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Structure and Dynamics of Ice Surfaces studied with Sum Frequency Generation Spectroscopy

The ice project involves studying the ice-air interface to provide better understanding of the nature of the quasi-liquid-layer (QLL), the presence of which was predicted on ice surfaces by Faraday as early as 1879. Despite the extensive theoretical and experimental research on characterizing the QLL, the thickness of the QLL and the onset temperature of the QLL remain highly controversial.

Single-crystalline boule of ice

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Our approach is to probe the ice-air interface using vibrational sum frequency generation spectroscopy (SFG), a noninvasive technique that is capable of providing vibrational information of specifically the outermost monolayer of water molecules, giving detailed information of the intermolecular hydrogen bond strengths.

In order to investigate the ice-air interface, well-defined single-crystalline ice is necessary. Ice boules were grown from the melt using the seed extraction method, based on the Czochralski process. The ‘seed’ was taken from growing “Lake Ice” and extracting the best single-domain structure out of it. Single-crystal ice boules 7 cm in diameter and 3 cm in length were obtained by slowly pulling out the seed crystal from the melt at an optimized rate and temperature setting. The single crystallinity was verified using the Rigsby Stage, which is a setup of two cross-polarizers. The crystal orientation was confirmed to using Formvar etching and finally by X-ray diffraction.

SFG experiments were conducted on basal single-crystalline hexagonal ice in the bonded-OH and free-OH spectral regions. Interestingly, the two regions gave contrasting results. The SFG intensity in the bonded-OH region decreased by a factor of 5 upon increasing the temperature – which could be directly related to a decrease in the hydrogen bond strength and a decrease in the ordering of interfacial molecules upon increasing the temperature. Also there was a shift of the hydrogen-bonded OH stretch band to higher frequencies at 257 K. The abrupt frequency shift indicates weakening of the hydrogen bond strength – indicating abrupt melting of the QLL at the transition temperature. Interestingly, the SFG intensity in the free-OH region showed only a weak, continuous dependence on temperature along the range 235 to 269 K. This weak affiliation to temperature, along with no frequency shift of the band, seems to suggest that the hydrogen bonding in the outermost surface structure is rather consistent.

Rigsby stage displaying what a multi-domained ice looks like

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SFG simulations (completed by collaborators) in the bonded and free OH regions were supportive of the experimental results and confirmed the bilayer melting fashion at 257 K for basal ice, whereas a gradual melting in case of secondary prism ice phase.

Combining results from both spectral regions led to the conclusion that the QLL is already present at temperatures lower than 230 K and that it melts in a bilayer-by-bilayer manner. Also, a comparison of the QLL SFG intensity to that of ice and supercooled water suggests that the QLL exhibits characteristics more similar to that of ice than water, thus having stronger hydrogen bonds than in water.