EGU2020: Sharing Geoscience Online

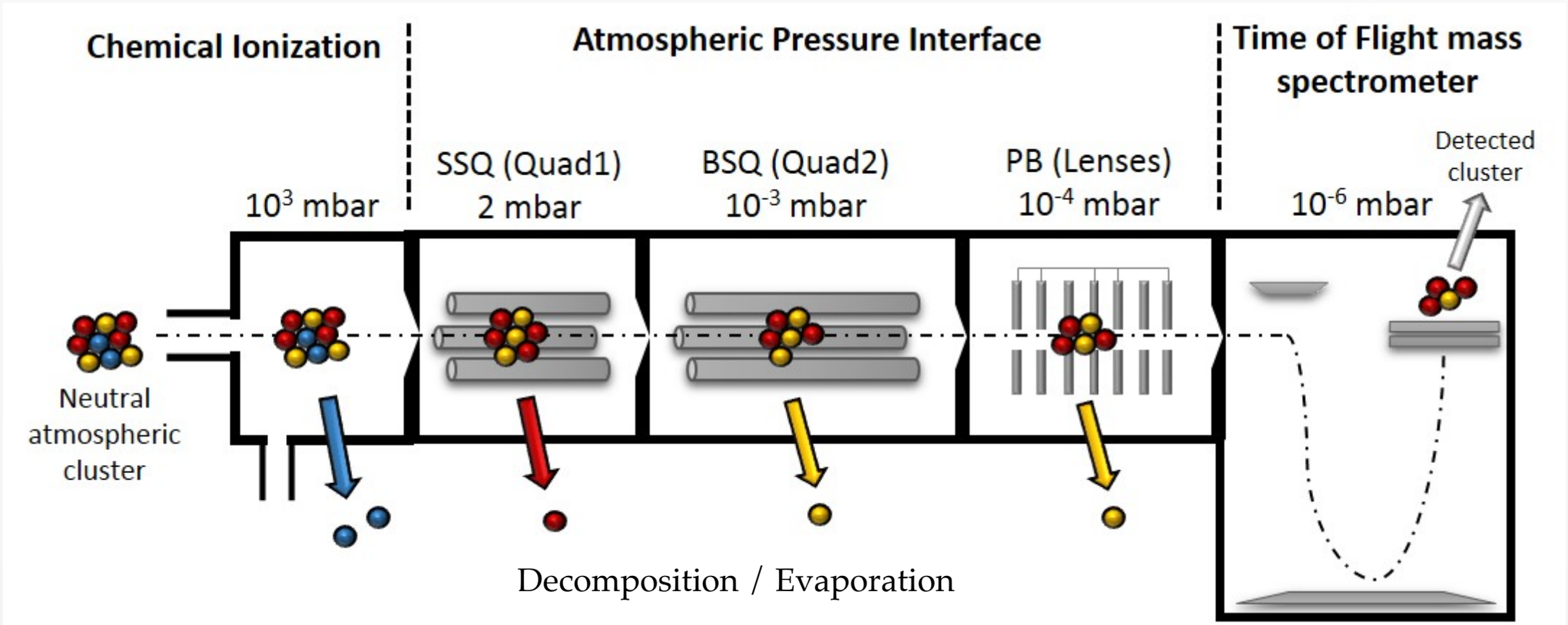
HOM Cluster Decomposition in APi-TOF Mass Spectrometers

Tommaso Zanca[1], Jakub Kubečka[1], Evgeni Zapadinsky[1], Monica Passananti[1,2], Theo Kurtén[3], and Hanna Vehkamäki[1]

[1] Institute for Atmospheric and Earth System Research/Physics, Faculty of Science, University of Helsinki, P.O. Box 64, 00014 Helsinki, Finland. *E-mail:* tommaso.zanca@helsinki.fi
[2] Dipartimento di Chimica, Università di Torino, Via Giuria 5, 10125 Torino, Italy
[3] Institute for Atmospheric and Earth System Research/Chemistry, Faculty of Science, University of Helsinki, P.O. Box 55, 00014 Helsinki, Finland

Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2019-502, in review, 2020.

Why Is It Important to Simulate Decomposition?



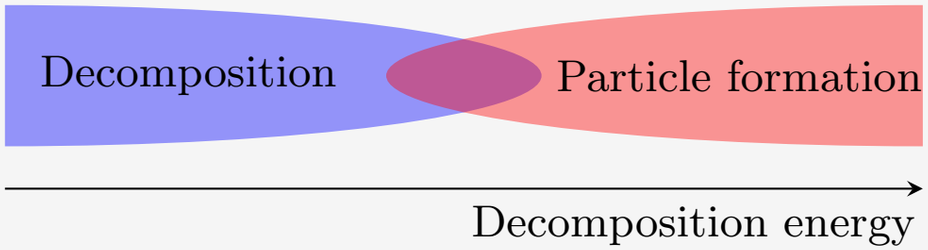
Identification of atmospheric molecular clusters and measurement of their concentrations by APi-TOF mass spectrometers may be affected by systematic error due to possible decomposition of clusters inside the instrument.

Cluster decomposition is caused by collisions with the carrier gas in the Atmospheric Pressure Interface (APi).

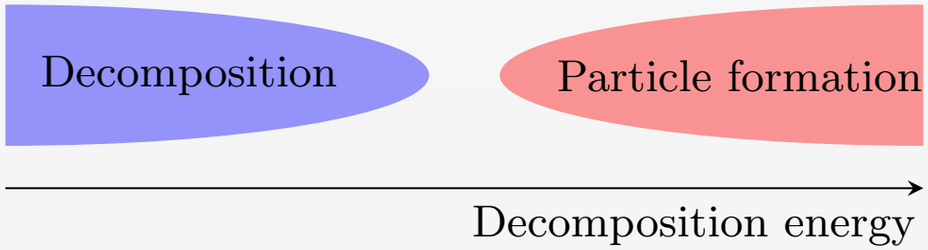
Are APi-TOF Measurements of Clusters Reliable?

- To what extent are we able to perform measurements of atmospheric cluster concentrations using APi-TOF mass spectrometers?
- Could the cluster decomposition in the APi-TOF be responsible for the lack of observations of some atmospheric clusters?

CASE A

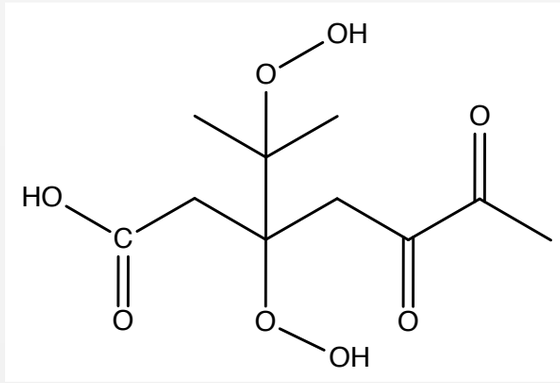


CASE B



We perform numerical simulations of decomposition in an APi-TOF and formation in the atmosphere of a set of clusters which involve a representative kind of highly-oxygenated organic molecule (**HOM**), with molecular formula $\mathbf{C_{10}H_{16}O_8}$.

We show that decomposition is highly unlikely for the considered clusters, provided their bonding energy is large enough to allow formation in the atmosphere in the first place.



$\mathbf{C_{10}H_{16}O_8}$ **($\mathbf{HOM_{10}}$)**

Decomposition in APi — Model

The decomposition of HOM_{10} clusters in the APi is simulated by a numerical model based on stochastic realizations of the cluster dynamics (*Zapadinsky E., et al. 2019*).

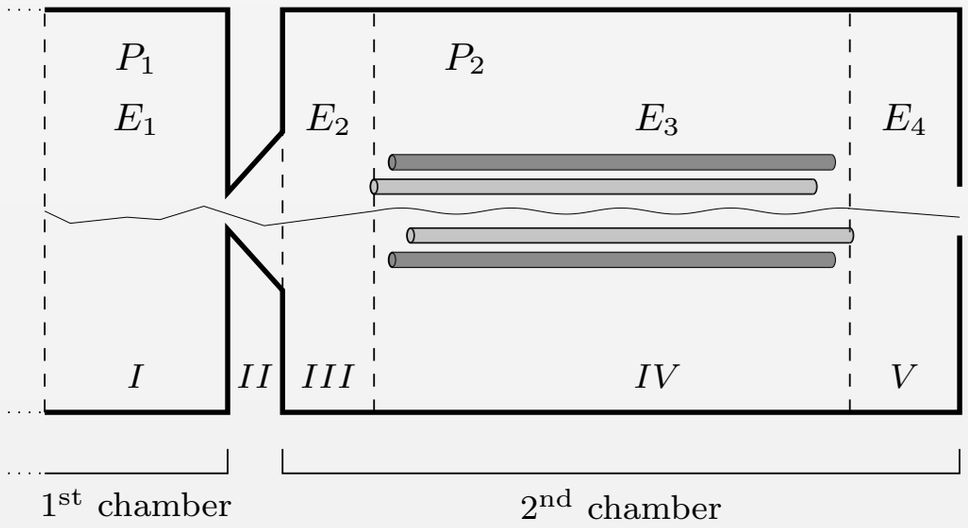
Decomposition Pathway:

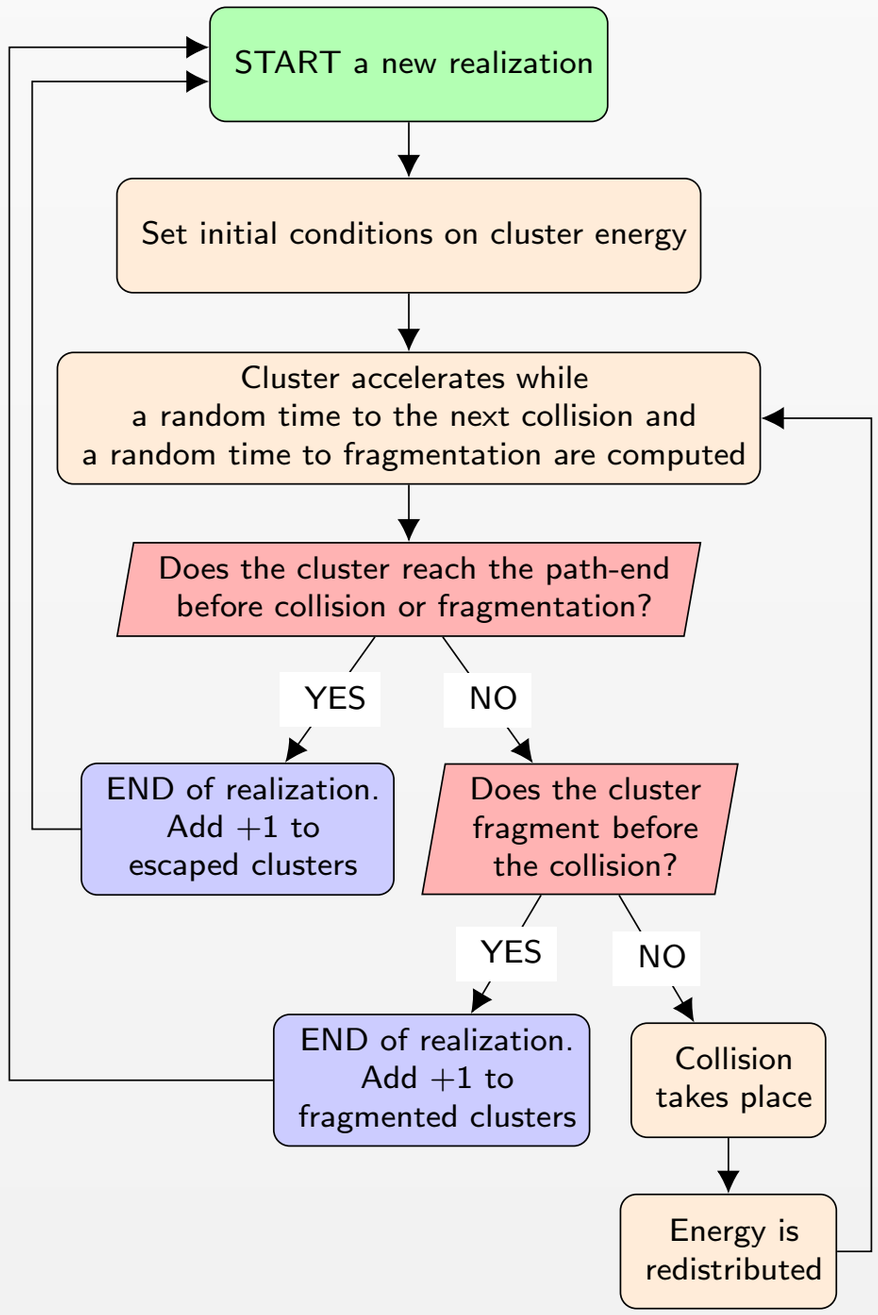
$$(HSO_4^-)(H_2SO_4)_n(HOM_{10})_m \rightarrow (HSO_4^-)(H_2SO_4)_n(HOM_{10})_{m-1} + (HOM_{10})$$

The simulations involve the end of first chamber and the second chamber of the APi, where cluster decomposition is likely to happen because of critical pressure values.

The voltage configuration is set as in CLOUD10 experiment.

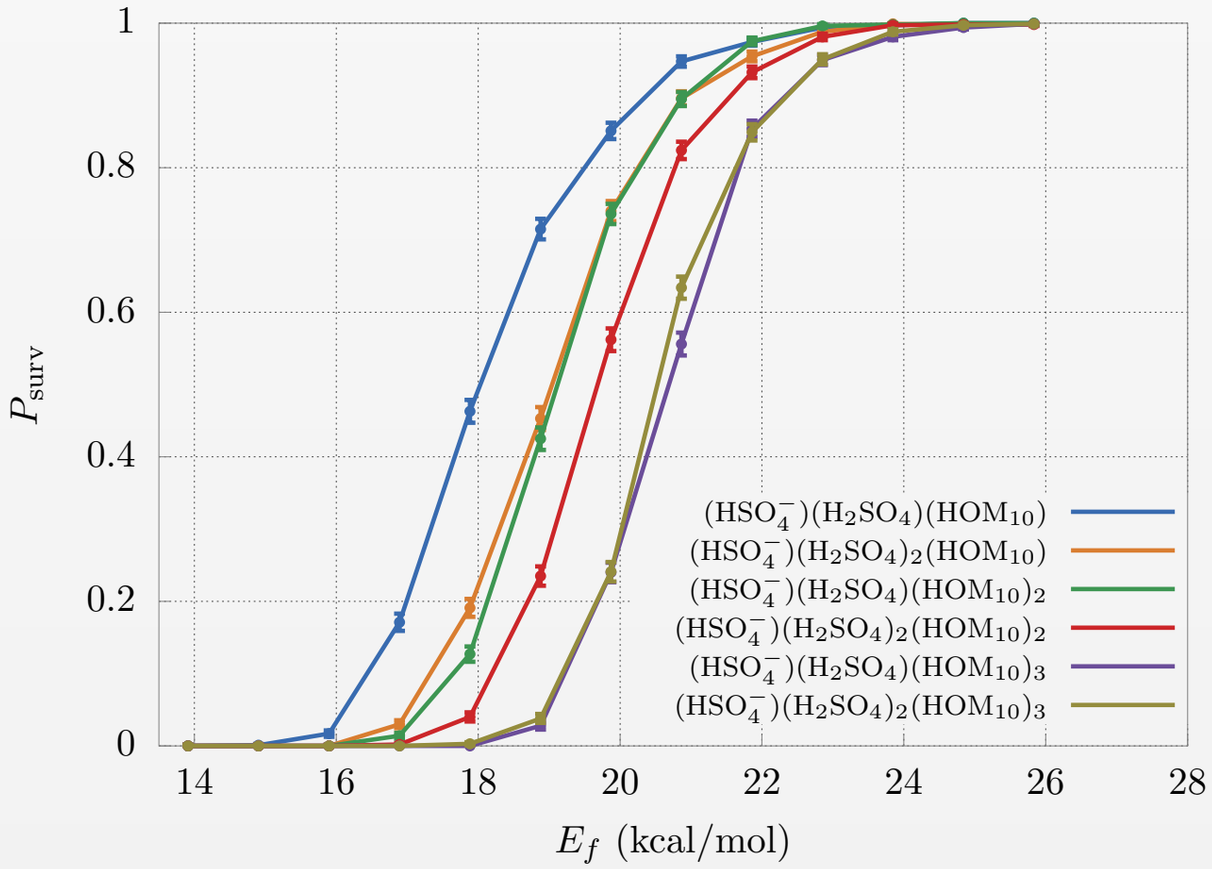
P_1	201 Pa
P_2	2.96 Pa
E_1	7189 V/m
E_2	804.9 V/m
E_3	18.04 V/m
E_4	1104 V/m

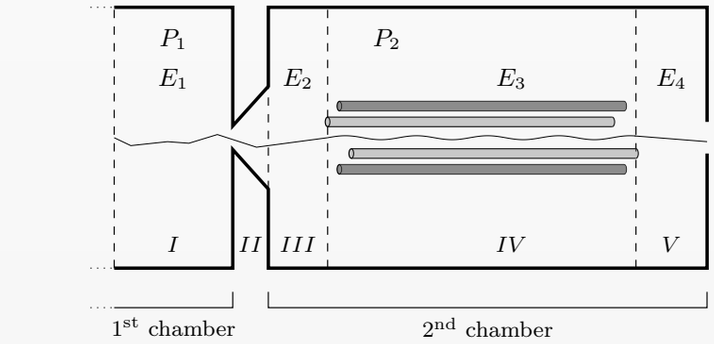


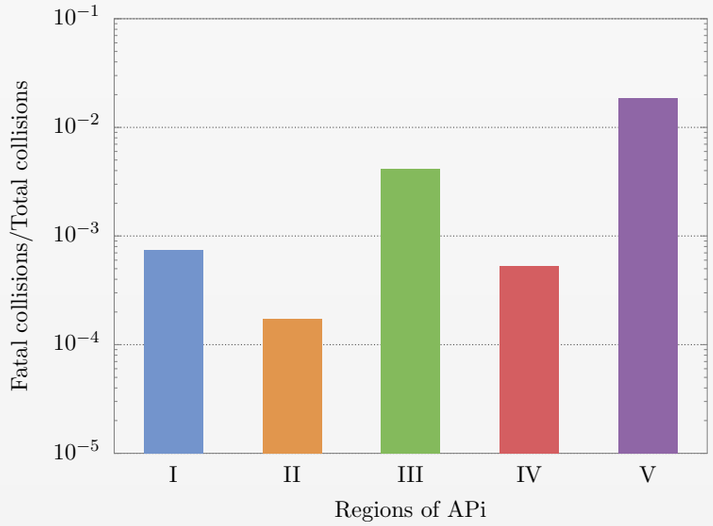


Decomposition in APi — Results

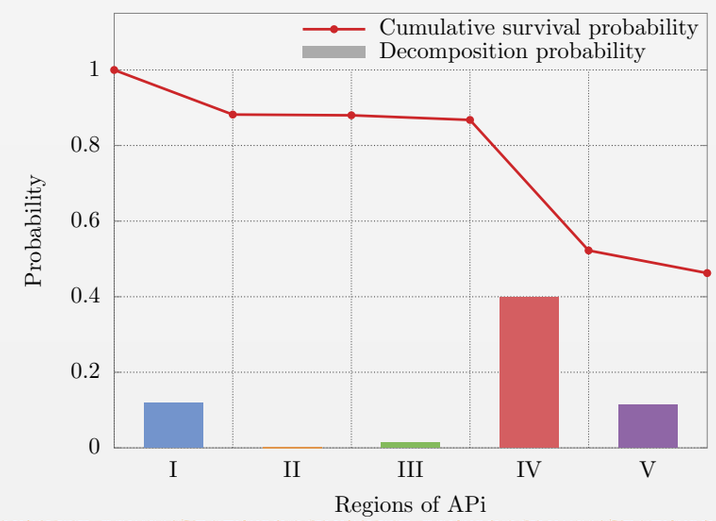
The results on clusters survival probability show that decomposition does not take place beyond $E_f \sim 24$ kcal/mol.







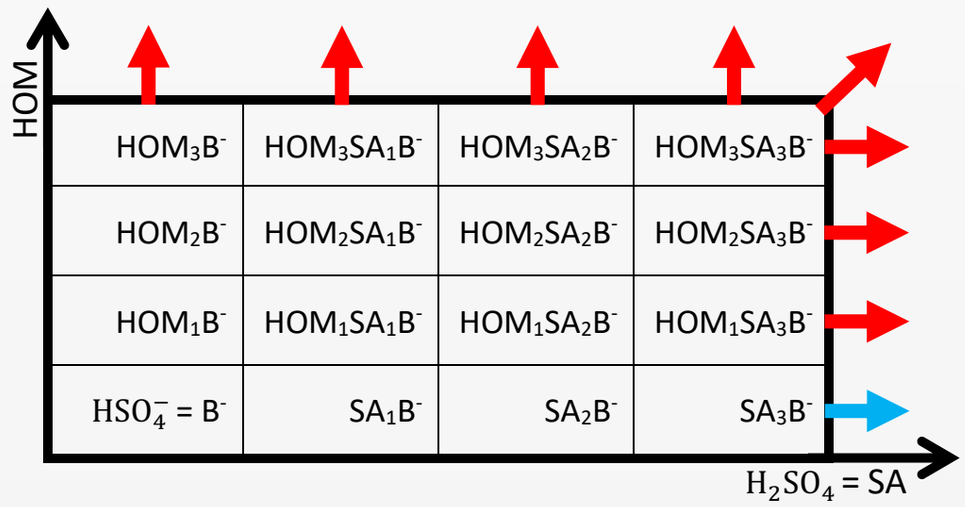
The most energetic collisions are located before and after the quadrupole of the second chamber.



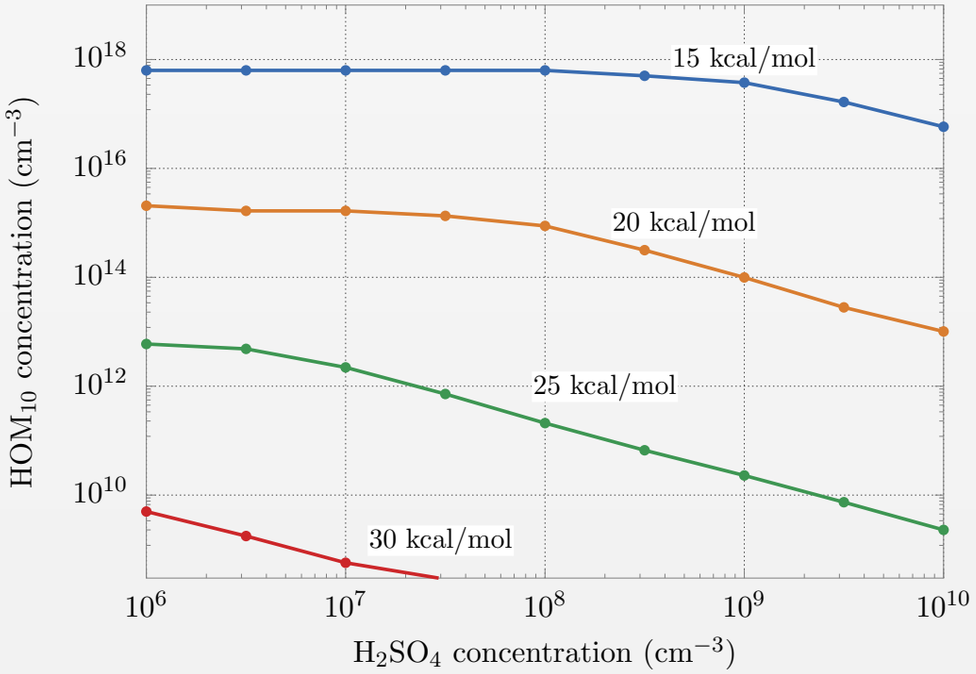
Most of the clusters decompose in the quadrupole region.

Formation in the Atmosphere

Using the ACDC program (*McGrath M. J., et al. 2012*) we computed the concentrations of HOM_{10} needed to provide a significant enhancement (1 cm^{-3} s^{-1}) of new-particle formation rate in the atmosphere.



The blue arrow indicates the flux of the outgrowing cluster that contributes to the formation rate of only sulfuric acid particles (J_{sa}). Adding HOM_{10} monomers to the system, new outgrowing HOM clusters (red arrows) are participating in new-particle formation, resulting in a total formation rate $J_{sa+hom} = J_{sa} + 1$ cm^{-3} s^{-1}.



The concentrations of HOM_{10} needed to increment the new-particle formation rate by 1 cm^{-3} s^{-1} decrease while increasing their decomposition energy.

The experimental concentrations ($< 10^8$ cm^{-3}) are reached at decomposition energies $E_f > 30$ kcal/mol, while decomposition in APi takes place at $E_f < 24$ kcal/mol

CONCLUSIONS

- The decomposition of HOM clusters in the APi requires a range of cluster decomposition energies which is incompatible with efficient cluster formation in the atmosphere given sub-ppb vapor concentrations.

- The biggest number of cluster decompositions are localized in the quadrupole of the second chamber.

- Similar simulations could be performed in future for other types of clusters, for example to assess whether they should be detectable in an APi-TOF or not, or whether they could possibly affect new-particle formation, despite not being directly detected.

THANK YOU