Surface Vibrational Spectroscopic Study of Surface Melting of Ice

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Surface melting on the (0001) face of hexagonal ice (I_h) was studied by sum-frequency vibrational spectroscopy in the OH stretch frequency range. The degree of orientational order of the dangling OH bonds at the surface was measured as a function of temperature. Disordering sets in around 200 K and increases dramatically with temperature. The results show that the disordered (quasiliquid) layer on ice is structurally different from normal liquid water.

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Faraday first proposed the existence of a liquidlike layer on an ice surface below the bulk melting temperature, which we know today as surface melting or premelting of ice [1]. It is believed to play an important role in phenomena such as reduction of the frictional coefficient of ice, electrification of thunder clouds, glacier flows, frost heaves, and ozone depletion [2]. The problem has been the subject of numerous theoretical investigations [3–6] and experimental studies including photoemission [7], proton backscattering [8], ellipsometry [9,10], optical reflectometry and interference microscopy [11], nuclear magnetic resonance [12,13], low energy electron diffraction [14], glancing angle x-ray diffraction [15], helium atom scattering [16], and atomic force microscopy [17,18]. While most of these experiments seem to have confirmed the existence of the liquidlike layer on the ice surface, the details such as the onset temperature and the temperature dependence of the layer thickness vary widely from experiment to experiment. Today, the exact nature of surface melting of ice remains controversial, and the structure and properties of the quasiliquid layer are far from being fully understood.

Recently, sum-frequency generation (SFG) vibrational spectroscopy has been established as a powerful tool for probing surfaces and interfaces [19]. It is highly surface specific and sensitive and does not require an ultrahigh vacuum environment. Therefore, it is ideally suited for studies of surfaces and interfaces of ice and water. We report here our study on surface melting of ice using this technique. Our results show that disordering of the (0001) surface of hexagonal ice (I_h) becomes detectable at 200 K and increases as the temperature increases. A comparison of the results for the ice surface and the supercooled water surface, however, reveals that the structures of the quasiliquid layer on ice and the surface layer of liquid water are not the same.

The SFG vibrational spectroscopy technique has been described in earlier publications [19,20]. It has been shown that the SFG output in reflection from a surface excited by two overlapping input beams, one visible at ω_1 and the other infrared at ω_2, is proportional to the square of an effective surface nonlinear susceptibility, $\chi^{(2)}_{\mathrm{eff}}(\omega_s = \omega_1 + \omega_2)$, defined as

$$\chi^{(2)}_{\mathrm{eff}} = [\mathbf{L}(\omega_s) \cdot \mathbf{e}_s] \cdot \boldsymbol{\chi}^{(2)} : [\mathbf{L}(\omega_1) \cdot \mathbf{e}_1][\mathbf{L}(\omega_2) \cdot \mathbf{e}_2], \tag{1}$$

where $\mathbf{e}_i$ is the polarization unit vector of the optical field at ω_i, $\mathbf{L}(\omega_i)$ is the tensorial Fresnel factor, and $\boldsymbol{\chi}^{(2)}$ denotes the surface nonlinear susceptibility tensor. If the infrared input is tuned across the surface vibrational resonances, the following resonant behavior of $\boldsymbol{\chi}^{(2)}$ is expected:

$$\boldsymbol{\chi}^{(2)}(\omega_2) = \boldsymbol{\chi}^{(2)}_{\mathrm{NR}} + \sum_q \frac{\mathbf{A}_q}{\omega_2 - \omega_q + i\Gamma_q}, \tag{2}$$

where $\boldsymbol{\chi}^{(2)}_{\mathrm{NR}}$ is a nonresonant background and $\mathbf{A}_q$ is the amplitude of the qth vibrational mode. We are interested in the OH stretch vibrational modes.

For the experiment, ice single crystals were grown by the Bridgman method from deionized water [21]. The basal-face samples were cut and oriented to within 2° in a cold compartment. The oriented surface was covered by a fused silica plate coated with an octadecyltrichlorosilane monolayer. The sample was then mounted in a sealed chamber (described in Ref. [22]) which could be cooled to 173 K with an accuracy of 0.1 K. For the spectroscopic measurement, the sample chamber was brought to the SFG setup. With the chamber in thermal equilibrium, the fused silica plate was separated from the sample, exposing the smooth (0001) ice surface in equilibrium with the saturated water vapor. This preparation procedure is similar to that described in Ref. [15] except that our silica cover plate was hydrophobic and therefore easy to separate from the ice crystal. We have chosen to study the (0001) basal face of ice not only because it is the most stable surface of ice I_h, but also because its hexagonal symmetry makes the SFG output azimuthally isotropic.

The SFG experimental setup has been described elsewhere [19]. In this experiment, a 1.5 mJ visible laser pulse with a wavelength of 532 nm and a 100 μJ infrared pulse tunable from 2900 to 3850 cm^{-1} (with a linewidth $\approx$6 cm^{-1}) were overlapped at the sample surface with incidence angles of 45° and 57°, respectively. Both input pulses had a beam diameter of $\sim$1 mm, a pulse duration of

$\sim$15 ps, and a repetition rate of 20 Hz. The SFG output was detected in the reflected direction. In the strong infrared absorption range of ice (2900 to 3570 cm^{-1}), the infrared input pulse energy was reduced to about 20 μJ to avoid laser heating or damage. Furthermore, the sample chamber was put on a computer-controlled two-dimensional raster stage to prevent input pulses from repeatedly hitting the same spot. With such precautions, the SFG output was found to be linearly proportional to the infrared input, indicating negligible laser heating or damage.

Shown in Fig. 1 is a typical SFG spectrum of the (0001) basal surface of ice at 232 K in comparison with that of the liquid water surface at 293 K. The polarization combination is ssp, which stands for s-, s-, and p-polarized sum-frequency output, visible input, and infrared input, respectively. The SFG output was calibrated against a reference z-cut quartz crystal [20], yielding the spectra of $|\chi_{\mathrm{eff}}^{(2)}|^2$ in MKS units. As seen in Fig. 1, the spectrum of the ice surface is dominated by a strong but relatively broad peak at $\sim$3150 cm^{-1} that resembles the main OH stretch peak observed in the Raman spectrum of ice I_h [23]. This peak is associated with the bonded OH stretching modes in the hydrogen bonding lattice. The same peak appears in the SFG spectrum for the silica/ice interface [22]. In both cases, the peak decreases as the temperature increases [22], but it remains significantly different from that of liquid water (Fig. 1). We do not know how the temperature dependence of this peak is related to the appearance and change of the quasiliquid layer on the ice surface. A molecular dynamics calculation is probably needed to find the answer.

The SFG spectra for the ice and water surfaces in Fig. 1 also exhibit a sharp peak around 3695 cm^{-1} associated with the stretch vibration of the free OH (or dangling OH) bonds protruding from the surfaces [24]. This is a feature that belongs to the ice surface layer and therefore can be used to characterize the surface structure. By measuring the free OH peak with different input/output polarization combinations we can deduce an approximate orientational distribution for the free OH bonds. We expect that the orientational distribution would be very narrow if the surface layer has an ordered crystalline structure but would broaden appreciably if the layer becomes liquidlike. Figure 2 displays a set of ssp and ppp spectra of the free OH peak for the ice surface at different temperatures. A similar set of spectra for the water surface is presented in Fig. 3. The solid lines in Figs. 2 and 3 are fits of the spectra using Eq. (2), from which we obtained the amplitudes $A_{q,\mathrm{eff}}(ssp)$ and $A_{q,\mathrm{eff}}(ppp)$ as a function of temperature for the free OH stretch mode. From Eqs. (1) and (2), we could further deduce the tensor elements $A_{q,xxz} = A_{q,yyz}$ and $A_{q,zzz}$ for each temperature.

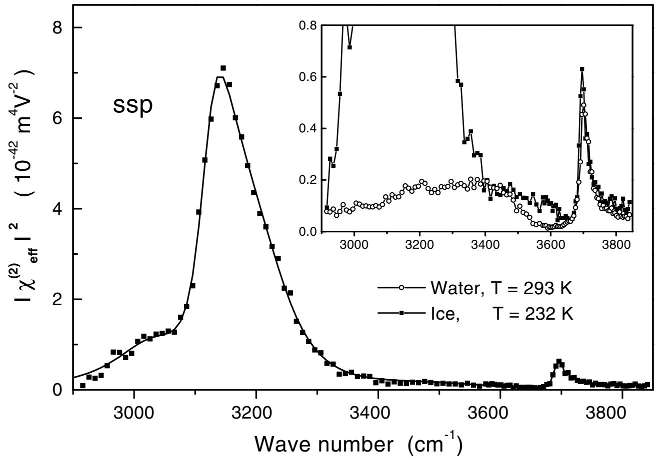

FIG. 1. SFG spectrum of the (0001) surface of ice at 232 K (solid symbols). The inset shows a comparison of the spectrum with that of the water surface at 293 K (open symbols). The polarization combination is ssp.

To obtain information about the orientational distribution of the free OH bonds, we note that [25]

$$A_{q,xxz} = A_{q,yyz} = \frac{1}{2} N_{\mathrm{S}} \int_0^{\frac{\pi}{2}} [a_{\zeta\zeta\zeta}(\cos\theta - \cos^3\theta) + a_{\xi\xi\zeta}(\cos\theta + \cos^3\theta)] f(\theta) \sin\theta \, d\theta \,, \tag{3}$$

$$A_{q,zzz} = N_{\mathrm{S}} \int_0^{\frac{\pi}{2}} [a_{\zeta\zeta\zeta} \cos^3\theta + a_{\xi\xi\zeta}(\cos\theta - \cos^3\theta)] \times f(\theta) \sin\theta \, d\theta \,. \tag{4}$$

Here N_{S} is the surface density of the free OH bonds; $f(\theta)$ is the polar orientational distribution of the free OH bonds in the tilt angle θ $(0 \le \theta < \pi/2)$ from the surface normal (the azimuthal distribution is isotropic); $a_{\zeta\zeta\zeta}$ and $a_{\xi\xi\zeta} = a_{\eta\eta\zeta}$ are the two independent nonvanishing hyperpolarizability elements of the OH bonds with $\hat{\zeta}$ along the bond direction, and from the Raman data, $a_{\xi\xi\zeta} = a_{\eta\eta\zeta} = 0.32 a_{\zeta\zeta\zeta}$ [24]. If we simply assume a truncated flat distribution for $f(\theta)$, i.e., $f(\theta) = \mathrm{const}$ for $0 \le \theta \le \theta_{\mathrm{M}}$ and $f(\theta) = 0$ for $\theta > \theta_{\mathrm{M}}$, then we can determine θ_{M} from Eqs. (3) and (4) knowing the values of $A_{q,xxz}$ and $A_{q,zzz}$. The deduced value of θ_{M} (Fig. 4) gives us a measure of the angular spread of the free OH bond orientation.

We can also use the orientational order parameter defined as

$$S = \int_0^{\frac{\pi}{2}} \frac{3\cos^2\theta - 1}{2} f(\theta) \sin\theta \, d\theta \tag{5}$$

to describe the degree of ordering of the OH bond orientation. If $\theta_{\mathrm{M}} \to 0$, then $S \to 1$ corresponding to perfect orientational order. The other extreme is $\theta_{\mathrm{M}} = \frac{\pi}{2}$ leading to $S = 0$ for total disorder. We have calculated S from the deduced θ_{M} for free OH bonds at both ice and water surfaces at various temperatures and displayed the result in Fig. 4. We notice that S is close to 1 below 200 K

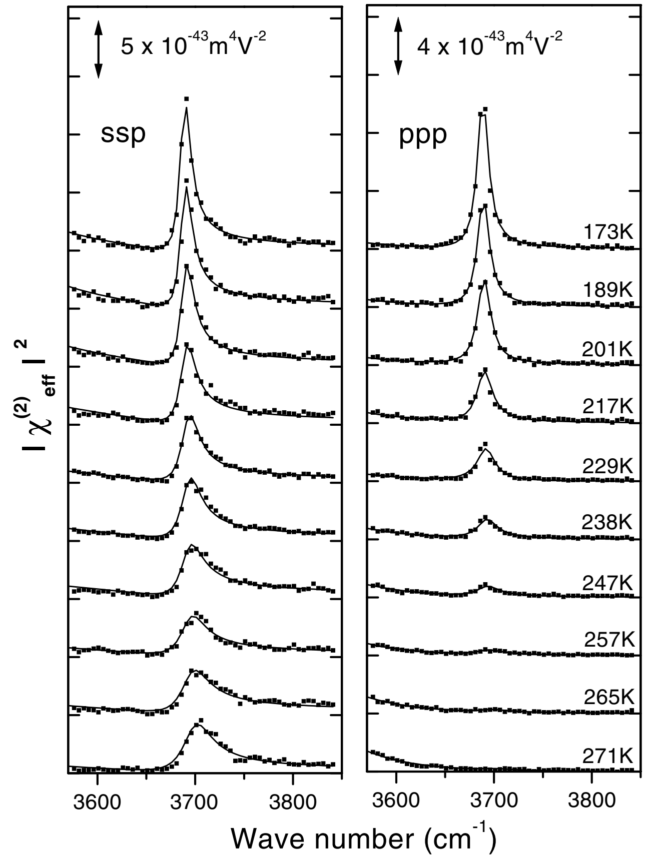

FIG. 2. SFG spectra of the free OH stretch mode for the (0001) surface of ice at various temperatures. The polarization combinations are *ssp* and *ppp*.

and drops appreciably as the temperature increases above 200 K.

Figure 4 also shows that within the experimental uncertainty, there is no abrupt jump in the order-disorder transition, in agreement with the prediction from molecular dynamics simulations [5,6]. An apparent onset of surface melting can be defined as the point at which surface disorder becomes detectable. Our experiment indicates that the onset of surface melting of ice is around 200 K, below which the surface monolayer is still solid but above which it becomes increasingly disordered. Our onset temperature is lower than those obtained by other techniques. This is presumably because our SFG technique is more surface specific and sensitive to the disorder of the surface monolayer. For example, the recent measurement of x-ray scattering at glancing angles found that for the (0001) ice surface, the onset of surface melting was at 259.5 ± 2.5 K below which no surface melting could be observed [15]. However, the measurement did not have enough sensitivity to detect a few monolayers of the quasiliquid. Extrapolation of the data to zero quasiliquid layer thickness to obtain the onset temperature for surface melting could yield too high a value.

Unlike other techniques that measure how the quasiliquid layer grows in thickness and extends into the bulk, SFG measures only disorder in the top surface layer. However, as shown in Fig. 4, we have observed a continuous decrease of ordering in the surface layer with an increase of temperature. This indicates that it is a quasiliquid layer with a strong temperature-dependent structure and suggests that there should be a structural variation across the quasiliquid layer grown on the ice surface. This picture is consistent with the results of molecular dynamics simulations [5,6] but different from the simple models of surface melting used in the analyses of many experimental results. The latter assume a quasiliquid layer with uniform structural properties.

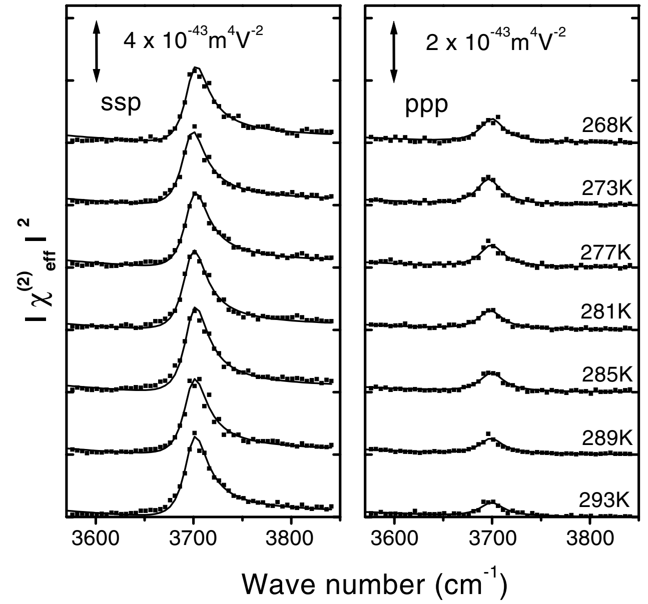

FIG. 3. SFG spectra of the free OH stretch mode for the water surface at various temperatures. The polarization combinations are *ssp* and *ppp*. Note that at 268 K water is supercooled.

It has been suggested that impurities may affect surface melting of ice [4]. In our experience, molecular impurities

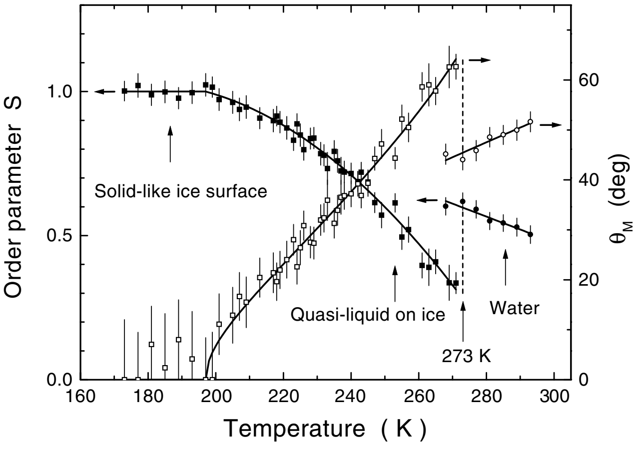

FIG. 4. Orientational order parameter *S* (solid symbols) and maximum tilt angle θ_M (open symbols) for the free OH bonds on the (0001) ice and water surfaces. The solid lines are guides to the eye.

at the water or ice surface are likely to suppress the dangling OH bonds. In the current experiment, the impurity effect is believed to be unimportant because of the clear presence of the free OH bonds. We are in the process of investigating the impurity effect by purposely dosing adsorbates on the ice surface.

Another important result displayed in Fig. 4 is that near the bulk melting temperature 273 K, the order parameter S of the ice surface is even lower than that of the supercooled water surface. Although not physically impossible, this seems surprising and needs a good theoretical explanation. In any case, it indicates that the quasiliquid layer on ice is different from the surface layer of water. There is a long-debated issue whether surface melting of ice has a complete or incomplete wetting property (i.e., whether the thickness of the quasiliquid layer diverges or remains finite as the temperature approaches 273 K) [11]. Our result here favors the incomplete wetting scenario because otherwise one would expect the surface structure of the quasiliquid layer to approach that of normal water as the layer thickness diverges.

In summary, we have used SFG vibrational spectroscopy to study surface melting of ice by probing the structure of the very first monolayer of the (0001) surface of ice I_h. Orientational disordering of the surface molecules as a signature of surface melting appears to set in around 200 K. The degree of disorder increases with temperature and shows that the quasiliquid layer on the ice surface is structurally different from the normal water surface layer. Our results suggest that the usual model treating the quasiliquid layer as a structurally uniform film should be modified.

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[25] Equations (3) and (4) are derived under the assumption that the orientation of a free OH bond is static within the OH stretch relaxation time $1/\Gamma_q$. In the case of rapid orientational motion, Eqs. (3) and (4) should be modified with motional average, although the correction is very small.