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THE VIBRONIC ABSORPTION SPECTRUM AND DICHROISM OF POTASSIUM TETRACHLOROPLATINATE(II)*

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The absorption spectrum at 25 °C from 700 to 270 $m\mu$ for a single crystal of K_2PtCl_4, with light polarized parallel and normal to the symmetry axis of the $PtCl_4^{2-}$ ion, has been observed. Absorption peaks for three strong transitions ($\varepsilon \sim 5$–$30\ M^{-1}cm^{-1}$) were well resolved which can be associated with the peaks observed in the solution spectrum of this ion. The absence of one peak for light polarized parallel to the symmetry axis indicates that a vibronic process in which asymmetric vibrations mix in odd wave functions is responsible for the absorption. The transition $^1A_{1g} \rightarrow {}^1A_{2g}$($D_{4h}$ symmetry) is accordingly assigned unambiguously. However, peaks are well resolved, so a shift in maxima between polarizations is observable. An assignment of the other peaks as singlet–singlet one-electron transitions has been proposed on the basis of the shift of maxima, which orders the d-orbitals $d_{z^2} > d_{xy} > d_{xz,yz}$. The Jahn-Teller effect for the ^1E_g state does not produce an observable splitting of the peaks which are assigned to the $^1A_{1g} \rightarrow {}^1E_g$ transition as a consequence of the Frank Condon principle. However, it may account for an anomalously large shift of the peaks in different polarizations. The absorption peaks are less intense and sharpened considerably at 77 °K in support of the vibronic mechanism. A number of weaker peaks have been observed which can be assigned to singlet–triplet transitions.

The spectra of a thicker crystal of K_2PtCl_4 with z and the xy polarizations were recorded for the region 12,000–22,000 cm^{-1}. Gaussian analyses of the peaks at about 20,000 cm^{-1} are shown in Fig. 1. It is clear that there is a weak transition in xy polarization at about 17,500 cm^{-1}. With a vibronic model this must be assigned as the spin-forbidden $^1A_{1g} \rightarrow {}^3A_{2g}$ transition corresponding to the 25,700 cm^{-1} spin-allowed transition. In addition, there are deviations of the Gaussian components from the observed spectra at 16,300–16,500 cm^{-1}. These deviations are so small that the existence of a transition in this region is uncertain. However, they might be associated with spin forbidden transitions of the peaks at *ca.* 20,000 cm^{-1}. It is noted that Perumareddi and Liehr[1] have observed peaks in the

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* A portion of the presentation is included in D. S. Martin and C. A. Lenhardt, *Inorganic Chemistry*, 3 (1964) 1368.

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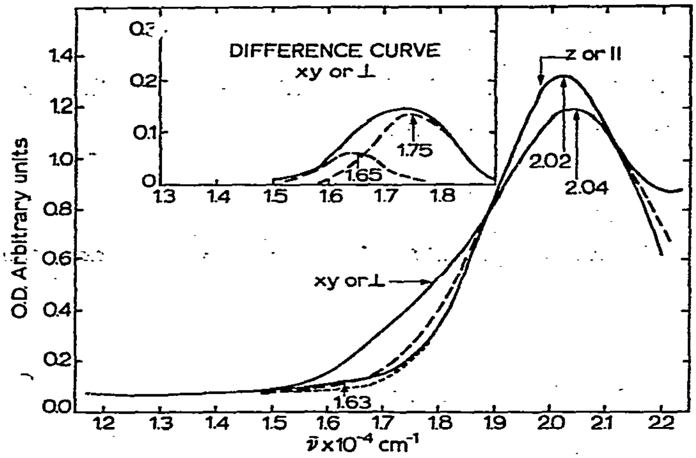

Fig. 1. Polarized absorption spectrum of a thick K_2PtCl_4 crystal.

reflectance spectrum of K_2PtCl_4 at 9,600 and 12,600 cm^{-1}. We have not observed these in the absorption of a crystal 0.74 mm thick and can therefore assign an upper limit to their intensities. It is also noted that in the z polarization a weak transition has been repeatedly recorded at about 24,000 cm^{-1}. This region is masked in xy polarization at room temperature by the much more intense peak at 25,700 cm^{-1}. This could logically be assigned as a spin-forbidden transition of the 29,200 cm^{-1} peak. The energies and intensities of the weak transitions are given below the line in Table I. The complete splitting of the energy levels, given by the diagonal terms only of the energy matrices, has been given in Fig. 2 including the

TABLE I

INTENSITIES: ABSORPTION SPECTRUM K_2PtCl_4

Energy cm^{-1}	*Polarization*	*Osc. Str. $f \times 10^4$ (298 °K)*
20,200	z	1.3
20,400	xy	1.5
25,700	xy	5.2
29,200	z	7.9
28,900	xy	5.3
9,600*	—	<.001
12,600*	—	<.001
16,500	z	.02
16,500	xy	.02
17,500	xy	.08
24,000	z	.2
(24,000)	xy	—

* Reported by J. R. Perumareddi and A. D. Liehr. From Reflectance Spectrum. Private Communication.

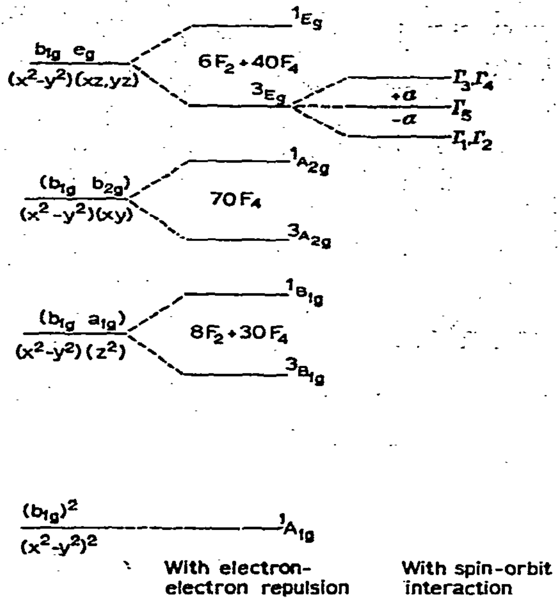

Fig. 2. Energy levels of square-planar d^8 system with electron–electron repulsion and spin–orbit coupling. (Diagonal matrix elements only.)

electron–electron repulsion and spin–orbit coupling. With the reasonable values for the parameters $F_2 = 10F_4 = 700$ cm^{-1} and $\alpha = 1{,}500$ the energies of the spin-forbidden transitions, are included in Table II. Agreement with the observed weak transitions is very unsatisfactory and admittedly does raise a question about the validity of the vibronic model.

TABLE II

POLARIZED ABSORPTION SPECTRUM OF K_2PtCl_4

Energy (cm^{-1})		*Vibronic Assignment*	*Calcd. Energy Triplet States* $F_2 = 10\ F_4 = 700$ $\alpha = 1{,}500$	*Observed Weak Transitions (cm^{-1})*
z	*xy*			
20,200	20,400	$^1A_{1g} \rightarrow {}^1B_{1g}$	13,300	16,300 (*z*, *xy*)
	25,700	$^1A_{1g} \rightarrow {}^1A_{2g}$	20,800	17,500 (*xy*)
			19,800	
29,200	28,900	$^1A_{1g} \rightarrow {}^1E_g$	21,300	24,000 (*z*, *xy*)
			22,800	

Spectra have also been recorded for the crystal at liquid nitrogen temperatures, with the crystal at somewhat higher temperatures than 77 °K because of heat transfer problems. These spectra are shown in Figs. 3 and 4. It is seen that in accordance with the vibronic model, intensities are reduced at the lower temperature, and resolution has been improved. Peaks have also shifted somewhat

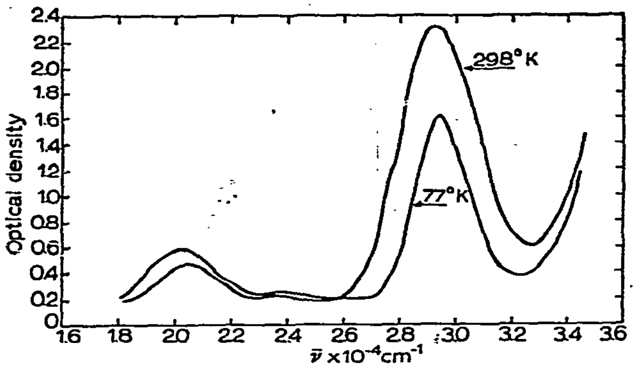

Fig. 3. Absorption spectrum in z polarization of a K_2PtCl_4 crystal.

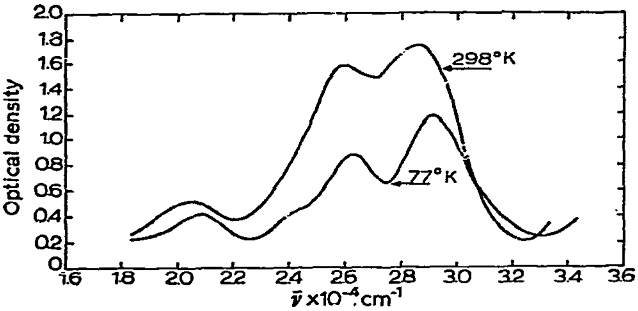

Fig. 4. Absorption spectrum in xy polarization of a K_2PtCl_4 crystal.

toward shorter wavelengths by 200–400 cm^{-1}. A frequency ν_i was calculated for each transition from the formula for the oscillator strength ratio:[2]

$$\frac{f(T_2)}{f(T_1)} = \frac{\coth(h\nu_i/2kT_2)}{\coth(h\nu_i/2kT_1)} \tag{1}$$

These results have been tabulated in Table III. Although the calculated frequencies are of the expected order of magnitude, which is perhaps all that can be expected from data of this nature, the frequencies for each of the transitions, excited by ε_u vibrations under this proposal, are all smaller than those for the out-of-plane

TABLE III

TEMPERATURE DEPENDENCE OF INTENSITIES K_2PtCl_4

Energy (cm⁻¹)	*Polarization*	*Vibronic Assignment*	*Exciting Vibration*	ν_1 *(cm⁻¹)*
20,200	z	$^1B_{1g}$	β_{2u}	260
20,400	xy	$^1B_{1g}$	ε_u	120
25,700	xy	$^1A_{1g}$	ε_u	50
29,200	z	^1E_g	ε_u	170
28,900		^1E_g	α_{2u}, β_{2u}	390

bending vibrations. It should be noted that formula (1) is based on the assumption that the force constant and minimum in the potential functions for the exciting vibrational mode are identical for the ground state and for the excited electronic state. Such assumptions are certainly open to question and a real possibility also exists that the equilibrium configuration of excited states might not be square-planar at all. In such a case the potential function of Q_2 or Q_4 might be a function with a double minimum as shown in Fig. 5. Such a function for Q_4 would correspond to distortion toward a tetrahedral configuration which seems the more likely than for the pyramidal distortion that would occur with the Q_2 vibration. This sort of distorted excited state would possibly account for the lower temperature dependence of the intensities of transitions excited by the out-of-plane bending.

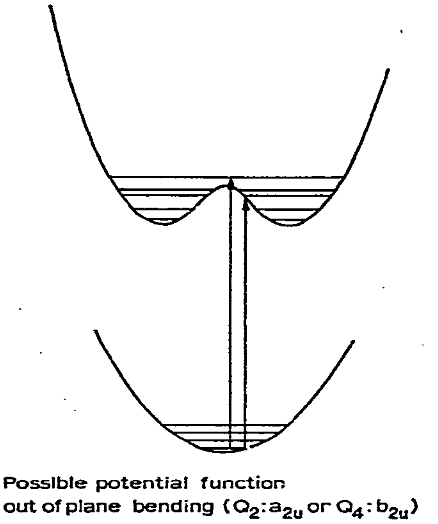

Fig. 5. Possible out-of-plane bending potential functions for the ground and excited states of a square-planar ion.

It appears that there are unresolved questions in the assignment of transitions. Further work in which the measurements are extended to liquid helium temperatures are planned which may clarify the possible assignments.

REFERENCES

1 J. R. PERUMAREDDI AND A. D. LIEHR, Private communication.
2 C. J. BALLHAUSEN, *Introduction to Ligand Field Theory*, McGraw-Hill, New York, 1962, p. 187.