

Determining the Three-Dimensional Electronic Transition Dipole Moment Orientation: Influence of an Isomeric Mixture**

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A new mixed experimental and theoretical approach for determining the exact three-dimensional orientation of electronic transition dipole moments (tdms) within the molecular frame is discussed. Results of applying this method on Chlorophyll a and the dye Coumarin 314 (C314) are presented. For C314 the

possible influence of a mixture of *E*- and *Z*-isomers in the sample on the determined electronic tdm is investigated. Moreover, the robustness of the method is investigated with the C314 data.

1. Introduction

The exact three-dimensional (3D) orientation of electronic transition dipole moments (tdms) within the molecular frame is difficult to come by.^[1] Traditional methods to obtain this kind of information often rely on attempting a macroscopic uniaxial alignment of the molecule of interest, before performing a linear dichroism investigation.^[1–3] This alignment is for instance imposed by stretching polymer films^[3] doped with the molecule of interest, incorporating them in liquid crystals^[2] or lipid bilayers, by using hydrodynamic shear in flowing solutions,^[1] or by applying a strong electric field across the sample.^[1] All these methods have in common that accomplishment of complete uniaxial alignment is hard to guarantee. Moreover, at best the alignment is achieved only along a single axis,^[1] and this therefore precludes extracting the true 3D orientation of the tdm vector. In the gas phase full 3D alignment of molecules has been accomplished in molecular beams,^[4–7] in principle allowing a straightforward determination of tdm orientations of the aligned molecules. Although these results represent an extraordinary experimental feat, extension of this method to protein-cofactors in large biological systems or molecules in the condensed phase is unlikely, and therefore an alternative method is desirable.

Recently, we presented an alternative mixed experimental–theoretical approach to resolving this issue, based on polarization resolved fs UV/visible pump–IR probe spectroscopy on isotropic samples in combination with density functional theory (DFT) calculations of vibrational tdm vectors in the electronic ground state.^[8,9] Briefly, the method consists of determining experimentally the angles between the electronic tdm and vibrational tdm vectors, where the latter have been calculated using DFT. For a single vibrational tdm the angle produces a cone of possible orientations of the electronic tdm. Combining cones for minimally three linearly independent vibrational tdm vectors yields at most a single unique 3D electronic tdm vector solution.^[8,9]

Thus far, the results of this method were reported for the Q_y transition of Chlorophyll a^[8] and for the $S_0 \rightarrow S_1$ transition of Coumarin 314 (C314)^[9] (see Figure 1 for the molecular structures). The importance of determining the Q_y electronic tdm orientation is self-evident, given its enormous importance for all kinds of photosynthetic biological apparatus. Knowledge of the Q_y tdm vector is a crucial input parameter for simulations of absorption spectra, energy transfer kinetics, and calculation of excitonic couplings. C314 presents an additional challenge for the method, as this molecule can adopt either the *E*- or *Z*-isomer conformation.^[10,11] Being capable to experimentally distinguish between isomers is particularly relevant, for instance, if one wishes to identify the 3D conformation of protein cofactors associated with specific active states.^[12–14] For C314 a distinction between the *E*- and *Z*-isomers cannot be made on the basis of standard vibrational absorption spectra.^[9] However, polarization-resolved spectroscopy does provide a handle, particularly due to the drastic polarization difference for the C=O mode, labelled ν_5 . Gas phase calculations predicted a 0.07 eV energy difference^[9] between the *E*- and *Z*-isomer of C314. Based on this, we previously estimated that at room temperature in thermodynamic equilibrium $\sim 7\%$ of the C314 would adopt the *Z*-isomer conformation.^[9]

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[**] Using Femtosecond Polarization-Resolved UV/Vis Pump–IR Probe Spectroscopy

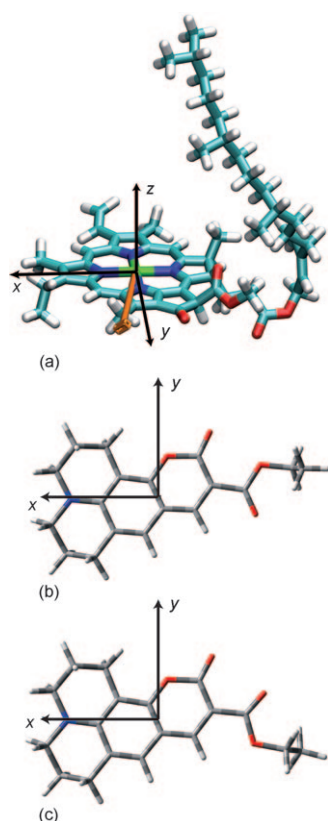


Figure 1. a) Structure of Chlorophyll a with the experimentally determined 3D orientation of the Q_y transition dipole moment (tdm) within the molecular frame (orange line). The orange box indicates the 1σ range of the Q_y tdm solution volume; b) *E*-isomer of Coumarin 314; c) *Z*-isomer of Coumarin 314.

Deducing the isomeric composition from experimentally determined dichroic ratios poses some serious problems. First of all, experimentally determined dichroic ratios depend on the relative signal contributions of both isomers, and thus depend on both the relative presence of the isomers, and on their respective extinction coefficients at both the pump and the probe wavelengths. Second, even if this is known, together with the calculated vibrational tdm vectors, it may still be that the electronic tdm vector differs significantly for the two isomers. Therefore one cannot simply add contributions from projecting correlated vibrational vectors on cartesian axes, but needs to consider projections relative to the electronic tdm vectors. If these have different orientations in the chosen cartesian frame one can either ignore this, introducing a systematic error, or implement calculated values, thereby more or less using the answer to obtain the solution. Neither seems acceptable. In our previous report the analysis was made to only confirm whether the data matched either the *E*-isomer or the *Z*-isomer. As mentioned, for C314 only the mode $\nu_5(\text{C}=\text{O})$ allows distinction between the two isomers. Here, we adopt two approaches to investigate the influence of a mixture of the two isomers on the experimental results. First, we compare the experimental dichroic ratio for $\nu_5(\text{C}=\text{O})$ straightforward to a dependence based entirely on theoretical electronic and vibrational tdm results. Second, we repeated the data analysis with

the $\nu_5(\text{C}=\text{O})$ tdm/electronic tdm angle varied from 49° to 72° , the lower and upper limit of its value according to the experimental error margins. Results of this procedure demonstrate that the determined electronic tdm for C314 is fairly insensitive to these changes, enhancing the reliability of the final result.

Experimental Section

Acetonitrile, Coumarin 314, and Chlorophyll a from spinach were obtained from Sigma–Aldrich and used as received. Polarization resolved femtosecond UV/Vis pump/mid-IR probe experiments were performed at room temperature (23°C), using a Coherent Legend USP Ti:Sa laser/amplifier system (55 fs pulses, centred at 800 nm, with 1 kHz repetition rate) to generate 5–9 μm mid-IR probe pulses and 455 nm UV (for C314) or 665 nm visible (for Chl a) pump pulses in three and four frequency conversion stages, respectively. The obtained tunable mid-IR probe pulses typically had 160 fs pulse duration, 100 cm^{-1} spectral width, and 0.6 μJ energy. The UV pump–IR probe time resolution was 0.3–0.4 ps, and mainly limited by group velocity mismatch. Pump pulses were attenuated to restrict excitation of the C314 molecules to $\sim 3\%$. The probe beam is split into two beams with polarizations perpendicular to each other and overlapped with the pump beam within the sample, for measuring signals for both parallel and perpendicular pump–probe polarizations simultaneously. After passing the sample both probe pulses are dispersed with an imaging spectrograph (grating 150 lines/mm, $f=320\text{ mm}$) and recorded with a 2×32 element MCT array detector (resolution $\sim 1.6\text{ cm}^{-1}$). More details can be found in ref. [9].

2. Results and Discussion

The determination of the Q_y electronic tdm orientation was performed^[8] using three molecular vibrations of the chlorin ring segment, that is, the chlorin ring $\nu(\text{C}=\text{C})^f$ absorbing at 1288 cm^{-1} , and two carbonyl stretching modes $\nu(\text{C}=\text{O})^a$ and $\nu(\text{C}=\text{O})^b$, absorbing at 1698 and 1739 cm^{-1} , respectively. The vibrational tdm vectors were obtained^[8] for these modes in the gas phase lowest energy conformation by DFT calculations performed with Gaussian03, using the B3LYP exchange–correlation functional and 6–31G* or 6–31G** basis sets. The normalized tdm vectors ($x/y/z$) are (0.66/0.75/–0.03) for $\nu(\text{C}=\text{C})^f$, (0.11/0.91/0.39) for $\nu(\text{C}=\text{O})^a$, and (0.33/0.89/–0.31) for $\nu(\text{C}=\text{O})^b$. The modes $\nu(\text{C}=\text{O})^a$ and $\nu(\text{C}=\text{O})^b$ are the asymmetric and symmetric stretch modes involving both the carbonyl group of the chlorin ring and the carbonyl of the proximal ester side-group. Transient absorption spectra for the IR absorption bands of these three vibrations were measured^[8] with parallel and perpendicular pump–probe polarization over the first 100 ps after excitation at 665 nm. Transient spectra at zero delay time were extracted from these data^[8], allowing the calculation of the dichroic ratios $D=A_{\parallel}/A_{\perp}$ (A_{\parallel} and A_{\perp} the absorption change for parallel and perpendicular polarization, respectively), and based on these the angles between the individual vibrational tdm and the electronic tdm can be calculated using Equation (1):

$$\theta = \arccos[(2D-1)/(D+2)]^{1/2} \quad (1)$$

Notice that the obtained angles are restricted to the range 0° – 90° , as experiments for the actual angles $\pm\theta$ and $180^\circ \pm\theta$ (or equivalently, $90^\circ \pm\chi$ and $270^\circ \pm\chi$, with $\chi = 90^\circ - \theta$) all yield the same ratio D . In the same manner this problem exists for traditional attempts to determine the electric tdm direction within the molecular frame based on orienting the molecules in liquid crystals^[2] or stretched polymeric films.^[3] In our method combining angles of at least three linearly independent vibrational tdm's does allow extraction of a unique 3D solution of the electronic tdm in the end.^[8,9] Exhaustive search analysis^[9,15] (ExSeA) provides the following 99% confidence intervals (i.e. 3σ range): 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 $\nu(\text{C}=\text{O})^b$. Next, these three ranges are each divided into 200 intervals and for each of the 8.12 million

($=201^3$) angle combinations of this three-parameter space it is determined if a solution of the electronic tdm exists. A relative probability plot can then be created from all possible electronic tdm solutions, whereby each tdm solution is assigned a weight based on the multiplication of the individual probabilities within their 3σ ranges associated with the three actual angles used in the particular solution (see ref. [9] for a more extensive description). Note that combining two angles ranges can produce 0, 1, or 2 tdm orientations as solutions, while with three angles only 0 or 1 solutions can be obtained, if the used vibrational tdm's are linearly independent. Figure 2 shows projections of the obtained Q_y electronic tdm probability distribu-

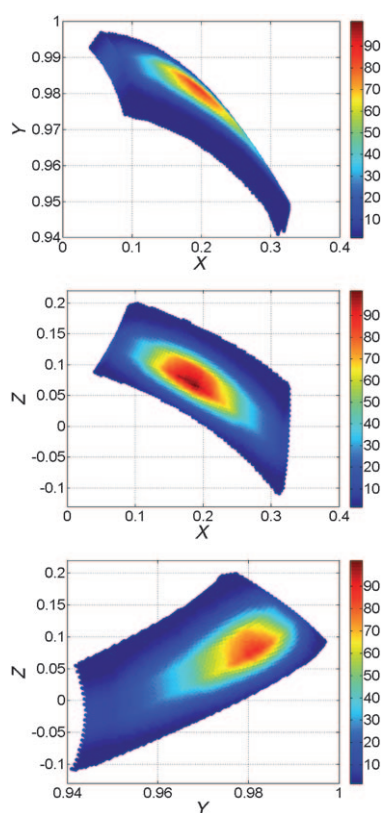


Figure 2. Projections of the 3D solution of the Q_y tdm orientation of Chl a on the cartesian planes.

tion on cartesian axes, chosen such that the X – Y plane coincides with the chlorin ring, and the x -axis goes through atoms C3 and C7, the position of the phytol chain attachment (see Figure 1 a and ref. [2]). Figure 2 illustrates that the most probable normalized Q_y electronic tdm vector is $(x/y/z) = (0.19/0.98/0.07)$; this vector is also depicted in Figure 1 a. While the error margins differ strongly for the various cartesian vector coordinates, that is, <0.01 for the y -coordinate compared to ~ 0.06 for the x -coordinate, representing the solution on a half-sphere produces a fairly symmetrical solution and therefore symmetrical error margins expressed in space angle. The Q_y tdm makes an angle of $(78 \pm 3)^\circ$ with the x -axis, $(12 \pm 3)^\circ$ with the y -axis, and $(86 \pm 2)^\circ$ with the z -axis. Previous determinations gave for Chl a in lamellar phase liquid crystals^[2] a Q_y angle of 70° with the x -axis, and for Chl a in nitrocellulose films^[3] an angle of $(105 \pm 2)^\circ$ with the x -axis. Note that these determinations could not give information if the Q_y tdm makes an angle with the X – Y plane, nor could they in principle distinguish between the angles $90^\circ \pm\theta$ with respect to the axis of orientation. Consequently, angles 105° and 75° are in effect equivalent, in these previous determinations.^[2,3] In contrast, our approach can distinguish between these possibilities, and our solution indicates a slightly larger angle of 78° with the x -axis, as well as an angle of 4° out of the X – Y plane.

The investigations on Coumarin 314 (C314) bring a further complication as this compound can exist both as E - and Z -isomer (Figures 1 b and c), with crystal structures^[10,11] determined for both these isomers. An analysis of the experiment based on the assumption that the molecule is present either in the E - or the Z -isomer gave no electronic tdm vector solution for the Z -isomer, and therefore we concluded that the compound is predominantly in the E -isomer configuration.^[9] Gas phase DFT calculations predicted that the E -isomer is 0.07 eV more stable than the Z -isomer, supporting our results, and based on this energy difference at most 7% of the C314 is expected to adopt the Z -isomer configuration in thermodynamic equilibrium.^[9] Here we will investigate in further detail if more can be said about the actual isomeric mixture on the basis of the experimental data, thereby highlighting explicitly strengths and limitations of this new approach.

Before showing the analysis based on the polarization-resolved experimental data we demonstrate what behaviour might be expected on the basis of vibrational tdm vectors and the relevant electronic C314 tdm vector (455 nm excites the $S_0 \rightarrow S_1$ transition) for both the E - and Z -isomer, that were obtained by DFT calculations.^[9] The normalized calculated $S_0 \rightarrow S_1$ electronic tdm vectors $(x/y/z)$ are $(-0.9822/0.1854/-0.0298)$ and $(-0.9900/0.1400/-0.0164)$ for the E - and Z -isomer, respectively, and these vectors make an angle of 2.8° with each other. Four vibrational modes (with normalized tdm vectors) were used in the analysis of the experimental data, that is, $\nu_1(\text{C}=\text{C})$ $(-0.9966/0.0653/-0.0512)$, $\nu_4(\text{C}=\text{C})$ $(0.9900/-0.1375/0.0316)$, $\nu_5(\text{C}=\text{O})$ $(0.4797/0.8723/0.0950)$, and $\nu_6(\text{C}=\text{O})$ $(-0.5673/0.8204/0.0713)$ for the E -isomer, and $\nu_1(\text{C}=\text{C})$ $(-0.9981/0.0414/-0.0460)$, $\nu_4(\text{C}=\text{C})$ $(0.9889/-0.1468/0.0233)$, $\nu_5(\text{C}=\text{O})$ $(-0.9665/0.2320/-0.1095)$, and $\nu_6(\text{C}=\text{O})$ $(-0.6482/0.7596/0.0527)$ for the Z -isomer. Of these vibrational modes only $\nu_5(\text{C}=\text{O})$, associated

with the ester-group that is flipped around in going from the *E*- to the *Z*-conformation, changes its angle with the electronic tdm more than the experimental 1σ error margin as determined by ExSeA,^[15] namely from 108.2° for the *E*-isomer to 7.6° for the *Z*-isomer. Consequently, only $\nu_5(\text{C}=\text{O})$ can be used to distinguish between these isomers in our experiments. Using these angles as input in Equation (1) we conclude that the *E*/*Z*-isomer theoretical electronic tdm and $\nu_5(\text{C}=\text{O})$ vibrational tdm predict a dichroic ratio $D=0.628$ if the experimental pump-probe signals are solely related to the *E*-isomer of C314, and $D=2.913$ if only *Z*-isomers are responsible for these signals. This ratio D lies in between these two values if both isomers contribute to the pump-probe signals. Note that at a given pump or probe wavelength the extinction coefficients of the electronic or vibrational transitions need not be identical, and therefore a measured dichroic ratio D cannot directly be correlated to an isomeric mixture ratio without further consideration and knowledge of the relevant extinction coefficients. The linear dependence of the theoretically calculated dichroic ratio with a linear increase of the fraction of the total signal coming from the *Z*-isomer can be converted in an angle dependence on this fraction with the help of Equation (1), which is shown in Figure 3. The angle extracted from the experimen-

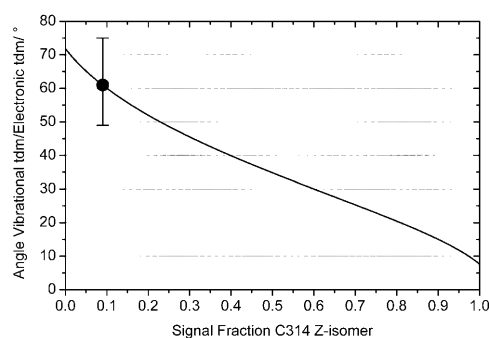


Figure 3. Angle dependence between the C314 electronic transition dipole moment (tdm) and the vibrational mode $\nu_5(\text{C}=\text{O})$ as a function of the signal fraction contributed by *Z*-isomers to the polarization-resolved pump-probe signals (—), calculated from Equation (1) with the (theoretically calculated) dichroic ratio D linearly changing from 0.628 (pure *E*-isomer) to 2.913 (pure *Z*-isomer). The experimentally determined value of D for this mode gives 61° (●), with ExSeA 1σ error margins of $+14^\circ/-12^\circ$, indicating *Z*-isomer signal contributions are $< 25\%$.

tal data for the mode $\nu_5(\text{C}=\text{O})$ was 61° ($+14^\circ/-12^\circ$), and is marked by the solid circle in Figure 3. As can be seen from Figure 3, based on the theoretical calculation this experimental data point corresponds to 91% of the experimentally determined dichroic ratio coming from *E*-isomers and 9% of the signal contributions coming from *Z*-isomers. Given the 1σ error margins 0–25% of the signals could come from the *Z*-isomer. Note that the 9% most probable value does not deviate much from the 7% *Z*-isomer estimated from the gas phase calculations.

A direct estimate of the isomeric composition of the sample on the basis of the femtosecond polarization-resolved pump-probe data and the theoretically calculated vibrational tdm

for the two isomers is a far from trivial task. An approach based on linear combinations of the *E*- and *Z*-isomer vibrational tdm vectors according to the isomeric fractions for the different modes does not work since there is no straightforward easy relation of these to the experimental quantity D (dichroic ratio). This is a result of the fact that the optical pump induced photoselection does not select a single unique electronic tdm but an ensemble of orientations described by a $\cos^2\theta$ distribution. The necessary averaging over this distribution is incorporated in Equation (1). Note furthermore that an approach based on the calculated vibrational tdm only entails the implicit assumption that the electronic tdm for the *E*- and *Z*-isomer have the same spatial orientation within the cartesian frame chosen for calculus. In the present case theoretical calculations indicated an orientational difference of only 2.8° , but in general this implicit assumption may lead to systematic errors.

As a further attempt to estimate the reliability of the electronic tdm vector solution we decided to perform a modified analysis starting from the experimental data for the three vibrations $\nu_1(\text{C}=\text{C})$, $\nu_5(\text{C}=\text{O})$, and $\nu_6(\text{C}=\text{O})$ and their vibrational tdm as determined for the *E*-isomer. Next to the analysis with the actual experimental results, the analysis is redone with the central angle value for $\nu_5(\text{C}=\text{O})$ of the experimental ExSeA generated probability distribution function shifted from 61° to 72° , that is, the theoretically calculated pure *E*-isomer angle, and with this central value shifted to 49° , the lower limit of the ExSeA 1σ solution range for the $\nu_5(\text{C}=\text{O})$ mode (see Figure 3). As mentioned above, of the four vibrations used in the original analysis only the $\nu_5(\text{C}=\text{O})$ mode makes it possible to distinguish between the two isomers. From the 8.12×10^6 investigated angle combinations an electronic tdm solution is obtained for 12.5×10^3 combinations with central angle of $\nu_5(\text{C}=\text{O})$ at 49° , for 13.9×10^3 combinations with the experimental angle of 61° , and for 18.9×10^3 combinations with 72° . The resulting probability distribution functions for these solutions, projected on cartesian planes, are shown in Figure 4, whereby the color scale is set by the absolute probability range obtained for 61° . The most probable electronic tdm vector ($x/y/z$) changes from $(-0.99/0.11/0.00)$ for 49° , to $(-0.99/0.11/0.01)$ for 61° , and $(-0.98/0.18/0.05)$ for 72° . As can be seen from Figure 4 the deviations in these results are actually significantly smaller than their 1σ error margins. The angle between these outcomes for 49° and 61° is 0.4° , and these vector solutions are therefore virtually identical. With the 72° solution these two vectors make an angle of 4.7° and 5.1° , respectively. Note from Figure 4 that although more angle combinations give a solution with 72° , the resulting probability distribution is actually showing a much larger maximum probability plateau region, while at the same time this maximum probability is lower than values reached with 49° and 61° . Therefore the electronic tdm vector is actually more poorly defined with 72° than with the other two central angle values. The vector solutions can further be compared to the original result^[9] obtained with four vibrational tdm of $(-0.99/0.11/-0.02)$. The relatively small variation of maximally 5.1° in obtained electronic tdm orientation while varying the angle of $\nu_5(\text{C}=\text{O})$ over 23° , encompassing 1/3 of the theoretically calculated range for C314 and 1/4 of the max-

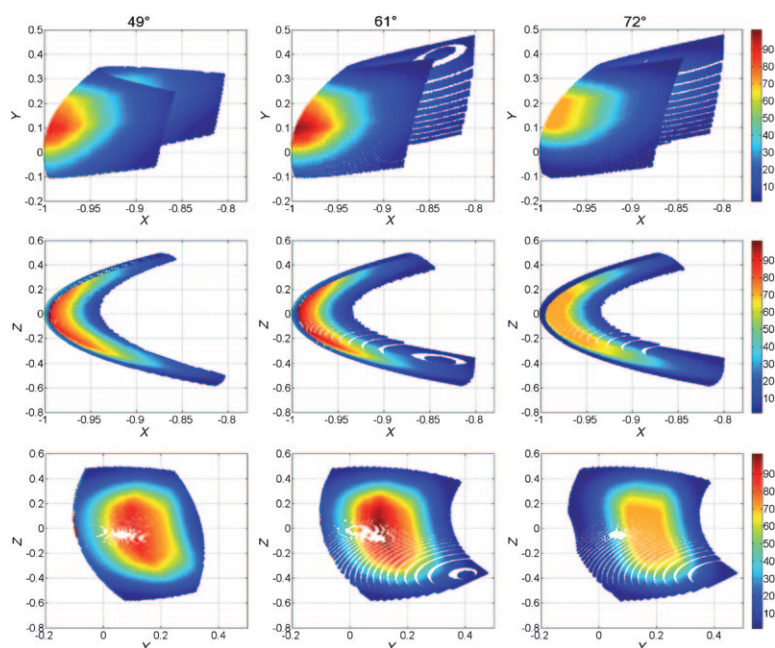


Figure 4. Projections of the 3D solution of the C314 electronic tdm on the Cartesian planes using the three vibrational tdm vectors $\nu_1(\text{C}=\text{C})$, $\nu_5(\text{C}=\text{O})$, $\nu_6(\text{C}=\text{O})$. The experimental values with a probability distribution function around 61° are presented in the central column. The left and right columns represent solutions with the central value of the experimental probability distribution functions for $\nu_5(\text{C}=\text{O})$ shifted to 49° and 72° , respectively.

imum possible solution range of 90° , indicates that the obtained solution is fairly robust. A rationale for this robustness could be the following: The combination of the two vibrational tdm vectors of $\nu_1(\text{C}=\text{C})$ and $\nu_6(\text{C}=\text{O})$ already yields maximally two electronic tdm vector solutions, reducing the influence of the third vibrational mode $\nu_5(\text{C}=\text{O})$ to only confirming which of these (maximally two) solutions are compatible with its vector. While the correct solution obtained for $\nu_1(\text{C}=\text{C})$ and $\nu_6(\text{C}=\text{O})$ most likely varies over a relatively limited range corresponding to the right answer, the other potential solution is expected to vary rather erratic, and therefore has a sharply reduced chance of providing a match with the solution cone of $\nu_5(\text{C}=\text{O})$. These occasional “outlier” solutions show up as relatively high probability pixels at the edges of the probability distribution plots in Figure 4.

3. Conclusions

A new method was presented that allows a truly three-dimensional determination of an electronic tdm orientation within the molecular structure, and is not dependent on experimental orientation distribution parameters. The method combines ExSeA^[15] on polarization-resolved fs UV/Vis pump–IR probe experimental data of at least three relative angles between the pumped electronic tdm and probed vibrational tdm vectors, with electronic ground state vibrational tdm vectors obtained from DFT calculations. The method was demonstrated for the Q_y transition of Chlorophyll a and the $S_0 \rightarrow S_1$ transition of Coumarin 314.

The electronic tdm obtained for the Q_y transition of Chl a makes an angle of $(12 \pm 3)^\circ$ with the y -axis, which is smaller

than in previous experimental determinations.^[2,3] Moreover, the Q_y tdm lies slightly outside the X – Y plane, making an angle of $(4 \pm 2)^\circ$. Precise knowledge of the Q_y tdm orientation allows for comparative experiments on Chl a in a protein environment for establishing if protein-cofactor interactions influence this orientation.

Two isomers can exist of C314, the E - and the Z -isomer, with very similar electronic tdm vectors, according to theoretical calculations.^[9] The $S_0 \rightarrow S_1$ electronic tdm vector determined with our method using data for four vibrational modes is $(x/y/z) = (-0.994/0.107/-0.020)$, with the reduced 1σ probability covering 2.24% of the half-sphere solution surface, when analyzing with vibrational tdm vectors of the E -isomer. The determined solution deviates 2.8° from the theoretical result.^[9] With the Z -isomer vibrational tdm vectors no solution could be found. Gas phase calculations suggest that in thermal equilibrium $\sim 7\%$ of the C314 molecules adopts the Z -isomer conformation. A calculation based on theoretical tdm vectors demonstrates that Z -isomers contribute less than 25% to the experimental signals, with 9% being the most probable contribution, close to the estimate from gas phase calculations. Although the precise composition of an isomeric mixture may be difficult to determine with this method, it can readily be used for following a real time evolution of an ultrafast isomerization, which is photoinduced from a known unique isomer, and determination of the tdm vector orientation in the end conformation. For C314 analysis of the influence of deliberate strong changes in the angle determined with $\nu_5(\text{C}=\text{O})$, the only vibrational mode used with a significantly different angle for the E - and Z -isomer, indicates that the 3D solution of the electronic tdm orientation is very robust.

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[1] J. Michl, E. W. Thulstrup, *Spectroscopy with Polarized Light*, VCH Publishers, Inc., New, York, 1986.

- [2] M. Fragata, B. Nordén, T. Kurucsev, *Photochem. Photobiol.* **1988**, *47*, 133.
- [3] M. A. M. J. Van Zandvoort, D. Wrobel, P. Lettinga, G. Vanginkel, Y. K. Levine, *Photochem. Photobiol.* **1995**, *62*, 299.
- [4] J. J. Larsen, K. Hald, N. Bjerre, H. Stapelfeldt, T. Seideman, *Phys. Rev. Lett.* **2000**, *85*, 2470.
- [5] J. G. Underwood, B. J. Sussman, A. Stolow, *Phys. Rev. Lett.* **2005**, *94*.
- [6] F. Dong, R. E. Miller, *Science* **2002**, *298*, 1227.
- [7] C. Z. Bisgaard, O. J. Clarkin, G. R. Wu, A. M. D. Lee, O. Gessner, C. C. Hayden, A. Stolow, *Science* **2009**, *323*, 1464.
- [8] M. Linke, A. Lauer, T. von Haimberger, A. Zacarias, K. Heyne, *J. Am. Chem. Soc.* **2008**, *130*, 14904.
- [9] M. Theisen, M. Linke, M. Kerbs, H. Fidder, M. E. A. Madjet, A. Zacarias, K. Heyne, *J. Chem. Phys.* **2009**, *131*, 124511.
- [10] B. C. Yip, H. K. Fun, K. Sivakumar, Z. Y. Zhou, O. B. Shawkataly, S. G. Teoh, *Acta Crystallogr. C* **1995**, *51*, 956.
- [11] T. Honda, I. Fujii, N. Hirayama, N. Aoyama, A. Miike, *Acta Crystallogr. C* **1996**, *52*, 395.
- [12] M. Lim, T. A. Jackson, P. A. Anfinrud, *Science* **1995**, *269*, 962.
- [13] D. von Stetten, M. Günther, P. Scheerer, D. H. Murgida, M. A. Mroginski, N. Krauß, T. Lamparter, J. Zhang, D. M. Anstrom, R. D. Vierstra, K. T. Forest, P. Hildebrandt, *Angew. Chem.* **2008**, *120*, 4831; *Angew. Chem. Int. Ed.* **2008**, *47*, 4753.
- [14] P. Hamm, M. Lim, W. F. DeGrado, R. M. Hochstrasser, *Proc. Nat. Acad. Sci. USA* **1999**, *96*, 2036.
- [15] T. A. Roelofs, C. H. Lee, A. R. Holzwarth, *Biophys. J.* **1992**, *61*, 1147.

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