

Unveiling subsurface hydrogen-bond structure of crystalline ice

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Determinations of structural reconstruction and molecular orientation at surfaces of ubiquitous water ice are challenging due to the inherent difficulty in probing surfaces of the fragile and insulating material through traditional experimental approaches. Because buried subsurface structures govern the physicochemical properties of topmost surfaces [1], unveiling the subsurface structures is of crucial importance for an ultimate understanding of various heterogeneous ice-surface processes vastly taking place on earth and in the universe. For the basal face of crystalline ice Ih, we have tackled this problem with a non-invasive surface-sensitive method of sum-frequency generation (SFG) vibrational spectroscopy with state-of-the-art phase detection [2] in combination with molecular dynamics simulations and *ab initio* quantum calculations [3].

Here we demonstrate that the SFG spectra of isotope-diluted crystalline ice Ih are highly sensitive to the symmetry breaking of inter-bilayer hydrogen bonds at subsurface. The observed $\text{Im}\chi^{(2)}$ spectrum for the hydrogen bonded OH-stretch vibration of HDO ice Ih(0001) at 120 K shows positive and negative peaks at lower and higher frequencies, respectively. As a H-bond that connects neighbouring molecules becomes stronger, the frequency of local OH-stretch vibration involved in the H-bond decreases [4]. Therefore, our result suggests that the OH oscillators pointing toward the bulk (negative peak) form weaker H-bond than those pointing toward the surface (positive peak). From the analysis of the observed spectra, we will discuss that, in contrast to the bulk, the strength of hydrogen bond strongly depends on the orientation of water molecules at subsurface due to asymmetric librational fluctuation and the cooperative nature of hydrogen bond.

References

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