Neutral and ion-induced H_2SO_4 - H_2O particle formation 1: New theory

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Keywords: Atmospheric nucleation, nucleation theory.
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We have derived a new version of Classical Nucleation Theory (CNT) to treat particle formation in neutral and ion-induced binary sulfuric acid-water systems. The model is validated against CLOUD measurements in Duplissy *et al* (2016), also presented in a companion abstract (Duplissy *et al*), and parameterized for the use in large scale atmospheric models as presented in a companion abstract by Määttänen *et al*.

In our new theoretical description we use a quantum chemistry-normalized form of Classical Nucleation Theory utilizing most reliable quantum chemistry calculations (Kurtén *et al.*, 2007) on sulphuric acid hydration. The model is based on a similar approach as Noppel et al. (2002) and extended into the kinetic regime where particle formation is no longer impeded by a free energy barrier.

The theory predicts that the binary water-sulfuric acid system can produce strong new particle formation in free tropospheric conditions both through barrier crossing and through kinetic pathways. In the kinetic regime particle formation rates become proportional to sulfuric acid concentration to second power in the neutral system or first power in the ion-induced system.

At cold stratospheric and upper free tropospheric conditions neutral formation dominates the binary particle formation rates. At mid-tropospheric conditions the ion-induced pathway becomes the dominant mechanism. However, even the ion-induced binary mechanism does not produce significant particle formation in warm boundary layer conditions.

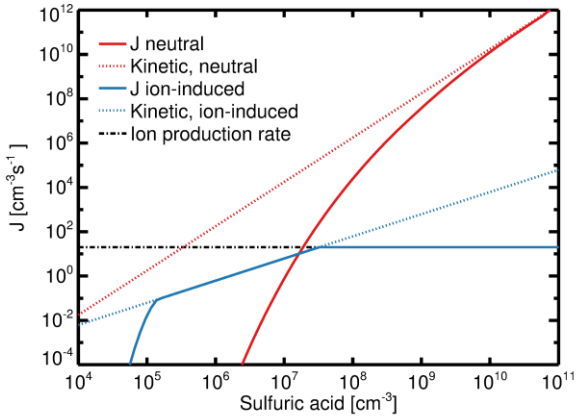

Figure 1. Neutral (red) and ion-induced (blue) particle formation rates at T=249K, RH=50%, ion concentration of 1000 cm^{-3} and ion production rate of 20 $cm^{-3}s^{-1}$.

The theory suggests that the interplay between the dominating mechanism (neutral or ion-induced) is not a simple one: it depends on the temperature and concentrations of participating species in a complex manner. As an example, Figure 1 compares the formation rates (full lines) at a fixed temperature 249K and relative humidity of 50%. The figure shows that below sulfuric acid concentration of $2x10^7$ molecules cm^{-3} the ion-induced particle formation dominates, while neutral pathway becomes dominant at higher sulfuric acid concentrations. This is because the steady state formation rates are ultimately limited by kinetic collision frequencies as well as ion pair production rate (neglecting recombination and aerosol sinks) in the ion-induced case.

The theoretical binary formation rates are very sensitive to relative humidity. The ion-induced rates at 279K and sulfuric acid concentration of $2x10^7$ molecules cm^{-3}, for example, can be effectively zero at 30% relative humidity, but take place at close to ion pair production rate at 90% relative humidity (Fig 2).

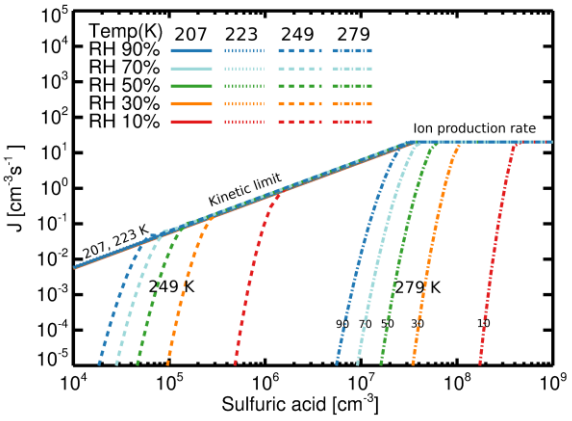

Figure 2: Dependence of ion-induced binary formation rates on relative humidity

Duplissy, J., *et al* (2016), *J. Geophys. Res. Atmos.* **121**, doi:10.1002/2015JD023539.
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Noppel, M., *et al* (2002) *J. Chem. Phys.*, **116**, 218-228.