Computational Studies on Atmospheric Sulfuric Acid – Ammonia Clusters

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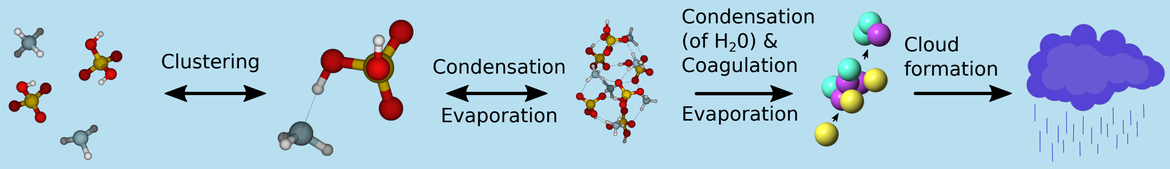
Motivation

Single molecules collide and might form **atmospheric clusters** and subsequently grow into **Cloud Condensation Nuclei**.



Computational studies can reveal the role of specific atmospheric compounds (here: **sulfuric acid** and **ammonia**) in the growth path from single gas molecules to bigger molecular clusters and shed light onto their role in cloud formation.

Procedure:

1. Search for characteristic structure of the cluster
2. Quantum chemistry characterization
3. Calculation of clusters fluxes with the ACDC program

Goal of the present work

1. Obtain optimal atmospheric cluster structures and their properties
2. Investigate the influence of Quantum Chemistry parameters such as rotational symmetry number and quasi-harmonic correction on predicted particle formation rates
3. Investigate the influence of model inherent parameters such as cluster set size
4. Compare new data and newly modeled particle formation rates with previous studies and experimental data

Methods

Configurational Sampling

Goal: Find global minimum (lowest energy) structure
Method: Built-up approach:

Molecular Mechanics
→ Search for Local Minima[1]
→ Generate 10^4 structures

→ Semi-empirical method
→ Optimization

Filtering to ~1000 structures

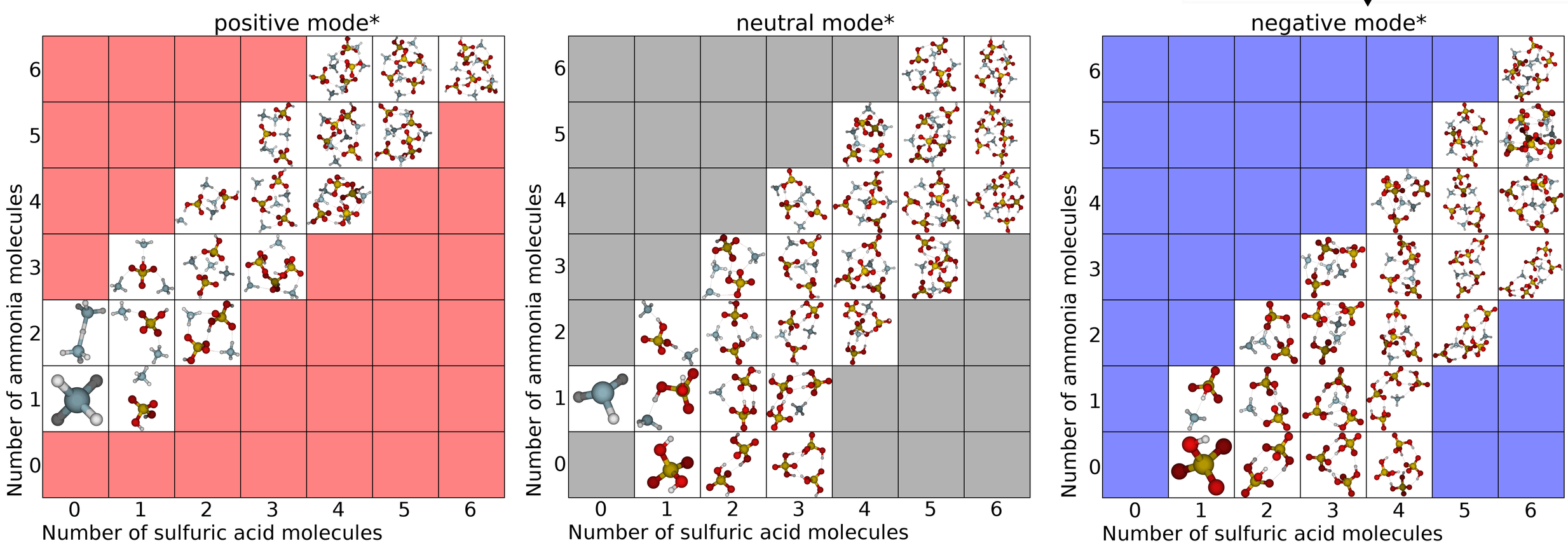
→ Density Functional Theory
→ Optimization

→ Global minimum structure

Yield:

Speed:

Global minima obtained



ACDC[2] (Atmospheric Cluster Dynamics Code)

Calculates (numerically):

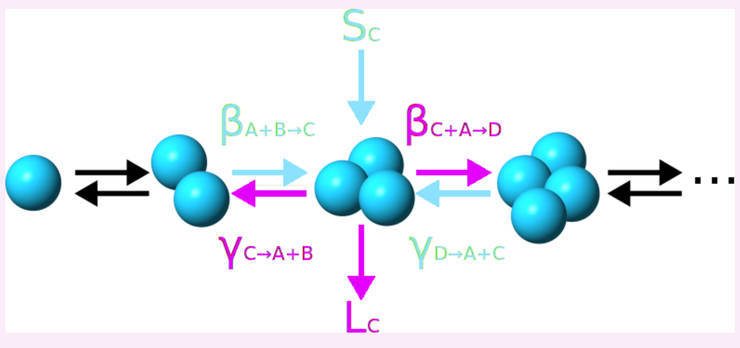
- Evolution of cluster population
- Steady state concentrations and fluxes
- New particle formation rate (nucleation rate)

Input:

- Gibbs free energy *G*, dipoles, polarizabilities of clusters provided by Quantum Chemistry based on global minimum structures
- Gibbs free energies of formation $\Delta G = G_{cluster} - \sum_i G_{monomer,i}$
- Monomer concentrations, pressure, temperature

*Omitted structures have been shown being of minor role / unstable in previous studies[3]

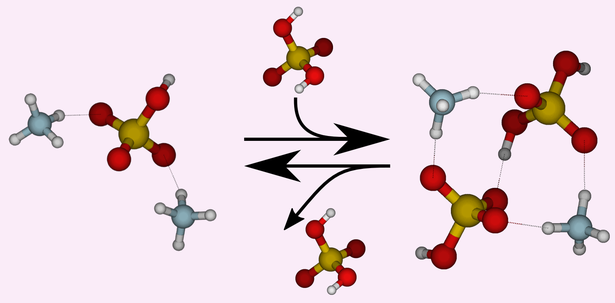
Outputs see next page



Considered processes:

- external sources S_C
- collision coefficients β
- external losses L_C
- evaporation rates γ

Example for present system



Results

Recap of the full procedure and the investigated parameters

Configurational Sampling

Investigated by Kubečka et al.[4]

→ provides molecular/ cluster structures

Quantum Chemistry

We correct identification of symmetry and apply a quasi-harmonic approximation (see below)

→ provides
Cluster stability ΔG
dipoles
polarizabilities

ACDC

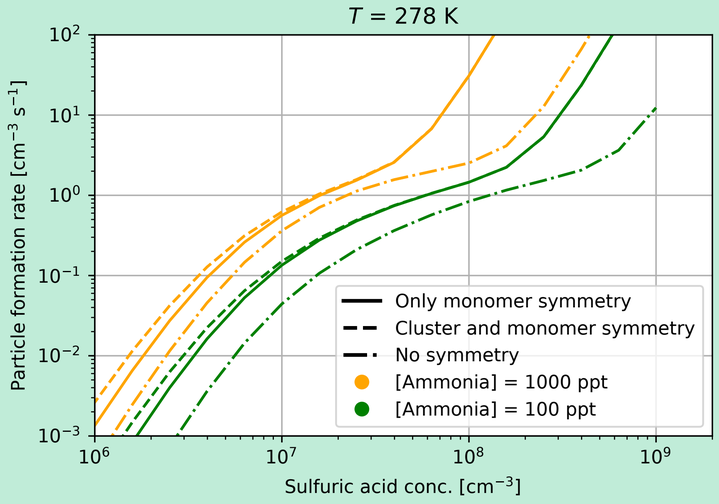
depends **exponentially** on ΔG

We investigate influence of the size of the provided cluster

→ Particle formation rates (number of cluster growing out at the upper right of the cluster set corner [$s^{-1}cm^{-3}$])

Symmetry

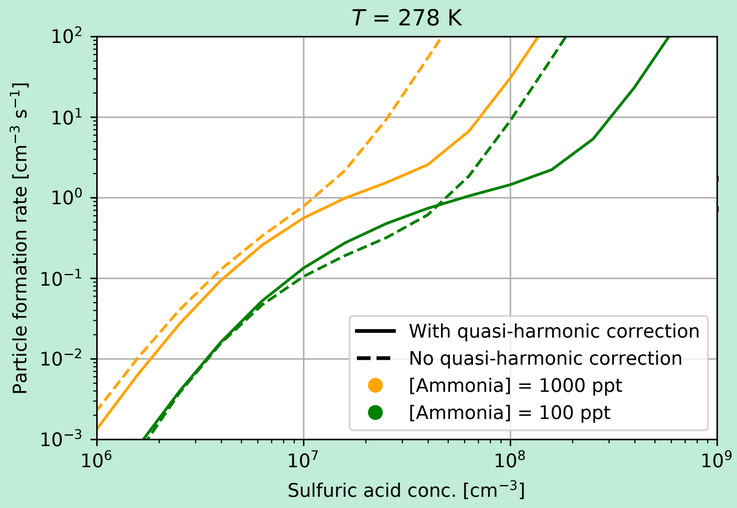
Quantum Chemistry programs are not consistently identifying symmetry in molecules/clusters. Forcing them to do so decreases the respective G and influences $\Delta G = G_{cluster} - \sum_i G_{monomer,i}$



→ consideration of monomer symmetry increases ΔG of all clusters
  → evaporation is reduced and particle formation rate rises
  → consideration of monomer symmetry leads to great change as it changes ΔG for all clusters
→ consideration of cluster symmetry only changes the decreases ΔG of the particular cluster and is negligible for overall particle formation rates

Quasi-harmonic correction

Quantum Chemistry programs misinterpret large amplitude intermolecular motions as molecular vibrations. This can be partially corrected for and the correction generally increases G, where molecular clusters less tightly bound are stronger affected. We use GoodVibes python[5] script to do so.

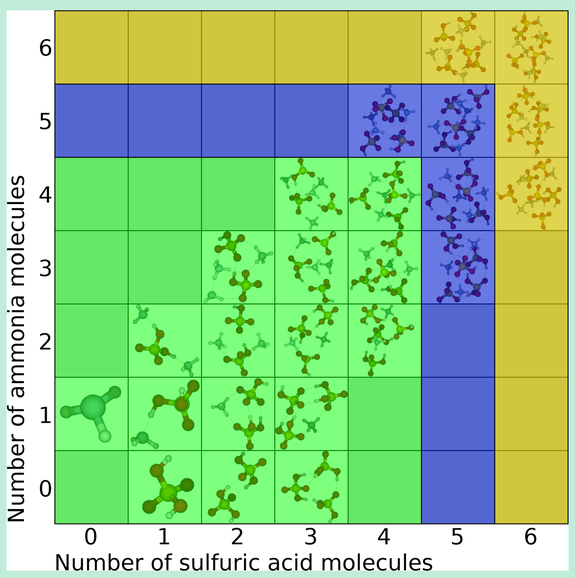


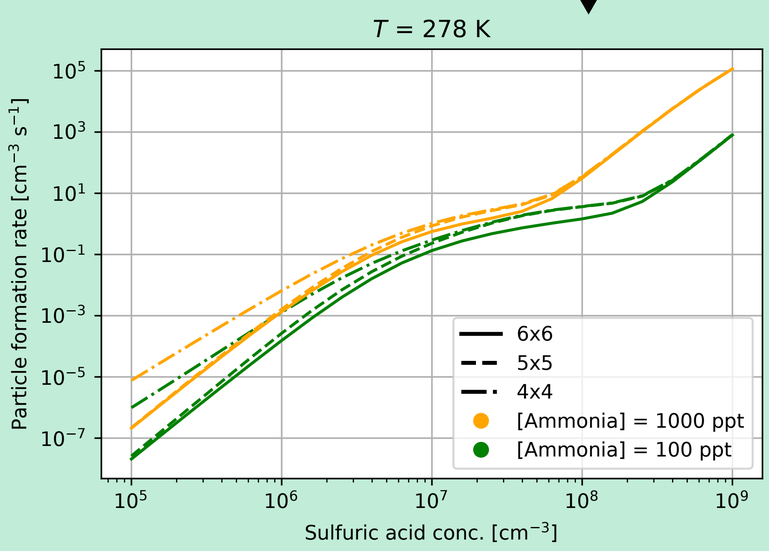
→ using the quasi-harmonic approximation has considerable impact for high monomer concentrations
  → cluster growth pathways change from growth through charged clusters to growth through neutral clusters with increasing monomer conc. → neutral clusters seem to be affected stronger

Cluster Set Size

Core input for ACDC are the molecular clusters to be considered. We investigate impact of the cluster set size used.
Three cluster set sizes:
GREEN : 4x4
GREEN + BLUE : 5x5
GREEN + BLUE + YELLOW : 6x6

To the right the neutral clusters as example, the same procedure was applied to charged clusters as well

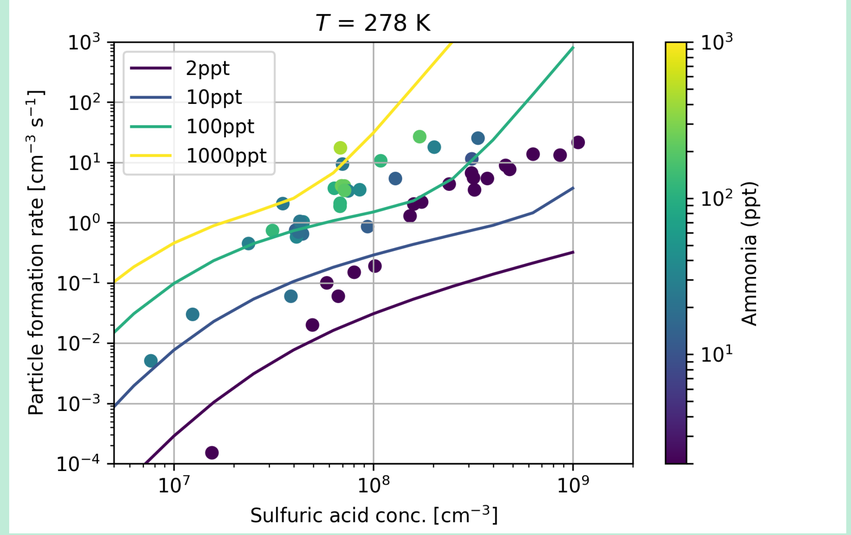




→ particle formation rates for all set sizes converge with higher sulfuric acid concentrations → Smaller cluster set is adequate to describe particle growth
→ particle formation rate rise with smaller cluster sets because the clusters is given less "room" to evaporate and stays in the simulation

Comparison to experiment

Comparison:
- This study (lines)
- CLOUD chamber experiment (Dots)[6]



→ model matches experiment well for low temperatures (other T are not shown in this document) and for moderate high ammonia concentrations
  → suggests model is suitable for low evaporation rates
→ reason for discrepancy can be various:
  → neglect of water in cluster
  → accuracy of quantum chemistry methods
  → fine tuning of model parameters

Conclusions

→ Quantum chemistry parameters/corrections can heavily influence outcome of new particle formation simulation

→ Size of cluster set used has to be chosen adequately

→ Particle formation rates are close to experiment, however, there is room for improvement

Acknowledgments:
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Literature
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