# Control of Energy Transport and Transduction in Photosynthetic Down-Conversion

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# Project Narrative

## 1 Introduction

**Overview:** The research program outlined here involves developing and integrating a number of theoretical and computational methods to enable the efficient first principles computation of ensembles of accurate model Hamiltonians for multi-chromophore light harvesting systems. These ensembles sample thermally accessible conformations of chromophore geometries and fluctuations of the protein environment that supports the chromophores. Electronic structure calculations provide access to chromophore excitation energies and electronic couplings, and their dependence on nuclear geometry gives information about the coupling of electronic transitions that transfer excitation between chromophores, which can also excite chromophore and environment vibrations responsible for dissipating electronic excitation. Different chromophores, and local protein environments enable these pigment protein complexes to function as excitation energy funnels in which inter-chromophore electronic coupling and local environmental dissipation directs excitation energy transfer, regulating the flow of excitonic energy, like the flow of electrons in electronic circuits.

The evolution of this downhill energy flow in these nanoscale excitonic circuits can be monitored using ultrafast 2D electronic spectroscopy (2DES) experiments that can provide exquisite detail of the time evolving vibrational and electronic (vibronic) quantum wave packets enabling direct determination of energy transfer pathways and mechanisms. These ultrafast nonlinear optical experiments provide detailed dynamical maps of how the sample absorbs and emits light as the excitation moves through the system. Despite splaying this information in multiple dimensions to relieve spectral congestion, in these complex biological systems many features still overlap so theoretical modeling plays a critical role in disentangling mechanistic detail from these signals. The first principles calculation of these signals takes as input the model Hamiltonian ensemble and makes the reasonable assumption that the quantum dynamics that determines the signal evolution proceeds quickly on the timescale of fluctuations in the model parameters. New methods for performing open system quantum dynamics of many coupled electronic and vibrational degrees of freedom can now be implemented to compute these 2DES signals and the results compared directly with experiments to provide detailed assignment, mechanistic interpretation and iteratively guide model refinement.

With molecularly detailed and validated models in hand we plan to explore the development of new capability using quantum optimal control theory implemented with our open quantum system density matrix dynamics methods to conduct "open-loop" optimal quantum control studies of the feasibility of employing adaptive feedback controlled pulse shaping methods to prepare specific initial excited states with the goal of developing understanding of their influence on subsequent dynamics as probed in the 2DES signals. The other key feature of these open loop studies is that they will help to provide fundamental understanding of the mechanism of control realized in the adaptive feedback control, "closed-loop", experiments and can reveal important design elements.

These closely coupled theoretical open-loop, and experimental closed-loop studies will explore the possibility of reducing decoherence by using model Hamiltonian-inspired shaped laser pulses to prepare initial coherent superposition states that are close to Zurek's "pointer" states[1–3] and thus in principle can sustain long-lived quantum coherent dynamics. The tools we plan to develop in this project thus support the long-term goal of understanding mechanisms of quantum control and initial state preparation in noisy complex systems.

As outlined below the photosynthetic light harvesting systems we plan to study as a proof of concept of these protocols are of great practical and fundamental interest so this project not only addresses the development of combined theoretical/computational and experimental methods to explore the feasibility of quantum state preparation in highly complex molecular systems, but also the information we learn about manipulation of energy transfer pathways and mechanisms will have significant impact on design concepts for new bio inspired nano structured materials that might be engineered to create new excitonic circuit elements for enhanced energy transport and transduction in light harvesting applications.

**The Systems:** Photosynthetic organisms employ chlorophyll-based light harvesting machinery[4–14] to transport photo-excitation energy and convert it to electrical energy by separating charge in reaction centers. Chlorophyll molecules perform these functions using absorption and emission primarily in the lower energy, red part of the spectrum. Many organisms have coopted other higher energy, blue light-absorbing chromophores, like carotenoid molecules, to extend the wavelength range over which they can harvest sunlight[15,16]. This has resulted in the evolutionary design and engineering of "down converting" pigment-protein nano-structures that enable the chlorophyll based excitonic circuitry to "plug into" a variety of different colored ambient light sources depending on the environmental lighting conditions in which different organisms must function.

The energy transfer pathways and mechanisms employed by these bio-molecular down-converters are only partially understood. A goal of the research program outlined here is to first reveal these processes in detail enabling the construction of accurate, predictive models and the exploration of how these processes might be influenced by changes in conditions, chemical changes, protein structural changes and mutations. With this demonstrated level of detailed mechanistic understanding the basic design concepts employed in these important photosynthetic components might be extended to new technologies for harvesting light and manipulating photo-excitation for energy and other applications.

Adaptive feedback control of energy flow has been demonstrated in natural and artificial light harvesting complexes involving energy transfer between carotenoid and chlorophyll/porphyrin molecules[17,18] focusing in particular *e.g.* on control over the branching of population between two competing pathways, internal conversion (IC) from the initially excited bright carotenoid $S_2$ state, to its $S_1$ state, and energy transfer (ET) from the carotenoid to the chlorophyll/porphyrin. Our goal is to explore extending this control capability to the preparation of arbitrary initial coherent superposition states, *e.g.* excitation to a non-stationary state localized on a given chromophore, and monitoring the subsequent dynamics.

The basic mechanism of down conversion process in pigment protein complexes involves resonantly transferring the absorbed energy from the initially excited higher energy electronic state of a donor subunit to a lower electronic energy state of an acceptor, and making up the electronic energy difference by exciting acceptor vibrations that can dissipate the excess energy, thus vibronic transitions of the network of coupled chromophore play a key role. The relevant time and energy scales that govern these processes can profoundly influence critical aspects of this basic mechanism.

The inverse of the strength of the vibronic coupling between the donor state and the vibrationally excited acceptor state is proportional to the characteristic coherent population transfer time (Rabi cycling time) between these states, $\tau_{\text{coh}}$. In addition, these coupled chromophore states are also solvated in a noisy protein environment that causes their energies to fluctuate with a characteristic solvent relaxation or incoherent "dephasing" time, $\tau_{\text{incoh}}$.[19] If these incoherent processes are fast as a result of strong environmental interactions of the chromophores compared to their weaker vibronic coupling, so that $\tau_{\text{incoh}} \ll \tau_{\text{coh}}$, the wave function does not have time to spread out over multiple pigments before the solvent fluctuates and changes the states resulting in localization so that transfer occurs by incoherent hopping between localized states at a rate that can often be reliably predicted by Förster theory. On the other hand, if the coherent processes are fast, resulting from stronger vibronic coupling compared to weaker environmental couplings, so $\tau_{\text{coh}} \ll \tau_{\text{incoh}}$, the transport occurs coherently involving wave function delocalization over multiple chromophores.

The goal of this project is to use direct ultrafast 2D electronic spectroscopy measurements[20–23], together with statistical mechanical, quantum chemical, and quantum dynamical calculations to characterize two very different classes of down converting pigment protein complexes that may function in these fundamentally different quantum dynamical regimes. By comparing and contrasting these different evolutionarily optimized down converters our studies will reveal how the different mechanisms at work tradeoff various aspects to achieve high quantum efficiency and/or robustness in different functional contexts. Exploring the control elements predicted by optimal quantum control solutions obtained from validated models and using them to guide experimental adaptive feedback control studies preparing different types of initial states for these systems that may function in different dynamical regimes will require intimate coupling of theoretical and experimental studies that will be realized in regular team meetings as outlined section 2.5.

The first class of systems we plan to study are the well characterized phycobili pigment proteins from cryptophyte algae[24–27]. These bio-excitonic down converters employ a flexible protein structure that can accommodate various bilin linear tetrapyrrole donor and acceptor chromophores whose electronic excitation energies are controlled by different conjugation lengths. In these systems the distances between chromophores with different electronic excitation, or site energies, are generally quite large so the vibronic couplings between donor and acceptor states are typically fairly small. The strength of the interactions of these states with the solvation environment of a given chromophore can vary significantly depending on if it is buried in different parts of the protein, or exposed to aqueous solvent. As such, the separation of timescales in this system may not always be completely clear. The weaker vibronic coupling combined with a donor-acceptor pair experiencing stronger environmental interactions will put such a transfer clearly in the incoherent limit. However, if the environmental interactions are weaker, and similar in strength to the vibronic coupling, no clear separation of timescales exists and a rich and complex dynamics[23,28–39] [20–23]not easily described by perturpation theory may result. In fact, our recent simulation studies have shown that at longer timescale these fluxional systems can sample local Hamiltonians that operate in different dynamical regimes so that a given component energy transfer process may be better represented by an ensemble of models characterized by Hamiltonians describing coherent and incoherent limits, and everything in between.

**We hypothesize that these cryptophyte algae pigment - protein complexes, that enable down conversion, function with the key vibronic energy transfer steps operating in the coherent regime to make this process occur rapidly and efficiently so the energy is quickly made compatible to flow through to the rest of the lower energy chlorophyll light harvesting circuitry.**

We will explore this hypothesis using a variety of studies including using quantum control to select different target initial states and monitor subsequent energy transfer pathways.

Also crucial for our proposed research to test this hypothesis is the report by Scholes and collaborators that the structures of the phycobiliproteins can be controllably manipulated *e.g.* by single point mutation, which transforms the compact “closed” forms, such as the phycocyanin chromophore based PC645 from *Chroomonas sp.* or the phycoerythrin based PE545 from *Rhodomonas sp.* to the “open” *Hemiselmis* structures such as PC612 from *H. virescenes* or PE555 from *H. andersenii.* Remarkably, they have also demonstrated that these “dimer of dimers” structures can be reversibly dissociated producing stable $\alpha-$ and $\beta-$protein subunits in solution, and even more extraordinary, different subunits from different species can be re-associated with one another to produce new functioning un-natural “chimera” complexes. This provides the opportunity to explore variations in vibronic couplings between chromophores and variations in chromophore - environment couplings over a wide range of naturally occurring and un-natural hybrids. We will present preliminary results of a detailed computational study on the PC645 system that suggests that some of the vibronic EET pathways in these systems function in the boundary region between a coherent and incoherent mechanism and variations in chromophore solvation environment like those resulting from these structural changes should push the system controllably between these different mechanistic regimes.

The second down converter system to be studied in this project is the Peridinin - Chlorophyll-a - Protein (PCP) complex from dinoflagellate algae, which exhibits a qualitatively different structural design concept with each unit composed of eight peridinin and two chlorophyll-a molecules densely packed into an $\alpha$-helical protein basket with the peridinin donor and chlorophyll-a acceptor chromophores essentially within van der Waals contact, so the vibronic coupling between these molecules may be very strong. However, the solvation environment is also very different with the close contact between the more rigid chromophores possibly dominating intermolecular environmental fluctuations. Despite numerous theoretical[40–42] and experimental[43–45] studies of this system there is currently no consensus on the mechanism of down conversion. This situation arises because of an important dynamical complication. Photoexcitation in the blue takes the peridinin donor to its bright $S_2$ state - its large transition dipole in this state, together with the close proximity, could indeed produce strong vibronic coupling with the chlorophyll-a resulting in rapid energy transfer in the coherent regime, **consistent with our hypothetical design concept for these down converters**. However, many model mechanisms proposed to explain time resolved pump-probe experimental[43,46] results suggest rapid internal conversion to the $S_1$ state of peridinin, which is essentially a dark state so we expect significantly weaker vibronic coupling to the acceptor chlorophyll-a. These mechanistic schemes go on to propose nuclear distortion to other intermediate structures with intramolecular charge transfer (ICT) character on the $S_1$ surface causing potentially stronger vibronic coupling to enable excitation energy transfer on the experimental timescale. The presence of such ICT state contributions may increase environmental interactions so this competing transfer mechanism could be operating in the incoherent regime, but the issue is clearly complicated.

The indirect pump-probe spectroscopic methods used to date[43–45], for example, to study the PCP system require constructing mechanistic schemes and employing global analysis to fit model parameters. Such approaches, however, do not in general yield unique interpretations so a study like that proposed here employing a direct spectroscopic approach like 2DES, which identifies precisely the energies of the states involved, as well as providing detailed dynamical information about their couplings to other states in general provide a better way to extract mechanistic information. Due to the complexity of this ultrafast non-linear optical experiment there may be several overlapping signals that can, in general, be difficult to pick apart. However, by combining results from detailed molecular dynamics simulations and high level quantum chemistry calculations that can directly explore the distribution of effective Hamiltonians underlying these signals, as well as general purpose, non-perturbative quantum dynamical techniques that can reliably describe the complex dynamics of these systems in, and beyond the different dynamical regimes where standard perturbative approaches apply, we should be able translate the computed first principles model Hamiltonian distribution into observables like rates of competing component processes as well as directly predict the 2DES ultrafast responses that can probe detailed vibronic wave packet dynamics providing a complete connection between a first principles derived mechanistic description and direct dynamical experimental results.

But our computational methodology provides much more than simply accurate ways to calculate experimental signals. We will demonstrate that the approach provides a simple first principles estimator of whether a particular mechanistic step is functioning in the coherent or incoherent regimes.

# 2 Project Description and Justification

## 2.1 Significance

Fundamental understanding of the capture of sunlight, its efficient transport through excited state energy transfer, and its transformation in biological light harvesting processes is a central focus of the DOE Photosynthetic Systems program. Down conversion of higher energy absorbed light, so it can be processed by the chlorophyll-based photosynthetic machinery, is a strategy used by many organisms to enable broad utilization of the solar spectrum. Transformation of electronic excitation to vibrational energy through vibronic excitation energy transfer is the first step in dissipating excess energy in these down conversion systems. Our project will probe the fundamental pathways and mechanisms that nature has evolved to accomplish efficient down conversion. Coherent superpositions of electronically (vibronically) excited donor and vibronically excited acceptor are central to efficient down conversion and our project uses ultrafast nonlinear spectroscopy experiments to probe these vibronic superposition states. Our theoretical team develops accurate molecularly detailed models of these vibronic states and how they fluctuate in the protein environment to understand the role of coherence in the mechanism. Finally the systems we will study are exquisitely tunable by changes in structure and nature of chromophores so will enable the most comprehensive study of pathways and mechanisms of these down conversion processes. We will advance the field by (a) developing and demonstrating design principles for vibronic control of energy transfer, and (b) discovering whether nature has evolved to use these principles in photosynthetic energy conversion.

## 2.2 Theoretical and Computational Methods:

The Frenkel exciton Hamiltonian, $\hat{H} = \hat{H}_{\text{ex}} + \hat{H}_{\text{ex}-\text{vib}} + \hat{H}_{\text{vib}}$, is a widely used approximate form for modeling excited state energy transfer in photosynthetic light harvesting. Its terms describe the exciton subsystem of coupled chromophores, parameterized by their excitation energies $\epsilon_\alpha$ and inter-chromophore couplings $\Delta_{\alpha\beta}$, the exciton-environment interaction that assumes the energies of the chromophores vary linearly with nuclear coordinates, and the Hamiltonian for the motions of these coordinates themselves, or the vibrations, which are assumed to be sets of independent harmonic normal modes. The electron-nuclear linear coupling constants vary with nuclear mode frequency and whether these modes are intramolecular, and strongly coupled to excitonic subsystem, or intermolecular, or environmental in nature, and more weakly coupled. The strength of these electronic - nuclear coupling terms is governed by the chromophore dependent inter- and intramolecular spectral densities, $J^{(\alpha)}_{\text{inter}}(\omega)$ and $J^{(\alpha)}_{\text{intra}}(\omega)$. The many parameters appearing in this model are usually adjusted to best fit a range of experiments and calculations[47–50] so, in this semi-empirical implementation, the Hamiltonian is a highly averaged, effective model that is not in general unique and may be difficult to interpret physically.

In a recent series of papers[51–53], however, we presented an alternative approach that treats the Frenkel exciton Hamiltonian as a local interpolating form and uses configurations from MD trajectories, together with quantum chemistry methods, to explore the global first principles Hamiltonian, but then representing it locally in the convenient Frenkel form. The approach, and its implementation, is outlined in the sections below and its quantitative and interpretative capabilities are demonstrated in a preliminary study of cryptophyte algae spectroccopy and vibronic energy down conversion. This approach will be our conceptual workhorse that will enable us to determine when different component processes and pathways are operating in coherent or incoherent dynamical regimes.

### 2.2.1 Model Hamiltonian Ensemble Sampling

We start[51] by generating configurations of the entire solvated pigment-protein system employing a long MD trajectory using molecular mechanics (MM) force fields to sample conformational fluctuations. Though the reliability of MM force fields can be questionable[54–56], such trajectories do provide a reasonable sampling of equilibrium fluctuations. This is the same starting point that has been employed in much of the previous published work that attempts to use first principles based approaches to study these systems[57–62]. Our approach, however, is fundamentally different since we avoid the inconsistency associated with directly using the configurations sampled from the approximate MM model ground state surface in electronic structure calculations to compute the Franck-Condon excitation energies[63]. Rather, we only use the sampled MM configurations to initiate QM ground state optimization of chromophore geometries in the presence of the instantaneous local fields provided by the MM partial charges of the surrounding protein environment to locate the "inherent structures" or local minima[64–67] of the chromophores in the presence of their surroundings. The pigment-protein complex will sample different inherent structure as long as enough thermal energy is available to overcome transition barriers.

Ground and excited state properties are then computed at these optimized geometries to parameterize an ensemble of instantaneous local Frenkel or system-bath model Hamiltonians that can be incorporated in model studies of the vibrational and vibronic relaxation processes. Alternatively, one could exploit "on-the-fly" QM/MM MD[68,69] approaches for sampling configurational space[65,70]. However, complete exploration of the potential energy surfaces becomes prohibitively expensive with such approaches, compared to our highly efficient sampling scheme just outlined.

These ideas can be generalized to go beyond the fixed MM partial charge assumption using polarizable embedding methods,[71,72] which can be important for treating some photoactive proteins[63,73–78]. If the charge distributions of the ground and excited states are not very different, however, this higher order environmental polarization effect can be small.[79] However, environmental polarization effects might be significant for excitations with large transition dipole moment. As outlined below, careful consideration of local environmental polarization effects will be required when treating the peridinin states in our studies of the PCP system.

### 2.2.2 Electronic Structure Calculations

For the bilin and chlorophyll systems studied in previous work[51–53] we have found that local chromophore geometry optimizations, vibrational analyses, single point excited state gradients (that govern electron - nuclear couplings) as well as ground to first excited state transition densities[80,81] (that determine inter-chromophore electronic couplings $\{\Delta_{\alpha\beta}\}$), and excitation energies, $\{\epsilon_\alpha\}$, were optimally performed with a two layer ONIOM partitioning in which the QM layer chromophore atoms are described respectively at the B3LYP, HF, CIS, and SOS-CIS(D)[82–84] levels of theory. This combination of methods provides sufficiently accurate characterizations of the ground and excited states at several hundred sampled inherent structures thus efficiently producing reliable parameterizations of an ensemble of Frenkel exciton models that have been used to calculate experimental spectroscopic signals with excellent accuracy as demonstrated in the preliminary results presented in **Section 2.2.7**.

The PCP system poses a significant challenge to computational chemistry. The extended polyene-like chemical structure of the peridinin chromophore (Figure 1a) leads to a manifold of the low-lying doubly-excited electronic states, and the lowest excited state, $S_1$, which can participate in the radiationless relaxation from the bright $S_2$ state, is of the doubly-excited character. Doubly-excited states are problematic for many electronic structure methods (CIS, TDDFT, EOM-CCSD), however they can be reliably described with multireference approaches. In addition to challenging electronic structure, the description of the interactions with the protein environment requires special care. Excitation into the bright $S_2$ state, playing the key role in the excitation energy transfer[85,86], is accompanied by profound dipole moment change[87–89] (Figure 1d). Proper description of such charge-transfer states in complex protein environment should go beyond the conventional electronic embedding QM/MM approaches where the environment is represented by fixed point charges. Polarizable embedding schemes are prerequisite. We have recently showed that the solvent polarization contributes profoundly to energetic parameters describing redox processes[90,91] and to energies of the charge-transfer states in proteins (*Tazhigulov and Bravaya, 2019, in preparation*). This in consistent with our preliminary TDDFT/non-equilibrium PCM calculations (Figure 1c) which indicate that the effects of the environment polarization on the computed excitation energies are non-negligible (0.2 eV). The Bravaya group has extensive expertise in multireference calculations[92–95] and polarizable embedding methods[90–92] and is uniquely positioned to successfully perform this part of the computational work.

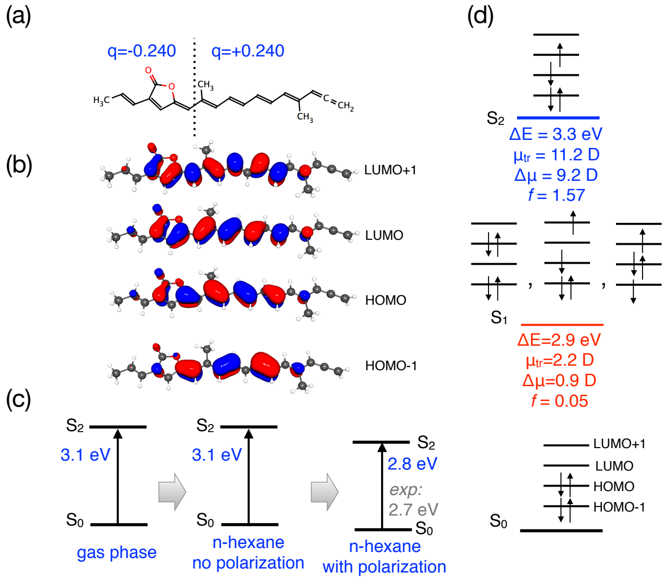

Figure 1: Lowest excited states of the model peridinin system from Refs.[88,96] characterized with extended 2nd order multiconfigurational quasidegenerate perturbation theory, XMCQDPT2, and TDDFT. (a) Structure and charge distribution of the peridinin $S_2$ state. (b) State-averaged SA-5-CASSCF(10/10)/6-311+G(d,p) natural orbitals. All active space orbitals are delocalized. (c) $\omega$B97X/6-31+G(d) excitation energies of peridinin in the gas phase, in non-polarizable n-hexane ($\epsilon = 1.88$, $\epsilon_{opt} = 1$), and in fully polarizable n-hexane ($\epsilon = 1.88$, $\epsilon_{opt} = 1.88$) obtained using non-equilibrium PCM scheme. (d) XMCQDPT2/SA-5-CASSCF(10/10)/6-311+G(d,p) transition characteristics for the dark $S_1$ and bright $S_2$ states.

We will exploit accurate multireference electronic structure methods, including extended multiconfigurational quasidegenerate perturbation theory, XMCQDPT2[97], and n-electron valence perturbation theory, NEVPT2 [98,99], to characterize the electronic structure of the chromophores. These methods can reliably treat both the bright $S_2$ and the dark doubly-excited $S_1$ states of peridinin. The methods will be thoroughly benchmarked with respect to the size of the active space relative to density matrix renormalization group, DMRG, multireference perturbation theory implementations[100]. Our preliminary estimates of $S_0 - S_2$ excitation energies (Figure 1d) for the isolated chromophore are in good agreement with both experimental data (2.7 eV $\lambda_{max}$ for peridinin in n-hexane)[101] and with the earlier NEVPT2/DMRG-CASSCF(16/16) estimates [102], considering that the account for the polarizable (non-polar) environment brings excitation energy down by 0.2 eV (Figure 1c). The effects of the protein environment on the excitation energies and electronic couplings will be evaluated by employing polarizable embedding effective fragment potential approach[103] and its extension to biomolecular system[104]. Polarizable environment models combined with multireference *ab initio* methods, which can be done, for example, using GAMESS package, will yield accurate energetic parameters that will be further used for dynamical simulations.

### 2.2.3 Spectral Density Calculations

The couplings of the chromophore excitonic subsystem to different classes of nuclear degrees of freedom result in them playing different roles in influencing the mechanism of excited state resonant energy transfer. The dynamics of the continuum of *intermolecular* solvation environment modes causes the energies of the discrete molecular states to fluctuate and the magnitude of these fluctuations, as summarized by the chromophore's intermolecular reorganization energy, $\lambda^{(\alpha)} = \frac{1}{\pi}\int_0^\infty d\omega J^{(\alpha)}_{\text{inter}}(\omega)/\omega$, determines the dephasing time, $\tau_{\text{incoh}} = h/\lambda^{(\alpha)}$. In this picture, the discrete *intramolecular* chromophore vibrational modes, on the other hand, enter our description in a completely different way - they appear in our definition of the initial and final discrete molecular quantum states and so influence the vibronic coupling matrix element, but they also determine the basis state energies, and thus the resonance energy condition. If the vibronic states involved in a particular transition are on resonance then the characteristic coherent population transfer time between these states is $\tau_{\text{coh}} = h/\Delta_{\alpha\beta}\langle \mathbf{v}^{(\alpha)}|\mathbf{u}^{(\alpha)}\rangle\langle \mathbf{u}^{(\beta)}|\mathbf{v}^{(\beta)}\rangle$. The nuclear part of $\tau_{\text{coh}}$ involves the Franck-Condon (FC) factors and these are related directly to the intramolecular reorganization energies, $\Lambda_I^{(\alpha)}$. Thus, the coherent and incoherent timescales for vibronic transitions are governed by the electronic coupling $\Delta_{\alpha\beta}$, and both the intermolecular and intramolecular reorganization energies. So the inter- and intramolecular spectral densities that determine these different components of electron-nuclear couplings are central.

In our approach to computing spectral densities[53,105] we break the electron-nuclear interactions into short- and long-range (intramolecular and intermolecular) contributions[106–108] and for optimal accuracy the electron-nuclear linear coupling constants for these different DOF are estimated in different ways. We use the local inherent structure molecular normal modes for the intramolecular nuclear DOF, performing normal mode analysis to extract the intramolecular bath frequencies, $\{\Omega_I^{(\alpha)}\}$ and then the corresponding intramolecular electron-nuclear linear coupling constants, $\{C_I^{(\alpha)}\}$, are obtained from single point excited state gradient calculations, and projecting these forces into in these normal mode directions. For these intramolecular modes, the electron-nuclear coupling weighted density of states or intramolecular spectral density is then obtained as $J^{(\alpha)}_{\text{intra}}(\omega) = \frac{\pi}{2}\sum_I (C_I^{(\alpha)2}/\Omega_I^{(\alpha)})\delta(\omega - \Omega_I^{(\alpha)})$.

We estimate the inter-molecular spectral density, on the other hand, using the correlation function of the fluctuations in the long-range contributions to the chromophore excitation energy, $K^{(\alpha)}(t) = \langle \delta\epsilon^{(\alpha)}_{\text{inter}}(t)\delta\epsilon^{(\alpha)}_{\text{inter}}(0)\rangle$, so that $J^{(\alpha)}_{\text{inter}}(\omega) = \beta\omega\int_0^\infty dt K^{(\alpha)}(t)\cos(\omega t)$. The charge density coupling (CDC) method[107–111] is used to calculate the fluctuations in the long-range contributions to site excitation energies, $\delta\epsilon^{(\alpha)}_{\text{inter}}(t)$, along the MD trajectory from the interactions of the partial charges in the local protein environments with the ground and excited state difference charges on each chromophore. To construct the full model Hamiltonian description we discretize the intermolecular continuum and extract the couplings $\{c_i^{(\alpha)}\}$ using $J^{(\alpha)}_{\text{inter}}(\omega)$ in a similar expression to that just given for $J^{(\alpha)}_{\text{intra}}(\omega)$. The reorganization energies of the intra- and inter-molecular modes are then $\Lambda_I^{(\alpha)} = C_I^{(\alpha)2}/2\Omega_I^{(\alpha)2}$, and $\lambda_i^{(\alpha)} = c_i^{(\alpha)2}/2\omega_i^{(\alpha)2}$.

This completes our first principles approach for characterizing the Frenkel exciton model Hamiltonian interpolating form describing the behavior of the coupled electron-nuclear system in the region of each sampled inherent structure. The underlying dynamics of the model is simple - the system oscillates like a multi-state spin-boson while it is in the basin of a particular inherent structure and then makes stochastic transitions between basins. The lifetime in a given basin is determined by the MD trajectory, and its characteristics are summarized in the Frenkel form.

### 2.2.4 Semiclassical Path Integral Quantum Dynamics

Our model Hamiltonians can now be employed in quantum dynamics calculations that treat the fully coupled non-adiabatic electron - nuclear dynamics in the different inherent structure regions. This Hamiltonian ensemble representation enables us to explore, in detail, what particular local structures are responsible for different energy transfer kinetics and ultrafast non-linear spectroscopic signatures observed in ensemble average experiments so we can pick apart contributions to these dynamics from different sub-ensembles to provide a deeper understanding of the contributing microscopic pathways and mechanisms.

Different quantum dynamics methods can be used to treat the multistate dynamics of each of our Frenkel model Hamiltonians *e.g.* HEOM, MCTDH, *etc.*[112–117]. We have developed a highly efficient semiclassical trajectory based partial linearized density matrix (PLDM) dynamics approach[118–125], a review of which, with particular emphasis on applications to photosynthetic light harvesting systems, has recently appeared[53].

The Meyer-Miller mapping Hamiltonian formalism[126,127] provides and exact representation of general non-adiabatic dynamical problems. It can be implemented highly efficiently using semiclassical coherent state trajectory based methods[128,129] in which both nuclear and electronic mapping variables are treated on consistent dynamical footing. Our PLDM approach uses these semiclassical nonadiabatic propagators to evolve the density matrix, which requires forward and backward propagation. The approach linearizes the phase of the density matrix evolution in the difference between the forward and backward paths of the continuum of classical-like low frequency variables and keeps the quantum interference effects between different forward and backward paths of the electronic mapping variables and higher frequency vibrational modes that can be incorporated in the vibronic representation.

After sampling quantum initial conditions, an ensemble of semiclassical trajectories is evolved with a simple MD approach, and the contributions from each trajectory to the final time evolved quantum density matrix are accumulated with phase weights that account for quantum interference. The scheme can thus automatically describe the coherent and incoherent dynamical regimes of energy transfer and it enables a highly flexible representation in which the dynamics of different variables can be treated fully quantum mechanically or through a linearized semiclassical description, all with in the context of an MD simulation. In recent applications to computing ultrafast 2DES of model systems[130] we found that the approach was able to provide results with comparable accuracy to exact HEOM calculations[112–114] with faster computation times and a dramatic reduction in memory utilization suggesting that the PLDM approach could be able to treat significantly larger, more realistic models. PLDM can also handle arbitrary realistic spectral densities, it does not make the secular or Markov approximations and is non-perturbative.

### 2.2.5 Vibronic Exciton Model

Ultrafast 2DES experiments generate wave packet motion on ground and excited electronic states of the different chromophores. The simplest approach to incorporate the wave packet dynamics of the specific modes that are most strongly coupled to the electronic transitions is to regroup these modes into the exciton subsystem Hamiltonian, $H_{\text{ex}}$,[131–134] and produce a model describing vibronic excitons evolving in the presence of the bath of other more weakly coupled vibrations. We thus partition each chromophore's nuclear DOF into a subset of $n_d^{(\alpha)}$ "discrete" modes, the states of which are incorporated into the vibronic exciton subsystem, and the remaining $n_c^{(\alpha)}$ weakly coupled "continuum" modes that, together with the solvation environmental DOF, are described by coordinates $\mathbf{Q}_c$, and treated semiclassically in our implementation of the PLDM dynamics.

Treating the vibronic problem by simply incorporating important discrete vibrational DOF into the excitonic system part of the Hamiltonian very rapidly becomes unwieldy due to the exponential growth in number of available states. This problem can be somewhat tamed if the FC factors are small so only states 0 and 1 are appreciably populated during the time scale of interest or by making the "one-particle" or "two-particle" approximations[132,135–137] that limit the number of chromophores that are excited in the basis states. Thus, for example, pairs of chromophores can be vibrationally excited in their ground or excited electronic states enabling ground state vibrational excitation during energy transfer processes[138].

We have recently developed a semiclassical coherent state density matrix (CSDM) propagation scheme[139] that replaces the static vibronic basis states for the discrete modes in the approach outlined above with evolving coherent state basis functions, the parameters of which are propagated with simple classical like trajectories, similar to the semiclassical path integral quantum dynamics methods outlined above. This new dynamical approach provides a substantially improved representation over the standard static vibronic description and it is highly optimized for treating generalized Frenkel exciton models with complex, highly structured spectral densities that include strongly coupled high frequency discrete quantum modes. In fact, the CSDM approach for the high frequency quantum environmental modes is easily implemented in tandam with PLDM being used to treat the low frequency classical-like continuum modes.[139]

### 2.2.6 Quantum Optimal Control Theory Implementation within Semiclassical Density Matrix Dynamics

The application of quantum optimal control theory (QOCT)[140–142] to photosynthetic pigment-protein complexes (PPC) is well documented in the literature[143–146] and the approach we follow is detailed in references[143,144]. To summarize we extend the model Frenkel exciton Hamiltonians in our ensemble to include a dipole field interaction term of the form $\mathbf{E}(t)\cdot(\mathbf{d}_{\alpha\beta}|\alpha\rangle\langle\beta|+h.c.)$ where $|\alpha\rangle$ and $|\beta\rangle$ are now delocalized exciton states that can be written as linear combinations of the chromophore site basis states, and $\mathbf{d}_{\alpha\beta}$ is the PPC transition dipole between these excitons. The optimal control field that takes the system from its initial ground state to some specific target excited state *e.g.* localized at a given site basis state is obtained by solution of a self-consistent equation for the field of the form $\mathbf{E}(t) \sim f(t)\mathbf{K}(t_f, t; \mathbf{E})$ where the envelope function, $f(t)$, guarantees the pulse vanishes for $t < t_0$ and $t > t_f$, and the control kernel reads $K(t_f, t; \mathbf{E}) = \frac{i}{\hbar N_r}\sum_j \mathrm{Tr}\{\hat{\sigma}^{(j)}(t)[\hat{\mu}^{(j)}, \hat{\rho}^{(j)}(t)]_-\}$, which contains the forward propagation of the density operator $\hat{\rho}$ from the initial time up to the intermediate time, $t$, and a backward propagation of the auxiliary density operator $\hat{\sigma}$ from $t_f$ back to $t$, where the final boundary condition for the auxiliary operator is $\hat{\sigma}(t_f) = \hat{\Pi}_{tar}$, the target state projector. In the above the sum runs over all realization, $N_r$, in our Hamiltonian ensemble, so the optimal pulse is determined by a compromise with respect to all the model Hamiltonians in our ensemble. This is a significant numerical challenge as both density operators ($\hat{\rho}$ and $\hat{\sigma}$) must be propagated for all Hamiltonian ensemble members simultaneously. The highly efficient classical trajectory -like propagation of the basis set parameters of our hybrid CSDM and PLDM approaches will be explored as an alternative to the standard approximate Lindblad quantum master equation approaches that abound in the literature.[143–146]

### 2.2.7 Demonstration of *Ab Initio* Mechanistic Exploration: PC645

As a justification of our approach for the detailed mechanistic exploration of EET using the theoretical and computational protocols outlined in the previous sections, here we present a summary of results from a preliminary study of the PC645 light harvesting antenna complex (**Figure 2d**).

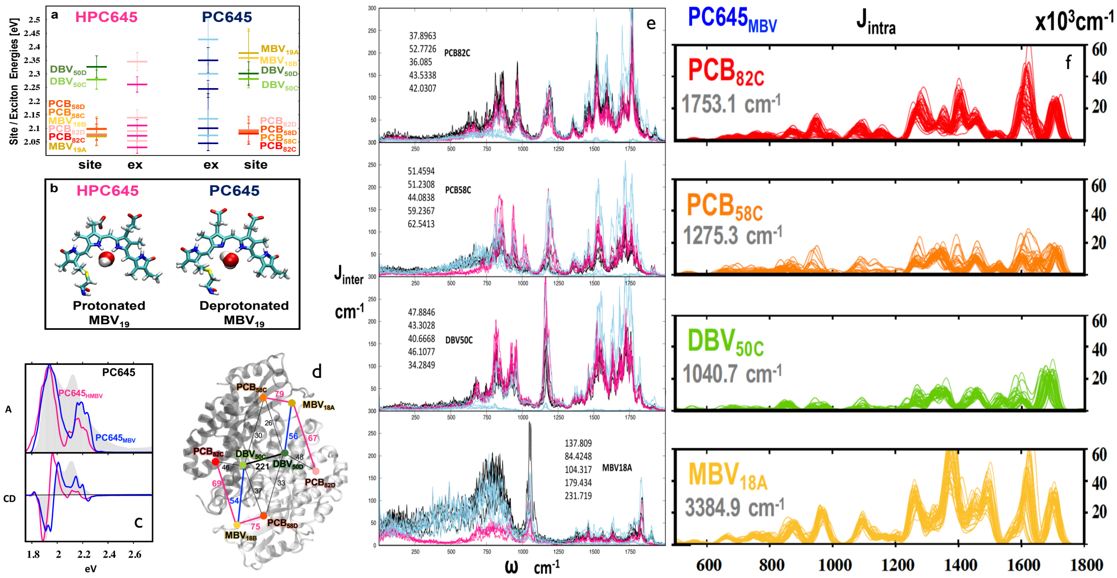

**Figure 2: PC645 Hamiltonian Ensemble Simulations** (a) Mean site and exciton energies and their ensemble dispersion for (b) protonated MBVs (HPC645) and unprotonated (PC645). (c) Influence of MBV protonation on calculated Absorption and CD compared to experiment (grey). (d) Structure showing color coding, electronic couplings and protonation affect on delocalization. (e) Inter- and (f) intra-molecular spectral densities showing ensemble variation. Insert values give representative / average reorganization energies.

**Figures 2a-c** explore the influence of protonation state of the MBV chromophores on excitation energies and CD and spectra of this complex. Unlike the other chromophores the MBVs are not coordinated with aspartic acid groups and our computed unprotonated spectra agree quantatively with experiment.[51] **Below we will show that protonation state significantly influences whether vibronic down conversion occurs coherently or incoherently.**

From the ensemble average of several hundred sampled configurations, the site energies and their fluctuations shown in **Figure 2a**, we find that $\mathrm{MBV}_{18}$ deprotonation increases this chromophore's average site excitation energy by nearly 0.3 eV and its site energy fluctuations more than double. The average electronic couplings change relatively little on deprotonation (**Figure 2d**), however, the average pattern of exciton delocalization can change significantly because the MBVs change from being quasi degenerate with the PCBs when protonated to being quasi degenerate with the DBVs when deprotonated.

**Figures 2e** and **2f** present our calculated inter- and intra-molecular spectral densities and computed reorganization energies. The intramolecular spectral densities were used to determine a limited set of most strongly coupled discrete modes for inclusion in the vibronic exciton model Hamiltonian and PLDM propagation was used to compute the linear response, $R^{(1)}(t)$, from which we obtained the absorption and CD spectra reported in **Figure 2c**, which are in semiquantitative agreement with experiment, with best agreement supporting MBV deprotonation.

The computed quantities presented in **Figure 2** can be used to understand which vibronic energy transfer pathways are coherent, and which are incoherent. Using the expressions given in **Section 2.2.3** we can estimate the ratio of the coherent vibronic population cycling time to the incoherent relaxation time as[70] $\tau_{\mathrm{coh}}/\tau_{\mathrm{incoh}} = \lambda^{(\alpha)}/\Delta_{\alpha\beta}\langle\mathbf{v}^{(\alpha)}|\mathbf{u}^{(\alpha)}\rangle\langle\mathbf{u}^{(\beta)}|\mathbf{v}^{(\beta)}\rangle$. The relevant Franck-Condon factors are $|\langle 0|v_i\rangle|^2 = e^{-S_i}(S_i)^{v_i}/v_i!$, where the Huang-Rhys (HR) factors are $S_i = \Lambda_i/\hbar\Omega_i$.

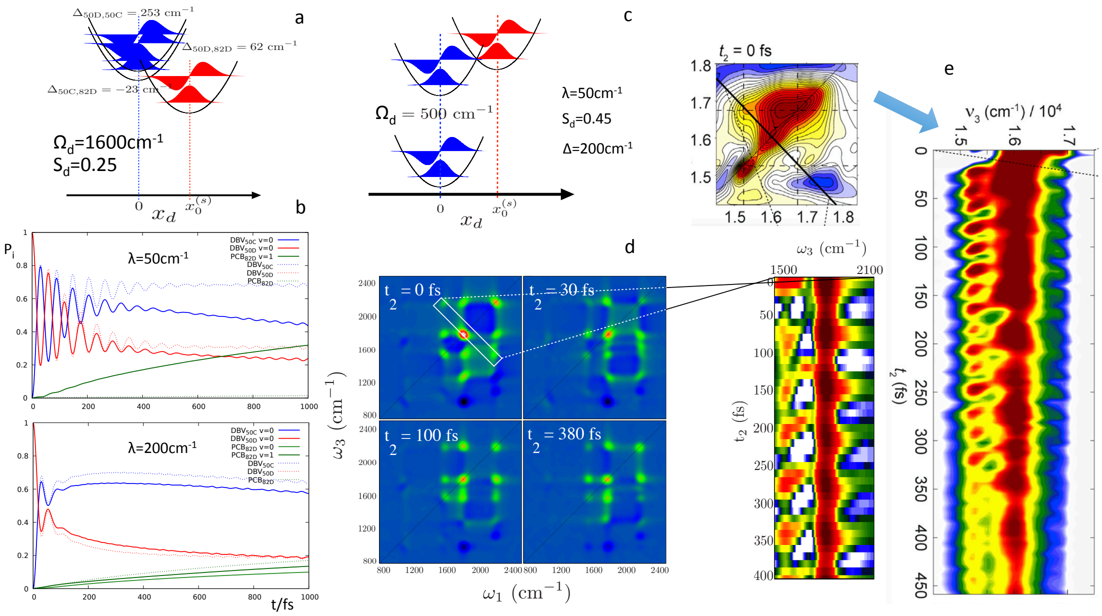

**Figure 3: PC645 Quantum Dynamics and 2DES Simulations** (a) Model for DBV$_{50}$ core dimer vibronically resonant EET to PCB$_{82}$ 1600cm$^{-1}$ mode. (b) Vibronic state population dynamics for different environmental coupling, $\lambda$ (see text). (c) Resonant vibronic EET model for exploring signatures in (d) computed 2DES. Right strip is computed anti-diagonal cut. (e) Experimental 2DES results[27]showing vibronic wave packet dynamics of PCB$_{82}$ 1600cm$^{-1}$ mode.

From the data in **Figure 2f** we see that the vibrational mode at 1600cm$^{-1}$ on chromophore PCB$_{82C}$ has the largest acceptor spectral density corresponding to a HR factor of S$_i$ $\sim$ 0.3, so $|\langle 0|1\rangle| \sim 0.5$. For simplicity we consider a process in which all the other modes are unexcited and assume their HR factors are small (for most bilin modes $S_i \sim 0.1$), maximizing the **0-0** FC factor product. Interestingly, the energy gap between the green and red bands of PC645 sites is $\sim$ 1600cm$^{-1}$ (**Figure 2c**) so this strongly coupled vibrational mode is resonant with the down conversion process.

Our deprotonated MBV Hamiltonian ensemble suggests two different pathways, one from each of the possible donor states in the upper manifold to the PCB$_{82C}$ acceptor chromophore in the lower manifold. From **Figure 2d** the electronic coupling from either DBV$_{50C}$ or MBV$_{18B}$ to the PCB$_{82C}$ chromophore, *e.g.* is typically about $\sim$50cm$^{-1}$, so the vibronic coupling for these transitions is $\Delta_{\alpha\beta}\langle \mathbf{v}^{(\alpha)}|\mathbf{u}^{(\alpha)}\rangle\langle \mathbf{u}^{(\beta)}|\mathbf{v}^{(\beta)}\rangle \sim 25\text{cm}^{-1}$. From **Figure 2e**, however, the different donor intermolecular reorganization energies for these two pathways are significantly different with $\lambda^{\text{DBV}} \sim 40\text{cm}^{-1}$ while $\lambda^{\text{MBV}} \sim 200\text{cm}^{-1}$. This critical difference arises due to the full protonation of the DBVs compared to the deprotonation of the MBVs. Thus, our simulations give the following estimates for the ratios of coherent to incoherent timescales for these different pathways: $[\tau_{\text{coh}}/\tau_{\text{incoh}}](\text{DBV}_{50} \rightarrow \text{PCB}_{82}) \sim 1.6$, and $[\tau_{\text{coh}}/\tau_{\text{incoh}}](\text{MBV}_{18} \rightarrow \text{PCB}_{82}) \sim 8.3$ respectively. This suggest that the vibronic relaxation pathway involving electronic relaxation of DBV$_{50}$ and vibronic excitation of PCB$_{82}$ and its 1600cm$^{-1}$ mode can often occur *coherently* involving delocalized vibronic dynamics, since the timescales for the coherent and incoherent processes are similar. Due to the stronger environmental couplings of the unprotonated MBVs, however, the EET pathways from these chromophores should mostly involve *incoherent* hopping dynamics between dynamically localized vibronic states since the incoherent timescale is nearly 10 time faster than that of the coherent process.

A model exploration of environmental tuning of these coherent/incoherent vibronic EET pathways using realistic parameters extracted from our Hamiltonian ensemble is presented in **Figure 3**. Upper panel in **Figure 3b** shows profound influence of vibronic resonance between the $\mathrm{DBV}_{50}$ dimer and vibronic excitation of $\mathrm{PCB}_{82}$ $1600\mathrm{cm}^{-1}$ mode when the environmental coupling is weak. The dashed curves show very slow EET in the absence of vibronic coupling, while solid curves show dramatic vibronic enhancement in this coherent regime. The Lower panel shows results for the incoherent regime when environment coupling is strong. Resonant vibronic enhancement in EET rate is marginal in this incoherent case as demonstrated by the similar dashed and solid curves. Comparing the rise of the green curves makes it clear that the coherent vibronic down conversion process occurs about twice as fast as the incoherent process.

**Figures 3c** and **3d** demonstrate our PLDM dynamics calculation of the signature of resonant vibronic energy transfer in 2DES and the qualitative comparison with the results of the Scholes group experimental 2DES measurements in **Figure 3e** where the oscillations of the vibronic wave packet generated as a result of **coherent** vibronic down conversion from $\mathrm{DBV}_{50}$ to the $\mathrm{PCB}_{82}$ $1600\mathrm{cm}^{-1}$ are clearly in evidence. Again, **our hypothesis is that nature takes this coherent vibronic enhancement seriously when designing its down conversion systems so as to get the excitation quickly matched up with the lower energy chlorophyll circuitry, and removing potential bottlenecks**.

## 2.3 Experimental Methods:

### 2.3.1 Phycobiliprotein Harvesting Network Manipulation by Protein Subunit Isolation, Characterization and Cross-Reconstitution

Given the suggestion from the simulation study outlined in the previous section that the vibronic EET pathways in the PC645 system may be functioning at the boundary between the coherent and incoherent quantum dynamical regimes, and that this is influenced significantly by chromophore-environment interactions we plan a series of experiments in which chromophore environments are manipulated by protein structural modifications.

The Scholes group has recently engaged in a collaboration with Prof. Palli Thordarson (UNSW, Sydney) and demonstrated that the four subunits of these phycobiliprotein down converting complexes can be reversibly dissociated with high integrity by varying solution pH. This enables the study of individual protein subunits from the light harvesting complexes where the chromophores and their local environments will be exposed in different ways to the solvent. By performing ultrafast spectroscopic studies of the phycocyanin $\beta$-subunits, for example, it will be possible to resolve the functional role of the chromophore dimer (*e.g.* $\mathrm{DBV}_{50\mathrm{C/D}}$ core donor in PC645) formed by the association of the $\beta$-subunit pair in the native protein. Moreover, it has been shown that the subunits may be refolded and self-assembled in unnatural combinations. For example, phycoerythrin $\beta$-subunits may be associated with phycocyanin $\alpha$-subunits. We can thereby produce unnatural combinations of subunits to change the "open" *Hemiselmus* structure to closed structures; we can change the electronic coupling in the complex's central dimer; or modify the energy funnel by changing chromophore types and also potentially influence their environments. This provides a powerful new way to explore structure-function relationships. By comparing natural and artificial "chimera" cryptophyte antenna complexes using ultrafast spectroscopy, we will elucidate the way energy transfer pathways and rates have evolved by selection of subunit structures and chromophore content. Simulation studies on each of these hybrid systems, like those outlined in the pervious section, will enable detailed mechanistic interpretation of these complex experiments. Of critical importance in these studies is the fact that all the parameters in the dynamical models used in their interpretation are determined from first principles, substantially reducing ambiguity about the potential mechanism. Where there is ambiguity, *e.g.* influence of different protonation states, we can always perform detailed first principles simulations to test out the different possibilities.

For example, in the process of undertaking preliminary experimental studies, we discovered that the vibrational activities of the $\alpha$ subunit bilins are different from that of bilins in the intact phycobiliprotein. This might be caused by interaction of the bilins with amino acid side chains in combination with distortions of the bilin structures. However, the vibronic amplitudes of the pigment-collective in the intact protein may significantly modulate the amplitudes of those vibronically active modes due to vibronic interactions. Hence, a spectroscopic catalog of the $\alpha$-subunits, as a first step, would provide a baseline against which we will subsequently compare the vibrational activity or extent of vibronic intensity borrowing in the bilins when the phycobiliprotein is in its native fold. In parallel to construction of this catalog, complementary molecular dynamics studies and model Hamiltonian ensemble analysis will be invaluable for determining the conformations the $\alpha$-subunits adopt in solution and assigning their energetic parameters and spectroscopic properties, thus enabling detailed comparison of these solvated subunit bilin conformational properties with those of the native protein structure.

Even though the $\beta$-subunits are prone to aggregate in aqueous solutions, we will attempt to explore re-solubilizing them using ATP or other hydrotropes. We speculate that the presence of hydrotropes in the thylakoid lumen may enhance the renaturation process of the phycobiliproteins PE545 and PC577, or even enable the renaturation of other phycobiliproteins *in vivo*.

### 2.3.2 Ultrafast multidimensional spectroscopy

In our experimental studies we will use the various ultrafast laser experiments we have developed, based on broad-band pump probe (BBPP) and 2D electronic spectroscopy (2DES) techniques, that capitalize on the ability of short laser pulses to prepare and probe wave packets - superpositions of quantum mechanical levels in molecules. These advanced techniques enable us to go beyond the “timing” experiments that obtain kinetic schemes, to experiments that elucidate mechanisms underpinning ultrafast processes. For example, as mentioned above these techniques incisively revealed the presence of coherent vibronic dynamics in the PC645 light harvesting complex[27]. However, the sheer observation of vibronic coupling/coherence does not help us understand how it affects the energy transfer rate, nor the mechanism and possible role of delocalization. This is why it is critical to combine these experiments with detailed, predictive atomistic simulations, where we know we can trust the *ab initio* integrity of the model parameterization and we can turn on and off the vibronic transitions and explore the influence of environmental interactions (*e.g.* **Figure 3b**) to provide intuitive mechanistic understanding of coherent enhancement of vibronic EET.

We have further been able to identify and detune these vibronic resonances using a high magnetic field that exclusively shifts molecular exciton states.[147] We implemented ultrafast pump-probe spectroscopy into a specialized 25 Tesla magnetic field facility and studied the light-harvesting complex PC645, where the strongly coupled core chromophores form molecular exciton energy donor states. We detect a marked change in high-frequency coherent oscillations when the field is engaged. Quantum chemical calculations coupled with a vibronic model explain the experiment as a magnetic field-induced shift of the exciton states that, in turn, modifies vibronic coupling between pigments. Our results demonstrate the exquisite sensitivity of inter-pigment vibronic coupling to electronic-vibrational detuning in light harvesting.

In another report[148] we re-examined the Fenna-Matthew-Olson complex and compared its spectroscopy to a series of mutants, cleverly designed by the Blankenship lab to have markedly disparate spectraand therefore different light harvesting pathways. A novelty of the work is the combination of biological mutagenesis and a very sensitive femtosecond spectroscopy. By studying a series of special mutants using selective pump-probe spectroscopy we were able to show, solely from experiment, the origin and properties of the detected coherent oscillations. We discovered how at least three chromophores interact collectively to harvest light, and this interaction is detected, even at ambient temperature, *via* long-lived coherent oscillations assigned to vibrational wavepackets in the ground electronic state.work will influence a large community of researchers, especially theoreticians, who have been inspired by the FMO coherences, setting a new benchmark for the theory.

### 2.3.3 Reducing Decoherence by using Hamiltonian-inspired Shaped Laser Pulses

Generally superposition states[1] are fleeting in open quantum systems due to environmental interactions that drive decoherence and result in the selection of certain preferred or equilibrium states,[3] which are left essentially untouched by environmental interactions and are known as pointer states.[2]

In the last decade, spectroscopic techniques like 2DES and BBPP have enabled the generation and observation of quantum superpositions in photosynthetic systems,[149–152] where, despite strong energetic disorder, superpositions between electronic states have been observed for timescales longer than expected. It has been suggested that this long-lived quantum coherence is supported by resonant vibrations through vibronic coupling that induces delocalization.[152–154] These superposition states underpin coherent energy transport and can attribute robustness and efficiency to the complex excited state energy transduction processes that enable the function of light harvesting down conversion systems.[150–152,155] **This raises the question, can we suppress decoherence processes to produce a quantum superposition that survives for a timescale long enough to derive further function? A possible answer may be to prepare superpositions that are close to pointer states.** Interesting candidates might be localized donor and acceptor electronic/vibronic states of photosynthetic systems. Typically 2DES and BBPP experiments use spectrally broard laser pulses that create superpositions amongst all accessible electronic states and all Franck-Condon active modes, which can couple to the environment and hence contribute to the decoherence.[156–159] Therefore, despite their high time-resolution, our laser pulses lack spectral selectivity for targeting specific superposition states.

To produce coherent superpositions close to the pointer states, we will shape broadband excitation laser pulses *via* controlled modulation of phase, amplitude, and polarization using Spatial Light Modulators (SLMs). **We hypothesize that the implementation of tailored excitation pulses by SLMs could produce superpositions close to the pointer states only, and reduce decoherence. Thus we aim to create a superposition of pointer states that are isolated from the background of superpositions that include Franck-Condon active environment coupled modes, enabling protection of specific coherences.**

Pulse shaping methods have been implemented in multidimensional coherent spectroscopies[160–163] but few studies have focused on creating selected coherent superpositions. As shown schematically in **Figure 4**[164] a spatially patterned mask is applied to the dispersed pulse, which modulates the amplitude, phase, and polarization of the spectral components. The modulated components are then reassembled at another grating. This 4f pulse shaping arrangement has an advantage that it is ideally free of temporal dispersions, which means we can simultaneously maintain the short time duration of the laser pulses as well as change their phase, amplitude and/or polarization. The implementation of the easy-to-use pulse shaper in BBPP and 2DES setups in our laboratory will enable us to probe and ascertain the longevity of the quantum coherences.

With our system we can implement either adaptive feedback, or open loop control[161,164] and our studies will employ results from optimal quantum control calculations with model Hamiltonian

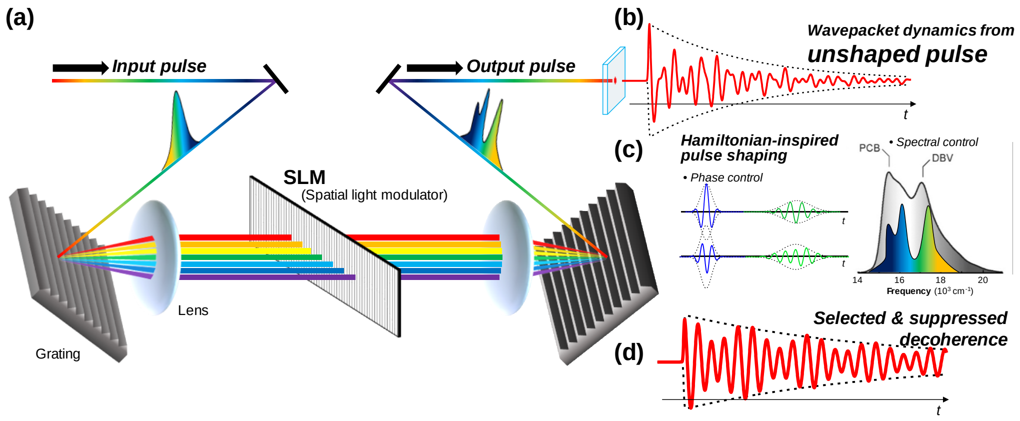

**Figure 4:** (a) Scheme of the Fourier transform optical pulse shaping technique. (b) Typically, temporally compressed unshaped pulses give rise to the wavepacket dynamics containing multitude of vibrational coherence. (c) Through open control based on a model Hamiltonian, phase and shape of pulses can be optimized to selectively excite superposition states close to pointer states, (d) which suppresses decoherence.

ensembles to generate initial trial pulse shapes whose reliability will be tested in adaptive feedback studies. This close coupling between predicted theoretical and experimental optimal pulse shape will provide information about control mechanism from calculations while the experiments assess predictive accuracy of the models. **Our ambitious goal involves implementing open loop designed, and adaptive feedback refined pulses to shape excitation laser pulses for 2DES experiments to develop fundamental understanding of how initial state preparation might enable reduction of decoherence in these down conversion systems that are close to the boundary between coherent and incoherent energy transfer mechanisms.**

We will study down-conversion energy transfer dynamics in photosynthetic systems using Hamiltonian - inspired shaped laser excitation pulses, at first in BBPP and then in the 2DES configuration. Previous work has shown that changing the phase of the excitation pulse alters the branching ratio of energy transfer in a photosynthetic complex.[17,165] In our study, we will focus on the implications caused by tailored pulse shapes on the coherent dynamics of photosynthetic systems, and also explore possibilities of reducing decoherence in superposition states. As outlined in the preliminary study in Section 2.2.7 the PC645 system offers a great opportunity to explore the influence of initial state preparation on decoherence dynamics using pulse shaping. Experiments[158,166] and theory thus suggest that vibronic transport is enabled by bridging of the donor-acceptor energy gap ($\sim$1500 cm$^{-1}$), through high-frequency quantum vibrations of 1580 cm$^{-1}$, which not only creates a resonant interaction, but also induces delocalization of the wavefunction between the donor and acceptor states.[158] This delocalization could be the possible source of coherent contribution to the down-conversion energy transfer dynamics.[151] We will perform BBPP experiments on PC645 using the computationally-derived Hamiltonian-based shaped laser pulses (**Figure 5**). The shape of the femtosecond optical waveform will be modified to create preferential excitation of the DBV and PCB chromophores only. This selective excitation will not only ensure direct correlation of the DBV and PCB transitions, but it will also generate selective superposition of the donor and acceptor pointer states.

All the photosynthetic proteins have large densities of Franck-Condon active vibrations. However, only a few selective degrees of freedom participate in vibronic coupling and may partici-

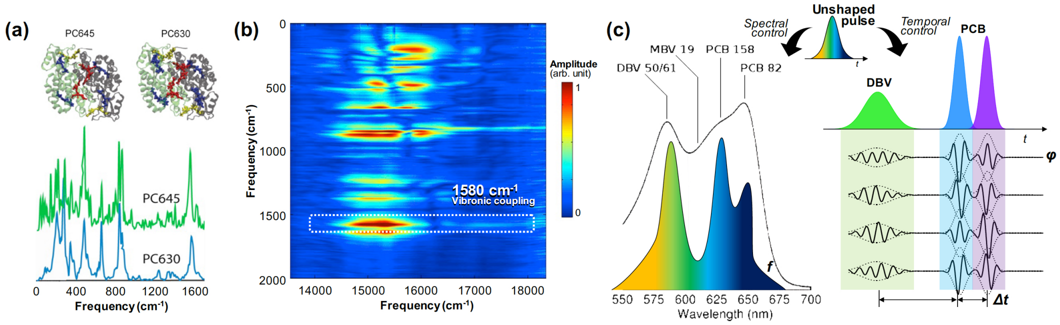

**Figure 5:** (a) X-ray crystal structures of light harvesting protein PC645 and PC630 (top) and the corresponding integrated Raman signal produced by unshaped short pulse (bottom). (b) Spectrally dispersed Raman signal of light harvesting complexes produced by unshaped short pulses. Intense 1580 cm$^{-1}$ mode, which vibronically couples to facilitate energy transfer, is present. (c) Schematic spectral and temporal profiles of shaped pulse to suppress decoherence of PC645. Pulse shaping enables selective excitation of individual spectral components of the system and control over pulse duration, pulse sequence, and phases.

pate in enhancing the survival of coherent superpositions via delocalization. The frequency of such FC active vibrations matches the energy gap between the donor and acceptor chromophores. Hamiltonian-inspired laser pulse shapes will be implemented that will produce a coherent excitation of only the important FC active vibrations, leaving aside all the other FC active modes as well as other electronic transitions. In addition, these shaped laser pulses can be tailored to create targeted excitation of other FC active modes as well and reveal the impact of those modes on the coherent dynamics, if any. Therefore, shaping laser pulses to produce discrete coherent superpositions of preferred states of electronic or vibronic nature, will open this whole new paradigm of understanding the decoherence process and its potential control.

We will extend the capabilities we develop for targeting specific quantum states through Hamiltonian - inspired laser pulse shaping to explore vibronic delocalization by turning off different states during the initial excitation and monitoring subsequent dynamics. These techniques will also be extended across the whole family of cryptophyte algal proteins including the chimera systems outlined in Section 2.3.1 where we will have detailed libraries exploring different conformations, chromophore identities, environment interactions *etc.* enabling the most complete study of control mechanisms in coherent quantum energy transport and transduction yet devised.

## 2.4 Statement of Work:

### 2.4.1 Cryptophyte Chimera Library Characterization, and Mechanistic Exploration

As outlined in **Section 2.3.1** a library of isolated component protein subunits will be developed and spectroscopically characterized. Since the protein scaffold changes the conformation of the bilins and, in turn, their vibrational activity, a spectroscopic catalog of $\alpha$-subunits will provide a baseline for microscopic insights into possible tuning of these vibrations for ultrafast energy transfer in the phycobiliproteins. Cross reconstitution of characterized and catalogued $\alpha$-subunits with various $\beta$-subunits will provide a collection of functional hybrid down converter pigment-protein complexes in which the different chromophores are coupled to one another in controlled, well-defined different ways. Their interactions with different local protein interfaces and solvation micro-environments can also be well controlled and characterized in these studies. Members of this pigment-protein library can then be selected for controlled studies of trends in mechanism with network structural and chromophore compositional variation using BBPP, and 2DES spectroscopy and Hamiltonian - inspired initial state preparation methods described in **Sections 2.3.2 and 2.3.3** respectively.

Parallel theory/computational studies using the methods and protocols outlined in **Section 2.2** and demonstrated in the mechanistic study of **Section 2.2.7** will provide comprehensive predictive modeling capability for mechanistic interpretation of the experimental studies. **These studies will advance the field by (a) developing and demonstrating design principles for vibronic control of energy transfer through detailed exposition of mechanism and pathways, and (b) discovering whether nature has evolved to use these principles in photosynthetic energy conversion. We will advance the field by providing a detailed mechanistic explanation for new ways of controlling and enhancing energy transfer.**

A key idea explored in these studies is nature's use of parallel networks of vibronic resonances that may be engineered into these cryptophyte phycobiliprotein energy transfer and down conversion structures. Redundancy is a potent way to produce robustness in a system. It is likely that these systems employ parallel vibronic resonance structures to dissipate energy. If fluctuations turn one pathway off, another high fidelity way of dissipating energy must come online to maintain steady service. The structural and compositional variation experimental studies outlined above will provide an indirect way to observe the functional components of these parallel networks using the ensemble average spectroscopic tools. Our Hamiltonian ensemble sampling methods, however, will provide a direct way from the simulations to explore how fluctuations may turn on one pathway while another lies dormant. These different pathways may also fluctuate in and out of different dynamical regimes, for example, fluctuations in local protein structure influencing chromophore - amino-acid coordination or solvation environment may push these pathways between coherent and incoherent vibronic energy transfer and down conversion regimes. Variation in coherence may be a switching mechanism exploited to effectively turn different pathways on and off. Understanding how nature deals with controlling energy dissipation at the nanoscale may provide important guidance on a significant problem facing component miniaturization in electronics and photonics.

### 2.4.2 Peridinin (Per) Chlorophyll-a (Chl-a) Protein Experimental Studies

The structure and spectra of the PCP complex[167,168] are shown in **Figure 6**. Despite the extensive information acquired from prior studies into PCP, questions[169,170] remain about the pathways and mechanisms by which energy initially harvested by Per is funnelled to Chl-a. Much of the debate involves the rich, yet complex photophysics of the Per[171,172] carotenoid primary donor. On the basis of the observed solvent-dependence of its fluorescence spectrum, researchers[43,171,173,174] have argued that the Per $S_1$ state possesses charge transfer (CT) character, or even a separate intramolecular charge transfer (ICT) state, that enhances the transition dipole moment, allowing the nominally dark Per $S_1$ state to act as the primary energy donor state to Chl-a. Recent pump-probe and pump-dump-probe measurements by Redeckas *et al.*[43] have reinforced the case for the existence of the ICT state. Nevertheless, experiments with shorter pulse durations are needed to fill gaps in the model by uncovering very early-time ultrafast dynamics. In particular, internal conversion from Per $S_2$ to $S_1$, as alluded to in the work of Van Tassle *et al.*[46] has not yet been incisively revealed.

We will combine 2DES[177,178] and BBPP to study PCP complexes isolated from *Amphidinium carterae* and suspended in aqueous buffer. Our 2DES experiments will focus on interchromophore electronic couplings and/or energy transfer pathways in the form of off-diagonal spectral cross-peaks between the chlorophyll and carotenoid absorption bands. In preliminary experiments we tuned the laser spectrum to span from the tail of the Per absorption to the Chl-a absorption band, as shown in **Figure 6b**, thus allowing resolution of electronic couplings between the Per $S_2$ and Chl-a

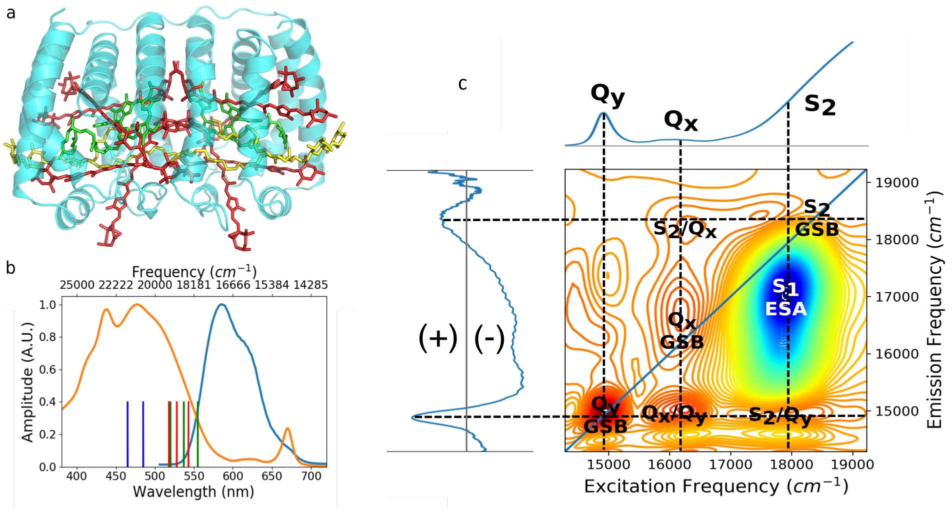

**Figure 6:** (a) Structure of Peridinin-Chlorophyll-a Protein (PCP) showing eight peridinin molecules (red), and two digalactosyl diacyl glycerol molecules (yellow) surrounding two chlorophyll-a molecules (green), at distances of about 3-4Å. (b) PCP absorption (orange) with the NOPA spectrum (blue). Estimates of peridinin site energies - blue, green[175] and red[176] sticks. NOPA spectrum spans lowest few peridinin excitations to the $Q_y$ transition of chlorophyll-a. (c) Real-valued absorptive 2DES spectra summed over the entire $t_2$ range with assigned EET features, juxtaposed with linear absorption spectrum (top) and summed TA spectrum (left). Cross peaks labeled with donor/acceptor assignments.

Q states in PCP. Despite the additional spectral dimension afforded by 2DES, the Per $S_2$ to Chl-a $Q_x$ cross peaks are still partially hidden by the Per $S_1$ excited-state absorption (ESA). However, careful examination of the population time traces around the Per $S_2$ - Chl-a Q cross peaks will help reveal previously obscured details of the ultrafast photophysics that occur after excitation of PCP.

2D spectra were integrated over all $t_2$ generating a summary 2D spectrum that reveals cross-peaks arising predominantly from energy transfer occurring within the $t_2$ time window, **Figure 6c**. Comparing this summary 2D spectrum with the linear absorption spectrum, (top trace), shows cross-peaks between the Per $S_2$ state at 18000 $cm^{-1}$ (555 nm) and the Chl-a $Q_x$ and $Q_y$ states, in addition to on-diagonal peaks corresponding to Chl-a $Q_x$ and $Q_y$ transitions at 16250 $cm^{-1}$ (615 nm) and 15000 $cm^{-1}$ (667 nm) respectively. In addition to corroborating the work by Kleima *et al.*[175] in which the least energetic Per $S_2$ state is determined to lie around 555 nm, this observation directly demonstrates energy transfer between this low-lying Per $S_2$ state and the Chl-a states. We will analyze the coherent oscillations as a function of pump-probe time delay to explore the peridinin-chlorophyll vibronic coupling. Another interesting issue amenable to detailed investigation with the methods we will develop is the significance of vibronic coupling between the Chla $Q_x$ and $Q_y$ states[179,180] that has been implicated in enhanced coherence loss.

### 2.4.3 Peridinin Chlorophyll-a Protein Theory and Computational Studies

The theory and computational methods of **Section 2.2** will be used to explore the influence of solvation environment, vibronic dynamics and relaxation on EET pathways and mechanisms in PCP. The competition between internal conversion, energy transfer, involvement of CT states and the influence of solvation environment on these processes will be explored. Model Hamiltonian ensembles constructed in these studies will be used to compute nonlinear optical signals as highlighted in **Section 2.2.7** for direct comparison and interpretation of experiment and also incorporated in OQCT studies of initial state preparation and its influence on branching and decoherence.

Accurate treatment of the excited state electronic structure of carotenoids like peridinin is a significant challenge (**Section 2.2.2**)[87,181] so we plan to explore a variety of approaches. In preliminary studies[102] using DMRG methods[182–186] we compared the manifold of excited states in peridinin to that of its parent polyene and find that the canonical $3A_g^-$ state achieves greatly enhanced oscillator strength stemming from the electron-withdrawing effect of the lactone ring. This ICT-like state, in conjunction with the correlated-triplet-pair (CTP) $B_u^-$ state,[187,188] may be involved in peridinin nonradiative decay processes at twisted conformations.

The agreement between moderate active space multi-reference perturbation theory calculations and DMRG results (**Section 2.2.2**) for the doubly excited $S_1$ state is promising as polarizable embedding techniques can readily be incorporated with these multi-reference methods to model the influence of the solvating protein environment. This is not currently possible with DMRG. Co-PI Sharifzadeh has experience extending many-body perturbation theory within the GW/BSE approximation for computing optical properties of organic molecules[189,190]. These techniques can also be extended to incorporate environmental polarization[191] and double excitations[192] and Sharifzadeh plans to continue working with the BerkeleyGW team to realize this alternative functionality.

A recently proposed mechanistic model of PCP ET dynamics supported by global analysis of heterodyne transient grating spectroscopy results[44,45] suggests that more than half the time the energy transfers to the Chl-a through an ultrafast, non-Förster-like, quantum coherent mechanism involving optical preparation of delocalized Per $S_2$ - Chl-a $Q$ exciton states that undergo fast relaxation in the intermediate to strong electronic coupling regime, resulting in rapid EET to Chl-a molecules on the few tens of femtosecond timescale. The model suggests that for the rest of the time the initially excited Per $S_2$ molecules undergo excited state nuclear framework distortion involving C-C and C=C stretching displacement along the bond-length alternation coordinate, as well as out-of-plane twisting of the conjugated polyene. Such distortions of a Per molecule in the $S_2$ state moves it towards the intersection seam with the almost dark $S_1$ state from which energy transfer is only possible on the several tens of picosecond timescale, contrary to the observed dynamics. This model thus suggests that before reaching this unproductive $S_1$ sink the molecules are trapped by confining low barriers resulting from environmental interactions in the so called $S_x$ intermediate conformation on the Per $S_2$ state. Electronically, a Per molecule adopting this $S_x$ conformation involves a mixture of the bright $S_2$, and the dark $S_1$ states of the polyene so the oscillator strength for transitions to and from this state, and hence its electronic coupling to other Per and Chl-a molecules, decreases significantly relative to $S_2$ putting the chromophore network into the weak electronic coupling limit. These restricted nuclear distortions result in charge localization so the $S_x$ state is characterized by partial intramolecular charge transfer (ICT) character producing stronger environmental coupling. In this more Förster-like incoherent regime efficient energy transfer to Chl-a occurs on the few picosecond timescale, consistent with the experimental observations.

To explore suggested mechanisms like this we will need a molecularly detailed treatment of environmental interactions to develop understanding of the caging-like phenomena that supposedly stabilize bond alternation and twisting distortions. We will explore these environmental confinement processes in a similar way to our Hamiltonian ensemble sampling approach. Configurations from MD simulations using MM force fields will be geometry optimized, and a vibrational analysis conducted using DFT which should be reliable for the ground state. Multi-reference electronic structure techniques including XMCQDPT2 and RASPT2 will be applied, treating the atomistic environment interactions from the MD configurations using the polarizable embedding effective fragment potential approach (see **Section 2.2.2**). The influence of distortion along the collective twisting and bond alternation coordinates on these solvated excited state energies will be mapped out to explore these suggested excited state environmental confinement effects.

An approach to compute intermolecular spectral densities generalizing the charge density coupling method (see **Section 2.2.3**) to include a polarizable atomistic environment will be developed.

## 2.5 Timeline of Major Activities and Researcher Responsibilities:

### 2.5.1 Hybrid Phycobili pigment-protein studies

**Year 1:(1)** Representative closed PC645, PE545, and open PC612, PE555, and PC577 complexes will be dissociated and the unfolded, soluble $\alpha$-subunits characterized spectroscopically. Studies of hydrotropes for solubilizing $\beta$-subunits will be conducted. Hybridization giving mixed $\alpha/\beta$ chimera complexes will be catalogued spectroscopically. Structural characterization of several hybrids will be undertaken to explore predictive trends. BBPP and 2DES studies of cryptophyte subunits and reconstituted hybrid complexes. *(Scholes Lab)*; **(2)** Parallel tempering MD of $\beta$-subunits in solution. Vibrational analysis in local minima enabling comparisons and assignment of experimental spectra. *(Coker Lab)*; **(3)** CSDM-PLDM codes for OQCT developed and tested (*Coker Lab*)
**Year 2:(1)** 2DES and BBPP of selected hybridized homologous series. Vibrational catalog of $\beta$-subunits will be compared with vibrational/vibronic excitations identified in multidimensional signals indicating how key modes are affected by hybridization. Adaptive feedback control developed in PCP study Y1 will be implemented in initial state preparation studies on cryptophyte systems*(Scholes Lab)*; **(2)** MD simulations conducted with hybrid structures and Hamiltonian ensemble sampling and characterization. Properties of Hamiltonian ensemble analyzed to identify strongly coupled vibrations and predictions used to assign experimental features. Theoretical estimates of $\tau_{\text{coh}}/\tau_{\text{incoh}}$ for different pathways identified by cross-peaks will enable prediction of coherent or incoherent regimes for vibronic energy down conversion. Exploring mechanistic trends with variations in hybrid structures and chromophore compositions will point to design principles. These can be tested by making predictions about different homologous series. Supporting OQCT studies on initial state preparation for cryptophyte systems will be conducted. *(Coker Lab)*
**Year 3:(1)** Trends in variation of pathways and mechanisms rationalized on the basis of different structural and compositional characteristics of hybrids in homologous series. *(Coker and Scholes Labs)*; **(2)** OQCT prediction of initial state preparation for DBV-PCB coherence and Open-loop/adaptive feedback refinement experiments and 2DES probe. *(Coker and Scholes Labs)*

### 2.5.2 Peridinin Chlorophyll-a Protein studies

**Year 1:(1)** Analysis of off-diagonal spectral cross-peaks in 2DES to elucidate relaxation timescales and oscillatory features reporting on various vibronic transitions and excited ground state vibrational contributions to signals in $S_2$ Chl-a Q coupling region. Adaptive feedback control of IC-ET branching *(Scholes Lab)*; **(2)** MD simulations with ground state characterization. Develop CSDM-PLDM implementation of OQCT. Multireference/GW-BSE benchmarking and polarizable embedding studies. Predict $S_1$ and ICT and CTP character states to guide experiments on these states. *(Bravaya, Sharifzadeh, Coker and Scholes Labs)*
**Year 2:(1)** BBPP experiments on PCP. Chla $Q_x$-$Q_y$ vibronic coupling 2DES study. *(Scholes Lab)*; **(2)** Develop polarizable CDC model for $J_{\text{inter}}$. Excited state gradients for $J_{\text{intra}}$, compute electronic and vibronic coupling to estimate $\tau_{\text{coh}}/\tau_{\text{incoh}}$ for $S_2$. Chl-a Q transitions incorporating vibronic coupling. *(Bravaya and Coker Labs)*
**Year 3:(1)** Environmental confined excited states for twist and BA distortion *(Coker, Bravaya Sharifzadeh Labs)*; **(2)** 2DES studies of $S_x$ or other excited state conformations *(Scholes Lab)*

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