

Delayed formation and localisation of positronium in polymers at low temperatures

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Abstract

A theoretical model of the positron annihilation lifetime spectrum including the mechanisms of slow positronium (Ps) localisation and delayed Ps formation from a positron and a trapped electron was developed. The model was applied to two series of spectra for low-density polyethylene and high-density polyethylene (HDPE) collected at constant temperature (much below the glass temperature) as a function of measurement time. The Ps internal relaxation time and time of localisation of Ps in a free volume centre were determined. The results show that after long irradiation of the polymer a dominant fraction of positrons (unbound in Ps) annihilate from the trapped states. On the basis of parameters determined from the HDPE lifetime spectra, two $S(t)$ curves (for sample in darkness and in light) were calculated. The predicted shapes of $S(t)$ well agree with literature data obtained with the age-momentum correlation (AMOC) experiment. According to the new model the shapes of the *para*-Ps and the *ortho*-Ps (*p*-Ps) components are non-exponential. In spite of this, the multi-exponential decomposition of a polymer spectrum enables to determine correctly the value of the *o*-Ps lifetime, however the other parameters determined from the spectrum have no simple physical meaning.

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1. Introduction

A positron injected into a polymer can annihilate with an electron either directly or via a bound state e^+e^- called positronium (Ps). The intrinsic lifetime of Ps in its singlet state, i.e. *para*-Ps (*p*-Ps), is only 0.125 ns, whereas the intrinsic lifetime of its triplet state, i.e. *ortho*-Ps (*o*-Ps), is 142 ns. The observed lifetime of *o*-Ps in substances is reduced to a few nanosecond due to the so called pickoff process, i.e. annihilation of e^+ from the interior of Ps by an electron in the environment of Ps.

The positron annihilation lifetime (PAL) spectrum of a polymer is usually resolved into three exponential components relating to annihilations of *p*-Ps, “free” positron and *o*-Ps. The lifetime parameter of the third component is easily detectable. The parameter supplies valuable information about the polymer-free volume (Schrader and Jean,

1988; Jean, 1990; Tao, 1972; Eldrup et al., 1981). However, physical interpretation of the shorter living components is not so straightforward. In the present work we propose a new method of positron lifetime analysis basing on some models concerning the processes of Ps formation and Ps localisation in polymers. The interpretation makes use of the whole PAL spectrum. The analysis is applied to PAL spectra of low-density polyethylene (LDPE) and high-density polyethylene (HDPE) measured in situ, one by one, at low and constant temperature.

PAL investigation of polyethylene in the external electric field by Ito and Suzuki (2003) showed that, at a temperature far below the polymer glass transition, two different mechanisms of Ps formation were involved.

The first mechanism was assigned to Ps formation from a positron, diffusing through the material and one of the electrons loosely trapped in the polymer structure. The loosely trapped electrons originated from a fraction of excess electrons produced by bombardment of material with positrons. Because the concentration of trapped

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electrons in sample increases with the time of its exposition to the radioactive source, the intensity of *o*-Ps component elevated with time of measurement. Illumination of the material by visible light releases the trapped electrons and the *o*-Ps component abruptly falls down (Hirade et al., 1998, 2000; Ito et al., 1999; Suzuki et al., 2003).

The second mechanism Ito and Suzuki (2003) presumably connected with a process of Ps production in a terminal positron spur so-called blob (Mogensen, 1974, Stepanov et al., 2000).

Recently a process of delayed Ps formation has been observed in age momentum correlation (AMOC) experiments by Suzuki et al. (2003) and Dauwe et al. (2003). According to Suzuki et al. the observed delay is caused by the first mechanism mentioned above, i.e. Ps formation from an e^+ and a trapped e^- . Dauwe et al. assigned the delay to some sub-nanosecond processes in the positron blob.

In the present paper we take into account both mechanisms as possible reasons for the delayed Ps formation. However, contrary to Dauwe et al. (2003), we assume that the processes inside the blob do not lead to creation of Ps in its stable state, but to a quasi-Ps, i.e. a non-localised and weakly bound pair e^+e^- (Stepanov et al., 2000). Then this quasi-Ps loses its kinetic energy, due to interactions with molecules. Gradually the contact density between e^+ and e^- inside Ps increases and simultaneously Ps becomes more and more localised. For a description of the process a model (called ETLA¹) had been proposed (Dauwe et al., 1998; Kansy et al., 2000a, b; Kansy and Suzuki, 2003). In earlier papers concerning the model it was assumed that the time needed for formation of stable Ps from its precursor (internal *relaxation* time) was much shorter than its *localisation* time. In a recent paper (Kansy and Suzuki, 2003) we tested another assumption, i.e. that the relaxation and localisation times were equal. Here we will employ the ETLA model without any prior constraints on the relation between the relaxation and localisation times.

2. Theoretical model

We assume that the positron injected into a polymer after a short period of order a few picoseconds can leave the blob as a loosely bound pair e^+e^- (quasi-Ps—with population ratio *o*-Ps to *p*-Ps = 3) or alternatively as a “free” epi-thermal positron. Then the following processes take place:

2.1. Slow localisation of positronium (SLP)

The quasi-Ps gradually loses its kinetic energy. The contact density between e^+ and e^- gets higher and higher

and the Ps is more and more localised.² This way: (1) its intrinsic annihilation rate changes from almost 0 to its characteristic value $\lambda_{o/p \text{ intr}}(\infty)$ at vacuum ($\lambda_{o/p \text{ intr}}(\infty) = 1/142$ or $1/0.125 \text{ ns}^{-1}$ for *o*- or *p*-Ps, respectively), (2) the pick-off annihilation rate decreases from a value $\lambda(0)$ to its asymptotic value $\lambda(\infty)$. The latter depends on the average hole size of polymer free volume.

Because of the above-mentioned processes the Ps lifetime becomes a function of time. Exact determination of this time dependence is a very difficult quantum-mechanical task. For a reasonable approximation of the dependence we propose the following simple function, which satisfies the assumptions 1 and 2 (Kansy et al., 2000a, b):

$$\lambda_{o/p}(t) = \lambda_{o/p \text{ intr}}(t) + \lambda_{\text{pickoff}}(t), \quad (1)$$

where

$$\begin{aligned} \lambda_{o/p \text{ intr}}(t) &= \lambda_{o/p \text{ intr}}(\infty)[1 - \exp(-t/\tau_{\text{relax}})], \\ \lambda_{\text{pickoff}}(t) &= \lambda(\infty) + [\lambda(0) - \lambda(\infty)]\exp(-t/\tau_{\text{local}}). \end{aligned}$$

τ_{relax} is the time of internal relaxation of Ps and τ_{local} the time needed for Ps localisation. Thus the *p*- or *o*-Ps component in the PAL spectrum is

$$C_{o/p\text{-Ps}} = \lambda_{o/p}(t) \exp\left[-\int_0^t \lambda_{o/p}(t) dt\right]. \quad (2)$$

The right side of Eq. (2) can be expanded into the following series of exponential functions:

$$C_{o/p\text{-Ps}} = \sum_{k,j=0}^{\infty} \frac{\delta_{kj}}{\xi_{kj}} \exp\left(-\frac{t}{\xi_{kj}}\right), \quad (3)$$

where $\delta_{kj} = (s^k/k!)(r^j/j!)\exp(-s-r)$, $s = -\lambda_{o/p \text{ intr}}(\infty)\tau_{\text{relax}}$, $r = [\lambda(0) - \lambda(\infty)]\tau_{\text{local}}$ and $\xi_{kj}^{-1} = [\lambda_{o/p \text{ intr}}(\infty) + \lambda(\infty)] + k/\tau_{\text{relax}} + j/\tau_{\text{local}}$.

(To simplify the notation the indexes *o/p* at the *s* and *r* are omitted).

In the case of *o*-Ps $s = \frac{1}{142}\tau_{\text{relax}}$. Because τ_{relax} is expected to be much lower than 142, *s* is expected to be almost 0. In such case Eq. (3) can be simplified to

$$C_{o\text{-Ps}} = \sum_{j=0}^{\infty} \frac{\delta_j}{\xi_j} \exp\left(-\frac{t}{\xi_j}\right), \quad (4)$$

where $\delta_j = (r^j/j!)\exp(-r)$, $r = [\lambda(0) - \lambda(\infty)]\tau_{\text{local}}$ and $\xi_j^{-1} = [\frac{1}{142} + \lambda(\infty)] + j/\tau_{\text{local}}$.

It is worthy to notice that $C_{o\text{-Ps}}$ is a superposition of many exponential components of “lifetimes” given by ξ_j and “intensities” given by δ_j . The components have no physical meaning separately therefore we will call them as *pseudo-components*.

¹In the present paper we decided to rename the model more adequate as SLP (Slow localisation of positronium).

²Because of interaction between quasi-Ps and its environment the state of the quasi-Ps is a mixed quantum state. Therefore the evolution of the state can be considered as a continuous classical process.

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