Monitoring aromatic ring-currents in Mg-porphyrin by time-resolved circular dichroism†

Yeonsig Nam,‡a Jérémy R. Rouxel,‡b Jin Yong Lee,‡ab and Shaul Mukamelab†

Time-resolved circular dichroism signals (TRCD) in the X-ray regime can directly probe the magnitude and the direction of ring currents in molecules. The electronic ring currents in Mg-porphyrin, generated by a coherent superposition of electronic states induced by a circularly polarized UV pulse, are tracked by a time-delayed circularly polarized attosecond X-ray pulse. The signals are calculated using the minimal coupling Hamiltonian, which directly makes use of transition current densities. The TRCD signals obtained from the left and right circularly polarized light pump have opposite signs, revealing the direction of the ring current. Molecular aromaticity and its role in photochemical reactions such as ring opening or closure can be studied using this technique.

Introduction

Exploring and controlling the dynamics of aromatic ring currents has received great attention for decades. Ring currents have been used to quantify the aromaticity of ring molecules. Their magnitude has been compared with the nucleus-independent chemical shift or diamagnetic susceptibility exaltation value and used to determine the aromaticity of molecules. Aromatic ring currents and their induced magnetic fields have been recently used for nanodevices, such as molecular magnets, quantum devices, and photo-switches, and to generate ultrafast magnetic field pulses.

An aromatic ring current is generated by a magnetic field perpendicular to the molecular plane due to the delocalized π electrons. A more effective way to create ring currents using circularly polarized light was suggested by the Manz group: the chirality of the laser pulse is transferred to the molecular system, inducing a clockwise or counterclockwise ring current. This current is much stronger than what can be induced by an external magnetic field with present technology. For example, in a Mg-porphyrin molecule, the net ring current induced by a circularly polarized laser π-pulse corresponds to one induced by a magnetic field of 8048 T, which is 100 times higher than the maximum permanent magnetic field currently available.

So far, monitoring the ultrafast circular coherent dynamics of ring currents in real time has been a challenge. Many experimental and computational approaches have been developed for the indirect measurement of aromatic ring currents: nuclear magnetic shielding, current density, and bond order, and polarizability analysis.

Several studies have attempted the direct observation of aromatic ring currents. Yuan et al. measured molecular angular and energy-resolved photoelectron spectra by using time-delayed X-ray pulses. Neufield et al. proposed that high-harmonic generation in the presence of a ring current causes the emission of elliptically polarized harmonics. Koksal et al. showed the possible manipulation of a ring current and induced magnetic field by changing the frequency and the orbital angular momentum of the light beams. However, both photoelectron circular dichroism and high-harmonic generation require elaborate experimental setups and are hard to interpret. Here, we discuss the use of time-resolved X-ray circular dichroism (TRCD) to directly measure the fast electronic motions associated with ring currents.

Attosecond X-ray pulses provide real-time and real-space resolution of electronic structure, enabling the creation of molecular movies. The high-spatial resolution of X-rays can reveal local properties in delocalized aromatic systems.

CD spectra are usually weak signals on top of a large achiral background. Transient CD signals are usually measured on top of a static background. The use of X-ray excitation from valence excited states allows one to generate transitions below the pre-edge region, a frequency regime with no or low static background. The absence of a static achiral background induces a large asymmetry.
ratio (>100%, eqn (10) below) compared to standard CD
techniques (a few % or less).

In this paper, we study the use of time-resolved circular
dichroism (TRCD) signals to probe ring currents: a UV pump
pulse induces a ring current and a delayed X-ray probe measures
the induced dichroic signal. The magnitude and the sign of the
signal reveal the amplitude and the direction of the ring current.
We employ the minimal coupling Hamiltonian for the light-
matter interaction, which expresses the signal directly in terms
of transition current densities. Simulations are carried out for
Mg-porphyrin where the X-ray probe is tuned to the nitrogen
K-edge at 409 eV or to the magnesium K-edge at 1327 eV.

Theory and computational details

The time-resolved CD signal

The minimal coupling Hamiltonian for the resonant radiation-
matter interaction is

\[ H_{\text{int}} = -\int dr (r) \cdot A(r, t) \]  

(1)

where \( A(r, t) \) is the electromagnetic vector potential of the
incoming field and \( j(r) \) is the current-density operator:

\[ j(r) = \frac{e\hbar}{2m} [\psi^*(r) \nabla \psi(r) - (\nabla \psi^*(r)) \psi(r)] \]  

(2)

where \( \psi^*(r) \) and \( \psi(r) \) are the electron field creation and anni-
hilation operators at position \( r \).

The time-dependent density matrix after two interactions with
the pump pulse (Fig. S2, ESI†) is given by

\[ \rho_{\text{ee}'}(T) = \langle \text{ee'} | \rho(T) | \text{ee'} \rangle \]

\[ = \langle \text{ee'} \rangle \langle \psi^*(r) \nabla \psi(r) - (\nabla \psi^*(r)) \psi(r) \rangle \]

(3)

where \( \psi^*(r) \) and \( \psi(r) \) are the electron field creation and anni-
hilation operators at position \( r \).

In the impulsive limit, the density matrix at waiting time \( T \)
becomes:

\[ \rho_{\text{ee}'}(T) = \frac{1}{2\pi} \int d\omega_1 d\omega_2 \langle \psi^*(r) \nabla \psi(r) - (\nabla \psi^*(r)) \psi(r) \rangle \]

\[ \times \left[ j_{\text{ee}'}(k_{\text{pu}}) \cdot e_{\text{pu}}^* \cdot j_\text{ee'}(-k_{\text{pu}}) \cdot e_{\text{pu}} e^{i(\omega_2 - \omega_1)T} \right. \]

\[ \times \left. \left( (\omega_1 - \omega_2 - \omega_{\text{ee}'} + i\Gamma_{\text{ee}'})(\omega_1 - \omega_{\text{ee}'} + i\Gamma_{\text{ee}'}) \right) \right] \]

\[ + j_{\text{ee}'}(-k_{\text{pu}}) \cdot e_{\text{pu}} \cdot j_{\text{ee}'}(k_{\text{pu}}) \cdot e_{\text{pu}} e^{-i(\omega_2 - \omega_1)T} \]

\[ \left. \left( (\omega_1 + \omega_2 - \omega_{\text{ee}'} + i\Gamma_{\text{ee}'})(\omega_1 + \omega_{\text{ee}'} + i\Gamma_{\text{ee}'}) \right) \right] \]  

(4)

where \( e \) are the electric field polarization vectors, which can be
left or right polarization. \( \omega_1 \) and \( \omega_2 \) run over the bandwidth
of the UV pump, which is set on resonance with a specific valence
excited state. The dephasing rate, \( \Gamma = 200 \text{ cm}^{-1} \), is taken to be
the same for all transitions.\(^{26}\)

The heterodyne detected signal\(^{27,28}\) is given by:

\[ S(\Gamma) = \frac{2}{h} \text{Im} \int dr \langle j(r, t) \cdot A_{\text{pr}}^*(r, t) \rangle \]

(5)

where \( \Gamma \) indicates the set of pulse parameters, \( \text{i.e.} \) central
frequencies, durations, \text{etc.}, and \( A_{\text{pr}} \) is the vector potential
of the probe pulse. Expanding to first order in the probe and
taking the difference between the left and the right polarization
of the probe we obtain:

\[ S_{\text{CD}}(k_s, \omega_s, T) = \frac{2}{h} \text{Re} \int dr \text{dr}1 \text{dt}1 \text{A}_{\text{pu}}^*(r, t) A_{\text{pu}}(r_1, t_1) \]

\[ \times \langle e_s^* e_L - e_s^* e_R \rangle \langle j(r) | G(t) | j(r_1) \rangle |\rho(t_1)\rangle |\rho(t-1)\rangle \rangle \]

(6)

where the subscript \( L \) (\( R \)) refers to left (right) circular polarization.

Assuming incoming pulses incident along \( z \), using \( e_s^* e_s^* - e_s^* e_R = (-1)_{\text{E}} \) \( \delta_{s,s} \), where \( \delta_{s,s} \) is the Levi-Cività symbol, and sum-
ing over electronic eigenstates gives:

\[ S_{\text{CD}}(k_s, \omega_s, T) = \frac{2}{h} \text{Im} \sum_{\text{ee'}c \text{c}'} \int dr \text{dr}1 \text{dt}1 \text{A}_{\text{pu}}^*(r, t) A_{\text{pu}}(r_1, t_1) \rho_{\text{ee}'}(t_1) \]

\[ \times \left[ j_{\text{ee}'}(k_s) \right. \left. \times j_{\text{ee}'}(-k_s) e^{i(\omega_s - \omega_{\text{ee}'} + \Gamma_{\text{ee}'})(t_1 - t)} \right] \]

\[ \left. \left. \times j_{\text{ee}'}(-k_s) \right. \left. \times j_{\text{ee}'}(k_s) e^{i(\omega_s - \omega_{\text{ee}'} - \Gamma_{\text{ee}'})(t_1 - t)} \right] \]

(7)

where \( \omega_{\text{ee}'} \) denotes the detection frequency of the probe pulse,
\( e \) and \( e' \) denote valence excited states \( \{e_1, e_2, \ldots, e_0\} \) and \( c \)
denotes core excited states \( \{c_1, c_2, \ldots, c_{10}\} \) and \( \rho_{\text{ee}'} \) is given
by eqn (4). \( j_{\text{ee}'} \) refer to the core/valence transition
current density matrix elements and the transition frequencies,
respectively. \times between transition current density terms,
\[ i.e. \, j_{\psi c}(k_s) \times j_{\phi c}(k_s), \] indicates a cross product. The final TRCD expression becomes:

\[
S_{\text{CD}}(\omega_k, T) = \frac{2}{\hbar^2 (2\pi)^2} \operatorname{Re} \sum_{\nu} A_{\psi}^{\nu}(\omega_k) A_{\phi}^{\nu}(\omega_k) \rho_{\psi \nu}(T) \times \left[ j_{\psi c}(k_s) \times j_{\phi c}(k_s) \right] \times \left[ \omega_k - \omega_{\psi \nu} + i\Gamma_{\psi \nu} \right] - \left[ \omega_k - \omega_{\phi \nu} + i\Gamma_{\phi \nu} \right] \frac{1}{C_0 k_s}
\]

(8)

Details on the TRCD signal derivation can be found in the ESI.†

**The pump–probe setup**

We assume a left circularly polarized UV pump propagating along the \( z \) direction. The Mg-porphyrin molecule (Fig. 1a) is in the \( xy \) plane. If the molecule were placed out of this plane, projections of the incoming field polarizations onto the molecular plane would have to be considered without providing extra insights on the ring current dynamics. After a waiting time \( T \), left and right circularly polarized X-ray probes are used to induce the CD signal. Two Gaussian pumps were considered (Fig. 1c): a narrow 0.1 eV bandwidth Fourier-transform-limited pump (central frequency at 3.125 eV, 18.2 fs duration) selectively excites the \( \varepsilon_1 \) or \( \varepsilon_2 \) states and a broad 1.0 eV bandwidth pump (central frequency at 5.400 eV, 1.82 fs duration) excites all valence excited states except \( \varepsilon_1 \) and \( \varepsilon_2 \). The X-ray probe at the N K-edge has a central frequency of 409 eV and 10 eV bandwidth (182 as pulse duration). At the Mg K-edge, we used a 1327 eV central frequency and 10 eV bandwidth (182 as duration).

**Electronic structure calculations**

Numerical simulations were carried out for Mg-porphyrin (Fig. 1a). Porphyrins are biologically important molecules involved in the primary events of photosynthesis, and biological sensing. Mg-porphyrin has been used as a model system for the generation of ring currents under an external magnetic field or circularly polarized light. Its aromatic ring currents and induced magnetic field with spectroscopic properties have been reported in numerous experimental29 and theoretical studies.30,31

The ground state geometry was optimized at the Hartree–Fock level with the 6-31G(d) basis set using the MOLPRO program.32 A CASSCF (13o/18e) calculation was used to compute transition current density matrix elements between valence states and to validate our results by comparison with previous studies. Because MOLPRO does not provide the one-body reduced transition density matrix needed to compute the current and charge density matrix elements between different wavefunction symmetries, the transition density matrix elements were calculated for \( C_1 \) wavefunction symmetry. Transition current density matrix elements were then computed from the transition density matrix based on the optimized geometry. Nine valence excited states and

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**Fig. 1** (a) The Mg-porphyrin used in this study. Gray, white, blue, and yellow spheres represent carbon, hydrogen, nitrogen, and Mg atoms, respectively. (b) Ladder diagram, and (c) the pump/probe setup used to calculate the TRCD signal and electronic energy levels contributing to the signal. Valence manifolds are denoted \( \{\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_9\} \), while core excited states are denoted \( \{c_1, c_2, \ldots, c_{10}\} \). \( \omega_{\psi \nu}, \sigma_{\psi \nu}, \) and \( t_{\psi \nu} \) denote the central frequency, bandwidth, and the time duration of the pump/probe pulse, respectively.
ten core excited states at the nitrogen K-edge were included for the spectroscopic calculations to match the bandwidth of the incoming pulses. The four degenerate N 1s molecular orbitals were rotated into the active space to calculate the transition density matrix element between valence and core excited states. Similarly, the single Mg 1s molecular orbital was rotated into the active space to generate ten core excited states at the Mg K-edge. Our quantum simulation results were consistent with the previous work of Rubio\textsuperscript{33} in terms of transition energies, transition dipole moments, and the orbital configuration of each excited state. Note that \( e_1, e_2, e_3, e_4 \), and \( e_5 \) are optically allowed \( E_u \) states, where \( e_1 \) and \( e_2 \) originate from a doubly degenerate state, while \( e_3, e_5, \) and \( e_4 \) do not have degenerate pairs within our computation. \( e_6, e_7, e_8, \) and \( e_9 \) are optically dark states (see Tables S1 and S2 in the ESI\textsuperscript{7} for more details).

### Results and discussion

The transition current densities which generate the ring current are shown in Fig. 2. We display three coherences: \( j_{e_1 e_2}, j_{e_3 e_4}, \) and \( j_{e_5 e_6} \). These ring currents have the same magnitude and a constant direction of the transition current density vectors along the porphyrin ring. \( e_1 \) and \( e_2 \) are degenerate and belong to the same \( E_u \) symmetry (\( B_{1u} \) and \( B_{2u} \) for \( D_{2h} \)), and hence their coherence generates a directional ring current, which maintains a clockwise ring current for a long time.\textsuperscript{34} In contrast, \( e_3 \) and \( e_4 \) have \( A_{2g}/B_{2g} \) (\( B_{1g} \) in \( D_{2h} \)) symmetry, while \( e_5 \) and \( e_6 \) have \( A_{1g}/B_{1g} \) (\( A_{g} \) in \( D_{2h} \)) symmetry. \( e_4 \) and \( e_6 \) have a degenerate transition from the same \( 3B_{3g} \) orbital to degenerate \( 4B_{2g} \) and \( 4B_{3g} \) orbitals. Similarly, \( e_5 \) and \( e_7 \) have a degenerate transition from the same \( 3B_{2g} \) orbital to degenerate \( 4B_{3g} \) and \( 4B_{3g} \) orbitals. Although they have different wavefunction symmetries, it is possible to generate a ring current by coherent excitation of two quasi-degenerate excited states with different symmetries.\textsuperscript{34} \( e_7 \) and \( e_8 \) have 0.17 eV splitting and \( e_5 \) and \( e_9 \) have 0.52 eV splitting, and thus \( j_{e_5 e_6} \) and \( j_{e_7 e_8} \) generate a coherent ring current which shows beating signals by reversing its rotational direction periodically,\textsuperscript{33} as will be discussed below. Because \( e_4, e_6, e_8, \) and \( e_9 \) are all optically dark states, we mainly probe the ring current generated by \( e_1 e_2 \) in the following discussions.

There exist quasi-ring currents \( j_{e_1 e_2}, j_{e_3 e_4}, j_{e_5 e_6}, \) and \( j_{e_7 e_8} \); they have a constant clockwise \( (j_{e_1 e_2} + j_{e_3 e_4}) \) or counter-clockwise \( (j_{e_5 e_6} + j_{e_7 e_8}) \) ring current but the magnitude of the vectors differs and some local vectors exist which do not follow the whole ring current direction. This is apparent for \( j_{e_1 e_2} \) and \( j_{e_3 e_4} \), where the local ring currents at the top and bottom could be dominating over the vorticity of the whole ring current.

The current density diagonal matrix elements vanish in all cases. Eqn (8) shows that the cross product of \( j_{e_1 e_2}(k) \times j_{e_3 e_4}(-k) = 0 \) (eqn (8)). This is confirmed by the oscillatory variation of the TRCD signal (Fig. 3b). The TRCD signal decays slowly after the incident pump is switched off\textsuperscript{35} because \( e_1 \) and \( e_2 \) are almost degenerate (0.03 eV splitting). The coherence between states with large energy splitting will produce a quickly oscillating signal. The TRCD signal variation with the probe frequency \( \omega_k \) (Fig. 3c) shows overlapping double peaks near 407.6 eV, reflecting small energy splitting between the \( e_1 \) and \( e_2 \) states and the degeneracy of the \( e_1 \) and \( e_2 \) core states. The contributions from the other core excited states, \( e_3 \) to \( e_{10} \), are negligibly small and they are invisible in the signal.

Fig. 3d–f present the TRCD signal for the right circularly polarized narrowband UV pump (0.1 eV) are shown in Fig. 3a–c. Due to the narrow bandwidth only the coherence \( e_1 e_2 \) contributes to the signal because the Raman pathways of the pump do not contribute to the signal: the only final state available for Raman interaction with the pump is the ground state, where \( j_{e_1 e_2}(k) \times j_{e_3 e_4}(-k) = 0 \) (eqn (8)). This is confirmed by the oscillatory variation of the TRCD signal (Fig. 3b). The TRCD signal decays slowly after the incident pump is switched off\textsuperscript{35} because \( e_1 \) and \( e_2 \) are almost degenerate (0.03 eV splitting). The coherence between states with large energy splitting will produce a quickly oscillating signal. The TRCD signal variation with the probe frequency \( \omega_k \) (Fig. 3c) shows overlapping double peaks near 407.6 eV, reflecting small energy splitting between the \( e_1 \) and \( e_2 \) states and the degeneracy of the \( e_1 \) and \( e_2 \) core states. The contributions from the other core excited states, \( e_3 \) to \( e_{10} \), are negligibly small and they are invisible in the signal.

Fig. 3d–f presents the TRCD signal for the right circularly polarized narrowband UV pump. This signal exhibits a reversed sign but with the same magnitude. The sign of the TRCD signal is thus a direct measure of the direction of the ring current. It also indicates that degeneracy is the key to maintaining long-lasting ring current, because a large energy gap will lead to a quickly oscillating signal. The expectation value of transition current density \( j_{e_1 e_2} \) in real space vs. the pump–probe waiting time is determined by \( \rho(T) \),

\[
\langle j_{e_1 e_2}(r, T) \rangle = \sum_{a, b=g, e_1, e_2} j_{ab}(r)\rho_{ab}(T) \tag{9}
\]

Fig. 4 shows that \( \rho(T) \) changes its sign around 100 fs and 200 fs. The magnitude of the ring current decreases in time and eventually changes its direction from clockwise to counterclockwise at 120 fs. Because the magnitude of the cross product \( j_{e_1 e_2}(k) \times j_{e_3 e_4}(-k) \) is time-independent, the signal will vary with the pump–probe waiting time, \( T \). The absolute value of the TRCD signal thus directly reflects the magnitude of the ring current in real space.

To investigate the element-sensitivity of TRCD in the presence of ring currents, we compare TRCD signals with the probe tuned at the N or Mg K-edges. To compare signals in such different frequency regimes, it is customary to define the CD...
asymmetry\textsuperscript{29} as the ratio between the chiral contribution and the achiral background:

\[ a_{\text{CD}}(\omega_s, T) = \frac{S_{\text{abs}}(\omega_s, T, L) - S_{\text{abs}}(\omega_s, T, R)}{1/2(S_{\text{abs}}(\omega_s, T, L) + S_{\text{abs}}(\omega_s, T, R))} \]  \hspace{1cm} (10)

where \( S_{\text{abs}} \) indicates the absorption amplitude after interaction with the left or right circularly polarized X-ray probe pulse.

Note that the static X-ray absorption signal (XAS) cannot be used because it vanishes in the region of the spectrum where the transient appears. The asymmetry ratio would be ill-defined in most regions of the spectra. Thus, we use as a denominator of \( a_{\text{CD}} \) the value of the transient absorption in the spectral region of significant CD.

The asymmetry ratios \( a_{\text{CD}} \) at the N and Mg K-edge are shown in Fig. 5. The signals display unusually large asymmetry ratios (above 100\%) compared to standard CD. This stems from the fact that no static signal (CD and XAS) exists in that spectral region, \textit{i.e.} the transition from \( e_1 \) and \( e_2 \) to the core states is made possible only by the actinic pump. Additionally, ring currents of opposite directions induce a significant difference in the transient absorption of the X-ray probe. We also observe that the asymmetry ratio is larger for Mg than for N, reaching a maximum of 164\% for the former and 110\% for the latter. This difference indicates that the Mg atom experiences a higher asymmetry, which can be assigned to the larger local magnetic field. The magnetic field created by the ring currents is the physical quantity breaking the parity of the molecular system and reaches its maximum at the ring center.

Fig. 6 depicts the TRCD signal for a broadband UV pump. It is generated by all possible coherences arising from the large bandwidth (1.0 eV), which covers the \( e_5 \) to \( e_9 \) valence states. The signal variation with time (Fig. 6b) is complex. The signal variation with \( \omega_s \) (Fig. 6c) shows peaks near 405.3 and 405.7 eV, which correspond to transitions from the \( e_3, e_5, \) and \( e_7 \) valence excited states to the \( e_1 \) and \( e_2 \) core excited states. Again, the other core excitations make negligible contributions.
to the signal due to their small transition current density. As shown in Fig. 6a, we find two coherences that contribute to the signal.

According to eqn (8), the signal is determined by \( r_{ee0}(T) \) and the cross product, \( j_{ee}\times j_{ee}^\dagger \), for possible coherences are shown in Fig. S4 (ESI†). It shows that \( r_{ee3}, r_{ee5}, \) and \( r_{ee7} \) coherences, are dominant. This is because of the large transition dipole moments between the ground state and the \( e_3, e_5, \) and \( e_7 \) valence excited states.

The \( x \) component of the cross product \( j_{ee}\times j_{ee}^\dagger \) is determined by the \( x \) component of \( j_{ee} \), and the \( y \) component of \( j_{ee}^\dagger \) and vice versa (Table S3, ESI†). For the \( e_3, e_5, \) and \( e_7 \) valence excited states, the cross products \( j_{ee}\times j_{ee}^\dagger \) and \( j_{ee}\times j_{ee}^\dagger \) are larger than \( j_{ee}\times j_{ee}^\dagger \) because \( j_{ee}^\dagger \) and \( j_{ee}^\dagger \) both have a large \( y \) component but small \( x \) component, but \( j_{ee}^\dagger \) has a large \( x \) component. Eventually, our signal mostly comes from the coherences \( e_3e_5 \) and \( e_3e_7 \), which do not generate a ring current.

In the real system, the \( e_1, e_3, e_5, \) and \( e_7 \) states are doubly degenerate, i.e. \( \{e_1, e_0\}, ..., \{e_7, e_0\} \) as reported by quantum calculations with high symmetry.33,36 Each coherence between degenerate states generates a ring current. By using a broadband pump, the TRCD signal probes multiple coherences which generate multiple ring currents.

It is clearer to use the TRCD signal to measure the ring current when it is accompanied by measurement of the induced magnetic field strength37 because it can reflect the vorticity of the ring currents. The induced magnetic field at the center of

Fig. 5  Comparison of the TRCD asymmetry (\( \Delta_{\text{CD}} \)), eqn (10), at the N (top, a–c) and Mg (bottom, d–f) K-edges. The asymmetry is larger when probing the magnesium than for the nitrogen atoms.

Fig. 6  The TRCD signal calculated for the left circularly polarized broadband light pump, where the central frequency was set to the transition energy between the ground and the 5th excited states. (b and c) show the TRCD signal versus time and probe frequency plots along the maximum absolute value of the TRCD signal, respectively.
Mg-porphyrin \((x, y, z = 0)\) can be calculated with the Biot–Savart law: \(B(x, y, z = 0)\)

\[
B(x, y, z = 0) = \frac{\mu_0}{4\pi} \int \left(\frac{1}{(x^2 + y^2 + z^2)^{3/2}} \right) \nabla \times B(x, y, z) \, dx \, dy \, dz
\]

where \(\mu_0\) is the vacuum permeability, and \(\hat{x}, \hat{y},\) and \(\hat{z}\) are the unit vectors along the \(x, y,\) and \(z\) axes, respectively. The induced magnetic field strengths for the ring-current-generating coherences \(e_1e_2, e_4e_6,\) and \(e_6e_8\) and the ring-current-non-generating coherences \(e_3e_5\) and \(e_5e_7\) are given in Table 1. The induced magnetic field strength along the \(z\) direction of the \(e_1e_2\) and \(e_3e_5\) coherences is 0.0185 and almost 0 T, respectively. In contrast, those of the \(e_4e_6, e_6e_8,\) and \(e_5e_7\) coherences, −0.2578, 0.1349, and 0.2376 T, are around 10–20 times higher. The calculated magnetic field strengths are similar to a previous study, \(^6\) 0.159 T. However, note that the transition current density in eqn (11) does not reflect the small transition dipole moment between the ground state and the dark states \((e_4, e_6, e_8,\) and \(e_9)\). The generation of the ring current \(j_{e_1e_2}\) and \(j_{e_3e_5}\) might be possible by relaxation from the other excited states to these optically dark states. Nevertheless, the measurement of the induced magnetic field helps to identify the ring current: the sign of the induced magnetic field marks the absolute direction of the ring current, where \(j_{e_1e_2}\) is a clockwise current while \(j_{e_3e_5}\) and \(j_{e_5e_7}\) are counterclockwise ring currents as shown in Fig. 2.

Fig. 7a and d show that the TRCD signals induced by a linearly polarized pump are about 1000 times smaller than the one induced by circular polarization. It indicates that circular polarization is an effective way of generating a ring current and induced magnetic field as suggested by the Manz group. \(^6\)

It is apparent from the ladder diagram (Fig. 1b) that linear polarization is an effective way of generating a ring current and induced magnetic field. However, note that the transition current density in eqn (11) does not reflect the small transition dipole moment between the ground state and the dark states \((e_4, e_6, e_8,)\) and \(e_9\). The generation of the ring current \(j_{e_1e_2}\) and \(j_{e_3e_5}\) might be possible by relaxation from the other excited states to these optically dark states. Nevertheless, the measurement of the induced magnetic field helps to identify the ring current: the sign of the induced magnetic field marks the absolute direction of the ring current, where \(j_{e_1e_2}\) is a clockwise current while \(j_{e_3e_5}\) and \(j_{e_5e_7}\) are counterclockwise ring currents as shown in Fig. 2.

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Table 1 The induced magnetic field strength (in Tesla) for different coherences, calculated at the center of Mg-porphyrin

<table>
<thead>
<tr>
<th>The type of coherence</th>
<th>(B_x)</th>
<th>(B_y)</th>
<th>(B_z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(e_1e_2)</td>
<td>0.0315</td>
<td>−0.0060</td>
<td>−0.2578</td>
</tr>
<tr>
<td>(e_4e_6)</td>
<td>−0.0170</td>
<td>0.0046</td>
<td>0.1349</td>
</tr>
<tr>
<td>(e_6e_8)</td>
<td>−0.0265</td>
<td>0.0049</td>
<td>0.2376</td>
</tr>
<tr>
<td>(e_3e_5)</td>
<td>−0.0030</td>
<td>0.0028</td>
<td>0.0185</td>
</tr>
<tr>
<td>(e_5e_7)</td>
<td>0.0001</td>
<td>−0.0007</td>
<td>−0.0</td>
</tr>
</tbody>
</table>

Fig. 7 The TRCD signal calculated for the linearly polarized light pump (a–c: linear polarization along the \(x\)-axis, d–f: linear polarization along the \(y\)-axis). (b and e) show the time variation of the TRCD signal along the maximum absolute value of the TRCD signal. (c and f) show the probe frequency \(\omega_s\) versus TRCD signal.
non-vanishing signal. Indeed, TRCD is sensitive to coherences in general, of which ring currents are a special case. However, the coherences induced by an x-y pump scheme would not be a signature of a ring current and do not survive complete or partial rotational averaging. If the molecules are averaged around the probe (or pump) wavevectors, the pump + molecules have cylindrical symmetry, and an x-y polarized pump is totally equivalent to an x or y polarized pump. Ring currents in molecules are created by a transfer of angular momentum from the field to the matter and an x-y linearly polarized pulse does not carry such momentum.

By the same argument, the TRCD signal is non-zero when coherences are present in the molecular system whether the system is aromatic or not, as long as the transition dipoles of the two transitions involved in the probe interaction are not pointing in the same direction. However, when a narrowband pump was used, an aromatic ring molecule would have a slow-decaying TRCD signal with larger magnitude while a non-aromatic ring molecule would have a fast-oscillating TRCD signal with much smaller magnitude because the cross product in eqn (8) is maximized for the degenerate states.

Conclusions

We have shown that time-resolved circular dichroism signals provide a direct measure of the magnitude and the direction of the electronic ring current. These measurements are simpler to interpret than photoelectron CD or high-harmonic-generation spectroscopy. The electronic ring current is generated by the coherent superposition of electronic states induced by circularly polarized light and is tracked by a time-delayed circularly polarized X-ray probe pulse. The signal is calculated using the minimal coupling Hamiltonian, which allows one to express it directly in terms of the relevant material quantity, transition current densities. The TRCD signals obtained from the left and right narrowband circularly polarized light pump have opposite signs, indicating that the signal is a direct signature of the ring current. The absolute value of the signal gives the magnitude of the ring current. The narrowband pump can selectively excite the doubly degenerate excited states to probe a specific ring current or the broadband pump can detect multiple coherences/ring currents at the same time.

X-rays allow one to study transient signals in regions where no static achiral background is present, leading to extremely large asymmetry ratios for such techniques. Additionally, X-rays can address different sites in the molecules. Here, we have focused on the amplitude of the TRCD signals for different atomic positions (at the center or on the ring); such sensitivity can also provide extra information for systems involving multiple rings with different atoms.

The strength of the induced magnetic field, calculated based on the Biot–Savart law, directly reflects the vorticity of an electronic coherence, which helps to identify a ring current and its absolute direction. Circular polarization is around 1000 times more sensitive than linear polarization to probe electronic coherences.

We expect that an aromatic and an anti-aromatic molecule will show the opposite TRCD signal under the same circularly polarized light pump. Hence, our direct approach to access the electronic coherences/ring currents opens a window to measure molecular aromaticity. Furthermore, ring currents can be generated and probed by TRCD while a molecule is experiencing ultrafast nuclear dynamics, and can thus be a potential probe for photochemical ring opening or closure reactions.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research was supported by Korea Initiative for fostering University of Research and Innovation Program of the National Research Foundation (NRF) funded by the Korean government (MSIT) (No. 2020M3H1A1077095). We wish to acknowledge the support of the National Science Foundation through Grant No. CHE-1953045 and of the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award DE-FG02-04ER15571. S. M. was supported by the DOE grant. We gratefully acknowledge Daehun Cho and Stefano M. Cavaletto for providing their code for calculating and visualizing transition density matrix elements.

Notes and references

Monitoring Aromatic Ring-Currents in Mg-porphyrin by Time-Resolved Circular Dichroism

Yeonsig Nam$^{1,2}$, Jérémie R. Rouxel$^1$, Jin Yong Lee$^2$, and Shaul Mukamel$^1$

$^1$Department of Chemistry, University of California, Irvine, California 92697-2025, USA
$^2$Department of Chemistry, Sungkyunkwan University, Suwon, South Korea, 16419

October 27, 2020

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1 Details of the time-resolved circular dichroism signal calculation

We start with the minimal coupling Hamiltonian, retaining only the current density term:

\[ H_{\text{int}} = -\int dr j(r) \cdot A(r, t) \]  

(1)

where \( j(r) \) is transition current density and \( A(r, t) \) is a vector potential of incoming pulse. The heterodyne-detected signal is defined as the change of the number of photons in a given time,

\[ S(\Gamma) = \int dt \langle N_s \rangle \]  

(2)

where, \( \Gamma \) indicates the set of parameters, i.e. incoming pulses central frequencies, durations, etc.

\[ N_s = \frac{i}{\hbar} [H_{\text{int}}, N_s] = \frac{i}{\hbar} \int dr j(r) A(r, t), a_s^\dagger a_s \]  

(3)

The vector potential \( A(r, t) \) can be expressed as the following:

\[ A(r, t) = \sqrt{\frac{\hbar}{2\epsilon_0\omega_s\Omega}} (a_s \epsilon e^{i(k_s \cdot r - \omega_st)} + a_s^\dagger \epsilon^* e^{-i(k_s \cdot r - \omega_st)}) \]  

(4)

where \( \epsilon \) is the electric field polarization vectors. Hence, it gives

\[ N_s = -\frac{i}{\hbar} \int dr j(r) \cdot [A(r, t), a_s^\dagger a_s] = -\frac{2}{\hbar} \text{Im} \int dr j(r) \cdot A^\dagger(r, t) \]  

(5)

Therefore, the heterodyne-detected signal is

\[ S(\Gamma) = -\frac{2}{\hbar} \text{Im} \int dr dt (j(r, t) \cdot A^\dagger(r, t)) \]  

(6)

The heterodyne-detected signal for Fig. S1 corresponds to

\[ S(\Gamma) = -\frac{2}{\hbar} \text{Im} \int dr dt \int dr_3 dt_3 dr_2 dt_2 dr_1 dt_1 (-\frac{i}{\hbar})^3 \langle j_{\text{left}}(r, t) j_{\text{left}}^\dagger (r_3, t_3) j_{\text{right}}^\dagger (r_2, t_2) j_{\text{right}}(r_1, t_1) \rangle A_s^\dagger(r, t) A_s(r_3, t_3) A_{pu}(r_2, t_2) A_{pu}^\dagger(r_1, t_1) \]  

(7)

The \( A_s \) and \( A_{pu} \) is the vector potential of a probe and pump pulse respectively. The subscript left and right indicates the Liouville space superoperators defined by \( O_{\text{left}} \rho = \hat{O} \rho \) and \( O_{\text{right}} \rho = \rho \hat{O} \). Upon expanding to first order in the probe and taking the difference between left and right polarization of the probe, we get
Figure S1: Possible pump-probe ladder diagrams. $t_1$, $t_2$, and $t_3$ refer to the time interval between interaction. Red and blue arrow indicate UV pump and X-ray probe interaction, respectively.

$$S_{ij}(T) = -\frac{2}{\hbar} \text{Im} \int dr dt dr_1 dt_1 \left(\frac{i}{\hbar}\right) \left[ \langle j_{\text{left}}(r,t)f_{\text{left}}^t(r_1,t-t_1) \rangle A_\epsilon^*(r,t)A_s(r_1,t-t_1) \right.$$ 

$$-\langle j_{\text{left}}(r,t)f_{\text{right}}^t(r_1,t-t_1) \rangle A_s^*(r,t)A_s(r_1,t-t_1) \right]\]

$$= \frac{2}{\hbar^2} \text{Re} \int dr dt dr_1 dt_1 \left[ \langle j(r)\mathcal{G}(t_1)f_{\text{left}}^t(r_1)|\rho(t-t_1)\rangle A_\epsilon^*(r,t)A_s(r_1,t-t_1) \right.$$ 

$$-\langle j(r)\mathcal{G}(t_1)f_{\text{right}}^t(r_1)|\rho(t-t_1)\rangle A_s^*(r,t)A_s(r_1,t-t_1) \right]\]

$$= \frac{2}{\hbar^2} \text{Re} \int dr dt dr_1 dt_1 \left[ \langle j(r)\mathcal{G}(t_1)f_{\text{left}}^t(r_1)|\rho(t-t_1)\rangle \right.$$ 

$$\left.-\langle j(r)\mathcal{G}(t_1)f_{\text{right}}^t(r_1)|\rho(t-t_1)\rangle \right]\left(\varepsilon_\epsilon^*\varepsilon_L - \varepsilon_R^*\varepsilon_R\right) A_\epsilon^*(r,t)A_s(r_1,t-t_1) e^{-ik_sr + ik_r r_1 e^{i\omega_1 t_1}}$$

(8)
Using that $e^{ia\sigma^b_i - e^{ia\sigma^b_i}} = (-i)\epsilon_{abc}$, where $\epsilon_{abc}$ is a Levi-Civita symbol and summing over electronic eigenstates, we get

$$S_{\text{CD}} = \frac{2}{\hbar^2} \text{Im} \int dr dt d_1 \epsilon_{abc} \left( \langle \langle j^a(r) | G(t_1) j_{\text{left}}^b(r_1) | \rho(t - t_1) \rangle \rangle \right)$$

$$- \langle \langle j^a(r) | G(t_1) j_{\text{right}}^b(r_1) | \rho(t - t_1) \rangle \rangle | A_z^*(r, t) A_s(r_1, t - t_1) e^{-iklr + ik_1r} e^{i\omega t_1}$$

(9)

and

$$\langle \langle ab | j_L - j_R | cd \rangle \rangle = j_{ac} \delta_{bd} - j_{bd} \delta_{ac}$$

(10)

then,

$$S_{\text{CD}} = \frac{2}{\hbar^2} \text{Im} \int dr dt d_1 \left( \langle \langle j(r) \times | G(t_1) j_{\text{left}}^c(r_1) | \rho(t - t_1) \rangle \rangle | A_z^*(r, t) A_s(r_1, t - t_1) e^{-iklr + ik_1r} e^{i\omega t_1} \right)$$

$$\left( \langle \langle j(r) \times | G(t_1) j_{\text{right}}^c(r_1) | \rho(t - t_1) \rangle \rangle | A_z^*(r, t) A_s(r_1, t - t_1) e^{i\omega t_1} \right)$$

(11)

where $j_-$ denotes the Liouville space current density superoperator defined by $j_- \rho = j \rho - \rho j$.

$$S_{\text{CD}} = \frac{2}{\hbar^2} \text{Im} \sum_{abc} \int dt d_1 \left( j_{ba}^c(k_3) - j_{ac}^t(-k_3) e^{i(\omega_3 - \omega_4) t_1 - \Gamma_{ab} t_1} \rho_{cb} (t - t_1) \right)$$

$$- \langle \langle j_{ac}^t(-k_3) e^{i(\omega_3 - \omega_4) t_1 - \Gamma_{ab} t_1} \rho_{ac} (t - t_1) | A_z^*(t) A_s(t - t_1) \rangle \rangle$$

(12)

Rearranging the sums to factorized out the density matrix after the pump, we get

$$S_{\text{CD}}(k_s, \omega_s) = \frac{2}{\hbar^2} \text{Im} \sum_{abc} \int dt d_1 A_z^*(t) A_s(t - t_1) \rho_{cb}(t - t_1)$$

$$\left( j_{ba}^c(k_3) - j_{ac}^t(-k_3) e^{i(\omega_3 - \omega_4) t_1 - \Gamma_{ab} t_1} \rho_{cb} (t - t_1) \right)$$

$$- j_{ac}^t(-k_3) e^{i(\omega_3 - \omega_4) t_1 - \Gamma_{ab} t_1} \rho_{ac} (t - t_1) | A_z^*(t) A_s(t - t_1) \rangle \rangle$$

(13)

In the impulsive limit, $A_s(t) = \delta(t - T) A_s$, $A_s(t - t_1) = \delta(t - 1 - T) A_s$, where $t \to T$, and $t_1 \to 0$.

We now express explicitly $\rho_{cb}(T)$. At second order in the pump interaction (Fig S4), we have

$$\rho_{cb}(T) = \langle \langle cb | \rho(T) \rangle \rangle$$

$$= (-\frac{i}{\hbar})^2 \int dr_1 dr_2 dt_1 dt_2 \langle \langle cb | j_-(r_2, t_2) j_-(r_1, t_1) | \rho(T - t_1 - t_2) \rangle \rangle A_{pu}^*(r_2, T - t_2) A_{pu}(r_1, T - t_2 - t_1)$$

$$= (-\frac{i}{\hbar})^2 \int dr_1 dr_2 dt_1 dt_2 \left( \langle \langle cb | G(t_2) j_{\text{right}}^c(r_2) G(t_1) j_{\text{left}}^t(r_1) | \rho(t_0) \rangle \rangle A_{pu}^*(r_2, T - t_2) A_{pu}(r_1, T - t_2 - t_1) \right)$$

$$+ \langle \langle cb | G(t_2) j_{\text{left}}^t(r_2) G(t_1) j_{\text{right}}^c(r_1) | \rho(t_0) \rangle \rangle A_{pu}^*(r_2, T - t_2) A_{pu}(r_1, T - t_2 - t_1)$$

(14)
Figure. S 2: Ladder diagrams for pump interaction. \( t_1 \) and \( t_2 \), refer to the time interval between two pump interactions.

Since, \( \rho(t_0) = |gg\rangle \)

\[
\rho_{cb}(T) = \left( \frac{1}{\hbar} \right)^2 \int dt_1 dt_2 \int dr_1 dr_2 \int \left( G_{cb,cb}(t_2) j_{bg}(r_2) G_{cg,cb}(t_1) j_{cg}^+(r_1) A_{pu}^*(r_2, T - t_2) A_{pu}(r_1, T - t_2 - t_1) \right. \\
+ G_{cb,cb}(t_2) j_{cg}^+(r_1) G_{bg,cb}(t_1) j_{bg}(r_1) A_{pu}(r_2, T - t_2) A_{pu}^*(r_1, T - t_2 - t_1) \right) \\
= \frac{1}{\hbar^2} \int dt_1 dt_2 \left( e^{-i\omega_{cb}t_2 - \Gamma_{cb}t_2} e^{-i\omega_{cg}t_1 - \Gamma_{cg}t_1} j_{bg}(k_{pu}) j_{cg}^*(-k_{pu}) A_{pu}^*(T - t_2) A_{pu}(T - t_2 - t_1) \right. \\
+ e^{-i\omega_{cb}t_2 - \Gamma_{cb}t_2} e^{-i\omega_{cg}t_1 - \Gamma_{cg}t_1} j_{cg}^+(k_{pu}) j_{bg}(k_{pu}) A_{pu}(T - t_2) A_{pu}^*(T - t_2 - t_1) \right) \\
\tag{15}
\]

In the impulsive limit, \( A_{pu}(t) = \delta(t) A_{pu} \), where \( t_2 \to T \), and \( t_1 \to 0 \). The Fourier transform of pump pulse in time-domain to frequency domain gives,

\[
A_{pu}(T - t_1) = \int \frac{d\omega_1}{2\pi} A_{pu}(\omega_1) e^{-i\omega(T-t_1)} \\
\tag{16}
\]

and

\[
\int_0^\infty dt_2 e^{i(\omega_1 - \omega_2 - \omega_{cb}t_2 - \Gamma_{cb}t_2)} = \frac{i}{\omega_1 - \omega_2 - \omega_{cb} + i\Gamma_{cb}} \\
\tag{17}
\]
Hence, the density matrix at waiting time $T$ becomes,

$$\rho_{cb}(T) = -\frac{1}{\hbar^2} \int \frac{d\omega_1}{2\pi} \frac{d\omega_2}{2\pi} A_{pu}(\omega_1)A_{pu}(\omega_2) \left[ j_{bg}(k_{pu}) \cdot \epsilon_{pu} \cdot j_{cg}^\dagger(-k_{pu}) \cdot \epsilon_{pu} e^{i(\omega_2-\omega_1)T} \right. \left. \frac{(\omega_1 - \omega_2 - \omega_{cb} + i\Gamma_{cb})(\omega_1 - \omega_{cg} + i\Gamma_{cg})}{(-\omega_1 + \omega_2 - \omega_{cb} + i\Gamma_{cb})(-\omega_1 - \omega_{gb} + i\Gamma_{gb})} \right]$$

(18)

Likewise, the final TRCD signal becomes,

$$S_{CD}(\omega_s, T) = \frac{2}{\hbar^2 (2\pi)^2} N \Re \sum_{abc} A_{s}^\dagger(\omega_s)A_{s}(\omega_s) \rho_{cb}(T) \left[ j_{ba}(k_s) \times j_{ac}^\dagger(-k_s) - j_{ac}(k_s) \times j_{ab}^\dagger(-k_s) \right. \left. \frac{\omega_s - \omega_{ab} + i\Gamma_{ab}}{-\omega_s - \omega_{ca} + i\Gamma_{ca}} \right]$$

(19)

Finally, substituting $a$, $b$, and $c$ into $c$, $e'$, and $e$, respectively, gives the final expression in the manuscript.
2 Quantum simulation results

We compared our quantum calculations with previous work of Rubio [1] which performed CASSCF calculations within the same active space (13o/18e) for the electronic structure calculation of the Mg-porphyrin. To that end, we computed transition energies (Table S1 and S2) and transition dipole moment (Fig. S3) of the Mg-porphyrin calculated at the CASSCF (13o/18e) level with C1 and D2h symmetry option (note that the highest symmetry option in MOLPRO is D2h). By comparing the orbital configuration of each excited state of the active orbitals, we assigned our e1, e3, e5, and e7 states to e1 to e4 states (Q band to N band) of Rubio’s work and those of D2h symmetry. The e1, e3, e5, and e7 states are originally doubly degenerate, however, they might split into several non-degenerate states due to the loss of symmetry [1, 2]: for example, the Q bands split into e1 and e2 states. Discrepancies of the computed transition energies compared to experimental data are due to the lack of dynamics correlation in CASSCF. However, our computation matches the results of the CASSCF calculation of Rubio [1] in terms of transition energies and orbital configurations. Moreover, the square of transition dipole moment with D2h symmetry shows the same trend (e1 < e3, e3 > e5, and e5 < e7). The small deviation from Rubio’s work mainly originates from the different basis set and since the oscillator strength was calculated with CASPT2 in that study. It is also consistent with experiment that the absorption of e1 is very weak and e3 shows the most intense absorption [3].

<table>
<thead>
<tr>
<th>CASSCF (13o/20e) with C1 symmetry</th>
<th>Rubio’s work(^{1}): CASSCF (13o/18e)</th>
<th>Experiment(^{1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transition Energy</td>
<td>Square of the transition dipole moment, (\mu^2)</td>
<td>Transition dipole moment direction</td>
</tr>
<tr>
<td>e1 3.125</td>
<td>0.199</td>
<td>x</td>
</tr>
<tr>
<td>e2 3.157</td>
<td>0.748</td>
<td>y</td>
</tr>
<tr>
<td>e3 5.051</td>
<td>14.054</td>
<td>x</td>
</tr>
<tr>
<td>e4 5.274</td>
<td>0.000</td>
<td>y</td>
</tr>
<tr>
<td>e5 5.492</td>
<td>0.000</td>
<td>x</td>
</tr>
<tr>
<td>e6 5.527</td>
<td>6.413</td>
<td>x</td>
</tr>
<tr>
<td>e7 5.664</td>
<td>0.000</td>
<td>y</td>
</tr>
</tbody>
</table>

Table S1: Comparison of transition energies (eV), transition dipole moment (a.u.), main orbital configuration of Mg-porphyrin between this study (with C1 symmetry), Rubio’s work [1] and experimental results [3]. The main orbital configuration of C1 symmetry was converted to the orbital notations of D2h symmetry for convenience.
Table S 2: Comparison of transition energies (eV), transition dipole moment (a.u.), main orbital configuration of Mg-porphyrin between this study (with D_{2h} symmetry), Rubio’s work [1] and experimental results [3].

<table>
<thead>
<tr>
<th>Energy</th>
<th>Square of the transition dipole moment, μ^2</th>
<th>Transition dipole moment direction</th>
<th>Main orbital configuration (Wavefunction symmetry)</th>
<th>Transition Energy</th>
<th>Oscillator Strength</th>
<th>Main orbital configuration</th>
<th>Transition Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>E_1</td>
<td>2.869</td>
<td>x</td>
<td>2A_0 → 4B_{1g}(B_{2u}) 6B_{1g} → 4B_{1g}(B_{2u})</td>
<td>3.05</td>
<td>0.008</td>
<td>4A_{1g} → 4E_g 1A_{2u} → 4E_g</td>
<td>2.14</td>
</tr>
<tr>
<td>E_2</td>
<td>2.869</td>
<td>y</td>
<td>2A_0 → 4B_{1g}(B_{2u}) 6B_{1g} → 4B_{1g}(B_{2u})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E_3</td>
<td>4.836</td>
<td>x</td>
<td>6B_{1g} → 4B_{2g}(B_{2u}) 2A_0 → 4B_{1g}(B_{2u}) 4B_{1g} → 4B_{1g}(B_{2u})</td>
<td>4.95</td>
<td>0.923</td>
<td>4A_{1g} → 4E_g 1A_{2u} → 4E_g 3A_{2u} → 4E_g</td>
<td>3.18</td>
</tr>
<tr>
<td>E_4</td>
<td>4.836</td>
<td>y</td>
<td>6B_{1g} → 4B_{2g}(B_{2u}) 2A_0 → 4B_{1g}(B_{2u}) 4B_{1g} → 4B_{1g}(B_{2u})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E_5</td>
<td>5.281</td>
<td>x</td>
<td>5B_{1g} → 4B_{2g}(B_{2u})</td>
<td>5.28</td>
<td>0.200</td>
<td>2A_{2u} → 4E_g</td>
<td>3.40</td>
</tr>
<tr>
<td>E_6</td>
<td>5.281</td>
<td>y</td>
<td>5B_{1g} → 4B_{2g}(B_{2u})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E_7</td>
<td>5.815</td>
<td>x</td>
<td>4B_{2g} → 4B_{2g}(B_{2u})</td>
<td>5.83</td>
<td>0.379</td>
<td>3A_{2u} → 4E_g</td>
<td>3.81</td>
</tr>
<tr>
<td>E_8</td>
<td>5.815</td>
<td>y</td>
<td>4B_{2g} → 4B_{2g}(B_{2u})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure. S 3: Stick spectra of the oscillator strength for the valence excitations from the ground state. Blue: CASSCF calculation with D_{2h} symmetry, Red: CASSCF calculation with C_{1} symmetry, Yellow: CASSCF result [1].

3 Time-dependent density matrix elements and Average transition current density
Figure. S 4: The time-dependent density matrix for various coherences of valence excited states. The density matrix originating only from $e_1$, $e_2$, $e_3$, $e_5$, and $e_7$ are shown.

<table>
<thead>
<tr>
<th>$J_{ab}$</th>
<th>$c_1$</th>
<th>$c_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$x$</td>
<td>$y$</td>
</tr>
<tr>
<td>$e_3$</td>
<td>-7.137</td>
<td>2.086</td>
</tr>
<tr>
<td>$e_5$</td>
<td>-0.300</td>
<td>-4.448</td>
</tr>
<tr>
<td>$e_7$</td>
<td>0.245</td>
<td>-5.231</td>
</tr>
</tbody>
</table>

Table S 3: The average transition current density value for the transition from $e_3$, $e_5$, and $e_7$ valence state to $c_1$ and $c_2$ core states in the real space (x and y component are separately shown, Unit: $10^{-7} e$/bohr$^3$), where $e$ is the electron charge.

References

