Spectroscopy at Very High Pressures. Part III.[1] Raman Spectra of Complexes $M_2^I[PtCl_6]$ and the Relation of Symmetry Species to Pressure-sensitivity †

By **David M. Adams** * and **S. John Payne**, Department of Chemistry, The University, Leicester LE1 7RH

The first systematic Raman study of inorganic complexes using a diamond anvil high-pressure cell is reported. It is shown that the pressure-sensitivity of the ν(Pt–Cl) modes in $M_2^I[PtCl_6]$ (M^I = K, Rb, Cs, Tl, NH_4), decreases in the order $A_{1g} > E_g > T_{1u}$, and this is correlated with the nature of the atom displacements. A probable phase change has been located in $Tl_2[PtCl_6]$.

ALTHOUGH attention is increasingly being devoted to study of the effects of high pressures upon the i.r. spectra of inorganic solids[2] contained in a diamond anvil cell (DAC), the equivalent Raman experiments have not yet been attempted. Prior to our work the sole publications in this area described the effect of

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† No reprints available.

[1] Part II, D. M. Adams and S. J. Payne, *J.C.S. Dalton*, 1974, 407.

[2] For a recent review see D. M. Adams and S. J. Payne, *Ann. Rep. A*, 1972, 3, The Chemical Society, London.

pressure upon the Raman spectrum of red mercuric iodide;[3,4] these used straight-through scattering geometry but this is not a method of general applicability. We have shown recently that high quality Raman spectra can be obtained by using a DAC in the 180° (back-scattering) mode;[5] the present paper gives our first systematic results using this technique.

One of our principal interests in this field is to seek relationships between the pressure dependencies of vibrational modes and their symmetry species, with the eventual object of using the pressure technique to establish assignments (to symmetry species) for compounds which present difficulties in respect of the usual means of assignment. For example, it would not be possible to determine the symmetry of a mode by the Raman polarisation technique if the material was insoluble, but a simple pressure study of the spectrum could well provide the desired information if there existed a body of reliable pressure–symmetry correlations. It has been shown by others that in complexes such as [$ZnCl_2$(terpyridyl)][6] and *cis*-[$PtBr_2(Me_2S)_2$][7] the symmetric M–hal stretch is more pressure-sensitive than the antisymmetric M–hal stretch, although in both these cases the sensitive band lost intensity rather than shifted. No equivalent Raman work has yet been attempted, and no systematic study has been made to seek relations between symmetry type and pressure-sensitivity.

For our purpose the isomorphous cubic compounds of the series $M_2^I[PtCl_6]$ (M^I = K, Rb, Cs, Tl, or NH_4), form an ideal system. The optically active modes for the unimolecular cell of factor group O_h are:

A_{1g}	ν(Pt–Cl)	ν_1	T_{1u}	ν(Pt–Cl)	ν_3
E_g	ν(Pt–Cl)	ν_2	T_{1u}	δ(Pt–Cl)	ν_4
T_{2g}	δ(Pt–Cl)	ν_5	T_{1u}	Lattice mode	
T_{2g}	Lattice mode				

where the *g*-modes are Raman-active and the *u*-modes are i.r.-active. Frequencies and assignments of these modes have been reliably established for some years.

Vibrational frequencies/cm^{-1} at ambient pressure, and pressure-sensitivities $\frac{\Delta\nu}{\Delta P}$[a] in cm^{-1} kbar^{-1} for solids $M_2^I[PtCl_6]$

	Raman						I.r.[1]					
	ν_1	$\frac{\Delta\nu}{\Delta P}$	ν_2	$\frac{\Delta\nu}{\Delta P}$	ν_5	$\frac{\Delta\nu}{\Delta P}$	ν_3	$\frac{\Delta\nu}{\Delta P}$	ν_4	$\frac{\Delta\nu}{\Delta P}$	ν_L	$\frac{\Delta\nu}{\Delta P}$
$K_2[PtCl_6]$	351	0·85	320	0·7			345	0·4	187	0·8	88	0·9
$Rb_2[PtCl_6]$	345	1·45	316	1·05			342	0·4	187	1·0	78	1·0
$Cs_2[PtCl_6]$	337	0·8	311	0·5			332	0·35	186	1·1	70	0·9
$(NH_4)_2[PtCl_6]$	346	1·15	316	0·9			340	0·5	201	1·7	135	0·85
$Tl_2[PtCl_6]$	347	1·6	317	1·1	163	1·2	335	0·65	181	0·5	49	0·6

[a] Values of the slopes of the lines in Figure 1 and similar plots.

EXPERIMENTAL

The compounds used were those made for a previous i.r. study.[1] Details of the DAC and the technique of its Raman use have been published.[5] It is very important that the surfaces of the diamond and tungsten carbide anvils be adjusted parallel to each other within two or three fringes. In the i.r. experiments[1] residual bands were often seen (*i.e.* absorption spectra of extruded material). In the Raman experiments the laser can be focussed to a precise point at the centre of the sample and most of the scattered light appears to come from that part which experiences the highest pressures. Spectra were excited with 632·8 nm radiation, *ca.* 20 mW at the sample. Pressures are quoted in kbar (1 kbar = 10^8 N m^{-2}).

RESULTS AND DISCUSSION

The principal results are shown in the Table and are combined with our earlier i.r. data for the same systems. Figure 1 shows a typical plot of band frequencies *versus* pressure. The three Pt–Cl stretching frequencies all fall within a narrow frequency interval so it is realistic to compare their shifts directly. For all five compounds the invariable order of pressure-sensitivity is $\nu_1(A_{1g}) > \nu_2(E_g) > \nu_3(T_{1u})$. However, the values of $(\Delta\nu_j/\Delta P)$ vary considerably within the series: for both ν_1 and ν_2 the order is Cs < K < NH_4 < Rb < Tl. The same order is probably followed by ν_3 but here the frequency shifts are smaller and the accuracy of their measurement is lower owing to problems of overlap with residuals from unpressurised material. It is clear that the pressure-sensitivity of the ν(Pt–Cl) modes is a complex function of the entire cell contents, which is not unreasonable as the compressibility is determined by all of them.

Anharmonicity causes a crystal normal mode $\nu_j(k)$ of wave vector k to be volume dependent according to equation (1) where V is the volume of the crystal and

$$\gamma_j(k) = -\frac{\mathrm{d}\ln\nu_j(k)}{\mathrm{d}\ln V} \qquad (1)$$

$\gamma_j(k)$ is the Grüneisen parameter, which may also be related by equation (2) to the experimentally available

$$\gamma_j(k) = \frac{1}{\chi_T\nu_j(k)}\left(\frac{\mathrm{d}\nu_j(k)}{\mathrm{d}P}\right)_T \qquad (2)$$

data, and the isothermal compressibility χ_T.[8] Values of $\gamma_j(k)$ may be computed (subject to various assumptions) on the basis of the theory of long wavelength optic modes in ionic crystals: if the theory applies at all to our compounds $M_2^I[PtCl_6]$ it is to the lattice

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[3] J. W. Brasch, A. J. Melveger, and E. R. Lippincott, *Chem. Phys. Letters*, 1968, **2**, 99.

[4] C. Postmus, V. A. Maroni, J. R. Ferraro, and S. S. Mitra, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 269.

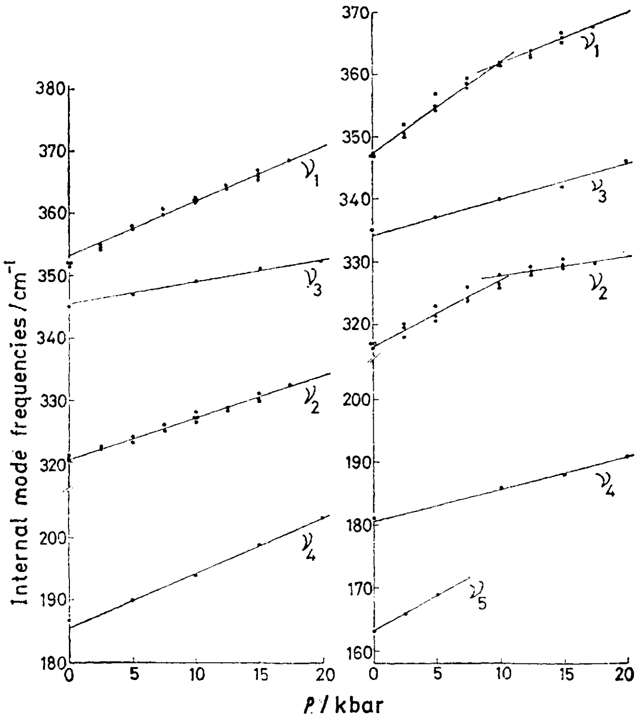
[5] D. M. Adams, S. J. Payne, and K. Martin, *Appl. Spectroscopy*, 1973, **27**, 377.

[6] C. Postmus, K. Nakamoto, and J. R. Ferraro, *Inorg. Chem.*, 1967, **6**, 2194.

[7] J. R. Allkins, R. J. Obremski, C. W. Brown, and E. R. Lippincott, *Inorg. Chem.*, 1968, **8**, 1450.

[8] S. S. Mitra, *Indian J. Pure Appl. Phys.*, 1971, **9**, 922.

modes ν_L; the pressure-dependence of the modes of the covalently-bonded anion are outside the limits of applicability of this theory. It is known, for example, that the experimentally determined Grüneisen parameters for crystals such as ZnS are significantly different from those calculated on the ionic model.[9] It appears that no explicit theory has been formulated that is suitable for discussion of the pressure-dependence of complex ionic crystals. It is sometimes assumed that all values of $\gamma_j(O)$ are the same for all values of j, but our data clearly show that this is not the case for the compounds $M_2{}^I[PtCl_6]$; if $\frac{1}{\nu_j(k)}\left(\frac{d\nu_j(k)}{dP}\right)_T$ = constant it follows that the higher mode frequencies will have the highest pressure dependencies, but this is the reverse of what is found experimentally. Thus, for the T_{1u} species, ν_4 is more sensitive than ν_3.



(a) (b)

FIGURE 1 Pressure dependence of anion internal mode frequencies/cm^{-1} for (a) $K_2[PtCl_6]$, (b) $Tl_2[PtCl_6]$

Although we are not at present able to rationalise the absolute values of the observed shifts, a simple qualitative explanation holds for the observed order of ν(Pt–Cl) sensitivities. The atom displacements, shown diagramatically in Figure 2, indicate that since ν_1 is a volume pulsation mode it will be the most highly pressure sensitive. In the ν_2 mode there is partial compensation of volume during the vibration but the net effect is still a volume pulsation, although less than for ν_1. If only the motion of the three atoms on the C_4-axis is considered, ν_3 is entirely self-compensated. The order of volume increase during one cycle of vibration is thus $\nu_1 > \nu_2 > \nu_3$ in accord with the observed order of shifts. Although this approach is qualitative it is at least a move in the right direction because the route to explicit calculation of the Grüneisen parameters starts with the first anharmonic potential (3) and involves knowledge of atom displacements $U_\alpha\binom{l}{k}$, *etc.*, where the Greek subscripts refer to co-ordinate directions, and the summation is over all atoms k in all unit cells l. Φ Is a matrix of force constants related to the normal elastic constants of the solid.

$$\sum_{\substack{\alpha\beta\gamma\\ ll'l''\\ kk'k''}} \Phi_{\alpha\beta\gamma}\begin{pmatrix} l & l' & l'' \\ k & k' & k'' \end{pmatrix} U_\alpha\binom{l}{k} U_\beta\binom{l'}{k'} U_\gamma\binom{l''}{k''} \qquad (3)$$

The bending frequencies ν_4 and ν_5 [only for one salt (M^I = Tl) was ν_5 clearly seen, due to overlap with a plasma line] are highly pressure-sensitive. This also may be rationalised on a simple model. The structure of $M_2{}^I[PtCl_6]$ can be described as that of a $[PtCl_6]^{2-}$ ion with one K^+ located over each triangular face and along the C_3-axes. Upon compressing the lattice each cation will tend to force the three nearest neighbour chlorines apart; this will, of course, happen symmetrically on each face. The net result will be to increase the constraint on the bending modes (ν_4, ν_5) more rapidly than on the stretching modes.

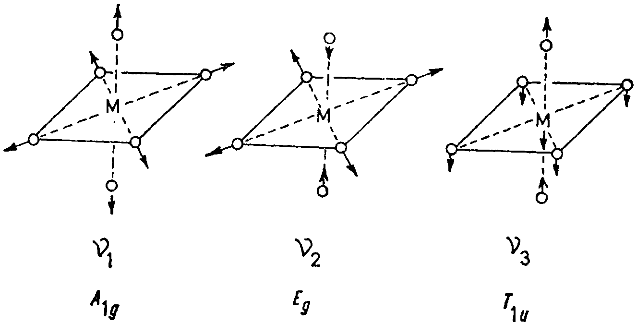


FIGURE 2 Approximate forms of the $A_{1g}(\nu_1)$, $E_g(\nu_2)$, and $T_{1u}(\nu_3)$ internal modes of an octahedral complex

For $Tl_2[PtCl_6]$ the change in slope of the ν_j *vs.* P plot, Figure 1(b), indicates a phase change; it is desirable that this be confirmed by X-ray methods.

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[9] B. Donovan and J. F. Angress, ' Lattice Vibrations,' Chapman and Hall, London, 1971.