Effect of excitation and charge transfer states on vibrationally-resolved electronic spectra in organic aggregates

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We propose a non-Markovian stochastic Schrödinger equation [1] together with TDDFT calculations for the calculation of absorption spectra of molecular aggregates immersed in harmonic quantized vibrational modes. The feasibility and the validity of newly proposed method are affirmed in the analytical monomer spectra. In the simulations, various types of local excitations, charge-transfer (CT) excitations, and exciton–phonon couplings are explicitly included in a comprehensive model Hamiltonian, parameterized by TDDFT calculations, together with a diabatic strategy of the fragment particle−hole densities [2]. The applications to Zinc Phthalocyanine aggregates [3] clarify that the two absorption bands in the Q-band region observed in experiments can be assigned to the contribution from the CT-mediated interactions, rather than the mixtures of different-type aggregates, as prevailingly assumed. From the investigation of the decoherence process after optical excitation, it is found that CT states can induce coherence regeneration as the time scale of charge separation is much faster than that of the vibration-induced decoherence. However, they would instead boost the decoherence process as the two time scales become comparable.

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