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ANOMALOUS TEMPERATURE VARIATION OF NQR FREQUENCIES AND BONDING IN METAL COMPLEXES

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A. INTRODUCTION

Since NQR was discovered by Dehmelt and Krüger [1] in 1950, it has attracted attention among chemists as a powerful means for studying chemical bonds in molecules because detailed information is available about the electronic charge distribution near resonant nuclei. It has been applied in a wide field of chemistry [2, 3]. In particular, a number of investigations have been carried out in coordination chemistry for clarifying the nature of coordination bonds, and the results have been summarized in several reviews [4—10].

Nuclear quadrupole resonance is directly related to the tensor components of electric field gradient formed by extranuclear charges at a resonant nucleus. The field gradient can be obtained from the hyperfine structure of molecular rotational spectra [11, 12] and also the quadrupole splitting of Mössbauer spectra [13, 14]. The former refers to gaseous molecules and is suitable for evaluating with a high precision the electric field gradient tensor in simple molecules and for discussing the electronic state of isolated molecules. However, the method is not experimentally or theoretically feasible for rather complicated coordination compounds which usually cannot be vaporized. Like NQR, the Mössbauer effect is observed with solid materials, and provides a convenient means for obtaining field gradients in coordination compounds. However, experiments using γ-rays of high energy naturally involve a low accuracy compared with NQR measurements. Accordingly, it is difficult to resolve the quadrupole splittings of nonequivalent atoms in crystals differing slightly in electric field gradients. On the other hand, an advantage of NQR spectroscopy arises from the high accuracy of frequency measurements obtainable in radiowave spectroscopy. Indeed, it is feasible to determine the chlorine resonance frequencies of, for instance, potassium chlorate and sodium chlorate giving rise to sharp resonance lines to an accuracy of eight significant figures [15]. The high accuracy implies that it is possible by NQR to discuss slight changes in field gradients due to the phase transition of crystals, the effect of temperature and external pressure, etc., in addition to crystal environments.

Normally, the NQR frequencies of monovalent halogens decrease with increasing temperature, the rate of decrease, $\nu^{-1}(\mathrm{d}\nu/\mathrm{d}T)$, being of the order of $10^{-4} - 10^{-5}$ deg^{-1}. Unlike molecular rotational spectra, observed NQR frequencies yield electric field gradients averaged over the thermal motion of atoms, molecules and ions. The average field gradient q_{zz} experienced by the resonant nuclei of terminal atoms in molecules and complex ions decreases in general with increasing excitation of thermal motion. However, when the excitation of molecular vibrations alters the bonding state of resonant atoms, the temperature coefficient of NQR frequencies gives information on the bonding of the resonant atoms. If the effect of bonding is marked, the temperature dependence of NQR frequencies shows anomalies revealing the effect of change in the bonding state. For instance, the chlorine NQR frequency of potassium hexachlororhenate(IV) shows a positive temperature coefficient above liquid nitrogen temperature [16]. This has been explained as due to the partial scission of Re—Cl bonds having a strong π covalent character [17—19]. Thus, one can obtain from NQR some knowledge about bonding types as well as information on molecular motions.

In this review, we shall focus our attention on the anomalous temperature variation of NQR frequencies observed with coordination compounds. The effect can be divided broadly into two main categories: one relating to the bonding type, whereas the other is due to phase transitions. First, let us outline the basic principle underlying NQR spectroscopy and the dependence of NQR frequency on temperature, and then discuss some examples of coordination compounds showing a positive temperature coefficient presumably due to bonding. The discussion will proceed to some examples of complexes showing an anomalous temperature behavior due to phase transition. Examples lying outside these two categories will be treated in the last section.

B. NQR SPECTROSCOPY

When a nucleus having a nuclear spin quantum number I equal to or greater than unity is placed in an inhomogeneous electric field, the electric quadrupole moment eQ of the nucleus interacts with the electric field gradient, and the nuclear spin is quantized along the direction of a principal axis of field gradient. Accordingly, transitions can be observed between discrete levels differing in the quantized interaction energy.

Let the electrostatic potential at a nucleus due to extranuclear charges be denoted by V. With respect to the principal coordinates, x, y and z, only diagonal terms,

$$V_{xx} = \left(\frac{\partial^2 V}{\partial x^2}\right)_0, \quad V_{yy} = \left(\frac{\partial^2 V}{\partial y^2}\right)_0, \quad V_{zz} = \left(\frac{\partial^2 V}{\partial z^2}\right)_0 \tag{1}$$

are nonzero components of the electric field gradient tensor. Since the Laplace equation, $V_{xx} + V_{yy} + V_{zz} = 0$, must hold, the electric field gradient tensor is traceless, and the number of independent components is reduced to two. If the coordinate system is chosen so that $|V_{zz}| > |V_{xx}| \geqslant |V_{yy}|$, the nuclear spin is quantized along the z axis. For this system, the NQR interaction can be expressed by the Hamiltonian $\mathcal{H}_Q$ given by

$$\mathcal{H}_Q = \frac{eQqh}{4I(2I-1)}[3I_z^2 - I^2 + \frac{\eta}{2}(I_+^2 + I_-^2)] \tag{2}$$

where I_z, I, I_+ and I_- are nuclear spin operators and eQq stands for the nuclear quadrupole coupling constant in frequency units expressing the magnitude of the nuclear quadrupole interaction energy. Although q ($\equiv q_{zz} = V_{zz}$) is the negative of the z component of the field gradient, it is simply called the field gradient by convention. The asymmetry parameter η is defined by

$$\eta = \frac{|V_{xx} - V_{yy}|}{|V_{zz}|} \tag{3}$$

Accordingly, electric field gradients along the principal axes can be evaluated from two observable parameters, eQq and η.

When the distribution of extranuclear charges has a threefold or higher axis of symmetry about the z axis, the asymmetry parameter vanishes, and the quadrupole interaction energy E_{m_I} is given by

$$E_{m_I} = \frac{eQqh}{4I(2I-1)}[3m_I^2 - I(I+1)] \tag{4}$$

where m_I is the z component of the nuclear spin I and can assume $(2I + 1)$ different values from $-I$ to $+I$. Because m_I appears in eqn. (4) as its square, all of E_{m_I} levels are doubly degenerate except for the level with vanishing m_I. The selection rule, $\Delta m_I = \pm 1$ restricts transitions as in the case of NMR. Accordingly, observable NQR frequencies are given by

$$\nu(m_I \leftrightarrow m_I') = \frac{E_{m_I'} - E_{m_I}}{h} = \frac{|3eQq(m_I' + m_I)|}{4I(2I-1)} \tag{5}$$

where $m_I' - m_I = \pm 1$. One can observe a single frequency $\nu_0 \equiv \nu(0 \leftrightarrow \pm 1)$, for

TABLE 1

NQR frequencies of nuclear species having I equal to 1, 3/2 or 5/2.

Nuclear spin	Nuclear species	NQR frequency
1	^{2}D, ^{14}N	$\nu_0 = 3eQq/4$, $\nu_{\pm} = 3eQq(1 \pm \eta/3)/4$
3/2	^{35}Cl, ^{37}Cl, ^{63}Cu, ^{65}Cu, ^{79}Br, ^{81}Br, ^{191}Ir, ^{193}Ir, ^{197}Au	$\nu = eQq(1 + \eta^2/3)^{1/2}/2$
5/2	^{27}Al, ^{55}Mn, ^{121}Sb, ^{127}I, ^{185}Re, ^{187}Re	$\nu_1 = (3eQq/20)(1 + 1.0926\eta^2 - 0.6340\eta^4 \ldots)$ $\nu_2 = (3eQq/10)(1 - 0.2037\eta^2 + 0.1622\eta^4 \ldots)$

$I = 1$; a single frequency, $\nu \equiv \nu(\pm 1/2 \leftrightarrow \pm 3/2)$, for $I = 3/2$; and two frequencies, $\nu_1 \equiv \nu(\pm 1/2 \leftrightarrow \pm 3/2)$ and $\nu_2 \equiv \nu(\pm 3/2 \leftrightarrow \pm 5/2)$, for $I = 5/2$.

When the asymmetry parameter η is finite, mixing takes place between states having $\Delta m_I = \pm\ 2$; m_I is no longer a good quantum number. In this case, energy levels must be evaluated by solving a secular equation. Table 1 shows some nuclear species amenable to NQR studies along with resonance frequencies as functions of eQq and η. For $I = 1$, double degeneracy occurring for $\eta = 0$ is lifted, and two resonance frequencies can be observed. On the other hand, double degeneracy persists for half-integral nuclear spins even when the asymmetry parameter is finite. A single resonance line is observed for equivalent nuclei of $I = 3/2$ regardless of whether the asymmetry parameter is zero or finite. Accordingly, the quadrupole coupling constant can be evaluated only when the asymmetry parameter may be assumed to be zero or negligibly small from theoretical consideration based on crystal structures. In other cases, the asymmetry parameter must be determined separately by studying the Zeeman effect of NQR in single crystals.

Observed resonance lines are assigned to various isotopic nuclear species in the following way. Chlorine has two isotopes, ^{35}Cl and ^{37}Cl, both having $I = 3/2$ in comparable natural abundance. Because electric field gradients in crystals are independent of the kind of isotopic nuclear species, the ratio of frequencies due to isotopic species is constant: for instance $\nu(^{35}\text{Cl})/\nu(^{37}\text{Cl}) = 1.269$. Bromine has two isotopes, ^{79}Br and ^{81}Br, both having $I = 3/2$, the frequency ratic $\nu(^{79}\text{Br})/\nu(^{81}\text{Br})$ being equal to 1.197. With these criteria, it is feasible to assign observed lines to isotopic nuclear species unambiguously. Iodine compounds present no problem regarding isotopes, because ^{127}I having $I = 5/2$ exists in a natural abundance of 100%. However, because two resonance frequencies, ν_1 and ν_2, can be observed, some means of identifying ν_1 and ν_2 must be found when nonequivalent iodine atoms exist in crystals. A theoretical relation, $2\nu_1 \geqslant \nu_2$ (equal sign for vanishing η), holding for equivalent atoms is very effective for this purpose. However, it is often insufficient, and must be supplemented by information obtainable from crystal analysis. Table 2

TABLE 2

NQR frequencies, quadrupole coupling constants, and asymmetry parameters of ^{127}I in cesium triiodide at room temperature [20, 21].

	Central iodine atom	Terminal iodine atoms	
	I_c	I_b	I_a
ν_1 (MHz)	368.21	214.62	119.48
ν_2 (MHz)	735.6	428.63	238.8
eQq (MHz)	2452	1429.5	796.0
η	0.02	0.034	0.02

shows observed resonance frequencies of cesium triiodide and their assignments [20, 21]. In the crystal of this compound, all I_3^- ions are crystallographically equivalent, and each I_3^- ion is linear and asymmetric [22] suggesting small asymmetry parameters for the three iodine atoms. Correspondence between ν_1 and ν_2 can be found by taking into account a relation that $2\nu_1 \approx \nu_2$. When the number of nonequivalent iodine atoms is large [23] or both ν_1 and ν_2 appear as closely spaced multiplets with a finite asymmetry parameter, it is difficult to find correspondence between ν_1 and ν_2. When a large single crystal is obtainable, correspondence between ν_1 and ν_2 can be found by observing Zeeman splittings. At the same time, the observed frequencies can be assigned to nonequivalent iodine atoms in the crystal.

For atoms having $I = 1$, a single resonance frequency, ν_0 is observed when $\eta = 0$ whereas two frequencies, ν_+ and ν_-, are observed when $\eta \neq 0$. The characterization of observed lines to ν_0, ν_+ or ν_- can be achieved by examining the line shape of absorptions recorded with Zeeman modulation [24—26]. When $\eta = 0$, the resonance frequency is given by

$$\nu_0 = \frac{3eQq}{4} \tag{6}$$

in the absence of external magnetic field. When a weak external magnetic field H is applied to this system, one has

$$\nu_0' = \frac{3eQq}{4} \pm \frac{\gamma H \cos\theta}{2\pi} \tag{7}$$

where γ denotes the gyromagnetic ratio of the nucleus, and θ stands for the angle between the external magnetic field and the z axis of the field gradient. In the case of powder samples, the z axis is distributed in space. Accordingly, ν_0 appears as a broad absorption covering a frequency range from $3eQq/4 - \gamma H/2\pi$ to $3eQq/4 + \gamma H/2\pi$. In pen recording, sensitivity in detection is usually increased by use of a phase-sensitive detector [27], which is set so as to move the pen to the right in response to a signal applied during a half period of Zeeman modulation, in which $H = 0$, and to the left when a signal is given

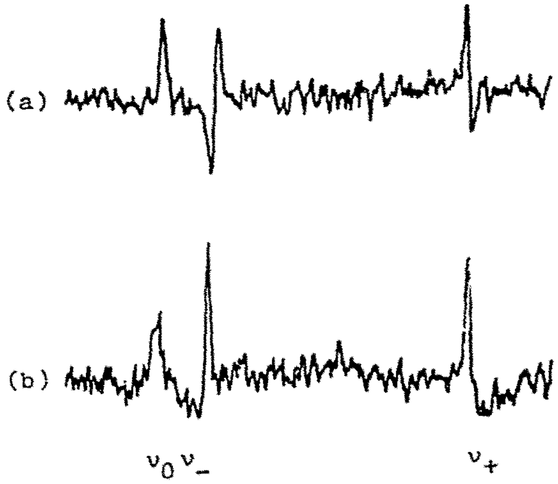


Fig. 1. NQR spectrum of ^{14}N in potassium tetracyanomercurate(II) recorded at liquid nitrogen temperature by Zeeman modulation with a modulation field of about (a) 15 G and (b) 60 G [29]. The line shape of ν_0 ($\eta = 0$) is more or less symmetric. When the asymmetry parameter is finite, ν_+ has a negative wing on the high-frequency side, while ν_- is accompanied by a negative wing on the low-frequency side.

during the other half period, in which $H \neq 0$. In this recording, negative wings appear symmetrically on both sides of $\nu_0 = 3eQq/4$. The line shape is characteristic of resonance lines of nuclei having η equal to zero. When the asymmetry parameter is finite, a negative wing appears on the low-frequency side of ν_-, whereas ν_+ is accompanied by another negative wing on the high-frequency side. Thus, it is possible to characterize observed lines as ν_0, ν_+ or ν_-. Figure 1 shows the line shape of three resonance lines of potassium tetracyanomercurate(II) recorded at liquid nitrogen temperature [28, 29]. It is evident from the line shape that two kinds of nonequivalent nitrogen atoms exist: one which has η equal to zero, while the other has a finite asymmetry parameter.

C. TEMPERATURE DEPENDENCE OF NQR FREQUENCIES

Figure 2 shows the dependence of the ^{14}N NQR frequency in potassium tetracyanozincate(II) on temperature [30]. In general, terminal resonant atoms yield NQR frequencies decreasing with increasing temperature. Bayer [31] has explained the behavior theoretically.

Suppose we have a molecule R—X having a resonant atom X. Without much loss in generality, let it be assumed that the atom X has a nuclear spin $I = 3/2$, that the z axis of the electric field gradient coincides with the R—X bond axis, and that $\eta = 0$ for simplicity. The molecule performs a rotational oscillation about its center of mass, i.e. the atom X undergoes a bending vibration relative

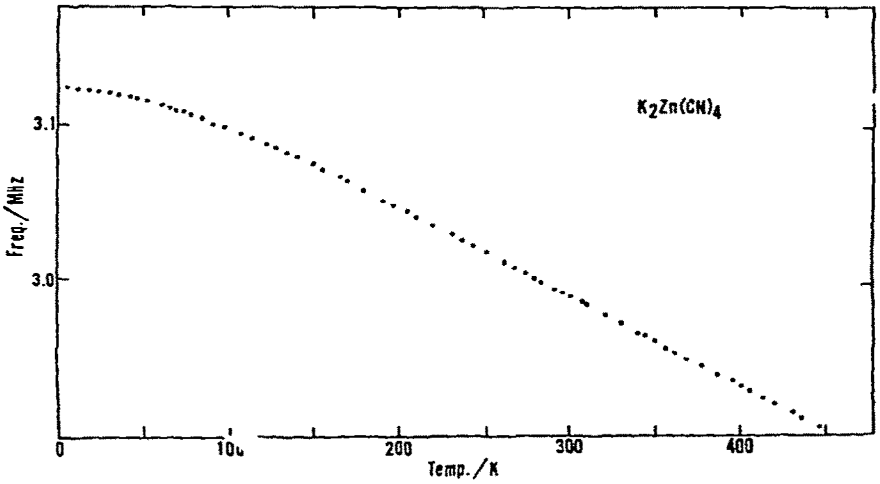


Fig. 2. Temperature variation of the NQR frequency of ^{14}N in potassium tetracyanozincate(II) [30].

to R. In order to examine the effect of the vibrational motion on the electric field gradient experienced by the nucleus X, a coordinate system (x, y, z) fixed in space and another system (x', y', z') fixed to the R—X bond are chosen with a common origin at the nucleus X as shown in Fig. 3. The motion of R relative to X is rotational oscillation in the $y'z'$ plane with an angular frequency ω. Let it be assumed that θ changes with time harmonically:

$$\theta = a \sin(\omega t + \phi) \tag{8}$$

where a is the angular amplitude of the oscillation, and ϕ is a phase factor. At an arbitrary time t, the nucleus X experiences an electric field gradient V_{zz} rather than the field gradient $V_{z'z'}$ in the absence of oscillation. Transforma-

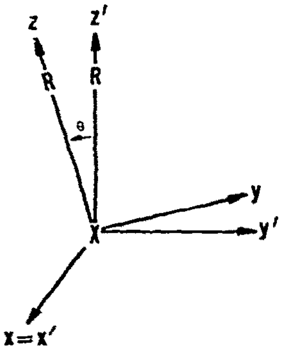


Fig. 3. Coordinate systems, x, y, z and x', y', z'.

tion between $V_{z'z'}$ and V_{zz} is straightforward, and one obtains a relation

$$V_{zz} = \frac{1}{2} V_{z'z'}(3\cos^2 \theta - 1) \tag{9}$$

The equation is simplified for small values of θ as

$$V_{zz} = V_{z'z'}(1 - \tfrac{3}{2}\theta^2) \tag{10}$$

For harmonic motion, θ^2 averaged over time is given by

$$\langle\theta^2\rangle = \frac{\hbar}{2\omega\Theta} \coth \frac{\omega\hbar}{2kT} \tag{11}$$

at a temperature T. Here, Θ denotes the moment of inertia of the molecule R—X about the x axis. Since an observable resonance frequency $\nu(T)$ is equal to ½ eQV_{zz}, one has

$$\nu(T) = \nu_0\left(1 - \frac{3\hbar}{4\omega\Theta} \coth \frac{\omega\hbar}{2kT}\right) \tag{12}$$

where ν_0 is equal to ½ $eQV_{z'z'}$, i.e. the resonance frequency in a fictitious vibrationless state of all atoms involved. In the limit of $T = 0$, one has

$$\nu(0) = \nu_0\left(1 - \frac{3\hbar}{4\omega\Theta}\right) \tag{13}$$

Accordingly,

$$\nu(T) - \nu(0) = -\frac{3\hbar\nu_0}{4\omega\Theta}\left(\coth \frac{\omega\hbar}{2kT} - 1\right) \tag{14}$$

Because $\coth(\omega\hbar/2kT) \geqslant 1$, $\nu(T) - \nu(0)$ is negative. For $\omega\hbar \ll kT$, the expansion of $\exp(\omega\hbar/2kT)$ yields

$$\nu(T) = \nu(0) - \frac{3kT}{2\omega^2\Theta}\nu_0 = \nu(0) - \frac{3kT}{2f}\nu_0 \tag{15}$$

where f denotes the force constant of the rotational oscillation. At high temperature, the resonance frequency decreases linearly with the temperature, and the slope of the straight portion of the ν versus T curve becomes steeper with decreasing force constant f.

Various modes of vibration including intramolecular vibrations as well as lattice vibrations are possible for crystals. Bayer [31] took into account only vibrational modes in which the direction of the field gradient q_{zz} rather than its magnitude changes at a resonant nucleus. Kushida [32] and Wang [33] generalized Bayer's theory, considering all normal modes of vibration, to evaluate the temperature variation of resonance frequencies. Among intramolecular vibrations, bending vibrations having a low frequency contribute to the change of resonance frequencies with temperature to a greater extent than do stretching vibrations. In the case of lattice vibrations, contribution from librational modes is larger in general than from translational modes.

The temperature variation of NQR frequencies is usually observed at a constant pressure, whereas Bayer and others' theories are developed at a constant volume. Accordingly, agreement between theoretical calculations and experimental data is rather poor when thermal expansion is no longer negligible at high temperature. In fact, the observed ν versus T curve often is not linear at high temperature but is convex upwards ($d^2\nu/dT^2 < 0$). The example shown in Fig. 2 presents a rather exceptional case in which the linearity of the curve is excellent in a high temperature range.

Kushida et al. [34] and Brown [35] refined Bayer's theory by introducing thermodynamic relations involving the thermal expansion coefficient and the isothermal compressibility. According to the authors, the observed temperature coefficient $(\partial\nu/\partial T)_p$ is given by

$$\left(\frac{\partial \nu}{\partial T}\right)_p = \left(\frac{\partial \nu}{\partial T}\right)_V + \left(\frac{\partial \nu}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \tag{16}$$

The first term is usually negative according to Bayer's theory. When the contribution from this term is large, one has a normal negative temperature coefficient of NQR frequencies. Equation (16) can be rewritten as

$$\left(\frac{\partial \nu}{\partial T}\right)_p = \left(\frac{\partial \nu}{\partial T}\right)_V - \frac{\alpha}{\chi}\left(\frac{\partial \nu}{\partial p}\right)_T \tag{17}$$

where α stands for the thermal expansion coefficient and χ is the isothermal compressibility. Both α and χ are normally positive. Therefore, when $(\partial\nu/\partial p)_T$ is negative and the absolute value of the second term in the right-hand side of eqn. (17) is greater than that of the first term. observed NQR frequencies increase with increasing temperature.

D. POSITIVE TEMPERATURE COEFFICIENT

Hamlen and Koski [36] found that the NQR frequency of chlorine in tungsten hexachloride decreased monotonically with decreasing temperature from room temperature to liquid nitrogen temperature in contradiction to Bayer's general theory. At the present time, various compounds are known to show a positive temperature coefficient of NQR frequencies for halogens, and the reason for these anomalies has been clarified for some compounds. In this section, the anomalous temperature behavior is discussed by classifying such complexes into several groups according to the origin of the anomalous temperature dependence of halogen NQR frequencies.

(i) π bonding

Hamlen and Koski [36], who found the anomalous behavior of tungsten hexachloride, noticed that the ^{35}Cl NQR frequency (10.545 and 10.172

MHz at 35 and −196° C, respectively) was much lower than can be anticipated from the electronegativity difference, $\Delta\chi = 1.2$, between chlorine and tungsten [37, 38], and invoked π character for the W—Cl bonds. However, they failed to discuss the positive temperature coefficient of NQR frequency in relation to π bonds. Barnes and Engardt [39] found that the resonance lines of ^{79}Br in titanium tetrabromide showed a temperature dependence having a broad maximum at about −50° C. In this case also, observed NQR frequencies (47.127 and 46.309 MHz at liquid nitrogen temperature) are lower than expected from $\Delta\chi$. They found that the observed $(\partial\nu/\partial p)_T$ was negative, and attributed the anomalous low frequencies and the anomalous temperature dependence to intermolecular interactions. Reddoch [40] observed that $\nu(^{35}\mathrm{Cl})$ in thorium tetrachloride showed a maximum at about −50° C. Because the observed resonance frequency, 5.9 MHz, deviated from Dailey and Townes' curve of $\Delta\chi$ plotted against the ionicity i, he suggested π character for the Th—Cl bonds, and showed that the positive temperature coefficient could be explained adequately on the basis of the π bond character.

Ikeda et al. [16] found that the NQR frequencies of chlorine and bromine in hexahalorhenates(IV) increase with increasing temperature. They called attention to the fact that the $d\nu/dT$ of chlorine in K_2MCl_6 type complexes having a third-row transition metal as the central metal M increases with decreasing atomic number of the central metal atom from platinum to tungsten almost linearly as shown in Fig. 4 [17]. Table 3 shows the resonance frequencies of these complexes and the temperature coefficients

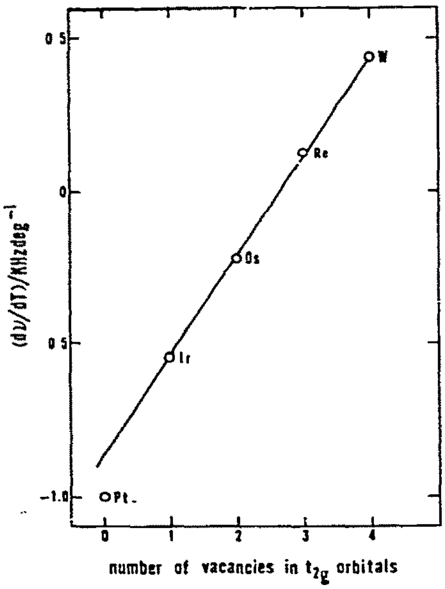


Fig. 4. Temperature coefficient of ^{35}Cl NQR frequencies at room temperature plotted against the number of vacancies in the π antibonding orbitals.

TABLE 3

Temperature coefficient of NQR frequencies in potassium hexahalorhenates(IV), hexachlorotungstate(IV) and related complexes at 20°C [17].

Compound	ν (MHz)	$d\nu/dT$ (kHz deg^{-1})	Temp. range (°C)
K_2PtCl_6	25.82	−1.00	—75.0—23.5
K_2IrCl_6	20.73	−0.54	—69.0—24.2
K_2OsCl_6	16.84	−0.22	—70.0—26.0
K_2ReCl_6	13.89	+0.13	—76.0—21.2
K_2WCl_6	10.22	+0.44	10.5—35.0
K_2ReBr_6	112.71	+2.8	— 3.0—181.0

thereof at room temperature. It is seen that the resonance frequency decreases linearly with decreasing atomic number of the central metal. All of these complexes form crystals of the K_2PtCl_6 structure shown in Fig. 5. Accordingly, the characteristic changes in the resonance frequency and its temperature dependence must be attributed to the difference in the kind of central metal atoms. However, the electronegativities [41, 42] of the central metals are not much different from one another. Accordingly, the decrease in resonance frequency is not attributable to an increase in the ionicity of M—Cl bonds. Since these complex ions have O_h symmetry in crystals, the degenerate 5*d* orbitals of a central metal atom are split into t_{2g} and e_g levels (or $d\epsilon$ and $d\gamma$ levels) in the strong field approximation. In

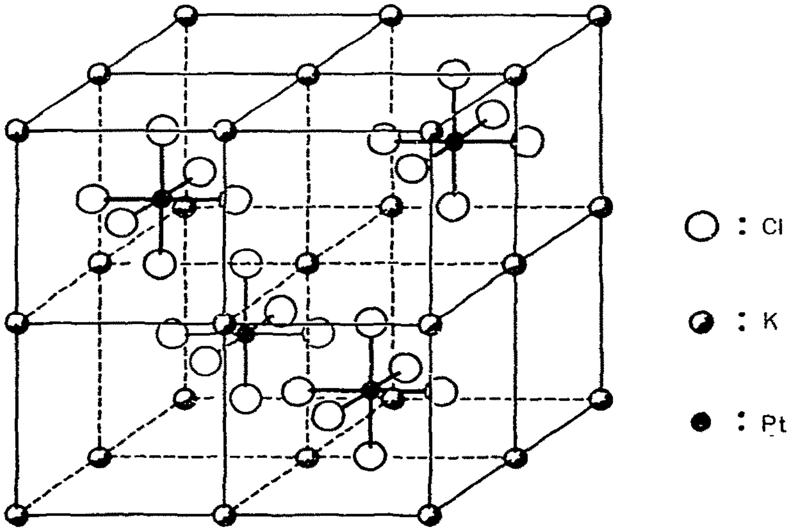


Fig. 5. Crystal structure of potassium hexachloroplatinate(IV).

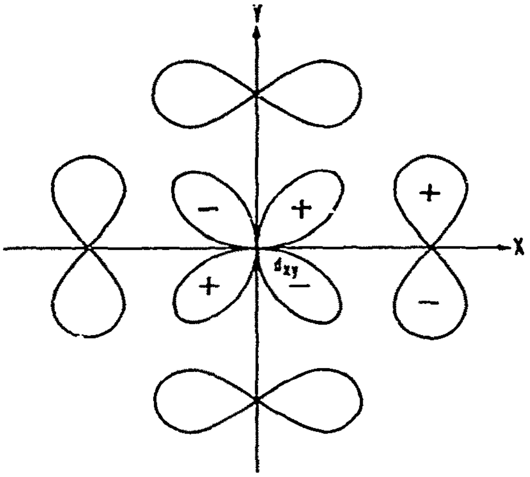


Fig. 6. Formation of $d\pi$—$p\pi$ bonds.

the case of Pt^{4+} having $5d^6$, the t_{2g} subshell is completely filled with electrons. With decreasing atomic number of the central metal atom, an electron hole or holes are formed successively in the t_{2g} orbitals. Back donation then takes place from the occupied $3p$ orbitals ($3p_x$ and $3p_y$) of ligands as shown in Fig. 6, forming $d\pi$—$p\pi$ bonds between the central metal atom and the ligands. The theoretical prediction for the formation of π bonds has been verified by an experimental investigation carried out by Owen, Griffiths and others [43—47], who confirmed the π character of Ir—Cl bonds in a hexachloroiridate(IV) ion from the hyperfine structure of ESR, and succeeded in evaluating quantitatively the extent of π bond character.

According to the Townes—Dailey approximation [48], the quadrupole coupling constant eQq observable in NQR is given by

$$|eQq| = U_p|eQq_p| \tag{18}$$

where eQq_p stands for the quadrupole coupling constant per single p electron distributed along the z axis of the field gradient q. For halogens, $|eQq_p|$ is equal to the absolute value of the atomic quadrupole coupling constant, $|eQq_{\text{atom}}|$, amenable to direct measurements [49—51]. The number U_p of unbalanced p electrons is defined by

$$U_p = \tfrac{1}{2}(N_x + N_y) - N_z \tag{19}$$

where N_x, N_y and N_z denote electron populations in the outermost p orbitals, p_x, p_y and p_z, respectively. When a halogen atom forms a σ bond, one may assume that $N_x = N_y = 2$. On the other hand, when a $d\pi$—$p\pi$ partial bond is formed between the central metal and a chlorine atom as in a hexachloroiridate(IV) ion involving the transfer of π electrons from the chlorine atom to the central metal atom, one has $N_x = N_y = 2 - \pi/2$ from symmetry, the number of transferred π electrons being denoted by π. The decrease in population from two implies that the charge distribution approaches spherical symmetry about the chlorine atom, and hence the observed resonance frequency decreases. A theoretical calculation yields the following relation for the ionicity i of the metal—halogen bonds [52].

$$|eQq| = [(1-s)(1-i-\pi) - \pi/2]\,|eQq_p| \tag{20}$$

where s denotes the s character of the σ bonding orbital of the halogens. Dailey and Townes [37] assumed that the atomic orbital of a halogen atom has 15% s character when the halogen atom is bonded to an atom more electropositive than the halogen by as much as 0.25. Cotton and Harris [53] carried out molecular orbital calculations on the complexes of the potassium hexachlorometallate(IV) series, and showed that the assumption of $s = 0.15$ is reasonable from the standpoint of orbital population. However, analysis of the experimental data suggests that the s value might be overestimated [54—56].

Ikeda et al. [17, 52] attributed a marked dependence of $\nu(^{35}Cl)$ in potassium hexachlorometallates(IV) on the nature of the central metal to a change in the π bond character of M—Cl bonds, and evaluated the ionic character i of M—Cl bonds assuming that the π bond character π is proportional to the number of electronic holes in the t_{2g} orbital. The values of ionicity thus obtained were found to be reasonable from electronegativity considerations. However, when the same method is applied to a tungsten hexachloride molecule, one gets an unbelievably small ionic character. Moreover, a negative net charge is obtained for the central metal of a hexaiodorhenate(IV) ion. Therefore, it is presumed that the π bond character and possibly the s character are also overestimated. Machmer [57, 58] found a linear relation between Jørgensen's optical electronegativity [59—62] and $\nu(^{35}Cl)$ in potassium hexachlorometallates(IV). Brown et al. [63] proposed a formula for estimating the π bond character π_M of M—Cl bonds from the optical electronegativity.

$$\pi_M = 0.054\, n \frac{\Delta\chi_{Ir}}{\Delta\chi_M}$$

$$\Delta\chi_M = \chi_M^{opt} - \chi_{Cl} \tag{21}$$

Here the numerical factor is the observed π bond character of Ir—Cl bonds in hexachloroiridate(IV) ion [43—46], n denotes the number of holes in the t_{2g} orbital of the central metal M, and χ_M^{opt} stands for the optical electronegativity of the metal M. They observed $\nu(^{35}Cl)$ in $[WCl_6]^-$ to complete a series from $n = 0$ to $n = 6$. Their data for bond parameters are compared in Table 4 with those obtained by Ikeda et al. [17, 52]. The optical electronegativity has been obtained on the basis of experimental charge transfer spectra resulting from the transfer of electrons localized in the $p\pi$ orbitals of

TABLE 4

Ionicity and π bond character of M—X bonds in some paramagnetic hexacoordinated complexes.

Complex	Number of $d\pi$ holes	π Bond character [a]		Ionicity [a]		Net charge on M [a]		χ_M^{opt}
$[IrCl_6]^{2-}$	1	0.054		0.47		0.82		2.4
$[OsCl_6]^{2-}$	2	0.081	0.108	0.51	0.47	1.06	0.82	2.2
$[ReCl_6]^{2-}$	3	0.097	0.16	0.55	0.45	1.34	0.70	2.0
$[WCl_6]^{2-}$	4	0.100	0.22	0.62	0.43	1.72	0.58	1.7
$[WCl_6]^-$	5	0.16	0.27	0.50	0.33	2.0	0.98	2.0
WCl_6	6	0.21	0.32	0.44	0.26	2.6	1.56	2.1

[a] Data in the first column were evaluated by the method of Brown et al. [63], whereas those in the second column were calculated by Ikeda et al. [17].

ligands to the $d\pi$ orbitals of central atoms [59]. Accordingly, the estimation of Brown et al. is expected to provide a better result than that of Ikeda et al. which is based on an assumption that the π character is proportional to the number of vacancies in the t_{2g} orbitals.

Thus, it is indubitable that the M—Cl bonds in paramagnetic hexachlorometallates(IV) have $d\pi$—$p\pi$ bond character and that its strength or the number of electrons transferred from a ligand to a central metal atom (or to the overlap region) increases with increasing number of vacancies in the t_{2g} orbitals of the central metal M, although the estimation of s character and π character still involves various problems. These conclusions permit one to ascribe the origin of the positive temperature coefficient of NQR frequencies to the π bond character of M—Cl bonds in this series of paramagnetic complexes.

When an M—X bond is formed as a hybrid between a σ covalent bond and a π covalent bond, the excitation of M—X stretching and bending vibrations gives rise to a decrease in the overlap population of both σ and π bonds. The decrease of π bond overlap leads to an increase in N_x as well as N_y, and hence the quadrupole coupling constant and NQR frequencies increase. On the other hand, in the case of σ bonds, decrease in overlap may increase N_z of halogen atoms and hence the NQR frequencies are expected to decrease. However, the latter effect can be disregarded for the following reason. Potassium hexachloroplatinate(IV), having completely filled t_{2g} orbitals (i.e., free from π bond character of Pt—Cl bonds), shows a normal negative temperature coefficient of the NQR frequency. Armstrong et al. [64—70] investigated the dependence of ^{35}Cl NQR frequency in potassium hexachloroplatinate(IV) on temperature and pressure as well as ^{35}Cl quadrupole spin—lattice relaxation, and evaluated the frequency of rotational vibration of the complex ion. From the observed temperature coefficient, they subtracted a contribution from intramolecular vibrations without considering the decrease of σ bond overlap. The remainder, which was assumed to be due to the rotational mode, yielded a frequency of 58 cm^{-1} in good agreement with 63 cm^{-1} calculated theoretically from the data of a vibrational spectrum [71]. This indicates that vibrational excitation affects the σ overlap population of M—Cl bonds to a negligibly small extent. Therefore, the temperature coefficient of NQR frequencies of potassium hexachlorometallates(IV) is determined by two factors, i.e., the Bayer effect and the effect of partial scission of π bonds. In other words, the temperature coefficient of $\nu(^{35}Cl)$ in paramagnetic potassium hexachlorometallates(IV) is determined by the balance between two contributions differing in sign. When the Bayer effect predominates over the π bond effect, the temperature coefficient of NQR frequencies is negative, whereas when the reverse relation holds as in

TABLE 5

^{35}Cl and ^{81}Br NQR data [72] at 300 K.

Compound	ν (MHz)	dν/dT (kHz deg^{-1})
WCl_6	10.539	1.80
WBr_6	72.12	13.0
$CsNbCl_6$	8.589	0.92
	9.245	1.20
$CsTaCl_6$	9.127	0.3
	8.803	0.62
$CsWCl_6$	11.748	0.94
	11.605	0.60
	11.281	0.56
$RbWCl_6$	11.546	0.54
	11.320	0.48
$KWCl_6$	11.455	0.78
	11.335	0.46
Cs_2WCl_6	10.913	0.35
Cs_2WBr_6	75.28	3.04
Rb_2WCl_6	10.575	0.49
Cs_2ReCl_6	14.592	0.00
K_2OsBr_6	111.78	0.29
Cs_2OsBr_6	116.83	—0.42
K_2PtBr_6	167.25	—5.1
Cs_2PtCl_6	26.552	—0.83
Cs_2PtBr_6	173.18	—4.3
Cs_2SnCl_6	16.057	—0.43
Cs_2SnBr_6	110.01	—2.2
Cs_2MoCl_6	10.732	0.76
K_2MoCl_6	9.541	0.12
	9.795	—0.15
	9.876	
Mo_2Cl_{10}	14.085	—1.44
Cs_2TeCl_6	15.566	—0.21
Cs_2PbCl_6	17.705	—0.50

potassium hexachlororhenate(IV), a positive temperature coefficient is observed.

Table 5 shows the temperature coefficients of $\nu(^{35}Cl)$ and $\nu(^{81}Br)$ in various compounds having $[MX_6]^0$, $[MX_6]^-$ or $[MX_6]^{2-}$ units observed by Brown and Kent [72]. When M—X bonds have a strong $d\pi$—$p\pi$ character with sufficient vacancies in the t_{2g} orbitals, the temperature coefficient of NQR frequencies is positive, whereas it is negative in the case of complexes having a d^6—d^{10} central metal atom (Pt, Sn, Te and Pb) with completely filled t_{2g} orbitals. These facts provide strong evidence for the foregoing presumption that the positive temperature coefficient arises from metal—halogen π bonding.

In order to clarify the mechanism by which the partial scission of π bonds takes place, Haas and Marram [19] performed quantitative calculations and concluded that the excitation of bending vibrations plays a major role. On the other hand, Brown and Kent [72] laid importance on a contribution from M—X stretching modes appearing below 350 cm^{-1} [63, 73—75], the excitation of which is not negligible at room temperature. Owing to the anharmonicity of vibrations, equilibrium bond distances increase with increasing temperature leading to a decrease in π bond overlap and hence to an increase in NQR frequencies. Oka et al. [76, 77] recorded the microwave spectra of bromine cyanide and iodine cyanide, and found that the quadrupole coupling constant of halogens is greater in the excited state than in the ground state. They explained their finding as due to a decrease in the π bond character of X—C bonds with the excitation of vibration. This suggests the importance of stretching vibrations for the positive temperature coefficient of NQR frequencies.

Armstrong et al. [66, 68] determined the dependence of chlorine resonance frequencies in K_2MCl_6 (M: Pt, Ir, Os, Re) on pressure ($1 \leqslant p \leqslant 5000$ kg cm^{-2}) in a temperature range covering 275—350 K. It was found that $(\partial\nu/\partial p)_T$ was very nearly constant, the value being equal to 5.0, —3.7, —7.1 and —11.2 Hz kg^{-1} cm^2 for M = Pt, Ir, Os and Re, respectively. This suggests that the positive temperature coefficient originates from the second term in the right-hand side of eqn. (17) or that the partial scission of π bonding takes place in accordance with a mechanism dependent on the volume. Haas and Marram's theoretical calculations [19] were performed at a constant volume, whereas Brown and Kent [72] proposed a mechanism dependent on the volume. Accordingly, the result of Armstrong et al. supports the latter mechanism. At the present stage, however, it is difficult to decide whether the mechanism is due to vibronic interaction or thermal expansion and whether bending vibration or stretching vibration is more important for the vibronic interaction.

O'Leary and Wheeler [78] observed $\nu(^{35}Cl)$ in potassium hexachlororhenate(IV) over a wide temperature range. The complex undergoes three crystallographic transitions at 76, 103, and 110.9 K as revealed by the determination of specific heat [79]. The phase transitions can also be located by the temperature variation of $\nu(^{35}Cl)$ shown in Fig. 7. O'Leary and Wheeler attributed

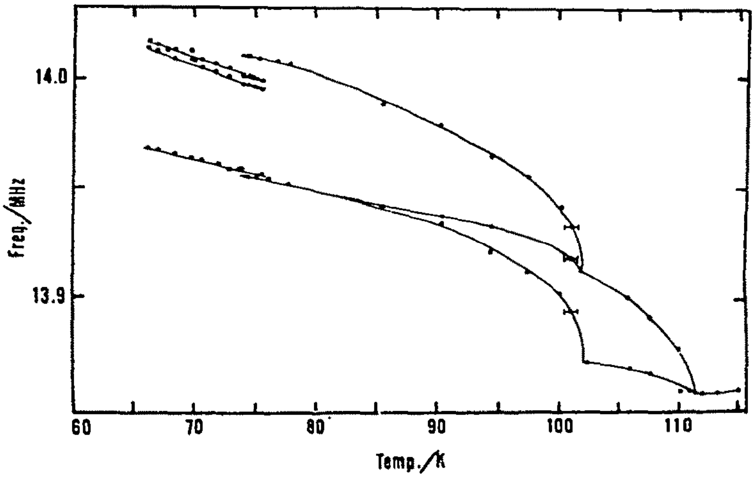


Fig. 7. ^{35}Cl NQR frequency data taken on K_2ReCl_6 below a phase transition at 110.9 K [78]. Evidence for thermal hysteresis is shown in the temperature range about the 76 K transition.

the positive temperature coefficient observed for this complex above a transition point at 110.9 K to a soft rotary mode giving rise to the transition from a less symmetric structure to a face-centered cubic structure because the NQR

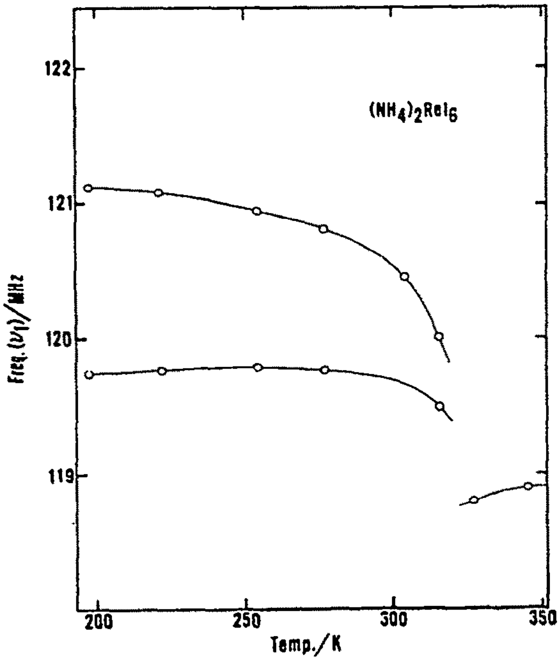


Fig. 8. Temperature dependence of ν_1 NQR frequencies of ^{127}I in ammonium hexaiodorhenate(IV) [18].

frequencies decrease with increasing temperature below the transition point. However, their conclusion seems to be inadequate for the following reason. Ammonium hexaiodorhenate(IV) has iodine atoms showing a positive temperature coefficient of the NQR frequency even when it forms crystals not having the face-centered cubic structure [18]. Figure 8 shows the dependence of ν_1 frequency on temperature; the resonance frequency at about 119.7 MHz clearly increases with increasing temperature. The corresponding ν_2 also shows a positive temperature coefficient.

Besides potassium hexachloroplatinate(IV) type complexes already discussed, the following compounds have been reported to show a positive temperature coefficient of NQR frequencies presumably owing to the π bond character of metal—halogen bonds: the cubic form of titanium tetrabromide [39], thorium tetrachloride [40], the monoclinic modification of titanium tetrabromide [80] square-planar tetrachlorocopper(II) complexes [81], ammonium trichlorocuprate(II) [81] and hexamminecobalt(III) pentachlorocuprate(II) [81].

(ii) Hydrogen bonding

Fryer and Smith [82] and independently Sasane et al. [83, 84] observed ^{35}Cl NQR in sodium tetrachloroaurate(III) dihydrate, and found that the lowest among four observed frequencies increased with increasing temperature, whereas three others showed normal negative temperature coefficients. Figure 9 shows the temperature variation of $\nu(^{35}\text{Cl})$ in this complex. The resonance frequencies of various tetrachloroaurates(III) are given in Table 6 at three different temperatures. Among various tetrachloroaurates(III), only sodium tetrachloroaurate(III) dihydrates shows a positive temperature coefficient of resonance frequency, indicating that unlike the case with rhenates(IV) the positive temperature coefficient is characteristic of this complex rather than of tetrachloroaurates(III). The aforementioned lowest frequency of sodium tetrachloroaurate(III) dihydrate showing the positive temperature coefficient is considerably lower than the remaining three frequencies and also than the resonance frequencies of other tetrachloroaurates(III). This indicates either that the chlorine atom giving rise to the lowest frequency line has a large ionicity (increase in the population of the $3p_z$ orbital) or that populations in the $3p_x$ and $3p_y$ orbitals perpendicular to the bonding direction are not completely occupied for some reason.

Bonamico et al. [85] carried out the X-ray crystal analysis of this complex, and found that the crystal is orthorhombic belonging to the space group *Pnma* ($Z = 4$) and that four complex ions in a unit cell are equivalent to one another. The structure is shown in Fig. 10. Four chlorine atoms in a complex ion are nonequivalent, the Au—Cl distances amounting to 2.288, 2.260, 2.283 and 2.278 Å, respectively. Planar $[\text{AuCl}_4]^-$ ions lie on $(0, b/4, 0)$ and $(0, 3b/4, 0)$ planes along with sodium ions. Although hydrogen atoms have not been located, oxygen atoms are approximately on $(0, b, 0)$ and $(0, b/2, 0)$ planes. Unlike other chlorine atoms, a Cl_1 atom having the longest Au—Cl distance is surrounded by four oxygen atoms at relatively short distances, $\text{Cl}_1 \cdots \text{O}$

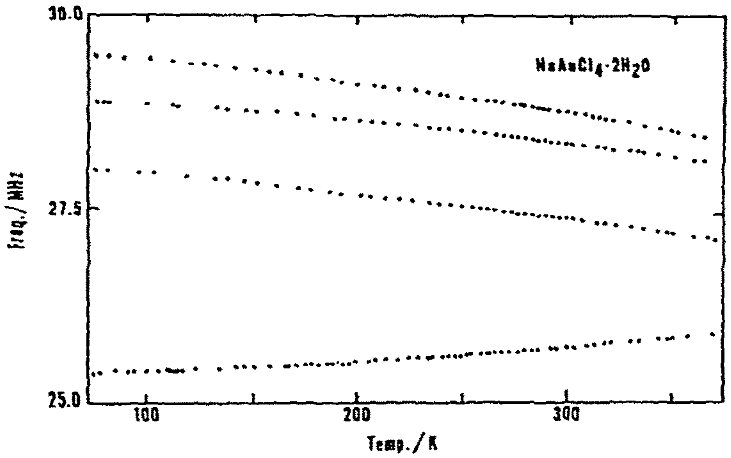


Fig. 9. Temperature dependence of ^{35}Cl NQR frequencies of sodium tetrachloroaurate(III) dihydrate *[84]*.

distances being 3.36 or 3.42 Å as contrasted with other Cl···O distances longer than 3.45 Å. The Cl_1 atom and the four oxygen atoms form a very flat slightly distorted square pyramid, the Au–Cl_1 bond axis almost coinciding with the axis of the pyramid. The angle, ∠Cl_1···O(1)···Cl'_1, equal to 118° is close to the ∠HOH bond angle in a water molecule. If the water molecule is oriented with

TABLE 6

NQR frequencies of ^{35}Cl in some tetrachloroaurates(III) [84].

Compound	Frequency (MHz)		
	77 K	193 K	293 K
$NaAuCl_4 \cdot 2H_2O$	25.356	25.501	25.685
	27.998	27.696	27.400
	28.867	28.633	28.368
	29.466	29.118	28.770
$KAuCl_4$	27.320	27.205	27.088
	27.598	27.415	27.231
	27.907	27.724	27.545
	28.214	27.881	27.573
$KAuCl_4 \cdot 2H_2O$	27.137	27.056	26.967
	28.183	27.948	27.686
NH_4AuCl_4	27.300	27.180	26.993
	28.130	27.980	27.809
$RbAuCl_4$	27.651	27.435	27.197
	28.319	28.056	27.946
$CsAuCl_4$	28.419	28.151	27.885
	27.800	27.330	27.098

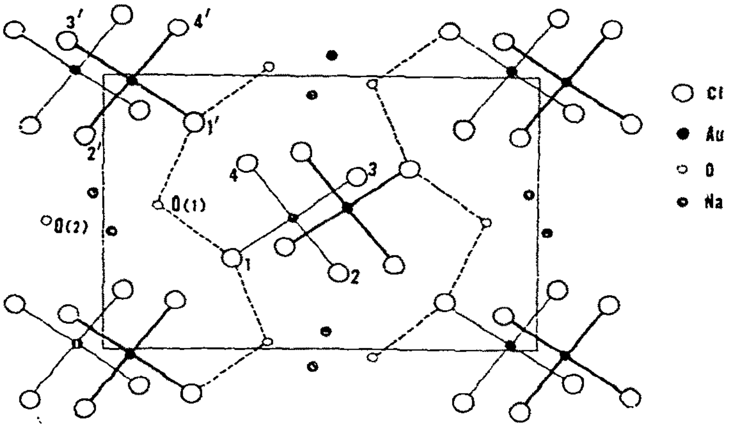


Fig. 10. Crystal structure of sodium tetrachloroaurate(III) dihydrate [85].

its OH vectors pointing to the Cl_1 and Cl_1' atoms, the lone pair orbitals of the oxygen atom are directed to two neighboring sodium ions, leading to an electrostatically stable orientation of the water molecule.

The formation of weak hydrogen bonds $O—H \cdots Cl_1$ has been confirmed by infrared spectroscopy [86] and broad-line NMR [84]. Fryer and Smith [82] observed the ^{35}Cl NQR in $NaAuCl_4 \cdot 2D_2O$, and found that the lowest frequency line shifted on deuteration to the low-frequency side by 0.03 MHz (at liquid nitrogen temperature), whereas three other lines underwent no appreciable changes. From these results, one can assign the resonance line showing the positive temperature coefficient of NQR frequency unequivocally to the Cl_1 atoms. An interesting feature of the crystal structure of this complex is that the $Cl_1 \cdots Na^+$ distances are long: the Cl_1 atom is separated from the nearest sodium ion by 4.37 Å, whereas other chlorine atoms are distant from sodium ions by an average distance equal to 3.05 Å. This suggests that the ionicity of the Cl_1 atom is not larger than that of other chlorine atoms. Therefore, the considerably low NQR frequency of the Cl_1 atoms must be interpreted in terms of a decrease in the populations of the $3p_x$ and $3p_y$ orbitals.

Taking the z axis along an $Au—Cl_1$ bond direction, one can calculate the quadrupole coupling constant of Cl_1 from eqns. (18) and (19) as

$$|eQq| = |(N_x + N_y)/2 - N_z||eQq_{\text{atom}}| \qquad (22)$$

If hydrogen atoms in water molecules are present in the x and y directions from the Cl_1 atom, electrons in the $3p_x$ and $3p_y$ orbitals of the chlorine atom are excited to outer orbitals owing to perturbation by electrostatic interaction with protons involved in hydrogen bonding. Accordingly, N_x and N_y decrease leading to a decrease in the quadrupole coupling constant in agreement with the small observed $\nu(^{35}Cl)$ of Cl_1 atoms as compared with the NQR frequencies of other chlorine atoms. With increasing temperature, the lattice vibrations, i.e. translational and librational modes of water molecules are excited to an increasing extent and reduce the electrostatic interaction between hydrogen and chlorine in the H···Cl_1 system. This along with the effect of thermal expansion increases the electron populations in the $3p_x$ and $3p_y$ orbitals of Cl_1, leading to an increase in the quadrupole coupling constant and hence in the observed NQR frequency. Thus, the partial scission of hydrogen bonds gives rise to a positive temperature coefficient of NQR frequencies to compete with the normal negative temperature coefficient of the Bayer term. If the former predominates over the latter, a positive temperature coefficient of NQR frequencies is observed as in sodium tetrachloroaurate(III) dihydrate. In this complex, the effect of hydrogen bonding is particularly marked because the Cl_1 atom is surrounded by four hydrogen atoms located nearly in the x and y directions from the Cl_1 atom. Accordingly, the positive temperature coefficient of NQR frequencies of halogens is expected for other systems involving hydrogen bonding of a similar spatial arrangement. In fact, the positive temperature coefficient of NQR frequencies has been observed in copper(II) chloride dihydrate [87] and cobalt(II) chloride dihydrate [88]. The presence of O—H···Cl type hydrogen bonds has been confirmed in these dichloride dihydrates by neutron diffraction experiments [89—91].

Sodium tetrabromoaurate(III) dihydrate shows the temperature dependence of ^{79}Br NQR frequencies bearing a strong resemblance to that of sodium tetrachloroaurate(III) dihydrate [84]. These compounds are isomorphous to each other as confirmed by X-ray powder patterns. Cornwell and Yamasaki [92] observed four ^{35}Cl NQR frequencies in sodium tetrachloroiodate(III) dihydrate. Their data suggest a positive temperature coefficient of the lowest frequency of four observed lines, but they failed to discuss the anomalous behavior. Sasane et al. [93] observed the temperature variation of $\nu(^{35}\mathrm{Cl})$ in this compound, and obtained a frequency pattern resembling that of sodium tetrachloroaurate(III) dihydrate. In addition, they recorded the X-ray powder patterns and confirmed that this compound is isomorphous with the foregoing two complexes. Table 7 shows the lattice constants of the three complexes. It is presumed that, in sodium tetrabromoaurate(III) dihydrate and sodium tetrachloroiodate(III) dihydrate, the halogen atom giving rise to the lowest frequency resonance line forms hydrogen bonds with four surrounding hydrogen atoms as in sodium tetrachloroaurate(III) dihydrate.

TABLE 7

Lattice constants of $NaAuCl_4 \cdot 2H_2O$ type complexes [84, 85, 93].

Compound	*a* (Å)	*b* (Å)	*c* (Å)
$NaAuCl_4 \cdot 2H_2O$	12.818	7.067	8.993
$NaICl_4 \cdot 2H_2O$	13.51	7.15	9.21
$NaAuBr_4 \cdot 2H_2O$	13.29	7.27	9.43

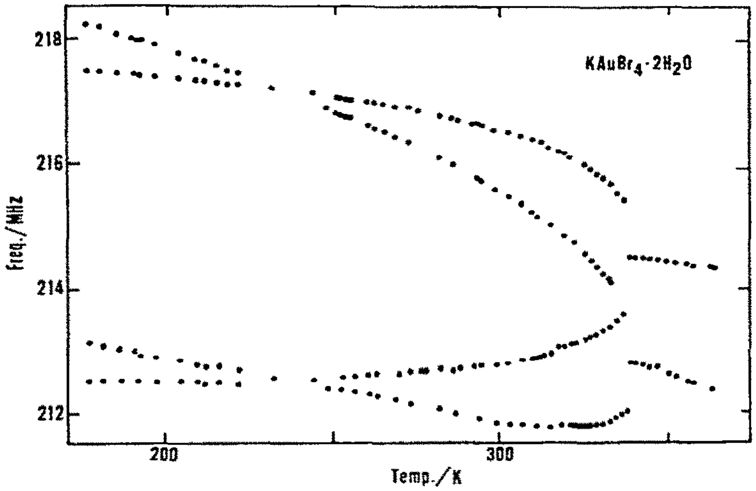


Fig. 11. Temperature dependence of ^{79}Br NQR frequencies in potassium tetrabromoaurate(III) dihydrate [84].

Figure 11 shows the dependence of the ^{79}Br NQR frequencies in potassium tetrabromoaurate(III) dihydrate on temperature [84]. Four nonequivalent bromine atoms exist in crystals below a transition point at 337 K, whereas two kinds of nonequivalent bromine atoms are present above the transition point. Two resonance lines of the low-temperature phase on the low-frequency side show a very mild temperature variation, and the temperature coefficient is positive in the high-temperature region. The crystal structure analysis of this compound has not been carried out as yet, but it is highly probable that bromine atoms yielding the two resonance lines are involved in weak hydrogen bonding of the O—H···Br type. Broad-line NMR observed at room temperature shows a broad signal having a maximum-slope width equal to 11 G supporting the formation of hydrogen bonds in the crystals.

Graybeal et al. [94] observed the ^{35}Cl NQR in $MSnCl_6 \cdot 6H_2O$ type complexes (M: divalent metal), and reported the positive temperature coefficients of NQR frequencies for magnesium hexachlorostannate(IV) hexahydrate and calcium hexachlorostannate(IV) hexahydrate. Although they attributed the positive temperature coefficients to the π bond character of Sn—Cl bonds, their explanation seems to be implausible because no positive temperature coefficients have been observed for R_2SnCl_6 type complexes (R: alkali metal) [95]. Sasane et al. [96] observed the temperature variation of ^{35}Cl NQR frequencies in $MPtCl_6 \cdot 6H_2O$ type complexes, and found that the lowest frequency of three resonance lines observed in barium hexachloroplatinate(IV) hexahydrate shows a positive temperature coefficient as shown in Fig. 12. Although the crystal structure of this complex has not been elucidated as yet, hydrogen bonding is suspected to be the origin of the positive temperature coefficient, because the frequency showing the positive temperature coefficient

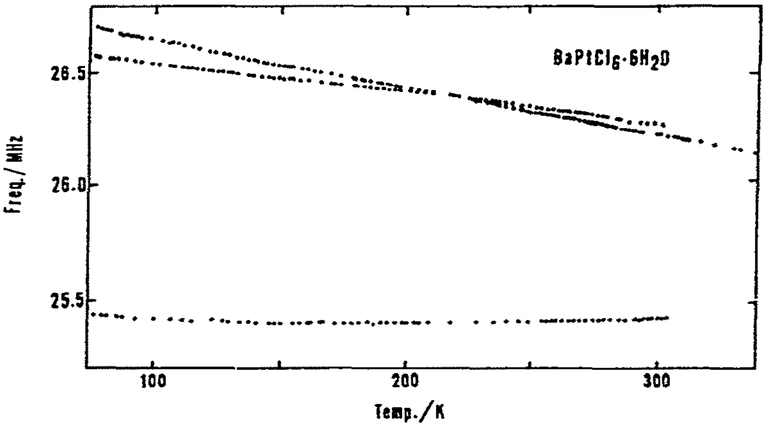


Fig. 12. Temperature dependence of ^{35}Cl NQR frequencies in barium hexachloroplatinate(IV) hexahydrate [96].

is considerably lower than those of the two other lines and also than those of R_2PtCl_6 type complexes [97, 98]. The negative temperature coefficients of ^{35}Cl NQR frequencies observed in $MPtCl_6 \cdot 6H_2O$ type complexes other than barium hexachloroplatinate(IV) hexahydrate are smaller in absolute values than those of potassium hexachloroplatinate(IV) indicating a possible effect of hydrogen bonding on the temperature variation of NQR frequencies.

Positive temperature coefficients of NQR frequencies presumably due to hydrogen bonding have also been reported for tetrachloroiodic(III) acid tetrahydrate (or hydroxonium tetrachloroiodate(III) trihydrate) [99] and tetrachloroauric(III) acid tetrahydrate (or hydroxonium tetrachloroaurate(III) trihydrate) [100]. In the case of the former compound, four resonance lines were observed between 130 K and room temperature. Two of the four resonance lines on the high-frequency side show positive temperature coefficients of resonance frequencies, suggesting a type of participation of hydrogen bonding different from the case of sodium tetrachloroaurate(III) dihydrate.

Brill and Long [101] report that, in a low-temperature region, the bromine resonance frequencies in tri(diethylammonium) hexabromoantimonate(III) and tri(diethylammonium) hexabromobismuthate(III) increase with increasing temperature, and that the intensity of signals decreases with decreasing temperature. The origin for the positive temperature coefficient of NQR frequencies seems to lie in the formation of hydrogen bonds of the N—H···Br type in these complexes.

Johnson and Rogers [102] observed the positive temperature coefficient of the rhenium resonance in ammonium perrhenate(VII), and attributed it to hydrogen bonding of the N—H···O type.

(iii) Arrangement of neighboring ions

Ammonium, rubidium, cesium and thallium(I) triiodides are isomorphous with one another, having linear asymmetric triiodide ions in crystals [20—23, 103—105]. All NQR frequencies of iodine in rubidium and cesium triiodides show normal negative temperature coefficients of resonance frequencies. However, in ammonium and thallium(I) triiodides, the most negatively charged iodine atom I_a gives rise to ν_1 and ν_2 frequencies increasing with increasing temperature as shown in Figs. 13 and 14 [20, 23]. It is noteworthy that the change in the resonance frequency of ammonium triiodide with temperature is particularly marked.

Figure 15 shows the crystal structure of ammonium triiodide along with the arrangement of neighboring cations around a triiodide ion. The crystal is orthorhombic belonging to the space group *Pnma* [103, 104]. An iodine atom I_a is surrounded by four ammonium ions in directions lateral to the $I_c—I_a$ bond axis. Two of the four ammonium ions are close to I_a, the distances being equal to 3.62 and 3.68 Å. The characteristic arrangement of cations may give a positive temperature coefficient of NQR frequencies of I_a atoms in the following three ways.

(a) In ionic crystals, the field gradient q at an I_a nucleus is the sum of a contribution from all other charges in the central triiodide ion and another from

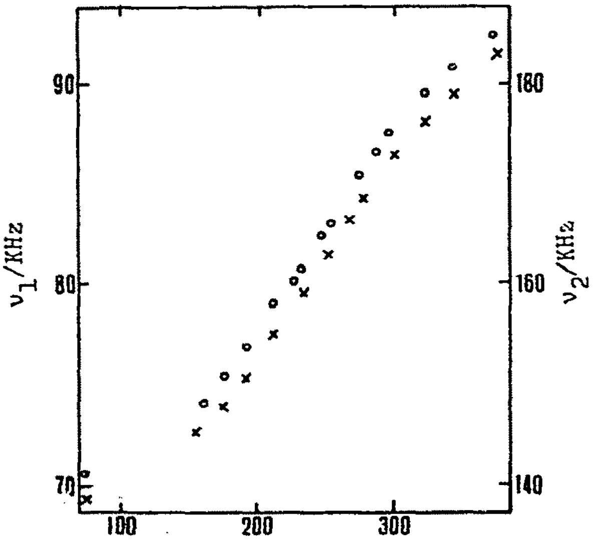
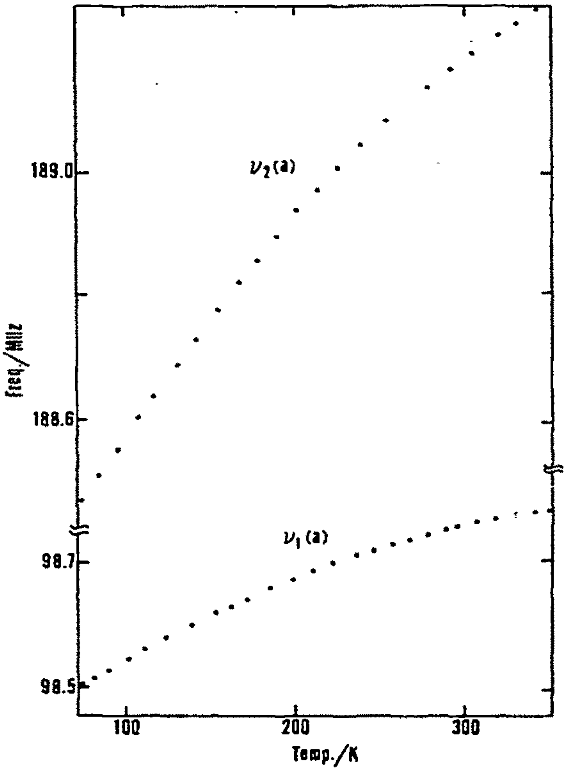


Fig. 13. Temperature dependence of the ν_1 (circles) and ν_2 (crosses) NQR frequencies of the most negatively charged iodine atoms I_a in ammonium triiodide [20].



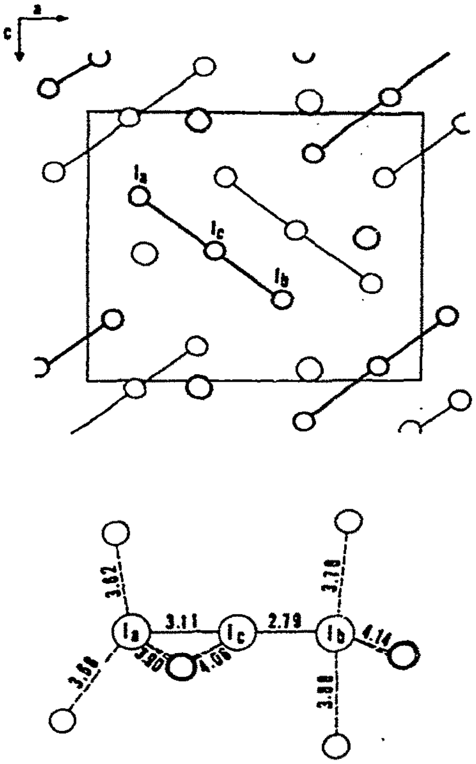


Fig. 14. Temperature dependence of the ν_1 and ν_2 frequencies of the most negatively charged iodine atoms I_a in thallium(I) triiodide [23].

Fig. 15. Crystal structure of ammonium triiodide and the arrangement of neighboring cations about a triiodide ion.

charges on all ions other than that in question.

$$q = q_{\text{c.i.}} + q_{\text{n.i.}} \tag{23}$$

For simplicity, let it be assumed that $q_{\text{c.i.}}$ and $q_{\text{n.i.}}$ have a set of principal axes in common and that only neighboring cations, which may be approximated with point charges, contribute to $q_{\text{n.i.}}$ to an appreciable extent. Theoretical considerations lead to a conclusion that $q_{\text{c.i.}}$ is positive whereas $q_{\text{n.i.}}$ is negative [98]. Interionic distances increase with thermal expansion. This gives rise to a decrease in $|q_{\text{n.i.}}|$ and hence an increase in the observed quadrupole coupling constant. The effect is expected to be marked when $q_{\text{c.i.}}$ is small or the halogen is strongly ionic.

(b) Owing to electrostatic interaction with neighboring cations, electrons in the $5p_x$ and $5p_y$ orbitals of I_a are excited to outer orbitals as in the case of sodium tetrachloroaurate(III) dihydrate, the z axis being taken along the

I_a—I_c bond axis. In other words, the electronic cloud of the $5p_x$ and $5p_y$ orbitals is distorted so as to extend outwards. As a result, the number of electrons in $5p_x$ and $5p_y$ orbitals decreases from the maximum value of two, and hence the observed frequencies decrease. The electrostatic interaction is reduced when thermal vibrations are excited. Accordingly, NQR frequencies increase with increasing temperature.

(c) When the electrostatic interaction becomes extraordinarily strong, it is expected that neighboring cations exert a great influence not only on the electron population in the $5p_x$ and $5p_y$ orbitals of the I_a atom, but on the charge distribution in an I_3^- ion. This may cause the geometry of the I_3^- ion to be more asymmetric, because NQR and X-ray studies on a variety of triiodides [106, 107] have revealed that, when the electrostatic effect of neighboring cations on a triiodide ion increases, the ion becomes more asymmetric and the ionicity of I_a increases. Therefore, when thermal motion is excited to decrease the electrostatic effect, the triiodide ion becomes more nearly symmetric, and the electronic charge on the I_a atom decreases because the excess negative charge on I_a is in the $5p_z$ orbital.

The large positive temperature coefficients of ν_1 and ν_2 observed for I_a in ammonium triiodide are attributable to (c) for the following reason. The quadrupole coupling constant of I_a at room temperature is greater than that at liquid nitrogen temperature by about 23%. That of another terminal iodine atom I_b decreases by as much as 8% with increasing temperature from liquid nitrogen temperature to room temperature. The value is one order of magnitude greater than the corresponding values of I_b in rubidium triiodide and cesium triiodide (0.4% and 0.5%, respectively). Evidently, this is anomalous although the temperature coefficient is negative, because, if the negative temperature coefficient arises from the Bayer term alone, the three triiodides are expected to show temperature coefficients of the same order of magnitude. Accordingly, the marked decrease of the quadrupole coupling constant observed for I_b in ammonium triiodide must be explained as due to an increase in the ionicity of I_b with increasing temperature. This implies that the electronic distribution of an I_3^- ion is affected indirectly by the electrostatic interaction between I_a and neighboring cations. In other words, the contribution from the resonance structure, $I_a—I_c\cdots I_b^-$ increases at the sacrifice of contribution from $I_a^-\cdots I_c—I_b$ with increasing temperature. Effects (b) and (c) are continuous to each other, and the former effect is surely involved in the present case as well. However, it is impossible to explain the large positive temperature coefficient observed for I_a with (b) alone. Quite recently, bromine NQR was observed in ammonium tribromide [108, 109]. It was found that the terminal bromine atoms Br_a bearing the highest negative charge yield resonance lines varying with temperature in almost the same manner as the lines of I_a in ammonium triiodide.

The positive temperature coefficient of NQR frequencies observed for thallium(I) triiodide is attributable mainly to the effect (b) [23], because the lattice constants of the crystal of this compound are considerably smaller than

TABLE 8

Unit cell dimensions of some orthorhombic triiodide crystals [20, 22, 103—105].

Compound	a (Å)	b (Å)	c (Å)
NH_4I_3	6.64	9.66	10.82
RbI_3	6.65	9.71	10.88
CsI_3	6.86	9.98	11.09
$Tl(I)I_3$	6.48	9.45	10.56

those of other triiodides as shown in Table 8. Since $Tl(I)\cdots I_a$ distance is anticipated to be smaller than the $NH_4\cdots I_a$ distance [110], the distortion of the $5p$ electron cloud of I_a due to cationic charges is expected to be considerable. The quadrupole coupling constant of I_a in thallium(I) triiodide observed at liquid nitrogen temperature amounts to 632.7 MHz. This value along with calculated $q_{n.i.}$ yields a fairly large $q_{c.i.}$, suggesting that the effect (a) is not the major factor for the anomalous temperature behavior.

Tovborg-Jensen [111] observed the ^{35}Cl NQR in cesium trichloroplumbate(II) which has a cubic perovskite structure, and found that the resonance frequency increases with increasing temperature. The observed low frequency of 7.7 MHz indicates that the field gradient is mainly due to contribution from surrounding ions [112]. In the perovskite structure, a chlorine atom is surrounded by four cesium ions in directions perpendicular to the Pb—Cl bond axis. The significant contribution from $q_{n.i.}$ indicates that the positive temperature coefficient of the NQR frequency is due mainly to the effect (a).

E. PHASE TRANSITION

In a majority of cases, a high-temperature modification having a symmetric structure undergoes a phase transition to a low-temperature phase of a less symmetric crystal structure [113]. This type of phase transition has been observed in a variety of R_2MX_6 type complexes [5]. As an example, Fig. 16 shows the temperature variation of ^{79}Br NQR frequencies in potassium hexabromostannate(IV) [114]. Phase transitions take place at 375 and 399 K with discontinuities in observed resonance frequencies. Immediately below the transition at 399 K, the high-frequency line is twice as intense as the low-frequency line. Galloni et al. [115] carried out an X-ray analysis and found that the compound forms potassium hexachloroplatinate(IV) type crystals above the transition point whereas it forms crystals having tetragonal symmetry at lower temperatures, although a detailed structural analysis has not been performed on the latter crystal. The high-frequency NQR signal observed in the tetragonal phase disappears whereas the low-frequency signal undergoes only a slight frequency shift on heating above the transition point. This suggests that bromine atoms in the tetragonal phase yielding the low-frequency

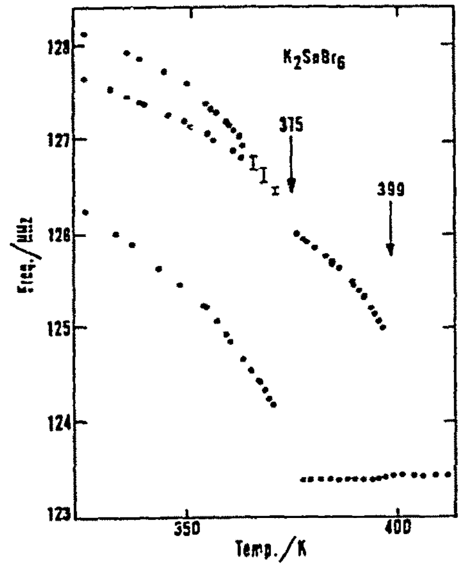


Fig. 16. Temperature dependence of ^{79}Br NQR frequencies in potassium hexabromostannate(IV) [114].

NQR signal have an environment of surrounding ions resembling that in the cubic phase and that the arrangement of neighboring cations undergoes no appreciable change. Similar transitions showing no detectable discontinuity in NQR signals have been found in potassium hexabromoselenate(IV) [116] and potassium hexabromorhenate(IV) [17]. The characteristic behavior can be explained if it is assumed that each of $[MX_6]^{2-}$ octahedra is rotated about an M—X axis through a small angle in a cage formed by surrounding cations on cooling the cubic crystals below the transition point [117].

O'Leary and Wheeler [78] carried out an extensive NQR study on a phase transition of potassium hexachlororhenate(IV) at 110.9 K (see Fig. 7). Two resonance lines, ν_z and $\nu_{x,y}$, of the low-temperature tetragonal phase show an intensity ratio of 1:2. They found that $[ReCl_6]^{2-}$ octahedra are rotated about the z axis through about 2° at a temperature a few degrees below the transition point as shown in Fig. 17. The angle of rotation increases with decreasing temperature. In other words, the complex anions are not rotated through a definite angle abruptly at the transition point, but the angle of rotation gradually increases with decreasing temperature. They attributed the occurrence of the phase transition to the induction of a soft rotary mode of the complex ions, the force constant of which depends to a great extent on temperature tending to zero at the transition point. Armstrong et al. [118, 119] observed a similar behavior of NQR frequencies for a phase transition of potassium hexabromoplatinate(IV) at 169 K. They assumed that the geometry of $[PtBr_6]^{2-}$ octahedra is unchanged even in the less symmetric

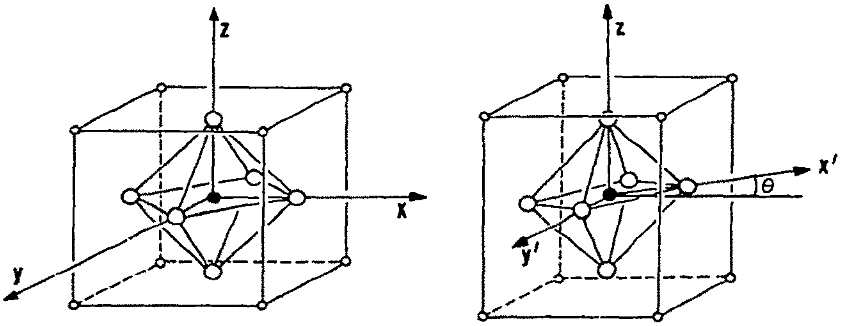


Fig. 17. Orientation of $[ReCl_6]^{2-}$ ions in the cubic (left) and tetragonal (right) crystals of potassium hexachlororhenate(IV).

low-temperature crystal structure, that the tetragonal distortion of the cage of cations is inappreciable, and hence that the difference between $\nu_{x,y}$ and ν_z is due to the difference between the field gradient originating directly from four neighboring cations, which can be approximated with point charges, at $Br_{x,y}$ and at Br_z. A simple calculation leads to a conclusion that the difference between $\nu_{x,y}$ and ν_z is proportional to the square of the angle θ of rotation of $[PtBr_6]^{2-}$ octahedra. Armstrong et al. estimated θ to be equal to about 7° at a temperature a few degrees below the transition point. A phase transition of a similar nature has been found for potassium hexachloroosmate(IV) at 45 K by NQR measurements [120].

Potassium hexabromostannate(IV) shows three resonance lines below a transition at 375 K [114] as is shown in Fig. 16, suggesting that the crystal has a lower than tetragonal symmetry. Nakamura et al. [121] observed three NQR signals of bromine in potassium hexabromotellurate(IV) at room temperature indicating that the crystal has a lower than tetragonal symmetry. An X-ray structural analysis carried out by Brown [122] on the latter compound has shown that the crystal is monoclinic and belongs to the space group $P2_1/n$, the structural parameters being $a = 7.521$, $b = 7.574$, $c = 10.730$ Å and $\beta = 89°40'$. The structure is very closely tetragonal, while $[TeBr_6]^{2-}$ ions retain their O_h symmetry. Each octahedron is rotated from the symmetric position through small angles about two axes successively. In other words, it is rotated slightly about the x' axis of the tetragonal phase shown in Fig. 17. From the result, one is led to conclude that in the low-temperature phase of potassium hexabromostannate(IV) below 375 K, each of $[SnBr_6]^{2-}$ octahedra is rotated about two axes through small angles in a cage of cations having orthorhombic or nearly tetragonal symmetry. An early X-ray analysis [123] reported that the compound forms tetragonal crystals at room temperature. Presumably, analysis was carried out assuming the tetragonal symmetry instead of the nearly tetragonal symmetry.

Very often, R_2MX_6 type complexes show multiplet lines in NQR spectra. The multiplet structure has been attributed to the crystal field effect, be-

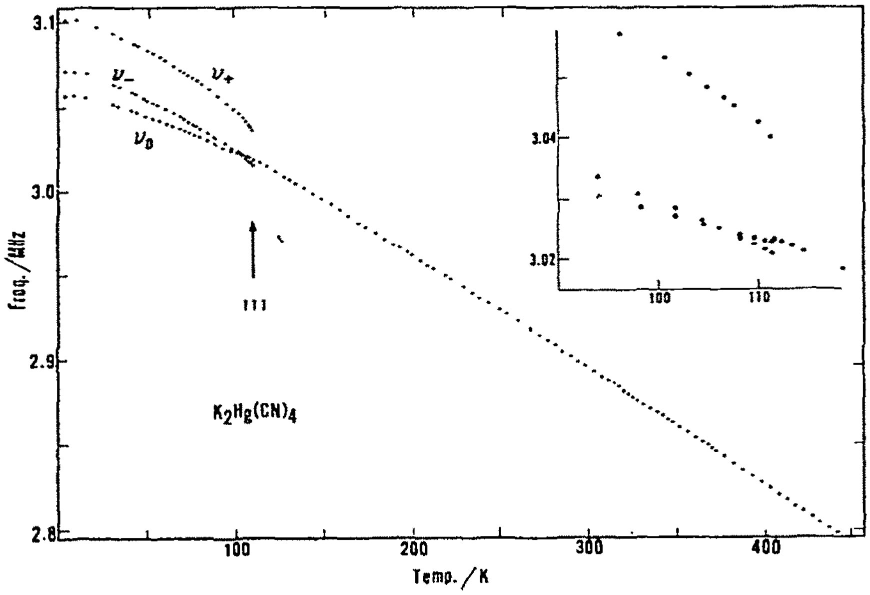


Fig. 18. Temperature dependence of ^{14}N NQR frequencies in potassium tetracyanomercurate(II) showing a phase transition at 111 K [124].

cause line separations are very small [5]. X-ray studies by Brown [122] and by O'Leary and Wheeler [78] have provided experimental evidence for the adequacy of this point of view.

Saruwatari et al. [124] observed the temperature variation of ^{14}N NQR frequencies in potassium tetracyanomercurate(II), and located a phase transition at 111 K as shown in Fig. 18. The crystal of this compound is cubic at room temperature belonging to the space group *Fd*3*m* [125]. An $[\mathrm{Hg(CN)_4}]^{2-}$ ion has T_d symmetry with CN groups lying on the body diagonals of unit cubes having threefold axes of symmetry. Accordingly, all nitrogen atoms are crystallographically equivalent. In fact, a single ^{14}N NQR line was observed with a vanishing asymmetry parameter above 111 K. Below the transition point, two kinds of nonequivalent nitrogen atoms exist in crystals as revealed by NQR. From intensity measurements, one can conclude that nitrogen atoms yielding a signal with $\eta = 0$ and those giving rise to two signals for a finite asymmetry parameter are in an abundance ratio of 1:3. This indicates that one of four cyanogen groups in a complex ion lies on the threefold axis even below the transition point. The resonance line of $\eta = 0$ undergoes a trivial frequency shift and a small change in the temperature coefficient of NQR frequencies at the transition point. These observations indicate that the low-temperature phase of this complex has a crystal structure obtained by distorting the aforementioned cubic structure slightly in the direction of a body diagonal, thereby leaving the threefold axis inherent in trigonal symmetry

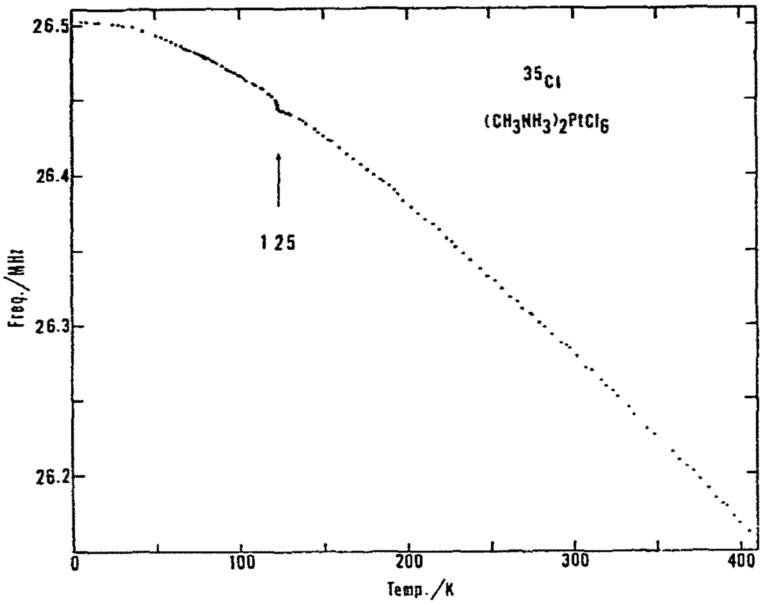


Fig. 19. Temperature dependence of ^{35}Cl NQR frequency in di(methylammonium) hexachloroplatinate(IV), $(CH_3NH_3)_2PtCl_6$ [126].

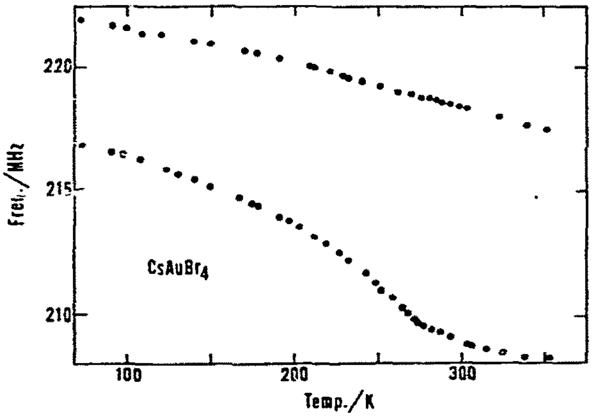
intact. It is an advantage of ^{14}N NQR spectroscopy as contrasted with the case of chlorine or bromine that both the quadrupole coupling constant and the asymmetry parameter can be determined for discussing the structure of low-temperature phases and the nature of phase transitions.

Ikeda et al. [126] determined the temperature variation of ^{35}Cl NQR frequencies in di(methylammonium) hexachloroplatinate(IV) as shown in Fig. 19. An anomaly at 125 K is characterized by a marked change in $d\nu/dT$ rather than in ν, and is accompanied by no change in intensity near the second-order phase transition. The structure of this complex is obtained by a rhombohedral distortion of the cubic potassium hexachloroplatinate(IV) structure with $[PtCl_6]^{2-}$ ions retaining O_h symmetry and the C—N bond axes of methylammonium ions lying on the threefold axis of a coordination octahedron [127]. The fact that a single NQR frequency was observed even below the transition point indicates that the threefold axis is retained in the low-temperature phase as well. The transition has been attributed to the rotation of $[PtCl_6]^{2-}$ ions through a small angle about their respective threefold axes. The present example is instructive in showing that accurate determination of the temperature variation of NQR frequencies at small temperature intervals is required for locating this type of phase transition.

F. MISCELLANEOUS

Sasane et al. [84] observed two frequencies in the NQR spectrum of ^{7} in cesium tetrabromoaurate(III). The result is shown in Fig. 20. A line o high-frequency side shows normal temperature dependence, whereas the frequency of the other line decreases sharply near 273 K, above which t curve is concave upwards. The anomaly is explained by a slight rotation square planar $[AuBr_4]^-$ ions about their respective Br—Au—Br axes. A s temperature behavior of NQR frequencies has also been found for neody tribromide [128] and 1,2-dichloroethane [129, 130].

Hynes et al. [131] observed three resonance lines in the NQR of ^{35}Cl potassium trichlorocuprate(II) as is shown in Fig. 21. The crystal of this plex is monoclinic belonging to the space group $P2_1/c$. Discrete dimeric $[Cu_2Cl_6]^{2-}$, having a center of symmetry exist in the crystal [132]. All dimeric units are equivalent, and each is located at a center of symmetry unit cell. Accordingly, there are three kinds of nonequivalent chlorine at in crystals, i.e. two terminal chlorine atoms, $Cl_{(1)}$ and $Cl_{(2)}$, and a bridgi chlorine atom, $Cl_{(3)}$. A characteristic feature of the temperature variatio resonance frequencies is that they decrease sharply near the liquid heliu temperature and again the slope becomes less steep below liquid nitroge temperature. The trend is particularly marked for the resonance frequen $Cl_{(3)}$. It is noteworthy that the anomaly occurs at a very low temperatu at which the excitation of thermal motion is inconceivable for averaging



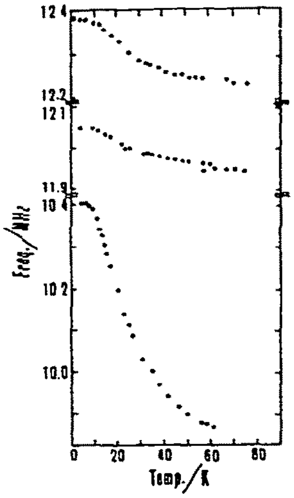


Fig. 20. Temperature dependence of ^{79}Br NQR frequencies in cesium tetrabromoau (III) [84].

Fig. 21. Temperature dependence of ^{35}Cl NQR frequencies in potassium trichlorocuprate(II) [131].

field gradient. The ESR [133—135] and magnetic susceptibility [136] measurements have indicated that unpaired electrons of copper in a discrete dimeric unit undergo pairwise exchange interaction. Hynes et al. [131] explained the anomalous temperature variation of NQR frequencies in terms of the change of population in the singlet and triplet states. From the dependence of NQR on temperature, they evaluated the energy difference between the singlet state and the triplet state as $\Delta E/k$ = 32 K if the ground state is triplet, and 48 K if it is singlet.

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