PROBING TRANS-HOOO/DOOO AND HOOO-$(O_2)_n$ CLUSTERS: A HENDI APPROACH

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Trans-HOOO and HOOO-$(O_2)_n$ 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 ν_1+ν_6 band at 3699.06 cm^{-1}. The band origins for ν_1 and ν_1+ν_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-O_2 species,[c] were found within a broad survey scan. The HOOO-$(O_2)_n$ clusters grow in to the red of the ν_1 band of trans-HOOO as the O_2 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 O_2 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.

[a] E. L. Derro, C. Murray, T. D. Sechler, and M. I. Lester, J. Phys. Chem. A. **111**, 11592, (2007).
[b] E. L. Derro, T. D. Sechler, C. Murray, and M. I. Lester, J. Chem. Phys. **128**, 244313, (2008).
[c] B. J. Braams and H. G. Yu, Phys. Chem. Chem. Phys. **10**, 3150, (2008).
[d] E. L. Derro, T. D. Sechler, C. Murray, and M. I. Lester, J. Phys. Chem. A. **112**, 9269, (2008).