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**Signature of Nonadiabatic Coupling in Excited-State Vibrational Modes** TAMMIE NELSON, Theoretical Division, Los Alamos National Lab, MIGUEL SOLER, Centro de Fisica da Materia Condensada, Universidade de Lisboa, ADRIAN ROITBERG, Quantum Theory Project, University of Florida, Gainesville , SERGEI TRETIAK, Theoretical Division, Los Alamos National Lab, SEBASTIAN FERNANDEZ-ALBERTI, Universidad Nacional de Quilmes, Argentina — Using analytical excited-state gradients, vibrational normal modes are obtained at the minimum of the electronic excited-state potential energy surfaces for a set of extended conjugated molecules. In regions of strong coupling, the contribution to the forces in the direction of the corresponding non-adiabatic (NA) coupling vector (i.e., the Pechuckas force) is the dominant driving force for nuclear motion and should be reflected in the specific adiabatic excited-state equilibrium normal modes (ES-ENMs) responsible for the coupling. Specifically, the projection of the NA coupling vector on the basis on ES-ENMs with a significant agreement with a single ES-ENM indicates an effective decoupled direction for NA energy transfer. The influence of the nonadiabatic coupling on the excited-state equilibrium normal modes is revealed as a unique highest frequency adiabatic vibrational mode that overlaps with the coupling vector. Comparison with vibrational modes computed in a locally diabatic representation demonstrates that the effect of nonadiabaticity is confined to only a few modes. Such an approach is encouraging as it suggests that the nonadiabatic character of a system may be detected spectroscopically by identifying these unique high frequency modes.

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