

SUPPORTING INFORMATION

Measuring Coherently Coupled Intramolecular Vibrational and Charge Transfer Dynamics with Two-Dimensional Vibrational-Electronic Spectroscopy

*Trevor L. Courtney, Zachary W. Fox, Laura Estergreen, and Munira Khalil**

Department of Chemistry, University of Washington, Seattle, Washington 98195, United States

AUTHOR INFORMATION

Corresponding Author

*Email: mkhalil@uw.edu

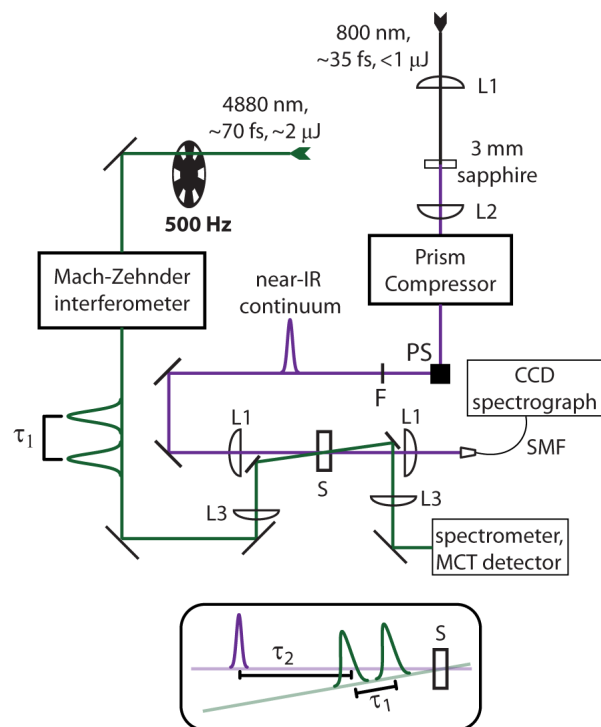


Figure S1. Experimental setup for 2D VE spectroscopy. A mid-IR pulse train is chopped at 500 Hz and enters a Mach-Zehnder interferometer with two computer-controlled translation stages. Collinear pump pulse pairs separated by delay τ_1 , precede the probe pulse by a computer-controlled delay τ_2 . The white-light continuum probe is generated from $<1 \mu\text{J}$ of the Ti:Sapphire output in a 3 mm sapphire window and then prism-compressed and spectrally filtered. At the sample, S, all pulses have vertical polarization, and lenses are used to focus the intersecting beams. The pulse interactions result in 3rd-order signals that propagate with the probe and are coupled via single mode fiber (SMF) to a CCD spectrograph. After the sample, IR pulses are routed to a spectrometer and mercury cadmium telluride (MCT) detector. PS: periscope, F: longpass (850 nm) filter, L1: fused silica (FS) plano-convex (PC) lens, $f=100 \text{ mm}$, L2: FS PC lens, $f=50 \text{ mm}$, L3: CaF_2 PC lens, $f=150 \text{ mm}$. Silver (near-IR path) and gold (mid-IR path) mirrors are unlabeled.

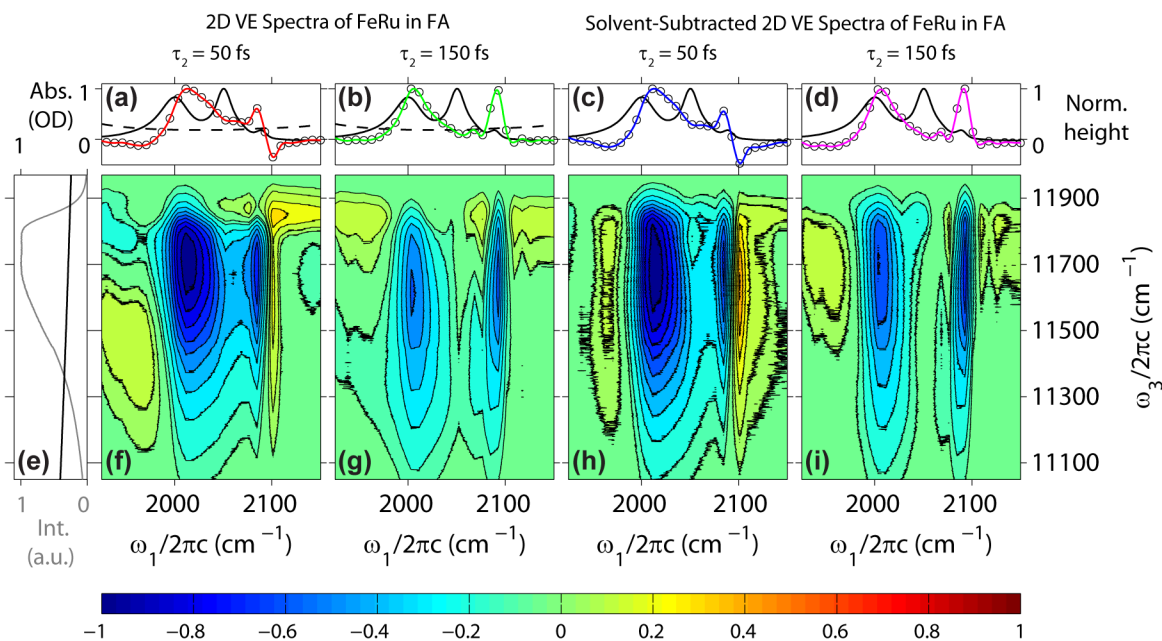


Figure S2. 2D vibrational-electronic (VE) spectra of $[(\text{CN})_5\text{Fe}^{\text{II}}-\text{CN}-\text{Ru}^{\text{III}}(\text{NH}_3)_5]^-$ (FeRu) in formamide (FA) (f, g) and with neat FA spectra subtracted (h, i). Note that (h) and (i) are the solvent-subtracted versions of (f) and (g), respectively. (a, b) FTIR spectra of neat FA (dashed black lines). (a-d) FTIR spectra of solvent-subtracted FeRu (solid black lines) plotted with height-normalized 1D projections of 2D VE spectra (open circles) or of a cubic spline interpolated (across ω_1) 2D VE spectrum (solid color lines that correspond to Fig. S3a). See Figs. 4 and S3 captions for more details. (e) Near-IR probe pulse spectra (solid gray lines), and linear solvent-subtracted electronic spectrum of FeRu in FA (solid black line). (f, g) Early waiting time 2D VE spectra of FeRu normalized to (f) are borrowed from Fig. 3d,e but are plotted here with an additional ± 0.05 contour level. (h, i) 2D VE solvent subtraction plots normalized to (h) and plotted with same contours as (f,g). (h) Fig. 3d - Fig. 3g. (i) Fig. 3e - Fig. 3h. These solvent-subtracted spectra are approximations of solvent-free 2D VE data: they are direct subtractions of 2D VE spectra with approximately equal LO intensity. However, as the probe propagates through the sample in neat FA, it is not absorbed as in FeRu; thus, the neat FA experiment has higher probe intensity followed by attenuation of both the LO and signal fields by a neutral density filter. Probe intensity, signal attenuation, sample cell alignment, and other possible experimental condition differences between sample and solute experiments limit the accuracy of direct subtraction. Lineshape changes are addressed in Fig. S3.

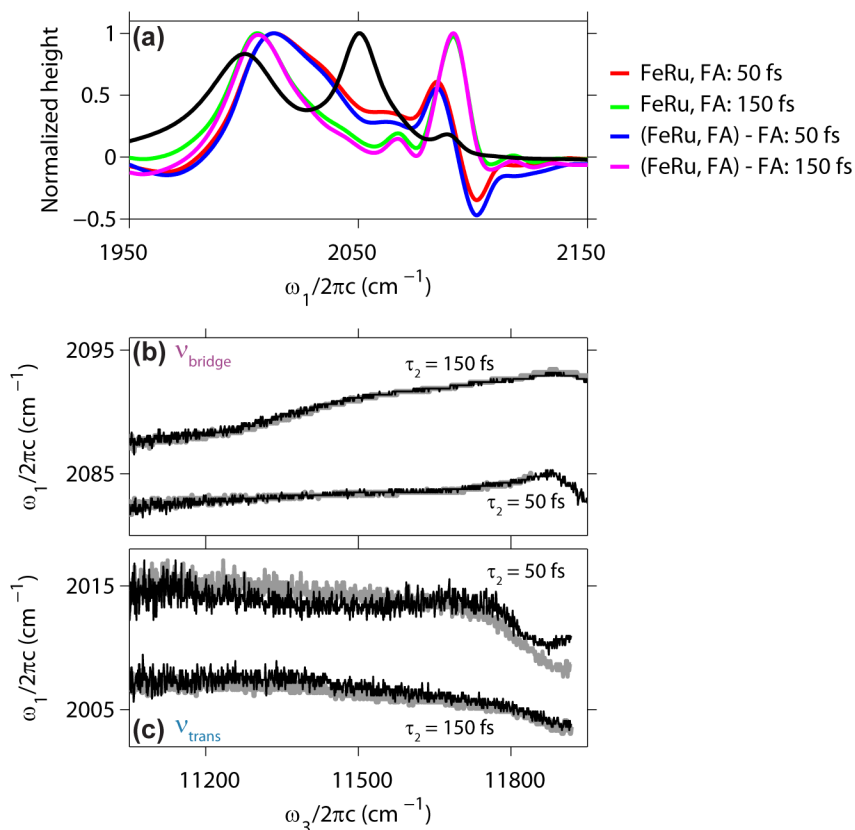


Figure S3. 1D representations of 2D VE data of $[(\text{CN})_5\text{Fe}^{\text{II}}-\text{CN}-\text{Ru}^{\text{III}}(\text{NH}_3)_5]^-$ (FeRu) in formamide (FA) and with neat FA spectra subtracted. (a) The solvent-subtracted FTIR spectrum of FeRu (solid black line) is plotted with projections of the 2D VE spectra. Interpolated pixel slices of 2D VE spectra are summed, multiplied by -1 for ease of comparison to the FTIR spectrum, and plotted on ω_1 for four 2D VE spectra: $\tau_2 = 50$ fs (red), $\tau_2 = 150$ fs (green), FA-subtracted $\tau_2 = 50$ fs (blue), and FA-subtracted $\tau_2 = 150$ fs (magenta). The ν_{radial} mode (2050.6 cm^{-1}) in the linear spectrum is absent in all projections, while the other three ν_{CN} modes are present in the projections but in different proportions than in the FTIR spectrum for each waiting time. The largest effect of solvent subtraction is a vertical offset, as seen between the two $\tau_2 = 50$ fs traces (red and blue). (b, c) ω_1 positions of the maximum magnitudes of the ν_{bridge} (b) and ν_{trans} (c) signals in interpolated FeRu in FA 2D VE spectra at $\tau_2 = 50$ fs and $\tau_2 = 150$ fs at each pixel slice are plotted as functions of ω_3 (gray traces). The black traces in (b,c) are the corresponding peak maxima for FA-subtracted 2D VE spectra. (c) The largest solvent-induced slope effect is at $\tau_2 = 50$ fs for the ν_{trans} mode.

Simulation details.

The response function for each relevant Liouville pathway follows the Bloch formalism. The response is calculated for both rephasing (R) and nonrephasing (NR) signals of ground state bleach (GSB) and excited state absorption (ESA). The difference in frequency of the IR active vibration in the ground and electronic excited states is given here by $\Delta = 75 \text{ cm}^{-1}$; Δ is not relevant for, and is omitted from, the GSB pathway response functions. The parameters used in the simulated spectrum shown in Fig. 1e rely on dipole moments for both IR and electronic transitions (μ_{IR} , and μ_{elec}) equal to 1. The center frequencies for these IR and electronic transitions (ω_{IR} and ω_{elec}) are 2002 and 8430 cm^{-1} , respectively. The linewidths for the IR and electronic transitions (g_{IR} and g_{elec}) are 20.5 and 200 cm^{-1} , respectively. All parameters reported above in wavenumber units are converted to radial frequencies to calculate the response functions of each pathway. The sums of R and NR response functions are each 2D Fourier transformed with respect to t_1 and t_3 . The real part of the R and NR frequency responses are added together to give the fully absorptive 2D VE spectrum presented in Fig. 1e.