

Line-Shape Analyses of Solid-state ^{17}O NMR Spectra for Hexagonal Ice

Kazuhiko Yamada^a, Kenzo Deguchi^b, Tadashi Shimizu^b, and Junji Watanabe^c

^a Interdisciplinary Science Unit, Multidisciplinary Sciences Cluster, Research and Education Faculty, in charge of Science Research Center, Kochi University, Oko Campus, Nankoku, Kochi 783-8505, Japan

^b National Institute for Materials Science, Tsukuba, Ibaraki 305-0003, Japan

^c Department of Organic and Polymeric Materials, Graduate School of Science and Engineering, Tokyo Institute of Technology, Meguro-ku, Tokyo 152-8552, Japan

Reprint requests to Kazuhiko Yamada. Phone: +81-88-880-2184. Fax: +81-88-880-2185.

E-mail: kyamada@kochi-u.ac.jp

Z. Naturforsch. **2014**, *69b*, 786–792 / DOI: 10.5560/ZNB.2014-4070

Received March 15, 2014

We present the results of experimental and theoretical investigations of line shapes in solid-state ^{17}O NMR spectra of hexagonal ice, I_h . Stationary ^{17}O NMR spectra of I_h at temperatures from 143 to 280 K were obtained at 11.7 and 16.4 T. Line shapes changed drastically as the temperature was increased from 143 to 243 K; at 253 K and above, pseudo-isotropic line shapes appear, indicating the presence of reorientational motions. We find that Ratcliffe's model, which involves twelve orientations and four-step jumps for water reorientational motions, is effective for analyzing the NMR spectra at temperatures below 243 K. The present analysis demonstrates that the isotropic line shapes arise from proton disorder with respect to the solid-state ^{17}O NMR time scale, producing pseudo-icosahedral motional averaging that can completely average out second-order quadrupole interactions.

Key words: Hexagonal Ice, Solid-state ^{17}O NMR, Molecular Dynamics

Introduction

Solid-state ^{17}O NMR ($I = 5/2$, natural abundance = 0.038 %, $\gamma = -3.6279 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1}$, and $Q = -2.558 \times 10^{-30} \text{ m}^2$) has achieved several breakthroughs in the past decade [1–9]. It is possible to obtain ^{17}O NMR parameters including chemical shielding (CS) and electric-field-gradient (EFG) tensors by analyzing complicated line shapes of molecules. Such NMR parameters can provide highly useful information in chemistry and biochemistry.

Ice, which is water in solid state, is one of the most widely distributed constituents of the surface of the earth. Water molecules form hexagonal crystals as the freezing point is reached under normal atmospheric conditions; this solid state is referred to as hexagonal ice, I_h . Reorientations of water molecules in I_h have been extensively investigated by ^1H and ^2H NMR [10–13]. Analyses of solid-state NMR line shapes at increasing or decreasing temperatures can

provide correlation times for water reorientations and activation energies, together with the corresponding motional modes.

Very recently, Ratcliffe and co-workers pioneered applications of solid-state ^{17}O NMR to the analysis of dynamic behavior and demonstrated the effectiveness of the method for investigating reorientations of water molecules in I_h and in tetrahydrofuran (THF) clathrate hydrate [14]. Although detailed information on water reorientational motions in I_h and in THF hydrate were unambiguously determined by solid-state ^{17}O NMR, pseudo-symmetric line shapes were reported at 250 K and above; such line shapes are inconsistent with the patterns predicted by spectral simulations. The line shapes for I_h were mainly governed by second-order quadrupole interactions and molecular motions such as C_3 rotation or restructuring of tetrahedra, partially average out interactions, causing changes in line shapes. However, in general, such motional averaging cannot completely average out second-order quadrupole in-

teractions. To obtain isotropic line shapes, icosahedral or higher averaging is theoretically required [15]. In their study [14], the reason for the presence of isotropic line shapes was discussed, and the effects of satellite transitions were proposed, *i. e.*, satellite transitions as well as central transitions were averaged out at higher temperatures, making the central transition appear as a pseudo-isotropic line shape. Apparently, there still seems to be room for discussion. In this paper, we present experimental and theoretical investigations of line shape analysis of solid-state ^{17}O NMR for hexagonal ice and discuss the reasons for the presence of pseudo-isotropic line shapes for I_h at higher temperatures.

Experimental

Water composed of 90% ^{17}O atoms was purchased from Taiyo Nippon Sanso Corp (Tokyo, Japan). A volume of 50 μL of this water was packed into zirconium oxide (4 mm o. d.) with a sealed spacer made of polychlorotrifluoroethylene. Solid-state ^{17}O NMR experiments were carried out at 67.8041 and 94.9802 MHz on 11.7 and 16.8 T Jeol ECA 500 and 700 spectrometers, respectively, using 4-mm MAS probes. A sample kept at room temperature was employed for chemical shift referencing. The recycle delay was 10 s. The radio frequency field strength for ^{17}O was approximately 100 kHz, and the number of scans was typically 128–512. For stationary ^{17}O NMR experiments, Oldfield echo [16] and/or direct polarization (DP) methods were used with high-power ^1H decoupling during acquisition. In cases where the baseline was distorted, a baseline correction was carried out. For the echo experiments, the delay time between pulses was set to be 10–20 μs . The temperature was changed from 143 to 280 K. Whenever the temperature changed, the system was held for more than 10 min to allow it to reach thermal equilibrium. All NMR spectra were processed by DELTA software (Jeol Inc., USA). For spectral simulations of ^{17}O NMR spectra of I_h , a semi-classical exchange formalism [17] was used; details can be found in ref. [15]. To calculate the theoretical line shapes, relevant chemical sites must be assumed for the chemical exchange process, and each molecular orientation should be expressed geometrically using Euler angles. For a theoretical model for water reorientational motions in I_h [14], we used the twelve Euler angles suggested by Ratcliffe and co-workers: $\alpha_1 = 0.00^\circ$, $\beta_1 = 0.00^\circ$, $\gamma_1 = 0.00^\circ$; $\alpha_2 = 215.26^\circ$, $\beta_2 = 60.00^\circ$, $\gamma_2 = 35.26^\circ$; $\alpha_3 = 144.74^\circ$, $\beta_3 = 60.00^\circ$, $\gamma_3 = 324.74^\circ$; $\alpha_4 = 35.26^\circ$, $\beta_4 = 60.00^\circ$, $\gamma_4 = 215.26^\circ$; $\alpha_5 = 324.74^\circ$, $\beta_5 = 60.00^\circ$, $\gamma_5 = 144.74^\circ$; $\alpha_6 = 90.00^\circ$, $\beta_6 = 90.00^\circ$, $\gamma_6 = 90.00^\circ$; $\alpha_7 = 270.00^\circ$, $\beta_7 = 90.00^\circ$, $\gamma_7 = 270.00^\circ$; $\alpha_8 = 324.74^\circ$, $\beta_8 = 120.00^\circ$, $\gamma_8 = 35.26^\circ$; $\alpha_9 = 35.26^\circ$, $\beta_9 = 120.00^\circ$,

$\gamma_9 = 324.74^\circ$; $\alpha_{10} = 144.74^\circ$, $\beta_{10} = 120.00^\circ$, $\gamma_{10} = 215.26^\circ$; $\alpha_{11} = 215.26^\circ$, $\beta_{11} = 120.00^\circ$, $\gamma_{11} = 144.74^\circ$; $\alpha_{12} = 0.00^\circ$, $\beta_{12} = 180.00^\circ$, $\gamma_{12} = 180.00^\circ$. All spectral simulations were performed using a program written by the authors on MATLAB (The MathWorks, Inc.).

Results and Discussion

Fig. 1 shows stationary ^{17}O NMR spectra of I_h at various temperatures, acquired at 11.7 T. The figure clearly shows drastic changes in line shapes as the temperature is increased, indicating that there were reorientational molecular motions. Note that there have been no reports of structural changes or phase transitions in I_h over this range of temperatures at atmospheric pressure. At 273 K, the spectrum showed a very sharp peak (data not shown), which was assigned to liquid water. At 143 K, the lowest temper-

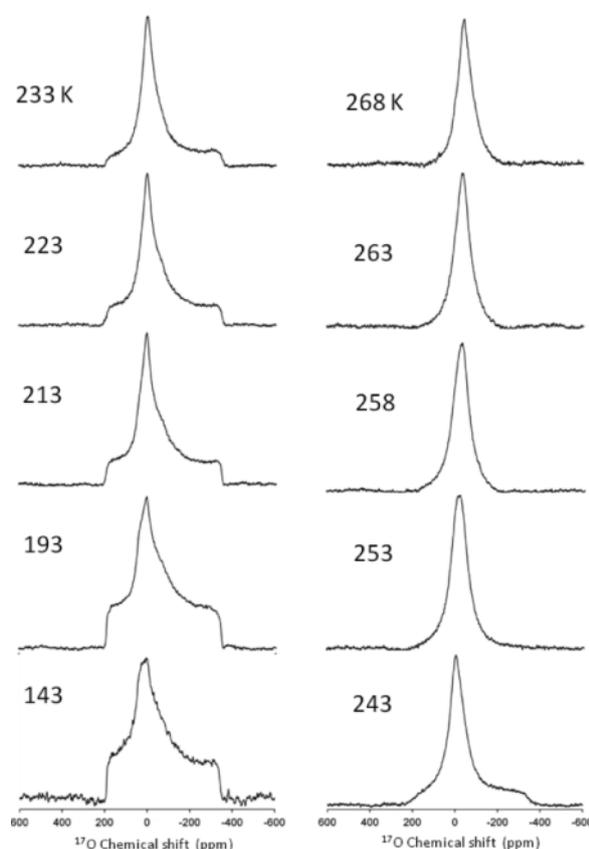


Fig. 1. Stationary ^{17}O NMR spectra of hexagonal ice, I_h , acquired at 11.7 T. Temperatures were varied from 143 to 268 K.

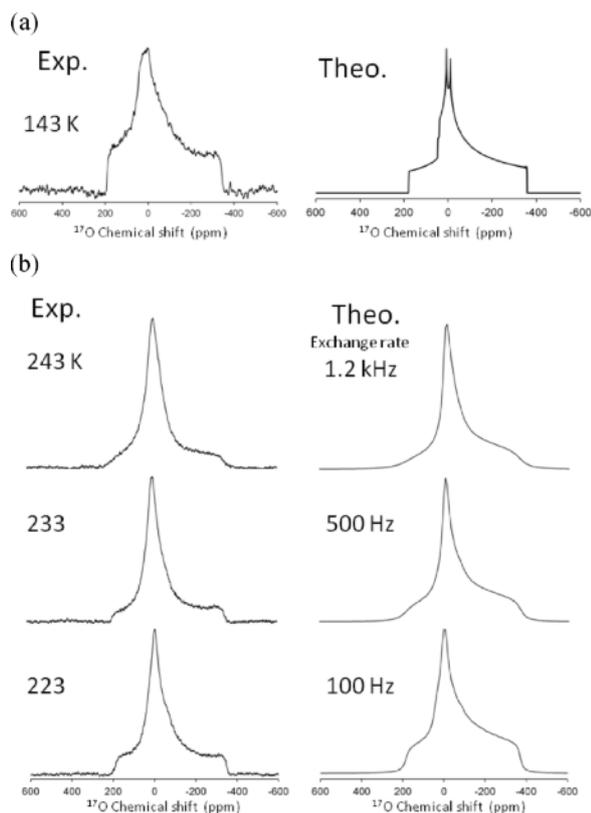


Fig. 2. (a) Experimental (left) and best-fit calculated (right) stationary ^{17}O NMR spectra of I_h at 143 K. No molecular motions were assumed in the spectral simulations. (b) Experimental (left) and corresponding theoretical (right) stationary ^{17}O NMR spectra at 223, 233, and 243 K. The Ratcliffe model was used for the spectral simulations. See details in the text.

ature reached in this study, molecular motions seem to be frozen. At temperatures above 193 K, the line shapes were roughly similar to that at 143 K, but, as the temperature is increased, the central peak becomes more symmetric, and both shoulders fade away. In the temperature range between 253 and 268 K, pseudo-symmetric line shapes appear, which are consistent with the previous observations by Ratcliffe and co-workers [14]. The pseudo-isotropic chemical shifts were found to be approximately -43 ppm.

Fig. 2(a) shows the experimental (left) and best-fit calculated (right) stationary ^{17}O NMR spectra of I_h at 143 K. The ^{17}O chemical shift tensors for water molecules were previously calculated by Pennanen *et al.* [18], and the chemical shift span, $\Omega = \delta_{11} - \delta_{33}$, was reported to be approximately 40 ppm.

Thus, the effects of ^{17}O chemical shift tensors were safely ignored during the above simulations since their magnitudes were much smaller compared to those of second-order quadrupole interactions. Here second-order quadrupole interactions, which can be described by the quadrupole coupling constant (C_Q) and the asymmetry parameter (η_Q), were only considered in the present analysis yielding $C_Q = 6.6(1)$ MHz and $\eta_Q = 0.95(2)$; these are in reasonable agreement with previous results [19, 20]. In principle, a theoretical model must be predefined to analyze NMR line shapes that show reorientational motions. A number of studies on the analysis of molecular motions in ice by solid-state NMR have been reported [10–14]. We believe that the theoretical treatment proposed by Ratcliffe and co-workers, as shown in Fig. 3, is the most straightforward and appropriate procedure [14]. Therefore, we followed that procedure, which can be briefly summarized as follows. (1) The molecular structure of water is assumed to be perfectly tetrahedral. (2) The two hydrogen atoms are distinguished from each other. In this figure, the radii of hydrogen atoms are drawn to be slightly different. (3) A three-fold jump, in a manner similar to methyl group and NH_3^+ rotations, is considered for each bond. For example, site 1 in Fig. 3 can be chemically exchanged into sites 2 and 3 by a C_3 rotation about one O–H bond and into sites 4 and 5 by the other O–H bond, and so on.

Fig. 2 (b) shows experimental stationary ^{17}O NMR spectra measured at a few temperatures (left) together with the corresponding spectra calculated from the Ratcliffe model (right). The exchange rates used for the calculations are also given in the figure. In the spectral simulations, the line shapes measured from 193 to 243 K were used with the ^{17}O NMR parameters obtained above, and the pseudo-symmetric line shapes were excluded. From an Arrhenius plot (data not shown), the activation energy was found to be $56(2)$ kJ mol^{-1} , which is consistent with results from ^2H and ^{17}O NMR experiments [12–14].

Fig. 4 (left) shows the theoretical line-shapes calculated from the Ratcliffe model at various exchange rates. In the spectral simulations, the obtained ^{17}O NMR parameters were used with the Larmor frequency of 67.8 MHz. Apparently, the anti-symmetric line-shapes at exchange rates faster than the line widths, *i.e.*, the fast exchange limit, do not reproduce the experimental ^{17}O NMR spectra at 253 K and higher. An FWHM of approximately 5 kHz was found

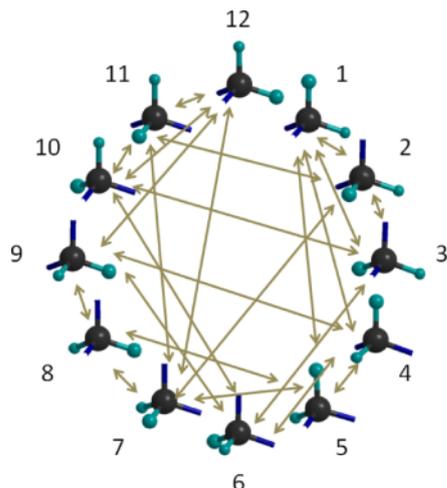


Fig. 3 (color online). Molecular orientations for the Ratcliffe model. See details in the text.

at 263 K, suggesting that the water was not in the liquid state, and molecular motions were not random. Moreover, since pseudo-isotropic chemical shifts were not observed at 0 ppm, quadrupole interactions must still exist. For reference, the correlation time for the reorientation motion at 273 K can be estimated to be approximately 30 kHz using an Arrhenius plot correlating time and inverse temperature, assuming that the same molecular motions occur at higher temperatures. The following possibilities can be considered as reasons for the presence of the symmetric line-shapes at higher temperatures: (1) proton disorder, (2) pulse interference, (3) effects of anisotropies in chemical shifts, and (4) effects of satellite transitions. We discuss each of these possibilities below.

Effects of proton disorder

As mentioned above, there have been no reports of phase transitions or structural changes for I_h in the temperature range between 253 and 268 K at atmospheric pressure. However, it is well known that protons can move between oxygen atoms at temperatures above about 130 K, and such proton disorder is described by Bernal-Fowler rules [21]. If the correlation time of the disorder is close to the ^{17}O NMR time scale, then we expect that proton disorder can affect changes in line shapes. Assuming that a proton moves at random at higher temperatures, it would be very difficult to distinguish each water site shown in

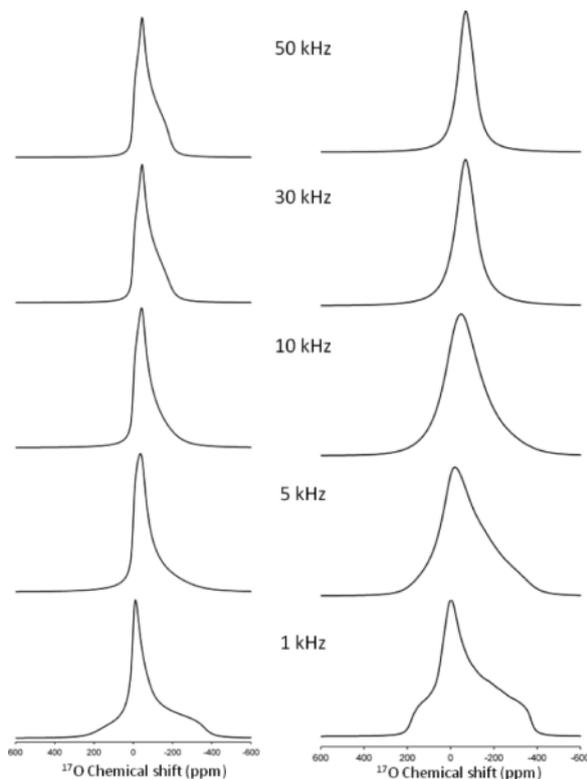


Fig. 4. Theoretical ^{17}O stationary NMR spectra of I_h at various exchange rates, calculated from the Ratcliffe model (left) and the conventional twelve-site chemical exchange model (right).

Fig. 3. As a result, chemical exchange among twelve sites can be spuriously achieved. Schurko *et al.* [15] demonstrated that exchange processes with icosahedral or higher symmetries can average out both first- and second-order quadrupole interactions, giving isotropic line-shapes in the fast-exchange limit. In the present case, it appears that, at 253 K and higher, second-order quadrupole interactions can be averaged out due to pseudo-icosahedral averaging, leading to symmetric line-shapes with approximately 5 kHz for FWHM observed at non-zero chemical shift. Fig. 4 (right) shows the theoretical line-shapes calculated from the twelve-site exchange model at various rates. In the spectral simulations, the same parameters as those in the Ratcliffe model (left) were used. As expected, symmetric line shapes were observed in the fast-exchange limit, and agreement with the corresponding experimental NMR spectra was reasonable.

Effects of pulse interference

In principle, ^1H or ^{17}O pulse radiation can potentially affect line-shapes, provided the correlation time for molecular motions coincides with the pulse power or an integral multiple of it. However, in the present case, there was no change in line shapes even when pulse powers were randomly changed. Furthermore, pseudo-isotropic line shapes appeared at all temperatures above 253 K. Accordingly, pulse interference was safely excluded from the possible explanations for the symmetric line-shapes.

Effects of anisotropies in chemical shifts

Although the effects of ^{17}O chemical shift tensors on line shapes were ignored in the present study, it should be discussed for the cases at higher temperatures. For a half-integer quadrupole nucleus in a strong magnetic field, both chemical shielding and second-order quadrupole interactions must be considered in calculating the central-transition NMR spectra. In the present case, an isotropic chemical shift was not needed since it is set to 0 ppm. When the line widths become narrow at higher temperatures, the effects of chemical shielding may become significant. To investigate such effects, NMR experiments were carried out at a high magnetic field of 16.4 T, because as the applied magnetic field increases, the magnitude of second-order quadrupole interactions decreases while that of chemical shielding increases. Fig. 5 shows experimental and theoretical stationary ^{17}O NMR spectra of I_h , measured at 16.4 T. In the high-field experiments, pseudo-isotropic line shapes appeared above approximately 260 K. The twelve-site exchange model was used for the spectral simulation, which is in reasonable agreement with the experimental results. An FWHM of approximately 6 kHz was obtained at 263 K, while the magnitude of the ^{17}O chemical shielding tensor for water was reported to be approximately 40 ppm, *i. e.*, 3.8 kHz [18]. Moreover, the anisotropy can also be averaged out by molecular reorientational motions. Therefore, it is safe to say that the effects of ^{17}O chemical shift tensors do not cause the symmetric line-shapes, even at higher temperatures.

Effects of satellite transitions

So far, we have discussed line shapes arising from the central transition. As pointed out by Ratcliffe and

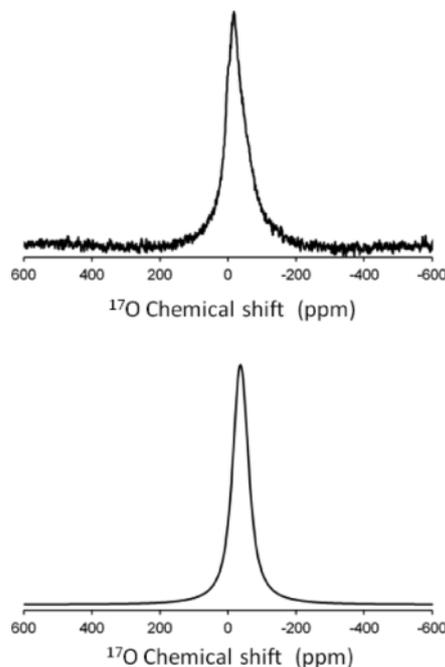


Fig. 5. Experimental (top) and theoretical (bottom) stationary ^{17}O NMR spectra of I_h , acquired at 16.4 T. The twelve-site chemical exchange model was used for the spectral simulation.

co-workers [14], satellite transitions should be considered in the spectral simulations, particularly at higher temperatures. The master equations for satellite transitions with contributions from first- and second-order quadrupole interactions ($v_{m-1,m}^1$ and $v_{m-1,m}^2$) are given by Eqs. 1–3 [22]:

$$v_{m-1,m}^{\text{total}} = v_{m-1,m}^1 + v_{m-1,m}^2 \quad (1)$$

where

$$v_{m-1,m}^1 = \frac{3C_Q}{4I(2I-1)} \frac{\sqrt{6}}{3} (1-2m)V_0 \quad (2)$$

$$v_{m-1,m}^2 = -\frac{2}{\omega_Q} \left[\frac{C_Q}{4I(2I-1)} \right]^2 \left\{ V_{-1}V_1[24m(m-1) - 4I(I+1)+9] + \frac{1}{2}V_{-2}V_2[12m(m-1) - 4I(I+1)+6] \right\} \quad (3)$$

In the above equations, m and I are the magnetic number and spin number, respectively. The quantities V_{-2} , V_{-1} , V_0 , V_1 , and V_2 are appropriately modified, depending on the theoretical models involved [15]. For

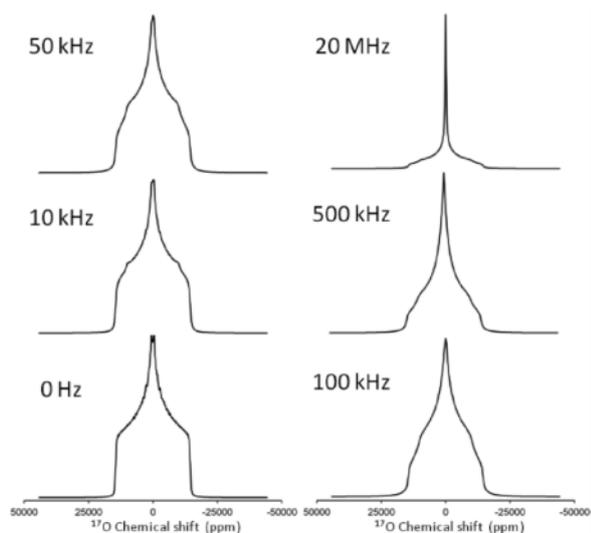


Fig. 6. Theoretical stationary ^{17}O NMR spectra arising from inner satellite transitions calculated at various exchange rates. The Ratcliffe model was used for the spectral simulations.

$I = 5/2$, two (inner and outer) satellite transitions exist. Fig. 6 shows the theoretical stationary ^{17}O NMR spectra of the inner satellite transition ($m = -1/2$ and $3/2$) including first- and second-order quadrupole interactions, calculated at various exchange rates. The Ratcliffe model was used for the spectral simulations with the same NMR parameters as used in Fig. 4. It can be seen that line shapes change as the exchange rates increase. Note that the spectral width, approximately 3000 ppm, is so wide that correlation times of tens of megahertz are required to partially average out the quadrupole interactions. Assuming that the correlation time was 30 kHz, as expected at 273 K from the Arrhenius plot, it was found that the line shape was almost the same as in the stationary NMR spectrum. The line shapes for the outer satellite transitions were omitted. Their line widths were much wider than those for the inner transitions, implying that correlation times of tens of kilohertz hardly affect the line shapes of satellite transitions.

Fig. 7 shows (a) the theoretical ^{17}O NMR spectrum of I_h including the central transition and inner and outer satellite transitions at the exchange rate of 50 kHz, and (b) a magnified view of the central spectrum. The Ratcliffe model was used for the spectral simulations with the same NMR parameters used in Fig. 4. The sharp signal at the center arose from the

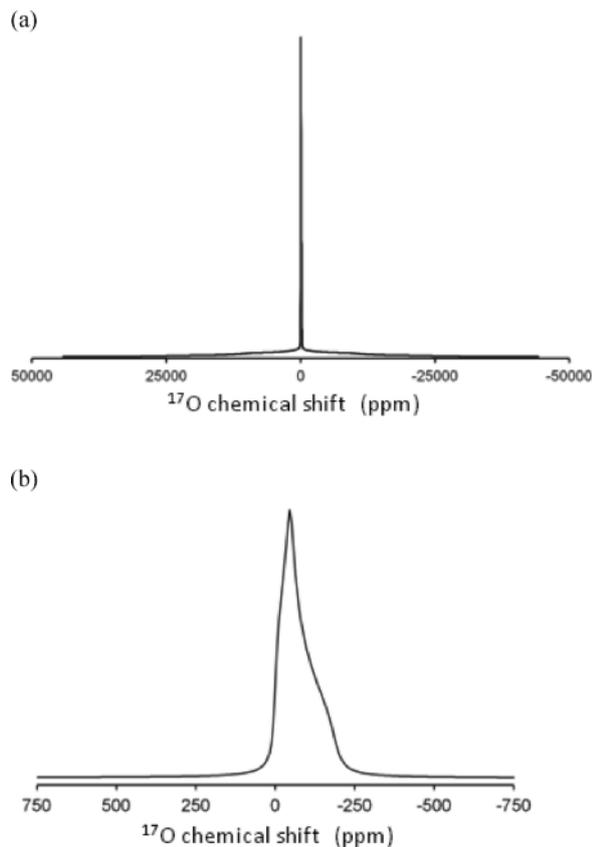


Fig. 7. (a) Theoretical stationary ^{17}O NMR spectrum arising from the central transition and inner and outer satellite transitions, calculated at the exchange rate of 50 kHz. (b) Magnified view of the central part in the above spectrum.

central transition, while the low and broad signals ranging roughly from $-30,000$ to $30,000$ ppm correspond to the satellite transitions. The relative intensities of the transitions for $I = 5/2$ are as follows: $\text{Sat}_{\text{out}} : \text{Sat}_{\text{in}} : \text{Cent} : \text{Sat}_{\text{in}} : \text{Sat}_{\text{out}} = 5 : 8 : 9 : 8 : 5$ [23]. Thus, approximately 74% of the total intensity accounts for both satellite transitions. Nevertheless, it can be demonstrated that, as shown in Fig. 7(b), motional averaging from the satellite transitions could not affect the line shape of the central transition unless the correlation time is in tens of megahertz.

Cause of symmetric line shapes

As the reason for the presence of the symmetric line shapes, we conclude that proton disorder best explains the experimental facts. In our understanding, pulse in-

terferences, effects of chemical shift tensors and satellite transitions are not realistic. Finally, we comment on the appropriate model for reorientational motion in ice at lower temperatures. As shown in Fig. 4, intermediate ranges in the twelve-site exchange model tend to give broader line widths compared to the experimental NMR spectra; it is safe to say that the model fails to reproduce them. We believe that the Ratcliffe model provides the best description for water reorientational motions of ice at temperatures below that at which symmetric line shapes appear. At 253 K and higher, proton disorder cannot be ignored with respect to the ^{17}O NMR time scale, and the model becomes a twelve-site exchange model giving pseudo-isotropic line-shapes.

Conclusion

We have performed line shape analyses of solid-state ^{17}O NMR spectra of hexagonal ice, I_h . Station-

ary ^{17}O NMR spectra of I_h at various temperatures were obtained at 11.7 and 16.4 T. Using the Ratcliffe model, the activation energy was estimated to be $56(2) \text{ kJ mol}^{-1}$ for I_h , which is in agreement with previous reports [12–14]. Pseudo-isotropic line-shapes have been obtained at 258 K and higher. In the current understanding, proton disorder occurs with respect to the ^{17}O NMR time scale at high temperatures, and such proton disorder makes the twelve sites in the Ratcliffe model indistinguishable from one another. As a result, chemical exchange among the twelve sites, by which second-order quadrupole interactions are averaged out, is spuriously achieved.

Acknowledgement

This study was financially supported by the Ministry of Education, Culture, Sports, Science and Technology (MEXT) via a Grant-in-Aid for Young Scientists (B) (22750009).

-
- [1] K. Yamada, S. Dong, G. Wu, *J. Am. Chem. Soc.* **2000**, *122*, 11602–11609.
- [2] V. Lemaître, M. R. R. de Planque, A. P. Howes, M. E. Smith, R. Dupree, A. Watts, *J. Am. Chem. Soc.* **2004**, *126*, 15320–15321.
- [3] J. Hu, E. Y. Chekmenev, Z. Gan, P. L. Gor'kov, S. Saha, W. W. Brey, T. A. Cross, *J. Am. Chem. Soc.* **2005**, *127*, 11922–11923.
- [4] E. Y. Chekmenev, K. W. Waddell, J. Hu, Z. Gan, R. Wittebort, T. A. Cross, *J. Am. Chem. Soc.* **2006**, *128*, 9849–9855.
- [5] E. Y. Chekmenev, P. L. Gor'kov, T. A. Cross, A. M. Alaouie, A. I. Smirnov, *Biophys. J.* **2006**, *91*, 3076–3084.
- [6] T. H. Sefzik, J. B. Houseknecht, T. M. Clark, S. Prasad, T. L. Lowary, Z. Gan, P. J. Grandinetti, *Chem. Phys. Lett.* **2007**, *434*, 312–315.
- [7] A. Brinkmann, A. P. M. Kentgens, *J. Am. Chem. Soc.* **2006**, *128*, 14758–14759.
- [8] I. P. Gerothanassis, *Prog. Nucl. Magn. Reson. Spectrosc.* **2010**, *56*, 95–197.
- [9] I. P. Gerothanassis, *Prog. Nucl. Magn. Reson. Spectrosc.* **2010**, *57*, 1–110.
- [10] D. E. Barnaal, I. J. Lowe, *J. Chem. Phys.* **1968**, *48*, 4614–4618.
- [11] M. I. Valic, S. Gornostansky, M. M. Pintar, *Chem. Phys. Lett.* **1971**, *9*, 362–364.
- [12] R. J. Wittebort, M. G. Usha, D. J. Ruben, D. E. Wemmer, A. Pines, *J. Am. Chem. Soc.* **1988**, *110*, 5668–5671.
- [13] M. Bach-Vergés, S. J. Kitchin, K. D. M. Harris, M. Zugic, C. A. Koh, *Phys. Chem. Chem. Phys.* **2004**, *6*, 871–872.
- [14] Y. Ba, J. A. Ripmeester, C. I. Ratcliffe, *Can. J. Chem.* **2011**, *89*, 1055–1064.
- [15] R. W. Schurko, S. Wi, L. Frydman, *J. Phys. Chem. A* **2002**, *106*, 51–62.
- [16] A. C. Kunwar, G. L. Turner, E. Oldfield, *J. Magn. Reson.* **1986**, *69*, 124–127.
- [17] H. M. McConnell, *J. Chem. Phys.* **1958**, *28*, 430–431.
- [18] T. S. Pennanen, J. Vaara, P. Lantto, A. J. Sillanpaa, K. Laasonen, J. Jokisaari, *J. Am. Chem. Soc.* **2004**, *126*, 11093–11102.
- [19] H. W. Spiess, B. B. Garrett, R. K. Sheline, S. W. Rabideau, *J. Chem. Phys.* **1969**, *51*, 1201–1205.
- [20] D. T. Edmonds, A. Zussman, *Phys. Lett.* **1972**, *41A*, 167–169.
- [21] J. D. Bernal, R. H. Fowler, *J. Chem. Phys.* **1933**, *1*, 515–548.
- [22] P. P. Man in *Encyclopedia of Nuclear Magnetic Resonance*, (Eds.: D. M. Grant, R. K. Harris), Vol. 6, John Wiley & Sons, Chichester, **1996**, p. 3838–3847.
- [23] A. J. Vega in *Encyclopedia of Nuclear Magnetic Resonance*, (Eds.: D. M. Grant, R. K. Harris), Vol. 6, John Wiley & Sons, Chichester, **1996**, p. 3869–3889.