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Positronium Bubble Oscillation in Room Temperature Ionic Liquids

Tetsuya Hirade[1,2,*]

[1]*Nuclear Science and Engineering Center, Japan Atomic Energy Agency, Tokai, Ibaraki, 319–1195 Japan*
[2]*Institute of Applied Beam Science Graduate School of Science & Engineering, Ibaraki University, 4–12–1 Nakanarusawa, Hitachi, Ibaraki, 316–8511 Japan*

E-mail: t.hirade@kurenai.waseda.jp

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Positronium bubble oscillation before the stabilization of the bubble was successfully observed by the change of the triplet Ps (*ortho*-Ps) pick-off annihilation rate in a room temperature ionic liquid, *N*,*N*,*N*-trimethyl-*N*-propylammonium bis(trifluoromethanesulfonyl)imide (TMPA-TFSI). It was reported that the Ps bubble stabilization in TMPA-TFSI took more than 500 ps. For materials having Ps formation, singlet Ps (*para*-Ps) gives the fastest annihilation mean lifetime of about 125 ps. Although it is intrinsic annihilation, the Ps bubble oscillation affects the *para*-Ps annihilation rate. The oscillation on the *ortho*-Ps pick-off annihilation was expected to appear at positron ages older than about 400 ps after the *para*-Ps annihilation fraction becomes small enough. An oscillation with 5.85 GHz frequency of the *ortho*-Ps pick-off annihilation rate was successfully observed at the positron ages older than 500 ps in 25 °C TMPA-TFSI.

1. Introduction

Ps is a bound state of an electron and a positron and has two different spin states. One is the singlet Ps (*para*-Ps) having an intrinsic annihilation rate of 1/125 ps^{-1} and the other is the triplet Ps (*ortho*-Ps) having intrinsic annihilation rate of 1/142 ns^{-1}. In condensed matter, the positron in Ps has contact with electrons in surrounding molecules and there then exists possibility of annihilation. Therefore the annihilation lifetime of Ps is shortened by the additional annihilation rate. This annihilation process is called "pick-off annihilation". This annihilation process will have almost no effect on the *para*-Ps mean lifetime in condensed matter because the intrinsic annihilation rate of *para*-Ps is much larger. Pick-off annihilation mainly affects the *ortho*-Ps annihilation. The positrons that are free from Ps formation, so-called "free positron", show about 400 ps mean annihilation lifetime.

Ps has negative work function in insulating materials and the repulsion between Ps and surrounding molecules can form a bubble, the so called "Ps bubble", in liquid phase. The bubble size is well explained by the balance between Ps zero point energy in the bubble and the sum of the energies of surface tension and pressure of the bubble [1]. When Ps is localized in a larger vacant space pick-off annihilation probability will be smaller, because the positron in Ps has a smaller overlap with electrons at the wall of the vacant space. This means that *ortho*-Ps mean lifetime is a very strong tool to investigate the size of the small vacant space (0.1 nm–10 nm) in insulation materials. The relation between the size of the vacant space and the *ortho*-Ps pick-off annihilation rate can be expressed by the Tao-Eldrup formula [2, 3] or extended Tao-Eldrup formula [4, 5].

The formation of almost all Ps by the spur process is very fast, probably within several ps. However, delayed formation of Ps, caused by the reaction between positrons and electrons initially thermalized at long distances has been observed in very pure fused quartz by positron age momentum correlation (AMOC) [6]. In AMOC the lifetime and annihilation gamma ray energy distribution are

measured simultaneously. The *S* parameter, a parameter describing the sharpness of the gamma ray distribution and obtained by calculating the fraction of counts in the central part of the annihilation gamma ray peak, is obtained as a function of lifetime. Delayed Ps formation is observed as so called "young-age broadening" when a small reduction of the *S* parameter is found at early lifetimes. The Ps formation reaction between the escaped positrons from the Ps formation by the spur process and pre-existing trapped electrons at low temperatures was very much delayed because the positrons need to diffuse. This process was also observed as young age broadening in AMOC measurement [7, 8]. However, even in these cases, slow (delayed) Ps formation did not cause any increase in the fastest annihilation lifetime. The fastest lifetimes obtained for room temperature ionic liquids (IL's) are much longer than the usual reported values for liquids [9]. Young age broadening was also observed in IL and hence it was initially interpreted as due to delayed Ps formation [9].

The *S* parameter is not the only parameter which can obtained by AMOC. The *W* parameter (wing parameter) is determined from the fraction of counts in fixed energy windows at the tail regions of the annihilation gamma-ray peak. The tail regions contain counts by the positron annihilation with high momentum electrons, i.e. core electrons. By plotting the *S* parameter and the *W* parameter together, an *S*–*W* plot is obtained. Movements on the *S*–*W* plane are often used to describe changes in the positron annihilation process. Time dependent *S*–*W* information can be obtained by AMOC. At positron ages below about 1 ns, the *S*–*W* plot typically changes in straight line from *para*-Ps intrinsic annihilation to free positron annihilation. *para*-Ps intrinsic annihilation gives relatively larger *S* parameter and smaller *W* parameter values, and whereas free positron annihilation gives relatively smaller *S* and larger *W* [10]. However, in the IL's, *N*,*N*,*N*-trimethyl-*N*-propylammonium bis(trifluoromethanesulfonyl)imide (TMPA-TFSI) the *S*–*W* plot showed a very different tendency. The straight line change as seen for water and fused quartz was not observed [10]. *W* was larger in the very young age region in TMPA-TFSI, which was interpreted as being due to the slow expansion of the Ps bubble. Ps was squeezed and annihilation probability with core electrons at the young age region was increased [10].

When Ps is formed, the repulsion between Ps and surrounding molecules appears simultaneously. A stable bubble size is well explained by the balance between the Ps zero point energy in the bubble and the sum of the energies of surface tension and pressure of the bubble as mentioned above. In this case, the bubble is in stable state, but before the bubble becomes stable, it needs to lose energy, i.e. it is expected to oscillate. Usually the Ps bubble stabilization time is very short and then it should be impossible to detect the oscillation of the bubble by positron annihilation lifetime (PAL) or AMOC measurements with a time resolution of 150 ps–250 ps. However, Ps bubble stabilization in IL's may be long enough to observe the oscillation of the Ps bubble. There have been many observations of the oscillations of larger gas bubbles (μm size) in liquids and the oscillation usually gives information of the visco-elastic properties on the macroscopic scale. In the case of Ps bubbles in IL's, the oscillation can give information on the IL's sub-nm scale visco-elastic properties.

The *ortho*-Ps pick-off annihilation rate depends on the size of the Ps bubble as mentioned above. If there is an oscillation of the Ps bubble, it should be detected in the time dependence of the *ortho*-Ps pick-off annihilation probability. Indeed, the Ps bubble oscillation can also affect the *para*-Ps intrinsic annihilation rate. Therefore, any oscillation of the *ortho*-Ps pick-off annihilation was expected to appear at positron ages older than about 400 ps after the *para*-Ps annihilation fraction becomes small enough. In the present study, very careful PAL measurements with a time resolution of about 160 ps (fwhm) were performed on TMPA-TFSI to try to observe the expected Ps bubble oscillation.

2. Experimental

PAL spectra were measured with a ^{22}Na source of about 45 kBq. The source was shielded in 7.5 μm Kapton foils and was immersed in the IL samples. Two BaF_2 scintillation detectors with a circular truncated cone shape (20 mm diameter at the top, 30 mm diameter at the bottom, and 20 mm height)

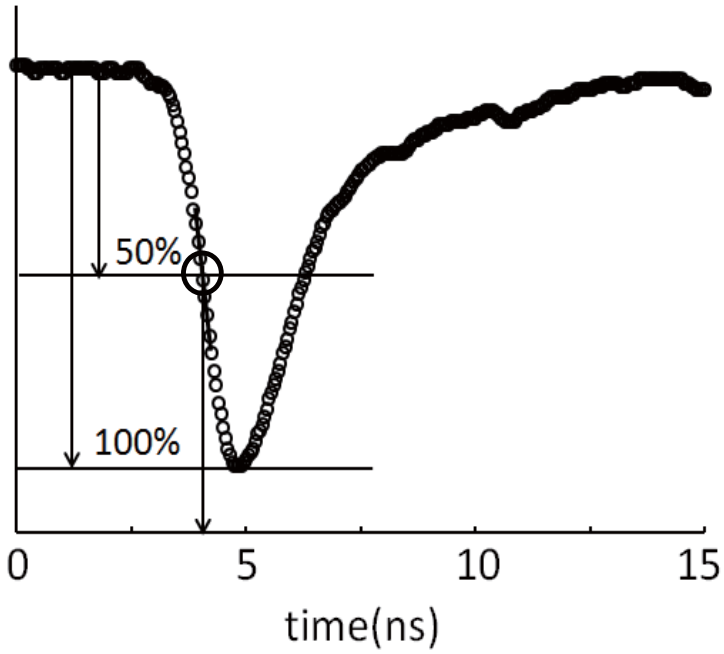

Fig. 1. Wave form from one of the scintillation detectors measured by a DSO. The time information of this signal was obtained at the crossing point indicated by the circle.

were used. One detector was used for the start signal by detecting the 1.275 MeV gamma-ray from ^{22}Na almost simultaneously with the time of a positron emission. The other detector was used for the stop signal by detecting one of the 511 keV annihilation gamma-rays. The waveforms from these detectors were stored in a digital storage oscilloscope (DSO), Wavepro7100A (LeCroy), with 20 G sampling/s. When the lifetime spectra were constructed, the timing information from every waveform was obtained from the crossing point at the 50 % level of the magnitude of the waveform as indicated in Fig. 1. If timing information is obtained from a lower level such as 25 %, the time resolution can be much better [11]. However, this could possibly induce an artificial oscillation on the lifetime spectra, because the shapes of the waveforms at 25 % level are not completely straight. The time resolution of the PAL apparatus with ^{22}Na was about 160 ps (fwhm). Every spectrum had about three million counts. The analyses of lifetime spectra were performed by use of PALSfit program [12].

TMPA-TFSI (Kanto-chemical) was used for this study, because the melting point is about 19 °C i.e. near room temperature. The sample was used just after the opening a new bottle without any treatment. Nitrogen gas bubbling was performed for about 30 min just before the PAL measurements to avoid the effect of oxygen gas, i.e. paramagnetic species. The sample temperature was controlled by use of a water bath with a temperature controller.

3. Results and Discussion

The lifetime spectrum of TMPA-TFSI at 25 °C is shown in Fig. 2. The total number of counts was 2.93×10^6 and the time resolution of this measurement was 160 ps (fwhm). From a three component analysis using PALSfit (without source correction) lifetimes of 0.207 ns (17.5 %), 0.447 ns (69.2 %), and 3.41 ns (13.3 %) were obtained. The longest lifetime is considered to be due to the *ortho*-Ps component in TMPA-TFSI because Kapton has no Ps formation probability. The solid line in Fig. 2

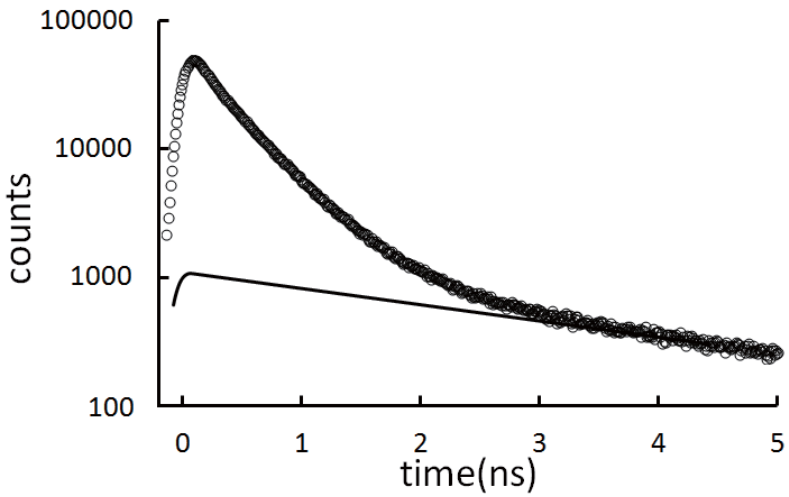

Fig. 2. Positron annihilation lifetime spectrum of TMPA-TFSI. The random coincidence background was subtracted. The solid line indicates the *ortho*-Ps component calculated from the values obtained by three component fit.

was calculated with 3.41 ns mean lifetime, total counts equal to 13.3 % of 2.93×10^6, i.e. 3.90×10^5, and 160 ps (fwhm) time resolution. This solid line is the *ortho*-Ps annihilation assuming no Ps oscillation.

It is then necessary to extract just the oscillation part from the lifetime spectra. The method applied here was to just subtract the lifetime spectra simulated from the results of the four exponentially decaying component fit by use of PALSfit. The lifetime spectra of ionic liquids are complicated [9] and the spectra also contain a source component so a four component fit was applied to obtain a better shape of the simulated lifetime spectra. The signal which remains after subtraction of the simulated curve from the measured curve should contain the oscillation. A similar procedure was already applied to see the slow expansion of Ps bubbles [10]. Figure 3 indicates the remaining signal obtained

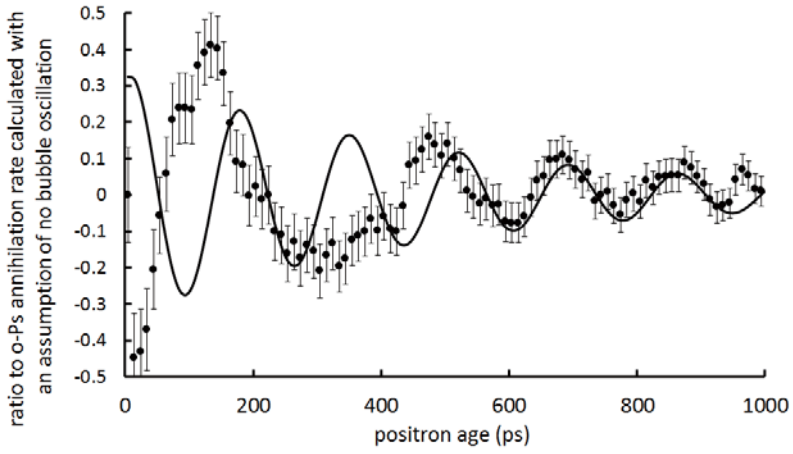

Fig. 3. Remaining lifetime spectrum after the subtraction of a simulated curve with four exponentially decaying components from the measured curve for TMPA-TFSI. The solid line is calculated with 5.85 GHz frequency and the decay rate of about 2 ns^{-1}.

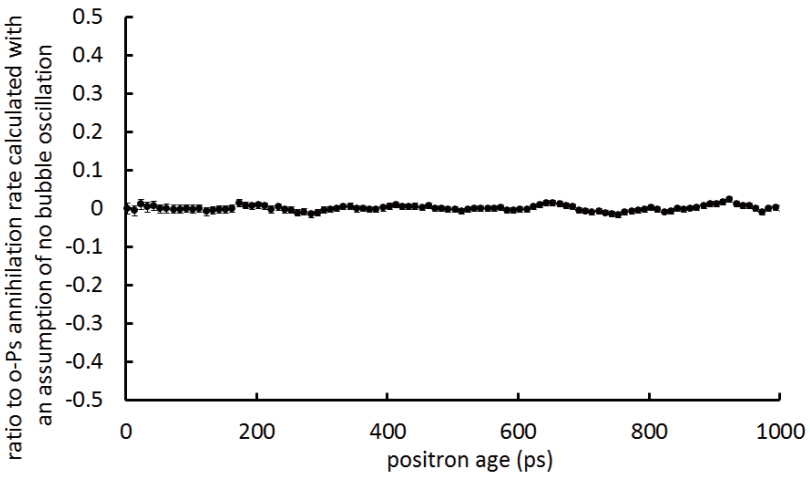

Fig. 4. Remaining lifetime signal after the subtraction of a simulated curve with four exponentially decaying components from the measured curve for fused quartz.

by the method explained above. In this spectrum a 5 point smoothing was performed. the curve was also standardized by expressing the value as a ratio to the solid line in Fig. 2, i.e. the *ortho*-Ps component calculated with a 3.41 ns mean lifetime, total counts of 3.90×10^5, and 160 ps (fwhm) time resolution as mentioned above. The *ortho*-Ps pick-off annihilation rate should be maximum at time zero, therefore it was possible to reproduce the oscillation curve as indicated in Fig. 3 by a product of a cosine curve and an exponential decay curve. The oscillation frequency was 5.85 GHz and the decay rate was about 2 ns^{-1} for 25 °C TMPA-TFSI. The result for fused quartz obtained by the exactly same procedure was indicated in Fig. 4. For fused quartz no oscillation is observed so the oscillation which appears for the IL must be caused by the oscillation of the Ps bubble before the Ps bubble stabilization.

4. Conclusion

Ps bubble oscillation with 5.85 GHz frequency and the decay rate of about 2 ns^{-1} was successfully observed on the change of the triplet Ps (*ortho*-Ps) pick-off annihilation rate in the room temperature ionic liquid, TMPA-TFSI, at 25 °C. This is the first experimental result showing that the Ps bubble oscillates just after Ps formation in liquids. The decay rate and the frequency of the oscillation will, probably, be able to give the visco-elastic properties of IL's in sub-nm scale. Indeed, further investigations are needed to understand how the measured is related to the properties of the IL. Positron annihilation lifetime measurements will be an important analytical method to study the physical properties of IL's in sub-nm scale.

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References

[1] R. A. Ferrell: Phys. Rev. **108** (1957) 167.
[2] S. J. Tao: J. Chem. Phys. **56** (1972) 5499.
[3] M. Eldrup, D. Lightbody, and J. N. Sherwood: Chem. Phys. **63** (1981) 51.
[4] K. Ito, H. Nakanishi, and Y. Ujihira: J. Phys. Chem. B **103** (1999) 4555.

[5] K. Wada, F. Saito, N. Shinohara, and T. Hyodo: Eur. Phys. J. D **66** (2012) 108.
[6] Y. Komuro, T. Hirade, R. Suzuki, T. Ohdaira, and M. Muramatsu: Radiat. Phys. Chem. **76** (2007) 330.
[7] N. Suzuki, T. Hirade, F. Saito, and T. Hyodo: Radiat. Phys. Chem. **68** (2003) 647.
[8] T. Hirade, N. Suzuki, F. Saito, and T. Hyodo: Phys. Status Solidi C **4** (2007) 3714.
[9] T. Hirade: Mater. Sci. Forum **607** (2009) 232.
[10] T. Hirade and T. Oka: J. Phys.-Conf. Ser. **443** (2013) 012060.
[11] H. Saito, Y. Nagashima, T. Kurihara, and T. Hyodo: Nucl. Instrum. Methods Phys. Res. Sect. A-Accel. Spectrom. Dect. Assoc. **487** (2002) 612.
[12] P. Kirkegaard, J. V. Olsen, M. Eldrup, and N. J. Pedersen: *PALSfit: A computer program for analysing positron lifetime spectra*, Risø-R-1652(EN), 2009.