Reaction of SO_3 with H_2SO_4 and Its Implication for Aerosol Particle Formation in the Gas Phase and at the Air-Water Interface

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Abstract

The reactions between SO_3 and atmospheric acids are indispensable in improving the formation of aerosol particle. However, relative to those of SO_3 with organic acids, the reaction of SO_3 with inorganic acids has not received much attention. Here, we explore the atmospheric reaction between SO_3 and H_2SO_4, a typical inorganic acid, in the gas phase and at the air-water interface by using quantum chemical (QC) calculations and Born-Oppenheimer molecular dynamics simulations. We also report the effect of $H_2S_2O_7$, the product of the reaction between SO_3 and H_2SO_4, on new particle formation (NPF) in various environments by using the Atmospheric Cluster Dynamics Code kinetic model and the QC calculation. The present findings show that the gas phase reactions of SO_3 + H_2SO_4 without and with water molecule are both low energy barrier processes. With the involvement of interfacial water molecules, H_2O-induced the formation of $S_2O_7^{2-}\cdots H_3O^+$ ion pair, HSO_4^- mediated the formation of $HSO_4^-\cdots H_3O^+$ ion pair and the deprotonation of $H_2S_2O_7$ were observed and proceeded on the picosecond time-scale. The present findings suggest the potential contribution of SO_3-H_2SO_4 reaction to NPF and aerosol particle growth as the facts that *i*) $H_2S_2O_7$ can directly participate in H_2SO_4-NH_3-based cluster formation and can present a more obvious enhancement effect on SA-A-based cluster formation; and *ii*) the formed interfacial $S_2O_7^{2-}$ can attract candidate species from the gas phase to the water surface, and thus, accelerate particle growth.

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1. Introduction

Sulfur trioxide (SO_3) is a major air pollutant (Zhuang and Pavlish, 2012; Chen and Bhattacharya, 2013; Cao et al., 2010; Kikuchi, 2001; Mitsui et al., 2011) and can be considered as the most important oxidation product of SO_2 (Starik et al., 2004). As an active atmospheric species, SO_3 can lead to the formations of acid rain and atmospheric aerosol (Sipilä et al., 2010; Mackenzie et al., 2015; England et al., 2000; Li et al., 2016; Renard et al., 2004) and thus plays a well-documented role in regional climate and human health (Zhang et al., 2012; Pöschl, 2005; Zhang et al., 2015; Pöschl and Shiraiwa, 2015; Haywood and Boucher, 2000; Lohmann and Feichter, 2005). In the atmosphere, the hydrolysis of SO_3 to product H_2SO_4 (SA) is the most major loss route of SO_3 (Morokuma and Muguruma, 1994; Akhmatskaya et al., 1997; Larson et al., 2000; Hazra and Sinha, 2011; Long et al., 2013a; Torrent-Sucarrat et al., 2012; Ma et al., 2020). As a complement to the loss of SO_3, ammonolysis reaction of SO_3 in polluted areas of NH_3 can form H_2NSO_3H, which not only can be competitive with the formation of SA from the hydrolysis reaction of SO_3, but also can enhance the formation rates of sulfuric acid (SA)-dimethylamine ($NH(CH_3)_2$, DMA) clusters by about 2 times. Similarity, the reactions of SO_3 with CH_3OH and organic acids (such as HCOOH) were reported (Liu et al., 2019; Hazra and Sinha, 2011; Long et al., 2012; Mackenzie et al., 2015; Huff et al., 2017; Smith et al., 2017; Li et al., 2018a), and both processes can provide a mechanism for incorporating organic matter into aerosol particles. However, the reaction mechanism between SO_3 and inorganic species are still unclear.

As a major inorganic acidic air pollutant (Tilgner et al., 2021), SA can act as an important role in the new particle formation (Weber et al., 1995; Weber et al., 1996; Weber et al., 2001; Sihto et al., 2006; Riipinen et al., 2007; Sipilä et al., 2010; Zhang et al., 2012) and acid rain (Calvert et al., 1985; Finlayson-Pitts and Pitts Jr, 1986; Wayne, 2000). The source of gas-phase SA is mainly produced by the gas-phase hydrolysis reaction of SO_3. For the direct reaction between SO_3 and H_2O, it takes place hardly in the atmosphere due to high energy barrier (Chen and Plummer, 1985; Hofmann and Schleyer, 1994; Morokuma and Muguruma, 1994; Steudel, 1995). However the addition of a second water molecule (Morokuma and Muguruma, 1994; Larson et al., 2000; Loerting and Liedl, 2000), the hydroperoxyl radical (Gonzalez et al., 2010), formic acid (Hazra and Sinha, 2011; Long et al., 2012) , sulfuric acid (Torrent-Sucarrat et al., 2012), nitric acid (Long et al., 2013a), oxalic acid (Lv et al., 2019) and ammonia (Bandyopadhyay et al., 2017) have been reported to catalyze the formation of SA from the hydrolysis reaction of SO_3 as they can promote atmospheric proton transfer reactions. Similarity, as SA can give out protons more readily than H_2O, which in turn is more conducive to the proton transfer, thus we predict that the addition reaction involving the proton transfer between SO_3 and SA is much easier under atmospheric conditions than that between SO_3 and H_2O. However, this gas-phase reaction has not been investigated as far as we know. Previous studies have shown that the concentration of water vapor decreases significantly with increasing altitude (Anglada et al., 2013), leading to longer atmospheric lifetimes of SO_3. The gas phase reaction of SO_3 with H_2SO_4 may contribute significantly to the loss of SO_3 in dry areas where $[H_2SO_4]$ is relatively high (especially at lower temperatures) and at higher altitude. So, it is important to study the reaction mechanism of SO_3 with H_2SO_4 and its competition with H_2O-assisted hydrolysis of SO_3. Meanwhile, in many gas phase reactions, single water molecule can play a catalyst role by increasing the stability of pre-reactive complexes and reducing the activation energy of transition states (Kanno et al., 2006; Stone and Rowley, 2005; Chen et al., 2014; Viegas and Varandas, 2012, 2016). For example, single water molecule in the $H_2O\cdots HO_2$ + SO_3 reaction can catalyze the formation of HSO_5 (Gonzalez et al., 2010). Thus, it is equally important to study the SO_3 + SA reaction without and with H_2O. In addition to the gas phase reactions, many new atmospheric processes and new reaction pathways have been observed at the air-water interface (Zhong et al., 2017; Kumar et al., 2017; Kumar et al., 2018; Zhu et al., 2016; Li et al., 2016; Zhu et al., 2017). Such as, the organic acids reacting with SO_3 can form the ion pair of carboxylic sulfuric anhydride and hydronium at the air-water interface (Zhong et al., 2019). This mechanism is different from the gas phase reaction in which the organic acid either serves as a catalyst for the hydrolysis of SO_3 or acts as a reactant reacting with SO_3 directly. So, water droplets may play important roles in atmospheric behaviors between SO_3 and SA. Thus, it is also important to study the interfacial mechanism between SO_3 and SA, and to compare its difference with the corresponding gas-phase reaction.

Previous experimental studies (Otto and Steudel, 2001; Abedi and Farrokhpour, 2013) found that disulfuric acid ($H_2S_2O_7$, DSA) is the product of the reaction between SO_3 and SA. From the perspective of structure, DSA possesses two HO functional groups. Both HO groups can act as hydrogen donors and acceptors to interact with atmospheric particle precursors. It has been shown that the reaction between SO_3 and some important atmospheric species (Li et al., 2018a; Yang et al., 2021; Liu et al., 2019; Rong et al., 2020) not only can cause appreciable consumption of SO_3 and thus reduce the abundance of SA from the hydrolysis of SO_3 in the atmosphere, but also can promote NPF process by their products. For example, the products of NH_2SO_3H, $HOOCOOSO_3H$, CH_3OSO_3H and $HOCCOOSO_3H$ from the reactions of SO_3 with NH_3 (Li et al., 2018a), $H_2C_2O_4$ (Yang et al., 2021), CH_3OH (Liu et al., 2019) and HOOCCHO (Rong et al., 2020) all have a catalytic effect on the formation of new particles in aerosols. However, whether DSA produced by the reaction between SO_3 and SA contributes to aerosol formation or not is still unclear. Thus, another main question that we intend to address here is the role of DSA in atmospheric SA-NH_3 (A) nucleation, which have been recognized as dominant precursors in highly polluted areas, especially in some megacities in Asia.

In this work, using quantum chemical calculations and Master Equation, we first studied the gas-phase reaction between SO_3 and SA to product DSA with H_2O acting as a catalyst. Then, we use the Born-Oppenheimer Molecular Dynamic (BOMD) simulations to evaluate the reaction mechanism of SO_3 with SA at the air-water interface. Finally, we used Atmospheric Clusters Dynamic Code (ACDC) and quantum chemical calculations to investigate atmospheric implications of SO_3-SA reaction to the atmospheric particle formation. Particular attention of this work is focused on the study of *i*) the mechanism difference of the SO_3 + SA reaction in the gas phase and at the air-water interface; *ii*) the fate of DSA in atmospheric NPF and its influence at various environmental conditions.

2. Computational Details

2.1 Quantum Chemical Calculation. The M06-2X functional has been proved to be one of the best functionals to describe the noncovalent interactions and estimate the thermochemistry and equilibrium structures for atmospheric reactions (Elm et al., 2012; Mardirossian and Head-Gordon, 2016). So, for the SO_3 + SA reaction without and with water molecule in the gas phase, the optimized geometries and vibrational frequencies of reactants, pre-reactive complexes, transition states (TSs), post-reactive complexes and products were calculated using M06-2X method (Zhao and Truhlar, 2008; Elm et al., 2012) with 6-311++G(2*df*,2*pd*) basis set by Gaussian 09 packages (Frisch, 2009). It is noted that the calculated bond distances and bond angles at the M06-2X/6-311++G(3*df*,2*pd*) level (Fig. S1) agree well with the available experimental values (Kuczkowski et al., 1981). At the same level, the connectivity between the TSs and the suitable pre- and post-reactant complexes was performed by intrinsic reaction coordinate (IRC) calculations. Then, single point energy calculations were calculated at the CCSD(T)-F12/cc-pVDZ-F12 level (Adler et al., 2007; Knizia et al., 2009) by using ORCA (Neese, 2012).

A multistep global minimum sampling technique was used to search for the global minima of the $(DSA)_x(SA)_y(A)_z$ ($z \leq x + y \leq 3$) molecular clusters. Specifically, a multistep global minimum sampling technique was used to search for the global minima of the (SA)*x*(A)*y*(DSA)*z* ($0< y \leq x + z \leq 3$) clusters. Specifically, the initial n*1000 ($1 < n < 5$) configurations for each cluster were systematically generated by the ABCluster program (Zhang and Dolg, 2015), and were optimized at the semi-empirical PM6 (Stewart, 2013) methods using MOPAC 2016 (Stewart, 2013; Stewart, 2007). Then, up to n*100 structures with relatively lowest energy among the n*1000 ($1 < n < 5$) structures were selected and reoptimized at the M06-2X/6-31+G(*d*,*p*) level. Finally, n*10 lowest-lying structures were optimized by the M06-2X/6-311++G(2*df*,2*pd*) level to determine the global minimum. To obtain the reliable energies, single-point energy calculations were refined at the DLPNO-CCSD(T)/aug-cc-pVTZ level based on the optimized geometries at the M06-2X/6-311++G(2*df*,2*pd*) level. The optimized structures and the formation Gibbs free energy of the stable clusters were summarized in Fig. S9 and Table S8 of the *SI Appendix*, respectively.

2.2 Rate constant calculations. Using the Rice-Ramsperger-Kassel-Marcus based Master Equation (ME/RRKM) model (Miller and Klippenstein, 2006), the kinetics for the SO_3 + SA reaction without and with water molecule were calculated by adopting a Master Equation Solver for Multi Energy-well Reactions (MESMER) code (Glowacki et al., 2012). In the MESMER calculation, the rate coefficients for the bimolecular barrierless association step (from reactants to pre-reactive complexes) were evaluated by the Inverse Laplace Transform (ILT) method (Horváth et al., 2020), meanwhile the unimolecular step was performed by the RRKM theory combined with the asymmetric Eckart model. The ILT method and RRKM theory can be represented in Eq (1) and Eq (2), respectively.

$$k^{\infty}(\beta) = \frac{1}{Q(\beta)}\int_0^{\infty} k(E)\rho(E)\exp(-\beta E)dE \quad (1)$$

$$k(E) = \frac{W(E-E_0)}{h\rho(E)} \tag{2}$$

Where h is denoted as Planck's constant; $\rho(E)$ is denoted as the active density of state of the reactant at energy level E; E_0 is denoted as the reaction threshold energy and $W(E\text{-}E_0)$ is denoted as the sum of the rovibrational states of the transition state (TS) geometry (excluding the degree of freedom related to passing the transition state). The input parameters for electronic geometries, vibrational frequencies, and rotational constants were calculated at the M06-2X/6-311++G(2*df*,2*pd*) level and single-point energy calculations were refined at the CCSD(T)-F12/cc-pVDZ-F12 level for the modeling.

2.3 Born-Oppenheimer Molecular Dynamic (BOMD) Simulation. The CP2K code (Hutter et al., 2014) was used in the BOMD simulations. The Becke-Lee-Yang-Parr (BLYP) functional (Becke, 1988; Lee et al., 1988) was chosen to treat with the exchange and correlation interactions, and the Grimme's dispersion was carried out to account for the weak dispersion interaction (Grimme et al., 2010). The Goedecker-Teter-Hutter (GTH) conservation pseudopotential (Goedecker et al., 1996; Hartwigsen et al., 1998) with the Gaussian DZVP basis set (VandeVondele and Hutter, 2007) and the auxiliary plane wave basis set was applied to correct the system valence electrons and the core electrons, respectively. For the plane wave basis set and Gaussian basis set, the energy cut off (Zhong et al., 2017; Zhong et al., 2018; Zhong et al., 2019) were set to 280 and 40 Ry, respectively. For each simulation in the gas phase, a 15 × 15 × 15 $Å^3$ supercell with periodic boundary condition was adopted with a time step of 0.5 fs. As the droplet system with 191 water molecules are sufficient to describe the interfacial mechanism (Zhong et al., 2017), the air-water interfacial system here included 191 water molecules, SO_3 and SA in the BOMD simulation. It is pointed out that the droplet system with 191 water molecules has been equilibrated before SO_3 and H_2SO_4 was added at the water surface. The details of the equilibrium process for the droplet system with 191 water molecules are shown in the *SI Appendix* Part 4. To avoid periodic interactions between adjacent water droplets, the size of the simulation box (Kumar et al., 2017; Kumar et al., 2018; Ma et al., 2020) was set as 35 × 35 × 35 $Å^3$ with a time step of 1.0 fs. Notably, the timestep of 1.0 fs has been proved to achieve sufficient energy conservation for the water system (Zhong et al., 2015; Li et al., 2016; Zhu et al., 2016; Kumar et al., 2017). For all the simulations in the gas phase and at the air-water interface, the Nose-Hoover thermostat (Zhong et al., 2017; Zhong et al., 2018; Zhong et al., 2019; Kumar et al., 2017; Kumar et al., 2018; Ma et al., 2020) was selected the NVT ensemble to control the temperature around 300 K. To eliminate the influence of the initial configuration on the simulation results of interfacial reaction, 40 BOMD simulations for the air-water interface reactions were carried out.

2.4 Atmospheric Clusters Dynamic Code (ACDC) Model

The Atmospheric Cluster Dynamics Code (ACDC) (McGrath et al., 2012) was used to simulate the cluster formation rates and mechanisms of $(DSA)_x(SA)_y(A)_z$ ($z \leq x + y \leq 3$) clusters at different temperatures and monomer concentrations. The thermodynamic data of quantum chemical calculation at the DLPNO-CCSD(T)/aug-cc-pVTZ//M06-2X/6-311++G(2*df*,2*pd*) level of theory can be used as the input of ACDC. The birth-death equation (Eq. 3) for clusters solves the time development of cluster concentrations by numerical integration using the ode15s solver in MATLAB program (Shampine and Reichelt, 1997).

$$\frac{dc_i}{dt} = \frac{1}{2}\sum_{j<i}\beta_{j,(i-j)}C_jC_{(i-j)} + \sum_j \gamma_{(i+j)\rightarrow i}C_{i+j} - \sum_j \beta_{i,j}C_iC_j - \frac{1}{2}\sum_{j<i}\gamma_{i\rightarrow j}C_i + Q_i - S_i \quad (3)$$

Where c_i is the concentration of cluster i; $\beta_{i,j}$ is the collision coefficient between clusters i and j; $\gamma_{(i+j)\rightarrow i}$ is the evaporation coefficient of cluster i+j evaporating into clusters i and j, and Q_i is all other source term of cluster i. (See more details of β and γ in *SI Appendix* Part 4). Besides, a constant coagulation sink coefficient 2×10^{-2} s^{-1} (corresponding to the median observed in contaminated areas) was used for taking into account external losses (Yao et al., 2018; Zhang et al., 2022; Liu et al., 2021b). The boundary conditions in the ACDC require that the smallest clusters outside of the simulated system should be very stable so that not to evaporate back immediately (McGrath et al., 2012). Based on cluster volatilization rate (shown in Table S10) and the formation Gibbs free energy of the clusters (shown in Table S8), the cluster boundary conditions simulated in this study were set as $(SA)_4\cdot(A)_3$, $(SA)_4\cdot(A)_4$, $SA\cdot(A)_3\cdot(DSA)_3$, $(SA)_3\cdot(A)_4\cdot(DSA)_1$ and $(SA)_2\cdot(A)_3\cdot(DSA)_2$. According to field observations, the concentration of SA and A was respectively set in a range of 10^6-10^8 molecules·cm^{-3} and 10^7-10^{11} molecules·cm^{-3} (Almeida et al., 2013; Kuang et al., 2008; Bouo et al., 2011; Zhang et al., 2018). As the prediction in Table S7, the concentration of DSA is set to 10^4-10^8 molecules·cm^{-3}. However, DSA is easily hydrolyzed with abundant water in the troposphere to form H_2SO_4, the concentration of DSA listed in Fig. S9 was overestimated.

So, the maximum concentration of DSA (10^8 molecules·cm^{-3}) was not included in the effect of $H_2S_2O_7$ on new particle formation (NPF) in various environments. Besides, the temperature was set to be 218.15-298.15 K, which span most regions of the troposphere and the polluted atmospheric boundary layer.

3. Results and discussion

3.1 Reactions in the gas phase

The addition reaction involving the proton transfer between SO_3 and SA (Channel DSA) proceeded through the formation of $SO_3\cdots H_2SO_4$ complex followed by unimolecular transformation through transition state TS_{DSA} to form $H_2S_2O_7$ (Fig. 1(a)). The reactant complex $SO_3\cdots H_2SO_4$ was a double six-membered ring complex with a relative Gibbs free energy of -1.6 kcal·mol^{-1}. After the formation of $SO_3\cdots H_2SO_4$ complex, Channel DSA overcame a Gibbs free energy barrier of 2.3 kcal·mol^{-1}, which was lower by 4.2 kcal·mol^{-1} than that of H_2O-catalyzed hydrolysis of SO_3 (Fig. S1). Rate constant for the SO_3 + SA reaction was calculated at various temperatures (Table 1). Within the temperature range of 280-320 K, the rate constants for the SO_3 + SA reaction were calculated to be 2.57×10^{-12}-5.52×10^{-12} cm^3·molecule^{-1}·s^{-1}, which were larger by 3.43-4.03 times than the corresponding values of H_2O-catalyzed hydrolysis of SO_3. Therefore, it can be said that the direct reaction between SO_3 and SA occurs easily under atmospheric conditions.

The $SO_3 + H_2SO_4$ reaction with H_2O produced two distinct products, labeled (*i*) $H_2S_2O_7$ (DSA, Channel DSA_WM) and (*ii*) H_2SO_4 (SA, Channel SA_SA). A single water molecule in (*i*) acted as a catalyst, while it played as a reactant in (*ii*). The schematic potential energy surface for the $SO_3 + H_2SO_4$ reaction with H_2O was shown in Fig. 1. As the probability of simultaneous collision (Pérez-Ríos et al., 2014; Elm et al., 2013) of three molecules of SO_3, SA and H_2O was quite low under realistic conditions, both Channel DSA_WM and Channel SA_SA can be considered as a sequential bimolecular process. In other words, both Channel DSA_WM and Channel SA_SA occurred via the collision between SO_3 (or H_2SO_4) and H_2O to form dimer ($SO_3\cdots H_2O$ and $H_2SO_4\cdots H_2O$) first, and then the dimer encountered with the third reactant H_2SO_4 or SO_3. The computed Gibbs free energies of dimer complexes $SO_3\cdots H_2O$ and $H_2SO_4\cdots H_2O$ were respectively 0.8 kcal·mol^{-1} and -1.9 kcal·mol^{-1}, which were respectively consistent with the previous values (the range from -0.2 to 0.62 kcal·mol^{-1} for $SO_3\cdots H_2O$ complex (Bandyopadhyay et al., 2017; Long et al., 2012) and the range from -1.82 to -2.63 kcal·mol^{-1} for $H_2SO_4\cdots H_2O$ complex (Long et al., 2013b; Tan et al., 2018)). The Gibbs free energy of $H_2SO_4\cdots H_2O$ was lower by 2.7 kcal·mol^{-1} than that of $SO_3\cdots H_2O$, thus leading to that the equilibrium constant of the former complex was larger by 1-2 orders of magnitude than that of the latter one in Table S2. Additionally, the larger equilibrium constant of $H_2SO_4\cdots H_2O$ complex leaded to its higher concentration in the atmosphere. For example, when the concentrations of SO_3 (Yao et al., 2020), H_2SO_4 (Liu et al., 2015) and H_2O (Anglada et al., 2013) were 10^6, 10^8 and 10^{17} molecules·cm^{-3}, respectively, the concentrations of $SO_3\cdots H_2O$ and $H_2SO_4\cdots H_2O$ were 2.41×10^3-2.01×10^4 and 5.01×10^5-3.01×10^8 molecules·cm^{-3} within the temperature range of 280-320 K (see Table S3), respectively. So, we predict that Channel DSA_WM and Channel SA_SA mainly take place via the collision of $H_2SO_4\cdots H_2O$ with SO_3. In order to check this prediction, the effective rate constants for two bimolecular reactions of $H_2SO_4\cdots H_2O$ + SO_3 and $SO_3\cdots H_2O$ + H_2SO_4 were calculated, and the details were shown in *SI Appendix*, Part 3 and Table 1. As seen in Table 1, the $SO_3\cdots H_2O$ + H_2SO_4 reaction in both Channel DSA_WM and Channel SA_SA can be neglected as their effective rate constants were smaller by 16.7-48.5 and 1.02-3.05 times than the corresponding values in the $H_2SO_4\cdots H_2O$ + SO_3 reaction within the temperature range of 280-320 K, respectively. Therefore, we only considered the $H_2SO_4\cdots H_2O$ + SO_3 bimolecular reaction in both Channel DSA_WM and Channel SA_SA.

As for Channel DSA_WM, the $H_2SO_4\cdots H_2O$ + SO_3 reaction occurred in a stepwise process as displayed in Fig. 1(b), which was similar to the favorable routes in the hydrolysis of COS, HCHO and CH_3CHO catalyzed by sulfuric acid (Long et al., 2013b; Li et al., 2018b; Tan et al., 2018). When the $H_2SO_4\cdots H_2O$ complex and SO_3 served as reactants, the reaction was initiated by complex IM_{DSA_WM}' where a van der Waals interaction (S2···O4, 2.75 Å) was found between the O4 atom of SA moiety in $H_2SO_4\cdots H_2O$ and the S atom of SO_3. After complex IM_{DSA_WM}', the ring enlargement from IM_{DSA_WM}' to $SO_3\cdots H_2SO_4\cdots H_2O$ complex occurred through transition state TS_{DSA_WM}' with a Gibbs free energy barrier of 1.2 kcal·mol^{-1}. Complex IM_{DSA_WM} was 6.1 kcal·mol^{-1} lower in energy than IM_{DSA_WM}'. In IM_{DSA_WM}, SO_3 acted as double donors of hydrogen bond to form a cage-like hydrogen bonding network with $H_2SO_4\cdots H_2O$. Then, starting with IM_{DSA_WM} complex, the $H_2SO_4\cdots H_2O$ + SO_3 reaction occurred through transition state TS_{DSA_WM} with a Gibbs free barrier energy of 0.5 kcal·mol^{-1} to form a quasi-planar network complex, $H_2S_2O_7\cdots H_2O$. TS_{DSA_WM} was in the middle of a double proton transfer, where H_2O played as a bridge for proton transfer, along with the simultaneous formation of the O4⋯S2 bond. In order to estimate the catalytic ability of H_2O in the SO_3 + SA reaction, the effective rate constant ($k'_{DSA\_WM\_s}$) of the $H_2SO_4 \cdots H_2O$ + SO_3 reaction were compared with the rate constant (k_{DSA}) of the SO_3 + H_2SO_4 reaction. As seen in Table 1, under the experimental concentration (Anglada et al., 2013) ([H_2O] = 5.20 × 10^{16}-2.30 × 10^{18} molecules·cm^{-3}) within the temperature range of 280-320 K, the calculated $k'_{DSA\_WM\_s}$ was 1.03 × 10^{-11}-4.60 × 10^{-12} cm^3·molecule^{-1}·s^{-1}, which was larger by 1.79-1.86 times than that of k_{DSA}. This result shows that H_2O exerts catalytic role in promoting the rate of the SO_3 + H_2SO_4 reaction.

Regarding Channel SA_SA, the stepwise reaction occurred firstly via the ring enlargement from six-membered ring complex IM_{SA_SA}' to a cage-like hydrogen bonding network IM_{SA_SA}, and then took place by going through a transition state, TS_{SA_SA}, to from the product complex $(H_2SO_4)_2$. TS_{DSA_WM} was in the middle of a double hydrogen transfer, where H_2SO_4 acted as a bridge of hydrogen atom from the H_2O to SO_3 along with O1 atom of H_2O addition to the S atom of SO_3. It was worth noting that the energy barriers of two elementary reactions involved in the stepwise route of Channel SA_SA were only 1.8 and 0.6 kcal·mol^{-1}, respectively, showing that the stepwise route of Channel SA_SA is feasible to take place from energetic point of view. To check whether Channel DSA_WM is more favorable than Channel SA_SA or not, their rate ratio listed in Eq. 4 has been calculated in Table 1. The calculated rate ratio v_{DSA_WM}/v_{SA_SA} shows that Channel DSA_WM is more important than Channel SA_SA because the rate ratio v_{DSA_WM}/v_{SA_SA} is 1.53-3.04 within the temperature range of 280-320 K. So, we predicted that the SO_3 + H_2SO_4 reaction with H_2O producing $H_2S_2O_7$ is more favorable than that forming H_2SO_4.

$$\frac{v_{DSA\_WM}}{v_{SA\_SA}} = \frac{v_{DSA\_WM\_s} + v_{DSA\_WM\_o}}{v_{SA\_SA\_s} + v_{SA\_SA\_o}} = \frac{k_{DSA\_WM\_s} \times K_{eq(H_2SO_4 \cdots H_2O)} + k_{DSA\_WM\_o} \times K_{eq(SO_3 \cdots H_2O)}}{k_{SA\_SA\_s} \times K_{eq(H_2SO_4 \cdots H_2O)} + k_{SA\_SA\_o} \times K_{eq(SO_3 \cdots H_2O)}} \quad (4)$$

3.2 Reactions at the Air-water interface

The mechanism for the SO_3 + SA reaction at the air-water interface was lacking. Notably, SO_3, SA and DSA molecules can stay at the interface for 35.8%, 30.1% and 39.2% of the time in the 150 ns simulation (Fig. S2), respectively, revealing that the existence of SO_3, SA and DSA at the air-water interface cannot be negligible. So, the BOMD simulations were used to evaluate the reaction mechanism of SO_3 with SA at the aqueous interfaces. Similar with the interfacial reaction of SO_3 with organic and inorganic acids (Cheng et al., 2023; Zhong et al., 2019), the reaction between SO_3

and SA at the aqueous interface may occur in three ways: (*i*) SO_3 colliding with adsorbed SA at the air-water interface; (*ii*) SA colliding with adsorbed SO_3 at the aqueous interface; or (*iii*) the SO_3-SA complex reacting at the aqueous interface. However, due to the high reactivity both of SO_3 and SA at the air-water interface, the lifetimes of SO_3 (Zhong et al., 2019) and SA (Fig. S3) (on the order of a few picoseconds) on the water droplet were extremely short and can be formed SA^- ion quickly. Besides, as the calculated result above, $SO_3\cdots H_2SO_4$ complex can be generate DSA easily before it approaches the air-water interface. So, two possible models were mainly considered for the SO_3 + SA reaction on the water surface: (*i*) gaseous SO_3 colliding with SA^- at the air-water interface and (*ii*) the DSA (the gas-phase product of SO_3 and SA) dissociating on water droplet.

Gaseous SO_3 Colliding with SA^- at the Air-Water Interface. At the water droplet's surface, the interaction between SO_3 and SA^- included two main channels: (*i*) H_2O-induced formation of $S_2O_7^{2-}\cdots H_3O^+$ ion pair (Fig. 2, Fig. S4 and Movie S1) and (*ii*) SA^--mediated formation of $SA^-\cdots H_3O^+$ ion pair (Fig. 3, Figs. S5-S6 and Movies S2-S3). The BOMD simulations for H_2O-induced formation of $S_2O_7^{2-}\cdots H_3O^+$ ion pair was illustrated in Fig. 2, the H1 atom of SA^- ion can combine with a nearby interfacial water molecule at 8.18 ps by hydrogen bond ($d_{(O3\text{-}H1)}$ = 1.17 Å) interaction, thus forming hydrated hydrogen sulfate ion ($SA^-\cdots H_2O$). Then, the H1 atom of SA^- ion was moved to the O3 atom of the interfacial water molecule at 8.28 ps, revealing the formation of $SO_4^{2-}\cdots H_3O^+$ ion pair. Additionally, SO_4^{2-} gradually approached to SO_3 molecule with the shortening of S1-O1 bond. At 9.26 ps, the S1-O1 bond length was 1.84 Å, which was close to the length of S-O1 (1.65 Å) bond in $S_2O_7^{2-}$ ion (Fig. S8), revealing the formation of $S_2O_7^{2-}\cdots H_3O^+$ ion pair.

Both direct (Fig. 3(a), Fig. S5 and Movie S2) and indirect (Fig. 3(b), Fig. S6 and Movie S3) forming mechanisms were observed in SA^--mediated formation of $SA^-\cdots H_3O^+$ ion pair. The direct SA^--mediated formation of $SA^-\cdots H_3O^+$ ion pair was a loop structure mechanism, which was consistent with gas phase hydrolysis of SO_3 assisted by acidic catalysts of HCOOH, HNO_3, $H_2C_2O_4$ and SA in the previous works (Long et al., 2012; Long et al., 2013a; Torrent-Sucarrat et al., 2012; Lv et al., 2019), and the interfacial reactions of HNO_3-mediated Criegee hydration (Kumar et al., 2018) and the hydration of SO_3 via the loop-structure formation (Lv and Sun, 2020). As for the direct formation mechanism of $SA^-\cdots H_3O^+$ ion pair seen in Fig. 3(a) and movie S2, an eight-membered loop complex, $SO_3\cdots H_2O(1)\cdots SA^-$, was found at 1.46 ps with the formations of two hydrogen bonds ($d_{(O3\cdots H2)}$ = 2.13 Å; $d_{(O4\cdots H3)}$ = 2.18 Å) and a van der Waals interaction ($d_{(S1\cdots O1)}$ =

2.14 Å). Subsequently, SO_3 and interfacial $H_2O(1)$ were close to each other. At 1.59 ps, a transition state-like loop structure was observed and proton transfer from interfacial $H_2O(1)$ to another suspended $H_2O(2)$ was found, where the bond lengths of S1-O1, O1-H1 and H1-O2 were 1.94 Å, 1.19 Å and 1.32 Å, respectively. At 1.70 ps, the bond lengths of S-O1 and H1-O2 were reduced to 1.73 Å and 1.01 Å, while the bond length of H1-O2 was extended to 1.61 Å, showing the formation of $SA^{-}\cdots H_3O^{+}$ ion pair. During the direct formation route of $SA^{-}\cdots H_3O^{+}$ ion pair, SA^{-} played as a spectator, while interfacial water molecules acted as both a reactant and a proton acceptor. As compared with the hydration reaction mechanism of SO_3 at the air-water interface reported by Lv et al. (Lv and Sun, 2020), the loop-structure formation with proton transferred in the loop was not observed in the direct mechanism of SA^{-}-mediated formation of $SA^{-}\cdots H_3O^{+}$ ion pair. This was probably because SA^{-} ion was more difficult to give the proton.

As seen in Fig. 3(b) and Movie S3, the indirect forming process of $SA^{-}\cdots H_3O^{+}$ ion pair contained two steps: (*i*) SO_3 hydration along with SA formation and (*ii*) SA deprotonation. Specifically, as for step (*i*), at 0.70 ps, a transition state like structure of SO_3 hydration was observed with SO_3, SA^{-} and an interfacial water molecule involved. Note that at this time the H1 atom in interfacial H_2O molecule migrated to the O2 atom of SA^{-} ion instead of the surrounding water molecule. At 0.96 ps, the O1-H1 bond of H_2O was broken with the length of 1.56 Å, while the S1-O1 bond was formed with the length of 1.75 Å, demonstrating the completion of hydrolysis reaction of SO_3 and the formation of SA molecule. Then, at 8.08 ps, the H2 proton transferred from SA to the O4 atom of SA^{-} ion and to the O5 atom of the nearby water molecule was occurred, where the O3-H2 and O1-H3 bonds extended to 1.13 Å and 1.22 Å, and the length of O4-H2 and O5-H3 bonds shortened to 1.45 Å and 1.20 Å. Finally, SA deprotonation was completed at 8.23 ps with the formation of $SA^{-}\cdots H_3O^{+}$ ion pair. During the whole indirect forming process of $SA^{-}\cdots H_3O^{+}$ ion pair, SA^{-} played as protons donor and acceptor, and water molecules acted as hydration reactants and proton acceptors. Compared with the direct mechanism of $SA^{-}\cdots H_3O^{+}$ ion pair, the indirect forming process of $HSO_4^{-}\cdots H_3O^{+}$ ion pair required more time. This was consistent with the interfacial reactions of $CH_2OO + HNO_3$ (Kumar et al., 2018) and the hydration of SO_3 (Lv and Sun, 2020) where the direct forming mechanism needed less time than indirect forming mechanism.

The $H_2S_2O_7$ Dissociating on Water Droplet. In addition to the gaseous SO_3 colliding with SA^{-} at the air-water interface, DSA, the product of the barrierless reaction between SO_3 and SA, can further quickly react with interfacial water molecule at the air-water interface. As seen in Fig. 4, Fig. S7 and Movie S4, DSA was highly reactive at the air-water interface and can undergo two deprotonations to form $S_2O_7^{2-}$ ion. Specifically, the DSA can firstly form a H-bond with interfacial water molecule at 0.45 ps. After that, the H1 atom of DSA transferred to interfacial water and produced $HS_2O_7^-$ and H_3O^+ ions. The formed $HS_2O_7^-$ ion can survive for ~3 ps on water droplet. At 4.14 ps, the H2 atom of $HS_2O_7^-$ ion moved to O4 atom of nearby interfacial water molecule and produced the formation of $S_2O_7^{2-}\cdots H_3O^+$ ion pair, which was stable at the air-water interface over a simulated time scale of 10 ps. Note that the second deprotonation of DSA indeed needs more time than its first deprotonation as the pK_a1 (pK_a1 = -16.05) of DSA is much smaller than its pK_a2 (pK_a2 = -4.81) (Abedi and Farrokhpour, 2013). In brief, at the air-water interface, both these two routes of the formation of $S_2O_7^{2-}\cdots H_3O^+$ ion pair occurred on the picosecond time scale.

3.3 Atmospheric Implications

The application of the SO_3 + SA reaction in atmospheric chemistry. In the gas-phase, the main sink route of SO_3 was H_2O-assisted hydrolysis of SO_3 (Morokuma and Muguruma, 1994; Akhmatskaya et al., 1997; Larson et al., 2000; Hazra and Sinha, 2011; Long et al., 2013a; Torrent-Sucarrat et al., 2012; Ma et al., 2020). To study the atmospheric importance of the SO_3 + SA reaction without and with H_2O, the rate ratio (v_{DSA}/v_{SA}) between the SO_3 + SA reaction and H_2O-assisted hydrolysis of SO_3 was compared, which was expressed in Eq. (5).

$$\frac{v_{DSA}}{v_{SA}} = \frac{k_{DSA}\times[SO_3]\times[H_2SO_4]+k_{DSA\_WM\_s}\times K_{eq1}\times[SO_3]\times[H_2SO_4]\times[H_2O]}{k_{SA\_WM}\times K_{eq2}\times[SO_3]\times[H_2O]\times[H_2O]} \quad (5)$$

In Eq. (5), K_{eq1} and K_{eq2} were the equilibrium constant for the formation of $H_2SO_4\cdots H_2O$ and $SO_3\cdots H_2O$ complexes shown in Table S2, respectively; k_{DSA}, $k_{DSA\_WM\_s}$ and k_{SA_WM} were respectively denoted the bimolecular rate coefficient for the H_2SO_4 + SO_3, $H_2SO_4\cdots H_2O$ + SO_3 and $SO_3\cdots H_2O$ + H_2O reactions; $[H_2O]$ and $[H_2SO_4]$ were respectively represented the concentration of H_2O and SA taken from references (Anglada et al., 2013; Liu et al., 2015); The value of v_{DSA}/v_{SA} was listed in Table S7 (0 km altitude) and Table S8 (5-30 km altitude). As seen in Table S7, the hydrolysis reaction of SO_3 with $(H_2O)_2$ was more favorable than the SO_3 + H_2SO_4 reaction at 0 km altitude as the $[H_2O]$ (10^{16}-10^{18} molecules·cm^3) was much larger than that of $[H_2SO_4]$ (10^4-10^8 molecules·cm^3). Although the concentration of water molecules decreased with the increasing of altitude in Table S8, the concentration of $[H_2O]$ was still much greater than that of $[H_2SO_4]$, resulting in the $SO_3 + H_2SO_4$ reaction cannot compete with H_2O-assisted hydrolysis of SO_3 within the altitude range of 5-30 km. Even considering of high H_2SO_4 concentration at the end and outside the aircraft engine and flight at 10 km (Curtius et al., 2002), the $SO_3 + H_2SO_4$ reaction was not the major sink route of SO_3. Notably, as the concentration of sulfuric acid was even greater than that of water vapor in the atmosphere of Venus, the SO_3 + SA reaction was probably favorable than the H_2O-assisted hydrolysis of SO_3 in the Venus' atmosphere. To check whether the $SO_3 + H_2SO_4$ reaction was more favorable than H_2O-assisted hydrolysis of SO_3 or not in the Venus' atmosphere, the rate ratio of ν_{DSA}/ν_{SA} listed in Eq. 4 has been calculated in Table 2. It can be seen from Table 2 that the rate ratio of ν_{DSA}/ν_{SA} was 3.24×10^8-5.23×10^{10} within the altitude range of 40-70 km in the Venus' atmosphere, which indicates that the $SO_3 + H_2SO_4$ reaction is significantly more favorable than the hydrolysis reaction of $SO_3 + (H_2O)_2$ within the altitudes range of 40-70 km in the Venus' atmosphere.

Enhancement Effect of DSA on NPF. From the multistep global minimum sampling technique, for $(DSA)_x(SA)_y(A)_z$ ($z \leq x + y \leq 3$) molecular clusters, 27 most stable structures in the present system have been found (Fig. S11). To evaluate the thermodynamic stability of these clusters, Gibbs formation free energies (ΔG) at 278.15 K and evaporation rate coefficient (γ, s^{-1}) for $(DSA)_x(SA)_y(A)_z$ ($z \leq x + y \leq 3$) molecular clusters were calculated in Fig. 5 and Table S11-12, respectively. As for dimers formed by SA, A and DSA, the ΔG of $(A)_1\cdot(DSA)_1$ was -16.1 $kcal\cdot mol^{-1}$, which was lowest in all dimers followed by $(SA)_2$ (-8.5 $kcal\cdot mol^{-1}$) and then $(SA)_1\cdot(A)_1$ (-6.3 $kcal\cdot mol^{-1}$), meanwhile, the γ of $(A)_1\cdot(DSA)_1$ (1.17×10^{-3} s^{-1}) was lower than those of $(SA)_2$ (3.81×10^2 s^{-1}) and $(SA)_1\cdot(A)_1$ (4.19×10^4 s^{-1}). Regarding for the SA-A-DSA-based clusters, the values of ΔG and γ of SA-A-DSA-based clusters containing more DSA molecules were relatively lower than the corresponding values of other SA-A-DSA-based clusters with the same number of acid and base molecules. In the free-energy diagram for cluster formation steps of the SA-A-DSA system (Fig. 5), thermodynamic barriers were weakened mainly by the subsequential addition of A or DSA monomer. Also, the SA-A-DSA-based growth pathway was thermodynamically favorable with decreasing ΔG. These results indicate that DSA not only can promote the stability of SA-A-DSA-based clusters but also may synergistically participate in the nucleation process.

The potential enhancement influence of DSA to the SA-A-based particle formation was shown in Fig. 6. The formation rate (J, $cm^{-3}\cdot s^{-1}$) of SA-A-DSA-based system illustrated in Fig. 6 was negatively dependent on temperature, demonstrating that the low temperature is a key factor to accelerate cluster formation. It is noted that, at low temperatures of 218.15 K (Fig. S12) and 238.15 K (Fig. S13), the actual Δ*G* of clusters has been calculated to ensure meaningful cluster dynamics of the 3 × 3 systems, where the actual Δ*G* surface represented that the simulated set of clusters always included the critical cluster. In addition to temperature, the *J* of SA-A-DSA-based system shown in Fig. 6 rise with the increase of [DSA]. More notably, the participation of DSA can promote *J* to a higher level, indicating its enhancement on SA-A nucleation. Besides, there was significantly positive dependence of the *J* of SA-A-DSA-based system on both [SA] and [A] in Fig. 7 (238.15 K) and Fig. S15-Fig. S18 (218.15, 258.15, 278.15 and 298.15 K). This was because the higher concentration of nucleation precursors could lead to higher *J*. Besides, Fig. S19 showed the nucleation rate when the sum ([SA] + [DSA]) was kept constant. $J_{DSA/SA}$ at substituted condition was higher than that at unsubstituted condition. These results indicated that DSA may can greatly enhance the SA-A particle nucleation in heavy sulfur oxide polluted atmospheric boundary layer, especially at an average flight altitude of 10 km with high [DSA].

Two main cluster formation pathways, the pure SA-A-based cluster (*i*) and DSA-containing cluster (*ii*), at different [DSA] and different temperatures (218.15 K, 238.15 K and 258.15 K) were shown in Fig. 8(a). As seen, the DSA molecule exhibited an ability to directly participate in cluster formation under high [SA] and [DSA], and median [A]. Interestingly, at different temperature and different [DSA], the DSA molecule showed different effect mechanism and contribution in SA-A system. As seen in Fig. 8(b) and Fig. S20(b), the cluster growth pathways were dominated by DSA-containing cluster formation under the conditions of 238.15 K ([DSA] is 10^6-10^7 molecules·cm^{-3}), 258.15 K ([DSA] is 10^5-10^7 molecules·cm^{-3}), 278.15 K ([DSA] is 10^4-10^7 molecules·cm^{-3}) and 298.15 K ([DSA] is 10^4-10^7 molecules·cm^{-3}). By the way, the cluster growth pathways were completely dominated by the DSA-containing cluster at 298.15 K where [DSA]= 10^5-10^7 molecules·cm^{-3}, and its contribution for growth flux out of the system reached to 100% (Fig. S22). In short, on one hand, the contribution of the DSA participation pathway has been increased with increasing temperature. On the other hand, the contribution of the pathway with participation of DSA increased with increasing [DSA], while the number of DSA molecules contained in clusters [$(SA)_2\cdot(A)_3\cdot DSA$, $SA\cdot(A)_2\cdot DSA$, $SA\cdot(A)_3\cdot(DSA)_2$, and $(A)_3\cdot(DSA)_3$] that can contribute to cluster growth had a positive correlation with [DSA]. These results suggested that DSA has the ability to act as a potential contributor to SA-A-based NPF in the atmosphere at low *T*, low [SA], high [A] and high [DSA], and the DSA participation pathway can be dominant in heavy sulfur oxide polluted atmospheric boundary layer and in season of late autumn and early winter.

At the air-water interface, important implication of the BOMD simulations was that the reaction between SO_3 and SA at the air-water interface can be accomplished within a few picoseconds, among which the interfacial water molecules played a significant role in promoting the formation of $S_2O_7^{2-}\cdots H_3O^+$ and $SA^-\cdots H_3O^+$ ion pairs. Furthermore, the adsorption capacity of the $S_2O_7^{2-}$, H_3O^+ and SA^- to gasous precursors in the atmosphere was further investigated by the calculated interaction free energies. Herein, the species of SA, NH_3, HNO_3 and $(COOH)_2$ have been regarded as the candidate species. (Kulmala et al., 2004; Kirkby et al., 2011). Our calculated Gibbs free energies in Table 3 showed that the interactions of $S_2O_7^{2-}\cdots H_2SO_4$, $S_2O_7^{2-}\cdots HNO_3$, $S_2O_7^{2-}\cdots(COOH)_2$, $H_3O^+\cdots NH_3$, $H_3O^+\cdots H_2SO_4$, $SA^-\cdots H_2SO_4$, $SA^-\cdots(COOH)_2$, and $SA^-\cdots HNO_3$ were stronger than those of $H_2SO_4\cdots NH_3$ (major precursor of atmospheric aerosols) with their binding free energies enhanced by 18.6-42.8 kcal·mol^{-1}. These results reveal that interfacial $S_2O_7^{2-}$, SA^- and H_3O^+ can attract candidate species from the gas phase to the water surface. Moreover, we evaluated the nucleation potential of $S_2O_7^{2-}$ on SA-A cluster by considering geometrical structure and the formation free energies of the $(SA)_1(A)_1(S_2O_7^{2-})_1$ clusters. As compared with $(SA)_1(A)_1(X)_1$ (X = HOOCCH$_2$COOH, HOCCOOSO$_3$H, CH$_3$OSO$_3$H, HOOCCH$_2$CH(NH$_2$)COOH and HOCH$_2$COOH) clusters (Zhong et al., 2019; Zhang et al., 2018; Rong et al., 2020; Gao et al., 2023; Liu et al., 2021a; Zhang et al., 2017), the number of hydrogen bonds in $(SA)_1(A)_1(S_2O_7^{2-})_1$ cluster presented in Fig. S8 increased and the ring of the complex was enlarged. It was demonstrated that $S_2O_7^{2-}$ has the highest potential to stabilize SA-A clusters and promote SA-A nucleation in these clusters due to its acidity and structural factors such as more intermolecular hydrogen bond binding sites. Subsequently, comparing to $(SA)_1(A)_1(X)_1$ clusters (Table 2), the Gibbs formation free energy ΔG of $(SA)_1(A)_1(S_2O_7^{2-})_1$ cluster was lower, showing $S_2O_7^{2-}$ ion at the air-water interface has stronger nucleation ability than X in the gas phase. Therefore, we predict that $S_2O_7^{2-}$ at the air-water interface has stronger nucleation potential.

4. Summary and Conclusions

In this work, we employed QC calculations, BOMD simulations and ACDC kinetic model to characterize the SO_3-H_2SO_4 interaction in the gas phase and at the air-water interface and to study the effect of $H_2S_2O_7$ on H_2SO_4-NH_3-based clusters. Results revealed that the energy barrier of the gas phase SO_3 + H_2SO_4 reaction without and with H_2O was less than 2.3 kcal·mol^{-1}. Rate constants indicated that though the SO_3 + H_2SO_4 reaction cannot compete with H_2O-assisted hydrolysis of SO_3 within the temperature range of 280-320 K, its rate constant was close to the upper limits for bimolecular reactions and H_2O exerted obvious catalytic role in promoting the reaction rate. Moreover, ACDC kinetic simulations showed that DSA has unexpected facilitate effects on the NPF process and can present a more obvious enhancement effect on SA-A-based cluster formation in polluted atmospheric boundary layer. Of particular note, DSA can directly participate in the SA-A-based cluster formation pathway and the contribution of the pathway with participation of DSA increases with increasing [DSA] in regions with atmospheric pollution boundary layer of high concentrations of SO_3, especially in late autumn and early winter.

At the air-water interface, H_2O-induced the formation of $S_2O_7^{2-}\cdots H_3O^+$ ion pair, SA^- mediated the formation of $SA^-\cdots H_3O^+$ ion pair and the deprotonation of $H_2S_2O_7$ were observed, both of which can occur within a few picoseconds. The formed interfacial $S_2O_7^{2-}$, SA^- and H_3O^+ can attract candidate species (such as H_2SO_4, NH_3, and HNO_3) for particle formation from the gas phase to the water surface, and thus accelerated the growth of particle. Moreover, potential of *X* (*X* = $S_2O_7^{2-}$, $HOOCCH_2COOH$, $HOCCOOSO_3H$, CH_3OSO_3H, $HOOCCH_2CH(NH_2)COOH$ and $HOCH_2COOH$) in ternary SA-A-*X* cluster formation indicated that $S_2O_7^{2-}$ has the highest potential to stabilize SA-A clusters and promote SA-A nucleation among *X*.

The present work will expand our understanding of new pathway for the loss of SO_3 in acidic polluted areas. Moreover, this work will also help to reveal some missing sources of metropolis industrial regions NPF and to understand the atmospheric organic-sulfur cycle more comprehensively.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Table 1 The rate constant ($cm^3 \cdot molecule^{-1} \cdot s^{-1}$) for the SO_3 + H_2SO_4 reaction and the effective rate constant ($cm^3 \cdot molecule^{-1} \cdot s^{-1}$) for the SO_3 + H_2SO_4 reaction with H_2O (100%RH) within the temperature range of 280-320 K

T/(K)	280 K	290 K	298 K	300 K	310 K	320 K
k_{DSA}	5.52×10^{-12}	4.60×10^{-12}	3.95×10^{-12}	3.80×10^{-12}	3.13×10^{-12}	2.57×10^{-12}
$k'_{DSA\_WM\_o}$	2.12×10^{-13}	2.68×10^{-13}	2.88×10^{-13}	2.89×10^{-13}	2.89×10^{-13}	2.75×10^{-13}
$k'_{DSA\_WM\_s}$	1.03×10^{-11}	8.55×10^{-12}	7.42×10^{-12}	7.11×10^{-12}	5.79×10^{-12}	4.60×10^{-12}

k_{DSA} is the rate constant for the SO_3 + H_2SO_4 reaction; $k'_{DSA\_WM\_o}$ and $k'_{DSA\_WM\_s}$ are respectively the effective rate constants for H_2O-assisted SO_3 + H_2SO_4 reaction occurring through one-step and stepwise routes.

Table 2 The rate ratio between the SO_3 + H_2SO_4 reaction and the hydrolysis of SO_3 at different altitudes in the atmospheres of Earth and Venus

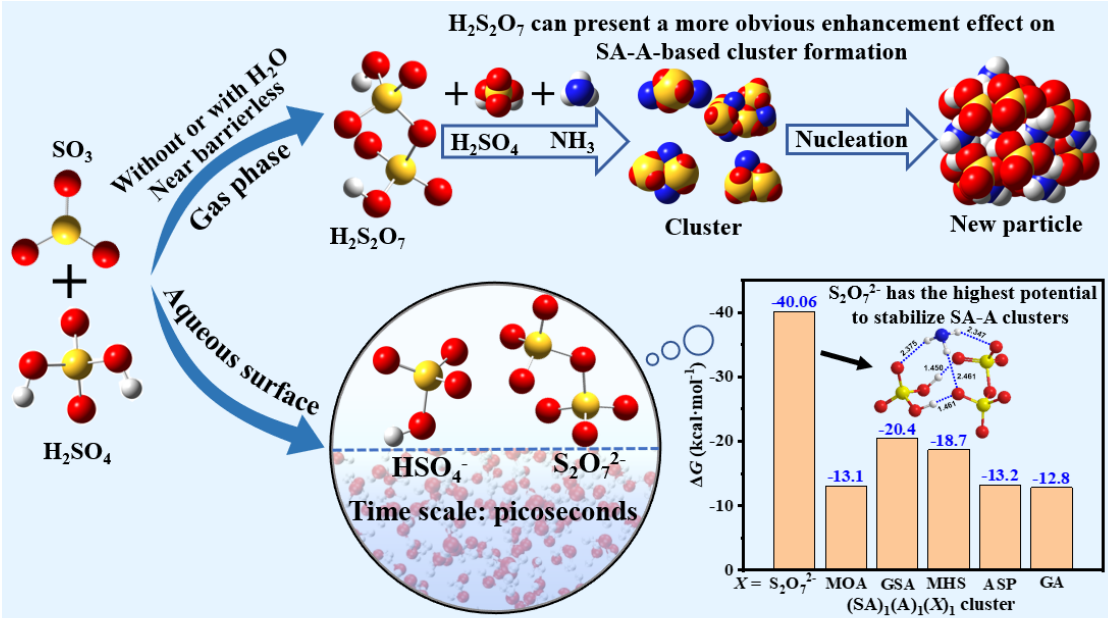
H (km)	*T*(K)	P (Torr)	$[H_2O]^a$	$[H_2SO_4]^a$	k_{DSA}	$k_{DSA\_WM\_s}$	k_{SA_WM}	v_{DSA}/v_{SA}
40	410	2025	1.08×10^{15}	6.15×10^{13}	5.22×10^{-12}	1.43×10^{-12}	2.31×10^{-13}	3.24×10^{8}
50	340	750	5.17×10^{14}	1.23×10^{14}	1.12×10^{-12}	3.87×10^{-12}	5.43×10^{-13}	3.81×10^{10}
60	320	104	1.72×10^{14}	1.85×10^{14}	1.23×10^{-12}	7.80×10^{-12}	1.37×10^{-12}	5.12×10^{10}
70	270	19	8.61×10^{13}	8.61×10^{13}	1.07×10^{-12}	8.61×10^{-12}	1.82×10^{-12}	5.23×10^{10}

k_{DSA}, $k_{DSA\_WM\_s}$ and k_{SA_SA} are respectively the rate constants for SO_3 + H_2SO_4 reaction, H_2O-assisted SO_3 + H_2SO_4 reaction occurring through stepwise route and the hydrolysis reaction of SO_3 + $(H_2O)_2$.

Table 3 Gibbs free energy (ΔG, kcal·mol^{-1}) for the formation of $S_2O_7^{2-}\cdots H_2SO_4$, $S_2O_7^{2-}\cdots HNO_3$, $S_2O_7^{2-}\cdots(COOH)_2$, $H_3O^+\cdots NH_3$, $H_3O^+\cdots H_2SO_4$, $HSO_4^-\cdots H_2SO_4$, $HSO_4^-\cdots(COOH)_2$, $HSO_4^-\cdots HNO_3$, $H_2SO_4\cdots NH_3$, $SO_7^{2-}\cdots H_2SO_4\cdots NH_3$, $HOOCCH_2COOH\cdots H_2SO_4\cdots NH_3$, $HOCCOOSO_3H\cdots H_2SO_4\cdots NH_3$, $CH_3OSO_3H\cdots H_2SO_4\cdots NH_3$ and $HOOCCH_2CH(NH_2)COOH\cdots H_2SO_4\cdots NH_3$ at 298 K

	$S_2O_7^{2-}\cdots H_2SO_4$	$S_2O_7^{2-}\cdots HNO_3$	$S_2O_7^{2-}\cdots(COOH)_2$	$H_3O^+\cdots NH_3$	$H_2SO_4\cdots NH_3$
ΔG	-46.3	-30.6	-39.9	-51.7 (-49.2)[a]	-8.9 (-8.9)[a]
	$H_3O^+\cdots H_2SO_4$	$HSO_4^-\cdots H_2SO_4$	$HSO_4^-\cdots(COOH)_2$	$HSO_4^-\cdots HNO_3$	$S_2O_7^{2-}\cdots H_2SO_4\cdots NH_3$
ΔG	-27.5 (-27.0)[a]	-41.6	-33.6	-27.8	-40.1
	$HOOCCH_2COOH\cdots H_2SO_4\cdots NH_3$	$HOCCOOSO_3H\cdots H_2SO_4\cdots NH_3$	$CH_3OSO_3H\cdots H_2SO_4\cdots NH_3$	$HOOCCH_2CH(NH_2)COOH\cdots H_2SO_4\cdots NH_3$	$HOCH_2COOH\cdots H_2SO_4\cdots NH_3$
ΔG	-13.1 (-13.6)[b]	-20.4 (-22.5)[c]	-18.8 (-20.7)[d]	-13.2 (-14.0)[e]	-12.8 (-13.5)[f]

Energies are given in kcal·mol^{-1}, and calculated at the M06-2X/6-311++G(2*df*,2*pd*) theoretical level. References are as follows: [a] Zhong et al., 2019.; [b] Zhang et al., 2018.; [c] Rong et al., 2020.; [d] Gao et al., 2023.; [e] Liu et al., 2021a; [f] Zhang et al., 2017.



Graphic abstract

Figure Caption

Fig. 1 Schematic potential energy surface for the $SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$ reaction; Distances is in angstrom at the M06-2X/6-311++G(2*df*,2*pd*) level, while the energy values correspond to the calculations at the CCSD(T)-F12/cc-pVDZ-F12//M06-2X/6-311++G(2*df*,2*pd*) level. The pre-reactive complex and TS for the route of DSA formation from the $SO_3 + H_2SO_4$ reaction with H_2O was denoted by "IM_{DSA_WM}" and "TS_{DSA_WM}", respectively, while the corresponding pre-reactive complex and TS for the process of SA formation from the hydrolysis of SO_3 with H_2SO_4 was respectively labeled as "IM_{SA_SA}" and "TS_{SA_SA}"

Fig. 2 Top panel: Snapshot structures taken from the BOMD simulations, which illustrate H_2O-induced the formation of $S_2O_7^{2-}\cdots H_3O^+$ ion pair from the reaction of SO_3 with HSO_4^- at the air-water interface. Lower panel: time evolution of key bond distances (S-O1, O2-H1, and O3-H1) involved in the induced mechanism

Fig. 3 Top panel: Snapshot structures taken from the BOMD simulations, which illustrate the hydration reaction mechanism of SO_3 mediated by HSO_4^- at the air water interface. Lower panel: time evolution of key bond distances (S-O1, O1-H2, O5-H2, O2-H1, O3-H4 and O4-H3) involved in the hydration mechanism

Fig. 4 Top panel: Snapshot structures taken from the BOMD simulations, which illustrate the deprotonation of $H_2S_2O_7$ at the air water interface. Lower panel: time evolution of key bond distances (O1-HI, O1-H2, O3-H2 and H2-O4) involved in the hydration mechanism

Fig. 5 The Gibbs free energy (kcal·mol^{-1}) diagram of $(DSA)_x(SA)_y(A)_z$ ($z \leq x + y \leq 3$) clusters at 278.15K and 1 atm. "A" refers to sulfuric acid, "D" refers to disulfuric acid and "N" refers to ammonia

Fig. 6 Cluster formation rates J (cm^{-3} s^{-1}) against the of DSA monomer concentration (unit： molecules·cm^{-3}) under different temperatures (218.15, 238.15, 258.15, 278.15 and 298.15 K) where [SA] = 10^7 molecules·cm^{-3} and [A] = 10^9 molecules·cm^{-3}

Fig. 7 Simulated cluster formation rates J (cm^{-3} s^{-1}) as a function of (a) [SA], (b) [A], with different concentrations of disulfuric acid [DSA] of 10^4 (red), 10^5 (blue), 10^6 (green) ,10^7 (purple) and 0 molecules·cm^{-3} (black, pure-SA-A), at T = 238.15 K

Fig. 8 (a) The main pathways of clusters growing out of the research system under the conditions where 218.15 K,238.15K and 258.15 K, [SA] = 10^8 molecules·cm^{-3}, [A] = 10^9 molecules·cm^{-3}, and [DSA] = 10^6 molecules·cm^{-3}; (b) The contribution of different concentrations of DSA to the main cluster formation pathway at 218.15 K, 238.15 K and 258.15 K is shown in the pie charts

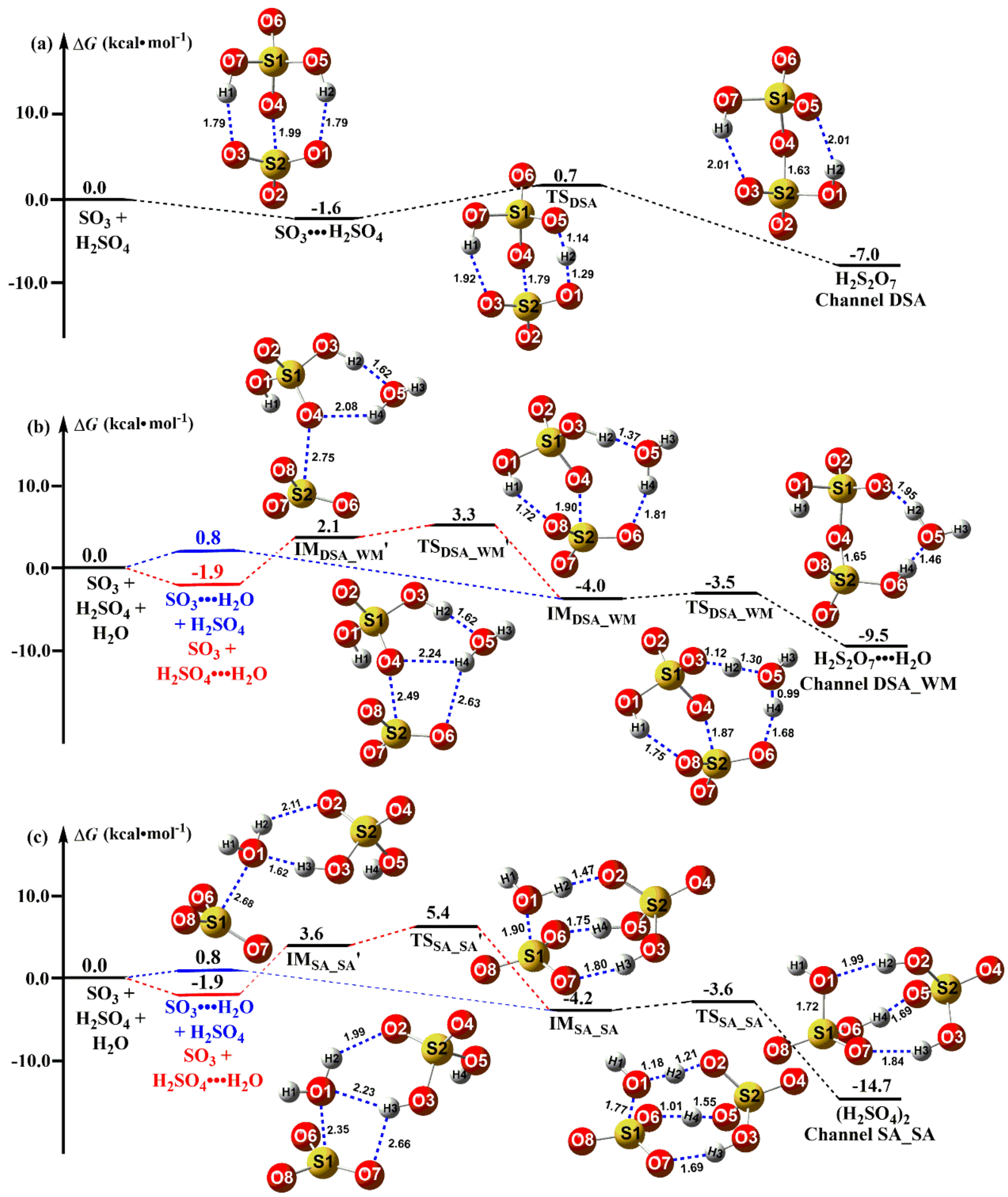

(a) ΔG (kcal•mol-1)
10.0
0.0
-10.0
0.0
SO3 + H2SO4
-1.6
SO3•••H2SO4
0.7
TSDSA
-7.0
H2S2O7
Channel DSA
(b) ΔG (kcal•mol-1)
0.8
-1.9
SO3•••H2O + H2SO4
SO3 + H2SO4•••H2O
2.1
IMDSA_WM'
3.3
TSDSA_WM'
-4.0
IMDSA_WM
-3.5
TSDSA_WM
-9.5
H2S2O7•••H2O
Channel DSA_WM
(c) ΔG (kcal•mol-1)
SO3 + H2SO4 + H2O
3.6
IMSA_SA'
5.4
TSSA_SA'
-4.2
IMSA_SA
-3.6
TSSA_SA
-14.7
(H2SO4)2
Channel SA_SA

Fig. 1

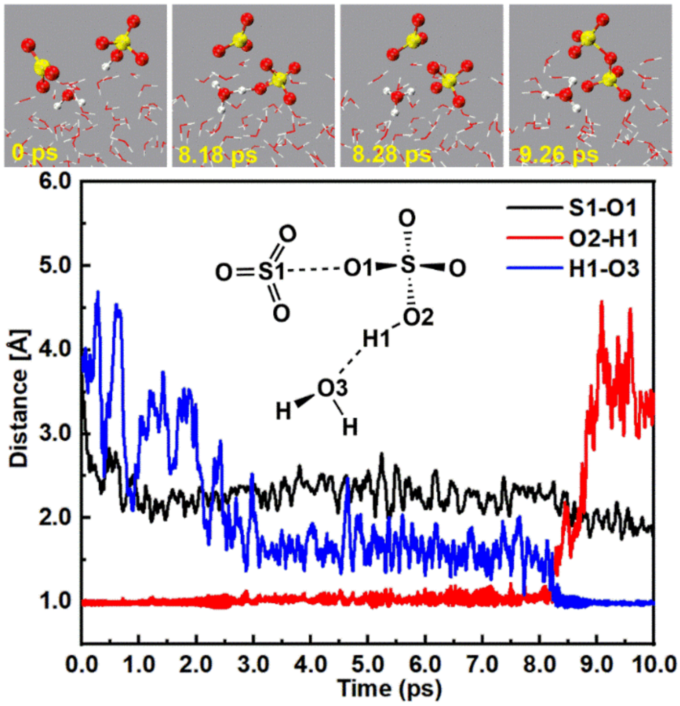
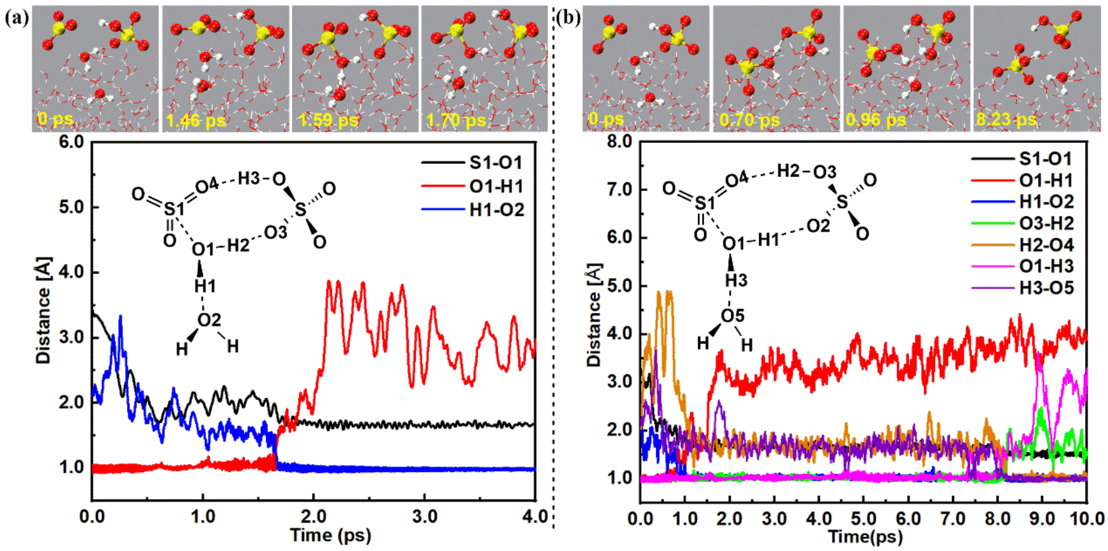

0 ps
8.18 ps
8.28 ps
9.26 ps
6.0
5.0
4.0
3.0
2.0
1.0
Distance [Å]
S1-O1
O2-H1
H1-O3
O=S1-----O1
O
O
S
O
O2
H1
O3
H
H
0.0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0
Time (ps)

Fig. 2



(a)
0 ps
1.46 ps
1.59 ps
1.70 ps
S1-O1
O1-H1
H1-O2
Distance [Å]
Time (ps)
(b)
0 ps
0.70 ps
0.96 ps
8.23 ps
S1-O1
O1-H1
H1-O2
O3-H2
H2-O4
O1-H3
H3-O5
Distance [Å]
Time(ps)

Fig. 3

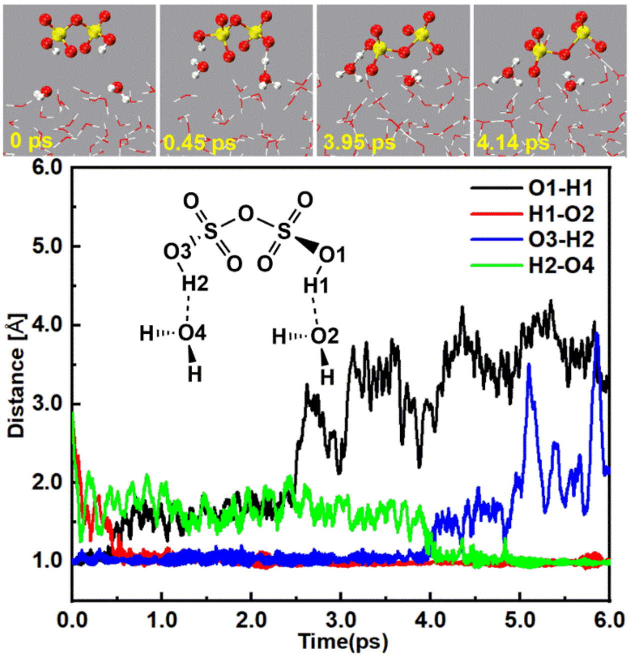
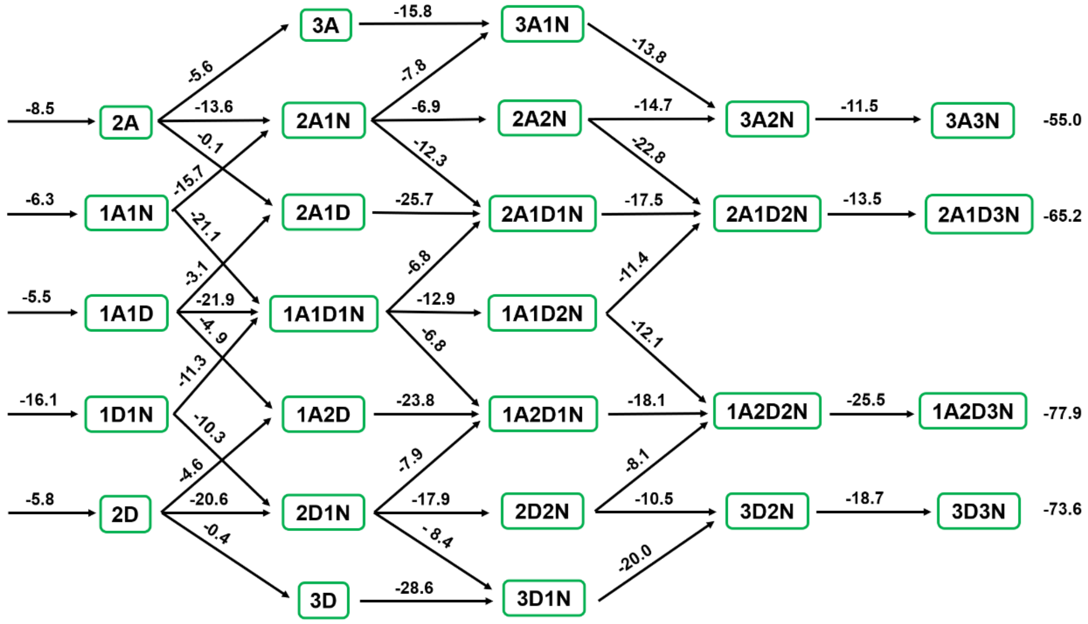
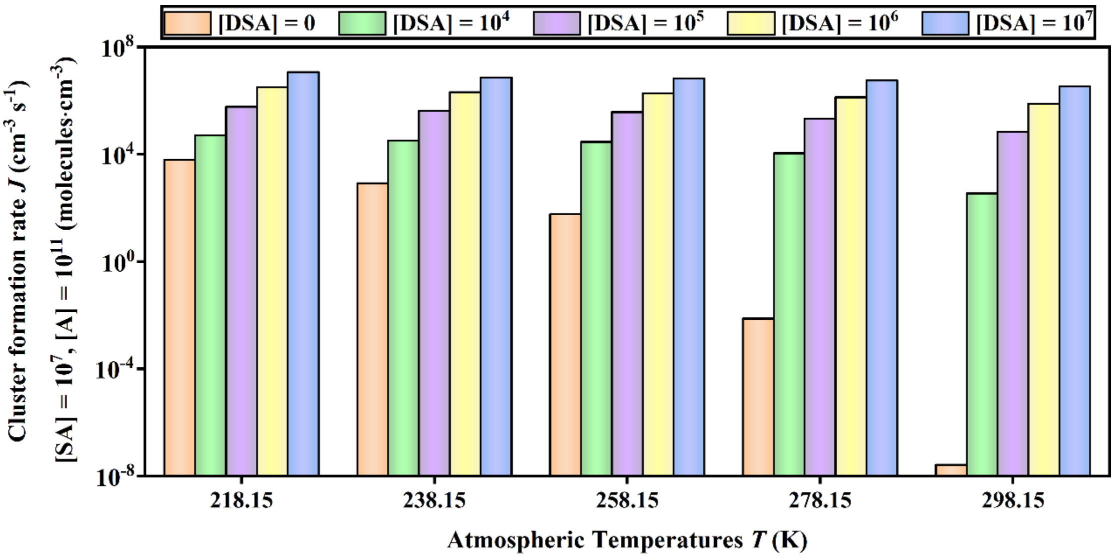


Fig. 4



-8.5
-6.3
-5.5
-16.1
-5.8
2A
1A1N
1A1D
1D1N
2D
-5.6
-13.6
-0.1
-15.7
-21.1
-3.1
-21.9
-4.9
-11.3
-10.3
-4.6
-20.6
-0.4
3A
2A1N
2A1D
1A1D1N
1A2D
2D1N
3D
-15.8
-7.8
-6.9
-12.3
-25.7
-6.8
-12.9
-6.8
-23.8
-7.9
-17.9
-8.4
-28.6
3A1N
2A2N
2A1D1N
1A1D2N
1A2D1N
2D2N
3D1N
-13.8
-14.7
-22.8
-17.5
-11.4
-12.1
-18.1
-8.1
-10.5
-20.0
3A2N
2A1D2N
1A2D2N
3D2N
-11.5
-13.5
-25.5
-18.7
3A3N
2A1D3N
1A2D3N
3D3N
-55.0
-65.2
-77.9
-73.6

Fig. 5



[DSA] = 0
[DSA] = 10^4
[DSA] = 10^5
[DSA] = 10^6
[DSA] = 10^7
Cluster formation rate J (cm^{-3} s^{-1})
[SA] = 10^7, [A] = 10^{11} (molecules·cm^{-3})
10^8
10^4
10^0
10^{-4}
10^{-8}
218.15
238.15
258.15
278.15
298.15
Atmospheric Temperatures T (K)

Fig. 6

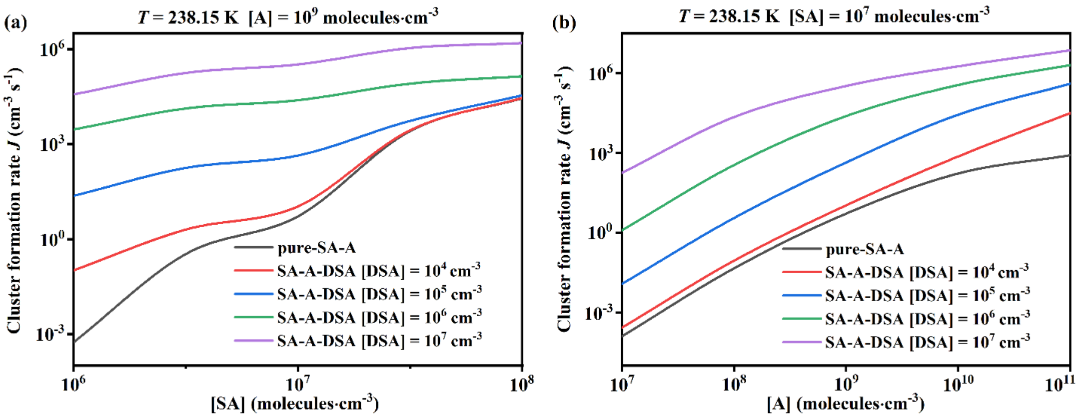

(a)
T = 238.15 K [A] = 10^9 molecules·cm^-3
Cluster formation rate J (cm^-3 s^-1)
[SA] (molecules·cm^-3)
pure-SA-A
SA-A-DSA [DSA] = 10^4 cm^-3
SA-A-DSA [DSA] = 10^5 cm^-3
SA-A-DSA [DSA] = 10^6 cm^-3
SA-A-DSA [DSA] = 10^7 cm^-3
(b)
T = 238.15 K [SA] = 10^7 molecules·cm^-3
Cluster formation rate J (cm^-3 s^-1)
[A] (molecules·cm^-3)
pure-SA-A
SA-A-DSA [DSA] = 10^4 cm^-3
SA-A-DSA [DSA] = 10^5 cm^-3
SA-A-DSA [DSA] = 10^6 cm^-3
SA-A-DSA [DSA] = 10^7 cm^-3

Fig. 7

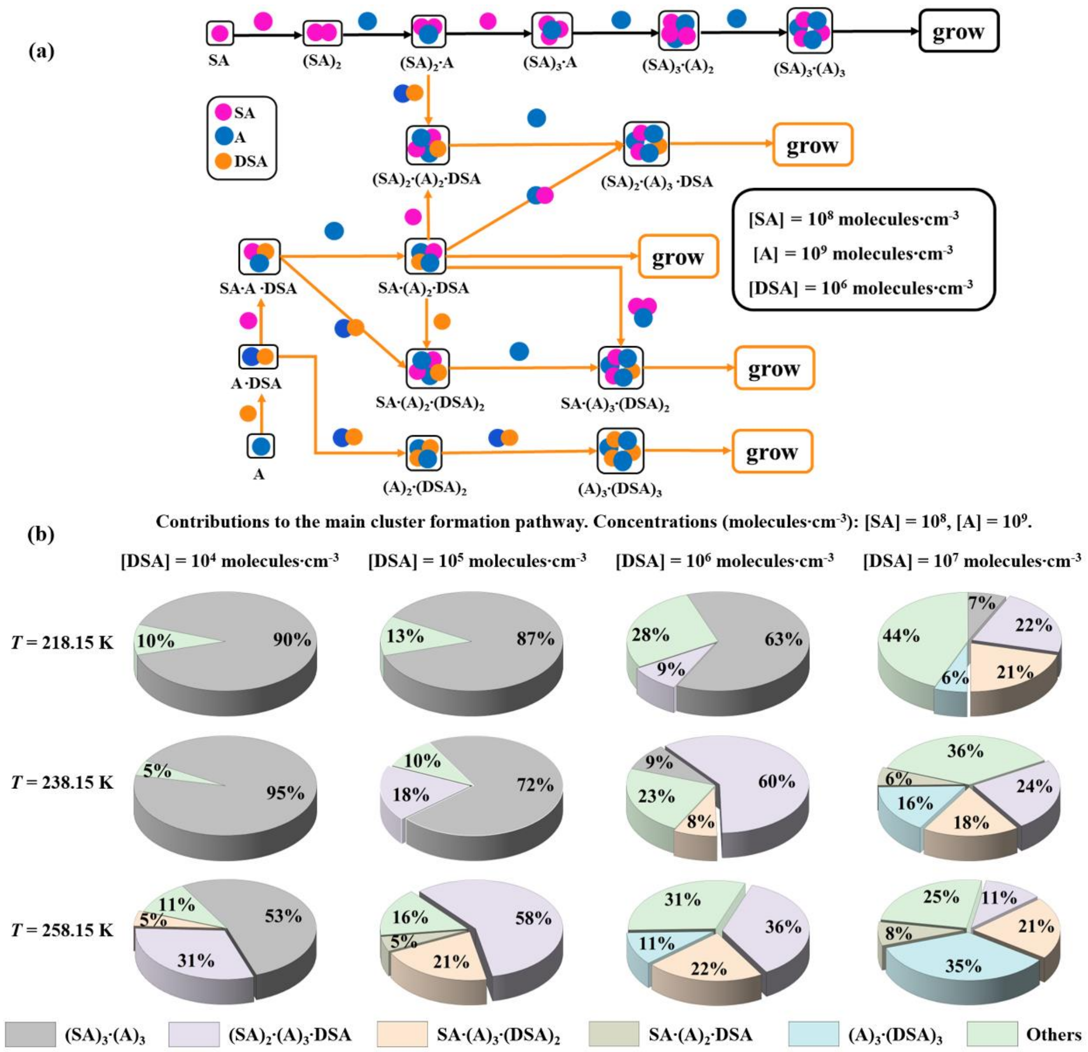

(a)
SA
(SA)2
(SA)2·A
(SA)3·A
(SA)3·(A)2
(SA)3·(A)3
grow
SA
A
DSA
(SA)2·(A)2·DSA
(SA)2·(A)3·DSA
grow
[SA] = 10^8 molecules·cm^-3
[A] = 10^9 molecules·cm^-3
[DSA] = 10^6 molecules·cm^-3
SA·A·DSA
SA·(A)2·DSA
grow
A·DSA
SA·(A)2·(DSA)2
SA·(A)3·(DSA)2
grow
A
(A)2·(DSA)2
(A)3·(DSA)3
grow
(b)
Contributions to the main cluster formation pathway. Concentrations (molecules·cm^-3): [SA] = 10^8, [A] = 10^9.
[DSA] = 10^4 molecules·cm^-3
[DSA] = 10^5 molecules·cm^-3
[DSA] = 10^6 molecules·cm^-3
[DSA] = 10^7 molecules·cm^-3
T = 218.15 K
10%
90%
13%
87%
28%
9%
63%
7%
22%
44%
6%
21%
T = 238.15 K
5%
95%
10%
18%
72%
9%
60%
23%
8%
36%
6%
24%
16%
18%
T = 258.15 K
11%
5%
53%
31%
16%
58%
5%
21%
31%
36%
11%
22%
25%
11%
21%
8%
35%
(SA)3·(A)3
(SA)2·(A)3·DSA
SA·(A)3·(DSA)2
SA·(A)2·DSA
(A)3·(DSA)3
Others

Fig. 8