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Three-Dimensional Orientation of the Q_y Electronic Transition Dipole Moment within the Chlorophyll a Molecule Determined by Femtosecond Polarization Resolved VIS Pump–IR Probe Spectroscopy

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Chlorophyll a (Chl a) is the most abundant pigment on earth. It plays an essential role in photosynthesis as a photophysically and photochemically active pigment in plants, algae, and cyanobacteria.¹ Primary energy transfer in photosynthetic complexes and electron transfer in the reaction center is governed by chlorophyll molecules. The efficiency of energy transfer between chlorophyll molecules depends critically on the distance and orientation of their Q_y electronic transition dipole moments (tdm's). Therefore, knowledge of the precise three-dimensional (3D) orientation of the Q_y tdm within the molecular structure is a prerequisite for calculating chlorophyll–chlorophyll interactions, which serve as an input parameter for simulations of absorption spectra and energy transfer.^{2,3} Previous theoretical calculations⁴ predict that the Q_y tdm is parallel to the y -axis. However, this prediction requires calculation of the first electronic excited-state wave function, and such calculations are less reliable than those of the electronic ground-state wave function. Here, we present a method that combines density functional theory (DFT) calculations in the ground state and polarization resolved femtosecond visible pump–infrared probe spectroscopy^{5,6} to obtain the three-dimensional orientation of the Q_y tdm of Chl a .

DFT calculations, using the B3LYP/6-31G* method as implemented in Gaussian03,⁷ were performed to obtain the ground-state structure of Chl a , its vibrational normal modes, and the 3D orientation of their tdm's. Polarization resolved femtosecond visible pump–infrared probe spectroscopy was performed on isotropic samples of Chl a in d_8 -toluene to determine the angles Θ between the Q_y tdm and selected vibrational tdm's, where the 3D orientations of the vibrational tdm's were taken from the DFT calculations. A unique solution of the 3D Q_y tdm requires determining at least three angles Θ with vibrational tdm's of different, linearly independent orientations.

Optical experiments to determine the Q_y tdm of Chl a have previously been performed on partially aligned samples, e.g. on stretched films⁸ or oriented liquid crystals (lc's).⁹ Typically, these experiments measure a single angle of the Q_y tdm, with respect to the macroscopic orientation of the sample in the laboratory frame. Subsequently the measured angle has to be correlated to the molecular frame, which requires knowledge of the full orientation distribution function. As has been stated by Michl and Thulstrup,¹⁰ "it is in principle a hopeless task to try to derive the full orientation distribution function from optical experiments alone". Fragata et al.⁹ concluded from experiments in lamellar phase lc's an angle of 70° for the Q_y tdm of Chl a with the x -axis, while van Zandvoort et al.,⁸ using nitrocellulose films, arrived at an angle of (105 ± 2)°

with respect to the same axis. In both cases it was assumed that the Q_y tdm lies within the x – y plane of the molecule that coincides with the chlorin ring. However, without perfectly aligned samples and by measuring only one angle it is not possible to determine the 3D orientation of the Q_y tdm.

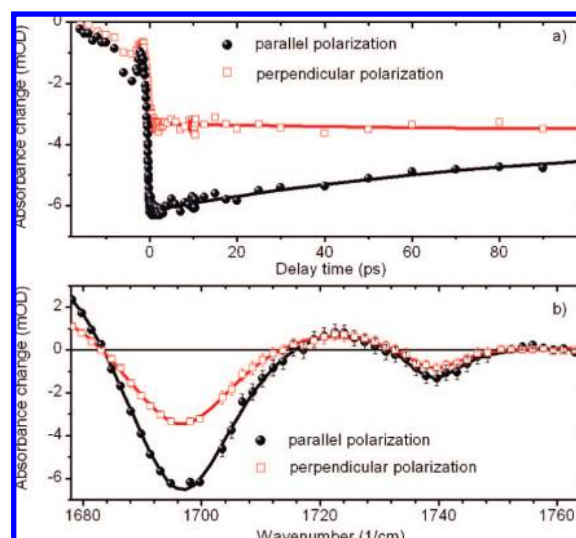


Figure 1. (a) Transients of Chl a after electronic excitation at 665 nm, probed at 1698 cm^{-1} for parallel (black) and perpendicular (red) polarization with respect to the pump pulse. Simulations for both polarizations with rotation relaxation time of 90 ps and lifetime of 5 ns (solid lines). (b) Vibrational difference spectra at $t = 0$ ps for parallel (black) and perpendicular (red) polarization, obtained from the decay associated spectra. Difference spectra simulated for both polarizations with two bleaching and two excited-state absorption bands (solid lines). Occasionally, the symbols are larger than the error bars. Spectral positions and line widths of bleaching bands are taken from the linear absorption spectrum.

We investigated 1–2 mM samples of Chl a from spinach (Sigma-Aldrich) in d_8 -toluene and excited the samples with linearly polarized femtosecond pump pulses in the Q_y absorption band at 665 nm, far away from saturation. The pump pulse induces a polarization on the Q_y transition of Chl a molecules and photoselects predominantly those molecules with their Q_y tdm oriented parallel to the pump polarization. Since the Q_y tdm and the vibrational tdm's are characterized by fixed orientations within the molecular frame, the vibrational tdm's, affected by the excitation, are oriented along a cone with an angle Θ to the Q_y tdm. We probed the vibrational tdm's with femtosecond mid-infrared pulses polarized parallel and perpendicular to the pump pulse polarization, in the range from 1800 cm^{-1} to 1150 cm^{-1} (time resolution ~300 fs). The relative angles Θ of the three strongest bleaching signals were determined

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by evaluation of the dichroic ratios D ($D = A_{\parallel}/A_{\perp}$, with A_{\parallel} and A_{\perp} as the absorption change for parallel and perpendicular polarization, respectively, and $\Theta = \arccos[(2D - 1)/(D + 2)]^{1/2}$). Our pump–probe setup detects only pump induced absorption differences. Therefore, only vibrational bands that undergo a noticeable shift in vibrational frequency contribute to the experimental signal upon Q_y excitation, which implies mainly vibrations of the chlorin ring.

Strong bleaching signals were obtained for the chlorin ring stretching mode $\nu(\text{C}=\text{C})^r$ at 1288 cm^{-1} and the two carbonyl stretching modes $\nu(\text{C}=\text{O})^a$ at 1698 cm^{-1} and $\nu(\text{C}=\text{O})^b$ at 1739 cm^{-1} . The transient signals (Figure 1a) of these modes are well described by a global fitting of the data set with two time constants, of which the first was found to be $(90 \pm 10)\text{ ps}$ and the second was fixed to 5 ns , the excited-state lifetime of Chl *a*.^{11,12} We assign the shorter time constant of 90 ps to the rotational relaxation time of Chl *a* in toluene, which causes the bleach to increase with the delay time for perpendicular polarization and to decrease for parallel polarization.

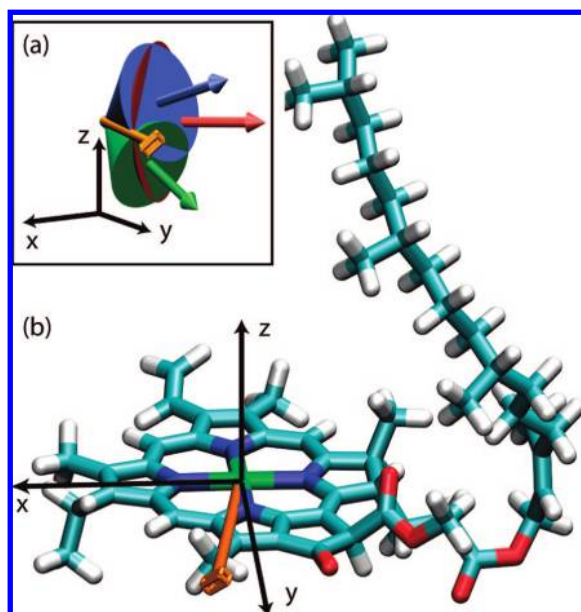


Figure 2. (a) Visualization of three cones around three vibrational tdm's (blue, red, and green arrows, corresponding to $\nu(\text{C}=\text{O})^b$, $\nu(\text{C}=\text{C})^r$, and $\nu(\text{C}=\text{O})^a$ vibrations, respectively) with different cone angles, all three intersecting along one direction. (b) Calculated Chl *a* structure together with the 3D orientation of the Q_y tdm (orange vector) within the molecular frame. The 1σ range of the Q_y tdm is indicated by the orange box.

Decay associated spectra are presented in Figure 1b for both polarizations. From the initial dichroic ratio D we determined the relative angles Θ by an exhaustive search analysis with a confidence interval of 99% (3σ range).¹³ The cone angles are distributed over angle ranges, due to the error margins. We found angles Θ of 35.2° – 60.3° for $\nu(\text{C}=\text{C})^r$, 29.8° – 36.7° for $\nu(\text{C}=\text{O})^a$, and 26.3° – 65.8° for $\nu(\text{C}=\text{O})^b$. A single angle Θ_r , related to $\nu(\text{C}=\text{C})^r$, indicates that the Q_y tdm lies somewhere on a cone with an angle Θ_r around the vibrational tdm. A second

cone, based on the angle Θ_a that the Q_y tdm forms with another vibrational tdm, has at most two intersections with the first cone. A third cone with angle Θ_b for a third vibration cannot yield more than a single unique intersection of all three cones that fixes the three-dimensional Q_y tdm orientation within the molecular structure (see Figure 2a).

The intersections fixing the Q_y orientation create a solution volume in the 3D space with a given probability for each individual intersection.¹⁴ The resulting 3D Q_y tdm orientation within the molecule is shown as an orange vector in Figure 2b, with the 1σ volume as an orange box. Projection angles of the Q_y tdm on the Cartesian axes are $(78 \pm 3)^\circ$ with the x -axis, $(12 \pm 3)^\circ$ with the y -axis, and $(86 \pm 2)^\circ$ with the z -axis.

Our investigations present the first truly three-dimensional determination of the Q_y tdm of Chl *a* in solution and does not depend on experimental orientation distribution parameters. The determined Q_y tdm is $\sim 10^\circ$ closer to the y -axis than the value of Fragata et al.⁹ and lies opposite to the side of the y -axis proposed by van Zandvoort et al.⁸ Furthermore, we found that the Q_y tdm deviates slightly from the x – y plane. This deviation could originate from small distortions of the chlorin ring.

The precise Q_y tdm orientation allows for refined calculations of absorption spectra and energy transfer processes of Chl *a* containing systems. With the exact Q_y orientation of Chl *a* in solution known, distortions induced by protein–cofactor interactions can be analyzed.

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Supporting Information Available: Complete ref 7. Description of the data analysis and of the conditional probability calculations. Coordinates of the Chl *a* ground-state structure. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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