JAHN-TELLER COUPLING IN THE METHOXY RADICAL: INSIGHTS INTO THE INFRARED SPECTRUM OF MOLECULES WITH VIBRONIC COUPLING

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The ground $\tilde{X}^2E$ vibrations of the methoxy radical have intrigued both experimentalists and theorists alike due to the presence of a conical intersection at the C_{3v} molecular geometry. This conical intersection causes methoxy's vibrational spectrum to be strongly influenced by Jahn-Teller coupling which leads to large amplitude vibrations and extensive mixing of the two lowest electronic states. The spectrum is further complicated due to spin-orbit and Fermi couplings. The standard diabatic normal mode quantum numbers are poor labels due to this vibronic mixing.

Using the potential energy force field and calculated spectra of the methoxy radical by Nagesh and Sibert[1] as a starting point, we look to develop a method for assigning states to a spectrum with vibronic coupling. We simplify the analysis by considering only the lowest two *e* modes of methoxy (the rock and the bend). When we include first-order Jahn-Teller coupling between these two modes in a new zero-order Hamiltonian, we are able to use an expanded version of the linear Jahn-Teller quantum numbers to assign the states.[2] This zeroth order representation is nontrivial; therefore, we study the properties of its eigenstates using correlation diagrams with respect to the strength of the Jahn-Teller coupling constant.

[1] Nagesh, J.; Sibert, E. L. *J. Phys. Chem. A* **2012**, *116*, 3846–3855.

[2] Barckholtz, T. A.; Miller, T. A. *Int. Revs. in Phys. Chem.* **1998**, *17*, 435–524.