THEORETICAL INVESTIGATION AND CORRELATION OF MOLECULAR PARAMETERS OF POLYCYCLIC AROMATIC HYDROCARBONS

A Dissertation

Presented to the

Faculty of the Department of Biophysical Sciences

College of Arts and Sciences

University of Houston

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

by

Henry Adolph Germer, Jr.

August, 1968

463819

To my Family

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ABSTRACT

The first part of the theoretical investigation is an interpretation of the calculated singlet $\pi \rightarrow \pi^*$ electronic transitions of five pentacyclic aromatic hydrocarbon molecules in terms of composite system approximations to these molecules. This study is motivated by the experimental observation that the electronic transitions of some pentacyclic aromatic hydrocarbons may be, on the basis of extinction coefficients, vibrational structure, and general band shape, correlated with the transitions of tetracyclic aromatic hydrocarbons contained within the structure of the pentacyclic. The molecules studied are benz(a)napthacene, benzo(b)chrysene, dibenzo(b,g)phenanthrene, dibenz(a,c)-anthracene, and 3,4-benzopyrene.

In this "molecules in molecule" investigation, the electronic transitions of the five pentacyclic aromatic hydrocarbons are first calculated using the semi-empirical SCFMO method with limited configuration interaction. Composite system models or approximations are formed for each pentacyclic hydrocarbon by conceptually breaking certain pairs of bonds in the subject molecule. The electronic transitions of these composite systems are then calculated. The electronic transitions of each subject pentacyclic hydrocarbon are next correlated to the transitions of the composite system model whose transitions most closely approximate those of the subject molecule.

The electronic transitions of the composite system are resolved into local excitations of either of the two composite system moieties

or as electron-transfer excitations from one moiety to the other. From this analysis, interpretations are made concerning the composite system origins of the pentacyclic transitions and predictions made concerning the observable characteristics of experimental pentacyclic transitions corresponding to the calculated transitions. A comparison of the theoretically predicted pentacyclic aromatic hydrocarbon transition characteristics with an available interpretation of the actual experimentally observed transitions indicate only fair agreement between experiment and the proposed theoretical interpretation.

In the second part, the theoretically calculated and experimental values of the ionization potential and electron affinity of the polyacene series of molecules, as well as other quantities derived from these parameters, are compared as a function of molecular size. The calculated values are determined for all molecules of the series from benzene through nonacene using the semi-empirical SCFMO method. Experimental data are available for benzene through pentacene. As has been frequently noted, the semi-empirical SCFMO theory cannot correctly predict the absolute values of the ionization potential and electron affinity when using theoretical parameters which give the best fit of spectroscopic data. However, the results of this investigation indicate that the theory can predict quite well the behavior of these molecular parameters as a function of a systematic change in molecular size.

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I.

INTRODUCTION

INTRODUCTION

A. Statement of Research Problems

The large polynuclear condensed ring aromatic hydrocarbons are a class of compounds which are of great interest to both biologists and chemists. The biological interest in these molecules stems primarily from the fact that many of these large benzenoid hydrocarbons are powerful carcinogens while some have little or no carcinogenic effects. As a consequence of this fact, much biological research has been done with these compounds in an attempt to find the mechanism whereby these compounds initiate cancerous growth and, hopefully, to thereby also gain an understanding of the cancer process itself.

To the chemist, the large benzenoid hydrocarbons have been a beautiful class of compounds in which to test the application of quantum mechanical theories to large molecules. From the early 1930's up to the present time, these molecules have been the subject of extensive study by theoretical chemists and physicists.

Since this class of compounds is of interest to both biologists and theoretical chemists, it was natural that attempts would be made to explain the biological effects in terms of theoretical chemistry. Probably the most famous of these attempts is the work of the Pullmans,[1] in which they have sought to correlate the carcinogenic action of these molecules with various theoretical parameters.

The work to be described in this dissertation, however, will not attempt to explain any of the biological effects of the benzenoid hydrocarbons but will rather address itself to two problems of interest primarily from a chemical point of view. This is not to say that the results may not have biological implications but rather that these implications will not be of primarily concern in this work.

The first problem is based upon the following experimental observation. In examining the absorption spectra of the large polycyclic condensed ring aromatic hydrocarbons, one may, on the basis of extinction coefficient, vibrational structure, and general appearance, find transitions in the large molecule which appear to be quite similar to transitions which appear in the absorption spectra of smaller moieties contained within the larger. For example, one may correlate transitions in the spectra of a pentacyclic aromatic hydrocarbon with those of a tetracyclic aromatic hydrocarbon which is contained within the structure of the pentacyclic. It must be noted that generally the transitions of the pentacyclic aromatic hydrocarbons which can apparently be correlated to those of a tetracyclic are considerably red or blue shifted relative to the actual transitions of the tetracyclic aromatic hydrocarbon.

In the first part of this work, an attempt has been made to gain a better understanding of the origin of such similar transitions by means of a theoretical study of the electronic transitions of five representative pentacyclic aromatic hydrocarbons. In this study, the transitions for the subject molecule treated as a single quantum

mechanical system and the transitions of various composite systems formed from the subject molecules are first calculated. The proper composite system is then chosen and the transitions of the molecule treated as a single system are interpreted in terms of the transitions of the composite system. On the basis of these interpretations, some observable predictions concerning the transitions are made which are then compared to the experimental data.

The second part of this work consists of a correlation of experimental and theoretical quantities and some general observations for the linear polyacenes, that is, anthracene, napthacene, pentacene, etc. Specifically, electron affinity and ionization potential data will be correlated with theoretical quantities.

Before beginning a discussion of the specific problems studied, it will be informative to first generally discuss quantum chemistry, that is, the application of quantum mechanics to chemical problems.

B. Summary of Theoretical Chemistry

1. Quantum Mechanics

The appropriate physical theory for dealing with atomic and molecular phenomena is quantum mechanics. The objective of quantum chemistry, therefore, is the successful solution of the time independent Schrodinger equation,

$$H\Psi = E\Psi$$

where H is the quantum mechanical Hamiltonian operator of the system

obtained by use of the quantum mechanical postulates and Ψ is the wave function of the stationary state of energy E. Unfortunately, the exact solution of the Schrodinger equation is impossible for all but the simplest systems, for example, the hydrogen atom and harmonic oscillator.

The basic problem of quantum chemistry has, therefore, become the determination of the best possible approximate solutions of the Schrodinger equation for systems of chemical interest. At the same time, it is desirable to find a systematic means of obtaining the approximate solutions which will give a physical insight into the fundamental chemical processes.

2. Approximate Methods

In general, there are two principle methods of obtaining approximate solutions to the Schrodinger equation, the perturbation method and the variational method. In the perturbation method, the complex system is treated as a soluble simple system which is perturbed by the formation of the complex system. This method has been used fairly extensively in studying very small molecules, for example, diatomics, small atoms such as helium, and intermolecular forces and interactions. However, with few exceptions, the perturbation method has not been used in the theoretical study of the electronic structure of large molecules. One exception was the Method of Spinvalence developed by a group of German mathematicians and physicists in the early 1930's.[2] The method is presented as, or at least in terms of, a perturbation problem. In this method, one begins conceptually with

a collection of atoms which are perturbed upon forming bonds to become a molecule. However, this method is virtually unknown today as a means of studying large molecules. This is probably due to criticism of a basic assumption that the energy involved in molecular binding is small compared with that involved in the atomic multiplet structure of the atoms which compose the molecule so that all but the lowest energy atomic levels can be neglected in discussing molecular formation. In this approximation, the directional properties of the bonds do not appear.[3] A probable contributing factor to the disappearance of this method was the apparent breakup of the German group which had developed this approach.

The second principle method for determining approximate solutions to the Schrodinger equation is the variational method based on the variational theorem. The most common form of this theorem states that if one chooses a trial function Φ and computes the quantity

$$W = \frac{\int \Phi^* H \Phi dV}{\int \Phi^* \Phi dV} ,$$

this W will be greater than or equal to the ground state energy, E_0. The quantity W will be equal to the ground state energy, E_0, only if the assumed wave function, Φ, is the exact solution or eigenfunction, Φ, of the Schrodinger equation for the system.

For all practical purposes, the variational method is the only method of approximation used in the theoretical study of larger molecules. Of the different forms of the variational method, the linear

variational method is by far the most important. In this method the trial function, Φ, is a linear combination of a finite set of known starting functions, Ψ_i, written as

$$\Phi = \sum_{i=1}^{M} c_i \Psi_i$$

and the energy, W, is minimized with respect to the coefficients c_j. This produces a set of M simultaneous linear equations for the M unknown coefficients c_j,

$$\sum_{j=1}^{M} c_j (H_{ij} - S_{ij} W) = 0$$

where

$$H_{ij} = H_{ji}^{*} = \int \Psi_i^* H \Psi_j dV$$

and

$$S_{ij} = S_{ji}^{*} = \int \Psi_i^* \Psi_j dV.$$

H_{ij} and S_{ij} can be computed from the known Hamiltonian and the starting functions. The condition that a nontrivial solution of these simultaneous equations exist is that the determinant of the coefficients vanish, that is

$$|H_{ij} - S_{ij} W| = 0.$$

This is the secular equation for the problem and the M roots of this equation give M possible energy levels, W_i, for the system. As the

number, M, of independent functions, Ψ_i, is increased, the M energy levels, W_i, converge from above, that is, higher energy, to the true energy levels, E_i, which would be obtained from an exact solution of Schrodinger's equation for the system.

Once the linear variational method was generally accepted as the best formal method of obtaining approximate solutions to the quantum mechanical problems of chemistry, because of mathematical convenience and/or accuracy of results, the next great problem was how to best choose the set of known starting functions Ψ_i used to form the trial functions

$$\Phi = \sum_{i=1}^{M} c_i \Psi_i .$$

Two major method which have been developed in response to this problem are the Valence Bond Method and the Molecular Orbital Method. Most surveys of the field of quantum chemistry begin with discussions of these two methods.

3. Pi-electron Approximation

Before continuing, it must be noted that although the general methods discussed are applicable to all molecular problems, the emphasis is on those theoretical methods which are applicable to larger organic molecules, in particular, the unsaturated conjugated hydrocarbons. Such hydrocarbons are those whose structures may be formally written as having alternating single and double bonds between the carbon atoms, for example, benzene, anthracene, and butadiene. The primary reason that this class of molecules has been so extensively and

reasonably successfully treated theoretically is because of the validity of the pi-electron or sigma-pi separability approximation. Basically, this approximation states that the electrons in the 1s levels of carbon and those localized in the sigma bonds directly along the carbon-carbon axes do not appreciably interact with the 2p electrons involved in the pi bonds and consequently, the two sets of electrons may be treated separately. More precisely, this means that in considering the total Hamiltonian of the system, the interaction between any pi-electron and all of the sigma-electrons may be accounted for by an average potential field independent of the exact coordinates of the sigma-electrons and the interaction of a sigma-electron with all the pi-electrons may be accounted for in a similar manner. Assuming the total wave function to be a product of the wave functions for the sigma-electrons and the pi-electrons, the Schrodinger equation for the system becomes separable under the foregoing approximation. The pi-electrons give rise to the more readily observable spectroscopic phenomena. Therefore, the pi-electron approximation has allowed the reduction of the quantum mechanical problem from, for example, in benzene a 36 electron problem to a 6 electron problem, while still giving results which may be directly correlated with experiment. This approximation is used in the theoretical study of unsaturated conjugated hydrocarbons, regardless of the method used for building trial wave functions.

4. The Valence Bond Method

The valence bond method of constructing approximate wave functions for chemical systems is essentially a generalization of the method used by Heitler and London[4] in the first successful treatment of the H_2 molecule. In considering the formation of a bond in the two electron system composed of atoms a and b, the trial wave function is built up in the following manner. First one considers the product of atomic wave functions, excluding spin,

$$\Psi_a(1)\Psi_b(2).$$

$\Psi_a(1)$ denotes the atomic wave function of atom a with electron 1, having space coordinates x_1, y_1, z_1 assigned to it and $\Psi_b(2)$ denotes the atomic wave function of atom b with electron 2, having space coordinates x_2, y_2, z_2 assigned to it. However, since the electrons are indistinguishable, the following product

$$\Psi_a(2)\Psi_b(1)$$

will be an equally good wave function. Therefore, the general form

$$N[\Psi_a(1)\Psi_b(2) \pm \Psi_a(2)\Psi_b(1)],$$

where N is a normalizing constant, is chosen for the space part of the trial wave function. However, the spin coordinates of the electrons must also be considered in the total wave function.

The following spin functions can be written for a system of two electrons:

$$\alpha(1)\alpha(2)\ , \qquad \beta(1)\beta(2)$$

$$\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \alpha(2)\beta(1)]$$

$$\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \alpha(2)\beta(1)].$$

α denotes the spin eigenfunction with eigenvalues (+1/2) and β the spin eigenfunction with eigenvalue (-1/2).

To combine the two space functions and four spin functions correctly, the Pauli principle must be satisfied. The Pauli principle states that the <u>total</u> spin-orbital wave function of a system must be antisymmetric with respect to the exchange of the coordinates of two of the electrons. In accordance with this principle, the following total wave functions may be written:

$$\Psi_S = \frac{N}{\sqrt{2}}[\Psi_a(1)\Psi_b(2) + \Psi_a(2)\Psi_b(1)][\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

$$\Psi_T = N[\Psi_a(1)\Psi_b(2) - \Psi_a(2)\Psi_b(1)]\left\{\begin{array}{l} \alpha(1)\alpha(2) \\ \beta(1)\beta(2) \\ \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \alpha(2)\beta(1)] \end{array}\right\}$$

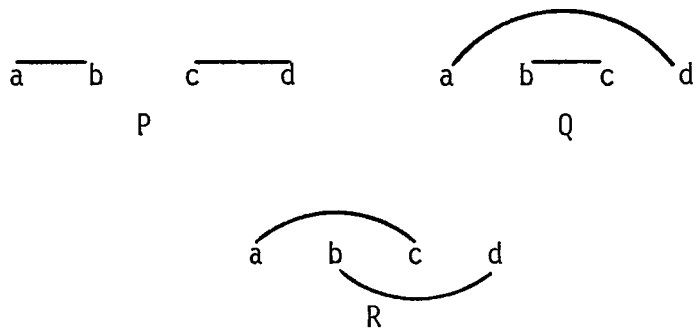
where Ψ_S is for a singlet state and the three possible forms of Ψ_T describe a triplet state. Writing the total wave function as a simple product amounts to neglecting the interaction between the magnetic moments of the orbital motion and spin.

It is instructive to rewrite Φ_s in the form of the Slater determinants:

$$\Psi_s = \frac{1}{2}\left\{\begin{vmatrix} \Psi_a(1)\alpha(1) & \Psi_b(1)\beta(1) \\ \Psi_a(2)\alpha(2) & \Psi_b(2)\beta(2) \end{vmatrix} - \begin{vmatrix} \Psi_a(1)\beta(1) & \Psi_b(1)\alpha(1) \\ \Psi_a(2)\beta(2) & \Psi_b(2)\alpha(2) \end{vmatrix}\right\}$$

The first determinant is an antisymmetric wave function with spin function α associated with atom a and β with b and the second determinant is an antisymmetric wave function with spin function β fixed at atom a and α at b. That is to say, the wave function may be considered as a linear combination of the wave functions of the two possible structures formed by the pairing of unlike spins to form a bond. The triplet state functions, Ψ_T, describe a non-bonding situation for this system.

The original generalization and application of this method to systems with more than one bond was done primarily by Slater[3] and Pauling.[5] Excellent examples of the application of this method to polyatomic molecules can be found in books by Sandorfy[6] and Eyring, Walter, and Kimball.[7] Very briefly, the forming of trial wave functions for polyatomic systems by the valence bond method is as follows. First the system to be described must be defined, for example, a system of four atoms with two bonds. There are three "structures" which may be drawn that are compatible with this system.



The total trial wave function will be taken as a linear combination of the wave functions for the above "structures", that is,

$$\Phi = c_P\Psi_P + c_Q\Psi_Q + c_R\Psi_R,$$

and the energy of the system minimized with respect to the constants c_P, c_Q, and c_R by application of the linear variational method.

By proper combination of the determinant space function of a "structure" with the various spin functions compatible with a particular "structure", one may derive the "structure" wave functions as linear combinations of Slater determinants. One finds that only a certain set of "structure" wave functions are linearly independent and that all others may be expressed in terms of these. The "structures" corresponding to the linearly independent "structure" wave functions are called the canonical structures and the number of canonical structures is given by the expression

$$\frac{(2N)!}{N!\,(N+1)!}$$

for a system of 2N atoms, each contributing one electron, and in which N bonds are formed.

The reason for treating the valence bond method with such extreme brevity is that this method is virtually unused today in forming trial wave functions for large unsaturated conjugated hydrocarbons even though this method does have some advantages. One advantage is that the "structures" corresponding to the "structure" wave functions from

which the total wave function is built, resemble conventional structural formulas and thus, allow the chemist to interpret the molecular state as a superposition of acceptable structural formulas. Another advantage of this method is that it allows the use of directed atomic orbitals[8,9] and introduces the concept of directed valence. This is done by combining (hybridizing) the atomic orbitals in such a manner as to produce equivalent orbitals directed in the direction of the bond. Also, in dealing with small molecules, such as the diatomics, it is the method of choice, since with little or no additional sophistication, it will give good quantitative results.

For larger systems, however, this method, in its present form, is mathematically unworkable. For example, anthracene, a molecule with three condensed aromatic rings (14 carbon atoms) will have 429 canonical structures. This means that the secular determinant that must be solved for the energy is 429 x 429. The Slater determinants from which the "structure" wave functions are built will be 14 x 14 and proper normalization of these wave functions will necessitate expansion of these determinants. The method has also been criticized on theoretical grounds because it does not account for any polar structures, i.e, the wave functions contain no terms of the form

$$\Psi_a(1)\Psi_a(2)$$

which may be interpreted as two electrons on one atomic center.

5. Molecular Orbital Method

The second main method used to form the trial wave functions, which are used to obtain the approximate solutions to the Schrodinger equation for chemical systems, is the molecular orbital method. In this method the electrons conceptually belong to the whole molecule and each electron is assigned a one-electron wave function, or molecular orbital, which spans the entire molecule. The molecular framework consists of a certain geometrical arrangement of the nuclei and also, in general, electrons in certain localized orbitals consistent with the arrangement of the nuclei. For example, electrons localized in the 1s atomic orbitals of carbon in a hydrocarbon molecule. Hund[10] and Mulliken[11] are generally credited with the early development of the molecular orbital concept.

This method has marked advantages in dealing with the energy states of certain molecules, particularly unsaturated conjugated hydrocarbons because it determines the sequence of energy levels of the individual electrons just as in atoms and thus, indicates the sequence of closed shells of electrons in molecules. In a manner consistent with the Pauli principle, the lower energy orbitals are filled with the electrons to give the state of lowest energy.

The energy content of the molecule can then be calculated relative to any convenient standard. Also, in some cases, the spectroscopic properties of molecules have been quite successfully interpreted in terms of the individual orbitals to which the electrons in a molecule have been assigned. Selection rules have been obtained in an elegant

way from the symmetry properties of the electronic orbitals. All of these advantages, plus the fact that by approximating the molecular orbitals as a linear combination of atomic orbitals the mathematical problem is still tenable for quite large systems, have made the molecular orbital method the most extensively used technique for the theoretical study of large molecules.

6. Hückel Molecular Orbital Theory

In discussing the molecular orbital method, at least as applied to conjugated systems, it is convenient to divide its development into five stages. The first and simplest form of the molecular orbital theory to be developed is commonly known as the Hückel Molecular Orbital Theory (HMO) since Hückel was the first to introduce the set of approximations used in this form of the theory.[12] First, the molecular orbitals are approximated as a linear combination of atomic orbitals (LCAO) and the Hamiltonian is of the form

$$H = \sum_i H_{eff}(i),$$

that is, a sum of terms, each of which depends only on the coordinates of one electron. The total wave function for the system is assumed to be a simple product of the occupied LCAO molecular orbitals, and this together with the form assumed for the Hamiltonian allows the total energy of the system to be taken as a simple sum of the orbital energies of the electrons. The Pauli principle is accounted for rather unsatisfactorily by distributing the electrons in pairs to each of

the lower molecular energy levels, the assumption being that one electron has spin function α and the other β.

The energy of the system is, of course, minimized with respect to the coefficients of the atomic orbitals in the assumed form for the molecular orbitals,

$$\phi_i = \sum_j c_{ij} \Psi_j .$$

The linear variational problem produces the set of equations

$$\sum_j c_{ij}(H_{ij} - S_{ij}E) = 0$$

which has nontrivial solutions when the orbital energies, ε_k, are roots of the secular equation

$$|H_{ij} - S_{ij}E| = 0.$$

The matrix elements H_{ij} and S_{ij} are given by the following integrals over the atomic orbitals:

$$H_{ij} = H_{ji}^* = \int \Psi_i^*(1)\, H_{eff}(1) \Psi_j(1) dv(1)$$

$$S_{ij} = S_{ji}^* = \int \Psi_i^*(1)\, \Psi_j(1) dv(1)$$

The Hückel MO method is then made into essentially an empirical theory by the following approximations for the matrix elements H_{ij} and S_{ij}:

(1) The coulomb integral $H_{ii} = \alpha_o$

(2) The resonance integral, $H_{ij} = \beta_o$ if $|i-j| = 1$

$H_{ij} = 0$ if $|i-j| > 1$

(i.e., H_{ij} finite only if Ψ_i and Ψ_j are atomic orbitals centered on neighboring nuclei)

(3) The overlap integral, $S_{ij} = \delta_{ij}$

The parameters α_0 and β_0 are chosen for the best fit of the theoretical quantities to experimental data.

Considering the drastic approximations used in this form of molecular orbital theory an amazing amount of reasonably successful interpretation of physical and chemical phenomena has been done and is being done with it.[13] Probably its chief advantage is simplicity. However, the complete neglect of electron-electron interactions makes it impossible for this method to account for the proper relative location and separation of many molecular states, in particular, the singlet and triplet states. These factors together with theoretical errors such as the use of a simple product wave function and the heavy use of empiricism made further sophistication of the Hückel molecular orbital method inevitable.

7. Antisymmetric Molecular Orbital Theory

The second stage of molecular orbital development is due largely to the work of Goeppert-Mayer and Sklar.[14] This stage of molecular orbital theory development is often called the antisymmetric molecular orbital theory (ASMO) because the Pauli principle is correctly satisfied by assuming the total wave function of the system to be an antisymmetric Slater determinant,

$$\Phi = \frac{1}{\sqrt{(2n)!}} \begin{vmatrix} \phi_1(1)\alpha(1) & \phi_1(1)\beta(1) & \phi_2(1)\alpha(1) & \cdots & \phi_n(1)\alpha(1) & \phi_n(1)\beta(1) \\ \phi_1(2)\alpha(2) & \phi_1(2)\beta(2) & & & & \\ \vdots & & & & & \\ \phi_1(2n)\alpha(2n) & \phi_1(2n)\beta(2n) & \cdots & & \phi_n(2n)\alpha(2n) & \phi_n(2n) \quad \beta(2n) \end{vmatrix} .$$

In forming the molecular orbitals, $\phi_i(k)\alpha(k)$, each space orbital, $\phi_i(k)$, is used twice, once with spin function α and once with spin function β. Further, these space molecular orbitals are assumed to be the same LCAO molecular orbitals found as solutions when treating the system in terms of the simple HMO theory. The Hamiltonian used is of the form:

$$H = \sum_i H_{core}(i) + \frac{1}{2} \sum_{\substack{i \\ i \neq j}} \sum_j \frac{1}{r_{ij}}$$

where $H_{core}(i)$ contains the kinetic energy operator of the ith electron and the potential field for the ith electron resulting from the nuclei (and sigma electrons in conjugated systems). The r_{ij}^{-1} term accounts for the coulombic electron-electron interaction. Goeppert-Mayer and Sklar[14] applied this method to the benzene molecule using essentially no empirical information except the experimental bond length. The coulomb, resonance, and overlap integrals (all identified above) as well as exchange integrals,

$$(ij|kl) = \iint \phi_i^*(1)\phi_k^*(2)\left(\frac{1}{r_{12}}\right)\phi_j(1)\phi_l(2)dv(1)dv(2) ,$$

arising from the electron interaction terms of the Hamiltonian, were

analytically evaluated using proper theoretical functions as far as possible. Unfortunately, the calculations are extremely difficult, being impractical beyond molecules the size of naphthalene, and the results are not good. Consequently efforts to improve the molecular orbital method were continued.

8. Configuration Interaction

The third stage of development of the molecular orbital method was the addition of configuration interaction (CI) to the ASMO method. In the molecular problem, as in the case of atoms, the electrons are placed in the allowed orbitals to form particular configurations. It is found that different configurations of the same symmetry regarding both space and spin parts are not mutually independent but the presence of electron repulsion alters the energy of each configuration and also introduces a resonance between different configurations. In the ASMO method describe above, the form of the wave functions of the molecular states was restricted to be either a single or the sum or difference of two Slater determinants. To account for the effects of configurational interaction the state wave functions are assumed to have the more general form of a linear combination of Slater determinants representing the various electron configurations. The coefficients of the determinants are then determined from energy minimization by the variational method. Substantial improvement in the approximate solution of the quantum mechanical problem for molecular systems can be achieved in this manner. An excellent discussion of the various aspects and results of the application of configuration interactions to simple unsaturated

conjugated hydrocarbon systems is given in a series of papers by Craig, Coulson and Jacobs.[15,16,17]

9. Self-Consistent Field Molecular Orbital Theory

The first three stages in the development of the Molecular Orbital Method all had one feature in common and this was the molecular orbital functions used in the calculations. The molecular orbitals used were always those obtained from the solution of the problem by the simple HMO method. That is, when using the ASMO or ASMO-CI methods, one would always obtain a solution to the quantum mechanical problem for the molecular system first by the HMO method and then take these LCAO orbital solutions and form the properly antisymmetric determinant type state wave functions from them. Finally the energy of the system is determined by use of the correct or full Hamiltonian of the system. An obvious improvement in this method would be to develop a more satisfactory means for determining the basic molecular orbitals.

The fourth stage in the development of the molecular orbital method was the application of the Hartree-Fock self-consistent field method, normally used for solving the quantum mechanical problem for atoms, to the molecular orbital problem. This development is usually called the self-consistent field molecular orbital theory (SCFMO). The detailed formulation of this theory was given by Roothaan,[18] but Lennard-Jones[19] and Coulson[16,17] also contributed to the development of this theory.

The following discussion of the self-consistent field molecular orbital theory will parallel the development given by Roothaan[18] but

will be considerably abbreviated. The system to be considered is one which has a closed-shell ground state. An electron shell is defined as a set of molecular orbitals in which (1) every space orbital occurs twice, that is, once with each spin function, and (2) if there is degeneracy on account of molecular symmetry, the molecular orbitals in the shell form a complete degenerate set. Unlike atoms most molecules have a closed-shell structure, that is, two electrons per shell, in the ground (lowest energy) state. Consequently, the wave function for the ground state of the system will be assumed to be reasonably approximated by a single Slater determinant made up of complete electron shells, that is,

$$\Phi = \frac{1}{\sqrt{(2n)!}} \begin{vmatrix} \phi_1(1)\alpha(1) & \phi_1(1)\beta(1) \ldots & \phi_n(1)\alpha(1)\phi_n(1)\beta(1) \\ \phi_1(2)\alpha(2) & \phi_1(2)\beta(2) \ldots & \phi_n(2)\alpha(2)\phi_n(2)\beta(2) \\ \cdot & & \\ \cdot & & \\ \cdot & & \\ \phi_1(2n)\alpha(2n) & \phi_1(2n)\beta(2n) \ldots & \phi_n(2n)\alpha(2n)\ \phi_n(2n)\beta(2n) \end{vmatrix} \tag{1.1}$$

Further, we assume that Φ is normalized, that is,

$$\int \Phi^* \Phi d\tau = 1 \tag{1.2}$$

and that the molecular orbitals are orthonormal, that is,

$$\int \phi_i^* \phi_j d\tau = \delta_{ij}. \tag{1.3}$$

The Hamiltonian of the system is assumed to be of the form

$$H = \sum_i H_{core}(i) + \frac{1}{2} \sum_i \sum_{\substack{j \\ i \neq j}} \frac{1}{r_{ij}} \tag{1.4}$$

where $H_{core}(i)$ is the Hamiltonian operator for the ith electron moving in the field of the nuclei alone, that is,

$$H_{core}(i) = -\frac{1}{2} \nabla^2 - \sum_k V_k(r_{ik}) \tag{1.5}$$

where the summation k is over all the nuclei. From the expression

$$E = \frac{\int \Phi^* H \Phi d\tau}{\int \Phi^* \Phi d\tau} \tag{1.6}$$

the following expression for the energy of the system is obtained,

$$E = 2\sum_i H_i + \sum_i \sum_j (2J_{ij} - K_{ij}), \tag{1.7}$$

where

$$H_i = H_i^* = \int \phi_i^* H \phi_i dv \tag{1.8}$$

$$J_{ij} = J_{ji} = J_{ij}^* = J_{ji}^* = \iint \frac{\phi_i^*(1)\phi_j^*(2)\phi_i(1)\phi_j(2)}{r_{12}} dv(1)dv(2) \tag{1.9}$$

$$K_{ij} = K_{ji} = K_{ij}^* = K_{ji}^* = \iint \frac{\phi_i^*(1)\phi_j^*(2)\phi_j(1)\phi_i(2)}{r_{12}} dv(1)dv(2) \tag{1.10}$$

The H_i are the nuclear-field orbital energies, the J_{ij} are the molecular coulomb integrals, and the K_{ij} are the molecular exchange integrals.

In order to obtain the best wave function, Φ, that is, the Slater determinant for which the energy is a minimum, the expression for the energy, equation (7), is varied by varying each molecular orbital, ϕ_i,

by an infinitesimal amount $\delta\phi_i$, subject to the restriction that the molecular orbitals form an orthonormal set. From this variation one obtains the following equations:

$$\delta E = 2\sum_i \int (\delta\overline{\phi}_i^*)\{H + \sum_j (2J_j - K_j)\}\phi_i dv$$

$$+ 2\sum_i \int (\delta\phi_i)\{H^* + \sum_j (2J_j^* - K_j^*)\}\phi_i^* dv \tag{1.11}$$

$$\int (\delta\phi_i^*)\phi_j dv + \int (\delta\phi_j)\phi_i^* dv = 0 \tag{1.12}$$

where the coulomb operator J_i and exchange operator K_i are defined by

$$J_{ij} = \int \phi_i^* J_j \phi_i dv \tag{1.13}$$

$$K_{ij} = \int \phi_i^* K_j \phi_i dv . \tag{1.14}$$

In order that E may reach its absolute minimum, it is necessary, although not sufficient, that $\delta E = 0$ for any choice of the $\delta\phi_i$'s in (1.11) which is compatible with the restrictions of (1.12). This problem is solved by the method of Lagrangian multipliers.

After considerable mathematical manipulation,[18] it may be derived that the set of "best" molecular orbitals satisfy the set of equations

$$F\phi_i = \varepsilon_i \phi_i , \tag{1.15}$$

which are known as Fock's equations, and the Hartree-Fock Hamiltonian operator F is given by

$$F = H + \sum_i (2J_i - K_i). \tag{1.16}$$

Fock's equations (1.15) state that the molecular orbitals, ϕ_i, which give the best determinant wave function, Φ, are all eigenfunctions of the same Hermitian operator, F, which in turn is defined in terms of these molecular orbitals.

Since F is defined in terms of the molecular orbitals which are themselves the solutions of Fock's equations (1.15), Fock's equations are solved by trial and error. One assumes a set of n functions, ϕ_i, from which the Hermitian operator F is first calculated. The eigenvalue problem for the operator, F,

$$F\phi = \varepsilon\phi \tag{1.17}$$

is then solved. In general there will be more than n solutions ε_i and ϕ_i, i = 1, 2, . . ., m (m > n), of the eigenvalue problem (1.17). Of these solutions, the set of n functions, ϕ_i, will be chosen which correspond to the n lowest eigenvalues, ϕ_i, and this set of functions compared to the functions originally used to calculate the operator F. Guided by this comparison, a new set of n functions is chosen and the procedure is repeated. This process is repeated until the assumed and calculated ϕ_i's agree. This method for solving Fock's equations is called the <u>Hartree-Fock self-consistent field method</u>. The set of m ε_i's determined in the final solution of the eigenvalue problem (1.17) are known as <u>Hartree-Fock orbital energies</u>. The set of n ϕ_i's corresponding to the n lowest ε_i are called <u>ground-state orbitals</u> and the remaining ϕ_i are known as <u>excited orbitals</u>.

For atoms, the solution of Fock's equations (1.15) by the above procedure is greatly simplified by the central symmetry, unfortunately, most molecules lack such symmetry and the solution of Fock's equations for molecules, using completely general functions, ϕ_i, for the molecular orbitals is out of the question except in extremely simple cases. Therefore, the next step is to pick a particular form for the molecular orbitals, ϕ_i, and re-derive Fock's equations using these approximations to the "best" molecular orbitals, ϕ_i, which would be obtained from the Hartree-Fock SCF Method. In particular, the molecular orbitals will be approximated by a linear combination of atomic orbitals (LCAO), that is

$$\phi_i = \sum_j \Psi_j c_{ji} \tag{1.18}$$

where the Ψ_j are normalized atomic orbitals, that is,

$$\int \Psi_j^* \Psi_j dv = 1. \tag{1.19}$$

It is then useful to introduce the following matrix notation:

$$\left.\begin{aligned} \underline{\Psi} &= (\Psi_1 \Psi_2 \cdots \Psi_m) \\ \underline{c}_i &= \begin{pmatrix} c_{1i} \\ c_{2i} \\ \vdots \\ c_{mi} \end{pmatrix} \\ \underline{C} &= \begin{pmatrix} c_{11} & c_{12} & \cdots & c_{1n} \\ c_{21} & c_{22} & \cdots & c_{2n} \\ \cdots & \cdots & \cdots & \cdots \\ c_{m1} & c_{m2} & \cdots & c_{mn} \end{pmatrix} \end{aligned}\right\} . \tag{1.20}$$

Equation (18) may then be rewritten as

$$\phi_i = \underline{\Psi}\,\underline{c}_i \tag{1.18'}$$

$$\phi_i = \underline{\Psi}\,\underline{C} \tag{1.18''}$$

Note that the total number of molecular orbitals and atomic orbitals are n and m, respectively, and since n linearly independent molecular orbitals must be constructed from m atomic orbitals, it must hold that $m \geq n$.

It is also useful to define a matrix for each one electron operator of the form

$$\underline{M} = \begin{pmatrix} M_{11} & M_{12} & \cdots & M_{1m} \\ M_{21} & M_{22} & \cdots & M_{2m} \\ \cdots & \cdots & \cdots & \cdots \\ M_{m1} & M_{m2} & \cdots & M_{mm} \end{pmatrix} \tag{1.21}$$

where

$$M_{ij} = \int \Psi_i^* M \Psi_j \, dv.$$

It can be shown that $\underline{M}$ is Hermitian if M is Hermitian, that is, $\underline{M}^* = \underline{M}$ ($\underline{M}^*$ denotes the Hermitian conjugate of the matrix $\underline{M}$). The following matrices may then be written:

$$\left.\begin{array}{ll} \underline{M} = \underline{H} & \text{if} \quad M = H \\ \underline{M} = \underline{J}_i & \text{if} \quad M = J_i \\ \underline{M} = \underline{K}_i & \text{if} \quad M = K_i \\ \underline{M} = \underline{F} & \text{if} \quad M = F \\ \underline{M} = \underline{S} & \text{if} \quad M = 1. \end{array}\right\} \tag{1.22}$$

$\underline{S}$ is the overlap matrix and its diagonal elements are unity by equation (19).

The usefulness of the matrix notation is shown by the fact that all integrals over the molecular orbitals, ϕ_i, may be written as

$$\int \phi_i^* M \phi_j dv = \underline{c}_i^* \, \underline{M} \, \underline{c}_j . \tag{1.23}$$

The orthonormality condition of the molecular orbitals, still assumed to hold under the LCAO approximation, becomes

$$\int \phi_i^* \phi_j dv = \underline{c}_i^* \underline{S} \, \underline{c}_j = \delta_{ij} \quad . \tag{1.24}$$

In view of equation (1.23), equations (1.8), (1.13), and (1.14) become

$$\begin{aligned} H_i &= \underline{c}_i^* \, \underline{H} \, \underline{c}_j \\ J_{ij} &= \underline{c}_i^* \, \underline{J}_j \underline{c}_i = \underline{c}_j^* \, \underline{J}_i \, \underline{c}_j \\ K_{ij} &= \underline{c}_i^* \, \underline{K}_j \, \underline{c}_i = \underline{c}_j^* \, \underline{K}_i \, \underline{c}_j \end{aligned} \tag{1.25}$$

and the expression for the energy of the system (1.7), may be rewritten as

$$\begin{aligned} E = 2 \sum_i \underline{c}_i^* \, \underline{H} \, \underline{c}_i + \sum_i \sum_j [\underline{c}_i^* (2\underline{J}_j - \underline{K}_j) \, \underline{c}_i \\ + \underline{c}_j^* (2\underline{J}_i - \underline{K}_i) \, \underline{c}_j] \quad . \end{aligned} \tag{1.26}$$

In order to determine the "best" LCAO molecular orbitals, that is, those orbitals which will minimize the energy of the system, a variational treatment analogous to that described previously is carried out. This time, however, the variation is restricted to the coefficients, c_{ij}, of the LCAO molecular orbitals, that is, the energy is varied by varying the matrices $\underline{c}_i$ by an infinitesimal amount, $\underline{c}_i$. The variation of equations (1.26) and (1.24) yields

$$\delta E = 2\sum_i (\delta \underline{c}_i^*)\{\underline{H} + \sum_j (2\underline{J}_i - \underline{K}_j)\}\underline{c}_i$$

$$+ 2\sum_i (\delta \underline{c}_i^+)\{\underline{\overline{H}} + \sum_j (2\underline{\overline{J}}_j - \underline{\overline{K}}_j)\}\underline{\overline{c}}_i \qquad (1.27)$$

and

$$(\delta \underline{c}_i^*)\ \underline{S}\ \underline{c}_j + \underline{c}_i^*\ \underline{S}\ (\delta \underline{c}_j) = 0. \qquad (1.28)$$

($\underline{\overline{M}}$ denotes the complex conjugate and $\underline{M}^+$ the transpose of matrix $\underline{M}$). As before, a necessary condition for the energy to be a minimum is that $\delta E = 0$ for any choice of $\delta \underline{c}_i$ which is compatible with the restrictions of (1.28).

Using an argument analogous to that used in deriving Fock's equations,[18] one may derive an analogous set of matrix equations

$$\underline{F}\ \underline{c}_i = \varepsilon_i\ \underline{S}\ \underline{c}_i \qquad (1.29)$$

which the LCAO molecular orbital coefficients must satisfy in order that the energy of the system, E, be a minimum. The matrix $\underline{F}$

$$\underline{F} = \underline{H} + \sum_j (2\underline{J}_j - \underline{K}_j) \qquad (1.30)$$

is defined in terms of the matrices, $\underline{c}_i$, so the equations(1.29) must be solved by trial and error.

To solve the set of equations(1.29), a set of n matrices, $\underline{c}_i$, is assumed and used to calculate $\underline{F}$ and $\underline{S}$. These matrices are then used to formulate the following problem:

$$\underline{F}\,\underline{c} = \varepsilon\,\underline{S}\,\underline{c} \quad \text{or} \quad (\underline{F} - \varepsilon\underline{S})\,\underline{c} = 0 \tag{1.31}$$

Equation(1.31) is a generalization of the eigenvalue problem for a Hermitian matrix and it can be shown that the important properties of the eigenvalues and eigenvectors of a Hermitian matrix still hold, namely, the eigenvalues of equation(1.31) are the roots of the secular determinant,

$$|\underline{F} - \varepsilon\underline{S}| = 0, \tag{1.32}$$

and the eigenvectors belonging to different eigenvalues are mutually orthogonal in the sense that

$$\underline{c}_i^{*}\,\underline{S}\,\underline{c}_j = 0. \tag{1.33}$$

Since $\underline{F}$ and $\underline{S}$ are mxm matrices, there will be m solutions, ε_i and $\underline{c}_i$, of equation (1.31). Of these m solutions, the set of n matrices $\underline{c}_i$ corresponding to the n lowest eigenvalues, ε_i, is chosen and compared with the set of n matrices, $\underline{c}_i$, used to originally calculate $\underline{F}$ and $\underline{S}$. Based on this comparison a new set of n matrices, $\underline{c}_i$, is chosen and the process is repeated until the assumed values of $\underline{c}_i$ and the solutions of equation(1.31) coincide. These self-consistent solutions are

now solutions of equation (1.29) which in turn are the conditions for minimization of the energy, E, of the system. This method of obtaining the coefficnets of the LCAO molecular orbitals, together with the use of the determinantal type wavefunction, equation (1.1), and correct Hamiltonian, equation (1.2), for the calculation of the energy of the system, constitute what is generally called the self-consistent field molecular orbital theory.

The eigenvalues, ε_i, obtained in the final solution of equation (1.31) are called the LCAO orbital energies. The set of n molecular orbitals, ϕ_i, determined from the set of n matrices, $\underline{c}_i$, corresponding to the n lowest values of ε_i are used to form the ground state wave function and are called ground state orbitals. The m-n set of molecular orbitals obtained from the remaining m-n solutions of equation (1.31) are referred to as excited state orbitals. These excited state orbitals obtained from the ground state solution for a molecular problem are used as a basis for forming the excited state wave functions. Basically, to do this one conceptually promotes an electron from a ground state orbital to an excited state orbital by replacing a ground state orbital in the Slater determinant describing that electron configuration with an excited state orbital. However, consideration of the spin functions α and β will produce four possible wave functions for the excitation of an electron from orbital, ϕ_i, to excited orbital, ϕ_e. Using an obvious notation for the determinant, the following determinantal wave functions are formed:

$$\Delta_1 = |(\phi_1\alpha)(\phi_1\beta)\ldots(\phi_{i-1}\alpha)(\phi_{i-1}\beta)(\phi_i\alpha)(\phi_e\alpha)\ldots(\phi_n\alpha)(\phi_n\alpha)|$$

$$\Delta_2 = |(\phi_1\sigma)(\phi_1\beta)\ldots(\phi_{i-1}\alpha)(\phi_{i-1}\beta)(\phi_i\alpha)(\phi_e\beta)\ldots(\phi_n\alpha)(\phi_n\beta)|$$

$$\Delta_3 = |(\phi_1\alpha)(\phi_1\beta)\ldots(\phi_{i-1}\alpha)(\phi_{i-1}\beta)(\phi_i\beta)(\phi_e\alpha)\ldots(\phi_n\alpha)(\phi n\beta)| \tag{1.34}$$

$$\Delta_4 = |(\phi_1\alpha)(\phi_1\beta)\ldots(\phi_{i-1}\alpha)(\phi_{i-1}\beta)(\phi_i\beta)(\phi_e\beta)\ldots(\phi_n\alpha)(\phi_n\beta)| .$$

These four wave functions must be considered to be equally probable so a linear combination is taken of all four and the energy minimized by a variational treatment. This gives rise to a singlet state

$$^1\Phi_{ie} = \frac{1}{\sqrt{2}}(\Delta_2 - \Delta_3) \tag{1.35}$$

and a triplet state with three wave functions

$$^3\Phi_{ie_1} = \frac{1}{\sqrt{2}}(\Delta_2 + \Delta_3)$$

$$^3\Phi_{ie_2} = \Delta_1 \tag{1.36}$$

$$^3\Phi_{ie_3} = \Delta_4$$

each of which have the same energy since spin-orbit coupling is neglected. Also, the triplet energy is normally lower than that of the singlet state.

The wave functions obtained in the manner described above will not, in general, produce the minimum energy for that state since the excited orbital, ϕ_e, was determined from the minimization of the ground state energy and not that of the excited state. Actually

the excited state energy should be minimized with respect to the coefficients of the LCAO molecular orbitals used to form that particular excited state electron configuration; however, in practice this is rarely done, the feeling evidently being that the amount of improvement in energy values would not be worth the additional computational difficulties.

Unfortunately, the rigorous application of the SCFMO method, that is, the analytical solution of all integrals and the use of no empirical data except bond length, does not give very satisfactory results. For example, Coulson and Jacobs[16] calculated the state energy levels for butadiene by the ASMO method, ASMO-CI method, and SCFMO method and found the SCFMO levels to be better than the ASMO levels but not as good as the ASMO-CI levels. This difficulty is, of course, readily overcome by generalizing our state wave functions in the SCFMO method to a linear combination of Slater determinants to allow for configuration interaction in this method. Another example of the rigorous application of the SCFMO method is the calculation of the energy levels of butadiene by Parr and Mulliken.[20] The SCFMO-CI method was used by Parr, Craig, and Ross to calculate the lower excited levels of benzene.[21]

The SCFMO method also shares the computational difficulties of the ASMO method which prevent its application to molecules much larger than naphthalene. This is the so-called "n^4 difficulty." For a large unsaturated conjugated molecule containing n pi-orbitals, the total number of integrals, when reduced to integrals over atomic orbitals, will total on the order of $n^4/8$, although this number is usually divided

into a smaller number of groups of similar integrals. Also, these integrals are quite difficult to compute, many of them being of a multicenter form.

The generally poor results for the energy levels obtained by the rigorous application of even the relatively sophisticated SCFMO method is usually attributed to two shortcomings in the theory. The first is the orbital approximation or one-electron approximation. In solving for the molecular orbitals, they are treated as single electron orbitals; however, in forming the determinant wave function, each space orbital is considered to contain two electrons with antiparallel spins. The molecular orbitals, therefore, contain no coordinates associated with the distance between these electrons and thus no account is taken of the correlation energy of these electrons.

The second criticism of the molecular orbital method is that it overestimates the polar character of the chemical bond. This is best illustrated by the simple product wave function of a two-electron system

$$\Phi = \phi_1(1)\phi_1(2) \tag{1.37}$$

where the molecular orbital, ϕ_1, is given by

$$\phi_1 = \frac{1}{\sqrt{2}}(\Psi_a + \Psi_b). \tag{1.38}$$

Substituting ϕ_1 into Φ and multiplying out one obtains

$$\begin{aligned}\Phi &= \frac{1}{2}[\Psi_a(1) + \Psi_b(1)][\Psi_a(2) + \Psi_b(2)] \\ &= \frac{1}{2}[\Psi_a(1)\Psi_a(2) + \Psi_a(1)\Psi_b(2) + \Psi_b(1)\Psi_a(2) + \Psi_b(1)\Psi_b(2)]\end{aligned} \tag{1.39}$$

where the polar terms, $\Psi_a(1)\Psi_a(2)$ and $\Psi_b(1)\Psi_b(2)$, constitute one-half of the terms of Φ.

10. The Semi-empirical or Pariser-Parr-Pople (P-P-P) LCAO Self-Consistent Field Molecular Orbital Theory

The computational difficulties and poor results of the rigorous application of the SCFMO theory led to the fifth and latest stage of development of the molecular orbital method. This development consisted of the application of a series of mathematical simplifications or approximations to the SCFMO theory along with the introduction of a limited amount of empirical data. The need for mathematical approximations was obvious since one desires a theoretical method which could be applied to a wide range of chemical systems and not just a few simple ones. The use of empirical data was viewed as a means of partially compensating for the errors introduced by the theoretical weaknesses discussed above. To do this, some of the integrals which appear in the SCFMO theory were given a physical interpretation and their computed values replaced by experimental values. This introduction of experimental data was said to "calibrate" the theory. The basic work in the development of the semi-empirical self-consistent-field molecular orbital theory was done by Pariser and Parr[22,23] and Pople[24].

The following discussion of the approximations made in formulating the semi-empirical SCFMO theory will concentrate primarily on those applicable to an unsaturated conjugated hydrocarbon in which only the pi-electrons are considered, that is, the pi-electron approximation is made. These results can, of course, be extended to

other classes of molecules; however, most of the theoretical work has concentrated on this class of molecules, as does the present work.

It will be useful to first write the expressions for the elements of the $\underline{F}$ and $\underline{S}$ matrices which appear in the set of equations [equation 1.29)]

$$\underline{F}\ \underline{c}_i = \varepsilon_i\ \underline{S}\ \underline{c}_i,$$

derived by Roothaan.[18] These equations are the conditions imposed on the coefficients of the linear combination of atomic orbitals (LCAO) molecular orbitals [equation (1.18)]

$$\phi_i = \sum_j \Psi_j c_{ji}$$

in order that the energy, E, of the system be minimized. These matrix elements are

$$F_{ij} = H_{ij} + \sum_k \sum_l P_{kl} \{ (i\ k\ |G|\ j\ l) - \frac{1}{2} (i\ k\ |G|\ l\ j) \} \tag{1.40}$$

where

$$H_{ij} = \int \Psi_i^*(1)\ \{ - \frac{1}{2} \nabla^2(1) - \sum_k V_k(1) \}\ \Psi_j(1)\ dV(1) \tag{1.41}$$

$$(i\ k\ |G|\ j\ l\ ) = \iint \frac{\Psi_i^*(1) \Psi_k^*(2)\ \Psi_j(1) \Psi_l(2)}{r_{12}}\ dV(1) dV(2) \tag{1.42}$$

$$P_{kl} = 2 \sum_i c_{ik}^* c_{il} \tag{1.43}$$

and

$$S_{ij} = \int \Psi_i^*\ \Psi_j\ dV \tag{1.44}$$

The approximations amount to a simplification of the matrix elements, F_{ij} and S_{ij}.

The first approximation is that the sigma electron system may be treated as a non-polarizable core and its effects included in the term H_{ij} (1.41). This means that $V_k(1)$ no longer represents the potential felt by electron (1) due to the nuclear charge of the kth atom, but rather the potential due to the core formed by the kth nucleus and all the sigma electrons associated with it.

The second approximation is to neglect all overlap integrals S_{ij} (44) unless i = j, that is

$$S_{ij} = \int \Psi_i^* \Psi_j dV = \delta_{ij}. \tag{1.45}$$

This means that the overlap matrix $\underline{S}$ is now equal to the identity matrix $\underline{I}$. The condition that the molecular orbitals, ϕ_i, be normalized is now

$$\sum_j C_{ij}^* C_{ij} = 1. \tag{1.46}$$

This approximation is not quantitatively correct, but it simplifies the computation considerably and is considered to be worth the loss of accuracy incurred by it.

The third approximation is to neglect all two-electron integrals (1.42) which depend on the overlapping of charge distributions of different orbitals. This means that the integrals (ik |G| jl) are neglected unless i = j and k = l. The second approximation of setting $S_{ij} = \delta_{ij}$ and this approximation are really consistent with one another because if

the magnitude, S_{ij}, of the charge distribution, $\Psi_i^* \Psi_j$, is neglected, its interaction with other charge distributions should also be neglected. If the second approximation were made without the third, it would be equivalent to counting the interactions of more electrons than are actually present.

The fourth approximation is based upon the following argument given by Pariser and Parr[22] concerning that part of the Hamiltonian which appears in equation (41)

$$H_N = -\frac{1}{2}\nabla^2(1) - \sum_k V_k(1) \tag{1.47}$$

where the summation k is over all cores of the molecule. Equation (1.47) is rewritten in the form

$$H_N = -\frac{1}{2}\nabla^2(1) - V_i(1) - \sum_{\substack{k(\neq i)\\(\neq j)}} V_k(1) - \sum_{\substack{j(\neq i)\\(\neq k)}} V_j'(1) \tag{1.48}$$

where V_j' is the potential due to uncharged cores in the molecule. (e.g., a hydrogen atom in the unsaturated hydrocarbon). Further the V_k may be written as

$$V_k(1) = V_k'(1) - \int \frac{\Psi_k^*(2)\ \Psi_k(2)}{r_{12}}\, dV(2) \tag{1.49}$$

where $V_k'(1)$ again denotes the potential due to the kth core if it were neutral. Using equations (1.48) and (1.49), equation (1.41) for H_{ii} may be rewritten as

$$H_{ii} = -I_i - \sum_k (i\ k\ |G|\ i\ k) - P_i \tag{1.50}$$

where

$$I_i = \int \Psi_i^*(1)[\frac{1}{2}\nabla^2(1) + V_i(1)]\Psi_i(1)dV(1) \tag{1.51}$$

$$P_i = \int \Psi_i^*(1)[\sum_k V_k'(1)]\Psi_i(1)dV(1) \tag{1.52}$$

and (i k |G| i k) is defined in equation (1.42). The fourth approximation is to interpret I_i as the atomic valence state ionization potential and to assume that it is a constant for all carbon atoms in unsaturated hydrocarbons. The integral for I_i is thus replaced by a constant based upon experimental data. The integral, P_i, called the neutral penetration integral, is the total attraction of an electron in Ψ_i for <u>all</u> (carbon and hydrogen) cores of the molecule in a neutral state. This quantity is either approximated as a small positive value or, more often, set equal to zero.

It should be noted that Pople[24] treats the approximations dealing with H_{ii} somewhat differently. His argument, however, depends upon specifically setting the integrals (i j |G| i j) = r_{ij}^{-1}. This is quite restrictive and consequently is not given here.

The sixth approximation concerns equation (1.41) for H_{ij}, that is,

$$H_{ij} \equiv \beta_{ij} = \int \Psi_i^*(1)[-\frac{1}{2}\nabla^2(1) - \sum_k V_k(1)]\Psi_j(1)dV(1). \tag{1.41}$$

These resonance integrals represent, according to Pople,[24] the fact that electrons can move in levels of lower energy by virtue of being in the field of two cores simultaneously. By theoretical elucidation,

these integrals may be shown to depend on the atoms i and j and the type and length of the bond between adjoining atoms i and j, but not sensibly on neighboring bonds or atoms.[22] Consequently, the resonance integrals, β_{ij}, are approximated as basic empirical parameters, the value of which depends on the atoms i and j and the length and type of bond, but the value of which remains constant between different molecules. The most common way of handling this approximation in unsaturated conjugated hydrocarbons is to set H_{ij} equal to a constant β for bonds between nearest-neighbor atoms and zero otherwise. The β is used as an adjustable parameter with which to fit the calculated values of quantities, for example, electronic transitions, to the observed values of the transitions for a number of similar molecules. There are other ways of approximating β_{ij} but they will be discussed under Recent Developments.

With the incorporation of the above six approximations, equation (1.40) may be rewritten as

$$F_{ii} = -I_i - P_i + \frac{1}{2} P_{ii} (ii\ |G|\ ii) + \sum_{j(\neq i)} (P_{jj} - 1)(ij\ |G|\ ij) \quad (1.53)$$

and

$$F_{ij} = \beta_{ij} - \frac{1}{2} P_{ij}(ij\ |G|\ ij) \quad \text{for } i \neq j. \quad (1.54)$$

The final stage in formulating the semi-empirical SCFMO theory is the development of approximations for the integrals of the form (ii |G| ii) and (ij |G| ij). Although this discussion does not exhaust the

approximations which have been tried, it does include the most successful, and, therefore, most commonly used ones.

The approximation for (ii |G| ii) was developed by Pariser[25] and is based on the energetics of a simple atomic charge-transfer process which takes an electron from a 2p orbital of one carbon atom to another carbon atom to form a positive and a negative ion. Based on this process, (ii |G| ii) may be interpreted as

$$(ii\ |G|\ ii) = I_i - A_i \tag{1.55}$$

where I_i is the valence state ionization potential of neutral carbon and A_i is the electron affinity. The integral (ii |G| ii) is then approximated by the experimental values for I_i and A_i. This development, of course, is for carbon atoms in an unsaturated conjugated hydrocarbon, but the same argument has been extended to other types of atoms.

The development of an approximation for the two-center coulomb integral, (ij |G| ij), has produced considerable activity in the field of quantum chemistry. The cause of this activity is apparently the failure to develop a really good single approximation which is applicable to more than one or two general classes of molecules. Four of the most common approximations for this integral in unsaturated conjugated hydrocarbons are as follows:

(i) Theoretical Slater:[26] For $r_{ij} \geq 2.80$ Å, the values are computed by performing the actual integration using Slater-type orbital functions (for example, see Ref. 27) for the atomic orbitals and using

the interpolation formula

$$(ij\ |G|\ ij) = \frac{1}{2}[(ii\ |G|\ ii) + (jj\ |G|\ jj)] - \lambda r_{ij} - \mu r_{ij}^2$$
$$= \frac{1}{2}[I_i - A_i + I_j - A_j] - \lambda r_{ij} - \mu r_{ij}^2 \qquad (1.56)$$

for $0 \leq r_{ij} < 2.80$ Å where μ and λ are parameters used to fit the values at $r_{ij} = 2.80$ Å and 3.70 Å to the values obtained from the actual integration.

(ii) Pariser-Parr:[22,28] For $r_{ij} \geq 2.80$ Å, the values are computed by performing the actual integration after replacing the 2p atomic orbitals of carbon by a pair of tangent uniformly charged nonconducting spheres of diameter

$$d_i = \frac{4.597}{Z_i}\ \text{Å} \qquad (1.57)$$

where Z_i is the Slater effective nuclear charge of the 2p atomic orbitals replaced. For $0 \leq r_{ij} < 2.80$ Å, values are again determined by the interpolation formula (1.56).

(iii) Pople:[24]

$$(ij\ |G|\ ij) = \frac{14.3986}{r_{ij}}\ \text{ev} \qquad (1.58)$$

where r_{ij} is in angstroms.

(iv) Mataga:[29]

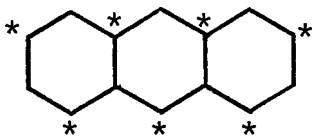
$$(ij\ |G|\ ij) = \frac{14.3986}{r_{ij} + a}\ \text{ev} \qquad (1.59)$$

where

$$a = \frac{14.3986}{\frac{1}{2}[I_i - A_i + I_j - A_j]} \tag{1.60}$$

and r_{ij} is in angstroms. Very good results for singlet state energy differences can be obtained using the Matage approximation, especially for the condensed ring aromatic hydrocarbons.

If one further restricts the class of molecules to the so-called even alternant unsaturated conjugated hydrocarbons, two further simplifications may be deduced. In these hydrocarbons, the carbon centers may be divided into two equal sets in which one member of a set is not bound to any other member of that set. For example, in anthracene,



the "starred" carbons form one set and the unstarred another. The first simplification for this class of molecules is that, subject to all the above approximations,

$$P_{ii} = 2 \sum_j C_{ij}^* C_{ij} = 1. \tag{1.61}$$

This was first proven by Pople.[24] P_{ii} is interpreted as the pi-electron charge density on the ith carbon atom. The second simplification for this class of molecules is the so-called <u>pairing theorem</u> which states that the orbital energies or eigenvalues of the matrix $\underline{F}$ are symmetrically arranged about the value for F_{ii}. That is, if $F_{ii} + \varepsilon$ is an eigenvalue, so is $F_{ii} - \varepsilon$. This is, of course, subject to all the above

approximations which ensure that F_{ii} is a constant, that is, all the diagonal elements of $\underline{F}$ are equal to the same constant value. This theorem was first proven for even alternant hydrocarbons in the HMO theory by Coulson and Rushbrooke[30] and extended to the semi-empirical SCFMO theory by Pople.[24,31]

By incorporating all the above approximations, and restricting the applicability to the even alternant unsaturated conjugated hydrocarbons, the $\underline{F}$ and $\underline{S}$ matrix elements in the semi-empirical SCFMO theory may finally be written as

$$\begin{aligned} F_{ii} &= -\frac{1}{2}(I_i + A_i) - P_i \\ F_{ij} &= \beta_{ij} - \frac{1}{2} P_{ij}\gamma_{ij} \\ S_{ij} &= \delta_{ij} \end{aligned} \tag{1.62}$$

where γ_{ij} is one of the approximations for the integral $(ij\ |G|\ ij)$ discussed above. As stated earlier, the penetration integral P_i is usually neglected.

It should be noted that these same semi-empirical approximations can and are applied equally well to the ASMO and ASMO-CI theories. Since the same Hamiltonian and LCAO type molecular orbitals are used in these theoretical methods, the same basic integrals, over the atomic orbitals, $(ii\ |G|\ ii)$, $(ij\ |G|\ ij)$, H_{ii}, and H_{ij}, will appear as in the SCFMO theory with LCAO molecular orbitals.

11. Recent Developments

The recent developments in the application of quantum mechanics to larger molecular systems have not produced any fundamental improvements

in the theory. Rather it has concentrated on the further development of a semi-empirical theory based on Roothaan's[18] formalism for a SCFMO theory using molecular orbitals approximated by a linear combination of atomic orbitals (LCAO). This work may be roughly divided into two categories. The first category is that motivated by the same one which led to the original development of the semi-empirical SCFMO theory, that is, a desire to overcome the poor results caused by the theoretical deficiencies of the LCAO molecular orbital theory. These deficiencies are over-estimation of the polar character of the bonds and the one-electron approximation. This work consists, primarily, of the improvement of the approximations used for the basic integrals over atomic orbitals and the improvement of the wave functions. The second category consists of developing techniques which may be thought of as lessening the severity of approximations made in the interest of computational simplicity.

Under the first category, improvements in integral approximations and wave functions, the large amount of research activity devoted to developing a good approximation for the integral $(ij\ |G|\ ij)$ has been mentioned in the preceeding section and four examples given. Some work has been done on the integral $(ii\ |G|\ ii)$ but molecular calculations in the literature almost invariably use the Pariser[25] approximation, which was also described in the preceeding section.

A number of different approaches have been taken to improve the wave functions. The most common way is to allow for the effects of configuration interaction, which was discussed in a previous section.

Almost all molecular calculations in the recent literature allow for configuration interaction, at least on a limited basis.

Another approach is to use orthogonalized atomic orbitals to form the molecular orbitals.[32] The effect of this is to set the overlap matrix $\underline{S}$ equal to the identity matrix, $\underline{I}$, exactly and not by approximation.

Dewar has introduced what he calls the "split-p" method in which the pi-electrons are alternantly assigned to the upper and lower lobes of the 2p orbitals of carbon, for example, in the upper lobes of carbon atoms 1, 3, and 5 and lower lobes of carbons 2, 3, and 6 in benzene.[33] This scheme will give computed values for the integral $(ij\ |G|\ ij)$ in remarkable agreement with empirical values; however, wave functions built from the split-P functions are no longer orthogonal to the sigma orbitals, thus invalidating the pi-electron approximation. Proper consideration of the nonorthogonality weakens Dewar's results.[34]

A final method to improve the wave functions is the alternant molecular orbital method of Löwdin.[35] In this method, Löwdin[35] puts one electron on one atom when the other is on a neighboring atom. The basic idea may be illustrated with a two-electron case, where instead of the usual molecular orbital wave function (excluding spin), $\Phi = \Psi(1)\Psi(2)$, the wave function has the form

$$\Phi(1,2) = \phi(1)\phi'(2) + \phi'(1)\phi(2).$$

That is, instead of the usual choice for the molecular orbital, $\phi = \Psi_a + \Psi_b$, where Ψ_a and Ψ_b are atomic orbitals, two orbitals are formed

$$\phi = \Psi_a + \lambda\Psi_b \,, \qquad \phi' = \Psi_b + \lambda\Psi_a$$

where λ is a parameter. This method apparently gives good results, and although mathematically difficult, it is being extended to larger unsaturated conjugated hydrocarbons.[36]

There are certainly other schemes for improving the wave functions, but these are probably the most significant in terms of applicability to the unsaturated conjugated hydrocarbons.

Under the second rather arbitraty category of improvements, that is, removing approximations made in the interest of computational simplicity, two will be considered. They are inclusion of overlap and the effects of bond length. It should be noted that before the advent of the large electronic computers, these considerations would have involved a prohibitive amount of labor for all but the smallest molecules.

Ever since the original formulation of the semi-empirical SCFMO theory, many workers felt that the neglect of the overlap of the atomic orbitals, that is, setting [equation (1.45)]

$$S_{ij} = \int \Psi_i^* \Psi_j dV = \delta_{ij}$$

altered the results considerably and it was only natural that the exact overlap matrix $\underline{S}$ would be used more often when the means of computation were sufficiently advanced. An added advantage of including overlap is that one may make use of the remarkably accurate Mulliken approximation[37]

$$\Psi_i(1)\Psi_j(1) \simeq \frac{S_{ij}}{2} [\Psi_i(1)\Psi_i(1) + \Psi_j(1)\Psi_j(1) \qquad (1.63)$$

in evaluating other integrals in which the term $\Psi_i(1)\Psi_j(1)$ occurs.

The true complete wave function of a molecule actually depends upon both the coordinates of the nuclei and the electrons; however, Born and Oppenheimer[38] have shown that, owing to the smallness of the ratio of the mass of an electron to that of any nucleus, the total wave function Ψ_T may be approximated quite well as a product of the nuclear wave function, Ψ_n, and the electronic wave function, Ψ_e, and the quantum mechanical problem essentially becomes uncoupled to form two separate problems

$$\begin{aligned} H_N\Psi_N &= E_N\Psi_n \\ H_e\Psi_e &= E_e\Psi_e\,. \end{aligned} \tag{1.64}$$

Most of the theoretical work of chemistry is directed toward the solution of the problem for the electronic wave function, Ψ_e, and this is what has been referred to, somewhat incorrectly, as the wave function in the previous discussions. In the approximate solution of the quantum mechanical problem for the electronic wave function discussed previously, the nuclei have been assumed to be fixed in a certain geometrical arrangement, usually based upon experimental evidence. The electronic energy of a molecule, however, does depend on the distances between nuclei and there are certain equilibrium distances or bond lengths at which the electronic energy is a minimum.

Quite early in the development of the molecular orbital method, Coulson[39] interpreted the quantity

$$P_{ij} = 2 \sum_k C_{ki}^* C_{kj} \tag{1.43}$$

as the bond order and derived a formula, within the restrictions of the HMO theory by which the bond length of an unsaturated conjugated hydrocarbon could be calculated from P_{ij}. That is, the bond order, P_{ij}, found from the solution of the quantum mechanical problem with a fixed assumed bond length, could in turn be used to calculate the correct bond length. More recently, Nishimoto and Forster[40] and Longuet-Higgins and Salem[41] have derived relations within the SCFMO formalism of the form

$$r_{ij} = r(s) - [r(s) - r(d)]P_{ij} \tag{1.65}$$

where r_{ij} is the bond length, r(s) is the bond length of a single carbon-carbon bond as in ethane and r(d) is the length of a "pure" double carbon-carbon bond as in ethylene. With the new electronic computers, it is no longer necessary to restrict the bond length to a fixed value but rather it may be allowed to vary in a manner consistent with a relation such as (65) and the energy minimized with respect to bond length simultaneously during the iterative solution for the self-consistent LCAO molecular orbitals. This additional technique of allowing the bond length to vary (within limits) represents about the highest level of development of the semi-empirical SCFMO theory.

Another problem related to the effects of the molecular geometry on the solution of the quantum mechanical problem is how to refine the manner in which the resonance integral, β_{ij}, is approximated. As was pointed out earlier, β_{ij} is a function of bond length and it is usually

approximated as a constant parameter. However, β_{ij} may be taken as a function of the overlap, S_{ij}, or the bond order, P_{ij}, and its effects on the quantum mechanical problem enters more realistically. If the bond length is allowed to vary, β_{ij} may be written as a function of the overlap integrals, S_{ij}, and since these integrals will change with varying bond lengths, β_{ij} is thus a function of bond length. If the quantum mechanical problem is solved with an assumed fixed molecular geometry, β_{ij} may still be made a function of the bond order, P_{ij}, since P_{ij} is related to bond length through equation (1.65). Examples of these approximations for β_{ij} are the "variable β approximation" of Nishimoto and Forster[40]

$$\beta_{ij} = k_1 P_{ij} + k_2 \; ; \tag{1.66}$$

the approximation used by Bloor, et al.[43]

$$\beta_{ij} = \frac{-(I_i + I_j)}{2} \; \frac{S_{ij}}{1+S_{ij}} \quad ; \tag{1.67}$$

and the approximation introduced by Fischer-Hjalmars[44]

$$\beta_{ij} = - S_{ij} \{k_1[(ii\,|G|\,ii) + (jj\,|G|\,jj)] + k_2(ij\,|G|\,ij)\}. \tag{1.68}$$

k_1 and k_2 in equations (1.66) and (1.68) are parameters for correlating theoretical and experimental quantities.

This concludes a very brief summary of the development of the quantum mechanical treatment of chemical systems with particular emphasis on those methods applicable to large unsaturated conjugated

hydrocarbon molecules. No attempt has been made to cover the large amount of work being done to extend these theoretical methods to conjugated systems containing atoms other than carbon and hydrogen or to saturated hydrocarbons. Also untouched is the vast amount of very rigorous and precise work done on very small organic and inorganic systems.

From the point of view of desiring a rigorous theory in which accurate quantities may be calculated from first principles, one must say that the theory in its present stage of development falls short and that improvements must be made. As will be seen in the next section, the chief redeeming quality is that the semi-empirical SCFMO theory with LCAO molecular orbitals presently used can give fairly quantitative results with a reasonable amount of effort.

12. Applications of Theory

The following examples of the calculated energies of electronic transitions (singlet-singlet) and oscillator strengths for various molecules taken from the recent literature are meant to serve two purposes. First, they should illustrate the merits of some of the more recent theoretical methods relative both to each other and relative to experimental values. Secondly, the subject molecules for this comparison are some which are involved in the present work and, therefore, may be used as a check on the methods used in this work.

The oscillator strength, f, is a measure of the intensity of electronic transitions. The term originated in classical electromagnetic theory in which it represents a measure of the effective number of

electrons whose oscillations produce a given line or band in the spectrum. The oscillator strength was reinterpreted in terms of quantum mechanics and for transitions between nondegenerate states Ψ_i and Ψ_j, it is determined from the expression

$$f_{ij} = \frac{8\pi^2 m_e c}{3he^2} \omega \sum_{i=x,y,z} Q_i^2 = 1.085 \times 10^{11} \omega \sum_{i=x,y,z} Q_i^2 \qquad (1.69)$$

where m_e is the mass of the electron, e is the electronic charge, c is the speed of light, h is Planck's constant, ω is the frequency of the transition in cm^{-1} (wave numbers) and the transition moment integral, Q_i, is given by

$$Q_i = \int \Psi_i^* \, \bar{i} \, \Psi_j dV \quad (i = x,y,z) \qquad (1.70)$$

where $\bar{i}$ is the algebraic sum of the ith coordinates of the several electrons. The experimental expression for the oscillator strength is given by

$$f_{ij} = \frac{.1028c^2 m_e}{N_n \pi e^2} \int \varepsilon(\omega) d\omega = 4.32 \times 10^{-9} \int \varepsilon(\omega) d\omega \qquad (1.71)$$

where it is assumed that $N_n = 2.69 \times 10^{-19}$ molecules per cm^3 and ε is the molar extinction coefficient in units of liter-mole^{-1}-cm^{-1}. The methods for the calculation of the intensities of electronic transitions are summarized in the work of Mulliken and Rieke.[45]

In the following tables of transitions for various molecules, the methods of calculation cited are as follows:

Method 1: This method was developed by Bloor[43] and the calculations done by him. The general method is the semi-empirical SCFMO method with LCAO molecular orbitals and configuration interaction. The atomic orbital functions used are 2p Slater functions with an effective nuclear charge of 3.18. Overlap is included and the bond length allowed to change according to equation (1.65) with numerical value

$$r_{ij} = 1.517 - 0.18\ P_{ij}. \tag{1.72}$$

The resonance integral, β_{ij}, was set equal to zero for nonadjacent atomic centers and calculated from equation (67) for nearest neighbors. The one-center repulsion integral, (ii |G| ii), was calculated from the Pariser[25] approximation, equation (1.55), and the two center integrals, (ij |G| ij), from the Mataga[29] approximation, equation (1.59).

Method 2: These calculations were performed by Nishimoto[42] and the method is also an example of the semi-empirical SCFMO theory with LCAO molecular orbitals; however, in these calculations the molecular geometry is fixed, that is, the bond length is a constant. Also, the resonance integral, β_{ij}, is calculated from equation (1.66) and the two-center integral, (ij |G| ij), is approximated by a complicated expression derived in an earlier work[46] which incorporates Dewar's idea of electrons in opposite 2p lobes[33] and an effective refractive index of the electrons' environment. He also assumes A_i is zero in the Pariser approximation for (ii |G| ii).

Method 3: These calculations were done by Nishimoto and Forster[40] and the method is identical to Method 2 except that the Mataga approximation, equation (1.59) is used for $(ij\ |G|\ ij)$.

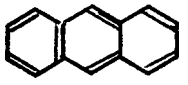
Method 4: This method was proposed by Fischer-Hjalmars[44] and first applied to aromatic molecules by Skancke;[47] however, these particular calculations were performed by Bloor.[43] This method differs from Method 1 only in the form of the resonance integral, β_{ij}, the form used was equation (1.68), and atomic spectroscopic data was used directly for the repulsion integral, $(ii\ |G|\ ii)$, rather than first calculating the valence state ionization potential, I_i, for use in the Pariser approximation, equation (1.55).

Method 5: These calculations are but a few of the large number done by Hummel and Ruedenberg.[48] The general method used was a semi-empirical version of the ASMO-CI theory, that is, the molecular orbitals were determined from the HMO theory and the complete Hamiltonian and antisymmetric wave functions used for energy calculations. The effects of overlap were taken into account, but the molecular geometry was fixed. The resonance integral was taken as a constant for nearest neighbors and zero otherwise. The precise approximations used for the various integrals are those developed by Ruedenberg in a series of six papers on the quantum mechanics of unsaturated conjugated molecules.[49]

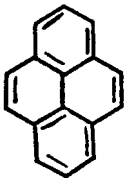
Other examples of calculations for these molecules exist; however, it is felt that most are too limited in scope or do not differ significantly from the examples given. Also, molecular calculations such as

those presented here have been made during each stage of development of theoretical chemistry but the examples given have been limited to those employing the more recent theoretical developments.

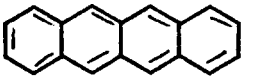
Figure 1.1 gives the conventional chemical structures of the molecules whose electronic transitions are tabulated in Tables 1.1 through 1.12.



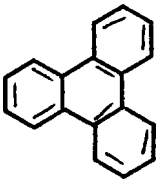
Anthracene



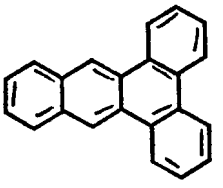
Pyrene



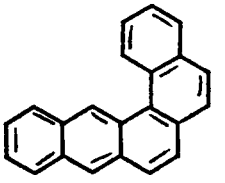
Napthacene



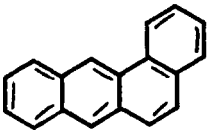
Triphenylene



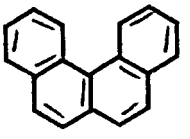
Dibenz(a,c)anthracene



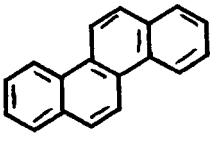
Dibenzo(b,g)phenanthrene



1,2-Benzanthracene



3,4-Benzophenan-
threne

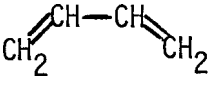


Chrysene

Styrene

$CH_2=CH_2$

Ethylene



cis-Butadiene

FIGURE 1.1 CHEMICAL STRUCTURES OF MOLECULES REFERRED TO IN TABLES 1.1 - 1.12

TABLE 1.1 - ELECTRONIC TRANSITIONS FOR ANTHRACENE

Method 1		Method 2		Method 3	
Energy (ev)	f	Energy (ev)	f	Energy (ev)	f
3.578	0.274	3.58	0.000	3.484	0.317
3.634	0.000	3.59	0.313	3.604	0.000
4.968	2.745	4.50	0.000	4.656	0.000
5.903	0.087	4.79	0.000	4.677	0.000
6.001	0.297	4.81	0.000	4.814	0.000
6.083	0.000	4.84	2.523	4.831	2.522
		5.19	0.044	5.264	0.000
		5.36	0.000	5.850	0.221
		5.87	0.604	5.916	0.560
		6.21	0.000	6.059	0.000
				6.206	0.000
				6.574	0.000

TABLE 1.1 - ELECTRONIC TRANSITIONS FOR ANTHRACENE (CONTINUED)

Method 4		Method 5		Experimental[a]	
Energy (ev)	f	Energy (ev)	f	Energy (ev)	f
3.685	0.000	3.231	0.359	3.34	0.10
3.842	0.200	3.507	0.162	4.83	2.28
5.543	0.001	4.738	0.018	5.61	0.28
5.613	3.230	5.351	2.818		
6.170	0.540	5.760	0.348		
7.940	1.180	6.263	0.222		
		6.540	0.026		
		6.721	0.670		
		7.517	0.089		
		7.580	0.614		
		7.781	0.035		
		8.092	0.023		

[a] See reference 50

TABLE 1.2 - ELECTRONIC TRANSITIONS FOR PYRENE

Method 1		Method 2		Method 3	
Energy (ev)	f	Energy (ev)	f	Energy (ev)	f
3.470	0.000	3.49	0.000	3.470	0.000
3.685	0.701	3.64	0.675	3.556	0.680
4.839	0.956	4.10	0.000	4.271	0.000
5.376	1.616	4.27	0.000	4.306	0.000
		4.77	0.954	4.703	0.948
		4.90	0.000	4.832	0.000
		5.00	0.000	4.946	0.000
		5.08	0.000	5.199	0.000
		5.25	1.485	5.207	1.468
		5.33	0.000	5.266	0.000
		5.98	0.000	5.939	0.000
		6.47	1.046	5.985	0.000
				5.997	0.000
				6.040	0.000
				6.319	0.940

TABLE 1.2 - ELECTRONIC TRANSITIONS FOR PYRENE

(CONTINUED)

Method 5		Experimental[a]	
Energy (ev)	f	Energy (ev)	f
3.325	0.034	3.33	0.002
3.398	0.796	3.71	0.330
4.838	0.909	4.55	0.350
5.440	0.183	5.14	0.850
5.655	1.170	6.26	
5.717	0.002		
6.564	0.161		
6.687	2.135		
7.051	0.209		
7.252	0.000		
7.457	0.039		
7.650	1.855		
7.965	0.013		
8.393	0.042		

[a] See reference 51

TABLE 1.3 - ELECTRONIC TRANSITIONS FOR NAPTHACENE

Method 1		Method 5		Experimental[a]	
Energy (ev)	f	Energy (ev)	f	Energy (ev)	f
2.951	0.293	2.659	0.366	2.951	-
3.294	0.000	3.229	0.312	4.463	-
4.464	3.331	4.140	0.036		
4.847	0.000	4.961	3.285		
4.889	0.050	5.169	0.512		
		5.272	0.079		
		5.723	0.057		
		6.144	0.067		
		6.625	0.952		
		6.785	0.488		
		7.091	0.169		
		7.714	0.030		
		7.795	0.021		
		8.076	0.017		

[a] See reference 52

TABLE 1.4 - ELECTRONIC TRANSITIONS FOR TRIPHENYLENE

Method 1		Method 5		Experimental[a]	
Energy (ev)	f	Energy (ev)	f	Energy (ev)	f
3.944	0.000	3.897	0.000	3.633	-
4.296	0.000	4.084	0.000	4.339	-
4.484	0.000	4.855	0.008	4.773	-
4.901	1.697	5.016	0.428		
5.383	0.045	5.063	2.085		
		5.107	1.780		
		5.317	0.098		
		5.568	0.000		
		5.586	0.013		
		5.777	0.027		
		6.161	0.013		
		6.162	0.010		
		6.193	0.000		
		7.006	0.047		

[a] See reference 52

TABLE 1.5 - ELECTRONIC TRANSITIONS FOR DIBENZ(a,c)ANTHRACENE

Method 5	
Energy (ev)	f
3.583	0.193
3.705	0.100
4.339	0.001
4.647	2.744
4.820	0.126
4.840	0.027
4.899	0.344
5.046	1.067
5.318	0.265
5.474	0.001
5.690	0.282
5.795	0.000
6.003	0.024
6.271	0.109

TABLE 1.6 - ELECTRONIC TRANSITIONS FOR DIBENZO(b,g)PHENANTHRENE

Method 5	
Energy (ev)	f
3.330	0.258
3.598	0.280
3.999	0.543
4.338	1.233
4.633	0.099
4.731	0.205
4.947	0.948
5.273	0.160
5.368	0.385
5.810	0.037
6.223	0.017
6.365	0.003
6.954	0.003

TABLE 1.7 - ELECTRONIC TRANSITIONS FOR 1.2-BENZANTHRACENE

Method 5	
Energy (ev)	f
3.449	0.423
3.652	0.199
4.276	0.475
4.598	1.465
4.795	0.106
4.931	0.258
4.993	0.284
5.919	0.287
5.863	0.311
5.969	0.091
6.172	0.121
6.284	0.049
6.834	0.003

TABLE 1.8 - ELECTRONIC TRANSITIONS FOR 3.4-BENZOPHENANTHRENE

Method 5	
Energy (ev)	f
3.546	0.005
3.879	0.022
4.427	1.392
4.693	0.408
4.819	0.052
4.955	1.274
5.224	0.169
5.451	0.336
5.573	0.003
5.780	0.002
5.918	0.486
5.866	0.000
6.362	0.002

TABLE 1.9 - ELECTRONIC TRANSITIONS FOR CHRYSENE

Method 5	
Energy (ev)	f
3.750	0.291
3.795	0.495
5.070	0.651
5.178	1.511
5.329	1.222
5.797	0.038
6.567	0.304

TABLE 1.10 - ELECTRONIC TRANSITIONS FOR STYRENE

Method 1		Method 5		Experimental[a]	
Energy (ev)	f	Energy (ev)	f	Energy (ev)	f
4.432	0.000	4.495	0.015	4.42	0.02
4.970	0.641	4.783	0.743	5.21	0.24
6.058	0.449	5.824	0.068	(6.20)	
6.307	0.649	6.149	0.781	6.32	
6.347	0.000	6.544	0.537	(6.57)	2.40
		6.929	0.263	6.88	
		7.111	0.109	7.60	
		7.844	0.018		
		8.212	0.212		
		8.536	0.572		

[a] See reference 53

TABLE 1.11 - ELECTRONIC TRANSITION FOR ETHYLENE

Method 1		Method 2		Experimental[a]	
Energy (ev)	f	Energy (ev)	f	Energy (ev)	f
7.700	-	7.25	-	7.28	-

[a] See reference 54

TABLE 1.12 = ELECTRONIC TRANSITION FOR cis-BUTADIENE

Method 2	
Energy (ev)	f
5.22	-

II.

INTERPRETATION OF PENTACYCLIC AROMATIC HYDROCARBON TRANSITIONS IN TERMS OF COMPOSITE SYSTEM APPROXIMATIONS

INTERPRETATION OF PENTACYCLIC AROMATIC HYDROCARBON TRANSITIONS IN TERMS OF COMPOSITE SYSTEM APPROXIMATIONS

A. Classification of Polycyclic Aromatic Hydrocarbon Spectra

Ever since chemists have begun determining the ultraviolet and visible absorption spectra of large groups of the polycyclic condensed ring aromatic hydrocarbons, they have been aware of striking similarities in the spectra of various molecules of this class. These spectral similarities have led to attempts to formulate classification systems whereby the bands in the spectra of the various molecules could be classified according to a given set of transitions common to all molecules of this class. The first classifications were naturally empirical in nature; however, attempts were soon made to develop a theoretical justification for these classifications.

The strictly empirical classification system which is almost universally used was developed by Clar[55] during his many years of extensive chemical study of the polycyclic aromatic hydrocarbons. In this system, bands in the various molecules which show similar intensities and vibrational fine structure, and which react, that is, shift in wavelength in a similar fashion upon substitution or enlargement of the pi-electron system by condensation of additional benzene rings, are given the same label. These band labels are α-band, p-band, β-band, and β'-band and, generally, the bands appear in this order with the α-band at the longest wavelength and β'-band at the shortest. Clar[55] and his associates have been able to deduce rules for the behavior of these bands as a

function of the number and arrangement of the condensed benzene rings so that these spectral bands could in turn be used to predict the gross structure and shape of unknown pi-electron systems. However, Clar's[55] empirical classification system in no way attempts to correlate these spectral bands with the quantum mechanical description of the molecules.

One of the first and certainly most well-known theoretical classification systems is the one introduced by Platt.[56] This system is limited to the cata-condensed polycyclic aromatic hydrocarbons, which are those compounds of empirical formula $C_{4n+2}H_{2n+4}$, having no carbon atom belonging to more than two rings and thus, each carbon atom is on the periphery of the conjugated system. Samples of these compounds are anthracene, benz(a)anthracene, and naphthacene.

Platt's classification system is theoretical, not in the sense that one may calculate electronic transitions from it, but rather in that it attempts to correlate the experimentally observed transitions with the transitions of a very simple quantum mechanical model of the molecule. His treatment is based on the assumption that, to a crude approximation, the one-electron molecular orbitals of a cata-condensed aromatic hydrocarbon may be treated as analogous to the wave function of an electron moving in a circle whose circumference is equal to the length of the perimeter of the molecule. With the further assumption that the potential energy is a constant all around the circle, the problem is reduced to that of a plane rotator with wave functions

$$\Psi = \frac{1}{\sqrt{2\pi}} e^{im\phi} \tag{2.1}$$

and energy values

$$E = \frac{m^2h^2}{2m_e l^2} \tag{2.2}$$

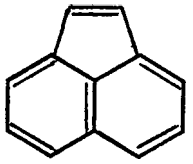
where m = 0, ±1, ±2, . . . , ϕ is the polar angle about the center of the circle, l is the circumference at the circle, m_e is the mass of the electron, and h is Planck's constant. The quantum number m in this case is also a measure of the angular momentum about the axis of rotation posessed by the rotator.

The ground state description of the molecule is formed by placing two electrons in each of the molecular orbitals beginning with the orbitals of lowest energy, that is, m = o, m = +1, m = -1, etc., until all of the electrons of the molecule have been assigned. Note that the orbitals corresponding to m = +i and m = -i are degenerate. Excited state descriptions may be formed by promoting an electron from a molecular orbital of lower energy to one of higher energy. The molecular states are then characterized by the total angular momentum of all the electrons, that is, the algebraic sum of the quantum numbers, m, of all the electrons. From these simple quantum mechanical descriptions, Platt then formed his classification system by characterizing or labeling electronic transitions according to the change in the total angular momentum which occurs upon excitation from one molecular state to another. The transition labels derived in this way for the

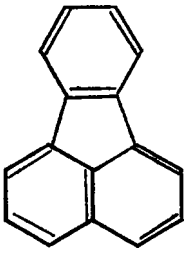
simple model are then extended to the transitions which occur in the actual molecule. The Platt labels may generally be matched to the Clar labels as follows: $^1L_b \rightarrow \alpha$, $^1L_a \rightarrow p$, $^1B_b \rightarrow \beta$, and $^1B_a \rightarrow \beta'$.

While both Clar[55] and Platt's[56] classification systems have been attempts to essentially develop a uniform labeling system for the electronic transitions of large numbers of the polycyclic aromatic hydrocarbons, the later more sophisticated studies have concentrated on interpreting the electronic transitions of particular molecules in terms of the various parts of the molecule. This type of approach is best exemplified by the works of Simpson[57] and of Longuet-Higgins and Murrel.[58] In this "independent systems" or "molecules in molecules" approach, it is assumed that the molecule is a composite system, R-S, and that the electronic transitions may be described in terms of local excitations in the two parts, R and S, and electron transfer transitions arising from excitation of an electron from a molecular orbital in one part to a molecular orbital in the other part. Longuet-Higgins and Murrell[58] gave a theoretical development for such composite systems and discussed the electronic transitions of biphenyl, butadiene, and styrene in terms of it.

The latest attempt to analyze the electronic spectra by assuming the molecule to be a composite two part system is the study of acenaphthylene and fluoranthene (see Figure 2.1) by Heilbronner, et al.[59]



Acenaphthylene



Fluoranthene

Figure 2.1

They characterized these two molecules as "weakly" non-alternant which means that they consist of alternant subunits linked by non-essential double bonds in such a way that although alternancy is lost for the compound system, the subunits retain much of their individuality. The component parts of these two molecules are thought to be quite loosely coupled and this led Heilbronner, et al.[59] to attempt to describe the lower energy electronic transitions of the two subject molecules in terms of the lower energy transitions of naphthalene, benzene, and ethylene alone. They declared the approach a failure when it was found that higher energy local excitations and electron-transfer excitations mixed considerably with the lower energy local excitations to produce the lower energy transitions of the compound molecules. Their method of correlating the orbital energy levels of the subject molecules with the orbital energy levels of the component parts was rather unique. They first divided the coefficients of each of the LCAO molecular orbitals for the subject molecule into two sets, each set corresponding to the carbon centers of one of the two assumed parts of the molecule. On the basis of a "resemblance" between the coefficients for a part of the complete molecule and the

coefficients of the molecular orbitals of that part when treated as a separate molecule, the molecular orbital of the subject molecule was interpreted as being a combination of the molecular orbitals of the two parts. The orbital energy of the complete molecule was then interpreted as arising from the combination of the orbital energies of the two molecular orbitals of the two parts forming the complete molecule. From this correlation, the excitations of electrons from one orbital to another in the subject molecule could be interpreted in terms of excitations among the various orbitals of the component parts. A composite systems approach, essentially identical to that of Longuet-Higgins and Murrell, was used by Mori[60,61] to calculate the electronic transitions of benzyl radical. He first calculated the transitions neglecting the effects of the electron-transfer configurations[60] and then recalculated the transitions allowing for the effects of the electron-transfer configurations.[61] He concluded that the consideration of the electron-transfer configurations did not materially alter the results. Recent experimental work by Johnson and Albrecht[62] on the benzyl radical indicates that the composite systems approach of Mori predicts the transitions of this radical much better than the conventional molecular orbital treatment.

The research to be described in this work was prompted by the observation that many of the electronic transitions of the pentacyclic aromatic hydrocarbons, on the basis of extinction coefficient, vibrational structure, and general appearance, appear to be quite similar to some of the electronic transitions observed in the tetracyclic

aromatic hydrocarbons. These similar transitions appear, however, to be shifted considerably in wavelength in going from the smaller molecule to the pentacyclic. In order to theoretically interpret a phenomenon such as this, the obvious theoretical approach is the "molecules in molecule" approach in which these compounds are treated as a composite two-part system.

This theoretical study, utilizing a "molecules in molecule" approach, has been performed on a representative group of five pentacyclic hydrocarbons. These compounds are benz(a)napthacene (I), benzo(b) chrysene(II), dibenzo(b,g)phenanthrene(III), dibenz(a,c)anthracene(IV), and 3,4-benzopyrene(V). (See Figures 2.2 through 2.6). In essence the theoretical study consists of first dividing the pentacyclic into a two-component system and calculating the electronic transitions for this system when the two components are first, non-bonded, second, weakly bonded, and third, when the two components are completely bonded to form the molecule as it is assumed to actually exist. In this manner the origin of the electronic transitions of the pentacyclic aromatic hydrocarbon may be interpreted in terms of local excitations of the component parts and electron-transfer transitions between the component parts. It must be emphasized that it is not desired to be able to classify all the transitions in terms of the transitions of the components, but rather to see if there are certain transitions which can conceivably be interpreted in terms of the local excitations in a composite system model of the complete molecule. The existence of such electronic transitions offer a theoretical interpretation for the observed transitions of

the pentacyclic aromatic hydrocarbons which appear similar to the transitions of smaller polycyclic aromatic hydrocarbons. Implicit in all this work is the assumption that the treatment of the molecule as a single quantum mechanical system is essentially best.

In applying the "molecules in molecule" approach to these polycyclic aromatic hydrocarbons, a unique problem arises. This is the fact that on the basis of structure or chemical evidence there is no obvious way to determine how the larger molecule should be divided into its two component parts. Even when the component parts are limited, as in this study, to even alternant conjugated hydrocarbons, one of which must be a tricyclic or tetracyclic aromatic hydrocarbon, there are generally two or three ways to divide the pentacyclic molecule which are, on the surface at least, equally suitable. Consequently, the calculation of the electronic transitions discussed above has to be repeated for each assumed two-component system corresponding to a given pentacyclic molecule, and the problem of which system is the best representative must be resolved. Unfortunately, no rigorous theoretical answer has been found; however, this problem can be somewhat resolved on the basis of some semi-quantitative arguments as well as examination of the calculated absorption spectra.

B. Theory: The Interaction of Excited Electronic Configurations in a Composite System

The quantum chemical problem presented in this work is treated within the theoretical formalism of the semi-empirical SCFMO theory

with configuration interaction and LCAO molecular orbitals. The general aspects of this theory were discussed earlier in the section entitled Summary of Theoretical Chemistry and will not be discussed here. However, in dealing with a composite system it is important to understand how the states arising from the local excitations of electrons in the component parts of the system and the states arising from the transfer of electrons from one part to the other interact with one another. The first part of this discussion will be devoted to the theory of these interactions and will closely follow the development given by Longuet-Higgins and Murrell.[58] Although their theoretical development was for a composite system consisting of two parts joined by a single bond, no inconsistency could be found in our work by applying it to a composite system joined by two identical bonds. This theory has been found to correctly predict the behavior of a composite system formed by setting the resonance integrals of two bonds to zero.

Before proceeding it is convenient to introduce the following notation for the singlet excited configurational wave functions. $\phi_i^{-1}\phi_k$ will represent the configurational wave function in which one electron is excited from an occupied molecular orbital ϕ_i to an unoccupied orbital ϕ_k. In the case of singlet excited configurations, to which this discussion is limited, $\phi_i^{-1}\phi_k$ is thus an abbreviated symbol representing the difference of two Slater determinants. [See equations (1.34) and (1.35) in Summary of Theoretical Chemistry].

To begin let R-S be an alternant unsaturated conjugated hydrocarbon made up of two unsaturated hydrocarbon residues joined by two identical bonds. If the two component parts, R and S, are initially regarded as separate, or non-bonded, the self-consistent molecular orbitals for the composite system, R-S, are just those for the separate subsystems, R and S. The molecular orbitals of R will be designated ϕ_i and those of S as ω_i.

The first question is: how are these molecular orbitals modified when R and S are joined together? Suppose the bonds are formed between atoms μ and λ in R and ν and σ in S. Then, Pople[24] has shown that if Ψ_μ, Ψ_ν, Ψ_λ, and Ψ_σ are the 2p atomic orbital functions of these atoms, the changes in the molecular orbitals are entirely determined by the value of the resonance integrals [equation (1.41)]

$$\begin{aligned} \beta_{\mu\upsilon} &= \int \Psi_\mu^*(1) H_{core}(1) \Psi_\nu(1) dV(1) \\ \beta_{\lambda\sigma} &= \int \Psi_\lambda^*(1) H_{core}(1) \Psi_\sigma(1) dV(1) \end{aligned} \tag{2.3}$$

where H_{core} is the one electron core Hamiltonian

$$H_{core}(1) = -\frac{1}{2}\nabla^2(1) - \sum_k V_k(1). \tag{2.4}$$

In this development it will always be assumed that $\beta_{\mu\nu} = \beta_{\lambda\sigma}$. It is convenient to first ignore the change in $H_{core}(1)$ as the subsystems, R and S, are brought together and to introduce it later as a perturbation which leads to a finite value for the resonance integrals $\beta_{\mu\nu}$ and $\beta_{\lambda\sigma}$. That is to say, the combination of the excited states of the

component parts, R and S, to form the excited state of the composite system, R-S, will be examined first for $\beta_{\mu\nu} = \beta_{\lambda\sigma} = 0$ and then the effects of finite resonance integrals examined.

If $\beta_{\mu\nu} = \beta_{\lambda\sigma} = 0$, there will be two kinds of excited electronic configurations for the system R-S. First there are the excited configurational wave functions, $\phi_i^{-1}\phi_k$ and $\omega_m^{-1}\omega_n$, arising from the local excitations in the component parts, R and S, and second, there will be the configurational wave functions, $\phi_i^{-1}\omega_n$ and $\omega_m^{-1}\phi_k$, arising from the transfer of an electron from an occupied molecular orbital of one part to an unoccupied molecular orbital of the other part. However, these individual excited configurational wave functions cannot, in general, be assumed to be independent. Therefore, in a manner analogous to that used to account for the interaction of excited electronic configurations in the usual theoretical treatment of molecules, the excited state wave function of the composite system, R-S, is taken as a linear combination of the various configurational wave functions of the form $\phi_i^{-1}\phi_k$, $\omega_m^{-1}\omega_n$, $\phi_i^{-1}\omega_n$, and $\omega_m^{-1}\phi_k$. The "best" excited state wave functions of R-S, that is, the wave functions which minimize the energy, are found by means of the linear variational method discussed under <u>Approximate Methods</u> in the <u>Summary of Theoretical Chemistry</u>. The excited state energies of the composite system, R-S, are the roots, E_i, of the secular determinant

$$|\underline{H} - \underline{I}E| = 0 \tag{2.5}$$

where the matrix $\underline{H}$ is formed from the interactions of the various excited configurations

$$\int_N \theta_a^{-1}\theta_b H \theta_c^{-1}\theta_d dV^N, \tag{2.6}$$

and H is the total Hamiltonian of the system. $\underline{I}$ in this case is the identity matrix and θ_i is a general molecular orbital. Thus, in discussing the interaction of the various excited electronic configurations the matrix element (2.6) is the quantitative expression which must be examined.

For the composite system, R-S, in which $\beta_{\mu\nu} = \beta_{\lambda\sigma} = 0$, the general expression for the interaction between two different singly excited configurations, $\theta_a^{-1}\theta_b$ and $\theta_c^{-1}\theta_d$, which is applicable is[31]

$$\begin{aligned}\int_N \theta_a^{-1}\theta_b H \theta_c^{-1}\theta_d dV^N = {} & 2\iint \theta_a(1)\theta_b(1)(1/r_{12})\theta_c(2)\theta_d(2)dV(1)dV(2) \\ & - \iint \theta_a(1)\theta_c(1)(1/r_{12})\theta_b(2)\theta_d(2)dV(1)dV(2)\end{aligned} \tag{2.7}$$

where

$$H = \sum_i H_{core}(i) + \frac{1}{2}\sum_i \sum_j \frac{1}{r_{ij}} \tag{2.8}$$

is the total Hamiltonian for this system and $H_{core}(i)$ is given by equation (2.4). From the expression (2.7), the following deductions may be made concerning the interaction of the excited configurations:

(i) If $\theta_a^{-1}\theta_b$ and $\theta_c^{-1}\theta_d$ are locally excited configurations in the same component part, that is, if both configurations are of the form $\phi_i^{-1}\phi_k$ or both of the form $\omega_m^{-1}\omega_n$, then the interaction between them will be independent of whether or not the subsystems, R and S, are joined. This means that configuration interaction occurs among the excited configurations of each component part to produce local excited state

wave functions for each of the subsystems R and S just as if the subsystems had been treated as conventional molecular problems. Furthermore, the interactions of the local excited configurations which determine the local excited states of each subsystem will not be altered when the other subsystem is joined to it to form the composite system R-S.

(ii) If $\theta_a^{-1}\theta_b$ and $\theta_c^{-1}\theta_d$ are locally excited configurations in different component parts, that is, if they are of the form $\phi_i^{-1}\phi_k$ and $\omega_m^{-1}\omega_n$, they will interact by virtue of the first integral of equation (2.7), but the second integral will be zero if the molecular orbitals of the different component parts do not overlap. Thus, in general, there will be interactions between the excited electronic configurations of the two component parts, and therefore, between the local excited state wave functions of the component parts, although this interaction may vanish for other reasons in some cases.

(iii) If $\theta_a^{-1}\theta_b$ and $\theta_c^{-1}\theta_d$ represent configurations in which electrons are transferred in the same direction, that is, if they are both of the form $\phi_i^{-1}\omega_n$ or both of the form $\omega_m^{-1}\phi_k$, then they will interact by virtue of the second integral in equation (2.7), the first integral being zero.

(iv) If $\theta_a^{-1}\theta_b$ and $\theta_i^{-1}\theta_d$ represent configurations one of which is a locally excited configuration and the other is an electron transfer configuration, for example, $\phi_i^{-1}\phi_k$ and $\phi_i^{-1}\omega_n$, or if they represent configurations in which electrons are transferred in opposite directions,

that is, of the form $\phi_i^{-1}\omega_n$ and $\omega_m^{-1}\phi_k$, then there will be no interaction between the excited electronic configurations. These interactions will be finite only if the resonance integrals between the two component parts is allowed to be finite. It may be concluded from this that if the resonance integrals, $\beta_{\mu\nu} = \beta_{\lambda\sigma} = 0$, as it has been assumed to so far, the electron transfer configurations may be ignored since transitions to excited states formed by them from the ground state will be forbidden, that is, the oscillator strength will be zero.

The affects of permitting finite resonance integrals, $\beta_{\mu\nu}$ and $\beta_{\lambda\sigma}$, [equation (2.3)] to exist between the two subsystems must now be examined. As noted earlier, the self-consistant field molecular orbitals and orbital energies of the composite system are dependent on the values of the resonance integrals between the subsystems. In fact, in the presence of finite resonance integrals between the subsystems, the self-consistent field molecular orbitals will no longer simply be the self-consistent field molecular orbitals, ϕ_i and ω_i, of the two subsystems R and S which would be found if both were treated as single quantum mechanical systems. Rather, each of the set of molecular orbitals will now span the entire molecule. As long as self-consistent field molecular orbitals are employed, Pople[31] has shown that the interaction of the various excited electronic configurations to form the excited state wave functions is completely determined by equation (2.7). From this, it can be seen that the finite resonance integrals do not directly inter the interactions of the various configurations in the case when self-consistent molecular orbitals are used. Longuet-Higgins and

Murrell[58], however, in their treatment of a molecule as a composite system made the assumption that the molecular orbitals of the composite system did not change upon introducing finite resonance integrals between the two subsystems but are the molecular orbitals, ϕ_i and ω_i of the subsystems R and S. Since the molecular orbitals ϕ_i and ω_i are no longer the self-consistent field orbitals of the composite system, equation (2.7) is no longer valid for the interaction of the excited electronic configurations of the system but will contain an additional finite term arising from the finite resonance integrals. The following theoretical development for this situation, given by Longuet-Higgins and Murrell[58], is presented primarily as an aid in understanding their work since it will not be directly applicable in the present study.

According to Longuet-Higgins and Murrell[58], the resonance integrals, $\beta_{\mu\nu}$ and $\beta_{\lambda\sigma}$, being one-electron elements, will have the effect of allowing the interaction of excited configurations which differ by the position of just one electron. The relevant formulas for these interactions are:

$$\int_N \Theta_o H_{core} \theta_a^{-1} \theta_b dV^N = \sqrt{2} \int \theta_a(1) H_{core}(1) \theta_b(1) dV(1) \tag{2.9}$$

where θ_o is the ground state wave function of the system, and

$$\int_N \theta_c^{-1} \theta_a H_{core} \theta_c^{-1} \theta_b dV^N = \int \theta_a(1) H_{core}(1) \theta_b(1) dV(1) \tag{2.10}$$

$$\int_N \theta_a^{-1} \theta_c H_{core} \theta_b^{-1} \theta_c dV^N = - \int \theta_a(1) H_{core}(1) \ _b(1) dV(1). \tag{2.11}$$

These three expressions will be zero unless θ_a belongs to one subsystem and θ_b to the other, since the change in $H_{core}(i)$ as the subsystems are brought together affects only the resonance integrals, $\beta_{\mu\nu}$ and $\beta_{\lambda\sigma}$. From equation (2.9) one sees that all of the electron-transfer configurations, that is, of the form $\phi_i^{-1}\omega_n$ and $\omega_m^{-1}\phi_k$, will interact with the ground state configuration. The interaction of locally excited configurations with electron-transfer configurations is given by equations (2.10) and (2.11). That is, configurations $\phi_i^{-1}\phi_k$ and $\phi_i^{-1}\omega_n$ or $\omega_m^{-1}\omega_n$ and $\omega_m^{-1}\phi_k$ interact by virtue of equation (2.10) while configurations $\phi_i^{-1}\phi_k$ and $\omega_m^{\theta 1}\phi_n$ or $\omega_m^{-1}\omega_n$ and $\phi_i^{-1}\omega_n$ interact by virtue of equation (2.11).

A final equation which is relevant to a discussion of the theory of a composite system, R-S, is the one for the energy of an electron-transfer configuration. This energy is given by the expression

$$\int_N \phi_i^{-1}\omega_n H\ {}_i^{-1}\omega_n dV^N = E_i - E_n - \iint \phi_i(1)\phi_i(1)(1/r_{12})\omega_n(2)\omega_n(2)dV(1)dV(2) \quad (2.12)$$

where E_i and E_n are the orbital energies of the self-consistent molecular orbitals ϕ_i and ω_n respectively and are determined from the general expression

$$\underline{c}_i^* \underline{F}\, \underline{c}_i = E_i \ . \quad (2.13)$$

(See discussion in <u>Summary of Theoretical Chemistry</u> for further details.) Also it must be noted that only those configurations in which one electron has been excited have been considered. This approximation is usually made since to include multiple excitations would complicate

the theory and calculations considerably. The justification for this approximation is that since these multiply excited configurations are of higher energy, it is unlikely that they will appreciably effect the lower energy states.

C. Theory: Selection of Proper Composite System

This discussion deals with the problem mentioned earlier of how to choose the component parts R and S when approximating a given molecule by a composite system R-S. In other words, what is the "best" way to divide a molecule when treating it as a composite system and there are, within certain limitations, more than one way to divide the molecule? The problem is actually not unique to the present treatment of the polycyclic aromatic hydrocarbons but occurs in all cases where the molecule is treated as a composite system. However, for the molecules previously studied, the choice of the component parts was always rather obvious on the basis of experimental evidence or intuition. For example, the two alternant hydrocarbon parts of the non-alternant hydrocarbons studied by Heilbronner, et al.[59] were rather obvious choices for the component parts. In Longuet-Higgins and Murrell's work,[58] the two benzene rings of biphenyl, the two ethylene residues in butadiene, and the benzene ring and ethylene residue of styrene were also rather obvious choices for the component parts. It should also be noted that the viewpoint of these previous studies was that the composite system with relatively little interaction between the component parts was, or should have been at least, a truer

representation of the molecule than the usual assumed picture of the molecule being a single quantum mechanical system.

The theoretical formalism apparently does not provide a direct answer to the problem of choosing the proper composite system. Thus, in this present study it will be necessary, as in the previous work, to rather arbitrarily base the choice of a proper composite system on the particular objective of the study.

To develop the criteria for choosing the proper composite system to approximate a given molecule, one may proceed as follows. One may conceptually break various bonds in the given molecule to form the various pairs of component parts which form the different possible composite systems, determine the locally excited electronic configurations and electron-transfer configurations for the various composite systems, allow the excited electronic configurations to interact with the resonance integrals between the component parts set to zero, and then determine the resulting excited states and electronic transitions for the various composite systems. Since the experimental observations indicate that the pentacyclic aromatic hydrocarbons may, to a certain extent, act as a weakly interacting composite system and since the objective of this study is to try to explain the similarity of some of the electronic transitions of the pentacyclics to the electronic transitions of smaller molecules contained within the larger, one is naturally led to choose that composite system whose electronic transitions most closely approximate those determined by treating the subject molecule as a single quantum mechanical system.

Now that the criterion for the selection of the preferred composite system has been defined, the problem is how to determine which of the possible composite systems meets this criterion. The most obvious approach is to compare the calculated transitions of all the composite systems, with zero resonance integrals between the component parts, to the calculated transitions of the subject molecule treated as a single quantum mechanical system. The preferred composite system would, of course, be the one whose transitions most closely "resemble" that of the subject molecule. Unfortunately, the calculated results of the various composite systems may not always be so different as to allow unambiguous judgements to be made concerning the preferred composite system. One would generally like, if possible, a more quantitative means of comparing the possible composite systems.

A possible quantitative approach, which will be examined in this work, to the problem of comparing the possible composite systems and the subject molecule is to define a quantity ΔE as follows. Let $E_1, E_2 \ldots E_n$ be the n self-consistent field molecular orbital energy levels for the molecule when treated as a single quantum mechanical system with $E_1 \leq E_2 \leq \ldots \leq E_n$. Let $A_1, A_2, \ldots A_n$ be the n self-consistent field molecular orbital energy levels for the Ath possible composite system which is an approximation to the subject molecule. Then one may define a quantity ΔE_A as follows

$$\Delta E_A = \sum_{i=1}^{n} (E_i - A_i)^2. \tag{2.14}$$

Since this study deals only with even alternant conjugated hydrocarbons, the energy levels will all occur in pairs symmetrically placed about a certain median value. That is, if $\alpha + \varepsilon$ is an energy level, so is $\alpha - \varepsilon$. (See Semi-empirical SCFMO Theory in Summary of Theoretical Chemistry). This fact is sufficient to ensure that ΔE_A is a minimum for the given sets of energy levels, $\{E_i\}$ and $\{A_i\}$ with respect to some constant shift of the E_i's or A_i's. That is, ΔE_A cannot be minimized further by adding a constant value δ to each energy level A_i. (See Appendix 1).

The justification for using the quantity E_A as a means for determining the proper composite system approximation to the subject molecule is as follows. Since the lower energy electronic transitions of both the composite systems and the subject molecule are derived from the interaction of the one-electron excitations from an occupied molecular orbital to an unoccupied molecular orbital to form the singly excited electronic configurations, it is quite reasonable to assume that the particular composite system whose one-electron molecular orbital excitations match the one-electronic molecular orbital excitations of the subject molecule most closely will also have the electronic transitions which would match those of the subject molecule most closely. The excitation energy from the ith molecular orbital to the jth molecular orbital is given by

$$E_{i\to j} = E_j - E_i - \iint \frac{\phi_i^*(1)\phi_j^*(2)\phi_i(1)\phi_j(2)}{r_{12}}\, dV(1)dV(2) + 2\iint \frac{\phi_i^*(1)\phi_j^*(2)\phi_j^*(1)\phi_i(2)}{r_{12}}\, dV(1)dV(2) \tag{2.15}$$

where E_i and E_j are the energies of the ith and jth SCF molecular orbitals respectively. It has been shown by numerous authors[43,63,64] that the value of the combined integral terms of equation (2.15) is approximately constant within a class of structurally related compounds, for example, the pentacyclic aromatic hydrocarbons. Since the one-electron molecular orbital excitation energies may be considered proportional to the energy values of the orbitals involved, the degree of correspondence of these excitations in the composite systems and the subject molecule may be determined by a measure of the correspondence of the molecular orbital energy levels. ΔE_A, as defined in equation (2.14), is a measure of the overall correspondence of the molecular orbital energy levels of a composite system and the subject molecule when treated as a single quantum mechanical system.

The quantity ΔE_A, as defined, does not take into account the symmetry of the molecular orbitals which determines the oscillator strength or intensity of the transition. Thus the quantity, ΔE_A, in unaffected by the changes in the oscillator strength of the electronic transitions as one passes from the composite system to the single component representation of the molecule. Also, the theoretical significance of ΔE_A, if any, is not obvious from its definition.

One may, perhaps, by the following approach, be able to attach some theoretical meaning to the problem of which composite system is the correct approximation to the subject molecule, that is, the one whose electronic transitions correspond most closely to those of the subject molecule. Recall from the discussion of the SCFMO theory with

LCAO molecular orbitals (see The Self- Consistent Field Molecular Orbital Theory in the Summary of Theoretical Chemistry) that the coefficients and energies of the molecular orbitals satisfy the set of matrix equations

$$\underline{F}\ \underline{c}_i = \varepsilon_i\ \underline{S}\ \underline{c}_i \tag{2.16}$$

where the elements F_{ij} of the matrix $\underline{F}$ are the integrals of the Hartree-Fock Hamiltonian operator F over the atomic orbital functions Ψ_i and Ψ_j,

$$F_{ij} = \int \Psi_i^* F \Psi_j dV\ ; \tag{2.17}$$

$\underline{S}$ is the overlap matrix with elements

$$S_{ij} = \int \Psi_i \Psi_j dV \tag{2.18}$$

and $\underline{c}_i$ and ε_i are the coefficients and the energy respectively of the ith LCAO molecular orbital. Recall also that $\underline{F}$ is defined in terms of the matrices, $\underline{c}_i$.

Consider first the case where the subject molecule is treated as a single quantum mechanical system. For this situation, one will have a particular $\underline{F}$ matrix, $\underline{F}^\circ$, and a particular set of LCAO molecular orbital coefficients and energy values, $\underline{c}_i^\circ$ and ε_i°, which satisfy the set of equations

$$\underline{F}^\circ\ \underline{c}_i^\circ = \varepsilon_i^\circ\ \underline{S}\ \underline{c}_i^\circ . \tag{2.19}$$

Consider next the kth possible composite system, R-S, with the resonance

integrals between the two component parts equal to zero. For this situation, one will have a particular $\underline{F}$ matrix, $\underline{F}^k$, and a particular set of LCAO molecular orbital coefficients and energy levels, $\underline{c}_i^k$ and ε_i^k, which satisfy the set of equations

$$\underline{F}^k \underline{c}_i^k = \underline{\varepsilon}_i^k \underline{S} \underline{c}_i^k \tag{2.20}$$

In this case the set of $\underline{c}_i^k$ and ε_i^k will be composed of the self-consistent field molecular orbitals and orbital energies of the two component parts R and S which would have been obtained if R and S had each been treated as a single quantum mechanical system. Next consider the set of matrix equations

$$(\underline{F}^\circ - \underline{\Delta F})\, \underline{c}_i = \varepsilon_i \underline{S} \underline{c}_i . \tag{2.21}$$

It can readily be seen that if $\underline{\Delta F} = \underline{0}$, then $\underline{c}_i = \underline{c}_i^\circ$ and $\varepsilon_i = \varepsilon_i^\circ$, but if $\underline{\Delta F} = \underline{\Delta F}^k = \underline{F}^\circ - \underline{F}^k$, then $\underline{c}_i = \underline{c}_i^k$ and $\varepsilon_i = \varepsilon_i^k$. This would indicate that a study of the elements of the matrices, $\underline{\Delta F}^k$, for the various possible composite systems may make it possible to find a theoretical reason for a particular composite system being the best approximation to the subject molecule treated as a single system. An overall general comparison of the various matrices, $\underline{\Delta F}^k$, is rather difficult. One possible way may be to calculate the spherical norms, $||\underline{\Delta F}^k||$, of the matrices. This norm of a matrix is defined by

$$||\underline{\Delta F}^k|| = \sqrt{\sum_i \sum_j |\Delta F_{ij}^k|^2} = \sqrt{S_p \underline{\Delta F}^{k*} \underline{\Delta F}^k} \tag{2.22}$$

and discussed at length by Faddeev and Faddeeva.[65] Just as for the vector norms, the condition $||\underline{A}' - \underline{A}|| \to 0$ is necessary and sufficient in order that $\underline{A}' \to \underline{A}$; likewise from $\underline{A}' \to \underline{A}$ it follows that $||A'|| \to ||\underline{A}||$. Unfortunately, nothing can be said about how $||\underline{A}'||$ approaches $||\underline{A}||$.

It should be noted that the concept of a composite system with varying degrees of interaction between the components as developed by Longuet-Higgins and Murrell[58] is not really the same as that implied by equation (2.21). In the treatment of Longuet-Higgins and Murrell, they begin with $\underline{\Delta F} = \underline{F}^{\circ} - \underline{F}^{k}$ in equation (2.21), which yields $\underline{c}_i = \underline{c}_k{}^{k}$ and $\varepsilon_i = \varepsilon_i{}^{k}$ where, as noted earlier, $\underline{c}_i{}^{k}$ and $\varepsilon_i{}^{k}$ are the same self-consistent field molecular orbitals and energies of the two component subsystems obtained when each is treated as a single quantum mechanical problem. The various excited electronic configurations for the composite system were then determined and first allowed to interact in a configuration interaction procedure with zero resonance integrals between the component parts, to produce the excited states of the composite system. To this point nothing is different from the approach of the present study; however, the difference occurs in what is meant by increased interaction between the component parts. In passing to a more strongly interacting composite system, Longuet-Higgins and Murrell[58] still conceive of the composite system as essentially two parts having the same molecular orbitals, orbital energies, and excited electronic configurations, but the various excited electronic configurations are allowed to undergo further interactions under the influence of

finite resonance integrals and consequently, changing the excited state wave functions for the composite system. Thus, Longuet-Higgins and Murrell's concept of the degree of interaction in a composite system is essentially only the degree to which the excited electronic configurations of the composite system interact in forming the excited state wave functions of the composite molecule. In other words, the limit of the strongly interacting composite system is not the subject molecule treated conventionally as a single quantum mechanical system. The reason for this is that the conventional treatment of the molecules they studied was considered not to be appropriate for those molecules.

For the purposes of this present study, the passing from a weakly interacting composite system to a completely interacting system is best conceived of as allowing the matrix $\underline{\Delta F}$ in equation (2.21) to change from $\underline{\Delta F} = \underline{\Delta F}^k = \underline{F}^\circ - \underline{F}^k$ to $\underline{\Delta F} = \underline{0}$. The self-consistent molecular orbitals and energies will change as $\underline{\Delta F}$ changes in addition to changes in the interactions between the excited electronic configurations. The degree of change in the molecular orbitals, orbital energies, and configuration interactions which occur when passing from $\underline{\Delta F} = \underline{\Delta F}^k$ to $\underline{\Delta F} = \underline{0}$ depends on how well the kth possible composite system approximates the actual molecule. This concept of the limit of the composite system is compatible with the viewpoint that the single system treatment is essentially best but that there exists a composite system which is a close approximation to the subject molecule. This is apparently the same viewpoint as that taken by Heilbronner, *et al.* in their work.[59]

A final remark may be made concerning the relationship of the quantity ΔE_k, defined in equation (2.14), and $\underline{\Delta F}^k = \underline{F}^\circ - \underline{F}^k$. The complete set of LCAO molecular orbital coefficients for a given system may be written as a square matrix, $\underline{C}$, given by

$$\underline{C} = (\underline{c}_1 \ \underline{c}_2 \ . \ . \ . \ \underline{c}_n) \tag{2.22}$$

where the $\underline{c}_i$ are the usual 1 x n column matrices of the coefficients of the individual molecular orbitals. If the $\underline{c}_i$ are the self-consistent field molecular orbitals then we have the following relationship:

$$\underline{C}^* \ \underline{F} \ \underline{C} = \underline{D} \tag{2.23}$$

where $\underline{D}$ is a diagonal matrix with the orbital energies of the molecular orbitals appearing on the diagonal. Thus, for the subject molecule treated as a single quantum mechanical system and for the kth possible composite system with zero resonance integrals between the component parts, one has, respectively,

$$\begin{aligned} \underline{C}^{\circ *} \ \underline{F}^\circ \ \underline{C}^\circ &= \underline{D}^\circ \\ \underline{C}^{k*} \ \underline{F}^k \ \underline{C}^k &= \underline{D}^k \end{aligned} \tag{2.24}$$

where $\underline{D}^\circ$ and $\underline{D}^k$ contain the molecular orbital energies of the subject molecule and the kth possible composite system respectively. One may define a matrix $\underline{\Delta D}^k$ as follows:

$$\underline{\Delta D}^k = \underline{D}^\circ - \underline{D}^k = \underline{C}^{\circ *} \ \underline{F}^\circ \ \underline{C}^\circ - \underline{C}^{k*} \ \underline{F}^k \ \underline{C}^k. \tag{2.25}$$

The quantity ΔE_k defined in equation (2.14) is simply the square of the norm of the matrix $\underline{\Delta D}^k$, that is,

$$\Delta E_k = ||\underline{\Delta D}^k||^2. \tag{2.26}$$

One may carry this a step further by defining a matrix $\underline{\Delta C}^k$ by

$$\underline{\Delta C}^k = \underline{C}^\circ - \underline{C}^k \tag{2.27}$$

and substituting $\underline{C}^\circ - \underline{\Delta C}^k$ for $\underline{C}^k$ in equation (2.25). A small amount of algebraic manipulation will yield

$$\underline{\Delta D}^k = \underline{C}^{\circ *}\underline{\Delta F}^k \underline{C}^\circ - [\underline{\Delta C}^{k*}\underline{F}^k\underline{\Delta C}^k - \underline{C}^{\circ *}\underline{F}^k\underline{\Delta C}^k - \underline{\Delta C}^{k*}\underline{F}^k\underline{C}^\circ]. \tag{2.28}$$

If $\underline{\Delta C}^k \simeq \underline{0}$, then $\underline{\Delta D}^k \simeq \underline{C}^\circ\underline{\Delta F}^k\underline{C}^\circ$, and from the properties of the norm, one may derive the inequality

$$||\underline{\Delta D}^k|| = \sqrt{\Delta E_k} \lesssim ||\underline{\Delta F}^k||\cdot||\underline{C}^\circ||^2. \tag{2.29}$$

If $\underline{\Delta C}^k$ is not negligible, then any relationship between ΔE_k and $\underline{\Delta F}^k$ will be considerably more complicated and the limited value of expressions such as equation (2.29) do not justify further developments along these lines.

D. Calculation of Spectra

The electronic transitions for the systems studied in this work were calculated by means of a computer program based on the semi-empirical SCFMO theory with LCAO molecular orbitals with inclusion of configuration interaction. The $\underline{F}$ and $\underline{S}$ matrix elements used are

those given by equation(1.62) in the Summary of Theoretical Chemistry. That is,

$$F_{ii} = -\frac{1}{2}(I_i + A_i) - P_i$$

$$F_{ij} = \beta_{ij} - \frac{1}{2} P_{ij}\gamma_{ij}$$

$$S_{ij} = \delta_{ij}$$

where I_i is the valence state ionization potential of carbon, A_i is the electron affinity of carbon, P_i is the penetration integral, β_{ij} is the resonance integral, γ_{ij} is an approximate form of the integral (ij |G| ij), and P_{ij} is the bond order given by [equation (1.43) in the Summary of Theoretical Chemistry]

$$P_{ij} = 2 \sum_k C_{ki}^* C_{kj}.$$

The following values were used for I_i and A_i in the calculations:

$$I_i = 11.42 \text{ ev} \qquad (2.30)$$

$$A_i = 0.58 \text{ ev.}$$

The Mataga approximation [see equation(1.59) in the Summary of Theoretical Chemistry) was used for the integral (ij |G| ij), that is,

$$\gamma_{ij} = \frac{14.3986}{r_{ij} + a} \text{ ev} = \frac{14.3986}{r_{ij} + 1.3283} \qquad (2.31)$$

where

$$a = \frac{14.3986}{\frac{1}{2}[I_i - A_i + I_j - A_j]} = 1.3283 \qquad (2.32)$$

and r_{ij} is the distance between the ith and jth carbon centers. The penetration integral, P_i, was set to zero in these calculations as is usually done. All of these values and approximations are quite standard in calculations for polycyclic aromatic hydrocarbons (for example, see Ref. 59), and no attempts were made to improve them since the primary objective was not to fit experimental spectra but to examine the "molecules in molecule" concept. The calculated spectra are, however, reasonably comparable to the experimental spectra.

The value of the resonance integrals, β_{ij}, between the carbon centers depends on the quantum mechanical model being treated. In calculating the electronic transitions for the molecule treated as a single quantum mechanical system, β_{ij} is given the value -2.318 ev for all nearest neighbor carbon centers and zero for all non-neighboring carbon centers. In calculating the electronic transitions for the various composite systems with zero resonance integrals between the subsystems, β_{ij} is again given the value -2.318 ev for all nearest neighbor carbon centers and zero otherwise with the exception that β_{ij} is also set to zero for the two pairs of nearest neighbor carbon centers between which the bonds would be conceptually broken to form the two component parts of the composite system. For the case of weak bonding between the component parts of the various possible composite systems, β_{ij} is set to -1.000 ev for the two pairs of nearest neighbor carbon centers between which the component parts of the composite system are bonded and the other β_{ij} are set to -2.318 ev for all other nearest neighbor

carbon centers and zero for non-neighboring carbon centers. The value -2.318 ev for the resonance integral, β_{ij}, between nearest neighbor carbon centers is again a standard empirical value used for this class of compounds and no attempt was made to obtain a better value.

These calculations were made for a fixed molecular geometry, that is, the bond length was not allowed to vary. The sigma bond framework of the molecules studied was assumed to be planar, with the bond length between all bonded carbon centers assumed to be 1.40 Å and the three sigma bonds terminating at each carbon center were considered to be in the plane of the molecule with equal bond angles of 120° between the bonds.

The configuration interaction calculations from which the excited state wave functions and energies are determined is limited by computer time and capacity when the molecules are as large as the pentacyclic aromatic hydrocarbons. In these calculations an upper limit was placed upon both the energies of the excited electronic configurations and the number of configurations considered in forming the excited state wave functions. That is, all the singly excited electronic configurations having an energy within 8.00 ev of the ground state configuration up to a maximum of 50 configurations were used to form the excited state wave functions. This limited configuration interaction procedure means, of course, that the excited state wave functions of lower energy are the most accurate since the neglected high energy configurations do not affect these states very much, but the state functions of the system generally become less accurate as the state energy increases since the

neglected configurations would contribute increasingly to the higher energy states.

The quantities ΔE_k and matrices, $\underline{\Delta F}^k$, were calculated by hand from the SCF molecular orbital energy levels and the $\underline{F}$ matrices obtained from the computer calculations.

It must be noted that calculations of some of the five pentacyclic molecules, which are the subject of the present investigation, have been done by others also. In 1954, Moffitt[66] calculated values of the α, p, and β bands (Clar's[55] classification) of benz(a)napthacene, benzo(b)chrysene, and dibenz(a,c)anthracene by means of a rather unusual and simple theoretical method. This method was based on the perimeter model of the polycyclic aromatic hydrocarbons, used by Platt[56] for the classification of spectra, in which the cross-linkages of the actual molecule were treated as perturbations. The object of Moffitt's[66] study was not to calculate precise values for the transitions of these molecules but rather to demonstrate that his simplified theoretical method could successfully predict the relative locations of the three prominent low energy bands of the various pentacyclic aromatic hydrocarbon isomers. Consequently, Moffitt[66] made no particular effort to fit the experimental values for the transition energies of the molecules, but rather presented his results as a set of relative values which demonstrated his method's ability to predict band changes in the pentacyclic isomers. Koutecky, et al.[67] calculated the value of the p band for twenty polycyclic aromatic hydrocarbons including 3,4-benzopyrene. The basic method used was the semi-empirical ASMO

method and the object of these rather limited calculations for individual molecules was to study the effect of varying degrees of configuration interaction on the value of this particular band. The values obtained for this band agreed well with experiment. Hummel and Ruedenberg[48] calculated the absorption spectra of a large number of polycyclic aromatic hydrocarbons including dibenz (a,c)anthracene and dibenzo(b,g)phenanthrene. Their calculated values for the allowed transitions, that is, transitions with finite oscillator strengths, of these two molecules were given previously in Tables 1.5 and 1.6 of the section entitled Summary of Theoretical Chemistry. The basic method employed by Hummel and Ruedenberg[48] was a semi-empirical ASMO method with configuration interaction and the inclusion of overlap. A comparison of the transition energies of dibenz (a,c)anthracene and dibenzo(b,g)phenanthrene calculated in the present investigation and those calculated by Hummel and Ruedenberg[48] shows a fair correspondence at best. It is possible that their calculations may fit the experimental data somewhat better; however, they made no detailed comparison of their calculated transition energies with experimental values and merely stated that there was reasonable agreement with the experimental spectra of these molecules.

As stated earlier, no particular effort was made in the present investigation to calculate precise values for the transition energies, since the object of this investigation was to find suitable composite system approximations to the subject molecules by means of internally consistent theoretical calculations. The fact that the values of the

transition energies calculated in this investigation do correspond fairly well to experimental values will be demonstrated in a later section.

E. Results

Figures 2.2 through 2.6 give the structures and names of the pentacyclic aromatic hydrocarbons which are the subject of this theoretical investigation. Also, introduced in these figures are the structural diagrams representing the various possible composite systems considered in this study as well as the Roman numeral designations for the molecules and composite systems which will be used in the later discussions.

Figures 2.7 through 2.11, each consisting of many parts, give a graphical representation of the calculated electronic transitions of the subject molecules and the composite systems. These figures are essentially the theoretically determined absorption spectra, each line representing the transition occurring at that energy while the length of the line is proportional to the oscillator strength of the transition. The transitions represented by dots on the energy axis are forbidden transitions having zero oscillator strength.

The numerical values for the electronic transitions and oscillator strengths for the subject molecules and composite systems are given in Tables 2.1 through 2.5. Also shown in these tables are the leading terms of the excited state wave functions given in the form of a linear combination of singly excited electronic configurational wave functions.

The symbol (i-j) used for the configurational wave functions represents the two-determinant singlet wave function formed by exciting a single electron from the ith ground state molecular orbital to the jth excited molecular orbital. A maximum of six contributing configurations are given for each excited state wave function and also those configurations which have coefficients less than 0.15 in magnitude are excluded. The reasons for these limitations are that, first, it will probably be impossible to make any interpretation of the sort desired for excited states which have a large number of excited configurations contributing substantially to them, and second, since the weight of any given configuration in the total excited state wave function is given by the square of the coefficients, those configurations with a coefficient less than 0.15 will represent less than 2.25% of the excited state wave functions.

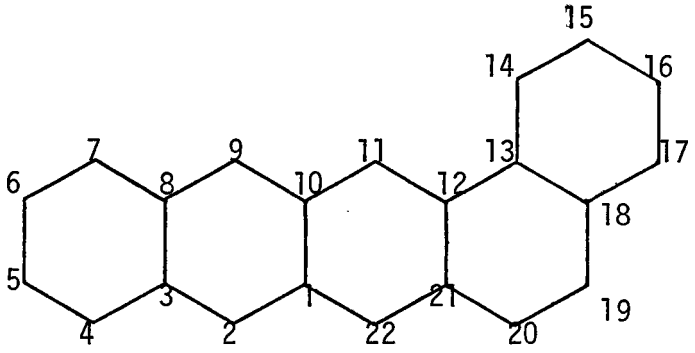
The orbital energies for the self-consistent field molecular orbitals of the molecules and composite systems are given in Tables 2.6 through 2.10. In the orbital energies given for the composite systems with the resonance integral between the component parts, β_{RS}, equal to zero, the energies of the SCF molecular orbitals of the smaller component part are marked with an asterisk (*) while the unmarked orbital energies are those of the SCF molecular orbitals of the larger component part. By convention, the orbital with the lowest energy is designated as the number one molecular orbital, the orbital with the next lowest energy as number two, etc. From this information, one may then determine the origin of the excited configurations which form

the Configurational Interaction Excited State Wave Functions given for the composite systems in Tables 2.1 through 2.5. That is, one may identify the configurations as local excitation configurations for either of the two component parts or electron-transfer configurations. From the molecular orbital energies in Tables 2.6 through 2.10, the values of ΔE, for the various composite systems appearing in Table 2.11, are calculated.

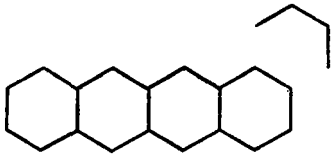
The $\underline{\Delta F}$ matrices for the composite systems of benz(a)napthacene(I), benzo(b)chrysene(II), and dibenzo(b,g)phenanthrene(III) were calculated; however, only the matrices for benz(a)napthacene(I) are given in Table 2.12. Since these matrices are symmetric, only half of each matrix is actually shown.

The various possible composite systems, for which the above calculated results were obtained, were formed by conceptually breaking two bonds in the complete molecules subject to the restrictions that both of the component parts should be an even alternant conjugated hydrocarbon, and that the larger component part should be a tetracyclic or tricyclic aromatic hydrocarbon. These restrictions in the choice of the composite systems were imposed for several reasons. First, and most important, was the fact that the experimental phenomena which this theoretical investigation attempts to elucidate indicates that the electronic transitions of some pentacyclic aromatic hydrocarbons may be related to those of a tetracyclic or perhaps a tricyclic aromatic hydrocarbon. Second, the restriction of the component parts to

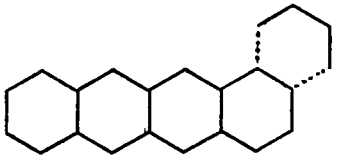
being even alternant hydrocarbons was primarily to ensure that the theoretical methods, with the various approximations and assumptions, would be applicable and consistent throughout the theoretical treatment. Also, this seemed justified by the fact that the pentacyclics were even alternant hydrocarbons and the experimental spectra are apparently interpretable in terms of even alternant polycyclic aromatic hydrocarbons. The final reason for restricting the number of composite systems was economic since the five molecules with the limited number of composite systems treated in this work already required 33 long calculations on an electronic computer.



Benz(a)napthacene (I)

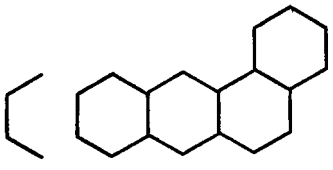


β_{RS} = 0.0 ev

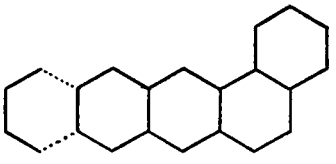


β_{RS} = -1.000 ev

Composite System (Ia)

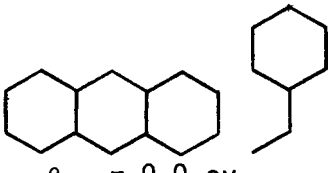


β_{RS} = 0.0 ev

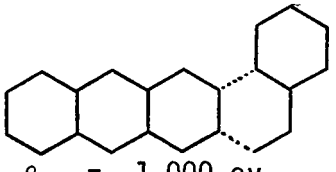


β_{RS} = -1.000 ev

Composite System (Ib)



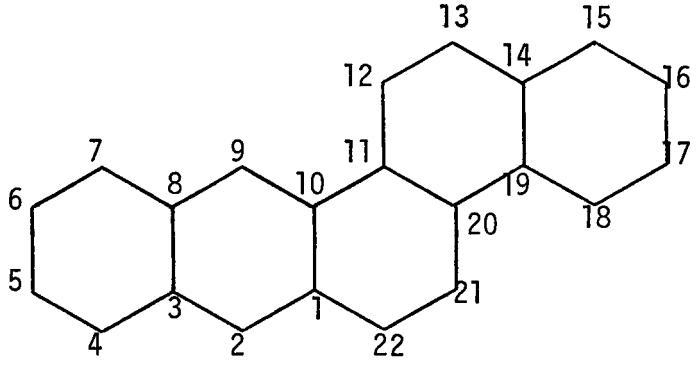
β_{RS} = 0.0 ev



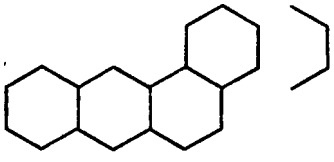
β_{RS} = -1.000 ev

Composite System (Ic)

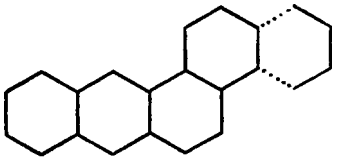
FIGURE 2.2. BENZ(a)NAPTHACENE AND COMPOSITE SYSTEMS



Benzo(b)chrysens (II)

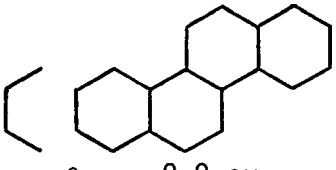


β_{RS} = 0.0 ev

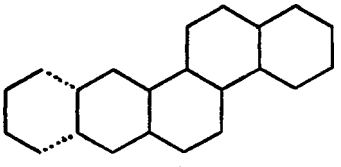


β_{RS} = -1.000 ev

Composite System (IIa)

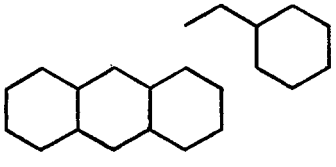


β_{RS} = 0.0 ev

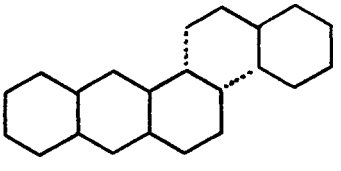


β_{RS} = -1.000 ev

Composite System (IIb)



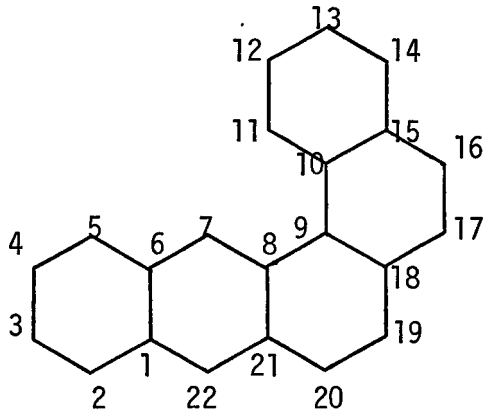
β_{RS} = 0.0 ev



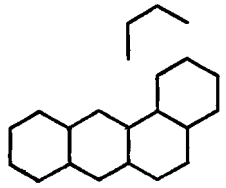
β_{RS} = -1.000 ev

Composite System (IIc)

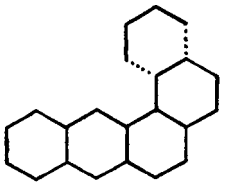
FIGURE 2.3. BENZO(b)CHRYSENE AND COMPOSITE SYSTEMS



Dibenzo(b,g)phenanthrene (III)

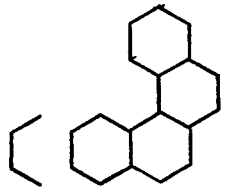


β_{RS} = 0.0 ev

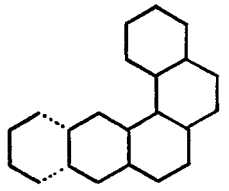


β_{RS} = -1.000 ev

Composite System (IIIa)

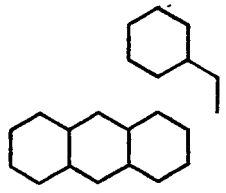


β_{RS} = 0.0 ev

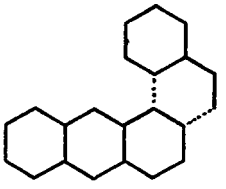


β_{RS} = -1.000 ev

Composite System (IIIb)



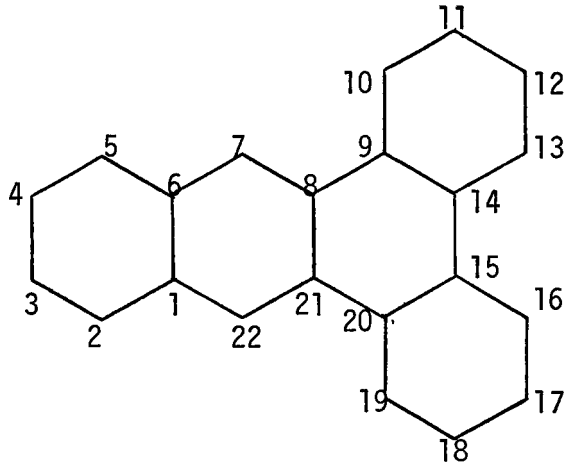
β_{RS} = 0.0 ev



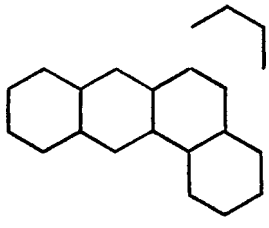
β_{RS} = -1.000 ev

Composite System (IIIc)

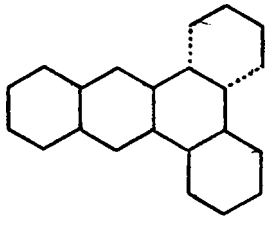
FIGURE 2.4. DIBENZO(b,g)PHENANTHRENE AND COMPOSITE SYSTEMS



Dibenz(a,c)anthracene (IV)

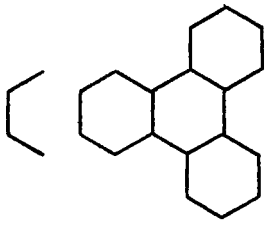


β_{RS} = 0.0 ev

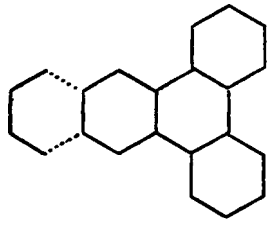


β_{RS} = -1.000 ev

Composite System (IVa)



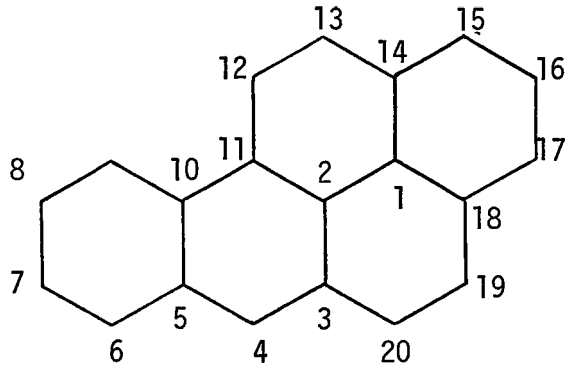
β_{RS} = 0.0 ev



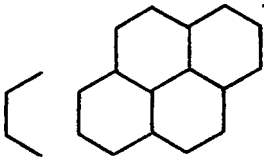
β_{RS} = -1.000 ev

Composite System (IVb)

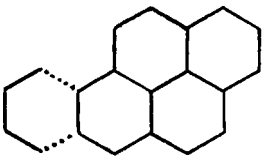
FIGURE 2.5. DIBENZ(a,c)ANTHRACENE AND COMPOSITE SYSTEMS



3.4-Benzopyrene

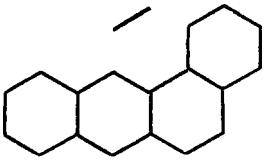


β_{RS} = 0.0 ev

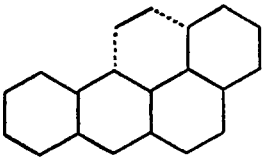


β_{RS} = -1.000 ev

Composite System (Va)

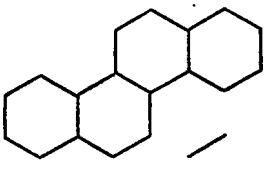


β_{RS} = 0.0 ev

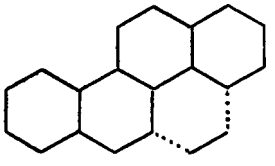


β_{RS} = -1.000 ev

Composite System (Vb)



β_{RS} = 0.0 ev



β_{RS} = -1.000 ev

Composite System (Vc)

FIGURE 2.6. 3,4-BENZOPYRENE AND COMPOSITE SYSTEMS

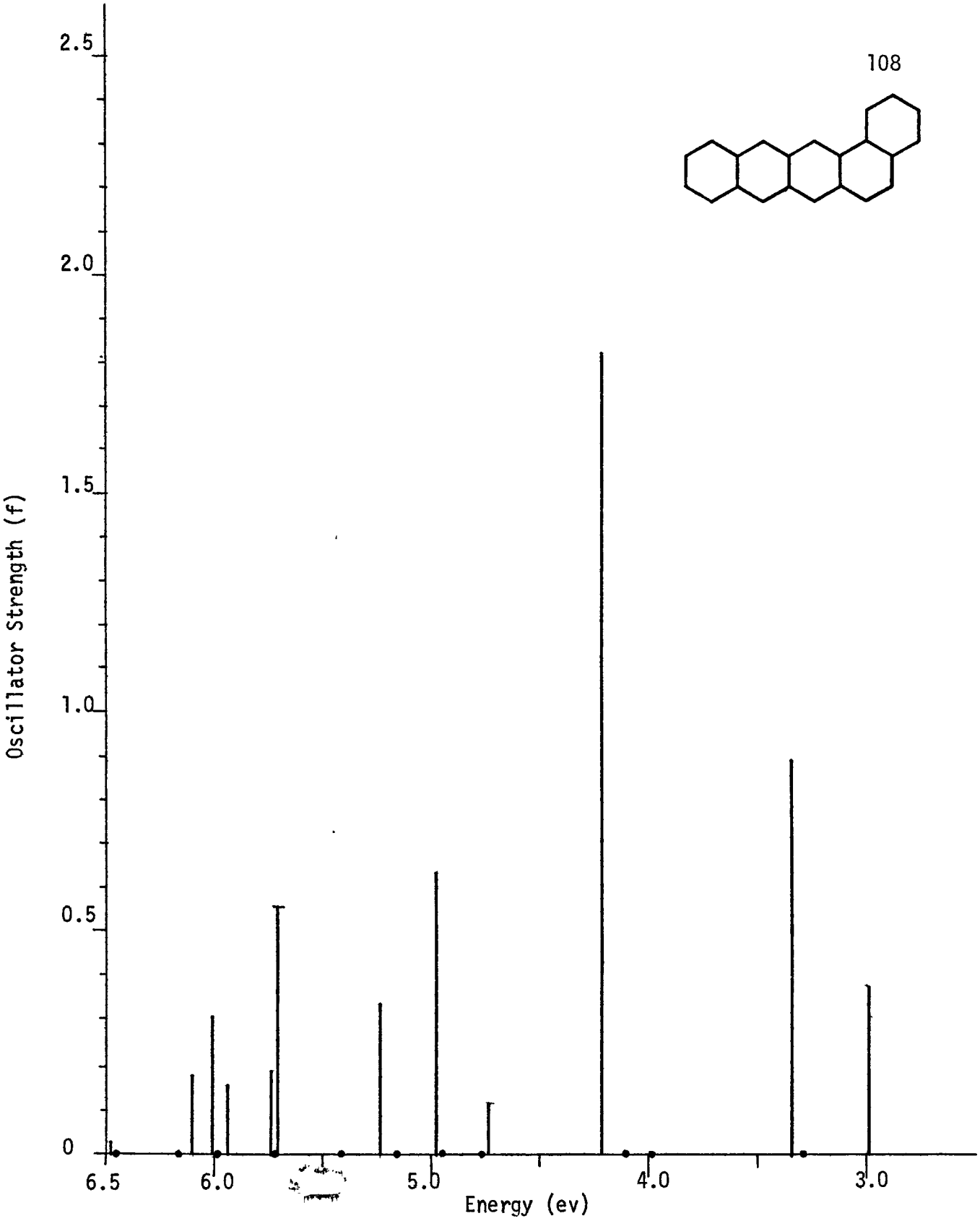


FIGURE 2.7a. CALCULATED ABSORPTION SPECTRA OF BENZ(a)NAPTHACENE (I)

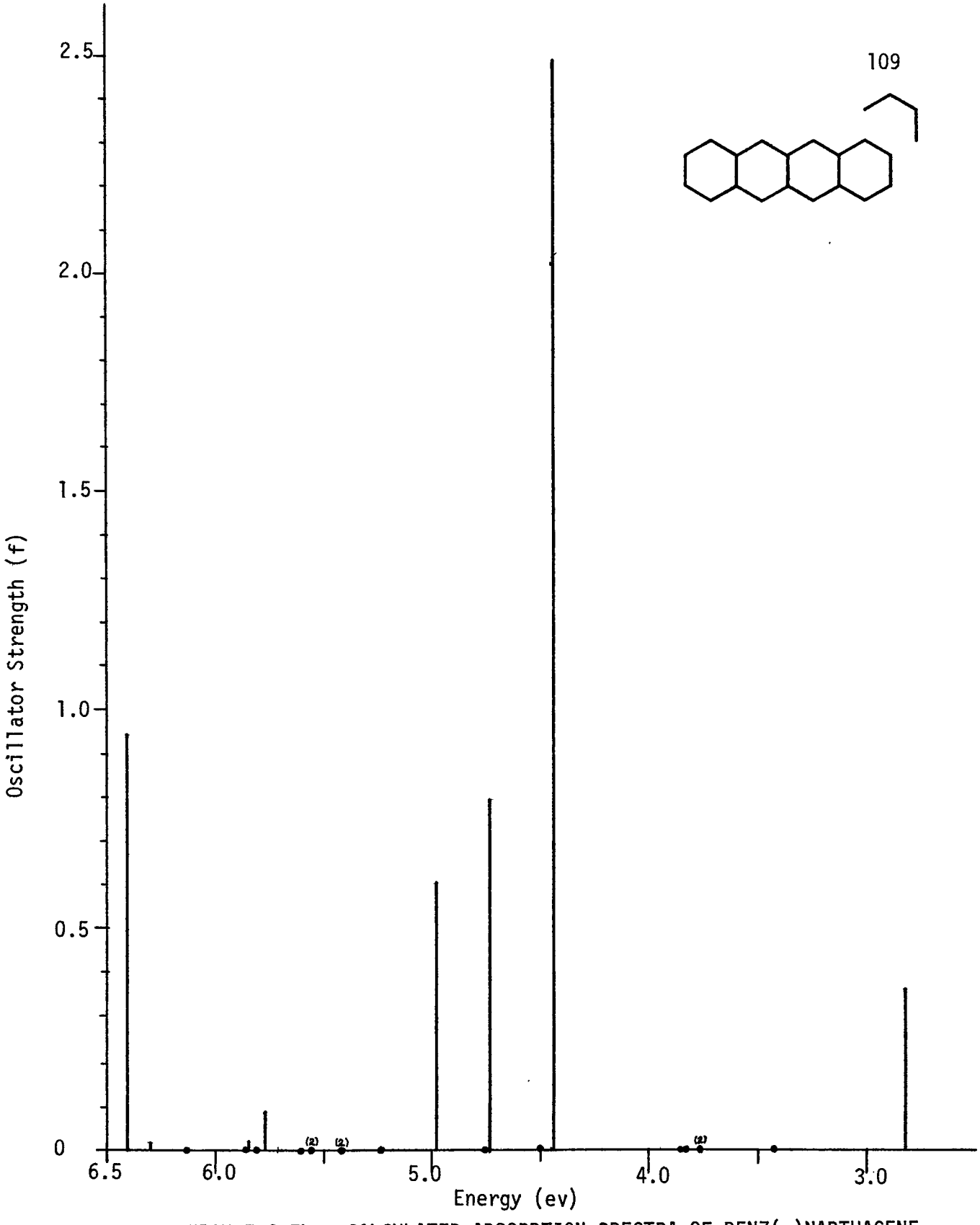


FIGURE 2.7b. CALCULATED ABSORPTION SPECTRA OF BENZ(a)NAPTHACENE COMPOSITE SYSTEM (Ia) WITH β_{RS} = 0.0 ev

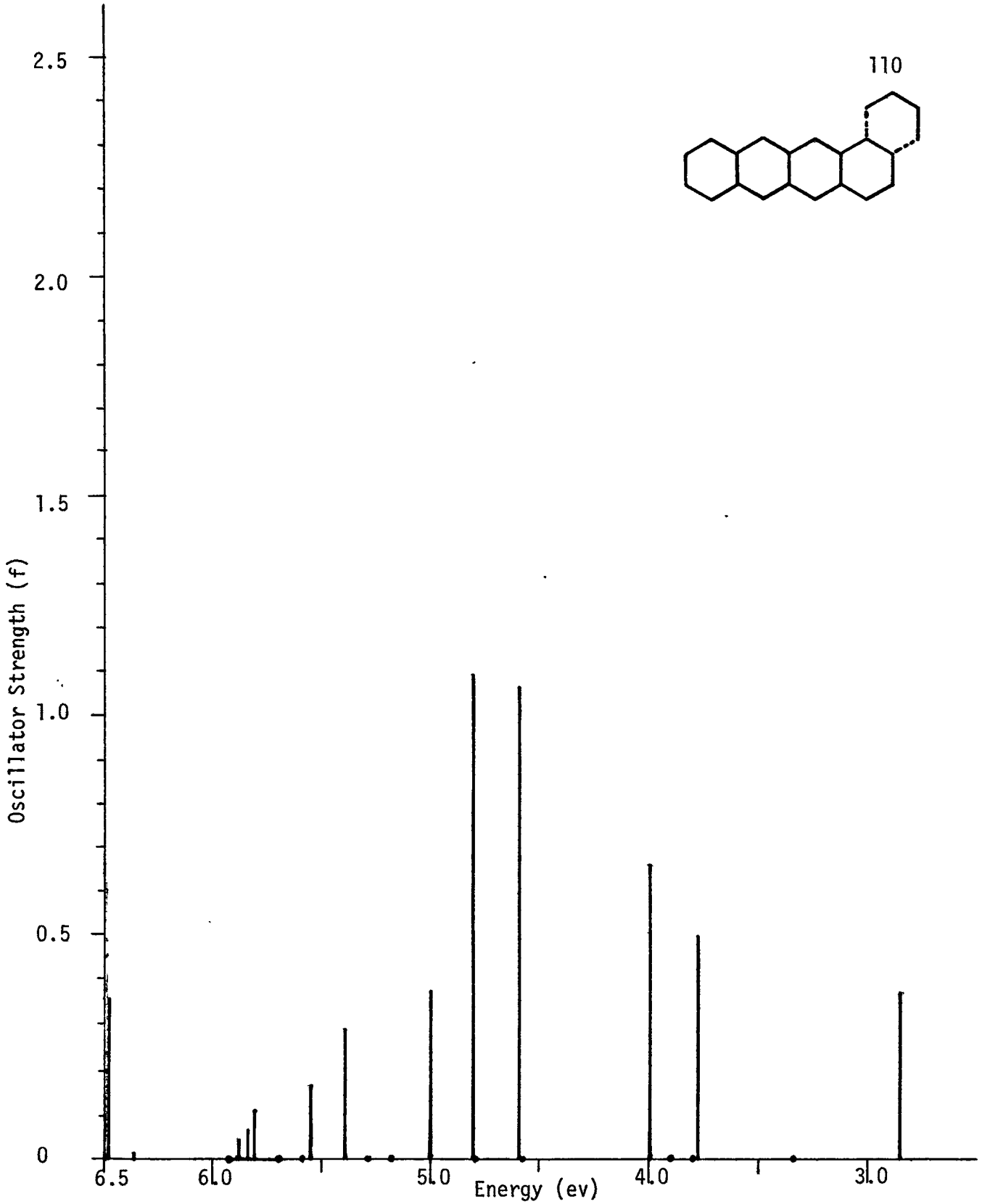


FIGURE 2.7c. CALCULATED ABSORPTION SPECTRA OF BENZ(a)NAPTHACENE COMPOSITE SYSTEM (Ia) WITH β_{RS} = -1.0 ev

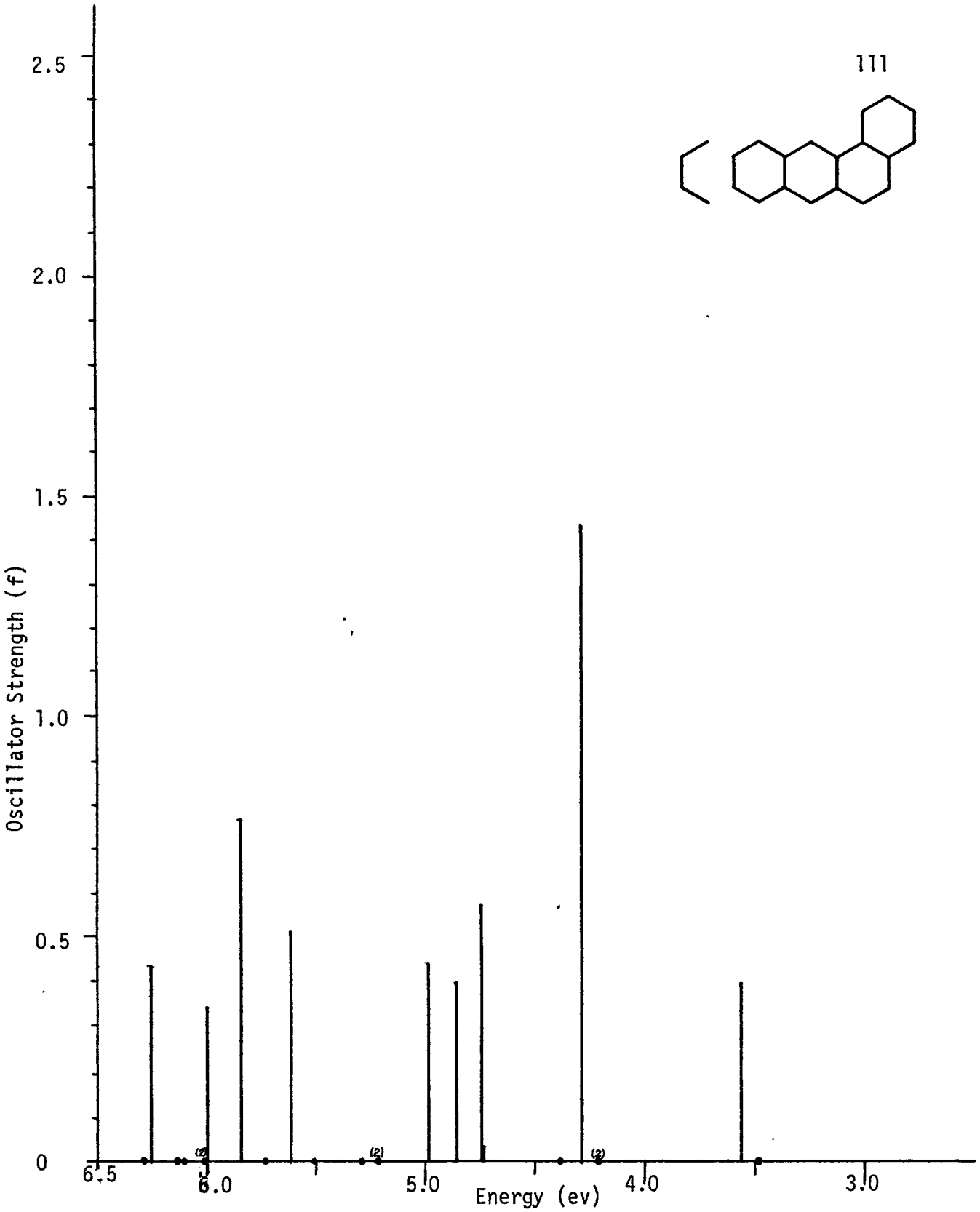


FIGURE 2.7d. CALCULATED ABSORPTION SPECTRA OF BENZ(a)NAPTHACENE COMPOSITE SYSTEM (Ib) WITH β_{RS} = 0.0 ev

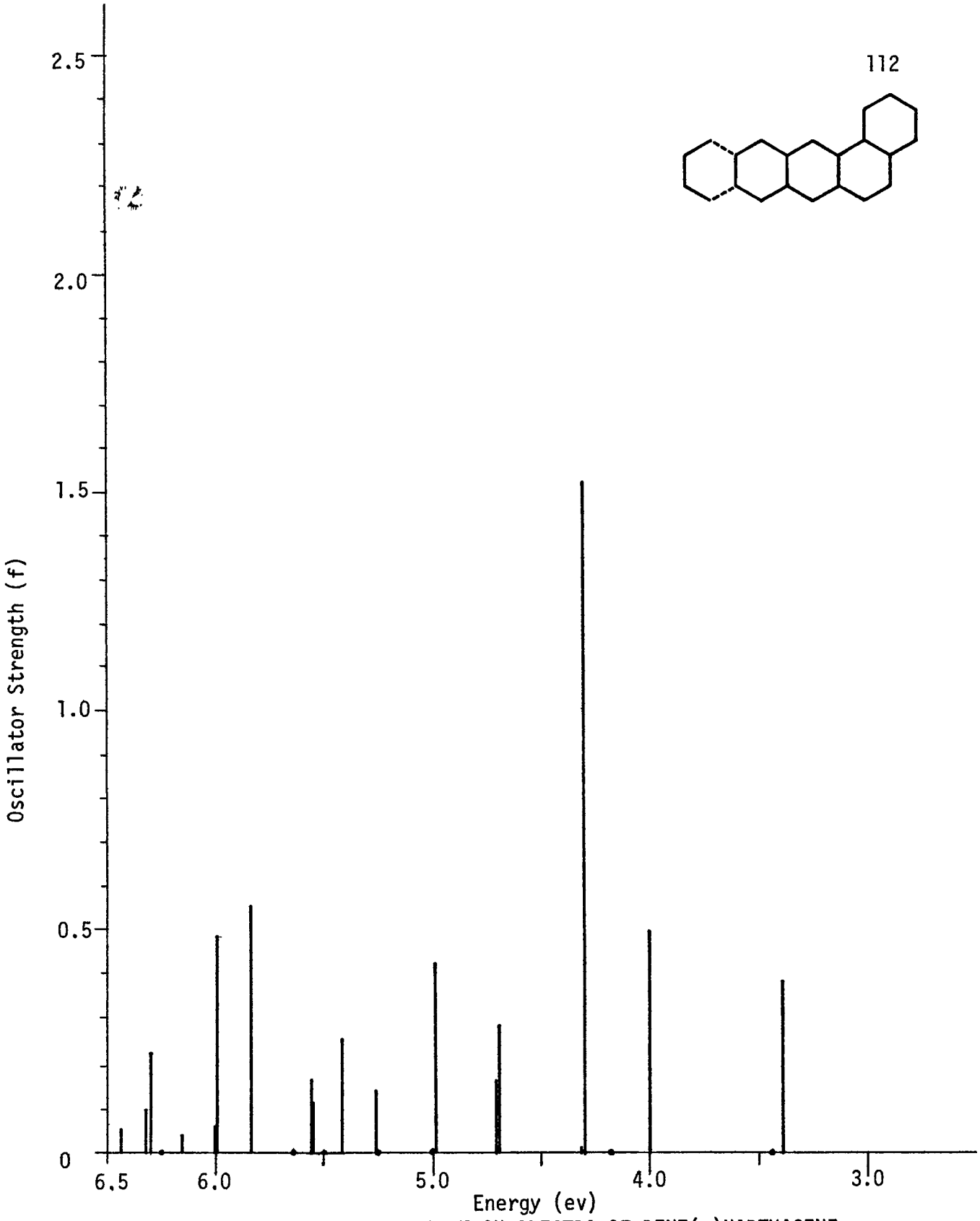


FIGURE 2.7e. CALCULATED ABSORPTION SPECTRA OF BENZ(a)NAPTHACENE COMPOSITE SYSTEM (Ib) WITH β_{RS} = -1.0 ev

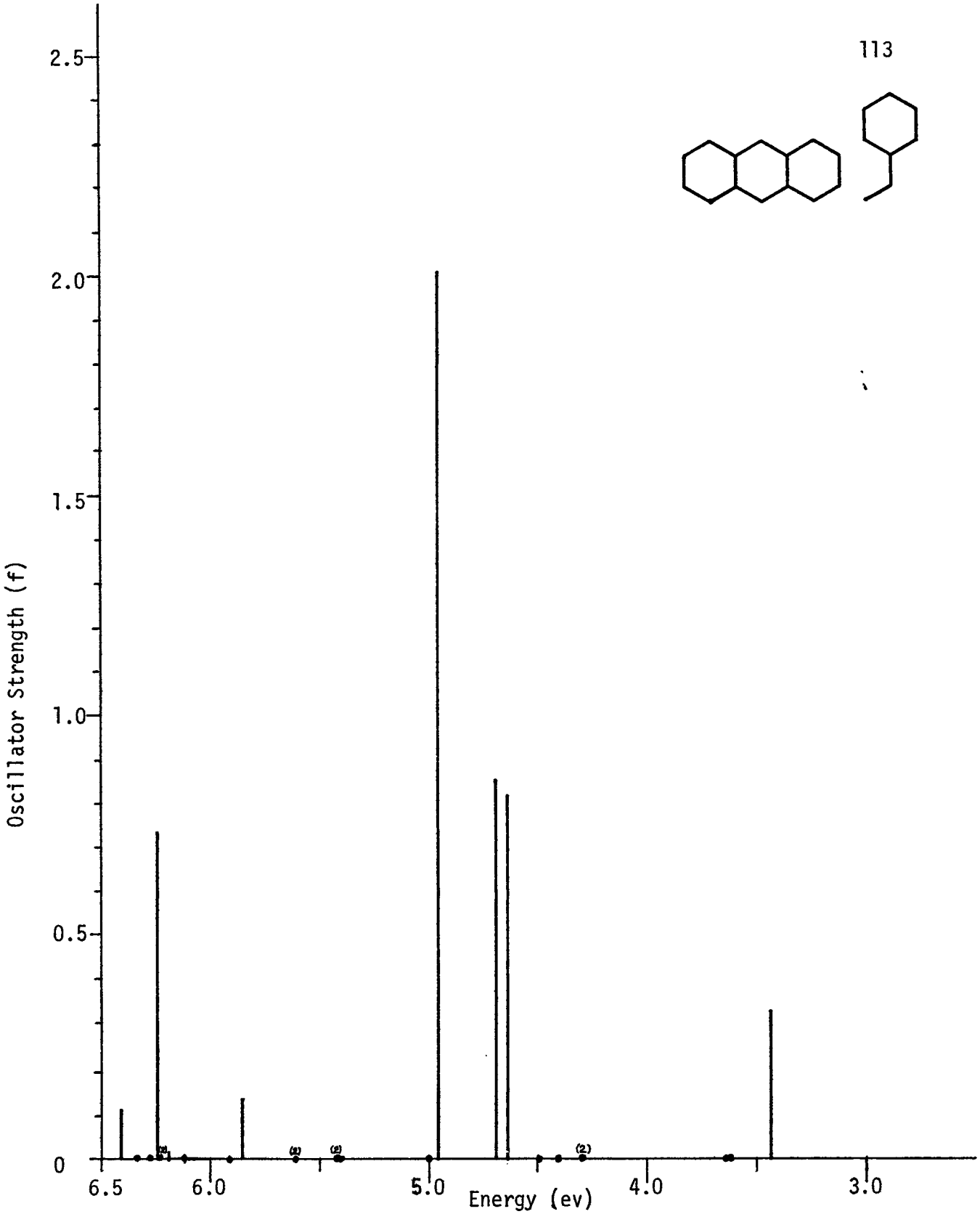


FIGURE 2.7f. CALCULATED ABSORPTION SPECTRA OF BENZ(a) NAPTHACENE COMPOSITE SYSTEM (Ic) WITH β_{RS} = 0.0 ev

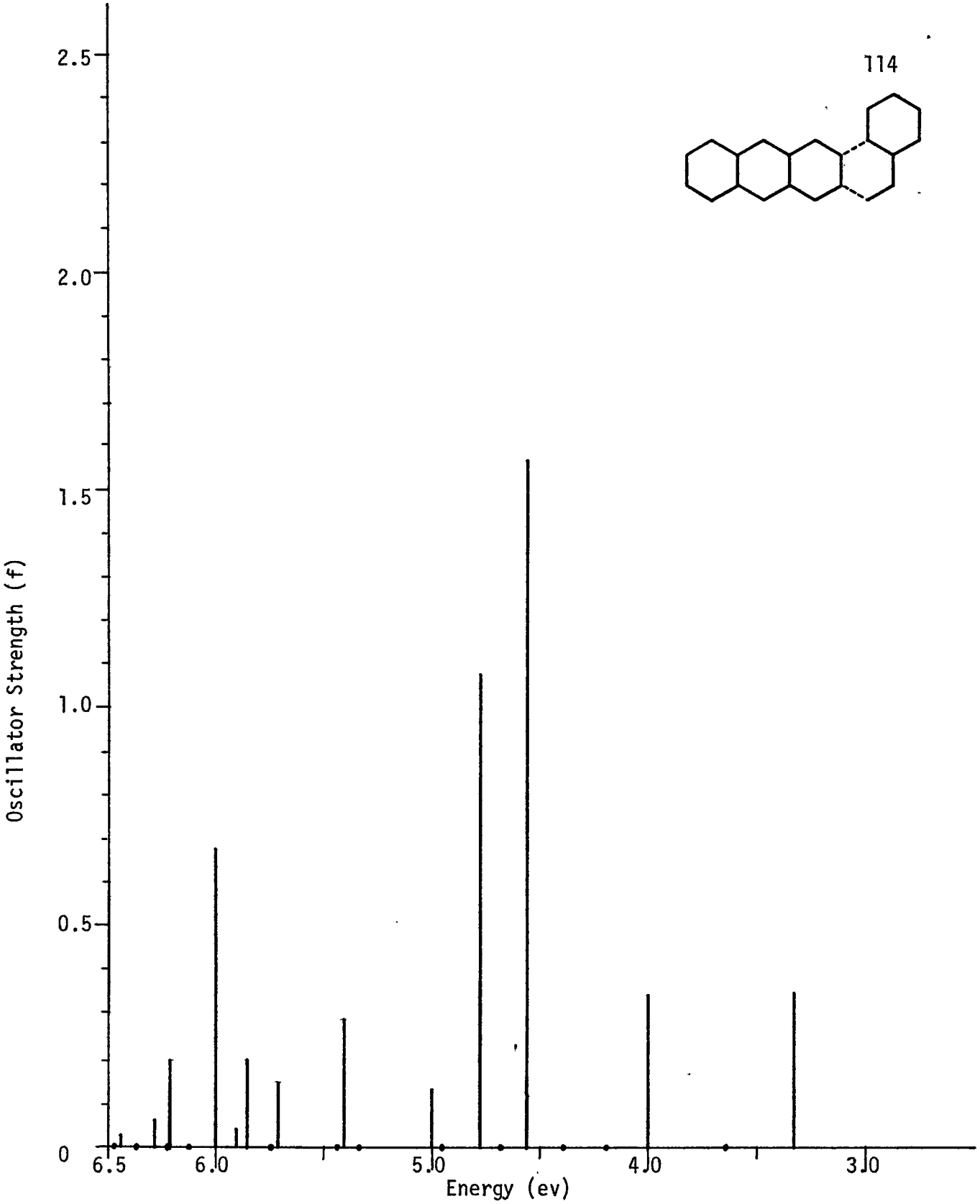


FIGURE 2.7g. CALCULATED ABSORPTION SPECTRA OF BENZ(a)NAPTHACENE COMPOSITE SYSTEM (Ic) WITH β_{RS} = -1.0 ev

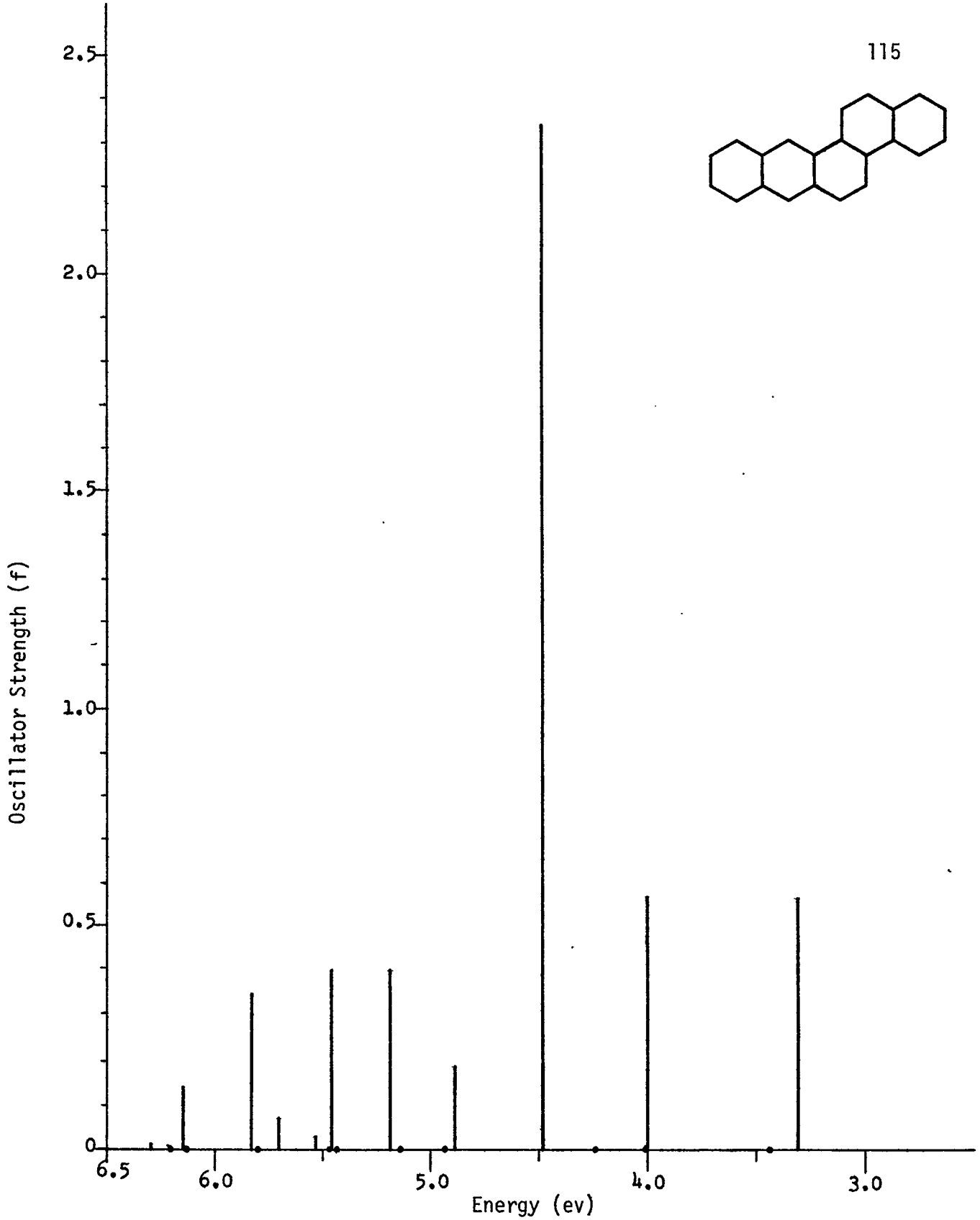


FIGURE 2.8a. CALCULATED ABSORPTION OF BENZO(b)CHRYSENE (II)

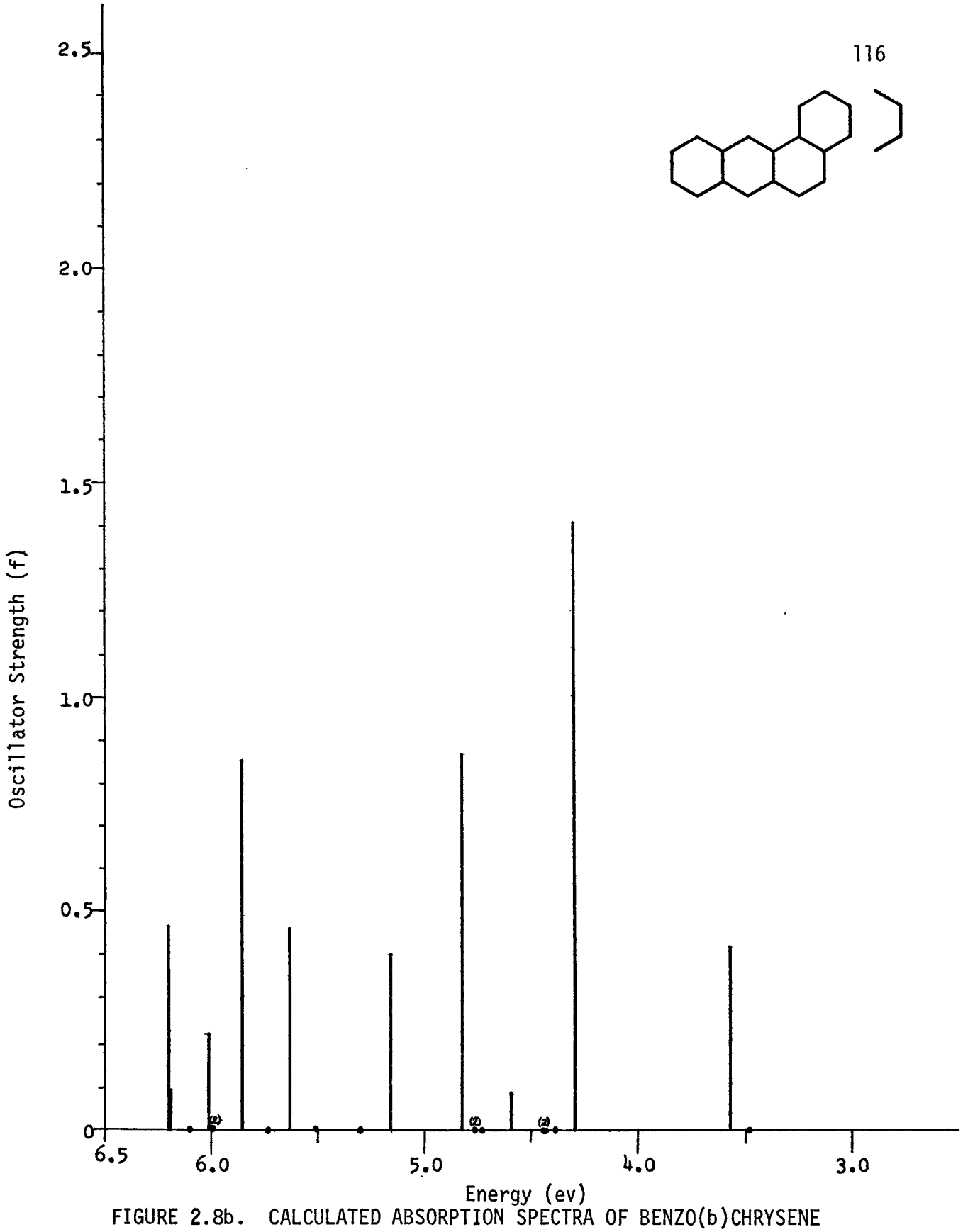


FIGURE 2.8b. CALCULATED ABSORPTION SPECTRA OF BENZO(b)CHRYSENE COMPOSITE SYSTEM (IIa) WITH β_{RS} = 0.0 ev

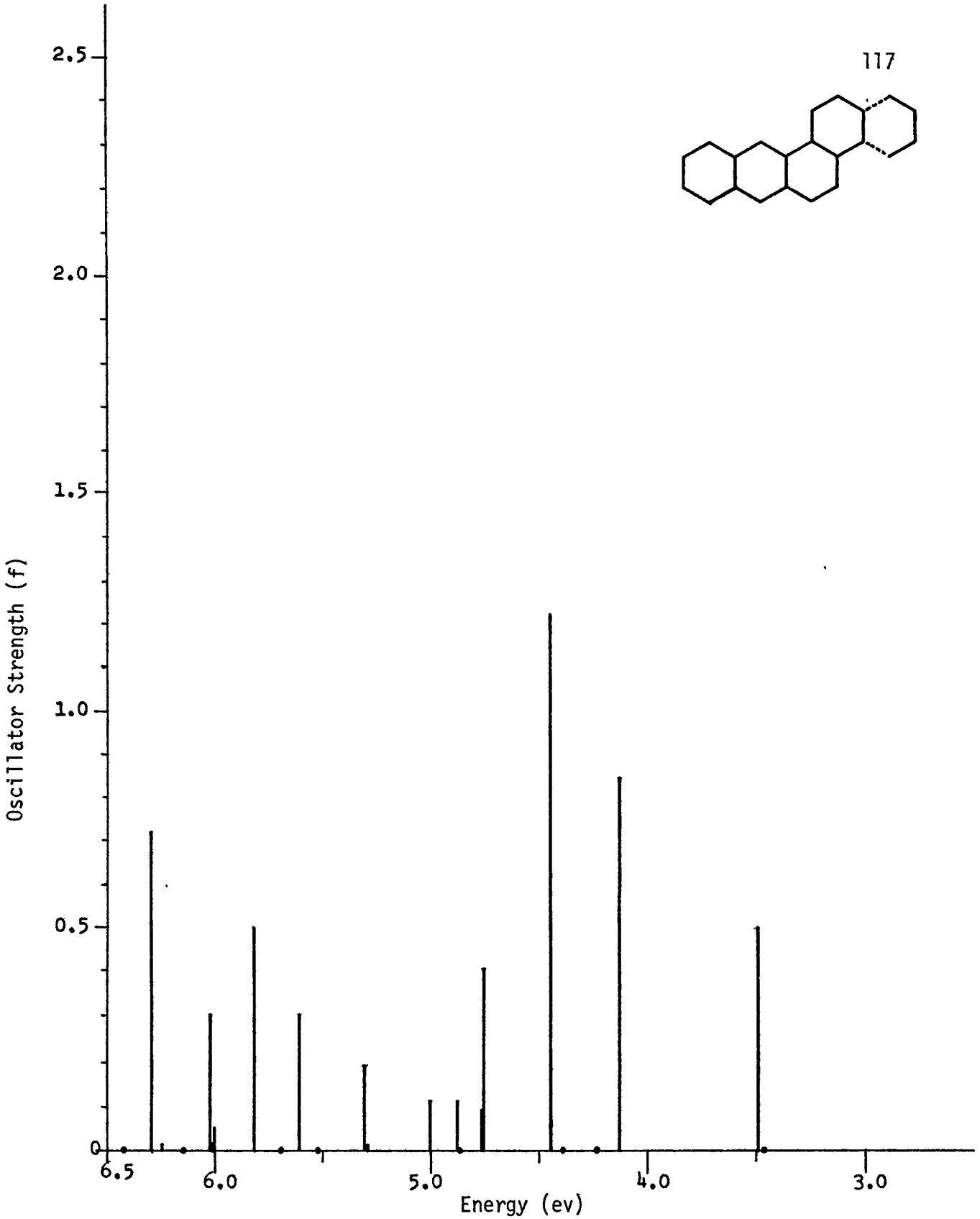


FIGURE 2.8c. CALCULATED ABSORPTION SPECTRA OF BENZO(b)CHRYSENE COMPOSITE SYSTEM (IIa) WITH β_{RS} = -1.0 ev

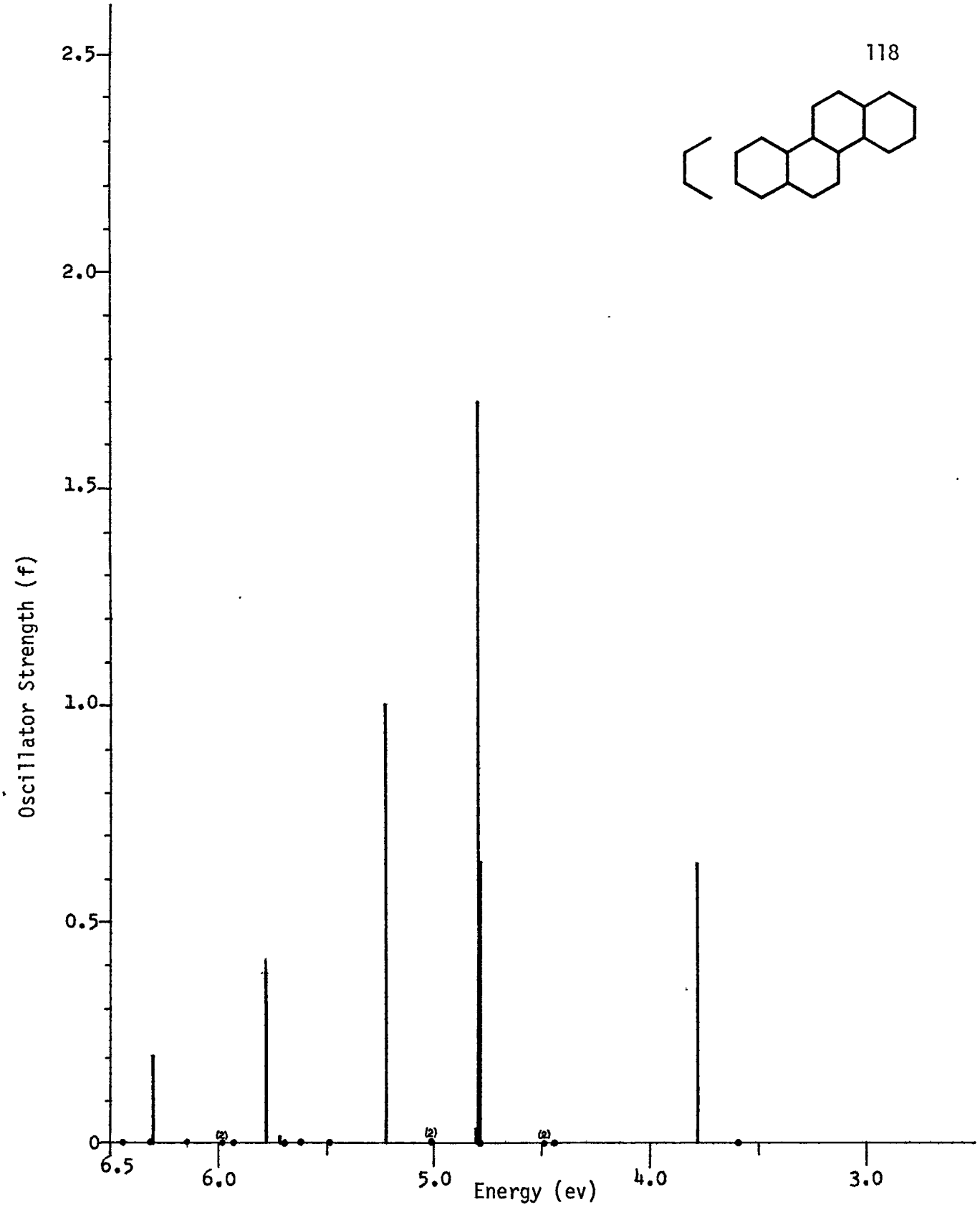


FIGURE 2.8d. CALCULATED ABSORPTION SPECTRA OF BENZO(b)CHRYSENE COMPOSITE SYSTEM (IIb) WITH β_{RS} = 0.0 ev

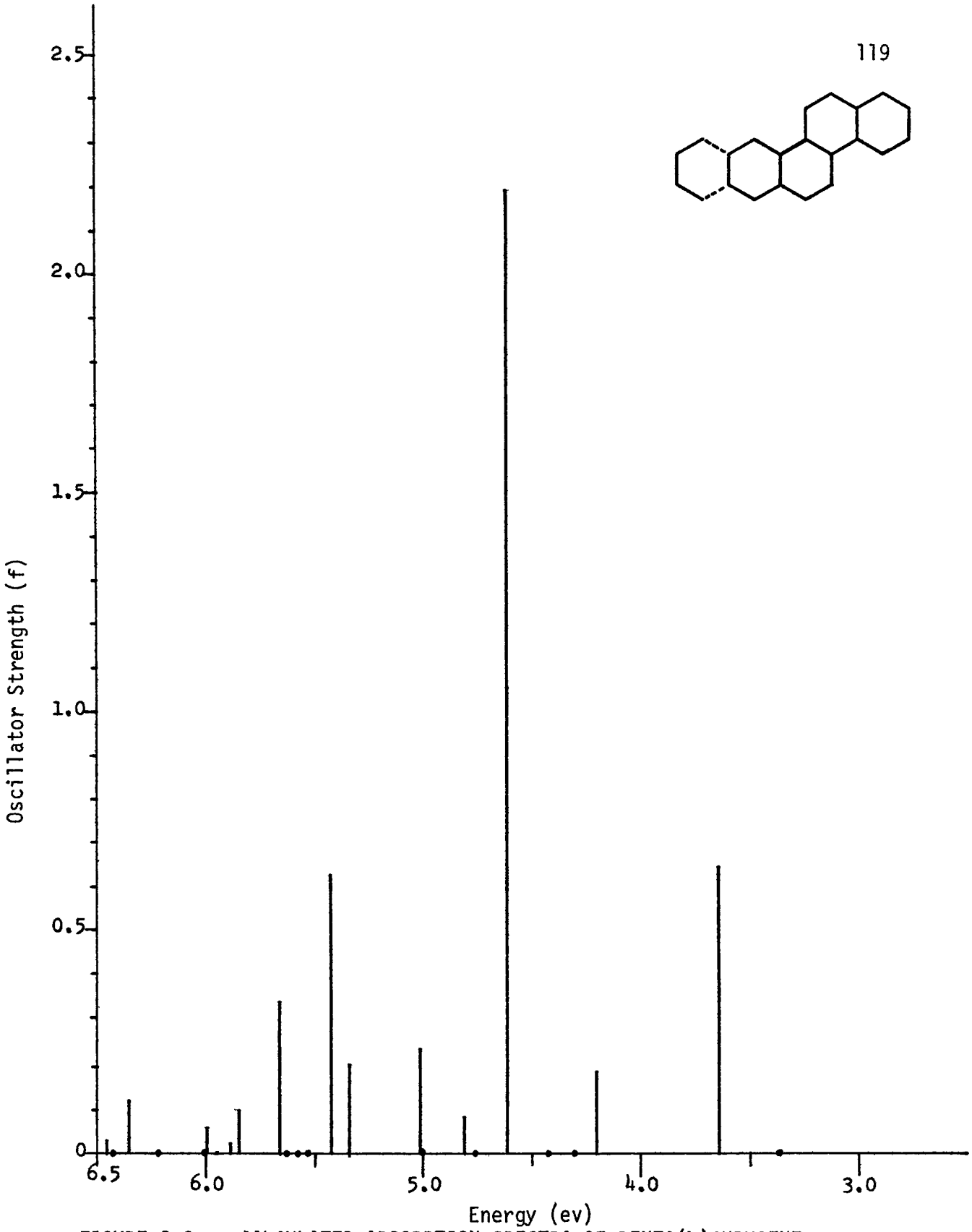


FIGURE 2.8e. CALCULATED ABSORPTION SPECTRA OF BENZO(b)CHRYSENE COMPOSITE SYSTEM (IIb) WITH β_{RS} = -1.0 ev

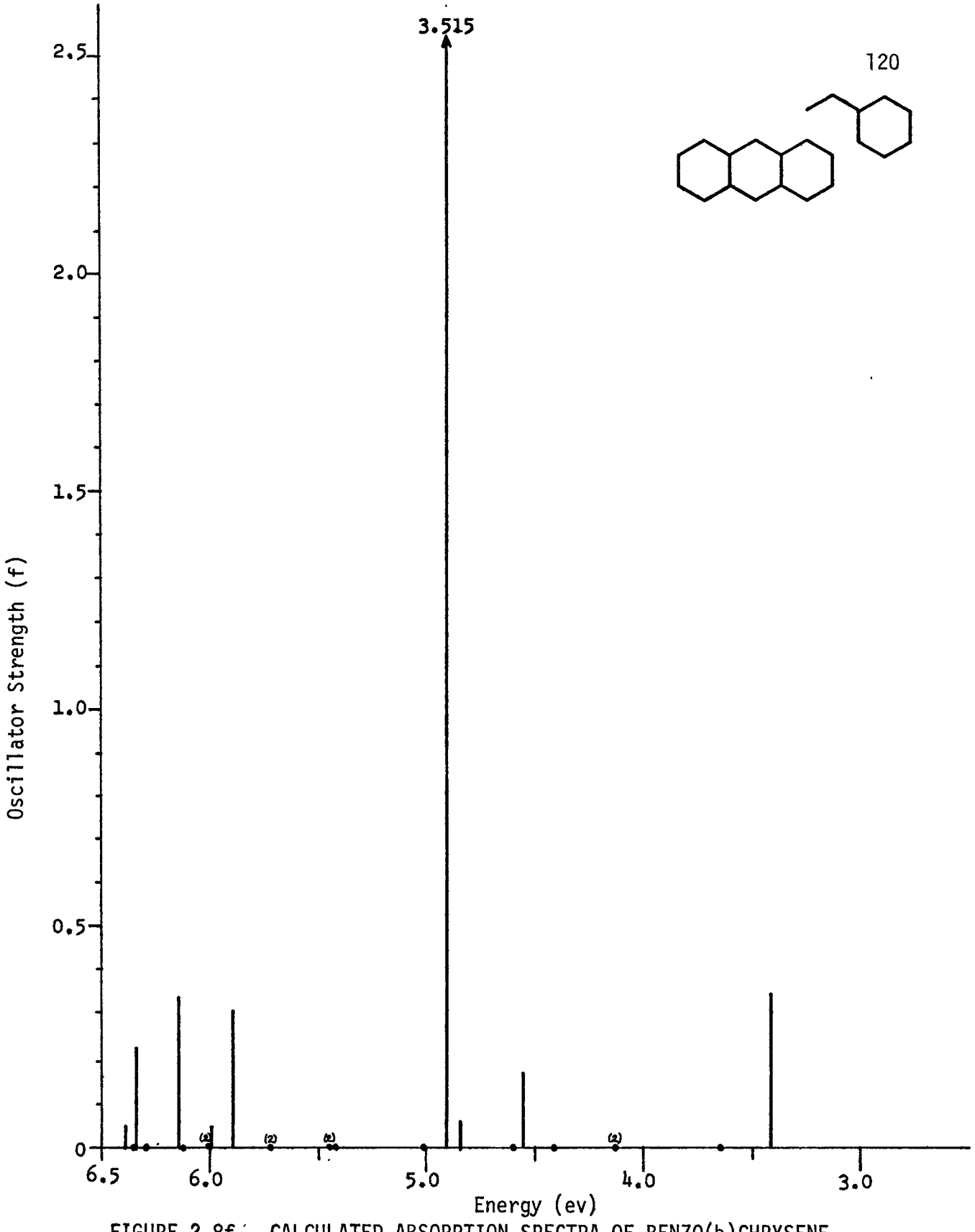


FIGURE 2.8f. CALCULATED ABSORPTION SPECTRA OF BENZO(b)CHRYSENE COMPOSITE SYSTEM (IIc) WITH β_{RS} = 0.0 ev

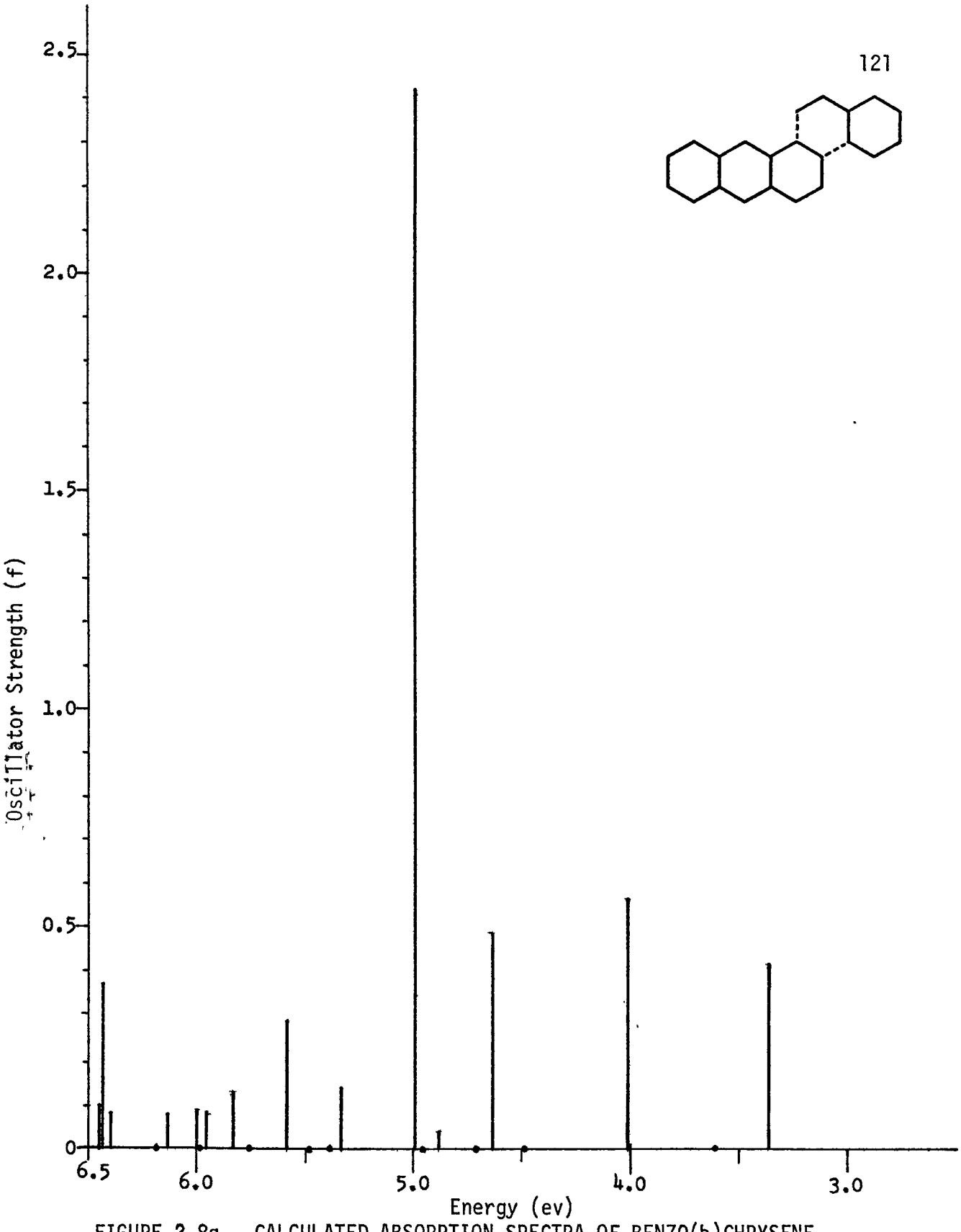


FIGURE 2.8g. CALCULATED ABSORPTION SPECTRA OF BENZO(b)CHRYSENE COMPOSITE SYSTEM (IIc) WITH β_{RS} = -1.0 ev

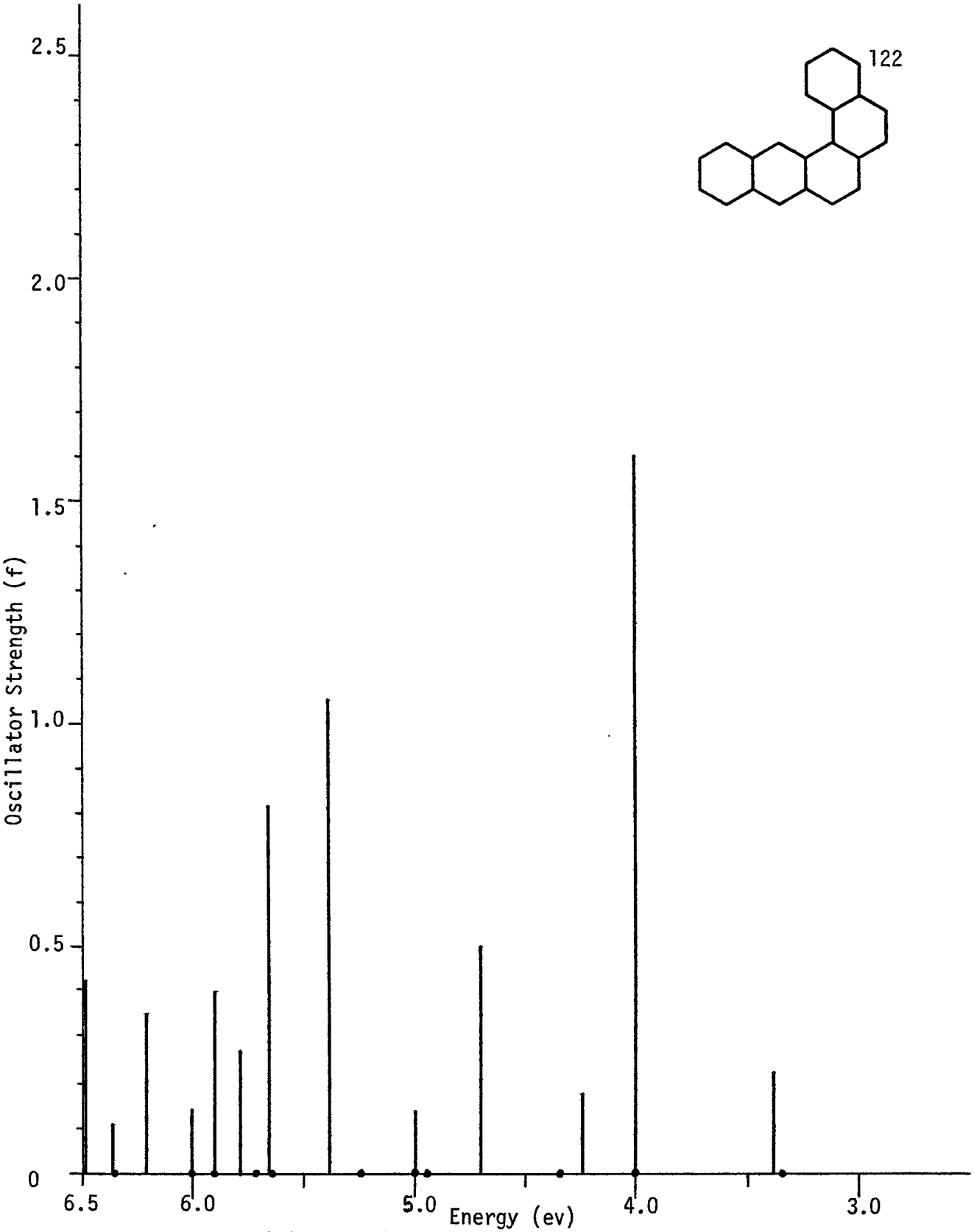


FIGURE 2.9a. CALCULATED ABSORPTION SPECTRA OF DIBENZO(b,g)PHENANTHRENE(III)

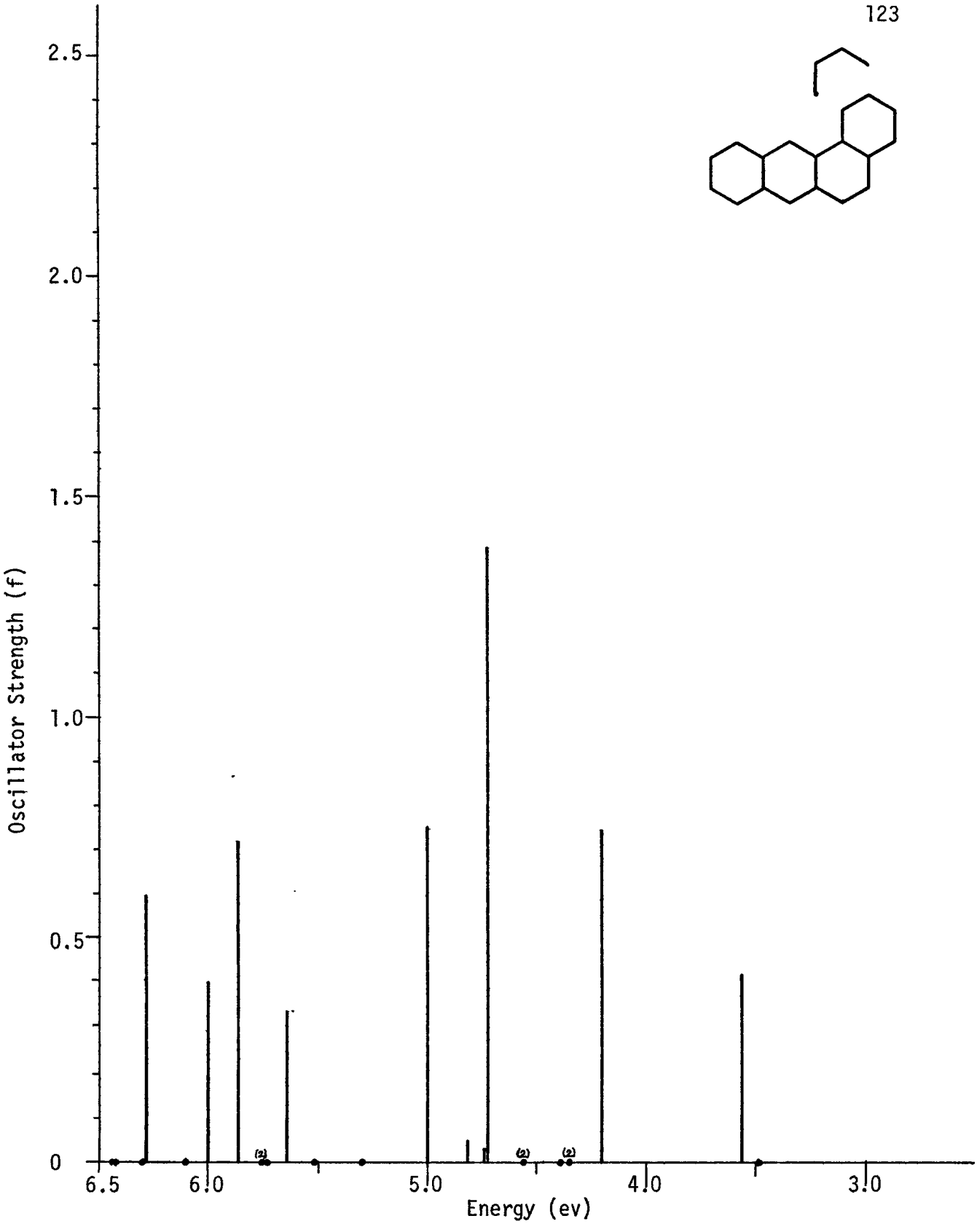


FIGURE 2.9b. CALCULATED ABSORPTION SPECTRA OF DIBENZO(b,g)PHENANTHRENE

COMPOSITE SYSTEM (IIIa) WITH β_{RS} = 0.0 ev

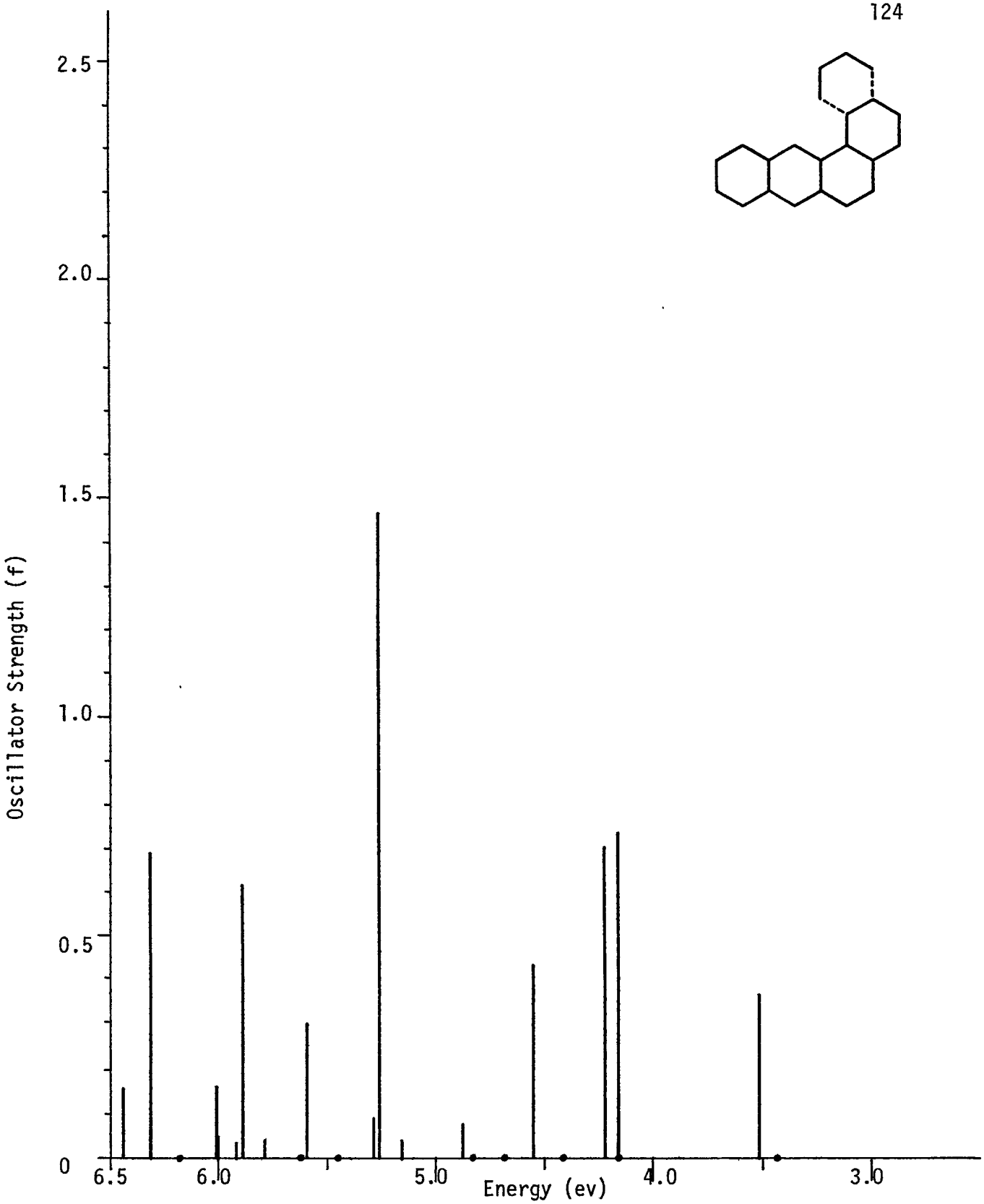


FIGURE 2.9c. CALCULATED ABSORPTION SPECTRA OF

DIBENZO(b,g)PHENANTHRENE

COMPOSITE SYSTEM (IIIa) WITH β_{RS} = -1.0 ev

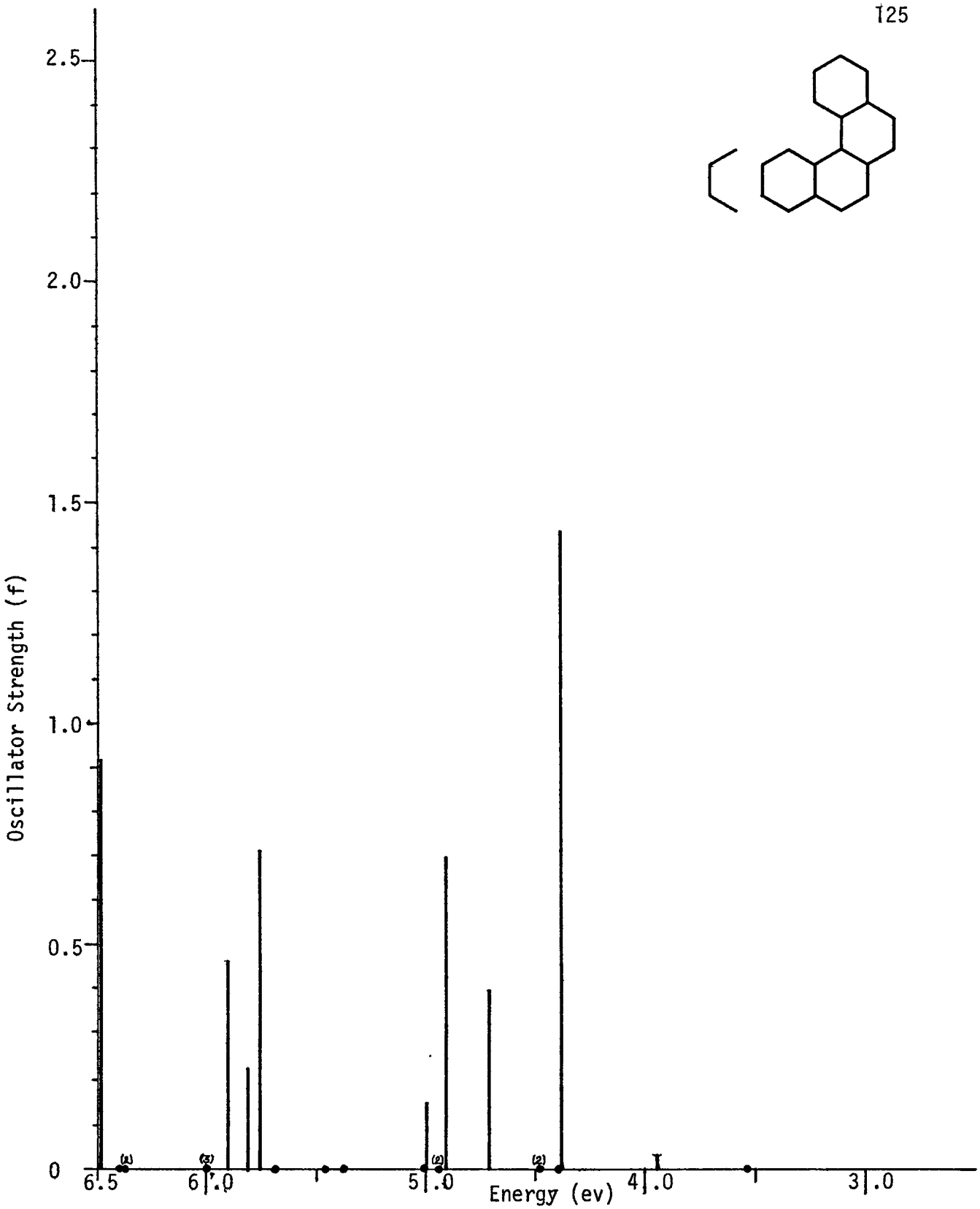


FIGURE 2.9d. CALCULATED ABSORPTION SPECTRA OF DIBENZO(b,g)PHENANTHRENE

COMPOSITE SYSTEM (IIIb) WITH β_{RS} = 0.0 ev

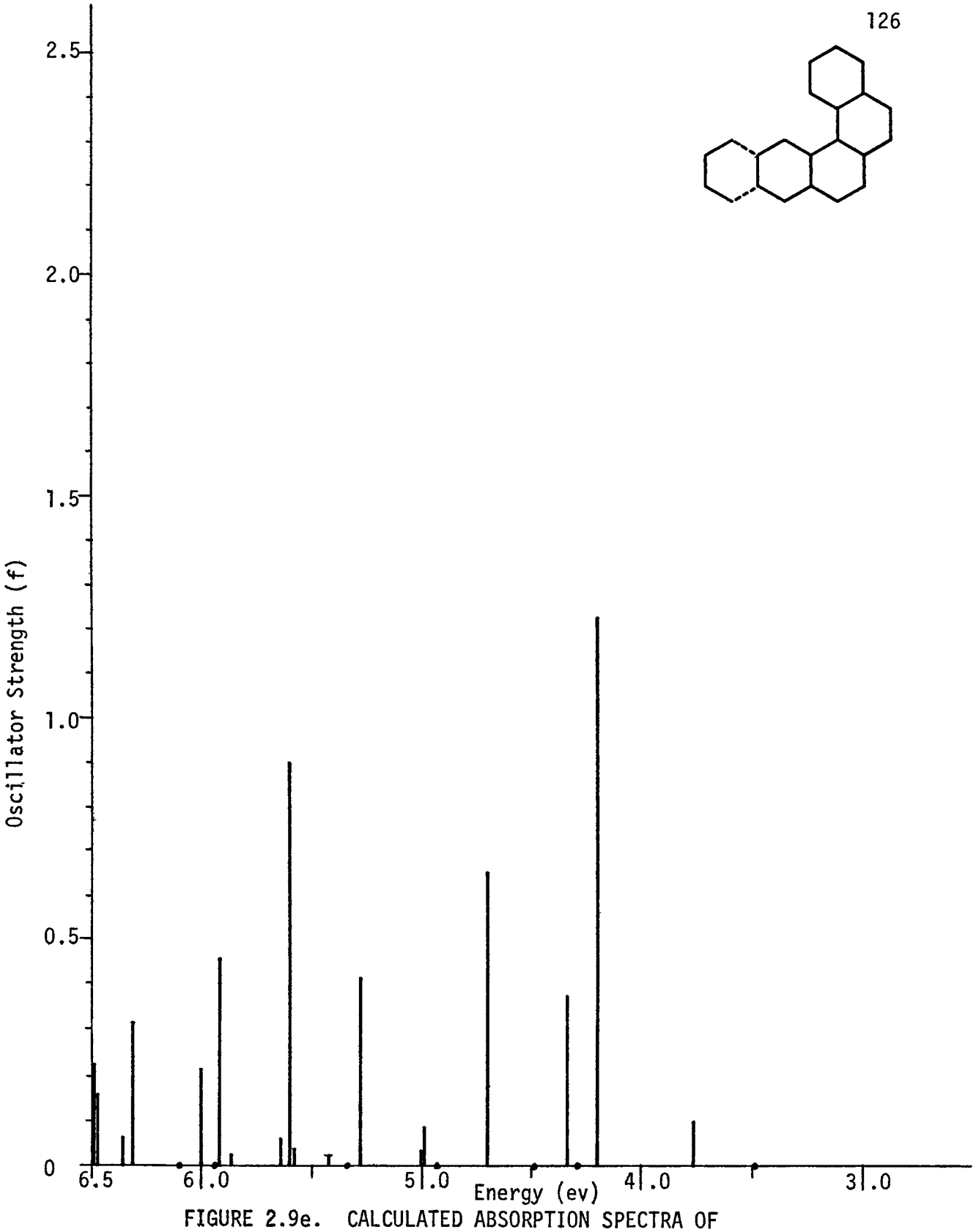


FIGURE 2.9e. CALCULATED ABSORPTION SPECTRA OF DIBENZO(b,g)PHENANTHRENE

COMPOSITE SYSTEM (IIIb) WITH β_{RS} = -1.0 ev

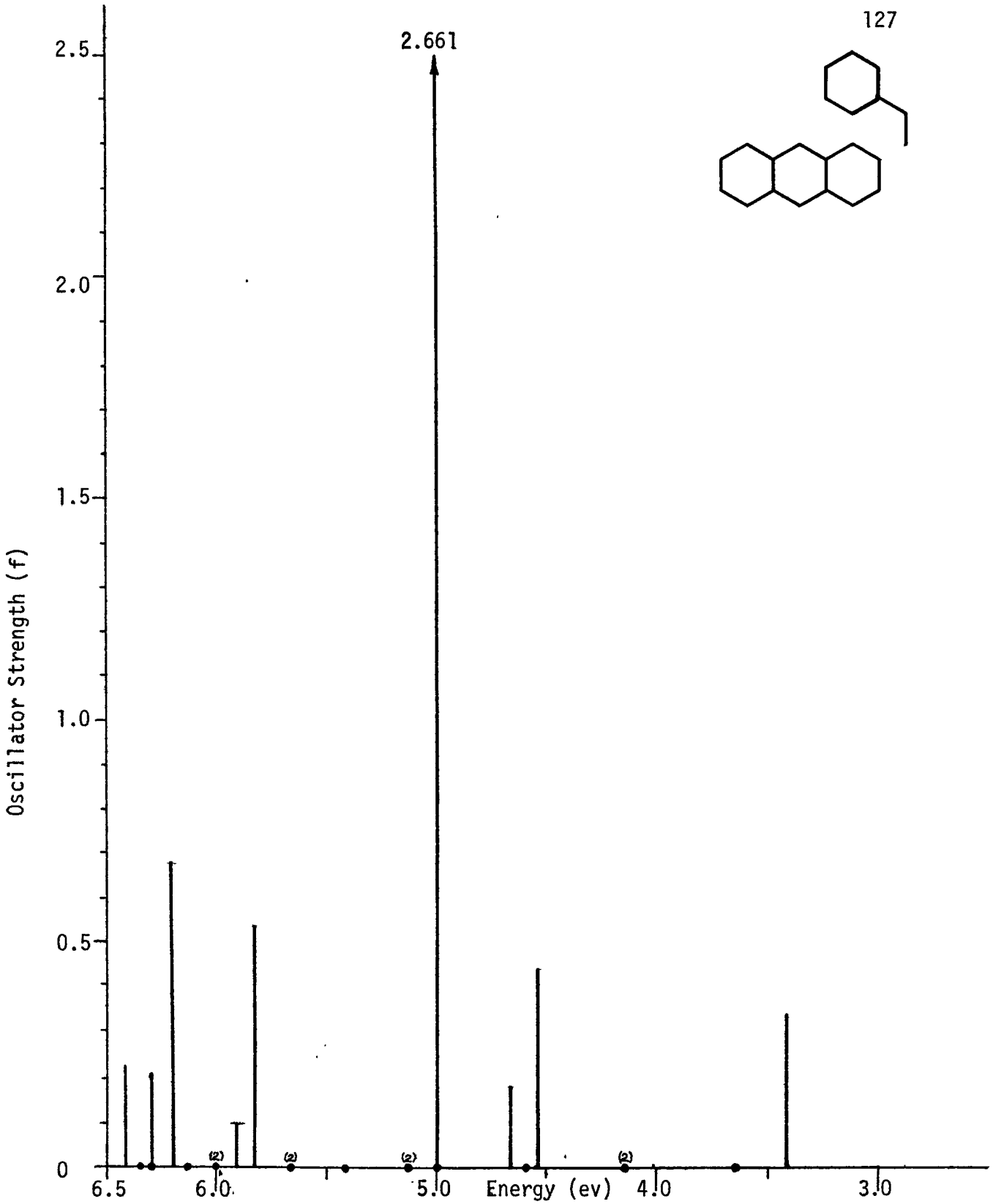


FIGURE 2.9f. CALCULATED ABSORPTION SPECTRA OF DIBENZO(b,g)PHENANTHRENE

COMPOSITE SYSTEM (IIIc) WITH β_{RS} = 0.0 ev

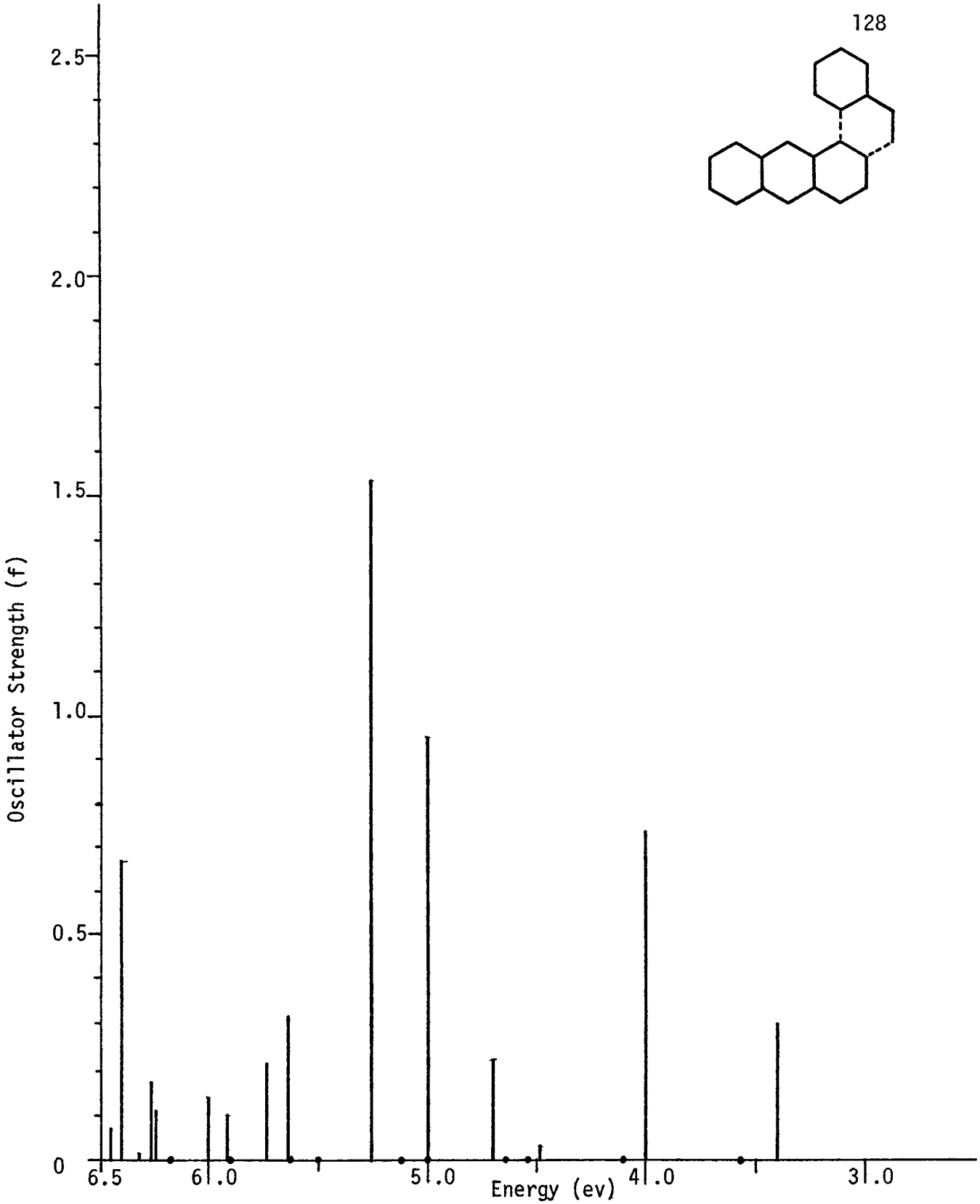


FIGURE 2.9g. CALCULATED ABSORPTION SPECTRA OF DIBENZO(b,g)PHENANTHRENE

COMPOSITE SYSTEM (IIIc) WITH β_{RS} = -1.0 ev

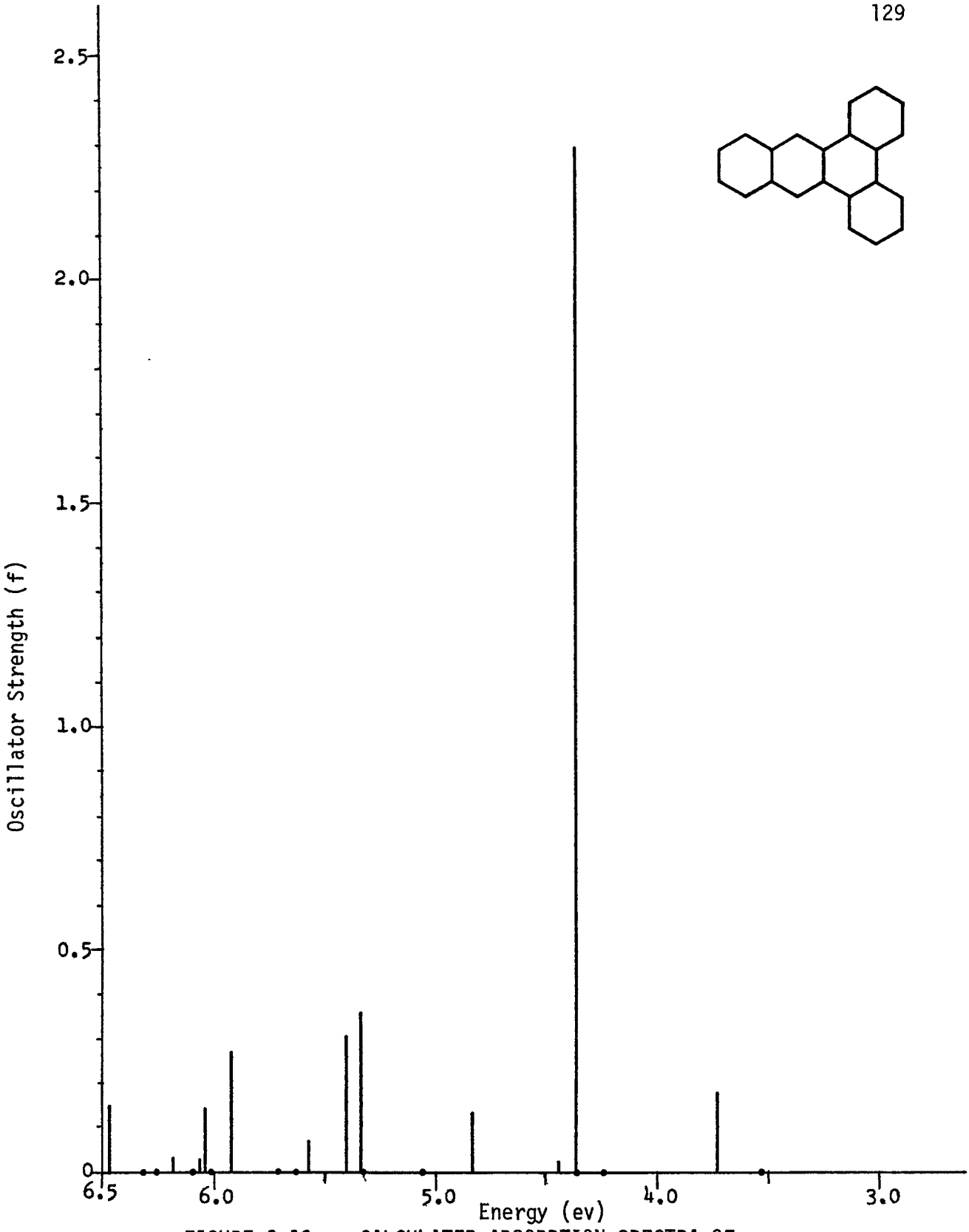


FIGURE 2.10a. CALCULATED ABSORPTION SPECTRA OF DIBENZ(a,c)ANTHRACENE (IV)

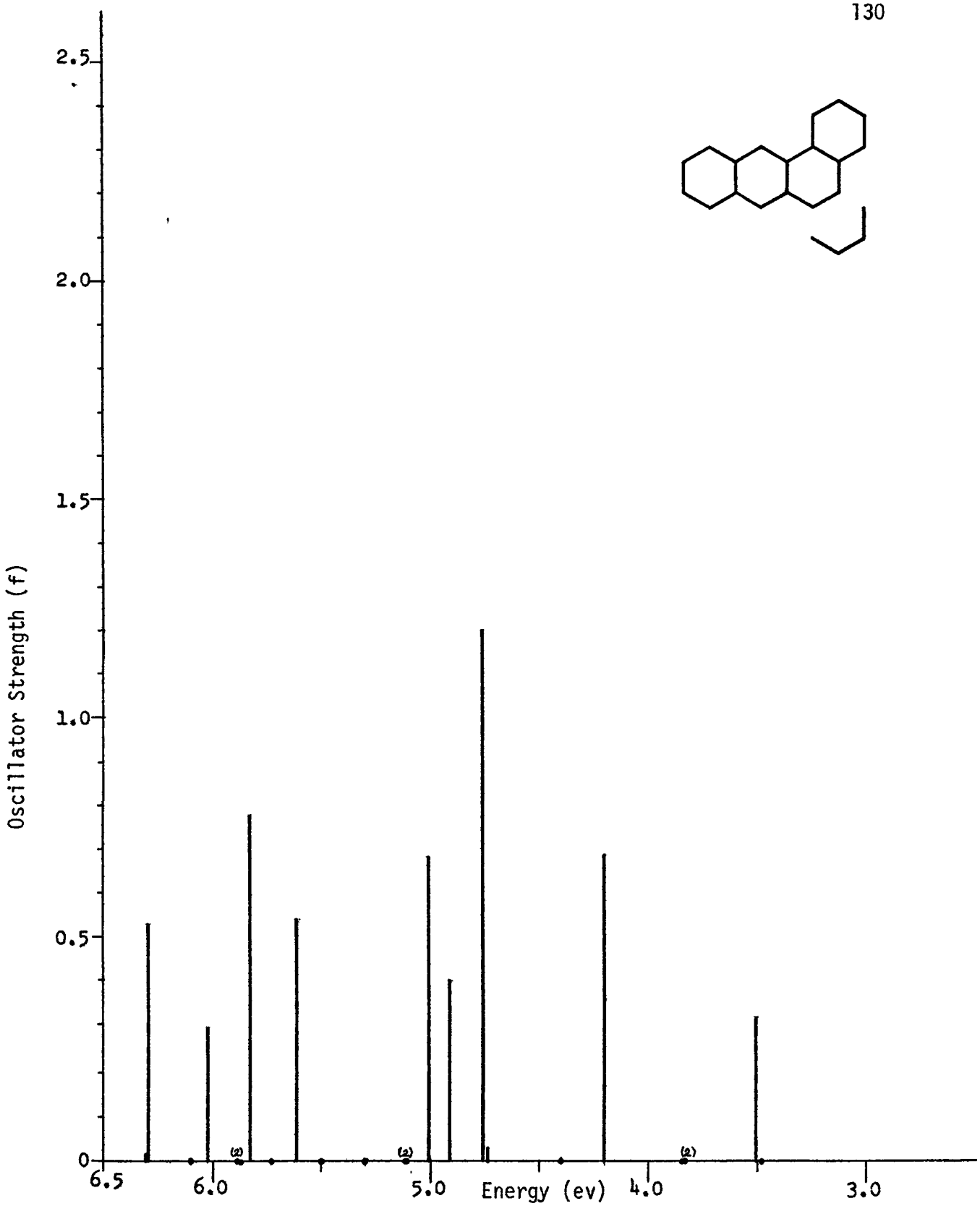


FIGURE 2.10b. CALCULATED ABSORPTION SPECTRA OF DIBENZ(a,c)ANTHRACENE

COMPOSITE SYSTEM (IVa) WITH β_{RS} = 0.0 ev

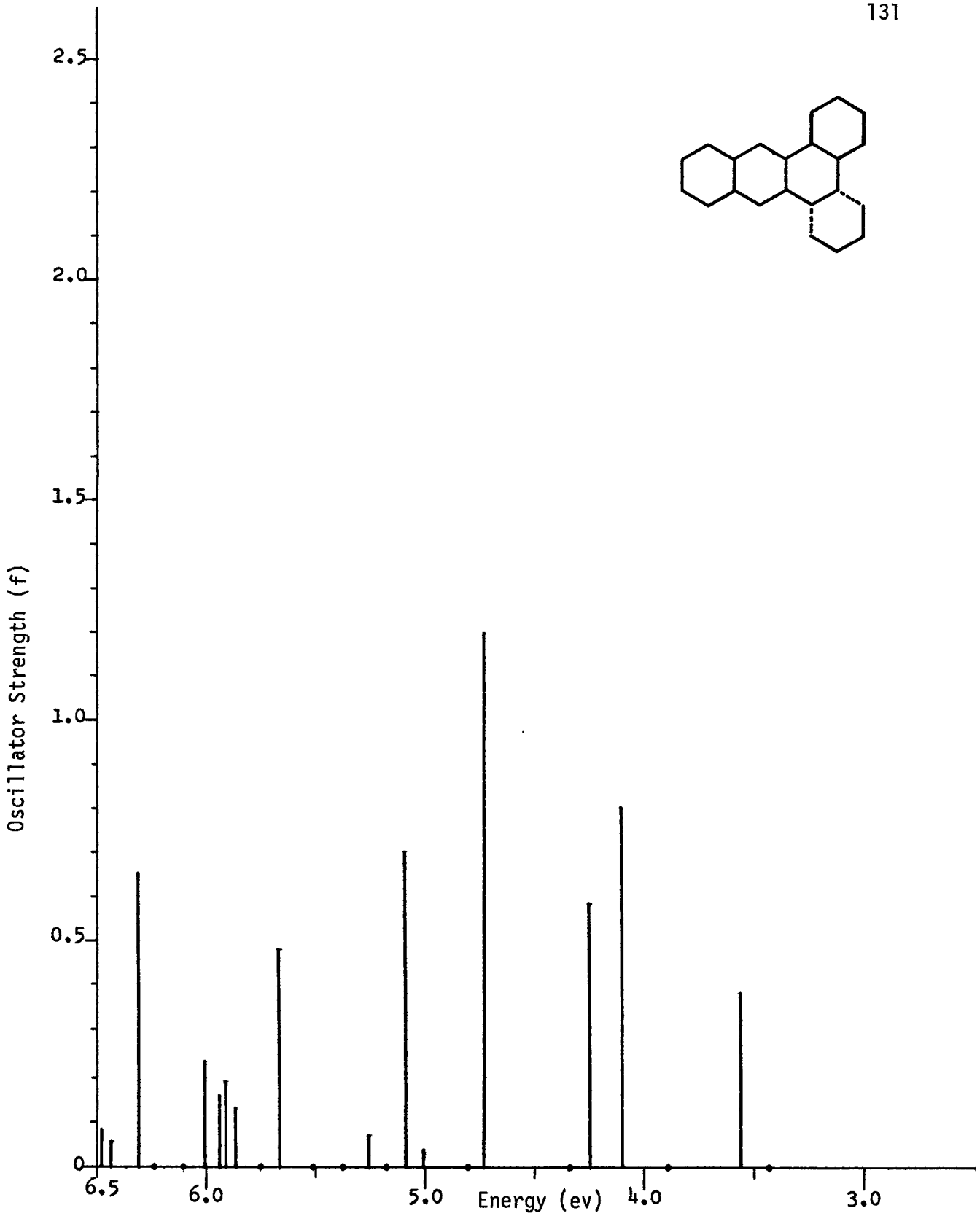


FIGURE 2.10c. CALCULATED ABSORPTION SPECTRA OF DIBENZ(a,c)ANTHRACENE

COMPOSITE SYSTEM (IVa) WITH β_{RS} = -1.0 ev

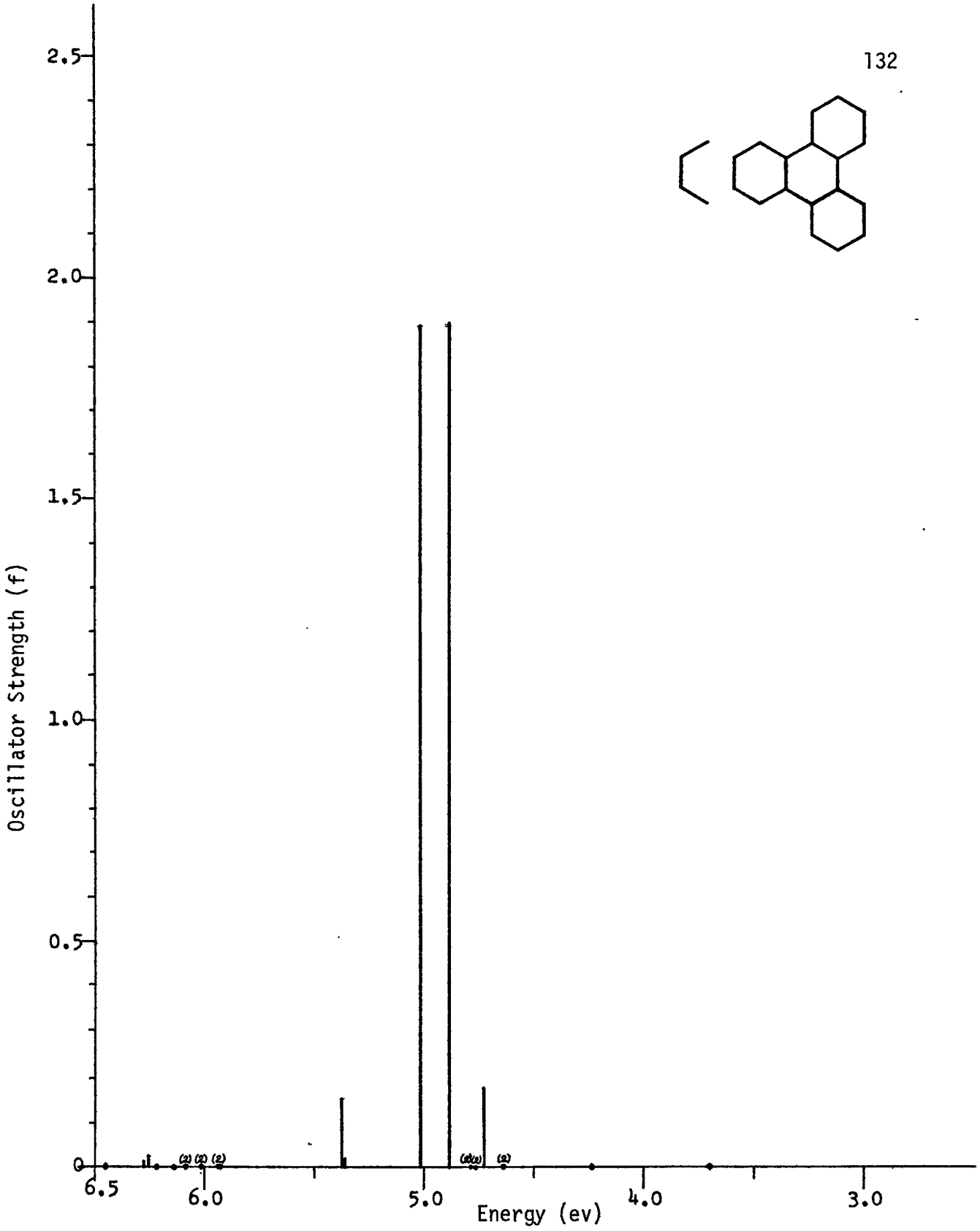


FIGURE 2.10d. CALCULATED ABSORPTION SPECTRA OF DIBENZ(a,c)ANTHRACENE

COMPOSITE SYSTEM (IVb) WITH β_{RS} = 0.0 ev

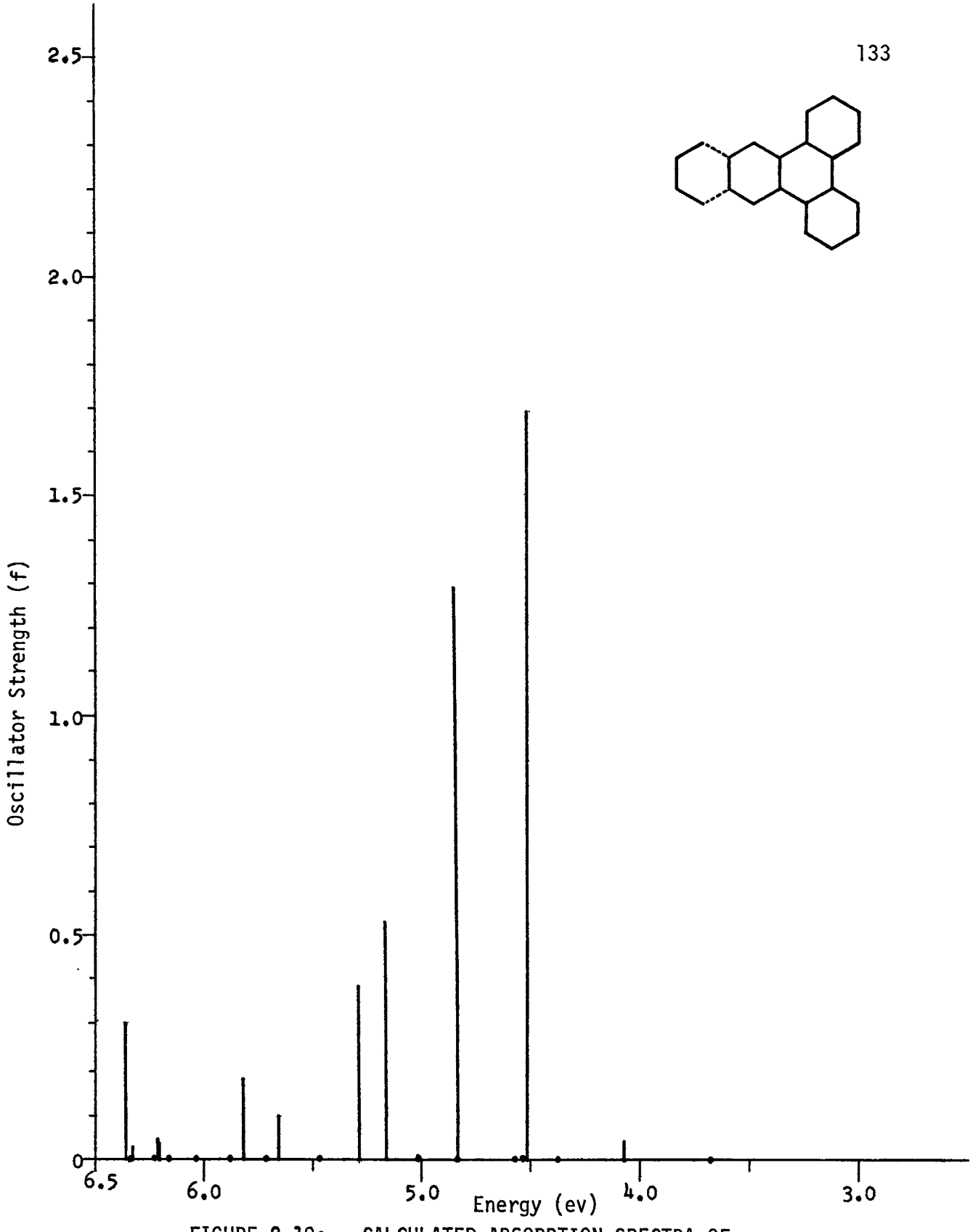


FIGURE 2.10e. CALCULATED ABSORPTION SPECTRA OF DIBENZ(a,c)ANTHRACENE

COMPOSITE SYSTEM (IVb) WITH β_{RS} = -1.0 ev

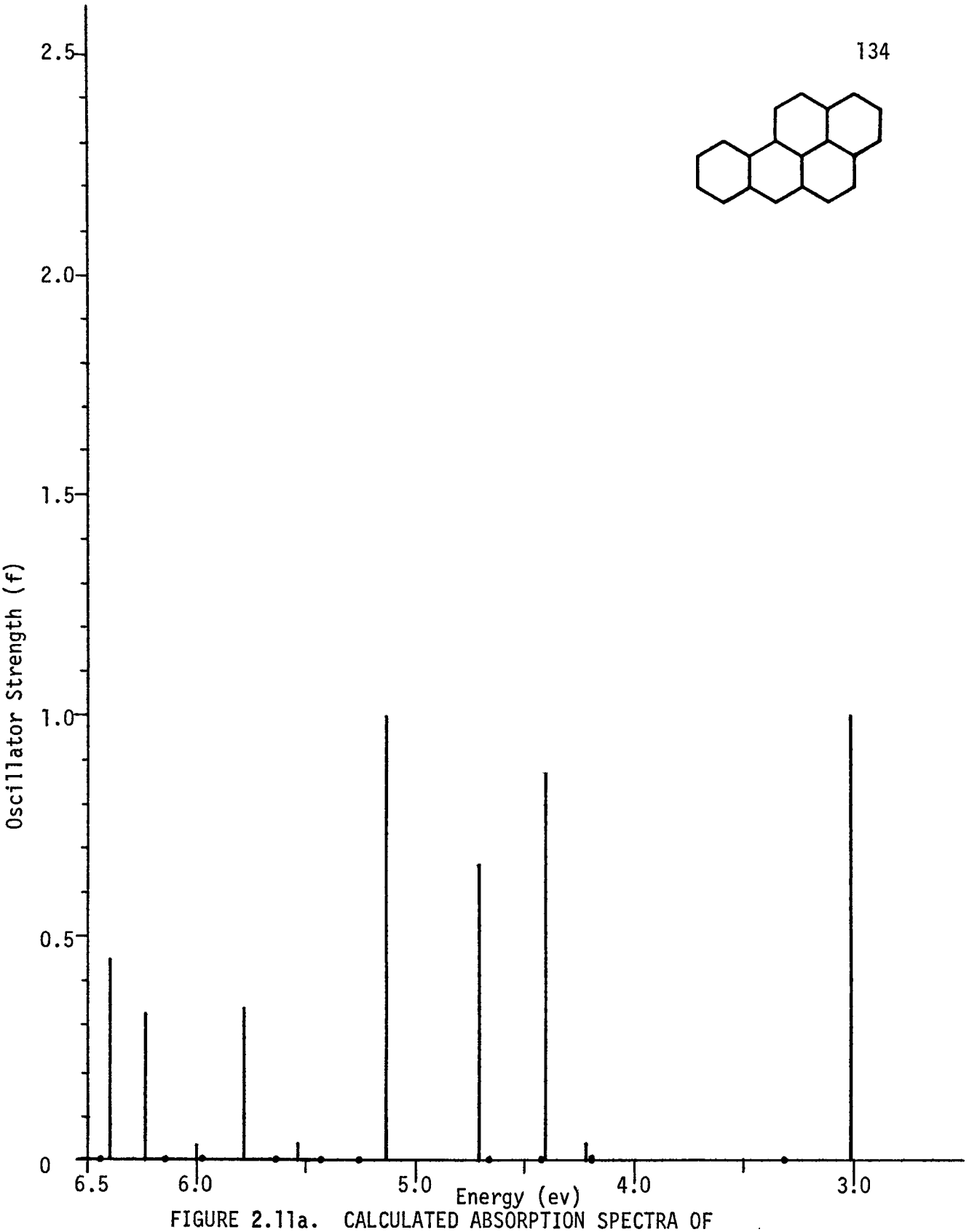


FIGURE 2.11a. CALCULATED ABSORPTION SPECTRA OF

3,4-BENZOPYRENE (V)

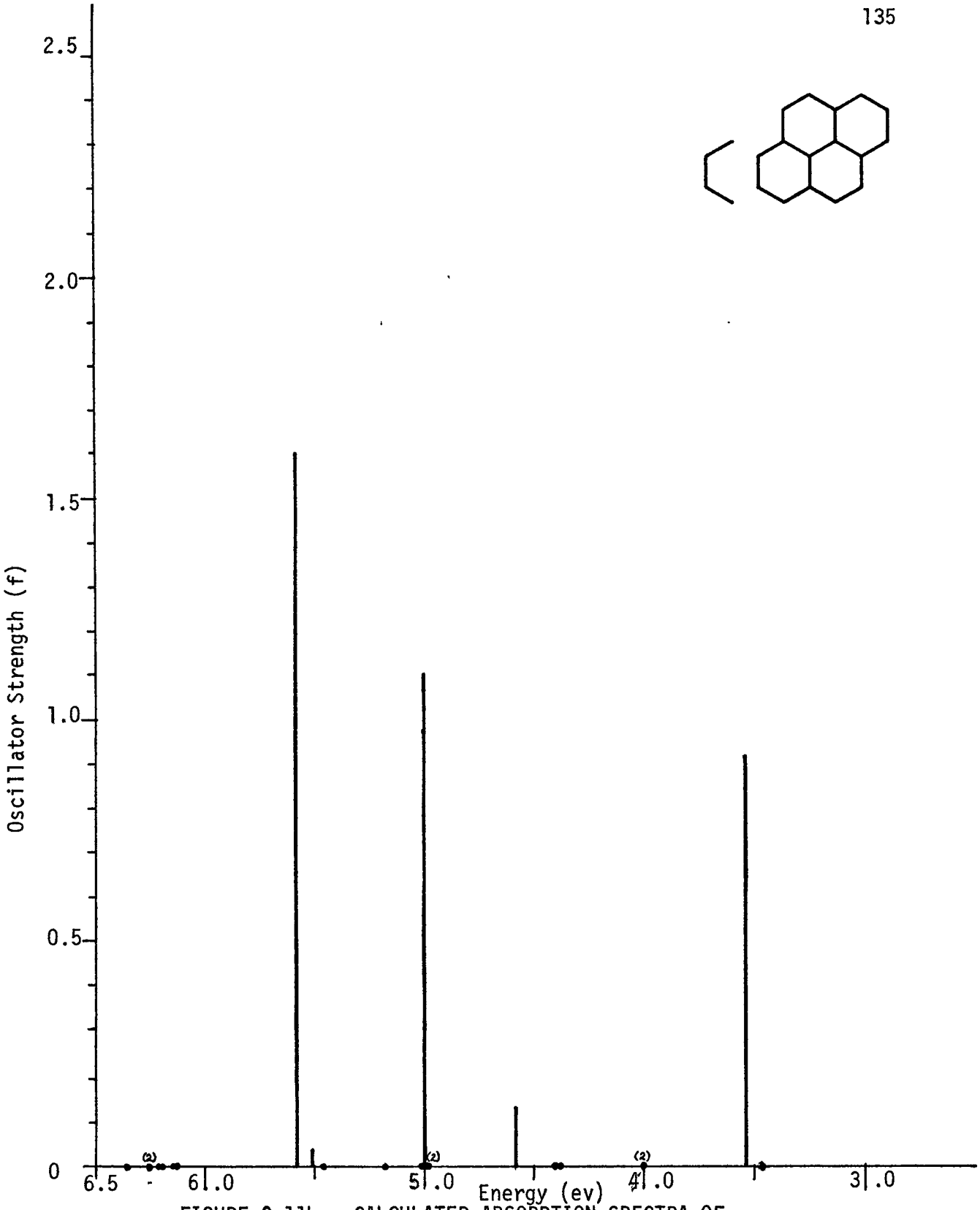


FIGURE 2.11b. CALCULATED ABSORPTION SPECTRA OF 3,4-BENZOPYRENE

COMPOSITE SYSTEM (Va) WITH β_{RS} = 0.0 ev

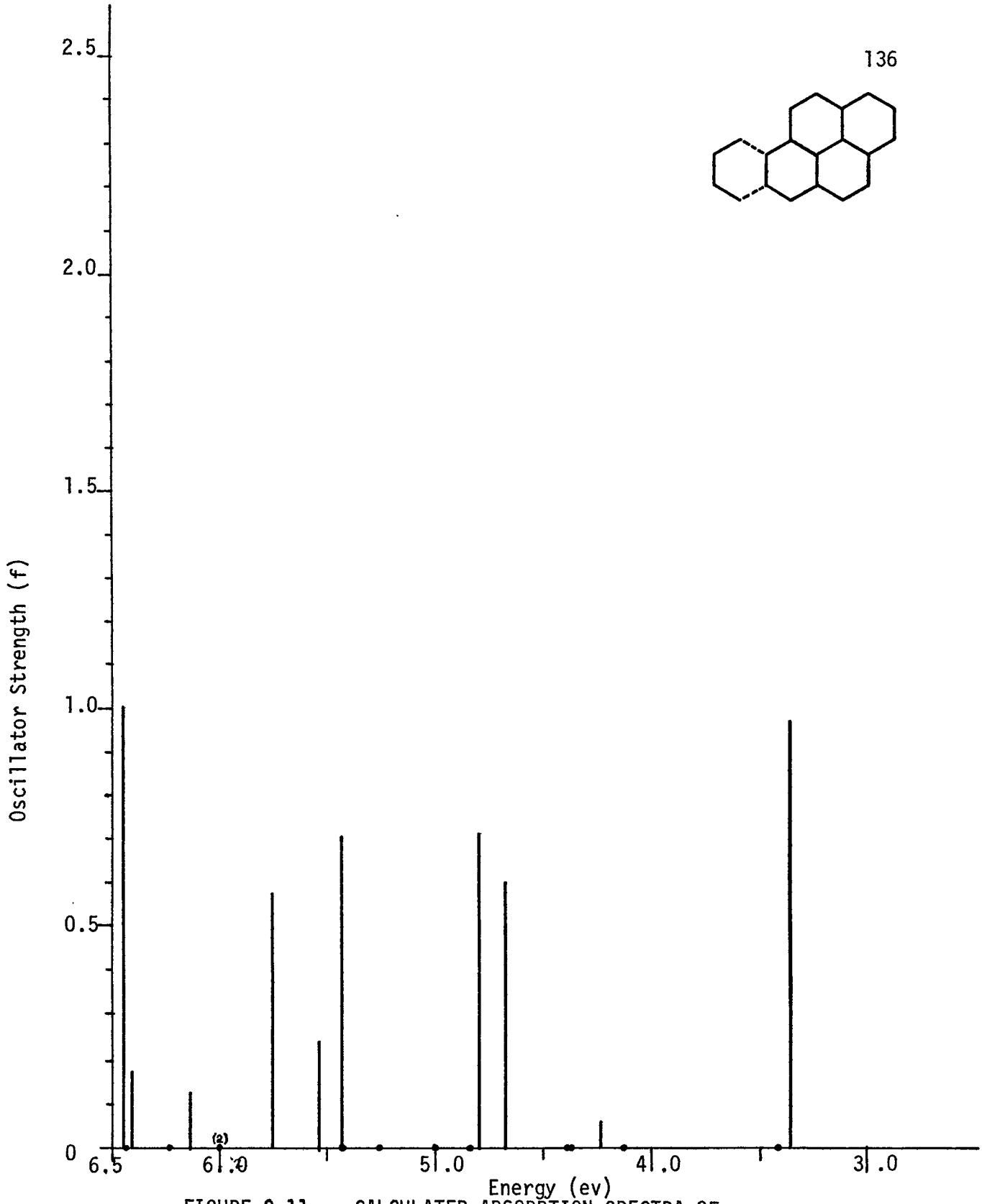


FIGURE 2.11c. CALCULATED ABSORPTION SPECTRA OF 3,4-BENZOPYRENE

COMPOSITE SYSTEM (Va) WITH β_{RS} = -1.0 ev

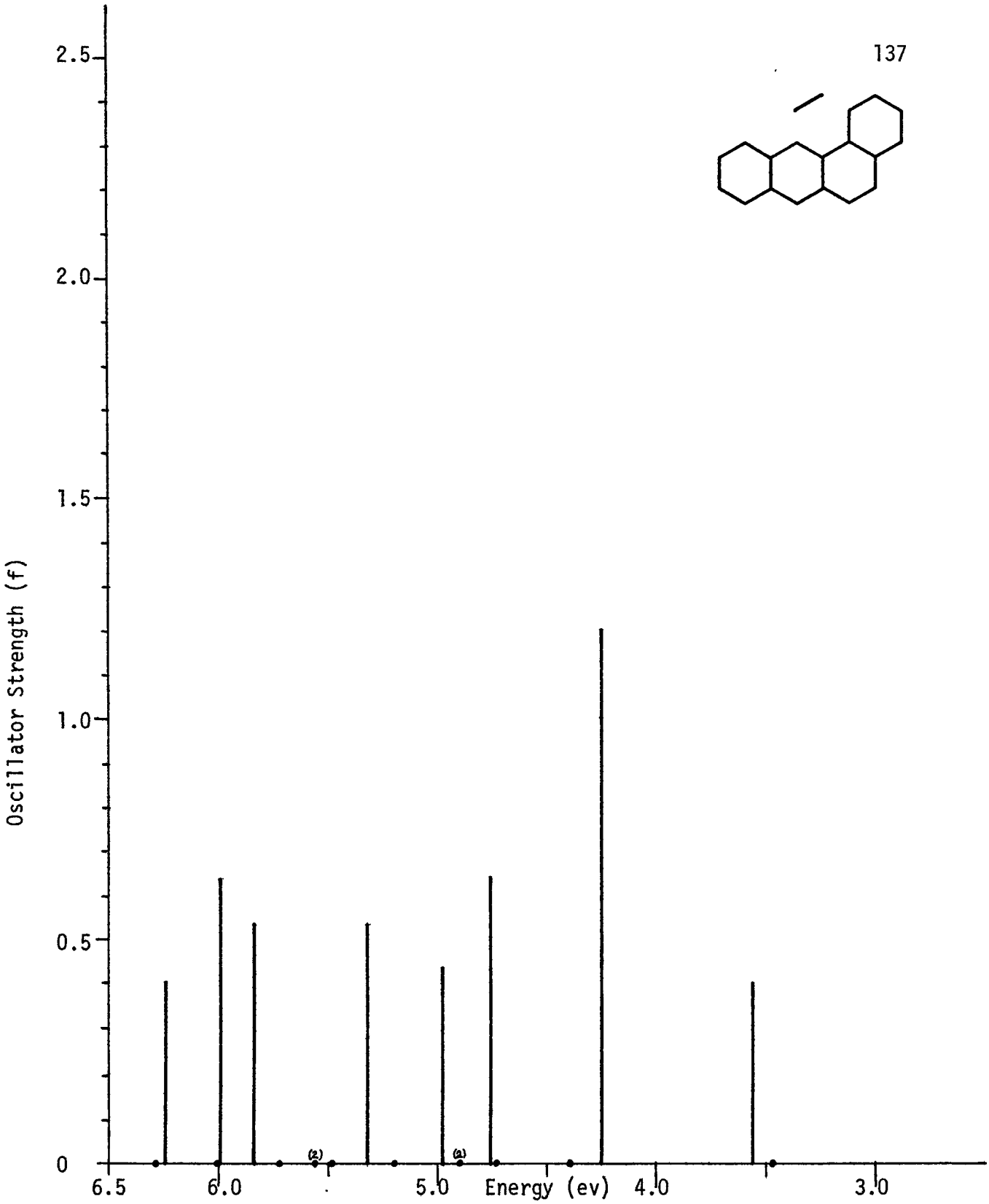


FIGURE 2.11d. CALCULATED ABSORPTION SPECTRA OF 3.4-BENZOPYRENE

COMPOSITE SYSTEM (Vb) WITH β_{RS} = 0.0 ev

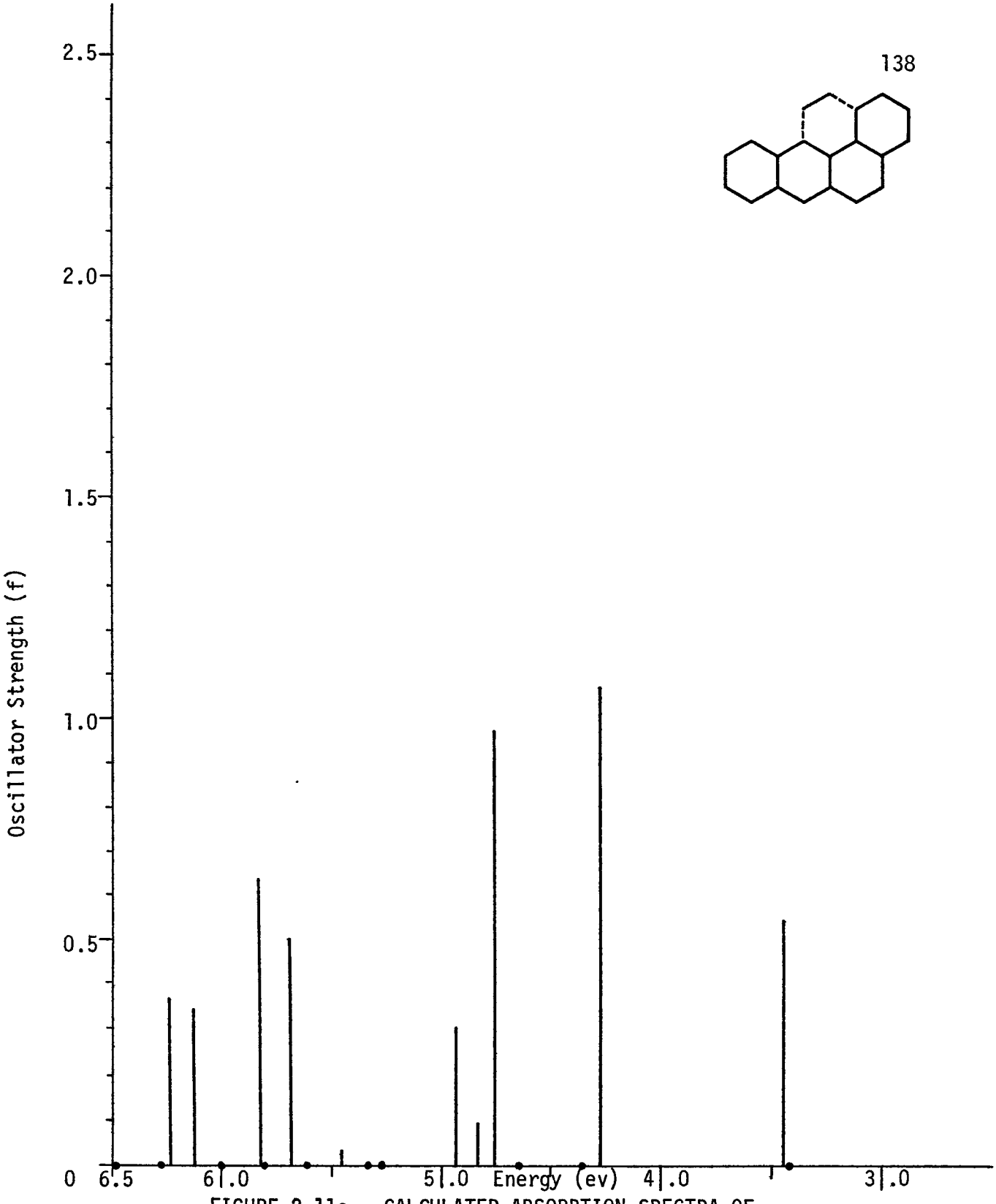


FIGURE 2.11e. CALCULATED ABSORPTION SPECTRA OF 3,4-BENZOPYRENE

COMPOSITE SYSTEM (Vb) WITH β_{RS} = -1.0 ev

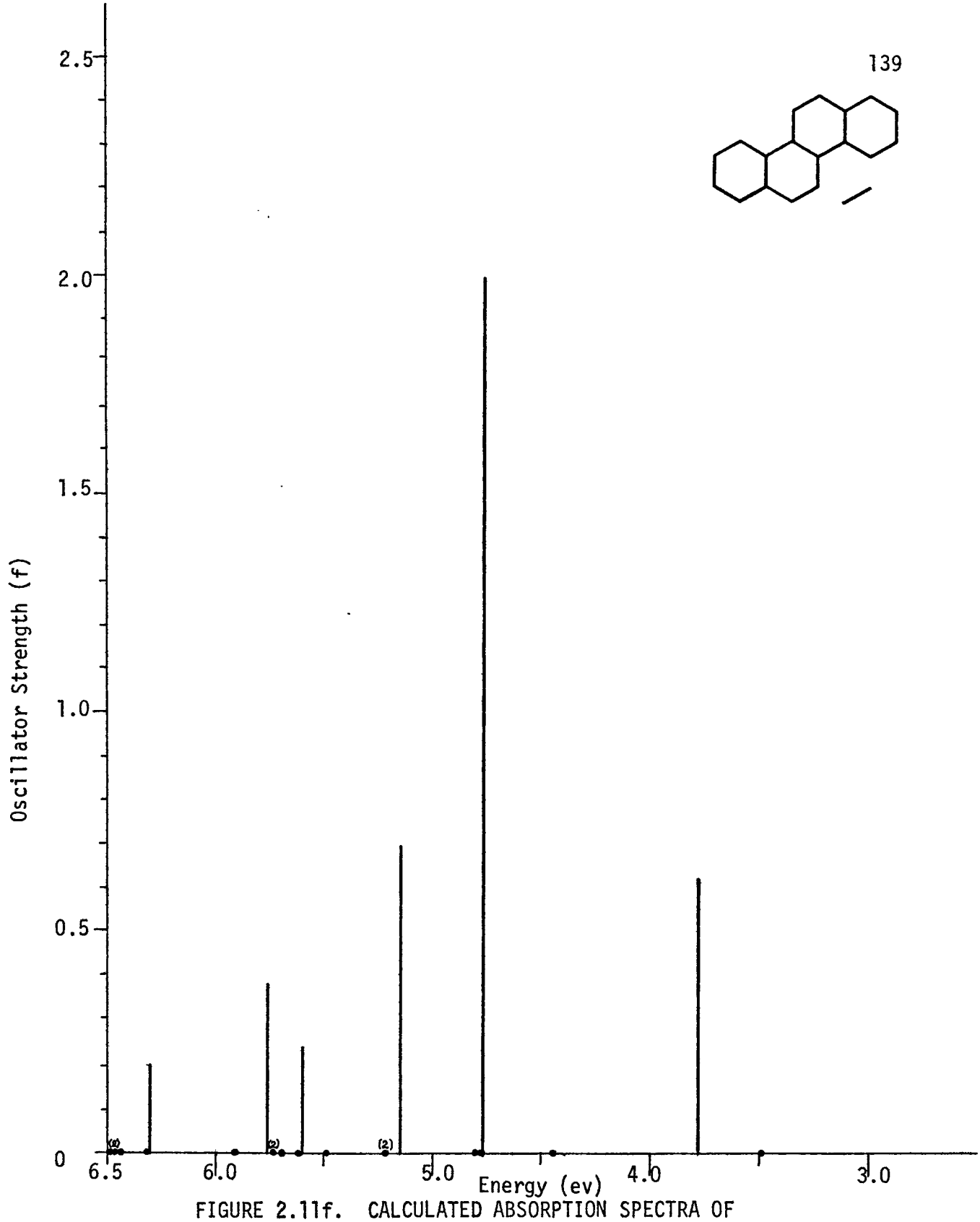


FIGURE 2.11f. CALCULATED ABSORPTION SPECTRA OF 3,4-BENZOPYRENE

COMPOSITE SYSTEM (Vc) WITH β_{RS} = 0.0 ev

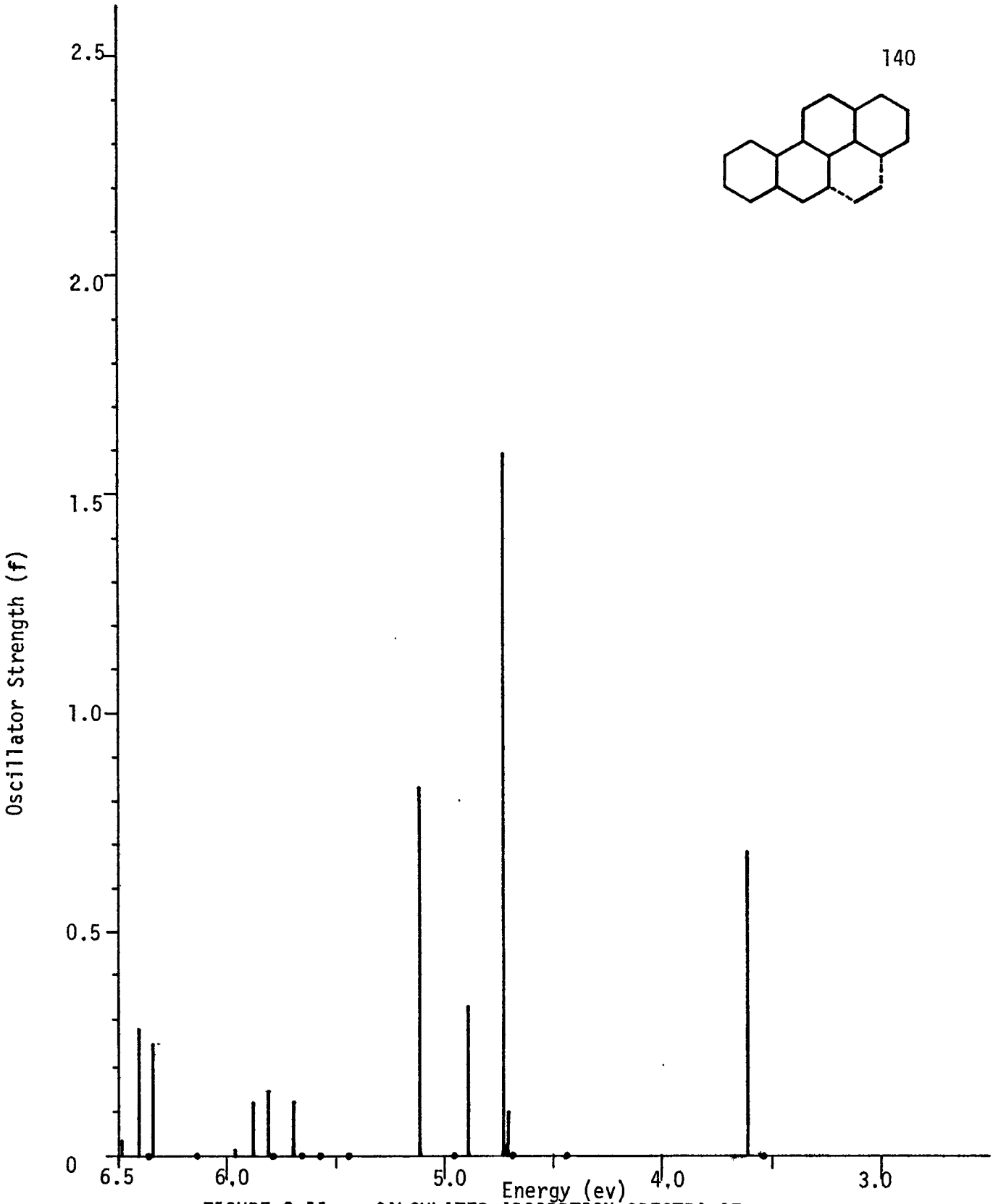


FIGURE 2.11g. CALCULATED ABSORPTION SPECTRA OF 3,4-BENZOPYRENE

COMPOSITE SYSTEM (Vc) WITH β_{RS} = -1.0 ev

TABLE 2.1a - WAVE FUNCTIONS AND EXCITATION ENERGIES OF BENZ(a)NAPTHACENE(I)

Excitation Energy (ev)	f	CI Excited State Wave Functions
2.978	0.371	+983(11-12)
3.289	0.000	-.572(11-13)+.572(10-12)+.288(11-14)+.288(9-12)-.215(11-15)+.215(8-12)
3.843	0.892	+.647(11013)+.647(10-12)+.248(11-14)-.248(9-12)
3.985	0.000	+.526(11-14)+.526(9-12)+.321(11-13)-.321(10-12)-.197(10-14)-.197(9-13)
4.101	0.000	+.439(11-15)-.439(8-12)+.370(10-14)+.370(9-13)+.310(11-14)+.310(9-12)
4.211	1.815	-.638(11-14)+.638(9-12)+.234(11-13)+.234(10-12)
4.732	0.119	-.672(10-13)+.338(9-14)+.316(11-15)+.316(8-12)+.309(11-16)+.309(7-12)
4.774	0.000	-.468(11-16)+.468(7-12)-.394(11-15)+.394(8-12)+.238(10-14)+.238(9-13)
4.960	0.000	-.397(9-15)-.397(8-14)-.357(10-16)+.357(7-13)-.352(11-17)+.352(6-12)
4.979	0.634	-.584(10-13)-.427(11-15)-.427(8-12)+.235(10-14)-.235(9-13)-.166(11-16)
5.165	0.000	-.384(11-17)+.384(6-12)-.287(11-16)+.287(7-12)-.283(10-14)-.283(9-13)
5.246	0.327	+.428(11-16)+.428(7-12)-.427(11-15)-.427(8-12)-.252(10-14)+.252(9-13)
5.411	0.000	-.458(11-18)+.458(5-12)+.314(11-16)-.314(7-12)+.287(10-14)+.287(9-13)
5.711	0.554	-.345(9-14)-.385(10-14)+.385(9-13)-.298(11-17)-.298(6-12)-.246(11-18)
5.721	0.000	-.269(11-19)-.269(4-12)-.266(10-15)+.266(8-13)+.260(11-17)-.260(6-12)
5.732	0.182	-.365(10-15)+.365(8-13)+.341(10-14)-.341(9-13)+.335(11-16)+.335(7-12)
5.935	0.157	-.512(9-14)+.398(11-18)+.398(5-12)+.246(10-15)+.246(8-13)+.239(11-17)
5.989	0.000	+.317(9-17)+.317(6-14)-.281(10-15)+.281(8-13)+.270(8-16)-.270(7-15)
6.051	0.309	-.432(9-14)-.407(10-15)-.407(8-13)-.269(11-17)-.269(6-12)+.221(11-16)
6.101	0.179	+.403(11-17)+.403(6-12)-.378(9-14)-.341(11-18)-.341(5-12)+.193(10-14)
6.168	0.000	-.433(10-15)+.433(8-13)-.271(11-17)+.271(6-12)-.223(10-18)+.223(5-13)
6.455	0.000	+.465(11-19)+.465(4-12)-.279(10-17)+.279(6-13)-.200(8-16)+.200(7-15)
6.472	0.026	-.448(10-16)-.448(7-13)+.293(8-15)-.266(11-19)+.266(4-12)+.204(7-15)

TABLE 2.1b - WAVE FUNCTIONS AND EXCITATION ENERGIES OF BENZ(a)NAPTHACENE

COMPOSITE SYSTEM (Ia) WITH β_{RS} = 0.0 EV

Excitation Energy (ev)	f	CI Excited State Wave Functions
2.826	0.357	-.986(11-12)
3.425	0.000	+.685(11-15)-.685(8-12)
3.761	0.000	+.903(10-12)-.385(10-14)
3.761	0.000	-.903(11-13)-.385(9-13)
3.830	0.000	+.690(11-14)+.690(9-12)
3.865	0.004	+.689(11-14)-.689(9-12)-.184(10-13)
4.462	2.487	-.651(11-15)-.651(8-12)+.309(10-13)
4.504	0.000	+.516(11-17)-.516(6-12)-.473(9-15)-.473(8-14)
4.471	0.795	-.585(10-13)+.428(9-14)+.406(11-16)+.406(7-12)-.212(11-15)-.212(8-12)
4.760	0.000	-.688(11-16)+.688(7-12)-.165(9-18)-.165(5-14)
4.984	0.604	+.644(10-18)+.429(11-16)+.429(7-12)+.303(9-14)
5.241	0.000	-.689(11-18)+.689(5-12)-.159(9-16)-.159(7-14)
5.426	0.000	+.738(10-14)+.419(10-12)+.401(10-16)+.260(10_15)-.169(10-17)
5.426	0.000	-.738(9-13)+.419(11-13)+.401(7-13)+.260(8-13)-.169(6-13)
5.560	0.000	+.841(10-15)-.431(10-17)-.285(10-14)
5.560	0.000	-.841(8-13)+.431(6-13)-.285(9-13)
5.615	0.000	-.445(8-16)+.445(7-15)+.411(9-17)+.411(6014)-.364(11-20_+.364(3-12)
5.776	0.088	+.722(9-14)-.406(8-15)-.351(11-16)-.351(7-12)
5.815	0.001	+.568(11-18)+.568(5-12)+.330(11-17)+.330(6-12)+.248(9-16)-.248(7-14)
5.851	0.027	-.571(11-17)-.571(6-12)+.315(11-18)+.315(5-12)+.194(10-13)-.150(9-15)
5.861	0.000	-.519(9-15)-.519(8-14)-.475(11-17)+.475(6-12)
6.136	0.000	-.707(10-19)+.707(4-13)
6.309	0.024	-.674(9-15)+.674(8-14)
6.418	0.944	-.855(8-15)-.342(9-14)-.172(7-16)+.164(9-18)-.164(5-14)

TABLE 2.1c - WAVE FUNCTIONS AND EXCITATION ENERGIES OF BENZ(a)NAPTHACENE

COMPOSITE SYSTEM (Ia) WITH β_{RS} = -1.000 EV

Excitation Energy (ev)	f	CI Excited State Wave Functions
2.857	0.368	+.986(11-12)
3.332	0.000	+.487(11-13)-.487(10-12)-.420(11-15)+.420(8-12)+.209(11-14)-.209(9-12)
3.776	0.486	-.628(11-13)-.628(10-12)+.270(11014)+.270(9-12)+.161(10-13)
3.798	0.000	-.411(11-13)+.411(10-12)-.384(11-15)+.384(8-12)+.311(11-14)-.311(9-12)
3.909	0.000	-.567(11-14)+.567(9-12)-.331(11-15)+.331(8-12)+.176(10-14)-.176(9-13)
3.994	0.653	+.625(11-14)+.625(9-12)+.238(11-13)+.238(10-12)+.181(10-14)+.181(9-13)
4.577	0.000	+.452(11-17)+.452(6-12)-.386(9-15)+.386(8-14)-.208(11-16)+.208(7-12)
4.594	1.151	+.574(11-15)+.574(8-12)-.440(10-13)-.197(9-14)+.183(11-16)+.183(7-12)
4.793	0.000	-.630(11-16)+.630(7-12)-.236(11-17)-.236(6-12)
4.801	1.184	-.516(10-13)-.382(11-15)-.382(8-12)-.371(9-14)+.358(11-16)+.358(7-12)
5.002	0.368	-.530(10-13)-.415(11-16)-.415(7-12)-.272(10-14)-.272(9-13)+.198(9-14)
5.173	0.000	+.353(10-14)-.353(9-13)-.318(11-18)+.318(5-12)-.310(10-16)+.310(7-13)
5.289	0.000	+.595(11-18)-.595(5-12)+.191(10-14)-.191(9-13)-.161(9-16)+.161(7-14)
5.497	0.279	-.514(10-14)-.514(9-12)+.310(10-13)-.302(9-14)+.251(10-16)+.251(7-13)
5.567	0.164	-.563(10-15)-.563(8-13)+.261(10-17)-.261(6-13)+.206(9-14)
5.590	0.000	-.439(10-15)+.429(8-13)-.298(10-14)+.298(9-13)+.292(10-17)+.292(6-13)
5.691	0.000	+.383(9-17)+.383(8-14)-.347(8-16)+.347(7-15)-.279(10-15)+.279(8-13)
5.818	0.103	-.469(11-18)-.469(5-12)+.363(9-14)+.233(11-16)+.233(7-12)+.190(9-16)
5.847	0.067	-.445(9-14)-.434(11-18)-.434(5-12)+.264(11-17)-.264(6-12)-.235(11-16)
5.886	0.045	-.569(11-17)+.569(6-12)-.376(9-14)-.212(8015)
5.925	0.000	+.420(11-17)+.420(1-12)+.393(9-15)-.393(8-14)-.239(10-15)+.289(8-13)
6.368	0.019	-.618(9-15)-.618(8-14)+.165(10-16)+.165(7-13)
6.487	0.354	-.710(8-15)+.242(10-17)-.252(6012)+.184(9-14)-.175(7-16)-.167(10-15)

TABLE 2.1d - WAVE FUNCTIONS AND EXCITATION ENERGIES OF BENZ(a)NAPTHACENE

COMPOSITE SYSTEM (Ib) WITH β_{RS} = 0.0 EV

Excitation Energy (ev)	f	CI Excited State Wave Functions
3.481	0.000	-.654(11-13)+.648(10-12)+.185(11-15)+.179(8-12)
3.567	0.397	-.969(11-12)+.194(10-13)
4.212	0.000	+.906(9-12)+.306(9-15)+.221(9-13)
4.212	0.000	+.906(11-14)-.306(8-14)+.221(10-14)
4.289	1.437	-.671(10-12)-.665(11013)+.197(8-12)-.193(11-15)
4.397	0.000	+.471(8-13)+.470(10-15)+.446(11-16)-.442(7-12)+.197(8-12)+.92(11-15)
4.732	0.035	+.729(11-15)+.499(8-12)-.196(10-12)-.165(8-13)
4.746	0.576	-.583(8-12)-.546(10-13)+.407(9-14)+.287(11-15)-.157(11-13)
4.860	0.401	-.837(9-14)-.330(8-12)+.320(11-15)
4.989	0.444	+.760(10-13)-.336(8-12)+.315(11-15)+.236(9-14)
5.215	0.000	-.753(9-13)+.512(9-16)+.287(9-15)-.175(9-18)
5.215	0.000	-.753(10-14)+.512(7-14)-.287(8-14)-.175(5-14)
5.299	0.000	+.439(11-16)+.418(11-17)-.409(7012)+.400(6-12)-.346(10-15)-.337(8-13)
5.510	0.000	-.462(5-12)+.450(11-18)+.393(8-16)+.392(7-15)+.346(10-17)+.324(6-13)
5.621	0.515	-.670(7-12)-.646(11-16)
5.732	0.001	+.472(11-17)+.446(6.12)-.284(11-18)+.277(8-13)+.267(10-15)+.264(5-12)
5.849	0.770	+.479(6-12)-.446(11-17)+.446(10-15)-.438(8-13)-.196)8-15)+.164(11-18)
6.032	0.346	-.509(10-16)-.470(7-13)+.307(11-18)+.279(5-12)+.265(8013)-.238(10-15)
6.097	0.000	+.772(9-15)-.408(9-17)-.399(9-12)+.260(9-12)
6.097	0.000	-.772(8-14)+.408(6-14)-.399(11-14)+.260(10-14)
6.102	0.002	+.489(7-13)-.425(10-16)-.289(5-12)-.276(6-13)-.275(10-17)+.269(11-17)
6.136	0.000	-.707(9-19)+.707(4-14)
6.256	0.434	+.430(10-15)-.430(8-13)-.401(7013)-.388(10-16)+.304(11017)-.309(6-12)
6.294	0.002	+.409(10-16)+.393(10-18)-.377(5-13)-.354(7-13)-.251(5-12)+.234(11-18)

TABLE 2.1e - WAVE FUNCTIONS AND EXCITATION ENERGIES OF BENZ(a)NAPTHACENE

COMPOSITE SYSTEM (Ib) WITH β_{RS} = -1.000 EV

Excitation Energy (ev)	f	CI Excited State Wave Functions
3.387	0.377	-.970(11-12)
3.437	0.002	-.557(11-13)+.557(10-12)+.325(11-14)+.319(9-12)-.162(11-15)-.158(8-12)
3.997	0.491	-.609(11-13)-.608(10-12)-.321(11014)+.321(9-12)
4.179	0.000	+.575(11-14)+.572(9-12)+.317(11-13)-.319(10-12)-.159(9-15)+.160(8-14)
4.300	1.523	-.589(9-12)+.567(11-14)-.318(10-12)-.308(11-13)+.202(10-14)
4.311	0.018	-.416(7-12)-.402(11-16)+.346(8-13)+.334(10-15)-304(9-13)+.267(11-15)
4.698	0.166	+.774(11-15)+.355(10-13)+.205(11-16)-.188(9-14)+.173(10-12)+.173(8-12)
4.702	0.278	+.749(8-12)-.465(10-13)+.240(9-14)+.179(7-12)-.155(11-13)
4.981	0.424	+.596(10-13)+.365(8-12)-.360(11-15)+.359(9-13)-.342(10-14)
5.037	0.000	+.341(10-14)+.329(9-13)+.316(9-15)-.314(8-14)-.304(9-16)+.307(7-14)
5.252	0.000	-.381(11-17)-.382(6-12)+.375(7-12)+.358(11-16)+.326(10-15)+.328(8-13)
5.269	0.142	-.365(9-14)+.225(11-16)-.224(11-15)+.218(8-12)-.213(8-14)-.212(9-13)
5.415	0.250	+.479(11-16)-.443(7-12)-.334(10-14)+.282(9-13)-.257(10-13)+.236(8-13)
5.580	0.150	-.380(7-12)+.307(7-15)+.305(9-14)+.294(10-14)+.265(11-18)-.225(8-16)
5.585	0.162	-.364(9-13)+.343(11-16)+.340(9-14)+.289(8-16)+.261(10-13)+.246(5-12)
5.634	0.000	-.385(5-12)+.379(11-18)+.361(11-17)+.343(6-12)+.306(7012)+.252(11-16)
5.835	0.551	+.508(6-12)-.459(11-17)-.292(8-13)+.283(10-15)+.248(9-14)+.228(10-14)
5.987	0.482	+.490(10-16)-.360(8-14)-.319(9-15)-.289(11-18)-.283(10-17)-.269(10-15)
6.016	0.060	-.467(7-13)+.346(6-13)+.265(10-14)+.255(9-17)-.243(10-16)-.237(5-12)
6.157	0.046	+.317(9-15)+.318(8-14)-.249(11-17)+.244(6012)-.231(10-15)-.233(6-14)
6.249	0.000	+.366(8-13)+.350(10-15)+.284(8-14)-.282(9-15)-.262(10-17)-.251(6-13)
6.293	0.230	+.469(7-13)+.324(8-13)-.310(7-14)-.306(11-17)-.301(10-15)-.278(5-13)
6.321	0.109	+.489(10-16)-.305(5-12)+.300(10-18)-.268(6-12)+.251(9-16)+.245(8-14)
6.432	0.055	+.509(5-12)+.495(11-18)+.335(9-16)+.328(7-14)+.196(6-12)

TABLE 2.1f - WAVE FUNCTIONS AND EXCITATION ENERGIES OF BENZ(a)NAPTHACENE

COMPOSITE SYSTEM (Ic) WITH β_{RS} = 0.0 EV

Excitation Energy (ev)	f	CI Excited State Wave Functions
3.434	0.324	-.985(11-12)-.169(9-14)
3.531	0.000	+.692(11-14)-.692(9-12)
4.310	0.000	+.944(11-13)-.295(7-13)
4.310	0.000	-.944(10-12)-.295(10-16)
4.410	0.000	+.678(10-15)+.678(8-12)-.200(8-19)+.200(4-15)
4.593	0.000	-.693(11-16)-.693(7-12)
4.642	0.813	+.637(10-13)+.484(11-16)-.484(7-12)-.236(11-14)-.261(9-12)
4.694	0.852	+.568(10-13)-.504(11-16)+.504(7-12)-.261(11-14)-.261(9-12)
4.971	2.052	+.585(11-14)+.585(9-12)+.461(10-13)-.162(8-15)+.161(10-15)-.161(8-13)
5.051	0.000	+.511(9-16)+.511(7-14)+.489(11-17)+.489(11-17)+.489(6-12)
5.420	0.000	-.707(11-18)+.707(5-12)
5.425	0.000	-.958(11-15)+.243(7-15)
5.425	0.000	+.958(8-12)+.243(8-16)
5.618	0.000	+.904(9-13)+.403(6-13)
5.618	0.000	-.904(10-14)+.403(10-17)
5.860	0.137	-.616(10-15)+.616(8-13)-.193(8-15)-.177(11-18)-.177(5-12)+.163(9-14)
5.921	0.006	-.615(11-18)-.615(5-12)+.365(7-16)+.154(10-15)-.154(8-13)
6.124	0.000	-.560(9-18)+.560(5-14)+.355(7-17)-.355(6-16)-.244(10-20)
6.192	0.015	-.637(8-15)+.479(9-14)-.294(11-17)+.294(6-12)-.206(10-19)
6.234	0.000	+.892(7-13)-.314(5-13)+.307(11-13)
6.234	0.000	+.892(10-16)+.314(10-18)-.307(10-12)
6.253	0.732	+.721(9-14)+.409(8-15)-.250(7-16)+.222(11-17)-.222(6-12)-.207(11-18)
6.286	0.000	-.511(11-17)-.511(6-12)+.489(9-16)+.489(7-14)
6.341	0.000	-.707(10-19)-.707(4-13)
6.420	0.114	-.532(11-17)+.532(6-12)+.365(8-15)-.336(9-16)+.336(7-14)

TABLE 2.1g - WAVE FUNCTIONS AND EXCITATION ENERGIES OF BENZ(a)NAPTHACENE

COMPOSITE SYSTEM (Ic) WITH β_{RS} = -1.000 EV

Excitation Energy (ev)	f	CI Excited State Wave Functions
3.327	0.349	+.983(11-12)
3.642	0.000	+.552(11-14)+.543(9-12)+.290(11-15)+.287(8-12)-.262(11-13)+.261(10-12)
4.074	0.339	+.670(10-12)+.656(11-13)+.244(10-13)
4.195	0.000	-.583(11-13)+.561(10-12)+.228(10-14)+.227(9-13)-.211(9-12)-.208(11-14)
4.393	0.001	-.391(10-14)-.387(9-13)+.329(11-15)-.325(10-16)-.319(7-13)+.315(8-12)
4.562	1.566	-.576(9-12)+.549(11-14)-.368(10-13)+.251(7-12)-.251(11-16)+.214(8-12)
4.689	0.000	-.461(11-16)-.457(11-15)-.455(7-12)-.454(8-12)
4.778	1.173	-.459(8-12)+.457(11-15)-.362(9-12)+.347(11-14)-.308(7-12)+.305(11-16)
4.952	0.000	-.373(8-14)+.369(9-15)-.317(11-17)-.316(6-12)+.256(10-16)+.247(7-13)
5.029	0.135	-.768(10-13)-.242(8-12)+.240(11-15)+.188(9-14)+.176(7-13)+.174(11-13)
5.343	0.000	+.424(11-18)+.422(5-12)-.309(11-16)-.289(7-12)+.268(9-13)+.265(10-14)
5.410	0.284	-.544(11-16)+.513(7-12)+.394(11-15)-.381(8-12)+.187(10-13)
5.433	0.001	+.493(11-18)+.484(5-12)+.306(7-12)-.280(10-14)-.274(9-13)+.237(11-16)
5.713	0.151	-.578(9-13)+.576(10-14)+.216(10-15)-.211(8-13)
5.735	0.000	+.399(10-15)+.339(8-13)+.291(10-17)+.274(8-16)+.258(6-13)-.254(7-15)
5.863	0.206	-.423(8-13)+.363(10-15)+.320(7-13)-.294(10-16)-.260(9-14)-.236(6-16)
5.900	0.048	-.474(5-12)+.465(11-18)-.275(10-14)+.264(9-13)+.261(9-14)-.216(8-13)
6.064	0.675	+.745(9-14)-.252(11-18)+.243(5-12)+.212(6-12)+.212(10-15)-.194(11-17)
6.122	0.000	-.504(11-17)-.475(6-12)+.251(8-14)-.238(9-15)-.216(7-13)+.208(10-19)
6.213	0.208	+.447(7-13)-.421(10-16)+.340(9-14)+.278(10-13)-.266(6-12)+.226(5-13)
6.220	0.004	+.382(10-15)+.369(8-13)+.269(11-19)+.255(10-16)+.239(10-18)+.198(5-13)
6.279	0.060	+.489(11-17)-.488(6-12)+.295(5-12)-.283(11-18)-.259(7-13)+.235(10-16)
6.367	0.000	+.371(11-19)+.342(4-12)+.298(10-19)-.280(10-17)+.279(4-13)-.260(6-13)
6.448	0.028	-.513(9-15)-.448(8-14)+.265(10-15)+.268(7-14)+.227(9-16)-.221(8-13)
6.466	0.000	+.434(8-14)+.379(10-16)+.362(7-13)-.348(9-15)-.253(11-19)-.232(4-12)

TABLE 2.2a - WAVE FUNCTIONS AND EXCITATION ENERGIES OF BENZO(b)CHRYSENE (II)

Excitation Energy (ev)	f	CI Excited State Wave Functions
3.305	0.565	+.971(11-12)
3.433	0.000	-.478(11-13)-.478(10-12)+.472(11-14)+.472(9-12)
4.035	0.560	-.676(11-13)+.676(10-12)
4.089	0.000	+.442(10-14)-.442(9-13)-.322(11-16)+.322(7-12)-.291(11-15)-.291(8-12)
4.243	0.000	+.431(11-13)+.431(10-12)+.429(11-14)+.429(9-12)-.262(10-14)+.262(9-13)
4.484	2.343	+.648(11-14)-.648(9-12)-.187(9-14)-.151(10-13)
4.881	0.188	+.667(10-13)+.336(11-15)-.336(8-12)-.287(11-16)-.287(7-12)+.265(9-14)
4.934	0.000	-.511(11-15)-.511(8-12)+.348(11-16)-.348(7-12)+.153(9-15)-.153(8-14)
5.143	0.000	+.402(9-15)-.402(8-14)+.370(10-16)+.370(7-13)+.266(11-18)-.266(5-12)
5.180	0.393	-.492(10-13)+.418(10-14)+.418(9-13)+.298(11-15)-.298(8-12)-.212(9-14)
5.432	0.000	+.449(11-16)-.449(7-12)+.332(10-14)-.332(9-13)+.269(11-17)+.269(6-12)
5.460	0.399	-.497(9-14)-.394(11-15)+.392(8-12)+.367(10-13)+.282(10-14)+.282(9-13)
5.474	0.000	-.533(11-17)-1533(6-12)+.210(11-19)-.210(4-12)+.207(10-14)-.207(9-13)
5.528	0.027	+.640(9-14)-.332(11-16)-.332(7-12)-.301(11-15)+.301(8-12)-.266(10-13)
5.710	0.065	+.393(11-16)+.393(7-12)-.314(10-15)-.314(8-13)+.291(10-14)+.291(9-13)
5.803	0.000	-.369(9-17)+.369(6-14)-.345(11-18)+.345(5-12)-.269(8-16)-.269(7-15)
5.926	0.342	+.432(11-17)-.432(6-12)+.291(10-14)+.291(9-13)+.259(11-16)+.259(7-12)
6.130	0.000	-.329(10-17)+.329(6-13)+.322(11-19)-.322(4-12)-.294(11-18)+.298(5-12)
6.142	0.140	+.449(10-15)+.449(8-13)-.317(11-17)+.317(6-12)+.219(10-16)-.219(7-13)
6.209	0.000	-.595(10-15)+.595(8-13)-.259(11-19)+.259(4-12)
6.292	0.012	-.442(11-18)-.442(5-12)-.256(10-16)+.256(7-13)+.248(11-19)+.248(4-12)

TABLE 2.2b - WAVE FUNCTIONS AND EXCITATION ENERGIES OF BENZO(b)CHRYSENE

COMPOSITE SYSTEM (IIa) WITH β_{RS} = 0.0 EV

Excitation Energy (ev)	f	CI Excited State Wave Functions
3.481	0.000	-.654(11-13)-.648(10-12)-.185(11-15)+.179(8-12)
3.567	0.418	-.968(11-12)+.199(10-13)
4.290	1.404	-.671(10-12)+.664(11-13)-.197(8-12)-.195(11-15)
4.397	0.000	+.471(10-15)+.470(8-13)+.446(11-16)+.442(7-12)-.198(8-12)+.192(11-15)
4.428	0.000	-.680(11-14)+.667(10-14)-.231(7-14)+.180(8-14)
4.431	0.000	-.680(9-12)-.667(9-13)+.232(9-16)+.180(9-15)
4.584	0.081	+.712(9-14)-.616(10-13)
4.732	0.001	+.656(11-15)-.606(8-12)-.175(10-12)-.168(11-13)-.152(11-16)
4.764	0.000	+.616(10-14)+.616(11-14)-.347(8-14)-.301(7-14)+.170(6-14)
4.764	0.000	-.616(9-12)+.615(9-13)+.347(9-15)-.301(9-16)
4.821	0.868	+.644(8-12)+.599(11-15)+.305(9-14)+.177(11-13)-.175(10-12)
5.149	0.401	-.702(10-13)-.553(9-14)+.162(6-12)+.160(8-15)
5.299	0.000	+.441(11-16)+.423(11-17)+.406(7-12)+.394(6-12)-.350(10-15)-.332(8-13)
5.510	0.000	-.462(5-12)-.450(11-18)-.393(8-16)-.393(7-15)+.346(10-17)-.325(6-13)
5.623	0.461	-.668(7-12)+.643(11-16)
5.732	0.001	-.470(11-17)-.448(6-12)-.284(11-18)-.276(8-13)-.268(10-15)-.264(5-12)
5.852	0.855	+.459(10-15)-.454(8-13)+.438(6-12)-.412(11-17)+.165(7-13)-.150(11-18)
6.000	0.000	+.805(8-14)-.404(6-14)+.385(11-14)
6.000	0.000	+.805(9-15)+.404(9-17)+.386(9-12)
6.024	0.222	+.455(10-16)+.426(7-13)+.339(11-18)-.309(6-12)-.300(5-12)-.245(8-13)
6.102	0.001	-.480(7-13)+.434(10-16)+.287(5-12)+.276(10-17)-.276(6-13)-.273(11-17)
6.293	0.097	-.500(7-13)+.366)5-13)-.329(10-18)+.256(11-17)-.242(11-18)+.232(10-15)
6.297	0.460	-.522(10-16)-.400(8-13)+.361(10-15)-.321(6-12)+.218(10-18)-.217(7-13)

TABLE 2.2c - WAVE FUNCTIONS AND EXCITATION ENERGIES OF BENZO(b)CHRYSENE

COMPOSITE SYSTEM (IIa) WITH β_{RS} = -1.000 EV

Excitation Energy (ev)	f	CI Excited State Wave Functions
3.454	0.001	+.528(11-13)+.523(10-12)+.404(11-14)+.399(9-12)
3.491	0.493	+.965(11-12)+.178(10-13)
4.123	0.846	+.670(10-12)-.665(11-13)
4.224	0.000	-.511(10-14)+.503(9-13)-.393(11-16)-.390(7-12)-.193(10-15)+.192(8-13)
4.390	0.002	-.483(11-14)-.435(9-12)+.410(10-12)+.404(11-13)-.215(10-15)+.208(8-13)
4.443	1.215	-.602(9-12)+.561(11-14)+.350(10-13)+.338(9-14)
4.752	0.402	-.609(11-15)+.438(10-13)-.340(10-14)+.319(8-12)+.204(11-16)+.158(7-14)
4.761	0.097	+.551(8-12)-.308(9-13)-.284(7-12)-.260(10-15)+.260(8-13)+.228(10-13)
4.860	0.005	+.528(11-15)+.515(8-12)-.287(9-12)+.254(9-15)-.217(8-14)-.206(10-14)
4.888	0.112	+.674(9-14)-.333(11-14)+.312(10-13)+.294(9-13)+.261(9-12)+.209(10-14)
5.037	0.111	-.632(10-13)+.496(9-14)+.315(8-12)-.311(11-15)
5.288	0.011	+.451(6-12)-.407(7-12)-.376(8-13)-.363(11-17)-.358(11-16)+.249(10-14)
5.308	0.191	+.482(9-13)+.406(10-14)-.365(10-15)+.291(11-17)+.233(11-16)+.227(8-14)
5.521	0.003	-.495(11-18)-.491(5-12)+.321(8-16)-.319(7-15)+.195(10-17)+ .193(9-17)
5.610	0.297	-.680(7-12)+.618(11-16)+.160(10-15)
5.685	0.001	-.434(11-17)+.404(6-12)+.298(11-16)-.236(10-17)-.235(6-13)-.230(9-15)
5.812	0.504	+.407(6-12)+.394(11-17)-.357(10-15)-.342(8-13)-.293(9-13)-.283(10-14)
6.030	0.053	+.457(9-15)-.366(6-12)-.292(11-17)-.289(10-17)+.279(8-14)-.270(11-18)
6.043	0.012	-.463(8-14)-.348(6-13)-.288(10-17)-.275(11-18)-.270(5-12)-.242(10-16)
6.056	0.295	+.473(7-13)+.432(10-16)-.308(5-12)+.272(7-14)+.269(9-15)+.252(8-13)
6.143	0.000	-.407(7-13)+.377(10-16)+.334(8-13)-.324(10-15)+.231(9-17)+.222(6-14)
6.288	0.715	+.410(10-15)+.384(8-14)+.366(8-13)-.319(7-13)+.309(9-15)+.284(11-17)
6.333	0.013	+.395(10-16)-.312(7-13)-.276(10-18)+.259(5-13)-.226(7-14)+.221(5-14)
6.422	0.001	+.366(7-14)-.350(9-16)+.295(9-18)-.294(5-14)-.256(9-15)+.234(10-16)

TABLE 2.2d - WAVE FUNCTIONS AND EXCITATION ENERGIES OF BENZO(b)CHRYSENE

COMPOSITE SYSTEM (IIb) WITH β_{RS} = 0.0 EV

Excitation Energy (ev)	f	CI Excited State Wave Functions
3.594	0.000	-.685(11-14)+.685(9-12)+.159(8-16)-.159(7-15)
3.772	0.635	-.962(11-12)-.227(9-14)
4.447	0.000	+.525(9-15)-.525(8-14)+.435(11-16)-.435(7-12)
4.494	0.000	+.860(11-13)-.460(8-13)+.173(6-13)
4.494	0.000	+.860(10-12)-.460(10-15)-.173(10-17)
4.775	0.637	-.753(10-13)-.408(11-14)-.408(9-12)+.187(11-15)+.187(8-12)
4.775	0.000	+.668(11-15)-.668(8-12)-.156(9-15)+.156(8-14)
4.783	1.695	-.541(9-14)-.469(11-14)-.469(9-12)+.391(10-13)-.194(11-15)-.194(8-12)
4.798	0.033	-.621(11-15)-.621(8-12)-.309)10-13)+.214(9-16)+.214(7-14)
5.089	0.000	+.878(10-14)+.451(10-16)-.152(10-12)
5.089	0.000	+.878(9-13)+.451(7-13)-.152(11-13)
5.223	1.023	-.761(9-14)-.345(10-13)+.313(11-14)+.313(9-12)+.214(11-12)
5.488	0.000	+.492(9-17)+.492(6-14)-.362(8-16)+.362(7-15)-.270(11-17)-.270(6-12)
5.620	0.000	+.638(11-17)_.638(6-12)+.215(9-17)+.215(6-14)
5.690	0.000	=.513(11-16)∓.513(7-12)+.362(9-15)-.362(8-14)+.246(11-18)+.246(5-12)
5.719	0.012	+.665(9-15)+.665(8-14)-.167(11-16)-.167(7-12)
5.774	0.376	-.572(8-15)+.557(11-17)-.557(6-12)
5.924	0.003	+.659(11-16)_.659(7-12)+.185(9-15)+.185(8-14)
5.978	0.000	-.794(8-13)-.486(11-13)+.353(6-13)
5.978	0.000	-.794(10-15)-.486(10-12)-.353(10-17)
6.136	0.000	-.707(10-19)+.707(4-13)
6.305	0.210	-.780(8-15)-.388(11-17)+.388(6-12)-.152(8-16)-.152(7-15)
6.319	0.000	+.549(11-18)+.549(5-12)-.219(9-16)+.219(7-14)+.214(9-18)+.214(5-14)
6.444	0.000	-.453(9-16)+.453(7-14)+.391(9-18)+.391(5-14)-.308(11-18)-.308(5-12)

TABLE 2.2e - WAVE FUNCTIONS AND EXCITATION ENERGIES OF BENZO(b)CHRYSENE

COMPOSITE SYSTEM (IIb) WITH β_{RS} = -1.000 EV

Excitation Energy (ev)	f	CI Excited State Wave Functions
3.569	0.000	+.533(11-14)-.533(9-12)+.411(11-13)+.411(10-12)
3.643	0.646	-.954(11-12)-.171(9-14)
4.204	0.186	-.636(11-13)+.636(10-12)+.214(11-14)-.208(10-13)
4.303	0.000	+.450(10-14)+.450(9-13)-.413(11-16)+.413(7-12)-.238(9-15)+.238(8-14)
4,430	0.000	-.502(11-13)-.502(10-12)+.392(11-14)-.392(9-12)-.221(10-15)-.221(8-13)
4.617	2.187	-.598(11-14)-.598(9-12)-.204(10-13)-.194(10-14)+.194(9-13)-.190(9-14)
4.767	0.000	+.631(11-15)-.631(8-12)-.198(10-14)-.198(9-13)
4.813	0.086	-.535(11-15)-.535(8-12)+.223(9-14)+.158(10-14)-,158(9-13)
5,018	0.000	+.389(9-15)-.389(8-14)-.321(10-16)-.321(7013)+.258(10-14)+.258(9-13)
5.099	0.235	-.521(10-13)-.325(10-14)+.325(9-13)+.294(9-14)+.255(11-15)+.255(8-12)
5.341	0.207	-.814(9-14)-.419(10-13)+.175(11-16)+.175(7-12)
5.422	0.622	-.491(10-15)+.491(8-13)+.320(10-14)-.320(9-13)-.180(11-17)+.180(6-12)
5.534	0.000	-.571(11-17)-.571(6-12)-.184(10-15)-.184(8-13)-.171(9-18)-.171(6-14)
5.581	0.000	-.362(9-17)-.362(6-14)-.312(8-16)+.312(7-15)+.300(11-17)+.300(6-12)
5.630	0.000	-.429(11-16)+.429(7-12)-.227(10-15)-.227(8-13)+.208(9-15)-.208(8-14)
5.666	0.336	+.363(10-13)-.305(10-14)+.305(9-13)+.303(11-16)+.303(7-12)-.270(11-15)
5.851	0.106	+.421(9-15)+.421(8-14)+.369(11-16)+.369(7-12)+.295(11-17)-.295(6-12)
5.890	0.028	-.422(11-16)-.422(7-12)+.368(9-15)+.368(8-14)+.239(10-16)-.239(7-13)
6.017	0.069	-.421(11-17)+.421(6-12)-.302(8-15)+.252(9-15)+.252(8-14)+.232(10-17)
6.099	0.000	-.356(11-18)+.356(5-12)-.294(10-15)-.294(11-14)+.217(10-14)+.217(9-13)
6.224	0.000	+.415(11-18)-.415(5-12)-.353(10-.5)-.353(8-13)-.199(9-15)+.199(8-14)
6.357	0.121	-.555(8-15)+.290(11-17)-.290(6-12)+.278(10-17)+.278(6-13)-.166(9-15)
6.429	0.000	-.447(10-16)-.447(7-13)+.255(9-16)-.255(7-14)+.250(9-18)-.250(5-14)
6.464	0.035	+.415(10-16)-.415(7-13)-.338(11-18)-.338(5-12)-.327(9-16)-.327(7-14)

TABLE 2.2f - WAVE FUNCTIONS AND EXCITATION ENERGIES OF BENZO(b)CHRYSENE

COMPOSITE SYSTEM (IIc) WITH β_{RS} = 0.0 EV

Excitation Energy (ev)	f	CI Excited State Wave Functions
3.408	0.347	+.976(11-12)+.164(9-14)
3.631	0.000	-.692(11-14)+.692(9-12)
4.123	0.000	+.943(10-12)+.265(10-16)
4.123	0.000	+.943(11-13)-.265(7-13)
4.410	0.000	+.678(10-15)+.678(8-13)+.200(8-19)-.200(11-14)
4.550	0.172	-.594(10-13)-.550(11-16)+.550(7-12)
4.593	0.000	+.693(11-16)+.693(7-12)
4.845	0.061	+.655(10-13)-.403(11-16)+.403(7-12)-.284(11-14)-.284(9-12)
4.909	3.515	+.620(11-14)+.620(9-12)+.371(10-13)-.151(11-16)+.151(7-12)
5.051	0.000	+.511(9-16)+.511(7-14)+.489(11-17)+.489(6-12)
5.420	0.000	-.707(11-18)+.707(5-12)
5.438	0.000	+.960(11-15)-.245(7-15)
5.438	0.000	+.960(8-12)+.245(8-16)
5.711	0.000	-.937(9-13)-.319(6-13)
5.711	0.000	-.937(10-14)+.319(10-17)
5.874	0.301	-.622(10-15)+.622(8-13)-.183(8-15)
5.922	0.057	+.632(11-18)+.632(5-12)-.354(7-16)
6.051	0.000	+.899(10-16)+.332(10-18)-.256(10-12)
6.051	0.000	+,899(7-13)-.332(5-13)+.256(11-13)
6.124	0.000	+.560(9-18)-.560(5-14)-.355(7-17)+.355(6-16)+.244(11-20)
6.134	0.331	+.741(9-14)-.568(8-15)+.171(10-19)=.171(4-13)-.156(7-16)
6.286	0.000	-.511(11-17)-.511(6-12)+.489(9-16)+.489(7-14)
6.335	0.254	-.619(8-15)-.506(9-14)+.269(7-16)+.210(10-19)-.210(4-13)+.202(11-18)
6.341	0.000	+.707(10-19)+.707(4-13)
6.387	0.050	-.625(11-17)+.625(6-12)=.275(9-16)+.275(7-14)

TABLE 2.2g - WAVE FUNCTIONS AND EXCITATION ENERGIES OF BENZO(b)CHRYSENE

COMPOSITE SYSTEM (IIc) WITH β_{RS} = -1.000 EV

Excitation Energy (ev)	f	CI Excited State Wave Functions
3.369	0.415	-.974(11-12)
3.620	0.000	+.505(11-14)+.502(9-12)-.385(11-13)-.374(10-12)+.241(11-15)-.235(8-12)
4.056	0.017	+.589(10-12)+.379(11-13)+.284(10-14)-.252(9-13)+.249(9-12)+.245(11-14)
4.077	0.566	+.731(11-13)-.582(10-12)-.158(8-12)
4.490	0.000	-.374(10-14)+.360(9-13)-.319(10-16)+.317(7-13)+.316(8-12)-.304(11-15)
4.639	0.487	+.483(11-14)-.465(8-12)-.406(10-13)-.308(11-15)-.237(8-12)-.226(11-16)
4.713	0.003	+.506(8-12)-.476(11-15)-.318(7-12)-.292(11-16)+.242(10-16)-.235(7-13)
4.881	0.047	-.682(10-13)+.393(11-15)+.385(8-12)+.275(11-16)-.268(7-12)
4.964	0.001	-.355(9-15)-.354(8-14)-.327(11-18)-.327(5-12)+.271(11-16)+.267(7-12)
4.993	2.421	+.462(10-13)-.461(9-12)+.451(11-14)+.391(8-12)+.377(11-15)
5.336	0.146	-.525(11-16)+.498(7-12)+.280(9-13)+.264(11-15)+.250(8-12)+.250(10-14)
5.385	0.001	+.381(5-12)+.375(11-18)+.336(7-12)-.311(11-17)-.304(6-12)+.288(11-16)
5.495	0.001	-.402(6-12)-.398(11-17)-.383(11-16)-.382(7-12)-.223(10-14)+.208(11-19)
5.592	0.281	-.591(9-13)-.528(10-14)+.281(9-14)+.235(8-13)-.220(10-15)+,209(7-12)
5.763	0.000	-.395(10-14)+.348(9-13)-.300(10-15)+.260(10-16)-.255(8-13)-.238(7-13)
5.835	0.130	-.400(11-17)+.398(6-12)-.352(8-13)+.340(10-15)-.199(4-12)+.196(9-16)
5.960	0.089	+.694(9-14)+.233(7-16)+.231(8-13)-.209(7-12)+.200(11-16)+.196(10-14)
5.985	0.000	+.538(8-13)+.537(10-15)+.257(10-16)-.253(7-13)-.224(6-13)+.223(10-17)
6.020	0.098	-.438(10-15)+.428(8-13)-.339(9-14)-.327(11-17)+.321(6-12)+.225(10-13)
6.130	0.082	+.465(7-13)+.445(10-16)-.359(11-18)+.336(5-12)+.190(6-13)
6.197	0.000	-.336(11-18)-.332(5-12)-.316(11-17)-.299(6-12)+.284(8-14)+.282(9-15)
6.408	0.087	+.488(5-12)-.374(11-17)-.337(11-18)+.316(6-12)-.289(9-16)-.281(7-14)
6.437	0.368	+.477(7-14)_.423(9-16)-.339(11-19)-.330(9-15)-.231(10-16)+.221(8-15)
6.452	0.059	-.403(8-14)-.400(4-12)+.398(11-18)-.284(11-19)-.272(4-13)-.240(9-16)

TABLE 2.3a - WAVE FUNCTIONS AND EXCITATION ENERGIES OF DIBENZO(b,g)PHENANTHRENE (III)

Excitation Energy(ev)	f	CI Excited State Wave Functions
3.343	0.000	+.624(11-13)-.624(10-12)-.194(11-14)-.194(9-12)+.171(11-15)-.171(8-12)
3.349	0.228	-.968(11-12)-.186(10-13)
4.041	1.606	+.659(11-13)+.659(10-12)-.284(10-13)+.107(10-15)+.107(8-13)
4.085	0.000	-.501(11-15)+.501(8-12)+.438(10-14)+.438(9-13)
4.235	0.177	+.684(11-14)-.684(9-12)-.131(10-13)
4.336	0.000	-.647(11-14)-.647(9-12)-.206(11-13)+.206(10-12)+.112(9-16)-.112(7-14)
4.706	0.505	-.880(10-13)-.198(11-13)-.198(10-12)+.172(11-12)+.160(9-14)
4.950	0.000	-.382(11-15)+.382(8-12)-.368(10-14)-.368(9-13)-.284(11-16)
5.056	0.000	+.373(11-17)+.373(6-12)+.370(9-15)+.370(8-14)+.248(10-14)+.248(9-13)
5.086	0.144	+.481(11-15)+.481(8-12)+.378(11-16)-.378(7-12)
5.236	0.000	-.558(11-16)-.558(7-12)+.258(11-18)+.258(5-12)-.173(11-17)-.173(6-12)
5.385	1.052	+.497(10-14)-.497(9-13)-.408(11-15)-.408(8-12)+.202(11-16)-.202(7-12)
5.634	0.000	-.571(10-15)+.581(8-13)-.218(10-17)-.218(6-13)-.163(10-18)-.173(5-13)
5.654	0.816	-.411(9-14)+.366(11-16)-.366(7-12)-.323(10-14)+.323(9-13)
5.716	0.000	-.512(11-18)-.512(5-12)-.220(9-17)-.215(6-12)+.183(8-16)+.183(7-15)
5.787	0.266	-.557(10-15)-.557(8-13)+.288(9-14)+.221(9-13)-.221(10-14)
5.901	0.000	+.319(10-18)+.319(5-13)-.267(11-18)-.267(5-12)-.252(8-16)-.252(7-15)
5.909	0.405	-.704(9-14)-.312(11-16)+.312(7-12)-.232(10-15)-.232(8-13)
6.025	0.000	+.406(10-16)+.406(7-13)-.382(11-17)-.382(6-12)+.251(11-18)+.251(5-12)
6.058	0.146	-.596(11-17)+.596(6-12)-.182(9-15)+.182)9-14)+.152(10-17)-.162(6-13)
6.214	0.352	+.541(11-18)-.541(5-12)-.271(10-16)+.271(7-13)-.185(11-17)+.185(6-12)
6.360	0.000	+.491(9-15)+.491(8-14)+.292(10-16)-.292(7-13)-.247(11-17)-.247(6-12)
6.371	0.117	-.459(10-16)+.459(7-13)-.265(11-18)+.265(5-12)+.222(9-15)-.222(8-14)
6.496	0.426	+.462(9-15)-.462(8-14)+.357(10-16)-.357(7-13)+.261(8-15)

TABLE 2.3b - WAVE FUNCTIONS AND EXCITATION ENERGIES OF DIBENZO(b,g)PHENANTHRENE

COMPOSITE SYSTEM (IIIa) WITH β_{RS} = 0.0 EV

Excitation Energy (ev)	f	CI Excited State Wave Functions
3.481	0.000	-.655(11-13)+.647(10-12)+.185(11-15)+.179(8-12)-.114(7-12)+.112(11-16)
3.566	0.420	-.969(11-12)-.191(10-13)
4.204	0.746	-.628(10-12)-.617(11-13)+.358(9-14)+.192(8-12)-.182(11-15)
4.353	0.000	-.928(11-14)-.265(9-14)+.193(10-14)-.140(6-14)
4.353	0.000	+.926(9-12)-.265(9-15)-.199(9-13)-.141(9-17)
4.397	0.001	+.471(8-13)+.470(10-15)+.445(11-16)-.443(7-12)+.194(11-15)+.196(8-12)
4.553	0.000	+.914(10-14)+.311(7-14)+.222(11-14)
4.560	0.000	+.913(9-13)+.314(9-16)+.228(9-12)
4.726	1.382	-.678(10-13)-.510(9-14)-.298(8-12)-.254(11-13)-.211(10-12)
4.732	0.032	-.697(11-15)-.550(8-12)+.201(10-12)+.148(11-16)+.148(8-13)-.147(7-12)
4.814	0.060	+.603(8-12)-.509(11-15)-.477(9-14)+.171(7-12)-.159(10-15)+.145(11-16)
5.086	0.751	+.653(10-13)+.525(9-14)-.249(8-12)+.247(11-15)-.206(11-13)-.207(10-12)
5.299	0.000	-.440(11-16)-.418(11-17)+.408(7-12)-.400(6-12)+.347(10-15)+.337(8-13)
5.510	0.000	-.462(5-12)+.450(11-18)+.393(7-15)+.393(8-16)+.346(10-17)+.324(6-13)
5.633	0.328	-1664(7-12)-.636(11-16)-.144(10-15)+.124(8-13)
5.732	0.001	+.473(11-17)+.445(6-12)-.284(11-18)+.281(8-13)+.262(10-15)+.263(5-12)
5.748	0.000	-.881(8-14)-.352(6-14)+.273(11-14)-.127(10-14)
5.748	0.000	+.881(9-15)+.352(9-17)+.274(9-12)-.127(9-13)
5.863	0.713	+.515(6-12)-.472(11-17)+.400(10-15)-.389(8-13)-.219(8-15)+.183(11-18)
6.033	0.396	+.553(10-16)+.516(7-13)-.294(11-18)-.262(5-12)-.253(8-13)+.229(10-15)
6.102	0.002	+.488(7-13)-.426(10-16)-.286(5-12)-.277(10-17)-.274(6-13)+.268(11-17)
6.290	0.592	+.466(10-15)-.460(8-13)-.372(7-13)-.328(10-16)+.297(11-17)-.279(6-12)
6.294	0.003	-.416(10-16)-.393(10-18)-.378(5-13)+.345(7-13)+.243)5-12)-.240(11-18)
6.427	0.000	-.889(7-14)+.323(10-14)-.295(5-14)
6.437	0.000	-.890(9-16)+.331(9-13)-.295(9-18)

TABLE 2.3c - WAVE FUNCTIONS AND EXCITATION ENERGIES OF DIBENZO(b,g)PHENANTHRENE

COMPOSITE SYSTEM (IIIa) WITH β_{RS} = -1.000 EV

Excitation Energy (ev)	f	CI Excited State Wave Functions
3.428	0.000	+.595(11-13)-.593(10-12)-.273(11-14)+.261(9-12)-.185(11-15)-.181(8-12)
3.512	0.361	-.968(11-12)-.152(10-13)
4.164	0.001	+.397(9-13)-.390(10-14)+.322(11-14)-.279(9-12)+.267(8-12)+.266(11-16)
4.165	0.729	+.573(9-12)+.562(11-14)-.357(10-12)-.349(11-13)+.179(9-14)
4.222	0.639	+.502(10-13)+.492(11013)+.498(10-12)+.312(9-12)+.291(11-14)
4.414	0.000	-.547(9-12)+.545(11-14)-.271(9-13)+.269(10-14)+.212(11-13)-.197(10-12)
4.549	0.430	-.798(10-13)+.326(10-12)+.324(11-13)+.192(9-12)+.180(11-14)
4.680	0.001	-.414(10-14)+.398(9-13)-.274(11-15)+.272(9-15)+.269(8-14)-.267(8-12)
4.825	0.001	+.555(11-15)+.452(8-12)-.329(11-16)+.294(7-12)+.237(8-14)+.228(9-15)
4.873	0.076	-.594(8-12)+.508(11-15)_.284(9-14)+.257(9-13)+.241(10-14)-.240(7-12)
5.158	0.041	+.585(9-14)-.501(9-13)-.477(10-14)+.178(8-13)-.154(10-15)
5.257	1.468	-.603(9-14)+.334(11-15)-.326(8-12)-.306(9-13)-.258(10-14)+.219(11-16)
5.274	0.086	-.442(7-12)+.408(11-16)-.381(11-17)-.371(6-12)-.233(8-13)+.224(9-15)
5.448	0.000	-.349(10-15)-.328(8-13)+.326(10-17)+.309(6-13)-.287(8-16)-.285(7-15)
5.592	0.291	+.517(7-12)+.510(11-16)-.339(8-13)+.290(10-15)+.198(9-14)-.172(8-14)
5.613	0.003	-.454(11-16)+.452(5-12)+.340(10-15)+.302(8-13)-.298(11-17)-.255(6-12)
5.789	0.046	+.459(8-13)-.433(10-15)+.355(7-12)+.338(11-16)+.224(9-13)+.216(10-14)
5.886	0.617	-.536(6-12)-.434(9-15)+.367(11-17)+.256(8-14)+.220(7-12)+.215(5-12)
5.922	0.034	-.436(8-14)-.411(11-17)+.261(9-17)-.257(9-15)+.245(6-14)-.238(11-16)
6.029	0.057	+.693(10-16)-.389(11-18)+.265(6-12)-.228(9-16)+.179(9-17)+.174(10-18)
6.058	0.162	+.688(7-13)-.381(5-12)+.274(8-14)-.260(7-14)-.205(6-14)-.172(11-17)
6.179	0.001	-.316(11-17)-.299(5-12)+.297(10-18)-.292(6-12)-.291(5-13)+.274(11-18)
6.318	0.688	+.412(10-16)+.413(7-18)+.380(9-15)-.379(8-14)-.237(10-15)+.232(8-13)
6.434	0.158	+.454(11-18)+.452(5-12)-.414(11-17)+.410(6-12)-.239(9-15)+.204(8-14)

TABLE 2.3d - WAVE FUNCTIONS AND EXCITATION ENERGIES OF DIBENZO(b,g)PHENANTHRENE

COMPOSITE SYSTEM (IIIb) WITH β_{RS} = 0.0 EV

Excitation Energy (ev)	f	CI Excited State Wave Functions
3.540	0.000	-.673(10-12)+.668(11-13)
3.951	0.039	+.878(11-12)+.450(10-13)
4.384	1.442	-.686(11-13)-.682(10-12)
4.396	0.000	+.522(11-16)-.522(7-12)-.444(10-15)+.444(8-13)
4.487	0.000	+.854(11-14)+.345(8014)+.332(10-14)
4.487	0.000	+.855(9-12)+.346(9-15)+.332(9-13)
4.722	0.410	-.647(9-14)+.626(10-13)-.349(11-12)
4.918	0.705	-.647(9-14)-.584(10-13)+.278(11-12)+.185(8-12)+.176(11-15)
4.941	0.000	-.799(10-14)-.396(7-14)+.267(8-14)+.266(11-14)-.235(5-14)
4.942	0.000	+.395(9-16)-.266(9-12)-.266(9-15)+.235(9-18)
5.006	0.152	-.674(11-15)-.678(8-12)-.253(9-14)
5.094	0.000	-.668(8-12)+.640(11-15)-.168(6-13)-.164(10-17)
5.374	0.000	+.512(10-15)-.466(8-13)-.445(7-12)+.440(11-16)+.171(10-18)-.168(7-17)
5.459	0.000	-.394(8-16)+.393(7-15)-.371(6-13)-.360(10-17)-.352(11-18)+.341(5-12)
5.687	0.000	+.658(10-16)-.619(7-13)-.174(5-12)+.167(11-18)-.157(11-13)+.151(10-12)
5.765	0.717	+.579(11-16)+.561(7-12)-.385(8-13)-.364(10-15)
5.819	0.225	+.537(8-13)+.497(10-15)+.326(6-12)+.309(7-12)+.274(11-16)-.222(11-17)
5.900	0.468	-.656(7-13)-.598(10-16)-.184(9-14)
6.002	0.001	-.704(11-17)-.635(6-12)-.162(5-15)+.151(8-18)
6.017	0.000	-.817(8-14)+.432(11-14)-.248(10-14)-.211(6-14)
6.022	0.000	-.821(9-15)+.433(9-12)-.242(9-13)+.213(9-17)+.186(9-16)
6.375	0.000	-.807(7-14)+.426(10-14)-.295(5-14)-.249(8-14)
6.377	0.000	-.811(9-16)+.428(9-13)-.294(9-18)-.240(9-15)
6.391	0.000	-.545(11-18)+.466(10-17)+.455(5-12)+.452(6-13)
6.481	0.921	+.663)8-15)-.334(11-17)+.311(6-12)-.239(11-16)+.232(10-18)-.231(7-12)

TABLE 2.3e - WAVE FUNCTIONS AND EXCITATION ENERGIES OF DIBENZO(b,g)PHENANTHRENE

COMPOSITE SYSTEM (IIIb) WITH β_{RS} = -1.000 EV

Excitation Energy (ev)	f	CI Excited State Wave Functions
3.499	0.000	+.624(11-13)+.628(10-12)-.178(9-13)-.177(10-14)+.172(11-14)-.169(9-12)
3.769	0.107	+.919(11-12)-.334(10-13)
4.206	1.227	-.630(11-13)+.623(10-12)+.256(10-13)+.196(9-12)+.194(11-14)
4.294	0.000	-.428(11-16)-.425(7-12)+.362(10-14)+.356(9-13)-.264(8-13)+.256(10-15)
4.338	0.370	-.654(11-14)-.641(9-12)+.218(10-12)-.205(11-13)
4.481	0.000	-.638(9-12)+.627(11-14)
4.710	0.651	-.842(10-13)-.318(11-12)+.202(9-14)+.192(10-12)-.160(11-13)
4.925	0.001	+.401(10-14)+.338(9-13)+.328(9-15)+.327(8-14)-.271(7-14)-.271(9-16)
4.998	0.083	+.795(11-15)-.325(10-14)-.209(9-14)+.188(9-13)-.175(8-12)-.156(10-13)
5.009	0.036	-.816(8-12)+.243(9-13)-.231(11-15)-.182(7-12)+.169(10-12)
5.273	0.419	-.674(9-14)-.381(9-13)+.331(10-14)-.254(7-12)-.203(7-14)+.215(9-16)
5.334	0.003	+.462(11-16)+.407(7-12)+.390(10-15)-.358(8-13)+.225(10-14)-.182(11-18)
5.422	0.024	-.367(9-13)+.353(10-14)-.327(10-15)-.325(8-13)-.313(9-15)+.312(8-14)
5.574	0.044	+.353(7-15)-.344(8-16)-.318(5-13)+.305(10-18)-.285(10-16)-.250(6-12)
5.602	0.901	-.474(7-12)+.468(11-16)-.367(10-15)+.327(9-13)+.249(8-12)-.244(10-14)
5.633	0.060	+.552(10-16)-.480(7-13)-.389(8-13)-.263(10-15)+.188(7-12)+.181(10-12)
5.862	0.024	-.341(8-13)-.334(10-15)+.292(7-12)-.284(9-14)-.276(11-16)-.262(5-12)
5.922	0.459	+.596(7-13)+.544(10-16)-.303(9-14)+.170(8-12)-.159(11-15)
5.941	0.005	+.537(11-18)+.498(5-12)+.348(11-17)-.266(9-15)-.248(6-12)-.160(8-14)
6.038	0.212	+.485(9-15)-.456(8-14)-.282(7-14)-.270(8-13)+.250(9-14)-.215(10-15)
6.109	0.001	+.356(8-14)-.297(7-13)+.291(11-18)-.273(10-14)+.258(9-15)+.243(5-12)
6.317	0.318	-.516(11-17)-.382(8-14)-.281(9-16)+.275(7-14)-.267(6-12)-.250(10-15)
6.359	0.062	-.509(6-12)+.430(9-15)+.259(7-14)+.227(8-14)-.224(10-18)-.223(6-13)
6.470	0.166	+.509(11-18)+.409(9-16)+.384(7-14)-.225(9-18)-.198(5-12)+.200(6-12)
6.490	0.237	-.592(5-12)-.365(9-16)+.333(11-18)-.277(7-14)+.222(11-17)+.217(10-15)

TABLE 2.3f - WAVE FUNCTIONS AND EXCITATION ENERGIES OF DIBENZO(b,g)PHENANTHRENE

COMPOSITE SYSTEM (IIIc) WITH β_{RS} = 0.0 EV

Excitation Energy (ev)	f	CI Excited State Wave Functions
3.414	0.336	+.979(11-12)-.168(9-14)
3.631	0.000	-.692(11-14)-.692(9-12)-.126(7-17)+.126(6-16)
4.146	0.000	-.950(10-12)-.256(10-16)
4.146	0.000	+.950(11-13)-.256(7-13)
4.410	0.000	+.678(10-15)+.678(8-13)-.200(8-19)+.200(4-15)
4.540	0.443	+.757(10-13)+.355(11-14)-.355(9-12)-.256(11-16)+.256(7-12)
4.593	0.000	+.693(11-16)+.693(7-12)
4.666	0.181	+.642(11-16)-.642(7-12)+.248(10-13)+.209(11-14)-.209(9-12)
5.051	0.000	+.511(9-16)-.511(7-14)-.489(11-17)-.489(6-12)
5.097	2.661	-.551(11-14)+.551(9-12)+.356(10-13)-.181(8-15)
5.123	0.000	-.973(8-12)-.164(8-16)
5.123	0.000	+.973(11-15)-.164(7-15)
5.420	0.000	-.707(11-18)-.707(5-12)
5.663	0.000	-.934(10-14)+.308(10-17)
5.663	0.000	+.934(9-13)-.318(6-13)
5.828	0.540	-.602(10-15)+.602(8-13)-.235(11-18)+.235(5-12)-.181(7-16)
5.902	0.101	+.579(11-18)-.579(5-12)+.315(7-16)-.275(8-15)+.219(9-14)-.200(10-15)
6.002	0.000	+.865(10-16)-.302(10-18)-.280(4-12)-.244(10-12)
6.002	0.000	+.865(7-13)-.302(5-13)-.280(11-19)+.244(11-13)
6.124	0.000	+.560(9-18)-.560(5-14)-.355(7-;7)+.355(6-16)-.244(11-20)+.244(3-12)
6.197	0.680	-.794(9-14)-.404(8-15)-.262)7-16)+.155(11-17)-.155(6-12)
6.285	0.215	+.569(8-15)-.400(9-14)-.297(11-17)+.297(6-12)+.233(11-18)-.233(5-12)
6.286	0.000	-.511(11-17)-.511(6-12)-.489(9-16)+.489)7-14)
6.341	0.000	+.707(10-19)+.707(4-13)
6.419	0.223	+.532(11-17)+.532(6-12)-.389(8-15)+.339(9-16)+.339(7-14)

TABLE 2.3g - WAVE FUNCTIONS AND EXCITATION ENERGIES OF DIBENZO(b,g)PHENANTHRENE

COMPOSITE SYSTEM (IIIc) WITH β_{RS} = -1.000 EV

Excitation Energy (ev)	f	CI Excited State Wave Functions
3.401	0.306	+976(11-12)
3.569	0.000	-.506(11-13)+.505(10-12)+.465(11-15)-.452(8-12)
4.090	0.742	+.683(10-12)+.613(11-13)-.279(10-13)
4.109	0.007	+.480(8-12)-.474(11-15)-.419(11-13)-.347(9-13)-.331(10-14)+.286(10-12)
4.486	0.030	+.621(11-14)-.602(9-12)-.381(10-13)-.156(11-16)-.153(7-12)
4.543	0.000	-.647(9-12)-.639(11-14)+.215(11-16)-.217(7-12)
4.640	0.010	+.404(10-16)-.400(7-13)+.396(10-14)+.378(9-13)-.262(11-13)-.232(11-15)
4.708	0.228	-.699(10-13)-.344(8-12)-.275(11-15)-.263(11-14)-.238(10-12)+.239(9-12)
5.040	0.000	+.329(9-15)+.328(8-14)+.322(6-12)-.321(11-17)-.304(11-16)+.285(7-12)
5.059	0.951	+.494(11-16)+.463(8-12)+.457(11-15)+.401(7-12)-.266(10-13)+.231(9-14)
5.122	0.005	-.592(7-12)+.499(11-16)-.252(5-12)+.245(11-18)+.182(9-12)+.181(9-15)
5.256	1.533	+.448(11-16)+.432(7-12)-.401(8-12)-.386(11-15)+.344(10-13)
5.5-6	0.000	-.638(11-18)+.632(5-12)-.162(7-12)+.158(11-16)
5.625	0.000	-.629(10-15)+.598(8-13)+.233(10-17)-.227(6-13)
5.631	0.318	+.615(8-13)+.584(10-15)-.222(10-14)+.228(9-13)
5.741	0.221	-.568(9-13)+.564(10-14)+.210(10-15)+.206(8-13)+.160(11-18)+.143(5-12)
5.909	0.003	+.365(10-16)-.353(7-13)-.350(10-14)-.328(9-13)-.269(10-18)-.265(11-19)
5.920	0.109	+.538(5-12)+.534(11-18)+.422(9-14)+.222(9-13)-.215(7-16)+.169(6-12)
6.053	0.146	-.465(10-16)-.446(7-13)+.325(9-14)-.279(11-17)-.247(6-12)+.181(6-13)
6.178	0.003	-.485(11-17)+.461(6-12)+.236(8-16)-.237(7-15)+.224(8-18)-.211(5-15)
6.246	0.112	-.468(11-18)+.428(10-16)+.382(7-13)-.374(6-12)+.311(9-14)-.158(8-15)
6.266	0.174	-.442(9-14)-.394(6-12)-.394(11-17)+.346(5-12)+.344(11-18)+.303(8-15)
6.323	0.011	+.429(8-14)+.419(9-15)-.316(6-12)+.256(10-19)+.256(7-13)+.249(10-17)
6.406	0.671	-.725(8-15)+.335(7-14)-.279(11-19)-.274(9-16)-.210(4-13)-.194(9-14)
6.454	0.079	+.370(4-12)-.328(9-18)+.321(5-15)-.302(6-13)-.274(11-19)+.247(8-15)

TABLE 2.4a - WAVE FUNCTIONS AND EXCITATION ENERGIES OF DIBENZ(a,c)ANTHRACENE (IV)

Excitation Energy (ev)	f	CI Excited State Wave Functions
3.532	0.000	+.666(11-13)+.666(10-12)
3.737	0.168	+.930(11-12)-.327(10-13)
4.242	0.000	+.579(10-14)+.579(9-13)-.355(11-16)+.355(7-12)
4.373	2.285	+.689(11-13)-.689(10-12)
4.373	0.000	+.598(11-14)-.598(9-12)+.266(9-15)+.266(8-14)+.191(10-17)-.191(6-13)
4.444	0.022	-.643(11-14)-.643(9-12)-.210(10-13)+.181(9-14)-.172(11-15)+.172(8-12)
4.844	1.263	-.882(10-13)-.314(11-12)+.205(11-14)+.205(9-12)
5.061	0.000	+.605(11015)+.605(8-12)+.251(11-14)-.251(9-12)+.178(9-18)+.178(5-14)
5.335	0.000	-.429(11-16)+.429(7-12)+.274(10-15)-.274(8-13)-.234(10-14)-.234(9-13)
5.345	0.364	+.622(9-14)+.532(11-15)-.532(8-12)
5.408	0.307	-.647(10-14)+.647(9-13)+.183(10-15)+.183(8-13)
5.579	0.075	+.715(9-14)-.381(11-15)+.381(8-12)+.203(10-13)+.180(11-14)+.180(9-12)
5.625	0.000	-.562(11-18)-.562(5-12)-.290(9-15)-.290(8-14)+.208(11-14)-.208(9-12)
5.721	0.000	+.374(11-16)-.374(7-12)-.337(11-17)-.337(6-12)+.328(10-15)-.328(8-13)
5.924	0.268	-.590(11-16)-.590(7-12)+.326(10-15)+.326(8-13)+.152(11-17)-.152(6-12)
6.023	0.000	-.516(10-15)+.516(8-13)-.408(11-17)-.408(6-12)
6.043	0.144	+.352(11-17)-.352(6-12)+.322(10-15)+.322(8-13)+.319(11-16)+.319(7-12)
6.069	0.029	-.567(11-18)+.567(5-12)-.334(9-15)+.334(8-14)-.156(10-16)+.156(7-13)
6.089	0.000	-.379(11-18)-.379(5-12)+.371(10-17)-.371(6-13)+.267(11-15)+.267(8-12)
6.184	0.031	-.612(10-16)+.612(7-13)+.254(11-18)-.254(5-12)-.151(9-14)
6.285	0.000	-.487(10-18)+.487(5-13)-.349(11-17)-.349(6-12)-.186(8-16)-.186(7-15)
6.310	0.000	+.564(10-16)+.564(7-13)+.321(9-15)+.321(8-14)-.164(10-17)+.164(6-13)
6.480	0.151	+.515(11-17)-.515(6-12)-.427(10-15)-.427(8-13)-.167(10-18)-.167(5-13)

TABLE 2.4b - WAVE FUNCTIONS AND EXCITATION ENERGIES OF DIBENZ(a,c)ANTHRACENE

COMPOSITE SYSTEM (IVa) WITH β_{RS} = 0.0 EV

Excitation Energy (ev)	f	CI Excited State Wave Functions
3.480	0.003	+.650(10-12)+.646(11-13)+.186(11-15)+.176(8-12)
3.509	0.313	+.940(11-12)+.209(9-14)-.197(10-13)
3.833	0.000	-.886(11-14)+.174(5-14)-.167(8-14)
3.834	0.000	-.886(9-12)-.368(9-13)-.175(9-18)+.167(9-15)
4.192	0.686	+.616(10-12)-.613(11-13)-.343(9-14)+.190(11-15)-.186(8-12)
4.397	0.000	+.472(8-13)-.469(10-15)+.447(11-16)-.441(7-12)-.199(8-12)-.190(11-15)
4.732	0.029	+.691(11-15)+.561(8-12)-.204(10-12)+.154(11-16)
4.765	1.206	+.566(10-13)-.566(8-12)+.401(11-15)+.216(11-13)-.180(10-12)-.154(9-14)
4.920	0.406	-.704(9-14)-.365(11-15)+.344(8-12)+.330(10-13)+.184)11-12)-.151(10-15)
5.001	0.685	-.676(10-13)-.467(9-14)-.246(8-12)+.230(11-13)-.226(10-12)+.212(11-15)
5.120	0.000	-.903(10-14)-.387(11-14)
5.121	0.000	-.903(9-13)+.387(9-12)
5.299	0.001	+.439(11-16)+.422(11-17)-.408(7-12)+.385(6-12)-.343(8-13)+.340(10-15)
5.511	0.000	+.453(11-18)+.459(5-12)-.393(8-16)-.392(7-15)-.346(10-17)+.323(6-13)
5.622	0.542	-.673(7-12)-.644(11-16)
5.732	0.001	-.473(11-17)-.446(6-12)-.281(11-18)-.273(8-13)+.270(10-15)-.265(5-12)
5.833	0.772	-.464(6-12)-.462(10-15)-.457(8-13)-.440(11-17)+.184(8-15)
5.886	0.000	-.954(8-14)+.205(6-14)+.176(11-14)
5.886	0.000	-.954(9-15)+.205(9-17)-.177(9-12)
6.023	0.293	-.517(10-16)+.485(7-13)-.326(11-18)+.288(5-12)+.243(6-12)+.233(8-13)
6.102	0.002	+.488(7-13)+.427(10-16)+.288(5-12)+.277(10-17)-.275(6-13)-.266(11-17)
6.291	0.528	+.489(10-16)+.396(8-13)+.379(10-15)-.352(7-13)+.271(6-12)-.220(11-17)
6.294	0.018	+.428(7-13)+.381(5-13)-.380(10-18)+.322(10-16)-.276(5-12)-.206(7-17)

TABLE 2.4c - WAVE FUNCTIONS AND EXCITATION ENERGIES OF DIBENZ(a,c)ANTHRACENE

COMPOSITE SYSTEM (IVa) WITH β_{RS} = -1.000 EV

Excitation Energy (ev)	f	CI Excited State Wave Functions
3.442	0.000	+.658(11-13)+.657(10-12)
3.559	0.288	+.943(11-12)-.263(10-13)
3.890	0.000	-.569(11-14)+.563(9-12)-.272(10-14)-.270(9-13)-.184(11-15)+.177(8-12)
4.099	0.809	-.514(10-12)+.508(11-13)-.416(9-13)-.410(11-14)+.190(9-14)+.173(10-13)
4.245	0.585	+.511(9-12)+.502(11-14)+.394(11-13)-.390(10-12)-.209(9-14)-.168(11-15)
4.338	0.000	+.398(11-16)-.395(7-12)-.332(10-14)-.322(9-13)+.298(8-13)+.297(10-15)
4.744	1.206	-.804(10-13)+.323(11-15)+.266(8-12)-.224(11-12)-.166(10-12)+.160(11-13)
4.809	0.002	-.617(8-12)+.612(11-15)+.208(9-12)-.202(11-14)
5.012	0.047	+.529(8-12)+.505(11-15)-.490(9-14)+.344(10-13)
5.094	0.701	-.570(9-13)+.535(10-14)+.235(9-14)+.189(6-12)-.181(10-12)+.178(10-15)
5.178	0.000	-.509(10-14)-.494(9-13)-.299(11-16)+.289(7-12)-.199(10-15)-.191(8-13)
5.256	0.075	-.730(9-14)-.288(10-13)+.276(10-14)-.259(9-13)-.215(11-15)-.211(8-12)
5.379	0.001	-.438(11-17)+.400(6-12)-.390(11-16)+.345(7-12)+.310(8-13)+.295(10-15)
5.513	0.000	+.422(5-12)-.420(11-18)-.314(8-16)+.313(5-15)+.283(10-17)+.281(6-13)
5.665	0.481	-.649(7-12)-.604(11-16)-.218(10-15)+.163(8-13)
5.751	0.004	-.459(10-15)-.394(8-13)-.358(11-17)+.340(6-12)+.267(11-18)+.259(11-16)
5.865	0.134	-.533(9-15)-.340(10-15)-.329(8-14)+.324(8-13)+.264(7-12)-.236(6-12)
5.909	0.191	+.493(8-14)-.405(11-18)+.397(11-17)-.371(10-15)+.302(6-12)-.159(7-13)
5.928	0.157	-.519(8-13)-.374(9-15)+.344(5-12)-.298(6-12)+.277(8-14)-.259(10-16)
6.066	0.233	+.469(10-16)-.448(7-13)+.330(5-12)+.312(11-18)-.305(9-16)-.279(7-14)
6.107	0.004	-.432(7-13)-.376(10-16)-.332(11-17)+.331(6-12)-.250(8-14)+.248(9-15)
6.240	0.009	-.405(10-18)-.404(10-16)-.395(5-13)-.359(7-13)+.214(11-18)-.198(5-12)
6.318	0.653	-.398(8-14)-.333(9-15)+.318(10-15)-.297(8-13)-.256(5-12)-.253(7-13)
6.442	0.070	+.406(7-14)-.348(11-18)+.339(5-14)-.308(11-17)+.295(10-16)+.223(9-15)
6.478	0.084	+.413(5-12)-.402(9-16)+.337(7-13)+.333(6-12)-.278(9-18)+.264(7-14)

TABLE 2.4d - WAVE FUNCTIONS AND EXCITATION ENERGIES OF DIBENZ(a,c)ANTHRACENE

COMPOSITE SYSTEM (IVb) WITH β_{RS} = 0.0 EV

Excitation Energy (ev)	f	CI Excited State Wave Functions
3.714	0.000	-.690(11-13)+.680(10-12)+.167(8-18)-.167(5-15)
4.244	0.002	+.720(11-12)+.669(10-13)
4.640	0.000	-.593(11-15)-.593(8-12)-.215(11-16)+.215(7-12)+.214(10-17)-.214(6-13)
4.640	0.000	-.593(10-15)-.593(8-13)+.215(11-17)-.215(6-12)+.215(10-16)-.215(7-13)
4.727	0.178	+.720(9-14)+.557(10-13)-.379(11-12)
4.733	0.000	+.914(11-14)+.306(5-14)+.267(6-14)
4.733	0.000	+.914(9-12)-.306(9-18)+.267(9-17)
4.777	0.000	+.817(9-13)+.506(9-15)+.278(9-16)
4.777	0.000	-.817(10-14)+.506(8-14)-.278(7-14)
4.881	1.895	-.659(11-13)-.659(10-12)-.241(11-15)+.241(8-12)
5.023	1.894	-.616(9-14)=.497(11-12)+.404(10-13)-.297(10-15)+.297(8-13)
5.357	0.044	-.644(11-15)+.644(8-12)+.234(11-13)+.234(10-12)
5.372	0.154	-.615(10-15)+.615(8-13)+.266(11-12)-.250(10-13)+.164(9-14)
5.926	0.000	+.432(11-16)-.432(7-12)-.429(10-17)+.429(6-13)-.348(11-15)-.348(8-12)
5.926	0.000	-.431(11-17)+.431(6-12)-.430(10-16)+.430(7-13)-.348(10-15)-.348(8-13)
6.001	0.006	-.934(8-15)+.176(10-16)+.176(7-13)
6.019	0.000	-.487(10-17)+.487(6-13)-.485(11-16)+.485(7-12)
6.097	0.000	+.791(9-15)-.568(9-13)+.229(9-16)
6.097	0.000	+.791(8-14)+.568(10-14)-.229(7-14)
6.136	0.000	+707(9-19)-.707(4-14)
6.212	0.000	+.500(10-16)-.500(7-13)-.500(11-17)+.500(6-12)
6.251	0.059	-.455(11-16)-.455(7-12)+.452(10-17)+.452(6-13)+.197(10-18)-.197(5-13)
6.271	0.016	+.495(10-16)+.495(7-13)+.418(11-17)+.418(6-12)-.160(8-16)+.160(7-15)
6.452	0.005	+.518(11-17)+.518(6-12)-.418(10-16)-.418(7-13)-.302(8-15)

TABLE 2.4e - WAVE FUNCTIONS AND EXCITATION ENERGIES OF DIBENZ(a,c)ANTHRACENE

COMPOSITE SYSTEM (IVb) WITH β_{RS} = -1.000 EV

Excitation Energy (ev)	f	CI Excited State Wave Functions
3.673	0.000	-.638(11-13)-.638(10-12)-.229(10-14)+.229(9-13)
4.073	0.047	-.807(11-12)+.543(10-13)
4.374	0.000	+.572(10-14)-.572(9-13)-.281(11016)+.281(7-12)
4.510	1.697	-.666(11-13)+.666(10-12)
4.534	0.007	+.643(11-14)-.643(9-12)-.270(10-13)-.198(11-12)
4.573	0.000	-.434(11-14)-.434(9-12)+.321(11-15)-.321(8-12)-.319(9-15)-.319(8-14)
4.844	1.295	-.759(10-13)-.492(11-12)-.257(11-14)+.257(9-12)
4.846	0.000	+.535(11-15)-.535(8-12)+.382(9-12)+.195(9-17)+.195(6-14)
5.014	0.000	+.565(10-15)+.565(8-13)-.203(9-16)-.203(7-14)+.201(8-16)-.201(7-15)
5.168	0.528	-.597(9-14)-.542(11-15)-.542(8-12)
5.290	0.385	+.670(10-14)+.670(9-13)-.168(11-13)+.168(10-12)
5.472	0.002	-.662(10-15)+.662(8-13)-.161(11-18)+.161(5-12)
5.659	0.107	-.610(9-15)+.610(8-14)-.197(10-16)+.197(7-13)
5.716	0.000	+.447(11-17)-.447(6-12)-.336(11-14)-.336(9-12)+.213(11-15)-.213(8-12)
5.822	0.186	+.664(9-14)-.396(8-15)-.394(11-15)-.394(8-12)-.164(10-13)
5.876	0.000	-.573(11-16)+.572(7-12)+.234(10-15)+.234(8-13)-.219(10-14)+.219(9-13)
6.030	0.000	+.621(10-17)+.621(6-13)-.227(11-16)+.227(7-12)-.205(10-15)-.205(8-13)
6.158	0.000	+.571(10-16)+.571(7-13)+.280(11-17)-.280(6-12)-.204(10-18)+.204(5-13)
6.210	0.041	+.555(11-16)+.555(7-12)+.390(10-17)-.390(6-13)
6.211	0.044	-.499(11-17)-.499(6-12)+.430(10-16)-.430(7-13)-.165(8-17)-.165(6-15)
6.226	0.000	-.492(11-18)-.492(5-12)-.371(9-16)-.371(7-14)+.175(11-13)+.175(10-12)
6.322	0.031	-.652(8-13)+.344(9-17)-.344(6-14)-.273(10-16)+.273(7-13)-.211(9-14)
6.341	0.000	+.398(11-17)-.398(6-12)-.396(9-15)-.396(8-14)-.248(10-18)+.248(5-13)
6.357	0.309	+.475(11-18)-.475(5-12)+.265(9-16)-.265(7-14)+.228(11-16)+.228(7-12)

TABLE 2.5a - WAVE FUNCTIONS AND EXCITATION ENERGIES OF 3.4-BENZOPYRENE (V)

Excitation Energy (ev)	f	CI Excited State Wave Functions
3.120	0.997	+.978(10-11)
3.312	0.000	+.671(10-12)+.671(9-11)-.160(10-13)-.160(8-11)
4.199	0.000	+.608(10-14)-.608(7-11)-.254(10-15)-.254(6-11)-.169(9-13)+.169(8-12)
4.225	0.048	-.638(10-14)-.638(7-11)+.210(10-13)-.210(8-11)+.185(10-12)-.185(9-11)
4.419	0.871	-.631(10-12)+.631(9-11)-.242(10-14)-.242(7-11)-.154(10-13)+.154(8011)
4.424	0.000	-.648(10-13)-.648(8-11)-.177(10-14)+.177(7-11)
4.671	0.000	-.498(10-15)-.498(6-11)-.372(9-13)+.372(8-12)-.294(10-14)+.294(7-11)
4.719	0.662	-.626(10-13)+.626(8-11)+.218(10-12)-.218(9-11)
5.141	1.055	+.915(9-12)
5.263	0.000	+.478(10-16)-.478(5-11)+.440(9-14)+.440(7-12)
5.432	0.000	-.445(9-14)-.445(7-12)+.430(10-16)-.430(5-11)+.188(10-15)+.188(6-11)
5.542	0.046	-.623(10-15)+.623(6-11)-.286(10-16)-.286(5-11)
5.638	0.000	-.300(9-13)+.300(8-12)-.299(9-16)-.299(5-12)+.261(8-15)-.261(6-13)
5.782	0.334	-.521(10-16)-.521(5-11)+.323(9-13)+.323(8-13)+.292(10-15)-.292(6-11)
5.973	0.000	-.414(9-13)+.414(8-12)+.296(8-14)+.296(7-13)+.291(10-15)+.291(6-11)
6.031	0.044	-.531(9-14)+.531(7-12)-.314(9-13)-.314(8-12)-.234(10-16)-.234(5-11)
6.146	0.000	-.494(8-14)-.494(7-13)+.312(9-16)+.312(5-12)+.241(7-16)-.241(5-14)
6.244	0.324	+.460(9-13)+.460(8-12)-.415(9-14)+.415(7-12)+.317(7-14)
6.401	0.450	+.516(7014)+.448(9-15)+.448(6-12)-.221(9-13)-.221(8-12)+.178(8-16)
6.448	0.000	+.561(10-18)+.561(3-11)-.343(10-17)+.343(4-11)+.189(9-16)+.189(5-12)

TABLE 2.5b - WAVE FUNCTIONS AND EXCITATION ENERGIES OF 3.4-BENZOPYRENE

COMPOSITE SYSTEM (Va) WITH β_{RS} = 0.0 EV

Excitation Energy (ev)	f	CI Excited State Wave Functions
3.471	0.000	-.693(10-13)-.693(8-11)
3.533	0.919	+.969(10-11)-.222(8-13)
4.081	0.000	-.965(9-11)-.215(9-15)
4.081	0.000	-.965(10-12)-.215(6-12)
4.398	0.000	+.700(10-14)+.700(7-11)
4.417	0.000	+.658(10-14)-.658(7-11)+.227(10-16)-.227(5-11)
4.587	0.134	+.682(9-12)-.494(10-13)+.494(8-11)
4.996	0.000	-.903(9-13)-.403(9-16)
4.996	0.000	-.903(8-12)+.403(5-12)
5.019	1.109	+.649(9-12)+.478(10-13)-.478(8-11)-.184(8-13)
5.070	0.000	-.593(10-15)+.593(6-11)-.384(8-14)-.384(7-13)
5.179	0.000	+.526(11-16)-.526(5-11)+.396(8-15)+.396(6-13)-.257(10-14)+.257(7-11)
5.466	0.000	+.593(8-14)+.593(7-13)-.382(10-15)+.382(6-11)
5.516	0.033	+.674(10-15)+.674(6-11)-.150(8-16)+.150(5-13)
5.585	1.603	-.927(8-13)-.201(9-12)-.188(10-11)+.172(7-14)
6.136	0.000	-.707(9-17)+.707(4-12)
6.141	0.000	-.628(7-15)+.628(6-14)+.233(10-19)+.233(2-11)-.180(8-18)+.180(3-13)
6.205	0.004	-.489(8-14)+.489(7-13)-.468(10-16)-.468(5-11)
6.218	0.010	-.488(8-14)+.488(7-13)+.466(10-16)+.466(5-11)+.163(8-15)-.163(6-13)
6.259	0.000	+.987(9-14)
6.259	0.000	+.987(7-12)
6.366	0.000	-.572(8-15)-.572(6-13)+.415(10-16)-.415(5-11)

TABLE 2.5c - WAVE FUNCTIONS AND EXCITATION ENERGIES OF 3.4-BENZOPYRENE

COMPOSITE SYSTEM (Va) WITH β_{RS} = -1.000 EV

Excitation Energy (ev)	f	CI Excited State Wave Functions
3.357	0.966	+.970(10-11)
3.419	0.000	-.523(10-12)+.523(9-11)-.454(10-13)+.454(8-11)
4.125	0.000	-.488(10-13)+.488(8-11)+.422(10-12)-.422(9-11)-.164(9-13)+.164(8-12)
4.237	0.057	-.570(10-12)-.570(9-11)+.323(10-13)+.323(8-11)+.219(10-14)+.219(7-11)
4.376	0.003	+.659(10-14)+.659(7-11)+.189(9-11)
4.387	0.000	+.642(10-14)-.642(7-11)-.197(10-16)-.197(5-11)
4.678	0.595	+.542(10-13)+.542(8-11)+.364(9-12)+.320(10-12)+.320(9-11)
4.809	0.710	+.877(9-12)-.214(10-13)-.214(8-11)
4.835	0.000	-.506(9-13)+.506(8-12)+.232(10-16)+.232(5-11)-.227(10-15)+.227(6-11)
5.081	0.000	+.549(10-15)-.549(6-11)-.280(8-14)+.280(7-13)-.226(9-14)+.226(7-12)
5.260	0.000	+.410(10-16)+.410(5-11)+.307(8-15)+.257(9-16)+.257(5-12)
5.442	0.000	-.432(9-14)+.432(7-12)-.408(8-14)+.408(7-13)-.335(10-15)+.335(6-11)
5.447	0.704	+.505(9-13)+.505(8-12)-.306(10-15)-.306(6-11)-.226(10-16)+.226(5-11)
5.542	0.236	-.599(10-15)-.599(6-11)-.266(9-13)-.266(8-12)+.159(8-16)-.159(5-13)
5.760	0.571	+.847(8-13)+.252(9-13)+.252(8-12)+.218(7-14)
6.059	0.000	-.405(7-15)+.405(6-14)-.365(8-14)+.365(7-13)+.300(9-14)-.300(7-12)
6.061	0.004	+.544(10-16)-.544(5-11)-.345(9-14)-.345(7-12)-.209(8-13)+.165(9-15)
6.133	0.122	-1535(9-14)-.535(7-12)-.279(10-16)+.279(5-11)-.267(8-14)-.267(7-13)
6.234	0.000	-.383(10-16)-.383(5-11)+.366(8-15)-.366(6-13)+.292(9-15)-.292(6-12)
6.417	0.173	+.598(8-14)+.598(7-13)-.224(9-14)-.224(7-12)-.223(9-15)-.223(6-12)
6.445	0.000	+.437(9-15)-.437(6-12)-.321(10-17)+.321(4-11)+.267(10-18)+.267(3-11)
6.478	0.998	-.725(7-14)-.271(9-15)-.271(6-12)-.193(6-15)-.179(10-18)+.179(3-11)

TABLE 2.5d - WAVE FUNCTIONS AND EXCITATION ENERGIES OF 3.4-BENZOPYRENE

COMPOSITE SYSTEM (Vb) WITH β_{RS} = 0.0 EV

Excitation Energy (ev)	f	CI Excited State Wave Functions
3.470	0.000	-.650(10-12)+.650(9-11)-.185(10-13)-.185(8-11)
3.557	0.402	-.966(10-11)-.204(9-12)
4.247	1.208	+.663(10-12)+.663(9-11)-.188(10-13)+.188(8-11)
4.394	0.000	-.468(9-13)-.468(8-12)+.444(10-15)+.444(6-11)-.198(10-13)-.198(8-11)
4.726	0.000	+.629(10-13)+.629(8-11)-.175(10-12)+.175(9-11)+.151(10-15)+.151(6-11)
4.754	0.640	+.571(9-12)+.521(10-13)-.521(8-11)
4.893	0.000	-.921(10-14)-.332(9-14)+.151(6-14)
4.893	0.000	+.921(7-11)+.332(7-12)+.151(7-15)
4.970	0.439	-.741(9-12)+.380(10-13)-.380(8-11)+.162(10-12)+.162(9-11)
5.286	0.000	-.418(10-16)-.418(5-11)-.411(10-15)-.411(6-11)-.334(9-13)-.334(8-12)
5.477	0.000	+.417(10-17)+.417(4-11)+.391(8-15)-.391(6-13)-.368(9-16)-.358(5-12)
5.558	0.000	+.913(7-12)-.347(7-11)
5.558	0.000	-.913(9-14)+.347(10-14)
5.611	0.536	+.653(10-15)-.653(6-11)+.151(10-16)-.151(5-11)
5.713	0.000	+.432(10-16)+.432(5-11)+.332(10-17)+.332(4-11)-.299(9-13)-.279(8-12)
5.828	0.540	+.455(10-16)-.455(5-11)+.446(9-13)-.446(8-12)+.195(8-13)+.182(10-17)
5.934	0.638	+.540(9-15)-.540(6-12)+.261(10-17)-.261(4-11)-.239(9-13)+.239(8-12)
6.096	0.000	+.437(9-15)+.437(6-12)-.280(10-16)-.280(5-11)+.279(10-17)+.279(4-11)
6.245	0.403	+.445(9-13)-.445(8-12)-.346(10-16)+.346(5-11)+.314(9-15)-.314(6-12)
6.277	0.000	-.394(9-12)-.394(4-12)+.392(9-15)+.392(6-12)-.216(10-17)-.216(4-11)

TABLE 2.5e - WAVE FUNCTIONS AND EXCITATION ENERGIES OF 3.4-BENZOPYRENE

COMPOSITE SYSTEM (Vb) WITH β_{RS} = -1.000 EV

Excitation Energy (ev)	f	CI Excited State Wave Functions
3.421	0.000	-.656(10-12)-.656(9-11)-.183(10-13)+.183(8-11)
3.449	0.543	+.970(10-12)-.189(9-12)
4.276	1.072	+.632(10-12)-.632(9-11)-.226(10-13)-.226(8-11)+.157(10-14)-.157(7-11)
4.366	0.000	+.437(9-13)+.437(8-12)+.413(10-15)-.413(6-11)-.304(10-14)-.304(7-11)
4.651	0.000	+.655(10-13)-.655(8-11)-.183)10-12)-.183(9-11)
4.759	0.972	+.523(10-13)+.523(8-11)-.391(9-12)-.272(10-14)+.273(7-11)+.214(10-12)
4.783	0.000	+.591(10-14)+.591(7-11)+.235(9-13)+.235(8-12)+.186(10-15)-.186(6-11)
4.842	0.098	-.536(9-12)+.528(10-14)-.528(7-11)-.150(10-12)+.150(9-11)
4.934	0.302	+.651(9-12)+.342(10-13)+.342(8-11)+.285(10-14)-.285(7-11)+.154(10-15)
5.276	0.000	-.363(10-16)+.363(5-11)-.362(10-15)+.362(6-11)-.360(9-14)+.360(7-12)
5.347	0.000	-.453(9-14)+.453(7-12)+.296(10-16)-.296(5-11)+.198(10-15)-.198(6-11)
5.457	0.038	-.490(9-14)-.490(7-12)+.441(10-15)+.441(6-11)-.173(9-12)
5.616	0.000	-.384(9-16)-.384(5-12)+.332(8-15)-.332(6-13)+.308(9-14)-.308(7-12)
5.688	0.504	+.457(10-15)+.457(6-11)+.433(9-14)+.433(7-12)+.164(10-16)+.164(5-11)
5.817	0.000	+.458(10-16)-.458(5-11)+.339(9-13)+.339(8-12)-.298(10-15)+.298(6-11)
5.827	0.633	+.461(10-16)+.461(5-11)-.458(9-13)+.457(8-12)-.151(8-13)
6.081	0.000	+.421(10-17)-.421(4-11)-.278(9-16)-.278(5-12)-.271(9-15)-.271(6-12)
6.123	0.339	-.474(9-15)+.474(6-12)+.268(10-16)+.268(5-11)+.246(9-13)-.246(8-12)
6.239	0.365	+.413(9-13)-.413(8-12)+.385(9-15)-.385(6-12)+.276(10-16)+.276(5-11)
6.272	0.000	+.475(8-14)+.475(7-13)-.236(9-17)-.236(4-12)-.228(10-17)+.228(4-11)
6.488	0.000	-.584(9-15)-.584(6-12)-.265(10-17)+.265(4-11)+.191(10-18)-.191(3-11)

TABLE 2.5f - WAVE FUNCTIONS AND EXCITATION ENERGIES OF 3.4-BENZOPYRENE

COMPOSITE SYSTEM (Vc) WITH β_{RS} = 0.0 EV

Excitation Energy (ev)	f	CI Excited State Wave Functions
3.594	0.000	-.685(10-12)-.685(9-11)-.160(8-15)-.160(6-13)
3.773	0.615	-.962(10-11)+.227(9-12)
4.447	0.000	-.525(9-13)-.525(8-12)-.435(10-15)-.435(6-11)
4.774	1.989	+.594(10-12)-.594(9-11)+.491(9-12)
4.776	0.000	-.667(10-13)+.667(8-11)+.156(9-13)+.156(8-12)
4.797	0.005	-.676(10-13)-.676(8-11)+.193(9-15)+.193(6-12)
5.152	0.687	-.800(9-12)+.362(10-12)-.362(9-11)-.225(10-11)
5.212	0.000	+.990(7-11)
5.212	0.000	+.990(10-14)
5.489	0.000	-.492(9-16)-.492(5-12)-.363(8-15)-.363(6-13)+.269(10-16)-.216(5-11)
5.600	0.235	+.585(9-13)-.585(8-12)-.244(7-14)-.236(10-15)+.236(6-11)+.166(8-13)
5.621	0.000	-.638(10-16)+.638(5-11)-.214(9-16)-.214(5-12)
5.690	0.000	-.513(10-15)-.513(6-11)+.362(9-13)+.362(8-12)+.246(10-17)-.246(4-11)
5.730	0.000	+.813(7-12)-.538(7-13)-.202(7-16)
5.730	0.000	+.813(9-14)+.538(8-14)+.202(5-14)
5.766	0.371	+.546(8-13)+.53)(10-16)+.530(5-11)-.220(9-13)+.220(8-12)
5.914	0.001	+.628(10-15)-.628(6-11)+.270(9-13)-.270(8-12)
6.306	0.210	+.779(8-13)-.390(10-16)-.390(5-11)
6.319	0.000	-.549(10-17)+.549(4-11)+.219(9-15)-.219(6-12)-.214(9-17)-.214(4-12)
6.444	0.000	-.453(9-15)+.453(6-12)+.391(9-17)+.391(4-12)-.308(10-17)+.308(4-11)
6.460	0.000	-.740(7-13)-.549(7-12)-.315(7-16)-.197(7-15)
6.460	0.000	-.740(8-14)+.549(9-14)-.315(5-14)+.197(6-14)
6.490	0.003	+.615(9-15)+.615(6-12)-.254(8-16)-.254(5-13)+.183(10-13)+.183(8-11)

TABLE 2.5g - WAVE FUNCTIONS AND EXCITATION ENERGIES OF 3.4-BENZOPYRENE

COMPOSITE SYSTEM (Vc) WITH β_{RS} = -1.000 EV

Excitation Energy (ev)	f	CI Excited State Wave Functions
3.536	0.000	-.683(10-12)+.683(9-11)+.153(8-15)+.153(6-13)
3.615	0.690	-.968(10-11)-.210(9-12)
4.438	0.000	-.494(9-13)+.494(8-12)-.412(10-15)-.412(6-11)+.255(10-14)-.255(7-11)
4.689	0.000	-.673(10-13)+.673(8-11)
4.712	0.104	-.595(10-13)-.595(8-11)+.324(10-14)+.324(7-11)
4.727	1.583	+.608(10-12)+.608(9-11)+.193(10-13)+.193(8-11)+.153(10-14)+.153(7-11)
4.899	0.330	-.571(10-14)-.571(7-11)-.263(10-13)-.263(8-11)+.247(10-12)+.247(9-11)
4.955	0.000	+.645(10-14)-.645(7-11)+.196(9-13)-.196(8-12)
5.115	0.828	+.894(9-12)-.211(10-11)+.209(10-12)+.209(9-11)
5.447	0.000	+.391(9-14)-.391(7-12)-.340(10-16)+.340(5-11)-.319(9-16)+.319(5-12)
5.576	0.000	-.472(10-16)+.472(5-11)+.306(9-16)-.306(5-12)+.252(10-15)+.252(6-11)
5.653	0.000	+.460(9-14)-.460(7-12)-.347(8-14)+.347(7-13)+.279(10-16)-.279(5-11)
5.696	0.121	+.446(9-13)+.446(8-12)+.328(10-16)+.328(5-11)-.267(10-15)+.267(6-11)
5.793	0.000	-.452(10-15)-.452(6-11)+.345(9-13)-.345(8-12)-.254(10-16)+.254(5-11)
5.818	0.148	+.413(9-13)+.413(8-12)-.408(8-13)-.399(10-16)-.399(5-11)-.181(7-14)
5.878	0.121	-.600(10-15)+.600(6-11)-.239(10-16)-.239(5-11)-.230(8-13)-.157(7-14)
5.967	0.014	-.485(9-14)-.485(7-12)+.348(8-14)+.348(7-13)+.236(9-13)+.236(8-12)
6.141	0.000	-.451(8-14)+.451(7-13)-.262(9-14)+.262(7-12)+.222(7-16)-.222(5-14)
6.342	0.245	+.671(8-13)+.351(8-14)+.351(7-13)-.293(10-16)-.293(5-11)+.194(9-14)
6.360	0.000	+.648(10-17)-.648(4-11)-.157(8-16)+.157(5-13)
6.402	0.277	+.414(8-13)-.371(8-14)-.371(7-13)-.322(9-14)-.322(7-12)-.221(10-16)
6.483	0.040	-.596(9-15)+.596(6-12)+.265(8-16)+.265(5-13)+.184(7-14)-.156(10-13)

TABLE 2.6 - ENERGIES (ev) OF SCF MOLECULAR ORBITALS FOR BENZ(a)NAPTHACENE

AND ITS COMPOSITE SYSTEMS

(I)	Composite System (Ia), β_{RS} = 0.0 ev	Composite System (Ia), β_{RS} = -1.000 ev	Composite System (Ib), β_{RS} = 0.0 ev
-14.812	-14.709	-14.721	-14.750
-14.273	-13.986	-14.032	-13.951
-13.387	-12.848	-13.024	-12.822
-12.463	-12.491*	-12.475	-12.491*
-12.021	-12.035	-12.009	-12.049
-11.661	-11.460	-11.468	-11.586
-11.118	-11.245	-11.219	-11.063
-10.776	-10.391	-10.497	-10.546
-10.116	-10.009	-10.052	- 9.823*
- 9.682	- 9.823*	- 9.741	- 9.756
- 8.581	- 8.490	- 8.507	- 8.982
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- 3.419	- 3.510	- 3.493	- 3.018
- 2.318	- 2.177*	- 2.259	- 2.244
- 1.884	- 1.991	- 1.948	- 2.177*
- 1.224	- 1.609	- 1.503	- 1.454
- 0.882	- 0.755	- 0.781	- 0.937
- 0.339	- 0.540	- 0.532	- 0.414
+ 0.021	+ 0.035	+ 0.009	+ 0.049
+ 0.463	+ 0.491*	+ 0.475	+ 0.491*
+ 1.387	+ 0.848	+ 1.024	+ 0.822
+ 2.273	+ 1.986	+ 2.032	+ 1.951
+ 2.812	+ 2.709	+ 2.721	+ 2.750

TABLE 2.6 - ENERGIES (ev) OF SCF MOLECULAR ORBITALS FOR BENZ (a)NAPTHACENE

AND ITS COMPOSITE SYSTEMS (CONTINUED)

Composite System (Ib), β_{RS} = -1.000 ev	Composite System (Ic), β_{RS} = 0.0 ev	Composite System (Ic), β_{RS} = -1.000 ev
-14.756	-14.579	-14.603
-13.998	-13.879*	-13.991
-13.011	-13.482	-13.446
-12.473	-11.887*	-12.112
-12.004	-11.878	-11.897
-11.580	-11.861	-11.716
-11.043	-10.675	-10.858
-10.629	-10.666*	-10.657
- 9.962	-10.438	-10.300
- 9.692	- 9.770*	- 9.779
- 8.864	- 8.891	- 8.812
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- 3.137	- 3.109	- 3.188
- 2.308	- 2.230*	- 2.221
- 2.038	- 1.562	- 1.700
- 1.371	- 1.334*	- 1.343
- 0.957	- 1.325	- 1.142
- 0.420	- 0.139	- 0.284
+ 0.004	- 0.122	- 0.103
+ 0.473	- 0.113*	+ 0.112
+ 1.011	+ 1.482	+ 1.446
+ 1.998	+ 1.879*	+ 1.991
+ 2.756	+ 2.579	+ 2.603

TABLE 2.7 - ENERGIES (ev) OF SCF MOLECULAR ORBITALS FOR BENZO(b)CHRYSENE

AND ITS COMPOSITE SYSTEMS

(II)	Composite System (IIa), β_{RS} = 0.0 ev	Composite System (IIa), β_{RS} = -1.000 ev	Composite System (IIb), β_{RS} = 0.0 ev
-14.850	-14.750	-14.762	-14.785
-14.247	-13.951	-13.997	-13.931
-13.382	-12.822	-13.017	-12.688
-12.379	-12.491*	-12.431	-12.491*
-12.065	-12.049	-12.034	-12.230
-11.703	-11.586	-11.596	-11.460
-11.025	-11.063	-11.028	-11.189
-10.884	-10.546	-10.649	-10.307
- 9.997	- 9.824*	- 9.884	- 9.904
- 0.750	- 9.756	- 9.723	- 9.823*
- 8.809	- 8.982	- 8.929	- 9.162
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- 3.191	- 3.018	- 3.071	- 2.838
- 2.250	- 2.244	- 2.277	- 2.177*
- 2.003	- 2.176*	- 2.116	- 2.096
- 1.116	- 1.454	- 1.351	- 1.693
- 0.975	- 0.937	- 0.972	- 0.811
- 0.297	- 0.414	- 0.404	- 0.540
+ 0.065	+ 0.049	+ 0.034	+ 0.230
+ 0.379	+ 0.491*	+ 0.431	+ 0.491*
+ 1.382	+ 0.822	+ 1.017	+ 0.688
+ 2.247	+ 1.951	+ 1.997	+ 1.931
+ 2.850	+ 2.750	+ 2.762	+ 2.785

TABLE 2.7 - ENERGIES (ev) OF SCF MOLECULAR ORBITALS FOR BENZO(b)CHRYSENE AND ITS COMPOSITE SYSTEMS (CONTINUED)

Composite System (IIb), β_{RS} = -1.000 ev	Composite System (IIc), β_{RS} = 0.0 ev	Composite System (IIc), β_{RS} = -1.000 ev
-14.792	-14.579	-14.611
-13.975	-13.879*	-13.987
-12.963	-13.482	-13.444
-12.389	-11.888*	-12.074
-12.173	-11.878	-11.897
-11.486	-11.861	-11.760
-11.140	-10.675	-10.844
-10.481	-10.666*	-10.670
- 9.955	-10.438	-10.292
- 9.761	- 9.770*	- 9.758
- 9.056	- 8.891	- 8.867
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- 2.944	- 3.109	- 3.133
- 2.239	- 2.230*	- 2.242
- 2.045	- 1.562	- 1.708
- 1.519	- 1.334	- 1.330
- 0.860	- 1.325	- 1.156
- 0.514	- 0.139	- 0.240
+ 0.173	- 0.122	- 0.103
+ 0.389	- 0.112*	+ 0.074
+ 0.963	+ 1.482	+ 1.444
+ 1.975	+ 1.879*	+ 1.987
+ 2.792	+ 2.579	+ 2.611

TABLE 2.8 - ENERGIES (ev) OF SCF MOLECULAR ORBITALS FOR DIBENZO(b,g)PHENANTHRENE AND ITS COMPOSITE SYSTEMS

(III)	Composite System (IIIa), β_{RS} = 0.0 ev	Composite System (IIIa), β_{RS} = -1.00 ev	Composite System (IIIb), β_{RS} = 0.0 ev
-14.868	-14.750	-14.765	-14.803
-14.209	-13.951	-13.991	-13.861
-13.388	-12.822	-13.001	-12.870
-12.489	-12.491*	-12.489	-12.491*
-11.994	-12.049	-12.005	-11.883
-11.610	-11.586	-11.552	-11.818
-11.218	-11.063	-11.091	-10.882
-10.733	-10.546	-10.605	-10.646
-10.152	- 9.823*	- 9.985	- 9.823*
- 9.567	- 9.756	- 9.615	- 9.576
- 8.867	- 8.982	- 8.952	- 9.317
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- 3.133	- 3.018	- 3.048	- 2.683
- 2.433	- 2.244	- 2.385	- 2.424
- 1.848	- 2.177*	- 2.015	- 2.177*
- 1.267	- 1.454	- 1.395	- 1.354
- 0.782	- 0.937	- 0.809	- 1.118
- 0.390	- 0.414	- 0.448	- 0.182
- 0.006	+ 0.049	+ 0.005	- 0.117
+ 0.489	+ 0.491*	+ 0.489	+ 0.491*
+ 1.383	+ 0.822	+ 1.001	+ 0.870
+ 2.209	+ 1.951	+ 1.991	+ 1.861
+ 2.868	+ 2.750	+ 2.764	+ 2.803

TABLE 2.8 - ENERGIES (ev) OF SCF MOLECULAR ORBITALS FOR DIBENZO(b,g)PHENANTHRENE AND ITS COMPOSITE SYSTEMS (CONTINUED)

Composite System (IIIb), β_{RS} = -1.000 ev	Composite System (IIIc), β_{RS} = 0.0 ev	Composite System (IIIc), β_{RS} = -1.000 ev
-14.810	-14.579	-14.616
-13.909	-13.879*	-13.977
-13.042	-13.483	-13.446
-12.490	-11.888*	-12.117
-11.853	-11.878	-11.894
-11.775	-11.861	-11.708
-10.878	-10.675	-10.926
-10.731	-10.666*	-10.519
- 9.969	-10.438	-10.411
- 9.550	- 9.770*	- 9.709
- 9.163	- 8.891	- 8.882
---	---	---
- 2.837	- 3.109	- 3.118
- 2.450	- 2.230*	- 2.291
- 2.031	- 1.562	- 1.589
- 1.269	- 1.334*	- 1.481
- 1.122	- 1.325	- 1.074
- 0.225	- 0.139	- 0.292
- 0.147	- 0.122	- 0.106
+ 0.490	- 0.112*	+ 0.117
+ 1.042	+ 1.482	+ 1.446
+ 1.909	+ 1.879*	+ 1.977
+ 2.810	+ 2.579	+ 2.616

TABLE 2.9 - ENERGIES (ev) OF SCF MOLECULAR ORBITALS FOR DIBENZ(a,c)ANTHRACENE AND ITS COMPOSITE SYSTEMS

(IV)	Composite System (IVa), β_{RS} = 0.0 ev	Composite System (IVa), β_{RS} = -1.00 ev	Composite System (IVb), β_{RS} = 0.0 ev
-14.923	-14.750	-14.774	-14.856
-14.073	-13.951	-13.969	-13.436
-13.442	-12.822	-12.979	-13.436
-12.711	-12.491*	-12.613	-12.491*
-11.751	-12.049	-11.887	-11.637
-11.526	-11.586	-11.569	-11.428
-11.145	-11.063	-11.066	-11.428
-10.901	-10.546	-10.637	-10.348
-10.029	- 9.823*	- 9.902	- 9.823*
- 9.686	- 9.756	- 9.689	- 9.625
- 9.115	- 8.982	- 9.008	- 9.625
------	------	------	------
- 2.885	- 3.018	- 2.992	- 2.375
- 2.314	- 2.244	- 2.311	- 2.375
- 1.971	- 2.177*	- 2.098	- 2.177*
- 1.099	- 1.454	- 1.363	- 1.652
- 0.855	- 0.937	- 0.934	- 0.572
- 0.474	- 0.414	- 0.431	- 0.572
- 0.249	+ 0.049	- 0.113	- 0.363
+ 0.711	+ 0.491*	+ 0.613	+ 0.491*
+ 1.442	+ 0.822	+ 0.979	+ 1.436
+ 2/-73	+ 1.951	+ 1.969	+ 1.436
+ 2.923	+ 2.750	+ 2.774	+ 2.856

TABLE 2.9 - ENERGIES (ev) OF SCF MOLECULAR ORBITALS FOR DIBENZ(a,c)ANTHRACENE AND ITS COMPOSITE SYSTEMS (CONTINUED)

Composite System (IVb), β_{RS} = -1.000 ev
-14.864
-13.567
-13.437
-12.580
-11.573
-11.471
-11.365
-10.500
- 9.949
- 9.633
- 9.406

- 2.594
- 2.367
- 2.051
- 1.500
- 0.635
- 0.529
- 0.427
+ 0.580
+ 1.437
+ 1.567
+ 2.864

TABLE 2.10 - ENERGIES (ev) OF SCF MOLECULAR ORBITALS FOR 3.4-BENZOPYRENE

AND ITS COMPOSITE SYSTEMS

(V)	Composite System (Va), β_{RS} = 0.0 ev	Composite System (Va), β_{RS} = -1.000 ev	Composite System (Vb), β_{RS} = 0.0 ev
-14.976	-14.872	-14.886	-14.750
-14.015	-13.478	-13.582	-13.951
-13.017	-12.942	-12.961	-12.822
-12.750	-12.491*	-12.593	-12.049
-11.669	-11.681	-11.589	-11.586
-11.257	-11.262	-11.289	-11.063
-10.700	-10.706	-10.705	-10.957*
-10.551	-10.122	-10.231	-10.546
- 9.931	- 9.823*	- 9.848	- 9.756
- 8.634	- 8.889	- 8.807	- 8.982
------	-----	-----	-----
- 3.366	- 3.111	- 3.193	- 3.018
- 2.069	- 2.177*	- 2.152	- 2.244
- 1.449	- 1.878	- 1.769	- 1.454
- 1.300	- 1.294	- 1.295	- 1.043*
- 0.743	- 0.728	- 0.711	- 0.937
- 0.331	- 0.319	- 0.411	- 0.414
+ 0.750	+ 0.491*	+ 0.593	+ 0.049
+ 1.017	+ 0.942	+ 0.961	+ 0.822
+ 2.015	+ 1.478	+ 1.582	+ 1.951
+ 2.976	+ 2.872	+ 2.886	+ 2.750

TABLE 2.10 - ENERGIES (ev) OF SCF MOLECULAR ORBITALS FOR 3.4-BENZOPYRENE

AND ITS COMPOSITE SYSTEMS (CONTINUED)

Composite System (Vb), β_{RS} = -1.000 ev	Composite System (Vc), β_{RS} = 0.0 ev	Composite System (Vc), β_{RS} = -1.000 ev
-14.786	-14.785	-14.815
-13.962	-13.931	-13.945
-12.838	-12.688	-12.702
-12.272	-12.231	-12.423
-11.597	-11.460	-11.523
-11.126	-11.189	-11.222
-10.835	-10.956*	-10.839
-10.547	-10.307	-10.348
- 9.771	- 9.904	- 9.912
- 9.914	- 9.163	- 9.045
------	------	------
- 3.086	- 2.837	- 2.955
- 2.229	- 2.096	- 2.088
- 1.453	- 1.693	- 1.652
- 1.165	- 1.044*	- 1.161
- 0.874	- 0.811	- 0.778
- 0.403	- 0.540	- 0.477
+ 0.272	+ 0.231	+ 0.423
+ 0.838	+ 0.688	+ 0.702
+ 1.962	+ 1.931	+ 1.945
+ 2.786	+ 2.785	+ 2.815

TABLE 2.11 - ΔE VALUES FOR VARIOUS COMPOSITE SYSTEMS

Molecules Divided by 2 Bonds With β_{RS}=0.000 ev		Molecules Divided by 2 Bonds With β_{RS}=-1.000 ev	
Molecule	ΔE	Molecule	ΔE
(Ia)	1.2356	(Ia)	0.6744
(Ib)	1.4830	(Ib)	0.7166
(Ic)	2.0536	(Ic)	0.8950
(IIa)	1.2288	(IIa)	0.6046
(IIb)	2.3690	(IIb)	1.1008
(IIc)	1.7830	(IIc)	0.8438
(IIIa)	1.2304	(IIIa)	0.5564
(IIIb)	1.7514	(IIIb)	0.9878
(IIIc)	2.1288	(IIIc)	0.9964
(IVa)	1.5372	(IVa)	0.7624
(IVb)	2.3488	(IVb)	1.2302
(Va)	1.2642	(Va)	0.7392
(Vb)	1.6948	(Vb)	0.8880
(Vc)	1.7502	(Vc)	0.9794

TABLE 2.12a - $\underline{\Delta F}$ FOR BENZ(a)NAPTHACENE COMPOSITE SYSTEM (Ia) WITH β_{RS} = 0.0 ev

0.0000	-0.0380	0.0000	-0.0063	0.0000	-0.0054	0.0000	+0.0126	0.0000	-0.0274
0.0000	+0.0185	0.0000	-0.0607	0.0000	+0.0396	0.0000	+0.0395	0.0000	-0.0432
0.0000	+0.0665								
	0.0000	-0.0259	0.0000	-0.0077	0.0000	+0.0040	0.0000	-0.0112	0.0000
+0.0183	0.0000	-0.0224	0.0000	-0.0216	0.0000	+0.0292	0.0000	-0.0114	0.0000
+0.0192	0.0000								
		0.0000	-0.0121	0.0000	+0.0080	0.0000	-0.0179	0.0000	+0.0133
0.0000	-0.0088	0.0000	+0.0284	0.0000	-0.0188	0.0000	-0.0160	0.0000	+0.0169
0.0000	-0.0183								
			0.0000	+0.0084	0.0000	-0.0014	0.0000	+0.0037	0.0000
-0.0048	0.0000	+0.0062	0.0000	+0.0063	0.0000	-0.0084	0.0000	+0.0031	0.0000
-0.0045	0.0000								
				0.0000	-0.0111	0.0000	+0.0088	0.0000	-0.0059
0.0000	+0.0044	0.0000	-0.0147	0.0000	+0.0099	0.0000	+0.0079	0.0000	-0.0082
0.0000	+0.0076								
					0.0000	+0.0084	0.0000	-0.0080	0.0000
+0.0076	0.0000	-0.0083	0.0000	-0.0086	0.0000	+0.0089	0.0000	-0.0022	0.0000
+0.0040	0.0000								
						0.0000	-0.0132	0.0000	+0.0074
0.0000	-0.0054	0.0000	+0.0162	0.0000	-0.0096	0.0000	-0.0073	0.0000	+0.0073
0.0000	-0.0056								
							0.0000	+0.0285	0.0000
-0.0197	0.0000	+0.0184	0.0000	+0.0174	0.0000	-0.0162	0.0000	+0.0033	0.0000
-0.0075	0.0000								
								0.0000	-0.0438
0.0000	+0.0243	0.0000	-0.0646	0.0000	+0.0346	0.0000	+0.0271	0.0000	-0.0260
0.0000	+0.0203								
									0.0000
+0.0792	0.0000	-0.0544	0.0000	-0.0418	0.0000	+0.0317	0.0000	-0.0020	0.0000
+0.0160	0.0000								
0.0000	-0.0937	0.0000	+0.2700	0.0000	-0.1176	0.0000	-0.0998	0.0000	+0.0821
0.0000	-0.0492								
	0.0000	+0.2412	0.0000	+0.1176	0.0000	-0.0409	0.0000	-0.0276	0.0000
-0.0206	0.0000								

TABLE 2.12a - $\underline{\Delta F}$ FOR BENZ(a)NAPTHACENE COMPOSITE SYSTEM (Ia) WITH β_{RS} = 0.0 ev (CONTINUED)

		0.0000	+0.5810	0.0000	-0.0935	0.0000	-0.0392	0.0000
+0.1164	0.0000							
			0.0000	-0.6212	0.0000	+0.4922	0.0000	-0.1743
0.0000	+0.0632							
				0.0000	+0.5696	0.0000	+0.1356	0.0000
-0.0851	0.0000							
					0.0000	-3.8655	0.0000	+0.2655
0.0000	-0.0885							
						0.0000	+0.2750	0.0000
-0.1155	0.0000							
							0.0000	-0.1425
0.0000	+0.0386							
								0.0000
+0.1436	0.0000							
0.0000	-0.0918							
	0.0000							

TABLE 2.12b - $\underline{\Delta F}$ FOR BENZ(a)NAPTHACENE COMPOSITE SYSTEM (Ia) WITH β_{RS} = -1.000 ev

0.0000	-0.0285	0.0000	+0.0049	0.0000	-0.0041	0.0000	+0.0094	0.0000	-0.0206
0.0000	+0.0140	0.0000	-0.0289	0.0000	+0.0157	0.0000	+0.0305	0.0000	-0.0329
0.0000	+0.0507								
	0.0000	+0.0195	0.0000	-0.0060	0.0000	+0.0031	0.0000	-0.0028	0.0000
+0.0137	0.0000	-0.0170	0.0000	-0.0077	0.0000	+0.0134	0.0000	-0.0085	0.0000
+0.0146	0.0000								
		0.0000	-0.0095	0.0000	+0.0063	0.0000	-0.0132	0.0000	+0.0101
0.0000	-0.0068	0.0000	+0.0251	0.0000	-0.0074	0.0000	-0.0124	0.0000	+0.0130
0.0000	-0.0137								
			0.0000	+0.0069	0.0000	-0.0010	0.0000	+0.0029	0.0000
-0.0037	0.0000	+0.0046	0.0000	+0.0022	0.0000	-0.0038	0.0000	+0.0023	0.0000
-0.0033	0.0000								
				0.0000	-0.0084	0.0000	+0.0063	0.0000	-0.0045
0.0000	+0.0033	0.0000	-0.0069	0.0000	+0.0038	0.0000	+0.0062	0.0000	-0.0063
0.0000	+0.0058								
					0.0000	+0.0063	0.0000	-0.0060	0.0000
+0.0058	0.0000	-0.0063	0.0000	-0.0030	0.0000	+0.0040	0.0000	-0.0017	0.0000
+0.0030	0.0000								
						0.0000	-0.0100	0.0000	+0.0057
0.0000	-0.0041	0.0000	+0.0076	0.0000	-0.0038	0.0000	-0.0057	0.0000	+0.0055
0.0000	-0.0044								
							0.0000	+0.0216	0.0000
-0.0252	0.0000	+0.0141	0.0000	+0.0063	0.0000	-0.0073	0.0000	+0.0025	0.0000
-0.0056	0.0000								
								0.0000	-0.0333
0.0000	+0.0183	0.0000	-0.0303	0.0000	+0.0138	0.0000	+0.0209	0.0000	-0.0199
0.0000	+0.0155								
									0.0000
+0.0602	0.0000	-0.0415	0.0000	-0.0154	0.0000	+0.0141	0.0000	-0.0014	0.0000
+0.0119	0.0000								
0.0000	-0.0950	0.0000	+0.1305	0.0000	-0.0483	0.0000	-0.0775	0.0000	+0.0632

TABLE 2.12b - $\underline{\Delta F}$ FOR BENZ(a)NAPTHACENE COMPOSITE SYSTEM (Ia) WITH β_{RS} = -1.000 ev (CONTINUED)

0.0000	-0.0380								
	0.0000	+0.1858	0.0000	+0.0461	0.0000	-0.0177	0.0000	-0.0213	0.0000
-0.0153	0.0000								
		0.0000	-2.1335	0.0000	+0.2142	0.0000	+0.4005	0.0000	-0.1674
0.0000	+0.0569								
			0.0000	+0.4517	0.0000	-0.0802	0.0000	-0.0172	0.0000
+0.0558	0.0000								
				0.0000	-0.4692	0.0000	+0.2138	0.0000	-0.0693
0.0000	+0.0236								
					0.0000	+0.4444	0.0000	+0.0535	0.0000
-0.0334	0.0000								
						0.0000	-2.1255	0.0000	+0.1287
0.0000	+0.0414								
							0.0000	+0.2127	0.0000
-0.0889	0.0000								
								0.0000	-0.1082
0.0000	+0.0292								
									0.0000
+0.1093	0.0000								
0.0000	-0.0691								
	0.0000								

TABLE 2.12c - $\underline{\Delta F}$ FOR BENZ(a)NAPTHACENE COMPOSITE SYSTEM (Ib) WITH β_{RS} = 0.0 ev

0.0000	-0.1853	0.0000	+0.1648	0.0000	-0.1194	0.0000	+0.3300	0.0000	+0.0908
0.0000	-0.0387	0.0000	+0.0086	0.0000	-0.0054	0.0000	+0.0090	0.0000	-0.0092
0.0000	+0.0860								
	0.0000	+0.3441	0.0000	+0.2792	0.0000	-0.1493	0.0000	+0.0799	0.0000
-0.0278	0.0000	+0.0039	0.0000	-0.0049	0.0000	+0.0069	0.0000	-0.0184	0.0000
+0.0458	0.0000								
		0.0000	-3.6574	0.0000	+0.3764	0.0000	+0.2064	0.0000	-0.0753
0.0000	+0.0280	0.0000	-0.0073	0.0000	+0.0047	0.0000	-0.0073	0.0000	+0.0076
0.0000	-0.0529								
			0.0000	+0.4096	0.0000	-0.0499	0.0000	-0.1496	0.0000
+0.0382	0.0000	-0.0052	0.0000	+0.0063	0.0000	-0.0084	0.0000	+0.0218	0.0000
-0.0494	0.0000								
				0.0000	-0.4354	0.0000	+0.3764	0.0000	-0.1199
0.0000	+0.0488	0.0000	-0.0147	0.0000	+0.0099	0.0000	-0.0133	0.0000	+0.0105
0.0000	-0.0647								
					0.0000	+0.4095	0.0000	+0.2789	0.0000
-0.647	0.0000	+0.0104	0.0000	-0.0086	0.0000	+0.0089	0.0000	-0.0236	0.0000
+0.0483	0.0000								
						0.0000	-3.6486	0.0000	+0.1659
0.0000	-0.0504	0.0000	+0.0162	0.0000	-0.0096	0.0000	+0.0114	0.0000	-0.0041
0.0000	+0.0374								
							0.0000	+0.3446	0.0000
-0.0529	0.0000	+0.0070	0.0000	-0.0044	0.0000	+0.0041	0.0000	-0.0124	0.0000
+0.0278	0.0000								
								0.0000	-0.1863
0.0000	+0.0466	0.0000	-0.0140	0.0000	+0.0077	0.0000	-0.0093	0.0000	+0.0027
0.0000	-0.0272								
									0.0000
+0.0876	0.0000	-0.0089	0.0000	+0.0052	0.0000	-0.0054	0.0000	+0.0154	0.0000
-0.0384	0.0000								
0.0000	-0.0570	0.0000	+0.0143	0.0000	-0.0065	0.0000	+0.0077	0.0000	-0.0003

TABLE 2.12c - $\underline{\Delta F}$ FOR BENZ(a)NAPTHACENE COMPOSITE SYSTEM (Ib) WITH β_{RS} = 0.0 ev (CONTINUED)

0.0000	+0.0112								
	0.0000	+0.0153	0.0000	-0.0072	0.0000	+0.0077	0.0000	-0.0220	0.0000
+0.0512	0.0000								
		0.0000	-0.0090	0.0000	+0.0035	0.0000	-0.0026	0.0000	-0.0028
0.0000	-0.0014								
			0.0000	+0.0079	0.0000	-0.0038	0.0000	-0.0069	0.0000
-0.0094	0.0000								
				0.0000	-0.0074	0.0000	+0.0038	0.0000	-0.0005
0.0000	+0.0031								
					0.0000	+0.0084	0.0000	-0.0066	0.0000
+0.0063	0.0000								
						0.0000	-0.0095	0.0000	+0.0026
0.0000	-0.0179								
							0.0000	+0.0164	0.0000
-0.0126	0.0000								
								0.0000	-0.0106
0.0000	+0.0166								
									0.0000
+0.0158	0.0000								
0.0000	-0.0559								
	0.0000								

TABLE 2.12d - $\underline{\Delta F}$ FOR BENZ(a)NAPTHACENE COMPOSITE SYSTEM (Ib) WITH β_{RS} = -1.000 ev

0.0000	-0.1483	0.0000	+0.0890	0.0000	-0.0509	0.0000	-0.0635	0.0000	+0.0734
0.0000	-0.0310	0.0000	+0.0070	0.0000	-0.0043	0.0000	+0.0072	0.0000	-0.0074
0.0000	+0.0691								
	0.0000	+0.2749	0.0000	+0.1285	0.0000	-0.0778	0.0000	+0.0628	0.0000
-0.0220	0.0000	+0.0031	0.0000	-0.0038	0.0000	+0.0055	0.0000	-0.0145	0.0000
+0.0366	0.0000								
		0.0000	-2.0448	0.0000	+0.1925	0.0000	+0.1673	0.0000	-0.0610
0.0000	+0.0228	0.0000	-0.0059	0.0000	+0.0038	0.0000	-0.0059	0.0000	+0.0060
0.0000	-0.0423								
			0.0000	+0.3288	0.0000	-0.0433	0.0000	-0.0781	0.0000
+0.0204	0.0000	-0.0028	0.0000	+0.0034	0.0000	-0.0045	0.0000	+0.0117	0.0000
-0.0267	0.0000								
				0.0000	-0.3447	0.0000	+0.1922	0.0000	-0.0592
0.0000	+0.0236	0.0000	-0.0071	0.0000	+0.0047	0.0000	-0.0063	0.0000	+0.0048
0.0000	-0.3000								
					0.0000	+0.3283	0.0000	+0.1285	0.0000
-0.0300	0.0000	+0.0048	0.0000	-0.0042	0.0000	+0.0043	0.0000	-0.0114	0.0000
+0.0234	0.0000								
						0.0000	-2.0453	0.0000	+0.0895
0.0000	-0.0271	0.0000	+0.0087	0.0000	-0.0052	0.0000	+0.0061	0.0000	-0.0022
0.0000	+0.0199								
							0.0000	+0.2755	0.0000
-0.0423	0.0000	+0.0056	0.0000	-0.0036	0.0000	+0.0034	0.0000	-0.0101	0.0000
+0.0116	0.0000								
								0.0000	-0.1488
0.0000	+0.0372	0.0000	-0.0113	0.0000	+0.0063	0.0000	-0.0074	0.0000	+0.0021
0.0000	-0.0215								
									0.0000
+0.0702	0.0000	-0.0072	0.0000	+0.0042	0.0000	-0.0045	0.0000	+0.0064	0.0000
-0.0307	0.0000								
0.0000	-0.0459	0.0000	+0.0115	0.0000	-0.0052	0.0000	+0.0063	0.0000	-0.0003
0.0000	+0.0087								

TABLE 2.12d - $\underline{\Delta F}$ FOR BENZ(a)NAPTHACENE COMPOSITE SYSTEM (Ib) WITH β_{RS} = -1.000 ev (CONTINUED)

	0.0000	+0.0121	0.0000	-0.0057	0.0000	+0.0063	0.0000	-0.0178	0.0000
+0.0412	0.0000								
		0.0000	-0.0074	0.0000	+0.0028	0.0000	-0.0021	0.0000	-0.0021
0.0000	-0.0011								
			0.0000	+0.0063	0.0000	-0.0031	0.0000	+0.0057	0.0000
-0.0074	0.0000								
				0.0000	-0.0058	0.0000	+0.0028	0.0000	-0.0002
0.0000	+0.0025								
					0.0000	+0.0069	0.0000	-0.0051	0.0000
+0.0052	0.0000								
						0.0000	-0.0079	0.0000	+0.0020
0.0000	-0.0044								
							0.0000	+0.0132	0.0000
-0.0101	0.0000								
								0.0000	-0.0084
0.0000	_0.0132								
									0.0000
+0.0127	0.0000								
0.0000	-0.0449								
	0.0000								

TABLE 2.12e - $\underline{\Delta F}$ FOR BENZ(a)NAPTHACENE COMPOSITE SYSTEM (Ic) WITH β_{RS} = 0.0 ev

0.0000	+0.0517	0.0000	-0.0080	0.0000	+0.0072	0.0000	-0.0188	0.0000	+0.0507
0.0000	-0.0495	0.0000	-0.0607	0.0000	+0.0396	0.0000	-0.0745	0.0000	+0.1153
0.0000	-0.1135								
	0.0000	-0.0311	0.0000	+0.0080	0.0000	-0.0026	0.0000	+0.0077	0.0000
-0.0152	0.0000	+0.0206	0.0000	-0.0216	0.0000	+0.0292	0.0000	-0.0837	0.0000
-0.0366	0.0000								
		0.0000	+0.0132	0.0000	-0.0094	0.0000	+0.0216	0.0000	-0.0181
0.0000	+0.0154	0.0000	+0.0284	0.0000	-0.0188	0.0000	+0.0283	0.0000	-0.0281
0.0000	+0.0243								
			0.0000	-0.0084	0.0000	+0.0007	0.0000	-0.0029	0.0000
+0.0044	0.0000	-0.0052	0.0000	+0.0063	0.0000	-0.0084	0.0000	+0.0218	0.0000
-0.0494	0.0000								
				0.0000	+0.0121	0.0000	-0.0094	0.0000	+0.0068
0.0000	-0.0064	0.0000	-0.0147	0.0000	+0.0099	0.0000	-0.0133	0.0000	+0.0105
0.0000	-0.0083								
					0.0000	-0.0084	0.0000	+0.0077	0.0000
-0.0083	0.0000	+0.0104	0.0000	-0.0086	0.0000	+0.0089	0.0000	-0.0236	0.0000
-0.0069	0.0000								
						0.0000	+0.0121	0.0000	-0.0069
0.0000	+0.0060	0.0000	+0.0162	0.0000	-0.0096	0.0000	+0.0114	0.0000	-0.0041
0.0000	+0.0035								
							0.0000	-0.0285	0.0000
+0.0229	0.0000	-0.0266	0.0000	+0.0174	0.0000	-0.0162	0.0000	+0.0476	0.0000
+0.0167	0.0000								
								0.0000	+0.0459
0.0000	-0.0315	0.0000	-0.0646	0.0000	+0.0346	0.0000	-0.0452	0.0000	+0.0170
0.0000	-0.0132								
									0.0000
-0.1008	0.0000	+0.1041	0.0000	-0.0418	0.0000	+0.0314	0.0000	-0.1161	0.0000
-0.0520	0.0000								
0.0000	+0.2164	0.0000	+0.2700	0.0000	-0.1176	0.0000	+0.1871	0.0000	-0.0712
0.0000	+0.0366								

TABLE 2.12e - $\underline{\Delta F}$ FOR BENZ(a)NAPTHACENE COMPOSITE SYSTEM (Ic) WITH β_{RS} = 0.0 ev (CONTINUED)

	0.0000	-3.3942	0.0000	+0.1176	0.0000	-0.0409	0.0000	+0.3408	0.0000
+0.1742	0.0000								
		0.0000	+0.1979	0.0000	-0.0691	0.0000	+0.1356	0.0000	+0.0185
0.0000	-0.0790								
			0.0000	-0.0960	0.0000	+0.0185	0.0000	-0.0798	0.0000
+0.1164	0.0000								
				0.0000	+0.0876	0.0000	-0.0523	0.0000	+0.0115
0.0000	+0.0632								
					0.0000	-0.0713	0.0000	+0.0807	0.0000
-0.0851	0.0000								
						0.0000	+0.0950	0.0000	-0.0438
0.0000	-0.0885								
							0.0000	-0.2528	0.0000
+0.2520									
								0.0000	+0.2971
0.0000	+0.3256								
									0.0000
-3.4918	0.0000								
0.0000	+0.2496								
	0.0000								

TABLE 2.12f - $\underline{\Delta F}$ FOR BENZ(a)NAPTHACENE COMPOSITE SYSTEM (Ic) WITH β_{RS} = -1.000 ev

0.0000	+0.0428	0.0000	-0.0066	0.0000	+0.0059	0.0000	-0.0157	0.0000	+0.0412
0.0000	-0.0401	0.0000	-0.0312	0.0000	+0.0209	0.0000	-0.0397	0.0000	+0.0641
0.0000	-0.0924								
	0.0000	-0.0259	0.0000	+0.0066	0.0000	-0.0023	0.0000	+0.0063	0.0000
-0.0126	0.0000	+0.0129	0.0000	-0.0118	0.0000	+0.0151	0.0000	-0.0434	0.0000
-0.0298	0.0000								
		0.0000	+0.0111	0.0000	-0.0077	0.0000	+0.0179	0.0000	-0.0150
0.0000	+0.0124	0.0000	+0.0145	0.0000	-0.0099	0.0000	+0.0152	0.0000	-0.0161
0.0000	+0.0200								
			0.0000	-0.0069	0.0000	+0.0007	0.0000	-0.0023	0.0000
+0.0035	0.0000	-0.0033	0.0000	+0.0035	0.0000	-0.0044	0.0000	+0.0114	0.0000
+0.0058	0.0000								
				0.0000	+0.0100	0.0000	-0.0077	0.0000	+0.0056
0.0000	-0.0053	0.0000	-0.0075	0.0000	+0.0052	0.0000	-0.0071	0.0000	+0.0061
0.0000	-0.0068								
					0.0000	-0.0074	0.0000	+0.0063	0.0000
-0.0068	0.0000	+0.0061	0.0000	-0.0048	0.0000	+0.0047	0.0000	-0.0124	0.0000
-0.0056	0.0000								
						0.0000	+0.0100	0.0000	-0.0057
0.0000	+0.0050	0.0000	+0.0084	0.0000	-0.0050	0.0000	+0.0061	0.0000	-0.0027
0.0000	+0.0029								
							0.0000	-0.0238	0.0000
+0.0189	0.0000	-0.0153	0.0000	+0.0096	0.0000	-0.0086	0.0000	+0.0250	0.0000
+0.0135	0.0000								
								0.0000	+0.0380
0.0000	-0.0257	0.0000	-0.0332	0.0000	+0.0181	0.0000	-0.0242	0.0000	+0.0110
0.0000	-0.0112								
-0.0823	0.0000	+0.0589	0.0000	-0.0233	0.0000	+0.0167	0.0000	-0.0610	0.0000
-0.0419	0.0000								
0.0000	+0.1725	0.0000	+0.1371	0.0000	-0.0607	0.0000	+0.0987	0.0000	-0.0438
0.0000	+0.0307								

TABLE 2.12f - $\underline{\Delta F}$ FOR BENZ(a)NAPTHACENE COMPOSITE SYSTEM (Ic) WITH β_{RS} = -1.000 ev (CONTINUED)

	0.0000	-1.9149	0.0000	+0.0655	0.0000	-0.0226	0.0000	+0.1803	0.0000
+0.1393	0.0000								
		0.0000	+0.1594	0.0000	-0.0562	0.0000	+0.1103	0.0000	+0.0129
0.0000	-0.0478								
			0.0000	-0.0776	0.0000	+0.0146	0.0000	-0.0149	0.0000
+0.0595	0.0000								
				0.0000	+0.0713	0.0000	-0.0426	0.0000	+0.0097
0.0000	+0.0341								
					0.0000	-0.0575	0.0000	+0.0647	0.0000
-0.0449	0.0000								
						0.0000	+0.0771	0.0000	-0.0355
0.0000	-0.0451								
							0.0000	-0.2032	0.0000
+0.1346									
								0.0000	+0.2390
0.0000	+0.1657								
									0.0000
-1.9635	0.0000								
0.0000	+0.2011								
	0.0000								

F. Analysis of Results

1. General

In this analysis the choice of the composite system model for the molecule will be noted and an interpretation of the molecular electronic transitions will be given in terms of the transitions of the appropriate composite system with no bonds between the component parts, that is, with zero value resonance integrals between the component parts. Basically, the proper composite system model of the subject molecule is chosen by means of a systematic comparison of the calculated absorption spectra of all the various possible composite systems with the calculated absorption spectra of the molecule treated conventionally as a single component quantum mechanical system. In this comparison, the energy and oscillator strength of all the transitions, including the formally forbidden transitions, is considered. The composite system whose absorption spectrum most closely approximates that of the complete molecule is considered to be the appropriate composite system model or approximation to the original molecule. This is the only method of choosing a composite system model which is compatable with the objective of this study, that is, the interpretation of the electronic transitions of a pentacyclic aromatic hydrocarbon in terms of the electronic transitions of a smaller polycyclic aromatic hydrocarbon contained within the structure of the pentacyclic.

The importance of the calculated absorption spectra of the composite systems with weak bonding, that is, the value of the resonance integrals

between the component parts equal to -1.000 ev, must be emphasized. First it is by means of these calculated spectra that one may determine with confidence which transitions of the complete molecule correspond to those of the composite system with no bonds between the component parts. This can be somewhat of a problem when the transitions are considerably shifted in energy, and/or undergo significant changes in oscillator strength when passing from the composite system model to the molecule treated as a single component system. Second, the calculated absorption spectra of the weakly bonded composite systems are a distinct aid in determining the appropriate composite system model for the molecule. This happens because, for the best composite system approximation to the molecule, one finds the spectra of the weakly bonded composite system to be remarkably close to that of the subject molecule.

Once the appropriate composite system model of the molecule has been chosen and the transitions of the molecule correlated to those of the composite system with no bonding between the parts, the next step is to determine the origins of the electronic transitions of the composite system. To do this, the wave functions of the non-bonded composite system excited states, to which the transitions occur, are examined to determine the types of excited electronic configurations from which the various excited states are formed (see Tables 1.1 through 1.5). That is, the wave function is examined to determine its composition in terms of local excited configurations, formed by local excitations between the molecular orbitals of one or the other of the component parts of the composite system,and electron-transfer

configurations, formed by the excitation of an electron from a molecular orbital of one component part to a molecular orbital of the other part. By this analysis of the non-bonded composite system excited states, the transitions of the composite system may be interpreted as (1) local transitions belonging to one of the two component parts, (2) transitions to states formed by combinations of local excitation configurations of the two parts, or (3) transitions to states formed from the electron-transfer configurations.

The final step is to extend the analysis of the non-bonded composite system transitions to the transitions of the molecule treated conventially as a single component quantum mechanical system. That is to say, a transition of the complete molecule is then interpreted or predicted to have the characteristics of the transition of the non-bonded composite system to which it is correlated. For example, consider an allowed transition of the complete molecule which is correlated to a particular allowed transition of the appropriate composite system. Next, suppose this particular transition of the non-bonded composite system was found, on the basis of the configurations of the excited state to which the transition occurred, to be essentially a local electronic transition of one of the component parts. Then, the electronic transition of the complete molecule is interpreted as being derived from this same local transition of the component part which produces the particular transition of the non-bonded composite system. From this, one may then predict that the

experimentally observed transition corresponding to the calculated transition of the complete molecule and the experimentally observed transition corresponding to the local transition of the component part should have similar characteristics. That is to say, characteristics such as extinction coefficient, vibrational structure, and general shape should be similar. To verify such predictions, it is, of course, necessary to first correctly assign the experimentally observed transitions to the calculated transitions. Unfortunately, this is by no means an easy task in many cases.

The above example is, of course, the ideal case in which the transition of the complete molecule can be correlated with a transition in one of the component parts of the composite system. It is much more difficult to interpret the transitions of the complete molecule in the case where the transitions are correlated with transitions in the non-bonded composite system which are to excited states formed by combinations of local excited configurations of both component parts. Generally, in this situation, an excited state from each of the two component parts to which allowed transitions occur when the component parts are isolated interact by virtue of the electron repulsion terms alone to form a pair of "mixed states" in the composite system. The transitions to these "mixed states" of the non-bonded composite system may then reasonably be predicted as having some combination of the characteristics of the two transitions which occur to the unaltered states of the isolated component parts. The predominant characteristics

may perhaps be predictable by means of the relative weights with which the configurations of the two component parts contribute to the excited state of the composite system.

There are also some transitions of the complete molecules which can be correlated with transitions to the excited states of the non-bonded composite system formed from the electron-transfer configurations. In the composite systems with zero value resonance integrals between the component parts, these electron transfer states occur in degenerate pairs, transitions to each of which are forbidden. As soon as a finite resonance integral is introduced between the component parts, this degeneracy is destroyed and the transition to one of these states becomes allowed while the transition to the other remains forbidden. Thus, there are some allowed transitions of the complete molecule which can be correlated with the forbidden transition to an electron-transfer state in the composite system with zero value resonance integrals between the component parts. Unfortunately, it does not seem possible to make any predictions concerning the characteristics of allowed transitions in the complete molecule derived from transitions to forbidden electron-transfer states of the non-bonded composite system. It would seem unreasonable to predict that a transition of the complete molecule correlated to an electron-transfer transition in the non-bonded composite system should appear similar to a local transition of either of the two component parts or some combination of transitions of the two parts. This is because the electron-transfer states exist

only by virtue of the two component parts forming a composite system and in the absence of a composite system those states do not exist. Consequently, it is difficult to argue that transitions to states derived from the electron-transfer states of the non-bonded composite system should have any particular characteristic other than perhaps those unique to that particular composite system.

The only transitions of the subject molecules which will be discussed are those which are allowed, that is, have a finite oscillator strength, and are,therefore,potentially observable. The calculated oscillator strengths of the transitions are given only for electric dipole transitions from the ground state to the excited states. It is entirely possible that those calculated transitions which are forbidden may be allowed as a multipole transition or perhaps a magnetic dipole transition. However, these other types of transitions are generally very weak relative to the electric dipole transitions and thus, very difficult to observe experimentally. It would seem even more unlikely that should such a weak electric dipole forbidden transition actually be observable in the complete or actual molecule, that the weak corresponding transition of a component part of the composite system would also be experimentally observable. Thus, even though the forbidden transitions of the complete molecule could be correlated to the transitions of the non-bonded composite systems, they will not since any interpretations or predictions concerning these transitions most probably could not be verified by experimental observations and would also tend to be rather confusing.

The correlation of the calculated electronic transitions of the five subject molecules with the electronic transitions of the appropriate non-bonded composite system will now be discussed. As stated earlier, the proper composite system is chosen essentially by a comparison of all the electronic transitions of the complete molecule, including formally forbidden transitions, with those of the various composite system models. The non-bonded composite system whose transitions are the best approximation to the complete molecule and undergo the least alteration upon the formation of bonds between the component parts is considered to be the proper model for the subject molecule. After the correlation of the complete molecule transitions with the transitions of a particular non-bonded composite system approximation, predictions will be made concerning the characteristics of the experimentally observable transitions equivalent to the calculated transitions of the complete molecule. The details of those predictions will be considerably abbreviated since the method and rational have been discussed quite thoroughly above.

2. Benz(a)napthacene (Figure 2.2)

On the basis of a comparison of the calculated electronic transitions, presented graphically in Figures 2.7a through 2.7g and numerically in Tables 2.1a through 2.1g, of benz(a)napthacene (I) and its possible composite system models, the composite system denoted by (Ia) is chosen as the best approximation to the benz(a)-napthacene molecule. The component parts of this composite system

are a napthacene molecule and a cis-butadiene molecule. Throughout the following discussion the benz(a)napthacene molecule treated as a complete molecule or a single component system will be denoted by (I) while the non-bonded composite system model will be denoted by (Ia).

The first allowed transition of (I) is correlated to the first allowed transition of (Ia). This transition of (Ia) is found to be a local transition of the napthacene part. Consequently, the first transition of (I) may be predicted to have the characteristics of the first transition of napthacene. Note that this transition is blue shifted about 0.15 ev while the oscillator strength remains relatively unchanged in passing from the non-bonded composite system to the complete molecule.

The second allowed transition of (I) corresponds to one of the degenerate transitions to the third and fourth electron-transfer states of (Ia). As noted earlier, the electron-transfer transitions of the non-bonded composite system are forbidden. For reasons given earlier in the general discussion of the analysis, no predictions will be made concerning the characteristics of these transitions.

The third allowed transition of (I), which has the largest value oscillator strength of all the transitions of (I), corresponds to the very weak (f = 0.004) second allowed transition of (Ia). This second allowed transition of (Ia) is essentially an unaltered local transition of napthacene. Thus one may correlate the strong third transition of (I) with the weak second transition of napthacene. The predicted

similarity or correspondence between these two transitions may not be obvious because of the large change in oscillator strength of this transition in passing from the non-bonded composite system (Ia) to the complete molecule (I). Also, the third transition of (I) is blue shifted about 0.35 ev relative to the corresponding napthacene transition of the non-bonded composite system.

The fourth relatively weak transition of (I) corresponds to the third allowed transition of (Ia). The third transition of (Ia) is the strongest and corresponds to a local transition of the napthacene moiety. In other words, the relatively weak fourth transition of (I) should be similar in appearance to the third very intense transition of napthacene which in turn is the basis of the third transition of the composite system. Not only is there a considerable change in the oscillator strength of this transition when passing from (I) to (Ia) but these is also a blue shift of about 0.27 ev.

The fifth and sixth allowed transitions of (I) correspond to the fourth and fifth allowed transitions of (Ia) respectively. The fourth and fifth allowed transitions of (Ia), however, are to excited states formed by the combination of local excited configurations of both component parts of (Ia). The leading four configurations of each of these excited states is the same, although their coefficients differ. Further, the leading configuration of each of these states is the lowest energy excited configuration of cis-butadiene; however, in the excited state to which the fourth transition of (Ia) occurs it

contributes about 41%. The remaining contributing configurations of these excited states are local excited configurations of napthacene, and particularly the same three configurations. One may thus interpret the fifth and sixth transitions of (Ia) as being formed from the interaction of the fourth allowed transition of napthacene and the first allowed transition of cis-butadiene. From this, one may predict that the fifth and sixth transitions of (I) should be quite similar to each other and should both perhaps appear to have characteristics similar to the fourth allowed transition of napthacene, although considerably altered by the characteristics of the first transition of cis-butadiene.

The discussion of benz(a)napthacene (I) transitions will be limited to the above six primarily because transitions higher than these in energy are not readily observable by the conventional techniques of solution molecular spectroscopy. Also, as mentioned earlier, the calculated transitions become progressively less accurate with increasing energy because of the exclusion of higher energy excited configurations in the limited configuration interaction procedure employed in these calculations.

3. Benzo(b)chrysene (figure 2.3)

A comparison of the calculated electronic transitions of benzo(b)chrysene (II) and its possible composite system models is presented graphically in Figures 2.8a through 2.8g and numerically in Tables 2.2a through 2.2g. These show that the non-bonded composite

system denoted by (IIb) is the best approximation to the benzo(b)-chrysene molecule. The component parts of this composite system are a chrysene molecule and a cis-butadiene molecule. In the following discussion the complete molecule or single component system will be denoted by (II) while the non-bonded composite system will be denoted by (IIb).

The first allowed transition of (II) is correlated to the first allowed transition of (IIb). This transition of (IIb) is found to be a local transition of the chrysene moiety of the composite system. Consequently one may predict that the first allowed transition of (II) will resemble the first allowed transition of chrysene quite closely. Note that this transition is red shifted about 0.47 ev in passing from the non-bonded composite system to the complete molecule, although the oscillator strength does not change materially.

The second allowed transition of (II) corresponds to one of the degenerate and forbidden transitions to the fourth and fifth electron-transfer states of (IIb). Consequently, no predictions or interpretations are made concerning this transition.

The third allowed transition of (II), which has the greatest oscillator strength of all the transitions of (II), corresponds to the third allowed transition of (IIb). The third transition of (IIb) is found to be the second, and strongest, allowed local transition of the chrysene part of (IIb). From this, one may predict that the third allowed transition of (II) should be quite similar to the second allowed, and most intense,transition of chrysene. This transition

is red shifted about 0.30 ev when passing from the non-bonded composite system (IIb) to the complete molecule (II) and the oscillator strength increases about 0.65.

The fourth allowed transition of (II) is correlated to the very weakly allowed fourth transition of (IIb). This fourth transition of (IIb) is predominantly a local transition of the chrysene moiety. Thus the fourth allowed transition of (II) may be predicted to resemble a weak third transition of chrysene. As a matter of fact, the calculated oscillator strength of this transition of chrysene when treated separately and not as part of the composite system would probably be zero. This transition is blue shifted about 0.08 ev when going from the non-bonded composite system (IIb) to the complete molecule (II) and the oscillator strength is approximately doubled.

The fifth allowed transition of (II) arises from a pair of degenerate and forbidden transitions to the tenth and eleventh electron-transfer states of (IIb). As before, no prediction is given for this type transition.

The sixth allowed transition of (II) corresponds to the fifth allowed transition of (IIb). This transition is blue shifted about 0.24 ev in going from the non-bonded composite system (IIb) to the complete molecule (II) and the oscillator strength decreases substantially. The fifth transition of (IIb) is to an excited state to which the lowest energy excited configuration of cis-butadiene contributes about 12% weight while the remaining 88% weight is contributed by chrysene

excited configurations. From this one may predict that the sixth transition of (II) should appear as the slightly perturbed or modified fourth allowed transition of chrysene.

The seventh, eighth, and ninth allowed transitions of (II) are very difficult to correlate to transition of (IIb). This difficulty is caused by the lack of a reasonably systematic change in these transitions as one goes from the composite system with no bonding between the component parts, to the composite system with weak bonding and finally to the complete molecule. This may be caused by a breakdown of this particular composite system model for the higher energy transitions or perhaps is due to the decreased accuracy of the higher-energy transitions caused by the exclusion of excited configurations above 8.00 ev in energy.

The following interpretations are given for the seventh, eighth, and ninth transitions of (II), although not with the same confidence as those for the first six transitions. The seventh allowed transition of (II) is correlated to the third allowed transition of (IIb). This interpretation is made essentially by a process of elimination. If this interpretation is correct, the transition is blue shifted approximately 0.75 ev and the oscillator strength decreased by almost a factor of 30 in going from the non-bonded composite system (IIb) to the complete molecule (II). Also, the third allowed transition of (IIb) is to a state to which the low energy excited configuration of cis-butadiene contributes about 55%, the other contributing configu-

rations being these of local excitations in the chrysene moiety. Thus, one may predict the seventh allowed transition of (II) to appear as an extremely altered first transition of cis-butadiene or perhaps be unrecognizable in terms of the transitions of other molecules.

The best correlation of the eighth and ninth allowed transitions of (II) appears to be, respectively, to the extremely weak sixth and eighth allowed transitions of (IIb). Both the sixth and eighth transitions of (IIb) are local transitions of the chrysene part; however, these chrysene transitions are essentially forbidden. Since these two chrysene transitions are most likely unobservable, the best one may do is predict that the eighth and ninth transitions of (II) should not appear similar to any observed chrysene transition, although these transitions do arise from the chrysene moiety.

4. Dibenzo(b,g)phenanthrene (Figure 2.4)

From the examination of the calculated electronic transitions of dibenzo(b,g)phenanthrene (III) and its possible composite system approximations, shown graphically in Figures 2.9a through 2.9g and numerically in Tables 2.3a through 2.3g, it is concluded that the composite system denoted by (IIIb) is the best model for this molecule. This composite system consists of a benzo(c)phenanthrene molecule and a cis-butadiene molecule. In the following discussion, the non-bonded composite system model will be denoted by (IIIb) and the complete dibenzo(b,g)phenanthrene molecule will be denoted by (III).

The lowest energy transition of (III), which is forbidden, is correlated to the lowest energy transition of (IIIb), which is also forbidden. This is an exception to the general rule of only discussing the allowed transitions; however, this transition is experimentally observable as will be seen later. The lowest energy forbidden transition of (IIIb) corresponds to the lowest energy forbidden transition of benzo(c)phenanthrene, which is also experimentally observable. Thus, one may predict that the lowest energy observable transition of (III) should appear similar to the lowest energy observable transition of benzo(c)phenanthrene. Both of these transitions, being forbidden as electric dipole transitions, are extremely weak. This transition is red shifted approximately 0.20 ev in going from (IIIb) to (III).

The first allowed transition of (III) corresponds to the first allowed transition of (IIIb). The first allowed transition of (IIIb) corresponds to the first allowed local transition of the benzo(c)-phenanthrene moiety and, consequently, one may predict that the first allowed transition of (III) should be similar to the first allowed transition of benzo(c)phenanthrene. This transition is red shifted about 0.60 ev in passing from (IIIb) to (III) and the oscillator strength increases by about a factor of 8.

The second allowed transition of (III), which has the largest oscillator strength of all the transitions of (III), is correlated with the second allowed transition and most intense transition of (IIIb). This transition of (IIIb), in turn corresponds to the second and most intense transition of the benzo(c)phenanthrene part of the composite

system. From this, one may predict that the second allowed transition of (III) should have the characteristics of the second allowed transition of benzo(c)phenanthrene. This transition is red shifted about 0.34 ev in passing from (IIIb) to (III), but the oscillator strength is changed by very little.

The third allowed transition of (III) is derived from two forbidden and degenerate transitions to the fifth and sixth electron-transfer states of (IIIb). No prediction is given concerning the appearance of this transition.

The fourth allowed transition of (III) and the third allowed transition of (IIIb) correspond. The third allowed transition of (IIIb) is to an excited state to which the lowest energy excited configuration of cis-butadiene contributes about 42% and the remaining weight is contributed by the excited configurations of the benzo(c)-phenanthrene moiety. From this, one would probably have to predict that the fourth allowed transition of (III) should appear to be a highly modified third allowed transition of benzo(c)phenanthrene. This transition is very slightly blue shifted in going from (IIIb) to (III) and the oscillator strength is increased about 20%.

The fifth allowed transition of (III) is interpreted as another transition arising from a pair of degenerate, forbidden electron-transfer transitions in (IIIb). In this case, the transitions are to the ninth and tenth electron-transfer states of (IIIb). No prediction is made concerning the characteristic of the fifth allowed transition of (III).

The sixth allowed transition of (III) is correlated to the fifth allowed transition of (IIIb). This particular transition of (IIIb) arises from the essentially unaltered fourth transition of benzo(c)-phenanthrene. This transition is blue shifted about 0.38 ev and the oscillator strength increases about seven times in passing from (IIIb) to (III). One may thus predict that the sixth allowed transition of (III) can be correlated to the fourth allowed transition of benzo(c)-phenanthrene; however, such a correlation may be rather tenuous if the actual differenct in oscillator strength is similar to the calculated difference.

No interpretation will be given for the allowed transition of (III) higher in energy than the sixth. This approach is taken because, as in the case of benz(a)napthacene, the questionable accuracy of the calculated transitions and the small possibility of readily observing these transitions do not appear to justify an interpretation.

5. Dibenz(a,c)anthracene (Figure 2.5)

The comparison of the calculated electronic transitions for dibenz(a,c)anthracene (IV) and its possible composite systems, presented graphically in Figures 2.10a through 2.10e and numerically in Tables 2.4a through 2.4e, shows that the composite system denoted by (IVb) is the best approximation to the complete molecule (IV).

This composite system consists of a triphenylene molecule and a cis-butadiene molecule. That this composite system is the best model of the complete molecule is rather obvious from the fact that the

absorption spectra of the composite system with weak bonding between the component parts duplicates the absorption spectra of the complete molecule extremely well. In the following discussion,the dibenz(a,c)-anthracene molecule considered as a single component system will be denoted by (IV) and the non-bonded composite system model will be denoted by (IVb).

Once again, an exception will be made to the general rule of only discussing the origins of the allowed transitions. The lowest energy transition of (IV) which, although it is forbidden, can be experimentally observed corresponds to the forbidden lowest energy transition of (IVb). In (IVb), this transition is found to be a local transition corresponding to the lowest energy forbidden, but experimentally observable, transition of triphenylene. Thus, one may predict that the lowest energy transition of (IV) should be very similar to the lowest energy transition of triphenylene. This transition is red shifted about 0.23 ev in passing from the composite system to the complete molecule.

The first allowed transition of (IV) is correlated to the first allowed transition of (IVb). This transition is red shifted by approximately 0.27 ev in going from (IVb) to (IV) and the oscillator strength increased from 0.002 to 0.313. The first allowed transition of (IVb) corresponds to a second formally forbidden transition of the triphenylene component which, because of configurational mixing, has a finite oscillator strength in the non-bonded composite system.

This formally forbidden triphenylene transition is experimentally observable, consequently, one may predict that the first allowed transition of (IV) should have the characteristics of the second extremely weak observable transition of triphenylene.

The second allowed transition of (IV) is interpreted as arising from the degenerate, forbidden transitions to the sixth and seventh electron transfer states of (IVb). No prediction will be given regarding the appearance of this transition.

The third allowed transition of (IV) is correlated to the second allowed transition of (IVb). The second transition of (IVb) is to a state to which the lowest energy local excited configuration of cis-butadiene contributes about 52% weight. The remaining weight is contributed by local excited configurations which form an excited state for the second allowed transition of an isolated triphenylene molecule. From this, one concludes that the third allowed transition of (IV) should appear either as an extremely modified first allowed transition of cis-butadiene or be unrecognizable in terms of other molecular transitions. It is also doubtful if this transition will be observable since the oscillator strength decreases from 0.178 to 0.022 in going from (IVb) to (IV). The transition is red shifted about 0.28 ev in (IV) relative to (IVb).

The fourth allowed transition of (IV) is also interpreted as arising from electron-transfer states in (IVb). In this case it is the transitions to the eighth and ninth electron-transfer states of (IVb).

The fifth allowed transition of (IV) corresponds to the third allowed transition of (IVb). The third allowed transition of (IVb) in turn is the first allowed local transition of the triphenylene moiety. Consequently, the fifth allowed transition of (IV) should have characteristics quite similar to that of the first allowed transition of triphenylene. However, this transition is blue shifted about 0.66 ev in passing from the non-bonded composite system (IVb) to the complete molecule (IV) and the oscillator strength decreased by a factor of five.

The sixth allowed transition of (IV) is correlated with the fourth allowed transition of (IVb). This transition of (IVb) is to an excited state formed from the same combination of local excited cis-butadiene and triphenylene configurations which form the state to which the third allowed transition of (IVb) occurs. However, in this case the local excited configuration of cis-butadiene only contributes about 39% to the state. From this, one would conclude that the sixth allowed transition of (IV) should appear to be a highly modified second allowed transition of triphenylene. This transition is blue shifted by approximately 0.39 ev in passing from the non-bonded composite system (IVb) to the complete molecule (IV) and the oscillator strength decreased by about a factor of six.

If should be noted here that due to the symmetry of the triphenylene molecule, the first and second allowed transitions of the isolated molecule are normally degenerate. However, upon forming a non-bonded composite system with cis-butadiene, the interaction through the electron repulsion type terms alone is apparently sufficient to shift one of

these intense triphenylene transitions, assumed to be the second, to a higher energy where it becomes the fourth allowed transition of (IVb). The other intense transition of triphenylene, assumed to be the first, remains relatively unchanged and is the third allowed transition of (IVb). Finally the second allowed transition of (IVb) is the highly altered first transition of cis-butadiene which is red shifted by the interaction with the triphenylene moiety in the non-bonded composite system.

The highest energy transitions of (IV) which will be discussed are the seventh and eighth allowed transitions which are correlated to the fifth and sixth allowed transition of (IVb) respectively. These two transitions are considered together because the fifth and sixth allowed transitions of (IVb) also correspond to a pair of local transitions of triphenylene which would normally be degenerate in the isolated molecule due to molecular symmetry. These two degenerate transitions are the third and fourth allowed transitions of triphenylene. From this, one may predict that the seventh and eighth allowed transitions of (IV) should appear similar to the degenerate third and fourth transitions of triphenylene. The seventh transition of (IV) is blue shifted by about 0.22 ev and oscillator strength increased about 70% in passing from (IVb) to (IV) while the eighth transition is blue shifted about 0.55 ev and oscillator strength increased about 74%.

6. 3,4-Benzopyrene (Figure 2.6)

From the comparison of the calculated electronic transitions of 3,4-benzopyrene (V) and its possible composite system models, shown in Figures 2.11a through 2.11g and Tables 2.5a through 2.5g, it is evident that the composite system denoted by (Va) is the best approximation to the 3,4-benzopyrene molecule. This composite system model consists of a pyrene molecule and a cis-butadiene molecule. The 3,4-benzopyrene molecule presents a slightly different situation since it is what is termed a peri-condensed aromatic hydrocarbon. That is, not all of the carbon atoms are located on the outer perimeter of the molecule as is the case for the cata-condensed aromatic hydrocarbons. All the previously considered molecules are examples of cata-condensed hydrocarbons. In the following discussion the complete 3,4-benzopyrene molecule, or single component system, will be noted by (V) and the non-bonded composite system model by (Va).

The first strong allowed transition of (V) corresponds quite well to the strong allowed first transition of (Va). The oscillator strength of this transition remains almost unchanged in going from the non-bonded composite system (Va) to the complete molecule (V) and it is red shifted approximately 0.35 ev. The first allowed transition of (Va) is the first allowed local transition of the pyrene moiety and from this one may predict that the first allowed transition of (V) should be quite similar to the first allowed transition of pyrene.

The next transition of (V) to be discussed is the lowest energy forbidden transition. This exception to the rule of discussing only

the theoretically allowed transitions is made for the same reasons as in the previously discussed molecules; that is, the transition is, generally, experimentally observable as a very weak transition. This transition is correlated to the lowest energy forbidden transition of (Va) which in turn arises from the lowest energy forbidden local transition of the pyrene moiety. From this, one may predict that the lowest energy forbidden transition of 3,4-benzopyrene should have characteristics similar to the lowest energy forbidden transition of pyrene. This transition is red shifted about 0.25 ev in passing from (Va) to (V). Note also that the relative positions of the first allowed transition and the lowest energy forbidden transition are changed in passing from the composite system (Va) to the complete molecule (V).

The second allowed transition of (V), which has an oscillator strength of only 0.048 and may not be experimentally observable, is interpreted as arising from the transitions to the third and fourth electron-transfer states of (Va). Since these transitions are forbidden and degenerate in (Va) no prediction is made concerning the characteristics of the second allowed transition of (V).

The third allowed transition of (V) corresponds to the second allowed transition of (Va). The second transition of (Va) is to an excited state to which the lowest energy local excited configuration of the cis-butadiene component contributes about 45% while the remaining configurations are local excited configurations of the pyrene moiety. These local excited configurations of pyrene are the ones which would

normally form the excited state to which the second allowed transition of pyrene would occur. Consequently, the third allowed transition of (V) may be interpreted as having the characteristics or appearance of a highly modified second allowed transition of pyrene. This transition is red shifted approximately 0.17 ev in going from (Va) to (V) and the oscillator strength increases by a factor of almost seven.

The fourth allowed transition of (V) is also interpreted as being derived from forbidden transitions to electron-transfer states in (Va). In this case, the two degenerate electron-transfer states of (Va) are the eighth and ninth excited states.

The fifth allowed transition of (V) is correlated to the third allowed transition of (Va). This transition of (Va) is to an excited state composed of the same combination of local excited cis-butadiene configurations and local excited pyrene configurations as the excited state to which the second transition of (Va) occurs. That is to say, when the cis-butadiene and pyrene molecules are combined to form a non-bonding composite system (Va), the excited state of pyrene to which the second allowed transition of pyrene occurs and the excited state to which the first allowed transition of cis-butadiene occurs interact to form a pair of states. The second and third transitions of (Va) occur to these states. In the case of the third transition of (Va), which becomes the fifth transition of (V), the cis-butadiene configuration contributes about 42%. Consequently, one may predict that the fifth allowed transition of (V) should appear as a highly

modified second allowed pyrene transition, as was the case for the third allowed transition of (V). This transition is blue shifted approximately 0.12 ev is passing from (Va) to (V) and the oscillator strength remains relatively unchanged.

The sixth allowed transition of (V), which is very weak, corresponds to the fourth allowed transition of (Va), which is also very weak. This fourth transition of (Va) is a weak local transition of the pyrene component corresponding to a,theoretically, at least, very weak or perhaps forbidden transition of the pyrene molecule. Thus, one may predict that the sixth transition of (V) should resemble a very weak third transition of pyrene. The fourth transition of the non-bonded composite system (Va) remains relatively unchanged in both energy and oscillator strength in passing to the complete molecule (V).

The last allowed transition of 3,4-benzopyrene (V) to be considered here is the seventh. This transition corresponds to the fifth allowed transition of the non-bonded composite system (Va). The fifth transition of (Va) in turn is a very strong local transition corresponding to the fourth allowed transition of pyrene. From this, one may predict that the seventh transition of (V) should have the characteristics of the fourth allowed transition of pyrene, although the oscillator strength decreases from 1.603 to 0.334 in going from (Va) to (V). Also, this transition is blue shifted slightly by about 0.20 ev in going from the non-bonded composite system (Va) to the complete molecule (V).

G. Discussion

Unfortunately, no relationship could be found between the values of ΔE_i for the various composite system models (Table 2.11) and the composite system whose electronic transitions were the best approximation to those of the subject molecule. Evidently the quantity ΔE_i, defined in equation (2.14), was too naive an approach to the problem of determining which composite system approximates the subject molecule best. There are three reasons why the use of this quantity probably fails as a means of comparison. The first reason was already mentioned in the previous discussion of ΔE_i. This concerned the fact the ΔE_i does not take into account the symmetry of the molecular orbitals when comparing the composite systems to the subject molecule. Since the oscillator strength or intensity of the various transitions is a function of the symmetry of the molecular orbitals, ΔE_i in no way compares the oscillator strengths of transitions in the composite systems and the subject molecule. Second, ΔE_i is a measurement of the degree to which equivalent energy levels of the composite system and the complete molecule correspond. However, the energy of the transition between two molecular orbitals is actually proportioned to the difference between the two orbital energy levels (see equation 2.15). Consequently, it is quite possible that the orbital energy levels of the composite system may differ considerably in magnitude when compared to the corresponding energy levels of the complete molecule and yet the difference of the energy levels in the complete molecule could be

quite close to the difference of the energy levels in the composite system. Third, the quantity ΔE_i is a measurement of the correspondence of <u>all</u> the equivalent energy levels. However, the electronic transitions of the complete molecule which are being approximated in this investigation are the lower energy transitions formed predominantly by excitations from the higher energy filled molecular orbitals to the lower energy unfilled molecular orbitals. Thus, a measure of the correspondence of a certain limited number of orbital energy levels may be superior to a measure of the correspondence of all the levels. However, it would be rather difficult to determine in a nonarbitrary manner the weight with which each energy level should enter the comparison.

The $\underline{\Delta F^i}$ matrices, discussed previously in conjunction with equation (2.21), also failed to provide a quantity which could be correlated with the composite system which was the best approximation to the subject molecule. The $\underline{\Delta F^i}$ matrices were calculated for benz(a)napthacene, benzo(b)chrysene, and dibenzo(b,g)phenanthrene, however, only the matrices for benz(a)napthacene are given in Table 2.12a through 2.12f since this is sufficient for illustrative purposes. The relative values for the norms of these matrices are determined completely by the values of the $\underline{\Delta F^i}$ matrix elements between two pairs of carbon centers. These pairs of carbon centers are the ones between which the bond is conceptually broken, or weakened, in forming the composite system from the complex molecule. The relative values of these particular matrix elements for the various composite systems are, in turn, determined by the values of the bond order, P_{ij}, of the bonds which are

broken to form the composite system. Unfortunately, as reasonable as the correlation of bond orders and the composite systems may seem, since the bond order is indicative of bond length and pi-bond character, no correlation can be found between the bond order values of the bonds broken to form a particular composite system and the suitability of that composite system as an approximation to the complete molecule.

In addition to the above approaches, attempts were made to divide the LCAO molecular orbitals of the subject pentacyclic aromatic hydrocarbons into the LCAO molecular orbitals of the component parts of a composite system. This was done by comparing the atomic orbital coefficients of the molecular orbitals for the complete molecule to the atomic orbital coefficients of the molecular orbitals of the component parts. This was analogous to the procedure reported by Heilbronner, et al.[59] and which was described earlier. This procedure proved to have little merit, since in the polycyclic aromatic hydrocarbons, there were some molecular orbitals which could not be resolved at all and others which could be resolved in terms of more than one composite system approximation. In other words, the form of the molecular orbitals of the pentacyclic aromatic hydrocarbons do not seem to indicate the composite system which may be the best approximation to the molecule.

Two general observations may be made concerning the composite systems which apparently are the best approximations to the subject molecules. First, the component parts of the best composite system approximations

in all five cases studied are a tetracyclic aromatic hydrocarbon molecule and a cis-butadiene molecule. Dibenz(a,c)anthracene should, of course, be excluded from this observation since those were the only type composite systems considered as possible approximations for this molecule. However, composite systems consisting of an anthracene molecule and a styrene molecule were considered as approximations to benz(a)napthacene, benzo(b)chrysene, and dibenzo(b,g)phenanthrene and composite systems consisting of a tetracyclic aromatic hydrocarbon molecule and an ethylene molecule were considered as approximations to 3,4-benzopyrene. The composite systems consisting of component parts other than a tetracyclic aromatic hydrocarbon molecule and a cis-butadiene molecule in no case produced a set of electronic transitions which were the best approximation to those of the complete molecule.

The second observation is that in every case, the composite system which is the best approximation to the complete molecule is the one which contains the tetracyclic aromatic hydrocarbon molecule of highest symmetry. For example, the composite system containing napthacene, which belongs to the symmetry point group D_{2h}, is a better approximation to benz(a)napthacene than the composite system containing benz(a)-anthracene, which belongs to the symmetry poing group C_s. Thus, one is inclined to believe that the most symmetrical tetracyclic sub-structure may be the dominant factor in determining the spectroscopic characteristics of the pentacyclic molecules.

H. Comparison with Experiment

1. General

The only interpretations available of the experimental pentacyclic aromatic hydrocarbon transitions in terms of the transitions of tetracyclic moieties contained within the structure of the pentacyclic were made by Becker.[86] In the following discussions, the analyses of the various experimentally observed transitions will be briefly given and the analyses compared to the predictions made for the transitions in the section entitled Analysis of Results. The observed and calculated transitions for the five subject molecules are correlated in Tables 2.13 through 2.17. In these tables the energy and extinction coefficient of the 0-0 transitions of the various observed bands will be given along with the theoretically calculated value of the transition energy and oscillator strength. The experimental transition energies and extinction coefficients were determined from the room temperature absorption spectra of the hydrocarbon dissolved in p-dioxane. The analysis of the experimental tetracyclic aromatic hydrocarbon spectra was done by Becker, Singh, and Jackson.[87]

2. Benz(a)napthacene

The experimental transition energies and the corresponding calculated values for benz(a)napthacene are given in Table 2.13. The correspondence of the calculated and observed values are relatively good but certainly not excellent.

TABLE 2.13. EXPERIMENTALLY OBSERVED 0-0 TRANSITIONS OF BENZ(a)NAPTHACENE AND CORRESPONDING CALCULATED TRANSITIONS

Transition Number	Observed Transition Energy (ev)	Extinction Coefficient of Observed Transition (l/mole·cm)	Calculated Transition Energy (ev)	Calculated Oscillator Strength
I	2.75	36,095	2.98	0.371
II	3.92	61,657	3.84	0.892
III	4.09	117,057	4.21	1.815
IV	4.81	61,657	4.98	0.634
V	5.55	36,095	5.25	0.327

TABLE 2.14. EXPERIMENTALLY OBSERVED 0-0 TRANSITIONS OF BENZO(b)CHRYSENE AND CORRESPONDING CALCULATED TRANSITIONS

Transition Number	Observed Transition Energy (ev)[a]	Extinction Coefficient of Observed Transition (l/mole·cm)	Calculated Transition Energy (ev)	Calculated Oscillator Strength
I	3.16	3,599	3.31	0.565
II	4.08	45,136	4.04	0.560
III	4.26	76,967	4.48	2.343
IV	4.65 (?)	27,237	4.88	0.188
V	4.98	29,961	5.18	0.393

[a] (?) signifies uncertainty in assignment of this transition as a separate transition

TABLE 2.15. EXPERIMENTALLY OBSERVED 0-0 TRANSITIONS OF DIBENZO(b,g)-PHENANTHRENE AND CORRESPONDING CALCULATED TRANSITIONS

Transition Number	Observed Transition Energy (ev)	Extinction Coefficient of Observed Transition (l/mole·cm)	Calculated Transition Energy (ev)	Calculated Oscillator Strength
I	3.09	2,716	3.34	0.000
II	3.16	5,028	3.38	0.228
III	3.84	7,989	---[a]	---
IV	4.01	99,812	4.04	1.606
V	4.51	22,180	4.24	0.177
VI	4.66	16,635	4.71	0.505
VII	4.98	53,571	5.09	0.144
VIII	5.47	79,793	5.39	1.052

[a] Observed transition apparently does not correspond to any allowed calculated transition

TABLE 2.16. EXPERIMENTALLY OBSERVED 0-0 TRANSITIONS OF DIBENZ(a,c)ANTHRACENE AND CORRESPONDING CALCULATED TRANSITIONS

Transition Number	Observed Transition Energy (ev)	Extinction Coefficient of Observed Transition (l/mole·sec)	Calculated Transition Energy (ev)	Calculated Oscillator Strength
I	3.29	697	3.53	0.000
II	3.52	3,465	3.74	0.168
III	4.31	146,315	4.37	2.285
IV	4.98	52,255	4.84	1.263
V	5.68	40,264	5.35	0.364
VI	6.00	---	5.92	0.268

TABLE 2.17. EXPERIMENTALLY OBSERVED 0-0 TRANSITIONS OF 3,4-BENZOPYRENE AND CORRESPONDING CALCULATED TRANSITIONS

Transition Number	Observed Transition Energy (ev)	Extinction Coefficient of Observed Transition (l/mole·sec)	Calculated Transition Energy (ev)	Calculated Oscillator Strength
I	3.07	4,029	3.31	0.000
II	3.22	27,637	3.12	0.997
III	4.18	57,871	4.42	0.871
IV	4.67	43,889	4.72	0.662
V	5.47	24,352	5.14	1.055
VI	5.93	---	5.78	0.334

The most important point, of course, is whether or not the composite system chosen as the best approximation to the complete molecule on the basis of the theoretical investigation agrees with the composite system implied by the interpretation of the experimental transitions. Becker[86] has interpreted the transitions of benz(a)napthacene as being napthacene-like transitions which implies that the composite system model of this molecule would be a napthacene molecule and a cis-butadiene molecule. These are the component parts of the composite system model chosen in the theoretical study as the best approximation to benz(a)napthacene. The individual transitions will now be discussed.

Transition I: Becker[86] has interpreted this transition as being equivalent to the first observed transition of napthacene. This benz(a)napthacene transition is blue shifted approximately 0.124 ev relative to its position in napthacene. Transition I has two vibrational sequences with vibrational spacings of 260 cm^{-1} and 1430 cm^{-1}. These correspond to two vibrational sequences of the equivalent transition in napthacene, however, two additional vibrational sequences exist in the napthacene transition. Transition I corresponds to the first allowed calculated transition of benz(a)napthacene. On the basis of the theoretical analysis, this transition was predicted to be similar to the first transition of napthacene and blue shifted about 0.15 ev relative to its position in the composite system (Ia). The theoretical prediction and experimental compare quite well in this case.

Transition II: In the experimental interpretation, this transition is correlated to the second observed transition of napthacene. The benz(a)napthacene transition is red shifted about 0.285 ev and its intensity increased considerably relative to the second transition of napthacene. Transition II corresponds to the second allowed calculated transition of benz(a)napthacene which was interpreted as arising from an electron-transfer transition at 3.761 ev in the non-bonded composite system (Ia). Consequently, no predictions were made concerning the appearance of Transition II.

Transition III: Becker[86] interprets this benz(a)napthacene transition as being equivalent to the third observed transition of napthacene. The vibrational sequence in Transition III has a spacing of 1345 cm^{-1} while the third transition of napthacene has a vibrational spacing of 1300 cm^{-1}. Also the benz(a)napthacene transition is red shifted approximately 0.397 ev relative to the napthacene transition. Transition III corresponds to the third allowed theoretical transition. In the theoretical analysis, this transition was correlated to a very weak second transition of the napthacene moiety of the composite system (Ia). Thus, the experimentally observed third transition of benz(a)napthacene was predicted to have the characteristics of the weak second transition of napthacene, although the intensity of this transition would be increased by a very large factor in going from napthacene to benz(a)-napthacene. Becker's analysis[86] of Transition III, however, does not agree with this prediction.

Transition IV: In the experimental interpretation this transition is correlated to the fourth observed transition of napthacene. Two vibrational sequences are noted in Transition IV with vibrational spacings of 1098 cm^{-1} and 1598 cm^{-1}. The corresponding transition of napthacene has a single observed vibrational sequence with a spacing of 900 cm^{-1}. Becker[86] notes that Transition IV of benz(a)-napthacene is red shifted nearly 0.620 ev relative to the fourth transition of napthacene. Transition IV has been correlated to the fifth allowed theoretical transition of benz(a)napthacene. (No observed transition could be correlated to the fourth allowed theoretical transition.) This calculated transition was in turn correlated to a composite system (Ia) transition essentially formed by the mixing of the fourth allowed napthacene transition and the first allowed cis-butadiene transition. On the basis of the relative weights with which the local excited configurations of each component part contribute to the excited state, it was predicted that the fifth allowed transition of benz(a)napthacene should appear as a highly modified fourth transition of napthacene. This seems to agree fairly well with the interpretation given for Transition IV. The shift in the calculated transition in going from the composite system (Ia) to the complete molecule does not correspond to the shift in the observed transtión; however, this discrepancy may be due to the large error in the calculated values of Transition IV.

Transition V: In the interpretation of the experimentally observed transitions, Transition V is correlated to the fifth observed transition of napthacene. The vibrational spacing of the one observed vibrational sequence of Transition V is about 1596 cm^{-1}. No vibrational structure is observed for the fifth transition of napthacene. Also, Transition V is red shifted approximately 0.248 ev relative to the fifth transition of napthacene. Transition V of benz(a)napthacene corresponds to the sixth allowed calculated transition. In the theoretical analysis, this transition was correlated to another composite system transition arising from the interaction of the fourth allowed transition of napthacene and the first allowed transition of cis-butadiene. Again, based on the relative weights with which the local excited configurations contributed to this excited state, it was predicted that the sixth allowed transition of benz(a)napthacene would appear as a highly modified fourth transition of napthacene. This does not agree with Becker's interpretation of Transition V.

In summary, the theoretical analysis of benz(a)napthacene has indicated that the composite system composed of napthacene and cis-butadiene is the best approximation to benz(a)napthacene. On this important point, the theoretical treatment agrees with the interpretation of the observed transitions. However, of the six experimentally observed transitions discussed above, Becker's[86] interpretations of the transitions in terms of particular napthacene transitions have agreed in only two cases with the predictions made in the theoretical analysis.

3. Benzo(b)chrysene

The experimental transition energies and corresponding theoretical values for benzo(b)chrysene are listed in Table 2.14. The overall correspondence of the calculated and experimental transition energies of benzo(b)chrysene is quite good. With the exception of Transition II, all of the experimentally observed transition energies are less than the corresponding calculated transition energies by a fairly constant amount.

In his examination of the five experimentally observed transitions of benzo(b)chrysene, Becker[86] has interpreted the transitions in terms of benz(a)anthracene transitions thus implying a composite system composed of a benz(a)anthracene molecule and a cis-butadiene molecule. However, it was found in the theoretical analysis that the composite system model whose electronic transitions most closely approximated those of benzo(b)chrysene consisted of a chrysene molecule and a cis-butadiene molecule. The composite system composed of a benz(a)anthracene molecule and a cis-butadiene molecule was also examined in the theoretical investigation, but it was not considered to be the best approximation to the benzo(b)chrysene molecule. Thus, in this case the theoretical interpretation and the interpretation of the experimentally observed transitions are in complete disagreement. Becker's[86] interpretation of the individual experimentally observed transitions of benzo(b)chrysene will be presented, although in all instances they differ from the results of the theoretical analysis.

It should be noted that Becker[86] did find some similarities between certain benzo(b)chrysene transitions and those of chrysene; however, overall he described the benzo(b)chrysene absorption spectra as having the general appearance of a red shifted benz(a)anthracene absorption spectra with a missing first transition.

Transition I: Becker[86] has interpreted this observed transition as being equivalent to the second observed transition of benz(a)-anthracene. The general structure of Transition I resembles that of the second benz(a)anthracene transition and both transitions are Franck-Condon forbidden. This benzo(b)chrysene transition is red shifted 0.029 ev relative to the equivalent benz(a)anthracene transition. Transition I corresponds to the first allowed calculated transition of benzo(b)chrysene. The theoretical investigation indicated that this calculated benzo(b)chrysene transition arises from the first allowed transition of chrysene.

Transition II: This observed transition is interpreted as corresponding to the third observed transition of benz(a)anthracene. The vibrational sequence of Transition II is short as it is in the benz(a)anthracene transition. Transition II of benzo(b)chrysene is red shifted 0.061 ev relative to the equivalent benz(a)anthracene transition. The calculated benzo(b)chrysene transition to which Transition II corresponds is the second allowed transition. In the theoretical analysis, the second allowed transition was interpreted as arising from a degenerate forbidden electron-transfer transition in the composite system model composed of a chrysene molecule and a cis-butadiene molecule.

Transition III: This transition is interpreted by Becker[86] as being equivalent to the fourth observed benz(a)anthracene transition. Transition III of benzo(b)chrysene has a long vibrational sequence as does the corresponding benz(a)anthracene transition; however, the 0-0 bond is not the most intense in Transition III as it is in the fourth observed benz(a) anthracene transition. Transition III is red shifted 0.050 ev relative to the equivalent benz(a)anthracene transition. Transition III corresponds to the third allowed theoretical transition of benzo(b)chrysene. On the basis of the theoretical analysis, the third allowed calculated transition of benzo(b)chrysene was interpreted as arising from the second allowed transition of chrysene.

Transition IV: The actual assignment of this benzo(b)chrysene transition is considered questionable by Becker.[86] Assuming that Transition IV does exist, it is considered to be equivalent to the fifth observed transition of benz(a)anthracene. This benzo(b)-chrysene transition is red shifted 0.191 ev relative to the corresponding benz(a)anthracene transition. Transition IV corresponds to the fourth allowed calculated transition of benzo(b)chrysene. The theoretical investigation indicated that this calculated transition was derived from an extremely weak, or perhaps forbidden, transition in chyrsene.

Transition V: Becker[86] has correlated this final observed benzo-(b)chrysene transition with the sixth observed transition of benz(a)-anthracene. Transition V is blue shifted 0.046 ev relative to the equivalent benz(a)anthracene molecule. The theoretical transition to which Transition V corresponds is the fifth allowed transition. In the theoretical analysis of benzo(b)chrysene, the fifth allowed transition was interpreted as arising from a forbidden degenerate electron-transfer transition in the chrysene and cis-butadiene composite system.

In summary, the comparison of the results of the theoretical analysis of the calculated transitions with the interpretation of the experimentally observed transitions of benzo(b)chrysene indicates disagreement in the most basic and important point. This point is the particular composite system model chosen as the best approximation to the complete benzo(b)chrysene molecule. From the theoretical analysis, a composite system composed of a chrysene molecule and a cis-butadiene molecule was found to be the best approximation to the benzo(b)chrysene molecule. However, in his examination of the experimentally observed transitions of benzo(b)chrysene, Becker[86] has interpreted the transitions as being similar to the observed transitions of benz-(a)anthracene and thus, implying that a composite system composed of a benz(a)anthracene molecule and a cis-butadiene molecule approximates benzo(b)chrysene best.

4. Dibenzo(b,g)phenanthrene

The experimental transition energies and corresponding theoretical values for dibenzo(b,g)phenanthrene are listed in Table 2.15. The overall correspondence of the theoretical and experimental transition energies of dibenzo(b,g)phenanthrene is somewhat better than the correspondence noted in the other molecules. However, Transition III, observed by Becker,[86] does not appear to correspond to any allowed calculated transition.

In his examination of the eight experimentally observed transitions of dibenzo(b,g)phenanthrene, Becker[86] has interpreted the transitions as benz(a)anthracene transitions thus, implying a composite system composed of a benz(a)anthracene molecule and a cis-butadiene molecule. However, it was found in the theoretical analysis that the composite system model whose electronic transitions most closely approximated those of dibenzo(b,g)phenanthrene consisted of a benzo(c)phenanthrene molecule and a cis-butadiene molecule. The composite system composed of a benz(a)anthracene molecule and a cis-butadiene molecule was also examined in the theoretical investigation, but it was not considered to be the best approximation to the dibenzo(b,g)phenanthrene molecule. Consequently, in this case the theoretical interpretation and the experimental interpretation are in complete disagreement. However, in the interest of completeness, Becker's interpretation of the experimentally observed transitions of dibenzo(b,g)phenanthrene will be discussed, although in all instances they differ from the interpretations given in the theoretical analysis.

Transition I: Becker[86] has correlated this transition with the first observed transition of benz (a)anthracene. Transition I of dibenzo(b,g)phenanthrene is extremely weak and there is some question as to the assignment of this transition. If Transition I is correctly assigned, it is red shifted 0.143 ev relative to the weak first observed transition of benz(a)anthracene. No vibrational structure is observed in Transition I. The calculated transition to which Transition I corresponds is the lowest energy forbidden transition. The theoretical investigation indicated that this calculated dibenzo-(b,g)phenanthrene transition arises from the lowest energy forbidden transition of benzo(c)phenanthrene.

Transition II: This observed transition is interpreted as being equivalent to the second observed transition of benz(a)anthracene. One vibrational sequence is observed in Transition II with a spacing of 1327 cm^{-1} compared to two vibrational sequences in the equivalent benz(a)anthracene with spacings of 1050 cm^{-1} and 1415 cm^{-1}. This dibenzo(b,g)phenanthracene transition is red shifted 0.298 ev relative to the second observed benz(a)anthracene transition. Transition II corresponds to the first allowed calculated transition. This calculated transition of dibenzo(b,g)phenanthrene was interpreted on the basis of the theoretical analysis as arising from the first allowed local transition of benzo(c)phenanthrene.

Transition III: Becker[86] has correlated this transition with the third observed transition of benz(a)anthracene. Transition III is red shifted 0.310 ev relative to the third observed transition of benz(a)anthracene. This dibenzo(b,g)phenanthrene transition generally looks like the third benz(a)anthracene transition and has a single observable vibrational sequence with a spacing of 530 cm^{-1} compared with a spacing of 425 cm^{-1} in the single observed vibrational sequence of the equivalent benz(a)anthracene transition. As noted earlier, Transition III cannot be associated with an allowed calculated transition. Consequently, there is no prediction of observable transition characteristics in the theoretical analysis which is applicable to Transition III. It is interesting to note that a similar situation exists for the third observed transition of benz(a)anthracene, that is, it apparently does not correspond to an allowed calculated transition of benz(a)anthracene.

Transition IV: This transition is correlated with the fourth observed transition of benz(a)anthracene. Becker[86] notes a similarity in the characteristics of these two transitions, for example, both are Franck-Condon allowed. Transition IV of dibenzo(b,g)phenanthrene has a single observed vibrational sequence with a spacing of 1318 cm^{-1} while the fourth transition of benz(a)anthracene has a single observed series with a spacing of 1350 cm^{-1}. Transition IV is red shifted 0.136 ev relative to the benz(a)anthracene transition. The calculated transition to which transition IV corresponds is the second allowed

calculated transition of dibenzo(b,g)phenanthrene. In the theoretical analysis, this calculated transition of dibenzo(b,g)phenanthrene was found to be derived from the second allowed transition of benz(c)-phenanthrene.

Transition V: Becker[86] has correlated this transition with the fifth observed transition of benz(a)anthracene. The assignment of this dibenzo(b,g)phenanthrene transition is questionable and it is insufficiently resolved to facilitate any further description. Transition V corresponds to the third allowed calculated transition of dibenzo(b,g)phenanthrene. In the theoretical analysis, this calculated transition was interpreted as being derived from a forbidden transition to an electron-transfer state in the composite system composed of a benzo(c)phenanthrene molecule and a cis-butadiene molecule.

Transition VI: This transition is interpreted as corresponding to the sixth observed transition of benz(a)anthracene. As in the case of Transition V, the assignment of Transition VI of dibenzo(b,g)-phenanthrene is also tentative and it is insufficiently resolved for further description. Transition VI corresponds to the fourth allowed calculated transition of dibenzo(b,g)phenanthrene. On the basis of the theoretical analysis, the observable transition corresponding to the fourth allowed calculated transition was predicted to have the characteristics of a highly modified third allowed transition of benzo-(c)phenanthrene.

Transition VII: This transition is interpreted by Becker[86] as being equivalent to the seventh observed transition of benz(a)anthracene and is red shifted 0.459 ev relative to the equivalent benz(a)anthracene transition. The calculated transition to which Transition VII of dibenzo(b,g)phenanthrene corresponds is the fifth allowed transition. In the theoretical analysis, this calculated dibenzo(b,g)phenanthrene transition was interpreted as arising from a degenerate forbidden transition to an electron-transfer state in the composite system composed of a benzo(c)phenanthrene molecule and a cis-butadiene molecule.

Transition VIII: This final observed transition is correlated with the eighth observed transition of benz(a)anthracene and is red shifted 0.149 ev relative to the benz(a)anthracene transition. Transition VIII corresponds to the sixth allowed theoretical transition of dibenzo(b,g)phenanthrene. In the theoretical interpretation, the sixth allowed transition of dibenzo(b,g)phenanthrene was correlated with the essentially unaltered fourth allowed local transition of benzo(c)phenanthrene.

To summarize the discussion of the dibenzo(b,g)phenanthrene molecule, it has been found that the theoretical interpretation of the calculated transitions in terms of a composite system approximation and the composite system interpretation of the experimentally observed transitions disagree in the most basic point. This fundamental difference is in the composite system model chosen as the best approximation to the complete dibenzo(b,g)phenanthrene molecule. On the basis of the

theoretical analysis, a composite system composed of a benzo(c)-phenanthrene molecule and a cis-butadiene molecule is determined to be the best model. However, in the experimental analysis, a composite system composed of a benz (a) anthracene molecule and a cis-butadiene molecule is determined to be the best approximation to a dibenzo(b,g)phenanthrene molecule. The benz(a)anthracene and cis-butadiene composite system was also considered in the theoretical investigation. This difference in the composite system approximations is undoubtedly the most fundamental and worst discrepancy between the proposed theoretical composite system analysis of pentacyclic aromatic hydrocarbon transition and the composite system interpretation of the actual experimentally observed transitions of these molecules.

5. Dibenz(a,c)anthracene

The experimental transition energies and corresponding theoretical values for dibenz(a,c)anthracene are listed in Table 2.16. The degree of correspondence of the calculated and observed transition energies is essentially the same as that noted for the other molecules. That is, the correspondence is not particularly good, but is about average for calculations of the level of sophistication used in this investigation.

In his examination of the six observed transitions of dibenz(a,c)-anthracene, Becker[86] has interpreted the first three transitions as triphenylene transitions, however, he has interpreted the other three

transitions as benz(a)anthracene transitions. The interpretation of the first three transitions as triphenylene transitions implies a composite system composed of a triphenylene molecule and a cis-butadiene molecule. These are the component parts of composite system (IVa) which was chosen as the best approximation to dibenz(a,c)anthracene in the theoretical investigation. However, in the theoretical investigation all the transitions of dibenz(a,c)anthracene were interpreted in terms of the triphenylene and cis-butadiene composite system and not just some as has been done by Becker[86] in the analysis of the observed transitions. The composite system composed of a benz(a)-anthracene molecule and a cis-butadiene molecule was also examined in the theoretical investigation but it was not considered to be the best approximation to the dibenz(a,c)anthracene molecule. Consequently, on this basic point, that is, which composite system is the best approximation to the dibenz(a,c)anthracene molecule there is only partial agreement between the theoretical and experimental analyses. The individual observed transitions of dibenz(a,c)anthracene will now be discussed.

Transition I: This transition is correlated with the first observed triphenylene transition by Becker.[86] Transition I is red shifted 0.341 ev relative to the triphenylene transition. Only one vibrational sequence with spacing of 760 cm^{-1} is observed in the dibenz(a,c)anthracene transition while three vibrational sequences with spacings of 525 cm^{-1}, 650 cm^{-1}, and 1375 cm^{-1} are

observed in the equivalent triphenylene transition. Also the intensity of the dibenz(a,c)anthracene transition is somewhat stronger. Becker[86] does note a similarity in general appearance between the triphenylene and dibenz(a,c)anthracene transitions. The calculated transition to which Transition I corresponds is the lowest energy forbidden transition. The theoretical investigation indicated that this transition corresponded to the lowest energy forbidden transition of triphenylene which was red shifted approximately 0.27 ev in passing from the composite system (IVb) to the complete dibenz(a,c)anthracene molecule. The theoretical and experimental analyses apparently agree in this particular case.

Transition II: This observed transition is interpreted as being equivalent to the second observed transition of triphenylene. Three vibrational sequences are observed in Transition II with spacings of 1030 cm^{-1}, 1170 cm^{-1}, and 1445 cm^{-1} compared to two vibrational sequences in the equivalent triphenylene transition with vibrational spacings of 525 cm^{-1} and 1375 cm^{-1}. Experimentally, the intensity of the dibenz(a,c)anthracene transition is somewhat weaker than the second observed triphenylene transition, and it is red shifted 0.747 ev relative to the second triphenylene transition. Transition II corresponds to the first allowed calculated transition of dibenz(a,c)anthracene. On the basis of the theoretical study, this transition was interpreted as arising from the first allowed local transition of triphenylene which was red shifted about 0.27 ev and became more intense in going from

the composite system to the complete molecule. Thus, the theoretical and experimental interpretations agree as to the composite system origin of Transition II, although there is some difference in the predicted and observed behavior of this transition in passing from the composite system model to the complete dibenz(a,c)anthracene molecule.

Transition III: This transition is red shifted 0.508 ev and the intensity slightly diminished relative to the third observed transition of triphenylene with which it is correlated. A single vibrational sequence with spacing of 1380 cm^{-1} is observed in Transition III while a single vibrational sequence with spacing of 1325 cm^{-1} is observed in the equivalent triphenylene transition. Transition III corresponds to the second allowed calculated transition of dibenz(a,c)anthracene. In the theoretical investigation, this transition was interpreted as arising from an electron-transfer transition in the composite system and consequently, no interpretation of the observable characteristics of this dibenz(a,c)anthracene transition was given.

Transition IV: Becker[86] interprets this transition as corresponding to the sixth observed transition of benz(a)anthracene. Transition IV is blue shifted 0.015 ev relative to the benz(a)anthracene transition. The dibenz(a,c)anthracene has a single vibrational sequence with a spacing of 1200 cm^{-1} and the benz(a)anthracene transition has a single observed vibrational sequence with a spacing of 1300 cm^{-1}. Transition IV corresponds to the fourth allowed calculated transition of dibenz-

(a,c)anthracene. In the theoretical analysis, this transition was also interpreted as being derived from an electron-transfer state of a triphenylene and cis-butadiene composite system and consequently no prediction was given for the observable characteristics of the fourth allowed theoretical transition. Although no prediction of observable characteristics was given, the theoretical and experimental analyses fundamentally disagree because the interpretations were given in terms of different composite system models.

Transition V: Becker[86] indicates that this transition may correspond to the eighth observed transition of benz(a)anthracene, in which case the transition would have been blue shifted 0.064 ev relative to its position in benz(a)anthracene. Transition V corresponds to the fifth theoretical transition of dibenz(a,c)anthracene. This transition was also interpreted in terms of a triphenylene and cis-butadiene composite system and thus does not agree with the analysis of the observed transition. In the theoretical analysis, the fifth allowed transition was interpreted as arising from the first allowed local transition of the triphenylene moiety and which was blue shifted about 0.66 ev in passing from the composite system model to the complete molecule.

Transition VI: It is indicated that this transition may be equivalent to the ninth observed transition of benz(a)anthracene. If this is the case, Transition VI is red shifted 0.038 ev relative to its position in benz(a)anthracene. Transition VI is correlated

with the eighth allowed calculated transition. As with Transitions IV and V, the interpretation of the observed Transition VI does not agree with the predictions made on the basis of the theoretical investigation of dibenz(a,c)anthracene. This is because the theoretical interpretation were again made in terms of a composite system containing triphenylene and the experimental interpretations were made on the basis of a composite system containing benz(a)anthracene. In the theoretical analysis, the sixth allowed transition of dibenz(a,c)-anthracene was predicted to have the observable characteristics of a highly modified second allowed transition of triphenylene.

To summarize this comparison, it must be concluded that the interpretation of the electronic transitions of dibenz (a,c) anthracene on the basis of theoretically calculated transitions coincides with the interpretation of the observed transitions only partially at best. Becker[86] has interpreted the first three transitions of this molecule in terms of a triphenylene and cis-butadiene composite system which agrees with the composite system chosen in the theoretical investigation as the best approximation to dibenz(a,c)anthracene. Of these first three transitions, the predictions made in the theoretical study concerning the characteristics of two compared favorably with the interpretations of the corresponding observed transitions. However, Becker[86] interpreted the other three observed dibenz(a,c)anthracene transitions in terms of a second composite system composed of a benz-

(a)anthracene molecule and a cis-butadiene molecule. Although two or more composite system models of each pentacyclic aromatic hydrocarbon molecule were examined in the theoretical analysis, the transitions of the subject molecule were interpreted only in terms of the single composite system model which was chosen to be the best approximation to the subject pentacyclic molecule.

It was noted during the study of the calculated transitions that occasionally small groups of transitions of the subject molecule may appear to be quite similar to a small group of transitions in a composite system other than the one which was chosen to be the best overall approximation to the molecule. However, the idea of interpreting the calculated transitions in terms of more than one composite system was rejected because of the difficulty of prescribing a logical set of rules or guidelines for such an interpretive scheme in the case of the theoretically determined transitions. This occurs because the calculated transitions are characterized only by the energy and oscillator strength of the transition and comparing individual transitions of the complete molecule to individual transitions in a number of composite systems only on the basis of two parameters could reduce the correspondence to pure coincidence. Consequently, it was felt that the correlation of the calculated transitions of a molecule in terms of many composite system approximations would seriously diminish any theoretical significance which could be attached to the interpretation of the molecular transitions in terms of those of a composite system model of that molecule.

It must also be noted that Becker[86] presented an alternative interpretation of the dibenz(a,c)anthracene transitions in terms of the transitions of benzo(c)phenanthrene. This particular tetracyclic aromatic hydrocarbon is not contained within the structure of dibenz(a,c)-anthracene. The interpretation of the transitions of a molecule in terms of a composite system not related to the structure of the subject molecule is entirely incompatible with the composite system approach of the present theoretical investigation and no understanding of such observations can be gained from this investigation.

6. 3,4-Benzopyrene

The observed transition energies and corresponding theoretical values for 3,4-benzopyrene are listed in Table 2.17. The calculated and observed values generally agree as well as they have for the other molecules studied, with one rather important exception. The calculated transitions indicate that the lowest energy allowed transition is at lower energy than the lowest energy forbidden transition; however, Becker[86] has found that experimentally, the very weak observed transition corresponding to the forbidden calculated transition is at lower energy than the observed lowest energy intense transition corresponding to the calculated lowest energy allowed transition. (Recall that throughout this investigation the terms "forbidden" and "allowed" indicate zero and finite values respectively for the calculated oscillator strengths.) A discrepancy between theory and experiment such as this is disturbing

and no clue as to its cause has been discovered in this work. For the purposes of this comparison, however, the lowest energy allowed and lowest energy forbidden theoretically determined transitions will be correlated to their obvious experimental counterparts regardless of the error in the predicted relative positions. In his analysis of the observed transitions of 3,4-benzopyrene, Becker[86] has interpreted the transitions in terms of pyrene transitions which imply a composite system composed of a pyrene molecule and a cis-butadiene molecule. These are the component parts of the composite system (Va) which was chosen as the best approximation to 3,4-benzopyrene on the basis of the theoretical investigation. The individual transitions of 3,4-benzopyrene will now be discussed.

Transition I: Becker[86] has interpreted this transition as being equivalent to the first observed transition of pyrene. Transition I is red shifted approximately 0.273 ev relative to the position of the equivalent pyrene transition. In 3.4-benzopyrene, there is only one observed vibrational sequence and its vibrational spacing is about 565 cm^{-1} while in pyrene there are four vibrational sequences with spacings of 500 cm^{-1}, 725 cm^{-1}, 1050 cm^{-1} and 1550 cm^{-1}. Transition I corresponds to the lowest energy forbidden calculated transition which, on the basis of the theoretical analysis, was predicted to have characteristics similar to the lowest energy forbidden transition of pyrene. This prediction corresponds to Becker's[86] interpretation of the observed transition. Also, the theoretical transition is found to be red shifted about 0.25 ev going from the composite system (Va) to the complete molecule.

Transition II: This transition has been interpreted as being equivalent to the second observed transition of pyrene. Transition II is red shifted about 0.484 ev relative to the corresponding pyrene transition. Becker[86] notes a similar general pattern for the pyrene and 3,4-benzopyrene transitions. Transition II has three observed vibrational sequences with spacings of 220 cm^{-1}, 375 cm^{-1}, and 1460 cm^{-1} while the second transition of pyrene has two vibrational sequences with spacings of 375 cm^{-1} and 1450 cm^{-1}. Transition II corresponds to the first allowed theoretical transition of 3,4-benzopyrene. The theoretical analysis of this transition indicated that it was derived from the first allowed transition of the pyrene component part and consequently, the observed transition corresponding to the first allowed transition of 3,4-benzopyrene should appear quite similar to the first intense transition of pyrene. This corresponds to the experimental interpretation.

Transition III: This transition is correlated to the third observed transition of pyrene by Becker.[86] Transition III is red shifted about 0.360 ev relative to the pyrene transition. Again, a similar general pattern is noted for the two transitions. One vibrational sequence with a spacing of 1460 cm^{-1} is positively observed in the 3,4-benzopyrene transition while two sequences with spacings of 375 cm^{-1} and 1450 cm^{-1} are observed in the pyrene transition. The theoretical transition of 3,4-benzopyrene which corresponds to Transition III is the third allowed transition. The theoretical interpretation

of this transition was that it arose from the interaction of the first allowed transition of cis-butadiene and the second allowed transition of pyrene and, on the basis of the relative weights with which the local excited configurations contributed to this excited state, the transition should appear as a highly modified second allowed pyrene transition when observed. This generally corresponds to Becker's interpretation; however, the observed transition is apparently not modified very extensively relative to the pyrene transition. The theoretical transition is red shifted about 0.17 ev in going from the composite system (Va) to the complete 3,4-benzopyrene molecule.

Transition IV: The transition is red shifted 0.484 ev relative to the fourth observed transition of pyrene with which it is correlated by Becker.[86] The vibrational pattern of Transition IV is similar to that in the corresponding pyrene transition. Two vibrational sequences are noted in the 3,4-benzopyrene transition with spacings of 400 cm^{-1} and 1550 cm^{-1} while the two vibrational sequences observed in the fourth pyrene transition have spacings of 400 cm^{-1} and 1550 cm^{-1}. Transition IV corresponds to the fourth allowed calculated transition. The theoretical analysis of this transition indicated that the transition was derived from a forbidden electron-transfer transition in the composite system and consequently, no prediction was made concerning the observed characteristics of the transition.

Transition V: Becker interprets this transition as being equivalent to the fifth observed transition of pyrene. Transition V is red shifted 0.521 ev relative to the fifth transition of pyrene. One vibrational sequence with spacing of 1350 cm^{-1} is observed in 3,4-benzopyrene but none are observed in the pyrene transition. Transition V corresponds to the fifth allowed theoretical transition. However, the theoretical analysis of this 3,4-benzopyrene transition in terms of the composite system approximation indicated that the transition was derived from the interaction of the first allowed cis-butadiene transition and the second allowed pyrene transition. From this, it was predicted that the observed transition, that is, Transition V, should appear quite similar to the second allowed transition of pyrene. This does not correspond to Becker's interpretation of the observed transition.

Transition VI: This transition is correlated by Becker[86] to the sixth observed transition of pyrene. The pyrene transition has no resolved vibrational structure while the 3,4-benzopyrene transition has a single poorly resolved vibration with a spacing of approximately 1220 cm^{-1}. Transition VI is red shifted 0.397 ev relative to the sixth pyrene transition. This observed transition corresponds to the seventh allowed calculated transition. Intthe theoretical analysis, the seventh allowed transition was related to the fourth allowed transition of pyrene. Consequently, the seventh allowed transition of 3,4-benzopyrene was predicted to have the observable characteristics of the fourth allowed pyrene transition. This does not correspond to Becker's interpretation of Transition VI.

In summary, the theoretical and experimental analyses of the electronic transitions of 3,4-benzopyrene agree on the most basic point. This point is that 3,4-benzopyrene is best approximated by a composite system composed of a pyrene molecule and a cis-butadiene molecule. Furthermore, in three of the six observed 3,4-benzopyrene transitions, the specific predictions made concerning the transitions on the basis of the theoretical investigation agrees with Becker's interpretation of the observed transitions. Also, the comparison of calculated and observed transitions for this molecule suggest the interesting possibility that in some cases the composite system model with very weak bonding between the component parts may be a better quantum mechanical picture of the molecule as it actually exists than the conventional picture of equal bonding between all carbon centers. This observation is prompted particularly by the fact that the composite system approximation of 3,4-benzopyrene correctly predicts the relative positions of the lowest energy allowed transition and the lowest energy forbidden transition while the conventional single component model of the molecule does not.

I. Conclusion

It has been experimentally observed that many electronic transitions of the pentacyclic aromatic hydrocarbons have characteristics similar to those observed for tetracyclic aromatic hydrocarbons contained within the structure of the pentacyclic. In order to gain

an understanding of this experimentally observed phenomenon, an interpretive method utilizing theoretically calculated electronic transitions has been suggested. In this scheme, composite system models of each of the subject pentacyclic molecules were formed by conceptually breaking certain pairs of bonds in the complete molecule. The electronic transitions of the various composite systems were then calculated and compared to the transitions determined for the pentacyclic molecule treated conventionally as a single component system. The transitions of the pentacyclic molecule were then correlated with the transitions of the non-bonded composite system model whose transitions best approximated those of the pentacyclic molecule. To aid in the above correlation, the electronic transitions were determined for the situation where there was "weak" or intermediate bonding between the component parts of the composite systems.

The transitions of the non-bonded composite systems were next analyzed to determine if the transitions arose as a local excitation in the component parts of the composite system or as an electron-transfer excitation from one component part to the other part. It was then suggested that the origins determined for the non-bonded composite system transitions may be assigned to the transitions of the complete pentacyclic molecule corresponding to the composite system transitions. From this theoretical interpretation, predictions were made concerning the characteristics of the experimentally

observable transitions corresponding to the theoretically calculated transitions of the pentacyclic aromatic hydrocarbons. For example, a pentacyclic transition may be predicted to have the characteristics of a particular tetracyclic transition.

The comparison of the proposed theoretical composite system interpretations of the pentacyclic aromatic hydrocarbon transitions with the available composite system interpretation of the experimentally observed transitions[86] reveals fair agreement at best. In the cases of benz(a)napthacene and 3,4-benzopyrene, both the theoretical and experimental interpretations reached the same conclusion as to which particular composite system models were the best approximations to the subject molecules. Although the interpretation of individual transitions disagreed in some instances, overall the theoretical and experimental interpretations agreed quite well. However, in the two cases of benzo(b)-chrysene and dibenzo(b,g)phenanthrene, the theoretical and experimental analyses reach different conclusions as to the best composite system approximations to the subject molecules. In the case of dibenz(a,c)-anthracene there is partial agreement in that half of the experimentally observed transitions are interpreted in terms of the composite system found to be the best approximation in the theoretical analysis while the remaining observed transitions are interpreted in terms of a different composite system model. All the theoretical interpretations were made in terms of a single composite system model for each subject

molecule. It is extremely difficult to judge the merits of the proposed composite system interpretation of electronic transitions on the basis of the results found from the comparison of the theoretical and experimental analyses.

If one is forced to draw a conclusion from the disagreement of the theoretical and experimental interpretations in the present work, the only reasonable conclusion would be that the suggested theoretical interpretation is apparently too naive or simply to give an adequate explanation for the experimentally observed "molecules in molecule" phenomenon. The composite system interpretive scheme suggested in this theoretical investigation of the pentacyclic aromatic hydrocarbons, as well as the previous studies of composite system approximations referred to earlier, all suffer from a common limitation. This limitation is the fact that the composite system concept is essentially an ad hoc assumption made to explain certain experimentally observed peculiarities in the spectra of limited classes of molecules. Thus, the only test which can be applied to the composite system model is to see if it leads to the same conclusions as the experimental interpretations. If it does not, the only alternative is to ascribe the disagreement between the theoretical and experimental interpretations to deficiencies in the theoretical models. If on the other hand, one would be able to derive the composite system concept from more basic physical principles or to justify the composite system model rigorously

in terms of other physical theory, one may be inclined to use the theoretical composite system analysis as a guide in the interpretation of the experimental results. Another possible means of strengthening the composite system approximation would be to have more than one type of experimental phenomenon with which to test the predictions of the composite system approximation. Unfortunately, the molecular orbital theory does not appear to be the proper quantum chemical theory with which to rigorously study the composite system concept. In fact, at first glance the molecular orbital picture of electron orbitals extending over the entire molecule is rather at odds with the composite system picture of a molecule composed of two rather independent parts. The logical theory in which to formulate the composite system problem is apparently the valence bond theory. In this theory, the various elements of the wave functions for a molecule can be correlated with particular canonical structures which resemble the classical chemical structure of the molecule. From this, a state of the molecule is visualized as a resonance between the various canonical structures or forms of the molecule, the weight with which the various canonical structures contribute depending, of course, on the particular molecular state described. Unfortunately, as noted in the Summary of Theoretical Chemistry, the valence-bond method is mathematically untenable at the present time for molecules the size of the pentacyclic aromatic hydrocarbons.

III.

CORRELATION OF THEORETICAL AND EXPERIMENTAL VALUES FOR THE ELECTRON AFFINITY AND IONIZATION POTENTIAL OF THE POLYACENES

CORRELATION OF THEORETICAL AND EXPERIMENTAL VALUES FOR THE ELECTRON AFFINITY AND IONIZATION POTENTIAL OF THE POLYACENES

A. Testing of Chemical Theory

Scientific theories are generally developed in order to provide a framework of unifying principles for the observations of natural phenonmena, thereby aiding in the understanding of these phenomena and providing a means of predicting the results of future observations under given conditions. The application of quantum mechanics to chemical systems and the development of theoretical chemistry was probably motivated most of all by a desire to understand the absorption and emission of light by molecules. Consequently, in the earlier days of the development of chemical theory, and also today, most theoretical work centers on trying to correctly calculate the ground state and excited state energies of molecules in order to explain the electronic transitions between states observed by means of molecular spectroscopy. The common way of "testing" the theory is to then use the refined theory to predict the electronic transitions of other molecules for which experimental data may be obtained for purposes of comparison.

However, in addition to the use of the spectroscopically observable electronic transitions as a means of testing chemical theory, that is, determining the adequacy and appropriateness of the quantum mechanical model of the chemical system, there are two other experimental quantities which may be compared to theoretical quantities that appear in the self-consistent field molecular orbital theory. These observable quantities are the ionization

potential and the electron affinity of a molecule. It will be of value to first discuss these two observables before discussing their interpretation in terms of theoretical parameters.

B. Ionization Potential

The ionization potential of a molecule may be defined with the aid of the potential energy curves shown in Figure 3.1. In this figure, curve M represents the electronic ground state of a given molecule, AB, and curve I represents the ground state of the positive ion, AB^+, of that molecule. The ionization potential (IP) is defined as the energy difference, E_{00}, between the zero vibration levels of the ground states of the neutral molecule and the positive ion. The ionization potential defined in this manner is more precisely called the adiabatic IP and corresponds to the transition shown by line A in Figure 3.1 In general, however, the minimum in the potential energy curves for the molecule and ion will occur at different internuclear distances as is shown in Figure 3.1. According to the Franck-Condon principle the most probable transition is the vertical transition, indicated by line V, from the zero vibrational level of the neutral molecule to an excited vibrational level of the positive ion. In this case the energy of the transition is called the vertical IP. Generally speaking, the adiabatic IP is the IP of most interest and the one that is referred to in theoretical discussions; unfortunately, the vertical IP is the quantity generally measured and this value must be corrected to obtain the adiabatic IP. This correction is done with

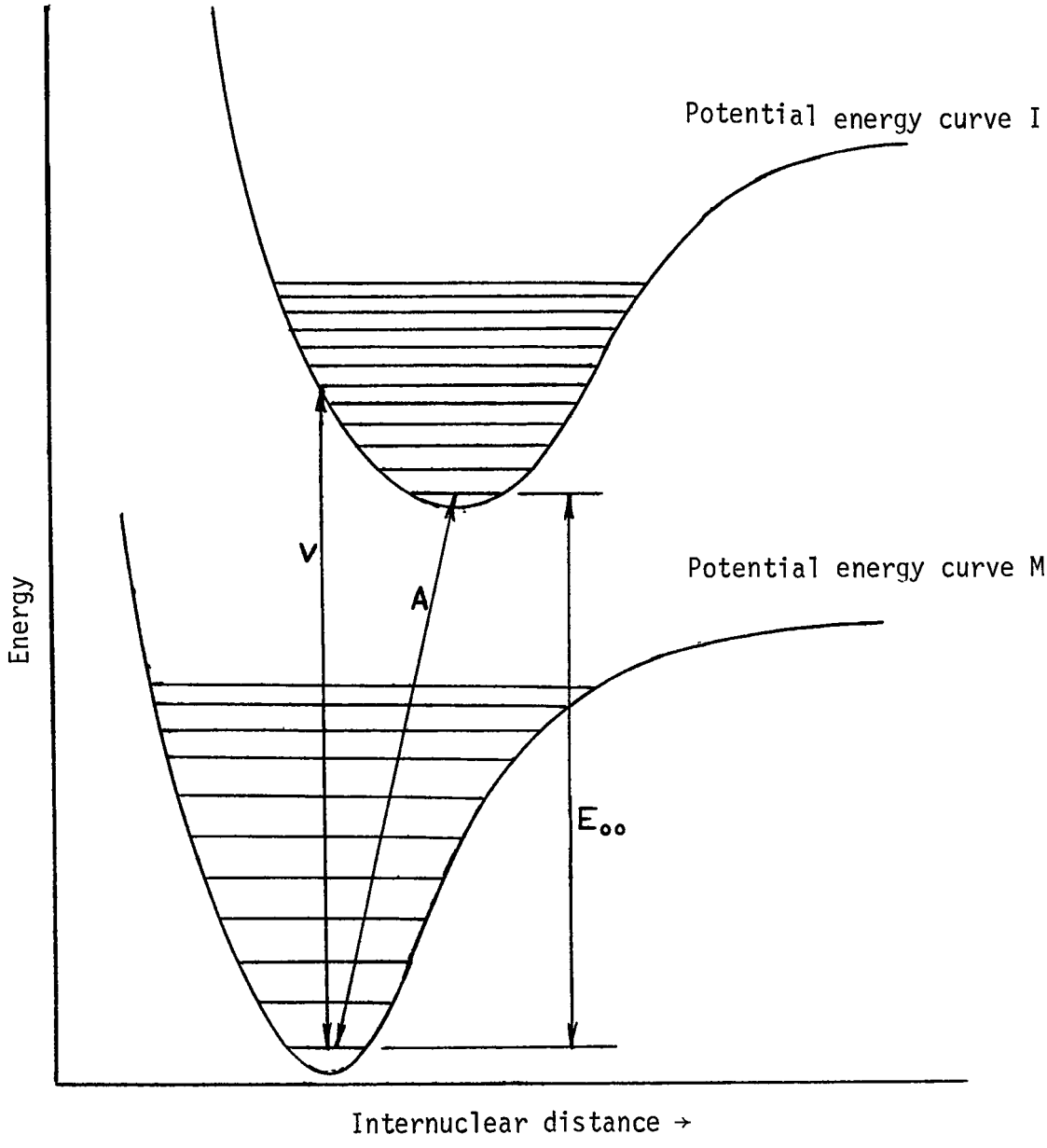


FIGURE 3.1. POTENTIAL ENERGY CURVES OF NEUTRAL MOLECULE (M) AND ITS SINGLY CHARGED ION (I)

varying degrees of success, depending somewhat on the particular method used for the measurement.

There are four primary methods which are used for the experimental measurement of the IP. First is the electron impact method. This is a threshold technique in which the sample is irradiated with electrons and the energy of the incident electrons is gradually increased until the liberation of an electron is detected by the measurement of an ion current. This method has been used extensively during the last 50 years and continues to be employed utilizing the mass spectrometer; however, differences and difficulties in the interpretation of electron impact data cause the IP's determined by this method to be probably the least accurate.

The spectroscopic method of IP determination consists of establishing the convergence limit of one or more Rydberg series in an absorption spectrum. Very accurate values (0.01 to 0.001 ev) may be obtained by this method if a sufficient number of well defined Rydberg bands are found to fit a series formula. Unfortunately, this method is not widely applicable because the vacuum ultraviolet absorption spectra of most molecules are very diffuse and do not exhibit Rydberg series. Even the absorption spectra of some simple molecules, such as NO and I_2, are so complex that Rydberg series have not been identified. The possibility also exists of using an incorrect combination of bands in identifying a Rydberg series.

A third method, known as the photoionization method, is also a threshold technique; however, in this case the sample is irradiated

with monoenergetic photons rather than electrons and the energy of the irradiating photons increased until an ion current is detected. The accuracy obtainable by this method is comparable with that of the spectroscopic method since the attainable energy band-width of monochromatic light is as narrow as 0.001 ev. Moreover, this method can give results in many cases where the spectroscopic method fails. Much of the development and refinement of the photoionization method as a means for measuring the IP, as well as the actual measurement of the IP of many molecules, was done by Watanabe.[68]

The fourth and most recent method to be employed in the determination of IP's is the photoelectron method suggested by Turner and Joboury.[69] In this method, the sample is irradiated with monochromatic light with energy in excess of the IP of the sample molecule. The IP is then determined by measuring the excess kinetic energy, $E = h\nu - IP$, of the ejected electrons. This excess kinetic energy can be measured by means of a retarding electric field of variable strength placed between the irradiated sample and the electron collecting circuitry. The photoelectron method is undoubtedly the most precise method for determining the IP, since this method is even capable of resolving energy transitions to the different excited vibrational levels of the ion.

C. Electron Affinity

The electron affinity (EA) of a molecule is defined in a manner completely analagous to the IP. Referring to Figure 3.1, curve M may now be considered to be the ground state potential energy curve of the

negative ion, AB^-, formed by the attachment of an electron to the neutral molecule, AB, the ground state potential energy curve of which is given by curve I. The electron affinity (EA) is then defined as the energy difference E_{00} between the zero vibrational levels of the ground states of the neutral molecule and the negative ion.

The remarks made earlier concerning the adiabatic and vertical transitions are also applicable to the EA. The adiabatic EA is of primary interest and, fortunately, in this case the experimental methods generally yield the adiabatic EA. However, this advantage is offset by the difficulty in devising suitable experiments to determine the EA.

There are only two significant methods by which experimental values for the EA of complex molecules have been determined. The first method used to obtain good estimates of this parameter is by measurement of the polarographic half wave reduction potential. Details of this method can be found in a discussion by Matsen[70] and the references therein. However, Matsen also pointed out [71] that in order to obtain the true EA of the molecule from the half wave reduction potential, it is necessary to evaluate the difference in the energy of solution of the neutral molecule and the negative ion. Unfortunately, it is rather difficult to evaluate this difference in the energy of solution.

The best method available for determining the electron affinities of complex molecules is the method first suggested by Wentworth and Becker[72] and more fully developed later by Wentworth, et al.[73] This method utilizes a gas chromatography detector developed by Lovelock[74] in which thermal energy electrons are produced and the ability of a

molecule in the gas phase to attach these electrons is determined by periodically sampling the electron concentration in the cell by means of a pulsed electric field. That the quantity determined is in fact the EA of the molecules, at least for the aromatic hydrocarbons, is established quite well by the successful correlation of these parameters with the IP's and ^1L_a (Platt's nomenclature) electronic transitions of a number of aromatic molecules by Becker and Wentworth,[75] and Becker and Chen.[76] The values obtained for the EA by this method are apparently quite good.

D. Theoretical Interpretations and Correlations

The first point to be discussed is the interpretation of the IP and EA as the energies of the SCF molecular orbitals of the molecule. The following theoretical development was that given by Roothaan[18] in his presentation of the formal self-consistent field molecular orbital theory. The ith ionization potential, IP_i, of a singly ionized molecule is given by the expression

$$IP_i = E(^1\Phi_0) - E(^2\Phi_i) \tag{3.1}$$

where $E(^1\Phi_0)$ is the energy of the ground state of the neutral molecule, described by the wave function $^1\Phi_0$, and $E(^2\Phi_i)$ is the ground state energy of the positive ion formed by the removal of an electron from the ith molecular orbital and which is described by the wave function $^2\Phi_i$. Recall from the discussion of the SCF molecular orbital theory in the Summary of Theoretical Chemistry that the ground state wave

function of the neutral molecule is given by equation (1.1) of that section as a single Slater determinant (in an obvious shorthand notation)

$$^{1}\Phi_{o} = \left|(\phi_1\alpha)(\phi_1\beta)(\phi_2\alpha)\ldots(\phi_n\alpha)(\phi_n\beta)\right|$$

and the energy of the ground state is given by equation (1.7) of that section as

$$E(^{1}\Phi_{o}) = 2\sum_i H_i + \sum_i \sum_j (2J_{ij} - K_{ij})$$

where the H_i, J_{ij}, and K_{ij} are given by equations (1.8), (1.9) and (1.10), respectively in the Summary of Theoretical Chemistry.

To obtain the ground state wave function of the positive ion, $^{2}\Phi_{i}$, a very important approximation is made. Rather than set up and solve the appropriate variational problem for the ion to determine all the molecular orbitals for that particular state, one instead forms the wave function of the ion from the molecular orbitals obtained from the variational problem for the ground state of the neutral molecule. To do this one simply deletes the molecular orbital for the electron removed by the ionization process from the determinant wave function of the neutral molecule. In spite of this rather drastic assumption good results are obtained for singly ionized states, and Roothaan[18] remarks that IP's calculated by this method are in closer agreement with experiment than those calculated by solving the variational problems for the energies of the ground states of the neutral molecule and ion separately and subtracting.

The wave functions for the ionized state using the above approximation are

$$
\begin{aligned}
{}^2\Phi_i &= |(\phi_1\alpha)(\phi_1\beta)\ldots(\phi_{i-1}\alpha)(\phi_{i-1}\beta)(\phi_i\alpha)(\phi_{i+1}\alpha)(\phi_{i+1}\beta)\ldots(\phi_n\alpha)(\phi_n\beta)| \\
{}^2\Phi_i &= |(\phi_1\alpha)(\phi_1\beta)\ldots(\phi_{i-1}\alpha)(\phi_{i-1}\beta)(\phi_i\beta)(\phi_{i+1}\alpha)(\phi_{i+1}\beta)\ldots(\phi_n\alpha)(\phi_n\beta)|.
\end{aligned}
\tag{3.2}
$$

This state is a doublet, the two wave functions (3.2) having the same energy

$$
\begin{aligned}
E({}^2\Phi_i) &= 2\sum_{j\neq i} H_j + H_i + \sum_{j\neq i}\sum_{k\neq i}(2J_{jk} - K_{jk}) + \sum_{j\neq i}(2J_{ij} - K_{ij}) \\
&= 2\sum_j H_j + \sum_j\sum_k (2J_{jk} - K_{jk}) - H_i - \sum_j (2J_{ij} - K_{ij}) \\
&= E({}^1\Phi_0) - H_i - \sum_j(2J_{ij} - K_{ij}).
\end{aligned}
\tag{3.3}
$$

From equations (3.1) and (3.3) one may obtain the following expression for the IP_i:

$$
IP_i = E({}^1\Phi_0) - E({}^2\Phi_i) = -H_i - \sum_j(2J_{ij} - K_{ij}) \tag{3.4}
$$

However, recalling equations (1.30), (1.31), and (1.33) from the <u>Survey of Theoretical Chemistry</u> one finds that, for the LCAO approximation,

$$
\begin{aligned}
H_i + \sum_j(2J_{ji} - K_{ji}) &= \underline{c}_i^* \{\underline{H} + {}_j(2\underline{J}_j - \underline{K}_j)\}\, \underline{c}_i \\
&= \underline{c}_i^*\, \underline{F}\, \underline{c}_i = \varepsilon_i\, \underline{c}_i^*\, \underline{S}\, \underline{c}_i = \varepsilon_i \quad .
\end{aligned}
\tag{3.5}
$$

Or in other words equation (3.1) reduces to

$$
IP_i = -\,\varepsilon_i \tag{3.6}
$$

where ε_i is the energy of the ith molecular orbital. Thus one obtains the result that, subject to the approximation of using the molecular orbitals of the ground state of the neutral molecule, the various ionization potentials of a molecule are equal to the negative of the energy of the molecular orbital from which the electron is ejected. This relationship is generally known as Koopman's theorem.

In a completely analogous manner, Hush and Pople[77] showed that the various electron affinities of a molecule were equal to the negative of the SCF molecular orbital energies, that is,

$$EA_i = - \varepsilon_i \tag{3.7}$$

with one important difference. In this case the orbital energy is that of an excited molecular orbital which is unoccupied when the neutral molecule is in the ground state while for the IP_i the orbital energy is that of an orbital which is occupied in the ground state of the neutral molecule. Since the development of equation (3.7) is completely analogous to that given for the IP, no further details will be given.

The above theoretical discussion of the ionization potential and electron affinity is quite general and applies to all the possible IP's and EA's of a given molecule. However, the experimental values of the IP and EA are generally the first IP and the first EA, that is, the IP is the energy relative to the lowest energy positive ion and the EA is the energy relative to the lowest energy negative ion. The lowest energy positive ion is that formed by removal of an electron from the

filled molecular orbital with highest energy while the lowest energy negative ion is formed by placing an electron in the unfilled molecular orbital with lowest energy. Consequently, for a closed shell molecule with 2n electrons, the IP and EA will be generally interpreted to be

$$\begin{aligned} IP &= -\varepsilon_n \\ EA &= -\varepsilon_{n+1} \end{aligned} \tag{3.8}$$

where ε_n and ε_{n+1} are the molecular energies of the highest energy filled SCF molecular orbital and the lowest energy unfilled SCF molecule orbital respectively. This investigation will only deal with the first IP and EA, thus only the interpretation implied in equation (3.8) will be of interest.

Over the years since the introduction of the semi-empirical SCF molecular orbital theory, numerous comparisons have been made of calculated values of the SCF molecular orbital energies and experimental values of the IP and EA. The comparisons made by Pople[24] and Hush and Pople[77] for a number of conjugated hydrocarbons are probably some of the earliest. All of these comparisons lead to the same results as obtained by Hush and Pople;[77] that is, only fair agreement, at best, is observed between the absolute values of the calculated orbital energies and the experimental values of the IP and EA. However, generally the ordering of the calculated and experimental values for different molecules is the same. This failure of the semi-empirical SCF molecular orbital theory to correctly predict the absolute

values of the IP and EA when using parameters which are considered to be optimum for the calculation of the electronic transition energies is quite disturbing and is often referred to as the "ionization catastrophe."[78]

The next quantity to be discussed is the absolute molecular electronegativity defined by Mulliken,[79] as

$$\chi = \frac{1}{2}(IP + EA). \tag{3.9}$$

Based on the previously discussed interpretation of the IP and EA as SCF molecular orbital energies, as interesting prediction may be made concerning χ. Hush and Pople[77] were the first to show that, subject to the approximations of the semi-empirical SCF molecular orbital theory, for the even alternant conjugated hydrocarbons

$$\varepsilon_n + \varepsilon_{n+1} = 2F_{ii} = \text{constant} \tag{3.10}$$

where ε_n and $_{n+1}$ are the orbital energies of the highest energy filled molecular orbital and the lowest energy unfilled molecular orbital respectively. Since F_{ii} is independent of molecular geometry and only depends on the properties of the carbon atoms, the constant value of $\varepsilon_n + \varepsilon_{n+1}$ is independent of a particular molecule. This in turn implies that the electronegativity, χ, of the even alternant conjugated hydrocarbons should be a constant independent of a particular molecule. That χ is in fact essentially a constant for this class of molecules has been rather convincingly demonstrated by the work of

Becker and Wentworth[75] and Becker and Chen[76] in which χ was determined from the experimental values for the IP and EA and from which an average value of 4.17 ev was found for χ.

The real utility of knowing the constant value of χ is that for those cases in which for one reason or another, one is unable to measure either the IP or EA of a molecule, a good estimate of the unmeasurable parameter may be obtained using the values for χ and the measured parameter.

The final quantity to be discussed is the socalled two-electron term

$$-J_{ij} + 2K_{ij} \tag{3.11}$$

where J_{ij} is the coulomb integral given by equation (1.9) in the Survey of Theoretical Chemistry and K_{ij} is the exchange integral given by equation (1.10) in the same section. This term arises in the theoretical expression for the energy of the electronic transition from the ground state to the singlet excited electronic configuration formed by exciting an electron from the ith ground state molecular orbital to the jth excited orbital. The expression for this energy is given by (see Ref. 18)

$$E({}^1\Phi_{ij}) - E({}^1\Phi_o) = \Delta E_{ij} = \varepsilon_j - \varepsilon_i - J_{ij} + 2K_{ij} \tag{3.12}$$

where ε_i and ε_j are again the orbital energies. In particular, this discussion will be concerned with the excited electronic configuration formed by exciting an electron from the highest energy filled molecular

orbital, the nth, to the lowest energy unfilled molecular orbital, the (n+1)th. For the polycyclic aromatic hydrocarbons, it has been found that generally very little, if any, configuration interaction occurs between this configuration and other configurations. This means that this particular electronic excitation from the nth to the (n+1)th molecular orbital may be considered as being directly observable as a transition between states in the molecule.

The above considerations have allowed Michl and Becker[64] to determine an experimental value for the two-electron term

$$-J_{n,n+1} + 2K_{n,n+1} \tag{3.13}$$

for the excitation from the nth to the (n+1)th molecular orbital This is done simply by substituting experimental values of the IP and EA for the orbital energies and the spectroscopically determined energy of the ^1L_a (Platt's nomenclature) transition for $[E(^1\Phi_{n,n+1}) - E(^1\Phi_0)]$ in equation (3.12). The experimental value may then be compared to the calculated value. The object of Michl and Becker's work was to show the approximately constant nature of the two-electron term for groups of structurally related compounds, for example, tetracyclic aromatic hydrocarbons; however, the usefulness of this interpretation need not be limited to this.

E. Proposed Correlations

Over the years considerable work has been done in the area of correlating and comparing the absolute values of molecular parameters,

such as the IP and EA, with theoretical calculated values for various molecules.[24,77] If one includes correlations made with values calculated by specialized techniques other than the SCF molecular orbital theory and its semi-empirical version, the amount of work is much larger.[75,76] Since the SCF molecular orbital theory is by far the most sophisticated chemical theory available today and the best grounded in fundamental physical theory, these correlations would seem most important.

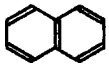
The previous correlations of experimental and theoretical molecular parameters have for the most part concentrated on the comparison of the absolute values of the parameters for various molecules. However, perhaps a better or more meaningful test of chemical theory would be to compare the trends of experimental and calculated molecular parameters, such as the IP and EA, for a series of molecules which change in a certain systematic manner. Some of the reasons for the inability of the SCF molecular orbital theory to correctly predict the absolute values of molecular parameters are recognized and the development of the semi-empirical form of the SCF molecular orbital theory has provided a means whereby the calculated values can perhaps be forced to approach the experimental values for restricted groups of molecules rather closely. However, if the theory cannot correctly predict trends in the changes of molecular parameters caused by changes in molecular structure and size, it is unlikely that this defect could be overcome by adjustments of parameters in the semi-empirical theory,

but would rather necessitate a drastic modification of the basic SCF molecular orbital theory.

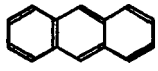
A classic group of molecules in which trends caused by a systematic change in molecular size are studied is the polyacenes. This is the series of conjugated aromatic hydrocarbons which begins with benzene and is formed by condensing additional rings to it in a linear fashion to form naphthalene (2 rings), anthracene (3 rings), etc. (See Figure 3.2). For example, Klevens and Platt[50] experimentally studied the trends of the electronic transitions in the polyacenes while Pariser[80] studied the trends of the calculated transitions in this series.

In this work, a study will be made of the ability of the semi-empirical SCF molecular orbital theory to predict the trends in the IP and EA, the quantity (IP - EA), and the experimental value of the two-electron term $(-J_{n,n+1} + 2K_{n,n+1})$ which is determined by means of the IP, EA, and ^1L_a transition energy. By equation (3.8), the quantity (IP - EA) is equivalent to the theoretical quantity $(\varepsilon_{n+1} - \varepsilon_n)$ where ε_{n+1} is the energy of the lowest unfilled molecular orbital and ε_n is the energy of the highest filled molecular orbital. The ability of the theory to predict the trends in the IP and EA will be investigated by a straight-forward comparison of the calculated and experimental values of these molecular parameters as a function of the molecular size.

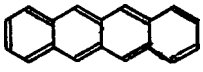
Benzene



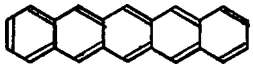
Napthalene



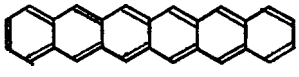
Anthracene



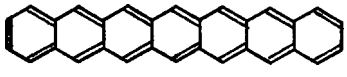
Napthacene



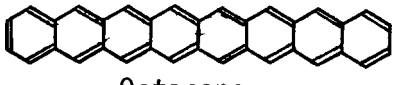
Pentacene



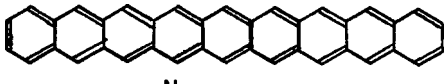
Hexacene



Heptacene



Octacene



Nonacene

FIGURE 3.2. THE POLYACENES

F. Results

Table 3.1 gives the theoretical calculated values of the energy of the highest filled molecular orbital, ε_n(-IP), the energy of the lowest energy unfilled molecular orbital, ε_{n+1}(-EA), the difference of these two quantities, $\varepsilon_{n+1} - \varepsilon_n$, the value of the two-electron term, $-J_{n,n+1} + 2K_{n,n+1}$, and the energy of the electronic transition, $\Delta E_{n,n+1}$, from the nth molecular orbital to the (n+1)th for the polyacenes. These values were determined by means of the computer program based on the semi-empirical SCF molecular orbital theory with LCAO molecular orbitals used in the calculations of Part II. The $\underline{F}$ and $\underline{S}$ matrix elements were again approximated by

$$\begin{aligned} F_{ii} &= -\frac{1}{2}(I_i + A_i) - P_i \\ F_{ij} &= \beta_{ij} - \frac{1}{2} P_{ij}\gamma_{ij} \\ S_{ij} &= \delta_{ij}. \end{aligned} \tag{3.14}$$

The valence state ionization potential, I_i, and electron affinity, A_i, of the $2p\pi$ carbon atom were assumed to have the widely used values of

$$\begin{aligned} I_i &= 11.42 \text{ ev} \\ A_i &= 0.58 \text{ ev} \end{aligned} \tag{3.15}$$

and the penetration integral, P_i, was assumed to be zero. The resonance integral, β_{ij}, was assumed to be -2.318 ev for nearest neighbor, or bonded, carbon atoms and zero between non-neighboring carbon atoms.

TABLE 3.1 - CALCULATED RESULTS FOR POLYACENES

Molecule	No. of C Atoms	ε_n (ev)	ε_{n+1} (ev)	$\Delta E_{n,n+1}$ (ev)	$-J_{n,n+1}+2K_{n,n+1}$ (ev)	$\varepsilon_{n+1}-\varepsilon_n$(ev)
Benzene	6	-10.658	-1.342	6.412	-2.905	9.317
Naphthalene	10	- 9.538	-2.462	4.520	-2.557	7.077
Anthracene	14	- 8.891	-.3109	3.525	-2.257	5.782
Napthacene	18	- 8.490	-3.510	2.921	-2.059	4.979
Pentacene	22	- 8.226	-3.774	2.534	-1.918	4.452
Hexacene	26	- 8.045	-3.955	2.275	-1.815	4.090
Heptacene	30	- 7.916	-4.084	2.098	-1.734	3.832
Octacene	34	- 7.822	-4.178	1.974	-1.670	3.644
Nonacene	38	- 7.751	-4.249	1.887	-1.615	3.502

The Mataga approximation[29] [equations (1.59) and (1.60) in Survey of Theoretical Chemistry]

$$\gamma_{ij} = \frac{14.3986}{r_{ij} + 1.3283} \quad \text{ev} \tag{3.16}$$

was used for the two-center integral, γ_{ij}, since this is reputed to give the best calculated results for the singlet transitions of conjugated hydrocarbons. The configuration interaction procedure was not used in these calculations since the transition energy determined in this manner would not be equivalent to the transition energy, $\Delta E_{n,n+1}$, which appears in equation (3.12). Furthermore, as noted earlier, $\Delta E_{n,n+1}$ is essentially unaffected by configuration interaction in polycyclic aromatic hydrocarbons, that is, naphthalene through nonacene, and thus, is actually the calculated value of the observable ^1L_a transition. In benzene, however, there are four excited electronic configurations with excitation energies equal to $\Delta E_{n,n+1}$ and, consequently, $\Delta E_{n,n+1}$ does not correspond to an observable transition but rather the observed transition will be to an excited state formed by the interaction of the four degenerate configurations. The observed transition is lower in energy than $\Delta E_{n,n+1}$:

The transition energies of the polyacenes have been calculated by numerous other workers. Pariser[80] calculated the transition energies for the molecules benzene through pentacene by means of the semi-empirical ASMO method with configuration interaction. Moffitt[66] also calculated the main low energy transitions of the molecules benzene

through pentacene using a simple method based on the perimeter model for polycyclic aromatic hydrocarbons with cross-linkages of the actual molecules treated as perturbations. The object of Moffitt's[66] work, however, was not the determination of extremely accurate values for the transition energies but rather to show that his relatively simple method was capable of predicting the correct trends of the transitions in the polyacene series. Pople[31] calculated the transition energies of the molecules benzene through anthracene using the semi-empirical SCFMO method with limited configuration interaction. Ham and Rudenberg[85] and Hummel and Rudenberg[48] made calculations of the transition energies of the molecules benzene through pentacene using methods which are essentially modifications of the standard ASMO method with configuration interactions. Koutecky, et al.[67] calculated the energy of the p band (Clar's[55] nomenclature) for a large group of polycyclic aromatic hydrocarbons, including the polyacene series through pentacene, by means of the semi-empirical ASMO method with configuration interaction. The p band is equivalent to the ^1L_a band (Platt's[56] nomenclature) or the transition energy referred to as $\Delta E_{n,n+1}$ in the present investigation. A comparison of the values for $\Delta E_{n,n+1}$ calculated previously and in the present work is given in Table 3.2. The experimentally observed values for the ^1L_a transition are also shown in Table 3.2. Note that none of the prior calculations have been for molecules greater than pentacene in size and none have included calculated values of the ionization potential and electron affinity. An examination of Table 3.2 shows that the values calculated

TABLE 3.2 - COMPARISON OF CALCULATED VALUES OF $\Delta E_{n,n+1}$ FOR THE POLYACENES

Source of Values	$\Delta E_{n,n+1}$ Transition Energy (ev)				
	Benzene	Naphthalene	Anthracene	Napthacene	Pentacene
Pariser[80]	5.96	4.49	3.65	3.11	2.82
Pople[31]	5.33	4.65	3.72		
Ham and Ruedenberg[85]	6.20	4.54	3.60	3.05	2.70
Hummel and Ruedenberg[48]	6.06	4.23	3.15	2.53	2.13
Koutecky, *et al.*[67]	5.99	4.32	3.31	2.74	2.52
This Work	6.41	4.52	3.53	2.92	2.53
Experimental[a]	5.957	4.290	3.273	2.616	2.120

[a]See Table 3.4

in this study generally fall within the range of previously calculated values. The effect of neglecting configuration interaction in calculating the benzene transition is shown by the substantially higher value obtained in the present investigation. Considering all five molecules, the values calculated by Hummel and Rudenberg[48] show the best correspondence to experimental values.

Pople[24] calculated the IP($-\varepsilon_n$) of the molecules benzene, naphthalene and anthracene by means of the semi-empirical SCF molecular orbital method, that is, a method equivalent to that used in this investigation. Hush and Pople[77] later calculated the IP($-\varepsilon_n$) and EA($-\varepsilon_{n+1}$) of these same three molecules using the same method but slightly different values for the theoretical parameters. Hoyland and Goodman[83,84] also calculated the IP($-\varepsilon_n$) of naphthalene and anthracene and the EA($-\varepsilon_{n+1}$) of benzene, naphthalene, and anthracene using the semi-empirical SCF molecular orbital methods. Hedges and Matsen[88] used the semi-empirical ASMO method to calculate the IP($-\varepsilon_n$) and EA($-\varepsilon_{n+1}$) of all the polyacene molecules through pentacene. A comparison of the previously calculated values of the IP($-\varepsilon_n$) and EA($-\varepsilon_{n+1}$) with those obtained in this study is given in Table 3.3. The experimental values for the IP and EA are also shown in Table 3.3. The wide variation between the various calculated values is caused by the different approximations for integrals and empirical values used in the respective calculations. Although some of the previously calculated values for the IP and EA are in closer agreement with the experimental values than those calculated for the present investigation, later discussions will indicate why, in one sense, these latter values are also quite good.

TABLE 3.3 - COMPARISON OF CALCULATED VALUES OF IONIZATION POTENTIAL AND ELECTRON AFFINITY

Source of Values	Benzene		Naphthalene		Anthracene		Napthacene		Pentacene	
	IP(ev)	EA(ev)	IP(EA)	EA(ev)	IP(EA)	EA(ev)	IP(EA)	EA(ev)	IP(ev)	EA(ev)
Pople[24]	+9.76	-	+8.28	-	+7.38					
Hush and Pople[77]	+9.87	-1.40	+8.61	-0.14	+7.83	+0.64				
Hoyland and Goodman[83,84]	-	+0.51	+10.53	+1.47	+9.80	+2.20				
Hedges and Matsen[88]	+9.37	-1.63	+8.12	-0.38	+7.25	+0.49	+6.92	+0.82	+6.73	+1.01
This Work	+10.66	+1.34	+9.54	+2.46	+8.89	+3.11	+8.49	+3.51	+8.23	+3.77
Experimental[a]	+9.24	-0.90	+8.26	+0.15	+7.55	+0.863	+6.95	+1.39	+6.55	+1.79

[a]See Table 3.4

The experimental values for the IP, EA, IP-EA, $-J_{n,n+1} + 2K_{n,n+1}$, and ^1L_a ($\Delta E_{n,n+1}$) transition energy are given in Table 3.4. All of the values for the IP and the ^1L_a transition energy are directly obtained experimental values, the sources of which are given in Table 3.4. Of the EA values only two, naphthalene and anthracene, were directly obtained from experiment. The other values were obtained using the experimental value of the electronegativity, χ, obtained by Becker and Chen[74] and the experimental value of the IP. This procedure has been reasonably well justified by the above authors. The experimental value of the two-electron term was obtained by the procedure proposed by Michl and Becker[64] and described in an earlier Section.

It should be noted that the calculated values of ε_n(-IP), ε_{n+1}(-EA), $\varepsilon_{n+1} - \varepsilon_n$, $-J_{n,n+1} + 2K_{n,n+1}$, and $\Delta E_{n,n+1}$ are determined for the polyacene molecules through nonacene while experimental data is available only through pentacene. The calculations were carried out to this rather extreme level primarily to be able to show the trends in the molecular parameters as clearly as possible. Unfortunately, it is doubtful if experimental data will ever be available for the polyacenes much larger than pentacene due to the extreme instability of these large linear molecules.

The above molecular parameters and quantities are shown graphically in Figures 3.3 through 3.8 as functions of the molecular size, that is, the number of carbon atoms, and as functions of the $\Delta E_{n,n+1}$ or ^1L_a transition energy. These various results will now be discussed.

TABLE 3.4 - EXPERIMENTAL RESULTS FOR POLYACENES

Molecule	No. of C Atoms	IP (ev)	EA (ev)	^1L_a Transition(ev)	$-J_{n,n+1}+2K_{n,n+1}$(ev)	(IP-EA) (ev)
Benzene	6	+9.24 [a]	-0.90 [g]	5.957 [j]	-4.183	10.14
Napthalene	10	+8.26 [b] +8.12 [a]	+0.15 [h]	4.290 [j]	-3.820 -3.680	8.11 7.97
Anthracene	14	+7.55 [b] +7.66 [c]	+0.863 [i]	3.273 [j]	-3.414 -3.524	6.687 6.797
Napthacene	18	+7.15 [c] +6.95 [d] +6.88 [e]	+1.19 [g] +1.39 [g] +1.46 [g]	2.616 [j]	-3.344 -2.944 -2.804	5.96 5.56 5.42
Pentacene	22	+6.55 [f]	+1.79 [g]	2.120 [j]	-2.640	4.76

[a] From H. Watanabe, J. Chem. Phys., 22, 1565 (1954)
[b] From M. E. Wacks and V. H. Dibeler, J. Chem. Phys., 31, 1557 (1959)
[c] D. P. Stevenson values, less 0.56 ev (Private communication from R. S. Becker to F. A. Matson, 1957)
[d] M. E. Wacks, J. Chem. Phys. 41, 1661 (1964)
[e] F. I. Vilesov, Dokl. Akad. Nauk SSSR, 132, 632 (1960)
[f] E. Gallegos, J. Phys. Chem. (to be published)
[g] Determined from IP and X = 4.17 ev, See Ref. 74
[h] From Ref. 74
[i] Value determined in this work by method of Wentworth, et al. (Ref. 73)
[j] From Ref. 50

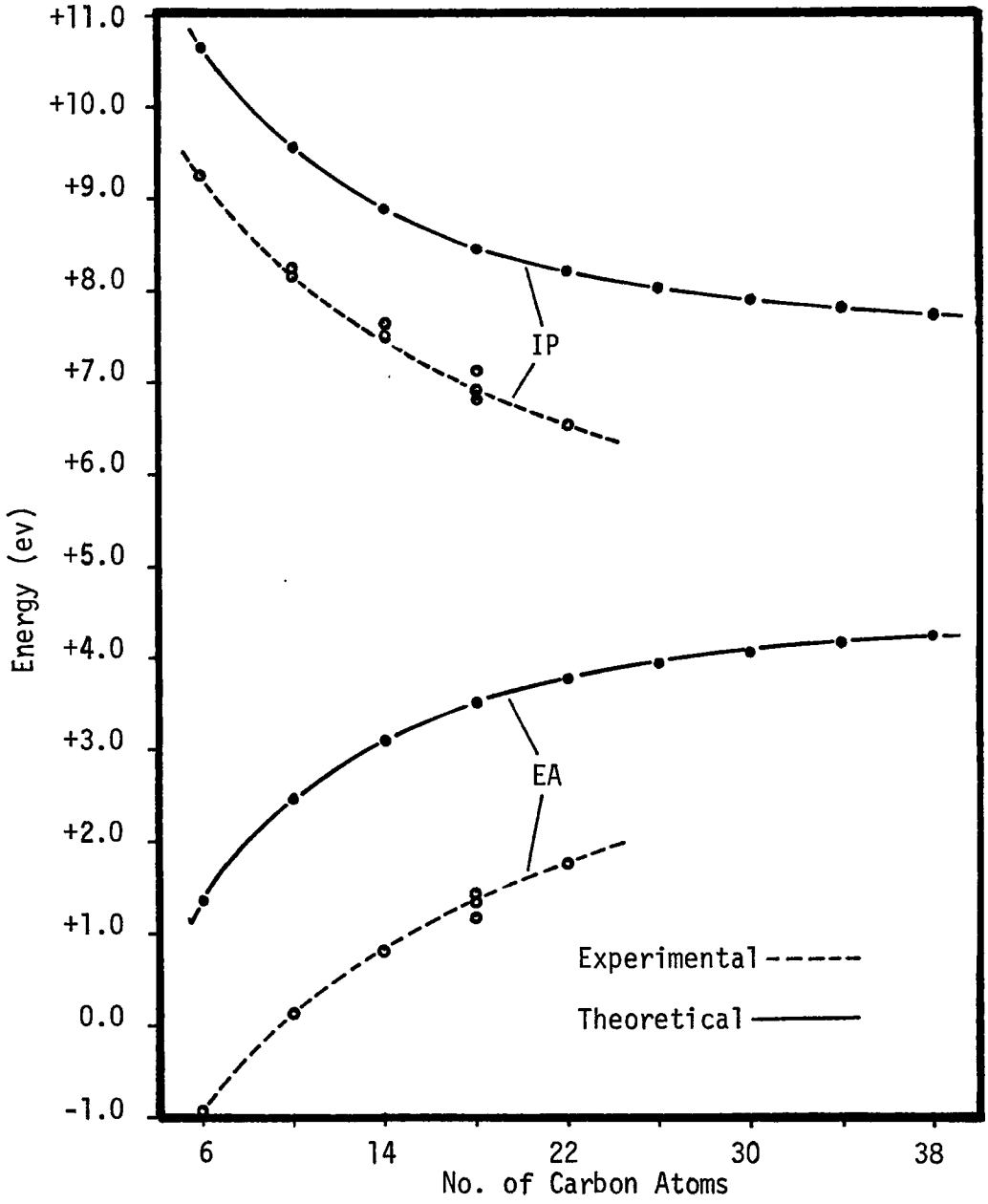


FIGURE 3.3. PLOT OF IONIZATION POTENTIAL AND ELECTRON AFFINITY VERSUS NUMBER OF CARBON ATOMS

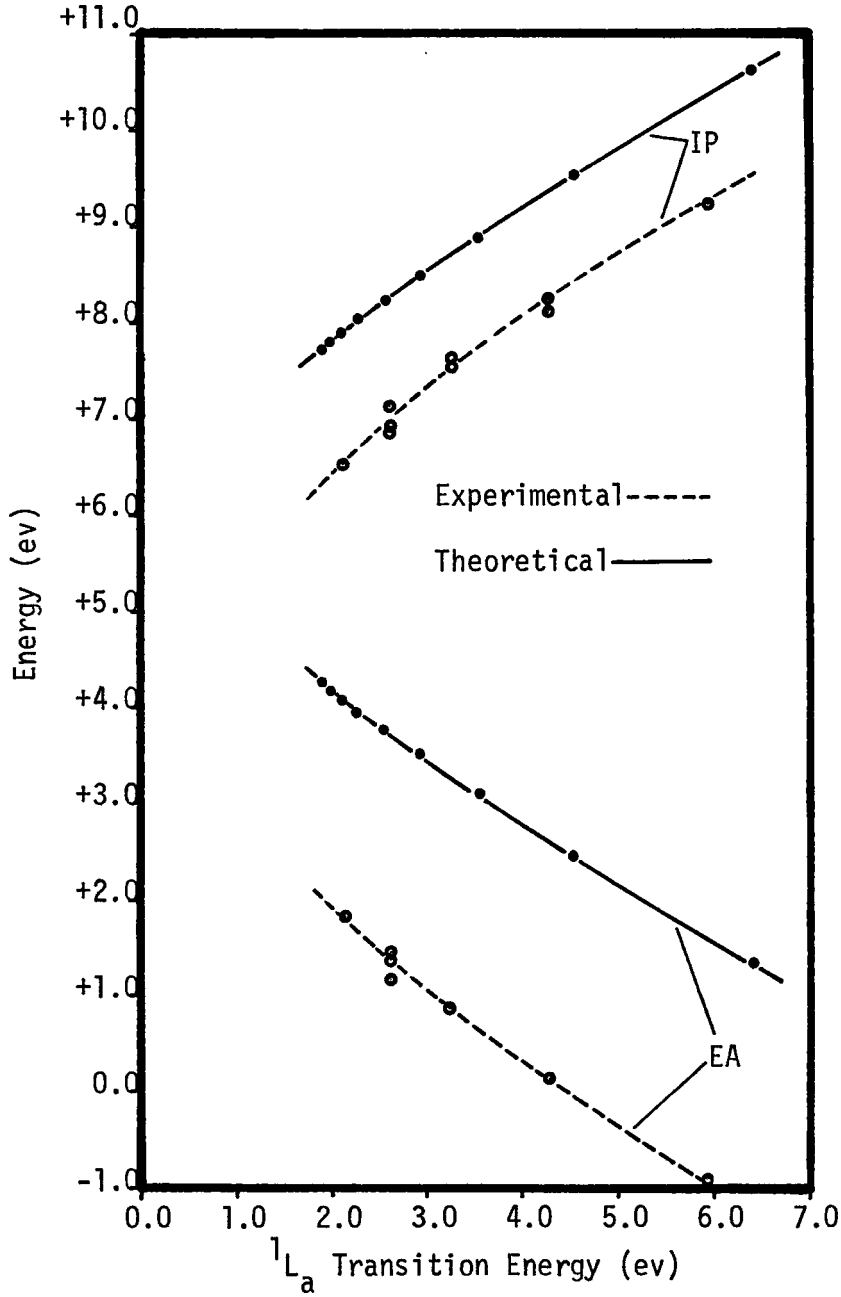


FIGURE 3.4. PLOT OF IONIZATION POTENTIAL AND ELECTRON AFFINITY VERSUS ^1L_a TRANSITION ENERGY

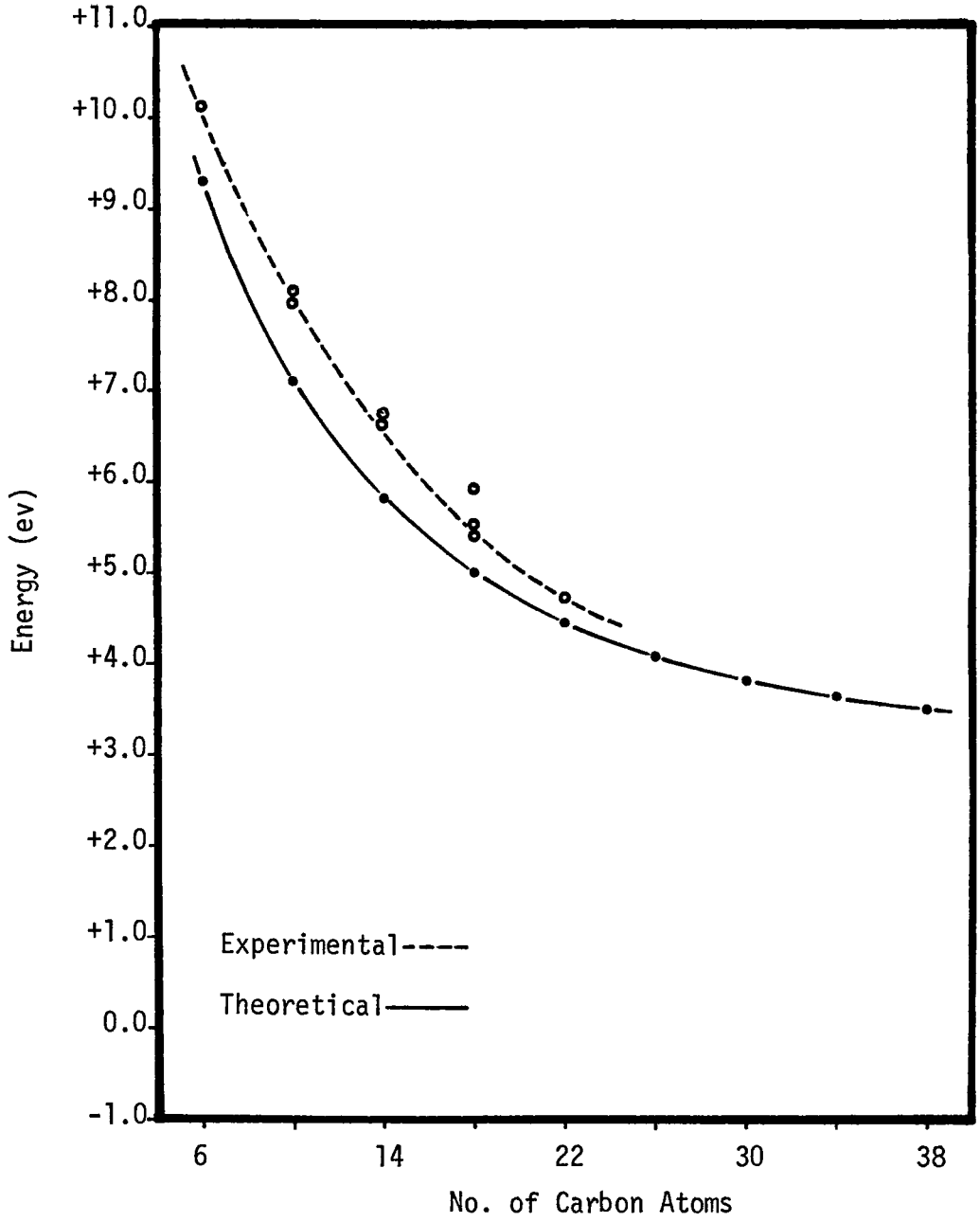


FIGURE 3.5. PLOT OF IONIZATION POTENTIAL MINUS ELECTRON AFFINITY VERSUS NUMBER OF CARBON ATOMS

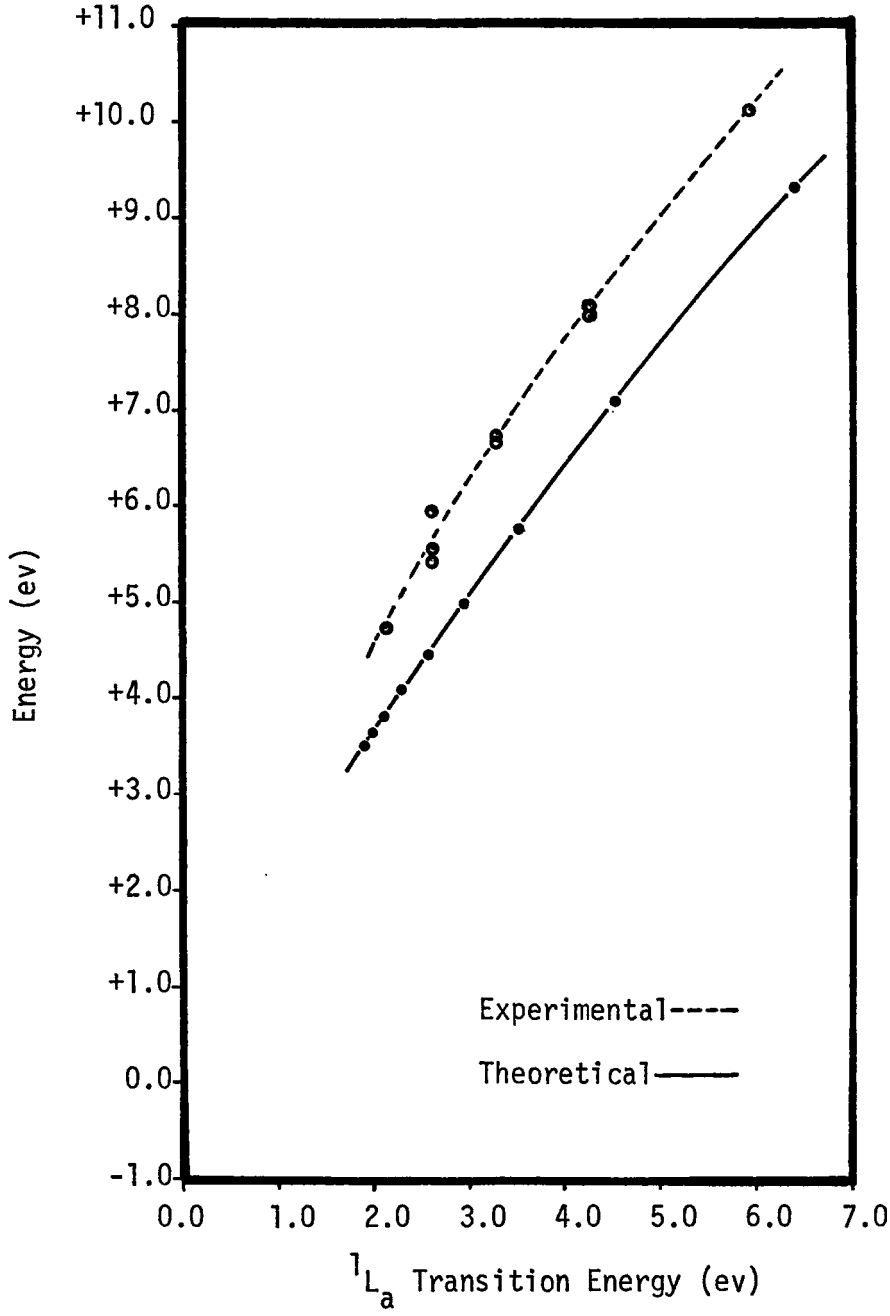


FIGURE 3.6. PLOT OF IONIZATION POTENTIAL MINUS ELECTRON AFFINITY VERSUS ^1L_a TRANSITION ENERGY

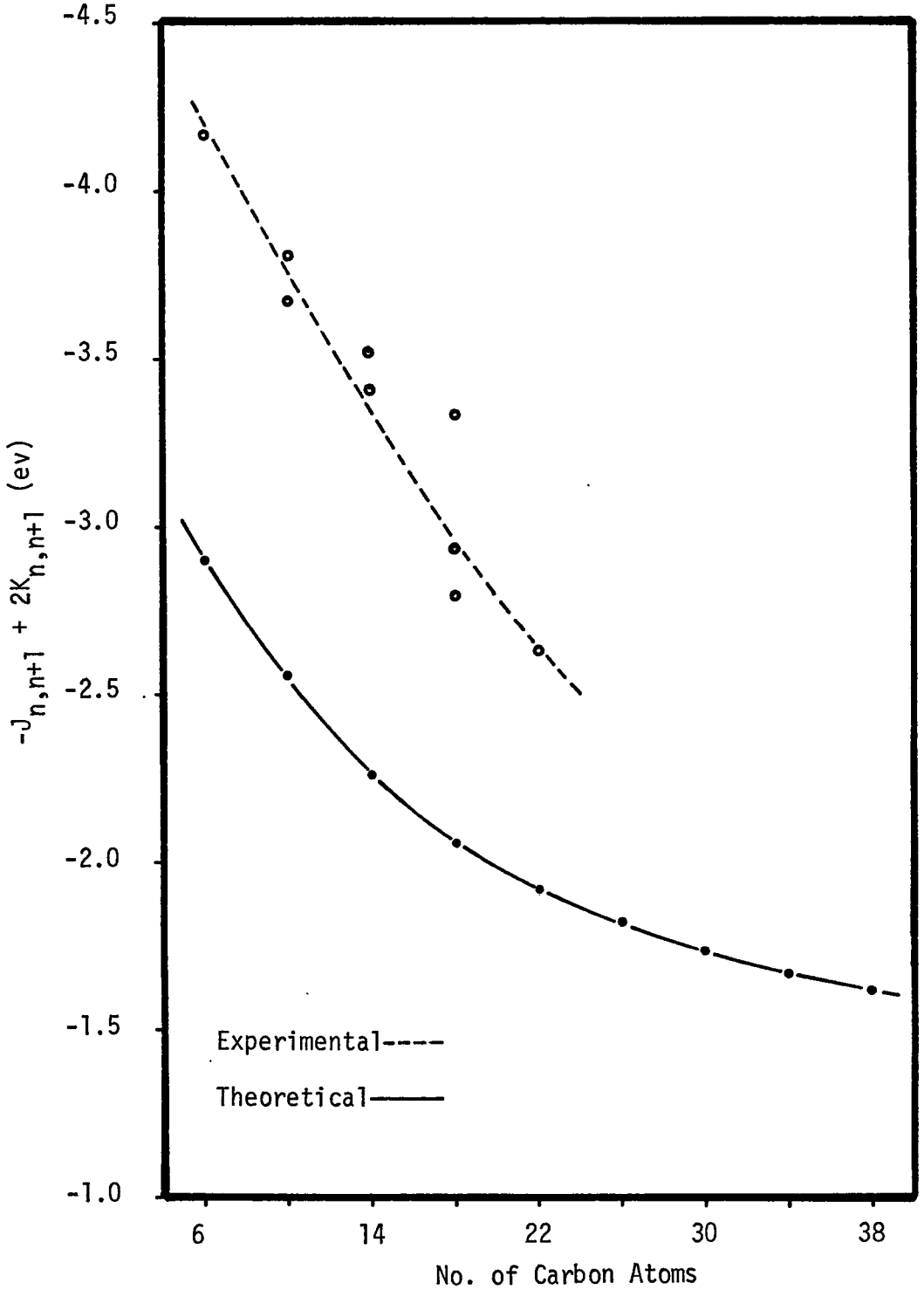


FIGURE 3.7. PLOT OF TWO-ELECTRON TERM $(-J_{n,n+1} + 2K_{n,n+1})$ VERSUS NUMBER OF CARBON ATOMS

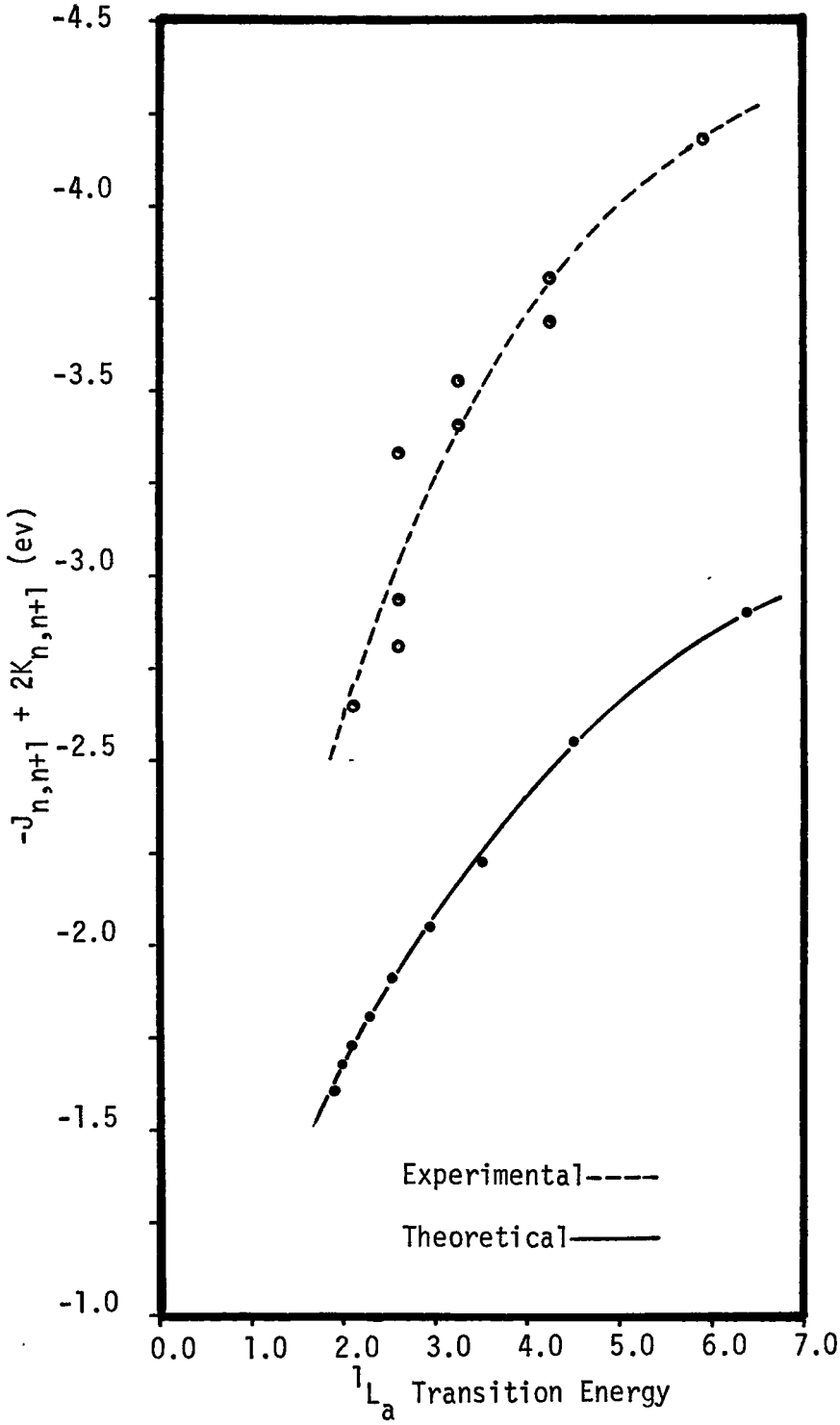


FIGURE 3.8. PLOT OF TWO-ELECTRON TERM $(-J_{n,n+1} + 2K_{n,n+1})$ VERSUS ^1L_a TRANSITION ENERGY

G. Discussion of Results

Figure 3.3 illustrates the behavior of the experimental and calculated values of the IP and EA as a function of the number of carbon atoms in the polyacenes. This graph presents a striking demonstration of the ability of the semi-empirical SCF molecular orbital theory to predict the trends in the value of the IP and the EA caused by a systematic change in the molecular size. This also gives a striking illustration of the inability of the theory to correctly predict the absolute values of the IP and EA.

If, conceptually, the number of rings in the polycyclic aromatic hdyrocarbons are allowed to increase, one will obtain as a limiting case an infinitely long polyacene molecule mathematically equivalent to graphite vapor. In this limiting case, Peacock and McWeeny[81] have shown that the value of ε_n, generally called the work function of graphite, and consequently also ε_{n+1}, will be equal to F_{ii}. The value of F_{ii} which the calculated values of the $-IP(\varepsilon_n)$ and $-EA(\varepsilon_{n+1})$ for the polyacenes approach asympotically is equal to -6.00 ev from equations (3.14) and (3.15). However, the measured value of the work function of graphite, which is supposed to be equal to $-F_{ii}$, is actually about 4.39 ev.[82] This value is much nearer to the experimental value of 4.17 ev for χ which the experimental values of the IP and EA approach asymptotically than to the value of F_{ii} obtained by means of the Pariser approximation.[25] Using this approximation, F_{ii} is equal to $-1/2(I_p + A_p)$ where I_p and A_p are the valence state ionization potential and electron affinity respectively of the $2p\pi$

carbon atom. The only problem is that the work function of graphite is determined from the solid which corresponds roughly to a stacked structure consisting of many layers of infinite two-dimensional carbon molecules. However, it is felt that the work functions of solid and vapor graphite should not differ very substantially.

If in Figure 3.3, instead of forcing the value of F_{ii} (which ε_n and ε_{n+1} approach asymptotically) to be equal to -6.00 ev, one would allow the value of F_{ii} to be equal to -4.17 ev (the negative of the experimental value of χ) then the correspondence of the calculated and the experimental values of the IP($-\varepsilon_n$) and EA($-\varepsilon_{n+1}$) is considerably improved. This certainly indicates that the SCF molecular orbital theory can correctly predict the trends in molecular parameters produced by systematic structural changes, but it also points out the dilemma faced by theoretical chemists since the semi-empirical SCF molecular orbital theory was first formulated. That is, to make the theory fit experimental data better, one would have to abandon the rather rigorous argument presented by Pariser[25] (See Summary of Theoretical Chemistry) which allowed the matrix element F_{ii} to be interpreted in terms of the experimental valence state atomic parameters of the carbon atom and instead, treat F_{ii} as an arbitrarily chosen quantity. Inclusion of the penetration integral, P_i, in F_{ii} would make matters worse since it is a positive quantity preceded by a minus sign in the expression for F_{ii} (equation 3.14). Rather than abandon Pariser's approximation, most workers have concentrated on obtaining new values for the valence state ionization potential and

electron affinity of atomic carbon in a conjugated hydrocarbon (that is, a $2p\pi$ carbon) either by reinterpretation of the existing experimental data from which these atomic parameters are determined or by attempting to obtain improved experimental data. For example, see Ref. 43 and 46. However, these attempts do not appear to have even changed the value of F_{ii} to -4.39 ev, the negative of the measured work function of graphite, much less to probably the better value of -4.17 ev, the negative of the measured value of χ.

Figure 3.4 shows the calculated values of the $IP(-\varepsilon_n)$ and $EA(-\varepsilon_{n+1})$ plotted as a function of the energy, $\Delta E_{n,n+1}$, of the electronic transition from the nth to the (n+1)th molecular orbitals and the measured IP and EA as a function of the energy of the ^1L_a transition of the polyacenes. This is the type of plot generally given in correlation studies since these molecular parameters are related to the electronic transition energy by equation (3.12). However, in this particular study it does not reveal much more information than the plot as a function of molecular size since this transition energy is simply a decreasing function of increasing polyacene size which is equal to zero for the two-dimensional infinite molecule. It is of interest to note that the measured ^1L_a transition energy of these molecules is lower than the calculated value, $\Delta E_{n,n+1}$, by a fairly constant value of 0.25 to 0.40 ev. Thus, we see again an example of a good prediction of the trend by the theory but some difficulty in predicting absolute values.

As mentioned earlier, if one could shift the calculated or the experimental values of the IP and EA so that both the calculated and

experimental values would approach the same value asymptotically with increasing molecular size, the correlation of these two sets of data would be considerably improved; however, they will not coincide exactly. Rather the value of the measured IP is greater than the calculated value, ranging from a value of about 0.50 ev greater than the calculated value for naphthalene down to a value about 0.15 ev greater for pentacene. The measured EA is less than the calculated value, ranging from a value about 0.50 ev less than the calculated value for naphthalene down to a value about 0.15 ev less for pentacene. These errors are, of course, generally symmetric, that is, the measured IP will be greater than the calculated value by the same amount that the measured EA will be less than its calculated value. These discrepancies between the measured and calculated parameters become evident in the plots of the measured and calculated values of the quantity (IP - EA) versus molecular size shown in Figure 3.5. This is also shown in the plots of the measured values of (IP - EA) versus the ^1L_a transition energies and the corresponding calculated values versus $\Delta E_{n,n+1}$ transition energies given in Figure 3.6.

It has often been argued that the errors in the calculated absolute values of the IP and EA occur in such a manner that they mostly cancel when taking the difference of the two.[83,84] That is to say, the calculated and experimental values of (IP - EA) should coincide quite well, although the absolute values of the individual parameters may differ substantially. This argument is presented to show that these errors in absolute values should not affect the accuracy of the calculated

electronic transitions very much since only the differences of the molecular orbital energies enter the expression for the transition energy given by equation (3.12). However, Figures 3.5 and 3.6 indicate that this argument is only partially valid since the plots of the calculated and measured values of (IP - EA) obviously do not coincide. In fact, the only error which cancels is that caused by the calculated values of the IP($-\varepsilon_n$) and EA($-\varepsilon_{n+1}$) approaching a different asymptotic value with increasing molecular size than that approached by the measured EA and IP. Those errors in the absolute values, discussed in the preceeding paragraph, which would still remain if the measured and calculated values approached the same asympotic value will, in general, not cancel and may be additive as is evidenced by Figures3.5 and 3.6. The fact that the calculated and measured (IP - EA) curves comverge with increasing molecular size indicates that both quantities are approaching the same value in the limit of the infinitely long polyacene molecule. The limiting value is, of course, zero. This sort of behavior again demonstrates the basic correctness in the molecular orbital model of molecular structure, at least for the class of conjugated aromatic hydrocarbon molecules. That is to say, the molecular orbital method apparently gives a valid picture of molecular structure even though the absolute accuracy of the method is seriously impaired by such problems as the LCAO approximation for the best molecular orbitals, the neglect of the correlation of electrons within the same orbital, etc.

Figures 3.7 and 3.8, which show plots of the experimental and calculated values of the two-electron term, $-J_{n,n+1} + 2K_{n,n+1}$, versus molecular size and transition energy respectively, indicate what should have been obvious from the behavior of the previously discussed parameters and quantities. That is, the calculated values of the two-electron termare rather substantially less in magnitude than the experimental value of this term for the series of polyacenes. It was noted earlier that the ^1L_a transition energy was consistently less than the calculated transition energy, $\Delta E_{n,n+1}$ and from Figures 3.5 and 3.6, it can be seen that the measured value of IP - EA is larger than the calculated value. The calculated value of IP - EA is, of course, equal to $\varepsilon_{n+1} - \varepsilon_n$. Thus, if in equation (3.12), the calculated values for the electronic transition energy, $\Delta E_{n,n+1}$, and $\varepsilon_{n+1} - \varepsilon_n$ were corrected in the directions dictated by the experimental values, it could be predicted that the two-electron term would have to have a larger negative value. That is, the rather small errors between the calculated and experimental values for the transition energy and the orbital energy difference have been combined in such a manner so as to produce a rather substantial apparent error between the calculated value of the two-electron term and its experimental counterpart. This is called an apparent error since the experimental value of the two-electron term is actually not a measurement but is calculated by substituting the measured values of the electronic transition energy and the measured orbital energy difference, (IP - EA), in the theoretical expression given by equation (3.12). Therefore,

the experimental two-electron term merely reflects the already discussed differences between the calculated values of $\Delta E_{n,n+1}$ and the observed ^1L_a transitions and the differences in the calculated and measured values of (IP - EA). One may wish to interpret this discrepancy between the calculated and experimental values of the two-electron term as rather substantial underestimation of the effects of electron-electron interaction in the molecule by the theory since this is the origin of the two-electron term. However, it is doubtful if one may attribute any additional fundamental meaning to the differences between the calculated and experimental two-electron terms on the basis of this particular study of the polyacenes.

H. Conclusions

The obvious conclusion to be drawn from this study is that the semi-empirical SCF molecular orbital theory is fully capable of correctly predicting the trend in the changes of molecular parameters, such as the ionization potential (IP) and electron affinity (EA), caused by a systematic change in molecular size (as occurs in the series of polyacenes). This property of the theory is quite important and demonstrates again the soundness of the molecular orbital quantum mechanical model for chemical systems, particularly the conjugated hydrocarbons. However, the well-known inability of the theory to predict absolute values for the molecular parameters is quite evident and the errors do not all cancel when one considers the orbital energy difference, $\varepsilon_{n+1} - \varepsilon_n$, as has been previously argued.

It may be argued that one may be able to obtain a better correlation of calculated and experimental values by further experimentation with the theoretical approximations and parameters. The errors noted may possibly be decreased by this procedure; however, it is doubtful if such adjustments could ever completely eliminate the amount of discrepancy noted between the experimental and calculated values. Furthermore, the correlation of the experimental values of the IP, EA, and related quantities with the theoretical values calculated in this investigation of the polyacene molecules would be considered significant in any case. This is because the empirical values and approximations used in these calculations are the ones used routinely by many workers for the determination of reasonably accurate theoretical values of electronic transitions.

APPENDIX 1

Let $E_1, E_2, \ldots E_n$ and $A_1, A_2, \ldots A_n$ be two sets of molecular orbital energy levels with $E_1 \leq E_2 \leq \ldots \leq E_n$ and $A_1 \leq A_2 \leq \ldots \leq A_n$. It is now desired to examine the quantity ΔE_A, defined by equation (2.14),

$$\Delta E_A = \sum_{i=1}^{n} (E_i - A_i)^2 \tag{1}$$

with respect to a constant shift, x, of all the energy levels, A_i. Let a new set of energy levels, $A_1', A_2', \ldots, A_n'$ be given by $A_1' = A_1 + x$, $A_2' = A_2 + x$, $\ldots$, $A_n' = A_n + x$. Then from equation (1) one may write

$$\Delta E_{A'}(x) = \sum_{i=1}^{n} [E_i - (A_i + x)].^2 \tag{2}$$

To find the minimum of $\Delta E_{A'}(x)$ with respect to x, the partial derivative of $E_{A'}(x)$ with respect to x is set to zero, that is,

$$\frac{\partial[\Delta E_{A'}(x)]}{\partial x} = -2 \sum_{i=1}^{n} [E_i - (A_i + x)] = 0. \tag{3}$$

Solving equation (3) gives

$$x = \frac{1}{n} \sum_{i=1}^{n} (E_i - A_i). \tag{4}$$

For the even alternant conjugated hydrocarbons, the energy levels are given by n/2 pairs of the form

$$\begin{aligned} E_i &= \alpha + \varepsilon_j \qquad 1 \leq i \leq n/2, \qquad j = \frac{n}{2} + 1 - i \\ E_i &= \alpha - \varepsilon_j \qquad \frac{n}{2} + 1 \leq i \leq n, \quad j = i - n/2 \end{aligned} \tag{5}$$

and

$$A_i = \alpha + a_j \qquad 1 \leq i \leq n/2, \qquad j = \frac{n}{2} + 1 - i$$
$$A_i = \alpha - a_j \qquad n/2 + 1 \leq i \leq n, \quad j = i = n/2 \tag{6}$$

where α is the Coulomb integral for carbon. One may rewrite (4) as

$$x = \frac{1}{n} \{ \sum_{i=1}^{n/2} (E_i - A_i) + \sum_{i=n/2+1}^{n} (E_i - A_i) \} , \tag{7}$$

and substitute for E_i and A_i from equations (5) and (6) to get

$$x = \frac{1}{n} \sum_{i=1}^{n/2} [(\alpha + \varepsilon_{n/2+1-i}) - (\alpha + a_{n/2+1-i})]$$
$$+ \sum_{i=n/2+1}^{n} [(\alpha - \varepsilon_{i-n/2}) - (\alpha - a_{i-n/2})]\} \tag{8}$$
$$= \frac{1}{n} \sum_{i=1}^{n/2} [\varepsilon_{n/2+1-i} - a_{n/2+1-i}] - \sum_{i=n/2+1}^{n} [\varepsilon_{i-n/2} - a_{i-n/2}]\} \tag{9}$$

By defining a new summation index $j = n/2+1-i$ in the first summation and a new summation index $j = i - n/2$ in the second summation, one obtains

$$x = \frac{1}{n} \{ \sum_{j=1}^{n/2} (\varepsilon_j - a_j) - \sum_{j=1}^{n/2} (\varepsilon_j - a_j) \} = 0 \tag{10}$$

That is, ΔE_A, as defined, is a minumum with respect to a constant shift of the set of energy levels, $\{A_i\}$ in the case of an even alternant conjugated hydrocarbon

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