Influence of the humidity on the sticking of HO_2 on fatty acids aerosols: a molecular dynamics study

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Keywords: aerosol, adsorption, water, molecular simulations.
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Models of atmospheric chemistry are widely used to perform projections of future changes in the chemical composition of the global troposphere, including changes in climate related to greenhouse gases and aerosol particles. However, large uncertainties are still associated with the chemistry implemented in these models (Boucher 2013), which in turn can lead to inaccurate long-term predictions.

The proposed work seeks to improve our understanding of the oxidative capacity of the atmosphere, which drives the lifetime of trace gases, and therefore the composition of the atmosphere.

Recent measurements (Stone 2012) of free radicals made in forested environments characterized by low levels of nitrogen oxides (NOx = NO and NO_2) indicate that current models of atmospheric chemistry tend to overestimate the concentration of peroxy radicals (HO_2 and RO_2). An overestimation of peroxy radicals is an important issue since these radicals are the main precursors of the hydroxyl radical (OH), the most important atmospheric oxidant during daytime.

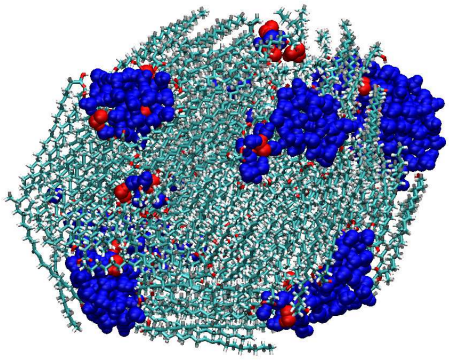

Figure 1: Sticking of water molecules (blue) and hydroperoxy radicals (red) on an oleic acid aggregate, as modelled in the MD simulations at 235 K.

An analysis of the dataset indicates that the missing sink could be due to an underestimation of the rates of RO_2+HO_2 reactions, and/or the uptake of peroxy radicals onto aerosol particles. However, there is still a lack of kinetic and mechanistic data to correctly assess the contribution of these two loss pathways of peroxy radicals in low NOx environments.

Classical molecular dynamics simulations have been performed to study the interaction of HO_2 with an organic aerosol particle composed of carboxylic acids, i.e. oleic acids. The results indicate that HO_2 radicals are efficiently accommodated on the aerosol particle; ii) this mechanism being enhanced in presence of water molecules. This work will help in understanding the first stage of the peroxy radical chemistry at organic aerosol surfaces.

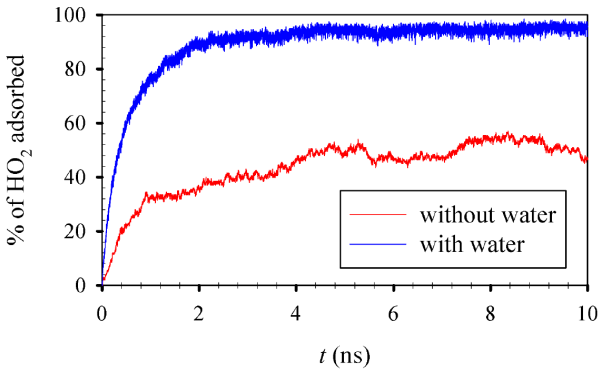

Figure 2: Percentage of adsorbed HO_2 radicals on an oleic acid particle at 235 K in presence or not of water.

This work has been supported by the CaPPA project (Chemical and Physical Properties of the Atmosphere), funded by the French National Research Agency (ANR) through the PIA (Programme d'Investissement d'Avenir) under contract ANR-10-LABX-005.

Boucher, O., et al (2013), 5th Assessment Report IPCC.
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