

FTIR Spectroscopy of the *tert*-Butyl Hydroperoxide Dimer in the Gas-phase

Casper Vindahl Jensen^a, Henrik G. Kjaergaard^b

^a Department of Chemistry, University of Copenhagen, CVJ@chem.ku.dk

^b Department of Chemistry, University of Copenhagen, HGK@chem.ku.dk

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Secondary Organic Aerosols (SOAs) formed from oxidized Volatile Organic Compounds (VOCs) remain one of the largest contributions to uncertainty to the radiative forcing of the planet. These compounds are functionalized by acid- alcohol- and (hydro)peroxide-groups. These functional groups are potential hydrogen bond donors and acceptors, critical to the initial condensation and cluster formation in the atmosphere. Hydroperoxides have been shown to have stronger hydrogen bonding interactions compared to alcohols. In this study, we present the first observation of *tert*-butyl hydroperoxide (TBHP) dimer in the gas-phase. The theoretical lowest Gibbs energy structure of the dimer is a closed ring-structure with two hydrogen bonding interactions (fig.1, left), similar to that found for formic acid dimer. By combining a calculated oscillator strength and the measured OH-stretching intensity,¹ we have estimated a unitless formation constant at room temperature of $K = 0.74 \pm 0.30$ (theory, osc. strength) ± 0.08 (exp.)

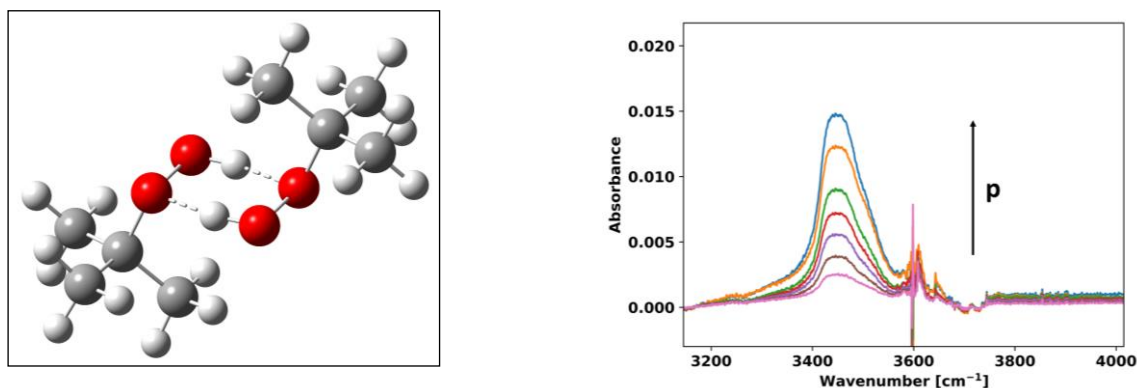


Figure 1 Left: Calculated lowest energy structure of TBHP dimer. Right: OH-stretch band from dimer with increasing monomer pressure.

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REFERENCES

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