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THE ABSORPTION SPECTRUM AND DICHROISM OF POTASSIUM TETRACHLOROPLATINATE(II) CRYSTALS AT 15 °K.

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The absorption spectra of thin crystals of K_2PtCl_4 with plane-polarized light at room temperature were presented to the 1964 Bressanone Conference (see p. 39). Discussions at that conference emphasized the uncertainties in the assignments of transitions in the spectra and the desirability for measurements at low temperatures where thermal excitation of molecular vibrations would not be significant. We are presently reporting the spectra obtained in the past few months with single crystals maintained at a nominal temperature of 15 °K in a liquid helium cryostat.

It is, of course, well established that the $PtCl_4^{2-}$ ion has a square-planar arrangement of ligands with a $5d^8$-electronic configuration. The arrangement of energy levels depends upon the degree of tetragonal distortion which is superimposed upon the octahedral splitting of the *d*-orbitals. Fig. 1 shows three possible arrangements of the *d*-orbitals for $PtCl_4^{2-}$ as an increasing tetragonal distortion is applied to the familiar O_h arrangement of orbitals. Various workers[1,2,3,4] have proposed each of these arrangements in assigning the transitions in the spectra.

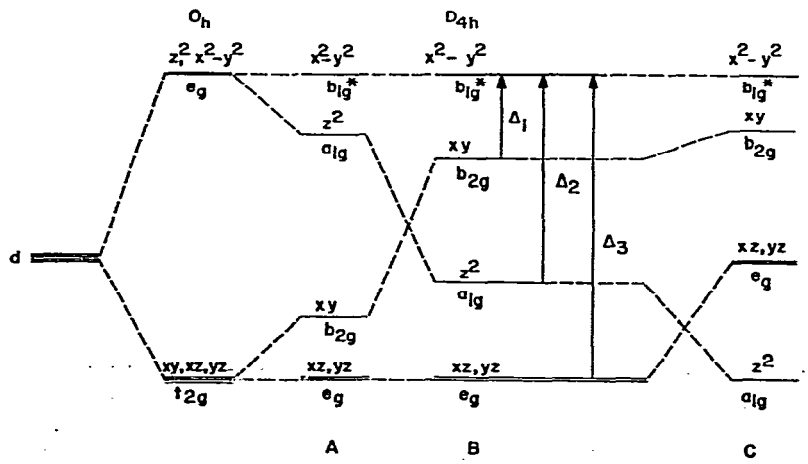

Fig. 1. Possible ordering of the *5d* orbital energies as a tetragonal distortion is applied to an octahedral coordination.

Also, since platinum as a heavy element has a moderately high spin–orbit coupling, the possibility of spin-forbidden transitions exists. In solution and crystal spectra two strong *d-d* bands and some much weaker bands are observed which clearly are spin-allowed and spin-forbidden respectively. However, there is one band observed which is intermediate in intensity between the two groups and its presence has contributed an additional uncertainty in the assignment of transition states. At present, molecular orbital calculations have not reached a degree of refinement where these ambiguities can be resolved by theoretical means.

The new data are presented as Figs. 2 and 3 where molar extinction coefficients for the crystals with light polarized in the z direction (∥ to the symmetry axis) and in the x, y direction (⊥ to the symmetry axis) are plotted for observations at 298° and 15 °K. In addition, the unpolarized absorption of a crystal 0.55 mm thick was recorded, and ε was <0.01 cm^{-1} M^{-1} for the region 8,000 to 14,300 cm^{-1}.

It is apparent that the intensity of each major transition was reduced by a factor of approximately .3 to .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 band in the region of 28,000–31,000 cm^{-1} for either polarization.

Fig. 3 presents spectra for a thicker crystal which was used to give higher absorption intensities in the long wavelength 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 ⊥-polarization the structure was still 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 ⊥-polarization. Fine structure was weakly evident in this region. The absorption in z-polarization at this wavelength 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 Figs. 2 and 3 have been included in Table I together with the extinction coefficients for the bands at 15° K.

The d^8 configuration can be treated by the two-hole formalism. Wave functions are expressed as products of the orbital and spin functions and the symmetry

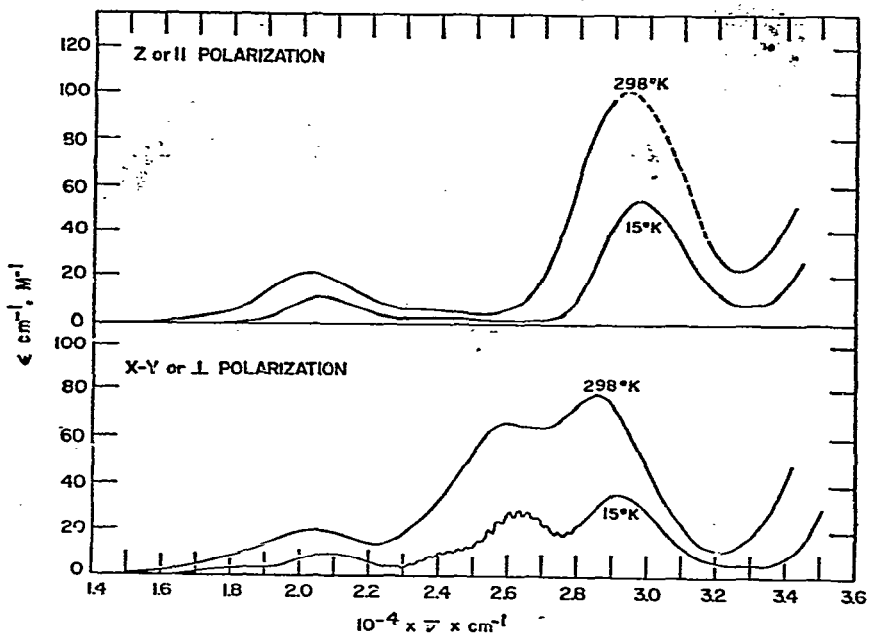

Fig. 2. Absorption spectra of a K_2PtCl_4 crystal with polarized light. Crystal thickness = 46.5 microns.

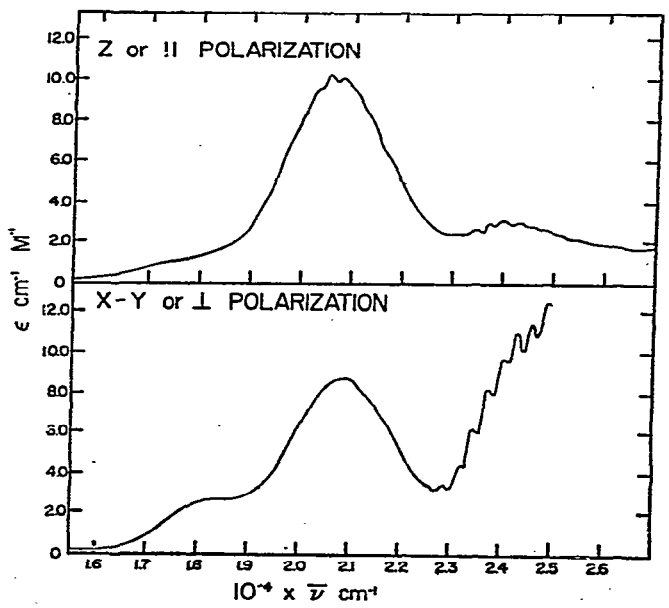

Fig. 3. Absorption spectra of a K_2PtCl_4 crystal with polarized light at 15 °K. Crystal thickness = 113 microns.

TABLE I

OBSERVED ABSORPTION PEAKS AT 15 °K FOR K_2PtCl_4 AND CALCULATED ENERGY LEVELS

z-Polarization		*x, y-Polarization*		*Vibrational Fine Structure*	*Calculated Energy* (cm^{-1})	*Principal Component*
$\bar{\nu}$ (cm^{-1})	ε ($M^{-1}cm^{-1}$)	$\bar{\nu}$ (cm^{-1})	ε ($M^{-1}cm^{-1}$)			
17,000	<1				$\Gamma_1 - 16{,}100$	$^3(b_{1g}e_g)$
19,000				none	$\Gamma_5 - 18{,}700$	$^3(b_{1g}e_g)$
		18,000	2	very weak	$\Gamma_2 - 17{,}800$	$^3(b_{1g}e_g)$
20,600	10	20,900	8.7	weak *z*	$\Gamma_4 - 20{,}800$	$^3(b_{1g}e_g)$
				very weak	$\Gamma_5 - 21{,}100$	$^3(b_{1g}b_{2g})$
				xy	$\Gamma_3 - 21{,}300$	$^3(b_{1g}e_g)$
24,000	3	24,100	7.1	strong	$\Gamma_1 - 23{,}500$	$^3(b_{1g}b_{2g})$
		26,300	28	strong	$\Gamma_2 - 26{,}300$	$^1(b_{1g}b_{2g})$
29,800	55	29,200	37	none	$\Gamma_5 - 29{,}400$	$^1(b_{1g}e_g)$
					$\Gamma_4 - 36{,}100$	$^3(b_{1g}a_{1g})$
d-state transitions above 34,000 cm^{-1} are hidden under the edge of the intense allowed charge transfer band.					$\Gamma_5 - 36{,}400$	$^3(b_{1g}a_{1g})$
					$\Gamma_3 - 46{,}285$	$^1(b_{1g}a_{1g})$

properties of the total wave function determined by the rules of group theory for direct products. Thus the singlet spin function transforms as a_{1g} and the triplet functions as a_{2g} and e_g in the D_{4h} group. The triplet states are therefore split as a consequence of the spin orbit coupling.

Bethe's Γ-notation is used for describing the total spin–orbital wave-functions, *i.e.*: $\Gamma_1 = a_{1g}$, $\Gamma_2 = a_{2g}$, $\Gamma_3 = b_{1g}$, $\Gamma_4 = b_{2g}$ and $\Gamma_5 = e_g$. In addition, the x and y axes have been chosen to pass through the ligand positions.

The energy levels of the $PtCl_4^{2-}$ were calculated including the contributions of one-electron orbital energies (the Δ_1, Δ_2, Δ_3 in Fig. 1), the electron–electron repulsions (the Slater-Condon parameters F_2 and F_4) and spin–orbit coupling.

The set of parameters which gave most satisfactory agreement with energies and intensities of the observed bands is given in Table II.

The calculated energies together with the symmetry representations and the principle contributing state for each level are also presented in Table I. The d_{z^2} or a_{1g} orbital has the lowest energy in this scheme and has arbitrarily been assigned zero energy.

TABLE II

PARAMETERS UTILIZED IN CALCULATING THE ENERGY LEVEL SCHEME IN TABLE I

Parameter	*Energy* (cm^{-1})
d_{z^2} orbital (a_{1g})	0
$d_{xz,yz}$ orbitals (e_g)	17,300
d_{xy} orbital (b_{2g})	24,700
$d^*_{x^2-y^2}$ orbital (b_{1g})	51,000
F_2	1,200
F_4	65
Spin-Orbit Coupling	
$\alpha = \zeta/2$	1,300

The energy levels for the system have been plotted as a function of the spin–orbit coupling parameter in Fig. 4 to illustrate the importance of this quantity. The squares in the figure indicated the observed band maxima. Thus, the states originating from the two triplet states of nearly equal energy in the absence of spin–orbit coupling split by as much as 8,000 cm^{-1}. The band of intermediate intensity at *ca.* 20,700 cm^{-1} arises from transitions to the four Γ_3, Γ_4 and Γ_5 states.

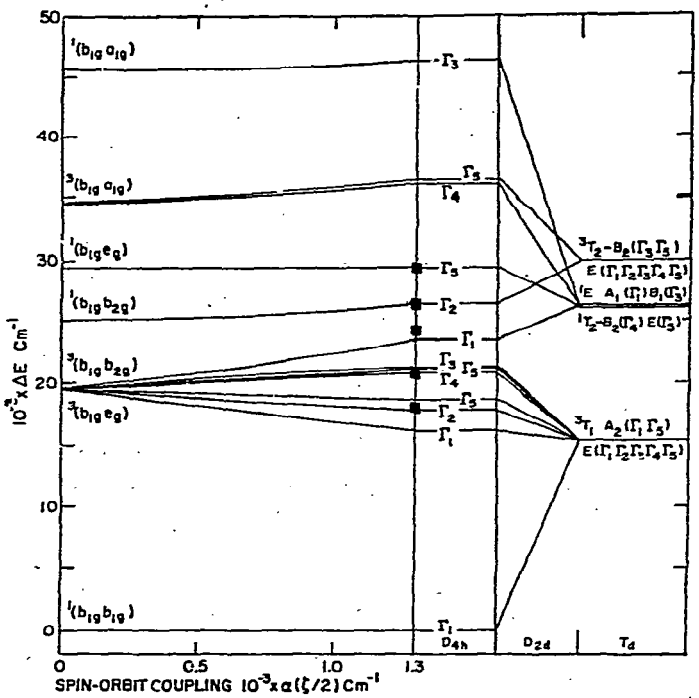

Fig. 4. The splitting of the square-planar electronic states by spin–orbit coupling with their D_{4h}-Γ-designation and the correlation of the square-planar states with the tetrahedral states (without spin-orbit coupling). The representations of the orbital part of the tetrahedral states under the D_{2d} 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}.

It is necessary to have a theoretical model which will account for the intensities of the observed spectra. According to the simple vibronic model, asymmetric vibrations provide a perturbation which mixes an asymmetric component into the wave functions so that a non-zero dipole transition moment can be obtained. From the symmetry properties of the normal vibrational coordinates for $PtCl_4^{2-}$, the simple vibronic model predicts that transitions to Γ_2 and Γ_4 states will be polarized in the x, y-direction which is consistent with the assignment of the peak at 26,300 cm^{-1}. The moderate absorption at 18,000 cm^{-1} is also assigned as a Γ_2 although there is a much weaker absorption in this region which is attributed to the Γ_1 at

16,100 and the Γ_5 at 18,700 cm^{-1}. Under favorable circumstances, where the potential functions for all the vibrations of an excited electronic state except the totally symmetric stretching vibration have similar force constants and equilibrium positions as the corresponding vibrations in the ground state, the vibronic model predicts a strong vibrational structure, as was observed for the transitions at 24,000 and 26,300 cm^{-1}. The vibrational structure can be attributed to a series of vibrational progressions in the symmetric stretching mode. Thus if the equilibrium distance for the Pt–Cl bonds is greater in the excited electronic state, the Frank-Condon principle requires that there will be a maximum probability for the ion to be carried into a highly excited Q_1-vibration state. The separations of the maxima in these bands amount to 270–290 cm^{-1} which, as expected, are somewhat lower than the Q_1-frequency of 335 cm^{-1} which is available from Raman spectra.

The out-of-plane β_{2u} bending vibration carries the square-planar, D_{4h}, arrangement into the symmetry D_{2d}. If continued, this vibration carries the ion into a tetrahedral, T_d arrangement. The ground state for T_d symmetry, without spin–orbit coupling, is $^3T_1$. It is proposed that the tetrahedral ground state lies below some of the excited states for the square-planar arrangement. The nine wave functions which comprise the $^3T_1$ in the T_d arrangement must each correlate via basis functions for the D_{2d} symmetry group of the intermediate configuration with states in the square-planar arrangement. If the $^3T_1$ state is below the D_{4h} state with which it correlates, the potential functions for the β_{2u} out-of-plane bending vibration for the D_{4h} ion will possess one or two maxima. Transitions to a number of vibration levels, which are not uniformly spaced, in the excited electronic state are to be expected; and the vibrational fine structure of the absorption bands may be lost. All of the D_{4h} states up to and including the Γ_3 at 21,300 cm^{-1} (Table I) correlate with the $^3T_1$ ground state of T_d.

The correlation of the D_{4h} states with the T_d states is also included in Fig. 4. For the T_d states, zero spin–orbit coupling was assumed and the values of F_2 and F_4 from the D_{4h} system were employed. The parameter, Δ_t, was set equal to 17,000 cm^{-1} which is somewhat greater than the crystal field value of $4/9\Delta_1$. The ground state of T_d was placed just below the first excited Γ_1-state of D_{4h}. The Γ_1 at 23,500 cm^{-1} and the Γ_2 state at 26,400 cm^{-1} correlate with T_d states of higher energy. These are just the ones reached by transitions with strong vibrational structure. The Γ_5 state at 29,400 cm^{-1} logically correlates with a state of lower energy so that the absence of structure can be explained.

One additional piece of evidence can now be cited for the assignment of the 29,400 cm^{-1} transition to Γ_5 states. Very recently Professor J. G. Foss of the Iowa State University Department of Biochemistry-Biophysics has recorded a magnetic circular dichroism which is associated with the solution absorption band at 30,300 cm^{-1}. The shape and magnitude of this dichroism indicates that it originates from the Zeeman splitting of a degenerate state. Such a splitting would require a state with the Γ_5-symmetry in the D_{4h} group.

A number of other transition assignments have been considered, but it is believed that the scheme included in Table I, with the modifications in the vibronic model which are required for the tetrahedrally deformed excited states, provides the most satisfactory explanation of the energies and intensities in the observed spectra.

Acknowledgement

Figs. 1, 2, 3 and 4 are reproduced, with permission, from D. S. MARTIN *et al.*, *Inorg. Chem.*, 4 (1965) 1682.

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