

PROBING TRANS-HOOO/DOOO AND HOOO-(O₂)_n CLUSTERS: A HENDI APPROACH

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Trans-HOOO and HOOO-(O₂)_n clusters have been assembled in helium nanodroplets and probed with a tunable narrow linewidth PPLN-OPO laser system in the O-H stretching region. We observed the ν_1 band at 3569.45 cm⁻¹, which consists of rotationally resolved a- and b-type components, in addition to the broad c-type $\nu_1+\nu_6$ band at 3699.06 cm⁻¹. The band origins for ν_1 and $\nu_1+\nu_6$ are shifted to the blue by only 0.15 cm⁻¹ and 1.03 cm⁻¹, respectively, compared to the gas phase values by Lester and co-workers.^{a,b} Neither of the two other predicted stable isomers, namely cis-HOOO and the hydrogen-bound OH-O₂ species,^c were found within a broad survey scan. The HOOO-(O₂)_n clusters grow in to the red of the ν_1 band of trans-HOOO as the O₂ pick-up pressure is increased. Cluster signals are resolved for up to $n = 4$, while signals for clusters with $n > 4$ pile up to form a broad feature. High level *ab initio* multireference calculations are needed to help understand the geometries for these multiple O₂ clusters. The O-D stretch of trans-DOOO was measured at 2635.02 cm⁻¹, which is extremely close to the gas phase value at 2635.06 cm⁻¹.^d The linewidths of the transitions within this band are narrower than those within the O-H stretching band of trans-HOOO, which suggests that the lifetime of the excited vibrational state is longer for trans-DOOO than trans-HOOO.

^aE. L. Derro, C. Murray, T. D. Sechler, and M. I. Lester, *J. Phys. Chem. A* **111**, 11592, (2007).

^bE. L. Derro, T. D. Sechler, C. Murray, and M. I. Lester, *J. Chem. Phys.* **128**, 244313, (2008).

^cB. J. Braams and H. G. Yu, *Phys. Chem. Chem. Phys.* **10**, 3150, (2008).

^dE. L. Derro, T. D. Sechler, C. Murray, and M. I. Lester, *J. Phys. Chem. A* **112**, 9269, (2008).