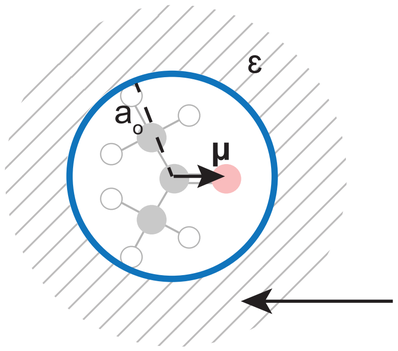
TokmakoffGroup

Electrolytes in Complex Environments

Vibrational probes of aqueous electrolytes



Mulder, W. H. and Parkanyi, C.
J. Phys. Chem. A. 2002, 106, 11932-11937

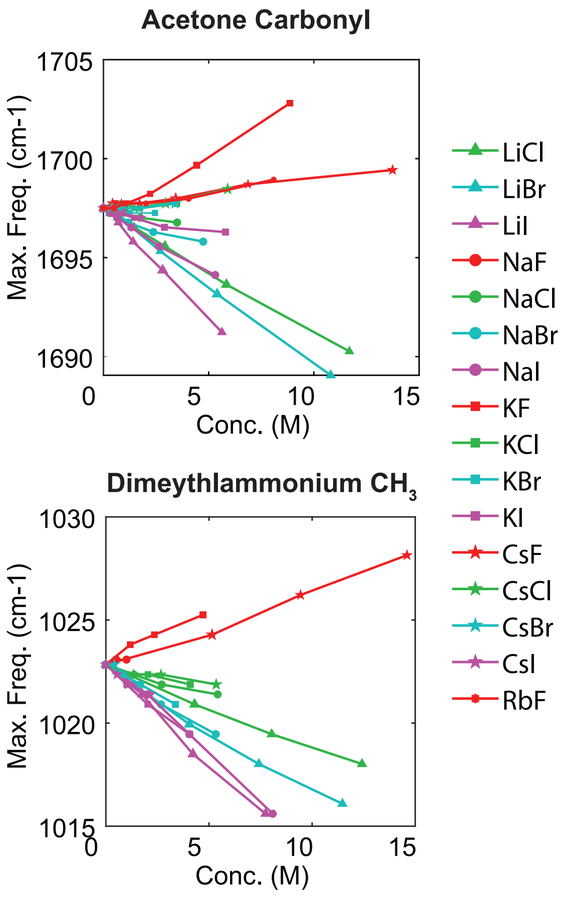
Vibrational probes such as C=O vibrations are excellent reporters on the external electric field of their environment.

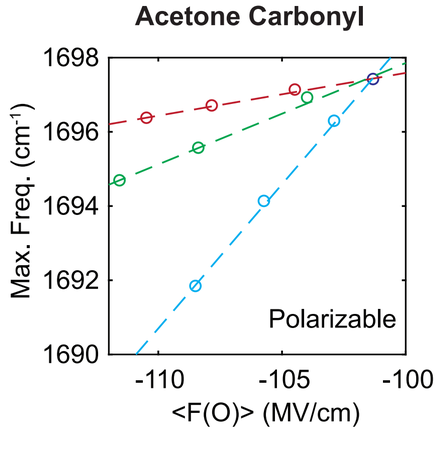
Classical theories relate the shift in frequency to the external field experienced by the dipole moment of the vibrational mode.

$$\Delta\nu = - \mu \cdot F_{ext}$$

However, classical predictions ignore the complicated molecular level interactions between ions, water, and the vibrational probe and therefore fail to capture the full range of ion-specific behavior such as the different signs of the frequency shift for select salts and the larger dependence on either cation or anion identity.

We are interested in exploring the origin of ion-specific effects including the interactions between ions and vibrational probes in order to increase their usefulness as

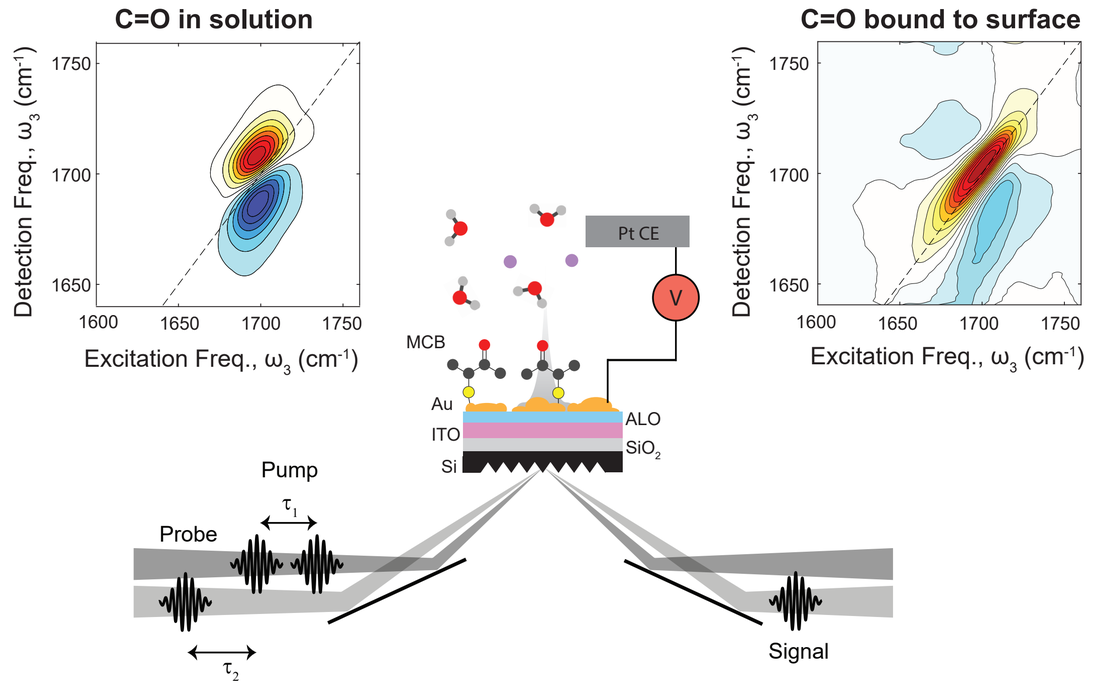




The electrostatic field on the CO of acetone in different solutions can be calculated with MD simulations. The ion dependence in the response implies that the field alone is not a complete descriptor of vibrational solvatochromism and further work is needed to understand the molecular origins.

Interfacial spectroelectrochemistry

Understanding the structure and dynamics of water at electrode interfaces has major ramifications in the development of new battery technologies and water remediation. We have developed ATR mode 2D IR that can be used to investigate the electric double layer at electrode interfaces with the use of surface-tethered vibrational probes and by taking advantage of surface plasmonic enhancements.



FTIR difference spectra vs 0mV difference spectra show the carbonyl shift with applied potential. The 2D IR spectra show the same shifting, but in comparison to solution C=O spectra show heterogeneous diagonal line broadening and a negative-positive-negative pattern along ω_3 that arises from coupling to the surface plasmon.