Temperature dependence of ortho-Positronium Annihilation in Room Temperature Ionic Liquids

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Temperature dependence of triplet positronium (ortho-Ps) lifetime in N,N,N-Trimethyl-N-propylammonium bis(trifluoromethanesulfonyl)imide (TMPA-TFSI) was obtained with positron energies of 2 keV and 12 keV using the vertical slow positron beamline installed at AIST. Positrons could be injected from the liquid surface of TMPA-TFSI and then the surface structure could be detected even at 100 °C. The ortho-Ps lifetime became shorter at higher temperature in near surface and bulk. It indicated that the Ps bubble structure in room temperature ionic liquids was different from that in usual molecular liquids. Ps bubble size obtained from ortho-Ps lifetime can give information of the size of soft region consisting of van der Waals force surrounded by the stiff structure consisting of the Coulomb force.

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1. Introduction

Melting temperatures of Room Temperature Ionic Liquids (RTILs) are lower than 100 °C. They have unique properties and show many interesting phenomena. There are many new applications for many different fields. One of them is the spent nuclear fuel reprocessing. Therefore, the irradiation effects such as the research of excess electrons, for example the mechanism of electron solvation, is very important \cite{1}. Electron solvation is usually very fast process. According to the spur reaction model \cite{2}, positronium (Ps) formation in insulating materials are caused by the very fast, \textasciitilde{}ps, reaction of a thermalized positron and one of excess electrons. Therefore, the positron annihilation method can be a strong tool to investigate fast reactions of excess electrons. It was initially the reason of the positron annihilation experiments for RTILs \cite{3}.

Ps has negative work functions in materials, including molecular liquids. Therefore the Ps in molecular liquids creates an empty space called “Ps bubble” within very short time \cite{4}. The size of Ps bubble is controlled by the balance between Ps zero-point energy and surface tension energy, i.e., larger Ps bubble at higher temperature because of smaller surface tension. Recently, it was reported that the Ps bubble in RTILs showed some phenomena that were very different from them observed in molecular liquids \cite{5,6}.

The positron annihilation lifetime (PAL) measurements of RTILs showed too long lifetime values, such as 250–30 ps for the shortest lifetime component that should be the para-Ps intrinsic annihilation component that is 125 ps in vacuum. Later, AMOC measurements were performed to know if the long lifetime values were really the lifetime of para-Ps in RTILs \cite{7} The answer was that the para-Ps annihilation lifetime values in RTILs were not so long, and it was concluded that the longer lifetime values were apparently observed by PAL. Therefore, it was needed to understand more in detail of Ps in RTILs. Then the possibility of slow Ps bubble formation in RTILs was needed to be considered, because the intrinsic annihilation probability of para-Ps before Ps bubble creation must be much smaller than that after Ps bubble formation. Experimentally, the slow Ps bubble formation could be observed by AMOC. Ps before the bubble creation must be distributed widely on molecules and has more annihilation probability with core electrons. Positron annihilation in N,N,N-Trimethyl-N-propylammonium bis(trifluoromethanesulfonyl)imide (TMPA-TFSI) at young positron ages showed larger annihilation probability with core electrons \cite{8}. Hence, it was concluded that the Ps bubble formation time in TMPA-TFSI was about 1 ns \cite{8}.

For the formation time of Ps bubble of about 1 ns, there must be time dependent annihilation rates of para-Ps intrinsic annihilation and ortho-Ps pick-off annihilation, and it was the reason of apparent long annihilation lifetimes in RTILs obtained by PAL. Hence, a trial to extract the time dependent annihilation rates on PAL spectra was performed \cite{8,9}. Then the delayed increment of annihilation probability near time zero was observed because of the change of para-Ps intrinsic annihilation

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rate caused by the Ps bubble creation [8] and the oscillation of ortho-Ps pick-off annihilation rate was also observed after 400–500 ps because of the oscillation of the Ps bubble [9].

There were two difficulties to understand the oscillation of the Ps bubble [6]: (i) the oscillation frequency of every RTIL showed a quite similar dependence on the temperatures from the melting temperature of each RTIL even though the bubble size was different; (ii) the oscillation frequency was quite stable, even though there must be the bubble size expansion. The reasonable answer for these phenomena was that the oscillation is caused by the repulsive forces by the stiff structure consist of the Coulomb interaction between ions [6].

Now the reason of many interesting phenomena can be understood. The structure caused by the ionic interaction between anions and cations can exist even at the higher temperatures than the melting temperatures. It was the reason why the oscillation of Ps bubble was observed at the temperatures near the melting temperatures in RTILs. The small temperature dependence of the Ps bubble size is also probably caused by this ionic structure [6]. Therefore, we decided to investigate the temperature dependence of the ortho-Ps annihilation lifetime in wider temperature range, i.e., higher temperatures. The 22Na positron source wrapped by the thin polymer films cannot be used for the measurements at high temperatures, because it can be easily broken at high temperatures, and hence it is needed to inject positrons from outside of the RTILs samples. The vertical positron beams installed at AIST is suitable apparatus to investigate RTILs at high temperatures, because it is possible to inject positrons from the side of liquid surface and it is possible to place a small container for RTILs inside of the vacuum chamber. Moreover, we can investigate the structure in near surface of RTILs at high temperatures as 100°C. Already it was reported that there was a structure in near surface at the room temperature [10].

2. Experimental

N,N,N-trimethyl-N-propylammonium bis(trifluoro-methanesulfonyl)imide (TMPA-TFSI, Kanto Chemical Co.), was used without any purification in this study. The melting point of TMPA-TFSI is 19°C.

Positron annihilation lifetime measurements were performed using the vertical slow positron beamline installed at AIST [11]. The diameter of the positron beam was about 10 mm which is small enough so that almost all positrons can be injected into the RTIL surface. The RTIL was poured into a metal cup which was placed in the vacuum chamber as indicated in Fig. 1. Measurements were performed with the positron energies of 2 keV and 12 keV and every spectrum had about 2 million counts. The time resolution was about 300 ps (FWHM) which was enough to obtain lifetimes and intensities for the longest lifetime component due to the annihilation of ortho-Ps.

3. Results and Discussion

As mentioned above, the analysis of lifetime spectra of RTILs is not simple, because of the slow bubble formation. We preferred to obtain lifetimes of the longest lifetime components and did not need to obtain the other lifetimes, i.e., para-Ps intrinsic annihilation and free positron annihilation lifetimes. Hence, we decided to add too much freedom on the analysis, i.e., four free component analysis was applied on the analysis of the PAL spectra here. Moreover, the ResolutionFit in the PALShift program [12] was used without fixing the resolution curve. The results obtained by this analysis are indicated in Table I and Fig. 2.

The longest lifetimes of the ortho-Ps annihilation component were shorter at higher temperatures, although the surface tension of TMPA-TFSI shows a negative temperature dependence, i.e., smaller surface tension at higher temperature [13]. As mentioned above, the Ps bubble size in molecular liquids is larger at higher temperature, because of smaller surface tension. It was reported that the Ps bubble size in 1-Ethyl-3-methylimidazolium thiocyanate which has a smaller anion was smaller than in TMPA-TFSI [14]. Ps bubble is formed at soft region consisting of nonionic parts of RTILs by the van der Waals force and hence Ps bubble cannot be larger than the allowed size surrounded by the structure consist of ionic interaction by the Coulomb force in RTILs [6].
Therefore it could be expected that there would be almost no temperature dependence of the Ps bubble size. However, the ortho-Ps lifetimes were shorter at higher temperatures. Similar temperature dependence was observed just in water [15, 16]. The reason why only water shows this opposite temperature dependence is ortho-Ps reactions with reactive species formed by water radiolysis formed by the injected positron [17]. Ortho-Ps can convert to positron by oxidation and to para-Ps by spin conversion reaction, therefore the longest lifetime can be shortened by these reactions. Faster diffusion of reactive species at higher temperatures gives more reactions, i.e., shorter lifetimes. Although reactions of ortho-Ps can be a reason of shorter annihilation lifetime at higher temperatures in TMPA-TFSI because of something like the cage effect [18], further investigations are needed.

It was reported that the ortho-Ps annihilation showed shorter lifetime in near surface than in bulk of TMPA-TFSI at the room temperature [11]. The melting temperature of TMPA-TFSI is 19°C. Here, we tried to investigate if the structure in near surface could be present at 100°C. As indicated in Table I and Fig. 2, the ortho-Ps annihilation showed shorter lifetime in near surface even at 100°C which is 80°C above the melting temperature. Jeon et al. reported by using X-ray diffraction measurements that there could be a crystalline structure on the surface of RTILs even at temperature of about 37°C higher than the melting point [19]. On the other hand, the positron annihilation lifetime measurements, i.e., ortho-Ps lifetime, can indicate the existence of the structure consisting of ionic interaction in near surface of RTIL at 80°C above the melting temperature, even though the diffraction peaks cannot be observed.

4. Conclusion

We indicated that the ortho-Ps lifetime in TMPA-TFSI at 100°C was shorter than that at 23°C, even though the surface tension is smaller at higher temperatures [13]. It is clearly indicated that the Ps bubble in RTILs are very different from that in usual molecular liquids. The size of the Ps bubble probably gives size information of the soft region surrounded by the stiff structure consisting of ionic interaction by the Coulomb force. The reason of shortening the ortho-Ps lifetime at higher temperatures can be explained by the ortho-Ps reactions by something like the cage effect. Further investigations are needed to understand the detail of the mechanism.

The lifetime in near surface in TMPA-TFSI was shorter than that in bulk even at 100°C, 80°C above the melting temperature. It can show that the structure in near surface is different from that in bulk in RTILs. Positron annihilation lifetime measurements performed using the vertical slow positron beamline installed at AIST will be a strong tool to investigate the microscopic structure in RTILs.

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