

1 **Responses to Referee #1's comments**

2 We are grateful to the reviewers for their valuable and helpful comments on our manuscript “A
3 novel formation mechanism of sulfamic acid and its enhancing effect on methanesulfonic acid-
4 methylamine aerosol particle formation in agriculture-developed and coastal industrial areas”
5 (Manuscript ID: EGUSPHERE-2024-2638). We have revised the manuscript carefully according to
6 reviewers' comments. The point-to-point responses to the Referee #1's comments are summarized
7 below:

8 **Referee Comments**

9 The manuscript egusphere-2024-2638, “A novel formation mechanism of $\text{NH}_2\text{SO}_3\text{H}$ and its
10 enhancing effect on methanesulfonic acid-methylamine aerosol particle formation in agriculture-
11 developed and coastal industrial areas”. The work studied the formation of sulfamic acid via HNSO_2
12 hydrolysis in the gas phase and at the air-water interface by using theoretical methods. Then, the
13 author investigated the new particle formation for the role of sulfamic acid in $\text{CH}_3\text{SO}_3\text{H}-\text{CH}_3\text{NH}_2$
14 system. The work is very interesting for understanding the chemical processes of sulfamic acid in
15 the atmosphere. However, there are some issues that should be addressed before publication.

16 **Response:** We would like to thank the reviewer for the positive and valuable comments, and we
17 have revised our manuscript accordingly.

18 **Major issues**

19 **Comment 1.**

20 In Line 39, “the concentration of $\text{NH}_2\text{SO}_3\text{H}$ was expected to reach up to $10^8 \text{ molecules} \cdot \text{cm}^{-3}$ ”, the
21 concentration of sulfamic acid was only estimated by theoretical method, not measured by field
22 observations. Therefore, it is required to elucidate this point.

23 **Response:** Thanks for the suggestion of the reviewer. As the suggestion of the reviewer, in Lines
24 38-40 Page 2 of the revised manuscript, the sentence of “the atmospheric concentration of $\text{NH}_2\text{SO}_3\text{H}$
25 was expected to reach up to $10^8 \text{ molecules} \cdot \text{cm}^{-3}$ (Li et al., 2018).” has been changed as “the
26 atmospheric concentration of SFA estimated by theoretical method of CCSD(T)-F12/cc-pVDZ-
27 F12//M06-2X/6-311++G(3df,3pd) (Li et al., 2018) was expected to reach up to $10^8 \text{ molecules} \cdot \text{cm}^{-3}$ ”.

28 **Comment 2.**

29 Lines 41-42, "the sources of $\text{NH}_2\text{SO}_3\text{H}$ in the atmosphere have been well investigated (Lovejoy and
30 Hanson, 1996; Pszona et al., 2015; Li et al., 2018; Larson and Tao, 2001; Manonmani et al., 2020;
31 Zhang et al., 2022)." In fact, sulfamic acid has been not investigated by field measurements.
32 Therefore, it is not well investigated in the atmosphere.

33 **Response:** Thanks for the suggestion of the reviewer. Indeed, it is true that SFA has not been
34 measured in the field. Therefore, atmospheric sulfamic acid has not been well studied. In Lines 41-
35 43 Page 2 of the revised manuscript, "So, the sources of $\text{NH}_2\text{SO}_3\text{H}$ in the atmosphere have been
36 well investigated (Lovejoy and Hanson, 1996; Pszona et al., 2015; Li et al., 2018; Larson and Tao,
37 2001; Manonmani et al., 2020; Zhang et al., 2022)." has been changed as "So, the sources of SFA
38 in the atmosphere has been focused by several groups (Lovejoy and Hanson, 1996; Pszona et al.,
39 2015; Li et al., 2018; Larson and Tao, 2001; Manonmani et al., 2020; Zhang et al., 2022).".

40 **Comment 3.**

41 Lines 46-47, "for the hydrolysis of SO_3 assisted by water molecule (10^{-11} - 10^{-10} cm^3 molecule $^{-1}$ s $^{-1}$)
42 (Kim et al., 1998; Hirota et al., 1996; Shi et al., 1994)." Some important references are missing such
43 as J. Am. Chem. Soc. 2023, 145, 19866-19876. and J. Am. Chem. Soc. 1994, 116, 10314-10315.

44 **Response:** Thanks for the suggestion of the reviewer. We apologize for missing some important
45 references. As the suggestion of the reviewer, some important references have been added in Lines
46 46-49 Page 2 of the revised manuscript, which has been organized as "which was close to the value
47 for the hydrolysis of SO_3 assisted by water molecule (10^{-11} - 10^{-10} cm^3 molecule $^{-1}$ s $^{-1}$) (Kim et al.,
48 1998; Hirota et al., 1996; Shi et al., 1994; Kolb et al., 1994; Long et al., 2013; Long et al., 2023;
49 Ding et al., 2023; Cheng et al., 2023; Wang et al., 2024).".

50 **Comment 4.**

51 What is the concentration of HNSO_2 in the atmosphere? This is very necessary for determining the
52 importance of HNSO_2 in the atmosphere.

53 **Response:** Thanks for the suggestion of the reviewer. As the suggestion of the reviewer, we have
54 conducted an extensive review of the relevant literature. However, the concentrations of HNSO_2 in
55 the atmosphere have not been reported. As the absence of the concentration of HNSO_2 , the

56 competitiveness between MSA-assisted HNSO₂ hydrolysis and the NH₃-assisted ammonolysis of
57 SO₃ (the traditional source of SFA) cannot be further confirmed. The related discussion has been
58 found in Line 236 Page 8 to Line 237 Page 9 of the revised manuscript, which has been organized
59 as “**However, due to the absence of the concentration of HNSO₂, the competitiveness of these two**
60 **reactions cannot be further confirmed.**” Although the concentration of HNSO₂ has not been reported,
61 it is still important to study HNSO₂ hydrolysis with MSA in the gas phase and at the air-water
62 interface. The detailed importance of HNSO₂ hydrolysis with MSA has been presented as follows.

63 In the gas phase, with the significant decrease in atmospheric water molecules with increasing
64 altitude, MSA has a significantly greater catalytic ability than H₂O in accelerating the rate of HNSO₂
65 hydrolysis within 5-15 km. At the air-water interface, two types of reactions, the ions forming
66 mechanism and the proton exchange mechanism to form NH₂SO₃⁻···H₃O⁺ ion pair were observed
67 on the timescale of picosecond, which is at least two orders of magnitude faster than the
68 corresponding gas-phase reaction. Nobly, considering the overall environment of sulfuric acid
69 emission reduction, the present findings suggest that SFA may play a significant role in NPF and
70 the growth of aerosol particles as *i*) SFA can directly participate in the formation of MSA-CH₃NH₂-
71 based cluster and enhance the rate of NPF from these clusters by approximately 10³ times at 278.15
72 K; and *ii*) the NH₂SO₃⁻ species at the air-water interface can attract gaseous molecules to the aqueous
73 surface, and thus promote particle growth.

74 **Comment 5.**

75 The reliability of the chosen methods should be clarified in the HNSO₂ + CH₃SO₃H reaction.
76 Although the traditional method CCSD(T)//M06-2X has been widely used for atmospheric reactions,
77 it should be noted that there are quite large uncertainties for estimating barrier height. This should
78 clearly tell the potential readers.

79 **Response:** Thanks for the suggestion of the reviewer. As the suggestion of the reviewer, the
80 reliability of CCSD(T)/aug-cc-pVDZ//M06-2X/6-311+G(2df,2pd)-based calculation method has
81 been verified as follows. Firstly, the geometry and frequency calculation involved in the HNSO₂
82 hydrolysis were verified (Fig. S2) at three different theoretical levels of M06-2X/6-
83 311++G(3df,2pd), M06-2X/6-311++G(3df,3pd) and M06-2X/aug-cc-pVTZ and experimental
84 values. Then, based on the M06-2X/6-311++G(2df,2pd) optimized geometries, the corresponding

111 **Table S1** The Energy barriers (ΔE) and unsigned error (UE) ($\text{kcal}\cdot\text{mol}^{-1}$) for the HNSO_2 hydrolysis
112 at different theoretical the potential energy profile (ΔG) correction

Methods	ΔE^a	ΔE^b	ΔE^c	UE
CCSD(T)/CBS//M06-2X/ 6-311++G(2df,2pd)	3.4	29.7	-23.0	0.00
CCSD(T)-F12/cc-pVDZ-F12//M06-2X/ 6-311++G(2df,2pd)	3.6	30.6	-22.0	0.71

113 ^{a, b and c} respectively denote the species of pre-reactive complexes, transition states and products involved in the
114 HNSO_2 hydrolysis.

115 (b) To further confirm the reliability of the CCSD(T)-F12/cc-pVDZ-F12//M06-2X/6-
116 311++G(2df,2pd) level of theory, single-point energy calculations for the HNSO_2 hydrolysis in the
117 gas phase have been performed at two different levels of CCSD(T)/CBS and CCSD(T)-F12/cc-
118 pVDZ-F12 based on the optimized geometries at the M06-2X/6-311++G(2df,2pd) level. Notably,
119 the complete basis set (CBS) obtained by basis set extrapolation is used as the reference basis set.
120 As presented in Table S1, compared with unsigned error calculated at the CCSD(T)/CBS//M06-
121 2X/6-311++G(2df,2pd) level, unsigned errors calculated at CCSD(T)-F12/cc-pVDZ-F12//M06-
122 2X/6-311++G(2df,2pd) was $0.71 \text{ kcal}\cdot\text{mol}^{-1}$. This suggests that the relative energies obtained at the
123 CCSD(T)/aug-cc-pVDZ//M06-2X/6-311++G(2df,2pd) level was reasonable. Considering the
124 computational accuracy and cost, the CCSD(T)/aug-cc-pVDZ//M06-2X/6-311++G(2df,2pd) method
125 was chosen to calculate the single point energies of all the species involved in the HNSO_2 hydrolysis.
126 Thus, in Lines 130 to 133 Page 5 of the revised manuscript, the sentence of “The CCSD(T)/aug-cc-
127 pVDZ method was chosen to calculate the relative energies as the fact that, compared with unsigned
128 error (Table S1) calculated at the CCSD(T)/CBS//M06-2X/6-311++G(2df,2pd) level, unsigned
129 errors calculated at CCSD(T)-F12/cc-pVDZ-F12//M06-2X/6-311++G(2df,2pd) was $0.71 \text{ kcal}\cdot\text{mol}^{-1}$.”
130 has been added.

131 **Comment 6.**

132 In kinetics calculations, it is unclear. There are lots of issues that must be addressed. Provide the
133 details of VRC calculations. For example, how to set pivot points and what is the electronic structure
134 method for VRC-TST calculations? The author should provide the input files for VRC-TST and
135 MESMER calculations in Supporting information to help the potential readers to understand the
136 computational details.

137 **Response:** Thanks for the suggestion of the reviewer. The pivot point setting method and the
138 electronic structure method for VRC-TST calculation are provided in detail (shown in Part S1 in the
139 Supplement). Meanwhile, the input files for VRC-TST and MESMER calculations have been
140 provided in Supporting information. The main revision has been made as follows.

141 (a) Herein, we describe the implementation details of the VRC-TST calculation in in Part S1
142 in the Supplement. Specifically, there are two assumptions in VRC-VTST calculation: (1) the
143 contribution of the vibrational modes of reactants to the partition function is canceled by the
144 corresponding contribution of transition states to the partition function; (2) the internal geometries
145 of reactants are fixed along the reaction coordinate. The reaction coordinate in VRC-VTST is
146 different from that in RP-VTST and determined by the pivot points of each reactant fragment. For
147 the HNSO₂ hydrolysis reaction, the pivot points of HNSO₂ (points 1 and 2) are located at a distance
148 $\pm d$ along its S axis. Meanwhile, the pivots of H₂O (points 3 and 4) are located at a distance $\pm d$
149 perpendicular to H₂O molecule lane. As shown in Fig. S6, the Multiwfn package combined with the
150 VMD software is adopted to visualize the reaction system and help determine the location of pivot
151 points. The reaction coordinate value (s) is defined as the minimum of the distance (r_{ij}) between the
152 pivot point i ($=1$ or 2) and pivot point j ($=3$ or 4), where i and j represent the pivot points of HNSO₂
153 and H₂O molecules, respectively. Hence, each of the four dividing surfaces is obtained by
154 symmetrically placing two pivot points of each radical fragment (1-3, 1-4, 2-3, and 2-4). For
155 example, if the reaction coordinate s is equal to r_{23} , one of the four dividing surfaces (2-3), is
156 determined by the locations of pivot points 2, 3 and the reaction coordinate s . There are total four
157 pair of pivot points, the other three dividing surfaces (1-3, 1-4, 2-4) are defined by their
158 corresponding pivot points and reaction coordinates s . Note that the locations of pivot points are
159 critical to the rate constant calculation. Considering the difference between HNSO₂ and H₂O
160 molecules, the distance s between pivot points varies from 2.5 to 6 Å for HNSO₂ and H₂O in each
161 case with a 0.5 Å grid increment. So, in Lines 139 to141 Page 5 of the revised manuscript, the
162 sentence of the “Meanwhile, two pivot points (Bao et al., 2016; Long et al., 2021; Georgievskii and
163 Klippenstein, 2003; Meana-Pañeda et al., 2024) were selected to calculate the high-pressure limiting
164 rate for the HNSO₂ hydrolysis (shown in Part S1 in the Supplement).” has been added. Also, the
165 computational details of VRC-VTST calculations have been added in Line 159 Page S15to 180 Page
166 S16 of the revised Supplement.

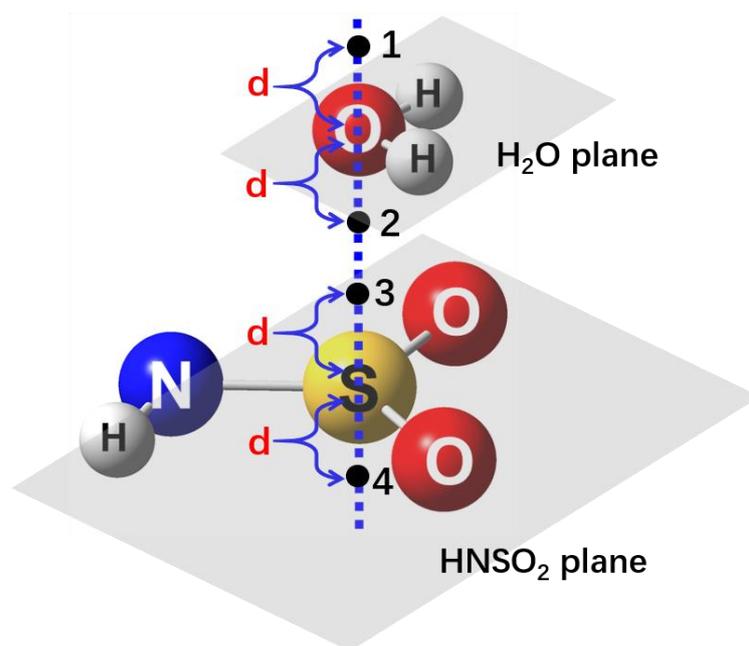


Fig. S6 The placements of the pivot points for the HNSO₂ hydrolysis

(b) The electronic structure method for VRC-TST calculations is based on Gaussian 09 program using the M06-2X/6-311++G(2df,2pd). So, in Lines 137-139 Page 5 of the revised manuscript, the sentence of the “It's worth noting that the electronic structure method for VRC-TST calculations is based on Gaussian 09 program using the M06-2X/6-311++G(2df,2pd).” has been added.

(c) The input files for VRC-TST and MESMER calculations have been provided in Supplement.

Comment 7.

According to the authors' previous research (Phys. Chem. Chem. Phys., 2022, 24, 4966-4977), the reaction of HNSO₂ with nH₂O also has a sufficiently low free energy barrier, which implies that HNSO₂ can undergo hydrolysis or decomposition directly at the gas-liquid interface or in the bulk phase. This seems to contradict the explanation on line 228 (page 8), given that the concentration of water is sufficiently high.

Response: Thanks for the suggestion of the reviewer. According to the previous work (Phys. Chem. Chem. Phys., 2022, 24, 4966-4977), the hydrolysis of HNSO₂ assisted by H₂O, (H₂O)₂ and (H₂O)₃ involved a loop structure mechanism. These reactions were known to occur via the initial formation of ring hydrogen bonding complex HNSO₂⋯(H₂O)_n (n = 1-3) with the calculated relative free energy of 0.2-3.6 kcal·mol⁻¹ followed by their rearrangement to form NH₂SO₃H. As the higher entropy effect, hydrogen bonding complex HNSO₂⋯(H₂O)_n (n = 1-3) were formed hardly under

187 actual atmospheric conditions, and thus the loop structure mechanism for the hydrolysis of HNSO₂
188 assisted by H₂O, (H₂O)₂ and (H₂O)₃ is not easy to occur in the gas phase. This is similar with
189 CH₃SO₃H-assisted gaseous hydrolysis of HNSO₂ which does not occur within the 100 ps.

190 At the air-water interface, the HNSO₂ molecule is stable and does not dissociate within 10 ps,
191 where the loop structure of hydrogen bonding complex HNSO₂⋯(H₂O)_n (*n* = 1-3) has not been
192 observed. This is proved by the BOMD simulation illustrated in Fig. S8 where the hydrated form of
193 HNSO₂ was not conducive to HNSO₂ hydrolysis at the air-water interface. So, even if the
194 concentration of water molecules at the air-water interface is sufficiently high, the probability that
195 HNSO₂ can be hydrolyzed or decomposed either directly at the air-water interface or in the bulk
196 phase is small. This is agreed with the simulation results. Based on this analysis above, in Lines
197 272-274 Page 10 of the revised manuscript, the sentence of the “Meanwhile, although HNSO₂
198 remains stable at the air-water interface (seen in Fig. S8) and does not dissociate within 10 ps, the
199 hydrated form of HNSO₂ illustrated in Fig. S8 was not conducive to HNSO₂ hydrolysis at the air-
200 water interface.” has been added to prove that the hydrated form of HNSO₂ was not conducive to
201 HNSO₂ hydrolysis at the air-water interface.

202 **Comment 8.**

203 Why did the authors not consider a third access channel in the gas phase, that is, the reaction pathway
204 of HNSO₂⋯CH₃SO₃H + H₂O? Considering the reactions at the gas-liquid interface, it seems more
205 plausible that HNSO₂⋯CH₃SO₃H would first form a complex before reacting with water molecules.
206 Considering the reactions at the gas-liquid interface, it seems more plausible that HNSO₂⋯
207 CH₃SO₃H would first form a complex before reacting with water molecules.

208 **Response:** Thanks for the suggestion of the reviewer. Indeed, the reaction pathway of HNSO₂⋯
209 MSA + H₂O is feasible. However, the concentration of water molecules in the atmosphere is about
210 10¹⁸ molecules·cm⁻³, which is much higher than those of HNSO₂ and MSA (10⁵-10⁹ molecules·cm⁻³).
211 Considering the harsh conditions for the initial formation of dimers between HNSO₂ and MSA
212 (i.e., HNSO₂ and MSA are sufficiently concentrated in the atmosphere.), we predict that the primary
213 preliminary dimers will continue to be dominated by HNSO₂⋯H₂O and MSA⋯H₂O complexes.
214 So, in Line 203 Page 7 to Line 207 Page 8 of the revised manuscript, the sentence of the “As the
215 concentration of water molecule (10¹⁸ molecules·cm⁻³ (Anglada et al., 2013)) in the atmosphere is

216 much higher than those of HNSO₂ and MSA (10⁵-10⁹ molecules·cm⁻³ (Shen et al., 2020)), the
217 reaction pathway of HNSO₂···MSA + H₂O is hard to occur in actual atmospheric conditions. So,
218 Channel MSA proceeds through the initial formation of dimers (HNSO₂···H₂O and MSA···H₂O)
219 via collisions between HNSO₂ (or MSA) and H₂O.” has been added.

220 **Comment 9.**

221 In Section 3.3, the authors examined the impact of MSA-MA-SFA clusters on nucleation.
222 Interestingly, DMA, which has a stronger nucleation capability, and NH₃, which has a higher
223 concentration, were excluded. I would like the authors to provide some appropriate justifications
224 for this.

225 **Response:** Thanks for the suggestion of the reviewer. Previous studies have demonstrated that
226 MSA-driven new particle formation (NPF) has attracted growing attention, as MSA significantly
227 contributes to NPF in scenarios with only natural sources of SO₂ were present. Currently,
228 atmospheric bases, including methylamine (MA), monoethanolamide, and dimethylamine (DMA),
229 have a key role in MSA-driven aerosol particle generation and growth, where MA exhibits the
230 strongest enhancing capability (*Environ. Sci. Technol.*, 2017, 51, 243-252; *J. Phys. Chem. B*, 2016,
231 120, 1526-1536; *Environ. Sci. Technol.*, 53, 14387-14397, 2019; *Atmos. Environ.*, 2023, 311,
232 120001). So, we choose MA over DMA and NH₃. This choice is similar to that previously reported
233 in the relevant references (*Atmos. Chem. Phys.*, 22, 2639-2650; 2022*Atmos. Environ.*, 2023, 311,
234 120001). Based on this analysis above, in Lines 94-96 Page 4 of the revised manuscript, the sentence
235 of the “Initially, the binary nucleation of MSA with inorganic ammonia and organic amines in the
236 atmosphere has been reported, where MA exhibits the strongest enhancing capability (Chen et al.,
237 2016; Chen and Finlayson-Pitts, 2017; Shen et al., 2019; Hu et al., 2023).” has been reorganized to
238 prove that the MSA-MA system was chosen over MSA-DMA.

239 **Comment 10.**

240 Since the ammonolysis of SO₃ is the primary pathway for SFA formation, the authors could have
241 compared it with the current pathway, which would be necessary for accurately assessing the
242 atmospheric significance of the current reaction.

243 **Response:** Thanks for the suggestion of the reviewer. As the suggestion of reviewer, we compared
244 the NH₃-assisted ammonolysis of SO₃ with the MSA-assisted HNSO₂ hydrolysis. In Line 233 Page
245 8 to Line 237 Page 9 of the revised manuscript, “Besides, MSA-assisted HNSO₂ hydrolysis is
246 reduced by 4.9 kcal·mol⁻¹ in energy barrier than the NH₃-assisted ammonolysis of SO₃ with its rate
247 constant at 298 K (2.85×10^{-11} cm³·molecule⁻¹·s⁻¹) close to the value of ammonolysis of SO₃ with
248 NH₃ (4.35×10^{-10} cm³·molecule⁻¹·s⁻¹) (Li et al., 2018). However, due to the absence of the
249 concentration of HNSO₂, the competitiveness of these two reactions cannot be further confirmed.”
250 has been added.

251 **Comment 11.**

252 In Fig. 6b and Fig. 7b, it is necessary for the authors to carefully examine whether the significant
253 abrupt changes caused by the concentrations of SFA and MA are reasonable.

254 **Response:** Thanks for the suggestion of the reviewer. It is noted that in Fig. 6(b), due to the
255 competitive relationship between MSA and SFA, at low concentrations of SFA, the binding capacity
256 of MSA with MA is stronger than that of SFA with MA, resulting in only a small amount of SFA
257 participating in cluster formation. However, as the concentration of SFA increases, the number of
258 (MSA)_x·(MA)_y·(SFA)_z (where $y \leq x + z \leq 3$) ternary clusters increases, leading to the formation of
259 more hydrogen bonds and a significant increase in R_{SFA} . Similarly, in Fig. 7(b), at a certain
260 concentration of SFA and MA, as the concentration of MSA increases, the hydrogen bonds between
261 SFA and MA are disrupted, leading to more binding of MA and MSA rather than SFA, resulting in
262 a sharp decrease in R_{SFA} . In Lines 364-369 Page 12 of the revised manuscript, “It is noted that in
263 Fig. 6(b), due to the competitive relationship between MSA and SFA, at low concentrations of SFA,
264 the binding capacity of MSA with MA is stronger than that of SFA with MA, resulting in only a
265 small amount of SFA participating in cluster formation. However, as the concentration of SFA
266 increases, the number of (MSA)_x·(MA)_y·(SFA)_z (where $y \leq x + z \leq 3$) ternary clusters increase,
267 leading to the formation of more hydrogen bonds and a significant increase in R_{SFA} .” has been added.

268 **Comment 12.**

269 In the introduction, the authors mention that the pK_a may affect the transfer of protons, thereby
270 affecting the catalytic ability. Whether similar trends will also directly affect the nucleation

271 capability should be considered, such as in the cases of MSA-MA-SFA, MSA-MA-SA, and SA/FA-
272 MA-SFA.

273 **Response:** Thanks for the suggestion of the reviewer. We apologize for the misunderstanding about
274 pK_a in Lines 63-65 Pages 2-3. Indeed, our aim is to illustrate the importance of MSA as a catalyst
275 from pK_a perspective. In order not to create ambiguity, as for the discussions of pK_a , the sentence
276 of the “It was noted that as the acidity of $\text{CH}_3\text{SO}_3\text{H}$ ($pK_a = -1.92$) was significantly stronger than
277 that of water ($pK_a = 15.0$) and formic acid ($pK_a = 3.74$), it may be predicted that the proton transfer
278 reaction for the hydrolysis of HNSO_2 with $\text{CH}_3\text{SO}_3\text{H}$ was much easier than those with water and
279 formic acid. It was also noted that although $\text{CH}_3\text{SO}_3\text{H}$ was less acidic than H_2SO_4 ($pK_a = -3.00$),
280 with the global reduction in the concentration of H_2SO_4 resulting from SO_2 emission restrictions,
281 the contribution of $\text{CH}_3\text{SO}_3\text{H}$ to aerosol nucleation has received the widespread attention of
282 scientists.” had been deleted. Meanwhile, the importance of MSA as a catalyst in HNSO_2 hydrolysis
283 has been organized as “It was noted that, with the global reduction in the concentration of H_2SO_4
284 resulting from SO_2 emission restrictions, the contribution of MSA to aerosol nucleation has received
285 the widespread attention of scientists.” in Lines 63-66 Page 3 of the revised manuscript.