

# Hydrogen Isotope Effect on the Temperature Dependence of the $^{35}\text{Cl}$ -NQR Frequency in $(\text{NH}_4)_2\text{IrCl}_6$

Yoshio Kume and Tetsuo Asaji<sup>a</sup>

Department of Environmental Policy, College of Environmental Health, Azabu University,  
1-17-71 Fuchinobe, Sagamihara, Kanagawa 229-8501, Japan

<sup>a</sup> Department of Chemistry, College of Humanities and Sciences, Nihon University,  
Sakurajosui, Setagaya-ku, Tokyo 156-8550, Japan

Reprint requests to Prof. Y. K.; Fax: +81 42 769 1973, E-mail: kume@azabu-u.ac.jp

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The  $^{35}\text{Cl}$ -NQR frequencies and spin-lattice relaxation times of  $(\text{NH}_4)_2\text{IrCl}_6$  and  $(\text{ND}_4)_2\text{IrCl}_6$  were measured in the temperature range 4.2 - 300 K. It was confirmed that no phase transition takes place down to 4.2 K. The observed frequency at 4.2 K in  $(\text{ND}_4)_2\text{IrCl}_6$  was higher by 18 kHz than that in the non-deuterated analogue. This discrepancy was attributed to a difference between the lowest rotational states of the ammonium ions in these compounds. The energy separation between the ground state and excited state of rotational motion, in which N-H of the ammonium ion rotates among the three directions slightly apart from the triad axis, was estimated by fitting analysis to be  $31\text{ cm}^{-1}$  and  $93\text{ cm}^{-1}$  for  $(\text{ND}_4)_2\text{IrCl}_6$  and  $(\text{NH}_4)_2\text{IrCl}_6$ , respectively. The activation energy of the reorientation of the ammonium ion among the four directions of the triad axis was estimated to be 6.9 and 7.6  $\text{kJ mol}^{-1}$ , respectively.

**Key words:** Isotope Effect; Tunneling Motion; Chlorine NQR; Ammonium Hexachloroiridate.

## Introduction

Some compounds having the formula  $(\text{NH}_4)_2\text{MCl}_6$  ( $\text{M} = \text{Te}$  [1, 2],  $\text{Se}$  [3, 4],  $\text{Pb}$  [5, 6],  $\text{Pd}$  [7, 8],  $\text{Pt}$  [9, 10]) exhibit so-called deuteration induced phase transitions, in which the deuterated compound undergoes a phase transition but there is no corresponding phase transition in the non-deuterated compound. This phenomenon can be comprehended qualitatively as follows. These compounds crystallize to the cubic antiferroite structure ( $\text{Fm}\bar{3}\text{m}$ ), in which ammonium ions are very loosely hindered at the  $T_d$  symmetry sites [11]. Neutron diffraction measurements at room temperature have revealed that the directions of the potential minimum for ammonium ion's rotation are not on the crystal triad axis directions but on three directions slightly apart from the triad axis direction [12]. At high temperatures, ammonium ions not only rotate between these three directions but also reorient between four triad axis directions, meaning that the high temperature state is in disorder. At low temperatures, the motion of deuterated ammonium

ions is reduced and ammonium ions localize on one of the three minimum directions. This change leads to an order-disorder phase transition. Since the hydrogen atom is very light, the tunnelling motion of non-deuterated ammonium ions inhibits the localization. There is consequently no phase transition in these non-deuterated analogues. The magnitude of tunnel splitting estimated from the transition entropy correlates with the metal-chlorine bond length [6].

Like  $(\text{NH}_4)_2\text{SnCl}_6$ ,  $(\text{ND}_4)_2\text{SnCl}_6$  undergoes no phase transition down to liquid helium temperature [13, 14]. Evidently the very low hindering potential barrier in the crystal permits the rotational tunneling of the deuterated ammonium ion through it. Because the compound is paramagnetic down to 2.16 K [15], strong NQR signals can be expected even at very low temperatures without suffering from saturation.

## Experimental

$(\text{NH}_4)_2\text{IrCl}_6$  (98% purity) from Aldrich Chem. Co was used without further purification. The deuter-

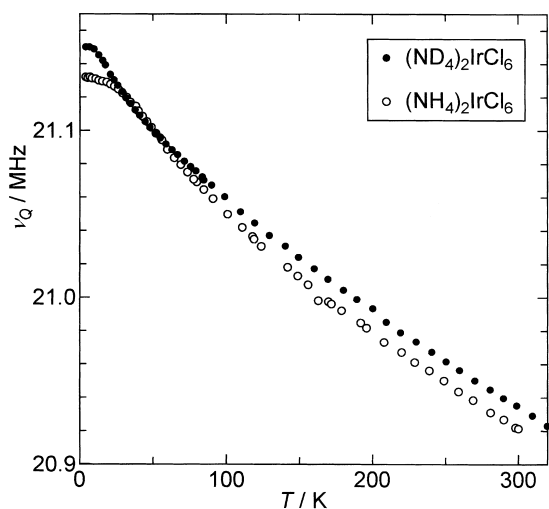


Fig. 1. The temperature dependence of  $^{35}\text{Cl}$  NQR frequencies determined between 4.2 K and ca. 300 K for  $(\text{NH}_4)_2\text{IrCl}_6$  and  $(\text{ND}_4)_2\text{IrCl}_6$ .

ated analogue was prepared by recrystallization of  $(\text{NH}_4)_2\text{IrCl}_6$  from heavy water (> 99.8% atomic D). The dark brown crystal obtained was dried over  $\text{P}_2\text{O}_5$  in a desiccator. The isotopic purity was estimated to be 99% atomic D by use of high-resolution  $^1\text{H}$  NMR measurements.

$^{35}\text{Cl}$  NQR measurement was done with a pulsed spectrometer based on the Matec gated amplifier 515A [16]. The spin-lattice relaxation time was determined by observing the recovery of the signal height of free induction decay after the pulse sequence  $\pi$ - $\tau$ - $\pi/2$ , since no echo signal could be observed using the pulse sequence  $\pi$ - $\tau$ - $\pi/2$ - $\tau'$ - $\pi$ .

## Results

Figure 1 shows the temperature dependences of the  $^{35}\text{Cl}$  nuclear quadrupole resonance frequency,  $\nu_Q$ , for  $(\text{NH}_4)_2\text{IrCl}_6$  (abbreviated to ACIr in the following) and  $(\text{ND}_4)_2\text{IrCl}_6$  (DACIr). In the whole temperature range measured, 4.2 K - 300 K, only one resonance signal, exhibiting a smooth temperature dependence, was observed for both compounds, indicating that no phase transition occurs in the temperature range. The second derivatives with temperature of both compounds are positive above 50 K. This feature has been found commonly in ammonium hexahalometalates(IV) [8, 14]. The difference of the NQR frequencies between the two compounds varies with tem-

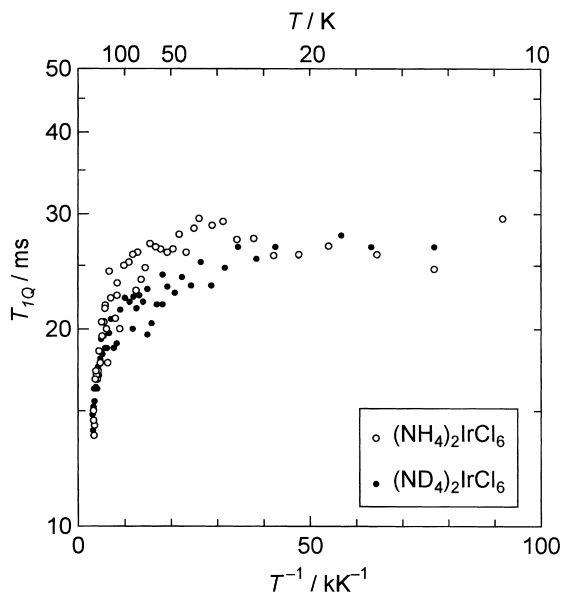


Fig. 2. The temperature dependence of  $^{35}\text{Cl}$  NQR spin-lattice relaxation times for  $(\text{NH}_4)_2\text{IrCl}_6$  and  $(\text{ND}_4)_2\text{IrCl}_6$ .

perature, especially at low temperatures. The NQR frequency of DACIr is higher by 18 kHz than that of ACIr at liquid He temperature.

The absence of an echo signal indicates that  $T_{2Q}^*$  is almost equal to  $T_{2Q}$ . The spin-lattice relaxation times,  $T_{1Q}$ , for both compounds are fairly short compared with those of the similar compounds  $(\text{NH}_4)_2\text{MCl}_6$  ( $\text{M} = \text{Pd}, \text{Pt}, \text{Pb}, \text{Se}$ ) and vary scarcely with the temperature. These reflect the existence of a magnetic hyper-fine interaction between the chlorine nuclei and the paramagnetic iridium ion [17]. Figure 2 shows the temperature dependences of the spin-lattice relaxation time for both compounds.

## Discussion

The most remarkable characteristic in the temperature dependence of the nuclear quadrupole frequency is a quite large disagreement of the frequencies at 4.2 K in ACIr and DACIr in spite of the same crystal structure. Since motions of a resonant nucleus causes the frequency to shift with temperature according to Bayer's theory, the NQR frequency should be essentially invariable at very low temperatures. The frequencies of these isotopomers at these low temperatures should be close to each other, because the difference in isotopomers is expected to be due only to the magnitude of the motion in the crystals.

The disagreement observed strongly suggests that the distributions of the hydrogen atoms in the crystals are different at this temperature. A similar temperature behaviour has been reported for ammonium hexachlorostannate(IV) [14]. It was explained as deviation from Bayer's theory depending on the strain of the potential around the stannate ion modified by the motion of the ammonium ions.

Another characteristic is the onset of the decrease of the NQR frequency at fairly low temperature in the deuterated compound, suggesting the occurrence of motional changing at low temperatures. In this paper, we will attempt to analyze phenomenologically the unusual temperature dependence. Our model, in which the librational ground state of the ammonium ion splits into two states giving different contributions to the electric field gradient at the chlorine nucleus, is essentially equal to the two-state model proposed by Negita et al. [18, 19]. The fitting function consists of two terms, Bayer's term and the term of the two-state model.

Bayer's term [20] can be written for the chlorines in the octahedral complex ion as

$$\nu_B(T) = \nu_0 \left[ 1 - \frac{3\hbar}{2I\omega} \coth\left(\frac{\hbar\omega}{2kT}\right) \right], \quad (1)$$

where  $\nu_0$  is the NQR frequency in a fictitious vibrationless state.  $I$  and  $\omega$  denote the moment of inertia and the librational angular frequency of  $[\text{IrCl}_6]^{2-}$ , respectively. The moment of inertia of the hexachloroiridate ion was calculated as  $1.273 \cdot 10^{-44} \text{ kg m}^2$ , using an Ir-Cl bond length of 0.2325 nm estimated from a neutron diffraction measurement [21]. The deviation,  $\Delta\nu_t(T)$ , from Bayer's theory of the two states averaging effect is expressed as

$$\Delta\nu_t(T) = \frac{\Delta\nu g \exp(-E_t/RT)}{1 + g \exp(-E_t/RT)}, \quad (2)$$

where  $\Delta\nu$  denotes the difference of contributions to the NQR frequency from the ground state and the first excited state,  $g$  and  $E_t$  denote the degeneracy of the excited state and magnitude of splitting, respectively. The fitting function was derived from a summation of the two terms:

$$\nu_Q(T) = \nu_B(T) + \Delta\nu_t(T). \quad (3)$$

Table 1. The results of non-linear least square fitting calculation.

	$\nu$ MHz	$\omega$ 2 $\pi$ THz	$\Delta\nu$ kHz	$g$	$E_t$ Jmol $^{-1}$	$\Delta\nu_t$ MHz	$\alpha$	$E_a$ kJmol $^{-1}$
$(\text{ND}_4)_2\text{IrCl}_6$	21.176	1.59	-83.8	1.80	374	2.2	8.1	6.9
$(\text{NH}_4)_2\text{IrCl}_6$	21.157	1.57	-55.5	4.95	1107	0.080	0.13	7.6

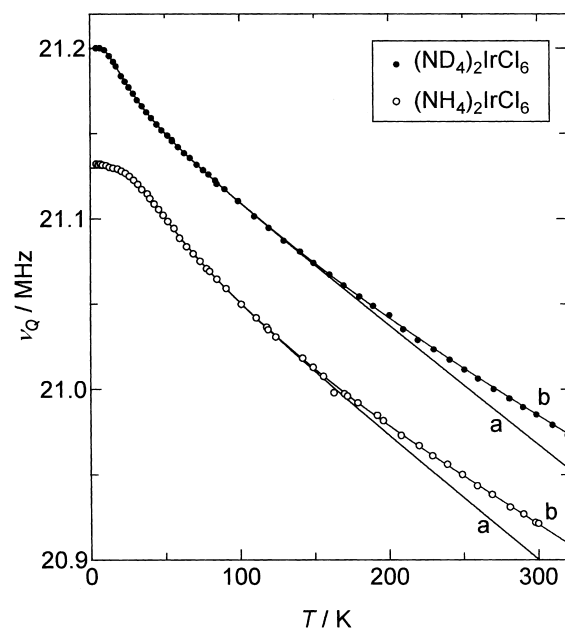


Fig. 3. Solid curves a and b were calculated with the fitting parameters in the Table 1 using (3) and (5), respectively. The curves and data points for  $(\text{ND}_4)_2\text{IrCl}_6$  are shifted upward by 0.05 MHz for the sake of clarity.

This equation contains five fitting parameters:  $\nu_0$ ,  $\omega$ ,  $\Delta\nu$ ,  $g$ ,  $E_t$ . Non-linear least squares fitting calculations were done with 30 data points below 100 K for DACIr and 28 data points below 125 K for ACIr.

The fitting results are shown in Table 1. Figure 3 shows the fitted curves. The librational frequency of  $[\text{IrCl}_6]^{2-}$  in the deuterated compound is almost equal to that of the non-deuterated compound. 1.59 THz corresponds to  $53.1 \text{ cm}^{-1}$ , which agrees well with the librational frequency of  $[\text{IrCl}_6]^{2-}$  of  $59 \text{ cm}^{-1}$  in  $\text{K}_2\text{IrCl}_6$  [22], indicating that the potentials around the  $[\text{IrCl}_6]^{2-}$  in these compounds are almost equal.

The value obtained for the splitting,  $E_t = 374 \text{ J mol}^{-1}$  (corresponding to  $31.3 \text{ cm}^{-1}$ ), is too large to be attributed to the splitting due to the reorientational tunneling of the ammonium ion between the four directions of the triad axis. The tunneling frequency of the reorientation in  $(\text{ND}_4)_2\text{SnCl}_6$

has been estimated from  $^2\text{H}$ -NMR measurement to be 7.5 MHz ( $2.5 \cdot 10^{-4} \text{ cm}^{-1}$ ) at 4.2 K [23]. Recently it was reported that the ammonium ions in  $(\text{ND}_4)_2\text{MX}_6$  type compounds rotate between three directions,  $[1\ 1\ 1 - \xi]$ ,  $[1\ 1 - \xi\ 1]$ ,  $[1 - \xi\ 1\ 1]$  around the crystal triad axis at high temperatures [12]. If the potential barriers between the three directions are low enough for the deuterated ammonium ion to tunnel frequently, the librational ground state splits to a tunneling ground state and excited states with fairly high energy. It was also reported that tunneling splitting for some  $(\text{ND}_4)_2\text{MCl}_6$  type compounds estimated from transition entropies of the deuteration induced phase transitions correlates with the M-Cl bond length [6]. The estimated splittings are distributed in the range of 20 - 65  $\text{cm}^{-1}$ , which agrees well with the obtained  $E_t$  of 31.3  $\text{cm}^{-1}$ . Very recent heat capacity measurement for DACIr revealed a Schottky anomaly around 20 K corresponding to an energy splitting of 29  $\text{cm}^{-1}$  [24]. Ingman et al. concluded from the observed shallow  $T_1$  minimum of  $^2\text{H}$ -NMR at about 15 K in  $(\text{ND}_4)_2\text{SnCl}_6$  that the ammonium ion's rotation between the three directions around the triad axis is not in fact a tunneling motion but a classical jumping over the hindered potential barrier of 18 - 26 K (12.5 - 18  $\text{cm}^{-1}$ ) in height [25]. This means that the ammonium ion in  $(\text{ND}_4)_2\text{SnCl}_6$  is considerably excited to the rotational state at 18 - 26 K. It is expected that the first excited state of the ammonium ion in DACIr is also the rotational state around the triad axis, since  $E_t$  is of the same order of magnitude as the barrier in  $(\text{ND}_4)_2\text{SnCl}_6$ . The difference in the hydrogen distribution between the ground state and the first excited state causes  $\Delta\nu$ .  $\Delta\nu$  is greater in DACIr than in ACIr. This can be attributed to the difference of the hydrogen distribution in the ground state since the hydrogen distribution in the rotational state is expected to be almost equal in DACIr and ACIr. Hydrogen is delocalized between the three directions around the triad axis due to the tunneling effect in the ground state of ACIr. Deuterium in DACIr, on the other hand, is fairly localized in a shallow potential minimum of the three equilibrium directions.

The second derivatives of the frequency with temperature are positive for both compounds even at higher temperatures (above ca. 120 K). This can't be attributed to the ammonium ion's rotational motion mentioned above. Positive second derivatives, which are commonly observed in ammonium hexahalometallates(IV) [26, 16] have been explained by either an

effect of the ammonium ion's reorientational motion [27] or non-harmonicity of the librational potential of the octahedral complex ions, which reflects lattice instability [19]. In the latter model the librational frequency of the complex ion increasing with temperature causes the positive second derivative. The model expresses more rigorously the idea of Bayer's theory, and the former model treats the ammonium ion's reorientation as an additional characteristic which is not expressed in Bayer's theory. We attempted to apply the latter model with the proposed temperature dependence of the librational frequency,  $\omega = \sqrt{a + bT}$  [19, 28], in the whole temperature range, but no good convergence was obtained. We also tried to combine this model with the two-state model mentioned above. However, the fitting calculation did not result in meaningful parameters either.

Since the ammonium ion in the crystal occupies a site with low hindering potential, the N-H bond direction reorients between four triad axis directions at high temperatures. The effect of the reorientation on the NQR frequency has been formulated [18] as

$$\Delta\nu_{\text{reo}} = \nu_r + \frac{\nu_t - \nu_r}{1 + \tau_0\tau_t^{-1} \exp(E_a/RT)}, \quad (4)$$

where  $\nu_r$  is the amount of contribution to the NQR frequency from ammonium ions staying in their equilibrium orientation and  $\nu_t$  is that from ammonium ions moving between the equilibrium orientations.  $\tau_0$  and  $\tau_t$  are the average residence time at infinite temperature and the time for a single reorientation, respectively.  $E_a$  is the activation energy for the reorientation. If it is assumed that  $\nu_t$  is independent of temperature [18] and  $\nu_r$  is contained in Bayer's term, the temperature dependent part of  $\Delta\nu_{\text{reo}}$  due to the ammonium reorientation,  $\Delta\nu'_{\text{reo}}$ , is expressed using the fitting parameters  $\Delta\nu_{\text{rt}} = \nu_t - \nu_r$ ,  $\alpha = \tau_0/\tau_t$  and  $E_a$  as

$$\Delta\nu'_{\text{reo}}(T) = \frac{\Delta\nu_{\text{rt}}}{1 + \alpha \exp(E_a/RT)}. \quad (5)$$

The deviation of the observed frequencies from the curve a in Fig. 3 was least-squares fitted by use of (5) for 22 and 18 data points of DACIr and ACIr, respectively. Good agreement was obtained for the fitting parameters listed in Table 1, as shown by line b in Figure 3. The values of  $\Delta\nu_{\text{rt}}$  and  $\alpha$  obtained in DACIr and ACIr are very different from each other. The fitted

data in the high temperature range are highly dependent on the base line which was extrapolated to the high temperature region. Nevertheless,  $E_a$  obtained for each compound agrees well with the activation energy ( $5.9 \text{ kJ mol}^{-1}$ ) of the reorientational motion determined from  $^2\text{H}$ -NMR spin-lattice relaxation measurement in  $(\text{ND}_4)_2\text{SnCl}_6$  [25].

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