Data Article

Spectroscopy data for the time and frequency characterization of vibrational coherences in bacteriochlorophyll a

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**ABSTRACT**

Bacteriochlorophyll is the primary pigment in the light-harvesting pigment-protein complexes (PPCs) of the bacterial photosynthetic apparatus. 2D electronic spectroscopy (2DES) represents one of the most exploited and powerful techniques to characterize the ultrafast relaxation dynamics in PPCs, in particular, to assess the presence of coherent mechanisms during energy transport. The data reported in this work and the associated research article, “Characterization of the coherent dynamics of bacteriochlorophyll a in solution” [Meneghin et al., 2019] are an important contribution to the literature on coherent dynamics of light-harvesting complexes and can be useful in the interpretation of coherent motion in more complex systems with bacteriochlorophyll a (BChla) as a basic unit. The analysis of the provided data allows the identification of vibrational coherences associated with several Franck-Condon active modes and the characterization of their frequencies and dephasing times. Here we report additional data analysis and additional measures that complement the associated research article [Meneghin et al., 2019] and support its main conclusions. In particular, we compare vibrational coherences extracted from 2DES response with Raman modes detected for BChlα powders at cryogenic temperature in resonant and non-resonant conditions. Finally, we show the time-resolved fluorescence decay of the chromophore to support the...
Sub-picosecond dynamics of Bchl monomeric form in methanol solution was investigated at room temperature by means of 2DES. The signal can be divided into a coherent (oscillating) and a non-coherent (non-oscillating) portion.

The non-coherent part of the 2DES signal was characterized and described in the associated research article, [1]. The interpretation has been guided and supported by time-resolved fluorescence
measurements, assessing the dynamics of excited states in a longer timescale. Fig. 1 shows the fluorescence decay trace of Bchl in methanol solution at room temperature. A three-exponential behavior could be retrieved, with time constants $\tau_1 = 2.1$ ns (89%), $\tau_2 = 3.9$ ns (7.5%), and $\tau_3 = 37.0$ ns (3.5%).

The coherent part of the 2D signal in the specific case of monomeric BChl molecules in methanol is expected to include only vibrational and vibronic contributions. For this reason, the comparison with resonant and non-resonant Raman spectra is particularly meaningful. Raman spectra of BChl powders at 77 K were recorded in resonance (exc. 514 nm) and off-resonance (exc. 633 nm) conditions. The main modes are listed in Table 1.

To analyze the coherent part of the 2DES signal, we subtracted the non-coherent decay from the rephasing and non-rephasing datasets, obtaining the associated arrays of oscillating residues.

The rephasing and non-rephasing residues are then Fourier transformed along the population time, $t_2$, to get the frequency of the oscillations in the $\omega_2$ domain. The retrieved spectra are integrated along excitation ($\omega_1$) and emission ($\omega_3$) axes and squared to compute the power spectrum. The integrated power spectrum of oscillations is a quick way of identifying the main components contributing to the overall beating behavior of the 2DES dataset.

Fig. 2 allows a direct comparison between the integrated Fourier spectra of the rephasing and non-rephasing portions of the 2DES signal and the resonant and non-resonant Raman spectra.

Time-frequency bilinear transform analysis [2] provides simultaneously time and frequency resolution of coherent beatings. The time behavior of the modes with frequency below 500 cm$^{-1}$ can be investigated analyzing a trace at a selected ($\omega_1$, $\omega_3$) coordinate where the contribution of low frequency modes is prominent. The resulting TFT plot (Fig. 3) highlights the long dephasing time of higher frequency modes and the short damping time of beatings below 500 cm$^{-1}$.

2. Experimental design, materials and methods

2.1. 2DES setup and experimental conditions

2DES measurements were conducted with the setup described in Refs. [1,3]. Briefly, a 3 kHz Ti:Sapphire laser system (Coherent Libra) is used to pump a non-collinear optical amplifier (Light Conversion TOPAS White).
Table 1
Raman shift of vibrational modes recorded on powders of Bchl at 77 K.

| Resonant Raman (exc. @ 633 nm) [cm\(^{-1}\)] | Non-resonant Raman (exc. @ 514 nm) [cm\(^{-1}\)] |
|---------------------------------------------|---------------------------------------------|
| 196                                         | 196                                         |
| 217                                         | 923                                         |
| 250                                         | 945                                         |
| 267                                         | 985                                         |
| 283                                         | 1000                                        |
| 304                                         | 1045                                        |
| 350                                         | 1067                                        |
| 378                                         | 1079                                        |
| 397                                         | 1124                                        |
| 429                                         | 1154                                        |
| 443                                         | 1190                                        |
| 479                                         | 1214                                        |
| 513                                         | 1230                                        |
| 537                                         | 1272                                        |
| 561                                         | 1290                                        |
| 573                                         | 1308                                        |
| 584                                         | 1326                                        |
| 601                                         | 1346                                        |
| 624                                         | 1376                                        |
| 680                                         | 1389                                        |
| 700                                         | 1399                                        |
| 702                                         | 1418                                        |
| 716                                         | 1434                                        |
| 730                                         | 1473                                        |
| 738                                         | 1520                                        |
| 746                                         | 1552                                        |
| 756                                         | 1567                                        |
| 796                                         | 1617                                        |
| 838                                         | 1653                                        |
| 838                                         | 1699                                        |

Fig. 2. Rephasing (orange) and non rephasing (green) power spectra of coherences of Bchl in methanol solution at room temperature. Resonant (exc. 633 nm) and non-resonant (exc. 514 nm) Raman spectra recorded on powders at 77K [1] are also reported in red and light blue, respectively.
The TOPAS was tuned to produce pulses centered at 13800 cm\(^{-1}\) with a time duration of 20 fs, corresponding to a spectral bandwidth of 750 cm\(^{-1}\).

The spectral range and time duration of the pulse were characterized at the sample position with a FROG measurement on a 1 mm cuvette filled with solvent. The result is reported in Fig. 4. The pulses energy at the sample position was reduced to 7 nJ per pulse by a broadband half-waveplate/polarizer system.

The 2DES experiment relies on the passively phase stabilized setup, where the laser output is split into four identical phase-stable beams in a BOXCARS geometry using a suitably designed 2D grating. Pairs of 4° CaF\(_2\) wedges modulate time delays between pulses with a temporal resolution of 0.07 fs.

2.2. Raman spectroscopy setup

Raman spectra were recorded directly on Bchl\(_a\) powders with a home-built micro-Raman system, based on a Triax-320 ISA spectrograph, equipped with a holographic 1800 g/mm grating and a CCD.

![Fig. 3. Time-frequency transform of a beating trace extracted at coordinates (12950, 12950) cm\(^{-1}\) of the rephasing dataset.](image)

![Fig. 4. FROG measurement performed at the sample position in a 1mm cuvette filled with solvent. The pulse duration is estimated to be 20 fs. The intensity is normalized to 1 on the maximum.](image)
detector (Spectrum One ISA Instruments). The excitation sources were a Spectra Physics Ar+ laser operating at 514.5 nm and an He–Ne laser at 632.8 nm for non-resonant and resonant conditions, respectively. Appropriate edge filters were used to reduce the stray-light level. An Olympus BX 40 optical microscope equipped with a long working distance 50 x/0.50 objective was optically coupled to the spectrograph. The Raman spectra were recorded on Bchl a powders between 100 and 1800 cm⁻¹ and with an instrumental resolution of about 2 cm⁻¹. To avoid optical damage, readily occurring at room temperature, the sample was held in a cryostat cell (Linkam Scientific Instruments) at 77 K and the power of the exciting radiation was maintained between 0.2 and 0.4 mW.

2.3. Time-resolved fluorescence spectroscopy setup

Time-resolved fluorescence measures were performed with the time-correlated single photon counting (TCSPC) methodology. The setup is based on a modified configuration of a Jobyn Yvone FluoroMax 3. The standard excitation lamp and detector are replaced by a pulsed nanoled source at 455 nm (Horiba) and a single-photon detector (FluoroHub-B), respectively. The apparatus has a time resolution of about 1.5 ns and the decay was measured in a time window of 200 ns.

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Transparency document

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