Restricted Rotational Motion of Interlayer Water Molecules in Vanadium Pentoxide Hydrate, $V_2O_5 \cdot nD_2O$, as Studied by Deuterium NMR

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The rotational behavior of the interlayer water molecules of deuterated vanadium pentoxide hydrate, $V_2O_5 \cdot nD_2O$, was studied by solid-state deuterium NMR for the mono- and double-layer structures of the adsorbed water molecules. The rotational motion was anisotropic even at 355 K for both the mono- and double-layer structures. The 180° flipping motion about the C_2-symmetry axis of the water molecule and the rotation around the figure axis, which makes an angle θ with the C_2-axis, occurred with the activation energy of (34 ± 4) and (49 ± 6) $\mathrm{kJmol^{-1}}$, respectively. The activation energies were almost independent of the mono- and double-layer structures of the water molecules, but the angle θ made by the two axes varied from 33° for the monolayer to 25° for the double-layer at 230 K. The angle started to decrease above 250 K (e. g. the angle was 17° at 355 K for the double-layer structure). The results indicate that the average orientation of the water molecules in the two dimensional interlayer space depends on the layer structure and on the temperature. From the deuterium NMR spectrum at 130 K, the quadrupole coupling constant e^2Qq/h = 240 kHz and the asymmetry parameter η = 0.12 were deduced. These values indicate the average hydrogen bond distance $R(\mathrm{O \cdots H})$ = 2.0 Å for the D_2O molecules in the 2D-interlayer space.

Key words: Rotational Motion; Interlayer Water; $V_2O_5 \cdot nD_2O$; Solid-State Deuterium NMR.

1. Introduction

Vanadium pentoxide hydrate, $V_2O_5 \cdot nH_2O$, exhibits a layer structure, the water molecules being confined in the two-dimensional (2D) interlayer space [1 - 3]. The intercalation properties of this material are similar to those of the smectic type clay minerals [4, 5]. The physicochemical properties of $V_2O_5 \cdot nH_2O$ were studied by XRD, calorimetry, polarized FTIR, etc [1, 6 - 9]. The adsorption isotherm of the water molecules for the $V_2O_5 \cdot nH_2O$ slightly depends on the sample, probably due to the grain size of the powder specimens, but is almost in step with the first, second and higher water layers [1]. This stepwise behavior was confirmed by powder XRD measurements. The c axis was elongated from 11.7 Å for the monolayer to 14.5 Å for the double-layer structure of the water molecules [6, 10]. The relative vapor pressure p/p_0 = 0.4 ∼ 0.5 coresponds to the boundary between the two structures, where the saturation vapor pressure p_0 is 23.7 and 20.5 torr for H_2O and D_2O, respectively. The c axis of the orthorhombic unit cell is perpendicular to the 2D-interlayer space (a-b plane). The a and b axes are 42.3 Å and 3.6 Å, respectively [6]. The host layer is composed of a stacking of double sheets of the V_2O_5 units in the c direction. This compound shows remarkable properties, for example intercalation of various polar molecules, chemical reactivities accompanied by oxidation-reduction reactions [11], and high electrical conductivity [9, 12]. The conductivity depends on the adsorption of the water molecules, and the mechanism of the conduction is believed to be a hopping motion of H^+ due to the rotational motion of the water molecules in the 2D-interlayer space. The rotational and translational motions have been detected by quasi-elastic neutron scattering [13]. However, detailed information on the rotational mode of the interlayer water molecules does not exist.

The aim of this study is to clarify the various rotational modes of the adsorbed water molecules and their frequency in the 2D-interlayer space of the mono- and double-layer structures. For this purpose we measured the line shape of the solid-state deuterium NMR spectrum (D NMR) for the deuterated compounds, $V_2O_5 \cdot nD_2O$, since the deuterium atom exhibits nuclear quadrupole interaction and the D NMR spectrum is very sensitive to the various rotational modes.

2. Experimental

2.1. Material

$V_2O_5 \cdot nH_2O$ was prepared from an aqueous solution of recrystallized NH_4VO_3 by an ion-exchange polymerization method, as described in [1]. To obtain a concentrated solution of vanadic acid, NH_4VO_3 was dissolved in an NaOH solution and then heated to remove NH_4^+ as NH_3. A reddish brown sol thus formed and was aged under ambient conditions for more than two months until it changed to a thick gel and was finally freeze-dried. For deuteration of the sample, $V_2O_5 \cdot nH_2O$ was evacuated to dryness in a glass ampule of 5 mm diameter and was exposed to heavy water (D_2O) vapor for 2 h at 298 K. This procedure was repeated several times for the complete deuteration. Then the glass ampule was sealed off at a D_2O vapor pressure of 5.0 torr for the measurements of the D NMR spectrum. This sample corresponds to $V_2O_5 \cdot 1.5D_2O$, which has monolayer water on the basis of the adsorption isotherm. The sample of $V_2O_5 \cdot 2.6D_2O$ was similarly prepared under the D_2O vapor pressure of 18.6 torr, where the D_2O double layer was completed and / or the third D_2O layer started to be formed. The saturation vapor pressure was 20.5 torr. The deuteration of the water molecules was examined by the IR spectrum.

2.2. D NMR

The solid-state deuterium NMR spectrum was measured with a Bruker DSX 300 spectrometer at the resonance frequency of 46 MHz in the temperature range of 130 - 355 K. The quadrupole echo pulse sequence with a $\pi/2$-pulse length of 2.2 µs was used. The separation of the two $\pi/2$-pulses was 20 µs. The number of scans for accumulating the signal was 80 - 1600.

Simulation of the D NMR spectrum was performed with the FORTRAN program [14]. The calculated free induction decay was processed on the program package of Bruker WinNMR for PC.

3. Results and Discussion

The temperature dependence of the D NMR spectrum of monolayer D_2O molecules of $V_2O_5 \cdot 1.5D_2O$ in the 2D-interlayer space is shown in Figure 1. The sharp signal at the center of the spectrum was assigned to the water molecules present in the grain boundary or at the grain surface. The integrated intensity of this signal was 4% of the total intensity, and the sharp signal was not observed for a sample with better crystallinity of the V_2O_5 layers in our preliminary experiment. Our discussion is focussed on the major part of the spectrum, which was assigned to the D_2O molecules in the 2D-interlayer space. A spectrum at 130 K is typical for the D_2O molecules that are rigid in the crystalline lattice [15] and gives the quadrupole coupling constant e^2Qq/h = 240 kHz and the asymmetry parameter of $\eta = 0.12$. The quadrupole-coupling constant of the deuterium atom is sensitive to the hydrogen bond length. A good correlation between the quadrupole coupling constant e^2Qq/h and the cube of the hydrogen bond distance $R(\mathrm{O}\cdots\mathrm{H})^3$ is known [16]. This relation gives $R(\mathrm{O}\cdots\mathrm{H}) = 2.0$ Å for the hydrogen bond distance of the D_2O molecules in the 2D-interlayer space. The shape of the spectrum changed between 170 and 225 K as shown in the left column of Figure 1. The outer doublet at a high temperature did not merge into a single peak that was expected for the isotropic rotation, but remained almost stationary at higher temperatures. This result indicates that the rotation of the D_2O molecules is not isotropic in the 2D-interlayer space. The most typical motion of the D_2O molecule in the crystalline lattice is a 180°-flip motion [15]. However, this motion can not explain the observed spectrum, therefore another

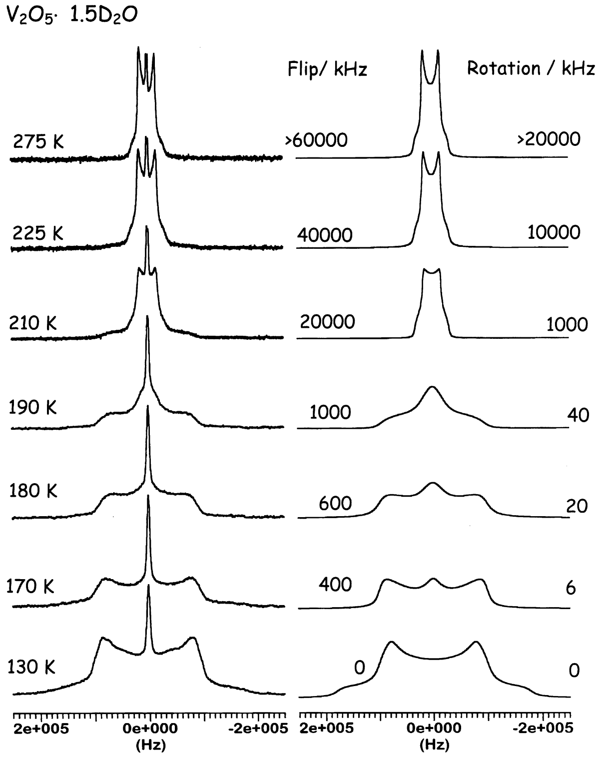

Fig. 1. Temperature dependence of the solid-state D NMR spectrum of $V_2O_5 \cdot 1.5D_2O$ with the monolayer D_2O molecules in the 2D-interlayer space. The left column is the experimental one, and the right column is the result of simulation, where the jumping rates of the 4-fold rotation and the 180°-flip motion are shown in kHz units. The quadrupole coupling constant e^2Qq/h = 240 kHz and the asymmetry parameter $\eta = 0.12$ were used for the simulation.

rotational mode must occur to give the observed spectrum. Here we considered two motional modes as the simplest model. One is the 180°-flip motion about the C_2 symmetry axis of the D_2O molecule, and another is the 4-fold rotation around the figure axis, which makes an angle θ with the C_2 symmetry axis as schematically depicted in Figure 2. Thus, the eight sites for the possible positions of the deuterium atom were assumed as shown in Figure 3. The 180°-flip motion and the 4-fold rotation were considered to be independent and only the 90° jump was taken into account as an elementary process for the 4-fold rotation. The transition matrix is described in Table 1. For the calculation of the D NMR spectrum of the powder samples, the direction of the rotation axis with respect to the V_2O_5 host lattice is not required, but only the angle θ made by the two axes is important. The direction of the rotation axis in the V_2O_5 host lattice is discussed later in relation to the polarized FTIR spectrum.

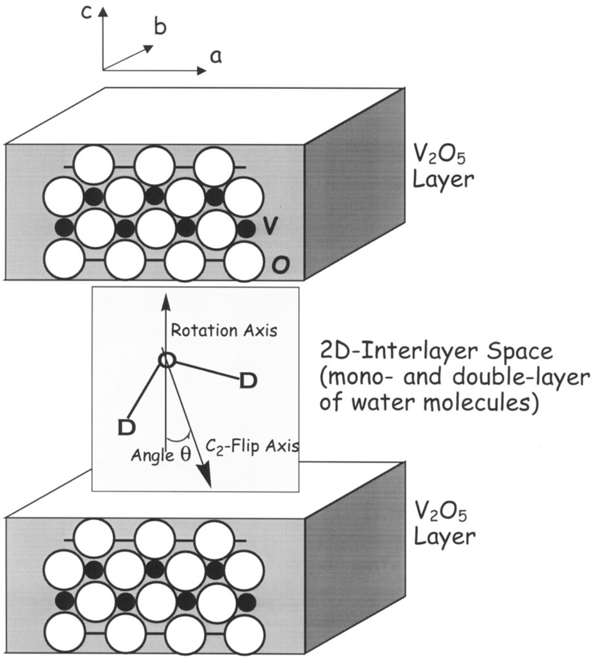

Fig. 2. Schematic view of the layer structure of V_2O_5 and the geometry of the axes of the 180°-flip motion and the rotation of the D_2O molecule.

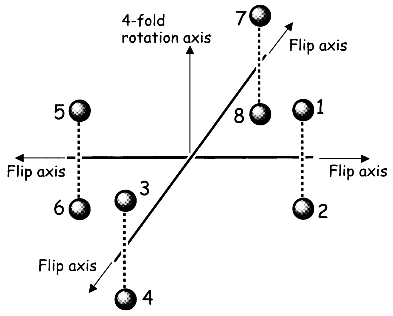

Fig. 3. Eight-site model for the 180°-flip motion and the 4-fold rotation of the D_2O molecule. The numbers 1 to 8 indicate the possible positions of the deuterium atom of the D_2O molecule.

Simulations of the D NMR spectrum were performed to reproduce the observed spectrum at each temperature by adjusting the jump frequencies based on the model described above. The angle θ was determined from the separation between the outer peaks observed for rapid motions in the high temperature region, and was 33° at 210 and 225 K. The angle of 33°

Table 1. Transition matrix elements for the 180°-flip and 4-fold rotational motions. τ_f^{-1} is the jump frequency of the 180°-flip motion and τ_r^{-1} is the jump frequency of the 4-fold rotation. Further $\tau = -\tau_f^{-1} - 2\tau_r^{-1}$.

	Site 1	2	3	4	5	6	7	8
Site 1	τ	τ_f^{-1}	τ_r^{-1}				τ_r^{-1}	
2	τ_f^{-1}	τ		τ_r^{-1}				τ_r^{-1}
3	τ_r^{-1}		τ	τ_f^{-1}	τ_r^{-1}			
4		τ_r^{-1}	τ_f^{-1}	τ		τ_r^{-1}		
5			τ_r^{-1}		τ	τ_f^{-1}	τ_r^{-1}	
6				τ_r^{-1}	τ_f^{-1}	τ		τ_r^{-1}
7	τ_r^{-1}				τ_r^{-1}		τ	τ_f^{-1}
8		τ_r^{-1}				τ_r^{-1}	τ_f^{-1}	τ

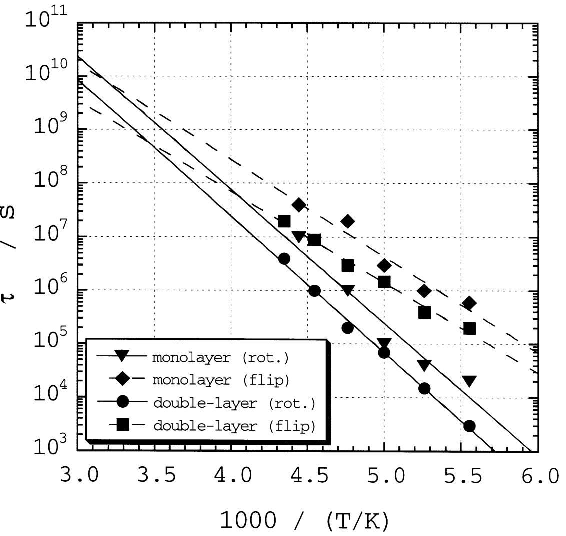

Fig. 4. Plot of the jumping rate for the 180°-flip motion and the 4-fold rotation as a function of inverse temperature. The symbols ◆ and ▼ depict the 180°-flip and the 4-fold rotation, respectively, for the monolayer D_2O molecules of $V_2O_5 \cdot 1.5D_2O$, while the symbols ● and ■ show those for the double-layer D_2O molecules of $V_2O_5 \cdot 2.6D_2O$.

was fixed for the calculations below 210 K. The bond angle of the water molecule was assumed to be 110° for all calculations. The result is shown in the right column of Figure 1. The calculated spectrum agrees well with the observed one shown in the left column. The jump frequencies of the 180°-flip and 4-fold rotational motions were thus determined between 170 and 225 K and were shown in the figure in kHz units. The jump frequencies were plotted in Fig. 4 as a function of inverse temperature. The activation energy of the 180°-flip motion is 35 ± 4 kJmol^{-1}, while that of the 4-fold rotation is 48 ± 6 kJmol^{-1}.

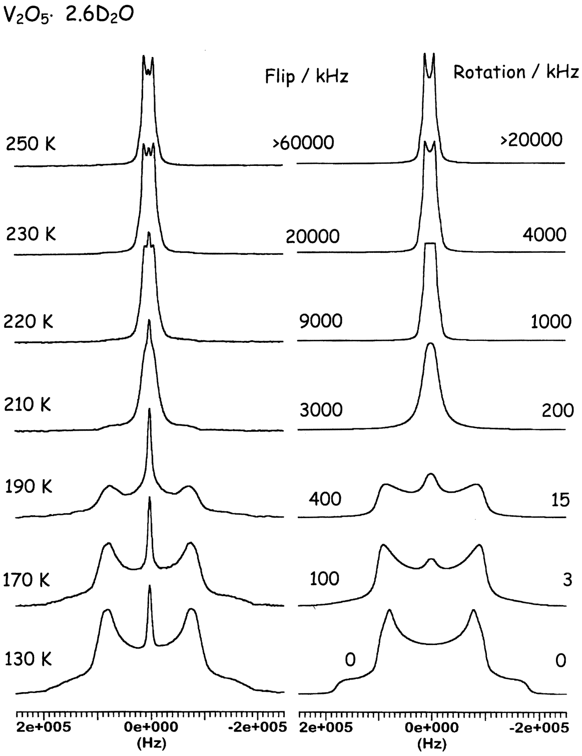

Fig. 5. Temperature dependence of the solid-state D NMR spectrum of $V_2O_5 \cdot 2.6D_2O$ with the double-layer D_2O molecules in the 2D-interlayer space. The left column is the experimental one and the right column is the result of simulation, where the jumping rates of the 4-fold rotation and the 180°-flip motion are shown in kHz units. The quadrupole coupling constant e^2Qq/h = 240 kHz and the asymmetry parameter η = 0.12 were used for the simulation.

Similar results were obtained for the double-layer D_2O molecules of $V_2O_5 \cdot 2.6D_2O$, as shown in Figure 5. The sharp signal at the center of the spectrum at 130 K was 3% in integrated intensity and was assigned to the D_2O molecules in the grain boundary or at the grain surface, as in the case of $V_2O_5 \cdot 1.5D_2O$. The model of the 180°-flip motion and the 4-fold rotation explained the observed spectrum. In this case, the angle θ, made by the two axes, was found to be 25° at 230 K, and this value was fixed for the calculation of the spectrum below 230 K. The temperature dependence of the derived jump frequency is shown in Figure 4. The activation energies (33 ± 4) kJmol^{-1} and (49 ± 6) kJmol^{-1} for the 180°-flip and 4-fold rotations, respectively, are very similar to those for

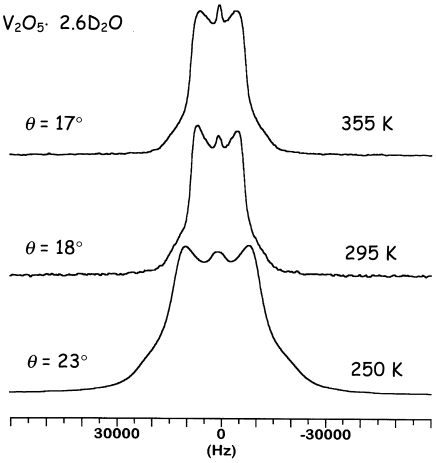

Fig. 6. Temperature dependence for the solid-state D NMR spectrum of $V_2O_5 \cdot 2.6D_2O$ in the high temperature region. The angle θ made by the 180°-flip axis and the 4-fold rotation axis is shown on the left side.

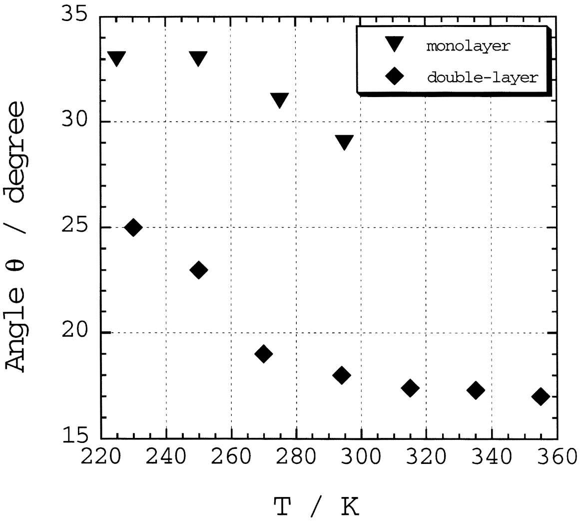

Fig. 7. The angle θ made by the 180°-flip axis and the 4-fold rotation axis as a function of the temperature for the mono- (▼) and double-layer (◆) structures.

the monolayer structure. However, the difference of the angle θ made by the two axes between the mono- and double-layer structures of the D_2O molecules was significantly detected. The angle of 25° for the double layer structure near 230 K is smaller than 33° for the monolayer. The spectrum should be independent of temperature for the rapid motion limit. However, the observed separation between the outer peaks was temperature dependent even in the rapid motional region, as shown in Fig. 6, indicating that the angle θ was temperature dependent in the high temperature region. The temperature variation of the outer-peaks separation is determined by that of the angle θ. The derived angle θ is plotted as a function of temperature in Fig. 7 for the mono- and double-layer structures.

The averaged orientation of the H_2O molecules in the 2D-interlayer space was discussed on the bases of the polarized FTIR spectrum [9]. A component of the transition moment of the O-H stretching vibration randomly distributes in the *a*-*b* plane parallel to the 2D-interlayer space and the averaged component along the *c* axis remains unique. This fact is compatible with the direction of the rotation axis depicted in Figure 2. The rotation axis is produced by the surfaces of the V_2O_5 layers. In the case that the axis is almost perpendicular to the layers, although this must be examined by theoretical calculation of potential energy, the arrangement of the oxygen atoms of the surface of V_2O_5 layers may determine the jump angle around the rotation axis. There exists no 4-fold symmetry axis along the *c* direction of $V_2O_5 \cdot nH_2O$, but the oxygen atoms are locally arranged in the distorted squares [6]. Thus, the assumption of 4-fold rotation may be plausible as a simple model. We note that the 2-fold rotation never reproduced the observed D NMR spectrum, and that the model of 3-fold rotation gave almost the same spectrum as the 4-fold model in the limit of rapid motion.

The derived activation energies of (34 ± 4) $\mathrm{kJmol^{-1}}$ and (49 ± 6) $\mathrm{kJmol^{-1}}$ for the 180°-flip and 4-fold rotation, respectively, are larger than the value of the ca. 20 $\mathrm{kJmol^{-1}}$ for the electrical conductivity along the a axis and similar to the 30 $\sim$ 50 $\mathrm{kJmol^{-1}}$ for the electrical conductivity along the *b* axis [9]. However, the relaxation rate of $10^6 \sim 10^7$ $\mathrm{s^{-1}}$ deduced from the impedance measurement near room temperature is almost three or four orders smaller than the extrapolation of the rotational jumping rate of the D_2O molecules, determined by the present D NMR experiment in the low temperature region as shown in Fig. 4 [9]. A similar relation between the molecular rotation and conductivity is known for liquid H_2O, in which the rotational motion of the H_2O molecule itself is much faster than the hopping frequency contributing to the electrical conduction [17]. The hopping motion of H^+ occurs only when the neighboring H_2O molecules take the mutual orientations appropriate to the hydrogen bonding.

Quasi-elastic neutron scattering (QENS) experiments have been performed for $V_2O_5{\cdot}1.5H_2O$ at 298 K [13]. The rapid rotational motion with $\tau_R^{-1} = 4.2 \times 10^{11}\ s^{-1}$ was deduced from the QENS measurement. The extrapolation of the jumping rates of the 180°-flip motion and the 4-fold rotation determined by the D NMR in the low temperature region is smaller by one or two orders of magnitude than the value determined by the QENS experiment at 298 K. The angle θ made by the 180°-flip axis and the 4-fold rotation axis was found to decrease above ca. 250 K, as shown in Figure 7. This fact indicates that the effective radius of the rotating water molecule around the figure axis starts off to be slightly small, above 250 K. Thus, the potential barrier hindering the rotation of the water molecule is considered to decrease in the high temperature region, and then the jumping rate may exceed the extrapolation of the Arrhenius plot from the low temperature region.

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