

## A ZERO-ORDER PICTURE OF THE INFRARED SPECTRA OF CH<sub>3</sub>O AND CD<sub>3</sub>O: ASSIGNMENT OF STATES

BRITTA JOHNSON, EDWIN SIBERT, *Department of Chemistry, University of Wisconsin–Madison, Madison, WI, USA.*

Experimentalists and theorists alike have been intrigued by the infrared spectra of the methoxy radical; due to the presence of a conical intersection at the C<sub>3v</sub> molecular geometry, methoxy's IR spectrum is strongly influenced by Jahn-Teller vibronic coupling which leads to large amplitude vibrations and extensive mixing of the two lowest electronic states. This radical's complex IR spectra, which also contains moderate mixing from spin-orbit and Fermi couplings, serves as an important test for models which seek to understand complex molecular vibrations.

The assignment of the IR spectra in methoxy, and its partially and fully deuterated analogues, is considered. All vibronic states below 2575 cm<sup>-1</sup> in CH<sub>3</sub>O and 2035 cm<sup>-1</sup> in CD<sub>3</sub>O are assigned. The mixing between the zero-order normal modes complicates the assignment using this representation. Alternative zero-order representations, that include specific Jahn-Teller couplings, are explored and used to create definitive assignments for the low lying vibronic states. In many instances it is possible to plot the wavefunctions on which the assignments are based. The plots also enable one to visualize the conical seam and its effect on the wavefunctions. The first and second order Jahn-Teller coupling in the rocking motion dominates the spectral features in CH<sub>3</sub>O, while first order and modulated first order couplings dominate the spectral features in CD<sub>3</sub>O. The methods described here are general and can be applied to other Jahn-Teller systems.