ISOLATING THE INTRINSIC SPECTRAL RESPONSES OF VIBRATIONAL PROBES: BENCHMARKS FOR REPORTERS OF CONDENSED PHASE AND BIOLOGICAL PROCESSES

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We use cryogenic infrared vibrational predissociation spectroscopy of isolated, nitrile-containing vibrational probe molecules to provide benchmarks for the probe molecule spectral response. Popular probes, such as paracyanophenylalanine, and other nitrile-containing molecules are manipulated in solution to modify conformation and charge state prior to extraction and isolation using electrospray ionization and He buffer gas cooling to 10 K. The vibrational spectra of the cold, He- or H2-tagged molecules are collected in a linear predissociation regime and interpreted with the aid of electronic structure calculations. The results provide insight into the intrinsic spectral response of isolated nitrile vibrational reporters decoupled from solvent effects.

Vibrational probe molecules are popularly employed to provide spectroscopic readouts of local electrostatic environments in phenomena including bulk solvation dynamics, interfacial proton transfer, and enzyme catalysis. A range of these molecules has been developed, allowing investigators to exploit absorption-free ”windows” in the infrared spectrum to ease measurement. However, in the condensed phase it is often a challenge to separate the components of the reporter’s response arising from external factors, such as local electric fields or hydrogen bonding, from those due to intrinsic factors such as molecular electrostatic potential or reporter isomerization.