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Zhong-Quan Wang, Yi-Rong Liu, Chun-Yu Wang, Shuai Jiang, Ya-Juan Feng, Teng Huang, Wei Huang

PII: S1352-2310(21)00380-0

DOI: https://doi.org/10.1016/j.atmosenv.2021.118558

Reference: AEA 118558

To appear in: Atmospheric Environment

Received Date: 11 March 2021

Revised Date: 19 May 2021

Accepted Date: 14 June 2021

Please cite this article as: Wang, Z.-Q., Liu, Y.-R., Wang, C.-Y., Jiang, S., Feng, Y.-J., Huang, T., Huang, W., Multicomponent nucleation of malonic acid involved in the sulfuric acid - dimethylamine system and its atmospheric implications, *Atmospheric Environment*, https://doi.org/10.1016/j.atmosenv.2021.118558.

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# **CRediT** authorship contribution statement

**Zhong-Quan Wang:** Conceptualization, Methodology, Data curation, Writing - original draft, Writing - review & editing. **Yi-Rong Liu:** Methodology, Validation, Formal analysis, Writing - review & editing. **Chun-Yu Wang:** Formal analysis, Data curation. **Shuai Jiang:** Software, Investigation, Visualization. **Ya-Juan Feng:** Visualization. **Teng Huang:** Resources. **Wei Huang:** Methodology, Software, Supervision, Project administration, Funding acquisition.

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# Multicomponent nucleation of malonic acid involved in the sulfuric

# acid - dimethylamine system and its atmospheric implications

Zhong-Quan Wang<sup>a, b, c</sup>, Yi-Rong Liu<sup>b, \*\*</sup>, Chun-Yu Wang<sup>b</sup>, Shuai Jiang<sup>b</sup>, Ya-Juan

Feng<sup>b</sup>, Teng Huang<sup>a</sup> and Wei Huang<sup>a, b, d, \*</sup>

<sup>a</sup>Laboratory of Atmospheric Physico-Chemistry, Anhui Institute of Optics & Fine Mechanics, Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei, Anhui, 230031, China.
<sup>b</sup>School of Information Science and Technology, University of Science and Technology of China, Hefei, Anhui, 230026, China.

<sup>c</sup>Department of Physics, Huainan Normal University, Huainan, Anhui, 232001, China

<sup>d</sup>Center for Excellence in Urban Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen, Fujian, 361021, China

Email addresses: yrliu@ustc.edu.cn (Y.R. Liu), huangwei6@ustc.edu.cn (W. Huang).

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### ABSTRACT

Malonic acid (MOA) is one of the main dicarboxylic acids in 2 aerosols. Some field observations and experiments have revealed that 3 malonic acid may be involved in new particle formation (NPF) events. 4 However, there are few reports on the mechanism of atmospheric cluster 5 formation involving MOA. In this study, high-precision quantum 6 chemical calculations and dynamics simulations were used to investigate 7 the mechanism by which MOA participates in a sulfuric acid (SA) -8 dimethylamine (DMA) multicomponent system. The most stable 9 molecular structures show that MOA can form relatively stable clusters 10 with the SA-DMA system by hydrogen bonding and proton-transfer 11 interactions. Compared with the results of the CERN-CLOUD 12 experiments, the formation rate of the SA-MOA-DMA system is between 13 those of SA-DMA-W and SA-NH<sub>3</sub>-W systems at high concentration of 14 DMA. This means that nucleation of the ternary SA-MOA-DMA system 15 cannot be ignored in atmospheric aerosol nucleation. It was also found 16 that temperature was crucial to the formation rate of the SA-MOA-DMA 17 system. The strong inverse relationship of the formation rate and 18 temperature indicates that if the temperature decreases the ternary 19 SA-MOA-DMA system becomes increasingly important in NPF events. 20

Keyword: Nucleation mechanism; Proton transfer; Evaporation rate;
Atmospheric relevance

### 23 **1. Introduction**

Atmospheric aerosols have a significant impact on many processes, 24 influencing the weather, cloud formation, health quality and so on 25 (Kulmala, 2003; Kulmala et al., 2004; Oberdörster and Utell, 2002; 26 Saxon and Diaz-Sanchez, 2005; Zhang et al., 2007). New particle 27 formation contributes to the large amount of atmospheric aerosols. Thus, 28 the formation and growth mechanisms of NPF are key research topics in 29 atmospheric chemistry (Temelso et al., 2012; Wang et al., 2010; Yue et 30 al., 2010; Zhang, 2010). Sulfuric acid has been considered the key species 31 in atmospheric aerosol formation. Many experimental and theoretical 32 studies have been carried out to explain the nucleation of sulfuric acid 33 and water from a molecular point of view (Kirkby et al., 2011; 34 Kupiainen-Määttä et al., 2013; Loukonen et al., 2010; Yue et al., 2010; 35 Zhang, 2010; Zhao et al., 2011). However, those studies do not 36 sufficiently explain nucleation events at low SA concentrations, which 37 are typically at the ppt level (Kulmala et al., 2004; Zhang et al., 2012). 38 Therefore, other atmospheric components, including organic acids 39 (Arquero et al., 2017b; Chen et al., 2017b; Xu et al., 2010; Zhang et al., 40 2004; Zhao et al., 2020), amines (Chen et al., 2012; Jen et al., 2014; Miao 41 et al., 2018), aldehydes (Kurtén et al., 2015), and highly oxidized 42 multifunctional organic molecules (HOMs) (Bianchi et al., 2016; Kirkby 43 et al., 2011; Ortega et al., 2016), have been considered to take part in 44

45 NPF.

Amines involved in NPF have been reported in experimental and 46 theoretical research. It was found that amines play an important role in 47 atmospheric conditions. The global emissions of typical amines 48 approximately  $83 \pm 26$  Gg N a<sup>-1</sup> for methylamine (MA),  $33 \pm 19$  Gg N a<sup>-1</sup> 49 for dimethylamine (DMA), and  $169 \pm 33$  Gg N a<sup>-1</sup> for trimethylamine 50 (TMA) (Schade and Crutzen, 1995). Jen et al. found that basic gases such 51 as ammonia and amines stabilize sulfuric acid clusters (Jen et al., 2014; 52 Xie et al., 2017). The base concentrations play an important role in the 53 formation of sulfuric acid clusters, suggesting NH<sub>3</sub><MA<TMA≤DMA in 54 formation of stabilized sulfuric acid dimers (Chen et al., 2016). 55 Laboratory studies and observations have found that amines have a 56 substantial effect on new particle formation, which enhances neutral and 57 ion-induced sulfuric acid-water nucleation (Kupiainen-Määttä et al., 2013; 58 Loukonen et al., 2010; Yao et al., 2018; Zhao et al., 2011). 59

In recent years, increasing number of theoretical studies have confirmed the role of organic acids in atmospheric aerosol nucleation (Arquero et al., 2017a; Chen et al., 2017a; Deshmukh et al., 2018; Liu et al., 2017; Wen et al., 2019). The thermochemistry of the nucleation process is mainly demonstrated by the strong hydrogen bonding between the organic acids and the atmospheric nucleation precursors (Han et al., 2018; Hong et al., 2018; Miao et al., 2018; Xu and Zhang, 2012; Zhang et

al., 2018b). However, the detailed dynamic process and the corresponding 67 mechanism of new particle formation involving organic acids are still 68 unclear. In addition, the action mechanisms of organic acids with 69 different functional groups and properties in NPF are also different 70 (Zhang et al., 2004). Therefore, the structure, formation rate and 71 participation mechanism of organic acids in atmospheric clusters need to 72 be determined. Dicarboxylic acids (Arquero et al., 2017a; Peng et al., 73 2015; Xu and Zhang, 2012), which have relatively low vapor pressures, 74 are expected to participate in nucleation. In particular, malonic acid 75 (MOA) is an important dicarboxylic acid in the atmosphere. Experimental 76 and theoretical results show that malonic acid is much stronger than 77 oxalic acid and succinic acid, and is even stronger than nitric acid in the 78 gas phase (Ezell et al., 2010). Deshmukh et al. (Deshmukh et al., 2018) 79 found that oxalic acid was dominant, followed by malonic acid and 80 succinic acid in Alaskan aerosols. The concentration of malonic acid was 81 between 1.52 and 35.3 ppt. Hoque et al. (Hoque et al., 2015) also 82 measured malonic acid in the North Pacific, to have a concentration 83 between 2.6 and 37.4 ppt. Kawamura et al. (Kawamura et al., 2013) 84 observed the high abundances of water-soluble dicarboxylic acids in the 85 mountaintop aerosols over the North China Plain during wheat burning 86 season. The concentration of malonic acid was between 7.4 and 475 ng 87 cm<sup>-3</sup>. Fang et al. (Fang et al., 2020) reported the observational evidence 88

for the involvement of dicarboxylic acids (diacids) in particle nucleation 89 at a rural site of the North China Plain in winter. They propose that 90 diacids could actively participate in particle nucleation and may dominate 91 the initial steps under high [diacids]/[SA] ratios. The concentrations of 92 gaseous MOA was estimated to be in the range from 6.0  $\times$  10  $^7$  to 3.5  $\times$ 93  $10^9$  cm<sup>-3</sup>. Zhang et al. (Zhang et al., 2018a) reported the potential role of 94 malonic acid in the formation of atmospheric sulfuric acid - ammonia 95 They found that MOA can sufficiently clusters. enhance the 96 intermolecular interaction between SA and NH<sub>3</sub> at 218 K. Despite the 97 large amount of MOA, the atmospheric properties of MOA are poorly 98 understood. In particular, the contribution of MOA to atmospheric 99 nucleation with DMA is not clear. 100

In this paper, the role of malonic acid in NPF and the formation mechanism of malonic acid, sulfuric acid and dimethylamine clusters are studied by density functional theory combined with the Atmospheric Clusters Dynamic Code. The structures and thermodynamics of the (SA)<sub>x</sub>(MOA)<sub>y</sub>(DMA)<sub>z</sub> ( $0 \le x, y, z \le 3$ ) clusters are calculated. The formation rate of the SA-MOA-DMA system is calculated by the ACDC simulation, and the influence of temperature on the formation rate is also analyzed.

108 2. Methods

To obtain the most reliable structure for the  $(SA)_x(MOA)_y(DMA)_z$ (0 $\leq$ x,y,z $\leq$ 3) system, we follow a three-step procedure. First, the initial

geometries were obtained using the Basin-Hopping (BH) algorithm 111 (Huang et al., 2010; Wales and Doye, 1997; Yoon et al., 2007) coupled 112 with semiempirical PM7 (Hostaš et al., 2013) implemented in 113 MOPAC2016 (Wales and Doye, 1997). This method has been used to 114 effectively search molecular clusters (Liu et al., 2014; Lv et al., 2015; 115 Wang et al., 2019; Xu et al., 2020). In this method, a new configuration 116 was generated by the random displacement of the molecules in the 117 clusters with different Boltzmann temperatures (ranging from 3000 to 118 6000 K) for funnel sampling. For each cluster size, 4000 sample 119 structures were generated by 5 separate BH searches at the Boltzmann 120 temperature. Then, the sample structures were optimized to the local 121 minimum by the PM7 method. Next, 40 low-energy geometries were 122 selected for optimization. The initial geometries were optimized with the 123 PW91PW91/6-311+G level of theory. Then, the stable isomers within 10 124 kcal mol<sup>-1</sup> of the lowest binding energy were optimized at the 125 PW91PW91/6-311++G(2d,2p) level. For each stationary point, frequency 126 calculations were executed to ensure that there were no imaginary 127 frequencies. Geometry and frequency calculations were performed using 128 the Gaussian 09 program (Frisch et al., 2016). Based on the optimized 129 single-point calculated geometries, the energies were at the 130 RI-MP2/cc-pVTZ level of theory using the Orca 4.0 (Charlson et al., 131 2001; Peterson et al., 2008; Yousaf and Peterson, 2008) suite of 132

133 programs.

The PW91PW91 method has been used to describe the binding 134 energies of molecular clusters with both acid-acid and acid-base 135 interactions. In order to make sure the results are consistent, another four 136 methods (B3LYP, M02-2X,  $\omega$ B97XD and MP2) are performed for the 137 smallest clusters. The results are list in Table S1. It is obviously that the 138 results of PW91PW91 is close to that of MP2. For the  $(SA)_1(DMA)_1$ 139 cluster, the Gibbs free energy change is -11.80 kcal mol<sup>-1</sup>, which is close 140 to -11.38 kcal mol<sup>-1</sup> reported by Nadykto et al. (Nadykto et al., 2011). The 141 Gibbs free energy change is -7.42 kcal mol<sup>-1</sup> for the (SA)<sub>1</sub>(MOA)<sub>1</sub> cluster, 142 which is close to -7.24 kcal mol<sup>-1</sup> reported by Zhang et al. (Zhang et al., 143 144 2018a).

The Atmospheric Cluster Dynamics Code (ACDC) simulation (McGrath et al., 2012) was used to investigate nucleation and the corresponding mechanism. The birth-death equations can be written as:

148 
$$\frac{dc_i}{dt} = \frac{1}{2} \sum_{j < i} \beta_{j,(i-j)} c_j c_{(i-j)} + \sum_j \gamma_{(i+j) \to i} c_{i+j} - \sum_j \beta_{i,j} c_i c_j - \frac{1}{2} \sum_{j < i} \gamma_{i \to j} c_i + Q_i - S_i$$
(1)

where  $c_i$  is the concentration of cluster i,  $\beta_{ij}$  is the collision coefficient of clusters i with j, and  $\gamma_{(i+j)\rightarrow i}$  is the evaporation coefficient of cluster i+j evaporating into clusters i and j.  $Q_i$  is the possible additional source of cluster i, and  $S_i$  is the sink term of cluster i.

Hard sphere collisions were used to calculate the collision coefficients, and the evaporation coefficient was calculated as the Gibbs free energy of the cluster formation.

$$\gamma_{(i+j)\to i} = \beta_{ij} \frac{c_i^e c_j^e}{c_{i+j}^e} = \beta_{ij} c_{\text{ref}} \exp\left(\frac{\Delta G_{i+j} - \Delta G_i - \Delta G_j}{k_b T}\right)$$
(2)

where  $\beta_{ij}$  is the collision coefficient between clusters *i* and *j*,  $c_i^e$  is the equilibrium concentration of cluster *i*,  $\Delta G$  is the Gibbs free energy for the formation of cluster *i*, and  $c_{ref}$  is the monomer concentration of the reference vapor corresponding to a pressure of 1 atm at which the Gibbs free energies were determined.

### 163 **3. Results and discussion**

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# 164 **3.1** Cluster structures and proton transfer parameters

In the calculation, there were a total of 58 clusters in the (SA)<sub>x</sub>(MOA)<sub>y</sub>(DMA)<sub>z</sub> ( $0 \le x, y, z \le 3$ ) system. All of the Cartesian coordinates of the most stable structures are list in the supplementary data.

The global minima for the binary clusters  $(MOA)_x(DMA)_y$ , (SA)<sub>x</sub>(MOA)<sub>y</sub> and  $(SA)_x(DMA)_y$  ( $1 \le x, y \le 3$ ) are displayed in Fig. 1. For the  $(MOA)_1(DMA)_1$  cluster, no proton transfer occurs, and an N····H-O hydrogen bond with a distance of 1.554 Å is formed to stabilize the cluster. When MOA and DMA are added to the dimer form (MOA)<sub>2</sub>(DMA)<sub>2</sub> and (MOA)<sub>3</sub>(DMA)<sub>3</sub> clusters, proton transfer occurs in

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the two clusters; thus,  $[H_3C_3O_4]^{-}[HCH_3NCH_3]^{+}$  ion pairs are formed. For the SA-MOA complex, the intermolecular interactions between SA and MOA molecules occur via hydrogen bonding. Moreover, proton transfer occurs in all of the SA-DMA complexes. The hydroxyl of SA transfers to the nitrogen of DMA, forming an  $[HSO4]^{-}[HCH_3NCH_3]^{+}$  ion pairs.



Fig. 1. The most stable structures of the binary  $(MOA)_x(DMA)_y$ , (SA)<sub>x</sub>(MOA)<sub>y</sub> and  $(SA)_x(DMA)_y$  ( $1 \le x, y \le 3$ ) clusters calculated at the PW91PW91/6-311++G (2d, 2p) level.

Fig. 2 shows the geometries of the global minima for the (SA)<sub>x</sub>(MOA)<sub>y</sub>(DMA)<sub>z</sub> ( $1 \le z \le x+y \le 3$ ) clusters. MOA molecules can form relatively stable clusters with the SA-DMA system by hydrogen bonding and proton-transfer interactions. For all of the stable

conformations of the clusters, the structure gradually changes from a 188 cyclic ring structure to cage structures as the number of molecules 189 increases. SA and MOA molecules can transfer a hydroxyl group to the 190 nitrogen of DMA. forming [HSO4]<sup>-</sup>[HCH<sub>3</sub>NCH<sub>3</sub>]<sup>+</sup> and 191  $[H_3C_3O_4]^{-}[HCH_3NCH_3]^{+}$  ion pairs. Thus, the MOA molecule can be 192 similar to the SA molecule in providing protons to DMA. 193



Fig. 2. The most stable structures of  $(SA)_x(MOA)_y(DMA)_z$   $(1 \le z \le x+y) \le 3$  clusters calculated at the PW91PW91/6-311++G (2d, 2p) level.

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Proton transfer is very important for stabilizing clusters. The proton transfer parameter  $\rho_{PT}$  is used to discuss the degree of proton transfer in the hydrogen bond (Hunt et al., 2003; Kurnig and Scheiner, 1987). In addition, based on the distance between atoms, the degree of ionization is evaluated. Hydrogen bond shortening and covalent hydrogen bond prolongation of the acid are used to measure the degree of proton transfer. The formula is as follows:

204 
$$\rho_{\rm PT} = (r_{\rm OH} - r_{\rm OH}^0) - (r_{\rm H\cdots N} - r_{\rm H\cdots N}^0)$$
(3)

where  $r_{\rm OH}$  and  $r_{\rm OH}^0$  are the O-H distance in MOA or SA and the O-H 205 distance in the free monomer, respectively, and  $r_{H\cdots N}^0$  and  $r_{H\cdots N}^0$  are the 206 hydrogen bond distances in the MOA-DMA or SA-DMA clusters and the 207 H-N distances in the fully protonated DMA, respectively. For a hydrogen 208 bonded cluster, the first term is approximately zero, and  $\rho_{\rm PT}$  is negative. 209 For a cluster with protons completely transferred to dimethylamine, the 210 second term is zero and  $\rho_{\rm PT}$  is positive. The value of  $\rho_{\rm PT}$  is close to 211 zero, which means that the proton sharing between the acid and base is 212 equal. 213

Table 1 The proton-transfer parameter ( $\rho_{PT}$ , Å) and the total number of proton transfers (n) for the  $(SA)_x(MOA)_y(DMA)_z$  ( $1 \le z \le x+y \le 3$ ) clusters. The proton donor and acceptor are also list.

	r	r	0	Proton	n
Clusters	<b>и</b> ОН	<b>и</b> <sub>N-Н</sub>	$ ho_{ ext{PT}}$	donor	
$(SA)_1(MOA)_1(DMA)_1$	1.594	1.070	0.577	SA	1
$(SA)_1(MOA)_1(DMA)_2$	1.685	1.056	0.682	SA	2
	1.565	1.089	0.528	MOA	
$(SA)_1(MOA)_2(DMA)_1$	1.660	1.058	0.655	SA	1
$(SA)_1(MOA)_2(DMA)_2$	1.684	1.058	0.679	SA	2
	1.554	1.090	0.516	MOA	
$(SA)_1(MOA)_2(DMA)_3$	1.646	1.063	0.636	SA	3
	1.589	1.085	0.556	MOA	
	1.537	1.094	0.495	MOA	
$(SA)_2(MOA)_1(DMA)_1$	1.668	1.062	0.658	SA	1
$(SA)_2(MOA)_1(DMA)_2$	1.673	1.058	0.667	SA	2
	1.707	1.057	0.702	MOA	
$(SA)_2(MOA)_1(DMA)_3$	1.723	1.053	0.723	SA	3
	1.690	1.053	0.690	SA	
	1.675	1.064	0.663	MOA	

Table 1 shows the value of for the 217 ternary  $ho_{ ext{PT}}$  $(SA)_x(MOA)_y(DMA)_z$  (1  $\leq z \leq x+y \leq 3$ ) clusters. All of the values are 218 positive, indicating that proton transfer has occurred in all of the clusters. 219 The number of proton transfers depends on the number of base molecules 220 in the cluster. SA is the preferential proton donor molecule in proton 221 transfer. When the number of DMA molecules is larger than the number 222 of the SA molecules in the cluster, are available, the excess DMA 223 molecules can accept the proton from the MOA molecules. Thus, the 224 MOA molecule can act similarly to the SA molecule in providing protons 225 to DMA. 226

# 227 3.2 Thermodynamic data

To effectively evaluate the possibility of formation for the cluster, 228 the formation Gibbs free energies ( $\Delta G$ ) at 298, 278, 268 K are listed in 229 Table S1 in the supplementary material. In addition, the cluster formation 230 Gibbs free energy values at 278 K are shown in Fig. 3, where A refers to 231 SA, m is the number of SA molecules, B refers to DMA and n is the 232 number of DMA molecules. The different colors represent the number of 233 MOA molecules. It can be seen that with the same number of DMA 234 molecules, an increase in MOA molecules causes the  $\Delta G$  to decrease. 235



236

Fig. 3. Formation free energies ( $\Delta G$ , kcal mol<sup>-1</sup>) of the A<sub>m</sub>B<sub>n</sub> clusters (A = SA, B = DMA, 0 $\leq$ x, y $\leq$ 3) with the number of MOA molecules set from zero to three at 278 K at the PW91PW91/6-311++G (2d, 2p) level of theory.

At low sulfuric acid concentrations, there are more base molecules than sulfuric acid molecules in the actual atmosphere, and a large number of  $(SA)_n(DMA)_m$  (1 $\leq$ n<m) clusters can be formed. However, these clusters are too unstable to grow into larger clusters. To promote the stability of the clusters, more acidic molecules are required to provide protons. In Fig. 3, it can be seen that with the addition of one to three MOA molecules to the A1B2, A1B3, and A2B3 clusters, the cluster

formation Gibbs free energies decrease rapidly. This is because the MOA molecules can provide protons for the excess DMA molecules and form hydrogen bonds with the SA molecules. Thus, additional MOA molecules can saturate the interaction sites of the  $(SA)_n(DMA)_m$  (1 $\leq$ n<m) clusters and promote the stability of the clusters.



# 253 **3.3 Evaporation rates**

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Fig. 4. The total evaporation rates for the  $(SA)_x(MOA)_y(DMA)_z$  ( $0 \le x, y, z \le 3$ ) clusters with different SA numbers on the MOA-DMA grid at 278 K at the PW91PW91/6-311++G (2d, 2p) level.

In the atmosphere, it is not enough to consider only the free energy of cluster formation ( $\Delta G$ ) to evaluate whether the clusters can grow into larger stable clusters. In some cases, the collision and evaporation rates

can be used to infer the stability of clusters. These rates mainly depends 261 on the collision rate constant and the concentration of the acid-base 262 molecules. The total evaporation rates for the  $(SA)_x(MOA)_y(DMA)_z$  (1  $\leq$ 263 x, y,  $z \le 3$ ) clusters with different SA numbers on the MOA-DMA grid at 264 278 K are shown in Fig. 4. The evaporation rate for most clusters without 265 the SA molecule is larger than that for the other three cases containing the 266 SA molecule. This indicates that the SA molecule can enhance the 267 nucleation ability of the MOA-DMA complex. It is also obvious that the 268 clusters with the same number of acid and base molecules have low 269 evaporation rates. 270



Fig. 5. The total evaporation rates for the  $(SA)_1(DMA)_2$ , (SA)<sub>1</sub>(DMA)<sub>3</sub> and  $(SA)_2(DMA)_3$  clusters with different MOA numbers at

274 278 K at the PW91PW91/6-311++G (2d, 2p) level.

When the number of base molecules is larger than the number of 275 acid molecules, the evaporation rates increase significantly. The main 276 evaporation pathway is evaporates the DMA molecule from the cluster. 277 Therefore,  $(SA)_n(DMA)_m$  (1 $\leq n < m$ ) clusters cannot exist and grow in an 278 actual atmosphere with low a sulfuric acid concentration. Thus, more acid 279 molecules are required to stabilize these clusters. As shown in Fig. 5, 280 when MOA molecules are added to the  $(SA)_1(DMA)_2$ ,  $(SA)_1(DMA)_3$  and 281  $(SA)_2(DMA)_3$  clusters, the evaporation rates decrease rapidly. For the 282  $(SA)_1(DMA)_3$  cluster, the evaporation rate is  $1.86 \times 10^6$  s<sup>-1</sup>. With the 283 addition MOA molecules, the evaporation two rate of the 284  $(SA)_1(MOA)_2(DMA)_3$  cluster is  $4.11 \times 10^1$  s<sup>-1</sup>. Moreover, the evaporation 285 rates of the  $(SA)_2(DMA)_3$  and  $(SA)_2(MOA)_1(DMA)_3$  clusters are 286  $6.55 \times 10^6$  and 2.94 s<sup>-1</sup>, respectively. Thus, the MOA molecule can 287 stabilize the SA-DMA cluster when there are more DMA molecules than 288 SA molecules. 289

### 290 3.4 Atmospheric Cluster Dynamics Simulation

The formation rate of clusters is an important parameter of NPF. The ACDC simulation is carried out under a range of atmospheric precursor concentrations to calculate the formation rate (*J*) of the SA-MOA-DMA system. The simulation system is a " $3 \times 3 \times 3$  box", where 3 is the

maximum number of acid or amine molecules in the cluster. The 295 maximum cluster size is approximately 1.1 nm. In the ACDC simulations, 296 some clusters stable enough will grow out of the studied system. These 297 clusters can be taken into account to contribute to the clusters' formation 298 rate. The simplest way to check if the "box size" is sufficiently large is to 299 compare the ratio of the collision and evaporation rates of the clusters at 300 the boundary of the "box" included in the simulation (Besel et al., 2020). 301 If this ratio is >> 1 for at least some of the clusters, then the 3 x 3 x 3 box 302 size is sufficiently large. Table S3 list the ratio of the collision and 303 evaporation rates of the clusters at the boundary of the "box". The 304 condensation sink coefficient is set to a constant value of  $1.5 \times 10^{-3}$  s<sup>-1</sup>, and 305 variations between  $1.0^{-3}$  s<sup>-1</sup> and  $5 \times 10^{-3}$  s<sup>-1</sup> are unlikely to affect the main 306 conclusions. 307



308

Fig. 6. Formation rates of the SA-MOA-DMA system vs 309 the concentration of SA and comparison with SA-W, SA-NH<sub>3</sub>-W and 310 SA-DMA-W in the CERN-CLOUD experiments at 278 K. The CLOUD 311 data is measured with [DMA]=5 - 140 ppt and [NH3]=2 - 250 ppt. The 312 curve 1 is the theoretical expectations of SA-DMA complex with 313 [DMA]=50 ppt. The yellow bands corresponds to the formation rates of 314 SA-DMA with the concentration of DMA range from 5 to 140 ppt. The 315 blue bands corresponds to the formation rates of SA-MOA-DMA with 316 [MOA]=10 and [DMA]=5 ppt to [MOA]=30 and [DMA]=140 ppt. The 317 curve 2, 3, 4 corresponds to the formation rates of SA-MOA-DMA with 318 different concentration of MOA and DMA. 319



Fig. 6 shows the formation rate as a function of the SA concentration

at 278 K. The measured formation rates of SA-W, SA-NH<sub>3</sub>-W and 321 SA-DMA-W in the CERN-CLOUD experiments (Almeida et al., 2013) 322 are also show in Fig. 6. The CLOUD data is measured with [DMA] = 5 - 100323 140 ppt and  $[NH_3] = 2 - 250$  ppt. For the SA-DMA system, the 324 simulation system is a " $5 \times 5$  box", where 5 is the maximum number of 325 acid or amine molecules in the cluster. The curve 1 is the theoretical 326 expectations of SA-DMA system with [DMA] = 50 ppt. The yellow 327 bands corresponds to the formation rates of SA-DMA with the 328 concentration of DMA range from 5 to 140 ppt. The results of theoretical 329 simulation are in agreement with the experimental results. The blue bands 330 corresponds to the formation rates of SA-MOA-DMA with [MOA] = 5331 and [DMA]=5 ppt to [MOA]=30 and [DMA]=140 ppt. The curve 2, 3, 4 332 corresponds to the formation rates of SA-MOA-DMA with different 333 concentration of MOA and DMA. It is obvious that the formation rate of 334 SA-MOA-DMA is lower than that observed in the SA-NH<sub>3</sub>-W 335 experiments at low concentration of MOA and DMA. At high 336 concentration of DMA, the formation rate of the SA-MOA-DMA system 337 is between those of SA-DMA-W and SA-NH<sub>3</sub>-W systems. In addition, 338 the linear slope of nucleation rate of the SA-MOA-DMA system is lower 339 than that of the SA-DMA system. Compared with the formation rate of 340 CERN-CLOUD experiments which correspond to a cluster size of 1.7 nm, 341 the formation rate for the smaller size may be overestimated. 342



343

Fig. 7. Formation rates of the SA-MOA-DMA system vs the concentration of SA at temperatures of 288, 283, 278, 273 and 268 K.

Temperature is crucial to new particle formation in the atmosphere 346 (Dunne et al., 2016). Many experimental (Chen et al., 2017a) and 347 theoretical (Lu et al., 2020; Zhang et al., 2018a) results show that low 348 temperature is a key factor for fast cluster formation. This is because the 349 Gibbs free energy of the formation of clusters becomes more negative 350 when the temperature decreases. Therefore, it becomes difficult to 351 evaporate the monomer or cluster from the system, leading to an increase 352 in the formation rate of larger clusters. Thus, the effect of temperature 353 (when T is 288, 283, 278, 273 and 268 K) on the formation rate of the 354

SA-MOA-DMA system was studied. The results are shown in Fig. 7. 355 Notably, as the temperature decreases, the formation rate of the 356 SA-MOA-DMA system increases significantly. Specifically, when the 357 concentration of SA ranges from  $10^6$  to  $10^9$  molecules cm<sup>-3</sup>, the formation 358 rate varies between  $10^{-7}$  and  $10^{0}$  cm<sup>-3</sup> s<sup>-1</sup> at 288 K, and varies between  $10^{0}$ 359 and  $10^5$  cm<sup>-3</sup> s<sup>-1</sup> at 268 K. Therefore, the formation rate at 268 K is  $10^5$  to 360  $10^7$  times higher than that at 288 K. The strong inverse relationship of the 361 formation rate and temperature indicates that if the temperature decreases, 362 for example, in the winter, the ternary SA-MOA-DMA system becomes 363 increasing important in NPF events. 364

In summary, the SA-MOA-DMA system can take part in new particle formation. The formation rate of SA-MOA-DMA is between that of SA-DMA-W and SA-NH<sub>3</sub>-W at 278 K at high concentration of DMA. As the temperature decreases, the formation rate of SA-MOA-DMA noticeably increases. This indicates that the SA-MOA-DMA system may play an important role in NPF events in the winter.

**4.** Conclusions

In this paper, the mechanism by which MOA participate in the formation of an atmospheric SA-DMA system was investigated. The low-lying structures and thermodynamics were optimized at the PW91PW91/6-311++G(2d,2p) level. The single-point energies were calculated at the RI-MP2/cc-pVTZ level of theory. In all of the stable

conformations of the ternary SA-MOA-DMA clusters, the SA, DMA and
MOA molecules form cyclic ring structures through hydrogen bonding.
Proton transfer occurs in all of the ternary SA-MOA-DMA clusters. The
MOA molecule is similar to the SA molecule in providing protons to
DMA.

The ACDC simulation indicates that MOA can participate in the 382 formation of the atmospheric SA-DMA system. The formation rate of 383 SA-MOA-DMA is between that of SA-DMA-W and SA-NH<sub>3</sub>-W at 278 384 K at high concentration of DMA. In addition, the influence of 385 temperature on the formation rate was analyzed. As the temperature 386 decreases, the formation rates increase, which corresponds to the 387 phenomenon that haze in winter is more serious than in summer. This 388 indicates that the SA-MOA-DMA system may play an important role in 389 NPF events in the winter. 390

This work provides a readily available method for understanding the mechanism by which MOAs participant in the formation of atmospheric SA-DMA systems. To study the possible reactions under atmospheric conditions, further field observations, theoretical calculations and experimental research are needed.

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# 397 CRediT authorship contribution statement

398 Zhong-Quan Wang: Conceptualization, Methodology, Data curation,

Writing - original draft, Writing - review & editing. Yi-Rong Liu:
Methodology, Validation, Formal analysis, Writing - review & editing.
Chun-Yu Wang: Formal analysis, Data curation. Shuai Jiang: Software,
Investigation, Visualization. Ya-Juan Feng: Visualization. Teng Huang:
Resources. Wei Huang: Methodology, Software, Supervision, Project
administration, Funding acquisition.

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### 406 Acknowledgments

This work was supported by the National Key Research and 407 Development Program (Grant No. 2016YFC0202203), the National 408 Natural Science Foundation of China (Grant Nos. 41775122, 41605099, 409 41705097, 41705111, 41877305 and 41527808), the National Science 410 Fund for Distinguished Young Scholars (Grant No. 41725019), the Key 411 of Frontier Research Program Science, CAS (Grant No. 412 QYZDB-SSW-DQC031), the National Research Program for Key Issues 413 in Air Pollution Control (DQGG0103) and the Fundamental Research 414 Funds for the Central Universities (Grant No. WK210000008). 415

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### 417 Appendix A. Supplementary data

418 Supplementary data to this article can be found online at 419 https://doi.org/10.1016/j.atmosenv.xxxx.xxxxx.

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### HIGHLIGHTS

- 1. MOA may play an important role in particle formation and growth.
- 2. The MOA molecule is similar to the SA molecule in providing protons to DMA.
- 3. Formation rates are negatively correlated with temperature.

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# **CONFLICTS OF INTEREST**

There are no conflicts of interest to declare.

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