

RESONANT FEMTOSECOND STIMULATED RAMAN BAND INTENSITY AND S_n STATE ELECTRONIC STRUCTURE

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Femtosecond Stimulated Raman Spectroscopy (FSRS) is a powerful technique capable of providing dynamic vibrational information on molecular excited states. When combined with transient electronic spectroscopies such as Pump-Probe or Pump-Repump-Probe, the excited state dynamics can be viewed with greater clarity. Due to the low intensities of Raman scattering typical for FSRS, experiments are commonly performed with the Raman pump in resonance with the excited state absorption to take advantage of resonance enhancement. However, the inherent information about the resonant state embedded in the Raman scattering is not a well explored component of the technique. 2,5-diphenylthiophene (DPT) in solution is used as a model system to study the wavelength dependence of the excited state Raman resonance enhancement. DPT has strong excited state absorption and stimulated emission bands within the tunable range of the Raman pump, allowing a wide variety of resonance conditions to be probed. Varying the Raman pump wavelength across the excited state absorption band produces different trends in both the absolute and relative magnitudes of the resulting FSRS vibrational modes. Comparing with calculations of the S_1 vibrational modes, we determine the structure of the resonant S_n state potential energy surface based on the motions of the resonantly enhanced vibrations.