# Contrary Role of H$_2$O and O$_2$ in the Kinetics of Heterogeneous Photochemical Reactions of SO$_2$ on TiO$_2$

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Ⓢ *Supporting Information*

ABSTRACT: Although the heterogeneous conversion of SO$_2$ on TiO$_2$ has been considered a potential source of sulfate in the troposphere, little is known about the kinetics of SO$_2$ uptake on TiO$_2$ under ambient conditions. In this study, heterogeneous reactions of SO$_2$ on a TiO$_2$ surface at 298 K were investigated by a coated-wall flow tube reactor and in situ diffuse reflectance Fourier transformed infrared spectroscopy (DRIFTS). The effect of UV irradiation, relative humidity (RH), and O$_2$ on the uptake coefficients and adsorption amount of SO$_2$ have been analyzed comprehensively. UV irradiation exhibits a slight effect on the initial uptake coefficient (γ_{BET}), which increases from 1.23×10^{-6} to 1.48×10^{-6} in air conditions and 5.89×10^{-7} to 6.42×10^{-7} in a N$_2$ stream under dry conditions. Surface water exhibits a competition effect on the adsorption of SO$_2$ on TiO$_2$. An increase in RH (in the range of 0−75%) led to a decrease in the γ_{BET} and adsorption amount of SO$_2$ both in the dark and the light reaction. In contrast, oxygen plays an important role in the uptake of SO$_2$. Both the uptake coefficients and adsorption amount of SO$_2$ on TiO$_2$ decreased in the N$_2$ stream compared to those in air conditions. Only sulfite was formed during the adsorption of SO$_2$ in dark and dry conditions. The presence of UV irradiation was found to promote the conversion of SO$_2$ to sulfate and the adsorption amount of sulfur species on the TiO$_2$ surface. These results suggest that heterogeneous reaction on TiO$_2$ as a sink for SO$_2$ is not important in the atmosphere.
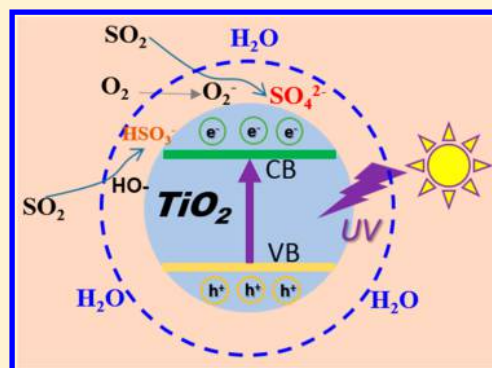
INTRODUCTION

Sulfate aerosol in the atmosphere has a significant impact on climate change. It exhibits a cooling effect on earth's energy balance by reflecting radiation and acting as cloud condensation nuclei (CCN).[1−4] Besides, sulfate is a predominant inorganic species in fine atmospheric particles, which causes severe negative effects on regional air quality and the visibility.[5−7] The sources of sulfate aerosol in the atmosphere include the primary direct emissions and secondary formation, which mainly comes from the oxidation of SO$_2$.[8,9] The conversion of SO$_2$ to sulfate in the atmosphere usually occurs through several well-known pathways, including gas-phase oxidation by OH or a Criegee intermediate radical to sulfuric acid followed by condensation into the particulate phase or neutralization by NH$_3$ or amine,[10−13] aqueous-phase oxidation by H$_2$O$_2$ or transition metal ions in cloud and fog droplets,[14,15] and various heterogeneous reactions on the surfaces of aerosol particles.[16,17] In the past decades, heterogeneous reactions of SO$_2$ on atmospheric particles have attracted a lot of attention. However, the formation processes of sulfate in the atmosphere are still not completely understood.

Mineral dust contributes a significant mass fraction of atmospheric aerosols and plays an important role in changing the chemical compositions by providing reactive surfaces to promote the conversion of trace gases to secondary aerosol.[18−21] Field observation found that mineral dust is always associated with sulfate.[22,23] Consequently, a lot of laboratory work has focused on the heterogeneous reactions of SO$_2$ on mineral dust. It was recognized that sulfite (SO$_3^{2-}$) and/or bisulfite (HSO$_3^{2-}$) species were the main surface products for heterogeneous reaction of SO$_2$ on mineral dust, while sulfate was hardly formed on the surface of mineral dust other than Fe$_2$O$_3$ and MgO.[24−27] Coexisting oxidants like O$_3$, NO$_2$, or H$_2$O$_2$ can promote the conversion of SO$_2$ or sulfite to sulfate on mineral dust.[25,26,28−31]

Most previous laboratory studies about heterogeneous reactions of SO$_2$ on mineral dust were conducted under dark conditions. Recently, it was recognized that solar light could contribute to the heterogeneous conversion of SO$_2$ on dust particles in the atmosphere.[32−35] For example, Dupart et al.[33] found that mineral dust could promote the formation of gaseous OH radicals upon UV irradiation, which further

initiate the conversion of SO_2 to H_2SO_4 in the vicinity of dust particles. The uptake coefficients of SO_2 corresponding to sulfate production on the Gobi Desert Dust (GDD) and Arizona Test Dust (ATD) particles determined in a chamber study were significantly increased in the presence of UV light compared to the results in dark conditions.[35,36] Titanium dioxide (TiO_2) has been considered the most important photocatalyst in mineral dust due to its high photocatalytic efficiency despite its relatively low abundance.[34,37,38] On the surface of TiO_2, water can be converted to highly reactive hydroxyl radicals in the presence of UV light at photoinduced valence band holes, which then react with SO_2 to form sulfate.[39−41] It was demonstrated that UV irradiation could significantly promote the conversion of SO_2 to sulfate on mineral dust or TiO_2.

Besides irradiation, surface-adsorbed water also plays important roles in the reactions on mineral dust surfaces.[42] Water was considered the source of reactive hydroxyl radicals in photooxidation of SO_2 on mineral dust;[33] however, the effect of water on the photochemical conversion of SO_2 is still controversial. For example, smog chamber simulation showed that the kinetic uptake coefficient of SO_2 on GDD and ATD particles greatly increased with increasing relative humidity (RH) under both light and dark conditions.[35,36] For TiO_2, Shang et al. found the promotion effect of surface water on the photooxidation of SO_2.[43] However, this was inconsistent with the X-ray photoelectron spectroscopy (XPS) results of Baltrusaitis et al., in which water was found to block the sites for SO_2 adsorption due to a competition between SO_2 and H_2O adsorption.[40] Thus, the role of water on the heterogeneous photochemical reaction of SO_2 on TiO_2 needs further study.

Moreover, the kinetics of heterogeneous reactions of SO_2 on TiO_2 is not well-known. Usher et al.[25] used a Knudsen cell to study the uptake of SO_2 on mineral dust and determined the initial uptake coefficient (γ_{BET}) of SO_2 on TiO_2 to be $1.0 \pm 0.2 \times 10^{-4}$. Nevertheless, the dry requirement in Knudsen cell experiments represents a serious limitation in studying atmospheric heterogeneous reactions. In another study, Shang et al.[43] measured the reactive uptake coefficient of SO_2 on TiO_2 based on diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) results. It should be noted that the concentration of SO_2 used by Shang et al. was higher than 50 ppm, which was quite beyond the ambient concentration of SO_2. Therefore, the kinetic behavior of the photochemical reaction of SO_2 on TiO_2 under ambient concentration should be further investigated. The objectives of this study are to investigate the kinetics of the heterogeneous reaction of SO_2 on TiO_2 using a coated-wall flow tube and in situ DRIFTS. It mainly focuses on the role of UV irradiation, RH, and oxygen on the heterogeneous reaction of SO_2 on TiO_2. The results could help understand the photochemistry of mineral dust and sulfate formation and resolve the discrepancy in previous studies.

■ EXPERIMENTAL SECTION

Coated-Wall Flow Tube Reactor. The uptake of SO_2 on TiO_2 was studied in a horizontal cylindrical coated-wall flow tube reactor, which has been described in detail elsewhere.[44−46] The experiments were performed at ambient pressure and maintained at 298 K by circulating a water bath through the outer jacket of the flow tube reactor. The tube with the deposited TiO_2 sample was introduced into the main

reactor along its axis. Synthetic air or N_2 was used as the carrier gas, which was introduced into the flow tube reactor at a total flow rate of 1400 mL/min, ensuring a laminar regime at ambient pressure. SO_2 was introduced into the gas flow by a movable injector with a 0.3 cm radius. The SO_2 concentration was 210 ± 5 ppb and recorded by a SO_2 analyzer (THERMO 43i). No uptake of SO_2 was observed when the reactant gas was introduced into the blank quartz tube. The reactor was surrounded by six UV lamps (365 nm, T5, UVA, 8 W) with a broad UV emission spectrum between 330 and 420 nm. The UV lamps were installed into a stainless light-tight box covering the main reactor tube. The irradiance intensity in the reactor could be regulated by switching off some lamps, and the intensity was measured by a fiber optic spectrometer (BLUE-Wave-UVNb). When all lamps switched on, the irradiance intensity in the reactor was 1.27 W/m^2 at 370 nm.

Uptake Coefficient. The kinetic behavior can be well described by assuming a pseudo-first-order reaction with respect to the gas-phase SO_2 concentration. The first-order rate constant (k) is related to the geometric uptake coefficient (γ_{geo}) using eq 1[44]

$$\frac{d}{dt} \ln \frac{C_0}{C_t} = k = \frac{\gamma \langle c \rangle}{2r_{tube}} \tag{1}$$

where r_{tube}, t, and $\langle c \rangle$ are the flow tube radius, the exposure time, and the SO_2 average molecular velocity, respectively. C_0 and C_i are the SO_2 concentrations at $t = 0$ and i, respectively.

If the loss of SO_2 at the TiO_2 surface is too rapid to be recovered with the SO_2 supply, a radial concentration gradient in the gas phase will be formed, which may cause diffusion limitations. Therefore, a correction for diffusion in the gas phase should be taken into account. Here, the Cooney−Kim−Davis (CKD) method was used to correct uptake coefficients,[47,48] which has been widely described in previous articles.[38,49,50] Because diffusion of SO_2 into underlying layers of the TiO_2 particle can take place, γ is dependent on sample mass and exhibits a linear increase in range of 0.5−8 mg. Therefore, the uptake coefficient normalized to the Brunauer−Emmmett−Teller (BET) surface area (γ_{BET}) was calculated using eq 2

$$\gamma_{BET} = \frac{S_{geo} \times \gamma_{geo}}{S_{BET} \times m_{TiO_2}} \tag{2}$$

where S_{geo} is the geometric area of the flow tube reactor, S_{BET} is the BET surface area of TiO_2, and m_{TiO_2} is the TiO_2 mass.

The uptake capacity of the TiO_2 surface to SO_2 was quantified by the consumption of SO_2, which was calculated by eqs 3 and 4

$$A_s = \int_{t_0}^{t_i} (C_i^{SO_2} - C_0^{SO_2}) \, dt \tag{3}$$

$$SO_2/sample = \frac{A_s \times v}{V_m} \times \frac{M}{m} \tag{4}$$

where A_s is the integrated area of the consumption of SO_2 (the uptake curves of SO_2 on the TiO_2 surface), $C_i^{SO_2}$ and $C_0^{SO_2}$ represent SO_2 concentrations (ppbv) under different times, and t_0 and t_i (min) are the times when the SO_2 exposure to TiO_2 particles starts and ongoing, respectively. $SO_{2/sample}$ (mg/g) is the uptake capacity of SO_2 on the TiO_2 surface per gram. v is the rate of gas flow, which is 1400 mL/min in this

experiment. V_m is the molar volume of gas, which is 24.5 L/mol at 298 K. M is the molar mass of SO_2, which is 64 g/mol. m is the mass of the TiO_2 particles.

In Situ DRIFTS. The heterogeneous reactions of SO_2 on TiO_2 particles were measured by in situ DRIFTS (NEXUS 6700, Thermo Nicolet Instrument Corporation), equipped with an in situ diffuse reflection chamber and a high-sensitivity mercury cadmium telluride (MCT) detector cooled by liquid N_2. The TiO_2 sample (about 15 mg) was finely ground and placed into a ceramic crucible in the in situ chamber. The total flow rate was 100 mL/min in all flow systems. The reference spectrum was measured after the pretreated sample was cooled to 298 K in a synthesized air or N_2 stream. The infrared spectra were collected and analyzed using a data acquisition computer with OMNIC 6.0 software (Nicolet Corp.). All spectra reported here were recorded at a resolution of 4 cm^{-1} for 100 scans in the spectral range of 4000–600 cm^{-1}. The spectra are presented in Kubelka–Munk (K–M) scale, which can reduce or eliminate the mirror effect and give a better linear relation with concentration.[51] Before DRIFTS measurement, the TiO_2 sample was pretreated in an in situ infrared cell by heating in 100 mL/min of carrier gas at 373 K for 2 h. The UV light was introduced into the DRIFTS reaction cell via a UV fiber (Φ = 5 mm). The light acquired with the mercury lamp (λ > 200 nm, CHF-XM-500 W, the Trusttech. Co. Ltd., Beijing) was used as the light resource. The spectrum of the light in the DRIFTS experiments was measured with a fiber optic spectrometer (BLUE-Wave-UVNb, Stellar Net Inc., USA).

Materials. The TiO_2 (P25:80% anatase, 20% rutile, Degussa) particles used in this study were purchased from commercial sources. A total mass of 1.0 g of TiO_2 powder was dispersed in 20.0 mL of water. This suspension was dripped uniformly into a quartz tube (20.0 cm length, 1.1 cm i.d.) and dried overnight in an oven at 373 K. The resulting homogeneous film covered the entire inner area of the tube. The nitrogen adsorption–desorption isotherms were obtained at 77 K over the whole range of relative pressures using Micromeritics ASAP 2000 automatic equipment. Specific areas were computed from these isotherms by applying the BET method. The BET area of the sample was 54.6 m^2/g. SO_2 (50.4 ppmv + N_2, Beijing Huayuan), O_2 (99.999%, Beijing Huayuan), and N_2 (99.999%, Beijing Huayuan) were used as received. The RH was controlled by regulating the ratio of dry and wet stream flow, which was recorded during the whole experiment by a hygrometer (Omega RH-USB).

■ RESULTS

The effect of UV light and O_2 on the uptake of SO_2 on TiO_2 was first investigated. Figure 1 shows the typical uptake curves of SO_2 on TiO_2 under dark and irradiation conditions in air and a N_2 stream. When the TiO_2 sample was exposed to SO_2, a decrease in SO_2 concentration was observed in all cases. However, the recovery of SO_2 concentration varied with different reaction conditions. In dark reactions, the concentration of SO_2 was close to its initial level after about 70 min in air stream and 30 min in the N_2 stream, respectively. This suggests that the presence of O_2 could promote the adsorption of SO_2 on TiO_2 under dark conditions. Moreover, when the injector was withdrawn to its original position, an increase in SO_2 concentration was observed in the reactions in both air and the N_2 stream. This was due to desorption of a fraction of SO_2 adsorbed. This means that, besides the reactive uptake,
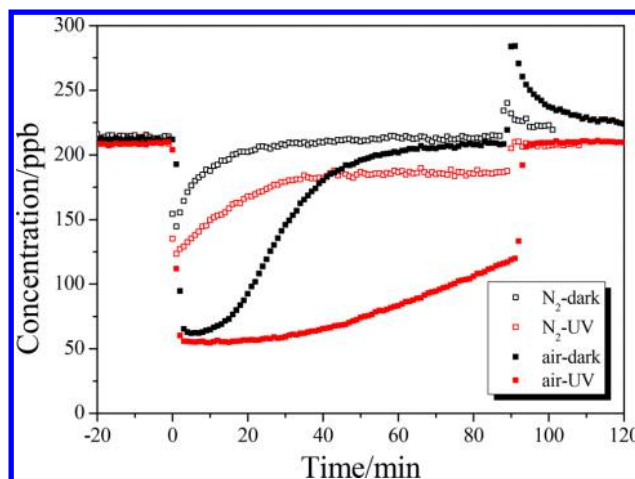
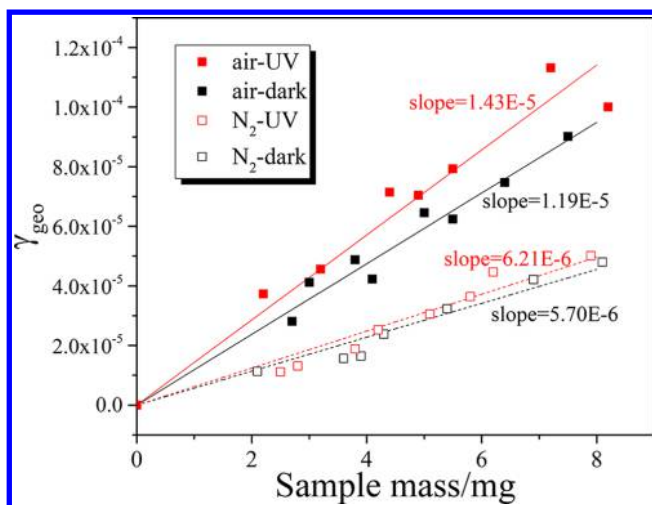**Figure 1.** Uptake curves of SO_2 on the TiO_2 surface under various conditions: dark reaction in N_2 (black empty), UV reaction in N_2 (red empty), dark reaction in air (black solid), and UV reaction in air (red solid). T = 298 K, RH = 0.5%, sample mass range: 4.85–5.05 mg.

the physical adsorption process also contributed to the uptake of SO_2 on the surface in the dark reactions.

For the uptake process upon UV irradiation, a sharp decrease in SO_2 concentration was also observed, which was similar to that in the dark reaction. However, the SO_2 concentration did not reach the initial level in 90 min, which recovered slowly in air and reached a plateau in N_2. In addition, when the injector was removed outside of the reaction region, no desorption was observed after the concentration of SO_2 returned to the initial value. These results indicated that the reactive uptake was the main contributor to the uptake of SO_2 on the sample under irradiation conditions.

In order to determine whether the underlying layers of TiO_2 were involved in the interaction with SO_2 molecules, the uptake coefficients of SO_2 were measured as a function of the mass of the TiO_2 sample under dark conditions or UV irradiation. The dependence of the initial geometric uptake coefficient (γ_{geo}) on the TiO_2 sample mass at dry conditions (RH < 5%) is shown in Figure 2. It shows that γ_{geo} was linearly dependent on the sample mass due to the resulting multilayer thickness. Then, the γ_{geo} was corrected with the BET surface area according to eq 2, denoted as γ_{BET}. The slopes of the uptake coefficient of SO_2 in the dark were 1.19 × 10^{-5} (air) and 5.70 × 10^{-6} (N_2), which increased weakly up to 1.43 × 10^{-5} (air) and 6.21 × 10^{-6} (N_2) in the presence of UV light. Consequently, the γ_{BET} showed a slight increase from 1.23 × 10^{-6} to 1.48 × 10^{-6} in air conditions and 5.89 × 10^{-7} to 6.42 × 10^{-7} in the N_2 stream, indicating a weak promotion effect of UV irradiation on the uptake coefficients of SO_2 on TiO_2.

It should be noted that the concentration of SO_2 reached the original level after a long uptake time under dark conditions, while the concentration of SO_2 reached a plateau in UV reaction conditions in the N_2 reaction. For the photochemical reaction in the air stream, the concentration of SO_2 reached a plateau after about 10 h (Figure S1). This indicated that steady-state uptake occurred in the photochemical reaction and a catalytic process could be involved. As for the adsorption of SO_2, adsorption sites are difficult to regenerate because the surface product, sulfate, would be accumulated on the surface and cause the surface to deactivate gradually. Dupart et al. found that mineral dust photochemistry could induce the

Figure 2. Initial uptake coefficients of SO_2 on a TiO_2 surface as a function of sample mass under various conditions: dark reaction in N_2 (black empty), UV reaction in N_2 (red empty), dark reaction in air (black solid), and UV reaction in air (red solid). $T = 298$ K, RH = 0.5%.

conversion of SO_2 to SO_3 or H_2SO_4 in the gas phase.[33] Thus, we proposed that the steady-state uptake in the present study could be due to the conversion of SO_2 to SO_3 or H_2SO_4 in the gas phase.

The influence of the RH on the γ_{BET}(initial) of SO_2 on TiO_2 at various RHs was compared in Figure 3. The γ_{BET}(initial) of
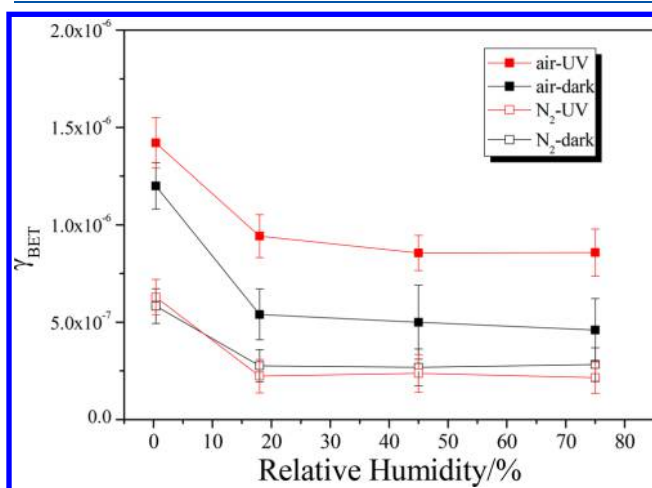
**Figure 3.** Γ_{BET}(initial) of SO_2 on a TiO_2 surface as a function of RH at 298 K. $[SO_2]$ = 210 ± 5 ppbv; sample mass = 5.05 ± 0.3 mg.

SO_2 with or without UV light decreased obviously when the RH increased from 0.5 to 20%, suggesting a block effect of H_2O on SO_2 adsorption. However, when the RH was larger than 20%, the γ_{BET}(initial) exhibited little change as the RH increased. This may be due to the block effect of water on the SO_2 reaction decreasing after the surface water monolayer formed because the RH corresponding to monolayer adsorption of water on TiO_2 particles was close to ~20%.[52] This suggests that the initial adsorption step of SO_2 on TiO_2 is weakly dependent on the RH at an elevated RH. Nevertheless, it should be pointed out that the RH impact on long-term uptakes is different from the initial values, as seen in Figure S2

and S3. Thus, surface water has an inhibition effect on the conversion of SO_2 on TiO_2.

Figure 4 shows the change of uptake capacity of TiO_2 to SO_2 as a function of time at RHs between 0.5 and 75%. UV irradiation exhibited a significant promoting effect on the uptake capacity under both dry and wet conditions. This is not unexpected because UV irradiation could promote the conversion of SO_2 and sulfite to sulfate on the TiO_2 surface. The absence of O_2 also led to the decrease of SO_2 adsorption amount, which confirmed the contribution of O_2 to the reaction of SO_2. Meanwhile, increasing humidity reduced the uptake capacity of TiO_2 to SO_2 under both light and dark conditions. The negative dependence of the uptake capacity on RH observed in this experiment could be attributed to competition between water and SO_2 molecules for the active sites on the surface, which counteracted the role of water as a source of OH radicals. In a previous study, Baltrusaitis et al.[40] used XPS to study the surface products in the adsorption of SO_2 on TiO_2 under different conditions. They found that sulfate was formed and the total amount of adsorbed sulfur decreased by a factor of 2 when 11.5 Torr of water vapor was present under dark conditions. This result suggests that there is competition between SO_2 and H_2O adsorption because molecularly adsorbed water can block sites for SO_2 adsorption.[24,40] This block effect of water was also observed in the photo-oxidation of SO_2 on TiO_2.[40] In addition, Nanayakkara et al. proposed that adsorbed SO_2 or sulfite species could react with water to form a surface complex ($SO_2 \cdot H_2O$) in the presence of water vapor.[41] In the present study, the decrease in the uptake capacity of TiO_2 to SO_2 with increasing RH suggested that this surface complex may not be involved in the photochemical conversion to sulfate upon irradiation.

In situ DRIFTS experiments were also conducted to investigate the heterogeneous reaction of SO_2 on TiO_2 with SO_2. The TiO_2 sample was exposed to 500 ppb SO_2 for 90 min in the absence and presence of UV light under various RH conditions, followed by purging with carrier gas (synthetic air or N_2) for 2 h to remove gaseous and weakly adsorbed surface species. The spectra are shown in Figure 5. When TiO_2 was exposed to SO_2 under dark conditions, one weak peak at around 1065 cm^{-1} was observed after flushing with carrier gas. This peak could be assigned to the stretching mode of adsorbed sulfite or bisulfite on the surface of oxides.[41,43] This is also in good agreement with the XPS experimental results of Baltrusaitis et al.[40] It is interesting to note that two negative peaks at 3695 and 3630 cm^{-1} were observed, which were attributed to the vibration of hydroxyl on Ti atoms.[41,53] This implies that surface OH groups were involved in the reaction of SO_2 on TiO_2 in dark reactions under dry conditions.

When the heterogeneous reaction of SO_2 with TiO_2 happened in the presence of UV irradiation, several new peaks at 1320, 1288, and 1269 cm^{-1} increased in intensity, which were attributed to sulfate.[29] This indicates that the UV irradiation can greatly promote the conversion of SO_2 to sulfate on TiO_2. In the absence of O_2, these peaks due to sulfate were also observed but with smaller intensities. This suggests that gas-phase O_2 is not necessary but can also enhance the photochemical formation of sulfate. Meanwhile, several peaks at 3185, 3310, and 1650 cm^{-1} were observed in light reactions and could be attributed to surface water. Surface water may be formed in the photochemical reaction or
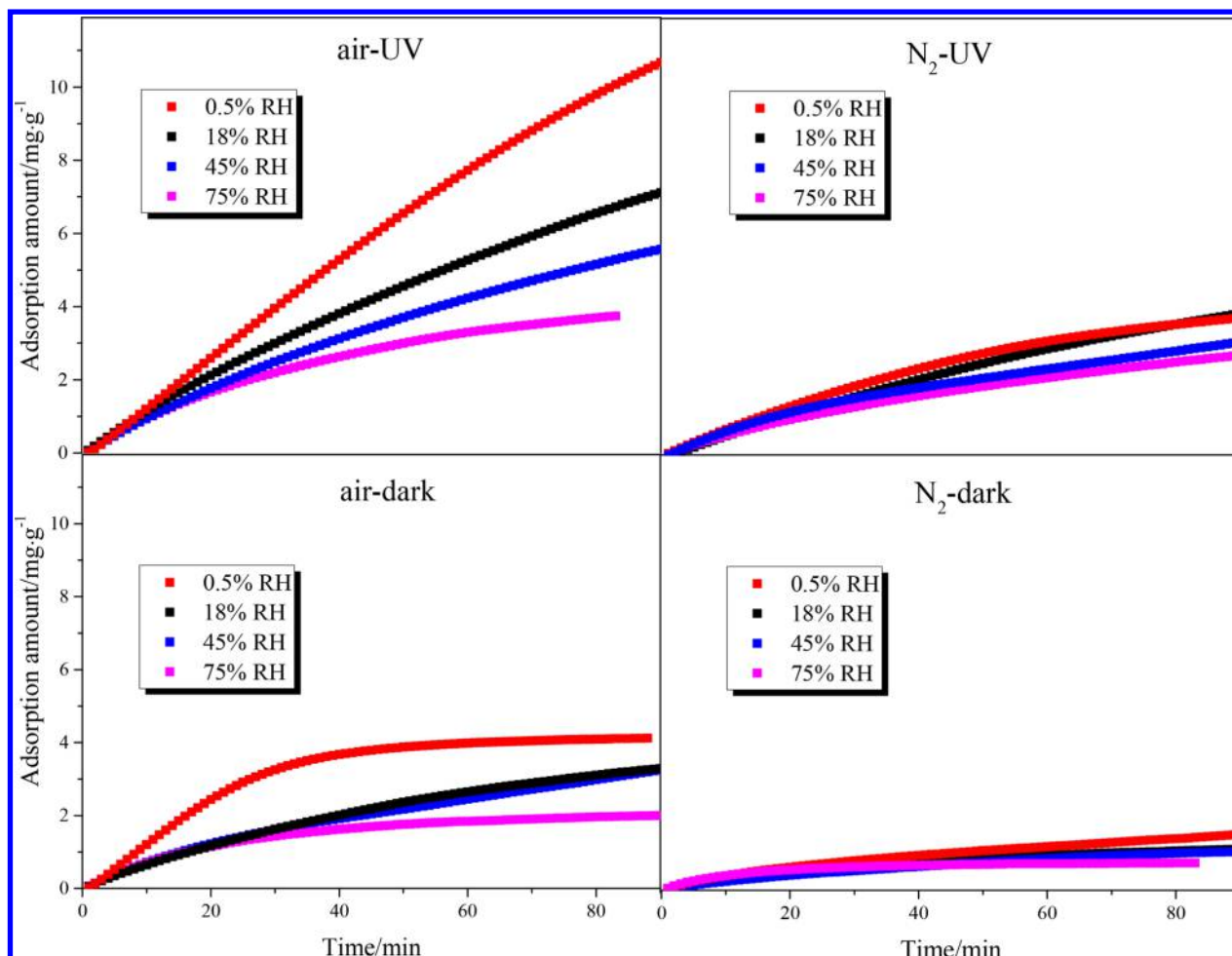
Figure 4. Change of uptake capacity of TiO$_2$ to SO$_2$ as a function of time at different conditions at 298 K, [SO$_2$] = 210 ± 5 ppbv; sample mass = 5.05 ± 0.3 mg.
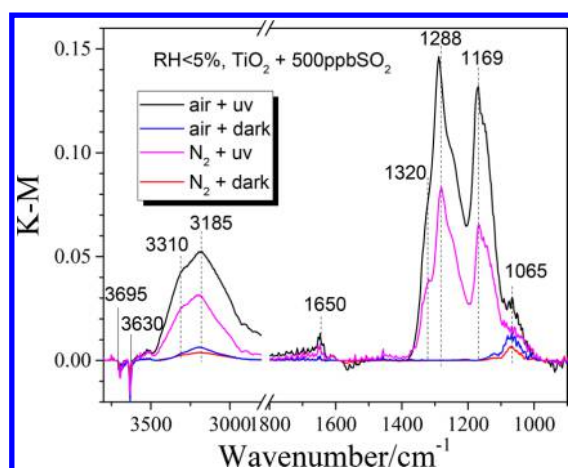
Figure 5. In situ DRIFTS spectra of TiO$_2$ exposure to 500 ppb SO$_2$ for 90 min under various conditions: air stream in the presence and absence of UV irradiation; N$_2$ stream in the presence and absence of UV irradiation. Total flow of 100 mL·min^{-1} at 298 K, RH < 5%.

enhanced adsorption of water due to the increased hygroscopicity by sulfate.

The effect of water on the heterogeneous reactions of SO$_2$ on TiO$_2$ was further analyzed by comparing the integrated areas of peaks (in the range of 1000.89−1400.089 cm^{-1}) due
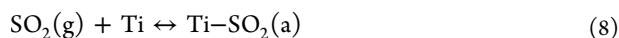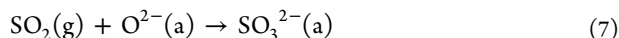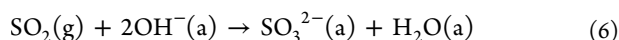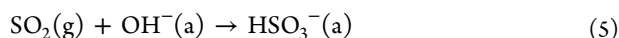
to surface sulfur species. Figure 6 shows the change of the integrated areas of peaks due to sulfite and sulfate as a function of time under various conditions. Both UV irradiation and O$_2$ exhibit promotive effects, while the RH shows an inhibition effect on the formation of surface sulfur species. These results are consistent with the flow tube experimental results. Nevertheless, the decrease factor in the flow tube reactor (Figure 4) is larger than that in DRIFTS studies (Figure 6). One reason might be that these two methods focus on different species. DRIFTS characterized surface species, whereas the flow tube reactor measured the gaseous species. DRIFTS may underestimate the measurements of surface species because the detection depth of IR may be shorter than the depth of SO$_2$ diffusion. The thickness of samples on the flow tube is less than 0.1 mm, while the thickness of powders in the in situ cell is larger than 2 mm. Another reason is that other gaseous products like SO$_3$ or H$_2$SO$_4$ may form during the uptake process of SO$_2$, as indicated by the steady-state uptake results.

■ DISCUSSION

Adsorption of SO$_2$ on metal oxides usually produces surface-coordinated sulfite or bisulfite on basic oxide anions (oxygen atoms or adsorbed hydroxyl) or adsorbed SO$_2$ on acidic metal sites. The proposed reaction mechanisms under dark conditions are shown in eq 5−8[39−41]
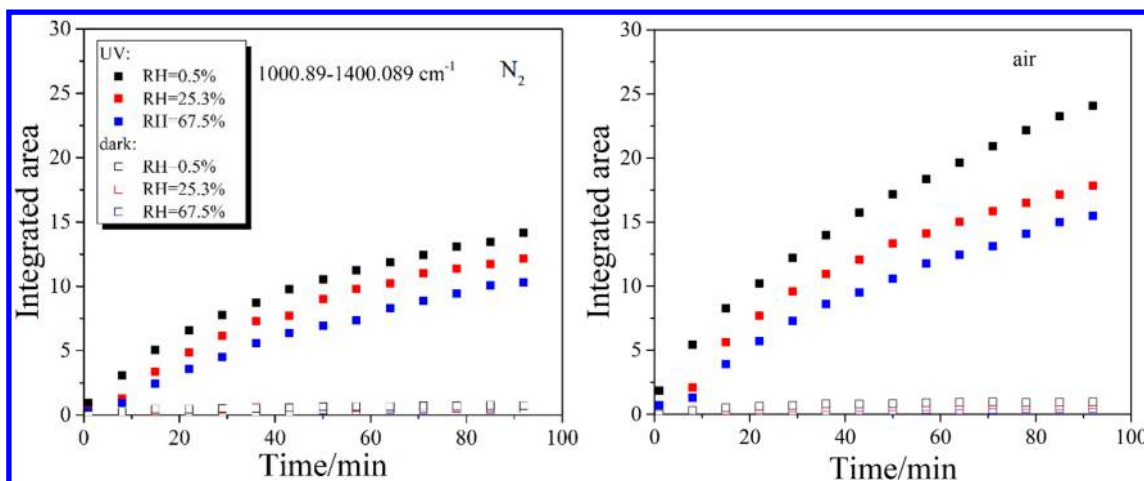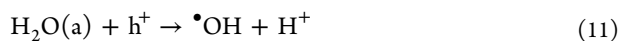
Figure 6. Comparison in the integrated areas of peaks (in the range of $1000.89-1400.089$ cm^{-1}) due to surface sulfur species. Reaction conditions: 500 ppb SO_2, total flow of 100 mL·min^{-1}, at 298 K, RH < 5%.

$$SO_2(g) + OH^-(a) \rightarrow HSO_3^-(a) \tag{5}$$

$$SO_2(g) + 2OH^-(a) \rightarrow SO_3^{2-}(a) + H_2O(a) \tag{6}$$

$$SO_2(g) + O^{2-}(a) \rightarrow SO_3^{2-}(a) \tag{7}$$
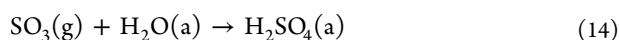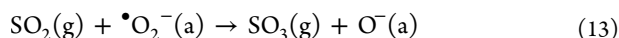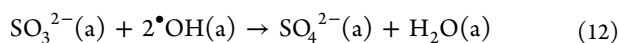
$$SO_2(g) + Ti \leftrightarrow Ti-SO_2(a) \tag{8}$$

These reactions are the initial steps of SO_2 adsorption in which UV irradiation is not necessary. Thus, UV irradiation has only a slight effect on the initial uptake coefficients of SO_2 on TiO_2. However, surface water is also adsorbed on OH sites which competed with the adsorption of SO_2 on TiO_2. Therefore, increasing RH results in a decrease of uptake coefficients. For O_2, it may participate in reaction 7 by supplying surface O^{2-} species to form sulfite. Hence, the presence of O_2 can greatly increase the uptake coefficients and the uptake capacity of TiO_2 to SO_2.

If TiO_2 is exposed to the irradiation, electron−hole pairs are created because of the short penetration depth of the UV light, and these electrons and holes react further with other components (water vapor and molecular oxygen) in the air, generating some oxidizing free radicals, such as OH radicals and O_2^- radicals.[37,54]

$$TiO_2 + h\nu \rightarrow h^+ + e^- \tag{9}$$

$$O_2(a) + e^- \rightarrow {}^\bullet O_2^- \tag{10}$$

$$H_2O(a) + h^+ \rightarrow {}^\bullet OH + H^+ \tag{11}$$

These oxidizing species can react with SO_2 and SO_3^{2-} and enhance the formation of sulfate.[40,41,43] On the basis of the present studies and previous literature, the possible photochemical reaction mechanism of the SO_2 reaction on the surface of TiO_2 can be described as follows

$$SO_3^{2-}(a) + 2{}^\bullet OH(a) \rightarrow SO_4^{2-}(a) + H_2O(a) \tag{12}$$

$$SO_2(g) + {}^\bullet O_2^-(a) \rightarrow SO_3(g) + O^-(a) \tag{13}$$

$$SO_3(g) + H_2O(a) \rightarrow H_2SO_4(a) \tag{14}$$

Several previous studies focused on the uptake coefficients of SO_2 on TiO_2, which gave different values. Usher et al. determined the true uptake coefficient (γ_{BET}) of SO_2 on TiO_2

to be $1.0 \pm 0.2 \times 10^{-4}$ using a Knudsen cell reactor.[25] This value is much larger than that measured in the present study. Unlike the Knudsen cell reactor under high vacuum conditions, the coated-wall flow tube reactor in the present study was used under ambient pressure. Thus, the residual water adsorbed on the surface could not be removed completely. Surface-adsorbed water may decrease the adsorption of SO_2 due to the competition effect, as seen in Figure 3. TiO_2 has a fully hydrated structure due to the abundant amount of surface hydroxyl groups.[52,53] In a previous study, Liu et al. found that dehydrated TiO_2 shows much higher reactivity to NO_2 than the hydrated TiO_2.[53] Because the initial adsorptions of both SO_2 and H_2O are mainly on surface hydroxyl sites, the block effect of H_2O could be reasonable. Recently, Lasne et al. observed that the measured uptake coefficients of O_3 on mineral dust were much smaller than those tested by a Knudsen cell.[55] They attributed the pressure effect to the large difference in the values of the uptake coefficients measured because the regeneration of sites for O_3 decompositions is pressure-dependent. Nevertheless, because the adsorption site for SO_2 could not be regenerated, the pressure effect may not be the main reason for the discrepancy observed in this study. On the basis of the DRIFTS study about the heterogeneous reaction of SO_2 on TiO_2 particles, Shang et al.[43] calculated the reactive uptake coefficient (γ_{BET}) to be 1.94×10^{-6} under dark and dry conditions and the initial uptake coefficient to be 1.35×10^{-5} upon UV irradiation and 40% RH.[43] Although the γ_{BET} in Shang et al. under dark conditions is close to that measured in the present study, the γ_{BET} under light and humid conditions is larger than that in our results. One reason for this discrepancy is the concentration of SO_2, which was 50 ppm in Shang et al. and 0.2−0.5 ppm in this study. It was reported that the surface product formation rate increased with gaseous reactant concentration in DRIFTS experiments.[27,56] Another reason is the different calculation methods. In the coated-wall flow tube reactor, the uptake coefficient was based on the loss rate of SO_2. In contrast, in DRIFTS study, γ_{BET} was based on the formation rate of sulfate. For the heterogeneous conversion of SO_2 to sulfate, the adsorption of SO_2 on the surface represents the first step and is not equal to the formation of sulfate. The formation of sulfate greatly depends on the oxidants presented. The presence of UV irradiation could promote the formation of sulfate during

the adsorption of SO_2. Consequently, the γ_{BET} in DRIFTS study would increase in UV reactions. Thus, the initial uptake measured in the present study should be considered as the low limit.

CONCLUSIONS AND ATMOSPHERIC IMPLICATIONS

In the present study, the kinetics of SO_2 uptake on TiO_2 with or without UV irradiation has been investigated using flow reactors. The influence of water and O_2 was also considered. The uptake experiment results showed that UV irradiation exhibited a slight increasing effect on the initial uptake coefficients of SO_2. Oxygen was demonstrated to be involved in the adsorption of SO_2. However, the adsorption amount of SO_2 as well as the formation of sulfate was significantly increased upon irradiation. Increasing the RH decreased the initial uptake coefficients and the adsorption amount of SO_2 in both dark and light reactions because of the competition effect. Therefore, surface-adsorbed water should be considered as an inhibition factor for the heterogeneous conversion of SO_2 on TiO_2.

The true uptake coefficients of SO_2 on TiO_2 measured in this study are on the order of about 10^{-7} under typical humid conditions in the atmosphere. This value is relatively low, which limits its contribution to the formation of sulfate. The lifetime for removal of SO_2 via heterogeneous reactions on dust is given by $\tau_{het} = 4/\gamma\omega A$, where A is the surface area density of the dust, ω is the mean molecular speed, and γ is the uptake coefficient.[57] The content of TiO_2 in mineral dust was about 0.68%.[16] The relation between the mass concentration and surface area of aerosol in Beijing was based on the values measured by Wu et al., in which ${\sim}10^{-5}$ m^2 μg^{-1} of particles was determined.[58] If the mass loading of mineral dust was assumed to be 1000 $\mu g/m^3$, the lifetime of SO_2 due to the heterogeneous reactions on TiO_2 was about 54 years. In comparison, the lifetime of SO_2 with respect to reaction with OH is ${\sim}11$ days if $[OH] = 1 \times 10^6$ molecules cm^{-3}.[57] Thus, heterogeneous reaction on TiO_2 as a sink for SO_2 could be neglected.

ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.8b11433.

Uptake curve of SO_2 on the TiO_2 surface in air upon UV irradiation with a relatively long time asn uptake curves of SO_2 on the TiO_2 surface in air with and without UV irradiation under various RHs (PDF)

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