Positrons in naphthalene. Critical remarks on the relation between *o*-Ps lifetime and void size

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Abstract. Lowering the temperature or applying high pressure leads to elimination of positronium component in the e^+ lifetime spectrum in solid naphthalene. Disappearance of positronium means reaching the free volume size limit at which there is no energy level in the potential well. It allows to estimate that size, which is found inconsistent with predictions of the popular Tao-Eldrup model. The range of applicability of that model is discussed. The dependence of the free e^+ decay constant on pressure indicates that positronium is formed not only in the blob processes, but during the whole free positron life. The lifetime of free positrons begins to rise with temperature earlier than Ps intensity.

Key words: high pressure • naphthalene • positronium quenching • free volume

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Introduction

Naphthalene is the first solid in which the formation of positronium (Ps) was observed by both angular distribution of annihilation radiation and positron lifetime methods [4, 13]. In majority of cases positronium is localized in condensed matter, it needs a free (electronless) volume in which it is trapped. The delocalized positronium, as a wave in periodic crystal structure, was observed too, however, this form was found in the crystals of some simple molecules only (ice, quartz, with low intensity – alkali halides). In organic crystals of more complex structure Ps was always found trapped in free volumes representing for Ps a potential well. In particular, no delocalized Ps was observed in naphthalene and pyrene, discussed in this paper (no characteristic very narrow *para*-positronium (*p*-Ps) peak in angular distribution of annihilation quanta).

Wasiewicz *et al*. [9] have shown that free volumes accommodating Ps in naphthalene are produced thermally, i.e. no positronium at low temperatures; with increasing temperature the long-lived component intensity I_3 in positron annihilation lifetime spectra (PALS) spectrum begins to rise closing to saturation value at room temperature. Positronium is located in thermally produced defects (like vacancies), or alternatively, pre-existing small intermolecular free volumes expanded to such dimensions which make localization of Ps in them possible. The Arrhenius plot $I_3/(I_{3\max} - I_3)$ vs. $1/T$ gives the activation enthalpy of Ps accommodation centres as $H = (0.17 \pm 0.03)$ eV. In the case of naphthalene the sublimation enthalpy H_s is much higher, about 0.7 eV. For vacancies in plastic crystals Eldrup [17] estimated
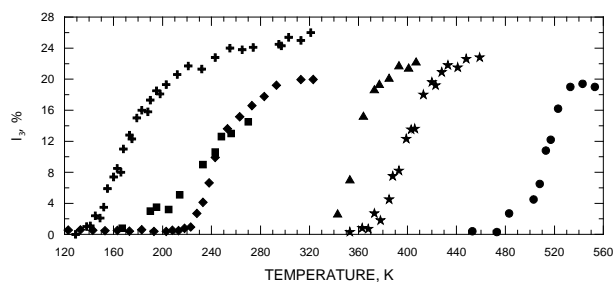
Fig. 1. Temperature dependence of positronium intensity in selected aromatic hydrocarbons. Crosses – biphenyl, asterisks – *p*-terphenyl; dots – *pp'*-quaterphenyl; diamonds – naphthalene, triangles – pyrene, squares – chrysene.

the values of vacancy formation enthalpy as (0.5–0.7) H_s, in very soft plastic crystals-close to H_s [3]. The value $H = 0.24 H_s$ found by us indicates that the Ps formation centres in naphthalene are not vacancies, but rather intermolecular free volumes (in the case of void left after removal of the molecule as big as naphthalene, the lifetime would be much longer than observed, about 2.7 ns).

Disappearance of positronium at lowering the temperature was observed by us in many solid aromatic hydrocarbons: polyphenyls, polycyclic chrysene and pyrene (Fig. 1). This kind of behaviour at temperature changes is not, however, a general rule: no Ps at any temperature in solid anthracene, Ps presence at all temperatures in phenanthrene (both molecules are three-ring polycyclic structures differing in mutual ring arrangement only). In a pair of similar solid hydrocarbons: naphthalene (two six carbon rings) and azulene (five- and seven-carbon rings) in the first case positronium forms, in the other – does not.

In all cases the *ortho*-positronium (*o*-Ps) lifetimes are short and temperature dependent. Typical lifetimes are 1.0–1.2 ns, decreasing with lowering temperature. An extreme case is pyrene, in which the lifetime of long-lived component is barely (0.5–0.7) ns. A separate measurement with pyrene was performed by the three gamma intensity method [8]. The triple coincidence rate was measured in pyrene as a function of temperature; the reference was pyrene at room temperature. Full consistency of $I_{3\gamma}$ intensity increase and long-lived component intensity was found, thus in spite of extremely short lifetime that component should be of Ps origin.

In this paper we present the experimental results for naphthalene. Using this example we discuss the reliability of existing models describing the relation between the free volume size and *o*-Ps life time.

Experimental

The positron annihilation lifetime spectra were measured using a standard fast-slow delayed coincidence spectrometer and processed using the LT v.9 [12] program. The spectra were decomposed into three (if not stated otherwise) exponentials convoluted with instrumental resolution curve. The constraints on spectrum parameters are described in the discussion of particular results. The temperature was regulated by fixing the sample container to the upper end of a cold finger contacting with liquid nitrogen (or its vapour) and

heating by a coil controlled by Shimaden FP21 stabilizer. The high pressure measurements were performed at room temperature using a U-11 (Unipress, Warsaw) compressor with argon as a working gas. The samples were placed in a special capsule with pistons, preventing the penetration of argon to the sample.

Results and discussion

Temperature and pressure effects

It was shown [10] that positronium formation in naphthalene can be quenched out by pressure (similar effect was observed in biphenyl). At about 110 MPa, the long-lived component in PALS spectrum disappears. In Fig. 2 the dependences of *o*-Ps intensity and lifetime on pressure, obtained from spectrum decomposition into three exponentials, are shown. Bisi *et al*. [1] reported that magnetic quenching of Ps in solid naphthalene gives electron density at the positron site as low as 0.25 of that for Ps in vacuum. It should increase the *p*-Ps lifetime to 0.335 ns, thus becoming not distinguishable from free e^+ annihilation component. However, careful lifetime measurements [11] have shown that the short-lived *p*-Ps component is easy to separate from the spectrum remainder and its lifetime is not far from that in vacuum. The ratio of longest to shortest-lived component intensities, assumed as *o*-Ps to *p*-Ps intensity ratio, was found at all pressures similar, the average ratio was 2.55, i.e. not far from statistically expected 3:1. This value, 2.55, was fixed at final spectra processing.

At room temperature and without external pressure, the *o*-Ps lifetime is about 1 ns only, and shortens when the pressure is applied. The pressures up to 65 MPa have little influence on *o*-Ps intensity (I_3 is over 85% of that without pressure), while above 80 MPa positronium disappears rather rapidly. Application of pressure squeezes free volumes. If the radius of a spherical void becomes smaller than
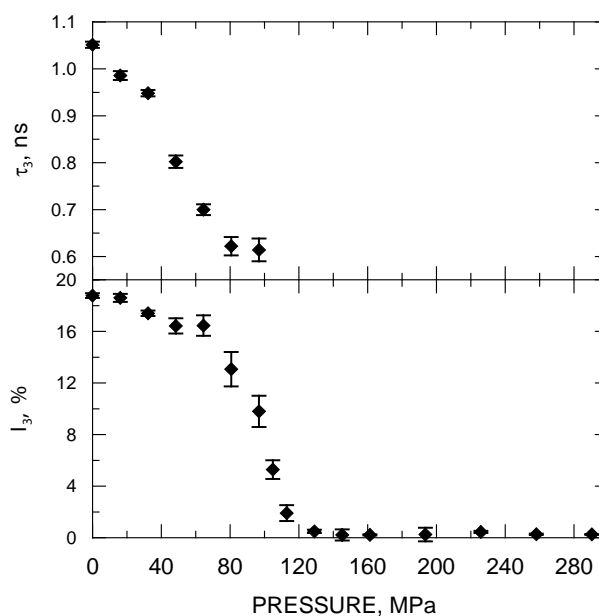

Fig. 2. *Ortho*-positronium lifetime τ_3 and intensity I_3 in naphthalene as a function of pressure at room temperature [10].

$$(1) \qquad R_{min} = \frac{\hbar\pi}{2\sqrt{m_{Ps}U}} = \frac{0.216}{\sqrt{U}} \text{ nm}$$

where: U – depth of the rectangular potential well in the solid, (for U in eV the radius in nm) there is no energy level for particle in the well; Ps cannot be localized there. The calculations by Nakanishi and Jean [21], basing mainly on the measurements by Mogensen and Jacobsen [19, 20], suggest that for rectangular potential the depth U for many organic media is of the order of 1 eV. For U equal exactly 1 eV, R_{min} at the point of long-lived component disappearance should be 0.216 nm. Abrupt disappearance of long-lived component at certain pressure means that Ps accommodating free volumes are of rather uniform sizes.

Figure 3 shows the lifetime of free positrons in a broad range of pressures, exactly – instead of mean lifetime its reciprocal, the decay constant λ_2, is placed on the ordinate axis. It is seen, that at the pressure when the positronium component disappears, a step down in λ_2 occurs. A quadratic function was fitted to the experimental data in the range 110–500 MPa and extrapolated to smaller values. The experimental result can be explained by the presence of an additional process removing free positrons from the second component and acting in this pressure range where positronium appears:

$$(2) \qquad \lambda_2 = \lambda_f + K_{23}$$

where λ_f is the decay constant of free positrons. The constant K_{23} is thus the rate of transfer of positrons from free state to bound one (positronium). Figure 3 shows the pressure dependence of K_{23} (as a difference between experimental data and extrapolated curve); it is seen that it follows exactly similar dependence I_3 vs. pressure.

The Ps formation, as proposed by Stepanov *et al.* [22], occurs at the end of ionization track (in blob):
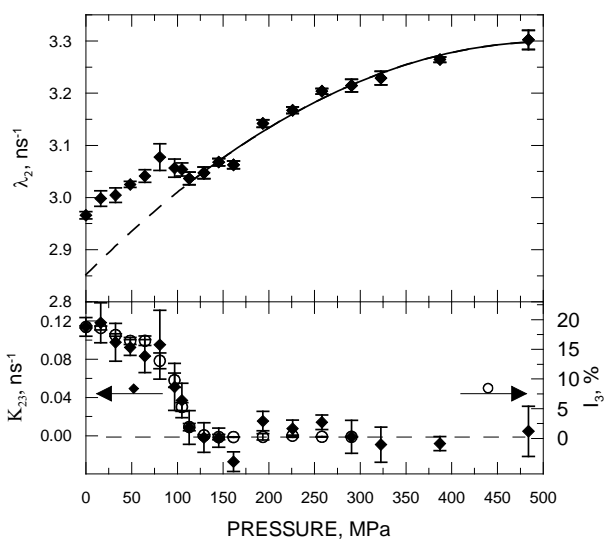
the positron picks one of electrons from a rather rich cluster of radiolytic species. The simulation by Garcia *et al.* [7], describing the fate of positron injected into *n*-hexane (linear hydrocarbon), estimates that majority of electrons in the blob decay on a time scale of $\approx$20 ps due to recombination with the cations, and similar should be the time of Ps formation. However, from this simulation it follows that not all excess electrons recombine in the first 20 ps, some of them survive as long as the lifetime of "free" positrons. After 200 ps still 10% of initial number of electrons remains. The *o*-Ps fraction continues this way to increase up to the times exceeding a few hundred ps. The non-zero value of K_{23} means that the third component in the spectrum is supplied by new positronium atoms as long as free positrons are present in the sample. The transition rate K_{23} should be proportional to the excess electron density, i.e. K_{23} is time dependent, thus the decay of *o*-Ps component is not strictly exponential. Our spectra were analysed as composed a priori of three exponentials, and the deviation from exponentiality is not visible. This deviation is not expected to be significant and its detection is out of the possibility in a standard experiment. Due to low concentration of electrons left after the blob decay, the value of K_{23} (essentially – time averaged one) is low, about 0.1 ns^{-1}.

The same effect of transitions from free positron state to positronium should be present also in temperature dependence of free positron lifetime, however it is much more difficult to observe. Unlike the pressure effect, the rise of *o*-Ps intensity occurs in a broad range of temperatures. In Fig. 4, the lifetime τ_2 is shown; the range of temperatures in which the intensity I_3 rises is dashed. It is seen that the τ_2 vs. T dependence has a kink-shaped form; initially it rises rather fast, in the indicated range the rise is stopped and then slow rise is again observed.

The increase of τ_2 begins at $\approx$200 K, thus it precedes the appearance of positronium by about 20 K. The accelerated rise of τ_2 is not the result of appearance of a new, unresolved, component; the attempt to split it into two (four component analysis) failed. It was noticed by
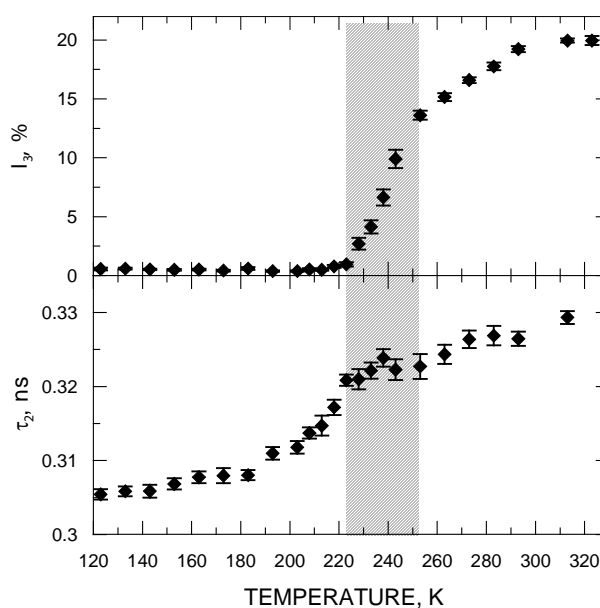

Fig. 3. Top – decay constant of free positrons λ_2 in naphthalene as a function of pressure. Solid line is a square function fitted to the data in the range 110–500 MPa, dashed line – its extrapolation toward lower pressures. Bottom – transition rate from free positron state to positronium K_{23} (diamonds) and intensity of *ortho*-positronium component I_3 (circles) as a function of pressure.

Fig. 4. *Ortho*-positronium intensity I_3 and free positron lifetime τ_2 in naphthalene as a function of temperature. The temperature range in which I_3 grows rapidly is dashed.

Brock and Dunitz [2] that in the case of naphthalene it is not possible to perform X-ray diffraction measurements at the temperatures over 239 K, due to excessive molecular motions. Disordering of the structure increases preexisting intermolecular small free volumes, their rise diminishes local electron density, allowing the lengthening of τ_2 lifetime. Initially, the increase of these volumes is too small to represent a void able to accommodate positronium, but at further rise the o-Ps component appears.

Void size estimation

The size of free volume is estimated usually using the Tao-Eldrup model (TE, [5, 24]). According to that model, the expected value of o-Ps lifetime at approaching the R_{min} (for $U = 1$ eV) is equal to ≈ 1.35 ns, while, as it is seen in Fig. 2, the measured values at the pressure ≈ 100 MPa are about 600 ps, moreover, the lifetime without pressure is 1.04 ns, also well below that estimated from the model. Even if we assume $U = 2$ eV (that seems to be exaggerated), the R_{min} is 0.154 nm and respective TE lifetime 0.926 ns, still more than experimental data above $p = 50$ MPa. All the values lie well below Tao-Eldrup expectations. Still worse is the discrepancy in the case of pyrene – in the whole range of long-component existence the lifetimes are contained in the range 0.5 to 0.7 ns. The value 0.5 ns is the same as $1/\lambda_{bulk}$, where λ_{bulk} is "hypothetical" decay constant of Ps in the bulk, as it is assumed in the TE model. Thus, o-Ps is localized, nevertheless the probability to find it outside the free volume is near 100%.

The experimental results in the range of lifetimes 1 ns or less do not fit to the Tao-Eldrup predictions[1].

The discrepancy needs to be discussed. Basic assumptions made in the TE model are:
– the potential well is spherically symmetric, rectangular (stepwise), of the depth U;
– o-Ps decay constant λ_3 is $\lambda_{bulk}P$, P is the probability to find Ps outside the electronless well,
– decay constant of o-Ps in the bulk is the average of p-Ps and o-Ps constants in vacuum

$$(3) \qquad \lambda_b = \tfrac{1}{4}\lambda_{pPs} + \tfrac{3}{4}\lambda_{oPs} = 2 \text{ ns}^{-1}$$

(may be the decay constant of negative Ps$^-$ ion would be more appropriate as λ_{bulk}, however, it is slightly larger [18], $\lambda_{Ps-} = 2.5$ ns^{-1}). Note that λ_{bulk} in this model does not depend on electron density of the medium (an alternative approach to λ_{bulk} taking into account the electron density, see the paper by Lévay and Vértes [15]). The penetration P is

$$(4) \qquad \int_R^\infty \psi_{out}^2(r) r^2 dr$$

where ψ_{out} is the Ps wave function outside the well, $\psi_{out} \sim \exp(-\kappa r)/r$.

In order to facilitate the calculations of the integral (4) Tao (and then Eldrup) have proposed to substitute

the well of depth U by infinitely deep one, and broaden it by Δ preserving the radius of electron-free volume R; Δ is to be chosen to get the P value the same as in exact solution:

$$(5) \qquad \int_R^\infty \psi_{out}^2(r)r^2 dr = \int_R^{R+\Delta} \psi_{in}^2(r)r^2 dr$$

$$= \left[1 - \frac{R}{R+\Delta} + \frac{1}{2\pi}\sin\frac{2\pi R}{R+\Delta} \right]$$

(the wave function inside the well is $\psi_{in} \sim \sin r/r$).

The parameter Δ is chosen experimentally. In a series of papers on plastic crystals [3, 5, 6, 16, 17] Eldrup proposed in the case of vacancies in these crystals $\Delta = 0.17$ nm. Nakanishi and Jean [21] fitted the value of Δ for rich a set of liquids [19] as $\Delta = 0.1656$ nm (precision is greatly exaggerated). In both cases the o-Ps lifetimes were lying in relatively narrow range of several nanoseconds, and respective void radii were (0.35–0.5) nm[2].

The Δ parameter is nothing real; it follows from the simplification of calculations and approximates the depth of penetration of Ps wave function into the bulk. In many papers one can find the statement "the radius of potential well is $R_0 = R + \Delta$, and Δ is the electron layer inside the well", which is wrong. The potential well radius is R, no "layer" inside. The Δ parameter is a substitute to $1/\kappa$ (appearing in ψ_{out} wave function), which is the mean penetration depth of Ps wave function into the bulk. The value of κ depends on the distance of Ps energy level from the upper rim of the well (U-E), and thus depends on R, and also on U. When the Ps energy approaches the upper rim κ tends to zero, and Δ, if this concept is still valid, should rise.

The discrepancy between the TE model and experimental data for the shortest o-Ps life times lies in the assumption of an infinite potential well depth. In the infinitely deep well the energy level, on which o-Ps locates always exists, in finite one – it exists for $R > R_{min}$ only. In the TE model the o-Ps lifetime tends to the value 0.5 ns when void radius tends to zero, while for the finite depth – much earlier, for the radius approaching R_{min}.

Of course, the rectangular, stepwise potential is an approximation, much better would be the Saxon-Woods potential of diffused walls, however, the whole model has an approximate character and excessive increasing the number of model parameters is not justified.

What is the void radius? The Tao-Eldrup model assumes a priori a spherical shape of the void. In the case of vacancies in plastic crystals Eldrup has used the Wigner-Seitz radius, i.e. the radius of a sphere with the volume equal to that of crystal unit cell divided by the number of molecules in the cell. The radii in plastic crystals investigated in Refs. [3, 5, 6, 16, 17] are rather similar to each other, thus assuming a constant value of Δ is fully justified. In liquids the spherical symmetry seems to be a natural one, however, in the case of big molecules it is not so obvious. The void radius in liquids is calculated applying the "bubble model"; the estimate given by Na-

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[1] Unexpectedly, the value of o-Ps lifetime in ice, although very short [5] fits rather well to the TE model. This case deserves particular attention in the discussion of free volume definition.

[2] Nakanishi [21] has used also the data for zeolites (≈ 0.6 nm), but they were taken by selecting the lifetime value at the maximum of its temperature dependence, which varies in very broad limits; such a choice seems to be rather arbitrary.

kanishi and Jean [21] was obtained assuming in the model the macroscopic surface tension (i.e. for flat surface) and neglecting the presence of radiolytical reactions, which can be a source of systematic error. All what we can say about the free volume, judging after the *o*-Ps lifetime, is to estimate the average equivalent radius.

The penetration coefficient P in the Tao-Eldrup model is determined assuming Ps as a structureless particle. The calculations by Larrimore, Bug *et al*. [14, 23] for two-particle Ps structure show that at a given radius of rectangular well the distribution of positron density, when it is a constituent of Ps, is evidently narrower than that of a single particle. However, the introduction of empirical Δ eliminates the problem how accurate are the wave functions; if there is an error in the determination of P, it is corrected by a modified value of Δ.

Conclusions

The lifetimes observed in organic liquids lie in the same range as in plastic crystals, rarely in solids, and as long as determined *o*-Ps lifetime fall into the range 2–5 ns, the Tao-Eldrup model works well and the "universal" value of Δ can be used (not fully universal, as Nakanishi and Jean proposed for solids the value of $\Delta = 0.166$ nm, but 0.183 nm for liquids, which is rather forgotten...). At the lifetimes of the order of 1 ns, the Tao-Eldrup model gives void radii too small.

Positronium formation, although dominant in the blob, takes place also in the time scale comparable to the lifetime of free positrons.

When free positron lifetime is observed as a function of temperature, the beginning of τ_2 rise precedes the appearance of positronium.

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