A Core-Shell box model for simulating Viscosity dependent secondary organic Aerosol (CSVA) and its applications

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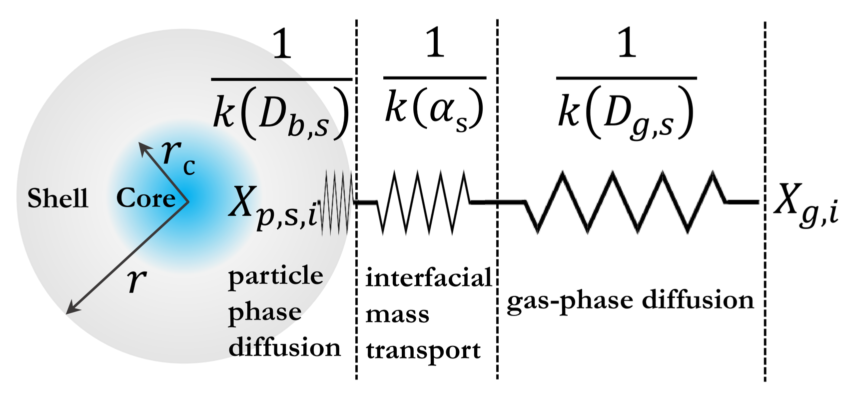
Motivation

Recent studies show that secondary organic aerosol (SOA) is a highly viscous material, and the SOA particle possesses a core−shell configuration. The understanding and modeling of (SOA) properties and evolution are still limited. Previous attempts of modeling particle-phase diffusion were based on Fick's second law with very complex partial differential equations.

Based on these facts, we assumed that SOA particle has a core−shell structure to represent the role of viscosity in the mass transfer, which is characterized by the monomer-rich shell and oligomer-rich core.

Schematic Process Representation

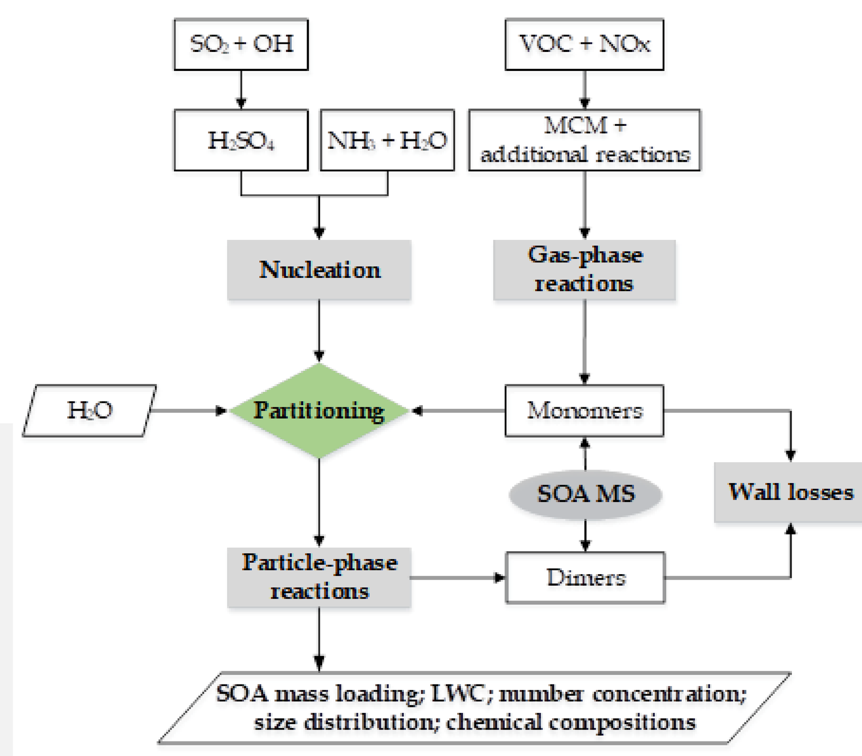
Mass transfer schematic in the Core−Shell structure



Kinetic nucleation: $\frac{dC_p}{dt} = \left\{\frac{dC_p}{dt}\right\}_{nr} + \left\{\frac{dC_p}{dt}\right\}_{co} + \left\{\frac{dC_p}{dt}\right\}_{wl}$

Gas phase : $\frac{dX_{g,i}}{dt} = \left\{\frac{dX_{g,i}}{dt}\right\}_{gr} + \left\{\frac{dX_{g,i}}{dt}\right\}_{mt} + \left\{\frac{dX_{g,i}}{dt}\right\}_{wl}$

Particle phase : $\frac{dX_{p,s,i}}{dt} = \left\{\frac{dX_{p,s,i}}{dt}\right\}_{pr} + \left\{\frac{dX_{p,s,i}}{dt}\right\}_{mt} + \left\{\frac{dX_{p,s,i}}{dt}\right\}_{wl}$

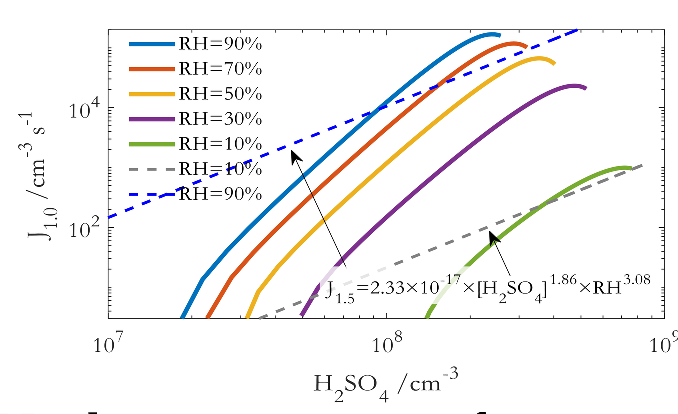


Overall schematic of the CSVA model

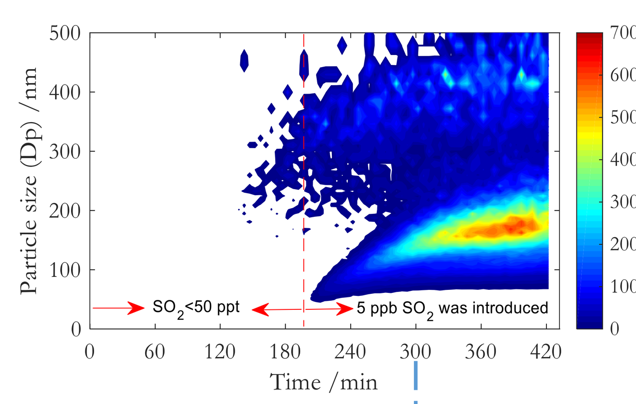
Model development and applications

1. RH-dependent kinetic nucleation by H_2SO_4 hydrate and NH_3

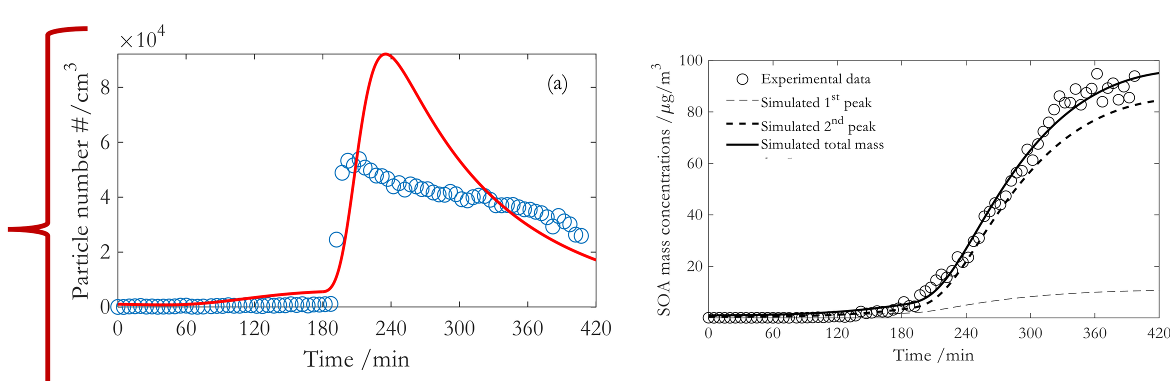
No.	Reactions
(1)	$H_2SO_4 + H_2O \rightarrow H_2SO_4{\bullet}H_2O$
(2)	$H_2SO_4{\bullet}H_2O \rightarrow H_2SO_4 + H_2O$
(3)	$H_2SO_4{\bullet}H_2O + H_2SO_4{\bullet}H_2O \rightarrow (H_2SO_4{\bullet}H_2O)_2$
(4)	$(H_2SO_4{\bullet}H_2O)_2 \rightarrow H_2SO_4{\bullet}H_2O + H_2SO_4{\bullet}H_2O$
(5)	$(H_2SO_4{\bullet}H_2O)_2 + NH_3 \rightarrow NH_3\ (H_2SO_4{\bullet}H_2O)_2$
(6)	$NH_3(H_2SO_4{\bullet}H_2O)_2 + H_2SO_4{\bullet}H_2O \rightarrow NH_3(H_2SO_4{\bullet}H_2O)_3$
(7)	$NH_3(H_2SO_4{\bullet}H_2O)_3 \rightarrow NH_3(H_2SO_4{\bullet}H_2O)_2 + H_2SO_4{\bullet}H_2O$
(8)	$NH_3(H_2SO_4{\bullet}H_2O)_3 + H_2SO_4{\bullet}H_2O \rightarrow NH_3(H_2SO_4{\bullet}H_2O)_4$



Nucleation rates as a function of sulfuric acid vapor concentrations at different RH



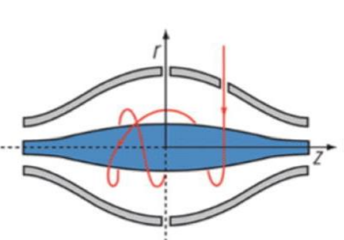
4. Influences of SO_2 on SOA formation from toluene



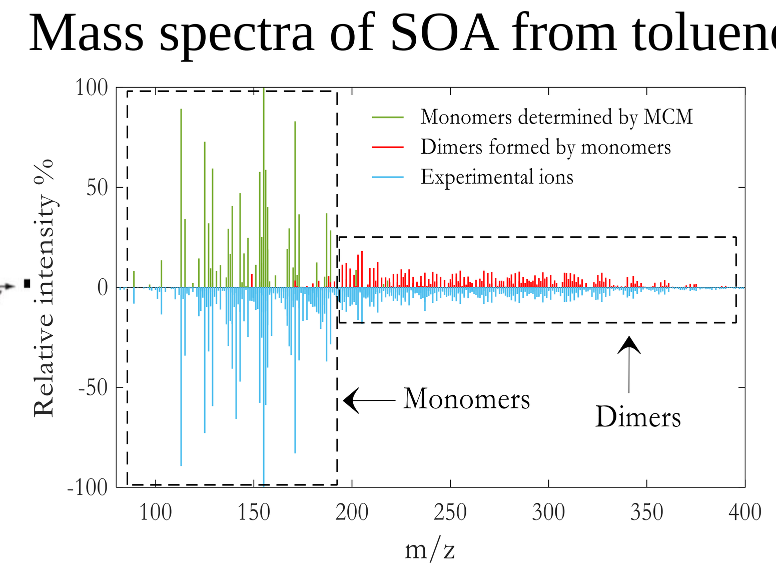
Measured (circles) and modeled (line) particle number and mass concentrations

2. Identification of SOA composition and particle-phase reactions

Mass spectra of SOA from toluene

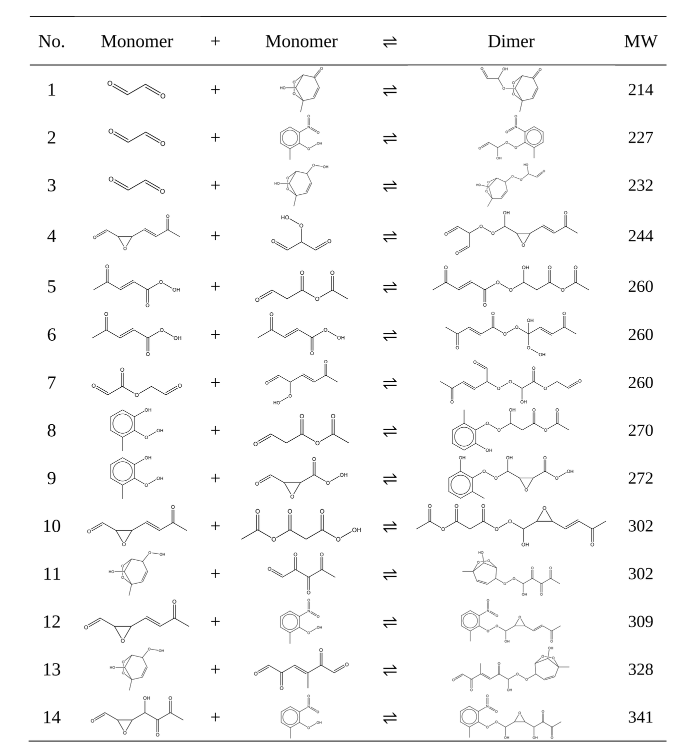


Orbitrap mass



+

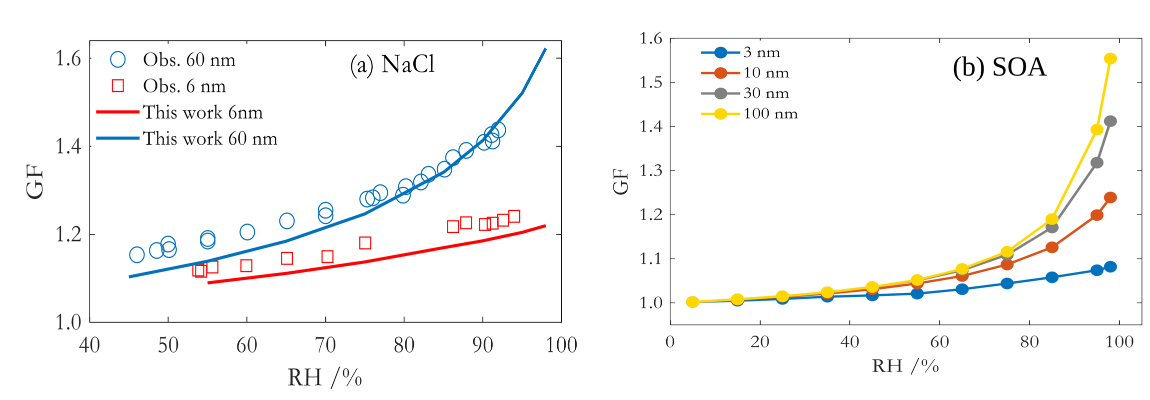
M C M



A total of 65 dimers (with relative intensity being over 5% in 220 dimers) and 440 particle-phase reactions are determined. The CSVA model includes 2855 reactions and 961 species for the toluene oxidation system.

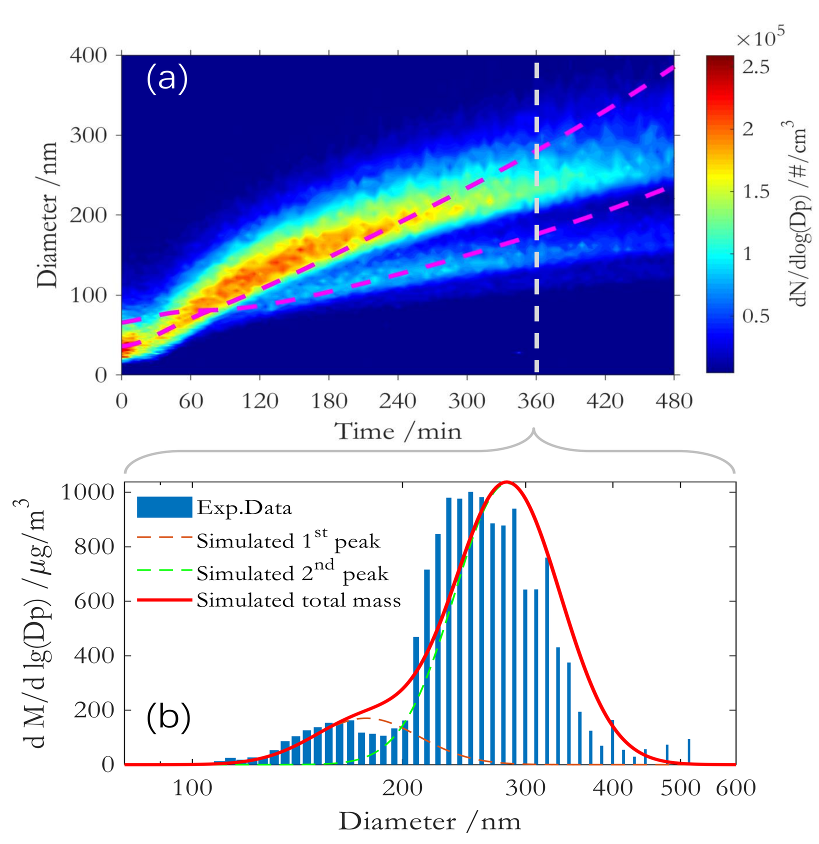
3. Size-dependent hygroscopic growth of salts and SOA

Different from the thermodynamic models (e.g., E-AIM or AIOMFAC), the aerosol water is kinetically predicted in the CSVA model, which can be easily coupled to gas-particle partitioning and other chemical processes.



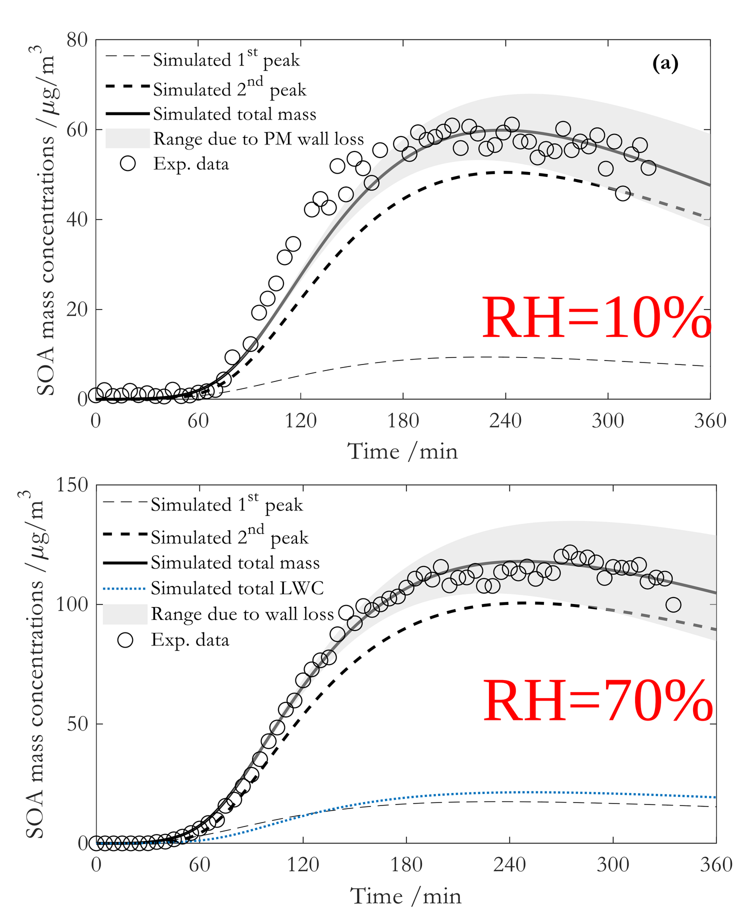
Modelled GF of NaCl and SOA from toluene-NO_2 irradiations for different particle sizes

5. Viscosity-dependent size distribution of SOA



Our model is successfully able to reproduce the evolution of SOA particle size distribution from a one-peak mode into a two-peak mode.

6. Effect of RH on SOA formation



When RH increases from 10% to 70%, the measured SOA mass increases by 67%, and the corresponding modelled SOA mass increases by 69%. This demonstrates that the simulated SOA results are in excellent agreement with the experimental results.

Highlights of CSVA

1. An equation is developed to describe the gas-particle mass transport processes
2. All processes are represented by the form of chemical reactions in the model
3. Aerosol components are determined by mass spectra and master chemical mechanism
4. A humid dependent homogeneous nucleation model by H_2SO_4-NH_3-H_2O is developed
5. Evolution of organic particle size distribution is controlled by viscosity

Acknowledgments

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