Supplementary Information for "Time-resolved enantiomer-exchange probed by using the orbital angular momentum of X-ray light"

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S-I. TRANSIENT ABSORPTION SIGNALS

We begin the derivation of transient absorption at any pump-probe time delay T from[1]

$$S(T) = -\frac{2}{\hbar}\,\mathrm{Im}\int_{t_0}^{+\infty} \mathrm{d}t\mathrm{d}\boldsymbol{r}\,\langle \mathbf{j}(\boldsymbol{r},t)\cdot\mathbf{A}^*(\boldsymbol{r},t)\rangle \tag{S1}$$

under the light-matter interaction Hamiltonian[2]

$$H_{\mathrm{int}} = -\int \mathrm{d}\boldsymbol{r}\;\mathbf{j}(\boldsymbol{r})\cdot\mathbf{A}(\boldsymbol{r},t), \tag{S2}$$

in which $\mathbf{j}(\boldsymbol{r})$ is the current density operator and $\mathbf{A}(\boldsymbol{r},t) = \mathbf{A}(\boldsymbol{r})A(t)$ is the electromagnetic vector potential of the light. In Eq. (S1), $\mathbf{j}(\boldsymbol{r},t)\cdot\mathbf{A}^*(\boldsymbol{r},t)$ is written in interaction picture as

$$\mathbf{j}(\boldsymbol{r},t)\cdot\mathbf{A}^*(\boldsymbol{r},t) = U^\dagger(t,t_0)\mathbf{j}(\boldsymbol{r})\cdot\mathbf{A}^*(\boldsymbol{r},t)U(t,t_0), \tag{S3}$$

and

$$\langle \mathbf{j}(\boldsymbol{r},t)\cdot\mathbf{A}^*(\boldsymbol{r},t)\rangle = \langle \psi_I(t)|\mathbf{j}(\boldsymbol{r},t)\cdot\mathbf{A}^*(\boldsymbol{r},t)|\psi_I(t)\rangle\,. \tag{S4}$$

Let $\psi(t_0) = \psi_0$, under linear response we have

$$|\psi_I(t)\rangle = |\psi_0\rangle + \left(\frac{-\mathrm{i}}{\hbar}\right)\int_{t_0}^{t}\mathrm{d}t'\mathrm{d}\boldsymbol{r}'U^\dagger(t',t_0)(-\mathbf{j}(\boldsymbol{r}')\cdot\mathbf{A}(\boldsymbol{r}',t'))U(t',t_0)\,|\psi_0\rangle\,. \tag{S5}$$

Then the transient absorption can be written as

$$\begin{aligned} S(T) = &-\frac{2}{\hbar}\,\mathrm{Im}\int_{t_0}^{+\infty}\mathrm{d}t\int_{t_0}^{t}\mathrm{d}t'\int\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}'\mathbf{A}^*(\boldsymbol{r},t)\\ &\times\left(\frac{-\mathrm{i}}{\hbar}\right)\Big[\mathbf{A}(\boldsymbol{r}',t')\,\langle\psi_0|U^\dagger(t,t_0)\mathbf{j}(\boldsymbol{r})U(t,t_0)U^\dagger(t',t_0)(-\mathbf{j}(\boldsymbol{r}'))U(t',t_0)|\psi_0\rangle\\ &\qquad -\mathbf{A}^*(\boldsymbol{r}',t')\,\langle\psi_0|U^\dagger(t',t_0)(-\mathbf{j}(\boldsymbol{r}'))U(t',t_0)U^\dagger(t,t_0)\mathbf{j}(\boldsymbol{r})U(t,t_0)|\psi_0\rangle\Big]\\ = &-\frac{2}{\hbar^2}\,\mathrm{Re}\int_{t_0}^{+\infty}\mathrm{d}t\int_{t_0}^{t}\mathrm{d}t'\int\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}'\mathbf{A}^*(\boldsymbol{r},t)\\ &\times\Big[\mathbf{A}(\boldsymbol{r}',t')\,\langle\psi_0|U^\dagger(t,t_0)\mathbf{j}(\boldsymbol{r})U(t,t')\mathbf{j}(\boldsymbol{r}')U(t',t_0)|\psi_0\rangle\\ &\qquad -\mathbf{A}^*(\boldsymbol{r}',t')\,\langle\psi_0|U^\dagger(t',t_0)\mathbf{j}(\boldsymbol{r}')U^\dagger(t,t')\mathbf{j}(\boldsymbol{r})U(t,t_0)|\psi_0\rangle\Big]. \end{aligned} \tag{S6}$$

After the substitution of $\tau = t - t'$ and $\mathrm{d}t' = -\mathrm{d}\tau$, we have

$$\begin{aligned} S(T) = &-\frac{2}{\hbar^2}\,\mathrm{Re}\int_{t_0}^{+\infty}\mathrm{d}t\int_{0}^{t-t_0}\mathrm{d}\tau\int\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}'\mathbf{A}^*(\boldsymbol{r},t)\\ &\times\Big[\mathbf{A}(\boldsymbol{r}',t-\tau)\,\langle\psi_0|U^\dagger(t,t_0)\mathbf{j}(\boldsymbol{r})U(\tau)\mathbf{j}(\boldsymbol{r}')U(t-\tau,t_0)|\psi_0\rangle\\ &\qquad -\mathbf{A}^*(\boldsymbol{r}',t-\tau)\,\langle\psi_0|U^\dagger(t-\tau,t_0)\mathbf{j}(\boldsymbol{r}')U^\dagger(\tau)\mathbf{j}(\boldsymbol{r})U(t,t_0)|\psi_0\rangle\Big]. \end{aligned} \tag{S7}$$

After defining

$$d_{ij} = \langle\varphi_i(\boldsymbol{r})|\mathbf{A}(\boldsymbol{r})\cdot\mathbf{j}(\boldsymbol{r})|\varphi_j(\boldsymbol{r})\rangle\,, \tag{S8}$$

using the Born-Oppenheimer approximation

$$|\psi(\boldsymbol{r},\boldsymbol{q},t)\rangle = \sum_e c_e(t)\,|\chi_e(\boldsymbol{q},t)\rangle\,|\varphi_e(\boldsymbol{r},\boldsymbol{q})\rangle \tag{S9}$$

for separating the nuclei and electron wavefunction, expanding $U(\tau)$ in core states, and inserting $t_0 \to -\infty$, we can rewrite Eq. (S7) as

$$\begin{aligned} S(T) = &-\frac{2}{\hbar^2}\,\mathrm{Re}\int_{-\infty}^{+\infty}\mathrm{d}t\int_0^{+\infty}\mathrm{d}\tau \mathrm{e}^{-\mathrm{i}\omega_{ee'}t}A^*(t)\\ &\times\sum_{ee'c}\Big[A(t-\tau)c^*_{e'}(t)c_e(t-\tau)\,\langle\chi_{e'}(t)|d^*_{ce'}U_{cc}(\tau)d_{ce}|\chi_e(t-\tau)\rangle\,\mathrm{e}^{\mathrm{i}\omega_e\tau}\\ &\qquad -A^*(t-\tau)c^*_{e'}(t-\tau)c_e(t)\,\langle\chi_{e'}(t-\tau)|d^*_{ce'}U^\dagger_{cc}(\tau)d^*_{ec}|\chi_e(t)\rangle\,\mathrm{e}^{-\mathrm{i}\omega_{e'}\tau}\Big], \end{aligned} \tag{S10}$$

where $\omega_{e(e')} = E_{e(e')}/\hbar, \omega_{ee'} = \omega_e - \omega_{e'}$, and we also used $U(t,t_0)\,|\psi_0\rangle = \sum_e c_e\mathrm{e}^{-\mathrm{i}\omega_e t}\,|\chi_e\rangle\,|\varphi_e\rangle$.

Then we consider a Gaussian type light wave packet whose center at pump-probe time delay T

$$A(t) = A_0\mathscr{A}(t)\mathrm{e}^{-\mathrm{i}\omega t},\ \ \mathscr{A}(t) = \frac{1}{\sqrt{2\pi}\xi}\exp\left[-\frac{(t-T)^2}{2\xi^2}\right], \tag{S11}$$

and introduce the step function

$$\theta(\tau) = \begin{cases} 1 & \tau > 0\\ 0 & \tau < 0\end{cases}$$

to change the integral lower limit of τ to $-\infty$ with

$$\begin{aligned} \theta(\tau)U_{cc}(\tau)\mathrm{e}^{\mathrm{i}\omega_e\tau} &= \theta(\tau)\exp[-\mathrm{i}(\omega_c-\omega_e)\tau], \omega_c = E_c/\hbar\\ &= -\frac{1}{2\pi\mathrm{i}}\int_{-\infty}^{+\infty}\frac{\mathrm{d}\Omega}{\Omega-\omega_{ce}+\mathrm{i}\Gamma_c}\exp(-\mathrm{i}\Omega\tau), \omega_{ce} = \omega_c - \omega_e. \end{aligned} \tag{S12}$$

We can rewrite Eq. (S10) as

$$\begin{aligned} S(\omega,T) = &\frac{1}{\pi\hbar^2}\sum_{ee'c}\mathrm{Im}\int_{-\infty}^{+\infty}\mathrm{d}\Omega\int_{-\infty}^{+\infty}\mathrm{d}t\int_{-\infty}^{+\infty}\mathrm{d}\tau\mathrm{e}^{-\mathrm{i}\omega_{ee'}t}\mathrm{e}^{-\mathrm{i}\Omega\tau}\\ &\Big[\mathscr{A}^*(t)c^*_{e'}(t)\,\langle\chi_{e'}(t)|\frac{d^*_{ce'}d_{ce}}{\Omega+\omega-\omega_{ce}+\mathrm{i}\Gamma_c}|\chi_e(t-\tau)\rangle\,c_e(t-\tau)\mathscr{A}(t-\tau)\\ &-\mathscr{A}^*(t-\tau)c^*_{e'}(t-\tau)\,\langle\chi_{e'}(t-\tau)|\frac{d^*_{ce'}d^*_{ec}}{\Omega-\omega-(\omega_c+\omega_{e'})+\mathrm{i}\Gamma_c}|\chi_e(t)\rangle\,c_e(t)\mathscr{A}^*(t)\mathrm{e}^{\mathrm{i}(2\omega)t}\Big] \end{aligned} \tag{S13}$$

The third line in Eq.(S13) should be ignored. First of all, we define a time domain function $f_e(t) = \mathscr{A}(t)c_e(t)\,|\chi_e(t)\rangle$ and then the time domain integral of the third line in Eq.(S13) can be written as

$$\int_{-\infty}^{+\infty}\left[\int_{-\infty}^{+\infty}f^*_{e'}(t-\tau)f_e(t)\mathrm{e}^{-\mathrm{i}(\omega_{ee'}-2\omega)t}\mathrm{d}t\right]\mathrm{e}^{-\mathrm{i}\Omega\tau}\mathrm{d}\tau \tag{S14}$$

after defining

$$\mathcal{F}[f(t)]\,(\omega) = \int_{-\infty}^{+\infty}f(t)\mathrm{e}^{-\mathrm{i}\omega t}\mathrm{d}t.$$

By using the cross-correlation and frequency-shift property, Eq.(S14) can be written as

$$\mathcal{F}[f_e(t)]^*(\Omega)\cdot\mathcal{F}[f_{e'}(t)]\,(\Omega+\omega_{ee'}-2\omega). \tag{S15}$$

Since

$$\mathcal{F}[\mathscr{A}(t)](\omega) = \exp\left(-\frac{\xi^2\omega^2}{2}\right)\mathrm{e}^{-\mathrm{i}\omega T}, \tag{S16}$$

the Fourier transform of $f_{e(e')}(t)$ also gives Gaussian similar result with a full width at half maximum (FWHM) of $2\sqrt{2\ln 2}/\xi \sim 2$ eV. So, to guarantee the nonvanishing of Eq.(S15), there are limitations of $\Omega \sim 0$ and $\omega \sim \omega_{ee'}/2$. But the limitations will result a large denominator of third line of Eq.(S13) since the core state energy ω_c is always much larger than valence state enery $\omega_{e(e')}$, which will give a vanishing contribution to total signal. By throwing away the the third line of Eq.(S13) and redefining the Fourier transform (FT) as

$$\mathcal{F}[f(t)](\omega) = \int_{-\infty}^{+\infty} f(t)\mathrm{e}^{\mathrm{i}\omega t}\mathrm{d}t,$$

The transient absorption can be finally written as

$$S_{\mathrm{abs}}(\omega, T) = \frac{1}{\pi\hbar^2}\sum_{ee'c}\mathrm{Im}\int \mathrm{d}\boldsymbol{q} d^*_{ce'}d_{ce}\int_{-\infty}^{+\infty}\mathrm{d}\Omega\frac{\mathcal{F}[f_{e'}(t)]^*(\Omega+\omega_{ee'})\mathcal{F}[f_e(t)](\Omega)}{\Omega+\omega-\omega_{ce}+\mathrm{i}\Gamma_c}, \tag{S17}$$

which is mentioned in the main text.

S-II. EXPNADING THE LAGUERRE-GAUSSIAN BEAM AND THE TRANSITION CURRENT DENSITY IN HERMITE-GAUSSIAN BASIS

In general, the size of the molecule is much smaller than the range of the beam. Since we choose $w_0 = 60$ nm in our simulation, we can do the approximation in the Laguerre-Gaussian (LG) beam as $w(z) \to w_0$, $R(z) \to \infty$, $\frac{z}{z_R} \to 0$, and the LG beam is simplified to

$$\mathrm{LG}_{lp}(r,\phi,z) = \frac{1}{w_0}\sqrt{\frac{2p!}{\pi(p+|l|)!}}\exp\left(-\frac{r^2}{w_0^2}\right)\left(\frac{\sqrt{2}r}{w_0}\right)^{|l|}L_p^{|l|}\left(\frac{2r^2}{w_0^2}\right)\mathrm{e}^{\mathrm{i}l\phi}\mathrm{e}^{\mathrm{i}kz}. \tag{S18}$$

There are examples of the spatial profiles of the LG beams with $l = \pm 1$ shown in Fig. 1 of main text, as well as compared with circularly polarized light.

For the definition of the Laguerre polynomials

$$L_p^l(x) = \frac{e^x x^{-l}}{p!}\frac{\mathrm{d}^p}{\mathrm{d}x^p}\left(\mathrm{e}^{-x}x^{p+l}\right), \tag{S19}$$

and the Hermite polynomials

$$H_t(x) = (-1)^t\exp\left(x^2\right)\left(\frac{\mathrm{d}}{\mathrm{d}x}\right)^t\exp\left(-x^2\right), \tag{S20}$$

we can write the follow expansion[3]:

$$\begin{aligned}\mathcal{L}_{lp}(x,y) &\equiv \mathrm{e}^{\mathrm{i}l\phi}r^{|l|}L_p^{|l|}(r^2)\\ &= \frac{(-1)^p}{2^{2p+|l|}p!}\sum_{u=0}^{p}\sum_{v=0}^{|l|}\mathrm{i}^{\mathrm{sgn}(l)v}\binom{p}{u}\binom{|l|}{v}H_{2u+|l|-v}(x)H_{2p-2u+v}(y),\end{aligned} \tag{S21}$$

in which sgn() is the sign function. The LG beam is finally written as

$$\mathrm{LG}_{lp}(x,y,z) = \frac{1}{w_0}\sqrt{\frac{2p!}{\pi(p+|l|)!}}\exp\left(-\frac{x^2+y^2}{w_0^2}\right)\mathcal{L}_{lp}\left(\frac{\sqrt{2}x}{w_0},\frac{\sqrt{2}y}{w_0}\right)\mathrm{e}^{\mathrm{i}kz}, \tag{S22}$$

and the vector potential of LG beam reads

$$\mathbf{A}(\boldsymbol{r},l) = \mathrm{LG}_{lp}(x,y,z)\frac{\hat{\mathbf{e}}_x+\mathrm{i}\sigma\hat{\mathbf{e}}_y}{\sqrt{1+|\sigma|}}, \tag{S23}$$

where $\sigma = 0, +1, -1$ corresponds to linearly polarized, left circularly polarized, and right circularly polarized light.

Next we consider the transition current density. First the electronic wavefunctions are expanded in Gaussian basis as

$$\varphi_\mu(\boldsymbol{r}) = \sum_A c_{\mu A} \sum_a \beta_a G_{ijk}(\boldsymbol{r}_A, a), A \equiv \{\boldsymbol{r}_A, \{a, \beta_a, i, j, k\}\}, \tag{S24}$$

in which

$$G_{ijk}(\boldsymbol{r}, a, \boldsymbol{A}) = G_{ijk}(a, \boldsymbol{r}_A) = x_A^i y_A^j z_A^k \exp\left(-a r_A^2\right), \begin{cases} a > 0 \\ \boldsymbol{r}_A = \boldsymbol{r} - \boldsymbol{A} \\ i \geq 0, j \geq 0, k \geq 0 \end{cases} \tag{S25}$$

is the Cartesian Gaussian-type orbitals (CGTO) , and $c_{\mu A}$ are the expansion coefficients on different Gaussian center A with various CGTO parameters. Second the CGTO can be separated into three Cartesian directions

$$G_{ijk}(a, \boldsymbol{r}_A) = G_i(a, x_A) G_j(a, y_A) G_k(a, z_A) \tag{S26}$$

with one-dimension CGTO (1d-CGTO)

$$\begin{aligned} G_i(a, x_A) &= x_A^i \exp\left(-a x_A^2\right) \\ \frac{\partial G_i(a, x_A)}{\partial x} &= -2a G_{i+1}(a, x_A) + i G_{i-1}(a, x_A) \end{aligned} \tag{S27}$$

and the product of two 1d-CGTO can be expanded in Gaussian-Hermite functions as

$$\Omega_{ij}(x; a, b, A_x, B_x) \equiv G_i(a, x_A) G_j(b, x_B) = \sum_{t=0}^{i+j} E_t^{ij} \Lambda_t(p, x_P) \tag{S28}$$

in which $p = a + b$, $P_x = (aA_x + bB_x)/p$, E_t^{ij} are the expansion coefficients, and $\Lambda_t(p, x_P)$ is the Gaussian-Hermite function reads

$$\begin{aligned} \Lambda_t(p, x_P) &\equiv \left(\frac{\partial}{\partial P_x}\right)^t \exp\left(-p x_P^2\right) \\ &= p^{t/2} H_t(p^{1/2} x_P) \exp\left(-p x_P^2\right). \end{aligned} \tag{S29}$$

So, the transition current density

$$\boldsymbol{j}_{\mu\nu}(\boldsymbol{r}) \equiv \frac{e\hbar}{2m_\mathrm{e}\mathrm{i}} \left[\varphi_\mu^* (\boldsymbol{\nabla} \varphi_\nu) - (\boldsymbol{\nabla} \varphi_\mu^*) \varphi_\nu\right] \tag{S30}$$

can be written as

$$\begin{aligned} \boldsymbol{j}_{\mu\nu} = \frac{1}{2\mathrm{i}} [\varphi_\mu (\boldsymbol{\nabla} \varphi_\nu) - (\boldsymbol{\nabla} \varphi_\mu) \varphi_\nu] = \frac{1}{2\mathrm{i}} \sum_{AB} c_{\mu A} c_{\nu B} \sum_{ab} \beta_a \gamma_b \Big\{ \\ \Big[l G_i(a, x_A) G_{l-1}(b, x_B) - 2b G_i(a, x_A) G_{l+1}(b, x_B) - i G_{i-1}(a, x_A) G_l(b, x_B) + 2a G_{i+1}(a, x_A) G_l(b, x_B)\Big] \\ \times G_j(a, y_A) G_m(b, y_B) G_k(a, z_A) G_n(b, z_B) \hat{\mathbf{e}}_x + \\ \Big[m G_j(a, y_A) G_{m-1}(b, y_B) - 2b G_j(a, y_A) G_{m+1}(b, y_B) - j G_{j-1}(a, y_A) G_m(b, y_B) + 2a G_{j+1}(a, y_A) G_m(b, y_B)\Big] \\ \times G_i(a, x_A) G_l(b, x_B) G_k(a, z_A) G_n(b, z_B) \hat{\mathbf{e}}_y + \\ \Big[n G_k(a, z_A) G_{n-1}(b, z_B) - 2b G_k(a, z_A) G_{n+1}(b, z_B) - k G_{k-1}(a, z_A) G_n(b, z_B) + 2a G_{k+1}(a, z_A) G_n(b, z_B)\Big] \\ \times G_i(a, x_A) G_l(b, x_B) G_j(a, y_A) G_m(b, y_B) \hat{\mathbf{e}}_z \Big\}. \end{aligned} \tag{S31}$$

By using the multiplication theorem of Hermite polynomials

$$H_s(\lambda x) = s! \sum_{t=0}^{\lfloor s/2 \rfloor} \frac{\left(\lambda^2 - 1\right)^t \lambda^{s-2t}}{t!(s-2t)!} H_{s-2t}(x) \tag{S32}$$

and the overlap integals between Hermite Gaussians[4]

$$\int \Lambda_m(a,x_A)\Lambda_n(b,x_B)\mathrm{d}x = (-1)^n\left(\frac{\pi}{a+b}\right)^{1/2}\Lambda_{m+n}(\frac{ab}{a+b},B_x-A_x), \tag{S33}$$

the light-matter interaction quantity defined in Eq. (S8) is finally written as

$$\begin{aligned} d_{\mu\nu} = &\int \boldsymbol{A}(\boldsymbol{r};\sigma,q,L,w_0,\kappa)\cdot \boldsymbol{j}_{\mu\nu}(\boldsymbol{r})\mathrm{d}\boldsymbol{r} = \frac{1}{2\mathrm{i}}\frac{1}{w_0}\sqrt{\frac{2q!}{\pi(q+|L|)!}}\frac{(-1)^q}{2^{2q+|L|}q!}\sum_{AB}c_{\mu A}c_{\nu B}\sum_{ab}\beta_a\gamma_b \\ &\left[\sum_{t=0}^{k+n}E_{Zt}^{kn}I_t(p,P_z,\kappa)\right]\sum_{u=0}^{q}\sum_{v=0}^{|L|}\mathrm{i}^{\mathrm{sgn(L)}v}\binom{q}{u}\binom{|L|}{v}\Bigg\{ \\ &\quad\left[\sum_{t=0}^{i+l+1}\left(lE_{Xt}^{i,l-1}-2bE_{Xt}^{i,l+1}-iE_{Xt}^{i-1,l}+2aE_{Xt}^{i+1,l}\right)I_{2u+|L|-v,t}(p,P_x,w_0)\right] \\ &\quad\times\left[\sum_{t=0}^{j+m}E_{Yt}^{jm}I_{2q-2u+v,t}(p,P_y,w_0)\right] \\ &+\mathrm{i}\sigma\left[\sum_{t=0}^{j+m+1}\left(mE_{Yt}^{j,m-1}-2bE_{Yt}^{j,m+1}-jE_{Yt}^{j-1,m}+2aE_{Yt}^{j+1,m}\right)I_{2q-2u+v,t}(p,P_y,w_0)\right] \\ &\quad\times\left[\sum_{t=0}^{i+l}E_{Xt}^{il}I_{2u+|L|-v,t}(p,P_x,w_0)\right]\Bigg\}, \end{aligned} \tag{S34}$$

in which the LG beam is LG_{Lq}, κ is the wavevector of LG light, w_0 is the beam waist, σ is the LG light polarization, the integral I_{st} in x-y plane is

$$\begin{aligned} I_{st}(p,P_x,w_0) &\equiv \int \exp\left(-\frac{x^2}{w_0^2}\right)H_s\left(\frac{\sqrt{2}x}{w_0}\right)\Lambda_t(p,x_P)\mathrm{d}x \\ &= \left(\frac{\pi}{w_0^{-2}+p}\right)^{1/2}\left(\sqrt{2}w_0\right)^s s!(-1)^t\sum_{u=0}^{\lfloor s/2\rfloor}\left(\frac{1}{2w_0^2}\right)^u\frac{1}{u!(s-2u)!}\Lambda_{s+t-2u}\left(\frac{p}{1+pw_0^2},P_x\right), \end{aligned} \tag{S35}$$

and the integral I_t in z direction is

$$\begin{aligned} I_t(p,P_z,\kappa) &\equiv \int \Lambda_t(p,z_P)\mathrm{e}^{i\kappa z}\mathrm{d}z \\ &= \sqrt{\pi}p^{\frac{t-1}{2}}\mathrm{e}^{\mathrm{i}\kappa P_z}\mathrm{e}^{-\frac{\kappa^2}{4p}}\left(\frac{\mathrm{i}\kappa}{\sqrt{p}}\right)^t. \end{aligned} \tag{S36}$$

S-III. NUCLEAR WAVEPACKET DYNAMICS

The out-of-plane bending motion of the CHO group at the 1170 cm^{-1} normal mode (orange arrows in Fig. 2(a) of main text) is used to construct an one-dimensional nuclear degrees of freedom for our effective Hamiltonian. All quantities, including the potential surfaces of the electronic states and transition dipole moments between valence and core-excited states were evaluated at a total of 351 nuclear grid points. The interaction with the pump-pulse is numerically included in the propagation scheme, by using a 10-fs FWHM Gaussian laser pump in resonance with the $S_0 \to S_1$ transition,

$$\mathcal{E}_{\mathrm{pu}}(t) = a_{\mathrm{pu}}e^{-\frac{(t-t_0)^2}{2\sigma^2}}\cos(\omega_{\mathrm{pu}}(t-t_0)) \tag{S37}$$

where $a_{\mathrm{pu}} = 4.875\times 10^{-2}$ au is the electric field amplitude. $\omega_{\mathrm{pu}} = 5.85$ eV is the central frequency corresponding to the energy gap between the ground state and the S_1 state at the Franck-Condon point, and $\sigma = 10$ fs is the temporal

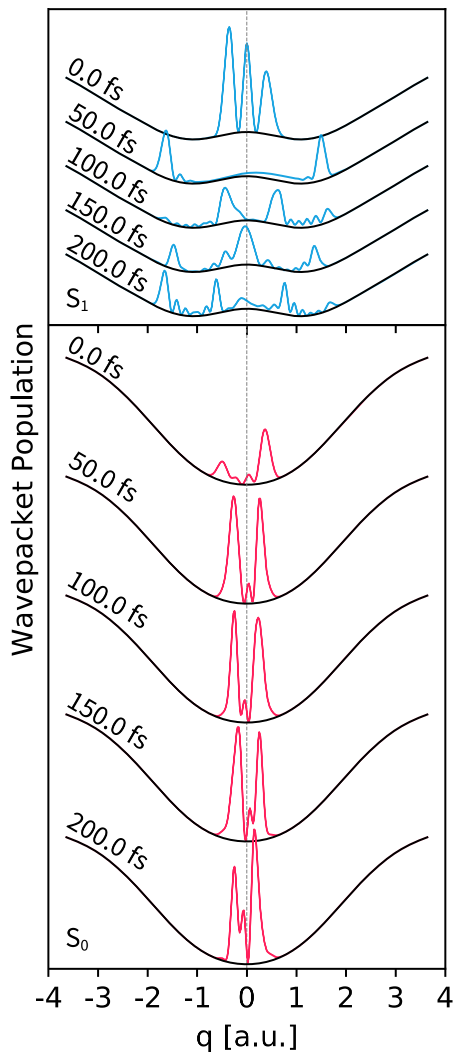

FIG. S1. The wavepacket snapshots of the ground state S_0 (bottom panel) and the valence excited state S_1 (top panel).

duration of the pump pulse. The nuclear wavepacket is then propagated by numerically solving the time-dependent Schrodinger equation on the one-dimensional nuclear grid[5]:

$$i\hbar\frac{\partial}{\partial t}\psi = \boldsymbol{H}\psi = \left[\boldsymbol{T} + \boldsymbol{V} - \boldsymbol{\mu}\boldsymbol{\varepsilon}(t)\right]\psi, \tag{S38}$$

$\boldsymbol{T}$ is the kinetic energy operator of the nuclei, $\boldsymbol{V}$ is the potential energy operator, and $\boldsymbol{\mu}\boldsymbol{\varepsilon}(t)$ describes the light-matter interaction. In our simulation, the propagation of nuclear wavepackets on core-exited states are neglected. The Chebychev propagation[5] with a 0.048 fs time step is employed to propagate this wavepacket until the final time of 458.79 fs. Some wavepacket snapshots are shown in Fig. S1.

S-IV. TIME-RESOLVED HELICAL DICHROISM (TR-HD) AND TIME-RESOLVED CIRCULAR-HELICAL DICHROISM (TR-CHD) FOR ALL HELICAL INDEX l

In our simulation, we choose $p = 0$ in the LG beam LG_{lp}, and we give all simulation results of tr-HD and tr-CHD with $l = 1$ to 4 in the following figures.

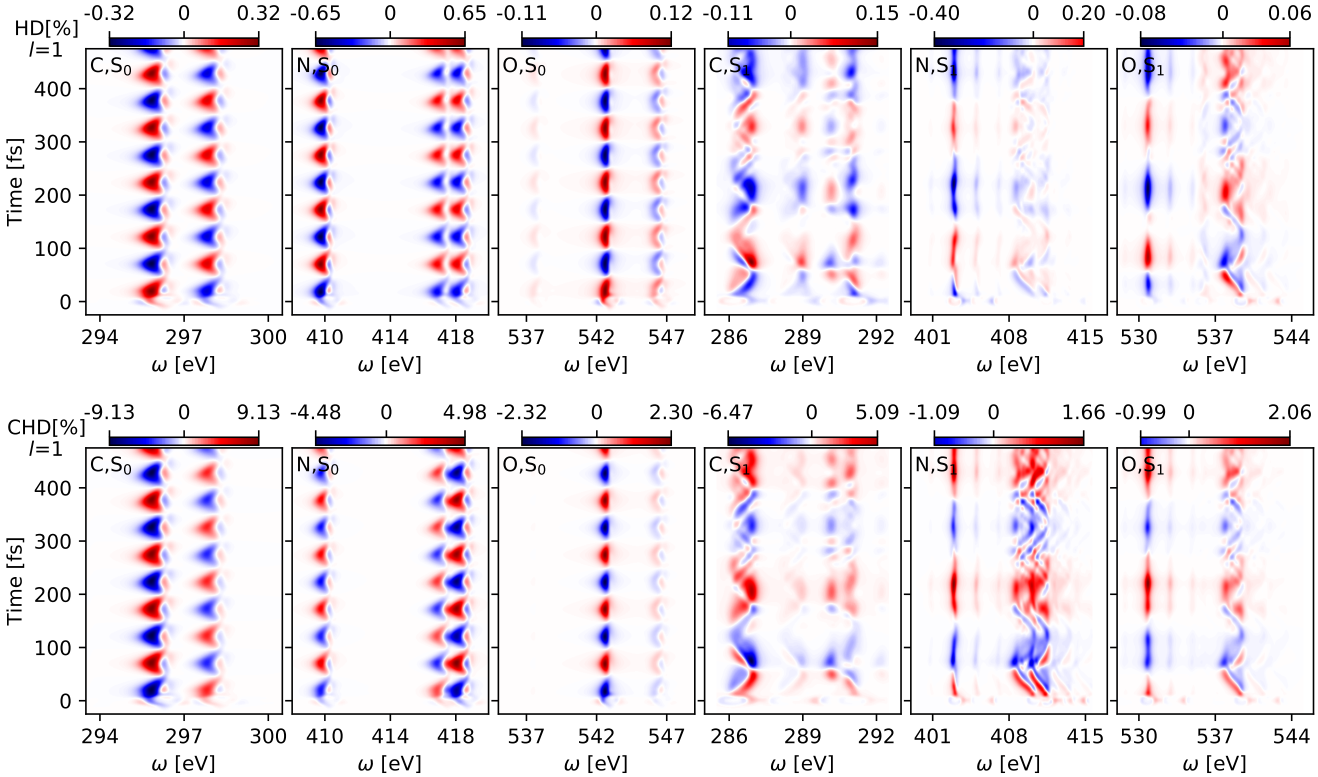

FIG. S2. The tr-HD (top panels) and tr-CHD (bottom panels) signals for $l = 1$ by probing C, N, and O. Left three panels: contributed by ground state S_0. Right three panels: contributed by valence excited state S_1

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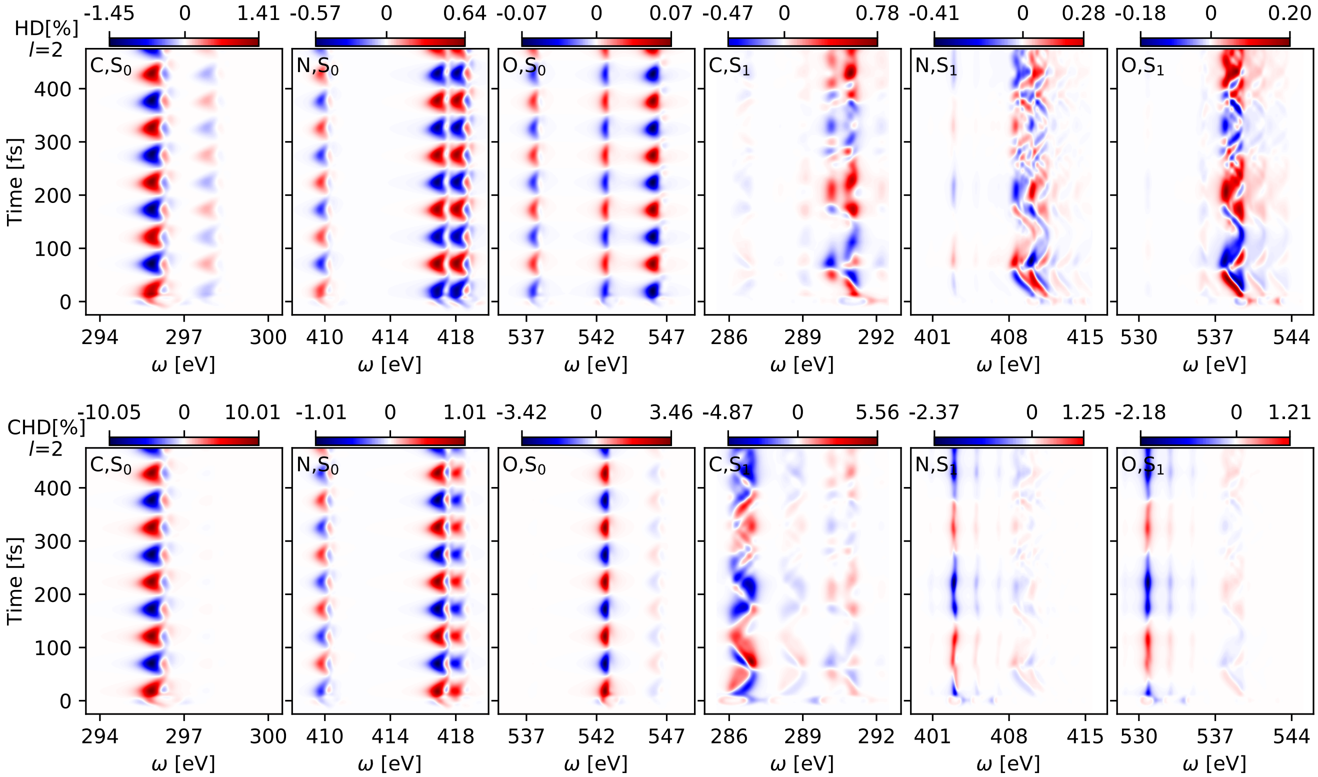

FIG. S3. The tr-HD (top panels) and tr-CHD (bottom panels) signals for $l = 2$ by probing C, N, and O. Left three panels: contributed by ground state S_0. Right three panels: contributed by valence excited state S_1

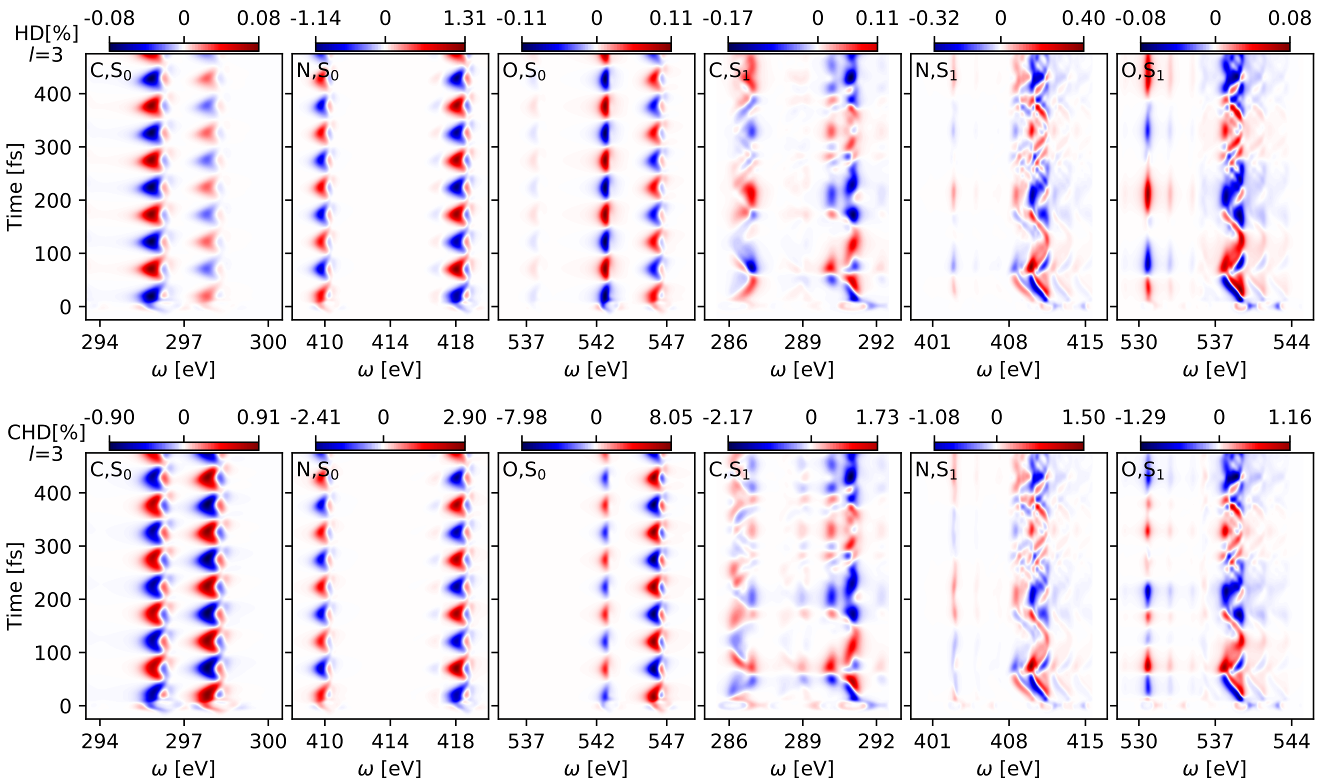

FIG. S4. The tr-HD (top panels) and tr-CHD (bottom panels) signals for $l = 3$ by probing C, N, and O. Left three panels: contributed by ground state S_0. Right three panels: contributed by valence excited state S_1

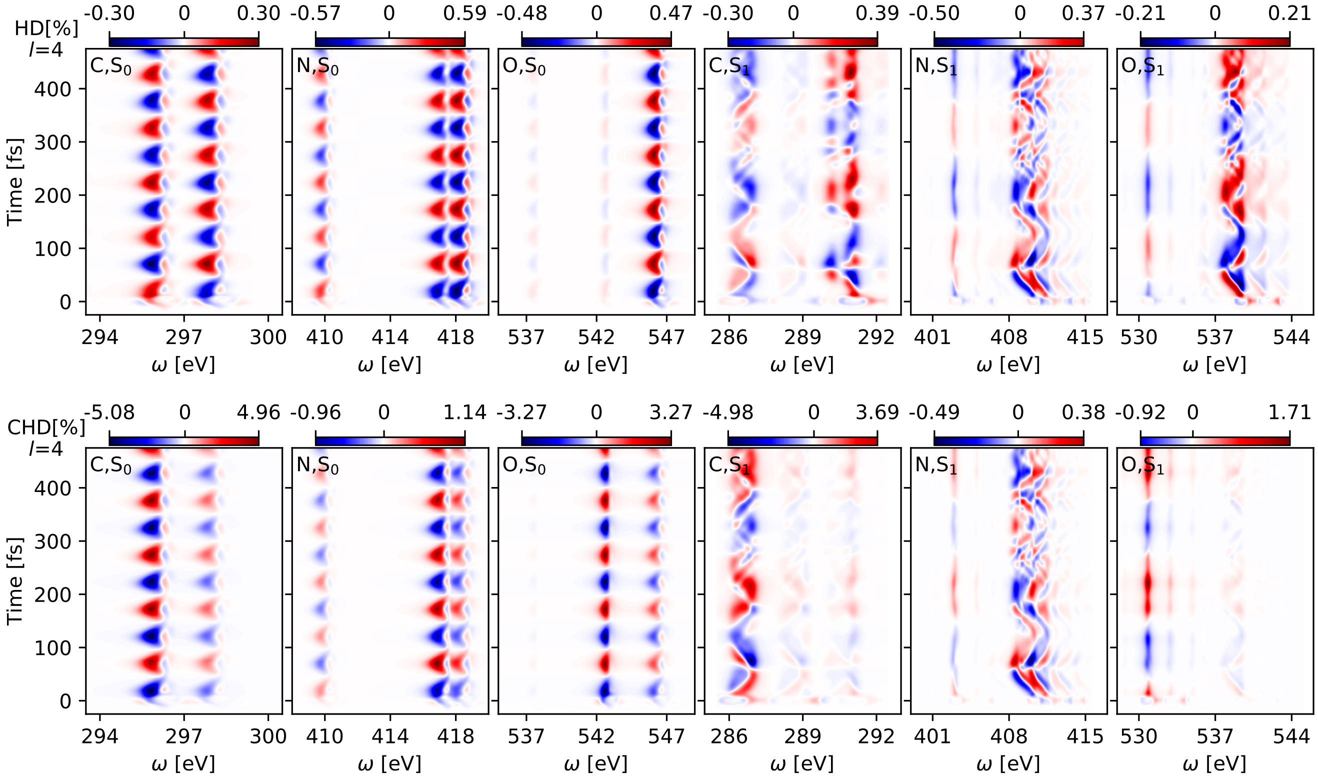

FIG. S5. The tr-HD (top panels) and tr-CHD (bottom panels) signals for $l = 4$ by probing C, N, and O. Left three panels: contributed by ground state S_0. Right three panels: contributed by valence excited state S_1