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# Catalytic effect of $(\text{H}_2\text{O})_n$ ( $n = 1-3$ ) clusters on the $\text{HO}_2 + \text{SO}_2 \rightarrow \text{HOSO} + {}^3\text{O}_2$ reaction under tropospheric conditions†

Rui Wang,<sup>id</sup>\*<sup>a</sup> Qiuyue Yao,<sup>‡</sup><sup>b</sup> Mingjie Wen,<sup>‡</sup><sup>a</sup> Shaobo Tian,<sup>‡</sup><sup>a</sup> Yan Wang,<sup>‡</sup><sup>a</sup> Zhiyin Wang,<sup>a</sup> Xiaohu Yu,<sup>id</sup><sup>a</sup> Xianzhao Shao<sup>a</sup> and Long Chen<sup>cd</sup>

The  $\text{HO}_2 + \text{SO}_2 \rightarrow \text{HOSO} + {}^3\text{O}_2$  reaction, both without a catalyst and with  $(\text{H}_2\text{O})_n$  ( $n = 1-3$ ) as a catalyst, has been investigated using CCSD(T)/CBS//M06-2X/aug-cc-pVTZ methods, and canonical variational transition state theory with small curvature tunneling (CVT/SCT). The calculated results show that  $\text{H}_2\text{O}$  exerts the strongest catalytic role in the hydrogen atom transfer processes of  $\text{HO}_2 + \text{SO}_2 \rightarrow \text{HOSO} + {}^3\text{O}_2$  as compared with  $(\text{H}_2\text{O})_2$  and  $(\text{H}_2\text{O})_3$ . In the atmosphere at 0 km altitude within the temperature range of 280.0–320.0 K, the reaction with  $\text{H}_2\text{O}$  is dominant, compared with the reaction without a catalyst, with an effective rate constant 2–3 orders of magnitude larger. In addition, at 0 km, it is worth mentioning that the relevance of the  $\text{HO}_2 + \text{SO}_2 \rightarrow \text{HOSO} + {}^3\text{O}_2$  reaction with  $\text{H}_2\text{O}$  depends heavily on its ability to compete with the primary loss mechanism of  $\text{HO}_2$  radicals (such as the  $\text{HO}_2 + \text{HO}_2$  and  $\text{HO}_2 + \text{NO}_3$  reactions) and  $\text{SO}_2$  (such as the  $\text{SO}_2 + \text{HO}$  reaction). The calculated results show that the  $\text{HO}_2 + \text{SO}_2 \rightarrow \text{HOSO} + {}^3\text{O}_2$  reaction with  $\text{H}_2\text{O}$  cannot be neglected in the primary loss mechanism of the  $\text{HO}_2$  radical and  $\text{SO}_2$ . The calculated results also show that for the formation of  $\text{HOSO}$  and  ${}^3\text{O}_2$ , the contribution of  $\text{H}_2\text{O}$  decreases from 99.98% to 27.27% with an increase in altitude from 0 km to 15 km, due to the lower relative concentration of water. With the altitude increase, the  $\text{HO}_2 + \text{SO}_2 \rightarrow \text{HOSO} + {}^3\text{O}_2$  reaction with  $\text{H}_2\text{O}$  cannot compete with the primary loss mechanism of  $\text{HO}_2$  radicals. The present results provide new insight into  $(\text{H}_2\text{O})_n$  ( $n = 1-3$ ) catalysts, showing that they not only affect energy barriers, but also have an influence on loss mechanisms. The present findings should have broad implications in computational chemistry and atmospheric chemistry.

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## 1. Introduction

As a significant gaseous pollutant from both industrial and natural sources,<sup>1</sup> sulfur dioxide ( $\text{SO}_2$ )<sup>2,3</sup> can cause a wide range of issues for human health, agriculture and the global climate.<sup>4</sup> It leads to acid rain that damages forest and crops, and plays a role in the formation of atmospheric aerosols.<sup>5,6</sup> Furthermore, short-term exposure to high levels of  $\text{SO}_2$  in the air can be life-

threatening, as it can cause breathing difficulties and obstruct airways, while long-term exposure to persistent levels of  $\text{SO}_2$  can cause chronic bronchitis, emphysema and respiratory illness.<sup>7</sup> Similar to  $\text{SO}_2$ , the hydroperoxyl radical ( $\text{HO}_2$ ) is also an important atmospheric species, which plays important roles in both the troposphere and the stratosphere.<sup>8</sup> In the troposphere, the  $\text{HO}_2$  radical is central to the production of ozone and the generation of hydroxyl radicals, whereas in the stratosphere, it is involved in catalytic cycles.  $\text{HO}_2$  also acts as a significant transient intermediate in the combustion of hydrocarbon fuels, atmospheric photolysis cycles, and biochemical processes.<sup>9,10</sup> The reaction between  $\text{HO}_2$  and  $\text{SO}_2$  has aroused great interest from many research groups due to its great importance to supply a reverse path between  $\text{SO}_2$  and  $\text{HOSO}$  (or  $\text{SO}_3$ ) in the sulfur cycle. This reaction may take place *via* a number of pathways including the three main product paths shown in eqn (1)–(3), namely,  $\text{O}_2 + \text{HOSO}$  formation,  $\text{O}_2 + \text{HSO}_2$  formation, and  $\text{OH} + \text{SO}_3$  formation.<sup>3,11</sup> It is noteworthy that, as one of the most important products of the  $\text{HO}_2 + \text{SO}_2$  reaction,  $\text{HOSO}$  has been found to be relatively stable<sup>12</sup> and its subsequent reactions<sup>13</sup> are important for atmospheric chemistry. Therefore, its structure,<sup>14,15</sup> harmonic vibrational frequencies,<sup>16</sup>

<sup>a</sup>Shaanxi Key Laboratory of Catalysis, School of Chemical & Environment Science, Shaanxi University of Technology, Hanzhong, Shaanxi, P. R. China. E-mail: wangrui830413@163.com; Fax: +86-0916-2641083; Tel: +86-0916-2641083

<sup>b</sup>Henan Key Laboratory of Boron Chemistry and Advanced Energy Materials, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan 453007, China

<sup>c</sup>Key Lab of Aerosol Chemistry & Physics, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an, Shaanxi, P. R. China

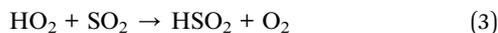
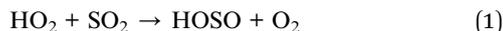
<sup>d</sup>State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an, Shaanxi, P. R. China

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‡ Qiuyue Yao, Mingjie Wen, Shaobo Tian, and Yan Wang contributed equally to this work.



thermochemistry<sup>12,17</sup> and subsequent reactions<sup>13,18</sup> have been widely investigated.



The kinetics and mechanism of the  $\text{HO}_2 + \text{SO}_2$  reaction have been studied experimentally and theoretically for a range of temperatures and pressures. In an experimental study, Payne *et al.*<sup>19</sup> found that the rate constant of the  $\text{HO}_2 + \text{SO}_2$  reaction was  $(8.7 \pm 1.8) \times 10^{-16} \text{ cm}^3$  per molecule per s at 300 K and a pressure of 30 Torr. Meanwhile, the rate constant of the  $\text{HO}_2 + \text{SO}_2$  reaction at 298 K was found to be  $2.01 \times 10^{-17} \text{ cm}^3$  per molecule per s, as measured by Burrows *et al.*<sup>20</sup> at low pressure. The kinetics and mechanism for the reaction of  $\text{HO}_2$  with  $\text{SO}_2$  were investigated by Wang *et al.*<sup>11</sup> with *ab initio* molecular orbital and transition state theory calculations. Their results showed that the reaction firstly proceeds to form a five-membering complex  $\text{SO}_2 \cdots \text{HO}_2$ , and then the complex undergoes barrierless decomposition to produce  $\text{O}_2 + \text{HOSO}$ . These investigations provide meaningful information about the mechanisms and kinetics for the  $\text{HO}_2 + \text{SO}_2$  reaction under atmospheric conditions. However, this effort has only focused on the non-catalytic process of the  $\text{HO}_2 + \text{SO}_2$  reaction.

Water has long been considered as a subject of chemical interest due to its abundance and unique properties in atmospheric chemistry.<sup>21</sup> It not only forms hydrogen-bonded complexes with  $\text{HO}_2$ ,<sup>22,23</sup>  $\text{OH}$ ,<sup>24–26</sup> formic acid<sup>21</sup> and nitric acid,<sup>8</sup> but also can actively participate in atmospheric reactions as a catalyst,<sup>27,28</sup> of which  $\text{HO}_2 \cdots \text{H}_2\text{O}$  is a well-studied example.<sup>29–31</sup> An interesting result<sup>29</sup> concerning this complex is that the  $\text{HO}_2$  self-reaction can be up to three times faster in the presence of water, since 30% of  $\text{HO}_2$  radicals may exist in the form of  $\text{HO}_2 \cdots \text{H}_2\text{O}$ .<sup>32</sup> Moreover, many experimental and theoretical studies have been reported on the electronic structure of the clusters  $\text{SO}_2 \cdots \text{H}_2\text{O}$ <sup>33–37</sup> and the gaseous hydrolysis reaction of  $\text{SO}_2 + \text{H}_2\text{O}$ .<sup>34</sup> These situations stimulated our interest in modeling the gas-phase reaction of the  $\text{H}_2\text{O} \cdots \text{HO}_2 \cdots \text{SO}_2$  ternary system, in which a single water molecule serves as a catalyst.

Recently, Chen *et al.*<sup>3</sup> employed the CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ method to investigate the reactions of  $\text{HO}_2 + \text{SO}_2$  and  $\text{HO}_2 \cdots \text{H}_2\text{O} + \text{SO}_2$ . Their calculations showed that  $\text{H}_2\text{O}$  slightly accelerates the  $\text{SO}_2 + \text{HO}_2$  reaction to form a  $\text{HSO}_4 \cdots \text{H}_2\text{O}$  radical complex. Although Chen *et al.*<sup>3</sup> provided meaningful information on the mechanism and kinetics of  $\text{HO}_2 \cdots \text{H}_2\text{O} + \text{SO}_2$  and  $\text{HO}_2 + \text{SO}_2$  reactions under tropospheric conditions, the most favorable, water-assisted channel ( $\text{HO}_2 + \text{SO}_2 \rightarrow \text{HOSO} + \text{O}_2$ ) has not yet been investigated in this way. Thus, it is still difficult to judge whether water molecules have an obvious positive catalytic effect on the  $\text{HO}_2 + \text{SO}_2$  reaction or not. Furthermore, many experimental and theoretical studies have appeared in the literature on the electronic structure of the clusters  $\text{HO}_2 \cdots (\text{H}_2\text{O})_n$  ( $n = 2–3$ )<sup>38,39</sup> and  $\text{SO}_2 \cdots (\text{H}_2\text{O})_n$  ( $n = 2–3$ ).<sup>40,41</sup> On the other hand, some studies have shown that water

dimers<sup>38,42–49</sup> and trimers<sup>39,49–52</sup> can also have a significant catalytic effect in hydrogen abstraction reactions and hydrolysis of sulfur dioxide.<sup>53,54</sup> Thus, the investigation of the effect of  $(\text{H}_2\text{O})_n$  ( $n = 1–3$ ) on the  $\text{HO}_2 + \text{SO}_2 \rightarrow \text{HOSO} + {}^3\text{O}_2$  reaction is a logical path to pursue.

In the present study, the detailed effects of  $(\text{H}_2\text{O})_n$  ( $n = 1–3$ ) on the hydrogen atom transfer processes of the  $\text{HO}_2 + \text{SO}_2 \rightarrow \text{HOSO} + {}^3\text{O}_2$  reaction have been investigated at the CCSD(T)/CBS//M06-2X/aug-cc-pVTZ level of theory, which is organized as follows. Firstly, incorporation of  $(\text{H}_2\text{O})_n$  ( $n = 1–3$ ) into the  $\text{HO}_2 + \text{SO}_2 \rightarrow \text{HOSO} + \text{O}_2$  reaction produced two different types reactions:  $\text{HO}_2 \cdots (\text{H}_2\text{O})_n$  ( $n = 1–3$ ) +  $\text{SO}_2$  and  $\text{SO}_2 \cdots (\text{H}_2\text{O})_n$  ( $n = 1–3$ ) +  $\text{HO}_2$ . Then, these  $(\text{H}_2\text{O})_n$  ( $n = 1–3$ )-catalyzed channels were evaluated by investigating the direct hydrogen abstraction process and the double hydrogen transfer mechanism. Secondly, the rate constants and effective rate constant of the hydrogen abstraction reaction of  $\text{HO}_2 + \text{SO}_2 \rightarrow \text{HOSO} + \text{O}_2$  without and with  $(\text{H}_2\text{O})_n$  ( $n = 1–3$ ) were calculated to identify the favorable routes. Finally, the atmospheric relevance of the effect of  $(\text{H}_2\text{O})_n$  ( $n = 1–3$ ) was investigated by their competition with the primary loss mechanism of  $\text{HO}_2$  radicals (such as the  $\text{HO}_2 + \text{HO}_2$  and  $\text{HO}_2 + \text{NO}_3$  reactions) and  $\text{SO}_2$  (such as the  $\text{SO}_2 + \text{HO}$  reaction). Overall, this work may lead to a better understanding of the effects of  $(\text{H}_2\text{O})_n$  ( $n = 1–3$ ) on gas-phase reactions under tropospheric conditions.

## 2. Computational details

The geometries of all the reactants, pre-reactive intermediates, post-reactive intermediates, transition states and products were optimized at the M06-2X/aug-cc-pVTZ level of theory,<sup>55</sup> and frequency analysis at the same level was performed to study the stationary point as well as the transition states. Moreover, the minimum energy path (MEP) was achieved by the intrinsic reaction coordinate (IRC)<sup>56</sup> theory with a gradient step size of  $0.01–0.05 \text{ (amu)}^{1/2} \text{ Bohr}$ , to confirm that the TS connects to minima along the reaction path. To obtain more reliable energy information, single-point energy calculations for the stationary points were obtained using the CCSD(T)<sup>57</sup>/CBS method at the M06-2X/aug-cc-pVTZ optimized geometries. It is worth pointing out that single point energy calculations of CCSD(T)/CBS were carried out for all species at the CCSD(T) level of theory using the aug-cc-pVDZ and aug-cc-pVTZ basis sets. The energy values obtained at the DZ and TZ levels were used to extrapolate the results to a complete basis set (CBS) limit. The method used here for CBS extrapolation was proposed and developed by Varandas and Pansini.<sup>58</sup> In this method, the energy at the CBS limit is obtained by extrapolating the correlation (Corr) energy and Hartree-Fock (HF) energy separately using two different equations. To extrapolate the Corr energy and HF energy, the following equations were used:

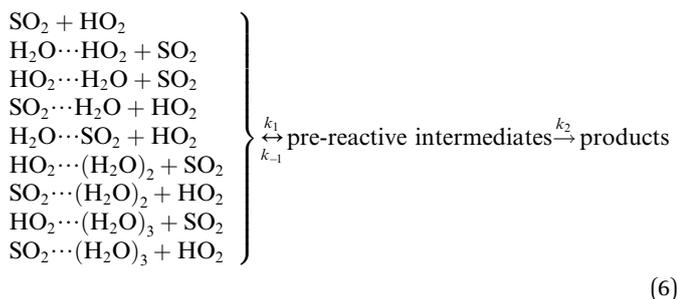
$$\text{CBS(Corr)} = \frac{2.71^3 E_{X+1} - 1.91^3 E_X}{2.71^3 - 1.91^3} \quad (4)$$

$$\text{CBS(HF)} = \frac{2.71^5 E_{X+1} - 1.91^5 E_X}{2.71^5 - 1.91^5} \quad (5)$$



To estimate the effect of  $(\text{H}_2\text{O})_n$  ( $n = 1-3$ ), the theoretical rate constants of canonical variational transition (CVT)<sup>59-61</sup> state theory with small curvature tunneling (SCT)<sup>62,63</sup> correction for every reaction channel were calculated using the VKLab<sup>64</sup> program coupled with the steady state approximation.

As described in eqn (6), the  $\text{HO}_2 + \text{SO}_2 \rightarrow \text{HOSO} + \text{O}_2$  reaction without and with  $(\text{H}_2\text{O})_n$  ( $n = 1-3$ ) all began with the formation of pre-reactive intermediates before occurring through the transition state.



Similar to the water-catalyzed  $\text{OH} + \text{HOCl}$  reaction,<sup>26</sup> the free energy results displayed in Table S4<sup>†</sup> suggest that the intermediates are, in part, shifted to the reactants. Assuming that the pre-reactive intermediates of the  $\text{HO}_2 + \text{SO}_2 \rightarrow \text{HOSO} + \text{O}_2$  reaction without and with  $(\text{H}_2\text{O})_n$  ( $n = 1-3$ ) are in equilibrium with the corresponding reactants and are at steady state, the overall rate constant of the  $\text{SO}_2 + \text{HO}_2$  reaction is expressed as:

$$k = k_{\text{eq}}k_2 \quad (7)$$

$$K_{\text{eq}}(T) = \sigma \frac{Q_{\text{IM}}}{Q_{\text{R1}}Q_{\text{R2}}} \exp\left(\frac{E_{\text{R}} - E_{\text{IM}}}{RT}\right) \quad (8)$$

Here, the various  $Q$  values denote the partition functions of the intermediates, reactants R1 and R2.  $E_{\text{R}}$  and  $E_{\text{IM}}$  stand for the total energies of the reactants and intermediate, respectively, while  $\sigma$  is the symmetry factor. The rate constant  $k_2$  of the second step of eqn (7) was evaluated by the VKLab<sup>64</sup> program in the framework of the CVT. To include tunneling effects for motion along the reaction coordinate of the title reaction at the CCSD(T)/CBS//M06-2X/aug-cc-pVTZ level, the SCT tunneling approximation was adopted. The electronic structure calculations were performed using Gaussian09 (ref. 65) software.

### 3. Results and discussion

The transition state in each reaction channel was denoted by “TS” followed by a number, and each pre-reactive intermediate was denoted by “IM” followed by a number. The letter “a” was used to distinguish the transition states and pre-reactive intermediates which are conformers of each other and therefore have the same features; species in the presence of  $\text{H}_2\text{O}$ ,  $(\text{H}_2\text{O})_2$ , and  $(\text{H}_2\text{O})_3$  were respectively denoted by a “WM”, “WD”, and “WT” suffix.

#### 3.1 Potential energy surfaces for the $\text{SO}_2 + \text{HO}_2 \rightarrow \text{HOSO} + \text{O}_2$ reaction

Consistent with previous studies on the  $\text{HO}_2 + \text{SO}_2$  reaction,<sup>3,11</sup> three kinds of product pairs,  $\text{HOSO} + \text{O}_2$ ,  $\text{HSO}_2 + \text{O}_2$ , and  $\text{SO}_3 + \text{HO}$  could be found. Two H-abstraction channels and one O-abstraction route were modeled for the  $\text{HO}_2 + \text{SO}_2$  reaction without water, as shown in Fig. S1.<sup>†</sup> From an energetic point of view, the channel for  $\text{HOSO} + \text{O}_2$  formation was determined to be the major channel, and this is in good agreement with previous results reported by Wang *et al.*<sup>11</sup> Herein, as seen in Fig. 1, the  $\text{SO}_2 + \text{HO}_2 \rightarrow \text{HOSO} + \text{O}_2$  reaction was mainly discussed, in order to focus on the catalytic role of  $(\text{H}_2\text{O})_n$  ( $n = 1-3$ ) in the  $\text{SO}_2 + \text{HO}_2 \rightarrow \text{HOSO} + \text{O}_2$  reaction under atmospheric conditions. As shown in Fig. 1, for the formation of HOSO and  $\text{O}_2$ , the reaction begins with the formation of the pre-reactive intermediate IM1. IM1 exhibits a five-membered ring structure. The relative energy of IM1 to the reactants ( $\text{HO}_2 + \text{SO}_2$ ) is  $-5.6 \text{ kcal mol}^{-1}$ , which is in reasonable agreement with the previous value ( $-6.2 \text{ kcal mol}^{-1}$ ) of CR1b reported by Wang *et al.*<sup>11</sup> The pre-reactive intermediate IM1 goes through an H-abstraction transition state TS1 to form the post-reactive intermediate IMF1. From an energetic standpoint, the transition state TS1 has been predicted to be  $0.3 \text{ kcal mol}^{-1}$  below the reactants, which is slightly different from the corresponding values ( $-0.5 \text{ kcal mol}^{-1}$ ) obtained by Wang *et al.*<sup>11</sup> Intermediate IMF1 retains a five-membered ring structure with a binding energy of  $1.4 \text{ kcal mol}^{-1}$ , and it dissociates to produce  $\text{HOSO} + \text{O}_2$ , which lies  $3.6 \text{ kcal mol}^{-1}$  above the energy of the  $\text{HO}_2 + \text{SO}_2$  reactants.

#### 3.2 Geometrical analysis of the $\text{HO}_2 \cdots (\text{H}_2\text{O})_n$ ( $n = 1-3$ ) and $\text{SO}_2 \cdots (\text{H}_2\text{O})_n$ ( $n = 1-3$ ) complexes

It is noteworthy that the rates of pure termolecular interactions are insignificant as compared to the rates of sequential bimolecular interactions.<sup>67</sup> In this sense, in the presence of  $(\text{H}_2\text{O})_n$  ( $n = 1-3$ ), both  $\text{HO}_2$  and  $\text{SO}_2$  mainly interact with  $(\text{H}_2\text{O})_n$  ( $n = 1-3$ ) *via* hydrogen bonding to form two-body complexes of  $\text{HO}_2 \cdots (\text{H}_2\text{O})_n$  ( $n = 1-3$ ) and  $\text{SO}_2 \cdots (\text{H}_2\text{O})_n$  ( $n = 1-3$ ), respectively, in the entrance channels, before interacting with the third body,  $\text{SO}_2$  or  $\text{HO}_2$ . Therefore, it is highly necessary to first find stable configurations of the complexes  $\text{HO}_2 \cdots (\text{H}_2\text{O})_n$  ( $n = 1-3$ ) and  $\text{SO}_2 \cdots (\text{H}_2\text{O})_n$  ( $n = 1-3$ ). In order to

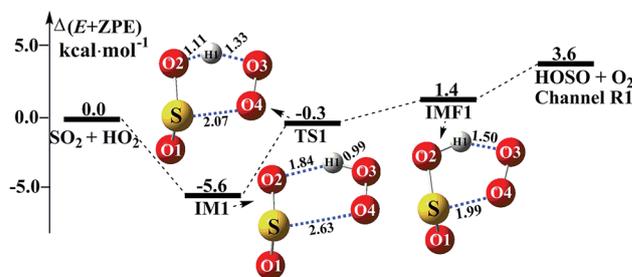


Fig. 1 Schematic energy diagrams of the  $\text{SO}_2 + \text{HO}_2 \rightarrow \text{HOSO} + \text{O}_2$  reaction without water at the CCSD(T)/CBS//M06-2X/aug-cc-pVTZ level.



find all possible stable configurations of the complexes  $\text{HO}_2 \cdots (\text{H}_2\text{O})_n$  ( $n = 1-3$ ) and  $\text{SO}_2 \cdots (\text{H}_2\text{O})_n$  ( $n = 1-3$ ), global minimum searching of geometric structures was carried out using Tsinghua Global Minimum (TGMin).<sup>68,69</sup> Then, the initial structures for  $\text{HO}_2 \cdots (\text{H}_2\text{O})_n$  ( $n = 1-3$ ) and  $\text{SO}_2 \cdots (\text{H}_2\text{O})_n$  ( $n = 1-3$ ) were selected for geometry optimization using the M06-2X/6-31G(d) method. The isomer structures within 6.0 kcal mol<sup>-1</sup> of the global minimum were re-optimized using the M06-2X/aug-cc-pVTZ method. Fig. 2 and S2† show the possible stable geometrical structures of  $\text{HO}_2 \cdots (\text{H}_2\text{O})_n$  ( $n = 1-3$ ) and  $\text{SO}_2 \cdots (\text{H}_2\text{O})_n$  ( $n = 1-3$ ), which are in good agreement with the available experimental results<sup>70</sup> and the previously calculated values.<sup>33,42,43,47</sup> Interestingly, each type of equilibrium structure of the  $\text{HO}_2 \cdots (\text{H}_2\text{O})_n$  ( $n = 1-3$ ) and  $\text{SO}_2 \cdots (\text{H}_2\text{O})_n$  ( $n = 1-3$ ) complexes mainly differs in the relative orientations of the dangling hydrogen atoms of  $(\text{H}_2\text{O})_n$  ( $n = 1-3$ ). Thus, for each type of equilibrium structure of  $\text{HO}_2 \cdots (\text{H}_2\text{O})_n$  ( $n = 1-3$ ) and  $\text{SO}_2 \cdots (\text{H}_2\text{O})_n$  ( $n = 1-3$ ), as shown in Fig. 2, we focus our attention on only one configuration, which has a larger stabilization energy than its isomers.

As shown in Fig. 2, consistent with previous reports,<sup>70,71</sup> the stable complex between  $\text{HO}_2$  and  $\text{H}_2\text{O}$  is  $\text{H}_2\text{O} \cdots \text{HO}_2$ , which involves a five-membered ring structure. Its bonding energy, listed in Table S3,† is 6.9 kcal mol<sup>-1</sup>, which is much more stable than hydrogen bonded (van der Waals interaction) complexes of  $\text{HO}_2 \cdots \text{H}_2\text{O}$ ,  $\text{SO}_2 \cdots \text{H}_2\text{O}$  and  $\text{H}_2\text{O} \cdots \text{SO}_2$ . Stable termolecular complexes of  $\text{HO}_2 \cdots (\text{H}_2\text{O})_2$  and  $\text{SO}_2 \cdots (\text{H}_2\text{O})_2$  are made up of  $\text{HO}_2$  or  $\text{SO}_2$  and a water dimer ( $\text{H}_2\text{O} \cdots \text{H}_2\text{O}$ ). Similar to a binary complex of  $\text{H}_2\text{O} \cdots \text{HO}_2$ , both  $\text{HO}_2$  ( $\text{SO}_2$ ) and the water dimer in these two complexes act simultaneously as a hydrogen bond acceptor and a hydrogen bond donor. From an energetic standpoint, due to ring tension, the stabilization energy of the seven-membered-ring  $\text{HO}_2 \cdots (\text{H}_2\text{O})_2$  complex is 12.6 kcal mol<sup>-1</sup>, whereas the

bonding energy of the six-membered ring  $\text{SO}_2 \cdots (\text{H}_2\text{O})_2$  complex is 6.9 kcal mol<sup>-1</sup>. With  $\text{HO}_2$  or  $\text{SO}_2$  inserted into  $(\text{H}_2\text{O})_3$ , two stable geometries,  $\text{HO}_2 \cdots (\text{H}_2\text{O})_3$  and  $\text{SO}_2 \cdots (\text{H}_2\text{O})_3$ , are obtained. Complex  $\text{HO}_2 \cdots (\text{H}_2\text{O})_3$  exhibits a nine-membered-ring structure with a bonding energy of 12.3 kcal mol<sup>-1</sup>, which is less stable than that of complex  $\text{HO}_2 \cdots (\text{H}_2\text{O})_2$ . Similarly, the binding energy of the eight-membered-ring  $\text{SO}_2 \cdots (\text{H}_2\text{O})_3$  complex is 6.5 kcal mol<sup>-1</sup>, which is 0.4 kcal mol<sup>-1</sup> lower than that of  $\text{SO}_2 \cdots (\text{H}_2\text{O})_2$  due to the effect of ring strain. The present study mainly focuses on the catalytic roles of  $(\text{H}_2\text{O})_n$  ( $n = 1-3$ ) in the  $\text{SO}_2 + \text{HO}_2 \rightarrow \text{HOSO} + \text{O}_2$  reaction. Only the favorable reaction channels will be discussed according to their energy barriers and thermodynamic properties. Details on the remaining reaction channels are presented in the ESI.†

### 3.3 Mechanism for $\text{H}_2\text{O}$ -assisted $\text{SO}_2 + \text{HO}_2 \rightarrow \text{HOSO} + \text{O}_2$ reaction

The significance of the water-catalyzed  $\text{SO}_2 + \text{HO}_2 \rightarrow \text{HOSO} + \text{O}_2$  reaction depends on the extent to which the respective bimolecular complexes,  $\text{H}_2\text{O} \cdots \text{HO}_2$ ,  $\text{HO}_2 \cdots \text{H}_2\text{O}$ ,  $\text{SO}_2 \cdots \text{H}_2\text{O}$  and  $\text{H}_2\text{O} \cdots \text{SO}_2$  exist, which can be determined by computing their stability, as above (Fig. 2), and their corresponding equilibrium constants, as shown in Table S2.† The equilibrium constants of these complexes at 298 K are  $8.59 \times 10^{-19}$ ,  $6.56 \times 10^{-23}$ ,  $3.08 \times 10^{-24}$  and  $4.88 \times 10^{-24}$  cm<sup>3</sup> per molecule, respectively (Table S2†). Taking into account typical tropospheric concentrations of  $7.73 \times 10^{17}$  molecules per cm<sup>3</sup> of  $\text{H}_2\text{O}$ ,  $3 \times 10^8$  molecules per cm<sup>3</sup> of  $\text{HO}_2$ ,<sup>72</sup> and  $1.0 \times 10^{12}$  molecules per cm<sup>3</sup> of  $\text{SO}_2$ ,<sup>33</sup> it is estimated that the atmospheric concentration of the  $\text{H}_2\text{O} \cdots \text{HO}_2$  complex is  $1.99 \times 10^8$  molecules per cm<sup>3</sup>. Meanwhile, the concentrations of the  $\text{HO}_2 \cdots \text{H}_2\text{O}$ ,  $\text{SO}_2 \cdots \text{H}_2\text{O}$  and  $\text{H}_2\text{O} \cdots \text{SO}_2$  complexes are estimated to be  $1.52 \times 10^4$ ,  $2.38 \times 10^6$ , and  $3.77 \times 10^6$  molecules per cm<sup>3</sup>. Thus, as shown in Fig. 3 and 4, when

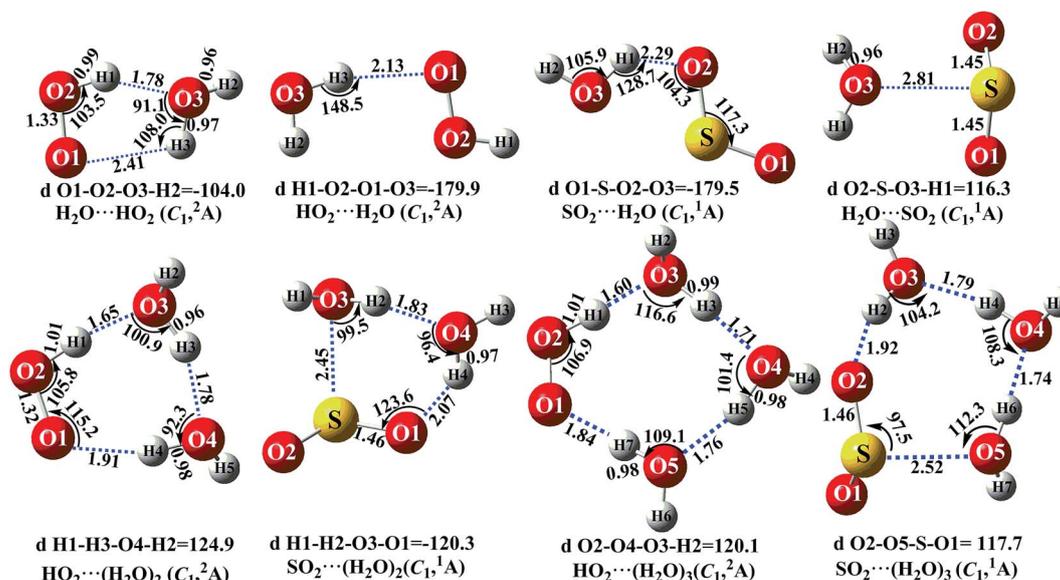


Fig. 2 The optimized geometrical reactants for the  $\text{SO}_2 + \text{HO}_2$  reaction without and with catalyst X ( $X = \text{H}_2\text{O}$ ,  $(\text{H}_2\text{O})_2$  and  $(\text{H}_2\text{O})_3$ ) at the M06-2X/aug-cc-pVTZ level of theory.



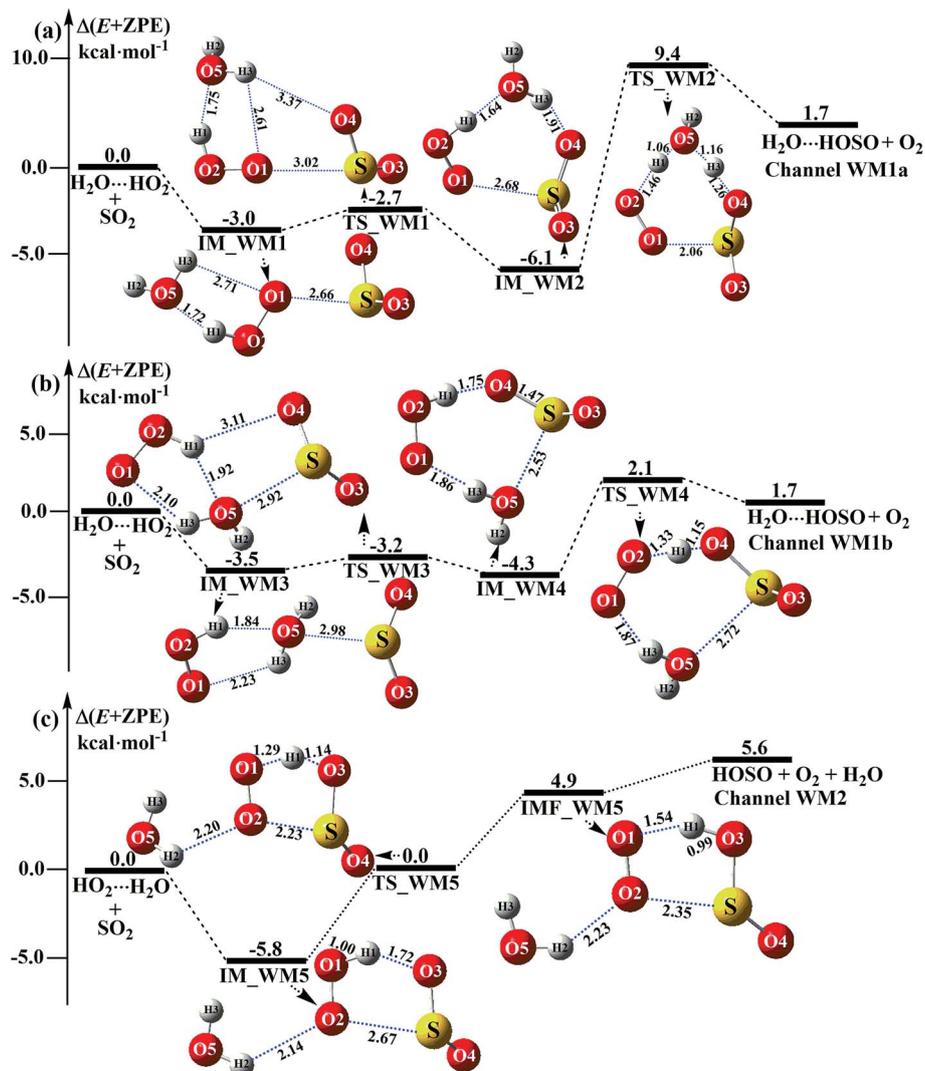
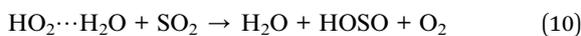


Fig. 3 Schematic energy diagrams of the water-assisted channel of HOSO + O<sub>2</sub> formation, occurring through H<sub>2</sub>O...HO<sub>2</sub> + SO<sub>2</sub> and HO<sub>2</sub>...H<sub>2</sub>O + SO<sub>2</sub> at the CCSD(T)/CBS//M06-2X/aug-cc-pVTZ level.

one water molecule is introduced into the SO<sub>2</sub> + HO<sub>2</sub> → HOSO + O<sub>2</sub> reaction, there are four possible types of bimolecular reactions, labeled as Channels WM1, WM2, WM3, and WM4.



**3.3.1 Mechanism of H<sub>2</sub>O...HO<sub>2</sub> + SO<sub>2</sub> and HO<sub>2</sub>...H<sub>2</sub>O + SO<sub>2</sub> reactions.** For the formation of HOSO...H<sub>2</sub>O + O<sub>2</sub> occurring through the H<sub>2</sub>O...HO<sub>2</sub> + SO<sub>2</sub> reaction, Fig. 3 displays two Channels, namely Channel WM1a and Channel WM1b. Similar to other water-catalyzed reactions reported before,<sup>26,33,73</sup> the influence of the water monomer in the H<sub>2</sub>O...HO<sub>2</sub> + SO<sub>2</sub>

reaction was investigated by a stepwise mechanism, where the reaction occurs *via* a ring enlargement at first, and then proceeds through a hydrogen abstraction mechanism. However, the stepwise mechanism of Channel WM1a is different from Channel WM1b in three aspects. First, for the ring enlargement, the form of the S...O in complex IM\_WM3 is different from that in complex IM\_WM1. In complex IM\_WM3, the S...O bond is formed by the S atom of SO<sub>2</sub> and the O atom of the H<sub>2</sub>O moiety in the HO<sub>2</sub>...H<sub>2</sub>O complex, whereas the S...O bond in the IM\_WM1 complex is formed by the S atom of SO<sub>2</sub> and the terminal O atom of the HO<sub>2</sub> moiety in the HO<sub>2</sub>...H<sub>2</sub>O complex. However, the stabilization energies of complexes IM\_WM3 and IM\_WM1 are close to each other, but with a difference of 0.5 kcal mol<sup>-1</sup>. Secondly, the complex IM\_WM4 has similar seven-membered cyclic structures as IM\_WM2, except that SO<sub>2</sub> and H<sub>2</sub>O have exchanged their positions. This is possibly the reason that the stabilization energy of complex IM\_WM4 is 1.8 kcal mol<sup>-1</sup> lower than that of complex IM\_WM2.



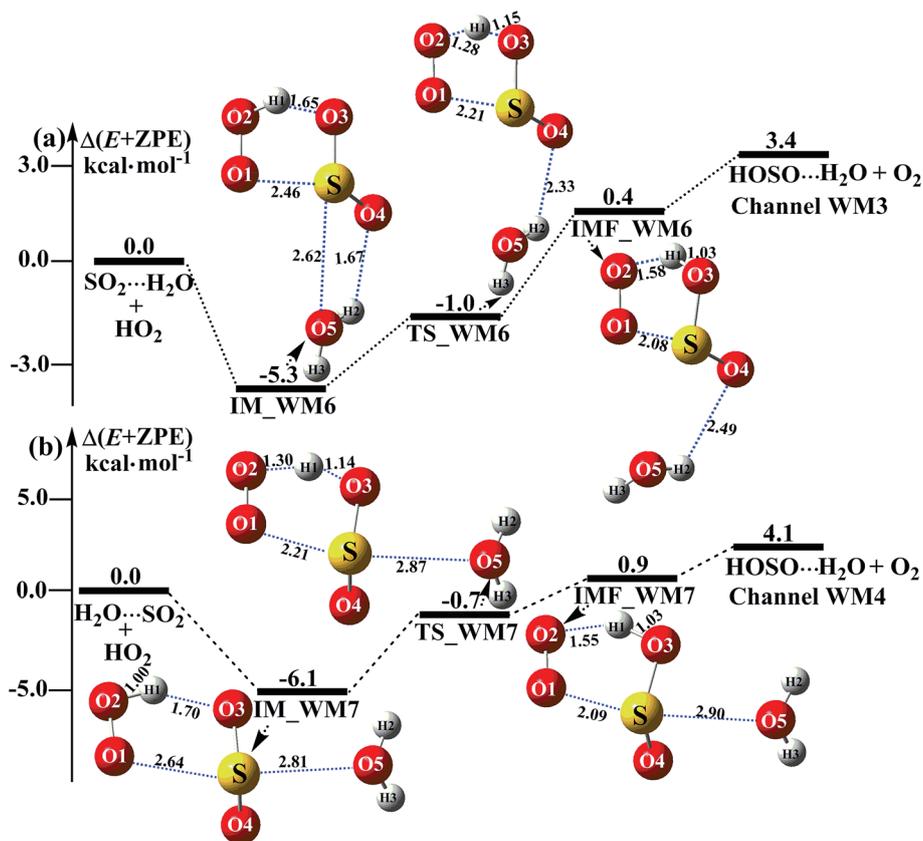


Fig. 4 Schematic energy diagrams of the water-assisted channel of HOSO + O<sub>2</sub> formation, occurring through SO<sub>2</sub>...H<sub>2</sub>O + HO<sub>2</sub> and H<sub>2</sub>O...SO<sub>2</sub> + HO<sub>2</sub> at the CCSD(T)/CBS//M06-2X/aug-cc-pVTZ level.

The third one is that, for the rate-determining step of hydrogen abstraction, the barrier height of Channel WM1b is 2.1 kcal mol<sup>-1</sup>, which is 7.3 kcal mol<sup>-1</sup> lower than the process of IM\_WM2 → TS\_WM2 → H<sub>2</sub>O...HOSO + O<sub>2</sub> in Channel WM1a. This indicates that the double hydrogen transfer mechanism in Channel WM1a is less favorable than the direct hydrogen abstraction involved in Channel WM1b. This conclusion is consistent with our previous reports.<sup>71,73,74</sup> As a result, in the following section, the reaction type of the multiple hydrogen transfer mechanism, where water molecules serve as a “bridge”, will be neglected in the stepwise reaction between SO<sub>2</sub> and HO<sub>2</sub>...((H<sub>2</sub>O)<sub>2</sub>) (or HO<sub>2</sub>...((H<sub>2</sub>O)<sub>3</sub>).

As for Channel WM2, it can be seen in Fig. 3c that a hydrogen bond complex, IM\_WM5, has been identified, with a stabilization energy of 5.8 kcal mol<sup>-1</sup>. From a geometrical point of view, complex IM\_WM5 exhibits a five-membered ring structure, which is similar to the five-membered ring structure of complex IM1 in the reaction without a catalyst, as shown in Fig. 1. Compared with complex IM1, an additional O...H bond (O2...H2, 2.14 Å) is involved in IM\_WM5. This leads to the stabilization energy of complex IM\_WM5 being enhanced by 0.2 kcal mol<sup>-1</sup>. Starting from complex IM\_WM5 seen in Fig. 3c, the products HOSO + H<sub>2</sub>O + O<sub>2</sub> can be obtained *via* transition state TS\_WM5. From a geometrical point of view, similar to the naked transition state TS1, TS\_WM5 follows direct hydrogen abstraction. Compared with TS1, the additional water molecule

in the transition state TS\_WM5 is bonded to the terminal O atom of the HO<sub>2</sub> radical. Such a weak hydrogen bonding (O2...H2, 2.23 Å) interaction may lead to the energy of the TS\_WM5 to HO<sub>2</sub>...H<sub>2</sub>O + SO<sub>2</sub> reactants being 0.3 kcal mol<sup>-1</sup> higher than that of the TS1 to the HO<sub>2</sub> + SO<sub>2</sub> reactants.

**3.3.2 Potential energy surfaces for SO<sub>2</sub>...H<sub>2</sub>O + HO<sub>2</sub> and H<sub>2</sub>O...SO<sub>2</sub> + HO<sub>2</sub> reactions.** Beyond the water-assisted reaction channels described above, two additional water-assisted channels for HOSO + O<sub>2</sub> formation were found by taking into account the bimolecular reactions of SO<sub>2</sub>...H<sub>2</sub>O + HO<sub>2</sub> (Channel WM3) and H<sub>2</sub>O...SO<sub>2</sub> + HO<sub>2</sub> (Channel WM4).

As for Channel WM3, the reaction of the SO<sub>2</sub>...H<sub>2</sub>O + HO<sub>2</sub> entry channel proceeds through the formation of complex IM\_WM6 before the transition state TS\_WM6 and complex IMF\_WM6. From a geometric point of view, complex IM\_WM6 has one five-membered ring, H(1)–O(2)–O(1)··S–O(3), and one four-membered ring, O(4)··H(2)–O(5)··S, with a computed relative energy of 5.3 kcal mol<sup>-1</sup> below the reactants of SO<sub>2</sub>...H<sub>2</sub>O + HO<sub>2</sub>, as shown in Table S4† and Fig. 4. Starting from complex IM\_WM6, with the H atom of HO<sub>2</sub> migrating to one O atom of the SO<sub>2</sub> moiety in the SO<sub>2</sub>...H<sub>2</sub>O complex, the reaction can proceed *via* the transition state TS\_WM6 to form complex IMF\_WM6. As shown in Fig. 4, only the five-membered ring was retained in both the transition state TS\_WM6 and complex IMF\_WM6 with the elongation of the S...O5 bond. Compared with the transition state TS1 in Fig. 1, the additional water



molecule in TS\_WM6 did not change the active features of the five-membered ring. Furthermore, with the water molecule added, the relative energy of TS\_WM6 to  $\text{SO}_2 \cdots \text{H}_2\text{O} + \text{HO}_2$  is  $0.7 \text{ kcal mol}^{-1}$  less than the corresponding value of TS1 ( $-0.3 \text{ kcal mol}^{-1}$ ) to  $\text{SO}_2 + \text{HO}_2$ .

The fourth channel of the water-assisted  $\text{SO}_2 + \text{HO}_2 \rightarrow \text{HOSO} + \text{O}_2$  reaction (Channel WM4, Fig. 4b) begins with complex IM\_WM7 *via* the interaction between the O atom of  $\text{H}_2\text{O}$  and the S atom of the  $\text{SO}_2$  moiety in  $\text{H}_2\text{O} \cdots \text{SO}_2$ . The relative energy of complex IM\_WM7 to the  $\text{H}_2\text{O} \cdots \text{SO}_2 + \text{HO}_2$  reactants is  $6.1 \text{ kcal mol}^{-1}$ . Complex IM\_WM7 then decomposes *via* transition state TS\_WM7 to form complex IMF\_WM7. As shown in Fig. 4, similar to the structure of TS\_WM6 and complex IMF\_WM6, a five-membered ring is still involved in both TS\_WM7 and complex IMF\_WM7. Compared with TS1 in Fig. 1, the additional water molecule in TS\_WM7 leads to the relative energy of TS\_WM7 to  $\text{H}_2\text{O} \cdots \text{SO}_2 + \text{HO}_2$  being  $0.7 \text{ kcal mol}^{-1}$ , which is  $0.4 \text{ kcal mol}^{-1}$  less than the corresponding value of TS1 ( $-0.3 \text{ kcal mol}^{-1}$ ) to  $\text{SO}_2 + \text{HO}_2$ .

### 3.4 Mechanism for $(\text{H}_2\text{O})_2$ -catalyzed the $\text{SO}_2 + \text{HO}_2 \rightarrow \text{HOSO} + \text{O}_2$ reaction

As shown in Fig. 5,  $(\text{H}_2\text{O})_2$  catalyzed channels were determined, starting from  $\text{HO}_2 \cdots (\text{H}_2\text{O})_2 + \text{SO}_2$  and  $\text{SO}_2 \cdots (\text{H}_2\text{O})_2 + \text{HO}_2$  reactants, which are labeled as Channel WD1 and Channel WD2.

For the  $\text{HO}_2 \cdots (\text{H}_2\text{O})_2 + \text{SO}_2$  reaction (Channel WD1), two reaction types, namely Channel WD1a and Channel WD1b were found, depending on how the S atom of  $\text{SO}_2$  approaches the complex of  $\text{HO}_2 \cdots (\text{H}_2\text{O})_2$ . In the same way as the  $\text{H}_2\text{O} \cdots \text{HO}_2 + \text{SO}_2$  reaction above (Fig. 3), both Channels WD1a and WD1b occur *via* a stepwise mechanism, which involves a direct hydrogen abstraction with one O atom of  $\text{SO}_2$  abstracting the H atom of a  $\text{HO}_2$  moiety in the  $\text{HO}_2 \cdots (\text{H}_2\text{O})_2$  complex. However, as shown in Fig. 5, unlike the hydrogen abstraction in Channel WD1a, where the number of rings increases with decreasing ring size, in Channel WD1b the hydrogen abstraction does not change the ring size or the ring number. This discrepancy of hydrogen abstraction between Channels WD1a and WD1b may mean that, in Channel WD1a, the barrier height of the rate determining step ( $\text{IM\_WD2} \rightarrow \text{TS\_WD2} \rightarrow (\text{H}_2\text{O})_2 \cdots \text{HOSO} + \text{O}_2$ ) is  $8.4 \text{ kcal mol}^{-1}$  higher than the corresponding barrier height of the rate determining step ( $\text{IM\_WD4} \rightarrow \text{TS\_WD4} \rightarrow (\text{H}_2\text{O})_2 \cdots \text{HOSO} + \text{O}_2$ ) in Channel WD1b. As a result, for the  $\text{HO}_2 \cdots (\text{H}_2\text{O})_2 + \text{SO}_2$  reaction, Channel WD1b is mainly taken into account here.

For Channel WD1b, with the interaction between the S atom of  $\text{SO}_2$  and O(5) of the  $\text{H}_2\text{O}$  moiety in the  $\text{HO}_2 \cdots (\text{H}_2\text{O})_2$  complex, the reaction begins with the seven-membered cyclic complex IM\_WD3, whose stability has been computed to be  $2.7 \text{ kcal mol}^{-1}$ . Then, the reaction proceeds through the ring enlargement from IM\_WD3 to IM\_WD4 *via* the transition state TS\_WD3, with an energy barrier of  $1.5 \text{ kcal mol}^{-1}$ . Complex IM\_WD4 has a similar structure to IM\_WM4 (Fig. 3), but with a water monomer substituted by a water dimer. The binding energy of IM\_WD4 is  $1.8 \text{ kcal mol}^{-1}$ , which is  $0.9 \text{ kcal mol}^{-1}$  less

stable than the complex IM\_WD3. Starting from the complex IM\_WD4, the reaction can proceed *via* the transition state TS\_WD4 to form the products of  $(\text{H}_2\text{O})_2 \cdots \text{HOSO} + \text{O}_2$ . Similar to complex IM\_WD4, TS\_WD4 also shows a nine-membered ring structure with three components of  $(\text{H}_2\text{O})_2$ , the SO moiety of  $\text{SO}_2$  and the  $\text{HO}_2$  radical. The relative energy of TS\_WD4 to  $\text{HO}_2 \cdots (\text{H}_2\text{O})_2 + \text{SO}_2$  is  $0.4 \text{ kcal mol}^{-1}$ , which is  $2.5 \text{ kcal mol}^{-1}$  lower than that of the  $\text{H}_2\text{O}$ -assisted transition state TS\_WM4 to  $\text{H}_2\text{O} \cdots \text{HO}_2 + \text{SO}_2$  reactants. Meanwhile, from the viewpoint of ring sizes, for TSW2 and TSWD, with the ring size increase, the rate constant of the rate-determining step increases when one water molecule has been replaced by a water dimer. This is possibly because when the seven-membered ring has been replaced by a nine-membered ring, the number of hydrogen bonds increases, leading to the stabilization of the ring increasing. These facts indicate that the second water molecule plays a positive catalytic role by significantly reducing the barrier height of the  $\text{SO}_2 + \text{HO}_2 \rightarrow \text{HOSO} + \text{O}_2$  reaction.

As for Channel WD2, starting from  $\text{SO}_2 \cdots (\text{H}_2\text{O})_2 + \text{HO}_2$  reactants, the reaction begins with the formation of complex IM\_WD5. As shown in Fig. 5c, complex IM\_WD5 exhibits a double-ring structure with a five-membered ring,  $\text{O}_2 \cdots \text{H}_1\text{O}_3\text{S} \cdots \text{O}_1$ , and a six-membered ring,  $\text{O}_4 \cdots \text{H}_2\text{O}_5 \cdots \text{H}_4\text{O}_6 \cdots \text{S}$ . Aside from these characteristics, complex IM\_WD5 has a similar structure to that of IM\_WM5, but with an additional water molecule inserted at the site between  $\text{H}_2\text{O}$  and  $\text{SO}_2$ . This leads to the stabilization energy of complex IM\_WD5 (Table S4† and Fig. 5) being enhanced by  $0.3 \text{ kcal mol}^{-1}$  compared with complex IM\_WM5. After complex IM\_WD5, with the H atom of  $\text{HO}_2$  migrating to one O atom of the  $\text{SO}_2$  moiety in the  $\text{SO}_2 \cdots (\text{H}_2\text{O})_2$  complex, the products of  $\text{HOSO} \cdots (\text{H}_2\text{O})_2 + \text{O}_2$  can be obtained *via* transition state TS\_WD5 and complex IMF\_WD5. As shown in Fig. 5, the double-ring structure is retained in transition state TS\_WD5 and complex IMF\_WD5. Compared with TS\_WM5 in Fig. 4, with the introduction of the second water molecule, the active features of the five-membered ring in TS\_WD5 exhibit no change. The relative energy of TS\_WD5 to  $\text{SO}_2 \cdots (\text{H}_2\text{O})_2 + \text{HO}_2$  is  $0.9 \text{ kcal mol}^{-1}$ , which is only changed by  $0.6\text{--}0.9 \text{ kcal mol}^{-1}$  compared with the corresponding values of TS\_WM5 with  $\text{H}_2\text{O}$  and TS1 without a catalyst. This implies that Channel WD2 proceeds easily.

### 3.5 Mechanism for $(\text{H}_2\text{O})_3$ -catalyzed the $\text{SO}_2 + \text{HO}_2 \rightarrow \text{HOSO} + \text{O}_2$ reaction

Similar to the instance of the  $(\text{H}_2\text{O})_2$ -assisted reaction that occurs through the  $\text{HO}_2 \cdots (\text{H}_2\text{O})_2 + \text{SO}_2$  and  $\text{SO}_2 \cdots (\text{H}_2\text{O})_2 + \text{HO}_2$  reactions discussed above, the  $(\text{H}_2\text{O})_3$ -assisted  $\text{SO}_2 + \text{HO}_2 \rightarrow \text{HOSO} + \text{O}_2$  reaction can be obtained both by the insertion of  $\text{SO}_2$  into the  $\text{HO}_2 \cdots (\text{H}_2\text{O})_3$  complex, and by the collision of the  $\text{HO}_2$  radical with the  $\text{SO}_2 \cdots (\text{H}_2\text{O})_3$  complex. Through the  $\text{SO}_2 \cdots (\text{H}_2\text{O})_3 + \text{HO}_2$  reaction (which proceeds easily, as shown in Table S6,† with an energy barrier of  $1.3 \text{ kcal mol}^{-1}$ , as shown in Table S2†), the concentration of  $\text{SO}_2 \cdots (\text{H}_2\text{O})_3$  at 298 K is 4 orders of magnitude smaller than that of  $\text{HO}_2 \cdots (\text{H}_2\text{O})_3$ . Therefore, the  $\text{SO}_2 \cdots (\text{H}_2\text{O})_3 + \text{HO}_2$  reaction can be neglected under tropospheric conditions, and herein, we only focus our attention on



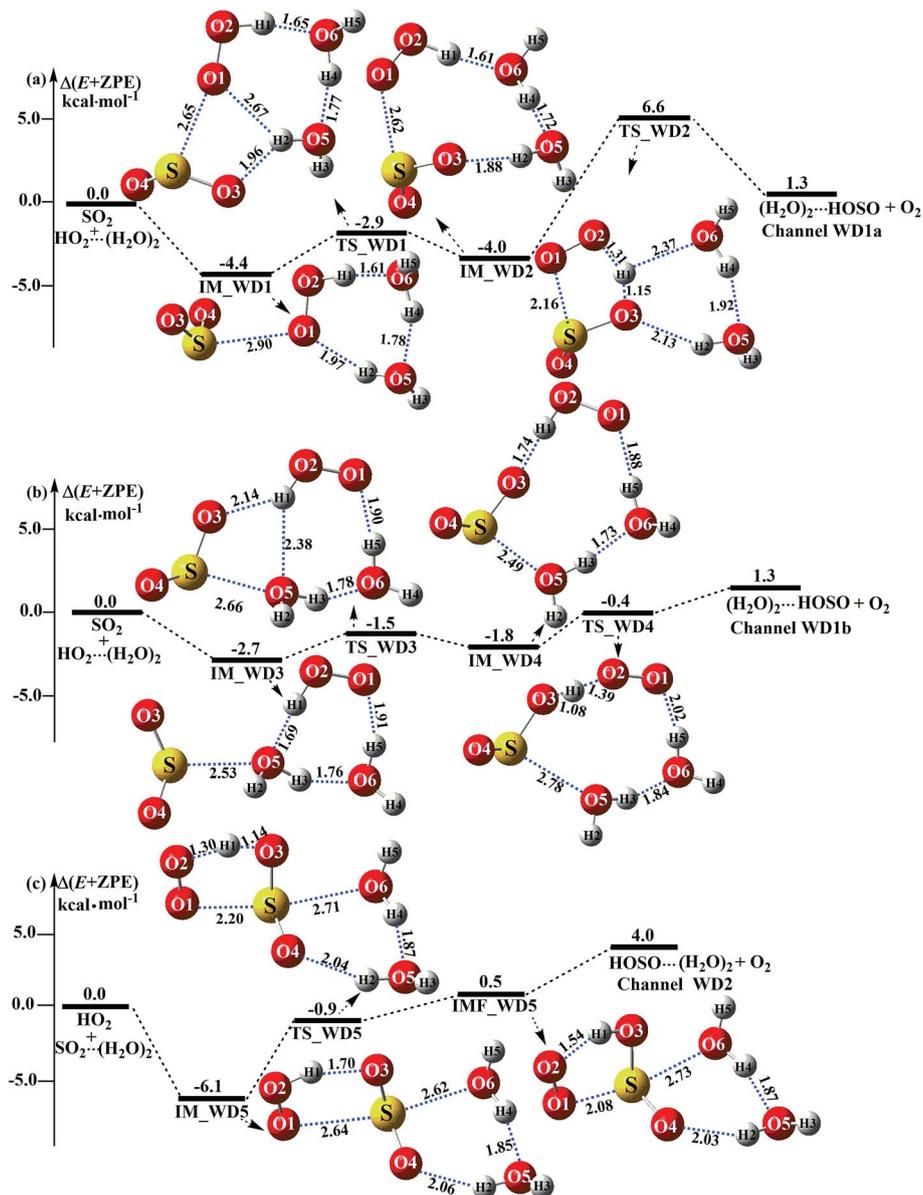


Fig. 5 Schematic energy diagrams of the dimer water-assisted channel of HOSO + O<sub>2</sub> formation, occurring through HO<sub>2</sub>·(H<sub>2</sub>O)<sub>2</sub> + SO<sub>2</sub> and SO<sub>2</sub>·(H<sub>2</sub>O)<sub>2</sub> + HO<sub>2</sub> at the CCSD(T)/CBS//M06-2X/aug-cc-pVTZ level.

the HO<sub>2</sub>·(H<sub>2</sub>O)<sub>3</sub> + SO<sub>2</sub> reaction. For comparison, a schematic energy diagram of HO<sub>2</sub> + SO<sub>2</sub>·(H<sub>2</sub>O)<sub>3</sub> reaction is displayed in Fig. S6.†

Similar to H<sub>2</sub>O·(H<sub>2</sub>O)<sub>2</sub> + SO<sub>2</sub> and HO<sub>2</sub>·(H<sub>2</sub>O)<sub>2</sub> + SO<sub>2</sub> reactions above, HO<sub>2</sub>·(H<sub>2</sub>O)<sub>2</sub> + SO<sub>2</sub> reaction (Channel WT1) shown in Fig. 6 also proceeds through a stepwise mechanism to form HOSO·(H<sub>2</sub>O)<sub>3</sub> + O<sub>2</sub>. In the first step, the reaction starts with complex IM\_WT1, which has a binding energy of 3.0 kcal mol<sup>-1</sup>. From a geometrical point of view, complex IM\_WT1 has one nine-membered ring-like structure. After complex IM\_WT1, the ring enlargement from complex IM\_WT1 to the eleven-membered ring complex IM\_WT2 occurs *via* the double-ring transition state TS\_WT1 (nine-membered ring, right; four-membered ring, left) with a barrier height of 0.7 kcal mol<sup>-1</sup>.

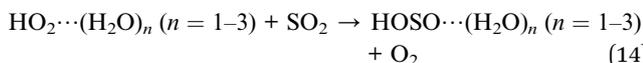
Complex IM\_WT2 has similar quasi-planar structures to IM\_WD4, with an additional water molecule inserted between SO<sub>2</sub> and HO<sub>2</sub>. Complex IM\_WT2 is 1.0 kcal mol<sup>-1</sup> less stable than IM\_WT1, and is also 0.8 kcal mol<sup>-1</sup> less stable than IM\_WD4. In the second step, following complex IM\_WT2, Channel WT1 proceeds through transition state TS\_WT2 to produce the product of HOSO·(H<sub>2</sub>O)<sub>3</sub> + O<sub>2</sub>. At transition state TS\_WT2, the eleven-membered ring structure is still conserved, and the structure is similar to TS\_WD4, but with an additional water molecule inserted between SO<sub>2</sub> and HO<sub>2</sub>. From the viewpoint of ring sizes, for TS\_WT2 and TS\_WD4, although the hydrogen bonds increase in the ring when the nine-membered ring becomes an eleven-membered ring, the eleven-membered ring is unstable, and the tension is large, so TS\_WT2 lies



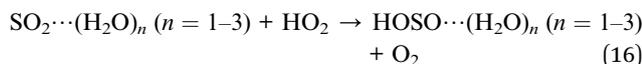
16.0 kcal mol<sup>-1</sup> above the HO<sub>2</sub>⋯(H<sub>2</sub>O)<sub>3</sub> + SO<sub>2</sub> reactants, which is 16.4 kcal mol<sup>-1</sup> higher in energy than the relative energy of TS\_WD4 to HO<sub>2</sub>⋯(H<sub>2</sub>O)<sub>2</sub> + SO<sub>2</sub> reactants. Meanwhile, the rate constant of the rate-determining step decreases when the water dimer has been replaced by the water trimer (Fig. 6).

### 3.6 Reaction kinetics

With regard to the reactions involving (H<sub>2</sub>O)<sub>n</sub> (n = 1–3), we consider HO<sub>2</sub>⋯(H<sub>2</sub>O)<sub>n</sub> (n = 1–3) and SO<sub>2</sub> or SO<sub>2</sub>⋯(H<sub>2</sub>O)<sub>n</sub> (n = 1–3) and HO<sub>2</sub>. When HO<sub>2</sub>⋯(H<sub>2</sub>O)<sub>n</sub> (n = 1–3) and SO<sub>2</sub> act as reactants, the reactions occur *via* the following reaction mechanism:



Meanwhile when SO<sub>2</sub>⋯(H<sub>2</sub>O)<sub>n</sub> (n = 1–3) and HO<sub>2</sub> are considered to be the reactants, the reaction mechanism is as follows:



The rate *via* the reaction processes (13) and (14) is expressed in eqn (17).

$$v_a = \frac{d[\text{HOSO} \cdots (\text{H}_2\text{O})_n (n = 1-3)]}{dt} = K_{\text{eq}}(\text{HO}_2 \cdots (\text{H}_2\text{O})_n (n = 1-3))k_a[(\text{H}_2\text{O})_n (n = 1-3)] [\text{HO}_2][\text{SO}_2] \quad (17)$$

Here,  $K_{\text{eq}}(\text{HO}_2 \cdots (\text{H}_2\text{O})_n (n = 1-3))$  is the equilibrium constant for the formation of the HO<sub>2</sub>⋯(H<sub>2</sub>O)<sub>n</sub> (n = 1–3) complex from isolated HO<sub>2</sub> and (H<sub>2</sub>O)<sub>n</sub> (n = 1–3) and  $k_a$  represents the rate

constant of eqn (14). The rate *via* the reaction processes (15) and (16) is expressed in eqn (18).

$$v_b = \frac{d[\text{HOSO} \cdots (\text{H}_2\text{O})_n (n = 1-3)]}{dt} = K_{\text{eq}}(\text{SO}_2 \cdots (\text{H}_2\text{O})_n (n = 1-3))k_b[(\text{H}_2\text{O})_n (n = 1-3)][\text{HO}_2][\text{SO}_2] \quad (18)$$

Here,  $K_{\text{eq}}(\text{SO}_2 \cdots (\text{H}_2\text{O})_n (n = 1-3))$  is the equilibrium constant for the formation of the SO<sub>2</sub>⋯(H<sub>2</sub>O)<sub>n</sub> (n = 1–3) complex from isolated SO<sub>2</sub> and (H<sub>2</sub>O)<sub>n</sub> (n = 1–3) and  $k_b$  represents the rate constant of eqn (16). It is worth noting that, herein, we do not consider how pressure effects influence the formation of these complexes, because there are no experimental results showing that the equilibrium constants of these complexes depend on pressure.

The computed rate constants are provided in Table 1. For the reaction without a catalyst, the computed rate constant ( $k_{\text{R1}}$ ) is  $9.09 \times 10^{-18}$  to  $5.22 \times 10^{-17}$  cm<sup>3</sup> per molecule per s in the temperature range of 218.6–320.0 K. At 298 K, the calculated value of  $k_{\text{R1}}$  is  $3.87 \times 10^{-17}$  cm<sup>3</sup> per molecule per s, which is close to the experimental value ( $1.0 \times 10^{-18}$  cm<sup>3</sup> per molecule per s).<sup>66</sup> For the reaction with (H<sub>2</sub>O)<sub>n</sub> (n = 1–3), the rate ratio  $v_a/v_b$  of the HO<sub>2</sub> + SO<sub>2</sub> + (H<sub>2</sub>O)<sub>n</sub> (n = 1–3) reaction shows that the entrance of HO<sub>2</sub>⋯(H<sub>2</sub>O)<sub>n</sub> (n = 1–3) and SO<sub>2</sub> is more important than that of SO<sub>2</sub>⋯(H<sub>2</sub>O)<sub>n</sub> (n = 1–3) and HO<sub>2</sub> because the rate ratios  $v_{a1}/v_{b1}$ ,  $v_{a2}/v_{b2}$ , and  $v_{a3}/v_{b3}$  are  $2.15 \times 10^9$  to  $1.27 \times 10^7$ ,  $5.00 \times 10^8$  to  $4.95 \times 10^6$ ,  $4.03 \times 10^{13}$  to  $4.12 \times 10^9$ , respectively, between 275.0 and 320.0 K (Table 1).

In the HO<sub>2</sub>⋯(H<sub>2</sub>O)<sub>n</sub> (n = 1–3) + SO<sub>2</sub> reaction, it is necessary to calculate its effective rate constant  $k'$ , which can be considered as a measure of the efficiencies of the different catalysts of (H<sub>2</sub>O)<sub>n</sub> (n = 1–3) under atmospheric conditions, as it includes the concentration of (H<sub>2</sub>O)<sub>n</sub> (n = 1–3), equilibrium constants of HO<sub>2</sub>⋯(H<sub>2</sub>O)<sub>n</sub> (n = 1–3), and the rate constant from eqn (14). Based on this, the rates for the channels of the H<sub>2</sub>O⋯HO<sub>2</sub> + SO<sub>2</sub> reaction ( $k_a(\text{WM1b})$ ), the

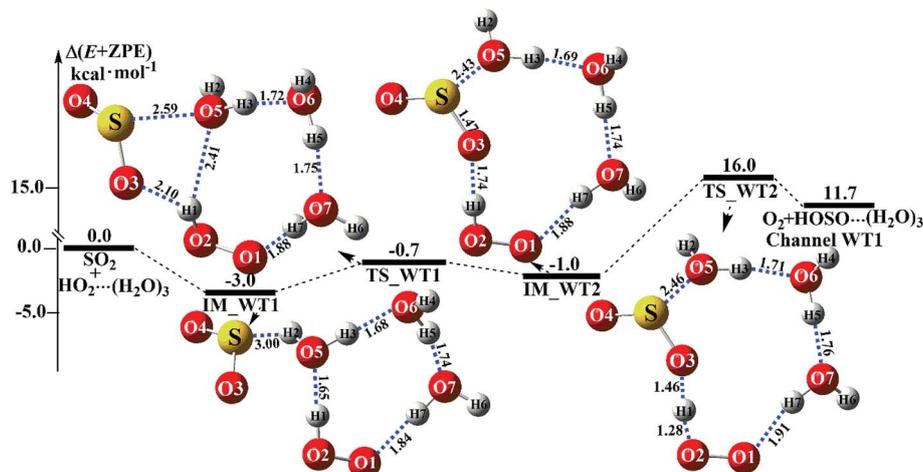


Fig. 6 Schematic energy diagrams of the trimer water-assisted channel of HOSO + O<sub>2</sub> formation, occurring through HO<sub>2</sub>⋯(H<sub>2</sub>O)<sub>3</sub> + SO<sub>2</sub> at the CCSD(T)/CBS//M06-2X/aug-cc-pVTZ level.



**Table 1** Ratio of reaction rate and effective rate constants ( $\text{cm}^3$  per molecules per s) for HOSO +  $\text{O}_2$  formation from the  $\text{SO}_2$  +  $\text{HO}_2$  reaction without and with  $(\text{H}_2\text{O})_n$  ( $n = 1-3$ ) within the temperature range of 275.0–320.0 K<sup>a</sup>

$T$ (K)	$k_R$	$\nu_{a1}/\nu_{b1}$	$\nu_{a2}/\nu_{b2}$	$\nu_{a3}/\nu_{b3}$	$k'_a(\text{WM1})$	$k'_a(\text{WD1})$	$k'_a(\text{WT1})$
218.6	$9.09 \times 10^{-18}$	$2.15 \times 10^9$	$5.00 \times 10^8$	$4.03 \times 10^{13}$	$5.84 \times 10^{-13}$	$2.99 \times 10^{-23}$	—
223.7	$1.02 \times 10^{-17}$	$1.48 \times 10^9$	$3.69 \times 10^8$	$1.73 \times 10^{14}$	$5.38 \times 10^{-13}$	$3.57 \times 10^{-22}$	—
229.7	$1.08 \times 10^{-17}$	$9.78 \times 10^7$	$3.96 \times 10^8$	$1.78 \times 10^{12}$	$4.93 \times 10^{-13}$	$5.07 \times 10^{-18}$	$1.68 \times 10^{-21}$
235.1	$1.31 \times 10^{-17}$	$6.82 \times 10^8$	$1.97 \times 10^8$	$9.96 \times 10^{11}$	$4.57 \times 10^{-13}$	$1.81 \times 10^{-18}$	—
249.9	$1.75 \times 10^{-17}$	$2.78 \times 10^9$	$9.59 \times 10^7$	$1.58 \times 10^{12}$	$3.83 \times 10^{-13}$	$5.73 \times 10^{-18}$	—
259.3	$1.76 \times 10^{-17}$	$1.66 \times 10^8$	$4.07 \times 10^5$	$3.24 \times 10^{11}$	$3.47 \times 10^{-13}$	$3.09 \times 10^{-18}$	$5.95 \times 10^{-21}$
275.0	$2.72 \times 10^{-17}$	$7.64 \times 10^7$	$3.47 \times 10^7$	$8.65 \times 10^{10}$	$3.02 \times 10^{-13}$	$3.90 \times 10^{-17}$	$1.63 \times 10^{-19}$
280.0	$2.95 \times 10^{-17}$	$6.07 \times 10^7$	$2.92 \times 10^7$	$3.10 \times 10^{10}$	$2.90 \times 10^{-13}$	$4.57 \times 10^{-17}$	$1.55 \times 10^{-18}$
290.0	$3.44 \times 10^{-17}$	$3.92 \times 10^7$	$2.09 \times 10^7$	$4.12 \times 10^9$	$2.71 \times 10^{-13}$	$6.58 \times 10^{-17}$	$1.54 \times 10^{-19}$
298.2	$3.87 \times 10^{-17}$	$2.82 \times 10^8$	$1.63 \times 10^8$	$7.88 \times 10^{13}$	$2.57 \times 10^{-13}$	$8.95 \times 10^{-17}$	$1.59 \times 10^{-18}$
300.0	$3.98 \times 10^{-17}$	$2.62 \times 10^8$	$1.54 \times 10^7$	$3.19 \times 10^{13}$	$2.54 \times 10^{-13}$	$9.50 \times 10^{-17}$	$1.58 \times 10^{-18}$
310.0	$4.57 \times 10^{-17}$	$1.80 \times 10^8$	$1.16 \times 10^7$	$4.87 \times 10^{10}$	$2.41 \times 10^{-13}$	$1.32 \times 10^{-16}$	$1.57 \times 10^{-19}$
320.0	$5.22 \times 10^{-17}$	$1.27 \times 10^7$	$4.95 \times 10^6$	$2.72 \times 10^{11}$	$2.30 \times 10^{-13}$	$1.72 \times 10^{-16}$	$1.48 \times 10^{-18}$

<sup>a</sup> The letters “a” and “b” are used to distinguish the complexes: “a” is the complex of  $\text{HO}_2 \cdots (\text{H}_2\text{O})_n$  ( $n = 1-3$ ), while “b” is the complex of  $\text{SO}_2 \cdots (\text{H}_2\text{O})_n$  ( $n = 1-3$ ).  $\nu_{a1}$ ,  $\nu_{a2}$  and  $\nu_{a3}$  are the reaction rates of  $\text{HO}_2 \cdots (\text{H}_2\text{O})_n$  ( $n = 1-3$ ),  $\nu_{b1}$ ,  $\nu_{b2}$  and  $\nu_{b3}$  are the equilibrium constants of  $\text{SO}_2 \cdots (\text{H}_2\text{O})_n$  ( $n = 1-3$ ). Species in the presence of a water molecule, water dimer and water trimer are respectively denoted by “1”, “2”, and “3”.  $k'_a(\text{WM1})$  is the effective rate constant for the process of  $\text{HO}_2 \cdots \text{H}_2\text{O} + \text{SO}_2 \rightarrow \text{HOSO} \cdots \text{H}_2\text{O} + \text{O}_2$ ,  $k'_a(\text{WD1})$  is the rate constant for the process of  $\text{HO}_2 \cdots (\text{H}_2\text{O})_2 + \text{SO}_2 \rightarrow \text{HOSO} \cdots (\text{H}_2\text{O})_2 + \text{O}_2$ .  $k'_a(\text{WT1})$  is the rate constant for the process of  $\text{HO}_2 \cdots (\text{H}_2\text{O})_3 + \text{SO}_2 \rightarrow \text{HOSO} \cdots (\text{H}_2\text{O})_3 + \text{O}_2$ .

$\text{HO}_2 \cdots (\text{H}_2\text{O})_2 + \text{SO}_2$  reaction ( $k_a(\text{WD1b})$ ) and the  $\text{HO}_2 \cdots (\text{H}_2\text{O})_3 + \text{SO}_2$  reaction ( $k_a(\text{WT1})$ ) are respectively written as follows.

$$\begin{aligned} \nu_a(\text{WM1b}) &= k_a(\text{WM1b})[\text{H}_2\text{O} \cdots \text{HO}_2][\text{SO}_2] \\ &= k'_a(\text{WM1b})[\text{SO}_2][\text{HO}_2] \end{aligned} \quad (19)$$

$$\begin{aligned} \nu_a(\text{WD1b}) &= k_a(\text{WD1b})[\text{HO}_2 \cdots (\text{H}_2\text{O})_2][\text{SO}_2] \\ &= k'_a(\text{WD1b})[\text{HO}_2][\text{SO}_2] \end{aligned} \quad (20)$$

$$\begin{aligned} \nu_a(\text{WT1}) &= k_a(\text{WT1})[\text{HO}_2 \cdots (\text{H}_2\text{O})_3][\text{SO}_2] \\ &= k'_a(\text{WT1})[\text{HO}_2][\text{SO}_2] \end{aligned} \quad (21)$$

In these equations,  $k'_a(\text{WM1b}) = k_a(\text{WM1b})K_{\text{eq}}(\text{H}_2\text{O} \cdots \text{HO}_2)[\text{H}_2\text{O}]$ ;  $k'_a(\text{WD1b}) = k_a(\text{WD1b})K_{\text{eq}}(\text{HO}_2 \cdots (\text{H}_2\text{O})_2)[(\text{H}_2\text{O})_2]$ ; and  $k'_a(\text{WT1}) = k_a(\text{WT1})K_{\text{eq}}(\text{HO}_2 \cdots (\text{H}_2\text{O})_3)[(\text{H}_2\text{O})_3]$ .  $K_{\text{eq}}(\text{H}_2\text{O} \cdots \text{HO}_2)$ ,  $K_{\text{eq}}(\text{HO}_2 \cdots (\text{H}_2\text{O})_2)$  and  $K_{\text{eq}}(\text{HO}_2 \cdots (\text{H}_2\text{O})_3)$  are the equilibrium constants for the formation of the  $\text{H}_2\text{O} \cdots \text{HO}_2$ ,  $\text{HO}_2 \cdots (\text{H}_2\text{O})_2$  and  $\text{HO}_2 \cdots (\text{H}_2\text{O})_3$  complexes, respectively.  $[\text{H}_2\text{O}]$ ,  $[(\text{H}_2\text{O})_2]$  and  $[(\text{H}_2\text{O})_3]$  are the concentrations of  $\text{H}_2\text{O}$ ,  $(\text{H}_2\text{O})_2$ , and  $(\text{H}_2\text{O})_3$ , respectively. As shown in Table 1, within the temperature range of 275.0–320.0 K, the effective rate constant of  $k'_a(\text{WM1b})$  is  $1.32 \times 10^{-14}$  to  $2.01 \times 10^{-14}$   $\text{cm}^3$  per molecule per s, which is 2–3 and 3–6 orders of magnitude larger than the corresponding values of  $k'_a(\text{WD1b})$  and  $k'_a(\text{WT1})$ , respectively, indicating that the catalytic effect of  $\text{H}_2\text{O}$  is the largest among the  $(\text{H}_2\text{O})_n$  ( $n = 1-3$ ) catalysts, and the catalytic effect of  $(\text{H}_2\text{O})_2$ , and  $(\text{H}_2\text{O})_3$  is negligible. Compared with the rate constant of the naked reaction of  $\text{SO}_2 + \text{HO}_2 \rightarrow \text{HOSO} + \text{O}_2$ , the value of  $k'_a(\text{WM1b})$  is 2–3 orders of magnitude larger within the temperature range of 275.0–320.0 K, indicating that at 0 km altitude within this temperature range, the positive effect of water is significant under atmospheric conditions.

The average concentrations of water at 5, 10 and 15 km altitudes are known to be  $2.41 \times 10^{16}$ ,  $4.92 \times 10^{15}$  and  $1.96 \times 10^{13}$  molecules per  $\text{cm}^3$ , respectively.<sup>75</sup> Considering the average concentrations of water at 5, 10 and 15 km altitudes in the troposphere, the calculated effective rate constants of the  $\text{H}_2\text{O}$ -

assisted Channel WM1, the  $(\text{H}_2\text{O})_2$ -assisted Channel WD1 and the  $(\text{H}_2\text{O})_3$ -assisted Channel WT1 are listed in Table 2. Compared with an altitude of 0 km, the dominant channel does not change in the three different cases, which is similar to the dominant channel in Table 1. Meanwhile, the values of  $k'(\text{WM1})$  are  $7.49 \times 10^{-17}$ ,  $2.68 \times 10^{-17}$  and  $2.95 \times 10^{-18}$  at altitudes of 5, 10 and 15 km, respectively. Compared with the value of  $k'(\text{WM1})$  at 0 km, we found that the values of  $k'(\text{WM1})$  show a declining trend, decreasing by about 4–5 orders of magnitude, as we move towards higher altitude. Furthermore, as shown in Table 2, it has been estimated that the enhancement factors of water vapor are 99.98%, 78.23%, 69.63% and 27.27% at altitudes of 0, 5, 10 and 15 km, respectively. This implies that, as we move towards higher altitudes, the contribution of water on increasing the reaction rate becomes gradually lessened.

### 3.7 Atmospheric implications

In gas-phase reactions of the atmosphere, previous investigations have shown that the dominant sink of  $\text{HO}_2$  is its reaction with  $\text{HO}_2$  (ref. 71) and  $\text{NO}_3$ .<sup>76</sup> Therefore, it is of great importance to discuss the effective rate constant of the  $\text{H}_2\text{O} \cdots \text{HO}_2 + \text{SO}_2$  reaction ( $k'_a(\text{WM1b})$ ) with the rate constant of these dominant sink processes of  $\text{HO}_2$ . To meet this goal, the reaction mechanisms of  $\text{HO}_2 + \text{HO}_2$  and  $\text{HO}_2 + \text{NO}_3$  at the CCSD(T)/CBS//M06-2X/aug-cc-pVTZ level are shown in Fig. S7,<sup>†</sup> while their rate constants within the temperature range of 218.6–320.0 K are listed in Table 3, with rate ratios between  $\text{H}_2\text{O} \cdots \text{HO}_2 + \text{SO}_2$  and  $\text{HO}_2 + \text{HO}_2$  ( $\text{HO}_2 + \text{NO}_3$ ) as shown in eqn (22). The calculated rate constants are in good agreement with the available experimental values.<sup>77–79</sup>

$$\begin{aligned} \frac{\nu_{a1}}{\nu_{R1}} &= \frac{K_{\text{eq}}(\text{H}_2\text{O} \cdots \text{HO}_2)k_a(\text{WM1b})[\text{H}_2\text{O}][\text{HO}_2][\text{SO}_2]}{k_{R1}[\text{HO}_2][\text{HO}_2]} \\ &= \frac{K_{\text{eq}}(\text{H}_2\text{O} \cdots \text{HO}_2)k_a(\text{WM1b})[\text{H}_2\text{O}][\text{SO}_2]}{k_{R1}[\text{HO}_2]} \end{aligned} \quad (22)$$



**Table 2** Effective rate constants (cm<sup>3</sup> per molecules per s) for HOSO + O<sub>2</sub> formation from the SO<sub>2</sub> + HO<sub>2</sub> reaction without and with (H<sub>2</sub>O)<sub>*n*</sub> (*n* = 1–3) within the altitude range of 0–15 km<sup>a</sup>

Alt. (km)	<i>T</i> (K)	<i>k</i> ' <sub>a</sub> (WM1)	<i>k</i> ' <sub>a</sub> (WD1)	<i>k</i> ' <sub>b</sub> (WD2)	<i>k</i> ' <sub>a</sub> (WT1)	<i>k</i> ' <sub>a</sub> (WM)/ <i>k</i> ' <sub>tot</sub>
0	298.2	1.67 × 10 <sup>-13</sup>	1.15 × 10 <sup>-21</sup>	4.03 × 10 <sup>-17</sup>	1.59 × 10 <sup>-18</sup>	99.98%
5	259.3	7.49 × 10 <sup>-17</sup>	3.09 × 10 <sup>-18</sup>	1.10 × 10 <sup>-18</sup>	3.53 × 10 <sup>-20</sup>	78.23%
10	229.7	2.68 × 10 <sup>-17</sup>	5.07 × 10 <sup>-18</sup>	1.40 × 10 <sup>-18</sup>	1.68 × 10 <sup>-21</sup>	69.63%
15	212.6	2.95 × 10 <sup>-18</sup>	8.95 × 10 <sup>-17</sup>	2.63 × 10 <sup>-22</sup>	2.42 × 10 <sup>-26</sup>	27.27%

<sup>a</sup> *k*'<sub>a</sub>(WM1) is the effective rate constant occurring through Channel WM1. *k*'<sub>a</sub>(WD1) and *k*'<sub>b</sub>(WD2) are the effective rate constants of Channel WD1 and WD2, respectively; *k*'<sub>a</sub>(WT1) is the effective rate constant of Channel WT1. *k*'<sub>tot</sub> = *k*'<sub>R1</sub> + *k*'<sub>a</sub>(WM)(100% RH).

$$\frac{v_{a1}}{v_{R2}} = \frac{K_{eq}(\text{H}_2\text{O}\cdots\text{HO}_2)k_a(\text{WM1b})[\text{H}_2\text{O}][\text{HO}_2][\text{SO}_2]}{k_{R2}[\text{HO}_2][\text{NO}_3]}$$

$$= \frac{K_{eq}(\text{H}_2\text{O}\cdots\text{HO}_2)k_a(\text{WM1b})[\text{H}_2\text{O}][\text{SO}_2]}{k_{R2}[\text{NO}_3]} \quad (23)$$

Here, *k*<sub>R1</sub> and *k*<sub>R2</sub> are the rate constants of the HO<sub>2</sub> + HO<sub>2</sub> reaction and the HO<sub>2</sub> + NO<sub>3</sub> reaction, respectively, obtained from Table 3. The rate ratios *v*<sub>a1</sub>/*v*<sub>R1</sub> and *v*<sub>a1</sub>/*v*<sub>R2</sub> depend on the H<sub>2</sub>O, SO<sub>2</sub>, NO<sub>3</sub> and HO<sub>2</sub> concentrations in the atmosphere. At 298 K, when the concentration of water is at a relative humidity of 100%, SO<sub>2</sub> and NO<sub>3</sub> are 7.73 × 10<sup>17</sup>, 1 × 10<sup>12</sup> and 2.46 × 10<sup>7</sup> molecules per cm<sup>3</sup>, respectively, and the gas-phase concentration of HO<sub>2</sub> is 3 × 10<sup>8</sup> molecules per cm<sup>3</sup>, the H<sub>2</sub>O⋯HO<sub>2</sub> + SO<sub>2</sub> reaction can compete with the HO<sub>2</sub> + HO<sub>2</sub> reaction, because the rate ratio *v*<sub>a1</sub>/*v*<sub>R1</sub> is about 4.35 × 10<sup>2</sup> at 298 K. Meanwhile, the H<sub>2</sub>O⋯HO<sub>2</sub> + SO<sub>2</sub> reaction can compete well with the HO<sub>2</sub> + NO<sub>3</sub> reaction because the rate ratio *v*<sub>a1</sub>/*v*<sub>R2</sub> is about 6.83 × 10<sup>3</sup> at 298 K. Thus, compared with the primary loss mechanism of HO<sub>2</sub> radicals, the HO<sub>2</sub> + SO<sub>2</sub> → HOSO + <sup>3</sup>O<sub>2</sub> reaction with H<sub>2</sub>O cannot be neglected. Meanwhile, with increasing altitude, the values of *v*<sub>a1</sub>/*v*<sub>R1</sub> and *v*<sub>a1</sub>/*v*<sub>R2</sub> obviously decrease. At 218.6 K, the values of *v*<sub>a1</sub>/*v*<sub>R1</sub> and *v*<sub>a1</sub>/*v*<sub>R2</sub> are 5.22 × 10<sup>-4</sup> and 1.73 × 10<sup>-3</sup>, showing that the HO<sub>2</sub> + SO<sub>2</sub> → HOSO + <sup>3</sup>O<sub>2</sub> reaction with H<sub>2</sub>O cannot compete with the primary loss mechanism of HO<sub>2</sub> radicals.

In order to test the competition of the H<sub>2</sub>O⋯HO<sub>2</sub> + SO<sub>2</sub> reaction with the primary loss mechanism of SO<sub>2</sub> (such as the

SO<sub>2</sub> + HO reaction), it is of great importance to discuss the rate ratio between H<sub>2</sub>O⋯HO<sub>2</sub> + SO<sub>2</sub> and SO<sub>2</sub> + OH, as shown in eqn (24).

$$\frac{v_{a1}}{v_{R3}} = \frac{K_{eq}(\text{H}_2\text{O}\cdots\text{HO}_2)k_a(\text{WM1b})[\text{H}_2\text{O}][\text{HO}_2][\text{SO}_2]}{k_{R3}[\text{HO}][\text{SO}_2]}$$

$$= \frac{K_{eq}(\text{H}_2\text{O}\cdots\text{HO}_2)k_a(\text{WM1b})[\text{H}_2\text{O}][\text{HO}_2]}{k_{R3}[\text{HO}]} \quad (24)$$

Here, *k*<sub>R3</sub> is the rate constant of the SO<sub>2</sub> + OH reaction, which is obtained from Table 3. The rate ratio *v*<sub>a1</sub>/*v*<sub>R3</sub> depends on the H<sub>2</sub>O, OH, and HO<sub>2</sub> concentrations in the atmosphere, At 298 K, when the concentration of water is at a relative humidity of 100%, OH is 7.73 × 10<sup>17</sup> and 1 × 10<sup>6</sup> molecules per cm<sup>3</sup>, respectively, and the gas-phase concentration of HO<sub>2</sub> is 3 × 10<sup>8</sup> molecules per cm<sup>3</sup>, the H<sub>2</sub>O⋯HO<sub>2</sub> + SO<sub>2</sub> reaction can compete with the SO<sub>2</sub> + HO reaction, because the rate ratio *v*<sub>a1</sub>/*v*<sub>R3</sub> is about 6.20 at 298 K. Consequently, the hydrogen atom transfer processes of the H<sub>2</sub>O⋯HO<sub>2</sub> + SO<sub>2</sub> reaction are more obvious in the atmosphere during the day than those of the SO<sub>2</sub> + HO reaction. Meanwhile, when the OH concentration decreases to 1 × 10<sup>4</sup> molecules per cm<sup>3</sup> during the night,<sup>80</sup> the H<sub>2</sub>O⋯HO<sub>2</sub> + SO<sub>2</sub> reaction can compete well with the SO<sub>2</sub> + HO reaction because the rate ratio *v*<sub>a1</sub>/*v*<sub>R3</sub> is about 6.20 × 10<sup>2</sup> at 298 K. Thus, the H<sub>2</sub>O⋯HO<sub>2</sub> + SO<sub>2</sub> reaction can also make a contribution to the sink of SO<sub>2</sub> during the night under the conditions of OH (10<sup>4</sup> molecules per cm<sup>3</sup>), HO<sub>2</sub> (molecules per cm<sup>3</sup>), and H<sub>2</sub>O (molecules per cm<sup>3</sup>).

**Table 3** Rate constants (cm<sup>3</sup> per molecules per s) for H<sub>2</sub>O<sub>2</sub> + O<sub>2</sub> formation from the HO<sub>2</sub> + HO<sub>2</sub> reaction (R1), HNO<sub>3</sub> + O<sub>2</sub> formation from the NO<sub>3</sub> + HO<sub>2</sub> reaction (R2) and HSO<sub>3</sub> formation from the SO<sub>2</sub> + OH reaction (R3) within the temperature range of 218.6–320.0 K

<i>T</i> (K)	<i>k</i> <sub>R1</sub>	<i>v</i> <sub>a1</sub> / <i>v</i> <sub>R1</sub>	<i>k</i> <sub>R2</sub>	<i>v</i> <sub>a1</sub> / <i>v</i> <sub>R2</sub>	<i>k</i> <sub>R3</sub>	<i>v</i> <sub>a1</sub> / <i>v</i> <sub>R3</sub>	<i>v</i> <sub>a1</sub> / <i>v</i> <sub>R3</sub> (night)
218.6	1.38 × 10 <sup>-10</sup>	5.22 × 10 <sup>-4</sup>	5.06 × 10 <sup>-10</sup>	1.74 × 10 <sup>-3</sup>	2.06 × 10 <sup>-12</sup>	3.15 × 10 <sup>-3</sup>	3.15 × 10 <sup>-1</sup>
223.7	8.29 × 10 <sup>-11</sup>	8.24 × 10 <sup>-4</sup>	2.55 × 10 <sup>-10</sup>	1.09 × 10 <sup>-3</sup>	2.09 × 10 <sup>-12</sup>	3.27 × 10 <sup>-4</sup>	3.27 × 10 <sup>-2</sup>
229.7	4.69 × 10 <sup>-11</sup>	1.63 × 10 <sup>-1</sup>	1.22 × 10 <sup>-10</sup>	2.55 × 10 <sup>-1</sup>	2.14 × 10 <sup>-12</sup>	3.58 × 10 <sup>-2</sup>	3.58 × 10 <sup>0</sup>
235.1	2.88 × 10 <sup>-11</sup>	4.54 × 10 <sup>-4</sup>	6.72 × 10 <sup>-11</sup>	7.92 × 10 <sup>-4</sup>	2.20 × 10 <sup>-12</sup>	5.95 × 10 <sup>-5</sup>	5.95 × 10 <sup>-3</sup>
249.9	8.50 × 10 <sup>-11</sup>	2.53 × 10 <sup>-3</sup>	1.68 × 10 <sup>-11</sup>	5.20 × 10 <sup>-2</sup>	2.32 × 10 <sup>-12</sup>	9.26 × 10 <sup>-4</sup>	9.26 × 10 <sup>-2</sup>
259.3	4.22 × 10 <sup>-11</sup>	1.02 × 10 <sup>0</sup>	8.20 × 10 <sup>-12</sup>	2.13 × 10 <sup>1</sup>	2.37 × 10 <sup>-12</sup>	1.82 × 10 <sup>-1</sup>	1.82 × 10 <sup>1</sup>
280.0	1.08 × 10 <sup>-11</sup>	1.27 × 10 <sup>1</sup>	2.32 × 10 <sup>-12</sup>	2.41 × 10 <sup>2</sup>	2.53 × 10 <sup>-12</sup>	5.43 × 10 <sup>-1</sup>	5.43 × 10 <sup>1</sup>
290.0	6.01 × 10 <sup>-12</sup>	2.53 × 10 <sup>1</sup>	1.42 × 10 <sup>-12</sup>	4.35 × 10 <sup>2</sup>	2.64 × 10 <sup>-12</sup>	5.76 × 10 <sup>-1</sup>	5.76 × 10 <sup>1</sup>
298.2	3.85 × 10 <sup>-12</sup>	4.35 × 10 <sup>2</sup>	9.96 × 10 <sup>-13</sup>	6.83 × 10 <sup>3</sup>	2.70 × 10 <sup>-12</sup>	6.20 × 10 <sup>0</sup>	6.20 × 10 <sup>2</sup>
300.0	3.49 × 10 <sup>-12</sup>	4.88 × 10 <sup>2</sup>	9.23 × 10 <sup>-13</sup>	7.51 × 10 <sup>3</sup>	2.71 × 10 <sup>-12</sup>	6.29 × 10 <sup>0</sup>	6.29 × 10 <sup>2</sup>
310.0	2.11 × 10 <sup>-12</sup>	8.88 × 10 <sup>2</sup>	6.29 × 10 <sup>-13</sup>	1.21 × 10 <sup>4</sup>	2.79 × 10 <sup>-12</sup>	6.72 × 10 <sup>0</sup>	6.72 × 10 <sup>2</sup>
320.0	1.32 × 10 <sup>-12</sup>	1.53 × 10 <sup>2</sup>	4.46 × 10 <sup>-13</sup>	1.84 × 10 <sup>3</sup>	2.90 × 10 <sup>-12</sup>	6.95 × 10 <sup>-1</sup>	6.95 × 10 <sup>1</sup>



## 4. Summary and conclusions

In this article, the hydrogen atom transfer processes of the  $\text{HO}_2 + \text{SO}_2 \rightarrow \text{HOSO} + {}^3\text{O}_2$  reaction without and with  $(\text{H}_2\text{O})_n$  ( $n = 1-3$ ) have been investigated using the CCSD(T)/CBS//M06-2X/aug-cc-pVTZ method and canonical variational transition state theory with small curvature tunneling (CVT/SCT). The calculated results show that, for the  $(\text{H}_2\text{O})_n$  ( $n = 1-3$ ) +  $\text{HO}_2 + \text{SO}_2$  reaction, the main entrance channel is the reaction of the  $\text{HO}_2 \cdots (\text{H}_2\text{O})_n$  ( $n = 1-3$ ) complex with  $\text{SO}_2$ . Additionally,  $\text{H}_2\text{O}$  exerts the strongest catalytic influence in the hydrogen atom transfer processes of the  $\text{HO}_2 + \text{SO}_2 \rightarrow \text{HOSO} + {}^3\text{O}_2$  reaction compared with  $(\text{H}_2\text{O})_2$  and  $(\text{H}_2\text{O})_3$ , which is due to the fact that the effective rate constant of the  $\text{HO}_2 \cdots \text{H}_2\text{O} + \text{SO}_2$  reaction is 2–3 and 4–6 orders of magnitude larger than the corresponding rate constants of the  $\text{HO}_2 \cdots (\text{H}_2\text{O})_2 + \text{SO}_2$  and  $\text{HO}_2 \cdots (\text{H}_2\text{O})_3 + \text{SO}_2$  reactions, respectively.

In the gas-phase reactions of the atmosphere, the importance of the  $\text{HO}_2 \cdots \text{H}_2\text{O} + \text{SO}_2$  reaction depends on its competition with the  $\text{HO}_2 + \text{SO}_2 \rightarrow \text{HOSO} + {}^3\text{O}_2$  reaction. We show that, at 0 km altitude within the temperature range of 275–320 K, the effective rate constant of the  $\text{HO}_2 \cdots \text{H}_2\text{O} + \text{SO}_2$  reaction was 2–3 orders of magnitude larger than that of the  $\text{HO}_2 + \text{SO}_2 \rightarrow \text{HOSO} + {}^3\text{O}_2$  reaction without a catalyst, indicating that the water monomer plays an obvious positive role in increasing the rate of the  $\text{HO}_2 + \text{SO}_2 \rightarrow \text{HOSO} + {}^3\text{O}_2$  reaction. Compared with the primary loss mechanism of  $\text{HO}_2$  radicals and  $\text{SO}_2$ , the  $\text{HO}_2 + \text{SO}_2 \rightarrow \text{HOSO} + {}^3\text{O}_2$  reaction with  $\text{H}_2\text{O}$  cannot be neglected with its rate constant close to the rate constant of those reactions of  $\text{HO}_2 + \text{HO}_2$ ,  $\text{HO}_2 + \text{NO}_3$  and  $\text{SO}_2 + \text{HO}$ . In addition, with the altitude increase, for the formation of  $\text{HOSO} + {}^3\text{O}_2$ , the contribution of  $\text{H}_2\text{O}$  decreases from 99.98% to 27.27% at the lower relative concentration of water, which indicates that the  $\text{HO}_2 \cdots \text{H}_2\text{O} + \text{SO}_2$  reaction cannot compete with the primary loss processes of  $\text{HO}_2$  radicals and  $\text{SO}_2$  at higher altitudes.

The findings of the present work not only show a specific  $(\text{H}_2\text{O})_n$  ( $n = 1-3$ ) catalyzed reaction for its reaction mechanism and kinetics, but also show that  $\text{H}_2\text{O}$  can obviously promote the hydrogen atom transfer processes of the  $\text{HO}_2 + \text{SO}_2 \rightarrow \text{HOSO} + {}^3\text{O}_2$  reaction. Thus, the present investigation has wide applications in the hydrogen atom transfer processes of atmospheric processes, such as  $\text{HO}_2 + \text{HO}_2$  and  $\text{HO}_2 + \text{NO}_3$  reactions.

## Conflicts of interest

There are no conflicts to declare.

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