

THE POSITRON ANNIHILATION IN SiO_2 SAMPLES WITH HIGH SPECIFIC SURFACE AREAS

BY M. DĘBOWSKA, W. ŚWIĄTKOWSKI AND J. WESOŁOWSKI

Institute of Experimental Physics, Wrocław University*

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Angular Distributions of Annihilation Quanta (ADAQ) were measured for three samples of powdered SiO_2 in vacuum and in air. The results obtained from analysing the distributions were compared with the results of lifetime spectra measured for the same samples by Paulin. Although shape changes of the ADAQ were found to be qualitatively consistent with the lifetime spectra interpretation given by Paulin, they are definitely higher than expected. An analysis of the results indicates that this can be explained by assuming that hot o-Ps atom interaction with the pore surface is considerable for the two-quanta annihilation process in these samples.

1. Introduction

Positron mean lifetime spectra studies of powdered metal oxides such as Al_2O_3 , MgO and SiO_2 [1-3] gave evidence of occurrence in these spectra, beside the two components: $\tau_1 \approx 10^{-10}$ s and $\tau_2 \approx 10^{-9}$ s characteristic of polycrystalline samples, a third one with a mean lifetime τ_3 varying in the range: 10^{-8} - 10^{-7} s. Both the value of the longest mean lifetime τ_3 and the intensity of this component I_3 were found to be dependent on parameters which describe the degree of porosity of the powders as well as the structure of the samples investigated and the medium in which the samples were placed (vacuum or air) during measurements. For example, when the samples were placed in vacuum, τ_3 reached a value approaching that of free o-Ps mean lifetime $\tau_3^0 = 1.4 \times 10^{-7}$ s [1, 2]. The complexity of the positron mean lifetime spectra for the powdered oxides is generally explained by assuming the possibility of positronium formation in them as the shape of appropriate ADAQ suggests. The short-lived component τ_1 is accounted for by free annihilation of positrons with electrons, annihilation of p-Ps and the possible fast quenching of o-Ps, whereas the τ_2 component is attributed to o-Ps annihilation by pick-off process in powder grains. Following Paulin, the presence of the third component τ_3 is accounted

* Address: Instytut Fizyki Doświadczalnej, Uniwersytet Wrocławski, Cybulskiego 36, 50-205 Wrocław, Poland.

for by diffusion into the pores of o-Ps atoms formed inside powder grains [2]. Most authors accept the high value of τ_3 in the mean lifetime spectra but there is no uniform opinion explaining the mechanism which causes its value to change with change of medium (e. g. when passing from vacuum to air). Some authors interpret the results obtained for powdered materials by assuming that in vacuum the o-Ps atom which have managed to escape into pores dont experience any interactions which could influence their lifetime while their interaction with oxygen molecules in air or oxygen leads to a shortening of the lifetime τ_3 owing to orto-para conversion. Other authors [3] attribute the shortening of the o-Ps lifetime to interaction of the o-Ps atoms with grain surface which can vary with change of medium. ADAQ studies performed for powdered samples [3, 4] indicated that the shape of the ADAQ also depends on the same agents which cause the positron lifetime spectra changes. Till now, drawing conclusions by comparing the effects observed for mean lifetime spectra and annihilation quanta angular correlation curves was not easy because lifetime measurements and the correlation measurements were as a rule performed on different samples. In the present work such a comparison is performed on SiO₂ samples (aerosils) kindly provided by Paulin who had used them before in measuring the lifetime spectra. It was expected that results of such studies would allow one to explain some phenomena connected with the positron annihilation in powdered substances, in particular the annihilation mechanism of o-Ps in pores.

2. Experiment

The ADAQ measurements were performed for three samples of powdered SiO₂ (aerosils) having different surface specific areas. In Table I the characteristic parameters of the studied samples are given: surface areas — S , specific volumes of pores — V , mean pore diameters — \bar{d} and mean grain radii — \bar{R} .

TABLE I

Parameters characteristic of the studied samples

Number of sample	S $\left(\frac{\text{m}^2}{\text{g}}\right)$	V $\left(\frac{\text{cm}^3}{\text{g}}\right)$	\bar{d} (Å)	\bar{R} (Å)
1	50	—	—	270
2	253.2	0.167	26.4	55
3	335	0.260	31.0	41

Each sample was shaped like a thin pellet (2 mm). They were produced by hand compression of the appropriate powder inside an aluminium ring which augmented the mechanical strength of the sample. The measuring apparatus described by Rozenfeld

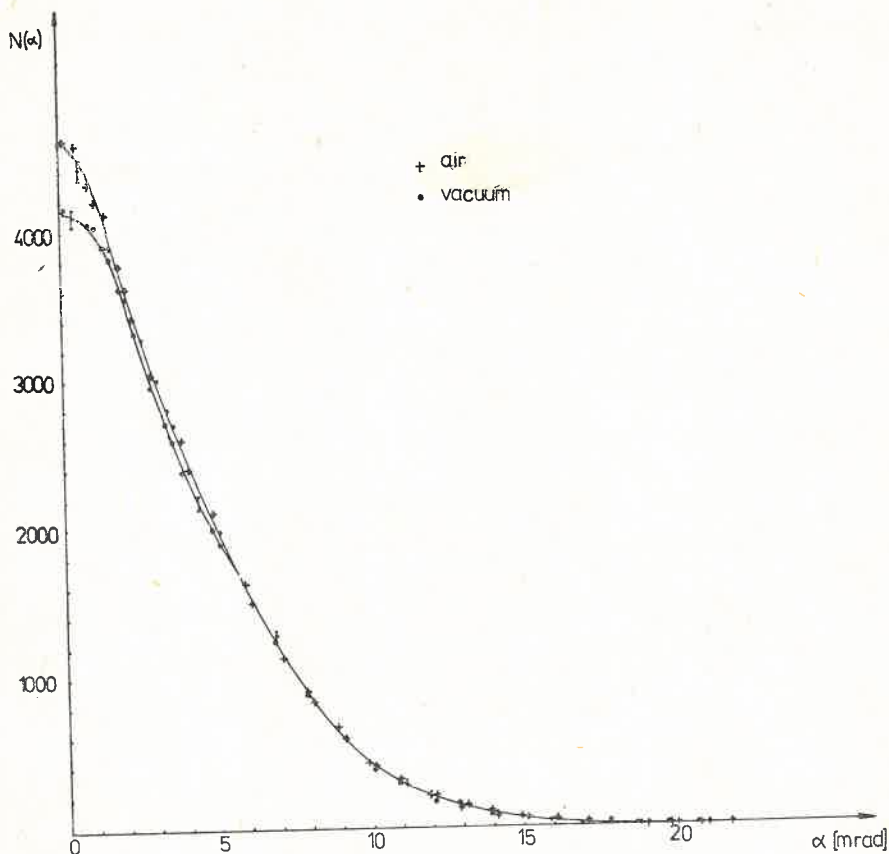


Fig. 1. The angular distribution of annihilation quanta for sample No 1

et al. [5] had been so chagned that a studied sample and a positron source (3 mCi of ^{22}Na on one side of the sample) were placed in a glass chamber connected to a vacuum system. The ADAQ measurements have been performed for all the samples in vacuum and in air with the geometry of the measurement system unchanged. All the ADAQ were measured at room temperature. In vacuum the measurements were performed at about 10^{-5} Torr. Prior to the ADAQ measurements, the samples were heated for two hours in situ in a dynamic vacuum at 200°C . The obtained ADAQ are shown in Figs 1-3. Since the position of the sample and source in vacuum and in air was the same, it was possible to compare the observed count rate (as a function of an angle α) without additional normalization of curves. All the distributions have been measured roughly with the same accuracy. The standard deviation for points near the maximum of the distribution equal to $\sigma(0) = 0.015 N(0)$ changes with α approximately in accordance with the formula

$$\sigma(\alpha) = \sigma(0) \sqrt{\frac{N(\alpha)}{N(0)}}, \quad (1)$$

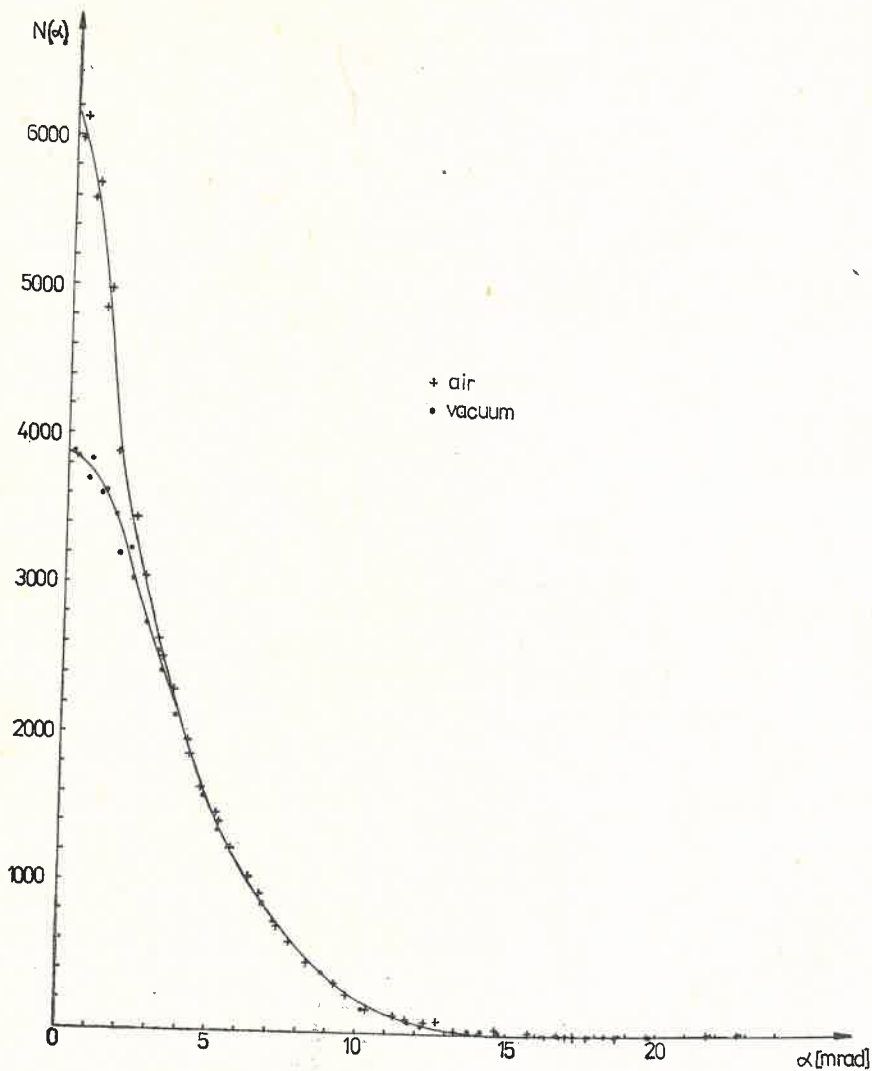


Fig. 2. The angular distribution of annihilation quanta for sample No 2

where $N(0)$ and $N(\alpha)$ denote the count rate of coincidences in the maximum of distribution and for the angle α respectively. The background conditioned by accidental coincidences is about 3% of the maximum count rate and was measured with an accuracy of about 10%. Results of an introductory analysis of the distributions obtained have been presented in [6]. On the basis of them conjectures have been made that some features of the measured distributions could be accounted for by the occurrence of two-quanta annihilation connected with high noncolinearity of quanta. Obviously, even though the probability of this effect would be considerable, the number of coincidence counts for any given angle may be small. In view of this, a measurement was performed to ascertain if at angles

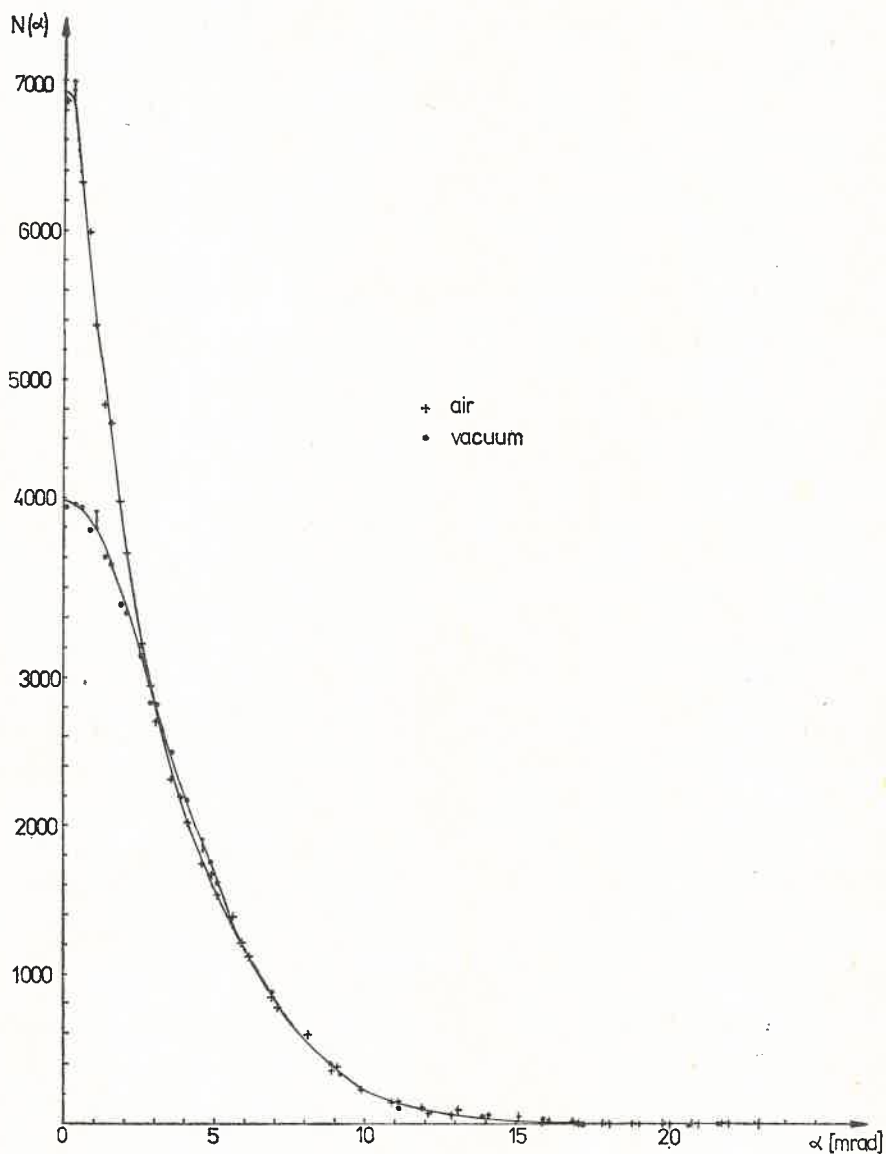


Fig. 3. The angular distribution of annihilation quanta for sample No 3

greater than 20 mrad (at these angles the distributions seemed to reach the background) we have to deal with pairs of correlated quanta. To separate this possible small effect from the background, conditions of the experiment were changed compared with the ADAQ measurement conditions. The slit of the sliding diaphragm was wider and a weaker ^{22}Na source was used. The use of a weaker source decreased the number of accidental coincidences. The measurement performed on sample No 3 (cf. Table I) showed that at

the angle $(38 \pm 3 \text{ mrad})$ the angular distribution function is equal to

$$N(38 \text{ mrad}) = (22 \pm 6) \times 10^{-5} N(O), \quad (2)$$

where $N(O)$ denotes the maximum value of the distribution function. Since the observed effect was small in comparison with background conditioned by accidental coincidences, the count rate of accidental coincidences was measured with a delay-line in one channel. This was to test its reliability. To this end, a similar measurement was performed under the same conditions for an Al sample for which one should not expect the existence of pairs of correlated quanta for $\alpha \cong 38 \text{ mrad}$. The result of this measurement equals

$$N(\alpha = 38 \text{ mrad})_{\text{Al}} = (5 \pm 7) \times 10^{-5} N(O)_{\text{Al}}. \quad (3)$$

Both of the measurements were performed in air since we were afraid that the chamber itself could cause the scattering of the annihilation quanta thus making it impossible to notice this effect for the sample.

3. Results and their interpretation

As shown in Figs 1-3 for all of the studied samples a considerable difference exists between the shapes of the ADAQ measured in vacuum and in air. For each sample, the angular correlation curves obtained from measurements in vacuum and in air coincide for the angular deviation of colinearity $\alpha \gtrsim 5 \text{ mrad}$. For angles $\alpha \lesssim 5 \text{ mrad}$ the correlation curves obtained in air run higher than the corresponding curves obtained in vacuum. Therefore, we observe a general increase in two-quanta annihilation events contributing to the observed angle in the range from -20 mrad to $+20 \text{ mrad}$. Such a result should be expected from the lifetime measurement data obtained by Paulin [2] for samples of the same material. If one assumes an increase in surface for the ADAQ observed when passing from vacuum to air is conditioned by quenching of o-Ps atom resulting from its interaction with oxygen molecules and that the intensity I_3 of the long-lived component is the measure of the number of all o-Ps atoms which left the grains, then the experimentally observed increase in surface ΔS with reference to the surface S_0 of the ADAQ measured in vacuum should be connected with the long lifetime component intensity I_3 , the lifetime $\tau_3 = (\lambda_3)^{-1}$ in air and the conversion rate λ_K by the formula

$$\frac{\Delta S}{S_0} (1 - I_3) = I_3 \frac{\lambda_K}{\lambda_3},$$

which after transforming gives

$$\frac{\Delta S}{S_0} = \frac{I_3 \lambda_K}{\lambda_3} \frac{1}{1 - I_3}. \quad (4)$$

The factor $(1 - I_3)$ in this formula results from the fact that in vacuum among the positrons coming into sample only a fraction $(1 - I_3)$ annihilate with emission of two quanta. The values of quantities occurring on both sides of the formula (4) calculated on the basis of

the ADAQ measured by us and the lifetime measurement results obtained by Paulin [2] are presented in Table II.

As one can see from this table for sample No 1 formula (4) seems to be practically fulfilled. Moreover, the run of correlation curves for this sample indicates that the passing

TABLE II

The collation of the results of the ADAQ and of the positron lifetime spectra for investigated samples

Number of sample	$\frac{\Delta S}{S_0}(1-I_3)$	I_3 [2]	$\lambda_k(s^{-1})$ [2]	$\lambda_3(s^{-1})$ [2]	$I_3 \frac{\lambda_k}{\lambda_3}$
1	0.035 ± 0.009	0.04 ± 0.005	} 7.16×10^8	} 0.142×10^8	0.020 ± 0.005
2	0.169 ± 0.012	0.12 ± 0.01			0.062 ± 0.01
3	0.142 ± 0.011	0.12 ± 0.01			0.060 ± 0.01

from vacuum to air has little effect on the ADAQ which corresponds to small intensity I_3 for this sample. For samples no 2 and 3 the relative increase in surface $\frac{\Delta S}{S_0}$ evaluated from correlation measurements is considerably greater than could be expected from the lifetime values obtained by Paulin. To explain this disaccord we assume that the intensity I_3 of the long-lived component in the time spectrum does not represent all the o-Ps atoms which are in pores. As mean grain radii of samples No 2 and 3 are several times smaller than of aerosil No 1, one may assume that among the o-Ps atoms which diffused into pores in these samples there are atoms which had not managed to thermalize completely in the grains. These form a group of hot o-Ps atoms. Their existence was postulated several times for gases and water solutions. Results of [4, 7, 8] confirm the possibility of the existence of hot o-Ps atoms for powdered metal oxides. Chuang and Tao explained the inconsistency of silicagels to follow the diffusion model with respect to the dependence of the quantity $\theta_3 = I_3/(I_2 + I_3)$ on temperature by occurrence of hot o-Ps atoms. The possibility of interaction of these atoms with grain surfaces in vacuum can not be excluded either for o-Ps atoms diffusing into the pores in the moment when they leave the grains or o-Ps atoms which had managed to diffuse into the pores and can collide with grain surfaces many times. One ought to expect that their interaction will be especially intensive for very narrow pores. The micropores ($d < 20 \text{ \AA}$) according to the additional data obtained for aerosils No 2 and 3 by using the method of Cranstone and Inkley, give a contribution to the pore specific volume: 32% and 22% and to the pore specific surface: 53% and 43% respectively. For narrow pores, the energy of the dispersion interaction reaches large values and thus o-Ps adsorption on the grain surface becomes more possible. As a result of adsorption, o-Ps is quenched via the pick-off process on account of the increase of the o-Ps wave function penetration into grain. As a result of the o-Ps interaction with the surface, chemical o-Ps quenching can also occur if there are chemical quenching centres on the surface. It follows from the data obtained by Chuang

and Tao for silicagels [3] that o-Ps is quenched chemically by free radicals: $\equiv \text{Si}^{\circ}$ and

$\equiv \text{Si}-\text{O}^{\circ}$ produced as a result of breaking of strained siloxane bridges: $\equiv \text{Si}-\text{O}^*-\text{Si}\equiv$.

On account of the absence of essential differences in chemical surface properties of silicagels and aerosils one can assume that similar bridges exist also on the aerosil grain surface since their appearance is favoured by the method of preparing the samples, namely:

a) In the process for obtaining aerosils the material is exposed to the action of diametrically differing temperatures. The result is that in the product obtained there is a certain quantity of strained siloxane bridges [9].

b) The samples were heated, and during this process condensation of silanol groups occurred in accordance with the formula: $2\equiv \text{Si}-\text{OH} \rightarrow \equiv \text{Si}-\text{O}^*-\text{Si}\equiv + \text{H}_2\text{O}$.

c) The pressing of samples causes an increase in the number of the grain nearest neighbours and the OH groups occurring on the grain surfaces are in contact joint by hydrogen bonds. One can assume that at the applied heating temperature ($\sim 200^{\circ}\text{C}$) condensation of these silanol groups takes place because as it is well known when the temperature increases during the dehydroxylation process, the hydroxyl groups in the neighbourhood joined by hydrogen bonds are removed at first [10].

It is generally accepted that the chemical quenching rate of o-Ps, λ_{chem} , is proportional to the concentration of active quenching agents. Chuang and Tao found that for silicagels [3] the λ_{chem} value depends on the activation energy of quenching centres — E_A , which they identified with the radical formation energy. Besides they assumed that the E_A

value depends on the energy state of the $\equiv \text{Si}-\text{O}^*-\text{Si}\equiv$ group which is also dependent on the surface structure. On the grounds of the evaluated E_A values they showed that the strained siloxane bridges are more excited on a narrow pore surface than on larger pores. Taking the small E_A values (about 10^{-1} eV) into account one can suppose that the quenching centres on the pore surface become active owing to the inelastic collisions of hot o-Ps atoms with pore surface. In consequence of this process the o-Ps atoms undergo 2γ -annihilation via chemical quenching caused by transitional excited complexes: $\equiv \text{Si}-\text{O}-\text{Ps}$ or or $\equiv \text{Si}-\text{Ps}$ formed on the surface. The chemically quenched o-Ps contributes to the component with a mean lifetime τ_1 ($\approx 10^{-10}$ s). Thus the intensity of the long-lived component — I_3 evaluated by Paulin does not account for all the o-Ps atoms which managed to escape into the pores. We assume that I_3 represents only the contribution from quasi-thermalized o-Ps atoms. The evaluation of the 2γ -annihilation contribution caused by chemical quenching of hot o-Ps atoms on the grounds of the mean lifetime measurements is not possible because these measurements do not reveal the complex character of the τ_1 component. One can not exclude that a certain number of annihilation events arising from the fast annihilation of o-Ps atoms bonded with the pore surface and giving a contribution to the τ_1 component is not observed for ADAQ in the angular range ± 20 mrad. If one assume that as a result of o-Ps bonding with the pore surface, the surface atoms can transfer a considerable momentum to emitted annihilation quanta, then their directions can evidently deviate from colinearity. This should cause annihilation quanta pairs to

appear in which flight directions of quanta form an angle differing from π by more than 20 mrad. To check this supposition experimentally we have performed additional measurements (for the angle $\alpha \simeq 38$ mrad) as mentioned in the description of the experiment. The obtained effect, although inconsiderable, does not exclude that the annihilation of o-Ps bonded with the surface can lead to a large noncolinearity of annihilation quanta. In air, on account of the partial coating of the pore surface with an adsorbate, the o-Ps interaction with the surface is considerably less efficient and the conversion by oxygen molecules in air becomes the prevailing mechanism of o-Ps quenching. It causes quenching for both fast and thermalized o-Ps atoms. Goldanskii suggested many times (for instance in [11]), that during the o-Ps interaction with the paramagnetic molecule the transitional complex: o-Ps molecule can be formed, the dissociation of which is accompanied by the orto-para conversion of Ps atoms. The mean lifetime of the hot o-Ps atoms depends in this case on many factors. Besides the known λ_K dependence on the convertor molecule concentration, its value is determined certainly by such factors as the possibility of the complex formation and the complex lifetime. The complexes of oxygen with hot o-Ps atoms probably formed in pores as intensely excited are short-lived. In the course of their dissociation the orto-para conversion followed by the emission of two γ quanta occurs increasing the narrow component intensity in the correlation curves and contributes to the τ_1 component in lifetime spectra. If the quantities of hot o-Ps atoms quenched chemically in vacuum and by conversion in air are the same, then the intensity I_1 should not change when passing from vacuum to air in accordance with the Paulin results. The quasi-thermalized atoms of o-Ps also undergo the conversion but their mean lifetime is longer. If one assumes that their conversion occurs like Paulin suggested, then interpreting the lifetime measurement data, it should increase the narrow component intensity in air. Thus the narrow component intensity increase in air gives information about the whole quantity of o-Ps atoms which underwent the conversion caused by their interaction with oxygen molecules. The change of the annihilation mechanism when passing from vacuum to air should then effect the correlation curve run. In air "the tails" of the curves should run below the curve tails in vacuum. It seems that on account of the energy and chemical heterogeneity and low adsorbate pressure the pore surface does not become completely coated with an adsorbate and its part is still accessible for o-Ps. In sum total, the relative increase $\frac{\Delta S}{S_0}$ of the narrow component of correlation curve observed when passing from vacuum to air is caused by two effects: the fast orto-para conversion of the hot o-Ps atoms being in pores $-\frac{\Delta S_h}{S_0}$ and the orto-para conversion of the quasithermalized o-Ps atoms $-\frac{\Delta S_t}{S_0}$ which is equal to $I_3 \frac{\lambda_K}{\lambda_3} \frac{1}{1-I_3}$.

Thus

$$\frac{\Delta S}{S_0} = \frac{\Delta S_h}{S_0} + \frac{\Delta S_t}{S_0}. \quad (5)$$

Utilizing the measured ADAQ and the mean lifetime measurement data obtained by Paulin and on the grounds of the above mentioned model describing the o-Ps annihilation in pores, the relative quantity of hot o-Ps atoms in samples No 2 and 3 can be evaluated.

If N_t denotes the relative number of positrons forming thermalized o-Ps atoms being in pores and quenched in air by conversion with 2γ emission referred to the whole quantity of positrons annihilating in sample thus

$$N_t = I_3 \frac{\lambda_K}{\lambda_K + \lambda_3^0}. \quad (6)$$

If in turn N_h denotes the relative number of positrons which form the hot o-Ps atoms being in pores chemically quenched in vacuum and undergoing fast o-Ps conversion in air thus $\Delta S_t \sim N_t$ and $\Delta S_h \sim N_h$.

As the surface S_0 found in the experiment (in range ± 20 mrad) is connected with the contribution of all the 2γ annihilation events except the events resulting from fast chemical quenching of hot o-Ps atoms in vacuum then $S_0 \sim [(1-I_3) - N_h]$. From where it follows:

$$\frac{\Delta S}{S_0} = \frac{\Delta S_t}{S_0} + \frac{\Delta S_h}{S_0} = \frac{N_t}{(1-I_3) - N_h} + \frac{N_h}{(1-I_3) - N_h}. \quad (7)$$

Transformation of formula (7) gives

$$\frac{\Delta S}{S_0} = \frac{\Delta S_t + \Delta S_h}{S_0} = \frac{N_t + N_h}{(1-I_3) - N_h}. \quad (8)$$

From where

$$N_h = \frac{\frac{\Delta S}{S_0} (1-I_3) - I_3 \frac{\lambda_K}{\lambda_K + \lambda_3^0}}{1 + \frac{\Delta S}{S_0}}. \quad (9)$$

According to Paulin's results $\lambda_K = \lambda_3^0 = 7.16 \times 10^6 \text{ s}^{-1}$. Finally we obtain

$$N_h = \frac{\frac{\Delta S}{S_0} (1-I_3) - \frac{I_3}{2}}{1 + \frac{\Delta S}{S_0}} = \frac{\frac{\Delta S}{S_0} - I_3 \left(\frac{\Delta S}{S_0} + \frac{1}{2} \right)}{1 + \frac{\Delta S}{S_0}}. \quad (10)$$

From this relation we obtain that $N_h \approx 0.07$ and 0.08 for samples No 2 and 3 respectively.

In other words for samples No 2 and 3 the number of positrons forming the hot o-Ps atoms equals $\approx 7\%$ and 8% of the whole number of positrons annihilating in the sample. Thus in these samples, the hot o-Ps atoms contribute of about 30% to the whole number of o-Ps atoms formed in the sample.

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