

# FORMATION AND QUENCHING OF ORTHO-POSITRONIUM IN MOLECULAR MATERIALS

BY R. G. LAGU, V. G. KULKARNI, B. V. THOSAR, F.A.Sc. AND G. CHANDRA

(Tata Institute of Fundamental Research, Bombay-5, India)

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## ABSTRACT

A correlation is observed between the lifetime and two-photon annihilation intensity by pick-off process of ortho-positronium in molecular materials. An empirical model, in terms of free volume, is developed to explain this correlation. The variation in lifetime and intensity with change of temperature and pressure, and due to melting of crystals, and glass-transition in polymers is considered, on the basis of this model.

## INTRODUCTION

POSITRONS annihilate with electrons in a material medium with the emission of gamma-rays. It is now generally known<sup>1</sup> that prior to annihilation a positron is slowed down in the medium, by successive inelastic collisions, and is degraded to low energies, of the order of a few electron volts. The slowing down times in metals and other condensed materials appear to be very small as compared to the annihilation lifetimes. Annihilation in free collisions, which may be either singlet or triplet, results in the emission of two or three photons respectively. The lifetime of such free annihilation is of the order of  $10^{-10}$  sec., and the process is termed prompt annihilation. The ratio of cross-sections for the singlet and triplet prompt annihilation,  $\sigma_{2\gamma} / \sigma_{3\gamma} = 372$ , has been experimentally verified.

An alternative mode of annihilation is possible in some media, where a positron slowed down to low velocities, forms a hydrogen-like bound state with an electron of the medium. This bound state, called the Positronium atom (Ps), is most likely to be formed in its ground state, which consists of two sub-states; the singlet  $1s$  or the para state and the triplet  $3s$  or the ortho state. In free space the annihilation lifetimes of these states are

For singlet  $(\tau_1) = 1.25 \times 10^{-10}$  sec.

For triplet  $(\tau_3) = 1.4 \times 10^{-7}$  sec.

The singlet state decays into two photons, while the triplet state decays into three photons. The lifetime  $\tau_1$  of the singlet state is of the same order as that of the prompt process, and so these are normally not distinguishable in an experiment designed to measure the life-times of positrons. The triplet positronium decays into three photons with a long lifetime  $\tau_3 \sim 10^{-7}$  sec. When formed in a condensed medium this state is rapidly quenched by the electrons in the medium, which results in two photon annihilation with a lifetime reduced to  $\sim 10^{-9}$  sec.

#### FORMATION OF POSITRONIUM

The energetics of positronium formation in gases has been discussed by Ore<sup>2</sup> who has shown that the formation of positronium is energetically probable when the energy of the positron lies within a small band or gap given by  $E_1 - (V_i - 6.8) \text{ ev}$ . Here  $E_1$  and  $V_i$  are respectively the first excitation and ionisation potentials of the molecules and  $6.8 \text{ ev}$  is the binding energy of the positronium. The width of the Ore gap determines in the first place the probability of positronium formation though other inhibiting factors when present also affect this probability. Ore's treatment for gases can be applied in a modified form to condensed materials. A positronium atom experiences repulsive forces from a region of high electron density and hence seeks out holes or sites<sup>3</sup> where the electron density is comparatively small. Such a site has to be large enough to accommodate the Ps atom, whose classical diameter is  $(1.06 \text{ \AA})$ . A triplet Ps atom lodged in a site in a condensed medium is likely to annihilate into two photons by a pick-off process, rather than the natural self-annihilation into three photons. In a pick-off process, the positron in the triplet Ps atom annihilates with an electron of opposite spin from the surrounding medium emitting two photons. The resulting lifetime  $\sim 10^{-9}$  sec. which is intermediate between prompt lifetime ( $\sim 10^{-10}$  sec.) and the free triplet Ps lifetime ( $\sim 10^{-7}$  sec.), is called the delayed component,  $\tau_2$ .  $\tau_2$  is thus sensitive to the electron density distribution in the neighbourhood of the sites.

#### EXPERIMENTAL SET-UP

A thin source of  $\text{Na}^{22}$ , deposited on a thin mylar film, is sandwiched between two discs of the sample to be studied. The discs are sufficiently thick ( $\sim 2 \text{ mm.}$ ) to absorb all positrons. The source assembly, which is suitably modified for the study of liquids, is placed between two NaI (TI) scintillation detectors coupled to 6810A photomultiplier tubes. The 1280 keV gamma-ray emitted by  $\text{Na}^{22}$  in prompt coincidence with the positron,

detected in one detector marks the emission of the positron. The 511 keV annihilation gamma is detected in the other detector. Delayed coincidence between the two gamma-rays is observed with a conventional slow fast coincidence set-up and a bridge-type time to amplitude converter, and the time distribution of annihilation quanta is mapped out with a multi-channel analyser. The slope of the delayed component gives the value of  $\tau_2$ , the effective lifetime of ortho-positronium in the sample. Figure 1 shows a typical time distribution curve. The ratio of the area under the delayed component to the total area under the curve gives the intensity  $I_2$ , which is a ratio of the two photon events due to the quenching of the triplet Ps atoms to the total number of two photon events due to all processes. Since the probability of the triplet Ps atom decaying by three-photon emission in a condensed medium is small,  $I_2$  is essentially a measure of the probability of Ps formation in the medium.

### ORTHO-POSITRONIUM IN MOLECULAR MATERIALS

Among condensed media,  $\tau_2$  component is seen to exist for molecular materials—organic liquids and crystals and solid state polymers. In such materials, electron exchange is restricted to within individual molecules and there are no attractive covalent forces between them, a situation favouring the existence of low electron density regions. Measurements for the lifetime  $\tau_2$  and intensity  $I_2$  for a number of such molecular materials are listed in Table I and shown graphically in Fig. 2. Except for cyclo-octatetraene, P.V.C., trioxane polymer, stilbene and  $Sb_4O_6$  which have been studied for the first time, our results for other materials as given in Table I agree fairly well with previously reported values.<sup>1</sup> It can be seen from Fig. 2 that  $I_2$  decreases as  $\tau_2$  increases, and the observed  $I_2 - \tau_2$  correlation is represented by three distinct curves corresponding to liquids and fully amorphous materials, semi-crystalline polymers and molecular crystals.

### DISCUSSION OF $I_2 - \tau_2$ CORRELATION

To describe the  $I_2 - \tau_2$  correlation observed for molecular materials, an empirical model for the process of positronium formation and decay is developed. The specific volume,  $V_{sp}$ , of a medium is considered to consist of the excluded volume,  $V_{ex}$ , *i.e.*, volume actually occupied by the atoms or molecules of the medium, and the free volume  $V_f$ , *i.e.*,  $V_{sp} = V_{ex} + V_f$ . The process of formation and decay of Ps is confined mainly to the free volume  $V_f$ . The important role of free volume in the phenomena of positron

annihilation has been recognised and discussed by Brandt,<sup>4</sup> by Wilson *et al.*<sup>5</sup> and by the present authors.<sup>6, 7</sup>

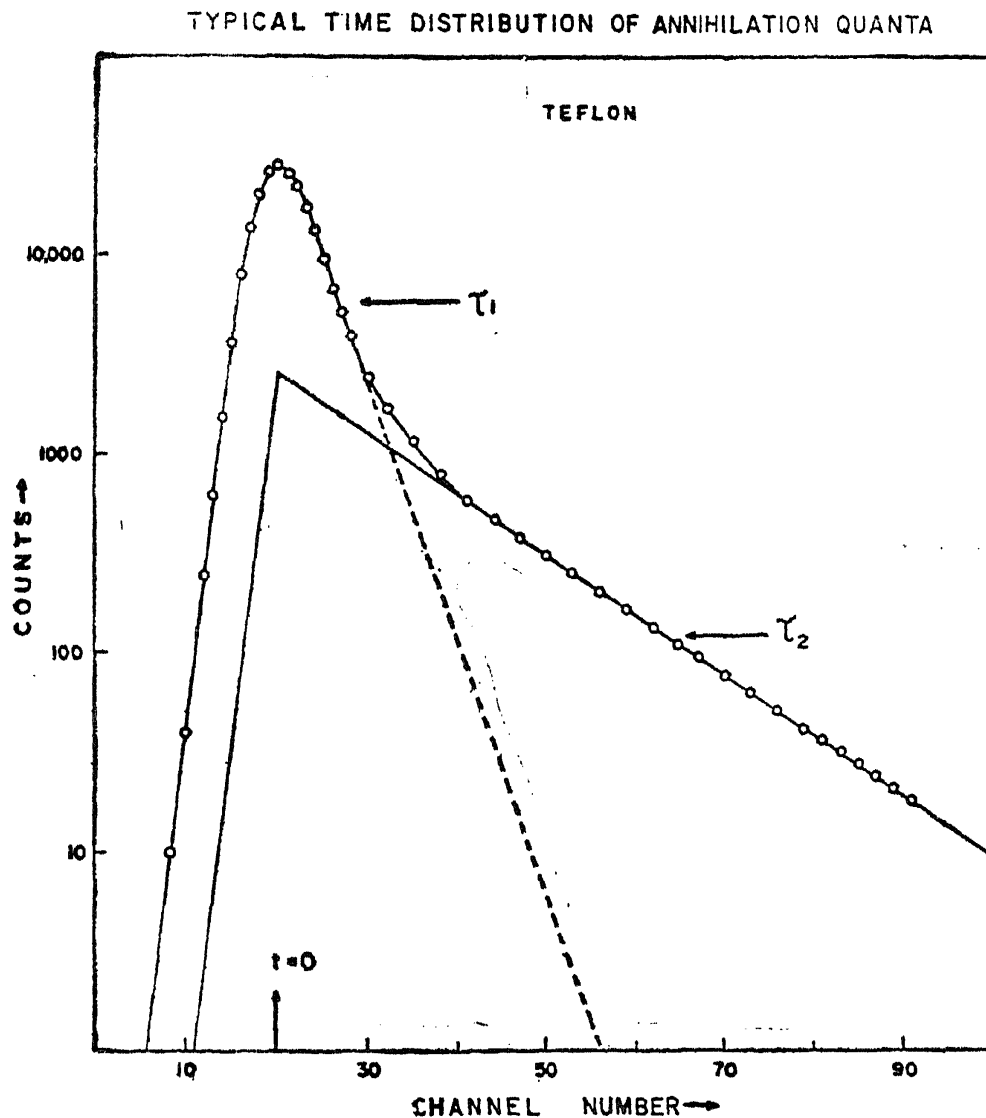


FIG. 1. Typical time distribution of annihilation quanta.

Free volume in the medium may be considered as divided into a number of cavities, void-cells or sites where the Ps atoms lodge themselves, presumably after thermalisation and annihilate by pick-off with surrounding electrons. The experimentally observed pick-off annihilation rate  $\lambda_2 = (1/\tau_2)$ , depends upon the overlap of the wave function of the positron in the Ps atom, trapped in the potential well representing the site, and the wave functions of the electrons of the surrounding medium. As ' $v$ ', the average volume of the site, decreases the electron density leaking into the site and hence the overlap will increase, resulting in an increase in  $\lambda_2$ . In the limiting situation when  $v \simeq v_1$ , the Ps atom will begin to lose its identity due to the crowding in of the surrounding medium, and the limiting value of  $\lambda_2$  will approach the value  $\lambda_1$  observed for the decay of positronium-molecular complexes. Thus  $\lambda_1$  is of the order of  $10^9 \text{ sec.}^{-1}$ . On the other hand as  $v$  increases to a high value