LATTICE DYNAMICS OF SOME HEXACHLOROPLATINATE
COMPOUNDS AS REVEALED BY NUCLEAR QUADRUPOLE RESONANCE

by

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The nuclear quadrupole resonance (NQR) frequencies (ν) of the $^{35}\text{Cl}$ nuclei in the compounds rubidium hexachloroplatinate ($\text{Rb}_2\text{PtCl}_6$) and cesium hexachloroplatinate ($\text{Cs}_2\text{PtCl}_6$) were measured as functions of temperature in the range 4-500 K, under vacuum. The corresponding spin-lattice relaxation times (T₁) were measured at the same temperatures above 60 K in $\text{Rb}_2\text{PtCl}_6$ and above 77 K in $\text{Cs}_2\text{PtCl}_6$. Both ν and T₁ were measured as functions of hydrostatic pressure in the range 1-500 kg cm⁻² at four temperatures between room temperature and 380 K. A brief description of the apparatus and techniques used is presented. The data for $\text{Rb}_2\text{PtCl}_6$ and $\text{Cs}_2\text{PtCl}_6$ are analysed with existing data for potassium hexachloroplatinate ($\text{K}_2\text{PtCl}_6$). Differences in the static lattice values (ν₀) of the NQR frequencies are compared with field gradient calculations. In each case, the temperature dependence of ν is explained in terms of a motional averaging of the electric field gradient at the chlorine site due to the internal modes of vibration of the $\text{PtCl}_6$ octahedron as well as the rotary lattice mode of this ion. The positive pressure coefficients of the ν(P) data are accounted for by increases in the restoring forces acting on the $\text{PtCl}_6$ octahedra. The ν(P) and ν(T) data are combined using a thermodynamic expression to obtain, for each substance, an average value of the rotary mode frequency ($\omega_{\text{rot}}$) as a function of $\alpha/\beta$ (the ratio of the thermal expansion coefficient
to the coefficient of isothermal compressibility). $T_1(T)$ data are analysed using a modification of the Van Kranendonk theory which takes account of internal and rotary mode contributions. Treatment of the $T_1(P)$ data follows the $\nu(P)$ analysis.

$\omega_{\text{rot}}(\alpha/\beta)$ is deduced from the combined $T_1(T)$ and $T_1(P)$ data for $\text{Rb}_2\text{PtCl}_6$ and $\text{Cs}_2\text{PtCl}_6$. Debeau and Poulet (1969) have obtained $\omega_{\text{rot}}$ values from infrared and Raman data. For $\text{K}_2\text{PtCl}_6$, $\text{Rb}_2\text{PtCl}_6$ and $\text{Cs}_2\text{PtCl}_6$ these values are, respectively $63 \text{ cm}^{-1}$, $71 \text{ cm}^{-1}$, $80 \text{ cm}^{-1}$. The $\omega_{\text{rot}}(\alpha/\beta = 15)$ values from the $\nu(T,P)$ data agree favourably: $61 \text{ cm}^{-1}$, $68 \text{ cm}^{-1}$, $81 \text{ cm}^{-1}$. The $\omega_{\text{rot}}(\alpha/\beta = 15)$ values from the $T_1(T,P)$ data for $\text{Rb}_2\text{PtCl}_6$ and $\text{Cs}_2\text{PtCl}_6$ are $63 \text{ cm}^{-1}$ and $75 \text{ cm}^{-1}$.
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CHAPTER I

INTRODUCTION

This thesis describes the nuclear quadrupole resonance (NQR) measurements performed on the chlorine nuclei in the compounds rubidium hexachloroplatinate ($\text{Rb}_2\text{PtCl}_6$) and cesium hexachloroplatinate ($\text{Cs}_2\text{PtCl}_6$). The results are analysed in conjunction with existing data for potassium hexachloroplatinate ($\text{K}_2\text{PtCl}_6$). The present work is part of a general program in this laboratory to investigate the potential of NQR as a spectroscopic tool which may be of particular use for the study of low frequency librational modes of vibration. In this chapter the origin of the nuclear quadrupolar interaction is described and the various types of information which can be obtained from NQR measurements are outlined. Chapter II describes the experimental apparatus and techniques used in this work. Chapters III and IV present the theory of and discuss the data for the NQR frequency as a function of temperature and pressure. Chapter V outlines the theory of quadrupolar relaxation; Chapter VI applies this theory to the spin-lattice relaxation time data.

I-1 The Nuclear Quadrupolar Hamiltonian

The Hamiltonian for the total electrostatic interaction between a nucleus and its environment can be written in the form
\[ H_E = \sum_{\ell, m} A^m_\ell B^{-m}_\ell. \]

This is derived by the expansion of the classical expression for the interaction energy in terms of spherical harmonics. The \( A^m_\ell \) are the components of the irreducible tensor operators corresponding to the multipole moments of the nucleus. Because nuclei have definite parity, they do not possess odd moments, i.e. \( A^m_\ell = 0 \) for odd \( \ell \). The \( B^m_\ell \) are the components of the irreducible tensor operators composed of the \( \ell \)th order derivatives of the electrostatic potential.

The \( \ell = 0 \) term of the Hamiltonian is the Coulomb interaction between point charges. The next non-vanishing term (\( \ell = 2 \)) gives rise to the interaction between the nuclear quadrupole moment and the electric field gradient at the nuclear site which is set up by the surrounding charge distribution. This term, the quadrupolar Hamiltonian is usually written

\[ H_Q = \sum_{\mu=2}^{2} Q^\mu (\nabla^2)^{-\mu} \]  \hspace{1cm} (1-1)

and it will be discussed from different viewpoints in succeeding chapters.

**I-2 Nuclear Quadrupole Resonance Experiments**

The quadrupolar Hamiltonian may be regarded as the sum of a secular part \( H_Q \) and a non-secular part \( H_Q - \overline{H}_Q \), i.e.
\[ H_Q = \bar{H}_Q + (H_Q - \bar{H}_Q). \]

The secular part gives rise to a set of stationary energy levels, the separation of which corresponds to radio frequency (rf) quanta. Resonance absorption of magnetic dipole radiation can be observed. Such experiments, first reported by Dehmelt and Kruger (1950), are referred to as pure nuclear quadrupole resonance experiments. In this work the NQR absorption frequencies of the \(^{35}\text{Cl}\) nuclei have been measured in \(\text{Rb}_2\text{PtCl}_6\) and \(\text{Cs}_2\text{PtCl}_6\) as functions of the external parameters, temperature and hydrostatic pressure.

The non-secular contribution to the Hamiltonian couples the nuclear spin system to its environment, the lattice. If the nuclear spin system is perturbed by rf magnetic field, it returns to equilibrium by exchanging energy with the lattice. It is possible to perform experiments to measure the characteristic time (the spin-lattice relaxation time) of the return of the spin system to equilibrium. Part of this work involved the measurement of spin-lattice relaxation times for the \(^{35}\text{Cl}\) nuclei in \(\text{Rb}_2\text{PtCl}_6\) and \(\text{Cs}_2\text{PtCl}_6\) over a wide range of temperatures and pressures.

Measurement of the NQR absorption frequency provides information about the quadrupole coupling constant \(e^2qQ\), which is the product of the nuclear quadrupole moment \(eQ\) and the electric field gradient parameter \(eq\), and also about the degree of asymmetry of the electric field gradient. If the nuclear
quadrupole moment is known a priori and the asymmetry parameter $\eta$ can be separated or is known to be zero, then such an experiment gives some insight into the electric charge distribution about the nucleus. For nuclei with spin $I = 3/2$, there is only one resonance frequency therefore $e^2qQ$ and $\eta$ cannot be determined separately. This is the case for chlorine nuclei in the $R_2PtCl_6$ compounds, however because of the symmetry of the structure, to a good approximation $\eta = 0$.

In an ionic solid, the neighbouring ions determine $eq$; in a covalent molecular solid, most of the field gradient comes from the molecular bond which involves the nucleus in question (Das and Hahn 1958). Therefore in some cases, NQR spectra may provide a check for molecular orbital calculations (Schempp and Bray 1968). Information about molecular bonds may sometimes be obtained from NQR spectra using the theory of Townes and Dailey (1951). Kubo and Nakamura (1966) have determined in this way that the metal-ligand bond of many $R_2MX_6$ compounds, which is responsible for the dominant part of the field gradient at the X site, is about 60 per cent covalent in character.

Some rudimentary information about crystal structure may be extracted from NQR spectra. The number of lines in an NQR spectrum determines the number of inequivalent sites occupied by the resonant nuclear species.

Both the NQR frequency and spin-lattice relaxation time are sensitive to changes in temperature and pressure through the dependence of the populations and amplitudes of normal
modes of vibration of the lattice. In most cases, lattice vibrations cause a motional averaging of the electric field gradient resulting in a decrease of the NQR frequency with temperature. The scattering of lattice phonons by the spin system provides a mechanism for spin-lattice relaxation.

Various models have been proposed to explain the temperature dependence of the NQR frequency and spin-lattice relaxation time due to the effects of lattice dynamics. The only quantitative theory for the pressure variation of the NQR frequency is the work of Kushida, Benedek and Bloembergen (1956). They showed that measurements of the NQR frequency as a function of temperature and pressure could be used, in conjunction with an equation of state of the solid, to obtain the frequency as a function of temperature at constant volume as well as the volume dependence of the electric field gradient at the nuclear site.

A comprehensive list of the $R_2MX_6$ compounds investigated by NQR methods may be compiled from this thesis and the following references: Kubo and Nakamura (1966), Segel and Barnes (1968), Lucken (1969) and Brown and Kent (1970). The measurements described by Kubo and Nakamura and by Brown and Kent are NQR frequency measurements at a few temperatures. Very little information about the lattice dynamics of these compounds is extracted from their data.
I-3 Present Investigation

The present work was undertaken to investigate the lattice dynamics of the $R_2MX_6$ compounds as well as the contribution of the $R$ ions to the NQR frequency. This could be best accomplished by performing experiments on the hexachloroplatinate compounds $\text{Rb}_2\text{PtCl}_6$ and $\text{Cs}_2\text{PtCl}_6$ and analysing the data together with the existing results for $\text{K}_2\text{PtCl}_6$ (Jeffrey and Armstrong 1968, Armstrong and Jeffrey 1969). The molecular bonding in the $\text{PtCl}_6$ complex ion is relatively simple in these compounds. The NQR frequency is not dependent on $\pi$-bonding effects as is the case in $\text{K}_2\text{IrCl}_6$ (Armstrong and Baker 1970), $\text{K}_2\text{OsCl}_6$ (Baker and Armstrong 1970) and $\text{K}_2\text{ReCl}_6$ (Armstrong, Baker and Van Driel 1971). Also there can be no magnetic hyperfine relaxation mechanism in the hexachloroplatinates as has been observed in $\text{K}_2\text{IrCl}_6$ (Jeffrey, Armstrong and Kisman 1969). Differences in the NQR measurements performed on $\text{R}_2\text{PtCl}_6$ compounds reflect small changes in the static and dynamic properties of the lattices.
CHAPTER II

EXPERIMENTAL PROCEDURES

II-1 Quadrupolar Energy Levels

The general quadrupolar Hamiltonian was given in Chapter I as

$$H_Q = \sum_{\mu=-2}^{2} Q^\mu (\hat{\mathbf{e}}^E)_x - \mu$$

The irreducible tensor components $Q^\mu$ are

$$Q^0 = \frac{eQ}{2I(2I-1)} [3I^2_z - I(I+1)]$$

$$Q^{\pm 1} = \frac{\sqrt{6}eQ}{4I(2I-1)} [I_z I_x \pm I_z I_y]$$

$$Q^{\pm 2} = \frac{\sqrt{6}eQ}{4I(2I-1)} I_z^2$$

The electric field gradient tensor has irreducible components:

$$\mathbf{eE}^0 = \frac{i}{2} \mathbf{V}_{zz}$$

$$\mathbf{eE}^{\pm 1} = \frac{1}{\sqrt{6}} [\mathbf{V}_{xz} \pm i \mathbf{V}_{yz}]$$

$$\mathbf{eE}^{\pm 2} = \frac{1}{2\sqrt{6}} [\mathbf{V}_{xx} - \mathbf{V}_{yy} \pm 2i \mathbf{V}_{xy}]$$

where $\mathbf{V}_{\alpha\beta} = \partial V/\partial \mathbf{x}_\alpha \mathbf{x}_\beta$ are the cartesian components of the electric field gradient. It is always possible to transform to a set of principal axes $(X,Y,Z)$ such that
\[ \begin{align*}
\nu_E^0 &= \frac{1}{2}V_{zz} = \frac{1}{2} \eta_{eq} \\
\nu_E^\pm &= 0 \\
\nu_E^{\pm 2} &= \frac{1}{2\sqrt{6}}[V_{xx} - V_{yy}] = \frac{1}{2\sqrt{6}} \eta_{eq}
\end{align*} \]

where \( \eta = (V_{xx} - V_{yy})/V_{zz} \) is defined as the asymmetry parameter.

In the principal axis co-ordinate system, the Hamiltonian becomes

\[ H_Q = \frac{e^2 gQ}{4I(2I-1)}[3I_Z^2 - I(I+1) + \frac{1}{2} \eta (I_+^2 + I_-^2)] \]

In the hypothetical case of a rigid \( R_2PtCl_6 \) lattice, the \( Cl \) sites have \( C_4 \nu \) symmetry hence the asymmetry parameter is zero. In fact, distortions of the \( PtCl_6 \) octahedra due to lattice vibrations will create a small asymmetry parameter, however in the next chapter it will be shown that it is completely negligible. Therefore in the case of \( R_2PtCl_6 \) lattices, the \( Cl \) NQR energy levels are given by

\[ E_m = \frac{e^2 gQ}{4I(2I-1)}[3m^2 - I(I+1)] \]

Since \( I = 3/2 \) for \( Cl \) nuclei the energy level scheme shown in Figure II-1(a) results. This energy level scheme is analogous to a combination of two nuclear magnetic resonance systems, each of spin \( I = 1/2 \). That is, the energy levels may be considered to be made up of the two subsystems shown in Figure II-1(b).
Figure II-1: (a) Quadrupolar energy levels for a nucleus with $I = 3/2$ in an axially symmetric field gradient.

(b) Subsystems comprising NQR energy level scheme.
Magnetic dipole transitions, $\Delta m = \pm 1$, may be stimulated by applying a radio frequency magnetic field of frequency

$$\nu_Q = \frac{\nu}{2e^2qQ}$$

The interaction between the applied rf field and the nuclear spins is given by the Hamiltonian

$$H_{rf} = -\gamma \tilde{H}_1 \cdot \vec{I}$$

where $\tilde{H}_1(t)$ may be written as the sum of two circularly polarized fields. That is

$$\tilde{H}_1(t) = \tilde{H}_1 \cos \omega_Q t$$

$$= \frac{H_1}{2} [\hat{i} \cos \omega_Q t + \hat{j} \sin \omega_Q t]$$

$$+ \frac{H_1}{2} [\hat{i} \cos \omega_Q t - \hat{j} \sin \omega_Q t]$$

where $\omega_Q = 2\pi\nu_Q$.

II-2 Macroscopic Magnetization and Relaxation Times

As an aid to understanding the macroscopic behaviour of the observed magnetization, a fictitious Curie magnetization, $M_0$, may be associated with each of the NQR subsystems:

$$\tilde{M}_0^+ = \frac{N\gamma \hbar^2}{4kT} \hat{h}, \quad \tilde{M}_0^- = \frac{N\gamma \hbar^2}{4kT} \hat{\kappa}$$

The superscripts (+) and (−) refer to the subsystems.
(+3/2, +1/2) and (-3/2, -1/2), respectively. The configuration of $M_0^+$ and $M_0^-$ in the absence of an rf field is shown in Figure II-2(a); this is consistent with the fact that there is no net equilibrium magnetization in an NQR system. Application of the rf field $H_1(t)$, at the NQR frequency, has the effect of applying torques to $\vec{M}_0^+$ and $\vec{M}_0^-$, forcing them to rotate slowly about the x axis, meanwhile they continue to precess rapidly about the z axis but in opposite senses. If the rf field is applied for the proper interval $\vec{M}_0^+$ and $\vec{M}_0^-$ can be rotated into the X, Y plane. Here they continue to precess about the Z axis after the rf pulse is removed, adding constructively along ±X directions and cancelling along the Y axis. This is seen in Figure II-2(b). The resultant magnetization is linearly polarized along the X axis:

$$\vec{M}_X(t) = \vec{r}_2M_0^+\cos \omega t$$

This alternating magnetization induces a voltage in the same coil which supplies the rf field $H_1(t)$. Due to a dephasing of the nuclear spins, the magnetization becomes incoherent and the signal induced in the coil dies away. For this reason the signal observed after the rf pulses is called the free induction decay signal.

The dephasing of the nuclear spins is caused by differences in the local electric field gradients experienced by the resonant nuclei and also by magnetic dipolar interactions among the spins. These mechanisms may be characterized
Figure II-2:  
(a) Macroscopic magnetizations in equilibrium configuration.

(b) Magnetizations after a 90° pulse. The directions of precession about the Z axis are indicated.
respectively by a reversible dephasing time, $T_2^\dagger$, and an irreversible dephasing time, $T_2$, known as the spin-spin relaxation time. If the NQR line shape as well as the distribution of local electric field gradients is assumed to be Gaussian then the free induction decay may be described by the single time constant $T_2^*$:

$$T_2^*-1 = \left(T_2^* - T_2^{*2} + T_2^{*2} - 2\right)^{1/2}$$

In a powder sample, the situation is complicated by the random orientation of crystallites with respect to the applied rf field. Woessuer and Gutowsky (1963) have shown, by integrating over all orientations that the averaged value of $\bar{M}_x$ before dephasing for a spin 3/2 nucleus is:

$$\bar{M}_x = \frac{\sqrt{3}}{4} n_0 f(x)$$

where

$$x = \sqrt{3} \gamma H_1 t$$

and

$$f(x) = -8 \sum_{n=1}^{\infty} \frac{J_{2n-1}(x)}{(2n-1)(3n+1)(2n-3)}$$

The $J_n$ are the Bessel functions.

The $\pm Z$ components of the magnetization grow back to their equilibrium values exponentially with a time constant $T_1$, termed the spin-lattice relaxation time. The $M_Z^\pm$ components can be observed by applying a second rf pulse, identical to the first and at a time interval $\tau$ after the first. This second pulse creates a free induction decay signal whose
amplitude is proportional to $M^+_Z(\tau)$. Since the amplitude of the first free induction decay is proportional to $M^+_Z$ then it can be shown that

$$\frac{M_0 - M^+_Z(\tau)}{M_0} = [1-\frac{1}{2}f(2x)/f(x)] \exp(-\tau/T_1).$$

Since the function $f(x)$ is quasi-periodic, its first maximum and minimum define pulse widths which are directly analogous to 90° and 180° pulses in an ordinary NMR experiment. Therefore the same pulse sequences as are used in NMR experiments can be employed in NQR experiments to measure spin-lattice and spin-spin relaxation times.

II-3 The NQR Spectrometer

The behaviour of the free induction decay signal discussed above imposes certain limitations on the construction of a pulsed NQR spectrometer. In the first place, the pure quadrupole resonance frequency is determined by the substance being investigated. Since this frequency varies with temperature and pressure, the useful spectrometer will operate over a wide band of frequencies. The free induction decay signal may die away in a time of the order of $\sim 50$ µs, therefore the spectrometer must be capable of supplying high power pulses of short duration relative to $T_2^*$. Finally, a single coil must be used both to excite the resonance and to detect the ensuing signal. A crossed-coil scheme cannot be employed since there
is no magnetization component perpendicular to the transmitting coil.

The spectrometer used in this work was constructed by K.R. Jeffrey and has been fully described in his Ph.D. thesis (1969). A schematic diagram displaying the major components is given in Figure II-3. Low-level rf power is generated in the cw oscillator which is continuously variable from 20-27 MHz. The rf is allowed to pass through the gate when it is turned on by a pulse from the dc pulse generating system. This consists of an array of Tektronix Series 160 waveform and pulse generators. The rf leakage through the gate in the off condition is suppressed by 80 db from the 25 V rf pulse which it outputs in the on condition. The rf pulses are fed to the power amplifier by a tuned length of co-axial cable. The power amplifier, or transmitter, amplifies the pulses to \(\approx 500\) V peak to peak into a 50 \(\Omega\) load.

The rf bridge (Jeffrey and Armstrong 1967) is an important component of the spectrometer. Its function is to couple the maximum possible amount of power to the sample coil during the pulse while protecting the pre-amplifier from the direct impact of the pulse. In addition, the bridge must efficiently couple the nuclear signal following the pulse to the input of the preamplifier. At a given frequency, the bridge is balanced by means of tuneable capacitors. At balance, the voltage seen at the preamplifier input is \(\approx 1\) V peak to peak.

The output from the preamp is mixed in the first stage
Figure II-3: Block diagram of the spectrometer.
of the receiver-detector with a cw reference signal from the oscillator. Both of these signals are attenuated before entering the receiver amplifier so that they are approximately the same level and in order that the mixed signal level is within the linear operating region of the diode detector. The reference signal can also be phase shifted with respect to the nuclear signal so that phase coherent detection is attained.

The detected signal is further amplified by 20 db in the video amplifier and is monitored by an oscilloscope at that point. The box-car integrator measures a portion of the signal selected by a gate from the dc pulse generator. The output of the integrator is preserved by an X-Y recorder.

II-4 Measurement Techniques

(a) NQR Frequency Measurement

The NQR frequency is measured by observing the free induction decay signal following a 90° pulse. When the oscillator frequency is within the span of the NQR resonance line, but off-centre, then a beat pattern is observed in the free induction decay. Ideally, the centre of the resonance line can be found by adjusting the oscillator frequency until the beat frequency is reduced to zero. However this is limited by the length of the free induction decay. For instance, if the free induction signal decays completely in 200 μs, then no beats will be observed if the oscillator frequency is within 4 kHz of the resonance line centre. This technique can be
improved by measuring the amplitude of a portion of the signal using the box-car integrator. The amplitude will be a maximum when the oscillator frequency is set at the line centre if the two signals are in phase. The precision of such a determination of the NQR frequency is ±1 kHz. Throughout this procedure the oscillator frequency is continuously monitored by an electronic counter (Hewlett Packard 3735 A in conjunction with a General Radio type 1156-A decade scaler).

(b) \( T_1 \) Measurement

The technique used to perform most of the \( T_1 \) measurements was the three pulse sequence. The first pulse in the sequence is a 180° pulse which reverses the directions of the two components of the equilibrium magnetization \( \vec{M}_0^+ \) and \( \vec{M}_0^- \). At a variable time \( \tau \) later, a 90° pulse followed closely by a 180° pulse create a spin echo (Hahn 1950) whose amplitude is proportional to

\[
M_z^+(\tau) + M_z^-(\tau) = 2M_z^+(\tau).
\]

After the first 180° pulse, \( M_z^+(\tau) \) is given by

\[
\vec{M}_z^+(\tau) = M_0^+[1-2\exp(-\tau/T_1)].
\]

Therefore \( T_1 \) may be found by taking the slope of a plot of \( \ln(M_0^+-M_z^+(\tau)) \) vs. \( \tau \). \( M_0 \) is measured as the amplitude of the spin echo in the absence of the first 180° pulse in the sequence. Oscilloscope traces of free induction decay and spin echo signals are displayed in Figure II-4. The difference in
Figure II-4: Free induction decay and spin-echo signals in Cs$_2$PtCl$_6$ at $T = 77$ K, 300 K.
Signal attenuation = 10 dB.
Oscilloscope settings: 1 v/div.; 0.1 ms/div.
amplitudes between the signals is due to the temperature
dependence of the Curie magnetization (2-1). $M^+_Z(\tau)$ is mea-
sured over a range of $\tau$ from $\simeq 0.1T_1$ to $\simeq 3T_1$. This is done
by repeating the 180°, 90°-180° pulse sequence at intervals
of $\simeq 10T_1$ (to ensure that the magnetization has reached equi-
librium at the beginning of each sequence). The spin echo
amplitude is monitored by the integrator and recorder at
each repetition; meanwhile $\tau$ is slowly increased from $\simeq 0.1T_1$
to $\simeq 3T_1$ by a long sawtooth waveform from one of the Tektronix
162 waveform generators which also drives the X axis of the
recorder. At least 250 samplings of $M^+_Z(\tau)$ are made in each
determination of $T_1$. This is a restriction imposed by the
conditions on the proper operation of the box-car integrator
outlined by Hardy (1965). That is

$$\frac{50Rc}{\omega} < N$$

and

$$Rc > 5\omega$$

where Rc is the time constant of the integrator and $\omega$ is the
integrating gate width.

Values of $T_1$ up to $\simeq 3$ seconds were measured with this
technique. In order to accomplish this, sweep times of the
order of $250 \times 10T_1 = 7500$ seconds were required. For the
creation of the long sweep times and repetition times, it was
necessary to modify two of the Tektronix 162 waveform generators.
This was done, following the method of Blume (1961), by connecting a 10 μF polystyrene capacitor across the 1 μF timing capacitor of each of these circuits. The sweep time and repetition time capabilities were thus increased by a factor of eleven.

The measurement of $T_1$ over such relatively long periods introduced problems of stability of the oscillator frequency and receiver gain. The frequency stability was improved by removing the oscillator-gate from the vicinity of the power amplifier which produced a large amount of heat causing thermal fluctuations which were reflected in drifting of the frequency. Since a short tuned length of coaxial cable connected the output of the oscillator-gate to the input of the power amplifier, it was necessary to introduce a half wavelength of cable in this connection in order to separate the two components. The gain of amplifiers tended to drift slightly over the period of these long measurements but in most cases the consequences to the precision of the measurements of $T_1$ were not serious.

Typical recorder traces and corresponding semi-logarithmic plots of $T_1$ measurements taken using the three pulse sequence technique are shown in Figures II-5 and II-6. These indicate the wide range of conditions under which $T_1$ measurements were made. It was possible to measure the longer $T_1$ values with a precision of ±5%. The precision of the shorter $T_1$ values was rather better than this.

Another method which was used to measure long relaxation times is the saturation sequence. The first set of pulses in
Figure II-5: Typical T₁ data.
Figure II-6: Typical $T_1$ data.
the sequence consists of about 10 closely spaced pulses, each of width slightly less than 90°. The effect of this set of pulses is supposedly to completely randomize the magnetization so that no coherent component is left in any direction. This effect should be independent of the initial magnetization. A 90° pulse at a variable time $\tau$ after the saturating "comb" of pulses creates a free induction decay whose amplitude is proportional to $\exp(-\tau/T_1)$. Since the initial value of the magnetization before the saturating comb should be unimportant, then the sequence can be triggered immediately after the 90° sampling pulse rather than waiting for an interval of $10T_1$.

However, in practice, this technique suffers from some disadvantages. It was found that the amplitude of the free induction decay signal was not independent of the repetition time of the sequence if this time were less than $\sim 3T_1$, indicating that there was some correlation between magnetization before and after the saturating comb. Another indication of this was the presence of a small secondary echo (Hahn 1950) at a time $\tau_0$ after the 90° sampling pulse, where $\tau_0$ was the spacing between pulses in the saturating comb. This imposed restrictions on the position of the integrating gate. For these reasons the saturating comb technique was used only for $T_1$ values greater than $\sim 4$ seconds.
Sample Preparation and Environment Control

Powder samples of Rb₂PtCl₆ and Cs₂PtCl₆ were purchased from Atomergic Chemetal Co., Division of Galland-Schlesinger Chemical Manufacturing Corp. The NQR signal was not observed in Rb₂PtCl₆ until the sample had been annealed at 500 K for several hours. This treatment apparently reduced the strains in the crystallites, creating a more favourable distribution of field gradients. Heat treatment was not necessary in the Cs₂PtCl₆ sample.

(a) Temperature Control

Standard cryogenic techniques were employed to control the temperature of the sample in the range 4-300 K. The sample itself was contained in a thin walled teflon holder around which the rf coil was wound. A copper can which acted as a shield was placed around the sample holder. A 500 Ω heater was wound on the shield and the space between it and the sample holder was filled with boron nitride to facilitate thermal conduction. This unit was thermally isolated by a stainless steel tube (which also served as an rf transmission line) and a vacuum space.

The simple feedback system shown schematically in Figure II-7 was used to regulate the temperature. A copper-constantan thermocouple measured the temperature of the copper shield. The dc bucking voltage source was connected to the thermocouple such that the polarities of the voltages were opposite. The null detector measured the difference between
Figure II-7: Schematic diagram of the temperature regulation system.
the thermocouple voltage and the bucking voltage source and
output a signal proportional to this difference. The heater
control unit used this signal to make an adjustment to the
heater current. By placing the regulating thermocouple as
close as possible to the heater, the response time of the
regulation process was minimized. A separate thermocouple
was used to measure the sample temperature.

In the temperature range above 300 K, the sample was con-
tained in a similar temperature regulated unit which was ther-
mally insulated by several nested stainless steel cans separated
by layers of glass wool. Temperatures up to 500 K were attained
with this arrangement.

(b) **Pressure Apparatus**

Hydrostatic pressures up to 5000 kg cm$^{-1}$ were generated
with a Hart compressor. The sample was contained in a teflon
holder which was immersed in the hydraulic fluid (Dow Corning
200 silicone oil). The rf coil was wound on the teflon sample
holder which was contained in a pressure cell constructed from
hardened beryllium copper. The rf power was fed to the coil
through a high pressure seal. The seal was constructed by
bonding a lead inside a short length of high pressure tubing
with Eccobond 104 epoxy.

The pressure was measured to within 100 kg cm$^{-2}$ using a
manganin coil pressure gauge in conjunction with a Foxboro
recorder. Temperatures in the range 300 K - 400 K could be attained by using an external heater supplied by a variac. Because of the large thermal mass of the pressure cell, the temperature could be regulated manually, thus maintaining fluctuations to within acceptable limits during the time in which measurements were taken.
CHAPTER III

THEORY OF NQR FREQUENCY

III-1 Introduction

In most cases, and in particular in the present work, the NQR frequency, measured as a function of temperature at a constant pressure, is observed to decrease with increasing temperature. Exceptions to this rule will not be discussed here. The decrease in frequency is proportional to a decrease in the average electric field gradient at the resonant nucleus caused by thermal motions of the lattice. This chapter will trace the development of the quantitative explanations for the temperature dependence of the NQR frequency as it relates to the cubic $R_2PtCl_6$ type of system. To facilitate the presentation a discussion of both the static and dynamic structure of these compounds is given.

III-2 Structure of $R_2PtCl_6$ Compounds

A particular unit cell of the cubic $R_2PtCl_6$ lattice is shown in Figure III-1. The Bravais lattice is face-centred cubic. The basis consists of a $PtCl_6$ octahedron at $(0,0,0)$ and two $R$ ions at $(t_1, t_2, t_3)$. The $PtCl_6$ octahedra are centrally located in alternate cubes of $R$ ions. Lattice parameters for $R = K, Rb, Cs$ are given in Table III-1.
Figure III-1: A unit cell of the cubic R$_2$PtC$_6$ lattice.
Table III-1: \( R_2PtCl_6 \) Lattice Parameters*

<table>
<thead>
<tr>
<th></th>
<th>( a_0 (\text{Å}) )</th>
<th>Pt-Cl distance (( \text{Å} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_2PtCl_6 )</td>
<td>9.755</td>
<td>2.34 ± .05</td>
</tr>
<tr>
<td>( Rb_2PtCl_6 )</td>
<td>9.901</td>
<td>2.33 ± .05</td>
</tr>
<tr>
<td>( Cs_2PtCl_6 )</td>
<td>10.215</td>
<td>2.35 ± .05</td>
</tr>
</tbody>
</table>

The primitive unit cell, containing one Bravais lattice point and one formula unit is shown inscribed in the fcc unit cell in figure III-2. Since there are 9 atoms per primitive unit cell, there is a total of 27 normal modes of vibration of the lattice. The structure of the normal modes is given in Table III-2.

Table III-2: \( R_2PtCl_6 \) Normal Mode Classification

<table>
<thead>
<tr>
<th>Type</th>
<th>Number</th>
<th>Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acoustic</td>
<td>3</td>
<td>( T_{1u} )</td>
</tr>
<tr>
<td>Optic translational</td>
<td>6</td>
<td>( T_{2g} + T_{1u} )</td>
</tr>
<tr>
<td>Optic rotational</td>
<td>3</td>
<td>( T_{1g} )</td>
</tr>
<tr>
<td>PtCl(_6) internal</td>
<td>15</td>
<td>( A_{1g} + E_g + 2T_{1u} + T_{2g} + T_{2u} )</td>
</tr>
</tbody>
</table>

*Wyckoff (1965).*
Figure III-2: The primitive unit cell shown in relation to the conventional fcc unit cell of the Bravais lattice.
III-3 **Electric Field Gradient at the Chlorine Site**

The chlorine site symmetry is \( C_{4v} \) and therefore the electric field gradient experienced by a chlorine nucleus with the \( \text{PtCl}_6 \) octahedron in its equilibrium configuration will be axially symmetric about the \( C_4 \) axis. A small asymmetry parameter will result from distortions of the octahedra during vibrations but this is estimated to have a negligible effect on the NQR frequency. Some support for this conjecture comes from the work of Nakamura, Ito and Kubo (1960) who have determined the asymmetry parameter for \( \text{K}_2\text{PtI}_6 \) to be about .02. This determination is possible in \( \text{K}_2\text{PtI}_6 \) since \( I = 5/2 \) for the iodine nucleus, so that two NQR frequencies are observed from which both the quadrupole coupling constant \( e^2qQ \) and asymmetry parameter \( \eta \) may be obtained separately. For a spin 3/2 nucleus the single resonance frequency is,

\[
v = \frac{1}{2} e^2 q Q \left( 1 + \frac{1}{3} \eta^2 \right)^{1/2}.
\]

Clearly an asymmetry parameter of .02 will have a negligible effect on \( v \).

The electric field gradient \( e\mathbf{q} \) may be regarded as the sum of two contributions: the major portion \( e\mathbf{q}_C \) comes from the electron charge distribution within the \( \text{PtCl}_6 \) octahedron; the residual part \( e\mathbf{q}_N \), is due to the neighbouring \( \text{R} \) ions, is opposite in sign to \( e\mathbf{q}_C \) and has magnitude \( \sim 5-10\% \) of \( e\mathbf{q}_C \). That is,

\[
e\mathbf{q} = e\mathbf{q}_C + e\mathbf{q}_N.
\]
In principle it is possible to calculate the electric field gradient parameter using

\[ eq = e_i \sum_{l} (3\cos^2 \theta_l - 1)/r_i^{-3} \]

where the summation is taken over all charges in the vicinity of the resonant nucleus. In practice, this calculation is prohibitive because it requires detailed knowledge of charge distributions: molecular orbitals, induced multipoles in neighbouring ions, etc. Smith and Stoessiger (1969a,b) have presented a calculation of the neighbouring ion contribution to the field gradient for \( \text{K}_2\text{PtCl}_6 \), \( \text{Rb}_2\text{PtCl}_6 \) and \( \text{Cs}_2\text{PtCl}_6 \). Their results will be discussed in the following chapter.

III-4 Thermodynamic Considerations

In a perfectly motionless lattice, the NQR frequency is defined to have the hypothetical value \( \nu_0 \). In a real lattice, vibrations at frequencies which are orders of magnitude higher than the NQR frequency have the effect of changing the average field gradient experienced by the resonant nucleus. The populations of the normal modes of vibration of the lattice depend on the temperature, with the result that the NQR frequency also varies with temperature. Changes in the volume of a lattice with temperature and pressure will also cause changes in the NQR frequency.

Experimental measurements of the chlorine NQR frequency \( \nu \) in cubic \( \text{R}_2\text{PtCl}_6 \) compounds suggest that \( \nu \) is uniquely
determined by the macroscopic temperature $T$ and hydrostatic pressure $P$. Therefore assuming an equation of state of the form

$$V = V(P, T)$$

it follows that

$$v = v(V, T) \text{ or } v = v(P, T).$$

The differentials of these expressions may be written:

$$d v = \left(\frac{3v}{3V}\right)_T dV + \left(\frac{3v}{3T}\right)_V dT \tag{3-1}$$

$$d v = \left(\frac{3v}{3P}\right)_T dP + \left(\frac{3v}{3T}\right)_P dT. \tag{3-2}$$

Also if $V = V(P, T)$ then

$$dV = \left(\frac{3V}{3P}\right)_T dP + \left(\frac{3V}{3T}\right)_P dT \tag{3-3}$$

Substituting (3-3) into (3-1) gives

$$d v = \left(\frac{3v}{3V}\right)_T \left(\frac{3V}{3P}\right)_T dP + \left[\left(\frac{3v}{3V}\right)_T \left(\frac{3V}{3P}\right)_P + \left(\frac{3v}{3T}\right)_V\right] dT. \tag{3-4}$$

Equating coefficients in (3-2) and (3-4) yields

$$\left(\frac{3v}{3P}\right)_T = \left(\frac{3V}{3V}\right)_T \left(\frac{3V}{3P}\right)_T \tag{3-5}$$

and

$$\left(\frac{3v}{3T}\right)_P = \left(\frac{3V}{3V}\right)_V + \left(\frac{3V}{3V}\right)_T \left(\frac{3V}{3T}\right)_P \tag{3-6}$$

Substitution of (3-5) in (3-6) then gives

$$\left(\frac{3v}{3T}\right)_V = \left(\frac{3v}{3P}\right)_P + \frac{\alpha}{\beta} \left(\frac{3v}{3P}\right)_T \tag{3-7}$$

where $\alpha$ and $\beta$ are, respectively, the coefficient of thermal...
expansion and the isothermal compressibility defined by

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p$$  and  $$\beta = \frac{1}{V} \left( \frac{\partial V}{\partial F} \right)_T$$

It should be emphasized that $\alpha$ and $\beta$ are macroscopic parameters. The theories for the temperature variation of NQR frequency, which will be discussed below, all assume a constant volume for the sample. If the macroscopic quantities $\alpha$ and $\beta$ are known, then the relation (3-7) allows comparison of the data with the existing theories.

III-5 Models for the Temperature Variation of NQR Frequency

Several models have been proposed, all of which originate from the simple Bayer theory. The Bayer theory (Bayer 1951, Kushida 1955) assumes an axially symmetric field gradient and that the lattice motion causes a torsional oscillation of the field gradient tensor about a fixed axis at a single angular frequency $\omega_t$. The field gradient is assumed to remain axially symmetric during the oscillation. The problem is discussed in terms of two reference frames: a space-fixed frame $(x', y', z')$ and a frame $(x, y, z)$ moving with the field gradient. The $(x, y, z)$ and $(x', y', z')$ axes are aligned with the principal axes of the corresponding field gradient tensors. The torsional oscillation is considered to occur about the common $y, y'$ axis. In the moving frame

$$\mathbf{\hat{v}}_E = \begin{bmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$
Transforming this to the space-fixed system gives

\[ \hat{\mathbf{v}}_E' = R \cdot \hat{\mathbf{v}}_E \cdot R^{-1} \]

where

\[
R = \begin{bmatrix}
\cos \Theta_y & 0 & -\sin \Theta_y \\
0 & 1 & 0 \\
\sin \Theta_y & 0 & \cos \Theta_y
\end{bmatrix}
\]

Therefore,

\[
\hat{\mathbf{v}}_E' = \begin{bmatrix}
-1/2 + 3/2 \Theta_y^2 & 0 & -3/2 \Theta_y \\
0 & -1/2 & 0 \\
-3/2 \Theta_y & 0 & 1 - 3/2 \Theta_y^2
\end{bmatrix}
\]

The secular part of \( \hat{\mathbf{v}}_E' \), which determines the NQR frequency, is found by taking the time average of the angular functions to give

\[
\langle \hat{\mathbf{v}}_E' \rangle = \begin{bmatrix}
-1/2 + 3/2 \langle \Theta_y^2 \rangle & 0 & 0 \\
0 & -1/2 & 0 \\
0 & 1 - 3/2 \langle \Theta_y^2 \rangle & 0
\end{bmatrix}
\]

The average field gradient parameter is then \( \varepsilon \langle \hat{\mathbf{v}}_E' \rangle = \varepsilon \langle 1 - 3/2 \langle \Theta_y^2 \rangle \rangle \). Since the NQR frequency is proportional to the field gradient parameter, the NQR frequency, as predicted by the simple Bayer theory is

\[ \nu = \nu_0 [1 - 3/2 \langle \Theta_y^2 \rangle] \]

To evaluate \( \langle \Theta_y^2 \rangle \), the torsional oscillation energy is equated
with that of a Planck oscillator of frequency $\omega_t$. That is,

$$\frac{1}{2} I \omega_t^2 \langle \theta_y^2 \rangle = \hbar \omega_t \left[ \frac{1}{2} + \frac{1}{\exp(\hbar \omega_t / kT) - 1} \right]$$

with $I$ the moment of inertia of the torsional oscillation.

Finally

$$v(T) = v_0 \left[ 1 - \frac{3\hbar}{4I \omega_t} \coth \left( \frac{\hbar \omega_t}{2kT} \right) \right] \quad (3-8)$$

This function is still often used to approximate experimental data and in the case of $K_2PtCl_6$ (Jeffrey and Armstrong 1968), provides an amazingly good fit to the experimental data. However the value of $\omega_t$ obtained is a weighted average of all normal mode frequencies of the crystal and as such is not a particularly useful parameter.

A modification of the Bayer model was proposed by Wang (1955) who considered oscillations about all three principal axes of the field gradient tensor. The result of this consideration gives

$$v(T) = v_0 \left[ 1 - \frac{3\hbar}{4I} \left( \frac{1}{I_x \omega_t(x)} \coth \left( \frac{\hbar \omega_t(x)}{kT} \right) + \frac{1}{I_y \omega_t(y)} \coth \left( \frac{\hbar \omega_t(y)}{kT} \right) \right) \right] \quad (3-9)$$

This expression employs the same assumption as the Bayer theory, the only difference being that two modes of vibration of different frequency and associated moments of inertia are considered. When (3-8) or (3-9) is used, the implicit assumption is made that one or two low lying normal modes dominate the field gradient averaging. For example, if the
field gradient averaging in PtCl₆ substances were due only to torsional oscillations of the PtCl₆ octahedron about its principal axes then the Wang formula (3-9) could be used to determine \( \omega_t \). In such a case, because of symmetry the motions about the \( x \) and \( y \) axes would be degenerate. That is, \( \omega_t(x) = \omega_t(y) \). However, as will be seen, other lattice modes contribute significantly to the field gradient averaging in such substances.

Kushida (1955) generalized the above approaches by expanding the mean square angular displacements \( <\theta^2> \) and the field gradient parameter eq in terms of normal modes of the lattice. Then, the contribution from each normal mode to the vibrational energy was equated to the energy of a corresponding Planck oscillator. In this way, Kushida derived the following general expression for the NQR frequency as a function of temperature.

\[
v(T) = v_0 \left[ 1 - \frac{3\hbar}{4} \sum_i \frac{A_i}{\omega_i} \coth \left( \frac{\hbar \omega_i}{2kT} \right) \right]
\]  

(3-10)

where the summation is over all normal modes and \( A_i \) are parameters dependent on the details of the motion of the particular modes. The application of this expression requires gross approximations, especially in the evaluation of the \( A_i \) parameters for complicated modes. In general \( A_i \) has no obvious physical interpretation. For a simple torsional oscillation mode, \( A_i \) becomes \( 1/I_i \) and the Kushida theory reduces to the

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Bayer formula (3-8) or to the Wang formula (3-9) in the case of two such modes.

III-6 Application of Kushida Approach to $R_2\text{PtCl}_6$ Substances

It is possible to calculate contributions to the field gradient averaging from two sources: the internal modes of the PtCl$_6$ octahedron and its triply degenerate rotary mode. Acoustic modes provide virtually no contribution since they produce no relative displacement of the neighbouring charges within the unit cell. Optical translatory modes may also be ignored since they involve relative translations of the PtCl$_6$ octahedra and the R ions and therefore they alter only the small portion of the field gradient $e^m_n$.

Following the suggestion of O'Leary (1969), Armstrong, Baker and Jeffrey (1970) have shown that the internal modes play a significant role in the field gradient averaging. To the extent that coupling between R atoms and the PtCl$_6$ octahedra may be neglected, these internal modes may be taken to be the normal vibrational modes of an octahedral molecule (Herzberg 1945). Knowing the details of the motion of these modes, it is possible to calculate explicitly their contribution, resulting from bond bending, to the mean square angular displacement of the field gradient tensor. Since no method is available for calculating the contribution from bond stretching, these contributions are assumed to be small. The
validity of this assumption is discussed below. The rotary mode, on the other hand, lends itself to the direct application of the Kushida theory and its contribution is therefore readily calculated.

(a) **Internal Mode Contribution**

In the harmonic approximation of lattice dynamics (Maradudin, Montroll and Weiss 1963), the $\alpha$th component of the displacement of the $k$th atom in the $l$th unit cell is given by

$$<u_{\alpha}^2(k)> = \frac{m}{2Nn_k} \sum_{k,j} e_{\alpha}^*(k|j)e_{\alpha}(k|j) \frac{c\coth(n\omega_j(k)/2kT)}{\omega_j(k)}$$  \hspace{1cm} (3-11)

where $N$ is the number of molecules per unit volume, $m_k$ is the mass of the $k$th atom, $e_{\alpha}(k|j)$ is the $\alpha$th component of the eigenvector of the displacement of the $k$th atom in the normal mode of wave vector $k$ branch $j$ and frequency $\omega_j(k)$. Following O'Leary it is then possible to consider the effect of bond bending by applying (3-11) to the PtCl$_6$ octahedron to obtain an expression for the mean square angular displacement of the chlorine atom

$$<\theta_{\alpha}^2> = \frac{\pi}{2NR^2} \sum_{k,j} \left| \frac{e_{\alpha}(C|j)}{m_{Cl}} - \frac{e_{\alpha}(Pt|j)}{m_{Pt}} \right|^2 \frac{c\coth(n\omega_j(k)/2kT)}{\omega_j(k)}$$  \hspace{1cm} (3-12)

where $R$ is the Pt-Cl distance. The internal modes of the PtCl$_6$ octahedron are shown in figure III-3 together with their symmetries and mean frequencies for the three substances (Debeau and Poulet 1969). For the frequency of $Q_6$, the experimental value of 120 cm$^{-1}$ (Dorain and Wheeler 1966) has been
Figure III-3: Internal modes of the PtCl$_6$ octahedra with symmetries and mean frequencies.
used rather than the value of 90 cm\(^{-1}\) which Debeau and Poulet calculated. The experimental value comes from structure observed in optical transitions in a Re doped K\(_2\)PtCl\(_6\) crystal. Since the measured internal mode frequencies of the Q\(_1\) to Q\(_5\) normal modes in K\(_2\)PtCl\(_6\), K\(_2\)IrCl\(_6\), K\(_2\)OsCl\(_6\), K\(_2\)ReCl\(_6\) have been found\(^a\) to be substance independent to within ±5%, it is reasonable to expect that the Q\(_6\) frequency will also be substance independent. Therefore the experimental value of \(\omega_6 = 120\) cm\(^{-1}\) has been taken rather than the calculated value of Debeau and Poulet. The modes are identified as pure-stretching, bending-stretching and pure-bending modes. This should be obvious from the indicated atomic displacements. It is probably a justifiable approximation to consider only the effect of bond-bending motion on the field gradient averaging for the following reasons. Q\(_1\) and Q\(_2\) are pure-stretching modes and Q\(_3\) is a bending-stretching mode – all of relatively high frequency. Therefore, unless stretching motions provide a significantly larger contribution to changes in the magnitude of the field gradient than do bending motions, it is safe to ignore these stretching contributions because of their higher frequencies. Although a non-negligible contribution due to bond-stretching may come from Q\(_4\), its effect relative to that of the pure bond-bending modes Q\(_5\) and Q\(_6\) might reasonably be expected to be small.

Since the dispersion of the internal modes is small, the summation over \(k\) may be replaced by multiplication by N.
Table III-3: Eigenvalues $e(\kappa | j)$ for the internal modes of the PtCl$_6$ octahedron

| Mode | $e(\text{Cl} | j)$ | $e(\text{Pt} | j)$ |
|------|-----------------|-----------------|
| $Q_3$ | $6 + \frac{4m_{\text{Cl}}}{m_{\text{Pt}}}$ | $\frac{2}{\frac{6m_{\text{Pt}}}{m_{\text{Cl}}} + 4}$ |
| $Q_4$ | $\frac{2m_{\text{Cl}} - m_{\text{Pt}}}{8m_{\text{Cl}}}$ | $\frac{3m_{\text{Pt}}^2 + 20m_{\text{Cl}}m_{\text{Pt}} + 12m_{\text{Cl}}^2}{16m_{\text{Cl}}}$ | $\frac{3m_{\text{Pt}}^2 + 20m_{\text{Cl}}m_{\text{Pt}} + 12m_{\text{Cl}}^2}{16m_{\text{Cl}}}$ |
| $Q_5$ | $1/2$ | 0 |
| $Q_6$ | $1/2$ | 0 |
By symmetry $<\theta_x^2> = <\theta_y^2>$, therefore (3-12) becomes

$$<\theta_x^2> = \frac{\hbar}{2R^2} \sum_{j=3}^{6} \left| \frac{e_x(C|j)}{m_{Cl}^{1/2}} - \frac{e_x(P|j)}{m_{Pt}^{1/2}} \right|^2 \frac{\coth(\hbar\omega_j/2kT)}{\omega_j}$$

The contribution to the decrease in the NQR frequency as a function of temperature due to the internal modes is

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

(3-13)

The eigenvector coefficients are given in Table III-3. These are calculated subject to the conditions of orthonormality and closure:

$$\sum_{k',\alpha} e_\alpha^* (k'|j) e_\alpha (k|j) = \delta_{ij}$$

$$\sum_{j} e_\beta^* (k'|j) e_\alpha (k|j) = \delta_{\alpha\beta} \delta_{k'k}.$$  

(b) **Rotary Mode Contribution**

It is believed that the rotary optic mode $Q_9$, a three fold degenerate torsional oscillation of the PtCl$_6$ octahedron about its principal axes, makes a large contribution to the temperature dependence of the chlorine NQR frequency. This mode satisfies all the assumptions of the simple Bayer theory, and therefore since it is a single normal mode it may be treated rigorously in this way. Taking into account the
degeneracy by using the Wang formula (3-9), the portion of
the frequency shift due to this mode can be shown to be

\[ \Delta v_{\text{rot}} = \frac{3}{2} \frac{v_0 \hbar}{I \omega_{\text{rot}}} \coth \left( \frac{\hbar \omega_{\text{rot}}}{2kT} \right) \]  

(3-14)

III-7 General Expression for \( v(T) \)

Finally, assuming the internal modes and the rotary mode
to be the sole contributors to the temperature dependence of
\( v \), then the observed frequency shift can be written

\[ \Delta v_{\text{expt}}(T) = \Delta v_{\text{int}}(T) + \Delta v_{\text{rot}}(T) \]  

(3-15)

In other words

\[ v(T) = v_0 \left[ 1 - \frac{3}{2} \frac{\hbar}{I \omega_{\text{rot}}} \coth \left( \frac{\hbar \omega_{\text{rot}}}{2kT} \right) \right. \]

\[ - \frac{3}{2} \frac{\hbar}{R^2} \sum_{j=3}^{6} \left| \frac{e_x(C_2j)}{m_{C_2j}^{1/2}} - \frac{e_x(P_tj)}{m_{P_tj}^{1/2}} \right|^2 \coth \left( \frac{\hbar \omega_j}{2kT} \right) \]  

(3-16)

This expression is applied to the analysis of the data in
the following chapter.
CHAPTER IV

PRESENTATION OF NQR FREQUENCY DATA

IV-1 Introduction

The $^{35}$Cl NQR frequency has been measured in $K_2PtCl_6$ (Jeffrey and Armstrong 1968) and $Rb_2PtCl_6$ and $Cs_2PtCl_6$ in the present work. In all three substances the NQR frequency $\nu$ has been measured as a function of temperature (in the range 4-500 K) at a constant pressure. The first part of this chapter will discuss these data in relation to the constant volume theory developed in the previous chapter. The NQR frequency has also been measured as a function of pressure at a number of constant temperatures for these substances. The pressure dependence of the NQR frequency is discussed in terms of the pressure dependence of the rotary mode frequency $\omega_{rot}$. Finally, the $\nu(T)$ and $\nu(P)$ data are related using the general thermodynamic expression (3-7).

IV-2 The Static Lattice NQR Frequency

Figures IV-1 and IV-2 show the $\nu(T)$ data for $Rb_2PtCl_6$ and for $Cs_2PtCl_6$, respectively. The curves traced out by the data are remarkably similar in shape; the only obvious difference is that, at any temperature, the $Cs_2PtCl_6$ data are about 0.3 MHz higher in frequency than the $Rb_2PtCl_6$ data. A similar curve, displaced to still lower frequencies has been previously observed in $K_2PtCl_6$ by Jeffrey and Armstrong (1968). These displacements may be attributed to differences
Figure IV-1: The $^{35}\text{Cl}$.NQR frequency vs temperature data for $\text{Rb}_2\text{PtCl}_6$. 
Figure IV-2: The $^{35}$Cl NQR frequency vs. temperature data for Cs$_2$PtCl$_6$.
in the nuclear quadrupole coupling constants and will be further discussed below. In each case, the slope of the data approaches some asymptotic value at the highest temperatures. This linear region extends to a much lower temperature (∼100 K) in K₂PtCl₆. A linear behavior at high temperatures is not surprising since the general expression for v(T) from all normal mode contributions considered (3-16) becomes linear at high temperatures, that is,

\[ v(T) = v_0 \left[ 1 + \sum_i \frac{2kT}{\hbar \omega_i} \right] \]  
(4-1)

for \( T \gg \frac{2k}{\hbar \omega_i} \).

It is clear, then, that extrapolating the linear high temperature portions of the data, will yield good estimates of \( v_0 \), the static lattice value of the NQR frequency. The extrapolations are shown in figure IV-3, where straight lines have been fit, by the method of least squares, to the data above 400 K for the Rb₂PtCl₆ and Cs₂PtCl₆. This has been done for a lower temperature range (between 250 K and 350 K) in the case of K₂PtCl₆ because of the effect of the onset of hindered rotations of the PtCl₆ octahedra (Jeffrey and Armstrong 1968) which becomes significant at temperatures greater than ∼350 K for this substance. The values of \( v_0 \) obtained in this manner are given below.
Figure IV-3: Straight lines fit by least squares method to high temperature \( \nu(T) \) data to determine \( \nu_0 \) values.
Table IV-1: Static Lattice NQR Frequencies

<table>
<thead>
<tr>
<th>Compound</th>
<th>υ₀ (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K₂PtCl₆</td>
<td>26.107</td>
</tr>
<tr>
<td>Rb₂PtCl₆</td>
<td>26.534</td>
</tr>
<tr>
<td>Cs₂PtCl₆</td>
<td>26.834</td>
</tr>
</tbody>
</table>

It is relevant to note at this point that explicit volume effects are not expected to be of importance in the determination of υ₀. An example of the experimental evidence in support of this conjecture is indicated in figure IV-4 where the high temperature data for K₂PtCl₆ is plotted for P = 1 kg cm⁻² and P = 5000 kg cm⁻². The line through the P = 1 kg cm⁻² points is the line used to determine the υ₀ value given above. The upper line is drawn from υ₀ through the data points at P = 5000 kg cm⁻²; it provides a good fit to them.

Smith and Stoessiger (1969a,b) have calculated the R⁺ ion contribution to the electric field gradient for K₂PtCl₆, Rb₂PtCl₆ and Cs₂PtCl₆. They have assumed the field gradient from the charge distribution in the PtCl₆ octahedra to be the same in each compound and that the observed differences among the NQR frequencies are due only to differences in the neighbouring ion contributions υₙ. The neighbouring ion contribution
Figure IV-4: \( \nu(T) \) data for \( K_2PtCl_6 \) at low and high pressures. The straight lines through the data indicate that the value of \( \nu_0 \) is a good approximation in each case.
to the field gradient at the nucleus is enhanced by a quadrupole moment induced in the electron charge distribution about the nucleus. That is

\[ q_n = q_{\text{ext}} (1 - \gamma) \]

where \( \gamma \) is the Sternheimer anti-shielding factor and \( q_{\text{ext}} \) is the unenhanced field gradient due to the external charges. Smith and Stoessiger have used a theoretical value of 28 for the anti-shielding factor, which has been calculated using contracted wave functions. Their lattice sum was taken over 125 complete unit cells. Both point charge and induced dipole contributions were considered. The results are summarized in Table IV-2.

<table>
<thead>
<tr>
<th>Pt charge</th>
<th>Cl charge</th>
<th>( K_2\text{PtCl}_6 ) ( \nu ) (MHz)</th>
<th>( \text{Rb}_2\text{PtCl}_6 ) ( \nu ) (MHz)</th>
<th>( \text{Cs}_2\text{PtCl}_6 ) ( \nu ) (MHz)</th>
<th>( \nu (\text{Rb}) - \nu (\text{K}) )</th>
<th>( \nu (\text{Cs}) - \nu (\text{K}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>-0.42</td>
<td>-3.08</td>
<td>--</td>
<td>-2.64</td>
<td>--</td>
<td>0.44</td>
</tr>
<tr>
<td>0.60</td>
<td>-0.43</td>
<td>-3.09</td>
<td>-2.91</td>
<td>-2.63</td>
<td>0.17</td>
<td>0.45</td>
</tr>
<tr>
<td>0.69</td>
<td>-0.45</td>
<td>-3.02</td>
<td>-</td>
<td>-2.63</td>
<td>-</td>
<td>0.39</td>
</tr>
<tr>
<td>0.80</td>
<td>-0.47</td>
<td>-3.04</td>
<td>-2.89</td>
<td>-2.61</td>
<td>0.15</td>
<td>0.43</td>
</tr>
<tr>
<td>0.90</td>
<td>-0.48</td>
<td>-3.02</td>
<td>-</td>
<td>-2.57</td>
<td>-</td>
<td>0.45</td>
</tr>
<tr>
<td>1.00</td>
<td>-0.50</td>
<td>-3.01</td>
<td>-2.82</td>
<td>-2.54</td>
<td>0.19</td>
<td>0.46</td>
</tr>
</tbody>
</table>

Ignoring induced dipole contribution:

<table>
<thead>
<tr>
<th>Pt charge</th>
<th>Cl charge</th>
<th>( K_2\text{PtCl}_6 ) ( \nu ) (MHz)</th>
<th>( \text{Rb}_2\text{PtCl}_6 ) ( \nu ) (MHz)</th>
<th>( \text{Cs}_2\text{PtCl}_6 ) ( \nu ) (MHz)</th>
<th>( \nu (\text{Rb}) - \nu (\text{K}) )</th>
<th>( \nu (\text{Cs}) - \nu (\text{K}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.69</td>
<td>-0.45</td>
<td>-3.32</td>
<td>-</td>
<td>-2.75</td>
<td>-</td>
<td>0.57</td>
</tr>
<tr>
<td>1.00</td>
<td>-0.50</td>
<td>-3.42</td>
<td>-3.18</td>
<td>-2.82</td>
<td>0.24</td>
<td>0.60</td>
</tr>
</tbody>
</table>
The calculations are carried out for various possible effective charges on the Pt and Cl atoms. This is done because the details of the molecular orbitals in the PtCl\textsubscript{6} complex are not known. The lower part of the table presents the calculations which do not include the induced dipole moment contribution in the R ions. The last two columns contain the differences from the K\textsubscript{2}PtCl\textsubscript{6} values of the Rb\textsubscript{2}PtCl\textsubscript{6} and Cs\textsubscript{2}PtCl\textsubscript{6} values, respectively, since it is only the differences which can be compared with experiment. The corresponding experimental differences are

\[ v_0(\text{Rb}) - v_0(\text{K}) = 0.427 \text{ MHz} \]

and

\[ v_0(\text{Cs}) - v_0(\text{K}) = 0.727 \text{ MHz}. \]

The calculated values are too small by an approximate factor of two, however they are in the same sequence and roughly in the same ratio as the experimental numbers, perhaps reflecting to some extent the uncertainty in the Sternheimer anti-shielding factor. However the major part of this discrepancy is likely due to the fact that the contribution \( \varepsilon_0 \) is assumed to be independent of its environments. It might be noted that the inclusion of induced dipole effects makes the agreement with the experiment worse. This is not uncommon in these types of calculations.
The Rotary Mode Frequency Neglecting
Explicit Volume Effects

Using the expressions (3-14) and (3-15), it is possible to solve for the rotary mode frequency \( \omega_{\text{rot}} \). In the limit of high temperatures (3-14) becomes

\[
\Delta \nu_{\text{rot}} = \frac{3v_0 kT}{I \omega_{\text{rot}}^2}
\]

and therefore

\[
\omega_{\text{rot}}^2 = \frac{3v_0 kT}{I}[\Delta \nu_{\text{expt}}(T) - \Delta \nu_{\text{int}}(T)]^{-1}
\]

Figures IV-5, IV-6 and IV-7 are plots of \( \Delta \nu_{\text{expt}} \) and \( \Delta \nu_{\text{int}} \) for the three substances. The experimental data is assumed to be in the asymptotic region at high temperatures. In each case, the dashed line which converges with the \( \Delta \nu_{\text{expt}} \) plot represents the extrapolated high temperature data and is assumed to be the asymptote. The dashed lines which converge with the \( \Delta \nu_{\text{int}} \) plots are the exact, calculated asymptotes. For each of the three substances, at temperatures greater than \( \sim 200 \) K, \( \Delta \nu_{\text{int}} \) comprises less than 30% of the total frequency shift. The remainder is assumed to be due entirely to the effect of the rotary mode. In the case of \( K_2 \text{PtCl}_6 \), figure IV-5 indicates a small overlap of \( \Delta \nu_{\text{expt}} \) and \( \Delta \nu_{\text{int}} \) at the low temperature end. This unphysical result is an indication of the limitations of the analysis.

The resulting values of \( \omega_{\text{rot}} \) deduced at 300 K are given together with values calculated by Debeau and Poulet (1969).
Figure IV-5: \( \Delta \nu_{\text{expt}}(T) \) and \( \Delta \nu_{\text{int}}(T) \) for \( K_2PtCl_6 \).
Figure IV-6: $\Delta \nu_{\text{expt}}(T)$ and $\Delta \nu_{\text{int}}(T)$ for $\text{Rb}_2\text{PtCl}_6$. 

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Figure IV-7: $\Delta v_{\text{expt}}(T)$ and $\Delta v_{\text{int}}(T)$ for Cs$_2$PtCl$_6$. 

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in Table IV-3. Debeau and Poulet have obtained force constants of the lattice from available infrared and Raman data and used them to deduce values of $\omega_{\text{rot}}$ at the Brillouin zone centre. The experimental values of $\omega_{\text{rot}}$ agree with the calculated values in order of magnitude and they increase in the same sequence. If the calculated value of $\omega_6 = 90 \text{ cm}^{-1}$ had been used in the evaluation of $\Delta \nu_{\text{int}}$ rather than the experimental value of $\omega_6 = 120 \text{ cm}^{-1}$, the resulting $\omega_{\text{rot}}$ values would have been of the order of 10% smaller. This would not present difficulties since all three $\omega_{\text{rot}}$ values are affected to the same degree and it is really the comparison of the three numbers which is significant.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\omega_{\text{rot}}^{(\text{expt})}$ (cm$^{-1}$)</th>
<th>$\omega_{\text{rot}}^{(\text{calc})}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$_2$PtCl$_6$</td>
<td>58</td>
<td>63</td>
</tr>
<tr>
<td>Rb$_2$PtCl$_6$</td>
<td>62</td>
<td>71</td>
</tr>
<tr>
<td>Cs$_2$PtCl$_6$</td>
<td>64</td>
<td>80</td>
</tr>
</tbody>
</table>

It should be noted that these experimental values of $\omega_{\text{rot}}$ are averages over the first Brillouin zones of the lattices. O'Leary and Wheeler (1969) have calculated the dispersion of this mode in K$_2$ReCl$_6$. They have shown that the frequency of the
rotary mode varies from \( \sim 40 \text{ cm}^{-1} \) to \( \sim 70 \text{ cm}^{-1} \) over the Brillouin zone. An NQR experiment averages over all values of the rotary mode frequency, more heavily weighting the low frequency values. It is necessary to know the details of the dispersion curve to see how the experimental \( \omega_{\text{rot}} \) values are related to \( \omega_{\text{rot}} \) calculated at the zone centre. Values of \( \omega_{\text{rot}} \) evaluated for temperatures \( > 250 \text{ K} \) are independent of temperature to within \( \pm 1 \text{ cm}^{-1} \). That is, to within the limitations inherent in the model the \( \omega_{\text{rot}} \) values are temperature independent constants.

IV-4 NQR Frequency as a Function of Pressure

The \( v(P) \) data for \( \text{Rb}_2\text{PtCl}_6 \) and \( \text{Cs}_2\text{PtCl}_6 \) are shown in figures IV-8 and IV-9. The \( v(P) \) data for \( \text{K}_2\text{PtCl}_6 \) has been published previously by Armstrong and Jeffrey (1969). Figure IV-10 shows a comparison of the pressure dependence of \( v \) at room temperature in the three compounds. In all three cases the slope of the frequency vs. pressure graphs is positive. A decrease in the dimensions of the \( R \) atom cage in which the \( \text{PtCl}_6 \) octahedron resides is expected to increase the restoring force on the octahedron and therefore its torsional oscillation frequency. Direct experimental evidence of this has been found in a study of \( \text{K}_2\text{PtCl}_6 \) (Armstrong and Jeffrey 1969). Inspection of the expression for \( \Delta v_{\text{rot}} \) (3-14) in the high temperature limit reveals that an increasing \( \omega_{\text{rot}} \) has the overall effect of increasing the NQR frequency. The pressure dependence of \( \omega_{\text{rot}} \) in the \( \text{R}_2\text{PtCl}_6 \) substances can be estimated.
Figure IV-8: The $^{35}\text{Cl}$ NQR frequency vs. pressure data for $\text{Rb}_2\text{PtCl}_6$. 

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Figure IV-9: The $^{35}\text{Cl}$ NQR frequency vs. pressure data for $\text{Cs}_2\text{PtCl}_6$. 
Figure IV-10: Comparison of $v(P)$ data at room temperature in three compounds.
in the following way (Armstrong 1971), from (3-14)

\[ \omega_{rot}^2 = \frac{\nu_0 \cdot 3kT}{I \Delta \nu_{rot}} \]

Differentiation of this expression yields

\[ \frac{\delta \omega_{rot}}{\delta P} = \omega_{rot} \left( \frac{1}{2} \frac{\delta \nu_{rot}}{\delta P} \right) \]

Now since \( \Delta \nu_{rot} = \Delta \nu_{\text{expt}} - \Delta \nu_{\text{int}} \), then

\[ \frac{\delta \nu_{rot}}{\delta P} = \frac{\delta \nu_{\text{expt}}}{\delta P} - \frac{\delta \nu_{\text{int}}}{\delta P} \]

\( (\delta \nu_{\text{expt}}/\delta P) \) may be obtained easily from the \( \nu(P) \) data.

\( (\delta \nu_{\text{int}}/\delta P) \) is considerably smaller than \( (\delta \nu_{\text{expt}}/\delta P) \) and therefore a first order estimate of this term will suffice. Differentiation of equation (3-13) yields

\[ \frac{\delta \nu_{\text{int}}}{\delta P} = \sum_{j=3}^{6} \frac{\delta \nu_{\text{int}}}{\delta P} \]

\[ = - \sum_{j=3}^{6} \frac{2}{j} \Delta \nu_{\text{int}} j \frac{\delta \nu_{\text{int}}}{\delta P} \]  \( \text{(4-2)} \)

This is valid if the high temperature approximation is taken and if the pressure variation is assumed to be due entirely to the pressure variation of the internal mode frequencies \( \omega_{\text{int}}^j \). For the infra-red active modes \( Q_3 \) and \( Q_4 \) \( (\delta \omega_{\text{int}}^j / \delta P) \)
has been measured in $\text{K}_2\text{PtCl}_6$ (Ferraro, 1970) to be $0.60 \text{ cm}^{-1} \cdot \text{kbar}^{-1}$. Assuming the coefficients to be the same for the modes $Q_5$ and $Q_6$ and using the published values of $\omega_{\text{int}}^j$ (Debeau and Poulet) in conjunction with the calculated values of $\Delta\nu_{\text{int}}^j$ gives an estimate of $\frac{\delta \nu_{\text{int}}}{\delta P}$ at $T = 300 \text{ K}$.

$$\frac{\delta \nu_{\text{int}}}{\delta P} = 0.60 \text{ kHz kbar}^{-1}$$

Substituting this number together with the experimental values of $\frac{\delta \nu_{\text{expt}}}{\delta P}$ into equation (4-1) yields the following values of $\frac{\delta \omega_{\text{rot}}}{\delta P}$.

**Table IV-4: Pressure Derivatives of $\nu_{\text{expt}}$ and $\omega_{\text{rot}}$**

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\frac{\delta \nu_{\text{expt}}}{\delta P} (\text{kHz kbar}^{-1})$</th>
<th>$\frac{\delta \omega_{\text{rot}}}{\delta P} (\text{cm}^{-1} \text{kbar}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{K}_2\text{PtCl}_6$</td>
<td>4.85</td>
<td>0.6</td>
</tr>
<tr>
<td>$\text{Rb}_2\text{PtCl}_6$</td>
<td>8.04</td>
<td>1.2</td>
</tr>
<tr>
<td>$\text{Cs}_2\text{PtCl}_6$</td>
<td>14.6</td>
<td>2.5</td>
</tr>
</tbody>
</table>

It is reasonable that the frequency of the rotary mode should be more sensitive to pressure than the internal modes.
IV-5 The Rotary Mode Frequency Including Explicit Volume Effects

Using the general thermodynamic expression (3-7) it is possible to combine the $v(T)$ data with the $v(P)$ data and obtain information on $\omega_{\text{rot}}$ taking explicit volume effects into account. In the high temperature approximation, (3-7) becomes

$$\frac{3v_0 k}{I \omega_{\text{rot}}^2} = -\frac{3v}{\beta T} P - \frac{\alpha}{\beta} \frac{3v}{\beta T} P - \left( \frac{3\Delta v_{\text{int}}}{\beta T} \right) V$$

(4-3)

since

$$\frac{\frac{3v}{\beta T}}{V} = -\frac{\frac{3\Delta v_{\text{int}}}{\beta T}}{V} - \left( \frac{\frac{3\Delta v_{\text{rot}}}{\beta T}}{V} \right)$$

where $\Delta v_{\text{int}}$ and $\Delta v_{\text{rot}}$ are taken to be positive quantities.

Since neither values of $\alpha$ nor $\beta$ for these substances have been reported, the quantity $\alpha/\beta$ will be treated as an unknown parameter. A table of the terms appearing in (4-3) and evaluated at $T = 300 \text{ K}$ is given below.

Table IV-5: Values of Derivatives Appearing in Equation (4-3) at 300 K.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\frac{3v}{\beta T} P$ (MHz K$^{-1}$)</th>
<th>$\frac{3v}{\beta T} P$ (MHz kg$^{-1}$ cm$^2$)</th>
<th>$\frac{3\Delta v_{\text{int}}}{\beta T} V$ (MHz K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$_2$PtCl$_6$</td>
<td>$-9.80 \times 10^{-4}$</td>
<td>$4.96 \times 10^{-6}$</td>
<td>$2.65 \times 10^{-4}$</td>
</tr>
<tr>
<td>Rb$_2$PtCl$_6$</td>
<td>$-9.07 \times 10^{-4}$</td>
<td>$8.20 \times 10^{-6}$</td>
<td>$2.67 \times 10^{-4}$</td>
</tr>
<tr>
<td>Cs$_2$PtCl$_6$</td>
<td>$-8.72 \times 10^{-4}$</td>
<td>$14.9 \times 10^{-6}$</td>
<td>$2.70 \times 10^{-4}$</td>
</tr>
</tbody>
</table>
Figure IV-11: Deduced values of $\omega_{\text{rot}}$ vs. the thermodynamic parameter $\alpha/\beta$. 
The values of $\omega_{\text{rot}}$ resulting from the solution of (4-3) are plotted as functions of $\alpha/\beta$ in Fig. IV-11. The dramatic differences among these curves are, of course, due to the rather different pressure dependences of the NQR frequencies. Once $\alpha/\beta$ has been measured experimentally for $\text{K}_2\text{PtCl}_6$, $\text{Rb}_2\text{PtCl}_6$ and $\text{Cs}_2\text{PtCl}_6$, the appropriate values of $\omega_{\text{rot}}$ may be taken directly from this graph. An estimate of $\alpha/\beta \approx 15$ is not unreasonable on the basis of the rather scant measurements reported for substances of similar structure. Values of $\omega_{\text{rot}}$ for $\alpha/\beta=15$ are compared with the values at $\alpha/\beta=0$ and with the calculated values of Debeau and Poulet. The agreement between the last

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\omega_{\text{rot}}(0)\ (\text{cm}^{-1})$</th>
<th>$\omega_{\text{rot}}(15)\ (\text{cm}^{-1})$</th>
<th>$\omega_{\text{rot}}\ (\text{calc})\ (\text{cm}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{K}_2\text{PtCl}_6$</td>
<td>58</td>
<td>61</td>
<td>63</td>
</tr>
<tr>
<td>$\text{Rb}_2\text{PtCl}_6$</td>
<td>62</td>
<td>68</td>
<td>71</td>
</tr>
<tr>
<td>$\text{Cs}_2\text{PtCl}_6$</td>
<td>64</td>
<td>81</td>
<td>80</td>
</tr>
</tbody>
</table>

two columns must be considered to be fortuitous but, nonetheless, it does suggest that NQR frequency data provides a practical means to obtain information on the low-lying rotary mode in substances of the antiflourite structure.
CHAPTER V

QUADRUPOULAR RELAXATION THEORY

V-1 Introduction

In a solid, the lattice vibrations modulate the electric and magnetic interactions between the resonant nuclei and their environment, thereby providing a mechanism for spin-lattice relaxation. It has been shown theoretically (Abragam 1961) that the magnetic dipolar interaction, which dominates the magnetic interaction, gives a negligible contribution to $T_1$ compared to the contribution from the electric quadrupolar interaction. Jeffrey and Armstrong (1968) have shown experimentally that the spin-lattice relaxation in $K_2PtCl_6$ is entirely due to the electric quadrupolar interaction. Therefore, this chapter will discuss the quadrupolar relaxation mechanism as it relates to $R_2PtCl_6$ compounds.

The first quantitative theory of quadrupolar relaxation was presented by Van Kranendonk (1954). This theory was specifically developed for ionic crystals of the NaCl structure where the quadrupole coupling can be reasonably calculated assuming a point charge model. Only nearest neighbour contributions were considered and the lattice vibrations were approximated by a Debye spectrum. Other workers have used the Van Kranendonk theory with modifications to account for covalency effects (Yosida and Moriya 1956), more sophisticated phonon spectra (Wikner, Blumberg and Hahn 1960; Kochelaev; Joshi, Gupta and Das 1964; Bridges and Clark 1967) and anharmonic lattice effects.
(Van Kranendonk and Walker 1967). Armstrong and Jeffrey (1970) have adapted the Van Kranendonk theory to the relaxation of the X nuclei in $R_2MX_6$ compounds. This chapter will describe their theory in detail after a brief resume of the Van Kranendonk theory.

V-2 Van Kranendonk Theory

The quadrupolar Hamiltonian may be written

$$H_Q = H_Q^\prime + (H_Q - H_Q^\prime)$$

where $H_Q^\prime$, the secular part, gives rise to the stationary nuclear quadrupole energy levels; the remaining part, $H_Q - H_Q^\prime$, describes the coupling between the nuclear spin system and the lattice. The nuclear spin system is described by

$$H_S = H_Q + H_{SS}$$

where $H_{SS}$ represents the coupling between the resonant nuclei. The nuclear spins are sufficiently strongly coupled that they may be considered as a thermodynamic system characterized by a spin temperature $T_S$ (Aragam 1961). Equilibrium occurs in the spin system in a time $T_2$, the spin-spin relaxation time, which in the present case is much shorter than the spin-lattice relaxation time $T_1$.

Now the quadrupolar Hamiltonian may also be written

$$H_Q = \sum_{\mu=-2}^{2} Q^{\mu F - \mu}$$

(5-1)
where
\[ Q^0 = A(3I_z^2 - I^2) \]
\[ P^0 = V_{zz} \]
\[ Q^{\pm 1} = A(I_{I}^2 + I_{z}^2) \quad \text{and} \quad P^{\pm 1} = V_{xz} \pm iV_{yz} \quad (5-2) \]
\[ Q^{\pm 2} = AI_{I}^2 \quad P^{\pm 2} = \frac{1}{2}(V_{xx} - V_{yy}) \pm 2iV_{xy} \]

in which \( A = eQ/4I(2I-1) \). The \( V_{ij} \) are the electric field gradient components at the nucleus. Van Kranendonk expanded the \( P^u \) in a power series of the relative displacements of the point charges about their equilibrium positions:
\[ P^u = P_0^u + \sum_i f_i^u \cdot \vec{r}_i + \sum_{ij} f_{ij}^u \cdot \vec{r}_i \cdot \vec{r}_j + \ldots \quad (5-3) \]
The first term in this series is just the static field gradient and gives rise to the pure quadrupole resonance which has been discussed. The remaining terms couple the nuclear spin system to the lattice vibrations. A first order perturbation treatment of the second term, using eigenfunctions of the harmonic lattice gives rise to the "direct" process. This involves the creation or annihilation of a phonon in conjunction with an NQR transition. Since there are a negligible number of phonons at the NQR frequency, then the probability of occurrence of the direct spin-phonon process is vanishingly small. Use of the third term in (5-3) in a first order perturbation calculation with the wave functions of an harmonic lattice, leads to the first-order Raman spin-phonon process. This process involves
the inelastic scattering of a phonon by the spin system; it was considered to be the dominant source of quadrupolar spin-lattice relaxation by Van Kranendonk.

A general expression for the transition probability \( W(m, m+\mu) \) may be written

\[
W(m, m+\mu) = \frac{2\pi}{\hbar^2} \int_0^{\omega_m} \int_0^{\omega_m} \rho(\omega) \rho(\omega') \delta(\omega-\omega'+\omega_\mu) \]

\[
\times \{ |H_Q^{\mu}(\lambda, \lambda')|^2 \} d\omega d\omega'
\]

where \( H_Q^{\mu}(\lambda, \lambda') \) is the matrix element of the \( \mu \)th component of the quadrupolar Hamiltonian between the states of the lattice before and after the phonon is scattered; \( \rho(\omega) = \rho(\omega') \) is the phonon density of states which is assumed to be a Debye distribution. The parentheses \( \{ \} \) denote an average over all phonon wavevectors and the summation is over all polarizations. This transition probability may be expressed as

\[
W(m, m+\mu) = C |Q_{\mu m}|^2 T^* E_{\mu}^*(T^*) \quad (5-4)
\]

where \( Q_{\mu m} = \langle m+\mu | Q^{\mu} | m \rangle \) and \( T^* \) is the ratio of the temperature to the Debye temperature \( \Theta_D \). The functions \( E_{\mu}^*(T^*) \) are defined by

\[
E_{\mu}^*(T^*) = N_{\mu 1}(D_1+D_3+D_5) + N_{\mu 2}(D_2+D_4+D_6)
\]

where \( N_{\mu 1} \) and \( N_{\mu 2} \) are functions of the tensor components \( F_{ij}^{\mu} \).
The $D_n(T^*)$ are the integrals

$$D_n(T^*) = T^* \int_0^{1/T^*} \frac{x^2 e^x}{(e^x - 1)^2} L_n(cT^*x) dx,$$

with the $L_n$ functions determined by the lattice structure and the normal modes of vibration. The transition probabilities can be used in the following expression (Hebel and Slichter 1959) to determine $T_{1R}$, the first-order Raman contribution to the spin-lattice relaxation time:

$$\frac{1}{T_{1R}} = \gamma \sum_{n,m} \frac{(E_n - E_m)^2 w_{nm}}{\sum_n w_n^2},$$

To deduce numerical values of $T_1$, the field gradient calculated in the ionic model is multiplied by a factor $\gamma$. This factor takes account of antiscreening effects, covalency effects, contributions of other than nearest neighbors etc. For an NMR experiment the best estimate of $\gamma$ is the experimental Sternheimer factor.

In general, the estimated values, $T_{1R}$, are found to be ~2 orders of magnitude larger than the experimental measurements of $T_1$. That is, the strength of the calculated spin-lattice coupling is too weak to explain the observations. Nonetheless, the Van Kranendonk theory has given good agreement with experiment with respect to the temperature dependence of $T_1$ (cf. Bridges and Clark 1967, Jeffrey and Armstrong 1968). At high temperatures the theory predicts that $T_1^{-1} \propto T^2$ independent of the details of the phonon spectrum. For temperatures $< \theta_D/2$, deviations from
the $T^2$ behaviour begin to appear. The nature of the deviation depends on the details of the phonon spectrum. For example, with a Debye spectrum, at very low temperatures $T^{-1} \approx T^7$.

V-3 Adaptation of Van Kranendonk Theory to $R_2PtCl_6$ Compounds

Following Van Kranendonk, Armstrong and Jeffrey (1971) have expanded the components of the electric field gradient tensor in terms of the relative displacements of the resonant nucleus $\kappa$ in the unit cell $\ell$ and all other nuclei specified by $\ell'\kappa'$. That is, they have written

$$F^\mu_{\ell\kappa} = F^\mu_{0\ell\kappa} + \sum_{\ell'\kappa'} f^\mu_{\alpha}(\mathbf{R}(\ell\ell',\kappa\kappa')) R^\alpha(\ell\ell',\kappa\kappa')$$

$$+ \sum_{\ell''\kappa''} f^\mu_{\alpha\beta}(\mathbf{R}(\ell\ell',\kappa\kappa'), \mathbf{R}(\ell\ell'',\kappa\kappa'')) R^\alpha(\ell\ell',\kappa\kappa') R^\beta(\ell\ell'',\kappa\kappa'')$$

(5-5)

where $\mathbf{R}(\ell\ell',\kappa\kappa') = \mathbf{U}(\ell'\kappa') - \mathbf{U}(\ell\kappa)$. The terms of equation (5-5) have the same interpretation as those of (5-3). The components $U_\alpha(\ell\kappa)$ are expanded in terms of the normal modes of the lattice following Maradudin, Montroll and Weiss (1963):

$$U_\alpha(\ell\kappa) = \left(\frac{\mathbf{R}}{2Nm_\kappa}\right)^{\frac{1}{2}} \sum_{\kappa,j} e^{i\mathbf{k}_j} A(\mathbf{k}_j) \frac{\exp[i\mathbf{k}_j \cdot \mathbf{S}]}{[\omega_i(\mathbf{k})]^{\frac{1}{2}}}$$

This expression is similar to (3-11) with $A(\mathbf{k}_j) = a(\mathbf{k}_j) + a^+(\mathbf{k}_j)$ being the sum of a phonon annihilation and a phonon creation operator. In the nearest neighbour approximation, the first
order Raman term of (5-5) becomes

\[
\frac{1}{N} \sum_{kk',jj'} \mathcal{F}^\mu(kk',jj') \exp[i(k + k') \cdot \vec{s}(l)] A(kj) A(k'j')
\]

where

\[
\mathcal{F}^\mu(kk',jj') = \frac{\frac{R}{2[\omega_j(k) \omega_j(k')]}}{\sum_{\alpha \beta} f_{\alpha \beta} \{ \tilde{k}(l, Cl-Pt), k(l, Cl-Pt) \}}
\]

\[
\times \left| \frac{e_{\alpha}(Cl|\tilde{k}_j)}{m_{Cl}} - \frac{e_{\alpha}(Pt|\tilde{k}_j)}{m_{Pt}} \right|^2
\]

\[
\left| \frac{e_{\beta}(Cl|\tilde{k}_j)}{m_{Cl}} - \frac{e_{\beta}(Pt|\tilde{k}_j)}{m_{Pt}} \right|^2
\]

Expression for the transition probabilities are similar to those given by Van Kranendonk. Making use of the H{\v c}el-Sl{\v c}chter formula gives the following expression for \( T_{1R} \):

\[
T_{1R}^{-1} = \sum_{\mu} \sum_{kk',jj'} 4\pi (eQ)^2 |\mathcal{F}^\mu(kk',jj')|^2 n[\epsilon_j(k)] n[\epsilon_j(k) + 1]
\]

\[
\chi \delta[\epsilon_j(k') - \epsilon_j(k) - E_Q]
\]

Where \( E_Q \) is the energy difference between the NQR levels. The \( n[\epsilon_j(k)] \) are phonon occupation numbers:

\[
n[\epsilon_j(k)] = \left\{ \exp[\beta \epsilon_j(k)] - 1 \right\}^{-1}
\]

where \( \epsilon_j(k) = \hbar \omega_j(k) \).

It is now possible to write the contribution \( T_{1R}^{int} \) to \( T_{1R} \) due to the PtCl\(_6\) internal modes. Since these modes have
relatively little dispersion, they may be represented by Einstein oscillators. It then follows that

\[
(T_{1R}^{\text{int}})^{-1} = \sum_{j=1}^{6} \frac{\pi N^2 (eQ)^2}{3\hbar \varepsilon_j \sinh^2(\beta \varepsilon_j/2)} \sum_{u=1,2} |f^u(j)|^2
\]  

(5-8)

Employing the point charge model, with a Pt atom situated at \((0 \ 0 \ 0)\) and a Cl atom at \((0 \ 0 \ a)\) the coefficients \(f^u_{\alpha \beta}\) then become

\[
f^1_{\alpha \beta} = \frac{3ye}{a^5} \begin{array}{ccc}
0 & 0 & -2 \\
0 & 0 & -2i \\
-2 & -2i & 0 \\
\end{array}
\]

\[
f^2_{\alpha \beta} = \frac{3ye}{2a^5} \begin{array}{ccc}
1 & i & 0 \\
i & -1 & 0 \\
0 & 0 & 0 \\
\end{array}
\]

where \(\gamma\) is the correction factor introduced by Van Kranendonk.

Substituting for the \(|f^u(j)|^2\) quantities in (5-8) gives

\[
(T_{1R}^{\text{int}})^{-1} = \frac{\pi y^2 e^2 (eQ)^2}{12a^10m^2} \sum_{j=1}^{6} \frac{a_j}{\omega_j^3 \sinh^2(\hbar \omega_j/2kT)}
\]  

(5-9)

where \(a = 2.34\ \text{Å}\) is the Pt-Cl separation, \(\cdot m = 1.67\times10^{-24}\text{g}\) is one a.m.u. and the \(a_j\) are numerical coefficients.

An expression similar to (5-9) may be written for the contribution to \(T_{1R}\) of \(T_{1R}^{\text{rot}}\) from the rotary mode of the PtCl\(_6\)
octahedron if an average over its dispersion curve is taken. It follows that

\[
(T_{\text{LR}}^{-1}) = \frac{\pi \gamma^2 e^2 (eQ)^2 a_{\text{rot}}}{12a^1 m^2 \omega_{\text{rot}} \sinh^2 (M \omega_{\text{rot}}/2kT)}
\]

In the high temperature limit, \( \sinh^2 (M \omega_{\text{rot}}/2kT) \to (M \omega_{\text{rot}}/2kT)^2 \) and \((T_{\text{LR}}^{-1})\) becomes inversely proportional to the fifth power of the rotary mode frequency. In this limit, it is then possible to derive an expression for \( \omega_{\text{rot}} \), which is easy to evaluate, by inverting (5-10), viz.

\[
\omega_{\text{rot}} = \left[ \frac{0.33 \pi^2 e^2 (eQ)^2 a_{\text{rot}} (kT)}{a^1 m^2 \omega_{\text{rot}}^2 T_{\text{LR}}^{-1}} \right]^{1/5}
\]

Making the same assumptions used in the evaluation of \( T_{\text{LR}} \), the NQR frequency is calculated to be

\[
v_0 = \frac{eQ (2\gamma e)}{2h a^3}
\]

Substitution of the measured NQR frequency then provides an experimental value for the parameter \( \gamma \).

V-4 Anharmonic Effects on \( T_1 \)

As noted above, the \( T_1 \) values calculated using the Van Kranendonk theory are generally about two orders of magnitude too large. Van Kranendonk and Walker (1967) have shown that this discrepancy may be accounted for in the Alkali halides by considering anharmonic lattice effects. Anharmonic lattice
forces allow three-phonon scattering processes to occur. This mechanism, in conjunction with the direct process mentioned above, gives rise to the anharmonic Raman contribution to spin-lattice relaxation. The calculation is carried out treating the lattice anharmonicity as a perturbation of the harmonic lattice to obtain 'anharmonic' wave functions and then performing a first-order perturbation calculation using the linear spin-lattice coupling term. From their result they showed that
\[ T_{1AR}^{-1} = 35 \gamma_G^2 T_{1R}^{-1} \]

The subscript AR refers to the anharmonic Raman process and \( \gamma_G \) is the Grüneisen constant. Since \( \gamma_G = 1.7 \) for alkali halides, this treatment reduces the theoretical \( T_1 \) values by two orders of magnitude and thereby brings them into approximate agreement with the experimental values. Armstrong and Jeffrey (1969) have shown that a similar relationship exists between \( T_{1AR} \) and \( T_{1R} \) in the case of Cu₂O.

It is therefore reasonable to conclude that the experimental values, \( T_1^{\text{expt}} \), should be compared with the \( T_{1AR} \) calculated values rather than the \( T_{1R} \) calculated values. The previous work suggests that a very rough estimate of \( T_{1AR} \) may be taken to be \( 10^{-2} T_{1R} \). Since the primary purpose of the analysis of \( T_1^{\text{expt}} \) data given in the following chapter is to deduce \( \omega_{\text{rot}} \) values and, since \( \omega_{\text{rot}} \) depends on the 5th root of \( T_{1R}^{\text{rot}} \), then the deduced values of \( \omega_{\text{rot}} \) are rather insensitive to the factor which relates \( T_{1AR} \) to \( T_{1R} \).
CHAPTER VI

ANALYSIS OF RELAXATION TIME DATA

VI-1 Introduction

The spin lattice relaxation times ($T_1$) have been measured at most of the same temperatures and pressures as the NQR frequencies for Rb$_2$PtCl$_6$ and Cs$_2$PtCl$_6$, in the present work, and for K$_2$PtCl$_6$ (Armstrong and Jeffrey 1968). The constant pressure $T_1(T)$ data will be discussed in terms of the quadrupolar relaxation theory presented in Chapter V. Paralleling the frequency data analysis, the pressure dependence of $T_1$ will be discussed in terms of the increase of the rotary mode frequency with pressure. Finally, the $T_1(T)$ and $T_1(P)$ data will be related thermodynamically to determine $\omega_{rot}$ as a function of the parameter $\alpha/\beta$.

VI-2 Temperature Variation of $T_1$

The $T_1(T)$ constant pressure data for the $^{35}$Cl nuclei in Rb$_2$PtCl$_6$ and Cs$_2$PtCl$_6$ are presented in Figs. VI-1 and VI-2, respectively. The lines fit to the data are given by the following expressions:

$$Rb_2PtCl_6: \quad T_1(T) = 9,214T^{-2} \text{ (sec)}$$

$$Cs_2PtCl_6: \quad T_1(T) = 21,200T^{-2} \text{ (sec)}$$

To within experimental accuracy, over most of the temperature range, the relaxation rate varies as the square of the absolute
Figure VI-1: Spin-lattice relaxation time vs. temperature data for $^{35}$Cl nuclei in Rb$_2$PtCl$_6$. 
**Figure VI-2**: Spin-lattice relaxation time vs. temperature data for $^{35}\text{Cl}$ nuclei in $\text{Cs}_2\text{PtCl}_6$. 

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Figure VI-2: Spin-lattice relaxation time vs. temperature data for $^{35}$Cl nuclei in $\text{Cs}_2\text{PtCl}_6$. 
temperature, as predicted by the Van Kranendonk theory for the Raman spin-phonon relaxation mechanism in the high temperature limit.

In the case of Rb$_2$PtCl$_6$, an attempt was made to measure $T_1$ values at temperatures below the range for which data is shown in Figure VI-1. In the vicinity of 4K, the relaxation exhibited a non-exponential behaviour, indicating the presence of paramagnetic impurities in the sample. In this region the $T_1$ values deviated from the $T^{-2}$ behaviour and approached a constant value of 5.63 sec at 4K. Since at this temperature the quadrupolar $T_1$ will be several orders of magnitude larger, therefore the 4K value of $T_1$ can be taken to be due entirely to the impurity relaxation mechanism. The impurity contribution to $T_1$ is expected to be essentially temperature independent. Following Bridges and Clark (1967), the impurity relaxation rate was subtracted from each of the measured relaxation rates leaving the quadrupolar rates. This correction increased the measured $T_1$ values by about 30 percent at the lowest temperature shown for Rb$_2$PtCl$_6$; above 200 K the impurity contribution was negligible. In the case of Cs$_2$PtCl$_6$, due to the higher purity of the sample, the impurity relaxation mechanism was not important in the temperature region for which the data is plotted. The Rb$_2$PtCl$_6$ $T_1$ data deviates from the $T^{-2}$ line at the low temperature end. This is predicted by the Van Kranendonk theory. Such a deviation was not seen in the Cs$_2$PtCl$_6$ data since measurements were not taken below 77 K.
The $T_1$ data are compared over the temperature range 100-350 K in three compounds $K_2PtCl_6$, $Rb_2PtCl_6$ and $Cs_2PtCl_6$ in Figure VI-3. The $K_2PtCl_6$ data does not have the same temperature dependence as the other compounds. This is thought to be due to the onset of hindered rotational motions of the $PtCl_6$ octahedra which has been identified in $K_2PtCl_6$. Figure VI-4 reproduces the $K_2PtCl_6$ data from Jeffrey and Armstrong (1968). The relaxation times were measured for both the $^{35}Cl$ and $^{37}Cl$ isotopes. At $\approx$350 K the $T_1$ data becomes isotope independent and in the temperature range above 350 K, $T_1$ varies exponentially with temperature. This behaviour is consistent with a non-resonant relaxation process related to the thermal activation of reorientation of the $PtCl_6$ octahedra between equilibrium positrons within the surrounding cage of $K$ ions. This phenomenon was explained using the theory of Alexander and Tzalmona (1967). Because of this behaviour, it is believed that below 350 K, the torsional oscillation amplitudes of the $PtCl_6$ octahedra in $K_2PtCl_6$ are large and that the use of perturbation theory is not valid. Therefore the $T^{-2}$ behaviour is not to be expected in this compound.

There is an indication of hindered rotations in $Rb_2PtCl_6$ as evidenced by the slight deviation from the $T^{-2}$ law at the highest temperatures. The $Cs_2PtCl_6$ data shows rather less inclination towards this behaviour. We may conclude that the restoring forces acting on the $PtCl_6$ octahedra increase through the series $K$, $Rb$, $Cs$. 

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Figure VI-3: A comparison of the $T_1(T)$ data in the three compounds.
Figure VI-4: $T_1(T)$ data for $K_2PtCl_6$ reproduced from Jeffrey and Armstrong (1968).
VI-3 Determination of the Rotary Mode Frequency

The contribution of the internal vibrational modes to the relaxation rate can be evaluated using (5-9). The coefficients $a_j$ are given in Table VI-1 together with the separate contributions from each mode at $T = 300$ K.

<table>
<thead>
<tr>
<th>$j$</th>
<th>$a_j$</th>
<th>$\frac{1}{T_{LR}^{\text{int}}} \text{ (sec}^{-1}\text{)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>$2.37 \times 10^{-3}$</td>
<td>$1.11 \times 10^{-4}$</td>
</tr>
<tr>
<td>4</td>
<td>$2.99 \times 10^{-4}$</td>
<td>$3.09 \times 10^{-4}$</td>
</tr>
<tr>
<td>5</td>
<td>$4.47 \times 10^{-4}$</td>
<td>$7.25 \times 10^{-4}$</td>
</tr>
<tr>
<td>6</td>
<td>$4.47 \times 10^{-4}$</td>
<td>$4.37 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td><strong>Total</strong></td>
<td><strong>5.51 \times 10^{-3}</strong></td>
</tr>
</tbody>
</table>

Therefore $T_{LR}^{\text{int}} = 181$ sec. This result is essentially the same for all three substances (because of the similarity of their internal mode frequencies) and is three orders of magnitude larger than the experimental values, $T_{1}^{\text{expt}}$. Even $T_{1LR}^{\text{int}} = 10^{-2} T_{LR}^{\text{int}}$ (as we have seen in Chapter V) is $\sim 10$ times larger than $T_{1}^{\text{expt}}$ values. Also $T_{1}^{\text{expt}}$ is markedly dependent on the R ions while $T_{LR}^{\text{int}}$ is relatively insensitive to the R ions. These two facts suggest that the internal modes offer a negligible contribution...
to the spin-lattice relaxation mechanism.

We may conclude then, that the rotary mode plays the dominant role in the quadrupolar relaxation theory. With this assumption, $T_{1AR}^{\text{rot}} = 100T_{1R}^{\text{rot}}$ can be associated with the experimentally measured values of $T_1$ and the expression (5-11) can be used to evaluate the rotary mode frequency:

$$\omega_{\text{rot}} = \left[ \frac{33\pi^2e^2(\epsilon\Omega)^2a_{\text{rot}}}{a_{10}^2m^2} \right]^{1/5} T_1^{\text{expt}}$$  \hspace{1cm} (6-1)

with $a_{\text{rot}} = 4.47 \times 10^{-4}$ and substituting the $T_1^{\text{expt}}$ values at $T = 300$ K, the $\omega_{\text{rot}}$ values presented in Table VI-2 are obtained.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\omega_{\text{rot}}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>from $T_1$ data</td>
</tr>
<tr>
<td>$K_2\text{PtCl}_6$</td>
<td>56</td>
</tr>
<tr>
<td>$Rb_2\text{PtCl}_6$</td>
<td>65</td>
</tr>
<tr>
<td>$Cs_2\text{PtCl}_6$</td>
<td>77</td>
</tr>
</tbody>
</table>

As with the $\omega_{\text{rot}}$ values deduced from the NQR frequency data the numbers given above must be considered as averages over the Brillouin zone. However, since $T_1^{-1}$ is inversely proportional to the 5th power of $\omega_{\text{rot}}$, it is clear that these values are more heavily weighted toward the low frequency end of the

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dispersion curve. This is believed to be at the zone centre (O'Leary and Wheeler 1970) hence the \( \omega_{\text{rot}} \) values determined in this way may be favourably compared with values calculated from infrared and Raman data. In view of the gross nature of the assumptions made in obtaining these values of \( \omega_{\text{rot}} \), their agreement with the calculated values of Debeau and Poulet and with the values deduced from the NQR frequency results (see Table IV-3) is remarkable. Part of the reason for this is due to the nature of the calculation.

**VI-4: Pressure Dependence of \( T_1 \)**

The \( T_1 \) data as a function of pressure are shown in Figures VI-5 and VI-6 for \( \text{Rb}_2\text{PtCl}_6 \) and \( \text{Cs}_2\text{PtCl}_6 \). In a manner analogous to the discussion of the NQR frequency data variation with pressure, the pressure dependence of \( T_1 \) may be understood in terms of an increase in the rotary mode frequency with pressure. This is obvious since from (6-1) \( \omega_{\text{rot}} = T_1^{1/5} \) and \( T_1 \) is observed to increase with pressure. It is then a simple matter to deduce \( \frac{\partial \omega_{\text{rot}}}{\partial P} \) from the \( T_1(P) \) data. The results are given in Table VI-3 for \( T = 300 \text{ K} \) and \( P = 1 \text{ kg cm}^{-2} \).

**Table VI-3: Pressure Coefficients of \( T_1 \) and \( \omega_{\text{rot}} \)**

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \frac{\partial T_1}{\partial P} ) (sec/kbar)</th>
<th>( \frac{\partial \omega_{\text{rot}}}{\partial P} ) (cm(^{-1})/kbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Rb}_2\text{PtCl}_6 )</td>
<td>( 5.92\times10^{-5} )</td>
<td>0.76</td>
</tr>
<tr>
<td>( \text{Cs}_2\text{PtCl}_6 )</td>
<td>( 6.15\times10^{-5} )</td>
<td>1.00</td>
</tr>
</tbody>
</table>

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Figure VI-5: Spin-lattice relaxation time vs. pressure data for $\text{Rb}_2\text{PtCl}_6$. 
Figure VI-6: Spin-lattice relaxation time vs. pressure data for Cs$_2$PtCl$_6$. 
The values shown agree in order of magnitude with those deduced from the $v(P)$ data given in Table IV-4. The $K_2PtCl_6$ data is not treated in this discussion because it behaves differently, as mentioned above.

VI-5 Determination of $\omega_{\text{rot}}$ Including Explicit Volume Effects

Making the same assumptions as outlined in section III-4 an expression analogous to equation (3-7) may be written for $T_1$. That is,

$$\frac{\partial T_1}{\partial T} V = \left(\frac{\partial T_1}{\partial P} P\right) + \frac{\partial}{\partial \beta} \left(\frac{\partial T_1}{\partial \beta} \right) T$$

(6-2)

The left side of (6-2) is given by the quadrupolar relaxation theory and may be solved for $\omega_{\text{rot}}^*$; the terms of the right side are the experimental quantities; $\alpha/\beta$ is again taken to be an unknown parameter. The following empirical equations are then obtained for $\omega_{\text{rot}}(\alpha/\beta)$ at 300 K and 1 kg cm$^{-2}$:

$$\omega_{\text{rot}}(\alpha/\beta) = \{1.697 \times 10^{11}[ -6.67 \times 10^{-3} + \frac{\alpha}{\beta} 5.80 \times 10^{-5}] \}^{1/5} \text{cm}^{-1}$$

(6-3)

for $Rb_2PtCl_6$

$$\omega_{\text{rot}}(\alpha/\beta) = \{3.993 \times 10^{11}[ -6.67 \times 10^{-3} + \frac{\alpha}{\beta} 6.04 \times 10^{-5}] \}^{1/5} \text{cm}^{-1}$$

(6-4)

for $Cs_2PtCl_6$

The graphical solutions of (6-3) and (6-4) are presented in Figure VI-7 together with the $\omega_{\text{rot}}(\alpha/\beta)$ curves from the NQR
Figure VI-7: $\omega_{\text{rot}}^{(a/\beta)}$ deduced from $T_1(T,P)$ compared with $\omega_{\text{rot}}^{(a/\beta)}$ deduced from $\nu(T,P)$ for the two compounds $\text{Rb}_2\text{PtCl}_6$ and $\text{Cs}_2\text{PtCl}_6$. 

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frequency data for Rb₂PtCl₆ and Cs₂PtCl₆. Note that ωᵣot deduced from the T₁ data is much less sensitive to α/β than ωᵣot deduced from the NQR frequency data.

The ωᵣot(T₁, α/β) and ωᵣot(ν, α/β) represent two different sorts of averages over the dispersion curves for the rotary modes. Since the ωᵣot(T₁, α/β) are more heavily weighted at the low frequency ends of the dispersion curves, then the points of intersection in Figure VI-7 may possibly represent lower limits for the parameter α/β. That is, this graph suggests that α/β > 10 which is as we expect.

VI-6 Concluding Remarks

The results of Chapters IV and VI provide a consistent picture of the behaviour of the rotary mode in K₂PtCl₆, Rb₂PtCl₆ and Cs₂PtCl₆. This suggests that NQR spectroscopy can be a useful technique for the investigation of low frequency lattice modes. This is especially true in cases like the present one, where NQR measurements are sensitive to modes which, by virtue of their particular symmetry, are not directly observable by other means.
BIBLIOGRAPHY

Herzberg, G., 1945, Infrared and Raman Spectra of Polyatomic
634.
Rev. B 1, 3770.
Kubo, M. and Nakamura, D., 1966, Advances in Inorganic and
Radiochemistry 8, 257.
104, 1364.
Luken, E.A.C., 1969, Nuclear Quadrupole Coupling Constants
State Physics, ed. F. Seitz and D. Turnbull (Academic
Chem. Soc. 82, 5783.