HIGH-RESOLUTION LASER-INDUCED FLUORESCENCE SPECTROSCOPY OF CYCLOHEXOXY: ROTATIONAL AND FINE STRUCTURE OF MOLECULES IN NEARLY DEGENERATE ELECTRONIC STATES

JINJUN LIU, *Department of Chemistry, University of Louisville, 2320 S. Brook St., Louisville, Kentucky 40292.*; DMITRY G. MELNIK, and TERRY A. MILLER, *Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Ave., Columbus, Ohio 43210.*

The previously obtained $\tilde{B}^2\mathrm{A}' - \tilde{X}^2\mathrm{A}''$ and $\tilde{B}^2\mathrm{A}' - \tilde{A}^2\mathrm{A}'$ laser-induced fluorescence (LIF) spectra of jet-cooled cyclohexoxy radical (c-$\mathrm{C_6H_{11}O}$)[a] have been analyzed and simulated using the coupled-two-state model presented in the preceding talk. The rotational and fine structure of the nearly degenerate $\tilde{X}^2\mathrm{A}''$ and $\tilde{A}^2\mathrm{A}'$ states is reproduced using one set of molecular constants including rotational constants, spin-rotation constants, effective spin-orbit constants ($a\zeta_e d$) and the vibronic energy separation between the two states (ΔE). While the energy level structure could be reproduced by only *effective* spin-rotation constants (without the spin-orbit constant), the spin-orbit interaction introduces transitions that have no intensity using the separate-states asymmetric rotor model. Rotational and fine-structure analysis using the two-state model has proven to be an effective method to separate the first order electron-spin-molecular-rotation constants from the effective spin-rotation constants, and to decouple the spin-orbit splitting ($a\zeta_e d$) and the vibronic energy separation (ΔE), both of which contribute to the experimentally observed energy separation between the two coupled states ($\Delta E^{\tilde{A}-\tilde{X}}$). Isopropoxy (discussed in the preceding talk), cyclohexoxy, and other molecules in nearly degenerate electronic states provide unique cases bridging the gap from symmetrically degenerate states, e.g., ground $\tilde{X}^2\mathrm{E}$ state of methoxy, and the Born-Oppenheimer limit of unperturbed electronic states.

[a] "Jet-cooled laser spectroscopy of the cyclohexoxy radical", L. Zu, J. Liu, G. Tarczay, P. Dupré, and T. A. Miller, *J. Chem. Phys.* **120**, 10579 (2004).