

DECONVOLUTING VIBRATIONAL PROBE RESPONSES USING CRYOGENIC ION INFRARED SPECTROSCOPY

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Noncovalent interactions between metal ions and complex molecules play a central role in condensed matter systems from enzyme catalysis to membrane permeability. Vibrational probes are used to gain information on the local electrostatic environment during such condensed phase phenomena. While this approach has proven successful, there are shortcomings that have not been addressed. In the condensed phase, the intrinsic molecular level response (polarization, isomerization, etc.) is obscured by the effects of hydrogen bonding, solvent exchange, and other external factors such as heterogeneity in the medium.

Cryogenic ion vibrational predissociation spectroscopy (CIVP) is a useful way to obtain the detailed information needed to unambiguously measure the intrinsic response of vibrational electric field probes. In particular, this paper describes how CIVP can be used to quantify the separate roles of proximal molecular ions and interactions with solvent. We apply this approach to monitor the responses of palmitic acid and benzo-15-crown-5-nitrile to various metals in the +1 and +2 charge states. Both of these species contain popular vibrational probes (carboxylate in the former and nitrile in the latter), and are relevant, molecular-level models of scaffolds present in biological systems. Vibrational spectra of the cold (20K), H₂ or He tagged ions are collected and assignments are made with the assistance of electronic structure calculations. This technique provides a new window into the intrinsic response of vibrational probes that are widely used in biophysical applications.