LOW-FREQUENCY VIBRATIONS IN CLUSTERS AND FLEXIBLE BIOMOLECULES: A VIEW FROM ELECTRONIC SPECTROSCOPY OF JET-COOLED MOLECULES

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Low frequency vibrations ($<100$ cm$^{-1}$) can be either intramolecular or intermolecular in character. In the condensed phase, these two contributions are often difficult to distinguish from one another. This talk will focus on the insights to such vibrations that can be gleaned from a study of the isolated, jet-cooled molecules and their solvent-containing complexes, using examples from the authors' recent work. By interrogating the isolated molecule after cooling in a supersonic expansion, the conformational populations are trapped in the zero-point levels of one or a few of the lowest energy conformational minima, and solvent effects are removed. Electronic excitation of an aromatic substituent often produces vibronic structure associated with the low frequency vibrations of flexible side-chains against the aromatic. Double resonance methods enable the acquisition of ultraviolet and infrared spectra of the individual conformations in order to determine how the low frequency motions change with molecular conformation. The intermolecular vibrations can then be explored by addition of solvent molecules to the aromatic solute. Franck-Condon activity involving these vibrations is often observed as the solvent molecules respond to electronic excitation of the aromatic solute.