

Reply to “Comment on ‘Mass Accommodation Coefficient of Water: Molecular Dynamics Simulation and Revised Analysis of Droplet Train/Flow Reactor Experiment’”

Akihiro Morita*

Department of Computational Molecular Science, Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan

Masakazu Sugiyama

Department of Electronics Engineering, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

Seiichiro Koda

Department of Chemistry, Faculty of Science and Technology, Sophia University, 7-1 Kioicho, Chiyoda-ku, Tokyo 102-8554, Japan

David R. Hanson

Atmospheric Chemistry Division, National Center for Atmospheric Research, Boulder, Colorado 80303-2000

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Our previous article¹ argued that the mass accommodation coefficient (α) of water into liquid water surface is predicted to be unity by molecular dynamics simulation. Furthermore, the droplet train flow reactor experiment, which insists on values for α in the range 0.17–0.32 near room temperature,² is not inconsistent with the simulation after revised evaluation of the gas-phase diffusion. In this Reply, we answer the questions raised by the Comment about both the molecular dynamics simulation and the treatment of the gas-phase diffusion in the flow tube.

Molecular Dynamics Simulation

The questions about the molecular dynamics simulation are twofold: the accuracy of the potential function and the spatial and temporal scale that the molecular dynamics simulation covers. In the following, we deal with these two issues in turn.

First, we point out that the picture of unit α is not affected by potential functions employed. Accuracy of the potential function is not a critical issue here, in contrast to some other aspects of water properties. We agree that the conventional potential functions are not accurate enough to reproduce nucleation rates, as the precise evaluation of the free energy barrier of nucleation is particularly critical. However, the main focus of our MD simulation is not evaluating thermodynamic quantities but examining whether friction during entry is large enough to prevent accommodation. We have reported that the friction is far too small to prevent the accommodation, which accompanies a relatively large stabilization energy during the entry from vapor to liquid. In fact, previous MD simulation studies have predicted unit α for thermal collisions of hydrogen-bonding systems.^{3–7} This picture of accommodation is qualitatively robust, irrespective of the potential functions or the

definition of a hydrogen bond. Furthermore, when direct molecular-level observation of the accommodation kinetics is available by surface scattering experiments, which can be unambiguously compared to the simulation, MD simulation with conventional potential functions is demonstrated to reproduce the accommodation processes very well over a wide energy range.⁸ (In connection to the experiments by Wernet et al.,⁹ we think that the quantum nature of hydrogen, rather than the potential functions, needs to be considered in the definition of a hydrogen bond. It is a different matter from the accommodation kinetics.)

Second, the spatial and temporal scale of mass accommodation is an important issue for the interpretation of the accommodation experiments. Our simulation, and those of others, regard that the accommodation dynamics is a fairly local phenomena that occurs at the molecular scale.^{3,8} This issue has been thoroughly examined by Wilson and Pohorille³ in the case of ethanol accommodation into water, an analogous hydrogen-bonding system. They revealed that the impinging molecule is thermally equilibrated at the surface in a time period of the order of ~ 10 ps and then it obeys the ordinary diffusion equation in the liquid in a manner identical to other molecules such as a labeled solvent molecule. This result is consistent with our simulation, implying a qualitative separation between mass accommodation and thermal evaporation, as the characteristic time for thermal evaporation is far longer than the thermal equilibration time in the order of magnitude.

We think that this problem is rather an issue of the microscopic definition of the mass accommodation coefficient. It is deeply related to the validity of the resistance formula, eq 1 in ref 1, that assumes a fundamental distinction between the mass accommodation resistance ($1/\alpha$) and the solubility resistance ($1/\Gamma_{\text{sol}}$). Whereas the two resistances are thought to be reasonably separated by the difference in their time scales, however, we cannot rule out the possibility that another criterion of separation exists that allows for a consistent interpretation of the experiment. If this were the case, then the molecular basis of the resistance formula, eq 1 of ref 1, should also be reconsidered.

Gas-Phase Transport in Flow Tube

While gas-phase diffusive resistance is an important ingredient in uptake experiments using the droplet train flow reactor, the understanding of the transport kinetics is still far from complete. This is partly because the gas-phase resistance is not amenable to an analytical formula due to complicated boundary conditions and because it is difficult to directly measure the gas-phase resistance by decoupling the other transport factors. The droplet train experimental results are an indirect measure of interfacial processes, and many careful calibration procedures are needed to extract molecular-level information. In particular, an accurate understanding of the gas-phase resistance becomes crucial in deriving the water accommodation coefficient, where the gas-phase resistance governs the phenomenological kinetics, as we have shown in the previous paper.¹

Davidovits and co-workers have reported an important insight into the gas-phase resistance by their droplet train flow reactor experiments. Although the gas-phase transport in the droplet train flow reactor involves many parameters of geometric and ambient conditions, they found that the gas-phase transport is well described by the “modified” or “effective” Knudsen

* To whom correspondence should be addressed. Fax: +81-564-55-7025. E-mail: amorita@ims.ac.jp.

number, which is defined by $\text{Kn}^* = 2\lambda/d_o$, twice the molecular mean free path (λ) divided by the orifice diameter (d_o) rather than the droplet diameter.¹⁰ This dramatically simple expression is surprising, and therefore, our aim in performing the computational fluid dynamics is to elucidate and examine all the gas-phase transport issues in the flow reactor. The power of the technique is that one can straightforwardly investigate the gas-phase transport in a well-defined set of geometric and ambient conditions.

As discussed in the Comment, our fluid dynamics simulation has supported some features of the experimental results, that is, that the concentration decay is exponential along the flow tube axis and that the uptake rate is fairly insensitive to the droplet velocity or orifice diameter (the latter provides an essential justification for the modified Knudsen number). These key experimental features were confirmed to be invariant with experimental conditions within experimental and calculation accuracy (typically $\pm 15\%$). However, the simulations also evaluated their quantitative accuracy of the modified Knudsen number, implying that one should employ it with caution in some cases, where quantitative accuracy is particularly required such as for the water uptake experiments.

As an illustration, the uptake coefficients (γ) were derived from the axial concentration decay slope in two configurations (A and B) with different orifice frequencies (see Table 1 of ref 1). Our simulation reported $\gamma = 0.238 \pm 0.01$ for A and $\gamma = 0.202 \pm 0.01$ for B at a common $\alpha = 1$ value, as shown in Figure 9 of ref 1. The simulation generally shows a moderate tendency that a larger orifice frequency (i.e., smaller droplet diameter and distance) leads to a larger uptake rate. However, the two values coincide within 18%, which is not inconsistent with experimental findings, since A and B employ the same orifice diameter and thus the modified Knudsen number. However, if we take the difference in slopes of A and B, as shown in eq 11 of ref 1, a γ value of 0.283 results, as the experiments are routinely (and nearly exclusively) conducted in an orifice frequency switching mode. This implies that a significant variation of γ could arise depending on the frequency range employed and other experimental conditions, on the basis of the assumption that the modified Knudsen number uniquely determines the uptake coefficient. It is worth pointing out that a variation of 15%, the estimated accuracy of the measurements and simulations, in the measured γ or in the empirical formula can lead to significant consequences. For example, for droplet train data taken at 285 K with droplets formed from a 60 μm orifice (i.e., $\text{Kn}^* \sim 0.08$), the empirical formula, if altered by 15%, can lead to an apparent decrease in α from a value of 1 to a value of 0.4.

Davidovits and co-workers insist from their experimental results that eq 11 very well defines a γ value over all of the accessible orifice frequency range, and accordingly, they did not report the above problem. The reason for the discrepancy between the experimental and simulation results is not clear at present, but one probable reason is that the current experiments and/or simulations do not have sufficient accuracy ($\lesssim 15\%$) to allow for quantitative comparison. We think that such basic knowledge of the gas-phase transport is very important for deriving meaningful microscopic information. In a realistic description with sufficient accuracy, the gas-phase transport might be represented beyond a simple function of the modified Knudsen number.

Another working test of the accuracy is the dependence of the uptake rate upon the droplet speed. Experimental analysis has ignored the droplet speed dependence, as it does not affect

the modified Knudsen number, whereas our simulation predicts that the uptake coefficient changes by 11–12% between $v_d = 16$ and 44 m/s¹ in an analogous way to the Ranz–Marshall formula.^{11,12} Again, the experiment and simulation agree within the current error range. However, we suggest that the droplet experiments should at least have sufficient accuracy to discuss any droplet speed dependence, on the condition that other ambient and geometrical parameters are kept constant.

While the experiments by Davidovits and co-workers should be regarded as a milestone in the field of heterogeneous chemistry, a quantitative understanding of the gas-phase resistance should be further pursued. If one uses the empirical gas-phase resistance formula beyond its inherent accuracy, one may overlook fundamental uncertainties underlying the gas-phase transport phenomena. We think that the results of additional flow reactor experiments under well-defined conditions are needed so that they can be critically compared to the predictions of our fluid dynamic simulations. In this endeavor, the accuracy of both might be properly assessed, and a better and more firm understanding of the uptake process can be gained.

H–D Exchange

Finally, we make a few comments on the wall loss, though it is not a focus of our paper. The Comment insists that the H–D exchange is not measurably present on the wall tube in the D₂O case, whereas it is substantial in *d*-ethanol. We think that this surprising and puzzling result deserves extensive investigation on its own, since it is commonly thought that the H–D exchange is quite facile and hard to control. Since the surface area of the droplets is much smaller than that of the apparatus, precise differential measurement is again critical. (Note that the kinetic interference between the droplet uptake and the wall loss will be another important issue.¹³) We assume that the wall loss problem requires more accuracy than the simple water uptake measurement. Quantitative understanding of the gas-phase transport is a basic requisite for the wall loss problem.

Besides the wall loss problem to elucidate the enhanced uptake of D₂O, another reason for the difference in D₂O and H₂¹⁷O could be the difference in the liquid-phase solubility resistance. The “solubility” of D₂O or H₂¹⁷O in water should be actually considered as finite with a value of ~ 500 M/atm or less (≈ 55 M/(0.01–0.03 atm)). H₂¹⁷O can accordingly desorb from liquid during its transit time in the flow tube, whereas D₂O can little desorb once it is accommodated into the liquid, due to the subsequent H–D exchange reaction in the liquid. The uptake experiments with isotope exchange pose many problems of their own, and further discussion will be needed.

References and Notes

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