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Journal

The Journal of Chemical Physics, 159(10)

ISSN

0021-9606

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Publication Date

2023-09-14

DOI

10.1063/5.0170807

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EDITORIAL | SEPTEMBER 08 2023

Photosynthetic light harvesting and energy conversion

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Graham R. Fleming ; Jun Minagawa ; Thomas Renger  ; Gabriela S. Schlau-Cohen 



J. Chem. Phys. 159, 100401 (2023)

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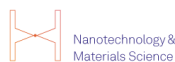
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Cite as: J. Chem. Phys. 159, 100401 (2023); doi: 10.1063/5.0170807

Submitted: 4 August 2023 • Accepted: 15 August 2023 •

Published Online: 8 September 2023



View Online



Export Citation



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Note: This paper is part of the JCP Special Topic on Photosynthetic Light-Harvesting and Energy Conversion.

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<https://doi.org/10.1063/5.0170807>

The primary photophysical and photochemical reactions in photosynthesis provide the basis for oxygenic life on our planet. The study of these reactions is challenging in many respects. Two important points dealt with in the present Special Topic issue on “Photosynthetic Light-Harvesting and Energy Conversion” are the following:

- (i) Pigment–protein complexes undergo conformational transitions on many different timescales that include transitions between functionally relevant modes of light harvesting and photoprotection. X-ray crystallography and cryogenic electron microscopy have made enormous strides in revealing the molecular structures of subunits and supercomplexes of many different photosynthetic systems. These structural models and spectroscopic experiments provide the basis for deciphering structure–function relationships. However, additional experimental and theoretical studies are needed in order to characterize the structural dynamics that are crucial for function.
- (ii) Pigment–protein complexes are difficult to describe theoretically. A full *ab initio* description is impossible because these systems are too complex and *ab initio* methods are not accurate enough. Therefore, multiscale methods are needed that must be tested and calibrated by comparison with experimental data. Two essential points of such modeling concern the parametrization of an effective Hamiltonian known as Frenkel exciton (charge transfer state) Hamiltonian and the study of the quantum dynamics of excited states with this Hamiltonian.

This Special Topic issue provides a collection of recent efforts to master the above challenges.

Pandit¹ provides a review on the application of magic angle spinning nuclear magnetic resonance (NMR) spectroscopy and related techniques, with which it is possible to access the motion of proteins, pigments, and lipids on sub-nanoseconds to millisecond timescales on very different length scales ranging from solubilized complexes to whole cells. Of particular interest is the change in dynamics induced by high light or metabolic processes.

A complementary technique focusing on the photodynamics of single light-harvesting complexes in an Anti-Brownian Electrokinetic (ABEL) trap is reviewed by Moerner and co-workers.² With this technique, it is possible to counteract Brownian motion and investigate the change in fluorescence lifetime and intensity of single complexes on physiologically relevant timescales. They illustrate the power of this technique with a comparison of different oligomerization states of cyanobacterial light-harvesting proteins: PE545 trimer vs monomer, whole phycobilisome, and whole phycobilisome including the accessory orange carotenoid protein (OCP), a well-known quencher of excitation energy. A quenching site could be identified in PE545 trimers, and many such sites could be identified in whole phycobilisomes. In the presence of OCP, two distinct subpopulations of quenched phycobilisome states arise, most likely reflecting quenching by one and two bound OCP complexes.

A paper by Schlau-Cohen, Scholes, and co-workers³ also uses single-molecule spectroscopy to investigate photodynamics. From the correlation between fluorescence intensity and lifetime, different

photophysical states related to light-harvesting and photoprotection can be identified and a kinetic model for the transitions between these states can be inferred. Application to the light-harvesting complex PE545 from cryptophyte algae revealed a transition from an unquenched (long lifetime, high intensity) to a quenched (short lifetime, small intensity) state that accelerates if the intensity of the excitation laser is increased.

Concerning the molecular mechanism of photoprotection, many different photophysical and/or photochemical pathways most likely contribute the underlying processes, which are collectively known as non-photochemical quenching (NPQ). In the contribution by Ruban and Saccon,⁴ a critical review is presented on the different photoprotective de-excitation reactions of chlorophyll that have been proposed for the major light-harvesting complex LHC-II of plants. These reactions include the formation of interchlorophyll charge transfer states, energy transfer between excited chlorophyll and optically dark excited states of carotenoids, and quenching by chlorophyll–carotenoid charge transfer. The review concludes that the three essential open points are “(1) the identity of the quencher, (2) the physics of the quenching process, and (3) which mechanism takes place *in vivo*. . .” Hence, a lot of research remains before we will understand photoprotection. The following reports address this topic.

Walla and co-workers⁵ introduce a new method to quantify the coupling between the optically dark state of carotenoids and the chlorophyll S_1 state from two-photon excitation fluorescence spectra. Short, Fleming, and co-workers⁶ report on a first kinetic model of NPQ in a simple marine alga involving the xanthophyll cycle, in which the enzymatic conversion of the carotenoid violaxanthin into zeaxanthin turns on non-photochemical quenching. The kinetic model is used to explain time-correlated single photon counting data collected under varying excitation intensities.

Sardar, Cerullo, and co-workers⁷ report time-resolved fluorescence and transient absorption data of the CP29 antenna complex of plants solubilized in detergent or inserted in discoidal lipid bilayers. The latter “nanodisks” are thought to mimic the native membrane environment. Interestingly, in the nanodisks, a shortening of the chlorophyll fluorescence time is observed, along with a decrease in carotenoid triplet formation. These results are interpreted in terms of a quenching involving chlorophyll–carotenoid energy transfer.

Besides switching the antenna complexes from a light-harvesting mode into a quenching mode, conformational transitions may also serve to acclimate into a particular light-harvesting mode. Kimura, Wang-Otomo, and co-workers⁸ investigate such conformational transitions in the Ca^{2+} binding core light-harvesting complex LH1 from the thermophilic purple sulfur bacterium *Thermochromatium (Th.) tepidum*. It is thought that the binding of Ca^{2+} ions leads to increased thermal stability. Kimura *et al.* investigated the structural changes of the complex upon Ca^{2+} binding/release using isotope-edited vibrational spectroscopy. They report the first vibrational footprints of this conformational transition. Yoneda, Dewa, and co-workers⁹ also report on purple bacteria. They extended the light-harvesting capacity of the light-harvesting complex LH2 through non-covalent incorporation of hydrophobic ATTO dye molecules into the surrounding lipid bilayer. The dyes broadly absorb light and then efficiently transfer excitation energy to the B850 pigments in LH2.

The complex dynamics of photosystems were also studied in this collection. In a 2D electronic spectroscopy study on PSII, Do, Tan, and co-workers¹⁰ find that internal conversion (IC) between the two lowest excited-states of chlorophyll occurs within 60 fs and that the excitation energies of the two states are uncorrelated. A new type of photoprotection in photosystem II (PSII) core complexes from the cyanobacterium *Thermosynechococcus (T.) vulcanus* is reported by Akhtar, Lambrev, and co-workers.¹¹ In their transient absorption/2DES study, they compare the decay of excited states in open reaction centers (RCs) and RCs with oxidized special pair P^+ . From this comparison, the authors conclude that P^+ is an efficient quencher of excitation energy and may play a role in photoprotection when water splitting in the oxygen-evolving complex is inhibited. A related study on photosystem I core complexes of the cyanobacterium *Spirulina (Sp.) platensis*, which contains strongly redshifted antenna states, is reported by Russo, Maiuri, and co-workers.¹² From time correlated single photon counting (TCSPC) and 2D electronic spectroscopy, they find picosecond energy transfer to and between red states as well as transfer to the pre-oxidized special pair and non-radiative internal conversion. In addition to the above processes, the authors identify a component ascribed to a rapid non-radiative decay of the antenna states that they speculate may serve a photoprotective role. Both when this process occurs and what is its molecular mechanism remain to be discovered.

An ancestor of PSI is the heliobacterial reaction center (hRC). It is a homodimeric RC that includes a PSI type core antenna. The major light-harvesting pigment is bacteriochlorophyll (BChl) g. Interestingly, the two primary electron acceptors in the two symmetric branches in the RC are Chl a, which absorb at higher energies than BChl g. Kondo, Matsushita, and co-workers¹³ use this energy difference to selectively excite the two Chl a pigments in the RC and monitor the polarization-resolved fluorescence from BChl g in single-molecule experiments at cryogenic temperature. On this basis, previous proposals for low energy BChl g sites in the antenna could be narrowed down to one BChl g that has a parallel transition dipole moment to its symmetry-related counterpart in the other half of the antenna.

Besides the above experimental studies, the present Special Topic issue also contains ground-breaking theoretical work. The two main problems addressed in the different contributions are (i) the parametrization of the Frenkel exciton (charge transfer) Hamiltonian of various light-harvesting complexes and (ii) the description of the quantum dynamics of excited states and their spectroscopic signatures.

In the perspective by Cignoni, Mennucci, and co-workers,¹⁴ the state-of-the-art and the open problems concerning the Hamiltonian parameterization are discussed, including calculation of site energies, excitonic couplings, and their dynamic and static disorder. One way to obtain the spectral density, which characterizes the dynamic disorder, is to combine molecular dynamics (MD) simulations of the nuclear positions with QC calculations of pigment transition energies. A prevailing problem has been the “geometry mismatch” between the classical force field used for the MD simulations and the QC calculations.

Sarangadharan, Malty, and Kleinekathöfer¹⁵ report a solution to this problem: a quantum mechanics/molecular mechanics (QM/MM) approach in which the pigment dynamics is described

by density functional theory based tight-binding (DFTB) instead of the purely classical force field used before. In the present Special Topic issue, this method is applied to the CP43 core complex of PSII. The spectral density of the chlorophylls in the high-frequency region agrees well with experimental data. A remaining problem, however, is to find an appropriate lineshape theory for the description of optical spectra. For the low-frequency part of the spectral density, different approximate lineshape theories exist, but the high-frequency part is more difficult to include. An underlying problem is the dynamic localization of excited states, which is difficult to describe with approximate lineshape theories.

Zhu, Higashi, and Saito¹⁶ aim to find absolute rather than just relative site energies of the pigments by improving the QC calculations. In their study, they investigate the Q_y transition energy of Chl *a* and Chl *b* in different solvent environments using a QM/MM scheme. A QC geometry optimization is included and the range-separation parameter of the exchange–correlation functional, used in the QC calculations, is varied to capture the experimental data with a remarkably low error margin.

A parametrization of previously unknown photosynthetic and artificial light-harvesting systems is provided by Mikalciute, Chmeliov, and co-workers¹⁷ and by Slama, Rajabi, and Mancal,¹⁸ respectively. In order to adapt to the light conditions in water, marine algae have replaced some Chl *a* by Chl *c* in their fucoxanthin–chlorophyll (FCP) light-harvesting complex. Chl *c* has a larger oscillator strength in the blue spectral region at the expense of the one in the red. Mikalciute *et al.* report the first structure-based calculation of excitonic couplings between Q_y transitions of Chl pigments in the FCP complex and the corresponding Förster theory rate constants of excitation energy transfer. Interestingly, the largest couplings (and fastest transfer) occur between Chl *a* and Chl *c*, despite the small oscillator strength of the Q_y transition of Chl *c*. Slama *et al.* introduce a 2D fluorographene system with graphene impurities as a promising artificial light-harvesting complex. In their QC study, they first show that the graphene islands behave like molecules exhibiting transition densities of low energy excited states that remain localized to these islands. By varying the size and relative orientation and distances between these defects, light-harvesting antennae can be created that show directed energy transfer to a low energy site with high efficiency. The population dynamics of excited states was described with the hierarchical equation of motion (HEOM) approach, which allows for effects such as the dynamical localization of excited states to be explicitly described, which is impossible with standard perturbative approaches. A drawback of HEOM is its high numerical cost and the fact that it is restricted to a particular type of spectral density.

Kundu, Dani, and Makri¹⁹ report an alternative non-perturbative approach, which is based on a path integral technique, in which there is no restriction with respect to the functional form of the spectral density. Using this technique, excitation energy transfer between the bacteriochlorophyll *a* pigments of the LH2 complex of purple bacteria is studied. Remarkably, the spectral density includes 50 high-frequency vibrational modes per pigment, besides a low-frequency part characterizing the pigment–protein coupling. This study, which reveals kinetics with unprecedented molecular details, serves as an important benchmark for perturbative approaches such as generalized Förster theory.

An alternative formally exact approach is presented by Mulvihill, Geva, and co-workers.²⁰ Their modified generalized quantum master equation (M-GQME) method is applied to study exciton relaxation in the Fenna–Matthews–Olson protein. Despite a partly classical description of nuclear motion, a good agreement is obtained with a full quantum HEOM treatment. The M-GQME method falls into a class of semiclassical descriptions, where the quantum aspect of nuclear motion is “rescued” by mapping it onto quantities that can be propagated by classical equations of motion. An alternative mapping procedure that is expected to be accurate in the limit of high temperatures and in cases where static disorder dominates the optical lineshapes is reported by Mannouch and Richardson.²¹ They apply their partially linearized spin mapping approach to the calculation of linear and non-linear optical spectra of the FMO protein and obtain good agreement with the fully quantum HEOM approach. Another semiclassical approach is reported by Polley and Loring,²² who calculate 2D electron–vibrational spectra of a three electronic state model system. Wang and Zhao²³ introduce a diagrammatic quantum Monte Carlo method that is capable of describing exciton dynamics in arbitrarily large systems using an imaginary time propagator to evaluate thermodynamic averages. Although the method is applied to study transport properties in disordered semiconductors, it could be readily applied to exciton transport in large photosynthetic light-harvesting complexes, e.g., the chlorosomes of green sulfur bacteria.

A fundamental question on light–matter interaction is addressed by Ko, Cook, and Whaley.²⁴ How does the exciton state population dynamics detected after coherent laser light excitation differ from that initiated by a randomly generated solar photon? They find that in the limit of weak system–field interaction, which applies to natural photosynthesis, both types of light excitation lead to equal exciton state populations. Another fundamental question concerning system–light interaction is how it can be used to investigate correlations in site energy fluctuations in excitonic systems. In their contribution, Heshmatpour, Hauer, and Sanda²⁵ investigate this question theoretically by considering fifth-order 2D electronic spectroscopy on a molecular dimer. The sign and magnitude of the correlations can be extracted from the tilt of the peaks in the 2D spectra. Interestingly, this spectroscopy also allows us to characterize the bi-exciton binding energy, about which our current knowledge is very limited.

Whereas the investigation of excitation energy transfer in photosynthesis greatly benefits from the fact that the involved electronic states can be probed spectroscopically, an investigation of charge transfer states (CT) is more indirect. CT states can only gain oscillator strength by their coupling to excited states. Manrho, Jansen, and Knoester²⁶ investigate the signature of this coupling in the absorption spectrum of linear chromophore aggregates using a Green’s function approach. A complementary approach that starts with a quantum chemical description of a donor–acceptor–donor triad is presented by Picconi.²⁷ In his approach, a diabaticization procedure is used to construct a vibronic coupling model between the local excited state of the donor and two CT states between the latter and the two acceptor molecules. The charge separation dynamics and its signature in transient absorption spectra are then studied by the non-perturbative multiconfigurational time-dependent Hartree method.

Due to the polar nature of CT states, their energies can be strongly shifted by static electric fields applied in Stark spectroscopy and by internal electric fields of the pigment–protein complex. By their coupling to CT states, excited states can “borrow” exciton–vibrational coupling from the former. In their contribution Braver, Valkunas, and Gelzinis²⁸ provide a general theoretical framework for the calculation of absorption and fluorescence Stark spectra of excitonic systems, including CT states. They find that the standard Liptay theory becomes invalid if the excited states have a large permanent dipole moment, e.g., by coupling to CT states. Large reorganization energies of excited states, which can also be induced by coupling to CT states, lead to large deviations between approximate lineshape theories and the numerically exact HEOM approach. Interestingly, a semiclassical lineshape theory that is based on a Poisson bracket mapping equation is found to give very accurate results in a wide parameter range.

The present Special Topic issue demonstrates that research on the primary photophysical and photochemical principles of photosynthesis is of general interest to a wide community of researchers from many different fields. It is this synergy that will bring us closer to the understanding of this process, which will ultimately allow us to create the solar energy converting devices of the future.

This special issue, in addition to highlighting remarkable progress, clearly shows that many highly challenging problems and open questions remain. To fully understand, and perhaps optimize, natural photosynthetic light harvesting, it seems likely that we will see greater focus on whole systems in live cells or fully functional membranes. New experimental methods and methods of analysis will be needed in a transition perhaps analogous to the transition from small molecule to macromolecular crystallography where iterative fitting and refinement play key roles. Perhaps advanced AI methods will have a transformative role as they do now in structural biology. Theoretical methods will be challenged by the need to confront large multiscale and multicomponent systems. Progress in recreating responsive systems *in vitro* by expression and reconstitution of pigment–protein complexes will also be a powerful complement to studies *in vivo*.

The challenging questions posed by light harvesting systems have long been a major stimulus to spectroscopic developments from single molecule to multidimensional spectroscopy. Third-order nonlinear spectroscopies have had a major impact on light harvesting research. Will higher-order studies become similarly impactful now that Brixner and co-workers (Malý *et al.*²⁹) have shown how to cleanly and simply separate the orders of the

nonlinear response? In a similar vein, will quantum light spectroscopies revealing photon statistics become important tools? What about the use of circular light polarization to analyze excitation energy relaxation/transport in greater detail? Chlorophyll and bacteriochlorophyll pigments show practically no intrinsic rotational strength due to the planarity of their structure. However, the wavefunction of the exciton due to the contribution of different pigments exhibits a strong rotational strength in stationary circular dichroism spectra of many light-harvesting systems. The obvious next step is to exploit this property in time-resolved spectra. The task is not easy since the signal to noise ratio is small due to the double difference nature of this type of spectra.

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