Hydrophobic hydration of alkanes: Its implication for the property of amorphous solid water

Ryutaro Souda

Articles you may be interested in

Optimization of linear and branched alkane interactions with water to simulate hydrophobic hydration
J. Chem. Phys. **135**, 054510 (2011); 10.1063/1.3623267

Atomistic simulation of nanoporous layered double hydroxide materials and their properties. II. Adsorption and diffusion
J. Chem. Phys. **127**, 224701 (2007); 10.1063/1.2799985

Comparative study of the interaction of pyridine with polycrystalline Ag and amorphous solid water
J. Chem. Phys. **127**, 174514 (2007); 10.1063/1.2784119

Interaction of benzene with amorphous solid water adsorbed on polycrystalline Ag
J. Chem. Phys. **127**, 074707 (2007); 10.1063/1.2759914

Water properties and potential of mean force for hydrophobic interactions of methane and nanoscopic pockets studied by computer simulations
J. Chem. Phys. **127**, 054505 (2007); 10.1063/1.2749250

Hydrophobic hydration of alkanes: Its implication for the property of amorphous solid water

Ryutaro Souda[a)]

Advanced Materials Laboratory, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

We measured the incorporation of adsorbed alkanes in and their desorption from the amorphous solid water (ASW) by means of secondary ion mass spectroscopy and temperature programmed desorption. The heavier alkanes such as butane and hexane are incorporated completely in the bulk of the *nonporous* ASW layer below 100 K probably due to the preferential formation of ice structures around the solute molecules. The self-diffusion of water molecules occurs above the glass transition temperature (136 K). The liquid water emerges above 165 K, as evidenced by simultaneous occurrence of the dehydration of alkanes and the morphological change of the water layer induced by the surface tension. © *2004 American Institute of Physics.*
[DOI: 10.1063/1.1814051]

The interaction of nonpolar molecules with liquid and solid water has attracted considerable attention. There exist giant natural methane clathrate deposits on the deep ocean floor, and the deep sea deposition of CO_2-clathrate is promising to remove this greenhouse gas from the atmospheric cycles. Gas–ice interactions that lead to clathrate hydrate formation are also of importance in cometary research. Moreover, a number of important processes in aqueous solutions, such as protein folding and formation of micelles and biological membranes, rely on the interactions between water and nonpolar moieties of organic molecules. The driving force behind these processes is a large entropy loss, which is explained as an enhanced structuring of water surrounding a hydrophobic entity (the ''iceberg'' model).[1] However, the formation of a highly ordered cage of water molecules is not supported by the recent experiments.[2–5] Thus, the exact nature of hydrophobic hydration in aqueous solution has remained unclear. More insights into the hydration phenomena would be gained from the adsorption experiments on the surface of amorphous solid water (ASW) since it can be a supercooled extension of liquid water. However, there is still debate about the properties of ASW above the glass-transition temperature ($T_g = 136$ K).[6–8] So far, molecular level investigations of hydration have been performed theoretically and computationally[9–15] but experimental probes of the local properties in the neighborhood of specific molecules at a surface or interface of the liquid and solid water are scarce.

In this paper, we report on the properties of the ASW surface and the alkane-ASW interactions at the molecular level, on the basis of the temperature-programmed time-of-flight secondary ion mass spectrometry (TP-TOF-SIMS) combined with the temperature-programmed desorption (TPD). TOF-SIMS is so sensitive to the outermost surface layer that dissolution and reorganization of solute and sol-vent molecules at the surface can be monitored, whereas TPD can distinguish between the dehydration of solute molecules incorporated in the bulk and the simple desorption of adsorbed molecules from the surface if combined with TOF-SIMS. It is demonstrated that the ASW is highly dynamic in nature even below the glass transition temperature and that the liquidlike layer evolves just before evaporation of the water molecules. The butane and hexane are incorporated completely in the bulk of ASW in the temperature range 50–100 K. The incorporation of lighter alkanes such as methane and ethane is much less efficient because they desorb prior to incorporation. The self-diffusion of water molecules takes place above 136 K, leading to the dehydration of alkanes at 165 K without irreversible crystallization. The results are interpreted in terms of the polyamorphism of supercooled and glassy water.

Experiments were conducted in a stainless steel ultrahigh-vacuum chamber of base pressure below 1×10^{-8} Pa. The vacuum system was equipped with an electron-impact-type ion source, a linear-TOF tube, and a differentially pumped quadrupole mass spectrometer (QMS) for TPD. The details of the TP-TOF-SIMS experiments were described in separate full papers.[16,17] Briefly, a pulsed He^+ beam (2 keV) was incident on the sample, which was floated with a bias voltage of $+500$ V, and the positive ions extracted into the field-free region of the TOF tube were detected with a channel electron multiplier. The substrate was a Ni(111) surface mounted on a sample holder cooled to 15 K by means of a closed-cycle He refrigerator.

Figure 1(a) displays the experimental result of TP-TOF-SIMS for the $H_2^{18}O/H_2^{16}O$ layer: the ASW film of $H_2^{16}O$ with a thickness of 50 monolayer (ML) was grown, and then the $H_2^{18}O$ molecules (1 ML) were adsorbed on it after cooling down to 15 K. The water molecules become mobile at $T > T_g$ as revealed from the occurrence of intermixing between the $H_2^{18}O$ and $H_2^{16}O$ molecules. A hump evolves in the Ni^+ intensity above 160 K before the water layer evapo-

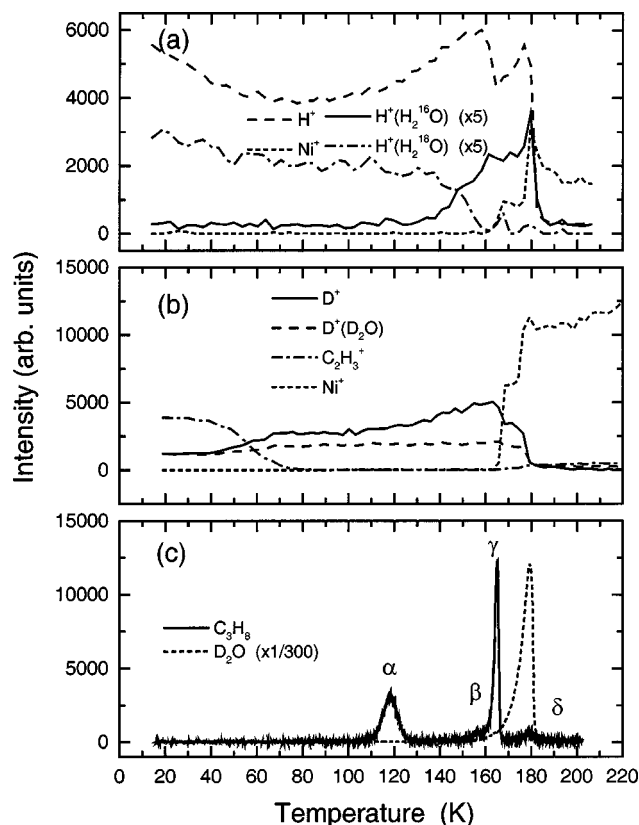[a)]Electronic mail: SOUDA.Ryutaro@nims.go.jp

FIG. 1. (a) The TP-TOF-SIMS intensities for the *nonporous* ASW layer of $H_2{}^{16}O$ (50 ML, annealed at 100 K) on which the $H_2{}^{18}O$ molecules (1 ML) were adsorbed at 15 K. The temperature was linearly ramped at a rate of 0.1 Ks^{-1}. (b) Evolutions of typical secondary-ion intensities from the butane (1 ML) adsorbed D_2O layer (ASW: 50 ML) as a function of temperature. (c) The TPD spectra of butane and heavy water taken under the same temperature ramp as in (b).

rates completely at 180 K. This result suggests that desorption of the water multilayer does not proceed via the layer-by-layer fashion but is preceded by the drastic morphological change leading to the microscopic "water droplet" formation.[18] A dip is observed in the H^+ intensity, concomitantly with the hump of Ni^+, but the $H^+(H_2O)$ intensity shows no structures at this temperature, indicating that the origins of bare and hydrated protons are different to each other: The former is emitted from the dangling OH bond of the water molecules on the topmost surface layer whereas the latter is caused by the proton transfer reactions during collisions of hydrogen-bonded water molecules, $2H_2O \rightarrow H_3O^+ + OH^-$.[16,17] The invariance of the $H^+(H_2O)$ intensity around 165 K indicates that the Ni(111) surface is basically covered with the water multilayer, whereas the dip in the H^+ intensity arises because the water molecules at the topmost surface undergoes the hydrogen-bond reorganization.

Figure 1(b) shows the TP-TOF-SIMS result for the butane (1 ML) adsorbed D_2O layer (50 ML: ASW). The butane disappears completely from the surface up to 80 K as evidenced by the decay of the fragment $C_2H_3^+$ ion. This result is not explained by the desorption because the TPD spectrum of butane exhibits four distinct peaks, α-δ, above 100 K as shown in Fig. 1(c). Note that peak β, γ, and δ, respectively, appear at temperatures for the occurrence of self-diffusion

(150 K), morphological change (165 K), and evaporation (180 K) of the D_2O layer. The roughening/desorption kinetics of the D_2O layer itself is not influenced by the incorporated butane as manifested by the similarity in the features of the TP-TOF-SIMS spectra between Figs. 1(a) and (b).

In the temperature range 140–150 K, the ASW may be hot enough to be no longer a glass and can crystallize to ice Ic (cubic ice), but there is still debate in terms of the temperatures for emergence of the liquid water and crystalline ice. Fisher and Devlin[6] assumed that ASW freezes directly to crystalline ice near 150 K without passing through the liquid state, whereas Jenniskens *et al.*[7] suggested that viscous liquid water may coexist with the crystalline ice. Kay and co-workers[8,19] concluded that the ice is formed irreversibly at around 160–165 K and a liquid phase appears just before the crystallization. At this temperature, they observed a bump in the water TPD spectra[8] and an explosive desorption of the CCl_4 molecules embedded underneath the thick ASW layer.[19] The same bump can be seen clearly in the D_2O TPD spectrum and peak γ exhibits an "explosive" feature, though the film preparation in the present experiment is completely different from the previous study.

The morphological change of the ASW film observed here might be associated with the ice crystallization. But this presumption is denied on the basis of the following two experiments. First, the monolayer of amphiphiles (surfactants) such as HCOOH and CH_3OH, which stays at the water-vacuum interface up to the evaporation temperature of the water layer,[16,17] quenches the morphological change of the film as confirmed from the absence of the hump in the sputtered Ni^+ intensity (not shown explicitly), suggesting that the morphological change is not related to the bulk crystallization but driven by the surface tension of liquidlike water molecules with high mobility. This picture is consistent with the hydrogen-bond reorganization leading to the drastic decrease in the number of the dangling OH and OD bonds at this temperature. Second, the same experiments as in Fig. 1(a) were performed for the "crystalline ice" surfaces prepared by annealing the ASW film at 165 K,[20] and the self-diffusion behavior of the adsorbed $H_2{}^{18}O$ molecules was observed for $T > T_g$ quite similarly to that in Fig. 1(a). If the crystalline water-ice layer were created irreversibly, the intermixing of the water molecules should be frozen out. Thus, the present TOF-SIMS study concludes the dominance of the liquidlike water layer without crystallization above 165 K.

In Fig. 2 are shown (a) the TP-TOF-SIMS intensities of the $C_2H_3^+$ ions from the butane (1 ML) adsorbed on the D_2O (ASW) layer with different thickness and (b) the TPD spectra from the corresponding surfaces. Two characteristic temperatures exist in Fig. 2(a) for incorporation (50–75 K) and desorption (100–110 K) of butane. At the thin D_2O layer, most of the butane molecules tend to stay on the surface without incorporation, resulting in the small TPD peaks β-δ relative to peak α. The D_2O layer with the thickness more than 25 ML is necessary to accommodate the 1-ML butane molecules completely in the bulk. With further increasing the thickness of the D_2O layer, the relative intensity of peak α decreases as seen in Fig. 3. From these results, it is concluded that peaks β-δ are caused by the tightly bound butane molecules form-
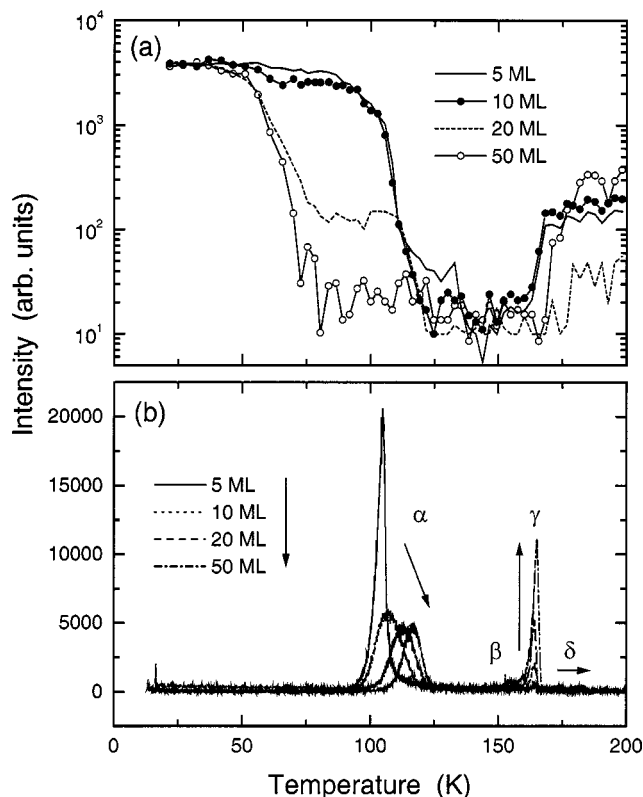
FIG. 2. (a) The $C_2H_3^+$ intensity from butane in the TP-TOF-SIMS experiments. The butane (1 ML) was adsorbed on the D_2O (ASW) layer with different thickness. The butane molecules are incorporated in the bulk completely up to 80 K when the D_2O layer is thicker than 25 ML. (b) The TPD spectra for butane adsorbed on the D_2O (ASW) layer with different thickness. The intensity of peak γ increases almost linearly with the thickness of the D_2O layer because it is cased by the bulk hydrates of butane. With increasing the thickness, peak δ shifts to the higher temperatures due to the shift of the D_2O TPD peak. The position of peak α moves towards higher temperatures with increasing the thickness of D_2O but it is fixed for thicker layers (>25 ML) when the butane is incorporated completely in the bulk.

ing bulk hydrates and peak α is their precursor state.

The ASW prepared at such a low temperature as 15 K contains nanometer-sized cavities.[21,22] The cavitation is the important first step for solvating any nonpolar molecules in water, so that more insights into the hydrophobic hydration would be gained from the comparison of the molecular uptake behaviors between the nonporous (ASW) and porous (PASW) layers. The yields of peak γ relative to the total TPD yields for some alkanes adsorbed on the ASW and PASW surfaces are summarized in Table I, together with the temperatures of peak α for the ASW surface. The temperatures at which peaks β-δ appear are independent of the alkane species. The heavier the alkane molecules are, the easier they form bulk hydrates. The uptake of methane and ethane in the bulk ASW hardly occurs, but they are incorporated considerably in the PASW. These molecules can permeate into the bulk through cavities and stabilize at higher coordination sites. The pores of ASW collapse up to 70 K (Ref. 22) and, hence, a part of such molecules are confined in the bulk during heating, thereby resulting in the bulk hydrates. Note that such cavities have very little effects on the hydration of heavier alkanes. The complete incorporation of hexane in the bulk ASW requires higher temperature (100 K) than that of
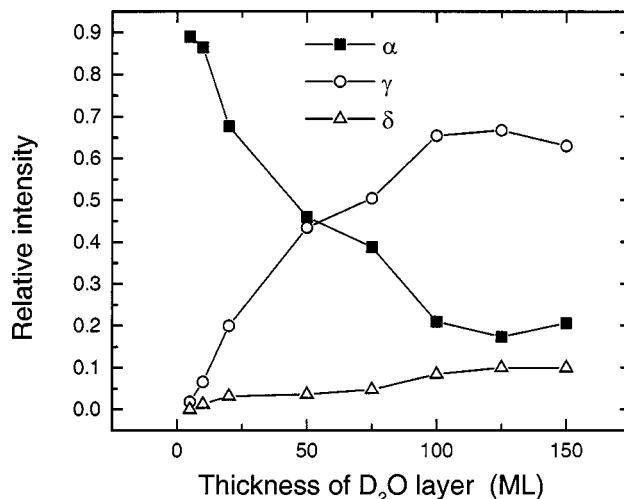

FIG. 3. The relative intensities of peaks α, γ, and δ in the TPD spectra of butane. The desorption of 1-ML butane molecules was measured as a function of the thickness of the D_2O layer (ASW).

butane. Thus, the dissolution of alkanes in ASW occurs most probably in the temperature range 50–100 K and the very little uptake of the methane and ethane in the ASW is caused by the occurrence of desorption prior to hydration. The capability to accommodate alkanes increases strongly with their molecular weight is interesting in comparison with the normal water (at ambient temperature/pressure conditions) in which the solubility is known to decrease for the sequence ethane/propane/n-butane.[23]

The dissolution of nonpolar molecules into the bulk ASW should be explained in the framework of the hydrophobic hydration. In the case of liquid water, the associated hydrophobic effect has so far been discussed extensively in terms of solute size, shape, and temperature effects.[9–15] It is believed that hydrophobic solutes increase the hydrogen bonding structure of water in the first hydration shell, but recent experiments revealed that the hydration cage, existing in the liquid, is rather loosely defined.[2–4] A poor solubility of nonpolar molecules in water may be amplified by the small size of water molecules themselves.[14,15] In any case, the immiscibility of nonpolar solutes in water has been explained by the large cavitation energy to modify the stable hydrogen-bond network. According to this picture, it seems difficult to elucidate the dissolution of such large molecules as butane and hexane in the bulk ASW at temperatures as low as below

TABLE I. The intensity of peak γ relative to the total intensity of the TPD spectra from alkane molecules (1 ML) adsorbed on the D_2O layer (50 ML). Two types of the D_2O films were compared to each other: the film deposited at 15 K (PASW) has cavities in which methane and ethane are incorporated whereas the film annealed at 100 K (ASW) have no cavities but heavier alkanes tend to dissolve in the bulk. T_α represents the temperatures of peak α which is a precursor state for hydration of adsorbed alkanes in ASW.

	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_6H_{14}
ASW	<0.01	<0.01	0.089	0.45	0.68
PASW	0.19	0.47	0.64	0.63	0.63
T_α (K)	50.4	82.0	103.8	118.0	134.5

100 K where the mobility of water molecules should be suppressed considerably.

The hydration phenomenon may be better explained on the basis of the polyamorphism of glassy and supercooled water at low temperatures.[24–27] Unlike other substances, water can form at least two distinct forms of glass, known as low-density and high-density amorphous ice (LDA and HDA, respectively), and the nature of the supercooled and stable water can be understood by the transition between LDA and HDA. Although the properties of the vapor-deposited ASW film depend sensitively on the growth condition and substrate, etc., the annealed ASW is basically identical to LDA in structure.[26,27] As far as the short-range structures are concerned, there exist significant similarities between LDA and ice Ih, and between HDA and liquid water.[28] Therefore, the formation of crystalline ice or clathratelike hydration shell would be facilitated in the bulk LDA with a relatively open structure, in which the nonpolar solute may play a role as a nucleus for the ice crystallization. The distinct phases of LDA and HDA terminate above the critical point, so that the properties of stable liquid water should be different largely from those of LDA. It is thus concluded that the formation of water cage presumed in the conventional "iceberg" model of hydrophobic hydration is rather realized in LDA or ASW but, in liquid water and probably HDA, the imperfect hydration shell causes a much poorer solubility of nonpolar molecules. The abrupt dehydration above 165 K invokes the emergence of the other phases of water. They are most likely liquid water, as inferred from the poor solubility of alkane molecules and the occurrence of the morphological change of the water layer induced by the surface tension. In this respect, Angell and co-workers[29] have recently suggested that the glass transition temperature should be reassigned to 165 ± 5 K instead of the commonly accepted value of 136 K though it is hardly observable experimentally due to the preceding crystallization above 150 K. In reality, the crystallization is not complete up to 165 K so that such a phase transition is observed clearly in the present experiment.

[1] H. S. Frank and M. W. Evans, J. Chem. Phys. **13**, 507 (1945).
[2] A. K. Soper and J. L. Finney, Phys. Rev. Lett. **71**, 4346 (1993).
[3] D. T. Bowron, A. Filipponi, M. A. Roberts, and J. L. Finney, Phys. Rev. Lett. **81**, 4164 (1998).
[4] A. Filipponi, D. T. Bowron, C. Lobban, and J. L. Finney, Phys. Rev. Lett. **79**, 1293 (1997).
[5] L. F. Scatena, M. G. Brown, and G. L. Richmond, Science **292**, 908 (2004).
[6] M. Fisher and J. P. Devlin, J. Phys. Chem. **99**, 11584 (1995).
[7] P. Jenniskens, S. F. Banham, D. F. Blake, and M. R. S. McCoustra, J. Chem. Phys. **107**, 1232 (1997).
[8] R. S. Smith and B. D. Kay, Nature (London) **398**, 788 (1999).
[9] N. T. Southall, K. A. Dill, and A. D. J. Haymet, J. Phys. Chem. B **106**, 521 (2002).
[10] H. S. Ashbaugh, T. M. Truskett, and P. G. Debenedetti, J. Chem. Phys. **116**, 2907 (2002).
[11] S. Garde, G. Hummer, A. E. Garcia, M. Paulaitis, and L. R. Pratt, Phys. Rev. Lett. **77**, 4966 (1996).
[12] Q. Cui and V. H. Smith, Jr., J. Phys. Chem. B **106**, 6554 (2002).
[13] H. A. Patel, E. B. Nauman, and S. Garde, J. Chem. Phys. **119**, 9199 (2003).
[14] M. Lucas, J. Phys. Chem. **80**, 359 (1976).
[15] B. Lee, Biopolymers **31**, 993 (1991).
[16] R. Souda, J. Chem. Phys. **119**, 2774 (2003).
[17] R. Souda, H. Kawanowa, M. Kondo, and Y. Gotoh, J. Chem. Phys. **119**, 6194 (2003).
[18] The Ni^+ ion is sputtered provided that the Ni(111) substrate is covered with the water molecules. The ion exhibits a maximum in intensity at around 1-ML coverage of water and is ejected if the water thickness is less than 4–5 ML.
[19] R. S. Smith, C. Huang, E. K. L. Wong, and B. D. Kay, Phys. Rev. Lett. **79**, 909 (1997).
[20] The evaporation of the water molecules was so severe at 165 K that the water layer was annealed in the $H_2\,^{16}O$ ambient of 1×10^{-4} Pa.
[21] E. Mayer and R. Pletzer, Nature (London) **319**, 298 (1986).
[22] K. P. Stevenson, G. A. Kimmel, Z. Dohnalek, R. S. Smith, and B. D. Kay, Science **283**, 1505 (1999).
[23] E. Wilhelm, R. Battino, and R. J. Wilcock, Chem. Rev. (Washington, D.C.) **77**, 219 (1977).
[24] O. Mishima, L. D. Calvery, and E. Whalley, Nature (London) **314**, 76 (1985).
[25] P. H. Poole, F. Sciortino, U. Essmann, and H. E. Stanley, Nature (London) **360**, 324 (1992).
[26] O. Mishima and H. E. Stanley, Nature (London) **396**, 329 (1998).
[27] P. G. Debenedetti, J. Phys.: Condens. Matter **15**, R1669 (2003).
[28] J. L. Finney, A. Hallbrucker, I. Kohl, A. K. Soper, and D. T. Bowron, Phys. Rev. Lett. **88**, 225503 (2002).
[29] V. Velikov, S. Borick, and C. A. Angell, Science **294**, 2335 (2001).