The cool state of water: Infrared insights into Ice

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Summary

Water is an extraordinary substance. It owes its characteristic anomalous properties to a network of strong hydrogen bonds present between water molecules. Ice is frozen water. In bulk ice, water molecules hold regular positions in the crystal. Nevertheless, the behaviour of ice can be dynamic and exciting, especially at the surface. At temperatures well below bulk melting, the surface of ice is covered by a liquid premelted layer. This water layer governs many geophysical processes and may be a significant factor in the low friction of ice.

This thesis describes the properties of ice and related systems at the molecular level. For this purpose we employ a variety of spectroscopic techniques and make use of stretching vibrations as sensitive probes of the molecular structure. The position, amplitude, and width of the stretching bands are utilized to describe the molecular properties and structure. The scientific insights from these studies are summarized below.

As a first experiment, we study the dissipation of vibrational energy using pump–probe spectroscopy. An intense pump pulse resonantly excites OD stretches of dilute HDO molecules and the population dynamics are probed using a time-delayed probe pulse. In ice we find the dissipation of the vibrational energy to decelerate with increasing temperature. The vibrational lifetime is observed to increase from $480 \pm 40$ fs at 25 K to $860 \pm 60$ fs at 265 K. These lifetimes are remarkably shorter than the vibrational lifetime in the liquid phase, which has a value of 1.7 ± 0.1 ps at 274 K and increases to 2.24 ± 0.09 ps at 343 K. The increase in vibrational lifetime with temperature is quite unusual because the vibrational lifetime generally decreases with temperature.

We also investigate the vibrational lifetime of similar water molecules in a hydrated lithium nitrate crystal. The crystal water contains OD groups with three distinct hydrogen bonds. The vibrational lifetime of the three hydrogen-bonded species is observed to increase with decreasing hydrogen-bond strength. Furthermore, the vibrational lifetime is found to decrease with temperature, which is qualitatively the opposite to the observed behaviour in ice.

The observed temperature dependencies can be well explained from a relaxation mechanism in which the OD vibration relaxes via energy transfer to a combination tone involving a bending mode of HDO or H2O. The vibrational lifetime are determined by the spectral overlap of the OD stretching mode and the acceptor mode. For ice, the spectral overlap decreases when temperature increases. For the OD stretching modes in hydrated lithium nitrate, the opposite holds and the spectral overlap increases with temperature. The frequency dependence of the spectral overlap also explains the differences in vibrational lifetime of the OD vibrations. The OD modes with strong hydrogen bonds have better spectral overlap with the acceptor mode than the OD modes with weaker hydrogen bonds.
weak hydrogen bonds, hence the vibrational lifetime is observed to increase with decreasing hydrogen-bond strength.

The surface structures of ice and liquid water are studied using phase-resolved sum-frequency generation spectroscopy. In this technique a broadband infrared pulse is overlapped at the surface with a visible pulse to generate sum-frequency light. The efficiency of this light-conversion process is strongly enhanced when the infrared light is resonant with a surface vibration. The spectral response is used to characterize the molecular surface structure of basal ice. At 150 K we observe 7 modes in the sum-frequency spectrum, of which 2 modes are absent in the bulk. These 2 modes are assigned to the outermost water molecules with an incomplete hydrogen-bond configuration. When increasing the temperature we find the crystalline surface to become disordered above ~185 K. At temperatures starting from 245 K we observe the surface of ice to be covered by a layer of liquid water, i.e. the hydrogen bonds of this premelted layer are indistinguishable from supercooled water.

In another experiment we study the extent of resonant molecular coupling towards the surfaces of ice and liquid water using isotope substitution. For isotopically dilute HDO in D$_2$O, the OH stretch vibration is effectively uncoupled from the surrounding OD oscillators owing to the frequency mismatch. The sum-frequency spectra of isotopically diluted ice and H$_2$O ice at 245 K strongly differ. This indicates that the OH stretches at the surface of H$_2$O ice are strongly influenced by intermolecular couplings, which leads to a delocalization of the vibrations. For liquid water, the difference between the surface spectra of neat and isotopically diluted water is found to be much smaller. The intermolecular coupling of the H$_2$O vibrations at the surface of liquid water is thus concluded to be smaller in comparison with the bulk, resulting in localized vibrations. The OH stretch vibrations are thus found to be much more delocalized at the surface of H$_2$O ice than at the surface of liquid H$_2$O. This is explained from a difference in surface order. The surface of ice is highly ordered and the homogeneity of the hydrogen-bond network leads to a large delocalization of the vibrations. The surface of liquid water is more disordered and the resulting heterogeneity of the hydrogen-bond strengths leads to a localization of the vibrations. Furthermore, for isotopically diluted liquid water and ice the surface spectra bear a striking similarity with the corresponding bulk spectra. This implies that the hydrogen-bond strengths at the surface of both liquid water and ice to resemble the bulk values.

Finally, we employ sum-frequency scattering spectroscopy to study the surface structure of nanoscopic water and oil droplets in emulsion. In this technique the infrared and visible pulses generate sum-frequency photons all around the droplets’ surface. The scattered sum-frequency photons yield a spectrum of the vibrations at the water–oil interface. We investigate the effect of freezing of the constituents on the interfacial structure of oil-in-water emulsions. The freezing of oil is observed to lead to deviations from the spherical shape of liquid oil droplets. The freezing of the water matrix leads to a strong distortion of the oil droplets in case the oil is liquid, but has little effect on frozen oil particles.

In a final experiment we characterize the surface structure of water droplets...
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in oil. The hydrogen-bond network at the surface of water droplets is found to possess a much enhanced tetrahedral structure compared to a planar air–water interface. The increase is much larger than observed in previous studies of planar liquid hydrophobic–water interfaces. The observed spectral difference is similar to that of a planar air–water surface at a temperature that would be 60 K lower.