JET-COOLED LASER-INDUCED FLUORESCENCE SPECTROSCOPY OF LARGE SECONDARY ALKOXY RADICALS

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The $\tilde{B} \leftarrow \tilde{X}$ laser-induced fluorescence (LIF) spectra of jet-cooled 2-pentoxy and 2-hexoxy have been recorded. The observed rotational and fine structure of the strongest vibronic bands has been simulated with *ab initio* calculated rotational constants for both the $\tilde{X}$ and $\tilde{B}$ states, as well as the electron spin-rotation constants of the $\tilde{X}$ state and the transition dipole moments, which are predicted based on the transferability of these quantities in an "orbital-fixed coordinate system" using iso-propoxy as the reference molecule. It is suggested by *ab initio* calculations that the lowest two electronic ($\tilde{X}$ and $\tilde{A}$) states of secondary alkoxy radicals have a small energy separation on the order of 100 cm^{-1}. The energy ordering of these two nearly degenerate states has been determined by comparing the experimentally determined rotational constants and the transition dipole moments to the predicted ones. Molecular constants derived in fitting the rotational and fine structure of the experimental spectra using an evolutionary algorithm (EA) enabled unambiguous assignment of the observed vibronic bands to different conformers of 2-pentoxy and 2-hexoxy. Based on the results of these two radicals, the strongest vibronic bands in the LIF spectra of larger secondary alkoxies were also assigned.