Supplement of Atmos. Meas. Tech., 19, 3363–3396, 2026
https://doi.org/10.5194/amt-19-3363-2026-supplement

Atmospheric Measurement Techniques
Open Access
EGU

Supplement of

Calibrating interdependent photochemistry, nucleation, and aerosol microphysics in chamber experiments

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S1 Excimer (UVX) stages simulation

Fig. S1 shows the simulation results for the group of stages with O_3 photolysis driven by the Excimer laser (UVX). This light is less uniform than the UVH illumination, filling as a rough approximation about half the CLOUD chamber. Model agreement with the UVH case confirms that any non-uniformities are not a severe impediment to the data interpretation.

S2 Photochemical model

S2.1 gas-phase reactions

The gas-phase photochemistry for the OH actinometry calibration run can be modeled with the following set of reactions. The initial photochemistry is driven by odd-oxygen (O_x) reactions:

$$O_2 \xrightarrow{h\nu} 2\,O(^3P) \qquad \text{SR1}$$

$$k = \text{photolysis}(O_2\,O^3P)$$

$$O_3 \xrightarrow{h\nu} O_2 + O(^3P) \qquad \text{SR2}$$

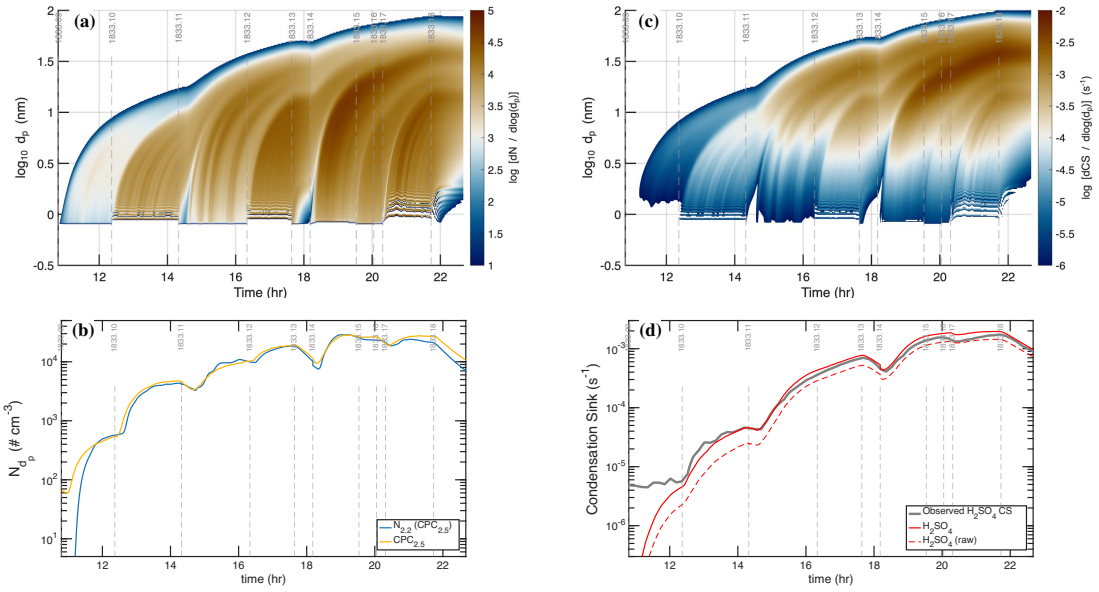

Figure S1: Optimal modeled particle size and corresponding condensation sink distributions with wet $(NH_4)_2 \cdot SO_4 \cdot (H_2O)_n$ growth, and their agreement with measurements during the UVX stages. (a) Simulated particle size distribution ($dN/d\log\ d_p$) for optimal parameters, with empirical nucleation coefficients and an H_2SO_4 calibration factor of 1.2. (b) Simulated (blue) and observed (gold) total particle number measurable by a $CPC_{2.5}$. (c) Simulated condensation-sink distribution ($dCS/d\log\ d_p$). (d) Simulated (red) and observed (gray) condensation sink. Simulated values are shown both with (solid) and without (dashed) a Van der Waals correction; the observed values include the correction; the condensation sink is reproduced with good fidelity aside from the enhanced loss during the cleaning stage, which was not simulated. Other than the low-intensity stages (01 and 02), charged and neutral nucleation are competitive because charged nucleation is limited by ion-pair production. That saturation value serves as an additional constraint on the nucleation parameters.

$$k = \text{photolysis}(O_3\,O^3P)$$

$$O_3 \xrightarrow{\text{UVH}} O_2 + O(^1D) \quad \text{SR3}$$

$$k = \text{photolysis}(O_3\,O^1D\,\text{UVH})$$

$$O_3 \xrightarrow{\text{UVX}} O_2 + O(^1D) \quad \text{SR4}$$

$$k = \text{photolysis}(O_3\,O^1D\,\text{UVX})$$

$$O_3 \xrightarrow{\text{LS}_1} O_2 + O(^1D) \quad \text{SR5}$$

$$k = \text{photolysis}(O_3\,O^1D\,\text{LS1})$$

$$O_3 \xrightarrow{\text{LS}_3} O_2 + O(^1D) \quad \text{SR6}$$

$$k = \text{photolysis}(O_3\,O^1D\,\text{LS3})$$

$$O_2 + O(^3P) \longrightarrow O_3 \quad \text{SR7}$$

$$k_0 = 5.7 \times 10^{-34} \times (T/300)^{-2.8}$$

$$k_\infty = 2.8 \times 10^{-12}$$

$$F_c = \exp(-T/696)$$

$$N_2 + O(^1D) \longrightarrow N_2 + O(^3P) \quad \text{SR8}$$

$$k = 1.8 \times 10^{-11}\, e^{+107/T}$$

$$O_2 + O(^1D) \longrightarrow O_2 + O(^3P) \quad \text{SR9}$$

$$k = 3.2 \times 10^{-11}\, e^{+67/T}$$

This includes three distinct O_3 photolysis representations so that the model will keep track of the separate contributions of individual lights during stages when more than one light is illuminated. This feeds into odd-hydrogen (HO_x) chemistry:

$$H_2O + O(^1D) \longrightarrow 2\,OH \quad \text{SR10}$$

$$k = 1.63 \times 10^{-10}\, e^{+60/T}$$

$$O_3 + OH \longrightarrow HO_2 + O_2 \quad \text{SR11}$$

$$k = 1.7 \times 10^{-12}\, e^{-940/T}$$

$$HO_2 + OH \longrightarrow H_2O + O_2 \quad \text{SR12}$$

$$k = 4.8 \times 10^{-11}\, e^{+250/T}$$

$$HO_2 + O_3 \longrightarrow 2\,O_2 + OH \quad \text{SR13}$$

$$k = 1.0 \times 10^{-14}\, e^{-490/T}$$

$$H + O_2 \longrightarrow HO_2 \quad \text{SR14}$$

$$k_0 = 7.4 \times 10^{-31} \times (T/300)^{-2.4}$$

$$k_\infty = 7.5 \times 10^{-11}$$

$$F_c = \exp(-T/517)$$

$$H_2O_2 \xrightarrow{h\nu} 2\,OH \quad \text{SR15}$$

$$k = \text{photolysis}(H_2O_2\,OH)$$

$$2\,HO_2 \longrightarrow H_2O_2 + O_2 \quad \text{SR16}$$

$$k = (3.0 \times 10^{-13}\, e^{+460/T} + 2.1 \times 10^{-33}\, e^{+920/T} \times c_M)$$

$$H_2O + 2\,HO_2 \longrightarrow H_2O + H_2O_2 + O_2 \quad \text{SR17}$$

$$k = 2.8 \times 10^{-18} \times (3.0 \times 10^{-13}\, e^{+460/T} + 2.1 \times 10^{-33}\, e^{+920/T} \times c_M)$$

$$\mathrm{H_2 + OH \longrightarrow H + H_2O} \quad \text{SR18}$$
$$k = 2.8 \times 10^{-12}\, e^{-1800/T}$$
$$\mathrm{2\,OH \longrightarrow H_2O + O(^3P)} \quad \text{SR19}$$
$$k = 1.8 \times 10^{-12}$$
$$\mathrm{H_2O_2 + OH \longrightarrow H_2O + HO_2} \quad \text{SR20}$$
$$k = 1.8 \times 10^{-12}$$

Reaction with CO is a major OH sink, and in the base model is the only "hydrocarbon" reaction treated.

$$\mathrm{CO + OH \longrightarrow CO_2 + H} \quad \text{SR21}$$
$$k = 1.3 \times 10^{-13} \times (1 + 0.6 \times (c_{\mathrm{M}}/2.5 \times 10^{19}))$$

Finally, OH is also the sink of SO_2 and ultimately source of H_2SO_4:

$$\mathrm{OH + SO_2 \longrightarrow HSO_3} \quad \text{SR22}$$
$$k_0 = 4.5 \times 10^{-31} \times (T/300)^{-3.9}$$
$$k_\infty = 1.3 \times 10^{-12} \times (T/300)^{-0.7}$$
$$F_c = 0.525$$
$$\mathrm{HSO_3 + O_2 \longrightarrow HO_2 + SO_3} \quad \text{SR23}$$
$$k = 1.3 \times 10^{-12}\, e^{-330/T}$$
$$\mathrm{2\,H_2O + SO_3 \longrightarrow H_2O + H_2SO_4} \quad \text{SR24}$$
$$k = 8.5 \times 10^{-41}\, e^{+6540/T}$$

Wall loss in general is modeled as a process relevant to all species in the photochemical system, with wall collision frequencies scaled by the (empirically constrained) H_2SO_4 wall loss (collision frequency) and an uptake coefficient (assumed to be $\gamma = 1$) for H_2SO_4. In addition, based on the observed 1:1 stoichiometry of SO_2 and O_3 loss when especially the 385 nm UV light emitting diodes (LS3) are on at full power, a photon-mediated uptake of SO_2 and O_3 (presumably to make wall-adsorbed H_2SO_4) is included in the mechanism.

$$\mathrm{O_3 + SO_2 \xrightarrow{h\nu}} \quad \text{SR25}$$
$$k = \mathrm{photolysis(SO_2\,O_3\,wall)}$$

S2.2 ion reactions

Nucleation as well as ion production and loss can be treated with a set of pseudo-reactions creating and removing primary ions ($n^{\pm}$) as well as nucleated clusters (2 nm particles in three charge states, $p_2^{\circ,\pm}$ above and $c_{n,m,p}$ here). Here the subscripts n, m, and p indicate charge, as "neutral", "minus (negative)" and "positive" (i.e. $\circ$, $-$, and $+$ elsewhere):

$$3\,\mathrm{H_2SO_4} + \mathrm{NH_3} \longrightarrow \mathrm{c}_n \quad \text{SR26}$$
$$k = \mathrm{nucleationCoefficient(ternary\,neutral)}$$
$$3\,\mathrm{H_2SO_4} + \mathrm{NH_3} + \mathrm{n}_m \longrightarrow \mathrm{c}_m \quad \text{SR27}$$
$$k = \mathrm{nucleationCoefficient(ternary\,anion)}$$
$$3\,\mathrm{H_2SO_4} + \mathrm{NH_3} + \mathrm{n}_p \longrightarrow \mathrm{c}_p \quad \text{SR28}$$
$$k = \mathrm{nucleationCoefficient(ternary\,cation)}$$
$$\mathrm{n}_m + \mathrm{n}_p \longrightarrow \quad \text{SR29}$$
$$k = 1.6 \times 10^{-6}$$
$$\mathrm{c}_m + \mathrm{n}_p \longrightarrow \mathrm{c}_n \quad \text{SR30}$$
$$k = 1.75 \times 10^{-6}$$
$$\mathrm{c}_p + \mathrm{n}_m \longrightarrow \mathrm{c}_n \quad \text{SR31}$$
$$k = 1.45 \times 10^{-6}$$
$$\mathrm{c}_n + \mathrm{n}_p \longrightarrow \mathrm{c}_p \quad \text{SR32}$$
$$k = 2 \times 10^{-9}$$
$$\mathrm{c}_n + \mathrm{n}_m \longrightarrow \mathrm{c}_m \quad \text{SR33}$$
$$k = 2 \times 10^{-9}$$
$$\mathrm{c}_m + \mathrm{c}_p \longrightarrow \mathrm{c}_n \quad \text{SR34}$$
$$k = 4 \times 10^{-7}$$
$$2\,\mathrm{c}_n \longrightarrow \mathrm{c}_n \quad \text{SR35}$$
$$k = 1.2 \times 10^{-9}$$

S2.3 modal microphysics

The modal representation continues with growth from 2 nm to a nanoparticle nucleation mode at 5 nm, $\mathrm{np}_{n,m,p}$. The growth is a first-order "reaction" with H_2SO_4 but with a rate constant reflecting of order 100 collisions required for 3 nm of growth. Coagulation as well as diffusion charging and neutralization by both primary ions and charged 2 nm particles is also treated.

$$\mathrm{H_2SO_4} + \mathrm{c}_n \longrightarrow \mathrm{np}_n \quad \text{SR36}$$
$$k = \mathrm{growthCoefficient(cluster)}$$
$$\mathrm{H_2SO_4} + \mathrm{c}_m \longrightarrow \mathrm{np}_m \quad \text{SR37}$$
$$k = \mathrm{growthCoefficient(cluster)}$$
$$\mathrm{H_2SO_4} + \mathrm{c}_p \longrightarrow \mathrm{np}_p \quad \text{SR38}$$
$$k = \mathrm{growthCoefficient(cluster)}$$
$$\mathrm{n}_m + \mathrm{np}_p \longrightarrow \mathrm{np}_n \quad \text{SR39}$$
$$k = 1.75 \times 10^{-6}$$
$$\mathrm{n}_p + \mathrm{np}_m \longrightarrow \mathrm{np}_n \quad \text{SR40}$$
$$k = 1.45 \times 10^{-6}$$
$$\mathrm{c}_m + \mathrm{np}_p \longrightarrow \mathrm{np}_n \quad \text{SR41}$$
$$k = 1.4 \times 4 \times 10^{-7}$$
$$\mathrm{c}_p + \mathrm{np}_m \longrightarrow \mathrm{np}_n \quad \text{SR42}$$
$$k = 1.4 \times 4 \times 10^{-7}$$

$$\mathrm{n}_m + \mathrm{np}_n \longrightarrow \mathrm{np}_m \quad \text{SR43}$$
$$k = 3 \times 10^{-8}$$
$$\mathrm{n}_p + \mathrm{np}_n \longrightarrow \mathrm{np}_p \quad \text{SR44}$$
$$k = 3 \times 10^{-8}$$
$$\mathrm{c}_m + \mathrm{np}_n \longrightarrow \mathrm{np}_m \quad \text{SR45}$$
$$k = 1 \times 10^{-8}$$
$$\mathrm{c}_p + \mathrm{np}_n \longrightarrow \mathrm{np}_p \quad \text{SR46}$$
$$k = 1 \times 10^{-8}$$
$$\mathrm{np}_m + \mathrm{np}_p \longrightarrow \mathrm{np}_n \quad \text{SR47}$$
$$k = 1 \times 10^{-7}$$
$$2\,\mathrm{np}_n \longrightarrow \mathrm{np}_n \quad \text{SR48}$$
$$k = 1.5 \times 10^{-9}$$
$$\mathrm{c}_n + \mathrm{np}_n \longrightarrow \mathrm{np}_n \quad \text{SR49}$$
$$k = 3 \times 10^{-9}$$

Finally, growth to an Aitken mode at 15 nm, $\mathrm{a}_{n,m,p}$, requires 1000s of collisions of H_2SO_4 with those growing nanoparticles, and the resulting Aitken mode particles can interact with all of the smaller nanoparticles and clusters, in all charge states. We ignore formation of doubly charged particles for all these sizes as negligible.

$$\mathrm{H_2SO_4} + \mathrm{np}_n \longrightarrow \mathrm{a}_n \quad \text{SR50}$$
$$k = \mathrm{growthCoefficient(nano)}$$
$$\mathrm{H_2SO_4} + \mathrm{np}_m \longrightarrow \mathrm{a}_m \quad \text{SR51}$$
$$k = \mathrm{growthCoefficient(nano)}$$
$$\mathrm{H_2SO_4} + \mathrm{np}_p \longrightarrow \mathrm{a}_p \quad \text{SR52}$$
$$k = \mathrm{growthCoefficient(nano)}$$
$$\mathrm{a}_p + \mathrm{n}_m \longrightarrow \mathrm{a}_n \quad \text{SR53}$$
$$k = 1.75 \times 10^{-6}$$
$$\mathrm{a}_m + \mathrm{n}_p \longrightarrow \mathrm{a}_n \quad \text{SR54}$$
$$k = 1.45 \times 10^{-6}$$
$$\mathrm{a}_p + \mathrm{c}_m \longrightarrow \mathrm{a}_n \quad \text{SR55}$$
$$k = 1.4 \times 4 \times 10^{-7}$$
$$\mathrm{a}_m + \mathrm{c}_p \longrightarrow \mathrm{a}_n \quad \text{SR56}$$
$$k = 1.4 \times 4 \times 10^{-7}$$
$$\mathrm{a}_p + \mathrm{np}_m \longrightarrow \mathrm{a}_n \quad \text{SR57}$$
$$k = 1.4 \times 1 \times 10^{-7}$$
$$\mathrm{a}_m + \mathrm{np}_p \longrightarrow \mathrm{a}_n \quad \text{SR58}$$
$$k = 1.4 \times 1 \times 10^{-7}$$
$$\mathrm{a}_m + \mathrm{a}_p \longrightarrow \mathrm{a}_n \quad \text{SR59}$$
$$k = 2 \times 10^{-8}$$
$$\mathrm{a}_n + \mathrm{n}_m \longrightarrow \mathrm{a}_m \quad \text{SR60}$$
$$k = 1 \times 10^{-7}$$
$$\mathrm{a}_n + \mathrm{n}_p \longrightarrow \mathrm{a}_p \quad \text{SR61}$$
$$k = 1 \times 10^{-7}$$

$$\mathrm{a}_n + \mathrm{c}_m \longrightarrow \mathrm{a}_m \qquad \text{SR62}$$
$$k = 3 \times 10^{-8}$$
$$\mathrm{a}_n + \mathrm{c}_p \longrightarrow \mathrm{a}_p \qquad \text{SR63}$$
$$k = 3 \times 10^{-8}$$
$$\mathrm{a}_n + \mathrm{np}_m \longrightarrow \mathrm{a}_m \qquad \text{SR64}$$
$$k = 7 \times 10^{-9}$$
$$\mathrm{a}_n + \mathrm{np}_p \longrightarrow \mathrm{a}_p \qquad \text{SR65}$$
$$k = 7 \times 10^{-9}$$
$$2\,\mathrm{a}_n \longrightarrow \mathrm{a}_n \qquad \text{SR66}$$
$$k = 2 \times 10^{-9}$$
$$\mathrm{a}_n + \mathrm{np}_n \longrightarrow \mathrm{a}_n \qquad \text{SR67}$$
$$k = 4 \times 10^{-9}$$
$$\mathrm{a}_n + \mathrm{c}_n \longrightarrow \mathrm{a}_n \qquad \text{SR68}$$
$$k = 8 \times 10^{-9}$$