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The Absorption Spectrum and Dichroism of Potassium Tetrachloroplatinate(II) Crystals. II[1,2]

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Absorption spectra of single crystals with light polarized parallel to (z) and perpendicular to (x,y) the fourfold symmetry axis of the $PtCl_4^{-2}$ ions in K_2PtCl_4 at room temperature and at liquid helium temperature (15°K.) have been recorded. Vibrational fine structure has been observed in some of the bands. A transition scheme is proposed on the basis of energy-level calculations, which include electron–electron repulsions and spin–orbit coupling, for which the ordering of the 5d orbitals is: $d^*_{x^2-y^2} > d_{xy} > d_{xz}, d_{yz} > d_{z^2}$. It is proposed that a number of excited states do not have the square-planar equilibrium arrangement of the ground state. Correlation with the states in a tetrahedral arrangement is presented. Transitions to the states which have a higher energy in square-planar than in tetrahedral geometry appear to have much more poorly resolved vibrational structure at 15°K.

Introduction

In the square-planar ion $PtCl_4^{-2}$ with the d^8 configuration the $d_{x^2-y^2}$ orbital is considered to be utilized for bonding, and the eight electrons occupy the four other d orbitals. The lowest unfilled orbital is then the antibonding orbital involving $d_{x^2-y^2}$ with b_{1g} symmetry. The ground state is described on the two-hole designation as $^1(b_{1g}b_{1g})$ or $^1A_{1g}$. Intense absorption above 36,000 cm.$^{-1}$ has generally been ascribed to charge-transfer bands and absorptions at lower energies to transitions in which electrons from other d orbitals are excited to the b_{1g}^* orbital. In solutions of K_2PtCl_4 (spectrum presented in ref. 2) four absorption regions can be recognized. Four different possibilities for the transition assignments of these absorptions, suggested by Chatt, Gamlen, and Orgel,[3] Fenske, Martin, and Ruedenberg,[4] Gray and Ballhausen,[5] and Martin and Lenhardt,[2] are included in Table I together with the observed $\bar{\nu}_{max}$, molar extinction coefficient, and oscillator strength from a Gaussian analysis of the solution spectrum. Differences in the assignments have arisen from different orderings of the d orbitals in the square-planar ions. In Figure 1 is shown the familiar splitting of the d orbitals under an octahedral "crystal field" into the higher e_g and lower t_{2g} groups of orbitals. As an increasing tetragonal distortion is impressed upon the system, the possible arrangements A, B, and C arise, and all three possibilities have been included in the various assignments listed in Table I. Another ambiguity arises from the question of whether the transition at *ca.* 21,000 cm.$^{-1}$ is spin-allowed or forbidden. It is definitely less intense than the peaks at 25,400 and 30,300 cm.$^{-1}$, having an oscillator strength only 0.3 and 0.2, respectively, of these, but it is still approximately an order of magnitude more intense than the questionable transition at about 18,000 cm.$^{-1}$. A heavy element, such as platinum, will have a high spin–orbit interaction which is expected to mix the different spin states so that relatively intense spin-forbidden bands may occur. A value of 4060 cm.$^{-1}$ for the spin–orbit coupling parameter of platinum, ζ, obtained from the atomic spectrum, was included in the tabulation of McClure,[6] who also commented that the parameters are generally somewhat smaller for coordination complexes than for the free atoms.

TABLE I

ABSORPTIONS IN THE SPECTRUM OF AQUEOUS $PtCl_4^{-2}$ (25°)

Peak	$\bar{\nu}_{max}$, cm.$^{-1}$	Extinction coeff. ϵ_{max}	Oscil. strength × 10^4	Assignment of excited state Ref. 3	Ref. 4	Ref. 5	Ref. 2
1	17,200	(2)	(0.3)	$^3A_{2g}$		$^3A_{2g}$	
2	21,000	15	2.8	^3E_g	($^3A_{2g}$ $^3B_{1g}$)	$^1A_{2g}$	$^1B_{1g}$
3	25,400	57	7.3	$^1A_{2g}$	$^1A_{2g}$	$^1B_{1g}$	$^1A_{2g}$
4	30,300	62	12	^1E_g	$^1B_{1g}$	^1E_g	^1E_g

In an earlier publication from this laboratory[2] the absorption spectrum for a single crystal of KPt_2Cl_4 was reported for light which was polarized both in the direction parallel to the tetragonal symmetry axis of the crystal and of the individual $PtCl_4^{-2}$ ions (designated as z or $\|$) and in the direction normal to the z axis and in the plane containing the square ions (designated x,y or $\perp$).

Absorption maxima in x,y polarization were found in the region of each of the strongest peaks of the solution spectrum whereas the central one of the three most intense transitions was missing in the z polarization. The energies of the peaks had been shifted somewhat in the crystals and indeed were significantly shifted between the two polarizations. The present paper presents an extension of the earlier work in that improvements in techniques have provided more reliable spectra over a broader wave length range. In addition, spectra, recorded for crystals at 15°K., have provided considerable additional information to assist in the transition assignments.

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[1] Contribution No. 1723. Work performed in the Ames Laboratory of the Atomic Energy Commission.

[2] No. I of the series: D. S. Martin, Jr., and C. A. Lenhardt, *Inorg. Chem.*, **3**, 1368 (1964).

[3] J. Chatt, G. A. Gamlen, and L. E. Orgel, *J. Chem. Soc.*, 486 (1958).

[4] R. F. Fenske, D. S. Martin, Jr., and K. Ruedenberg, *Inorg. Chem.*, **1**, 441 (1962).

[5] H. B. Gray and C. J. Ballhausen, *J. Am. Chem. Soc.*, **85**, 260 (1963).

[6] D. S. McClure, *Solid State Phys.*, **9**, 399 (1959).

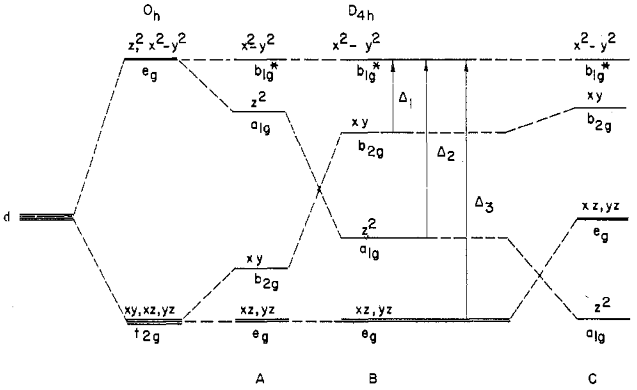

Figure 1.—Possible ordering of the 5d orbital energies as a tetragonal distortion is applied to an octahedral coordination.

Experimental

The thin crystal in the earlier work[2] was broken and several crystals, somewhat thicker than the former specimen, were selected for this study. One crystal was found to weigh 0.357 ± 0.001 mg. on a Cahn microelectrobalance. Its dimensions were determined by a Cambridge Measuring Instrument, from which its area was calculated to be 2.24 ± 0.02 mm.^{2}. From the handbook density of 3.30 g./cm.^{3} its thickness was therefore indicated to be 48 μ or 3.84×10^{-2} M cm. The thicknesses of other crystals were determined by comparison of their absorption spectra with that of this crystal. The difference between the optical density of the maximum at 20,200 cm.$^{-1}$ (z) or 20,400 cm.$^{-1}$ (x,y) and the optical density at 16,667 cm.$^{-1}$ was taken proportional to the thickness of a crystal. Consistent results were obtained with either x,y or z polarizations.

Crystals were cemented by a thinned varnish over holes, 0.025–0.030 in. in diameter, drilled in $^1/_{32}$-in. aluminum sheets. For the measurements at liquid helium temperature the aluminum sheet bearing the crystal was pressed by spring clips into the recess of a copper support frame. The copper frame had been machined from a solid rod which served as the bottom of the liquid helium well of a cryostat which in turn was surrounded by a polished copper radiation shield. Holes in the radiation shield and the copper frame together with silica windows in the outer wall permitted the light to pass through the crystal, which was mounted close to the slit image in the sample compartment of a Cary Model 14 spectrophotometer. With the cryostat evacuated, no fogging of windows occurred and a charge of liquid helium could be maintained for the 2–3 hr. needed for the measurements. Although it was not used in these studies, a thermocouple attached near the sample recess of the copper block had previously indicated a temperature of 15°K. when the cryostat was charged with helium, and this value is taken as a nominal temperature for the spectra.

Modifications in instrumentation from the earlier work included the following. The reference beam in the spectrophotometer was generally stopped down by a hole drilled in a metal plate. A Glan-polarizer, matching the unit in the sample beam, was placed in the reference beam. It was then possible to balance out some weak absorption bands in the polarizer which were observable at wave lengths greater than 550 mμ. Also, a high-intensity source, Cary Model 1471200, was used over the visible and most of the ultraviolet region.

Results

The spectra recorded for two different crystals at 298 and 15°K. with z and xy polarization are shown in Figures 2 and 3. In these figures the results have been reported as molar extinction coefficients which were calculated from the crystal thicknesses. The spectrum of a thick crystal (0.55 mm. thick as indicated by a micrometer) was recorded at room temperature in the red and infrared region without polarization. This crystal was mounted over a 0.030-in. diameter hole, and an optical density from 8000 to 16,100 cm.$^{-1}$ could be recorded with no pinhole in the reference beam. From 8000 to 14,300 cm.$^{-1}$ there was no change in absorption corresponding to a molar extinction coefficient as great as 0.01 cm.$^{-1}$ M^{-1}. At 16,100 cm.$^{-1}$, ϵ had increased to 0.7 cm.$^{-1}$ M^{-1}. The values plotted for ϵ in Figures 2 and 3 have been calculated on the basis ϵ = 0.0 M cm.$^{-1}$ at $\bar{\nu}$ = 12,500 cm.$^{-1}$.

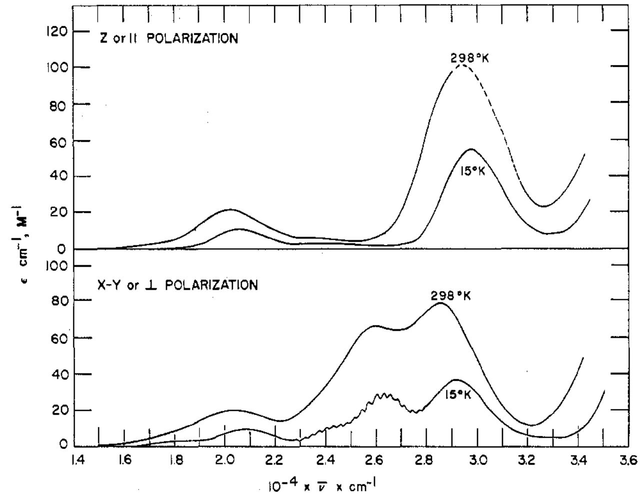

Figure 2.—Absorption spectra of a K_2PtCl_4 crystal with polarized light; crystal thickness 46.5 μ.

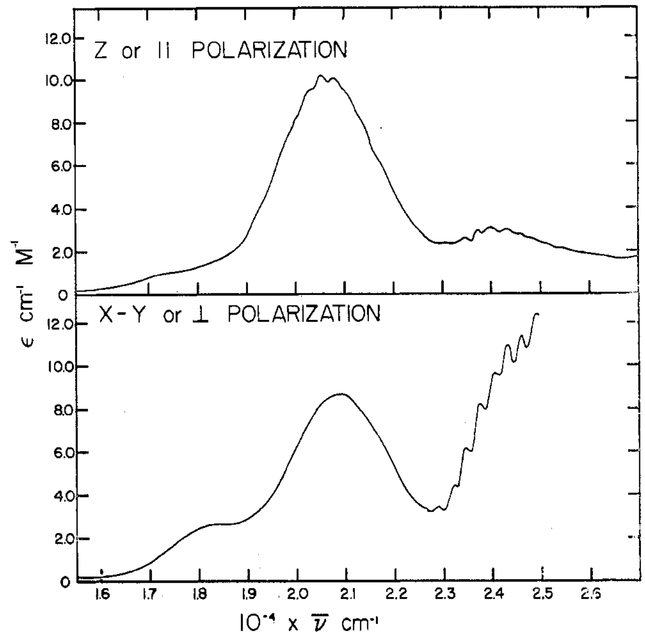

Figure 3.—Absorption spectra of a K_2PtCl_4 crystal with polarized light at 15°K.; crystal thickness 113 μ.

Figure 2 is for the thinner crystal. However, it was sufficiently thick that the spectrophotometer slits opened completely over the region of the dashed curve in z polarization at 298°K. The curves for 298°K. are in substantial agreement with respect to relative intensities and peak energies with the earlier work.[2]

Polarized absorption spectra for K_2PtCl_4 as well as for some related compounds at room temperature have been recently reported by Day, Orchard, Thompson, and Williams.[7] The locations of the major peaks of their spectra are in excellent agreement with ours at room temperature. In addition, very good agreement has been obtained for the intensities (ϵ) of the peak at about 20,300 cm.$^{-1}$ in each polarization. However, the peak heights of the present spectra were somewhat greater for the higher energy transitions at shorter wave lengths. This feature may reflect the somewhat higher resolution which is evident by the appearance of a maximum rather than a shoulder for the transition at about 25,700 cm.$^{-1}$.

It is apparent that the intensity of each major transition was reduced by a factor of approximately 0.3 to 0.5 at 15°K. In addition, the bands were significantly narrower and the maxima had shifted to higher energies at the lower temperatures.

One of the most striking features of the low-temperature spectra was the resolution of vibrational structure in the absorption bands over the region 22,300 to 27,000 cm.$^{-1}$ for the x,y polarization. Some 18 maxima can be resolved in this region. In addition, a weak transition band at about 24,000 cm.$^{-1}$ in x,y polarization is now clearly evident. In retrospect, it can be seen that this transition corresponds in energy to a very weak absorption which is discernible in the z polarization of the room temperature spectra, but it fell under the edge of the band with maximum at 25,700 cm.$^{-1}$ in x,y polarization. In contrast to the above, not the slightest structure could be discerned in the largest absorption bands in the region of 28,000–31,000 cm.$^{-1}$ for either polarization.

Figure 3 presents spectra for a thicker crystal which was used to give higher absorption intensities in the long wave length region. In these curves structure is clearly evident in the z or $\|$ polarization peak near 20,600 cm.$^{-1}$, although it is much less pronounced than in regions above 23,000 cm.$^{-1}$. For the x,y or $\perp$ polarization the structure was even fainter and only barely evident. The transition at 24,000 cm.$^{-1}$ in z polarization is clearly evident for this crystal and in consideration of the weakness of the transition exhibits a strong structuring. It is clear that there is a weak absorption band centered at 18,000 cm.$^{-1}$ in x,y or $\perp$ polarization. Fine structure was weakly evident in this region. The absorption in z polarization at this wave length is much weaker still; however, there is a greater intensity of absorption increasing from 15,000–19,000 cm.$^{-1}$ than corresponds to the tail of a Gaussian peak centered about 20,600 cm.$^{-1}$.

The energies of the transitions indicated from Figures 2 and 3 have been tabulated in Table II for 15 and 298°K. Also, the extinction coefficients for the absorption maxima have been included. With so large a number of transitions which overlap considerably, only very approximate intensities can be estimated for the bands. Such estimates, which were obtained from the integration of Gaussian components into which the spectra of Figures 2 and 3 were resolved, are included as the oscillator strengths in Table II.

TABLE II

ABSORPTION ENERGIES AND INTENSITIES FROM THE SPECTRA OF K_2PtCl_4 CRYSTALS[a]

$\bar{\nu}_{\text{max}}$, cm.$^{-1}$		Extinction coefficient, M^{-1} cm.$^{-1}$		Oscillator strength × 10^4	
z or $\|$	x,y or $\perp$	z or $\|$	x,y or $\perp$	z or $\|$	x,y or $\perp$
17,000–19,000	...	<1	...	...	...
...	18,000	...	2	...	0.2
20,600	20,900	10	8.7	1.2	1.0
(20,200)	(20,400)	(20)	(18)	(2.9)	(3.0)
24,100	24,000	3	7.1	0.4	0.5
(23,700)	(23,400)	(5)	(9?)	(0.8)	(0.8)
...	26,300	...	28	...	(3.2)
(...)	(25,700)	(...)	(62)	(...)	(9.0)
29,800	29,200	55	37	7.1	5
(29,300)	(28,700)	(101)	(74)	(15.4)	(10.2)

[a] The values without parentheses are for 15°K. and the values in parentheses are for 298°K.

Discussion

Transitions between the even (or gerade) states of the $PtCl_4^{-2}$ ion are forbidden for dipole radiation. Crystals of K_2PtCl_4 are especially advantageous for studies of the electronic spectra since in this crystal each Pt atom occupies a site with the full D_{4h} symmetry.[8] Static crystal fields, therefore, cannot introduce the asymmetries necessary to provide the observed intensities for the bands.

A vibronic model for the electronic states will account for the observed spectra in centrosymmetric ions since the asymmetric vibrations remove the inversion center and permit the mixing of symmetric and asymmetric wave functions. For vibronic model considerations the interactions of one $PtCl_4^{-2}$ ion with other ions in the crystal have been neglected. Such an assumption appears reasonable in view of the close similarity between the solution and the room-temperature crystal spectra. Further, since there is only one $PtCl_4^{-2}$ ion per unit cell no Davydov splitting of the absorption bands can occur.

If Q_i designates an asymmetric normal vibration coordinate, then according to first-order perturbation theory the electronic wave function is expressed as[9]

$$\psi_{\text{elect}} = \psi_{\text{g}} - \sum_{i} \sum_{\psi_{\text{u}}} cQ_i\psi_{\text{u}} \tag{1}$$

where ψ_{g} is the unperturbed wave function, ψ_{u} is an asymmetric wave function, and

$$c = \int \psi_{\text{g}}^* \frac{\partial H}{\partial Q_i} \psi_{\text{u}} \, d\tau / (E_{\text{u}} - E_{\text{g}}) \tag{2}$$

The product $Q_i\psi_{\text{u}}$ is required to possess the symmetry properties of ψ_{g}. In accordance with the Born–Oppenheimer approximation the total wave function, Ψ, is written as the product

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[7] P. Day, A. F. Orchard, A. J. Thompson, and R. J. P. Williams, *J. Chem. Phys.*, **42**, 1973 (1965).

[8] R. G. Dickinson, *J. Am. Chem. Soc.*, **44**, 2404 (1922).

[9] (a) W. Moffitt and C. J. Ballhausen, *Ann. Rev. Phys. Chem.*, **7**, 107 (1956); (b) C. J. Ballhausen, *Progr. Inorg. Chem.*, **2**, 251 (1960); A. D. Liehr, *Advan. Chem. Phys.*, **5**, 241 (1963).

$$\Psi = \psi_{\text{elect}}\chi \tag{3}$$

where $\chi(\ldots Q_j \ldots Q_i \ldots)$ is the vibrational wave function for the nuclei. The transition moment for a dipole process from an initial (lower) state Ψ'' to a final state Ψ' becomes

$$\int \Psi''^{*}\mathrm{r}\Psi'\,\mathrm{d}\tau = \sum_i \int \sum_{\mathrm{u}} [(c''\psi_{\mathrm{u}}'')^{*}\mathrm{r}\psi_{\mathrm{g}}' + \psi_{\mathrm{g}}''^{*}\mathrm{r}c'\psi_{\mathrm{u}}']\,\mathrm{d}\tau_{\text{elect}} \int \chi'' Q_i \chi''\,\mathrm{d}\tau_{\text{vib}} \tag{4}$$

The vibrational wave functions can be represented as a product of the wave functions of all the individual normal vibrations

$$\chi = \prod_j \chi_j \tag{5}$$

The transition moment will therefore contain nonzero terms, and low intensities are permitted for the "symmetry-forbidden" transitions. Symmetry coordinates for the vibrations of the $PtCl_4^{-2}$ ion were given in ref. 2, and the symmetries of the various vibrations together with frequencies assigned for the electronic ground state from recent Raman and infrared studies are given in Table III. In case the product $\psi''^{*}\psi' Q_i$ contains a basis function for the representation a_{2u}, which characterizes z, polarization with the electric vector in the z direction ($\|$) will be possible as a consequence of this vibration. If the product $\psi''^{*}\psi' Q_i$ contains a basis function for the e_u representation, which characterizes x,y, polarization in the plane of the ions ($\perp$) will occur.

TABLE III

VIBRATIONS FOR THE $PtCl_4^{-2}$ ION WITH D_{4h} SYMMETRY

Vibration[a]	Symmetry[a] representation	$\bar{\nu}$, cm.$^{-1}$	Determination
Q_1	α_{1g}	335	Raman[b]
Q_2	α_{2u}	175	Infrared[c,d]
Q_3	β_{2g}	164	Raman[b]
Q_4	β_{2u}	. . .	Inactive
Q_5	β_{1g}	304	Raman[b]
$Q_{6a,b}$	ϵ_u	325	Infrared[c,d] (primarily str.)
$Q_{7a,b}$	ϵ_u	193	Infrared[c,d] (primarily bend.)

[a] The enumeration of the vibrations follows that of A. Maccoll, *J. Proc. Roy. Soc. N.S. Wales*, **77**, 130 (1944). However, in the present work the symmetry designations are based on a choice of x and y axes which pass through the ligand sites. [b] H. Stammreich and R. Forneris, *Spectrochim. Acta*, **16**, 363 (1960). [c] A. M. Adams and H. A. Gebbie, *ibid.*, **19**, 925 (1963). [d] A. Sabatini, L. Sacconi, and V. Schettino, *Inorg. Chem.*, **3**, 1775 (1964).

The vibronic model predicts that under very favorable circumstances, fine structure for the absorption bands will be resolvable at temperatures approaching absolute zero. In such instances the $PtCl_4^{-2}$ ion will be in the lowest state of each of the nine vibrations for the electronic ground state. Presumably, the potential energy for each vibration can be represented by a parabolic function. Because of the zero-point energy, the vibration Q_i may still effectively excite the transition to an excited electronic state. If the potential function for the vibration, Q_i, has exactly the same force constants in the ground and the excited electronic states, the form of eq. 4 requires the rigorous selection rule $\Delta n_i = +1$ for the Q_i vibration. The transition will therefore carry Q_i into its first excited state in the higher electronic state as shown in Figure 4C. Now if another vibration Q_j also has potential functions with the same force constant and location of minimum for the two electronic states, eq. 4 requires that $\Delta n_j = 0$. The vibration Q_j will be carried into the ground vibrational state of the upper electronic state as shown in Figure 4B. For the totally symmetric stretching vibration, Q_1 (α_{1g}), it is anticipated that the equilibrium internuclear distances will be considerably greater in the excited state than in the ground state. It is expected, therefore, from the Franck–Condon principle that transitions to a number of highly excited states for the Q_1 vibration will occur. These situations have been illustrated in Figure 4A. The transition with the greatest probability will have approximately the energy of the "vertical transition" from the minimum of the lower potential curve to the upper curve. Transitions to higher or lower vibrational states will be the less probable as the energy separation increases.

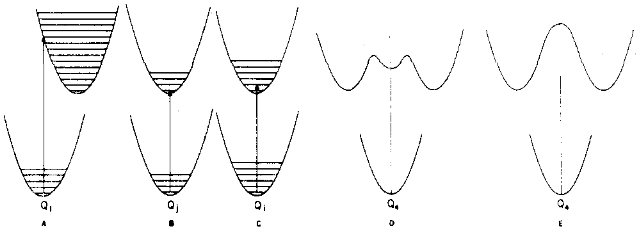

Figure 4.—Possible potential energy curves of ground and excited electronic states for various vibrational modes of a square-planar $PtCl_4^{-2}$ ion: A, for the totally symmetric stretching vibration, Q_1–α_{1g} (harmonic); B, for a Q_i vibration not involved in the vibronic excitation (harmonic with identical equilibrium coordinates and force constants for the ground and excited electronic states); C, for a Q_i vibration involved in a vibronic excitation (asymmetric and harmonic with identical force constants for the ground and excited electronic states); D, E, possible potential functions for the Q_4–β_{2u} vibration which carries the square-planar $PtCl_4^{-2}$ ion toward tetrahedral configurations with a lower energy.

A number of conditions may serve to reduce the vibrational structure which will be observed in an absorption band. For example, more than one asymmetric vibration with different frequencies might contribute to a band. Then since the energy $\bar{\nu}_i$ is added to each transition energy, there would be a separate series for each vibration. The corresponding members of two series would be separated by the differences in the $\bar{\nu}_i$ values, and a poorer resolution of the more closely spaced peaks would result. Of course, even if several vibrations should have nonzero transition moments, one of the vibrations might predominate so a fine structure would still be resolved. Also, as the absorption bands overlap it is expected that interference will reduce resolvable structure except for the rather unlikely circumstance that the energy differences of the vibrational levels of the different excited states should be in phase.

If the excited electronic state has a potential function different from that of the ground state the rigorous selection rules will fail. If the two states have only differing harmonic force constants, transitions will be possible for $\Delta n_i = 1, 3, 5\ldots$ and $\Delta n_j = 0, 2, 4\ldots$, although if the differences between the force constants are small, the probability of the transitions will fall off rapidly as the Δn values increase.

In an extreme case, the equilibrium configuration of the excited state might not be a planar-square arrangement at all. The Q_4 (β_{2u}) vibration carries the $PtCl_4^{-2}$ ion toward a tetrahedral or T_d configuration. In the intervening region the ion possesses the D_{2d} symmetry. Ballhausen, *et al.*,[10] have commented that an electron in the b_{1g}^* orbital may well destabilize the square-planar arrangement in a d^8 complex. In such a case the potential function of the excited state might appear as shown in Figure 4D. In such a case separation of vibration levels would not be constant and transitions to several vibrational states would reduce the resolvable structure in the band. The extent of this reduction would depend strongly on the barrier height and under some circumstances the structure might well disappear.

With the extreme case shown in Figure 4E the vibronic selection rules might fail completely for the transition. This is the situation proposed by Ballhausen, *et al.*,[10] to account for the polarized spectra of $Ni(CN)_4^{-2}$ ions where a peak, polarized in only the z direction, was encountered. They noted that such a polarization cannot occur by a vibronic model, but that it was possible if the transition terminated on a potential surface where the stable configuration was a distorted tetrahedron.

Finally, it should be noted that if an excited state is degenerate, the Jahn–Teller effect requires the potential function of the Q_3 (β_{2g}) as well as of the Q_5 (β_{1g}) vibrations to have minima which are displaced from the square-planar arrangement. In case of a strong Jahn–Teller effect, therefore, the Franck–Condon principle will require transitions to excited vibrational levels for the Q_3 and for the Q_5 vibrations as well as the Q_1 vibration with an almost certain reduction in the observed structure. On the other hand, should the Jahn–Teller effect be sufficiently small in the excited state, at least some fine structure might be observable.

At sufficiently high temperatures higher vibrational states of the electronic ground state are excited. In even the most favorable cases the selection rule for the exciting asymmetric vibration becomes $\Delta n_i = \pm 1$. There is in general a broadening of the bands. If the same conditions apply which permit the fine structure at low temperature as listed above, the oscillator strength for a band is given by the equation[11]

$$f(T) = f(T = 0) \coth (h\nu_i/2kT) \qquad (6)$$

where ν_i is the frequency of the exciting asymmetric vibration.

The vibronic model with the type of potential functions illustrated in Figure 4A, B, C accounts very well for the sort of fine structure which appeared at 15°K. for the transition with x,y polarization centered on 26,300 cm.$^{-1}$ and the transition at 24,000 cm.$^{-1}$ in both polarizations. The average separation between ten peaks from 25,440 to 27,780 cm.$^{-1}$ is 290 cm.$^{-1}$. The average for the 9 peaks in both z and x,y polarization from 22,880 to 25,150 cm.$^{-1}$ is 280 cm.$^{-1}$. For the region from 19,190 to 21,880 cm.$^{-1}$, involving 11 poorly resolved lines in z polarization, the average separation is 270 cm.$^{-1}$. There was no observable trend in the line separations with energy and hence only a small anharmonicity, at most, is indicated for the totally symmetric stretching vibration of these excited states. These observed vibrational frequencies, as expected, are of the same order of magnitude but somewhat smaller than the stretching frequency of 335 cm.$^{-1}$ for Q_1 of the ground electronic state (see Table III).

At 298°K. the oscillator strength of each band, which can be estimated satisfactorily, appears to be 2.0–3.0 times the intensity for 15°K. Such intensity ratios correspond to vibrational frequencies ($\bar{\nu}_1$), calculated from eq. 6, of 220–140 cm.$^{-1}$. These values just cover the range of the bending frequencies of the ground state and thus lend credence to the vibronic model.

It is proposed that the absorption peaks, in which vibrational structure is resolved only poorly or not at all, are associated with transitions to excited states for which the potential function of an exciting vibration is of the type 4D. Before a consideration of some possible effects of such excited state distortions, it is necessary to remark on the source of the intensity for the weak peaks which presumably are spin-forbidden. Such transitions can occur because spin–orbit coupling mixes the singlet and triplet states. The large spin–orbit coupling in the heavy elements leads to relatively high intensities for such bands and will in addition, under D_{4h} symmetry, lead to separations of several thousand wave numbers for the states originating from the same triplets. Any satisfactory treatment must therefore include spin–orbit coupling.

A complete crystal field treatment of the d^8 problem with electron–electron interactions and spin–orbit coupling was presented by Fenske, *et al.*[4] In the two-hole formalism there are a total of 45 states to be considered. However, the states with the lowest energy and those which will make the greatest contribution to the intensities are the one-electron transfer states in which one electron has been excited from another orbital to the b_{1g}^*.

In the absence of the spin–orbit perturbation the ground state for $PtCl_4^{-2}$ can be designated as $^1(b_{1g}b_{1g})$–$^1A_{1g}$. The one-electron transfer states are then $^3(b_{1g}b_{2g})$–$^3A_{2g}$, $^1(b_{1g}b_{2g})$–$^1A_{2g}$, $^3(b_{1g}a_{1g})$–$^3B_{1g}$, $^1(b_{1g}a_{1g})$–$^1B_{1g}$, $^3(b_{1g}e_g)$–^3E_g, and $^1(b_{1g}e_g)$–^1E_g. If the total wave function is written as the product of the orbital part and the spin part, the symmetry of the total state will be given by the rules for products. The singlet spin functions

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[10] C. J. Ballhausen, N. Bjerrum, R. Dingle, K. Eriks, and C. R. Hare, *Inorg. Chem.*, **4**, 514 (1965).

[11] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 187.

transform as a_{1g} and the triplet functions consist of a_{2g} and e_g components in D_{4h} symmetry. We shall use Bethe's Γ notation[12] to represent the symmetry properties of the total wave function

$$(\Gamma_1 = a_{1g}, \Gamma_2 = a_{2g}, \Gamma_3 = b_{1g}, \Gamma_4 = b_{2g}, \Gamma_5 = e_g \text{ for } D_{4h})$$

It is the symmetry of the total wave functions which must be considered in the selection rules for polarized light. Under the simple vibronic model, since the ground state of $PtCl_4^{-2}$ belongs to Γ_1, the polarization rules for a transition to a square-planar excited state are determined by the product $(\psi')(Q_i)$. The polarizations excited in this way by the various asymmetric vibrations of $PtCl_4^{-2}$ are given in Table IV. From this table it is seen that transitions to Γ_2 and Γ_4 states are predicted to be polarized completely in x,y or $\perp$. Transitions to Γ_1 and Γ_3 have z or $\|$ polarizations excited by single out-of-plane bending vibrations and x,y or $\perp$ polarization excited by the ϵ_d (stretching and in-plane bending), whereas for Γ_5 transitions the z polarization is excited by the ϵ_u vibrations and the x,y polarization by the two out-of-plane bendings. Now the "spin-forbidden" transitions may occur because of triplet character which is mixed into the ground state and because of singlet character mixed into the excited states. It is to be noted that there is no one electron-transfer singlet state mixed into a Γ_4 state. Therefore transitions to the Γ_4 states may be expected to have moderately low intensities.

TABLE IV

POLARIZATIONS INDICATED FOR TRANSITIONS TO THE VARIOUS EXCITED STATES OF $PtCl_4^{-2}$ INDUCED BY THE ASYMMETRIC VIBRATIONS IN THE VIBRONIC MODEL

		Excited state				
		Γ_1	Γ_2	Γ_3	Γ_4	Γ_5
Vibration				Polarization		
Q_2	α_{2u}	z	. . .	. . .	. . .	x,y
Q_4	β_{2u}	. . .	. . .	z	. . .	x,y
Q_6, Q_7	ϵ_u	x,y	x,y	x,y	x,y	z

The strong field matrix elements for the d^8 states in a square-planar configuration published by Fenske, *et al.*,[4] were modified by replacing the crystal field parameters in an appropriate fashion by the quantities Δ_1, Δ_2, and Δ_3 as defined for the one-electron orbitals in Figure 1. These quantities could then be treated as arbitrary parameters together with the two Slater–Condon parameters F_2 and F_4 and the spin–orbit coupling parameter, $\alpha = {}^1/_2\zeta$. Energies of the various states were calculated for different values of these parameters from these matrices in an attempt to find agreement with the observed spectra. It was intended to keep F_2 and F_4 within reasonable limits indicated for other heavy element spectra and to have α sufficiently high to account for the intensities of the "spin-forbidden" transitions.

First, any attempt to bring the three primarily singlet states all below 30,000 cm.$^{-1}$ yielded many more transitions than were observed. Generally, in such attempts a number of transitions which should possess moderately high intensity fell into the region of 23,000 to 27,000 cm.$^{-1}$ where the fine structure indicated that probably only two states occur. For this reason neither assignments of ref. 5 or ref. 2 indicated in Table I seem satisfactory.

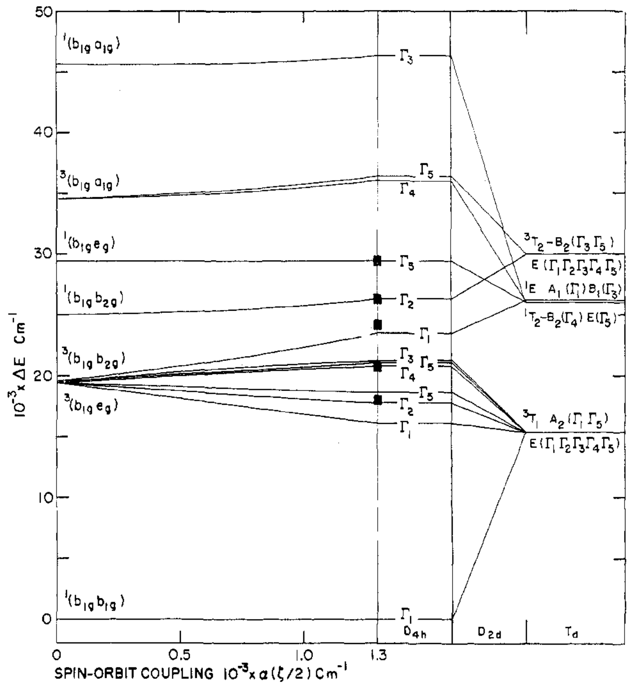

Figure 5.—The splitting of the square-planar electronic states by spin–orbit coupling with their D_{4h}–Γ designation and the correlation of the square-planar states with the tetrahedral states (without spin–orbit coupling). The representations of the orbital part of the tetrahedral states under the D_{2d} intermediate symmetry group are shown together with the Γ designations of the total wave functions under D_{2d}; $F_2 = 1200$, $F_4 = 65$, $\Delta_1 = 26{,}300$, $\Delta_2 = 51{,}000$, $\Delta_3 = 33{,}700$, and $\Delta_t = 17{,}000$ cm.$^{-1}$.

For the reasons discussed below the most satisfactory ordering of orbital energies was the one proposed by Chatt, Gamlen, and Orgel[3] (Figure 1C); and the results of the calculations for this level scheme are presented in detail. For the set of parameters Δ_1, Δ_2, Δ_3, F_2, and F_4 indicated in the caption, the energies of the various one-electron transfer states, which were calculated, are plotted as a function of the spin–orbit coupling parameter, α, on the left side of Figure 5. The absorption band centers, which were taken from the 15°K. spectra, are the points plotted in this figure. The energies calculated for the different states and the normalized eigenvector components for the one-electron transfer states are presented in Table V for α = 1300 cm.$^{-1}$. Each of the observed bands agrees closely with a calculated transition energy. Transition moments will include the sum of products of the eigenvectors for the ground state with the eigenvectors for the excited state which have the same spin eigenfunctions. The assignment scheme described in Table V and Figure 5 accounts for the following intensity features.

A very low absorption was observed in the region of

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[12] H. Bethe, *Ann. Physik*, **3**, 133 (1929).

Table V

Calculated Energy Levels and Eigenvector Components for the Ground-State and One-Electron Transition States of $PtCl_4^{-2}$ with Square-Planar Coordination for the Parameters: $\Delta_1 = 26{,}300$, $\Delta_2 = 51{,}000$, $\Delta_3 = 33{,}700$, $F_2 = 1200$, $F_4 = 65$, $\alpha = 1300$ cm.$^{-1}$

Representation of state	Transition energy, cm.$^{-1}$	Eigenvector lengths		
		Singlet states	Triplet states	
		a_{1g}	a_{2g}	e_g
Γ_3	46,285	$(b_{1g}a_{1g})$ 0.836		$(b_{1g}e_g)$ 0.097
Γ_5	36,441	$(b_{1g}e_g)$ 0.333	$(b_{1g}e_g)$ 0.151	$(b_{1g}a_{1g})$ 0.918
				$(b_{1g}b_{2g})$ 0.034
Γ_4	36,052		$(b_{1g}a_{1g})$ 0.971	$(b_{1g}e_g)$ 0.223
Γ_5	29,441	$(b_{1g}e_g)$ 0.904	$(b_{1g}e_g)$ 0.002	$(b_{1g}a_{1g})$ 0.030
				$(b_{1g}b_{2g})$ 0.080
Γ_2	26,348	$(b_{1g}b_{2g})$ 0.964		$(b_{1g}e_g)$ 0.264
Γ_1	23,482	$(b_{1g}b_{1g})$ 0.194	$(b_{1g}b_{2g})$ 0.731	$(b_{1g}e_g)$ 0.640
Γ_3	21,334	$(b_{1g}a_{1g})$ 0.123		$(b_{1g}e_g)$ 0.985
Γ_5	21,088	$(b_{1g}e_g)$ 0.090	$(b_{1g}e_g)$ 0.621	$(b_{1g}a_{1g})$ 0.118
				$(b_{1g}b_{2g})$ 0.743
Γ_4	20,836		$(b_{1g}a_{1g})$ 0.222	$(b_{1g}e_g)$ 0.968
Γ_5	18,701	$(b_{1g}e_g)$ 0.160	$(b_{1g}e_g)$ 0.778	$(b_{1g}a_{1g})$ 0.088
				$(b_{1g}b_{2g})$ 0.636
Γ_2	17,782	$(b_{1g}b_{2g})$ 0.256		$(b_{1g}e_g)$ 0.947
Γ_1	16,109	$(b_{1g}b_{1g})$ 0.001	$(b_{1g}b_{2g})$ 0.627	$(b_{1g}e_g)$ 0.746
Γ_1	0	$(b_{1g}b_{1g})$ 0.974	$(b_{1g}b_{2g})$ 0.153	$(b_{1g}e_g)$ 0.122

32,000–34,000 cm.$^{-1}$ of the spectrum. In the calculated level assignment there are no states between 29,500 and 36,000 cm.$^{-1}$. The Γ_4 and Γ_5 at 36,052 and 36,441 cm.$^{-1}$ correspond closely to the shoulder reported by Day, *et al.*,[7] in reflectance and solution spectra. The degenerate Γ_5 states at 29,400 cm.$^{-2}$ are primarily singlet states and should probably give the strongest band, which is seen at 29,800 (z) and 29,200 (x,y) cm.$^{-1}$. The Γ_2 at 26,300 cm.$^{-1}$ is also largely singlet and should be an intense transition polarized x,y, in close agreement with the observation. Close to the transition seen at *ca.* 24,000 cm.$^{-1}$ is the calculated Γ_1 at 23,500 cm.$^{-1}$. This state arises from the $^3(b_{1g}b_{2g})$, but it contains a considerable contribution from $^3(b_{1g}e_g)$ and lies at so high an energy because of the strong repulsion between the two Γ_1 states arising from these closely neighboring states. The peak occurring at 20,600 (z) and 20,800 (x,y) cm.$^{-1}$ is close in energy to calculated Γ_3, Γ_4, and Γ_5 states. At least a part of its somewhat anomalously high intensity for a spin-forbidden transition results from the combination of the four different states. Vibrational structure was weakly but clearly resolved in its z polarization. Since the Γ_4 transition would be polarized x,y, the interference of this additional state may be the cause for the reduction in the vibrational structure, which was barely discernible in x,y polarization. The Γ_2, calculated at 17,800 cm.$^{-1}$, lies close to an x,y absorption, and the much weaker absorption in z through this region can be attributed to the Γ_5 at 18,700 cm.$^{-1}$ and the Γ_1 at 16,100 cm.$^{-1}$. The singlet character of this Γ_1 at 16,100 cm.$^{-1}$ is so small that its intensity is undoubtedly low. From the low absorption below 15,000 cm.$^{-1}$, this first spin-forbidden state can probably not lie below 16,000 cm.$^{-1}$.

As Ballhausen, *et al.*,[10] have proposed, the ground state for a tetrahedral arrangement of a d^8 configuration may well lie below the excited states of the square-planar arrangement. The equilibrium coordination arrangement of ligands for a number of excited states therefore would not be square-planar. The $^3T_1$ ground state for the tetrahedral arrangement corresponds to nine separate eigenfunctions. As the ion moves from the tetrahedral through the intervening D_{2d} arrangement, each of the nine wave functions must serve as a basis function for a representation in this lower symmetry group and finally correlate with a state in the square-planar, D_{4h}, arrangement. Energy states with the same symmetry properties in D_{2d} cannot cross and the square-planar Q_4 vibrational potential energy curves must be of the type 4C or 4D if they correlate with a lower $^3T_1$ state in T_d symmetry.

A possible arrangement of the low states for the tetrahedral arrangement is shown in the right side of Figure 5. In addition to the T_d symmetry properties, the representation of the orbital part in D_{2d} is given and finally the representation of the combined spin–orbit functions in terms of the Γ designation for D_{2d}: $\Gamma_1 = a_1$, $\Gamma_2 = a_2$, $\Gamma_3 = b_1$, $\Gamma_4 = b_2$, and $\Gamma_5 = e$. Note that with the x and y axes which have been chosen for the square-planar arrangement the relevant D_{4h} representations correlate in the following manner: $\Gamma_1(D_{4h}) \rightarrow \Gamma_1(D_{2d})$, $\Gamma_2(D_{4h}) \rightarrow \Gamma_2(D_{2d})$, $\Gamma_3(D_{4h}) \rightarrow \Gamma_4(D_{2d})$, $\Gamma_4(D_{4h}) \rightarrow \Gamma_3(D_{2d})$, $\Gamma_5(D_{4h}) \rightarrow \Gamma_5(D_{2d})$. Thus the $^3T_1$ ground state, as indicated, includes A_2 and E orbital functions which further resolve into the nine states: $2\Gamma_1$, $1\Gamma_2$, $1\Gamma_3$, $1\Gamma_4$, and $2\Gamma_5$. With the $^3T_1$ state 15,500 cm.$^{-1}$ above the square-planar ground state the lowest nine states in D_{4h}, as shown in Figure 5, correlate with $^3T_1$. The first state in D_{4h} which must correlate with a higher state in T_d is the Γ_1 at 23,500 cm.$^{-1}$. This corresponds to the first of the two peaks in which the vibrational structure was well resolved and this Γ_1 state correlates with the ^1E excited state of the tetrahedron. This state together with $^1T_2$ which originates from the $^1(t_2{}^2)$ configuration is placed about 10,500 cm.$^{-1}$ above $^3T_1$ on the basis of the values of F_2 and F_4 used for the square-planar arrangement and a small interaction of $^3T_1$ and ^1E with higher states of the same symmetry. The other state with well-resolved vibrational structure, Γ_2, at 26,300 cm.$^{-1}$, correlates with $^3T_2$ in T_d which in Figure 5 is placed some 14,500 cm.$^{-1}$ above $^3T_1$. This state originates from $^3(et_2)$ in T_d. Since this state lies at approximately $-3F_2 + 15F_4 + \Delta_t$ above the ground state, a Δ_t of *ca.* 17,000 cm.$^{-1}$ is indicated. This value of Δ_t is required to place the $^3T_2$ well above the square-planar Γ_2 and is somewhat in excess of $^4/_9\Delta_1 = 11{,}700$ cm.$^{-1}$, which is required by the classical crystal-field models. A value of Δ_t that low would place $^3T_2$ very close to the ^1E and $^1T_2$ states. The strong peak at Γ_5 correlates with the lower $^1T_2$ and therefore the lack of vibrational structure would reasonably result.

The energy level scheme described by Table V and Figure 5 appears to account very satisfactorily for all the observed features of the spectra. The $^3T_1$ ground state in the T_d arrangement is fixed within rather narrow limits if it must lie below the $\Gamma_1(D_{4h})$ at 16,000 cm.$^{-1}$ and if the $^1E(T_d)$ must lies ignificantly above the $\Gamma_1(D_{4h})$ at 24,000 cm.$^{-1}$. Admittedly, the value of 15,500 cm.$^{-1}$ for $^3T_1(T_d)$ is somewhat arbitrary. The $^3T_1$ in the T_d arrangement is considerably higher than for $Ni(CN)_4^{-2}$, so it is not surprising that the tetrahedral arrangement is generally not formed in Pt^{II} complexes. This feature may also account for the fact that the type of anomaly found by Ballhausen, *et al.*,[10] for the $Ni(CN)_4^{-2}$ was not observed for $PtCl_4^{-2}$, and the vibronic selection rules for the square-planar arrangement seem generally valid.

According to the proposed scheme the energy of the d_{z^2} orbital is very low, as indicated by the high value of Δ_2. There are actually some two-electron states, which were omitted for clarity in Figure 5, in the vicinity of the 46,300 cm.$^{-1}$ Γ_3 state. A trial calculation was made with the $^1(b_{1g}a_{1g})$ state at about 36,000 cm.$^{-1}$. This inserted some moderately intense additional transitions to Γ_5 and Γ_4 states into the region of 23,000–27,000 cm.$^{-1}$ for which there was no evidence. The crossover of the a_{1g} and e_g levels, as illustrated in Figure 1C, is therefore rather extreme. This low energy of the a_{1g} orbital probably implies a considerable involvement of the 6s orbital with the $5d_{z^2}$ in this nonbonding orbital of the σ system. This is another feature whereby the Pt^{II} system appears to differ considerably from the Ni^{II}.

Also, since the peak at 20,600 (z)–20,900 (x,y) cm.$^{-1}$ is perhaps surprisingly strong even if it does include the four transitions to the four states (Γ_3, Γ_4, Γ_5), the possibility proposed earlier[2] that it might arise from the $^1(b_{1g}a_{1g})$ state was specifically considered. In such a case the presence of the Γ_3 in the same region from the $^3(b_{1g}e_g)$ yields two resolvable strong peaks under a reasonable spin–orbit coupling. Further spin-forbidden peaks would then be expected in the vicinity of 10,000 cm.$^{-1}$, whereas there were very low limits on any absorption between 8000 and 14,000 cm.$^{-1}$.

The failure of the rule $\Delta_t = {}^4/_9\Delta_1$ is perhaps not too disturbing in view of the covalency in the bonding. Perhaps it is only one of the predictions of the simple ion or dipole crystal field models which must be discarded. Such a model appears to exclude the crossover of the a_{1g} and e_g orbitals also.[4] The values of the parameters F_2 and F_4 appear to lie within reasonable limits under which these quantities can be inferred from interpretation of spectra for other systems. The value of $\alpha = 1300$ cm.$^{-1}$ is, as McClure predicted,[6] somewhat lower than the free-atom value of 2040 cm.$^{-1}$. In this model it is established within rather narrow limits by the observed splitting of the Γ_1 states calculated at 16,100 and 23,500 cm.$^{-1}$.

The experimental spectra do contain sufficient detail to provide rather severe tests for transition assignment theories. The level scheme presented was considered to be by far the most satisfactory of those tested, but alternatives are probably not completely excluded. The results do imply that distortions in the excited states may under certain circumstances exert a profound effect upon observed spectra for coordination complexes. These effects in certain cases may be useful in identifying transitions. However, the form of the potential functions for certain vibrations which must occur in such systems will greatly complicate the already formidable theoretical computations of intensities.

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