Generation of Positronium Annihilation Lifetime Spectra in Polymers

توليد أطياف زمن عمر فناء البوزترونيوم في البوليمرات

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Abstract:

Positronium annihilation lifetime spectroscopy is a powerful prope that ia used in the study of free volume in polymers. In this work we study the positronium annihilation lifetime spectra in polymers contain free volume and in pure polymers. The spectra that generated contain single Gaussian component fixed at 400ps convoluted with three lifetime components (τ_1,τ_2 and τ_3) and considering τ_1 originated from annihilation of para-positronium, τ_2 originated from annihilation of positrons in matter and τ_3 originated from annihilation of ortho-positronium in free volume also the background fixed at 0.001% of peak. Also study the effect of mean value of free volume size and its concentrations by study the effect of intensity of long-lived component (I_3) the theoretical spectra were compared with experimental spectra for polystyrene sample and we discussed the differences. We notice that as the long-lived component increase the right hand side of the spectrum rise. The difference between the experimental spectrum and the generated spectrum arises from that the background and time-zero channel in the generated spectra considered to be constant, but in experimental spectra, these parameter varied with thermal influences. Moreover the generated spectra described by single Gaussian component. The separating of 0.1 ns difference in lifetime components give specific description for positronium annihilation lifetime in polymers, also the difference of 5% in intensity give distinguished separating in the spectra, and these give distinguished components which have small intensities in experimental spectra . There are clear difference between positronium annihilation lifetime spectrum in pure polymers and positronium annihilation lifetime in defective polymers (contain free volume), this due to the effect of concentration and size of free volume on the spectrum. The small resolution (400ps) give a clear separation in smallest lifetime components (τ_1 ,τ_2) and smallest intensities in the generated spectra.

الخلاصة :

تعتبر تقنية حساب زمن عمر البوزترونيوم في البوليمرات طريقة جيدة جدا لدراسة الحجم الحر وتراكيزها في البوليمرات. في هذا العمل تم توليد و دراسة أطياف زمن عمر البوزترونيوم في البوليمرات التي تحتوي على حجم حر البوليمرات النقية. تم توليد هذه الأطياف نظريا بتصميم برنامج حاسوبي ، تحتوي هذه الأطياف المولدة على مركبة كاوسية واحدة وثبتت عرض النطاق لمنتصف الذروة لهذه الدالة على٤٠٠ بيكوثانية ولفت دالة الانحلال للبوزترونيوم ذات الثلاث مركبات (τ_1، τ_2،τ_3) حيث إن τ_1 ناشئة من فناء البارا- بوزترونيوم و τ_2 ناشئة من فناء البوزترونات في المادة أما τ_3 فناشئة من فناء الاورثو- بوزترونيوم في الحجم الحر. تم تثبيت الأحداث العشوائية على ٠.٠٠١% لقمة الطيف. أيضا تمت دراسة معدل قيمة الحجم الحر وتراكيزها وذلك بمعرفة تأثير شدة المحصلة الكبيرة (I_3). إن الأطياف المولدة نظريا قورنت مع أطياف عملية لعينة من مادة البوليستيرين ونوقشت الاختلافات بين الأطياف النظرية والأطياف العملية. لاحظنا إن بزيادة المحصلة الكبيرة فان الجزء الأيمن من الطيف يرتفع . إن سبب الاختلاف بين الطيف النظري و الطيف العملي هو ثبوتية الأحداث العشوائية و ثبوتية قناة الزمن الصفري في الأطياف المولدة نظريا أما في الطيف العملي تكون هذه العوامل متغيرة بسبب التأثيرات الحرارية. إضافة إلى ذلك فان دالة الاستجابة الزمنية في الطيف النظري وصفت بمحصله كاوسية واحدة. إن الاختلاف بقيمة ٠.١ نانوثانية التي تفصل محصلات زمن العمر في الأطياف النظرية تعطي وصف دقيق لمواقع فناء البوزترونيوم في البوليمر. أيضا اختلاف ٥% بالشدة يعطي فصل واضح في الأطياف. هنالك اختلاف واضح بين طيف البوليمر النقي وطيف البوليمر الذي يحتوي على حجم حر، هذا يعود إلى تأثير تركيز الحجم الحر في المادة. إن قيمة التحلل القليلة تعطي فصل واضح بين مركبتي زمن العمر القصيرتين (τ_1، τ_2) وكذلك في الشدة ذات القيم القليلة في الأطياف المولدة.

Key words: Positronium, Lifetime spectra, Free volume, Polymer.

1. Introduction

Positronium (Ps) is the bound state of an electron and its antiparticle. Positron annihilation spectroscopy is widely used to investigate subnanometer size of holes which appear in polymers as consequence of the irregular arrangement of molecular chains and form the so – called free volume [1]. The purpose of this work is to explain the effect of free volume and its concentration in polymers on the positronium annihilation lifetime spectra and compare with experimental spectra at the same conditions. In this work we designed a computer program to generate the positronium annihilation lifetime in polymers contains free volume and compared these spectra with experimental spectra. The spectra that obtained experimentally contain a resolution function convoluted with the decay curve of positronium for polystyrene sample. In polymers a fraction of the positrons entering the material form positronium, the lifetime of orthostate of this (o-Ps) [2] decrease typically from 2.6 ns in vacuum to the low ns – range in matter, due to annihilation during collisions of positronium with molecules (pick-off annihilation). The generated lifetime spectra are assumed to contain three different components which originated from the annihilation of parapositronium (p-Ps) (τ_1), free positrons (τ_2), and ortho-positronium (o-Ps) (τ_3) in free volume regions. The o-Ps pick-off lifetime very sensitively reflects the size of the local free volumes in which positronium is confined, so the generated spectra contain the values of long live component $\tau 3$ varied from 2.5ns to 2.8ns, where the two shortest lifetime components (τ_1,τ_2) fixed at 0.125ns and 0.2ns respectively. The generated spectra contain single resolution function convoluted with three components decay function and superimpose with background, where the resolution function fixed at 400ps and the background fixed at 0.001% of peak. In positronium annihilation lifetime one employs the anti-electron the positron as a probe and monitors the lifetime of the positron and positronium in the polymeric materials under study. Because of the positive – charged nature of the positron, the positron and positronium are repelled by the core of the electron of polymers and trapped in open spaces, such as hole, the free volume and voids. The annihilation photons come mainly from these open spaces. Results of positron annihilation lifetime measurements as a function of temperature[3], pressure [4] time of aging [5] and degree of crystalline [6] give evidence that the positron and positronium are localized in these preexisting local holes and free volume in polymers. Because of relatively small size of positronium probe ($1.06A^0$)[7] compared to other probes positron annihilation spectroscopy is particularly sensitive to small holes and a free volume of angstroms in size and at time of molecular motion from 0.1 ns and longer. In contrast to other methods, positron annihilation spectroscopy is capable of determining the holes and free volume in polymer with no significant interference related to the bulk, and the positron is also localized in free-volume holes [8]. The localization of the positron in polymers may bring practical applications of positron annihilation spectroscopy to certain polymeric materials where no positronium formed such as a conducting polymers [9], so that, we are generate the spectra for this case (spectra of conducting polymers), where the spectrum contain only on the two lifetime components and these spectra has been compared with the spectra of polymer contain positronium annihilation and discussed the difference. In current work some of our spectra contain o-Ps lifetime, because that its results are employed to interpret the free – volume hole distribution with higher accuracy than using the positron lifetime distribution. In generation of positronium annihilation lifetime spectra we are use a perfect mathematical model of resolution function and decay function to avoid most of error arises with experimental spectra. The time – zero point in the generated spectra was considered to be constant, also the generated spectra are do not contain lifetime components with very small intensities. Also the input parameters (lifetime components values and its intensities, and resolution) have not plus or minus error number as in experimental spectra, and the random coincidence was treated as constant parameter in the generated spectra. The total count for each spectrum was 100000 counts. The generated and experimental spectra are compared and the difference has been discussed

2. Theory

In positron annihilation spectroscopy , the observed lifetime is the reciprocal of the integral of the positron (ρ_+) and the electron (ρ_-) densities at site where the annihilation take place [10]

$$\tau = \text{constant} * \int (\rho_+ \rho_- \, dr)^{-1} \qquad (1)$$

According to eq.(1) a large hole , which has a lower average electron density, is expected to have a longer Ps lifetime. The correlation between the free volume in molecular systems and the observed o-Ps lifetime is expressed in semiempirical equation [11] between the mean o-Ps lifetime $\tau 3$ and mean radius of holes R as

$$\tau_3 = \frac{1}{2}[1 - \frac{R}{R_0} + \frac{1}{2\pi}\sin(2\pi\frac{R}{R_0})]^{-1} \qquad (2)$$

Where τ_3 is the positronium lifetime in free volume , R: hole radius, where $R_0=R+\Delta R$

3. Results and Discussion:

a- Effect of free volume

The difference between the positron annihilation spectrum in pure polymer and positronium annihilation spectrum in polymer contain free volume was shown in fig.(1)

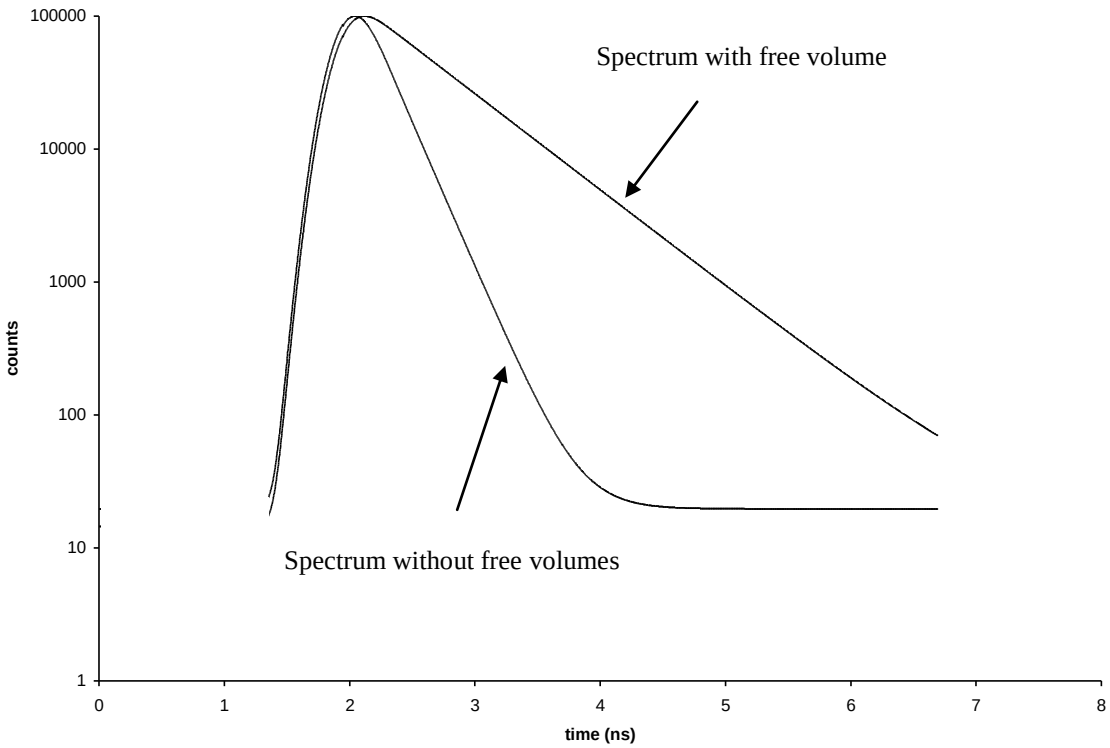

Fig.(1) shows the generated spectrum of positronium annihilation in polymer contain free volume and generated spectrum of positron in pure polymer.

These difference arises from that the positronium annihilation lifetime spectrum in polymer contain free volume described by long-lived component (τ_3), which determine the free volume, but in pure polymer the spectrum contain only τ_1 and τ_2 .

In fig.(2) the two shortest lifetime components (τ_1,τ_2) fixed at 0.12ns and 0.2 ns respectively, while the variation of long-lived component (τ_3) ranged from 2.5 ns to 2.8 ns. In fig. (2) the increasing in τ_3 has a

big effect on the positron annihilation decay spectra, there for the mean free – volume hole size has a large effect on the spectra, so as the mean free – volume hole size increase (increasing of τ_3), the right hand side part of the spectrum ride up although the intensities of τ_1 and τ_2 are larger than intensities of τ_3 as shown in fig. (2). The splitting in the right hand side of the spectra is due to the increasing in the long-lived component, also the amount of difference in the splitting has nearly constant ratios this due to regular increasing in the values of τ_3 , so as the right-hand side of spectrum rise up the mean value of free-volume become larger.

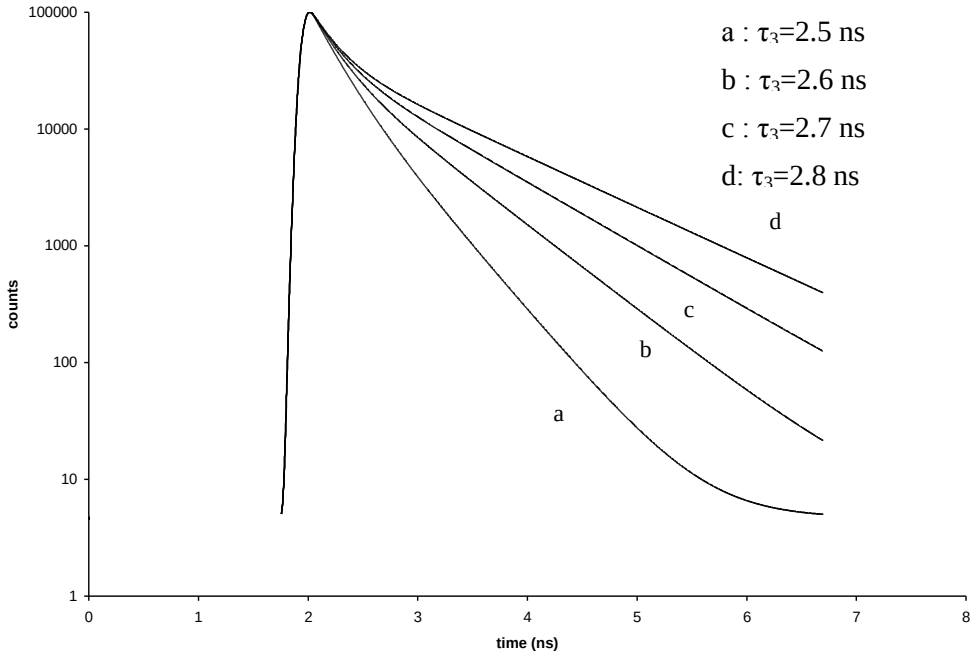

Fig.(2) illustrate the separation in the spectra with different values of τ_3

b- Intensity Effect

The concentration of free volumes has been determined by o-Ps intensity. Fig.(3) show the effect of increasing of intensity of long-lived (I_3) component. The parapositronium intensity (I_1) and the positrons intensity (I_2) varied from 10% to 35% while the o-Ps intensity I_3 which reflects the relative probability of o-Ps annihilation from free volume, varied from 5% to 30%, in each spectrum the right hand side part rise more this due to the increasing the relative intensity.

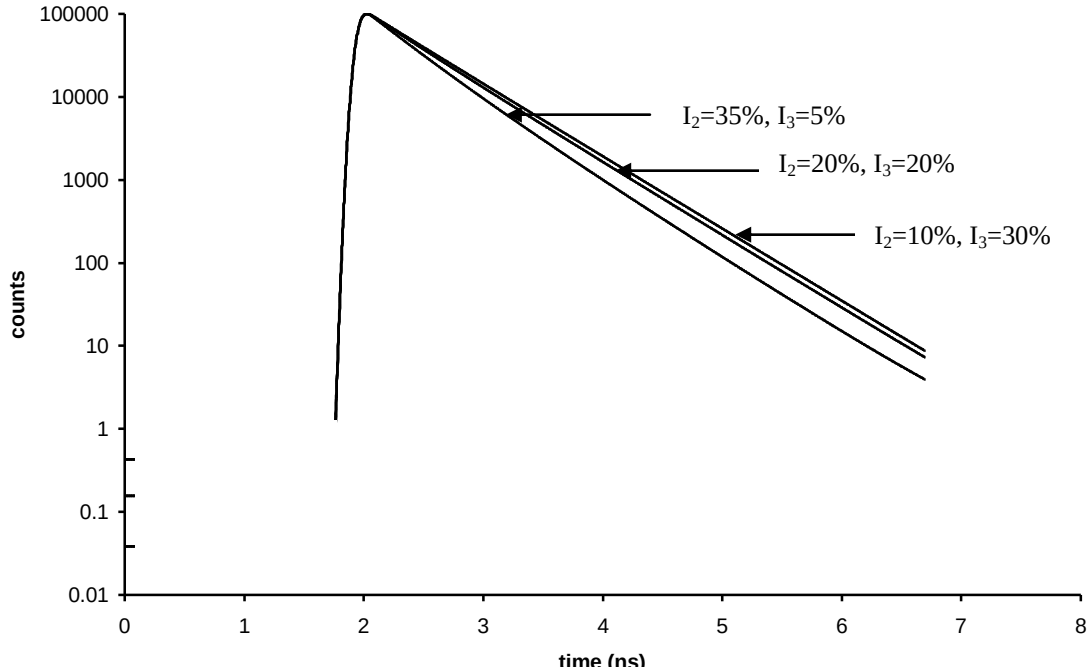

Fig.(3) illustrate the effect the variation of I_2 and I_3 on the spectra

4. Experimental Spectrum Details and Comparison with Theory

The experimental spectrum represents the positronium annihilation lifetime spectra in polystyrene sample [12]. The sample was manufactured by keeping 1.5 gm of polymer grain in the sample preparation system under pressure of 200 bar during a period of 3 minutes at temperature (T_m+25 ^{0}C) where T_m is the melting temperature. The diameter of the sample is 32 mm with thickness of 2mm. The sample was irradiated in air and in vacuum with Beta ray by using ^{90}Sr/^{90}Y Beta source with activity of 3mCi to total Beta-dose of 1.2Gy. All these parameters used as input parameters to generate positronium lifetime spectrum for polystyrene sample of 1.2Gy of irradiation. The lifetime spectrum measured was carried out using a fast-slow timing spectrometer of about 421ps resolution. The spectrum was analyzed using PFPOSFIT program [13] for three components where the shortest lifetime component (τ_1) is attributed to free annihilation of positron. The second lifetime component (τ_2) is considered to be due to the annihilation of free positron contributed with annihilation of parapositronium. The longest lifetime component (τ_3) is attributed to pick-off annihilation of o-Ps in the free volume. In the irradiation of 1.2Gy, the parameters were as following τ_1=125ps, I_1 =71.66%, τ_2 =363ps, I_2 =21.45%, τ_3=1.974 ns, I_3 =6.99%. Fig.(4) show these experimental spectrum for polystyrene sample compared with theoretical spectra. As show in figure the experimental spectrum higher than the theoretical spectrum especially at the region of long-lived component this due to the high value of τ_3, also the intensity of τ_1 and τ_2 higher than intensity of τ_3.

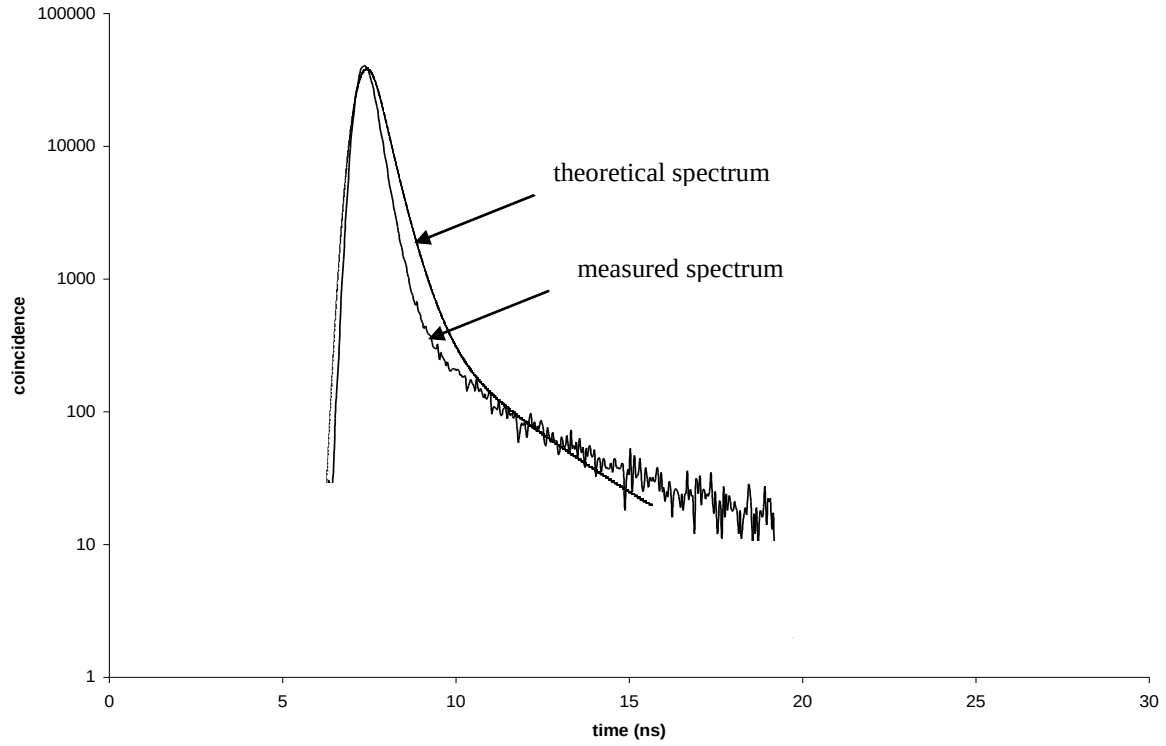

Fig.(4) illustrate the theoretical and measured spectra for polystyrene sample

5. Conclusions

We notice that the free-volumes in polymers have a significant effect on the positron lifetime spectrum, because it determines by long-lived component, whereas the long-lived component increase the right hand side of the spectrum rise. The splitting in the spectra due to the variation in the values of τ_3. Also the increasing in the intensity of long-lived component (I_3) make the right-hand side of the spectra rises up despite of the that I_1 and I_2 were larger than I_3 , this due to high value of τ_3. The difference between the experimental spectrum and the generated spectrum arises from that the background and time-zero channel in the generated spectra consider to be constant, but in experimental spectra these parameter varied with thermal influences. Also the generated spectra described by single Gaussian component. The separating of 0.1 ns difference in lifetime components give specific description for positronium annihilation lifetime in polymers, also the difference of 5% in intensity gives distinguished separating in the spectra, these give distinguished components which have small intensities in experimental spectra. The effect of I_2 were smaller than the effect of I_3, this due to that τ_3 greater than τ_2. There are clear difference between positronium annihilation lifetime spectrum in pure polymers and positronium annihilation lifetime in defective polymers (contain free volume), this due to the effect of concentration and size of free volume on the spectrum. The small resolution (400ps) gives a clear separation in smallest lifetime components (τ_1 ,τ_2) and smallest intensities in the generated spectra.

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