Line-Narrowing Spectroscopy of Water-Soluble Chlorophyll-Binding Protein (WSCP) Embedded in an Asymmetric Phonon Bath

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Abstract:

A tractable and computationally expedient electronic transition dipole moment time-correlation function of a dimeric photosynthetic complex, from which nonlinear optical time- and frequency-domain signals may be obtained, and the bath spectral density, which impacts the dynamics and the shape and symmetry of linear spectra, play key roles in extracting structural and dynamical information for condensed systems. Analytical expressions for the electronic transition dipole moment time-correlation function and the homogeneous absorption lineshape function of excitonically coupled systems, showing both lower and upper excitonic states, are derived. This correlation function is based on an experimentally determined 1-phonon profile of the surroundings of the photosynthetic protein. The resultant asymmetric spectral density of the surrounding protein phonons renders, caused by the unequal contribution from the protein phonons to the low- and high-energy sides of the spectra manifests itself in the phonon sideband (PSB) in the absorption spectrum. The protein *asymmetric* spectral density will give rise to an electronic transition dipole moment time-correlation function that can characterize the nature of electron-phonon, exciton-phonon, and phonon relaxation couplings. As such, one can fine-tune the exciton-phonon coupling strength caused by the protein phonon. To explore the dynamical attributes of the asymmetric spectral density and their impact on the transition dipole moment correlation function, linear homogeneous absorption, spectral hole-burning (SHB), line narrowing fluorescence (FLN), and difference FLN (DFLN) spectra of the water-soluble chlorophyll-binding protein (WSCP) are computed using 2- and 3-state models, showing excellent agreement with experiment (Pieper J.; Rätsep, M.; Trostmann, I.; Paulsen, H.; G. Renger, G.; Freiberg A. *J. Phys. Chem.* B 2011, 115, 14, 4042. , Pieper J.; Rätsep, M.; Trostmann, I.; Paulsen, H.; G. Renger, G.; Freiberg A. *J. Phys. Chem. B* 2011, *115*, 14, 4053.). The 2-state model considers only the ground electronic and lower excitonic states that account for pure electronic dephasing, whereas the 3-state model considers the ground electronic, lower excitonic, and upper excitonic states, in which pure electronic dephasing in the lower excitonic state and excitonic relaxation in the upper excitonic state are accounted for. WSCP proves to be an ideal system for assessing the correctness, applicability, and utility of the theoretical framework presented herein.