

**ELECTRONIC EMISSION SPECTROSCOPY OF CERTAIN
METALLO MESOPORPHYRINS AND PHTHALOCYANINES**

A Thesis

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by

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ABSTRACT

The low temperature emission spectra of the dimethyl ester of mesoporphyrin IX and its Co(II), Ni(II), Cu(II), Zn(II), Pd(II), and Cd(II)-derivatives have been obtained. The emission characteristics of Ag(II) derivative were investigated; however, no emission bands could be detected. The spectral properties of these compounds are discussed in terms of the degree of spin-orbital coupling present in such molecules. Several predictions are made regarding the magnetic character of the central metal ion and the metal-porphyrin geometry present in these porphyrin molecules.

In addition, a comparison is made of the intensities of the fluorescent spectra of Zn-mesoporphyrin with Zn-phthalocyanine. This indicates that there is a decrease in the size of the area between the pyrrole rings of the former molecule compared to the latter.

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I.

INTRODUCTION

INTRODUCTION

Nature of the Porphyrins

The porphyrins represent a class of compounds widely distributed in nature. As a result, much information concerning their chemical and physical properties is constantly being compiled. One such porphyrin-like compound, chlorophyll, is directly concerned with photosynthesis. Just what role it plays in this process is not completely understood at the present time. Also, little is actually known about the type of bonding that exists between the porphyrin nucleus and various metal atoms. In order to gain better insight to these, as well as to other problems, it is necessary to study not only the natural porphyrins, but also the artificial porphyrins.

The porphyrin molecules are made up of four pyrrole rings joined by four methine groups, as in Figure 1. Various groups are substituted onto the porphyrin nucleus to form the different parent porphyrins. It has been shown, from molecular orbital calculations, that all of these molecules possess a high degree of aromaticity (1, 2).

The absorption spectra of the porphyrins and their metal derivatives consists of a series of narrow, well

defined bands in the visible region of the spectrum. These absorption bands are due to π - π electronic transitions.

The Importance of the Lowest Excited States

When a molecule is excited (by the absorption of light), it cannot normally re-emit its electronic excitation energy until it resides in the lowest vibrational level of the lowest electronic state. Since the molecule is often excited to higher electronic states, it must, therefore, necessarily lose this excess energy by a rapid, radiationless process known as internal conversion in order to pass into the lowest electronic excited state of the series (for example, see the work by Kasha (3)). Internal conversion usually occurs about 10^4 times faster than the time required for direct emission from an upper excited state, so that the molecule normally does not have time to re-emit its excitation energy from any state other than the lowest excited state.

All molecules possessing an even number of paired electrons have diamagnetic ground states which are termed singlet. When such a molecule is excited, the electron pairing can be sustained and thus the excited state is also a singlet. Such a transition is designated as: singlet $\rightarrow$ singlet. However, it is possible that during an excitation,

or more probably during the time a molecule is in an excited singlet electronic state, the electrons in their different space orbitals will uncouple. In such a case, a state of higher multiplicity results; this is the triplet state. The transition from a molecular singlet to a triplet state occurs due to a phenomenon designated as intercombination. Due to the process of internal conversion, only the lowest excited triplet state is normally capable of re-emitting the excitation energy.

Figure 2 illustrates the fundamental processes involved in electronic transitions. Fluorescence is the term used for singlet $\longrightarrow$ singlet emissions, and phosphorescence indicates triplet $\longrightarrow$ singlet emission.

By application of Hund's rule, the triplet state will be lower in energy than the corresponding singlet state of the molecule in most every instance. This would mean that the phosphorescence is found at longer wavelengths than the fluorescence. This is the best distinction available between these two processes. If one compound of a similar series of compounds exhibits both fluorescence and phosphorescence, and if the emission for another member of this series occurs only in the region assigned to the phosphorescence of the first, then it can safely be assumed that the

emission of the latter was phosphorescence.

Fluorescent lifetimes are usually of the order of 10^{-8} to 10^{-10} seconds, whereas the lifetimes of phosphorescence are usually much longer -- 10^{-4} to several seconds. These lifetimes are an indication of the "allowedness" of a transition. If, for some reason, the singlet $\rightarrow$ singlet process is somewhat forbidden, then the corresponding emission (fluorescence) will be longer lived and have a lower intensity of emission. Also, the lifetime of phosphorescence can be shorter because of certain perturbations (vid. seq. page). In such cases, it becomes obvious why no clear cut distinction exists between fluorescence and phosphorescence solely on the basis of lifetimes.

Since the lifetimes of triplet states are usually long, some means must be taken to prevent loss of excitation energy by collisional deactivation. This is accomplished by studying phosphorescent emissions in a rigid glass media. The high viscosities in such systems prevent collisions between molecules which would drain off the excitation energy.

Direct excitation from the singlet ground state to the triplet excited state is an impracticable means to study the phosphorescent emission of a molecule because certain selection rules prevent direct singlet $\rightarrow$ triplet absorption.

A much more efficient mode to populate the triplet state is by the intersystem crossing process. The degree of intersystem crossing (excited singlet to lowest triplet) can be increased by spin-orbital perturbations.

The degree of spin-orbital interaction is dependent on three factors: the nuclear charge of atoms or ions present in the molecule; the distance of approach by the optical electron to the nucleus of atoms or ions and to other electrons in the molecule; and the presence of paramagnetic atoms or ions in the molecule.

The spinning motion of the optical electron creates a magnetic moment which then interacts with the magnetic field set up by the motion of the nucleons of a high atomic number atom or ion. The higher the atomic number, the greater the magnetic moment created, and the greater the spin-orbital interaction. (The other electrons in the system will also create a magnetic field which can interact with the field of the optical electron).

The spin-orbital interaction is also dependent on the distance of approach of the optical electron to the nucleus of heavy elements. The magnetic field of the nucleus is non-uniform; it diminishes rapidly as the distance from the nucleus is increased. Thus, the closer the optical electron can

approach the nucleus of a high atomic number atom or ion, the greater will be the spin-orbital interaction. This degree of approach can depend on the electronic arrangement of the high atomic number element. Yuster and Weissman (4) have demonstrated this dependence of spin-orbital interaction by employing atoms or ions in the molecule which had incom-
pleted inner shells.

The greatest effect on spin-orbital interaction is brought about by the presence of a paramagnetic ion or atom in the molecule. The unpaired electron creates such a large, non-homogeneous magnetic field that only phosphorescence is observed (i.e., there is complete intersystem crossing from the excited singlet to the triplet state). This effect is demonstrated in the papers of Yuster and Weissman (4), McClure (5), and Becker and Kasha (6).

The overall effects of increasing spin-orbital interaction may be summarized as follows:

- (1). there is a decrease in the quantum yield of fluorescence, with a consequent increase in the quantum yield of phosphorescence;
- (2). the lifetime of the phosphorescence is decreased.

Emission Spectra of Porphyrins and
their Metal Complexes

Most of the early work on the emission spectra of the porphyrin molecules was carried out by Dhere, Stern, and Kosaki (see references 27-32, 43-47, 48-50, and 52 in the thesis by Becker (7)). At this time, these investigators observed only the fluorescent emission of such molecules. Table I gives the emission data compiled by these authors, as well as that of several others.

The most complete study, to the present time, on the effects of a metal substituent on the emission spectra of porphyrin was carried out by Haurowitz (8). He studied the fluorescent spectra of fifteen metallo-derivatives of one of the mesoporphyrins. It was observed that all the diamagnetic derivatives possessed fluorescent bands, while the paramagnetic complexes had no such emission. This paper also gives a good discussion of the bonding between the metals and the porphyrin nucleus and of the absorption spectra of these metal complexes. Haurowitz stated that the absorption band maxima shifted to shorter wavelengths with increasing paramagnetic susceptibility of the metal ion.

Albers, Knorr, et al (9, 10) reported that the Ni-, Ag-, and Zn-derivatives of a tetraphenylporphine had fluorescent bands. Of these, only the Zn-complex had fluorescent bands in a region different from that of the parent

porphyrin. This, coupled with the fact that the emission intensities of the Ni- and Ag-derivatives were very weak, would necessarily lead to the conclusion that their reported emission was really just the fluorescence of the parent porphyrin present in a trace amount.

Becker and Kasha (6) were the first to report what appeared to be the true emission spectra of a nickel porphyrin. They found that it was totally phosphorescent and that its emission intensity was very low. Their results are recorded in Table II. (For a further discussion of this paper, see Section IV of this thesis).

Absorption Spectra of Porphyrins and their Metal Complexes

Many comprehensive studies of the absorption spectra of the metallo-porphyrins have been carried out by such investigators as Stern, Corwin (see references 55-74 and 75-81 in thesis by Becker (7)), and Haurowitz (8, 11). As long ago as 1918 Milroy (12) described the spectroscopic characteristics of the Zn-, Cd-, Ni-, Co-, Fe-, Cu-, Sn-, and Pb-derivatives of hematoporphyrin.

In recent years several review articles concerning the absorption spectra of the porphyrins have been published (1, 2, 13, 14). Of particular importance was that of

Williams (14). He found that the more electronegative the metal in the porphyrin molecule, the more the band maxima were shifted toward shorter wavelengths (i.e., the order of increasing shift was: $\text{Pd(II)} > \text{Ni(II)} > \text{Co(II)} > \text{Cu(II)} > \text{Zn(II)} > \text{Fe(II)} > \text{Mn(II)} > \text{Mg(II)} > \text{Ba(II)}$). The fact that the intensity of the first absorption band increased with an increase in the electron donor character of the metal was also noted.

Quite often the absorption spectrum of the metal porphyrin is used as a means to gain information concerning the nature of the bond between the porphyrin nucleus and the metal. Dorrough and co-workers (15) used the metallo-tetraphenylporphines for such a correlation. They concluded that those metals which had a d orbital available for bonding, had a very depressed first band in the first electronic transition (cf. their figures for Cu, Ag, Ni, and Co). The divalent metals which had no d orbital available for bonding were shifted to longer wavelengths compared to the "d group", and their first absorption band was much more intense (cf. their figures for Mg, Ba, Zn, Cd, and Sn). If the metalbporphyrin was completely ionic in character, it had an entirely different type of spectra from either of the above.

In addition, it was noted that the metals in a given group in the periodic table also presented certain general trends. As one proceeds down a group (i.e., increasing electropositivity), the entire spectrum shifted to longer wavelengths, the first band in the first electronic transition was more intense, and the extinction coefficient of the strong absorption band near 4000 Å (the Soret band) decreased.

Other studies of the absorption spectra of the metalloporphyrins which deserve mention are those by Seely (16), Thomas (17), and Gouterman (18).

Scope of the Present Investigation

Extensive X-ray and infrared analyses are normally carried out in an effort to ascertain the molecular geometry of a molecule. However, as was previously pointed out, several papers have recently appeared in which an attempt was made to determine the type of bonding present in these metalloporphyrins from molecular orbital calculations and from absorption spectral data. In particular, the papers by Simpson (1), Longuet-Higgins (2), Seely (19), Dorrough, et al (15), and Gouterman (18) are to be complimented. However, all of these papers fail to discuss or explain the

discrepancies encountered in such things as magnetic susceptibility and emission spectra. For example, in the paper by Dorough and co-workers (15), it was implied that Ni-, Co-, Cu-, and Ag-ions were bonded to the porphyrin nucleus in the same manner since their absorption spectra were so similar. All of these metals were said to utilize one of their d orbitals for bonding, and this would mean that the Ni-porphyrin must be diamagnetic (20).

If the Ni-porphyrin is diamagnetic, then its emission spectra should be fluorescent, while that of the paramagnetic Cu-, Ag-, and Co-porphyrin should be solely phosphorescent (8). No fluorescent bands for the Ni-porphyrins have been definitely established up to the present investigation.

X-ray studies have shown that most of the divalent metallo-phthalocyanines are planar molecules (21, 22, 23, 24). Since the porphyrins are so closely related to the phthalocyanines (see Figure 1), it follows that they should also be planar. This would lead to the conclusion that the transition metal derivatives of these compounds should have dsp^2 square planar bonding between the central metal atom and the four pyrrole nitrogens. A later, more detailed investigation indicates that while the metal ion in the Ni-porphyrin is

in the plane of the whole molecule, the four pyrrole nitrogens are out of the plane (25). This would necessitate a different type of bonding between the metal atom and the porphyrin ring, as previously proposed by Becker (7).

The present investigation deals with the emission spectra of the transition metallo derivatives of the dimethyl ester of mesoporphyrin IX and of certain metallo-phthalocyanines. By considering the type of emission (i.e., fluorescence and phosphorescence) obtained, their relative intensities and lifetimes, certain deductions can be made concerning the type of bonding between the porphyrin and the metal, and the magnetic susceptibility of the metal ion. It will be shown that the emission data generally provide a superior means of determining these than do absorption spectral studies.

In brief summary:

- (1). To the present time, absorption spectral studies have been incapable of predicting certain unusual spectral emission properties often found in many molecules.
- (2). Absorption spectral data do not present a definitive method of determining the magnetic character

of the metal ion in compounds such as these metallo-porphyrins.

- (3). It will be demonstrated that emission spectral studies can give a great deal of information concerning the nature of the metal-ligand bonding in molecules such as the metallo-porphyrins. Even though quantitative information can be obtained by X-ray studies, certain valuable qualitative information can be obtained in a much shorter time from emission spectral data. Moreover, it will be shown that qualitative deductions regarding magnetic susceptibility can be obtained from emission data in a much shorter time than required by conventional methods.

II.

EXPERIMENTAL

EXPERIMENTAL

Purification of Solvents

N, N-dimethylformamide was obtained from Distillation Products Industries, Rochester, N. Y., Division of Eastman Kodak Company. Two grades of purity were employed: (1) spectro-grade - for all spectral work; and (2) Eastman White Label - for all procedures preliminary to obtaining the spectra. These were used without further purification.

The 1-chloronaphthalene, Eastman White Label, also obtained from Distillation Products Industries, was used without further purification. The absorption spectra of this solvent versus air indicated no absorption in the region of 1000 to 370 millimicrons.

Diethyl ether was purified by refluxing Baker's A.R. anhydrous ether over calcium hydride or metallic sodium for several hours. This was then distilled through a 36-inch fractionating column packed with glass helices. The distillation head was a total condensation - partial take-off type. A reflux ratio of 1:10 was used for this and all other distillations.

Absolute ethanol was used from freshly opened bottles without further purification. It was obtained from U. S. Industrial Chemicals Co., Division of National Distillers Products Corp., N. Y.

Phillips Petroleum Special Products Division supplied instrument grade isopentane which was further purified by fractional distillation over calcium hydride. The fractionating column was a modified Widmer column with a distillation head comparable to that described for the ether distillation. In addition, the isopentane was passed through a column 18 inches in length with a diameter of 22 millimeters packed with silica gel (60 to 200 mesh, obtained from the Davison Chemical Co.). The silica had been activated by heating to 400° C.

The 3-methylpentane, Phillips Pure Grade (99 mol % minimum), was distilled over sodium through a 36-inch fractionating column packed with glass helices. The distillation head was equipped with an automatic timing mechanism which was adjusted to give a 1:10 reflux ratio. The 3-methylpentane was also passed through an activated silica gel column 18 inches long with a diameter of 22 millimeters.

Purification and Preparation of Compounds

Mesoporphyrins

The mesoporphyrin IX, dimethyl ester and its Fe(III)Cl-, Co(II)-, Ni(II)-, Cu(II)-, Pd(II)-, and Zn(II)-metal derivatives were kindly donated by the Monadnock Research Institute,

Inc., Antrim, N. H. Their absorption spectra in N, N-dimethylformamide indicated that they were of high purity. Subsequent investigation of their emission spectra disclosed the presence of trace amounts of the parent mesoporphyrin in the cobalt, nickel, and palladium derivatives. An attempt was made to purify them by the method of Corwin and Erdman (26). According to this procedure the metallo-mesoporphyrin is recrystallized several times from a chloroform-methanol mixture. This method takes advantage of higher degree of solubility of the parent mesoporphyrin in the chloroform. However, it was found that this method did not completely remove the contaminant.

The second procedure, which also proved unsuccessful, was an acid extraction of the parent mesoporphyrin as described by Erdman, et al (27). A 3 to 5 mgm. sample was extracted four successive times with 2 ml. portions of 98.8% formic acid, followed by four more extractions using 2 ml. portions of 50% formic acid. After these extractions, the sample was filtered with suction, washed with water and ethanol, and finally dried for two hours under high vacuum.

When the emission spectra showed trace quantities of the parent mesoporphyrin were still present, a longer extraction with the 98.8% formic acid was attempted. This time,

the sample (3 to 5 mgm.) was extracted for twenty hours, with continuous stirring, using 4 ml. formic acid. This was carried out in a 10 ml. erlenmeyer flask equipped with a magnetic stirrer. While this procedure greatly reduced the amount of contaminant, it still failed to give the degree of purity required for this study.

In view of the above facts, another step was employed in conjunction with the acid extraction for purification of the palladium mesoporphyrin. (The cobalt mesoporphyrin was found to be unstable in an acid media; therefore, the preliminary acid treatment was eliminated.). According to Erdman (27), if the formic acid treatment fails to remove the metal free mesoporphyrin, column chromatography may be beneficial. Therefore, the acid treated samples were dissolved in a minimum amount of hot reagent grade benzene and placed on a calcium carbonate column. After developing the column with benzene, the middle portion of the main dark red band was removed. This portion contained the desired product and it was extracted from the calcium carbonate column with benzene and filtered through Whatmann #42 filter paper. The resulting solution was carefully evaporated to dryness under vacuum. This time the emission spectra of the sample either showed no trace of parent mesoporphyrin, or only

exhibited these emission bands during extremely long exposure.

The cadmium and silver(II)-mesoporphyrin IX, dimethyl ester compounds were prepared in a manner similar to that described by Dorough, et al (15), for metallo-derivatives of tetraphenylporphine. Mesoporphyrin IX, dimethyl ester (30 mgm.) was used as the starting material for both products. The metal was introduced by refluxing the parent mesoporphyrin with four times the calculated amount of the metal acetate in 5 ml. of pyridine. Refluxing was carried out for 1.5 hours, and then the solution was allowed to stand at room temperature overnight.

In preparing the cadmium derivative, the original brownish-red solution changed to a deep maroon after heating. An aliquot of this reaction mixture had an absorption spectra which agreed well in both band position and shape to that reported by Haurowitz (8).

The silver complex represents an unusual type of reaction. In a pyridine media, the di-monovalent silver complex is formed first; however, on vigorous heating, it is converted to the divalent silver derivative. During the boiling process, the brownish-red solution changed to a deep red and a silver mirror formed on the walls of the reaction

flask (for a discussion of this see Dorough, et al (15)).

This reaction could be represented as: $\text{Meso-Ag}_2 \longrightarrow \text{Meso-Ag} + \text{Ag} \downarrow$. Conversion to the metallo-mesoporphyrin was verified by the absorption spectra (8) of an aliquot of this reaction mixture. The reaction mixture was transferred to a small separatory funnel with 5 ml. of benzene. Approximately 10 ml. of water was added to the separatory funnel to remove the bulk of the reaction solvent. The resulting benzene solution was washed several times with water to completely remove the pyridine and the inorganic salts. Following this, the benzene layer was dried over anhydrous sodium sulfate, filtered and evaporated to dryness under vacuum.

It should be remarked that the cadmium complex was found to be unstable to light. Consequently, all steps involving the benzene solution were carried out in subdued light.

It was not expected that the refluxing procedure employing the pyridine solution, would hydrolyze the ester groups of the mesoporphyrin. In order to confirm this, a sample of deuteroporphyrin IX, dimethyl ester was vigorously boiled for 15-20 minutes. The absorption spectra before and after this treatment were identical in all respects. It was therefore concluded that the above procedures had

no adverse effect on the dimethyl ester of mesoporphyrin.

An alternate procedure for the silver derivative was attempted using glacial acetic acid for the reaction solvent. In this solvent the reaction proceeds directly to the divalent silver derivative. An examination of the absorption spectra of the reaction solution did not look like that expected for the Ag(II)-derivative. As a result it was decided to carry out the reaction in pyridine as previously described.

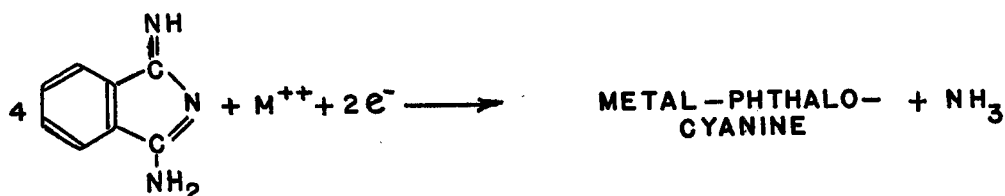
Phthalocyanines

Alpha-metal free phthalocyanine and its Mg-, Co-, Zn-, Fe(III)Cl-, and Sn(II)-metallo derivatives were kindly supplied by the Jackson Laboratories of the E. I. DuPont de Nemours & Company, Inc. These samples were purified by washing first with hot water to remove any extraneous inorganic salts, and then with ethanol. After air drying, the samples were suspended in hot 1-chloronaphthalene, filtered with suction, washed with ethanol, and air dried. This suspension procedure was repeated four times. The absorption spectra of these compounds in 1-chloronaphthalene agreed well with respect to both band maxima and relative intensity to those reported by Anderson, et al (28) and by Linstead, et al (29, 30, 31). These metallo-phthalocyanines were merely

used to establish a set of reference absorption spectra; all metallo-derivatives used in this study were prepared by the procedures outlined below.

The appropriate metal salt was added to a solution of the alpha-metal free phthalocyanine in N, N-dimethylformamide containing a small amount of trimethylphenylammonium hydroxide (32). This mixture was heated for various times over a range of temperatures in an effort to increase the yield of metal phthalocyanine. An examination of the absorption spectra of each of these reaction mixtures always exhibited bands characteristic of the parent phthalocyanine. Since it was desired to have the metal compounds completely free of the alpha-metal free phthalocyanine, this procedure was deemed too inefficient for use.

The method found to be the most simple and the most satisfactory for the synthesis of these compounds was that discussed by Bauman, et al (33). According to these authors, the metallo-phthalocyanine was prepared by the following reaction:



A 2.0 gm. sample of 1-amino-3-iminoisoindolene (kindly supplied by the E. I. DuPont de Nemours & Company, Inc.) was dissolved in 150 ml. of N, N-dimethylformamide. The appropriate molar quantity of the metal salt was added to this solution. This mixture was allowed to react, with constant stirring, within a temperature range of 140 to 150° C (reflux temperature). During the course of the reaction, the solution changed from a light brown to a viscous blue suspension (in the cases of the Mn(II)- and Fe(II)-derivatives, this color was dark brown). The reaction times ranged from 3 hours to 20 hours depending on the metal derivative being prepared.

After completion of this reaction, the mixture was filtered using a suction filter assembly. The precipitate was then washed with 25 ml. of hot dimethylformamide, washed with water, and finally washed with ethanol. To insure its purity, the precipitate was recrystallized several times from 1-chloronaphthalene. The absorption spectra of these compounds agreed with those reported in the literature and with the reference compounds obtained from DuPont.

Tables III and IV give information regarding the preparation and absorption spectra of the compounds prepared by the above method.

Spectral Techniques and Instruments

Instruments

A Beckman model DK-1 automatic recording spectrophotometer was used to obtain all absorption spectra. The sample cells, of either quartz or pyrex, were made by the American Instrument Company, Inc., Silver Spring, Maryland.

For the emission spectra two instruments were employed: (1) - a Steinheil Universal Spectrograph, model GH, obtained from C. A. Steinheil Sohne, Munich, Germany; and (2) - a Hilger Infrared Medium Glass 1-Prism Spectrograph, made by Hilger and Watts, Ltd., London, England.

The Steinheil spectrograph has three adjustable glass prisms, an $f = 3.5$, and a range of 3700 to 9200 Å. Minimum prism settings were used in order to obtain maximum dispersion on the photographic plate. In this case the spectrograph settings were: prisms - 1.5; camera brackett - $26^{\circ}23'$; camera extension - 123.4; camera inclination - 75.6° ; and the collimator at 12.

On the other hand, the Hilger spectrograph contains only one fixed glass prism, but it has the advantage in that its range extends from 3700 to 14000 Å.

A modified Becquerel phosphoroscope was used in conjunction with the spectrograph for obtaining solely phos-

phorescence of compounds whose lifetimes were sufficiently long. The phosphoroscope blades were rotated at 1800 rpm and had slots of a 9° sector of annulus cut in them. These slots were diametrically opposed to the uncut sections enabling a phosphorescence having a lifetime of approximately 5×10^{-4} seconds or longer to be photographed. A diagram of the phosphoroscope is shown in Figure 3.

Techniques

In order to procure the emission spectra, the compound being investigated was dissolved in a solvent system which formed a clear rigid glass when cooled to 77° K. The sample, held in a round pyrex or quartz sample tube, was suspended in a quartz Dewar flask filled with liquid nitrogen. The Dewar had an unsilvered portion which enabled the exciting light to be easily focused on the sample, and at the same time, enabled the light emitted by the sample to enter the spectrograph. Outside frosting on the Dewar was prevented by directing a dried stream of air around the flask.

All emission spectra were taken in one of the following solvent systems:

- (1). "EPA" - 2 parts absolute ethanol, 5 parts ethyl ether, and 5 parts isopentane.

- (2). 2 parts absolute ethanol, 6 parts ethyl ether,
and 5 parts 3-methylpentane.
- (3). 3-methylpentane.
- (4). 2 parts absolute ethanol, 2 parts 1-chloronaphthalene, 8 parts ether, and 6 parts isopentane.
- (5). 3 parts absolute ethanol, 3/4 part N, N-dimethylformamide, 6 parts ether, and 5 parts isopentane.

The exciting light was supplied by a 1-kw Xenon-Mercury Compact Arc lamp manufactured by the Hanovia Chemical Company, Newark, N. J. The wavelength of the exciting light was selectively controlled by placing a combination of solution and colored glass filters between the light source and the sample assembly. Table IV gives the specific filters employed for the various systems. The spectral properties of the glass filters are fully described in the booklet, "Glass Filters", Corning Glass Works, 1948. For information concerning the solution filters see Kasha (34).

The emission spectra were photographed on Kodak photographic plates of the types I-N, I-M, and I-Z. All of these plates are characterized by high sensitivity in the infrared

region. Type I-N plates have a high contrast and high sensitivity extending from 3000 to 8800 Å. The I-M and I-Z, both high contrast, have their highest sensitivity in the regions of 8600 to 10000 Å and 10100 to 11600 Å, respectively. The plates were always hypersensitized immediately before use. Plate specifications and methods of hypersensitizing and developing can be found in Kodak Photographic Plates for Scientific and Technical Use, 7th ed., Eastman Kodak Company, Rochester, N. Y. Reference wavelength lines were placed on the plate by superimposing the emission spectra of a standard Neon Geissler discharge lamp.

After developing the plates, the emission spectra were traced with an Applied Research Laboratories Microphotometer (densitometer) attached to a Bristol Recorder having 0.3 second response. The tracing speed was usually 2 inches per minute. In order to locate the wavelength of the band maxima, a second tracing of the photographed spectra was made by tracing both the sample and reference neon spectra. In order to locate the wavelengths of the bands whose maxima did not exactly correspond to one of the standard neon lines, a dispersion curve was prepared according to the instructions given in the thesis by Elder (35). In this case it was necessary to prepare two dispersion curves -- one for each spectrograph.

Two types of illuminating systems were used in this study to photograph the emission spectra. Figures 4 and 5 are diagrams of the illumination setups. In cases using the phosphoroscope, the direct illumination system was always used.

III.

RESULTS

RESULTS

The results of the emission spectra of all the dimethyl ester mesoporphyrin IX compounds are compiled in Table VI. The phosphoroscope (used in conjunction with the Steinheil Spectrograph) was used to confirm the phosphorescence of the dimethyl ester of mesoporphyrin IX and its Zn-, Cd-, and Pd-derivatives.

Figures 6 through 13 are plots of the emission spectra of the compounds investigated. The relative intensities of the emission bands can be seen by examining these figures. These plots were obtained from the densitometer tracings by using the dispersion curves to determine the wavelengths of the bands.

The emission spectra of Zn-phthalocyanine (cf., Figure 14) is included in these figures. Only the fluorescent spectra of the alpha-metal free phthalocyanine and the Zn-derivative could be observed. Since Becker and Kasha (16) could not detect the phosphorescent spectra for the metallo-phthalocyanines in the photographic infrared up to 9000 Å, the infrared region beyond 9000 Å was examined in this investigation. The Cu-phthalocyanine sample was exposed for periods no less than 8 hours using both an I-M

and I-Z photographic plate (with maximum sensitivity in the regions of 8600 - 10000 Å and 10100 - 11600 Å, respectively). As a result of these long exposures, the plate background was so high that only intense emission bands could have been detected. Due to this plate darkening and lack of emission bands this project was carried no further.

IV.

DISCUSSION

DISCUSSION

Mesoporphyrins

This investigation confirms the earlier work of Becker and Kasha (6) in which they reported what appeared to be a phosphorescent emission from Ni-etiochlorophyll II. The emission spectra from the dimethyl ester of Ni-mesoporphyrin IX is sufficiently different from that of the other metallo-mesoporphyrins to clearly establish its individuality. The emission consists solely of phosphorescence. In addition, the emission spectra of the dimethyl ester of Co-mesoporphyrin IX has been found to consist solely of phosphorescence.

The transition metallo-derivatives of mesoporphyrin provide an excellent series of compounds to illustrate the effect of increased spin-orbital interaction on the emission spectra. The parent mesoporphyrin exhibits both fluorescent and phosphorescent emission bands. The intensity of the fluorescence is so great that it is difficult to observe the phosphorescent bands. As a result, the phosphorescence of the parent mesoporphyrin could be identified only by use of the phosphoroscope. When a paramagnetic metal is complexed with the porphyrin molecule, spin-orbital interaction

is greatly increased and complete quenching of the fluorescence is observed. Cu-mesoporphyrin illustrates this effect. The emission spectra of the Cu-derivative consists solely of phosphorescence, and the lifetime of the triplet state becomes too short to observe phosphorescence with the phosphoroscope (the lifetime was estimated to be less than 10^{-4} seconds). A comparison of the total emission spectra of the parent mesoporphyrin with that of Zn-mesoporphyrin illustrates the atomic number effect on spin-orbital interaction. When Zn-is complexed with porphyrin, the quantum yield of phosphorescence is considerably greater than that of the parent compound.

As previously stated, the metallo-mesoporphyrins should exhibit dsp^2 bonding between the metal ion and the porphyrin nucleus if they are planar molecules. This bonding scheme requires that the divalent Ni ion have an electronic configuration similar to that for the Zn ion (i.e., no unpaired electrons). Complexing the Ni ion (via dsp^2 bonding) with the parent mesoporphyrin should have much the same effect on the emission spectra as did the introduction of the Zn ion. Since the emission spectra of the later contains both fluorescence and phosphorescence, and the atomic number of Ni is

less than that of Zn, then the Ni-derivative would be expected to contain fluorescent bands. Contrary to this prediction, the Ni-mesoporphyrin is solely phosphorescent. If the Ni ion is bonded to the porphyrin nucleus with dsp^2 bonds, then there are two possible explanations for this unexpected emission (see Becker (6)):

- (1). The Ni atom is not diamagnetic.
- (2). There are other perturbations present in the Ni-porphyrin which can increase the spin-orbital interaction in the system similar to that of a paramagnetic ion or atom.

If the metal atom in the Ni-mesoporphyrin is considered paramagnetic, the possible electronic configurations would require the presence of two unpaired electrons no matter what metal-porphyrin bonding scheme is employed. Since Cu-mesoporphyrin, with only one unpaired electron, has sufficient spin-orbital interaction to allow complete intersystem crossing from the excited singlet state to the excited triplet state, it might be inferred that the presence of two unpaired electrons could further increase this spin-orbital interaction. Such an increase in spin-orbital interaction would be expected to result in an intensity of

phosphorescence equal to or greater than the Cu-complex. However, the intensity of emission of the Ni-mesoporphyrin is much weaker than that of the Cu-complex, indicating that Ni and Cu are probably not alike with respect to their magnetic susceptibilities. (This intensity difference could be caused by some type of radiationless internal degradation process in the Ni compound. This, too, would indicate a difference between the Cu and the Ni bonding schemes).

The lifetime of the triplet state can provide a method by which the magnetic character of the metal complex can be determined. For instance, the phosphorescent emission of Zn-mesoporphyrin (diamagnetic) can be obtained with the phosphoroscope whereas that of the Cu-derivative (paramagnetic) cannot. Even though phosphorescence of Ni-mesoporphyrin could not be obtained through the phosphoroscope, there remains the possibility that the weak intensity of emission could explain this.

The X-ray data (25) concerning the odd arrangement of the pyrrole nitrogens around the central metal atom in Ni-porphyrin would require that the bonding scheme could no longer be dsp^2 square planar. The metal-porphyrin geometry of such a system would indicate that the bonding is that of an irregular tetrahedron (dp^3 or dsp^2). This arrangement

could tend to pull the pi electron system closer to the central metal ion. As a result, the metal ion would be able to perturb the system to a greater extent than if dsp^2 square planar bonding had been utilized. This perturbation could increase the spin-orbital interaction to such an extent that only phosphorescence would be observed. Again, the relative weakness of intensity could be explained by some radiationless internal degradation process inherent in the Ni-porphyrin molecule.

Pd-mesoporphyrin, like the Ni analogue, has an emission consisting solely of phosphorescence. The intensity of this emission appears to be even greater than that obtained from the paramagnetic Cu-complex. This implies that intercombination is equal to or greater than that of the Cu-derivative. However, the lifetime of the triplet state is much longer in the Pd-compound than that in the Cu-porphyrin. The lifetime for the Pd-mesoporphyrin was estimated to be approximately 5×10^{-4} seconds by considering the time of exposure and relative intensity of the emission observed with the phosphoroscope. This difference in lifetime could only lead to the conclusion that the Pd-mesoporphyrin is diamagnetic.

Thus, the question still remains -- why is the Pd-complex solely phosphorescent? Whether the increase in atomic number between Zn and Pd is sufficient to completely quench the fluorescence can easily be tested by examining the emission spectrum of the metal porphyrin with a similar atomic number but known to be diamagnetic. The Cd-porphyrin represents such a compound. The spectrum of the Cd-derivative contains weak fluorescent bands in addition to the intense phosphorescent emission. Furthermore, the lifetime of the triplet state of Cd-mesoporphyrin is sufficiently long to enable observation of the phosphorescence with the phosphoroscope; this is approximately 5×10^{-4} seconds. Thus, the atomic number effect alone is not the cause of the quenching of fluorescence. Since the Pd ion is more electronegative than the Cd ion (36), there remains the possibility that this factor could be an additional perturbation to the system of sufficient magnitude to quench the fluorescence. The similarity of the triplet state lifetimes, in addition to the Pd-Cu comparison makes it conclusive that the metal ion of Pd-mesoporphyrin is truly diamagnetic.

Thus, Pd could be bonded to the porphyrin by dsp^2 square planar bonding. On the other hand, if Pd-mesoporphyrin utilizes the same bonding scheme as that indicated for

Ni-porphyrin from X-ray measurements (25), then the totally phosphorescent emission could be attributed to increased spin-orbital interaction due to the odd molecular geometry. The differences in relative intensity of emission for these two derivatives is still explicable even though they may have the same metal-porphyrin geometry. The Pd-porphyrin has several features which should enable it to perturb the pi electron system to a greater extent than the Ni-complex. These are:

- (1). Due to an increase in atomic number, the spin-orbital interaction is enhanced with a consequent increase in intensity of the emitted phosphorescence.
- (2). The electronegativity of the Pd ion is greater than that of the Ni ion (36). This, too, would allow the Pd ion to distort the electron cloud resulting in closer approach of the optical electron to the magnetic field of Pd ion. This would result in a greater degree of spin orbital coupling.
- (3). The Pd ion has a larger diameter than the Ni ion. As a result, there should be a greater

overlap between the pyrrole nitrogen orbitals with those of the metal ion. This would distort the molecule even more, in the sense that the π system is pulled even closer into the central metal ion with a consequent increase in spin-orbital interaction. Also, because of size, the perturbing Pd ion would project further into the field of the π electron system.

However, if the metal-porphyrin bonding is identical for the Ni and Pd-derivative, then the lifetime of the triplet state for Ni-mesoporphyrin should be longer than that of Pd-mesoporphyrin. This would mean that the phosphorescence of Ni-porphyrin should be observed with the phosphoroscope. Further examination of the compound seems necessary to ascertain if the lifetime of Ni-porphyrin is longer than that of the Pd-derivative.

The emission spectrum of Co-mesoporphyrin consists solely of phosphorescence and has an estimated lifetime of less than 10^{-4} seconds. This is to be expected since the Co ion is paramagnetic (37) whether it has adopted the dsp^2 square planar bonding or an odd type of bonding such as that

exhibited by the Ni-derivative. However, the weak intensity of this emission compared to that obtained from the paramagnetic Cu-complex seems surprising if dsp^2 square planar bonding exists between the Co ion and the pyrrole nitrogens. Both the Cu ion and the Co ion have only one unpaired electron when a 3d orbital is utilized in bond formation. Thus, it would seem that both ions should produce the same degree of spin-orbital interaction with a consequent similarity between lifetime of the triplet state and quantum yield of phosphorescence. Since the emission intensity of Co-mesoporphyrin is comparable to that of Ni-mesoporphyrin, it would seem necessary to conclude that both metals have a similar bonding scheme. A closer examination of the phosphorescent intensity reveals that the emission from the Co-mesoporphyrin is stronger than that observed for the Ni-derivative. This intensity difference could be attributed to two factors:

- (1). Co and Ni-mesoporphyrin are similar with respect to metal-porphyrin bonding, but the presence of an unpaired electron in the Co ion creates an even greater spin-orbital interaction than that produced by the distorted molecular geometry.

- (2). Co and Ni-mesoporphyrin are somewhat similar with respect to metal-porphyrin bonding, but the radiationless internal degradation inherent in the Ni-molecule is different or greater than that of Co-mesoporphyrin.

There still exists another explanation for weak intensities in emission for Ni and Co-mesoporphyrin. If the metallo-porphyrins are planar molecules like the structurally similar phthalocyanines have been shown to be (19, 20, 21, 22), then the following analogy could be drawn. A comparison of experimentally observed magnetic susceptibilities of Mn-, Fe-, Co-, and Ni-phthalocyanine with those calculated for normal and penetration type complexes (i.e., for ionic and covalent type complexes) indicate that these four derivatives represent some intermediate type of bonding between these two forms (38). Applied to the Ni and Co-porphyrin molecules, this hybrid bonding scheme could give rise to a radiationless internal degradation process by which most of the excitation energy is drained off, resulting in the observed weak intensity for the phosphorescence. Furthermore, even if the Ni ion is diamagnetic, this type of bonding could allow the metal ion to perturb the π electron system to such an extent that its emission consists solely

of phosphorescence. On this basis, it could be predicted that the emission spectra of Mn- and Fe-mesoporphyrin should also display this same weak intensity for their phosphorescent emission.

Considering the intense phosphorescent emission of the Cu-complex, it would seem logical to suppose that any other paramagnetic metal of this same periodic group should exhibit an equal or greater intensity of phosphorescence when complexed with the porphyrin molecule. However, even with long periods of excitation, no emission bands for Ag(II)-mesoporphyrin could be located. If the divalent silver ion possesses electronic excitation levels lower than the phosphorescent level of the mesoporphyrin complex, it is possible that all excitation energy could be transferred to these atomic levels. The emission from these levels would occur farther into the infrared than the photographic plates could detect. (For examples of this type of energy transfer see Weissman (39), and Crosby and Kasha (40). On the other hand, several other possible explanations for this lack of emission are possible. For instance, the divalent silver ion represents an oxidation state for this metal which is uncommon. As a result, the metal ion should be

more electronegative than if it was in the univalent state, and moreover, more electronegative than Cu(II). Due to the greater electronegative and paramagnetic nature of the metal ion, an internal degradation mechanism could exist which would allow drain off of the excitation energy in a radiationless manner. Moreover, the type and geometry of the bonding with the pyrrole nitrogen atoms could be different than Cu(II) because of the expected high electronegativity of Ag(II). If the ionic radii of Ag(II) was sufficiently large, it would no longer be planar with respect to the molecule. Then the only alternative is for the central silver ion to be out of this plane. This, too, could give rise to some radiationless internal degradation process. In order to test these hypotheses, a more comprehensive study of Ag(II)-mesoporphyrin seems necessary.

Comparison of Fluorescent Intensities of
Zn-phthalocyanine and Zn-mesoporphyrin

As estimation of the quantum yields of fluorescence for Zn-phthalocyanine compared to that for Zn-mesoporphyrin would present a means to determine the structural similarity between these molecules. In order to make this estimate as

quantitative as possible, both metallo-compounds were studied in the same solvent system (EPA) and irradiated with measured quantities of light in their respective excitation regions (see Table V for filter systems). An estimate of the percentages of excitation light showed that almost twice as much light was used to excite the mesoporphyrin derivative as that for the corresponding metallo-phthalocyanine. The concentration of each sample was adjusted so that equal integrated absorption areas were present in the excitation regions. An examination of Figure 14 reveals that Zn-phthalocyanine has fluorescent bands almost twice as intense as those of Zn-mesoporphyrin. This would indicate that the quantum yield of phosphorescence for Zn-phthalocyanine should be, at most, one-half as great as that for Zn-mesoporphyrin. This difference in quantum yield of fluorescence is directly related to the amount of spin-orbital interaction present in these metal compounds. The greater intensity of phosphorescence for Zn-mesoporphyrin implies a greater degree of spin-orbital interaction. This could be accounted for by the differences in expected electron density on the pyrrole nitrogens for these two compounds. Porphyrins should have a greater electron density on these nitrogens than in the corresponding phthalocyanines

(See Becker (6)). This would enable the central metal ion (in porphyrin) to have a greater degree of orbital overlap with these pyrrole nitrogen orbitals; and, as a result, the bond distance between the metal ion and the four pyrrole nitrogens should be shorter than those in the metallo-phthalocyanine molecule. The effect of this would be an increase in the perturbing ability of the metal ion, with a consequent decrease in quantum yield of fluorescence.

Conclusion

It has been shown that emission spectral studies provide a valuable method to study the molecular geometry of the metal-porphyrin bonding and magnetic character of the metal ion. Such studies should not be limited to porphyrin-like molecules, but can be extended to any number of metallo-organic molecules.

This investigation has shown that the metal ion in Pd-mesoporphyrin must be diamagnetic, and is utilizing either dsp^2 square planar bonding between the metal ion and the porphyrin ring or an odd bonding similar to that apparently exhibited by Ni-porphyrin. An analysis of the emission data for Co-mesoporphyrin would indicate that it is also similar to Ni-porphyrin with respect to bonding.

A study of the relative fluorescent intensities for Zn-mesoporphyrin and Zn-phthalocyanine has led to the conclusion that four pyrrole nitrogens in the porphyrin molecule are closer in toward the central metal ion than those in the corresponding phthalocyanine molecule.

V.
TABLES

TABLE I

**FLUORESCENCE SPECTRA OF PORPHYRINS AND THEIR
METAL DERIVATIVES**

Metal	Porphyrin	Bands (wavelengths in Å)	Reference
	Dimethylmesoporphyrin	6170	(8)
Na(I)	"	5970, 6470	"
K(I)	"	5990, 6560	"
Mg(II)	"	5860	"
Zn(II)	"	5760	"
Cd(II)	"	5810	"
Sn(II)	"	5790	"
Ag(II)	"	Non-fluorescent	"
Cu(II)	"	"	"
Co(II)	"	"	"
Fe(II)	"	"	"
Tl(II)	"	"	"
Pb(II)	"	Questionable	"
Fe(III)OH	"	Non-fluorescent	"
Fe(III)Cl	"	"	"
Mn(III)Cl	"	"	"

TABLE I(Cont'd.)

**FLUORESCENCE SPECTRA OF PORPHYRINS AND THEIR
METAL DERIVATIVES**

Metal	Porphyrin	Bands (wavelengths in Å)	Reference
	Mesoporphyrin IX, dimethyl ester	5970, 6230, 6540, 6720, 6910	(See ref.43 in (7)).
Al(III)	"	5790, 6030, 6310	"
Al(III) in solid state	"	6200, 6410	"
Ga(II)	Mesoporphyrin	6050-6300, 5650-5800	(41)
	Hematoporphyrin	6180-6420, 6480-6550, 6660-6770, 6830-6940	(See refs.43 and 44 in (7)).
Fe(II)	"	Non-fluorescent	"
Co(II)	"	"	"
Cu(II)	"	"	"
Zn(II)	"	5790-5830, 6160-6360	"
Cd(II)	"	Fluoresces orange	"
Pb(II)	"	Fluoresces orange- red	"
Sn(II)	"	5720-5900, 6130-6480	"

TABLE I(Cont'd.)

FLUORESCENCE SPECTRA OF PORPHYRINS AND THEIR
METAL DERIVATIVES

Metal	Porphyrin	Bands (wavelengths in Å)	Reference
Zn(II)	Hematoporphyrin	6280, 5785	(42)
Pb(II)	"	6205, 5780	"
Cd(II)	"	6205, 5785	"
Zn(II)	Protoporphyrin	6295, 5845	"
Pb(II)	"	6300, 5835	"
Cd(II)	"	6295, 5840	"

TABLE II

**FLUORESCENCE AND PHOSPHORESCENCE OF
PORPHYRINS AND THEIR METAL DERIVATIVES**

Metal	Porphyrin	Fluorescence (in Å)	Phosphores- cence (in Å)	Reference
	Tetraphenylpor- phine	6600, 7300		(See ref.14 in (7)).
Mg(II)	"		7900	"
Zn(II)	"	6500	7900, 8800	
	Etioporphyrin II	6236	8060	(6)
Zn(II)	"	5730	7000	"
Cu(II)	"	None	6812	"
Ni(II)	"	None	6812	"
	Phthalocyanine	6918	Not observed	"
Mg(II)	"	6705	"	"
Zn(II)	"	6731	"	"

TABLE III

REACTION DATA AND CHARACTERISTICS OF
METALLO-PHTHALOCYANINES

Metal derivative prepared	Metal salt employed	Reaction time	Color of Compound
Mn(II)	$\text{Mn}(\text{C}_2\text{H}_3\text{O}_2)_2$	20 hours	dull brown-green
Fe(II)	FeCl_2	20 hours	black
Co(II)	CoCl_2	4 hours	blue with maroon luster
Ni(II)	$\text{Ni}(\text{C}_2\text{H}_3\text{O}_2)_2$	4 hours	blue with red luster
Cu(II)	$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$	15 hours	blue with red luster
Zn(II)	$\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$	20 hours	bright blue

TABLE IV

ABSORPTION SPECTRA OF METALLO-PHTHALOCYANINES
(in 1-chloronaphthalene)

Metal derivative	Absorption band maxima (wavelength in Å)				
Mn(II)	7210	6880	6450	6000	
Fe(II)	6550			5950	
Co(II)	6675	6400	6020	5750	5570
Ni(II)	6680	6380	6020	5800	5560
Cu(II)	6750	6470	6080	5800	6500
Zn(II)	6770	6480	6090	5850	5650

TABLE V

FILTER SYSTEMS FOR EMISSION SPECTRA

Compound	Solution Filter	Corning Glass Filters
Mesoporphyrin samples	5 cm. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (125 gm./l.)	#3961, 5562, 9782
Phthalocyanine samples	5 cm. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (25 gm./l.)	#2412, 3961, 9788
Special Filters for Zn-mesoporphyrin — Zn-phthalocyanine Comparison:		
Zn-mesoporphyrin	5 cm. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (125 gm./l.)	#5970, 7380
Zn-phthalocyanine	5 cm. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (25 gm./l.)	#2424, 9788

TABLE VI
SPECTRAL METHODS AND RESULTS

Compound	Solvent ^a	Instrument	Experimental Arrangement
Mesoporphyrin IX, dimethyl ester	(5)	Hilger	Total emission, side illumination
"	(1)	Steinheil	Phosphoroscope
Zn Mesoporphyrin IX, dimethyl ester	(1)	Hilger	Total emission, side illumination
"	(1)	Hilger	Total emission, side illumination
Cu Mesoporphyrin IX, dimethyl ester	(5)	Steinheil	Total emission, front illumination
Ni Mesoporphyrin IX, dimethyl ester	(5)	Steinheil	Total emission, side illumination
Co Mesoporphyrin IX, dimethyl ester	(5)	Steinheil	Total emission, side illumination
Cd Mesoporphyrin IX, dimethyl ester	(2)	Hilger	Total emission, side illumination
"	(2)	Hilger	Total emission, side illumination
Pd Mesoporphyrin IX, dimethyl ester	(5)	Steinheil	Phosphoroscope
Ag Mesoporphyrin	(5)	Steinheil	Total emission, side illumination
Zn Phthalocyanine	(4)	Hilger	Total emission, side illumination

^aSee pages 24-25 for a description of the solvent systems.

TABLE VI

SPECTRAL METHODS AND RESULTS

Type of Emission	Estimate of Lifetime ^b	Band Positions ^c (wavenumber in cm. ⁻¹)
Fluorescence		16196, 15985, (15704), 15462, 15235, (15068), 15008, 14875, 14642, 13956, 13665, (13578), 13512, 13100
Phosphorescence	10 ⁻³ - 10 ⁻⁴	13310, 12400, 11845
Fluorescence		17492, 16708, (16458), 16110, 15882, 15628
Phosphorescence	10 ⁻³ - 10 ⁻⁴	14260, 13538, 12905, 12712
Phosphorescence	< 10 ⁻⁴	14656, 14430, 13872, 13786, 13098
Phosphorescence	(?)	(15200), 14680, 14472, 13980, 13575, 13145, (12456)
Phosphorescence	< 10 ⁻⁴	14908, (14430), 14168, 13705, 13545, 13415
Fluorescence		(17345), 17185, (16865), 16418, 15945, (15898), 15858, (15720), 15672, 15636
Phosphorescence	10 ⁻³ - 10 ⁻⁴	13772, 13283, 13118, 13028, (12905), (12768), (12685), 12400
Phosphorescence	10 ⁻³ - 10 ⁻⁴	(15582), 15200, 14982, 14445, (14252), 14100, 13818, 13666
Not observed		
Fluorescence		14876, 14225, 13718, 13550, 13425

^bLifetimes of fluorescence are in the range of 10⁻⁸ to 10⁻⁹ seconds. No apparatus was available to estimate fluorescence lifetimes.

^cAll questionable bands are indicated by parenthesis.

TABLE VII

SINGLET-TRIPLET SPLIT AND PREDICTED PHOSPHORESCENT
REGION FOR METALLO-MESOPORPHYRIN DERIVATIVES

Compound	Last absorption band (wavelength in Å)	First Fluorescent band (wavelength in Å)
Zn-mesoporphyrin	5750	5715
Cu-mesoporphyrin	5590	
Ni-mesoporphyrin	5490	
Co-mesoporphyrin	5520	
Cd-mesoporphyrin	5848	5817
Ag-mesoporphyrin	5600	Not observed
Pd-mesoporphyrin	5430	

TABLE VII

**SINGLET-TRIPLET SPLIT AND PREDICTED PHOSPHORESCENT
REGION FOR METALLO-MESOPORPHYRIN DERIVATIVES**

First Phosphorescent band (wavelength in Å)	S-T split (wavelength in Å)	Predicted Phos- phorescent region (wavelength in Å)
6978	1283	
6821		6835
6810		6735
6673		6765
7260	1443	7100 ^a
Not observed		6845 ^a
6576		(6675 ^a 6838 ^b)

^aThis value is based on the S-T split of the Zn-derivative.

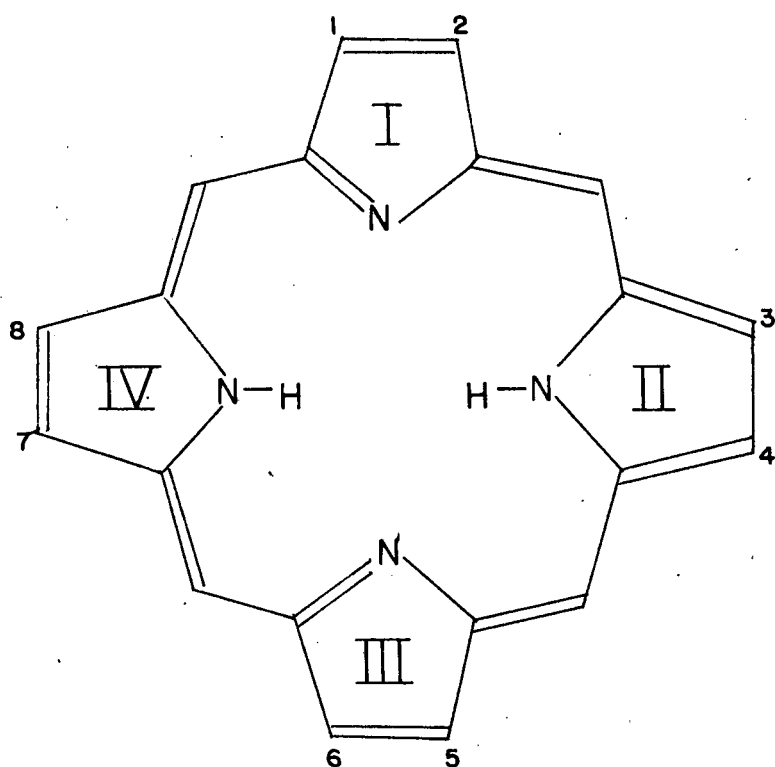
^bThis value is based on the S-T split of the Cd-derivative.

VI.
FIGURES

FIGURE 1

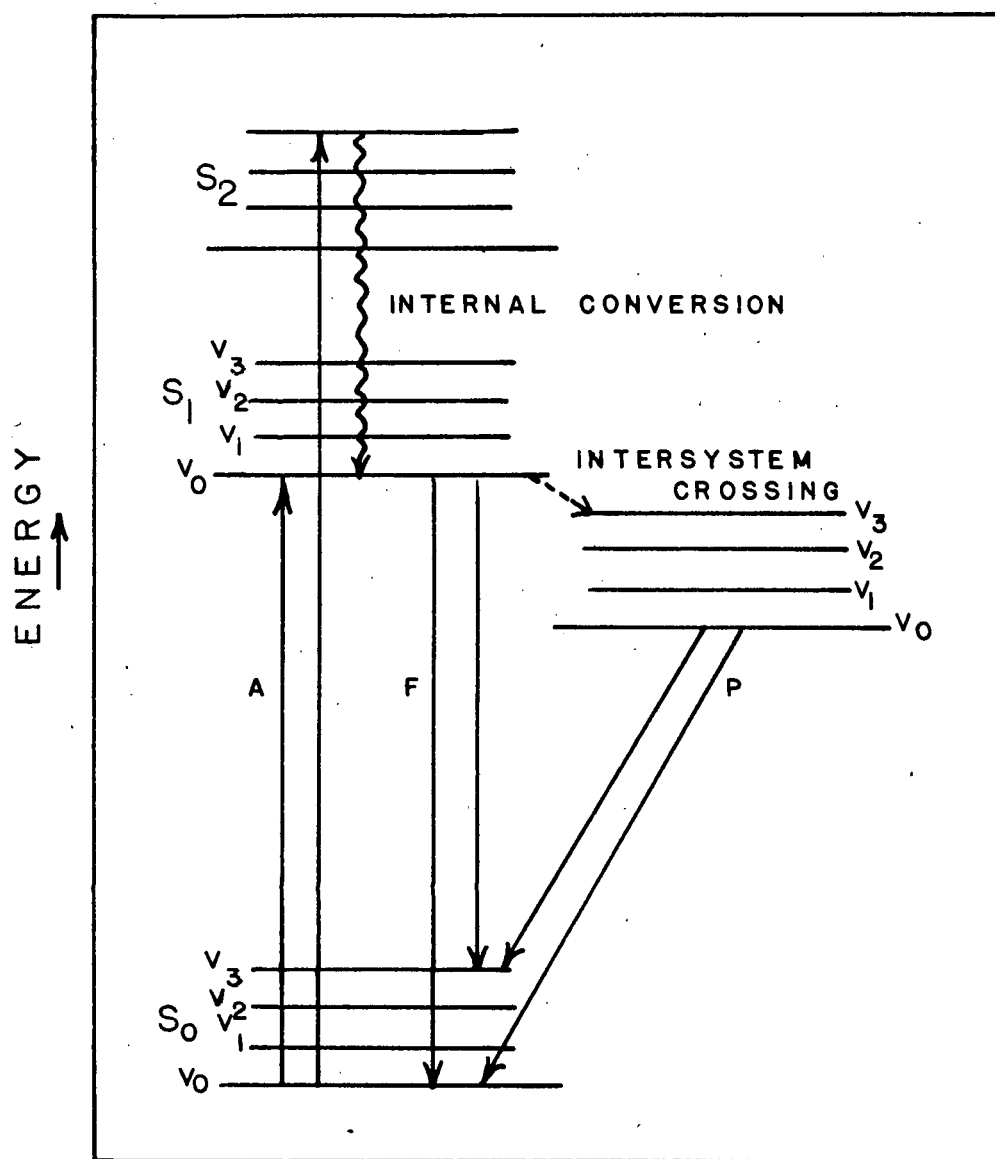
Structure of the Porphyrin Molecule

1. Mesoporphyrin IX, dimethyl ester: 1,3,5,8-tetramethyl-2,4-diethyl-6,7-di-(methyl propionate)-porphyrin.
2. Zn, Cu, Ni, Co, Cd, Ag, Pd mesoporphyrin IX, dimethyl ester: Same as mesoporphyrin IX, dimethyl ester with metal complexed in the center of the ring (hydrogen atom of rings I and III are removed).
3. Phthalocyanine: Same as porphyrin except that methine carbons are substituted by N atoms and four phenyl groups are attached to positions 1,2; 3,4; 5,6; 7,8.
4. Zn phthalocyanine: Same as phthalocyanine with the metal complexed in the center of the ring.



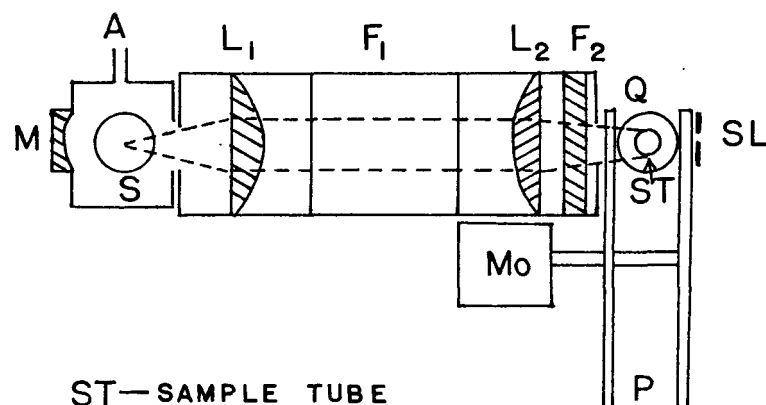
STRUCTURE OF THE
PORPHYRIN MOLECULE

FIGURE I



ELECTRONIC ENERGY
LEVELS

FIGURE 2



ST—SAMPLE TUBE

M—MIRROR

A—XENON MERCURY ARC
LAMP, AIR-COOLED

L₁, L₂—QUARTZ CONDENSING LENS

F₁—SOL'N FILTER WITH QUARTZ WINDOWS,
CONTAINING INORGANIC SALT SOL'N

F₂—GLASS FILTER(S)

P—PHOSPHOROSCOPE
Q—QUARTZ OPTICAL
DEWAR PARTIALLY
DESILVERED

Mo—PHOSPHOROSCOPE
MOTOR

SL—SLIT

A—AIR SOURCE

PHOSPHOROSCOPE ASSEMBLY

FIGURE 3

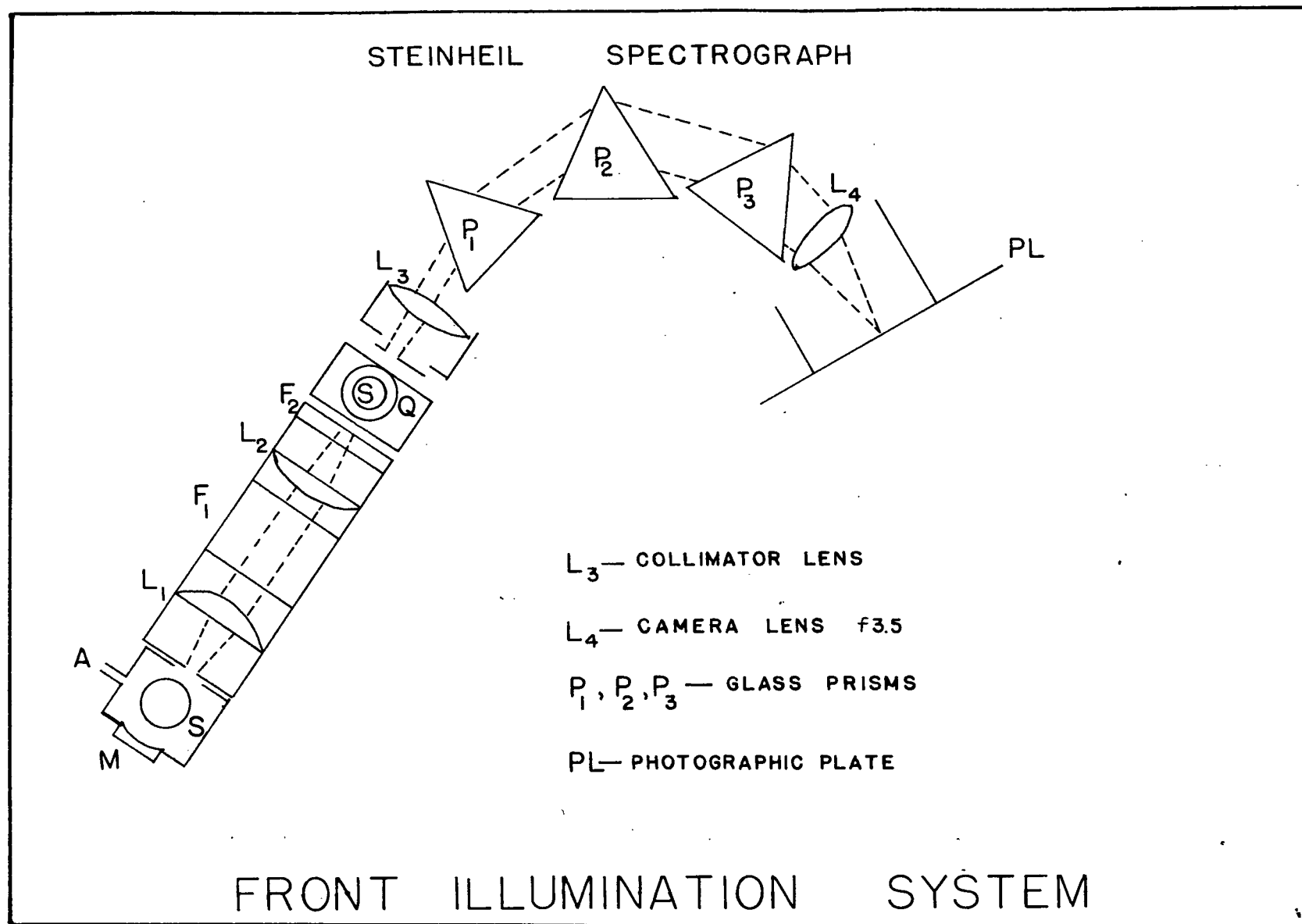
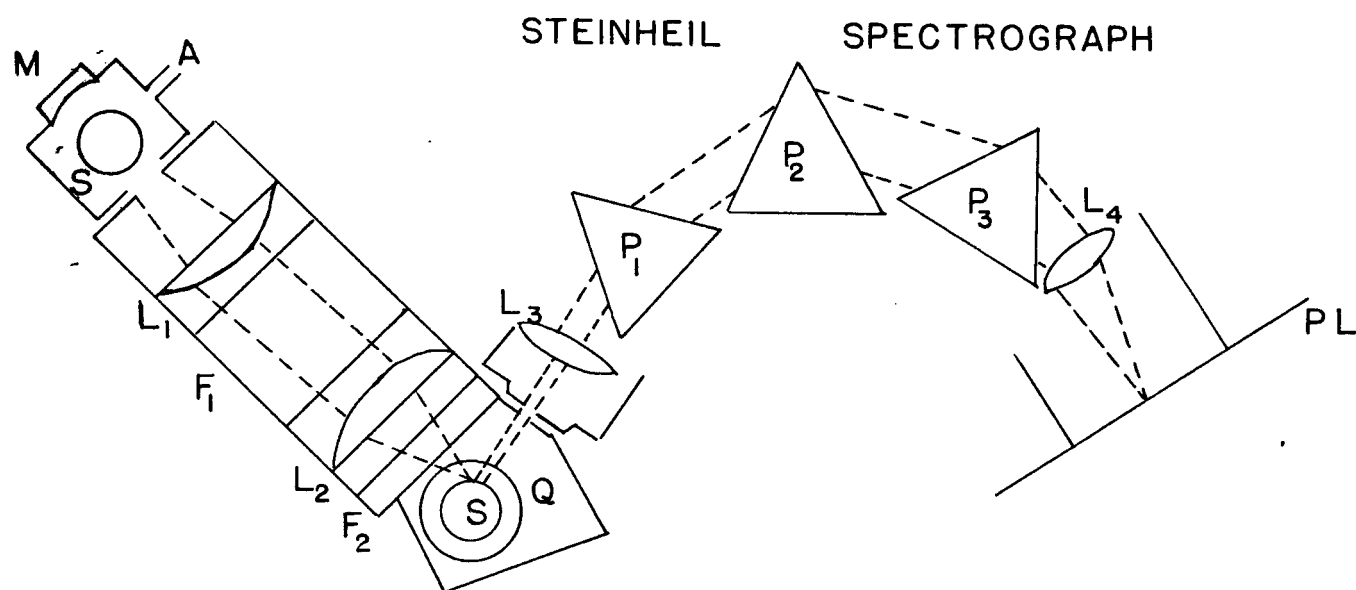


FIGURE 4



L_3 — COLLIMATOR LENS

PL— PHOTOGRAPHIC PLATE

L_4 — CAMERA LENS $f3.5$

P_1, P_2, P_3 — GLASS PRISMS

SIDE ILLUMINATION SYSTEM

FIGURE 5

EMISSION SPECTRA OF MESOPORPHYRINS

FIGURE		PAGE
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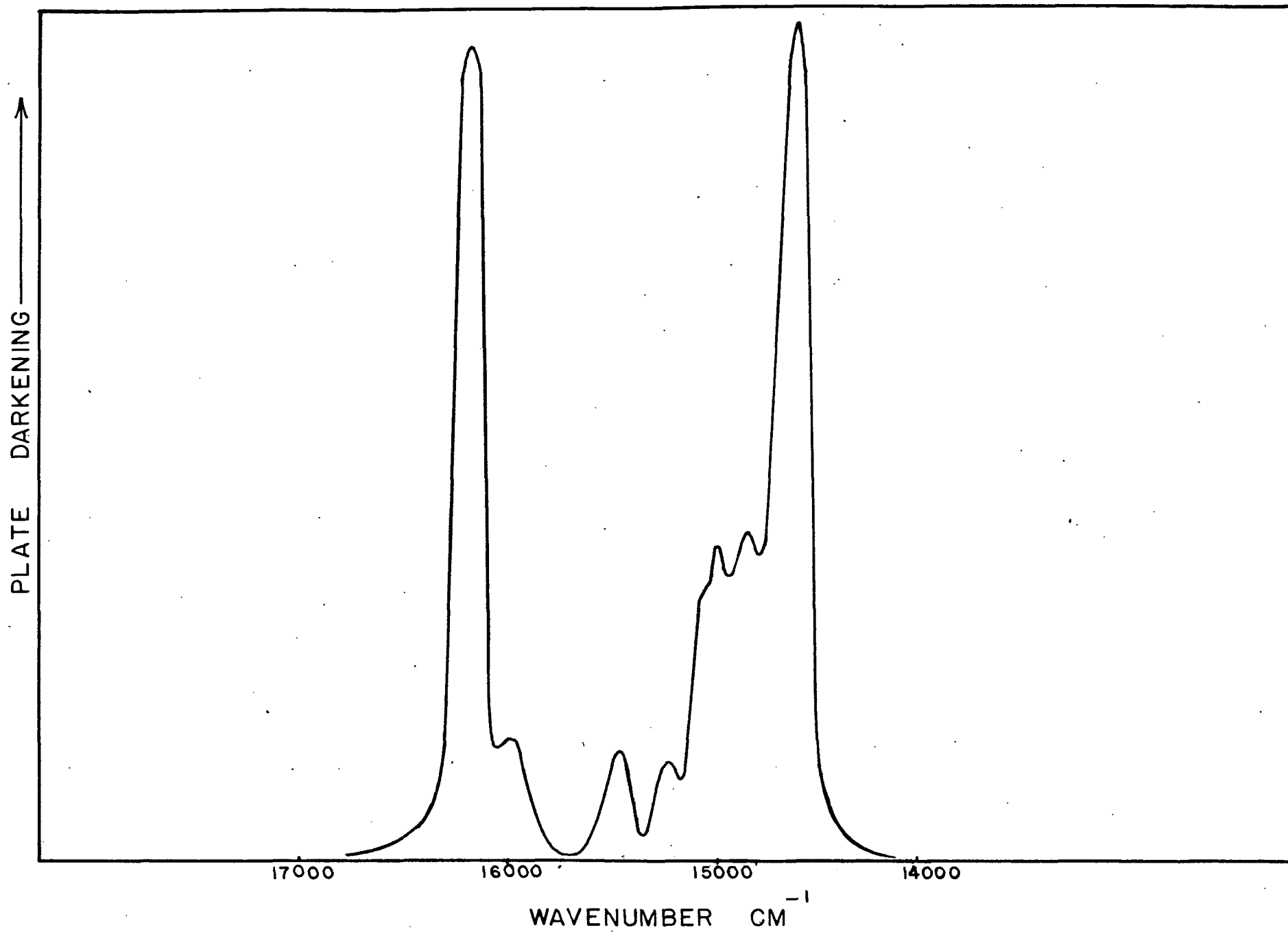


FIGURE 7

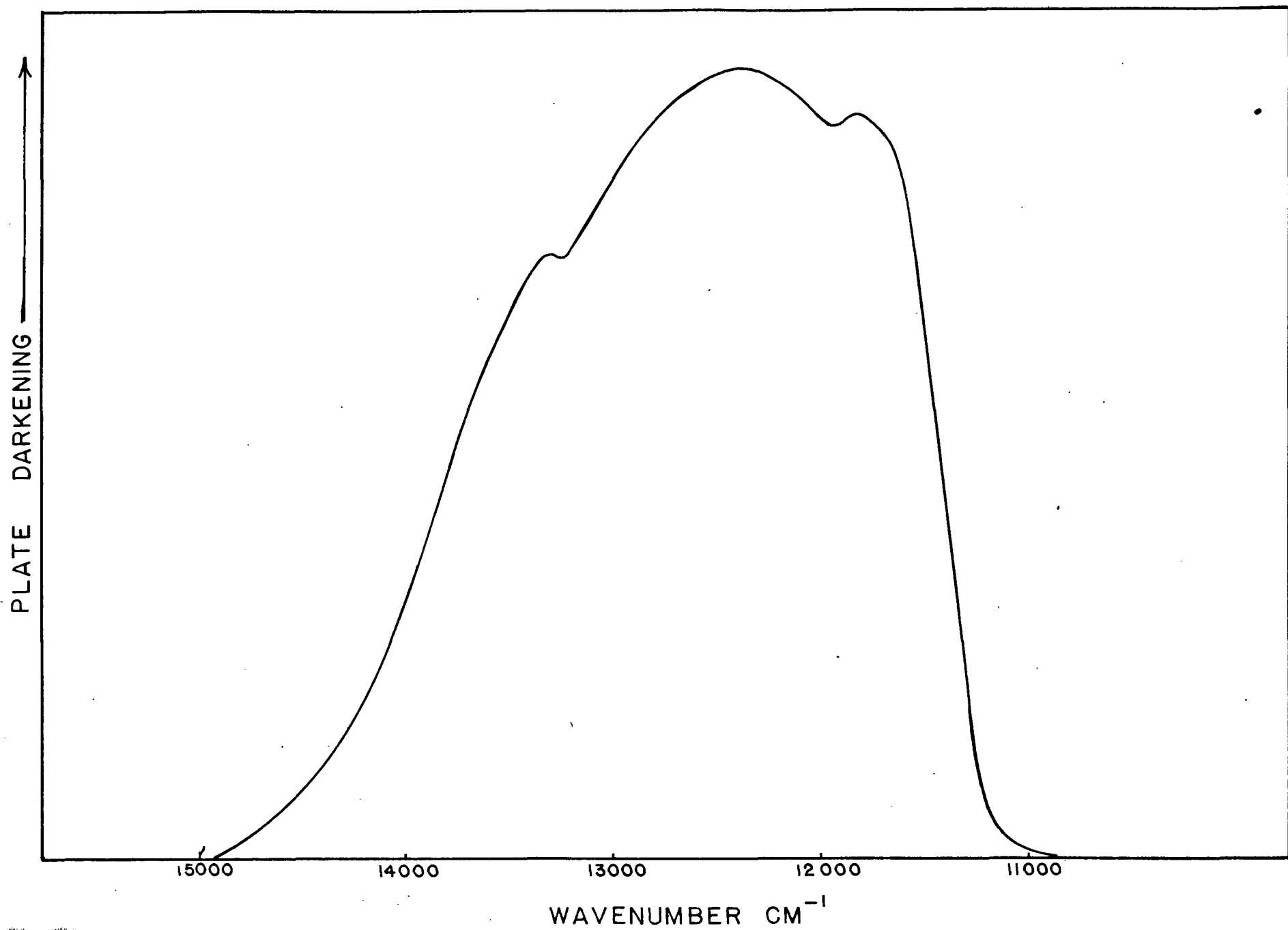


FIGURE 8

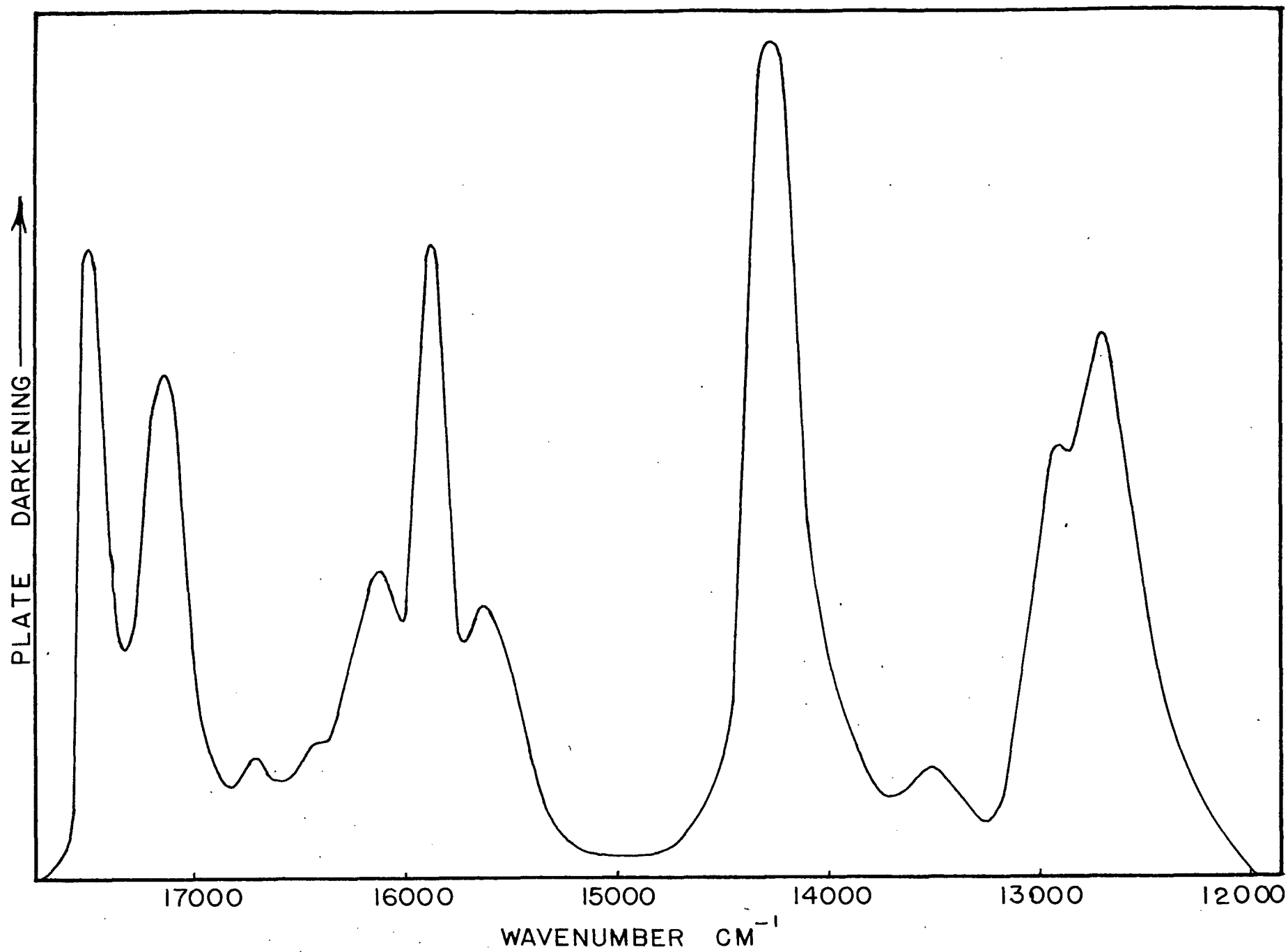


FIGURE 9

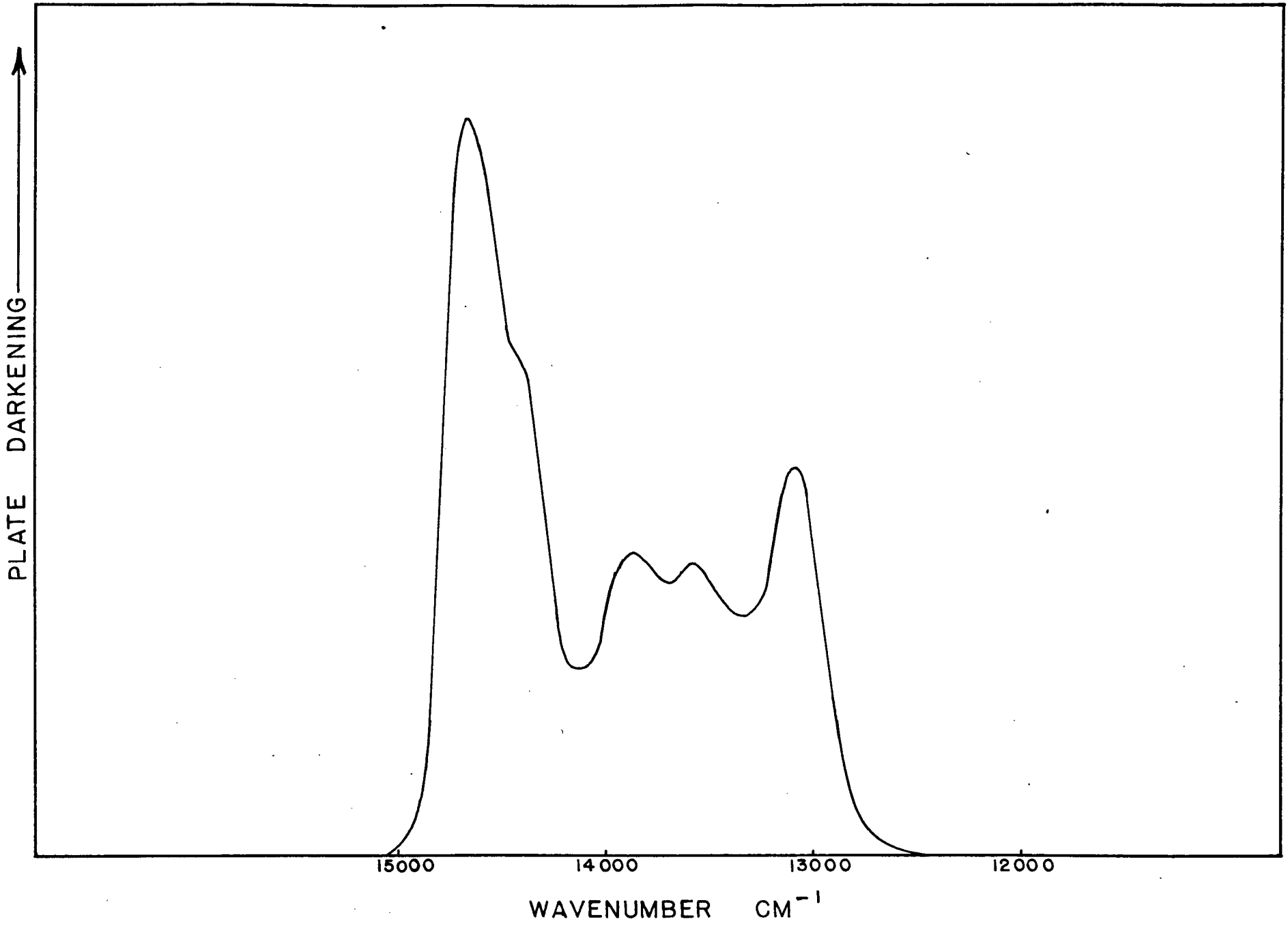
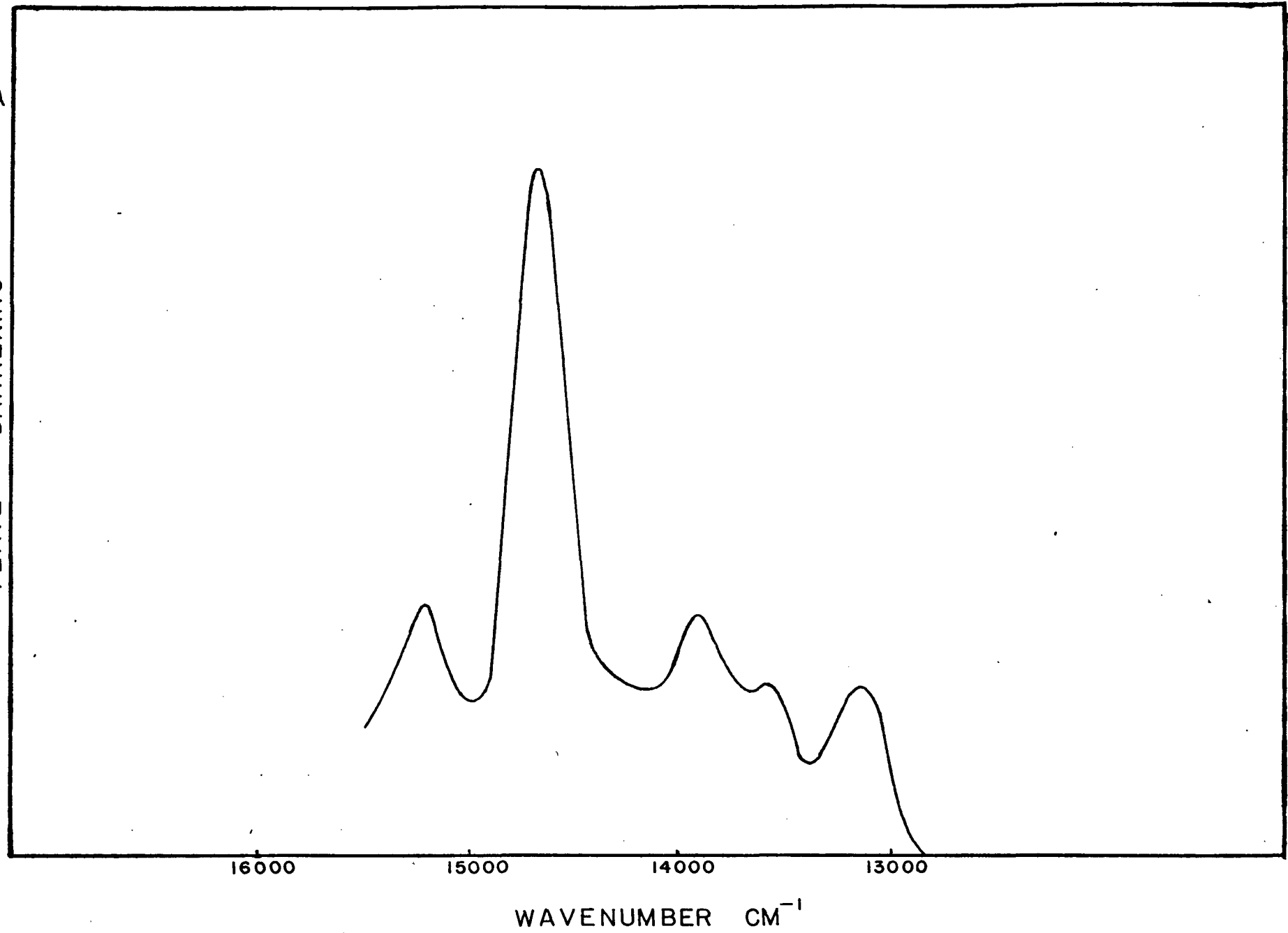
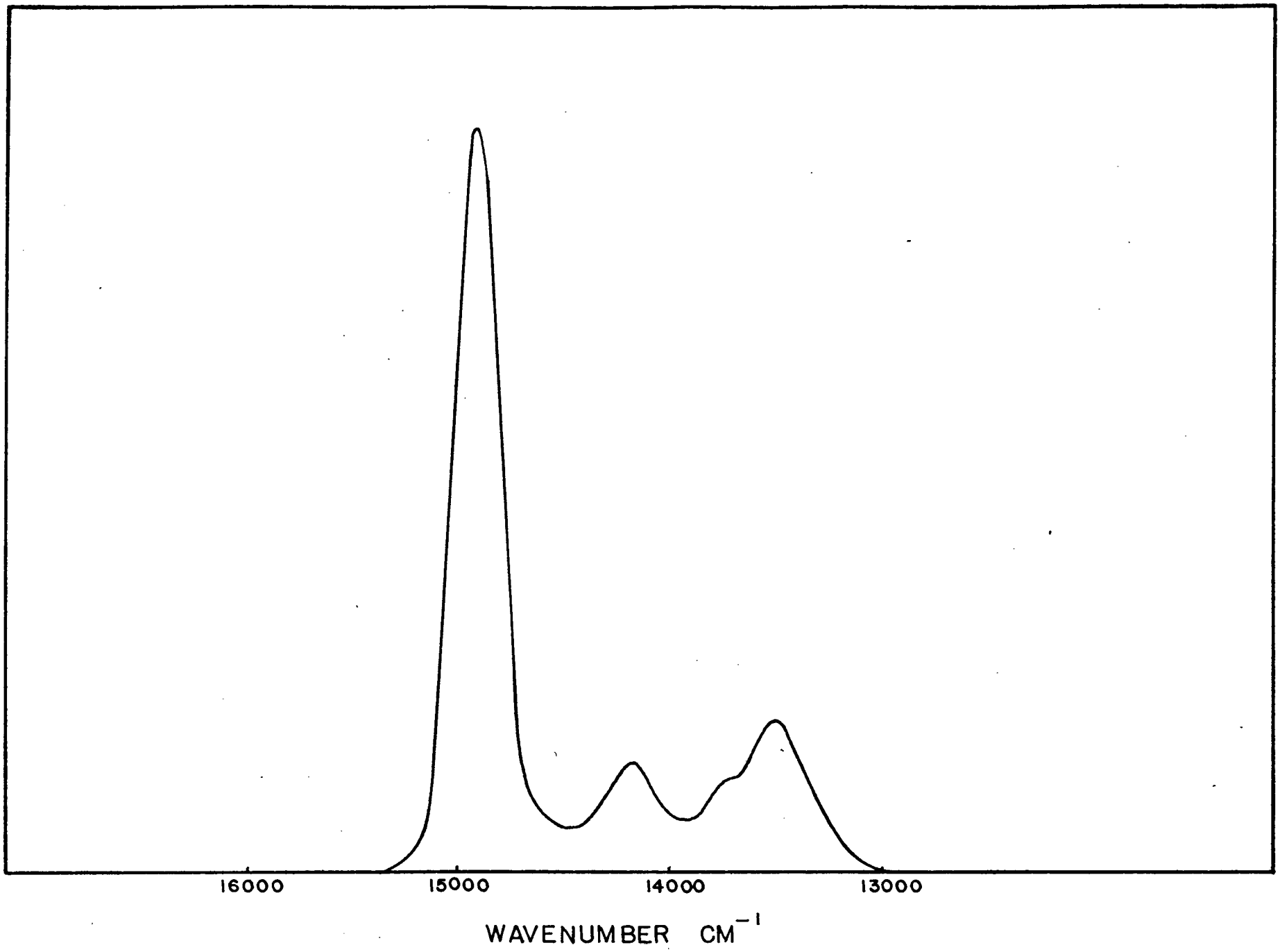


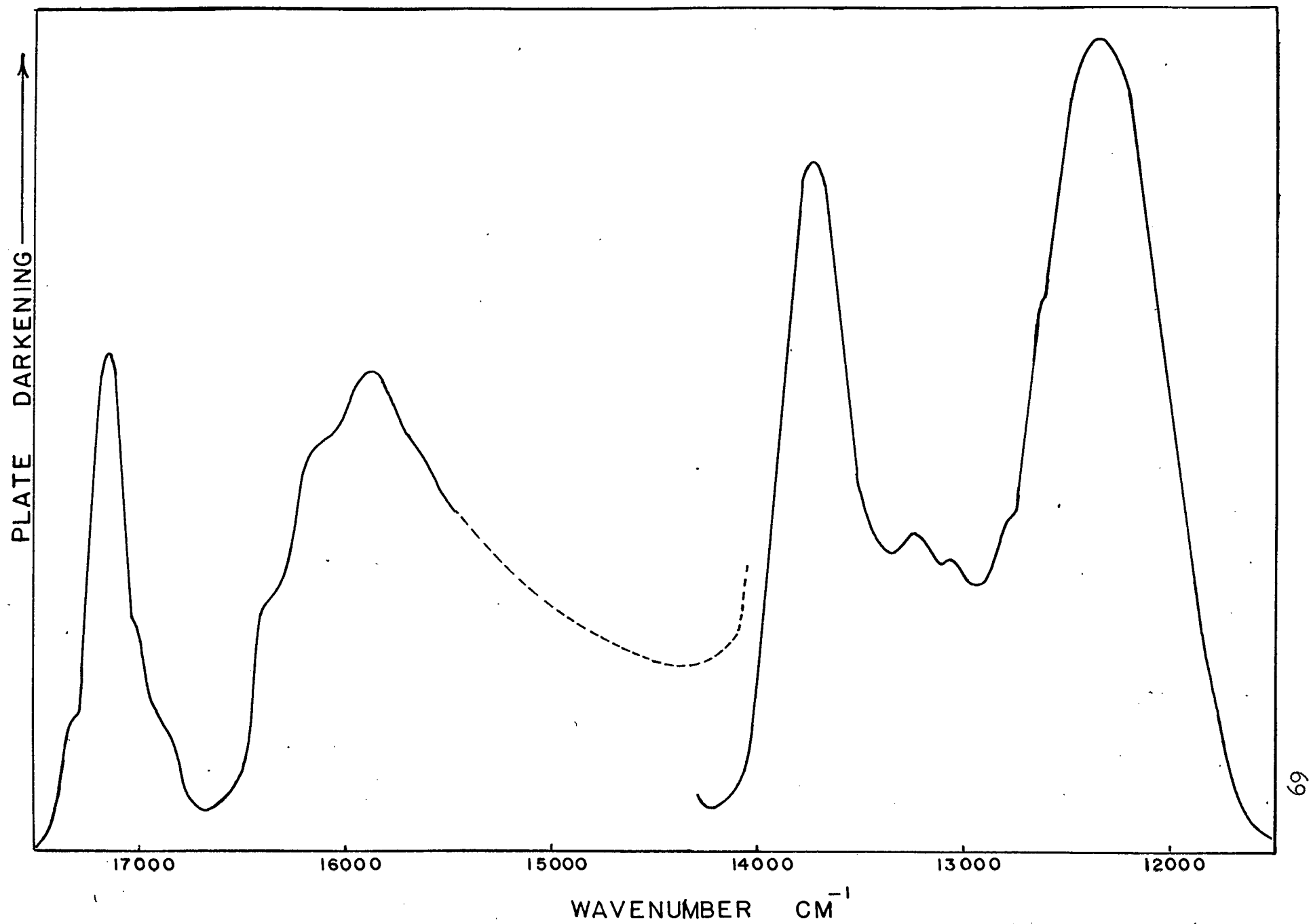
FIGURE 10

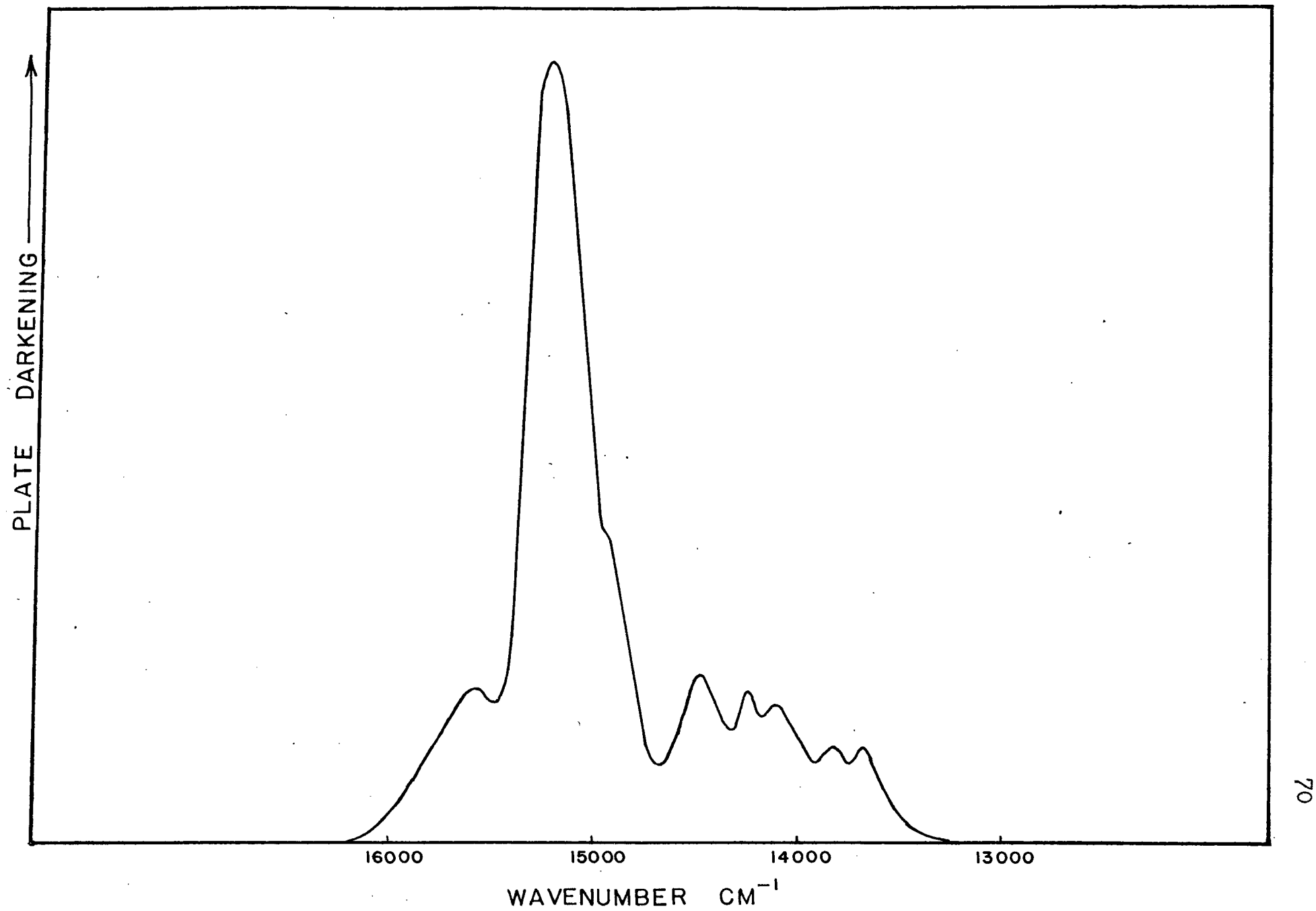
PLATE DARKENING



↑
DARKENING
PLATE







ZINC-MESOPORPHYRIN

ZINC-PHTHALOCYANINE

↑
DARKENING
PLATE

17000

16000

15000

15000

14000

13000

WAVENUMBER CM^{-1}

VII.
BIBLIOGRAPHY

BIBLIOGRAPHY

- (1) Simpson, W. T., J. Chem. Phys., 17, 1218 (1949).
- (2) Longuett-Higgins, H. C., Rector, C. W., and Platt, J. R., J. Chem. Phys., 18, 1174 (1950).
- (3) Kasha, M., Far. Soc. Discuss., No. 9, 14 (1950).
- (4) Yuster, P., and Weissman, S. I., J. Chem. Phys., 17, 1182 (1949).
- (5) McClure, D., J. Chem. Phys., 17, 905 (1949).
- (6) Becker, R. S., and Kasha, M., J. Am. Chem. Soc., 77, 3669 (1953).
- (7) Becker, R. S., Dissertation, Florida State University, May 1955.
- (8) Haurowitz, R., Ber., 68, 1795 (1935).
- (9) Knorr, H. V., and Albers, V. M., Phys. Rev., 57, 347 (1940).
- (10) Albers, V. M., Knorr, H. V., and Fry, D. L., J. Chem. Phys., 10, 700 (1942).
- (11) Haurowitz, F., Ber., 71, 1404 (1938).
- (12) Milroy, J. A., Biochem. J., 12, 318 (1918).
- (13) Rabinowitch, E., Rev. Mod. Phys., 16, 226 (1949).
- (14) Williams, R. J. P., Chem. Rev., 56, 299 (1956).
- (15) Dorrough, G. D., Miller, J. R., and Huennekens, R. M., J. Am. Chem. Soc., 73, 4315 (1951).
- (16) Seely, G. R., Chem. Abstr., 48, 1196^e (1954).
- (17) Thomas, D. W., Dissertation Abstr., 18, 71 (1958).

- (18) Gouterman, M., Dissertation, University of Chicago, August 1958.
- (19) Seely, G. R., J. Chem. Phys., 27, 125 (1957).
- (20) Haurowitz, F., and Klemm, W., Ber., 68, 2312 (1935).
- (21) Robertson, J. M., J. Chem. Soc., 615 (1935).
- (22) Ibid, 1195, (1936).
- (23) Linstead, R. P., and Robertson, J. M., J. Chem. Soc., 1736 (1936).
- (24) Robertson, J. M., and Woodward, I., J. Chem. Soc., 219 (1937).
- (25) Personal communication, Caughey, W. S., Monadnock Research Institute, Inc., Antrim, New Hampshire.
- (26) Corwin, A. H., and Erdman, J. G., J. Am. Chem. Soc., 68, 2473 (1946).
- (27) Erdman, J. G. Ramsey, V. G., Kalenda, N. K., and Hanson, W. E., J. Am. Chem. Soc., 78, 5844 (1956).
- (28) Anderson, J., Bradbrook, E., and Cook, A., J. Chem. Soc., 1151 (1938).
- (29) Barrett, P., Linstead, R. P., and Tuey, G., J. Chem. Soc., 1809 (1939).
- (30) Barrett, P., Linstead, R. P., Rundall, F. G., and Tuey, G., J. Chem. Soc., 1079 (1940).
- (31) Ficken, G. E., and Linstead, R. P., J. Chem. Soc., 4846 (1952).
- (32) Personal communication, Dr. H. L. Smith, Jackson Laboratories, E. I. DuPont de Nemours and Company, Inc., Wilmington, Delaware.
- (33) Bauman, F., Bienert, B., Rosch, G., Vollman, H., and Wolf, W., Angew. Chem., 68, 133 (1956).

- (34) Kasha, M., J. Opt. Soc., 38, 929 (1949).
- (35) Elder, E. S., Thesis for Master of Science Degree, University of Houston, August 1958.
- (36) Gordy, W., and Thomas, W. J. O., J. Chem. Phys., 24, 439 (1956).
- (37) Pauling, L., and Corgell, C. D., Proc. Natl. Acad. Sci. U. S., 22, 159 (1936).
- (38) Senff, H., and Klemm, W., J. Prakt. Chem., 73, 154 (1939).
- (39) Weissman, S. I., J. Chem. Phys., 10, 214 (1942).
- (40) Crosby, G. A., and Kasha, M., Spectrochimica Acta, 10, 377 (1958).
- (41) Haberlandt, H., Wien Chem. Ztg., 47, 80 (1944).
- (42) Vanotti, A., "Porphyrins", Hilger and Watts, Ltd., London (1954), p. 20.