

Charge induced enhancement of water adsorption on nanoparticle ions

Mario Nachbar³, Thomas Dresch¹, Denis Duft¹, and Thomas Leisner^{1,2}

¹Institute of Meteorology and Climate Research (IMK-AAF), KIT, Germany; ²Institute of Environmental Physics (IUP), University of Heidelberg, Germany; ³current address: Bruker AXS GmbH, Karlsruhe, Germany

Motivation

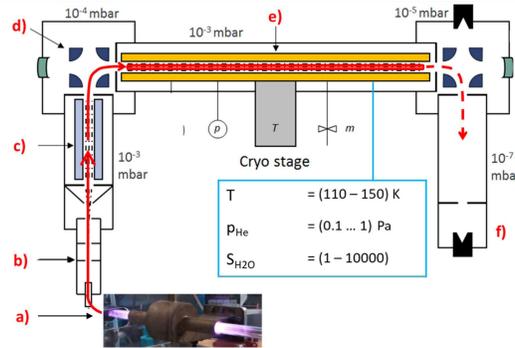
- Formation of noctilucent ice clouds. Ice clouds forming in the mesopause at an altitude of ~85 km by heterogeneous nucleation on meteoric smoke nanoparticles.
- Strong charge-dipole interaction between nanoparticle ions and polar water molecules.
- How does an electric charge impact the agglomeration of water molecules on nanoparticles compared to neutral particle interactions?
- How much does the charge induced attractive force enhance the collision cross section on nanoparticles whose radii exceed the Langevin capture radius [3]?
- What is the role of charged particles in cloud formation and the growth of atmospheric nanoparticles?
- We present new experimental results for the charge induced enhancement of the collision cross section between H₂O molecules and singly charged nanoparticles with radii between 1.4 nm and 3 nm; we also present a new theoretical model to describe our experimental findings.



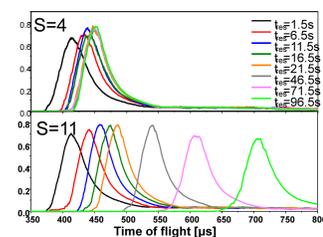
Mesospheric ice clouds seen from the ISS
Photo: NASA, 13. Jul 2012

Experiment: the Trapped Reactive Atmospheric Particle Spectrometer (TRAPS) [1,2]

- Microwave plasma nanoparticle generator (a)
- Aerodynamic lens (b)
- Octupole ion guide (c)
- 90° electrostatic deflector (d)
- Linear quadrupole ion trap configured as supersaturation Molecular-Flow-Ice-Cell (MICE) (e)
- Time-of-Flight mass spectrometer (TOF-MS) (f)
- Helium buffer gas thermalizes the nanoparticles in MICE
- Cryogenic temperature control

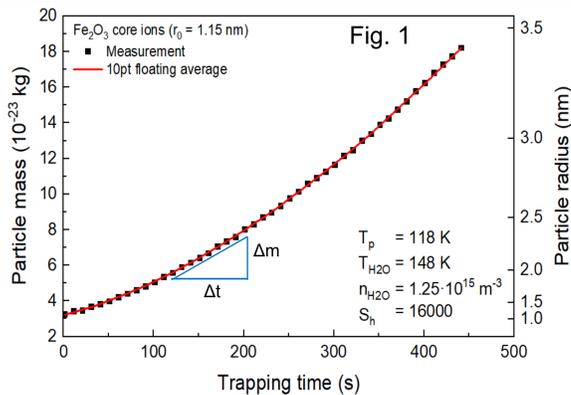


- Condensation of water ice on the nanoparticles is observed by measuring the particle mass as a function of trapping time with the TOF-MS



Typical Time-of-Flight mass spectra (smoothed) for the evaluation of particle growth; t_{res} is the time particles had been exposed to mesospheric conditions in the MICE ion trap prior to TOF mass analysis. S is the supersaturation.

Method



- Fig. 1 shows a typical growth rate measurement of H₂O ice on Fe₂O₃ core nanoparticle ions ($r_0=1.15$ nm).
- At very low particle temperatures and high supersaturations we can safely neglect the outgoing flux.
- The particle mass growth rate is simply {incoming flux density * effective surface area * molecular mass}, or:

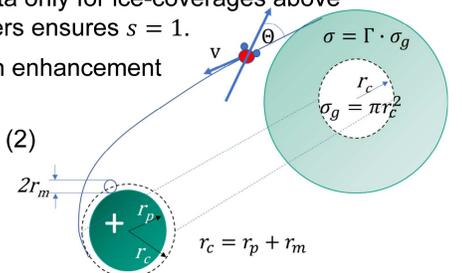
$$\frac{dm}{dt} = s \cdot m_{H_2O} \cdot n_{H_2O} \cdot v_t \cdot \sigma \quad (1)$$

s is the sticking coefficient, m_{H_2O} the mass of the water molecule, n_{H_2O} the number density of gas phase water molecules. $v_t = \sqrt{8kT_{H_2O}/\pi m_{H_2O}}$ is the mean thermal velocity. σ denotes the effective collision cross section of the nanoparticle with a gas phase molecule (various factors of 4 cancel out).

- Analyzing data only for ice-coverages above 1.5 monolayers ensures $s = 1$.

- Cross section enhancement factor Γ :

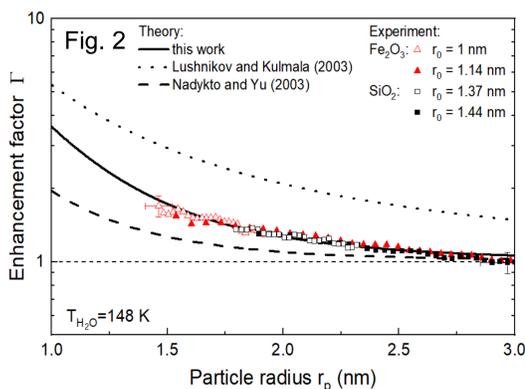
$$\sigma = \Gamma \cdot \sigma_g \quad (2)$$



- We derive Γ from the experimental data by determining growth rates dm/dt from the derivative of the smoothed growth curves and solving Eq. (1) and (2) for Γ .

Results and Discussion

- Measurements:** experimental results (Fig. 2) show that the enhancement factor Γ increases with decreasing particle radius; the charge effect is evident for particles with $r_p < 3$ nm.



- Collisions with attractive force:** The velocity-dependent differential enhancement factor $\gamma(v)$ for the collisions of a nanoparticle with a gas phase molecule (mass m , starting velocity v , kinetic energy K_0) is a function of the potential energy of the molecule at the collision radius $\varphi(r_c)$ [4] (mean free path length $\lambda \gg r_c$):

$$\gamma(v) = \frac{\sigma(v)}{\sigma_g} = 1 - \frac{\varphi(r_c)}{K_0} = 1 - \frac{2 \cdot \varphi(r_c)}{mv^2} \quad (3)$$

- Charge-dipole potential:** $\varphi(r_c)$ is obtained by integrating the force F_d acting on the dipole from the far field at $r=\lambda$ to the collision surface $r=r_c$ ($r_c \ll \lambda$):

$$\varphi(r_c) = \int_{\lambda}^{r_c} F_d dr = \int_{\lambda}^{r_c} \alpha E \frac{dE}{dr} dr + \int_{\lambda}^{r_c} \mu \cos \theta \frac{dE}{dr} dr \quad (4)$$

induced dipole permanent dipole

α is the polarizability, μ the dipole moment, $E=E(r)$ is the electric field.

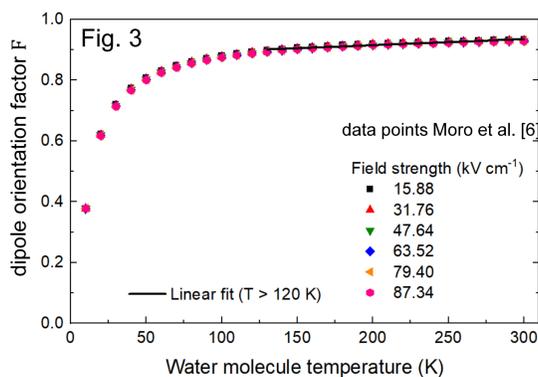
In order to evaluate Eq. (4) a suitable expression for the average dipole orientation $\overline{\cos \theta}$ must be applied.

- Dipole orientation:** at thermal equilibrium the mean dipole orientation $\overline{\cos \theta}$ is given by the Langevin function $L(x) = \overline{\cos \theta} = \left(\frac{e^x + e^{-x}}{e^x - e^{-x}} - \frac{1}{x} \right)$ with $x = \frac{\mu E}{kT}$. $L(x)$ provides an upper limit for $\overline{\cos \theta}$.

- Rotating dipoles:** rotating polar molecules establish a rotational state distribution at a distance $r \gg \lambda$ and then respond adiabatically, to the electric field at distances smaller than λ . This results in lower values for $\overline{\cos \theta}$ [6]:

$$\overline{\cos \theta} = F(x) \cdot L(x); \quad F(x) \leq 1 \quad (5)$$

- Stark effect model:** Quantum mechanical Stark shift calculations of $\overline{\cos \theta}$ were carried out by Moro et al. [5, 6]. The authors of reference [6] generously shared the results of their modelling (Fig. 3), which we will now use to determine the dipole orientation factor $F(T,E)=F(x)$.



- Dipole orientation factor:** According to ref. [6] $F(T,E)$ for water molecules is surprisingly independent of the electric field strength below 100 kVcm⁻¹. We represent $F(T)$ by a linear fit (see Fig. 3):

$$F(T) = 0.875 + 0.0002 \cdot T[K] \quad (120 \text{ K} < T < 300 \text{ K}) \quad (6)$$

- Potential $\varphi(r_c)$:** Assuming that Eq. (6) is a good approximation also for the strongest fields near a point charge (10^3 kVcm⁻¹), inserting into Eq. (5 & 4) and integrating results in:

$$\varphi(r_c) = -\frac{\alpha E(r_c)^2}{2} - F(T) \cdot kT \cdot \ln \left(\frac{\exp[x(r_c)] - \exp[-x(r_c)]}{2x(r_c)} \right) \quad (7)$$

- Enhancement Γ :** The differential enhancement factor $\gamma(v)$ depends on the initial velocity of the gas phase molecule. Integration over the Maxwell-Boltzmann distribution $f(v) = 4\pi v^2 \cdot (m/2\pi kT)^{3/2} \cdot \exp(-mv^2/2kT)$ yields the total enhancement factor Γ :

$$\Gamma(T) = \int \gamma(v) f(v) dv = \int \left(1 - \frac{2 \cdot \varphi(r_c)}{mv^2} \right) f(v) dv \quad (8)$$

- Conclusions:** The integration of Eq. (8) was performed numerically and the result is shown by the solid black line in Fig. 2 without further adjustable fit parameters.

For reference, Fig. 2 also displays two models, which are in general use in the atmospheric community [7, 8] and which are bracketing our results.

The new model for charge induced enhancement of water adsorption on nanoparticles based on Stark effect adiabatic dipole orientations appears in excellent agreement with our experimental findings.

Acknowledgments: We are deeply grateful to Vitaly Kresin and Ramiro Moro for sharing the original Stark effect model data. The work was partially funded by the German Federal Ministry of Education and Research (BMBF, grant number 05K16VHB), the German Research Foundation (DFG, grant number LE 834/4-1) and the Helmholtz Association in the framework of the program Atmosphere and Climate.

References:

- D. Duft, M. Nachbar, M. Eritt, T. Leisner, Aerosol Sci. Technol., 49(4):682-690 (2015)
- M. Nachbar, D. Duft, T. Leisner, Atmos. Chem. Phys. 18, 3419 (2018)
- G. Kummerlöwe, M. K. Beyer, Int. J. Mass Spec. 244, 84 (2005)
- L. D. Landau and E. M. Lifshitz, Mechanics (Pergamon Press, 1960).
- J. Bulthuis, J. A. Becker, R. Moro, V. V. Kresin, J. Chem. Phys. 129, 024101 (2008)
- R. Moro, J. Bulthuis, J. Heinrich, V. V. Kresin, Phys. Rev. A 75, 013415 (2007)
- A. B. Nadykto, F. Yu, J. Geophys. Res. Atmospheres 108 (2003)
- A. A. Lushnikov, M. Kulmala, Euro. Phys. J. D 29, 345 (2004)