



## ***Ab initio* modeling $O_2^-$ (H<sub>2</sub>O)<sub>n</sub> and $O_3^-$ (H<sub>2</sub>O)<sub>n</sub> clusters, $n \leq 12$**

Nicolai Bork (1), Martin B. Enghoff (1), Jens Olaf P. Pedersen (1), Kurt V. Mikkelsen (2), Theo Kurtén (2,3), and Henrik Svensmark (1)

(1) National Space Institute, Technical University of Denmark, Copenhagen, Denmark (nbor@space.dtu.dk), (2) Division of Scientific Computing, University of Copenhagen, Copenhagen, Denmark, (3) Division of Atmospheric Sciences, University of Helsinki, Helsinki, Finland

For almost two decades, empirical evidence has linked the influx of cosmic rays to cloud formation.[1] Cosmic rays are the primary source of atmospheric ionization and it has therefore been speculated that ions may provide the link between cosmic rays and clouds. The exact mechanism is largely unknown, but one plausible mechanism is through catalytic oxidation of SO<sub>2</sub> to H<sub>2</sub>SO<sub>4</sub>.[2]

Due to electron affinities and concentrations, O<sub>2</sub><sup>-</sup> and O<sub>3</sub><sup>-</sup> anions are likely primary products of cosmic ray ionization. Such ions will quickly attract a number of water and the attached water molecules will be important for any subsequent reactions.[3] It is well known that solvent molecules alter both thermodynamic and kinetic properties of most reactions, but further, the solvent water may also disperse the charge and /or screen the O<sub>2</sub><sup>-</sup> and O<sub>3</sub><sup>-</sup> species from further reactions. Despite several previous studies, the exact sizes and structures of the most important O<sub>2</sub><sup>-</sup>(H<sub>2</sub>O)<sub>n</sub> and O<sub>3</sub><sup>-</sup>(H<sub>2</sub>O)<sub>n</sub> clusters remain uncertain.[4] This information is crucial for studying all subsequent reactions in the proposed catalytic oxidation of SO<sub>2</sub> to H<sub>2</sub>SO<sub>4</sub>.[1,2]

We present an *ab initio* study of gaseous clusters of O<sub>2</sub><sup>-</sup> and O<sub>3</sub><sup>-</sup> with water. We have included up to 12 water, constituting the first and second solvation shells. We have determined the thermodynamics of cluster growth in excellent agreement with existing experimental data.[3] We find that anionic O<sub>2</sub><sup>-</sup>(H<sub>2</sub>O)<sub>n</sub> and O<sub>3</sub><sup>-</sup>(H<sub>2</sub>O)<sub>n</sub> clusters are thermally stabilized at typical atmospheric conditions for at least  $n = 8$ . This is considerably larger than previous assumptions of  $n = 4 - 5$ .[4]

The first 4 water molecules are strongly bound to the anion due to delocalization of the excess charge while stabilization of more than 4 H<sub>2</sub>O is due to normal hydrogen bonding. Although clustering up to 12 H<sub>2</sub>O, we find that the O<sub>2</sub> and O<sub>3</sub> anions retain at least ca. 80% of the charge. Further, the O<sub>2</sub><sup>-</sup> and O<sub>3</sub><sup>-</sup> species are located near at the surface of the cluster and are thus accessible for further reactions in the catalytic H<sub>2</sub>SO<sub>4</sub> oxidation cycle.

[1] Enghoff et al., *Atmos. Chem. Phys.*, 8, 4911–4923, 2008.

[2] Svensmark et al., *Proc. R. Soc. A*, 463, 385-396, 2007.

[3] Fehsenfeld and Ferguson, *J. Chem. Phys.*, 61, 8, 1974.

[4] Seta et al., *J. Phys. Chem. A*, 107, 7, 2003. Lee and Kim, *Mol. Phys.*, 100, 6, 875, 2002.