

Structural Relaxation of Vapor-Deposited Water, Methanol, Ethanol, and 1-Propanol Films Studied Using Low-Energy Ion Scattering

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Glassy thin films of water, methanol, ethanol, and 1-propanol were prepared by deposition from the gas phase at 20 K. Relaxation of their surface and bulk structures was investigated by measuring temperature evolutions of H^+ , H^- , and total yields in low-energy H_2^+ scattering. The surface structure of a methanol film changes at temperatures of about 20 K below the glass transition temperature ($T_g = 103$ K) because of enhanced diffusivity of molecules at the surface. Both surface and bulk structures change at around T_g for ethanol, but the structure of the 1-propanol film is unchanged at temperatures higher than T_g , indicating that the vapor-deposited 1-propanol glass is more stable than the liquid-quenched one. These behaviors strongly suggest that the configurations of molecules in the vapor-deposited glass differ significantly from those in the liquid-quenched glass and that the aliphatic-chain length plays an important role in structural relaxation. The surface (bulk) structure of the water film changes gradually (is invariant) across T_g , suggesting that the relaxation and glass transition processes differ significantly between those of water and alcohols.

1. Introduction

Upon rapid cooling, some liquids can be quenched to a metastable glassy state without losing a disordered configuration. The self-diffusion occurs at the glass transition temperature, T_g , but the molecules can be rearranged toward an equilibrium configuration in the sub- T_g region. This relaxation process is designated as “structural relaxation”, although its origin is not known in any detail for most materials. For widely varying glasses, structural relaxation is recognizable in calorimetric studies;¹ aging in the glassy state changes the behavior of the specific heat drastically upon heating. On the other hand, it is generally expected that a glass prepared by vapor deposition (referred to as vapor-deposited glass) has a higher enthalpy and a lower density than a glass formed by quenching an equilibrium liquid (liquid-quenched glass). However, glassy molecular systems deposited at temperatures slightly lower than T_g are known to have higher density and stability than those of liquid-quenched glasses.^{2,3} A semiequilibrium configuration of molecules is thought to be realized as a result of surface diffusion. Therefore, the molecular conformation might be different between the vapor-deposited and liquid-quenched glasses. To date, very little is known about how the molecules in vapor-deposited glasses are reorganized upon heating despite the phenomenon's importance for improving the properties of glassy materials.

As described in this paper, we investigate structural relaxation processes of vapor-deposited thin films of water and some simple alcohols using time-of-flight ion scattering spectroscopy (TOF-ISS), together with time-of-flight secondary ion mass spectrometry (TOF-SIMS). In an earlier report,⁴ we discussed molecular diffusion and film morphology change based on the secondary-ion yields as a function of temperature. Results of that study show that the self-diffusion onset of methanol depends on the thermal history:⁴ The molecules appear to be mobile at around 80 K (almost 20 K below the calorimetric $T_g = 103$ K⁵)

when the film is deposited at 15 K, suggesting that molecular configurations differ between the vapor-deposited and liquid-quenched methanol. This mobile behavior might be explained differently: the enhancement of mobility of molecules at the surface is relative to that in the bulk because TOF-SIMS probes only a few layers from the surface. However, the self-diffusion onset of water probed by TOF-SIMS⁴ agrees well with the calorimetric T_g (136 K).⁶ These results strongly suggest that molecular rearrangement processes between the water and alcohol films differ significantly. As described in this paper, we performed a TOF-ISS measurement to shed light on this point. A primary H_2^+ beam was incident on the surface; the intensities of scattered neutrals (H^0) and charged particles (H^+ and H^-) are measured as a function of temperature. The ionization probability of the H^+ ion is known to be dependent on the nature of bonding of target atoms with their surroundings.^{7–9} Therefore, H^+ scattering is expected to probe configurational changes of the molecules upon heating. Here, relaxation processes of vapor-deposited thin films of water, methanol, ethanol, and 1-propanol are compared to reveal the roles of hydrogen bonds and aliphatic groups. We demonstrate that the relaxation temperatures of alcohols increase relative to T_g with increasing aliphatic chain length and that the relaxation of vapor-deposited 1-propanol is not completed even at calorimetric T_g of the liquid-quenched 1-propanol. The origin of the different structural relaxation processes between water and alcohols is suggested.

2. Experimental Section

The experiments were conducted in an ultrahigh-vacuum (UHV) chamber with a base pressure of less than 1×10^{-8} Pa. An electron-impact-type ion gun (IQE 12/38; Specs GmbH) was used to generate primary He^+ and H_2^+ beams with a kinetic energy of 2 keV. The beams were chopped into pulses of 40 ns width and 15 kHz in repetition rate using electrostatic deflection plates. The TOF-SIMS measurement was performed using the pulsed He^+ beam at an incidence angle of 70° (measured from

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the surface), and the positive secondary ions emitted perpendicular to the surface were detected using a microchannel plate after traveling a field-free TOF tube. A bias voltage was applied to the sample (125 V/mm) to extract low-energy secondary ions. For the TOF-ISS measurement, on the other hand, the yields of scattered H^+ and H^- ions were so small (ion fractions are typically less than 5%) that a forward-scattering condition was adopted: The incidence and scattering angles were fixed, respectively, at 12 and 20°. The scattered particles were detected using a movable TOF tube connected to the UHV chamber via a bellows; the H^+ and H^- species were separated from H^0 by deflecting the tube and applying a voltage to a deflector placed at the entrance. Temperature evolutions of the H^+ , H^- , and total (including H^0 , H^+ , and H^-) yields were measured independently. A multichannel scaler was used to create histograms for the TOF-SIMS and TOF-ISS spectra. The substrate was a mirror-finished Ni(111) surface that was cleaned by several cycles of heating (electron bombardment from behind) and sputtering (using the He^+ beam). The sample was attached to a Cu coldfinger extended from a closed-cycle helium refrigerator via a sapphire plate for electric insulation. The sample temperature was controlled using a cartridge heater and a digital temperature controller by monitoring the temperature of the coldfinger close to the sample position using Au(Fe)-chromel thermocouples. The cleanliness of the surface was checked in situ using TOF-SIMS. The samples of methanol (99.8%), ethanol (99.5%), and 1-propanol (99.5%) (purchased from Kanto Kagaku Reagents Co. Ltd.), as well as distilled water, were further purified by several freeze–pump–thaw treatments. The molecules were introduced via high-precision variable leak valves and were condensed onto the cooled Ni(111) substrate by backfilling the UHV chamber. The purities of the molecules were monitored in situ from the TOF-SIMS spectra. The coverage of the molecules was determined from the evolution curves of the TOF-SIMS intensities as a function of exposure. A monolayer (ML) of the molecules, as determined from the saturation point of the TOF-SIMS intensities, was attained at exposures of 2.5–5 L (langmuir; 1 L = 1.3×10^{-4} Pa s). The molecular deposition rate was 0.2–0.4 ML per second. The temperature was ramped at a rate of 5 K min^{-1} for both TOF-SIMS and TOF-ISS. The measurements were completed within a fluence of 1×10^{12} ions cm^{-2} to avoid damaging the sample.

3. Experimental Results

In a forward scattering geometry, directly recoiled hydrogen can be observed together with scattered hydrogen. However, we cannot separate them in TOF-ISS spectra that consist of a broad, single peak (not shown). The yields of directly recoiled H species are negligibly small compared to those of scattered species, as confirmed from forward scattering experiments using He^+ . Figure 1 presents results of TOF-ISS obtained for 40 ML H_2O films deposited on Ni(111) at 20 K. The H^+ , H^- , and total yields are shown, respectively, as a function of temperature. No H_2^+ ions are scattered at all; H_2^0 species (cannot be separated from H^0 in this study) might be included in the total yield, although they have only a marginal contribution because of dissociation during violent collisions. The glass–liquid transition of water occurs at 136 K, as determined from calorimetric⁶ and TOF-SIMS⁴ studies, but nothing happens at T_g in the total yield. The same is true for the H^- yield, but the H^+ yield tends to decrease at around T_g . A steep drop occurs for all species at a crystallization temperature, T_c , of ca. 160 K. The TOF-SIMS and infrared absorption study¹⁰ revealed that the film morphology changes abruptly at T_c because of the evolution of a fluidized

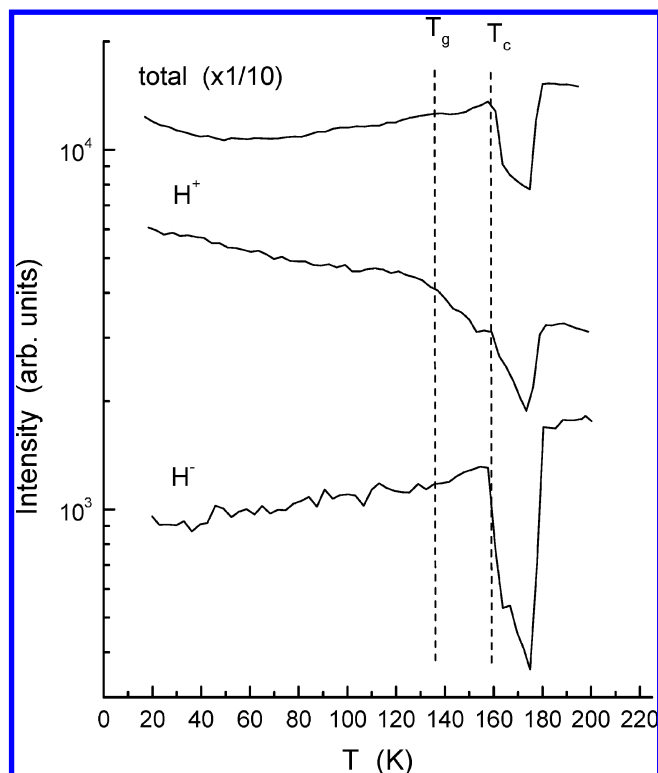


Figure 1. Temperature evolutions of H^+ , H^- , and total yields in TOF-ISS measurement of glassy H_2O films obtained with incidence of a 2 keV H_2^+ beam. The 40 ML thick films were deposited from the gas phase onto the Ni(111) substrate at 20 K.

liquid and the occurrence of immediate crystallization in it. The formation of droplets reduces the effective surface area under the small-angle-scattering condition, thereby engendering steep decays of all scattered species. Their yields recover at around 180 K as a result of the droplet evaporation. The total and H^- yields exhibit no indications of the film morphology change at T_g ; the gradual ($T < T_g$) and steep ($T_g < T$) decrease of the H^+ yield is thought to be associated, respectively, with reorganization of the molecules during structural relaxation and glass–liquid transition. The evolution of the H^+ yield differs greatly from that of the H^- and total yields because the former is influenced by ion–surface charge exchange processes in addition to the structural change.

Figure 2 presents the TOF-ISS yields from the 40 ML methanol films as a function of temperature. The temperature evolution of the H^- yield resembles that of the total yield. They start to increase at around T_g of methanol (103 K⁵), which is ascribable to the bulk structural change associated with self-diffusion of the molecules. On the other hand, the H^+ yield once decreases at ca. 80 K and then increases at around T_g . The evolution of the H^+ yield in the sub- T_g region is associated with structural relaxation. With further increasing temperature, the H^+ yield turns to decrease at 120 K, where the total and H^- yields plateau. At this temperature, the film morphology changes because of crystallization, as revealed from TOF-SIMS¹¹ and infrared absorption¹² studies. Therefore, the formation of droplets or crystal grains reduces the effective surface area of the film. The structural change is responsible for the increase of all species at $100 K < T < 120 K$, whereas a steep decay of the H^+ yield at $T > 120 K$ should be ascribed to the charge exchange process. The H^+ and total (and H^-) yields behave quite differently because the former (later) mainly reflects the structural transformation of the molecules at the surface (in the bulk), as described later.

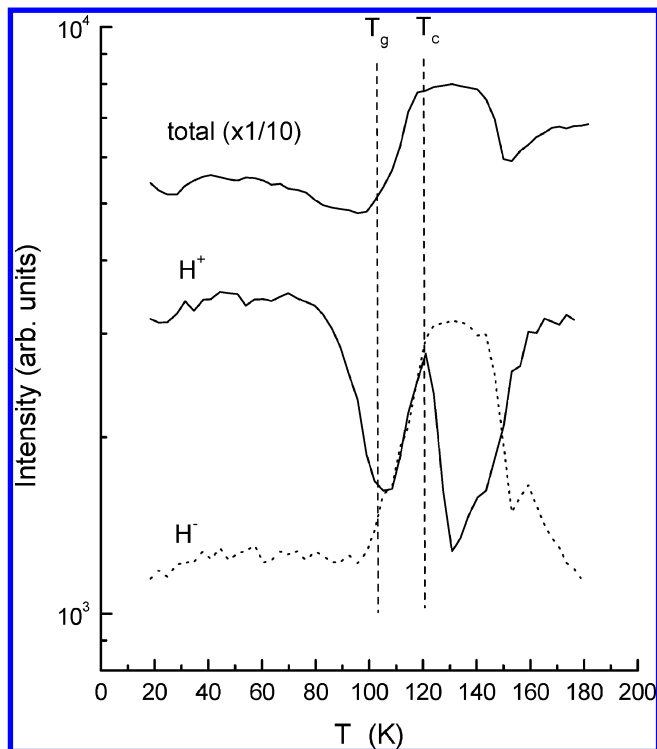


Figure 2. Evolutions of H^+ , H^- , and total yields from 40 ML CH_3OH films deposited on Ni(111) at 20 K as a function of temperature.

The TOF-ISS yields from 40 ML ethanol films are depicted in Figure 3 as a function of temperature. The total and H^- yields increase at temperatures corresponding to calorimetric T_g (97

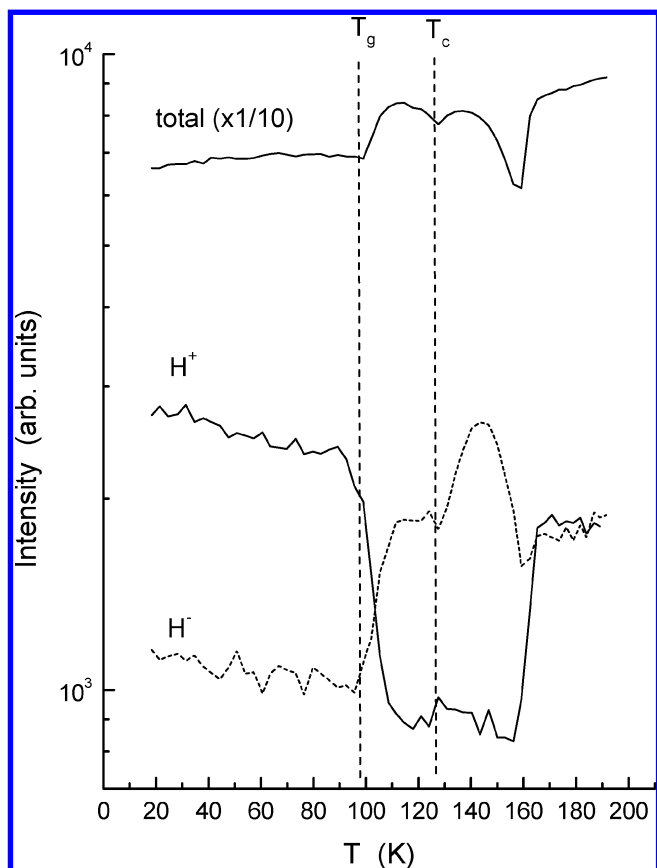


Figure 3. Evolutions of H^+ , H^- , and total yields from 40 ML C_2H_5OH films deposited on Ni(111) at 20 K as a function of temperature.

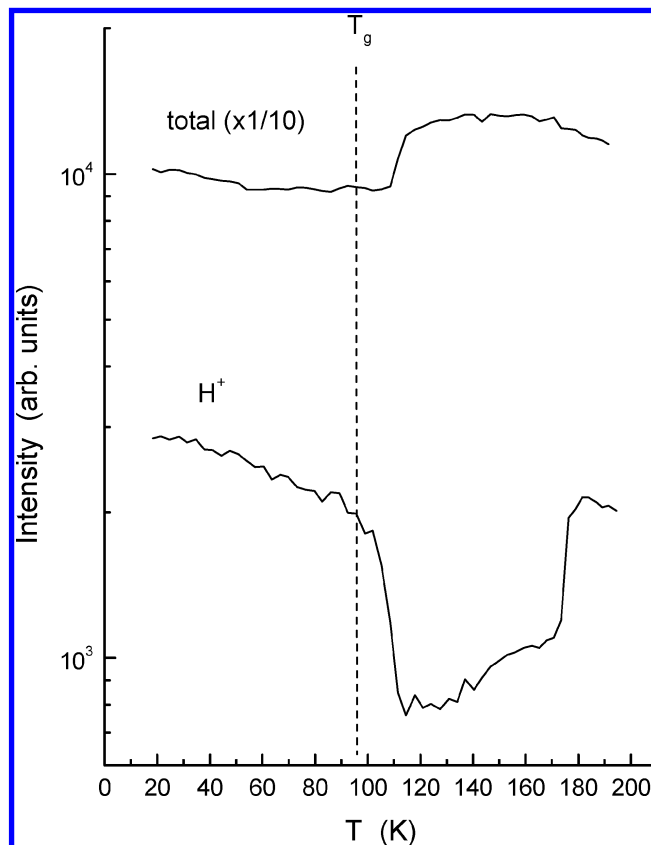


Figure 4. Evolutions of H^+ and total yields from 40 ML C_3H_7OH films deposited on Ni(111) at 20 K as a function of temperature.

K)¹³ and tend to be saturated in a narrow temperature range (ca. 10 K). The temperature evolution of the H^+ yield differs significantly from that of the total and H^- yields. From the analogy of the result for methanol, the decay of the H^+ yield is expected to be related to the surface structural change. Probably, both surface and bulk structures of ethanol change at around T_g ; the increase in scattering yield (as a result of the bulk structural change) is hindered by the prevailing decay for the H^+ yield. The yields of all species tend to increase at 120–125 K, where crystallization occurs. In contrast to the results for water, no decay behavior of the yield is observed during crystallization of ethanol, suggesting that the morphology of the film after crystallization is considerably different. After the crystallization is completed at 125 K, the total and H^- yields decay significantly at temperatures of 140–160 K. This phenomenon is explainable as premelting of crystals because the fusion temperature of ethanol is 158.7 K.

Figure 4 portrays TOF-ISS results for the 40 ML 1-propanol films. The total yield jumps in a narrow temperature range (109–115 K), where the H^+ yield decreases steeply following a gradual decrease. It is worth noting that this temperature is apparently higher than calorimetric T_g (96.2 K)¹⁴ of the liquid-quenched 1-propanol. The 1-propanol film does not crystallize up to the evaporation temperature (176 K), as confirmed from the infrared absorption spectra (not shown). Comparison of the vapor-deposited alcohol films revealed that the relaxation temperatures, as monitored from the steep decays of the H^+ yield, increase relative to T_g with increasing aliphatic chain length. That the relaxation temperature of 1-propanol is higher than T_g implies that the vapor-deposited 1-propanol glass is more stable than the liquid-quenched one.

Structural relaxation is an irreversible phenomenon controlled by the thermal histories. Figure 5 shows deposition-temperature

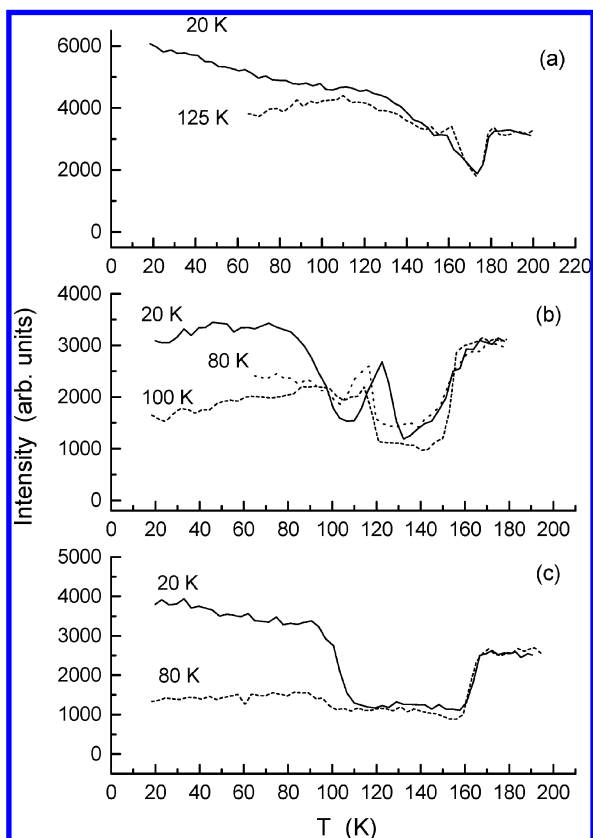


Figure 5. Temperature evolutions of H^+ yields from glassy films of (a) water, (b) methanol, and (c) ethanol. The films were deposited on Ni(111) at the temperatures shown in the figure.

dependencies of the TOF-ISS H^+ yields for (a) water, (b) methanol, and (c) ethanol films. In the case of water, the gradual decay region ($T < 100$ K) observed for the film deposited at 20 K is smeared out when the film is deposited at 125 K, but the glass-transition and crystallization region ($T > 136$ K) are little affected by the deposition temperature. The water film forms droplets when deposited at 135 K, as revealed from the small yields and the absence of their decay at T_c (not shown). For the methanol film, the decay of the H^+ yield at 80 K becomes much less remarkable when the film is deposited at 80 and 100 K; the increase in the yield at $T > T_g$ ($=103$ K) disappears for the film deposited at 100 K. Moreover, T_c is lowered for the films deposited at higher temperatures, as revealed from the shift of the decay temperature at around 120 K. The relaxation behavior of the ethanol film is also influenced by the deposition temperature. Consequently, the behaviors of the H^+ yield in the sub- T_g region depend on the thermal history; no structural relaxation was observed for the glassy films that were once heated to T_g (not shown).

The vapor-deposited films are characterized by low density. It might therefore be presumed that the relaxation observed here is related to volume shrinkage upon heating. TOF-SIMS measurements have been performed to gain insight into the microscopic film morphology as well as molecular configuration; the results for thin films of (a) water and (b) ethanol deposited at 20 K are displayed in Figure 6. For both films, protonated molecular ions in the form of $H^+(H_2O)_n$ and $H^+(C_2H_5OH)_n$ are sputtered in addition to H^+ . The cluster ion yields decrease more steeply than the H^+ yield with increasing temperature. The cluster ions are emitted preferentially from weakly bound (or lower-coordinate) molecular domains in low-density glass. Therefore, the gradual decrease of the cluster-ion yields is

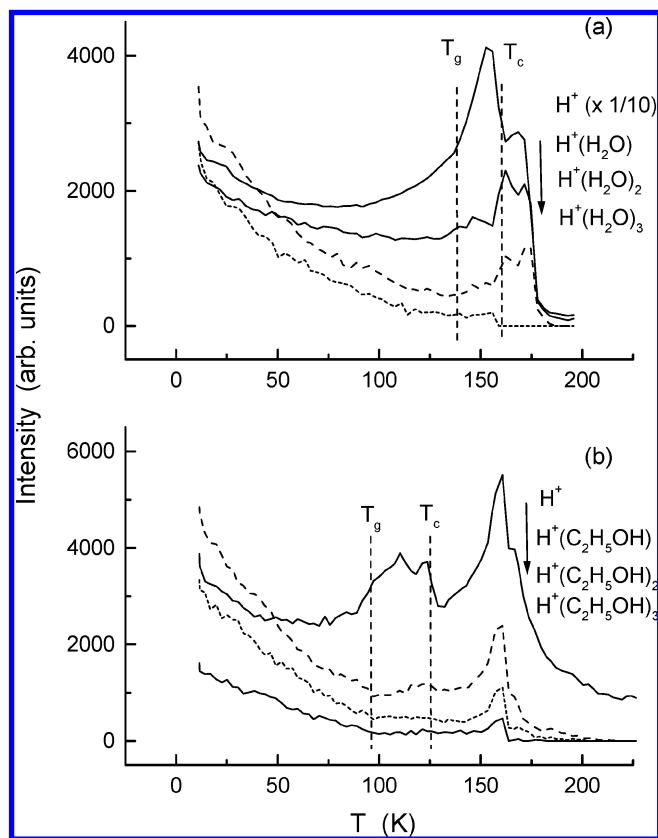


Figure 6. Temperature evolutions of TOF-SIMS intensities of bare proton and protonated molecular ions sputtered from (a) water and (b) ethanol films (40 ML) deposited at 20 K.

explainable as densification of the film resulting from pore collapse. This result is consistent with the effective surface-area measurements of porous amorphous solid water.^{15,16} The decay continues up to the calorimetric T_g for both water and ethanol films. This tendency corresponds well to the gradual decrease of the TOF-ISS H^+ yield from water at $T < T_g$ as presented in Figure 5a. However, the steep drop of the TOF-ISS H^+ yield at T_g for ethanol cannot be explained as the gradual pore collapse. This phenomenon is rather explained as the configurational changes of the molecules at the surface. The H^+ yield in TOF-SIMS increases for both water and ethanol when a liquid phase evolves at temperatures between T_g and T_c .

4. Discussion

It is expected that the molecular configuration in glass is fundamentally identical to that in liquid when the former is created by rapid quenching of the latter. However, such is not the case for water.^{17,18} For alcohols, the molecular configuration of vapor-deposited glasses might also differ from that of liquid-quenched glass. In fact, the porosity (or low density) of vapor-deposited glasses implies that numerous unpaired OH groups remain in the bulk; the molecules are reorganized to complete hydrogen bonds when the rotational and translational diffusions become possible upon heating. The structural change continues at temperatures higher than T_g to realize the equilibrium structure of normal liquid or crystals via the deeply supercooled-liquid state. Here, we demonstrated that such a relaxation process can be probed from temperature evolutions of the H^+ yields in both ISS and SIMS. However, it is necessary to clarify the ionization mechanism for deeper understanding of this phenomenon.

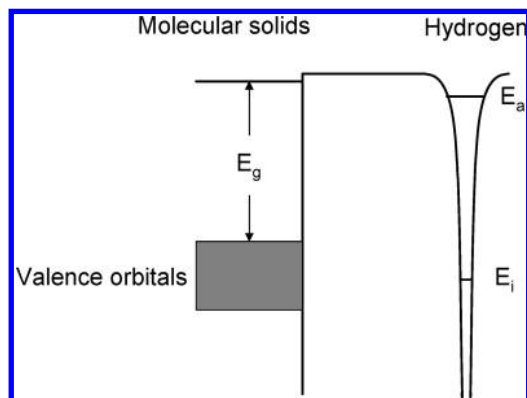


Figure 7. Schematic of the ionization level ($E_i = -13.595$ eV) and the affinity level ($E_a = -0.754$ eV) of hydrogen relative to the binding energy of valence orbitals of molecular solids. The hydrogen ion is readily neutralized at the surface via resonance tunneling of a valence electron, but it can be reionized during violent collisions via the electron promotion mechanism (see text).

The charge exchange of the energetic H^+ ion in solids and at the surface has been discussed extensively in previous papers.^{7-9,19-22} As schematically shown in Figure 7, the H 1s state ($E_i = -13.565$ eV) has an open-shell structure, satisfying a resonance condition with the valence orbitals. Therefore, the H^+ ion is neutralized in solids via the transient formation of a resonance (bound) state. The energetic H^0 atom can also be (re)ionized during violent collisions via the electron promotion mechanism.²¹ Consequently, the energetic hydrogen undergoes capture and loss sequences of valence electrons in solids;⁹ the charge state of scattered particles is fixed during the last collision (or bond breakage) with specific atoms immediately before leaving from the surface. Therefore, the H^+ yield is expected to be dependent on the configuration of the molecules on the surface. Moreover, the ionization probability is related to what degree a hole can be localized in the resonance state,^{20,21} which is controlled by the nature of the intramolecular bonds or intermolecular interactions. The hydrogen bonds are known to have some covalency, so that they reduce the H^+ yield as a result of the delocalization of a hole.⁸ Thus, reorganization of hydrogen bonds is expected to be probed from temperature evolutions of the H^+ yield. These behaviors are not expected for the H^- scattering because the affinity level of hydrogen is too shallow ($E_a = -0.754$ eV) to resonate with the valence states of the molecules. The yields of the H^- and H^0 species are rather determined by the density and configuration of the molecules existing on the trajectory of energetic hydrogen in the bulk. Therefore, the increase in total and H^- yields at T_g is tentatively ascribed to configurational change or densification of the molecules in the bulk. The film morphology also influences the yields of scattered particles. In any case, it is important that the structural changes of thin molecular films can be probed in microscopic and mesoscopic scales by measuring the temperature evolutions of the TOF-ISS yields.

In TOF-SIMS, the secondary H^+ ion is emitted from the surface via the bond-breaking mechanism.²³⁻²⁵ Therefore, the H^+ yield from water is expected to be related to the number or direction of the unpaired OH groups at the surface. The H^+ yield increases at $T_g = 136$ K, peaks at 153 K, and drops at 163 K, indicating that the configuration of the water molecules changes at the surface after the occurrence of self-diffusion (i.e., the evolution of a liquidlike phase) until crystallization. In the case of alcohol, the H^+ ion can be emitted from both O-H and C-H groups at the surface. The ionization probability is related to the ionicity in the parent species,²⁴ so that the small H^+ yield

from ethanol in comparison with that from water strongly suggests that H^+ is ejected mainly from the C-H bond. Therefore, the C_2H_5 group (the OH group) is thought to be exposed to the vacuum (concealed in the bulk) even when the molecules are deposited onto a low-temperature surface. The increase in the H^+ yield at around T_g is attributable to reorientation of the C_2H_5 group at the surface as a result of reorganization of hydrogen bonds in the bulk side.

The onset temperature of the structural relaxation of methanol (ca. 80 K), as revealed from the ISS H^+ yield, is apparently lower than calorimetric T_g (see Figure 2). The same tendency has been observed in TOF-SIMS,⁴ in which the H^+ yield increases at around 80 K simultaneously with the occurrence of intermixing of molecules. The surface structural changes are monitored preferentially on the basis of the H^+ yields in both SIMS and ISS. Therefore, these results indicate that the methanol molecules at the surface are mobile at temperatures lower than those in the bulk and that structural relaxation is associated with molecular diffusion. That the relaxation temperature of ethanol (ca. 90 K) is slightly lower than T_g might be explained similarly. However, the relaxation temperatures of both surface and bulk structures of the 1-propanol film become rather higher than T_g of the liquid-quenched glass. The hydrogen-bonded molecular chains are known to exist in a liquid phase of alcohol,²⁶ but molecules are frozen before completion of the hydrogen-bond chains on a low-temperature surface. Consequently, the vapor-deposited and liquid-quenched glasses might be regarded as distinct materials in terms of hydrogen bonds. The long aliphatic chain obstructs the structural transformation (i.e., reorganization of the hydrogen bonds). Therefore, the vapor-deposited glass of 1-propanol is thought to be more stable than the liquid-quenched one.

Recently, other groups have reported unusual properties of the vapor deposited glasses. Swallen et al.² demonstrated that 1,3-bis-(1-naphthyl)-5-(2-naphthyl)-benzene and indomethacin deposited at temperatures around $0.85 T_g$ had a lower enthalpy and higher density than those of liquid-quenched glasses. Ishii et al.³ showed that ethylbenzene molecules deposited at $0.91 T_g$ yield a high-density glass, which exhibited volume expansion rather than shrinkage at temperatures about 5 K higher than T_g of the liquid-quenched glass. These materials, termed unusually stable or anomalously high-density glasses, are thought to be formed under the semiequilibrium condition based on surface diffusion of the molecules. In contrast, we demonstrated that the low-density glass of 1-propanol is also more stable than the liquid-quenched glass. This behavior is expected to arise from the interplay between the hydrogen bond and aliphatic group, so that the underlying mechanism for stabilization differs from the high-density glasses described above. In this respect, we also described that the relaxation behaviors are dependent on the molecule deposition temperature (see Figure 5). The lowering of T_c for the methanol films deposited at higher temperatures indicates that the aging time for crystallization is shortened because the molecules can form hydrogen bonds to some extent during deposition.

The relaxation behaviors of water appear to be different from those of alcohols. The increase in the total TOF-ISS yield is missing at T_g ; the H^+ yield decreases rather gradually at $T > T_g$. Film morphology change at T_g has not been observed in TOF-SIMS for either water or alcohols.⁴ Therefore, we consider that the morphology of the water film is invariant at T_g although the molecular configuration at the surface changes greatly in the liquid-like phase, as evidenced by the TOF-SIMS H^+ yield (Figure 6a). The relaxation of water in the sub- T_g region (less

than 100–120 K) appears to be more gradual than that of either methanol or ethanol (see Figure 5). This behavior is in agreement with the gradual pore collapse.¹⁶ It is possible that hydrogen bonds of water are reorganized to some extent via rotational relaxation at $T < T_g$ because disturbance of the aliphatic group is missing. An equilibrium structure is generally considered to form immediately at T_g when supercooled liquid evolves. However, such is apparently not the case for water. The surface structure continues to change at $T > T_g$ (Figure 6a) based on the translational diffusion. The apparently different relaxation behaviors between water and alcohols at $T > T_g$ might be related to the “fragility” of liquids.²⁷ The water in the deeply supercooled region is regarded as a “strong liquid” whose heat capacity changes very little over a wide temperature range across T_g ,⁶ whereas “fragile liquid” including alcohols exhibits a substantial heat capacity jump at T_g .^{5,13,14,27} In this study, the structural transformation was observed rather than the glass transition itself, but the gradual relaxation of the surface structure at $T_g < T < T_c$ (see Figures 1 and 6a), together with the absence of bulk structural change at T_g , can be interpreted as a characteristic of strong liquid that exhibits slow evolution of liquid properties across T_g . This behavior is thought to be related to the fact that the liquid-like water formed prior to crystallization is a distinct phase.¹⁷ The fragile liquid (i.e., normal water) might be formed via a liquid–liquid phase transition immediately before crystallization occurs; its presence has been inferred indirectly from a drastic change in hydration properties at around T_c .²⁸

5. Conclusion

This study has demonstrated that structural relaxation of the vapor-deposited thin films of water and alcohols can be probed using low-energy H_2^+ scattering. The positive ion fraction of energetic hydrogen depends on atomic or molecular species during collisions and how they interact with the surroundings. Consequently, the yield of the scattered H^+ ion reflects the arrangement of the molecules at the surface. The total scattering yield of hydrogen is also influenced by the relaxation of the bulk structure or the film morphology change. The results showed that the surface structure of the vapor-deposited methanol film changes prior to the bulk structural change at T_g because the mobility of the molecules at the surface is enhanced relative to that in the bulk. The surface and bulk structures of the ethanol film change at around T_g . The structures of the glassy 1-propanol film appear to be more stable than those of the liquid-quenched glass, as evidenced by the relaxation temperatures

higher than T_g . This result suggests strongly that the aliphatic groups play an important role in the structural relaxation of alcohols. Probably, they disturb reorganization of the hydrogen bonds. In fact, the structure of the vapor-deposited water film changes gradually at temperatures considerably lower than T_g . However, no indication of the bulk structural change of the water film is recognizable at T_g , in contrast to the alcohol films; the surface structure of the liquid-like water changes gradually across T_g . It is likely that the liquid-like water formed at T_g is distinct from normal (or supercooled) liquid water.

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