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# The distinct vibrational signature of grain-boundary water in nano-crystalline ice films

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## Abstract

We have characterized the vibrational response of grain-boundary water in crystalline ice films consisting of nanometer-sized crystalline domains. The crystalline ice is grown isothermally on Ru(0001), and the crystalline domain size is controlled by varying the crystallization temperature. A distinct vibrational feature in the OD stretching region is observed, which we attribute to grain-boundary water. The relative contribution of the grain-boundary vibrational response to the overall spectrum increases with decreasing crystal domain size. Its central frequency is located around 2500 $\text{cm}^{-1}$, between that of amorphous solid water and crystalline ice.

The characterization of the grain boundaries of ice crystals is important for understanding a wide variety of environmental subjects such as electrification of clouds [1,2], phenomena such as soil freezing, frost heave and permafrost [3,4] as well as fundamental subjects such as the sintering, coarsening, transport behavior and many other properties of bulk ice [5–9]. The understanding of crystalline grain boundaries is also of importance for chemical reactions on ice, such as the formation of prebiotic organic molecules in the interstellar medium [10] and reactions that lead to ozone depletion in the stratosphere [11]. Ice grains grown on a solid surface always have a finite grain size, which depends on the condition of the preparation [5,6,12]. Thus, in addition to the surface of ice exposed to the vacuum, there exist many grain–grain interfaces. Molecules and/or ions that can react on ice may diffuse over the surfaces and interfaces of ice grains; bulk diffusion is much less likely from the viewpoint of thermodynamics. The interaction between such molecular moieties and the ice surface/interface (i.e., water molecules at the grain boundary) therefore determine the fate of these molecules. As a result, the behavior of the molecular monolayer of water at the surface of ice grains and clusters has received much attention. Particularly noteworthy are infrared (IR) spectroscopic studies as sensitive and non-destructive methods to characterize the vibrational properties of aqueous solids. Indeed, Devlin, Buch, and co-workers have extensively investigated size-selected water clusters in the gas-phase by IR spectroscopy and have found specific vibrational response of water at the surface and right below the surface (sub-surface) in small water clusters (Refs. [13,14] and references therein). Such information has not yet been obtained for water at the interfaces between crystalline grains in solid films.

Here, we report the vibrational response of grain-boundary water molecules between crystalline grains at temperatures around 150 K. We have prepared well-defined nanometer-sized crystalline ice (CI) grains by the isothermal crystallization of amorphous solid water (ASW) films grown on a Ru(0001) surface. The number

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and size of the CI grain can be controlled in our isothermal crystallization experiments through the different temperature dependences of the nucleation rate and growth rate of the CI in the bulk of the ASW films [5,12,15–18]. Our results reveal a distinct vibrational response of grain-boundary water molecules localized around the nanometer-sized CI grains.

The experimental apparatus used in this work has already been described elsewhere [17–19]. Briefly, the infrared light from the Fourier transform IR-spectrometer (JASCO FT/IR-550) was p polarized through a ZnSe polarizer. It was then focused on the sample surface in the ultrahigh vacuum (UHV) chamber by a concave mirror through a BaF viewport at an 85° grazing angle of incidence. The IR light reflected from the sample was detected by a mercury–cadmium–telluride (MCT) detector. The light paths outside the UHV chamber were purged by pure nitrogen gas to avoid absorption by ambient air, which contains $CO_2$ and $H_2O$. IRAS spectra were recorded at $4\ \mathrm{cm}^{-1}$ resolution with 20 scan (40 s) averages. The IR absorbance $A$ is defined as $A = -\ln(R/R_0)$, where $R$ and $R_0$ are the reflected intensities with and without the water layers on the substrate, respectively. We investigated fully deuterated water ($D_2O$) because the IR-spectrometer has a higher sensitivity in the O–D stretch frequency range than in the O–H stretch range of $H_2O$.

The Ru(0001) substrate was cleaned using standard sputtering, annealing, oxidation and flashing cycles in the UHV chamber with a base pressure of $\sim 1 \times 10^{-10}$ Torr. The temperature of the sample surface is measured by C-type (W5%Re–W26%Re) and K-type (Alumel–Chromel) thermocouples spot-welded to the edge of crystal. Each of the output Seebeck voltages is measured by a digital multimeter, referenced to liquid nitrogen temperature. The substrate temperature was then carefully calibrated by temperature-programmed desorption (TPD) measurements of $D_2O$ from Ru(0001) prior to the experiment [20].

The degree of thickness of the water layer is expressed here in monolayers (ML). one ML is determined by the desorption amount of the first water layer strongly interacting with the Ru(0001) surface that gives rise to one desorption feature near 180 K in the thermal desorption experiments [20]; this feature saturates with exposure, after which multilayer desorption occurs near 160 K. Thin films of ASW of $\sim$50 monolayers (ML) were deposited on the surface at $\sim$90 K. After the deposition of ASW, the layers were heated to the designated isothermal temperature, $T$, where IRAS spectra were recorded continuously at 40 s intervals. The IRAS spectra measured during the ASW crystallization can be reproduced very well by a linear combination of the spectrum at $t = 0$ (amorphous solid water) and the spectrum after staying at temperature $T$ sufficiently long that the spectral response does not change any longer (crystalline ice with possible contributions form grain-boundary water, see below). The 'converted fraction' is defined here as the long-time contribution divided by the weighted sum of the two [17,18,21]. The average CI grain size in the converted CI films was controlled by varying $T$ owing to the different activation energies for nucleation and growth; At high $T$, nucleation is dominant and many small crystalline grains appear, whereas at low $T$ the nucleation probability is low and relatively large (tens of nm) crystalline grains appear in the films [5,12,15–18].

Fig. 1 shows typical IRAS spectra of ASW and CI films on Ru(0001), where each spectrum is normalized by the spectrally integrated intensity in the O–D stretch region. An absorption band with a large width at 2400–2600 $\mathrm{cm}^{-1}$ in Fig. 1 is typical of the OD stretching vibrational mode ($\nu_{OD}$) of $D_2O$ forming a hydrogen bond network, where intramolecular and intermolecular coupling among $D_2O$ molecules cause a large peak-width of $\nu_{OD}$ [14,22]. The first moment of the absorbance peak is located at higher frequency for ASW: after crystallization the peak shifts to lower frequency due to the well-ordered and more strongly hydrogen-bonded network of CI, as shown in Fig. 1.

As shown in Fig. 1b in detail, the spectrum of CI consists of three major noticeable absorption peaks at $\sim$2340, $\sim$2440 and $\sim 2500\ \mathrm{cm}^{-1}$. With increasing crystallization temperature $T$, the high-frequency peak shoulder increases in amplitude relative to the low-frequency shoulder, as indicated by the arrows in Fig. 1b. We attribute this effect to the variations in average crystal size with varying temperature. This observation is reminiscent of previous TPD studies [15,16], where differently shaped TPD spectra of probe molecules desorbing from CI surfaces were observed, depending on the crystallization conditions. The difference of the TPD shape was attributed to the residual non-crystallized component surrounding the annealed CI grains, which resists conversion to CI [23,24]. As will be described below, our results provide new insight into the nature of this residual component: it is shown to be distinctly different from the amorphous phase, and we identify it as grain-boundary water.

We note two possible effects [25,26] that may complicate a straightforward interpretation of the IRAS spectra:

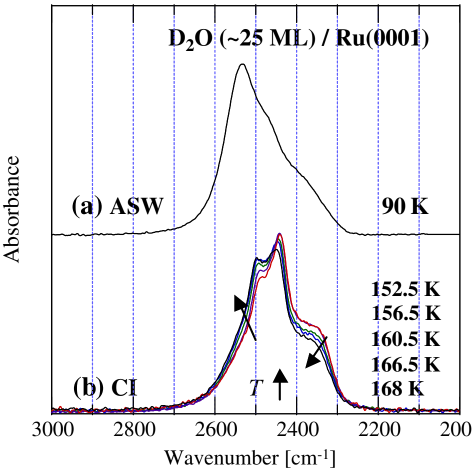

Fig. 1. Typical IRAS spectra of ASW ($\sim$25 ML) (a), crystalline ice (b). The spectra were normalized by the integral intensity of the absorbance.