Nanoscale vibrational spectroscopy of liquid water by monochromated aloof EELS

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Electron microscopy of liquids has been a rapidly growing area of interest as improving resolution opens the door to the atomic length scale. At these length scales, the physics of adsorption and desorption, interfacial double-layers, or other ordered liquid structures become important to electrochemistry, catalysis, and biology operate. A classic problem is the behavior of water, which is critical to many areas of science and engineering. Anomalous behavior in its phase diagram, questions in electrochemistry, and effects of nanoscale confinement make up some of the more important topics of the moment. For example, in nanoscale confined volumes unique hydrogen bonding states have been identified,[1] while in an aqueous medium, chemical reactions depend on the interaction of water with specific atomic scale surface sites.[2]

Historically, the most successful means of investigating bonding and local structure of water have used FTIR or Raman vibrational spectroscopies. However, the spatial resolution of these techniques is limited by light diffraction to several microns, which is far larger than the scale on which many phenomena of interest occur. While there are some tip-enhanced Raman[3] and scanning near-field IR[4] methods capable of nanoscale resolution, these also have drawbacks due to high sensitivity to the tip-sample interface.

Electron microscopes, on the other hand, can readily achieve nanoscale spatial resolution, but their energy resolution has not been good enough to resolve vibrational spectra. With the development of monochromated electron microscopes, this limitation has been overcome. In our work reported here, we employed a new approach to access the vibrational spectra of water encapsulated in novel boron nitride liquid cells. We demonstrate that the phonon spectra of bulk water as well as the effects of surfaces on the phonon spectra can be directly characterized at a spatial resolution of tens of nanometers. In addition, we demonstrate that our approach is sensitive to isotopes and we can easily distinguish between H_2O and D_2O liquid samples

Several innovations are key to these measurements. First, water readily decomposes under the electron beam, even at very low electron fluxes. This can be mitigated using the 'aloof' mode, where the beam is placed near (10-50 nm) but not on the sample while still collecting an EELS signal via long range interactions with the electric field.[5] A second issue involves the construction of the liquid cell. Graphene-based liquid cells have been utilized in many cases, but creates a problem for ultra low-loss EELS as graphene is a zero bandgap conductor causing a high background signal in the low loss region.[6] Here, this is mitigated by constructing liquid cells using insulating 2D boron nitride as the window material. Finally, the phonon signal is weak and near the zero-loss peak at energies of 0-3 eV, a cutting edge monochromated instrument is required to get sufficient energy resolution and to suppress the tail of the zero loss peak. The combination of these has allowed us to directly detect the phonon stretching signals of liquid water with nanoscale resolution.

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