The Early Picosecond Photophysics of Ru(II) Polypyridyl Complexes: A Tale of Two Timescales

William Henry,[†] Colin G. Coates,[‡] Clare Brady,[‡] Kate L. Ronayne,[‡,§] Pavel Matousek,[§] Michael Towrie,[§] Stanley W. Botchway,[§] Anthony W. Parker,[§] Johannes G. Vos,[†] Wesley R. Browne,*,[†,‡,‖] and John J. McGarvey*,[‡]

National Centre for Sensors Research, Dublin City University, Dublin 9, Ireland, School of Chemistry & Chemical Engineering, Queen's University Belfast, Belfast BT9 5AG, Northern Ireland, U.K., Central Laser Facility, Science & Technology Facilities Council, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire, OX11 0QX, U.K., and Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747AG Groningen, The Netherlands

The early picosecond time scale excited-state dynamics of the paradigm tris(2,2′-bipyridyl)Ruthenium(II) ([Ru(bpy)$_3$]$^{2+}$) and related complexes have been examined by picosecond Kerr-gated time-resolved resonance Raman (ps-TR^3) spectroscopy. The evolution of the signature Raman bands of the lowest thermally equilibrated excited (THEXI) state under two-color pump/probe conditions show that this state is not fully populated within several hundred femtoseconds as proposed previously but rather only within the first 20 ps following excitation. In addition to an emission observed within the instrument rise time ($\tau < 3$ ps), the early picosecond dynamics are characterized by a rise in the intensity of the Raman marker bands of the THEXI–^{3}MLCT state, a rise time which, within experimental uncertainty, is not influenced by either partial or complete ligand deuteriation or the presence of ligands other than bpy, as in the heteroleptic complexes [Ru(bpy)$_2$(L1)]$^+$ and [Ru(bpy)$_2$(Hdcb)]$^+$ (where H$_2$dcb is 4,4′-dicarboxy-2,2′-bipyridine and L1 is 2,-(5′-phenyl-4′-[1,2,4]triazole-3′-yl)pyridine). Overall, although the results obtained in the present study are consistent with those obtained from examination of this paradigm complex on the femtosecond timescale, regarding initial formation of the vibrationally hot ^{3}MLCT state by ISC from the singlet Franck–Condon state, the observation that the THEXI–^{3}MLCT state reaches thermal equilibration over a much longer time period than previously suggested warrants a re-examination of views concerning the rapidity with which thermal equilibration of transition metal complex excited states takes place.

Introduction

Since the first reports of the luminescence[1] and photochemistry[2,3] of the tris(2,2′-bipyridyl)Ruthenium(II) complex ([Ru(bpy)$_3$]$^{2+}$) half a century ago, this complex has become a paradigm for transition metal photochemistry and photophysics. Although the subject of intense debate initially, the character of the thermally equilibrated excited state (the THEXI–^{3}MLCT state) of this complex is generally accepted to be best described as a manifold of thermally equilibrated metal to ligand charge transfer states of varying triplet character, with the electron density localized on a single bpy ligand.[4–11] Despite such consensus, the series of events that lead from the Franck–Condon state formed upon electronic excitation of [Ru(bpy)$_3$]$^{2+}$ to the appearance of the THEXI–^{3}MLCT state has remained the subject of intense enquiry. The necessity of understanding these early processes has been underscored by the recognition[12–26] that excited-state processes such as, for example, energy transfer and electron injection into semiconductor materials may not always proceed from the THEXI–^{3}MLCT state but rather from 'hot excited states';[27–30] for example, Hammarstrom and co-

workers[31] have reported that electron transfer is faster than relaxation in ruthenium(II)-based multinuclear complexes. Indeed this recognition has stimulated the re-examination of the femto- and early picosecond photophysical behavior of [Ru(bpy)$_3$]$^{2+}$, building on the seminal transient absorption studies by McCusker and co-workers, which began in the late 1990s.[32]

The model put forward by McCusker and co-workers[32] based on transient absorption (TA) spectroscopy proposed that grow-in of the characteristic TA spectrum of the [Ru(bpy)$_3$]$^{2+}$ excited ^{3}MLCT state was essentially complete within 1 ps following excited-state relaxation dynamics, evolving directly from the initially populated Franck–Condon state (^{1}MLCT). Support for this picture was adduced from fluorescence upconversion spectroscopic studies by Bhasikuttan et al.,[33] in which a decay of a very weak high energy emission (distinct from the familiar ^{3}MLCT emission of [Ru(bpy)$_3$]$^{2+}$) was observed to follow fast femtosecond kinetics. The observation of a subpicosecond fluorescence from [Ru(bpy)$_3$]$^{2+}$ has since been confirmed in our earlier communication by time-resolved fluorescence spectroscopy[34] and later by McFarland et al.[35] by time correlated single photon counting. However, as for the ^{3}MLCT emission reported by Paris and Brandt[1] in the late 1950s, the assignment of the origin of this femtosecond emission has not proven straightforward.

Although the TA spectroscopic studies suggested that the formation of the THEXI state was complete within a matter of a few hundred femtoseconds, more recent investigations have indicated that this view may require some closer examination

* To whom correspondence should be addressed. E-mails: (W.R.B.) w.r.browne@rug.nl; (J.J.M.) j.mcgarvey@qub.ac.uk.
† Dublin City University.
‡ Queen's University Belfast.
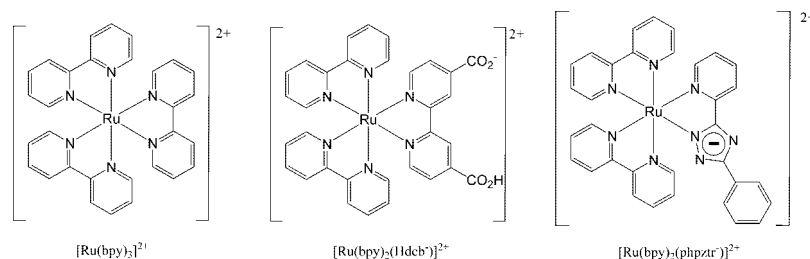§ Rutherford Appleton Laboratory.
‖ University of Groningen.

Figure 1. Structures of complexes examined.

(vide infra).[36] The application of time-resolved vibrational (resonance Raman[37] and IR[38]) and luminescence[34,35] spectroscopies and, more recently, coherent spectroscopic techniques[39] has pointed to the need for a re-evaluation of the timescales over which various excited-state relaxation processes (e.g., IC, ISC, and vibrational cooling) take place.[32]

In addition to confirming the observation of a high-energy, short-lived fluorescence from $[Ru(bpy)_3]^{2+}$, our earlier communication[34] also examined this system by time-resolved resonance Raman spectroscopy (TR^3), which demonstrated clearly that the formation of the THEXI$-^3$MLCT state was not complete within 1 ps but rather took up to 20 ps to evolve fully.

In the present study, we build on our earlier communication,[34] which focused on the observation of a cross correlated ($\tau < 3$ ps, λ_{max} 520 nm) luminescence, which preceded the familiar luminescence (λ_{max} 600 nm) from the THEXI$-^3$MLCT state of $[Ru(bpy)_3]^{2+}$.[4] Here we report the early picosecond dynamics following electronic excitation of $[Ru(bpy)_3]^{2+}$ and related complexes (Figure 1), probed by Kerr-gated TR^3. The major part of this study is focused on $[Ru(bpy)_3]^{2+}$ and several isotopologues due to the wealth of spectroscopic data available already for this complex[4] and the appearance of several recent detailed studies of its earliest (subpicosecond) excited-state processes.[32b,40] The central questions we have attempted to address in this study concern the nature of the high energy (<3 ps) emission observed in our earlier picosecond time-resolved emission studies[34] and the time frame within which the lowest THEXI$-^3$MLCT state is fully established. We have also attempted to explore the generality of the observations made for $[Ru(bpy)_3]^{2+}$ by including in the study the complexes $[Ru(bpy)_2(phpytr)]^+$ and $[Ru(bpy)_2(Hdcb^-)]^+$, (where phpytr$^-$ = 5-phenyl-3-pyrid-2′-yl-1,2,4-triazolato and H_2dcb = 4,4′-dicarboxy-2,2′-bipyridyl) which bear solvent sensitive ligands, and which force the localization of the THEXI state onto the bpy and Hdcb$^-$ ligands, respectively.

Experimental Section

All solvents employed were of spectroscopic grade and used as received. $[Ru(bpy)_3](PF_6)_2$, $[Ru(bpy)_3]Cl_2$, and their isotopologues were obtained from Gas Sensor Solutions, Dublin 9, Ireland. The syntheses and characterization of $[Ru(bpy)_2(phpytr)](PF_6)$[41] and $[Ru(bpy)_2(Hdcb)](PF_6)$[42] and their isotopologues are described elsewhere. Kerr-gated picosecond TR^3 spectroscopy was carried out as reported previously.[43] Briefly, a regenerative amplifier system supplied a 1 ps, 800 nm pulse with an energy of 2.5 mJ at a rate of 1 kHz, part of which was frequency doubled to 400 nm and used to pump optical parametric amplifiers, which are tuneable, independently, over a range of visible wavelengths. A computer-controlled optical delay line was used to vary the path length of the pump laser to provide time resolution. A CS_2 Kerr gate, pumped at 800 nm (~0.5 mJ), was used to reject sample fluorescence. The sample was introduced to the incident laser beam as a continuous
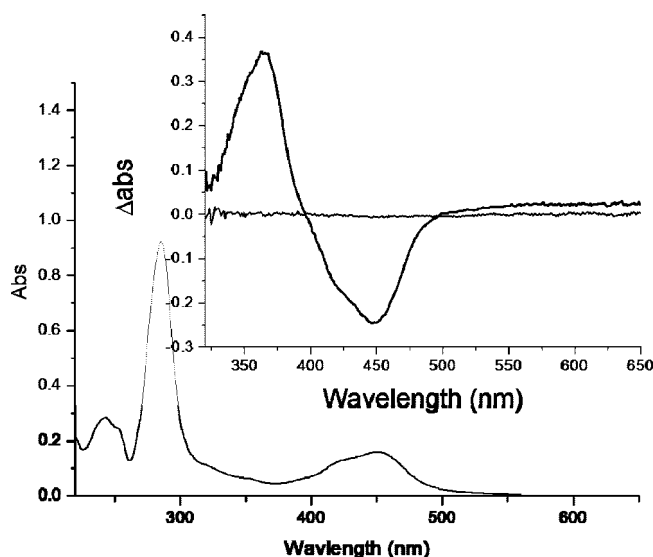

Figure 2. Absorption and transient differential absorption spectra (at 20 ns) of $[Ru(bpy)_3]^{2+}$.

open jet (500 μm diameter) using a peristaltic pump. Sample concentrations were determined by electronic absorption spectroscopy 0.3−0.5 OD in a 1 mm path length quartz cuvette and were typically between 1−5 mM. The energies of the ~1 ps duration laser pulse energies at the sample were typically 10 μJ (pump pulse) and 5−10 μJ (probe pulse).The spectra were recorded under continuous flow conditions; that is, the sample was introduced as a jet and hence was replaced continuously by fresh sample. Under the conditions employed, photochemistry can potentially occur; however, the quantum yields for these processes are low and the steady-state absorption spectra before and after measurement were unchanged. Furthermore, with the same solution recirculated several times, no changes in the TR^3 spectra were observed over several acquisitions. Raw data were processed by subtraction of a solvent spectrum from all traces prior to subtraction of the negative time (ground state, −50 ps) spectrum. No further spectral processing was carried out. Kinetic traces were derived from measurements at single Raman frequencies.

Results

The ground and ^{3}MLCT excited-state absorption spectra of $[Ru(bpy)_3]^{2+}$ are shown in Figure 2. The ps-TR^3 spectra of $[Ru(bpy)_3]^{2+}$ were recorded at several combinations of pump and probe wavelengths. The wavelengths of the actinic laser pulse were chosen to excite across the ^{3}MLCT absorption manifold from the visible (450−500 nm) to the near-UV (390, 400, and 410 nm). However, as the kinetics and spectra obtained show no dependence on the pump wavelength employed, the results obtained at 400 nm pump only and various probe wavelengths will be discussed.

The time-resolved excited-state rR spectra of $[Ru(bpy)_3]^{2+}$ (in acetonitrile, λ_{pump} 400 nm and λ_{probe} 350 nm) are shown in
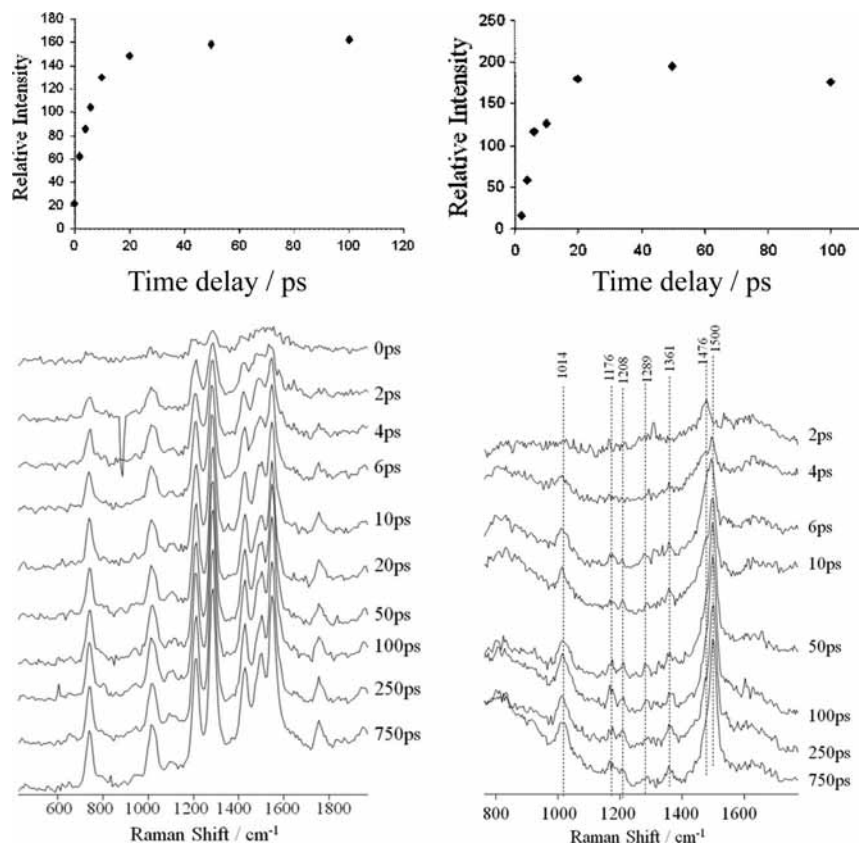
Figure 3. Time-resolved resonance Raman spectra of [Ru(bpy)$_3$]Cl$_2$ recorded in (left) acetonitrile, λ_{pump} 400 nm and λ_{probe} 350 nm and (right) in H$_2$O at λ_{pump} 400 nm, λ_{probe} 475 nm. Upper traces: Kinetic trace at 1285 and 1500 cm^{-1}, respectively. Ground state and solvent bands have been subtracted. Note that the spectra in acetonitrile and H$_2$O differ considerably due to the different probe wavelengths employed in each case. When recorded at the same probe wavelength, the spectra obtained in either solvent are essentially the same.

Figure 3. It can be seen from these spectra that the Raman scattering bands at 1223, 1291, and 1547 cm^{-1} (assigned to vibrational modes of the bpy$^{-\bullet}$ radical anion[44]) increase in intensity over the first 20 ps following excitation.[45]

In contrast to the rich spectra obtained with λ_{probe} 350 nm (i.e., in resonance with the ^{3}MLCT excited state, bpy-based, absorption band), the TR^3 spectra of [Ru(bpy)$_3$]$^{2+}$, recorded in H$_2$O solution (λ_{probe} 400 nm, with λ_{probe} 475 nm, Figure 3, right), are much simpler, with a single Raman scattering band observed at 1500 cm^{-1} (also characteristic of the bpy$^{-\bullet}$ anion radical). Nevertheless, as at λ_{probe} 350 nm, the kinetics of the grow-in of this band at λ_{probe} 475 nm indicates a lifetime of ∼10 ps for the process.

Although the kinetics for the evolution of the resonance Raman spectra of the THEXI ^{3}MLCT spectra were similar in both CH$_3$CN and H$_2$O, the solvent dependence of the grow-in of the excited-state Raman bands was examined for a series of alcohols and deuterated solvents. The kinetics of excited-state grow-in of [Ru(bpy)$_3$]$^{2+}$ were investigated in four homologous alcohols (λ_{pump} 410 nm, λ_{probe} 475 nm, Figure S3). The time constant for the grow-in of the resonance Raman spectrum of the THEXI–^{3}MLCT state was invariant (within experimental uncertainty) over the series, despite the very different viscosities, dielectric constants, and thermal diffusivities.[46] Indeed no significant differences in the grow-in kinetics were observed in either CH$_3$CN, CD$_3$CN, H$_2$O, or for several isotopologues of [Ru(bpy)$_3$]$^{2+}$ (*vide infra*). The kinetics were also insensitive to the counterion employed (chloride or hexafluorophophate). Figure 4 gives an example of the spectra and kinetics obtained in hexanol.

The ps-TR^3 spectra of [Ru(bpy)$_x$([D$_8$]-bpy)$_y$]$^{2+}$ (where $x =$ 0–2 and $y = 1–3$) show essentially identical kinetics for the

grow-in of the marker bands of the THEXI–^{3}MLCT state and are also identical to the kinetics observed for the perprotio complex [Ru([H$_8$]-bpy)$_3$]$^{2+}$. It is of note, however, that the mixed ligand complexes, for example, [Ru([D$_8$]-bpy)([H$_8$]-bpy)$_2$]$^{2+}$ (Figure 5), show the characteristic Raman bands of the THEXI–^{3}MLCT states of *both* [Ru([H$_8$]-bpy)$_3$]$^{2+}$ (at 1223, 1292, and 1551 cm^{-1}) and [Ru([D$_8$]-bpy)$_3$]$^{2+}$ (at 1436 cm^{-1}).

Heteropletic Ruthenium(II) Complexes. The complex [Ru(bpy)$_2$(Hdcb)]$^+$ is analogous to [Ru(bpy)$_3$]$^{2+}$; however, a key feature of this complex is that the THEXI–^{3}MLCT state has been identified by TR^2 through isotope labeling as residing on the 4,4′-dicarboxy-2,2′-bipyridine ligand and not on the bpy ligands.[41] Indeed, in contrast to the partially deuterated [Ru-(bpy)$_3$]$^{2+}$ (*vide supra*), in the present study (at λ_{pump} 410 nm and λ_{probe} 470 nm), a single excited-state Raman scattering band at 1486 cm^{-1} was observed for [Ru(bpy)$_2$(Hdcb)]$^+$, which, as for the 1557 cm^{-1} band of [Ru(bpy)$_3$]$^{2+}$, increased in intensity over several ps to reach a maximum intensity by 20 ps. Again, ligand deuteration of either or both the H$_2$dcb or bpy ligands had no effect on the rate of the grow-in of the THEXI–^{3}MLCT state (Figure 6).

Previous studies[47,26] have indicated that charge injection in solar cells occurs on the femtosecond timescale and from a level above the THEXI state. The present results, which suggest that [Ru(bpy)$_2$(Hdcb)]$^{2+}$ is not 'vibrationally cold' until several picoseconds after initial formation, are consistent with these studies. It is also important to note that the THEXI–^{3}MLCT state in this complex is localized on the Hdcb$^-$ ligand with the energy difference between the Hdcb$^-$ and bpy ligands precluding thermally activated interligand hopping.

For the complex [Ru(bpy)$_2$(phpytr)]$^+$, the location of the THEXI–^{3}MLCT state has been identified as residing on the

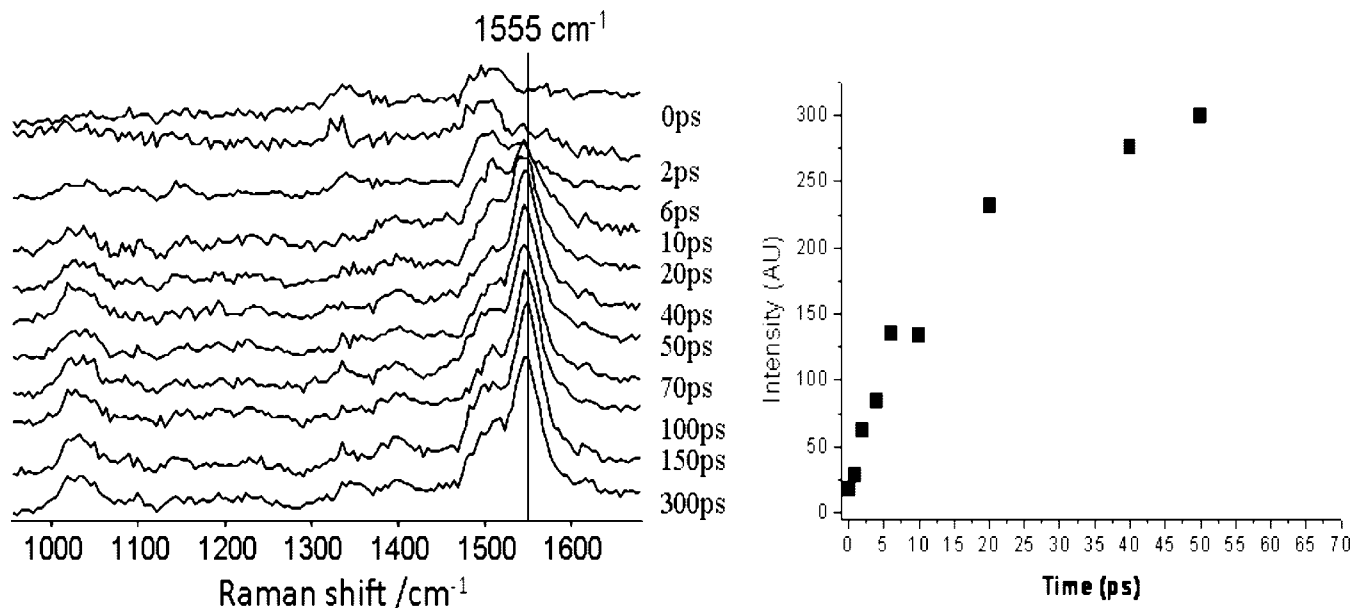**Figure 4.** Left panel: TR^3 spectra of [Ru(bpy)$_3$]$^{2+}$ in 1-hexanol; pump at 400 nm, probe at 475 nm. The shoulder at 1500 cm^{-1} is due to incomplete subtraction of the solvent band. Right panel: Kinetics of the 1555 cm^{-1} Raman band in 1-hexanol (for the kinetics in a series of homologous series of alcohols see Figure S3, Supporting Information) with the pump excitation at 400 nm and the probe wavelength at 475 nm.
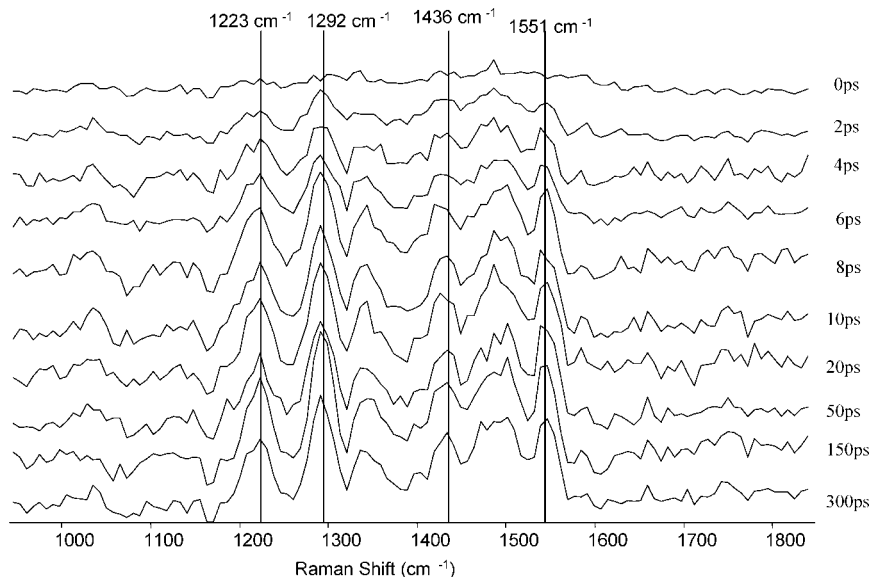

Figure 5. TR^3 (ground-state and solvent subtracted) spectra of [Ru([D$_8$]-bpy)([H$_8$]-bpy)$_2$]$^{2+}$ in H$_2$O, λ_{pump} 400 nm and λ_{probe} 350 nm.

bpy ligands.[41] The spectra of the deprotonated complex in H$_2$O and in acetonitrile (λ_{pump} 400 nm and λ_{probe} 350 nm) are shown in Supporting Information. The excited-state resonance Raman spectra of [Ru(bpy)$_2$(phpytr)]$^+$ show bands at 1212, 1287, and 1540 cm^{-1}, characteristic of the bpy$^{•-}$ anion radical. The grow-in of the excited-state features at early times is very similar to that observed for [Ru(bpy)$_3$]$^{2+}$, with the process (followed at 1288 cm^{-1}) being complete well within ~20 ps. Protonation of the triazole moiety of the complex, that is, [Ru(bpy)$_2$-(Hphpytr)]$^{2+}$, did not result in any changes in the rate of the grow-in of the spectrum of the THEXI–^{3}MLCT state, and as for [Ru(bpy)$_3$]$^{2+}$, ligand deuteration has no measureable effect on the kinetics of the grow-in (Figure 7). Notably, in this case, the subsequent decay[41] of the THEXI–^{3}MLCT state could be observed on the experimental timescale also, in line with the very short lifetime (ca. 10 ns) of the ^{3}MLCT state of this complex.[41]

The complex [Ru(bpy)$_2$(phpytr)]$^+$ is asymmetric in comparison with [Ru(bpy)$_3$]$^{2+}$, and the electron density of the negative triazole moiety increases the energy of the ^{3}MLCT states localized on the phpytr ligand relative to the bpy ligands. This results in an excited-state which may be delocalized over two near degenerate bpy ligands (the asymmetry of phpytr leads to a small energy difference between the ligands). However, no change is observed in the rate of formation of the THEXI–^{3}MLCT excited state (Figure 8). It is perhaps of interest to note that, in contrast to [Ru(bpy)$_3$]$^{2+}$, the negatively charged phphytr$^-$ ligand results in a considerable dipole in both the ground and excited states (the magnitude of the dipole is reduced significantly in the excited state). The similarity of the relaxation kinetics for these three series of complexes suggests that solvent reorganization is not a major factor in determining the rate of formation of the THEXI–^{3}MLCT state.

Discussion

While a strong consensus emerges from the majority of studies on both picosecond and femtosecond timescales con-
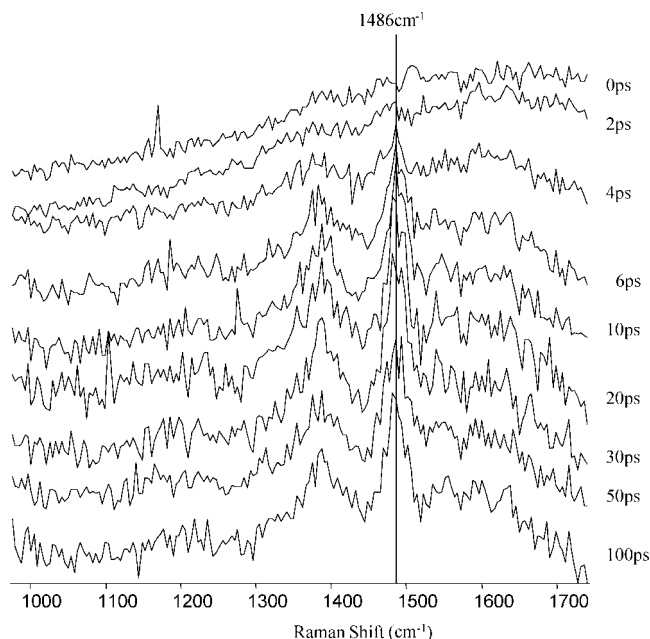
Figure 6. Time-resolved excited-state resonance Raman spectra of [Ru([D$_8$]-bpy)$_2$([D$_6$]-Hdcb)]$^+$ in D$_2$O with λ_{pump} 410 nm and λ_{probe} 470 nm.

cerning the initial formation of the ^{3}MLCT state of [Ru(bpy)$_3$]$^{2+}$ from the FC ^{1}MLCT state via ultrafast ISC, a considerable divergence of views appears in respect of the timescale over which formation of the fully, vibrationally relaxed (THEXI) ^{3}MLCT state occurs.

The transient absorption data of McCusker et al.[32] suggested that the THEXI state has fully evolved by ca. 300 fs with the experimental data indicating no further slower relaxation processes. More recent reports by Mathies et al.[48] suggest that the THEXI−^{3}MLCT state is formed over a period of 100−130 fs. The recent broadband femtosecond fluorescence study of the excited-state dynamics of the MLCT states of [Ru(bpy)$_3$]$^{2+}$ by Chergui et al.[39] appears to suggest an even shorter timescale, with the vibrationally relaxed ^{3}MLCT state forming within some 15 fs.

Notwithstanding these reports, the weight of the evidence from several other studies, carried out on both the picosecond and femtosecond timescales,[49] together with the present study, support a timescale for vibrational cooling to the fully relaxed THEXI−^{3}MLCT state of some 10−20 ps.

Thus, considering first the results of the present study covering the early picosecond timescale (1−500 ps), it is apparent that in the TR^3 spectra of [Ru(bpy)$_3$]$^{2+}$ in acetonitrile (Figure 3, λ_{pump} 400 nm and λ_{probe} 350 nm), bands at 1212, 1293, and 1500 cm^{-1}, characteristic of the bpy anion radical (bpy$^{-\bullet}$), reach a maximum in intensity on the picosecond timescale (1/e time ~20 ps). These observations are in accordance with the TR^3 and TRIR studies reported recently by Vlček et al.[38c] for Re(I) and Ru(II) complexes containing a single polypyridyl chromophore. In these studies, vibrational cooling of the metal → polypyridyl ligand ^{3}MLCT state was found to take place over ca. 10 ps, a timescale very similar to that observed in the present study.

Figure 4 (and Figure S3 in Supporting Information) highlights the effect of solvent on the excited-state grow-in, as observed in the present study. Again the process occurs on the picosecond timescale, with a 1/e lifetime of ca. 20 ps, independent of solvent. Given the range of dielectric constant and viscosity covered by the solvents investigated, this would suggest that

solvent reorganization and heat dissipation are not rate-limiting in the vibrational cooling step of the THEXI−^{3}MLCT state. This is not unexpected, considering the rate of solvent reorganization for acetonitrile has been estimated as 5×10^{-13} (200 fs), which further indicates that this process is completed on a a different timescale to excited-state relaxation, a point also made by Vlček et al.[38c]

Interestingly, on the basis of picosecond TR^3 studies on [Ru(bpy)$_3$]$^{2+}$ carried out some 20 years earlier, Carroll and Brus[37] concluded that vibrational relaxation of the ^{3}MLCT state was complete within some 6 ps. Moreover, they found no difference in the rR line shapes of this state going from aqueous to isopropyl alcohol environments.

Turning now to femtosecond timescale studies, Hammarström et al.[40] have noted an apparent discrepancy between their ultrafast transient absorption measurements at a 360 nm probe wavelength and the earlier findings of McCusker and co-workers. In the Hammarström study,[40] a 10 ps process was observed, in addition to the ultrafast subpicosecond step. The difference in the results obtained in the two studies was attributed to the difference in the probe wavelengths employed. In the earlier study of McCusker et al.,[32] the TA kinetics were probed in the 400−500 nm region, where ground-state depletion is the dominant process. In contrast, the 360 nm probe employed by Hammarstrom et al.[40] falls within the absorption band of the bpy anion radical (bpy$^{-\bullet}$) species and, thus, the absorption of the THEXI−^{3}MLCT state, which they suggest is where most of the solvation and vibrational relaxation processes can be expected to be observed. While this is the only wavelength where they detected significant 10 ps isotropic dynamics, the results from our own studies illustrated in Figure 3, with a 470 nm probe, interrogating the lower energy absorption band of the THEXI−^{3}MLCT state (assigned also as a bpy anion radical-centered transition), point to grow-in on a similar timescale. It is interesting to note at this point also that in a later study by the McCusker group[50] (400 nm pump) of the complexes tris(4,4'diphenyl-2,2'-bipyridyl)Ruthenium(II) ([Ru(dpbpy)$_3$]$^{2+}$) and tris(4,4'dimethyl-2,2'-bipyridyl)Ruthenium(II) ([Ru(dmb-py)$_3$]$^{2+}$), a 10 ps process was observed also, albeit being assigned to conformational changes involving the phenyl−pyridyl torsion angle. This process was found to be somewhat probe wavelength dependent with the process not being observed at 480 nm (where ground-state bleaching dominates) but observed at 532 nm (where excited-state absorption is found). Moreover, very recent investigations[36b] by femtosecond four-wave mixing of the relaxation processes leading to a thermalized ^{3}MLCT-state in the complex [Ru(tbbpy)$_3$]$^{2+}$ have also revealed two distinct timescales. An ultrafast process, which is attributed to intersystem crossing, rapidly depopulating the initially photo-excited ^{1}MLCT-state, is found to take place in less than 200 fs, followed by a second process on a picosecond timescale, assigned to vibrational cooling within the ^{3}MLCT-state.

Thus, the evidence in support of the formation of the THEXI−^{3}MLCT state requiring some 10 ps is considerable, on the basis of independent studies on both femtosecond and picosecond timescales from several laboratories. Figure 9 summarizes the picture which emerges from our own findings and these other studies. Notably, Papanikolas et al.,[51] on the basis of femtosecond TA studies on [Os(bpy)$_3$]$^{2+}$, also conclude that vibrational cooling in the ^{3}MLCT state of this complex takes place over 16 ps, following subpicosecond ISC, subsequent to initial ^{1}MLCT formation.

It is important also to consider the nature of the vibrational cooling process. The primary method for investigation of this
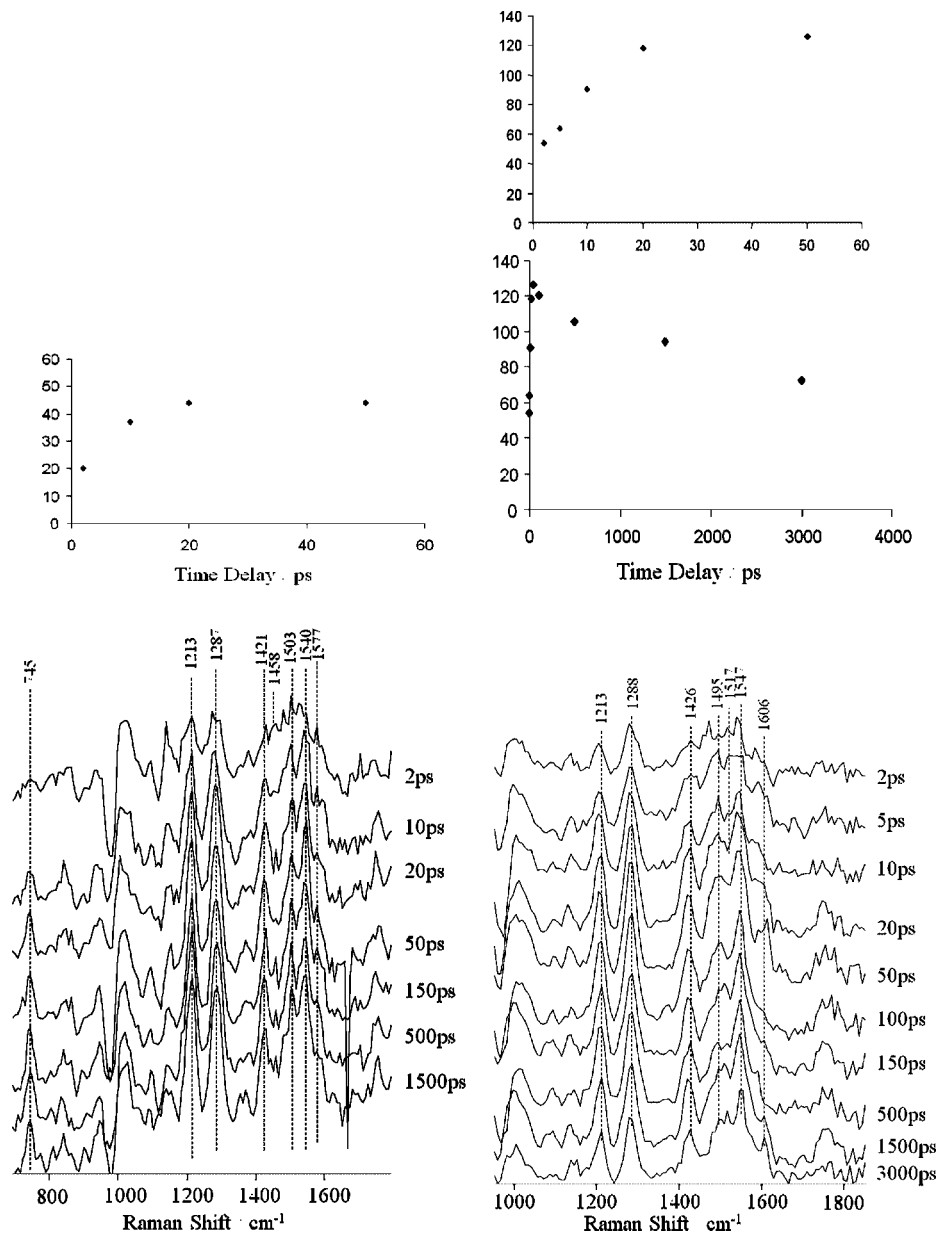
Figure 7. TR^3 spectra (lower) and kinetic traces at 1288 cm^{-1} (upper) of [Ru(bpy)$_2$(phpytr)]$^+$ in H$_2$O (left panels) and [Ru([D]$_8$-bpy)$_2$(Hphpytr)]$^{2+}$ in CD$_3$OD (right panels), λ_{probe} 350 nm, λ_{pump} 400 nm.

is the deuteriation of solvent and ligand (see Figure 7). Solvent vibrational modes act as energy acceptors in the deactivation of excited states. The insensitivity of the rate of THEXI state formation to solvent deuteriation (Figure 7) indicates that the rate of energy dumping from the upper excited levels of the ^{3}MLCT state is not significant in the thermalization process. Furthermore, the absence of any influence of ligand deuteriation on the dynamics (Figure 7) suggests that the high-frequency solvent-acceptor/ligand-donor modes are not the principal carriers for energy dissipation. Therefore, energy is probably lost via conversion into low-frequency vibrational modes. The combination of the large molecule and the mixing of vibrational modes results in a variety of closely spaced levels capable of deactivating the upper excited-state via a multitude of small steps.

The results obtained for the heteroleptic complexes [Ru-(bpy)$_2$(Hdcb)]$^+$ and Ru(bpy)$_2$(phpytr)]$^+$ provide a basis for assessing the generality of the conclusions just reached for [Ru(bpy)$_3$]$^{2+}$. Figure 6 shows the resonance Raman spectra of

[Ru(bpy)$_2$(Hdcb)]$^+$ in D$_2$O. As already pointed out, the THEXI$-^3$MLCT state of this molecule is located on the dcb ligand and not on the bpy ligands. Despite the presence of the electron-withdrawing COOH groups, the rate of THEXI state formation is little different from that for [Ru(bpy)$_3$]$^{2+}$. Previous work has suggested that charge injection in solar cells occurs on the femtosecond timescale and from a level above the THEXI state. The present results are consistent with these studies as they suggest that [Ru(bpy)$_2$(Hdcb)]$^{2+}$ is not vibrationally cold on this timescale.

From the resonance Raman spectra and kinetics of [Ru(bpy)$_2$(phpytr)]$^+$ in acetonitrile with pump at 400 nm and probe at 350 nm (Figure 7), it is clear that the grow-in kinetics occur on practically the same ps timescale as observed for [Ru(bpy)$_3$]$^{2+}$ and its deuteromers. [Ru(bpy)$_2$(phpytr)]$^+$ is a less symmetrical molecule than [Ru(bpy)$_3$]$^{2+}$ which leads to changes in the excited-state electronic structure. The electron density of the negative triazole moiety increases the energy of the phpytr ligand such that this ligand is at higher energy than the two
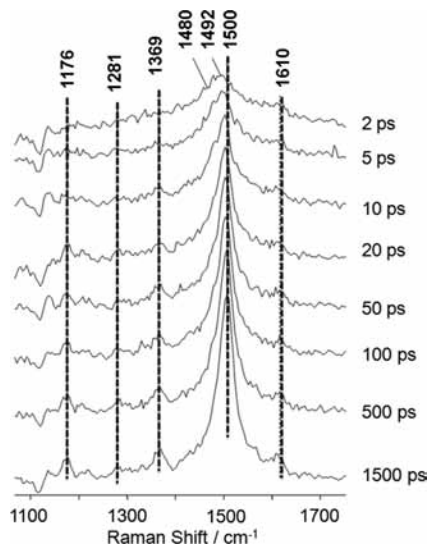
Picosecond Excited-State Dynamics of [Ru(bpy)₃]²⁺

J. Phys. Chem. A, Vol. 112, No. 20, 2008 **4543**

Figure 8. [Ru(bpy)₂Hphpytr]²⁺ in CD₃OD, λ_{probe} 475nm, λ_{pump} 400 nm. It is of note, in light of the observation in certain cases by TRIR spectroscopy,[38b,c] that changes in line shape, specifically band narrowing, occur; no example of changes in line shape or position was observed in the present study.
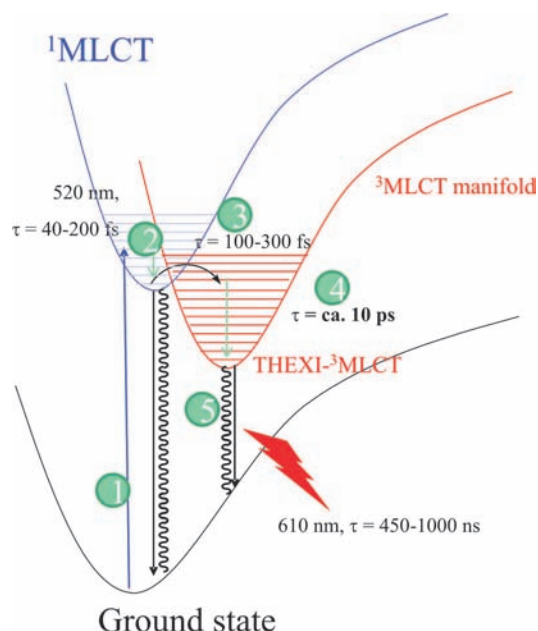

Figure 9. Overview of processes following excitation of [Ru(bpy)₃]²⁺ to the Franck–Condon (FC) state based on the present study and results obtained from TA and luminescence studies elsewhere (see text for details). (1) Excitation from the ground-state to the FC state, (2) relaxation of the FC state and fluorescence (520 nm), the lifetime of which is determined by the rate of ISC, ca. <300 fs, (3) to the vibrationally hot ³MLCT state followed by (4) vibrational cooling to the THEXI–³MLCT state (complete by 20 ps), which itself undergoes (5) both nonradiative and radiative relaxation with a lifetime of 400–1000 ns.

bipyridine ligands. This results in an excited-state which may be delocalized over two near degenerate bpy ligands (the asymmetry of L1 leads to a small energy difference between the ligands). However, no change is observed in the time taken to reach the relaxed ³MLCT spectrum. The strong σ-donor properties of the triazole lead to an increase in the energy gap between the ³MLCT and ³MC (metal centered) states. Another significant point is that the overall 1+ charge on this molecule due to the negative triazole moiety modifies the dipole of the molecule in both the ground and excited states.

The agreement of the results obtained for both the protonated [Ru(bpy)₂(Hphpytr)]²⁺ and deprotonated [Ru(bpy)₂(phpytr)]⁺ complexes highlights the fact that the protonation state, and hence charge, of the complex does not affect the time taken for formation of the THEXI state. Also the ability to control the σ-donor properties and ³MLCT–³MC energy gap of the triazole-containing complex gives an indication of the effect on ¹MLCT–³MLCT coupling of these properties. Again, since little change is seen for the triazole-containing complex in either protonation state, the influence of ³MC coupling during vibrational cooling in the picosecond time range must be seen as negligible.

Conclusions

In the present work, we have undertaken an extensive survey of the time-resolved resonance Raman spectroscopy of the paradigm [Ru(bpy)₃]²⁺ complex, its isotopologues, and a series of heteroleptic ruthenium(II) complexes. From these results, it is apparent that the THEXI state is not fully formed on the femtosecond timescale, as previously suggested, but changes in the vibrational spectra are seen up to some 10 ps.

This work is not only relevant in understanding the fundamental properties of the excited-state in transition metal complexes, but also important in regard to the design of supramolecular devices. The inclusion of [Ru(bpy)₂(Hdcb)]⁺ extends this work to cover complexes which have previously been incorporated into molecular light-energy storage devices and the observations are in agreement with studies which indicate that charge injection occurs from a non-THEXI state.[40] The similarity of the results obtained for this complex and [Ru(bpy)₃]²⁺ also highlights the importance of an intimate understanding of even ostensibly well-understood structures. Also, the observation of similar grow-in kinetics for complexes with the excited-state located on a single ligand discounts the possibility that the time taken to reach the fully vibrationally relaxed excited-state is due to localization.[40]

Supporting Information Available: Figures of [Ru(bpy)₃]-Cl₂ in 1-propanol and kinetics at 1470 cm⁻¹, Ru(bpy)₃ in H₂O, and kinetics of the 1555 cm⁻¹ Raman band for a homologous series of alcohols. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Paris, J. P.; Brandt, W. W. *J. Am. Chem. Soc.* **1959**, *81*, 5001–5002.

(2) (a) Van Houten, J.; Watts, R. J. *Inorg. Chem.* **1978**, *17*, 3381–3385. (b) Van Houten, J.; Watts, R. J. *J. Am. Chem. Soc.* **1976**, *98*, 4853–4858.

(3) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85–277.

(4) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159–244.

(5) Lehn, J. M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89–112.

(6) Balzani, V.; Campagna, S.; Denti, G.; Juris, A.; Ventura, M. *Coord. Chem. Rev.* **1994**, *132*, 1–13.

(7) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 759–834.

(8) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Acc. Chem. Res.* **1998**, *31*, 26–34.

(9) Sauvage, J.-P.; Collins, J.-P.; Chambron, J.-C.; Guillerez, S.; Coudret, C.; Balzani, V.; Barigelletti, F.; De Cola, L.; Fannigni, L. *Chem. Rev.* **1994**, *94*, 993–1019.

(10) *Supramolecular Photochemistry*; Balzani, V., Ed.; Reidel: Dordrecht, The Netherlands, 1997.

(11) Lehn, J.-M. *Supramolecular Chemistry*; Wiley-VCH: Weinheim, Germany, 1995.

(12) Hu, Y.-Z.; Tsukiji, S.; Shinkai, S.; Oishi, S.; Hamachi, I. *J. Am. Chem. Soc.* **2000**, *122*, 241–253.

(13) Meyer, T. J. *Acc. Chem. Res.* **1989**, *22*, 163.

(14) Tachibana, Y.; Haque, S. A.; Mercer, I. P.; Durrant, J. R.; Klug, D. R. *J. Phys. Chem. B* **2000**, *104*, 1198–1205.

(15) O'Regan, B.; Graetzel, M. *Nature* **1991**, *335*, 737.

(16) De Cola, L.; Belser, P. *Coord. Chem. Rev.* **1998**, *177*, 301–346.

(17) Bignozzi, C. A.; Schoonover, J. R.; Scandola, F. *Prog. Inorg. Chem.* **1997**, *44*, 1–95.

(18) Blanco, M.-J.; Jimenez, M. C.; Chambron, J.-C.; Heitz, V.; Linke, M.; Sauvage, J.-P. *Chem. Soc. Rev.* **1999**, *28*, 293–305.

(19) Martini, I.; Hodak, J. H.; Hartland, G. V. *J. Phys. Chem. B* **1998**, *102*, 9508–9517.

(20) Burfeindt, B.; Hannappel, T.; Storck, W.; Willig, F. *J. Phys. Chem.* **1996**, *100*, 16463–16465.

(21) Hilgendorff, M.; Sundström, V. *J. Phys. Chem. B* **1998**, *102*, 10505–10514.

(22) Ellingson, R. J.; Asbury, J. B.; Ferrere, S.; Ghosh, H. N.; Sprague, J. R.; Lian, T.; Nozik, A. J. *J. Phys. Chem. B* **1998**, *102*, 6455–6458.

(23) Hannappel, T.; Burfeindt, B.; Storck, W.; Willig, F. *J. Phys. Chem. B* **1997**, *101*, 6799–6802.

(24) Fessenden, R. W.; Kamat, P. V. *J. Phys. Chem.* **1995**, *99*, 12902–12906.

(25) Asbury, J. B.; Ellingson, R. J.; Ghosh, H. N.; Ferrere, S.; Nozik, A. J.; Lian, T. *J. Phys. Chem. B* **1999**, *103*, 3110–3119.

(26) Anderson, N. A.; Lian, T. Q. *Annu. Rev. Phys. Chem.* **2005**, *56*, 491–519.

(27) (a) Puntoriero, F.; Serroni, S.; Galletta, M.; Juris, A.; Licciardello, A.; Chiorboli, C.; Campagna, S.; Scandola, F. *Chem. Phys. Chem.* **2005**, *6*, 129–138. (b) Andersson, J.; Puntoriero, F.; Serroni, S.; Yartsev, A.; Pascher, T.; Polivka, T.; Campagna, S.; Sundstrom, V. *Chem. Phys. Lett.* **2004**, *386*, 336–341.

(28) Hagfeldt, A.; Gratzel, M. *Acc. Chem. Res.* **2000**, *33*, 269–277.

(29) Kuciauskas, D.; Monat, J. E.; Villahermosa, R.; Gray, H. B.; Lewis, N. S.; McCusker, J. K. *J. Phys Chem. B.* **2002**, *106*, 9347–9358.

(30) Ott, S.; Borgstrom, M.; Hammarstrom, L.; Johansson, O. *Dalton Trans.* **2006**, 1434–1443.

(31) Baudin, H. B.; Davidsson, J.; Serroni, S.; Juris, A.; Balzani, V.; Campagna, S.; Hammarstrom, L. *J. Phys. Chem. A.* **2002**, *106*, 4312–4319.

(32) (a) Damrauer, N. H.; Cerullo, G.; Yeh, A.; Boussie, T. R.; Shank, C. V.; McCusker, J. K. *Science* **1997**, *275*, 54. (b) McCusker, J. K. *Acc. Chem. Res.* **2003**, *36*, 876. (c) Yeh, A. T.; Shank, C. V.; McCusker, J. K. *Science* **2000**, *289*, 935–938.

(33) Bhasikuttan, C.; Suzuki, M.; Nakashima, S.; Okada, T. *J. Am. Chem. Soc.* **2002**, *124*, 8398–8405.

(34) (a) Browne, W. R.; Coates, C. G.; Brady, C.; Matousek, P.; Towrie, M.; Botchway, S. W.; Parker, A. W.; Vos, J. G.; McGarvey, J. J. *J. Am. Chem. Soc.* **2003**, *125*, 1706–1707. (b) Browne, W. R.; Coates, C. G.; Brady, C.; Matousek, P.; Towrie, M.; Botchway, S. W.; Parker, A. W.; Vos, J. G.; McGarvey, J. J. *J. Am. Chem. Soc.* **2004**, *126*, 10190.

(35) McFarland, S. A.; Lee, F. S.; Cheng, K. A. W. Y.; Cozens, F. L.; Schepp, N. P. *J. Am. Chem. Soc.* **2005**, *127*, 7065–7070.

(36) (a) Dietzek, B.; Kiefer, W.; Blumhoff, J.; Bottcher, L.; Rau, S.; Walther, D.; Uhlemann, U.; Schmitt, M.; Popp, J. *Chem.−Eur. J.* **2006**, *12*, 5105–5115. (b) Dietzek, B.; Akimov, D.; Kiefer, W.; Rau, S.; Popp, J.; Schmitt, M. *Laser Phys. Lett.* **2007**, *4*, 121–125.

(37) Carroll, P. J.; Brus, L. E. *J. Am. Chem. Soc.* **1987**, *109*, 7613–7616.

(38) (a) Wang, Y.; Asbury, J. B.; Lian, T. *J. Phys. Chem. A* **2000**, *104*, 4291–4299. (b) Alsindi, W. Z.; Easun, T. L.; Sun, X.-Z.; Ronayne, K. L.; Towrie, M.; Herrera, J.-M.; George, M. W.; Ward, M. D. *Inorg. Chem.* **2007**, *46*, 3696–3704. (c) Liard, D. J.; Busby, M.; Matousek, P.; Towrie, M.; Vlcek, A., Jr. *J. Phys. Chem. A* **2004**, *108*, 2363–2369.

(39) Cannizzo, A.; van Mourik, F.; Gawelda, W.; Zgrablic, G.; Bressler, C.; Chergui, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 3174–3176.

(40) Wallin, S.; Davidsson, J.; Modin, J.; Hammarstrom, L. *J. Phys. Chem. A* **2005**, *109*, 4697–4704.

(41) Browne, W. R.; Henry, W.; Passaniti, P.; Gandolfi, M. T.; Ballardini, R.; O'Connor, C. M.; Brady, C.; Coates, C. G.; Vos, J. G.; McGarvey, J. J. *Photochem. Photobiol. Sci.* **2007**, *6*, 386–396.

(42) Browne, W. R.; Passaniti, P.; Gandolfi, M. T.; Ballardini, R.; Henry, W.; Guckian, A.; O'Boyle, N.; McGarvey, J. J.; Vos, J. G. *Inorg. Chim. Acta* **2007**, *360*, 1183–1190.

(43) Towrie, M.; Parker, A. W.; Shaikh, W.; Matousek, P. *Meas. Sci. Technol.* **1998**, *9*, 816–823.

(44) The assignment is based on comparison with transient and nanosecond TR[3] studies. See, for example, Bradley, P. G.; Kress, N.; Hornberger, B. A.; Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 7441–7446.

(45) The limited number of data points available are insufficient to warrant the fitting of an exponential function; however, an estimate of the lifetime of this process indicates a figure of 10 ± 4 ps.

(46) Seilmeier, A.; Kaiser, W. *Ultrashort Laser Pulses and Applications*; Springer Verlag: New York, 1998; Chapter 7.

(47) Kallioinen, J.; Benkoe, G.; Myllyperkioe, P.; Khriachtchev, L.; Skrman, B.; Wallenberg, R.; Tuomikoski, M.; Korppi-Tommola, J.; Sundstroem, V.; Yartsev, A. P. *J. Phys. Chem. B* **2004**, *108*, 6365–6373, and ref. therein.

(48) Yoon, S.; Kukura, P.; Stuart, C. M.; Mathies, R. A. *Mol. Phys.* **2006**, *104*, 1275–1282.

(49) See, for example, Macoas, E. M. S.; Kananavicius, R.; Myllyperkio, P.; Pettersson, M.; Kunttu, H. *J. Phys. Chem. A* **2007**, *111*, 2054−2061.

(50) (a) Damrauer, N. H.; McCusker, J. K. *J. Phys. Chem. A* **1999**, *103*, 8440–8446. (b) Damrauer, N. H.; Boussie, T. R.; Devenney, M.; McCusker, J. K. *J. Am. Chem. Soc.* **1997**, *119*, 8253–8268.

(51) Shaw, G. B.; Styers-Barnett, D. J.; Gannon, E. Z.; Granger, J. C.; Papanikolas, J. M. *J. Phys. Chem. A* **2004**, *108*, 4998–5006.