Resonance hyper-Raman spectroscopy: a new probe for the origins of optical nonlinearity

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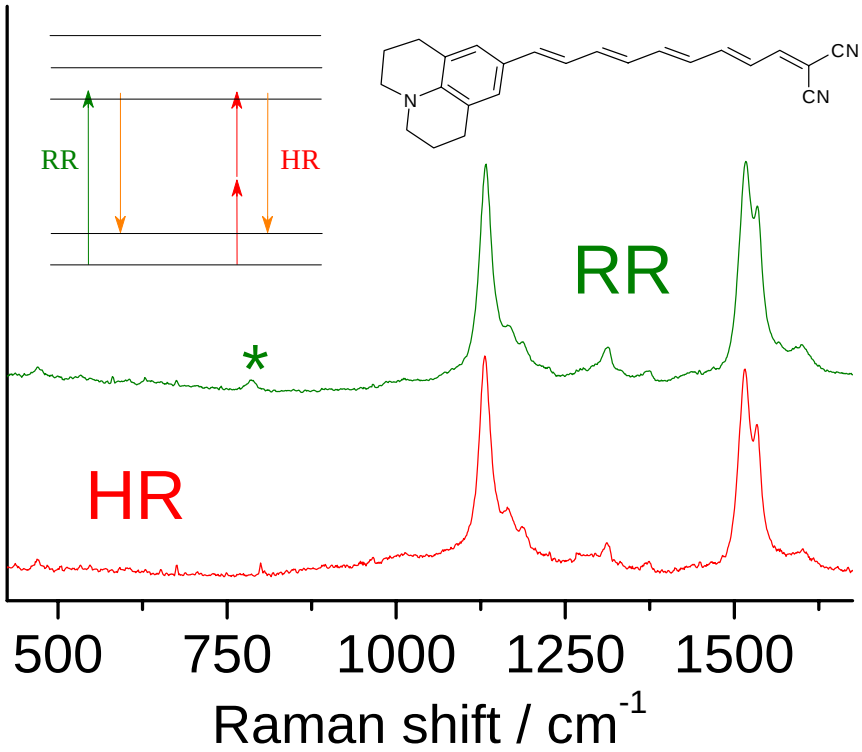

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Hyper-Raman scattering, the two-photon analog of ordinary Raman scattering, is normally a very weak process and has rarely been reported from solutions except with surface enhancement (e.g. on Ag colloids). We have found that many conjugated organic molecules with large first hyperpolarizabilities (β) generate strong resonance hyper-Raman spectra in dilute (< 1 mM) solution. Often the HR and RR spectral patterns are identical, indicating that the same resonant electronic state carries both the one-photon and the two-photon oscillator strength and supporting the popular two-level model for β. However, significant differences between the RR and HR spectra are seen for some chromophores at some excitation wavelengths, demonstrating different contributions from different resonant states to the one- and two-photon transitions.