Vibrational solvatochromism, intermolecular interaction, and femtosecond vibrational/electronic spectroscopy

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Current multidimensional vibrational spectroscopy in time domain provides critical information on vibrational frequency fluctuation dynamics, which is one of the vibrational solvatochromism phenomena. We here discuss a recent systematic development in vibrational solvatochromism theory and its applications to a few different systems.

Vibrational frequency is probably one of the most accurately measurable spectroscopic properties of molecules in condensed phases. Absorption and scattering spectra provide information on its distribution and ensemble-average value, which have been widely used to understand structure, conformation, and absolute configuration of chemical and biological molecules of interest. In addition, time-domain nonlinear vibrational spectroscopy, e.g., two-dimensional IR, IR pump-probe, and so on, further allows one to study ultrafast fluctuation of vibrational frequencies reflecting thermally driven incessant motions of surrounding solvent molecules or protein residues. Despite prolonged efforts to develop an all-encompassing theory for vibrational solvatochromism, vibrational electrochromism, and dynamic fluctuation of instantaneous vibrational frequencies, still we have highly approximate or even incorrectly misleading theoretical models. Over the last few years, we have developed a systematic theory based on effective fragment potential approach, which was applied to a variety of molecular systems that have been studied with time-resolved vibrational spectroscopic methods. We have elucidated the underlying mechanism and the interplay of local electric field with vibrational solvatochromism of certain IR probes. It is emphasized here that the contributions from non-Coulombic (such as Pauli exclusion repulsion, dispersive interaction, and polarization interaction-induced) intermolecular interactions to vibrational frequency shifts and fluctuations are not negligible and in some cases they are the dominant terms. We believe that this and related approaches will be of exceptional use in studying structure and dynamics of biomolecules when combined with (i) femtosecond IR pump-probe, (ii) two-dimensional IR spectroscopy, and (iii) molecular dynamics simulation method.