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Comment

## ***Interactive comment on “Kinetics and mechanisms of heterogeneous reaction of NO<sub>2</sub> on CaCO<sub>3</sub> surfaces under dry and wet conditions” by H. J. Li et al.***

### **Anonymous Referee #1**

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This manuscript discusses experiments on the heterogeneous reaction of nitrogen dioxide on calcite surfaces, emphasizing the effects of relative humidity and surface adsorbed water. The data – primarily infrared data collected using DRIFTS – presented in this manuscript are of interest to the atmospheric chemistry community. However the presentation, discussion and conclusions based on this data require significant revisions. In revising this manuscript the authors should address the following issues, which are presented roughly in order of appearance in the manuscript (not in order of relative importance).

1. The manuscript repeatedly mentions that SEM analysis of the particles was per-

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formed (e.g., Abstract line 10; page 7118, line 21; page 7119, line 7). However, no details are given in the experimental section and no data/results are presented. The authors assume a cubic shape for  $\text{CaCO}_3$  particles, which becomes important for calculating the uptake coefficient at higher RH. An SEM image should be included in the supplemental information and discussed in relation to the assumed cubic shape.

2. The authors calculate that 3.4-3.6% of the oxygen atoms correspond to  $-\text{Ca}(\text{OH})$  sites (page 7120, line 26). Since XPS analyzes the bulk sample, it would be more insightful to estimate the percentage of surface sites corresponding to  $-\text{Ca}(\text{OH})$  sites versus  $-\text{Ca}(\text{CO}_3\text{H})$  sites.

3. The  $\text{NO}_2$  concentrations used in these experiments are orders of magnitude higher than found even in the most polluted regions ( $4.81 \times 10^{15}$  to  $1.22 \times 10^{16}$  molecules  $\text{cm}^{-3}$  for  $\text{RH} < 10\%$  versus  $5 \times 10^{12}$  molecules  $\text{cm}^{-3}$  in extremely polluted regions and more typically  $2 \times 10^{11}$  molecules  $\text{cm}^{-3}$ ). This significant difference should be acknowledged and discussed in the paper. This also has great implications for the low RH studies, in which the authors conclude that  $\text{N}_2\text{O}_4$  is the reactive species. The concentration of  $\text{N}_2\text{O}_4$  in their experiments is never calculated – yet they range from  $5.7 \times 10^{12}$  to  $3.7 \times 10^{13}$  molecules  $\text{cm}^{-3}$ , which is considerably higher than equilibrium concentrations at tropospheric levels ( $1 \times 10^4$  molecules  $\text{cm}^{-3}$  in remote regions and  $6 \times 10^6$  molecules  $\text{cm}^{-3}$  in extremely polluted regions). If uptake coefficients were calculated for  $\text{N}_2\text{O}_4$  at low RH, does this reaction likely compete with  $\text{HNO}_3$ ?

4. Figure 1. It appears that the black squares (left axis) and open circles (right axis) are the same data with the left and right axes scaled differently, making the data redundant. The right axis should be scaled to correlate with the left, thus requiring only one set of data points. The line appears to be arbitrary; instead, the authors should include the BET best fit line. The authors should also review Al-Hosney, H. A., and Grassian, V. H.: Water, sulfur dioxide and nitric acid adsorption on calcium carbonate: A transmission and ATR-FTIR study, *Phys. Chem. Chem. Phys.*, 7, 1266-1276, 2005. This article presents an extensive discussion of surface adsorbed water that the authors should

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consider in their discussion.

5. Figure 2 and Figure 10. It appears that these two figures present the same data, merely plotted using different variables (although Fig. 2 has one less data point). This presentation is redundant. I suggest eliminating Figure 10 and moving Figure 2 along with its discussion (page 7121, line 13 through page 7122, line 7). The effect of surface adsorbed water on the reaction with  $\text{NO}_2$  might fit more naturally after Section 3.3.

6. Figure 4 and page 7123, lines 20-24. These plots appear to follow normal saturation curves consistent with the formation of a “passivation layer,” where calcium nitrate products remain immobile and unreactive. Such plots could be fit with an appropriate saturation model; thus, the benefits of dissecting these kinetic plots into three regions remain unclear.

7. Figure 5. When calculating  $\ln\{\text{dNO}_3^-/\text{dt}\}$  for region I of the  $4.81 \times 10^{15}$  molecules  $\text{cm}^{-3}$  data set, were all data points between 0 and 50 minutes used? Clearly the number of reactive surface sites is decreasing during this time period as evidenced by the saturation behavior. Given this observation, it would be best to fit the initial linear portion (e.g., 0 – 15 minutes) of this data to determine  $\ln\{\text{dNO}_3^-/\text{dt}\}$ . This analysis, however, would increase  $\ln\{\text{dNO}_3^-/\text{dt}\}$  for the first two data points in Figure 5, resulting in a lower slope. Such an analysis might significantly challenge the concluded second order w.r.t.  $\text{NO}_2$  for this reaction, which is already a stretch based on the slope  $1.63 \pm 0.23$ . *Given the uncertainty in this analysis, I am greatly concerned by the strong mechanistic conclusions presented for low relative humidity. The authors need to carefully consider the interpretation of their data, and should revisit this analysis and their mechanistic conclusions.*

8. Figure 6. Why are Kulbelka-Munk units used in this figure? Why are absorbance units used everywhere else? Although Kulbelka-Munk units theoretically apply to diffuse reflectance spectroscopy, several studies note the utility of absorbance units for adsorption studies and heterogeneous reactions. The authors should be consistent

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with the presentation of their data or they should include a discussion in the text explaining any differences.

9. Figure 7 & Figure 8. Nitrate formation in Figure 8 appears linear for the  $\text{NO}_3^- \nu_1$  peak at  $1048 \text{ cm}^{-1}$ . The analysis in Figure 7 suggests saturation behavior for the  $\text{NO}_3^- \nu_3$  peak at  $1344 \text{ cm}^{-1}$ . Why is there a discrepancy? It is also very interesting to note that the surface adsorbed water levels off after 30 minutes, especially since calcium nitrate is of interest given its hygroscopic properties.

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Interactive comment on Atmos. Chem. Phys. Discuss., 9, 7115, 2009.

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