

THE O<sub>2</sub> + ETHYL REACTION IN HELIUM NANODROPLETS: INFRARED SPECTROSCOPY OF THE ETHYLPEROXY RADICAL

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Helium-solvated ethylperoxy radicals (CH<sub>3</sub>CH<sub>2</sub>OO●) are formed via the *in situ* reaction between ethyl radicals and  $\tilde{X}^3\Sigma_g^-$  O<sub>2</sub>. The reactants are captured sequentially through the droplet pick-up technique. Helium droplets are doped with ethyl radical via pyrolysis of di-*tert*-amyl peroxide or *n*-propyl nitrite in an effusive, low-pressure source. A mid-infrared spectrum of ethylperoxy is recorded with species-selective droplet beam depletion spectroscopy. Spectral assignments in the CH stretching region are made via comparisons to second-order vibrational perturbation theory with resonances (VPT2+K) based on coupled-cluster quartic force fields. *Gauche* and *trans* conformers are predicted to be nearly isoenergetic; however, the spectrum indicates that one dominant conformer is present. Indeed, in several previous studies in our group, where chemical reactions were conducted inside droplets, only a single conformer of the product was observed. Exploration of the ethylperoxy potential energy surface, particularly along the CCOO torsional and CO stretching coordinates, motivates an explanation that is based upon an adiabatic funneling mechanism that leads to the exclusive production of one conformer. The slower torsional degree of freedom is cooled more rapidly than the higher frequency stretching and bending coordinates owing to the stronger coupling between the torsional modes and the collective modes of the helium droplet. The reactants are cooled into the torsional well that stabilizes first during their approach on the PES.