Visualizing Light Harvesting Processes Beyond Heisenberg’s Uncertainty

D. Paleček, R. Dědic
Charles University in Prague, Faculty of Mathematics and Physics, Department of Chemical Physics and Optics, Ke Karlovu 3, 121 16 Praha 2, Czech Republic.

Abstract. The Heisenberg’s uncertainty relation between energy and time restricts our ability to achieve high spectral and temporal resolution in a single experiment, although both are needed to investigate the ultrafast primary processes of photosynthetic light-harvesting. Two distinct experimental concepts providing either spectral or temporal resolution have been developed over the years. We review their basic concepts together with a recent development of new techniques, namely the two-dimensional coherent electronic spectroscopy and the differential fluorescence line-narrowing being applied to the light-harvesting complexes. Extensive collaboration between the Charles University in Prague and the Lund University in Sweden makes it possible to investigate bacterial reaction centers as well as artificial bacteriochlorophyll $c$ aggregates, taking advantages of the both above mentioned techniques. Future prospects for acquiring new knowledge about the recently observed quantum coherence effects in the light-harvesting are discussed.

Introduction

The primary processes in photosynthesis convert sun-light photons to energy of chemical bonds which subsequently drive all biological processes on the Earth. Photosynthetic light-harvesting (LH) includes a capture of a photon by a pigment, the excitation energy transfer (EET) through LH antennas towards a reaction center (RC), and charge separation together with charge transfer across a membrane therein [Blankenship, 2002]. These concepts are not only important for understanding the natural LH, but also for designing highly efficient photovoltaic solar cells (for reviews on various solar cells see Rühle et al. [2010]; Brabec et al. [2010]; Kim et al. [2011]; Hardin et al. [2012]) since the quantum efficiency of LH complexes is mostly higher than 95 % and the charge separation efficiency was found to be essentially unity [Sundström, 2008b].

Among others, two crucial factors need to be considered when performing the research related to LH. (1) Timescales of the processes under study ranging from fs-ps for the EET, up to $\mu$s in the case of the charge transfer, (2) Pigment content complexity used to funnel the excitation energy towards the RC or to favor the unidirectional charge transfer. The energy/electron funnelling concepts and intrinsic inhomogeneity of the LH complexes naturally lead to very congested and broad spectral features in the visible and the near infra-red region. This implies an always present trade-off between spectral and temporal resolution which are both extremely important in understanding the processes underlying LH. For example, the 10 fs Fourier transform-limited laser pulse centered at 800 nm corresponds to about 100 nm spectral bandwidth which prevents obtaining any spectrally resolved information from a standard experiment using such pulses.

In the first part of this article, we briefly describe well established experimental techniques with high spectral/temporal resolution, namely transient absorption (TA) and hole-burning (HB) spectroscopies with an accent on the various information obtainable from them. In the second part of the article, we introduce the novel techniques in the high resolution spectroscopies applied to the LH complexes such as the two-dimensional coherent electronic spectroscopy (2DES) and the differential fluorescence line-narrowing ($\Delta$FLN). The basic concepts and applications of these techniques, mainly for elucidating the question about the role of coherent dynamics in LH, will be discussed. 2DES is the state-of-the-art technique in this respect,
combining both the spectral and the temporal resolution beyond the Heisenberg’s uncertainty principle determined by the laser pulse.

Established Techniques with High Spectral/Temporal Resolution

Transient Absorption

Rapid development of laser technologies in 1990s (for review see Steinmeyer et al. [1999]) made it possible to produce sub-50 fs pulses with sufficient repetition rates to study the early LH processes in the real time [Sundström, 2008a]. A basic implementation of TA spectroscopy uses a short pulse to excite a part of the ground state population, effectively triggering the excited state evolution, which is then probed by the second pulse delayed in time. By scanning the time delay between the pulses and calculating differential absorption of the probe pulse with and without excitation ($\Delta A(\lambda, T)$) provides the information about the excited state dynamics. Depending on the experimental details, one can measure time traces (kinetics) of a system at one particular wavelength or the whole spectra of the sample if a white light probe is used. In general, ground-state bleach, stimulated emission, excited-state absorption, and photo product absorption contribute to the resultant spectrum [Berera et al., 2009].

It is clear that monitoring the temporal behaviour of these processes provides valuable information about the function of the systems under study. Over the years, TA has been established as one of the most basic characterization methods used in LH-related experiments and many questions have been resolved by its implementation. Energy transfer dynamics within antenna systems is a natural topic for the time-resolved spectroscopy providing timescales and pathways of the relevant processes, delocalization lengths, etc. [Sundström et al., 1999]. The first time constants of intra- and interband energy transfer for B800–B850 complex were found using TA methods [Bergström et al., 1986]. Ultrafast charge separation and asymmetric charge transfer in the almost $C_2$ symmetrical branches of RCs is also an issue where TA has played the crucial role [Kirmaier et al., 1985; Romero et al., 2010]. Another example is the role of carotenoids and their symmetry-forbidden transitions to the first excited state ($S_1$) in the photoprotection and energy transfer to proximate (bacterio)chlorophylls (B)Chls [Polívka and Sundström, 2004].

Time-resolution is limited by the duration of the laser pulse used in the particular experiment which is intrinsically connected to the bandwidth of the pulse spectrum and the ability to compress such pulse. On the contrary, methods with high spectral resolution benefit from the ability to resolve various species within congested spectral bands by selective excitation and possibility to assign role of the homogeneous and inhomogeneous broadening. HB and $\Delta$FLN techniques are discussed in this regard.

Hole-Burning

HB spectroscopy is a low-temperature site-selective method which discloses the information obscured by the inhomogeneous broadening present in all the photosynthetic complexes due to distribution of the local environments of individual pigments (for review see Jankowiak et al. [2011]). Experimentally, one compares absorption or emission spectra before and after the illumination by a narrow-band excitation laser in continuous wave mode at the liquid helium temperatures. The resulting difference spectrum reflects absorption or emission of the molecules photochemically or non-photochemically alternated by the spectral hole-burning process. It can be shown that narrow feature of the HB spectrum reflects zero-phonon line (ZPL) and side holes provide information about electron-phonon coupling between the molecule and its environment. The width of the ZPL is inversely proportional to the lifetime of the lowest excited state (LES) which makes HB the complementary method to TA in the frequency domain. From the distribution of the hole depths, one obtains position of the LES and its inhomogeneous broadening. Temperature dependence of the hole-widths provides pure dephasing time.
Because the homogeneous hole-width is inversely proportional to the lifetime of the excited state, the first ultrafast energy transfer times were determined from HB studies, for instance the $\approx 100$ fs excitonic relaxation within the FMO complex [Johnson and Small, 1991]. Besides that, optical dephasing in B850 band from LH2 complex [Purchase and Völker, 2009] and its LES, which transition is partially allowed due to a disorder within the ring structure, were investigated [Scholes and Fleming, 2000]. HB is also very sensitive to the trap states, which was utilized in the studies of photosystem II (PSII) [Groot et al., 1996; Hartog et al., 1998]. Another challenging problem is to resolve the structure of chlorosomes from green photosynthetic bacteria, the largest and one of the most efficient antenna systems found in nature. LES lifetime and inhomogeneous broadening has been determined using HB on the chlorosomes [Psencik et al., 1998].

Novel Techniques

It is clear that experimental techniques mentioned in the previous section brought about great knowledge about LH processes, but also further stimulated a development of new techniques to address novel questions. The most recent question is the role of excitonic, vibrational, or mixed vibronic coherences in the LH and their potential implications for the efficiency of the energy/electron transfer, which is closely connected to 2DES experiments. To elucidate and model the role of vibrations in dynamical processes one also needs to input the accurate structural parameters, mostly Huang-Rhys (HR) factors determining mixing between the electronic and the vibrational degrees of freedom. Another challenge is the structure-function relationship and its direct investigation enabled by the super-resolution imaging recently developed in single molecule spectroscopy [Leung and Chou, 2011] and/or the time-resolved X-ray diffraction applied to the bacterial RC [Huang et al., 2012].

$\Delta$FLN

FLN spectroscopy is another low-temperature, site-selective spectroscopy method where an energetically narrow sub-population of a sample is excited, which fluorescence is then monitored in the emission or excitation mode. The low temperature is needed to cool down the dynamical disorder which is proportional to the energy of $kT$ ($\approx 200 \text{ cm}^{-1}$ at room temperature), while the narrow-band laser photo-excitation eliminates the static disorder (inhomogeneous broadening) [Fidy et al., 1998]. Combining HB spectroscopy and FLN enables to eliminate the contributions from scattered light in FLN and antiholes absorption in HB experiments which preclude the precise determination of the HR factors [Jankowiak et al., 2011]. This is exactly what is needed to model the complex dynamics observed in the 2DES experiments (see the next section), since the spectral density profile (or direct inclusion of particular vibrational mode into the system Hamiltonian [Christensson et al., 2012]) is one of the crucial steps in designing a suitable model to simulate experimental data [Renger, 2009]. Moreover, $\Delta$FLN provides the electron-phonon and the electron-vibrational couplings (HR factors) for both the ground and the excited states. Comprehensive summary of the HR factors obtained for various photosynthetic complexes using different experimental methods can be found in [Jankowiak et al., 2011].

2DES

Splitting the first excitation pulse used in TA spectroscopy to two separate pulses and phase-sensitive detection led to advent of multidimensional coherent spectroscopies. Note that the first 2D experiments in the infra-red region were realized as a dynamical hole-burning utilizing tunable narrow band pump pulse, directly connecting hole-burning and line narrowing techniques to the development of 2DES [Hamm et al., 1998]. Four-wave mixing scheme in a so called “box car” geometry is usually employed, where the three excitation laser pulses generate a third-order non-linear polarization which is then emitted into the direction of the fourth pulse and interferometrically detected [Brixner et al., 2004]. The four pulse scheme implies the three
adjustable time delays. Fourier transform is performed over the first and the third one (the first Fourier transform is computational, the second one comes from spectrally-resolved detection on CCD) and the second time-delay is scanned as a population delay. In this way, a two dimensional correlation plot between the excitation and the emission energies with ≈15 fs time resolution is obtained. The spectral resolution on the excitation axis is the unique feature of 2DES within the time-resolved optical spectroscopies which basically circumvents the Heisenberg uncertainty principle given by the laser pulse used in the experiment. That is achieved by scanning the time delay between the first two pulses with interferometric precision and Fourier transforming with respect to this time delay.

Lineshapes of the diagonal peaks in 2D spectra provide the homogeneous and inhomogeneous linewidths, while cross-peaks reflect the couplings and the EET dynamics between pigments. Oscillatory features in the spectra stems from the vibrational, vibronic, or electronic coherences. Independent variation of all the four laser pulse polarizations in 2DES experiment can help to distinguish between the different coherences [Schlau-Cohen et al., 2012; Westenhoff et al., 2012].

Direct evidence for the energy transfer between various excitonic levels in FMO complex has started exciting development and application of 2DES to the photosynthetic systems [Brixner et al., 2005]. Oscillatory features in different regions of 2D spectra attract particular attention, since the purely electronic coherences were assumed to be responsible for the EET efficiency and led to the ideas of a coherent transport [Engel et al., 2007]. Recent development in 2DES data interpretation suggests an alternative explanations if the vibrational modes are taken into account [Christensson et al., 2012; Tiwari et al., 2013]. This fact revive the importance of the site-selective techniques with their ability to determine structural parameters and HR factors as a measure of coupling between the electronic and the vibrational degrees of freedom.

Future prospects

Extensive collaboration between the Department of Chemical Physics and Optics at Faculty of Mathematics and Physics of the Charles University in Prague and the Lund University in Sweden provides a unique opportunity to apply ∆FLN and 2DES techniques to both the natural and artificial LH systems within a single project, to shed a new light on coherent phenomena and its possible applications for the new generation of photovoltaics or even quantum computers. So far, chlorosomes and artificial BChl c aggregates have been extensively studied by both groups [Pšenčík et al., 2006; Alster et al., 2010; Dostál et al., 2012]. The Experimental as well as theoretical work on coherent phenomena related to both the energy and the charge transfer dynamics in bacterial RCs is in progress [Westenhoff et al., 2012]. The expertise of the Charles University side in HB and site-selective techniques can contribute to resolve the ongoing discussion about the nature and role of the quantum coherence in biology by implementing ∆FLN to both the natural (bacterial RCs) and the artificial (BChl c aggregates) LH systems.

Conclusion

In this minireview, we presented fundamental techniques used to study LH processes providing high spectral/temporal resolution, which have been employed to address a large number of questions throughout the years. Development of more sophisticated experimental techniques leads to the new unexplored areas of the primary processes in the LH promising also new applications for the future artificial LH materials and other fields dealing with the coherent ultrafast processes such as the quantum computing.

Acknowledgments. The work is supported by project number 87010 from Grant Agency of Charles University (GAUK) and project number P501/12/G055 from the Czech Science Foundation (GAČR). D.P. acknowledge financial support from the Swedish Research Council.
References


