Since the difference in frequencies of the individual components in both the infrared and Raman spectra are a measure of the coupling between the molecules in the unit cell, we are attempting to locate for these solids the infrared-active crystal modes.

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The Electronic Structure of Manganese(V) in $Ca_2(PO_4)Cl$

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Pursuant with our interest in the electronic structure of higher oxidation states[1–4] we wish to report on the single-crystal polarized spectrum of Mn(V) in the host $Ca_2(PO_4)Cl$. Single crystals of $Ca_2(PO_4)Cl$ containing small amounts of manganese were first prepared by Kingsley, *et al.*[5] Using various physical and chemical techniques they demonstrated that the manganese was present in the 5+ oxidation state and that it undoubtedly substituted for the phosphorous atom in the phosphate tetrahedron. In this study they also measured the absorption and emission spectrum of this compound but did not report polarization behavior as neither the structure of the host not that of the dopant was known at that time. Recently Greenblatt, *et al.*,[6] have determined the structures of both Ca_2PO_4Cl and Ca_2CrO_4Cl. On the basis of their data, the similarity of the polarization behavior between $Ca_2(PO_4,CrO_4)Cl$ and $Ca_2(PO_4,MnO_4)Cl$, and the electron spin resonance data of Banks,[7] *et al.*, for $Ca_2(PO_4,CrO_4)Cl$, we wish to suggest that the polarized spectrum of $Ca_2(PO_4,MnO_4)Cl$ is interpretable in terms of D_{2d} symmetry.

The spectrum of $Ca_2(PO_4,MnO_4)Cl$ at 80°K with light incident on the 001 crystal face is shown in Figure 1. No attempt was made to obtain the spectrum at lower temperatures as there is little physical difference between our 80°K spectrum and that reported for 2°K.[5]

The 80°K polarized spectrum of $Ca_2(PO_4,MnO_4)Cl$ was obtained using experimental techniques identical with those reported in earlier communications.[8,9]

Results and Discussion

Crystal field theory predicts that the energy level sequence for a d^2 ion in a tetrahedral environment should be ${}^3A_2 < {}^3T_2 < {}^3T_1(F) < {}^3T_1(P)$. The correlation between these states and those produced when tetrahedral symmetry is reduced to D_{2d} symmetry is shown in Table I.

TABLE I

T_d	D_{2d}
${}^3A_2$	${}^3B_1$
${}^3T_2$	${}^3B_2 + {}^3E$
${}^3T_1$	${}^3A_2 + {}^3E$

In the group D_{2d} the z component of the electric dipole transition operator is a function of symmetry B_2 while the x and y components of the operator belong to the E representation. The selection rules for allowed electric dipole transitions in D_{2d} symmetry are readily calculated. These are presented in Table II.

TABLE II

Initial and final states[a]	Transition symmetry	Allowed polarization directions
${}^3B_1 \rightarrow {}^3E$	E	x, y
${}^3B_1 \rightarrow {}^3B_2$	A_2	Forbidden
${}^3B_1 \rightarrow {}^3A_2$	B_2	z

[a] Initial electron spin resonance measurements are, assuming D_2d symmetry, consistent with a ${}^3B_1$ ground state: J. Milstein, B. R. McGarvey, and S. L. Holt, unpublished data.

In Figure 1 we note that there are three areas of relatively intense absorption, 10,000–15,000, 15,000–20,000, and above 25,000 cm^{-1}. These absorptions have previously been assigned[5] as

$$\begin{array}{rl}{}^3A_2(t_1^6e^2) \rightarrow {}^3T_2(t_1^6et_2) & 11{,}000\ \text{cm}^{-1}\\ \left.\begin{array}{r}\rightarrow {}^3T_1(t_1^5e^3)\\ \rightarrow {}^3T_1(t_1^6et_2)\end{array}\right\} & \begin{array}{l}13{,}800\ \text{cm}^{-1}\\ 17{,}500\ \text{cm}^{-1}\end{array}\\ \rightarrow {}^3T_1(t_1^5e^2t_2) & 32{,}400\ \text{cm}^{-1}\end{array}$$

Based upon this assignment but taking the molecular symmetry to be D_{2d} instead of T_d, we would expect that with $\vec{E} \perp z$ our spectrum should consist of absorptions in the regions of 11,000, 13,800, 17,500, and 32,400 cm^{-1}, *i.e.*, transitions from the ${}^3B_1$ ground state to the x,y-allowed low-symmetry components of the ${}^3T_2$ and ${}^3T_1$ states. On the other hand, with $\vec{E} \parallel z$ we should not see an 11,000-cm^{-1} band but should see the ${}^3A_2$ components at $\sim$13,800, 17,500, and 32,400 cm^{-1}. Looking at Figure 1 we note that this behavior is not what is observed. While it is difficult to draw any conclusions about the weak 11,000-cm^{-1} absorption, clearly the band at 17,500 cm^{-1} does not have ${}^3T_1$ parentage as no component appears with $\vec{E} \parallel z$. The question is then, what kind of assignment can be made to explain the spectrum. One possible assignment is to treat all of the absorptions in the 9000–35,000-cm^{-1} region as arising from transitions occurring within the d manifold. Such an assignment would require that the first charge-transfer band in MnO_4^{3-} occur somewhere above 35,000 cm^{-1}. When one considers that the first charge-transfer transition occurs at $\sim$18,000 cm^{-1} in both MnO_4^- and CrO_4^{3-} and at somewhat lower energies in MnO_4^{2-} it is

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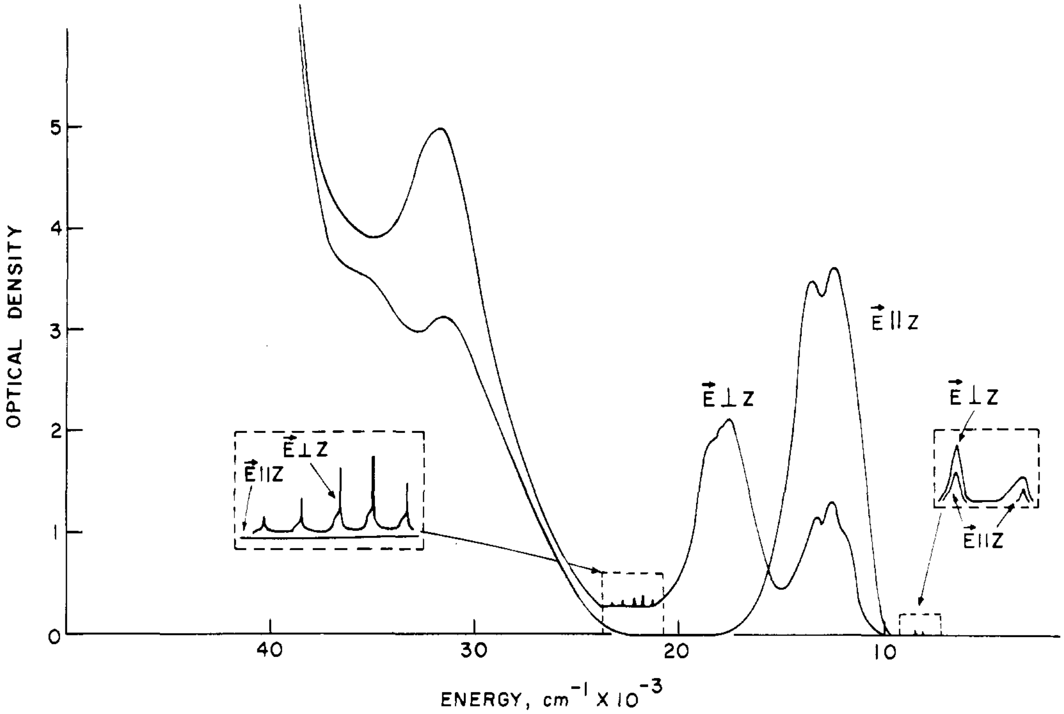

Figure 1.—The 80°K polarized crystal spectrum of $Ca_2(PO_4,MnO_4)Cl$.

difficult to rationalize 35,000 cm^{-1} as a value for a similar process in MnO_4^{3-}. Similarly, although the band at 17,500 cm^{-1} has the correct polarization behavior to be a low-symmetry component of the $^3T_2(t_1^6et_2)$ level such an alternative is ruled out on the basis that this would require a reversal of the normal ordering of energy levels to $^3T_1(F) < {}^3T_2(F) < {}^3T_1(P)$ rather than $^3T_2(F) < {}^3T_1(F) < {}^3T_1(P)$. The most reasonable assignment then is that the 10,000–15,000-cm^{-1} region of absorption consists of low-symmetry components of the $^3A_2 \rightarrow {}^3T_2(t_1^6et_2)$, the $^3A_2 \rightarrow {}^3T_1(t_1^6et_2)$ and the $^3A_2 \rightarrow {}^3T_1(t_1^5e^3)$ transitions. The absorption occurring at ~17,500 cm^{-1} is then assigned to the ^3E component of the orbitally forbidden $^3A_2 \rightarrow {}^3T_2(t_1^5e^3)$ transition. The maxima at higher energy are then undoubtedly associated with various charge-transfer processes.

Turning our attention to the finer details of the spectrum, we observe that there are two areas of rather sharp absorption occurring at ~8500 and 22,000 cm^{-1}. The splitting but not the polarization behavior of the two narrow bands occurring at ~8700 and 8410 cm^{-1} is in accord with their assignment as low-symmetry components of the $^3A_2 \rightarrow {}^1E(t_1^6e^2)$ transition.[5] Taking polarization behavior of the spin-allowed transitions into account, the selection rules in the double group, Table III, are such as to require that both peaks should be present in the x, y polarization but that only one of the two should be present in the z polarization. Here there is an obvious breakdown in the selection rules.

Table III

Double-Group States and Selection Rules

T_d	T_d (double group)	D_{2d} (double group)
$^3A_2$	Γ_5	$\Gamma_4 + \Gamma_5$
$^3T_2$	Γ_2	Γ_3
	Γ_3	$\Gamma_1 + \Gamma_3$
	Γ_4	$\Gamma_2 + \Gamma_5$
	Γ_5	$\Gamma_4 + \Gamma_5$
$^3T_1$	Γ_1	Γ_1
	Γ_3	$\Gamma_1 + \Gamma_3$
	Γ_4	$\Gamma_2 + \Gamma_5$
	Γ_5	$\Gamma_4 + \Gamma_5$
^1E	Γ_3	$\Gamma_1 + \Gamma_3$
$^1T_2$	Γ_4	$\Gamma_2 + \Gamma_5$
	Γ_5	$\Gamma_4 + \Gamma_5$

Selection rules

$\Gamma_4 \nrightarrow \Gamma_1$	$\Gamma_5 \xrightarrow{x,y} \Gamma_1$
$\nrightarrow \Gamma_2$	$\xrightarrow{x,y} \Gamma_2$
$\xrightarrow{z} \Gamma_3$	$\xrightarrow{x,y} \Gamma_3$
$\nrightarrow \Gamma_4$	$\xrightarrow{x,y} \Gamma_4$
$\xrightarrow{x,y} \Gamma_5$	$\xrightarrow{z} \Gamma_5$

Similarly the verification of the assignment for the higher energy progression at 21,500 cm^{-1} is somewhat hazy. This series of sharp maxima has been assigned to a $^1T_2(t^5e^3)$ parentage. Again, from Table III, we should expect a complex series of maxima in the x, y polarization but only a single electronic origin in the z direction. This view is somewhat modified if we look at a condensed formulation of the equation which governs the intensity of spin-forbidden transitions,[10] $f = f^0(a\zeta_{nl}/\Delta E)^2$. Here we have that the oscillator strength of the spin-forbidden transition is equal to the oscillator strength of the spin-allowed transition times

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[10] S. Holt and R. Dingle, *Acta Chem., Scand.*, **22**, 1091 (1968).

the square of the mixing coefficient divided by the square of the separation between the spin-allowed and spin-forbidden transitions. Thus while we would expect a z component, based upon our selection rules, the intensity of this component is dependent upon a coupling coefficient and the proximity of a spin-allowed transition containing the equivalent representation. The polarization behavior of the 21,500-cm^{-1} grouping is then explainable in terms of the behavior of the neighboring $^3T_2$ spin-allowed transition.

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Pt–O Stretching and OH Wagging Frequencies in Trimethylplatinum Hydroxide[1]

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There has been considerable recent interest in the characterization of trimethylplatinum hydroxide $(CH_3)_3PtOH$, first prepared by Pope and Peachey.[2] Several workers have investigated the infrared and nmr spectra of this compound,[3–6] and very recently the assumed tetrameric structure upon which their analyses were based has been confirmed.[7–9] In this structure the four platinum atoms lie at the corners of a tetrahedron, with the four oxygen atoms forming a slightly smaller, interpenetrating tetrahedron, each OH group bridging three platinum atoms.

In the course of a detailed Raman and infrared study[10] of the compounds $[(CH_3)_3PtX]_4$ (where X = OH, Cl, I), we found reason to question previous interpretations of the infrared spectrum of $[(CH_3)_3PtOH]_4$, specifically in regard to the assignment of bands at 719 and 365 cm^{-1} to Pt–O stretching and PtO deformation modes, respectively. Hoechstetter[3] originally assigned the band at 719 cm^{-1} to Pt–O stretching on the basis of a small shift upon deuteration of the hydroxyl group. Morgan, *et al.*,[4] accepted this assignment and in addition attributed a band at 365 cm^{-1} (beyond the range of the earlier work) to PtO deformation. In neither of these studies was a value assigned for the expected OH wagging mode.

Although the availability of vibrational spectra and assignments for metal–hydroxy complexes is limited, it is clear that the great majority of M–O stretching frequencies in such complexes appear well below the 719 cm^{-1} assigned here. The range 300–625 cm^{-1} includes most M–O stretching frequencies for simple hydroxy complexes[11] and complexes in which hydroxyl groups bridge two metals.[12,13] For hydroxyl or alkoxyl groups briding three metal atoms, one can compare the present case with $Pb_4(OH)_4^{4+}$[14] and $Tl_4(OR)_4$,[15] which have structures analogous to that of trimethylplatinum hydroxide and which show M–O stretching frequencies between 290 and 510 cm^{-1}. In $Tl_2Pt_2O_7$, where one also has Pt(IV) in octahedral coordination but where the Pt–O distances are considerably shorter (2.08 Å *vs.* 2.22 Å in $[(CH_3)_3PtOH]_4$), the highest infrared band is still only 684 cm^{-1}.[16] The structure of trimethylplatinum hydroxide shows no features which might account for an abnormally high Pt–O stretching frequency.

Clegg and Hall[17] have reported Raman spectra for aqueous solutions of $(CH_3)_3PtX$, where X is a poorly coordinating anion such as NO_3^-, ClO_4^-, or SO_4^{2-}. They interpreted the results in terms of a common cationic species, $(CH_3)_3Pt(OH_2)_n^+$, and assigned the value 357 cm^{-1} to a Pt–O stretching mode. It has since been shown[18] that, for the perchlorate at least, $n = 3$, as expected. The Pt environment in this species is thus very similar to that in trimethylplatinum hydroxide, and we would expect Pt–O stretching frequencies near 357 cm^{-1} for the latter.

Raman spectra of *solid* $[(CH_3)_3PtOH]_4$[10] also show a line near 719 cm^{-1} and another one at 706 cm^{-1}. However, these bands are evidently shifted in benzene solution, since no intensity is observed between 700 and 740 cm^{-1}. This is further evidence against the assignment of the 719-cm^{-1} frequency as Pt–O stretching (*i.e.*, a "cage" motion) since the remainder of the solution spectrum, as well as nmr results,[4] strongly indicates that the tetrametric cage structure is maintained in benzene solutions. New Raman lines are found at 744, 790, and 829 cm^{-1} in benzene solution. These frequencies may include one or both of the modes shifted from 706 and 719 cm^{-1}.

We now present evidence from a new deuteration experiment that the 719-cm^{-1} band (observed here at 724 cm^{-1}) in trimethylplatinum hydroxide is in fact due to OH wagging.

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