EFFECT OF JAHN-TELLER AND SPIN-ORBIT COUPLING ON $\tilde{X}^2E$ INFRARED SPECTRUM OF CH_3O

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The $\tilde{X}$ state is doubly degenerate for the CH_3O radical in its highest symmetry, for geometries belonging to C_{3v} point group. The symmetry is lowered and the degeneracy removed by displacements along asymmetric modes of vibration due to Jahn-Teller coupling between electronic and vibrational degrees of freedom. Spin-orbit coupling plays an important role as well, by removing degeneracy at high symmetry and partically quenching Jahn-Teller coupling at displaced geometries or lower symmetries. In this work, we examine the effect of Jahn-Teller and Spin-Orbit coupling on the infrared spectrum of the $\tilde{X}$ surface. The selection rules combine symmetries of vibrational and electronic degrees of freedom and are less straightforward. We calculate a 9-D dipole moment surface for x, y and z components using $ab\ initio$ methods. The components of the vibronic dipole moment operator, obey transformation properties belonging to different symmetry species of the C_{3v} point group and we use group-theoretical arguments to impose constraints on the allowed terms in its functional form, similar to that used in construction of the vibronic Hamiltonian [1]. We construct the dipole moment surface solely using geometries of C_s symmetry in a diabatic vibronic representation, using the two electronic states as diabatic basis. We fit only the x and z components for the two diabatic states and derive the rest of the dipole operator based on constraints imposed by three-fold symmetry. The merits and limitations of such an approach will be discussed. The vibronic states are calculated using a 9-D quartic force field as described in [1]., where both Jahn-Teller and spin-orbit coupling are included. The Davidson and Lanczos iterative methods are used to calculate the transitions between the ground vibronic to the higher levels in the infrared spectrum and the calculated transitions are compared to experiment.

[1] Jayashree Nagesh and Edwin L. Sibert III $Phys.\ Chem.\ Chem.\ Phys.$,**12**,8250 (2010)