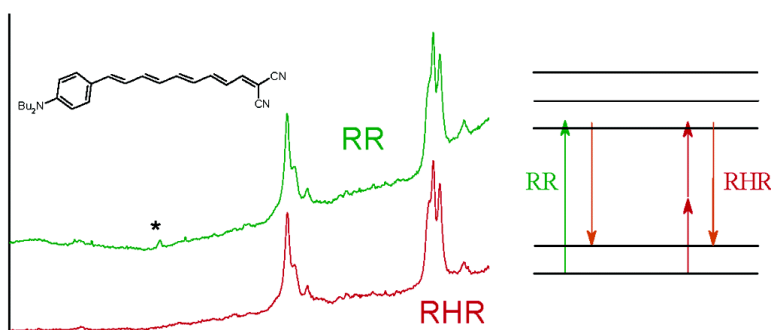


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Resonance Hyper-Raman Scattering from Conjugated Organic Donor–Acceptor “Push–Pull” Chromophores with Large First Hyperpolarizabilities

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“Push–pull” organic chromophores contain electron donor and acceptor groups connected through a π -conjugated linker. They often have large first hyperpolarizabilities (β) and hold great promise as the optically active components of polymer-based materials for electrooptic modulators and other second-order nonlinear optical devices.¹ The hyperpolarizabilities of these molecules are typically described by a two-level model in which only the ground and first excited electronic states contribute.² This two-level model is widely used to extrapolate the frequency dependence of β from measurements made at a single frequency, by either electric field-induced second harmonic generation or its incoherent analogue, hyper-Rayleigh scattering.³ It has theoretical and experimental support but has rarely been tested rigorously, particularly in complex chromophores optimized for large hyperpolarizabilities. One proposed test of the two-level model involves comparing the experimental β dispersion with that calculated from a Kramers–Kronig transform of the linear absorption spectrum.⁴ Accurate measurement of the hyper-Rayleigh intensity across a two-photon resonance is difficult, however, and has been attempted in only a few systems.⁵

Large organic molecules in solution phase tend to have broad, structureless linear absorption spectra and hyperpolarizability dispersions. Resonance Raman (RR) spectroscopy can provide detailed information about the vibronic structure that underlies featureless linear absorption spectra.⁶ Resonance hyper-Raman (RHR) scattering should carry similar information about states that are both one-photon and two-photon allowed (Scheme 1). As the vibrational intensities carry information about the structure of the resonant electronic state, comparison of RR and RHR intensities should allow us to determine whether the same resonant electronic state dominates both processes. Two-photon fluorescence is recognized as a complication in the measurement of hyper-Rayleigh intensities,⁷ but its incoherent analogue, resonance hyper-Raman scattering, apparently has not been reported from molecules of this type.

We have observed hyper-Raman scattering from several push–pull chromophores using excitation that is two-photon resonant with their strong linear absorptions.⁸ Figure 1 compares the resonance hyper-Raman and resonance Raman spectra for structures **1b-5** and **2b-5** of ref 9. The RR and RHR spectra are essentially identical in **1b-5** and extremely similar in **2b-5**. **2b-4**, the analogue of **2b-5** having only four polyenic double bonds, also gives RHR and RR spectra in cyclohexane that are very similar to one another, although both spectra are superimposed on fluorescence backgrounds that reduce the signal-to-noise ratio. All of the spectra are dominated by double-bond and single-bond stretching vibrations of the conjugated chain. Disperse Red 1, one of the benchmark chromophores for polymer-based nonlinear optical materials,¹⁰ exhibits weak RHR scattering in both methanol and CH_2Cl_2 . Several other

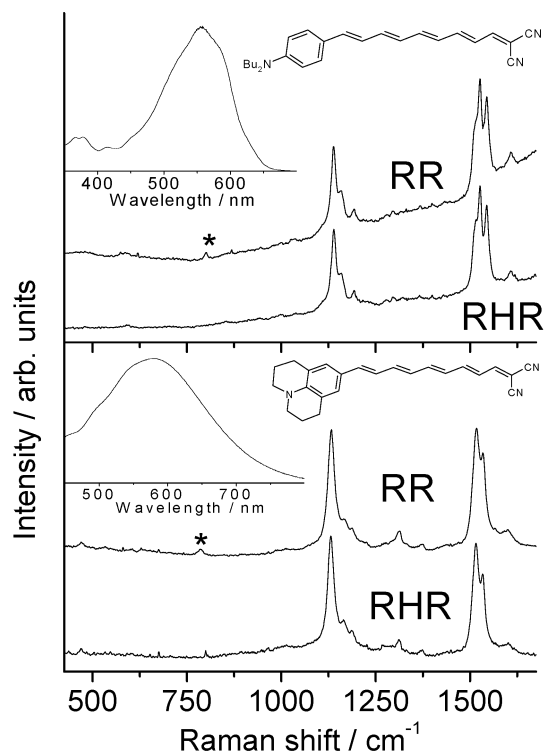
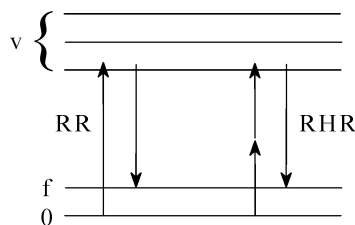


Figure 1. Resonance Raman (532 nm excitation) and hyper-Raman (1064 nm excitation) spectra of **1b-5** (upper panel, 0.45 mM in cyclohexane) and **2b-5** (lower panel, 0.4 mM in acetone). The insets are the linear absorption spectra. The asterisks mark solvent bands in the RR spectra. RR spectra are offset vertically for clarity.

Scheme 1. Resonance Raman (RR, Left) and Resonance Hyper-Raman Scattering (RHR, Right).



molecules examined produced either no detectable spectra or strong two-photon fluorescence under our experimental conditions.

Resonance hyper-Raman scattering has rarely been reported from molecules in solution, perhaps because of competition from other nonlinear processes at the high laser intensities required.¹¹ HR spectra of the pure solvents are undetectable (cyclohexane) or extremely weak (acetone) under our experimental conditions, although normal Raman spectra of the solvents are easily obtained and weak solvent bands appear in the RR spectra of the chro-

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mophores in Figure 1. A recent RHR study of all-trans retinal in solution used tightly focused picosecond laser pulses having considerably higher peak intensities than those employed in our work.¹² The strong RHR from retinal was attributed to its high second harmonic hyperpolarizability, $\beta(-2\omega; \omega, \omega) = 730 \times 10^{-30}$ esu at 1064 nm. The corresponding values for **1b-5** and **2b-5** at 1907 nm are considerably higher, 2180×10^{-30} esu and 1945×10^{-30} esu, respectively.⁹ These are all preresonant values, while the HR measurements were made within the two-photon resonance, but they are consistent with the expectation that resonant hyper-Rayleigh and hyper-Raman intensities should be highly correlated, as both require a resonant electronic state that is both one- and two-photon allowed.

In the vibronic theory of Raman scattering,¹³ the leading (A-term) contribution to the $0 \rightarrow f$ vibrational transition intensity for a single, strongly allowed resonant electronic state is given by

$$I_{\text{RR}} \propto \left| \sum_v \frac{M_{\text{ge}}^0 M_{\text{eg}}^0 \langle f|v\rangle \langle v|0\rangle}{\omega_{\text{ev},g0} - \omega_L - i\Gamma} \right|^2$$

where M_{ge}^0 is the $g \rightarrow e$ electronic transition dipole moment at the equilibrium nuclear configuration, and the sum is over all vibrational levels v of the resonant electronic state e having homogeneous line width Γ .¹⁴ The corresponding expression for resonance hyper-Raman when a single resonant state is both one- and two-photon allowed is¹¹

$$I_{\text{RHR}} \propto \left| \sum_{s,v} \frac{M_{\text{ge}}^0 M_{\text{es}}^0 M_{\text{sg}}^0 \langle f|v\rangle \langle v|0\rangle}{(\omega_{s,g0} - \omega_L)(\omega_{\text{ev},g0} - 2\omega_L - i\Gamma)} \right|^2$$

where the sum over s includes all intermediate electronic states in the two-photon process, none of which are one-photon resonant. The vibrational intensity patterns in both spectra depend only on the vibrational overlaps $\langle f|v\rangle \langle v|0\rangle$, which are functions of the change in molecular geometry between ground and excited states, and the resonant energy denominators, which are the same for RHR excited at ω_L and RR excited at $2\omega_L$. Thus, we expect identical spectra in this limit. If, instead, there are two or more excited states e that contribute differently to the one-photon and two-photon transitions, the RR and RHR spectra should have different intensity patterns unless all of the excited states involved have very similar geometries. While most of the low-lying electronic transitions of such molecules should be $\pi-\pi^*$ excitations dominated by changes in conjugated bond lengths, different states should have somewhat different geometries. The close agreement between the RR and RHR spectra of **1b-5** and **2b-5** suggests that a single resonant electronic state carries both the one- and two-photon oscillator strength in this region, i.e., the state responsible for the strong linear absorption also dominates the hyperpolarizability. This is also consistent with our RHR polarization measurements on **1b-5**, which give $I_{\text{VH}}/I_{\text{VV}} = 0.20 \pm 0.01$ as expected when β has a single nonzero tensor element.¹⁵

Structures such as **1b-5** and **2b-5** may be unusually good RHR scatterers because they combine a simultaneously strong one- and two-photon transition with a substantial change in geometry upon electronic excitation. Nevertheless, we anticipate that hyper-Raman scattering will be observable from many other dipolar molecules that have large first hyperpolarizabilities. Other methods to assess the relative contributions of different electronic states to the one-

and two-photon absorptivity include measuring the two-photon absorption spectrum or the frequency dispersion of $\beta(-2\omega; \omega, \omega)$, both of which require comparing intensities for weak processes measured with pulsed lasers at different wavelengths. Comparison of RR and RHR spectra at one or a few $\omega_L/2\omega_L$ pairs may provide an experimentally simpler way to determine whether a single electronic state dominates both transitions. More importantly, the RR and RHR spectra provide information about the structure and dynamics of the resonant state(s) not available from the low-resolution electronic spectra.

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