Air quenching of positronium in mesoporous materials: positron porosimetry

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Abstract
The o-Ps lifetimes in mesoporous materials in vacuum and in the presence of air have been measured. The measured lifetimes are examined in terms of various available models for positron porosimetry. The o-Ps lifetimes measured in vacuum agree well with those predicted from the extended Tao–Eldrup model. In the presence of air, the o-Ps lifetimes are seen to reduce. The enhancement in the annihilation rate of positronium caused by air is seen to increase with decrease in the pore size. The positronium lifetimes measured in the presence of air in the present experiment and the literature data are fitted to a model based on the statistical probability of positronium interacting with the pore wall. This describes the increase in the quenching rate with decrease in pore size by taking into account the reactivity of air as well as the reduction in the average pore size due to adsorption of air on the pore surface. This simple model can be used in positron porosimetry for measurements carried out in the presence of air.

1. Introduction

Positron annihilation spectroscopy is emerging as a valuable tool for pore size determination on the subnanometre to nanometre scale [1–4]. In any medium, the intrinsic lifetime of ortho-positronium (o-Ps) is reduced from 142 ns by the process called pick-off annihilation. The pick-off annihilation rate and, hence, the o-Ps lifetime are dependent on the size of the pore in which the positronium is confined. Calibration of pore size against the o-Ps lifetime under different experimental conditions is needed for the routine applicability of this technique in size spectroscopy.

Different models have been proposed to relate the measured positronium lifetime to the pore size. The first quantitative relation between the pore size and positronium lifetime was obtained from the Tao–Eldrup (TE) model [4–6] based on the positronium interactions with the pore wall in an infinite potential well. This model is extensively used in the determination of

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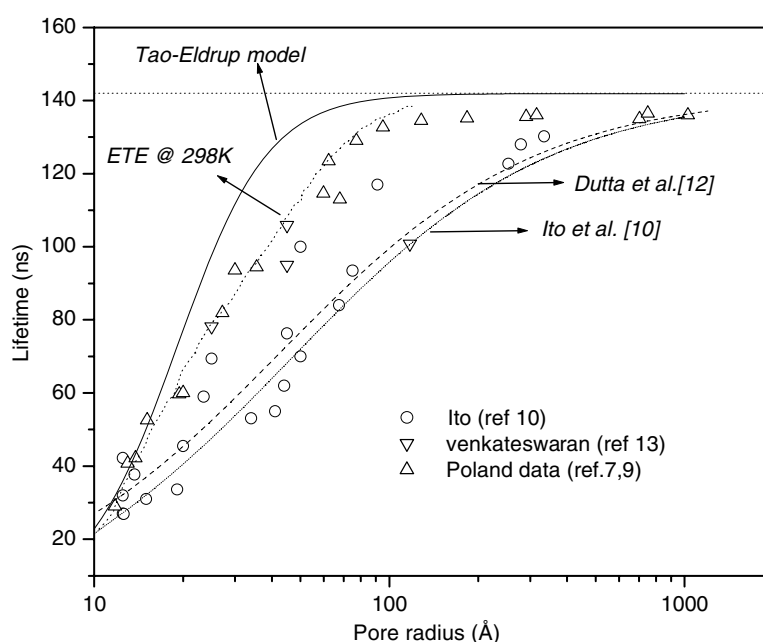
Figure 1. The calibration curves of different models used positron porosimetry and the literature data on o-Ps lifetime measurements in mesoporous materials.

free volume hole size in polymers and in porous materials with pore size less than 10 Å. At larger pore sizes the observed lifetimes are lower than expected from the TE model. Goworek *et al* have given an extended TE model (ETE model) taking into account the annihilations from excited states [7–9] at different temperatures. Though the model has a strong physical basis and explains the observed temperature dependence of o-Ps lifetimes, the calculation of pore size from determined lifetime is complex. Ito *et al* [10] have suggested a simplified relation between the radius and pick-off annihilation rate based on the bouncing quantum particle model for pores of radius larger than 8 Å. Dull *et al* [11] have suggested a model independent of pore geometry by taking the mean free path of positronium in the pores instead of the pore dimension to quantify the o-Ps lifetimes. Dutta *et al* [12] have given a classical model of positronium interacting with the surroundings.

The calibration of o-Ps lifetimes with pore size predicted by different models for spherical pores is shown in figure 1. It can be seen from the figure that the predicted o-Ps lifetimes differ significantly for the same pore size, depending on the model. The o-Ps lifetimes in various mesoporous materials reported [7, 9, 10, 13] are also shown in figure 1. It is seen from figure 1 that there is large scatter in the experimental data on o-Ps lifetimes in mesoporous materials. The reasons for this scatter are yet to be ascertained.

The positronium lifetime measurements on porous materials are usually carried out in vacuum, but the level of vacuum achieved or maintained is seldom reported. The vacuum level or presence of different quantities of air in the sample could be one of the reasons for the scatter in the literature data on positronium lifetimes in these materials. There is no model relating the measured o-Ps lifetimes with pore size, when measurements are carried out exposing the samples to air. Absence of a model for quantifying the air quenching in porous materials coupled with the dependence of the pore size determined from the o-Ps lifetime (measured in vacuum) on the model selected can lead to ambiguities in the interpretation of the results. For

example, the positronium lifetimes in MCM-41 of 19 Å average pore radius were determined by He *et al* [14] at different vacuum levels. It was observed that the lifetime in the presence of air gives the pore size expected using the model of Ito *et al*. The result was interpreted assuming that the air does not enter the pores of radius 19 Å. However, the o-Ps lifetime in vacuum in the same sample is close to the expected value for pore of radius 19 Å using ETE model at 298 K.

In the present work, the positronium lifetimes in some porous materials have been measured maintaining a vacuum level of <0.2 mbar. Lifetime spectra have also been measured while the samples are exposed to air at 1 atm. We examine the current experimental data in the light of various models. The positronium lifetimes measured with the samples exposed to air along with some literature data, where the measurements on samples are made in the presence of air, were fitted to a simple equation based on the classical description of positronium.

2. Experimental details

Five samples of Amberlite™ XAD™ polymeric resins and three silica gel samples were used in this study. The XAD resins were air dried before use. The silica gel samples are heated to around 250 °C under a rotary vacuum for 3 h and used for positron lifetime measurements. The surface area and pore size distributions in XAD resins were measured using SORPMATIC1990 (CE instruments, Germany) following the multiple-point BET method. Nitrogen gas was used as the adsorbate to form a monolayer on the sample at 77 K and $P/P_0 < 0.35$, and pore volume filling at $P/P_0 = 0.998$. The average pore radii were calculated using the BJH method using the relation $r = 2V/S$ where S and V are the measured surface area and pore volume respectively. The pore sizes certified by Aldrich were used for the silica gels.

The positron annihilation spectra of these resins were acquired using a conventional fast–fast coincidence set-up. ^{22}Na deposited between two 7.6 μm aluminium foils was used as the positron source. The time dispersion of the lifetime spectrometer was 500 ps/channel and the time resolution was about 350 ps (measured for ^{60}Co gamma rays with the time calibration of 25 ps/channel). For each sample the spectra were acquired in air and maintaining a vacuum level of <0.2 mbar using a rotary pump. About one million counts were acquired for each of the lifetime spectra. The counts corresponding to the long lived o-Ps component were in the range of 0.1–0.2 million in all the cases. Data analysis was carried out for three components using POSFIT [15]. Since the time dispersion was 500 ps/channel, para-positronium (p-Ps) and free positron components could not be extracted reliably from the lifetime spectra. Therefore, in accordance with the general practice, the first two ns of the spectrum was cut off when fitting the data to the long lived o-Ps component.

3. Results and discussion

The specific surface area and average pore size of the samples used in the current study are given in table 1. All the samples have average pore radii greater than 10 Å. Typical positron lifetime spectra of silica gel sample obtained under vacuum and in air are shown in figure 2. Both spectra are normalized in counts at the peak position. It can be seen from the figure that the long lived component due to o-Ps annihilation in mesopores persists even in the presence of air, though the lifetime is considerably reduced. In all the porous materials studied, τ_1 is in the region of 500 ps and is less reliable due to the large time dispersion used to determine the long lifetime components. τ_2 is in the range of 2–5 ns which is usually attributed to positronium annihilations in micropores. These two components (τ_1 and τ_2) do not show appreciable variation in the

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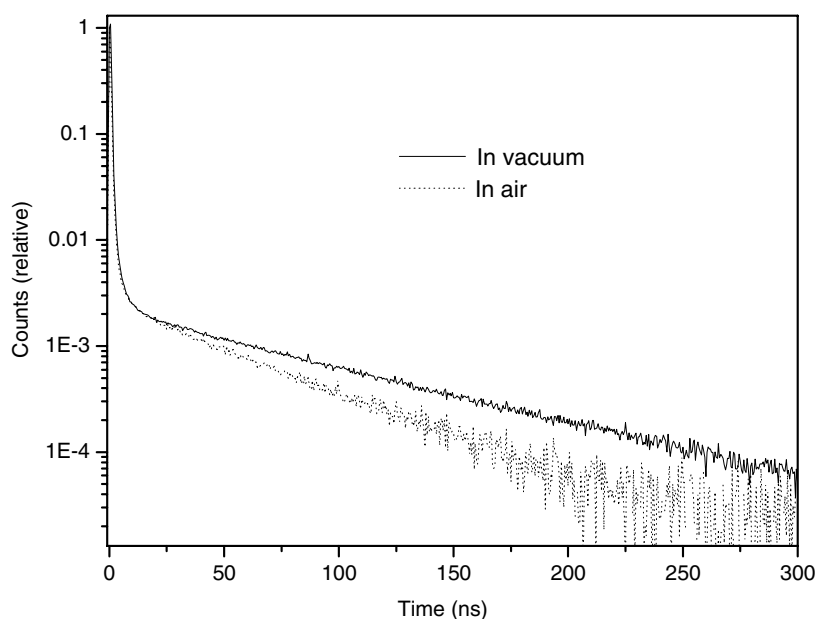
Figure 2. The positron annihilation lifetime spectra of silica gel under vacuum and in the presence of air.

Table 1. The physical properties of porous materials used in the current study.

Sample	Surface area $(m^2\,g^{-1})$	Specific volume of the pores $(cm^3\,g^{-1})$	Average pore radius (Å)
XAD-2	305	0.496	33
XAD-4	850	1.18	28
XAD-7	336	0.453	27
XAD-8	191	0.414	43
XAD-16	920	1.57	34
Silica gel (Aldrich, 40356-3)	750	0.68	20
Silica gel (Aldrich, 40359-8)	550	0.8	30
Silica gel (Aldrich, 40360-1)	300	0.75	50

presence of air. The longest lived component (τ_3), in the range of 40–100 ns, originates from the mesopores and is of interest in the present work as discussed in the later sections.

The measured o-Ps lifetimes (τ_3) are shown in figure 3(a) along with the calibration lines using different models. In all the porous materials studied, the long lived component (τ_3) has reduced considerably in the presence of air. The o-Ps lifetimes measured while the samples were under vacuum are close to the values expected using the ETE model at 298 K while the lifetimes in the presence of air are close to those predicted using the Ito model [10] or Dutta model [12]. Some of the lifetimes used in determining the fitting parameters by Ito *et al* [10] and Dutta *et al* [12] in their respective models were measured in the presence of air [16] and are also given in figure 3(a) as filled circles. The o-Ps lifetimes measured in the presence of air in the present experiment and in [16] fall on a common calibration line. The reduction in the o-Ps lifetimes in the presence of air is expected due to the quenching of positronium by oxygen present in the air. The positronium quenching rate constant of oxygen is reported to be
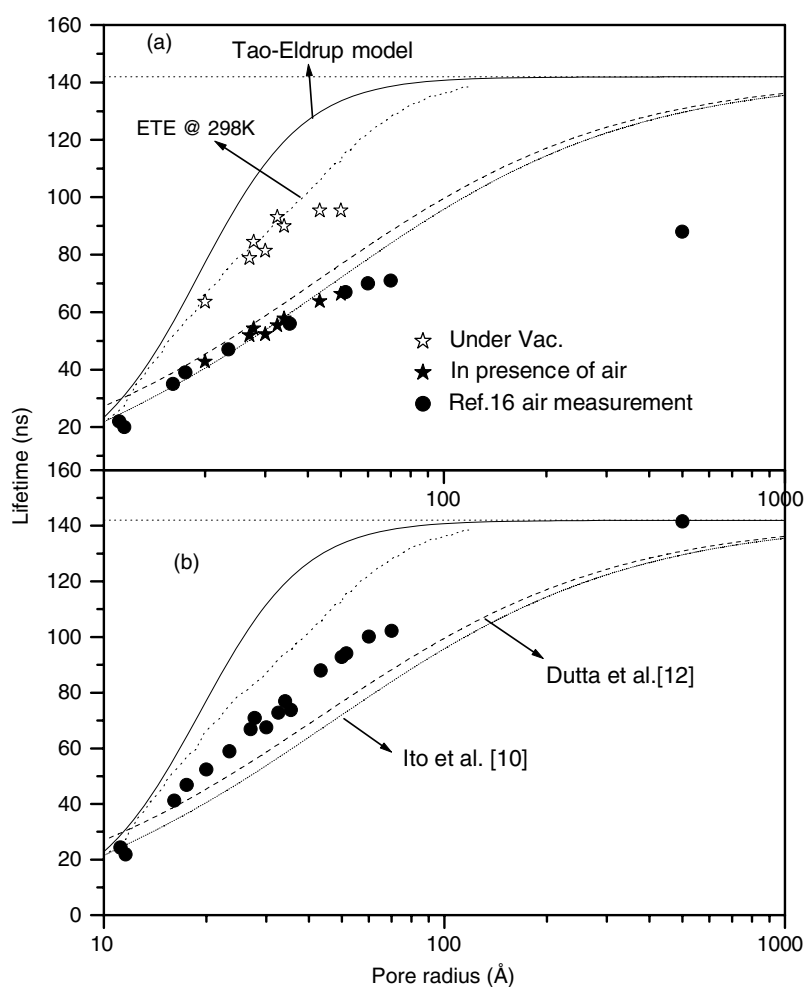
Figure 3. (a) The o-Ps lifetimes measured when the porous materials are in vacuum and in air. The o-Ps lifetime of porous materials in air from [16] is shown for comparison. (b) The o-Ps lifetimes measured in the presence of air are corrected for the air quenching rate of 0.0043 ns^{-1} atm^{-1}.

0.023 ± 0.003 ns^{-1} atm^{-1}, by Gelitans *et al* [17]. Taking the partial pressure of oxygen in air to be 0.2 atm and the same quenching constant to be valid for oxygen present in the mesopores, the rate constant would be 0.0046 ns^{-1} atm^{-1}. Dull *et al* [11] estimated the quenching rate constant of air to be 0.0040 ns^{-1} atm^{-1}. The o-Ps lifetimes measured in the presence of air in the present experiment and data from [16] have been corrected for air quenching taking the rate constant as 0.0043 ns^{-1} atm^{-1} and are shown in figure 3(b) as filled circles. This reproduces the expected lifetime in terms of ETE at very large pore sizes of 500 Å. However, the lifetimes are shorter than expected for smaller pore sizes or the quenching correction is insufficient.

The rates of positronium quenching by oxygen in some silica gels were measured by Hopkins *et al* [18] and Goldanskii *et al* [19]. It was found that the rate of positronium quenching by oxygen decreases with increase in the pore size of the silica gels. The positronium quenching rates from [18] and [19] are corrected for the partial pressure of oxygen in air and are shown in figure 4. From the lifetimes measured in the current experiment, the enhancements in the
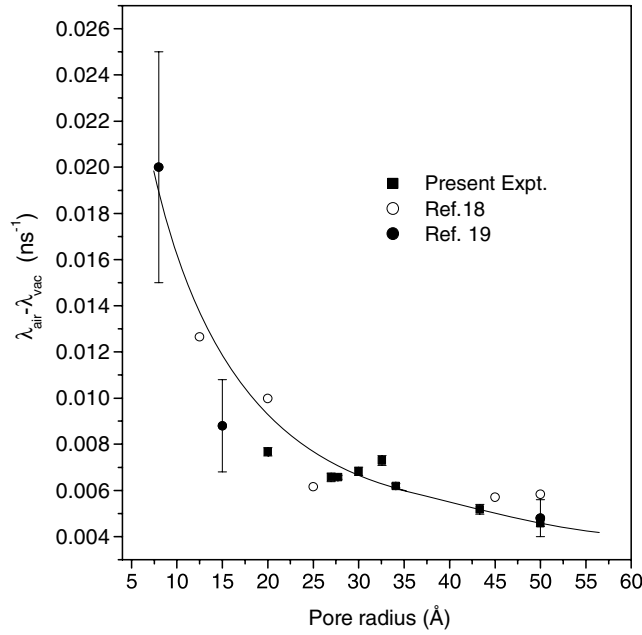
Figure 4. Enhancement in the o-Ps annihilation rates caused by air in different pores. The rates of positronium quenching by oxygen from the literature [18, 19] are converted to air annihilation rates taking the partial pressure of oxygen as 0.2 atm. The line is a guide to the eye only.

positronium annihilation rates caused by the presence of air in these porous materials were obtained as $\lambda_3^{air} - \lambda_3^{vac}$ and are given in figure 4. The enhancement in the annihilation rate of positronium caused by air is seen to decrease with increase in the pore size and seen to vary from 0.020 to 0.0040 ns^{-1} atm^{-1} in the pore size range studied. Hence the correction of 0.0043 ns^{-1} for the presence of air in pores was sufficient for large pores only.

Though pore size dependent correction for air quenching and use of the ETE model for estimation of pore size is possible, the calculation of the expected lifetime in terms of the ETE model is lengthy. Alternatively, the positronium lifetimes measured in the presence of air themselves can be fitted in terms of a calibration model and used in porosimetry. Considering the positronium to be a classical particle bouncing in between the walls of a pore of radius R, and having constant probability of pick-off annihilation in each collision, the annihilation rate of positronium can be given as

$$\lambda = \frac{1}{\tau} = \lambda_{po} + \lambda_{T} = \frac{k}{R} + \lambda_{T} \tag{1}$$

where λ_{T} is the self-annihilation rate of o-Ps and k is a constant characteristic of the material and is dependent on the probability of pick-off annihilation in each collision. The presence of air can influence the o-Ps annihilation rate in any of the following ways: (i) reduction in the apparent pore size caused by adsorption of air; (ii) quenching of positronium by oxygen (addition to pick-off annihilation); (iii) the probability of pick-off annihilation in each collision can change as the chemical nature of the pore surface is changed due to adsorption of air. These factors can be incorporated into equation (1) and it can be written as

$$\lambda = \frac{k'}{(R - r')} + \lambda_{T} + \lambda_{q} \tag{2}$$
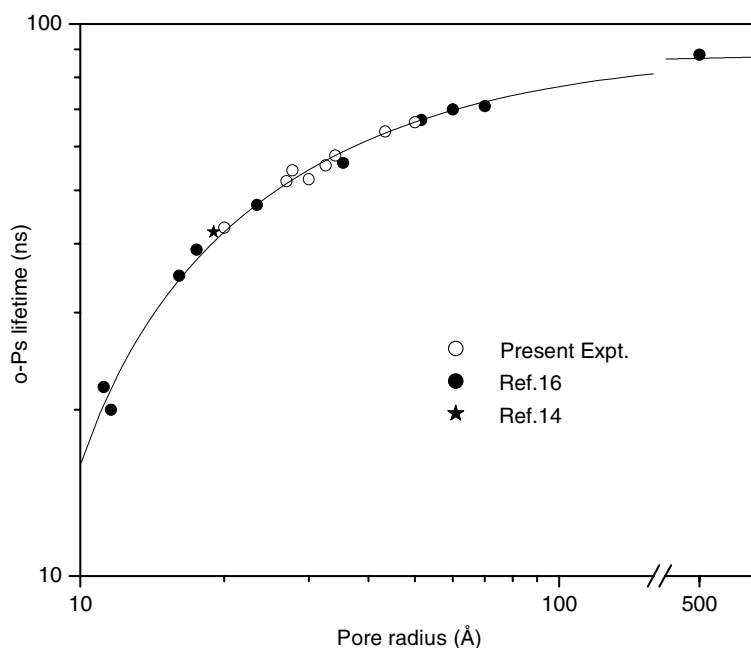
Figure 5. The o-Ps lifetimes of porous materials measured while the samples are exposed to air. The solid line is a fit to the data using equation (2).

where k' is characteristic of the electron density parameter for the samples with adsorbed air, r' is the parameter introduced to account for the pore size reduction due to adsorption of air on the pore surface and λ_q is the quenching rate constant of positronium in air. Since the fractional pore size reduction is large for smaller pores, this would account for the sharper change in annihilation rates with pore size in the presence of air (figure 4).

The present experimental data along with data from [16] are fitted to the equation (2). The plot of these data is shown in figure 5. The values of parameters k', r' and λ_q determined from the fitting are 0.164 ± 0.027 ns^{-1} Å, 6.8 ± 0.7 Å and $0.004\,27 \pm 0.0010$ ns^{-1} respectively. The value of the air quenching rate (λ_q) determined from the fit ($0.004\,27 \pm 0.0010$ ns^{-1}) is close to the value 0.0040 ns^{-1}, a value used by Dull *et al* [11], and 0.0046 estimated from the oxygen quenching rate measured by Gelitans *et al* [17]. The value of the parameter r' introduced to account for reduction in the pore size due to adsorption of air on the pore surface is 6.8 ± 0.7 Å, which is of the order of the van der Waals diameter of O_2 and N_2. This shows that the reduction in the pore size is approximately equivalent to the monolayer adsorption on the surface of the pores. k' is the electron density parameter characteristic of the pore surface adsorbed with air. The o-Ps lifetime in MCM-41 measured by He *et al* [14] in the presence of air at 1 atm is also shown in figure 5 by an asterisk, which agrees well with the current model. The positron lifetime measurements in air are easy to carry out and can be very useful as the value of k' is expected to be independent of the chemical nature of the pore surface when measurements are carried out in air.

4. Conclusion

The positron annihilation lifetimes in porous materials in the presence of air and in vacuum have been measured. The lifetimes measured in vacuum are close to the values expected using the

ETE model. In the presence of air, the annihilation rates of positronium are seen to increase, and the increase is larger for smaller pores. A model is proposed that efficiently gives a calibration of the pore size with the o-Ps lifetime in the presence of air measured over a wide range of pore size. We believe our description of the Ps annihilation in porous materials in the presence of air will help with the routine acceptability of this technique in porosimetric studies.

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