

"Aqueous Hydrogen Bonding Probed with Polarization and Matrix Isolation Spectroscopy"

Shultz, Mary Jane; Bisson, Patrick; Buch, Victoria; Groenzin, Henning; Li, Irene
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A major challenge in hydrogen-bond research is interpreting the vibrational spectrum of water, arguably *the* most fundamental hydrogen bonding system. This challenge remains despite over a half century of progress in vibrational spectroscopy, largely due to a combination of the huge oscillator strength and the enormous width of the hydrogen-bond region. Lack of assignment of the resonances in the hydrogen-bond region hinders investigation of interactions between water and solutes. This lack-of-interpretation issue is an even more significant problem for studies of the aqueous interface. Numerous solutes are known to have an effect, some very dramatic, on the shape of the surface spectrum. These effects, however, are but tantalizing teasers because lack of interpretation means that the changes cannot be used to diagnose the effect of solutes or impinging gas-phase molecules on the surface.

In the reported work two techniques are used to probe the origin of vibrational resonances in the H-bonded region: the surface sensitive technique sum frequency generation (SFG) and room-temperature matrix-isolation spectroscopy (RT-MIS). A polarization technique called polarization angle null (PAN) has been developed that extends SFG and enables identification of resonances. The result of applying PAN-SFG to single-crystal, I_h -ice is identification of at least nine underlying resonances and assignment of two of these. One resonance is correlated with the crystal temperature and is a sensitive probe for interactions that disrupt long range order on the surface – it is a morphology reporter. The second is associated with weakly bonded, double-donor water molecules. This resonance is sensitive to interaction of hydrogen bond donors, i.e. acids, with the surface. Both modes are more correctly pictured as collective modes. These two assignments are the first *definitive assignments in the hydrogen-bond region for the aqueous surface*.

The effect of salts on the vibrational spectrum of water is also probed with a recently developed room-temperature, matrix-isolation technique. The matrix environment demonstrates that salts containing large anions with small cations support water-water hydrogen bonds with a vibrational resonance that has similar characteristics as the SFG spectra of salt solutions.