ELECTRONIC SPECTROSCOPY OF THE $\tilde{A} - \tilde{X}$ TRANSITIONS OF JET-COOLED CALCIUM MONOALKOXIDE RADICALS: SPIN-VIBRONIC STRUCTURE OF NONLINEAR MOLECULES AS CANDIDATES FOR DIRECT LASER COOLING

ANAM C. PAUL, HAMZEH TELFAH, *Department of Chemistry, University of Louisville, Louisville, KY, USA*; KETAN SHARMA, *Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH, USA*; S M SHAH RIYADH, *Department of physics and astronomy, University Of Louisville, Louisville, KY, USA*; TERRY A. MILLER, *Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH, USA*; JINJUN LIU, *Department of Chemistry, University of Louisville, Louisville, KY, USA*.

We report a combined experimental and computational study of spin-vibronic structure and transition intensities of the lowest electronic states of nonlinear alkaline earth monoalkoxide (MOR) radicals, including calcium methoxide ($CaOCH_3$), calcium ethoxide ($CaOC_2H_5$), and calcium isopropoxide [$CaOCH(CH_3)_2$]. Experimentally, laser-induced fluorescence/dispersed fluorescence (LIF/DF) and cavity ring-down (CRD) spectra of the $\tilde{A}^2E$–$\tilde{X}^2A_1$ electronic transition of $CaOCH_3$ (C_{3v}), the ${\tilde{A}_1}^2A''/{\tilde{A}_2}^2A'$–$\tilde{X}^2A'$ transition of $CaOC_2H_5$ (C_s), and the ${\tilde{A}_1}^2A'/{\tilde{A}_2}^2A''$–$\tilde{X}^2A'$ transition of [$CaOCH(CH_3)_2$] were recorded under jet-cooled conditions. An essentially constant $\tilde{A}_2 - \tilde{A}_1$ energy separation for different vibronic levels is observed in the LIF spectrum of each radical, attributed to the spin-orbit (SO) interaction and, in the case of the two C_s molecules, the zero-point-energy-corrected "difference potential". The complete active space self-consistent field (CASSCF) and the coupled-cluster (CC) methods are used to calculate electronic transition energies and vibrational frequencies and to predict parameters governing the spin-vibronic energy level structure and simulate the recorded LIF/DF spectra. The Jahn-Teller (JT), pseudo-Jahn-Teller (pJT), and SO interactions, especially those between the $\tilde{A}_1/\tilde{A}_2$ and the neighboring $\tilde{B}$ states, induce a number of off-diagonal Franck-Condon (FC) matrix elements leading to additional vibronic transitions. The spin-vibronic Hamiltonian presented in the preceding talk has been employed for the spectral simulation. Computational and experimental results on all three free radicals will be compared, and the implications for future laser cooling experiments will be discussed.