

An Experimental and Modeling Study of Nanoparticle Formation and Growth From Dimethylamine and Nitric Acid

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Supporting Information

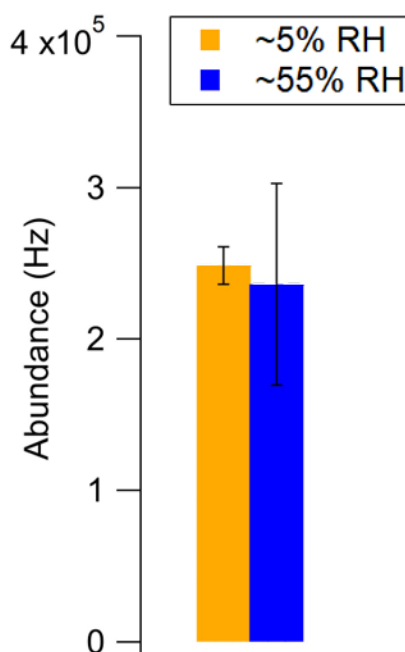


Figure S1. Measured DMA abundance under 5% and 55% RH conditions using a transverse ionization chemical ionization inlet coupled with mass spectrometry (TI-CIMS).¹ The reagent ion used for these experiments was H_3O^+ , and measured DMA abundances were within the linear range (that is, reagent ion was not saturated). No significant difference in DMA concentration was observed in the presence of water, which suggests that the different RH experiments did not operate under different vapor concentrations of DMA.

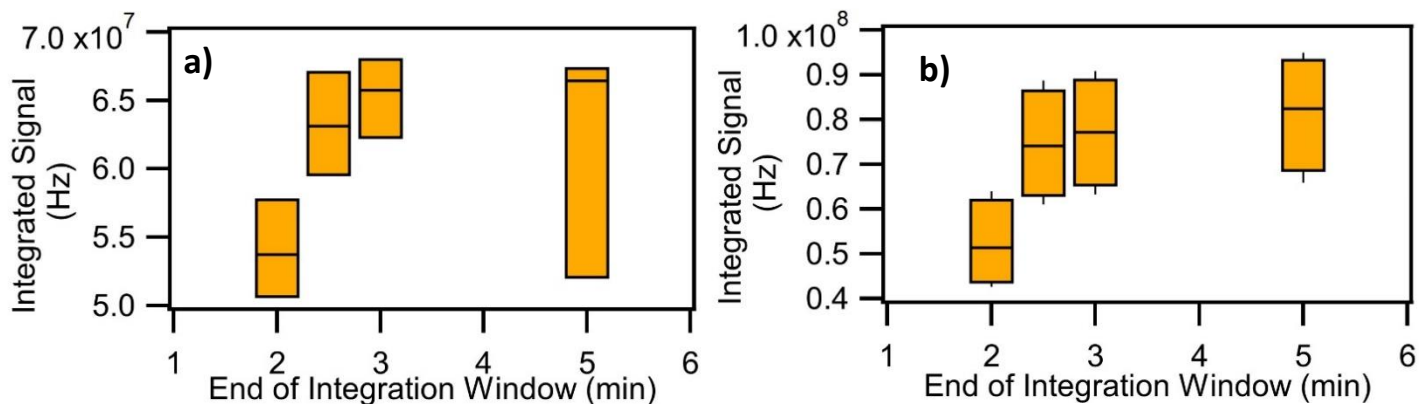


Figure S2. Box-and-whisker plots of the difference in integration end times, where 5 minutes is across the entire desorption period. a) shows the effect on variability and average signal for nitrate ion, while b) shows the effect on variability and average signal on dimethylaminium ion.

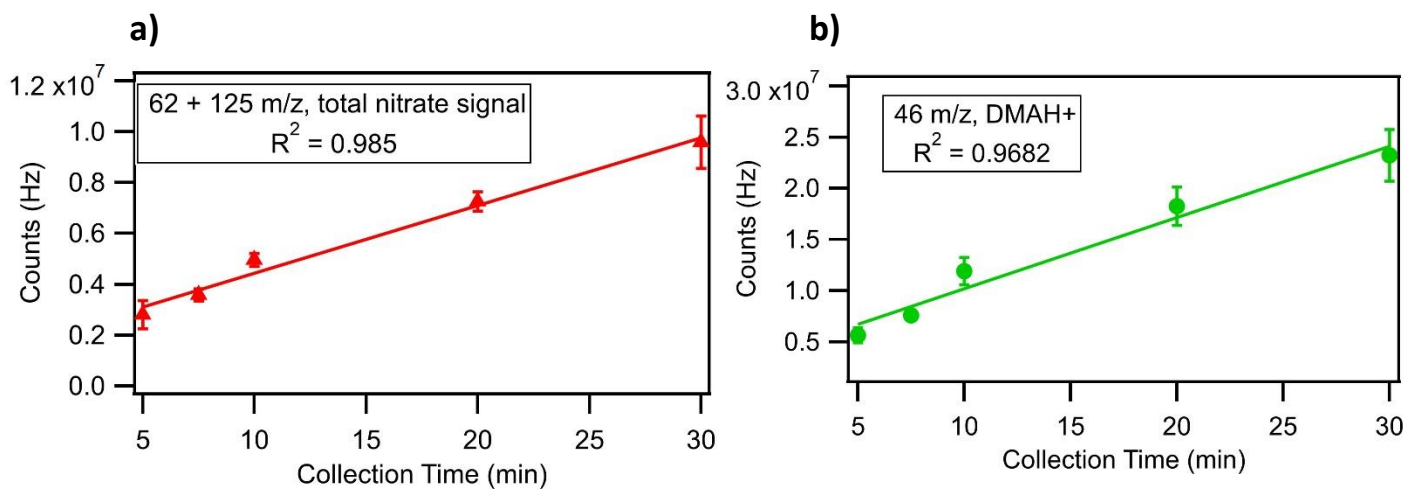


Figure S3. Linearity tests of signal vs collection time for particles generated with dimethylamine and nitric acid in dry conditions, where a) shows the linearity of m/z 46 with collection time, and b) shows the linearity of total nitrate signal (m/z 62 and m/z 125).

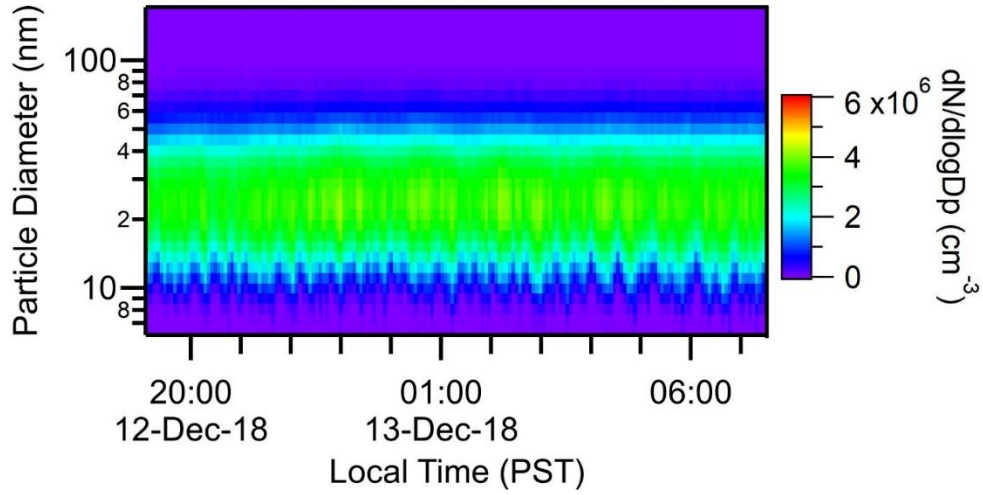


Figure S4. Particle size distribution produced from dimethylamine and nitric acid in humid conditions over a period of 10 hours.

Computational Methods

The Gibbs free binding energies for the global minimum energy clusters are calculated

$$\Delta G = G_{\text{cluster}} - \sum_i G_{\text{monomers},i}$$

The evaporation rates of the clusters are obtained from the Gibbs free binding energies ΔG of the evaporating cluster and its products as

$$\gamma_{(i+j) \rightarrow i,j} = \beta_{i,j} \frac{p_{\text{ref}}}{k_B T} \exp\left(\frac{\Delta G_{i+j} - \Delta G_i - \Delta G_j}{k_B T}\right).$$

The collision coefficients for neutral-neutral collisions are computed from kinetic gas theory as

$$\beta_{i,j} = \left(\frac{3}{4\pi}\right)^{1/6} \left[6k_B T \left(\frac{1}{m_i} + \frac{1}{m_j}\right)\right]^{1/2} (V_i^{1/3} + V_j^{1/3})^2,$$

where m_i and V_i are the mass and volume of cluster i , respectively. The volumes are calculated using bulk liquid densities assuming spherical clusters and ideal mixing.

Hydrated Nitric Acid-Dimethylamine Clusters

We have calculated the evaporation rates for all studied acid-base clusters with 1-4 water molecules. Figure S4 shows that all evaporation rates are very high, which is related to the rapid evaporation of water monomers as discussed in the main text.

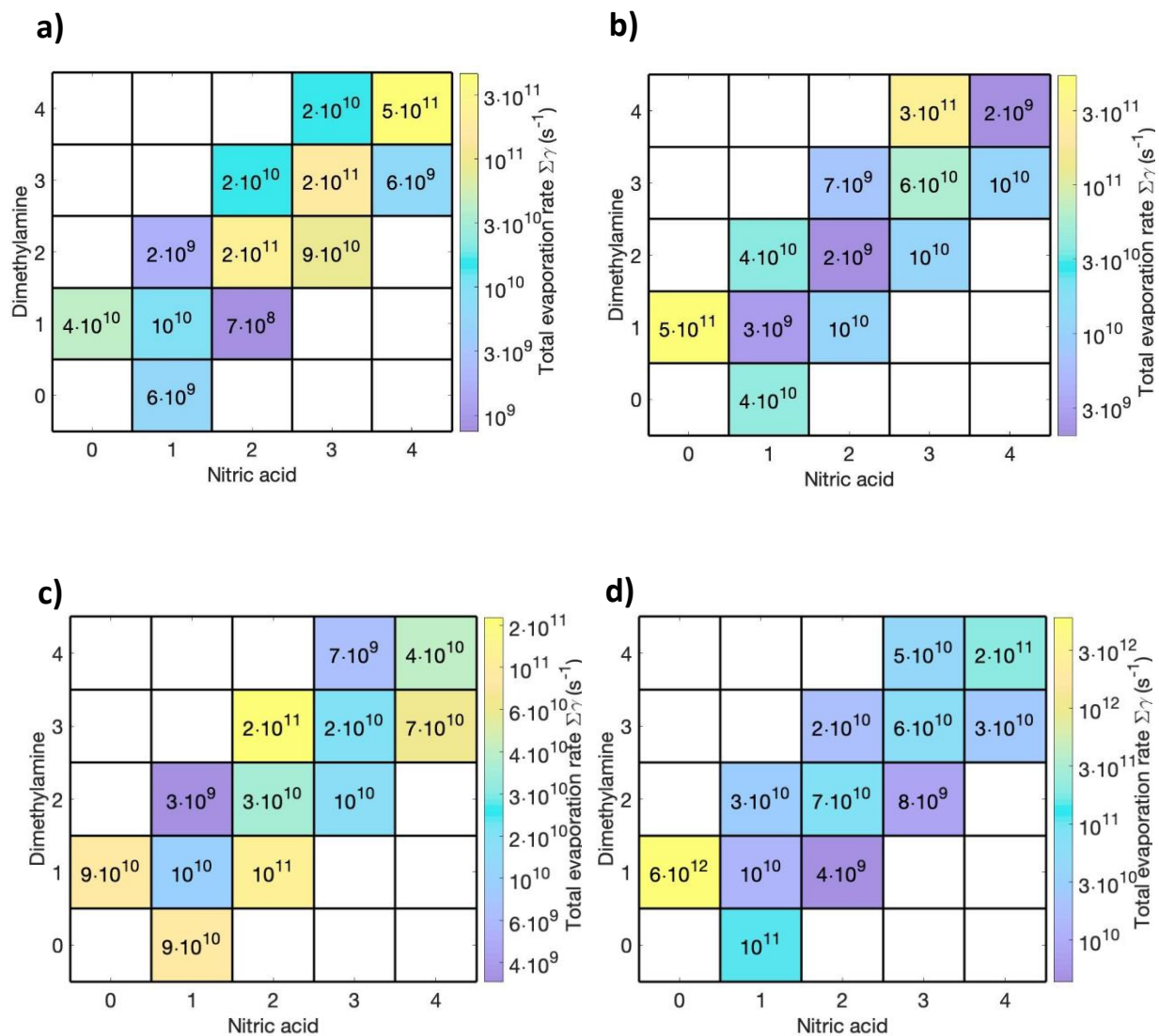


Figure S5. Evaporation rates for nitric acid-dimethylamine clusters containing a) one water molecule, b) two water molecules, c) three water molecules and d) four water molecules

In order to prove that water has no contribution in the initial steps of new-particle formation, we have simulated the nanoparticle formation rates in dry and wet conditions using ACDC. We tested

several different nitric acid and dimethylamine concentrations in order to detect even a small difference between RH=0% and RH=55% in particle formation rates. However, since water is so weakly-bound in nitric acid-dimethylamine clusters, particle formation is occurring via dry pathway even at low concentrations and thus the presence of water does not increase the particle formation rate. Figure S5 shows that very low nitric acid and dimethylamine concentrations are required and that the effect of hydration is not negligible. When dimethylamine concentration is set as low as 0.001 ppt_v and nitric acid concentration is less than 10⁶ cm⁻³, the particle formation rate is increased at RH=55%. However, the particle formation rate is so small that it has no relevance in the atmosphere or even in laboratory measurements. Thus, we can conclude that due to the small number of available hydrogen bonds acceptors and donors in nitric acid-dimethylamine clusters and weak intermolecular interaction of water with nitric acid and dimethylamine, water is not contributing in the initial steps of particle formation. Therefore, we can assume that the small increase in experimentally measured size-distribution is related to the uptake of water in large particles.

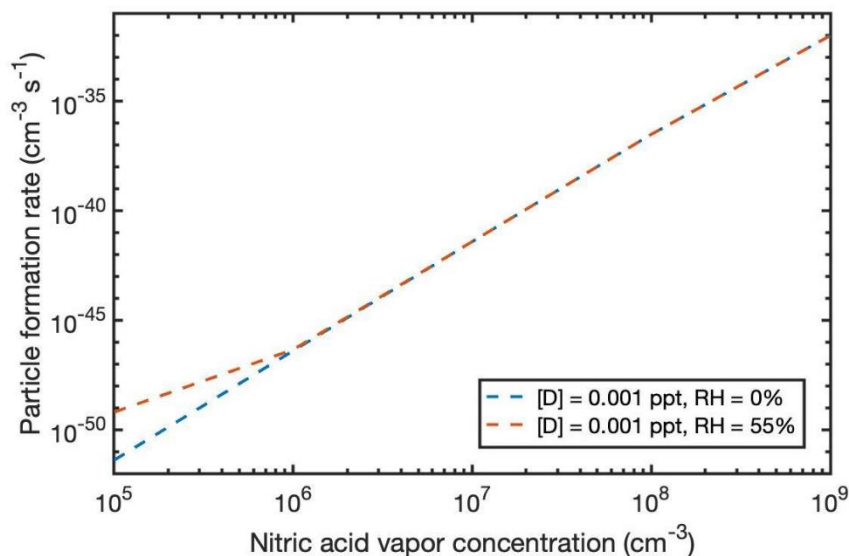


Figure S6. Nanoparticle formation rate as a function of nitric acid concentration at dimethylamine concentration of 0.001 ppt_v at 298.15 K at RH=0% and RH=55%.

Table S1. Gibbs free binding energies (kcal/mol) at 298.15 K.

Cluster	Gibbs free binding energy (kcal/mol)	Cluster	Gibbs free binding energy (kcal/mol)	Cluster	Gibbs free binding energy (kcal/mol)
1NA1D	-5.724157	2NA1D4W	-12.275211	4NA3D1W	-52.871277
1NA2D	-6.73516	2NA2D1W	-26.097955	4NA3D2W	-53.327972
2NA1D	-10.443673	2NA2D2W	-27.468284	4NA3D3W	-52.761529
2NA2D	-27.578118	2NA2D3W	-27.175271	4NA3D4W	-52.770011
2NA3D	-28.859774	2NA2D4W	-26.429614	4NA4D1W	-67.816153
3NA2D	-32.142466	2NA3D1W	-29.076732	4NA4D2W	-69.373003
3NA3D	-47.424814	2NA3D2W	-29.782558	4NA4D3W	-69.134867
3NA4D	-47.159572	2NA3D3W	-28.588995	4NA4D4W	-67.982571
4NA3D	-52.065425	2NA3D4W	-28.802786	2W	3.162067
4NA4D	-69.522126	3NA2D1W	-31.278613	3W	4.864611
1NA1D1W	-5.934857	3NA2D2W	-31.67997	4W	4.746037
1NA1D2W	-6.957322	3NA2D3W	-31.964862	1NA1W	-0.344143
1NA1D3W	-7.253366	3NA2D4W	-32.584604	1NA2W	0.426409
1NA1D4W	-7.432016	3NA3D1W	-46.213954	1NA3W	1.587919
1NA2D1W	-8.24401	3NA3D2W	-45.677012	1NA4W	2.779769
1NA2D2W	-7.870135	3NA3D3W	-45.948104	1D1W	0.719374
1NA2D3W	-9.097184	3NA3D4W	-45.403719	1D2W	2.896121
1NA2D4W	-8.949039	3NA4D1W	-47.642912	1D3W	3.879365
2NA1D1W	-12.26978	3NA4D2W	-46.207552	1D4W	7.281732
2NA1D2W	-12.492675	3NA4D3W	-47.286794		
2NA1D3W	-11.402652	3NA4D4W	-46.892945		

References

- (1) Li, X.; Chee, S.; Hao, J.; Abbatt, J. P. D.; Jiang, J.; Smith, J. N. Relative Humidity Effect on the Formation of Highly Oxidized Molecules and New Particles during Monoterpene Oxidation. *Atmos. Chem. Phys.* **2019**, *19*, 1555–1570. <https://doi.org/acp-19-1555-2019>.