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 #1 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.

—REPLY TO COMMENTS BY REFEREE #1—

Comment 1: Text is full of vague expressions (transition state, for example), that could mean many things and usually are used in different context. Authors should clearly revisit the text to use adequate language, proper for the context of current field.

REPLY: *We greatly thank the reviewer #1.*

Following the reviewer’s suggestion, we have checked the whole paper carefully and modified the vague expressions in revised version. “The initial state”, “the transition state”, and “the steady state” were revised to “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 (γ_{ts})*” was revised to “the transition region uptake coefficient* (γ_{tr})*”.*

Page 3510 line 7: “the saturation state uptake coefficient (γ_{ss})*” was revised to “the transition region uptake coefficient* (γ_{tr})*”, “the saturation region uptake coefficient* (γ_{sr})*”, respectively.*

Page 3523 Fig. 3: “t=IS”, “t=TS”, and “t=SS” were revised to “Ⅰ”, “Ⅱ”, and “Ⅲ”, respectively.

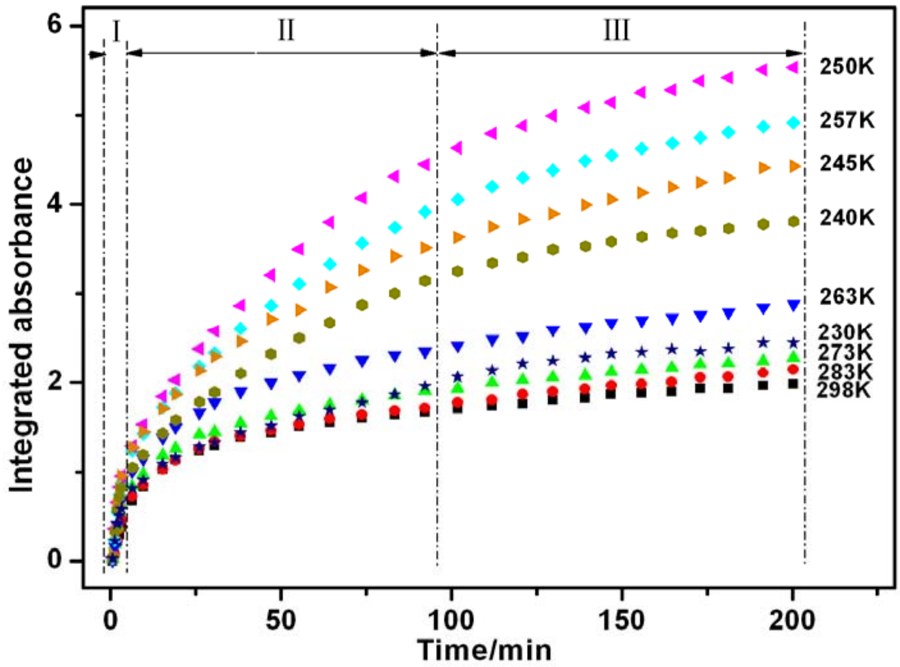

Fig.3. The integrated absorbance of 1012–1240 cm^{-1} for sulfate formed during the reaction at series temperatures as functions of reaction time. I , II , III stand for initial region, transition region, and saturation region, respectively.

Table 2. Reactive uptake coefficient for SO_2 (4.9×10^{14}molecules cm^{-3}) and O_3 (4.9×10^{14}molecules cm^{-3}) on $CaCO_3$ at series of tropospheric temperatures.

T/K	γ_0		γ_{tr}		γ_{sr}	
	Geometric 10^{-4}	BET 10^{-7}	Geometric 10^{-5}	BET 10^{-8}	Geometric 10^{-6}	BET 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

In addition, according to the reference (Usher et al., 2003), we revised other expressions to be more proper for the context of atmospheric chemistry field, such as:

Page 3494 line 12: "the model studies" was revised to "atmospheric chemistry modeling studies".

Page 3495 line 27: "models" was revised to "atmospheric chemistry models".

Page 3495 line 29: "the model" was revised to "the modeling studies".

Page 3512 line 11: "the model studies" was revised to "the modeling studies"

Page 3497 line 5, Page 3509 line 12 and Page 3509 line 14: "atmospheric models" was revised to "atmospheric chemistry models".

Page 3496 line 5, Page 3497 line 27, Page 3509 line 12, and Page 3510 line 5: "model studies" was revised to "atmospheric chemistry modeling studies".

References:

Usher, C. R., Michel, A. E., and Grassian, V. H.: Reactions on mineral dust, Chemical Reviews, 103, 4883-4939, 2003.

Comment 2: Figures 1 and 2 are not informative and, even more so, confusing. Why are there negative-positive peaks 870 cm-1 in Figure 1 and why are they alternating with no particular order in temperature? If they are subtraction artifacts, how can authors believe other data shown in their spectra?

REPLY: *Thank you very much for the Referee's conscientiousness on our present article. We are sorry for making the referee confused. To express more clearly, we revised the figure caption in Fig.1 and Fig.2.*

Page 3521: "Fig.1. In situ DRIFTS spectra (absorbance units) of surface products when $CaCO_3$ *particles were exposed simultaneously to* SO_2 *(*4.9×10^{14} *molecules* cm^{-3}*) and* O_3 *(*4.9×10^{14} *molecules* cm^{-3}*) for 200 min at different temperatures under dry conditions (RH<1%). The spectra were ordered by increasing sulfate intesity."*

Page 3522: "In situ DRIFTS spectra of surface products when $CaCO_3$ *particles were exposed sequentially to* SO_2 *(*4.9×10^{14} *molecules* cm^{-3}*) and* O_3 *(*4.9×10^{14} *molecules* cm^{-3}*). (a), (b), (c) showed the product spectra when the adsorption rate becomes stable after addition of* SO_2 *at 298 K, 263 K and 250 K, respectively. (d), (e), (f) show the product* *spectra when the SO_2 flow was cut off, and O_3 was introduced into the reaction system for 60 min at 298 K, 263 K and 250 K, respectively."*

As the referee pointed out, there existed there negative-positive peaks around 870 cm^{-1}(exactly at 878 cm^{-1}). 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} which were alternating with no particular order in temperature 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.

There was no absorbance bands of $CaCO_3$ sample appeared in the region between 900 cm^{-1} and 1300 cm^{-1} so that this kind of spectral noise couldn't affect the data of products on $CaCO_3$ surface.

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."

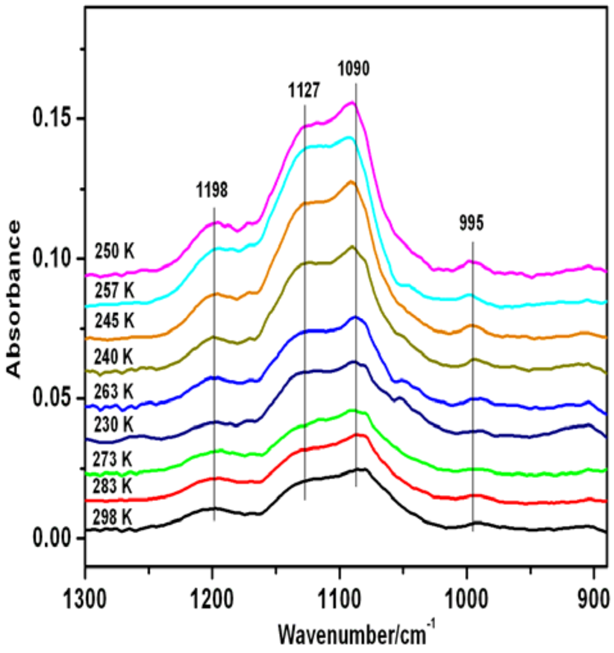

Fig.1. In situ DRIFTS spectra (absorbance units) of surface products when $CaCO_3$ particles were exposed simultaneously to SO_2 (4.9×10^{14} molecules cm^{-3}) and O_3 (4.9×10^{14} molecules cm^{-3}) for 200 min at different temperatures under dry conditions (RH<1%). The spectra were ordered by increasing 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 3: I personally don't think authors revealed the nature of sulfate formation "hump" shown in Figures 5 and 7. A proper molecular mechanistic explanation must be given borderline with chemistry or any other more rigid discipline to explain underlying phenomena.

REPLY: *We thank the referee's suggestion to improve our paper. As the referee's suggestion, we discussed the turning point in Fig.5 and Fig.7 in more detail from the point of view of physical chemistry. Analyzing the data in our experiments carefully, we found that the whole process of sulfite formation which involved both reaction (R1) and reaction (R2) determined the rate of sulfate formation. And we have 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 $\frac{\mathrm{k}_1 k_2}{k_{-1}} = Kk_2$*, 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). ΔH_{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.