Measuring the Ultrafast Correlation Dynamics between the Q_x and Q_y Bands in Chlorophyll Molecules

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ABSTRACT

We use two-dimensional electronic spectroscopy (2DES) to measure the ultrafast correlation dynamics between the Q_x and Q_y transitions in chlorophyll molecules. We derive a variation to the Centre Line Slope method to quantify the frequency fluctuation cross correlation function (FXCF), $C_{xy}(T)$. Compared with the frequency fluctuation correlation function (FFCF) of the Q_y transition, we observe that there is only a minimal correlation between the Q_x and Q_y transition, even at the ultrashort timescale of ~ 100 fs, which then decays to zero in a timescale of ~ 2 ps.

1. Introduction

Chlorophylls (Chls) are fundamental building blocks in plants and play a significant role in photosynthesis. The primary function of Chls in plant is to absorb energy from the sun and direct it to the reaction centre where the charge separation occurs. Due to its importance in understanding the energy capture and transfer processes in photosynthetic systems, there has been much experimental effort to measure the internal conversion rate in Chl. Han *et al.* studied Chl *a* using fluorescence up conversion techniques and reported an extremely fast internal conversion transfer from Q_x to Q_y band occurring in the range of 100 fs to 226 fs depending on the solvent.¹ This was then further corroborated by the transient absorption spectroscopy² and the non-adiabatic excited-state molecular dynamics simulation (NA-ESMD) studies.³ In addition, studies on the Bacteriochlorophyll *a* monomer by Kosumi *et al.* using time-resolved fluorescence shows a relaxation time scale for the Q_x to Q_y band of around 50 fs.⁴

It is known that the $Q_x \rightarrow Q_y$ relaxation rate is highly complex and depends on the energy gap, ΔE between the two states. There is also evidence that coherences between Q_x and vibronic

states of Q_y can affect the transfer rate.⁵ Moreover, due to line broadening effects of the Q_x and Q_y transitions, there will also be a distribution of ΔE in an ensemble which will affect the transfer rate and the dephasing process of any coherences involving Q_x and Q_y transitions. Therefore, it is necessary to better characterize the distribution of ΔE . The extent of the distribution of ΔE depends on several factors. These factors include the linewidth of Q_x and Q_y transitions and more importantly, on whether the Q_x and Q_y transitions are correlated. There have not been many studies on the correlation between the Q_x and Q_y transitions. Friedrich *et al.* reported the frequency correlation of the Q bands in Mg-mesoporphyrin horseradish peroxidase (MgMP-HRP) using spectral hole burning spectroscopy.⁶ Their results indicate a lack of correlation between the two bands. This is based on a broad non-resonant satellite hole in the Q_y band observed when a selective subpopulation of the Q_x band in an inhomogeneously broadened spectra was burnt. However, these experiments are steady-state experiments and do not give the indication of the time-dependent correlation. Studies by Sundström and co-worker using transient hole-burning experiment on Chl *b* in pyridine suggests that there is a lack of correlation between the Q_x and Q_y transitions at ultrashort timescales. However, the transient hole-burning experiment did not have the resolution to provide a definitive and quantitative study of the correlation.⁷ In this article, for the first time, we report on the ultrafast time-resolved measurement of the correlation between the Q_x and Q_y transitions of Chl *a* using 2DES.

An absorption peak in the condensed phase, as in the case of the Q_y transition of Chl *a* solution, is always broadened due to homogeneous, inhomogeneous and spectral diffusion contributions. There have been various studies using modern nonlinear optical techniques such as photon echoes and 2D electronic spectroscopy (2DES) to characterize these contributions.^{8–12} Under the Kubo lineshape theoretical framework, the frequency fluctuation correlation functions

(FFCF) of the Q_y and Q_x transition is given by $C_{yy}(T_w) = \langle \delta\omega_y(T_w) \delta\omega_y(0) \rangle$ and $C_{xx}(T_w) = \langle \delta\omega_x(T_w) \delta\omega_x(0) \rangle$, respectively. These functions contain the details to describe contributions to the spectral linewidth.¹³ Analogous to this function, we can also define a frequency fluctuation cross-correlation function (FXCF) $C_{xy}(T_w) = \langle \delta\omega_y(T_w) \delta\omega_x(0) \rangle$ that measures the cross-correlation dynamics between the transitions of the Q_x to the Q_y bands.

The analysis may be complicated by the fact that peaks assigned as Q_x and Q_y 0-1 bands (first vibronic band of Q_y) in Chl *a* are overlapping in the majority of solvents.¹⁴ Here, we chose the Chl *a* in pyridine system to study, as the Q_x peak is relatively distinct from Q_y 0-1 band at room temperature.¹⁵ However, as a reference experiment to minimize the consideration of possible interference by overlapping peaks, we also performed similar studies on one of the Chl *a* analogues, Chlorin-e6 (Chl-e6), which has a greater separation between the Q_x and Q_y bands than Chl *a*.¹⁴ The molecular structure of Chl *a* and Chl-e6 are shown in Supporting Information S1. The linear absorption spectrum superimposed with the spectra of the excitation pulses used for Chl *a* in pyridine and Chl-e6 in methanol are presented in Figure 1.

Figure 1: Linear absorption spectra of chlorophyll *a* (left) and chlorin-e6 (right) overlaid with the spectra of the excitation pulses used for 2DES measurement of Q_{yy} (red) and Q_{xy} (blue) experiments.

For both Chl *a* and Chl-e6, we conducted two sets of 2DES experiments. The first set with excitation pulses (pink spectra in Figure 1) covering the Q_y band which gives rise to a diagonal peak Q_{yy} at $(\omega_r, \omega_t) = (\omega_y, \omega_y)$ on the 2DES spectrum. The second set with excitation pulses (blue spectra in Figure 1) covering the Q_x band which gives rise to a cross peak Q_{xy} at $(\omega_r, \omega_t) = (\omega_x, \omega_y)$. From these peaks, it is then possible to characterize the FFCF and FXCF, respectively. In the systems that we study here, due to the fast internal conversion from Q_x to Q_y band (less than ~200 fs)^{5,14} and weak oscillator strength of the Q_x band compared to the Q_y band, the amplitude of the diagonal peak Q_{xx} which contains the FFCF $C_{xx}(T_w)$ term, is exceedingly small and thus its analysis was not performed.

2. Experimental method

Chl *a* (Chl-e6) was dissolved in pyridine (methanol) to match 0.2 OD at the maximum of either Q_x or Q_y excited transition in the 1 mm quartz cuvette. The Chl *a* and Chl-e6 samples, purchased from Sigma Aldrich and Fisher Scientific respectively, were used without further purification. Spectral positions of the pulses exciting Q_x and Q_y bands for Chl *a* and Chl-e6, generated by the Noncollinear Parametric Amplifier (TOPAS White), are summarized in Table 1.

Table 1 Summarized excitation wavenumbers for Chl-e6 and Chl *a*

Sample	Q_y (cm ⁻¹)	Q_x (cm ⁻¹)
Chl-e6 in methanol	15150	18800

Chl <i>a</i> in pyridine	14900	15630
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Excitation pulses in all the experiments were compressed to less than 1.3 times transform limited pulses using acousto-optic programmable dispersive filter pulse shaper (AOPDF) which was measured using a homemade autocorrelator (see Supporting information S2). To perform 2DES, the AOPDF was further used to generate a two-pulse sequence with an interpulse delay τ (1st coherence time) varying from 0 fs to 150 fs with an interval of 3 fs. Experiments were performed in a partially rotating frame with a reference frequency (λ_{ref}) set at 13990 cm⁻¹ for all experiments except Q_{xy} for Chl-e6 which was set at 17240 cm⁻¹. A 1 × 2 phase cycling scheme was used in all of the experiments to eliminate strong background pump-probe signal.¹⁶ In all experiments, the pump pulses were set to 40 nJ per pulse pair. The third interaction pulse (probe pulse) was generated by ~1 μ J of 12500 cm⁻¹ (800nm) light focusing onto a 2 mm thick sapphire window and collimated using a curved mirror afterwards. Two pairs of chirp mirrors were then used to correct the temporal chirp of the probe light. Afterwards, the probe light was passed through a half-wave plate and a polarizer, and set at the magic angle (54.7°) with respect to the pump polarization. The 2DES spectra containing the diagonal peak (Q_{yy}) and the crosspeak (Q_{xy}) of Chl *a* and Chl-e6 were recorded by collecting at a series of waiting times, T_w , defined as the time delay between the second and third excitation pulses and was controlled by a high precision motorized delay stage with a translational motion resolution of one femtosecond. For the Q_{yy} experiment, T_w was recorded from -200 fs to 400 ps whereas the Q_{xy} experiment was recorded from -200 fs to 50 ps. However, the data was only analyzed after $T_w \geq 100$ fs due to the presence of coherent artifact spectrally overlapped with the desired signal. After the pump and the probe beams were spatially overlapped in the 1 mm flow cell, the pump beam was blocked while the probe beam sent to the spectrometer

equipped with a CCD detector (Pixis 100B, Princeton Instrument) cooled to -75°C . The experiment was then repeated three times to ensure the reproducibility of our results. Finally, the linear absorption spectra was recorded before and after the experiment to check for sample integrity.

3. Theoretical Methods

The theory for the extraction of the FFCF from a diagonal peak of 2DES spectrum is well developed.¹⁷ Here, we further develop the theory and derive an expression for a 2DES cross peak function based on the FXCF, $C_{xy}(T) = \langle \delta\omega_y(T) \delta\omega_x(0) \rangle$. The rephasing and nonrephasing signal accounting for population transfer process from Q_x to Q_y can be pictured by the double-sided Feynman diagrams shown in Figure 2.

Figure 2. Double-sided Feynman diagrams for population transfer from Q_x to Q_y band for nonrephasing (left) and rephasing (right) pathways.

The third order rephasing and non-rephasing response function for the cross peak can be expressed as

$$R_{xy}^{R/NR}(t_1, t_2, t_3) \equiv i\mu_x^2\mu_y^2 (e^{\pm i\omega_x t_1} e^{-i\omega_y(t_3-t_2)}) F_{xy}^{R/NR}(t_1, t_2, t_3)$$

where μ_x and μ_y are the transition dipole moments for the Q_x and Q_y band respectively. The peakshape function $F_{xy}^{R/NR}(t_1, t_2, t_3)$ accounts for the shape of the cross peak. Eq. 1 can then be expanded using 2nd order of cumulant expansion. After applying the Kubo's stochastic theory of lineshapes¹⁸, Fourier transformation along τ and t , and some simplification (see Supporting Informations S3), we obtain the peak shape function of the purely absorptive cross peak as the following expression:

$$F_{xy}(\omega_\tau, T_w, \omega_t) \equiv \exp \left[\frac{-\omega_t^2 \Delta_x^2 - \Delta_y^2 \omega_t^2 + 2C_{xy} \omega_t \omega_\tau}{2(\Delta_x^2 \Delta_y^2 - C_{xy}^2)} \right] \quad 2$$

We can then characterize the frequency fluctuation cross correlation function (FXCF) by utilizing the center line slope (CLS) method devised by Kwak *et al.*¹⁹ This is done by obtaining the line through the peak where $d\bar{F}/d\omega_\tau = 0$. From this, the normalized FXCF, $\bar{C}_{xy}$ is shown to become proportional to the CLS by the following expression,

$$\frac{d\omega_\tau^{max}}{d\omega_t} = \frac{\Delta_x}{\Delta_y} \bar{C}_{xy}(T_w) \quad 3$$

$$\text{Where } \bar{C}_{xy}(T_w) = \frac{C_{xy}(T_w)}{\Delta_x \Delta_y} \quad 4$$

The terms Δ_x and Δ_y in Eq. 2-4 are the fluctuation amplitude of the Q_x and Q_y transitions respectively. In the case where Δ_x and Δ_y are equal, the expression in Eq. 4 will have a range of values $-1 \leq \bar{C}_{xy}(T_w) \leq +1$. In general, we can then classify correlations into three main types: correlated when $\bar{C}_{xy}(T_w)$ has positive values, anti-correlated when $\bar{C}_{xy}(T_w)$ has negative values and non-correlated when $\bar{C}_{xy}(T_w)$ equals to zero.²⁰ Here, we take slices parallel to the probe frequency axis ω_3 and employ what is known as the CLS ω_3 method^{17,19,21} to retrieve the normalized FFCF ($\bar{C}_{yy}(T_w)$) and the normalized FXCF ($\bar{C}_{xy}(T_w)$) from the Q_{yy} and Q_{xy} peaks, respectively. The analysis will be performed for both the Chl *a* and Chl-e6 systems.

It should be noted that transition dipoles values do not enter Eq. 2-4, therefore the relative magnitude of the transition dipole moments of the two transitions do not affect the measured CLS values.

4. Results and Discussion

Representative purely absorptive 2DES spectra of the Q_{yy} and Q_{xy} peaks at selected population times, T_w , for Chl *a* in pyridine, are shown in the upper and lower rows of Figure 3, respectively. The fitted CLS is denoted as the red line superimposed onto the 2DES spectra in Figure 3.

Figure 3. Normalized 2DES of the Q_{xy} (top) and Q_{yy} (bottom) experiment for Chl *a* in pyridine at T_w values of 0.17, 1 and 10 ps (left to right) with corresponding overlaid CLS fits (red line). White dashed line indicates diagonal. (2DES spectra for Chl-e6 are presented in Supporting Information S4)

In the lower row of Figure 3, the Q_{yy} peaks show a distinct evolution from an elliptical peak shape at early population time to circular-like shape at longer T_w . This process is attributed to spectral diffusion and is well studied.^{8,9} On the other hand, the Q_{xy} peak (upper row of Figure 3) shows an almost circular-like shape through all T_w steps. The extracted CLS data of the cross and diagonal peak for the Q_{xy} and Q_{yy} are plotted against T_w (for $T_w = 100$ fs to 15 ps) together with fitted exponential decay functions in Figure 4. It can be clearly seen that the CLS of Q_{xy} is much lower in value than that of Q_{yy} .

Figure 4. CLS data as T_w progresses for Chl *a* (a) and Chl-e6 (b) with the corresponding fitted exponential decays described in Table 2 for FFCF (red) and FXCF (blue).

The representative results of 2DES measurements for Chl-e6 at selected T_w are depicted in the Supporting Information S4. From them, it can be seen that the T_w dependent 2DES spectra of Chl-e6 have very similar trend with the previous observation of Chl *a*, which clearly show minimal correlation between Q_x and Q_y bands from short T_w . The extracted CLS data points against T_w (for $T_w = 100$ fs to 15 ps) with fitted exponential decay functions for Chl-e6 are depicted in Figure 4(b). The time scales and amplitudes of the components of the fitted exponential decays for the CLS, for both Chl *a* and Chl-e6, are summarized in Table 2.

Table 2. Fit parameters for the fitted exponential decays of CLS values for Q_{yy} and Q_{xy} experiment and the resulting $\bar{C}_{yy}(T_w)$ and $\bar{C}_{xy}(T_w)$ values.

Sample	A ₁	τ_1 (ps)	A ₂	τ_2 (ps)	A ₃	τ_3 (ps)	A ₄ >1 ns
Chl <i>a</i>							
$\bar{C}_{yy}(T_w)$	0.16	0.54	0.19	2.45	0.06	35	0.01
Q_{xy} CLS	0.08	1.81	-	-	-	-	-
$\bar{C}_{xy}(T_w)$	0.05	1.81					
Chl-e6							
$\bar{C}_{yy}(T_w)$	0.13	0.53	0.14	4.15	0.10	32	0.03
Q_{xy} CLS	0.05	2.45	-	-	-	-	-
$\bar{C}_{xy}(T_w)$	0.04	2.45					

Results presented here indicate a minimal correlation between Q_x and Q_y transitions for both Chl *a* and Chl-e6. The CLS values of Q_{yy} and Q_{xy} at the earliest measured population time show values of 0.43 (0.4) and 0.08 (0.05) for Chl *a* (Chl-e6) respectively. This then decays to zero in 1.81 ± 0.19 ps for Chl *a* and 2.45 ± 0.31 ps for Chl-e6. The CLS value of the diagonal peak, Q_{yy} for both samples do not decay to zero in the probed delay window of up to 400 ps and is left with the residual inhomogeneity which has been reported to decay in nanosecond timescale.^{8,9}

To obtain $\bar{C}_{xy}(T_w)$ (Table 2) from the CLS of the Q_{xy} peak, we need to include the value of the factor $\frac{\Delta_x}{\Delta_y}$ (Eq. 3). The values of Δ_x and Δ_y can be obtained from analyzing the linear lineshape and the 2DES diagonal peaks' CLS of the Q_x and Q_y transitions¹⁷. However, due to the small oscillator strength of the Q_x transition, as explained earlier in the text, we were not able to measure the CLS of the Q_{xx} diagonal peak. Instead we make the assumption that the ratio of homogeneous to non homogeneous contributions to the linear lineshape of the the Q_x and Q_y transitions are similar. This allows us to obtain from the experimental linear absorption bandwidth of Q_x and Q_y

transitions, an estimation of the $\frac{\Delta_x}{\Delta_y}$ factor (see Supporting Information S5). For both Chl *a* and Chl-e6, the factor is determined to be > 1 . In other words, the $\bar{C}_{xy}(T_w)$ values are lower than the CLS values (i.e. less correlation than suggested by the CLS values). Both $\bar{C}_{xy}(T_w)$ and CLS values are entered in Table 2 for comparison.

Additionally, because of a very short lifetime of the Q_x band ($T_1 < 150$ fs), we also analyzed the possible effect of lifetime broadening on the recovered CLS values. Simulated 2D spectra for different T_1 lifetimes (infinity, 100 fs, 50 fs and 5 fs) are shown in Supporting Information S6. Although the simulation results show broadening of the 2D peak along ω_1 and ω_3 with decreasing of the Q_x lifetime (Figure S5), the CLS analysis of the simulated 2D spectra for multiple T_w delay times (Figure S6) shows minimal effect for T_1 of 50 fs and longer. In the case of Chl *a* in pyridine, where the Q_x relaxation lifetime is reported to be around 107 fs¹⁴, the effect of the lifetime broadening on the analysis can be neglected. As for Chl-e6, although the internal conversion lifetime from the Q_x state in methanol is not yet known to the author, we hypothesize that it is between the ranges of ~ 50 -100 fs as reported in most of Chl analogue systems.^{1,3,14,22} Therefore, it is assumed here that this effect is also negligible.

The sub 100 fs correlation dynamics are not available in our present measurements. This is due firstly, to the strong coherent artifact overlapping with the signal that strongly distorts the peak shape for $T_w < 100$ fs, and secondly, the inherent limitation of the CLS analysis in recovering the FFCF (and by extension, the FXCF) at T_w shorter than the free induction decay (FID) timescale. In the short time approximation used in the CLS analysis¹⁷, in the cases of Chl *a* and Chlorin e6, whose FIDs have timescale of ~ 100 fs, the measured CLS for will not reflect the actual FFCF for $T_w < 100$ fs. Unfortunately, the measured Q_x relaxation lifetime of < 200 fs, is on the order of the

earliest T_w of our presented data, and it is difficult to draw any conclusion presently about whether or how the internal conversion process is related to the measured correlation dynamics measured here. It is however still interesting to understand what is the reason for the measured minimal correlation after 100 fs between the Q_x and Q_y transitions.

We offer here a possible reason for the minimal correlation between the Q_x and Q_y transitions. Due to the Stark effect, the electric field exerted by the environment will cause frequency shifts in the Q_x and Q_y transitions.²³ The fluctuation in the electric field exerted by the environment will therefore induce a fluctuation in the transition frequencies. The amount of the frequency shifts depends on the difference dipole moment, difference polarizability and other higher terms between the excited and ground states. Since in general, these terms are different between the Q_x and Q_y transitions, the fluctuation of the Q_x and Q_y transition frequencies may not necessarily be correlated. This can be clearly seen if we consider the lowest order term, the difference dipole moments. If we assume that the instantaneous electric field along any two perpendicular directions to be uncorrelated, the degree of correlation between the frequency fluctuation of Q_x and Q_y transitions will depend on the relative directions or dot product between the difference dipole moments vectors of the Q_x and Q_y transitions. This value can range from being maximally correlated to uncorrelated depending on the difference dipole moments vectors ranging from being collinear to perpendicular, respectively. Further studies, both theoretical and experimental will be needed to verify and quantify this.

5. Conclusions

In summary, we have carried out experiments on Chl *a* in pyridine to study the relationship of frequency fluctuation between the Q_x and Q_y transition implementing 2D electronic

spectroscopy. To the best knowledge of the author, this is the first characterization of the femtosecond correlation dynamics between the two coupled electronic excited states. Comparing the CLS values obtained from Q_{xy} and Q_{yy} experiment, we show that the Q_x and Q_y bands of Chl *a* have minimal correlation at sub 150 fs which decays away in ~ 2 ps. It is hoped that the observed 2DES spectra here can be further studied using theoretical and computational methods such as molecular dynamics simulation and ab-initio quantum mechanical calculations to determine the correlation between two coupled electronic states. In this paper, the FXCF measured is related to the energy gap fluctuation between the Q_x and Q_y transition. In general, FXCF can be measured for any pair of coupled transitions, such as between pairs of excitonic states arising from protein-bound pigment molecules in light harvesting complexes, undergoing excitation energy transfer processes. Measuring the energy gap fluctuation between these states will be important in resolving the question of whether coherences measured in 2DES are indeed due to the correlated fluctuations in their protein environment.²⁴⁻²⁶

ASSOCIATED CONTENT

Supporting Information

Structure of Chl *a* and Chl-e6, autocorrelation trace, expression to describe the Q_{xy} crosspeak, 2DES of Chl-e6 in methanol, comparison of peakshape analysis methods, fluctuation amplitudes Δ_x and Δ_y of Q_x and Q_y transitions respectively and lifetime coherence broadening effect.

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Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

This work is supported by grants from the Singapore Ministry of Education Academic Research Fund (Tier 2 MOE2015-T2-1-039 and Tier 1 RG16/15). M.F.K. acknowledges funding from the Ministry of Education Malaysia and the SLAB/SLAI fellowship scheme from the University of Malaya. Fruitful discussions with Maxim Gelin and Yuan-Chung Cheng are acknowledged.

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