Pressure Effects on the Vibrational Modes of K_2PtCl_4, K_2PdCl_4, K_2PtCl_6, and K_2PdCl_6*

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Pressure effects on the vibrational modes (internal and lattice) of tetragonal crystals of K_2PtCl_4 and K_2PdCl_4 were studied. The most pressure-sensitive external mode for these compounds was the translational mode along the long axis a_0, while the least sensitive was the translational mode along the short axis c_0. Results with cubic crystals of K_2PtCl_6 and K_2PdCl_6 showed that the lattice mode demonstrated higher pressure dependency than the internal modes.

INTRODUCTION

Recent pressure studies[1-6] of ionic crystals of the cubic type have demonstrated the sensitivity to pressure of external or lattice modes. With compression, a blue shift in the frequency of the lattice mode has been observed. In a cubic crystal, application of pressure will be the same in all directions since the axes are equal ($a_0=b_0=c_0$). The applications of high external pressures to noncubic-type crystals and a spectroscopic study of the effects on the lattice modes have not been made. For example, in solids that crystallize in a tetragonal structure the lattice parameters are different ($a_0=b_0\neq c_0$). Thus, it is conceivable that the effects of pressure will depend on the particular lattice mode considered. The pressure dependence of a lattice mode would be dependent on the amount of contraction or expansion that would take place along a crystalline axis.

Recently, Hiraishi and Shimanouchi[7] made a normal-coordinate treatment of the molecule K_2PtCl_4. On the basis of a D_{4h}^1 space group, three external or lattice modes ($\Gamma_{T'}=2E_u+A_{2u}$)[8] were assigned. The $2E_u$ vibrations were assigned as the translation motions along the a_0 and b_0 axes. The A_{2u} vibration was assigned to the translation mode along the c_0 axis. Since this solid was so well researched, it seemed to be the ideal substance to study under high external pressures. This study reports on the results obtained from the pressure effects on the solids K_2PtCl_4 and K_2PdCl_4. For comparison purposes similar studies were made on the cubic crystals K_2PtCl_6 and K_2PdCl_6.

EXPERIMENTAL

A multiple anvil high-pressure diamond cell was used in conjunction with the Beckman IR-11 and Perkin–Elmer No.301 far-infrared spectrophotometers. Details of the experimental techniques used have been published elsewhere.[1,2] The solids studied were C.P.-grade commercially available materials. Pressures are obtain-

TABLE I. Pressure dependencies for K_2PtCl_4 and K_2PdCl_4.

Compound	Vibration	Ambient pressure ν (cm^{-1})	Pressure dependence[a] $d\nu/dp$ (cm^{-1}/kbar)
K_2PtCl_4	$\nu_{PtCl}(E_u)$	325	0.25
	$\delta_{ClPtCl}(E_u)$ (in plane)	195	0.46
	$\delta_{ClPtCl}(A_{2u})$ (out of plane)	173	disappears[b]
	Lattice (E_u—a_0 axis)	116	0.86
	Lattice (A_{2u}—c_0 axis)	106	0.08
	Lattice (E_u—b_0 axis)	89	disappears[c]
K_2PdCl_4	$\nu_{PdCl}(E_u)$	340, 337	0.42 (coalesces into one band)
	$\delta_{ClPdCl}(E_u)$ (in plane)	190	0.35
	$\delta_{ClPdCl}(A_{2u})$ (out of plane)	170	disappears[b]
	Lattice (E_u—a_0 axis)	126	0.64
	Lattice (A_{2u}—c_0 axis)	115	0.15
	Lattice (E_u—b_0 axis)	96	disappears[c]

[a] Where a frequency shift occurs it is toward higher energy (blue shift)
$d\nu = (\nu_{33\ kbar} - \nu_{0.001\ kbar}) = dp = (P_{33\ kbar} - P_{0.001\ kbar})$.

[b] Band decreases in intensity and disappears.

[c] Band decreases in intensity and shifts into stationary A_{2u} band.

TABLE II. Pressure dependence for K_2PtCl_6 and K_2PdCl_6.

Compound	Vibration	Ambient pressure ν (cm^{-1})	Pressure dependence[a] $d\nu/dp$ (cm^{-1}/kbar)
K_2PtCl_6	$\nu_{PtCl}(F_{1u})$	345	0.62
	$\delta_{ClPtCl}(F_{1u})$	185	0.60
	Lattice(F_{1u})	87	0.76
K_2PdCl_6	$\nu_{PdCl}(F_{1u})$	360	0.43
	$\delta_{ClPdCl}(F_{1u})$	175[b]	...
	Lattice(F_{1u})	94	0.69

[a] Where a frequency shift occurs it is toward higher energy (blue shift) $d\nu = (\nu_{33\ kbar} - \nu_{0.001\ kbar})$, $dp = (P_{33\ kbar} - P_{0.001\ kbar})$.

[b] Observed by Hiraishi et al.[14] This absorption was not observed with the diamond cell used in the present work.

able to within 10%, and wavenumber units may be read to 1 cm^{-1}.

RESULTS AND DISCUSSION

K_2PtCl_4, K_2PdCl_4

The infrared results obtained for K_2PtCl_4 were made at ambient pressure and at high pressures. There is agreement that the three frequencies lower than 116 cm^{-1} are lattice modes.[7,9-11] From factor-group analysis for a D_{4h}^1 space group ($Z=2$) six infrared-active vibrations should appear. These would belong to the A_{2u} and E_u species. For the internal modes Γ_n[12]$ = 2E_u + A_{2u}$ and for the lattice modes $\Gamma_{T'} = 2E_u + A_{2u}$. From a normal-coordinate treatment Hiraishi and Shimanouchi[7] have assigned the 116-cm^{-1} absorption to the translation along the a_0 axis, the 113-cm^{-1} absorption to the translation along the c_0 axis, and the 90-cm^{-1} absorption to the translation along the b_0 axis.

Table I records the pressure dependencies of the various modes of vibration in K_2PtCl_4 and K_2PdCl_4. The results are given in the ratio $d\nu/dp$, where $d\nu$ is the difference in frequency at high pressure (33 kbar) and the frequency at ambient pressure. The slopes of the plot of $d\nu$ versus dp are found to be essentially linear, and have been obtained with a computer using the

method of least squares. All frequency shifts noted in this work are in the blue direction. It may be observed that in K_2PtCl_4 the most pressure-sensitive vibration is the translational lattice mode along the long axis (a_0), while the least sensitive mode is the translational mode along the short axis (c_0). In fact, the internal modes actually show a higher pressure dependence than the latter lattice mode. Very little may be expressed concerning the translational mode along the b_0 axis since it disappears with pressure (decreasing in intensity and shifting right into the stationary 106-cm^{-1} band). Similar results are obtainable with K_2PdCl_4 with pressure, and one may now make assignments for K_2PdCl_4

inasmuch as the previous assignments of the lattice modes were only assumed by previous workers.

From the results obtained it may be concluded that with an increase in pressure, contraction occurs along the a_0 axis, while only a slight contraction or even an expansion may occur along the c_0 axis. Drickamer and co-workers[13] have measured with x-ray diffraction the pressure dependence of the a_0 and c_0 axes in the tetragonal solids, MnO_2 and SnO_2, and have determined that up to 50 kbar the c_0 axis expands with pressure while the a_0 axis contracts. No measurement of the effect of pressure along the b_0 axis was made. The results of the high-pressure infrared studies of K_2PtCl_4 and K_2PdCl_4 agree with Drickamer's x-ray results for MnO_2 and SnO_2.

K_2PtCl_6, K_2PdCl_6

To compare the differences in pressure dependencies of noncubic and cubic crystals, the results with some related cubic crystals are included. The pressure effects on K_2PtCl_6 and K_2PdCl_6 are illustrated in Table II. Previous assignments for these compounds have been made by Hiraishi et al.[14] For cubic crystals of space group O_h^5 only one infrared lattice mode is expected, and this is what is found experimentally. Factor-group analysis shows that a total of three infrared-active vibrations should be observed. These would belong to the F_{1u} type; for the internal modes $\Gamma_n = 2F_{1u}$ and for the lattice modes $\Gamma_{T'} = F_{1u}$. Pressure effects show that the translational mode is more pressure sensitive than the internal modes, results which are not too surprising in view of previous results with related compressible compounds.[1-6]

CONCLUSIONS

The results serve to illustrate the usefulness of studying noncubic materials under high pressure and observing their low-frequency vibrational spectra. The technique can be used to complement the high-pressure x-ray studies or may be made in lieu of these studies, wherever x-ray studies are impossible. Further, the usefulness of the technique in assigning lattice modes in coordination compounds with internal modes occurring near lattice frequencies is demonstrated in this work.

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[1] J. R. Ferraro, S. S. Mitra, and C. Postmus, Inorg. Nucl. Chem. Letters 2, 269 (1966); 4, 55 (1968).

[2] L. J. Basile, C. Postmus, and J. R. Ferraro, Spectry. Letters 1, 189 (1968).

[3] J. R. Ferraro, C. Postmus, and S. S. Mitra, Phys. Rev. 174, 983 (1968).