

Supporting information

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Significant influence of water molecule on the SO₃ + HCl reaction in the gas phase and at the air-water interface

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Fig. S1 The optimized geometrical structures for the species of the SO₃ and HCl at several different levels of theory. The values in parentheses are the experimental values. ^a The values obtained at the MP2/6-311+G(3d,2p) level of theory; ^b The values obtained at the MP2/6-311+G(2df,2pd) level of theory, ^c The values obtained at the MP2/aug-cc-pVDZ level of theory, ^d The values obtained at the MP2/aug-cc-pVTZ level of theory, ^e The values obtained at the MP2/6-311++G(3df,2pd) level of theory; bond length is in angstrom and angle is in degree.

Table S1 Unscaled vibrational frequencies obtained at different levels

Table S2 The energy barriers (ΔE) and unsigned error (UE) (in kcal·mol⁻¹) for the SO₃ + HCl → ClSO₃H reaction at different theoretical methods with zero-point energy (ZPE) correction

Table S3 Relative energies (ΔE and $\Delta(E + ZPE)$ /(kcal·mol⁻¹)), enthalpies (ΔH /(kcal·mol⁻¹)), entropy (S(298 K)/(cal·mol⁻¹·K⁻¹)) and free energies (ΔG (298 K)/(kcal·mol⁻¹)) for the reactants, pre-reactive complexes, transition states, post-reactive complexes and products involved in the SO₃ + HCl → ClSO₃H reaction without and with H₂O and (H₂O)₂, as well as the hydrolysis reaction of SO₃ without and with H₂O

Table S4 Relative energies (ΔE and $\Delta(E + ZPE)$ /(kcal·mol⁻¹)), enthalpies (ΔH /(kcal·mol⁻¹)), entropy (S(298 K)/(cal·mol⁻¹·K⁻¹)) and free energies (ΔG (298 K)/(kcal·mol⁻¹)) for the reactants, pre-reactive complexes, transition states, post-reactive complexes and products involved in the SO₃ + HCl → ClSO₃H reaction at the CCSD(T)-F12/cc-pVDZ-F12//BLYP-D3/6-311+G(3d,2p) level

Table S5 Equilibrium coefficients for the complexes of SO₃···HCl, SO₃···H₂O, SO₃···(H₂O)₂, HCl···H₂O, and HCl···(H₂O)₂ within the altitudes range of 0-50 km

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Table S6 Concentrations ($\text{molecules}\cdot\text{cm}^{-3}$) of $\text{SO}_3\cdots\text{HCl}$, $\text{SO}_3\cdots\text{H}_2\text{O}$, $\text{SO}_3\cdots(\text{H}_2\text{O})_2$, $\text{HCl}\cdots\text{H}_2\text{O}$, and $\text{HCl}\cdots(\text{H}_2\text{O})_2$ within the temperature range of 280-320 K

Fig. S2 Schematic energy diagrams for the hydrolysis reaction of SO_3 without (a) and with (b) H_2O at the CCSD(T)-F12/cc-pVDZ-F12//MP2/6-311+G(3d,2p) level of theory

Fig. S3 The simulated trajectories of $\text{SO}_3 + \text{HCl}$ reaction (a), H_2O catalyzed $\text{SO}_3 + \text{HCl}$ reaction (b), $(\text{H}_2\text{O})_2$ catalyzed $\text{SO}_3 + \text{HCl}$ reaction (c), $\text{SO}_3 + \text{H}_2\text{O}$ reaction (d), and H_2O catalyzed $\text{SO}_3 + \text{H}_2\text{O}$ reaction (e) in the gas phase

Part 1. Calculations of reaction rate coefficients

Table S7 Rate coefficient ($\text{cm}^3\cdot\text{molecule}^{-1}\cdot\text{s}^{-1}$) for the $\text{SO}_3 + \text{HCl}$ reaction without and with H_2O , and $(\text{H}_2\text{O})_2$ as well as the hydrolysis of SO_3 without and with H_2O and HCl , along with the effective rate coefficient ($\text{cm}^3\cdot\text{molecule}^{-1}\cdot\text{s}^{-1}$) for the $\text{SO}_3 + \text{HCl}$ reaction with H_2O , and $(\text{H}_2\text{O})_2$ as well as the hydrolysis of SO_3 with H_2O and HCl within the temperature range of 280-320 K at 0 km

Table S8 Rate coefficient ($\text{cm}^3\cdot\text{molecule}^{-1}\cdot\text{s}^{-1}$) and atmospheric lifetimes (τ , s) of SO_3 for the hydrolysis of SO_3 without and with H_2O within the altitudes range of 0-50 km

Table S9 The rate coefficient for the hydrolysis of SO_3 starting from $\text{SO}_3\cdots\text{H}_2\text{O}$, $\text{SO}_3\cdots\text{H}_2\text{O} + \text{HCl}$ reaction, the hydrolysis of SO_3 with H_2O starting from $\text{SO}_3\cdots(\text{H}_2\text{O})_2$ and $\text{SO}_3\cdots(\text{H}_2\text{O})_2 + \text{HCl}$ reaction; Atmospheric lifetimes (τ , s) of $\text{SO}_3\cdots\text{H}_2\text{O}$ for the hydrolysis of SO_3 starting from $\text{SO}_3\cdots\text{H}_2\text{O}$ and the $\text{SO}_3\cdots\text{H}_2\text{O} + \text{HCl}$ reaction as well as the atmospheric lifetimes (τ , s) of $\text{SO}_3\cdots(\text{H}_2\text{O})_2$ for the hydrolysis of SO_3 with H_2O starting from $\text{SO}_3\cdots(\text{H}_2\text{O})_2$ and the $\text{SO}_3\cdots(\text{H}_2\text{O})_2 + \text{HCl}$ reaction within the altitude range of 0-50 km

Fig. S4 The simulated trajectories of the formation of $\text{ClSO}_3\cdots\text{H}_3\text{O}^+$ ion pair from the reaction of SO_3 , HCl and one interfacial water molecular at the air-water interface

Fig. S5 The simulated trajectories of the formation of $\text{ClSO}_3\cdots\text{H}_3\text{O}^+$ ion pair from the reaction of SO_3 , HCl and two interfacial water molecular at the air-water interface

Fig. S6 The simulated trajectories of the $\text{HSO}_4\cdots\text{H}_3\text{O}^+$ ion pair formation from SO_3 , HCl and two interfacial water molecules at the air-water interface

Fig. S7 The optimized geometrical structure for the ClSO_3^- ion at the MP2/6-311+G(3d,2p) level

Fig. S8 The optimized geometrical structure for the ClSO_3^- ion at the MP2/6-311+G(3d,2p) level

Fig. S9 The z coordinates of ClSO_3^- ion as the function of simulation time (a), the density profile of water (b) and the pie chart with the occurrence percentages of ClSO_3^- ion (c) at the air-water interface and in water phase

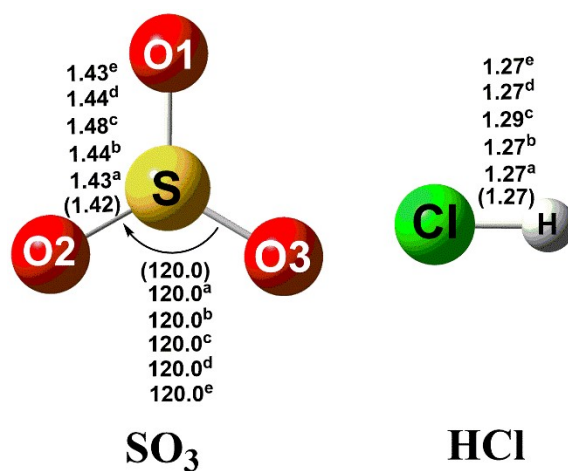


Fig. S1 The optimized geometrical structures for the species of the SO_3 and HCl at several different levels of theory. The values in parentheses are the experimental values. ^a The values obtained at the $\text{MP2}/6\text{-}311+\text{G}(3d,2p)$ level of theory; ^b The values obtained at the $\text{MP2}/6\text{-}311+\text{G}(2df,2pd)$ level of theory, ^c The values obtained at the $\text{MP2}/\text{aug-cc-pVDZ}$ level of theory, ^d The values obtained at the $\text{MP2}/\text{aug-cc-pVTZ}$ level of theory, ^e The values obtained at the $\text{MP2}/6\text{-}311++\text{G}(3df,2pd)$ level of theory; bond length is in angstrom and angle is in degree.

Table S1 Unscaled vibrational frequencies obtained at different levels

SO ₃		
Method	Theoretical Frequencies (unit: cm ⁻¹)	Experimental Frequencies (unit: cm ⁻¹)
MP2/6-311+G(3 <i>d</i> ,2 <i>p</i>)	494 513 513 1049 1379 1379	498 530 530 1065 1391 1391
MP2/6-311+G(2 <i>df</i> ,2 <i>pd</i>)	488 521 521 1053 1408 1408	
MP2/6-311++G(3 <i>df</i> ,2 <i>pd</i>)	503 523 523 1068 1421 1421	
MP2/aug-cc-pVDZ	454 469 469 974 1324 1324	
MP2/aug-cc-pVTZ	480 505 505 1037 1389 1389	
HCl		
Method	Theoretical frequencies (unit: cm ⁻¹)	Experimental frequencies (unit: cm ⁻¹)
MP2/6-311+G(3 <i>d</i> ,2 <i>p</i>)	3026	2990
MP2/6-311+G(2 <i>df</i> ,2 <i>pd</i>)	3055	
MP2/6-311++G(3 <i>df</i> ,2 <i>pd</i>)	3055	
MP2/aug-cc-pVDZ	3023	
MP2/aug-cc-pVTZ	3045	

The vibrational frequencies of SO₃ and HCl reactants among the methods of MP2/6-311+G(3*d*,2*p*), MP2/6-311+G(2*df*,2*pd*), MP2/aug-cc-pVTZ and MP2/6-311++G(3*df*,2*pd*) have been compared with the corresponding experimental values (From the NIST chemistry webbook, <http://webbook.nist.gov/chemistry>). As seen in Table S3, for the species of SO₃ and HCl, the average absolute deviation between the calculated harmonic vibrational frequencies at the MP2/6-311+G(3*d*,2*p*), MP2/6-311+G(2*df*,2*pd*), MP2/aug-cc-pVTZ and MP2/6-311++G(3*df*,2*pd*) levels of theory and the corresponding experimental ones are 1.66%, 2.13%, 2.26%, 3.05% and 4.72%, respectively. This further indicates that the calculated data for the title reaction at the MP2/6-311+G(3*d*,2*p*) level of theory is acceptable as the fact that the average absolute deviation between the calculated bond distances, bond angles and vibrational frequencies at the MP2/6-311+G(3*d*,2*p*) level and the corresponding experimental values is the smallest among the five different theoretical methods.

Table S2 The energy barriers (ΔE) and unsigned error (UE) (in kcal·mol⁻¹) for the SO₃ + HCl → ClSO₃H reaction at different theoretical methods with zero-point energy (ZPE) correction

Methods	ΔE^a	ΔE^b	ΔE^c	UE
CCSD(T)-F12/cc-pVQZ-F12//MP2/6-311+G(3d,2p)	-3.0	-19.0	-11.7	0.00
CCSD(T)/CBS//MP2/6-311+G(3d,2p)	-3.0	18.5	-12.1	0.30
CCSD(T)-F12/cc-pVDZ-F12//MP2/6-311+G(3d,2p)	-3.0	19.6	-11.3	0.30
CCSD(T)/aug-cc-pVTZ//MP2/6-311+G(3d,2p)	-3.0	19.5	-10.1	0.57
DLPNO-CCSD(T)-F12/cc-pVDZ-F12//MP2/6-311+G(3d,2p)	-2.7	19.9	-11.5	0.47
CCSD(T)/cc-pVTZ//MP2/6-311+G(3d,2p)	-2.1	20.4	-8.2	2.23
CCSD(T)/aug-cc-pVDZ//MP2/6-311+G(3d,2p)	-3.0	20.4	-5.7	2.47

^a, ^b and ^c respectively denote the species of pre-reactive complexes, transition states and product involved in SO₃ + HCl reaction.

Based on the MP2/6-311+G(3d,2p)-optimized geometries, single-point energy calculation was performed at a series of calculated methods of CCSD(T)-F12/cc-pVQZ-F12, CCSD(T)/CBS, CCSD(T)-F12/cc-pVDZ-F12, DLPNO-CCSD(T)-F12/cc-pVDZ-F12, CCSD(T)/aug-cc-pVTZ, CCSD(T)/aug-cc-pVDZ and CCSD(T)/cc-pVTZ. It is reported that the CCSD(T)-F12/cc-pVQZ-F12 (*Mol Phys.*, 2010, 108, 315-325.; *J. Chem. Theory. Comput.*, 2012, 8, 3175-3186) energy is the well-recognized “gold standard” with an accuracy better than 0.01 kcal·mol⁻¹. Thus, the single-point energy at the CCSD(T)-F12/cc-pVQZ-F12 level can be used as a benchmark for selecting the most appropriate method of calculating the energy. As seen in Table S4, the average absolute deviation between the calculated energies at the CCSD(T)/CBS, CCSD(T)-F12/cc-pVDZ-F12, DLPNO-CCSD(T)-F12/cc-pVDZ-F12, CCSD(T)/aug-cc-pVTZ, CCSD(T)/aug-cc-pVDZ and CCSD(T)/cc-pVTZ levels of theory and the corresponding CCSD(T)-F12/cc-pVQZ-F12 are 0.30 kcal·mol⁻¹, 0.30 kcal·mol⁻¹, 0.57 kcal·mol⁻¹, 0.47 kcal·mol⁻¹, 2.03 kcal·mol⁻¹ and 2.47 kcal·mol⁻¹, respectively. This further indicates that compared with the single-point energy at the CCSD(T)-F12/cc-pVQZ-F12 level, the average absolute deviation at the CCSD(T)-F12/cc-pVDZ-F12 level is the smallest in six different theoretical methods. So, the single-point energy obtained at the CCSD(T)-F12/cc-pVDZ-F12//MP2/6-311+G(3d,2p) level is reasonable and acceptable. Taking into account the computational accuracy and cost, the CCSD(T)-F12/cc-pVDZ-F12//MP2/6-311+G(3d,2p) method has been selected to optimize geometrical structures and calculate the relative energies of all the species for the title reactions.

Table S3 Relative energies (ΔE and $\Delta(E + ZPE)$ /(kcal·mol⁻¹)), enthalpies (ΔH /(kcal·mol⁻¹)), entropy (S(298 K)/(cal·mol⁻¹·K⁻¹)) and free energies (ΔG (298 K)/(kcal·mol⁻¹)) for the reactants, pre-reactive complexes, transition states, post-reactive complexes and products involved in the SO₃ + HCl → ClSO₃H reaction without and with H₂O and (H₂O)₂, as well as the hydrolysis reaction of SO₃ without and with H₂O at the CCSD(T)-F12/cc-pVDZ-F12//MP2/6-311+G(3d,2p) level

<i>Species</i>	ZPE	ΔE	S	ΔG	$\Delta(E + ZPE)$	ΔH
SO ₃ + HCl	11.9	0.0	106.1	0.0	0.0	0.0
SO ₃ ···HCl	12.7	-3.8	87.1	2.8	-3.0	-2.8
TS _{CSA}	12.2	19.2	74.3	27.9	19.6	18.4
ClSO ₃ H	16.2	-15.6	74.2	-2.9	-11.3	-12.4
SO ₃ + HCl + H ₂ O	25.4	0.0	168.2	0.0	0.0	0.0
SO ₃ ···H ₂ O + HCl	27.6	-9.6	124.9	-0.1	-7.4	-7.9
SO ₃ ···HCl + H ₂ O	26.2	-3.8	149.5	2.7	-3.0	-2.8
HCl···H ₂ O + SO ₃	27.4	-5.3	128.9	2.6	-3.3	-4.1
SO ₃ ···HCl···H ₂ O	28.9	-12.8	98.1	5.7	-9.4	-16.6
TS _{CSA_WM}	29.6	-9.1	84.9	12.5	-5.0	-12.3
ClSO ₃ H···H ₂ O	32.0	-28.7	89.0	-5.3	-22.1	-29.4
SO ₃ + HCl + (H ₂ O) ₂	41.2	0.0	175.3	0.0	0.0	0.0
SO ₃ ···(H ₂ O) ₂ + HCl	44.3	-16.6	135.9	-2.8	-13.5	-14.6
SO ₃ ···HCl + (H ₂ O) ₂	42.0	-3.8	156.7	2.7	-3.0	-2.8
HCl···(H ₂ O) ₂ + SO ₃	43.7	-8.7	143.4	2.2	-6.2	-7.4
SO ₃ ···HCl···(H ₂ O) ₂	45.0	-17.6	111.0	4.1	-13.9	-15.1
TS _{CSA_WD}	44.6	-17.4	104.2	5.2	-14.0	-16.0
ClSO ₃ H···(H ₂ O) ₂	48.0	-35.7	101.1	-8.9	-29.0	-31.0
SO ₃ + H ₂ O	21.1	0.0	106.6	0.0	0.0	0.0
SO ₃ ···H ₂ O	23.2	-9.6	80.3	-0.1	-7.4 (-7.6) ^a (-7.4) ^b	-7.9
TS _{SA}	21.7	16.0	70.9	25.6	16.6 (16.0) ^a (16.3) ^b	15.0
H ₂ SO ₄	24.8	-23.7	72.2	-11.2	-20.1 (19.5) ^a (-20.36) ^b	-21.5
SO ₃ + 2H ₂ O	34.7	0.0	198.0	0.0	0.0	0.0
SO ₃ + (H ₂ O) ₂	36.9	-5.0	167.4	2.9	-2.7 (-2.9) ^b	-3.3
SO ₃ ···H ₂ O + H ₂ O	36.8	-9.6	167.9	-0.1	-7.4 (-7.4) ^b	-7.9
IM _{SA_WM}	40.0	-21.6	128.0	0.2	-16.3 (-16.6) ^b	-17.8
TS _{SA_WM}	39.0	-15.0	118.1	7.6	-10.6 (-11.1) ^b	-13.7
H ₂ SO ₄ ···H ₂ O	40.7	-36.2	122.9	-12.9	-30.2 (-30.68) ^b	-32.3

^a The values are reported from reference (*J. Phys. Chem. A*, **2019**, *123*, 3131-3141)

^b The values are reported from reference (*Chem. Phys. Lett.*, **2013**, *581*, 26-29)

^c The values are reported from reference (*J Am Chem Soc.*, **2012**, *153*, 20632-44)

Table S4 Relative energies (ΔE and $\Delta(E + ZPE)$ /(kcal·mol⁻¹)), enthalpies (ΔH /(kcal·mol⁻¹)), entropy (S(298 K)/(cal·mol⁻¹·K⁻¹)) and free energies (ΔG (298 K)/(kcal·mol⁻¹)) for the reactants, pre-reactive complexes, transition states, post-reactive complexes and products involved in the SO₃ + HCl → ClSO₃H reaction at the CCSD(T)-F12/cc-pVDZ-F12//BLYP-D3/6-311+G(3d,2p) level

<i>Species</i>	ZPE	ΔE	S	ΔG	$\Delta(E + ZPE)$	ΔH
SO ₃ + HCl	11.1	0.0	106.5	0.0	0.0	0.0
SO ₃ ···HCl	11.9	-3.7	87.1	2.8	-2.9	-2.7
TS _{CSA}	11.3	20.9	74.3	29.2	19.	19.9
ClSO ₃ H	15.1	-15.0	74.2	-2.7	-11.5	-12.0

The DFT methods were used for the BOMD simulations benchmarked against the MP2 structures and CCSD(T) energies used to map the key structures along the PES for the SO₃ + HCl reaction. Specifically, the optimized geometries and vibrational frequencies of the reactants, pre-reactive complexes, transition states (TSs), post-reactive complexes and products were calculated using the BLYP-D3 method with 6-311+G(3d,2p) basis set by Gaussian 09 A.01 packages. At the same level, intrinsic reaction coordinate (IRC) calculations were used to determine the connectivity between the TSs and the suitable pre- and post-reactant complexes. Then, single point energy calculations were performed at the CCSD(T)-F12/cc-pVDZ-F12 level using ORCA. As seen in Table S2, the energies difference between CCSD(T)-F12/cc-pVDZ-F12//MP2/6-311+G(3d,2p) and CCSD(T)-F12/cc-pVDZ-F12//BLYP-D3/6-311+G(3d,2p) levels are less than 0.4 kcal·mol⁻¹. Thus, the BLYP-D3 method was reliable to model the reaction pathway.

Table S5 Equilibrium coefficients for the complexes of $\text{SO}_3 \cdots \text{HCl}$, $\text{SO}_3 \cdots \text{H}_2\text{O}$, $\text{SO}_3 \cdots (\text{H}_2\text{O})_2$, $\text{HCl} \cdots \text{H}_2\text{O}$, and $\text{HCl} \cdots (\text{H}_2\text{O})_2$ within the altitude range of 0-50 km

Altitude /km	T/K	$\text{SO}_3 \cdots \text{HCl}$	$\text{SO}_3 \cdots \text{H}_2\text{O}$	$\text{SO}_3 \cdots (\text{H}_2\text{O})_2$	$(\text{H}_2\text{O})_2$	$\text{HCl} \cdots \text{H}_2\text{O}$	$\text{HCl} \cdots (\text{H}_2\text{O})_2$
	280.00	1.58×10^{-22}	3.31×10^{-20}	7.12×10^{-18}	3.60×10^{-22}	7.53×10^{-22}	2.09×10^{-21}
	290.00	1.37×10^{-22}	2.11×10^{-20}	2.99×10^{-18}	3.06×10^{-22}	6.08×10^{-22}	1.38×10^{-21}
0	298.15	1.24×10^{-22}	1.51×10^{-20} (5.80×10^{-20}) ^a	1.56×10^{-18} (4.94×10^{-18}) ^b (2.16×10^{-18}) ^c	2.71×10^{-22} (5.70×10^{-22}) ^a	5.19×10^{-22} (5.50×10^{-22}) ^d	1.01×10^{-21}
	300.00	1.21×10^{-22}	1.39×10^{-20}	1.34×10^{-18}	2.63×10^{-22}	4.99×10^{-22}	9.34×10^{-22}
	310.00	1.07×10^{-22}	9.43×10^{-21}	6.28×10^{-19}	2.29×10^{-22}	4.16×10^{-22}	6.50×10^{-22}
	320.00	9.63×10^{-23}	6.57×10^{-21}	3.10×10^{-19}	2.02×10^{-22}	3.51×10^{-22}	4.63×10^{-22}
5	259.30	2.22×10^{-22}	9.11×10^{-20}	5.48×10^{-17}	5.59×10^{-21}	1.25×10^{-21}	5.59×10^{-21}
10	229.70	4.05×10^{-22}	5.92×10^{-19}	1.71×10^{-15}	2.94×10^{-20}	2.99×10^{-21}	2.94×10^{-20}
15	212.60	6.33×10^{-22}	2.19×10^{-18}	1.99×10^{-14}	9.60×10^{-20}	5.59×10^{-21}	9.60×10^{-20}
20	215.50	5.81×10^{-22}	1.71×10^{-18}	1.25×10^{-14}	7.68×10^{-20}	4.97×10^{-21}	7.68×10^{-20}
25	218.60	5.35×10^{-22}	1.35×10^{-18}	8.00×10^{-15}	6.19×10^{-20}	4.43×10^{-21}	6.19×10^{-20}
30	223.70	4.70×10^{-22}	9.18×10^{-19}	3.89×10^{-15}	4.37×10^{-20}	3.68×10^{-21}	4.37×10^{-20}
35	235.10	3.60×10^{-22}	4.19×10^{-19}	8.87×10^{-16}	2.14×10^{-20}	2.53×10^{-21}	2.14×10^{-20}
40	249.90	2.63×10^{-22}	1.61×10^{-19}	1.46×10^{-16}	8.97×10^{-21}	1.60×10^{-21}	8.97×10^{-21}
45	266.10	1.97×10^{-22}	6.61×10^{-20}	2.67×10^{-17}	3.96×10^{-21}	1.05×10^{-21}	3.96×10^{-21}
50	271.00	1.81×10^{-22}	5.12×10^{-20}	1.64×10^{-17}	3.13×10^{-21}	9.26×10^{-22}	3.13×10^{-21}

^a The value was taken from reference (*J. Phys. Chem. A*, **2019**, *123*, 3131-3141)

^b The value was taken from reference (*J. Am. Chem. Soc.*, **2012**, *134*, 20632-20644)

^c The value was taken from reference (*J. Phys. Chem. A*, **2017**, *121*, 3101-3108)

^d The value was taken from reference (*J. Phys. Chem. A*, **2018**, *122*, 350-363)

Table S6 Concentrations (molecules·cm⁻³) of SO₃···HCl, SO₃···H₂O, SO₃···(H₂O)₂, HCl···H₂O, and HCl···(H₂O)₂ within the temperature range of 280-320 K at 0 km

Catalysts	T/K	280	290	298	300	310	320
H ₂ O ^a	20% RH	5.16 × 10 ¹⁶	9.56 × 10 ¹⁶	1.55 × 10 ¹⁷	1.72 × 10 ¹⁷	2.92 × 10 ¹⁷	4.70 × 10 ¹⁷
	40% RH	1.03 × 10 ¹⁷	1.91 × 10 ¹⁷	3.09 × 10 ¹⁷	3.43 × 10 ¹⁷	5.84 × 10 ¹⁷	9.40 × 10 ¹⁷
	60% RH	1.55 × 10 ¹⁷	2.87 × 10 ¹⁷	4.64 × 10 ¹⁷	5.15 × 10 ¹⁷	8.77 × 10 ¹⁷	1.41 × 10 ¹⁸
	80% RH	2.07 × 10 ¹⁷	3.82 × 10 ¹⁷	6.18 × 10 ¹⁷	6.86 × 10 ¹⁷	1.17 × 10 ¹⁸	1.88 × 10 ¹⁸
	100% RH	2.58 × 10 ¹⁷	4.78 × 10 ¹⁷	7.73 × 10 ¹⁷	8.58 × 10 ¹⁷	1.46 × 10 ¹⁸	2.35 × 10 ¹⁸
(H ₂ O) ₂	20% RH	9.59 × 10 ¹¹	2.80 × 10 ¹²	6.51 × 10 ¹²	7.78 × 10 ¹²	1.95 × 10 ¹³	4.45 × 10 ¹³
	40% RH	3.82 × 10 ¹²	1.12 × 10 ¹³	2.59 × 10 ¹³	3.10 × 10 ¹³	7.81 × 10 ¹³	1.78 × 10 ¹⁴
	60% RH	8.65 × 10 ¹²	2.52 × 10 ¹³	5.83 × 10 ¹³	6.98 × 10 ¹³	1.76 × 10 ¹⁴	4.01 × 10 ¹⁴
	80% RH	1.54 × 10 ¹³	4.46 × 10 ¹³	1.03 × 10 ¹⁴	1.24 × 10 ¹⁴	3.14 × 10 ¹⁴	7.13 × 10 ¹⁴
	100% RH	2.40 × 10 ¹³	6.99 × 10 ¹³	1.62 × 10 ¹⁴ (4.72 × 10 ¹⁴) ^b (4.55 × 10 ¹⁴) ^c	1.94 × 10 ¹⁴	4.88 × 10 ¹⁴	1.11 × 10 ¹⁴
SO ₃ ···H ₂ O	20% RH	1.71	2.02	2.34	2.39	2.75	3.09
	40% RH	3.41	4.03	4.66	4.77	5.51	6.17
	60% RH	5.13	6.06	7.00	7.16	8.27	9.26
	80% RH	6.85	8.06	9.32	9.54	11.0	12.3
	100% RH	8.54	10.1	11.7	11.9	13.8	15.4
SO ₃ ···(H ₂ O) ₂	20% RH	6.83 × 10 ⁻³	8.37 × 10 ⁻³	1.02 × 10 ⁻²	1.04 × 10 ⁻²	1.23 × 10 ⁻²	1.38 × 10 ⁻²
	40% RH	2.72 × 10 ⁻²	3.34 × 10 ⁻²	4.04 × 10 ⁻²	4.13 × 10 ⁻²	4.91 × 10 ⁻²	5.53 × 10 ⁻²
	60% RH	6.16 × 10 ⁻²	7.54 × 10 ⁻²	9.11 × 10 ⁻²	9.32 × 10 ⁻²	0.11	0.12
	80% RH	0.11	0.13	0.16	0.17	0.20	0.22
	100% RH	0.17	0.21	0.25	0.26	0.31	0.35
HCl···H ₂ O	20% RH	3.89 × 10 ⁴	5.82 × 10 ⁴	8.04 × 10 ⁴	8.59 × 10 ⁴	1.21 × 10 ⁵	1.65 × 10 ⁵
	40% RH	7.76 × 10 ⁴	1.16 × 10 ⁵	1.60 × 10 ⁵	1.71 × 10 ⁵	2.43 × 10 ⁵	3.30 × 10 ⁵
	60% RH	1.17 × 10 ⁵	1.75 × 10 ⁵	2.41 × 10 ⁵	2.57 × 10 ⁵	3.64 × 10 ⁵	4.94 × 10 ⁵
	80% RH	1.56 × 10 ⁵	2.32 × 10 ⁵	3.21 × 10 ⁵	3.42 × 10 ⁵	4.86 × 10 ⁵	6.59 × 10 ⁵
	100% RH	1.94 × 10 ⁵	2.91 × 10 ⁵	4.01 × 10 ⁵	4.28 × 10 ⁵	6.07 × 10 ⁵	8.24 × 10 ⁵
HCl···(H ₂ O) ₂	20% RH	2.00	3.85	6.56	7.27	12.7	20.6
	40% RH	7.99	15.4	26.1	28.9	50.8	82.5
	60% RH	18.1	34.7	58.7	65.2	11.5	18.6 × 10 ²
	80% RH	32.3	61.5	1.04 × 10 ²	1.16 × 10 ²	2.04 × 10 ²	3.30 × 10 ²
	100% RH	50.1	96.2	1.63 × 10 ²	1.81 × 10 ²	3.1 × 10 ²	5.16 × 10 ²

^a The Concentrations (molecules·cm⁻³) of H₂O and (H₂O)₂ values were reported from reference (*J. Phys. Chem. A*, **2013**, *117*, 10381-10396)

^b The values are reported from reference (*J. Am. Chem. Soc.*, **2021**, *143*, 8402–8413)

^c The values are reported from reference (*RSC Adv.*, **2015**, *5*, 17623)

^d The values are reported from reference (*Proc. Natl. Acad. Sci. U.S.A.*, **2019**;116(50):24966-24971)

^e The values are reported from reference (*J. Phys. Chem. A*, **2018**; 122(1):350-363. *J. Phys. Chem. A*, **2012**, *116*, 4712–4719)

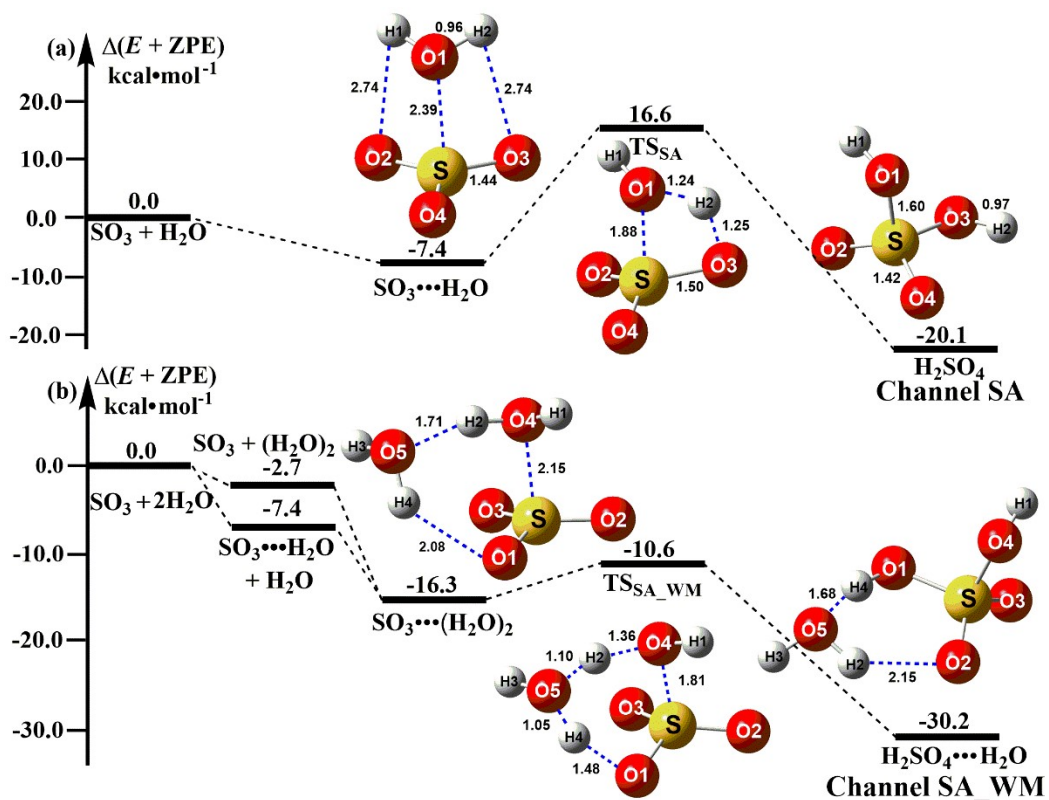


Fig. S2 Schematic energy diagrams for the hydrolysis reaction of SO_3 without (a) and with (b) H_2O at the CCSD(T)-F12/cc-pVDZ-F12//MP2/6-311+G(3d,2p) level of theory

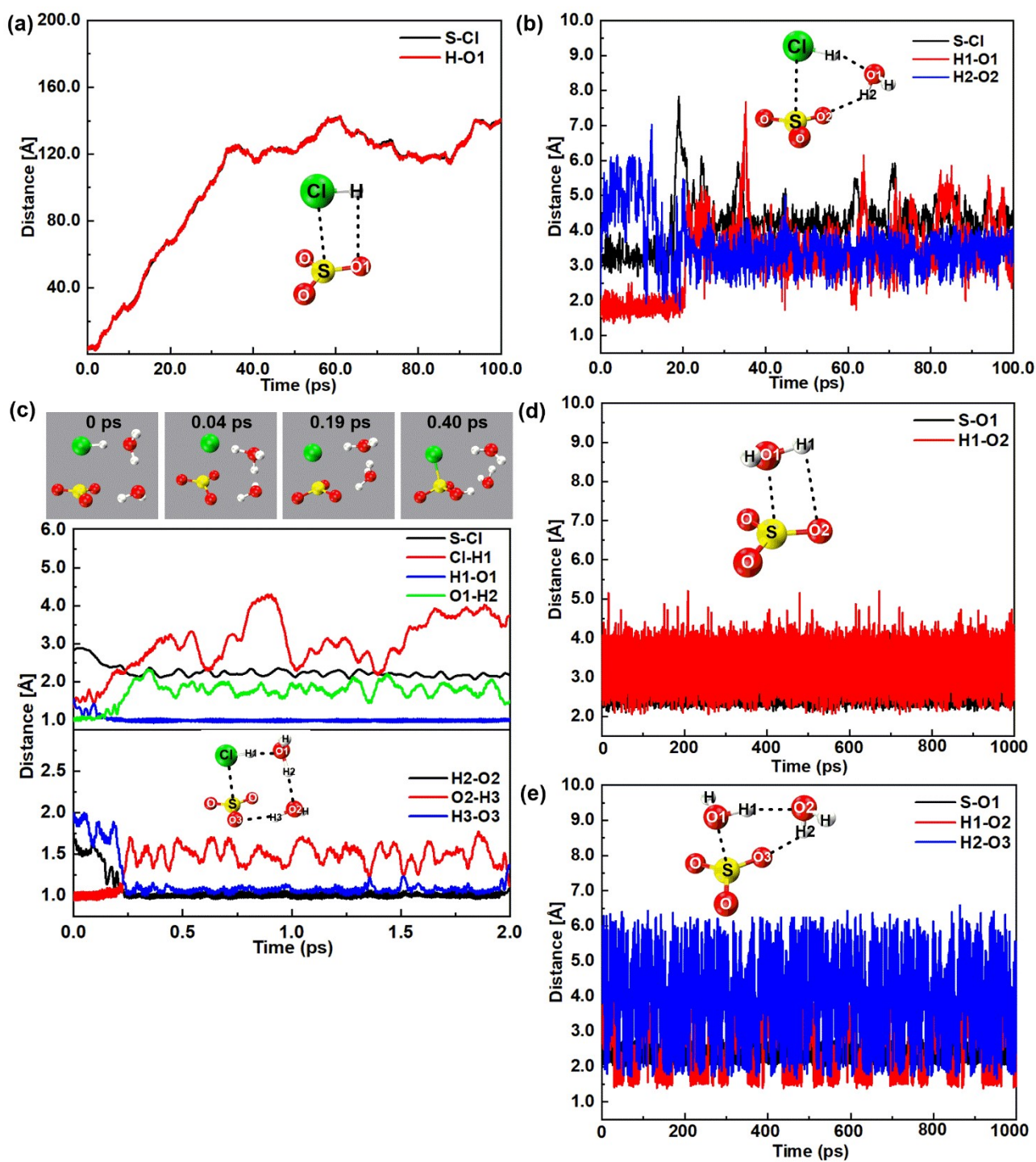


Fig. S3 The simulated trajectories of SO₃ + HCl reaction (a), H₂O catalyzed SO₃ + HCl reaction (b), (H₂O)₂ catalyzed SO₃ + HCl reaction (c), SO₃ + H₂O reaction (d), and H₂O catalyzed SO₃ + H₂O reaction (e) in the gas phase

Part 1. Calculations of reaction rate coefficients

The kinetics for the $\text{SO}_3 \cdots (\text{H}_2\text{O})_n$ ($n = 0-2$) + HCl reaction were calculated by adopting a Master Equation Solver for Multi Energy-well Reactions (MESMER) code.¹ The $\text{SO}_3 \cdots (\text{H}_2\text{O})_n$ ($n = 0-2$) + HCl reaction begins with the formation of the pre-reactive reactant complex $\text{SO}_3 \cdots (\text{H}_2\text{O})_n \cdots \text{HCl}$ ($n = 0-2$) through barrierless bimolecular association reactions between $\text{SO}_3 \cdots (\text{H}_2\text{O})_n$ ($n = 0-2$) and HCl, then $\text{SO}_3 \cdots (\text{H}_2\text{O})_n \cdots \text{HCl}$ ($n = 0-2$) goes through a unimolecular transformation through the TS to form $\text{ClSO}_3\text{H} \cdots (\text{H}_2\text{O})_n$ ($n = 0-2$).

The inverse Laplace transformation method has been used to carry out the kinetic calculations for the barrierless bimolecular reaction steps ($\text{SO}_3 \cdots (\text{H}_2\text{O})_n$ ($n = 0-2$) + HCl \rightarrow $\text{SO}_3 \cdots (\text{H}_2\text{O})_n \cdots \text{HCl}$ ($n = 0-2$)). Rate coefficients for unimolecular steps ($\text{SO}_3 \cdots (\text{H}_2\text{O})_n \cdots \text{HCl}$ ($n = 0-2$) \rightarrow $\text{ClSO}_3\text{H} \cdots (\text{H}_2\text{O})_n$ ($n = 0-2$)) have been calculated using the Rice-Ramsperger-Kessel-Marcus (RRKM) theory as implemented in MESMER software [1], and has been shown in eqn. (S1) and (S2), has been shown in eqn. (S1) and eqn. (S2), respectively.

$$k(E) = \kappa \cdot \frac{\sigma m^\ddagger g_e^\ddagger}{\sigma^\ddagger m g_e} \cdot \frac{E(E - E_0)}{h \rho(E)} \quad (\text{S1})$$

$$k(T) = \frac{1}{Q(\beta)} \int_0^\infty k(E) \rho(E) \exp(-\beta E) dE \quad (\text{S2})$$

In eqn. (S1) and eqn. (S2), σ and σ^\ddagger are respectively the external rotational symmetry numbers for the reactants and transition state; m and m^\ddagger is respectively the numbers of optical isomer for the reactants and transition state; g_e and g_e^\ddagger is respectively the electronic state degeneracy for the reactants and transition state; E_0 is the reaction critical energy; $E(E - E_0)$ is the sum of states of the transition state; $\rho(E)$ is the density of states of the reactants and $Q(\beta)$ is the corresponding canonical partition function. For the bath gas (N_2) and reactants (SO_3 and HCl), the collisional energy-transfer process was simulated in a single exponential-down model with the $\langle \Delta E_{\text{down}} \rangle = 200 \text{ cm}^{-1}$. The Lennard-Jones parameters for the reaction of SO_3 ($\epsilon/k_B = 318.4 \text{ K}$ and $\sigma = 4.175 \text{ \AA}$) and HCl ($\epsilon/k_B = 344.7 \text{ K}$ and $\sigma = 3.339 \text{ \AA}$) were estimated by Gilbert and Smith method² and the parameters ($\epsilon/k_B = 71.4 \text{ K}$ and $\sigma = 3.798 \text{ \AA}$) of bath gas (N_2) was taken from the reference.³

Reference:

- [1] Gilbert, R.G., Smith, S.C., Theory of unimolecular and recombination reactions. **1990**.
- [2] Glowacki, D.R., Liang, C.H., Morley, C., Pilling, M.J., Robertson, S.H., *J. Phys. Chem. A.*, **2012**, 116, 9545-9560.
- [3] Mai, T.V.T., Duong, M.V., Nguyen, H.T., Huynh, L.K., *Phys. Chem. Chem. Phys.*, **2018**, 20, 6677-6687

Table S7 Rate coefficient ($\text{cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$) for the $\text{SO}_3 + \text{HCl}$ reaction without and with H_2O , and $(\text{H}_2\text{O})_2$ as well as the hydrolysis of SO_3 without and with H_2O within the temperature range of 280-320 K at 0 km

Catalysts	T (K)	280 K	290 K	298 K	300 K	310 K	320 K
Channel CSA	k_{CSA}	2.16×10^{-27}	4.53×10^{-27}	8.20×10^{-27}	9.51×10^{-27}	1.98×10^{-26}	4.07×10^{-26}
Channel CSA_WM	$k_{\text{CSA_WM}}$	5.81×10^{-15}	5.23×10^{-15}	4.82×10^{-15}	4.73×10^{-15}	4.30×10^{-15}	3.93×10^{-15}
Channel CSA_WD	$k_{\text{CSA_WD}}$	5.65×10^{-11}	4.90×10^{-11}	4.33×10^{-11}	3.26×10^{-11}	2.72×10^{-11}	2.26×10^{-11}
Channel SA	k_{SA}	1.66×10^{-24}	2.18×10^{-24}	2.76×10^{-24} $(1.50 \times 10^{-23})^a$	2.94×10^{-24}	4.09×10^{-24}	5.81×10^{-24}
Channel SA_WM	$k_{\text{SA_WM}}$	3.74×10^{-13}	3.19×10^{-13}	2.81×10^{-13} $(1.40 \times 10^{-12})^a$	2.72×10^{-13}	2.32×10^{-13}	1.99×10^{-13}

k_{CSA} , $k_{\text{CSA_WM}}$, $k_{\text{CSA_WD}}$, k_{SA} and $k_{\text{SA_WM}}$ are denoted the rate coefficient for the $\text{SO}_3 + \text{HCl}$ reaction without and with H_2O , and $(\text{H}_2\text{O})_2$ as well as the hydrolysis of SO_3 without and with H_2O ;

^a The value was taken from reference (*J. Phys. Chem. A*, **2019**, 123, 3131-3141)

1 **Table S8** Rate coefficient ($\text{cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$) and atmospheric lifetimes (τ , s) of SO_3 for the hydrolysis of SO_3
 2 without and with H_2O within the altitudes range of 0-50 km

H (km)	T (K)	p (Torr)	$[\text{H}_2\text{O}]^{\text{a,b}}$	$[\text{HCl}]^{\text{b}}$	$[\text{HCl} \cdots \text{H}_2\text{O}]$	$k_{\text{SA}}(T, p)$	τ_{SA}	$k_{\text{SA_WM}}(T, p)$	$\tau_{\text{SA_WM}}$
0	298.15	760.00	4.40×10^{17}	3.20×10^7	7.31×10^3	2.76×10^{-24}	8.22×10^5	2.81×10^{-13}	1.22×10^{-3}
5	259.30	406.75	1.70×10^{16}	2.10×10^7	4.46×10^2	1.06×10^{-24}	5.55×10^7	5.50×10^{-13}	6.54×10^{-2}
10	229.70	202.16	3.00×10^{14}	2.60×10^7	2.33×10^1	7.02×10^{-25}	4.75×10^9	9.52×10^{-13}	1.97×10^1
15	212.60	91.20	1.50×10^{13}	2.70×10^8	2.26×10^1	6.19×10^{-25}	1.08×10^{11}	1.32×10^{-12}	1.41×10^3
20	215.50	41.04	4.20×10^{12}	2.00×10^9	4.17×10^1	6.45×10^{-25}	3.69×10^{11}	1.21×10^{-12}	2.51×10^4
25	218.60	19.00	2.50×10^{12}	1.30×10^9	1.44×10^1	6.71×10^{-25}	5.96×10^{11}	1.09×10^{-12}	1.01×10^5
30	223.70	8.36	1.50×10^{12}	7.90×10^8	4.36	7.07×10^{-25}	9.43×10^{11}	9.30×10^{-13}	4.83×10^5
35	235.10	3.80	8.90×10^{11}	5.10×10^8	1.15	7.87×10^{-25}	1.43×10^{12}	7.05×10^{-13}	4.28×10^6
40	249.90	2.28	4.80×10^{11}	2.70×10^8	2.07×10^{-1}	9.45×10^{-25}	2.21×10^{12}	4.99×10^{-13}	5.40×10^7
45	266.10	1.06	2.50×10^{11}	1.40×10^8	3.68×10^{-2}	1.24×10^{-24}	3.21×10^{12}	3.07×10^{-13}	7.88×10^8
50	271.00	0.55	1.20×10^{11}	7.50×10^8	8.33×10^{-3}	1.38×10^{-24}	6.06×10^{12}	2.20×10^{-13}	6.17×10^9

3 τ_{SA} and $\tau_{\text{SA_WM}}$ are atmospheric lifetimes of SO_3 for the reactions of $\text{SO}_3 + \text{H}_2\text{O}$ and $\text{SO}_3 \cdots \text{H}_2\text{O} + \text{H}_2\text{O}$, respectively.

4 ^a The value was taken from reference (*J. Am. Chem. Soc.*, 2021, **143**, 8402-8413.)

5 ^b The value was taken from reference (*Aeronomy of the Middle Atmosphere: Chemistry and Physics of the Stratosphere and Mesosphere, the third revised and*
 6 *enlarged edition, 2005.*)

7

8 **Table S9** The rate coefficient for the hydrolysis of SO₃ starting from SO₃⋯H₂O, SO₃⋯H₂O +HCl reaction, the hydrolysis of SO₃ with H₂O starting from SO₃⋯(H₂O)₂
9 and SO₃⋯(H₂O)₂ +HCl reaction; Atmospheric lifetimes (τ, s) of SO₃⋯H₂O for the hydrolysis of SO₃ starting from SO₃⋯H₂O and the SO₃⋯H₂O + HCl reaction as well
10 as the atmospheric lifetimes (τ, s) of SO₃⋯(H₂O)₂ for the hydrolysis of SO₃ with H₂O starting from SO₃⋯(H₂O)₂ and the SO₃⋯(H₂O)₂ + HCl reaction within the altitude
11 range of 0-50 km

<i>H</i> (km)	[H ₂ O] ^a	[HCl] ^b	<i>k</i> ₁	τ ₁	<i>k</i> ₂	τ ₂	<i>k</i> ₃	τ ₃	<i>k</i> ₄	τ ₄
0	4.40 × 10 ¹⁷	3.20 × 10 ⁷	1.91 × 10 ⁻⁴	5.23 × 10 ³	1.92 × 10 ⁻¹⁶	1.63 × 10 ⁸	1.80 × 10 ⁷	5.55 × 10 ⁻⁸	2.88 × 10 ⁻¹³	5.07 × 10 ⁵
5	1.70 × 10 ¹⁶	2.10 × 10 ⁷	1.45 × 10 ⁻⁵	6.88 × 10 ⁴	1.26 × 10 ⁻¹⁶	5.55 × 10 ⁸	5.98 × 10 ⁶	1.67 × 10 ⁻⁷	3.07 × 10 ⁻¹³	8.87 × 10 ⁵
10	3.00 × 10 ¹⁴	2.60 × 10 ⁷	2.54 × 10 ⁻⁶	3.93 × 10 ⁵	8.30 × 10 ⁻¹⁷	4.75 × 10 ⁸	1.92 × 10 ⁶	5.20 × 10 ⁻⁷	3.26 × 10 ⁻¹³	7.43 × 10 ⁵
15	1.50 × 10 ¹³	2.70 × 10 ⁸	1.04 × 10 ⁻⁶	9.59 × 10 ⁵	6.16 × 10 ⁻¹⁷	1.08 × 10 ⁷	8.09 × 10 ⁵	1.24 × 10 ⁻⁶	3.39 × 10 ⁻¹³	1.27 × 10 ⁴
20	4.20 × 10 ¹²	2.00 × 10 ⁹	1.20 × 10 ⁻⁶	8.30 × 10 ⁵	6.48 × 10 ⁻¹⁷	3.69 × 10 ⁶	7.45 × 10 ⁵	1.34 × 10 ⁻⁶	3.29 × 10 ⁻¹³	2.14 × 10 ³
25	2.50 × 10 ¹²	1.30 × 10 ⁹	1.41 × 10 ⁻⁶	7.09 × 10 ⁵	6.81 × 10 ⁻¹⁷	5.96 × 10 ⁷	6.37 × 10 ⁵	1.57 × 10 ⁻⁶	3.12 × 10 ⁻¹³	7.93 × 10 ³
30	1.50 × 10 ¹²	7.90 × 10 ⁸	1.84 × 10 ⁻⁶	5.43 × 10 ⁵	7.31 × 10 ⁻¹⁷	9.43 × 10 ⁷	5.20 × 10 ⁵	1.92 × 10 ⁻⁶	2.83 × 10 ⁻¹³	3.21 × 10 ³
35	8.90 × 10 ¹¹	5.10 × 10 ⁸	3.43 × 10 ⁻⁶	2.91 × 10 ⁵	8.36 × 10 ⁻¹⁷	1.43 × 10 ⁷	4.62 × 10 ⁵	2.17 × 10 ⁻⁶	2.29 × 10 ⁻¹³	1.92 × 10 ³
40	4.80 × 10 ¹¹	2.70 × 10 ⁸	8.15 × 10 ⁻⁶	1.23 × 10 ⁵	9.49 × 10 ⁻¹⁷	2.21 × 10 ⁷	4.64 × 10 ⁵	2.15 × 10 ⁻⁶	1.72 × 10 ⁻¹³	1.60 × 10 ⁴
45	2.50 × 10 ¹¹	2.47 × 10 ²	2.24 × 10 ⁻⁶	4.47 × 10 ⁴	9.61 × 10 ⁻¹⁷	3.21 × 10 ⁷	3.63 × 10 ⁵	2.75 × 10 ⁻⁶	1.06 × 10 ⁻¹³	1.72 × 10 ⁴
50	1.20 × 10 ¹¹	5.03 × 10 ¹	3.07 × 10 ⁻⁶	3.26 × 10 ⁴	8.49 × 10 ⁻¹⁷	6.06 × 10 ⁸	2.43 × 10 ⁵	4.12 × 10 ⁻⁶	7.50 × 10 ⁻¹⁴	1.34 × 10 ⁵

12 *k*₁ is the rate coefficient of the hydrolysis of SO₃ starting from SO₃⋯H₂O, *k*₂ is the rate coefficient of the SO₃⋯H₂O +HCl reaction, *k*₃ is the rate coefficient of the hydrolysis of SO₃ with H₂O
13 starting from SO₃⋯(H₂O)₂ and *k*₄ is the rate coefficient of the SO₃⋯(H₂O)₂ +HCl reaction; τ₁ and τ₂ is the atmospheric lifetime of SO₃⋯H₂O for the SO₃⋯H₂O and SO₃⋯H₂O + HCl reactions,
14 respectively; τ₃ and τ₄ is the atmospheric lifetime of SO₃⋯(H₂O)₂ for the reactions of SO₃⋯(H₂O)₂ and SO₃⋯(H₂O)₂ + HCl, respectively.

15 ^a The values are reported from reference (*J. Am. Chem. Soc.*, **2021**, *143*, 8402-8413)

16 ^b The values are reported from reference (*Aeronomy of the Middle Atmosphere: Chemistry and Physics of the Stratosphere and Mesosphere, the third revised and enlarged edition, 2005.*)

17 The atmospheric lifetimes of SO₃⋯H₂O for the hydrolysis of SO₃ starting from SO₃⋯H₂O (τ₁) and the SO₃⋯H₂O + HCl reaction (τ₂) have been calculated and
18 were represented as Eq. (S3) and Eq. (S4), respectively. Similarly, the atmospheric lifetimes of SO₃⋯(H₂O)₂ for the hydrolysis of SO₃ with H₂O starting from
19 SO₃⋯(H₂O)₂ (τ₃) and the SO₃⋯(H₂O)₂ + HCl reaction (τ₄) have been calculated and were represented as Eq. (S5) and Eq. (S6), respectively.

20
$$\tau_1 = (k_1)^{-1} \tag{S3}$$

21
$$\tau_2 = (k_2 \times [\text{HCl}])^{-1} \tag{S4}$$

22
$$\tau_3 = (k_3)^{-1} \tag{S5}$$

23
$$\tau_4 = (k_4 \times [\text{HCl}])^{-1} \tag{S6}$$

24 Where k_1 is the rate coefficient of the hydrolysis of SO_3 starting from $\text{SO}_3 \cdots \text{H}_2\text{O}$, k_2 is the rate coefficient of the
25 $\text{SO}_3 \cdots \text{H}_2\text{O} + \text{HCl}$ reaction, k_3 is the rate coefficient of the hydrolysis of SO_3 with H_2O starting from $\text{SO}_3 \cdots (\text{H}_2\text{O})_2$
26 and k_4 is the rate coefficient of the $\text{SO}_3 \cdots (\text{H}_2\text{O})_2 + \text{HCl}$ reaction; $[\text{HCl}]$ is the concentration of HCl taken from
27 reference.¹

28 As seen in Table S9, the value of τ_2 is larger by 2-5 orders of magnitude than τ_1 within the altitude range of
29 0-50 km. This indicates that $\text{SO}_3 \cdots \text{H}_2\text{O}$ is hydrolyzed before it collides with HCl molecules. So, the H_2O -assisted
30 $\text{SO}_3 + \text{HCl}$ reaction occurred through $\text{SO}_3 \cdots \text{H}_2\text{O} + \text{HCl}$ reaction is unfavorable. This is consistent with the fact that
31 H_2O -assisted $\text{SO}_3 + \text{HCl}$ reaction is dominated by the $\text{HCl} \cdots \text{H}_2\text{O} + \text{SO}_3$ reaction mentioned in the 3.2 section of the
32 manuscript. Similarly, the value of τ_4 is larger by 11-13 orders of magnitude than τ_3 within the altitude range of 0-
33 50 km, revealing $\text{SO}_3 \cdots (\text{H}_2\text{O})_2$ is hydrolyzed before it collides with HCl molecules. These results predict that
34 $\text{SO}_3 \cdots (\text{H}_2\text{O})_n$ ($n = 1-2$) + HCl reaction is unfavorable in $(\text{H}_2\text{O})_n$ ($n = 1-2$)-assisted $\text{SO}_3 + \text{HCl}$ reaction. Thus, the
35 $\text{SO}_3 \cdots (\text{H}_2\text{O})_n$ ($n = 1-2$) + HCl reactions were not considered in $(\text{H}_2\text{O})_n$ ($n = 1-2$)-assisted $\text{SO}_3 + \text{HCl}$ reaction and
36 only the $\text{HCl} \cdots (\text{H}_2\text{O})_n + \text{SO}_3$ reaction has been studied in the $(\text{H}_2\text{O})_n$ ($n = 1-2$)-assisted $\text{SO}_3 + \text{HCl}$ reaction.

37 **Reference**

38 1. S. Mallick, S. Sarkar, B. Bandyopadhyay and P. Kumar, *J. Phys. Chem. A*, 2018, **122**, 350-363.

39

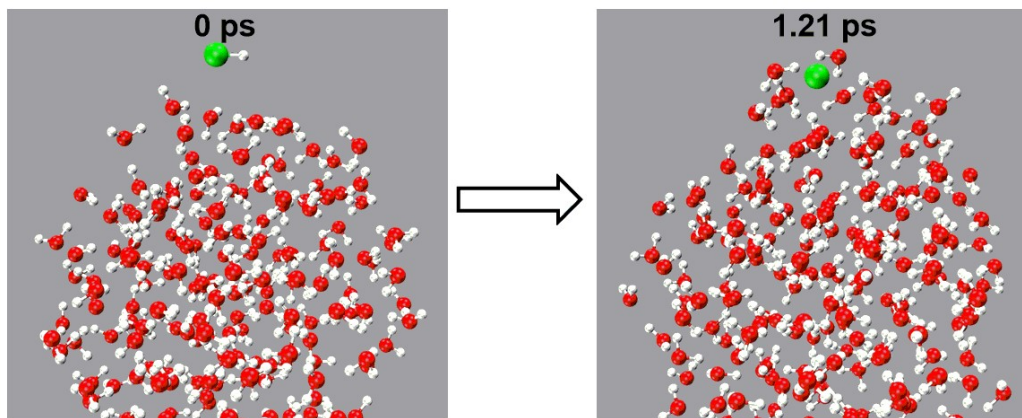


Fig. S4 Snapshot structures taken from the BOMD simulations of HCl reaction at the air-water interface. The white, red and green spheres represent H, O and Cl atoms, respectively.

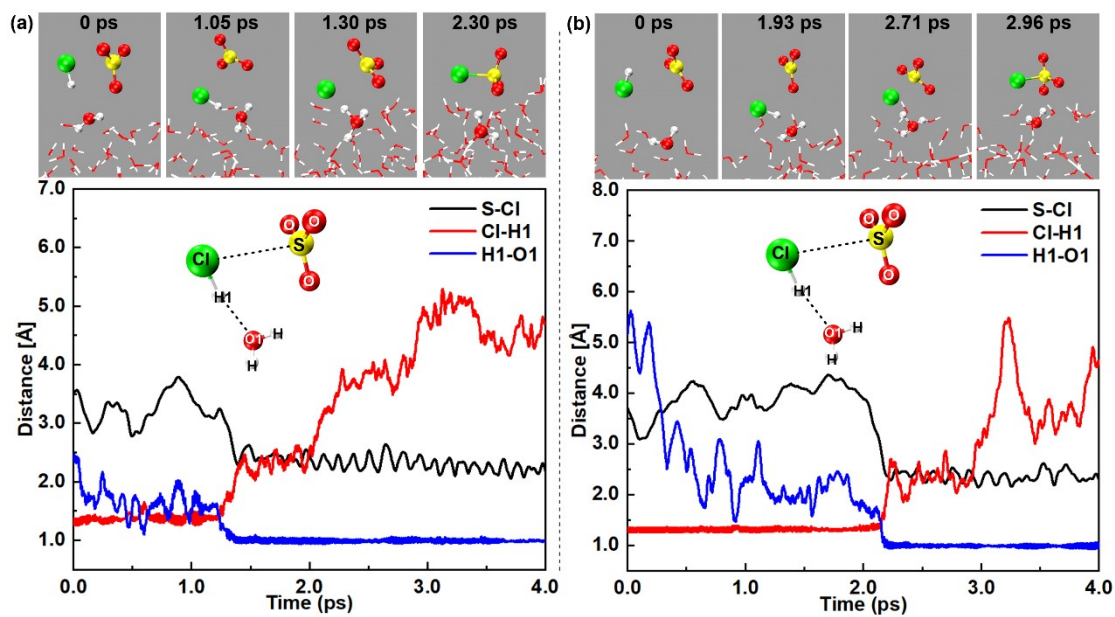


Fig. S5 The simulated trajectories of the formation of $\text{ClSO}_3^- \cdots \text{H}_3\text{O}^+$ ion pair from the reaction of SO_3 , HCl and one interfacial water molecular at the air-water interface

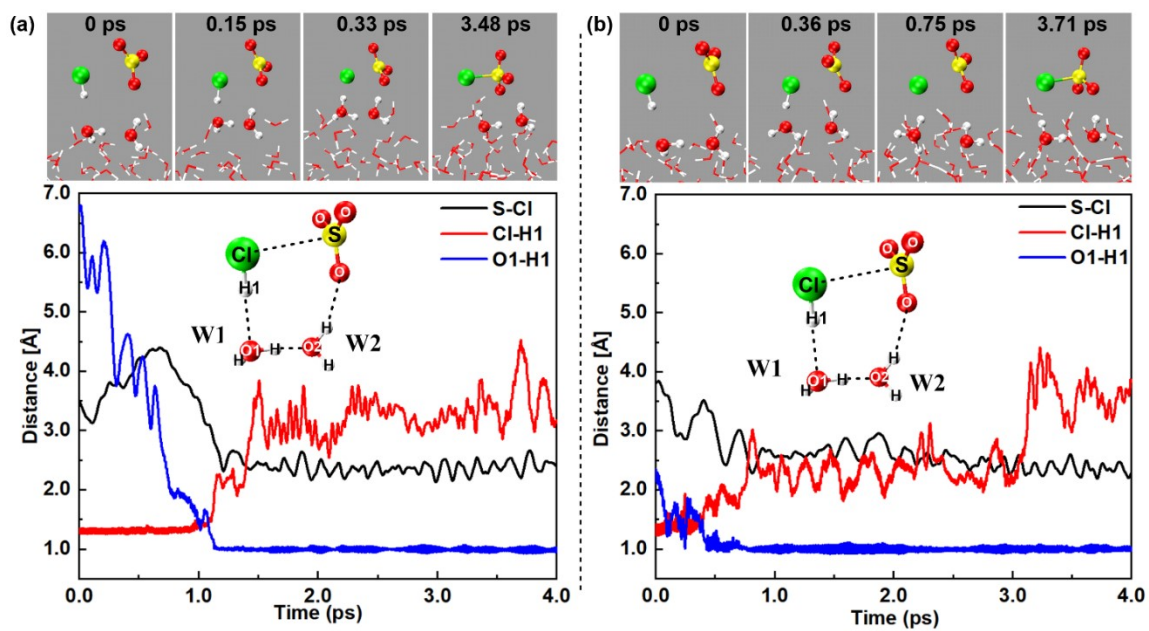


Fig. S6 The simulated trajectories of the formation of $\text{ClSO}_3^- \cdots \text{H}_3\text{O}^+$ ion pair from the reaction of SO_3 , HCl and two interfacial water molecular at the air-water interface

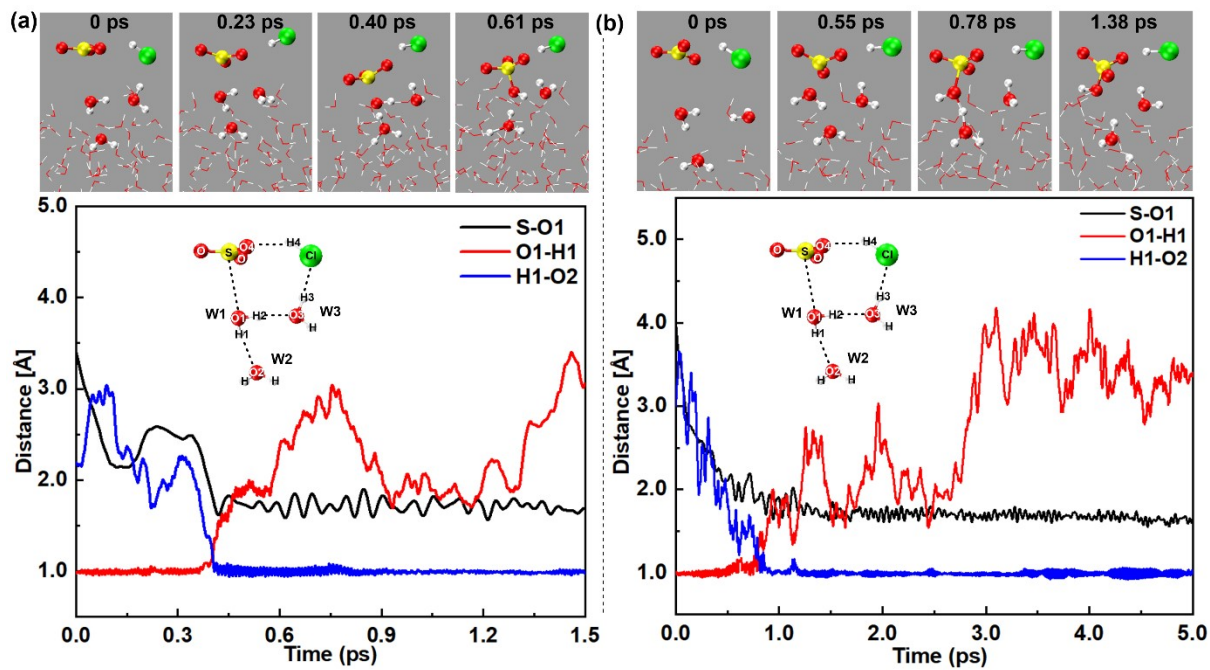


Fig. S7 The simulated trajectories of the $\text{HSO}_4^- \cdots \text{H}_3\text{O}^+$ ion pair formation from SO_3 , HCl and two interfacial water molecules at the air-water interface

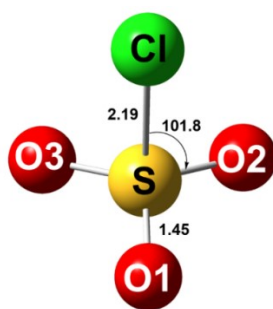


Fig. S8 The optimized geometrical structure for the ClSO_3^- ion at the MP2/6-311+G(3d,2p) level

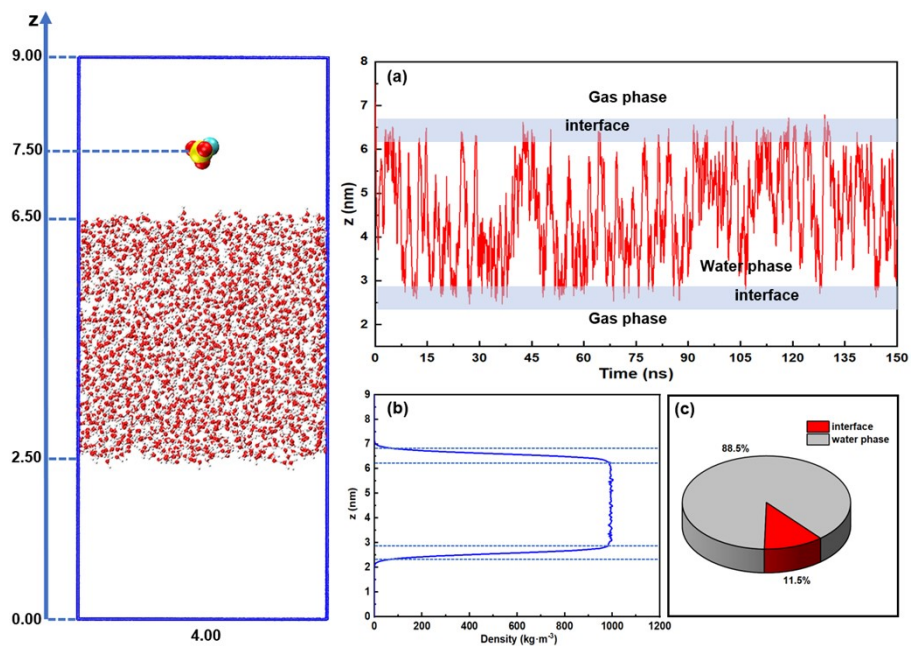


Fig. S9 The z coordinates of ClSO_3^- ion as the function of simulation time (a), the density profile of water (b) and the pie chart with the occurrence percentages of ClSO_3^- ion (c) at the air-water interface and in water phase