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Atmospheric Chemistry and Physics Discussions



# *Interactive comment on* "The adsorption of nitrogen oxides on crystalline ice" *by* T. Bartels et al.

**Anonymous Referee #2**

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The manuscript of Bartels et al. describes the adsorption of NOy species on ice. These experiments are very important towards assessing the atmospheric sinks of NOy species, especially those of cirrus cloud/contrail ice particles and polar snowpack. The impact of the gas-condensed phase partitioning of NOy has a direct effect on tropospheric photochemistry. In particular, the results for PAN are especially new to the community. Experimentally, these studies were conducted with various NOy species flowing through a packed column of small ice spheres with a negative temperature gradient. The NOy species contain the N-13 isotope which radioactively decays gamma rays. Gamma rays are then detected through the length of the column to assess adsorption properties. The use of isotopically-labeled NOy helps to separate background signals of adsorbates (e.g., any "ambient" nitrates in the water supply used to make ice will not show up in the data). The experiments appear to be carefully designed, but the



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actual results need more description and explanation. Although the results of these experiments are important to the field, the authors need to consider the comments outlined below before publication.

The most pressing issue about this manuscript concerns the characterization of the packed-ice column. First, what exactly is the temperature gradient along the column length? How linear is the gradient along the temperatures of interest? What is the setup for the temperature-controlled cryostat? More experimental details are needed. Because the results of the manuscript are so critically tied to the adsorption temperature, a plot of temperature versus column length under experimental conditions would be very helpful. How do the authors know that the temperature gradient of an empty column is representative (i.e. within a degree or so) of one with packed spheres of ice? The temperature gradients plotted in Figure 4 don't look very linear. Also, how does the temperature gradient change once a gas flow begins (with warmer, upstream gas impinging on colder, downstream ice particles)? A more direct measurement of column temperature of the packed ice is needed.

Secondly, I think more focus needs to be placed on experimental details and results, and less on speculative explanations that this experiment really can't address (e.g. number of free OH bonds on surface, quasi-liquid layers, etc.). The experimental data needs to be addressed very clearly and explained how/why it occurs when/where it does (e.g., NO peak adsorption at temperature T=?, NO2 T=?, etc.). To this end, I recommend plotting the column temperature in Figure 2 somewhere on the x-axis (temperature data is shown in Figure 4, but even that plot is confusing - I'd suggest simply converting the x-axis to temperature). The peak desorption temperatures should also be noted. I remain somewhat confused on how the "calculated" lines were drawn on Figure 2.

Finally, the boiling point discussion is irrelevant. Condensation will occur if the partial pressure of the NOy species is above its condensed phase vapor pressure at that temperature. To determine if NO2, for example, will condense, the partial pressure



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of NO2 should be compared to the vapor pressure of NO2 at a given column temperature. Clearly, the species should be condensing near the liquid nitrogen end of the column. 3 ppbv NO2 at atmospheric pressure leads to a partial pressure of 2.3e-6 Torr NO. In Figure 4, the peak adsorption temperature for NO2 is around 140 K. Based on extrapolated NO2 vapor pressure data from the NIST Chemistry Webbook (www.webbook.nist.gov), condensation will clearly be occurring at this temperature and partial pressure. Therefore, the NO2 results can simply be explained in terms of condensation.

Additional points:

1. What size sieves were used to select the ice particles? How does a calculation of geometric surface area (e.g. assume x mm id spheres, knowing the mass of ice, estimate surface area) agree with the BET surface area? A plot of a representative sample of BET surface area would also be helpful.

2. p. 8: The flow through the column is listed as 5-360 sccm. However, on page 12, it is noted that the gas flow of NO2 in the column is 5 sccm. Why the inconsistency?

3. Figure 5: HONO is also listed on the graph, but not the caption.

4. Because this study evaluates the uptake of NOy on ice in the laboratory, some mention or a short discussion/comparison (few sentences) of these results to the Weinheimer et al. (GRL, 25, 1725-8, 1998) field data of NOy uptake on an ice wave cloud should be made in the atmospheric implications section.

5. The discussion of thermodynamic parameters (enthalpy and entropy) is important in this manuscript, and the authors have explained their calculations in detail to their credit. However, the observable data (adsorption peak temperatures) are then fed into various models/assumptions. The derived enthalpies will thus only be as accurate as the intrinsic model assumptions, whether in the transport model or the entropy calculations. Because of the uncertainties in the transport process (e.g. the true temperature



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gradient under experimental conditions) and entropic calculations (as the authors note, adsorption at ice surfaces is incredibly complex), the derived adsorption enthalpies are subject to greater uncertainties than the sensitivity study presented here. The authors should be a bit more cautious with their final adsorption enthalpies numbers.

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Interactive comment on Atmos. Chem. Phys. Discuss., 2, 431, 2002.