NINE DIMENSIONAL THEORETICAL STUDIES ON METHOXY FREE RADICAL

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The Jahn-Teller type of degeneracy in electronic states in polyatomic molecules greatly affects its vibrational dynamics. The methoxy free radical possesses C_{3v} symmetry at the Jahn-Teller conical intersection ($\tilde{X}^2E$) and provides an ideal system for understanding how the Jahn-Teller phenomenon affects the dynamics. Despite many efforts to clearly elucidate the dynamics, calculation of the potential hypersurface and vibronic states in the molecule remains a theoretical challenge. We adopt a diabatic framework to describe the 9-dimensional hypersurface, which allows us to treat the dynamics in a more straightforward manner. A 9-dimensional force field is calculated for both the $\tilde{A}^2A_1$ and $\tilde{X}^2E$ surfaces using various levels of theory and basis sets. Quartic and quadratic force fields, expressed in internal coordinates, are obtained for the ground and excited states, respectively. The least squares fit was obtained solely using points with C_s symmetry, yet is shown to agree well with *ab initio* points obtained at lower symmetry. The Hamiltonian is shown to take on a particularly simple form when expressed in terms of circular raising and lowering operators for both the electronic and vibrational degrees of freedom. The variational calculation in the diabatic representation is carried out in a series of prediagonalization steps, adding vibrational degrees of freedom in a systematic manner. Theoretical and experimental fundamental frequencies are shown to be in good agreement.