Parameterization of N$_2$O$_5$ Reaction Probabilities for Inclusion in CMAQ

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OBJECTIVES

- Develop a comprehensive parameterization for the heterogenous reaction probability of N$_2$O$_5$, as a function of temperature (T), relative humidity (RH), particle composition, and phase state, using:
  - All of the available laboratory measurements of γ on ammoniated sulfate and nitrate particles at tropospheric T and RH conditions
  - Rigorous statistical methods (e.g., significance test of each independent variable, weighting of each data point by the measurement uncertainty, defining extrapolation limits).
- Consider the effects of:
  - Phase changes (i.e., crystalization and ice formation), such that on aqueous particles exceeds that on solid particles
  - Particle acidity, by comparing laboratory data on NH$_4$HSO$_4$ with data on NH$_4$NO$_3$
- Nitrates, by comparing our parameterizations on (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$

PARAMETERIZATIONS

Using the laboratory data shown in Figure 2, we developed a parameterization for the heterogenous reaction probability of N$_2$O$_5$ as a function of T, RH, particle composition, and phase state. For details on the development of these equations, please see the extended abstract. The final parameterization is summarized below with coefficients given in Table 1 and subscripts defined as follows:

\[
\gamma_{\text{ambient}} = \gamma_{\text{sof}} + \gamma_{\text{d}} + \gamma_{\text{mix}} \gamma_{\text{aq}} + \gamma_{\text{mix}} \gamma_{\text{ice}}
\]

For atmospheric applications:

\[
\gamma_{\text{ambient}} = \gamma_{\text{sof}} + \gamma_{\text{d}} + \gamma_{\text{mix}} \gamma_{\text{aq}} + \gamma_{\text{mix}} \gamma_{\text{ice}}
\]

where:

\[
\begin{align*}
\gamma_{\text{sof}} &= \sum_{i} \gamma_{\text{sof},i} \\
\gamma_{\text{d}} &= \gamma_{\text{d}} \\
\gamma_{\text{mix}} \gamma_{\text{aq}} &= \gamma_{\text{mix}} \gamma_{\text{aq}} \\
\gamma_{\text{mix}} \gamma_{\text{ice}} &= \gamma_{\text{mix}} \gamma_{\text{ice}}
\end{align*}
\]

Constraints are applied to prevent extrapolations beyond the maximum laboratory measurement:

\[
\begin{align*}
\gamma_{\text{sof},i} &= \min(0, \gamma_{\text{sof},i}) \\
\gamma_{\text{d}} &= \gamma_{\text{d}} \\
\gamma_{\text{mix}} \gamma_{\text{aq}} &= \gamma_{\text{mix}} \gamma_{\text{aq}} \\
\gamma_{\text{mix}} \gamma_{\text{ice}} &= \gamma_{\text{mix}} \gamma_{\text{ice}}
\end{align*}
\]

CONCLUSIONS

- Developed a robust parameterization for γ as a function of T, RH, particle composition, and phase state, which can be incorporated into CMAQ.
- Parameterization reproduces 79% of the laboratory data within a factor of 2 and 53% within a factor of 1.25.
- Nitrate effect is quantified as only a factor of 1.4 – 4.4, rather than the factor of 10 proposed previously by Riemer et al. (2003).
- Parameterization captures the ~50% enhancement of γ on acidic NH$_4$HSO$_4$ particle surfaces relative to that on (NH$_4$)$_2$SO$_4$ surfaces.
- Parameterization of γ on aqueous particles exceeds that on solid particles. This is the first parameterization in which phase changes are considered explicitly.
- Our parameterization yields slightly larger values of γ than have been estimated during intensive summer/fall field campaigns (e.g., NCAQS, CARAT).
- During winter, large differences between our parameterization and Evans & Jacob (2005) arise from different extrapolations of the available laboratory data into typical winter conditions.
- Future improvements to our γ parameterization will require accurate measurements of the low-T and high-RH conditions typical of winter.

LITERATURE CITED


