

Mechanism of Metal-to-Ligand Charge Transfer Sensitization of Olefin Trans-to-Cis Isomerization in the $fac\text{-}[\text{Re}^{\text{I}}(\text{phen})(\text{CO})_3(\text{1,2-bpe})]^+$ Cation

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Received: July 19, 2002; In Final Form: December 31, 2002

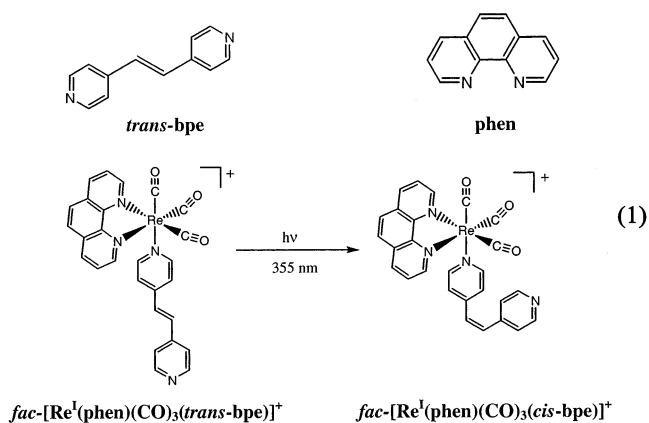
Near-UV, largely $\text{Re}^{\text{I}} \rightarrow \text{phen}$, bpe metal-to-ligand charge transfer (MLCT) excitation of $fac\text{-}[\text{Re}^{\text{I}}(\text{phen})(\text{CO})_3(\text{trans-bpe})]^+$ [where phen is 1,10-phenanthroline and bpe is 1,2-bis(4-pyridyl)ethylene] in CH_3CN results in isomerization at the bpe ligand and formation of $fac\text{-}[\text{Re}^{\text{I}}(\text{phen})(\text{CO})_3(\text{cis-bpe})]^+$. Time-resolved absorption and infrared (TRIR) measurements reveal the existence of an intermediate with a lifetime of ~ 28 ns ($k = 3.6 \times 10^7 \text{ s}^{-1}$). According to the results of the transient IR measurements, the intermediate is ligand-based, presumably the olefin-localized twisted triplet ^3p . TRIR measurements in the $\nu(\text{C}=\text{C})$ region point to a significant twisting around the $\text{C}=\text{C}$ bond in ^3p .

Introduction

In the photochemical isomerization of olefins, such as the stilbenes, there is experimental evidence for the occurrence of “nonvertical” energy transfer and a twisted triplet intermediate, ^3p , in addition to the spectroscopic or “vertical” triplet, $^3\pi\pi^*$.^{1–13} Saltiel and co-workers first suggested that a twisted geometry existed at the $\text{C}=\text{C}$ bond in $^3\text{p}^*$.^{1,12}

The triplet manifolds are accessible by inter- and intramolecular energy transfer and by heavy-atom effects,^{14,15} with the latter evidenced by the heavy-cation-substituted zeolites prepared by Ramamurthy *et al.*¹⁶ They are also accessible by coordinating the olefin in metal complexes, including inert complexes of ruthenium or rhenium.^{17–21} Schanze and co-workers have suggested that $\text{Re}^{\text{I}} \rightarrow \text{bpy}$ metal-to-ligand charge transfer (MLCT) excitation in $fac\text{-}[\text{Re}(\text{bpy})(\text{CO})_3(\text{py-CH}_2\text{-NH-C(O)-(trans-stilbene)})]^+$ and a series of related complexes results in energy transfer to a stilbene-based $^3\pi\pi^*$ state (transoid, $^3\text{t}^*$) that is in competition with MLCT excited-state decay. MLCT \rightarrow $^3\text{t}^*$ energy transfer is followed by reversible conversion to the perpendicular triplet $^3\text{p}^*$, and its decay results in trans-to-cis isomerization at the ligand.²²

We report here the results of an investigation on the dynamics of intramolecular sensitization of trans \rightarrow cis ligand isomerization in $fac\text{-}[\text{Re}^{\text{I}}(\text{phen})(\text{CO})_3(\text{bpe})]^+$ [where phen is 1,10-phenanthroline and bpe is 1,2-bis(4-pyridyl)ethylene], eq 1, by transient absorption (TA) and time-resolved infrared (TRIR) spectroscopies. These measurements provide direct evidence for a ligand-based photochemical transient and insight into the mechanism of sensitized trans-to-cis isomerization. Ligand and complex structures are illustrated in eq 1.²³



In the electronic spectrum of $fac\text{-}[\text{Re}^{\text{I}}(\text{phen})(\text{CO})_3(\text{trans-bpe})]^+$ in CH_3CN , there are overlapping $\text{Re} \rightarrow \text{phen}$, $\text{Re} \rightarrow {}^1\text{bpe}$ [where ${}^1\text{bpe}$ is *trans*-1,2-bis(4-pyridyl)ethylene], and $\pi \rightarrow \pi^*(\text{bpe})$ absorption bands in the 310–370 nm region. Excitation in this region results in bpe trans-to-cis isomerization as shown in the UV/visible spectrum by a decrease in absorbance in the 270–384 nm region and an increase in the 200–270 nm region. The isomerization process is accompanied by the disappearance of ${}^1\text{H}$ NMR resonances at δ 7.17–7.30 ($J = 16$ Hz) for the $\text{HC}=\text{CH}$ protons of the trans isomer and growth of those for the cis isomer at δ 6.52–6.80 ($J = 12$ Hz). The quantum yield for trans-to-cis isomerization, $\Phi_{\text{trans} \rightarrow \text{cis}}$, is 0.25 ± 0.02 at 365 nm.²⁴

At 77 K in a 1:1 propionitrile/butyronitrile glass, there is little or no isomerization in $fac\text{-}[\text{Re}^{\text{I}}(\text{phen})(\text{CO})_3(\text{trans-bpe})]^+$. A weak, structured emission appears at 390 nm, presumably from a $\pi\pi^*$ state localized on the *trans*-bpe ligand but red-shifted, presumably by coordination to the metal.

There is no detectable emission from this complex at room temperature in CH_3CN . Transient absorption measurements

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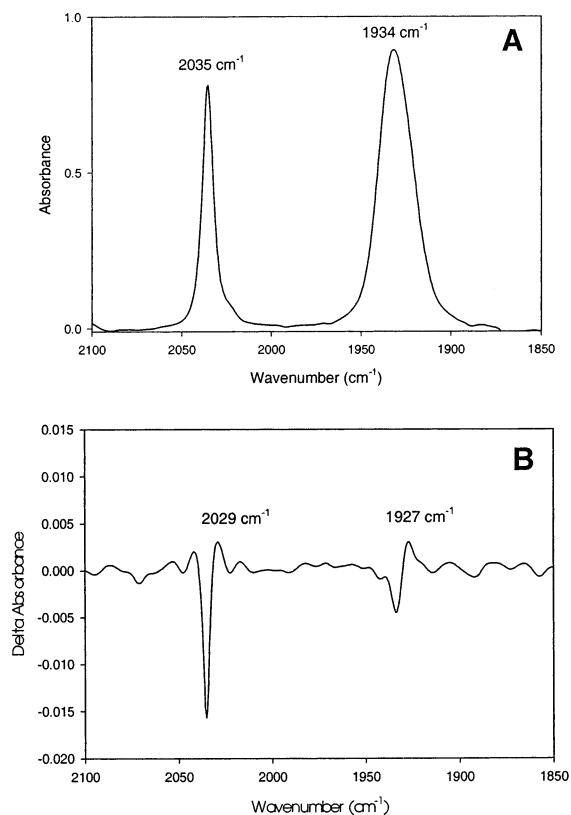


Figure 1. Ground-state (A) IR (± 2 cm^{-1}) and (B) TRIR (± 4 cm^{-1}) spectra of $\text{fac-}[\text{Re}^{\text{I}}(\text{phen})(\text{CO})_3(\text{trans-bpe})]^+$ in CH_3CN (~ 10 – 20 mM) at 298 K in the $\nu(\text{CO})$ region. The absorbance of $\nu(\text{CO})$ was ~ 0.8 absorbance units. Samples for TRIR were Ar-purged prior to measurement.

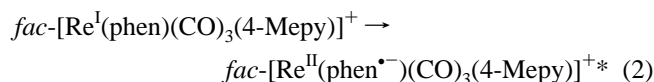
($\sim 1 \times 10^{-5}$ M in CH_3CN , 298 K, Ar deaerated) with excitation by the second harmonic of a Nd:YAG laser at 355 nm (7 ns pulse width, ~ 6 mJ/pulse) detect a short-lived transient with a narrow, intense absorption at 370 nm and a broad, featureless absorption at 480–500 nm. The low energy feature is presumably MLCT in origin as the planar $\pi\pi^*$ triplets absorb below 400 nm.²⁵ The transient decays with $\tau = 28 \pm 1$ ns ($k = 3.6 \times 10^7$ s^{-1}). Sustained photolysis at room temperature results in the growth of a characteristic MLCT emission for $\text{fac-}[\text{Re}^{\text{I}}(\text{phen})(\text{CO})_3(\text{cis-bpe})]^+$ at 550 nm ($\text{phen}^{\bullet-} \rightarrow \text{Re}^{\text{II}}$). According to transient emission measurements, the lifetime of the emitting MLCT state is $\tau = 928 \pm 16$ ns ($k = 1.08 \times 10^6$ s^{-1}).²⁶

In Figure 1 are shown ground-state and room-temperature transient IR (TRIR) spectra of $\text{fac-}[\text{Re}^{\text{I}}(\text{phen})(\text{CO})_3(\text{trans-bpe})]^+$ in Ar-deaerated CH_3CN . The concentration of the sample (~ 10 – 20 mM) was adjusted so that the absorbance of the CO bands in the region 1900–2100 cm^{-1} was ~ 0.8 – 1.0 absorbance units. The TRIR spectrum was acquired from the cessation of the 355-nm laser pulse to 50 ns.²⁷ The time-dependent decay characteristics of the transient spectrum were consistent with the 28-ns decay observed by transient absorption. The short excited-state lifetime contributed to the low signal-to-noise characteristics of the spectra in Figures 1B and 2B. Both the direction and magnitude of the $\nu(\text{CO})$ shifts in the transient spectrum between the ground and excited state in Figure 1B are revealing. For MLCT excited states, eq 2, these shifts are characteristically large and positive ($\Delta\bar{\nu} = +26$ to $+80$ cm^{-1} for $\text{fac-}[\text{Re}^{\text{I}}(\text{phen})(\text{CO})_3(4\text{-Mepy})]^+$, where Mepy is 4-methylpyridine) because of partial oxidation at Re and loss of $d\pi(\text{Re})-\pi^*(\text{CO})$ back-bonding.²⁸

TABLE 1: Summary of TRIR Results in the CO and Mid-IR Regions in CH_3CN at 298 K

complex ^a	$\bar{\nu}_{\text{gs}}$ (cm^{-1})	$\bar{\nu}_{\text{es}}$ (cm^{-1})	$\Delta\bar{\nu}^b$ (cm^{-1})	excited state
$[\text{Re}(\text{phen})(\text{CO})_3(4\text{-Etpy})]^+$	1931	1962	+31	MLCT
$[\text{Re}(\text{phen})(\text{CO})_3(\text{trans-bpe})]^+$	2036	2011	+80	$\pi\pi^*$
	1934	2062	+26	
	2035	2029	+6	
$[\text{Re}(\text{phen})(\text{CO})_3(\text{trans-bpe})]^+{}^d$ and	1639 ^c	1622 ^c	-17 ^c	$\pi\pi^*$
	2035	2029	-6	
$[\text{Re}(\text{phen})(\text{CO})_3(\text{cis-bpe})]^+{}^d$	1934	1974	+40	MLCT
	2035	2017	+83	
	2035	2066	+31	

^a As PF_6^- salts. ^b $\Delta\bar{\nu} = \bar{\nu}_{\text{es}} - \bar{\nu}_{\text{gs}}$. ^c In CD_3CN , C=C olefin. ^d In a mixture of $\sim 36\%$ $\text{fac-}[\text{Re}^{\text{I}}(\text{phen})(\text{CO})_3(\text{trans-bpe})]^+$ and $\sim 64\%$ $\text{fac-}[\text{Re}^{\text{I}}(\text{phen})(\text{CO})_3(\text{cis-bpe})]^+$. ^e Obscured by the bleach at 1934 cm^{-1} .



By contrast, the ground-to-excited-state shifts for the transient following laser flash excitation of $\text{fac-}[\text{Re}^{\text{I}}(\text{phen})(\text{CO})_3(\text{trans-bpe})]^+$ are $\Delta\bar{\nu} = -6$ and -7 cm^{-1} , with $\bar{\nu}(\text{CO})$ appearing at 1927 and 2029 (± 4 cm^{-1}) in the transient, Table 1. These values are comparable to shifts found following excitation of $\text{fac-}[\text{Re}(\text{dppz})(\text{CO})_3(\text{PPh}_3)]^+{}^*$ (dppz is dipyrido[3,2-a:2',3'-c]phenazine), which produces a dppz-localized ${}^3\pi\pi^*$ excited state.^{28,29} From this comparison, the transient observed for $\text{fac-}[\text{Re}^{\text{I}}(\text{phen})(\text{CO})_3(\text{trans-bpe})]^+$ appears to be an intermediate or excited state localized on the *trans-bpe* ligand. As for the dppz complex, the decrease in $\bar{\nu}(\text{CO})$ compared to the ground state shows that the ligand acts as an electron donor toward the metal in the transient.

TRIR measurements on a prephotolyzed mixture containing $\sim 36\%$ $\text{fac-}[\text{Re}^{\text{I}}(\text{phen})(\text{CO})_3(\text{trans-bpe})]^+$ and $\sim 64\%$ $\text{fac-}[\text{Re}^{\text{I}}(\text{phen})(\text{CO})_3(\text{cis-bpe})]^+$ provide evidence for both *cis-bpe* MLCT and *trans-bpe* $\pi\pi^*$ excited states following MLCT laser flash excitation. (The complex containing the pure *cis-bpe* ligand was not available for this study.) In the transient spectrum, $\nu(\text{CO})$ shifts appear at both *higher* and *lower* energies (Table 1), including $\nu(\text{CO})$ shifts of +40, +31 and +83 cm^{-1} for the MLCT excited state $\text{fac-}[\text{Re}^{\text{II}}(\text{phen}^{\bullet-})(\text{CO})_3(\text{cis-bpe})]^+{}^*$.

The TRIR measurements on $\text{fac-}[\text{Re}^{\text{I}}(\text{phen})(\text{CO})_3(\text{trans-bpe})]^+$ were extended into the mid-IR region from 1100 to 1700 cm^{-1} in CD_3CN [Figure 2 (1550–1700 cm^{-1})]. The band at 1639 cm^{-1} (± 4 cm^{-1}) is the olefin C=C stretch for a planar *trans*-stilbene conformation, with the $\nu(\text{C}=\text{C})$ stretches for additional rotamers appearing at 1643 and 1651 cm^{-1} .^{30,31} The bands at 1615 and 1597 cm^{-1} are $\nu(\text{phen})$ bands. The TRIR difference spectrum is complex but can be interpreted with $\nu(\text{C}=\text{C})$, planar) shifting to *lower* energy at 1622 cm^{-1} , the band at 1643 cm^{-1} shifting to 1631 cm^{-1} , and the excited-state band that correlates with the band at 1651 cm^{-1} possibly obscured by the bleach at 1639 cm^{-1} . The shifts of $\nu(\text{C}=\text{C})$ to lower energy are consistent with a partial loss in C–C multiple bonding in the ligand-localized excited state. The absence of assignable $\nu(\text{phen})$ bands in the difference spectrum, analogous to those observed for the MLCT excited state(s) of $[\text{Ru}(\text{phen})_3]^{2+}$,³² shows that $\nu(\text{phen})$ shifts are negligible in the transient, which is also consistent with a *bpe*-based intermediate.

The observations made here are consistent with the following conclusions:

(1) At the wavelengths used to excite $\text{fac-}[\text{Re}^{\text{I}}(\text{phen})(\text{CO})_3(\text{trans-bpe})]^+$ and mixtures of this isomer and $\text{fac-}[\text{Re}^{\text{I}}(\text{phen})-$

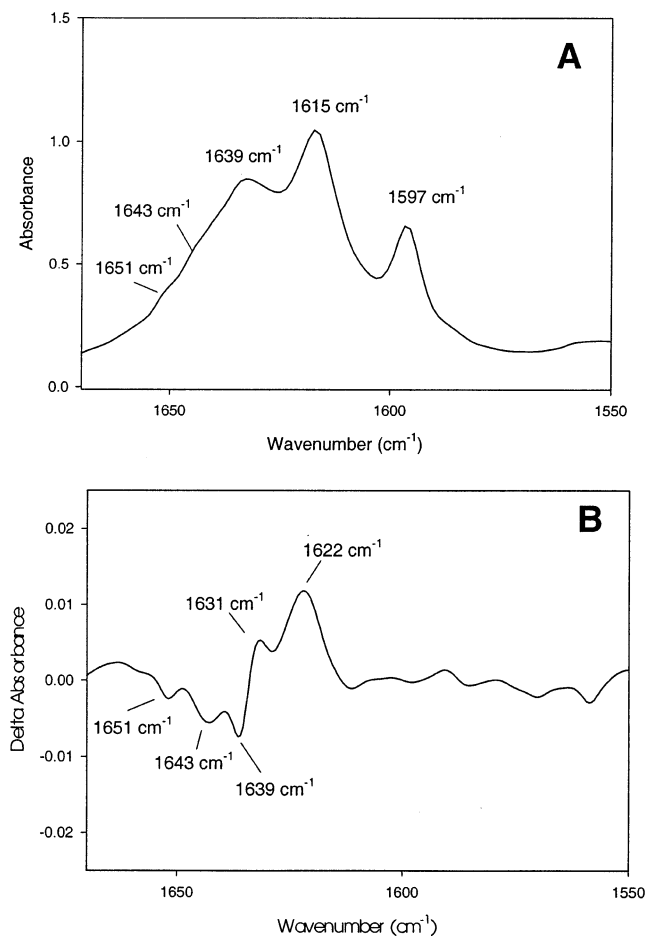


Figure 2. As in Figure 1, (A) IR and (B) TRIR spectra of *fac*-[Re^I(phen)(CO)₃(*trans*-bpe)]⁺ in the mid-IR region at 298 K in CD₃CN.

(CO)₃(*cis*-bpe)]⁺, singlet Re^{II}(phen^{•-}) and Re^{II}(bpe^{•-}) MLCT and ligand-localized $\pi\pi^*$ excited states are reached initially. The photochemistry and photophysics that are observed occur following relaxation to lower-lying states.

(2) In *fac*-[Re^I(phen)(CO)₃(*trans*-bpe)]⁺, the TRIR results show that the lowest-lying state is bpe-localized at room temperature. This state is short-lived with $\tau = 28$ ns ($k = 3.6 \times 10^7$ s⁻¹). It is presumably ³p, given its lifetime, and the direct precursor to bpe *trans* → *cis* isomerization. The lifetimes of ³p for a variety of substituted stilbenes have been measured and found to be ~60 ns.³³ In *fac*-[Re^I(phen)(CO)₃(*trans*-bpe)]⁺, this state is presumably formed by intramolecular sensitization and the sequence ¹MLCT, ¹ $\pi\pi^* \rightarrow$ ³MLCT → ³t* → ³p*.²²

If this interpretation is correct, the TRIR data in Figure 2 provide direct insight into the structure of ³p*. In the mid-IR region, the shift of $\nu(\text{C}=\text{C})$ to lower energy is consistent with a loss of some double bond character and a weakening of the C—C bond in the excited state. Some double-bond character is still present, as shown by the appearance of $\nu(\text{C}=\text{C})$ for the rotamers at 1643 and 1651 cm⁻¹. The energy of $\nu(\text{C}=\text{C})$ is the same as that calculated by Choi *et al.* for the central C=C bond in a nonplanar *trans*-stilbene conformation with a dihedral angle of ~30°. ^{30,34} This suggests that there is considerable C=C twisting in the ³p* excited state, consistent with the initial suggestion by Saltiel *et al.*^{1,9}

(3) In the propionitrile/butyronitrile rigid glass at 77 K, the weak fluorescence at 390 nm presumably arises from ¹t*, the singlet analogue of the *transoid* ³t*. There is no photochemistry. The absence of photochemistry should *not* be a consequence

of a change in excited-state ordering in the glass. In the glass, the energies of the dipolar Re^{II}(phen^{•-}) MLCT states are increased relative to those of centrosymmetric, olefin-based states,³⁵ and the ³t* < ³MLCT ordering should be maintained. *Trans*-to-*cis* isomerization in the glass is presumably inhibited by the low temperature and the existence of a thermal barrier to ³t* → ³p* interconversion.

(4) In *fac*-[Re^I(phen)(CO)₃(*cis*-bpe)]⁺, the ordering of low-lying states in CH₃CN at 298 K appears to be the reverse with ³MLCT < ³c* (where ³c* is the *cisoid* $\pi\pi^*$ analogue of ³t*). Re^{II}(phen^{•-}) MLCT emission occurs at 550 nm, with $\tau = 928$ ns ($k = 1.08 \times 10^6$ s⁻¹) at room temperature. The positive shifts in $\nu(\text{CO})$ in the TRIR spectrum of the ~36:64 *trans*/*cis* mixture provide direct evidence that this is an MLCT state.

Acknowledgment. The authors thank the Office of Basic Energy Sciences, U. S. Department of Energy (Grant DE-FG02-96ER14607), and Los Alamos National Laboratory for support of this research. Work in São Paulo was supported by FAPESP and CNPq.

Supporting Information Available: Figures showing ground-state IR and TRIR spectra of the photostationary state containing ~36% *fac*-[Re(phen)(CO)₃(*trans*-bpe)]⁺ and ~64% *fac*-[Re(phen)(CO)₃(*cis*-bpe)]⁺ in CH₃CN at 298 K and changes in the UV/vis absorbance spectrum corresponding to photoisomerization of coordinated bpe upon photolysis at 365 nm at 298 K. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(24) Quantum yields were obtained by following the reaction spectrophotometrically at three different wavelengths where the contribution to the absorbance from the cis isomer complex was minimal. For the quantum yield determinations [average of at least three independent experiments with tris-oxalate ferrate(III) as the actinometer], absorbance changes were monitored to less than 10% conversion in freshly prepared solutions. The photolyses were carried out with an Oriol 200 W Hg(Xe) arc lamp powered by an Oriol universal power supply model 78700. Irradiation at 313 or 334 nm was obtained by passing the beam through a quartz collimating lens and an appropriate interference filter. This procedure is described in ref 23 and Lima, J. F.; Nakano, A. K.; Murakami Iha, N. Y.; *Inorg. Chem.* **1999**, *38*, 403–405. There was no measurable *cis-to-trans* conversion.

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(26) Transient absorption and emission measurements were performed by using an experimental apparatus described in: Maxwell, K. A.; Sykora, M.; DeSimone, J. M.; Meyer, T. J. *Inorg. Chem.* **2000**, *39*, 71–75. Excitation was at 355 nm with monitoring of wavelengths from 370 to 600 nm.

(27) Time-resolved infrared measurements were performed according to a method described in detail in: Dattelbaum, D. M.; Meyer, T. J. In *Introduction to Step-Scan FTIR*; Johnson, T. J., Zachman, G., Eds.; Bruker Optics: Billerica, MA, 2000; pp 21–25. Samples for TRIR measurements were prepared in CH₃CN or CD₃CN, with the concentration adjusted so that the absorbances of the bands of interest were 0.8–1.0 OD units. Ground-state IR and TRIR spectra were recorded using a Bruker IFS 66v step-scan FTIR spectrometer. Ground-state spectra were recorded in the rapid-scan mode, whereas excited-state spectra were recorded in the step-scan mode. The infrared beam from the interferometer was overlapped with the 354.7-nm pump beam from a Surelite Continuum Nd:YAG laser operating at 10 Hz using a pinhole aperture. Detection was provided by using a Kolmar liquid-N₂-cooled MCT photovoltaic detector fitted with a fast preamplifier. Depending on the spectral range of interest, filters were mounted directly

in front of the detector. For the mid-IR and CO regions, a Ge low-pass filter with a 2250 cm⁻¹ cutoff was employed. The external optical train was enclosed in a plexiglass box and continuously purged with dry N₂. Experimental timing of the laser pulse and interferometer mirror step was controlled by a Stanford Research Systems model DG535 pulse generator. Signal intensities were collected in 20- or 50-ns time increments to approximately 600 ns and in-step coadditions (64–180) used to increase the S/N ratio. Following the completion of an experiment, interferograms were Fourier transformed and sorted in time to produce a 3D data set of single-channel spectra. The 3D file was further manipulated by a macro that converted the single channel spectra into absorbance changes (ΔA) as a function of time in the form $\Delta A = -\log[1 + I(v,t)/I(v)]$. Here, $I(v,t)$ and $I(v)$ are the infrared intensities at time t (from the 3D file) and time = 0, respectively. Time slices following the laser pulse were signal averaged over 50 ns.

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