

Effect of Pressure on the Rotary Lattice Mode of K_2PtCl_6 *

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A recent analysis¹ of the nuclear quadrupole resonance (NQR) frequency data for the ^{35}Cl resonance in the cubic crystal K_2PtCl_6 yielded an average frequency of $\sim 60\text{ cm}^{-1}$ at $300^\circ K$ for the rotary lattice mode. This result is of particular significance since the rotary mode (symmetry species F_{1g}) is forbidden both in infrared absorption and in Raman scattering. It is the purpose of this Note to extend the analysis of the NQR data to deduce the effect of pressure on the rotary mode frequency and to compare the result with corresponding results reported by Ferraro² for the three infrared active vibrational modes (symmetry species F_{1u}) of K_2PtCl_6 .

The rotary mode frequency may be obtained from the NQR frequency data using the formula

$$\omega_{rot}^2 = \nu_0 3kT/I\Delta\nu_{rot}, \quad (1)$$

where $\Delta\nu_{rot} = \Delta\nu_{expt} - \Delta\nu_{int}$ is the shift in the NQR frequency at temperature T from the static lattice value ν_0 due to the rotary lattice mode, and I is the moment of inertia of a $PtCl_6$ octahedron about one of its symmetry axes. The quantities $\Delta\nu_{expt}$ and $\Delta\nu_{int}$ are the experimental frequency shift and the shift due to the internal vibrational modes of a $PtCl_6$ octahedron.

When the NQR frequency is measured at constant temperature T as a function of the applied pressure, the small frequency shift $\delta\nu_{expt} = \Delta\nu_{expt}(P) - \Delta\nu_{expt}(0)$ that is observed may be attributed to the change in the vibrational mode frequencies resulting from the decrease in sample volume. [$\Delta\nu_{expt}(0)$ is the frequency shift measured at temperature T and ambient pressure; $\Delta\nu_{expt}(P)$ is the shift measured at the same temperature but at pressure P]. It will be assumed that ν_0 and I are independent of pressure. This should be a reason-

alter the dimensions of the $PtCl_6$ octahedra.³ It then follows by differentiation of Eq. (1) that

$$\delta\omega_{rot}/\delta P = -(\omega_{rot}/2)(1/\Delta\nu_{rot})(\delta\nu_{rot}/\delta P), \quad (2)$$

with

$$\delta\nu_{rot}/\delta P = \delta\nu_{expt}/\delta P - \delta\nu_{int}/\delta P;$$

$\delta\nu_{int}/\delta P$ and $\delta\nu_{rot}/\delta P$ are the contributions to $\delta\nu_{expt}/\delta P$ from the internal modes and the rotary mode, respectively.

The term $\delta\nu_{int}/\delta P$ is considerably smaller than $\delta\nu_{rot}/\delta P$, and therefore, it is sufficient to give a first order estimate of it. By differentiation of Eq. (7) of Ref. 1 it follows that

$$\begin{aligned} \delta\nu_{int}/\delta P &= \sum_{j=3}^6 (\delta\nu_{int}^j/\delta P) \\ &= - \sum_{j=3}^6 (2/\omega_{int}^j) \Delta\nu_{int}^j (\delta\omega_{int}^j/\delta P) \end{aligned} \quad (3)$$

if a high temperature approximation is taken and if the pressure variation of $\Delta\nu_{int}$ is assumed to be due entirely to the pressure variation of the internal mode frequencies ω_{int}^j .

For the infrared active internal modes Q_3 and Q_4 , $\delta\omega_{int}^j/\delta P$ has been measured² to be $\simeq 0.60\text{ cm}^{-1}\cdot\text{kbar}^{-1}$. Assuming that the corresponding coefficients for the modes Q_5 and Q_6 are also $\simeq 0.60\text{ cm}^{-1}\cdot\text{kbar}^{-1}$, and using the calculated values for $\Delta\nu_{int}^j$ and the measured values of ω_{int}^j quoted in Ref. 1, it follows from Eq. (3) that $\delta\nu_{int}/\delta P = 0.60\text{ kHz kbar}^{-1}$ at $300^\circ K$. About 85% of this contribution is due to the modes Q_5 and Q_6 . The quantity $\delta\nu_{expt}/\delta P$ has been measured³ to be $4.8(5)\text{ kHz kbar}^{-1}$ at $300^\circ K$; therefore, $\delta\omega_{rot}/\delta P = 4.2(0)\text{ kHz kbar}^{-1}$. Substituting $\omega_{rot} = 60\text{ cm}^{-1}$, $\Delta\nu_{rot} = -196\text{ kHz}$, and $\delta\nu_{rot}/\delta P$ into Eq. (2) gives $\delta\omega_{rot}/\delta P = 0.6(4)\text{ cm}^{-1}\cdot\text{kbar}^{-1}$. The reliability of this result depends somewhat on the correctness of the value $\delta\omega_{int}/\delta P$ taken for the Q_5 and Q_6 modes. For example, if a value of $0.50\text{ cm}^{-1}\cdot\text{kbar}^{-1}$ had been used, the deduced value of $\delta\omega_{rot}/\delta P$ would have been increased to $0.6(6)\text{ cm}^{-1}\cdot\text{kbar}^{-1}$.

Table I shows the comparison of the various values of $\delta\omega^j/\delta P$. It is seen that the pressure dependence of the rotary lattice mode as deduced from the NQR data is similar to the pressure dependence of the vibrational modes Q_3 , Q_4 , and Q_8 as obtained directly from the infrared measurements. This reasonable result provides further evidence to support the thesis that the NQR technique offers a practical means to investigate low-lying librational modes.

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¹ R. L. Armstrong, G. L. Baker, and K. R. Jeffrey, Phys. Rev. B **1**, 2847 (1970).

² J. R. Ferraro, J. Chem. Phys. **53**, 117 (1970).

³ R. L. Armstrong and K. R. Jeffrey, Can. J. Phys. **47**, 1095 (1969).

TABLE I. Pressure dependence of vibrational mode frequencies.

Vibrational mode	ω^j	
	Ambient pressure (cm ⁻¹)	$\delta\omega^j/\delta P$ (cm ⁻¹ ·kbar ⁻¹)
Q_3 (F_{1u})	345	0.62 ²
Q_4 (F_{1u})	185	0.60 ²
Q_8 (F_{1u})	87	0.76 ²
Q_9 (F_{1g})	60	0.6(4)

able approximation since the dominant effect of pressure is to change the $K-K$ separation rather than to