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Bilayer-by-Bilayer Surface Melting of Crystalline Ice

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Over 150 years ago, Faraday proposed the existence of a liquid-like layer at ice surfaces below the bulk melting temperature. This layer is important for surface chemistry and glacier sliding close to sub-freezing conditions. Since Faraday's discovery, the properties of this water-like layer have been intensely debated, entailing considerable controversy. The experimentally reported onset temperature for quasi liquid layer (QLL) formation varies between 200 K and 271 K. Moreover, most experimental work shows that with increasing temperature, the QLL thickness gradually and continuously increases from the onset temperature up to the bulk melting point, with reported thicknesses varying from 2 nm to over 45 nm at 271 K. In contrast, early simulations showed that the QLL is formed in a more quantized, bilayer-by-bilayer manner.

To elucidate the precise temperature variation of the QLL, and its nature, we investigate the surface melting of ice Ih by combining non-contact, surface-specific vibrational sum frequency generation (SFG) spectroscopy and spectra calculated from molecular dynamics simulations. In our SFG experiment an 800 nm and a 3 μm laser pulse are combined at the interface and the sum-frequency light is detected. Being a second-order nonlinear process, SFG is forbidden in centrosymmetric materials such as the proton disordered ice studied here. At the interface this symmetry is broken, thus allowing us to specifically probe the vibrational response of the interfacial region. The signal is strongly enhanced when the infrared laser pulse is resonant with a molecular vibration. Here we use the O-H stretch vibration of the interfacial water molecules to report on the (molten or non-molten) state of the interface.

Using SFG, we probe the outermost water layers of distinct single crystalline ice faces at different temperatures. Macroscopic single-crystalline ice samples are grown from a melt using the seed extraction method. Afterwards the samples are oriented and cut to obtain a specific face. For the basal face, a stepwise, sudden shift in the SFG spectrum to higher frequency occurs around 257 K, which means that the hydrogen-bonded structure of the outermost water layers weaken at this temperature. The spectral calculations from the molecular dynamics simulations reproduce the experimental findings. Moreover, both the experimental and the calculated spectra show only a very weak change in the dangling OH bond. From the combined experimental and simulated surface-specific vibrational spectroscopy, we conclude that the thickness of the quasi liquid layer changes in a non-continuous, stepwise fashion around 257 K. Below this temperature, the first bilayer is already molten; the second bilayer melts at this transition temperature.

Significance statement

For reactions taking place on ice surfaces the molecular level structure is very important, i.e. an ice- or liquid-like surface. Our results show a weakening of the hydrogen bond structure around 257 K, which we assign to a phase transition from one-to-two molten bilayers.

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