Role of coherent nuclear motion in the ultrafast intersystem crossing of ruthenium complexes†

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Ultrafast intersystem crossing (ISC) in transition metal complexes leads to a long-lived active state with a high yield, which leads to efficient light energy conversion. The detailed mechanism of ISC may lead to a rational molecular design of superior transition metal complexes. Coherent nuclear wave packets observed in femtosecond time-resolved spectroscopies provide important information on the excited-state dynamics. In particular, analyzing the nuclear wave packets in both the reactant and the product may unveil the molecular dynamics of an ultrafast reaction. In this study, experimental evidence proving the reaction coordinates of the ultrafast ISC of ruthenium(II) complexes is presented using coherent vibrational spectroscopy with a quantum chemical simulation of coherent vibrational motion. We observed vibrational modes strongly coupled to the ISC, whose vibrational coherences undergo remarkable attenuation after the ISC. The coupled modes contain metal–ligand stretching or symmetry breaking components, and the faster ISC rates of lower-symmetry ruthenium(II) complexes support the significance of the latter.

Introduction

Ru(II) complexes are widely used photosensitizers for various applications such as solar cells and photocatalysts.1–3 Tris(2,2′-bipyridyl)ruthenium(II) [Ru(bpy)3]2+, shown in Fig. 1a, is the most common Ru(II) complex utilized for the fundamental study of excited-state dynamics.4–12 The lowest allowed electronic transition of [Ru(bpy)3]2+ generates a singlet metal-to-ligand charge transfer (1MLCT) state. Subsequently, ultrafast intersystem crossing (ISC) occurs in less than 25 fs to form a long-lived triplet state (3MLCT),5,9 which is the photoactive state of a Ru(II) complex, and it can be utilized as a photocatalyst (Fig. 1b and c). The lifetime of the 3MLCT state is long enough to transport the complex, and it can be utilized as a photocatalyst (Fig. 1b and c).

Femtosecond time-resolved spectroscopies have been actively employed to uncover the reaction dynamics of ultrafast photochemical and photochemical processes owing to their high time-resolution.5,9,13 In particular, the capability of time-resolved spectroscopies for monitoring vibrational and electronic coherences provides more advanced information on the process of interest.14–16 Transient absorption (TA) and time-resolved fluorescence (TF) are two typical time-resolved spectroscopic techniques. TA is advantageous in observing coherent wave packet oscillations because of its high time resolution and simple experimental setup. TF is the most appropriate technique for studying the ultrafast kinetics of a photochemical reaction because it probes the excited state dynamics exclusively and is free from the coherent artifact. Therefore, the complementary use of TF and TA provides invaluable information on the molecular dynamics of photochemical reactions.17

In the time-resolved spectroscopy of Ru(II) complexes, they are excited to the 1MLCT state by a near-UV pump pulse. The displaced harmonic oscillator model is widely used for the description of nuclear motions coupled to an electronic transition in large molecules. Within this model, the potential energy surface (PES) of the 1MLCT state has the same shape but it is displaced from that of the S0 state along vibrational coordinates. A Huang–Rhys factor $S = d^2 = d^2 m \omega_0^2 / 2 \hbar$, where $d$ is the dimensionless vibrational displacement, $m$ is the reduced mass, and $\omega_0$ is the vibrational frequency, represents the coupling strength between a vibrational mode and the electronic transition to the 1MLCT state. If the pulse duration of the pump is short enough and $S$ is not zero, the population and holes generated in the excited (1MLCT) and ground (S0) states, respectively, behave like wave packets (Fig. 1b). Within the displaced harmonic oscillator model, both wave packets

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generated in the S₀ and ¹MLCT states reflect the initial nuclear motion of the excited Ru(n) complex because they originate from the same vibronic coupling. Therefore, it is possible to predict the coherent nuclear motion right after the photoexcitation by monitoring the wave packet oscillations in the ground state bleach (GSB) band of TA.

Since direct observation of the wave packet oscillation in the ¹MLCT state is not possible due to the ultrafast ISC of [Ru(bpy)₃]²⁺, the property of GSB is useful to investigate the excited-state dynamics of a Ru(n) complex.

We have recently reported that coherent nuclear motions coupled strongly to an ultrafast chemical reaction undergo vibrational decoherence and vibrational coordinate transformation in the course of the reaction. That is, the amplitude, phase, and frequency of the nuclear motions associated with the ultrafast process change as the reaction propagates, and nuclear coherences are lost. The photoinitiated vibrational coherences may be attenuated by dephasing by slow stochastic processes, wave packet broadening by the propagation on an anharmonic PES, and vibrational mode mixing between the reactant and the product. Thus, the vibrational coherence observed in the product state should contain the dynamic information about the ultrafast reaction, and the reaction dynamics can be deduced by analyzing the decoherence mechanism of the wave packet. The vibrational coherence of the product (³MLCT) state for the ultrafast ISC can be monitored through an excited-state absorption (ESA) band of the ³MLCT state. Comparing the CVS of ³MLCT via ESA and that of ¹MLCT via GSB reveals two significant nuclear motions associated with the ISC dynamics. Herein, the correlation between the nuclear motion and the ultrafast ISC of [Ru(bpy)₃]²⁺ is investigated by analyzing the coherent vibrational spectrum (CVS), which is the Fourier transform of the measured wave packet oscillations following the photoexcitation of ¹MLCT. The precise measurement of the ISC times of four Ru(n) complexes, [Ru(bpy)₃]²⁺ and its three structural analogues, by TF supports the role of coherent nuclear motion in the ultrafast ISC.

Experimental

Sample preparation

Four Ru(n) complexes were prepared to investigate the ligand-structure dependence in the ultrafast ISC of Ru(n) complexes. [Ru(bpy)₃]²⁺, tris(2,2'-bipyrazine)ruthenium(II) ([Ru(bpz)₃]²⁺), and tris(1,10-phenanthroline)ruthenium(II) ([Ru(phen)₃]²⁺) were purchased from Sigma-Aldrich and used without further purification. Tris(2,2',2'-tripyridyl)ruthenium(II) ([Ru(tpy)₂]²⁺) was purchased from Medigen Inc. and used without further purification. The counter ions of [Ru(bpy)₃]²⁺, [Ru(phen)₃]²⁺ and [Ru(tpy)₂]²⁺ are Cl⁻, while that of [Ru(bpz)₃]²⁺ is PF₆⁻. The Ru(n) complexes were dissolved in a sufficient amount of deionized water to reach an absorbance of 0.2 at 415 nm using a 100 µm thick sample cuvette. The absorbance was 0.1 for [Ru(bpz)₃]²⁺ due to its low solubility. The samples were placed in either a wire-guided cell (TA) or a quartz flow-cell (TF) and continuously circulated using a gear pump during the experiment. The wire-guided cell was in an acrylic box to minimize evaporation of the samples. The use of a wire-guided cell removes the contribution of pump scattering from the cell walls and enabled the sensitive detection of the ESA from ³MLCT.

Time-resolved spectroscopy

A home-built cavity-dumped Kerr-lens mode-locked Ti:sapphire laser was used as a fundamental light source. The center wavelength was set to 830 nm for both TA and TF experiments.
The pulse energy, pulse duration, and repetition rate of the laser output were 35 nJ, 14 fs, and 72 kHz, respectively. For TA, the fundamental output was focused on a 50 μm thick β-barium borate (BBO) crystal to generate the pump pulses at 415 nm with a pulse energy of 1.5 nJ and a pulse duration of 15 fs. A 100 μm thick BBO crystal was used to generate 23 fs long pump pulses for TF. Group velocity dispersions (GVDs) of both pump and fundamental beams were compensated by the combination of a pair of negative GVD mirrors and a pair of wedge-prisms. It has been reported that the fraction of solvated electrons increases with the excitation energy by the multi-photon effect. We checked that the transient absorption ratio between the 1MLCT-GSB band (left, Fig. 2a) and an ESA band at 800 nm (right, Fig. 2a) is constant in the excitation energy range from 1.3 μJ to 25 μJ (see ESI 1† for more details). Therefore, under the CVS measurement conditions with an excitation energy of 10 μJ cm\(^{-2}\), the multiphoton effect should be negligible, and the ESA band can be assigned as 3MLCT-ESA.

For TA, small fractions of the pump and fundamental beams that reflected off the wedge prisms were used as the probe beams. The probe beam was detected by a photodiode after a 415 (830) nm short-pass filter for the GSB (ESA) measurement. The time resolution of the ESA measurement was estimated from the sum-frequency generation (SFG) signal between the pump (415 nm) and probe (830 nm) pulses in a 50 μm thick BBO crystal, and its width was 25 fs of the full width at half maximum (FWHM) (red dashed line in Fig. 1c). The time delay between the pump and probe pulses was controlled using a motorized stage (XMS-100, Newport) and a motion controller (XPS, Newport). The TA spectrum at around 415 nm (left, Fig. 2a) follows the absorption spectra of the compounds closely, which indicates that they indeed arise from the GSB. It has been reported that the fraction of solvated electrons increases with the excitation energy by the multi-photon effect.26 We checked that the transient absorption ratio between the 1MLCT-GSB band (left, Fig. 2a) and an ESA band at 800 nm (right, Fig. 2a) is constant in the excitation energy range from 1.3 μJ to 25 μJ (see ESI 1† for more details). Therefore, under the CVS measurement conditions with an excitation energy of 10 μJ cm\(^{-2}\), the multiphoton effect should be negligible, and the ESA band can be assigned as 3MLCT-ESA.

The representative ESA spectra at 500 fs and 10 ps are the same. This strongly suggests that the dynamic processes occurring to form the 3MLCT state are complete well before 500 fs, and that the TA spectrum in the near IR region represents the ESA of the lowest 3MLCT state of [Ru(bpy)\(_3\)]\(^{2+}\). It is difficult to measure the CVS\(_x\) of [Ru(bpy)\(_3\)]\(^{2+}\) because of the weak transient absorption of the ESA band, which is about 15 times smaller than that of the GSB band (Fig. 2a), as well as the maximum wave-packet oscillation-amplitude of the band, which is about 0.5% of the maximum ESA amplitude at 800 nm (Fig. S5, ESI†). In order to clearly resolve the weak oscillating feature, we employed a fast-scan data acquisition scheme to minimize the effect of slow (<50 Hz) mechanical fluctuations. In this scheme, the time-delay and TA signal are simultaneously recorded while the translational stage is moving continuously. Finally, we were...
able to measure the wave packet oscillation upon 3MLCT with a reliable data quality [see Fig. S6, ESI † for details].

The apparatus for the fluorescence up-conversion experiment has been described elsewhere.27 Briefly, the pump beam was focused on the sample and its fluorescence was collected by a reflective Cassegrain microscope objective lens. The collected fluorescence and the fundamental beams were focused on a 100 µm thick BBO crystal to generate the SFG signal, which was detected by a photomultiplier tube and a monochromator (SP300, Princeton Instruments). The time resolution of the TF apparatus estimated by using the up-converted solvent Raman apparatus is 60 fs (FWHM, black dashed line in Fig. 1c). Fig. 1c shows the time-traces of TF and 3MLCT-ESA of [Ru(bpy)3]2+.27 The decay and rise of the 1MLCT fluorescence and 3MLCT-ESA with similar time constants support the feasibility of the detection scheme illustrated in Fig. 1b. A slow (250 fs) rise component in the ESA arises from the solvation-induced charge localization.6 The population and solvation components in the time profiles of GSB and ESA were removed via nonlinear least-square fitting for the wave packet analysis.

Quantum mechanical calculation

The LANL2 effective core potential with a double-ζ-quality basis-set (LANL2DZ) was employed for Ru and the 6-31G* basis set was used for the other atoms. The exchange–correlation functional used was mPW1PW91.28,29 The vibrational frequencies were calculated using the density functional theory (DFT) method without applying symmetrization to avoid degeneracy. For the time-dependent DFT calculations, the lowest-lying singlet state with a relevant oscillator strength was chosen as the 1MLCT state, while the highest triplet state below the 3MLCT state with a similar transition character was chosen as the 3MLCT state. All calculations were performed using the Gaussian 09 software.30

The CVS acquired at the GSB band can be predicted by calculating the vibrational displacements $d_i$ between the equilibrium geometries of the S0 and 1MLCT states.19 The procedure of the numerical calculation of CVS has been described elsewhere22 and in ESI 3.1 Briefly, the PES of each Ru(n) complex around the Franck–Condon geometry was calculated with respect to the vibrational modes below 750 cm$^{-1}$ in the ground state. To propagate all vibrational modes consistently, the propagation parameter of each vibrational mode was set to $\delta / (\nu_i)^{-1/2}$. The energy minimum of each mode in the 3MLCT state was calculated assuming that the PES along the mode is quadratic.

Results

Coherent nuclear wave packet of Ru(n) complexes

Fig. 2b shows the oscillation patterns of the GSB (black) and ESA (red) of [Ru(bpy)3]2+.27 The dashed lines in the data are the fitting results obtained using the linear-prediction singular value decomposition (LPSVD) method.21 The Fourier transforms of the TA oscillations at 1MLCT-GSB (CVS$_s$) and 3MLCT-ESA (CVS$_t$) are depicted in Fig. 2c. The vibrational peaks of CVS$_s$ at 122, 249, 276, 337, 378 and 669 cm$^{-1}$ have been observed previously in the resonance Raman study of [Ru(bpy)$_3$]2+ (Table S1, ESI†).32–34 Interestingly, CVS$_t$ is quite different from CVS$_s$. Most remarkably, several major peaks observed at 163, 276, 337 and 669 cm$^{-1}$ in CVS$_t$ are missing in CVS$_s$. There are two reasons why CVS$_t$ does not show the four peaks. One is that the vibrational coherences of the modes generated by photoexcitation are broken down by the ultrafast ISC. In this case, the coherent vibrational peaks showing a notable disparity between CVS$_s$ and CVS$_t$ should be related to the ultrafast ISC. The other is the weak vibronic coupling between the 3MLCT state and an upper state resonant with the probe wavelength about the four vibrational modes.

If the disappearance of the vibrational modes at 163, 276, 337, and 669 cm$^{-1}$ is due to the small vibrational displacements with respect to the ESA band, the corresponding peaks should not be detected in the resonant Raman spectrum of the 3MLCT state. Previous studies on [Ru(bpy)$_3$]2+ showed that 337, 378, and 669 cm$^{-1}$ modes exist in the excited-state Raman spectrum.4,35,36 The observations suggest that the coherences of the 337 and 669 cm$^{-1}$ modes may be attenuated by the ultrafast ISC. We recently reported that coherent nuclear motions coupled strongly to an ultrafast chemical reaction undergo vibrational decoherence and vibrational coordinate transformation in the course of the reaction.17,21

To facilitate the vibrational assignment, the CVS$_t$ of [Ru(bpy)$_3$]2+ was calculated based on DFT and time-dependent DFT calculations as described in the Experimental section. The experimental CVS$_t$ and CVS$_s$ and the calculated CVS$_t$ are displayed in Fig. 2c. The calculated CVS$_t$ yields 9 vibrational modes below 750 cm$^{-1}$ with significant amplitudes, out of 54 normal modes, rendering the vibrational assignment straightforward. The dashed lines in Fig. 2c represent the peak assignments. Symmetries of the vibrational modes were determined by considering the central Ru and six N atoms only. The nuclear motions of the vibrational modes indicated by the three point groups (Oh, D$_3$, and C$_3$) are illustrated in Fig. 2d.

Molecular structure dependence on ultrafast ISC

The molecular structures of the four ligands are depicted in Fig. 3a. The 1MLCT absorption and 3MLCT emission bands of the complexes shift slightly depending on the ligands, but they show nearly the same Stokes shifts (Fig. S1, ESI†). [Ru(bpy)$_3$]2+ possesses a D$_3$ symmetry close to Oh due to the flexibility of its ligand. The molecular configuration of [Ru(bpy)$_3$]2+ is very similar to that of [Ru(tpy)$_3$]2+, except that the carbon atoms at the para-position of pyridine are replaced by nitrogen. The ethylene group between the two pyridine rings in [Ru(phen)$_3$]2+ restricts ring stretching and twisting of the ligand molecules, so that the complex is forced to adopt D$_3$ symmetry. [Ru(tpy)$_3$]2+ has a lower symmetry (C$_3$) than the others. [Ru(tpy)$_3$]2+ shows a lower phosphorescence quantum yield than the other complexes because of the faster nonradiative decay of 3MLCT. Since there is no notable relaxation component within the vibrational...
coherence time, the effect of the lower phosphorescence quantum yield does not have to be considered for studying the ultrafast ISC.

Fig. 3b shows the fluorescence decay times, which are equivalent to the ISC times, of the four Ru(n) complexes measured by TF (Fig. S9, ESI†). The ISC times of [Ru(bpy)3]2+, [Ru(phen)3]2+, and [Ru(tpy)3]2+ are similar (24 fs), while that of [Ru(bpz)3]2+ is slightly faster (18 fs). The distinction of the decay times was reproducible for three independent data sets. The TF signals simulated by the convolution of exponential decay and IRF also demonstrate that the difference is beyond the experimental uncertainty (see ESI 4† for more details). The faster ISC of a Ru(II) complex with the d-orbitals of [Ru(bpy)3]2+ have approximately 276 cm$^{-1}$ mode. The SOC strength, which also supports the notion that the nuclear motions affect the dynamics of ultrafast ISC.

**Discussion**

**Identification of the vibrational modes coupled to the ISC**

To characterize the contribution of the observed vibrational modes to the structural change during the ultrafast ISC, we defined two geometrical parameters:

\[
\Delta R_i = \frac{1}{6} \sum_{j=1}^{6} \Delta R_{i,j} \delta_i (1 - \cos[2\pi \nu_i \tau_{ISC}])
\]

(1)

\[
\Delta \Delta R_i = \frac{1}{6} \sum_{j=1}^{6} \left( \frac{\Delta R_{i,j} \delta_i (1 - \cos[2\pi \nu_i \tau_{ISC}])}{1 - \sum_{j=1}^{6} |\Delta R_{i,j} \delta_i (1 - \cos[2\pi \nu_i \tau_{ISC}])|} \right)^2 .
\]

(2)

Here, i is the index of N atoms around the Ru atom and \(\tau_{ISC} = 24\) fs. The ISC times were obtained by TF (Fig. 1c). \(\nu_i\) and \(\delta_i\) are the frequency and displacement of the i-th vibrational mode, respectively. \(\nu_i\) and \(\delta_i\) were retrieved from the measured CVS$_i$ while the sign of \(\delta_i\) was obtained from the calculated CVS$_i$. Each \(\delta_i\) value was normalized to that of the measured 276 cm$^{-1}$ mode. \(\Delta R_{i,j}\) is the proportion of Ru-to-N-distance change of the j-th N atom for the i-th vibrational mode. \(\Delta R_i\) and \(\Delta \Delta R_i\) reflect the metal–ligand bond length (RML) change and the degree of symmetry breaking from O$_6$ to C$_2$, respectively, by the i-th vibrational mode during the ISC. The calculated parameters are listed in Table 1.

The correlation between the vibronically activated coherent nuclear motion and the ISC rate represents the role of nuclear motion in the ultrafast ISC. Cherghi and coworkers reported the TF of Re[X(CO)$_3$(bpy)] while varying the halogen atom (X). They found that the spin–orbit coupling (SOC) increases with the atomic number of X. However, the ISC rate increases with the metal-halogen stretching frequency rather than the SOC strength, which also supports the notion that the nuclear motions affect the dynamics of ultrafast ISC.

**Interplay between metal–ligand stretching and symmetry breaking for ultrafast ISC**

Metal–ligand stretching has been assumed as a reaction coordinate of the ultrafast ISC for various transition metal complexes. As a Ru(n) complex is excited to the 1MLCT state, the metal–ligand bond weakens because the 1MLCT transition, whose majority character is d–π* transition, decreases the metal–ligand bonding character. That is, the N atoms are pushed away from the metal upon photoexcitation to the 1MLCT state. Assuming that the d-orbitals of [Ru(bpy)3]2+ have approximately O$_6$ symmetry, the six valence electrons occupy the lower-lying t$_{2g}$ orbitals initially, which have a bonding character with the ligand field. When one of the electrons is excited to the π-orbital of the ligand, the molecule loses the metal–ligand bonding character,
which increases $R_{ML}$. As $R_{ML}$ increases, the interaction between d-orbitals of the Ru atom and p-orbitals of N atoms becomes weaker, so that the energy levels of the $t_{2g}$ orbitals approach those of the degenerate d-orbitals. Then, the unpaired electron remaining in the $t_{2g}$ orbital is localized on the Ru atom, and the localization increases SOC owing to the heavy atom effect of the ligands. The former emphasizes the dynamic role of the symmetry breaking rather than static molecular symmetry. The CVSs of the four complexes shows a tendency whereby the number of $C_2$ modes increases when the molecular symmetry is lowered (Fig. S8, ESI†). This emphasizes the role of $C_2$ vibrations in the ultrafast ISC. While photoexcitation to the 3MLCT state moves the ligand along $R_{ML}$, the symmetric stretching motion ($R_{ML}$) is disturbed by the molecular structure of the ligands. The $D_{2d}$-to-$C_2$ symmetry breaking of [Ru(tpy)$_2$]+ is rapid in [Ru(tpy)$_2$]+ due to the tridentate coordination of tripyridine.

Recently, the importance of symmetry breaking in ISC has been reported. Tahara and coworkers also observed a coherent $D_{2d}$-to-$D_2$ symmetry breaking motion of bis(2,9-dimethyl-1,10-phenanthroline)copper(I), [Cu(dmphen)$_2$]+.

The ISC takes place predominantly at the symmetry broken geometry. Cherghi and coworkers observed a solvent dependence in the ultrafast ISC of tetrakis[µ-pyrophosphophito]diplatinate(µ$_2$)-[P$_4$(µ$_2$-P$_2$O$_7$H$_4$)$_8$]+, where the solvation quickly lowering the symmetry results in faster ISC. Further, the contribution of coherent symmetry breaking was also observed in singlet fission systems.

The $C_2$ symmetry of the electronic configuration in the 3MLCT state of [Ru(bpy)$_3$] was observed via time-resolved X-ray absorption spectroscopy. This implies that the propagation of the $C_2$-symmetry breaking coordinate ($S_1$) should increase the 3MLCT character of the transient 3MLCT→MLCT coupled state initiated by $R_{ML}$. In view of the molecular orbital, the splitting of $t_{2g}$ orbitals induced by the symmetry breaking increases the localization character of a d-orbital, as described in Fig. 4a, resulting in the increased heavy atom effect of Ru.

**Spin–orbit coupled state**

Okada and coworkers observed a decay of the weakly fluorescent peak at $>575$ nm, where the contribution of solvation dynamics to the 3MLCT state had already been reported by McCusker and coworkers. They proposed that the weakly
fluorescent spectral feature can be attributed to the mixing of the higher levels in the $^3\text{MLCT}$ state with the $^3\text{MLCT}$ state. We also measured the TF of $[\text{Ru(bpy)}_3]^{2+}$ at 575 and 615 nm (Fig. S9, ESI†). The two emission profiles contain two decay components with the time constants of 330 fs and $>5$ ps, which are much slower than the ISC (24 fs). Since the fraction of the slow components is prominent at a longer wavelength (615 nm), they can be assigned to $^3\text{MLCT}$-phosphorescence.$^7,9$

One interesting point about the sub-ps component is that it appears as a decay in TF, whereas it appears as a rise in $^3\text{MLCT}$-ESA (250 fs rise, Fig. 1c). This indicates an exchange of oscillator strengths of the $^3\text{MLCT}$-emission and $^3\text{MLCT}$-ESA bands by the solvation-driven charge localization, and a partial singlet character of the initially formed $^3\text{MLCT}$ state. This observation is consistent with the argument by Okada and coworkers, and supports the presence of a spin–orbit ($^1\text{MLCT}$–$^3\text{MLCT}$) coupled state during the ISC.

The suggested ISC mechanism with respect to the two reaction coordinates ($R_{\text{ML}}$ and $S_C$) is illustrated by a 2D PES (Fig. 4b) along the $C_2$-symmetry breaking ($S_C$, 337 cm$^{-1}$) and $R_{\text{ML}}$ (669 cm$^{-1}$) modes of $[\text{Ru(bpy)}_3]^{2+}$. An appropriate coupling constant that increases with $R_{\text{ML}}$ and decreases with $S_C$ was applied. As the N atoms move away from the Ru atom, the Ru(n) complex is driven to a spin–orbit coupled state (yellow surface in the 2D PES) having a partial $^3\text{MLCT}$ character. As the $^3\text{MLCT}$ character of the spin–orbit coupled state increases with $S_C$, the Ru(n) complex relaxes to the $^3\text{MLCT}$ state to complete the ISC. In the Ru(n) complexes with lower symmetry ([Ru(tpy)]$^{2+}$ and [Ru(phen)]$^{2+}$), the ISC is accelerated due to their faster symmetry breaking motion.

Conclusions

We provide the rationale behind the ultrafast and efficient ISC of Ru(n) complexes using time-resolved spectroscopies (TA and TF) with ultimate time-resolution and model quantum chemical calculations. By comparing the vibrational coherence in the reactant and product PESs to those obtained via quantum mechanical calculations, we found that two types of nuclear motions, which are metal–ligand stretching ($R_{\text{ML}}$) and $C_2$ symmetry breaking ($S_C$), are strongly coupled to the ultrafast ISC. The photoexcitation-induced repulsion force between the Ru atom and ligands excites the vibrational modes involving $R_{\text{ML}}$. While $R_{\text{ML}}$ quickly drives the Ru(n) complex to a spin–orbit coupled state, the symmetry breaking inhibits the return to the $^3\text{MLCT}$ state. The faster ISC rates of the Ru(n) complexes with lower symmetry observed in TF support the contribution of the symmetry breaking. The suggested mechanism well explains the high efficiency of the ISC. We expect that the mechanism may be applicable generally for other transition metal complexes with ultrafast ISC, and provides appropriate insight for designing an appropriate transition metal complex.

Conflicts of interest

There are no conflicts to declare.

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