Investigating vibrational relaxation in cyanide-bridged transition metal mixed-valence complexes using two-dimensional infrared and infrared pump-probe spectroscopies

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Using polarization-selective two-dimensional infrared (2D IR) and infrared pump-probe spectroscopies, we study vibrational relaxation of the four cyanide stretching ($\nu_{CN}$) vibrations found in $\left[(\text{NH}_3)_5\text{Ru}^{II}\text{NCFe}^{II}(\text{CN})_5\right]^{-}$ (FeRu) dissolved in D$_2$O or formamide and $\left[(\text{NC})_5\text{Fe}^{II}\text{CNPt}^{IV}(\text{NH}_3)_3\text{NCFe}^{II}(\text{CN})_5\right]^{4-}$ (FePtFe) dissolved in D$_2$O. These cyanide-bridged transition metal complexes serve as models for understanding the role high frequency vibrational modes play in metal-to-metal charge transfers over a bridging ligand. However, there is currently little information about vibrational relaxation and dephasing dynamics of the anharmonically coupled $\nu_{CN}$ modes in the electronic ground state of these complexes. IR pump-probe experiments reveal that the vibrational lifetimes of the $\nu_{CN}$ modes are ~2 times faster when FeRu is dissolved in D$_2$O versus formamide. They also reveal that the vibrational lifetimes of the $\nu_{CN}$ modes of FePtFe in D$_2$O are almost four times as long as for FeRu in D$_2$O. Combined with mode-specific relaxation dynamics measured from the 2D IR experiments, the IR pump-probe experiments also reveal that intramolecular vibrational relaxation is occurring in all three systems on ~1 ps timescale. Center line slope dynamics, which have been shown to be a measure of the frequency-frequency correlation function, reveal that the radial, axial, and trans $\nu_{CN}$ modes exhibit a ~3 ps timescale for frequency fluctuations. This timescale is attributed to the forming and breaking of hydrogen bonds between each mode and the solvent. The results presented here along with our previous work on FeRu and FePtFe reveal a picture of coupled anharmonic $\nu_{CN}$ modes where the spectral diffusion and vibrational relaxation dynamics depend on the spatial localization of the mode on the molecular complex and its specific interaction with the solvent. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).

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I. INTRODUCTION

Understanding the pathways and timescales of vibrational energy relaxation is crucial for monitoring and controlling chemical reactivity. In polyatomic molecules in solution, vibrational phase and energy transfer and relaxation can occur through intramolecular and intermolecular processes. The vibrational energy transfer processes can be coherent and incoherent in nature and coupled to electronic dynamics in the case of ultrafast photoinduced chemical reactions. Recent experiments on transition metal donor-bridge-acceptor complexes have shown how the vibrations of the bridging species can affect the charge transfer between the donor acceptor...
moieties. These studies highlight the importance of understanding the time-dependent intra- and intermolecular vibrational energy transfer and relaxation pathways to develop a microscopic understanding of light-induced phenomena in small molecules and materials for efficient photochemical energy conversion.

Cyanide-bridged transition metal mixed-valence complexes serve as excellent model systems to study the coupling of vibrational and electronic coordinates in ultrafast charge transfer reactions. Previous ultrafast studies of cyanide-bridged mixed-valence complexes have explored the role played by high-frequency CN stretching ($\nu_{\text{CN}}$) vibrations in the photo-induced metal-to-metal charge transfer (MMCT) and the subsequent back electron transfer process.7–9,12–21 These studies have shown that there is a high degree of vibrational excitation and measured how the vibrational transfer and relaxation pathways evolve as the molecule equilibrates in the ground electronic state following back-electron transfer. However, the intra- and intermolecular vibrational relaxation dynamics of the $\nu_{\text{CN}}$ modes in the ground electronic state of cyanide bridged transition metal mixed valence complexes have not been explored. The goal of this paper is to determine what role solvent and other molecular properties play in the vibrational relaxation dynamics of the $\nu_{\text{CN}}$ modes of cyanide-bridged bimetallic and trimetallic transition metal mixed-valence complexes. Infrared pump-probe and two-dimensional infrared (2D IR) spectroscopies are used to measure ground state vibrational dynamics of the cyanide stretching vibrations of [(NH$_3$)$_5$Ru$^{\text{III}}$NCFe$^{\text{II}}$(CN)$_5$]$^{3-}$ (FeRu) dissolved in deuterium oxide (D$_2$O) or formamide (FA) and [(NC)$_5$Fe$^{\text{II}}$CNPt$^{\text{IV}}$(NH$_3$)$_3$NCFe$^{\text{II}}$(CN)$_5$]$^{3-}$ (FePtFe) dissolved in D$_2$O. FeRu and FePtFe both have four cyanide stretching frequencies that are labelled $\nu_{\text{trans}}$ ($\nu_t$), $\nu_{\text{radial}}$ ($\nu_r$), $\nu_{\text{axial}}$ ($\nu_a$), and $\nu_{\text{bridge}}$ ($\nu_b$) (illustrated in Figs. 1(a) and 1(b)).

The FTIR spectra of the $\nu_{\text{CN}}$ modes (see Figs. 1(c)–1(e)) of the bimetallic and trimetallic systems are strikingly different in terms of frequencies, amplitudes, and lineshapes and have been discussed in detail earlier.22 The center frequencies of the four $\nu_{\text{CN}}$ modes for the FeRu complex are arranged in the following ascending order: $\nu_t < \nu_r < \nu_a < \nu_b$. The frequency ordering changes to $\nu_r < \nu_t < \nu_a < \nu_b$ for FePtFe dissolved in D$_2$O. The higher oxidation state of Pt(IV) compared to Ru(III) explains why the frequency of the bridging $\nu_{\text{CN}}$ mode is farther to the blue by 20 cm$^{-1}$ for FePtFe than for FeRu dissolved in D$_2$O. The larger positive charge pulls more electron density out of the cyanide antibonding ($\pi^*$) orbital and increases the strength of the CN bond thus increasing the vibrational frequency of the $\nu_{\text{CN}}$ stretch.23–25 If the
electron withdrawing effect carries along the MMCT axis, the strength of the CN bond could also increase for the terminal cyanide ligands explaining why the $\nu_4$ mode (blue arrows in Figs. 1(a) and 1(b)) in FePtFe is at a much higher frequency than it is in FeRu and why the frequency ordering of the four $\nu_{CN}$ modes change between the two complexes.

Previous work by our group has measured the experimental 2D IR spectra of FeRu and FePtFe in various solvents at $\tau_2 \sim 100$ fs.\textsuperscript{22} The best fits of the 2D IR spectra reveal a picture of a set of weakly coupled anharmonic $\nu_{CN}$ modes. The vibrational mode anharmonicities of the individual $\nu_{CN}$ modes range from 14 to 28 cm$^{-1}$, and the mixed-mode anharmonicities range from 2 to 14 cm$^{-1}$. Measurements of the relative transition dipole moments of the four $\nu_{CN}$ modes reveal that the angles in FeRu in FA are significantly different than both FeRu in D$_2$O and FePtFe in D$_2$O suggesting that the molecular structure might be a function of solvent environment. In this study, we will explore how the solvent and other molecular parameters affect the intra- and inter-molecular vibrational relaxation and spectral diffusion processes for the $\nu_{CN}$ modes in FeRu and FePtFe.

The remainder of this article is organized as follows. Section II describes the methods used to prepare samples and collect both pump-probe and 2D IR spectra. Sections III A and III B describe the results from the IR pump-probe and the 2D IR relaxation experiments, respectively. Section IV contains the discussion of our results followed by a summary in Section V.

II. METHODS

A. Materials

Starting materials and solvents were purchased from Sigma Aldrich and used without further purification. The mixed-valence complexes, FeRu and FePtFe, were synthesized as described earlier.\textsuperscript{22,26,27} A saturated solution of FeRu was prepared in FA with a maximum optical density (OD) of 0.22 in the $\nu_{CN}$ region after solvent subtraction. A solution of FeRu was also prepared in D$_2$O to a concentration of 25 mM and maximum OD of 0.36 in the $\nu_{CN}$ region. A solution of FePtFe dissolved in D$_2$O was prepared to a concentration of 15 mM and a maximum OD of 0.45 in the $\nu_{CN}$ region for use in experiments.

B. 2D IR experiments

The experimental parameters and layout of the 2D IR experiments have been described in detail in Ref. 22. Briefly, the 2D IR experiments were performed in a boxcar geometry with $\sim$80 fs mid-IR pulses centered at 4.9 $\mu$m ($\Delta \omega = 250$ cm$^{-1}$). The three input beams were focused to a spot size ($1/e^2$) of $\sim$150 $\mu$m at the sample with each beam having energy of 0.4 $\mu$J/pulse (0.5 $\mu$J/pulse) for the FeRu (FePtFe) samples. The sample was contained in a home built sample cell equipped with two 1 mm thick CaF$_2$ windows and a 50 $\mu$m Teflon spacer for the D$_2$O solutions or a 100 $\mu$m Teflon spacer for the FeRu/FA solution. The 2D IR spectra of FeRu in FA were collected at the following $\tau_2$ delays (waiting times): 0.07, 0.14, 0.225, 0.3, 0.425, 0.475, 0.625, 1, 2.5, 5, 7.5, 10, 15, and 20 ps. The 2D IR spectra of FeRu/D$_2$O were collected at $\tau_2$ delays of 0.09, 0.15, 0.225, 0.3, 0.375, 0.65, 1, 3, 5, 7.5, 10, and 15 ps, and the 2D IR spectra of FePtFe dissolved in D$_2$O were taken at $\tau_2$ delays of 0.15, 0.34, 0.38, 1.36, 2.04, 5, 7.5, 10, and 15 ps. For each sample, the 2D IR spectra were collected in both parallel ($S_{||}$, $ZZZZ$) and crossed ($S_{\perp}$, $YYZZ$) polarization geometries. In the former case, all input beams and the signal field have the same polarization and in the latter, beams 1 and 2 have perpendicular polarization relative to beam 3 and the signal field. Magic angle spectra were constructed using the relationship: $S_M = \frac{1}{2}(S_{||} + 2S_{\perp})$ to remove effects of reorientational dynamics.

C. IR pump-probe experiments

The generation and manipulation of the mid-IR light pulses used in the IR pump-probe experiments were similar to the 2D IR experiments and has been described earlier.\textsuperscript{22,26} The pump beam (chopped at 500 Hz) and the probe beam were spatially and temporally overlapped in the sample to generate the pump-probe signal. An additional mid-IR pulse was also sent...
through the sample to act as a reference beam. The input pump and probe beams had energies of \(0.5\) and \(0.3\) \(\mu\)J/pulse for all three samples. All input beams were focused onto the sample with a spot size (1/e\(^2\)) of ~150 \(\mu\)m. The pump-probe signal and the reference beam were vertically offset before being dispersed by a spectrometer (Triax 190, Horiba Jobin Yvon) and detected on the upper and lower stripes of a 2 \(\times\) 64 element mercury cadmium telluride array detector (IR0144, Infrared Systems Development).

The pump-probe spectra for the FeRu samples were collected at magic angle where the polarization of the probe beam was rotated 54.7° relative to the polarization of the pump beam to eliminate contributions from reorientational dynamics. Collected data were generated by dividing both the pump on and pump off signals by their respective reference pulses and then subtracting the pump on signal from the pump off signal. Dividing each signal pulse by the reference helped mitigate the effects of shot-to-shot and long term noise fluctuations in the mid-IR field. The reference beam was set to arrive 150 ps before the pump beam to ensure that the sample had relaxed back to the ground state. For FeRu dissolved in FA and D\(_2\)O, the time delay between the pump and probe pulses was scanned from -150 to 150 fs in 10 fs steps, 150 to 2500 fs in 25 fs steps, 2.5 to 5 ps in 50 fs steps, 5 to 8 ps in 250 fs steps, 8 to 20 ps in 1 ps steps, 20 to 40 ps in 4 ps steps, and 40 to 100 ps in 10 ps steps. Each data point represents 1500 shots, and each spectrum was collected 100 times and averaged to obtain the experimental spectra presented here. The experimental spectral resolution is ~2.8 cm\(^{-1}\) for the FeRu samples.

Spectra for FePtFe were collected in both parallel and crossed polarization geometries and no reference beam was used for shot-to-shot normalization of the data. For FePtFe dissolved in D\(_2\)O, the time delay between the pump and probe pulses was scanned from -1.5 to 3.5 ps in 25 fs steps, 3.5 to 6 ps in 250 fs steps, 6 to 20 ps in 1 ps steps, and 20 to 100 ps in 4 ps steps. Each data point represents 2000 shots, and each spectrum was collected 25 times and averaged to obtain the experimental spectra presented here. Experimental spectral resolution is ~4.4 cm\(^{-1}\) for the FePtFe sample.

III. RESULTS

A. IR pump-probe experiments

The IR pump-probe spectra of FeRu/FA, FeRu/D\(_2\)O, and FePtFe/D\(_2\)O are shown in Figure 2. The time-dependence of the fundamental \(\nu_{\text{CN}}\) frequencies of each sample are shown on semi-log plots. The data were fit to the following expression:

\[
\Delta A(t_2, \omega_3) = \sum_i A_i \exp \left( -\frac{t_2}{t_i} \right) + A_{\text{rise}} \left( 1 - \exp \left( -\frac{t_2}{t_{\text{rise}}} \right) \right) + A_{\text{osc}} \exp \left( -\frac{t_2}{t_{\text{osc}}} \right) \cos \left( 2\pi \omega_{\text{osc}} t_2 + \phi \right),
\]

where \(A\) and \(t\) are the amplitude and timescale of each decay/rise, respectively, \(\omega_{\text{osc}}\) is the frequency of any oscillation that is present, and \(\phi\) is the phase of the oscillation. Because of a large nonresonant signal, we fit the data starting at a pump-probe delay of 200 fs. The best fit parameters are listed in Table I.

Figure 2(a) displays \(t_2\) dependent spectrally dispersed pump-probe traces of FeRu/FA in the left panel. The data reveal that the negative bleach signals (0 \(\rightarrow\) 1 transitions) of the \(\nu_r\) (2050 cm\(^{-1}\)) and \(\nu_a\) (2064 cm\(^{-1}\)) modes are spectrally overlapped and the weaker axial mode appears as a shoulder to the blue side of the radial mode. It is also evident from Figure 2(a) that the \(\nu_l\) mode (2004 cm\(^{-1}\)) decays at a much faster rate than the other three modes. The positive absorption signals represent the 1 \(\rightarrow\) 2 transitions to the various overtones and combination bands from the first excited vibrational states. We do not fit the dynamics of the 1 \(\rightarrow\) 2 transitions due to the fact that they have overlapping contributions from both combination bands and overtones and therefore do not represent dynamics of any single transition exclusively. The
vibrational relaxation dynamics detected at the four fundamental transitions are plotted in the right panel of Figure 2(a) and the data is fit using Eq. (1). The traces in the right panel of Figure 2(a) and the best fit parameters listed in Table I reveal that the detection of the pump-probe signals at the four fundamental $\nu_{\text{CN}}$ transition frequencies displays different timescales of vibrational relaxation dynamics. In general, there are two timescales for vibrational relaxation. In all cases, we attribute the short timescale to intramolecular vibrational relaxation and transfer steps.
processes where the vibrational energy leaks into other high-frequency $\nu_{\text{CN}}$ modes or low-frequency vibrational modes along the metal-ligand backbone and the longer timescale to intermolecular vibrational relaxation to the solvent. The signal detected at $\omega_3 = \nu_3$ decays on two main timescales: 0.31 and 0.99 ps. The fit at $\omega_3 = \nu_3$ reveals three timescales that consist of two exponential decays and a decaying cosine. We attribute the 10.8 ps decay to vibrational energy relaxation to the solvent. The faster 0.64 ps decay is attributed to cross-population relaxation processes to other intramolecular vibrational modes. The oscillation at $\sim 50 \text{ cm}^{-1}$ results from the coherent superposition of two coupled $\nu_{\text{CN}}$ modes. The amplitude of the oscillatory component is proportional to the anharmonic coupling and the transition dipole moment between coupled modes. The frequency difference between the radial and trans modes and between the radial and bridge modes is $\sim 50$ and $\sim 40 \text{ cm}^{-1}$, respectively. We have previously measured similar anharmonic couplings and angles between the radial and trans modes and between radial and bridge modes suggesting that the oscillation arises from both of these coherent contributions.\textsuperscript{22} In addition, clear cross-peaks between the $\nu_t$ and $\nu_r$ and $\nu_t$ and $\nu_b$ modes can be seen in the 2D IR spectra in Figure 3(a) at $\omega_3 = \nu_t$. The fit of the signal at $\omega_3 = \nu_3$ (2064 cm$^{-1}$) reveals two timescales consisting of an exponential decay of 9.32 ps and a very weak decaying oscillatory component. The weak oscillatory component at $\sim 90 \text{ cm}^{-1}$ likely results from spectral overlap with the combination bands between the various fundamental $\nu_{\text{CN}}$ modes. The signal trace at $\omega_3 = \nu_b$ (2091 cm$^{-1}$) displays an exponential decay of 12.4 ps, a growth at 1.4 ps, and a decaying oscillation at $\sim 84 \text{ cm}^{-1}$. The oscillation matches the difference in frequency between $\nu_t$ and $\nu_b$ indicating a superposition between the two modes which have parallel transition dipole moments. In summary, we note that the pump-probe signals detected at the radial, axial, and bridge modes of FeRu/FA display vibrational energy relaxation to the solvent ranging from 9 to 12 ps. The signal detected at the trans mode appears to be an outlier with the longest timescale (with significant amplitude) being $\sim 1$ ps. The intramolecular

| Mode | Freq (cm$^{-1}$) | $t_1$ (ps) | $t_2$ (ps) | $t_3$ (ps) | $t_{\text{osc}}$ (ps) | $\omega_{\text{osc}}$ (ps) | $\omega_{\text{osc}}$ (cm$^{-1}$) |
|------|-----------------|------------|------------|------------|----------------------|--------------------------|-----------------------------|
| FeRu/FA | Trans 2004 | 0.31 ± 0.02 | 0.99 ± 0.04 | 10 ± 1 | 0.2 ± 0.1 | 50 ± 10 |
| | Radial 2050 | 0.64 ± 0.04 | 10.8 ± 0.1 | 0.2 ± 0.1 | 50 ± 10 |
| | Axial 2064 | 9.32 ± 0.09 | 0.2 ± 0.1 | 7.0 ± 0.3 | 90 ± 4 |
| | Bridge 2091 | 12.4 ± 0.5 | 0.46 ± 0.2 | 1.4 ± 0.2 | 84 ± 1 |
| FeRu/D$_2$O | Trans 2028 | 0.42 ± 0.03 | 5.81 ± 0.05 | 0.82 ± 0.04 | 84 ± 1 |
| | Radial 2047 | 0.72 ± 0.03 | 6.51 ± 0.09 | 0.85 ± 0.04 | 84 ± 1 |
| | Axial 2064 | 5.25 ± 0.06 | 0.04 ± 0.01 | 0.06 ± 0.01 | 84 ± 1 |
| | Bridge 2093 | 0.41 ± 0.06 | 0.04 ± 0.01 | 0.06 ± 0.01 | 84 ± 1 |
| FePtFe | Trans 2060 | 0.85 ± 0.07 | 17.2 ± 0.2 | 0.82 ± 0.04 | 84 ± 1 |
| | Radial 2050 | 0.5 ± 0.1 | 19.4 ± 0.2 | 0.82 ± 0.04 | 84 ± 1 |
| | Axial 2073 | 16.1 ± 0.3 | 0.04 ± 0.01 | 0.06 ± 0.01 | 84 ± 1 |
| | Bridge 2115 | 18 ± 1 | 0.04 ± 0.01 | 0.06 ± 0.01 | 84 ± 1 |
vibrational transfer and relaxation timescales among the coupled modes range from 0.3 to 1.4 ps and the lifetimes of the coherent oscillations are less than 1 ps.

Figure 2(b) shows the dispersed pump-probe spectra of the FeRu/D_2O sample as a function of ω_3 and τ_2, and the fit values for the fundamental traces can be seen in the FeRu/D_2O section of Table I. We note that the ν_t (2028 cm⁻¹), ν_a (2047 cm⁻¹), and ν_b (2064 cm⁻¹) modes are spectrally overlapped and the ν_0 mode (2093 cm⁻¹) is extremely weak. In contrast to the pump-probe data for FeRu in FA, the pump-probe traces of FeRu in D_2O at the chosen frequencies show no rises or oscillations. The fit of the trace at ω_3 = ν_t reveals two timescales, where the short timescale is attributed to intramolecular vibrational relaxation processes, and the 6.51 ps timescale is attributed to vibrational energy relaxation to the solvent. The signal trace at ω_3 = ν_0 only decays on a timescale of 5.25 ps. The fit of the signal at ω_3 = ν_t consists of two exponential decays that have amplitude factors of opposite signs to the rest of the fundamental transitions. The fundamental transition for the ν_a mode is overlapped with overtones of other modes as well as contributions from combination bands which most likely results in the positive signal. Given that the vibrational relaxation times to the solvent at ω_3 = ν_t and ν_a are approximately half of their measured values in the FeRu/FA sample, we tentatively assign the 0.42 ps decay to be indicative of relaxation to the solvent at ω_3 = ν_t. Since the ω_3 = ν_0 region of the spectrum has a low signal to noise level, fit values for that trace likely have no physical meaning. In summary, we note that the pump-probe signals detected at the radial and axial modes of FeRu/D_2O have timescales of vibrational energy relaxation to the solvent of ~5 ps. Interestingly, these timescales are twice as fast as those seen in FeRu/FA.

Figure 2(c) shows τ_2 dependent dispersed pump-probe spectra of FePtFe and ω_3 dependent vibrational relaxation dynamics. The ν_t (2050 cm⁻¹), ν_1 (2060 cm⁻¹), and ν_0 (2073 cm⁻¹) modes are spectrally overlapped, but their individual contributions can be distinguished as shoulders in the strong bleach contribution in the dispersed pump-probe spectra. Similar to the FeRu sample dissolved in FA, we see that pump-probe signal detected at three of the modes in FePtFe have oscillations, but here two modes have visible rises. From the fit values seen in Table I, we can see that the signals detected at all four ν_CN modes share a similar long time constant of ~18 ps representing vibrational energy relaxation to the solvent. The signal detected at the ν_t mode does show a faster decay of 0.85 ps, which is attributed to relaxation processes to other intramolecular vibrational modes. The fit for signal detected at the ν_t mode also shows two exponential decays representing intramolecular vibrational relaxation (0.5 ps) and vibrational population relaxation to the solvent (19.4 ps). Additionally, the signal at ω_3 = ν_t displays an oscillation with a frequency of 33 cm⁻¹. Like seen in the FeRu/FA sample, this oscillation probably arises from contributions of both a ν_t/ν_b superposition, where the difference in frequency is 10 cm⁻¹, and a ν_t/ν_b superposition, where the difference in frequency is 67 cm⁻¹. Furthermore, a clear cross-peak can be seen between the ν_t and ν_b modes in the 2D IR spectra in Figure 3(c) at ω_3 = ν_t, while the cross-peaks between the ν_1 and ν_t modes are not as easily distinguished due to overlap with the ν_1 and ν_t diagonal peaks. The fit of the signal at ω_3 = ν_b shows one exponential decay representing the vibrational lifetime, a rise, and a decaying oscillation. The rise of ~1.1 ps is attributed to energy relaxation from the other three ν_CN modes into the axial mode. A similar rise of ~800 fs is seen in the fit of the signal at ω_3 = ν_b (2115 cm⁻¹) which also shows one exponential decay and a coherent oscillation. The oscillation frequency of ~54 cm⁻¹ is approximately the difference in frequency between the ν_1 and ν_0 modes indicating a superposition between the two modes like that seen in the bridge mode of FeRu/FA. In summary, we note that all four ν_CN modes of FePtFe/D_2O have similar vibrational lifetimes ranging from 16 to 19 ps. The lifetimes of the coherent oscillations found in the pump-probe traces detected at the ν_t, ν_0, and ν_b frequencies are ~500 fs.

The dispersed pump-probe data for the ν_CN modes of FeRu and FePtFe consist of four overlapping vibrations and the fast timescales extracted from the fit to the data probably consist of several contributions arising from vibrational population transfer in and out of various excited modes detected at the particular ω_3 frequency of interest. A 2D IR relaxation experiment which resolves the excitation frequency axis provides a better description of how vibrational energy transfers between the four coupled ν_CN modes and is discussed in detail in Section III B.
B. 2D IR relaxation experiments

Figure 3 displays representative crossed polarization 2D IR spectra as a function of $\tau_2$ for all three samples. Note that contour levels do not follow a linear scale and are listed in the figure caption. The 2D IR data for FeRu in FA is shown in Figure 3(a). There are three main features along the diagonal with positive (0 $\rightarrow$ 1 transitions) and negative (1 $\rightarrow$ 2 transitions) features. The spectral feature at lowest energy represents the $\nu_1$ mode, the feature in the middle of the spectrum represents overlapping contributions from the $\nu_i$ and the $\nu_a$ modes as well as their cross-peaks, and the one at highest energy represents the $\nu_b$ mode. It can be seen that the trans mode decays away relatively quickly compared to the other diagonal features. We attribute this to the shorter timescale vibrational relaxation of the $\nu_1$ mode (1 ps) compared to the other $\nu_{CN}$ modes (9–12 ps) as discussed in Section III A and presented in Table I. The time-evolving 2D lineshapes and amplitudes measure the spectral diffusion and vibrational relaxation dynamics of the $\nu_{CN}$ modes in FeRu/FA. The 2D peak representing both the radial and axial modes is elongated along the diagonal at $\tau_2 = 70$ fs and its spectral diffusion dynamics are completed by $\sim 5$ ps. The diagonal and cross-peaks are amplitude modulated as a function of $\tau_2$ in a 2D IR spectrum of coupled vibrational modes. Oscillatory behavior is clearly seen for the $\nu_b$ mode in the 2D IR spectra where the diagonal peak has more amplitude at 300 fs than it does at 70 fs. The beats are also seen in the pump-probe data (Fig. 2(a)) which show a clear oscillation at a frequency of 84 cm$^{-1}$. Recall that the dispersed pump-probe data at a particular $\tau_2$ delay is the projection of the 2D IR spectrum along $\omega_3$. Evidence of intramolecular vibrational energy
redistribution among the $\nu_{CN}$ modes of FeRu/FA can be observed by the growth of three cross peaks at $(\omega_1 = \nu_{s}, \omega_2 = \nu_{r}, \omega_3 = \nu_{b})$, $(\omega_1 = \nu_{r}, \omega_2 = \nu_{s}, \omega_3 = \nu_{b})$, and $(\omega_1 = \nu_{b}, \omega_2 = \nu_{r}, \omega_3 = \nu_{s})$ relative to the radial diagonal peak. The time-dependent intensities of the cross-peaks are also plotted in the left panel of Figure 5. The other two obvious cross-peaks at $(\omega_1 = \nu_{r}, \omega_2 = \nu_{b}, \omega_3 = \nu_{s})$ appear to decay at similar rates to the $\nu_{r}$ and $\nu_{b}$ modes.

The 2D IR spectra for FeRu in D$_2$O are shown in Figure 3(b) and seem very different from the 2D IR spectra of FeRu in FA. The FTIR spectrum of FeRu/D$_2$O shows significant overlap of the $\nu_{s}$, $\nu_{r}$, and $\nu_{a}$ modes and very weak amplitude in the $\nu_{b}$ mode. The resultant 2D spectra of FeRu in D$_2$O show one main peak that represents overlapping contributions from the $\nu_{s}$ and $\nu_{a}$ modes as well as their cross peaks. At the lower left-hand corner of the central peak, there is a small feature that quickly disappears indicating the $\nu_{s}$ mode has an estimated vibrational lifetime of $\sim$400 fs corresponding to the timescale measured in the pump-probe experiments at $\omega_3 = \nu_{s}$ (Table I). A bridge diagonal peak is not distinguishable in any of the spectra due to the $\nu_{b}$ mode’s very small transition dipole moment ($|\mu_{b}| = 0.89|\mu_{r}|$, $|\mu_{b}| = 0.40|\mu_{r}|$, and $|\mu_{b}| = 0.12|\mu_{r}|$) as diagonal peak amplitudes scale with $|\mu_{p}|$.

The central diagonal peak loses its spectral correlation and appears fully rounded by $\sim$5 ps. We note that it is difficult to disentangle the relative homogenous and inhomogeneous contributions from the radial and axial cross peak contributions. There are two cross peaks that show up as wings to the lower and higher energy sides of the central peak $(\omega_1 = \nu_{b}/\nu_{r}, \omega_2 = \nu_{s})$. The 2D spectra reveal a spectral feature growing in at higher $\omega_3$ frequencies for $\tau_2 > 3$ ps. We attribute this to a solvent feature as there is a large D$_2$O band centered at $\sim$2500 cm$^{-1}$. Temperature dependent FTIR spectra of D$_2$O show a growth in the transmission from $\sim$2100 to 2150 cm$^{-1}$ as the temperature increases. In the 2D spectra, we see that the amplitude in the same spectral region increases.

The 2D IR spectra for FePtFe are shown in Figure 3(c). Here, we see two main diagonal features, the central one representing overlapping contributions from the $\nu_{s}$, $\nu_{r}$, and $\nu_{a}$ modes as well as their respective cross peaks, and the higher energy peak representing the $\nu_{b}$ mode. The central feature starts off elongated along the diagonal with a similar homogeneous width for all three modes (see 2D IR plot at $\tau_2 = 0.15$ ps), and the spectral diffusion dynamics are completed by 5 ps. As seen in the 2D spectra for FeRu/FA, the 2D spectral feature of the bridge mode does not appear to have any elongation along the diagonal at early $\tau_2$ delays. The diagonal bridge peak exhibits amplitude beating with a time-period of 620 fs consistent with the beats seen in the dispersed IR pump-probe data (Fig. 2(e)). We see that the obvious cross peaks $(\omega_1 = \nu_{s}, \omega_2 = \nu_{r}, \omega_3 = \nu_{b})$ and $(\omega_1 = \nu_{r}, \omega_2 = \nu_{b}, \omega_3 = \nu_{s})$ grow in relative to the diagonal features and are most visible in the $\tau_2 = 10$ ps 2D IR spectrum. Below we will discuss the spectral diffusion and vibrational relaxation dynamics measured in the 2D IR spectra by following the $\tau_2$-dependent 2D IR line shapes and 2D peak amplitudes, respectively.

The line shapes in the 2D IR experiments are a measure of the transition frequency fluctuations arising from the relative movements of molecules’ positions and orientations in solution. Vibrational frequency-frequency correlation functions (FFCFs) can be used to characterize these fluctuations and provide a measure of the system-bath interaction for each vibration. This gives us a tool to look at solvation dynamics in the ground electronic state of molecules in solution. There are various metrics available to extract FFCF timescales, but here we use the center line slope (CLS) method to measure spectral diffusion of the CN stretches.

The CLS method is one way to quantify how elongated the 2D IR peak is along the diagonal at a particular $\tau_2$ delay. To accomplish this, several $\omega_3$ frequencies centered on the fundamental frequency of the vibrational mode are chosen, and the $\omega_3$ frequency at which maximum amplitude is reached is recorded for each $\omega_1$ frequency. These points determine a line on a $\omega_1$ versus $\omega_3$ plot, and the slope of that line is the CLS. This slope is calculated for each $\tau_2$, and the resulting decay is fit to the following expression to find timescales that are proportional to the FFCF:

$$ \text{CLS}(\tau_2, \omega_3) = \left( \sum_i A_i \exp \left( -\frac{\tau_2}{\tau_i} \right) \right) + A_{osc} \exp \left( -\frac{\tau_2}{\tau_{osc}} \right) \cos(2\pi \omega_{osc} \tau_2 + \phi) + A_{\infty}, \quad (2) $$
where $A$ and $t$ are the amplitude and timescale of each decay, respectively, $\omega_{osc}$ is the frequency of the oscillation, and $\phi$ is the phase of the oscillation. The term $A_\infty$ represents a static component referring to dynamics that do not occur within the timescale of this experiment. The cosine is only included in the fit if there is an oscillatory component present, and the $t_{osc}$ and $\omega_{osc}$ variables are held constant at the values determined in the IR pump-probe fits at that $t_{osc}$ (see Table I). Previous 2D IR and peak shift experiments have observed oscillations in their extracted FFFCs. Examples include an underdamped hydrogen bond oscillation in HOD/D$_2$O, modulation of the polarization of high frequency NH and OH modes due to strong anharmonic couplings with low frequency skeletal hydrogen bonding modes, and strongly coupled correlated high frequency vibrational modes.

Figure 4 shows the CLS decays determined from the parallel polarization 2D IR spectra for selected modes from each system and the fits to the experimental CLS traces are listed in

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**FIG. 4.** Plots of the center line slope (CLS) measuring spectral diffusion as a function of $t_2$ for selected modes from each sample. Error bars represent 90% confidence intervals on the CLS value for each $t_2$ point. (a) and (b) The $\nu_3$ and $\nu_4$ modes, respectively, for FeRu/FA. (c) and (d) The $\nu_3$ and $\nu_5$ modes, respectively, for FeRu/D$_2$O. (e) (f) The $\nu_3$ and $\nu_5$ modes, respectively, for FePtFe.
Table II. The $\nu_{CN}$ modes for which the CLS analysis was performed were chosen carefully to minimize contributions from other close lying modes. Large error bars are due to the limited number of $\tau_2$ points available for each sample. The CLS of the $\nu_r$ mode is the only one that can be compared between all three samples. The two CLS traces from the D$_2$O samples of both FeRu and FePtFe have a time constant around 3 ps and an offset that represents dynamics too long to be measured with the time resolution of this experiment. The FeRu/FA $\nu_r$ trace has two time constants and no offset. It still has a short time constant at 2 ps that is close to the D$_2$O samples, but its long time constant is $\sim$20 ps. For the $\nu_a$ mode, only the two D$_2$O samples can be compared. FeRu/D$_2$O has two timescales present in its fit: the shortest decay constant measured at $\sim$600 fs and a longer one at $\sim$4 ps that is close to the $\sim$3 ps decays seen in the $\nu_r$ mode. The FePtFe $\nu_a$ trace has one time constant at $\sim$2 ps and an offset. With the $\nu_b$ mode traces, we cannot compare across molecule or solvent due to low signal in the bridge region of the 2D spectra for FeRu/D$_2$O (Fig. 3(b)). The fits for the $\nu_b$ traces for the FeRu/FA and FePtFe samples reveal a matching decay time constant of $\sim$20 ps fit to them while keeping the decay for the beat constant. This long decay also matches the long time constant seen in the $\nu_r$ mode of FeRu/FA. Only the trans mode of the FeRu/FA sample was fully distinguishable from the other modes due to a lack of overlapping spectral features. This allowed a determination of a CLS trace for one $\nu_r$ mode. Overall, the CLS dynamics reveals that the individual $\nu_{CN}$ modes in the mixed valence complexes studied here interact differently with the solvent at a microscopic level resulting in the different timescales of the fits shown in Table II.

To look at the vibrational dynamics of specific modes using the spectra shown in Figure 3, a small area of each 2D spectrum was chosen for each peak and all signal intensity within that area was summed. These volumes were then plotted as a function of $\tau_2$ to monitor peak specific relaxation. Each of these decays was then fit to a sum of exponentials like the formula used to fit the pump-probe traces. Because of the low number of $\tau_2$ points available, these fits have very large uncertainties and only a few fits are shown in Figure 5 for illustration. These fits are discussed in a qualitative manner. Several illuminating time-dependent cross-peak volume plots for FeRu in FA show growths in addition to their decays (Fig. 5 left panel). These rises indicate population transfer between modes on the order of 1 ps. Most of these cross-peaks also have multiple decay timescales with the longest timescales corresponding to the long timescale extracted from the fit of the dispersed pump-probe data at the same $\omega_3$ frequencies. The mode-specific dynamics of FeRu in D$_2$O do not contain as many growths as the FA sample, but the ones that are observed are also on $\sim$1 ps timescales. Data for FePtFe are similar to that seen for FeRu in FA with multiple rises on the order of 1 ps, several decays, and long timescales on the order of the vibrational lifetimes for the $\nu_{CN}$ modes. All of the short decay timescales seen in the pump-probe match the $\sim$1 ps rises seen in the 2D volume mode-specific relaxation dynamics giving more strength to the argument that intramolecular vibrational transfer dynamics occur in all three systems on a similar timescale.

| Mode      | $t_1$ (ps) ($A_1$) | $t_2$ (ps) ($A_2$) | $\omega_{osc}$ (cm$^{-1}$)$^a$ | $A_\infty$ |
|-----------|-------------------|-------------------|------------------------------|------------|
| FeRu/FA   |                   |                   |                              |            |
| Trans     | 4 ± 2 (0.31)      |                   | ...                          | 0.07 ± 0.05 |
| Radial    | 2 ± 1 (0.23)      | 20 ± 10 (0.23)    | ...                          |            |
| Bridge    | 20 ± 40 (0.21)    | 0.30 (0.3)        | 84                           |            |
| FeRu/D$_2$O|                   |                   |                              |            |
| Radial    | 3 ± 1 (0.26)      |                   | ...                          | 0.09 ± 0.03 |
| Axial     | 4 ± 4 (0.09)      | 0.6 ± 0.7 (0.12)  | ...                          |            |
| FePtFe    |                   |                   |                              |            |
| Radial    | 3 ± 3 (0.83)      |                   | ...                          | 0.1 ± 0.3  |
| Axial     | 2 ± 1 (0.19)      |                   | ...                          | 0.04 ± 0.02 |
| Bridge    | 11 ± 9 (0.16)     | 0.46 (0.7)        | 54                           |            |

$^a$Oscillation frequencies are held constant at their respective pump-probe oscillation frequency.
IV. DISCUSSION

Our results show that the vibrational relaxation and the vibrational dephasing dynamics of the $\nu_{CN}$ modes are mode dependent in the solvated transition metal molecules studied here. Vibrational lifetimes change significantly between modes within the same system and between the same modes in different systems. Long spectral diffusion timescales also show large variations between the same mode in different systems and different modes within the same system. In this section, we will put this work in the larger context of vibrational spectroscopy of CN stretches.

A. Vibrational relaxation dynamics of the $\nu_{CN}$ modes in FeRu and FePtFe

The IR pump-probe experiments reveal that the vibrational lifetimes of the $\nu_{CN}$ modes are $\sim 2$ times faster when FeRu is dissolved in D$_2$O versus FA. This is likely due to the much larger spectral overlap between the IR bands of the $\nu_{CN}$ and D$_2$O than exists between the $\nu_{CN}$ and FA bands. The D$_2$O IR absorption spectrum has a band centered at $\sim 2500$ cm$^{-1}$ which is much broader ($\sim 500$ cm$^{-1}$) and more intense than the closest FA band (centered at $\sim 2210$ cm$^{-1}$ with a width of $\sim 80$ cm$^{-1}$) to the $\nu_{CN}$ modes studied here. This is particularly obvious in the 2D spectra for the FeRu/D$_2$O sample where a large solvent response grows in at high energies along the $\omega_3$ axis (see Figure 3(b)). A greater overlap of the solvent and solute vibrational spectrum would lead to more efficient energy transfer between the solute and solvent resulting in faster relaxation times as noted previously in experiments of isotope labeled CN ions dissolved in aqueous solutions. The vibrational lifetime of the trans mode is also likely faster when FeRu is dissolved in D$_2$O versus FA, but it is hard to say by how much because of spectral congestion in the FeRu/D$_2$O pump-probe spectra. We note that a faster relaxation time for the $\nu_1$ mode in D$_2$O versus FA was also observed in a similar molecule [(NH$_3$)$_5$Ru$_{III}$NCO$_{III}$(CN)$_5$]$^-$ after optical excitation and back electron transfer. This was attributed to better overlap between the $\nu_1$ band and solvent bands in D$_2$O compared with FA. Shorter vibrational lifetimes for the $\nu_1$ mode in FeRu indicate the $\nu_1$ mode has stronger interactions with the solvent than the other three vibrational modes.

The frequency shift of the $\nu_1$ mode in the FTIR and resonance Raman spectra of FeRu in...
different solvents provides evidence of the stronger coupling of the terminal CN ligand to the solvent.\textsuperscript{5,22} We also see evidence of strong coupling to the solvent of the \( \nu_t \) mode in recent 2D VE experiments of FeRu/FA.\textsuperscript{7}

The IR pump-probe and 2D IR relaxation experiments reveal that the lifetime of the \( \nu_{\text{CN}} \) modes in FePtFe/D\(_2\)O is significantly slower than that of FeRu in FA or D\(_2\)O (see Table I). Due to the larger size and increased complexity of FePtFe, it is expected that the vibrational relaxation for the \( \nu_{\text{CN}} \) modes would be faster than for FeRu. Greater complexity increases the number of intramolecular vibrational relaxation channels available for the \( \nu_{\text{CN}} \) modes to dump their energy into leading to more efficient energy transport out of the \( \nu_{\text{CN}} \) modes. FePtFe also has a larger charge than FeRu and previous work with other CN ions in solution has shown that they relax more quickly with increasing charge, likely due to the increased strength of interaction with the solvent.\textsuperscript{40} In addition to these molecular attributes, most of the FePtFe \( \nu_{\text{CN}} \) modes have better overlap with D\(_2\)O IR bands than the \( \nu_{\text{CN}} \) modes of FeRu. Again, this should increase the efficiency with which energy is funneled out of the \( \nu_{\text{CN}} \) modes and into the solvent. Given these factors, it is surprising to see that the vibrational lifetimes for most FePtFe \( \nu_{\text{CN}} \) modes are almost twice as long as the lifetimes for FeRu/FA and four times as long as the lifetimes for FeRu/D\(_2\)O. The \( \nu_t \) mode certainly decays significantly more slowly in FePtFe than in either FeRu sample. The larger charge on the Pt(IV) compared to the Ru(III) explains why the frequencies of the trans and bridging modes are farther to the blue for FePtFe than for FeRu, as described earlier. The large positive charge pulls more electron density out of the cyanide antibonding orbital increasing the strength of that bond and increasing its vibrational frequency. This effect might also explain why the characteristics of the trans mode are so different in FePtFe than for the two FeRu systems. If the reduced metal-ligand interaction in FePtFe results in weaker coupling to other carbon-metal modes or other low frequency modes along the MMCT backbone, this would limit interactions with the solvent for FePtFe in general helping explain why the lifetimes observed are so much longer than those measured for the FeRu systems.

Vibrational lifetimes ranging from 2.3 to 38.2 ps were observed for OCN\(^-\), SCN\(^-\), and SeCN\(^-\) in D\(_2\)O,\textsuperscript{40} a lifetime of 170 ps was measured for the \( \nu_{\text{CN}} \) mode in FeNO(CN)\(_2\)\(^2-\),\textsuperscript{41} and a lifetime of 4.2 ps was observed for a cyanide probe of the villin HP35 protein.\textsuperscript{42} Other simple metal-cyanide compounds have long vibrational lifetimes that range from 8.0 to 170 ps when dissolved in D\(_2\)O.\textsuperscript{43} All of the lifetimes observed in the current study fall within this range with the possible exception of the \( \sim 400 \) fs lifetime measured for the trans mode in FeRu/D\(_2\)O. Vibrational lifetimes for \( \nu_{\text{CN}} \) modes in FePtFe, all of which are \( \sim 18 \) ps, closely match the lifetime of 24 ps reported for Fe\(^{III}\)(CN)\(_6\)\(^3-\) in D\(_2\)O.\textsuperscript{41} However, the lifetimes for FeRu in D\(_2\)O and FA of \( \sim 6 \) ps and \( \sim 10 \) ps, respectively, match the lifetimes reported for Fe\(^{III}\)(CN)\(_6\)\(^3-\) in D\(_2\)O and FA of 8 ps and 10 ps, respectively.\textsuperscript{41} At first glance, such a comparison might indicate that the oxidation state of the iron in FeRu might be +3 instead of the +2 reported or at least more delocalized than assumed. However, work by multiple groups has shown that the extra electron is fairly localized on the Ru and not on the Fe.\textsuperscript{44,45} In a study of single metal-cyanides of the form M(CN)\(_x\)\(^y-\) dissolved in D\(_2\)O, it was found that the vibrational lifetimes for the \( \nu_{\text{CN}} \) mode was split into two camps where the first group have long vibrational energy relaxation times of \( \> 100 \) ps, and the second group have times of \( < 35 \) ps. The first group contains Pt(CN)\(_4\)\(^2-\), a square planar molecule, while the second includes Ru(CN)\(_6\)\(^4-\), Fe(CN)\(_6\)\(^2-\), and Fe(CN)\(_6\)\(^3-\), all octahedral molecules.\textsuperscript{43} While the oxidation state and molecular configuration of the platinum investigated in this study are different than the state of the platinum in FePtFe, the large discrepancy in relaxation rates between the Pt and the Fe containing species, despite the species with similar charges, might provide a clue as to why we observe longer lifetimes for the \( \nu_{\text{CN}} \) modes in FePtFe than in the \( \nu_{\text{CN}} \) modes in FeRu.

**B. Spectral diffusion dynamics of the \( \nu_{\text{CN}} \) modes in FeRu and FePtFe**

Due to the limited number of points available to fit and the large error bars that result for the CLS timescales measured, the comparisons that can be made between the samples studied here and other systems are limited. Approximately 3 ps timescales seen repeatedly in the CLS
measurements can be compared with similar timescales of 1–2 ps seen in the frequency-frequency correlation functions of vibrational probes in several compounds: a 1.5 ps spectral diffusion constant for the $\nu_{\text{CN}}$ mode in Fe$^{11}(\text{CN})_6^{4-}$ in D$_2$O, a ~2 ps timescale for $\nu_{\text{NO}}$ mode FeNO(CN)$_5^{2-}$ in several hydrogen bonding solvents, and a 1.6 ps timescale for the cyanide probe of a villin HP35 protein when water molecules were allowed into the pocket. In all of these cases, the timescale was compared to the characteristic timescale for the forming and breaking of hydrogen bonds. In light of this, the lack of a ~3 ps timescale for the bridge mode CLS could be attributed to its greater isolation from the solvent. The bridging cyanide is less likely to form hydrogen bonds with the solvent because the nitrogen is already bound to the ruthenium instead of being free to interact with the solvent like it is for the other CN ligands. Comparing the $\nu_{\text{r}}$ traces between all three samples, there is a dependence on solvent in that both D$_2$O samples only have one decay and an offset, whereas the FA sample has a similar short decay and a longer decay with no offset. This would suggest that, at least for this mode, spectral diffusion rates could rely on the structure of the molecule. But we can see a difference in the spectral diffusion timescales between the molecules by comparing the $\nu_{\text{r}}$ traces between FeRu and FePtFe in D$_2$O. The FePtFe sample only shows the ~1 ps decay and an offset. In contrast, the FeRu sample shows a shorter timescale, the ~1 ps decay, and no offset. The lineshape analysis of the CN modes in FeRu and FePtFe reveal a complex picture of solute-solvent interactions in these transition metal mixed-valence complexes. This complex picture is also borne out by the X-ray absorption spectroscopy of FeRu dissolved in water at the Ru L$_3$ edge which has revealed that the explicit hydrogen bonding environment of the solvent is essential to stabilize the complex with the correct oxidation states of the transition metal atoms.

V. SUMMARY

The goal of this study was to investigate the vibrational relaxation and dephasing dynamics for a set of four anharmonically coupled cyanide stretching vibrations of bimetallic and trinmetallic transition metal mixed-valence complexes. We measure vibrational lifetimes, intramolecular vibrational transfer dynamics, and spectral diffusion dynamics using infrared pump-probe and two-dimensional infrared spectroscopies. The values for vibration lifetimes reveal that the ~18 ps lifetimes for the $\nu_{\text{CN}}$ modes of FePtFe dissolved in D$_2$O are approximately four times longer than the modes of FeRu dissolved in D$_2$O and two times longer than the modes in FeRu dissolved in FA. Vibrational lifetimes for the trans mode in both FeRu systems are significantly faster than the other three modes, which is not the case for FePtFe. This is an indication that FePtFe has weaker solute-solvent interactions since the trans mode is the most accessible to the solvent. Mode specific dynamics from both the pump-probe and 2D IR experiments reveal that intramolecular vibrational transfer processes are occurring in all three systems on the order of 1 ps. Spectral diffusion dynamics reveal that the radial, axial, and trans $\nu_{\text{CN}}$ modes show a ~3 ps timescale that is indicative of the forming and breaking of hydrogen bonds between the solvent and each $\nu_{\text{CN}}$ mode that is not apparent in the bridge mode. These results along with our previous work on these complexes reveal a complex solute-solvent environment with coupled anharmonic $\nu_{\text{CN}}$ modes where the spectral diffusion and vibrational relaxation dynamics are different for specific modes depending on their spatial localization on the molecular complex. Recent 2D VE results clearly indicate that only some of the $\nu_{\text{CN}}$ modes are coherently coupled to the metal-to-metal charge transfer transition. The vibronic nature of the $\nu_{\text{CN}}$ modes adds an additional layer of complexity to analyzing the vibrational relaxation processes in the ground electronic state. The results in this work present a challenge to theorists interested in calculating structural dynamics of charge transfer systems where the electronic, vibrational, and solvent degrees of freedom are intrinsically coupled.

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