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by

LeRoy Dean Hunter

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

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Polarized absorption electronic spectra for single crystals of dichloro(ethylenediamine)platinum(II)*

LeRoy Dean Hunter

Under the supervision of Don S. Martin, Jr.
From the Department of Chemistry
Iowa State University of Science and Technology

The polarized electronic absorption spectra for single crystals of dichloro(ethylenediamine)platinum(II) at 300°, 77° and 15°K have been recorded. It is possible to measure both c and b polarizations for the compound which crystallizes in an orthorhombic structure consisting of chains of the square planar molecules uniformly spaced 3.39Å apart. Typical crystals for experiments were plates 1-3μ thick, grown from aqueous solution. The polarized crystal spectra indicate pronounced crystal effects compared with the solution spectrum. These effects are apparently the result of the close Pt-Pt spacings within the chains. A one-dimensional exciton theory is applied which accounts for the observed features. A dipole allowed transition, $d_{xy}^{*} \leftarrow L(\pi)$, has been shifted from ~ 49,000 to 37,500 cm^{-1} with c polarization by

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perturbations which are identified with a Frenkel excitation. In _b_ polarization there are two weak bands at 33,100 and 39,100 cm^{-1} which become narrower and more intense with lower temperature, indicating that they have some dipole allowed character. They have been assigned as unusual transitions to ionized exciton states based on the excitation of an electron into a d_{xy}^{*} orbital from the d_{xz} and $L(\pi)$ orbitals on adjacent molecules respectively. There is a slight shift of these bands to lower energy upon cooling, which is a logical consequence of shorter Pt-Pt spacings.

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INTRODUCTION

The purpose of this work has been to study the polarized electronic spectrum of single crystals of dichloro(ethylenediamine)platinum(II). This particular system provides an ideal example of the effects of a one-dimensional crystal perturbation upon the electronic absorption spectrum of a d^8 square planar platinum complex. As will be seen, this spectrum provides convincing evidence for excitations to both Frenkel exciton and ionized exciton states due to this crystal environment.

First the evidence involved in assigning the transitions of K_2PtCl_4, including single crystal absorption spectral evidence, will be reviewed. Then the perturbation upon this $PtCl_4^{2-}$ spectrum in tetrammineplatinum(II)chloroplatinate(II), Magnus' green salt, will be presented as it has been investigated by several workers. This will be followed by a brief discussion of other systems in which similar perturbation effects occur. The presentation of previously developed theory related to these effects will be included in a later section where the theories will be related to the $Pt(en)Cl_2$ problem.

Potassium tetrachloroplatinate, K_2PtCl_4, prepared from aqueous systems, forms red crystals, usually needles. The crystal structure (1) reveals that the $PtCl_4^{2-}$ ions stack along the c axis which is perpendicular to the planar ions. The Pt-Pt distance along the chains is 4.13Å as shown in Figure 1. Some flat, plate-like crystals of the compound, which were grown, had the c-axis or stacking axis coincidental with the long dimension of the crystal. The square planar $PtCl_4^{2-}$ ions are perfectly eclipsed as they stack along the axis, and each lies in D_{4h} crystal symmetry. This means that with an incident plane polarized light beam directed perpendicular to the crystal face, absorption of light with pure c polarization (z-polarization) or with a polarization (xy-polarization) can be measured.

Various techniques have been applied to the problem of assigning the spectrum of $PtCl_4^{2-}$, including polarized single crystal absorption spectra at various temperatures (2,3,4), powder reflectance spectra (4), solution spectra (5), magnetic circular dichroism of a solution (6), and low temperature solution spectra in a frozen organic solvent (7). Figure 2 shows the solution spectrum and reflectance spectrum, and Figure 3 gives the room temperature and 15°K polarized crystal spectra. These data provide clear evidence for the proposal

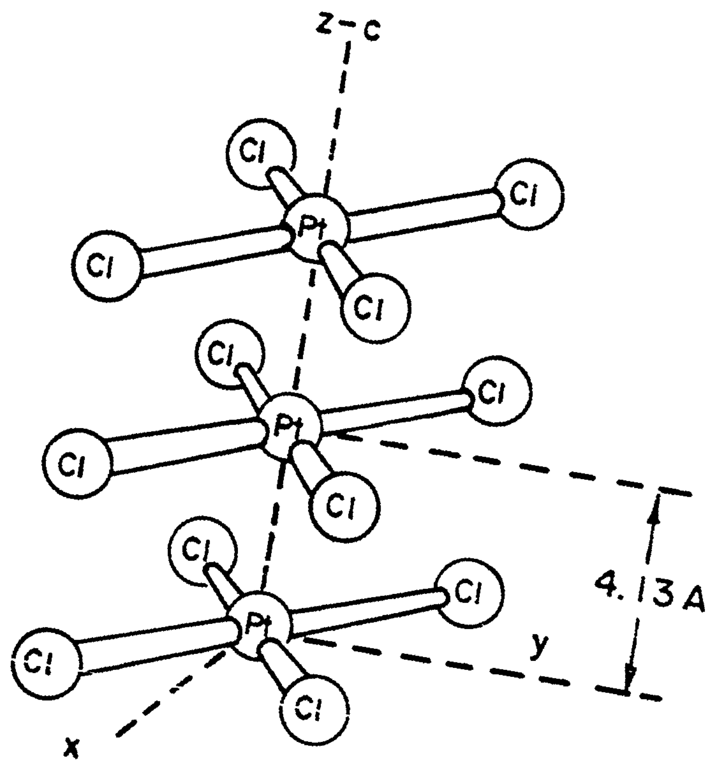

Figure 1. Stacking of $PtCl_4^{2-}$ ions

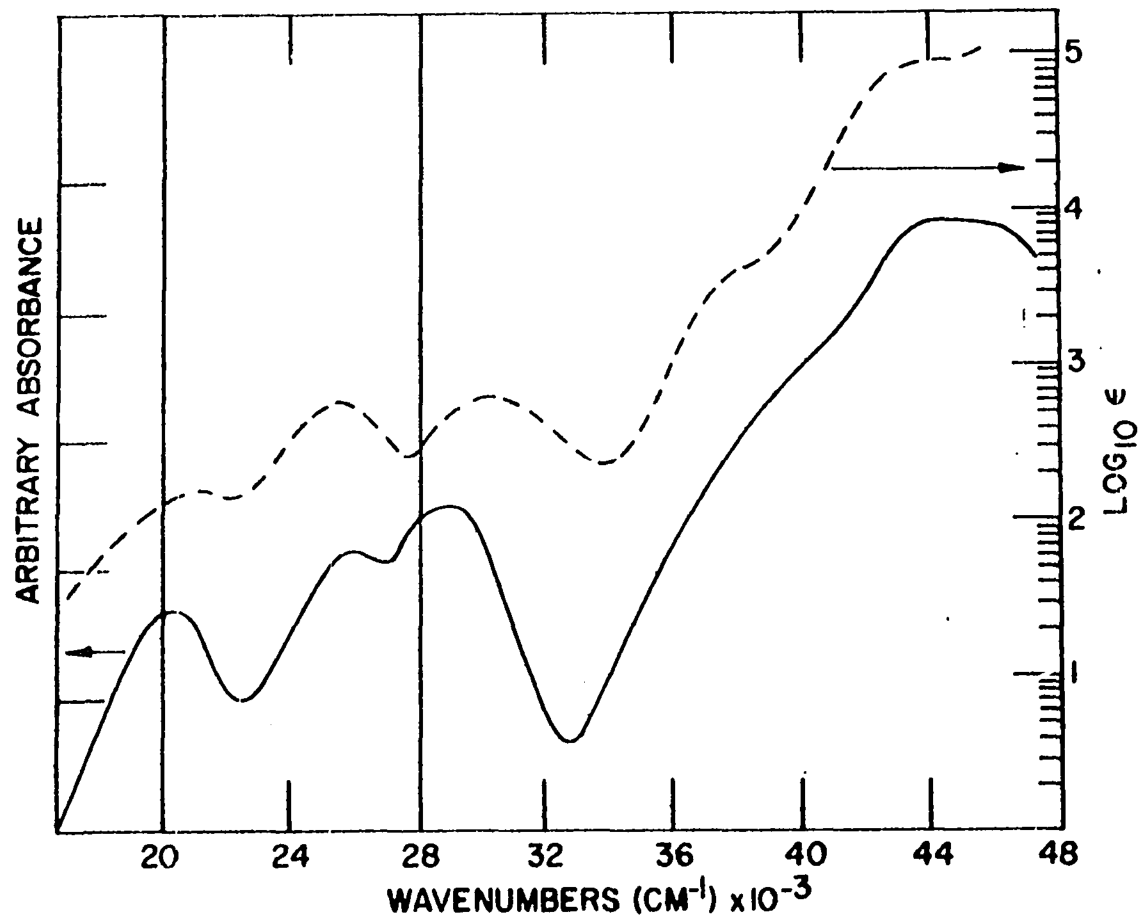

Figure 2. Spectra of K_2PtCl_4. The solution spectrum is the dashed line and the diffuse reflectance spectrum is the solid line

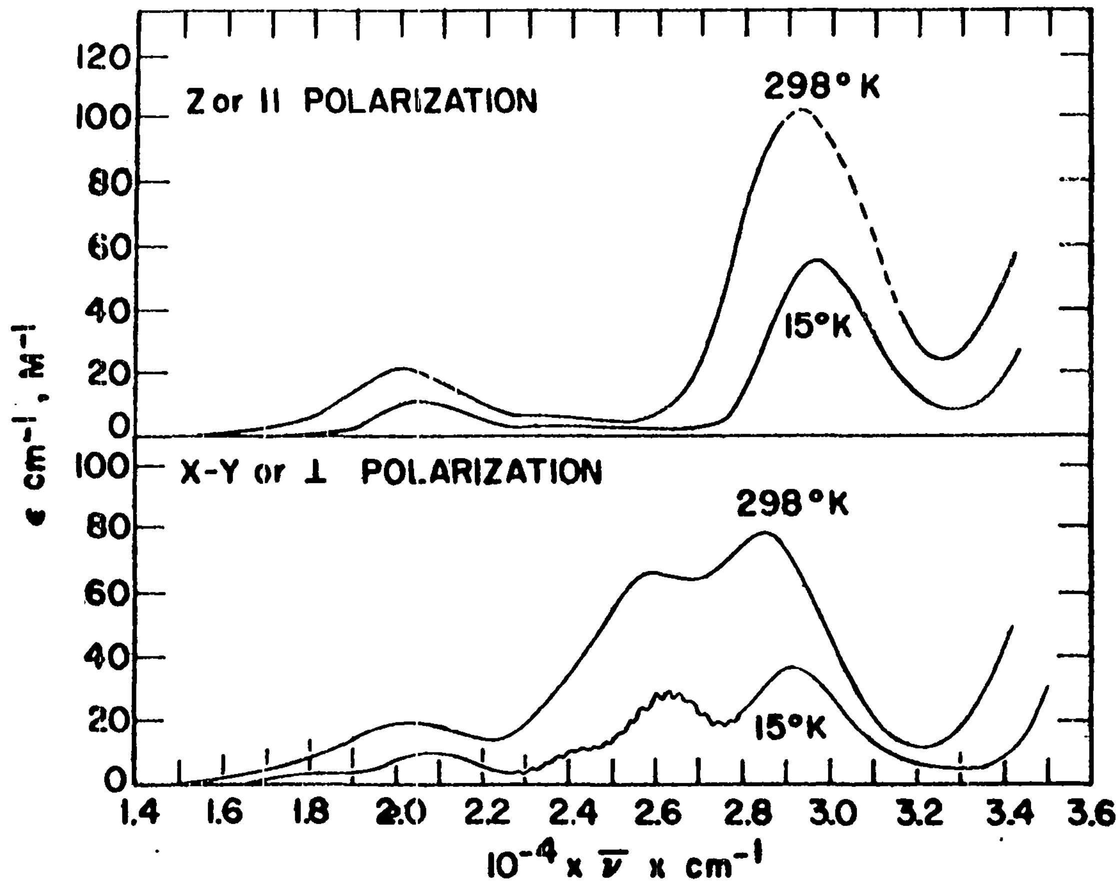

Figure 3. Polarized crystal spectra of K_2PtCl_4 at 298° and 15°K

that the bands which are assigned as d-d transitions occur *via* a borrowing mechanism from similarly polarized allowed transitions by means of vibronic coupling. This fact is evidenced by the temperature dependence of the bands, for they demonstrate lower intensity at the lower temperature where there is higher population of the ground states for the vibrational modes which serve as the mixing perturbation. The assignments of the bands for the $PtCl_4^{2-}$ spectra from Martin and coworkers (8,9), most of which have now become well accepted, appear in Table 1. The energy level scheme for such a d^8 square planar complex with weak field ligands such as Cl^- or NH_3 is shown in Figure 4. In the molecule, the x and y axes have been chosen to pass between the ligands, and therefore, the d_{xy}^* orbital is the lowest unfilled orbital since the d_{xy} orbital is involved in σ bonding of the ligands. The solution spectrum bands for K_2PtCl_4 are considered to be assigned analogous to the crystal data with only slight shifts of the energies. If these assignments are correct, it appears that the spectrum of solid K_2PtCl_4 arises from oriented $PtCl_4^{2-}$ ions which are sufficiently isolated that there are negligible interaction effects in the spectrum.

The transitions of primary interest here are d-d transi-

Table 1. The spectrum of $PtCl_4^{2-}$ in solution and in various crystalline environments (3,4,5,20). (Energies in $cm^{-1} x 10^{-3}$, molar absorbances in brackets)

		$^3A_{2g}$	^3E_g	$^3B_{1g}$	$^1A_{2g}$	^1E_g	$^1B_{1g}$
$PtCl_4^{2-}$(2M HCl soln.)		17.7(2.6)	21.0(15)	--	25.5(59)	30.2(64)	37.9
K_2PtCl_4	xy	17.3(5)	20.4(17.5)	23.8(30)	26.0(45)	28.5(57)	
	z	--	20.2(20)	23.8(10)	--	29.3(70)	--
$Pt(C_2H_5NH_2)_4$	xy	--	19.0(45)	--	24.8(135)	26.6(140)	33.5
$PtCl_4$	z	--	18.8(70)	--	--	27.2(190)	--
$Pt(CH_3NH_2)_4$	xy	--	17.3(35)	--	--	25.2(190)	30
$PtCl_4$	z	--	17.3(100)	23(120)	--	25.3(340)	--
$Pt(NH_3)_4PtCl_4$	xy	--	16.5(20)	--	--	24.9(170)	30
	z	--	16.5(150)	23(190)	--	24.9(305)	--

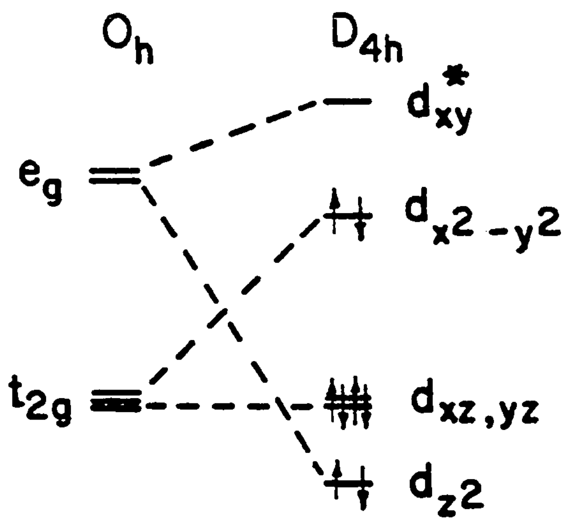

Figure 4. Energy correlation diagram for the 5d orbital states in O_h and D_{4h} symmetries

tions which one would normally expect to be symmetry forbidden for a centrosymmetric metal complex such as $PtCl_4^{2-}$. However, these transitions become partially allowed due to mixing of odd excited states with the even excited states through the perturbing influence of an odd vibration (10-12). The problem is complicated by the fact that components of several transitions may be mixed together by one or more asymmetric vibrational modes. A further complication arises from the fact that the spin-orbit coupling constant for platinum is so large, 4060 cm^{-1} in the free atom, that supposedly 'spin-forbidden' transitions appear with appreciable intensities, always at lower energies from their parent singlet transitions. Martin <u>et al</u>. (8,9) have treated the $PtCl_4^{2-}$ problem using the ligand field technique as it applies to $PtCl_4^{2-}$ described by Fenske <u>et al</u>. (13), including spin-orbit coupling and electron-electron repulsion. Their calculations give semi-quantitative as well as qualitative support for the assignments in Table 1. The logic for the given assignments is as follows. The singlet transition, ${}^1A_{2g} \leftarrow {}^1A_{1g}$ ($d^*_{xy} \leftarrow d_{x^2-y^2}$) should be <u>xy</u> polarized exclusively in the crystal spectrum, so we start by assigning it to the 26,300 cm^{-1} band corresponding to 25,500 cm^{-1} in solution. Magnetic circular dichroism in solution (6) indicates that the 30,200 cm^{-1} band is primarily a transition terminating in degenerate states, so it has been labeled singlet $^1E_g \leftarrow {}^1A_{1g}$ ($d^*_{xy} \leftarrow d_{xy,yz}$). Further evidence for this assignment is the fact that this transition in the crystal is seen in both _z_ and _xy_ polarizations, consistent with the prediction of theory. The primary components of the corresponding triplet transitions, logically occurring at lower intensity and lower energy due to the unpaired spins, account for the two broad absorptions centered at 21,000 cm^{-1} and 17,500 cm^{-1}.

These assignments so far have set the relative energies of $d^*_{xy} > d_{x^2-y^2} > d_{xz} = d_{yz}$ orbitals. The question of just how far the d_{z^2} orbital state drops in energy as one goes from an octahedral arrangement to the square planar configuration (see Figure 4) has been a primary concern for the effort that has been expended on the $PtCl_4{}^{2-}$ problem.

The assignment of the 37,900 cm^{-1} solution band to $^1B_{2g} \leftarrow {}^1A_{1g}$ ($d_{xy} \leftarrow d_{z^2}$) placed the d_{z^2} orbital lowest in energy. This assignment has been qualitatively supported by Martin's work and also by semi-empirical molecular orbital calculations by Gray (14) and Cotton (15). The corresponding triplet state for this transition presumably would lie near 25,000 cm^{-1}, under the $^1A_{2g}$ band. The relatively high intensity of the $^1B_{2g}$ band, compared to the other singlet d-d transitions, could very well be a logical consequence of the close proximity of the intense charge transfer band at about 46,000 cm^{-1}.

When $PtCl_4^{2-}$ ion is added in aqueous solution to $Pt(NH_3)_4^{2+}$, there is a very interesting result. Usually, an intensely colored green solid precipitates, whereas the salts K_2PtCl_4 and $[Pt(NH_3)_4]Cl_2$ are quite soluble. This green solid is Magnus green salt (MGS), named for the man who first reported its existence (16). The green color strikes one as being peculiar since the $PtCl_4^{2-}$ ion is red both in solution and in a crystal such as K_2PtCl_4, while $Pt(NH_3)_4^{2-}$ is colorless both in solution and in a solid such as $[Pt(NH_3)_4]Cl_2$. In MGS (17), the anions and cations stack alternately along an axis perpendicular to their planes. However, the Pt-Pt distance in MGS is 3.25Å compared to 4.13Å for K_2PtCl_4. Yamada (2) as early as 1951, speculated that some type of metal-metal interaction was causing the anomalous color band and crystalline stability after he had observed that this band was polarized along the stacking chain of the molecules perpendicular to the planes. He observed similar behavior in nickel(II) dimethylglyoximate which possesses a similar stacking of planar molecular units (18). His spectra were very qualitative since the bands were too intense to measure accurately.

In 1957 Rundle et al. (17) reported the crystal structures of both MGS and a pink form of the same compound called MPS, or Magnus pink salt. Presumably the pink color of the MPS was the result of direct mixing of red $PtCl_4^{2-}$ ions with colorless $Pt(NH_3)_4^{2+}$ ions in a lattice where the closest Pt-Pt spacing is greater than 5Å. Rundle suggested that in terms of molecular orbital theory, the metal-metal interaction in MGS could be thought of as a 'configuration interaction' involving some metal-metal bonding. He did not elaborate as to how this might actually lead to the green color.

Miller (19) proposed a band theory which attempted to quantitatively describe the bonding in a chain of metal ions such as in MGS, taking into account the different energies of the basis orbitals on the platinum atoms of the anion and cation. He made the assumption that the filled $5d_{z^2}$ orbitals of the d^8 square planar complexes overlapped to form a one dimensional band. For a large number, N, of atoms in the chain, the eigenvalues would be

$$E_n = (\alpha_C+\alpha_A)/2 \pm (\tfrac{1}{2})[(\alpha_A-\alpha_C)^2 \pm 16\beta^2\cdot\cos^2(n\pi/(N+1)]^{\frac{1}{2}}$$

where α_C and α_A are the orbital energies of cation and anion $5d_{z^2}$, and β is the resonance integral $\langle 5d_{z^2}(A)\ H\ 5d_{z^2}(C)\rangle$ between nearest neighbors. One observable consequence of such band formation would be a broadening of ligand field transitions within either $Pt(NH_3)_4^{2+}$ or $PtCl_4^{2-}$ involving d_{z^2}. Also the possibility exists for new excited states resulting from transitions between anion and cation states.

The former idea of Yamada (2) that the color band in MGS arises from some new transition between Pt atoms in the chain was fairly well dispelled by Day's evidence (4,20) that the bands in the MGS spectrum, which have been measured, correspond to rather normal absorption bands for a coordination complex and probably characterize perturbed bands of $PtCl_4^{2-}$. The evidence involved the polarized transmission spectra of MGS and its analogs $Pt(CH_3NH_2)_4PtCl_4$ and $Pt(C_2H_5NH_2)_4PtCl_4$, shown with the spectra of K_2PtCl_4 in Figure 5. The bands below 30,000 cm^{-1} appear to be clearly related in parentage to bands in the spectrum of K_2PtCl_4. The ethylamine MGS, which has a Pt-Pt spacing of 3.40Å, intermediate between MGS and K_2PtCl_4, shows an intermediate shift of the bands which move from K_2PtCl_4 to lower energies in methylamine MGS (Pt-Pt

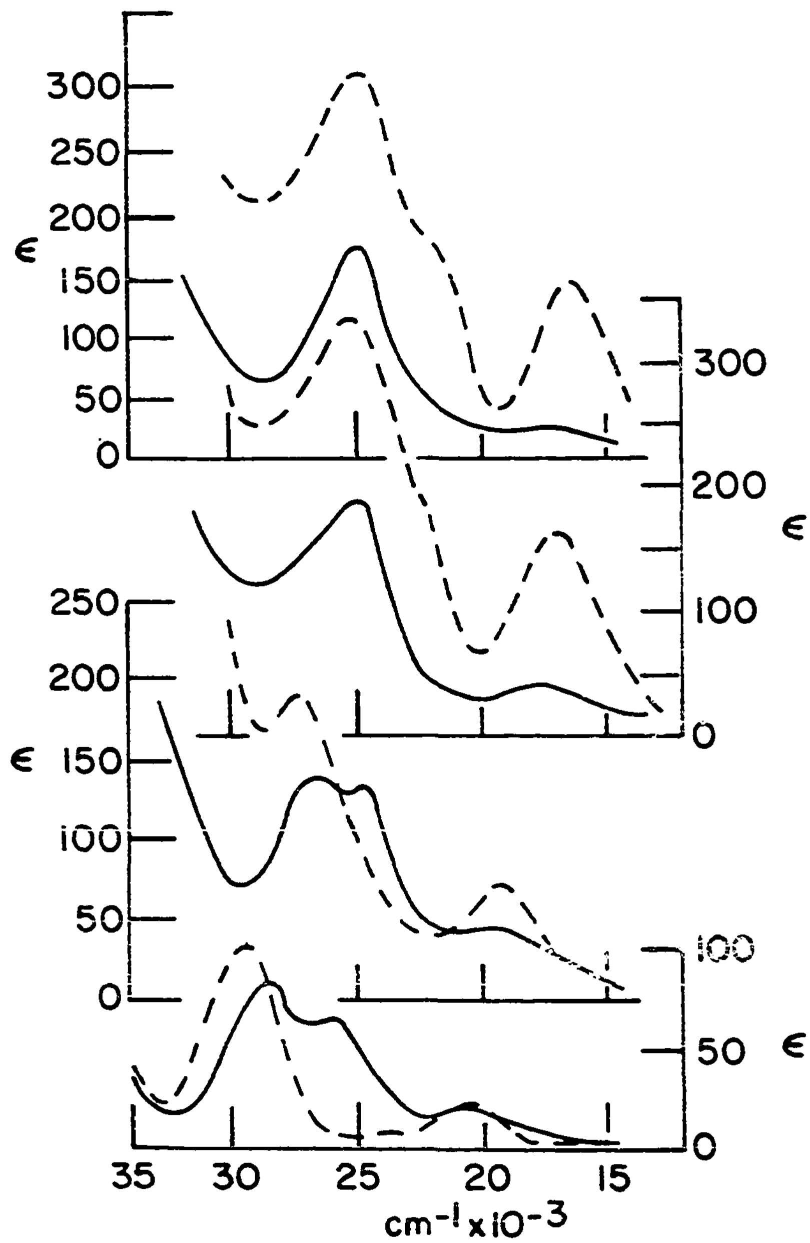

Figure 5. Room temperature polarized crystal spectra for K_2PtCl_4 and $PtCl_4 \cdot PtA_4$, where A = $C_2H_5NH_2$, CH_3NH_2 and NH_3 in order from the bottom to top. The dashed lines are for z polarization, solid lines are for x-y polarization

spacing of ~3.25Å) and MGS. Day has, therefore, made the assignments of the bands for these compounds analogous to those for $PtCl_4^{2-}$ (see Table 1). Day has postulated that a high energy allowed band in K_2PtCl_4 has shifted in MGS to lower energy toward the visible. Such a band is the $^1A_{2u} \leftarrow {}^1A_{1g}$ ($d^*_{xy} \leftarrow L\text{-}\pi_z$) charge transfer band which is at 42,500 cm^{-1} in K_2PtCl_4 and 34,500 cm^{-1} in MGS, based on reflectance spectra (4). Since it is such a band that mixes _via_ the vibronic model to give intensity to the bands seen in the visible, and further since the magnitude of the mixing is dependent upon the energy separation, Day has concluded that it is primarily the shift of this charge transfer band which causes an increased absorption and green color of MGS. Anex _et al_. (21) have shown by specular reflectance with single crystals that the 34,500 cm^{-1} band in solid MGS is _z_ polarized, thus supporting Day's suggestion, since the visible band in MGS is strongly _z_ polarized. As will be developed later, the $Pt(en)Cl_2$ system demonstrates strong evidence of a similar red shift of an intense high energy charge transfer band on going from solution to the solid state and subsequent enhancement of _z_ polarized band in the visible region of the spectrum.

There are several other crystal systems which seem to demonstrate similar effects of intra-molecular interaction on the absorption spectrum. One of these is nickel(II)dimethylglyoximate $Ni(dmg)_2$. The crystal structure of this compound shows that the planar molecules stack along an axis with a spacing of 3.245Å (18). The spectrum (22), however, is dominated by intense allowed bands which apparently obscure the d-d transitions. The evidence seems to indicate that the red color of the solid results from an intense band at 18,500 cm^{-1} which has shifted from the solution spectrum to the red by at least 7000 cm^{-1} and increased in intensity by about ten-fold. Anex (22) presents evidence for this transition being $(p_z,\pi^* \leftarrow d_{z^2},\sigma)$ metal to ligand. Other systems which have such effects as are under discussion here are the alkaline earth salts of $Pt(CN)_4{}^{2-}$ (23-25), and most other complexes between nickel, palladium, and platinum and the vic-dioximes, all of which have similar crystal structures with respect to the formation of "metal chains" (4,17,20,23,26-28).

Interest in these systems is primarily directed toward gaining a better understanding of the forces between the metal atoms in the chains and their influence on the absorption spectrum. One would like to develop a concise theory which accounts for the anomalous behavior of the spectra of the square planar molecules when they are stacked so closely. The $Pt(en)Cl_2$ system provides an ideal model for testing possible theories. The crystal structure of this compound has been solved recently by Jacobson and Benson[1]. The crystals belong to the space group $C222_1$ with 4 molecules per unit cell. The molecules are nearly planar and stack in a linear array just as $Ni(dmg)_2$ and MGS with an inter-planar spacing of 3.39Å. Figure 6 shows the orientation of the molecules along the stacking axis, or c axis and Figure 7 shows the orientation of the molecules in an a-b plane. The molecular axes have been chosen analogous to Figure 1 for K_2PtCl_4. This choice of axes has the very nice consequence that the molecular axes all coincide with the three crystallographic axes. The crystals typically grow as plates with the edges of the plates parallel to the c direction and b direction. The a direction is then perpendicular to the face of a plate. It is possible then to measure pure c absorption or b absorption for the molecules in the fixed lattice by directing a plane polarized light beam through a crystal

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[1]R. A. Jacobson and J. E. Benson, Ames, Iowa. X-ray crystal data. Private communication. 1970.

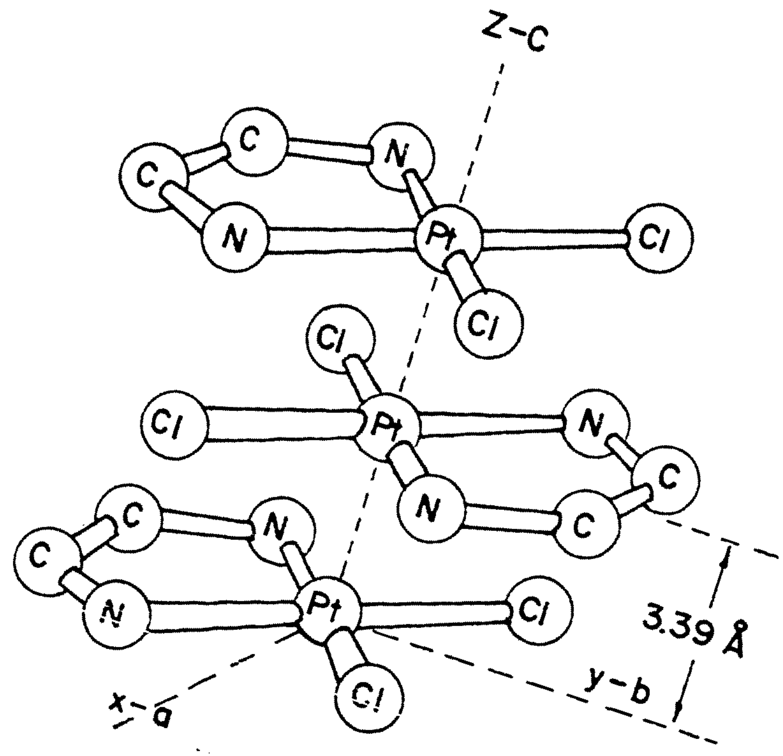

Figure 6. Stacking of the Pt(en)Cl_2 molecules along the c-direction

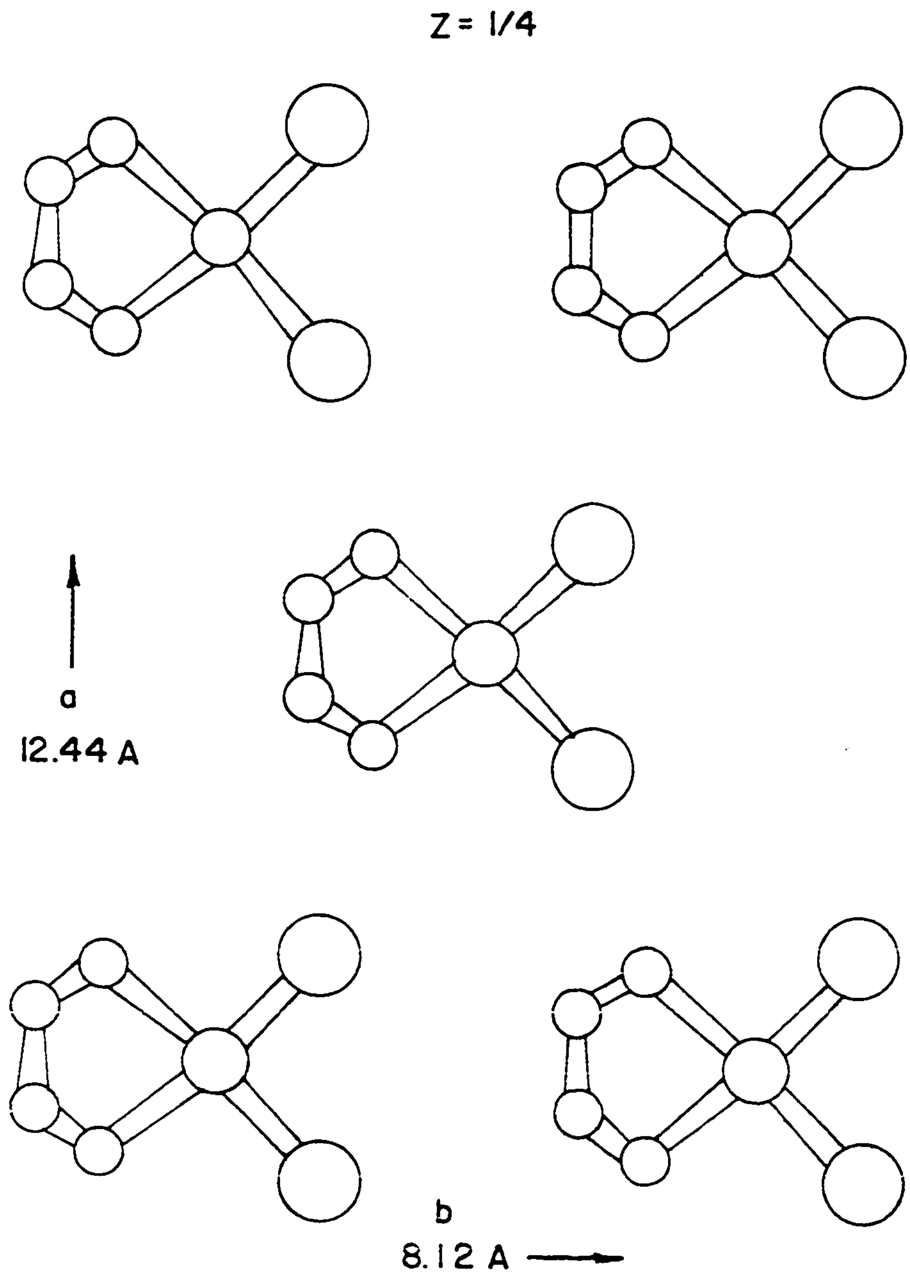

Figure 7. Orientation of $Pt(en)Cl_2$ molecules in an a-b plane

along the _a_ or _x_ axis. Interpretation of the effect of such a close Pt-Pt spacing as 3.39Å, in this case, should be more straightforward than for MGS since the molecules in the chain are the same with no ionic charges. What follows is the presentation of polarized absorption spectra for single crystals of $Pt(en)Cl_2$ at $300^\circ K$, $77^\circ K$, and $15^\circ K$. The results are examined in terms of an exciton theory which has been so effectively applied to aromatic organic molecular crystals (29-32).

II. EXPERIMENTAL INVESTIGATION

The $Pt(en)Cl_2$ was prepared according to the method of Basolo et al. (33). Very thin plates of the compound with well developed 100 faces were grown from solutions containing about .05 M KCl. Crystals were withdrawn from the liquor and mounted over a small hole in a platinum support plate. They were attached to the platinum at one point with low temperature varnish. This permitted the unequal contraction of the crystal and platinum plate upon cooling. The crystals were typically 1-2 mm^2 in area, necessitating pinholes of .6-.8 mm diameter. The platinum support plate was then mounted to the cold finger of a liquid helium cryostat. The tail section of the cryostat was lowered into the sample beam of a Cary 14 spectrophotometer and supported in that position by external braces. The tail section was equipped with quartz windows through which the light beam could pass. A Glan-type calcite polarizer was in the light path following the crystal. The polarizer could be rotated by an external crank to adjust the polarization. In the reference compartment the beam was balanced down by a pinhole and sometimes absorber screens. Also, an identical polarizer to the one in the sample compartment was provided to balance polarizer absorbance due either to calcite bands or systematic polarization within the spectrophotometer. The absorbance from 5500Å into the uv was recorded using a high intensity source Model 1471200. For the uv spectrum from 2900Å to 1900Å, the hydrogen arc was used. The spectra for c polarization and b polarization were recorded at room temperature, 77°K and 15°K. The low temperature spectra were obtained by adding liquid nitrogen and liquid helium to the cryostat. The very fragile crystals very often broke at 15°K. The absorbances were set equal to zero at 5500Å where there was no apparent absorption. Base lines were determined with the same setup without a crystal over the pinhole.

In order to determine the molar absorbancies for a crystal, it is necessary to know the concentration of the compound in the crystal and the crystal thickness or the equivalent of this information. Direct measurement of the crystal thickness was prohibited by the fact that the thickest crystals for which the c-polarization band at 25000 cm^{-1} could be measured was about 6 μ. This difficulty was averted by taking advantage of the fact that for a uniformly thick crystal, the thickness may be determined from its density, weight and surface area. The way in which the molar absorbancy, ϵ, may be determined from this information is shown in the following equations.

$$\varepsilon = \frac{OD}{\ell c}\ (cm^{-1}\underline{M}^{-1}) \tag{1}$$

(OD = optical density or absorbance, ℓ = crystal thickness and c = concentration).

$$c = x/V \tag{2}$$

(x = number of moles of the compound in the crystal or crystal weight divided by the molecular weight, V = crystal volume (liters))

$$\ell = V/A \tag{3}$$

(A = surface area of the crystal.)

$$\varepsilon = \frac{OD}{(V/A)(x/V)} = OD\left(\frac{A}{x}\right) \times 10^{-3} cm^{-1}\underline{M}^{-1} \tag{4}$$

For the molar absorbance determination, it was necessary to use relatively thick crystals in order to provide sufficient weight to be accurately weighed with the Cahn electrobalance available to us. Crystals of this size, about 1 mm^2 area and 3.5×10^{-4} g weight, were not generally as uniformly thick as the thinner crystals used for the spectra determinations, as judged by interference colors in a polarizing microscope. This resulted in an uncertainty of as much as 20% in the measured molar absorbancy. It was also, for this reason that the molar absorbancies have been related to the one crystal which was judged to be the most uniformly thick of the ones weighed for that purpose. That crystal, which weighed 3.66×10^{-5} g and measured $1.822 \times 10^{-2} cm^2$ in surface area, had an absorbance of 3.08 in the _c_-polarization at 25,000 cm^{-1}. The thicknesses of other crystals were then assumed to be proportional to this crystal's 6.44 μ with respect to the absorbance at 25,000 cm^{-1} in _c_ polarization.

III. RESULTS AND DISCUSSION

A. Spectra

The aqueous solution spectrum of $Pt(en)Cl_2$ is shown in Figure 8. The dashed lines represent a Gaussian analysis (34) of the d-d region of the spectrum from 20,000 cm^{-1} to 42,000 cm^{-1}. In this region, the spectrum was measured with .318 M KCl to suppress aquation. The region above 42,000 cm^{-1} was examined immediately following rapid dissolution without KCl to avoid chloride ion interference. The spectrum strongly resembles that of $Pt(NH_3)_2Cl_2$ except that the bands are more intense. The assignments taken for these bands followed those for $Pt(NH_3)_2Cl_2$ by Chatt et al. (5) and are consistent with the assignments previously discussed for the $PtCl_4^{2-}$ spectrum. These assignments are shown in Table 2 along with their predicted polarizations in the crystal spectra. Figure 9 shows the ordering of the molecular orbital energies for the 5d orbitals and 6pz orbital on platinum as well as the $3p\pi$ orbitals of the chloride ligands. The symmetry designations for D_{4h}, C_{2v} and C_2 are shown for these orbitals.

The diffuse reflectance spectrum and polarized crystal spectra at 300° and 77°K for a crystal 2.37 μ thick are shown in Figure 10. The general features of these spectra have

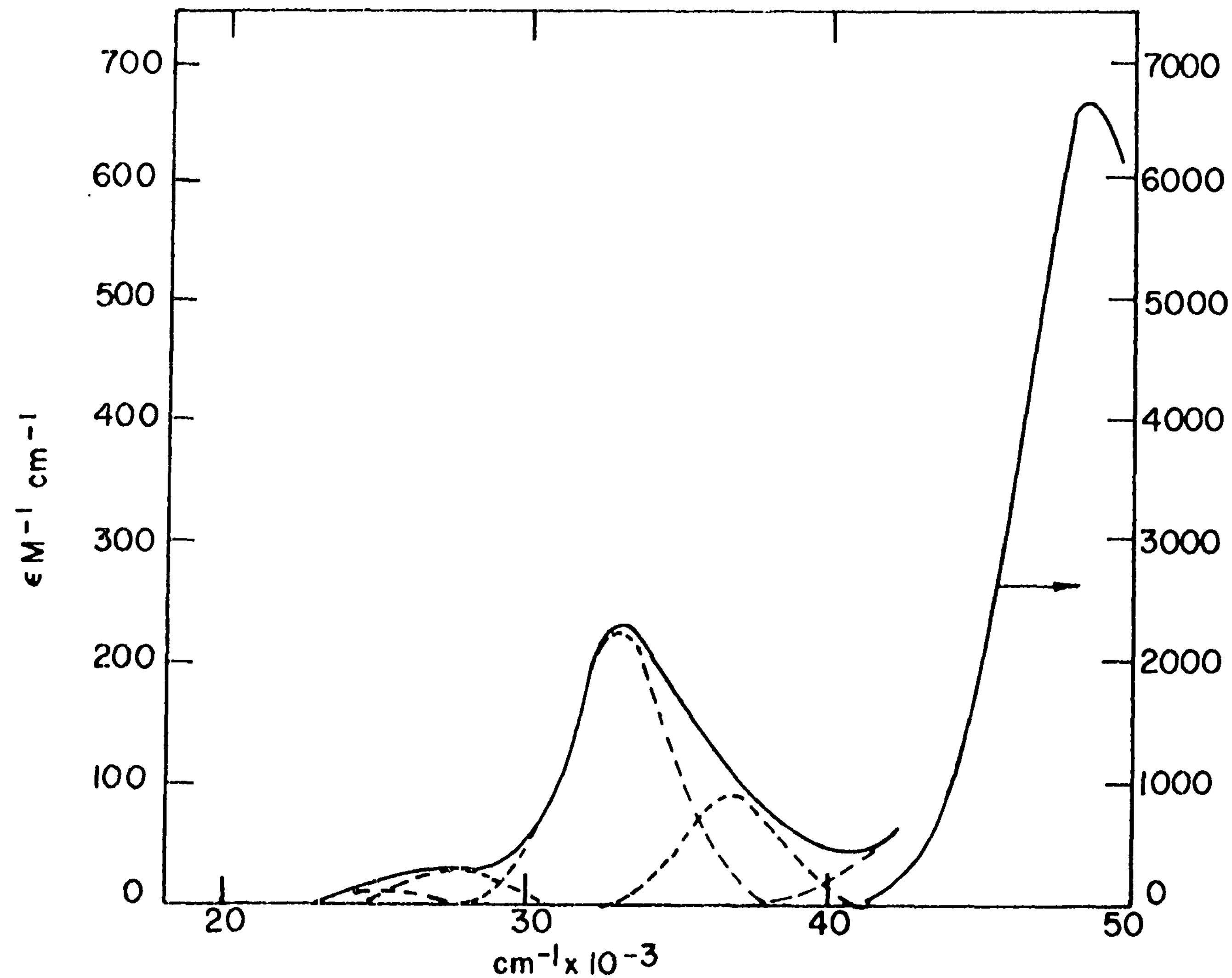

Figure 8. Solution spectrum of $Pt(en)Cl_2$ (solid lines). A Gaussian analysis is indicated by the dashed line

Table 2. Transitions in $Pt(en)Cl_2$ from solution spectrum

Wave number $\bar{\nu}_{max}$ - cm^{-1}	Molar absorbancy ϵ_{max} - $\underline{M}^{-1}$ cm^{-1}	Oscillator strength	Transition assignment C_{2v} symmetry $\leftarrow A_1$	Predicted ligand field polarization in crystal
24,900	12	1.7×10^{-4}	${}^3B_2(d_{\underline{xy}} \leftarrow d_{\underline{x}^2-\underline{y}^2})$	
27,300	31	5.1×10^{-4}	${}^3A_2(d_{\underline{xy}} \leftarrow d_{\underline{yz}})$	
			${}^3B_1(d_{\underline{xy}} \leftarrow d_{\underline{xz}})$	
33,200	226	4.1×10^{-3}	${}^1B_2(d_{\underline{xy}} \leftarrow d_{\underline{x}^2-\underline{y}^2})$	$\underline{x}$ - $\underline{z}$
36,900	94	1.6×10^{-3}	${}^1A_2(d_{\underline{xy}} \leftarrow d_{\underline{yz}})$	Forbidden
			${}^1B_1(d_{\underline{xy}} \leftarrow d_{\underline{xz}})$	$\underline{z}$ - $\underline{c}$
Not observed			${}^1B_2(d_{\underline{xy}} \leftarrow d_{\underline{z}^2})$	$\underline{x}$ - $\underline{a}$
49,200	6700	2.0×10^{-1}	${}^1B_1(d_{\underline{xy}} \leftarrow L\pi\text{-}a_2)$	$\underline{z}$ - $\underline{c}$
			${}^1A_1(d_{\underline{xy}} \leftarrow L\pi\text{-}b_2)$	$\underline{y}$ - $\underline{b}$
			${}^1B_2(d_{\underline{xy}} \leftarrow L\pi\text{-}a_1)$	$\underline{x}$ - $\underline{c}$
			${}^1A_2(d_{\underline{xy}} \leftarrow L\pi\text{-}b_1)$	Forbidden

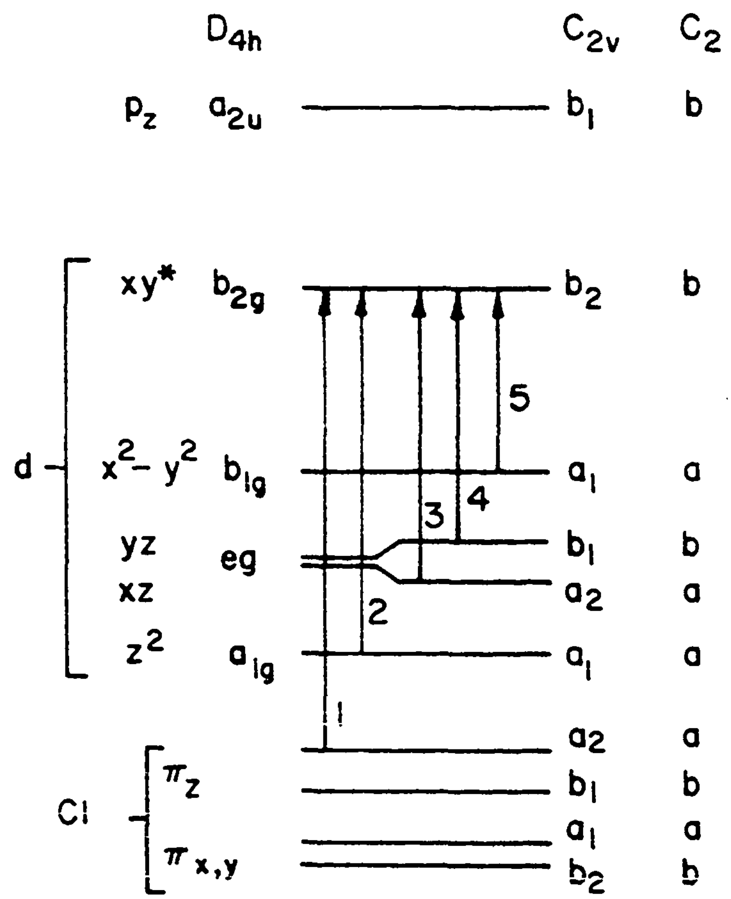

Figure 9. Energy diagram for D_{4h}, C_{2v} and C_2 symmetries. The five possible d-d transitions are indicated

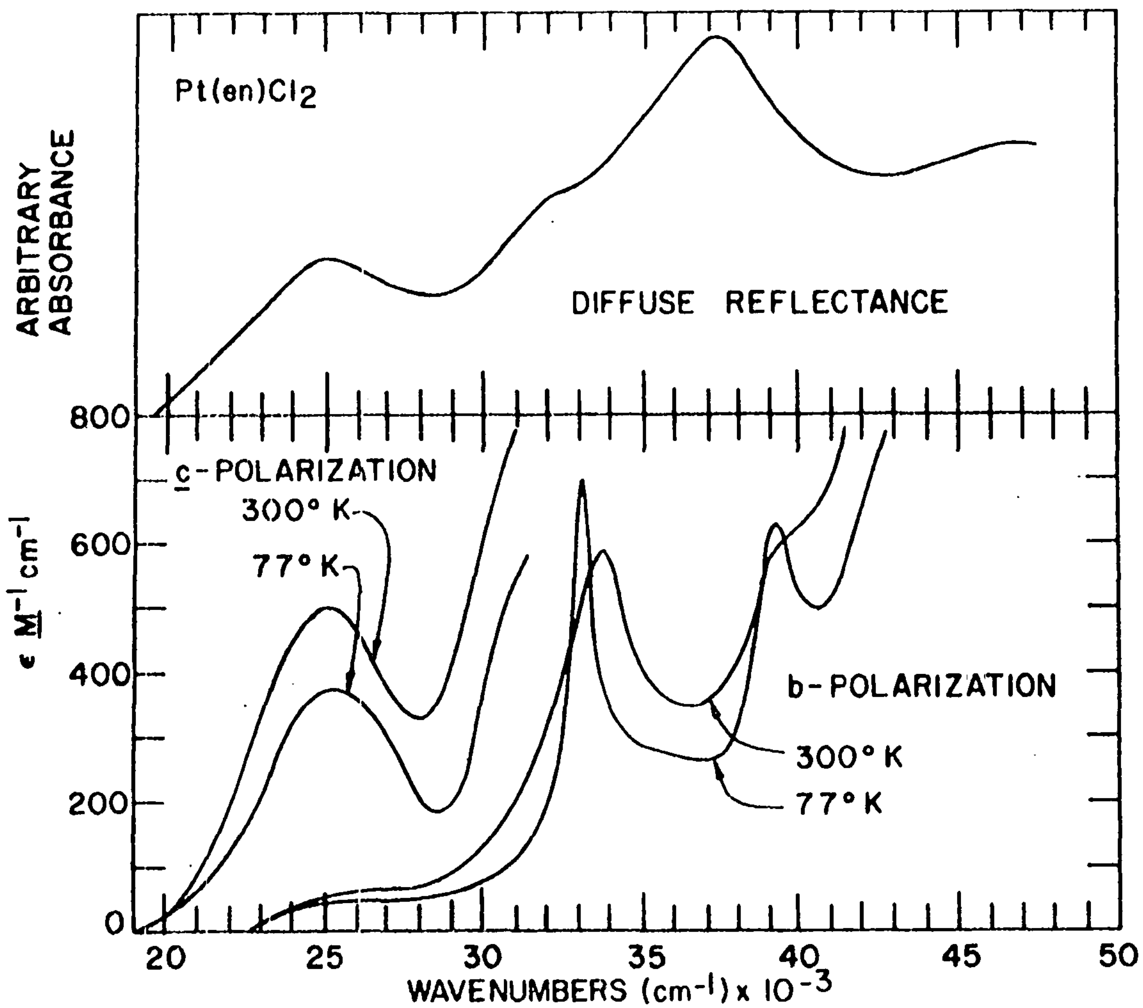

Figure 10. Diffuse reflectance spectrum and single crystal polarized absorption spectra for $Pt(en)Cl_2$

been duplicated with several different crystals. Spectra at liquid helium temperatures were successfully observed for three thicker crystals, however, the b polarized peak at 39,100 cm^{-1} was not recorded for these due to the thickness of the crystals. There was only a small variation between the 77°K and 15°K spectra. For future reference, the locations of the 33,100 cm^{-1} b polarized peak at the various temperatures are tabulated in Table 3.

Table 3. Temperature dependence of 33,100 cm^{-1} b polarized peak. (Energies in cm^{-1})

Exp.#	300 °K	77 °K	15 °K
7	33,670	33,113	32,970
10	33,647	33,090	33,014
14	33,625	33,110	32,900

The orientation of the $Pt(en)Cl_2$ molecule in a crystal with respect to the x, y and z axes was given in Figure 6. Strictly speaking, the symmetry of the $Pt(en)Cl_2$ molecule is C_2 due to the slight puckering of the carbon atoms, however the nitrogens are essentially co-planar with the platinum atom and chloride ligands so that the ligand field constraints should be fairly well represented by C_{2v} symmetry. For completeness, C_2 symmetry will be considered first in assigning the spectral bands, recognizing that, at most, the features due to C_2 symmetry, but absent for C_{2v}, will be of second order effect. Initially, the 'oriented gas' model which was successful with K_2PtCl_4 will be adopted.

In order to see if a transition is dipole allowed, it is necessary to evaluate the transition moment integral:

$$\mu_i = \int \psi^* \underline{r}_i \psi' d\tau \qquad (5)$$

where ψ' is the excited state function, ψ is the ground state function and $\underline{r}_i$ is the dipole moment component for $\underline{i}$ equal to either $\underline{x}$, $\underline{y}$ or $\underline{z}$. By using only group theory, one may solve the above integral for the symmetry representation of ψ', $\underline{r}_i$, and ψ to see if the integral is allowed by symmetry. The integral will be non-zero when the product $(\psi' \underline{r}_i \psi)$ is a basis for the totally symmetric representation for the symmetry group. For C_2 symmetry, the product must have the A symmetry representation to be non-zero. The dipole component $\underline{r}_y$ transforms like $\underline{y}$ or A. The $\underline{r}_x$ and $\underline{r}_z$ components transform like $\underline{x}$ and $\underline{z}$ or B. Referring to Figure 9, transition 2 ($d^*_{xy} \leftarrow d_{z^2}$), would have the transition moment integral

$$\mu_i = \int A^* \underline{r}_i B d\tau. \qquad (6)$$

This integral is non-zero only if r_i has B symmetry or in other words this transition would be $\underline{x}$ and $\underline{z}$ polarized.

Transitions 1, 3 and 5 would also be *x* and *z* polarized, whereas transition 4, $(d^{*}_{xy} \leftarrow d_{yz})$, would be *y* polarized. Transition 1, $(d^{*}_{xy} \leftarrow 3p_z)$, which is a ligand π-to-metal transition should be strongly allowed as would the other charge transfer transitions with non-zero symmetry transition moments, whereas the d-d transitions are allowed only to the extent that the C_2 or C_{2v} ligand field breaks the center of symmetry. It was seen that the d-d transitions in $PtCl_4^{2-}$ ion, where there is a center of symmetry, were very weak, and all resulted from the 'vibronic' mechanism.

The polarized crystal spectra of $Pt(en)Cl_2$ are reported in Figure 10. Table 4 presents the assignments of absorption bands. For *y* polarization, no strong transitions are seen below 42,000 cm^{-1} so it is presumed that the allowed transitions from the Cl π states in *y* polarization occur at higher energies and are not considered here.

There are two weak transitions in *y* polarization in the spectrum at 33,100 and 39,100 cm^{-1} which exhibit some dipole allowed character in that they become narrower and higher upon cooling. The ligand field model for C_2 can only account for one *y* polarized d-d transition, i.e. transition 4. Invoking the higher symmetry of C_{2v} cannot introduce additional transitions and transition 4 would even be forbidden in this

Table 4. Crystal spectra of $Pt(en)Cl_2$

$\tilde{\nu}$ cm^{-1}	Polarization	Osc. strength f 77^{o}	Proposed assignment: excitation
19,000-27,000	c	9×10^{-3}	d ← d, spin-forbidden, vibronic and ligand field
22,000-27,000	b	4×10^{-4}	d ← d, spin-forbidden, vibronic and ligand field
28,000	b	$\sim 5 \times 10^{-4}$	$d_{xy} \leftarrow d_{x^2-y^2}$, spin allowed: vibronic
33,100	b	1.7×10^{-3}	$d_{xy} \leftarrow d_{xz}$: ionized exciton $\beta = \pm 1$. Dipole allowed by overlap
37,500	c	(~0.2?)	$d \leftarrow L\pi - a_2[6p_z \leftarrow 5d_{z^2}]$ Frenkel exciton-dipole allowed
39,100	b	1.3×10^{-3}	$d_{xy} \leftarrow L\pi - a_2$: ionized exciton. $\beta = \pm 1$. Dipole allowed by overlap

case, so that it too falls short on this point.

Although in C_2 symmetry, four transitions would be allowed in z polarization, only two are seen. These bands occur at 25,000 cm^{-1} and 37,500 cm^{-1}. C_{2v} symmetry allows two z polarized transitions, 2 and 5. The 37,500 cm^{-1} band, however, appears to be strongly allowed since it is too intense to be measured with the single crystal spectra that we measured. The location of this peak has been judged from the powder reflectance spectrum shown in Figure 10. The peak falls at an energy where there is a valley in *y* polarization, and specular reflectance data for a single crystal[1] indicated that there was strong *z*-polarized absorption in that region. It is not likely that such an intense transition as this could be a d-d transition. The diffuse reflectance spectrum shows no other absorption even close in intensity to this band up to the limit of 48,000 cm^{-1}. This suggests that the 37,500 cm^{-1} band may be the *z* component of the intense charge transfer bands which appear in solution between 42,500 cm^{-1} and 49,000 cm^{-1} but has shifted by about 12,000 cm^{-1} in the crystal. The 25,000 cm^{-1} band is very broad and does not increase in intensity upon cooling. This is similar to the behavior seen in $PtCl_4^{2-}$ for 'spin-forbidden' bands at about the same energy so that it is not very likely that this is one of the transitions being considered.

Considering all of the above evidence, it becomes clear that something other than a straightforward assignment of the transitions for the solid state must be considered. The general features of the differences in the spectra for crystals

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[1]David Lynch, Ames, Iowa. Spectral data. Private communication. 1970.

compared to solution appear suspiciously similar to those for MGS and related compounds. There is a band in the visible region polarized in the direction of the stacking of molecules which becomes much more intense in the crystal and a very intense $\underline{z}$ polarized band at higher energy which evidently shifts to lower energy in the crystal. Unfortunately, to this date there has been no low temperature data on spectra of related systems reported, so that a comparison with the very striking low temperature behavior of $Pt(en)Cl_2$ cannot be made.

B. Application of Exciton Theory to $Pt(en)Cl_2$

1. The Frenkel exciton

In the previous section, it was shown that the so-called 'oriented gas' model is inadequate for assigning the spectra for $Pt(en)Cl_2$. Therefore, the 'weak coupling' model, as discussed by Craig and Hobbins (35), will be developed. This model treats the interaction energy between molecules as a small perturbation to the intramolecular energies, so that the molecular electronic structure is essentially undisturbed by crystal formation.

The interaction energy operator for the system is

$$V_{h\ell} = -\sum_{fj} Z_f e^2/r_{fj} - \sum_{gi} Z_g e^2/r_{gi} + \sum_{ij} e^2/r_{ij} + \sum_{fg} Z_f Z_g e^2/r_{fg} \dots \qquad (7)$$

where f and g label the nuclei, Z_f and Z_g the nuclear charges, and i and j label the electrons of the h-th and ℓ-th molecules respectively. The energy levels, E, and the wave functions, Φ, are defined by the equation:

$$\left(\sum_{j=1}^{N} H_j + \sum_{\ell > h} V_{h\ell} \right) \Phi = E \Phi \tag{8}$$

where H_j is the single molecule Hamiltonian.

Since the ground state wave function goes to that for N unexcited molecules upon infinite separation, it may be written as the product of antisymmetrized molecular wave functions:

$$\Phi_G = \varphi_1 \varphi_2 \varphi_3 \ldots \varphi_N \ . \tag{9}$$

First order perturbation theory may be used to approximate the ground state energy in accordance with Equation 10:

$$E_G = Nw_G + \sum_h \sum_\ell (\varphi_h \varphi_\ell | V_{h\ell} | \varphi_h \varphi_\ell) \tag{10}$$

where

$$w_G = (\varphi_j | H_j | \varphi_j) \tag{11}$$

The orientation of the $Pt(en)Cl_2$ molecules in the crystal, where the planar molecules stack in a chain and are spaced 3.39Å apart, was discussed in the Introduction and was shown in Figures 6 and 7. A primitive unit cell contains two adjacent molecules stacked in the c direction. Therefore, the localized excitation functions resulting from the transfer of an electron from the ground state to an excited state within one of the two non-equivalent molecules is written:

$$\phi'_{1p} = \varphi_{11}\varphi_{21}\varphi_{12}\varphi_{22}\cdots\varphi'_{1p}\varphi_{2p}\cdots\varphi_{2N/2} \tag{12}$$

$$\phi'_{2p} = \varphi_{11}\varphi_{21}\varphi_{12}\varphi_{22}\cdots\varphi_{1p}\varphi'_{2p}\cdots\varphi_{2N/2} \tag{13}$$

where p numbers the unit cells in the c direction and ϕ'_{1p} and ϕ'_{2p} are functions for excitations to the first and second non-equivalent molecules respectively. Linear combinations of these basis functions yield:

$$\phi'_{p+} = (1/2)^{\frac{1}{2}}(\phi'_{1p} + \phi'_{2p}) \tag{14}$$

and

$$\phi'_{p-} = (1/2)^{\frac{1}{2}}(\phi'_{1p} - \phi'_{2p}). \tag{15}$$

Initially, the motion of excitation in one dimension only, the c direction, will be considered. The crystal wave functions may be written:

$$\Phi_{k+} = (N/2)^{-\frac{1}{2}} \sum_{p}^{N/2} \exp(4\pi ikp/N)\ \phi'_{p+} \tag{16}$$

$$\Phi_{k-} = (N/2)^{-\frac{1}{2}} \sum_{p}^{N/2} \exp(4\pi ikp/N)\ \phi'_{p-} \tag{17}$$

where k is the momentum. These are the solutions to the secular determinant:

$$\left\| (\Phi_{k\pm} | \sum_{j=1} H_j + \sum_{\ell>h} V_{h\ell} | \Phi_{k\pm}) - E(\Phi_{k\pm}, \Phi_{k\pm}) \right\| = 0 \tag{18}$$

In $Pt(en)Cl_2$, the molecular axes of the planar molecules are parallel and the spacings between all adjacent molecules are equal. The only thing that is different about the two 'non-equivalent' molecules is that their permanent dipoles are 180° out of phase. One result of this unique situation is that the non-diagonal terms of the secular determinant are exactly zero since:

$$(\Phi_{k+}, \Phi_{k-}) = 0 \tag{19}$$

$$(\phi'_{1p} | H_p | \phi'_{1p}) = (\phi'_{2p} | H_p | \phi'_{2p}) \tag{20}$$

$$(\phi'_{1p+n} | V_{1p+n,2p} | \phi'_{2p}) = (\phi'_{2p+n} | V_{2p+n,1p} | \phi'_{1p}) \tag{21}$$

where n is an integer.

The diagonal terms can now be solved directly for the energies. The one-electron integrals are:

$$(\Phi_{k+} | \sum_{j=1}^{N} H_j | \Phi_{k+}) = (\Phi_{k-} | \sum_{j=1}^{N} H_j | \Phi_{k-})$$

$$= (2/N)(1/2)\Big(\sum_{p}^{N/2} \exp(-4\pi ikp/N)(\emptyset_{1p}^{'}+\emptyset_{2p}^{'}) \Big| \sum_{j} H_j \Big|$$

$$\sum_{p}^{n/2} \exp(4\pi ikp/N)(\emptyset_{1p}^{'}+\emptyset_{2p}^{'})\Big)$$

$$= (1/N) \sum_{p}^{N/2} \Big[(\emptyset_{1p}^{'} | \sum_{j\neq p}^{N/2} H_j | \emptyset_{1p}^{'}) + (\emptyset_{2p}^{'} | \sum_{j\neq p}^{N/2} H_j | \emptyset_{2p}^{'}) \Big]$$

$$+ (1/N) \sum_{p}^{N/2} \Big[(\emptyset_{1p}^{'} | H_{1p} | \emptyset_{1p}^{'}) + (\emptyset_{2p}^{'} | H_{2p} | \emptyset_{2p}^{'}) \Big] \qquad (22)$$

$$(\Phi_{k+} \sum_{j=1}^{N} H_j \; \Phi_{k+}) = (N-1)w_G + w_p^{'} \qquad (23)$$

This result derives from setting all integrals between $\emptyset_{1p}^{'}$ and $\emptyset_{1p}^{'}$ equal to integrals between $\emptyset_{2p}^{'}$ and $\emptyset_{2p}^{'}$.

The two-electron integrals are:

$$(\Phi_{k+} | \sum_{\ell>h} V_{h\ell} | \Phi_{k+})$$

$$= (2/N)(1/2)\Big(\sum_{p}^{N/2} \exp[-4\pi ik(p+n)/N](\emptyset_{1p+n}^{'}+\emptyset_{2p+n}^{'}) \Big| \sum_{\ell>h} V_{h\ell} \Big|$$

$$\sum_{p}^{N/2} \exp(4\pi ikp/N)(\emptyset_{1p}^{'}+\emptyset_{2p}^{'})\Big)$$

$$= N^{-1} \sum_{p}^{N/2} \Big[\sum_{\substack{n=-N/4 \\ n\neq 0}}^{N/4} \exp(-4\pi ikn/N)(\emptyset'_{1p+n}|V_{1p+n,1p}|\emptyset'_{1p})\Big]$$

$$+ N^{-1} \sum_{p}^{N/2} (\emptyset'_{1p}| \sum_{\ell>h} V_{h\ell}|\emptyset'_{1p})$$

$$+ N^{-1} \sum_{p}^{N/2} \Big[\sum_{\substack{n=-N/4 \\ n\neq 0}}^{N/4} \exp(-4\pi ikn/N)(\emptyset_{2p+n}|V_{2p+n,2p}|\emptyset'_{2p})$$

$$+ N^{-1} \sum_{p}^{N/2} (\emptyset'_{2p}| \sum_{\ell>h} V_{h\ell}|\emptyset'_{2p})$$

$$+ N^{-1} \sum_{p}^{N/2} \Big[\sum_{n=-N/4}^{N/4} \exp(-4\pi ikn/N)(\emptyset'_{1p+n}|V_{1p+n,2p}|\emptyset'_{2p})\Big]$$

$$+ N^{-1} \sum_{p}^{N/2} \Big[\sum_{n=-N/4}^{N/4} \exp(-4\pi ikn/N)(\emptyset'_{2p+n}|V_{2p+n,1p}|\emptyset'_{1p})\Big] \qquad (24)$$

In the last expression for Equation 24, the sum of the first and third terms will be called I and the sum of the fifth and sixth terms will be I'. The sum of the second and fourth terms is:

$$(N-1) \sum_{\ell} (\varphi_h \varphi_\ell | V_{h\ell} | \varphi_h \varphi_\ell) + \sum_{\ell} (\varphi_h \varphi'_\ell | V_{h,\ell} | \varphi_h \varphi'_\ell) \tag{25}$$

The result for Φ_{k-} is the same as for Φ_{k+} except that I' is replaced by -I'.

The energies become bands:

$$E_{\pm} = (N-1)w_G + w'_p + (N-1) \sum_{\ell} (\varphi_h \varphi_\ell | V_{h\ell} | \varphi_h \varphi_\ell)$$

$$+ \sum_{\ell} (\varphi_h \varphi'_\ell | V_{h,\ell} | \varphi_h \varphi'_\ell) + I \pm I' \tag{26}$$

where:

$$I = N^{-1} \sum_{p}^{N/2} \sum_{\substack{n=-N/4 \\ n\neq 0}}^{N/4} \cos(4\pi kn/N) [(\phi'_{1p+n} | V_{1p+n,1p} | \phi'_{1p})$$

$$+ (\phi'_{2p+n} | V_{2p+n,2p} | \phi'_{2p})] \tag{27}$$

and

$$I' = N^{-1} \sum_{p}^{N/2} \sum_{n=-N/4}^{N/4} \cos(4\pi kn/N) [(\phi'_{1p+n} | V_{1p+n,2p} | \phi'_{2p})$$

$$+ (\phi'_{2p+n} | V_{2p+n,1p} | \phi'_{1p})] . \tag{28}$$

The transition energies for excitation to the two excited states may be found by subtracting the ground state energy in Equation 10 from the excited state energies.

$$\Delta E_{\pm} = w'_p - w_G + D + I \pm I' \tag{29}$$

where

$$D = \sum_{\ell>h} (\varphi_h \varphi'_\ell | V_{h\ell} | \varphi_h \varphi'_\ell) - \sum_{\ell>h} (\varphi_h \varphi_\ell | V_{h\ell} | \varphi_h \varphi_\ell) \qquad (30)$$

Since optical transitions from a ground state with k = 0 must go into excited states with k = 0, the transition energy is not a band. For $Pt(en)Cl_2$, I = I', so that the transition energy to the Φ_{k-} state would be shifted from the gas phase transition energy by D. However, the transition moment for a transition to the Φ_{k-} state is exactly equal to zero since

$$(\Phi_G \underline{M} \phi'_{1p}) = (\Phi_G \underline{M} \phi'_{2p}) \qquad (31)$$

where $\underline{M}$ is the transition moment. If $(\Phi_G \underline{M} \phi'_{1p})$ is non-zero, then a transition to Φ_{k+} is allowed, and the transition energy is the same as if the system had been treated assuming equivalent molecules. A diagramatic description of the possible Frenkel exciton, $(d^*_{xy} \leftarrow L\text{-}\pi)$, appears in Figure 11.

In the most general treatment, motion of excitation in all three directions in the crystal would have to be considered.

The resulting transition energy would contain the D and I terms where the summations encompassed all directions. The transition energy would be

$$\Delta E = w'_p - w_G + D + I \qquad (32)$$

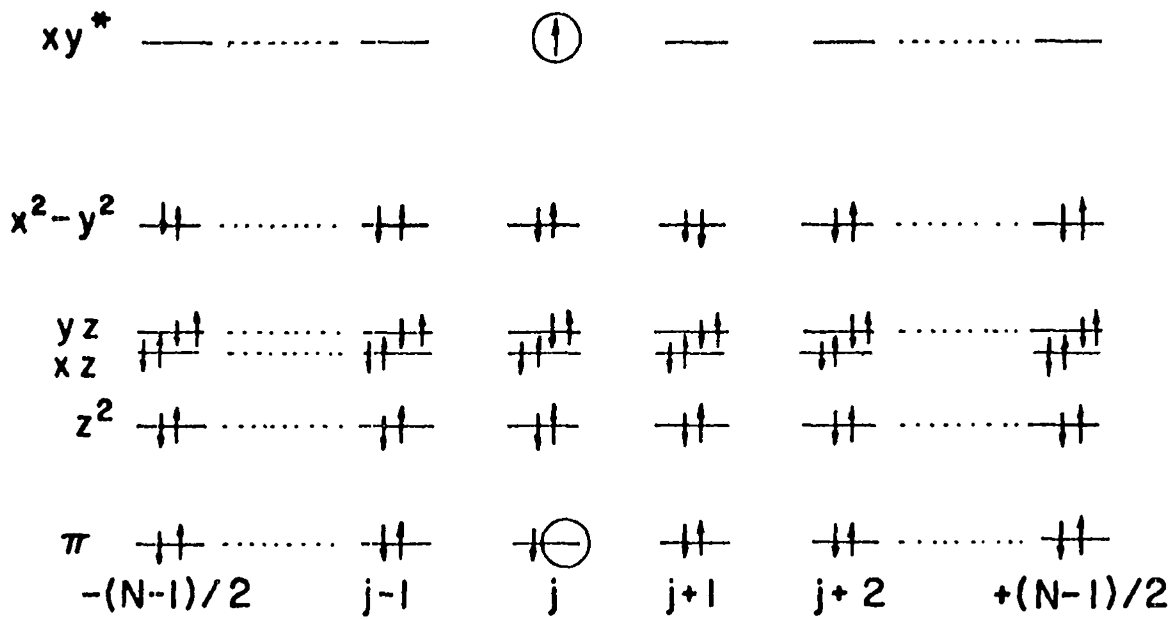

Figure 11. Schematic of Frenkel exciton, $(d^*_{xy})_j \leftarrow (L\pi)_j$

where D and I are defined according to the new definitions encompassing the entire crystal.

The quantity, D, of Equation 32 is just the type of term that Day (20) has postulated to be responsible for the large red shift of an allowed band in MGS. This term could be much more significant in the case of MGS than in $Pt(en)Cl_2$, however, since there are alternating charged ions in MGS causing the nuclear-electron attraction term to be particularly significant. The D term may be qualitatively described as the difference in Van der Waal's energy between the ground and excited states, which should be a negative quantity, but no attempt will be made to calculate its magnitude.

Integrals of the type I, have received considerable attention because they describe the Davydov splittings in crystal spectra. Approximate calculations for this term have involved an expansion of the potential energy operator as a transition multipole-multipole interaction with retention of only the first non-zero term. The dipole term only is retained for dipole allowed transitions with a dipole moment, $e\underline{r}'$. The approximation yields:

$$I_{nm} = e^2 r^{-3} (\underline{x_n x_m} + \underline{y_n y_m} - 2\underline{z_n z_m}) \qquad (33)$$

where x_n is the x component of the transition moment $\underline{r}'$ on the n-th molecule. The other components are defined analogously.

It may be seen from Equation 33 that z polarized bands in $Pt(en)Cl_2$ should be shifted to lower energy and x or y polarized bands to higher energy. This fact is consistent with the observation that the intense z polarized band at 37,500 cm^{-1} in the crystal spectrum has apparently shifted from the region of allowed ($d \leftarrow L\text{-}\pi$) transitions in the solution spectrum of 46,000-53,000 cm^{-1}. The shift due to this term should be proportional to the square of the transition moment and inversely proportional to the cube of the distance between the transition centers.

Approximate calculations were performed for this term from a transition moment of 1Å by means of a computer program which summed interactions from surrounding molecules. The results of those calculations appear in Tables 5 and 6. The calculations considered transition dipoles centered on the platinum atoms, (S=0), and at various displacements from the platinum atom in the plane along a line which passes midway between the two chlorine ligands of a molecule. For a metal to ligand transition, the transition moment should be centered near the mid-point between the platinum atom and center

Table 5. Values of I for a 1Å transition moment calculated with the dipole-dipole approximation for spherical limits. (Values are in units of $10^3 cm^{-1}$)

S	r = 50Å	20Å	12.4Å	8.14Å	3.94Å
0 Å	-11.5	-11.6	-11.4	-11.8	-12.0
.5 Å	-8.9	-8.8	-9.4	-7.9	-9.3
.8 Å	-5.8	-5.8	-6.2	-4.9	-5.8
1.0 Å	-4.4	-4.3	-4.5	-3.4	-4.6
1.25Å	-2.8	-2.7	-2.9	-1.7	-0.0
1.50Å	-1.9	-1.6	-1.9	-.5	-0.0

Table 6. Values of I for a 1Å transition moment calculated with the dipole-dipole approximation for rectangular limits. (Values are in units of $10^3 cm^{-1}$)

S	x = 100Å y = 100Å z = 100Å	120Å 120Å 120Å	140Å 140Å 140Å	40Å 100Å 100Å	100Å 40Å 100Å	100Å 100Å 40Å	14.1Å 100Å 14.1Å
0Å	-11.4	-11.5	-11.4	-12.8	-13.0	-8.5	-9.9
.5Å	-8.7	-8.9	-8.8	-10.2	-10.2	-5.8	-7.1
.8Å	-5.9	-6.2	-6.0	-7.4	-7.4	-2.9	-3.8
1.0Å	-4.3	-4.4	-4.4	-5.7	-5.8	-1.3	-2.3
1.2Å	-3.0	-3.1	-3.0	-4.4	-4.5	-.1	-

of mass of the two chlorine ligands. This point corresponds to a value of about .8Å for S. Typically, for such calculations (32), interactions at long distances are not negligible since the number of neighboring molecules increases with volume at about the same rate as the magnitude of the interaction falls off, i.e. in proportion to r^3. The result of this is that the calculation is dependent upon the shape of the limits, as may be seen in Tables 4 and 5. However, the calculation is consistent for large spheres and cubes, which are the limits commonly used for such calculations (32).

The result for a transition moment of 1Å centered on the platinum atom was -11,500 cm^{-1}. Placing the transition moment at S = .8Å reduced the term to -5,800 cm^{-1}. From this it would appear that the D term in Equations 9 and 10 must also be significant in accounting for the apparent shift of about -12,000 cm^{-1} for the z-polarized charge transfer band.

It is interesting to notice that the same value for I was calculated for the two nearest neighbor interactions, (r = 3.94Å), as for a large sphere. This would seem to indicate that the premise of a one-dimensional interaction is valid insofar as nearest neighbors are concerned.

The shift of the high intensity z polarized band to to lower energy should enhance the intensity of vibronic bands which gain intensity from coupling with it. The broad z polarized absorption in the region of 25,000 cm^{-1} is in fact greatly enhanced in the crystal spectrum, reinforcing the proposal that this band is due to 'spin-forbidden' d-d bands which are at least partially vibronic.

The shift of y or b polarized bands to higher energy due to the I term of Equation 14 results in there being no intense absorption evidenced in the b polarized spectrum below 42,000 cm^{-1}. The shift of such bands may also account for the relatively low intensity of the b polarized absorption in the region of 'spin-forbidden" bands, since such bands would be expected to rely upon allowed bands for borrowed intensity. This shift also makes it possible to observe the relatively weak b polarized bands which strangely appear.

The appearance of the solution maximum at the same energy as the 33,100 cm^{-1} band is surely accidental. As shown in Table 2 the solution maximum was assigned to the $(d^{*}_{xy} \leftarrow d_{x^2-y^2})$ transition, analogous with cis-$Pt(NH_3)_2Cl_2$. This transition should be a polarized and furthermore, symmetry predicts no b polarized dipole allowed d-d transitions due to C_{2v} symmetry. Even crystal perturbation effects cannot produce b polarized absorption to a d-d transition, because the crystal symmetry does not break the local molecular C_{2v} symmetry. Therefore, the very interesting possibility of excitation to ionized exciton states was considered.

2. Ionized excitons

Ideally, if one wished to consider transitions involving ionization, he would first calculate an estimated energy for such a process. Clearly, ionization in solid and other condensed phases should be much more favorable than in the gas, since there are forces which can stabilize the resulting ions. For an ionized exciton transition in a crystal, the process would amount to the promotion of an electron from an orbital of one molecule to an unoccupied orbital in another molecule in the crystal. An example of this type of excitation is shown in Figure 12. Lyons (36) has estimated the energy of such an excitation between neighboring molecules in anthracene and naphthalene by considering the cycle shown in Table 7.

The energies 2.2 and 3.9 eV are about the same as for the Frenkel exciton transitons in these systems. A similar calculation for $Pt(en)Cl_2$ would be very difficult, however, since the ionization potential and electron affinity of the

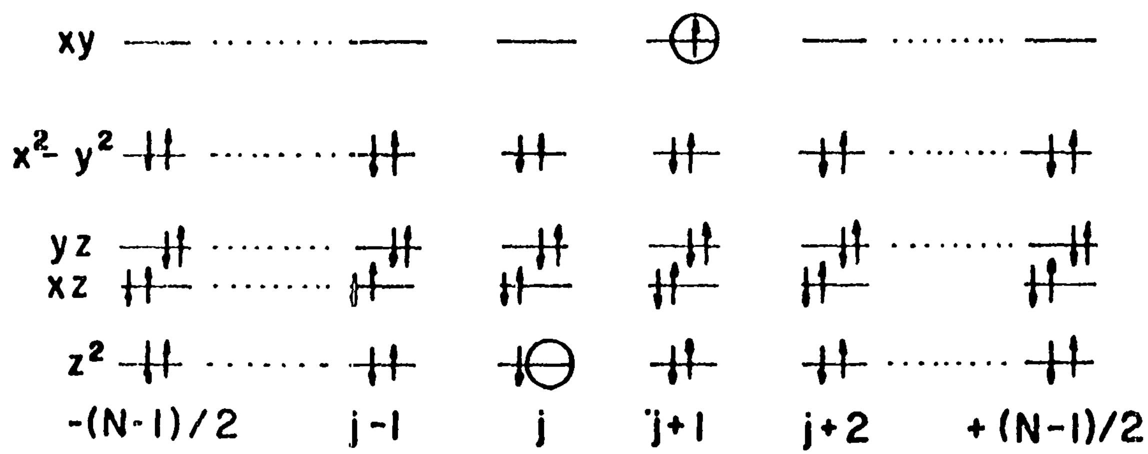

Figure 12. Schematic of ionized exciton, $(d^{*}_{xy})_j \leftarrow (d_{z^2})_{j+1}$

Table 7. Energy of formation of ionized states

	Work needed (eV) Anthracene	Naphthalene
Withdraw 2M from lattice	2x	2y
$M \rightarrow M^+ + e^-$	7.2	8.1
$M + e^- \rightarrow M^-$	-1.4	-0.7
Replace M^+ in lattice	-x	-y
Replace M^- in lattice at a point distant from M^+	-x	-y
Bring M^+ and M^- to neighboring sites	-2.8	-2.9
Polarize crystal surrounding ion pair	-.8	-.6
	2.2	3.9

gaseous molecule are not known and cannot be adequately estimated empirically. Lyons (36) has estimated transition moments for such states in naphthalene and anthracene from overlap integrals of $2p\pi$ molecular orbitals on adjacent molecules. He found that $f \approx 10^{-5}$-10^{-6}, which is about the same intensity as for singlet to triplet transitions. Hemandez and Choi have stated, however, that in organic molecular crystals, the occurrence of ionized exciton transitions of observable intensity would necessarily rely upon coupling with a Frenkel exciton due to small overlap of molecular orbitals on adjacent molecules. Attempts to establish conclusive experimental evidence for the occurrence of ionic excitons in these systems (37,38) have thus far been inconclusive.

The theoretical development of the ionized exciton follows similar logic for that of the Frenkel exciton except that the basis functions will be antisymmetrized initially to allow for the most general considerations. Only interactions along the chain of molecules in the c direction are considered. Excitations will involve only the transfer of an electron from a single filled molecular orbital, u^o, to a single unfilled orbital, u'. Other electrons in a molecule are assigned to a core. The molecules along the chain will be considered equivalent in view of the result obtained for the Frenkel exciton. A diagramatic description of an ionized exciton transition, $(d^*_{xy})_{j+1} \leftarrow (d_{z^2})_j$, is given in Figure 12.

The ground state wave function is considered to be the antisymmetrized product of one-electron molecular wave functions.

$$\Phi^o = (N!)^{-\frac{1}{2}} | u^o_{-(N-1)/2} \cdots u^o_{j-2} u^o_{j-1} u^o_j u^o_{j+1} u^o_{j+2} \cdots u^o_{(N-1)/2} | \quad (34)$$

Excitations from the j-th molecular orbital to an unfilled orbital on another molecule β units away is expressed:

$$\phi_j'(\beta) = (N!)^{-\frac{1}{2}} \left| u^o_{-(N-1)/2} \cdots u^o_{j-2} u^o_{j-1} u'_{j+\beta} u^o_{j+1} u^o_{j+2} \cdots u^o_{(N-1)/2} \right| \tag{35}$$

An excited state wave function for the crystal is then:

$$\Phi_k'(\beta) = N^{-\frac{1}{2}} \sum_j^N \exp(i\underline{kR}_j)\phi_j'(\beta) \tag{36}$$

Applying the selection rule $\underline{k} = 0$ for optical transitions:

$$\Phi_o'(\beta) = N^{-\frac{1}{2}} \sum_j^N \phi_j'(\beta) \tag{37}$$

This function, with $\beta = 0$, is identical to the function that would have resulted for the Frenkel exciton if antisymmetrized one electron functions had been used.

Merrifield (39) found exact solutions for the energies of a one-dimensional model such as considered here for the general exciton problem. The assumptions that he made in order to achieve exact solutions cause the problem to deviate somewhat from reality. However, it is instructive to look at his model and notice the changes necessary for a real crystal.

In order to find the stationary states of the system he considered the matrix elements of the Hamiltonian operator among the various basis functions. The diagonal components were:

$$(\Phi_o'(\beta)|H|\Phi_o'(\beta)) = V(\beta) \tag{38}$$

He made the assumption that

$$V(\beta) = \text{I.E.} - e^2/\epsilon|\beta|R_{j,j+1}) \qquad \beta \neq 0 \tag{39}$$
$$V(0) = -A_o$$

where I.E. is the energy required to ionize a molecule and separate the resulting electron and hole by an infinite distance in the crystal.

The symbol ϵ is the bulk dielectric constant of the crystal and $R_{j,j+1}$ is the distance between adjacent molecules in the chain. A_o is the energy of the molecular excited state. This type of potential function should be quite appropriate for the general exciton problem, which for the most part involves interactions between electrons and holes over relatively long distances in crystals. The interaction is basically electrostatic, corrected for the dielectric field of the medium through which it is communicated. Such an approximation is poorest for interactions between adjacent molecular sites, where a bulk dielectric constant is inappropriate. Unfortunately, it is just this type of interaction which is most important for our application. Compared to the value that would be estimated for this energy by the technique of Lyons (36) which was described earlier, dividing by a bulk dielectric constant would yield a higher energy than one would expect.

Off diagonal terms in Merrifield's treatment were:

$$\epsilon_e = (\phi_j^{'*}(\beta)|H|\phi_j^{'}(\beta \pm 1)) \tag{40}$$

$$\epsilon_h = (\phi_j^{'}(\beta)|H|\phi_{j\pm 1}^{'}(\beta \mp 1) \tag{41}$$

where ϵ_e and ϵ_h corresponded to the transfer of an electron and a hole between nearest neighbor molecules.

The assumption that ϵ_e and ϵ_h are independent of β is equivalent to setting them equal to one electron integrals involving overlap:

$$\epsilon_e = (u_j^{'}|V_{j,j\pm 1}|u_{j\pm 1}^{'}) \tag{42}$$

$$\epsilon_h = -(u_j^{o}|V_{j,j\pm 1}|u_{j\pm 1}^{o}) \tag{43}$$

This means that two electron interactions between electrons on adjacent molecules, such as $(e^2/R_{j,j+1})$, are neglected. This approximation should not be too bad for cases where the overlap is small.

The matrix elements for the system then simply become:

$$(\Phi_o^{'}(\beta)|H|\Phi_o^{'}(\beta)) = V(\beta) \quad \text{for } \beta \neq 0 \tag{44}$$

and

$$(\Phi_o^{'}(\beta)|H|\Phi_o^{'}(\beta \pm 1) = \epsilon_e + \epsilon_h. \tag{45}$$

For a given value of $|\beta|$, there are two degenerate basis functions, $\Phi_o'(\beta)$ and $\Phi_o'(-\beta)$. From these, two non-interacting exciton functions may be derived:

$$\psi_+(\beta) = (1/2)^{\frac{1}{2}}(\Phi_o'(\beta) + \Phi_o'(-\beta)) \tag{46}$$

$$\psi_-(\beta) = (1/2)^{\frac{1}{2}}(\Phi_o'(\beta) - \Phi_o'(-\beta)) \tag{47}$$

An ionized exciton then would correspond to a transition from the ground state to one of the states resulting from $\psi_+'(\beta)$ or $\psi_-'(\beta)$.

The ψ_+ state would transform identically with the corresponding Frenkel exciton, and so would mix with it to form two new states analogous with molecular orbital theory. The resulting energy diagram is shown in Figure 13.

Although Merrifield considered only one type of filled orbital and one type of unoccupied orbital in his model, in a real crystal there would be a set of states as in Figure 13 for each combination of filled and unfilled orbitals. The intensity of possible transitions between these states would depend on the conventional type transition moment integral.

$$\mu = (\Phi^o| \sum_i r_i|\psi') \tag{48}$$

where ψ' is the excited state wave function and $\underline{r}_i$ is summed

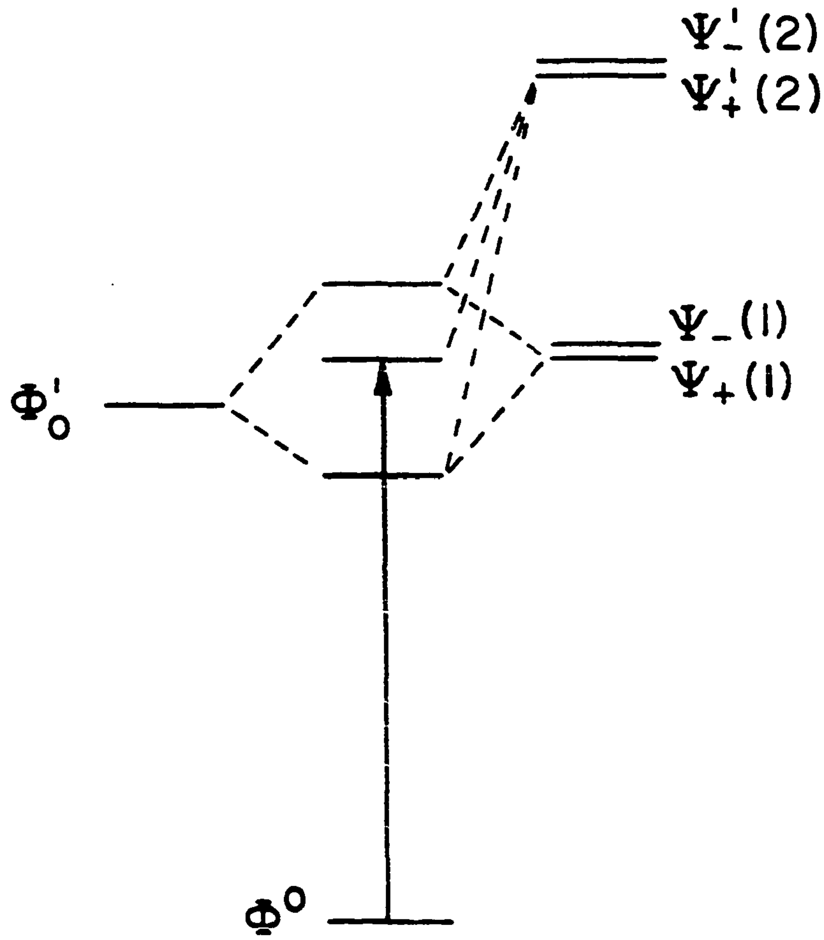

Figure 13. Energy diagram showing an ionized exciton transition $\psi_-(1) \leftarrow \Phi^0$. The interaction between the Frenkel exciton state $\bar{\Phi}_0'$ and $\psi_+(1)$ is also depicted

over the chain of molecules. All transitions to $\psi_+(\beta)$ states are forbidden just as the Frenkel states were.

Transitions to $\psi_-(\beta)$ states will be possible when the transition moment given in Equation 49 is non-zero.

$$(\Phi^0| \sum_i^N \underline{r}_i |\psi_-'(\beta)) = (2N)^{-\frac{1}{2}}[\sum_j (u_j^0|\underline{r}|u_{j+1}')$$

$$-(u_j^0 \ \underline{r} \ u_{j-1}') = (N/2)^{\frac{1}{2}}[\underline{r}_{j,j+1}' - \underline{r}_{j,j-1}'] \qquad (49)$$

This will be non-zero if

$$\underline{r}_{j,j+1}' = -r_{j,j-1}' \neq 0. \qquad (50)$$

A convenient way to determine if Equation 50 is satisfied is to examine the sketches in Figure 14. The square in each sketch represents a plane midway between adjacent molecules. The outline of the orbitals u_j^0 and u_{j+1}' on that plane are sketched in solid and dashed lines respectively. In each sector, in parentheses, are shown the signs of the $\underline{x}$, $\underline{y}$ and $\underline{z}$ components of $\underline{r}_{j,j+1}'$. For $(d_{xy}^*)_{j+1} \leftarrow (d_{z^2})_j$, the positive values of $\underline{x}$, $\underline{y}$ and $\underline{z}$ components are exactly cancelled by negative values in other sectors. Consequently the transition moment is zero and the ionic exciton transition is forbidden. The same result is obtained for the $(d_{xy}^*)_{j+1} \leftarrow (d_{x^2-y^2})_j$

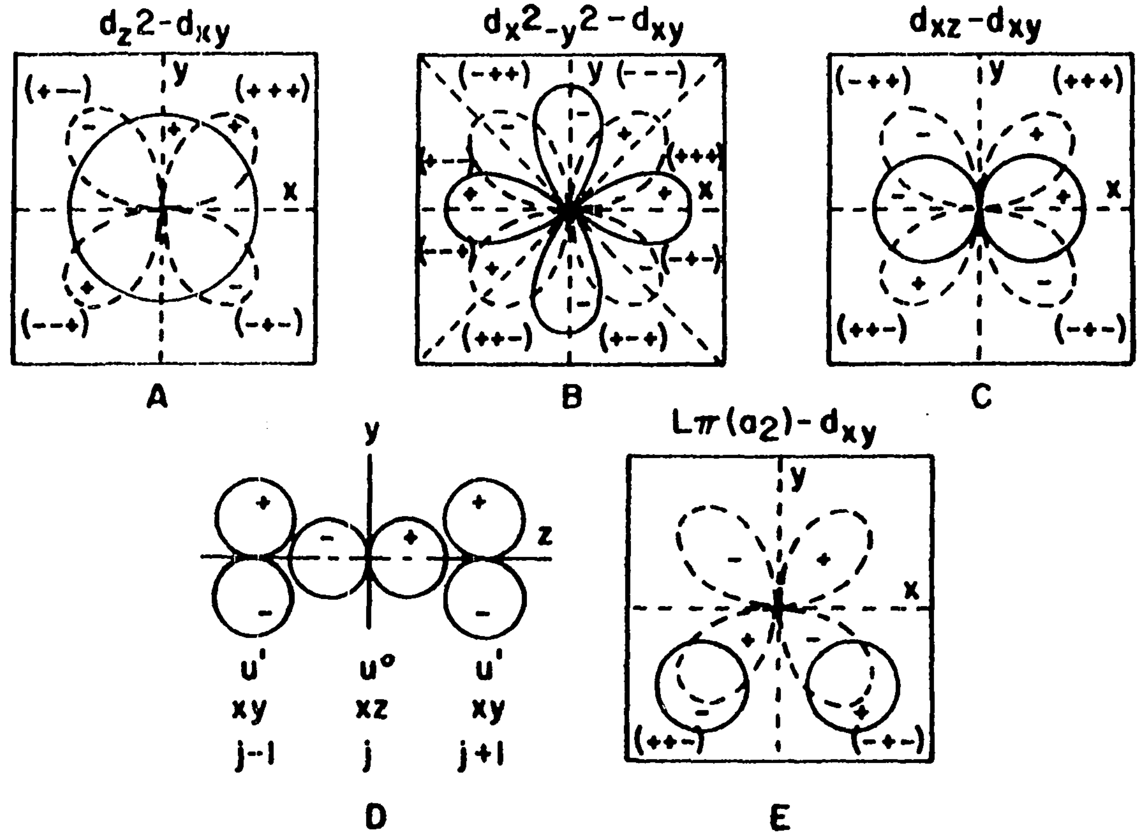

Figure 14. Symmetry properties of the ionic excitation transfer moments $\underline{r}^{1}_{j,j+1}$ to $(d^{*}_{xy})_{j+1}$ from orbitals on the jth molecule

transition. However, for the transition, $(d^*_{xy})_{j+1} \leftarrow (d_{xz})_j$, the $\underline{y}$ component, $\underline{y}'_{j,j+1}$, of the transition moment is + in every sector and will therefore be non-zero. With the aid of Figure 14D it is readily seen that $y'_{j,j+1} = -y'_{j,j-1}$ so that the transition moment is non-zero and the transition is allowed in $\underline{y}$ polarization. The transition, $(d^*_{xy})_{j+1} \leftarrow (d_{yz})_j$, will also be allowed for $\underline{x}$ polarization.

The actual intensity of the $\underline{y}$ polarized ionized exciton transition can be estimated by an approximate numerical calculation of the transition moment integral $\underline{y}'_{j,j+1}$. This was done using the approximate wavefunctions of Cotton and Harris (15) for platinum. A value of .107Å was calculated which corresponds to an oscillator strength of 8.6×10^{-3}. This result is to be compared with the observed oscillator strength for the $\underline{b}$ polarized band at 33,100 cm^{-1} of 1.7×10^{-3}. Calculated transition moments are typically too high (32), as in this case. The present calculation is quite crude since the antibonding d^*_{xy} orbital was treated as being pure d_{xy} and the wave functions were single nodeless slater-type d orbitals for which the shielding parameter was determined by fitting overlaps of self-consistent field wave functions between platinum and chlorine in $PtCl_4{}^{2-}$. The bond distance between chlorine and platinum in $PtCl_4^{2-}$ is 2.3Å, whereas our application is for a separation of 3.39Å so that the calculated transition moment may be trusted only qualitatively.

The 33,100 cm^{-1} band has been assigned to the $(d^*_{xy})_j \leftarrow (d_{xz})_{j+1}$ transition since this transition must be the lowest energy ionized exciton with a $\underline{y}$ moment. The molecular transition $d^*_{xy} \leftarrow d_{xz}$ was assigned to the 36,900 cm^{-1} band in solution. There are no other ionized transitions to $\beta = 1$ states among the d orbitals which would have a non-zero $\underline{y}$ transition moment. Transitions to states with β greater than one would have a very small transition moment. Therefore, the possibility of a $(d^*_{xy})_j \leftarrow (L)_{j+1}$ ionized exciton transition was considered for the 39,100 cm^{-1} $\underline{y}$ polarized band. Considering again the transition moment, $\underline{y}_{j,j+1}$, for such transitions, only one is found to satisfy the conditions of Equation 50, as may be determined with the aid of Figure 14E. That transition is $(d^*_{xy})_j \leftarrow (L\text{-}\pi(a_2))$ involving the non-bonding π molecular orbital on the chlorine atoms. Again using the wavefunctions of Cotton and Harris, an approximate numerical integration was performed to evaluate the transition moment for this transition. For the calculation, a pure p_z orbital on one chlorine atom was considered with the d^*_{xy} orbital of platinum.

The result was f = .13, which is quite large and probably not very reliable. For a more accurate calculation, one would have to use wavefunctions which were derived for overlaps at such long distances. The observed intensity of the 39,100 cm^{-1} band is about 1.3×10^{-3}.

Irregardless of difficulties with intensity calculations using empirical wave functions, this 39,100 cm^{-1} band is tentatively assigned to the $(d^{*}_{xy})_{j+1} \leftarrow (L\text{-}\pi(a_2))_j$ transition. It is interesting that the z polarized exciton at 37,500 cm^{-1} is also based on these same orbitals on one molecule. In this case the dipole-dipole interactions have carried it to a lower energy than the corresponding ionized exciton.

One possible alternative description of the observed b polarized bands might be as singlet-to-triplet charge transfer bands. Although these transitions are not seen in the solution spectrum, the shift of the strongly allowed x and y polarized bands to higher energy might allow them to be observed. However, such bands are not witnessed in crystals of K_2PtCl_4, which leads one to be skeptical that they appear for $Pt(en)Cl_2$, especially at as low an energy as 33,100 cm^{-1}. This region has been well characterized for K_2PtCl_4 (3,8) with no evidence of any bands with dipole allowed character, as may be seen in Figure 3.

C. Application of Band Theory to $Pt(en)Cl_2$

There is another point of view that can be used to describe interactions in crystals. This approach would describe the formation of bands due to the overlap of orbitals of adjacent molecules. Consider again a one dimensional chain of N $Pt(en)Cl_2$ molecules stacked along a z axis spaced 3.39Å apart. Significant overlap should result between the $5d_{z^2}$ orbitals on adjacent molecules so that a band is formed

$$(\psi_{z^2})_n = (1/N)^{\frac{1}{2}} \sum_{-\frac{1}{2}(N-1)}^{\frac{1}{2}(N-1)} \exp(i\gamma_n j)(d_{z^2})_j \qquad (51)$$

where j is the index of the molecules of the chain, n labels the particular state of which there are N, and

$$\gamma_n = 2\pi n/N \qquad (52)$$

All integrals between functions with different values of n will have the factor

$$\sum_{-\frac{1}{2}(N-1)}^{\frac{1}{2}(N-1)} \exp[(n-n')(2\pi ij)/N]$$

where n and n' label the states. This sum equals N if $n = n'$. It may be shown to be exactly equal to zero if

$n \neq n'$. Therefore, the non-zero integrals must require that $\gamma_n = \gamma_{n'}$ and the n subscripts will be deleted in what follows for convenience.

The secular determinant for the d_{z^2} system may be written:

$$\|(\psi_{z^2}|H|\psi_{z^2}) - E(\psi_{z^2}\psi_{z^2})\| = 0 \tag{53}$$

which becomes:

$$\alpha_{dd} + e^{i\gamma}\beta_{dd} + e^{-i\gamma}\beta_{dd} - E_d = 0 \tag{54}$$

where

$$\alpha_{dd} = ((d_{z^2})_j|H|(d_{z^2})_j) \tag{55}$$

and

$$\beta_{dd} = ((d_{z^2})_j|H|(d_{z^2})_{j+1}). \tag{56}$$

Using the relationships:

$$e^{i\gamma} = \cos\gamma + i\sin\gamma \tag{57}$$

$$e^{-i\gamma} = \cos\gamma - i\sin\gamma \tag{58}$$

$$e^{ir} + e^{-i\gamma} = 2\cos\gamma \tag{59}$$

Equation 54 may be solved for E_d:

$$E_d = \alpha_{dd} + \beta_{dd}(2\cos\gamma) \tag{60}$$

In an analogous manner, a band of states due to the $6p_z$ orbitals may be described:

$$\psi_p = (1/N)^{\frac{1}{2}} \sum_{-\frac{1}{2}(N-1)}^{\frac{1}{2}(N-1)} \exp(i\gamma j)(p_z)_j \tag{61}$$

$$E_p = \alpha_{pp} + \beta_{pp}(2\cos\gamma). \tag{62}$$

The d_{z^2} and p_z bands may interact to yield the secular determinant

$$\begin{vmatrix} \alpha_{dd} + 2\beta_{dd}\cos\gamma - E & -2i\beta_{dp}\sin\gamma \\ 2i\beta_{dp}\sin\gamma & \alpha_{pp} + 2\beta_{pp}\cos\gamma - E \end{vmatrix} = 0 \tag{63}$$

where

$$\beta_{dp} = ((d_{z^2})_j |H| (p_z)_{j+1}) \tag{64}$$

$$\beta_{pd} = ((p_z)_j |H| (d_{z^2})_{j+1} \tag{65}$$

$$\beta_{dp} = -\beta_{pd}\ . \tag{66}$$

Orthonormality of the orbitals analogous with Huckel assumptions has been adopted. Solution of the secular equation yields:

$$(a-E)(b-E) - c^2 = 0 \tag{67}$$

where

$$a = \alpha_{dd} + 2\beta_{dd}\cos\gamma \tag{68}$$

$$b = \alpha_{pp} + 2\beta_{pp}\cos\gamma \tag{69}$$

$$c = 2\beta_{dp}\sin\gamma \tag{70}$$

Solving Equation 67 by the quadratic formula gives:

$$E = \tfrac{1}{2}(a+b) \pm \tfrac{1}{2}[(a+b)^2 - 4ab + 4c^2]^{\frac{1}{2}} \tag{71}$$

Manipulation of the equation yields:

$$E = \tfrac{1}{2}(a+b) \pm \tfrac{1}{2}(a-b)[1 + 4c^2/(a-b)^2]^{\frac{1}{2}} \tag{72}$$

Assuming that β_{dp}, β_{dd} and β_{pp} are all integrals of comparable absolute value and very much smaller than the difference $(\alpha_{dd} - \alpha_{pp})$, the quantity within brackets becomes approximately

$$[1 + 4x]^{\frac{1}{2}}$$

where x is a number greater than zero but smaller than one. This means that the binomial expansion may be applied to Equation 72 retaining only the first terms to yield:

$$E = \tfrac{1}{2}(a+b) \pm \tfrac{1}{2}(a-b)[1 + \tfrac{1}{2}(4c^2)(a-b)^2] \tag{73}$$

The two solutions are:

$$E_+ = a + c^2/(a-b) \tag{74}$$

$$E_- = b - c^2/(a-b) \tag{75}$$

These solutions may be identified as

$$E_d = \alpha_{dd} + 2\beta_{dd}\cos\gamma - (2\beta_{dp}\sin\gamma)^2/(\alpha_{pp}-\alpha_{dd}) \tag{76}$$

$$E_p = \alpha_{pp} + 2\beta_{pp}\cos\gamma + (2\beta_{dp}\sin\gamma)^2/(\alpha_{pp}-\alpha_{dd}) \tag{77}$$

The terms α_{dd} and α_{pp} are the energies of non-interacting d and p orbitals. The second term in Equations 76 and 77 provides the band width since γ spans the limits $-\pi$ to π. The third term of these equations provides a lowering in energy for the d_{z^2} band and a rise in energy for the p_z band, recognizing that α_{pp} is greater than α_{dd}. The lowering in energy for the d_{z^2} band, which is filled with electrons, corresponds to a bonding type interaction and increased stabilization.

Although the band theory description does provide a qualitative rationalization for increased stabilization with a closer Pt-Pt spacing, it does not provide any real insight into the observed absorption spectrum. The description in terms of excitons should be more realistic since the concept of bound states is retained. The band theory tends to delocalize the electrons throughout the crystal, which in this case is not really appropriate.

IV. SUMMARY

A summary of the assignments in the crystal spectra based on the exciton theory with the inclusion of ionic exciton states is presented in Table 4. The selection rules and energy predictions from this theory present a coherent rationalization of the observed spectrum. The orientation of the molecules in this crystal have provided a very favorable experimental model for obtaining information about molecular polarization and the demonstration of transition selection rules.

The possibility of measurably intense ionic excitons for this system may represent a very significant development for molecular spectroscopy. Further study in related systems should help to test these assignment proposals. The $Pt(en)Br_2$ system appears to be very promising. The author has carried out a detailed X-ray crystal structure determination for this compound. The structure is isostructural with $Pt(en)Cl_2$. The space group is $C222_1$ with a:b:c = 12.89:8.27:6.99Å. The polarized crystal spectra for the compound are currently being characterized by another worker in this laboratory.

Another related compound of particular interest is MGS. It would be interesting to evaluate the temperature dependence of the band polarized normal to the chains in MGS at 24,900 cm^{-1} to determine if its temperature dependence resembles that of the 33,100 cm^{-1} band in $Pt(en)Cl_2$. Other systems that may very well exhibit similar spectral properties to $Pt(en)Cl_2$ are a number of tetracyano-platinate(II) salts with short Pt-Pt specings, which have been noted by Krogman (40) as having anomalous colors. However, comprehensive spectral studies require the preparation and manipulation of exceedingly thin and fragile crystals. Future work is likely to be limited by the availability of crystals with suitable form and structure for meaningful study.

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VII. APPENDIX A: COMPUTER PROGRAM FOR CALCULATING DIPOLE-DIPOLE INTERACTIONS

The Fortran computer program called 'DIP' which was used to calculate the magnitude of the transition dipole-dipole interactions in a crystal of $Pt(en)Cl_2$ is provided on the following pages. The program as given performs the calculation with cubic or rectangular limits provided in the input data. The values of the displacement of the transition moment from the platinum atom toward the center of mass of the chlorine ligands is also part of the input data. With a slight modification, the program will use spherical limits.

The output of the program provides the value of DIPTOT, which when multiplied by 1.16×10^5 provides the magnitude of the interaction of 1Å *z* transition moment in units of cm^{-1}.

The program follows:

```
C        ***********************  DIP  **********************
      DIMENSION XMAX(2),YMAX(2),ZMAX(2),D(5)
      READ(1,4) XMAX(1),XMAX(2),YMAX(1),YMAX(2),ZMAX(1),ZMAX(2),
     1          D(1),D(2),D(3),D(4),D(5)
    4 FORMAT(11F5.2)
      WRITE(3,6)  XMAX(1),XMAX(2),YMAX(1),YMAX(2),ZMAX(1),ZMAX(2),
     1          D(1),D(2),D(3),D(4),D(5)
    6 FORMAT('1','XMAX(1)=',F5.2,'XMAX(2)=',F5.2,'YMAX(1)=',F5.2,
     1   'YMAX(2)=',F5.2,'ZMAX(1)=',F5.2,'ZMAX(2)=',F5.2,/,'D(1)=',F5.2,
     1   'D(2)=',F5.2,'D(3)=',F5.2,'D(4)=',F5.2,'D(5)=',F5.2)
      A = 6.2185
      B = 4.06
      C = 3.388
      DO 300 M=1,5
      DE=D(M)
      DO 200 N=1,2
      NPTS = 0
      DIPTOT=0
C
      DO 100 NZ1=1,21
      NZ = NZ1 - 1
      DO 99 NY1=1,18
      NY = NY1 - 1
      DO 98 NX1=1,12
      NX = NX1 - 1
      MULT = 8
      NXPLNY = NX + NY
      NDIV2 = NXPLNY/2
      AXPLNY = NXPLNY
      ANDIV2 = AXPLNY/2.0
      DIF = ANDIV2 - NDIV2
      IF(DIF.GT..4) GO TO 98
      IF(NX.NE.0) GO TO 10
      MULT = MULT/2
   10 IF(NY.NE.0) GO TO 12
       MULT = MULT/2
   12 IF(NZ.NE.0) GO TO 14
```

```
      MULT = MULT/2
   14 CONTINUE
      X = NX*A
      Y = NY*B
      Z = NZ*C
      XS = X**2
      YMINY=(Y+((-1)**(NZ))*D(M)-D(M))
      YMINYS=YMINY**2
      ZS = Z**2
      R = SQRT(XS+YMINYS+ZS)
      IF(X.GT.XMAX(N)) GO TO 99
      IF(YMINY.GT.YMAX(N)) GO TO 100
      IF(Z.GT.ZMAX(N)) GO TO 101
      IF(R.LT..1) GO TO 98
      ZR = Z/R
      THETA = ARCOS(ZR)
      COSSQ = (COS(THETA))**2
      SINSQ = 1 - COSSQ
      DIP = (SINSQ - 2*COSSQ)/R**3
      DIPTOT = DIPTOT + DIP*MULT
      NPTS = NPTS + MULT
      IF(NY.GT.4) GO TO 16
      IF(NZ.GT.2) GO TO 16
      IF(NX.GT.5) GO TO 16
      WRITE(3,15) N,XS,YMINYS,ZS,R,ZR,THETA,COSSQ,DIP,MULT,DIPTOT
   15 FORMAT(' ','N=',I2,'XS=',F7.3,'YMINYS=',F7.3,'ZS=',F7.3,
     1 'R=',F7.3,'ZR=',F7.3,'THETA=',F7.3,'COSSQ=',F7.3,'DIP=',F7.3,
     1'MULT=',I3,'DIPTOT=',F7.3)
   16 CONTINUE
   98 CONTINUE
   99 CONTINUE
  100 CONTINUE
  101 CONTINUE
      WRITE(3,150) N,NX,NY,NZ,NPTS,DE,DIPTOT
  150 FORMAT(' ','N=',I4,'NX=',I4,'NY=',I4,'NZ=',I4,'NPTS=',I7,
     1 'D=',F7.3,'DIPTOT=',F7.3)
      WRITE(3,151)
```

```
151 FORMAT('1')
200 CONTINUE
300 CONTINUE
    STOP
    END
```

VIII. APPENDIX B: COMPUTER PROGRAMS FOR CALCULATING IONIZED EXCITON TRANSITION MOMENTS

The Fortran computer program called 'IN1' which was used to calculate the y transition moment for the ionized exciton transition, $(d^*_{xy})_{j+1} \leftarrow (d_{xz})_j$, and the program called 'INZ' which was used to calculate the y transition moment for the ionized exciton transition $(d^*_{xy})_{j+1} \leftarrow (L\text{-}\pi)_j$, are provided on the following pages. The wave functions in the program were adopted from the work of Cotton and Harris (15). The transition moments in 'IN1' are calculated for three intermolecular distances: 3.24Å, 3.39Å, and 3.495Å. These correspond to the spacings between molecules in the chains for MGS, $Pt(en)Cl_2$, and $Pt(en)Br_2$ respectively. The program 'IN2' is specific for $Pt(en)Cl_2$ only. There is no input data required for either of the programs.

The programs follow:

```
C           *******************    IN1    **********************
      DIMENSION AB(3)
      AB(1) = 3.24
      AB(2) = 3.39
      AB(3) = 3.495
      PI = 3.414
      DO 300 J=1,3
      SUMF = 0.0
      DO 200 IR=1,100
      DO 210 IZ=1,100
      A = AB(J)
      R = IR*(.04)
      Z = -A/2.0 + (2*A)*IZ*(0.01)
      R1=SQRT(Z**2 + R**2)
      R2 = SQRT((A-Z)**2 +R**2)
      FDXY = R2**4*EXP(-R2*3.15)*R**2/R2**2
      FDXZ = Z*(R**2)*(EXP(-3.15*R1))*(2-3.15*R1)
      FOFRZ = FDXY*R*FDXZ
      SUMF = SUMF + FOFRZ
  210 CONTINUE
  200 CONTINUE
      ANORXY = 13.2*SQRT(15./(4*PI))
      ANORXZ = 13.2*SQRT(15./(4*PI))
      ANGNOR = ANORXY * ANORXZ*PI/4.0
      SUMF = SUMF*A*.02*.04*ANGNOR
  215 WRITE(3,220) AB(J), SUMF
  220 FORMAT('1','A=',F7.4,'INTEGRAL=',E14.7)
  300 CONTINUE
      STOP
      END
```

```
C          *************************    IN2    ************************
C          FPZ TO FDXY IONIZED EXCITON
      DIMENSION AB(3),XO(3),YO(3),ZO(3)
      NX = 50
      NY = 50
      NZ = 100
      AB(1) = 3.39
      XO(1) =-.137*12.437
      YO(1) = .197*8.12
      ZO(1) =-3.39
      PI = 3.414
      DO 300 J=1,1
      A = AB(J)
      SUMF = 0.0
      DO 210 IZ=1,NZ
      DO 205 IY=1,NY
      DO 200 IX=1,NX
      X1 =-(1./NX)*4.*IX
      Y1 = (1./NY)*4.*IY
      Z1 = .50*A-(1./NZ)*2.00*A*IZ
      X2 = X1 - XO(J)
      Y2 = Y1 - YO(J)
      Z2 = Z1 - ZO(J)
      R1 = SQRT(X1**2+Y1**2+Z1**2)
      R2 = SQRT(X2**2+Y2**2+Z2**2)
      FDXY = R1**2*X1*Y1*EXP(-3.15*R1)
      FPZ = R2*Z2*EXP(-1.85*R2)
      FOFXYZ = FDXY*Y1*FPZ
      SUMF = SUMF + FOFXYZ
  200 CONTINUE
  205 CONTINUE
  210 CONTINUE
      ANORXY = 13.2*SQRT(15./(4*PI))
      ANORZ = 3.63*SQRT(3./4*PI)
      ANOR = ANORXY*ANORZ
      AINTEG = SUMF*ANOR*(1./NX)*(1./NY)*(1./NZ)*4.*4.*2.00*A
      WRITE(3,218)
```

```
218 FORMAT('1','FPZ TO FDXY IONIZED EXCITON')
    WRITE(3,220) A,AINTEG
220 FORMAT(' ','A=',F7.4,'INTEGRAL=',E14.7)
300 CONTINUE
    STOP
    END
```

IX. APPENDIX C. COMPUTER PROGRAM FOR PLOTTING SPECTRA

A listing of the Fortran computer program, 'IPLOT SPECTRA', is provided on the following pages. The program reads and interprets the output from a Cary 14 recording spectrophotometer which had been adapted to provide digital card punch output through a Datex interface and IBM 29 card punch.

In the program the data are first prepared for plotting and then plotted with the aid of a simplotter routine available with the IBM 360-65 computer at Iowa State University, Ames, Iowa. Among the operations in the program are: optional automatic or input controlled adjustment of absorbances values of fragmented spectra, automatic baseline subtraction, automatic evaluation of molar absorbancy and wavenumbers from absorbance-wavelength data, optional logarithmic plotting facility, output in the form of tables and a wide range of input controlled plotting options.

Most of the input data is optional and if not specified, it will be chosen by the program to provide a convenient plot. Most of the options made available through the simplotter routine are retained as options for input for the program.

The input instructions and explanation of these instructions follows in the next several pages. After these, the listing of the program is provided.

INPUT DATA FOR 'IPLOT SPECTRA'

A 1 card (I2,2I8,2I2)

NSETS	MINWAV	MAXWAV	NDATCK	MAT
1-2	3-10	11-18	21	23

B (Put this section NSETS times)

1st card (3I2,2I1,I2,2X,3I3,I5,F9.2)

MONTH	DAY	YEAR	COMPND	TYPSP	EXPNUM	SPECNO	BASENO
1-2	3-4	5-6	7	8	9-10	13-15	16-18

NINSTR	EXTWAV	EXTCOF
19-21	22-26	27-35

2nd card (and more if needed) - INSTRUCTIONS

TYPINS(J)	FRSTNO(J)	LASTNO(J)	ABSADD(J)
3-4	5-8	9-12	13-17
20-21	22-25	26-29	30-34
37-38	39-42	43-46	47-51
54-55	56-59	60-63	64-68

(i.e. 4 instructions per card, as many cards as needed)

Next cards after instructions are the raw data cards

Last card of section B is the 'Z' card (a Z in column 2)

C 1 card (I2)

NPLOTS
1-2

D (Put this section NPLOTS times)

1st card (2I2,F4.2,I3,I2,2F5.2,4F9.3,I3,9I2)

TYPLOT	NSUPER	KSIZE	MODE	EXLAB	XSIZE	YSIZE	XMIN
1-2	3-4	5-8	9-11	12-13	14-18	19-23	24-32

YMIN	XSF	YSF
34-41	43-50	52-59

SPECNO(I)...I=1,10

60-62	63-64	65-66	67-68	69-70	71-72	73-74
75-76	77-78	79-80				

2nd card (4(5A4))

XLAB	YLAB	GLAB1	GLAB2
1-20	21-40	41-60	61-80

3rd, 4th, and 5th cards (skip these if EXLAB equals zero) (6F6.2,2I3)

XO3	YO3	XO4	YO4	HEIGHT	THETA	NCHAR3	NCHAR4
1-6	7-12	13-18	19-24	25-30	31-36	37-39	40-42

GLAB3
1-80

GLAB4
1-80

EXPLANATION OF INPUT DATA VARIABLES FOR 'IPLOT SPECTRA'

NSETS Number of spectra to be read in.

MINWAV (If spectral points are within the limits 1800 A and 7000 A, leave this and MAXWAV blank.) MINWAV should be more than 100 A less than the value of the lowest wavelength of the spectrum.

MAXWAV (see above) MAXWAV should be more than 100 A greater than the largest wavelength value encountered in any data set.

note: the maximum range of points is 5200 A.

NDATCK If this is zero, output of intermediate stages of the data processing will be printed. If it is other than zero, intermediate output will be omitted.

MAT If this equals one, automatic matching of points in the spectrum will result at the place in the data set where a card has been inserted with a one in column 80. If MAT = 0, then no automatic matching will result.

SPECNO(I) This is the number given to the spectrum. The spectra should be numbered sequentially including baselines. (Actually, the program automatically assigns SPECNO values sequentially, and this number is primarily for bookkeeping purposes on this card.)

BASENO(I) The value of SPECNO of the spectrum which is the baseline for this spectrum. BASENO should be blank if there is no baseline for this spectrum or if this is a baseline itself.

NINSTR The number of instructions that will be given on the next card(s).

EXTWAV The wavelength value for which the extinction coefficient (EXTCOF) is given. (If not needed, leave this blank.)

EXTCOF The extinction coefficient for the compound at wavelength EXTWAV.

note: If EXTWAV and EXTCOF have been specified once for a compound with a given experiment number (EXPNUM), it need not be specified for other spectra of the same experiment number. In taking advantage of this, it is necessary that the spectrum for which EXTWAV and EXTCOF are provided is plotted before others of the same experiment number which need EXTWAV and EXTCOF but have not specified them.

TYPINS Tells what type instruction is intended.

TYPINS=2, throw out one or more points

TYPINS=1, add absorbance to one or more points

FRSTNO Number of the first point of a sequence to be operated on by instruction.

LASTNO Number of the last point of a sequence to be operated on by instruction.

note: 1. A sequence may be only one point, i.e. FRSTNO= LASTNO

2. Points of a data set are numbered sequentially counting 7 points per card, whether or not the point is blank.

3. If an instruction operates on a sequence ending with the last point of the data set, LASTNO may be set equal to a very large number, e.g. 999, and the program will automatically stop with the last point. This removes the necessity of counting all of the points correctly.

ABSADD ABSADD is an integer number equal to 1000 times the amount of the absorbance which it is desired to be added to one or more points. If TYPINS=2, ABSADD is not used.

NPLOTS The number of plots to be plotted. There may be more than one spectrum on a plot, but NPLOTS is the number of separate plots, irregardless of how many spectra are plotted on each plot.

TYPLOT Tells which type of plot is desired.

TYPLOT=1 wavelength vs. absorbance

TYPLOT=2 wavenumber vs. absorbance

TYPLOT=3 wavelength vs. molar absorbtivity

TYPLOT=4 wavenumber vs. molar absorbtivity

NSUPER The number of superpotions to be plotted, (i.e., the number of extra spectra plotted on this graph in addition to the usual one). For example, if two spectra are to be plotted on the same graph, NSUPER=1.

KSIZE Plotting symbol size. (Leave this blank and KSIZE= .05 inches).

MODE The plotting mode as explained in the simplotter manual. The two most likely values to be used are:

MODE=11 interpolated curve plotted with points

MODE=21 interpolated curve plotted without points

note: If MODE= blank, then it is assumed to be 11.

EXLAB Tells if extra labeling is desired in addition to the usual two lines.

EXLAB=0 no extra labeling

EXLAB=1 extra labeling is wanted.

XSIZE The length of the graph in the X direction.

YSIZE The length of the graph in the Y direction. (If YSIZE is negative, $\log_{10}$ plots will result. Program automatically evaluates the logarithms).

note: If XSIZE and YSIZE equal zero or blank, they are assumed to be 13.0 and 10.0 respectively.

XMIN Minimum value on the X axis.

YMIN Minimum value on the Y axis.

XSF Scale factor for X axis (in units per inch).

YSF Scale factor for Y axis (in units per inch).

note: If XMIN, YMIN, XSF, YSF are left blank, minimum values and scale factors are determined for you from the data sets.

SPECNO(I) These are the values of SPECNO of the spectra to be plotted on this graph.

note: The maximum number of spectra per graph is 10. If SPECNO(I) is blank it is assumed to equal 1.

XLAB The label for the X axis, maximum of 20 characters.

YLAB The label for the Y axis, maximum of 20 characters.

GLAB1 First graph label, maximum 20 characters.

GLAB2 Second graph label, maximum 20 characters.

GLAB3 First extra label, maximum 80 characters.

GLAB4	Second extra label, maximum 80 characters.
X03	X coordinate of the first letter of GLAB3.
Y03	Y coordinate of the first letter of GLAB3.
X04	X coordinate of the first letter of GLAB4.
Y04	Y coordinate of the first letter of GLAB4.
note:	If X03,Y03,X04, and Y04 equal zero or blank, then their values are determined by the program so that extra labeling is directly beneath other labels.
HEIGHT	Height of extra labeling. (If HEIGHT is blank, HEIGHT=1 is chosen.)
THETA	Leave this blank and labels will be horizontal.
NCHAR3	The number of characters in GLAB3.
NCHAR4	The number of characters in GLAB4.
note:	If NCHAR3 and NCHAR4 equal zero (blank), then NCHAR3=NCHAR4=80 is chosen. This means that the characters of GLAB3 and GLAB4 should be right adjusted on the input cards so that they will terminate at the point below where GLAB1 and GLAB2 terminate.

```
C       ************** IPLOT SPECTRA **************
C
C
C           DEFINE THE NATURE OF THE VARIABLES
C
       REAL*4 KSIZE,EXTCOF,X,Y,XSIZE,YSIZE,XMIN,YMIN,XSF,YSF,X03,Y03,
      1       X04,Y04,HEIGHT,THETA,SLAV,DASORB,TASORB,E,EXTABS,
      1       XSIZEO,YSIZEO,ABS,WAV,LC,DIFPAG,PAGE,PAGES,XLAB,YLAB,GLAB1,
      1       GLAB2,GLAB3,GLAB4
       INTEGER FNO4,LNO4,NPAGES,NROW,NEXPT,NPPLS1,SIGN
       INTEGER MINUS,POUND,DIGIT,CHAR,Z,NPTS,NP,MODE,NCHAR3,NCHAR4,KS
       INTEGER*2 A,B,C,  F,G,H,I,J,K,L,M,N,P,Q,S,T,U,W
       INTEGER*2 NSETS,MONTH,DAY,YEAR,TYPSP,COMPND,EXPNUM,NCARDS,NINSTR,
      1          SPECNO,BASENO,EXTWAV,TYPINS,FRSTNO,LASTNO,DUMWAV,NDMPTS,
      1          ORIGNI,SLAVLE,SLAVRB,WAVELE,ABSORB,      BASORB,DUMABS,
      1          ABSADD,NPLOTS,TYPLOT,NSUPER,      EXLAB,READFT,
      1                    NSCALE,CKNMBR,NUMBR1,NUMBR2,NUMBR3,IDMWAV
       INTEGER*2 NPMIN1,LNMINS,QPLUS1,MINWAV,MAXWAV,ORNPLT,SUPLS1,
      1          LNO,FNO,LN,FN,MINPLT,MORMIN,EXNUM,NPOINT,
      1          ABSADD,NPLOTS,TYPLOT,NSUPER,      EXLAB,READFT,II,ID,
      1          FNB,FNBPS1,LNB,LNBMN1,LNMIN,NDATCK,MAT,PLOTX
C
C
C
C
C
       DIMENSION XLAB(5),YLAB(5),GLAB1(5),GLAB2(5),GLAB3(20),GLAB4(20)
       DIMENSION X(1000),Y(1000),EXTCOF(30),LC(100),E(1000)
       DIMENSION NPTS(30),DIGIT(10),CHAR(7),NROW(5),SIGN(7)
       DIMENSION WAVELE(10000),ABSORB(10000),BASORB(5200)
C
       DIMENSION MONTH(30), DAY(30), YEAR(30), TYPSP(30), COMPND(30),
      1          EXPNUM(30),SPECNO(30),BASENO(30),EXTWAV(30),
      1          ORIGNI(30),NDMPTS(30),FNO(30),LNO(30)
C
       DIMENSION NUMBR1(7), NUMBR2(7), NUMBR3(7), NSCALE(7),IDMWAV(7)
       COMMON /HOLD/NCARDS(30),NINSTR(30),DUMWAV(1000),DUMABS(1000),
```

```
     1          TYPINS(100), FRSTNO(100), LASTNO(100), ABSADD(100),
     1          II(150),ID
C
C          INITIALIZE THE CHARACTER REPRESENTATIONS USED IN THE PROGRAM
      DATA MINUS /'-'/, POUND /'#'/,Z/'Z'/
      DATA DIGIT/'0','1','2','3','4','5','6','7','8','9'/
C
C
C
C
      DO 1 I=1,100
      LC(I) = 0.0
    1 CONTINUE
C
C          HOW MANY SETS OF DATA ARE TO BE READ IN?
C
      READ(1,100) NSETS,MINWAV,MAXWAV,NDATCK,MAT
  100 FORMAT(I2,2I8,I3,I2)
C          THE PURPOSE OF MINWAV AND MAXWAV IS TO PROVIDE FOR THE POSSIBILITY
C          THAT THE LIMITS OF THE WAVELENGTH VALUES OF A GIVEN SPECTRUM MAY BE
C          LESS THAN 1800 A OR MORE THAN 7000 A.  IF THIS IS THE CASE, EITHER
C          MINWAV OR MAXWAV MUST BE SPECIFIED AND THE RANGE OF THE DATA SET CAN
C          STILL NOT EXCEED 5200 A.  NOTE THAT IF BOTH MINWAV AND MAXWAV ARE
C          SPECIFIED, MAXWAV OVERRIDES MINWAV.
C
      IF(MINWAV.GT.0) GO TO 101
      MINWAV = 1800
      IF(MAXWAV.EQ.0) GO TO 101
      MINWAV = MAXWAV - 5200
  101 CONTINUE
      IF(NSETS.GT.0) GO TO 105
      NSETS = 1
  105 CONTINUE
C
C          BEGIN DO LOOP WHICH IN EACH LOOP READS DATA PERTAINING TO ONE SET,
C          PERFORMS ON THE DATA  INSTRUCTIONS WHICH HAVE BEEN READ IN OR SELF
C          GENERATED, AND ASSIGNS THE DATA POINTS TO ARRAYS
```

```
C
      S = 0
      DO 270 I=1,NSETS
      ID=I
C
C         READ DESCRIPTIVE INFORMATION FOR THIS SET
C
      READ(1,110) MONTH(I),DAY(I),YEAR(I),TYPSP(I),COMPND(I),EXPNUM(I),
     1             SPECNO(I),BASENO(I),NINSTR(I),EXTWAV(I),EXTCOF(I)
  110 FORMAT(3I2,2I1,I2,2X,3I3,I5,F9.2)
C         SPECNO(I) SHOULD ALWAYS EQUAL I.  IT HAS BEEN READ IN MERELY TO HAVE
C         IT ON THE CARD FOR BOOKKEEPING PURPOSES.  TO BE SURE THAT SPECNO(I)
C         HAS THE PROPER VALUE, WE SHALL DEFINE IT HERE.
C
C         REMEMBER THE ORIGINAL NUMBER OF INSTRUCTIONS
      ORIGNI(I) = NINSTR(I)
C
C
C         IF THERE ARE NO INSTRUCTIONS SKIP THE STATEMENT TO READ INSTRUCTIONS.
      IF(NINSTR(I).EQ.0) GO TO 125
C
C
C         READ INSTRUCTIONS
      G = NINSTR(I)
      READ(1,120) (TYPINS(J), FRSTNO(J), LASTNO(J),ABSADD(J),
     1             J=1,G)
  120 FORMAT(4(2X,I2,2I4,I5))
C
C         ECHO CHECK
      IF(NDATCK.GT.0) GO TO 126
      WRITE(3,121) I,(TYPINS(J),FRSTNO(J),LASTNO(J),ABSADD(J),
     1             J=1,G)
  121 FORMAT('1','ORIGINAL INSTRUCTIONS FOR DATA SET NUMBER',I2,/,4(2X,
     1 I2,2I4,I5))
      GO TO 126
C
C
```

```
  125 WRITE(3,122)I
  122 FORMAT('1 NO INSTRUCTIONS FOR DATA SET NUMBER',I2)
C
C
C
C          READ THE RAW DATA FOR SPECTRAL POINTS.  ASSIGN EACH RAW DATA POINT TO
C          THE ARRAYS DUMWAV AND DUMABS.  ALSO, MARK CERTAIN EXTRANEOUS
C          POINTS TO EVENTUALLY BE ELIMATED.  THE DATA IS READ ONE CARD AT
C          A TIME, THE DATA INTERPRETED INTO POINTS IDMWAV AND DUMABS FOR
C          EACH CARD BEFORE THE NEXT CARD IS READ.
  126 NCARDS(I) = 0
      W = 1
      DO 170 K=1,1000
C
C
C          READ THE RAW DATA POINTS ON CARD 'K'
C
      READ(1,130) (NSCALE(J),CHAR(J),NUMBR3(J),IDMWAV(J),J=1,7),II(K)
  130 FORMAT(7(I1,A1,I2,1X,I5,1X),2X,I1)
      IF(CHAR(1).EQ.Z) GO TO 175
      NCARDS(I) = NCARDS(I) + 1
C
C          PROCESS THE POINTS
      DO 165 J=1,7
C           INITIALIZE THE VALUE OF NUMBR(J) TO ZERO INCASE CHAR(J) IS BLANK.
      NUMBR2(J) = 0
C          WHAT IS THE NUMBER OF THIS POINT (B).
      B = (K-1)*7 + J
C          SET THE VALUE OF THE WAVELENGH (IDMWAV(J)) FOR THIS POINT EQUAL
C          TO DUMWAV(B).
      DUMWAV(B) = IDMWAV(J)
C
C          IF DUMWAV EQUALS 0, GENERATE INSTRUCTIONS TO THROW OUT THE POINT
C          SINCE THIS MEANS THAT IT IS MERELY A BLANK NOT A REAL POINT. THERE
C          IS NO REASON TO FIND DUMABS IN THIS CASE SO GO ON TO END OF LOOP.
      IF(DUMWAV(B).NE.0) GO TO 131
      DUMABS(B) = 10000
```

```
      NINSTR(I) = NINSTR(I) + 1
      C = NINSTR(I)
      TYPINS(C) = 2
      FRSTNO(C) = B
      LASTNO(C) = B
      ABSADD(C) = 0
      GO TO 165
C
C
C          IF THIS IS THE FIRST POINT OF THE DATA SET 'I', WE WANT TO SET
C          CKNMBR EQUAL TO NSCALE(1).  THE MEANING OF CKNMBR WILL BECOME EVIDENT
C          LATER
  131 IF(W.NE.1) GO TO 132
C
C          THIS IS THE FIRST POINT OF THE DATA SET 'I'.  WE WANT CKNMBR TO EQUAL
C          NSCALE(1).
      CKNMBR = NSCALE(J)
C
C
C
C          WHAT SCALE IS THE POINT ON ON THE SPECTROPHOTOMETER?  NSCALE EQUAL
C          TO 0 IS SCALE ONE AND NSCALE EQUAL TO 6 IS SCALE TWO.
  132 IF(NSCALE(J).EQ.0) GO TO 140
C
C
C          POINT IS ON SECOND SCALE, NSCALE SHOULD EQUAL 6, IF NOT PRINT ERROR.
      IF(NSCALE(J).EQ.6) GO TO 135
C
C          IF YOU GET HERE THERE IS AN ERROR.
      WRITE(3,133) I,B
  133 FORMAT(' ','ERROR     NSCALE IS NOT EQUAL TO EITHER 0 OR 6.',
     1           '  I = ',I2,' B =',I2)
C          SET NUMBR1 EQUAL TO 1000, THIS WILL HAVE THE EFFECT OF ADDING 1.0
C          TO THE ABSORBANCE, SINCE THE POINT IS ON THE SECOND SCALE.
  135 NUMBR1(J) = 1000
C
C          CHECK TO SEE IF THE PREVIOUS POINT WAS ON SECOND SCALE.  IF THIS IS
```

```
C          THE FIRST POINT SINCE A CHANGE FROM FIRST SCALE TO SECOND, WE WANT
C          TO THROW OUT THIS POINT AND THE NEXT ONE.  THEY ARE USUALLY IN ERROR
C          SINCE THEY ARE TAKEN WHILE THE PEN IS MOVING TO THE NEXT SCALE.
C          CKNMBR WILL EQUAL 6 IF THE PREVIOUS POINT WAS ON SECOND SCALE.
      IF(CKNMBR.EQ.6) GO TO 138
C
C          CKNMBR EQUALS 0, THEREFORE THE PREVIOUS POINT WAS NOT ON SECOND
C          SCALE, GIVE INSTRUCTIONS TO THROW OUT THIS POINT AND THE NEXT. ALSO
C          INDICATE THAT CKNMBR SHOULD NOW EQUAL 6, SINCE THIS POINT IS ON
C          SECOND SCALE.
      CKNMBR = 6
      DUMABS(B) = 10000
      NINSTR(I) = NINSTR(I) + 1
      C = NINSTR(I)
      TYPINS(C) = 2
      FRSTNO(C) = B
      LASTNO(C) = B + 1
      ABSADD(C) = 0
C
  138 CONTINUE
      GO TO 143
C
C
C          NSCALE EQUALS 0, POINT IS ON THE FIRST SCALE.
  140 CONTINUE
      NUMBR1(J) = 0
C
C          CHECK TO SEE IF THE PREVIOUS POINT WAS ON FIRST SCALE.  IF THIS
C          IS THE FIRST POINT SINCE A CHANGE FROM SECOND SCALE TO FIRST, WE WANT
C          TO THROW OUT THIS POINT AND THE NEXT ONE, SINCE THEY ARE USUALLY IN
C          ERROR.  CHNMBR WILL EQUAL 0 IF THE PREVIOUS POINT WAS ON FIRST SCALE.
      IF(CKNMBR.EQ.0) GO TO 143
C
C          CKNMBR EQUALS 6, THEREFORE THE PREVIOUS POINT WAS NOT ON FIRST
C          SCALE.  GIVE INSTRUCTIONS TO THROW OUT THIS POINT AND THE NEXT.  ALSO
C          INDICATE THAT CKNMBR SHOULD NOW EQUAL 0, SINCE THIS POINT IS ON
C          FIRST SCALE
```

```
      CKNMBR = 0
      DUMABS(B) = 10000
      NINSTR(I) = NINSTR(I) + 1
      C = NINSTR(I)
      TYPINS(C) = 2
      FRSTNO(C) = B
      LASTNO(C) = B + 1
      ABSADD(C) = 0
C
C
C
C
C
C         IS THE POINT WITHIN THE RANGE OF THE INDICATED SCALE, OR IS IT
C         ABOVE OR BELOW THAT RANGE.
  143 IF(CHAR(J).NE.POUND) GO TO 150
C
C         CHAR(J) EQUALS POUND (#).  THEREFORE POINT IS A POSITIVE NUMBER
C         ABOVE THE INDICATED SCALE.
      SIGN(J) = 1
C         WHICH SCALE IS POINT ON?
      IF(NSCALE(J).EQ.0) GO TO 145
C         NSCALE EQUALS 6, POINT IS SLIGHTLY ABOVE SECOND SCALE.
      NUMBR1(J) = 2000
      GO TO 147
C         NSCALE EQUALS 0, POINT IS SLIGHTLY ABOVE FIRST SCALE
  145 NUMBR1(J) = 1000
C
C
  147 CONTINUE
      GO TO 157
C
C
C          CHAR(J) DOES NOT EQUAL POUND, SEE IF CHAR(J) EQUALS MINUS ('-').
  150 IF(CHAR(J).NE.MINUS) GO TO 152
C
C         CHAR(J) EQUALS MINUS, SET SIGN(J) EQUAL TO -1
```

```
      SIGN(J) = -1
      GO TO 157
C         SINCE CHAR(J) DOESN'T EQUAL MINUS OR POUND, CHAR(J) EQUALS A CHARACTER
C         REPRESENTATION OF A NUMBER.  FIND OUT WHICH NUMBER AND SET
C         NUMBR2(J) EQUAL TO THAT NUMBER.  ALSO SET SIGN(J) EQUAL TO 1.0.
  152 SIGN(J) = 1
      DO 155 L=1,10
      IF(CHAR(J).NE.DIGIT(L)) GO TO 155
C
C         CHAR(J) EQUALS DIGIT(L), SET NUMBR2(J) EQUAL TO L - 1.
      NUMBR2(J) = 100*(L-1)
  155 CONTINUE
      GO TO 160
C
C         CHAR(J) EQUALS EITHER POUND OR MINUS, THEREFORE SET NUMBR(J) EQUAL
C         TO 0.
  157 NUMBR2(J) = 0
C
C
C         WE NOW HAVE ALL OF THE INFORMATION TO RECONSTRUCT THE VALUE OF
C         DUMABS(B).
  160 DUMABS(B) =  NUMBR1(J) + NUMBR2(J) + NUMBR3(J)*SIGN(J)
      W = 2
C
C
C         GO ON TO NEXT POINT
  165 CONTINUE
C
C
C         GO ON TO NEXT CARD
  170 CONTINUE
  175 CONTINUE
C         DATA FOR THIS SET HAVE BEEN READ IN AND NOW EXIST AS THE ARRAYS,
C         DUMWAV AND DUMABS.
C         REMEMBER THE NUMBER OF POINTS FOR THIS SET
      NDMPTS(I) = B
C
```

```
C
C
C
C
C
C
C         ECHO CHECK
      IF(NDATCK.GT.0) GO TO 180
      WRITE(3,1000) I, (DUMABS(C), DUMWAV(C), C=1,B)
 1000 FORMAT(' ',35X,'RAW DATA, DUMABS VS. DUMWAV FOR DATA SET ',
     1      'NUMBER',I2,/,7(I8,1X,I5))
  180 CONTINUE
C
C
C
      IF(MAT.EQ.0)GO TO 181
      CALLMATCH
      IF(MAT.NE.2)GO TO 181
      CALL SUBTRT
  181 CONTINUE
C
C
C         ARE THERE ANY INSTRUCTIONS?  IF NOT GO ON AND SKIP THE NEXT SECTION.
C
      IF(NINSTR(I).LT.1) GO TO 250
C
C         THERE ARE INSTRUCTIONS.  CARRY THEM OUT.
C
      H = NINSTR(I)
      DO 240 J=1,H
C
      L = FRSTNO(J)
      M = LASTNO(J)
      F = TYPINS(J)
C         WHAT IS THE INSTRUCTION?  IF IT IS TO ADD GO TO 200.  IF IT IS TO
C         THROW OUT POINTS GO TO 220.
      GO TO (200,220), F
```

```
C
C          INSTRUCTION IS TO ADD ABSADD(J) TO DUMABS(A), WHERE A GOES FROM
C          FRSTNO(J) TO LASTNO(J).
  200 DO 210 A=L,M
      IF(A.GT.NDMPTS(I)) GO TO 211
      DUMABS(A) = DUMABS(A) + ABSADD(J)
  210 CONTINUE
C          GO ON TO NEXT INSTRUCTION.
  211 GO TO 240
C
C
C          INSTRUCTION IS TO MARK THE POINTS DUMABS(A) AND DUMWAV(A) FOR
C          ELIMINATION, WHERE 'A" GOES FROM FRSTNO(J) TO LASTNO(J).
  220 DO 230 A=L,M
      IF(A.GT.NDMPTS(I)) GO TO 240
      DUMABS(A) = 10000
  230 CONTINUE
C          GO ON TO NEXT INSTRUCTION.
C
  240 CONTINUE
C          INSTRUCTIONS HAVE BEEN EXECUTED.
C
C          ECHO CHECK
      IF(NDATCK.GT.0) GO TO 250
      C = NINSTR(I)
      WRITE(3,242) I,(TYPINS(J),FRSTNO(J),LASTNO(J),ABSADD(J),
     1             J=1,C)
  242 FORMAT(' ',' TOTAL   INSTRUCTIONS FOR DATA SET NUMBER',I2,/,4(2X,
     1 I2,2I4,I5))
C
C          NOW ASSIGN THE POINTS OF SET 'I' TO THE ARRAYS WAVELE(S) AND
C          ABSORB(S), LEAVING OUT THE POINTS WITH DUMABS(J) = 1000.
  250 NDMPTS(I) = 7*(NCARDS(I))
      P = NDMPTS(I)
      T = 0
      DO 260 A=1,P
      IF(DUMABS(A).GT.8000) GO TO 260
```

```
      S = S + 1
      T = T + 1
      ABSORB(S) = DUMABS(A)
      WAVELE(S) = DUMWAV(A)
  260 CONTINUE
C
C          REMEMBER THE VALUE OF T, IT IS THE NUMBER OF POINTS (NPTS(I)) FOR
C          DATA SET I.  ALSO REMEMBER THE POSITION IN THE ARRAYS WAVELE(S)
C          AND ABSORB(S) OF THE FIRST AND LAST POINTS OF THE SPECTRUM.
      NPTS(I) = T
      FNO(I) = S - NPTS(I) + 1
      LNO(I) = S
C
C          GO ON TO NEXT SET OF DATA POINTS
C
  270 CONTINUE
C
C
C
C          ECHO CHECK
      IF(NDATCK.GT.0) GO TO 299
      DO 272 I=1,NSETS
      FN = FNO(I)
      LN = LNO(I)
      WRITE(3,1001) I, (ABSORB(C),WAVELE(C), C=FN,LN)
 1001 FORMAT('1',35X,'DATA AFTER INSTRUCTIONS HAVE BEEN EXECUTED FOR',
     1        ' DATA SET',I2,/,7(I8,1X,I5))
  272 CONTINUE
C
C
C
C
C          PUT THE POINTS OF EACH SET IN DESCENDING ORDER OF THEIR
C          WAVELE VALUES.
  299 CONTINUE
      DO 320 I=1,NSETS
C          DO NOT BOTHER TO ORDER POINTS IF NO ORIGINAL INSTRUCTIONS WERE
```

```
C           GIVEN.  (THEY ARE PROBABLY ALREADY IN ORDER).
      IF(ORIGNI(I).LT.1) GO TO 320
C
C           PROCEED TO ORDER THE POINTS
      NPMIN1 = NPTS(I) - 1
      FN = FNO(I)
      DO 310 S=1,NPMIN1
      LNMINS = LNO(I) - S
      DO 300 Q=FN,LNMINS
      QPLUS1 = Q + 1
C
C           IF WAVELE( Q ) IS NOT GREATER THAN WAVELE(  QPLUS1), EXCHANGE THEM.
      IF(WAVELE(Q).GT.WAVELE(QPLUS1)) GO TO 300
      SLAVLE = WAVELE(Q)
      SLAVRB = ABSORB(Q)
      WAVELE(Q) = WAVELE(QPLUS1)
      ABSORB(Q) = ABSORB(QPLUS1)
      WAVELE(QPLUS1) = SLAVLE
      ABSORB(QPLUS1) = SLAVRB
  300 CONTINUE
C           INNERMOST DO LOOP IS DONE, GO ON TO THE NEXT POINT
C
  310 CONTINUE
C           POINTS OF SET 'I' HAVE BEEN PUT IN ORDER, GO ON TO NEXT SET
C
  320 CONTINUE
C           ALL SETS OF POINTS HAVE BEEN PUT IN ORDER, PROCEED WITH PROGRAM
C
C           ECHO CHECK
      IF(NDATCK.GT.0) GO TO 500
      DO 322 I=1,NSETS
      FN = FNO(I)
      LN = LNO(I)
      WRITE(3,1002) I, (ABSORB(C),WAVELE(C), C=FN,LN)
 1002 FORMAT('1',35X,'DATA AFTER BEING PUT IN ORDER FOR DATA SET',I2,
     1       /,7(I8,1X,I5))
  322 CONTINUE
```

```
C
C
C
C          SUBTRACT BASELINES FROM THE SPECTRAL POINTS.
  500 CONTINUE
      DO 596 I=1,NSETS
C
C          IS THE DATA SET A BASELINE OR A SPECTRUM?  WE DON'T NEED TO SUBTRACT
C          ANYTHING IF IT IS A BASELINE.
C
C          THERE MAY NOT BE A BASELINE.  IF NOT GO TO 596.
      IF(BASENO(I).EQ.0) GO TO 596
C
C          THE DATA SET IS A SPECTRUM AND WE WANT TO SUBTRACT THE BASELINE.
C          FIRST INITIALIZE THE ARRAY BASORB AND THEN ASSIGN TO THIS ARRAY THE
C          APPROPRIATE BASELINE.
      DO 501 J=1,5200
      BASORB(J) = 10000
  501 CONTINUE
C
      N = BASENO(I)
      FN = FNO(N)
      LN = LNO(N)
      DO 502 J=FN,LN
      H = WAVELE(J) - (MINWAV-1)
      BASORB(H) = ABSORB(J)
  502 CONTINUE
      NP = NPTS(I)
      FN = FNO(I)
      LN = LNO(I)
C
C
      DO 595 J=FN,LN
      K = WAVELE(J) - (MINWAV-1)
      M = K
      L = 0
C          IS THERE A VALUE FOR THE BASELINE AT THIS POINT?  IF THERE IS GO TO
```

```
C          530 AND SUBTRACT IT FROM THE SPECTRAL POINT.  IF THERE IS NO POINT
C          HERE INTERPOLATE LINEARLY BETWEEN THE NEAREST POINTS TO DETERMINE
C          A VALUE AT THIS POINT FOR THE BASELINE TO  SUBTRACT FROM THE
C          SPECTRAL POINT.
  505 IF(BASORB(M).LT.10000) GO TO 530
C
C          THERE IS NO VALUE OF THE BASELINE AT THIS POINT, START COUNTING
C          HOW MANY TIMES IT TAKES TO FIND A POINT (L IS THE COUNTER).
      L = L + 1
      M = K + L
C           IF L EXCEEDS 100 EXTRAPOLATE FROM THE END POINTS
      IF(L.LT.100 ) GO TO 520
C
      WRITE(3,510) I,N
  510 FORMAT(' ','EXTRAPOLATION REQUIRED, DATA SET NUMBER ',I2,
     1        'BASENO ',I2,'L EXCEEDS 100')
      NPOINT = J+1-FN
      WRITE(3,999) NPOINT
  999 FORMAT('   POINT NUMBER ',I3)
      FNB = FNO(N)
      FNBPS1 = FNB + 1
      TASORB = (ABSORB(FNB) + ABSORB(FNBPS1))/2.0
      GO TO 581
C
C
C          NOW LOOK AT THE NEXT WAVELENGTH TO SEE IF THE BASELINE HAS A VALUE.
  520 GO TO 505
C
C          IF 'L' EQUALS 0, THEN NO EXTRAPOLATION IS NEEDED, GO TO 590
  530 IF(L.EQ.0) GO TO 590
C
C          THERE IS NO VALUE OF THE BASELINE AT THIS POINT, EXTRAPOLATION
C          PROCEEDS.  THE NEAREST WAVELENGTH IN THE '+' DIRECTION AT WHICH
C          THERE IS A VALUE OF THE BASELINE IS 'M' ('M' EQUALS K+1)..
C          NOW FIND THE NEAREST WAVELENGTH IN THE '-' DIRECTION.  'T' IS THE
C          COUNTER IN THIS DIRECTION.  'P' WILL EVENTUALLY EQUAL BE THE NEAREST
C          WAVELENGTH IN THE '-' DIRECTION.
```

```
      T = 1
      P = K - 1
C
  540 IF(BASORB(P).LT.10000) GO TO 580
      T = T + 1
      P = P - 1
C         ANOTHER SAFETY CHECK
C          IF T EXCEEDS 100 EXTRAPOLATE FROM THE END POINTS
      IF(T.LT.100 ) GO TO 570
C
      WRITE(3,560) I,N
  560 FORMAT(' ','EXTRAPOLATION REQUIRED, DATA SET NUMBER ',I2,
     1       'BASENO ',I2,'T EXCEEDS 100')
      NPOINT = J+1-FN
      WRITE(3,999) NPOINT
      LNB = LNO(N)
      LNBMN1 = LNB - 1
      TASORB = (ABSORB(LNB) + ABSORB(LNBMN1)) /2.0
      GO TO 581
C
C         NOW LOOK AT THE NEXT WAVELENGTH TO SEE IF THE BASELINE HAS A VALUE.
  570 GO TO 540
C
C         WE NOW KNOW THE POINTS OF THE BASELINE NEAREST THE SPECTRAL POINT.
C         CALCULATE THE EXTRAPOLATED VALUE FOR BASORB(K)
  580 TASORB   =((T*1.0)/((L+T)*1.0))*(BASORB(M)-BASORB(P)) + BASORB(P)
  581 BASORB(K) = TASORB + .5
C
C         NOW SUBTRACT THE BASELINE VALUE AT WAVELE(K) FROM THE SPECTRAL VALUE.
  590 ABSORB(J) = ABSORB(J) - BASORB(K)
C
C
C         GO ON TO THE NEXT POINT IN THE SET 'I'
  595 CONTINUE
C
C         GO ON TO THE NEXT SET
  596 CONTINUE
```

```
C          SPECTRA HAVE BEEN CORRECTED FOR BASELINES, WE ARE READY TO START
C          PLOTTING.
C
C
C          ECHO CHECK
      IF(NDATCK.GT.0) GO TO 599
      DO 598 I=1,NSETS
      FN = FNO(I)
      LN = LNO(I)
      WRITE(3,1003) I, (ABSORB(C),WAVELE(C), C=FN,LN)
 1003 FORMAT('1',35X,'DATA AFTER BASELINES HAVE BEEN SUBTRACTED FOR',
     1       ' DATA SET',I2,/,7(I8,1X,I5))
  598 CONTINUE
C
C
C
C          HOW MANY PLOTS ARE WANTED?
  599 CONTINUE
      READ(1,600) NPLOTS
  600 FORMAT(I2)
      ORNPLT = NPLOTS
      IF(NPLOTS.GT.0) GO TO 610
      NPLOTS = 1
C
C
C
C          NOW START LOOP THAT READS GRAPHING INFORMATION, CALCULATES
C          NECESSARY INFORMATION ON POINTS, WRITES A TABLE OF POINTS, AND
C          PLOTS THE POINTS FOR ONE GRAPH EACH TIME IT LOOPS.
  610 DO 820 W=1,NPLOTS
C
C          READ INFORMATION PERTAINING TO THE SPECIFIC PLOT 'W'.
  615 READ(1,620) TYPLOT,NSUPER,KSIZE,MODE,EXLAB,XSIZE,YSIZE,XMIN,YMIN,
     1            XSF,YSF, (SPECNO(I), I=1,10)
  620 FORMAT(2I2,F4.2,I3,I2,2F5.2,4F9.3,I3,9I2)
      READ(1,630) XLAB,YLAB,GLAB1,GLAB2
  630 FORMAT(4(5A4))
```

```
C          IF TYPLOT HAS NOT BEEN SPECIFIED, IT WILL EQUAL 0, IF SO ASSUME IT
C          EQUALS 1.
      IF(TYPLOT.GT.0) GO TO 632
      TYPLOT = 1
  632 IF(XSIZE.GT.0) GO TO 635
      IF(XSIZE.LT.-.5) GO TO 635
      XSIZE = 13.0
      YSIZE = 9.75
  635 CONTINUE
C
C          IS EXTRA GRAPH LABELING DESIRED?  IF SO READ DATA PERTAINING TO
C          EXTRA LABELS.
      IF(EXLAB.LT.1) GO TO 670
C
C          EXTRA LABELING IS DESIRED.  READ DATA.
      READ(1,640) XO3,YO3,XO4,YO4,HEIGHT,THETA,NCHAR3,NCHAR4,GLAB3,GLAB4
  640 FORMAT(6F6.2,2I3,/,20A4,/,20A4)
C          IF THE INFORMATION JUST READ IN WAS BLANK, INITIALIZE THE VALUES.
      IF(XO3.GT.(.1)) GO TO 670
      XO3 = ABS(XSIZE)-8.0
      XO4 = XO3
      YO3 = ABS(YSIZE) -.6
      YO4 = ABS(YSIZE) - .75
      HEIGHT = .1
      THETA = 0.0
      NCHAR3 = 80
      NCHAR4 = 80
C
C
C
C          START INNER LOOP WHICH, PLOTS ONE SPECTRUM OF A GIVEN PLOT FOR EACH
C          LOOP.
  670 SUPLS1 = NSUPER + 1
      DO 800 U=1,SUPLS1
C        IF SPECNO(U) HAS NOT BEEN SPECIFIED, IT WILL EQUAL 0.  IF THIS IS THE
C          CASE, SET IT EQUAL TO 1.
      IF(SPECNO(U).GT.0) GO TO 680
```

```
      SPECNO(U) = 1
  680 I = SPECNO(U)
      NP = NPTS(I)
      FN = FNO(I)
      LN = LNO(I)
C         NOW THE PLOTTING VARIABLES SHOULD BE CALCULATED IF NECESSARY AND
C         ASSIGNED.
      M = 0
      GO TO (685,690,700,690), TYPLOT
C
C
C         TYPLOT EQUALS 1, SET THE PLOTTING VARIABLES EQUAL TO WAVELE(I,J) AND
C         ABSORB(J)
C
  685 DO 687 J=FN,LN
      M = M + 1
      LNMIN = LN - J + FN
      X(M) = WAVELE(LNMIN)
      Y(M) = ABSORB(LNMIN)*(1.0E-3)
  687 CONTINUE
C         NOW GO DOWN TO TABULATE POINTS
      GO TO 730
C
C         TYPLOT EQUALS 2 OR 4, CALCULATE VALUES FOR X(N) IN WAVENUMBERS.
  690 CONTINUE
      N = 0
      DO 692 J=FN,LN
      N = N + 1
      X(N) = (1.0E8)/WAVELE(J)
  692 CONTINUE
C         IS TYPLOT 2 OR 4
      IF(TYPLOT.EQ.4) GO TO 700
C
C         TYPLOT IS 2, THEREFORE SET THE PLOTTING VARIABLES EQUAL TO ABSORB(J).
C         THE  X(J) VARIABLE HAS ALREADY BEEN SET EQUAL TO WAVENUMBERS.
      DO 695 J=FN,LN
      M = M + 1
```

```
      Y(M) = ABSORB(J)*(1.0E-3)
  695 CONTINUE
C          NOW GO DOWN TO TABULATE POINTS
      GO TO 730
C
C          TYPLOT IS 3 OR 4, THEREFORE CALCULATE VALUES OF E(J).  FIRST
C           DETERMINE THE NEAREST POINTS IN THE SPECTRUM TO EXTWAV,
C           AND THEN LINEARLY INTERPOLATE BETWEEN THEM.
  700 DO 705 J=FN,LN
      IF(EXTWAV(I).LT.1) GO TO 710
      K = J
      IF(EXTWAV(I).GT.WAVELE(J)) GO TO 708
C
C          WE HAVEN'T FOUND IT YET SO KEEP LOOKING.
  705 CONTINUE
      WRITE(3,707) W,I
  707 FORMAT('  EXTWAV(I) OUT OF RANGE OF DATA.  PLOT NUMBER',I2,
     1       '  SPECTRUM NUMBER',I2)
      WRITE(3,7071) EXTWAV(I)
 7071 FORMAT('1','EXTWAV(I) NON-ZERO, EXTWAV(I)=',I20)
      GO TO 800
  708 CONTINUE
      WRITE(3,7071) EXTWAV(I)
      KMINS1 = K - 1
      ABB = ABSORB(KMINS1) - ABSORB(K)
      WAV = WAVELE(KMINS1) - WAVELE(K)
      EXTABS = (ABB/WAV)*(EXTWAV(I) - WAVELE(K)) +ABSORB(K)
      EXNUM = EXPNUM(I)
      LC(EXNUM) = EXTABS/EXTCOF(I)
  710 CONTINUE
C
      EXNUM = EXPNUM(I)
      N = 0
      DO 715 J=FN,LN
      DASORB = ABSORB(J)
      N = N + 1
      E(N) = DASORB/LC(EXNUM)
```

```
  715 CONTINUE
C
C           POINTS HAVE VALUES FOR E(J), NOW SEE WHETHER TYPLOT EQUALS 3 OR 4.
      IF(TYPLOT.EQ.4) GO TO 722
C
C           TYPLOT EQUALS 3, THEREFORE SET THE PLOTTING VARIABLES EQUAL TO
C           WAVELE(J) AND E(J).
      IF(YSIZE.LT.0.0)GO TO 718
      DO 716 J=FN,LN
      M = M + 1
      LNMIN = LN - J + FN
      X(M) = WAVELE(LNMIN)
      N = NP + 1 - M
      Y(M) = E(N)
  716 CONTINUE
      GO TO 721
  718 IF(YSF.GT.0.OR.YSF.LT.0)GO TO 7185
      YSF=.5
 7185 DO 7195 J=FN,LN
      M=M+1
      LNMIN=LN-J+FN
      X(M)=WAVELE(LNMIN)
      N=NP+1-M
      IF(E(N).GT.1.0)GO TO 719
      E(N)=1.0
      WRITE(3,7265) M
  719 Y(M)=ALOG10(E(N))
 7195 CONTINUE
  721 GO TO 730
C           NOW GO DOWN TO TABULATE POINTS
C
C
C           TYPLOT EQUALS 4 THEREFORE SET THE PLOTTING VARIABLES Y(M) EQUAL TO
C           E(J).  THE VALUES FOR X(M) HAVE ALREADY BEEN SET EQUAL TO WAVENUMBERS.
  722 IF(YSIZE.LT.0.0) GO TO 726
      DO 725 M=1,NP
      Y(M) = E(M)
```

```
  725 CONTINUE
      GO TO 730
  726 IF(YSF.GT.0.OR.YSF.LT.0)GO TO 729
      YSF=.5
  729 CONTINUE
      DO 728 M=1,NP
      IF(E(M).GT.1.0) GO TO 727
      E(M) = 1.0
      WRITE(3,7265) M
 7265 FORMAT(' ','M=',I3,'TO AVOID TAKING THE LOG OF A NEGATIVE',
     1' NUMBER OR TOO SMALL OF A NUMBER, E(M) WAS SET EQUAL TO 1.0')
  727 Y(M)=ALOG10(E(M))
  728 CONTINUE
C          NOW GO DOWN TO TABULATE POINTS
C
C
  730 CONTINUE
C
C
C          THIS PART OF THE PROGRAM FIRST PRINTS A TABLE OF EACH SPECTRUM, THEN
C          PLOTS THE POINTS.
C
C
C          THIS SECTION WRITES TABLES OF DATA TO BE PLOTTED.  FIRST THE TABLE
C          PARAMETERS ARE DETERMINED, AND THEN THE TABLE IS WRITTEN.
C
      NPAGES = (NPTS(I)/200) + 1
      DO 735 H=1,NPAGES
      NROW(H) = 50
  735 CONTINUE
C
      PAGES = (1.0*NPTS(I))/(200.0)
      PAGE = FLOAT(NPAGES) - 1.0
      DIFPAG = PAGES - PAGE
      IF(DIFPAG.GT.0.0) GO TO 737
      NPAGES = NPAGES - 1
      GO TO 739
```

```
  737 CONTINUE
C
      NEXPT = NPTS(I) - (NPAGES-1)*200
      IF(NEXPT.GT.49) GO TO 739
      NROW(NPAGES) = NEXPT
  739 CONTINUE
C
      DO 760 G=1,NPAGES
C
C
      GO TO (740,741,742,743), TYPLOT
C
  740 CONTINUE
      WRITE(3,7401) COMPND(I), EXPNUM(I), SPECNO(U)
 7401 FORMAT('1',4X,'COMPOUND=',I2,2X,'EXPNUM=',I2,2X,'SPECNO=',I2,
     1/,'  (ANG)    ABS ',5X,' (ANG)    ABS ',5X,' (ANG)    ABS '5X,
     1' (ANG)    ABS ')
      GO TO 744
C
  741 CONTINUE
      WRITE(3,7411) COMPND(I), EXPNUM(I), SPECNO(U)
 7411 FORMAT('1',4X,'COMPOUND=',I2,2X,'EXPNUM=',I2,2X,'SPECNO=',I2,
     1/,' (1/CM)    ABS ',5X,'(1/CM)    ABS ',5X,'(1/CM)    ABS '5X,
     1'(1/CM)    ABS ')
      GO TO 744
C
  742 CONTINUE
      WRITE(3,7421) COMPND(I), EXPNUM(I), SPECNO(U)
 7421 FORMAT('1',4X,'COMPOUND=',I2,2X,'EXPNUM=',I2,2X,'SPECNO=',I2,
     1/,'  (ANG)  EXTCOF',5X,' (ANG)  EXTCOF',5X,' (ANG)  EXTCOF'5X,
     1' (ANG)  EXTCOF')
      GO TO 744
C
  743 CONTINUE
      WRITE(3,7431) COMPND(I), EXPNUM(I), SPECNO(U)
 7431 FORMAT('1',4X,'COMPOUND=',I2,2X,'EXPNUM=',I2,2X,'SPECNO=',I2,
     1/,' (1/CM)  EXTCOF',5X,'(1/CM)  EXTCOF',5X,'(1/CM)  EXTCOF'5X,
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```
     1'(1/CM)   EXTCOF')
C
  744 CONTINUE
C          THE FOLLOWING STATEMENTS THROUGH 745 DETERMINE FROM THE NUMBER
C          OF POINTS IN THE DATA SET THE PARAMETERS NEEDED TO WRITE THE TABLE
      NR = NROW(G)
      DO 755 H=1,NR
      FNO4 = (G-1)*200 + H
      LNO4 = FNO4 + 150
      NPPLS1 = NPTS(I) + 1
      IF(LNO4.LT.NPPLS1) GO TO 745
      LNO4 = FNO4 + 100
      IF(LNO4.LT.NPPLS1) GO TO 745
      LNO4 = FNO4 + 50
      IF(LNO4.LT.NPPLS1) GO TO 745
      LNO4 = FNO4
  745 CONTINUE
C
      GO TO (747,749,751,753), TYPLOT
C
  747 WRITE(3,748) (X(J),Y(J), J=FNO4,LNO4,50)
  748 FORMAT(' ',F6.1,' ',F7.3,5X,F6.1,' ',F7.3,5X,F6.1,' ',F7.3,5X,
     1F6.1,' ',F7.3)
      GO TO 755
C
  749 WRITE(3,750) (X(J),Y(J), J=FNO4,LNO4,50)
  750 FORMAT(' ',F6.0,' ',F7.3,5X,F6.0,' ',F7.3,5X,F6.0,' ',F7.3,5X,
     1F6.0,' ',F7.3)
      GO TO 755
C
  751 WRITE(3,752) (X(J),Y(J), J=FNO4,LNO4,50)
  752 FORMAT(' ',F6.1,' ',F7.1,5X,F6.1,' ',F7.1,5X,F6.1,' ',F7.1,5X,
     1F6.1,' ',F7.1)
      GO TO 755
C
  753 WRITE(3,754) (X(J),Y(J), J=FNO4,LNO4,50)
  754 FORMAT(' ',F6.0,' ',F7.1,5X,F6.0,' ',F7.1,5X,F6.0,' ',F7.1,5X,
```

```
     1F6.0,' ',F7.1)
C
C
  755 CONTINUE
  760 CONTINUE
C           GO DOWN TO PLOT POINTS
C
C
C
C           NOW PLOT THE POINTS, IF THIS IS FIRST SPECTRUM (U=1) OF MORE THAN ONE
C           ON THE SAME PLOT, USE STATEMENTS WHICH ALSO WRITE LABELS.  OTHERWISE
C           USE STATEMENT WHICH MERELY PLOTS POINTS.
  770 IF(U.GT.1) GO TO 790
C
C
C           THIS IS THE FIRST SPECTRUM OF THIS PLOT, SPECIFY THE PLOTTING
C           SYMBOL SIZE (KSIZE) FIRST.  IF KSIZE HAS NOT BEEN SPECIFIED, IT WILL
C           EQUAL 0, IF THIS IS SO SET IT EQUAL TO .50.
      IF(KSIZE.GT.0) GO TO 775
C
      KSIZE = .05
C           TELL THE PLOTTER WHICH SIZE PLOTTING SYMBOL TO USE
  775 CONTINUE
      CALL ORIGIN(KSIZE,BB,5)
C           NOW PLOT THE POINTS OF THE FIRST SPECTRUM AND WRITE LABELS.
C
C           SPECIFY THE PLOTTING SYMBOL
      KS = 4
C
C           IF THE PLOTTING MODE HAS NOT BEEN SPECIFIED, IT WILL EQUAL 0, IF THIS
C           IS TRUE, SET IT EQUAL TO 1.
      IF(MODE.GT.0) GO TO 780
C
C           MODE HAS NOT BEEN SPECIFIED, SET IT EQUAL TO 11.
      MODE = 11
C
C           PLOT THE POINTS AND WRITE LABELS ON THE GRAPHS.
```

```
  780 CONTINUE
      CALL GRAPH(NP,X,Y,KS,MODE,XSIZE,YSIZE,XSF,XMIN,YSF,YMIN,XLAB,YLAB,
     1           GLAB1,GLAB2)
C
C          IS EXTRA GRAPH LABELING DESIRED?
      IF(EXLAB.LT.1) GO TO 785
C
C          EXTRA GRAPH LABELING IS DESIRED, WRITE IT ON THE GRAPH.
      CALL LETTER (XO3,YO3,HEIGHT,GLAB3,THETA,NCHAR3,0,0,0,0,0,0,0,0,0,
     1             0)
      CALL LETTER (XO4,YO4,HEIGHT,GLAB4,THETA,NCHAR4,0,0,0,0,0,0,0,0,0,
     1             0)
  785 CONTINUE
C          THE FIRST SPECTRUM OF THIS PLOT HAS BEEN PLOTTED, GO TO COMPLETION
C          OF THIS LOOP.
      GO TO 800
C
C
C          THIS IS A SUPERPOTITION OF A SPECTRUM ON A GRAPH.  FIRST SPECIFY
C          A DIFFERENT PLOTTING SYMBOL
  790 KS = KS - 1
C          MAKE CERTAIN THAT KS IS NEVER LESS THAN 1.
      IF(KS.GT.0) GO TO 795
C
C          KS IS LESS THAN 1, SET IT EQUAL TO 1.
      KS = 1
C
C          NOW PLOT THE SUPERPOTITION.
  795 CONTINUE
      CALL GRAPH(NP,X,Y,KS,MODE,0,0,0,0,0,0,0,0,0,0)
C
C          SUPERPOTITION HAS BEEN PLOTTED,  GO TO COMPLETION OF THIS LOOP.
C
  800 CONTINUE
C          GRAPH HAS BEEN COMPLETED, GO TO COMPLETION OF OUTER LOOP TO
C          START THE NEXT GRAPH.
C
```

```
  820 CONTINUE
C          ALL PLOTS HAVE BEEN COMPLETED, TIME TO QUIT.
C
  900 CONTINUE
C
C
      STOP
      END
      SUBROUTINE MATCH
C
C               SUBPROGRAM PROVIDES INSTRUCTIONS FOR MATCHING
C               OVERLAPPING PARTS OF SPECTRA
C
      INTEGER*2 NCARDS, NINSTR,TYPINS,FRSTNO,LASTNO,DUMWAV,DUMABS,
     1          II,ID,ABSADD
      COMMON /HOLD/NCARDS(30),NINSTR(30),DUMWAV(1000),DUMABS(1000),
     1          TYPINS(100), FRSTNO(100), LASTNO(100), ABSADD(100),
     1         II(150),ID
      KK=NCARDS(ID)
      DO 5 J=1,KK
C
C               WILL MAKE A MATCH WHENEVER THERE IS A 1 IN COLUMN 80 OF DATA
C               CARD
C
      IF(II(J).EQ.0) GO TO 5
   10 NPH=7*J+2
      NST=NPH
      NPL=7*J-8
   30 CONTINUE
      IF(DUMWAV(NPH).EQ.0)GO TO 20
      IF(DUMABS(NPH).LT.-40.OR.DUMABS(NPH).GT.2000)GO TO 20
      GO TO 25
   20 NPH=NPH+1
      GO TO 30
   25 CONTINUE
      IF(DUMWAV(NPL).EQ.0)GO TO 21
      IF(DUMABS(NPL).LT.-40.OR.DUMABS(NPL).GT.2000)GO TO 21
```

```
      GO TO 35
   21 NPL=NPL-1
      GO TO 25
   35 CONTINUE
      IF (DUMWAV(NPH)-DUMWAV(NPL))40,50,60
   50 NINSTR(ID)=NINSTR(ID)+1
      L=NINSTR(ID)
      TYPINS(L)=1
      FRSTNO(L)=NST
      LASTNO(L)=999
      ABSADD(L)=DUMABS(NPL)-DUMABS(NPH)
      GO TO 5
   60 NPL=NPL-1
      GO TO 35
   40 CONTINUE
C
C              MAKES SURE THERE IS OVERLAP
C
      IF(DUMWAV(NPH)-DUMWAV(NPL+1))100,101,102
  100 WRITE(3,1)DUMWAV(NPL)
    1 FORMAT('0','NO OVERLAP AT ',I5)
      GO TO 5
  101 NPL=NPL+1
      GO TO 50
  102 NHH=NPL+1
C
C              DOES EXTRAPLOLATION
C
      DIFFLG=DUMWAV(NHH)-DUMWAV(NPL)
      DIFFSM=DUMWAV(NHH)-DUMWAV(NPH)
      DIFFAB=DUMABS(NHH)-DUMABS(NPL)
      CORR=DUMABS(NHH)-(DIFFAB*(DIFFSM/DIFFLG))
      NINSTR(ID)=NINSTR(ID)+1
      L=NINSTR(ID)
      TYPINS(L)=1
      FRSTNO(L)=NST
      LASTNO(L)=999
```

```
      ABSADD(L)=CORR-DUMABS(NPH)
    5 CONTINUE
      RETURN
      END
      SUBROUTINE SUBTRT
      INTEGER*2 NCARDS, NINSTR,TYPINS,FRSTNO,LASTNO,DUMWAV,DUMABS,
     1          II,ID,ABSADD
      COMMON /HOLD/NCARDS(30),NINSTR(30),DUMWAV(1000),DUMABS(1000),
     1          TYPINS(100), FRSTNO(100), LASTNO(100), ABSADD(100),
     1         II(150),ID
      CORR=-DUMABS(2)
      NINSTR(ID)=NINSTR(ID)+1
      L=NINSTR(ID)
      TYPINS(L)=1
      FRSTNO(L)=1
      LASTNO(L)=999
      ABSADD(L)=CORR
      RETURN
      END
```