Roles of Individual and Cooperative Motions of Molecules in Glass-Liquid Transition and Crystallization of Toluene

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Introduction…

❖ Glass-forming liquids are of two types: One in which viscosity behaves in a nearly Arrhenius fashion and their heat capacity changes very little across T_g and another in which are characterized by a strong non-Arrhenius behaviour in viscosity and a substantial drop in heat capacity at T_g.

❖ T_g has been determined from the onset temperature of the heat capacity jump in differential scanning calorimetric (DSC).

❖ Difficulties are often encountered in assignments of calorimetric T_g of poorly glass-forming materials

❖ It is quite important to determine the onset temperature of self-diffusion of molecules, T_d, and reveal its roles in the glass-liquid transition and crystallization.

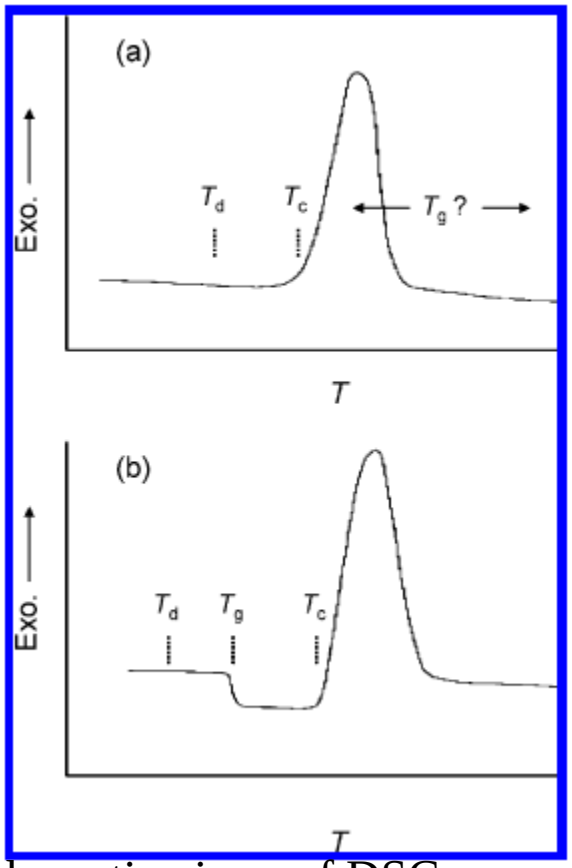


Figure 1. Schematic views of DSC scans. No appreciable glass transition endotherm is observed for water (a), although good glass formers like toluene (b) exhibit glass-transition endotherm (T_g) prior to crystallization exotherm (T_c). Because of decoupling, the translational molecular diffusion might occur at T_d prior to the glass transition at T_g, but the former is difficult to be identified using DSC.

In this paper…

❖ TOF-SIMS is used for the analysis of the glass-liquid transition dynamics and investigated correlations between microscopic molecular diffusion and macroscopic hydrodynamics of vapour-deposited toluene films.

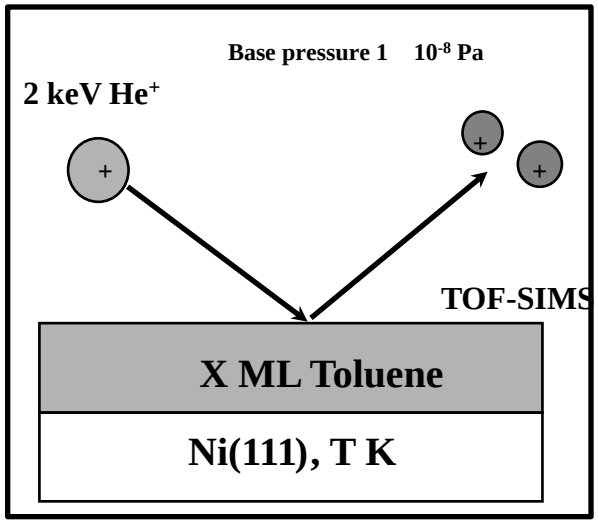
Experimental section…

❖ sample surface was floated with a bias voltage of +500 V.

❖ Positive secondary ions were extracted from the surface by a grounded stainless steel mesh placed immediately in front of the sample.

❖ They were pulse counted using a channel plate after travelling through a field free linear TOF tube.

❖ The TOF-SIMS spectrum was created using a multichannel scalar.



❖ To determine T_c, TPD spectra of toluene were taken using a differentially pumped quadrupole mass analyzer.

❖ The TOF-SIMS and TPD spectra were recorded at the same ramping speed of 5 K min^{-1}.

Experimental Results…

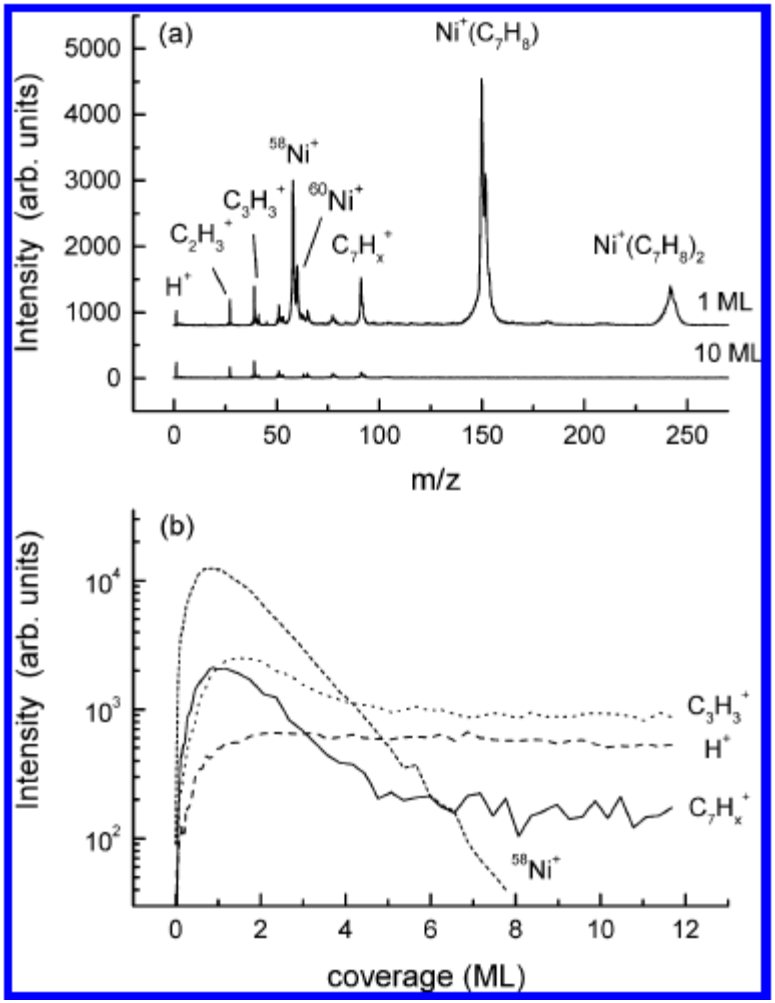


Figure 2. (a) Typical TOF-SIMS spectra from the toluene-deposited Ni(111) surface. The results between 1- and 10-ML toluene films are compared. (b) Evolutions of typical secondary ion intensities as a function of coverage of toluene deposited on the Ni(111) surface at 15 K.

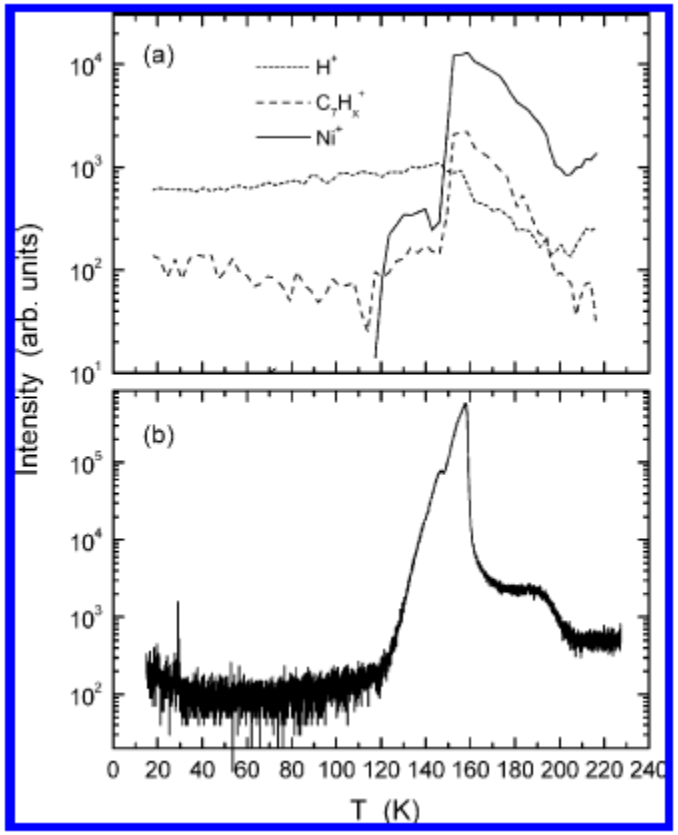


Figure 3. Temperature-programmed TOF-SIMS intensities from the 10-ML toluene film (a) and a corresponding TPD spectrum of toluene (m/z = 92) (b). The temperature was increased at a rate of 5 K min^{-1}.

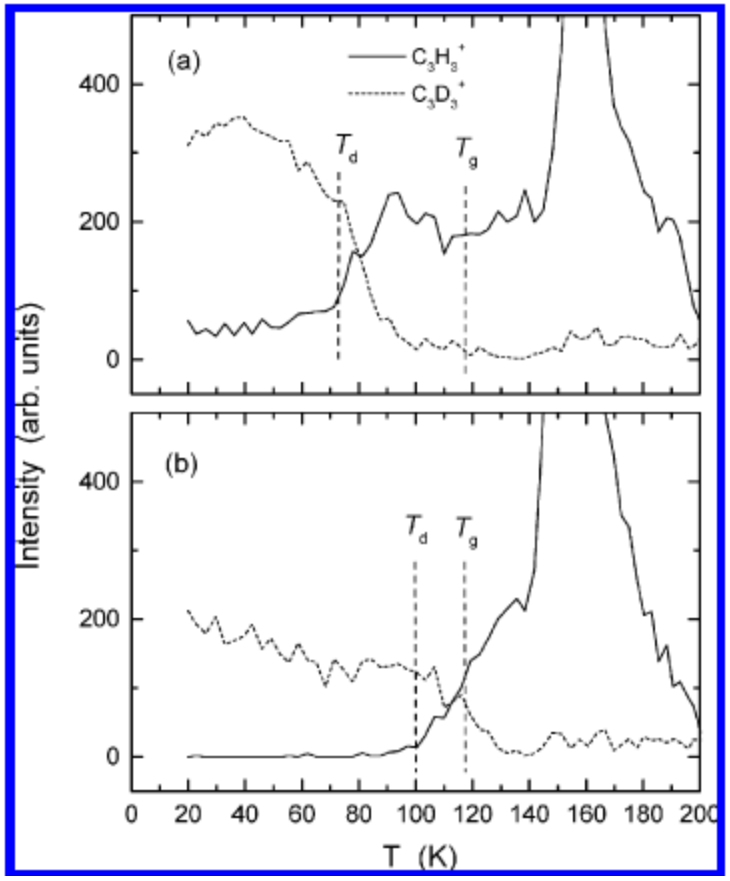


Figure 4. Temperature-programmed TOF-SIMS intensities of $C_3H_3^+$ and $C_3D_3^+$ ions sputtered from the 1-ML toluene-d_8 molecules deposited on the 20-ML toluene films deposited at 15 (a) and 100 K (b).

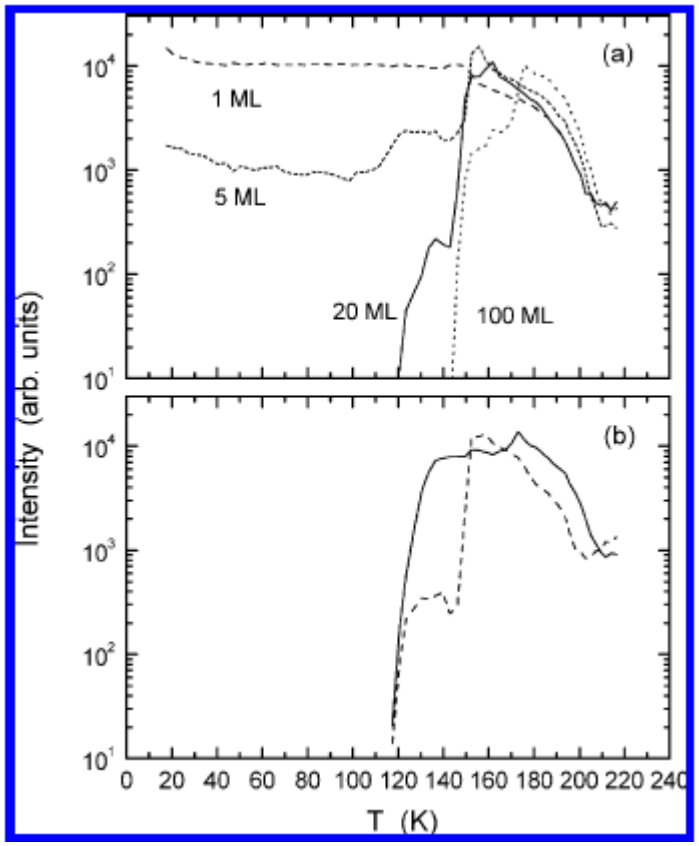


Figure 5. (a) Temp-programmed TOF-SIMS intensities of Ni^+ from the Ni(111) substrate on which 1-100 ML toluene molecules were deposited at 15 K. (b) The effect of pre-existing crystals on dewetting of the glassy toluene film is monitored by evolution of the Ni^+ intensity. The 10-ML glassy film deposited on crystalline toluene (solid line) is compared with that deposited directly on Ni(111) (dottedline). The crystalline toluene film was prepared by annealing the 10-ML glassy film at 130 K for 33 min.

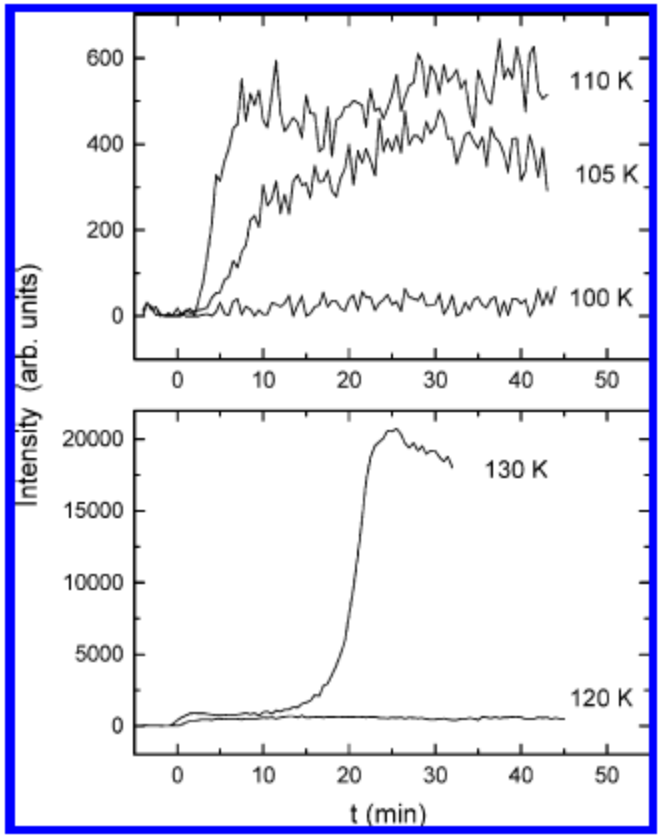


Figure 6. Isothermal TOF-SIMS intensities of the Ni^+ ion sputtered from the Ni(111) substrate on which 10-ML toluene films were deposited at 15 K. The negative time corresponds to the time required for heating the sample to temperatures indicated in the figure.

Conclusion…

❖ The microscopic origins of fragility and the α and β relaxations of deeply super cooled liquids were investigated by using TOF-SIMS.

❖ The toluene molecules move individually in the sub-T_g region ($T_d \approx 100$ K).

❖ The film deposited at 15 K is characterized by low density and exhibits lower T_d (~70 K).

❖ The film morphology changes at T_g = 117 K because super cooled liquid emerges, but no apparent change in diffusivity of the molecules is recognizable across T_g.

❖ The glass-liquid transition is a two-step process: Strong liquid is formed at T_d and super cooled (or fragile) liquid is created at T_g.

❖ The calorimetric assignment of water's T_g is fundamentally impossible because super cooled liquid water crystallizes immediately.

❖ The super cooled liquid toluene nucleates spontaneously at T_c = 147 K, where the growth of crystal grains results in a more significant change in the film morphology than that observed at T_g.

My opinion…

❖ Diffusivity of toluene (or benzene) through water and vice-versa (i.e. intermolecular diffusion) can be checked at temperature lower than the glass-liquid transition temperature.

❖ Low energy ion scattering experiment can also be done on toluene surface by using different projectile.

THANK YOU