Dynamic Property of H_2O in Layered $VOPO_4 \cdot 2H_2O$ Studied by Solid-State NMR

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The dynamics of interlayer H_2O in $VOPO_4 \cdot 2H_2O$ have been studied by ^1H and ^2H NMR measurements. This compound contains two different kinds of water molecules. One of the two water molecules has a coordination bond to the V in the layer. The ^2H NMR spectrum at 150 K was reproduced by one component with the quadrupole-coupling constant $QCC = 220\,\text{kHz}$ and the asymmetry parameter $\eta = 0.12$. This result suggests that all H_2O molecules are static at this temperature. In the temperature range of 160–240 K, both interlayer H_2O molecules show 180°-flipping motion from the ^2H NMR spectra. This motion of the two different H_2O molecules suggests the hydrogen-bonding network between these interlayer H_2O. The activation energies of this motion could be determined to be $30\,\text{kJ}\,\text{mol}^{-1}$ from the ^2H NMR spectrum simulation. Additionally, the diffusional component also appeared above 240 K. Above 270 K, two-dimensional diffusion of the interlayer species is suggested in this material.

Oxovanadium phosphate dihydrate, $VOPO_4 \cdot 2H_2O$, has a layered structure and can be dehydrated at 423 K topotactically.[1] This material contains two different kinds of H_2O molecules in the interlayer space (Fig. 1)[1,2] and it can intercalate several organic compounds.[3–6] This intercalation is strongly influenced by the interlayer H_2O molecules.[7] Additionally, this material has been reported to have a mixed protonic–electronic conductivity, which is influenced by the behavior of the interlayer H_2O molecules.[8] The protonic conductivity of this compound is supposed to be caused by the interlayer H_2O molecules, which form a two-dimensional network of hydrogen bonds. Nevertheless, there has been no detailed information on the dynamics of H_2O.

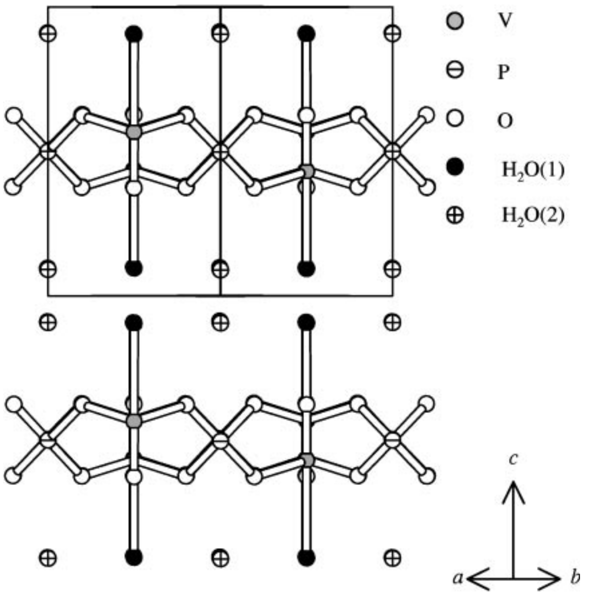

Fig. 1. Crystal structure of $VOPO_4 \cdot 2H_2O$. $H_2O(1)$ is coordinated to V in the layer, and $H_2O(2)$ is in a positional disordered state along the *c* axis.[1]

The aim of this study is to clarify the dynamics of two intercalated H_2O molecules and the intermolecular interaction between them. For this purpose, we have measured solid-state ^1H and ^2H NMR spectra, since these techniques are quite sensitive to molecular motions.

Experimental

$VOPO_4 \cdot 2H_2O$ was synthesized by the method described in the literature.[2] The synthesized sample was characterized by powder XRD. In order to get the deuterated analog, $VOPO_4 \cdot 2H_2O$ was dehydrated at 300 °C for several hours. Then, $VOPO_4 \cdot 2D_2O$ was obtained by leaving $VOPO_4$ over a D_2O atmosphere for one week.

The ^2H NMR spectra were observed at a Larmor frequency of 41.6 MHz, applying the quadrupole echo pulse sequence with $\pi/2$ pulse durations of 3 µs up to 250 K. The pulse separation between the 1st and 2nd pulses was 50 µs. Above 250 K, the spectra were observed by a single-pulse sequence because of the disappearance of the echo signal. The signals were accumulated up to 256 transients with 1–100 s recycling delays. The spectral simulation was done by use of MXQET.[9] The ^1H NMR spectra were observed by a single-pulse method at a Larmor frequency of 271.2 MHz with the $\pi/2$ pulse duration of 3 µs. The dead time of the ^1H NMR was 2 µs.

Results and Discussion

Figure 1 shows the crystal structure of $VOPO_4 \cdot 2H_2O$.[1] This crystal belongs to a tetragonal system (*P*4/*n*, #85) and contains two crystallographically non-equivalent H_2O molecules. $H_2O(1)$ is a coordinated water to the V in the layer and is located on the C_4 axis; hence, this $H_2O(1)$ is in an orientational disordered state. The other $H_2O(2)$ located on the S_4 axis is in a positional disordered state over the two positions separated by 1.36 Å along the S_4 axis. These H_2O molecules may be connected by hydrogen bonds and form a two-dimensional network. The dynamics of these H_2O molecules have been revealed by solid-state NMR methods.

^{2}H NMR. The temperature dependence of the ^{2}H NMR spectra for $VOPO_4 \cdot 2D_2O$ is shown in Fig. 2. The spectral profile changes drastically with increasing temperature. At 150 K, this spectrum is reproduced by one component with the quadrupole-coupling constant $QCC = 220(3)$ kHz and asymmetry parameter $\eta = 0.12(2)$, which are typical values for static D_2O; that is, all D_2O are static at this temperature from the spectrum.

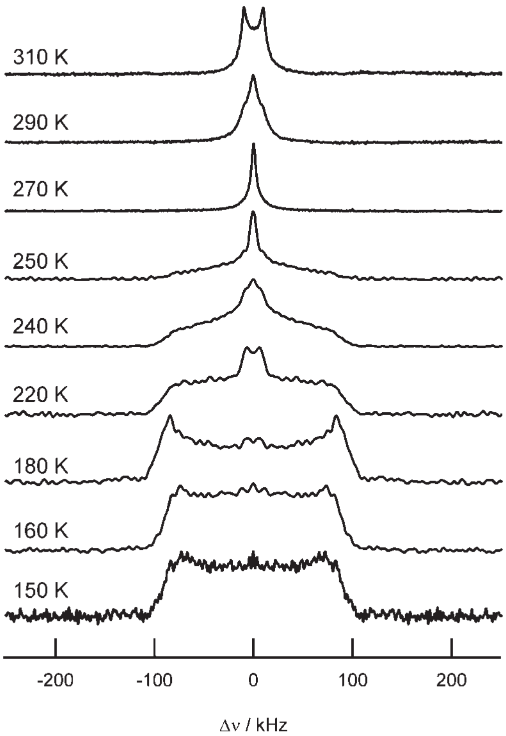

Fig. 2. Temperature dependence of ^{2}H NMR spectra from 150 to 310 K.

Upon increasing the temperature above 160 K, a new doublet appears near the center together with the weakening of the outer edges. At 240 K, the spectrum shows a characteristic quadrupole effect having a high η. This spectrum suggests the 180°-flip motion of the water molecule. Figure 3 shows the spectra between 160 and 240 K together with simulations. The spectra could be reproduced by changing the flipping rate k. The activation energy of the 180°-flip motion could be estimated to be 30(3) kJ mol^{-1} from the Arrhenius plot of the flipping rates. This value is comparable with other intercalated D_2O reported for vanadium oxide.[10] Thus, the 180°-flip motion of the interlayer D_2O is excited simultaneously, although there are two different types of H_2O molecules in this material (see, Fig. 1). This result is consistent with the structure in which two non-equivalent H_2O molecules are connected by the hydrogen bonds two-dimensionally.

Above ca. 240 K, a narrow component, which could be assigned to D_2O under the isotropic rotation or the diffusion, appears at the center of the spectrum. The intensity of this component increases with temperature and a single Lorentzian spectrum appears at 270 K with a FWMH of 5 kHz. Above 290 K, however, the new broad component appears again and it changes to a typical quadrupole pattern at 310 K. The QCC parameter of the spectrum was determined to be 30(3) kHz with $\eta = 0$. This spectrum at 310 K indicates that all deuterons see the same time-averaged electric field gradient as the result of the rapid motions, which are faster than the timescale of the NMR line width. This finding suggests the two-dimensional diffusion of D_2O or deuteron through several specific sites because isotropic diffusion or rotation of the D_2O lead to $QCC = 0$. This diffusional model is also confirmed by the ^{1}H NMR spectra (see, next section). However, it is difficult to determine the diffusing species (D_2O or deuteron) from only

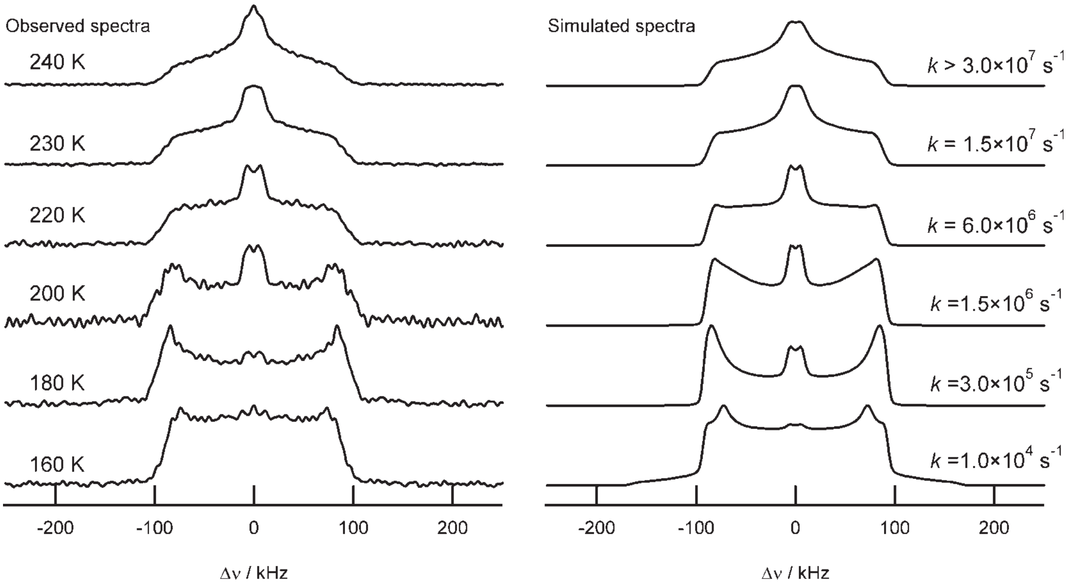

Fig. 3. Simulation of ^{2}H NMR spectra between 160–240 K. Spectra are reproduced by adjusting the motional rate (k) of the 180°-flip.

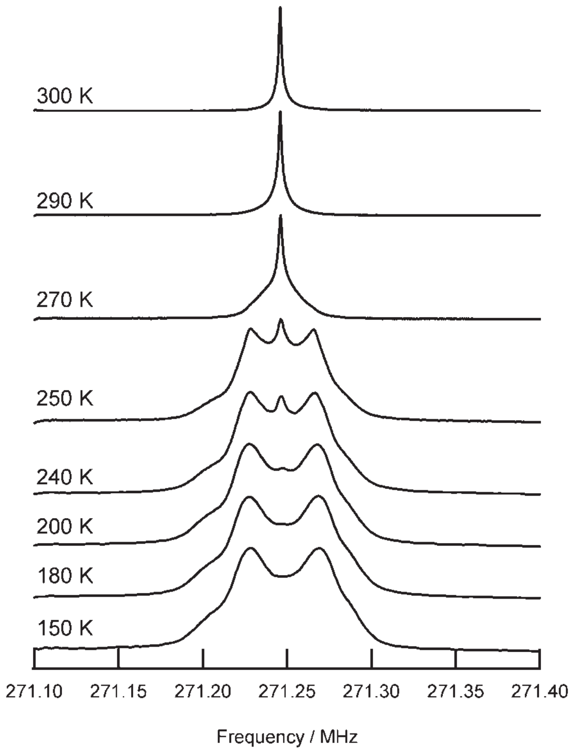

Fig. 4. Temperature dependence of ^{1}H NMR spectra from 150 to 300 K.

NMR measurement. Since the ionic conductivity for this material was reported to be 10^{-6} S cm^{-1} at 290 K,[8] proton transfer similar to ice is supposed to occur because the interlayer H_2O molecules form a two-dimensional network of hydrogen bonds.[11]

^{1}H NMR. Figure 4 shows the temperature dependence of the ^{1}H NMR spectra for $VOPO_4{\cdot}2H_2O$. In the temperature range between 150–250 K, the spectrum shows a typical Pake doublet indicating an isolated two-spin system. According to the ^{2}H NMR and its simulation (see, former session), the water molecule undergoes the rapid 180°-flip motion faster than $k = 10^7$ s^{-1} at 240 K. Despite the rapid 180°-flip motion of the H_2O, however, the Pake doublet still appears up to 250 K because the relative H positions do not change in this molecular motion. Furthermore, it should be emphasized that the C_4 reorientation of the H_2O around the V–O axis is not excited below 230 K, even though $H_2O(1)$ is located on the C_4 axis. With increasing the temperature above 240 K, the spectrum shows a sharp component at the center of the Pake doublet. This component is assigned to the isotropic rotation or the diffusion of H_2O (see, former section). The intensity of this component increases rapidly, decreasing that of the broader component. At 270 K, the spectrum consists of the narrow component at the center and the broader component. This narrow component with FWHM $= 2$ kHz could be assigned to the diffusional species. Above 290 K, however, a Lorentzian spectrum with a broad base was observed, probably due to the exchange between diffusional and non-diffusional species. This fact suggests the two-dimensional diffusion as described in the former section.

Conclusion

The dynamics of crystallographically non-equivalent H_2O molecules in $VOPO_4{\cdot}2H_2O$ have been investigated by ^{1}H and ^{2}H NMR measurements. Characteristic H_2O dynamics were observed with increasing temperature. Both H_2O molecules undergo the 180°-flip motion between 160 and 240 K. This result is consistent with the hydrogen-bonding network formed between the interlayer H_2O. Additionally, the diffusional component also appears above 240 K and becomes dominant above 290 K. The two-dimensional H_2O and/or proton diffusion have been suggested in this material.

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