

## ***Interactive comment on “Thermodynamics of the formation of sulfuric acid dimers in the binary (H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O) and ternary (H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O-NH<sub>3</sub>) system” by A. Kürten et al.***

**Anonymous Referee #2**

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This paper presents a comprehensive and detailed analysis of experiments, performed at the CERN CLOUD chamber, to determine the thermodynamic properties of the dimer formation in the systems listed in the title. In practice this means experimentally determining the evaporation rate of the dimer, calculating the equilibrium constant for dimer formation, and fitting to observations to determine the change in enthalpy  $dH$  and entropy  $dS$  for the dimer formation. These values are determined for the first time at temperatures  $<232\text{K}$ , which are relevant for the upper troposphere where new particle formation is known to occur and play an important role in both stratospheric and tropospheric processes. In addition these measurements, first estimates of the

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thermodynamics of the H<sub>2</sub>SO<sub>4</sub>-NH<sub>3</sub> cluster formation are also calculated.

The paper is very thorough and well-written, and covers an important topic in atmospheric chemistry and physics. I recommend it for publication with minor modifications. There are two relatively substantive changes I'd like to see; the other changes are technical.

1) There are several combinations of projects (CLOUD5 and CLOUD7), instruments (CIMS, API-TOF-MS, CI-API-TOF-MS), and conditions (with and without natural GCR-produced ions). It's very difficult for someone not intimately familiar with the CLOUD projects to understand which instruments contribute to which measurements and findings. Might it be possible to construct a text-based table which lists the various combinations of instruments and conditions that contribute to each finding? The rows might be the findings (e.g., evaporation rate of the dimer, thermodynamics of the ternary cluster) and the columns the various experiments (e.g., CLOUD5-charged; CLOUD7-neutral), and the content of each cell would be the instruments that were used. I simply lost track and spent much time flipping back and forth in the manuscript trying to make sense of the various combinations of measurements and analyses.

2) It should be possible to estimate the uncertainty in  $dH$  and  $dS$  determined from the H<sub>2</sub>SO<sub>4</sub>-NH<sub>3</sub> measurements. Without uncertainties the suggestion that the experimental measurements "agree" with quantum chemical calculations is pointless. Errors may be estimated as follows: experimental uncertainties are shown in Fig. 8. If the evaporation rates for H<sub>2</sub>SO<sub>4</sub>-NH<sub>3</sub> are adjusted to span the range of the observed uncertainty (rather than the arbitrary factor of 5 and 0.2 shown), you should be able to calculate a range of  $dH$  and  $dS$  that are consistent with the stated experimental uncertainties, even if these uncertainties are "high". This would be more scientifically useful than an estimate without uncertainties, which is essentially meaningless.

Technical corrections: a) p. 13962, line 18-19, please use Kelvins here as in the rest of the manuscript.

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b) Page 13963, and elsewhere. The instrument acronym definitions are repeatedly defined here, in the Abstract, and in Section 1. Just once, please. Same on p. 13965, line 17.

c) p. 13970, line 18. Was the tubing length not measured? Why is an estimate necessary?

d) p. 13975, line 16. "data are", not "data is". Check elsewhere in manuscript for consistency with this plural noun.

e) p. 13977, line 22. It might be helpful to plot the dimer evaporation rate at 220K as a function of RH to see the RH dependence and the validity of the exponent assumed.

f) p. 13987, line 14. The precision of the thermodynamic parameters given is excessive given the measurement uncertainties and the lack of error analysis.

g) Figure 7. Would it be possible to add error bars to Fig. 7b? I don't know whether the variations in the trend in signal with cluster size is significant or not.

Thank you for writing an interesting and well-written manuscript.

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