VIBRATIONAL DAMPING EFFECTS ON ELECTRONIC ENERGY RELAXATION IN MOLECULAR AGGREGATES

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The problem of describing intramolecular vibrations in molecular aggregates often lead to models where a finite number of vibrational quanta is included into the description. Such approach, denoted as one- or two-particle approximation (TPA), depending on the chosen upper limit of the number of vibrational quanta, yield an accurate approach that has been efficiently used to describe absorption and emission of J aggregates [1]. The approach, however, is limited to a small number of vibrational degrees of freedom.

We have extended description of molecular aggregate Hamiltonian by including both electronic-phonon and linear vibrational-phonon couplings (see Fig. 1), and have used computationally inexpensive (compared to TPA) stochastic time-dependent variational approach [2] to calculate the time evolution of electronic-vibrational wavepacket. This method allows us to approximately treat a large number (thousands) of vibrational modes explicitly, avoiding Born and Markovian approximations used in the perturbative reduced density operator approach.
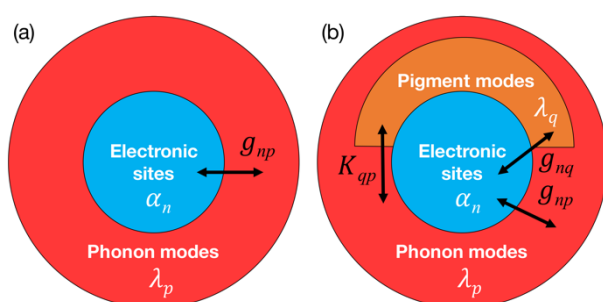

Fig. 1 (a) The standard scheme: a single bath, consisting of independent vibrational modes, is coupled to electronic sites; (b) Pigment-protein coupling scheme: two coupled vibrational manifolds, each consisting of a set of independent vibrational modes, are also coupled to electronic site.
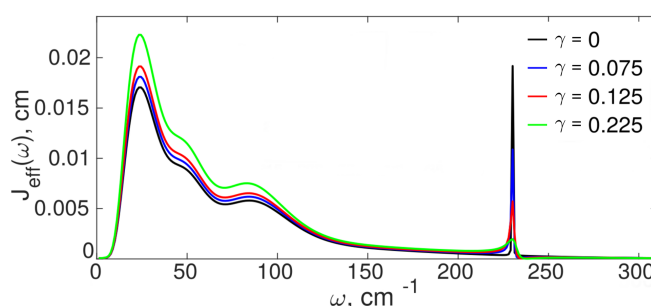
Fig. 2 Effective fluctuation spectral density function, calculated with no vibrational-phonon coupling (black line) and when vibrational-phonon coupling is present (blue, red, green lines).

Using this approach, we have simulated a model pigment-protein system made up of a single electronic state coupled to one high-frequency pigment vibrational mode and a whole spectra of phonon frequencies with coupling between pigment and phonon modes. We have shown that the intermode coupling leads to the quenching of pigment vibrational modes by phonon modes, and to the redistribution of fluctuation spectral density with respect to the electronic excitations (see Fig. 2).

Further, to study vibrational-phonon coupling effects on excitation energy relaxation rates, we have simulated naturally occurring water soluble chlorophyll binding protein (WSCP) aggregate reduced density matrix at 77 K with 20 high-frequency pigment vibrational and 1000 phonon modes included. We have found that the new energy relaxation pathways, opened by the vibrational-phonon interactions, allow to reach excitonic state equilibrium quicker, thus demonstrating that damping of molecular vibrations is an important effect to consider when describing intermolecular energy relaxation process. Additionally, vibrational-phonon coupling change the final excitonic state energy distribution, hinting at excitonic state transformation to vibronic states.

References:
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