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Positronium in Organic Crystals

Pozyt w kryształach organicznych

Позитрон в органических кристаллах

INTRODUCTION

Thirty years have passed since Deutsch demonstrated experimentally the existence of bound state of electron-positron pair in gaseous medium [1]. This result was followed soon by numerous publications reporting the observation of positronium atoms (as this bound state is called) in condensed media. Formation of positronium (Ps) is easily observed in liquids, where its behaviour is successfully described by bubble model [2], much more limited are the data concerning Ps in solids. Positronium can exist in insulators only, experimental evidence is for molecular crystals (including hydrogen bonded crystals), defected ionic crystals, and amorphous solids like polymers. First observation of positronium in organic crystal belongs to L a n d e s ,   B e r k o , and Z u c h e l l i [3]. They have found well pronounced long living component in the life-time spectrum of positrons in naphtalene. Many other examples of positronium formation were reported soon, the role of various factors in the annihilation characteristics was investigated, among others the sensitivity of annihilation processes on the structure of the medium was appreciated (effect of phase transitions [3,4]).

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In the early seventies, in spite of relatively rich material collected, the picture of positronium formation in organics was still not clear. There were known many solids in which positronium forms easily, and equally numerous ones in which Ps states do not form. Quantitative data were frequently inconsistent, further complication was introduced by the paper of D e B l o n d e et al. [5], stating that there is essential discrepancy between the results obtained using two fundamental experimental methods: lifetime method and angular distribution of two-gamma annihilation method.

In 1974 in the Department of Nuclear Physics headed by Professor Włodzimierz Żuk a team dealing with positron annihilation was created. The main task of this group was the investigation of factors influencing positronium formation in molecular solids, precisely – in aromatic hydrocarbons. In the pages below we want to present the scope of recent results of that group and the experimental equipment used in these investigations. Some features of positron annihilation in these compounds seem to be well established, nevertheless there are also some puzzling effects deserving further attention.

EXPERIMENTAL

In the investigations described below all three fundamental methods in the annihilation research were used:
- momentum distributions of annihilating electron-positron pairs,
- positron lifetime distributions,
- three quantum annihilation intensity measurements.

Measurements of momentum distributions

The momentum distribution of annihilating pairs was measured using well known angular correlation technique, where the deviation θ from colinearity of two-photon annihilation quanta is the measure of transverse component of the momentum. Creation of positronium manifests itself by the appearence of a narrow, low-momentum component in the momentum spectrum. The experimental set was of the "long-slit" type (vertical slits, counter movement in horizontal plane).
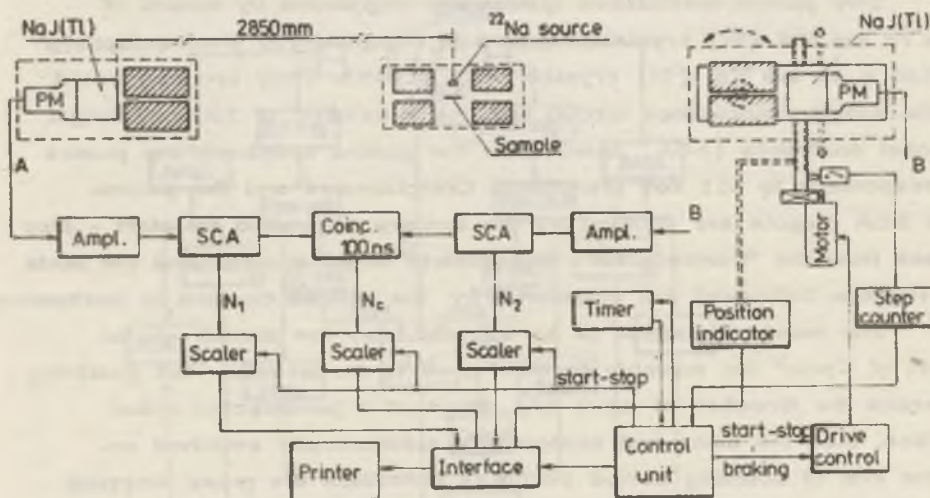
Fig. 1. Twophoton annihilation angular correlation apparatus

        Block diagram of our apparatus is shown in Fig. 1. Whole
mechanical arrangement is composed of three independent consoles
fixed to the main walls of the building, in its basement. The sample
- counter span is 2,8 m. The movable counter console contains a table,
which can be moved horizontally in the direction perpendicular to the
axis defined by fixed counter and sample. In the front of both counters
two thick lead baffles are located forming the slits. In the movable
counter the lead blocks are fixed to the vertical axis supported by
ball bearings and equiped with the arm, the end of which slides on
oblique bar. The angle of bar location is chosen to assure that in all
angular positions the symmetry axis of slit is oriented toward the
sample. The width of all slits can be regulated from 0 to 10 mm without
shift of the symmetry axis. The movement of the table is realized by
means of a screw of 1 mm pitch, driven by a 15 W reversible DC
motor. The table position is indicated by the mechanical numerator,
and by an electronic coding device coupled to the driving gear.
Moreover, every full revolution of the screw is signalized by a vol-
tage pulse appearing when the radial extension on the screw shortens
the contacts of precision microswitch. The pulses are registered by
"Step Counter", making possible to choose the number of revolutions
(1, 2, 3 or 4) separating subsequent measuring positions of movable
counter. The smallest step corresponds to the angle of 0,35 mrad.

Two photon annihilation quanta are registered by means of 75 x 75 mm NaI (Tl) crystals coupled to the FEU-110 photomultipliers or 160 x 40 mm NaI (Tl) crystals with FEU-93. They are connected to the simple coincidence circuit with the resolution of 100 ns. Single channel analysers (SCA) select from the gamma spectrum, the pulses corresponding to 511 keV photopeak. Coincidences and the pulses from SCA outputs are counted by the scalers controlled by start - stop pulses from the "Control Unit". The content of all scalers and the state of "Position Indicator" are registered by the printer coupled to perforator.

The measuring cycle is as follows: after the manual signal "Start of Cycle" the movable counter goes to the extreme left position, reverses the direction of move and stops at a preselected initial position, then the timer and scalers are automatically switched on. At the end of counting period the timer generates the pulse stopping the scalers and beginning the printing cycle. "End of Printing" signal switches the motor on, and after the number of screw revolutions determined by "Step Counter", the motor is blocked by transforming it into a short-circuit generator. The timer and scalers are switched on again with a two second delay. Reproducibility of the position is equivalent to 1/150 th of full screw revolution. In the extreme right position determined by "Position Indicator" the direction of revolutions is reversed, and the step counter is switched off, thus the table moves to the initial position without stopping and resumes next cycle of measurements. It is also possible to stop the system after completion of first cycle.

Positron source of 10 mCi ^{22}Na was produced by Amersham Co. Most of measurements were performed with slit width of 2 or 3 mm. Angular resolution of apparatus was determined by the method of Fujiwara and Sueoka [6]. The time necessary to obtain one angular distribution curve (ADAP) is 1-5 days, depending on statistics needed.

Positron lifetime measurements

The idea of positron lifetime measurements consists in registering the spacing of positron birth signal (1274 keV gamma transition following β^+ decay of ^{22}Na) and annihilation moment (511 keV two photon annihilation quantum). Block diagram of lifetime spectrometer used here is shown in Fig. 2. It is a modified two-counter fast slow gamma-gamma
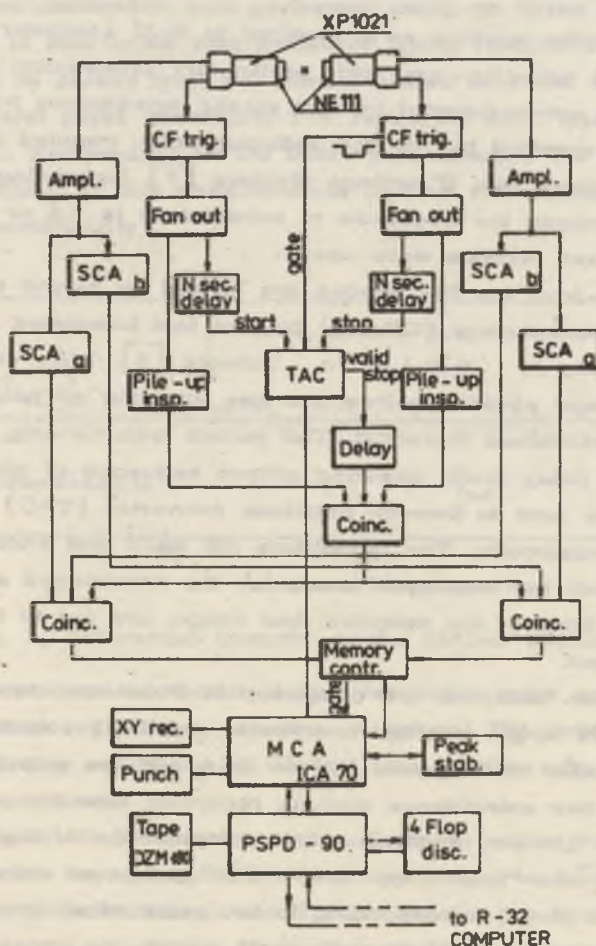
Fig. 2. Positron lifetime spectrometer

delayed coincidence setup, with the time to amplitude converter and
multichannel amplitude analyser. Commonly used spectrometers make
it possible to register the delayed coincidence spectrum using one
pair of energy windows selecting the pulses from 1274 keV gamma
quanta (start) in one counter, and 511 keV quanta (stop) in the
other. In our case, the doubled energy selection system enables
paralell registration of two spectra gated by two pairs of windows
selecting appropriate 1274 and 511 keV pulses in both channels.

    The time measuring tract is equiped with a single point digital
peak stabilizer and pile-up eliminating circuits. A multichannel amplitude
analyser (MCA) of ICA-70 type (4096 channels) is coupled to a

PSPD- 90 microcomputer working as a terminal to R-3? computer
and serving for data collection and their preliminary processing.

Gamma quanta are registered by fast plastic scintillators NE 111,
2,5 cm in diameter, covered by NE 560 reflector paint, coupled to
XP 1021 photomultipliers with B' voltage dividers [7]. Depending on
experimental requirements the thickness of scintillators is 2,5 or 1,2 cm
(in most cases thicker plastics were used).

Timing signals from the PM anodes are formed by means of
constant fraction discriminators (CF-trig) built of fast integrated
circuits ECL according to   B a l d i n   scheme [8]. They contain
also fast discriminators eliminating from the time analysis all pulses
not exceeding predetermined threshold. The pulses from CF-trig,
through appropriate delay lines, assuring proper sequence of start
and stop pulses, are sent to time-to- amplitude converter (TAC) and
to pile- up inspection circuits. The converters NE 4670 and Polon 1701
are used. To diminish the loading of converter the nondelayed stop
pulses, of duration fitted to the selected time range, are fed to the
converter gating input.

Energy selection channels are composed of Polon modules:
1101 amplifiers, 1201 single channel analysers, and 1402 coincidence
circuits. Every amplifier is followed by two SCA and the output
pulses are sent to two coincidence circuits receiving also the pulses
from fast $CC(2\mathcal{T} = 100$ ns) registering the coincidences of signals
"Pile-up Inspection" and "Valid Stop TAC". Two groups of coincidence
pulses obtained this way (corresponding to two pairs of windows)
are controlling, by means of "Memory Control" circuit, the process of
information storing in MCA, i.e. they open the gate of ADC converter
and then they select this sector of MCA memory (splitted into four
parts), in which particular coincidence signal is to be stored.

To stabilize the time spectrum "live" symmetrical integral
spectrum, composed mainly of prompt 511-511 events, is used. It
is stored in two memory sectors (analyser works in DOUBLE regime).
The error signal is obtained by comparison of the content of two
digital windows placed symmetrically on opposite slopes of the peak [9].
Correction voltage changes the baseline level of pulses entering
the ADC. Obtained long-term stability of time zero, estimated on the
basis of numerical analysis of many experimental spectra collected
during 6 days, was better than 4 ps.

Time calibration was performed using an Ortec 425A delay line, linearity of time scale was measured using random coincidence spectrum of pulses from two noncorrelated sources: scintillation counter and pulse generator. The result for TAC type 1701 is shown in Fig. 3. Nonlinearity in the initial part reaches 2,5 %, but in the range utilised in the measurements it does not exceed 1 % (the same as ADC nonlinearity).
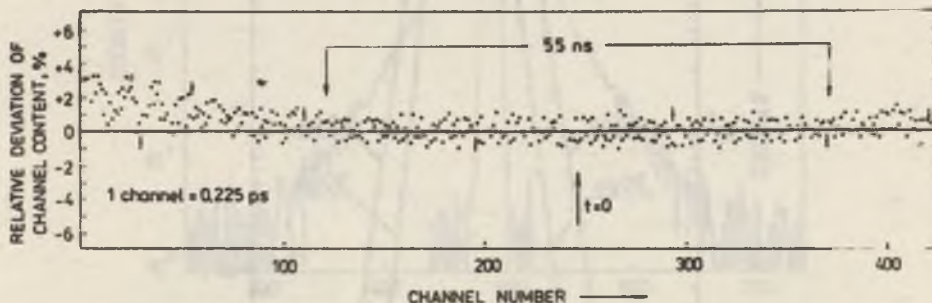

Fig. 3. Differential linearity of the lifetime spectrometer

Control measurements of time resolution were performed using ^{60}Co gamma rays. After selection of optimal PM voltage distributions and triggering conditions of CF-trig (the fraction $c/r = 0,1$ was used), we have obtained:

a) with 20 % windows on the Compton edges corresponding to ^{60}Co gamma rays, the FWHM of prompt curve is $2\tau_\rho = 170$ ps for 1,2 cm thick scintillators, and 210 ps for 2,5 cm thick ones,

b) in the conditions of positron lifetime measurements (30 % windows set as written in Fig. 4) the respective resolutions for one pair of windows were 200 and 270 ps, side slopes 30 and 42 ps. For second pair of windows ("left spectrum") the $2\tau_\rho$ values were higher by about 10 ps, because CF-trigs were optimalised for first pair. An example of positron lifetime spectrum as plotted directly from the analyser is shown in Fig. 5. The use of peak stabiliser deteriorates the resolution by 5 ps.

Decomposition of lifetime spectra is performed using a well known Positronfit program [10]. In most cases three exponential components are assumed (convoluted with instrumental resolution curve of gausian shape). The shortest component with fixed lifetime $\tau_0 = 123$ ps belongs to the decay of para-Ps states, an intermediate one 300–400 ps is
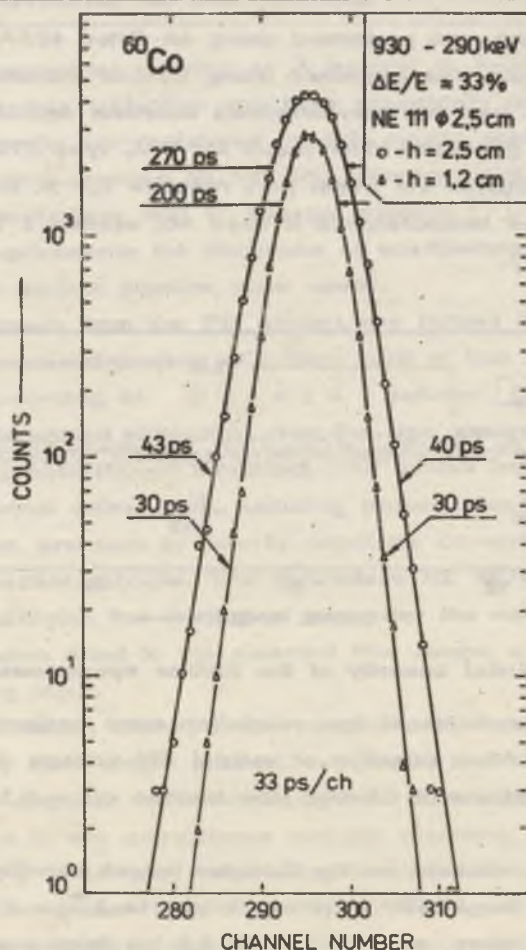
Fig. 4. Time resolution curve ("prompt curve") of the lifetime
spectrometer

ascribed to free annihilation in collisions, and the longest living one
- to the pick-off decay of ortho-Ps. In some of calculations the ratio
of shortest to longest component intensities I_0/I_2 was kept constant,
1/3, as it follows from the weights of para and ortho states.

Positron source, about 10 μCi of ^{22}Na in the form of aqueous
solution of NaCl, was evaporated on the surface of 1.2 μm thick
nickel foil covered by 50 $\overset{\circ}{R}$ gold layer. The foil was folded to form
a kind of envelope. Absorption of positrons in the source was
estimated experimentally by registering the statistically rich lifetime
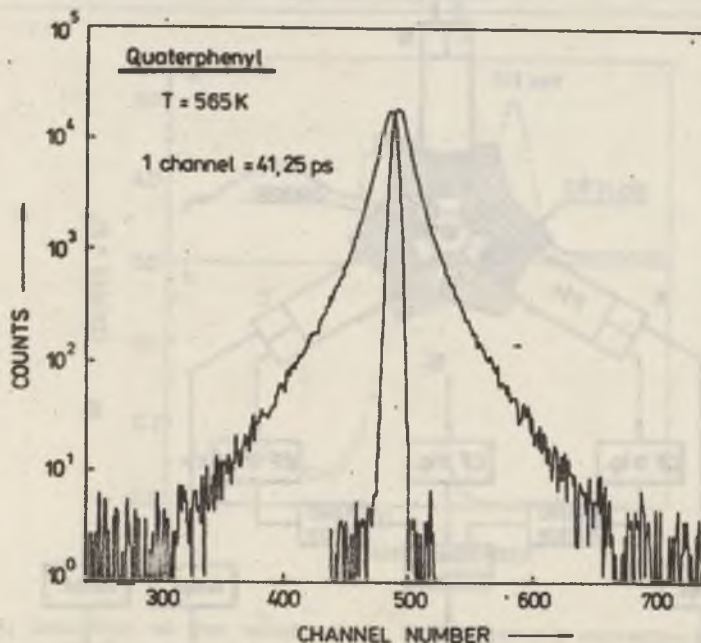spectrum of positrons in an organic sample, which contains one

Fig. 5. Example of double lifetime spectrum recorded in modified positron lifetime spectrometer

exponential component only. About 12 % of positrons are absorbed in the source, mainly with the lifetime 175 ps. During the numerical data processing the correction for source absorption was applied.

Measurements of three-quantum annihilation intensity

The measurements of three quantum annihilation intensity serve usually as a decisive test of positronium formation. An experimental arrangement to measure three-photon events consists of three NaI (Tl) 40 x 40 mm counters placed radially in a solid lead block serving as backscattering absorber and colimator, and of fast-slow triple coincidence circuit (Fig. 6). Counter axes are coplanar and form 120° angles. The sample with ^{22}Na source inside can be introduced through a vertical channel. Its holder enables precise displacement to fix the specimen exactly at the intersection of counter axes. All channels housing the counters are covered by Fe sheets. Triple coincidence measurements are performed with the electronic circuitry offering the time resolution of about 30 ns.

Energy calibration of spectrometer, necessary to place the energetic windows of SCA to select the gamma rays of about 340 keV,
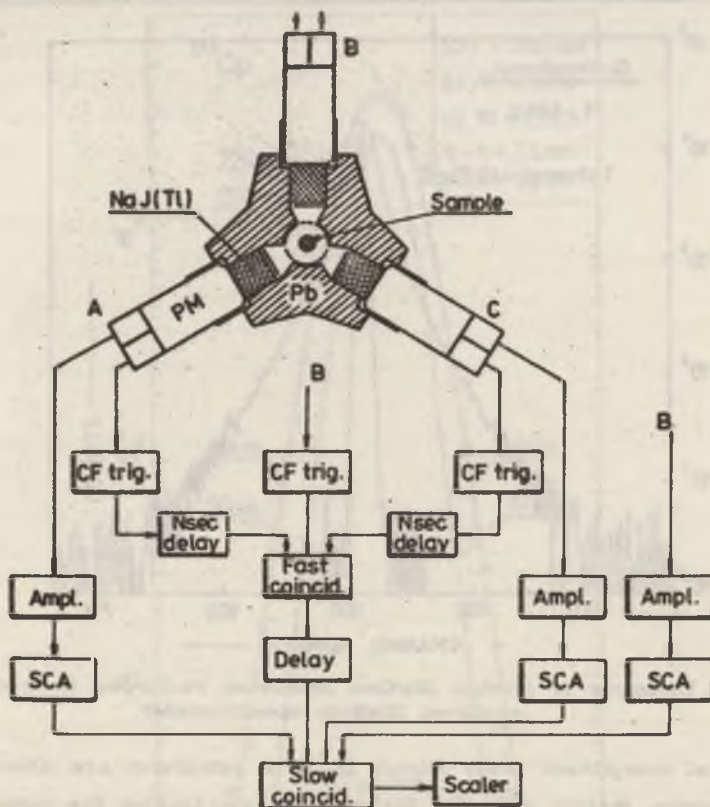
Fig. 6. Experimental arrangement for the measurements
of three-quantum annihilation intensity

is performed with standard radioactive sources and a multichannel
amplitude analyser. Window location on the annihilation gamma spectrum,
and the spectrum of triple coincidences are shown in Fig. 7. Random
coincidence rate is estimated by moving one of counters out of the
plane to an additional vertical channel.

, RESULTS AND DISCUSSION

It was shown earlier that at room temperature many solid
aromatic· hydrocarbons do not show the signs of positronium formation:
time spectrum consists of one exponential component only (Fig. 8.),
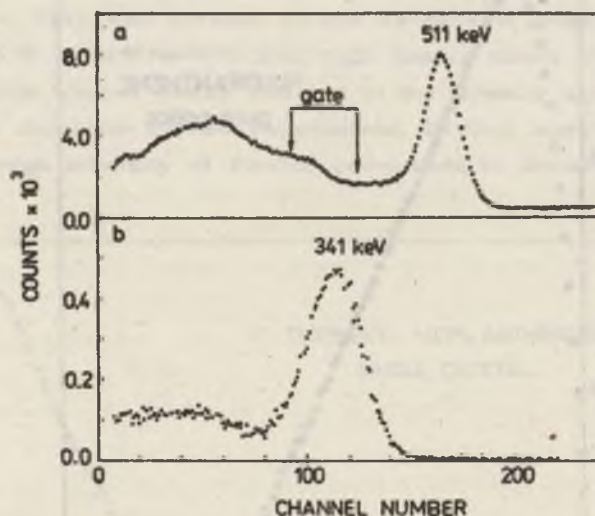in the momentum spectrum the narrow component is not discernible.

Fig. 7. Location of the windows in three gamma experiments   (a)
and energy spectrum of triple coincidence events when the coun-
ters are placed in 120° spacings (b)

To this group of organic solids belong e.g. anthracene, p-terphenyl,
pp-quaterphenyl, pirene, azulene, fluoranthene, benzophenone. The aim
of our investigation was to examine the influence of various factors
on positronium creation in this class of solids. Generally one can say
that disturbing the structure of idea! crystal makes formation of Ps
atoms possible. Two main factors acting effectively in Ps creation are
discussed below in detail: introduction of admixtures to the pure crystal,
and increase of   temperature.

In the case of the above mentioned pure compounds we have not
seen positronium in policrystalline samples produced from the   melt,
the long living component does not appear also in p-terphenyl samples
produced by resublimation on a glass backing, in the samples irradiated
with the gamma doses up to 20 Mrad. No long living component is
present in pressed powdered p-terphenyl, but s..ch a component was
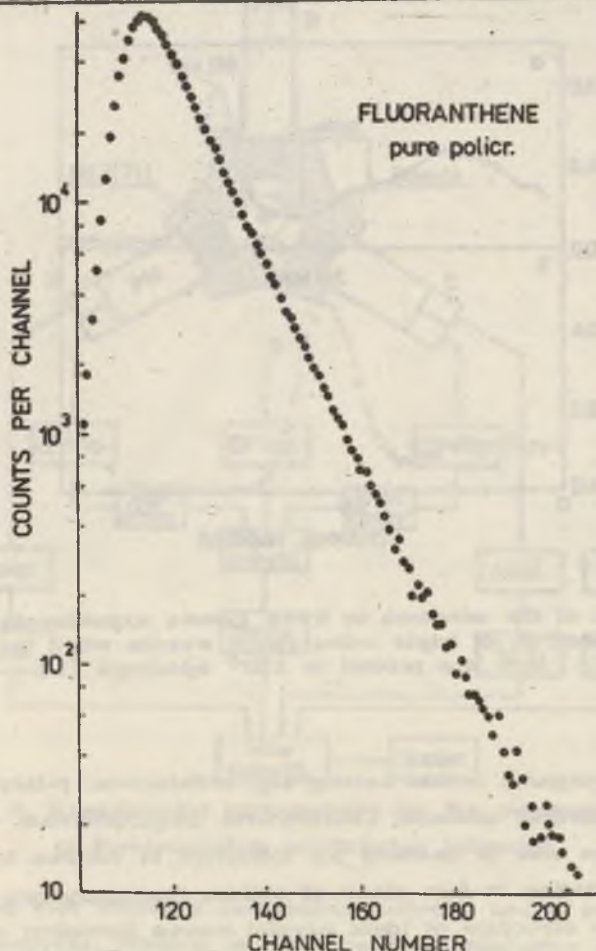seen in pp-quaterphenyl powder.

Fig. 8. Lifetime spectrum of positrons annihilating in pure solid
fluoranthene

Mixed crystals

General remarks

An effective method to produce long living positrons (1,0 - 1,7ns)
in the molecular solids which originally demonstrated one lifetime
component ($\sim$0,3 ns) only is to introduce foreign molecules crystallizing
together with the host medium. This effect was demonstrated by us
[11,12] on the example of p-terphenyl host. The long living component
can be ascribed to positronium-like states, as its growth with the
concentration of guest molecules is accompanied by similar growth of
the narrow component in the momentum spectrum of annihilating pairs.
There is a small but measurable increase of three quantum annihilation
yield observed too. All observed parameters: lifetimes and intensities

of the components are identical for policrystalline sample and for single crystal. This was verified on the example of p-terphenyl with the admixture 0,5 % of anthracene. The high quality mixed single crystal was grown from vapour phase[*] and cut in the primary cleavage plane to obtain flat discs for lifetime experiments. Lifetime spectrum for this sample with high intensity of Ps-like component is shown in Fig. 9.
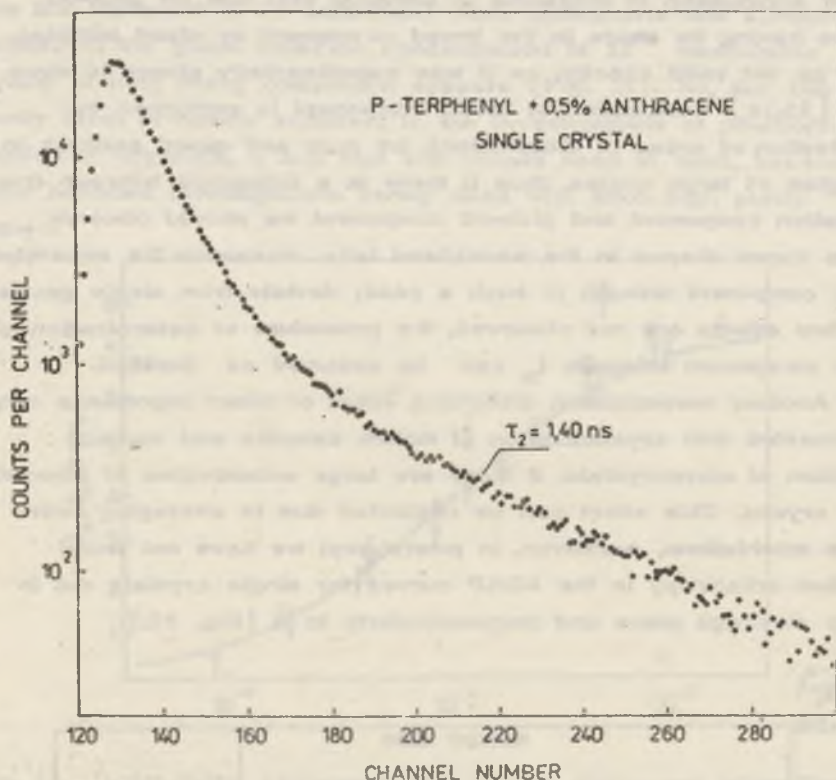

P - TERPHENYL + 0,5% ANTHRACENE
SINGLE CRYSTAL

$\tau_2 = 1,40$ ns

Fig. 9. Lifetime spectrum of positrons annihilating in a single crystal of p-terphenyl + 0,5 % anthracene. Long living component with τ = 1,40 ns is visible $(I_2 = 17,5 \%)$

We have not found the difference in annihilation parameters for poli-crystalline samples produced in various conditions: molten in the air and in inert atmosphere, cooled with various rates.

In the angular distribution experiments the so called narrow component is not especially narrow (3,5 - 5,0 mrad, comparing with about 10 mrad of the broad one), thus the separation and precise determination of its intensity I_N is not easy. We assumed that the momentum distribution of $e^+ - e^-$ pairs annihilating in pure samples (no positronium) can serve as a standard of the broad component. In this case a silent assumption is made: that the momentum distribution for free annihilation in collisions is identical with that for pick-off process having its share in the broad component in mixed samples. It may be not valid exactly, as it was experimentally shown in some cases [13,14]. Subtraction of broad component is performed by normalization of areas of distributions for pure and mixed samples in the region of large angles, thus if there is a difference between free annihilation component and pick-off component we should observe various curve shapes in the normalized tails, moreover the separated narrow component should, in such a case, deviate from single gaussian. If the two effects are not observed, the procedure of determination of narrow component intensity I_N can   be assumed as   justified.

Another normalization disturbing effect of minor importance may be connected with crystallization of molten samples and various orientation of microcrystals, if there are large anisotropies of momenta in the crystal. This effect can be neglected due to averaging over various orientations, moreover, in p-terphenyl we have not found momentum anisotropy in the ADAP curves for single crystals cut in primary cleavage plane and perpendicularly to it (Fig. 10.).
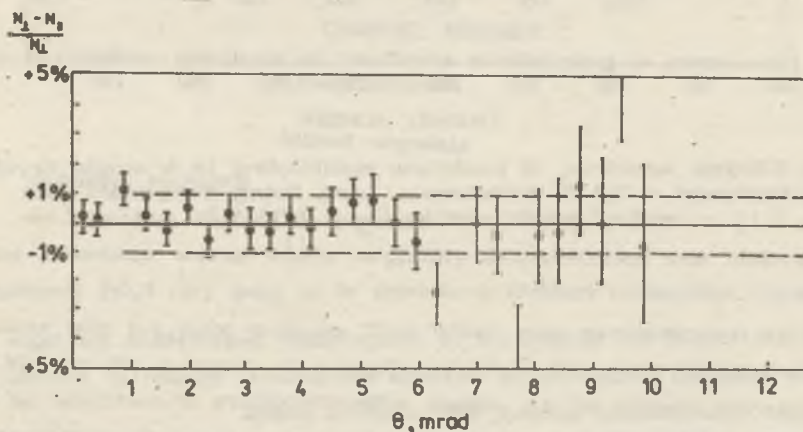
Fig. 10. Difference of momentum distributions for pure p-terphenyl single crystals cut in primary cleavage plane and perpendicularly to it

ι p-terphenyl host

The intensity of long living component, as well as the intensity of narrow component rise with the increase of guest molecule concentration approaching the saturation value which is determined mainly by the host material. Over 20 various aromatic species were introduced to the p-terphenyl lattice, the most sensitive admixtures (from the viewpoint of Ps formation) were anthracene and 2,3-benzo-fluorene. At the guest molecule concentration of 10^{-4} measurable intensity of long living component appears (Fig. 11). So, the 100 ppm impurity level is hardly sufficient in the investigations of positronium formation in organics, a fact that one should keep in mind, because earlier reported investigations rarely dealt with such high purity samples.
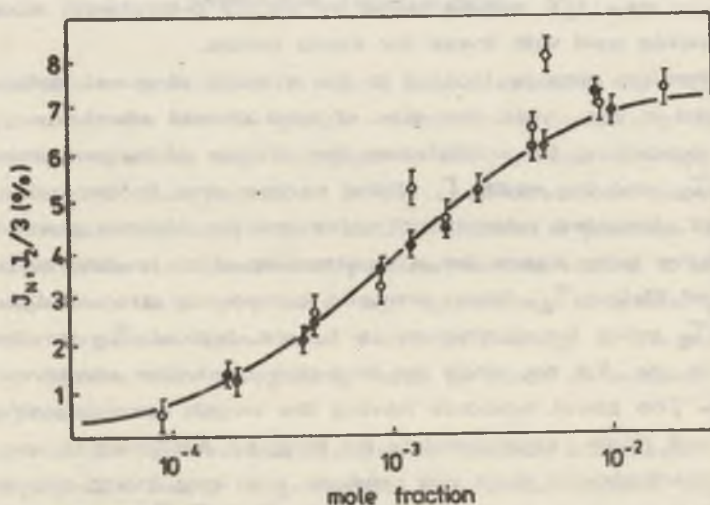

Fig. 11. Long living component and narrow component intensities vs. concentration of guest molecules. Full symbols: $I_2/3$, open symbols Admixture: circles — antharacene, diamonds — benzofluorene

To explain observed facts we proposed to assume that positronium atoms form in the free spaces in the vicinity of guest molecules when the linear dimensions of these molecules are smaller than those of host ones. Positron annihilation is a competition between disappearence in free collisions with the rate λ_f and capture in the voids with subsequent Ps formation by some of captured particles. Another possibility is that Ps atoms form inside the medium, but decay immediately unless

they diffuse out to the voids. The intensity I_2 of the ortho-positronium component is thus:

$$I_2 = I_{2max} \frac{x\nu}{\lambda_f + x\nu}$$

where x is the mole fraction of admixture, and ν – the Ps formation rate. In Fig. 10 the experimental data for anthracene and benzofluorene in p-terphenyl are presented. By chance, the value $\nu = (1,65 \pm 0,25) \cdot 10^{12}$ s^{-1} is the same for both guests, although generally one observes large spread of ν values over two orders of magnitude. The reciprocal of $x\nu$ represents the positronium formation time t_f. Its value at x=1 is a parameter equivalent to the formation time t_c in uniform media. This last was estimated for liquids on the basis of Ps quenching by electron scavengers as being of the order of 10^{-11} s or less. The $1/\nu$ values found by us for p-terphenyl mixed crystals coincide well with these for liquid media.

If positronium atom is located in the vicinity of guest molecule, i.e. is trapped in the void, the size of void should affect the parameters describing Ps annihilation: the lifetime of longest living component τ_2 and the width Γ of the narrow one. In the latice consisiting of elongated p-terphenyl molecules the shorter guest molecules leave more space for a positronium atom, leading to the lengthening of lifetime τ_2. When aromatic compounds are used as guests, the τ_2 value for naphtalene is 1,6 ns, typical τ_2 for three-ring compounds is $\sim$ 1,4 ns, while for four-ring ones one observes $\tau_2 \cong$ 1,1 ns. The guest molecule having the length corresponding to five condensed rings (approximately as long as p-terphenyl), e.g. 1,2,5,6-dibenzanthracene does not produce any long living component, although it crystallizes together with p-terphenyl [15]. Addition of one aromatic ring in transverse direction with respect to elongated axis of the molecule does not change τ_2 : the values of τ_2 for chrysene and benzo/des/chrysene are identical.

The size of positronium trap should also influence the width of the narrow component, according to the uncertainity relation. Observed Γ values, as for their order of magnitude, are an argument for Ps localization. Delocalized positronium was not observed yet in Van der Waals crystals, in hydrogen bonded ones (ice) or in ionic crystals delocalization manifests itself by very narrow p-Ps peaks. One should expect that the shorter lifetime τ_2 is, the broader should be the narrow component distribution Γ. This relation was positively verified by precise measurements of angular distributions

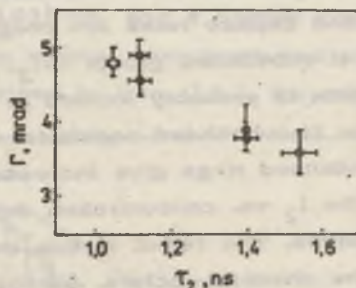(about 10^5 coincidences per point in the centre) for six mixed
crystals (Fig. 12).

Fig. 12. Orthopositronium lifetime and narrow component width for
p-terphenyl mixed crystals (full circles) and for anthracene   +
naphtalene (open circle)

Annihilation processes in liquid mixed systems were intensively
investigated for the last 10 years - addition of chemically active
compounds, containing e.g. halogens or NO_2 groups strongly
influenced positronium formation. In the case described above, in-
active hydrocarbons added to a medium unable to produce Ps atoms,
were responsible for creation of positronium-like states. It seems
that a major role is played here by geometric, structural factors,
free space available. This model works in analogy to the bubble
model for liquids, with preexisting voids in place of bubbles forced
by own pressure of Ps.

It would be an oversimplification to ascribe all effects observed
in mixed crystals solely to geometric, free-space factors. E.g.
admixture of tetracene does not produce the long living component,
although it has approximately the same length as benzofluorene
and is soluble in p-terphenyl. Large spread of capture rates ν needs
also an explanation.

The mixed crystals of p-terphenyl and naphtalene derivatives
were studied. Adding of naphtalene to p-terphenyl host produces very
small intensity of the long living component, but well-measurable
intensities are obtained for naphtalene derivatives with an extra group
substituted in position 2, or two groups in positions (2,3), (2,6),
(2,7). In the case of position 1 (α-derivatives) no long living
component is observed, as one should expect for non-miscible
compounds.

The relation between mole fraction and long living component intensity was investigated for naphtalene β -derivatives. Low I_2 intensities caused relatively large errors, but one can see from Fig. 13 that the intensities and capture rates are roughly independent on chemical character of substituted group: CH_3, NH_2, OH, SH, or even CH_3COOH. Positronium is probably located in the neighborhood of substituted group, because bi-substituted naphtalenes with the groups placed on both sides of condensed rings give increased capture rate, while 2,3-derivative follows the I_2 vs. concentration dependence appearing in simple 2-derivatives. The result of this experiment may suggest secondary role of the chemical factors, although there are also exceptions from the presented simple picture: admixture of β -naphtalenic acid give much smaller I_2 than other derivatives.
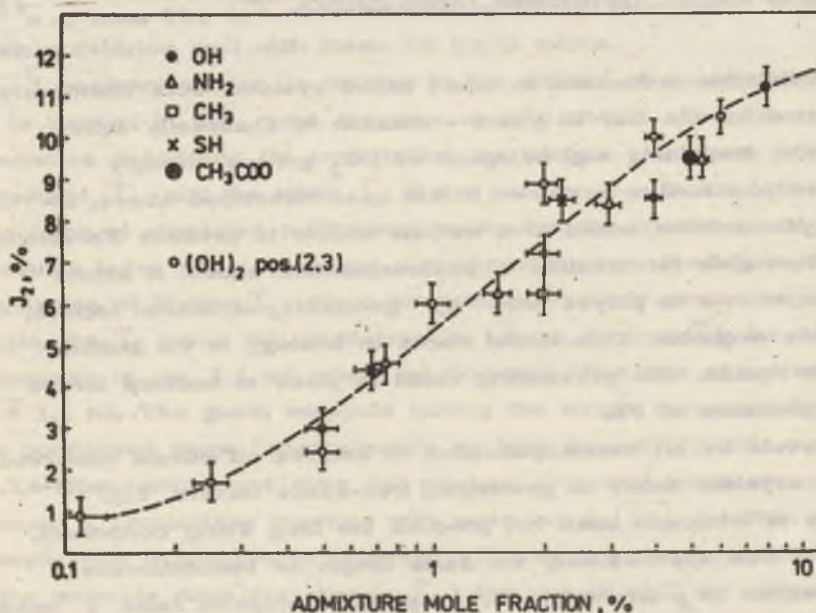
Fig. 13. Long living component intensity as a function of concentration of naphtalene β -derivatives in p-terphenyl

Other host media

Positronium formation in the presence of guest molecules is not a particular property of p-terphenyl. The same effect can be demonstrated in various other media. It seemed worthwhile to prove the existence of the discussed effect using as host the "standard" molecular crystal - anthracene. Anthracene is known as particularly resistant

against positronium formation by the increase of medium temperature
(see Sec. 3.2). Nevertheless, anthracene doping by 1 % of naphta-
lene gave well pronounced long living component with
τ = (1,05 $\pm$ 0,02) ns, and a narrow component with Γ = 4,8 mrad.
Separation of the narrow component was performed in the same
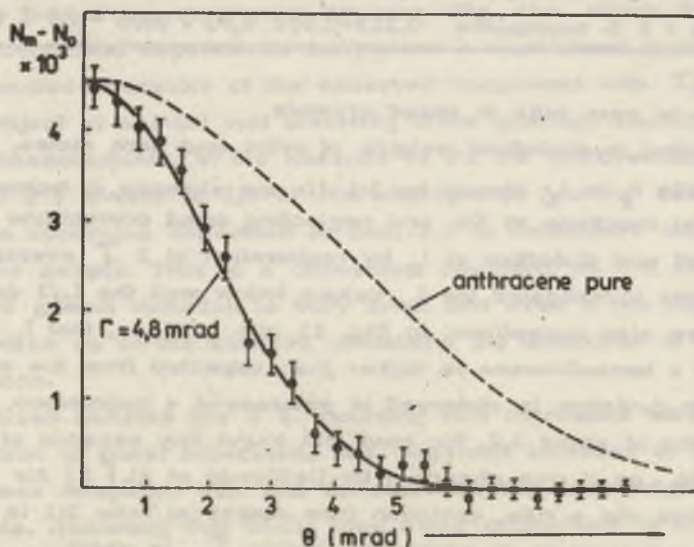manner as described in Sec. 3.1.1, the result is shown in Fig. 14.

Fig. 14. Narrow component in anthracene with 1 % admixture of naphtalene

Another investigated host medium was pp-quaterphenyl (chain
of four aromatic rings). The admixtures of one molar percent of
anthracene and p-terphenyl were introduced, giving easily observable
long living component in the positron lifetime spectrum. As one could
expect from earlier experiment with p-terphenyl host, the relation:
shorter guest molecule - longer lifetime is fulfilled too (Table 1).
Similarly, the same guest molecule produces longer living component,
when the host medium is composed of longer molecules (see anthra-
cene in p-terphenyl and in pp-quaterphenyl). The lifetime of Ps in
quaterphenyl doped with anthracene is longest of all observed yet
in mixed crystals. Due to the low intensity of narrow component it
is impossible to measure its width and check the $\Gamma - \tau_2$ relation
of this kind as shown in Fig. 12.

Finally the sample of fluoranthene doped with 2 % of naphtalene
shows the long living component too (Table 1).

Table 1. Positror. lifetimes and long living component intensity in
doped quaterphenyl and fluoranthene

Host + admixture	τ_1, ns	τ_2, ns	I_2, %
quaterphenyl + 1 % terphenyl	$0,312 \pm 0,002$	$1,48 \pm 0,02$	$9,8 \pm 0,2$
quaterphenyl + 1 % anthrac.	$0,310 \pm 0,002$	$1,69 \pm 0,04$	$4,0 \pm 0,1$
fluoranthene + 2 % naphtalene	$0,313 \pm 0,002$	$0,92 \pm 0,05$	$3,6 \pm 0,3$

Ortho to para ratio in mixed crystals

According to statistical weights of ortho and para states, the intensity ratio I_2 to I_N should be 3:1 (in the absence of conversion and chemical reactions of Ps, and neglecting small corrections for p-Ps pick-off and distortion of I_2 by registration of 3 γ events). In most cases investigated the I_N values follow well the $I_2/3$ data, but there are also exceptions: in Fig. 11 one can see, that I_N for p-terphenyl + benzofluorene is higher than expected from the statistical rule. Similar deviation is observed in anthracene + naphtalene, where the $I_2 : I_N$ ratio is about 2,2. We have not found any example of I_2 exceeding $3I_N$ as it was observed by DeBlonde et al. [5] for pure organic solids. As a rule, deviation from statistical ratio 3:1 is observed in these mixed crystals, in which the lifetime τ_2 is short.

The deviation of I_2/I_N ratio from the value 3 was observed by Mogensen et al [16] for many liquids, and ascribed by them to the secondary reactions of Ps with other reactants in the positron spur (Ps$^-$ formation, conversion on free radicals etc.). In most cases these authors observed $I_2/I_N < 3$, with one exception: liquid aromatic hydrocarbons. In our case of mixed crystals of aromatics the deviation, if it appears, follows the tendency of lowering I_2 to I_N ratio.

Essentially it would be possible to determine the p-Ps yield from the lifetime spectra, but low intensity of I_o component and its lifetime, much shorter than the instrumental resolution time, lead to large experimental errors. Misfitting the resolution time by 5 ps during the numerical data processing causes the change of I_o by 50 % or more. Resolution of about 220 ps, obtainable with 12 mm thick scintillators, could diminish the uncertainity of I_o, but not to the level of reliability, and at the expense of fourfold lengthening of measurement duration.

Pyrene host

Pyrene was chosen as another example of solid hydrocarbons, in which the positronium formation was studied. Pure samples do not show the presence of long living component in the positron lifetime spectrum registered at room temperature ($I_2 \leqslant 0.5$ %). With the admixtures (biphenyl, phenanthrene, naphtalene and its derivatives) added, the long living component appears. Fig. 15a shows the I_2 vs. guest concentration dependence for pyrene + naphtalene system. Positronium-like character of the observed component with $\tau_2 = 1.20$ ns was the object of special test involving three quantum annihilation intensity measurements. In the absence of Ps the relative intensity of 3 γ to 2 γ events is 1/372. The standard of "no Ps" counting rate in the apparatus described in Sec. 2.3 is determined using pure pirene sample. This is a convenient standard, as the absorption of 340 keV gamma radiation is very small and even if not negligible, it is the same as in the samples containing the admixture of other hydrocarbons.

In mixed samples the 3 γ counting rate increases with the concentration of guest molecules. The measured increase of 3 γ intensity was compared with that estimated on the basis of lifetime experiments. Assuming that whole long living component is of Ps-origin and that the para-to-ortho ratio is 1/3 we obtained very good consistency of so calculated $I_{3\gamma}$ with the experimental data (Fig. 15b).

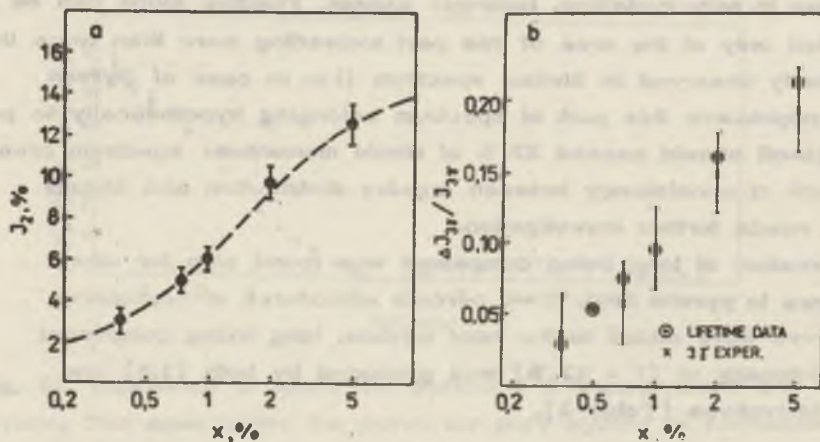
Fig. 15. a - long living component intensity vs. naphtalene concentration in pyrene, b - relative increase of 3 γ counting rate vs. naphtalene concentration. Double circles denote I_3/I_3 expected from the lifetime experiments

The next step in these investigations in pyrene was to determine
the intensity of narrow component in the momentum spectrum of
annihilating pairs. Angular distributions of two-gamma annihilation
radiation were measured with high statistical accuracy ($\sim 10^6$ coin-
cidences per spectrum) for pyrene + naphtalene (3 various concen-
trations), and pyrene |+ phenanthrene. It was found that the addition
of admixtures does not produce the typical narrow componen', but
causes rather general change of angular distributions. The shape
of ADAP curve changes continuously with the admixture concentration.

Let us assume initially, that the pick-off momentum distribution
is identical as in free annihilation (like in p-terphenyl or anthracene).
Subtraction of the pure pyrene ADAP curve from the mixture ADAP
curve, the first of which has the area   normalized to $(1 - \frac{1}{3}I_2)$ of
the other one, should give the momentum distribution of narrow
component. As it is seen in Fig. 16, such a "difference spectrum" is
not acceptable: for both admixtures – naphtalene, phenanthrene – in
the region of angles 3 mrad $\leqslant |\theta| \leqslant 7$ mrad one receives negative
intensities. More realistic assumption that the pick-off annihilation
spectrum differs significantly from that of free annihilation does not
improve the picture to much. Subtraction of "free annihilation" spectrum,
normalized to $(1 - \frac{4}{3}I_2)$ of the total area under the mixture spectrum
removes the negative intensities (Fig. 17), but the difference of
distributions has still the region of positive slope, physically
senseless in polycrystalline, isotropic sample. Positive slope can be
eliminated only at the area of this part exceeding more than twice the
I_2 intensity observed in lifetime spectrum (i.e. in case of pyrene
+ 2 % naphtalene this part of spectrum belonging hypothetically to p-Ps
and pick-off should exceed 22 % of whole momentum spectrum area).
This lack of consistency between angular distribution and lifetime
method needs further investigation.

Creation of long living component was found also for other
admixtures to pyrene host. Two percent admixtures of naphtalene
derivatives were added to the host medium; long living component
of the intensity of (7 – 12 %) was produced by both (1,5) and
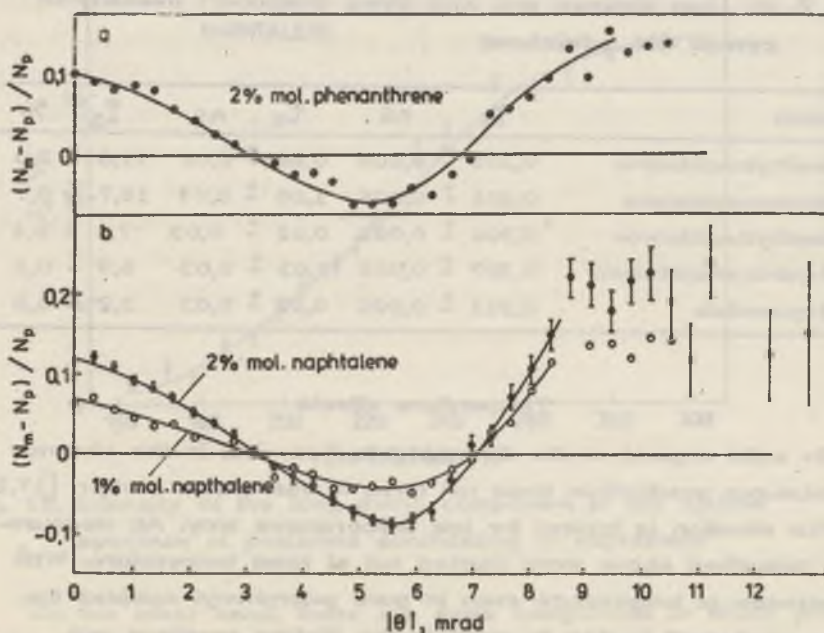(2,6) derivatives (Table 2).

Fig. 16. Difference of ADAP for pyrene mixed samples and pure pyrene. The area under the curve for pure sample is normalized to $(1 - I_2/3)$ of that for mixed ones
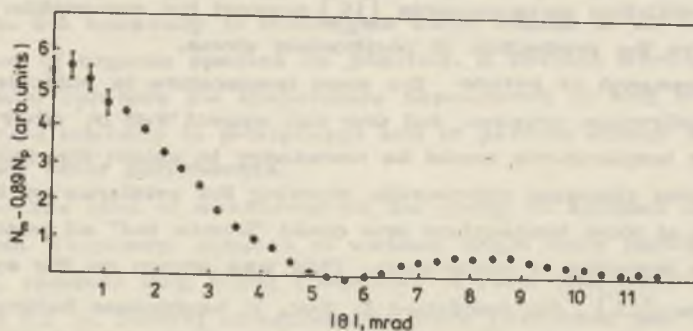

Fig. 17. Difference of ADAP for pyrene + 2 % naphtalene and pure pyrene. The area under the curve for pure pyrene is normalized to $(1 - 4I_2/3)$ of that for mixed one

Table 2. Positron lifetimes and long living component intensity in pyrene with admixtures

Admixture	τ_1 , ns .	τ_2 , ns	I_2 , %
1,5-dimethylnaphtalene	0,305 ± 0,006	0,88 ± 0,04	11,8 ± 2,0
1,5-diaminonaphtalene	0,308 ± 0,005	1,00 ± 0,04	10,7 ± 0,7
2,6-dimethylnaphtalene	0,306 ± 0,003	0,68 ± 0,03	7,0 ± 0,4
2,7-dihydroxynaphtalene	0,307 ± 0,005	1,03 ± 0,03	6,9 ± 0,5
2-naphtylacetate	0,313 ± 0,005	0,93 ± 0,03	3,2 ± 0,5

Temperature effects

In solid organic media discussed in Sec. 3.1, in the absence of admixtures positronium does not form. It was shown earlier [17,18] that this situation is typical for low temperatures only. All measurements described above were carried out at room temperature. With the increase of temperature even in pure p-terphenyl samples the narrow component begins to grow, in the lifetime spectrum one observes appearence and rise of intensity of long living component. The intensity vs. temperature relation is of sigmoidal type: initial rise has an exponential character, at higher temperatures I_N, I_2 approach to the saturation value $I_2(sat)$, the same as in case of mixed crystals. This effect was observed also in pyrene. Three quantum annihilation measurements [19] support the assumption that we have here the production of positronium atoms.

For p-terphenyl or pyrene   the room temperature is sufficient to eliminate positronium creation, but one can expect that in other cases lower temperatures would be necessary to obtain the same result. In some chemical compounds, showing the existence of Ps in solid phase at room temperature one could "freeze out" all positronium by adequate lowering of temperature. This was shown on the example of naphtalene [22] . As mentioned in Sec. 1, naphtalene belongs to these solids, which at room temperature demonstrate well pronounced long living component. Cooling the sample to 160 K reduces this component to the level of 1 % (Fig. 18). Preliminary results for phenanthrene and chrysene indicate the same character of temperature dependence of long living component.
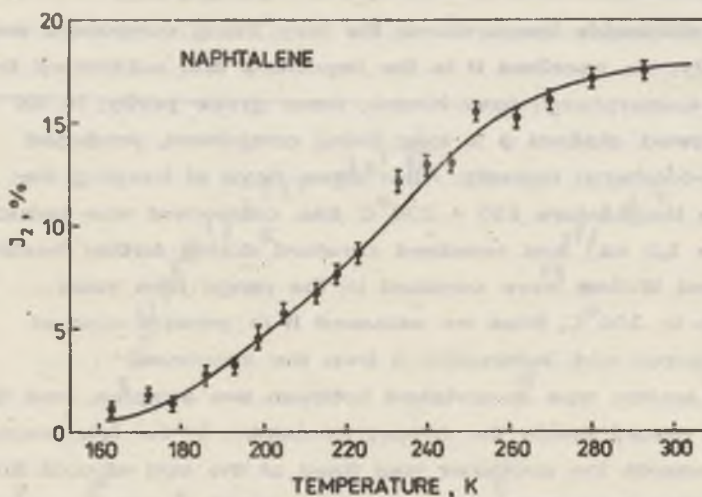
Fig. 18. Intensity of the long living component in the lifetime
spectrum of positrons annihilating in naphtalene

On the other hand, there are some compounds in which positronium
does not form in solid state in whole range of temperatures, up to the
melting point. To this class of organic solids belongs anthracene
[20,21] , and azulene [22] - the latter compound is the isomer of
naphtalene. There were also found the solids in which the positro-
nium cannot be "frozen out" - hexane, some plastic crystals [23] .

The complexity of temperature effects in positronium creation
leads to the necessity to investigate these effects in as large
spectrum of organic species as possible. It seemed worthwhile to
remeasure carefully the temperature dependence of long living
component intensity in p-terphenyl and to perform similar measure-
ments for other polyphenyls.

In this kind of measurements the purity of samples is particularly
important. Terphenyl samples of various origin were purified by zone
melting, residual long living component at room temperature did not
exceed 0,2 %. Control measurements were performed with single
crystals. The results were identical as with polycrystalline samples,
thus all further measurements with other compounds were carried out
with polycrystalline pellets formed by melting the material in disc
shaped formers.

Biphenyl from J.T. Baker, ULTREX grade, whose purity was
atested as better than 99,99 % was used without further treatment.

In the lowest obtainable temperatures the long living component was of 1 % intensity; we ascribed it to the impurities and subtracted from the spectrum. Quaterphenyl from Kodak, laser grade purity, in its initial form showed distinct 3 % long living component, produced probably by p-terphenyl impurity. After three days of keeping the material in the temperature 220 - 230°C this component was reduced to 1 % (τ_2 = 1.5 ns) and remained constant during further heating. Its intensity and lifetime were constant in the range from room temperature up to 200°C, thus we assumed it is present also at higher temperatures and subtracted it from the spectrum.

Positron source was sandwiched between two samples, and the sandwich was placed inside the copper container. In the low temperature measurements the container was fixed at the end of cold finger of a cryostat. The temperature was controlled with $\pm$ 0.5 K accuracy, the thermocouple sunk into the sample served to measure the temperature close to the annihilation site. The temperatures over 270 K were obtained by heating the container with DC current, stability of temperature was better than 1 K.

In the case of biphenyl the lifetime spectra were decomposed into 3 components without fixing the relative intensities. The only fixed parameter was τ_0 lifetime, equal 124 ps. The intensities I_0, although determined with very poor accuracy located around $I_2/3$ value. In other measurements the I_0/I_2 ratio was fixed to be 1:3 to reduce the number of fitting parameters. Even if this ratio deviates slightly from above given value, this fact has no particular importance for determination the I_2 and τ_2 values.

The result of measurement is shown in Fig. 19. In all three solid polyphenyls the long living component appears in certain range below the melting point. The experience gained during the investigation of mixed crystals suggests that we have here another effect of positronium trapping, this time on thermally produced defects. The p-Ps component in the momentum spectrum is broad, indicating strong localization of positronium atoms. The effect is reversible, the runs with rising temperature and with the temperature going down gave the same result within the limits of error. Most known equilibrium defects are vacancies, thus it seemed natural to assume that we observe positronium formation in vacancies. Such an interpretation proved valid in the case of plastic crystals [23] . The Arrhenius
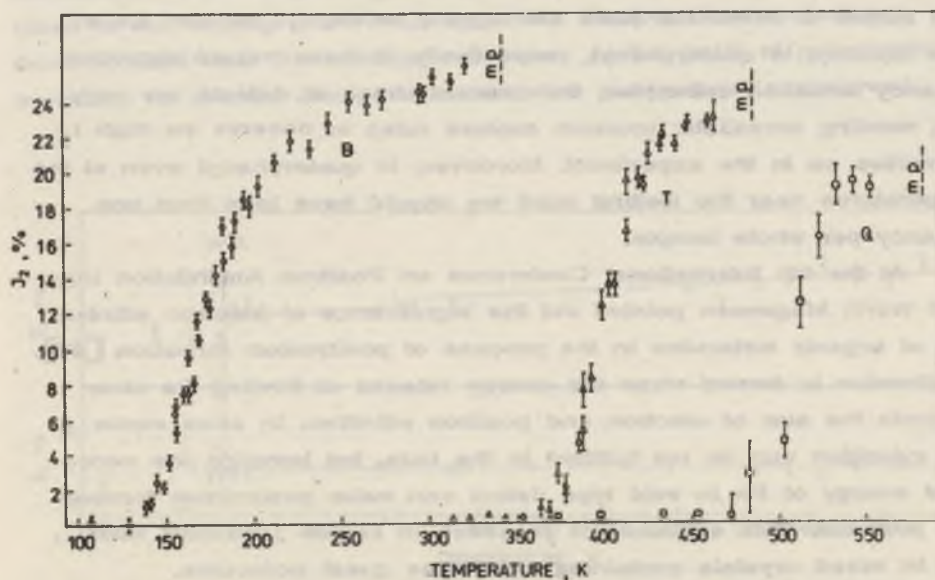
Fig. 19. Temperature dependence of long living component in polyphe-
nyls. B - biphenyl, T - p-terphenyl, Q - pp-quaterphenyl. I_2 saturation
values are not constant, but rise slowly with temperature (see biphenyl)

plot, e.e. ln $\left[I_2 / \left(I_2(sat) - I_2\right)\right]$ as a function of $1/T$ should
represent straight line with the slope proportional to the formation
enthalpy of defects. Unfortunately, thermal production of positronium
cannot be ascribed to vacancies. The formation enthalpy found for
naphtalene is $(0,17 \pm 0,03)$ eV, while in the case of vacancies it
should be 0,72 eV. The lifetimes observed in our experiment are
short, much shorter than expected for the voids left by large organic
molecules. Vacancies should provide the lifetimes of 2,5 ns and more,
while the observed values do not exceed 1 ns. Moreover, with the
increase of molecule dimensions (and of vacancy size) we should
expect that the lifetimes of trapped Ps rise too. Experimentally,
a reversed effect is observed: among polyphenyls the longest lifetime
appears in biphenyl, varying with temperature from 0,95 ns to 1,2 ns.
In p-terphenyl and quaterphenyl the lifetimes are initially equal about

0,65 ns (twice of free annihilation only!), and rise with the tempera-
ture relatively fast to 1,1 ns in terphenyl and 1,0 ns in quaterphenyl.
The slopes of Arrhenius plots are high: 0,19 eV, 1,1 eV and 2,4 eV
from biphenyl to quaterphenyl, respectively. If these values represent
vacancy formation enthalpies, the concentrations of defects are very
low, needing unrealistic positron capture rates to observe so high I_2
intensities as in the experiment. Moreover, in quaterphenyl even at the
temperatures near the melting point we should have less than one
vacancy per whole sample.

At the 6th International Conference on Positron Annihilation in
Fort Worth Mogensen pointed out the significance of electron affini-
ties of organic molecules in the process of positronium formation [24].
Positronium is formed when the energy release at binding Ps atom
exceeds the sum of electron and positron affinities. In some media
this condition can be not fulfilled in the bulk, but lowering the zero
point energy of Ps in void type defect can make positronium forma-
tion possible. This explains Ps presence in liquids ("bubble" model),
and in mixed crystals containing small size guest molecules.

The lower electron affinity (EA) is, the easier should be posi-
tronium formation. In a series of polynuclear aromatic hydrocarbons
the EA of molecules with the rings arranged linearly is usually higher
than of these forming kinked chains. This could explain the fact that
in phenanthrene and crysene Ps forms easily and is observed already
at room temperature, while in anthracene, with EA = 0,57 eV [25],
there is no Ps up to the melting point. No positronium in azulene,
which electron affinity is even higher than that of anthracene. One
can expect, that in the solid media composed of small molecules with
low, negative, electron affinities positronium is formed in the bulk and
at arbitrary temperature.

Polyphenyls and some polynuclear hydrocarbons seem belong to
that class of organic solids in which free volume type defects are
needed to reduce Ps zero-point energy and to bind the e^+e^- pair.
Thus, two questions arise: what kind of thermally produced free volume
is responsible for positronium formation in these solids, and what is
the meaning of activation energy determined from Arrhenius plots.

It is interesting that in the case of mixed crystals temperature
effects are significantly reduced. One observes slow rise of τ_2 with
the temperature increase, and small variations of I_2 intensity. This is
seen in Fig. 20, showing the result of measurements (in selected

temperature ranges) for single crystal of p-terphenyl + 0,5 % of anthracene. Constancy of τ_2 value indicates that up to temperatures close to the melting point the only active Ps formation centers are those located near the strange molecules. At the point of polymorphic transition no drastic change of annihilation parameters is observed.
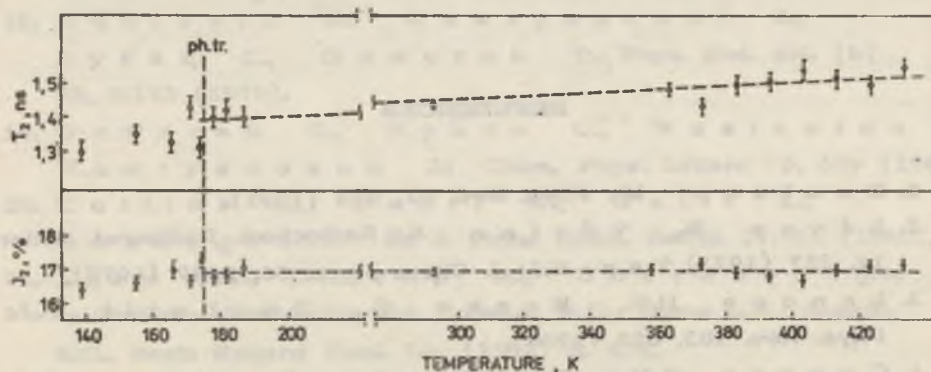

Fig. 20. Temperature dependence of long living component in mixed single crystal of p-terphenyl + 0,5 % of anthracene. Vertical broken line is placed at the temperature of phase transition in p-terphenyl

It is seen that the mechanism of positronium thermal production is still far from clarity. Further investigations are needed to expand the experimental basis for discussion.

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STRESZCZENIE

W pracy opisano badania nad tworzeniem się pozytu w wybranych węglowodorach aromatycznych. W poszukiwaniach czynników wpływających na tworzenie się stanów pozyto-podobnych zwrócono uwagę na dwa zjawiska: lokalizację pozytu w sąsiedztwie obcych molekuł, oraz termiczne wytwarzanie pozytu. Ten ostatni efekt dyskutowany jest z punktu widzenia modelu pułapkowego oraz możliwego wpływu powinowactwa elektronowego.

РЕЗЮМЕ

В работе представлены результаты исследований процессов образования позитрония в некоторых ароматических углеводородах. В поисках факторов влияющих на образование позитрониеподобных состояний обращено внимание на два эффекта: локализацию позитрония в соседстве чужих молекул и термическое образование позитрония. Второй эффект обсуждается с точки зрения модели ловушек и влияния электронного сродства.