Ultrafast Dynamics Investigations: Development of Femtosecond Time-Resolved Infrared Spectrometer

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In femtochemistry, studies of physical, chemical, or biological changes are at the fundamental time scale of molecular vibrations, the actual nuclear motions. Normally, electronic transitions are strongly broadened owing to the coupling with the fluctuating solvent and hence relatively featureless due to overlapping of different transitions. Spectral shifting and reshaping caused by solvent reorganization provide an ensemble averaged time-correlation function for liquid motion. Therefore, electronic spectroscopy can provide very limited information regarding the microscopic structure of the transient states and solute-solvent interactions. More insight into the dynamics of molecular Structure and dynamics can be obtained using ultrafast structurally resolving techniques. Ultrafast time-resolved vibrational spectroscopy by probing the fingerprint vibrational modes (1 – 30 mm) has several advantages over the electronic spectroscopy. Vibrational transition can be correlated to specific vibrational motions and hence conclusion can be drawn on specific structural motifs in the molecule. Narrow bandwidth (−10 – 20 cm$^{-1}$) ensures less overlapping with the neighboring bands and small molecular species can also be probed. Considering the above aspects, a femtosecond time resolved UV pump – IR probe transient absorption spectrometer has recently been developed in Radiation & Photochemistry Division, BARC. This spectrometer uses 400 nm light pulses of 50 fs duration to pump (or excite) the sample. An optical parametric amplifier (OPA) – difference frequency generator (DFG) system coupled to the femtosecond laser system generates the probe pulses of 80 fs in the 1–10 micrometer wavelength region. The probe wavelength can be selected using an IR monochromator. The instrument response has been measured to be about 150 fs. The spectrometer is currently being used for investigation of the dynamics of hydrogen bonds in the excited states of hydrogen-bonded complexes as well as charge transfer dynamics in donor-acceptor molecules.