

Two-Dimensional Fourier Transform Infrared-Visible and Infrared-Raman Spectroscopies

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Abstract: Femtosecond nonlinear spectroscopies using new IR and visible pulse sequences are demonstrated, including 2D IR-visible spectroscopy to study vibrational-electronic couplings and 2D IR-Raman spectroscopy to study anharmonic inter- and intramolecular vibrational couplings.

OCIS codes: (300.6420) Spectroscopy, nonlinear; (300.6450) Spectroscopy, Raman

Introduction

We report multidimensional spectroscopies to probe electronic and vibrational couplings and vibrational anharmonic inter- and intramolecular couplings to understand the roles played by coupled vibrations in ultrafast charge-transfer processes. An IR vibrational pump or collinear pump pulse pair for 2D Fourier transform (FT) spectroscopy [1, 2] excites a sample, which is then probed by either a visible (Vis) pulse or Raman pulse sequence [Fig. 1(a,b)]. Our Raman detection scheme is analogous to femtosecond stimulated Raman spectroscopy (FSRS) [3] but with IR excitation to study structural dynamics on the electronic ground state. Resulting 2D IR-Raman (5th-order) spectra enable the measurement of cross terms between the IR dipole moment and the polarizability of a particular Raman mode in a molecule. Fully resonant 2D IR-Vis (3rd-order) spectra should measure IR and optical dipole moment cross terms. In the present work, we demonstrate the recovery of these 3rd- and 5th-order signals in neat benzonitrile.

Experimental Methods

The output from a 1 kHz Ti:Sapphire regenerative amplifier (800 nm, 35 fs, 2.7 W) is used to generate all pulses in this experiment [Fig. 1(a)]. Mid-IR pump pulses are created via near-IR optical parametric amplification and subsequent difference frequency mixing; the resulting mid-IR pulses are tuned to $\nu = 2100 \text{ cm}^{-1}$ ($\lambda = 4.76 \text{ nm}$) with 310 cm^{-1} bandwidth and 65 fs pulse duration. An optional Mach-Zehnder interferometer in the IR path generates pulse pairs (0.45 $\mu\text{J}/\text{pulse}$) from the train of single IR pump pulses (1.8 $\mu\text{J}/\text{pulse}$) with a computer-controlled delay, τ_1 , which transforms to ω_1 in 2D FT experiments. A computer-controlled stage defines the delay, τ_2 , between the final IR pulse and the Raman continuum probe, generated in sapphire from 800 nm light. Prism compression and transmission through a 750-nm short-pass filter yield 35 fs pulses for anti-Stokes FSRS. Tunable ($\lambda = 800 \pm 15 \text{ nm}$), narrowband ($\leq 10 \text{ cm}^{-1}$), 3 ps Raman pump pulses ($\sim 0.5 \mu\text{J}/\text{pulse}$) from a grating filter [3] are fixed at delay ~ 0 fs with respect to the probe for maximum Raman signal. Lenses focus all three vertically polarized beams into the 250 μm sample. The probe serves as the local oscillator (LO) and copropagates with nonlinear signal fields; a double-chopping scheme [4] isolates 3rd- and 5th-order signals (Fig. 1) for single-shot detection with a CCD spectrograph.

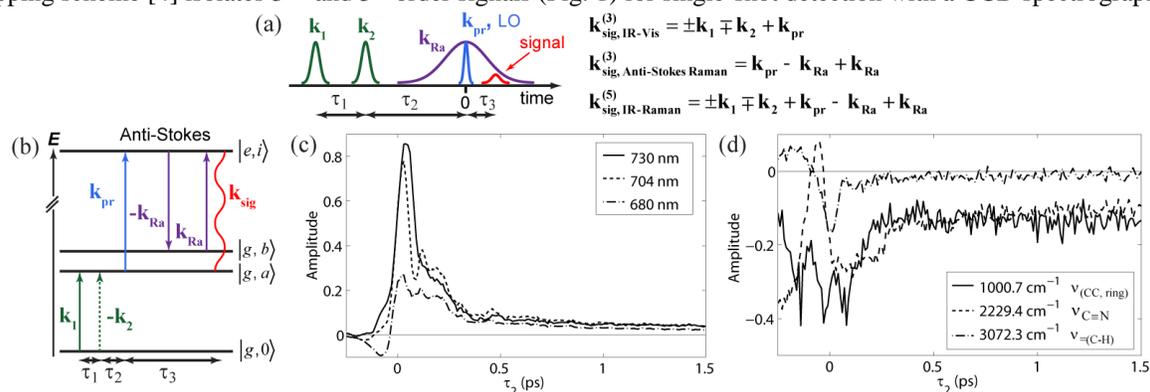


Fig. 1. Overview of IR-visible and IR-Raman spectroscopies. (a) Collinear IR pumps, \mathbf{k}_1 and \mathbf{k}_2 , are separated by the vibrational coherence time, τ_1 ; after a population time, τ_2 , the noncollinear visible probe and picosecond near-IR Raman pump (two interactions) impinge on the sample, generating a signal at detection time, τ_3 . Pump beam chopping ($\mathbf{k}_{1,2}$ at 250 Hz, \mathbf{k}_{Ra} at 500 Hz) and subtraction isolate the 3rd- and 5th-order signals. (b) Energy level diagram for resonant vibrational excitation with ω_b from ground state, $|g, 0\rangle$, to $|g, a\rangle$ and a subsequent stimulated Raman process, $\Delta\omega_{\text{Anti-Stokes}} = \omega_b - \omega_a$, involving a real or virtual electronic excited state, $|e, i\rangle$. (c) 3rd-order IR-Vis pump-probe spectra for three probe wavelengths versus τ_2 ; \mathbf{k}_{Ra} blocked, $\tau_1 = 0$. (d) 5th-order IR-Raman signal versus τ_2 at three benzonitrile Raman peak frequencies; $\tau_1 = 0$.

Results and Discussion

These experiments allow us to collect three nonlinear signal fields simultaneously: 3rd-order IR-Vis, 5th-order IR-Raman, and 3rd-order ground-state stimulated anti-Stokes Raman (shifts from 12500 cm⁻¹). Single IR pump ($\tau_1 = 0$) scans of τ_2 yield 1D spectra to measure dynamics of the 3rd-order IR-Vis [Fig. 1(c)] and 5th-order [Fig. 1(d)] signals. From a symmetric scan of two collinear IR pump pulses about $\tau_1 = 0$, we generate a 2D FT spectrum for a fixed τ_2 delay. Here, the 3rd-order [Fig. 2(a)] or 5th-order [Fig. 2(b)] signal is located at the ω_1 excitation frequency of the specific IR-active mode responsible for the change in visible probe transmission or Raman signal strength. Linearity of 3rd- and 5th-order signals with concentration was verified with stepwise benzonitrile/carbon tetrachloride mixtures to rule out contamination from 3rd-order cascades.

Since benzonitrile has no resonant transition in the probe frequency range, the IR-Vis signal follows the probe spectrum in ω_3 and lacks other spectral features. However, each probe frequency slice of the 2D spectrum maps the IR pump in ω_1 with absorption at benzonitrile vibrational modes [Fig. 2(a)]: $\nu_{\text{CN}} \approx 2230$ cm⁻¹, 1850 – 2000 cm⁻¹ combination bands, and a continuum baseline. Longer-lived vibrational coherences of frequencies within the pump bandwidth [5] appear in Figs. 1(c) and 2(a) at ~ 450 cm⁻¹ (benzonitrile) and 322 cm⁻¹ (CaF₂ window). By extension of Fig. 1(b), low-frequency peaks could arise from vibrational coherences between $|g, a\rangle$ and substate $|g, a'\rangle$ populations, accessed via ω_a and $\omega_{a'}$ IR pump frequencies, respectively. In the 5th-order experiments, the same benzonitrile modes as in the 3rd-order spectra are resonantly excited with the IR pump; the stimulated Raman process involves a virtual excited state. A broad signal appears near $\tau_2 = 0$ from the IR-Vis signal at all benzonitrile Raman peaks followed by an exponential decay of the 5th-order signal with τ_2 [Fig. 1(d)]. With increasing τ_2 , the 5th-order signal at the $\nu_{\text{CN}} = 2229.4$ cm⁻¹ Raman peak is more clearly coupled to the IR-active modes [Fig. 2(b)].

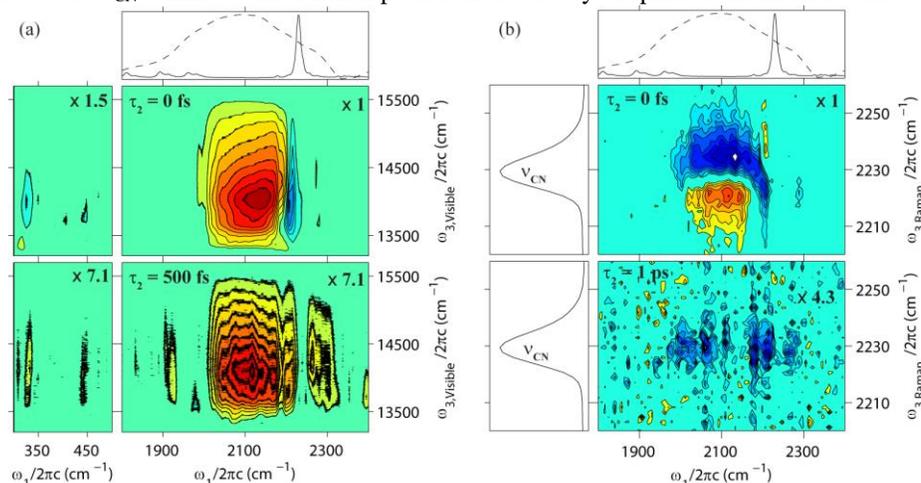


Fig. 2. 2D IR-Vis and 2D IR-Raman spectra of benzonitrile, each with FTIR (solid line) and IR pump (dashed line) spectra in top panel. (a) 3rd-order 2D IR-Vis spectra, including low-frequency CaF₂ and benzonitrile peaks. (b) 5th-order 2D IR-Raman spectra in the CN region (recovered ground-state stimulated Raman spectra in left panels) show a dispersive feature ($\tau_2 = 0$) giving way to IR-Raman mode couplings.

Conclusions

We have demonstrated new FT multidimensional spectroscopies using IR and visible pulse trains with sub-100 fs time resolution. Analysis of 2D IR-Raman and 2D IR-Vis benzonitrile spectra indicate that these experiments are well-suited to studies of vibrational energy pathways in charge transfer complexes [4]. The ability to probe vibronic couplings with high time and frequency resolutions should make these ultrafast spectroscopies invaluable to researchers studying correlated electronic and nuclear motions in chemistry, biology, and material science.

References

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