JET-COOLED LASER SPECTROSCOPY OF CYCLOHEXOXY RADICAL

LILY ZU, JINJUN LIU, GYÖRGY TARCZAY,[a] PATRICK DUPRÉ and TERRY A. MILLER, *Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University,120 W. 18th Avenue, Columbus, Ohio 43210.*

The laser induced fluorescence(LIF), and laser excited, dispersed fluorescence(DF) spectra of the cyclohexoxy free radical have been observed under free-jet cooling conditions for the $\widetilde{B} - \widetilde{X}$ electronic transition. In the LIF excitation spectrum, two different types of expansions, characterized by rotational temperatures of 1 and 100 K, have demonstrated that a number of lines, termed hot bands, either nearly or entirely disappear at the lowest jet temperature. The cold spectral bands have two distinct types of structure in rotationally resolved high-resolution spectra. Correspondingly, two distinct sorts of structure are observed in the DF spectra.
LIF transitions to both a' and a'' vibrational levels in the $\widetilde{B}$ state are observed and allowed due to a substantial pseudo-Jahn-Teller effect in the $\widetilde{X}$ state. We assign hot bands to transitions to the origin and excited vibrational levels of the $\widetilde{B}^2A'$ state from the vibrationless level of the low-lying $\widetilde{A}$ electronic state. Analyses of the spectra yield vibrational frequencies for the $\widetilde{X}$, $\widetilde{A}$, and $\widetilde{B}$ states as well as the energy separations of their vibrationless levels. Although 5 conformers of cyclohexoxy are possible, it appears that all presently observed spectral bands can be accounted for by a single conformer. A more complete rotational analysis is now in progress.

[a]Present address: Department of General and Inorganic Chemistry, Eötvös University, P. O. Box 32, H-1518 Budapest 112, Hungary