

Interactive comment on “Collision dynamics and uptake of water on alcohol-covered ice” by E. S. Thomson et al.

Anonymous Referee #2

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The authors report on some interesting kinetic data on mass accommodation and evaporation at temperatures of upper tropospheric/lower stratospheric relevance using a model condensed phase. It is probed using a superthermal molecular beam of D₂O, and both the retention (sticking or uptake) as well as inelastic scattering and thermal desorption of D₂O is probed for different configurations of the ice/alcohol interface. The experiments are performed in an environmental cell at up to 10(-2) mbar total pressure which provides the link to atmospheric pressures and temperatures. The report relates a good story and the paper is written in a clear style and conveys an interesting aspect of molecular beam probing. The discussion is a bit lengthy and diffuse in view of the modest quality and quantity of data available. However, there are parts of the manuscript that are in need of more extensive explanations (see below). The reader is not reminded often enough of the superthermal probe used to gauge the kinetic pa-

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rameters. The authors must clarify the many different consequences of using a high energy molecular probe beam as a surrogate to a thermal probe at different locations in the text. After all, the kinetic energy of D2O is roughly a factor of 20 larger than thermal (RT at 200K), and this could bias the kinetic results that are intended to be applied to a thermal system.

I would like the authors to address the following questions to the benefit of the readers:

- Regarding the experimental technique I am a bit surprised that the authors can go up to 10(-2) mbar without gas-beam scattering. Of course, this depends on the scattering length, but my experience with a thermal molecular beam tells me that scattering (= attenuation) starts to be observed at a few 10(-5) mbar total pressure across a 10-15 cm scattering length. In addition, does the collinear geometry of the mass spectrometer lead to additional noise of the MS signals due to the fact that fast neutrals are reaching the SEM.

- Pg. 27644, lines 10-13: How do you deduce absolute accommodation coefficients "alpha"(T) from integrated thermal distributions? How do you quantitatively subtract the inelastically scattered fraction (still having a factor of roughly four larger than thermal energy) from the total? Do you use different calibrations for high-energy vs. thermal D2O? Is this the procedure outlined in equation (4)? Explanations are in order. On lines 13-15 the mass accommodation coefficient and the uptake coefficient are only numerically equal in the limit of no thermal (or nonthermal) desorption. Accommodation coefficients are not observable, uptake coefficients are.

- Pg. 27644, last §: Are the high values of s (or "alpha" = mass accommodation coefficient) a consequence of the high-energy molecular probe? For thermal systems significantly lower absolute values for "alpha" have been measured (see for instance the following URL: http://www.iupac-kinetic.ch.cam.ac.uk/datasheets/pdf/H2O+ice_V.A1.6.pdf). See also pg. 27646, line 13 and pg. 27652, lines 27/28.

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- How does the molecular scattering approach hang together with the flow reactor approach outlined on pg. 27645/646? The parameter “b” in equation (5) should correspond to the collision frequency “ ω ” ($= (A/V)\langle c \rangle/4$, with $\langle c \rangle$, A and V being the average molecular speed, the ice target surface area and the volume of the reactor, respectively) or should be proportional to it depending on the used units. Does the fitted value agree with a (semi)quantitative estimate of “ ω ”? In addition, $1/k$ from equation (1) should be comparable, better equal, to $1/k_{des}$ (equation (5)) or $(A/V)k_{des}$, depending on the used units. Do the two data treatments agree on these benchmarks? It is incumbent on the authors to show that both treatments are self-consistent and lead to similar parameters.

- Pg. 27648, last §, and pg. 27649, first §: Is the absence of any backscattered/“thermally” desorbing D2O an artifact owing to the high energy D2O-beam? My naïve expectation suggests to me that D2O molecules are slammed deep into the 1 micron-thick ice slab, never to be recovered during the time scale of the experiment. Another loss mechanism could be H/D exchange during the residence time of D2O inside the bulk. Have the authors looked for HDO coming out of the ice slab? Please compare with Chaix et al. (J. Phys. Chem. 1998, 102A, 10300-10309) who practically recovered all D2O when deposited onto H2O ice at 180 K when using a pulsed valve leading to a thermal plume of D2O.

- Pg. 27649, lines 1-4: How do the authors explain the absence of a temperature dependence for desorption rates for methanol covered ice? Is it because there is no or only a weak MS signal returned from the substrate? For pure ice we expect an activation energy of the desorption rate (for H2O) of 11.9 kcal/mol for $T < 190\text{K}$ according to Pratte et al. (Figure 11 in J. Phys. Chem. A 2006, 110, 3042-3058).

- Pg. 27651, lines 13-16: Regarding Figure 5 it seems to me that the authors overinterpret their data as far as temperature dependence is concerned. If you disregard both points at 175 and 172 K which are the points with the largest uncertainty, I cannot discern any T-dependence. Only two out of eight points are higher than the other six

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which do not show any T-dependence!

- Figure 4: Do the green (thermal) arrival time distributions correspond to 165 and 180 K, respectively?

- In section 4 and 5, Discussion and Conclusions, the authors must remind the reader more often of the non-thermal nature of their probe beam in order to avoid misleading the reader. The discussion comes across as diffuse and unfocussed, I do not know exactly what to think of it or what to take home. Please try to focus the discussion and leave out any unnecessary speculation.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 27637, 2012.

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