

Integrating the spectroscopic and computational characterization of vibronically coupled molecular states

Miller, T.A.,^{1*} Sharma, K.,² Stanton, J.F.,³ Liu, J.⁴

*presenter

¹Miller.104@osu.edu, The Ohio State University, U.S.A.

²The Ohio State University, U.S.A.

³University of Florida, U.S.A.

⁴University of Louisville, U.S.A.

The foundation of molecular physics has long been the Born–Oppenheimer approximation, which neglects vibronic (non-adiabatic) coupling. However, in recent years it has been found that many chemical reactions, particularly photochemical ones, proceed when molecules are in the vicinity of a conical intersection (CI) of electronic states. In just such circumstances vibronic (non-adiabatic) coupling between the states becomes very significant for both the energetics and dynamics. This situation poses challenges for the computational chemist since most electronic structure calculations assume the validity of the Born–Oppenheimer approximation. Similarly, challenges for the experimental spectroscopist are posed because the ultrashort passage of molecules through CIs along reaction paths renders impossible the precise spectroscopic measurement of molecular parameters such as have been used traditionally to benchmark electronic structure calculations.

Fortunately, another venerable theorem by Jahn and Teller provides a solution to this experimental dilemma, as it guarantees that all nonlinear, polyatomic molecules that possess degenerate electronic states will distort leaving a CI at their high symmetry geometry within a potential that supports stationary states that can be probed by high resolution spectroscopy. Traditional adiabatic quantum chemistry calculations cannot describe this surface adequately because the non-adiabatic coupling diverges at the CI. However, calculations using a Hamiltonian, including both vibronic and spin-orbit coupling terms (parameterized by adiabatic electronic structure calculations), in a quasi-diabatic basis yield eigenvalues that can be compared directly to spectroscopic measurements of spin-vibronic energy levels. Furthermore, the corresponding eigenfunctions allow the calculation of the electron-spin and rotational fine structure exhibited by these spin-vibronic levels and the prediction of the transition moments between them. This talk will discuss the integration of the results of such calculations with detailed experimental observations of spectra involving Jahn-Teller active states of several reactive, chemical intermediates, including CH_3O , CaOCH_3 , NO_3 , and C_5H_5 , to provide enhanced understanding of the molecular physics occurring in these molecules.