

ROTATIONALLY RESOLVED $\tilde{B} \leftarrow \tilde{X}$ ELECTRONIC SPECTRA OF THE ISO-PROPOXY RADICAL AND OTHER SECONDARY ALKOXY RADICALS

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The $\tilde{B} - \tilde{X}$ laser-induced-fluorescence (LIF) spectrum of jet-cooled iso-propoxy radical (*i*-C₃H₇O \cdot) has been recorded. The observed rotational and fine structure of the origin band has been well simulated with rotational constants for both the \tilde{X} and \tilde{B} states and the electron spin-rotation constants of the \tilde{X} state. The line intensities are well simulated with a parallel transition type, requiring the same symmetry for the \tilde{X} as for the \tilde{B} state (A'), which confirms the previous suggestion^a that going from ethoxy (C₂H₅O \cdot) to iso-propoxy, the energy ordering of the in- and the out-of-plane half-filled *p*-orbitals is reversed and the ground state symmetry changes from A'' to A' . The fit rotational constants are consistent with those obtained from the quantum chemistry calculations. However, the fit spin-rotation constants, particularly the nonzero ϵ_{aa} with *a*-axis perpendicular to the C_s plane, can not be explained by second-order perturbation theory. Nevertheless they can be semi-quantitatively explained based on the transferability of the electron spin-molecular rotation tensor^b in the axis system defined by the half-filled *p*-orbital and the *p* π -orbital using ethoxy as the reference molecule. The failure of the second-order perturbation theory, as well as that of the pure precession approximation, is due to the strong vibronic interaction between the near-degenerate \tilde{X} and \tilde{A} states. The vibrationless levels of these two states are separated by only 68 cm⁻¹ as determined in previous disperse-fluorescence study.^c The near degeneracy of the \tilde{X} and \tilde{A} states of iso-propoxy and reversal of the energy ordering going from ethoxy to iso-propoxy have also been demonstrated in quantum chemistry calculations. Based on the result of iso-propoxy, spin-rotation constants of other secondary alkoxy radicals can be predicted and used for the simulation of the $\tilde{B} - \tilde{X}$ rovibronic spectra of these radicals. Specifically, analysis of the high-resolution LIF spectrum of cyclohexoxy (*c*-C₆H₁₁O \cdot)^d is ongoing.

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