THE INFRARED ABSORPTION OF PHTHALOCYANINE AND RELATED COMPOUNDS

by

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TABLE OF CONTENTS

SECTION	PAGE
INTRODUCTION	1
OBJECTS	1
PHTHALOCYANINES	2
General	2
Preparation and Chemistry	9
Metal-free phthalocyanine	9
Copper phthalocyanine	13
Nickel phthalocyanine	14
Platinum phthalocyanine	14
Magnesium phthalocyanine	14
Polymorphic Forms of the Phthalocyanines	15
THEORETICAL BACKGROUND OF INFRARED SPECTRA	17
GENERAL	17
DIATOMIC MOLECULES	18
Rotational Spectra	18
Vibrational-Rotational Spectra	20
POLYATOMIC MOLECULES	21
Normal Vibrations	21
Determination of Normal Vibrations	23
INFRARED SPECTRA OF SOLIDS	28
INSTRUMENT	32
DISCUSSION OF PRINCIPLES	32
General	32
Monochromator	33
Single Beam Operation	34
Double Beam Operation	36
DETAILS OF CONSTRUCTION	39
Mechanical System	39
Preamplifier	39
Main Amplifier	43
Auxiliary Circuits	44
PERFORMANCE OF THE INSTRUMENT	47
Calibration and Accuracy	47
Resolution	50
EXPERIMENTAL TECHNIQUES	55
SAMPLE PREPARATION FOR SOLIDS	55
SPECIAL TECHNIQUE FOR THE PHTHALOCYANINES	57

SECTION	PAGE
EXPERIMENTAL RESULTS	61
PREPARATION OF PLATINUM DERIVATIVE	61
PREPARATION OF DEUTERIUM DERIVATIVE	61
X-RAY POWDER DIFFRACTION PATTERNS	63
INFRARED SPECTRA OF POLYMORPHIC FORMS	71
Alpha-Beta Conversions	71
General Discussion of Spectra	73
SPECTRA OF THE PHTHALOCYANINES	90
THEORETICAL CONSIDERATIONS	90
Calculations for Normal Modes	90
Analysis of Vibrations	94
ASSIGNMENT OF FREQUENCIES	95
General	95
Characteristic Bond Frequencies	98
NH Frequencies	99
CH Frequencies	101
The region from 2000-3000 $cm.^{-1}$	101
Analysis of the 2000-400 $cm.^{-1}$ region	102
The region of 1650-1000 $cm.^{-1}$	104
The region of 1000-700 $cm.^{-1}$	106
The region of 700-400 $cm.^{-1}$	109
Combinations	111
COMPARISON: OBSERVED TO CALCULATED	111
CONCLUSIONS	113
BIBLIOGRAPHY	115

TABLES

TABLE NO.	TITLE	PAGE
1	Crystallographic Data for Phthalocyanines	8
2	Calculations for Normal Modes of a D_{4h} Molecule Using a Character Table	25
3	Interplanar Distances (in Angstroms) for Phthalocyanines Obtained on XRD Apparatus	65
4	Absorption Bands Observed for Phthalocyanines - Alpha Forms	88
5	Absorption Bands Observed for Phthalocyanines - Beta Forms	89
6	Calculation of Numbers of Modes of Each Species for Phthalocyanines of D_{4h} Symmetry	91
7	Calculation of Number of Modes of Each Species for Phthalocyanines of D_{2h} Symmetry	92
8	Calculation of Number of In-plane Characteristic Group Frequencies in Phthalocyanines	97
9	Normal Modes of Benzene	103
10	Analysis of 1650-1000 $Cm.^{-1}$ Region	105
11	Analysis of 1000-700 $Cm.^{-1}$ Region	107
12	Analysis of 700-400 $Cm.^{-1}$ Region	110

PLATES

Plate No.	Title	Page
1	Spectrometer	41

FIGURES

Figure No.	Title	Page
1	Structural Diagrams of Phthalocyanine and the Porphyrin Nucleus	5
2	Metal-Free Phthalocyanine	10
3	Ni Phthalocyanine	11
4	Pt Phthalocyanine	12
5	Normal Vibrations for a D_{4h} Molecule	23
6	Sector Disks	38
7	Circuit Diagram of Preamplifier	42
8	Circuit Diagram of Ten Cycle Amplifier	45
9	Auxiliary Circuits	46
10	Resolution for LiF Prism	52
11	Resolution for NaCl Prism	53
12	Resolution for KBr Prism	54
13	Sublimation Apparatus	59
14	X-Ray Diffraction Patterns of Metal-Free Phthalocyanine	66
15	X-Ray Diffraction Patterns of Copper Phthalocyanine	67
16	X-Ray Diffraction Pattern of Platinum Phthalocyanine - Alpha Form	68
17	X-Ray Diffraction Pattern of Magnesium Phthalocyanine Dihydrate	69
18	X-Ray Diffraction Pattern of Magnesium Phthalocyanine - Alpha Form	70
19	Metal-Free Phthalocyanine - Alpha Form	77
20	Metal-Free Phthalocyanine - Beta Form	78
21	Copper Phthalocyanine - Alpha Form	79
22	Copper Phthalocyanine - Beta Form	80
23	Nickel Phthalocyanine - Alpha Form	81
24	Nickel Phthalocyanine - Beta Form	82
25	Platinum Phthalocyanine - Alpha Form	83
26	Magnesium Phthalocyanine - Alpha Form	84
27	Magnesium Phthalocyanine - Dihydrate	85
28	Deuteration of Central Hydrogen of Metal-Free Phthalocyanine	86
29	Absorptions in C-H Stretching Region	87
30	Choice of Coordinates for In-plane Modes	96

THE INFRARED ABSORPTION OF PHTHALOCYANINE AND RELATED COMPOUNDS

INTRODUCTION

OBJECTS.

Since the absorption spectrum of a compound in the infrared region is related to important molecular parameters, infrared spectroscopy provides an excellent means for molecular structure studies. Phthalocyanine and its metallic derivatives have been chosen for such a study here. These compounds are commercial dyes and of theoretical importance because they bear close structural relationship to both leaf and blood pigments; i.e., to the pigment portion of the chlorophyll and hemoglobin molecules. Furthermore, these phthalocyanines have been the subject of extensive x-ray analysis from which bond length, bond angle, and crystal lattice details are available to enable one to use much of the theoretical developments of infrared spectroscopy.

Aside from the purely analytical value of these absorption spectra as fingerprints for the respective molecules, the more important use is to obtain information about the fundamental vibrational frequencies leading to force constant determinations from which, in theory at least, many physical and chemical properties of the molecules may be predicted.

PHTHALOCYANINES.

GENERAL. The first phthalocyanine was discovered by chance in 1928 during the course of the industrial production of phthalimide in the Grangemouth works of Messrs. Scottish Dyes, Ltd. The process consists of passing ammonia into molten phthalic anhydride in iron vessels and during certain operations traces of a dark blue substance were formed in the molten imide. This material was stable, crystalline, and contained iron which could not be eliminated by treatment with concentrated sulfuric acid. Study of this compound was turned over to R. P. Linstead of the Imperial college, London and from his laboratory a series of 19 papers was issued during the period 1934-1940 which contain practically all the basic chemistry of the phthalocyanines. During the same period J. M. Robertson of the University of Glasgow did extensive x-ray analysis of single crystals of various phthalocyanines furnished to him by Linstead which led to complete determination of the molecular and crystalline structures. Due to the unusual isomorphism of the metal-free and metallic complexes, Robertson was able to perform his classical structure determination by means of a Fourier synthesis contour map of electron densities.

When Allied technical teams entered German industries in 1945, another large source of experimental work on

phthalocyanine and phthalocyanine-like compounds was unearthed (27, pp.273-345,442-446). This information covered the efforts of the German dye industry to improve known phthalocyanine pigments and develop new ones.

The parent phthalocyanine is the metal-free compound shown by structural diagram A of Figure 1 and the manner in which metallic derivatives are formed is illustrated by diagram B. Robertson found the molecules to be planar with practically perfect tetragonal symmetry (49, p.1195). There is a cavity in the exact center of the molecule containing two hydrogen atoms which may be replaced by a variety of metals from every group in the periodic system. Only a slight distortion of the molecule accompanies this replacement (37, p.1737). X-ray and chemical evidence indicates that the whole molecule must be regarded as one continuous conjugated system and no definite position may be assigned to the single, double, or coordination bonds (48, p.618) (2, pp.1725-1726).

The phthalocyanines are remarkably stable, being insoluble in organic liquids, water, dilute acids or alkali. They resist oxidation and reduction to varying degrees depending on which metallic complex is concerned, and dissolve in H_2SO_4, H_3PO_4, HF, chlorosulfonic acid, and trichloroacetic acid. When heated under vacuum they will sublime around 500 degrees centigrade to form beautifully colored,

long needle-like crystals with little or no decomposition. Another characteristic property is their ability to dissolve in concentrated sulfuric acid and precipitate quantitatively when the solution is poured on ice water.

Their preparation is quite simple and may be performed a number of ways. The most successful method for metallic phthalocyanines is to heat phthalonitrile with a chloride or oxide of the metal to 250 degrees centigrade over the course of 30 minutes. The pigment forms with a highly exothermic reaction and may be purified easily because of its insolubility and inertness. Solution in sulfuric acid followed with precipitation by drowning in an ice bath or sublimation under vacuum yields an analytically pure material.

Their relation to the basic porphyrin ring is shown by diagram C in Figure 1. In porphyrin, the corner benzene rings are missing and the four outer nitrogen atoms are replaced by CH groups. The similarity in chemical properties of the two series is striking. The structural diagram of haemin from hemoglobin may be obtained by placing iron in the center of the porphyrin ring and a number of alkyl and acid groups around the outer edges of the ring (26, p.466). Iron phthalocyanine, its counterpart in the phthalocyanine series, displays its unique property of functioning as an

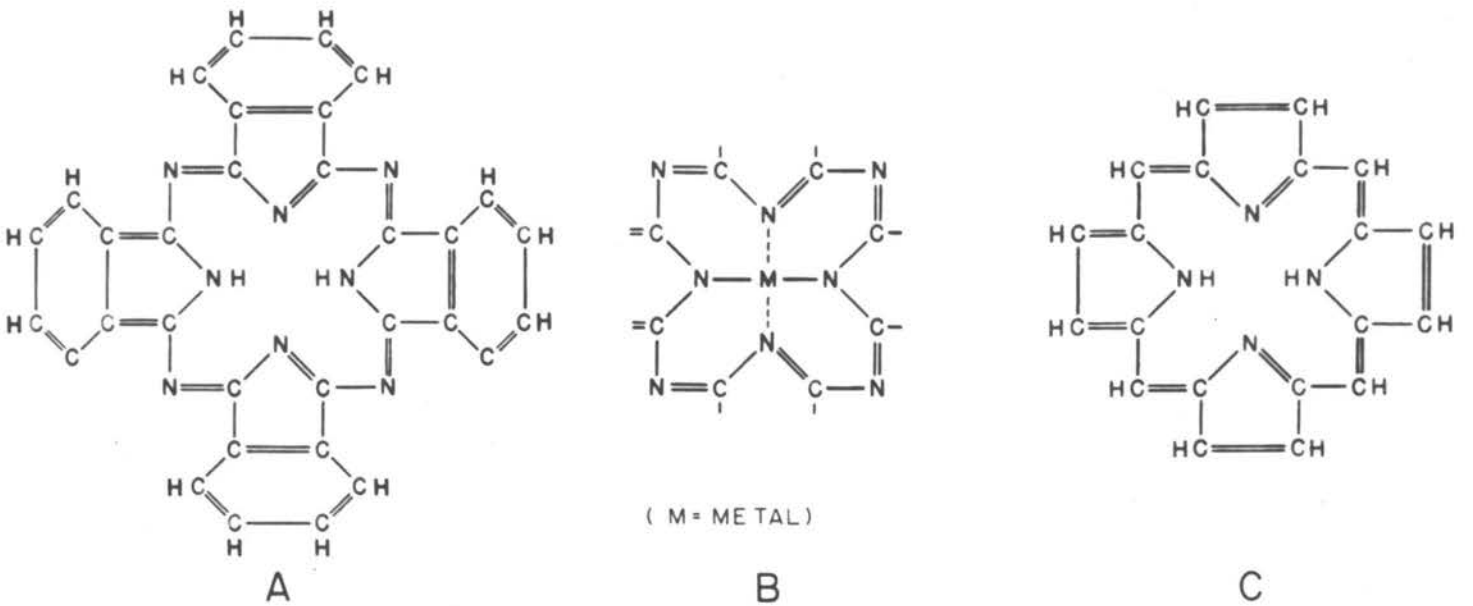

FIGURE I. STRUCTURAL DIAGRAMS OF PHTHALOCYANINE AND THE PORPHYRIN NUCLEUS

oxygen carrier (15, pp.1761-1768) (16, pp.1768-1774) (17, pp.1774-1780). Other phthalocyanines do not display this property.

The structural diagram of chlorophyll may be obtained by placing magnesium in the center of the porphyrin ring and other substitution groups around the edges (26, p.516). Magnesium phthalocyanine displays a brilliant chemiluminescence when oxidized which may suggest some relation to the role chlorophyll plays in photosynthesis (19, p.842).

Linstead not only developed the basic chemistry of the phthalocyanines but attempted to bridge the gap between these compounds and the porphyrins by synthesizing intermediates. Preparative methods are developed for the phthalocyanines in parts I to IV of his papers, (33, pp.1016-1017) (12, pp.1017-1022) (34, pp.1022-1027) (22, pp.1027-1031), and parts V and VI establish a molecular structure by organic chemistry techniques which was completely confirmed by x-ray analysis (35, pp.1031-1033) (23, pp.1033-1039). Part VII is a very complete investigation of 20 metallic derivatives, their preparation, properties and chemistry. This single paper contains a tremendous amount of experimental detail (2, pp.1719-1736). Part XIV is a further investigation of metallic derivatives (3, pp.1157-1163). Parts VIII, IX, and X represent efforts to prepare other compounds of the phthalocyanine type from naphthalene,

pyridine, thiophen, and others (9, pp.1744-1748) (36, pp. 911-921) (8, pp.922-929). Attempts to prepare intermediates between the phthalocyanines and porphyrins are described in parts XI, XII, XV, XVII, XVIII, and XIX (14, pp.929-933) (38, pp.933-936) (4, pp.1809-1820) (39, pp.1070-1076) (6, pp.1076-1079) (7, pp.1079-1092). Visible absorption spectra of the phthalocyanines and porphyrins are presented in part XIII (1, pp.1151-1156). Part XVI describes halogenation of the phthalocyanines (5, pp.1820-1828).

Since Robertson did complete determinations of molecular and crystal structure on metal-free, nickel, and platinum phthalocyanines, these were chosen for the infrared work (49, pp.1195-1209) (50, pp.219-230) (51, pp.36-48). Magnesium and copper phthalocyanine were studied to provide additional information about the effect on the spectra of compounds with different metals.[1]

Table 1 gives a summary of the crystallographic data for these compounds (37, p.1736). Data for the beryllium compound is given here because it is very similar in chemical and crystallographic properties to the magnesium compound, whose data were not available.

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1. The metal-free, nickel, copper, and magnesium phthalocyanine were very kindly furnished by Dr. O. Stallmann of E. I. duPont de Nemours Company who was one of the authors of reference 27. The platinum compound was prepared by the synthesis described under its discussion.

TABLE 1.

CRYSTALLOGRAPHIC DATA FOR PHTHALOCYANINES

	Metal-free	Copper	Nickel	Platinum	Beryllium
Atomic No. of metal	0	29	28	78	4
Atomic wt. of metal	0	64	59	195	10
a- Angstroms	19.85	19.6	19.9	23.9	21.2
b- "	4.72	4.79	4.71	3.81	4.84
c- "	14.8	14.6	14.9	16.9	14.7
β	122.2°	120.6°	121.9°	129.6°	121.0°
Space group	$P2_1/a$	$P2_1/a$	$P2_1/a$	$P2_1/a$	$P2_1/a$
Molecules per cell	2	2	2	2	2
Vol. of unit cell, A^3	1173	1180	1186	1186	1293
Density g./cc.	1.445	1.61	1.59	1.97	1.33
Molecular weight	514	576	571	707	521

Figures 2, 3, and 4 give the molecular details Robertson found for the metal-free, nickel, and platinum phthalocyanines. It is to be noted that the platinum compound shows the greatest differences in bond lengths and angles. The copper derivative is considered to be quite similar to the metal-free and nickel compounds.

PREPARATION AND CHEMISTRY. Although all the phthalocyanines except the platinum derivative were obtained from the duPont Company, it is thought advisable to review the methods of preparation described in the literature.

Metal-Free phthalocyanine. This compound may be prepared by heating phthalonitrile to high temperatures in the presence of such catalysts as silica gel or platinum. However, gross decomposition and deposition of carbon accompany the reaction and yields are low. It may also be prepared by demetallizing by means of acids or water one of the following derivatives: beryllium, sodium, magnesium, potassium, calcium, manganese, cadmium, tin, barium, or lead, (2, p.1719). At Ludwigshafen, Germany, commercial production of this pigment was carried out via calcium phthalocyanine. Calcium phthalocyanine is obtained by allowing phthalonitrile, calcium oxide, and formamide to undergo a highly exothermic reaction which is initiated around 50 degrees centigrade. Pigment formation takes place at a temperature above 125 degrees, and is completed by allowing the temperature to rise

Co-ordinates with Respect to Monoclinic Crystal Axes. Centre of Symmetry as Origin.

Atom (cf. Fig. 2).	x, A.	$2\pi x/a$.	y, A.	$2\pi y/b$.	z, A.	$2\pi z/c$.
1 CH	6·82	123·7°	3·12	238·1°	4·22	102·7°
2 CH	6·35	115·2	3·76	286·5	2·80	68·1
3 CH	4·91	89·0	3·43	261·5	1·46	35·6
4 C	3·94	71·3	2·48	189·0	1·53	37·3
5 C	4·40	79·8	1·84	140·6	2·95	71·8
6 CH	5·84	105·8	2·17	165·2	4·29	104·3
7 N	3·24	58·7	0·14	10·4	3·79	92·2
8 C	3·10	56·3	0·90	68·2	2·62	63·8
9 N	1·95	35·2	0·98	74·5	1·09	26·5
10 C	2·36	42·8	1·88	143·6	0·39	9·6
11 N	1·61	29·1	2·31	176·0	−1·10	− 26·7
12 C	0·20	3·7	1·79	136·7	−2·14	− 52·0
13 N	−0·66	− 12·0	0·87	66·1	−1·96	− 47·8
14 C	−2·01	− 36·4	0·68	52·0	−3·37	− 81·9
15 CH	−2·76	− 50·0	2·72	207·6	−6·99	−170·1
16 CH	−1·34	− 24·3	3·43	262·0	−6·21	−151·2
17 CH	−0·28	− 5·0	3·21	245·0	−4·61	−112·2
18 C	−0·61	− 11·1	2·29	174·5	−3·80	− 92·3
19 C	−2·02	− 36·6	1·57	119·9	−4·57	−111·2
20 CH	−3·08	− 55·8	1·79	136·6	−6·16	−150·0

FIG. 3.

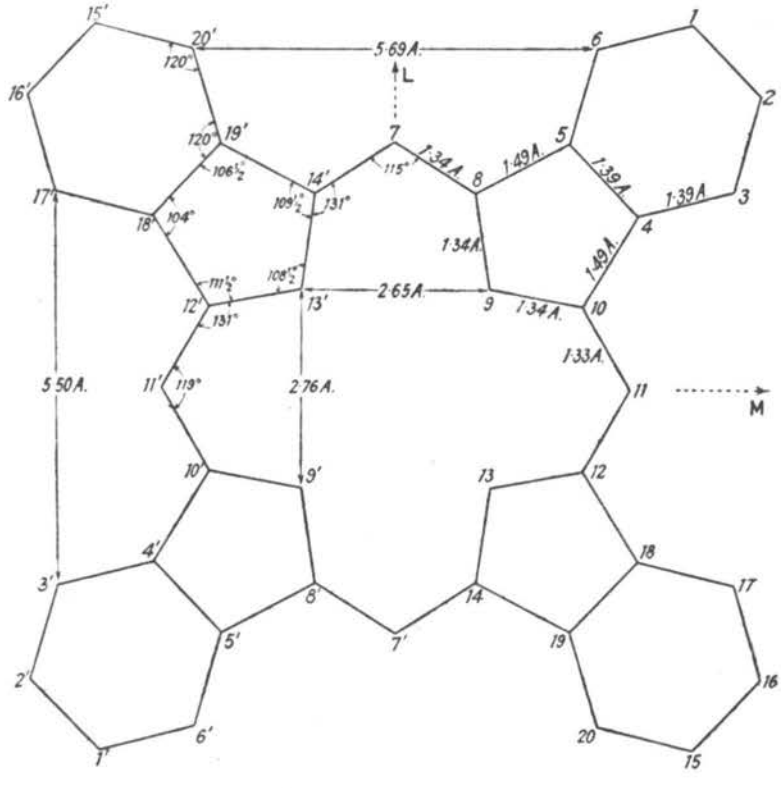


FIGURE 2. METAL-FREE PHTHALOCYANINE

Dimensions of the nickel phthalocyanine molecule.

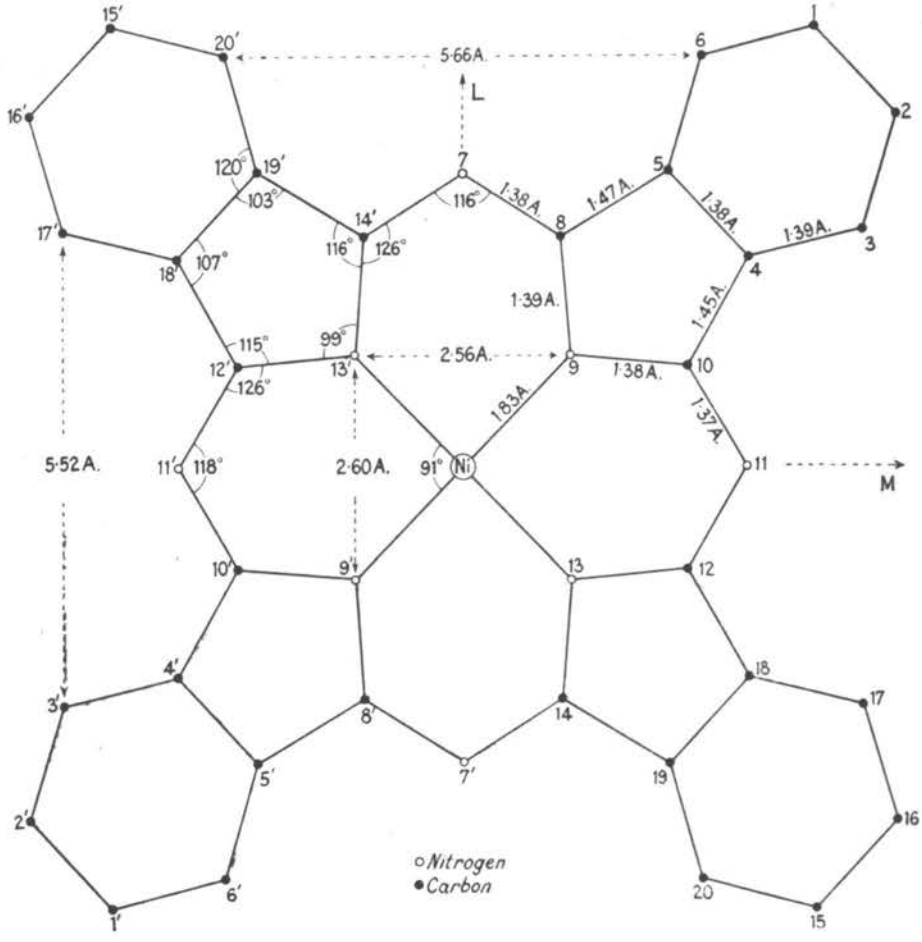


FIGURE 3. Ni PHTHALOCYANINE

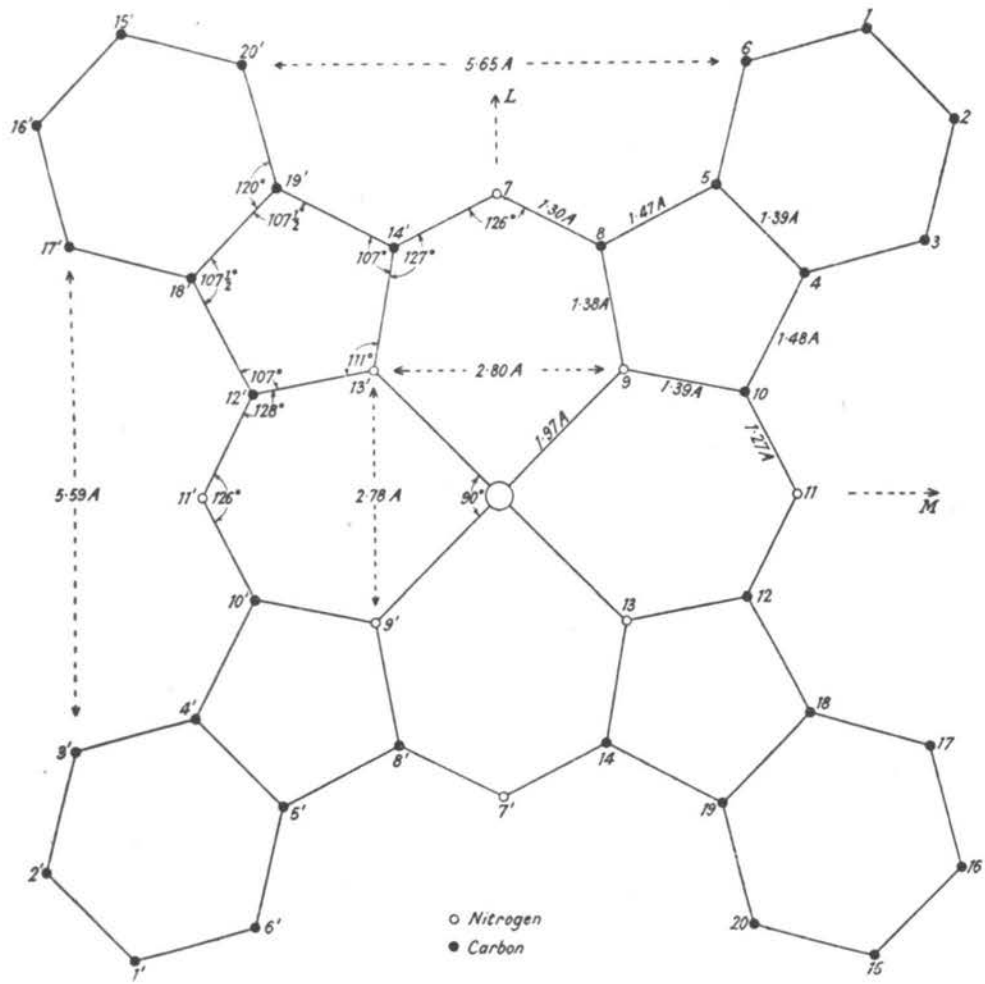


FIGURE 4. Pt PHTHALOCYANINE

to 170-180 degrees. Crude calcium phthalocyanine is obtained as a dark colored porous mass which, when treated with strong mineral acid to demetallize the product, yields metal-free phthalocyanine (27, p.292). Metal-free phthalocyanine decomposes slowly in concentrated sulfuric acid; rapidly when the solution is heated. It sublimes readily under reduced pressure, and 3.7 parts of it will dissolve in 100 parts of boiling quinoline.

Copper phthalocyanine. This pigment is produced commercially by the reaction of phthalonitrile with anhydrous CuCl. Equivalent amounts of these reactants are mixed and heated to 140 degrees centigrade at which temperature an exothermic reaction occurs with the formation of copper phthalocyanine (27, pp.274-275). It may also be prepared with high yields (90-96 % of theoretical) in a trichlorobenzene solvent by a catalytic process using urea, phthalic anhydride, CuCl, and As_2O_5 as a catalyst (27, p.275). Copper phthalocyanine is even more stable than most compounds of this series. It resists the action of molten KOH and boiling HCl, dissolves in concentrated sulfuric acid, remains quite stable for days in solution, and precipitates quantitatively upon dilution with water. At low pressure it sublimes around 580 degrees centigrade to form a beautifully crystalline and analytically pure sublimate (22, p. 1028).

Nickel phthalocyanine. The preparation and properties of this derivative are very similar to those of the copper derivative. It is formed by heating phthalonitrile to 150 degrees centigrade with anhydrous $NiCl_2$. The pigment precipitates quantitatively from concentrated sulfuric acid solution by dilution and sublimes readily. Being quite similar to the copper compound, and so much more expensive to manufacture, it possesses little commercial interest (27, p.309).

Platinum phthalocyanine. $PtCl_2$ and an excess of phthalonitrile are heated together to 280 degrees centigrade during 20 minutes. Pigment formation begins at 180 degrees, and solidification occurs at 230 degrees. The material may be purified by precipitation from sulfuric acid solution. It is quite stable, being the most resistant member of the group towards oxidation. It sublimes readily at 550 degrees under reduced pressure (2, p.1734).

Magnesium phthalocyanine. This compound is prepared by reacting phthalonitrile and lightly etched turnings of magnesium. The reactants are boiled for several hours, after which unreacted nitrile is removed by boiling benzene. Complete elimination of the metal occurs upon precipitation from concentrated sulfuric acid solution. Magnesium phthalocyanine will sublime at low pressures, with some decomposition, to form lustrous blue needles. When these needles

become exposed to air they start to crumble, split, and break up into a blue amorphous-appearing powder which is a dihydrate (34, pp.1023-1024). Beryllium is the only other complex to exhibit this property.

POLYMORPHIC FORMS OF THE PHTHALOCYANINES. The dye industry found that the phthalocyanines must be treated physically to obtain a substance suitable for their use. The long lustrous needles produced by sublimation and the product obtained by the pigment formation could not be ground fine enough to furnish a suitable raw material for dyeing. When used as a pigment in paints where a solvent was present these compounds would tend to grow into larger crystals and lose much of their tinctorial properties. However, it was discovered that the phthalocyanines precipitated from concentrated sulfuric acid were quite suitable.

When the Allied technical teams entered Germany in 1945 a systematic study of these facts came to light (27, pp.345-347,412,434-439). By use of x-ray powder diffraction patterns the following facts were established:

1. Phthalocyanines produce a crystalline form known as the beta form when vacuum sublimed or when originally formed by the standard methods of preparation. This hard monoclinic crystalline form is the one Robertson studied.

2. When precipitated from concentrated sulfuric acid solutions by dilution, the chemical substance is unchanged, but a polymorphic modification of the crystalline structure occurs. This is known as the alpha form.

3. The alpha form may be produced by a process called "permutoid" swelling which gives uniform products of a small particle size by proper choice of conditions (27, pp.444-445,462). It consists of allowing the beta form to remain in contact with sulfuric acid of concentration sufficient to cause swelling and rupture of the beta crystals to alpha crystals, but insufficient to cause solution.

4. Conversion of the alpha form back to beta may be done for the metal-free and copper compounds by heating them to above 200 degrees centigrade (27, pp.447-448).

5. Conversion of the beta form of metal-free phthalocyanine to the alpha form may be done by prolonged grinding (16 hours) in the presence of NaCl (27, p.448).

No crystallographic data has been published about the alpha forms of these compounds other than some rather diffuse powder diffraction patterns found in Germany (27, p.462).

THEORETICAL BACKGROUND OF INFRARED SPECTRA

GENERAL.

It should be borne in mind that the spectra dealt with in this paper are those of the crystalline solids of polyatomic molecules. These are among the most complicated to treat theoretically, and for that reason the great bulk of theory has originated with a study of the gaseous phase of diatomic and other fairly simple molecules. Our outline of the theory will necessarily begin with these simpler molecules and then be extended to the more complicated cases.

To account for observed infrared spectra a simplified model of a molecule is adopted and then the spectrum which this model would produce is calculated using the principles of quantum mechanics. Atoms are considered to be point masses and the forces between them may be crudely thought of as weightless springs which approximately obey Hooke's law. It is assumed that the atoms may be electrically polarized by an external electrical field such as that of a beam of light, and that they may or may not be permanently polarized by mutual interactions in such a manner that the whole molecule has a resultant electric moment. The electrical moment of an electrically neutral molecule is a vector quantity whose direction is that of a line joining the center of

charge of the negative charges with the center of charge of the positive charges and whose magnitude is the length of that line multiplied by the total negative or total positive charge.

The atoms in any molecule are always oscillating about their respective equilibrium positions with frequencies falling within the infrared portion of the electromagnetic spectrum. If a change in dipole moment of the molecule occurs during these oscillations, a periodically changing electric field will result; and it is the interaction of this field with that of radiant energy which causes absorption of the radiant energy to occur at the vibrating frequencies. Molecules such as hydrogen and oxygen, having no dipole moment, do not absorb energy because when their atoms vibrate there can be no change in dipole moment. However, a molecule such as carbon dioxide, even though it has no permanent dipole moment, will absorb radiant energy during its asymmetrical vibrations because they generate a dipole moment.

DIATOMIC MOLECULES.

ROTATIONAL SPECTRA. The rotational energy of a diatomic molecule about an axis perpendicular to a line joining the nuclei is given by,

$$E_J = \frac{h^2 J}{8\pi^2 I} \quad (J+1)$$

h = Planck's constant
I = moment of inertia
J = rotational quantum number; 0,1,2,....

The quantum number, J, represents a certain rotational energy level and absorption of radiation occurs by the molecule moving from a lower level to a higher one. Quantum theory gives rules, known as selection rules, which predict that only certain transitions between levels may occur. In this case, ΔJ may be ± 1. If a transition $J \longrightarrow J+1 = J'$ occurs,

$$\Delta E = \frac{h^2}{8\pi^2 I} 2J' \quad \text{or} \quad \frac{\Delta E}{hC} = 2BJ' \qquad B = \frac{h}{8\pi^2 CI}$$

and $\frac{\Delta E}{hC}$, usually expressed in wave numbers, ω, gives the frequency of the radiation absorbed in this process. The unit for ω is cm^{-1}, which represents the number of waves per centimeter. Frequency, ν, in waves per second is related to ω by $\nu = \omega C$. Experimental data are often expressed in wavelength units, microns, μ, for which the relationship $\omega = 10^4 \mu^{-1}$ holds.

By placing $J' = 1,2,3,....$ it can be seen that the rotational spectra should consist of lines 2B units apart. Once B is obtained in this manner, I may be calculated. In a diatomic molecule $I = (m_a m_b / m_a + m_b) r^2$, where r is the interatomic distance; thus this parameter may then be

calculated. Since these absorptions occur at wavelengths around 200 microns, experimental difficulties discourage their use for these calculations.

VIBRATIONAL-ROTATIONAL SPECTRA. According to the equations of wave mechanics, the energy and selection rule for a harmonic oscillator are,

$$E_v = (v+\tfrac{1}{2})\, hc\omega_o \qquad \Delta v = \pm 1$$

v = vibrational quantum number; 0,1,2,....

ω_o = fundamental frequency

For most purposes we may neglect anharmonicity of the oscillations, which produces overtones or harmonics of ω_o according to a slightly different equation. Then, neglecting interaction, the vibrational and rotational energies may be added to produce,

$$E = (v+\tfrac{1}{2})\, h\, c\omega_o + \frac{h^2}{8\pi^2 I}\, J\,(J+1)$$

and use of the selection rules governing J and v transitions result in expressions for the spectra:

$$\omega = \omega_o + 2BJ' \qquad J' = 1,2,3,....$$
$$= \omega_o - 2B(J'+1) \qquad J' = 0,1,2,3,..$$

Where J' represents the energy level to which the molecule goes in a transition.

The above band would have a "missing line" for (since selection rules forbid $\Delta J = 0$), with lines at 2B spacings on either side. Since these bands occur in the 1-23 micron region, for which the experimental techniques are well developed, this is the usual source of B values for moment of inertia and interatomic distance calculations. It is also possible to write for harmonic motion,

$$\omega_o = \left[\frac{k}{4\pi^2 c^2 \bar{m}}\right]^{\frac{1}{2}}$$

$\bar{m}$ = reduced mass
k = force constant

and thus the force constant, a measure of the atomic bonding forces, may be obtained from ω_o.

POLYATOMIC MOLECULES.

NORMAL VIBRATIONS. A diatomic molecule, having only one mode of vibration, gives a comparatively simple spectrum. If one could see a polyatomic molecule in motion, a wild disorderly motion would be observed as each atom responded to the many forces acting upon it. However, this complicated motion can be resolved into a definite number of fundamental or normal vibrations; 3n - 5 for linear molecules, and 3n - 6 for non-linear molecules of n atoms. These relationships arise from the fact that the number of different normal vibrations is equal to the number of vibrational degrees of freedom. For an n-atomic molecule the total number of degrees of freedom is 3n; there are always three

translational degrees of freedom and, for non-linear molecules, three rotational degrees of freedom corresponding to three independent rotations of the molecule about three perpendicular axes. But for linear molecules only two rotational degrees of freedom exist since the rotation around the molecular axis does not displace the atoms and must not be counted. In a normal vibration all atoms move in straight lines, in phase, with the same frequency, and with no change in the center of gravity of the molecule. Thus each normal vibration has a characteristic frequency, although the amplitude may have any value. The actual motion of the atoms in a molecule may be constructed from some linear combination of these normal modes. Since absorption in the infrared occurs at these normal vibrational frequencies, this is the information available for molecular studies.

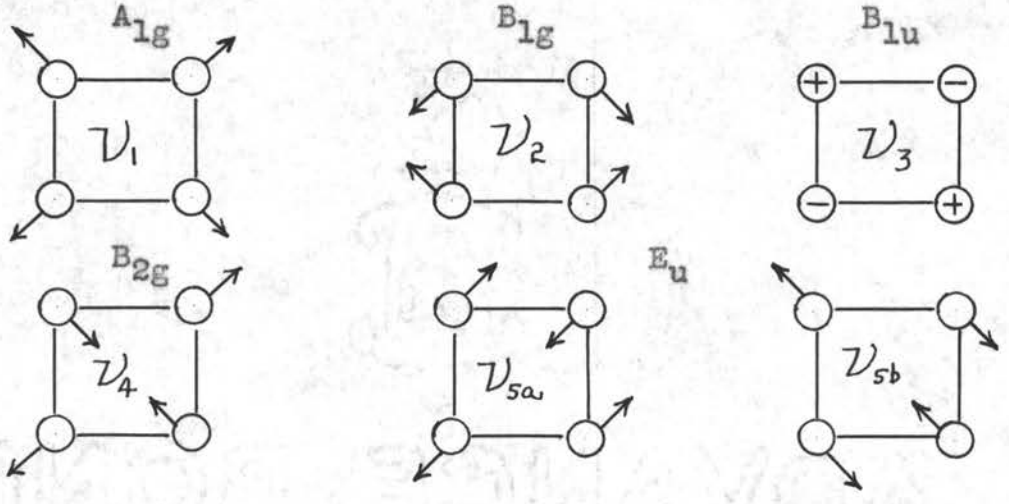
If in a molecule of known configuration the linear relation between restoring forces and displacements is given, it is possible to calculate the frequency and form of the normal vibrations. However, the calculation is very complicated for polyatomic molecules, since it involves the solution of a determinant equation of high order. In practice the reverse is usually done. The frequencies can be determined experimentally, and some additional information may be obtained about the form of the vibrations. From

these data we wish to find what kind of forces arise when atoms are displaced, but unfortunately we usually have too few facts to permit calculation of all the force constants. The problem can be greatly simplified by taking into account the molecular symmetry and symmetry of the normal vibrations.

DETERMINATION OF NORMAL VIBRATIONS. To illustrate the above discussion of normal vibrations, those of a square, planar molecule will be presented. In group theory designation this symmetry is given the synbol D_{4h}. A four atom molecule of this symmetry has the six normal vibrations (3n-6) shown in Figure 5 (30, pp.92-93). Displacements of atoms are indicated by arrows, and a + and - indicate motions perpendicular to the plane of the paper.

FIGURE 5.

Normal Vibrations for a D_{4h} Molecule.



The form of the vibrations may be obtained by considerations of symmetry and certain results of group theory which are quite simple to use. Table 2 presents a "Character" table (30, p.117) which gives in very concise form a symbolic picture of the symmetry and possible modes of vibration of any molecule possessing D_{4h} symmetry. The symbols across the top of the table represent certain symmetry "operations". A symmetry operation is defined as a geometrical transformation of the molecule which turns it into a configuration that one cannot distinguish from the original position. For example, C_4 means a 90 degree rotation, C_2 a 180 degree rotation, i an inversion through the center, σ a reflection through a plane, and S_4 a 90 degree rotation followed by reflection through a plane. The column of symbols under D_{4h} represent all possible species of vibrations. The number of each species which a four atom molecule of D_{4h} symmetry possesses is calculated as follows:

1. The χ_R row beneath the character table is calculated according to equation number 1 in Table 2. This is done by multiplying the number of unshifted atoms when the particular symmetry operation is performed by the expression $(\pm 1 + 2 \cos \alpha_R)$, where -1 is used for operations other than pure rotation and α_R is the angle involved in the symmetry operation.

TABLE 2

CALCULATIONS FOR NORMAL MODES OF A D_{4h} MOLECULE USING A CHARACTER TABLE

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	n^{γ}		n_v^{γ}	n_μ^{γ}
A_{1g}	1	1	1	1	1	1	1	1	1	1	1		1	0
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	0		0	0
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	1	R_z	0	0
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	1	T_z	0	1
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1	1		1	0
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1	1		1	0
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1	1		1	0
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1	0		0	0
E_g	2	0	-2	0	0	2	0	-2	0	0	1	R_xR_y	0	0
E_u	2	0	-2	0	0	-2	0	2	0	0	2	T_xT_y	1	1
	3	1	-1	-1	-1	-3	-1	1	1	1	$(\pm 1 + 2\cos\alpha_R)$			
	12	0	0	0	-2	0	0	4	0	2	χ_R			

(1) χ_R = No. of unshifted atoms $(\pm 1 + 2\cos\alpha_R)$

(2) $n^{\gamma} = \frac{1}{g} \sum_R \chi_R \chi_R^{(\gamma)}$ = No. of motions of species $\Gamma^{(\gamma)}$

(3) g = No. of symmetry operations.

(4) χ_R^g = Character of species γ for operation R(1, -1, etc. in table above).

(5) $n_\mu^{\gamma} = \frac{1}{g} \sum_R (\pm 1 + 2\cos\alpha_R)\chi_R^{(\gamma)}$ = Infrared active motion of species

2. The n^{γ} column is calculated by use of equations number 2, 3, and 4. A one in this column indicates there will be found one normal mode of that particular species. These modes total twelve (3n) of which the A_{2g}, A_{2u}, E_g, and E_u species posses one mode of zero frequency corresponding to translational or rotational motions as indicated by an R or T in the next column. E_g and E_u modes, being degenerate, must be counted twice.

3. The n_v^{γ} column then indicates the number of vibrational modes of each species.

While there are formal methods to obtain the forms of these modes, for the present purpose it will suffice to show how the diagrams of the normal modes in Figure 5 may be deduced from use of the character table and symmetry considerations. The symmetry of a species is given by the numbers (χ_R^g) running across the table. For example, a 1 under C_2 and opposite B_{1g} means that mode will retain its symmetry when rotated 180 degrees, while a reflection through a diagonal plane will reverse the phase of this mode as indicated by a -1 under σ_d. In this simple case one can arrive at the diagrams in Figure 5 by considering what pattern of displacements would possess the symmetry of the species indicated by the character table. For example, the motion of ν_1 in Figure 5 is easily seen to be the only one having all the symmetry of A_{1g}. It represents a totally

symmetric vibration. ν_2, ν_3 and ν_4 are partially symmetric vibrations because they are changed in phase under certain operations, as shown by a -1 in the table. ν_{5a} and ν_{5b} are called a degenerate pair since they occur with the same frequency.

Now that the normal modes have been determined it is possible to use the information in Table 2 to calculate which of these modes are infrared active. This is done by use of equation number 5 in Table 2 which leads to the column n_μ^γ . A one in this column indicates the vibrations of that species will be infrared active. Only the E_u mode will appear as an absorption band in the infrared spectrum.

ν_1 is inactive in the infrared spectrum since its dipole moment is unchanged by the motion. Its value may be determined frequently in the form of a combination frequency with other active modes, or by observation of the Raman spectrum. A combination frequency may be either the sum or difference of two normal modes arising from coupling and is usually much weaker than a normal mode.

The more atoms in a molecule the greater the number of vibrational modes, and consequently the number of vibrational-rotational bands in the spectrum. Non-linear molecules, having two or three different moments of inertia, exhibit a very complicated rotational fine structure of vibrational bands. It is obvious that identification of

frequencies for even relatively simple polyatomic molecules is difficult. However, some progress may be made with highly symmetrical molecules where the symmetry reduces the number of infrared active modes, as has just been shown in the case of the D_{4h} molecule.

INFRARED SPECTRA OF SOLIDS.

In solids a molecule is closely surrounded by others and its vibrations as well as electrical dipole are influenced so that its infrared spectrum is changed. If intermolecular forces are weak compared to interatomic forces in the molecule, the vibrations will remain essentially the same as in a gaseous phase. However, since free rotation does not occur in most solids, this motion becomes transformed into a vibration about an equilibrium orientation. Translational motion is likewise transformed into vibrational, so that in a solid all degrees of freedom may be considered vibrational. These six motions (3 translational, 3 rotational) of the molecules as rigid units constitute the so-called "lattice modes", which usually occur at frequencies below 200 $cm.^{-1}$. The rotational fine structure of vibrational modes disappears, but in its place appear combinations of lattice modes with internal normal vibrations. The first effect tends to narrow an internal normal mode; the latter to broaden it. Broadening and shifting as well

occurs from effects of environment where there is a large interaction between molecules.

When a crystal is studied at very low temperatures, both the lattice and molecule may be regarded as in their ground state. This simplifies the infrared spectrum, since anharmonic effects giving rise to coupling between lattice and normal modes are minimized, and normal modes should be exceedingly narrow bands. Furthermore, forbidden lines resulting from coupling of lattice modes with an unallowed frequency should disappear.

For each crystal vibrations occur where the motion mainly consists in displacements of cells with respect to each other. These are known as the acoustical branch because vibrations produced by sound belong to this continuum. Other vibrations occur consisting of relative motions of atoms within one cell. These comprise the "optical" branch, since they occur with frequencies in the infrared spectrum. In molecular crystals such vibrations may closely resemble those of isolated molecules; however, all molecules in the crystal participate with the same amplitude and regular phase shifts (52, pp.216-220).

From the whole continuum of crystal vibrations, only a few may appear as strong fundamentals in the infrared spectrum. Translational symmetry of the crystal requires that in an infrared active vibration all crystal cells shall

vibrate in the same phase. The acoustical branch never contributes fundamentals appearing in the infrared, since equal phase in all cells means a simple translation of the whole crystal. Complicated crystals present fundamentals which should be sharp lines. Their sharpness is due not to lack of interaction between crystal constituents, but to their perfectly ordered positions and regular vibrational motion.

Hornig has presented a detailed mathematical development of the theory of vibrational spectra of crystals (31, pp. 1063-1076). Selection rules for calculation of infrared active frequencies are developed which depend upon the symmetry of the environment of a molecule in a crystal, which is deduced from a knowledge of the unit cell group describing the symmetry of a unit cell. Just as a unit cell group is a factor group of the space group for the entire crystal, a site group is a factor group of the unit cell group. It describes the symmetry about any point in the crystal. The conclusions his theory reach are that the number of frequencies active in the infrared spectrum calculated from local symmetry of the molecules (site group) is exactly equal to the number calculated on the basis of the unit cell, which is equal to the allowed number for the entire crystal.

Infrared spectra of solids also give direct information about the direction in which a change in dipole moment

occurs during a vibration. This is done by observing the dependence of the absorption strength on the relative orientations of a single crystal when polarized infrared energy is used.

INSTRUMENT

DISCUSSION OF PRINCIPLES.

GENERAL. An infrared spectrometer consists of a source of infrared radiation, a monochromator to disperse it into its various wavelengths, and a detector to indicate the amount of radiant energy of each wavelength the compound transmits. Early instruments were quite cumbersome, their major difficulty being the use of a shock-sensitive galvanometer as a detector which had to be carefully mounted and shielded. A spectrum was obtained by recording the energy reaching the galvanometer with the sample in the beam and then out of the beam at each wavelength, then carrying out a point by point division to obtain a plot of percent transmission versus wavelength. Today much of this tedious labor may be avoided because of the excellent spectrometers available using thermocouple detectors and automatic recorders.

The instrument used in this work was a model 12C Perkin-Elmer monochromator. Accessory components were constructed for this basic unit according to the method of Savitsky and Halford so that the completed instrument would automatically record a spectrum (53, pp.203-212). If used with double beam operation, i.e., one beam for the sample and another for the standard, percent transmission of the

sample will be plotted directly by the recorder. It may also be used as a single beam instrument whereby the absolute energy passed by the sample alone is recorded. It is desirable to obtain a spectrum in this manner when high resolution is necessary.

MONOCHROMATOR. The source of infrared radiation is a carborundum rod[2] electrically heated to about 1300 degrees centigrade by a regulated power supply and cooled by a water jacket. It has approximately the same distribution of energy as that of a black body at this temperature. Mirrors focus the radiation on an entrance slit immediately in front of which rests the sample holder. The prism arrangement is the conventional Littrow type in which the radiation is passed through the prism and then reflected back so that one prism functions as a double dispersing agent. The dispersed radiation then goes through the exit slit and finally reaches the thermocouple[3] where it is detected by its heating effect. The entrance and exit slits open in unison and determine the strength of the signal reaching the thermocouple. Although more energy is allowed through the system

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2. Sold by Perkin-Elmer Company under the trade name of "Globar".
3. The thermocouple is permanently evacuated with a KBr window and is rated to have a sensitivity of 6-10 microvolts per microwatt of incident radiation. It has a 90% response at 10 cycles.

when open wider, the exit slit also passes a wider band of dispersed wavelengths, which lowers the resolution. The spectrum is scanned by rotation of the Littrow mirror, which causes a different wavelength to pass through the exit slit.

SINGLE BEAM OPERATION. Since the energy detected by the thermocouple appears as a very small voltage in the microvolt range a high degree of stable amplification is required to obtain a recordable voltage. This is done by placing in the light beam a rotating disk, so constructed that it interrupts the beam at ten cycles per second. This frequency is chosen because the response of the thermocouple falls off rapidly at higher frequencies. A ten cycle signal will reach the detector which may be amplified by a special low frequency amplifier. The amplified signal is then rectified to a d.c. voltage and delivered to a Brown recorder, which requires 10 millivolts for full scale deflection.

To obtain an absorption spectrum of a compound, one must first insert a cell filled with the standard in the monochromator. Since the spectrum is a percent transmission plot, the standard will consist of every material in the beam other than the sample. For example, if the spectrum of a material is being determined in solution, the standard would consist of the cell filled with the solvent. The

starting wavelength is set by means of a calibrated drum and the slit and amplifier gain are adjusted to obtain almost full scale deflection on the recorder.

It is desirable to use as narrow a slit as possible to obtain high resolution, but as the slit adjustment is narrowed the lessened energy reaching the thermocouple must be compensated by increasing the gain of the amplifier if the same deflection is to be maintained on the recorder. This process may be carried out to the point where the lessened radiant energy reaching the thermocouple produces voltages approaching those induced in the amplifier by random electromagnetic fields in the room, and various factors in the electronic components known collectively as "noise" voltages. In this event, the recorder may move in response to voltages of the thermocouple or to noise voltages, and the record is of no value. Under ordinary conditions, the slit setting is made as small as possible, consistent with the requirement that the noise does not exceed 2% of full scale signal.

With the cell in place, a gear train is then set in motion which changes the wavelength reaching the thermocouple by rotation of the Littrow mirror. As longer wavelengths are approached the energy of the source falls off. When a value around mid-scale on the recorder is reached, the slit is opened just enough to bring the signal to the

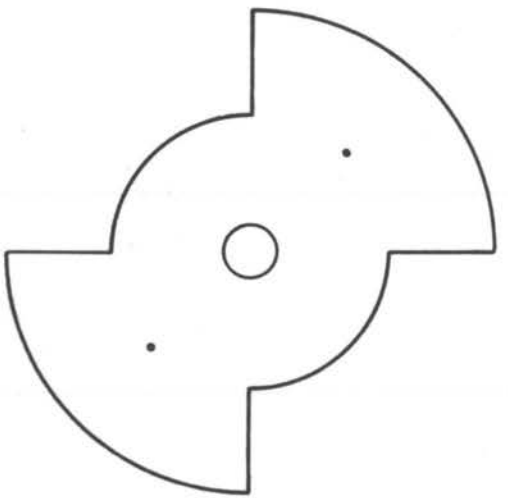
initial value again. This procedure is continued until the desired wavelength region is scanned. A sample is then placed in the cell and the recorder and spectrometer are reset to the initial conditions. The procedure is repeated for the sample, taking care to start its trace on the recorder paper at the same initial point as the trace of the standard, to employ the same slit settings as before, and to maintain the gain of the amplifier the same. This record must then be converted to a percent transmission versus wavelength plot by calculation of the ratio of the sample curve to that of the standard.

DOUBLE BEAM OPERATION. When one considers the labor involved in obtaining a spectrum by the single beam method, the desirability of having a spectrum appear on the recorder as a direct ratio reading is obvious. Furthermore, the single beam method has the difficulty that there may be variations in source intensity or in atmospheric absorption between the standard and sample runs, thereby causing an error in the calculated ratio. The Savitsky and Halford double beam method (53, pp.203-212) is capable of viewing the radiant energy passing through both sample and standard simultaneously and giving this information to the recorder so that the ratio of the two will appear.

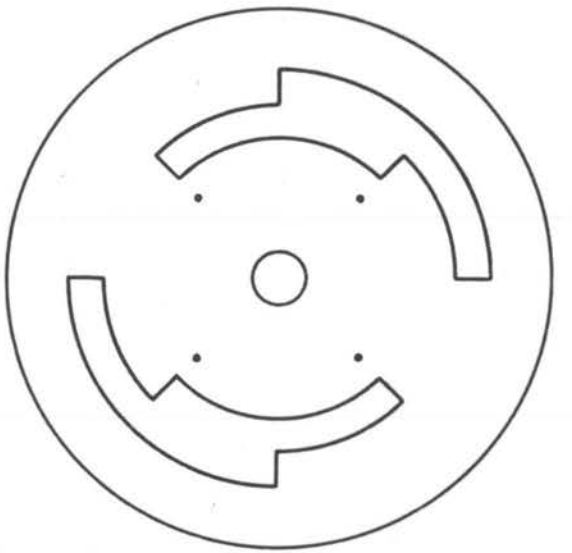
Figure 6 illustrates the sector which provides the double beam. It is shaped so that it divides the radiation

beam into upper and lower halves, each interrupted at ten cycles per second and with a 90 degree phase difference between them. A cell is constructed so that its upper half will contain the standard and lower half the sample, then placed on the monochromator in the respective beams provided by the sector. A ten cycle signal will go through the amplifier for each of these beams, the only difference being their amplitudes and a 90 degree phase difference. From the amplifier the signals go to two breaker switches which are each synchronized with one of the beams by mechanical coupling to the sector. It is this arrangement which will separate and rectify the two signals from the amplifier due to their 90 degree phase difference. The separated signals are filtered and the standard voltage placed across the slidewire in a Brown recorder. The sample voltage is balanced against it and the position of balance will indicate the ratio of the two voltages.

Since the radiation beam is divided, it can be seen that only half as much energy may reach the thermocouple from a sample as in an equivalent single beam operation. Therefore, when high resolution by using a very narrow slit is desired, the double beam sector is replaced by one shaped so the entire beam will be passed through the sample channel. This single beam sector is illustrated in Figure 6. The signal is then introduced to the recorder in the conventional manner.



Single Beam



Double Beam

Figure 6 – Sector Disks (1/3 Actual Size)

DETAILS OF CONSTRUCTION.

MECHANICAL SYSTEM. The mechanical system is shown above the source housing in Plate 1. To obtain good mechanical balance the sector is cut to provide two electrical cycles per revolution. It is driven by an 1800 r.p.m. synchronous motor through a six to one gear reduction. The breaker system is mounted on top of the shaft support and driven by a two to one spur gear from the same shaft as the sector. Phasing of the breakers is accomplished by means of a rotatable coupling to the gear train and an adjustment enabling one breaker to be rotated with respect to the other. The entire structure has adjustments to place the sector properly in the beam. Since the beam is quite large near the sector and smaller near the entrance slit, a double beam cell must place the sample near the sector to avoid a critical sample position. For single beam operation the sample is placed immediately in front of the entrance slit.

PREAMPLIFIER. Proper design of the preamplifier[4] is critical for stable amplification of the minute signals at the thermocouple. To eliminate magnetic pickup and microphonic disturbances the entire circuit was shielded and mounted on a pillar directly beneath the table carrying the

4. A more detailed discussion of this unit will appear in a thesis by Mr. T. E. Furlong entitled "The Infrared Spectrum of Hydrazine Dihydrofluoride", the completion of which is now in progress.

monochromator. This shortened the input lead to six inches and reduced vibrations from the mechanical system. The completed circuit appears in Figure 7. T_1 is a special low frequency transformer[5] tuned near ten cycles by a 0.01 microfarad condenser. This condenser drops the ten cycle gain of the untuned transformer to 70%, but the 60 cycle gain to 20%. This latter feature is highly desirable, since pickup of this frequency is a source of noise in the system.

The bias employed in these low level circuits is extremely critical. An incorrect bias results in grid currents which in turn result in excessive noise and low gain. Liston and White discovered that when the grid of the tube is allowed to float by use of a condenser, the free bias will adjust itself to the optimum value (40, p.38). This also makes tube selection and filament temperature less critical. However, experience has shown that if a very large signal is injected into the grid, the bias will go to cut-off and remain there for some time. The grid condenser can be discharged to correct this condition. Such a large signal is rarely encountered in normal operation of the spectrometer. The plate is operated at 50 volts with 25 volts on the screen grid. Filaments are heated by about 4 volts d.c. from a storage battery.

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5. Manufactured by United Transformer Company, New York City. Model No. D7719.

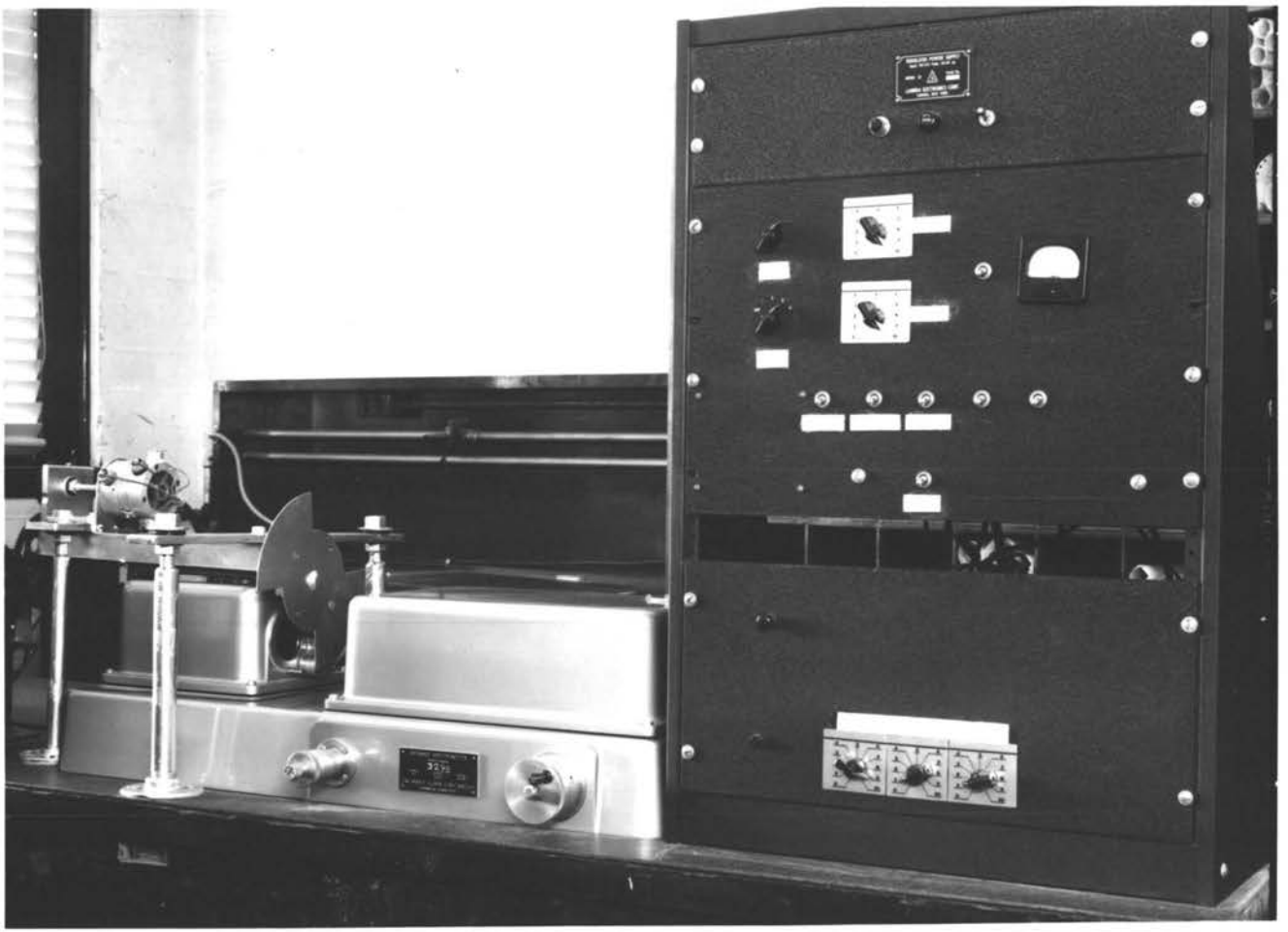

PLATE I. SPECTROMETER

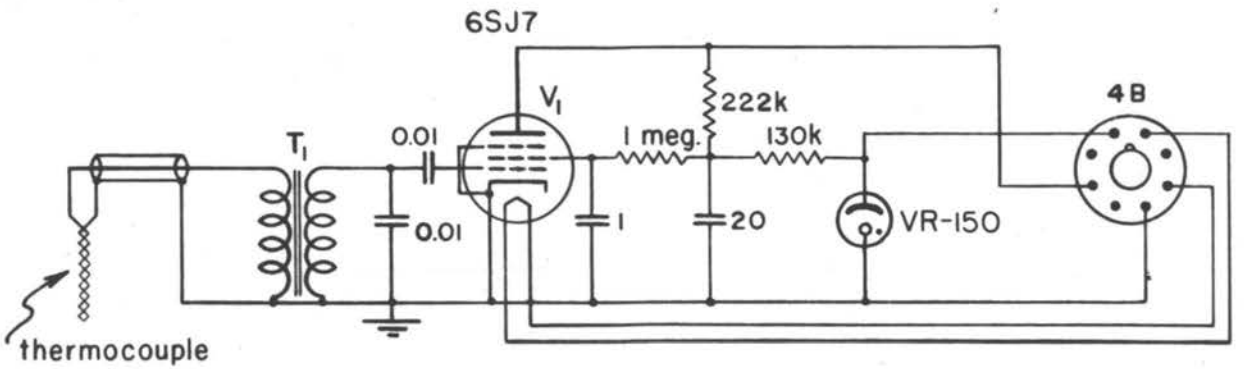

Figure 7 - Circuit Diagram of Preamplifier

The transformer has an input impedance of 10 ohms which appears as 750,000 ohms at the grid of V_1. Its voltage gain at ten cycles is 160 and that of the tube is 200. This gives a total gain of 3.2×10^4 for the preamplifier unit.

MAIN AMPLIFIER. Brown (10, pp.194-197) has successfully used the circuit of Sturtevant (56, pp.124-127) for amplification of weak thermocouple voltages. The design of Sturtevant provides a selective low frequency amplifier in which the center frequency and band width may be readily changed. Direct coupling and both frequency-dependent and independent feedback are used to provide a high degree of stability and linearity at low frequencies. Therefore it was chosen as the amplifier to construct for the spectrometer.

The circuit is represented schematically in Figure 8. Two separate feedback loops, each including a cathode follower, connect the plate of the second amplifier tube to the cathode of the input tube. Selectivity is obtained by a twin-T network, which is a ten cycle rejection filter; thus all other frequencies are fed back degeneratively. P_1 and P_2 are in the feedback paths and allow an adjustment of the circuit Q and band width. To find their optimum setting for ten cycles, they are adjusted alternately until about 90% of a maximum signal is observed at pin 1 of the test

socket with an oscilloscope. Experience has indicated that a setting of P_1 = 9.0 and P_2 = 1.0 is best for ten cycle operation. Care must be used not to tune the circuit too sharply, for near the maximum Q, instability and oscillations occur. P_4 serves as a balance control for the phase inverter, V_5, which delivers the signal to the cathode followers, V_6. These provide an impedance match for the rectifier and filter system to which the signal then goes. The main amplifier has a gain of 600 with the settings of P_1 and P_2 indicated and the phase inverter and cathode followers provide a combined gain of 12. Plate voltage is supplied by a well regulated power supply[6] and each stage has ample decoupling. Tube filaments are heated by a 6 volt battery. This battery should be maintained well charged, because when its specific gravity falls below 1.125, noise appears due to instability in the main amplifier. This amplifier is quite sensitive to electrical disturbances in its input stage, since any such shock will cause a ten cycle wave to be generated.

AUXILIARY CIRCUITS. Figure 9 shows the auxiliary circuits which take the signal from V , convert it to d.c., and then deliver it to the recorder. The signal enters a decoupling network through plug 9, and from there to the two

6. Manufactured by Lambda Electronics Corp., Elmhurst, New York. Model No. 28.

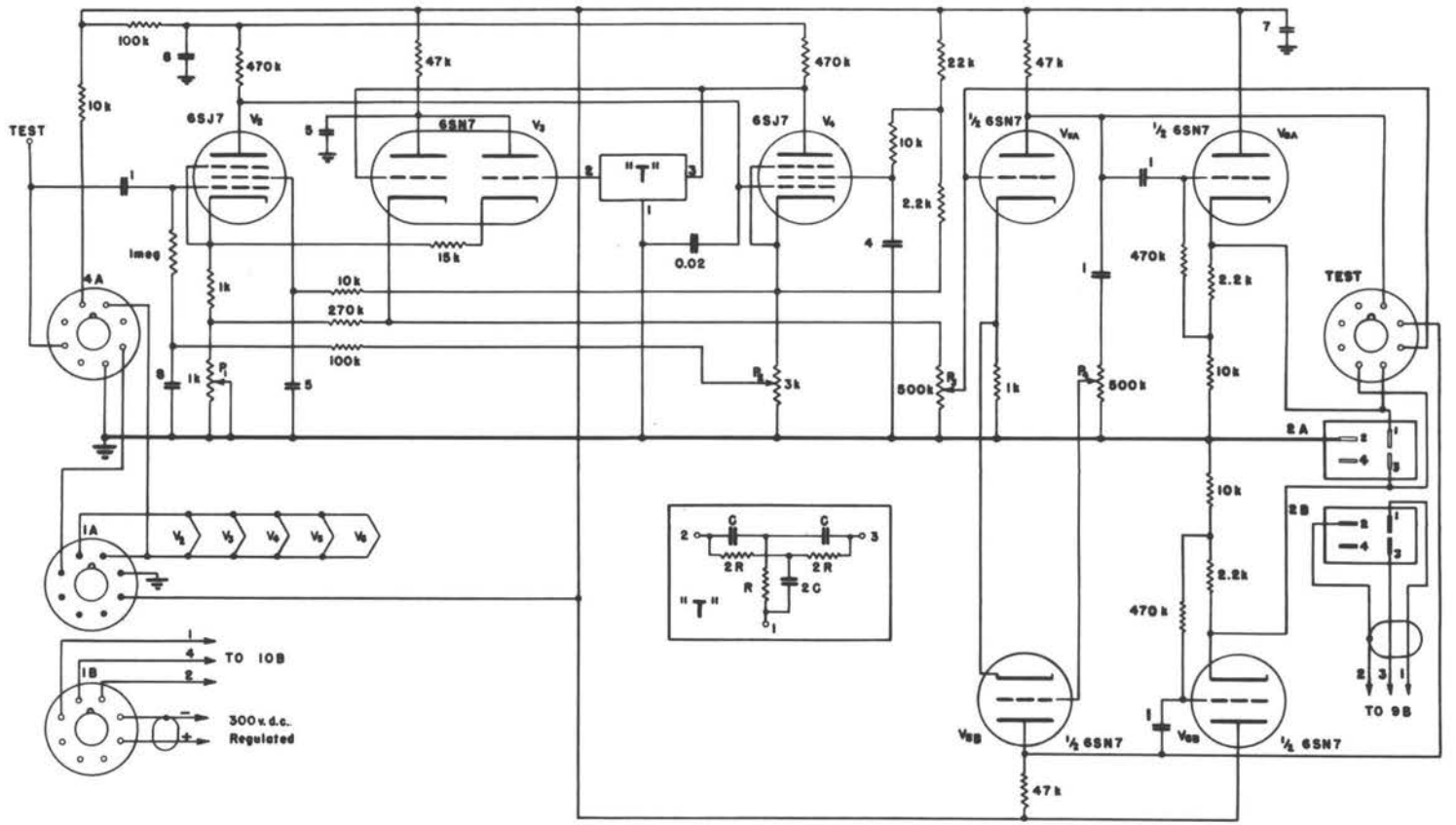

Figure 8 – Circuit Diagram of Ten Cycle Amplifier

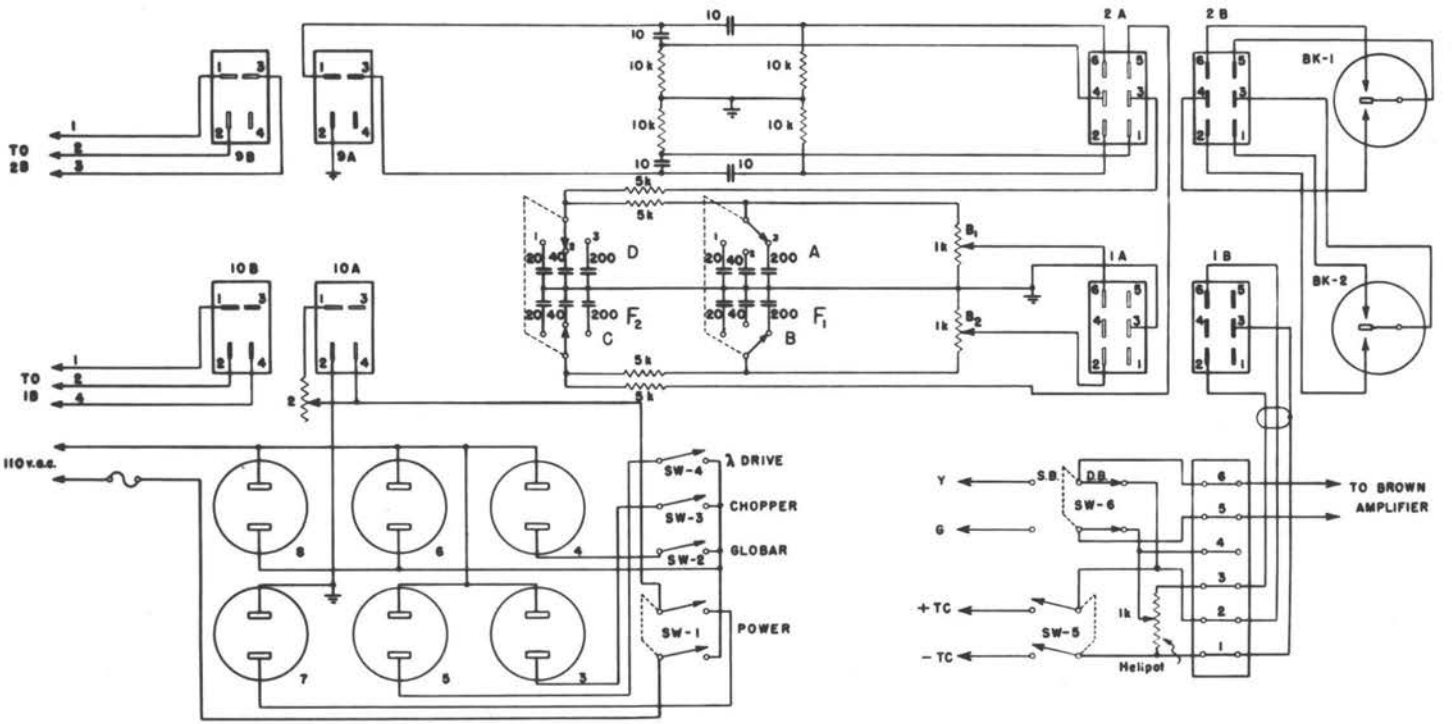

Figure 9 –Auxiliary Circuits

breaker switches through plug 2. Since each one of these is phased to one beam by a mechanical coupling to the sector shaft, they will rectify and separate the signals from the upper and lower beams. To phase the breakers accurately, one blocks the upper beam channel and sets the signal from the lower beam to full scale on the recorder. Doubling the slit then gives a signal which is four times full scale. The upper beam is next unblocked, connected to the recorder, and its breaker adjusted by rotation of the shaft coupling so that the signal is less than 1% of full scale. This procedure is then repeated for the other channel, rotating the switches with respect to one another for this adjustment.

The rectified signals from the breaker enter a filtering system whose time constant may be varied by F_1 and F_2 according to the desired noise level and scanning speed. The final signal goes through plug 1 to a switching system in the recorder. Switches sw-5 and sw-6 provide the necessary changes from single to double beam operation. A 1000 ohm potentiometer serves as a slidewire for the reference beam on double beam operation. It is mechanically coupled to the recorder slidewire.

PERFORMANCE OF THE INSTRUMENT.

CALIBRATION AND ACCURACY. To cover with good resolution the region of 400 to 4000 cm^{-1} where most fundamental

vibrations occur, there are three prisms available which are mounted on individual tables to allow a ready interchange in the monochrometer. The regions where each prism gives best resolution are:

$Cm.^{-1}$	Prism
400- 700	KBr
700-2000	NaCl
2000-4000	LiF

There is a micrometer attached to the shaft that drives the Littrow mirror which may be read to 0.01 of a revolution and estimated to 0.005. Micrometer units are correlated with points on the recorder trace of the spectrum by fiduciary marks. These marks are most conveniently made by hand with a sharp momentary reduction in the output control of the lower beam (B-1) at convenient readings on the wavelength micrometer.

A calibration of micrometer readings versus wavenumbers is necessary for each prism. It is carried out by determining the positions of absorption bands of several common substances. The Perkin-Elmer Company has supplied complete details of the spectra necessary for each prism in an instruction manual accompanying the monochromator (44, pp.30-31). A convenient source of methane and carbon monoxide for calibration of the LiF prism is gas from the commercial pipe lines. A 40 cm. cell was required for methyl

alcohol vapors for the KBr prism, but it was found one could place a small evaporating dish of methyl alcohol in the mirror housing adjacent to the globar as a substitute.

After each prism is calibrated, a large plot of the data is made and a table of micrometer units versus wavenumbers constructed from this master plot. In order to place the LiF prism on the micrometer scale, it is necessary to change the setting of the Littrow mirror from that used for the NaCl and KBr prisms. This is done by turning a screw adjustment at the base about three turns counterclockwise. When resetting any prism to precise calibration this screw is adjusted until one of the atmospheric absorption bands lines up with its exact micrometer setting.

One will find that at times it is impossible to adjust the Littrow mirror to reproduce the previous calibration exactly upon replacing a prism. In this event, regions where atmospheric absorptions occur should be recorded and reading from the calibration tables corrected accordingly. For the LiF prism, a complete check of the region may be made by use of the absorptions of atmospheric water vapor and carbon dioxide, and the methane and carbon monoxide in pipe-line gas. Since slight calibration shifts occur from day to day, very precise work requires these checks daily.

Consideration of error arising in reading band centers, in calibration, in changing prisms, and from

calibration drifts indicate that the frequency assignments are no more accurate than:

Prism	Region Cm.$^{-1}$	Accuracy Cm.$^{-1}$
LiF	3200	± 3
	2300	± 1
NaCl	1600	± 3.5
	700	± 0.5
KBr	700	± 1.8
	400	± 0.5

These values agree fairly well with those found by Mair and Hornig using the same monochromator (42, pp.1241-1242).

RESOLUTION. Resolution may be thought of as the ability of the monochromator to furnish the detector a single wavelength. This ability is determined by the dispersion of the prism and the slit opening. It will appear in the recorded spectrum as a factor which determines how close two absorption bands may be to each other and still appear as separate bands.

Figures 10, 11, and 12 indicate the resolution attained under normal operating conditions, and the prism resolution limit with an infinitely narrow slit, for the LiF, NaCl, and KBr prisms respectively. These figures were calculated with the aid of curves furnished with the monochromator (45, p.C5). Abrupt changes along the curves occur where slit changes are made.

This resolution is not as good by a factor of two as that attainable with the instrument (44, p.7). The slits one may use are determined by the requirement that the noise level be less than 2% of full scale deflection. It was measured to be $\pm$ 1 x 10^{-9} volts rms., which is quite close to the calculated Johnson noise ($\pm$ .33 x 10^{-9} volts) of the thermocouple (18, p.713). Since noise voltages were not the limiting factor in the poor signal to noise ratio, the response of the thermocouple was checked and found to be too low by a factor of 10-20, which adequately accounts for the observed signal to noise ratio.

The discussion of performance above refers to single beam operation. Since all of the spectra in this research were obtained by this method, the performance of double beam operation will not be discussed here.

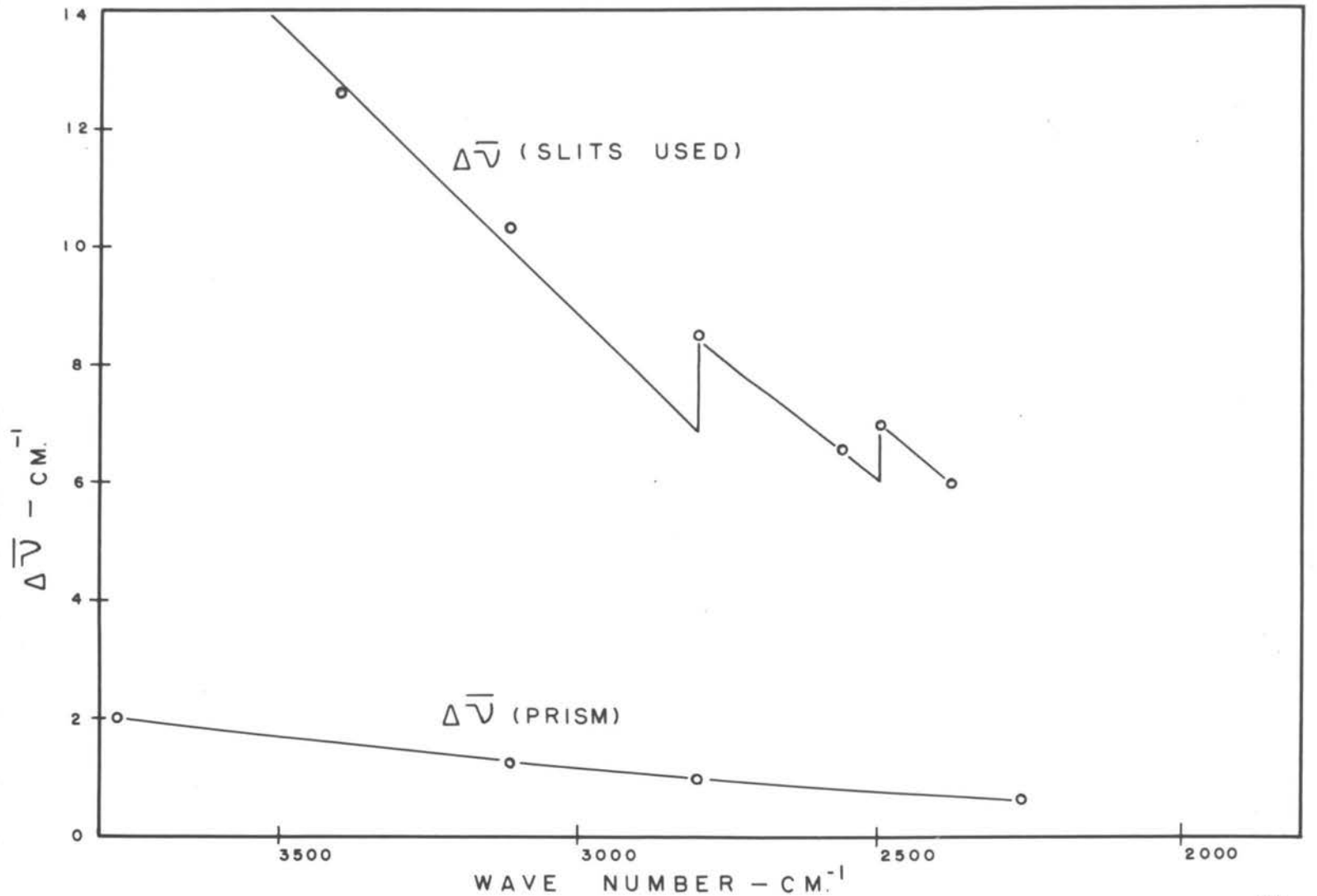

FIGURE 10. RESOLUTION FOR LiF PRISM

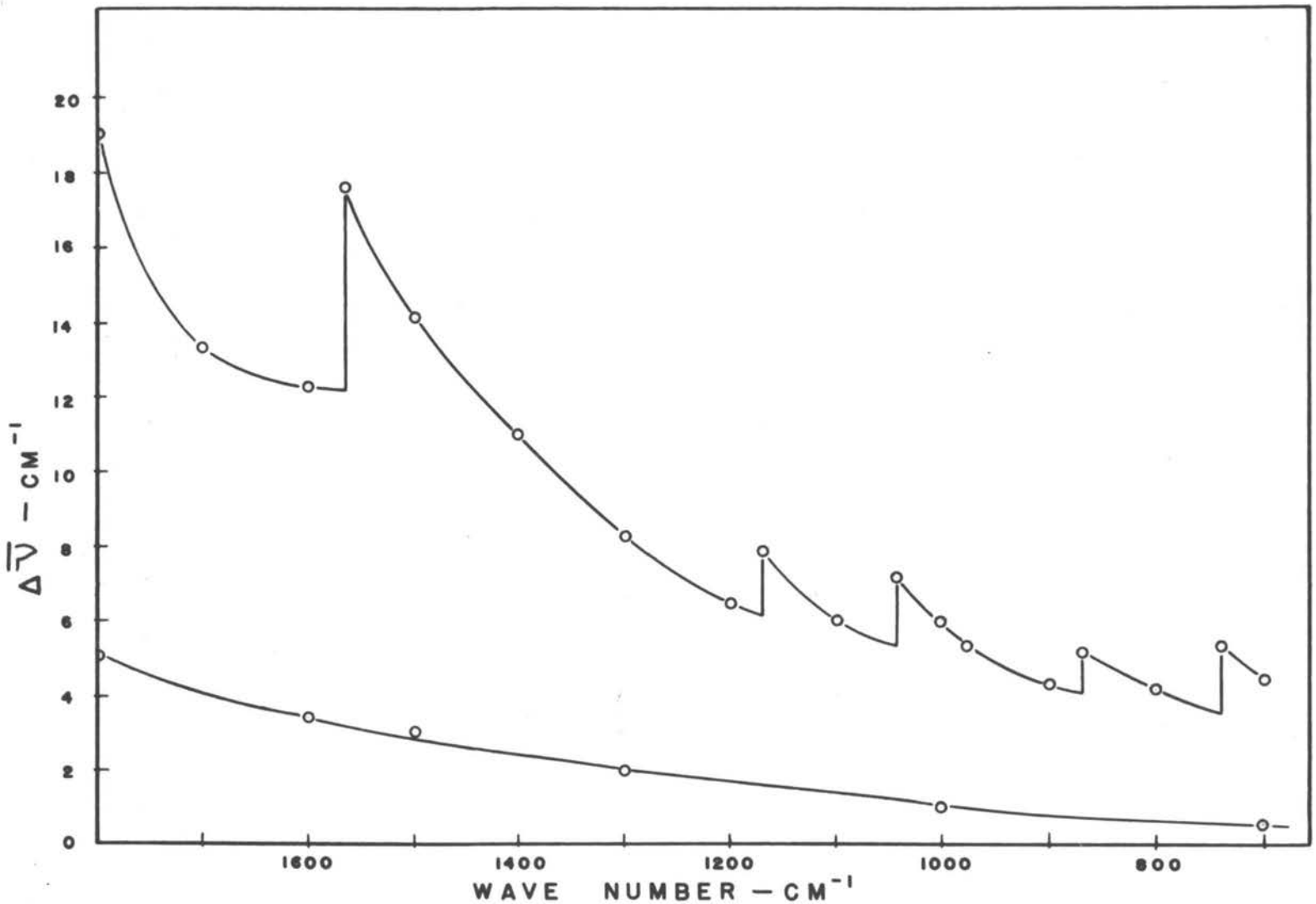

FIGURE 11. RESOLUTION FOR NaCl PRISM

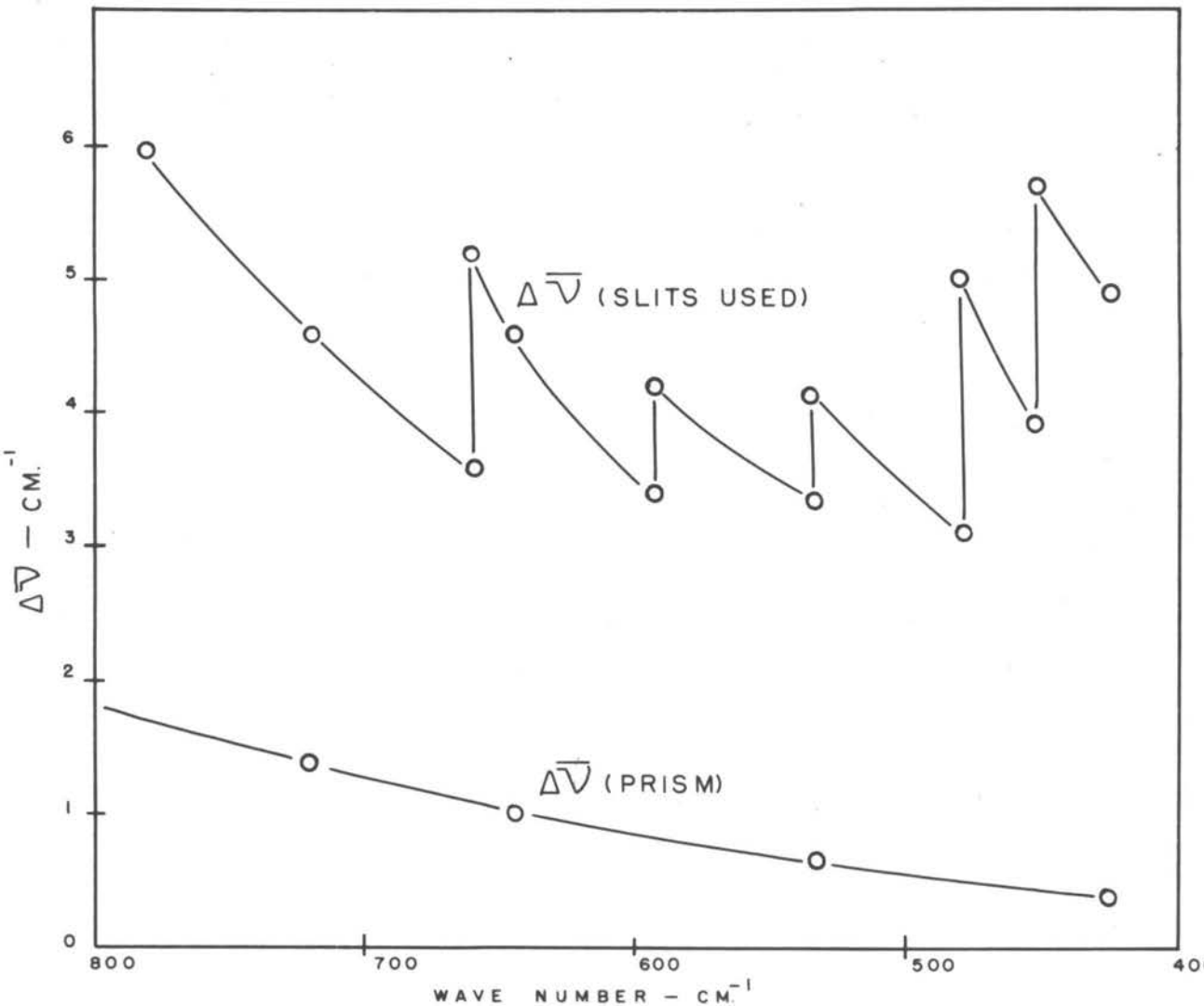

FIGURE 12. RESOLUTION FOR KBr PRISM

EXPERIMENTAL TECHNIQUES

SAMPLE PREPARATION FOR SOLIDS.

Materials transparent in the infrared region and their usable ranges are:

Material	Range, Cm.$^{-1}$
NaCl	50,000 - 590
KBr	50,000 - 400
LiF	83,000 - 1500

Synthetic crystals of these materials of high optical quality are grown commerically[7], and available for windows in the spectrometer and sample cells. A cell for solids consists of two round disks of NaCl or KBr, 7 mm. thick and 25 mm. in diameter. The surfaces must be polished to reduce losses due to scattering. This is best accomplished by stretching a polishing cloth tightly across a section of plate glass. Optical quality cerium oxide[8] is spread on the cloth and sprayed with a film of ethanol. Using a rubber glove, the window is then polished by rubbing against the moist cerium oxide until the mixture becomes dry. A little experience will enable one to determine the exact point to lift the window from the dry powder so that it does not become scratched by rubbing against a dry surface too

7. Manufactured by Harshaw Chemical Co., Elyria, Ohio.
8. Manufactured by Lindsay Light and Chemical Co., West Chicago, Illinois.

long. This technique produces a higher polish than by use of the conventional jeweler's rouge and lap board technique. Furthermore, the cerium oxide does not adhere to the window like the jeweler's rouge. However, prolonged polishing produces a rounded surface, so one must occasionally refinish it. This may be done by stretching No. 600 water-sandpaper on the plate glass and grinding the window surface flat.

The best way to measure the absorption spectrum of a solid is to dissolve it in a suitable solvent such as carbon tetrachloride or carbon disulfide and treat the solution as a volatile liquid. A lead spacer from 0.025-0.075 mm. thick is placed between the two cell windows. Solution is introduced in the cavity provided by the spacer and the whole ensemble clamped tightly in a sample holder. The disadvantage to this technique is that the solvents have their own characteristic absorption bands and obscure those of the sample for these regions.

When one has an insoluble material, or one that reacts with u s able solvents, various other procedures are available. If the material may be melted or dissolved in some solvent, it can be laid down on a window as a thin film. By far the most common procedure is the practice of mulling a powder with Nujol and placing a thin layer of this between two windows. Nujol is the trade name of a high

boiling paraffin and has only four absorption bands at 2910, 2860, 1460, and 1380 cm.$^{-1}$. If the first three regions are of interest, a fluorocarbon[9] may be used as a mulling agent since it has no absorptions there.

Recently another technique for preparation of organic powder samples has been developed (55, p.1050). The sample is finely ground and intimately mixed with powdered KBr. The mixture is then subjected to a very high pressure, resulting in the formation of a thin wafer with low scattering properties. This method was considered, but not thought necessary for the present investigation.

SPECIAL TECHNIQUE FOR THE PHTHALOCYANINES.

Perhaps the most serious difficulty in any technique dealing with powders is the effect of particle size. Hunt et al. (32, pp.1479-1497) demonstrated that when the particle size became larger than the wavelength of the radiation, almost complete scattering due to refraction occurs and absorption bands are not obtained. Transmission bands occur which arise from lack of refraction where the refractive index of the particle nears 1.0. These low refractive indexes arise on the short wavelength side of absorption bands due to the phenomenon of anomalous dispersion. These authors separated particles of less than 5 microns from

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9. Sold by the Perkin-Elmer Company.

minerals by sedimentation of finely ground material in the presence of a dispersing agent. Even with this technique, examination of their spectra indicates very low transmission at wavelengths less than 5 microns.

The phthalocyanines are almost completely insoluble in solvents and thus must be treated as powders. However, the crystals are extremely hard and difficult to reduce to a size that would produce reasonable spectra by mulling with Nujol. The metal-free compound is particularly difficult in this respect.

Since these compounds are known to sublime under vacuum, a technique of sample preparation was suggested which resulted in very good spectra from 3500 to 400 cm.$^{-1}$. Figure 13 illustrates the apparatus used to produce a film on a rock salt plate which has very little scattering losses. The sublimation tube with the phthalocyanine sample in the bottom is attached to a vacuum system and evacuated to 10^{-5} mm. pressure. The phthalocyanine is heated to drive off sublimable impurities and some of it then sublimed on the walls of the tube. A rock salt plate is then placed on the support above the phthalocyanine and a pressure of 10^{-5} mm. maintained for 30 minutes or more. Proper preparation of the plate is considered important. It should be highly polished before use and kept dry and clean. With a jet of air directed on the ground glass joint above to prevent the

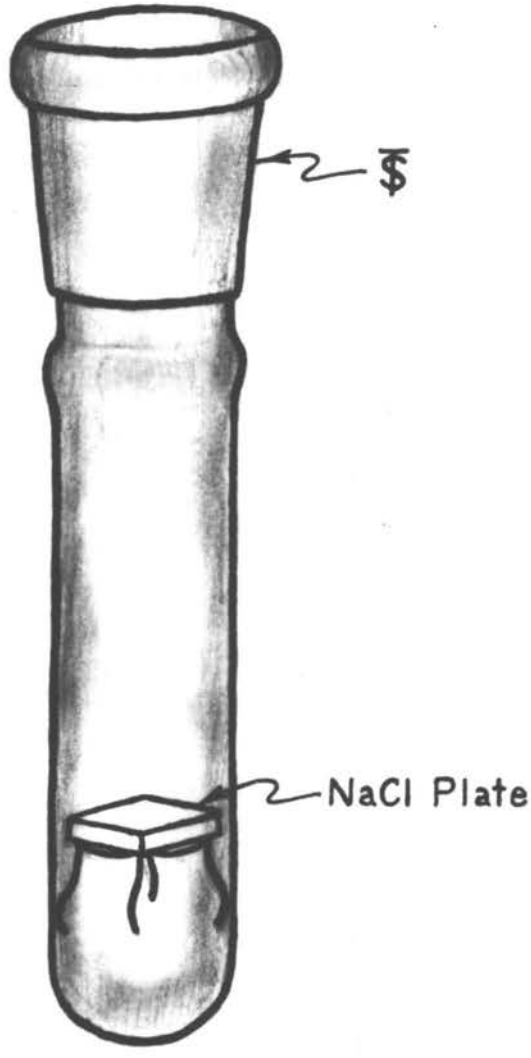

FIG. 13. SUBLIMATION APPARATUS

high vacuum grease from melting, the phthalocyanine is sublimed to the surface of the plate in stages. Using a soft flame one drives sublimate up the walls of the tube and finally over to the plate. It is essential to do this slowly and especially to maintain the very low pressure. These conditions favor the formation of very small crystals as evidenced by low scattering losses in the 3-5 micron region and x-ray diffraction patterns to be discussed later. This was the only way absorption bands in the 2-3 micron region could be obtained for the phthalocyanines studied. The sublimed films appeared dull and black when viewed directly, but quite shiny by reflected light.

It was found that most films sublimed in this manner were very adherent and could be polished on a polishing cloth to a high purplish-bronze luster. Although polishing removed material it did not seem to reduce the strength of absorption bands, but actually to sharpen them. It was concluded that polishing removed the larger particles and produced a more uniform film of the smaller ones. A plate could be coated entirely this way, protecting it from dulling effects of atmospheric vapors, and used as a calibration device when prisms were interchanged.

EXPERIMENTAL RESULTS

PREPARATION OF PLATINUM PHTHALOCYANINE.

In order to carry out the published preparation (12, p.1734) for the platinum derivative, it was necessary to obtain phthalonitrile. This was done by conversion of phthalimide to phthalamide with concentrated ammonia, followed by dehydration to phthalonitrile with acetic anhydride (58, pp.852-853). Purification of the crude nitrile was not necessary for preparation of platinum phthalocyanine.

Anhydrous $PtCl_2$ was conveniently prepared by heating $H_2PtCl_6 \cdot 6H_2O$ until evolution of HCl ceased. Further heating is to be avoided as it decomposes $PtCl_2$ to Pt. The mixture of $PtCl_2$ and phthalonitrile is placed in a test tube and heated slowly in an oil bath; a direct flame on the test tube causing decomposition of $PtCl_2$ before pigment formation can occur. Once heating of the mixture has begun it must be carried to completion; an interruption causes failure of the reaction.

The pigment was precipitated from concentrated sulfuric acid for purification and sublimed on a KBr plate to obtain the spectrum.

PREPARATION OF DEUTERIUM DERIVATIVE.

A deuterium derivative was desired to obtain information on the N-H frequencies in the metal-free compound. It

was formed by dissolving the magnesium derivative in D_2SO_4 and, upon precipitation by addition of D_2O, the magnesium is eliminated and replaced by two deuterium atoms.

To prepare D_2SO_4, P_2O_5 and fuming H_2SO_4 were placed in a flask and heated to distill SO_3 into a trap. Five cc. of D_2O were then placed in the sublimation tube shown in Figure 13 and SO_3 distilled into it from the trap until a total volume of 13 cc. was obtained. Violent reaction occurs in this process and an ice-bath must be used to keep the D_2O solution cool. About 250 mg. of magnesium phthalocyanine dihydrate was dissolved in the D_2SO_4 and precipitated by the addition of 20 cc. of D_2O ice. The precipitate was separated using a centrifuge and the dilute acid placed in a stoppered bottle in a dessicator. The precipitate was washed with H_2O until free of sulfate ion and dried in a vacuum dessicator. A film was sublimed on a NaCl plate at a pressure of 10^{-5} mm. and the spectrum recorded in Figure 28 indicates about 30-50% deuteration.

Several months later it was decided that the washing process may have resulted in the low deuteration yield due to incomplete precipitation with the D_2O ice, or exchange with the wash H_2O. The dilute D_2SO_4 kept in a desiccator was distilled, recovering 13 cc. of water and 5 cc. of acid. The above preparation was repeated, except this time D_2O was

used for all the washes. The result was a completely non-deuterated metal-free phthalocyanine.

The conclusions reached as a result of this work are:

1. D_2SO_4, especially when concentrated, exchanges quite rapidly with atmospheric H_2O.

2. Once the deuterated derivative is precipitated little exchange occurs by contact with water. This was also upheld by no change in the spectrum of the sublimed film after several months exposure to the atmosphere.

3. To obtain higher yields it would be desirable to design an apparatus to accomplish the formation of D_2SO_4, solution of the magnesium derivative, and precipitate under a vacuum or free from atmospheric H_2O.

X-RAY POWDER DIFFRACTION PATTERNS.

With the use of x-ray powder diffraction apparatus[10] patterns were obtained for the materials from which our spectra were produced. Table 3 reports the results of work done on the XRD apparatus with strip film, and Figures 14, 15, 16, 17, and 18 the work done on electronic recording

10. Part of this work was done on apparatus available in the chemistry department; model XRD unit manufactured by the General Electric Company and equipped with a recent model powder camera (cat. No. A4926E). Strip film was used with unfiltered radiation from a chromium x-ray tube. Exposures ran up to 6 hours. Confirmation and extension of this work was done with the valued assistance of Mr. L. Noble of the U.S. Bureau of Mines in Albany, Oregon, who used equipment of a very late design available there. Some of these materials were deposited in a very adherent film on a plate of NaCl which could be introduced directly as a sample in the

apparatus. Examination of these patterns reveals the previously unreported fact that sublimation at a pressure of 10^{-5} mm. produces the alpha form. This can be seen by comparison of values given in column 3 of Table 3 which are for the alpha form of copper phthalocyanine produced by precipitation from sulfuric acid with those obtained for the high vacuum sublimate in column 4. The patterns in Figure 15 were obtained from the originally prepared pigment (beta form) and the acid precipitated pigment (alpha form). Figure 14 shows patterns obtained from the original metal-free pigment (beta form), and from a high vacuum sublimate (alpha form) on a rock salt plate. The 200 lines of NaCl are seen on the pattern. Since this was a polished plate the intensity pattern may be influenced by partial orientation of the crystals. Figure 16 shows an acid precipitated platinum phthalocyanine pattern, and Figures 17 and 18, the magnesium dihydrate and high vacuum sublimate respectively. Greater reliance is placed on results obtained by the electronic recording equipment because the film patterns from the XRD apparatus were very difficult to read with precision. Some lines were too obscured and faint to be detected at all.

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apparatus. The equipment was manufactured by the Phillips Company and used a geiger counter as a detector. The output of the geiger counter was delivered to an automatic recorder, so the diffraction pattern appeared as a tracing in which the ordinate represents relative intensities of scattering, and the abscissa interplanar distances.

A copper x-ray tube was used with a filter to remove α radiation.

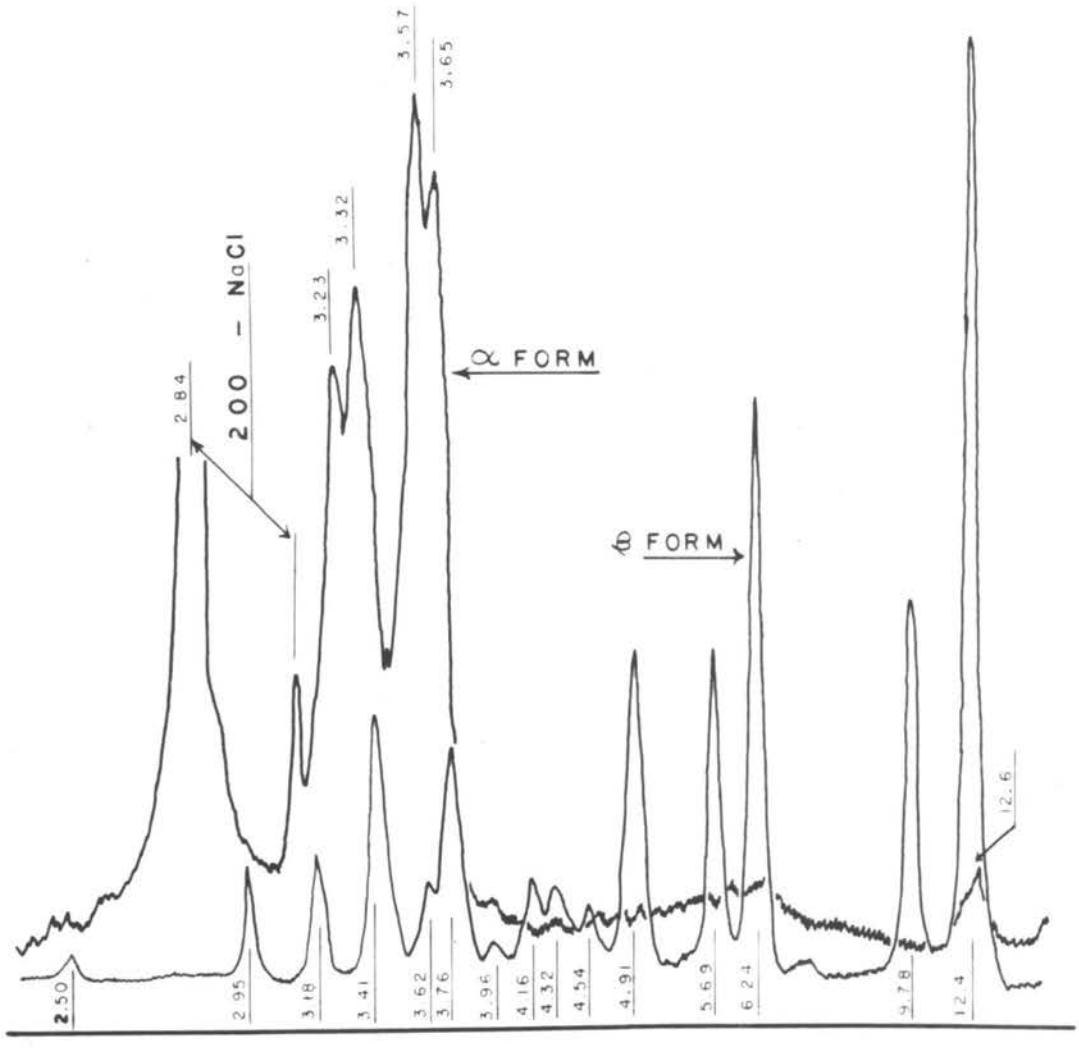
TABLE 3

Interplanar Distances (in Angstroms) for Phthalocyanines Obtained on XRD Apparatus.

Metal-free (beta form)	Copper (beta form)	Copper (acid precipitated)	Copper (high vac. form)	Magnesium (dihydrate)
12.6	12.5	12.6	12.5	12.0
9.71	9.51		5.52	
6.21	8.21		3.70	
5.68	7.00	3.51	3.52	3.44
4.86	4.79	3.31	3.29	3.26
3.70	4.72	3.19	3.19	
3.37	4.07			
3.16	3.70			
2.93	3.40			
	3.18			
	2.90			
	2.06			
	1.64			

FIGURE 14.

X-RAY DIFFRACTION PATTERNS OF METAL-FREE PHTHALOCYANINE



INTERPLANAR DISTANCE — ANGSTROMS

FIGURE 15 — X-RAY DIFFRACTION PATTERNS OF COPPER PHTHALOCYANINE

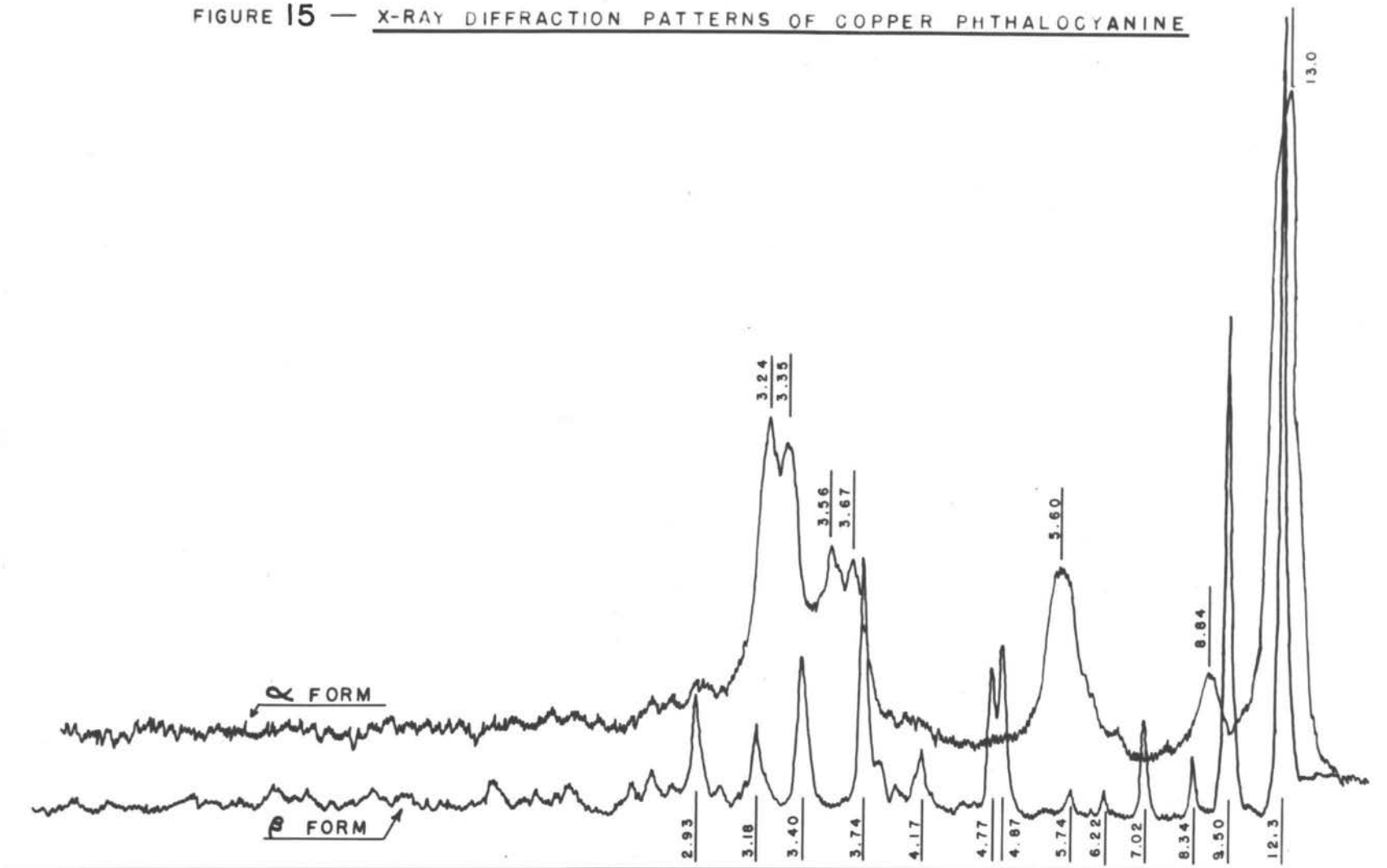


FIGURE 16.

X-RAY DIFFRACTION PATTERN OF PLATINUM PHTHALOCYANINE

ALPHA FORM

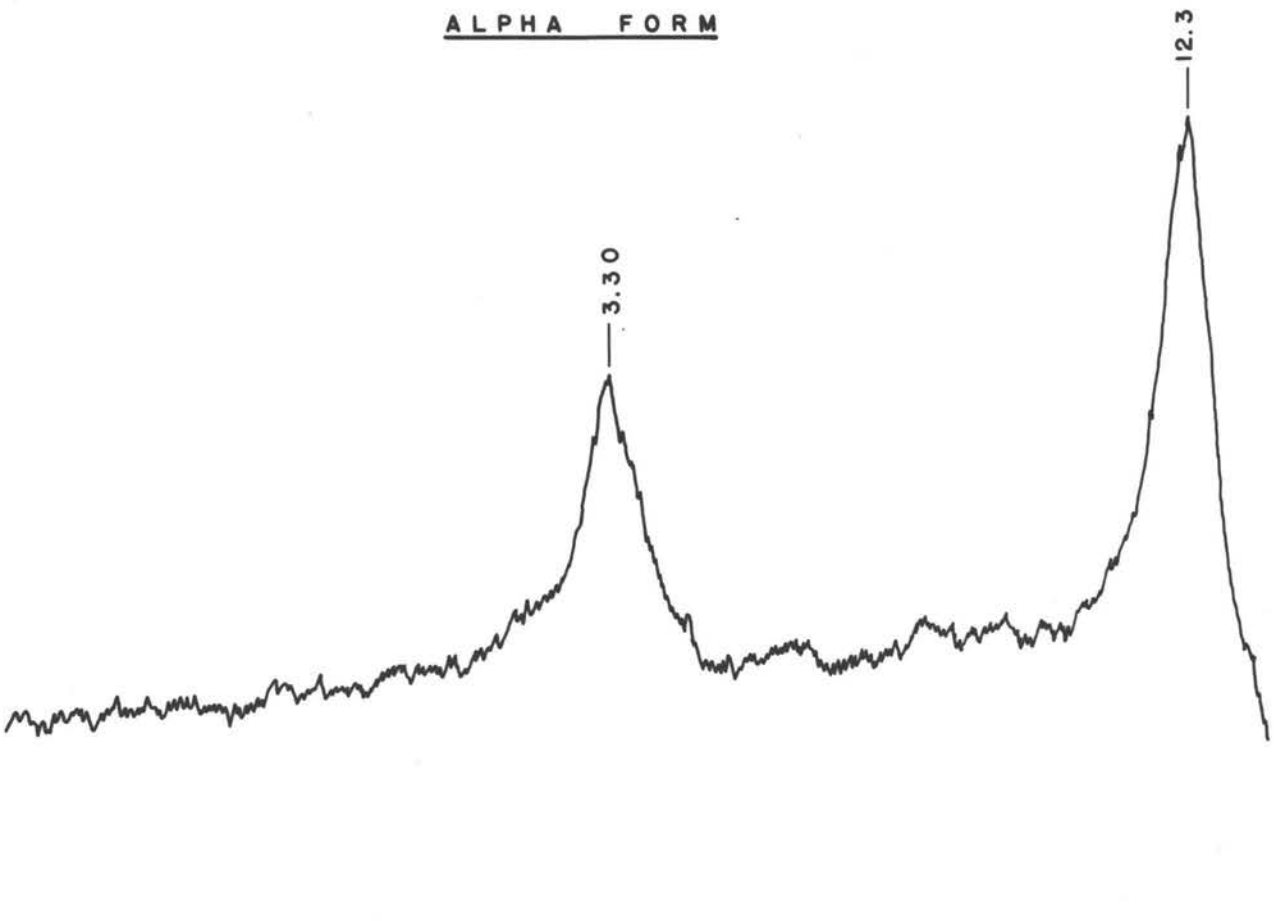


FIGURE 17. - X-RAY DIFFRACTION PATTERN OF MAGNESIUM PHTHALOCYANINE DIHYDRATE

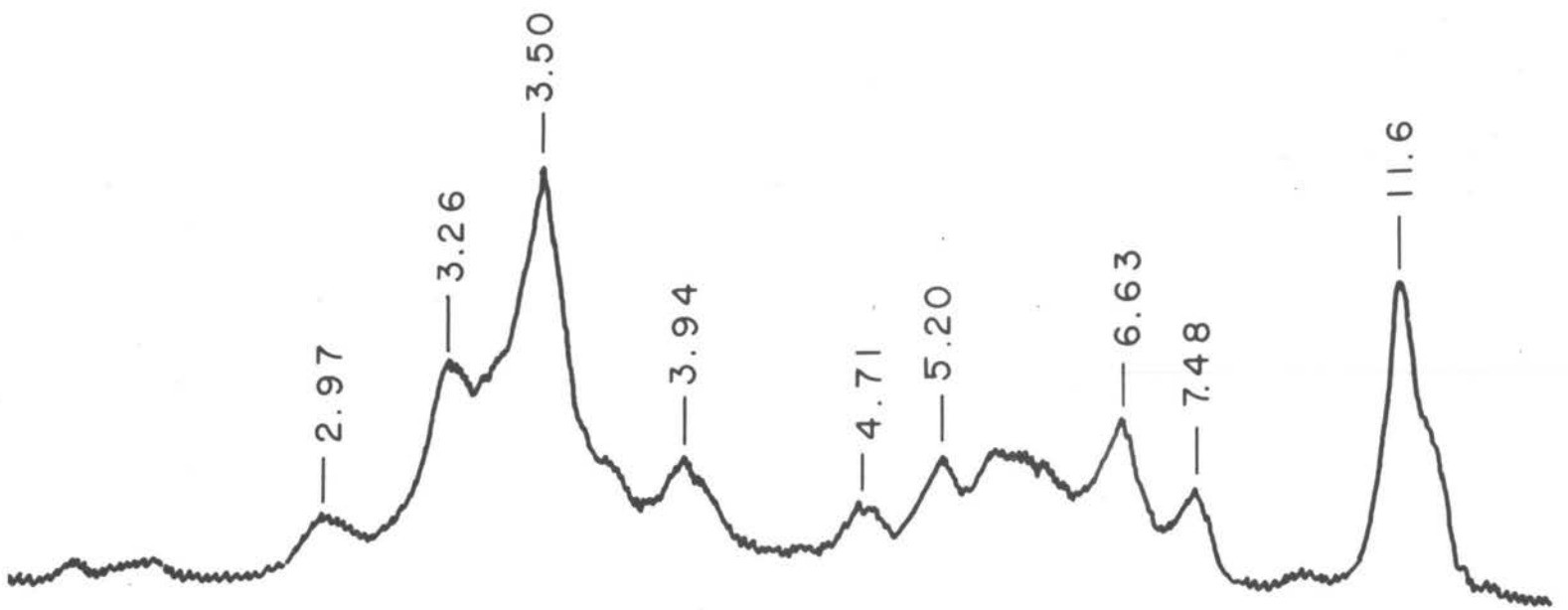
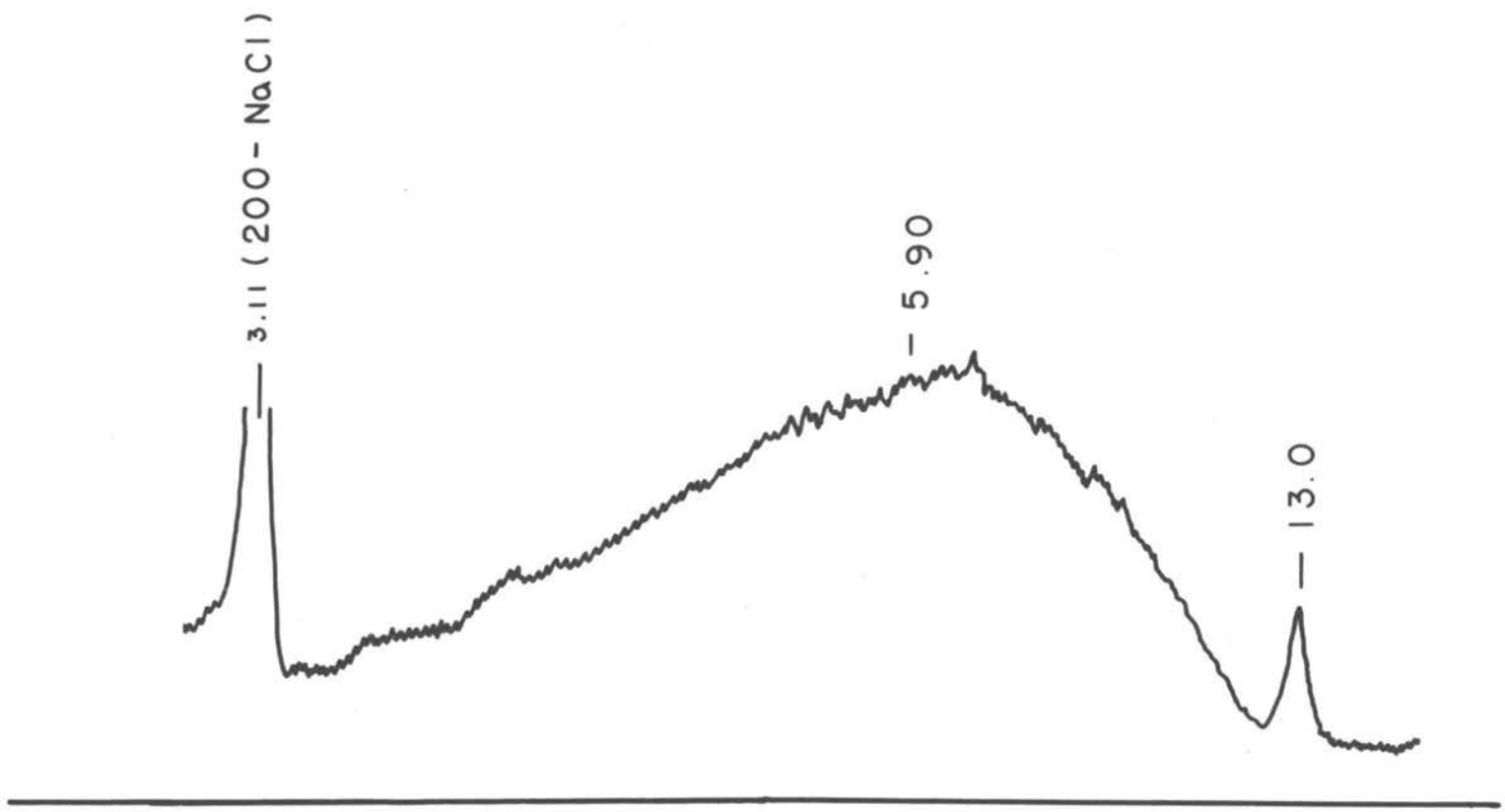


FIGURE 18. X-RAY DIFFRACTION PATTERN OF MAGNESIUM PHTHALOCYANINE — ALPHA FORM



INFRARED SPECTRA OF POLYMORPHIC FORMS.

It was noted that there were certain systematic and definite differences in the spectra of samples produced by sublimation at a pressure of 10^{-5} mm. and those from the original pigments. It was also found that the spectrum of alpha copper phthalocyanine produced by precipitation from sulfuric acid agreed with that produced by the 10^{-5} mm. sublimate. Both of these were proved to be alpha forms by their x-ray powder diffraction patterns, so the changes in the infrared spectra, then, are characteristic of the crystalline modification of the compounds. Further confirmation of this was obtained by private correspondence[11] with Dr. D.N. Kendall of the American Cyanamid company who presented a paper on the identification of polymorphic crystalline forms by infrared analysis at a meeting of the American Chemical Society in April of 1951.

ALPHA-BETA CONVERSIONS. According to Linstead the beta form is produced by sublimation at 550° C. under pressures around 5 mm. when the sublimate is allowed to condense on a surface heated to 400° C. (2, pp.1734-1735). Therefore, the only differences in our conditions of sublimation which produces the alpha form are the pressure of sublimation and

11. Prints of the spectra of alpha and beta copper phthalocyanine were received from Dr. Kendall, the essential details of which agree with the corresponding spectra presented here in Figures 21 and 22.

temperature of condensation. The rock salt plate is out of contact with the hot walls of the sublimation tube and above the zone of heating, so its temperature is relatively low. A study of sublimation at different pressures for metal-free phthalocyanine revealed that the alpha form was still obtained at a sublimation pressure of 50 mm.[12] However the particle size was much larger than produced by sublimation pressure of 10^{-5} mm. as evidenced by large scattering losses at wavenumbers above 1400 $cm.^{-1}$. On the other hand, copper phthalocyanine was found to produce a beta sublimate at pressures above 10^{-1} mm. Its spectrum, which shows less scattering losses, is given in Figure 22.

Conversion of alpha to beta form may be effected by heating the metal-free and copper phthalocyanine to 250-300 degrees. However, the platinum and nickel compounds will not undergo this transition. A rock salt plate coated with alpha nickel phthalocyanine sublimate was heated to 350 degrees centigrade for 30 minutes with no conversion, and even heated at sublimation temperatures under 1 mm. pressure for 20 minutes with no conversion. A sublimed film of alpha platinum phthalocyanine was heated to 400 degrees

12. This may seem to disagree with the fact that Linstead produced beta crystals by subliming at 5 mm. pressure, but it must be remembered that his condensation temperature of 400 degrees is well above the transition temperature (200-300 degrees) for the alpha to beta conversion. Our condensation temperature is below 200 degrees.

centigrade for 20 minutes, during which time over 50% of the film decomposed to metallic platinum with no change in the remaining material.

GENERAL DISCUSSION OF SPECTRA. Figures 19, 21, 23, 25, and 26 present infrared absorption spectra of the alpha forms of metal-free, copper, nickel, platinum, and magnesium phthalocyanine. All these alpha spectra were obtained by high vacuum sublimation directly on KBr or NaCl plates. Figures 20, 22, and 24 present the spectra of the beta forms of metal-free, copper, and nickel phthalocyanine. Figure 27 shows the spectrum of magnesium dihydrate. Comparison of the curves of the alpha with the beta spectra illustrates adequately the superiority of the alpha due to their small particle size resulting from the sublimation technique. Spectra of most beta compounds were obtained by mulling with Nujol and fluorocarbon, and were very difficult to determine because of a generally low transmission due to scattered radiation. Copper phthalocyanine was the only compound of the beta form where absorption bands could be obtained in the region 2000-3500 $cm.^{-1}$. This was done by use of a special technique. The sublimed film used to obtain the alpha copper phthalocyanine spectrum of Figure 21 was heated to 250 degrees centigrade over the course of ten minutes which converted it to the beta form. This then produced the fine detailed spectrum of curve A in

Figure 22. The sublimed film of metal-free phthalocyanine used to obtain the spectrum of Figure 19 was heated to 250 degrees over a period of 8 minutes. The beta crystals formed were so large that the transmission dropped abruptly to 0-10% at 1000 $cm.^{-1}$ as indicated in Figure 20. For this reason curve A of Figure 20 is not a true percent transmission reading because the absorptions are "blown-up" by widening the slit and thus increasing the energy in the sample path for the spectrometer. Curve B was obtained by mulling with Nujol, and curve C by mulling with fluorocarbon, because of the obscuring effect of Nujol bands in the 1400-1600 $cm.^{-1}$ region. Both mulling agents have bands obscuring the region of 1350-1380 $cm.^{-1}$ which fortunately contains no strong bands for the phthalocyanines studied. In fact, examination of the curves will indicate no change in the alpha and beta forms for the region 1250-2000 $cm.^{-1}$. Most changes between the two phases occur in the 700-1200 $cm.^{-1}$ region. Curve D of Figure 20 shows the severe transmission loss by scattering for the metal-free compound, even after grinding the sample with an agate mortar for 30 minutes. It was concluded that grinding the hard particles of the beta form with any available equipment would not succeed in producing a particle size (1-3 microns) to provide spectra in the 2000-3500 $cm.^{-1}$ region. This conclusion was upheld by experience of the German dye industry.

The comparatively soft alpha copper phthalocyanine was milled with a ball mill for 48 hours with an emulsifying agent to obtain an average particle size of 3 microns; while severe treatment in a 3000 r.p.m. disintegrator only produced a particle size of aroung 1 micron (27, pp.296-297).

Figure 26 shows the spectrum of a high vacuum sublimate of magnesium phthalocyanine. Curve A of this figure is a plot of the magnesium phthalocyanine dihydrate to indicate the correspondence of the two spectra in the 400-700 $cm.^{-1}$ region. Figure 27 gives the spectrum of magnesium phthalocyanine dihydrate obtained with emulsions. Curve A of this figure shows a new absorption which occurs for the high vacuum sublimate (alpha form) after it has been exposed to the atmosphere for several months. This absorption occurs in a region for OH absorptions and it is interesting to note that it occurs at 3600 $cm.^{-1}$ rather than around 3350 $cm.^{-1}$ as in the dihydrate.

Figure 28 shows the changes found in the spectrum when the central hydrogen atoms of metal-free phthalocyanine are replaced by deuterium atoms. No noticeable changes occur in regions not plotted.

Figure 29 is a direct trace from the recorder paper of the C-H stretching region for the alpha forms of platinum, nickel, metal-free, and copper phthalocyanine. The

beta copper form is shown to indicate the intensity changes between alpha and beta forms. These spectra were obtained by the "blowing-up" technique of increasing the energy in the sample path by increasing the slit and amplifier gain settings.

No quantitative significance may be attached to intensities of absorption bands in the 400-700 $cm.^{-1}$ region due to the effect of stray light passed by the spectrometer which was not eliminated. However, relative intensities between different curves can have meaning.

Tables 4 and 5 list the frequencies assigned to the alpha and beta phthalocyanines illustrated in the figures.

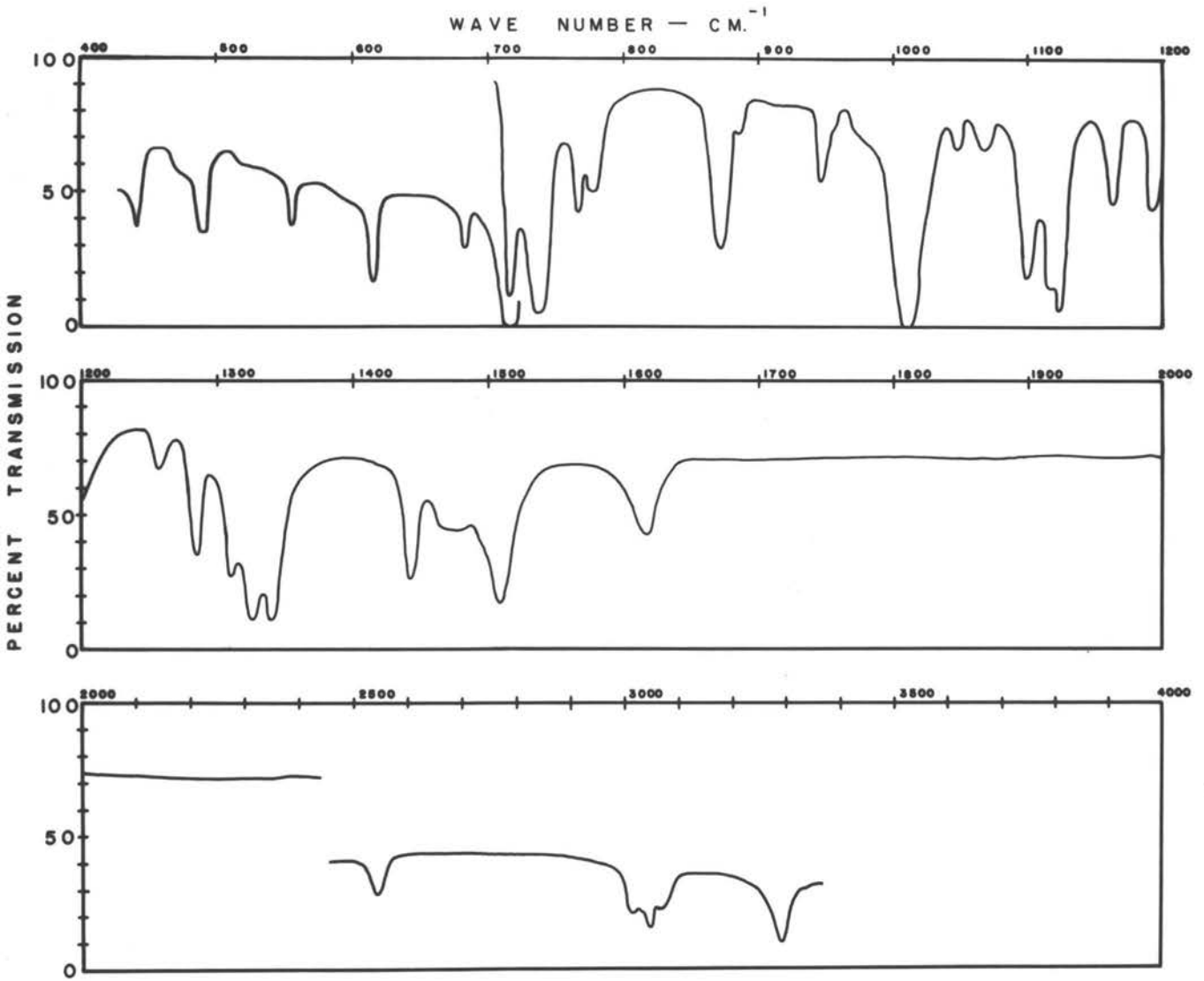


FIGURE 19. METAL-FREE PHTHALOCYANINE– ALPHA FORM

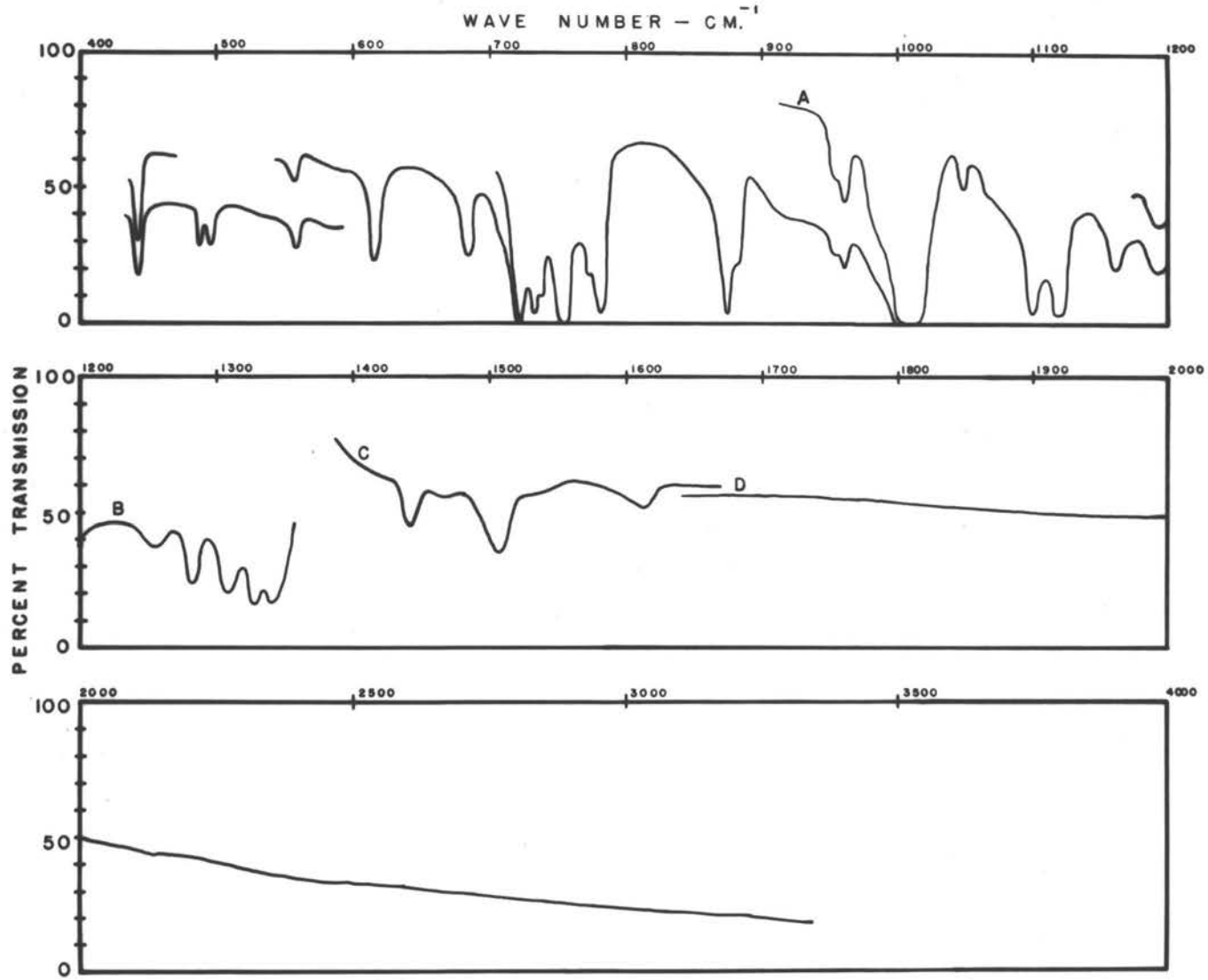


FIGURE 20. METAL-FREE PHTHALOCYANINE – BETA FORM

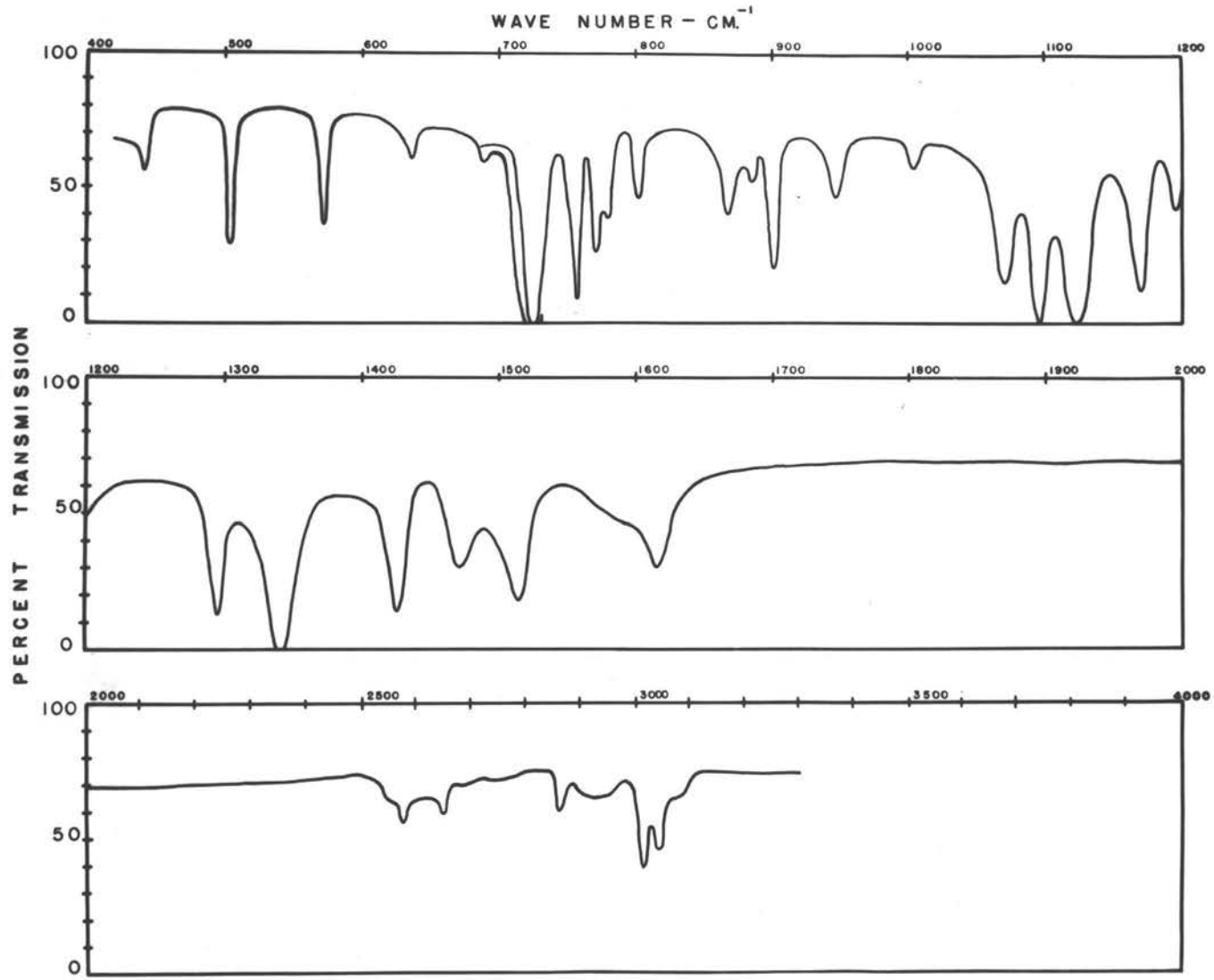


FIGURE 21. COPPER PHTHALOCYANINE – ALPHA FORM

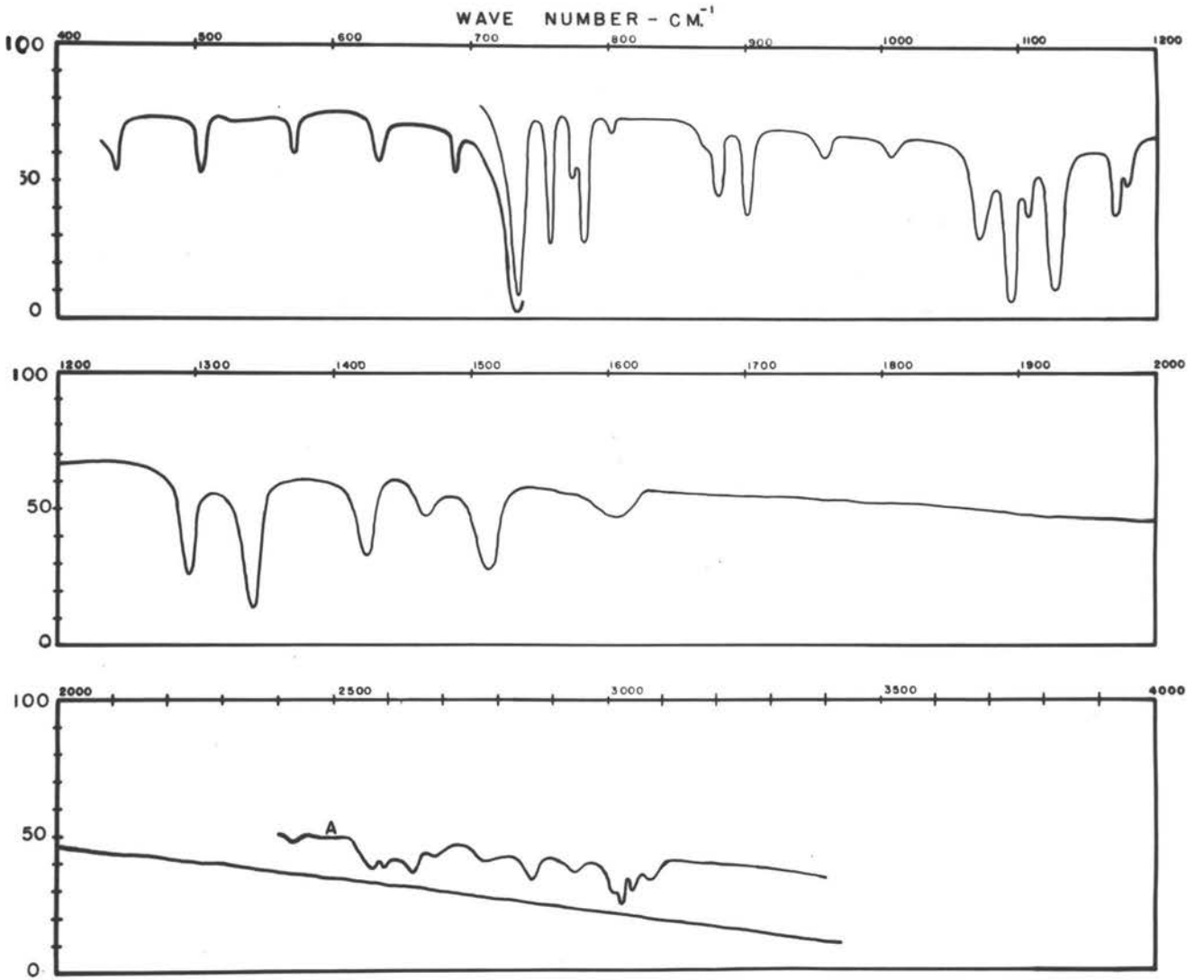


FIGURE 22. COPPER PHTHALOCYANINE - BETA FORM

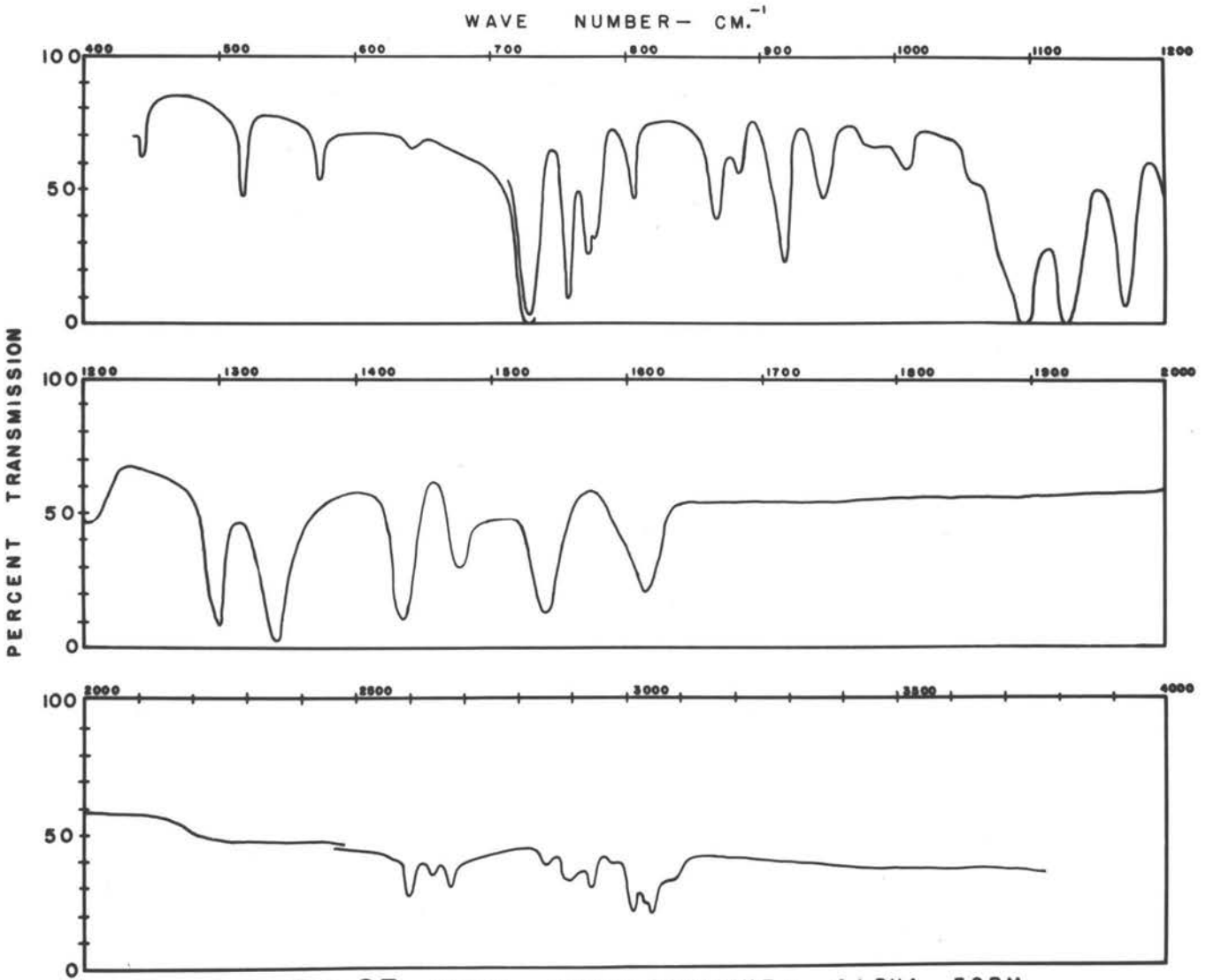


FIGURE 23. NICKEL PHTHALOCYANINE— ALPHA FORM

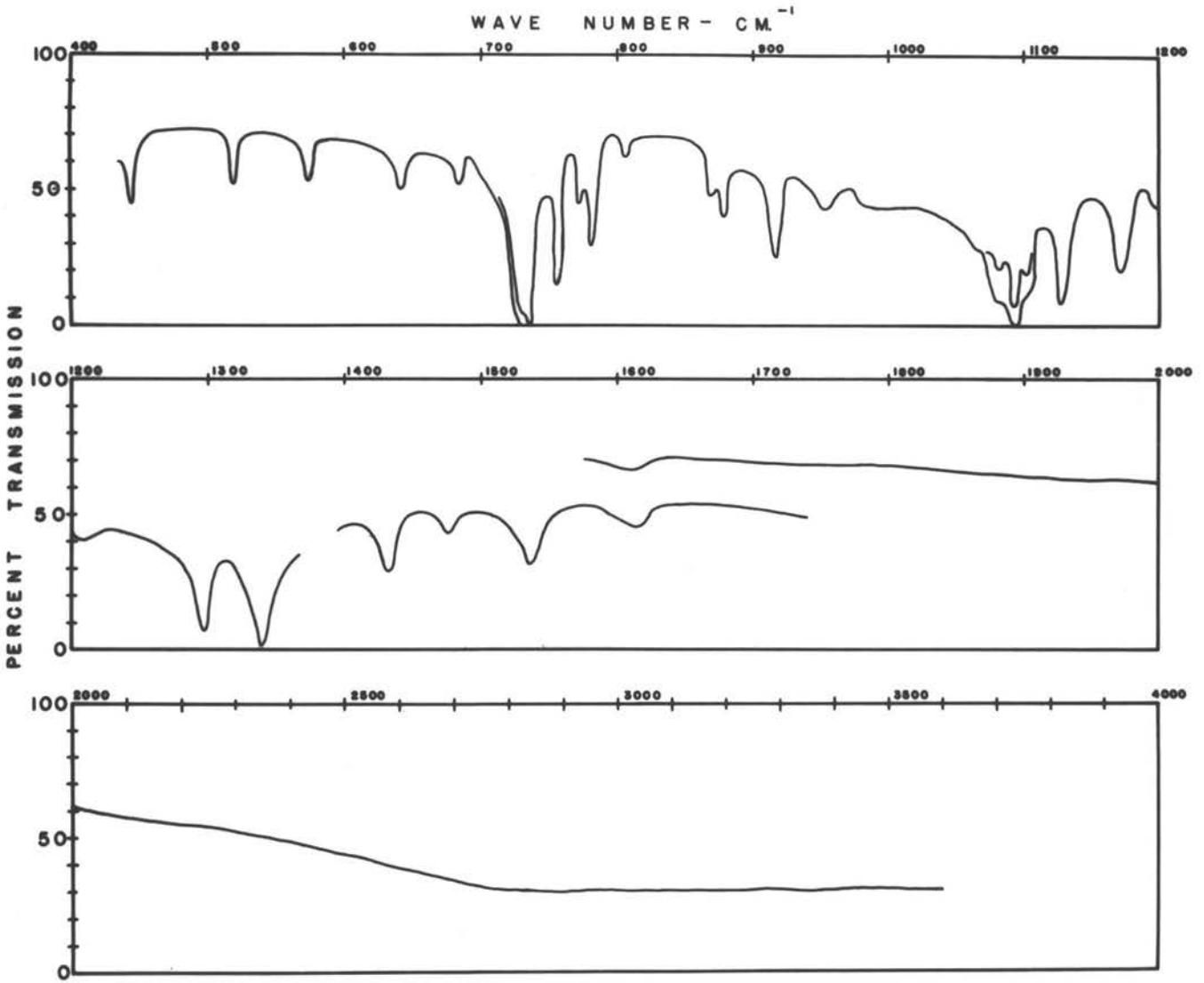


FIGURE 24. NICKEL PHTHALOCYANINE - BETA FORM

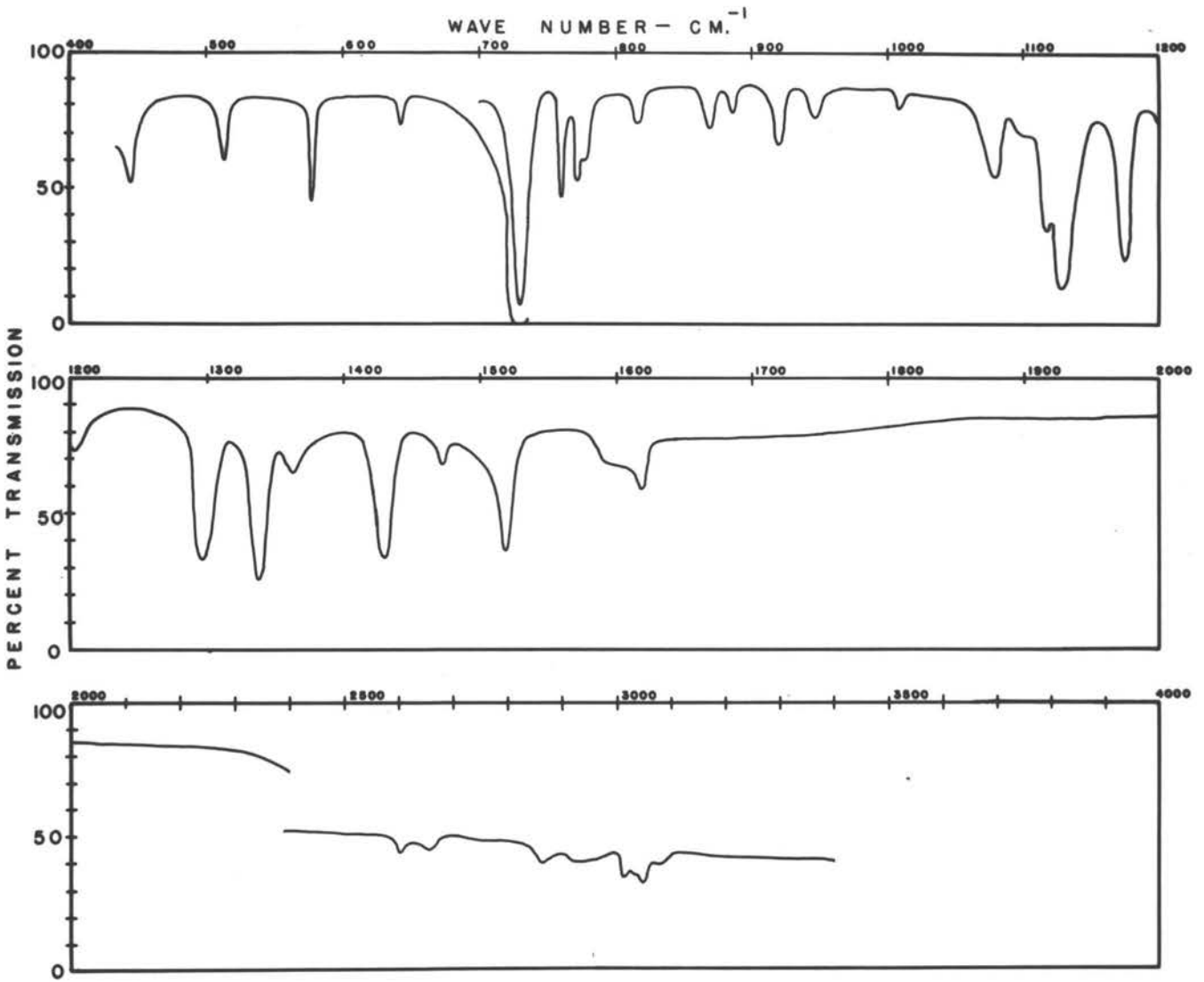


FIGURE 25. PLATINUM PHTHALOCYANINE — ALPHA FORM

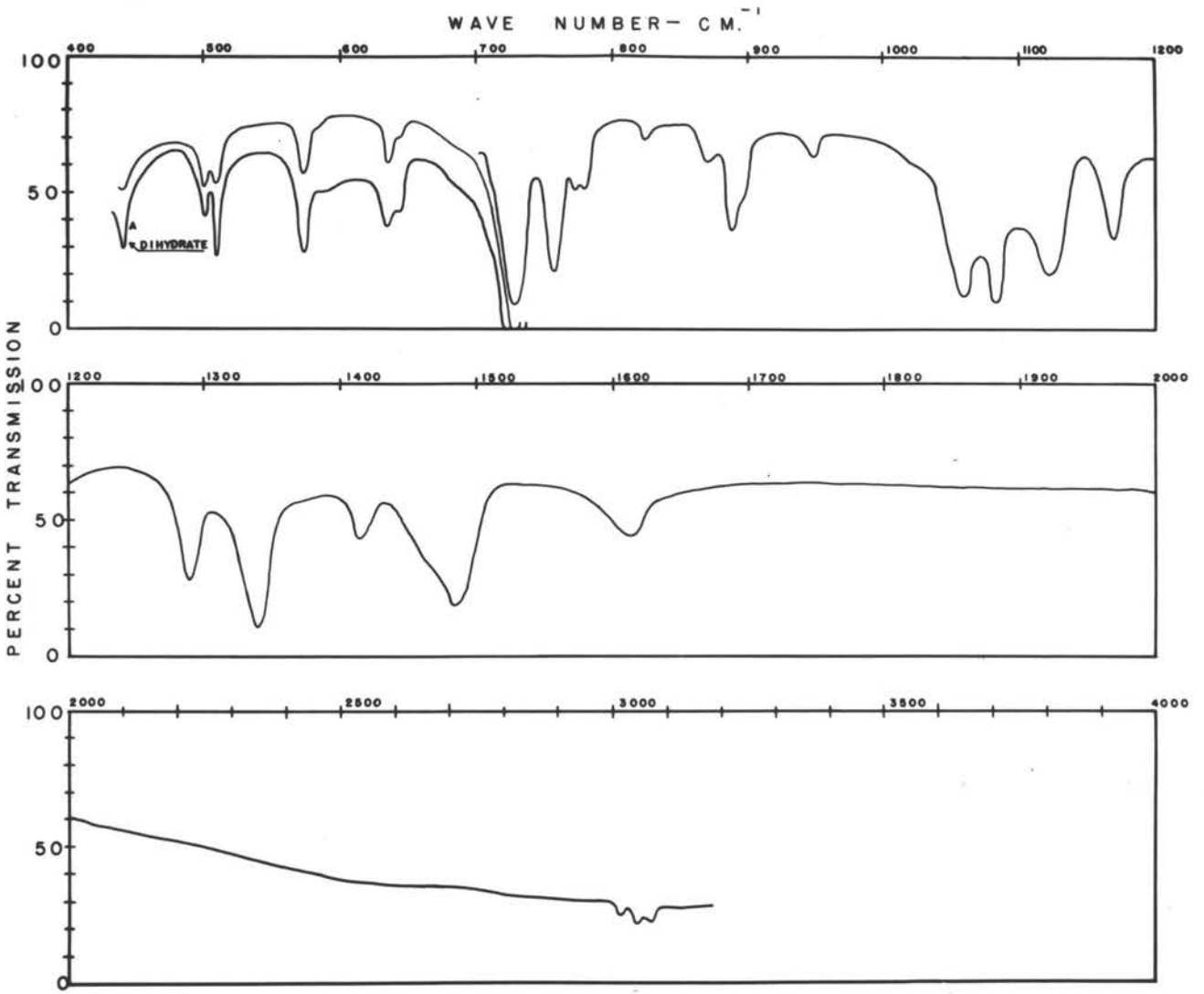


FIGURE 26. MAGNESIUM PHTHALOCYANINE — ALPHA FORM

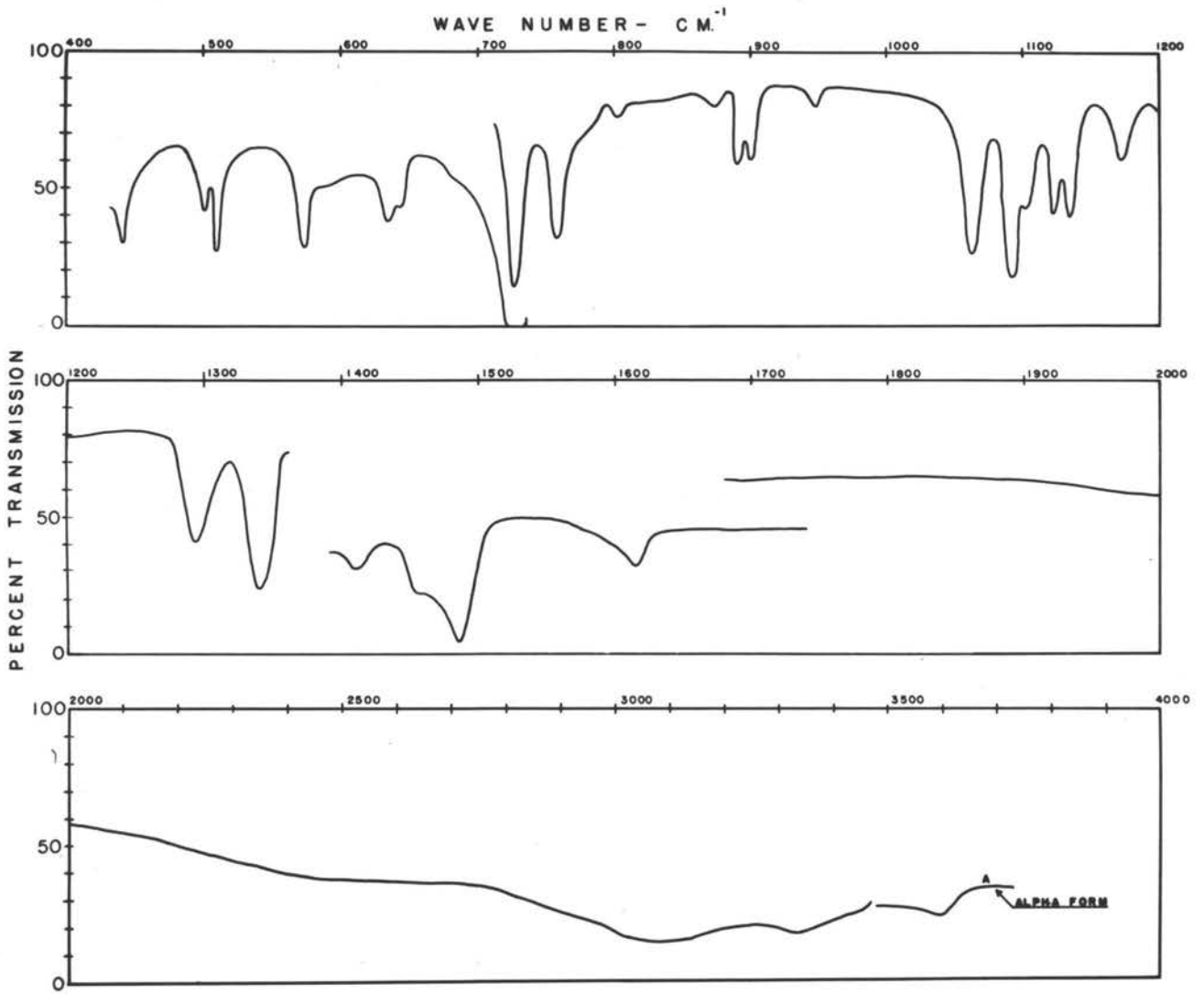


FIGURE 27. MAGNESIUM PHTHALOCYANINE - DIHYDRATE

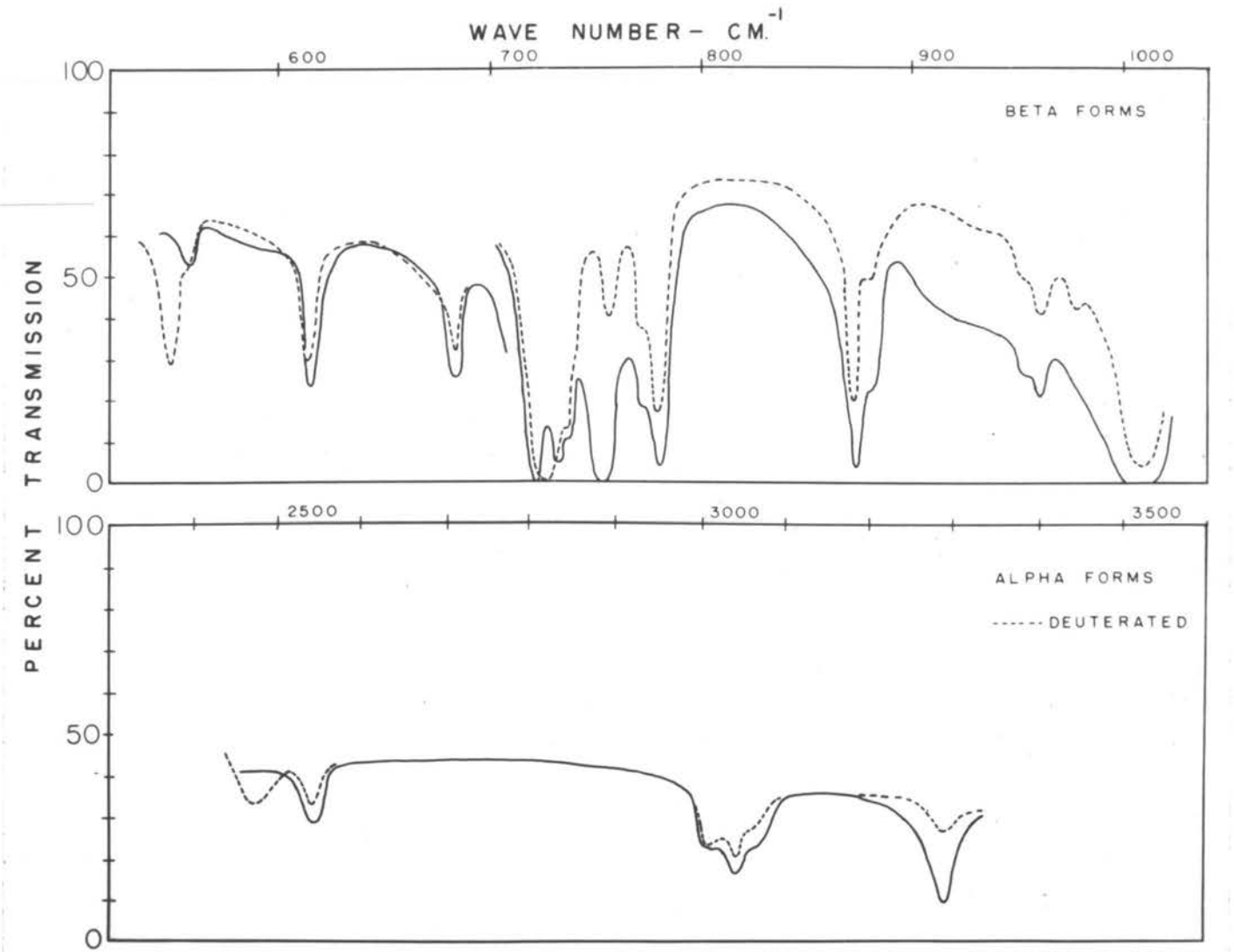


FIGURE 28. DEUTERATION OF CENTRAL HYDROGEN OF METAL-FREE PHTHALOCYANINE

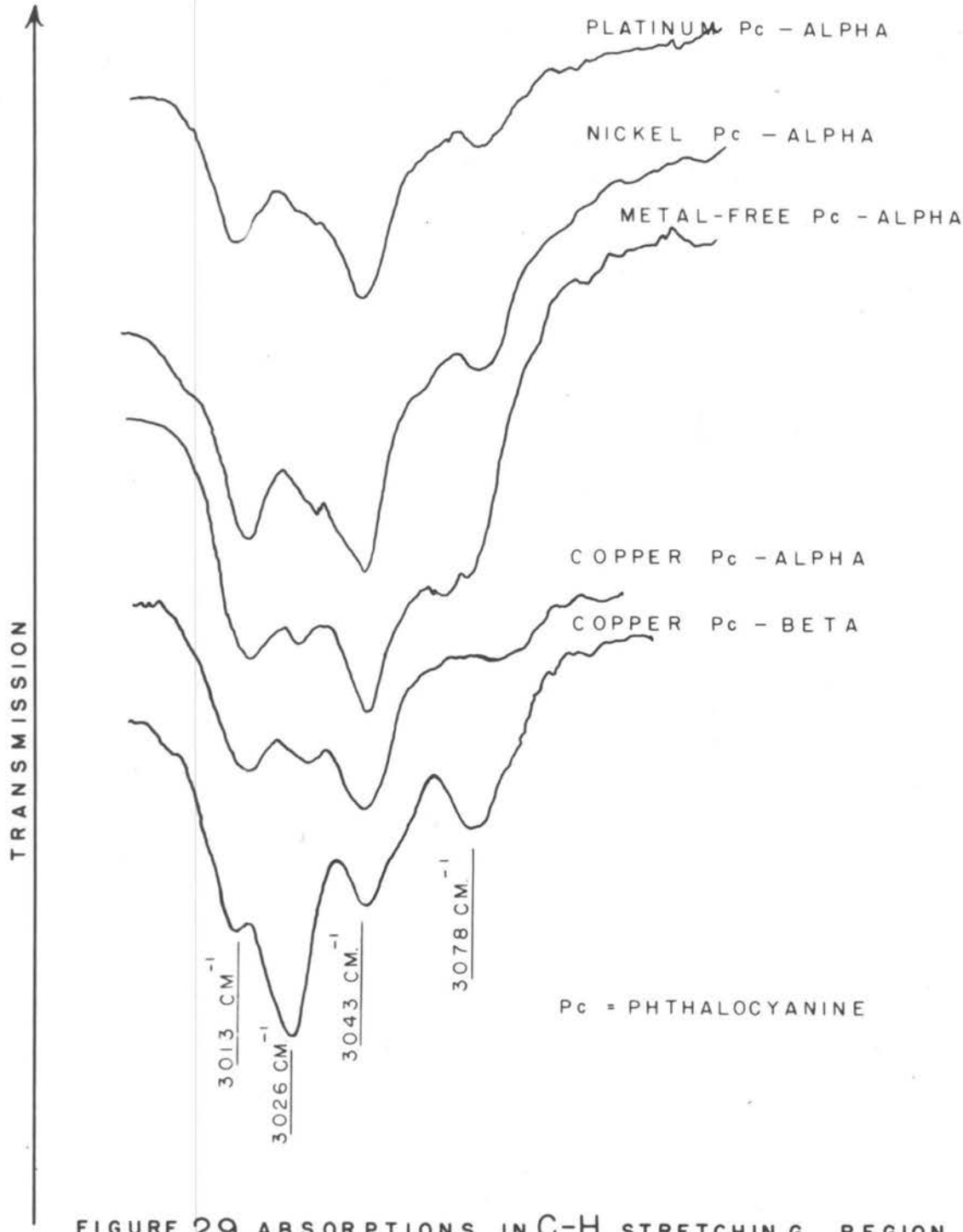


FIGURE 29. ABSORPTIONS IN C-H STRETCHING REGION

TABLE 4

ABSORPTION BANDS OBSERVED FOR PHTHALOCYANINES
ALPHA FORMS

Wave Numbers

Metal-free	Copper	Nickel	Platinum	Magnesium
443	443	443	445	441
476	505	518	513	502
492	573	574	577	509
556	637	642w	643	574
616	689w	727s	729s	635
684	724s	756	760	643
715s	756	772	772	728s
736s	770	780	776	757
767	780	804	816w	774
777	802	866	868	780
872	867	884	885	824w
886	884	917	920	870
946	901	946	947	889
955w	945	1009w	1008w	896
1009vs	1002w	1058	1079	949w
1048w	1070	1082	1117	1060s
1070	1095s	1095s	1128s	1083s
1098s	1122s	1126s	1175s	1122s
1116s	1170	1170	1202	1170
1123s	1196	1204	1296s	1290
1163	1295	1298s	1338s	1340s
1194	1342s	1341s	1363	1414
1203	1425	1435	1430	1464
1257	1471	1478	1472	1484
1285	1514	1539	1518	1590
1309	1590	1590	1590	1615
1327s	1615	1614	1616	3013
1340s	2575	2596	2603	3026
1442	2648	2642	2655	3043
1475	2858	2675	2862	3078
1507	3013	2853	3013	
1616	3026	2892	3026	
2545	3043	2935	3043	
3013	3078	3013	3078	
3026		3026		
3043		3043		
3078		3078		
3290				

w = weak; s = strong; vs = very strong

TABLE 5

ABSORPTION BANDS OBSERVED FOR PHTHALOCYANINES
BETA FORMS

Wave Numbers			
Metal-free	Copper	Nickel	Magnesium-Dihydrate
443	443	444	441
488	506	519	502
496	573	574	509
558	635	641	574
615	690	684	635
684	734s	728s	643
722s	757	735s	727s
733s	774	756	758
736	781	772	803w
753s	802w	781	872w
772	870	806w	891
781	880	869	900
874	901	878	946w
882	958w	917	1062
955w	1006w	953w	1092s
960w	1071	1082	1101
1010vs	1094s	1093s	1122
1048w	1106	1101	1134
1099s	1126s	1127s	1172
1120s	1171	1171	1293
1161	1178	1207	1340s
1194	1295	1297s	1410
1255	1342s	1340s	1458
1282	1423	1432	1486
1308	1466	1475	1590
1328	1512	1538	1615
1340	1612	1590	3330
1442	2427	1616	
1470	2573		
1506	2594		
1590	2649		
1614	2685		
	2771		
	2862		
	2941		
	3013		
	3026		
	3043		
	3078		

w = weak; s = strong

SPECTRA OF THE PHTHALOCYANINES

THEORETICAL CONSIDERATIONS.

CALCULATIONS FOR NORMAL MODES. The molecular model used earlier for a discussion of the application of group theory to infrared spectra was chosen because D_{4h} is the symmetry of the phthalocyanine molecules if one assumes:

1. The two hydrogen atoms in the parent compound lie on the principal axis of symmetry, at equal distances above and below the plane of the molecule.

2. The very slight distortion from perfect tetragonal symmetry may be ignored as an approximation.

Table 6 gives the results of calculations performed as indicated earlier to determine the number of frequencies of each symmetry species (30, p.117). Only two of these, namely A_{2u} and E_u, are infrared active, since the vibrational motion must have the same transformation properties as the translations, T_x, T_y, and T_z. These total 8 and 28 frequencies respectively for either the metal-free phthalocyanine or its metallic derivatives.

Table 7 shows the results of a calculation for metal-free phthalocyanine in which the molecule was assumed to have the two hydrogen atoms in the plane of the molecule with one bonded between nitrogen atoms number 13' and 9, and the other between 9' and 13 in Figure 2. This model has

TABLE 6. CALCULATION OF NUMBERS OF MODES OF EACH SPECIES FOR PHTHALOCYANINES OF D_{4h} SYMMETRY.

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	TOTAL MODES H_2	TOTAL MODES M.	LATTICE MODES	MOL. MODES H_2	MOL. MODES M.
A_{1g}	1	1	1	1	1	1	1	1	1	1	15	14		15	14
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	6	6		6	6
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	14	14	R_z	13	13
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	9	9	T_z	8	8
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1	14	14		14	14
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1	7	7		7	7
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1	14	14		14	14
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1	7	7		7	7
E_g	2	0	-2	0	0	2	0	-2	0	0	15	14	R_x R_y	14	13
E_u	2	0	-2	0	0	-2	0	2	0	0	29	29	T_x T_y	28	28
	3	1	-1	-1	-1	-3	-1	1	1	1	$(\pm 1 + 2\cos\alpha_R)$				
	58	2	2	2	2	0	0	56	4	4	U_R (H_2)				
	57	1	1	3	3	1	1	57	3	3	U_R' (M)				

H_2 = metal-free phthalocyanine M = metallic derivative

TABLE 7. CALCULATION OF NUMBER OF MODES OF EACH SPECIES FOR PHTHALOCYANINES OF D_{2h} SYMMETRY.

									TOTAL MODES				MOLECULAR MODES		
D_{2h}	E	C_2	C_2'	C_2''	i	σ_h	σ_v	σ_d	H_2 (O.P.)	H_2 (I.P.)	M	LATTICE MODES	H_2 (O.P)	H_2 (I.P)	M
A_g	1	1	1	1	1	1	1	1	29	29	28		29	29	28
A_u	1	1	1	1	-1	-1	-1	-1	13	13	13		13	13	13
B_{1g}	1	1	-1	-1	1	1	-1	-1	28	29	28	R_z	27	28	27
B_{1u}	1	1	-1	-1	-1	-1	1	1	16	16	16	T_z	15	15	15
B_{2g}	1	-1	1	-1	1	-1	-1	1	15	14	14	R_y	14	13	13
B_{2u}	1	-1	1	-1	-1	1	1	-1	29	29	29	T_y	28	28	28
B_{3g}	1	-1	-1	1	1	-1	1	-1	15	15	14	R_x	14	14	13
B_{3u}	1	-1	-1	1	-1	1	-1	1	29	29	29	T_x	28	28	28
	3	-1	-1	-1	-3	1	1	1	$(\pm 1 + 2\cos\alpha)$			O.P. = Out-of-plane			
	58	2	2	2	0	56	4	4	$U_R(H_2$:out-plane)			I.P. = In-plane			
	58	0	4	2	0	58	4	2	$U_R'(H_2$: in-plane)						
	57	1	3	3	1	57	3	3	$U_R''(M)$						

D_{2h} symmetry and is the symmetry of a rectangle. If the two hydrogen atoms are assumed to be on the principal axis of symmetry at equal distances above and below the plane of the molecule, and the metals at the center of symmetry in the metallic derivatives; then the slight distortion Robertson found would give all these molecules D_{2h} symmetry. Calculations for these models appear in Table 7. A comparison of the number of infrared active frequencies, as indicated by a T in the lattice mode column, shows the two models of the parent compound cannot be distinguished by the total number of frequencies observed. The total number of infrared active frequencies for a D_{2h} model increases to 71.

These calculations are for an isolated molecule which corresponds to conditions in the gaseous phase. To make calculations for the crystalline phase, the theory of Hornig can be used (31, pp.1063-1076). The symmetry one uses is that of the site group, which is C_i in the nomenclature of Halford (27a, pp.8-15) for the phthalocyanines. The calculated number of infrared active frequencies on this basis would be 84.

Since the total number of absorptions[13] found for these compounds is around 36, some of which may be combinations, for all practical purposes the assumption of a

13. There may also be a maximum of six frequencies below 400 $cm.^{-1}$ where no experimental data was obtained.

symmetry much less than D_{4h} is an unlikely one. This means that although the total of 84 frequencies predicted by the theory of Hornig may be present in the spectrum, many are so coincident that may not be resolvable because in a molecule of this size and stability the interatomic forces are quite strong compared to the intermolecular, and the molecular symmetry is the important factor.

ANALYSIS OF VIBRATIONS. By defining internal coordinates with reference to the valence bonding system assumed for the molecule, the normal modes may be analyzed further. Decius gives a simple method for defining these coordinates which leads to no redundancies in acyclic molecules, and 6μ redundancies in cyclic molecules, where μ is the number of bonds one must delete to render the molecule acyclic (21, pp.1315-1318). Figure 30 illustrates the choice of coordinates for in-plane motions which leads to the calculations of Table 8. Bond stretching means the motion of the bond labelled is defined by the difference of the distance between the atoms in a distorted configuration and an equilibrium one. Parallel bending is a motion defined by the difference between the distorted and equilibrium positions of the atoms defining the angle indicated. Once the coordinates are chosen, calculations are carried out exactly as performed in Table 2 to calculate n^{γ}, except now we use:

λ_R^a = No. of unshifted coordinates of type a.

Table 8 shows the number of different modes of the species E_u one may expect consisting mainly of motions of the coordinates shown. However, 7 of these are redundancies, and it cannot be said which ones they are. This information tells us there can be no more than the listed modes and since these motions occur in different parts of the spectrum some assistance is given to frequency assignments. Our choice of in-plane coordinates leads to a total of 3μ redundancies ($3 \times 9 = 27$) as shown in Table 8. Bonds for the metal were not considered as this would introduce too many redundancies.

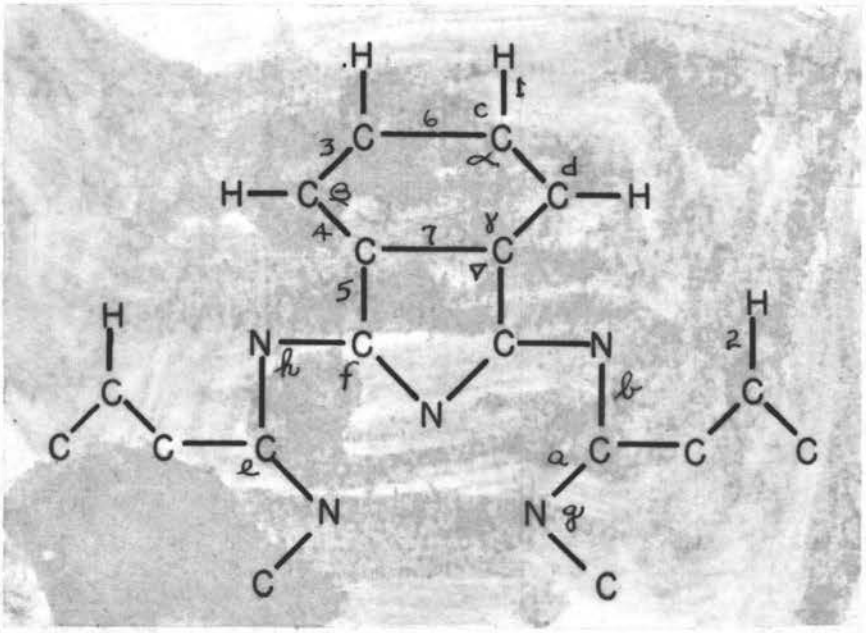
Coordinates for the out-of-plane modes could not be chosen so that the redundancies would be small enough to give useful information. Since there are only 8 predicted this is not a serious situation.

ASSIGNMENT OF FREQUENCIES.

GENERAL. In order to make a complete and unambiguous assignment of many of the absorptions found in the infrared spectra of the phthalocyanines, a great deal more data is necessary than is available here. This would involve determination of the Raman spectra, infrared work at very low temperatures, and work with isotopic substitution. We

FIGURE 30

CHOICE OF COORDINATES FOR IN-PLANE MODES.



Symbol	Bond
1	CH(1)
2	CH(2)
3	CC(1)
4	CC(2)
5	CC(3)
6	CC(4)
7	CC(5)
α	CCC(1)
β	CCC(2)
γ	CCC(3)
▽	CCC(4)

Symbol	Bond
a	CN(1)
b	CN(2)
c	CCH(1)
d	CCH(2)
e	CCN(1)
f	NCN(1)
g	CNC(1)
h	CNC(2)

TABLE 8

CALCULATION OF NUMBER OF IN-PLANE
CHARACTERISTIC GROUP FREQUENCIES IN PHTHALOCYANINES

	D_{4h} Symmetry Species				
Coordinates	A_{1g}	A_{2g}	B_{1g}	B_{2g}	E_u
CH(1)	1	1	1	1	2
CH(2)	1	1	1	1	2
CC(1)	1	1	1	1	2
CC(2)	1	1	1	1	2
CC(3)	1	1	1	1	2
CC(4)	1	0	0	1	1
CC(5)	1	0	0	1	1
CN(1)	1	1	1	1	2
CN(2)	1	1	1	1	2
CCH(1)	1	1	1	1	2
CCH(2)	1	1	1	1	2
CCC(1)	1	1	1	1	2
CCC(2)	1	1	1	1	2
CCC(3)	1	1	1	1	2
CCC(4)	1	1	1	1	2
CCN(1)	1	1	1	1	2
NCN(1)	1	1	1	1	2
CNC(1)	1	0	0	1	1
CNC(2)	1	0	1	0	1
Total Modes	19	15	16	18	34
Molecular Modes	14	13	14	14	27*
Redundancies	5	2	2	4	7

* Does not include 1 for the metal itself or 2 for central hydrogens.

cannot even state with certainty that all the very strong absorptions are normal modes, because in some cases a combination of two normal modes will give an absorption as strong as, or stronger than, another normal mode (42, p.1239). The theory whereby the number of infrared active modes may be calculated tells us nothing about the intensity of these modes. Some fundamental may be so weak as not to be observed, while others may correspond so closely to another in frequency they may not be resolved.

CHARACTERISTIC BOND FREQUENCIES. Assignment of observed infrared absorptions is greatly facilitated by a corollary of the invariance of force constants between the same bonds in different molecules which leads to characteristic bond frequencies. A study of the spectra of many compounds has resulted in the assignment of various spectral regions to various motions, i.e., in the 3000 to 3100 cm.$^{-1}$ region benzenoid CH bond stretching motion occurs, while between 600 and 900 cm.$^{-1}$, the out-of-plane bending of this bond is found (30, p.195) (47, p.20). It might appear that these concepts are contrary to the definitions of normal vibrations in which all nuclei of the molecule are taking part in the motion. A simple explanation may be illustrated by the case of a CH frequency. Since the mass of the hydrogen nucleus is so much smaller than that of the other nuclei in the molecule, the amplitude of vibrations of the

latter will be very much smaller than those of the hydrogen, and the hydrogen may be considered as oscillating against an infinitely large mass. Therefore, the vibration will depend primarily on the force between the hydrogen atom and the rest of the molecule.

Our analysis of the phthalocyanines is facilitated by a unique situation where several other compounds may be obtained merely by replacing one atom, without disturbing the remainder of the molecule to any great extent. Existence of polymorphic forms, with shifts and intensity changes of certain bands from one form to the other, also provides assistance in the frequency assignments.

NH Frequencies. As a result of isotopic substitution of the central hydrogen atoms in the metal-free phthalocyanine, the NH frequencies may be readily assigned. Figure 28 illustrates the weakening of bands at 3290, 1010, and 753 cm.$^{-1}$ and the appearance of new bands at 2475, 727, and 549 cm.$^{-1}$ upon replacing the central hydrogen atoms with deuterium. The ratios of each new band to its respective weakened one are 0.751, 0.731, and 0.729. An approximate calculation of this ratio may be made by use of:

$$\nu_o = \frac{1}{2\pi}\sqrt{\frac{k}{\overline{m}}}$$

k = force constant

$\overline{m}$ = reduced mass

Assuming k remains constant for replacement of H with D and using masses of N, H, and D, the ratio of the frequencies comes to 0.781. If the mass of N is replaced by the mass of the entire molecule, which is practically infinite compared with the H or D mass, this ratio would be 0.707; so the observed ratios are reasonable. This leads to assignments:

$CM.^{-1}$	Mode
3290	NH stretching
1010	NH in-plane bending
753	NH out-of-plane bending

These frequencies all lie in regions where these motions are known to occur in other compounds (47, pp.46-65). Vestling concluded from a study of porphyrins that since the NH stretching frequency he found was at 3320 $cm.^{-1}$ instead of around 3500 $cm.^{-1}$ as found in pyrrole, hydrogen bonding between two nitrogen atoms was indicated (57, pp. 3511-3513). This same conclusion may be applied to our 3290 $cm.^{-1}$ NH stretching frequency. Robertson attributed the greater rectangular distortion of the metal-free compound to the effect of hydrogen bonding (49, p.1199).

An interesting result of this work was that the alpha form does not have the 753 $cm.^{-1}$ band. The motion is either entirely absent due to a low intensity or shifted to around 736 $cm.^{-1}$. If the latter is the case, the ND shift

should show up around 520 cm.$^{-1}$ for the alpha phase. Unfortunately, this material was sublimed on a NaCl plate and the limit of transmission is around 535 cm.$^{-1}$.

CH Frequencies. The CH frequencies associated with the benzene ring occur in such a characteristic region they may be assigned easily to the four observed bands at 3078, 3043, 3026, and 3013 cm.$^{-1}$ which are indicated in Figure 29. An interesting feature of these absorptions is the intensity reversal found in the 3013 and 3026 cm.$^{-1}$ pair in the alpha to beta transition.

Four bands were predicted on the basis of D_{4h} symmetry, but this does not rule out the presence of more predicted from a lower symmetry. Bands of half-width less than 9 cm.$^{-1}$ will be resolved here as shown in Figure 10, and if low temperature work were successful in narrowing bands in this region below this width, one could expect to see if the splitting caused by lower symmetry could be detected with the spectrometer.

The region from 2000-3000 cm.$^{-1}$. The region of 2000-3000 cm.$^{-1}$ is one in which characteristic group frequencies are not expected from these compounds, but one where harmonics and combinations would easily fall. There are so many possibilities for the few absorptions occuring here no attempt will be made to analyze them. A very well prepared

sample was required to obtain absorptions in this region, and failure of some of the plotted alpha spectra to show bands here may be attributed to a poor sample.

ANALYSIS OF THE 2000-400 CM.$^{-1}$ REGION. This region is the most difficult to analyze because frequencies arising from the benzene ring and from the phthalocyanine inner CN ring occur here, some of them very close to one another. The phthalocyanine inner ring is shown in diagram B of Figure 1. As an aid to separation of the two types of modes, Table 9 presents a list of the fundamental frequencies of benzene. This table illustrates an empirical relationship derived by a study of the fundamentals of many compounds; namely that general regions may be assigned as follows:

Region, Cm.$^{-1}$	Type of Vibration
1650-1000	CC and CCH in-plane
1000-700	CCH out-of-plane
700-400	CCC or ring out-of-plane

In general, vibrations of the CN bonds will fall within the same general regions because they are isoelectronic with CC bonds; however, the frequencies may be expected to be somewhat lower on account of the greater mass of nitrogen. The regions above have no strict boundaries and occasional exceptions will be found. One cannot expect

TABLE 9

NORMAL MODES OF BENZENE

$Cm.^{-1}$	Type of Vibration
415	CCC perpendicular ring
606	CCC parallel bend
687	CH perpendicular bend
703	CCC perpendicular bend
854	CH perpendicular bend
975	CH perpendicular bend
990	CC parallel stretch
995	CH perpendicular bend
1010	CCC parallel bend
1036	CH parallel bend
1147	CH parallel bend
1174	CH parallel bend
1312	CC parallel stretch
1340	CH parallel bend
1478	CC parallel stretch
1596	CC parallel stretch

parallel = in-plane motion

perpendicular = out-of-plane motion

the exact benzene frequencies to show up in the spectra of the phthalocyanines because the benzene rings are only a part of a larger molecule.

A careful study of the spectra of the phthalocyanines will disclose certain relationships between the frequencies of alpha and beta forms, and between the metal-free and metallic compounds. These relationships will now be used together with a knowledge of the spectral region, and the character of the phthalocyanines, to arrive at frequency assignments in which the benzene frequencies may be separated from those of the phthalocyanine ring. H_2, used in connection with a phthalocyanine, will refer to the metal-free compound.

The region of 1650-1000 cm.$^{-1}$. Table 10 indicates the correlations found among the spectra. Using absorptions of the alpha form of metal-free phthalocyanine as a standard, frequency shifts for the alpha-beta transition and the metallic derivatives are listed. Little alpha-beta shift is noted for any bands in this region, but some large shifts are noted when a metal enters the center of the molecule. These shifts may now be used to arrive at the frequency assignments shown in Table 10.

The frequencies at 1616, 1475, 1340, 1123, and 1098 cm.$^{-1}$ show a small change accompanying the substitution of

TABLE 10

ANALYSIS OF 1650-1000 Cm.$^{-1}$ REGION

	Shifts from H_2-Alpha				H_2-Alpha	Assignment
	H_2	Cu	NI	Pt		
Alpha	0	-1	-2	0	1616	CC stretch - benzene
Beta	-2	-4	0	-		
Alpha	0	7	32	11	1507	CN stretch - inner ring
Beta	-1	5	31	-		(N bonded to metal)
Alpha	0	-4	3	-3	1475	CC stretch - benzene
Beta	-5	-9	0	-		
Alpha	0	-17	-7	-8	1442	CN stretch - inner ring
Beta	0	-19	-10	-		(N bonded to metal)
Alpha	0	2	1	-2	1340	CC stretch - benzene
Beta	0	2	0	-		(CCH bend)
Alpha	0	10	13	11	1285	CN stretch - inner ring
Beta	-3	10	12	-		
Alpha	0	2	10	8	1194	CC stretch - ortho
Beta	0	-	13	-		carbons
Alpha	0	7	7	12	1163	CN stretch - inner ring
Beta	-2	8	8	-		
Alpha	0	-1	3	5	1123	CCH parallel bend
Beta	-3	3	4	-		
Alpha	0	-3	-3	4	1098	CCH parallel bend
Beta	1	-4	-5	-		

a metal, so that they are assigned to motions connected with the benzene ring which is quite far removed from the metal in the molecule.

Frequencies at 1507, 1442, 1285, 1194, and 1163 $cm.^{-1}$ display varying shifts with the metals. Those at 1507 and 1442 $cm.^{-1}$ show shifts which vary from metal to metal and are quite near the frequency one may calculate for a C ═══ N stretching mode. Therefore, they are assigned to modes involving relatively large amplitudes of vibration of the nitrogen atoms (9, 9', 13, 13' of Figure 2) to which the metals are bonded. By the above reasoning, 1163 and 1285 $cm.^{-1}$ bands are assigned to motions involving the nitrogen atoms not directly bonded to the metal, but still in the inner ring (7, 7', 11, 11' of Figure 2).

There may also exist modes primarily involving the phthalic CC atoms. Robertson found these to have about one-quarter double bond character and their frequency might be expected to be about 1100-1200 $cm.^{-1}$. Therefore, the 1194 $cm.^{-1}$ band is tentatively assigned to this motion.

The region of 1000-700 $cm.^{-1}$. Correlations and assignments for this region are indicated in Table 11. The band at 715 $cm.^{-1}$ is one of the strongest in the spectrum and because of its region and strength is assigned to the out-of-plane bending of the CH bonds, quite similar to the 687 $cm.^{-1}$ frequency in benzene. The shift caused by metal

TABLE 11

ANALYSIS OF 1000-700 Cm.$^{-1}$ REGION

	Shifts from H_2-Alpha				H_2-Alpha	Assignment
	H_2	Cu	Ni	Pt		
Alpha	0	9	12	14	715	CH perpendicular
Beta	7	19	20	-		
Alpha	0	20	20	24	736	CN inner ring,
Beta	0	21	20	-		perpendicular
Alpha	(0	3	5	5	767)	CH perpendicular
	(0	3	3	-	777)	
Beta	(5	7	5			
	(9	4	4			
Alpha	(0	-5	-6	-4	872)	CH perpendicular
	(0	-2	-2	-	886)	
Beta	(2	-2	-3			
	(-4	-6	-8			
Alpha	0	-1	0	1	946	CH perpendicular
Beta	14	12	7	-		

substitution could be explained as due to the removal of a resonance effect when the strong NH mode at 753 cm.$^{-1}$ is removed. This would cause the frequency to move closer to 753 cm.$^{-1}$, which it does.

The CH stretching modes at 3013 and 3026 cm.$^{-1}$ exhibit an intensity reversal in the alpha to beta transition, and this same effect, coupled with smaller frequency shifts, is noted for the pairs of absorptions at 767, 777 and 872, 886 cm.$^{-1}$. Therefore, they are assigned to perpendicular CH modes. These frequencies where intensity changes occur in the alpha-beta transition may be attributed to anharmonic coupling of lattice modes with forbidden CH modes. Use of the D_{4h} character table leads to calculations which show that A_{1u} moles would be inactive, out-of-plane frequencies which could couple with the R_x, R_y, and R_z rotational modes to give an infrared active combination. Since this molecule is so large, one would expect very low frequency lattice modes.

The absorption at 946 cm.$^{-1}$ is assigned to a CH perpendicular mode because of its large alpha to beta shift.

This region contains fairly strong absorptions which occur only in the metallic derivatives as indicated below:

	Cu	Ni	Pt
Alpha	802	804	816
Beta	802	806	-
Alpha	901	917	920
Beta	901	917	-

We are forced to conclude these frequencies are connected with the metal to nitrogen bond. A simple calculation on the effect of a heavier metal on the reduced mass, and thus on the vibrational frequence of a metal to nitrogen bond (as done earlier for deuterium substitution), will indicate that no great change in the frequency from metal to metal could be expected from the mass effect.

The region of 700-400 cm.$^{-1}$. Table 12 indicates correlations and assignments made for the absorptions found in this region. It is the region for out-of-plane modes, and the few absorptions and definite effect caused only by the metals (no appreciable alpha-beta shifts) simplifies assignment. Frequencies at 616, 556, and 492 cm.$^{-1}$ show large shifts caused by metals. Those at 616 and 492 cm.$^{-1}$ are so much like those occuring with the 1507 and 1442 cm.$^{-1}$ bands, they are assigned to out-of-plane modes of the same bonds. It is remarkable that the 492 cm.$^{-1}$ band appears as a doublet in the beta phase of the parent compound. Just such a splitting could be expected for a mode involving large displacements of the nitrogens involved in

TABLE 12

ANALYSIS OF 700-400 Cm.$^{-1}$ REGION

	Shifts from H_2-Alpha				H_2-Alpha	Assignment (out-of-plane modes)
	H_2	Cu	Ni	Pt		
Alpha	0	0	0	2	443	CCC benzene ring
Beta	0	0	1	-		
Alpha	0	13	26	21	492	CN inner ring
Beta	4*	14	27	-		(N bonded to metal)
Alpha	0	17	18	21	556	CN inner ring
Beta	2	17	18	-		
Alpha	0	21	26	27	616	CN inner ring
Beta	-1	19	25	-		(N bonded to metal)
Alpha	0	5	-	-	684	(CCC parallel bend)
Beta	0	6	0	-		CH perpendicular

* Doublet

the hydrogen bonding. The frequency at 556 cm.$^{-1}$ is assigned to an out-of-plane mode of the same bonds as that at 1285 cm.$^{-1}$ by the same reasoning as above.

Combinations. By an examination of the general features of all the spectra, one can conclude that the frequencies at 1255, 1308, and 1328 cm.$^{-1}$ are strong combinations arising from frequencies present in the metal-free phthalocyanine and not in the metallic derivatives. The only combination apparent for the 1255 cm.$^{-1}$ absorption seems to be that of the 1010 cm.$^{-1}$ NH bending mode with a frequency at 245 cm.$^{-1}$. Examination of the spectra of the deuterated compound indicates this absorption at 1255 cm.$^{-1}$ becomes quite weaker as expected. We would expect the other combinations to arise from this NH band because it fulfills the requirements, but numerically the 872 and 882 cm.$^{-1}$ bands with the one at 443 cm.$^{-1}$ fit. These former two bands are much more intense in the metal-free compound than in the metallic derivatives.

COMPARISON: OBSERVED TO CALCULATED.

While it is not possible to assign frequencies as characteristic of individual bonds as calculated in Table 8, the following comparison may be made by grouping calculated modes:

Number Observed	Number Calculated	Type of Vibration
4	4	CH stretching
2	4	CH in-plane bending
9	7	Out-of-plane motion
4	10	Inner ring: in-plane motion
5	16	Benzene ring: in-plane motion

The in-plane modes as calculated contain 7 redundancies, most of which are likely to be found in the benzene ring modes.

CONCLUSIONS

1. A new method for preparing the alpha phase of the phthalocyanines has been presented. It involves subliming the compounds at a pressure of from 10^{-1} to 10^{-5} mm. onto a surface whose temperature is below 200 degrees centigrade.

2. A technique of sample preparation is given for these compounds resulting in samples which exhibit low scattering of radiation and produce excellent spectra.

3. An opportunity to test the theory of Hornig concerning calculation of the number of infrared active modes of vibration predicted on the basis of environmental symmetry was presented. Evidence is given to indicate that as a practical matter (because of instrumental resolution limits) use of approximate molecular symmetry appears adequate for theoretical considerations of these molecules. This is attributed to the size and great stability of the phthalocyanine molecule, which cause the interatomic forces in the molecules to be so much stronger than the intermolecular forces that the molecular symmetry is a major factor to be considered rather than environmental symmetry.

4. Replacement of the central hydrogen atoms in metal-free phthalocyanine with deuterium has been carried out. The spectrum resulting from this experiment led to

frequency assignments for the NH modes which appear to be quite accurate.

5. A scheme of analysis of the spectra obtained, which mades use of the unique molecular and crystalline characteristics of phthalocyanine and its metallic derivatives, has been used to obtain characteristic bond frequency assignments for metal-free phthalocyanine.

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