

# One conceivable mechanism of UV-light induced SO<sub>2</sub> Oxidation to H<sub>2</sub>SO<sub>4</sub>

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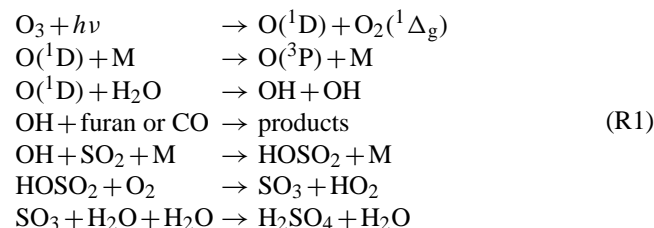
**Abstract.** The electron-excited chemistry of sulfur dioxide oxidation induced by UV irradiation of air with trace O<sub>3</sub> and SO<sub>2</sub> is considered. The importance of this mechanism is evaluated based on recent laboratory experiments on SO<sub>2</sub> oxidation in a laminar tube with air induced by UV irradiation. Results show that under respective conditions the route of SO<sub>2</sub> oxidation involving electron excited oxygen molecules may present an additional source of gaseous H<sub>2</sub>SO<sub>4</sub> production to known OH-radical mechanism.

## 1 Introduction

The gaseous sulfur compounds present in atmosphere mostly as sulfur dioxide. SO<sub>2</sub> is an important air pollutant and a source of gaseous sulfuric acid H<sub>2</sub>SO<sub>4</sub> (GSA), one of the main aerosol precursor gases (Seinfeld and Pandis, 1998). Understanding of subsequent oxidation reactions of SO<sub>2</sub> in the atmosphere is hence of fundamental importance. In this study, we discuss possible ways to influence the GSA formation by UV radiation through the mechanism involving electron-excited molecules.

Recently several special flow tube experiments have been performed to investigate the aerosol formation in the humid air with trace O<sub>3</sub> and SO<sub>2</sub> under UV irradiation (Berndt et al., 2005, 2006, 2008; Benson et al., 2008; Young et al., 2008; Enghoff et al., 2008). In these experiments, the GSA was in-situ produced in a tubular flow reactor (FR) triggered by ozone or water molecules UV photolysis. Important to note,

that in (Benson et al., 2008; Young et al., 2008) the GSA concentration was directly measured by using a CIMS technique. However, in (Berndt et al., 2005, 2006; Enghoff et al., 2008) the reported GSA concentration was estimated somewhat indirectly based on a combination of simulation results and measurement data. The GSA formation in these experiments has attributed to neutral-chemistry mechanism starting from the reaction of SO<sub>2</sub> molecules with hydroxyl radicals OH:



The given reaction scheme was applied in (Berndt et al., 2006, 2008) to deduce the time behavior of GSA along the FR. We have repeated these calculations with even more detailed reaction scheme and using different compilations of rate coefficients to see a sensitivity of the resulting GSA concentration. The results obtained totally were the same as in (Berndt et al., 2006), i.e. the formed GSA concentration is around a few 10<sup>7</sup> cm<sup>-3</sup>.

It should be noted that in (Laaksonen et al., 2008) it was hypothesized that HSO<sub>5</sub> radicals may be partly formed in a reaction between HSO<sub>3</sub> and O<sub>2</sub> in the presence of sufficient concentration of inert molecules whose collisions stabilize the reaction product. Indirect experimental support for such a mechanism is given in the paper (Berndt et al., 2008). Also in (Laaksonen et al., 2008) it was further suggested that the HSO<sub>5</sub> radicals may react with other trace species, and that



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the resulting molecules act as nuclei for heterogeneous nucleation of H<sub>2</sub>SO<sub>4</sub> vapor which will initiate the growth of the new particles (Salonen et al., 2009). Finally, in a very recent publication by Sipila et al. (2010) the explanation of the apparent difference between atmospheric and laboratory measurements of the sulfuric acid concentration needed to nucleate new particles, as seems, has been answered.

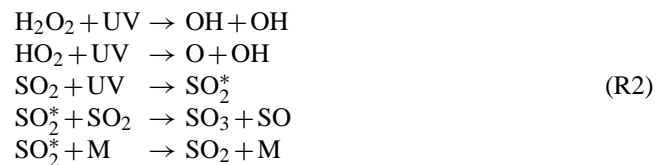
However, one result of our simulation seems to be also interesting, that is a formation of a sufficient amount of electronically excited oxygen molecules O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) (up to about 5 × 10<sup>9</sup> cm<sup>-3</sup> at steady-state). This implies a potential for an additional source of the GSA production via the mechanism involving electron-excited oxygen molecules. Another possibility may imply ion-chemistry effects and the formation of sulfur bearing ions in some a chain mechanism triggered by UV induced multiphoton ionization of air molecules. The objective of this study is to analyze the effect of the UV induced photo-excitation processes on GSA formation in a humid air with O<sub>3</sub> and SO<sub>2</sub>. The results obtained are based on simple calculations using either existing data or upper limit estimations for rate coefficients of the reactions involving excited molecules.

## 2 UV light induced “electron-excited” chemistry

The electron-excited molecules and atoms may essentially affect the kinetics of chemical reactions (Fridman and Kennedy, 2004). In air with SO<sub>2</sub> in the presence of UV irradiation both the photolysis and collision reactions may lead to the formation of electronically and vibrationally excited oxygen and sulfur dioxide molecules. Hence, it is reasonable to assess the possible involvement of electron-excited species in SO<sub>2</sub> oxidation.

### 2.1 Electron-excited SO<sub>2</sub> formation

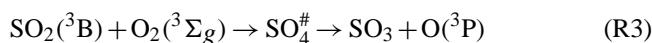
At first, one might suggest an additional formation of OH radicals either by UV-light induced dissociation of HO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> molecules or the formation of excited SO<sub>2</sub>\*



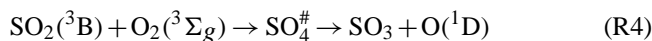
Here, SO<sub>2</sub>\* indicates SO<sub>2</sub> in <sup>1</sup>B or <sup>3</sup>B electronic states. Self-quenching of excited SO<sub>2</sub>\* is known to produce SO<sub>3</sub>, since ΔH<sub>rxn</sub> = -210 (-112) kJ/mol for <sup>1</sup>B (<sup>3</sup>B) states (James et al., 1974; Marvin and Reiss, 1978; Sander and Seinfeld, 1976). The formation of H<sub>2</sub>O<sub>2</sub> in the laboratory experiments occurs in the recombination reaction between two HO<sub>2</sub> radicals. On the other hand, some of OH radicals will disappear through the following reactions before reacting with CO, OH+OH+M=H<sub>2</sub>O<sub>2</sub>+M (Seinfeld and Pandis, 1998).

However, the simulation with these new reactions added to mechanism (Reaction R1) shows that given UV absorption channels are not important for GSA production in conditions of above experiments as the rate constants for quenching of the SO<sub>2</sub>\* are too large. The reason is in relatively small an absorption cross section (σ) of these molecules for UV light near 254 nm (compare the respective σ in cm<sup>2</sup>: O<sub>3</sub>-1.5 × 10<sup>-17</sup>, HO<sub>2</sub>-2 × 10<sup>-19</sup>, H<sub>2</sub>O<sub>2</sub>-7 × 10<sup>-20</sup>, and SO<sub>2</sub>-1.5 × 10<sup>-19</sup> (Manatt and Lane, 1993; NIST, 2007). Moreover, the excited SO<sub>2</sub>(<sup>1</sup>B) relaxes very rapidly in collisions with N<sub>2</sub> (with the rate of about 1 × 10<sup>10</sup> s<sup>-1</sup> at atmospheric conditions) to ground electronic state and partially (no more than 10 %) to SO<sub>2</sub>(<sup>3</sup>B) state and then to ground state with the rate of about 6 × 10<sup>6</sup> s<sup>-1</sup> (Marvin and Reiss, 1978; Christensen et al., 1994).

Also, the chemical quenching of excited SO<sub>2</sub>(<sup>3</sup>B) by O<sub>2</sub> to produce SO<sub>3</sub> is energetically possible, i.e.



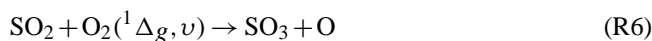
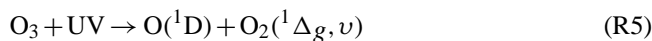
where SO<sub>4</sub><sup>#</sup> presents a transition state, and for this reaction ΔH<sub>rxn</sub> = -165 kJ/mol (Sidebottom et al., 1972; NIST, 2007). However, the rate of this reaction should be small as expected from the theory for spin forbidden reactions (Sidebottom et al., 1972). The spin allowed reaction



is endothermic (ΔH<sub>rxn</sub> = +25.1 kJ/mol) (Sidebottom et al., 1972; NIST, 2007) and likely has a negligible rate coefficient. The electronic state of the SO<sub>4</sub> transition state not indicated in these references, but presumably, it is singlet. The conclusion made, coincides with results of testing experiments performed in (Berndt et al., 2006, 2008), which indicate the absence of the formation of new particles with O<sub>3</sub> switched off. This eliminates as important any mechanisms without O<sub>3</sub> involvement.

### 2.2 Metastable electron-excited oxygen O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>, ν) formation

Another possibility is the reaction of SO<sub>2</sub> with electron-vibrationally excited oxygen O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>, ν > 0), where ν is a vibrational quantum number



In Hartley absorption band of ozone (the peak at 254 nm) more than 50% of oxygen molecules O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>, ν) are formed in states with ν ≥ 1 (Slanger and Copeland, 2003). The energy defect of Reaction (R5) can be estimated as ΔE = E<sub>UV</sub> - EO<sub>3</sub> - EO\* - E<sub>0</sub>. Here E<sub>UV</sub> is the photon energy, EO<sub>3</sub> is the dissociation energy of the ozone molecule (1.05 eV), EO\* is the energy of excitation of the O(<sup>1</sup>D) atom from the ground

state (1.97 eV), and  $E_0=0.98$  eV is the energy of oxygen electron-excited state  $O_2(^1\Delta_g, \nu=0)$  (0.98 eV) (Yankovsky et al., 2007). At  $\lambda=254$  nm (4.9 eV), the value of  $\Delta E$  is 0.90 eV and hence excited molecules  $O_2(^1\Delta_g, \nu)$  with vibration quantum numbers up to  $\nu=5$  can be formed (the mean energy of vibrational quanta is of about  $E_{\text{vib}}=0.2$  eV). The reaction enthalpy of Reaction (R6) may be estimated as  $\Delta H_{\text{rxn}} = \Delta H_f(\text{SO}_3) + \Delta H_f(\text{O}(^3\text{P})) - \Delta H_f(\text{SO}_2) - \Delta H_f(\text{O}_2(^1\Delta_g)) - \nu \times \Delta E_{\text{vib}} = 0.58 - \nu \times 0.2$  (in eV) (NIST, 2007). Hence, Reaction (R4) is exothermic for only  $\nu \geq 3$ . The quantum yield  $F$  of  $O_2(^1\Delta_g, \nu=3-5)$  molecules in a singlet channel of  $O_3$  photolysis (at  $\lambda=254$  nm) is estimated to be about  $F=0.19$  (Slanger and Copeland, 2003; Yankovsky et al., 2007).

Molecules  $O_2(^1\Delta_g)$  are produced mainly in Reaction (R5) and removed due to electron-relaxation to lower states and losses on walls. Hence, the steady-state concentration of excited oxygen is

$$[O_2(^1\Delta_g)] = P/R \quad (\text{R7})$$

Here  $P=[O_3] \times Q_{\text{UV}}$  presents the production rate of  $O_2(^1\Delta_g)$  in Reaction (R5) and  $R$  denotes its total removal rate. The parameter  $Q_{\text{UV}}=0.031 \text{ s}^{-1}$  is the rate of  $O_3$  photolysis in Reaction (R5), which, as an example, is derived by fitting Reaction (R1) to measured effective rate of ozone consumed (Berndt et al., 2008). The removal rate may be presented as  $R = R_{\text{REL}} + R_{\text{WL}}$ . Here, the  $R_{\text{REL}}$  takes into account the deexcitation of  $O_2(^1\Delta_g)$  to ground state and  $R_{\text{WL}}$  presents the effective rate of  $O_2(^1\Delta_g)$  wall losses (which is much smaller,  $R_{\text{WL}} < 0.03 \text{ s}^{-1}$ , Sharpless and Slanger, 1989). The rate coefficients of relaxation processes are from (Slanger and Copeland, 2003; Yankovsky and Manuilova, 2006). The quenching of electronically excited  $O_2(^1\Delta_g, \nu=0)$  by both  $N_2$  and  $O_2$  (i.e. ET process – the relaxation of electronically excited molecules, Fridman and Kennedy, 2004) is significant. At room temperature the rate coefficients  $k_{\text{ET}}(\text{N}_2)=1 \times 10^{-20} \text{ cm}^3/\text{s}$  and  $k_{\text{ET}}(\text{O}_2)=1.7 \times 10^{-18} \text{ cm}^3/\text{s}$  and hence in  $N_2-O_2(1\%)$  mixture the removal rate  $R=4.5 \text{ s}^{-1}$ . At  $[O_3]=6 \times 10^{11} \text{ cm}^{-3}$ , the  $O_2(^1\Delta_g)$  production rate is  $P=1.9 \times 10^{10} \text{ cm}^{-3} \text{ s}^{-1}$  and therefore the steady-state concentration of  $O_2(^1\Delta_g)$  should be about  $4 \times 10^9 \text{ cm}^{-3}$  (the simulated concentration is close to  $5 \times 10^9 \text{ cm}^{-3}$ ). In the atmosphere, the  $O_2$  concentration is about 20 times higher and hence the electronic quenching of singlet-delta oxygen should be much more efficient. The deexcitation of electronic-vibrationally excited  $O_2(^1\Delta_g, \nu \geq 1)$  in collisions with  $N_2$  is small in comparison with that of  $O_2$ . The vibrational deactivation of  $O_2(^1\Delta_g, \nu \geq 3)$  is defined mainly by collisions with  $O_2$  and its rate is estimated to be about  $R_{\text{REL}}(\nu \geq 3)=10^7-2 \times 10^8 \text{ s}^{-1}$  depending on  $O_2$  concentration in air. Therefore, the low limit for the concentration of  $[O_2(^1\Delta_g, \nu \geq 3)]$  can be estimated assuming the Boltzman's distribution over vibration levels in electronic state  $a^1\Delta_g$  with  $\Delta E_{\text{vib}}=0.2$  eV. The upper concentration limit (non-equilibrium case) can be estimated from

the ratio  $F \times [O_3] \times Q_{\text{UV}} / R_{\text{REL}}(\nu \geq 3)$ . As a result, we have  $0.1 \leq [O_2(^1\Delta_g, \nu \geq 3)] < 10-200 \text{ cm}^{-3}$ .

Reaction (R6), which involve the low vibration energy levels of  $O_2(^1\Delta_g, \nu=0-2)$ , is endothermic. Its rate is about of  $2.2 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$  (NIST, 2007). The rate of Reaction (R6) with  $O_2(^1\Delta_g, \nu \geq 3)$  involved is unknown. However, according to experimental data and results of the developed theory (Fridman and Kennedy, 2004), the vibrational excitation of molecular reactants has a potential to increase the reaction rate. To make an estimate of the maximum efficiency of the considered mechanism the upper limit for the rate coefficient of about  $3 \times 10^{-10} \text{ cm}^3/\text{s}$  can be used (i.e. nearly the collision limit). Hence, in maximum, the production rate of  $\text{SO}_3$ ,  $Q_{\text{SO}_3}$ , via the mechanism of Reactions (R5) and (R6) at  $[\text{SO}_2]=5 \times 10^{10} \text{ cm}^{-3}$  (the upper range of  $\text{SO}_2$  concentrations in Berndt et al., 2006) may be estimated to be about  $Q_{\text{SO}_3}=3 \times 10^3-6 \times 10^4 \text{ cm}^{-3} \text{ s}^{-1}$ . The  $\text{SO}_3$  wall losses may be estimated as  $R_{\text{WL}}(\text{SO}_3)=0.02 \text{ s}^{-1}$  (using the diffusion coefficient  $D_g=0.1 \text{ cm}^2/\text{s}$ ). Hence, the steady-state GSA concentration, formed via Reactions (R5) and (R6) should not be greater than  $3 \times 10^6 \text{ cm}^{-3}$ .

Thus, the performed analysis shows that the role of  $O_2(^1\Delta_g, \nu)$  molecules in production of GSA precursors in air with trace  $O_3$  and  $\text{SO}_2$  under UV irradiation is likely small in comparison with the oxidation route involving OH radicals (where GSA is about of few  $1 \times 10^7 \text{ cm}^{-3}$ ). Note that in (Christensen et al., 1994) the rate coefficient for Reaction (R6) was estimated to be smaller by about three orders of magnitude than that was used in above estimation, that only enhance the conclusion made.

### 2.3 Excited $O_2(b^1\Sigma_g^+, \nu)$ formation

Most of electron-excited  $O(^1\text{D})$  atoms are removed by electronic quenching in collisions with air molecules with the total rate of about  $2.9 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  (Sander et al., 2006). Most of the remaining atoms rapidly transfer their energy to  $O_2$ , resulting in electron-vibration excited molecules  $O_2(b^1\Sigma_g^+, \nu=0-2)$  and react with water molecules to give OH radicals. The total quantum yield of  $O_2(b^1\Sigma_g^+, \nu)$  in collisions of  $O_2$  with  $O(^1\text{D})$  was measured to be equal to 0.95 with the rate of about  $4.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  at room temperature (Yankovsky and Manuilova, 2006).

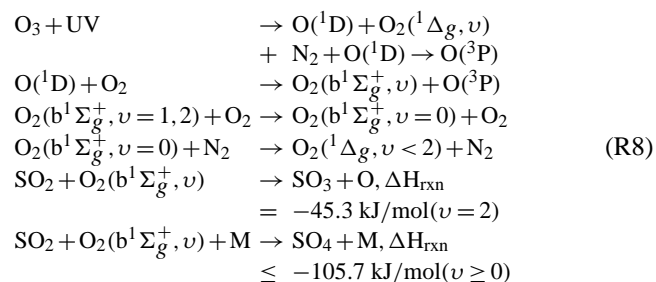
The most effective atmospheric quencher of  $O_2(b^1\Sigma_g^+, \nu=0)$  is  $N_2$ , while removal by  $O_2$  is about 50 times slower. For de-excitation of  $O_2(b^1\Sigma_g^+, \nu=0)$  by  $N_2$  the upper limit of the rate constant is measured to be about  $2.1 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$  (Sander et al., 2006). In contrast, the vibration-translational relaxation of  $O_2(b^1\Sigma_g^+, \nu=1, 2)$  to  $O_2(b^1\Sigma_g^+, \nu=0)$  by  $O_2$  is much more rapid with the room-temperature rate constant for  $\nu=1$  of about  $1.5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  (Kalogerakis et al., 2002). In a flow reactor with air and  $O_3$  under UV irradiation the steady-state concentrations of excited  $O(^1\text{D})$  and  $O_2(b^1\Sigma_g^+, \nu)$  are rapidly formed. The production and

**Table 1.** The estimated production of GSA in air with trace O<sub>3</sub> and SO<sub>2</sub> under UV irradiation in experiments (Berndt et al., 2005, 2006) due to different proposed chemical mechanisms.

Chemical mechanism	Production of GSA (cm <sup>-3</sup> )
Base case: SO <sub>2</sub> oxidation driven by OH (Reaction R1)	(1–5) × 10 <sup>7</sup> (Berndt et al., 2005, 2006)
Electron excited SO <sub>2</sub> chemistry (Reaction R2)	far less
Electron excited oxygen chemistry (Reactions R6, R8)	3 × 10 <sup>6</sup> and (1–5) × 10 <sup>7</sup> (this work)

removal processes of O<sub>2</sub>(b<sup>1</sup>Σ<sub>g</sub><sup>+</sup>, *v*) proceed with the rates of about  $P=2 \times 10^8 \times [\text{O}(\text{D})] \text{ cm}^{-3} \text{ s}^{-1}$  and  $R=5 \times 10^4 \text{ s}^{-1}$  respectively, where [O(<sup>1</sup>D)] denotes the concentration of O(<sup>1</sup>D) atoms in cm<sup>3</sup>. For conditions from (Berndt et al., 2006) these concentrations are estimated to be about [O(<sup>1</sup>D)]=15 and [O<sub>2</sub>(b<sup>1</sup>Σ<sub>g</sub><sup>+</sup>, *v*)]=6 × 10<sup>4</sup> per cm<sup>3</sup>.

The reaction of O<sub>2</sub>(b<sup>1</sup>Σ<sub>g</sub><sup>+</sup>, *v*) with SO<sub>2</sub> leading to formation of SO<sub>3</sub> and O(<sup>3</sup>P) is exothermic for all *v*. Hence, it is interesting to consider the following mechanism of UV induced SO<sub>2</sub> oxidation



The two reactions, involving SO<sub>2</sub>, are energetically favourable. The oxygen atoms in reactions with SO<sub>2</sub> in Reactions (R6) and (R8) are forming in a ground (triplet) electronic state. The enthalpy values were calculated based on data for formation enthalpies for reactants and reaction products in a ground energy states and with accounting afterward for energies of discrete electronic and vibration states of molecules. Assuming the rate coefficient for these exothermic reactions to be close to a collision limit, i.e. nearly 3 × 10<sup>-10</sup> cm<sup>3</sup>/s, the GSA production rate via the Reaction (R8) may be estimated to be about 6 × 10<sup>5</sup> cm<sup>-3</sup> s<sup>-1</sup> at [SO<sub>2</sub>]=(1–5) × 10<sup>10</sup> cm<sup>-3</sup>. With accounting for diffusion losses on walls, the steady-state concentration of GSA is about (1–5) × 10<sup>7</sup> cm<sup>-3</sup>. This value is of the same order as was deduced in recently in laboratory experiments (Berndt et al., 2005, 2006) for OH driven SO<sub>2</sub> oxidation route.

The efficiency of reactions with participating of SO<sub>2</sub> would expect to be low, as these reactions require a spin inversion and hence would likely violate the spin conservation rule. However polyatomic molecules have complex potential surfaces some of which can cross the predissociating surfaces. From the predissociating state, ground state atoms are eventually forming. Hence, the mechanism of Reactions (R6) and (R8) are only speculatively considered in

the paper and their reaction rates are likely much lower than collision rates. The final conclusion may be possible only after the proper experimental evidence. Further investigations are needed to confirm or reject the performed estimations.

The results obtained are summarized in Table 1. Note, the uncertainty of the above estimations seems to be large due to unknown rate coefficients for some reactions involving SO<sub>2</sub>. For example, the non-reactive quenching of O<sub>2</sub>(b<sup>1</sup>Σ<sub>g</sub><sup>+</sup>, *v*) by SO<sub>2</sub> is also probable. Also, the uncertainty of thermochemistry data used may introduce some errors in our estimations. Nevertheless, the performed analysis shows readily the potential for the enhanced SO<sub>2</sub> oxidation in air with O<sub>3</sub> under UV irradiation via the chemistry involving electron excited oxygen molecules. The most promising is likely the reaction of SO<sub>2</sub> with O<sub>2</sub>(b<sup>1</sup>Σ<sub>g</sub><sup>+</sup>, *v*).

Finally, it is important to note that in a very recent publication in Science by Sipila et al. (2010) the results of laboratory measurements have been reported which show the formation of new particles (approximately 1.5 nanometers) at atmospherically relevant sulfuric acid concentrations. Also, it is shown that the observed freshly formed particles contain one to two sulfuric acid molecules, a number consistent with assumptions that are based on atmospheric observations.

### 3 Conclusions

An analysis of different mechanisms of SO<sub>2</sub> oxidation have indicated the potential importance of chemical reactions involving electron excited oxygen molecules O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) and O<sub>2</sub>(b<sup>1</sup>Σ<sub>g</sub><sup>+</sup>). This oxidation route could provide an additional source of gaseous H<sub>2</sub>SO<sub>4</sub> in laboratory experiments to known OH radical mechanism with both driven by ozone UV photolysis.

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