VIBRONIC ANALYSIS OF MOLECULES WITH QUASI-DEGENERATE ELECTRONIC STATES

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Progress in laser cooling and trapping molecules has lead to a renewed interest in alkaline earth monoalkoxide (MOR) free radicals as promising candidates for direct laser-cooling of polyatomic molecules. Theoretical understanding of these molecules is challenging due to the presence of quasi-degenerate electronic states in these molecules. In addition to that, pseudo-Jahn Teller interactions and spin-orbit coupling also play a very important role. Understanding these couplings and their effects on the molecular spectra will provide critical information for future direct laser cooling of MORs and similar radicals. In this talk we discuss the theoretical intricacies involved in calculating the spin-vibronic spectra of such molecules from first principles. A Hamiltonian has been developed in a spin-vibronic representation for molecules with quasi-degenerate electronic states. We will describe calculating the parameters in this Hamiltonian using ab-initio methods and the software developed for solving such Hamiltonians (SOCJT3). Our discourse includes both frequency calculations and relative transition intensities from first principles for both excitation and emission spectra which can be compared to experimentally observed using LIF and DF spectra of $CaOCH_3$, $CaOC_2H_5$, and iso-$CaOC_3H_7$ to be reported in succeeding talk. Typical Franck-Condon factor calculations done under the Born-Oppenheimer approximation reproduce the dominant features of these spectra, but the inclusion of Jahn-Teller and pseudo-Jahn-Teller couplings and spin-orbit interactions in the calculations not only improves the accuracy of simulation but also leads to additional vibronic transitions that help to explain the finer structure observed in the spectra. A major limitation of these methods is the amount of computational resources required as the molecules become larger. Efforts to minimize the amount of resources required as well as approximations involved in simulating the spin-vibronic spectra for larger molecules like iso-$CaOC_3H_7$ have also been discussed.