COHERENT MULTIDIMENSIONAL OPTICAL PROBES OF BIOLOGICAL COMPLEXES

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Energy- transfer and charge-separation pathways in the reaction center of photosystem II may be revealed by coherent two-dimensional optical spectroscopy. The excited state dynamics and relaxation of electrons and holes are simulated using a two-band tight-binding model. The dissipative exciton and charge carrier motions are calculated using a transport theory, which includes a strong coupling to a harmonic bath with experimentally determined spectral density, and reduces to the Redfield, the Förster, and the Marcus expressions in the proper parameter regimes. The simulated third order two-dimensional signals, generated in the directions $-\boldsymbol{k}1+\boldsymbol{k}2+\boldsymbol{k}3$, $\boldsymbol{k}1-\boldsymbol{k}2+\boldsymbol{k}3$, and $\boldsymbol{k}1+\boldsymbol{k}2-\boldsymbol{k}3$, clearly reveal the exciton migration and the charge-separation processes. Novel 2D signals that make use of entangled photons will be presented.

We calculate the double-quantum-coherence signal of excitons generated at $\boldsymbol{k}4=\boldsymbol{k}1+\boldsymbol{k}2-\boldsymbol{k}3$ by two pulsed entangled photon pairs ($\boldsymbol{k}1$, $\boldsymbol{k}2$) and ($\boldsymbol{k}3$, $\boldsymbol{k}4$), where all four modes are chronologically ordered. Entangled photons offer an unusual combination of bandwidths and temporal resolution not possible by classical beams. Contributions from different resonances can be selected by varying the parameters of the photon wave function. The signal scales linearly rather than quadratically with the laser field intensity, which allows performance of the measurements at low powers. An assembly of non interacting atoms may become correlated upon interaction with entangled photons, and their density matrix can then show collective resonances. We explore experimental signatures of these resonances in the nonlinear response of a pair of two-level chromophores. We find that these resonances are canceled out in stimulated signals such as pump-probe and two photon absorption due to interference of two-photon-absorption and emission pathways in the joint two-particle space. However, they may be observed in photon statistics (Hanbury-Brown Twiss) measurements through the attenuation of two-time intensity correlations.

Two dimensional ultraviolet (2DUV) spectra of protein backbone and side chains are simulated by a combined quantum mechanics (QM) and molecular mechanics (MM) protocol. The signals provide new insights into the IR structure, dynamics and functions. Simulated Chirality-induced 2DUV spectra reveal characteristic patterns of helical and sheet secondary structures that can be used to probe the structure and aggregation mechanism of amyloid fibrils which are associated with over 20 diseases related to protein misfolding.

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