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Positronium bubble oscillation in room temperature ionic liquids -Temperature dependence-

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Abstract. The temperature dependent oscillation of the ortho-positronium pick-off annihilation rate was successfully observed for a room temperature ionic liquid (IL), N,N,N-trimethyl-N-propylammonium bis (trifluoromethanesulfonyl)imide (TMPA-TFSI). The fundamental frequencies at 25C and 30C were 5.85GHz and 4.00GHz, respectively. The decay of the oscillation was faster at higher temperature, 30C. Moreover, the higher harmonic frequencies could explain the change of ortho-positronium pick-off annihilation rate successfully. The macroscopic viscosity of the IL could not explain the appearance of the oscillation. It indicated that the positron annihilation methods were very strong tools to study the properties of IL's in sub-nano meter scale that must be very different from the macroscopic properties.

1. Introduction

Positronium (Ps, a bond state of an electron and a positron) forms mainly by the reaction with an injected positron and one of the excess electrons after the positron thermalization at the end of the track in insulating materials. The detail of the Ps formation in insulating materials, such as liquids or solids, is well explained by the spur reaction model [1]. There are two Ps states because of spins of the electron and the positron. Para-Ps has anti-parallel spins and ortho-Ps has parallel spins. Positrons are anti-particle of electrons and then the mass of an electron and a 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 in the case of the intrinsic annihilation. 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 Ps can overlap with electrons on surrounding molecules and pair annihilation with one of those electrons is also possible. This annihilation process is called "pick-off annihilation". Almost all of pick-off annihilations give 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. These positrons are often called "free positrons", because they are free from Ps formation. The lifetime of these positrons is about 400ps in condensed matter.

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Room temperature ionic liquids (IL's) 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, mainly because of their environmentally friendly property.

It was 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 forms before electron and positron solvation at the time range of ~10ps in liquids. Therefore Ps formation reaction is a good tool to study the electrons before full solvation. If these electrons can diffuse for long time, Ps formation is quite possible even at the later positron ages such as 10~100ps and hence the results obtained by the positron annihilation age-momentum correlation (AMOC) experiment for IL could be explained by the delayed Ps formation [3]. AMOC is a combination method of the positron annihilation lifetime and the Doppler broadening of annihilation gamma-rays, i.e. momentum distribution of the annihilating electron. It is possible to discuss the change of the shape of the annihilation gamma-rays energy distribution, i.e. momentum distribution of annihilating electrons, by use of time dependent *S*-parameter applied 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. However, It was not a straight line for N,N,N-trimethyl-N-propylammonium bis (trifluoromethane-sulfonyl)imide (TMPA-TFSI).

Ps has negative work function in many materials and can create a bubble in liquids. *S*-*W* plots at young ages in TMPA-TFSI did not appear on a straight line and it indicated that the Ps bubble formation would take longer time than other liquids [4]. There is very small space for Ps at very young ages and it is similar to the squeezed Ps [5]. The small p-Ps intrinsic annihilation probability caused by the squeezed state at very young positron ages was successfully observed. [4] On the other hand, there is a good correlation between o-Ps pick-off annihilation rate and the bubble size, which is the well-known Tao-Eldrup formula. [6,7] If the bubble formation is slow in the IL, it is possible to detect the bubble size change by observing the o-Ps pick-off annihilation rate. It was successfully observed as the oscillation of the o-Ps pick-off annihilation rate in TMPA-TFSI at older positron ages than 400-500ps as expected. [8]

Here, we are discussing the oscillation of o-Ps pick-off annihilation rate measured at different temperatures.

2. Experimental

N,N,N-trimethyl-N-propylammonium bis (trifluoromethanesulfonyl)imide (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. The sample temperature was controlled by use of a water bath with a temperature controller.

Positron annihilation lifetime (PAL) measurements were performed by use of a fast-fast coincidence method by use of two scintillation detectors. The every detector had a BaF_2 scintillator with the shape of a circular truncated cone with 20mm diameter at the top 30mm diameter at the bottom and 20mm height on the top of a Hamamatsu H3378 photomultiplier tube. The waveforms from these detectors were stored by use of the digital storage oscilloscope (DSO), Wavepro7100A (LeCroy), with 20G sampling/sec. The timing information from every waveform was obtained from the crossing point at the 50% level of the magnitude of the waveform. [4] About 45kBq ^{22}Na positron source sealed with two kapton films whose thickness is about 1.1mg/cm^2 was immersed in IL samples. The time resolution of PAL was about 160ps (fwhm). Every spectrum had about three million counts. The PAL spectra analysis was performed by the PALSfit programme. [9]

3. Results and Discussion

The typical PAL spectrum was shown in Fig.1. Apparently, it is quite usual spectrum. However, PAL spectra measured in IL's gives anomalous long shortest lifetimes. [3] It could be explained by the very

Figure 1. Positron annihilation lifetime spectrum of TMPA-TFSI measured at 25C. Back ground was not subtracted.

slow Ps bubble formation. [4] Moreover, it was indicated that there exist the Ps bubble oscillation until the bubble stabilized. [8] It was needed to extract just the oscillation part from the lifetime spectra indicated in Fig.1. The method used here was exactly same as indicated in [8]. The oscillation part was obtained by just subtracting the simulated lifetime spectrum with four exponentially decaying component fit by use of PALSfit [9] from the measured spectrum. The subtracted part should be just the oscillation of the annihilation counts. The oscillation was caused by the oscillation of the bubble i.e. the oscillation of the o-Ps pick-off annihilation rate. Hence, to obtain the o-Ps pick-off annihilation rate, annihilation counts from o-Ps pick-off annihilation should be divided by the o-Ps population at every positron age. Indeed, the simpler method applied here to standardize just the oscillation part of the annihilation rate was as follows. The oscillation of the annihilation count at every positron age was divided by the o-Ps pick-off annihilation count without the oscillation that is almost proportional to the o-Ps population at the positron age. The o-Ps pick-off annihilation count was calculated by the intensity and the lifetime of the longest lifetime component obtained by the PALSfit analysis.

The oscillation curves of the o-Ps pick-off annihilation rate obtained for TMPA-TFSI at 25C and 30C were indicated in Fig.2 and Fig.3, respectively. The oscillation curve observed at 25C showed beautiful sine curve at the positron ages of 500-900 ps. [8] However, the oscillation curve at 30C was not like the oscillation observed at 25C. The oscillation at 30C was complicated curve. In the case of the oscillation of the gas bubble, there must be the higher harmonics. [10] Therefore it is expected to have higher harmonics even for the Ps bubble oscillation. The solid line indicated in Fig.3 was sum of the second and the third higher harmonics. It successfully reproduced the complicated curve. The fundamental frequency for these higher harmonics was 4.00GHz. Moreover, the decay of the fundamental frequency oscillation was faster at 30C. On the other hand, the higher harmonics was expected even at 25C after the fundamental frequency oscillation decayed. The solid line in Fig.2 was

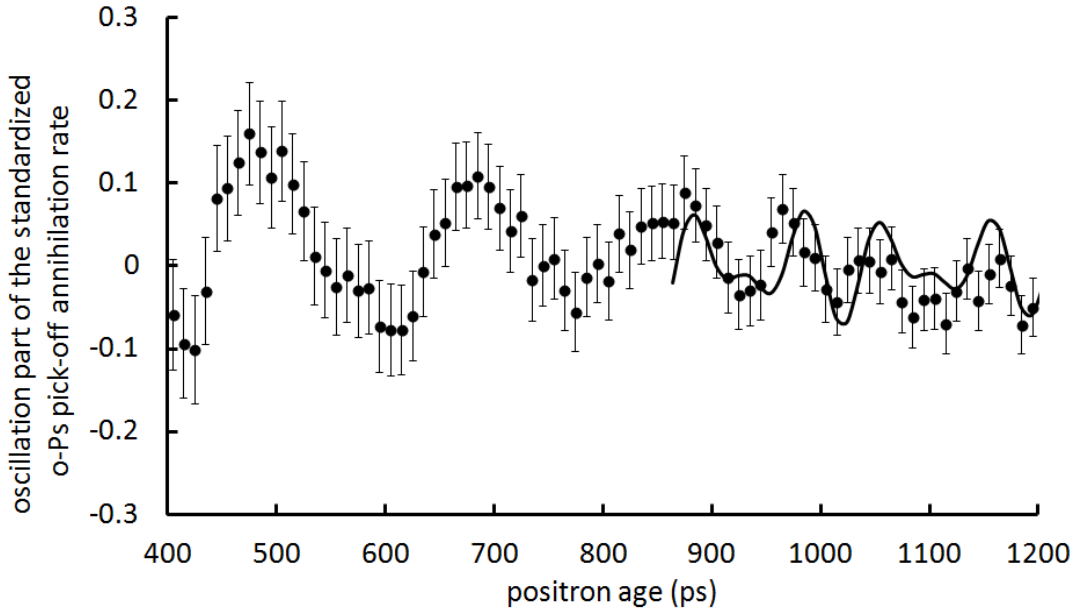

Figure 2. Oscillation part of the standardized o-Ps pick-off annihilation rate in TMPA-TFSI at 25C. The solid line was sum of the second and the third higher harmonics of the fundamental frequency of 5.85GHz.

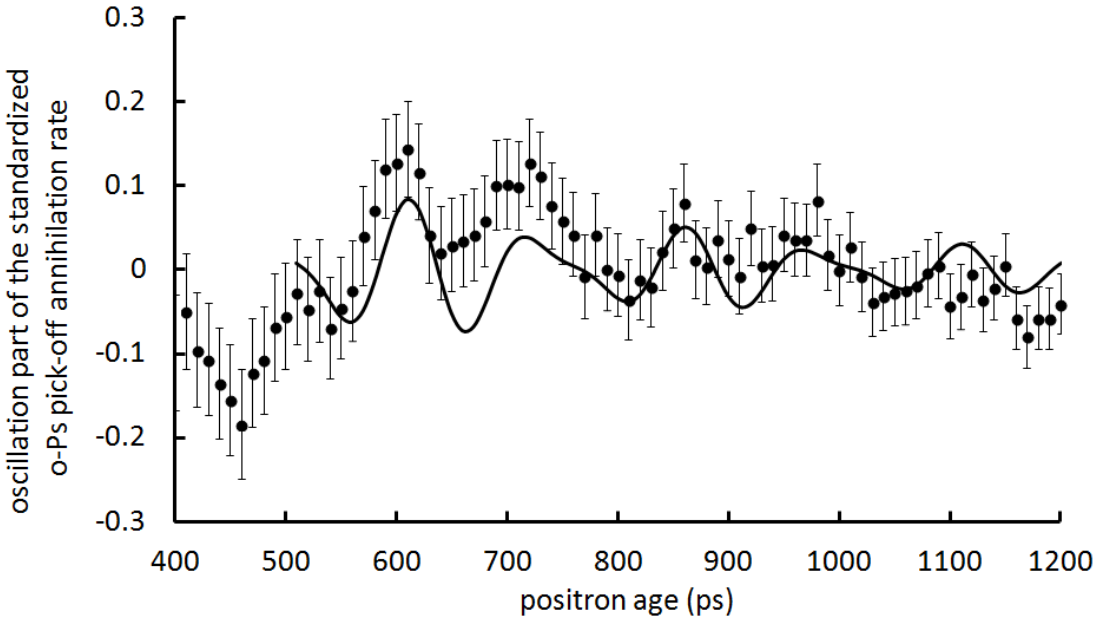

Figure 3. Oscillation part of the standardized o-Ps pick-off annihilation rate in TMPA-TFSI at 30C. The solid line was sum of the second and the third higher harmonics of the fundamental frequency of 4.00GHz.

also obtained by the summation of the second and the third higher harmonics of the fundamental frequency of 5.85GHz that was exactly same frequency for the sine curve appeared at 500-900 ps.

Two important things were obtained here. One was that the decay of the oscillation of the fundamental frequency decayed faster at higher temperatures. The other was that the fundamental frequency was higher at lower temperatures. The faster decay indicated that the energy loss caused by the movement of the molecules were larger at the higher temperatures. However the macroscopic viscosity of TMPA-TFSI is 72mPas that is not so small value. Theoretical studies by Stepanov et al. indicated that the liquids with these kinds of viscosities should not have oscillation. [11] Ps bubble size is sub-nano meter scale and the IL molecular motion in the very small scale around the Ps bubble should be very different from the molecular motion of the usual liquid materials. The higher frequency at the lower temperatures indicated that the modulus was larger.

4. Conclusion

The o-Ps pick-off annihilation rate measured for TMPA-TFSI showed the oscillation at the positron ages of 500-1200ps at 25C and 30C. The oscillation was probably caused by the oscillation of the Ps bubble. The fundamental oscillation could not be observed at 30C. However, the oscillation caused by the higher harmonic frequencies could explain the complicated oscillation of the o-Ps pick-off annihilation rate. Moreover the temperature dependence of the Ps bubble oscillation was observed. The decay of the oscillation was faster at higher temperatures. The frequency was higher at lower temperatures.

5. Acknowledgement

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