Vibronic Coupling in Molecules: From Symmetry to Computations to Spectroscopy

Ketan Sharma[1], Oleg A. Vasilyev[1], Terry A. Miller[1], Jinjun Liu[2], and John F. Stanton[3]

[1]Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH, USA
[2]Department of Chemistry, University of Louisville, Louisville, KY, USA
[3]Department of Chemistry, University of Florida, Gainesville, FL, USA

The interaction of electronic and nuclear motion – broadly categorised as 'vibronic coupling' phenomena pose significant challenges to both computational electronic spectroscopy and quantum chemistry, as the usual approximations (Franck–Condon and Born–Oppenheimer) are often rendered unsatisfactory. While vibronic level structure of such systems has been well studied both theoretically and experimentally, there remain practical challenges for calculations attempting to approach conventional spectroscopic accuracy. Even more challenges are encountered when attempts are made to calculate fine-structure effects that arise from couplings involving rotational, orbital, and electron-spin angular momenta, which more subtle and are primarily seen only with very high (rotationally-resolved) spectroscopy.

Calculating experimentally observable spectroscopic effects for rotationally resolved spectra of such molecules involves three basic steps, a) generating a potential energy surface in a quasi-diabatic basis, b) transformation of the potential energy surface from Cartesian to cylindrical coordinates c) diagonalizing the spin-vibronic Hamiltonian. In this talk we discuss pushing the boundaries for such calculations. We demonstrate that by using symmetry properties, we can simplify the problem to a great extent. The cylindrical representation of the potential energy matrix in the quasi-diabatic basis is more convenient due to the simple form of the rovibronic Hamiltonian. A major obstacle in these calculations is solving the eigenvalue problem due to the size of matrices that need to be diagonalized. We have implemented new algorithms that diagonalize huge matrices that include coupling terms up to quartic order. We demonstrate the strength of our computational techniques by comparing our theoretical calculations to recent experiments on calcium-alkoxide free radicals, which are promising candidates for direct laser-cooling of polyatomic molecules.

The computation techniques have been extended to calculate experimentally observable rotational parameters. We demonstrate that the fine-structure Hamiltonian within a doubly degenerate electronic state can be substantially simplified using symmetry properties and also lead to explicit expressions for the rotational parameters that can be calculated using the spin-vibronic eigenfunctions. This can be used to generate a simulation to understand and characterize the previously observed, but unanalyzed rotationally resolved spectra of open-shell radicals.