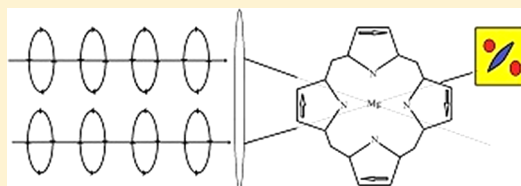


Probing Ring Currents in Mg-Porphyrins by Pump–Probe Spectroscopy

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ABSTRACT: Theoretical studies of Manz et al. have shown that upon excitation of a Mg-porphyrin molecule with a circularly polarized laser pulse, a ring current can be generated that is much stronger than what can be induced by means of an external magnetic field with present technology. We show that the circular dichroism signal of a Mg-porphyrin molecule that has been excited to a state with an inner ring current is proportional to the magnitude of the probability of this ring current and can be used for the detection of this current. In analogy to magnetic circular dichroism, it probes the symmetry of degenerate excited states.



1. INTRODUCTION

The induction of a ring current in molecular and atomic systems, by means of a circularly polarized laser π -pulse, has been proposed.^{1,2} The optical pulse can selectively excite degenerate states with inner ring currents in a short time scale where nuclear motions can be ignored. The chirality of the laser pulse is transferred to the molecular system, inducing a time-dependent asymmetry in the electronic structure. In a Mg-porphyrin molecule, a huge magnetic field of 8048 T is required to induce the same net ring current that can be induced with a circularly polarized laser pulse. A related phenomenon has been observed experimentally in helical wires.^{3,4} In that experiment, it was shown that the yield of optically induced electron transfer in a helical molecule adsorbed on a surface depends on the handedness of the chiral field and of the molecule. Tight-binding models have been used to simulate these circular currents.^{5,6}

In this article, we show that the circular dichroism of an excited ring current is a direct measurement of the magnitude of the ring current, and analyze the symmetry of the degenerate states in the molecular system. The analogy to magnetic circular dichroism is pointed out. In the proposed experiment Mg-porphyrin molecules are first excited with a circularly polarized laser pulse (the pump), and the differential transmittance of a left or a right circularly polarized second pulse (the probe) is then measured as illustrated in Figure 1. The experiment can be viewed as a circular dichroism (CD) of the excited electronic states, and we refer to it as *excited state* CD. Ordinary CD depends on a mixed electric-magnetic polarizability. CD spectroscopy is widely used, e.g., to study chiral conformational changes during photochemical and photobiological processes.⁷ Chiral molecule studies of vibrational CD are commonly applied to peptides.⁸ In the visible domain, the electronic CD spectrum of a variety of molecules, such as chlorophylls and fullerenes, have been studied.^{9,10} In the ultraviolet region, it has been applied to determine the secondary and tertiary structure of proteins.^{11,12} In the X-ray region, CD is used to characterize magnetic materials.^{13,14} Chiral signals for two-dimensional

pump–probe, photon-echo, double-quantum correlation signals, have been simulated for vibrations in polypeptides and for electronic transitions in chromophore aggregates.^{15–17} A two-dimensional coherent optical technique that reveals transition rates between chiral molecular configurations have been proposed.¹⁸

Magnetic circular dichroism (MCD) has been used to study the symmetry of molecular states.¹⁹ Similar information can be obtained by the proposed signal. This signal can also be amplified in a superchiral wave, as shown recently for ordinary CD.²⁰ In section 2, we first introduce the model for E-symmetry states of a Mg-porphyrin. In section 3, we derive the excited state CD signal. In section 4, we compare it with the MCD signal. In section 5, we calculate the probability of ring current of a Mg-porphyrin molecule excited with a circularly polarized laser. In section 6, conclusions are given.

2. MODEL HAMILTONIAN FOR OPTICAL EXCITATION OF MG-PORPHYRIN

We use the model suggested by Manz et al.^{1,2} The total Hamiltonian of the system is

$$H_{\text{total}} = H_0 + H_{\text{int}} \quad (2.1)$$

where H_0 represents the Mg-porphyrin molecule and H_{int} is the coupling with the optical field. The molecule has two degenerate perpendicular in-plane transition dipole moments that define the Q_x and Q_y transitions.^{21,22} We thus model it as a three-level system composed of a ground state, $|g\rangle$, and two degenerate excited states $|e_1\rangle$ and $|e_2\rangle$ that cause the Q_x and Q_y electronic transitions. We thus have

$$H_0 = (\hbar\omega_{eg}|e_1\rangle\langle e_1| + \hbar\omega_{eg}|e_2\rangle\langle e_2|) \quad (2.2)$$

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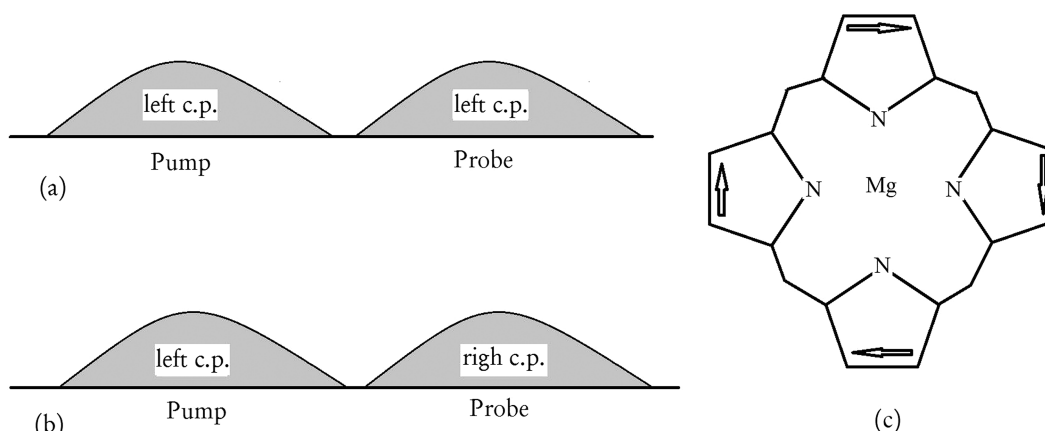


Figure 1. Two pump–probe measurements. The pump is left circularly polarized and the probe is either (a) left circularly polarized or (b) right circularly polarized. The difference between the induced transmittance of the two measurements is related to the magnetic circular dichroism signal and is proportional to the magnitude of the frequency dependent ring current in the Mg-porphyrin. (c) Ring current in the Mg-porphyrin.

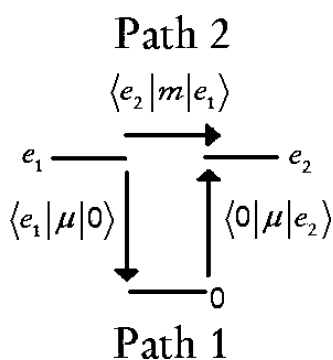


Figure 2. Two pathways for a transition from the state $|e_1\rangle$ to the state $|e_2\rangle$. The parameters are defined in section 2.

where $\hbar\omega_{eg}$ is the transition energy between the ground state and the excited electronic state. The state vectors $|e_1\rangle$ and $|e_2\rangle$ are taken to be real. The circularly polarized pulse laser is represented by

$$\vec{E}^{(l/r)}(t) = \vec{E}^{(l/r)} e^{-i\omega t} + \text{c.c.} \quad (2.3)$$

The amplitude of the field is

$$\vec{E}^{(l/r)} = \frac{|E|}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm i \\ 0 \end{pmatrix} \quad (2.4)$$

The signs ‘+’ and ‘−’ are associated with the superscripts l and r. If an external magnetic field B_z points along the z axis, the interaction Hamiltonian within the rotating wave approximation is

$$H_{\text{int}} = \vec{V} \cdot \vec{E}^{(l/r)*} + \vec{V}^* \cdot \vec{E}^{(l/r)} + \vec{M}_z B_z \quad (2.5)$$

where the transition electric and magnetic dipole operators in the laboratory frame are

$$\vec{V} = \langle g|\vec{\mu}|e^{(l)}\rangle|g\rangle\langle e^{(l)}| + \langle g|\vec{\mu}|e^{(r)}\rangle|g\rangle\langle e^{(r)}| \quad (2.6.a)$$

$$M_z = \langle e^{(l)}|\vec{m}_z|e^{(l)}\rangle|e^{(l)}\rangle\langle e^{(l)}| + \langle e^{(r)}|\vec{m}_z|e^{(r)}\rangle|e^{(r)}\rangle\langle e^{(r)}| \quad (2.6.b)$$

$\langle 0|\vec{m}|e^{(l)}\rangle$ and $\langle 0|\vec{m}|e^{(r)}\rangle$ vanish because the molecule is nonchiral. The state vectors with E-symmetry $|e^{(r)}\rangle$ and $|e^{(l)}\rangle$ are given by^{1,2}

$$|e^{(l)}\rangle = \frac{1}{\sqrt{2}}|e_1\rangle + i\frac{1}{\sqrt{2}}|e_2\rangle \quad (2.7.a)$$

$$|e^{(r)}\rangle = \frac{1}{\sqrt{2}}|e_1\rangle - i\frac{1}{\sqrt{2}}|e_2\rangle \quad (2.7.b)$$

The handedness of these states (l or r) should not be associated with chirality. Chirality is a time-invariant quantity, and the metal-substituted porphyrin is nonchiral.^{1,2} If the plane of polarization of a Mg-porphyrin molecule is perpendicular to the propagation direction of the laser, then a left (right) circularly polarized laser excites the molecule to the state $|e^{(l)}\rangle$ ($|e^{(r)}\rangle$). In a more general case, this apparent chirality is defined in terms of the projection of the wave vector of the laser along an axis that is perpendicular to the plane of polarization of the molecule. We further define the magnitude of the transition electric and magnetic dipoles of the degenerate states as

$$|\mu| = |\langle g|\vec{\mu}|e^{(l)}\rangle| = |\langle g|\vec{\mu}|e^{(r)}\rangle| \quad (2.8.a)$$

$$|m| = |\langle e^{(l)}|\vec{m}|e^{(l)}\rangle| = |\langle e^{(r)}|\vec{m}|e^{(r)}\rangle| = |\langle e_1|\vec{m}|e_2\rangle| \quad (2.8.b)$$

Figure 2 shows the transitions involved in the signal calculated here. For a perturbation to interact with a ring current or E-symmetry state, it must induce a transition between the states $|e_1\rangle$ and $|e_2\rangle$ (polarizing the molecule with circular symmetry). Two pathways for a transition between these states are possible. In the first, a static magnetic field interacts with the transition magnetic dipole $|\langle e_1|\vec{m}|e_2\rangle|$. In the

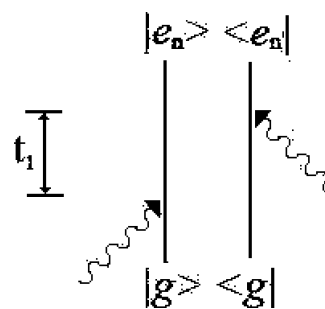


Figure 3. Feynman diagrams for the pump–probe experiment in a Mg-porphyrin molecule. The n and n' may refer to states 1 or 2, associated with the Q_x and Q_y transitions.

second one, an optical field stimulates a transition to the ground state by interacting with the transition electric dipole $\langle e_1 | \vec{\mu} | g \rangle$ and a second interaction excites the molecule to the other excited state by interaction with the transition dipole $\langle g | \vec{\mu} | e_2 \rangle$.

$$S_{(p_1, p_2)}(\omega_1, \omega_2) = \text{Im}\{E_i^{*(p_2)}(\omega_2) E_j^{(p_2)}(\omega_2) E_k^{(p_1)*}(\omega_1) E_l^{(p_1)}(\omega_1) [\chi_{m,o,p,r;1}^{(3)}(-\omega_2; \omega_2, -\omega_1, \omega_1) + \chi_{m,o,p,r;4}^{(3)}(-\omega_2; \omega_2, -\omega_1, \omega_1)] \\ + E_i^{*(p_2)}(\omega_2) E_j^{(p_2)}(\omega_2) E_k^{(p_1)}(\omega_1) E_l^{*(p_1)}(\omega_1) [\chi_{m,o,p,r;2}^{(3)}(-\omega_2; \omega_2, \omega_1, -\omega_1) + \chi_{m,o,p,r;3}^{(3)}(-\omega_2; \omega_2, \omega_1, -\omega_1)]\} \quad (3.1)$$

where p_1 , ω_1 , p_2 , and ω_2 are the polarizations (l or r) and the frequencies of the pump and probe. In Figure 1, we show two pump–probe configurations. In both the pump is left circularly polarized, but the probe is either right or left circularly polarized. We calculate the difference between these signals. Only the first two diagrams of Figure 3 contribute to this differential signal. The susceptibilities corresponding to these diagrams are

$$\chi_{m,o,p,r;1}^{(3)}(-\omega_2; \omega_2, -\omega_1, \omega_1) = -\left(\frac{1}{\hbar}\right)^3 \sum_{q_1=l,r} \frac{\langle e^{(q_2)} | \mu_m | g \rangle \langle g | \mu_o | e^{(q_2)} \rangle \langle g | \mu_p | e^{(q_1)} \rangle \langle e^{(q_1)} | \mu_r | g \rangle}{(\omega_{eg} - \omega_2 - i\gamma_0/2) i\gamma_0 (\omega_{eg} - \omega_1 - i\gamma_0/2)} \quad (3.2.a)$$

$$\chi_{m,o,p,r;2}^{(3)}(-\omega_2; \omega_2, \omega_1, -\omega_1) = -\left(\frac{1}{\hbar}\right)^3 \sum_{q_1=l,r} \frac{\langle e^{(q_2)} | \mu_m | g \rangle \langle g | \mu_o | e^{(q_2)} \rangle \langle g | \mu_p | e^{(q_1)} \rangle \langle e^{(q_1)} | \mu_r | g \rangle}{(\omega_{eg} - \omega_2 - i\gamma_0/2) i\gamma_0 (\omega_1 - \omega_{eg} - i\gamma_0/2)} \quad (3.2.b)$$

where $\gamma_0 = \gamma_r = \gamma_l$ is the relaxation rate for the $|e^{(l)}\rangle$ and $|e^{(r)}\rangle$ excited states. After algebraic manipulations, the signal illustrated in Figure 2 can be written as

$$S_{(l,l)}(\omega_1, \omega_2) - S_{(l,r)}(\omega_1, \omega_2) = \frac{8|E|^4}{\hbar^3} [\langle e_1 | \mu_x | g \rangle \langle g | \mu_y | e_2 \rangle + \langle e_1 | \mu_y | g \rangle \langle g | \mu_x | e_2 \rangle]^2 \\ \times \frac{\gamma_0}{2((\omega_1 - \omega_{eg})^2 + \gamma_0^2/4)((\omega_2 - \omega_{eg})^2 + \gamma_0^2/4)} \quad (3.3)$$

Upon averaging over an isotropic ensemble, it becomes

$$S_{(l,l)}(\omega_1, \omega_2) - S_{(l,r)}(\omega_1, \omega_2) = \frac{8|\mu|^4 |E|^4}{5\hbar^3} \frac{\gamma_0}{2((\omega_1 - \omega_{eg})^2 + \gamma_0^2/4)((\omega_2 - \omega_{eg})^2 + \gamma_0^2/4)} \quad (3.4)$$

The CD signal vanishes if the pump beam is linearly polarized. This signal is capable of detecting the E-symmetry states of the Mg-porphyrin molecule. It is also worth noting that the loss of coherent current by nuclear motion²³ is not a limiting factor in the proposed experiment. If the intensity of the pump does not vanish, the ring current is present as long the excited state populations are different from zero because the excited states are polarized with circular symmetry by the circularly polarized beam.

3. THE EXCITED STATE CD SIGNAL

Double-sided Feynman diagrams of excited state CD are given in Figure 3. The signal is

4. MAGNETIC CIRCULAR DICHROISM

MCD measures the differential absorption for left and right circularly polarized light in the presence of a magnetic field. MCD is used to probe the symmetry of the electronic levels of molecular systems. We briefly review the MCD technique.²⁴ The susceptibility for absorption perturbed by a constant magnetic field in Mg-porphyrin is

$$\chi_{i,j,k}^{(2)}(-\omega, \omega) \equiv \frac{2}{\hbar} \sum_{q_1=l,r} \text{Im} \left(\frac{\langle g | \mu_i | e^{(q_2)} \rangle \langle e^{(q_2)} | m_k | e^{(q_1)} \rangle \langle e^{(q_1)} | \mu_j | g \rangle}{i\gamma_0(\omega - \omega_{eg} - i\gamma_0/2)} \right) \quad (4.1)$$

The corresponding field correlation function is

$$E_{l,m,n}^{(p,p)}(\omega, \vec{r}) = E_l^{*(p)}(\omega, \vec{r}) E_m^{(p)}(\omega, \vec{r}) B_n \quad (4.2)$$

where the magnetic field B_k is constant and frequency independent. Assuming the molecule is fixed respect to the lab frame, the MCD signal is

$$S(\omega) = \frac{B_z |E|^2}{\hbar} [\langle g | \mu_y | e_2 \rangle \langle e_1 | \mu_x | g \rangle + \langle g | \mu_x | e_2 \rangle \langle e_1 | \mu_y | g \rangle] \\ \times \text{Im} \left(\frac{\langle e_2 | m_z | e_1 \rangle}{i\gamma_0(\omega_{eg} - \omega - i\gamma_0/2)} \right) \quad (4.3)$$

where x , y , and z are the coordinates of the lab frame. We had shown that excited state CD is proportional to the square of the term in squared brackets. The rotationally averaged signal can be obtained using the tensor in eq A.3, leading to

$$S(\omega) = \frac{2|\mu|^2 |m||E|^2 B_z}{3\hbar} \text{Im} \left(\frac{1}{\gamma_0(\omega_{eg} - \omega - i\gamma_0/2)} \right) \quad (4.4)$$

The signal is finite because the magnetic field interacts differently with the ring-current induced in the molecule by the left and the right circularly polarized beams.

5. PROBABILITY CURRENTS AND EVOLUTION OF COHERENCES

We now study the probability current in the Mg-porphyrin molecule under irradiation with a circularly polarized beam. An orbital can be written for an electron in the Mg-porphyrin molecule as a linear combination of the HOMO and the degenerate LUMO's

$$\psi = \sum_n c_n \psi_n(\mathbf{r}) \quad (5.1)$$

where $\psi_n(\mathbf{r})$ corresponds to the states $|n\rangle = |e^{(l)}\rangle$, $|e^{(r)}\rangle$, or $|g\rangle$. The elements of the density matrix, for the wave functions in

eqs 5.1, are then given by $\rho_{n',n} = c'_n c_n^*$. The probability current operator is

$$J(\mathbf{r}, \omega) = \frac{\hbar}{2m_e i} |e_1\rangle \langle e_2| \{ \psi_1(\mathbf{r}) \vec{\nabla} \psi_2(\mathbf{r}) - \psi_1(\mathbf{r}) \vec{\nabla} \psi_2(\mathbf{r}) \} \quad (5.2)$$

The frequency and position dependent current is given by $\vec{j}(\mathbf{r}, \omega) = \langle J(\mathbf{r}, \omega) \rho(\omega) \rangle_0$,

$$\vec{j}(\mathbf{r}, \omega) = \frac{\hbar}{m_e} \text{Im}(\rho_{2,1}(\omega)) \{ \psi_1(\mathbf{r}) \vec{\nabla} \psi_2(\mathbf{r}) - \psi_1(\mathbf{r}) \vec{\nabla} \psi_2(\mathbf{r}) \} \quad (5.3)$$

where m_e is the mass of an electron. x' and y' being the axes for the Q_x and Q_y transitions. The spatial dependence within the molecular system is given by the term in curl brackets in eq 5.3.

Let us now calculate the imaginary part of $\rho_{2,1}(\omega)$ under irradiation with a left circularly polarized laser. The relevant double-sided Feynman diagram are shown in Figure 4. Assuming

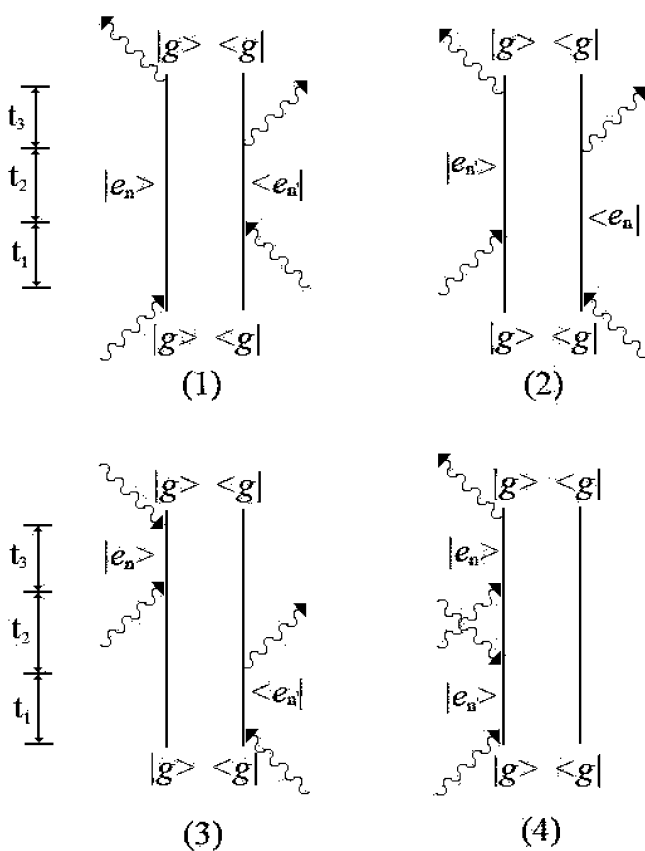


Figure 4. Double-sided Feynman diagram for the coherences between degenerate excited states of the Q-band. $|e_n\rangle \neq |e_{n'}\rangle$ for $n = 1$ or 2 and $n' = 1$ or 2 (the model is described in section 2). $|g\rangle$ is the ground state of the molecule.

a fixed orientation of the molecule with respect to the lab frame, we have

$$\text{Im}(\rho_{2,1}(\omega)) = \frac{2|E|^2}{\hbar} \{ \langle g|\mu_y|e_2\rangle \langle e_1|\mu_x|g\rangle + \langle g|\mu_x|e_2\rangle \langle e_1|\mu_y|g\rangle \} \times \text{Im} \left(\frac{1}{(\omega_{eg} - \omega - i\gamma_0/2)} \right) \quad (5.4)$$

Table 1. Summary of Signals

	signal	oriented sample	rotationally averaged
excited state CD	$\chi_{lll}^{(3)}(-\omega_2, \omega_2, \omega_1, -\omega_1) - \chi_{llr}^{(3)}(-\omega_2, \omega_2, \omega_1, -\omega_1)$	$S_{(l,l)}(\omega_1, \omega_2) - S_{(l,r)}(\omega_1, \omega_2)$ $= \frac{8 E ^4}{\hbar^3} [\langle e_1 \mu_x g\rangle \langle g \mu_x e_2\rangle + \langle e_1 \mu_y g\rangle \langle g \mu_y e_2\rangle]^2$ $\times \frac{\gamma_0}{2((\omega_1 - \omega_{eg})^2 + \gamma_0^2/4)((\omega_2 - \omega_{eg})^2 + \gamma_0^2/4)}$	$S_{(l,l)}(\omega_1, \omega_2) - S_{(l,r)}(\omega_1, \omega_2)$ $= \frac{8 E ^4}{\hbar^3} \times \frac{\gamma_0}{2((\omega_1 - \omega_{eg})^2 + \gamma_0^2/4)((\omega_2 - \omega_{eg})^2 + \gamma_0^2/4)}$
MCD	$\chi_{0ll}^{(2)}(0, -\omega, \omega) - \chi_{0rr}^{(2)}(0, -\omega, \omega)$	$S(\omega) = \frac{ E ^2 B_z}{\hbar} \times [\langle g \mu_y e_2\rangle \langle e_1 \mu_x g\rangle + \langle g \mu_x e_2\rangle \langle e_1 \mu_y g\rangle]$ $\times \text{Im} \left(\frac{\langle e_2 m_z e_1\rangle}{i\gamma_0(\omega_{eg} - \omega - i\gamma_0/2)} \right)$	$S(\omega) = \frac{2 E ^2 B_z \mu ^2 \text{Im}}{3\hbar} \times \text{Im} \left(\frac{1}{\gamma_0(\omega_{eg} - \omega - i\gamma_0/2)} \right)$
frequency and position dependent probability current		$\vec{j}(\mathbf{r}, \omega) = \frac{2 E ^2}{m_e \hbar} \text{Im} \left(\frac{1}{(\omega_{eg} - \omega - i\gamma_0/2)} \right) \times \{ \psi_1(\mathbf{r}) \vec{\nabla} \psi_2(\mathbf{r}) - \psi_2(\mathbf{r}) \vec{\nabla} \psi_1(\mathbf{r}) \}$ $\times [\langle g \mu_y e_2\rangle \langle e_1 \mu_x g\rangle + \langle g \mu_x e_2\rangle \langle e_1 \mu_y g\rangle]$	$\vec{j}(\mathbf{r}, \omega) = \frac{2 E ^2 \mu ^2}{\sqrt{5} \hbar} \times \text{Im} \left(\frac{1}{(\omega_{eg} - \omega - i\gamma_0/2)} \right) \{ \psi_1(\mathbf{r}) \vec{\nabla} \psi_2(\mathbf{r}) - \psi_2(\mathbf{r}) \vec{\nabla} \psi_1(\mathbf{r}) \}$

upon isotropic averaging over random orientations, $\text{Im}(\rho_{1,2}(\omega))$ vanishes. However, each molecule has an internal current. We therefore calculate the root-mean square of eq 5.4, using eq A.4,

$$\sqrt{\langle \text{Im}(\rho_{2,1}(\omega))^2 \rangle_{\text{avg}}} = \frac{2|E|^2|\mu|^2}{\sqrt{5}\hbar} \text{Im}\left(\frac{1}{(\omega_{\text{eg}} - \omega - i\gamma_0/2)}\right) \quad (5.5)$$

The magnetic dipole generated as a consequence of this ring current interacts with the external magnetic field in the MCD experiment discussed in the previous section. This ring current is proportional to the pump–probe signal discussed earlier.

6. CONCLUSIONS

The excited state CD technique described here lifts the degeneracy of E-symmetry excited states by using circularly polarized lasers. The resulting signal is of the same order of magnitude as MCD. As shown in Table 1, the factor that depends on the transition electric dipoles (the terms in squared brackets for the oriented samples) is common to the excited state CD signal, the MCD signal, and the probability of ring current. Thus, the experiment is analogous to MCD, and it allows for the detection of ring currents.

■ APPENDIX A: ROTATIONAL AVERAGING

The theory used to compute the rotationally averaged signal is now briefly summarized. Let the components of the n th rank tensor \mathbf{T} with respect to the a space fixed frame be

$$\mathbf{T}_{i_1 \dots i_n} = l_{i_1 \lambda_1} \dots l_{i_n \lambda_n} \mathbf{T}_{\lambda_1 \lambda_2 \dots \lambda_n} \quad (A.1)$$

where $l_{i_1 \lambda_1}$ is the cosine of the angle between the space-fixed axis i_1 and the molecule-fixed axis λ_1 . Thus, $\mathbf{T}_{\lambda_1 \lambda_2 \dots \lambda_n}$ is the corresponding tensor in the molecule fixed frame. The rotational average requires the average of the product of cosines

$$I^{(n)} = \langle l_{i_1 \lambda_1} \dots l_{i_n \lambda_n} \rangle \quad (A.2)$$

Because $I^{(n)}$ is rotationally invariant, it can be expressed as a linear combination of rotationally invariant tensors, known as *isotropic tensors*. The averaged products of cosines for the tensors used in this article are

$$I^{(3)} = \frac{1}{6} \varepsilon_{i_1 i_2 i_3} \varepsilon_{\lambda_1 \lambda_2 \lambda_3} \quad (A.3)$$

$$I^{(4)} = \frac{1}{30} \begin{pmatrix} \delta_{i_1 i_2} \delta_{i_3 i_4} \\ \delta_{i_1 i_3} \delta_{i_2 i_4} \\ \delta_{i_1 i_4} \delta_{i_2 i_3} \end{pmatrix}^T \begin{pmatrix} 4 & -1 & -1 \\ -1 & 4 & -1 \\ -1 & -1 & 4 \end{pmatrix} \begin{pmatrix} \delta_{\lambda_1 \lambda_2} \delta_{\lambda_3 \lambda_4} \\ \delta_{\lambda_1 \lambda_3} \delta_{\lambda_2 \lambda_4} \\ \delta_{\lambda_1 \lambda_4} \delta_{\lambda_2 \lambda_3} \end{pmatrix} \quad (A.4)$$

Further details on this rotational average formalism can be found elsewhere.²⁵

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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