Spectral signatures of exciton-phonon coupling in molecular aggregates: A polaron transformation approach

Maurits H. Silvis,[1] Erik A. Bloemsma,[1] Anna U. Stradomska,[1] and Jasper Knoester[1]
[1]*Centre for Theoretical Physics and Zernike Institute for Advanced Materials, University of Groningen, Groningen, The Netherlands*

Abstract. *We investigate the influence of a dynamical environment on the optical properties of molecular aggregates by using a polaron transformation approach that accounts for both weak and strong exciton-phonon coupling regimes as well as thermal effects.*

Ever since the discovery of molecular aggregates by Jelley and Scheibe in the 1930s much study has been devoted to their fascinating optical and energy transport properties.[1] These features have inspired the development of complex molecular systems having potential applications as light-harvesting systems or nanowires. Both the optical and energy transport properties arise from collective excitations, Frenkel excitons, of which the delocalization characteristics strongly depend on the interaction with the environment.

We qualitatively study the influence of a dynamical environment on molecular aggregates, focusing on their linear optical spectra in particular. The starting point for our model is the Holstein Hamiltonian that describes the excited states of the system. Several perturbative approaches exist to study the arising eigenstates – and thus the optical behavior – of an aggregate within this model, assuming either weak or strong exciton-phonon coupling.

We go beyond these perturbative limits by applying the polaron, or Lang-Firsov, transformation to the Holstein Hamiltonian.[2] In our approach, the intermolecular interactions are reduced to effective interactions by the presence of the environment, thereby also incorporating the effects of temperature. Furthermore, in this effective description excitations and vibrations are decoupled. This then leads to a novel approach to calculate optical spectra in a numerically inexpensive way.

Focusing on linear absorption spectra, a clear vibrational structure can be seen. When considering the monomer, for instance, the well-known zero-temperature spectrum with its vibrational progression following from the Franck-Condon principle is reproduced. Also for larger aggregates clear vibrational structure is observed. Introducing temperature has a two-fold effect on the system. First of all, it causes a broadening of the peaks in the absorption spectrum. Furthermore, as the molecular interactions are reduced by the presence of the exciton-phonon coupling, we observe thermal destruction of exciton coherence in molecular aggregates. Due to this latter effect, our model is capable of capturing both the perturbative limits described above: that of weak exciton-phonon coupling in which we have collective delocalized exciton states and that of weak intermolecular coupling for which the wavefunctions are highly localized.

We present linear absorption spectra of molecular aggregates obtained from our polaron transformation method and compare them to results from the well-known two-particle approximation[3] to determine the regime in which our method is applicable. A promising next step is to apply the current method to study energy transport properties of closely-spaced molecular aggregates.

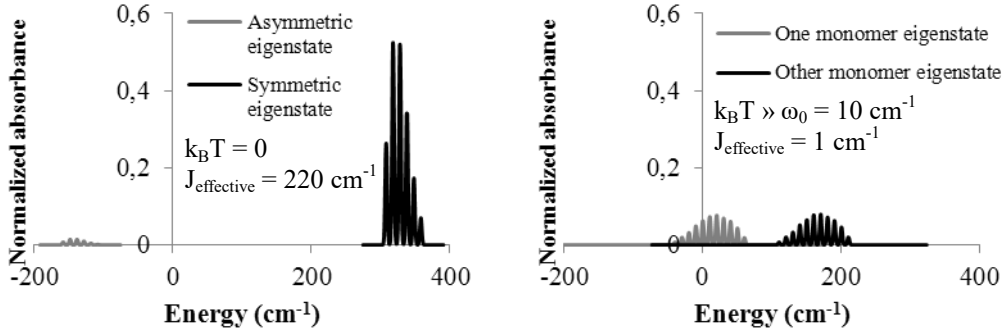

Fig. 1. *Thermal destruction of exciton coherence. (a) Delocalized exciton regime. (b) Localized exciton regime.*

References

1 F. Würthner, Theo E. Kaiser, and Chantu R. Saha-Möller, Angew. Chemie. Int. Ed. **50**: 3376–3410 (2011)
2 S. Jang, J. Chem. Phys. **135**, 034105 (2011)
3 M.R. Philpott, J. Chem. Phys. **55**: 2039–2054 (1971)