Zeeman shift of two-dimensional optical signals of Mg-porphyrin dimers with circularly polarized beams

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Two-dimensional (2D) electronic spectra of Mg-porphyrin dimers with circularly polarized laser pulses are simulated for two molecular geometries. The Zeeman shift of the non-chiral 2D spectra induced by a magnetic field highlights spectral regions that are dominated by exciton states with large total angular momentum, and are particularly sensitive to the geometry. These 2D shifts show much higher sensitivity to the molecular array than the absorption spectrum shifts. For different molecular geometries, only the intensity of the 2D spectrum peaks changes while the form of the Zeeman shifts in the 2D frequency space is modified. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4767066]

I. INTRODUCTION

Two-dimensional (2D) optical spectroscopy probes correlations between coupled vibrational and electronic transition dipoles,^{1,2} and provides high resolution information on molecular structure. The polarization of four optical pulses can be controlled to reveal detailed molecular properties. Combinations of linear polarization configurations have been used to increase the resolution of cross-peaks in infrared 2D spectra of organic compounds,³ and to measure the angles between chromophores in the CP29 light harvesting complex.⁴ Simulations based on genetic algorithms have also been used to construct optimal pulse polarizations and analyze selected features of two-dimensional spectra of porphyrin dimers.⁵

Here, we study two-dimensional spectra of Mgporphyrin dimers obtained with circularly polarized beams. A circularly polarized laser pulse can selectively excite degenerate states that carry angular momentum. Upon the absorption of light, the photon angular momentum can be transferred to the electrons and induce a ring current.^{6,7} Metal-substituted porphyrins are heterocycles with a large number of π -electrons and a divalent metal at the center. They are of particular interest in biology and material science. The degenerate states that carry an orbital angular momentum are split by an external magnetic field due to the so-called Zeeman effect.^{8–10} We study how circularly polarized pulses and Zeeman splitting can be combined to increase the sensitivity of the technique to molecular geometry.

Two-dimensional spectroscopy with circularly polarized beams may be used to probe correlations between transitions with orbital angular momentum. Correlations between Mgporphyrin dimers embedded in a phospholipid bilayer membrane have been simulated recently using two-dimensional spectroscopy with linearly polarized pulses.¹¹ In this article, we first present in Sec. II sum over state expressions for signals with circular polarization. We then obtain a set of independent polarization configurations for the two-dimensional signal in Sec. III. In Sec. IV, we describe the Hamiltonian of a Mg-porphyrin dimer in terms of angular momentum states and the Zeeman effect. 2D spectra are simulated and analyzed in Sec. V. Finally, in Sec. VI, conclusions are given.

II. TWO-DIMENSIONAL SPECTROSCOPY

We focus on coherent third order spectra induced by four short pulses. The output field is detected in the rephasing, $\mathbf{k}_{I} = -\mathbf{k}_{1} + \mathbf{k}_{2} + \mathbf{k}_{3}$ direction. $\mathbf{k}_{1}, \mathbf{k}_{2}$, and \mathbf{k}_{3} are the wave vectors of the first, second, and third pulses (in chronological order). In this article, we use the sum over states approach¹ to calculate the 2D spectra with circularly polarized beams. The photon-echo signal has three contributions

$$R_{K_{I},i}(B;t_{3},t_{2},t_{1}) \propto \sum_{e,e'} \left(\vec{e}_{4}^{(p_{4})} \cdot \vec{\mu}_{ge'}^{(p_{4})}\right) \left(\vec{e}_{3}^{(p_{3})} \cdot \vec{\mu}_{e'g}^{(p_{3})}\right) \left(\vec{e}_{2}^{(p_{2})} \cdot \vec{\mu}_{ge}^{(p_{2})}\right) \left(\vec{e}_{1}^{(p_{1})} \cdot \vec{\mu}_{ge}^{(p_{1})}\right) \times \exp(-i\omega_{e'g}(B)t_{3} - i\omega_{ge}(B)t_{1}),$$
(1a)

$$R_{K_{I},ii}(B;t_{3},t_{2},t_{1})$$

$$\propto \sum_{e,e'} \left(\vec{e}_{4}^{(p_{4})} \cdot \vec{\mu}_{ge'}^{(p_{4})}\right) \left(\vec{e}_{3}^{(p_{3})} \cdot \vec{\mu}_{eg}^{(p_{3})}\right) \left(\vec{e}_{2}^{(p_{2})} \cdot \vec{\mu}_{e'g}^{(p_{2})}\right) \left(\vec{e}_{1}^{(p_{1})} \cdot \vec{\mu}_{ge}^{(p_{1})}\right)$$

$$\times \exp(-i\omega_{e'g}(B)t_{3} - i\omega_{e'e}(B)t_{2} - i\omega_{ge}(B)t_{1}), \quad (1b)$$

$$\begin{aligned} &\mathcal{R}_{K_{I},iii}(B;t_{3},t_{2},t_{1}) \\ &\propto -\sum_{f,e',e} \left(\vec{e}_{4}^{(p_{4})} \cdot \vec{\mu}_{fe}^{(p_{4})}\right) \left(\vec{e}_{3}^{(p_{3})} \cdot \vec{\mu}_{e'f}^{(p_{3})}\right) \left(\vec{e}_{2}^{(p_{2})} \cdot \vec{\mu}_{e'g}^{(p_{2})}\right) \\ &\times \left(\vec{e}_{1}^{(p_{1})} \cdot \vec{\mu}_{ge}^{(p_{1})}\right) \\ &\times \exp(-i\omega_{fe}(B)t_{3} - i\omega_{e'e}(B)t_{2} - i\omega_{ge}(B)t_{1}). \end{aligned}$$
(1c)

The transition frequencies, $\omega_{ab}(B)$, depend on a constant external magnetic field *B* which causes the Zeeman splitting. $\vec{\mu}_{ab}^{(p_n)}$ are the transition dipole moments. $\vec{e}_n^{(p_n)}$ is the polarization of the pulse in the frequency domain. $p_n = r$, *l* denotes right- or left-circular polarizations. *e* and *e'* are single exciton

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states and f doubly excited states. The total signal is

$$S_{K_{I}}(B; t_{3}, t_{2}, t_{1}) \propto R_{K_{I}, i}(B; t_{3}, t_{2}, t_{1}) + R_{K_{I}, ii}(B; t_{3}, t_{2}, t_{1}) + R_{K_{I}, iii}(B; t_{3}, t_{2}, t_{1}),$$
(2)

the pulses are of the form

$$E^{(p_n)}(t) = \lambda_n \vec{e}^{(p_n)} A(t - t_n) \cos(\omega_n (t - t_n) + \phi_n), \qquad (3)$$

 ω_n are the corresponding carrier frequencies. $A(t - t_j)$ is the pulse envelop, with λ_n being the maximum intensity of the pulse. Multidimensional signals are displayed in the frequency domain by a Fourier transform with respect to the time intervals between the pulses

$$S_{\mathbf{k}_{\mathbf{s}}}^{(3)}(B;\Omega_{3},t_{2},\Omega_{1}) = \int_{-\infty}^{\infty} \mathrm{d}t_{3} \int_{-\infty}^{\infty} \mathrm{d}t_{1} e^{i\Omega_{3}t_{3}+i\Omega_{1}t_{1}} S_{\mathbf{k}_{\mathbf{s}}}^{(3)}(B;t_{3},t_{2},t_{1}), \quad (4)$$

 Ω_1 and Ω_3 are the transform variables conjugate to t_1 and t_3 . For the absorption spectra, we use Lorentzian line shapes

$$S_{abs}^{(1)}(B;\omega) = \frac{\omega \gamma_{eg} |\mu_{0e}|^2}{(\omega - \omega_{eg}(B))^2 + \gamma_{eg}^2}.$$
 (5)

III. INDEPENDENT CIRCULAR POLARIZATION CONFIGURATIONS

The response function contains a tensor product of four transition dipoles 1

$$S \propto \langle \boldsymbol{\mu}_4^{(q_4)} \boldsymbol{\mu}_3^{(q_3)} \boldsymbol{\mu}_2^{(q_2)} \boldsymbol{\mu}_1^{(q_1)} \rangle,$$
 (6)

where q_n denotes the rotational symmetry of the transition, $q_n = r$ clockwise (right) or $q_n = l$ anti-clockwise (left). This handedness is defined with respect to the wave vector of the laser that induces the excitation. After excitation with circularly polarized beams, electrons may acquire angular momentum. Rotational averaging is over molecular orientation performed using Eq. (A3). The three-independent polarization configurations are given by Eq. (A4). Independent sets can be built from linear combination of the independent vectors $\mathbf{F}_1^{(4)} = (1, 0, 0)$, $\mathbf{F}_2^{(4)} = (0, 1, 0)$, and $\mathbf{F}_3^{(4)}$ = (0, 0, 1). When the Zeeman effect is accounted for, the orientation of the molecules also affects the energy in the denominators and the orientational averaging must be carried out numerically. The independent polarization configurations in Table I only apply in the absence of a magnetic field.

Table I shows the independent polarization configurations of circularly polarized beams. l or r denote a left or a right circularly polarized beam propagating along the z axis. Unlike for linearly polarized pulses,¹ the configurations in Table I depend on the propagation direction. The reason is that

TABLE I. Independent polarization configurations for the non-chiral KI, KII, and KIII signals.

Polarization configurations	F ⁽⁴⁾
lrll	(0, 1, 1)
llrl	(1, 0, 1)
lllr	(1, 1, 0)

a right-circularly polarized beam propagating along \hat{z} and a left-circularly polarized beam propagating along $-\hat{z}$ produce the same polarization, as long as the light-matter interaction occurs within a spatial region that is small compared with the wavelength of the optical field. The polarization of the electric field of two circularly polarized beams cannot be identical if they propagate in different directions.

When the delay between the second and third pulses is zero, the first and second polarization configurations in Table I are identical. The llrl - lllr configuration cancels single exciton contributions and is especially sensitive to the geometry.

IV. MODEL HAMILTONIAN FOR AN OPTICALLY DRIVEN Mg-PORPHYRIN DIMER IN A MAGNETIC FIELD

We use the model previously reported in Ref. 11 but extended to include ring currents following Manz *et al.*^{6,7} The total Hamiltonian of the system is

$$H_{\text{total}} = H_0 + H_{\text{int}},\tag{7}$$

where H_0 represents the Mg-porphyrin dimer and H_{int} is the coupling with the optical field. Every Mg-porphyrin molecule is modeled as a three-level system comprised of a ground state, with state vector $|g\rangle$, and two degenerate excited states with state vectors $|e_1\rangle$ and $|e_2\rangle$ that correspond to the in-plane Qx and Qy electronic transitions, Figure 2(a).¹² We further define excited states with E-symmetry $|e^{(r)}\rangle$ and $|e^{(l)}\rangle^{6,7}$

$$|e^{(l)}\rangle = \frac{1}{\sqrt{2}}(|e_1\rangle + i|e_2\rangle), \tag{8a}$$

$$|e^{(r)}\rangle = \frac{1}{\sqrt{2}}(|e_1\rangle - i|e_2\rangle). \tag{8b}$$

In the presence of an external magnetic field the degeneracy of these states is lifted as illustrated in Figure 1(a). Since



FIG. 1. (a) Level scheme for a Mg-porphyrin molecule with a shift ΔE , illustrating the Zeeman effect. (b) Level scheme for a Mg-porphyrin dimer.

the monomers are non-chiral, the definitions of l and r are arbitrary.¹³ If a molecule plane is perpendicular to the propagation direction of the laser, then a left- (right-) circularly polarized laser excites the molecule to the state $|e^{(l)}\rangle$ ($|e^{(r)}\rangle$).

Figure 1(b) gives the level scheme for the Mg-prophyrin dimer. It has four single exciton states and four double exciton states. The Mg-porphyrin molecules are denoted a and b, with ε_a and ε_b the transition energies. We can then write the following complete basis of nine dimer states, $\{|i\rangle\}$, as given products of the ground states and E-symmetry excited states

of the monomers

$$|g\rangle = |g^{(a)}\rangle|g^{(b)}\rangle, |e_{1}\rangle = |e^{(l,a)}\rangle|g^{(b)}\rangle, |e_{2}\rangle = |e^{(r,a)}\rangle|g^{(b)}\rangle, |e_{3}\rangle = |g^{(a)}\rangle|e^{(l,b)}\rangle, |e_{4}\rangle = |g^{(a)}\rangle|e^{(r,b)}\rangle, |e_{5}\rangle = |e^{(l,a)}\rangle|e^{(r,b)}\rangle, |e_{6}\rangle = |e^{(r,a)}\rangle|e^{(l,b)}\rangle, |e_{7}\rangle = |e^{(l,a)}\rangle|e^{(l,b)}\rangle, |e_{8}\rangle = |e_{2}^{(r,a)}\rangle|e_{2}^{(r,b)}\rangle.$$
(9)

The dimer Hamiltonian is

The electronic couplings are given by

$$V_{nm} = \frac{|\mu|^2}{4\pi\varepsilon R^3} \kappa_{nm}^2,\tag{11}$$

where $|\mu|$ is the transition dipole of the Mg-porphyrin molecule. The orientational factor is

$$\kappa_{nm}^{2} = \langle n | \hat{\mu}^{(a)} | m \rangle \cdot \langle m | \hat{\mu}^{(b)} | n \rangle - 3[\langle n | \hat{\mu}^{(a)} | m \rangle \cdot \hat{R}][\hat{R} \cdot \langle m | \hat{\mu}^{(b)} | n \rangle],$$
(12)

where $\hat{\mu}^{(\xi)}$ is the unit dipole operator for the molecule ξ . \hat{R} is a unit vector from the center of one molecule to another.

The interaction with the optical field within the rotating wave approximation is

$$H_{\rm int} = \vec{V}(t) \cdot \vec{E}^{(p)*}(t) + \vec{V}^{*}(t) \cdot \vec{E}^{(p)}(t),$$
(13)

where the transition dipole operator in the laboratory frame is

$$\vec{V} = \sum_{f=5,6,7,8} \sum_{\xi=a,b} \sum_{s=1,2,3,4} \langle g^{(a)} g^{(b)} | \vec{\mu}^{(\xi)} | s \rangle | g^{(a)} g^{(b)} \rangle \langle s | + \langle s | \vec{\mu}^{(\xi)} | f \rangle | s \rangle \langle f |.$$
(14)

The electric field in the circularly polarized pulse laser is

$$E^{(p)}(t) = \lambda \vec{e}^{(p)} A(t - t_0) \cos(\omega(t - t_0) + \phi),$$
(15)

with parameters already defined in Sec. II. The polarization of the field is

$$\vec{e}^{(p)} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1\\ \pm i\\ 0 \end{pmatrix}.$$
 (16)

The signs "+" and "-" are associated with the superscripts p = l and p = r, respectively. The energy shifts, $\varepsilon_{n, Z}$, in Eq. (10) are caused by the Zeeman effect. In the presence of a constant magnetic field B_z in the propagation direction of the laser, the energy of a single or double exciton state $|n\rangle$ of the dimer is shifted by

$$\varepsilon_{n,Z} = -B_z \left(\langle n | \, \vec{m}_z^{(a)} \, | n \rangle + \langle n | \, \vec{m}_z^{(b)} \, | n \rangle \right). \tag{17}$$

V. SIMULATION OF THE SPECTRA

2D spectra, $S_{KI}(0; \Omega_3, 0, \Omega_1)$, for $t_2 = 0$ were calculated for two molecular geometries. The planes of the two Mg-porphyrin molecules are either parallel or perpendicular in these geometries (see Figure 2). The separation between the Mg atoms is 8 Å, and we used the *lrll-lllr* polarization configuration. We assume that when we use a magnetic field of 100 kG perpendicular to the porphyrin plane, it causes a Zeeman splitting of 44 cm⁻¹. This is consistent with previous observations.¹² The optical linewidth was taken from Ref. 15. The same dephasing rate is assumed for all transitions of 200 cm⁻¹. The electronic transition frequencies of the isolated chromophores, $\varepsilon_a = \varepsilon_b$, is 16500.7 cm⁻¹. Rotational averaging was carried out numerically; taking into account that the Zeeman shift (Eq. (17)) depends on the orientation. For this average, we first defined the molecular coordinates in consistency with Fig. 2, and rotated these coordinates along the axis of the Mg atoms and two other perpendicular axes 20 times by



FIG. 2. Geometry of a Mg-prophyrin dimer, illustrated by means of their ring currents. The red arrows represent the angular momentum of the electrons. (a) The angular momentum of both electrons point in the same direction. In (b) they point in perpendicular directions. The separation between the molecule centers is 8 Å.

18° creating a spherical grid with 20 × 20 × 20 sets of coordinates. The signals were calculated for every coordinate set, and subsequently averaged over all the sets. The four laser pulses have a frequency of 15 500 cm⁻¹, and Gaussian profiles with full width at half maximum of 300 cm⁻¹. The pulses have been introduced in the frequency domain.¹⁴ As in a previous work¹¹ optical dephasing, inhomogeneous broadening, and dissipative processes are included by multiplying the signal in the time domain by $\exp(-t_1^2 / \sigma^2)$, and $\exp(-t_3^2 / \kappa^2)$. We have not considered these broadening mechanisms in the calculation of the absorption spectra. These parameters have been chosen to be $\sigma = 108.1$ fs and $\kappa = 98.1$ fs.¹¹ The two-dimensional (Ω_3 , Ω_1) signal reveals correlations between the Mg-porphyrin molecules. The spectral shift induced by the external magnetic field is defined a

$$\Delta S_{KI}^{(3)}(B;\Omega_3,t_2,\Omega_1)$$

= $S_{KI}^{(3)}(B;\Omega_3,t_2,\Omega_1) - S_{KI}^{(3)}(0;\Omega_3,t_2,\Omega_1)\lambda_{2D}$, (18)

where

$$\lambda_{2D} = \frac{S_{KI}^{(3)}(B; 16\,500\,\,\mathrm{cm}^{-1}, t_2, -16\,500\,\,\mathrm{cm}^{-1})}{S_{KI}^{(3)}(0; 16\,500\,\,\mathrm{cm}^{-1}, t_2, -16\,500\,\,\mathrm{cm}^{-1})}.$$
 (19)

Since a displacement of the signal peaks also implies a change in its magnitude due to the variation of the pulse intensity in the frequency domain, the factor λ_{2D} has been introduced so that none of the signals in Eq. (20) is much larger than the other. The frequencies at which λ_{2D} is calculated can be modified to maximize the sensitivity to the molecular geometry. In analogy, the Zeeman shift for the absorption spectra is

$$\Delta S_{abs}^{(1)}(B;\omega) = S_{abs}^{(1)}(B;\omega) - S_{abs}^{(1)}(0;\omega) \lambda_{abs}, \qquad (20)$$

where

$$\lambda_{abs} = \frac{S_{abs}^{(3)}(B; 16\,500\,\,\mathrm{cm^{-1}})}{S_{abs}^{(3)}(0; 16\,500\,\,\mathrm{cm^{-1}})}.$$
(21)

Figures 3(a) and 3(b) show the absorption spectra that are obtained with circularly polarized beams for the two geometries. The two spectra show no appreciable difference and they cannot distinguish between the geometries. Figures 3(c) and 3(d) show the Zeeman shift associated with absorption. It can clearly distinguish between the two geometries. The implementation of this technique in 2D spectroscopy offers higher sensitivity to molecular geometry.

Figures 4(a) and 4(b) show the 2D spectra in the *lrll–lllr* polarization configuration for the molecular geometries in Figures 2(a) and 2(b). The difference in intensity between these spectra is only dependent on the geometry of the molecules, and it is able to distinguish the geometries. Figures 4(d) and 4(e) show the Zeeman shift of the 2D spectra in Figures 4(a) and 4(b) that is experienced in the presence of a magnetic field. These shifts are calculated using Eq. (18). They are different to their corresponding spectra



FIG. 3. Absorption spectra for the first and second geometries are shown in (a) and (b) and their corresponding Zeeman shifts are shown in (c) and (d) calculated using Eq. (20). The two spectra are in the same scale, and the Zeeman shift scale is a thousand times smaller.



FIG. 4. Two-dimensional spectra, $S^{(KI)}(0; \Omega_3, 0, \Omega_1)$, for the first and second geometries are shown in (a) and (b) for the *lrll-lllr* polarization configuration. The Zeeman shifts, $\Delta S^{(KI)}(B; \Omega_3, 0, \Omega_1)$, of these spectra in (c) and (d) has been calculated using Eq. (18). The two spectra are in the same scale, and the scale for their corresponding shifts is a thousand times smaller.

and highlight spectral regions that are dominated by exciton states with large total angular momentum. The form of the 2D shifts for the two geometries is similar, but there is an inversion in the sign of the spectral peaks. The shifts are more sensitive to the geometry than the spectra, as the sign of the peaks can be associated with one of the geometries. It is worth noting that both the double and single exciton states are shifted by the Zeeman effect and this is possibly a reason for the additional sensitivity to the molecular geometry of the Zeeman shift of the 2D spectra respect to the absorption.

VI. CONCLUSIONS

The independent polarization configurations for circularly polarized optical pulses have been derived. The *lrll– lllr*2D spectra were simulated for two geometries of a Mgporphyrin dimer and found to be sensitive to the geometry. The shift of the signal when a static external magnetic field is switched on has been calculated. The Zeeman shift of the 2D spectra is more sensitive to molecular geometry than the 2D spectra and the corresponding shift of the absorption spectra. This shift may also allow for the elimination form the signal of any contribution that implies transitions without angular momentum.

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APPENDIX: ROTATIONAL AVERAGE

The theory used to determine the independent polarization configurations is now summarized. Let the components of the *n*th rank tensor \mathbf{T} with respect to a space fixed frame be

$$T_{i_1\dots i_n} = l_{i_1\lambda_1}\dots l_{i_n\lambda_n} T_{\lambda_1\lambda_2\dots\lambda_n},\tag{A1}$$

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

$$I^{(n)} = \langle l_{i_1\lambda_1} \dots l_{i_n\lambda_n} \rangle, \tag{A2}$$

since $I^{(n)}$ is rotationally invariant it can be expressed as a linear combination of rotationally invariant tensors, known as isotropic tensors. In three dimensions, there are two fundamental isotropic tensors, the Kronecker delta δ_{ij} and the Levi-Cevita epsilon ε_{ijk} . All higher rank isotropic tensors can be expressed as products of fundamental isotropic tensors. The possible products of these tensors, called isomers, are obtained by permuting the indexes $i_1, i_2, ..., i_n$ in a chosen product. The averaged product of cosines for the tensors used in this work is¹⁵

$$I^{(4)} = \frac{1}{30} F^{(4)} \begin{pmatrix} 4 & -1 & -1 \\ -1 & 4 & -1 \\ -1 & -1 & 4 \end{pmatrix} G^{(4)},$$
(A3)

where

$$F^{(4)} = \begin{pmatrix} \delta_{i_1 i_2} \delta_{i_3 i_4} \\ \delta_{i_1 i_3} \delta_{i_2 i_4} \\ \delta_{i_1 i_4} \delta_{i_2 i_3} \end{pmatrix}^{\mathbf{T}}, \qquad (A4)$$

$$G^{(4)} = \begin{pmatrix} \delta_{\lambda_1 \lambda_2} \delta_{\lambda_3 \lambda_4} \\ \delta_{\lambda_1 \lambda_3} \delta_{\lambda_2 \lambda_4} \\ \delta_{\lambda_1 \lambda_3} \delta_{\lambda_2 \lambda_3} \end{pmatrix}.$$
 (A5)

Further details on this rotational average formalism can be found in Ref. 15. The elements of $F^{(4)}$ and $G^{(4)}$ represent the independent polarization configurations.

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