Water Molecular Motion and Hydrogen Bond in Paramagnetic $[Cu(H_2O)_6][PtCl_6]$ as Studied by Single Crystal ^{2}H NMR

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The temperature and angular dependences of the ^{2}H NMR spectrum were measured for single crystal $[Cu(H_2O)_6][PtCl_6]$. $(e^2Qq/h, \eta) = (132\,\text{kHz}, 0.72)$ were obtained for the D nucleus averaged by the fast 180° flip of the water molecule at 297 K. D_1(236 kHz, 0.10) and D_2(246 kHz, 0.09) were obtained for two unequal D nuclei of the water molecule at 133 K. Below T_c, at least three nonequivalent waters were found to exist. The jumping rate for the 180° flip of the water molecule (k) was obtained from the simulation of ^{2}H NMR spectra at $H_0 \| [111]$ direction. The activation energy E_a and the jumping rate at infinite temperature were estimated from the temperature dependence of k to be $24\,\text{kJmol}^{-1}$ and $1 \times 10^{13}\,\text{s}^{-1}$.

Key words: Phase Transition; ^{2}H NMR; Nuclear Quadrupole Interaction; Paramagnetic Shift; Molecular Dynamics.

Introduction

The shift of the phase transition temperature on deuteration has been reported for numerous compounds. Generally this shift is to higher temperatures due to the higher mass of the deuteron. For the phase transition of $[Cu(H_2O)_6][PtCl_6]$ caused by the cooperative Jahn-Teller effect, however, it is known that the transition temperature shifts from 135 to 129 K, and the activation energy for jumping between the three Jahn-Teller distorted configurations is lowered on deuteration [1 - 4]. These phenomena are considered to be closely related to the local structure around the H site rather than to the mass difference. Recently, We have studied the local structure at the site of the water molecules by measuring ^{2}H and ^{195}Pt NMR spectra and T_1 for the powder sample [4]. In this work, ^{2}H NMR investigations on single crystal $[Cu(D_2O)_6][PtCl_6]$ were carried out in order to obtain more information about the environment of the H site and the motion of the water molecule. This crystal is trigonal with space group $R\bar{3}$ in the high temperature phase, and the $[Cu(H_2O)_6]^{2+}$ and $[PtCl_6]^{2-}$ octahedra are stacked in columns parallel to the three-fold axis of the crystal [5]. The principal values and the direction cosines of the nuclear quadrupole interaction were obtained from the angular dependence of the quadrupole splitting in the ^{2}H NMR spectra measured at 297 and 133 K. The direction of the water molecule and the Cl···H hydrogen bond in the high temperature phase are discussed by using these results. A temperature variation of the spectra for the direction of $H_0 \|$ [111] was observed. The rate (k) of the 180° flip motion of the water molecule was estimated from the spectral simulation.

Experimental

The deuterated sample was obtained by repeated recrystallization from heavy water. A single crystal which was elongated along the [111] direction and had developed faces parallel to this axis was obtained. ^{2}H NMR spectra were measured by means of a CMX-300 spectrometer, 45.825 MHz. The sample was mounted on an uniaxial goniometer so as to allow rotation about a chosen axis perpendicular to the external magnetic field. A quadrupole echo sequence $((\pi/2)_x\text{-}\tau\text{-}(\pi/2)_y\text{-}\tau\text{-acq})$ and a shift-

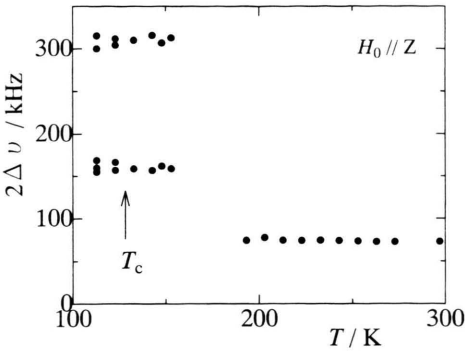

Fig. 1. Temperature dependence of the quadrupole splitting ($2\Delta\nu$) of ^{2}H NMR in $[Cu(D_2O)_6][PtCl_6]$ at $H_0 \parallel z$.

compensated echo sequence ($(\pi/2)_x$-$\tau'/2$-$(\pi)_y$-$\tau'/2$-$(\pi/2)_y$-$\tau'/2$-$(\pi)_y$-$\tau'/2$-acq) were used [6 - 11], which refocuses the dephasing due to the quadrupolar interaction and the paramagnetic shift. The $\pi/2$ pulse width, τ and $\tau'/2$ were 3.0, 40 and 20 µs, respectively.

Results and Discussion

Figure 1 shows the temperature dependence of the ^{2}H NMR quadrupole splitting $2\Delta\nu$ for the direction of the external magnetic field H_0 parallel to [111]. In the high temperature phase, six water molecules are equivalent at this orientation. Only one value $2\Delta\nu$ due to the fast 180° flip of the water molecules was observed at high temperatures. Between ca. 180 and 160 K, the spectrum could not be observed owing to the exchange broadening. Two values $2\Delta\nu$, which are attributable to the nonequivalent D nuclei of the water molecule were observed at low temperatures. A further splitting due to the nonequivalent water molecules was observed below T_c. Figure 2 shows the ^{2}H NMR spectrum for the direction of $H_0 \parallel$ [111] at 113 K. Below T_c (= 129 K), at least three nonequivalent waters were predicted to exist, since three pairs of lines appeared instead of a single pair for each D nucleus. Figure 3 (a) shows the angular dependences of ^{2}H NMR quadrupole splitting $2\Delta\nu$ around each crystal axis (x, y, z) at 297 K. The z axis was defined to be parallel to the [111] direction of the crystal. The fitting calculation of the x axis rotation was performed with the equation [12]

$$2\Delta\nu_x = 3eQ/4h\big[V_{xx} + (V_{zz} - V_{yy})\cos 2\theta_x + 2V_{yz}\sin 2\theta_x\big]. \tag{1}$$

Table 1. Principal components and their direction cosines for the EFG tensors of ^{2}H in $[Cu(D_2O)_6][PtCl_6]$.

T/K		$\lvert e^2Qq_{ii}\rvert/h$ (kHz)	— Direction cosines — x	y	z
		106	0.2679	0.9292	0.2546
133	D_1	130	–0.9608	0.2381	0.1420
		236	0.0713	–0.2826	0.9566
		111	0.0336	0.0643	0.9973
	D_2	135	0.8995	0.4330	–0.0583
		246	–0.4356	0.8991	–0.0433
		19	–0.4062	0.4524	0.7939
295		113	–0.2997	0.7548	–0.5835
		132	–0.8632	–0.4750	–0.1710

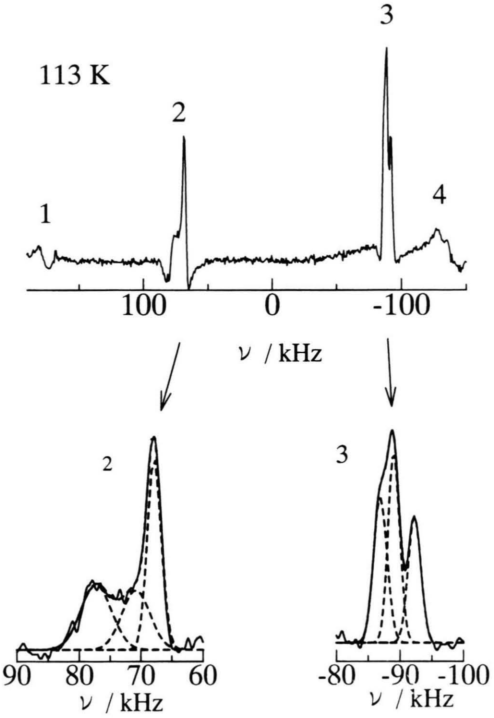

Fig. 2. ^{2}H NMR spectra of $[Cu(D_2O)_6][PtCl_6]$ for $H_0 \parallel z$ at 113 K. Above the observed spectrum. Below the best-fitted curves for the peaks 2 and 3 using three Lorentzian curves.

Here, θ_x is the angle between the direction of the external magnetic field and the y axis of the crystal. Similar relations for the other axis rotations are obtained by cyclic permutation. V_{ij} ($i, j = x, y, z$) shows the components of the electric field gradient (EFG) tensor in the crystal coordinates. All $V_{ij}(i, j = x, y, z)$ can be obtained by rotation around the three orthogonal axes. Table 1 shows the principal values of the quadrupole

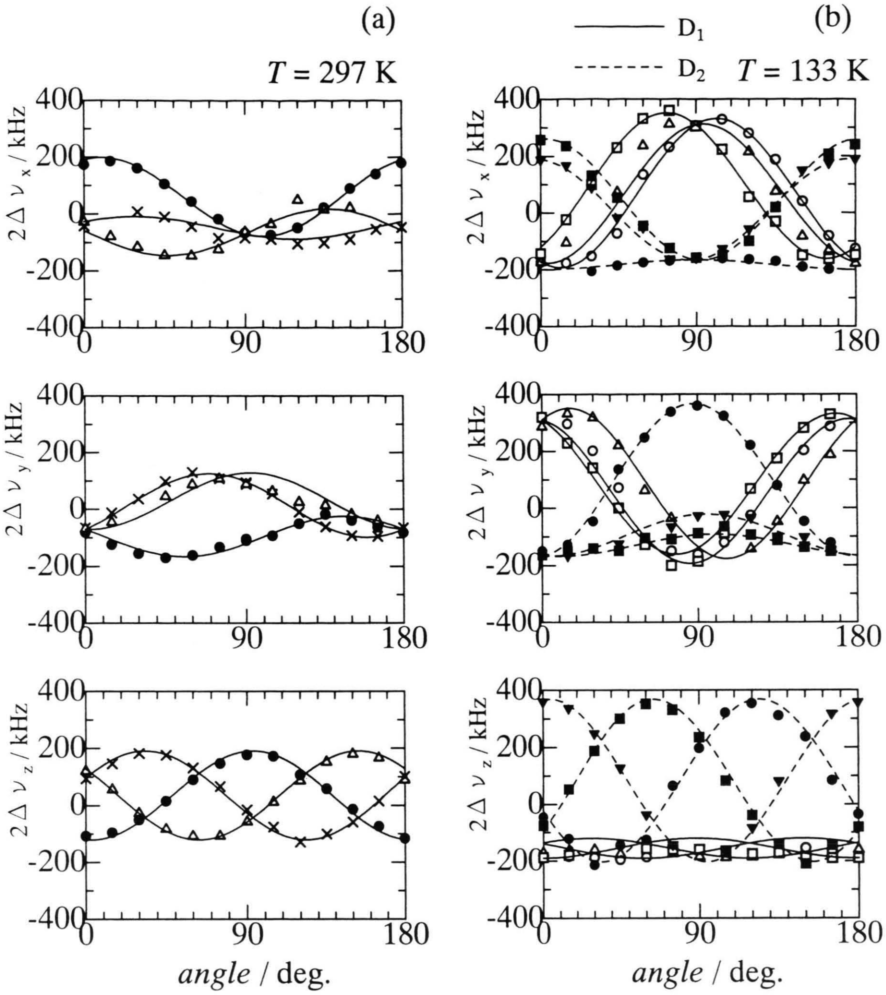

Fig. 3. Angular dependence of the quadrupole splitting ($2\Delta\nu$) of ^{2}H NMR in [Cu(D_2O)$_6$][PtCl$_6$] for the direction of $H_0\|x$, $H_0\|y$, and $H_0\|z$. (a) and (b) show $2\Delta\nu$ at 297 and 133 K, respectively. The solid and broken lines show the fitting curves by use of (1).

interaction e^2Qq_{ii}/h ($i = 1,2,3$) and the direction cosines of the principal axes (X_p, Y_p, Z_p) with respect to the crystal axes obtained by the diagonalization of the V_{ij} tensor. The parameters $(e^2Qq/h, \eta)$ = (132 kHz, 0.72) were obtained for the D nucleus, averaged by the fast 180° flip of the water molecule at 297 K. Figure 3(b) shows the angular dependences of $2\Delta\nu$ around each crystal axis (x, y, z) at 133 K. e^2Qq_{ii}/h ($i = 1,2,3$) and the direction cosines with respect to the crystal axes at 133 K are shown in Table 1. $(e^2Qq/h, \eta)$ for the two unequal D nuclei of the water molecule were obtained as D_1 (236 kHz, 0.10) and D_2 (246 kHz, 0.09). By assuming the Z_p axis of the EFG to be parallel to the O-D bond, a DOD angle of 109° was estimated. The deviations of the y principal axis of the EFG for D_1 and D_2 from the normal direction to the plane of a water molecule were 15° and 8°, respectively. The deviation of the z principal axis of the EFG averaged by the fast 180° flip of the water molecule from the normal direction to the plane of a water molecule was 7°. This crystal is build up by parallel columns of alternating [Cu(H_2O)$_6$]$^{2+}$ and [PtCl$_6$]$^{2-}$ [5]. From the direction cosines, the O-D_1 and O-D_2 bonds were found to be directed to the [PtCl$_6$]$^{2-}$ octahedron in the same and the neighboring column, respectively. The smaller e^2Qq/h of D_1 suggests that the D···Cl hydrogen bond in the same column is stronger than that to the neighboring column [13]. Figure 4 shows the temperature variation of the ^{2}H NMR spectra obtained by the quadrupole echo pulse sequence at $H_0\|$ [111]. A pair of sharp peaks at high temperatures broadened with decreasing temperature and became one broad peak. At still lower temperatures, two pairs of peaks appeared. The

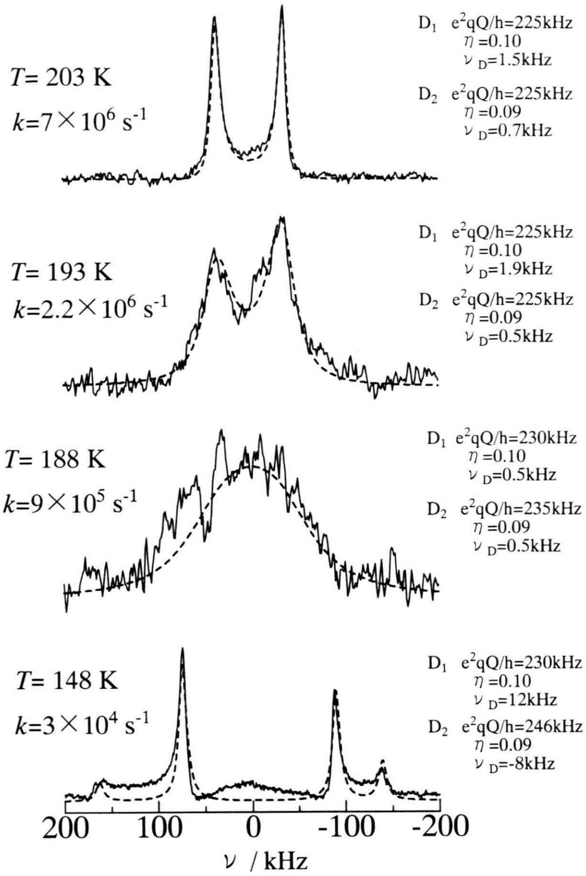

Fig. 4. Temperature dependence of the ^{2}H NMR spectrum in [Cu(D$_2$O)$_6$][PtCl$_6$] at $H_0\|z$. The broken lines show the theoretical spectra.

asymmetry of the spectra is considered to be caused by the paramagnetic shift. A simulation of the spectra was performed by using the two site jump model of the water molecules and considering the nuclear quadrupole interaction and the paramagnetic shift due to the Cu^{2+} ions. On the assumption of an isotropic **g** tensor, the site frequency ω_i is written by the second-order Wigner rotation matrix $D^{(2)*}_{nm}(\Omega)$ [8, 14, 15] as,

$$\omega_i = \mp\omega_Q - \omega_P, \tag{2}$$

$$\omega_Q = \sqrt{\frac{3}{2}}\sum_{n,m=-2}^{2} D^{(2)*}_{0n}(\psi,\theta,\phi)D^{(2)*}_{nm}(\alpha,\beta,\gamma)T^{(2)}_{mQ}, \tag{3}$$

$$T^{(2)}_{0Q} = \sqrt{\frac{3}{8}}e^2Qq/\hbar,\ T^{(2)}_{\pm2Q} = (\eta/4)e^2Qq/\hbar, \tag{4}$$

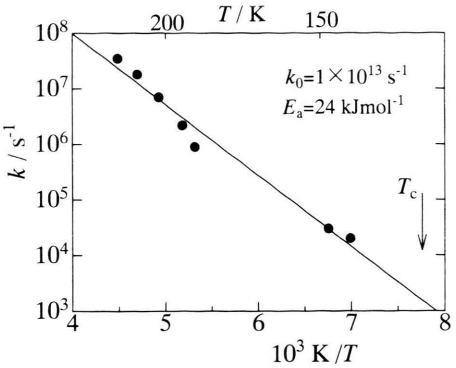

Fig. 5. Temperature dependence of the jumping rate (k) for the 180° flip of the water molecule in [Cu(D$_2$O)$_6$][PtCl$_6$].

where (α,β,γ) and (ψ,θ,ϕ) are the Euler angles for the transformation from the crystal axes to the principal axes system of the quadrupolar tensor, from the laboratory axes to the crystal axes, respectively. $\omega_P(=2\pi\nu_P)$ is the paramagnetic shift which is caused by Fermi's contact interaction and the dipole interaction between the ^{2}H nucleus and the Cu^{2+} ions. (ψ,θ,ϕ) becomes (0,0,0) at $H_0\|$ [111]. From the direction cosines of D$_1$ and D$_2$, (α,β,γ) of the two sites were obtained as (104°, −17°, −29°) and (−64°, −92°, 44°), respectively. The signal which is collected beginning at the top of the resulting echo $G(t,\theta,\phi)$ is written as [14, 16, 17]

$$G(t,\theta,\phi) = \boldsymbol{P}\cdot\hat{\mathbf{B}}^3\exp[\hat{\mathbf{A}}t]\exp[\hat{\mathbf{A}}(\tau+t_p)] \cdot \exp[\hat{\mathbf{A}}^*(\tau+t_p)]\cdot\boldsymbol{1}, \tag{5}$$

$$\hat{\mathbf{A}} = \begin{pmatrix} i\omega_1 - k & k \\ k & i\omega_2 - k \end{pmatrix}, \tag{6}$$

$$\hat{\mathbf{B}} = \begin{pmatrix} \sin(\pi K_1/2)/K_1 & 0 \\ 0 & \sin(\pi K_2/2)/K_2 \end{pmatrix}, \tag{7}$$

$$K_i^2 = 1 + (\Omega_i t_p/\pi)^2, \tag{8}$$

$$\boldsymbol{P} = (P_1, P_2),\ \boldsymbol{1} = (1,1). \tag{9}$$

Here, $\hat{\mathbf{B}}$ is the tensor which is attributed to the finite 90° pulse width. t_p and Ω_i represent the 90° pulse width and the imaginary part of the eigenvalue of the matrix $\hat{\mathbf{A}}$, respectively. $\boldsymbol{P}$ is a vector of site populations. We assumed $P_1 = P_2 = 1/2$. The spectrum is obtained by the Fourier transform of $G(t)$.

The simulated spectra are shown by the broken lines in Figure 4. e^2Qq/h, η, ν_p and k were obtained from the simulation at each temperature. The temperature dependence of k is shown in Figure 5. Assuming an Arrhenius relation, k is given by

$$k = k_0 \exp(-E_a/RT), \qquad (10)$$

where k_0 and E_a are the jumping rate at infinite temperature and the activation energy for the 180° flip of the water molecule. $k_0 = 1 \times 10^{13}$ s^{-1} and E_a = 24 kJmol^{-1} were obtained by fitting (10) to the temperature dependence of k. The jumping rate of the water molecule is predicted to reach the order of 10^3 s^{-1} at T_c, whereas the transition rate of jumping between the Jahn-Teller distorted configurations of the $[Cu(D_2O)_6]^{2+}$ ion is of the order 10^9 s^{-1} [4]. These results suggest that the hydrogen bond between D and Cl affects the reorientation of the Jahn-Teller distortion of $[Cu(D_2O)_6]^{2+}$. The distance between the hydrogen and chlorine is predicted to increase on deuteration owing to reduction of the distance between the hydrogen and oxygen [1]. A weakening of the hydrogen bond between the hydrogen and chlorine on deuteration is considered to result in lowering of the activation energy for the jumping between the different Jahn-Teller configurations and the transition temperature.

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