Probing and Exploiting the Interplay between Nuclear and Electronic Motion in Charge Transfer Processes

Published as part of the Accounts of Chemical Research special issue "Ultrafast Excited-State Processes in Inorganic Systems".

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CONSPECTUS: The Born−Oppenheimer approximation refers to the assumption that the nuclear and electronic wave functions describing a molecular system evolve and can be determined independently. It is now well-known that this approximation often breaks down and that nuclear−electronic (vibronic) coupling contributes greatly to the ultrafast photophysics and photochemistry observed in many systems ranging from simple molecules to biological organisms.


In order to probe vibronic coupling in a time-dependent manner, one must use spectroscopic tools capable of correlating the motions of electrons and nuclei on an ultrafast time scale. Recent developments in nonlinear multidimensional electronic and vibrational spectroscopies allow monitoring both electronic and structural factors with unprecedented time and spatial resolution. In this Account, we present recent studies from our group that make use of different variants of frequency-domain transient two-dimensional infrared (T-2DIR) spectroscopy, a pulse sequence combining electronic and vibrational excitations in the form of a UV−visible pump, a narrowband (12 cm^{-1}) IR pump, and a broadband (400 cm^{-1}) IR probe.

In the first example, T-2DIR is used to directly compare vibrational dynamics in the ground and relaxed electronic excited states of Re(Cl)(CO)$_3$(4,4′-diethylester-2,2′-bipyridine) and Ru(4,4′-diethylester-2,2′-bipyridine)$_2$(NCS)$_2$, prototypical charge transfer complexes used in photocatalytic CO$_2$ reduction and electron injection in dye-sensitized solar cells. The experiments show that intramolecular vibrational redistribution (IVR) and vibrational energy transfer (VET) are up to an order of magnitude faster in the triplet charge transfer excited state than in the ground state. These results show the influence of electronic arrangement on vibrational coupling patterns, with direct implications for vibronic coupling mechanisms in charge transfer excited states.

In the second example, we show unambiguously that electronic and vibrational movement are coupled in a donor−bridge−acceptor complex based on a Pt(II) *trans*-acetylide design motif. Time-resolved IR (TRIR) spectroscopy reveals that the rate of electron transfer (ET) is highly dependent on the amount of excess energy localized on the bridge following electronic excitation. Using an adaptation of T-2DIR, we are able to selectively perturb bridge-localized vibrational modes during charge separation, resulting in the donor−acceptor charge separation pathway being completely switched off, with all excess energy redirected toward the formation of a long-lived intraligand triplet state. A series of control experiments reveal that this effect is mode specific: it is only when the high-frequency bridging C≡C stretching mode is pumped that radical changes in photoproduct yields are observed. These experiments therefore suggest that one may perturb electronic movement by stimulating structural motion along the reaction coordinate using IR light.

These studies add to a growing body of evidence suggesting that controlling the pathways and efficiency of charge transfer may be achieved through synthetic and perturbative approaches aiming to modulate vibronic coupling. Achieving such control would represent a breakthrough for charge transfer-based applications such as solar energy conversion and molecular electronics.
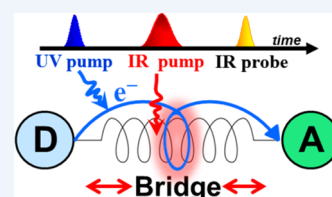
1. INTRODUCTION

1.1. Background and Significance

Classical analyses of photophysical and photochemical mechanisms treat nuclear and electronic wave functions independently, under the Born−Oppenheimer approximation. Such treatments are founded on the assumption that nuclear movement is slow enough to appear fixed on the rapid electronic movement time scale. This phenomenon results in the well-known Franck−Condon principle, which states that electronic transitions occur without changes in the molecular structure or that of its environment. Another often applied photophysical concept is Kasha's rule and derivations thereof. In the most encompassing terms, this rule assumes that vibrational relaxation (VR) is faster than internal conversion (IC) between electronic states, which itself is faster than intersystem crossing (ISC) between different spin manifolds: $k_{VR} \gg k_{IC} \gg k_{ISC}$. Thus, molecules are perceived to only emit
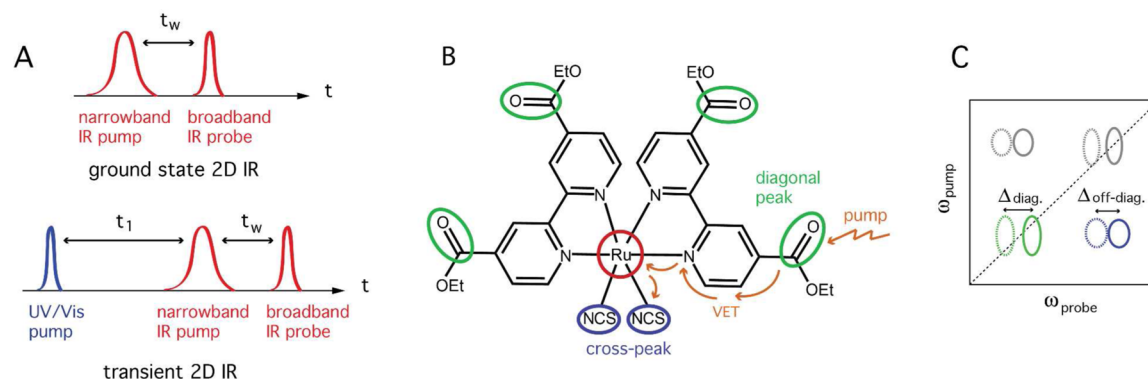
Figure 1. (A) Frequency-domain 2DIR and T-2DIR pulse sequences. (B) Simplistic scheme of VET in Ru(4,4′-diethylester-2,2′-bpy)$_2$(NCS)$_2$ upon IR excitation of ν(C=O). (C) Typical 2DIR spectrum containing diagonal peaks of the excited modes (green) and cross-peaks (purple). The frequency difference between solid and dashed contours are diagonal and off-diagonal anharmonicities.[32]

and react in appreciable yields from the lowest state of a given multiplicity. Under these approximations, nuclear–electronic (vibronic) interactions are negligible and do not contribute to the photophysics or photochemistry of molecular systems.[1]

We now know of course that there are many exceptions to these rules; in fact, in several classes of molecular systems (including charge transfer transition metal complexes, the focus of this Account), the exceptions outweigh the rule. On the ultrafast time scales, the experimentalist will often struggle to deconvolute VR, IC, and ISC processes, which frequently occur concomitantly on strongly interacting potential energy surfaces.[2−10] In such cases, there are opportunities for nuclear and electronic degrees of freedom to interact and affect each other.[4,5,11] In some extreme cases, such interactions fully dictate the rates and pathways of photoinduced transformations by allowing or disabling certain electronic transitions.[12−14]

This Account summarizes recent efforts of our group to gain a deeper understanding of how electronic density distribution affects vibrational dynamics, how excess vibrational energy affects electronic processes, and ultimately whether one can exploit vibronic interactions by external perturbation to control electron transfer (ET) processes with appreciable efficiency. These studies, performed on Re(I), Ru(II), and Pt(II) charge-transfer complexes, add to a fast-growing body of evidence that continuously demonstrates the importance of nuclear–electronic interactions in systems ranging from simple molecules to large biological organisms.[14−20] Gaining deeper insight into how to alter such interactions will offer unprecedented opportunities to control charge transfer processes, bearing direct significance to applications in solar energy harvesting and information processing and storage.

1.2. The Toolbox

To probe vibronic interactions affecting electron transfer in a time-dependent manner, one must use spectroscopic tools capable of correlating nuclear and electronic motion on ultrafast time scales. Recent phenomenal developments in time-resolved X-ray spectroscopies and electron diffraction, among other techniques, have allowed these correlations to be monitored through the use of structure-sensitive probes, but generally require major equipment such as free electron lasers to deliver the required pulses.[21,22] A more accessible yet powerful toolset consists of nonlinear multidimensional electronic and vibrational spectroscopies.[23,24] In particular, two-dimensional infrared (2DIR) spectroscopy[25,26] provides bond-specific information through chemical selectivity that

allows a degree of spatial resolution not attainable with UV–visible methods. Combining 2DIR with a UV–visible excitation pulse (a method often referred to as transient 2DIR, T-2DIR)[27] permits structural changes that accompany rapid photoinduced electronic processes to be resolved, providing a way to correlate nuclear and electronic degrees of freedom.

Comprehensive reviews of 2DIR and T-2DIR techniques have recently become available,[26,28−31] and only a fleeting overview is given here. The relation between 2DIR and linear IR spectroscopy is analogous to that between 2D NMR and NMR, with the added benefit of time resolutions on the order of ~100 fs to 1 ps achievable with commercial ultrafast lasers. These multidimensional spectra provide insights not accessible with linear methods by spreading the information over two frequency axes (excitation and detection). The information lying on the "diagonal" (excitation frequency = detection frequency) broadly corresponds to the information provided by linear IR spectra, while "off-diagonal" signals arise from the interaction between different vibrational modes (Figure 1).

There are several configurations available to perform 2DIR studies, with the frequency[25] and the time domain[33] schemes being the main variants. While both schemes yield the same information, they differ in experimental complexity as well as time and spectral resolution.[28,34] The experiments described herein use the simpler, lower-resolution double-resonance (frequency domain) arrangement,[25] which utilizes a narrowband IR pump (10−15 cm^{-1}, 1−1.5 ps pulsewidth) and broadband IR probe (300−400 cm^{-1}) (Figure 1A). The experiment is performed by scanning the IR pump in small frequency steps across a range of interest (typically 1200−2400 cm^{-1}) while probing at a set IR$_{pump}$−IR$_{probe}$ waiting time t_w; a schematic 2D map resulting from such an experiment is shown in Figure 1C. Figure 1B shows an example vibrational energy transfer (VET) scheme for Ru(4,4′-diethylester-2,2′-bpy)$_2$(NCS)$_2$ whereby a C=O stretching mode is excited by the IR pump and relaxes through intramolecular vibrational redistribution (IVR) to surrounding low-frequency modes, which subsequently transfer vibrational energy across the molecule toward a probed vibration, in this case a CN stretch. Low-frequency modes surrounding the latter are anharmonically coupled to the probed vibration, giving rise to a cross-peak (Figure 1C). 2DIR can help resolve such long-range VET schemes by extending t_w into tens of picoseconds.[31,35]

T-2DIR experiments can be performed by introducing a UV–vis laser pulse before or during the 2DIR pulse sequence to trigger an electronic process. The nature of the experiment

depends on the specific sequence used and the time delay between the UV−vis pump and IR pump.[29,30] In the simplest T-2DIR experiment, a long-lived (>1 ns) electronic excited state is populated with the UV−vis pump; initial solvation response and vibrational processes on the nascent excited state surface are permitted to relax (typically 100−200 ps) before introducing the 2DIR pulse sequence. The equivalent of ground state 2DIR but in an electronically excited state is then measured, correlating vibrational dynamics to electron density distribution. Examples of such studies on Re(I) and Ru(II) complexes are given in section 2. Introduction of a small time delay, t_1, between the UV and IR pumps permits a variety of experiments, including probing excited state solvation dynamics[36] and perturbing structural dynamics during a triggered electronic process. The latter is demonstrated in section 3.2 on the example of a Pt(II) donor−bridge−acceptor complex. Finally, reversing the order of the two pumps is used in T-2DIR exchange spectroscopy where a specific vibration is labeled in the ground state and its frequency is directly correlated to its excited state counterpart following electronic excitation.[37] There are many other creative uses of this highly adaptive method,[38−40] including a recently reported combination of 2D electronic with 2DIR spectroscopies, which provides a more direct correlation of nuclear and electronic degrees of freedom in virtually any system.[41]

The experiments discussed here were performed at the Rutherford Appleton Laboratory.[42] A 10 kHz ultrafast laser system uses optical choppers to modulate the UV−visible pump at 5 kHz and the IR pump at 2.5 kHz, providing complete freedom over the order of the three pulses while allowing recording background, time resolved IR (TRIR), 2DIR, and T-2DIR spectra simultaneously. TRIR and 2DIR data are collected under magic angle configuration between the pump and the probe beams to suppress rotational diffusion from population dynamics. T-2DIR is a fifth order experimental technique involving up to three transition dipole moments but only two independently controllable polarization degrees of freedom; therefore no real magic angle condition is possible.[43] In our experiments, UV and IR pumps are in parallel polarization to each other, while the IR probe is set at magic angle with respect to both pumps. Orientational effects are negligible in this configuration for the specific set of experiments described below, where only one time delay is varied at a time.[43]

2. DIRECT COMPARISON OF VIBRATIONAL DYNAMICS IN GROUND AND EXCITED STATES OF METAL CHROMOPHORES

We have recently implemented 2DIR and T-2DIR to study IVR and VET mechanisms in the ground and charge transfer excited states of two prototypical transition metal complexes: Re(Cl)-(CO)$_3$(4,4′-diethylester-2,2′-bpy) and Ru(4,4′-diethylester-2,2′-bpy)$_2$(NCS)$_2$, where bpy is bipyridine, abbreviated ReCOe and RuNCS-e, respectively. The former is a derivative of a well-known CO_2 reduction photocatalyst, while the latter is a derivative of the RuN3 dye, an efficient sensitizer in dye-sensitized solar cells. In both complexes, UV−visible light promotes the molecules to a singlet metal-to-ligand charge transfer (^{1}MLCT) state, which undergoes rapid intersystem crossing (<1 ps) to a long-lived ^{3}MLCT state of predominantly metal-to-bpy charge transfer character. Solvent reorganization and vibrational relaxation on the ^{3}MLCT surface are complete in <100 ps. Referring to Figure 1A, this means that in T-2DIR

experiments, t_1 can be kept at 100 ps < t_1 < 1 ns to allow IC, ISC, and VR following excitation to fully finish before introducing the 2DIR pulse sequence in ^{3}MLCT, thereby isolating the vibrational dynamics of interest from all other kinetic processes.

Both molecules contain infrared reporters that are well separated in space (8−10 Å) and frequency ($\nu(C\equiv O) \approx 2000$ cm^{-1} and $\nu(C=O) \approx 1730$ cm^{-1} in ReCOe, $\nu(CN) \approx 2200$ cm^{-1} and $\nu(C=O) \approx 1730$ cm^{-1} in RuNCS-e), allowing for selective vibrational excitation while probing long-range VET. The results for both molecules are strikingly similar, with the main finding that IVR and VET in ^{3}MLCT are up to an order of magnitude faster than in the ground state.[32,44] Due to the similarity in behavior of these two systems, only ReCOe is discussed further.

Figure 2 shows the ground state two-dimensional IR (GS2DIR) maps of ReCOe in CD$_2$Cl$_2$ at 1 and 10 ps waiting
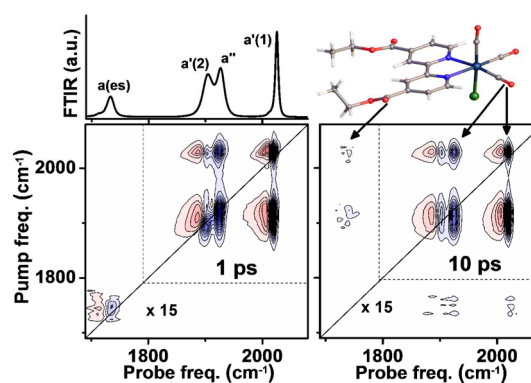

Figure 2. Ground state 2DIR maps for ReCOe in CD$_2$Cl$_2$ at 1 ps (left) and 10 ps (right) waiting time t_w. Colors correspond to transient absorption changes of +25 mOD (red) and −25 mOD (blue). The linear FTIR spectrum with corresponding band assignments in the range of interest and the X-ray structure of ReCOe are shown.[44]

time. The three $\nu(C\equiv O)$ vibrations, a′(1), a′(2), and a″, are directly coupled. Thus, at 1 ps waiting time, all three vibrations show cross peaks as well as diagonal peaks. The ester $\nu(C=O)$ mode, a(es), is far from the metal carbonyls and is therefore not anharmonically coupled to the $\nu(C\equiv O)$ modes. Through-space coupling over such large distances is also considered to be negligible.[31,45] Nonetheless, at 10 ps, small cross-peaks are observable at both $\nu(C=O)$ and $\nu(C\equiv O)$ positions; thus VET across the molecule has taken place, provoking a response from distant modes. Note that the diagonal a(es) peak has disappeared by 10 ps, implying that the a(es) mode is short-lived, whereas the $\nu(C\equiv O)$ modes still display intense diagonal peaks.

Varying t_w allows extraction of the IVR and VET kinetics. These are shown in Figure 3A,B for both VET directions: pumping a′(1) and monitoring a′(1) → a(es) VET, and vice versa. Note that cross-peaks are not necessarily an indication of the *population* of a particular vibrational mode. In the cases presented here, the a(es) mode is never populated following a′(1) excitation; only low-frequency modes in spatial proximity and anharmonically coupled to a(es) are populated, producing a cross-peak at the a(es) position on the probe axis. The same is true for VET in the opposite direction.

Figure 3C,D compares the a′(1) and a(es) mode lifetimes in the ground and excited states; the extracted IVR, VET, and cooling (equilibration with the solvent bath) lifetimes are
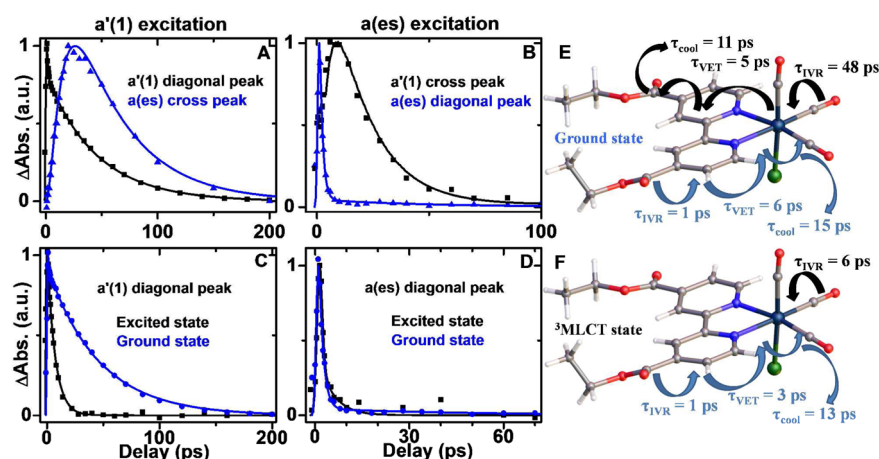
Figure 3. Normalized kinetic traces extracted from bleach kinetics of 2DIR and T-2DIR data for ReCOe in CD_2Cl_2. (A) Ground state $a'(1)$ diagonal peak and $a(es)$ cross peak. (B) Ground state $a(es)$ diagonal peak and $a'(1)$ cross peak. Comparison of $a'(1)$ (C) and $a(es)$ (D) diagonal peak lifetimes in the ground (blue) and ^{3}MLCT (black) states. Solid lines represent best fits deconvoluted from a Gaussian instrument response function.[44] Extracted lifetimes are represented schematically (E) for the ground state and (F) for the ^{3}MLCT state. Note that VET from $a'(1)$ to $a(es)$ in ^{3}MLCT was not satisfactorily resolved due to the low signal-to-noise of the $a(es)$ cross-peak in T-2DIR experiments.

represented schematically in Figure 3E,F. The results are surprising: the $a'(1)$ mode lifetime (equivalent here to all $\nu(C\equiv O)$ IVR lifetime) reduces from 48 ps in the ground state to 6.5 ps in the excited state. A recent study on a similar Re-tricarbonyl found the same increase in $\nu(C\equiv O)$ deactivation rate,[46] and in RuNCS-e, we observed a similar reduction in the $\nu(CN)$ lifetime, from 60 ps in the ground to 7 ps in the excited state.[32] Meanwhile, the $a(es)$ IVR lifetime in ReCOe remains the same, at around 1 ps, and the VET lifetime is reduced by at least a factor of 2, from 6 to 3 ps, upon promotion to the excited state.

The $a'(1)$ lifetime in the ground state is dependent on the polarity of the solvent (CH_2Cl_2, MeCN, or toluene). This observation is as expected since solvent−solute frequency fluctuations are known to affect the rate and amplitude of vibrational energy level fluctuations in the solute.[31,47] These interactions can speed up IVR and VET through favorable frequency matching conditions. Surprisingly, the solvent dependence disappears in ^{3}MLCT, suggesting that the mechanism responsible for the rapid deactivation of $\nu(C\equiv O)$ in ^{3}MLCT must be predominantly intramolecular.

The $\nu(C\equiv O)$ mode in ReCOe and $\nu(CN)$ mode in RuNCS-e are somewhat isolated from the rest of the molecule by the central heavy atom. Since IVR occurs through surrounding anharmonically (mechanically) coupled modes,[31,45] IVR originating from high frequency $C\equiv O$ and CN vibrations of the ligands must occur primarily through low-frequency modes that involve displacement of the metal center. The resulting large energy mismatch renders these transitions inherently inefficient, accounting for particularly slow IVR in the ground state.[48,49] So what is responsible for an observed acceleration of IVR in ^{3}MLCT?

The MLCT transition depletes electron density on the metal center, reducing metal → CO π back-donation to the antibonding orbital and resulting in higher $\nu(C\equiv O)$ frequencies. Several studies have shown that π back-donation facilitates intramolecular anharmonic coupling of the $C\equiv O$ modes to surrounding low-frequency modes. Reducing π back-donation should therefore result in slower IVR.[50,51] We observe the opposite effect. This contradiction suggests that a

mechanism other than increased anharmonic coupling facilitates IVR in the excited state of Re-carbonyls.

Electron density redistribution in the excited state, which results in greater dipole over the metal−CO or metal−NCS fragments of the molecules, can increase short distance dipole−dipole coupling surrounding the metal center. IVR through anharmonic coupling is slowed down in the ground state due to structural and thermodynamic barriers imposed by large displacements of the heavy metal atom. It is possible that through-space dipole−dipole coupling in ^{3}MLCT helps overcome these barriers by effectively circumventing low-frequency modes involving large displacements of the metal center, resulting in faster alternative IVR pathways from $\nu(C\equiv O)$ or $\nu(CN)$. Softening of low-frequency skeletal modes was also suggested as a potential mechanism for increased IVR in the excited state.[46] Additional investigations are currently underway to elucidate this intriguing effect.

These studies illustrate the power of T-2DIR to directly compare and contrast vibrational dynamics in the ground and excited state of metal complexes. Similar T-2DIR experiments have been performed to investigate vibrational dynamics of hot photoproducts following UV photolysis.[52,53] Such comparisons allow one to relate vibrational coupling mechanisms to electron density distribution and structure in molecules and what effect this may have on the sampling of structural movement along reaction coordinates, which define the efficiencies of various electronic processes.

3. THE INFLUENCE OF BRIDGE-LOCALIZED VIBRATIONS IN DONOR−BRIDGE−ACCEPTOR SYSTEMS

When electron transfer is mediated by molecular bridges in donor−bridge−acceptor (DBA) systems,[54,55] the bridge structure and its thermal and nuclear motions modulate ET probability[56] by affecting a number of parameters including electronic and vibronic coupling interactions. Much sophisticated work has been devoted to formulating frameworks capable of explaining the variety of ET mechanisms in DBA systems.[1,14,56−60]

One theoretical framework considers controlling ET processes using IR-excitation to affect vibronic interactions in

the nonadiabatic (weakly electronically coupled) electron tunneling medium. Skourtis, Beratan, and co-workers showed that the exchange of energy between tunneling electrons and bridge-localized nuclear modes (inelastic tunneling) may erase interferences that govern ET pathways between a donor and acceptor.[13] In such cases, theory predicts that labeling specific pathways by mode-specific excitation of bridge vibrations using IR-light can effectively direct ET.[12,13,61] In an elegant study by Rubtsov, Beratan, and co-workers,[62] vibrational excitation with broadband (~120 cm^{-1}) IR-pulses that perturbed the H-bonding network linking donor and acceptor molecules was shown to slow down the photoinduced intermolecular charge-separation process and decrease its yield by ~1.8%.[62] This study demonstrated the viability of using IR-excitation to perturb structural movement during charge separation and consequently modulate ET efficiency.

In this section, we summarize some recent findings from our group on the influence of bridge-localized nuclear modes in a Pt(II) *trans*-acetylide DBA system, PTZ−CH$_2$−Ph−C≡C−Pt(PBu$_3$)$_2$−C≡C−NAP (hereafter PTZ-CH$_2$-Pt-NAP), where PTZ is the electron donor group phenothiazine and NAP is the acceptor naphthalene monoimide (Figure 4).[63] The bridging ν(C≡C) and acceptor-localized ν(C=O) modes are strong infrared reporters, which allow monitoring of the excited state dynamics using TRIR spectroscopy.

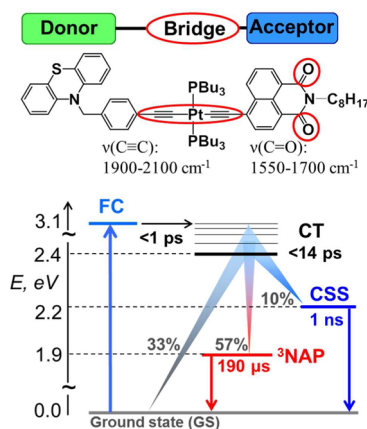**Figure 4.** DBA triad PTZ−CH$_2$−Ph−C≡C−Pt(PBu$_3$)$_2$−C≡C−NAP (PTZ-CH$_2$-Pt-NAP), its infrared reporters, and the summary of its excited state evolution in CH$_2$Cl$_2$ following 400 nm, 50 fs laser excitation at room temperature.[63,64] All states keep the same color-coding throughout this section.

The section is split in two parts. Part 3.1 briefly reviews the evidence of how bridge-localized excess energy influences ET dynamics, as revealed by TRIR spectroscopy; part 3.2 applies T-2DIR to selectively perturb bridging vibrations during charge separation and probe the resulting modulation in excited state dynamics.

3.1. Excited State Dynamics and the Effect of Excess Energy

The complex excited state dynamics of PTZ−CH$_2$−Pt−NAP in solution was elucidated by a combination of methods, predominantly ultrafast electronic transient absorption, TRIR, and density functional theory (DFT) calculations.[63] Laser excitation (400 nm) initiates bridge-to-NAP ET, populating a charge transfer (CT) manifold. CT is a gateway state from which multiple ET pathways originate: forward ET from the

donor, forming a full charge separated state (CSS); back ET, reforming the ground state (GS); and the formation of a long-lived $\pi-\pi*$ intraligand triplet state on the NAP moiety (^{3}NAP). These photophysical pathways including the energies, yields, and lifetimes are summarized in Figure 4.

An intriguing aspect in the excited state dynamics of this system is the decay of CT to CSS, ^{3}NAP, and the GS over a range of time scales concomitant with thermalization. This is most evident in the TRIR spectrum in the acetylide frequency region (Figure 5A), where the broad signal with maximum at
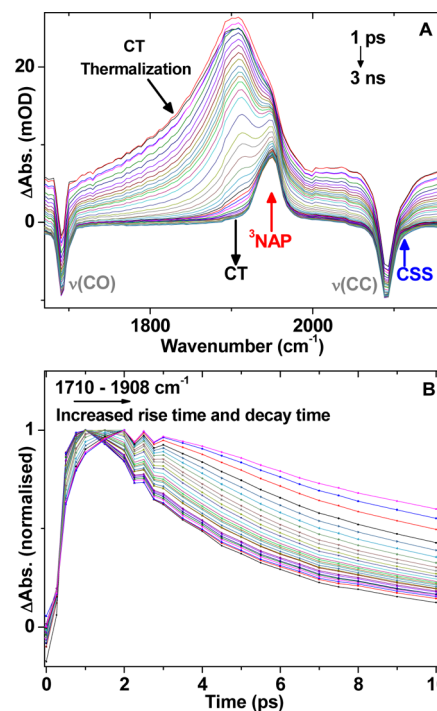
Figure 5. (A) TRIR spectrum in the acetylide frequency region and (B) corresponding single-pixel kinetic traces plotted every 10 cm^{-1} throughout the ν(C≡C) band in CT, from 1710 to 1908 cm^{-1} following 400 nm, 50 fs excitation of PTZ-CH$_2$-Pt-NAP in CH$_2$Cl$_2$.[63]

1908 cm^{-1} is assigned to ν(C≡C) in CT. Figure 5B shows that the rise and decay times of the signal systematically increase with an increase in the detection frequency, from instrument-limited ~200 fs to 14 ps. Such kinetic behavior and unusual band broadening is in part due to the high-frequency mode coupling to spatially close, anharmonically coupled low-frequency modes that are vibrationally excited.[65] As these low-frequency modes relax, the high-frequency band narrows, giving a direct probe of the thermalization of local low-frequency bridge modes.

The nonexponential decay of ν(C≡C) in CT (~200 fs to 14 ps) mirrors the grow-in of the product states (GS, ^{3}NAP, and CSS). This is direct evidence that electron transfer (ET) occurs from a nonthermalized CT state. The fastest rates take place when ν(C≡C) is broadest, indicating that ET rates scale with the amount of excess vibrational energy localized on the bridge.[66,67] This effect was confirmed by varying the excitation wavelength and monitoring the changes in the spectral shape of ν(C≡C) and concomitant ET dynamics.[63]

3.2. Modulation of ET Rates and Pathways by Infrared Stimulation of Bridge Vibrations

Several features in PTZ-CH$_2$-Pt-NAP make it an ideal candidate for attempting to perturb vibronic interactions in the bridge using mode-specific IR excitation. The excited state dynamics are complex, featuring multiple simultaneous ET pathways. The high-frequency bridging $\nu(C\equiv C)$ vibration is well isolated in energy and space, facilitating selective excitation. Furthermore, $\nu(C\equiv C)$ was previously identified as the ET reaction coordinate in related Pt(II) *trans*-acetylides.[68] Finally, as discussed above, the TRIR spectra showed that ET from the charge-transfer state occurs concomitantly with vibrational relaxation.

The experiment was performed using a variant of the T-2DIR pulse sequence. A 400 nm, 50 fs pulse prepares the CT state; a tunable narrowband IR pump ($\sim$12 cm^{-1}, $\sim$1.5 ps pulsewidth) then selectively excites the intense $\nu(C\equiv C)$ band in CT 2 ps after the 400 nm pump. The product states generated over all reaction pathways are then quantified with a broadband IR probe ($\sim$400 cm^{-1}). The changes in IR absorption were recorded as ΔAbs(IR$_{pumpON}$−IR$_{pumpOFF}$), which is the equivalent of {TRIR(IR pump ON) − TRIR(IR pump OFF)}, thereby solely extracting the effect of the intermediate IR-excitation.[64]

The main result is displayed in Figure 6. ΔAbs(IR$_{pumpON}$−IR$_{pumpOFF}$) (bottom panel) 198 ps after vibrational excitation
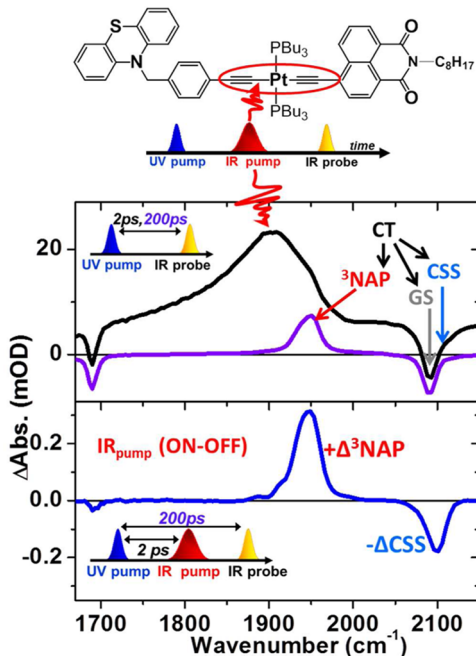

Figure 6. Results of the IR-modulation experiments. The top panel shows the TRIR at representative delay times. The bottom panel shows ΔAbs(IR$_{pumpON}$−IR$_{pumpOFF}$) 200 ps after UV excitation (198 ps after IR excitation) that demonstrate suppression of the CSS and an increase of the ^{3}NAP pathway by IR excitation.[64]

(i.e., long after any vibrations have lost memory of IR excitation through IVR and cooling) shows distinct signals associated with the ^{3}NAP and CSS electronic states. The former is positive, indicating that IR excitation increased the amount of ^{3}NAP formed compared with the IR-pump-OFF case. The CSS-associated signal is negative, indicating a suppression of this pathway.

A quantitative investigation reveals that for every molecule that absorbs an IR photon, the CSS pathway (10% yield without IR excitation) is fully switched off, with all excess energy redirected toward the formation of more ^{3}NAP.[64] In other words, the molecule acts as an *IR-photoswitch*. This effect is mode-specific: pumping other modes such as $\nu(C=O)$ in the same excited state does not affect product yields. It is also time-specific: reversing the UV−IR pump pulse sequence to vibrationally pre-excite $\nu(C\equiv C)$ in the ground state accelerates ET, as expected from the excess energy effects revealed with TRIR spectroscopy, but does not affect product yields because ET is accelerated uniformly across all pathways.[64]

These experiments conclusively prove that nuclear motion in the bridge radically affects the efficiencies and pathways of ET reactions in DBA molecules. Using IR excitation to transiently perturb bridge vibrational dynamics during ET processes may ultimately lead to predictive IR-control of excited state processes, with direct applications in a range of molecular devices.

4. CONCLUDING REMARKS

This Account reviews our recent studies probing the interplay between nuclear and electronic motion in charge transfer transition metal complexes. We have used the powerful yet accessible frequency-domain transient-2DIR method, which combines electronic and vibrational excitations to provide structure-specific information before, during, and after photo-induced electronic processes.

Section 2 discusses how the distribution of electron density has profound effects on vibrational energy flow in octahedral Re(I) and Ru(II) complexes: structural and thermodynamic constraints that slow down IVR in the vicinity of the metal center in the ground state are alleviated in the MLCT excited state.

Section 3 presents a Pt(II) *trans*-acetylide DBA system in which bridge-localized vibronic effects dramatically affect ET rates and pathways. Mode-specific excitation of the stretching vibration of the bridging acetylide during ET completely switches off the charge separation pathway, redirecting all energy toward a long-lived intraligand triplet state. This experiment illustrates that even in the condensed phase, where memory of vibrational excitation is typically short-lived due to rapid IVR, timely perturbation of structural movement along the reaction coordinate can substantially affect excited state dynamics, pathways, and product state yields.

The field has long moved on from the approximations that separate nuclear and electronic motion to describe ultrafast processes in condensed phase systems. Understanding and ultimately controlling the vibronic interactions that dictate the reaction pathways and efficiencies of various electronic processes is one of the great challenges of modern chemistry, which may open the door onto hitherto unexplored territories.

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All authors contributed to and approve the paper's submission.

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■ REFERENCES

(1) Barbara, P. F.; Meyer, T. J.; Ratner, M. A. Contemporary Issues in Electron Transfer Research. *J. Phys. Chem.* **1996**, *100*, 13148−13168.

(2) Damrauer, N.; Cerullo, G.; Yeh, A.; Boussie, T.; Shank, C.; McCusker, J. Femtosecond Dynamics of Excited-State Evolution in [Ru(bpy)$_3$]$^{2+}$. *Science* **1997**, *275*, 54−57.

(3) McCusker, J. K. Femtosecond Absorption Spectroscopy of Transition Metal Charge-Transfer Complexes. *Acc. Chem. Res.* **2003**, *36*, 876−887.

(4) Cannizzo, A.; Blanco-Rodríguez, A. M.; El Nahhas, A.; Sebera, J.; Zális, S.; Vlcek, A.; Chergui, M. Femtosecond Fluorescence and Intersystem Crossing in rhenium(I) Carbonyl-Bipyridine Complexes. *J. Am. Chem. Soc.* **2008**, *130*, 8967−8974.

(5) Schrauben, J. N.; Dillman, K. L.; Beck, W. F.; McCusker, J. K. Vibrational Coherence in the Excited State Dynamics of Cr(acac)3: Probing the Reaction Coordinate for Ultrafast Intersystem Crossing. *Chem. Sci.* **2010**, *1*, 405−410.

(6) Petersson, J.; Eklund, M.; Davidsson, J.; Hammarström, L. Ultrafast Electron Transfer Dynamics of a Zn(II)porphyrin-Viologen Complex Revisited: S2 vs S1 Reactions and Survival of Excess Excitation Energy. *J. Phys. Chem. B* **2010**, *114*, 14329−14338.

(7) Bhasikuttan, A. C.; Suzuki, M.; Nakashima, S.; Okada, T. Ultrafast Fluorescence Detection in tris(2,2′-bipyridine)ruthenium(II) Complex in Solution: Relaxation Dynamics Involving Higher Excited States. *J. Am. Chem. Soc.* **2002**, *124*, 8398−8405.

(8) Consani, C.; Auböck, G.; Bräm, O.; van Mourik, F.; Chergui, M. A Cascade through Spin States in the Ultrafast Haem Relaxation of Met-Myoglobin. *J. Chem. Phys.* **2014**, *140*, No. 025103.

(9) Chergui, M. On the Interplay between Charge, Spin and Structural Dynamics in Transition Metal Complexes. *Dalton Trans.* **2012**, *41*, 13022−13029.

(10) Heydová, R.; Gindensperger, E.; Romano, R.; Sýkora, J.; Vlcek, A.; Záliš, S.; Daniel, C. Spin-Orbit Treatment of UV-Vis Absorption Spectra and Photophysics of rhenium(I) Carbonyl-Bipyridine Complexes: MS-CASPT2 and TD-DFT Analysis. *J. Phys. Chem. A* **2012**, *116*, 11319−11329.

(11) Conyard, J.; Addison, K.; Heisler, I. A.; Cnossen, A.; Browne, W. R.; Feringa, B. L.; Meech, S. R. Ultrafast Dynamics in the Power Stroke of a Molecular Rotary Motor. *Nat. Chem.* **2012**, *4*, 547−551.

(12) Xiao, D.; Skourtis, S. S.; Rubtsov, I. V.; Beratan, D. N. Turning Charge Transfer on and off in a Molecular Interferometer with Vibronic Pathways. *Nano Lett.* **2009**, *9*, 1818−1823.

(13) Skourtis, S. S.; Waldeck, D. H.; Beratan, D. N. Inelastic Electron Tunneling Erases Coupling-Pathway Interferences. *J. Phys. Chem. B* **2004**, *108*, 15511−15518.

(14) Beratan, D. N.; Skourtis, S. S.; Balabin, I. A.; Balaeff, A.; Keinan, S.; Venkatramani, R.; Xiao, D. Steering Electrons on Moving Pathways. *Acc. Chem. Res.* **2009**, *42*, 1669−1678.

(15) Halpin, A.; Johnson, P. J. M.; Tempelaar, R.; Murphy, R. S.; Knoester, J.; Jansen, T. L. C.; Miller, R. J. D. Two-Dimensional Spectroscopy of a Molecular Dimer Unveils the Effects of Vibronic Coupling on Exciton Coherences. *Nat. Chem.* **2014**, *6*, 196−201.

(16) Prokhorenko, V. I; Nagy, A. M.; Waschuk, S. A.; Brown, L. S.; Birge, R. R.; Miller, R. J. D. Coherent Control of Retinal Isomerization in Bacteriorhodopsin. *Science* **2006**, *313*, 1257−1261.

(17) Roberts, G. M.; Hadden, D. J.; Bergendahl, L. T.; Wenge, A. M.; Harris, S. J.; Karsili, T. N. V.; Ashfold, M. N. R.; Paterson, M. J.; Stavros, V. G. Exploring Quantum Phenomena and Vibrational Control in σ* Mediated Photochemistry. *Chem. Sci.* **2013**, *4*, 993−1001.

(18) Fuller, F. D.; Pan, J.; Gelzinis, A.; Butkus, V.; Senlik, S. S.; Wilcox, D. E.; Yocum, C. F.; Valkunas, L.; Abramavicius, D.; Ogilvie, J. P. Vibronic Coherence in Oxygenic Photosynthesis. *Nat. Chem.* **2014**, *6*, 1−6.

(19) Kushmerick, J. G.; Lazorcik, J.; Patterson, C. H.; Shashidhar, R.; Seferos, D. S.; Bazan, G. C. Vibronic Contributions to Charge Transport Across Molecular Junctions. *Nano Lett.* **2004**, *4*, 639−642.

(20) Sukegawa, J.; Schubert, C.; Zhu, X.; Tsuji, H.; Guldi, D. M.; Nakamura, E. Electron Transfer through Rigid Organic Molecular Wires Enhanced by Electronic and Electron−vibration Coupling. *Nat. Chem.* **2014**, *6*, 899−905.

(21) Milne, C. J.; Penfold, T. J.; Chergui, M. Recent Experimental and Theoretical Developments in Time-Resolved X-Ray Spectroscopies. *Coord. Chem. Rev.* **2014**, *277−278*, 44−68.

(22) Miller, R. J. D.; Ernstorfer, R.; Harb, M.; Gao, M.; Hebeisen, C. T.; Jean-Ruel, H.; Lu, C.; Moriena, G.; Sciaini, G. 'Making the Molecular Movie': First Frames. *Acta Crystallogr., Sect. A* **2010**, *66*, 137−156.

(23) Hochstrasser, R. M. Two-Dimensional Spectroscopy at Infrared and Optical Frequencies. *Proc. Natl. Acad. Sci. U. S. A.* **2007**, *104*, 14190−14196.

(24) Mukamel, S. Multidimensional Femtosecond Correlation Spectroscopies of Electronic and Vibrational Excitations. *Annu. Rev. Phys. Chem.* **2000**, *51*, 691−729.

(25) Hamm, P.; Lim, M.; Hochstrasser, R. M. Structure of the Amide I Band of Peptides Measured by Femtosecond Nonlinear-Infrared Spectroscopy. *J. Phys. Chem. B* **1998**, *102*, 6123−6138.

(26) Hamm, P.; Zanni, M. *Concepts and Methods of 2D Infrared Spectroscopy*; Cambridge University Press: New York, 2011.

(27) Bredenbeck, J.; Helbing, J.; Behrendt, R.; Renner, C.; Moroder, L.; Wachtveitl, J.; Hamm, P. Transient 2D-IR Spectroscopy: Snapshots of the Nonequilibrium Ensemble during the Picosecond Conformational Transition of a Small Peptide. *J. Phys. Chem. B* **2003**, *107*, 8654−8660.

(28) Hunt, N. T. 2D-IR Spectroscopy: Ultrafast Insights into Biomolecule Structure and Function. *Chem. Soc. Rev.* **2009**, *38*, 1837−1848.

(29) Bredenbeck, J.; Helbing, J.; Kolano, C.; Hamm, P. Ultrafast 2D-IR Spectroscopy of Transient Species. *ChemPhysChem* **2007**, *8*, 1747−1756.

(30) Hunt, N. T. Transient 2D-IR Spectroscopy of Inorganic Excited States. *Dalton Trans.* **2014**, *43*, 17578−17589.

(31) Rubtsov, I. V. Relaxation-Assisted Two-Dimensional Infrared (RA 2DIR) Method: Accessing Distances over 10 Å and Measuring Bond Connectivity Patterns. *Acc. Chem. Res.* **2009**, *42*, 1385−1394.

(32) Fedoseeva, M.; Delor, M.; Parker, S. C.; Sazanovich, I. V.; Towrie, M.; Parker, A. W.; Weinstein, J. A. Vibrational Energy Transfer Dynamics in Ruthenium Polypyridine Transition Metal Complexes. *Phys. Chem. Chem. Phys.* **2015**, *17*, 1688−1696.

(33) Khalil, M.; Demirdöven, N.; Tokmakoff, A. Coherent 2D IR Spectroscopy: Molecular Structure and Dynamics in Solution. *J. Phys. Chem. A* **2003**, *107*, 5258−5279.

(34) Cervetto, V.; Helbing, J.; Bredenbeck, J.; Hamm, P. Double-Resonance versus Pulsed Fourier Transform Two-Dimensional Infrared Spectroscopy: An Experimental and Theoretical Comparison. *J. Chem. Phys.* **2004**, *121*, 5935−5942.

(35) Kurochkin, D. V.; Naraharisetty, S. R. G.; Rubtsov, I. V. A Relaxation-Assisted 2D IR Spectroscopy Method. *Proc. Natl. Acad. Sci. U. S. A.* **2007**, *104*, 14209−14214.

(36) Bredenbeck, J.; Helbing, J.; Hamm, P. Solvation beyond the Linear Response Regime. *Phys. Rev. Lett.* **2005**, *95*, No. 083201.

(37) Bredenbeck, J.; Helbing, J.; Hamm, P. Labeling Vibrations by Light: Ultrafast Transient 2D-IR Spectroscopy Tracks Vibrational Modes during Photoinduced Charge Transfer. *J. Am. Chem. Soc.* **2004**, *126*, 990−991.

(38) Van Wilderen, L. J. G. W.; Messmer, A. T.; Bredenbeck, J. Mixed IR/Vis Two-Dimensional Spectroscopy: Chemical Exchange beyond the Vibrational Lifetime and Sub-Ensemble Selective Photochemistry. *Angew. Chem., Int. Ed.* **2014**, *53*, 2667−2672.

(39) Bakulin, A. A.; Rao, A.; Pavelyev, V. G.; van Loosdrecht, P. H. M.; Pshenichnikov, M. S.; Niedzialek, D.; Cornil, J.; Beljonne, D.; Friend, R. H. The Role of Driving Energy and Delocalized States for Charge Separation in Organic Semiconductors. *Science* **2012**, *335*, 1340−1344.

(40) Xiong, W.; Laaser, J. E.; Paoprasert, P.; Franking, R. A.; Hamers, R. J.; Gopalan, P.; Zanni, M. T. Transient 2D IR Spectroscopy of Charge Injection in Dye-Sensitized Nanocrystalline Thin Films. *J. Am. Chem. Soc.* **2009**, *131*, 18040−18041.

(41) Oliver, T. A. A.; Lewis, N. H. C.; Fleming, G. R. Correlating the Motion of Electrons and Nuclei with Two-Dimensional Electronic-Vibrational Spectroscopy. *Proc. Natl. Acad. Sci. U. S. A.* **2014**, *111*, 10061−10066.

(42) Greetham, G.; Burgos, P.; Cao, Q.; Clark, I.; Codd, P.; Farrow, R.; George, M.; Kogimtzis, M.; Matousek, P.; Parker, A.; Pollard, M.; Robinson, D.; Xin, Z.-J.; Towrie, M. ULTRA: A Unique Instrument for Time-Resolved Spectroscopy. *Appl. Spectrosc.* **2010**, *64*, 1311−1319.

(43) Bredenbeck, J.; Helbing, J.; Hamm, P. Transient Two-Dimensional Infrared Spectroscopy: Exploring the Polarization Dependence. *J. Chem. Phys.* **2004**, *121*, 5943−5957.

(44) Delor, M.; Sazanovich, I. V.; Towrie, M.; Spall, S. J.; Keane, T.; Blake, A. J.; Wilson, C.; Meijer, A. J. H. M.; Weinstein, J. A. Dynamics of Ground and Excited State Vibrational Relaxation and Energy Transfer in Transition Metal Carbonyls. *J. Phys. Chem. B* **2014**, *118*, 11781−11791.

(45) Rubtsov, I. V.; Hochstrasser, R. M. Vibrational Dynamics, Mode Coupling, and Structural Constraints for Acetylproline-NH$_2$. *J. Phys. Chem. B* **2002**, *106*, 9165−9171.

(46) Kiefer, L. M.; King, J. T.; Kubarych, K. J. Equilibrium Excited State Dynamics of a Photoactivated Catalyst Measured with Ultrafast Transient 2DIR. *J. Phys. Chem. A* **2014**, *118*, 9853−9860.

(47) King, J. T.; Ross, M. R.; Kubarych, K. J. Water-Assisted Vibrational Relaxation of a Metal Carbonyl Complex Studied with Ultrafast 2D-IR. *J. Phys. Chem. B* **2012**, *116*, 3754−3759.

(48) Park, K.-H.; Jeon, J.; Park, Y.; Lee, S.; Kwon, H.-J.; Joo, C.; Park, S.; Han, H.; Cho, M. Infrared Probes Based on Nitrile-Derivatized Prolines: Thermal Insulation Effect and Enhanced Dynamic Range. *J. Phys. Chem. Lett.* **2013**, *4*, 2105−2110.

(49) Kasyanenko, V. M.; Lin, Z.; Rubtsov, G. I.; Donahue, J. P.; Rubtsov, I. V. Energy Transport via Coordination Bonds. *J. Chem. Phys.* **2009**, *131*, No. 154508.

(50) Rosenfeld, D. E.; Gengeliczki, Z.; Smith, B. J.; Stack, T. D. P.; Fayer, M. D. Structural Dynamics of a Catalytic Monolayer Probed by Ultrafast 2D IR Vibrational Echoes. *Science* **2011**, *334*, 634−639.

(51) Dlott, D. D.; Fayer, M. D.; Hill, J. R.; Rella, C. W.; Suslick, K. S.; Ziegler, C. J. Vibrational Relaxation in Metalloporphyrin CO Complexes. *J. Am. Chem. Soc.* **1996**, *118*, 7853−7854.

(52) Kania, R.; Stewart, A. I.; Clark, I. P.; Greetham, G. M.; Parker, A. W.; Towrie, M.; Hunt, N. T. Investigating the Vibrational Dynamics of a 17e(−) Metallocarbonyl Intermediate Using Ultrafast Two Dimensional Infrared Spectroscopy. *Phys. Chem. Chem. Phys.* **2010**, *12*, 1051−1063.

(53) Baiz, C. R.; McCanne, R.; Kubarych, K. J. Structurally Selective Geminate Rebinding Dynamics of Solvent-Caged Radicals Studied with Nonequilibrium Infrared Echo Spectroscopy. *J. Am. Chem. Soc.* **2009**, *131*, 13590−13591.

(54) McConnell, H. M. Intramolecular Charge Transfer in Aromatic Free Radicals. *J. Chem. Phys.* **1961**, *35*, 508−515.

(55) Newton, M. D. Quantum Chemical Probes of Electron-Transfer Kinetics: The Nature of Donor-Acceptor Interactions. *Chem. Rev.* **1991**, *91*, 767−792.

(56) Balabin, I. A.; Onuchic, J. N. Dynamically Controlled Protein Tunneling Paths in Photosynthetic Reaction Centers. *Science* **2000**, *290*, 114−117.

(57) Davis, D.; Toroker, M. C.; Speiser, S.; Peskin, U. On the Effect of Nuclear Bridge Modes on Donor−acceptor Electronic Coupling in Donor−bridge−acceptor Molecules. *Chem. Phys.* **2009**, *358*, 45−51.

(58) Vura-Weis, J.; Abdelwahed, S. H.; Shukla, R.; Rathore, R.; Ratner, M. A.; Wasielewski, M. R. Crossover from Single-Step Tunneling to Multistep Hopping for Molecular Triplet Energy Transfer. *Science* **2010**, *328*, 1547−1550.

(59) Beratan, D. N.; Liu, C.; Migliore, A.; Polizzi, N. F.; Skourtis, S. S.; Zhang, P.; Zhang, Y. Charge Transfer in Dynamical Biosystems, or The Treachery of (Static) Images. *Acc. Chem. Res.* **2015**, *48*, 474−481.

(60) Devault, D. Quantum Mechanical Tunnelling in Biological Systems. *Q. Rev. Biophys.* **1980**, *13*, 387−564.

(61) Carias, H.; Beratan, D. N.; Skourtis, S. S. Floquet Analysis for Vibronically Modulated Electron Tunneling. *J. Phys. Chem. B* **2011**, *115*, 5510−5518.

(62) Lin, Z.; Lawrence, C. M.; Xiao, D.; Kireev, V. V.; Skourtis, S. S.; Sessler, J. L.; Beratan, D. N.; Rubtsov, I. V. Modulating Unimolecular Charge Transfer by Exciting Bridge Vibrations. *J. Am. Chem. Soc.* **2009**, *131*, 18060−18062.

(63) Scattergood, P. A.; Delor, M.; Sazanovich, I. V.; Bouganov, O. V.; Tikhomirov, S. A.; Stasheuski, A. S.; Parker, A. W.; Greetham, G. M.; Towrie, M.; Davies, E. S.; Meijer, A. J. H. M.; Weinstein, J. A. Electron Transfer Dynamics and Excited State Branching in a Charge-Transfer Platinum(II) Donor-Bridge-Acceptor Assembly. *Dalton Trans.* **2014**, *43*, 17677−17693.

(64) Delor, M.; Scattergood, P. A.; Sazanovich, I. V.; Parker, A. W.; Greetham, G. M.; Meijer, A. J. H. M.; Towrie, M.; Weinstein, J. A. Toward Control of Electron Transfer in Donor-Acceptor Molecules by Bond-Specific Infrared Excitation. *Science* **2014**, *346*, 1492−1495.

(65) Koch, M.; Rosspeintner, A.; Adamczyk, K.; Lang, B.; Dreyer, J.; Nibbering, E. T. J.; Vauthey, E. Real-Time Observation of the Formation of Excited Radical Ions in Bimolecular Photoinduced Charge Separation: Absence of the Marcus Inverted Region Explained. *J. Am. Chem. Soc.* **2013**, *135*, 9843−9848.

(66) Spears, K. G.; Wen, X.; Zhang, R. Electron Transfer Rates from Vibrational Quantum States. *J. Phys. Chem.* **1996**, *100*, 10206−10209.

(67) Huang, Y.; Rettner, C. T.; Auerbach, D. J.; Wodtke, A. M. Vibrational Promotion of Electron Transfer. *Science* **2000**, *290*, 111−114.

(68) Kwok, W. M.; Phillips, D. L.; Yeung, P. K.; Yam, V. W. Resonance Raman Investigation of the MLCT Transition in $[Pt(dppm)_2(PhCC)_2]$ and the MMLCT Transition in $[Pt_2(\mu\text{-}dppm)_2(\mu\text{-}PhCC)(PhCC)_2]^+$. *J. Phys. Chem. A* **1997**, *101*, 9286−9295.