ANALYZING THE ROTATIONAL AND SPIN STRUCTURE OF THE TWO LOWEST ELECTRONIC STATES OF ASYMMETRICALLY SUBSTITUTED ALKOXY RADICALS

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The members of the alkoxy radical family play important roles in oxidation processes, both in combustion and the atmosphere, and their spectrocopy is well studied. The simplest species, CH_3O, has a degenerate $\tilde{X}^2$E ground electronic state, which has a near-UV transition to a non-degenerate electronic state presently referred to as $\tilde{B}^2$A. Larger family members formed by alkyl group substitution of the H atom(s) shift the $\tilde{A}$-$\tilde{X}$ electronic transition to the red as the size of the alkyl group grows. If the H atom(s) substitution is not symmetric, the degeneracy of the $\tilde{X}$ state is resolved into two non-degenerate electronic states, presently referred to as $\tilde{X}$ and $\tilde{A}$. Typically the energy separation, ΔE_0, between these two states, caused by the vibronic quenching mechanism[a,b], is small ($\leq 1000 cm^{-1}$). Historically, the approach to the spectra involving these three states has been to analyze the rotational structure in the $\tilde{X}$ and $\tilde{A}$ states separately via a Hamiltonian including an asymmetric top rotational term and a spin-rotation interaction. Recently Liu[c] has suggested that, as is done with the $\tilde{X}^2$E state of methoxy, the structure of both the $\tilde{X}$ and $\tilde{A}$ states, now separated by ΔE_0, and coupled by the spin-orbit and Coriolis interactions, is better considered together. This "coupled two-state model" also allows semi-quantitative prediction of effective spin-rotation constants using calculated molecular geometry and spin-orbit constants, which can be calculated with considerable accuracy. In the present work, we have simulated rotationally and fine-structure resolved laser-induced fluorescence (LIF) spectra of alkoxy radicals with the Liu model and fit the rotational constants, as well as the spin-orbit and Coriolis coupling parameters between the $\tilde{A}$ and $\tilde{X}$ states, holding the spin-rotation parameters at zero. The fits have been carried out for ethoxy, 2 conformers of propoxy, and 4 conformers of butoxy. Comparisons between the experimental spectra and simulations with both models (with separated and coupled electronic states) will be shown and relationships between the parameters from both models will be discussed.

[a] R. Renner, Z. Phys. 92, 172 (1934).

[b] D. A. Mills, C. M. Western, and B. J. Howard, J. Phys. Chem. 90, 3331 (1986)

[c] J. Liu, J. Chem. Phys. 148, 124112 (2018).