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# A Novel Pathway of Atmospheric Sulfate Formation Through Carbonate Radical

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**Abstract.** Carbon dioxide is considered an inert gas that rarely participates in atmospheric chemical reactions. However, we show here that $CO_2$ is involved in some important photo-oxidation reactions in the atmosphere through the formation of carbonate radicals ($CO_3^{\cdot-}$). This potentially active intermediate $CO_3^{\cdot-}$ is routinely overlooked in atmospheric chemistry regarding its effect on sulfate formation. Present work demonstrates that $SO_2$ uptake coefficient is enhanced by 17 times on mineral dust particles driven by $CO_3^{\cdot-}$. It can be produced through two routes over mineral dust surfaces: i) hydroxyl radical + $CO_3^{2-}$; ii) holes ($h^+$) + $CO_3^{2-}$. Employing a suite of laboratory investigations of sulfate formation in the presence of carbonate radical on the model and authentic dust particles, field measurements of sulfate and (bi)carbonate ions within ambient PM, together with density functional theory (DFT) calculations for single electron transfer processes in terms of $CO_3^{\cdot-}$-initiated S(IV) oxidation, a new role of carbonate radical in atmospheric chemistry is elucidated.

## 1. Introduction

Atmospheric composition changes are subjected to highly reactive light-induced radicals, such as hydroxyl (·OH), hydroperoxyl ($HO_2^{\cdot}$), or nitrate radicals ($NO_3^{\cdot}$), which are able to alter not only compositions but also physical and chemical properties of particulate matter (Thompson, 1992;Prinn et al., 2001;Platt et al., 1990;Davis and Francisco, 2011). However, when atmospheric chemical reactions occur over nanometer-sized particles at ambient condition, which creates a locally enriched aqueous medium of unique chemical activity, other radicals might likewise gain importance. The carbonate radical ($CO_3^{\cdot-}$) is typically such an active radical. The lifetime of $CO_3^{\cdot-}$ ranges from a microsecond to even a few milliseconds and its concentration can be two orders of magnitude higher than that of hydroxyl radicals over the water surface (Chandrasekaran and Thomas, 1983;Goldstein et al., 2001;Shafirovich et al., 2001;Sulzberger et al., 1997a). In addition, the one-electron

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reduction potential of $E^0(CO_3^{\cdot-}/CO_3^{2-})$ couple is 1.78 V vs. NHE at neutral pH, leaving $CO_3^{\cdot-}$ a strong oxidant in aquatic chemistry (Cope et al., 1973 ;Bisby et al., 1998;Merouani et al., 2010). Previous studies concerning carbonate radical in aqueous media demonstrate that it reacts rapidly with some organic compounds with higher selectivity (Merouani et al., 2010), especially for those electron-rich compounds amines (Stenman et al., 2003;Yan et al., 2019). Also, it has been pointed out that the scavenging of hydroxyl radicals by (bi)carbonate species leads to the formation of $CO_3^{\cdot-}$ ions (Graedel and Weschler, 1981b), which promotes the degradation of phenol (Xiong et al., 2016). Besides, a higher second order of rate constant, lying at $10^9$ $M^{-1}$ $s^{-1}$, has been reported for the reaction of $CO_3^{\cdot-}$ with porphyrins (Ferrer-Sueta et al., 2003), indicating that this radical ion has great oxidation capability that may trigger atmospherically relevant chemical reactions. However, it is only regarded as an intermediate in tropospheric anion chemistry so far (Graedel and Weschler, 1981a;Dotan et al., 1977;Lehtipalo et al., 2016;Beig and Brasseur, 2000) and its underlying role as an active oxidant for heterogeneous reaction in the atmosphere is barely explored. Very recently, our group observed the promotional effect of $CO_3^{\cdot-}$ on atmospheric nitrate formation (Fang et al., 2021). Motivated by this finding, attempts were made to further explore its role in other important atmospherically-relevant reactions.

It is well documented that sulfate ($SO_4^{2-}$) is also a key constituent of aerosols in the atmosphere (Huang et al., 2015;Su et al., 2016). It is able to serve as the precursors of efficient cloud condensation nuclei, with optical properties leading to a cooling effect (Wang et al., 2011). As a consequence, the mechanism aspect of secondary sulfate formation was the focus of numerous studies over the past decades (Hung et al., 2018;Stone, 2002;Zhang et al., 2015b). There is a consensus that high-valence sulfur (VI), produced from the oxidation of anthropogenic $SO_2$, is the dominant source for atmospheric secondary sulfate. However, a remarkable missing sulfate budget emerges for the atmospheric modeling, which underpredicts $SO_4^{2-}$ by over 50 % (normalized mean bias) in comparison to observational results when heterogeneous aerosol chemistry is not considered (Zheng et al., 2015). This large gap indicates that there are unknown heterogeneous reaction pathways of significance and unconsidered promoters that have great potential to accelerate sulfate formation.

Due to the high stability of $CO_2$ under ambient conditions (Hossain et al., 2020), there are rare studies concerning the influence of $CO_2$ in atmospheric chemical processes. $CO_2$ is demonstrated to form (bi)carbonate species over humidified dust particles (Baltrusaitis et al., 2011;Nanayakkara et al., 2014) and reduced to CO under solar illumination (Deng et al., 2020). However, its impact on atmospheric heterogeneous reactions remains poorly characterized. Our recent laboratory study shows that $CO_2$ impacts the sulfate formation on aluminum oxide particles in the dark (Liu et al., 2020) while upon solar illumination its role in $SO_2$ oxidation over mineral dust surfaces is still an open question. Carbonate salt is enriched in authentic dust aerosol (Cao et al., 2005) and reported to reach over 10 % wt. of Asian dust particles (McNaughton et al., 2009). It is generally accepted that $CO_3^{2-}$ affects atmospheric chemistry and aerosol characteristics mainly through its intrinsic alkalinity, which buffers aerosol acidity and favors the sulfate formation (Bao et al., 2010;Kerminen et al., 2001;Yu et al., 2018). In fact, either $CO_2$ or carbonate salt is able to produce the active $CO_3^{\cdot-}$ under the ambient circumstance and increase the oxidative capacity in the atmosphere. Combined with our earlier investigation of $CO_3^{\cdot-}$(Fang et al., 2021), this

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radical ion is likely to be a driving force for fast $SO_2$ oxidation. However, to the best of our knowledge, no work has considered how and to what extent the carbonate radical influences $SO_2$ heterogeneous oxidation in the atmosphere.

In the current study, through laboratory studies, we present that carbon dioxide and calcium carbonate, working as the precursor of carbonate radicals, extend their ability to accelerate sulfate formation over authentic particles in the atmosphere. Together with quantum chemistry calculations, a detailed molecular mechanism regarding a single electron transfer (SET) process between carbonate radical and sulfite ions is elucidated. Furthermore, field observations validate findings from the laboratory investigations.

## 2. Experimental methods

### 2.1 Laboratory Studies

A series of characterizations were initially performed to investigate the mineral dust of concern by using X-ray diffraction (XRD) and Raman. The heterogeneous reaction of $SO_2$ on mineral dust particles in the presence of $CO_2$ and carbonate species were then investigated by the *in situ* Fourier transform spectrum (DRIFTS), ion chromatography (IC), Raman, electron spin resonance (ESR), and nanosecond transient absorption spectroscopy (NTAS). Furthermore, we employed three types of authentic dust particles and four kinds of synthesized authentic simulants to probe the proposed scheme. All corresponding configuration setup, characterizations, and methodologies can be found in Supplement, text 1-12, Tables S1-S3 and Fig. S1-S10. In terms of oxygen isotope experiments, more detailed procedures are available in Supplement, text 15.

### 2.2 Quantum Chemical Calculation

We employed density functional theory (DFT) calculations in the term of single electron transfer (SET) process using Gaussian 09 package to investigate this novel route, detailed in Supplement text 13-14 and Fig. S11-S12.

### 2.3 Field Observations

Atmospheric aerosols were collected on the roof of our department using an 8-stage non-viable-cascade-impactor type sampler (TISCH TE Inc., USA), with details shown in supplement Text 16. The concentration of water-soluble sulfate ion was by measured IC analysis while that of (bi)carbonate ions were determined by the ionization balance approach (Supplement, text 17 and 18). The relationship between (bi)carbonate ions and sulfate ions during the daytime and nighttime hours were then determined.

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## 3. Results and discussion

### 3.2.1 Accelerated sulfate production in the presence of carbonate.

The phy-chemical properties of employed mineral dust proxies were first characterized (Fig. S1), consistent with earlier reported studies (Su et al., 2008;Balachandran and Eror, 1982;Shang et al., 2010), and spectral irradiance of the solar simulator applied in the present study is well covered by natural sunlight (Fig. S2), as much as possible having experimental results from the lab better applicability in the real atmosphere. The sulfate yield, measured by IC, upon irradiation on $TiO_2$-$CaCO_3$ mixture particles (50 wt. % $CaCO_3$) is significantly enhanced by 7 times and 23 times compared to that of pristine $TiO_2$ and $CaCO_3$ (Fig. 1a), respectively. In stark contrast, there is a negligible increase of sulfate production detected on the $TiO_2$-$CaCO_3$ mixture relative to that of pristine $CaCO_3$ and $TiO_2$ in dark experiments (Fig. 1a). This result allows us to consider that in addition to alkaline environment alternative important force resulting in the remarkable increase of sulfate yield upon irradiation is expected within the carbonate-containing system. Fig. 1b and 1c show the *in situ* diffuse reflectance infrared DRIFTS features of S(IV) and S(VI) species formed on theoretical and experimental $TiO_2$-$CaCO_3$ mixtures (wt./wt. = 50/50) upon irradiation for 90 min, respectively. The "theoretical" here is calculated based on the *in situ* DRIFTS of pristine $TiO_2$ and $CaCO_3$ through a simple linear superposition. These results suggest a synergistic effect presented in this mixture for sulfate formation under solar irradiation. In addition, a more evident fingerprint $SO_4^{2-}$ feature (Dong et al., 2009;Yann Batonneau et al., 2008) monitored by Raman spectroscopy appears over $TiO_2$-$CaCO_3$ particles compared to pristine $TiO_2$ particles (Fig. S3), in good agreement with the IC analyses and *in situ* DRIFTS measurements. Combining DRIFTS experiments with the obtained calibration curve (Fig. S4), we estimated that the uptake coefficient of $TiO_2$-$CaCO_3$ mixture (50 wt. % $CaCO_3$) is increased by about 17 times as compared to that of pure $CaCO_3$ or $TiO_2$(Table S3). More importantly, upon irradiation $SO_2$ uptake coefficients for these dust proxies lie at the order of magnitudes of $10^{-4}$, indicating that the photochemical pathway associated with carbonate species is likely a potential driving force to trigger fast $SO_2$ oxidation in the atmosphere.

High-resolution transmission electron microscopy (HRTEM) analysis of $TiO_2$-$CaCO_3$ particles after reaction, in combination with energy dispersive spectrometer mapping measurements of sulfur component, were conducted to investigate the synergistic effect between $TiO_2$ and carbonate ions (Fig. 1 d-f and Fig. S5). A region with a relatively high density of sulfur species was selected for further observation and the distribution of each component (Fig. 1g) was determined by fast Fourier transformation (FFT) and inverse FFT analyses of the selected HRTEM image in high resolution with lattice fringes shown in Fig. 1f. Observation of crystalline $Ti(SO_4)_2$ and $CaSO_4$ on the interface of $TiO_2$ and $CaCO_3$ components imply that the synergistic effect on sulfate production likely originates from interplays of those two types of components under solar illumination. We further assessed the importance of interfacial contact between $TiO_2$ and $CaCO_3$ in sulfate production by two synthesis approaches in which the interface abundance is modulated for comparison. Typically, a "grinding" method was used to make $TiO_2$-$CaCO_3$ mixture with tight contact between those two components, thus leading to a strong interaction. Meanwhile, the "shaking" method is designed to create a $TiO_2$-$CaCO_3$ mixture with weak interplay,

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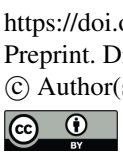

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leaving relatively fewer amounts interfaces within the mixtures. Indeed, the resulting mixing statuses of two samples meet our expectations, evidenced by the scanning electron microscope (SEM) technique (Fig. S6). IC quantification analysis suggests that particles with considerable junctions exhibit a more pronounced promotion for sulfate yield than those having relatively few junctions (Fig. S7). These results emphasize the importance of an indispensable interface connection between $TiO_2$ and $CaCO_3$ in fast production upon irradiation.

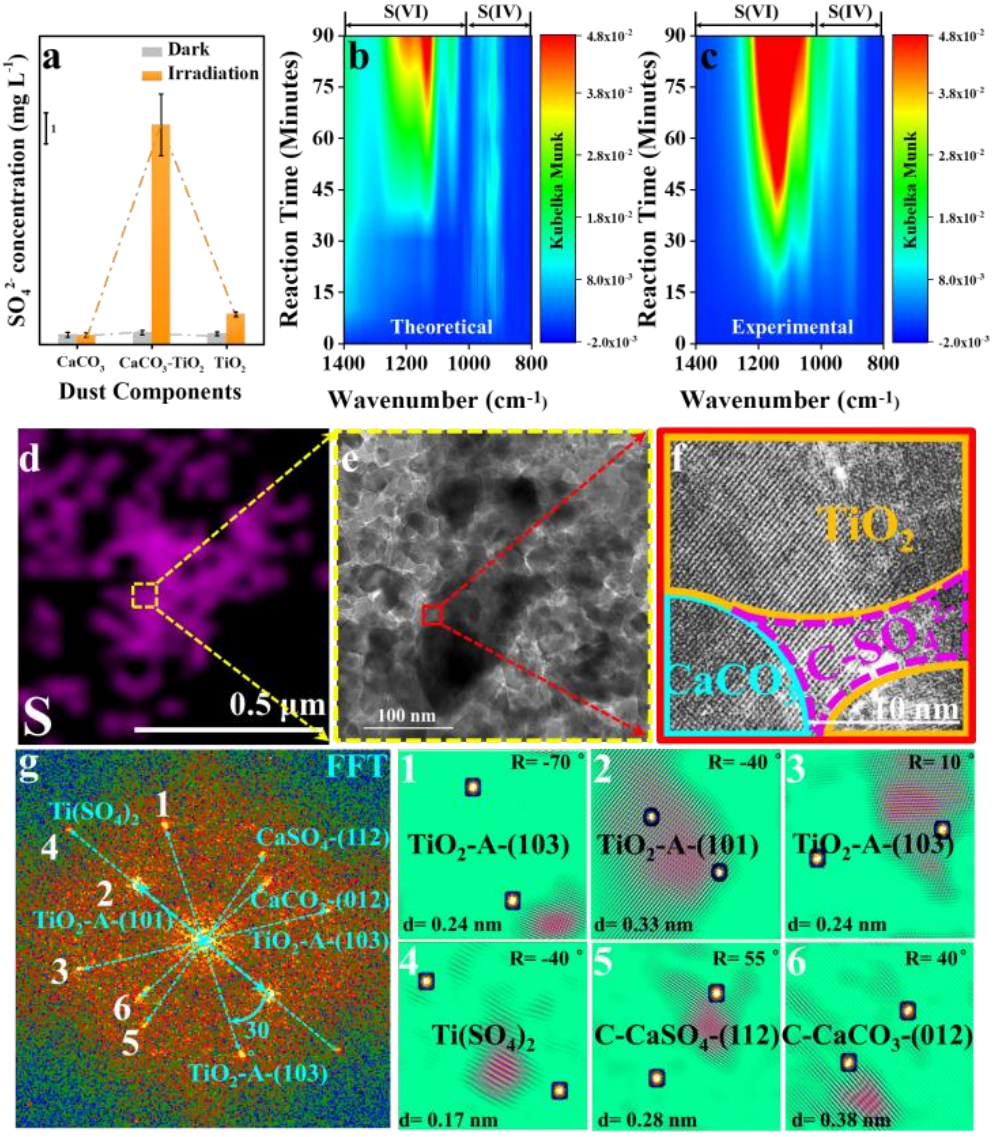


**Figure 1. (a)** Sulfate concentration quantified by IC on mineral dust particles after exposure to gaseous $SO_2$ under irradiation or dark for 30 min. *In situ* DRIFTS of S(IV) and S(VI) species yield on theoretical **(b)** and **(c)** experimental $TiO_2$-$CaCO_3$ mixtures (wt./wt. = 50/50) upon irradiation for 90 min. Reaction conditions: RH = 30 %, Light intensity (I) = 30 mW $cm^{-2}$, Total flow rate = 52.5 mL $min^{-1}$ and $SO_2$ = $2.21\times10^{14}$ molecules $cm^{-3}$. All spectra were processed by the Kubelka-Munk (K-M) algorithm. Noting that the production of sulfur species in theoretical $TiO_2$-$CaCO_3$ mixtures refer to 0.5 × K-M bands of sulfur species of $TiO_2$ + 0.5 × K-M bands of sulfur species of $CaCO_3$

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while that for experimental $TiO_2$-$CaCO_3$ mixtures refer to 1 × K-M bands of sulfur species of $TiO_2$-$CaCO_3$ mixtures (wt./wt. = 50/50). **(d)** Energy Dispersive Spectroscopy (EDS) mapping of sulfur. **(e)** Selected HRTEM region containing a high density of sulfur for further observation and the red rectangle refers to the region shown in panel f. **(f)** The HRTEM image in high resolution with lattice fringes and **(g)** corresponding FFT power spectra, lattice indexing, and (1-6) inverse FFT analysis of lattice signal shown in panel g. In panel f, the term C-$SO_4^{2-}$ stands for crystalline $SO_4^{2-}$, i.e. $CaSO_4$ and $Ti(SO_4)_2$. Particles for the HRTEM measurement refer to $TiO_2$-$CaCO_3$ mixture particles upon exposure to the $4.42\times10^{14}$ molecules $cm^{-3}$ $SO_2/N_2+O_2$ for 60 min while other reaction conditions are as same as that of above sulfate quantification experiments.

Except for the consideration of heterogeneous reaction over $TiO_2$, $CaCO_3$, and $TiO_2$-$CaCO_3$ mixtures, the rapid $SO_2$ oxidation pathway was further probed by employing mineral dust simulants where two dominant crust constitutents $SiO_2$ and $Al_2O_3$ were introduced into $TiO_2$-$CaCO_3$ particles to mimic the authentic mineral dust particles in the atmosphere, with specific component and corresponding ratio information shown in Table S1. It worth mentioning that the determination of the ratio of each component in the simulants relies on the EDS mapping results of ATD particles. In Fig. S8, the introduction of $TiO_2$ components ( $\approx$ 1 % wt.) into $SiO_2$-$Al_2O_3$ leads to 81.6 % enhancement of sulfate production while merely 24.8 % wt. increase of sulfate yield was observed once $\approx$ 8 % wt. of $CaCO_3$ was incorporated into $SiO_2$-$Al_2O_3$ dust particles. Surprisingly, mixing of $\approx$ 1 % mass fraction of $TiO_2$ and $\approx$ 8 % wt. of $CaCO_3$ into $SiO_2$-$Al_2O_3$ gives rise to a 235 % increase of sulfate formation relative to that of $SiO_2$-$Al_2O_3$. Hence, the synergistic effect on heterogeneous oxidation of $SO_2$ is likely to take effect in the atmosphere.

### 3.2.2 Accelerated sulfate production in the presence of $CO_2$.

Atmospheric $CO_2$ is also an important source of (bi)carbonate. Its influence on photochemical $SO_2$ uptake on mineral dust was thus studied. In the presence of atmospherically relevant $CO_2$ ($9.83\times10^{15}$ molecules $cm^{-3}$), sulfate yield was increased under irradiation as compared to $CO_2$-free case (Fig. 2a and b). We cautiously check the buffering effect of formed (bi)carbonate on sulfate production by time-resolved DRIFTS spectra (Fig. 2c and d). $CO_2$ suppresses both S(IV) and S(VI) products under the dark. Instead of accumulating much more sulfur species through buffering effect, (bi)carbonate ions that evolve active intermediates upon irradiation may be a plausible force to drive rapid sulfate formation. The reaction kinetics of $SO_2$ on mineral dust particles follows the pseudo-first-order, as evidenced by the $SO_2$ concentration dependence experiments (Fig. S9 a-f). Besides, a nearly 50 % increase of $SO_2$ uptake coefficient is observed for the mineral dust proxy $TiO_2$ after being exposed to $9.83\times10^{15}$ molecules $cm^{-3}$ (400 ppm) $CO_2+SO_2/N_2+O_2$ mixture.

As another step toward a real scenario in the atmosphere, experimental trials employing authentic dust particles, i.e. Arizona test dust (ATD), clays IMt-2 (Illite, Mont., USA) and K-Ga-2 (Kaolin, Georgia, USA), were carried out (Table S2). In Fig. S10, K-Ga-2 clay exhibits the most remarked promotional effect on sulfate yield (by nearly 120 % increased sulfate production in the $CO_2$-involved case under irradiation). This correlates with its considerable $TiO_2$ contents (3.43 %) in the K-Ga-2 clay, in which active intermediates are readily evolved from $TiO_2$ and (bi)carbonate species upon irradiation. However, the promotional effect of $CO_2$ on sulfate production under irradiation is weak for IMt-2 (the content of $TiO_2$ $\approx$ 0.99 %) and ATD (the content of $TiO_2$ $\approx$ 0.46 %) as compared to K-Ga-2 particles. This may correlate to their higher mass fraction of

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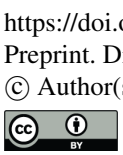

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alkaline earth metal oxide (denoted as A.E.), which enables dust particles to possess a large number of (bi)carbonate species in the natural environment where they have experienced long-term exposure to atmospheric $CO_2$. Therefore, the aforementioned synergetic effect takes effect over IMt-2 and ATD particles even without exposure to $CO_2$ due to the presence of abundant formed carbonate, and a less evident increase of sulfate yield is observed.

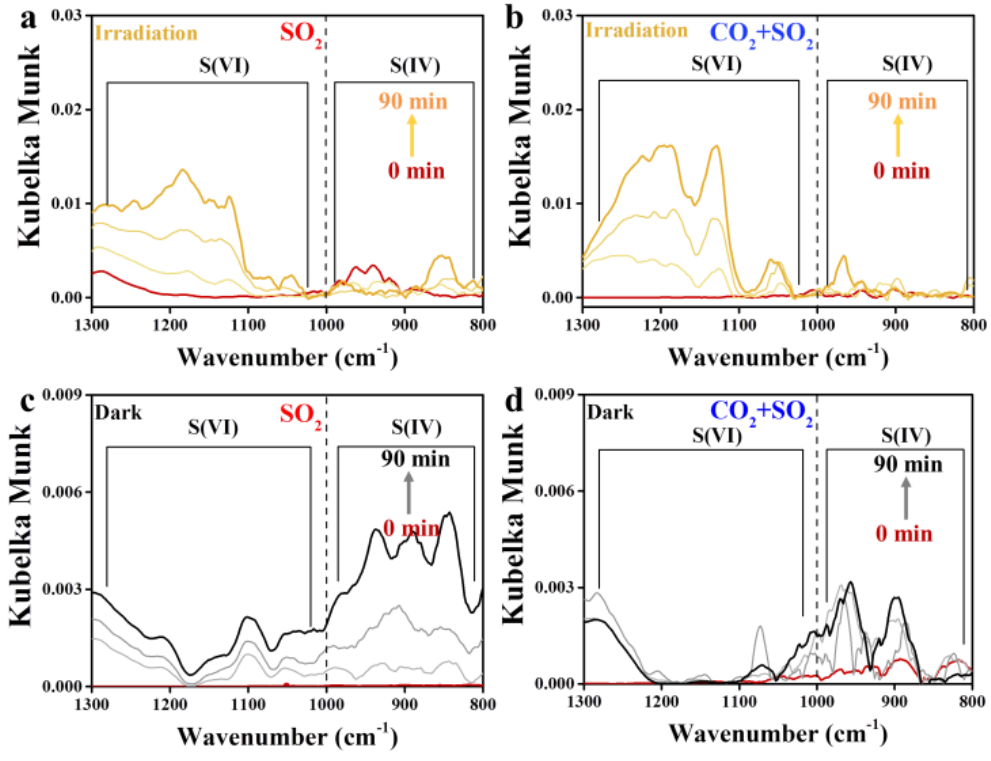


**Figure 2.** Time-resolved DRIFTS of S(IV) and S(VI) products over $TiO_2$ particles after exposure to $SO_2/N_2+O_2$ in the absence and presence of $CO_2$ upon irradiation (**a** and **b**) and those reactions under dark (**c** and **d**). Reaction conditions: RH = 30 %, Light intensity (I) = 30 mW $cm^{-2}$, total flow rate = 52.5 mL $min^{-1}$ and $SO_2$ = 7.37 ×$10^{13}$ molecules $cm^{-3}$.

### 3.2.3 Reaction Mechanism.

The heterogeneous reaction of $SO_2$ on dust particles in the atmosphere is a complicated process, covering a series of reactions taking place through both homogeneous and heterogeneous ways. Many studies pointed out that dust particles in the atmosphere are more likely to possess several water layers (Vlasenko et al., 2006;Pradhan et al., 2010;Yang et al., 2017) through a thermodynamic equilibrium process, and particles are subjected to provide quasi-aqueous medium when RH is over 20 % (Yu and Jang, 2018). Therefore, the adsorption process mediated by formed water layers can be a major route for gas-dust partitioning, and the aqueous radical-initiated reactions are very likely to responsible for the rapid oxidation of $SO_2$ on mineral dust surfaces. Earlier sulfate quantification results suggest that intermediates originated from carbonate salt and $CO_2$ gives rise to fast oxidation of $SO_2$ on dust particles upon irradiation. In our carbonate-containing reaction system, a plausible intermediate is an active carbonate radical. They are readily produced via the following two pathways. First of all,

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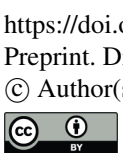

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carbonate anion can be directly oxidized by produced photo-induced holes (Eqs 2 and 3), as the redox potential of $CO_3^{\cdot-}$ /$CO_3^{2-}$ is 1.78 V (vs NHE, at pH = 7), which is lower than the $TiO_2$ valence band (VB) potential of 2.67 V (vs NHE, at pH = 7) (Li et al., 2016;Xiong et al., 2016):

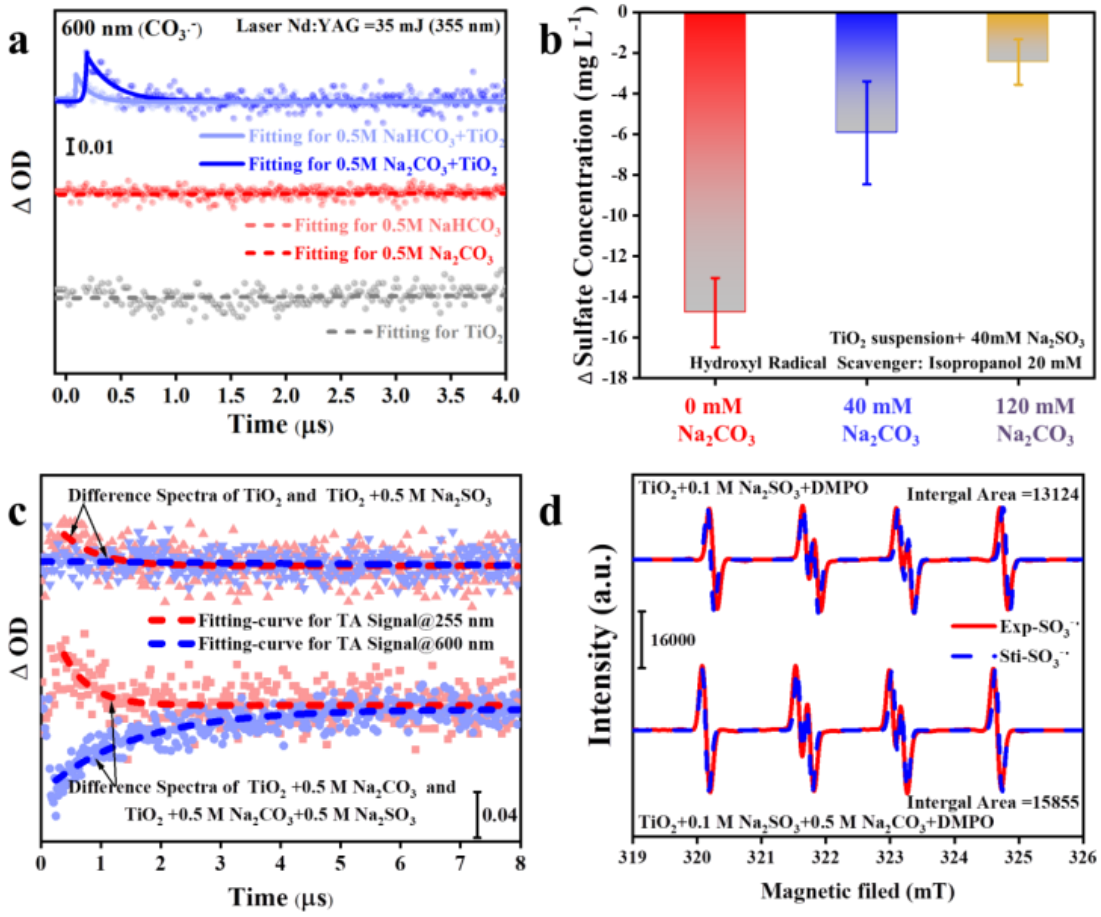


**Figure 3.** (**a**) Single-wavelength transient absorption spectra of various aqueous solutions. (**b**) Sulfate formation change $\Delta(SO_4^{2-})$ determined by different sulfate concentrations with and without the addition of isopropanol as hydroxyl radical scavenger. (**c**) The difference in transient absorption kinetics of sulfite radical and carbonate radical at the various aqueous solutions and their corresponding growth-decay fit curves. ΔA-signal was recorded at 255 and 600 nm after pulsed 355 nm laser excitation. (**d**) ESR spectrometry of [DMPO–$SO_3^{\cdot-}$] intermediate formed in a solution of d $TiO_2$ (3mg~4 mL) + 0.1 M $Na_2SO_3$ and $TiO_2$ (3mg~4 mL) + 0.5 M $Na_2CO_3$ + 0.1 M $Na_2SO_3$. For clarity, the integrated areas of ESR profiles were also presented for direct comparison. Exp. and Sti. stand for experimental results and corresponding fitting results using software Isotropic Radicals.

Mineral dust +$h\nu$→$h^+$+$e^-$ (Eq. 1)

$h^+$+ $CO_3^{2-}$→$CO_3^{\cdot-}$ (Eq. 2)

In the second pathway, carbonate radicals evolve through the reaction of (bi)carbonate anion with formed hydroxyl radicals ·OH over mineral dust surfaces (Zhang et al., 2015a) (Eqs 3 and 4).

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$h^+ + H_2O_{ad} \rightarrow \cdot OH + H^+$ (Eq. 3)

$\cdot OH + HCO_3^-/CO_3^{2-} \rightarrow CO_3^{\cdot-} + H_2O/OH^-$ (Eq. 4)

The above assumptions are supported by nanosecond transient absorption spectra (NTAS), in which signal (ΔOD) of carbonate radical $CO_3^{\cdot-}$ at 600 nm (Bhattacharya et al., 1998) only emerged for dust suspension containing (bi)carbonate species (Fig. 3a). The $CO_3^{\cdot-}$-induced chemistry was further evidenced by ·OH scavenging experiments using isopropanol as it shows a lower reaction rate with $CO_3^{\cdot-}$ ($K_{i\text{-}PrOH\sim CO3^{\cdot-}} < 4.0 \times 10^4\ M^{-1}\ s^{-1}$) relative to that with ·OH ($K_{i\text{-}PrOH\sim OH} < 1.9 \times 10^9\ M^{-1}\ s^{-1}$) (Buxton et al., 2009;Liu et al., 2015). Clearly, a significant loss of sulfate yield when $TiO_2$ suspension was added with ·OH scavenger (Fig. 3b). However, this is in strong contrast to the result of a carbonate-involved system where the reactivity is sustained, i.e., carbonate radicals offer an alternative reaction pathway for $SO_2$ oxidation. In addition to laboratory investigations, the carbonate radical formation process is proved to be thermodynamically favorable, supported by density functional theory (DFT) calculations (Fig. S11).

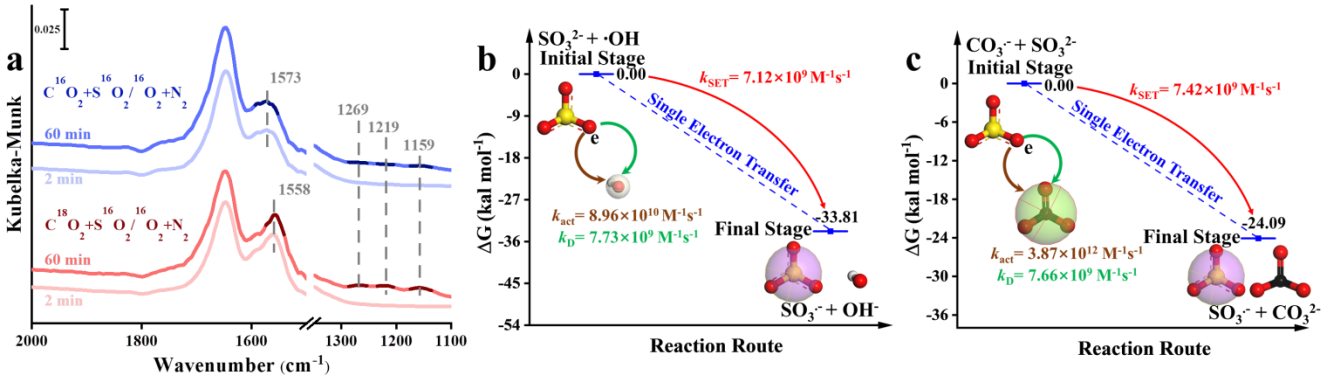


**Figure 4.** (**a**) *In situ* DRIFTS of heterogeneous reaction of $SO_2$ on the $TiO_2$ particles for 2 and 60 min after being exposed to $C^{16(18)}O_2/N_2$ for 20 min under irradiation. (**b**) Reaction pathway of interaction between hydroxyl radical (·OH) and sulfite ($SO_3^{2-}$) and (**c**) Interaction between carbonate radical ($CO_3^{\cdot-}$) and sulfite ($SO_3^{2-}$) through the SET process at the CCSD (T)-F12/cc-PVDZ-F12//M06-2X/6-311++G (3df, 3pd) level and $\Delta G_0^{SET}$ represents the difference in Gibbs free energy between reactant and product. The white, black, yellow, and red spheres represent H, C, S, and O atoms, respectively. In order to guide the attention of the variation of surface products in oxygen isotope experiments (panel a), DRIFTS features of these concerned species were plotted in dark colors.

On the other hand, the previous studies (Das, 2001;Neta and Huie, 1985;Chameides and Davis, 1982) agree with the key role of sulfite radical ($SO_3^{\cdot-}$) in rapid sulfate production in an aqueous medium, and the present reaction system creates a localized environment where $SO_3^{\cdot-}$ can be readily stemmed from the $TiO_2$ and S(IV) species upon solar illumination (Salama et al., 1995). Consequently, probe light of NTAS at wavelength 255 nm (ascribed to sulfite radical) and 600 nm (ascribed to carbonate radical) were simultaneously monitored (Hayon et al., 1972;Ghalei et al., 2016;Goldstein et al., 2001). A weak signal of sulfite radical was observed in the system of $TiO_2$+$Na_2SO_3$ suspension under irradiation (Fig. 3c,). On the contrary, the sulfite radical signal is strengthened after the introduction of $Na_2CO_3$ into the $TiO_2$+$Na_2SO_3$ suspension, along

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with a significant decrease of signal for carbonate radical. ESR data (Fig. 3d) further confirms the increase of $SO_3^{\cdot-}$ after 2 min UV irradiation in the presence of carbonate ion. Based on the above results, one may deduce that the interplay between carbonate radical and sulfite ions is a crucial step giving rise to the increased $SO_3^{\cdot-}$ which is responsible for rapid $SO_2$ oxidation through chain propagation reactions (Deng et al., 2017). Nevertheless, there are two possibilities that might explain the aforementioned interaction. One is the oxygen transfer and the other route is electron transfer, which needs further clarification.

We first examined the oxygen transfer path through $^{18}O$ isotope labeling experiments. $TiO_2$ particles were initially exposed to $C^{16}O_2/N_2$ and $C^{18}O_2/N_2$, followed by the exposure of $SO_2/N_2+O_2$ under irradiation (Fig. 4a). Bidentate carbonate band centered at 1573 $cm^{-1}$ appears after the introduction of $C^{16}O_2/N_2$, while this band shifts to 1558 $cm^{-1}$ when $C^{18}O_2/N_2$ is introduced, indicating the incorporation of $^{18}O$ into bidentate carbonate species, in good agreement with the previous report (Liao et al., 2002). However, none shift of IR features at 1269, 1219, and 1159 $cm^{-1}$, assigned to (bi)sulfate species on $TiO_2$ particles, were observed throughout the reaction. This implies that the oxygen transfer path does not account for the rapid $SO_2$ oxidation on particles of concern.

In light of the above analysis, the electron transfer might be a plausible pathway to explain the fast oxidation within the reaction system. DFT calculations provide an accessible approach to study the electron transfer pathway. The result in Fig. 4b shows $SO_3^{\cdot-}$ formation is a SET process of $CO_3^{\cdot-}$ and $SO_3^{2-}$, where O atom in $SO_3^{2-}$ transfers an electron to O atom in $CO_3^{\cdot-}$ to form $SO_3^{\cdot-}$ and $CO_3^{2-}$. This SET reaction is a thermodynamically favorable process, with the difference of Gibbs free energy between reactant and product lying at -24.09 kcal $mol^{-1}$. Taken above results and discussions together, the following reactions are proposed accordingly (Eqs. 5-8):

$$CO_3^{\cdot-} + SO_3^{2-} \rightarrow CO_3^{2-} + SO_3^{\cdot-} \quad \text{(Eq. 5)}$$

$$SO_3^{\cdot-} + O_2 \rightarrow SO_5^{\cdot-} \quad \text{(Eq. 6)}$$

$$SO_5^{\cdot-} + SO_3^{2-} \rightarrow SO_4^{\cdot-} + SO_4 \quad \text{(Eq. 7)}$$

$$SO_4^{\cdot-} + SO_3^{2-} \rightarrow SO_4^{2-} + SO_3^{\cdot-} \quad \text{(Eq. 8)}$$

Another important issue needs to be addressed as well. We noted that $SO_3^{\cdot-}$ can also be formed via the conventional reaction of ·OH and $SO_3^{2-}$ (Eqs. 9) and this process is also considered.

$$\cdot OH + SO_3^{2-} \rightarrow SO_3^{\cdot-} + OH^- \quad \text{(Eq. 9)}$$

In this SET process, electron donor $SO_3^{2-}$ reacts spontaneously with electron acceptor ·OH (Fig. 4c) and the calculated activation free energy barrier $\Delta G^{\neq}_{SET}$ for this SET reaction is 2.50 kcal $mol^{-1}$. Hence, the reaction process of ·OH with $SO_3^{2-}$ is diffusion-controlled, and the total rate constant $k_{SET-2}$ was calculated to be $7.12 \times 10^9$ $M^{-1}s^{-1}$. In comparison, the rate constant $k_{SET-1}$ of the diffusion-controlled SET process for $CO_3^{\cdot-}$ and $SO_3^{2-}$ was estimated to be $7.42 \times 10^9$ $M^{-1}s^{-1}$. Despite a slight net increase of the rate, the distinguishable concentration of $CO_3^{\cdot-}$ and ·OH should also be taken into account for the rate comparison in varied reaction paths. To visualize the difference, relative rates were calculated according to Eq. 10:

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$$r=\frac{v_{CO_3^{\cdot-}+SO_3^{2-}}}{v_{\cdot OH+SO_3^{2-}}}=\frac{k_{SET\text{-}1}[CO_3^{\cdot-}][SO_3^{2-}]}{k_{SET\text{-}2}[\cdot OH][SO_3^{2-}]} \quad \text{(Eq.10)}$$

Where *r* is the ratio of two reaction rates, $[CO_3^{\cdot-}]$, $[SO_3^{2-}]$, and $[\cdot OH]$ refer to the concentration of corresponding reactants. Previous literature suggests the concentration of carbonate radicals is able to show two orders of magnitude higher than that of hydroxyl radical at the surface of the water under solar irradiation (Chandrasekaran and Thomas, 1983;Goldstein et al., 2001;Shafirovich et al., 2001). Aqueous medium that attach to particle surfaces offer an ideal environment for accumulating carbonate radicals. Consequently, concentrations of $CO_3^{\cdot-}$ and $\cdot OH$ were set at the range from $1.0 \times 10^{-10}$ to $1 \times 10^{-12}$ mol $L^{-1}$ and from $1.0 \times 10^{-12}$ to $1 \times 10^{-14}$ mol $L^{-1}$ (Sulzberger et al., 1997b) and *r* value could thus reach to $1.04 \times 10^4$ at most (Fig. S12). As a result, we speculate that the formation pathway of $SO_3^{\cdot-}$ via interaction between $CO_3^{\cdot-}$ and $SO_3^{2-}$ is a more effective route, corresponding well with experimental results.

### 3.2.4 Field Measurements of Sulfate and (Bi)carbonate Ions.

Complement field sampling and analysis provide indirect evidence to support our hypothesis that intermediates $CO_3^{\cdot-}$ may affect sulfate formation in the atmosphere. Previously, it has been suggested that coarse-model particulate matter (PM) possesses a large mass fraction of mineral dust (Fang et al., 2017;Miller-Schulze et al., 2015), in which $TiO_2$ was found at mass mixing ratios ranging from 0.1 to 10 % depending on the exact location where particles were uplifted (Hanisch and Crowley, 2003). In this case, PM with relatively larger size dimensions is expected to contribute to secondary sulfate formation via heterogeneous reactions, which is supported by the recent field study where carbonate fraction of coarse PM is evidenced to promote secondary sulfate production(Song et al., 2018). Therefore, rather than determine the concentration of water-soluble ions in all stages, more attention was paid to PM collected in stages 1-4 (particles with their dimension $\geqslant$ 3.3 μm). (Bi)carbonate ions are known as key precursors in producing $CO_3^{\cdot-}$ and accelerate sulfate formation. Quantifications of those relevant species were thus conducted (supplement texts 17 and 18). We further considered the relationships between sulfate ions and (bi)carbonate ions by means of linear regression analysis. In Fig. 5, the negative correlations between the mass concentrations of sulfate ions and (bi)carbonate ions are observed in the nighttime hours, consistent with the suppression of sulfate formation by $CO_2$ in the dark experiments. This is also supported by our previous study where $CO_2$-derived (bi)carbonate species are demonstrated to block the active sites for yielding sulfate over mineral dust proxy aluminum oxide (Liu et al., 2020). Instead, positive correlations are seen for those ions within PM sampled during the daytime hours regardless of size ranges and carbonate types ($HCO_3^-/CO_3^{2-}$). Except for the case (nighttime period, size larger than 9 μm), most of the significance *P* values for their correlations were smaller than 0.1, indicating those correlations do exist for sulfate and (bi)carbonate ions. This matches with the scenarios in which sulfate production upon irradiation in the presence of (bi) carbonate ions are increased over both model and authentic dust particles. In fact, preceding field observations of highly correlated relationship between $Ca^{2+}$ and $SO_4^{2-}$ water-soluble ions (Liu et al., 2020) during the carbonate-enriched dust storm episodes, together with persistent reports on the significant role of photochemical channels in

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increasing the sulfate concentration during the daytime (Wei et al., 2019;Kim et al., 2017;Wu et al., 2017) indirectly reflects the possibility of accelerated $SO_2$ oxidation triggered by photo-response active intermediates related to carbonate species. While we note that the correlation coefficients between sulfate and (bi)carbonate are not high in this work, field measurements of sulfate and (bi)carbonate ions shed light on their distinct correlations during the daytime and nighttime hours. This is the first time that relationships between those ions are explored separately in these two periods. Taken together, carbonate radical is likely to impact the sulfate formation in the atmosphere during the daytime hours.

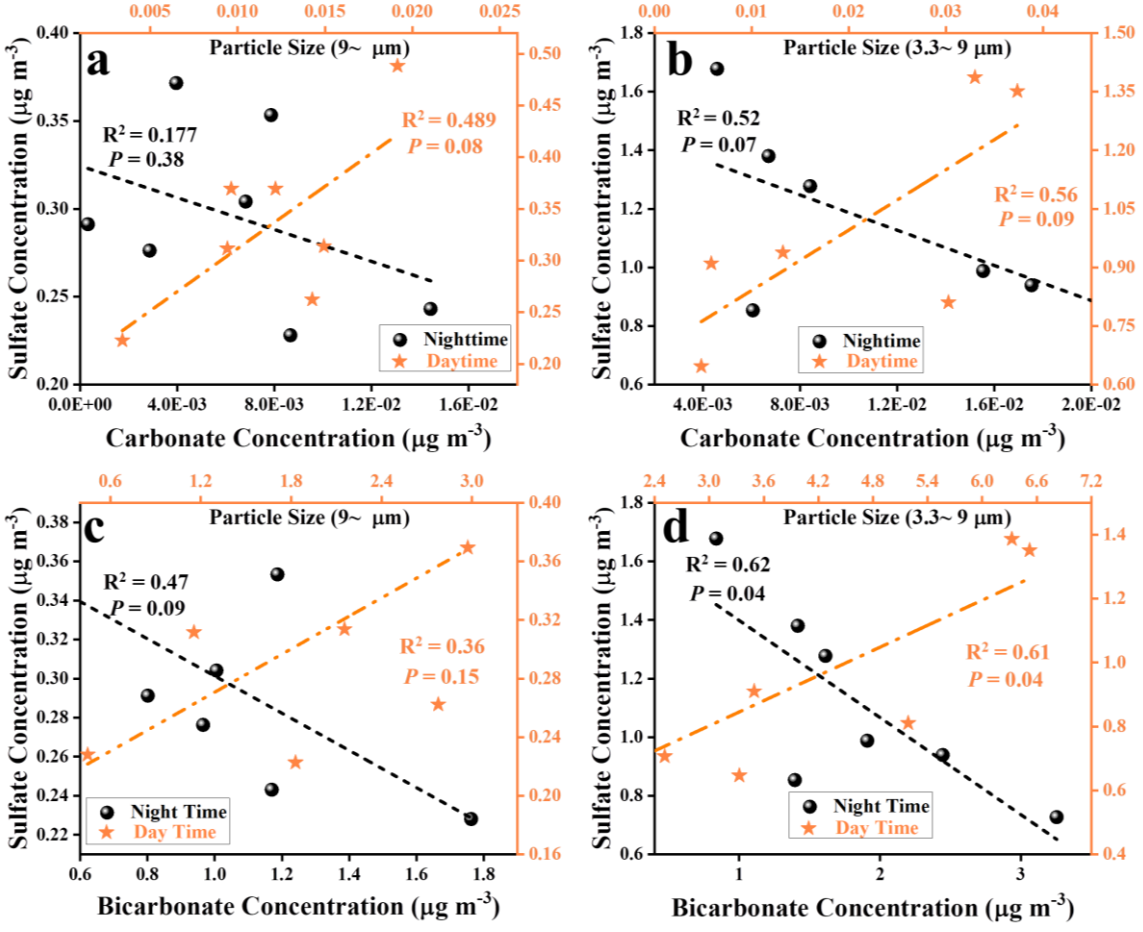


**Figure 5.** Field observation for the relationship between carbonate and sulfate ions during daytime and nighttime. Linear relationship analyses for measured sulfate ions and estimated carbonate ions (**a** and **b**) and for measured sulfate ions and estimated bicarbonate ions (**c** and **d**) during the daytime and nighttime at the varied range of particle size 9 μm~ and 3.3~ 9 μm, respectively.

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## 4. Conclusion

Overall, a reaction mechanism for the rapid sulfate formation in the presence of carbonate radicals is summarized and proposed in the scheme (Fig. 6). One may expect that during the nighttime hours $CO_2$-derived (bi)carbonate species are prone to have a slightly negative effect on sulfate formation due to the competitive adsorption between $CO_2$ and $SO_2$. On the other hand, both $CO_2$-derived carbonate species and carbonate salt works as the precursor of $CO_3^{\cdot-}$, which largely promotes sulfate formation during the daytime where energetic photons exist. Our observation of strengthened photochemistry launched by carbonate radicals suggests that such chemistry may be amplified on atmospherically relevant reactions over aerosols, where they often contain a large number of hydroxyl radicals and water-soluble (bi)carbonate ions. Since both sulfate aerosol and $CO_2$ are well known to affect the radiation budget and solar energy balance on the earth, their overall influence on the global climate considering the increased yield of sulfate aerosol triggered by $CO_2$, the precursor of carbonate radical, needs further investigation. Therefore, our study highlights the necessity for a comprehensive understanding of the $CO_3^{\cdot-}$ relevant chemistry in the underlying impacts of fine PM concentration, human health, and climate. Moreover, little is known about the interaction between carbonate radicals and other trace gas. Its further influence on the organic aerosol formation also needs consideration since it is known to efficiently participate in some organic compound oxidation reactions. All these assumptions need to be investigated in further detail. This study provides the first indication that carbonate radical not only plays a role as an intermediate in tropospheric anion chemistry but also as a strong oxidant for surfacial processing of trace gas in the atmosphere.

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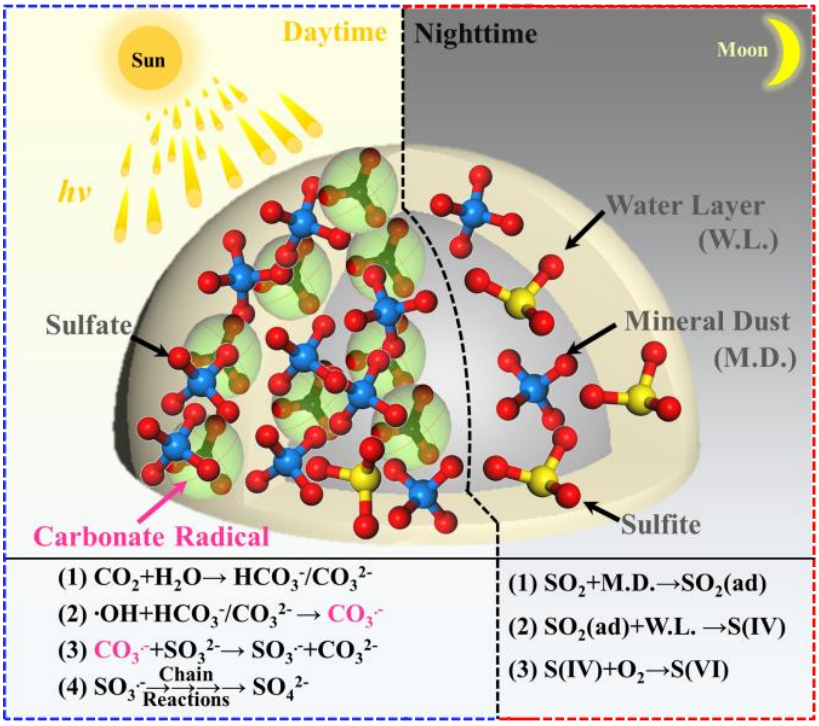


**Figure 6.** Schematic of the sulfate formation in the presence and absence of carbonate radical.

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*Data availability.* The data that support the results are available from the corresponding author upon request.

*Author contributions.* Y.L., Y.D. and L.Z. initially proposed the idea; Y.L. and Y.D. designed and performed most of the experiments; J.L. performed DFT calculations; Y.L., X.Z. and T.W. contributed to field samplings and data analysis; K.L., K.G., A.B., I.N., X.Z., C.G., and
325 L.Z. provided suggestions on the experiments and paper writing; All authors wrote the manuscript.

*Competing interests.* The authors declare that they have no conflict of interest.

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