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Atmospheric Chemistry and Physics Discussions

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

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*Responses to Referees, "Collision dynamics and uptake of water on alcohol-covered ice" E. S. Thomson et al.*

We appreciate the anonymous referees' comments, which have been instructive and illuminated areas for improvement within our manuscript. As a result we have prepared a revised manuscript that thoroughly addresses the referees' questions. Additionally, below we sequentially address and/or point to changes in the text that address each comment.

**Anonymous Referee #1**

Numbers correspond to the specific comments of the referee:

1. In section 3.1 reference was made to Winkler et al. (2002) and Jedlovszky et al. (2006) who have observed and simulated monolayer coverages of methanol on ice. However, this was not made explicit and thus the text has been modified to make this clear. Additionally, the background discussion of methanol layers and mixing on pp. 27640 has been rewritten to be more clear and succinct, including references to the aforementioned citations at this point.

2. We agree that the wording here was confusing. The choice of the word, 'better' was unfortunate. Certainly, $k$ does not have to be forced to be $\gg 10^3$ s$^{-1}$. The intention was to reflect that when time constants exceed the experimental resolution, their choice is somewhat arbitrary. Thus, supplying a cutoff prevents searching for an experimentally irrelevant root and the choice also computationally simplifies the fitting calculation. This issue is intimately connected with the next point.

3. For each analyzed distribution it is verified that the parameters represent a global minimum of physically realistic parameters. However, it must be said that in most cases the minima are shallow with respect to multiple parameters. This fact leads to the uncertainty which presents itself in the error analyses. At times these shallow minima lead the algorithm to find unphysical solutions that must be discarded. As is clear from Equation (2) in the text $\bar{v}$ and $T_{\text{is}}$ can in fact somewhat compensate for each other – parameter limits to prevent this can be implemented by considering the physical system. However, compensating changes to these variables do not, in general, affect the shape of the total best fit inelastic distribution and therefore do not alter the inelastic integral. Thus, for this work we have excluded further discussion of these parameters.

To address points 2 & 3 the text following equation (3) has been modified for clarity.

4. We agree with the referee that here a positive statement is better and the text has been changed accordingly.

5. The error bars in Figure 3 (We gather this, not Figure 2, is the figure to which the referee is referring) are calculated by appropriately propagating the error associated

with the confidence intervals of the thermal desorption component integrals of the non-linearly fitted curves. Thus the error estimates of individual points vary based upon the quality of the data. Although the TOF distributions are normalized with respect to one another this does not prevent some data runs from being more noisy than others, which leads to varying degrees of uncertainty. Furthermore, the error analysis focused on the quantifiable uncertainty in individual measurements and does not directly address the reproducibility between differently prepared surfaces. These experiments are quite time intensive and thus getting a statistical sense of the reproducibility between different surfaces is prohibitive. In this case repeated experiments have shown reliable reproducibility (see e.g., the overlapping points at 170 K and 190 K), but in general we have chosen to present the highest quality, best constrained data. The points at 175 K represent surfaces prepared on different days, and thus the most likely explanation is that the different uptake coefficients result from small differences in the prepared surface.

In the revised manuscript a statement is added to more clearly acknowledge the different potential sources of uncertainty.

6. The caption has been altered to reflect that ‘higher’ temperatures are temperatures above 175 K.

7. After further reflection we agree with Referee #1 that our exclusion of data in Fig. 5 is unwarranted. Thus, we have remade the figure with a single regression line and redacted the text accordingly. Initially, the low activation energy of the full fit seemed surprising. However, experiments concerning $D_2O$ desorption from pure bulk butanol conducted since the original manuscript submission are indicative of similar Arrhenius parameters. [Aside: This is quite different from observations of butanol monolayers on graphite which we did examine in detail during this work and are referred to in the text.] Such activation energies may result from $D_2O$ interactions with the hydrocarbon tails of the system. The work on bulk butanol, including an effort to theoretically constrain the molecular interactions leading to such $E_a$ values are the subject of a recent submission

to JPCC (Papagiannakopoulos et al., 2013). While the presence of the underlying ice makes the systems quite different, attempting to understand both is mutually beneficial.

**Anonymous Referee #2**

One repeated concern of Referee #2 is the effect of the hyperthermal incident beam. We argue that our own observations and previous work indicate that our results should not be biased by the larger than thermal kinetic energies of the incident beam molecules. Simulations and experiments agree that the upper most layer of ice surfaces dissipate energy very efficiently due to the phonon spectrum of the crystal lattice (e.g., Bolton et al., 1999). This has been observed over a range of temperature for solid surfaces and for multiple incident molecular species (e.g., He, Ne, Ar, HCl, $H_2O$ Bolton et al., 1999; Andersson et al., 2000; Gibson et al., 2011). Furthermore, less than 3% of simulated trajectories show penetration beyond the first bilayer for kinetic energies of 1 eV and 45° incidence angles. Thus, we would expect that noticeable changes to the system kinetics, like molecular penetration into the bulk will only occur at much higher energies than we employ in this study. For clarity, the above references and a statement regarding the non-thermal incident energies has been added to the experimental section, where the kinetic energies are introduced.

Numbers correspond to the specific comments of the referee:

1. It appears Referee #2 has a slightly incorrect vision of the geometry of the experimental system – likely this results from our simplified experimental schematic in Fig. 1. In fact, the mass spectrometer geometry is not collinear. After ionization and a series of focusing lenses the selected ions are accelerated through 90°and thus the electron multiplier does not interact with fast neutrals. We have submitted a revised Fig. 1 to more accurately reflect this QMS geometry.

Gas-beam scattering attenuation is avoided by limiting the high-pressure region path length and is discussed in detail in the included references, Kong et al. (2011) and Kong et al. (2012).

2. We believe a careful re-reading of this section will satisfy Referee #2. The paragraph beginning at 27644, line 18 details the $\alpha(T)$ calculation. However, as the Referee points out it is important to clearly explain what is meant by 'accommodation' versus 'uptake' and the intervening statement (27644, lines 12-17) is intended to make our efforts explicit.

3. The extra collision energy of the molecular probe is quickly dissipated (see above), and therefore does not affect the uptake coefficients. The active debate (as pointed to in the text on pp. 27646 line 13 and by the referee) in the literature concerning ice and water's 'alpha' values is interesting and important. To that end timescales may be important, and at these experimental time scales our observations support using a value of unity.

4. These questions regarding equation (5) have led us to make several changes to make things more clear. Originally we wrote equation (5) in a manner that emphasized the physical observable (pressure $P$). However from a dimensional perspective and for comparison with other work we realize from Referee #2's comment this may not have been the best choice. Thus we rewrite equations (5) through (7) in terms of $N$ the number of molecules. The pressure is simply $N/V$ the number of molecules scaled by the volume. Equation (8) and (9) remain with an additional equivalency introduced to tie the two viewpoints together. The changes now make plain that $b$ in equation (5) is in fact a loss rate (s$^{-1}$) and does not correspond to $\omega$, which we could estimate but do not measure, or use. The rewritten equation also more clearly presents the desorption rate constant. An estimate of the outgoing flux ($10^{17}$ molecules/s) from the inner chamber using a 'flow reactor' approach is consistent with the number based upon monolayer coverage ($10^{14}$ molecules) and the desorption rates we obtain from our measurements. Thus, while such an estimation assures us the two methods are self-consistent, in our view it is not well enough constrained to include in the manuscript. [Note: Although we utilize a flow reactor like approach, the presence of the surface within the inner chamber but close to the orifices prevents a direct analogy to Knudsen reactors and

limits the accuracy of such calculations.]

5. The absence of a D$_2$O signal in the case of methanol is not related to the beam's kinetic energy as we have discussed above. The possibility of isotopic exchange as a sink of D$_2$O was considered and investigated. However, no HDO was measured and thus we conclude that within the experimental resolution no isotopic exchange occurs. This observation agrees with previous work that shows isotopic exchange requires longer times. A comment on this should have been included in the original text, and the lack thereof was an oversight. This has been added to the revised manuscript.

The author's thank the referee for pointing out the Chaix et al. reference, which should also have been included originally and has been added in the relevant locations. A second reference by the same group has also been added (Pratte et al., 2006)

6. No temperature dependence could be determined for the desorption rate from methanol covered ice largely due to the general weakness of the QMS desorption signals.

7. Please see answer 7 to Referee #1. Also, we have added wording to acknowledge the weak temperature dependence and high uncertainty in Fig. 5.

8. A few words have been added to the Figure 4 caption to clarify the curves.

9. In addition to our previous attention to the non-thermal beam issue we have tried to condense and polish the Discussion section. Text has been eliminated and reordered for clarity and typical atmospheric temperatures have been added for context.

**Anonymous Referee #3**

We have responded to Referee #1's concern regarding justifying the methanol monolayer and also re-expressed the methanol partial pressure $p$ in a manner that should make the definition clear.

Referee #3 also questions the effect of hyper-thermal incident velocities and we hope that these concerns are addressed in our answers to #2's comments.

Changes have been made to the discussion section as mentioned above.

Conclusions is a section heading specified in the ACPD supplied latex template.

Minor Comments:

–A sentence concerning atmospheric temperatures has been added to the discussion.

–Abstract, lines 10-13: The suggested change has been adopted.

–Section 2.2 pp.27644 lines 15-16: ‘surface’ has been added to the sentence in question for clarity. Thus Referee #3's interpretation of $\alpha(T)$ is correct. However, we do not explicitly measure uptake and/or collision rates, so these can only be inferred from the ratio we obtain.

– pp.27644 The variables have been defined for clarity.

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