# Molecular Motions in Sodium Tetrachloroaurate Dihydrate as Studied by the Proton and Chlorine Nuclear Relaxation Times

Kenshô Sagisawa, Hideko Kiriyama,* and Ryôiti Kiriyama

*The Institute of Scientific and Industrial Research, Osaka University, Yamadakami, Suita 565*

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The $^{1}H$ and $^{35}Cl$ relaxation times in $NaAuCl_4 \cdot 2H_2O$ have been measured at temperatures between 79 and 350 K. The $^{1}H$ $T_1$ data revealed that the water molecule of crystallization reorients about its $C_2$ axis with an activation energy of 26 kJ mol$^{-1}$. The $^{35}Cl$ $T_1$ values of the four NQR absorptions indicated that the reorientation of the water molecule makes no important contribution to the chlorine $T_1$, in spite of the hydrogen bonds between them. A brief analysis of the $^{35}Cl$ $T_1$ led to a frequency of 58 cm$^{-1}$ for the torsional vibration of the $AuCl_4^-$ ion.

It has been reported that vibrational and reorientational motions of a molecule containing resonant quadrupolar nuclei produce their nuclear relaxation. However, the relaxation resulting from random motions of atoms near the relaxing nucleus has received less attention. Woessner and Gutowsky suggested that the $CH_3$ reorientation in $(CH_3)_2CCl_2$ is responsible for not only the proton $T_1$ but also the chlorine $T_1$.[1] They estimated the chlorine $T_1$ by assuming that the electric field gradient at the chlorine nucleus fluctuates while the $CH_3$ reorientation is actually taking place, but their calculated value did not agree with the observed one even in order of magnitude.

Recently we measured $T_1$ of both the proton and chlorine nuclei in $\alpha$-$NH_4HgCl_3$, and showed that the motion of the ammonium ion affects the chlorine $T_1$ as well as the proton $T_1$.[2] In $\alpha$-$NH_4HgCl_3$ the ammonium ion reorients about its $C_2$ and $C_3$ axes, and flips by 90° about its $S_4$ axis. Obviously the former, $C_2$ and $C_3$ reorientations, do not change the orientation of the ammonium ion, whereas the latter, $S_4$ flip, does change it. In the preceding paper, we therefore proposed that only the flip mode should affect the chlorine $T_1$. In order to substantiate this proposal, our study was extended to $NaAuCl_4 \cdot 2H_2O$, in which one of the chlorine atoms is probably hydrogen-bonded to water molecules, whereas the other three do not participate in any hydrogen bonds. The comparison of these chlorine $T_1$ values will enable us to examine the influence of the reorientation of the water molecules on the chlorine $T_1$.

## Experimental

A variable frequency pulsed spectrometer (Bruker, B-KR-322s) was employed to measure the $^{1}H$ and $^{35}Cl$ relaxation times. The spin-lattice relaxation time, $T_1$, was obtained by use of a 180°-$\tau$-90° pulse sequence for $^{1}H$, and a 90°-$\tau$-90° sequence for $^{35}Cl$. The $^{35}Cl$ spin phase-memory time, $T_2$, was measured by a 90°-$\tau$-180° method, and the inverse line width parameter, $T_2^*$, was determined from the free induction decay following a 90° pulse. The $^{35}Cl$ signal after the r.f. pulses was often time-averaged because of its small signal to noise ratio. The temperature of the specimen was varied from 79 to 350 K by using liquid nitrogen or Dry Ice, and measured by means of a copper-constantan thermocouple with an accuracy of ±0.3 K. Polycrystalline $NaAuCl_4 \cdot 2H_2O$ was prepared from an equimolar solution of NaCl and $HAuCl_4 \cdot 4H_2O$, and identified by use of an X-ray diffractometer.

## Results and Discussion

The orthorhombic crystal of $NaAuCl_4 \cdot 2H_2O$ contains one kind of planar complex ion, $AuCl_4^-$, the four chlorine atoms of which are crystallographically nonequivalent to one another.[3] The crystal structure shown in Fig. 1 suggests that only one of these four, Cl(1) atom, is hydrogen-bonded to four oxygen atoms; the distances between Cl(1) and the oxygen atoms (3.36 and 3.42 Å) are shorter than the van der Waals contact (4.0 Å). The lone-pair orbitals of the oxygen atom are probably directed to sodium atoms. The $^{35}Cl$ nuclear quadrupole resonance (NQR) gave four absorption lines corresponding to the four nonequivalent chlorine atoms, as listed in Table 1. Fryer and Smith and Sasane *et al.* have studied the temperature dependence of the resonance frequency, and suggested that the positive temperature coefficient of the lowest frequency line arises from the hydrogen bonds of the Cl(1) atom.[4,5]

In order to elucidate the orientation and motion of the water molecules of crystallization, the $^{1}H$ $T_1$ was measured at the resonance frequencies of 20 and 35 MHz. A plot of log $T_1$ *vs.* inverse temperature exhibited a minimum (0.44 s at 308 K for 20 MHz) as

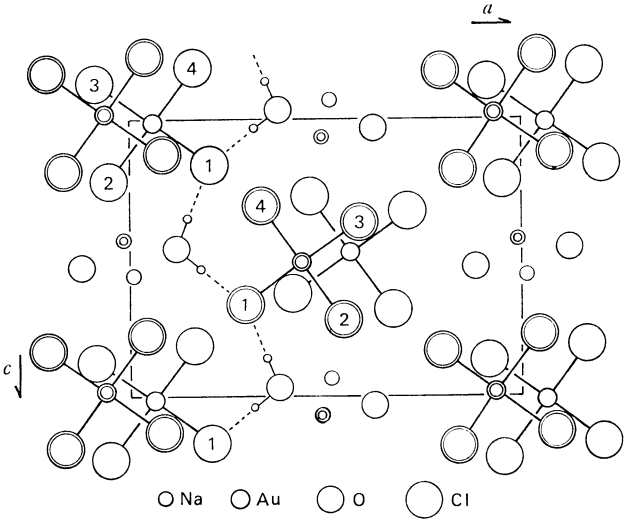


Fig. 1. The crystal structure of $NaAuCl_4 \cdot 2H_2O$ projected along the b axis. The tetrachloroaurate and sodium ions locate on the mirror plane at $y=1/4$ (single circle) or $y=3/4$ (double circle), while the oxygen atoms locate at $y \approx 0$ and $y \approx 0.5$.

Table 1. $^{35}Cl$ NQR frequencies and relaxation times in $NaAuCl_4 \cdot 2H_2O$

| $T$/K | | Frequency/MHz | $T_1$/s | $T_2$/μs | $T_2^*$/μs |
|---|---|---|---|---|---|
| 79 | $\nu_1$ | 25.353 | 1.86 | 400 | 61 |
| | $\nu_2$ | 28.001 | 0.94 | 930 | 79 |
| | $\nu_3$ | 28.866 | 1.20 | 970 | 150 |
| | $\nu_4$ | 29.467 | 0.56 | 850 | 76 |
| 297 | $\nu_1$ | 25.702 | 0.065 | 470 | 150 |
| | $\nu_2$ | 27.376 | 0.040 | 870 | 190 |
| | $\nu_3$ | 28.345 | 0.049 | 820 | 260 |
| | $\nu_4$ | 28.737 | 0.034 | 820 | 170 |

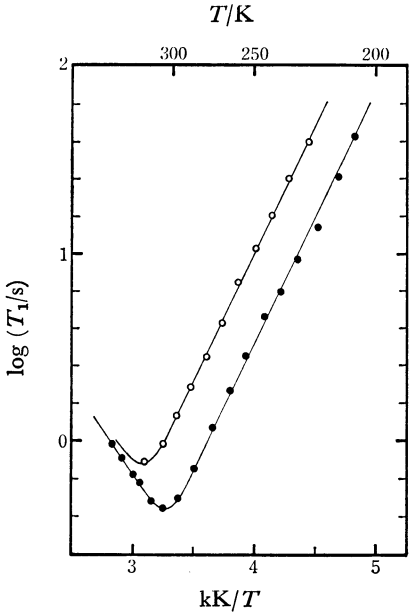


Fig. 2. The temperature dependence of $^1H$ $T_1$ in $NaAuCl_4 \cdot 2H_2O$.
●: 20 MHz, ○: 35 MHz.

shown in Fig. 2, and gave the activation energy of 26 kJ mol$^{-1}$. These results, together with the fact that the $^1H$ $T_2$ is almost unchanged in the temperature range studied, indicate clearly that the water molecule reorients about its $C_2$ axis.

The theoretical value of the $^1H$ $T_1$ for the reorienting water molecules was calculated as follows:[6]

$$\frac{1}{T_1} = \gamma^4\hbar^2\frac{3I(I+1)}{16N}\sum_{i\neq j}\left[B_{ij}^{(1)}\frac{\tau_c}{1+(1/4)\omega_0^2\tau_c^2} + (2A_{ij}^{(1)} + B_{ij}^{(2)})\frac{\tau_c}{1+\omega_0^2\tau_c^2} + 2A_{ij}^{(2)}\frac{\tau_c}{1+4\omega_0^2\tau_c^2}\right], \quad (1)$$

$$A_{ij}^{(q)} \equiv [F_{ij}^{(q)}(\beta,\beta) - F_{ij}^{(q)}(\delta,\delta)]^2 + [F_{ij}^{(q)}(\beta,\delta) - F_{ij}^{(q)}(\delta,\beta)]^2,$$

$$B_{ij}^{(q)} \equiv \frac{1}{2}[F_{ij}^{(q)}(\beta,\beta) + F_{ij}^{(q)}(\delta,\delta) - F_{ij}^{(q)}(\beta,\delta) - F_{ij}^{(q)}(\delta,\beta)]^2, \quad (2)$$

$$F_{ij}^{(o)}(\beta,\beta) \equiv r_{ij}^{-3}(\beta,\beta)[1-3\cos^2\theta_{ij}(\beta,\beta)],$$

$$F_{ij}^{(1)}(\beta,\beta) \equiv r_{ij}^{-3}(\beta,\beta)\sin\theta_{ij}(\beta,\beta) \times \cos\theta_{ij}(\beta,\beta)\exp[-i\phi_{ij}(\beta,\beta)],$$

$$F_{ij}^{(2)}(\beta,\beta) \equiv r_{ij}^{-3}(\beta,\beta)\sin^2\theta_{ij}(\beta,\beta)\exp[-2i\phi_{ij}(\beta,\beta)], \quad (3)$$

Table 2. Positional parameters of hydrogen atoms in $NaAuCl_4 \cdot 2H_2O$

| | | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|---|
| Model A | H(1) | 0.1534 | 0.4327 | 0.3829 |
| | H(2) | 0.1776 | 0.5697 | 0.5199 |
| Model B | H(1) | 0.1553 | 0.4646 | 0.3728 |
| | H(2) | 0.1770 | 0.5378 | 0.5380 |

where $N$ is the number of spins, $\omega_0 = \gamma H_0$, and $\tau_c$ is the correlation time. The $\beta$ and $\delta$ in parentheses refer to the two equilibrium lattice sites of a given proton. For polycrystalline specimens, one must take the spatial averages of the $\theta_{ij}$ and $\phi_{ij}$ terms.
Thus,

$$F_{ij}^{(o)}(\beta,\beta)^2 = \frac{4}{5}r_{ij}^{-6}(\beta,\beta),$$

$$F_{ij}^{(o)}(\beta,\beta)\cdot F_{ij}^{(o)}(\delta,\delta) = \frac{2}{5}[3\cos^2\alpha(\beta\beta,\delta\delta)-1] \times r_{ij}^{-3}(\beta,\beta)r_{ij}^{-3}(\delta,\delta),$$

$$F_{ij}^{(1)}(\beta,\beta)^2 = \frac{2}{15}r_{ij}^{-6}(\beta,\beta),$$

$$F_{ij}^{(1)}(\beta,\beta)\cdot F_{ij}^{(1)}(\delta,\delta) = \frac{1}{15}[3\cos^2\alpha(\beta\beta,\delta\delta)-1] \times r_{ij}^{-3}(\beta,\beta)r_{ij}^{-3}(\delta,\delta),$$

$$F_{ij}^{(2)}(\beta,\beta)^2 = \frac{8}{15}r_{ij}^{-6}(\beta,\beta),$$

$$F_{ij}^{(2)}(\beta,\beta)\cdot F_{ij}^{(2)}(\delta,\delta) = \frac{4}{15}[3\cos^2\alpha(\beta\beta,\delta\delta)-1] \times r_{ij}^{-3}(\beta,\beta)r_{ij}^{-3}(\delta,\delta), \quad (4)$$

where $\alpha(\beta\beta,\delta\delta)$ is the angle between vector $\beta\beta$ and vector $\delta\delta$.

Prior to the $T_1$ calculation, the hydrogen atoms were located by assuming that: A) the H–H vector is parallel to the Cl(1)–Cl(1) vector or B) the H–H vector is normal to the Na–Na vector. In both cases the typical values ($\angle$H–O–H=106° and O–H=1.00 Å) were used for the geometry of a water molecule. The positional parameters of protons thus obtained (Table 2) yielded the $T_1$ minima of 0.28 s for model A, and 0.65 s for model B at the Larmor frequency of 20 MHz; both of these values are close to the experimental one. In both models the water molecule is hydrogen-bonded to the Cl(1) atoms, although the positions of the hydrogen atoms are slightly different from each other. Therefore, the agreement between the observed and calculated values of the $T_1$ minima supports the formation of the hydrogen bonds. Moreover, the hydrogen bonding is suggested from the fact that the spin phase-memory time, $T_2$, of the Cl(1) atom is shorter than those of the other chlorine atoms (Table 1). Presumably, the shorter $T_2$ of the Cl(1) atom is due to the magnetic dipole interaction with protons.

Figure 3 shows the temperature dependence of $^{35}Cl$ $T_1$ for the four absorptions. All $^{35}Cl$ $T_1$ decrease monotonously with an increase in temperature with the coefficients, $\Delta\log T_1/\Delta\log T$, ranging from −2.1 to −2.5. It should be noticed that the $^{35}Cl$ $T_1$ for the lowest frequency line is comparable to those for the other lines,

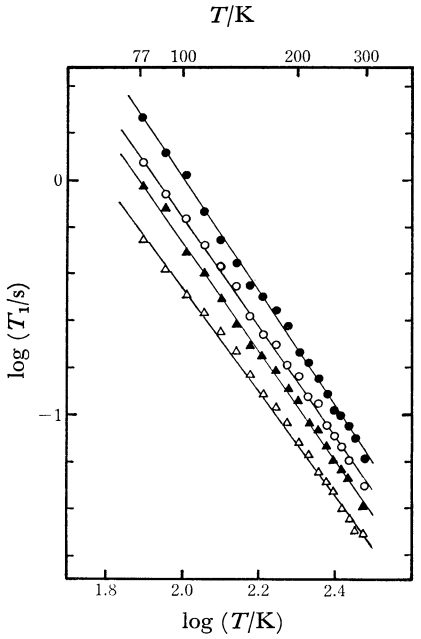


Fig. 3. The temperature dependence of $^{35}Cl$ $T_1$ in $NaAuCl_4 \cdot 2H_2O$.
●: $\nu_1$, ▲: $\nu_2$, ○: $\nu_3$, △: $\nu_4$.

and shows no anomalous temperature dependence. This finding, contrary to the suggestion of Woessner and Gutowsky,[1] permits us to conclude that the reorientation of the water molecule affects the chlorine $T_1$ very little, although the hydrogen bonds are formed between them. The very short $T_1$ observed in $(CH_3)_2CCl_2$ is probably caused not by the $CH_3$ reorientation but by molecular reorientations.

Then the chlorine $T_1$ in $NaAuCl_4 \cdot 2H_2O$ was interpreted on the basis of the torsional vibrations of the $AuCl_4^-$ ion. The quadrupole transition probabilities, $W_1(|\Delta m|=1)$ and $W_2(|\Delta m|=2)$, can be expressed by

$$W_1 = \frac{3}{2}\frac{\hbar\omega_Q^2}{I\omega_t^3}\frac{1}{\tau_a}\coth\left(\frac{x}{2}\right), \tag{5}$$

$$W_2 = \frac{3}{64}\left(\frac{\hbar\omega_Q}{I\omega_t}\right)^2\frac{\tau_a}{\sinh^4(x/2)}, \tag{6}$$

where $\omega_Q$ is the angular NQR frequency, $\omega_t$ is the angular torsional frequency, $I$ is the moment of inertia, $\tau_a$ is the average life time of torsional levels, and $x=\hbar\omega_t/kT$. The $T_1$ for quadrupolar nuclei of spin 3/2 is given in terms of $W_1$ and $W_2$ by

$$\frac{1}{T_1} = 2(W_1+W_2). \tag{7}$$

Equations 5, 6, and 7 yield the following quadratic equation:

$$A_2\tau_a^2 - \frac{1}{2T_1}\tau_a + A_1 = 0, \tag{8}$$

where $A_1$ and $A_2$ are parameters determined by $\omega_Q$, $\omega_t$, $I$, and $T$.

In order to obtain $\omega_t$, the Bayer approximation was used:[7]

$$\frac{(\Delta\nu_Q/\Delta T)}{\nu_Q} = -\frac{3}{2}\sum_i\frac{k}{(I\omega_t^2)_i}, \tag{9}$$

where the summation is taken over all effective modes.

Table 3. Calculated values of $\nu_t$, $\tau_a$, and $W_1=W_2$ at different temperatures

| $T$/K | $\nu_t$/cm$^{-1}$ | $\tau_a$/ps | $W_1=W_2$/s$^{-1}$ |
|---|---|---|---|
| 79 | 56.62 | 4.880 | 0.278 |
| 102 | 57.16 | 3.358 | 0.500 |
| 150 | 57.62 | 1.898 | 1.250 |
| 201 | 59.16 | 1.257 | 2.252 |
| 297 | 58.67 | 0.694 | 6.098 |

In the crystal lattice, the planar $AuCl_4^-$ ion may vibrate about the two Cl–Au–Cl axes and about the axis perpendicular to the plane. Supposing that these three rotary modes are degenerate, and taking account of the two effective modes, we estimated the value of $\nu_t(=\omega_t/2\pi)$ to be 38.1 cm$^{-1}$ from the average temperature coefficient ($-0.99\times10^{-4}$ K$^{-1}$) of all the resonance frequencies except the lowest one. Substituting the value of $\omega_t$ and the average value of the experimental $T_1$ into Eq. 8, however, yielded imaginary values of $\tau_a$ at all temperatures of measurement. This means that the $T_1$ value predicted by the theory is shorter than the observed one. Such a discrepancy has also been pointed out in the chlorine relaxation study for *p*-dichlorobenzene.[1]

It is noteworthy that the $\omega_t$ dependence of the temperature coefficient of the resonance frequency is quite different from those of the transition probabilities of $W_1$ and $W_2$. If the approximation $e^x \approx 1+x+x^2/2$ is used, we obtain

$$W_1 = 3\sum_i\frac{\omega_Q^2kT}{(I\omega_t^4\tau_a)_i}, \tag{10}$$

$$W_2 = \frac{3}{4}\sum_i\frac{\omega_Q^2k^4T^4}{(\hbar^2I^2\omega_t^6)_i}(\tau_a)_i. \tag{11}$$

The powers of $\omega_t$ in Eqs. 10 and 11 are much smaller than that in Eq. 9. This means that high frequency modes contribute to the temperature coefficient of resonance frequency more strongly than to $W_1$ and $W_2$. Hence, a new attempt to evaluate the $\omega_t$ from the $T_1$ data was made by assuming

$$\left(\frac{1}{2T_1}\right)^2 = 4A_1A_2. \tag{12}$$

This predicts the minimum value of $\omega_t$ which will give a real $\tau_a$. The quadratic equation then yields

$$\tau_a = \frac{1}{4T_1A_2} \tag{13}$$

and

$$W_1 = W_2 = \frac{1}{4T_1} \tag{14}$$

with the simplifying assumption of only one torsional mode, one finds

$$\omega_t = \sqrt[10]{36\frac{\omega_Q^4k^5T^5T_1^2}{\hbar^2I^3}}. \tag{15}$$

The calculated values of $\nu_t(=\omega_t/2\pi)$, $\tau_a$, and $W_1$ $(=W_2)$ are summarized in Table 3. Though one has no justification for the use of Eq. 12, the resulting ratio of $W_2/W_1$ $(=1)$ is comparable to those obtained in *p*-dichlorobenzene (2—12 at 300K and 0.5—2 at 77K),[8] and the values of $\nu_t$ are approximately constant in the

temperature range studied. These results support the present model for the chlorine relaxation time. The $\nu_t$ value of about 58 $cm^{-1}$ predicts a temperature coefficient of $-0.28 \times 10^{-4}$ $K^{-1}$, which is somewhat smaller than the average experimental one on the absolute scale. The residual part of the coefficient may be interpreted in terms of high frequency modes, as described above.

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