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Effective Electron Density for Free-Positron Annihilation in Low-Z Compounds.

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Summary. — Time spectra of positrons annihilating in various low-Z compounds, mostly liquids at room temperature, were investigated. They can be consistently resolved into three components which can be ascribed to the ortho- and para-positronium decay and to the annihilation of free positrons. The lifetime of this last component is interpreted in terms of Dirac's formula and it is shown that each atom contributes to the decay rate with an amount typical of the atom itself, *i.e.* independent of the structural properties of the molecule and of the material. For H, Li, B, C, O, Cl the number of effective electrons per atom is obtained.

1. – Introduction.

The picture which was accepted up to a few years ago on positron annihilation in those substances where positronium formation is allowed is very simple. Positrons when slowed down may form positronium within a range of kinetic energies of the order of $\frac{1}{2}$ Ryd, the so-called Ore gap. Positronium formation occurs in para- and ortho-states, presumably in the ratio of the statistical weights 1 to 3. The positron bound in parapositronium annihilates with its electron with a lifetime of $1.25 \cdot 10^{-10}$ s. The positron bound in orthopositronium annihilates prevailingly (at least in diamagnetic substances) with an electron of the surrounding molecules, whose spin state relative to it is a singlet (« pick-off » annihilation); this decay which occurs with fractional intensities of 10 to 30 %, is characterized by lifetimes ranging from 2 to 4 ns. The fraction of positrons which have missed the Ore gap annihilates as « free » with lattice electrons with a lifetime of a few 10^{-10} s.

From these considerations, it follows that the time annihilation spectrum must contain three components; the longer-lived one, attributed to the pick-off annihilation, has been always observed without difficulty, while the other two have appeared unresolved.

Recent improvements in fast-timing techniques have made available further resolution in the time spectra. In particular the annihilation spectrum for some molecular substances was resolved into three components ([1,2]). However, the analysis of these components has shown that the positron behavior does not agree with the simple picture given above. A discussion of this situation was given by BRANDT ([3]) and by BRANDT and SPIRN ([4]).

Our investigation started with the aim of analysing the structure of the annihilation time spectrum in several low-Z compounds. We have found that about one half of all the investigated substances (30 compounds) display a time spectrum which can be consistently resolved in three components and then cannot be interpreted in the « simple picture »; these materials, which will be referred to as type B substances, are mostly solids at room temperature. The other investigated materials display a time spectrum which is in agreement with the behaviour expected on the basis of the « simple picture »; they are mostly liquids at room temperature and will be referred to as type A substances. The present paper is devoted to the A type substances, with particular attention to the fraction of the positrons which annihilate as free.

2. – The experiment.

The measurements of the time annihilation spectra were performed in a conventional way. The positron source obtained from a carrier-free solution of ^{22}NaCl, was sealed between two Moplefan (polypropylene) foils (1.0 mg/cm^2). For the analysis of liquid samples the source sandwich was held at the center of a glass tank by means of Teflon rings; to complete the assembly a lid was sealed on. The fraction of positrons annihilating in Moplefan foils was estimated as described by BERTOLACCINI *et al.* ([5]). This fraction, in our case, does not exceed 4% so that the effect of this correction on the conclusions of the experiment is negligible.

([1]) I. SPIRN, W. BRANDT, G. PRESENT and A. SCHWARZSCHILD: *Bull. Am. Phys. Soc.*, **9**, 394 (1964).

([2]) A. W. SUNYAR: *Bull. Am. Phys. Soc.*, **9**, 394 (1964).

([3]) W. BRANDT: *Contribution to the Proceedings of Wayne Conference on Positron Annihilations, Detroit,* 1965.

([4]) W. BRANDT and I. SPIRN: *Phys. Rev.*, **142**, 231 (1966).

([5]) M. BERTOLACCINI, C. BUSSOLATI and L. ZAPPA: *Phys. Rev.*, **139**, A 696 (1965).

The γ-rays were detected by means of two counters consisting of Naton 136 plastic scintillators, $1\frac{1}{2}$ inch in diameter, 1 inch thick, optically coupled to XP 1020 photomultiplier tubes; 180° detector geometry was used with an off-center source displacement making detection of both the simultaneous 511 keV quanta unlikely. The time distribution spectrum of the annihilation radiation with respect to the 1.28 γ-rays was analysed by means of a time-to-height converter: pulse pile-up rejection was provided on both channels. The prompt resolution curve fits a Gaussian curve with full width at half-height $3.5\cdot10^{-10}$ s; this curve was obtained with a ^{60}Co source using the same energy windows as for ^{22}Na. A stability of about $3\cdot10^{-11}$ s/day was obtained.

The analysis of the spectral shape was performed with a maximum-likelihood method which was described in a previous paper (⁶) and will not be reported here.

3. – Results and discussion.

A representative time spectrum of positrons annihilating in water, which is a type A substance, is shown in Fig. 1. Two components, τ_1 and τ_2, are clearly identified; their intensities when summed do not attain 100%. However if the τ_2 component is attributed to the orthopositronium decay, the spectrum must contain the parapositronium component, whose shape is strongly affected by the instrumental resolution. Under the assumption that the para- and ortho-states are formed in the ratio of the statistical weights the intensity of the parapositronium component must be equal to $\frac{1}{3}I_2$: in all our spectra this is just the fraction lacking to attain 100%.

Table I collects the results for all the investigated type A substances; we wish to point out that if we take into account the sources of systematic errors the accuracy of the τ and I values is about 5%.

As far as regards the results pertaining to the long-lived components a comparison can be made for those samples (entries No. 4, 5, 7, 9, 10, 13) previously examined by LEE and CELITANS (⁷,⁸) who investigated the effect of dissolved gases on positronium quenching in organic liquids. The comparison is quite satisfactory if one refers to the mean life measured in air-saturated samples and not to that in degassed ones. The effect of dissolved oxygen in quenching positronium is interpreted by LEE and CELITANS as a strong triplet-to-singlet conversion, so that our τ_2 values are not representative of the pick-off decay

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(⁶) M. BERTOLACCINI, A. BISI and L. ZAPPA: *Nuovo Cimento*, **46** B, 237 (1966).

(⁷) J. LEE and G. J. CELITANS: *Journ. Chem. Phys.*, **42**, 437 (1965).

(⁸) J. LEE and G. J. CELITANS: *Journ. Chem. Phys.*, **44**, 2506 (1966).

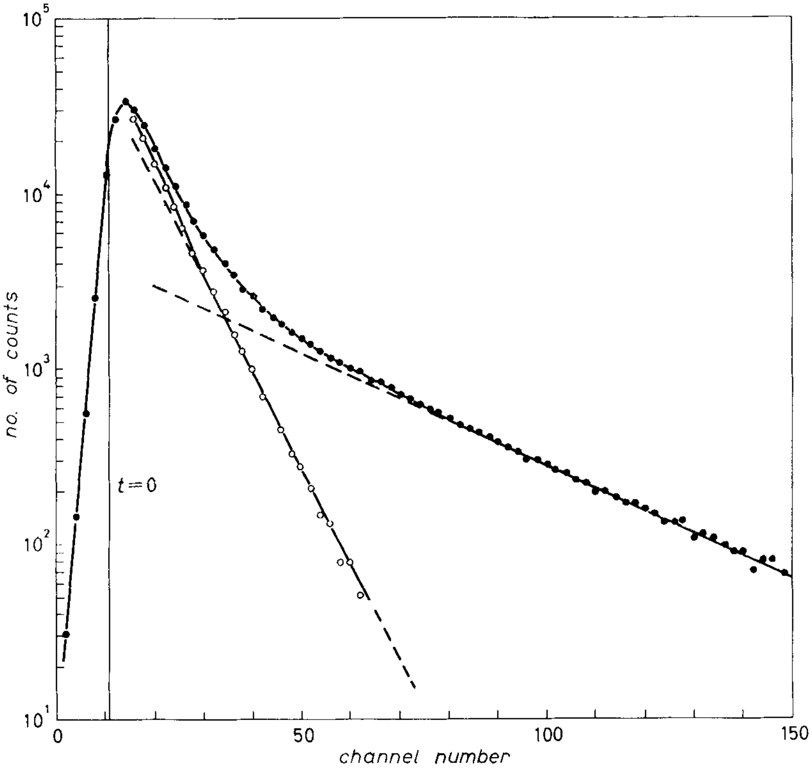

Fig. 1. – Time spectrum of positrons annihilating in water at room temperature. For convenience only one half of the representative points are plotted. • $I_2 = 21.5\%$, $\tau_2 = 1.87\cdot10^{-9}$ s; ○ $I_1 = 70\%$, $\tau_1 = 4.1\cdot10^{-10}$ s; 1 channel $= 0.54\cdot10^{-10}$ s.

only. However, the very small concentration of air under normal conditions is not able to affect the decay of positrons as free.

We wish now to turn our attention to the τ_1 component arising, according to the « simple picture », from free-positrons annihilation. If one neglects the contribution of triplet-state annihilation the decay rate of slow positrons in matter is given by the equation (⁹)

$$\lambda_1 = C_s \psi_s^2$$

where C_s is the fundamental interaction rate in the singlet state and ψ_s^2 is the density at the average position of the positron of the electrons with anti-parallel spin direction. As is well known, if one neglects the effect of Coulomb

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(⁹) P. A. M. Dirac: *Proc. Cambridge Phil. Soc.*, **26**, 361 (1930).

TABLE I. – *Positron lifetimes in low-Z compounds.* τ_1, τ_2, I_1 and I_2 indicate the mean lifetimes of short-lived positrons and of long-lived positrons, and their intensities respectively; the last column contains the τ_1 values calculated according to eq. (2).

Entry No.	Sample	Formula	I_2 %	τ_2 10^{-9} s	I_1 %	τ_1 10^{-10} s	Predicted τ_1 10^{-10} s
1	Water	H_2O	21,5	1.87	70	4.13	3.84
2	Maleic acid	HOOCCH:CHCOOH	—	—	101	3.13	3.10
3	Pyrene	$C_{16}H_{10}$	—	—	101	3.26	3.37
4	Methyl alcohol	CH_3OH	20.5	2.75	72	4.07	4.43
5	Ethyl alcohol	CH_3CH_2OH	20.6	2.86	73	4.09	4.31
6	*n*-amyl alcohol	$CH_3(CH_2)_3CH_2OH$	21.4	2.82	69	4.01	4.03
7	*n*-octyl alcohol	$CH_3(CH_2)_6CH_2OH$	21.9	2.87	68	3.94	3.95
8	*n*-nonyl alcohol	$CH_3(CH_2)_7CH_2OH$	24.8	3.20	62	3.92	3.92
9	Benzene	C_6H_6	36.5	2.54	49	4.22	4.42
10	Toluene	$C_6H_5CH_3$	40.1	2.55	45	4.17	4.33
11	Xylene	$C_6H_4(CH_3)_2$	40.5	2.56	44	4.44	4.22
12	Mesitylene	$(CH_3)_3C_6H_3$	37.9	2.64	45	4.32	4.16
13	Heptane	$CH_3(CH_2)_5CH_3$	35.5	2.39	51	4.40	4.43
14	*d*-tartaric acid	$HOOC(CHOH)_2COOH$	—	—	95	3.11	3.08
15	Lithium carbonate (*)	Li_2CO_3	31.4	0.47	55	2.54	—
16	Boron (*)	B	14.0	0.48	80	2.04	—
17	Boric acid	H_3BO_3	43.3	0.83	40	3.34	—
18	Chloroform	$CHCl_3$	3.0	2.20	95	4.39	—

(*) The assignement to the *A* class is uncertain.

forces, $\psi_s^2 = n_e/4$ where n_e is the number of electrons per cubic centimeter; if instead the Coulomb forces are taken into account n_e is the « effective » number of electrons, whose explicit evaluation is very hard. Therefore we attempt an empirical approach by writing

$$n_e = \frac{\varrho}{A} N \sum_i \nu_i z_i \,, \tag{1}$$

where N is Avogadro's number, ϱ is the mass density and A is the molecular weight.

In the sum the index i identifies the element contributing with ν_i atoms to the molecule; z_i is the number of electrons per atom effective for free-positron annihilation. Clearly eq. (1) contains the assumption that each atom contributes to the decay rate with an amount typical of the atom itself, *i.e.* independent of the structural properties of the molecule and of the material. Numerically we have

$$\lambda_1 = 4.50 \cdot 10^9 \frac{\varrho}{A} \sum_i \nu_i z_i \ \text{s}^{-1}. \tag{2}$$

We wish to point out that ϱ/A values in the investigated substances are different by as much as a factor of about 10. In order to test our assumption we first consider those compounds containing only H, C and O; from the measured values of the mean life τ_1 of the first three entries of Table I, it is straightforward to deduce the number of effective electrons per atom of H, C and O.

Now if the mean life of the remaining compounds is evaluated with these values of z_i and with the aid of eq. (2), it results that the calculated values agree within 5 % with the measured ones. A better agreement can be obtained by using all the experimental values of τ_1 (entries 1-14) in a least-squares adjustement. The obtained values of z_i are collected in Table II; they were used for the calculation of the mean lives τ_1 contained in the last column of Table I. No further comments are necessary about the procedure for obtaining the z_i values of Li, B and Cl which are contained in the last compounds listed in Table I. These values are also reported in Table II; however it is clear that they have not the same experimental background as the preceding ones. For all the light elements that are investigated the number of effective electrons per atom is of the same order of magnitude as the atomic number and increases as this increases; this fact appears reasonable in view of the essential role played by the valence electrons in annihilating with positrons.

TABLE II. – *Number Z_i of electrons per atom effective for free-positron annihilation.*

Atom	z_i
H	2.37 ± 0.14
Li	4.3
B	4.8
C	5.07 ± 0.24
O	5.64 ± 0.34
Cl	11.0

Our empirical approach appears then to be successfully tested, however the extension of its implications should be taken with some caution owing to the fact that implicitly we assumed that the positrons move freely through the medium. This may be a good picture for those compounds which display a covalent bond as those investigated here, but may not apply to other materials characterized by different chemical bond.

RIASSUNTO

Si studiano gli spettri temporali delle annichilazioni di positoni in composti diversi di basso numero atomico. Tali spettri vengono decomposti in tre componenti attribuite al decadimento dell'orto e parapositronio ed al decadimento di positoni liberi. La vita media di quest'ultimo decadimento è interpretata secondo la formula di Dirac: risulta che ciascun atomo porta alla costante di decadimento un contributo tipico dell'atomo stesso, indipendente cioè dalle proprietà strutturali della molecola e del composto. Il numero di elettroni per atomo, efficaci al fine della annichilazione, è ricavato per i seguenti elementi: H, Li, B, C, O, Cl.

Эффективная электронная плотность для аннигиляции свободного позитрона в соединениях с малым Z.

Резюме (*). — Исследовались временные спектры аннигиляции позитронов в различных соединениях с малым Z, которые, в основном, представлют жидкости при комнатных температурах. Спектры могут быть последовательно разложены на три компоненты, которые можно приписать к распадам орто- и пара-позитрония и к аннигиляции свободного позитрона. Рассматривается время жизни этой последней компоненты в терминах формулы Дирака, и показывается, что каждый атом дает вклад в интенсивность распада пропорциональных числу данных атомов, т.е. независимо от структурных свойств молекулы и материала. Определяется число эффективных электронов на один атом для H, Li, B, C, O, Cl.

(*) *Переведено редакцией.*