Electronic Spectroscopy of Jet-Cooled Combustion Radicals

Final Report

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There are no unexpended funds.

In the final grant period, we completed two major manuscripts detailing the spectroscopy of both the 1-methylvinoxy and 2-methylvinoxy free radicals. The experimental work is augmented by a variety of electronic structure calculations in collaboration with Dr. Larry Harding of Argonne National Labs and Prof. John Stanton of U. Texas-Austin.

The jet-cooled laser induced fluorescence spectrum of the $\tilde{B} \leftarrow \tilde{X}$ electronic transition of 1-methylvinoxy radical is assigned, including both hot and cold bands. The barrier to methyl internal rotation in both $\tilde{X}$ and $\tilde{B}$ states is determined by fitting pure torsional transitions to a one-dimensional hindered rotor model. The resulting threefold torsional barrier parameters are $V_3' = -740 \pm 30 \text{ cm}^{-1}$ for the $\tilde{B}$ state (minimum energy conformation having one methyl CH bond *cis* to the frame CO bond) and $V_3'' = +130 \pm 30 \text{ cm}^{-1}$ for the $\tilde{X}$ state (methyl CH bond *trans* to CO). The intensity pattern clearly indicates a change in the preferred methyl conformation upon excitation, while *ab initio* calculations provide the absolute conformations in each state. A variety of *ab initio* methods including CASSCF, multi-reference CI, and coupled cluster techniques were applied to both the $\tilde{X}$ and $\tilde{B}$ states of 1-methylvinoxy. Only the largest coupled-cluster calculations yield a $\tilde{B}$ -state barrier in good quantitative agreement with experiment. In unsubstituted vinoxy, a $\tilde{B}$ -state geometry adjusted earlier to fit experimental rotational constants (Ref. 10) is evidently in error.

The jet-cooled laser induced fluorescence spectrum of the $\tilde{B} \leftarrow \tilde{X}$ electronic transition of 2-methylvinoxy radical is assigned as a superposition of contributions from non-interacting *cis* and *trans* isomers. The spectrum of the *cis* isomer is identified by comparison with *ab initio* electronic structure calculations; both theory and experiment clearly indicate that the methyl conformation changes from the $\tilde{X}$ state to the $\tilde{B}$ state. Fits of both hot and cold bands to a one-dimensional torsional model yield methyl rotor barrier

magnitudes of $270 \pm 20 \text{ cm}^{-1}$ in the $\tilde{X}$ state and $200 \pm 20 \text{ cm}^{-1}$ in the $\tilde{B}$ state. The *ab initio* calculations show that in the ground state the preferred conformation places one methyl CH bond in the plane of the molecular frame *cis* to the vicinal CC bond. Assignment of the spectrum of *trans*-2-methylvinoxy is more tentative, since no resolved hot bands are available to corroborate the model. Our best estimate for the $\tilde{B}$ state barrier magnitude is $60 \pm 15 \text{ cm}^{-1}$. Multi-reference configuration interaction calculations and coupled cluster calculations are reasonably successful in obtaining methyl torsional barriers in agreement with experiment, although high accuracy is elusive for the $\tilde{B}$ state of both *cis* and *trans* isomers. By comparison with simpler cases, we infer that the π radical character of the $\tilde{B}$ state strongly influences the methyl torsional barrier.

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