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Coherent control of long-range photoinduced electron transfer by stimulated X-ray Raman processes

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We show that X-ray pulses resonant with selected core transitions can manipulate electron transfer (ET) in molecules with ultrafast and atomic selectivity. We present possible protocols for coherently controlling ET dynamics in donor–bridge–acceptor (DBA) systems by stimulated X-ray resonant Raman processes involving various transitions between the D, B, and A sites. Simulations presented for a Ru(II)–Co(III) model complex demonstrate how the shapes, phases and amplitudes of the X-ray pulses can be optimized to create charge on demand at selected atoms, by opening up otherwise blocked ET pathways.

electron transfer | coherent control | ultrafast X-ray spectroscopy | stimulated Raman

Long-range electron transfer (ET) over tens of angstroms in molecular assemblies plays an essential role in many biological processes, artificial light-harvesting schemes, and sensor applications (1–7). Using lasers to precisely control ET pathways and rates has been a long-term goal of chemists (8). The manner in which infrared light can excite molecular vibrations to affect ET in donor–bridge–acceptor (DBA) systems has been studied theoretically (9, 10) and experimentally (11–14).

The rapid development of bright X-ray lasers and high harmonic sources has opened up new opportunities for X-ray spectroscopy (15). We have recently demonstrated that stimulated X-ray Raman spectroscopy (16, 17) with broadband X-ray pulses can reveal the time-evolving oxidation states of various species in the long-range ET process of the protein azurin (18). Here we show that by coupling to core-excited states, resonant X-ray pulses can precisely target either the donor, bridge, or the acceptor site in an ET process by altering the valence electronic states in its vicinity by triggering the bridge-to-acceptor (BA), the donor-to-bridge (DB), or the bridge-to-bridge (BB) ET transfer. We show how the ET pathways in a model DBA system ($[(\text{CN})_4\text{Ru}^{\text{II}}(\text{tpphz})\text{Co}^{\text{III}}(\text{CN})_4]^{3-}$) can be coherently manipulated by X-ray pulses resonant with the acceptor.

Application is made to a Ru–Co light-harvesting complex (shown in Fig. 1 *A* and *B*) where an electron is transferred from the donor Ru^{II} to the acceptor Co^{III} to create $\text{Ru}^{\text{III}}/\text{Co}^{\text{II}}$. X-ray pulses can create valence excitations via a Raman process (19), thus altering the occupied molecular orbitals (MOs). We shall focus on the BA ET coherent control scheme illustrated in Fig. 2*A*. In a stimulated Raman process a core hole created by the X-ray pulse on the acceptor is instantaneously filled by a valence electron on the bridge, resulting in a B→A ET. Such an ET process is analogous to the valence-to-core X-ray spontaneous emission observed in transition metal complexes with ligand-to-metal charge transfer (20).

Effective Model Hamiltonian for the Ru–Co Complex

Long-range ET in the bimetallic Ru–Co complex $[(\text{bpy})_2^1\text{Ru}^{\text{II}}(\text{tpphz})^1\text{Co}^{\text{III}}(\text{bpy})_2]^{5+}$ (low spin in the ground state) was investigated recently by transient optical absorption, X-ray absorption, X-ray diffuse scattering, and X-ray emission (21–23). This complex has been proposed for artificial light-harvesting applications. The DB ET step is very fast (<50 fs) but the BA ET is much slower (picoseconds). The system ends up in a $[(\text{bpy})_2^2\text{Ru}^{\text{III}}(\text{tpphz})^4\text{Co}^{\text{I}}(\text{bpy})_2]^{5+}$ high-spin charge-separated state. Our goal is to accelerate the BA step by a stimulated X-ray Raman process. To reduce the computational cost

while keeping the essential ET physics of the original complex, we have studied the simplified model complex $[(\text{CN})_4\text{Ru}^{\text{II}}(\text{tpphz})\text{Co}^{\text{III}}(\text{CN})_4]^{3-}$ (Fig. 1 *A* and *B*) where the bpy ligands are replaced with $(\text{CN})^-$. This eliminates the complicated spin crossover transition at the Co center (23), because the strong ligands $(\text{CN})^-$ favor the low-spin state.

The relevant ET parameters were obtained from electronic structure calculations. Because the Ru and Co centers are far apart, electronic structure calculations can be carried out for smaller fragments $[(\text{CN})_4\text{Ru}^{\text{II}}(\text{tpphz})]^{2-}$ and $[(\text{tpphz})\text{Co}^{\text{III}}(\text{CN})_4]^{2-}$ (the tpphz ligand is negatively charged). Computational details are given in *Materials and Methods*.

We model the ET in this complex using two frontier orbitals on each of the donor, the bridge, and the acceptor site; these are the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Neglecting spin, each site has four possible states: the ground state $|0\rangle$, where the HOMO is occupied and LUMO is not; the negatively charged state $c_m^\dagger|0\rangle$ (both orbitals are occupied); the positive charged hole state $v_m^\dagger|0\rangle$ (both orbitals are unoccupied); and a single electron–hole pair (Frenkel exciton) state $c_m^\dagger v_m^\dagger|0\rangle$, where the HOMO electron is moved to the LUMO. The operators c_m^\dagger (c_m) and v_n^\dagger (v_n) create (annihilate) an electron on site m and a hole on site n , respectively. They satisfy the Fermi commutation relations $\{c_m, c_n^\dagger\} = \delta_{mn}$, $\{v_m, v_n^\dagger\} = \delta_{mn}$. Out of all of the orbitals only three states *D*, *B*, and *A* are relevant to the ET process and are described below. Whereas the DB coupling is strong and the BA coupling is weak, we neglect the direct donor–acceptor coupling.

Initial photoexcitation creates an electron–hole pair on the donor $|D\rangle = c_d^\dagger v_d^\dagger|0\rangle$. We assume that there are no electronic coherences and only donor population is generated. This can be achieved by, e.g., resonant optical or X-ray Raman pulse that is tuned to the vicinity of the Ru atom in the donor molecule. The electron then hops from orbital *d* to orbital *b* due to the strong *D/B* coupling, thereby creating

Significance

Electron transfer is ubiquitous in chemical reactions and many biophysical processes such as respiration and photosynthesis. In this work, we show how broadband X-ray pulses can be used to change the local electronic structures of donor–bridge–acceptor (DBA) molecular systems, thus enabling and controlling electron transfer between designated sites in the molecule. An X-ray-stimulated Raman process can control electron transfer with atomic specificity and ultrafast timescale. With an appropriate X-ray pulse setting, electron pathways can be selectively enhanced. The control can be implemented at the donor, bridge, or acceptor sites in a DBA system.

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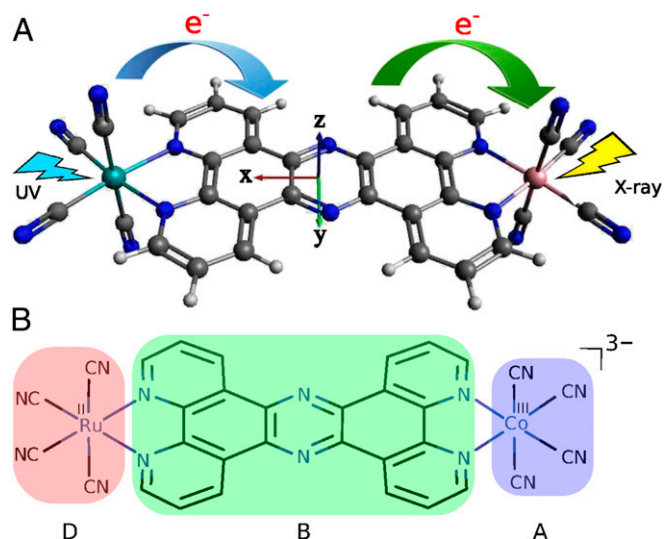


Fig. 1. (A) Three-dimensional molecular structure of the Ru-Co complex $[(\text{CN})_4\text{Ru}^{\text{II}}(\text{tpphz})\text{Co}^{\text{III}}(\text{CN})_4]^{3-}$, which is a simplified model of that studied in refs. 21–23. The D→B and B→A ET steps are represented by the blue and green arrows, respectively. The B→A ET step is aided by an X-ray pulse shot at the Co center. The coordinate axes are also shown. Color code: Ru, light blue; Co, pink; N, deep blue; C, black; H, light gray. (B) Chemical structure of the Ru-Co complex. The donor, bridge, and acceptor fragments are labeled and shaded with different colors.

state $|B\rangle = c_d c_b^\dagger |D\rangle \equiv c_b^\dagger v_d^\dagger |0\rangle$. The ET is completed when an electron hops from the bridge to acceptor due to the weak B/A coupling creating the final state: $|A\rangle = c_b c_a^\dagger |B\rangle \equiv c_a^\dagger v_d^\dagger |0\rangle$. We had calculated the matrix elements of the Hamiltonian in *SI Appendix, Eq. S1* in this diabatic basis $|D\rangle, |B\rangle, |A\rangle$.

Enabling Electron Transfer Pathways by an X-Ray Raman Process

In the absence of the X-ray pulse the ET process is described by a generalized Redfield master equation:

$$\dot{\rho} = -\mathcal{L}[\rho], \quad [1]$$

where the Liouvillian $\mathcal{L}[\rho] = i/\hbar[H_S, \rho] - K\rho$ is a rank 9 tensor in the space of D, B, A states (three populations and six coherences). Here $H_S = H_{DBA} + H_{hop}$ is a 3×3 Hamiltonian matrix which includes the DBA diagonal part H_{DBA} (*SI Appendix, Eq. S3*) plus the electron hopping off-diagonal part H_{hop} (*SI Appendix, Eq. S4*), and K denotes 9×9 Redfield ET rate matrix (*SI Appendix, Eqs. S6–S8*). The ET includes several pathways that involve both population hopping (sequential) as well as electronic coherences between adiabatic states (superexchange) (24).

The time evolution of the acceptor population can be observed by various spectroscopic measurements including fluorescence and transient absorption. Using Eq. 1 we had calculated acceptor population. After photoexcitation of the excited state population of the donor state D at time $t = 0$ in the diabatic basis, the electron wave packet goes through various states including the population and coherences between states D, B, A , and finally populates the acceptor state A at time t given by

$$P_A^{(0)}(t) = i\hbar \mathcal{G}_{AA,DD}(t), \quad [2]$$

where the zero superscript indicates that this is a reference calculation in the absence of the X-ray. $\mathcal{G}_{AA,DD}(t) = [e^{-\mathcal{L}t}]_{AA,DD}$ is the Liouville space Green's function matrix element that represents electron transfer dynamics between donor and acceptor populations and is given by *SI Appendix, Eq. S10*.

We now introduce an X-ray pulse at time t_1 after the photoexcitation. This pulse can promote an electron from the core orbital to the valence orbital of the acceptor, and the core hole is simultaneously filled by an electron from the bridge valence orbital. In this X-ray Raman process shown in Fig. 2A, the electron is transferred from orbital b to a via an inelastic process or from a to a and b to b via an elastic process. The ET can be controlled by an X-ray Raman excitation as long as the lifetime of the valence excited state created by the X-ray Raman process is comparable to or longer than the ET timescale. Interaction of the molecule with light is described by a dipole matter–field coupling in *SI Appendix, Eq. S13*. By placing a core electron on a valence orbital of the acceptor (orbital a) and filling this core hole with the valence electron from the bridge (orbital b), the pulse enables electrons to tunnel through the bridge and reach the acceptor. We had calculated the acceptor population induced by the X-ray pulse and its variation with t_2 (the time delay between the X-ray pulse arrival and observation time) and t_1 (the X-ray pulse delay relative to the initial photoexcitation). The ET dynamics consists of three steps (see the diagram in *SI Appendix, Fig. S1*). During t_1 (before the X-ray pulse) the system evolves according to the Redfield master equation (Eq. 1) and is promoted from population ρ_{DD} to some superposition of bridge and acceptor states ρ_{mn} , $m, n = A, B, D$. The second step is the evolution during the X-ray pulse. We use perturbation theory in the X-ray field–matter interaction with the diagram in *SI Appendix, Fig. S1*. In the first-order perturbation theory with respect to X-ray

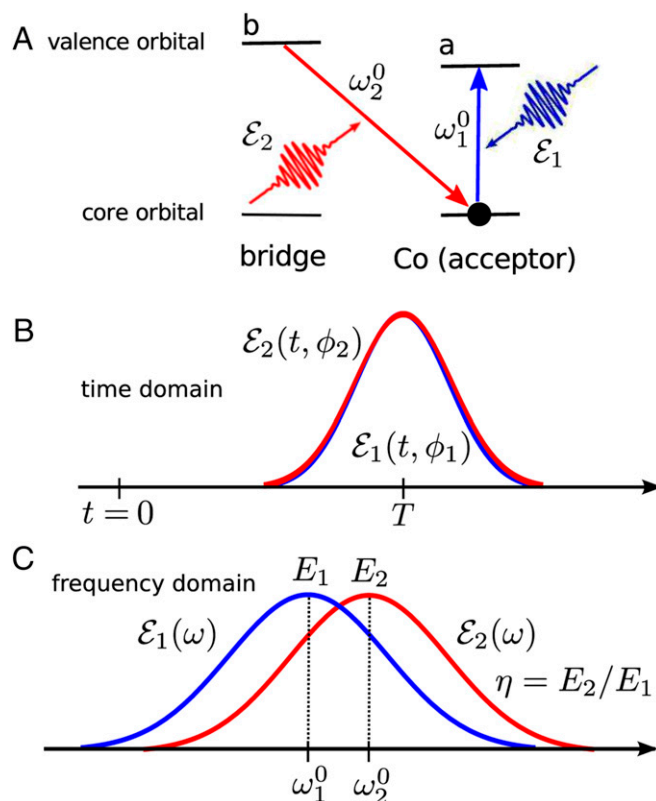


Fig. 2. (A) The acceptor control stimulated X-ray Raman process invoked by two X-ray pulses, of which the carrier frequencies ω_1^0 are resonant with the cobalt (acceptor) local core excitation and ω_2^0 is resonant with the bridge to cobalt emission transition, respectively. (B) The two pulses \mathcal{E}_1 (blue) and \mathcal{E}_2 (red) in the time domain with their phases ϕ_1 and ϕ_2 , respectively. See *SI Appendix, Eq. S14* for detailed expressions. (C) The two pulses in the frequency domain with the carrier frequencies $\omega_1^0 = 7,720.65$ eV and $\omega_2^0 = 7,721.53$ eV, bandwidths $\sigma_1 = \sigma_2 = 3$ eV, and the maximum field intensities $E_1 = E_2 = 5 \times 10^{11}$ V/cm. The amplitude ratio η is defined as E_2/E_1 . See *SI Appendix, Eq. S15* for expressions.

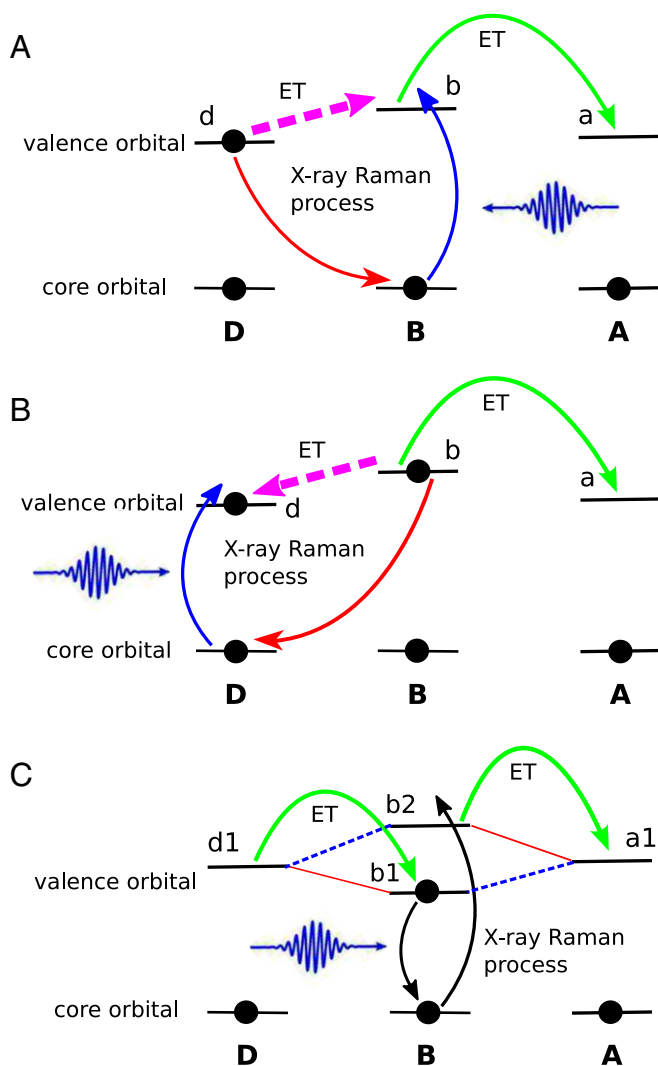


Fig. 5. The DB and BB coherent control schemes. ET processes with X-ray control are represented by magenta dashed arrows. (A) The DB control scheme which facilitates the $D \rightarrow B \rightarrow A$ ET process (core excitation on the bridge). (B) The DB control scheme which hinders the $D \rightarrow B \rightarrow A$ ET process (core excitation on the donor). (C) The BB control scheme. The red solid lines represent the strong interactions between orbitals, and blue dashed lines represent weak interactions. Relevant molecular orbitals are also labeled. Orbitals b_1 and b_2 can be on the same or different bridges.

used to coherently control the ET process in a DBA system. Alternatively, one can induce ET by an ionization with an off-resonant X-ray pulse. However, this may cause the system to decay through multiple channels, which complicates the process. Pulse delays, shapes, phases, and intensities can be tuned to enhance the ET. This coherent control tool for ET processes can be used for processing of functional electronic materials (27), disease diagnostics (28), and X-ray sterilization (29).

Infrared (IR) pulses have been used recently to excite selected vibrational modes after triggering ET by UV pulses (11, 12). In the superexchange ET mechanism, vibrations can affect the interferences between various ET pathways, so that some ET pathways could be totally switched off (9). Similar experimental observations have been reported, but for the sequential ET mechanisms (12). IR pulses only weakly perturb the electronic structure and the molecular geometry, which facilitates their application for biomolecular ET coherent control.

The X-ray pulses used here can substantially alter the electronic structure of the bridge, whereas vibrations generated by IR pulses only change phases of different ET pathways and therefore affect their interferences (9–12, 30, 31). UV-vis pulses may access the same valence excited states prepared by an X-ray Raman process. However, UV-vis excitations lack the site selectivity of X-rays. In addition, short X-ray pulses can capture ultrafast ET dynamics that goes beyond the reach of UV pulses.

Coherent control has been successfully used to manipulate the relative strength of competing optical processes (32) but the major goal has always been the steering of chemical reactions in desired directions by properly shaped and timed optical pulses (33–39). The X-ray control schemes presented here offer opportunities for manipulating and monitoring chemical reactions which involve an electron transfer step. These could provide new synthetic routes for molecules and materials. X-ray pulses allow for a molecular level control with atomic selectivity and high temporal resolution which is not possible by optical techniques (40). Our earlier studies had demonstrated that stimulated X-ray Raman spectroscopy can be used to elucidate the catalytic reaction mechanism of the cytochrome P450 complex (41) by probing the oxidation state history of reactants, products, and various intermediates. By combining narrowband and broadband pulses, the hybrid X-ray Raman technique (42) [previously denoted as attosecond stimulated X-ray Raman spectroscopy (43)] offers a unique combination of spectral and temporal resolution, making it possible to take snapshots of ultrafast chemical reaction dynamics, which is not possible by conventional IR and optical techniques. Raman lineshapes are not affected by the core lifetime and are thus much narrower than those of X-ray absorption, which significantly enhances their resolution and selectivity. Going beyond the detection of reaction intermediates, with the control schemes proposed here one can selectively enhance or suppress ET steps, thereby facilitating or hindering selected chemical reaction steps, and then probe the reacting system by additional sequences of X-ray pulses (18). These offer a class of applications to X-ray free-electron laser and high harmonic light sources.

Finally, we note that competing decay channels with the resonant X-ray Raman of a core-hole state, such as Auger electron emission, must be taken into account. Auger processes are dominant in the core-hole decay processes of light atoms, but are less important for heavy atoms. For Co, the atomic spontaneous K-edge X-ray fluorescence and Auger yields are 0.373 and 0.627, respectively (44). However, unlike the abovementioned spontaneous processes, in stimulated X-ray Raman processes intense pulses can be used to enhance the Raman cross-section and suppress the Auger decay channels. For example, it was observed that the charge-transfer excitations in NiO were enhanced by resonant X-ray Raman scattering (45). In this study we focused on the acceptor control scheme. However, we can also use the same strategy to control the electron transfer via the donor, Ru atom. For Ru, the spontaneous K-edge Auger decay yield is only 0.206 (44). Considering many heavy metal complexes used as photosensitizers in solar cell applications, it is safe to neglect the effect of Auger decay when applying our proposed X-ray electron transfer control scheme to these systems. For example, in solid-state systems, the saturation of the stimulated emission on the Si (100) surfaces with X-ray free-electron laser was observed (46), which indicates the Auger decay channels have been suppressed. It was demonstrated that the stimulated X-ray Raman in CO molecules can compete well with the Auger processes (47, 48).

Materials and Methods

The geometry of the Ru–Co model complex was optimized using the Becke three-parameter and Lee–Yang–Parr hybrid (B3LYP) exchange-correlation energy functional (49, 50). The Ru atom was described by the Stuttgart/Dresden relativistic pseudopotential and its corresponding basis set (51). The Co atom was described by the improved default triple-zeta valence basis set with small polarization (def2-TZVP) (52), and the 6–31G* basis set (53) was used for other

light atoms. Solvation effect was considered by using the polarized continuum model (54–56) with the solvent acetonitrile. Valence excited-state calculations were done at the time-dependent density functional theory (TDDFT) level of theory using the Coulomb-attenuating method version of the B3LYP functional (CAM-B3LYP) (57). All geometry optimization and valence excitation calculations were done with the quantum chemistry program package Gaussian (58). To compare the transition dipoles of charge transfer and localized core excitation around the Co center, the Co 1s core excitation calculations were done with the quantum chemistry program package NWChem (59) at the TDDFT/Tamm–Dancoff approximation (60) level of theory

using the exchange-correlation functional CAM-B3LYP. The def2-TZVP basis set was used for Co and N, and the 6–31G* basis set was used for other atoms.

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