HELIUM NANODROPLET ISOLATION SPECTROSCOPY AND AB INITIO CALCULATIONS OF HO_3-$(O_2)_N$ CLUSTERS (N=0-4)

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The HOOO hydridotrioxygen radical and its deuterated analog (DOOO) have been isolated in helium nanodroplets following the *in-situ* association reaction between OH and O_2. The infrared spectrum in the 3500-3700 cm^{-1} region reveals bands that are assigned to the ν_1 (OH stretch) fundamental and $\nu_1 + \nu_6$ (OH stretch plus torsion) combination band of the *trans*-HOOO isomer. The helium droplet spectrum is assigned on the basis of a detailed comparison to the infrared spectrum of HOOO produced in the gas phase [E. L. Derro, T. D. Sechler, C. Murray, and M. I. Lester, J. Chem. Phys. **128**, 244313 (2008)]. Despite the characteristic low temperature and rapid cooling of helium nanodroplets, there is no evidence for the formation of a weakly bound OH-O_2 van der Waals complex, which implies the absence of a kinetically significant barrier in the entrance channel of the reaction. There is also no spectroscopic evidence for the formation of *cis*-HOOO, which is predicted by theory to be nearly isoenergetic to the *trans* isomer. Stark spectroscopy of the *trans*-HOOO species provides vibrationally averaged dipole moment components that qualitatively disagree with predictions obtained from CCSD(T) computations at the equilibrium, planar geometry, indicating a floppy complex undergoing large-amplitude motion about the torsional coordinate. Under conditions that favor the introduction of multiple O_2 molecules to the droplets, bands associated with larger H/DOOO-$(O_2)_n$ clusters are observed shifted 1-10 cm^{-1} to the red of the *trans*-H/DOOO ν_1 bands. Detailed *ab initio* calculations are carried out for multiple isomers of *cis*- and *trans*-HO_3-O_2, corresponding to either hydrogen or oxygen bonded van der Waals complexes. Comparisons to theory suggest that the structure of the HO_3-O_2 complex formed in helium droplets is a hydrogen-bonded $^4A'$ species consisting of a *trans*-HO_3 core. The computed binding energy of the complex is approximately 240 cm^{-1}. Despite the weak interaction between *trans*-HO_3 and O_2, non-additive red shifts of the OH stretch frequency are observed upon successive solvation by O_2 to form the larger clusters with $n>1$.