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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* (BChl*a*) 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 BChl*a* powders at cryogenic temperature in resonant and non-resonant conditions. Finally, we show the time-resolved fluorescence decay of the chromophore to support the

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interpretation of non-coherent dynamics discussed in Ref. [Meneghin et al., 2019].

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Specifications table

Subject area	Ultrafast optical spectroscopy
More specific subject area	2D coherent spectroscopy
Type of data	Graphs, figures, table and text file
How data was acquired	2D electronic spectroscopy and frequency-resolved optical gating measurements were performed at room temperature with a home-built setup in BOXCARS geometry and diffractive optic element. Raman spectra were obtained with a home-built micro-Raman system. Fluorescence lifetimes were measured with Jobyn Yvone FluoroMax 3 equipped with a pulsed nanoled source at 455 nm (Horiba) and a single-photon detector (FluoroHub-B).
Data format	Analyzed data
Experimental factors	Bacteriochlorophyll <i>a</i> (Sigma Aldrich) was dissolved in methanol without any further purification
Experimental features	The dynamics of BChl <i>a</i> in methanol solution have been characterized at room temperature through 2D electronic spectroscopy. The oscillating part of the signal, carrying information on vibrational coherences has been isolated from the population decay signal and analyzed. Integrated Fourier spectrum, 2D beating maps and time-frequency distribution of the vibrational coherences have been determined. Resonant (exc. 633 nm) and non-resonant (exc. 514 nm) Raman spectra of BChl <i>a</i> powders have been recorded for comparison.
Data source location	Department of Chemical Sciences, University of Padova, Italy
Data accessibility	Data are provided in this data article
Related research article	Elena Meneghin, Danilo Pedron, Elisabetta Collini, Characterization of the coherent dynamics of bacteriochlorophyll <i>a</i> in solution, Chem. Phys. 519 (2019), 85–91. https://doi.org/10.1016/j.chemphys.2018.12.008 [1].

Value of the data

- 2D electronic spectroscopy can assess the early stages of energy transfer process in photosynthetic biological systems. Important pieces of information are encoded into their coherent dynamics but disentangling electronic and vibrational beatings is not a trivial task. A comprehensive analysis of the coherent signals recorded for monomeric forms of photosynthetic chromophores is a fundamental step towards a conscious interpretation of coherent dynamics in multi-chromophoric PPCs.
- Bacteriochlorophyll *a* (Bchl*a*) coherent response is investigated in the blue side of the first electronic transition Q_y to be more sensitive to the excited state vibrations. Vibrational modes could be assigned to electronic ground and excited states.
- A library of vibrational coherences of Bchl*a* is provided, and beatings are characterized both in time and frequency domain.
- The data confirm that several vibrational coherences with a frequency below 500 cm^{-1} are characterized by short damping times, at least at room temperature, and their dynamics is strongly dependent on the environment. This finding is an essential clue in the interpretation of multi-Bchl*a* PPC systems, including complex dynamic phenomena recently hypothesized, such as correlated fluctuations.

1. Data

Sub-picosecond dynamics of Bchl*a* 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

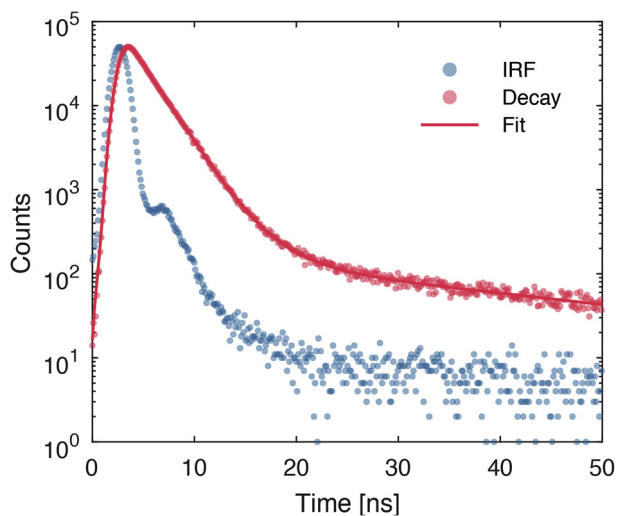


Fig. 1. Experimental fluorescence decay trace of Bchl a (red dots), instrumental response (blue dots) and multiexponential fitting trace (red line).

measurements, assessing the dynamics of excited states in a longer timescale. Fig. 1 shows the fluorescence decay trace of Bchl a 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 a 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 a 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 ω_2 domain. The retrieved spectra are integrated along excitation (ω_1) and emission (ω_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 (ω_1 , ω_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 1Raman shift of vibrational modes recorded on powders of Bchl*a* at 77 K.

Resonant Raman (exc. @ 633 nm) [cm^{-1}]	Non-resonant Raman (exc. @ 514 nm) [cm^{-1}]	
196	196	923
—	217	945
250	—	985
—	267	1000
283	—	1045
304	306	1067
350	352	1079
378	384	1124
397	397	1154
429	—	1190
443	442	1214
479	481	1230
513	513	1272
537	539	1290
561	—	1308
573	579	1326
584	—	1346
601	603	1376
624	—	1389
—	638	1399
680	—	1418
700	702	1434
—	716	1473
730	—	1520
738	—	1552
746	745	1567
756	758	1617
796	796	1653
838	839	

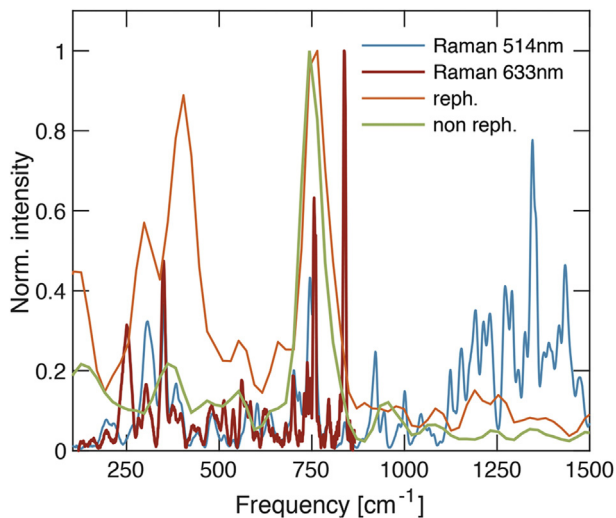


Fig. 2. Rephasing (orange) and non rephasing (green) power spectra of coherences of Bchl*a* in methanol solution at room temperature. Resonant (exc. 633 nm) and non-resonant (exc. 514 nm) Raman spectra recorded on powders at 77K [1] are also reported in red and light blue, respectively.

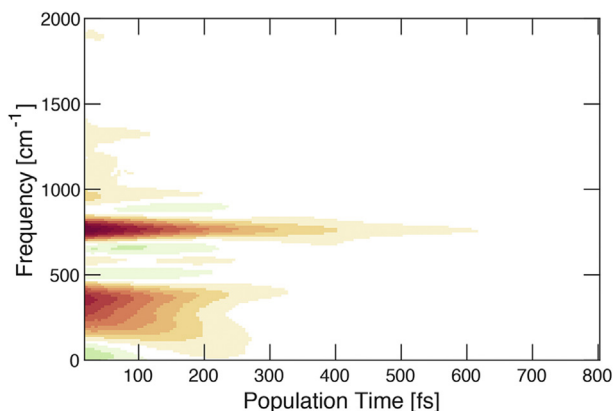


Fig. 3. Time-frequency transform of a beating trace extracted at coordinates (12950, 12950) cm⁻¹ of the rephasing dataset.

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 [4] 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 BOXCAR geometry using a suitably designed 2D grating. Pairs of 4° CaF₂ 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

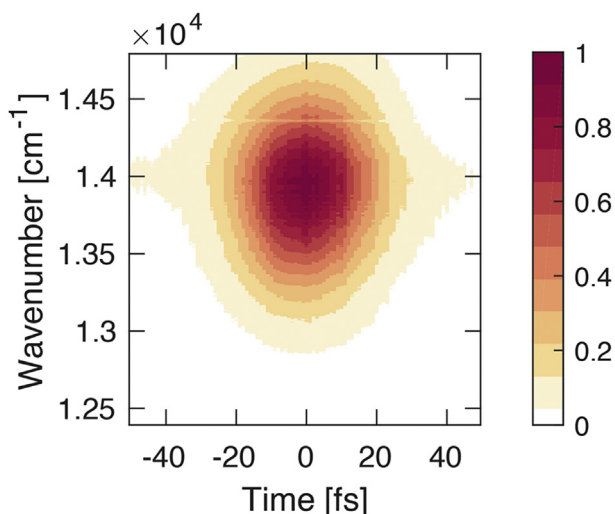


Fig. 4. FROG measurement performed at the sample position in a 1 mm cuvette filled with solvent. The pulse duration is estimated to be 20 fs. The intensity is normalized to 1 on the maximum.

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×/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.

Acknowledgments

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Transparency document

Transparency document related to this article can be found online at <https://doi.org/10.1016/j.dib.2019.103707>.

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