Interactive comment on “Effects of temperature on the heterogeneous oxidation of sulfur dioxide by ozone on calcium carbonate” by L. Y. Wu et al.

We would like to thank the Referee #2 for the comments and the constructive suggestions to improve our manuscript. We have implemented all the comments and suggestions in the revised manuscript. Our responses to the comments and changes to the manuscript are included below in the order that the comments were given. We repeat the specific points raised by the reviewer in bold font, followed by our responses in italic font. And we have added three figures (Fig.S1 to Fig.S3) to supplementary material.

**—REPLY TO COMMENTS BY REFEREE #2—**

**Comment 1: Figure 1. Ordering of spectra is confusing. It seems as if the authors have ordered them by increasing sulfate intensity rather than temperature. If they believe this to be preferable, please clearly state this decision in the text and figure caption. Peaks around 875 cm$^{-1}$, which randomly seem to be positive and negative for different experiments, are not discussed in text. Presumably this is a contaminant – do the authors know their origin?**

REPLY: *Thank you very much for the Referee’s conscientiousness on our present article.*

*To highlight the effect of temperature on the sulfate intensity, we ordered the spectra by increasing sulfate intensity rather than temperature. According to the suggestion of the referee, we have stated this decision in figure caption.*

*Page 3521: “Fig.1. In situ DRIFTS spectra (absorbance units) of surface products when* $CaCO_3$ *particles were exposed simultaneously to* $SO_2$ *(*$4.9\times10^{14}$ *molecules cm*$^{-3}$*) and* $O_3$ *(*$4.9\times10^{14}$ *molecules cm*$^{-3}$*) for 200 min at different temperatures under dry conditions (RH<1%). The spectra were ordered by increasing sulfate intesity.”*

*As the referee pointed out, there existed peaks around 875 cm*$^{-1}$*(exactly at 878 cm*$^{-1}$*). We are sorry for not discussing these bands in text and making the referee confused. It is reasonable for the referee to doubt the presence of contaminant. However, several details suggested that no contaminants existed in our experiments. Firstly, prior to initiation of the experiments, the Teflon tube and the chamber were* *washed at least three times and then evacuated under high vacuum overnight to make sure that the whole gas supply system and the chamber were clean. Secondly, ultra-pure chemicals were used in our experiments. The purity of* $SO_2$*,* $O_2$*, and* $N_2$ *were 99.9%, >99.998% and >99.999%, respectively. The* $CaCO_3$ *particles with the purity of 99.5% were purchased from Alfa Aesar. Furthermore, the sample was in situ pretreated by heating in synthesized air at 573K for 3 h before an experiment. This treatment can also remove surface-adsorbed substances on the sample (Borensen et al., 2000). To avoid confusing, we have added this information in our revise version.*

*Page 3501 line 7: the sentence "The sample was pretreated by heating in synthesized ......such as loosely bonded water, from the surface (Koretsky et al., 1997)" was revised to "Prior to initiation of the experiments, the Teflon tube and the chamber were washed at least three times and then evacuated under high vacuum overnight to make sure that the whole gas supply system and the chamber were clean. Ultra-pure sample was in situ pretreated by heating in synthesized air at 573K for 3 h before an experiment. This treatment can also remove surface-adsorbed substances such as adsorbed water from the surface (Koretsky et al., 1997; Borensen et al., 2000)."*

*Examining the spectra in the literatures that involved the heterogeneous reactions on* $CaCO_3$ *surface carefully, we found that the peaks at 878* $cm^{-1}$ *corresponded to the out-of-plane bend of* $CaCO_3$*. To investigate the absorbance bands of* $CaCO_3$ *sample used in our experiments, the spectrum of* $CaCO_3$ *has been collected on pure KBr background spectrum. The frequencies of the vibrational bands observed (2510* $cm^{-1}$*, 1795* $cm^{-1}$*, broad band around 1445* $cm^{-1}$*, 878* $cm^{-1}$*and 713* $cm^{-1}$*) are in good agreement with literature values (Martin et al., 1987;Li et al., 2007;Prince et al., 2007a;Prince et al., 2007b;Prince et al., 2008). Therefore, the peaks at 878* $cm^{-1}$ *were assigned to the absorbance of* $CaCO_3$ *substrate used in our experiments. The strong absorption of* $CaCO_3$ *substrate at 878* $cm^{-1}$ *may interfere the intensity of IR signal in this region, and then the positive and negative peaks at 878* $cm^{-1}$ *for different experiments were observed in our experiments. The positive and negative peaks around 878* $cm^{-1}$ *also existed in previous literature (Li et al., 2006). This kind of spectral noise has been reported to emerge in the region where the absorption of substrate existed (Borensen et al.,* *2000;Ma et al., 2008;Tong et al., 2010). And the region with spectral noise was usually cut off. To avoid misunderstanding, we have also cut off the bands below 883 cm$^{-1}$. The explanation has been added in the revised paper, and it will be stated in the following comment.*

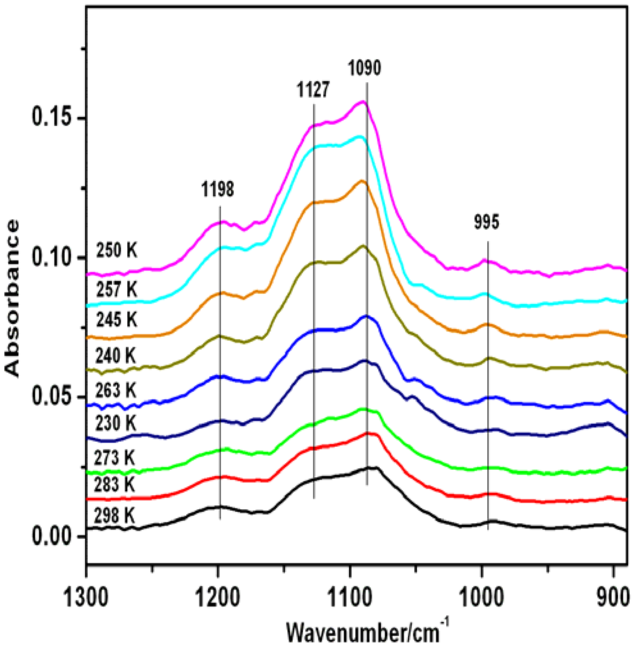


**Fig.1.** In situ DRIFTS spectra (absorbance units) of surface products when $CaCO_3$ particles were exposed simultaneously to $SO_2$ ($4.9\times10^{14}$ molecules cm$^{-3}$) and $O_3$ ($4.9\times10^{14}$ molecules cm$^{-3}$) for 200 min at different temperatures under dry conditions (RH<1%). The spectra were ordered by increasing sulfate intesity.

*References:*

*Borensen, C., Kirchner, U., Scheer, V., Vogt, R., and Zellner, R.: Mechanism and kinetics of the reactions of $NO_2$ or $HNO_3$ with alumina as a mineral dust model compound, J. Phys. Chem. A, 104, 5036-5045, 2000.*

*Li, L., Chen, Z. M., Zhang, Y. H., Zhu, T., Li, J. L., and Ding, J.: Kinetics and mechanism of heterogeneous oxidation of sulfur dioxide by ozone on surface of calcium carbonate, Atmos. Chem. Phys., 6, 2453-2464, doi:10.5194/acp-6-2453-2006, 2006.*

*Li, L., Chen, Z. M., Zhang, Y. H., Zhu, T., Li, S., Li, H. J., Zhu, L. H., and Xu, B. Y.: Heterogeneous oxidation of sulfur dioxide by ozone on the surface of sodium chloride and its mixtures with other components, J. Geophys. Res.-Atmos., 112, D18301, doi:10.1029/2006JD008207, 2007.*

*Ma, Q. X., Liu, Y. C., and He, H.: Synergistic effect between $NO_2$ and $SO_2$ in their adsorption and reaction on gamma-alumina, J. Phys. Chem. A, 112, 6630-6635，2008.*

*Martin, M. A., Childers, J. W., and Palmer, R. A.: Fourier-Transform Infrared Photoacoustic-Spectroscopy characterization of sulfur-oxygen species resulting from the reaction of $SO_2$ with CaO and $CaCO_3$, Appl. Spectrosc., 41, 120-126, 1987.*

*Prince, A. P., Grassian, V. H., Kleiber, P., and Young, M. A.: Heterogeneous conversion of calcite aerosol by nitric acid, Phys. Chem. Chem. Phys., 9, 622-634, 2007a.*

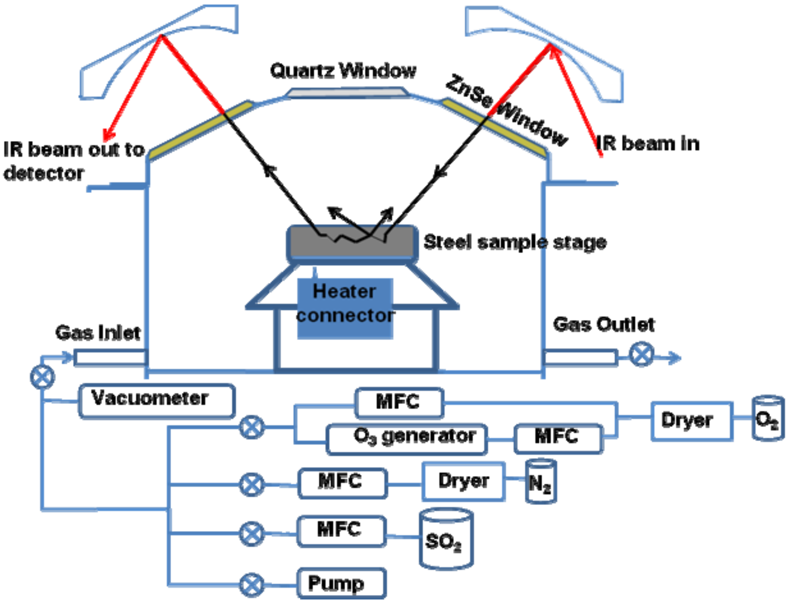
*Prince, A. P., Kleiber, P., Grassian, V. H., and Young, M. A.: Heterogeneous interactions of calcite aerosol with sulfur dioxide and sulfur dioxide-nitric acid mixtures, Phys. Chem. Chem. Phys., 9, 3432-3439, 2007b.*

*Prince, A. P., Kleiber, P. D., Grassian, V. H., and Young, M. A.: Reactive uptake of acetic acid on calcite and nitric acid reacted calcite aerosol in an environmental reaction chamber, Phys. Chem. Chem. Phys., 10, 142-152, 2008.*

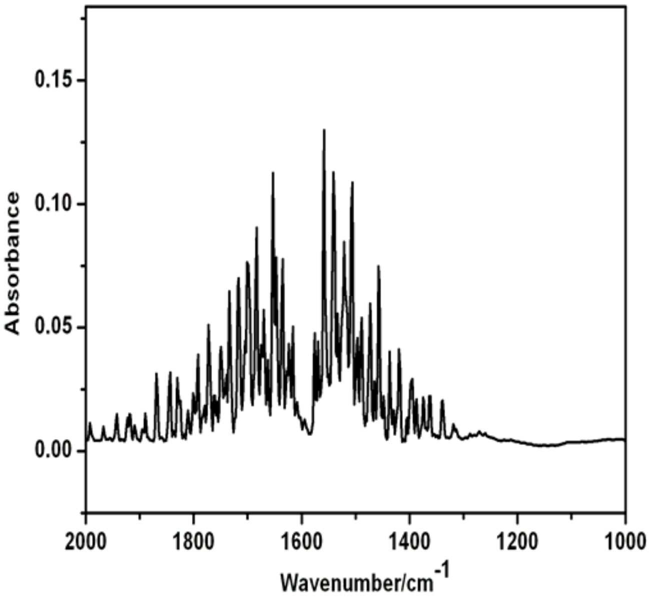
*Tong, S. R., Wu, L. Y., Ge, M. F., Wang, W. G., and Pu, Z. F.: Heterogeneous chemistry of monocarboxylic acids on alpha-$Al_2O_3$ at different relative humidities, Atmos. Chem. Phys., 10, 7561-7574, doi:10.5194/acp-10-7561-2010, 2010.*

**Comment 2: Figure 2. There appears to be absorption bands around 1790 cm-1 (and possibly around 1650 cm-1) underneath the poor water vapor subtraction. Again, the presence of organic contaminants might impact the experimental results – the authors should identify and discuss these bands in the text.**

REPLY: *As the referee's mentioned, there appears to be absorption bands around 1790 $cm^{-1}$ (and possibly around 1650 $cm^{-1}$). Examining the spectra in the literature carefully, we try to explain these bands in the range of 1400 to 1800 $cm^{-1}$from two aspects. Firstly, since we didn't substract the water vapor in our experiments, these bands may result from water vapor that existed in the environment out of the DRIFTS chamber (Chen et al., 2010). As shown in the schematic diagram of the experimental set-up, the IR beam must pass through air in the environment out of DRIFTS chamber simultaneously when* *collecting spectra. Although dry nitrogen was used to drive away the water vapor in our experiments, poor water vapor was unavoidable in the environment. To affirm the position of water vapor in the spectra, we got water vapor spectrum by a Nicolet FTIR Spectrometer 6700 equipped with a 10 cm single-pass gas cell. The bands in the region of 1400 and 1800 cm*$^{-1}$ *are similar to that in Fig.2 in our manuscript.*



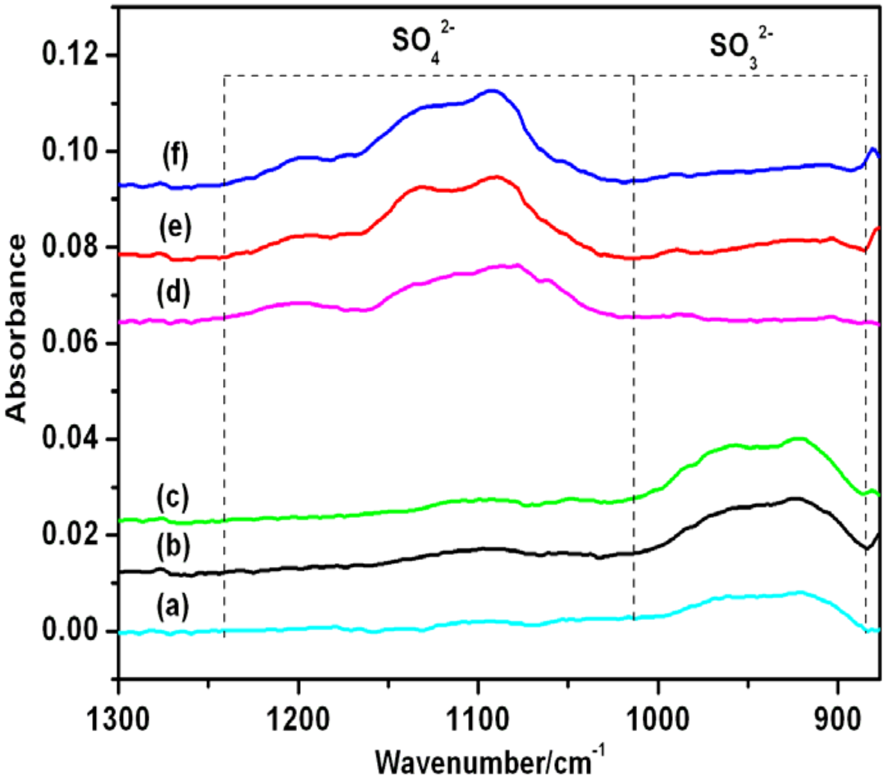
Schematic diagram of the experimental set-up including the DRIFTS apparatus, the $O_3$ generator, vacuometer, mass flow controller (MFC), silicon and zeolite dryer, pump and gas handling system. The red lines showed the IR beam through air in the environment out of DRIFTS chamber.



The spectrum of water vapor with a resolution of 4 cm$^{-1}$ and 100 scans.

*Secondly, as replying to comment 1, the absorbance peak was observed at 1795 cm$^{-1}$ which was best assigned to the combination mode (symmetric stretch + in-plane bend) (Ross and Goldsmith, 1964;Martin et al., 1987;Prince et al., 2007a;Prince et al., 2007b;Prince et al., 2008). The spectra noise of $CaCO_3$ substrate at 1795 cm$^{-1}$ could be responsible for the weak peak close to ~1790 cm$^{-1}$(exactly at 1795 cm$^{-1}$). The absorption bands of substrate after heterogeneous reactions were also observed in other literatures (Borensen et al., 2000;Ma et al., 2008;Tong et al., 2010). Since the bands in the range of 2000 to 1300 cm$^{-1}$ didn't provide much useful information for analyzing the products on the surface, they have been deleted in the revised paper. We have added explanation in the revised version.*

*Page 3501 line 16: after "shown in Fig.1.", we added one sentence "The frequency cutoff below 883 cm$^{-1}$ and above 1300cm$^{-1}$ was due to the strong absorption of $CaCO_3$ substrate (878 cm$^{-1}$,1795 cm$^{-1}$) and water vapor interference (1300 cm$^{-1}$ to 2000cm$^{-1}$) that existed in the environment out of the DRIFTS chamber."*



*References:*

*Borensen, C., Kirchner, U., Scheer, V., Vogt, R., and Zellner, R.: Mechanism and kinetics* *of the reactions of $NO_2$ or $HNO_3$ with alumina as a mineral dust model compound, J. Phys. Chem. A, 104, 5036-5045, 2000.*

*Chen, Y. J., Wang, H. S., and Umemura, J.: A New Method to Obtain Fourier Transform Infrared Spectra Free from Water Vapor Disturbance, Appl. Spectrosc., 64, 1186-1189, 2010.*

*Ma, Q. X., Liu, Y. C., and He, H.: Synergistic effect between $NO_2$ and $SO_2$ in their adsorption and reaction on gamma-alumina, J. Phys. Chem. A, 112, 6630-6635，2008.*

*Martin, M. A., Childers, J. W., and Palmer, R. A.: Fourier-Transform Infrared Photoacoustic-Spectroscopy characterization of sulfur-oxygen species resulting from the reaction of $SO_2$ with CaO and $CaCO_3$, Appl. Spectrosc., 41, 120-126, 1987.*

*Prince, A. P., Grassian, V. H., Kleiber, P., and Young, M. A.: Heterogeneous conversion of calcite aerosol by nitric acid, Phys. Chem. Chem. Phys., 9, 622-634, 2007a.*

*Prince, A. P., Kleiber, P., Grassian, V. H., and Young, M. A.: Heterogeneous interactions of calcite aerosol with sulfur dioxide and sulfur dioxide-nitric acid mixtures, Phys. Chem. Chem. Phys., 9, 3432-3439, 2007b.*

*Prince, A. P., Kleiber, P. D., Grassian, V. H., and Young, M. A.: Reactive uptake of acetic acid on calcite and nitric acid reacted calcite aerosol in an environmental reaction chamber, Phys. Chem. Chem. Phys., 10, 142-152, 2008.*

*Ross, S. D., and Goldsmith, J.: Factors affecting the infra-red spectra of planar anions with $D_{3h}$ symmetry—Ⅰ. carbonates of the main group and first row transition elements,, Spectrochimica Acta, 20, 781-784, 1964.*

*Tong, S. R., Wu, L. Y., Ge, M. F., Wang, W. G., and Pu, Z. F.: Heterogeneous chemistry of monocarboxylic acids on alpha-$Al_2O_3$ at different relative humidities, Atmos. Chem. Phys., 10, 7561-7574, doi:10.5194/acp-10-7561-2010, 2010.*

**Comment 3: Labeling of the various kinetic regions is confusing. Given the low RH of these experiments, the decreasing rate of reaction likely results from surface sulfate blocking adsorption sites for further sulfur dioxide reactions. “Transition state” and “steady state” labels have other common meanings. Perhaps “transition**

**region" and "saturation" would be less confusing descriptors.**

REPLY: *Thanks for the referee's advice.*

*According to the referee's suggestion, we have modified the label of the kinetic regions in Fig.3. "t=IS", "t=TS", and "t=SS" were revised to "Ⅰ", "Ⅱ", and "Ⅲ", respectively. "The initial state", "the transition state", and "the steady state" were revised to "initial region", "transition region", and "saturation region", respectively.*

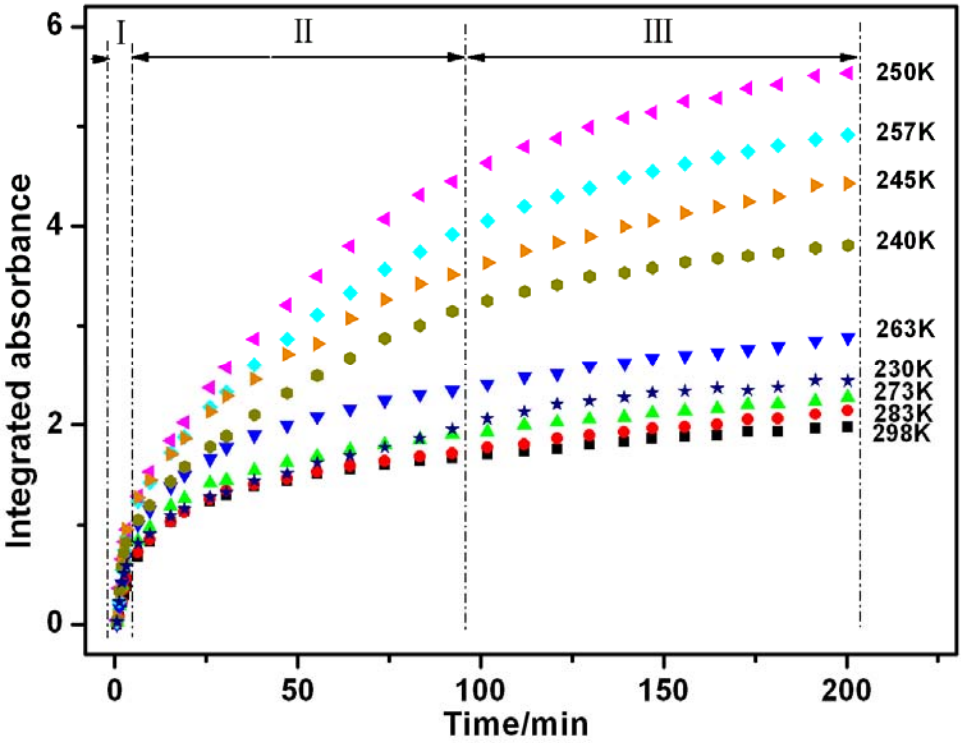


**Fig.3.** The integrated absorbance of 1012–1240 cm$^{-1}$ for sulfate formed during the reaction at series temperatures as functions of reaction time. Ⅰ, Ⅱ, and Ⅲ stand for initial region, transition region, and saturation region, respectively.

*All of expressions ("The initial state", "the transition state", and "the steady state") included in the manuscript have also been corrected in the revised version.*

*Page 3510 line 3: "the transition state uptake coefficient ($\gamma_{ts}$)" was revised to "the transition region uptake coefficient ($\gamma_{tr}$)".*

*Page 3510 line 7: "the saturation state uptake coefficient ($\gamma_{ss}$)" was revised to "the saturation region uptake coefficient ($\gamma_{sr}$)".*

*Page 3520 Table 2: "$\gamma_{ts}$" and "$\gamma_{ss}$" were revised to "$\gamma_{tr}$" and "$\gamma_{sr}$", respectively.*

**Table 2.** Reactive uptake coefficient for $SO_2$ ($4.9\times10^{14}$molecules $cm^{-3}$) and $O_3$ ($4.9\times10^{14}$molecules $cm^{-3}$) on $CaCO_3$ at series of tropospheric temperatures.

| T/K | $\gamma_0$ | | $\gamma_{tr}$ | | $\gamma_{sr}$ | |
|---|---|---|---|---|---|---|
| | Geometric | BET | Geometric | BET | Geometric | BET |
| | $10^{-4}$ | $10^{-7}$ | $10^{-5}$ | $10^{-8}$ | $10^{-6}$ | $10^{-9}$ |
| 298 | 1.31±0.13 | 1.27±0.13 | - | - | 1.87±0.14 | 1.81±0.11 |
| 283 | 1.32±0.10 | 1.28±0.10 | - | - | 2.46±0.32 | 2.37±0.29 |
| 273 | 1.62±0.10 | 1.56±0.09 | - | - | 2.31±0.31 | 2.23±0.30 |
| 263 | 1.78±0.05 | 1.73±0.05 | - | - | 3.35±0.17 | 3.24±0.16 |
| 257 | 2.27±0.20 | 2.19±0.19 | 2.16±0.47 | 2.09±0.46 | 5.70±1.06 | 5.53±1.02 |
| 250 | 2.44±0.07 | 2.36±0.07 | 2.86±0.24 | 2.78±0.24 | 6.12±1.12 | 5.93±1.08 |
| 245 | 2.45±0.28 | 2.37±0.28 | 2.38±0.13 | 2.30±0.16 | 5.53±0.99 | 5.35±0.97 |
| 240 | 2.15±0.28 | 2.08±0.28 | 1.75±0.32 | 1.69±0.31 | 3.81±0.54 | 3.69±0.53 |
| 230 | 1.59±0.13 | 1.53±0.13 | 0.60±0.20 | 0.58±0.19 | 4.11±1.06 | 3.98±1.02 |

**Comment 4: The authors state that reaction 2 is rate determining. While this seems reasonable given their proposed mechanism, they present no evidence supporting this conclusion. Did they run any duplicate experiments with different ozone concentrations? All conclusions must be supported by observations.**

REPLY: *We are sorry for making a mistake in proposing that the reaction (R2) is rate determining in our manuscript. Actually, the whole process of sulfite formation which involved both reaction (R1) and reaction (R2) determined the rate instead of the reaction (R2) solely. Following the referee's suggestion, we presented evidences supporting conclusions and corrected in our revised version.*

*Firstly, we have supplemented a series of experiments as a function of ozone concentration at four model temperatures to prove our proposed mechanism. Double-logarithmic plots of the rate of sulfate formation as a function of the* *concentration of $O_3$ at 298 K (Fig.S2a), 273 K (Fig.S2b), 263 K (Fig.S2c), and 240 K (Fig.S2d) give a series of slopes from a linear regression. All of these slopes are close to zero, indicating zero-order rate law for $O_3$ in the heterogeneous oxidation of $SO_2$ on $CaCO_3$ surface and the rate of sulfate formation is independence of the concentration of $O_3$.*

*From eq. (1) in our manuscript,* $\mathrm{r} = \dfrac{d\{\mathrm{SO}_4^{2-}\}}{dt} = \dfrac{k_1 k_2}{k_{-1} + k_2}[\mathrm{SO}_2] = k[\mathrm{SO}_2]$*, we can see that the reaction is zero order for $O_3$. Therefore, the reaction order deduced from the proposed mechanism is well consistent with the experiment results shown in Fig.S2.*

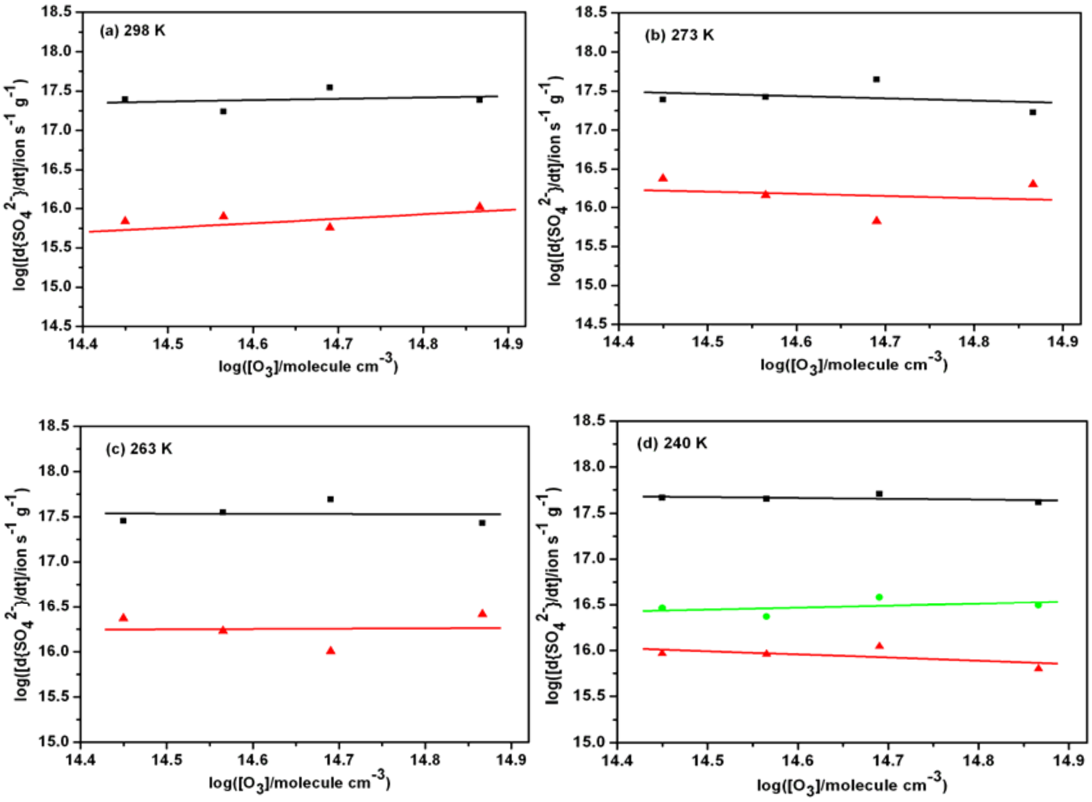


**Fig.S2.** Double-logarithmic plot of the rate of sulfate formation as a function of the concentration of $O_3$ at (a) 298 K, (b) 273 K, (c) 263 K, and (d) 240 K. ■, ●, and ▲ represent the data of the initial region, the transition region, and the saturation region, respectively.

*Secondly, two aspects suggested that the whole process of sulfite formation which involved both reaction (R1) and reaction (R2) determined the rate instead of the reaction (R2) solely. On the one hand, the evolution of the integrated absorbance of the sulfite band and sulfate during the sequential exposure experiment to $SO_2$ and $O_3$ was illustrated in Fig.S3.*

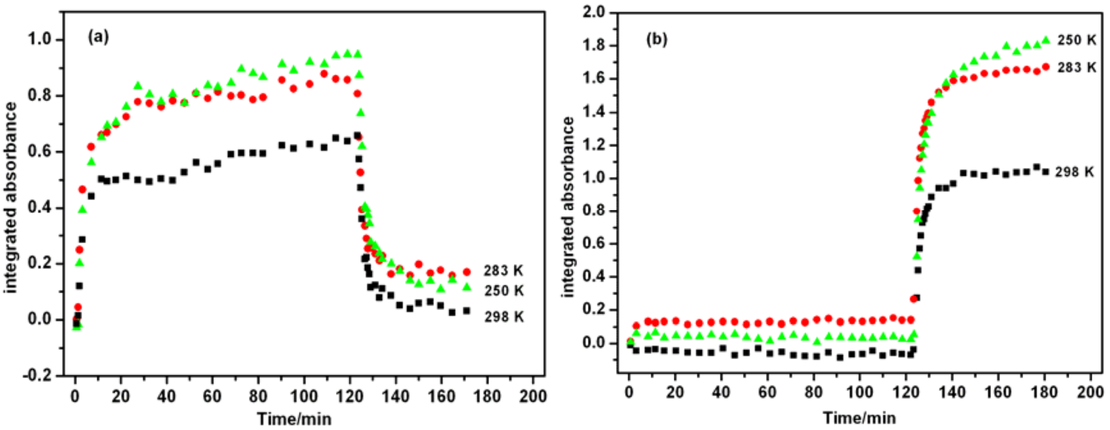


**Fig.S3.** The evolutions of the integrated absorbance of the sulfite band (a) and the sulfate band (b) during the sequential exposure experiments that the $O_3$ was introduced in the reaction system after the adsorption of $SO_2$ for 120 min.

*This experiment indicated that* $SO_2$ *can adsorb on* $CaCO_3$ *surface to form sulfite and then sulfite can immediatly be oxidized to sulfate in the presence of ozone. Compared to the oxidation of sulfite, it takes more time for the formation of sulfite to be saturation. On the other hand, no kinetic parameters are available for the S(IV) oxidation involving* $SO_2{\cdot}H_2O$*,* $HSO_3^-$ *or* $SO_3^{2-}$ *on particle surfaces so far, the corresponding aqueous-phase kinetic parameters are used as an estimation(Li et al., 2006). For the aqueous phase reaction:* $S(\mathrm{IV}) + O_3 \rightarrow S(\mathrm{VI}) + O_2$*, the expression for the rate of the reaction of S(IV) with dissolved ozone is:*

$$R_0 = -\frac{\mathrm{d[S(IV)]}}{\mathrm{dt}} = (k_0[SO_2.H_2O] + k_1[HSO_3^-] + k_2[SO_3^{2-}])[O_3]$$

*with* $k_0$*=2.4±1.1×*$10^4 M^{-1}s^{-1}$*,* $k_1$*=3.7±0.7×*$10^5 M^{-1}s^{-1}$*,* $k_2$*=1.5±0.6×*$10^9 M^{-1}s^{-1}$*(Hoffmann and Calvert, 1985). The rate constants above indicated that the reaction between* $SO_3^{2-}$ *and* $O_3$ *was the most rapid. Therefore, the whole process of sulfite formation determined the rate of sulfate formation. And we have stated them in our revised version.*

*Page 3504 between line 12 and line 13: we added one paragraph "A series of experiments were carried out as a function of ozone concentration at four model temperatures. Double-logarithmic plots of the rate of sulfate formation as a function of the concentration of* $O_3$ *at 298 K (Fig.S2a), 273 K (Fig.S2b), 263 K (Fig.S2c), and 240 K (Fig.S2d) give a series of slopes from a linear regression. All of these slopes are close to zero, indicating zero-order rate law for* $O_3$ *in the heterogeneous oxidation of* $SO_2$ *on* $CaCO_3$ *surface and the rate of sulfate formation is approximate independence of the* *concentration of* $O_3$*.”*

*Page 3505 line 3: The sentence “The reaction (R2) is the rate determining step in the whole mechanism.” was deleted*

*Page 3505 line 20-24: to express more clearly, the sentence in section 3.2.2 “Based discussion above, …… Where k is the rate constant:* $k = \frac{k_1 k_2}{k_{-1} + k_2}$*.” was rewritten in page 3505 between line 2 and line 3: “Thus, the rate of sulfate formation was deduced according to the steady-state approximation, which had been described in detail elsewhere (Li et al., 2006).*

$$\mathrm{r} = \frac{d\{\mathrm{SO_4^{2-}}\}}{dt} = \frac{k_1 k_2}{k_{-1} + k_2}[\mathrm{SO_2}] = k[\mathrm{SO_2}] \qquad (1)$$

*Where k is the rate constant:* $k = \frac{k_1 k_2}{k_{-1} + k_2}$.

*From eq. (1), we can see that the reaction is zero order for* $O_3$*. Therefore, the reaction order deduced from the proposed mechanism is well consistent with the experiment results shown in Fig.S2.*

*According to eq. (1), the sulfate formation rate is dependent on* $k_1$*,* $k_{-1}$*,* $k_2$*, which are related to the formation of sulfite. That means, reaction (R1) and reaction (R2) determined the rate simultaneously. On the one hand, the evolution of the integrated absorbance of the sulfite band and sulfate during the sequential exposure experiment to* $SO_2$ *and* $O_3$ *was illustrated in Fig.S3. This experiment indicated that* $SO_2$ *can adsorb on* $CaCO_3$ *surface to form sulfite and then sulfite can immediatly be oxidized to sulfate in the presence of ozone. Compared to the oxidation of sulfite, it takes more time for the formation of sulfite to be saturation. On the other hand, no kinetic parameters are available for the S(IV) oxidation involving* $SO_2{\cdot}H_2O$*,* $HSO_3^-$ *or* $SO_3^{2-}$ *on particle surfaces so far, the corresponding aqueous-phase kinetic parameters are used as an estimation(Li et al., 2006). For the aqueous phase reaction:* $S(\mathrm{IV}) + O_3 \rightarrow S(\mathrm{VI}) + O_2$*, the expression for the rate of the reaction of S(IV) with dissolved ozone is:* $R_0 = -\frac{\mathrm{d[S(IV)]}}{\mathrm{dt}} = (k_0[SO_2.H_2O] + k_1[HSO_3^-] + k_2[SO_3^{2-}])[O_3]$ *with*

*$k_0$=2.4±1.1×$10^4M^{-1}s^{-1}$, $k_1$=3.7±0.7×$10^5M^{-1}s^{-1}$, $k_2$=1.5±0.6×$10^9M^{-1}s^{-1}$(Hoffmann and Calvert, 1985). The rate constants above indicated that the reaction between $SO_3^{2-}$ and $O_3$ was the most rapid."*

*Page 3514 between line 9 and line 10: A new reference (Hoffmann and Calvert, 1985) due to modification was added to references in revised version. "Hoffmann , M. R., and Calvert, J. G.: Chemical transformation models for eulerian acid deposition models, The Aqueous-phase Chemistry, EPA/600/3-85/017, U.S. Environment Protection Agency, Research Triangle Park, NC, 2, 1985."*

*References:*

*Li, L., Chen, Z. M., Zhang, Y. H., Zhu, T., Li, J. L., and Ding, J.: Kinetics and mechanism of heterogeneous oxidation of sulfur dioxide by ozone on surface of calcium carbonate, Atmos. Chem. Phys., 6, 2453-2464, doi:10.5194/acp-6-2453-2006, 2006.*

*Hoffmann , M. R., and Calvert, J. G.: Chemical transformation models for eulerian acid deposition models, The Aqueous-phase Chemistry, EPA/600/3-85/017, U.S. Environment Protection Agency, Research Triangle Park, NC, 2, 1985.*

**Comment 5: Figures 5 & 7. As the authors state, "it is scarce that turning point appears at the experimental temperatures." Unexpected results require conclusive supporting evidence. The experimental and data discussion, however, is lacking many details which the authors need to address to support the robustness of this data. How were the error bars determined? Were they the result of replicate experiments at each temperature? The "relationship between formation rate of sulfate and temperature" (i.e., Fig. 5) matches that pattern of the t=200 minute concentration of sulfate vs. temperature (Fig. 7). I am concerned that the effect of temperature on rate may simply be a result of the effect of temperature on the final sulfate IR signal – is this trend supported by replicate experiments? I do not understand the authors' arguments for this trend. The authors should analyze each reacted sample using ion chromatography to confirm the linear correlation between their final sulfate IR signal (which was recorded at different temperatures)**

**and the final analyzed IC sulfate concentration? Finally, what are the solid lines included in these figures?**

REPLY: *The supporting evidence and data discussion for turning point will be given in replying to comment 7 in detail.*

*The experiments at each temperature were replicated at least three times to get closer to the true mean result***.** *Therefore, standard deviation (SD) was used for descriptive error bars in our manuscript.*

*First of all, we should apology for misleading the referee to understand that ion chromatography was used to the linear correlation between sulfate IR signal and sulfate concentration. Since* $CaSO_4$ *is slightly soluble in water, ion chromatography is not suitable equipment for quantifying the sulfate ions. Referencing the method of the linear correlation in the literature (Martin et al., 1987;Li et al., 2006), the amount of sulfate ions formed during the reaction on the particulate sample was determined by the DRIFTS calibration curves made by mixing the weighted pure* $CaSO_4$ *uniformly in* $CaCO_3$ *to a certain concentration in our experiments. To avoid misleading, we have revised some sentences in the revised paper.*

*Page 3499 line 16-20: the sentence "DRIFTS can provide mechanistic details not available through other methods and the kinetics data can also be obtained (Vogt and Finlaysonpitts, 1994), and it was also possible to determine the reactive uptake coefficient by calibrating the infrared absorbance with ion chromatographic analysis of reacted samples." was revised to "DRIFTS can provide mechanistic details not available through other methods and the kinetics data can also be obtained (Vogt and Finlaysonpitts, 1994), and it was also possible to determine the reactive uptake coefficient."*

*Page 3506 line 5-8: the sentence "In order to quantify the rate of sulfate ……*$CaCO_3$ *to a certain concentration." was revised to "In order to quantify the rate of sulfate formation* $d\{SO_4^{2-}\}/dt$*, the amount of sulfate ions formed during the reaction on the particulate sample was determined by the DRIFTS calibration curve. Referencing the method of the linear correlation in the literature (Martin et al., 1987;Li et al., 2006), the DRIFTS calibration curve was made by mixing the weighted pure* $CaSO_4$ *uniformly in*

*$CaCO_3$ to a certain concentration."*

*Thanks the referee for pointing out an important issue that the temperature would affect the final sulfate IR signal. But it is still a debatable question (Hermann and Harvey, 1969). Avery et al. stated that the width of infrared bands narrowed when molecules were cooled (Avdry and Ellis, 1942). However, Walsh and Willis (Walsh and Willis, 1949, 1950) reported that narrowing of IR bands was not of general occurrence and stated that narrowing occurs only in molecules which undergo changes of state in the temperature range of the particular study. At the beginning of our study on effects of temperature on the heterogeneous oxidation, an experiment had been carried out to investigate whether the temperature would affect the IR signal or not. In this experiment, the integrated absorbance of sulfate with the same concentration (2.4 mg/g) was investigated as a function of temperature (as shown in Fig.S1). The slope, which was close to zero, indicated that the IR signal intensity of sulfate was approximately independent of temperature in the temperature range used in our study. We are sorry for not declaring this conclusion in our manuscript. We have stated this conclusion in revised version.*

*Page 3503 line 17: After "at ambient pressure had been studied.", we added some sentence in revised version. "At the beginning of this study, an experiment was carried out to investigate whether the temperature would affect the IR signal or not. In this experiment, the integrated absorbance of sulfate with the same concentration (2.4 mg/g) was investigated as a function of temperature (as shown in Fig.S1). The slope, which was close to zero, indicated that the IR signal intensity of sulfate was approximately independent of temperature in the temperature range used in our study. On the basis of this conclusion, series of following experiments were done."*

*The solid lines included in Fig.5 and Fig.7 were obtained by connecting the data points through B-Spline in Origin 7.0 soft. To avoid misunderstanding, we have deleted the solid lines in Fig.5 and Fig.7 in revised paper. The revised figure will be shown in following comment.*

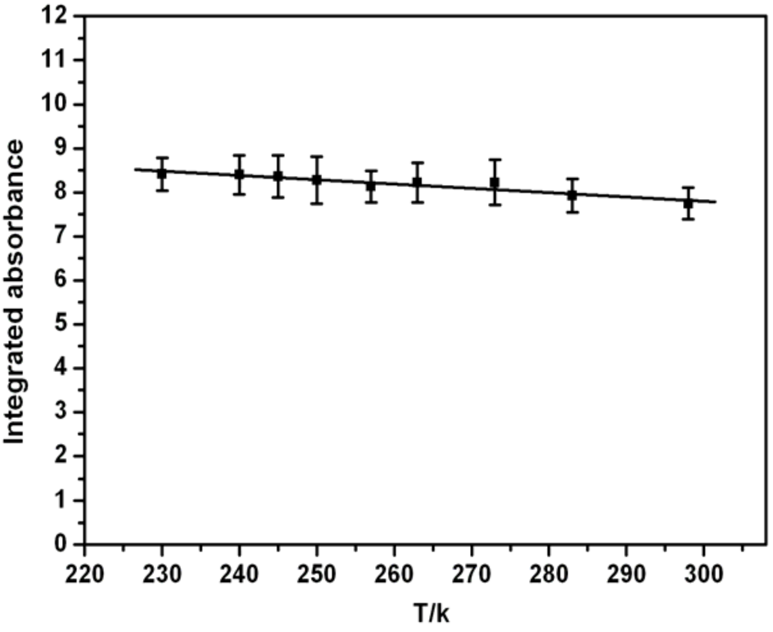


**Fig.S1.** The integrated absorbances of sulfate with the same concentration (2.4 mg/g) as a function of temperature. The slope from a linear regression was determined to -0.00969±0.0845(σ).

*References:*

*Avdry, W. H., and Ellis, C. F.: Infra-red spectra of hydrocarbons I Some investigations of the temperature dependence of absorption bands, J. Chem. Phys., 10, 10-18, 1942.*

*Hermann, T. S., and Harvey, S. R.: Infrared spectroscopy at sub-ambient temperatures I. literature review, Appl. Spectrosc., 23, 435-450, 1969.*

*Li, L., Chen, Z. M., Zhang, Y. H., Zhu, T., Li, J. L., and Ding, J.: Kinetics and mechanism of heterogeneous oxidation of sulfur dioxide by ozone on surface of calcium carbonate, Atmos. Chem. Phys., 6, 2453-2464, doi:10.5194/acp-6-2453-2006, 2006.*

*Martin, M. A., Childers, J. W., and Palmer, R. A.: Fourier-Transform Infrared Photoacoustic-Spectroscopy characterization of sulfur-oxygen species resulting from the reaction of $SO_2$ with CaO and $CaCO_3$, Appl. Spectrosc., 41, 120-126, 1987.*

*Walsh, A., and Willis, J. B.: Infra-red absorption spectra at low temperatures, J. Chem. Phys., 17, 838-838, 1949.*

*Walsh, A., and Willis, J. B.: Infra-red absorption spectra at low temperatures, J. Chem. Phys., 18, 552-556, 1950.*

**Comment 6: Figure 6 is redundant since it simply shows three data points from Figure 5.**

REPLY: *Thanks for the referee's suggestion. Fig.6 has been deleted in our revised paper and the corresponding number of figure has been modified in the text.*

*Page 3506 line 28: "Figure 6 shows the linear regression of the rate of sulfate formation d{*$SO_4^{2-}$ *}c/dt with the reciprocal value of temperature(1/T ).*" *was corrected to be "Figure 5 shows the linear regression of the rate of sulfate formation d{*$SO_4^{2-}$ *}/dt with the reciprocal value of temperature(1/T ) at temperatures between 245 K and 230 K.".*

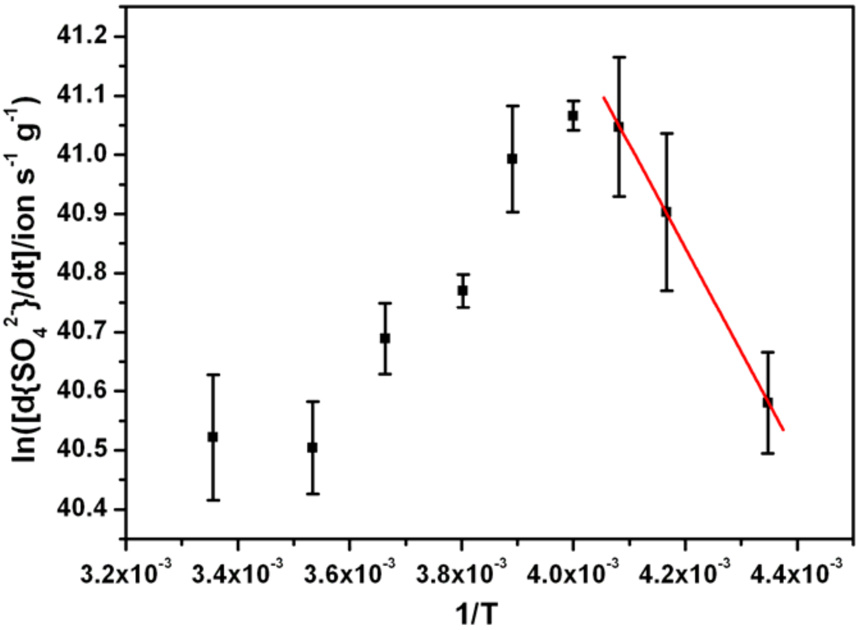


**Fig.5.** The relationship between formation rate of sulfate and temperature. The red solid line is the linear regression of the rate of sulfate formation *d*{$SO_4^{2-}$}/*dt* with the reciprocal value of temperature (1/T) at temperatures below 250 K. The slope is -1759.24±23.58(σ).

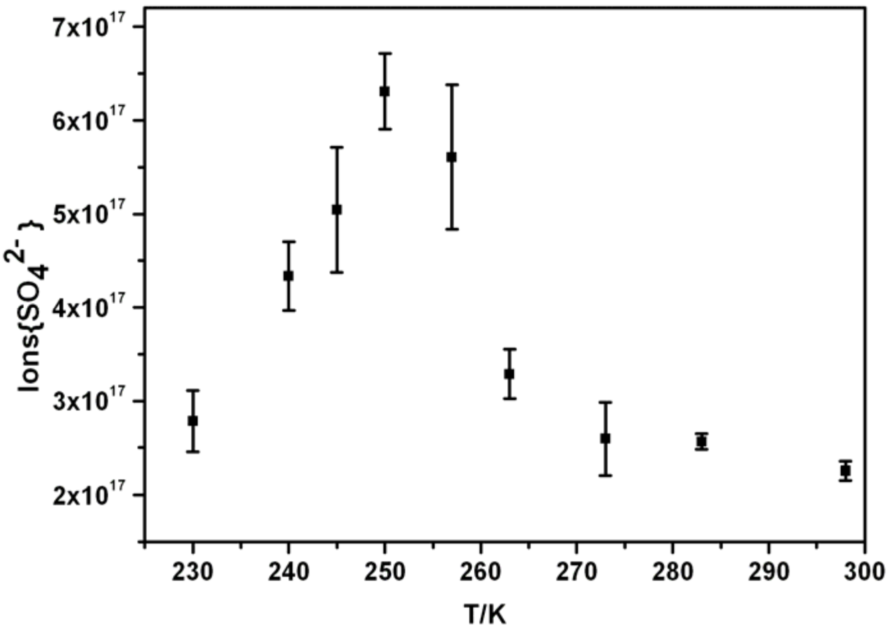


**Fig.6.** The concentrations of sulfate ions at different temperatures after $CaCO_3$ particles exposed simultaneously to $SO_2$ ($4.9\times10^{14}$ molecules $cm^{-3}$) and $O_3$ ($4.9\times10^{14}$ molecules $cm^{-3}$) for 200 min.

**Comment 7: A rigorous discussion of the turning point is lacking from this paper. At present, they simply discuss why one might expect the rate to increase with temperature and why one might expect the rate to decrease with temperature. They fail, however, to explain their major claim which is how their system transitions from one relationship to the next. The arguments put forth by the authors should be consistent with the steady state equation (1) considering the temperature dependence of k1, k-1, and k2 – and I am not sure this is the case. This article requires extensive work and revisions that must include a convincing discussion and explanation of this observation.**

REPLY: *Thanks for the referee's advice so that we could gain more insights into the turning point. As replying to comment 4, our proposed mechanism is reasonable and the whole process of sulfite formation determined the sulfate formation rate. On the basis of this conclusion, we discussed the turning point in more detail and revised the discussion in revised version.*

*Page 3507 line 10-26: the whole paragraph "Two aspects are tried to interpret temperature effect ……Therefore, a maximum value of sulfate concentration on* $CaCO_3$

*was appeared at about 250 K." was revised to "According to the eq.(1), the rate of sulfate formation was proportional to the rate constant and the concentration of gas-phase* $SO_2$*. Since the concentration of gas-phase* $SO_2$ *was kept constant, the rate constant was the only factor that influenced the rate of sulfate formation. All of rate constants (*$k_1$*,* $k_{-1}$*, and* $k_2$*) would decrease as the temperature decreasing in terms of Arrhenius expression. The reactions to the right that were favor of sulfate formation would slow as* $k_1$ *and* $k_2$ *decreasing while the reaction to the left that hindered from sulfate formation would also slow as* $k_{-1}$ *decreasing. The balance of these two opposite situation determined temperature effect on the rate of sulfate formation. According to* $k = \frac{k_1 k_2}{k_{-1} + k_2}$ *, two extreme cases of the rate constant needed to be considered. If the value of* $k_{-1}$ *was small enough to be neglected compared to* $k_2$*, then the rate constant k would approach* $k_1$*. In this case, the adsorption of gas-phase* $SO_2$ *to the surface of* $CaCO_3$ *was the rate determining step in the whole mechanism and the reaction to the left was nearly negligible. The apparent activation energy is expressed as:*

$$E_a = RT^2 \frac{d \ln k}{d(1/T)} = RT^2 \frac{d \ln k_1}{d(1/T)} = E_{a1} \qquad (3)$$

*Where* $E_a$ *is the apparent activation energy, and* $E_{a1}$ *is the activation energy for the adsorption of gas-phase* $SO_2$ *to the surface of* $CaCO_3$*. The apparent activation energy is a positive value in this case for* $E_{a1}$ *is larger than zero. On the contrary, if* $k_2$ *was small enough to be neglected compared to* $k_{-1}$*, the rate constant k would approach* $\frac{\mathrm{k}_1 k_2}{k_{-1}} = K k_2$*, where K is the equilibrium constant of reaction (R1). Thus the apparent activation energy can be expressed as:*

$$E_a = RT^2 \frac{d \ln k}{d(1/T)} = RT^2 \frac{d \ln(K\mathrm{k}_2)}{d(1/T)} = RT^2 \frac{d \ln(K)}{d(1/T)} + RT^2 \frac{d \ln(k_2)}{d(1/T)} = \Delta H_{ads} + E_{a2} \qquad (4)$$

*Where* $E_{a2}$ *is the activation energy for the reaction between the adsorbed-phase* $SO_2$ *and* $CaCO_3$*.* $E_{a2}$ *must be smaller than 20 kJ/mol for the reactions with the activation energy greater than 20 kJ/mol are regarded to be too slow to play a significant role in* *atmospheric chemistry (Smith, 2003).* $\Delta H_{ads}$ *is the enthalpy for gas-phase* $SO_2$ *adsorption on* $CaCO_3$ *surface. It has been reported that the reversible adsorption of gas-phase* $SO_2$ *is exothermic (Clegg and Abbatt, 2001). Therefore, it is reasonable to give that* $\Delta H_{ads}<0$*. To our knowledge, there is no direct value of the enthalpy for gas-phase* $SO_2$ *adsorption on* $CaCO_3$ *surface so that available enthalpy values (-26.13 kJ/mol) for* $SO_2$ *adsorption on water surface (Conklin and Bales, 1993) is used to estimate. Therefore,* $E_{a2}$ *can be a negative value and the reaction to the right play a critical role in this case. These two extreme cases should be combined to interpret temperature effect on the rate of sulfate formation.*

*As shown in Fig.5, the activation energy for the whole reaction is a negative value at temperatures from 298 to 250 K. According to the above two extreme cases, the value of* $E_a$ *could exist as negative value only if the second extreme case dominated in the whole reaction. That means, the reactions to the right that were favor of sulfate formation dominated in the whole heterogeneous reaction at high temperature. At temperature below 250 K, the activation energy for the whole reaction was determined to be 14.63 ± 0.20 kJ/mol. It suggested that the first extreme case became more and more important. Less high active sites could be acquired as the temperature decreasing so that the adsorption of gas-phase* $SO_2$ *became slow and then played an important role in the whole reaction at temperature below 250 K. When the reactions to the right that were favor of sulfate formation was equal to the reaction to the left that hindered from sulfate formation, the turning point emerged. And at this moment, the apparent activation energy approached zero."*

*Page 3508 line 11: "(3)" was revised to "(5)".*

*Page 3508 line 12: "(4)" was revised to "(6)".*

*Page 3508 line 13: "(5)" was revised to "(7)".*

*Page 3510 line 16: "Eqs. (2), (3), and (4)" was revised to "Eq. (5), (6), and (7)".*

*Page 3513 between line 11 and line 12: A new reference (Conklin and Bales, 1993) due to modification was added to references in revised version. "Conklin, M. H., and Bales, R. C.:* $SO_2$ *uptake on ice spheres - liquid nature of the ice-air interface, J. Geophys.*

*Res.-Atmos., 98, 16851-16855, 1993.”*

*Reference:*

*Clegg, S. M., and Abbatt, J. P. D.: Uptake of gas-phase* $SO_2$ *and* $H_2O_2$ *by ice surfaces: Dependence on partial pressure, temperature, and surface acidity, J. Phys. Chem. A, 105, 6630-6636, 2001.*

*Conklin, M. H., and Bales, R. C.:* $SO_2$ *uptake on ice spheres - liquid nature of the ice-air interface, J. Geophys. Res.-Atmos., 98, 16851-16855, 1993.*

*Smith I. W. M.: Laboratory studies of atmospheric reactions at low temperatures, Chem. Rev., 103, 4549-4564, 2003.*