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STUDIES OF SURFACE PROPERTIES OF ICE USING NUCLEAR MAGNETIC RESONANCE

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Résumé - Des expériences de résonance magnétique nucléaire pulsée ont été faites sur des petites particules de glace ayant un grand rapport surface/volume pour étudier la couche quasi liquide (Q.L.L.) à la surface de la glace. La dépendance avec la température des caractéristiques RMN et les propriétés dynamiques telles que le temps de corrélation pour le mouvement de rotation et le coefficient d'auto-diffusion de la Q.L.L. ont été décrites. La fréquence du mouvement moléculaire rotationnel dans le Q.L.L. et le coefficient d'auto-diffusion sont plus grands respectivement de 5 et 2 ordres de grandeur que dans la glace en volume.

Abstract - Pulsed nuclear magnetic resonance studies were carried out on small ice particles with large surface to volume ratios to investigate the so-called quasi-liquid layer (Q.L.L.) on an ice surface. The temperature dependence of features of the NMR spectra and dynamical properties such as the correlation time for rotational motion and the self diffusion coefficient of the Q.L.L. were described. The frequency of the rotational molecular motion and the self diffusion coefficient were larger than those of bulk ice by about five orders and by two orders, respectively.

I. Introduction

It is generally accepted that a mobile phase, the so-called quasi-liquid layer (Q.L.L.) on an ice surface, plays an important role in some phenomena which occur at temperatures near below the melting point, such as snow metamorphism, sintering, adhesion, accretion and crystal growth. Many studies related to the Q.L.L. have been carried out in the past 30 years to clarify its existence and the distinctive surface properties of ice.

Nakaya (1) and Weyl (2) have interpreted the adhesion observed between ice spheres and regelation in terms of mobile "liquid-like" surface structures. Jellinek (3) emphasized the existence of the mobile phase based on extensive studies on ice adhesion and reviewed the surface properties of ice.

On the other hand, Fletcher (4) has shown theoretically the existence of the proper surface structure and concluded that at temperatures above about -5°C the surface of ice is covered by the Q.L.L., whose thickness increases as the temperature approaches 0°C .

Direct evidence of the existence of the Q.L.L. on ice surfaces has been presented by many investigators using various experimental techniques: Photoemission by Nason and Fletcher (5), proton channelling by Golecki and Jaccard (6) and nuclear magnetic resonance by Kvlividze et al. (7), Anderson (8), Bell et al. (9) and Ocampo and Klinger (10).

A recent ellipsometrical study by Furukawa et al. (11) provided detailed information on the thickness and refractive index of the layer and its dependence on the crystallographic surface. Their results on the crystallographic surface support the theoretical treatment of the

growth kinetics of ice from the vapor phase presented by Kuroda and Lacmann (12).

Information on the dynamical properties of the Q.L.L., its difference from bulk ice or its "liquid-like" feature, is important to understand the above-mentioned snow and ice phenomena which are closely related to the surface properties of ice.

In this connection, this paper describes the dynamical properties of the Q.L.L., the correlation time for rotational molecular motion and the self diffusion coefficient in the Q.L.L. using pulsed nuclear magnetic resonance.

II. Experimental Procedures

In order to obtain the NMR signal due to ice surfaces, small ice particles of less than 150 μm in diameter were prepared at -30°C by freezing supercooled water droplets sprayed out from an atomizer on a clean teflon sheet. The particles were put into a glass cell for the NMR spectroscopy. To prevent sintering between ice particles, the glass cell was stored in a cold chamber whose temperature was kept below -80°C .

The NMR measurements were made using a JEOL FX100NMR spectroscope equipped with a spin locking unit and a temperature controlling unit and operated at 100 MHz. The temperature of a sample was controlled with an accuracy of $\pm 0.1^\circ\text{C}$, and for thermal equilibrium, every measurement performed at a certain temperature was started after keeping the sample for more than 30 minutes at that temperature.

To obtain the temperature dependence on both the intensity and the line width, most of the measurements were made in the process of the temperature rising from -100°C to -5°C .

Spin lattice relaxation time T_1 and that in a rotating frame $T_{1\rho}$ were measured by the inversion recovery and the spin locking methods, respectively.

III. Results

1. NMR signal due to surface mobile phase Figure 1 shows NMR spectra for the surface mobile phase accumulated 200 times at the various temperatures observed at 99.5 MHz, the broad signal due to crystalline ice is not seen within the range of observational frequency of 20 kHz.

The narrow signal was not detected at any temperature when only bulk ice was used, and the signals appearing in Fig. 1 were thought to be caused by a mobile phase at an interface between air and crystalline ice and/or at grain boundaries.

As is obvious in the figure, the line width and the intensity vary with temperature. It should be noted that the line width of the spectrum at -10°C is about 7 times that of ordinary water at $+5^\circ\text{C}$, which is shown for comparison on the left hand side. The intensity of the spectrum is proportional to the number of the mobile molecules. The relative intensity, which is normalized with the intensity at -5°C , and the line width variation with temperature are shown in Fig. 2. As the surface area was reduced by sintering in our experiment, the intensity, especially at -5°C , is expected to be larger. Although the relative intensity largely changed between -5°C and -10°C , line width variation was quite small.

2. Spin-lattice relaxation time(T_1) The spin lattice relaxation time, T_1 , was measured by the inversion recovery method at various temperatures. Figure 3 shows the relations between T_1 and the temperature for powder ice particles and a refrozen ice, where each point is an av-

erage of three times measurements in both cases. The refrozen ice was made by melting the powder ice slightly within the cell and thereafter freezing it rapidly at below -30°C . Microscopical observation revealed that a large number of tiny bubbles several $10\ \mu\text{m}$ in diameter were dispersed uniformly in the sample.

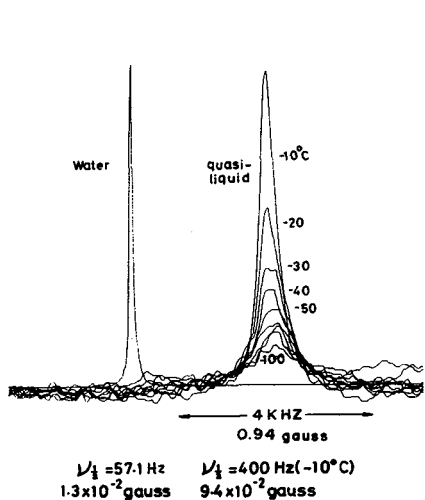


Figure 1. NMR spectra of the Q.L.L. observed at 99.5 MHz. Signal of liquid water was taken at $+5^{\circ}\text{C}$. Notice the difference in the line width between liquid water and the Q.L.L.

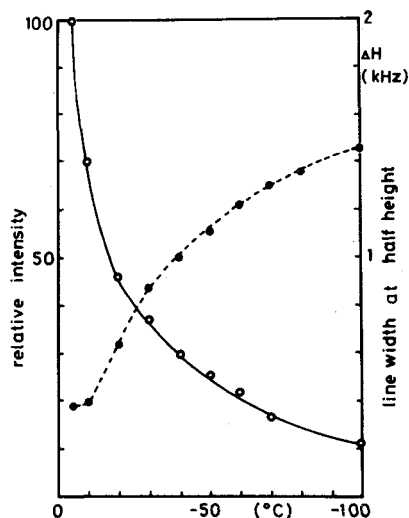


Figure 2. Intensity (solid line) and line width variation (dotted line) with temperature

The variance in T_1 between the two samples reflects some of the dynamical differences expected to be caused mainly by water vapor pressure around the inner and the outer surfaces. However, T_1 minimum appeared around -35°C in both samples.

The spin lattice relaxation time T_1 for proton is expressed in the following form (13),

$$\frac{1}{T_1} = \frac{3\gamma^4 \hbar^2}{10 r^6} \left(\frac{\tau}{1 + \omega_0^2 \tau^2} + \frac{4\tau}{1 + 4\omega_0^2 \tau^2} \right) \quad (1)$$

where, $\omega_0 = \gamma H_0$ is the resonant frequency, γ is the gyromagnetic ratio, r is the spin to spin distance and τ is the correlation time for rotational molecular motion. The correlation time at -35°C was evaluated to be 9.6×10^{-10} sec from the condition that T_1 is minimum for $\omega_0 \tau$ is about 0.6. Using this correlation time, the spin to spin distance, r , was evaluated to be about 1.66×10^{-10} m and 1.41×10^{-10} m for powder and refrozen ice, respectively. Assuming r does not change with temperature, τ at each temperature can be obtained by substituting the corresponding T_1 into eq. (1). In this case, $\omega_0 \tau \ll 1$ is reasonably considered at higher temperatures and $\omega_0 \tau > 1$ at lower temperatures compared to the minimum point given in Fig. 3.

Figure 4 illustrates the correlation time at various temperatures, where the value at 0°C was calculated by using T_1 at 0°C , which was obtained by extrapolating several points at lower temperatures.

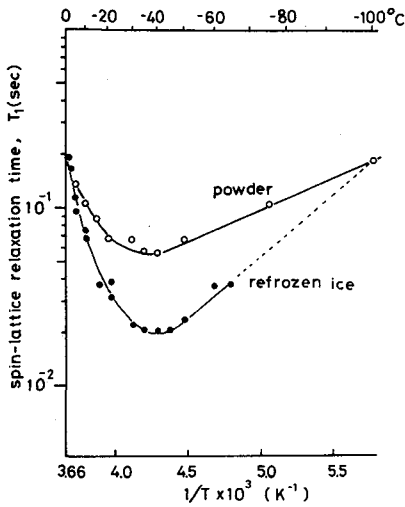


Figure 3. Spin lattice relaxation time, T_1 , vs. inverse temperature

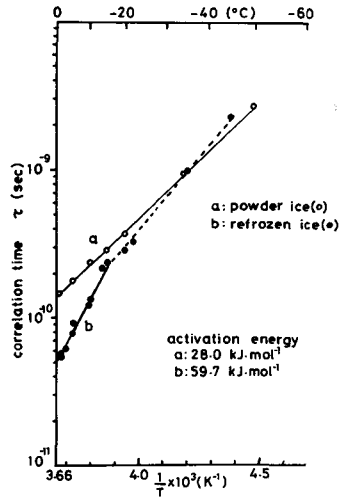


Figure 4. Correlation time for rotational motion, τ , vs. inverse temperature

The difference in τ for powder and refrozen ice is considerably large near the melting point; however, it decreases as temperature falls, and below -15°C , both samples become almost equal. The activation energy for rotational motion was 28.0 kJ/mol for powder ice and 59.7 kJ/mol for refrozen ice in the temperature range of 0 to -50°C and 0 to -15°C , respectively.

As is shown in Fig. 4, the correlation time of the Q.L.L. is in the order of 10^{-10} sec, which is much closer to that of water of 10^{-12} sec (14) than that of ice crystal of 10^{-5} sec (15). As compared with the correlation time of the Q.L.L. at 0°C and that of ordinary water, the Q.L.L. is movable with a frequency of about $1/25$ of that in ordinary water at 0°C .

3. Diffusion coefficient For proton, whose nucleus possesses spin $1/2$, the spin lattice relaxation time in a rotating frame, $T_{1\rho}$, is related to w_1 , the radio frequency, and D , the self diffusion coefficient, as follows (16):

$$d(1/T_{1\rho})/d(w_1^{1/2}) = (-\sqrt{2}\gamma^4 h^2 N)/(80\pi D^{3/2}) \quad (2)$$

where N is the number density of resonant nuclei. As is obvious in eq. (2), in plotting $1/T_{1\rho}$ vs. $w_1^{1/2}$, the slope gives a self diffusion coefficient, D . A typical result at -10°C is shown in Fig. 5. We obtained the self diffusion coefficient at temperatures between -1.5°C and -20°C . The results are listed in Table 1, where every value is an average of three measurements at each temperature.

Activation energy for diffusion by translational motion was evaluated to be 23.5 kJ/mol as is shown in Fig. 6. For comparison, the diffusion coefficient in a single crystal by Itagaki (17), in polycrystalline ice by Kuhn and Thürkauf (18) and in water (14) are also shown in the same figure.

The absolute value of the diffusion coefficient of the Q.L.L. is about four orders of magnitude smaller than that of water; however, it is remarkable that this value is larger than that of a single crystal of ice by two orders. In regard to the activation energy for diffusion, that

of the Q.L.L. is slightly larger than that of liquid water but is only about a third of a single crystal of ice.

Table 1

Temperature	Diffusion coefficient
-1.5°C	$3.08 \times 10^{-13} \text{ m}^2/\text{sec}$
-5.0°C	2.55×10^{-13}
-10.0°C	2.15×10^{-13}
-15.0°C	1.79×10^{-13}
-20.0°C	1.35×10^{-13}

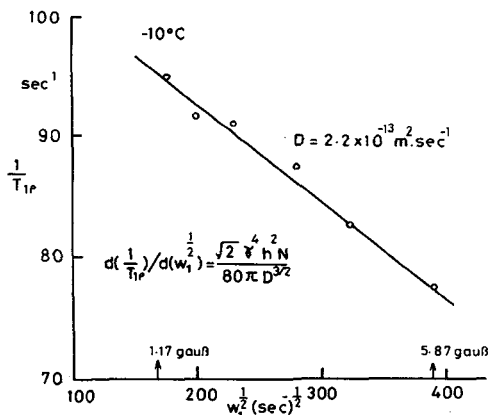


Figure 5. $T_{1\rho}$ variation with radio frequency at -10°C ; plotted $1/T_{1\rho}$ vs. $\omega_1^{1/2}$

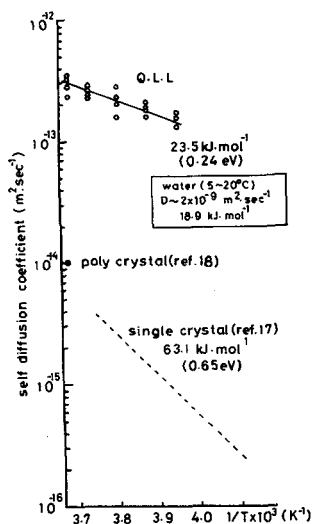


Figure 6. Diffusion coefficient of the Q.L.L. vs. inverse temperature

IV. Discussion and Conclusion

The intensity of the NMR signal was largely dependent on the particle size. In fact, in our experiment using ice particles larger than 200 μm in diameter, the signal was small and faint even at -10°C . However, the size of an individual crystal in an ice particle was mostly independent of the particles between 50 and 500 μm in diameter. Therefore the NMR signal is considered to be due mainly to inner or outer free surfaces and the contribution from grain boundaries seems to be small in this case. Undoubtedly, the existence of the mobile water phase at grain boundaries at very close to the melting point has been shown by Ohtomo and Wakahama(19). Further studies are needed to clarify the difference between the dynamical properties of a free surface and of a grain boundary, because molecules at the grain boundary are expected to have a higher crystallinity than those in a free surface.

As the surface area decreases due to sintering between ice particles, the intensity variation with temperature does not correspond to the thickness variation of the Q.L.L. with temperature. Regardless of

the large variation of the intensity between -5°C and -10°C , the line width does not change very much. This fact suggests that the thickness of the Q.L.L. changes largely within this temperature range ; however, very small changes occur in the dynamical properties.

In our experiment, the NMR signal due to the mobile molecules at the surface was observed even at a temperature of as low as -100°C . This finding indicates that some surface molecules can rotate at a much higher frequency than in bulk ice even at -100°C , however, it should not be considered that the Q.L.L. still remains at such a low temperature.

The number of mobile molecules is dependent not only on the temperature but also on the degree of the perfection and the crystallographic orientation of the surface. Our result differs largely from the ellipsometrical observation (11) of the temperature at which the mobile phase appears. The difference is caused mainly by the difference in the power of detection of each experimental method than by the difference in the sample. The question "how many mobile molecules make the surface very liquid-like ?" can not be answered from the results of our experiment using NMR; however, this method does provide information on the surface molecule motion.

It was found that the molecules at the surface rotate at a frequency of about five orders larger than that of crystalline ice at temperatures between 0 to -20°C , and this frequency corresponds to only about $1/25$ of that of a molecule in liquid water.

Regarding diffusion by the translational motion, the surface molecule diffuses at a rate of about two orders larger than that in bulk ice. It can be concluded that the surface molecule possesses some properties which are much closer to those of liquid water than to those of crystalline ice, but they are apparently different from those of liquid water even at temperatures very close to the melting point.

The activation energy both for the rotational and the translational motion of the surface molecule appear to be located between those of liquid water and crystalline ice.

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COMMENTS

E. OFFENBACHER

Can you estimate the thickness of the Q.L.L. from the relative intensity of your signals and your sample parameters ?

Answer :

Yes I can estimate the thickness of the Q.L.L. by assuming the specific surface area, but in our experiment, especially at higher temperature (-5°C and -10°C), the surface area reduces by sintering during experiment and further correction is required.

P. PISSIS

I think, it is important for such measurements to have a large surface/volume ratio. I wonder, in this connection, why you don't use emulsified water droplets where you can easily get droplets of a few μm in diameter. Is any reason for not using such systems ?

Answer :

To obtain the MNR signal due to ice surface, the sample with the larger surface/volume ratio is the better. However the purpose of our study is to know the properties of the quasi-liquid layer between air and crystalline ice. So we used rather large ice particle but with free outer surface.

P.L.M. PLUMMER

I am very pleased to see your very nice results. My interpretation of your results suggest that since the rotational times of the quasi liquid layer are very similar to those of liquid water but the diffusion times are between those of liquid and solid suggest the layer can also be described as quasi-solid amorphous layer with a high concentration of defects, no long range order and a high degree of rotational freedom. Do you agree and could you amplify on your opinion of the structure of this layer implied by your data ?

Answer :

Yes. I agree with you basically. We assume that diffusion takes place with molecular unit and we evaluated the spin to spin distance to be about 4 \AA , so some crystalline structure is expected to be remained in the quasi-liquid layer.

Remark of J.W. GLEN :

Relative to Dr PLUMMER's comment, the values of D at $10^{-12} \text{ m}^2 \text{ s}^{-1}$ from this paper are about half way between those of water ($\sim 10^{-9} \text{ m}^2 \text{ s}^{-1}$) and ice ($\sim 10^{-15} \text{ m}^2 \text{ s}^{-1}$), and the activation energy is more like that of water.