

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

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Alkoxy radicals are vital in the process of oxidation and have been well studied spectroscopically. The simplest species, CH_3O , has a degenerate $\tilde{X}^2\text{E}$ ground electronic state, which has a near-UV transition to a non-degenerate electronic state, $\tilde{B}^2\text{A}_1$. Larger alkoxy radicals are formed by substitution of the H atom(s) with the $\tilde{B}-\tilde{X}$ electronic transition shifting to the red as the size of the alkyl group increases. Most importantly, when the H atom(s) substitution is asymmetric, the degeneracy of the \tilde{X} state is resolved into two non-degenerate electronic states, \tilde{X} and \tilde{A} . Typically the spin-orbit-free energy separation, ΔE_0 , between these two states, is small ($\leq 1000 \text{ cm}^{-1}$ and even $\leq 100 \text{ cm}^{-1}$ in some cases). Historically, the approach to the analysis of spectra has been to treat 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 term. Recently Liu^a suggested that, as is done with the $\tilde{X}^2\text{E}$ 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 interaction and the Coriolis interaction, should be better considered together. This “coupled two-state model” also allows semi-quantitative prediction of effective spin-rotation constants using 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. The Coriolis coupling constant (ζ_t) was held equal to the quenched electronic orbital angular momentum (ζ_{ed}) of the spin-orbit constant. For these fits the spin-rotation parameters are held zero. The fits have been carried out for isomers and conformers of alkoxy radicals with four or less carbon atoms for which high-resolution LIF spectra have been obtained. Dependence of fit values of molecular constants (ζ_t , ζ_{ed} , and ΔE_0) on the size and conformation of alkoxy radicals will be discussed.

^aJ. Liu, *J. Chem. Phys.* 148, 124112 (16 pages) (2018).