Chlorine Nuclear Quadrupole Relaxation Studies on Ionic Dynamics and Phase Transition in NH\textsubscript{4}AuCl\textsubscript{4}\n
Atsushi Ishikawa, Tetsuo Asaji, and Daiyu Nakamura
Department of Chemistry, Faculty of Science, Nagoya University, Nagoya 464-01, Japan
Ryuichi Ikeda
Institute for Molecular Science, Myodaiji, Okazaki 444, Japan
Z. Naturforsch. 45a, 467–471 (1990); received August 25, 1989

Chlorine NQR frequencies, and NQR spin-lattice and spin-spin relaxation times (T\textsubscript{1Q} and T\textsubscript{2Q}) were measured for NH\textsubscript{4}AuCl\textsubscript{4} crystals at various temperatures between 4.2 and 337 K. Each of the two resonance lines observed at room temperature is split into a doublet below T\textsubscript{c} = 29 K, indicating a phase transition. A rapid decrease of T\textsubscript{1Q} above ca. 290 K is attributable to 90° reorientational jumps of the complex anion about its pseudo C\textsubscript{2v} axis. An activation energy of 80 kJ mol\textsuperscript{-1} was obtained for this motion. \textsuperscript{35}Cl T\textsubscript{1Q} exhibits a minimum at T\textsubscript{c}. The T\textsubscript{1Q} isotope ratio T\textsubscript{1Q}(\textsuperscript{35}Cl)/T\textsubscript{1Q}(\textsuperscript{37}Cl) becomes 1.6 and 1.0 on the high- and low-temperature sides of this minimum, respectively. These results were explained by fluctuations of the electric field gradient produced at the chlorine nuclei by the reorientational jumps of the NH\textsubscript{4}\textsuperscript{+} ions. The motion of the cations is much faster and much slower than the resonance frequencies on the high- and low-temperature sides, respectively. This suggests that the phase transition is of the order-disorder type relating to the orientation of the NH\textsubscript{4}\textsuperscript{+} ion.

**Introduction**

Recently, the dynamics of pyridinium ions (pyH\textsuperscript{+}) in crystals have been studied in (pyH)\textsubscript{2}MCl\textsubscript{6} (M: Sn, Te, Pb), (pyH)AuCl\textsubscript{4}, and (pyH)ICl\textsubscript{4} by measuring chlorine NQR and \textsuperscript{1}H NMR relaxation times [1–6]. It has been shown that reorientation of the cations about the pseudohexad axis causes fluctuations of the electric field gradient (EFG) at nearby chlorine nuclei and becomes a dominant mechanism of spin-lattice relaxation of the chlorine nuclei. The experimental results were explained by reorientational jumps of the cations with a finite electric dipole moment, taking place among nonequivalent potential wells. Also NH\textsubscript{4}\textsuperscript{+} cations, although having a higher symmetry than pyH\textsuperscript{+}, can be expected to produce fluctuations of the EFG at the resonant chlorine nuclei in the dynamically complex, disordered N\textsubscript{4} cations having been observed in many ammonium compounds [7]. However, owing to its small size and highly symmetrical charge distribution, the hindrance barrier for reorientation is expected to be lower for NH\textsubscript{4}\textsuperscript{+} than for pyH\textsuperscript{+} [2, 5, 8, 9], suggesting that relaxation associated with this process becomes effective at lower temperatures than for pyH\textsuperscript{+}.

\textsuperscript{35}Cl NQR frequencies in NH\textsubscript{4}AuCl\textsubscript{4} crystals have been reported at temperatures above 77 K [10], where the NH\textsubscript{4}\textsuperscript{+} reorientation is so rapid that it cannot become an effective relaxation mechanism. In this work, measurements have been carried out at lower temperatures where the NH\textsubscript{4}\textsuperscript{+} motions are slower and expected to contribute to the relaxation.

**Experimental**

The chlorine NQR spin-lattice relaxation time T\textsubscript{1Q} and spin-spin relaxation time T\textsubscript{2Q} were measured with a homemade pulsed NQR spectrometer described elsewhere [11]. Values of T\textsubscript{1Q} and T\textsubscript{2Q} were determined from the height of echo signals observed after the pulse sequences, π/2-τ-π/2-τ-π and π/2-τ-π, respectively, where the echo height was observed at various interpulse spacing times τ changed up to about twice of each relaxation time, while τ\textsubscript{e} was set constant (100 μs) throughout the measurements. Exponential decay of the echo amplitude against τ was observed in the whole temperature range studied for T\textsubscript{1Q} and T\textsubscript{2Q}.

0932-0784 / 90 / 0300-0467 S 01.30/0. – Please order a reprint rather than making your own copy
For 4.2–50 K, a homemade cryostat with liquid helium [12] was employed. Temperatures between 50 and 77 K were obtained by pumping off the ambient gas above liquid nitrogen and regulating the gas pressure with a homemade manostat. Above 77 K, another liquid nitrogen cryostat [11] was employed. The sample temperature was controlled within ±0.5 K and determined by a gold (0.07% Fe) vs. chromel thermocouple between 4.2 and 77 K, and a copper vs. constantan thermocouple above 77 K. The determined temperatures are estimated to be accurate within ±1 K.

\( \text{NH}_4\text{AuCl}_4 \cdot \frac{1}{3} \text{H}_2\text{O} \) crystals were prepared by the method described in [10, 13]. The water of crystallization was completely removed by keeping the sample in a vacuum at ca. 100 °C for 10 h. Powdered \( \text{NH}_4\text{AuCl}_4 \) thus obtained was identified by observing the \( ^{35}\text{Cl} \) NQR signals at the frequencies reported [10].

**Results**

**Temperature Dependence of Chlorine NQR Frequencies**

The observed temperature dependence of the \( ^{35}\text{Cl} \) NQR frequencies of \( \text{NH}_4\text{AuCl}_4 \) is plotted in Fig. 1 and listed in Table 1. The frequencies observed above 77 K have equal intensity and are in good agreement with those reported by Sasane et al. [10]. They are hereafter called as \( v_H \) and \( v_L \) (high- and low-frequency).

![Fig. 1. Temperature dependence of \( ^{35}\text{Cl} \) NQR frequencies, \( v_H \) and \( v_L \) above the phase transition temperature, \( T_c = 29 \) K, and \( v_{H1}, v_{H2}, v_{L1}, \) and \( v_{L2} \) below \( T_c \).](image)

![Fig. 2. Frequency dependences of the heights of \( ^{35}\text{Cl} \) NQR echo signals corresponding to \( v_H \) (right) and \( v_L \) (left) observed near \( T_c \).](image)

<table>
<thead>
<tr>
<th>( T/K )</th>
<th>( v/\text{MHz} )</th>
<th>( T_{1Q}/\text{ms} )</th>
<th>( T_{2Q}/\text{ms} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2</td>
<td>28.44</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4.2</td>
<td>27.99</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4.2</td>
<td>27.70</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4.2</td>
<td>26.98</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>22</td>
<td>28.01</td>
<td>640</td>
<td>-</td>
</tr>
<tr>
<td>22</td>
<td>27.70</td>
<td>360</td>
<td>0.37</td>
</tr>
<tr>
<td>22</td>
<td>26.99</td>
<td>370</td>
<td>0.37</td>
</tr>
<tr>
<td>*22</td>
<td>21.29</td>
<td>400</td>
<td>-</td>
</tr>
<tr>
<td>37</td>
<td>28.20</td>
<td>100</td>
<td>0.35</td>
</tr>
<tr>
<td>41</td>
<td>27.33</td>
<td>21</td>
<td>0.31</td>
</tr>
<tr>
<td>*41</td>
<td>21.55</td>
<td>38</td>
<td>-</td>
</tr>
<tr>
<td>129</td>
<td>28.08</td>
<td>170</td>
<td>0.49</td>
</tr>
<tr>
<td>129</td>
<td>27.27</td>
<td>110</td>
<td>0.32</td>
</tr>
<tr>
<td>332</td>
<td>27.72</td>
<td>0.58</td>
<td>0.22</td>
</tr>
<tr>
<td>332</td>
<td>26.90</td>
<td>0.60</td>
<td>0.20</td>
</tr>
</tbody>
</table>

* The data for \( ^{37}\text{Cl} \).

With decreasing temperature, at ca. 29 K the lines split into two lines each, indicating a phase transition. To determine \( T_c \) accurately, frequency dependences of the echo height for \( v_H \) and \( v_L \) near \( T_c \) were measured. The curves obtained at several temperatures are shown in Figure 2. With decreasing temperature, the peaks of both \( v_H \) and \( v_L \) suddenly broadened at 29 K, and below 29 K two peaks with equal height appeared. From these data we determined \( T_c = 29 \) K. Below \( T_c \), \( v_H \) and \( v_L \) were almost symmetrically split into \( v_{H1} \) and \( v_{H2} \), and \( v_{L1} \) and \( v_{L2} \), respectively. \( v_{H1} - v_{H2} \) and \( v_{L1} - v_{L2} \) became almost temperature independent below ca. 15 K and gave ca. 450 kHz and ca. 700 kHz, respectively.
Figure 3 shows the temperature dependences of $\text{T}_{1Q}$ and $\text{T}_{2Q}$ for $^{35}\text{Cl}$ nuclei in NH$_4$AuCl$_4$ crystals observed between 14 and 337 K. Numerical values are given in Table 1.

With increasing the temperature from 15 K to $T_c$, $^{35}\text{Cl} \text{T}_{1Q}$ for $v_{H2}$, $v_{L1}$, and $v_{L2}$ decreased rapidly and reached a minimum at $T_c$. Above $T_c$, $\text{T}_{1Q}$ of both $v_H$ and $v_L$ increased almost linearly with $T^{-1}$ and showed a $\text{T}_{1Q}$ maximum around 80 and 120 K for $v_H$ and $v_L$, respectively. With further increasing temperature, $\text{T}_{1Q}$ for both lines became the same above ca. 290 K and decreased rapidly down to ca. 400 $\mu$s at 337 K. Above this temperature, no $\text{T}_{1Q}$ could be determined because the echo signals weakened.

$^{37}\text{Cl} \text{T}_{1Q}$ was determined in the range 19–77 K for $v_{L2}$ or $v_L$. They showed analogous temperature dependences to those of the corresponding $^{35}\text{Cl}$ line. The $\text{T}_{1Q}$ isotope ratio

$$R = \frac{\text{T}_{1Q}(^{37}\text{Cl})}{\text{T}_{1Q}(^{35}\text{Cl})}$$

became 1.0 ± 0.2 and 1.6 ± 0.2 for the temperature ranges 19–25 and 31–77 K, respectively.

Discussion

High-Temperature Range ($T > 290$ K)

Above ca. 290 K, $\log \text{T}_{1Q}$ depended linearly on $T^{-1}$ for both $v_H$ and $v_L$. A quite similar $^{35}\text{Cl} \text{T}_{1Q}$ behavior was observed for RbAuCl$_4$ and CsAuCl$_4$ [14], whose crystal structures are isomorphous with that of the present complex around room temperature [15–17]. The temperature dependence of $\text{T}_{1Q}$ in the rubidium and cesium salts has been explained by sudden and infrequent 90° jumps of the square planar [AuCl$_4$]$^-$ ions about the pseudo $C_4$ axis. Applying the same analysis to the present $\text{T}_{1Q}$ data, we determined the activation energy of the in-plane 90° reorientational jumps of [AuCl$_4$]$^-$ ions as 80 ± 5 kJ mol$^{-1}$ above 290 K. This activation energy is slightly larger than that of RbAuCl$_4$ and much larger than that of CsAuCl$_4$, and may be due to the effect of crystal packing.

Intermediate-Temperature Range ($T_c < T < 100$ K)

With decreasing temperature, $\text{T}_{1Q}$ for both $v_H$ and $v_L$ decreased over a wide temperature range, namely, from ca. 80 K to $T_c$ for $v_H$, and from ca. 120 K to $T_c$ for $v_L$. This temperature dependence is unusual because in general the relaxation mechanism mainly contributing to $\text{T}_{1Q}$ in this temperature range is librations of the complex anions which usually reduce $\text{T}_{1Q}$ with increasing temperature. One could consider softening of some librational modes in crystals as one of the causes for this anomalous $\text{T}_{1Q}$ behavior. This, however, is no possible explanation for reason given in the following section.

The most probable mechanism we can propose is the motion of the counter cations, which fluctuate the EFG produced at the chlorine nuclei (cf. the Introduction).

$\text{T}_{1Q}$ of chlorine nuclei with spin $I = 3/2$, as determined by the motion of the counter ions, can be ex-
pressed as [18]

\[ T_{1Q}^{-1} = \frac{1}{12} \left( e^2 q Q / h \right)^2 \left( q'/q \right)^2 \left\{ \gamma_c / \left( 1 + \omega_Q \tau_c \right) \right\}. \]

(2)

Here, \( e^2 q Q / h \), \( q'/q \), \( \omega_Q \), and \( \tau_c \) denote the quadrupole coupling constant, the EFG fluctuation fraction related to the matrix elements of the EFG tensor, the angular NQR frequency, and the correlation time of the cationic motion, respectively. In (2), \( T_{1Q}^{-1} \) is proportional to \( Q^2 \) and \( \tau_c \) under the condition of \( \omega_Q \tau_c^2 \ll 1 \). In this case

\[ R = \frac{Q(35Cl)}{Q(37Cl)} = 1.61. \]

(3)

This agrees very well with the experimental data observed between 77 and 31 K given by

\[ T_{1Q}(35Cl \gamma_c)/(T_{1Q}(35Cl \gamma_c)) = 1.6 \pm 0.2. \]

(4)

Assuming the Arrhenius relationship for \( \tau_c \), we can write \( T_{1Q} \) as

\[ T_{1Q} \propto \exp \left( -E_a/R T \right), \]

(5)

where \( E_a \) is the activation energy for the cationic motion. By fitting (5) to the observed temperature dependence of \( T_{1Q} \) for \( \gamma_H \) and \( \gamma_L \), \( E_a \) values of 0.63 and 0.83 kJ mol\(^{-1}\), respectively, are obtained. These activation energies are assumed to be the same because they are believed to originate from the same cationic motion. In the derivation of these activation energies, no correction was made for the contribution to \( T_{1Q} \) from lattice vibrations, which increases with increasing temperature. Since \( T_{1Q}(\gamma_H) \), which is longer than \( T_{1Q}(\gamma_L) \), is thought to be affected by lattice vibrations more strongly than \( T_{1Q}(\gamma_L) \), the smaller \( E_a \) for \( \gamma_H \) is understandable in view of this lattice effect.

Some kind of reorientation of the \( \text{NH}_4^+ \) ions is acceptable as the cationic motion responsible for this \( T_{1Q} \) decrease. The activation energy of less than 1.0 kJ mol\(^{-1}\) is small as compared with those reported for analogous compounds, such as \((\text{NH}_4)_2\text{SnCl}_6\), \((\text{NH}_4)_2\text{PdCl}_6\), and \((\text{NH}_4)_2\text{PtCl}_6\), having \( E_a \) of 5.0 [19], 1.75 [20], and 1.6 kJ mol\(^{-1}\) [20], respectively, for the \( \text{NH}_4^+ \) reorientation. This comparison suggests the possibility that the jump angle of the expected cationic reorientation is smaller than 120° or 90°.

**Low Temperature Range \((T < T_c)\)**

Below \( T_c \), the \( T_{1Q} \) isotope ratio \( R \) for \( \gamma_L \) became 1.0 \( \pm \) 0.2 in the range 19–25 K. This can also be explained by the above cationic motion. By assuming \( \omega_Q \tau_c^2 \ll 1 \) in (2) for the present temperature range, \( T_{1Q} \) becomes proportional to \( \tau_c \) but independent of \( Q \). This \( T_{1Q} \) gives \( R = 1.0 \), in good agreement with the observation. Accordingly, the relaxation process below \( T_c \) is attributable to the classical reorientation of \( \text{NH}_4^+ \) ions with a slower rate than the NQR frequencies.

In this temperature range it is also possible that quantum mechanical tunneling of the \( \text{NH}_4^+ \) ion contributes to \( T_{1Q} \) through magnetic dipolar coupling between chlorine nuclei and protons. It has been reported that a \( ^{35}\text{Cl} \) \( T_{1Q} \) minimum observed in \((\text{NH}_4)_2\text{SnCl}_6 \) at ca. 55 K can be explained by this mechanism [21]. In the present complex, however, the \( T_{1Q} \) minimum was observed just at \( T_c \), and \( R = 1.0 \) was observed below \( T_c \). However, \( R \) usually differs from 1.0 for \( T_{1Q} \) governed by the tunneling assisted mechanism. For these reasons, the main relaxation mechanism in this temperature range is attributable to the fluctuation of chlorine EFG caused by the \( \text{NH}_4^+ \) reorientation in the neighborhood of \( T_c \).

**Mechanism of Phase Transition**

In the present complex, the \( R \) values were determined as 1.6 and 1.0 on the high- and low-temperature sides of \( T_c \), respectively. These values cannot be explained by attributing the relaxation mechanism near \( T_c \) to the softening of the lattice vibrations which is expected to give \( R = 1.6 \) if it works as the main process of the relaxation [11, 22].

In the foregoing analysis of \( T_{1Q} \), the classical reorientation of \( \text{NH}_4^+ \) ions has been accepted as the origin of relaxation where the \( \text{NH}_4^+ \) ions are assumed to reorient much more rapidly and slowly than \( \omega_Q \) in the high- and low-temperature phases, respectively. From this cationic motion around \( T_c \), we can propose a model of order-disorder type phase transition as for the orientation of the \( \text{NH}_4^+ \) ion in the present complex. The splittings of \( \gamma_H \) and \( \gamma_L \) observed at \( T_c \) and the gradual shift of the split lines with temperature below \( T_c \) seem to be attributable to a small deformation of the crystalline lattice occurring at the phase transition. Probably, the order-disorder of the \( \text{NH}_4^+ \) orientations and the lattice deformation take place correlatively at \( T_c \).