

VIBRONIC AND SPIN ANGULAR MOMENTUM IN ROTATIONALLY RESOLVED SPECTRA OF JAHN-TELLER ACTIVE MOLECULES

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Effects due to vibronic and spin angular momentum have long been observed in rotationally resolved spectra of Jahn-Teller active molecules. The breakdown of the Born-Oppenheimer approximation in these molecules leads to complications in their vibronic spectra. The molecular picture is further complicated due to the coupling of spin angular momenta with rotational and vibronic angular momentum. Values of these coupling constants have been determined by many high resolution rotationally resolved spectroscopic experiments. However, the presence of a conical intersection in the adiabatic potential energy surfaces has made getting a reliable quantum chemistry calculation of these terms challenging. In this talk we present methods that have been developed to make first principles calculations of vibronic angular momenta and Coriolis coupling constants from quantum chemistry. Further methods have been developed to calculate spin related terms (spin-orbit quenching and spin rotation coupling), using ab initio methods and model vibronic hamiltonian. We report a comparison of calculations of these parameters with corresponding results determined from high resolution spectroscopy for molecules like methoxy radical and cyclopentadienyl radical.