

## ***Interactive comment on “Determination of the evaporation coefficient of D<sub>2</sub>O” by W. S. Drisdell et al.***

**W. S. Drisdell et al.**

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We thank the reviewer for the comments on our manuscript detailing measurements of the evaporation coefficient of liquid D<sub>2</sub>O. When revising the paper, we will provide a more thorough and consolidated discussion of the accuracy of our experiment and modeling procedures as suggested. To address the specific concerns mentioned:

1. Regarding the effect of higher vapor pressure near the nozzle orifice: the first measurement taken in vacuum is 1 mm away from the nozzle orifice. This typically corresponds to a vapor pressure of  $\sim 7.5$  torr for D<sub>2</sub>O, which is sufficiently low to insure that the experiments are within the free evaporation regime. We do also observe a “time zero” data point obtained in ambient air, where the temperature of the droplet train is  $\sim 295$  K. This will be clarified in the revised manuscript

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and the “time zero” point will be marked in the figures with a separate symbol. Excluding this point from the data set results in a change of less than 0.03 in the value of  $\gamma_e$ .

2. Regarding the effect of droplet velocity: Given the high vacuum environment, drag forces are negligible and the droplets are, relative to one another, stationary. Some of the evaporate will impinge upon adjacent droplets in the train; this effect was quantified in Smith et al. (2006) as causing an underestimate in  $\gamma_e$  of less than 0.01, an effect much smaller than other uncertainties. Explicit reference to this calculation will be made in the revised manuscript.
3. Regarding a vapor sheet entrained by the droplet train: The calculation mentioned above addresses this issue.
4. The reviewer states: “The Drisdell et al. experiments are done completely off equilibrium. The surface is likely to be significantly perturbed by the rapid evaporation without the balancing effect of condensation. Under these conditions the water surface is likely to be very different from the surface under near equilibrium conditions found in nature. Could this affect the evaporation coefficient?” Molecular simulations suggest that the time scales for reorganization of the liquid surface will be on the order of a few picoseconds (Garrett et al., 2006). If one considers a 1 nm square patch of liquid H<sub>2</sub>O surface (larger than the water-water correlation length in the liquid phase (Head-Gordon and Hura, 2002)), the evaporation rate calculated from the Hertz-Knudsen equation (equation 3 of the manuscript) assuming  $\gamma_e = 1$ , is found to be a single evaporating molecule every 10 ns. Consequently, evaporation events are too rare to significantly perturb the molecular structure at the surface. Discussion of these effects will be presented in the revised manuscript.

The reviewer also notes some apparent discrepancies between the current work and that of Cappa et al. (2005). The first is that Cappa et al. (2005) predict a measurable

temperature dependence to the evaporation coefficient, whereas the current study and that of Smith et al. (2006) find it to be independent of temperature. This discrepancy is discussed in Cappa et al. (2007), which is referenced in the current manuscript. The predicted *absolute* temperature dependence from Cappa et al. (2005) involved several assumptions and a high level of uncertainty. It is important to note, however, that the *relative* evaporation rates of the isotopes discussed in Cappa et al. (2005) are expected to display a measurable temperature dependence. The discussion of these temperature dependences will be referenced and clarified in the revised manuscript.

The second discrepancy pointed out by the reviewer is that of definitions of the evaporation coefficient and accommodation coefficient. In Cappa et al. (2005), the mass accommodation process measured by Li et al. (2001) is compared to the free evaporation process monitored by our experiments, and it was concluded that the  $\gamma_e$  we measure is proportional to  $(1-\alpha_m)$  as measured by Li et al. (2001), rather than being equal to  $\alpha_m$ . This is, as the reviewer points out, incorrect.

Cappa et al. used the following representation of the mass accommodation process (Nathanson et al., 1996; Kolb et al., 2002):

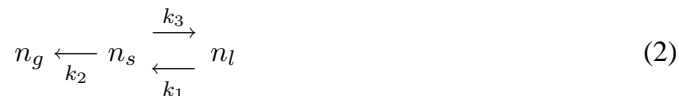


Here  $n_g$  is the gas phase water concentration,  $n_s$  is the surface concentration, and  $n_l$  is the liquid concentration. In this representation, only the mass accommodation process is considered because there is no term that moves molecules from the bulk liquid to the surface. Additionally, given the nature of the experiment of Li et al., in which isotopically labeled  $\text{H}_2^{17}\text{O}$  was used, the definitions of  $n_s$  and  $n_l$  refer specifically to concentrations of the labeled species; as such,  $n_l$  can be considered to be effectively zero (at short times), and  $n_s$  refers specifically to the concentration of the labeled species at the surface. The rate constant  $k_{ads}$  corresponds to the Hertz-Knudsen gas-phase collision rate with the surface. Upon striking the surface, the labeled species either desorbs from

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the surface (through the  $k_{des}$  pathway) or becomes solvated (through the  $k_{sol}$  pathway). Therefore  $k_{des}$  can be viewed as representing “rejected” condensation events (i.e.  $k_{des}$  allows for the accommodation coefficient  $\alpha_m$  to be less than unity).

Cappa et al. then formulated a similar picture for their free evaporation experiments:

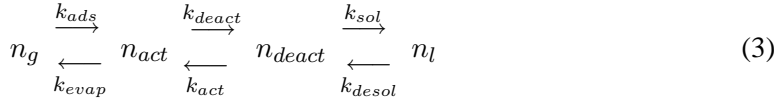


Due to the high vacuum in the experiments,  $n_g$  is effectively zero and as such the arrow for gas-phase collision with the surface has been omitted, i.e. there is no condensation. However, the liquid concentration is now high and the flux from the liquid to the surface is present as represented by  $k_1$ . Cappa et al. then equated the rate  $n_s \cdot k_2$  from Equation (2) with the rate  $n_s \cdot k_{des}$  from Equation (1). Herein lay the error;  $k_2$  represents the evaporation rate coefficient from the surface whereas  $k_{des}$  represents “rejected” condensation when evaporation is neglected and is expected to be smaller than the evaporation rate when molecular transfer out of the bulk liquid is considered. Additionally, the definitions of  $n_s$  are not consistent between the two equations; in Equation (1)  $n_s$  is the surface concentration of the isotopically labeled species arising entirely from gas-phase collisions with the surface, whereas in Equation (2)  $n_s$  is the surface concentration of water generated entirely from molecules transferred from the bulk liquid to the surface. By equating these rates, Cappa et al. found that their measured  $\gamma_e$  was proportional to  $(1-\alpha_m)$  as measured by Li et al, but we can now see that this is not appropriate.

To show that the measured quantities ( $\gamma_e$  and  $\alpha_m$ ) are in fact equal, one must rethink the arrow formulations in Equations (1) and (2). If one assumes that  $\gamma_e$  and  $\alpha_m$  are unity, then  $k_{des}$  in Equation (1) and  $k_3$  in Equation (2) are zero, and the picture simplifies significantly;  $n_s$  no longer must be considered. In this situation the measured rates in both cases are clearly equal to the equilibrium evaporation and condensation rates.



If one assumes that  $\gamma_e$  and  $\alpha_m$  are less than one, then a rate-limiting step must exist in the process. The Boston College / Aerodyne collaborators assume that all the impinging vapor molecules adsorb to the surface, and that the rate limiting step occurs between surface species formation and solvation into the bulk liquid. This idea is supported by experiments which have found the thermal accommodation coefficient to be unity, and is also consistent with the suggested mechanism given in the manuscript under review, i.e. that the limit to the evaporation rate is due to intermolecular modes at the surface needing to be excited before evaporation takes place. One can then describe the equilibrium system for the evaporation / condensation process as follows:



Here  $n_{act}$  and  $n_{deact}$  represent two types of surface species, “activated” and “deactivated”. Only “activated” surface molecules can evaporate, and only “deactivated” molecules can absorb into the bulk liquid. The rate-limiting steps in the process are represented by  $k_{act}$  and  $k_{deact}$ , which represent the interchange rates between the two surface species. Now, in the case of the Li et al. experiments,  $n_l$  is negligible and so  $k_{desol}[n_l] = 0$ ; however, the concentration of  $n_{act}$  should be close to equilibrium due to relatively rapid interchange with the vapor. The rate-limiting step in this case is represented by the rate  $n_{act} * k_{deact}$ , and should be equal to the rate in the equilibrium system. In the experiments of Cappa et al. and the current manuscript,  $n_g$  is negligible and therefore  $k_{ads}[n_g]=0$ . However, rapid interchange between the bulk liquid and the “deactivated” surface species should keep  $n_{deact}$  near the equilibrium value. Therefore the rate-limiting step is represented by the rate  $n_{deact} * k_{act}$  and should be equal to the equilibrium rate. Thus both experiments should indeed probe the equilibrium rates and should find equivalent values of  $\gamma_e$  and  $\alpha_m$  because the rate limiting step is the interconversion between activated and deactivated species.

It is also important to note that Li et al. do not use Equation (1) to define  $\alpha_m$ . Their

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definition of  $\alpha_m$  is consistent with that of Cappa et al. and our definition in the current manuscript and is derived from the Hertz-Knudsen equation. Li et al. invoke Equation (1) only as a way of representing their observed temperature dependence.

A brief summary of this discussion and acknowledgement of the error in Cappa et al 2005 will be included in the revised manuscript.

We also thank the reviewer for pointing out two references that were missed; the manuscript has been updated to include them.

Garrett, B. C., Schenter, G. K., and Morita, A.: Molecular simulations of the transport of molecules across the liquid/vapor interface of water, *Chem. Rev.*, 106, 1355-1374, 2006.

Head-Gordon, T., and Hura, G.: Water structure from scattering experiments and simulation, *Chemical Reviews*, 102, 2651-2669, 2002.

Kolb, C. E., Davidovits, P., Jayne, J. T., Shi, Q., and Worsnop, D. R.: Kinetics of trace gas uptake by liquid surfaces, *Progress In Reaction Kinetics And Mechanism*, 27, 1-46, 2002.

Nathanson, G. M., Davidovits, P., Worsnop, D. R., and Kolb, C. E.: Dynamics and kinetics at the gas-liquid interface, *Journal Of Physical Chemistry*, 100, 13007-13020, 1996.

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Interactive comment on *Atmos. Chem. Phys. Discuss.*, 8, 8565, 2008.

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