

Motional Averaging of the Electric Field Gradient at Chlorine Nuclear Sites in K_2PtCl_6 and K_2PdCl_6 by the Lattice Vibrations*

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Temperature variations of the ^{35}Cl nuclear-quadrupole-resonance (NQR) frequencies in K_2PtCl_6 and K_2PdCl_6 are discussed. The dominant thermal motions of the lattice responsible for the averaging of the electric field gradient at a nuclear site are assumed to take place in the plane perpendicular to the symmetry axis of the field gradient. Contributions to the NQR frequency shifts due to the internal modes Q_3 , Q_4 , Q_5 , and Q_6 of the $[MCl_6]^-$ octahedra are calculated using the results of the harmonic theory of lattice dynamics and the Bayer-Kushida theory of NQR frequencies. Differences between the experimental and calculated frequency shifts are assumed to be due to the rotary lattice modes; the frequencies of these modes are deduced in K_2PtCl_6 and K_2PdCl_6 for temperatures in the range $100^\circ K < T < 340^\circ K$. In each case the torsional oscillation frequency is found to be relatively insensitive to the temperature.

I. INTRODUCTION

THE nuclear-quadrupole-resonance (NQR) frequency is determined by the nuclear electric quadrupole moment of the resonant nuclei and the time-averaged component of the electric field gradient at the site of the nuclei, where the average is taken over times short compared to the reciprocal of the resonance frequency. This averaged field gradient exhibits a temperature variation since the amplitudes of the lattice vibrations and the volume of the sample change with temperature.

In the model first proposed by Bayer¹ to explain the observed temperature variation of the NQR frequency volume effects are not taken into account and the averaging of the field gradient is assumed to result from the lattice executing a single torsional oscillation mode in which an atom containing a resonant nucleus moves perpendicular to the bond joining it to another atom. The resonant nucleus is assumed to experience an axially symmetric electric field gradient both in the presence and absence of the lattice vibrations. According to this model the temperature dependence of the NQR frequency is described by the equation

$$\nu = \nu_0 \left[1 - \frac{3\hbar}{4I\omega_t} \coth\left(\frac{\hbar\omega_t}{2kT}\right) \right]. \quad (1)$$

The torsional oscillation frequency ω_t may often be identified with one of the low-frequency lattice modes observed by conventional spectroscopic methods. The moment of inertia I for the motion is taken as the appropriate geometric value and ν_0 as the static lattice resonance frequency. Although this single-mode model is rather unsatisfactory on physical grounds, its sim-

licity is appealing and it has been used more or less successfully as the basis for the analysis of a large amount of NQR data.

Modifications of the Bayer theory to include several lattice modes and nonaxially symmetric field gradients have been proposed by Wang² and Kushida.³ In the Kushida approach, which is the most general one, the angular displacements of the principal axes of the field gradient are expanded in the normal coordinates of the lattice modes. The resultant temperature variation of the NQR frequency as predicted for the case of an axially symmetric field gradient is given by

$$\nu = \nu_0 \left[1 - \frac{3\hbar}{4} \sum_i \frac{A_i}{\omega_i} \coth\left(\frac{\hbar\omega_i}{2kT}\right) \right], \quad (2)$$

where i runs over the normal modes. The quantities A_i contain the expansion coefficients and in general have no simple physical interpretation. In applying the Kushida formula it is generally assumed that bond-stretching motions are of negligible importance relative to bond-bending motions as a means of averaging out the field gradient. For a torsional oscillation mode in which the motion is perpendicular to the axis of symmetry of the field gradient, A_i can be identified as the reciprocal moment of inertia for the mode and its effect on the NQR frequency is the same as predicted by the Bayer model.

The model suggested by Wang (a special case of the Kushida approach) provides a realistic treatment of torsional oscillation modes. In the simplest case, the atom containing the resonant nucleus is assumed to execute torsional oscillations about the three principal axes of the electric field gradient. Assuming axial symmetry with respect to the z axis this model leads

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¹ H. Bayer, *Z. Physik* **130**, 227 (1951).

² T. C. Wang, *Phys. Rev.* **99**, 566 (1955).

³ T. Kushida, *J. Sci. Hiroshima Univ.* **A19**, 327 (1955).

to the equation

$$\nu = \nu_0 \left\{ 1 - \frac{3}{2} [\langle \theta_x^2 \rangle + \langle \theta_y^2 \rangle] \right\}, \quad (3)$$

where the mean-square angular displacements $\langle \theta_x^2 \rangle$ and $\langle \theta_y^2 \rangle$ are given by

$$\langle \theta_i^2 \rangle = \frac{\hbar}{2I_i \omega_i} \coth \left(\frac{\hbar \omega_i}{2kT} \right).$$

The Bayer-Kushida theory has been applied to a large number of experimental studies (cf. the work of Lee *et al.*⁴ on LaF₃ and Ward *et al.*⁵ on SnI₄).

The importance of volume changes to the NQR frequency was first considered theoretically and experimentally by Kushida, Benedek, and Bloembergen.⁶ They showed that

$$\left(\frac{\partial \nu}{\partial T} \right)_P = \left(\frac{\partial \nu}{\partial T} \right)_V - \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial \nu}{\partial P} \right)_T, \quad (4)$$

where $(\partial \nu / \partial T)_P$ is the rate of change of frequency with temperature as measured in experiments carried out at constant pressure and $(\partial \nu / \partial T)_V$ is the Bayer-Kushida contribution. In only a very few cases have other authors evaluated the contribution from the third term (cf. Gutowsky and Williams,⁷ Barnes and Engardt,⁸ Matzkanin *et al.*⁹). However, following the suggestion of Brown,¹⁰ some authors have assumed that the lattice frequencies decrease linearly as the temperature increases, in an attempt to take account of volume effects in an approximate fashion (cf. the analysis of data for solid chlorine by Nakamura and Chihara¹¹).

Measurements of the temperature dependence of the ³⁵Cl and ³⁷Cl NQR frequencies in K₂PtCl₆ and the ³⁵Cl NQR frequency in K₂PdCl₆ have been reported by Jeffrey and Armstrong¹² and Armstrong and Cooke,¹³ respectively. In each case a preliminary analysis using the Bayer model yielded a remarkably good representation of the data. From the torsional oscillation frequencies deduced it was concluded that the motional averaging of the field gradient at chlorine sites resulted predominantly from the rotary lattice mode of *F*_{1g} symmetry. Since the rotary mode corresponds to

threefold-degenerate torsional oscillations of the [MCl₆]⁼ ion about the principal axes of the field gradient, it seemed appropriate to apply the Wang formula with $\langle \theta_x^2 \rangle = \langle \theta_y^2 \rangle$ to the analysis of the data. Torsional oscillation frequencies of 32 cm⁻¹ for K₂PtCl₆ and 42 cm⁻¹ for K₂PdCl₆ were deduced. In each case the effective moment of inertia was about twice the geometrical value.

The raison d'être of this paper is to present the results of a multiple-mode analysis of the NQR frequency data for the ³⁵Cl resonances in K₂PtCl₆ and K₂PdCl₆. The stimulation for carrying out this analysis came from a recent letter by O'Leary¹⁴ in which he questioned the validity of a single-mode analysis.

II. THEORETICAL MODEL

The chlorine atoms in the face-centered-cubic (fcc) K₂MCl₆ crystals form the corners of a regular octahedron¹⁵ which surrounds the central metal atom. The M-Cl bonds are therefore oriented along the cubic crystal axes. The octahedra define a fcc lattice and the potassium atoms occupy tetrahedral interstices. The chlorine site symmetry is therefore C_{4v} and the electric field gradient is symmetric about the fourfold axis. The bonding within and [MCl₆]⁼ octahedron has appreciable covalent character. As a result, the contribution to the field gradient at a chlorine site from neighboring atoms outside the octahedron represents a small fraction of the total.¹⁶

If the dominant thermal motions of the lattice take place in the plane perpendicular to the symmetry axis of the electric field gradient at a ³⁵Cl site, then to first order the temperature dependence of the ³⁵Cl NQR frequency is described by Eq. (3). We emphasize that in adopting this approach we are implicitly assuming that bond-stretching motions internal to the [MCl₆]⁼ ions are of negligible importance relative to bond-bending motions as a means of averaging the field gradient. The acoustic and translatory lattice modes involve pure translations of the octahedra as rigid bodies, and therefore cause neither the length nor orientation of the M-Cl bonds to be changed. These modes have at most a small effect on the NQR frequency and may be safely ignored.

There are six lattice modes internal to the [MCl₆]⁼ octahedra.¹⁷ Two of them, designated Q₁ and Q₂ are pure stretching modes and will not be considered in the analysis. The other four internal modes designated Q₃, Q₄, Q₅, and Q₆ are depicted in Fig. 1. For each mode the motion of a chlorine nucleus has a component in the plane perpendicular to the M-Cl bond. These four

⁴ K. Lee, A. Sher, L. O. Andersson, and W. G. Proctor, *Phys. Rev.* **150**, 168 (1966).

⁵ R. W. Ward, C. D. Williams, and R. F. Tipword, *J. Chem. Phys.* **51**, 823 (1969).

⁶ T. Kushida, G. B. Benedek, and N. Bloembergen, *Phys. Rev.* **104**, 1364 (1956).

⁷ H. S. Gutowsky and G. A. Williams, *Phys. Rev.* **105**, 464 (1957).

⁸ R. G. Barnes and R. D. Engardt, *J. Chem. Phys.* **29**, 248 (1958).

⁹ G. A. Matzkanin, T. N. O'Neal, T. A. Scott, and P. J. Haigh, *J. Chem. Phys.* **44**, 4171 (1966).

¹⁰ R. J. C. Brown, *J. Chem. Phys.* **32**, 116 (1960).

¹¹ N. Nakamura and H. Chihara, *J. Phys. Soc. Japan* **22**, 201 (1967).

¹² K. R. Jeffrey and R. L. Armstrong, *Phys. Rev.* **174**, 359 (1968).

¹³ R. L. Armstrong and D. F. Cooke, *Can. J. Phys.* **47**, 2165 (1969).

¹⁴ G. P. O'Leary, *Phys. Rev. Letters* **23**, 782 (1969).

¹⁵ R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1965), 2nd ed., Vol. 3, p. 339.

¹⁶ D. Nakamura and M. Kubo, *J. Phys. Chem.* **68**, 2986 (1964).

¹⁷ G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Co., Inc., New York, 1945), p. 122.

modes, as well as the rotary mode, will be considered in the analysis.

From the theory of lattice dynamics in the harmonic approximation¹⁸ the mean-square value of the $\alpha \equiv x, y$ component of the displacement from equilibrium of atom κ in unit cell l is given by

$$\langle u_{\alpha}^2(l, \kappa) \rangle = \frac{\hbar}{2Nm_{\kappa}} \sum_{\mathbf{k}, j} e_{\alpha}^*(\kappa|\mathbf{k}, j) e_{\alpha}(\kappa|\mathbf{k}, j) \times \frac{\coth(\hbar\omega_j(\mathbf{k})/2kT)}{\omega_j(\mathbf{k})}.$$

In this expression m_{κ} is the mass of atom κ , N is the number of molecules per unit volume, $e_{\alpha}(\kappa|\mathbf{k}, j)$ the eigenvector component with eigenvalue $\omega_j(\mathbf{k})$ is the displacement of atom κ in the normal mode of wave vector \mathbf{k} and branch j . It then follows¹⁴ that

$$\langle \theta_{\alpha}^2 \rangle = \frac{\hbar}{2NR^2} \sum_{\mathbf{k}, j} \left| \frac{e_{\alpha}(Cl|\mathbf{k}, j)}{m_{Cl}^{1/2}} - \frac{e_{\alpha}(M|\mathbf{k}, j)}{m_M^{1/2}} \right|^2 \times \frac{\coth(\hbar\omega_j(\mathbf{k})/2kT)}{\omega_j(\mathbf{k})}, \quad (5)$$

where R is the M -Cl bond length. By symmetry $\langle \theta_x^2 \rangle = \langle \theta_y^2 \rangle$ for K_2MCl_6 crystals.

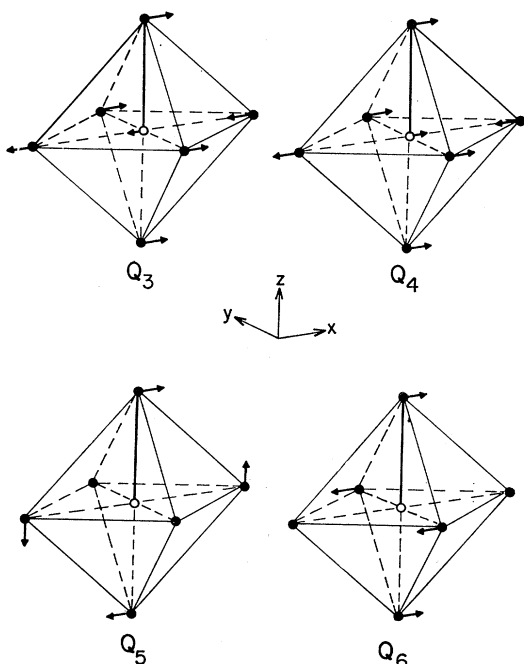


FIG. 1. Illustration of the normal modes Q_3 , Q_4 , Q_5 , and Q_6 of an MX_6 octahedron. In each case, only that form of the mode is shown which results in the rotation in the plane of the page of the MX bond indicated by the heavy solid line.

¹⁸ A. A. Maradudin, E. W. Montroll, and G. H. Weiss, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Suppl. 3, p. 237.

The dispersion of the internal mode is probably small enough so that they can be adequately represented by triply degenerate and temperature-independent Einstein modes. That is, $\omega_j(\mathbf{k})$ may be taken as independent of \mathbf{k} and approximately equal to $\omega_j(\mathbf{k}=0)$.

The rotary mode may exhibit considerable dispersion. This constitutes a serious difficulty except in the high-temperature limit where the population factor $\coth[\hbar\omega_j(k)/2kT]$ may be approximated by $2kT/\hbar\omega_j(\mathbf{k})$. In this limit

$$\langle \theta_x^2 \rangle_{\text{rot}} = \frac{kT}{I\langle \omega_{\text{rot}}^2 \rangle}, \quad (6)$$

with $\langle \omega_{\text{rot}}^2 \rangle$ the mean-square frequency of the transverse and longitudinal branches of the rotary mode.

Based on the following considerations it is reasonable to assume that to within 10% $(\partial\nu/\partial T)_P = (\partial\nu/\partial T)_V$. From a study of the pressure variation of the ³⁵Cl NQR frequency in K_2PtCl_6 ¹⁹ it is known that at 300°K $(\partial\nu/\partial P)_T \approx 4 \times 10^{-3}$ kHz kg⁻¹ cm². To obtain a value for $(\partial P/\partial T)_V$ requires knowledge of the ratio of the coefficient of thermal expansion α to the coefficient of isothermal compressibility β of the $[PtCl_6]^-$ octahedra in K_2PtCl_6 . To estimate this ratio we take an average of typical values of α and β for substances of similar structure, giving $\alpha/\beta \approx 20$ kg cm⁻² °K. It follows from Eq. (4) that $|(\partial\nu/\partial T)_P - (\partial\nu/\partial T)_V| \approx 0.08$ kHz °K⁻¹. In comparison, the atmospheric value of $(\partial\nu/\partial T)_P \approx 1$ kHz °K⁻¹.

III. ANALYSIS OF DATA

The NQR data used for the analysis are those reported by Jeffrey and Armstrong¹² and Armstrong and Cooke¹³ for temperatures less than 340°K. The data above 340°K are believed to be influenced by the onset of hindered rotations of the $[MCl_6]^-$ octahedra.¹⁹ The static lattice values ν_0 are 26.102 and 26.819 MHz for K_2PtCl_6 and K_2PdCl_6 , respectively. Equations (3) and (5) were used to obtain the following equation for the NQR frequency shift $\Delta\nu_{\text{int}}$ due to the internal modes Q_3 , Q_4 , Q_5 , and Q_6 :

$$\Delta\nu_{\text{int}} = \frac{3\hbar\nu_0}{2R^2} \sum_{j=3}^6 \left| \frac{e_x(Cl|j)}{m_{Cl}^{1/2}} - \frac{e_x(M|j)}{m_M^{1/2}} \right|^2 \times \frac{\coth(\hbar\omega_j/2kT)}{\omega_j}. \quad (7)$$

The frequencies of the internal modes²⁰ as used in the calculations are given in Table I. The values quoted for Q_6 are only estimates since this mode has apparently not been observed in either substance. The calculated

¹⁹ R. L. Armstrong and K. R. Jeffrey, *Can. J. Phys.* **47**, 1095 (1969).

²⁰ P. J. Hendra and P. J. D. Park, *Spectrochim. Acta* **23A**, 1635 (1967).

TABLE I. Contributions of the internal modes to the ^{35}Cl NQR frequency shifts in K_2PtCl_6 and K_2PdCl_6 at 300°K .

Mode	ω (cm^{-1})	$\Delta\nu_{\text{int}}$ (kHz)	$\frac{\Delta\nu_{\text{int}}}{\Delta\nu_{\text{expt}}}$
K_2PtCl_6			
Q_3	345	8	0.031
Q_4	183	4	0.015
Q_5	162	28	0.110
Q_6	130	44	0.167
Total			0.323
K_2PdCl_6			
Q_3	358	8	0.031
Q_4	175	1	0.004
Q_5	164	29	0.110
Q_6	130	46	0.171
Total			0.316

contributions to $\Delta\nu_{\text{int}}$ from the four modes at 300°K are given in Table I. It is interesting to note that the pure bending modes Q_5 and Q_6 give considerably larger contributions than the bending-stretching modes Q_3 and Q_4 . The sum of the four contributions in each case

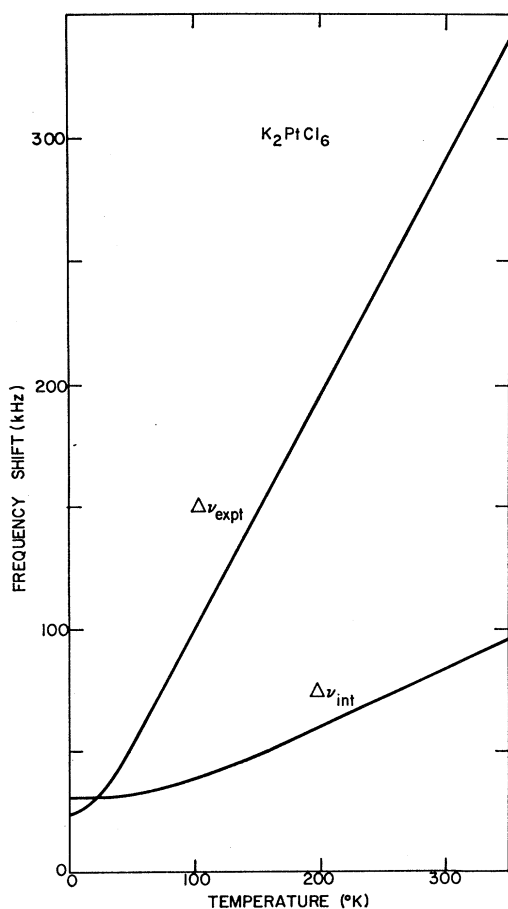


FIG. 2. Plots of the experimental frequency shift $\Delta\nu_{\text{expt}}$ and the calculated shift $\Delta\nu_{\text{int}}$ due to the internal lattice modes as a function of temperature for K_2PtCl_6 .

represents about one third of the experimental frequency shifts.

In Figs. 2 and 3 the calculated frequency shifts $\Delta\nu_{\text{int}}$ and the experimental frequency shifts $\Delta\nu_{\text{expt}}$ are plotted for K_2PtCl_6 and K_2PdCl_6 , respectively. The probable error associated with the $\Delta\nu_{\text{expt}}$ values is ± 2 kHz. From the figures it is seen that the internal modes make a significant contribution at all temperatures. At the lowest temperatures $\Delta\nu_{\text{int}} > \Delta\nu_{\text{expt}}$ for the K_2PtCl_6 data.

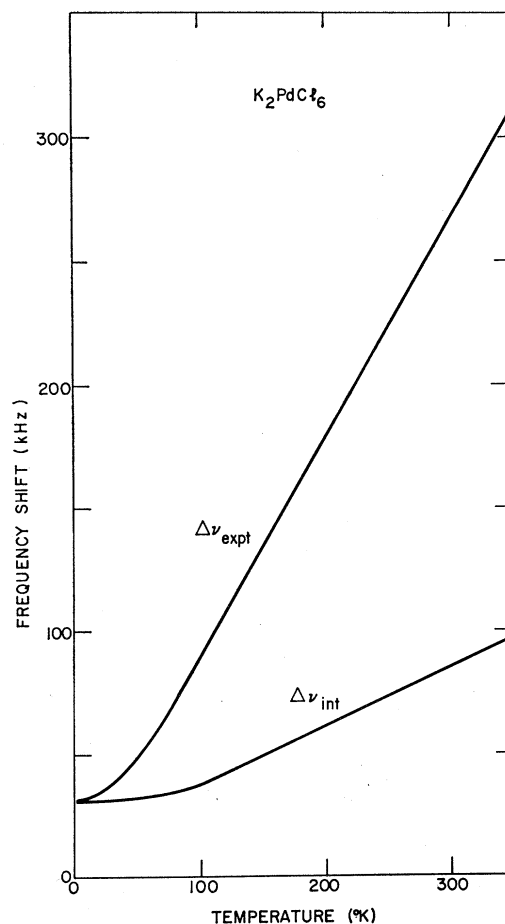


FIG. 3. Plots of the experimental frequency shift $\Delta\nu_{\text{expt}}$ and the calculated shift $\Delta\nu_{\text{int}}$ due to the internal lattice modes as a function of temperature for K_2PdCl_6 .

This is an impossible result and indicates that the present approach somewhat overestimates the contribution to the frequency shift from the internal modes. However, for temperatures greater than 100°K the differences ($\Delta\nu_{\text{expt}} - \Delta\nu_{\text{int}}$) are positive and reasonably large. These differences can therefore be expected to provide meaningful values for the frequency shift $\Delta\nu_{\text{rot}}$ due to the rotary lattice mode. Assuming that for temperatures greater than 100°K the high temperature approximation is valid for this mode, Eqs. (3) and (6)

may be combined to yield

$$\langle \omega^2_{\text{rot}} \rangle = \frac{\nu_0 3kT}{I \Delta \nu_{\text{rot}}(T)}. \quad (8)$$

Geometric moments of inertia $I = 1.28 \times 10^{-37}$ g cm² and $I = 1.25 \times 10^{-37}$ g cm² are deduced from the $M\text{-Cl}$ bond lengths^{15,21} in K_2PtCl_6 and K_2PdCl_6 , respectively. Substitution in Eq. (8) yields the $\langle \omega^2_{\text{rot}} \rangle^{1/2}$ values shown in Fig. 4. We see that $\langle \omega^2_{\text{rot}} \rangle^{1/2}$ is a slowly varying function of the temperature over the range $100^\circ\text{K} < T < 340^\circ\text{K}$ for both substances. The increase in $\langle \omega^2_{\text{rot}} \rangle^{1/2}$ at the lowest portion of the temperature range may not be entirely real, since in this range an overestimate of $\Delta \nu_{\text{int}}$ will have the largest effect on the deduced $\Delta \nu_{\text{rot}}$ values. At room temperature the deduced torsional oscillation frequencies are ~ 58 cm⁻¹ and ~ 64 cm⁻¹ for K_2PtCl_6 and K_2PdCl_6 , respectively. These values are significantly larger than the corresponding values of ~ 32 cm⁻¹ and ~ 42 cm⁻¹ obtained from the single-mode analysis. A recent calculation of these torsional oscillation frequencies by Debeau and Poulet²² has yielded values ~ 63 and ~ 62 cm⁻¹ for K_2PtCl_6 and K_2PdCl_6 , respectively. These values are in excellent agreement with those that we have obtained.

In conclusion, the multiple-mode analysis of the ³⁵Cl NQR frequency data for K_2PtCl_6 and K_2PdCl_6 presented in this paper provides a convincing explanation of the observed motional averaging of the electric field gradient at the chlorine nuclear sites. With such a satisfactory theoretical analysis of the NQR data it seems reasonable to assert that nuclear quadrupole resonance offers a practical means to investigate low-lying librational modes, such as the rotary modes in

²¹ I. D. Brown (private communication).

²² M. Debeau and H. Poulet, *Spectrochim. Acta* **25A**, 1553 (1969).

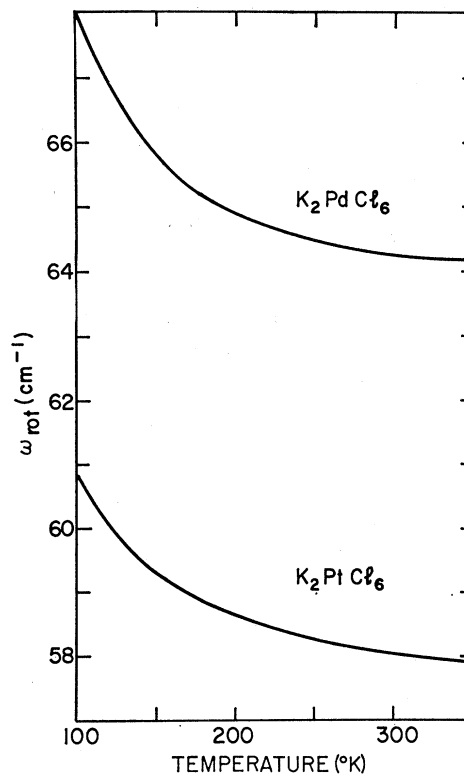


Fig. 4. The deduced temperature dependence of the rotary lattice mode frequencies $\omega_{\text{rot}} \equiv \langle \omega^2_{\text{rot}} \rangle^{1/2}$ in K_2PtCl_6 and K_2PdCl_6 .

cubic R_2MX_6 compounds, which are inaccessible to direct investigation by conventional spectroscopic methods because of symmetry considerations.

ACKNOWLEDGMENT

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