Improved parameterizations for neutral and ion-induced H_2SO_4-H_2O particle formation

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Sulfuric acid

- Earth
  - Tropospheric new particle formation
  - Stratospheric sulfate aerosol (Junge) layer
- Venus
  - Thick sulfuric acid clouds cover 100% of the planet
- Mars
  - Possible volcanism in the past causing sulfate aerosol formation, acid rain and formation of sulfate minerals at the surface

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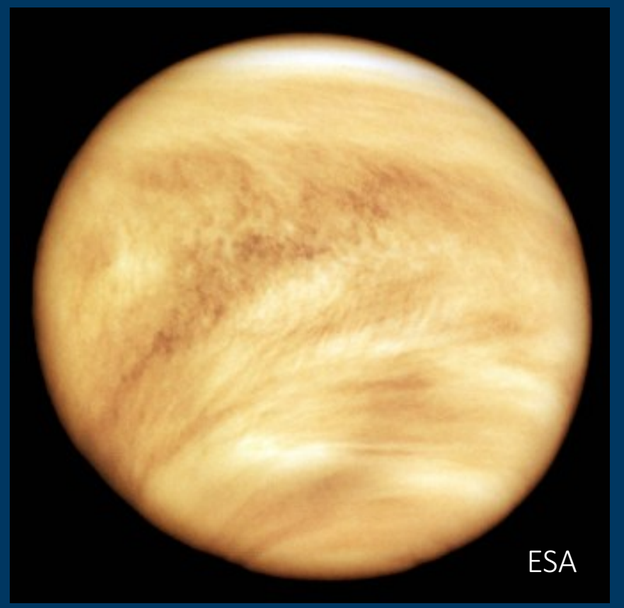

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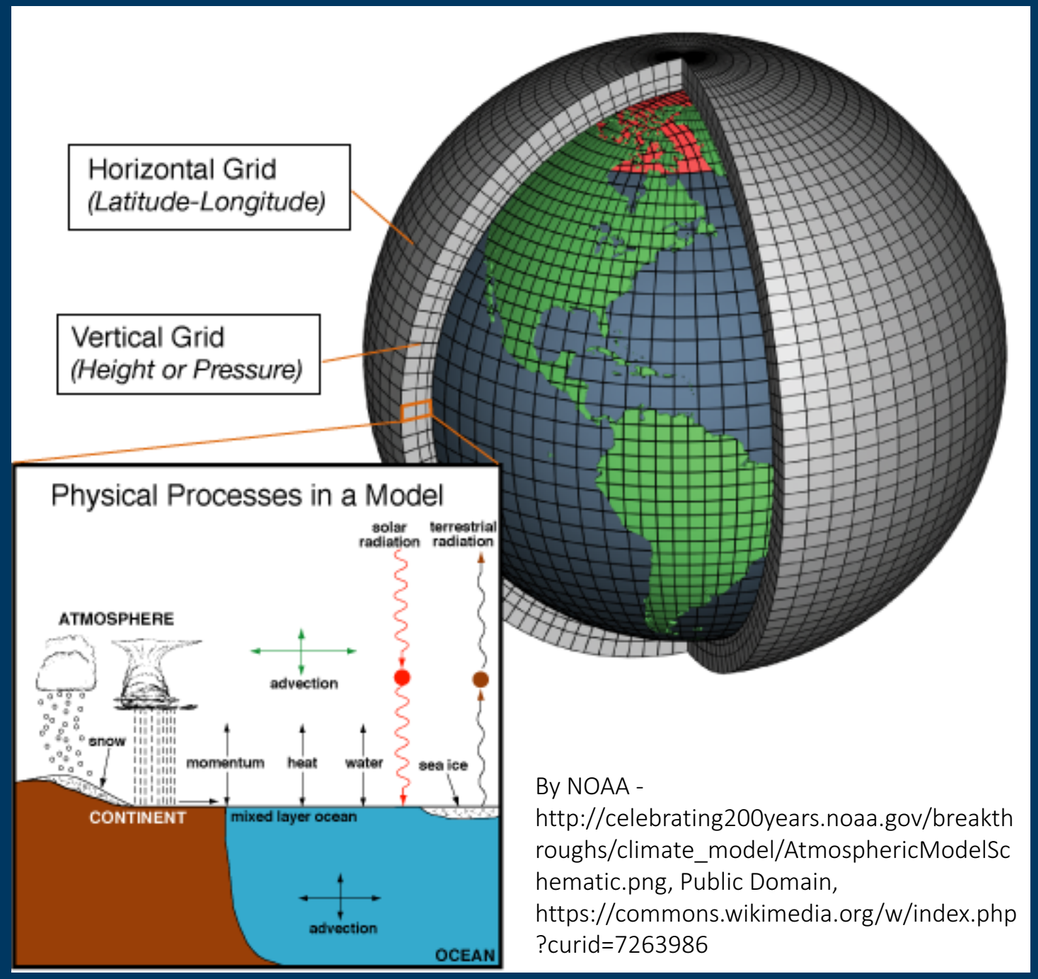
Particle formation parameterizations

- Parameterizations for new particle formation needed in Global Climate Models (GCMs)
  - Formation of a significant fraction of tropospheric CCN related to sulfuric acid
  - Formation of the stratospheric sulfate aerosol layer
- Parameterized functions or look-up tables
- Can be based on theoretical calculations and/or experimental data
- Best case: theoretical calculations that reproduce well measurements within the experimental range and give robust results outside this range
- A very popular one: Vehkamäki et al. (2002,2003)



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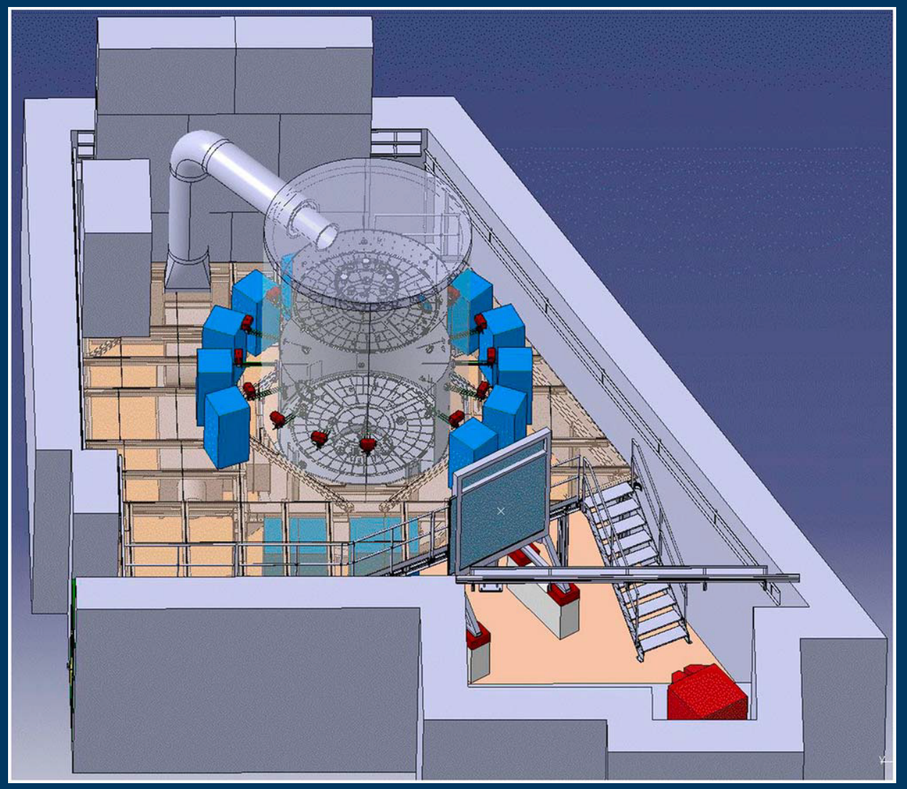
$$
\begin{aligned}
J\left[1/\left(\mathrm{cm}^3\mathrm{s}\right)\right] = \exp\{ & g_1^J(T,x^*) \\
& + g_2^J(T,x^*)\ln(\mathrm{RH}/100) + g_3^J(T,x^*)\left[\ln(\mathrm{RH}/100)\right]^2 \\
& + g_4^J(T,x^*)\left[\ln(\mathrm{RH}/100)\right]^3 + g_5^J(T,x^*)\ln(\rho_a) \\
& + g_6^J(T,x^*)\ln(\mathrm{RH}/100)\ln(\rho_a) \\
& + g_7^J(T,x^*)\left[\ln(\mathrm{RH}/100)\right]^2\ln(\rho_a) \\
& + g_8^J(T,x^*)\left[\ln(\rho_a)\right]^2 \\
& + g_9^J(T,x^*)\ln(\mathrm{RH}/100)\left[\ln(\rho_a)\right]^2 \\
& + g_{10}^J(T,x^*)\left[\ln(\rho_a)\right]^3 \},
\end{aligned}
$$

Data

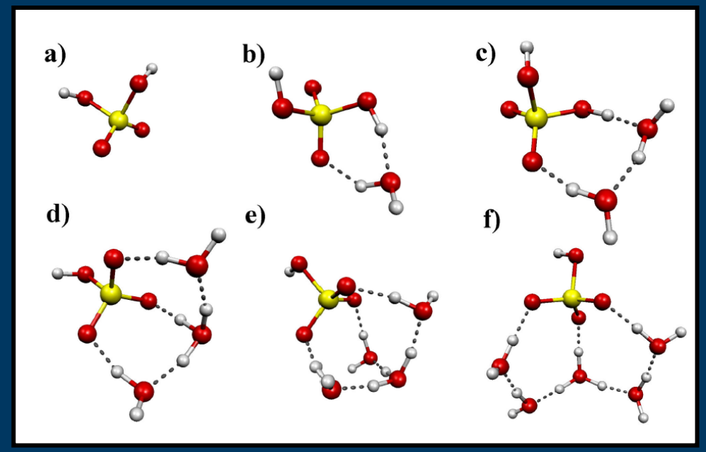
- Parameterization development has suffered from lack of measurements in well-controlled experimental conditions
- CLOUD experiment (Cosmics Leaving OUtdoor Droplets) at CERN has provided unprecedented data on sulfuric acid-water particle formation
- Both electrically neutral and ion-induced particle formation have been studied (Duplissy et al. 2016)
- Conditions: [H_2SO_4]: 10^5 - 10^9 cm^{-3}; RH: 11% - 58%; T: 207 K - 299 K; [ion]: 0 - 6,800 cm^{-3}.



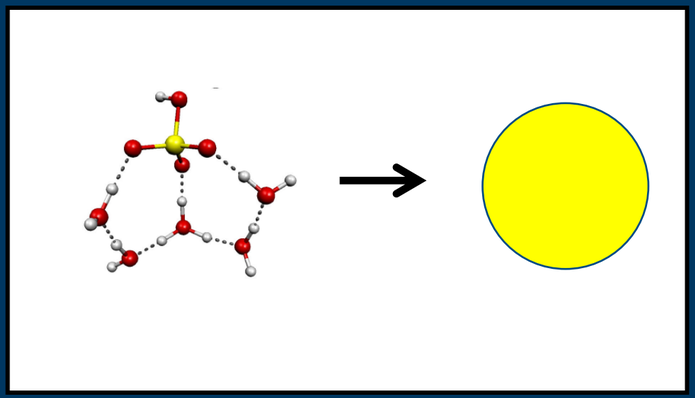
An illustration of the CLOUD chamber: Duplissy et al. 2016

Model

- Classical nucleation theory (CNT)
  - thermodynamically consistent classical nucleation theory (Noppel et al. 2002)
  - normalized with quantum chemical data on sulfuric acid hydration as described in Merikanto et al. (2016).
- The model has been successfully validated against the CLOUD experiments (Duplissy et al., 2016).
- CNT ensures a physically based behavior for the developed parameterizations even outside the experimental range of the CLOUD data set

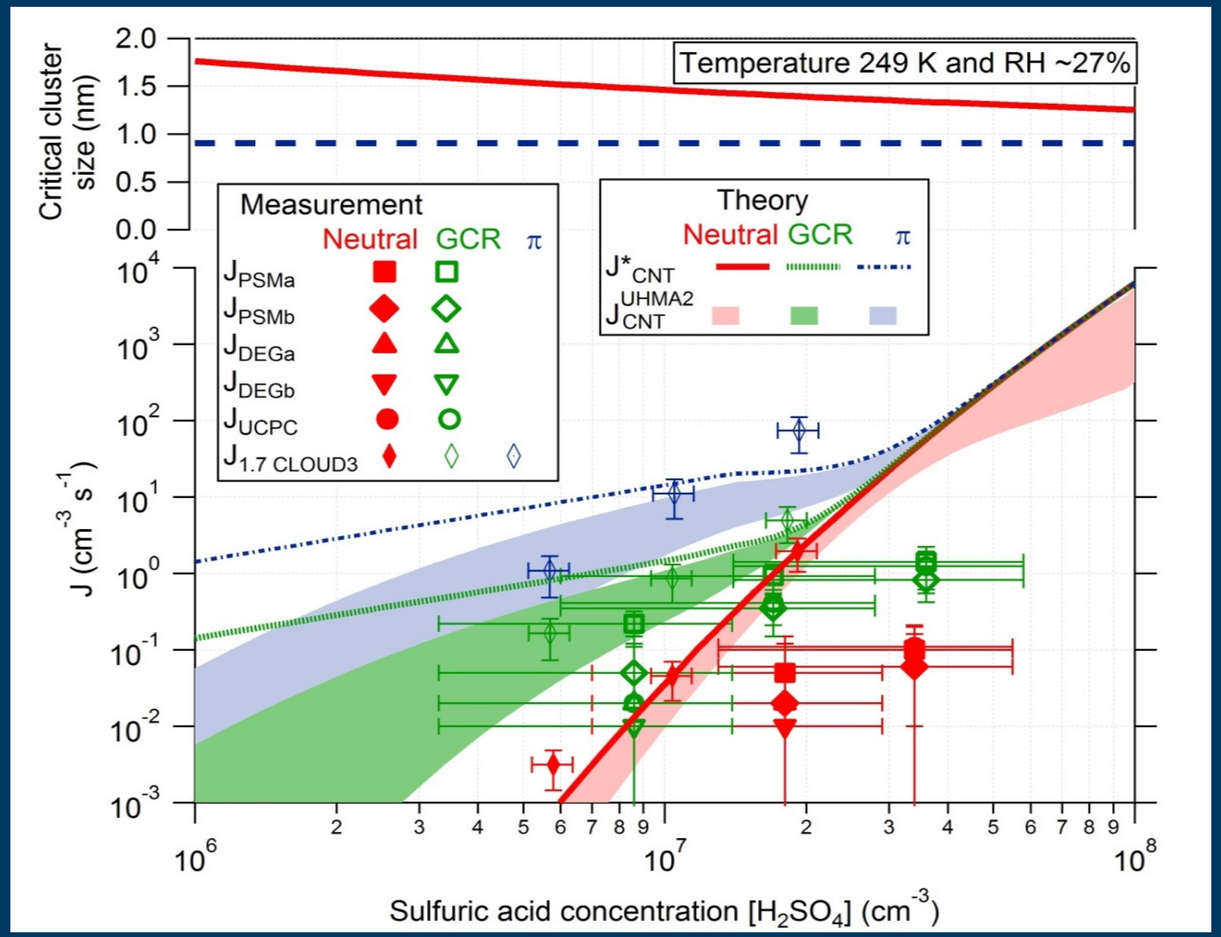


Loukonen et al., ACP 2010



Model validation against data (example)

- T=249 K, RH=27%
- Both neutral and ion-induced nucleation
- Ion-induced nucleation enhance total nucleation rates (one order of magnitude)
- Ion-induced nucleation is kinetic and rates are further limited by ion production rate



Duplissy et al. 2016

Building a parameterization on model results

- The model was used to produce a dataset of parameters related to new particle formation in a wide range of conditions
  - Conditions:
    - Neutral: [H_2SO_4] 10^4 - 10^{13} cm^{-3}, RH 0.001% - 100%, T 165 - 400 K
    - Ion-induced: [H_2SO_4] 10^4 - 10^{16} cm^{-3}, RH 10^{-5}-100%, T 195K - 400 K.

- Data were fitted with parameterized functions for particle formation rate J_{nuc}, critical cluster mole fraction x*, radius r*, and number of molecules n*

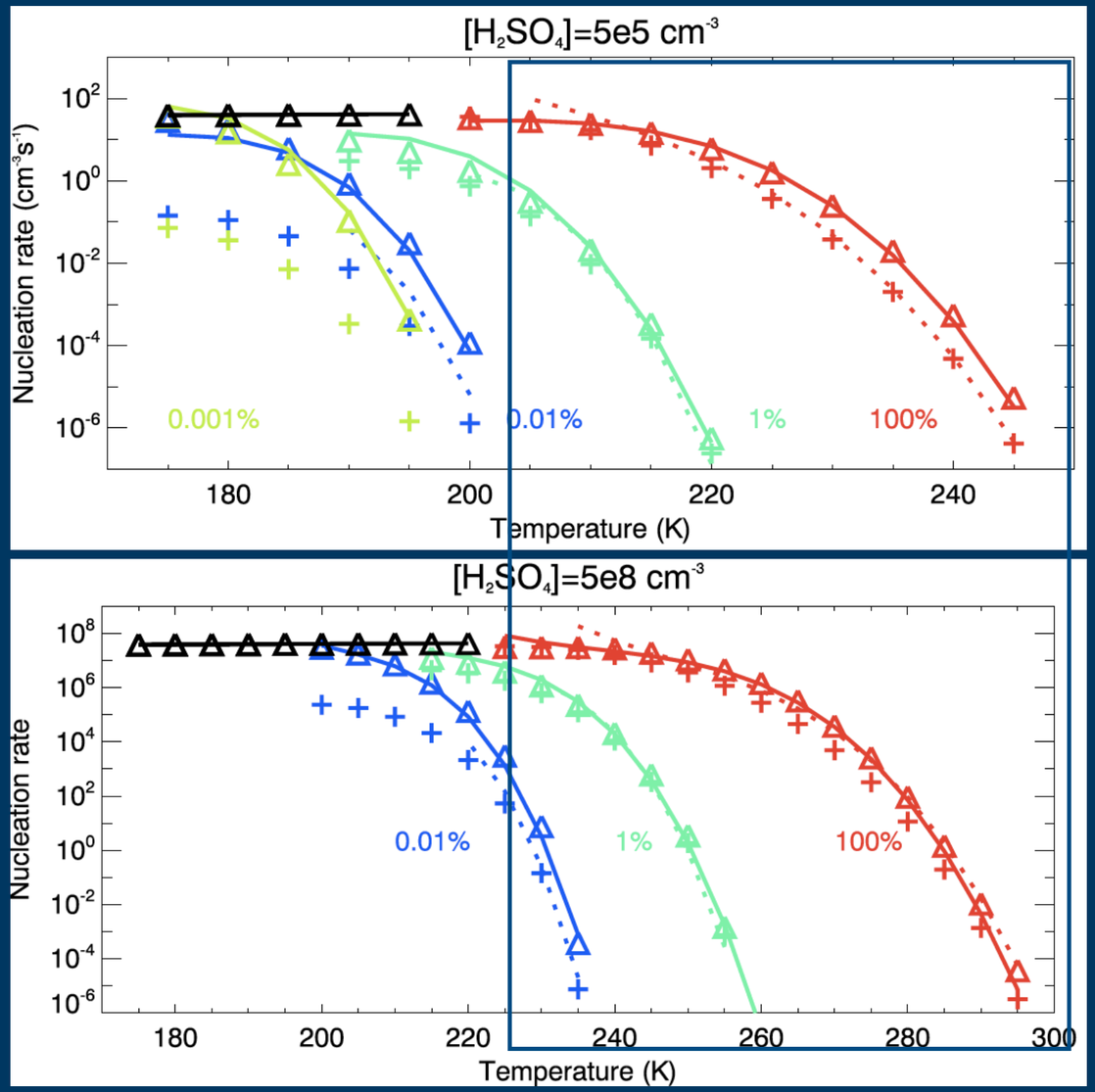
- The [H_2SO_4] threshold above which particle formation becomes barrierless (kinetic) has been parameterized

- Conditions for which neutral J_{nuc}=1 $cm^{-3}s^{-1}$ has also been parameterized

Parameterizations

Neutral case

- New and old parameterization agree at higher temperatures
- Lower temperatures and relative humidities reveal differences
- The lowest ranges not reached by the old parameterization
- Note the black lines and triangles: kinetic range accessible with the new parameterization
- New parameterization shows a good fit to the data (solid lines superposed with the triangles)



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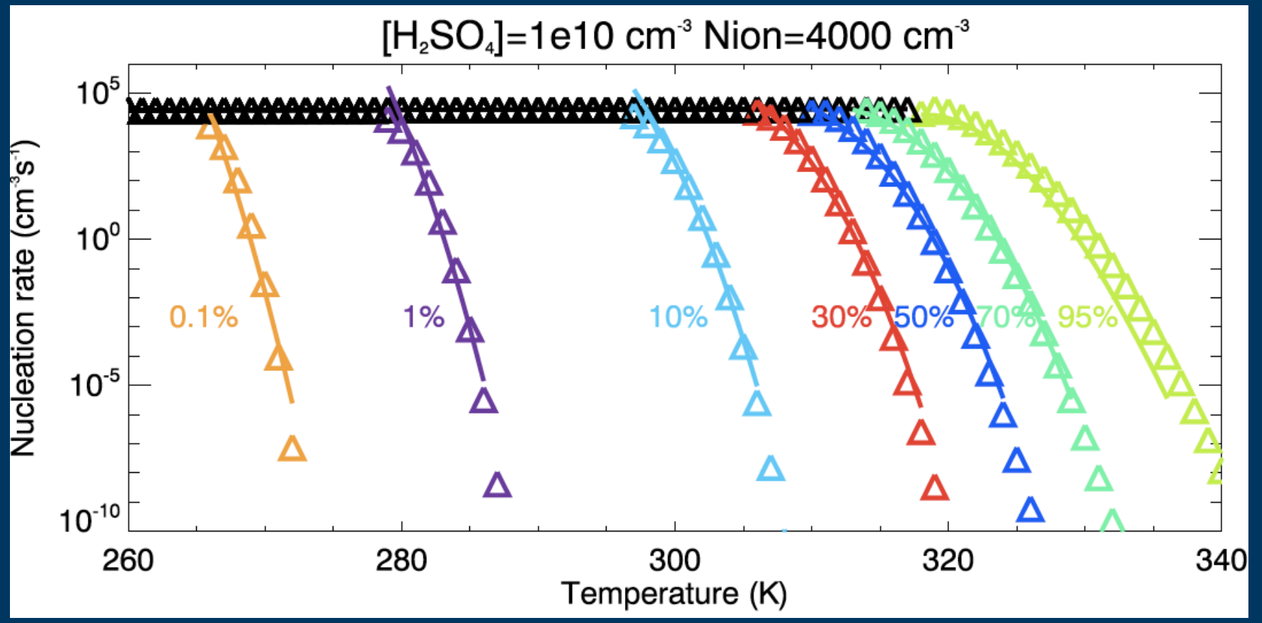
Ion-induced case

- Parameterization follows well the theoretical values
- Parameterization scalable to actual ion concentrations, and limited by the ion pair production rate
- The provided code including the parameterizations allows for calculating the ion concentration from the ion pair production rate



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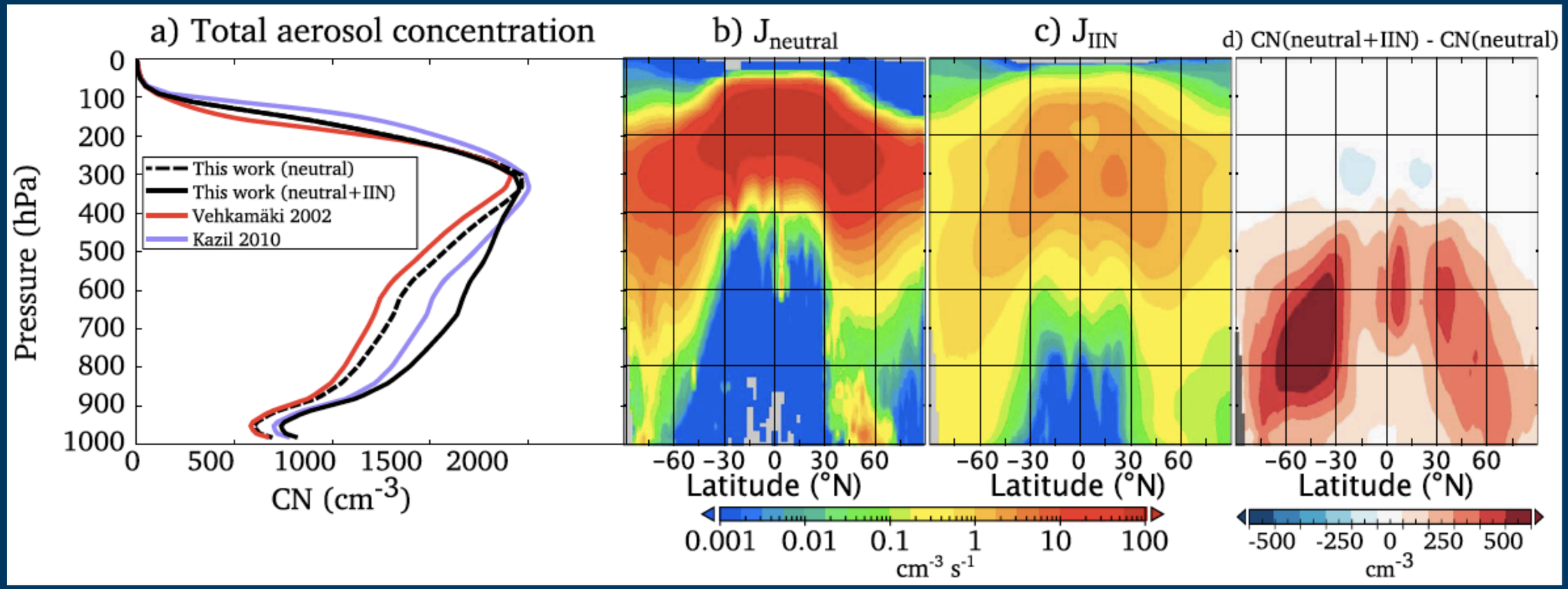
Application in a GCM (ECHAM5.5-HAM2)



- IIN increases particle formation between 1000 and 600 hPa by about 20%.
- Around 300-400 hPa minimal contribution from IIN on total particle formation rates

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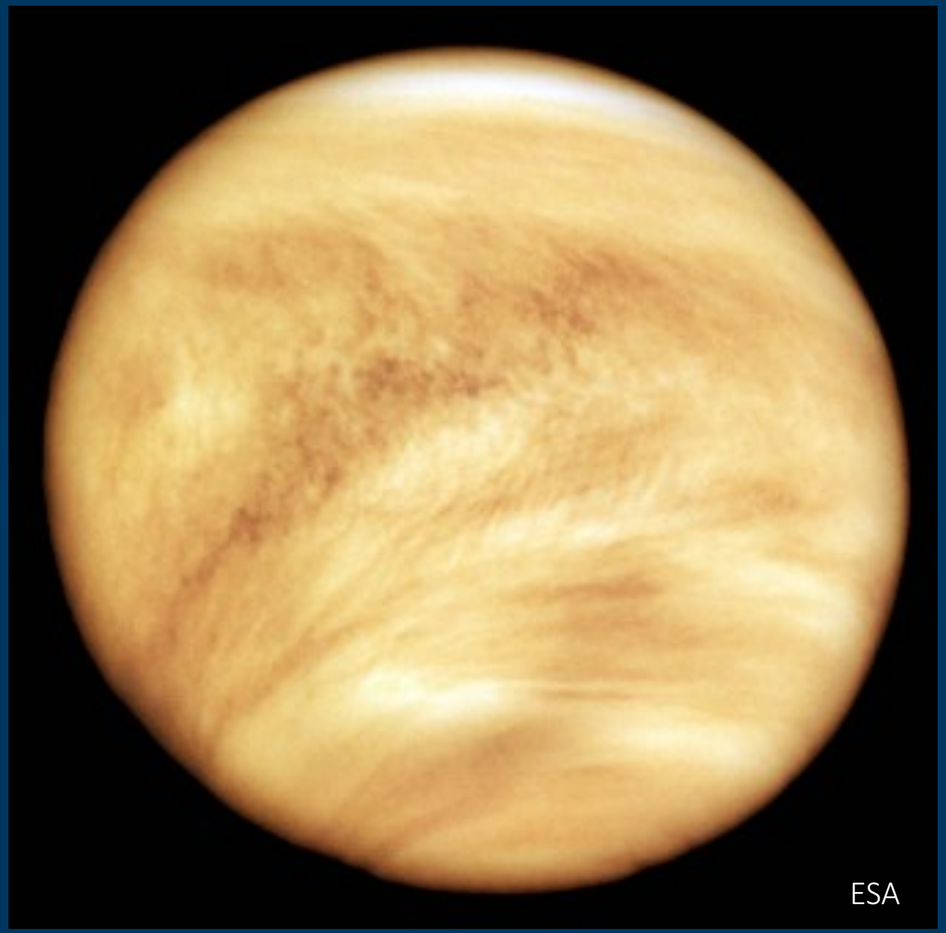
Venus

- CO_2 atmosphere
- Mean surface pressure ~90 bars
- Mean surface temperature ~450°C
- 10^6 times more sulfur than on the Earth
- Sulfuric acid clouds
  - Cover the whole planet
  - 20 km thick layer @45-65 km
  - Total optical thickness > 30
  - Albedo ~0.8
  - Very low RH (<1%)
  - Cloud droplet H_2SO_4 wt%: 75%-98%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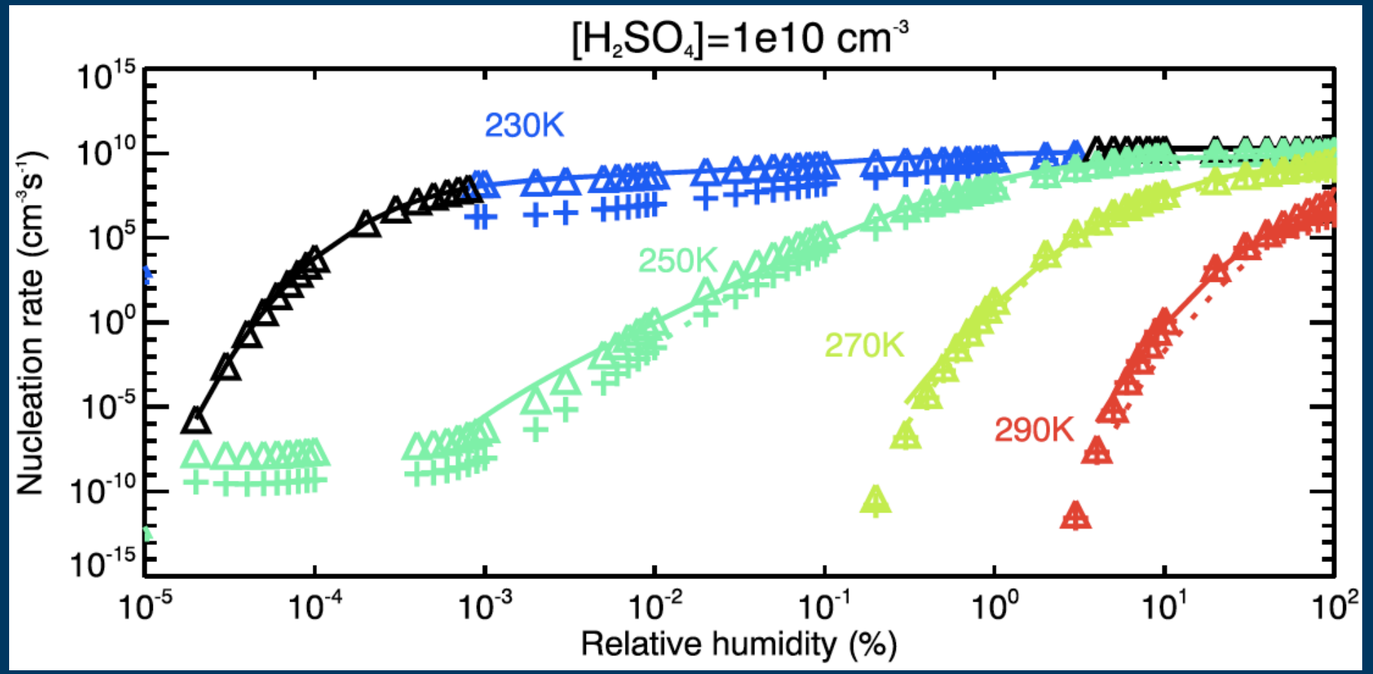
On Venus

- Parameterization extends to very low relative humidities
  - ➢Can be used for conditions in the atmosphere of Venus
  - ➢Upper cloud: [H2SO4]=10^7 cm^{-3}, RH=0.03%, T=230 K

- In the upper cloud layer, formation rates depend strongly on [H_2SO_4]

- In the lower cloud layer, due to the high temperatures (T>350K) formation rates are extremely low



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Summary

- New parameterizations with an updated QC-normalized CNT model validated with experimental data
- The new neutral parameterization widens the validity range of the Vehkamäki et al. (2002) and Vehkamäki et al. (2003) parameterizations: we recommend using the new parameterization!
- Parameterizations for J_{nuc}, r*, x*, n* and the kinetic limit and for J= 1/cm^{3}s
- Ion-induced parameterization for J_{nuc}, r*, n* and kinetic limit
- Application in a GCM shows that including the ion-induced pathway increases the particle formation rates clearly in the lower troposphere at middle and high latitudes (aerosol concentrations higher by 20% compared to the neutral pathway only).
- Fortran code provided with the article: please use it!
  - Article: Määttänen et al. 2018, *JGR Atmospheres*., https://doi.org/10.1002/2017JD027429
  - Code: https://doi.org/10.5281/zenodo.1044366

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