A ZERO-ORDER PICTURE OF THE INFRARED SPECTRUM FOR THE METHOXY RADICAL: ASSIGNMENT OF STATES

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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 vibronic coupling which leads to large amplitude vibrations and extensive mixing of the two lowest electronic states. This coupling combined with spin-orbit and Fermi couplings greatly complicates the assignments of states. Using the potential force field and calculated spectra of Nagesh and Sibert[1,2], we assign quantum numbers to the infrared spectrum. When the zero-order states are the diabatic normal mode states, there is sufficient mode mixing that the normal mode quantum numbers are poor labels for the final states. We define a series of zero-order Hamiltonians which include additional coupling elements beyond the normal mode picture but still allow for the assignment of Jahn-Teller quantum numbers. In methoxy, the two lowest frequency *e* modes, the bend (q_5) and the rock (q_6), are the modes with the strongest Jahn-Teller coupling. In general, a zero-order Hamiltonian which includes first-order Jahn-Teller coupling in q_6 is sufficient for most states of interest. Working in a representation which includes first-order Jahn-Teller coupling in q_6, we identify states in which additional coupling elements must be included; these couplings include first-order Jahn-Teller coupling in q_5, higher order Jahn-Teller coupling in q_5 and q_6, and, in the dueterated case, Jahn-Teller coupling which is modulated by the corresponding *a* modes.

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