ALKALINE EARTH MONOALKOXIDE FREE RADICALS AS CANDIDATES FOR LASER COOLING OF POLYATOMIC MOLECULES

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Alkaline earth monoalkoxide free radicals, e.g., $CaOCH_3$, $CaOCH_2CH_3$, and $CaOCH(CH_3)_2$, have been proposed recently as candidates for future laser cooling of polyatomic molecules.[a] Their $\tilde{A} \leftarrow \tilde{X}$ and $\tilde{B} \leftarrow \tilde{X}$ electronic transitions correspond to promotion of the unpaired electron in the $4s$ orbital of Ca^+ to each of the three components of its $4p$ orbital perturbed by the presence of the alkoxy group. These electronic transitions are limited to unbonding orbitals, from which the existence of quasiclosed transition loops for laser cooling has been surmised. Moreover, molecules suitable for Doppler cooling with lasers must feature (quasi-)diagonal Franck-Condon (FC) matrices for transitions between vibronic levels involved in the closed transition cycles, which is expected for alkaline earth monoalkoxides thanks to their bonding scheme. Laser-induced fluorescence (LIF) and dispersed-fluorescence (DF) spectra can provide valuable information to guild future laser cooling experiments. Experimentally obtained vibronic transition frequencies and intensities have been used to benchmark ab initio calculations carried out using both complete active space self-consistent field (CASSCF) and coupled cluster (CC) methods. Although FC factor calculations using the harmonic oscillator approximation reproduce major peaks in the spectra, it has been found that Jahn-Teller (JT) and pseudo-Jahn-Teller (pJT) effects introduce certain new transitions. Furthermore, The $\tilde{A}$ state of alkaline earth monoalkoxides is split by the spin-orbit interaction and, for those free radicals with symmetry lower than C_{3v}, the difference potential between two nearly degenerate electronic states. The rotational and fine structure of the involved electronic states as well as line intensities for rotational transitions between these states are predicted using a newly proposed spectroscopic model. The implications of the present experimental and computational investigations to future laser cooling experiments will be discussed.

[a] Kozyryev, L. Baum, K. Matsuda and J. M. Doyle, ChemPhysChem 17, 3641 (2016).