**Atmospheric
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Mechanism of UV-light induced SO$_2$ oxidation to H$_2$SO$_4$

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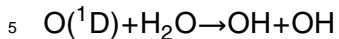| Abstract | Introduction |
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Abstract

The electron-excited chemistry of sulfur dioxide oxidation induced by UV irradiation of air with trace O$_3$ and SO$_2$ is considered. The importance of this mechanism is evaluated based on recent laboratory experiments on SO$_2$ oxidation in a laminar tube with air induced by UV irradiation. Results show that under respective conditions the route of SO$_2$ oxidation involving electron excited oxygen molecules may be as efficient as a known OH-radical mechanism. Hence, an influence of UV irradiation on SO$_2$ oxidation chemistry, if confirmed, may provide an additional external source affecting the oxidation and aerosol formation processes in atmosphere.

1 Introduction

The sulfur presents in atmosphere mostly as sulfur dioxide. SO$_2$ is an important air pollutant and a source of gaseous sulfuric acid H$_2$SO$_4$ (GSA), one of the main aerosol precursor gases (Seinfeld and Pandis, 1998). Understanding of subsequent oxidation reactions of SO$_2$ 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$_3$ and SO$_2$ 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 in somewhere 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$_2$ molecules with hydroxyl radicals OH:
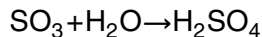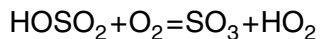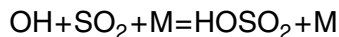
$$O_3 + h\nu \rightarrow O(^1D) + O_2(^1\Delta_g) \tag{R1}$$

$$O(^1D) + M \rightarrow O(^3P) + M$$

$$O(^1D) + H_2O \rightarrow OH + OH$$

$$OH + furan \text{ or } CO = products$$

$$OH + SO_2 + M = HOSO_2 + M$$

$$HOSO_2 + O_2 = SO_3 + HO_2$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$
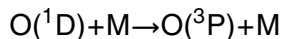
The given reaction scheme was applied in (Berndt et al., 2006, 2008) to deduce the time behavior of GSA along the FR. We have repeated these calculations with even more detailed reaction scheme and using different compilations of rate coefficients to see a sensitivity of the resulting GSA concentration. The results obtained totally were the same as in (Berndt et al., 2006), i.e. the formed GSA concentration is of about few 10^7 cm^{-3}.

However, one result seems to be interesting, that is a formation of a sufficient amount of electronically excited oxygen molecules O$_2$($^1\Delta_g$) (up to about 5×10^9 cm^{-3} 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$_3$ and SO$_2$.
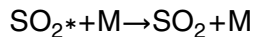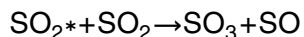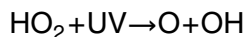
2 UV light induced "electron-excited" chemistry

The electron-excited molecules and atoms may essentially affect the kinetics of chemical reactions (Fridman and Kennedy, 2004). In air with SO_2 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 asses the possible involvement of electron-excited species in SO_2 oxidation.

2.1 Electron-excited SO_2 formation

At first, one might suggest an additional formation of OH radicals either by UV-light induced dissociation of HO_2 and H_2O_2 molecules or the formation of excited SO_2^*

$$H_2O_2 + UV \rightarrow OH + OH \tag{R2}$$

$$HO_2 + UV \rightarrow O + OH$$

$$SO_2 + UV \rightarrow SO_2^*$$

$$SO_2* + SO_2 \rightarrow SO_3 + SO$$

$$SO_2* + M \rightarrow SO_2 + M$$

Here, SO_2^* indicates SO_2 in ^1B or ^3B electronic states. Self-quenching of excited SO_2^* is known to produce SO_3, since $\Delta H_{rxn} = -210 (-112)\,kJ\,mol$ for ^1B (^3B) states (James et al., 1974; Marvin and Reiss, 1978; Sander and Seinfeld, 1976). However, the simulation with these new reactions added to mechanism (1) 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_2^* 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^2: $O_3 - 1.5 \times 10^{-17}$, $HO_2 - 2 \times 10^{-19}$, $H_2O_2 - 7 \times 10^{-20}$,

and $SO_2 - 1.5 \times 10^{-19}$ (Manatt and Lane, 1993; NIST, 2007). Moreover, the excited $SO_2(^1B)$ relaxes very rapidly in collisions with N_2 (with the rate of about $1 \times 10^{10}\,s^{-1}$ at atmospheric conditions) to ground electronic state and partially (no more than 10%) to $SO_2(^3B)$ state and then to ground state with the rate of about $6 \times 10^6\,s^{-1}$ (Marvin and Reiss, 1978; Christensen et al., 1994).

Also, it is energetically possible the chemical quenching of excited $SO_2(^3B)$ by O_2 to produce SO_3, i.e.

$$SO_2(^3B) + O_2(^3\Sigma_g) \rightarrow SO_4^\# \rightarrow SO_3 + O(^3P) \qquad (R3)$$

where $SO_4^\#$ presents a transition state, and for this reaction $\Delta H_{rxn} = -65\,kJ\,mol$. 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

$$SO_2(^3B) + O_2(^3\Sigma_g) \rightarrow SO_4^\# \rightarrow SO_3 + O(^1D) \qquad (R4)$$

is endothermic ($\Delta H_{rxn} = +25.1\,kJ\,mol$) and has a negligible rate coefficient. 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_3 switched off. This eliminates as important any mechanisms without O_3 involvement.

2.2 Metastable electron-excited oxygen $O_2\,(^1\Delta_g, \upsilon)$ formation

Another possibility is the reaction of SO_2 with electron-vibrationally excited oxygen $O_2(^1\Delta_g, \upsilon > 0)$, where υ is a vibrational quantum number

$$O_3 + UV \rightarrow O(^1D) + O_2(^1\Delta_g, \upsilon) \qquad (R5)$$

$$SO_2 + O_2(^1\Delta_g, \upsilon) \rightarrow SO_3 + O \qquad (R6)$$

In Hartley absorption band of ozone (the peak at 254 nm) more than 50% of oxygen molecules $O_2(^1\Delta_g, \upsilon)$ are forming in states with $\upsilon \geq 1$ (Slanger and Copeland, 2003).

The energy defect of Reaction (R5) can be estimated as $\Delta E = E_{UV} - EO_3 - EO^* - E_0$. Here E_{UV} is the photon energy, EO_3 is the dissociation energy of the ozone molecule (1.05 eV), EO^* is the energy of excitation of the $O(^1D)$ atom from the ground state (1.97 eV), and $E_0 = 0.98$ eV is the energy of oxygen electron-excited state $O_2(^1\Delta_g, \upsilon=0)$ (0.98 eV) (Yankovsky et al., 2007). At $\lambda=254$ nm (4.9 eV), the value of ΔE is 0.90 eV and hence excited molecules $O_2(^1\Delta_g, \upsilon)$ with vibration quantum numbers up to $\upsilon=5$ can be formed (the mean energy of vibrational quanta is of about $E_{vib}=0.2$ eV). The reaction enthalpy of Reaction (R6) may be estimated as $\Delta H_{rxn} = \Delta H_f(SO_3) + \Delta H_f(O) - \Delta H_f(SO_2) - \Delta H_f(O_2(^1\Delta_g)) - \upsilon \times \Delta E_{vib} = 0.58 - \upsilon \times 0.2$ (in eV) (NIST, 2007). Hence, Reaction (R6) is exothermic for only $\upsilon \geq 3$. The quantum yield F of $O_2(^1\Delta_g, \upsilon=3-5)$ 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 reduced due to electron-relaxation to lower states and losses on walls. Hence, the steady-state concentration of excited oxygen can result from

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

Here $P=[O_3] \times Q_{UV}$ presents the production rate of $O_2(^1\Delta_g)$ in Reaction (R5) and R denotes its total removal rate. The parameter $Q_{UV}=0.031$ 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 $R=R_{REL}+R_{WL}$. Here, the R_{REL} takes into account the deexcitation of $O_2(^1\Delta_g)$ to ground state and R_{WL} presents the effective rate of $O_2(^1\Delta_g)$ wall losses (which is much smaller, $R_{WL}<0.03$ 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 $O_2(^1\Delta_g, \upsilon=0)$ by both N_2 and O_2 is significant. At room temperature, $k_{ET}(N_2)=1\times10^{-20}$ cm^3/s and $k_{ET}(O_2)=1.7\times10^{-18}$ cm^3 s and hence in N_2-O_2 (1%) mixture the removal rate R=4.5 s^{-1}. At $[O_3]=6\times10^{11}$ cm^{-3},

the $O_2(^1\Delta_g)$ production rate is $P=1.9\times10^{10}\,cm^{-3}\,s^{-1}$ and therefore the steady concentration of $O_2(^1\Delta_g)$ should be about $4\times10^9\,cm^{-3}$ (the simulated concentration is close to $5\times10^9\,cm^{-3}$). The deexcitation of electronic-vibrationally excited $O_2(^1\Delta_g, \upsilon\geq1)$ at collisions with N_2 is small in comparison with that of O_2. The vibrational deactivation of $O_2(^1\Delta_g, \upsilon\geq3)$ is defined mainly by collisions with O_2 and its rate is estimated to be about $R_{REL}(\upsilon\geq3)=10^7-2\times10^8\,s^{-1}$ in dependence on O_2 concentration in air. Therefore, the low concentration limit of $[O_2(^1\Delta_g, \upsilon\geq3)]$ can be estimated assuming the Boltzman's distribution over vibration levels in electronic state $a^1\Delta_g$ with $\Delta E_{vib}=0.2\,eV$. The upper concentration limit (non-equilibrium case) can be estimated from the ratio $F\times[O_3]\times Q_{UV}/R_{REL}(\upsilon\geq3)$. In result, we have $0.1\leq[O_2(^1\Delta_g, \upsilon\geq3)]<10-200\,cm^{-3}$.

Reaction (R6), which involve the low vibration energy levels of $O_2(^1\Delta_g, \upsilon=0-2)$, is endothermic. Its rate is about of $2.2\times10^{-16}\,cm^3/s^{-1}$ (NIST, 2007). The rate of Reaction (R6) with $O_2(^1\Delta_g, \upsilon\geq3)$ involved is unknown but it should be smaller than $3\times10^{-10}\,cm^3/s$ (Fridman and Kennedy, 2004). Hence, the production rate of SO_3, Q_{SO3}, via the mechanism Reactions (R5–R6) at $[SO_2]=5\times10^{10}\,cm^{-3}$ (the upper range of SO_2 concentrations in Berndt et al., 2006) is estimated to be about $Q_{SO3}=3\times10^3-6\times10^4\,cm^{-3}/s^{-1}$. The SO_3 wall losses may be estimated as $R_{WL}(SO_3)=0.02\,s^{-1}$ (using the diffusion coefficient $D_g=0.1\,cm^2/s$). Hence, the formed via Reactions (R5–R6) steady-state GSA concentration should not be greater than $3\times10^6\,cm^{-3}$. Thus, the performed analysis shows that the role of $O_2(^1\Delta_g, \upsilon)$ molecules in production of GSA precursors in air with trace O_3 and SO_2 under UV irradiation is likely small in comparison with the neutral chemistry oxidation route involving OH radicals (where GSA is about of few $1\times10^7\,cm^{-3}$). 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 ($b^1\Sigma_g^+$, υ) formation

Most of electron-excited $O(^1D)$ atoms are removing by electronic quenching in collisions with air molecules with the total rate of about 2.9×10^{-11} cm^3 s^{-1} (Sander et al., 2006). The remaining atoms rapidly transfer their energy to O_2, resulting in electron-vibration excited molecules $O_2(b^1\Sigma_g^+$, $\upsilon=0$–2). The total quantum yield of $O_2(b^1\Sigma_g^+$, υ) in collisions of O_2 with $O(^1D)$ was measured to be equal to 0.95 with the rate of about 4.0×10^{-11} cm^3 s^{-1} at room temperature (Yankovsky and Manuilova, 2006). The most effective atmospheric quencher of $O_2(b^1\Sigma_g^+$, $\upsilon=0$) is N_2, while removal by O_2 is about 50 times slower. For de-excitation of $O_2(b^1\Sigma_g^+$, $\upsilon=0$) by N_2 the upper limit of the rate constant is measured to be about 2.1×10^{-15} cm^3 s^{-1} (Sander et al., 2006). In contrast, the vibration-translational relaxation of $O_2(b^1\Sigma_g^+$, $\upsilon=1$, 2) to $O_2(b^1\Sigma_g^+$, $\upsilon=0$) by O_2 is much more rapid with the room-temperature rate constant for $\upsilon=1$ of about 1.5×10^{-11} cm^3 s^{-1} (Kalogerakis et al., 2002). In FR with air and O_3 under UV irradiation the steady-state concentrations of excited $O(^1D)$ and $O_2(b^1\Sigma_g^+$, υ) are rapidly forming. The production and removal processes of $O_2(b^1\Sigma_g^+$, υ) proceed with the rates of about $P=2 \times 10^8 \times [O(^1D)]$ cm^{-3} s^{-1} and $R=5 \times 10^4$ s^{-1} respectively, where $[O(^1D)]$ denotes the concentration of $O(^1D)$ atoms in cm^3. For conditions from (Berndt et al., 2006) these concentrations are estimated to be about $[O(^1D)]=15$ and $[O_2(b^1\Sigma_g^+$, $\upsilon)]=6 \times 10^4$ per cm^3.

The reaction of $O_2(b^1\Sigma_g^+$, υ) with SO_2 leading to formation of SO_3 and $O(^3P)$ is exothermic for all υ. Hence, it is interesting to consider the following mechanism of UV induced SO_2 oxidation
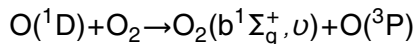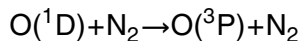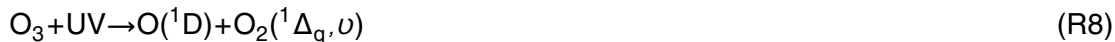
$$O_3 + UV \rightarrow O(^1D) + O_2(^1\Delta_g, \upsilon) \tag{R8}$$

$$O(^1D) + N_2 \rightarrow O(^3P) + N_2$$

$$O(^1D) + O_2 \rightarrow O_2(b^1\Sigma_g^+, \upsilon) + O(^3P)$$

$$O_2(b^1\Sigma_g^+,\upsilon=1,2)+O_2\rightarrow O_2(b^1\Sigma_g^+,\upsilon=0)+O_2$$

$$O_2(b^1\Sigma_g^+,\upsilon=0)+N_2\rightarrow O_2(^1\Delta_g,\upsilon<2)+N_2$$

$$SO_2+O_2(b^1\Sigma_g^+,\upsilon)\rightarrow SO_3+O, \Delta H_{rxn}=-45.3 kJmol(\upsilon=2)$$

$$SO_2+O_2(b^1\Sigma_g^+,\upsilon)+M\rightarrow SO_4+M, \Delta H_{rxn}\leq-105.7 kJmol(\upsilon\geq0)$$
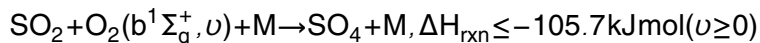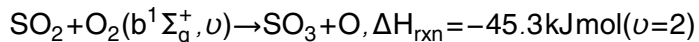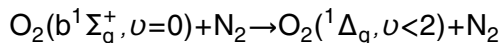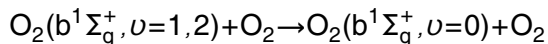
Two reactions, involving SO$_2$, are energetically favourable. Assuming the rate coefficient for that to be nearly 3×10^{-10} cm^3 s, the GSA production rate via the mechanism Reaction (R8) is estimated to be about 6×10^5 cm^{-3} s^{-1} at [SO$_2$]=(1–5)$\times10^{10}$ cm^{-3}. With accounting for diffusion losses on walls, the steady-state concentration of GSA is about (1–5)$\times10^7$ cm^{-3}. This value is of the same order as was deduced recently in laboratory experiments (Berndt et al., 2005, 2006) for OH driven SO$_2$ oxidation route. The results of evaluated models in application to these experiments are summarized in Table 1. However, the uncertainty of the above estimations seems to be large due to unknown rate coefficients for some reactions involving SO$_2$. For example, the non-reactive quenching of O$_2$(b$^1\Sigma_g^+$, υ) by SO$_2$ is also probable.

However, the performed analysis shows readily the potential for the enhanced SO$_2$ oxidation in air with O$_3$ under UV irradiation via the chemistry involving electron excited oxygen molecules. The most promising is likely the reaction of SO$_2$ with O$_2$(b$^1\Sigma_g^+$, υ).

3 Conclusions

An analysis of different mechanisms of SO$_2$ oxidation have indicated the potential importance of chemical reactions involving electron excited oxygen molecules O$_2$($^1\Delta_g$) and O$_2$(b$^1\Sigma_g^+$). ' This oxidation route could provide an additional source of gaseous H$_2$SO$_4$ in laboratory experiments with OH radical production driven by ozone UV photolysis. If valid, this may imply a potential for some a link of H$_2$SO$_4$ variability in atmosphere due to natural solar irradiance variance.

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Interactive Discussion

Table 1. The estimated production of GSA in air with trace O$_3$ and SO$_2$ under UV irradiation in experiments (Berndt et al., 2005, 2006) due to different proposed chemical mechanisms.

Chemical mechanism	Production of GSA (cm^{-3})
Base case: SO$_2$ oxidation driven by OH (1)	$(1–5)\times10^7$ (Berndt et al., 2005, 2006)
Electron excited SO$_2$ chemistry (2)	far less
Electron excited oxygen chemistry (6) and (8)	3×10^6 and $(1–5)\times10^7$ (this work)