

Abstract Submitted
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Simulation study of 2D spectrum of molecular aggregates coupled to correlated vibrations¹ DARIUS ABRAMAVICIUS, VYTAUTAS BUTKUS, LEONAS VALKUNAS, Physics Dept. Vilnius University, SHAUL MUKAMEL, Chemistry Dept. University of California Irvine — Oscillatory dynamics of two-dimensional (2D) spectra of photosynthetic pigment-protein complexes raise the questions of how to disentangle various origins of these oscillations, which may include quantum beats, quantum transport, or molecular vibrations. We study the effects of correlated overdamped fluctuations and under-damped vibrations on the 2D spectra of Fenna-Matthews-Olson (FMO) aggregate, which has well-resolved exciton resonances, and a circular porphyrin aggregate (P6), whose absorption shows vibrational progression. We use a generic exciton Hamiltonian coupled to a bath, characterized by a spectral density. Fluctuations have smooth, while vibrations have δ -type spectral densities. We show how various scenarios of correlated molecular fluctuations lead to some highly oscillatory crosspeaks. Molecular vibrations cause progression of diagonal peaks in the 2D spectrum and make their corresponding cross-peaks highly oscillatory. We, thus, demonstrate that bath fluctuations and molecular vibrations of realistic molecular aggregates are highly entangled in 2D spectroscopy.

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