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Ortho-Positronium Annihilation Lifetimes and Reemission Yields in Mesoporous silica

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Abstract

A novel model is introduced to describe *ortho*-positronium (o-Ps) reemission into vacuum from surfactant templated mesoporous silica films. This model is used to analyze lifetime spectra recorded using a positron beam based lifetime spectrometer specifically designed to record o-Ps reemission in the reflection mode. This model directly correlates the orthopositronium reemission yield into vacuum to the o-Ps annihilation lifetime in the film state from which reemission takes place. It is demonstrated that a lifetime spectroscopy, based on o-Ps reemission, gives unique information on the mesopore structure in the film bulk. The mesopore structure is characterized in surfactant templated mesoporous silica film deposited on glass by using the novel methodology. The reemission yield, studied as a function of the concentration of the cationic surfactant, cetyl trimethyl ammonium bromide, exhibits a threshold at a mole fraction of 0.06-0.08. The *o*-Ps annihilation lifetimes in the films increase significantly above the threshold, from ~42 to 60-80 ns. This change in the lifetimes likely reflects an extension of the *o*-Ps localization over several pores. It suggests that, above the reemission threshold, the mesopores become highly interconnected. Furthermore, it is shown that the refractive index linearly varies with the o-Ps annihilation yield.

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Mesoporous silica films are promising systems for applications as diverse as filters, chemical sensors, templates for nanostructures and optical coatings. Characterization of the pore organization, volume and size is one key step for controlling their properties. A few authors have used positron (e^+) annihilation to investigate the pore size distribution in mesoporous silica films vs. depth using low energy e^+ beams [1-9]. Positrons implanted into mesoporous silica form ortho-positronium (o -Ps), i.e. the triplet state of a positron-electron (e^+e^-) bound pair, that has been shown either to annihilate in the films or escape into vacuum [1, 10, 11].

The annihilation in vacuum gives rise to the lifetime of 142 ns. The o -Ps annihilation (o -PsA) in the films results in long lifetimes, >10 ns. The quenching of the o -Ps annihilation lifetime in the films is controlled by the pore size and surface chemistry. It can be used to determine an effective pore size in the films [12]. o -Ps quenching takes place in the mesoporous films as in other insulating materials. However, the quenching is much less efficient in the films than in polymers or molecular materials where the quenched lifetimes are much shorter (<3 ns). This reduced quenching property has recently been used to successfully convert a high intensity e^+ beam pulse into o -Ps gas confined in the mesopores with decay times and densities sufficient to observe Ps-Ps interactions [13-15]. A step further would be to initiate a novel physics by achieving Bose-Einstein condensation of positronium [16].

The property of o -Ps reemission singles out mesostructured silica films as potential structures to prepare clouds of low energy o -Ps (<0.1 eV) in vacuum. Attention has recently been attracted to the novel experiments in fundamental physics [17] that can be achieved once a low energy o -Ps cloud with high density is available. Its interaction with an antiproton beam provides a method for the direct or indirect production of neutral antihydrogen atoms, suitable for direct gravity measurements of antimatter [17, 18]. Methods need to be developed to progress in the understanding of the relationship between the mesopore structures and their efficiency for o -Ps reemission. This requires direct monitoring of the o -Ps reemission (o -PsR) yield into vacuum and annihilation in mesoporous films.

This letter reports such a novel investigation in which the o -PsR yield into vacuum is directly determined by using an e^+ beam-based wide acceptance lifetime spectrometer [11, 19], installed on the slow positron beam of ETHZ Zurich [20]. The o -PsA lifetimes in the films and the o -PsR yields into vacuum are correlated as a function of the e^+ beam energy (E_{e^+}) in mesostructured silica films (S) prepared by surfactant templating methods. The correlation uses a novel model to determine the annihilation lifetime characteristic of the film state from which reemission takes place.

The films are synthesised from mixtures containing the cetyl trimethyl ammonium bromide (CTAB) organic surfactant and a silica sol prepared by acidic hydrolysis of an ethanolic solution of tetraethoxysilane (TEOS) [21]. After spin-coating deposition on glass, the rapid removal of solvents allows both the micellar organization of the surfactant and its stabilization by the gelation of the percolative silica network. The subsequent removal of the organic template by calcination at 450°C results in mesoporous silica films where pores are separated by silica walls with a specific density for the silica skeleton. The total volume fraction occupied by the pores and the fraction of micropores (<2 nm) and mesopores (~ 2 -50 nm) is controlled in the CTAB-TEOS films by varying the surfactant mole fraction, CTAB/Si (x), in the initial mixtures. As x increases, three long range ordered micellar structures are observed for $0.1 \leq x \leq 0.18$ that, after 450°C calcination, result in highly organized mesoporous silica films [22, 23].

It is reported in this letter that the *o*-PsA lifetime and the *o*-PsR yield in the S(x) films exhibit a sharp correlated increase at a CTAB/Si mole fraction of 0.06-0.08. The correlation gives evidence that the mesopore size distribution evolves towards much larger values as x reaches the threshold value for vacuum *o*-Ps reemission. The pore effective diameters become much larger than those typically determined in the films by other methods. This difference points out to a pore distribution where a high fraction of interconnections begin to form between the pores for $0.06 \leq x \leq 0.08$. This mesostructure reorganisation has escaped detection by any other methods used to characterize the mesostructure and demonstrates the unique capability of the ortho-positronium reemission lifetime spectroscopy.

Seven CTAB-TEOS (S(x)) Film/Glass (S(x)/G) samples with different x in the range 0 to 0.14 were prepared as previously reported [22]. After calcination at 450°C, the thickness for the S(x) films determined from ellipsometry and profile measurements increases with x from 150 to 310 nm (Fig.1). Due to the texture of the S(x) films, X-ray patterns ($\lambda = 1.54 \text{ \AA}$) consist of one intense peak at low angle (2-4°). The coherence length ζ in Fig.1, i.e. the extent of the order in the thickness direction of a film, was deduced from the peak width at half maximum using the Scherrer formula. It was compared to the resolution of the diffractometer ($\zeta = 100 - 150 \text{ nm}$) to classify the films as “short (or long) range ordered” (Fig.1). Consistent with the well organised Hexagonal 3D (H3D) structure for the pore arrangement in S(0.1) and the less organised Cubic (C) in S(0.14), ζ has a value $>120 \text{ nm}$ in H3D S(0.1) and $\sim 44 \text{ nm}$ in C S(0.14). The film porosity was determined by in-situ coupling of ellipsometric porosimetry (EP) in the visible range with infrared ellipsometry [24]. The total volume fraction occupied by micropores (p_μ) and mesopores (p_m) was deduced from the changes of the refractive index in the film upon gas ethanol adsorption/desorption using for its value in the silica skeleton, 1.488. The total volume fraction occupied by micropores (p_μ) and mesopores (p_m) increases from 0.33 to 0.58 for $0.06 \leq x \leq 0.14$ (Fig.1). The relative populations (Fig.1) changes with x and reaches $(p_\mu, p_m)/(p_\mu + p_m)$ values of (0.35, 0.65) in S(0.10) and (0.25, 0.75) in S(0.14). Using the Kelvin equation and assuming spherical pores, a diameter of 4 nm has been determined for mesopores in S(0.10) films [24].

Ortho-positronium annihilation in the S(x)/G samples was measured at the ETHZ beam using a e^+ beam-based lifetime spectrometer specifically designed to detect *o*-Ps annihilating either inside the sample or outside (after reemission from the irradiation entrance surface) [11]. The e^+ beam energy (E_{e^+}) varies in the range 1-5 keV for the recording of the lifetime spectra (Fig.1). For each E_{e^+} , the model for the annihilation state lifetime distribution is a sum of exponential lifetime decay components (I_i, τ_i). After background corrections and convolution with the 5ns FWHM resolution function of the spectrometer, a sum of three lifetime components is resolved in the fitting of the spectra with the Lt9 program [25]. Given the 5 ns resolution, the short component, $\tau_{i=1} < 4 \text{ ns}$, is disregarded. Only the two longest ones, $\tau_{i=2,3} > \sim 10 \text{ ns}$, for which the decomposition is reliable, are considered. Both depend on E_{e^+} and the CTAB/Si mole fraction, x , in the film/glass. For $E_{e^+} \geq 2 \text{ keV}$ and $x \leq 0.06$, the longer component has a lifetime, τ_3 , fluctuating due to a low intensity, $I_3 \leq 1.5\%$. On the other hand, for $E_{e^+} \geq 2 \text{ keV}$ and $x \geq 0.08$, the longer component is well determined due to its high intensity, $10 \leq I_3 \leq 18\%$ and found to decay with a lifetime of $\tau_3 = 142 \pm 5 \text{ ns}$. This value is characteristic of the *o*-Ps self-annihilation lifetime in vacuum, $\tau_v = 142 \text{ ns}$. Accordingly, in

Fig. 1, all lifetime spectra were fitted with τ_3 constant and equal to τ_v in order to obtain a more reliable analysis of the variation of τ_2 with E_{e^+} and with x .

The e^+ implantation depth in S(x)/G varies with the positron beam energy, E_{e^+} . Assuming a Makhovian e^+ implantation profile and no diffusion, the calculations give that the implantation probability in a film/glass with a 250 nm S(x) film of 1.5 gcm^{-3} density is 92.5 % for 3 keV e^+ and 46% for 5 keV e^+ in the film. Since, for $E_{e^+} \geq 2 \text{ keV}$, we could find no long ($\tau_i > 10 \text{ ns}$) o -Ps component in the lifetime spectra in the glass substrate, it can be concluded that the results in Fig.1 are determined essentially by the o -Ps annihilation probability distribution and behavior in the films. In S(x)/G with $x \neq 0$, one notices in Fig.1 that the lifetime τ_2 varies with E_{e^+} in the range 1-2 keV and remains constant in the range 2-5 keV. It can be inferred from such behavior that there are two regions in the films where o -Ps behavior differs: (i) a surface region and (ii) a homogeneous bulk region. For $E_{e^+} < 2 \text{ keV}$ the film surface contributes most importantly, and for $E_{e^+} > 2 \text{ keV}$ it is the film bulk which dominates but with a probability that decreases in favor of the glass contribution as E_{e^+} increases. Given that the implantation probability in the glass substrate is below 10 % ($\sim 7.5\%$) at 3 keV, it follows that the lifetime components in Fig. 1 have lifetimes (τ_2, τ_v) and intensities (I_2, I_v) arising from the behavior of o -Ps in the film bulk for $2 \leq E_{e^+} \leq 3 \text{ keV}$.

As earlier shown [11], the existence of the 142 ns lifetime in the spectra recorded with the ETHZ wide acceptance lifetime spectrometer provides evidence that the films reemit o -Ps from the front surface. In Fig. 1, the I_v values at 3 keV depend on the CTAB/Si mole fraction. The steep increase marks a threshold for o -Ps reemission between $0.06 \leq x \leq 0.08$. This threshold is correlated to a change in the τ_2 and I_2 values at 3 keV. The τ_2 values are quasi-constant for $0.03 \leq x \leq 0.06$, and tend to decrease for $x \geq 0.08$. Also to be noted is that for $x \geq 0.03$, and at 3 keV, whereas I_2 and I_v individually vary with intensity, their sum ($I_2 + I_v$) remains quasi-constant (Fig. 2a).

To determine the τ_2 values in absence of o -Ps reemission, the S(0.1) and S(0.14) films were capped in AIST with a 20 nm thick silica layer to prevent o -Ps reemission without, if possible, damaging the film mesostructure. For $E_{e^+} = 2 \text{ keV}$, the 270 ps FWHM resolution of the AIST spectrometer allows us to resolve three lifetime components in capped S(0.1)/G and four components in capped S(0.14)/G. For the longer one, the intensity and lifetime values after capping, (I_{ci}, τ_{ci}) are ($i = 3$; $25 \pm 3\%$, $67 \pm 2 \text{ ns}$) for $x = 0.1$ and ($i = 4$; $18 \pm 1\%$, $87 \pm 2 \text{ ns}$) for $x = 0.14$. The comparison of the lifetimes in these films before and after capping suggests that the reemission process reduces considerably the o -Ps lifetime, τ_2 , in film bulk. This can be understood using a model describing the o -Ps reemission process in analogy to e^+ trapping by vacancy type defects [26] as a transition between two o -Ps states. The initial film state is characterized by the o -Ps annihilation lifetime, τ_f , and gives rise to the lifetime component (I_2, τ_2) in Fig.1 at 2-3keV before capping. The final state is the o -Ps ground state in vacuum characterized by the 142 ns annihilation lifetime and component ($I_v, 142 \text{ ns}$) in Fig.1. The transition from the film state to the vacuum state decreases the o -Ps energy. From the film state, o -Ps gets trapped into the vacuum state at a transition rate κ_v . The o -Ps annihilation

lifetime τ_f is given by $\tau_f = ((\tau_2^{-1} - \tau_v^{-1})I_2 / (I_2 + I_v) + \tau_v^{-1})^{-1}$. The τ_f values calculated in Fig.2b from the values τ_2 for 3keV in Fig.1 increase from 42.0 ± 0.5 to 70 ± 1 ns as x increases from 0.03 to 0.14. In S(0.1), the values before (τ_f) and after (τ_c) capping, are consistent at 67 ± 2 ns in both cases. This validates both the model and the silica capping as a procedure for probing the mesostructure without damaging it. After capping in S(0.14), the average values of the two longer lifetimes, $((I_{c3}\tau_{c3}) + (I_{c4}\tau_{c4})) / (I_{c3} + I_{c4}) = 69 \pm 2$ ns, agrees well with $\tau_f = 70 \pm 1$ ns. The *o*-Ps reemission yield can be defined as the annihilation probability in the vacuum state given by $Y_v = \kappa_v / (\tau_f^{-1} + \kappa_v)$ with $\kappa_v = (\tau_2^{-1} - \tau_v^{-1})I_v / (I_2 + I_v)$. Renormalized to the total intensity, $I_2 + I_v$, of the *o*-Ps components, it increases from 0 to 16% in Fig.2a.

In quenching models for *o*-Ps annihilation by electron pick-off, lifetimes in the range 40-80 ns are consistent with *o*-PsA from localized states in pores of diameter greater than 3 nm [12]. From the *o*-PsA lifetime behavior, it can be inferred that the size distribution of the mesopores that localize *o*-Ps is constant for $x = 0.03, 0.06$ and shifts to higher values for $x \geq 0.08$. For a cubic pore model [12], the *o*-Ps annihilation lifetime of 42 ns in S(0.03) and S(0.06) corresponds to effective sizes of ~ 4 nm whereas the lifetimes of 60 -70 ns for $x \geq 0.08$ correspond to larger ones, $\sim 5 - 6$ nm. It is interesting to correlate this size evolution to the evolution deduced from the other methods used here (EP, etc.). First, we wish to note that *o*-Ps is very sensitive to the presence of mesopores and gives an estimation of their size even at moles fractions as low as $x = 0.03$ where the other methods fail. Secondly, we call attention to the good agreement between the pore size determined from EP in S(0.1), of ~ 4 nm, and *o*-Ps localization in S(0.03) and S(0.06). It then follows that, before 450° calcination, micellar aggregates are already existing for $x = 0.03$. Finally, we note the surprising result that *o*-Ps localization for $x \geq 0.08$ appears to be sensitive to some organization of the mesopore distribution that escapes detection by the other methods. The space where *o*-Ps gets localized increases, although, the pore size remains quasi-constant according to the other methods. One possibility, consistent with these two results, is that the mesopores start to become interconnected at $0.06 \leq x \leq 0.08$. This transition is consistent the H3D mesostructure found for $x = 0.10$ where the total porosity reaches 55% with the mesopores (36%) connected to each other through the micropores (19%). For the micropores, an effective size, $d < 1.5$ nm, is inferred from the absence of any *o*-Ps annihilation lifetime in the range 5-10 ns in the films. The two type of regions where *o*-Ps localization takes place in capped S(0.14), over ~ 1.9 nm for $\tau_{c3} = 13.9 \pm 0.5$ ns ($I_{c3} = 4.5 \pm 0.5\%$) or ~ 8.5 nm for $\tau_{c4} = 87 \pm 2$ ns ($I_{c4} = 18 \pm 1\%$) suggests that some of the interconnecting pores have also sizes larger (~ 1.9 nm) than those of the micropores.

The total intensity, $I_2 + I_v$, for the *o*-Ps lifetime components for 3keV in Fig.2b is essentially independent of x and, consequently, rather insensitive to the increase in porosity. It suggests that, in analogy to e^+ trapping by vacancy-type defects [26], after *o*-Ps formation in the silica walls, *o*-Ps localization in pores occurs via a trapping process that reaches saturation. The pore density in the S(x) films ($\geq 10^{18}$ cm $^{-3}$) is so high that trapping prevails over annihilation due to a much higher rate than the *o*-Ps annihilation rate in silica (> 0.2 ns $^{-1}$).

In Fig.2c, the refractive index, n , (measured at 633 nm by spectroscopic ellipsometry), decreases with increasing x . The comparison of Fig.2c with Fig.2a,b shows that this variation

partially correlates the *o*-Ps annihilation lifetime and reemission yield in the S(x) films. Furthermore, the *n* values vary linearly as a function of the *o*-Ps reemission yield in Fig.3.

Fig. 4 shows that the transition rate κ_v from the mesopores to vacuum varies linearly with the volume fraction occupied by the mesopores. The rate vanishes when the volume fraction drops below 25%. The rate per mesopore is of the order of $0.18 \pm 1 \text{ ns}^{-1}$ per unit of mesopore volume fraction. The linear relation κ_v with p_m seems to indicate that the transition rate is independent of the size of the mesopore for lifetime in the range 40 - 70 ns.

In summary, a model is introduced to establish *o*-Ps reemission lifetime spectroscopy as a novel spectroscopy for *o*-Ps mesopores states reemitting *o*-Ps. By applying this spectroscopy to mesoporous CTAB-TEOS film/glass, it is shown that the space where *o*-Ps localizes in the films increases above a CTAB/Si mole fraction, $x = 0.06$. The variation suggests that pore interconnection occurs between 0.06-0.08. By examining how the *o*-PsR yield and refractive index correlate to the mesostructure, it is shown that the pore interconnection rather than the porosity and its ordering control these two quantities in mesoporous CTAB TEOS films.

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Figures

Figure 1

Ortho-positronium lifetime components, (τ_2, I_2) and (142 ns, I_v), as a function of the e^+ beam energy in mesoporous silica CTAB-TEOS S(x) film/glass for CTAB/Si (x) mole fraction in the range 0-0.14. The top panel gives the film thickness. The lower one gives the coherence length and the short or long range order (S/LRO) of the pore arrangement and the fraction of micropore (p_μ) and mesopore (p_m) volume.

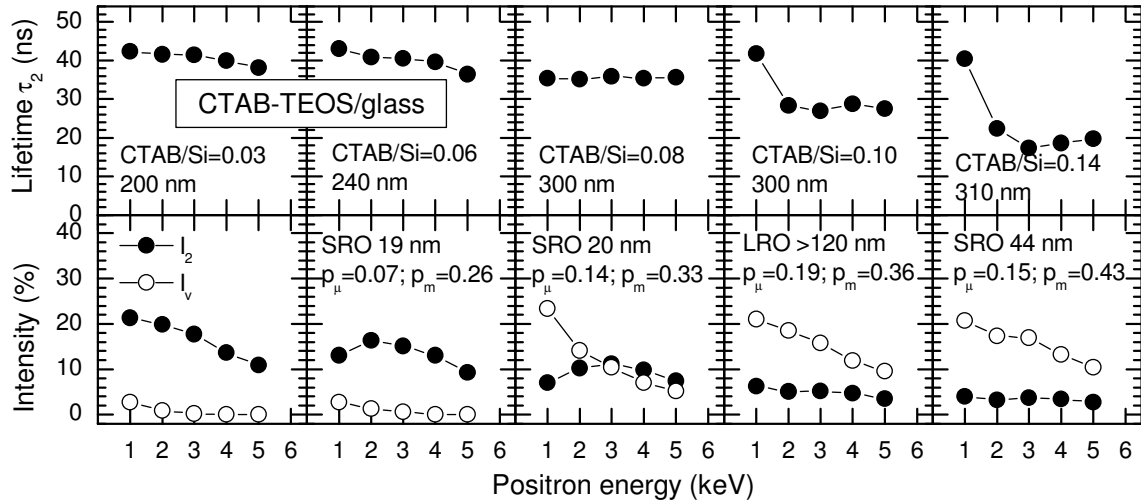


Figure 2

(a) Total intensity of lifetime components, $(I_2 + I_v)$, (○) and vacuum *o*-Ps reemission yield, Y_v , (●) at 3 keV e^+ beam energy (E_{e^+}) for *o*-Ps in film bulk vs. CTAB/Si (x); (b) *o*-Ps annihilation pore lifetime, τ_f , calculated before capping using the trapping model(●) vs. x ; (c) film bulk refractive index, n , measured at 633 nm (●) vs. x .

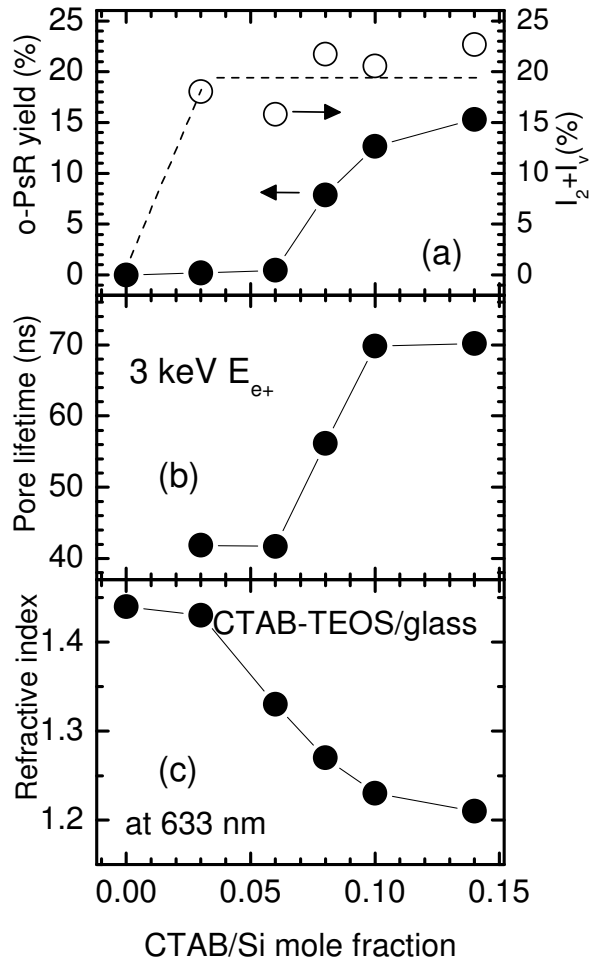


Figure 3

Refractive index (n) measured at 633 nm wavelength as a function of the *o*-Ps reemission yield (Y_v) calculated for the mesoporous silica films.

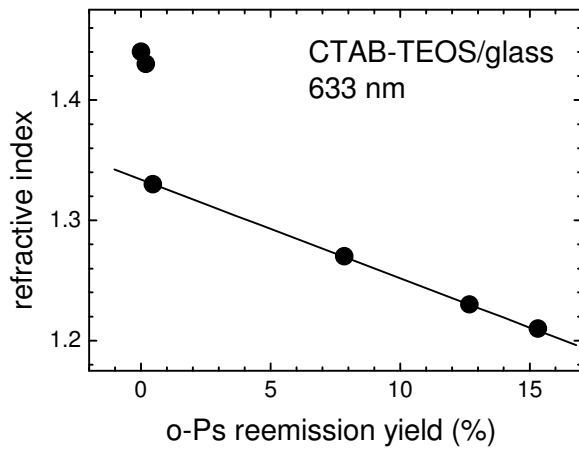


Figure 4

Ortho-Positronium transition rate (κ_v) from the film state into the vacuum state as a function of the mesopore volume fraction (p_m).

