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Ultrafast Excited State Dynamics of $[\text{Cr}(\text{CO})_4(\text{bpy})]$: Revealing the Relaxation between Triplet Charge-Transfer States

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Abstract

Ultrafast excited state dynamics of $[\text{Cr}(\text{CO})_4(\text{bpy})]$ upon metal-to-ligand Charge-Transfer (¹MLCT) transition have been studied by pump-probe absorption spectroscopy in CH_3CN , pyridine and CH_2Cl_2 solvents. Intersystem crossing (ISC) was found to be very fast (~ 100 fs) and efficient, while the formation of the photoproduct with one axial CO dissociated is significantly less competitive, indicating a barrier along the dissociative coordinate. As a refinement of the previous dynamic model [I. R. Farrell, et al, *J. Am. Chem. Soc.* 1999, **121**, 5296-5301], we show that a conventional downhill energy relaxation concept dominates the observed dynamics. Experimentally, we have revealed consecutive population of two triplet states as a result of triplet electronic relaxation convoluted with vibrational and solvent relaxation (overall time is 2.7–6.9 ps depending on solvent), as well as the overall depopulation of the excited state through the lowest triplet state (57–84 ps). Adaptive excitation pulse shaping could not achieve optimization of the photoproduct quantum yield via re-distribution of only low-frequency vibrational modes during excitation, indicating that the two low-lying ¹MLCT states, $\text{Cr}(3d) \rightarrow \pi_{\text{bpy}}^*$ and $\text{Cr}(3d) \rightarrow \pi_{\text{CO}}^*$, are not coupled.

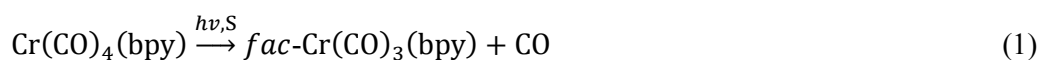
Key Words

Ultrafast dynamics of $[\text{Cr}(\text{CO})_4(\text{bpy})]$, triplet energy relaxation, coherent control, DFT-calculations

Introduction

The various luminescence properties of transition metal complexes are extensively studied, especially phosphorescence from a triplet metal-to-ligand Charge-Transfer ($^3\text{MLCT}$) state.^{1–3} Excitation of singlet MLCT states of several transition metal complexes have been shown to cause chemical reactions such as dissociation of metal-ligand bonds, isomerization or ionization.^{4–7} However, spin-orbit coupling present in heavy metal atoms increases intersystem crossing (ISC) rates, with the characteristic times ranging from tens of femtoseconds to a few picoseconds.^{8–13} In most cases ISC will strongly compete with photoreaction processes occurring from the $^1\text{MLCT}$ state.

$[\text{Cr}(\text{CO})_4(\text{bpy})]$ is a typical example of a transition metal complex undergoing a photo-induced chemical reaction. Excitation of the $^1\text{MLCT}$ state causes dissociation of an axial CO ligand, which is subsequently replaced by a solvent molecule to form a long-lived photoproduct:^{14–17}



The photoproduct quantum yield (Φ) of this dissociation reaction is low, ranging from 2% to 8% depending on the excitation wavelength.^{14–17} The wavelength dependency of Φ has been discussed in the frame of theoretical calculations, which suggest that the two lowest $^1\text{MLCT}$ states, $\text{Cr}(3d) \rightarrow \pi_{\text{bpy}}^*$ (with a small barrier along the CO dissociation coordinate) and $\text{Cr}(3d) \rightarrow \pi_{\text{CO}}^*$ are excited simultaneously upon short-wavelength excitation and that the higher energy $\text{Cr}(3d) \rightarrow \pi_{\text{CO}}^*$ state gives higher Φ .^{16–19} When the red side of the $\text{Cr}(3d) \rightarrow \pi_{\text{bpy}}^*$ band is excited, the decrease of Φ with the increasing excitation wavelength is attributed to vibronically activated crossing of the energy barrier arising from avoided crossing with a higher-lying dissociative state(s).¹⁴ Due to the short lifetimes and severe absorption spectral overlap of the states involved, it has, however, not been possible to fully characterize all aspects of the early excited state dynamics. In particular, the low value of Φ is, most probably, a consequence of ultrafast ISC, and therefore further study of ISC and subsequent triplet processes is needed for a better understanding of the photochemistry of this complex. Following ISC, population and depopulation of two triplet states has been reported to occur along two independent pathways.^{15,16} In the present work, however, we report that the triplet

decay process is more complex: besides each ISC to the ground state, electronic transition from the T_2 to T_1 state as well as vibrational and solvent relaxation also occur. Convolution of all the pathways results in consecutive population of the two triplet states.

To learn more about the details of this photo-dissociation reaction, we have applied the method of coherent control in this study. Coherent control has been recently established as a powerful tool to study, in particular, chemical reactions. This approach has been previously effectively used to optimize the branching of competing reaction channels.^{20–22} One of the first reactions that was successfully controlled using the feedback-optimized excitation pulse shaping algorithm was photo-dissociation of $\text{CpFe}(\text{CO})_2\text{Cl}$ in gas phase.²⁰ As the photo-dissociation yield of $[\text{Cr}(\text{CO})_4(\text{bpy})]$ in solution exhibits a strong excitation wavelength dependence, one would expect that changing the excited state population at the Frank-Condon region by a tailored excitation pulse could influence the photo-reaction pathways and thus change the yield of the photo-dissociation. Yet, in the present study, no optimization of the photo-dissociation reaction could be achieved. This lack of controllability of the reaction provides additional insight about the potential energy surface of the $[\text{Cr}(\text{CO})_4(\text{bpy})]$ excited state.

Methods

$[\text{Cr}(\text{CO})_4(\text{bpy})]$ was prepared by a previously reported procedure and analyzed using FTIR, ^1H -NMR and UV-Vis spectroscopies.¹⁴ Anhydrous CH_3CN , pyridine and CH_2Cl_2 were obtained from Sigma-Aldrich and degassed by bubbling of N_2 gas for at least 1h before every sample preparation. Samples for transient absorption measurements were prepared under inert conditions using Schlenk techniques. UV-Vis absorption spectra were recorded by Jasco V-530 UV-Vis spectrophotometer.

For the transient absorption experiment, tunable noncollinear optical parametric amplifiers (TOPAS white, Light Conversion and NOPA, CLARK-MXR) pumped by amplified fs-pulses (CPA 2001, Clark-MXR) were used to generate pump and probe pulses at 1 kHz repetition rate. The pump centered at 490 nm was compressed to the pulse duration of 25 fs. The broadband probe covering 500–780 nm for difference spectra measurements was a non-collinearly parametrically amplified single filament continuum with a post-measurement chirp correction

during the analysis. The measured difference spectra at most probe wavelength were influenced by cross-phase modulation and solvent artefacts leading to difficulties in assigning the first 100~150 fs. For the kinetics measurement, a probe compressed to 30 fs, centered at 560 nm was used.

Pulse shaping in the coherence control experiments was realized by a 4f zero-dispersion compressor (1200 grooves/mm gratings) combined with the liquid-crystal spatial light modulator (640 pixels, JENOPTIK Laser, Optik, System GmbH, Jena) placed in the Fourier plane of the compressor. A self-learning adaptive feedback loop was employed to optimize the photoproduct Φ , by monitoring its population at the delay time of 500 ps, when dissociation reaction is over, see below.

All the measurements were performed under magic angle excitation conditions. The excitation flux was 1.6×10^{14} photons/cm² per pulse and the sample absorbance was set to $A = 0.2 \sim 0.3$ at the excitation wavelengths. The sample solution was sealed in a flowing cell with the protection of N₂ and flows with a rate of 20~40 mL/h, depending on the solvents used. After each measurement, the degree of the solution degradation during experiment was monitored by UV-Vis spectra. Typically, less than 2% degradation of the starting solution was observed.

Density functional theory (DFT) calculations were carried out with the Gaussian09²³ package. Firstly, [Cr(CO)₄(bpy)] was optimized at the PBE0²⁴/6-31G(d,p) level of theory in C_{2v} symmetry, using a polarizable continuum model²⁵ for the solvents CH₃CN, pyridine, and CH₂Cl₂, respectively. Secondly, singlet excitations were calculated by the time dependent (TD)-DFT scheme, with the same solvents. Thirdly, the three lowest triplet states were optimized with unrestricted (u)-DFT for the CH₃CN case with the three state symmetries B₁, B₂, and A₁ imposed, respectively. At each of these three structural optima, single point calculations of the other two triplet states were performed.

Results and discussion

Our uDFT calculations are in broad agreement with the previous computational results.^{18,19}

We identify the HOMO→LUMO Cr(d_{z²-y²})→π_{bpy}^{*} triplet state of B₁ symmetry at 751 nm

(1.65 eV), the HOMO-1→LUMO $\text{Cr}(d_{xy}) \rightarrow \pi_{\text{bpy}}^*$ triplet of B_2 symmetry at 708 nm (1.75 eV), as well as a third HOMO-2→LUMO $\text{Cr}(d_{zx}) \rightarrow \pi_{\text{bpy}}^*$ triplet of A_1 symmetry at 670 nm (1.85 eV), all as relaxed in CH_3CN . The orbitals involved are depicted in Figure 1. These three triplet states of different symmetries optimize to slightly different geometries. Furthermore, each state is the lowest triplet state at respective optimized geometry, as verified by single point uDFT calculations of all three states at all three geometries. This may support their experimental occurrence. The axial Cr–C bonds are calculated to be 1.90, 1.96 and 1.94 Å respectively for the B_1 , B_2 and A_1 relaxed states, whereas the equatorial Cr–C bonds are 1.92, 1.86 and 1.86 Å. For the singlet excitations, TD-DFT assigns negligible intensity to the two lowest B_1 and B_2 excitations, both with a 98.5% correspondence to respectively HOMO→LUMO and HOMO-1→LUMO. This makes the A_1 $\text{Cr}(d_{zx}) \rightarrow \pi_{\text{bpy}}^*$ excitation responsible for the first absorption peak, with a 98.6% correspondence to HOMO-2→LUMO. As evident from Figure 1, the depopulation of the three HOMOs weakens the Cr–C bonds, whereas the LUMO does not affect this bond. The experimental solvatochromic shift apparent in Figure 2 is adequately captured with TD-DFT, with the first vertical absorption peaks occurring at 444 nm, 453 nm, and 457 nm for the solvents CH_3CN , pyridine and CH_2Cl_2 respectively. However, this constitutes a consistent blueshift compared to the experimental peaks (474, 490 and 504 nm, respectively). The fourth calculated singlet has a 89.4% correspondence to HOMO→LUMO+3, and it is the lowest excitation of $\text{Cr}(3d) \rightarrow \pi_{\text{CO}}^*$ character. It occurs at 391 nm, 392 nm, and 392 nm for CH_3CN , pyridine and CH_2Cl_2 respectively, but shows much smaller intensity than the $\text{Cr}(d_{zx}) \rightarrow \pi_{\text{bpy}}^*$ excitation.

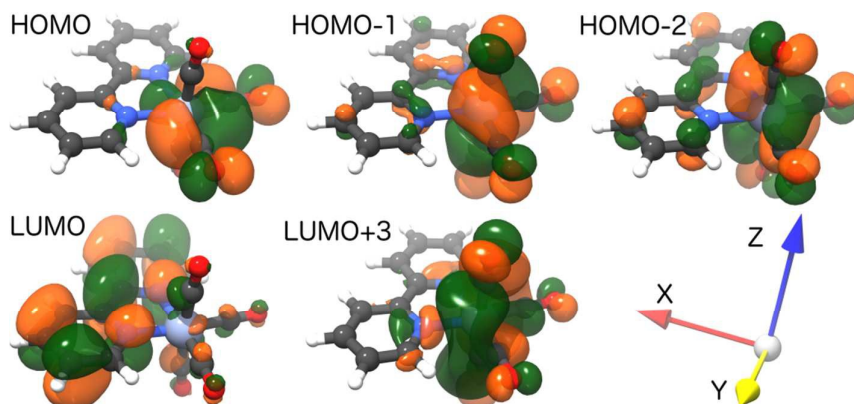


Figure 1. Selected molecular orbital plots involved in the low-energy excitations for $[\text{Cr}(\text{CO})_4(\text{bpy})]$ in CH_3CN .

The UV-Vis absorption spectra of $[\text{Cr}(\text{CO})_4(\text{bpy})]$ (Figure 2) contain two main bands around 333 and 500 nm with a shoulder in between. The high- and the middle-energy bands are not very sensitive to the solvents used in this work, while the low-energy band energy clearly increases with the increase of the solvent polarity from CH_2Cl_2 to pyridine and CH_3CN . To understand the solvent dependency better, each spectrum was decomposed into three Gaussian bands. Although this decomposition is rather tentative, it exhibits the main trends. The low- and the middle-energy bands were assigned to the photodissociative $^1\text{MLCT}$ states, $\text{Cr}(3\text{d}) \rightarrow \pi_{\text{bpy}}^*$ and $\text{Cr}(3\text{d}) \rightarrow \pi_{\text{CO}}^*$, in agreement with ^{16–19}. The MLCT transitions exhibit hypsochromic, whereas $\text{Cr}(3\text{d}) \rightarrow \pi_{\text{bpy}}^*$ and $\text{Cr}(3\text{d}) \rightarrow \pi_{\text{CO}}^*$ states exhibit bathochromic solvent polarity dependence with increasing solvent polarity respectively.

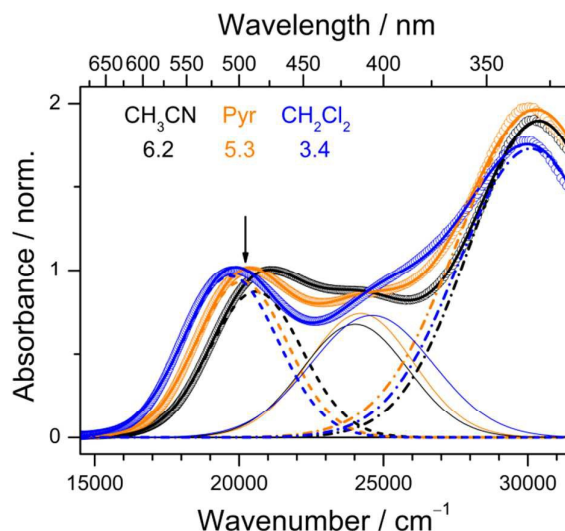


Figure 2. Normalized UV-Vis absorption spectra of $[\text{Cr}(\text{CO})_4(\text{bpy})]$ in different solvents (open circles) and their fitting curves (thick solid lines) with Gaussian decompositions. Arrow shows the excitation wavelength, and solvent polarities are also shown.

The transient absorption spectra of $[\text{Cr}(\text{CO})_4(\text{bpy})]$ in various solvents are shown in Figure 3. Upon excitation at 490 nm, a broad $^1\text{MLCT}$ excited state absorption (ESA) appears at pump-probe delay close to zero. At ~ 50 fs delay, a negative band builds up in the blue part of the difference spectrum, which could be assigned to the ground state bleaching (GSB) or/and the stimulated emission (SE) from the $^1\text{MLCT}$ state. The assignment of this negative feature is fairly uncertain, considering a probable contribution of the relatively large cross-phase modulation (XPM) artifact. It should be noted that the $\text{Cr}(3\text{d}) \rightarrow \pi_{\text{bpy}}^*$ and $\text{Cr}(3\text{d}) \rightarrow \pi_{\text{CO}}^*$ states cannot be distinguished in the transient spectra. Both the early ESA and negative signal are short-lived and disappear due to fast ISC. ISC rise dynamics cannot be accurately determined because of the XPM contribution, thus we estimate that ISC occurs in ~ 100 fs. It is particularly difficult to determine the ISC rates more accurately as the solvents used in this study exhibit fast photo-induced dynamics in the same spectral region as can be seen in Figure S2.

After 100 fs, a new broad ESA signal of a different shape with two peaks takes over the early signal. Figure 3 shows that the spectral shape of this ESA is solvent dependent. Transition metal complexes are well known for very fast ISC, e.g. 20 fs in $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ and

$[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$ ^{9,10} or 43 fs in $[\text{Ru}(4,4'-(\text{COOH})_2\text{-bpy})_2(\text{NSC})_2](\text{N3})$. ⁸ Therefore we attribute this new ESA to the triplet states. The broad triplet ESA decays on a ps time scale. Global fitting of the difference spectra results in a biexponential decay over the studied spectral range, with one short lifetime, τ_2 , of a few (2.5/6.2/2.6) ps, and one long lifetime, τ_3 , of several tens (57/84/73) of ps (in CH_3CN /pyridine/ CH_2Cl_2 , respectively), see Table 1. These two decay components are related to the population and depopulation of the two separate triplet states. Previous studies have assigned these two states as the two lowest lying ³MLCT states (T_2 and T_1), originating from $\text{Cr}(\text{d}_{xy}) \rightarrow \pi_{\text{bpy}}^*$ and $\text{Cr}(\text{d}_{z^2-y^2}) \rightarrow \pi_{\text{bpy}}^*$ at 1.69 (734) and 1.56 eV (795 nm), respectively. ¹⁵⁻¹⁹ Furthermore, as suggested by the open-shell TD-DFT calculation of a similar complex, $\text{Re}(\text{L})(\text{CO})_3(\text{bpy})$, the intense bands in the UV region may originate from $\pi_{\text{bpy}}^* \rightarrow \text{Cr}$ LMCT transition (with a possible contribution of intraligand (IL) component). ²⁶

After the decay of the triplet states, a new long-lived photo-induced broad absorption band maximized at 590/640/610 nm dominates the difference spectra in CH_3CN /pyridine/ CH_2Cl_2 , see Figure 3. It is attributed to *fac*- $\text{Cr}(\text{S})(\text{CO})_3(\text{bpy})$ photoproduct. In agreement with previous publications ^{15,16}, we propose that dissociation occurs from the ¹MLCT states, in competition with ISC. Owing to the severe spectral overlap with T_1 and T_2 in the studied spectral region and due to the small contribution to the overall intensity, the photoproduct absorption rise cannot be distinguished. Previous publications reported that the photoproduct formation is completed within 400 fs. ^{15,16} Now with better temporal resolution, we conclude that this time is shorter, ~ 100 fs. If we assume a simplified branching reaction from ¹MLCT between ISC leading towards the triplet states and the photo-dissociation of the CO-group, we can estimate the rate of dissociation from the yield of the photo-product. With the ISC rate of $(\sim 100 \text{ fs})^{-1}$ and Φ of 4.2% (both values are obtained from global fitting as stated below), the photo-dissociation should have an approximate rate constant as $(\sim 2.3 \text{ ps})^{-1}$. This rate scale implies that photo-dissociation process is limited by a small barrier, which has been confirmed by the temperature dependence of Φ . ¹⁴ CASSCF/MR-CCI calculations have also shown the presence of a small barrier along $\text{Cr}-\text{CO}_{\text{axial}}$ bond. ^{16,19} This conclusion is also in line with the results of our coherent control experiment (*vide infra*).

Regarding the appearance and time evolution of the two triplet states of $[\text{Cr}(\text{CO})_4(\text{bpy})]$, it

was concluded in the previous studies that these states are populated simultaneously and decay independently with different time constants.^{15,16} This scheme was later modified for $\text{Re}(\text{L})(\text{CO})_3(\text{bpy})$,^{13,27} by including an electronic transition process that couples two triplet states ($\text{b}^3\text{A}'' \rightarrow \text{hot a}^3\text{A}''$) with time constants of 0.3~1.6 ps, followed by cooling of hot $\text{a}^3\text{A}''$ with a time constant of ~10 ps. In the later scheme, $\text{a}^3\text{A}''$ was still suggested to be populated directly via ISC.

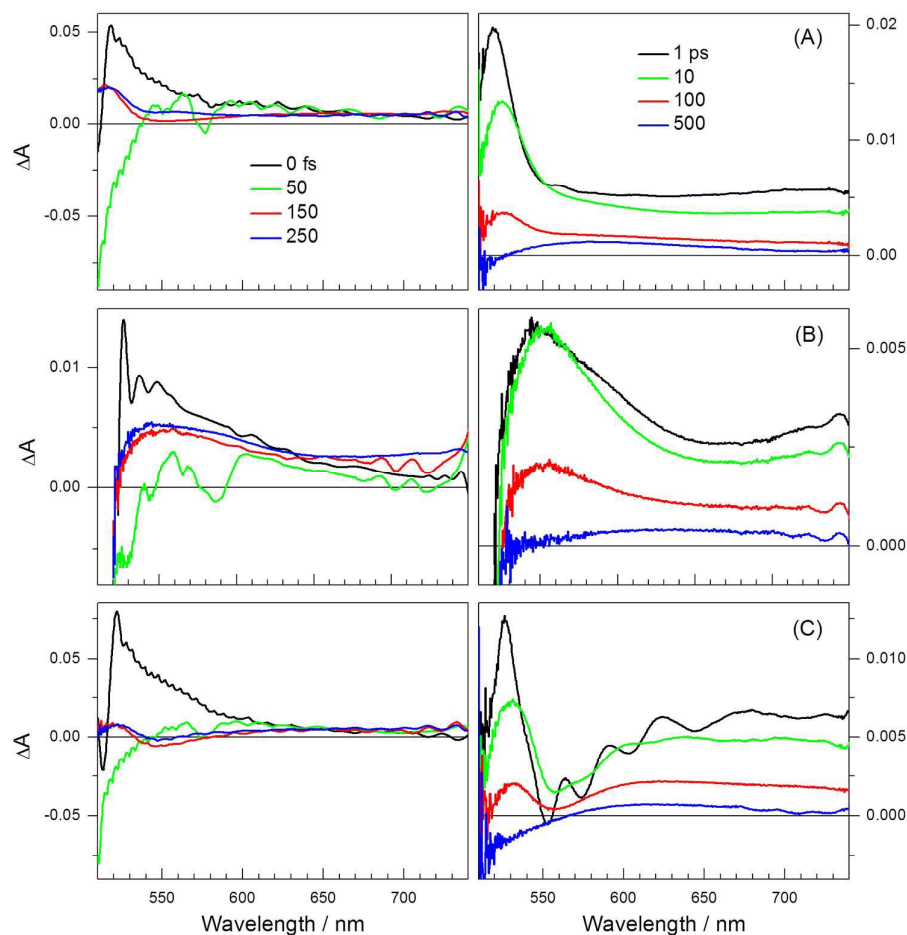


Figure 3. Transient absorption spectra of $[\text{Cr}(\text{CO})_4(\text{bpy})]$ dissolved in CH_3CN (A), pyridine (B) and CH_2Cl_2 (C) at different delay times.

In the present work, on the basis of the observed spectral dynamics in the broad spectral region measured in several solvents, a refinement scenario of the triplet population and relaxation dynamics is suggested. To account for the observed spectral evolution, we have to include vibrational and solvent relaxation in the model. This process can be seen in Figure 4

(we present only the CH₃CN and pyridine data, for CH₂Cl₂ see Figure S1).

In pyridine (Figure 4A and B), the triplet ESA band first undergoes a spectral narrowing to the blue, in ~1 ps. This corresponds most probably to the vibrational and solvent relaxation process occurring in the T₂ state. Then a state-to-state transition takes place, manifested by an apparent isosbestic point at 585 nm visible from 1 to 6.5 ps in Figure 4A. Also, the 580 nm kinetics remains nearly flat from 0.3 to 5.5 ps. No vibrational/solvent relaxation is observed for the T₁ state, so the T₂→T₁ conversion is dominant by the electronic transition.

In CH₃CN (Figure 4C and D), the triplet ESA band also undergoes a state-to-state transition. An indication of an isosbestic point can be recognized in the early times from 0.2-1.1 ps. Later this band broadens and shifts to the red. Therefore, the expected state-to-state isosbestic point in difference spectra is not pronounced any more due to the dominant contribution of the spectral shift towards red. Furthermore, the decay of the blue part at 520 nm and the rise of the red part at 540 nm correlate with each other. These features are in agreement with vibrational and solvent relaxation processes. The observed spectral dynamics indicates that vibrational and solvent relaxation predominantly occurs after the electronic relaxation into the T₁ state. The difference in the appearance of the isobestic points for these two solvents is correlated with the time scale of the triplet conversion process, which is much faster in CH₃CN than in pyridine. Thus, if energy relaxation processes occur on a few ps time scale, they can mix up with the triplet conversion in CH₃CN whereas in pyridine the relaxation is largely over before the triplet conversion.

The intramolecular part of the vibrational relaxation (IVR) is most probably not clearly visible in neither pyridine nor CH₃CN. This relaxation should be weakly dependent on solvent and thus should have similar appearance in both CH₃CN and pyridine. Yet, the early resolved spectral dynamics is clearly different in these two cases. This observation agrees with the expected fast (~100 fs) time scale of IVR for large aromatic molecular groups.^{28,29} Solvation dynamics is also hardly responsible for the observed changes during several ps as it has been reported to occur on a few hundreds of fs time scale in CH₃CN and CH₂Cl₂.²⁹ Vibrational cooling is the process that depends on both solvent and solute and has been reported to occur on a time scale of several ps.²⁸ This process, though, is usually associated with spectral narrowing and cannot solely explain the observed spectral shift in difference spectra.

Apparently, a combination of all relaxation processes has to be taken into account in assignment of the experimental results. In addition, there are two other minor features that could contribute to the change of the spectral shape: the decaying GSB signals due to tentative fast internal conversion to S_0 from S_1 , T_2 and T_1 joined with the short-wavelength part of the triplet ESA spectra and the time-dependent spectral change of the photoproduct induced by the solvation. Although we could not access the spectral range where the ground state recovery dynamics should be dominant, we can refer to the previous time-resolved IR spectroscopy study where the recovery has been determined to have 8 ± 3 ps and 76 ± 7 ps decay, using 200 fs pulse at 400 nm as pump and 200 fs IR pulse as probe.¹⁶ No faster components have been reported there. Based on this result, we do not expect much of the ground state recovery to contribute to the spectral dynamics.

It is possible to notice that in CH_3CN and CH_2Cl_2 the extinction coefficient of the T_2 state is larger (smaller) than that of the T_1 in the short (long) wavelength region, whereas in the pyridine case the observation is opposite. This is probably related to different solute-solvent interaction in the set of solvents used in our study.

On the basis of the observed spectral dynamics, electronic transition between the T_1 and T_2 states is evident, therefore the parallel model of energy evolution after excitation should be modified. In the suggested model, the $T_2 \rightarrow T_1$ conversion contains several combined components: (1) electronic transition from the T_2 to T_1 state, (2) IVR of the high vibrational levels in both triplet states, (3) solvation dynamics of the new distribution of charges and (4) vibrational (solvent) cooling. The overall triplet conversion process can be simplified as $T_2 \rightarrow \text{hot } T_1 \rightarrow T_1$ for CH_3CN and $\text{hot } T_2 \rightarrow T_2 \rightarrow T_1$ for pyridine.

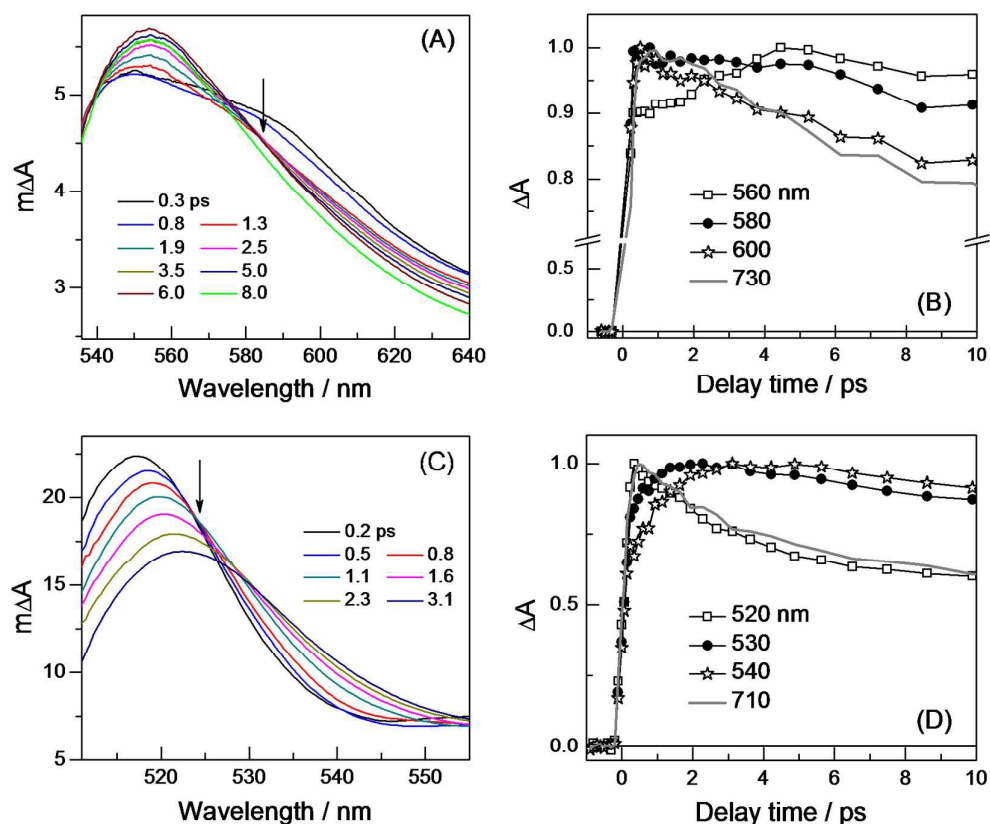


Figure 4. Transient absorption spectra at selected delay times (A), (C) and normalized kinetic curves (B), (D) at different wavelengths of $[\text{Cr}(\text{CO})_4(\text{bpy})]$ dissolved in pyridine (A and B) and CH_3CN (C and D). The arrows on (A) and (C) show isosbestic points in difference spectra. In (C) the isosbestic point is only visible at earlier times, later energy relaxation processes complicate the spectral dynamics.

Global fitting of the difference spectra was done to obtain the basic time constants. The hot and relaxed triplet states cannot be distinguished inside the applied model because global analysis is not directly applicable in a case of a spectral shift. Thus in the practical fitting, we treat the hot T_1 and T_1 (hot T_2 and T_2) states as one component. The obtained τ_2 , which actually corresponds to several combined processes, was used as the lifetime of the T_2 state.

This model presented in Scheme 1 is the simplest one that can explain the main kinetics observed, with k_d , k_r and k_1 as free parameters and k_{ISC} fixed as 100 fs^{-1} . Then the lifetimes of S_1 , T_2 and T_1 states are: $\tau_1 = (k_{\text{ISC}} + k_d)^{-1}$, $\tau_2 = k_r^{-1}$, $\tau_3^{-1} = k_1$, while the photoproduct quantum yield is: $\Phi = k_d / (k_{\text{ISC}} + k_d)$. The obtained species absorption spectra are shown in Figure 5 while the time constants are listed in Table 1. The absorption spectra of T_1 and T_2 states are rather

similar, although the T_1 peak shifts slightly to the red as compared to T_2 . The photoproduct absorption maximum is different for different solvents: 590 nm (CH_3CN), 640 nm (pyridine) and 610 nm (CH_2Cl_2).

Both τ_2 and τ_3 are solvent dependent, yet due to different mechanisms. The dependence of τ_3 is mainly determined by the spin-orbital coupling while τ_2 reflects complex solvent dependences of multiple processes. The rates of electronic transition (internal conversion), vibrational cooling and solvent relaxation decrease with increasing solvent viscosity^{29–31} while IVR is not sensitive to the solvents²⁸. The larger τ_2 observed for pyridine is mainly due to the slower internal conversion, which is implied to have a stronger dependence on solvent viscosity than the other processes. The photoproduct yields in all the three solvents are low, in agreement with the previous publications.^{14,15} However, the Φ s increases with increasing solvent polarity, which may be related to the increase of the photoreaction activation energy in more polar solvents.¹⁴

Scheme 1. The proposed excited state dynamics of $[\text{Cr}(\text{CO})_4(\text{bpy})]$ complex with the relations: $(\tau_1)^{-1} = k_{\text{ISC}} + k_{\text{d}}$, $\Phi = k_{\text{d}} / (k_{\text{ISC}} + k_{\text{d}})$, $(\tau_2)^{-1} = k_{\text{r}}$, $(\tau_3)^{-1} = k_1$.

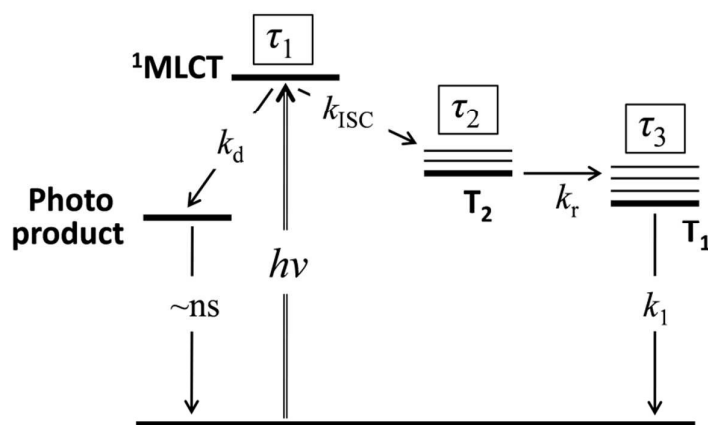


Table 1. Solvent polarity and time constants/photoproduct Φ obtained from global fitting.

Solvent	Polarity	viscosity	τ_1 (fs)	τ_2 (ps)	τ_3 (ps)	Φ (%)
CH_3CN	6.2	0.37	96	2.5	57	4.2
pyridine	5.3	0.97	96	6.2	84	3.7
CH_2Cl_2	3.4	0.44	97	2.6	73	3.4

The simplest model could explain the observed kinetics of the two consecutive triplet states, however, another electronic relaxation route of T_2 state, $T_2 \rightarrow$ ground state, is also supported by TD-DFT calculation results. Time-resolved IR spectroscopy showed that the ground state recovery has two decay components with the lifetimes similar to τ_2 and τ_3 ,¹⁶ also indicating the existence of the $T_2 \rightarrow$ ground state ISC. The same channel also appears in $\text{Re}(\text{L})(\text{CO})_3(\text{bpy})$.^{13,26} Therefore a modified model including $T_2 \rightarrow$ ground state relaxation appears to be more accurate. The global fitting results with this modified model (see Figure S3, Scheme S1 and Table S1 in supporting information) show that $T_2 \rightarrow$ ground state relaxation is much slower than $T_2 \rightarrow T_1$ state relaxation, and thus T_2 and T_1 states are still dominated by consecutive population.

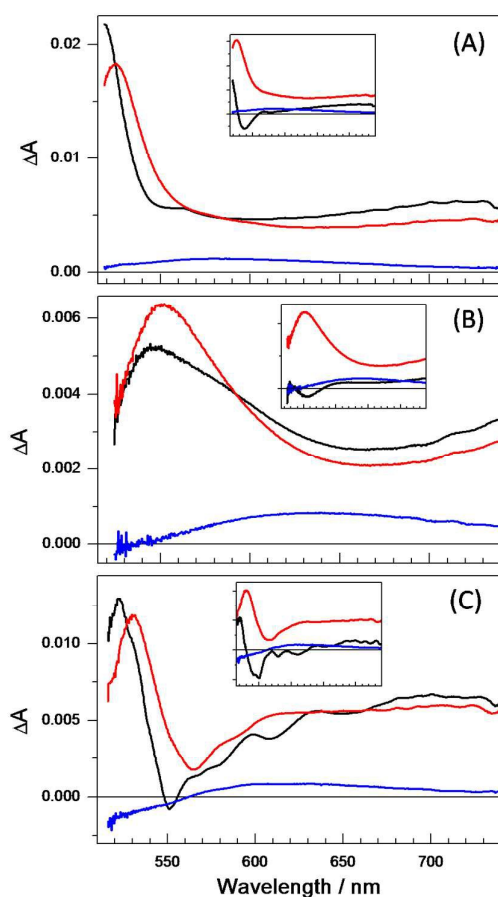


Figure 5. Absorption spectra of T_2 (black), T_1 (red) and photoproduct (blue) for $[\text{Cr}(\text{CO})_4(\text{bpy})]$ dissolved in CH_3CN (A), pyridine (B) and CH_2Cl_2 (C) obtained by global fitting according to Scheme 1. Insets shows the same spectra but fitted according to the parallel model¹⁵.

The alternative model where T_1 and T_2 are populated in parallel via ISC and then decay independently was also tested in global fitting, see the inset of Figure 5. The obtained spectra are not consistent with the above considerations that the absorption spectra of T_1 and T_2 states should be rather similar. In fact, in this model the T_2 spectrum is negative in the short-wavelength LMCT region. A negative component in the T_2 decay spectrum could be related to the internal conversion to the ground state on a few ps time scale, which would be in conflict with the earlier reported ground state recovery dynamics.¹⁶ Although global fitting is not quite applicable in the case of a complex spectral shift, the drastically different absorption spectra and yields of the T_1 and T_2 states indicate that the parallel model is not adequate to the observed spectral and dynamic evolutions. Further problem in the parallel model is related to the positive T_2 decay spectrum towards blue from 530 nm even if we assume a substantial ground state recovery associated with the decay of T_2 . Such component implies either that T_2 ESA is much stronger than the ground state absorption or a build up in the ground state bleach. Neither of these two implications seems reasonable.

The temporal resolution of the difference spectral measurements, Figure 4, is limited to ~ 100 fs due to the relatively long probe pulses used and due to XPM. To overcome these complications, we conducted additional kinetic measurements in which a selected part of the probe light was compressed to nearly transform-limited pulses and detected by a single detector without spectral resolution. Consequently, we can eliminate XPM³² and improve the temporal resolution by using probe pulses as short as ~ 30 fs. Kinetics measured with such pulses, see Figure 6, give information on the rise process. However, solvent induced artifact signals at $-100\sim 300$ fs make a nonnegligible contribution to the measured traces due to the small cross section of the $[\text{Cr}(\text{CO})_4(\text{bpy})]$ ground and excited state absorption.³² The artifacts are complex (see Figure S2) and cannot be unambiguously removed by subtraction from the kinetic curves. Nevertheless, the measured kinetics can be also used to disclose the population of T_1 directly from $^1\text{MLCT}$. The difference absorption spectra of the triplet states in CH_2Cl_2 exhibit a minimum at ~ 560 nm where the GSB contribution is still relatively strong, and the overall ΔA signal in this spectral region turns negative for the delay times from about 0.15 to 3 ps. Further, the same kinetics turns positive at longer delay times. Such behaviour of the difference absorption signal does not fit to a spectral shift but agrees well with a sequential

type of the population reaction of the two triplet states. The early negative signal corresponds to the absorption of the first triplet being slightly weaker than the ground state absorption at this wavelength whereas the absorption of the second triplet is slightly stronger than that of the ground state resulting in an overall positive signal. Absorption of the triplet states as well as of the ground state can be relatively similar yet slightly different to result in the measured dynamics.

The appearance of the negative signal from 0.15 ps in the CH₂Cl₂ 560 nm dynamics shows that the T₂ state has been populated in 0.15 ps. Although the ISC rate still cannot be determined precisely due to the artifacts, this dynamic feature supports the above estimation of the ISC rate, (~ 100 fs)⁻¹. The ICS of [Cr(CO)₄(bpy)] is comparable with that of Re(L)(CO)₃(bpy), while slower than that of [Ru^{II}(bpy)₃]²⁺ and [Fe^{II}(bpy)₃]²⁺, 20 fs.

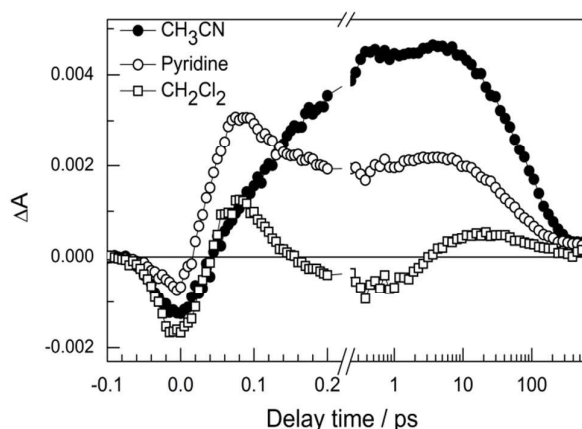


Figure 6. Kinetic curves at 560 nm of [Cr(CO)₄(bpy)], measured with a 30 fs pulse.

We have attempted to control the dissociation reaction via optimization of the yield Φ by excitation pulse tailoring, but could not obtain reliable increase of the feedback signal in either maximization or minimization of Φ by the optimization algorithm (for details, see supporting information). Since Φ is determined by the branching ratio of the dissociative and the ISC pathways, the lack of optimization indicates that either both branches cannot be influenced by the excitation pulse shape or, less probably, that pulse shaping induces identical changes along both pathways. The lack of optimization could be explained by the presence of a barrier along the dissociative coordinate. Such a barrier would be difficult to overcome by

changing the distribution of the low-frequency vibrational modes only. It should be noted that all experiments showing successful coherent control of photo-dissociation of coordination compounds have been performed in gas phase where the barriers may not exist.^{20–22} As our pump pulses should excite both $\text{Cr}(3d) \rightarrow \pi_{\text{bpy}}^*$ and $\text{Cr}(3d) \rightarrow \pi_{\text{CO}}^*$ states and tailoring of the excitation pulse may induce some interference between these transitions, the lack of coherent control of photo-dissociation also implies that $\text{Cr}(3d) \rightarrow \pi_{\text{bpy}}^*$ and $\text{Cr}(3d) \rightarrow \pi_{\text{CO}}^*$ states are most probably not coupled, in agreement with the results from temperature and pressure dependence of Φ .^{6,14}

Conclusions

Transient absorption spectra upon excitation of the $^1\text{MLCT}$ state of $[\text{Cr}(\text{CO})_4(\text{bpy})]$ in CH_3CN , pyridine and CH_2Cl_2 are presented. Very efficient ISC from the Franck-Condon point occurs in ~ 100 fs. The photo-dissociation pathway in these solvents is much less competitive, most probably due to the existence of a barrier. Triplet energy relaxation between the two lowest triplet states was observed on a time scale of 2.5–6.2 ps and is solvent dependent. The results together with DFT calculations provide a more detailed understanding of the photo-dissociation of $[\text{Cr}(\text{CO})_4(\text{bpy})]$, which is a refinement of the previous description.^{15,16} No coherent control of the photoproduct Φ could be achieved, suggesting that neither $\text{Cr}-\text{CO}_{\text{axial}}$ bond dissociation nor ISC can be influenced at the experimental conditions used. Apparently, modulation of the low-frequency vibrational modes of the $^1\text{MLCT}$ state by the shaped pulse excitation cannot alter the branching ratio of these reaction channels, also suggesting that the $\text{Cr}(3d) \rightarrow \pi_{\text{CO}}^*$ and $\text{Cr}(3d) \rightarrow \pi_{\text{bpy}}^*$ $^1\text{MLCT}$ states are not coupled.

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References

1. R.C. Evans, P. Douglas and C. J. Winscom, *Coord. Chem. Rev.*, 2006, **250**, 2093–2126.
2. A. Hagfeldt and M. Grätzel, *Acc. Chem. Res.*, 2000, **33**, 269–277.
3. A. M. Blanco-Rodríguez, M. Busby, C. Grădinaru, B. R. Crane, A. J. Di Bilio, P. Matousek, M. Towrie, B. S. Leigh, J. H. Richards, A. Jr. Vlček and H. B. Gray, *J. Am. Chem. Soc.*, 2006, **128**, 4365–4370.
4. A. Vogler and H. Kunkely, *Coord. Chem. Rev.*, 1998, **177**, 81–96.
5. S. Wieland, K. B. Reddy and R. van Eldik, *Organometallics*, 1990, **9**, 1802–1806.
6. W.-F. Fu and R. van Eldik, *Inorg. Chem.*, 1998, **37**, 1044–1050.
7. D. M. Manuta and A. Lees, *J. Inorg. Chem.*, 1986, **25**, 1354–1359.
8. A. C. Bhasikuttan and T. J. Okada, *Phys. Chem. B*, 2004, **108**, 12629–12632.
9. A. Cannizzo, F. van Mourik, W. Gawelda, G. Zgrablic, C. Bressler and M. Chergui, *Angew. Chem., Int. Ed.*, 2006, **45**, 3174–3176.
10. W. Gawelda, A. Cannizzo, V.-T. Pham, F. van Mourik, C. Bressler and M. Chergui, *J. Am. Chem. Soc.*, 2007, **129**, 8199–8206.
11. G. T. Burdzinski, R. Ramnauth, M. H. Chisholm and T. L. Gustafson, *J. Am. Chem. Soc.*, 2006, **128**, 6776–6777.
12. E. A. Juban and J. K. McCusker, *J. Am. Chem. Soc.*, 2005, **127**, 6857–6865.
13. A. Cannizzo, A. M. Blanco-Rodríguez, A. Nahhas, J. Šebera, S. Zális, A. Jr. Vlček and M. Chergui, *J. Am. Chem. Soc.*, 2008, **130**, 8967–8974.
14. J. Víchová, F. Hartl and A. Jr. Vlček, *J. Am. Chem. Soc.*, 1992, **114**, 10903–10910.
15. I. R. Farrell, P. Matousek and A. Jr. Vlček, *J. Am. Chem. Soc.*, 1999, **121**, 5296–5301.
16. I. R. Farrell, P. Matousek, M. Towrie, A.W. Parker, D. C. Grills, M. W. George, and A. Jr. Vlček, *Inorg. Chem.*, 2002, **41**, 4318–4323.
17. A. Jr. Vlček, *Coordin. Chem. Rev.*, 2002, **230**, 225–242.
18. D. Guillaumont, C. Daniel and A. Jr. Vlček, *Inorg. Chem.*, 1997, **36**, 1684–1688.
19. D. Guillaumont, A. Jr. Vlček and C. Daniel, *J. Phys. Chem. A*, 2001, **105**, 1107–1114.
20. A. Assion, T. Baumert, M. Bergt, T. Brixner, B. Kiefer, V. Seyfried, M. Strehle and G. Gerber, *Science*, 1998, **282**, 919–922.

21. H. Rabitz, R. de Vivie-Riedle, M. Motzkus and K. Kompa, *Science*, 2000, **288**, 824–828.
22. C. Daniel, J. Full, L. González, C. Lupulescu, J. Manz, A. Merli, Š. Vajda and L. Wöste, *Science*, 2003, **299**, 536–539.
23. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford CT, 2009.
24. C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158–6170.
25. E. Cancès, B. Mennucci and J. Tomasi, *J. Chem. Phys.*, 1997, **107**, 3032–3041.
26. S. Zálíš, C. Consani, A. Nahhas, A. Cannizzo, M. Chergui, F. Hartl, A. Jr. Vlček, *Inorg. Chim. Acta*, 2011, **374**, 578–585.
27. A. Nahhas, A. Cannizzo, F. van Mourik, A. M. Blanco-Rodríguez, S. Zálíš, A. Jr. Vlček and M. Chergui, *J. Phys. Chem. A*, 2010, **114**, 6361–6369.
28. T. Elsaesser and W. Kaiser, *Annu. Rev. Phys. Chem.*, 1991, **42**, 83–107.
29. M. L. Horng, J. A. Gardecki, A. Papazyan, M. Maroncelli, *J. Phys. Chem.*, 1995, **99**, 17311–17337.
30. M. Belletête, R. S. Sarpal and G. Durocher, *Chem. Phys. Lett.*, 1993, **201**, 145–152.
31. A. M. Blanco-Rodríguez, K. L. Ronayne, S. Zálíš, J. Sýkora, M. Hof and A. Jr. Vlček, *J. Phys. Chem. A*, 2008, **112**, 3506–3514.
32. B. Dietzek, T. Pascher, V. Sundström and A. Yartsev, *Laser Phys. Lett.*, 2007, **1**, 38–43.