Ammonium-Induced Stabilization of Imidazoles in the Particle Phase

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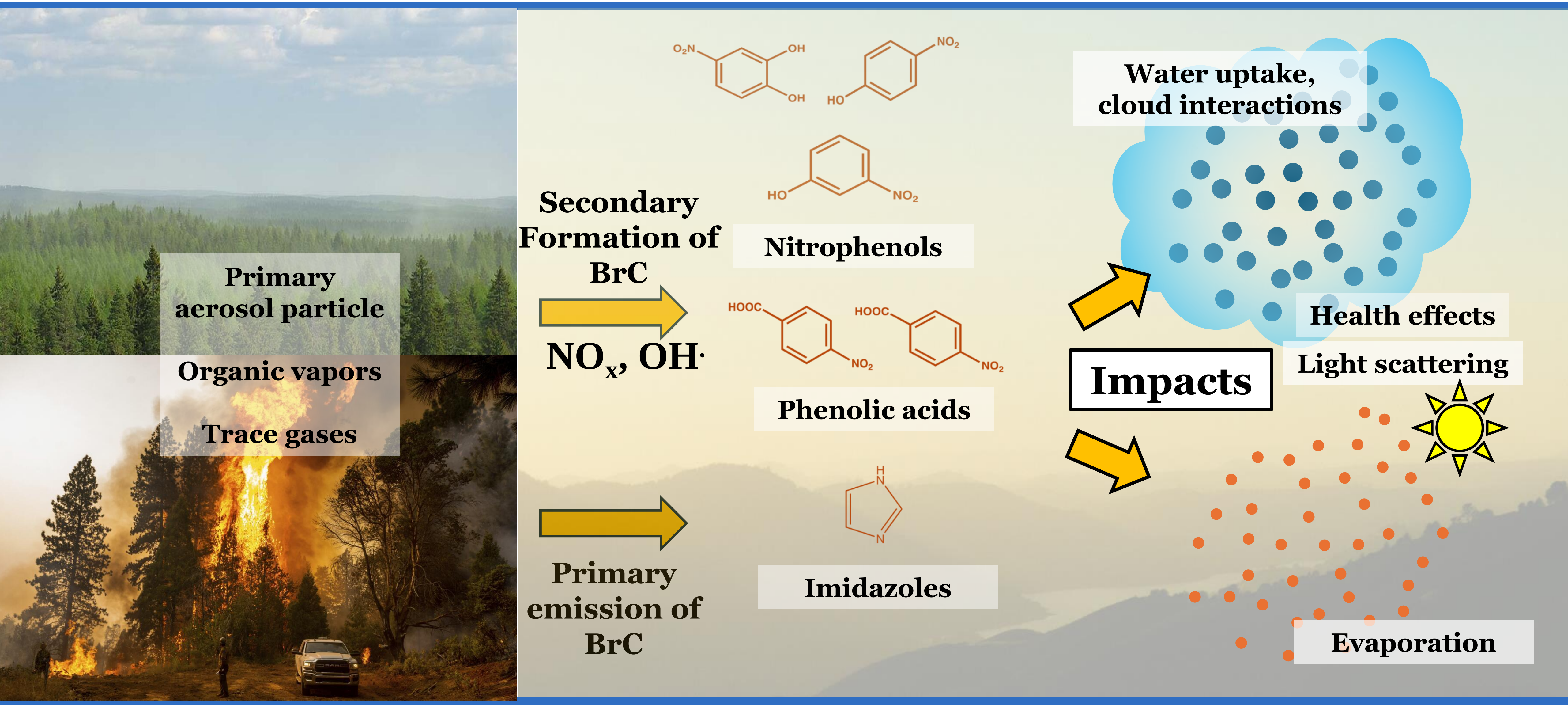
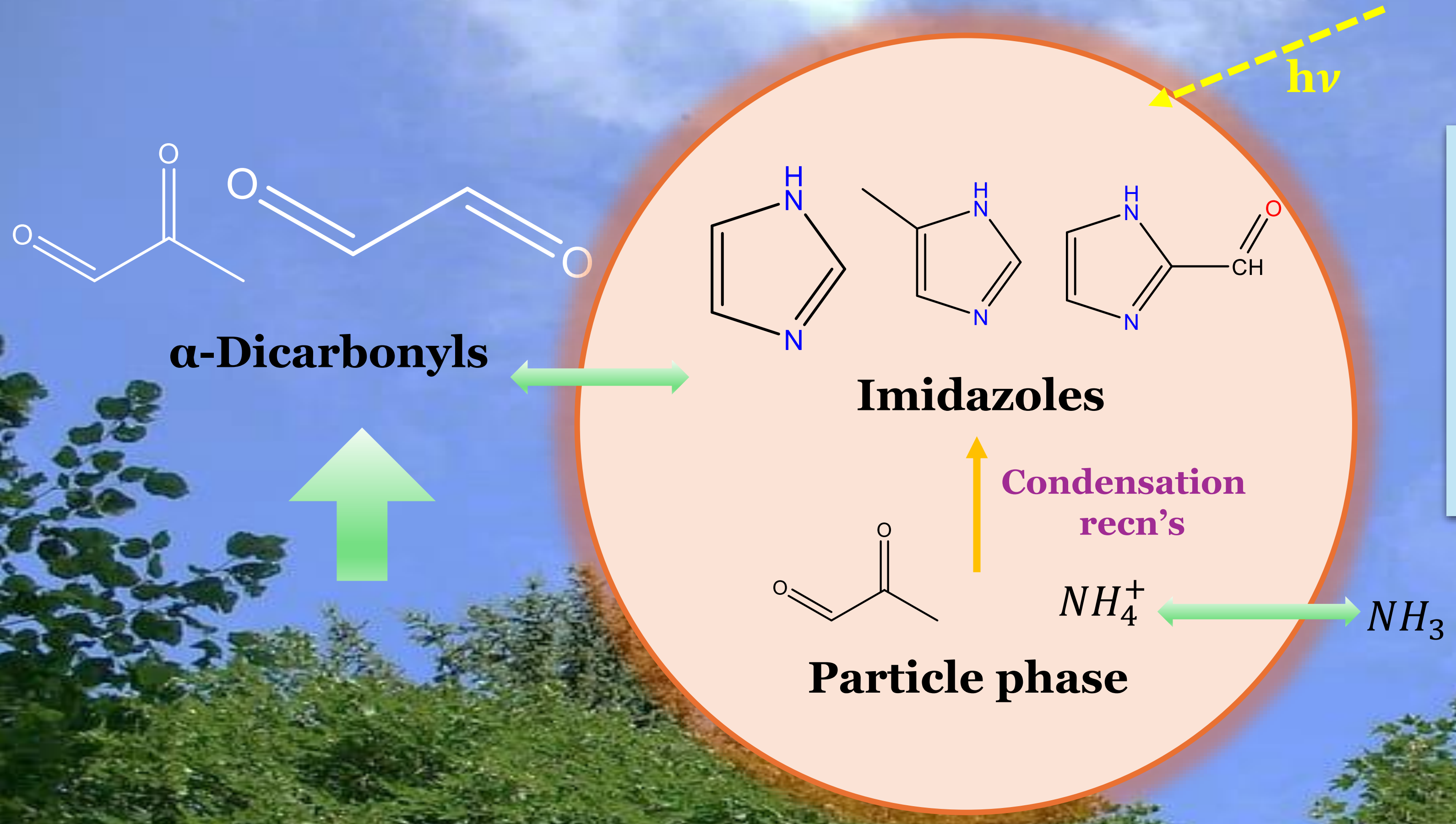
Brown Carbon and their Atmospheric Evolution



Lim et al., *Atmos. Chem. Phys.* **2010**, *10* (21), 10521–10539.

Particulate Imidazoles: Primary emission and Secondary formation

- Light-absorbing, N-containing aromatic heterocyclic organic compounds



Field studies:

- Concentrations of 0.01–20.99 ng m^{-3}
- The most abundant was 4(5)-methylimidazole
- Internally mixed with ammonium etc.
- Photochemistry

He et al., *Science of The Total Environment*, vol. 806, **2022**, p. 150804.

Understanding the Evaporation of Imidazoles

- Particle levitation in linear quadrupole electrodynamic balance coupled with Mie resonance spectroscopy to characterize the evolving size and RI under controlled RH and temperature

MeIM + Water (controlled RH)

- Vapor pressure

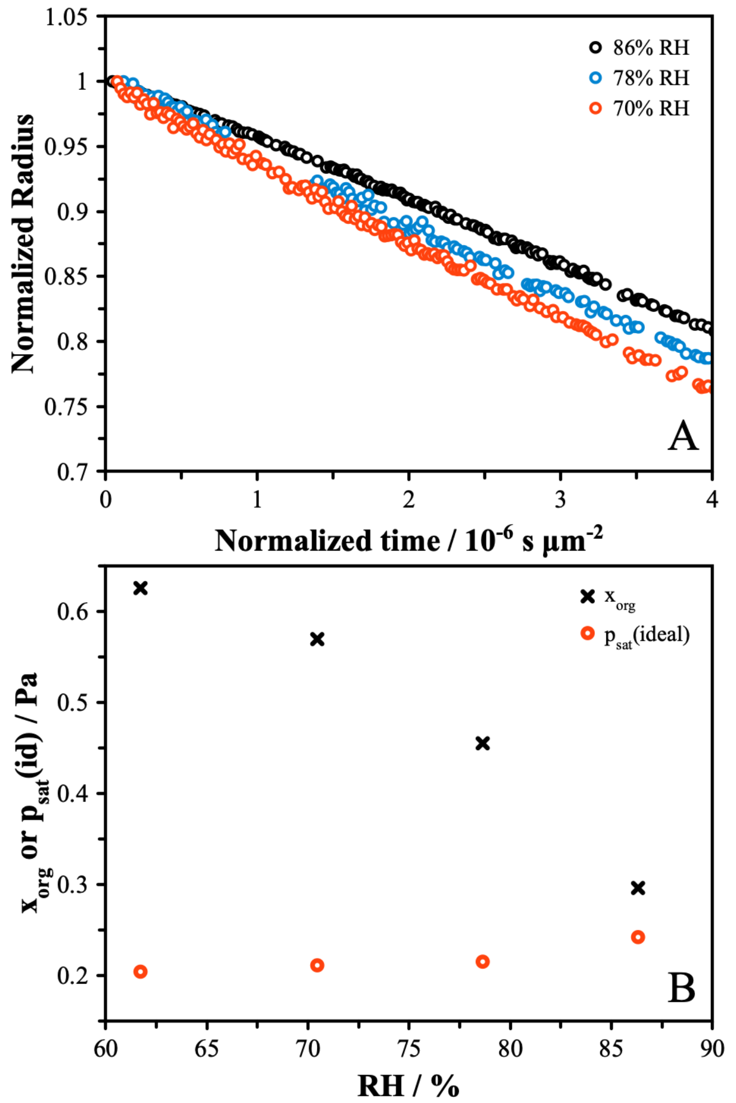
MeIM + Ammonium salts (dry RH)

- What is the influence of inorganic co-solutes on the liquid-vapor partitioning?

MeIM + Acids (dry RH)

- The role of acid/base chemistry and ammonium depletion on the evolution of MeIM particles.

Evaporation of Binary Particles Containing MeIM and Water

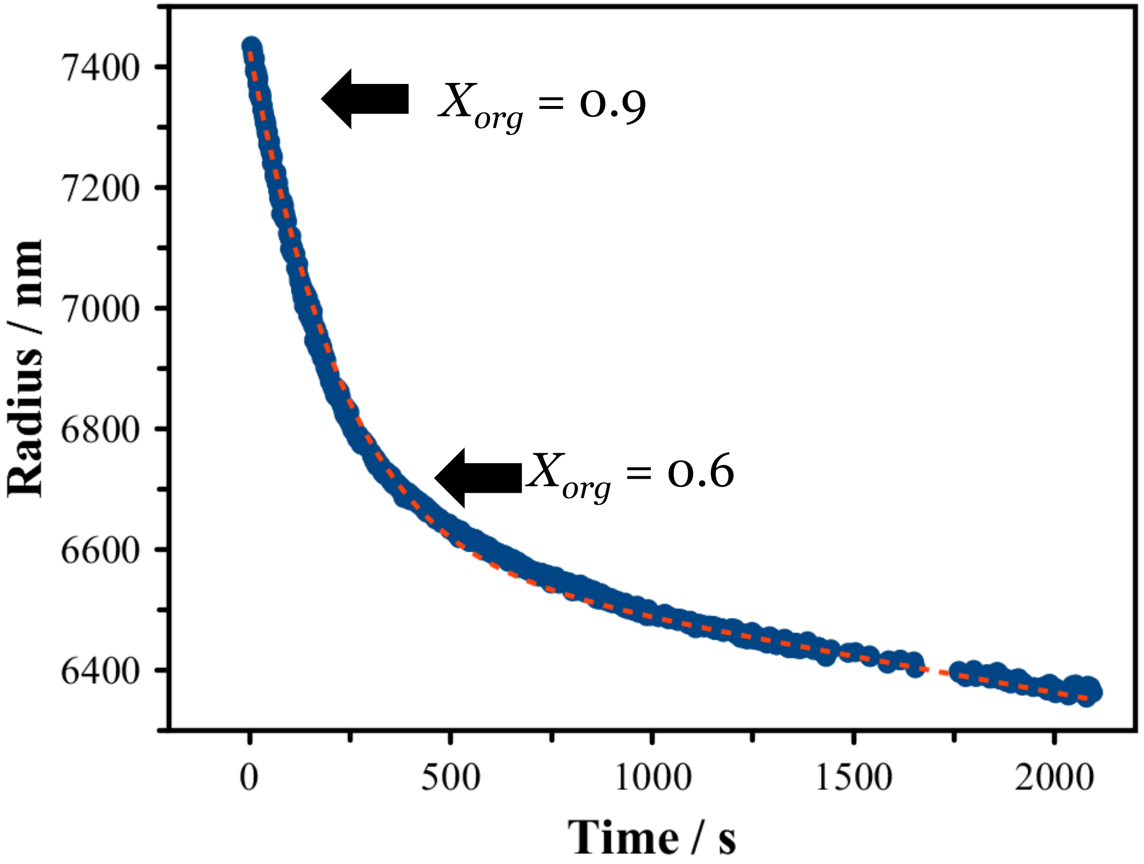


- The pure component vapor pressures are calculated using a simple evaporation model incorporating the refractive index data to estimate the mole fraction of organic

$$\frac{da^2}{dt} = \frac{2M_{org}D_{org}}{\rho_a RT}\gamma_{org}p^{\circ}_{org} \times \left[\frac{(1-x_{org})M_w}{M_{org}} + x_{org}\right]$$

- The vapor pressure of MeIM varies a small amount with RH, indicating that the assumption of ideality is not fully supported

Evaporation of MeIM w/ $(NH_4)_2SO_4$ at 0% RH

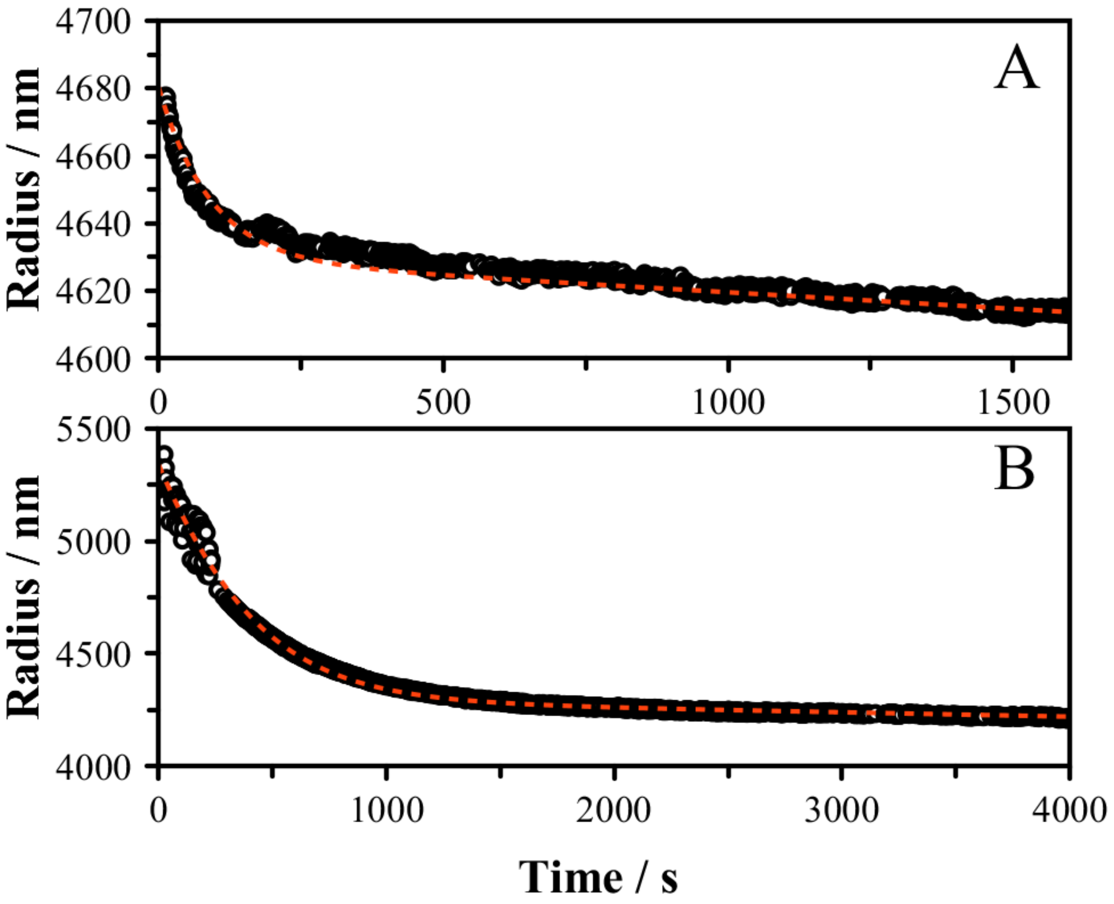


The evaporation of MeIM + AS (X_{org} =0.85), under dry RH

- Evaporation occurs over two distinct timescales
- A significant fraction of organic remains in the particle when the slow region occurs
- Modeling of the evaporation:

Component	X_{org}	P_{sat} / Pa
MeIM (fast component)	0.29	0.43
AS	0.15	
MeIM (slow component)	0.56	0.0054

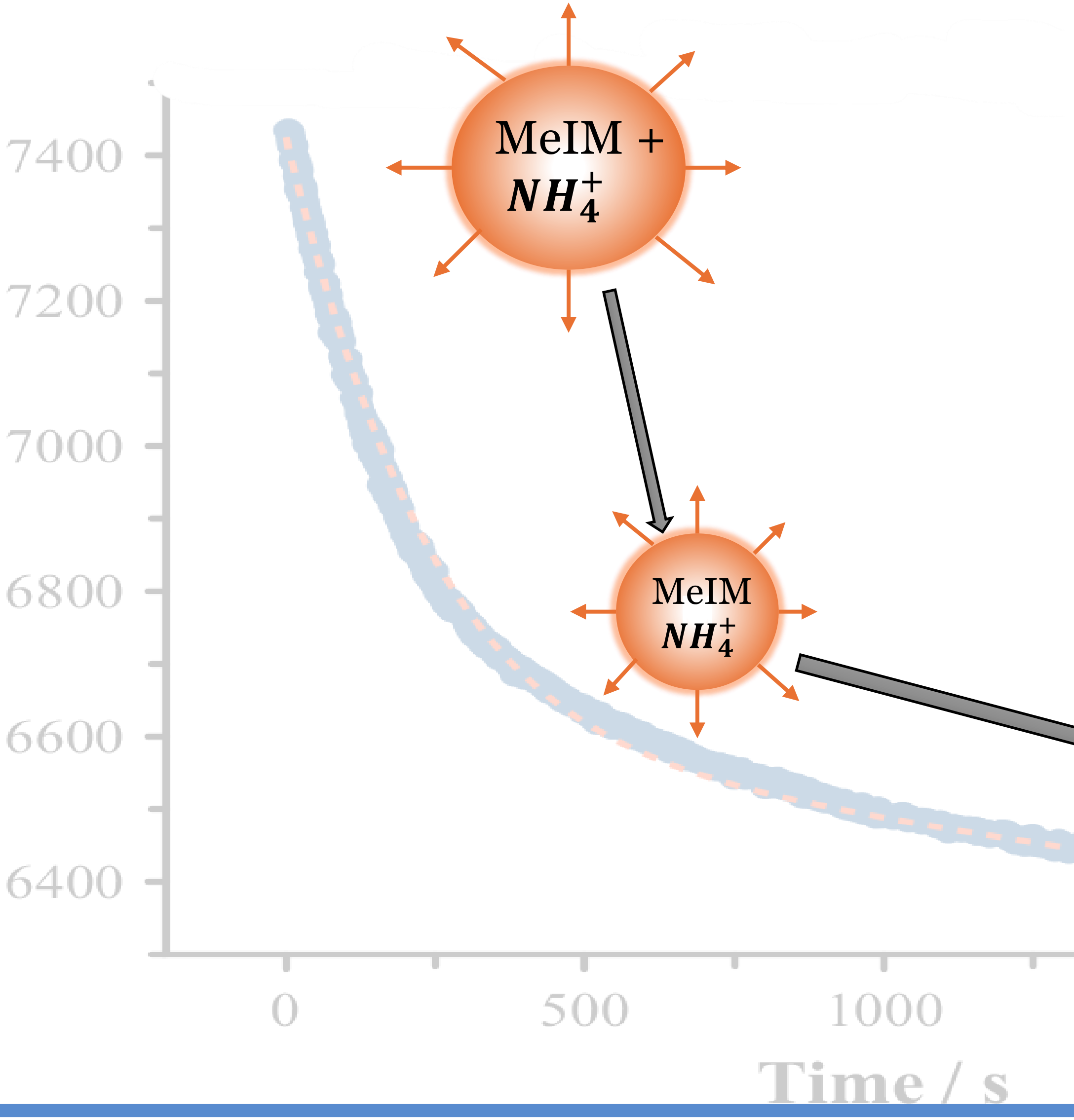
Evaporation of MeIM w/ NH_4Cl at 0% RH

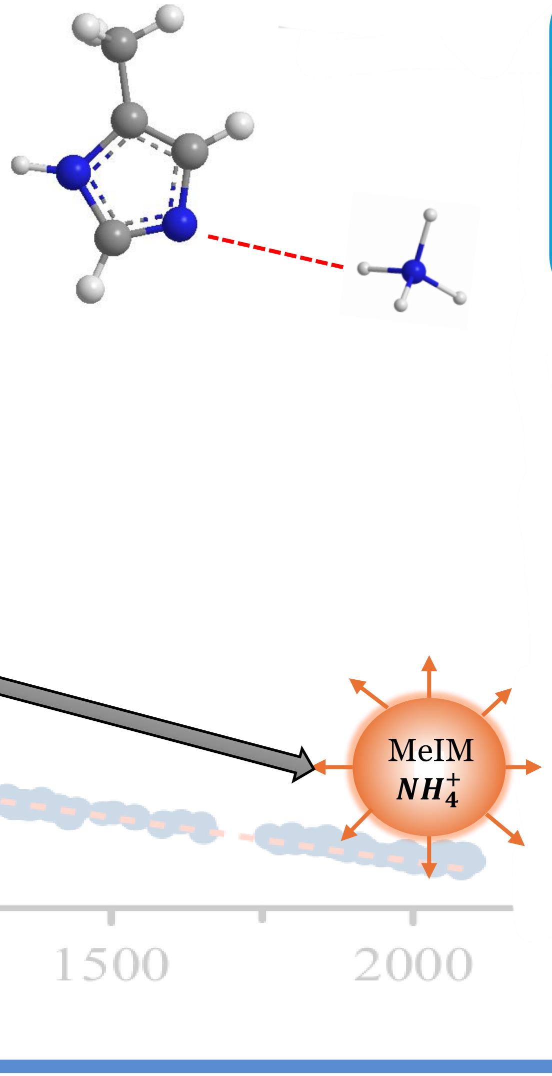


The evaporation of MeIM + NH_4Cl (A)X_{org} =0.49, (B) X_{org} =0.85, under dry RH

- Slow size change over tens of thousands of seconds
- Starting mole fraction controls the size change
- P_{sat} of fast region 0.2 Pa >> P_{sat} of slow region 0.0001 Pa
- IM and ICA mixtures also show slow down of evaporation
- Slowing effects was not observed in 4MI / NaCl and 4MI / K_2SO_4 mixtures

How does NH_4^+ Slow Down the Evaporation of MeIM?



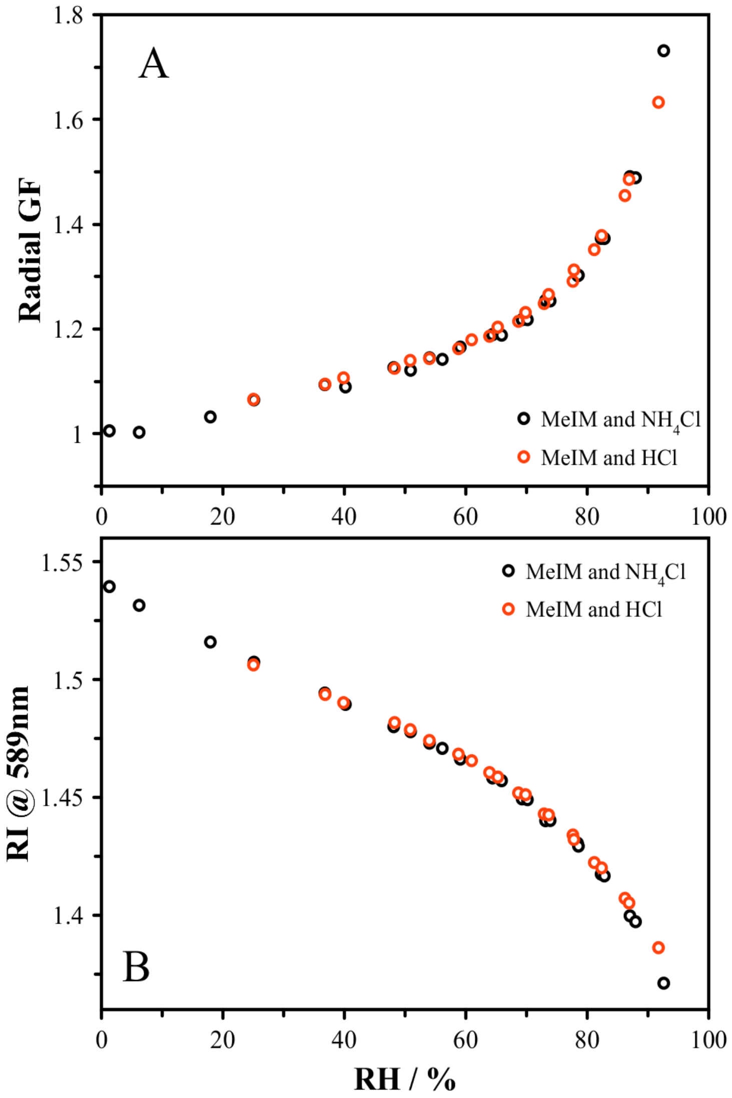


Hydrogen bonding between MeIM and NH_4^+ → cluster formation

Acid-base reaction of MeIM with NH_4^+ → Organic salt formation (favorable under dried conditions)

Reddy et al., *J. Phys. Chem. A* **2005**, *109* (39), 8893–8903.

Hygroscopicity and Optical Properties of of MeIM and NH_4Cl Versus MeIM and HCl



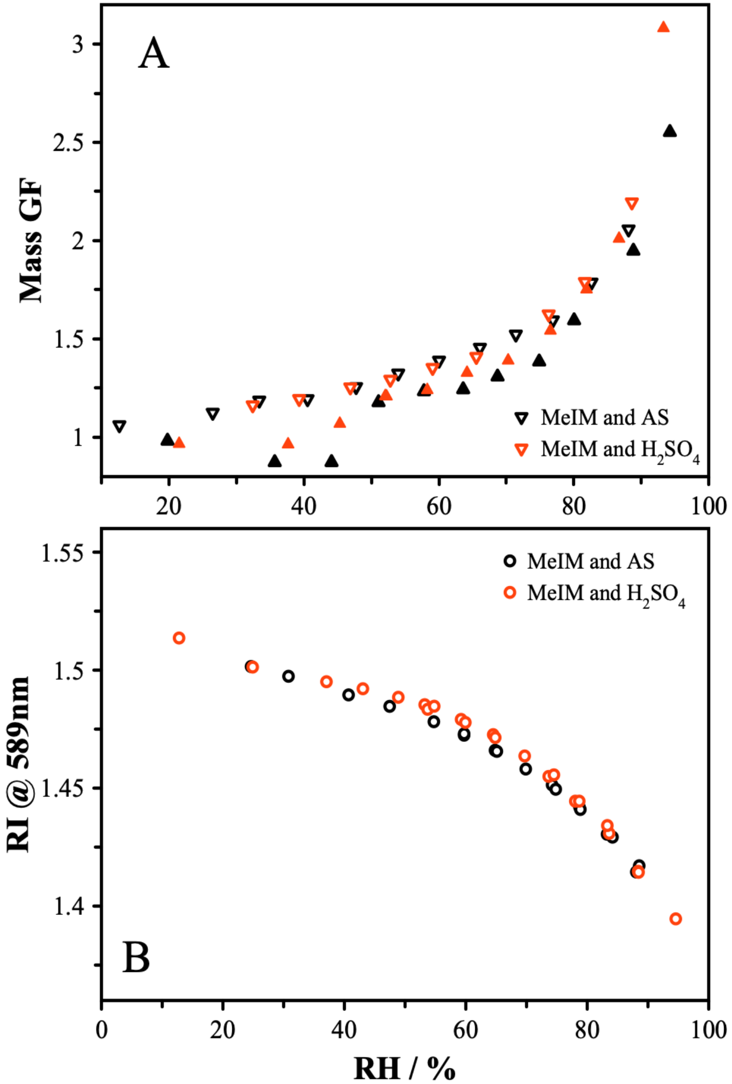
$$MeIM + NH_4Cl \leftrightharpoons MeIMH^+Cl^- + NH_3$$

$NH_{3(g)}$

$$MeIM + HCl \leftrightharpoons MeIMH^+Cl^-$$

- Degassing of ammonia drives the forward reaction
- Ammonium depletion is responsible for the observed behavior
- $MeIMH^+Cl^-$ can act as an **ionic liquid**, and particles remain spherical and amorphous across all RH conditions

Hygroscopicity and Optical Properties of of MeIM and $(NH_4)_2SO_4$ Versus MeIM and H_2SO_4



$$2MeIM + (NH_4)_2SO_4 \leftrightharpoons (MeIMH^+)_2SO_4^{2-} + 2NH_3$$

$NH_{3(g)}$

$$MeIM + H_2SO_4 \leftrightharpoons (MeIMH^+)_2SO_4^{2-}$$

- $(MeIMH^+)_2\ SO_4{}^{2-}$ does not act as an **ionic liquid**, and particles solidify to a non-spherical morphology at low RH

Summary and Conclusions

- While the volatility of pure imidazoles results in rapid evaporation from the particle phase, the presence of **ammonium ions can stabilize them in the particle phase via acid/base chemistry and ammonium depletion.**

- Given the formation mechanism of imidazoles in the atmosphere, it is highly likely that an abundance of ammonium is present in aerosols that exhibit a high mass loading of particle phase imidazoles

- 4-methylimidazole can form an **ionic liquid with chloride ions following protonation** either by a strong acid or ammonium. These particles remain **amorphous** across the full RH range.

$$MeIM + HCl \leftrightharpoons MeIMH^{+}Cl^{-}$$

$$MeIM + NH_4Cl \leftrightharpoons MeIMH^{+}Cl^{-} + NH_3$$

Acknowledgements

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