Electronic Supplementary Material (ESI) for Environmental Science: Nano.


# Electronic Supplementary Information:

# The heterogeneous reaction of dimethylamine/ammonia with sulfuric acid to promote the growth of the atmospheric nanoparticle

Weina Zhang, Yuemeng Ji, Guiying Li, Qiuju Shi and Taicheng An*

*Guangzhou Key Laboratory of Environmental Catalysis and Pollution Control, Guangdong Key Laboratory of Environmental Catalysis and Health Risk Control, School of Environmental Science and Engineering, Institute of Environmental Health and Pollution control, Guangdong University of Technology, Guangzhou 510006, China*

*Corresponding Author: **Prof. Taicheng An**

Tel: +86-20-39322298

E-mail: antc99@gdut.edu.cn

## Tests on the model

Considering about the homogeneity and cohesiveness of a real water droplet in the atmosphere, we compared space distribution and relative concentration of water molecules from n=64 to n=577 in the PBC box. The coherence improves with an increasing number of water molecules. Fig. S1 illustrates the space distribution of water molecules randomly located in the same size PBC box. It can be observed visually that “holes” occurs when n is smaller than 249. The occurrence of hole goes against the cohesiveness of the atmospheric droplet. For n=249 and 499 water molecules, they display good cohesiveness. However, for a real droplet, it should satisfy the homogeneity which can be analyzed by the relative concentration function. Accordingly, we then compared two relative concentration profiles for n=249 and n=499 water molecules in Fig. S2. The profile of more water molecules fluctuates less which implies a homogenous droplet. Finally, considering about the real density at ambient (about $\rho$=0.997 g/cm$^3$)[1], we determined n=577.

## Occurrence probability

In order to obtain the distribution of different components in the DMA/ammonia-SA-water system, occurrence probability was separately calculated for DMA/ammonia, SA and water. The occurrence probability of the specific component is the ratio of the local concentration and bulk concentration of the component along the specified direction. In this work, the direction is set perpendicular to the air-nanoparticle interface. The concentration is the number of the specific component per unit volume.

## Radial distribution function

Radial distribution function (RDF), $g(r)$, is commonly used to calculate the close interactions between two specific atoms. In the air-aqueous interface or aqueous bulk, close interactions between solutes and solutions occur. The first solution shell is thus formed around the specific solute. The components of the first solution shell can be quantified by the coordination numbers. The coordination numbers are calculated as the integrations of $g(r)$ within $r$=2.5 Å. The distance of 2.5 Å is considered as the threshold value to determine

whether close interactions occur between two specific atoms. It is also used as the threshold distance in the Martins-Costa et al's work[2] where they investigate the heterogeneous interactions of volatile organic compounds with water.

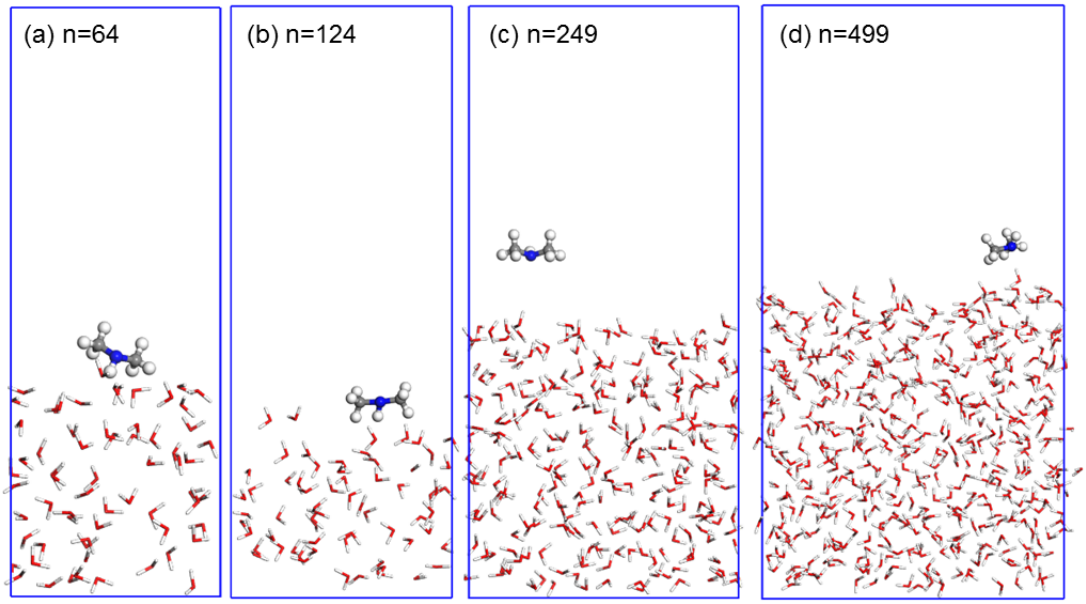



Fig. S1. Snapshots of the equilibrated droplet model involving varying numbers (denoted by *n*) of water molecules. Colors of blue, white and red represents N, H and O atom, respectively.

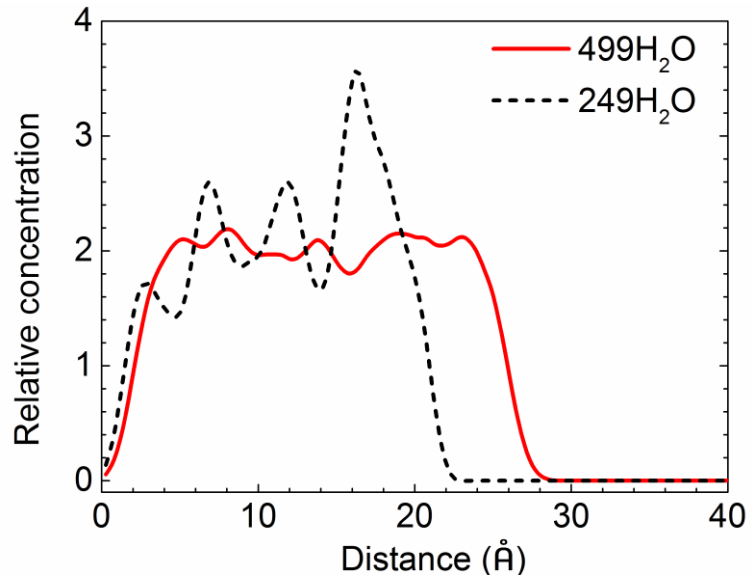



Fig. S2. Relative concentrations of water molecules along z-axis.

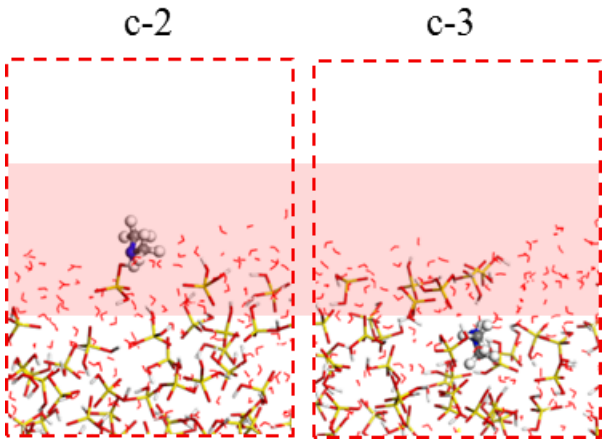



Fig. S3. The specific snapshots of DMA-SA-water system. Labels of c-2 on nanoparticle surface and c-3 inside bulk nanoparticle correspond to specific points remarked on free energy profile of DMA-SA-water system (Fig 4b in the manuscript). Color of gray, blue, yellow, white and red represents C, N, S, H and O atom, respectively.

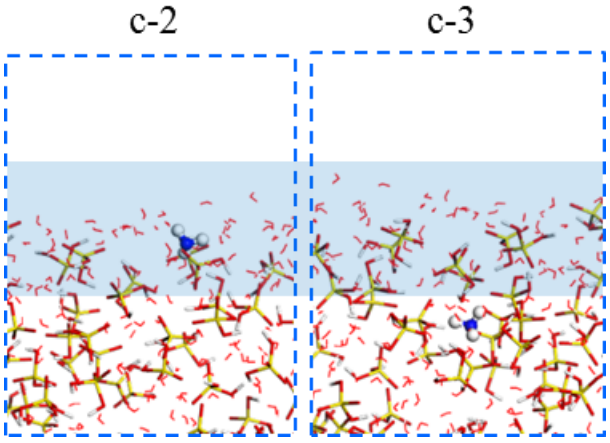



Fig. S4. The specific snapshots of ammonia-SA-water system. Labels of c-2 on nanoparticle surface and c-3 inside bulk nanoparticle correspond to specific points remarked on free energy profile of ammonia-SA-water system (**Figure 1b**). Color of blue, yellow, white and red represents N, S, H and O atom, respectively.

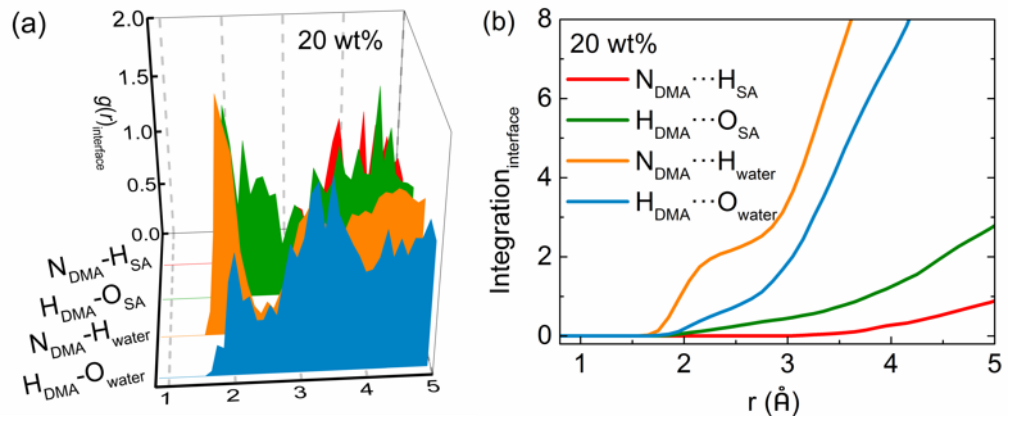



Fig. S5 (a) The radial distribution function $g(r)$s and (b) the integrations of the HBs formed in the interface of the 20 wt% SA nanoparticle. The curves of $N_{DMA}\cdots H_{SA}$, $H_{DMA}\cdots O_{SA}$, $N_{DMA}\cdots H_{water}$ and $H_{DMA}\cdots O_{water}$ HBs are displayed in red, green, orange and blue lines, respectively.

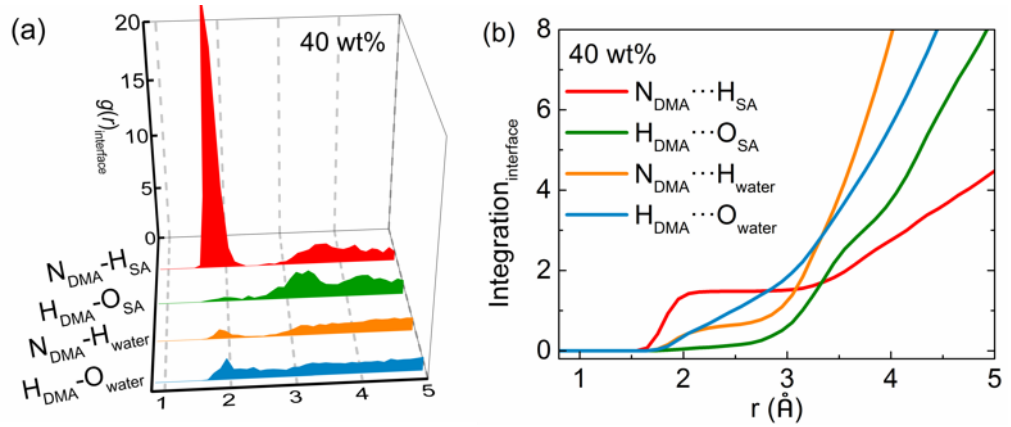
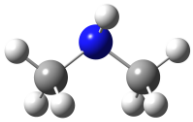
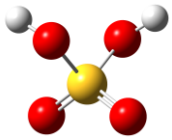



Fig. S6 (a) The radial distribution function $g(r)$s and (b) the integrations of the HBs formed in the interface of the 40 wt% SA nanoparticle. The curves of $N_{DMA}\cdots H_{SA}$, $H_{DMA}\cdots O_{SA}$, $N_{DMA}\cdots H_{water}$ and $H_{DMA}\cdots O_{water}$ HBs are displayed in red, green, orange and blue lines, respectively.

Table S1. Cartesian coordinates for the optimized DMA, SA and DMA-SA cluster geometries given in article Figure 5b. Color of gray, blue, yellow, white and red represents C, N, S, H and O atom, respectively.

| | | | | |
|---|---|---|---|---|
| DMA ((CH3)2NH)  | C | 1.19713100 | -0.22777300 | 0.01982100 |
| | N | 0.00001300 | 0.59051200 | -0.16315300 |
| | C | -1.19713900 | -0.22777700 | 0.01978800 |
| | H | 1.20679800 | -0.77546100 | 0.97287900 |
| | H | 1.26284500 | -0.96361200 | -0.78509100 |
| | H | 2.08948200 | 0.39770900 | -0.02617800 |
| | H | 0.00000600 | 1.28233500 | 0.58103000 |
| | H | -1.20621500 | -0.77637500 | 0.97236200 |
| | H | -2.08937500 | 0.39796600 | -0.02481600 |
| | H | -1.26358100 | -0.96284500 | -0.78576900 |
| Sulfuric acid ($H_2SO_4$)  | O | 0.34280400 | -0.83719600 | 1.21003800 |
| | S | -0.00006400 | -0.14510000 | 0.00134000 |
| | O | -0.34281500 | -0.86024000 | -1.19387200 |
| | O | 1.16938600 | 0.82822300 | -0.41933700 |
| | O | -1.16936100 | 0.83610400 | 0.40353600 |
| | H | 1.55729900 | 1.29610600 | 0.34281000 |
| | H | -1.55638700 | 1.29035900 | -0.36716300 |
| DMA-SA ((CH3)2NH·($H_2SO_4$)) | C | -2.29739000 | -1.31524200 | -0.02237500 |
| | N | -2.05088500 | 0.14843800 | -0.01087300 |
| | C | -3.29191500 | 0.95759000 | 0.00874100 |
| | H | -2.88754900 | -1.55822500 | -0.90350800 |
| | H | -1.34026000 | -1.83016600 | -0.05846000 |
| | H | -2.83823000 | -1.58231500 | 0.88291300 |
| | H | -1.45559900 | 0.37172000 | 0.79621300 |

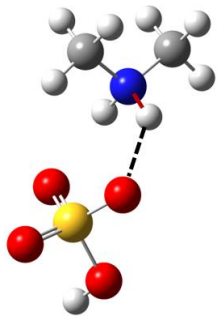
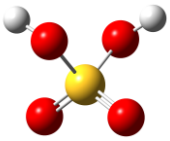
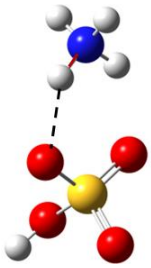
| | | | | |
|---|---|---|---|---|
|  | H | -3.02263600 | 2.01089300 | 0.01856600 |
| | H | -3.87127200 | 0.72210300 | -0.88149700 |
| | H | -3.85634000 | 0.70156300 | 0.90290300 |
| | O | 2.30932100 | -1.15648600 | 0.04777700 |
| | S | 1.33723600 | -0.06516200 | 0.01746500 |
| | O | 0.53512100 | 0.06884900 | 1.23748500 |
| | O | 0.53211200 | -0.03270200 | -1.21313000 |
| | O | 2.18993600 | 1.31340100 | 0.02072200 |
| | H | -1.47193800 | 0.38411200 | -0.82524900 |
| | H | 2.70814300 | 1.38525600 | -0.79623800 |

Table S2. Cartesian coordinates for the optimized ammonia, SA and ammonia-SA cluster geometries given in article Figure 3b. Color of blue, white, red and yellow represents N, H, O and S, respectively.

| | | | | |
|---|---|---|---|---|
| Ammonia ($NH_3$)  | N | 0.00000200 | -0.00003600 | -0.12086000 |
| | H | 0.92117900 | -0.14737500 | 0.28202200 |
| | H | -0.58832900 | -0.72376200 | 0.28206200 |
| | H | -0.33286100 | 0.87138800 | 0.28193900 |
| SA ($H_2SO_4$)  | O | 0.34280400 | -0.83719600 | 1.21003800 |
| | S | -0.00006400 | -0.14510000 | 0.00134000 |
| | O | -0.34281500 | -0.86024000 | -1.19387200 |
| | O | 1.16938600 | 0.82822300 | -0.41933700 |
| | O | -1.16936100 | 0.83610400 | 0.40353600 |
| | H | 1.55729900 | 1.29610600 | 0.34281000 |
| | H | -1.55638700 | 1.29035900 | -0.36716300 |
| Ammonia-SA  | N | -2.82058139 | 0.04172822 | -0.01344340 |
| | H | -3.32062059 | 0.93166890 | 0.01895758 |
| | H | -2.29066666 | -0.09317162 | 0.85505341 |
| | H | -3.48675931 | -0.72088968 | -0.14316900 |
| | O | -0.23287468 | -0.18475968 | 1.22290621 |
| | S | 0.57427981 | -0.11617529 | 0.00202177 |
| | O | 1.60279487 | -1.14695737 | -0.10983878 |
| | O | 1.35135196 | 1.29256417 | 0.18796022 |
| | O | -0.24042152 | 0.03164637 | -1.21639235 |
| | H | 1.93542634 | 1.45672054 | -0.56888684 |
| | H | -2.12859213 | 0.05243104 | -0.77728205 |

# Reference


1 j. a. riddick, w. b. bunger and t. k. sakano, organic solvents physical properties and methods of purification (techniques of chemistry.), *wiley-interscience*, 1970.

2 m. t. c. martins-costa, j. m. anglada, j. s. francisco and m. f. ruiz-lopez, reactivity of volatile organic compounds at the surface of a water droplet, *Journal of the American Chemical Society*, 2012, **134**, 11821-11827.