ASSIGNING STATES IN THE JAHN-TELLER COUPLED INFRARED SPECTRA OF CH$_3$O AND CD$_3$O

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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, this leading 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. In this talk we describe our efforts to assign the states of both CH$_3$O and CD$_3$O.

Using the potential energy force field and calculated spectra of Nagesh and Sibert\textsuperscript{1} as a starting point, vibrational mixing is considered using various zero-order representations. When the zero-order states are the diabatic normal mode states, there is sufficient mode mixing that the normal mode quantum numbers are no longer good labels. The mixing of the zero-order states can be reduced by including additional terms in the zero-order Hamiltonian, $H^o$. We consider the choice of including the first order Jahn-Teller coupling between one of the three degenerate normal modes. As the rocking motion has the largest Jahn-Teller coupling, this is the coupling that is included in $H^o$. Although the normal mode quantum numbers of the rocking basis functions are no longer good quantum numbers, due to the Jahn-Teller induced vibronic mixing, the zero-order states can be labeled with the linear Jahn-Teller quantum numbers.\textsuperscript{2} This work extends these ideas by considering an $H^o$ that includes linear Jahn-Teller coupling between two sets of degenerate vibrations. Plots of the resulting zero-order states are presented, and the spectral transitions recently observed\textsuperscript{3} for both CH$_3$O and CD$_3$O in a $p$-H$_2$ matrix are assigned using these basis functions. The extent of state-mixing found for the full Hamiltonian $H$ for various choices of $H^o$ is illustrated via the use of correlation diagrams obtained by plotting the eigenvalues of $H^o + \delta(H - H^o)$ as a function of $\delta$ where $\delta$ varies from zero to one.


\textsuperscript{3} Yu-Fang Lee, Wei-Te Chou, and Yuan-Pern Lee (private communication).