Positronium bubble formation in room temperature ionic liquids

T. Hirade
Nuclear Science and Engineering Directorate, Japan Atomic Energy Agency, Tokai, 319-1195 Japan
Graduate School of Science and Engineering, Ibaraki University, 4-12-1 Narusawa, Hitachi, Ibaraki, 316-8511 Japan
E-mail: hirade.tetsuya@jaea.go.jp

T. Oka
Research Institute for Science and Engineering, Waseda University
3-4-1, Shinjuku, Tokyo, 169-8555 Japan
E-mail: kotobuki@kurenai.waseda.jp

Abstract. Positron annihilation age-momentum correlation (AMOC) measurements were performed for a room temperature ionic liquid (IL) to investigate positronium (Ps) bubble formation process. The Ps just after the formation must be squeezed Ps that has larger probability of annihilation with core electrons in liquids. However, it has been believed that the bubble formation in liquids is very fast and difficult to observe the squeezed Ps experimentally. When the bubble formation is slow, it can give broader energy distribution of annihilation gamma-rays at young age region. There have been several experimental results showing young age broadening and some of them are interpreted as the delayed Ps formation. However, if the bubble formation is slow, it also can be a reason of the young age broadening. If the squeezed Ps and the free positron give different momentum distributions by annihilation with core electrons on different atoms, it is possible to detect the annihilation from squeezed Ps at the young age, i.e. the bubble formation can be observed. We found larger high momentum distribution at young age in IL and it might be caused by the delayed bubble formation in IL. Positron annihilation methods can be a tool to investigate the IL molecular dynamics at the time range of pico-nano second and in the scale of sub-nano to nano meter.

1. Introduction
Positron can form positronium (Ps, a bond state of an electron and a positron) with an electron. Ps formation in insulating materials, such as liquids or solids, is well explained by the spur reaction model.[1] Injected positrons thermalize at the terminal spur where many cations and excess electrons formed. Positrons have a chance of Ps formation with one of excess electrons before electron and positron localization, usually. There are two different Ps states because of spins of the electron and the positron. Para-Ps has anti-parallel spins and ortho-Ps has parallel spins. The mass of the electron and

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1 To whom any correspondence should be addressed.
the positron disappears and the energy appears as gamma rays instead. The allowed number of annihilation gamma rays is even for para-Ps and odd for ortho-Ps. One gamma ray emitting annihilation is not allowed because of the low of conservation of momentum. Therefore para-Ps gives the fastest intrinsic-annihilation by emitting two gamma rays with lifetime of 125ps, and the ortho-Ps intrinsic-annihilation by emitting three gamma rays has the lifetime of 142ns in vacuum. In condensed matter, the positron in the Ps can overlap with electrons on surrounding molecules and pair annihilation with those electrons is also possible. This annihilation process is called “pick-off annihilation”. Almost all of pick-off annihilation gives two gamma rays. The ortho-Ps lifetime in condensed matter is about 1 ~ 10 ns mainly by the pick-off annihilation. Some of the positrons do not form Ps and annihilate with electrons on the surrounding molecules. The lifetime of these positrons is about 400ps in condensed matter.

Room temperature ionic liquids are liquids consisting of ions. Negligible vapour pressure and other interesting properties are considered to be caused by the ionic nature. There are many considerable applications of ionic liquids. One of the reasons is their environmentally friendly property.

It is reported that thermalization distance of electrons that has sub-excitation energy is large and that electrons before full solvation in ionic liquids can diffuse [2]. Ps formation is a good tool to investigate the electrons before full solvation. If these electrons can diffuse for long time, Ps formation is quite possible even at the later positron age such as 10~100ps and hence the Positron annihilation age-momentum correlation (AMOC) experimental results measured for IL was explained by the delayed Ps formation [3].

There were just the arguments for the change of the shape of the annihilation line measured by Ge semiconductor detector by use of time dependent $S$-parameter in [3]. Larger $S$ means the sharper line shape. There is the other parameter, $W$-parameter, i.e. wing parameter. It gives the information of annihilation with core electrons. Hence for the change between two positron annihilation processes, the sets of $S$ and $W$ appear on one straight line on the $S-W$ plane.

Here, we are discussing the change of positron annihilation processes by plotting on the $S-W$ plane and discussing the possibility of the delayed Ps bubble formation.

2. Experimental

N,N,N-trimethyl-N-propylammonium bis ( trifluoromethanesulfonfyl)imid (TMPA-TFSI) (Kanto Chemical Co.) was used without any purification in this study. It has the viscosity of 72mPas and the melting temperature of 19C. The oxygen gas in the sample was removed by nitrogen gas bubbling for about 30 min.

AMOC was performed by use of a triple coincidence method by use of a digital oscilloscope (Wavepro7100A, LeCroy) [4], scintillation detectors, i.e. truncated-cone-shaped BaF$_2$ scintillators and Hamamatsu H3378 photomultiplier tubes, and LO-AX (SEIKO EG&G) type semiconductor detector. Positron annihilation lifetime (PAL) was performed by the same scintillation detectors for AMOC by just removing the semiconductor detector. $^{22}$Na was used as a positron source. About 50kBq $^{22}$Na was sealed with two kapton films whose thickness is about 1.1mg/cm$^2$. The time resolution of PAL and AMOC was about 250ps (fwhm). The counting rate was about 1cps for AMOC. The total count for every spectrum was about 1 million. The PAL spectra analysis was performed by the PALSfit programme. [5]

Every $S$ and $W$ parameter was obtained by fraction of the counts appeared at 0~4x10$^{-3}$mc and 15~30 x10$^{-3}$mc from the centre to the total counts for the annihilation peak. Here, $m$ is the mass of electron, $c$ is the velocity of the light.

3. Results and Discussion

$S$ and $W$ parameters at the young positron ages from about -150ps in fused quartz and water were indicated in Fig.1. There are straight lines indicated by arrows up to about 1ns. The time interval between plots is 150ps. The straight lines indicated by arrows show the change from the p-Ps intrinsic annihilation to the free positron annihilation. In the case of the intrinsic-annihilation of para-Ps, momentums of the electron and the positron are cancelled out with each other. Hence, only the
annihilation gamma-rays from para-Ps have a narrow energy distribution, i.e. large \( S \) and small \( W \). When you observe positron age dependent shape of annihilation gamma-rays, you can find narrower distribution of annihilation gamma-rays at younger age region where para-Ps intrinsic-annihilation is favourable.

\( S \) and \( W \) parameters at the positron ages from -150ps to 900ps in IL, TMPA-TFSI, were indicated in Fig.2. For TMPA-TFSI, smaller \( S \), i.e. the broader distribution was found at young age region, and interpreted as the delayed Ps formation [3]. In the case of the delayed Ps formation, it is expected to have longer lifetime of free excess electrons, i.e. they can diffuse longer time. Moreover positrons also need to diffuse longer time. It means that there is more fraction of the annihilation from free positrons and probably freely mobile positrons at young age region. Therefore the annihilation at young age should give \( S \) and \( W \) on or close to the arrow in dashed line in Fig.2. Therefore, the larger \( W \) at young age in Fig.2 is difficult to explain with the delayed Ps formation.

The possible explanation for the \( W \) at young age is, probably, delayed Ps bubble formation. If the bubble formation is slow, Ps is squeezed just after Ps formation. If the electron and the positron in squeezed Ps prefer to be on the ions like in CS\(_2\) at low temperatures [6], \( W \) should be similar to the \( W \) at the free positron state. However, \( W \) is larger and hence the positron and the electron do not
separated even though Ps is squeezed and Ps is distributed on surrounding molecules or ions, i.e. it is probably similar to the delocalized Ps in ionic crystals. The negatively charged nitrogen atom in the TFSI anion attract positrons, which might be a suitable site for the free positron. TFSI anion contains fluorine, oxygen, surfer atoms and hence the squeezed Ps can give larger $W$ parameter than that for the free positron state. Therefore the change on the $S$-$W$ plane during the bubble formation might be like the arrow in solid line as indicated in Fig.2. Indeed, the real p-Ps intrinsic annihilation can probably have larger $S$ and smaller $W$. The squeezed Ps also can have larger $W$ and smaller $S$. The circles are just indicated for easy understanding.

The annihilation rate of the squeezed Ps is smaller than that of the p-Ps intrinsic annihilation, therefore the shoulder like shape on the lifetime spectra is expected and it can not be fitted by the exponentially decaying components. If the $S$ and $W$ change in Fig.2 indicates the delayed bubble formation, it might be possible to see the effect on the lifetime spectra. Indeed, the shortest lifetime is much longer than the one obtained in usual materials [3]. As mentioned above, it is impossible to fit the lifetime spectra of TMPA-TFSI with the exponentially decaying components and the difference between measured curves and fitted curves can make the shoulder visible. The differences for 47.5C and 22.5C are plotted in Fig.3. The shoulders on the lifetime spectra can be seen as the peaks indicated in Fig.3. The lifetime spectra of IL are very difficult to fit and then three fixed lifetimes, 0.2959ns, 0.4000ns, 1.0000ns and one free lifetime for the longest lifetime component were used. Intensities were free. The peaks indicate just the tendencies but it is larger and shifts to the older age at the lower temperature, 22.5C. Probably it indicates that the bubble formation is slower at lower temperatures.

![Figure 3. Differences between measured curves and fitted curves by use of fitting programme with exponentially decaying components, i.e. PALsfit[5] for TMPA-TFSI. Open circles were obtained at 47.5C and closed circles were at 22.5C. The values were standardised by the total count of every spectrum.](image)

4. Conclusion
Large $W$ was found at young age in IL, TMPA-TFSI, by the AMOC measurement and probably the delayed Ps bubble formation is only the possible explanation now. The shoulder like shape on the lifetime spectra was expected and it was confirmed by the peaks obtained by subtracting the fitted curve by PALsfit[5] from the measured curve, as indicated in Fig.3. The peaks at 22.5C and 47.5C indicate that the bubble formation is slower at lower temperatures.

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