

THE TEMPERATURE DEPENDENCE OF POSITRON LIFETIMES IN SOLID PIVALIC ACID

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The temperature dependence of positron lifetimes in both the brittle and plastic phases of trimethylacetic (pivalic) acid* has been examined using the positron lifetime technique. In the plastic phase two long-lived components attributable to ortho-positronium (ortho-Ps) decay are observed. The longer of these (≈ 2.8 ns) increases with temperature and is believed to be characteristic of ortho-Ps trapped at defects, probably mono- and di-vacancies. A shorter lifetime component (≈ 1 ns) which shows little temperature dependence is also present in the brittle phase. Additionally in the brittle phase and close to the transition region a longer lifetime is detected. This may also be associated with trapping of ortho-Ps in thermally created defects, probably vacancies. In the plastic phase the intensity of a short-lived component associated with para-Ps is confirmed to be approximately one third of the total intensity of the two long-lived components associated with ortho-Ps, but in the brittle phase it is higher than one third. On using data for several plastic crystals a relationship is established between the lifetime of ortho-Ps trapped in a vacancy and the vacancy volume.

1. Introduction

Pivalic acid, $(\text{CH}_3)_3\text{C}\cdot\text{COOH}$, is a member of an interesting class of molecular solids composed of globular molecules and known as *plastic crystals* [1]. At temperatures close to the melting point this molecular symmetry reduces the reorientational barriers between neighbouring molecules allowing a high degree of orientational molecular disordering; the translational order of the lattice structure is maintained. In this phase the solid is highly plastic. All of these solids undergo first-order solid-solid phase transformations with decreasing temperature to form orientationally ordered (brittle) phases. In some cases disorder-disorder transitions are also observed. The properties of this plastically-crystalline state have recently been reviewed [1].

One aspect of these solids, and of molecular solids in general, which remains rather ill-defined is the nature and properties of the intrinsic point defects. Using the positron annihilation technique (PAT) we have started an investigation into a number of plastic crystals to provide a more detailed picture of the point defect state of these materials.

In recent years the use of PAT has proved to be an efficient tool in the study of vacancies and vacancy clusters in metals [2]. Positrons injected into a metal tend to become trapped at these electron deficient regions thus increasing the lifetime of the positron with respect to its bulk lattice value. The sensitivity of the positrons to the presence of such defects has allowed the determination of vacancy formation and migration energies [2]. In many condensed molecular substances a certain fraction of the injected positrons form a positron-electron bound state,

* Trimethylacetic acid; 2,2-dimethylpropanoic acid.

positronium (Ps), before they annihilate [3]. Ps exists in two states, the short-lived para-Ps (spins anti-parallel) and the long-lived ortho-Ps (spins parallel). These states have intrinsic lifetimes of 0.125 and 140 ns, respectively. In condensed matter, due to the high electron density of its environment the positron of ortho-Ps has a high probability of annihilating with an electron of the medium with opposite spin (pick-off annihilation) which reduces the ortho-Ps lifetime to the order of a few nanoseconds. This annihilation mechanism is sensitive to small variations in the electron density and hence molecular density of the Ps environment. This feature of PAT renders it a potentially useful probe for the examination of small-scale structural processes such as vacancy and void formation and phase transformations in molecular solids.

Extensive studies on pure, doped and irradiated ice [4] have illustrated that ortho-Ps does indeed undergo vacancy trapping in a similar way to the positron/metal case. This has allowed the assessment of vacancy formation and migration energies. Also the phenomenon of vacancy clustering has been observed.

Extension of this work to the *plastic crystals* succinonitrile [5], adamantane [6] and dl-camphene [7] has confirmed that ortho-Ps also undergoes vacancy trapping in organic materials. Solid-solid phase transformations in a number of *plastic crystals* have also been studied to complement investigations carried out in other organic systems (see ref. [8] and references therein). Hysteresis and impurity effects have been clearly defined [9].

This PAT study of the plastic crystal pivalic acid was undertaken to extend the range of materials and to provide further information on the behaviour of positrons and Ps in molecular solids.

2. Experimental

Reagent grade pivalic acid (BDH Ltd.), purity $\approx 97\%$ was purified by use of a Nester-Faust spinning band-distillation column. Subsequent

sublimation yielded material of ultra-high purity (<1 ppm total impurity content g.l.c.). Single crystals of this material grown by a Bridgman technique were sectioned to form discs of about 1 cm diameter \times 0.5 cm thick.

A positron source consisting of about $20 \mu\text{Ci}$ $^{22}\text{NaCl}$ encapsulated between two 1 mg/cm^2 Kapton foils was sandwiched between two such discs. The fraction of positrons annihilating in the source was estimated to be 10% of the total emitted. The source-sample sandwich was mounted in a thermostatically controlled liquid nitrogen cryostat ($\pm 0.5^\circ\text{C}$). The sample was allowed 3–4 hours to acclimatise before each measurement.

A fast-fast coincidence lifetime spectrometer with a time resolution of $\text{fwhm} = 0.4 \text{ ns}$ was used for the measurements [10]. Lifetime spectra were typically accumulated over a 15–20 hours period to give $\approx 4 \times 10^6$ counts in a spectrum.

Two temperature scans were made, each starting close to the melting point ($T_m \approx 310 \text{ K}$ [1]), reducing the temperature to about 100 K then increasing to the melting point. Between the two scans the sample was accidentally melted leaving it in a polycrystalline state during the second temperature scan. The two scans were identical.

3. Data analysis and results

The data were analysed using the computer programme "Positronfit" [11, 12]. The spectrometer time resolution function was determined several times during the period of measurement by analysis with the computer programme "Resolution" [12] of lifetime spectra obtained for single crystals of ultra-pure benzophenone. This solid yields only one lifetime component ($\approx 330 \text{ ps}$ at room temperature).

The measured lifetime spectra could be resolved, in an unconstrained analysis, into three lifetime components at the lower temperatures and into four components at the higher temperatures. For the parameters resulting from

these analyses we shall use the following nomenclature. Parameters from a three-component analysis are indicated by a prime (e.g. τ'_3 , I'_3), while parameters resulting from a four-component analysis have no prime (e.g. τ_3 , τ_4). In all cases a short-lived component, τ_1 (τ'_1) \approx 0.12–0.22 ns and an intermediate component, τ_2 (τ'_2) \approx 0.3–0.4 ns were obtained. In addition, either one or two long-lived components were observed, with lifetimes, τ_3 (τ'_3) \approx 1–1.5 ns and $\tau_4 \approx$ 2–3 ns. As discussed below, it is reasonable to associate one or both of the long-lived components with ortho-Ps and τ_1 (τ'_1) with para-Ps. τ_1 (τ'_1) is especially difficult to determine precisely since its value is very sensitive to small changes in spectrometer time resolution function. In order to reduce the scatter of the other parameters extracted from the analysis, the lifetimes were re-analysed with τ_1 (τ'_1) fixed at the theoretical vacuum para-Ps lifetime, 0.125 ns. This constraint did not increase the “variance of the fit” [11] significantly. The results are shown in fig. 1.

Below 230 K only three components are resolved, but at 243 K and above four components may be extracted. The total intensity of the long-lived component(s) (I'_3 or $I_3 + I_4$) follows a sigmoidal increase below the phase transition (280 K [13]). The phase transition region is shown in more detail in fig. 2. The changes in τ_3 , I_3 and I_4 occur sharply within a few tenths of a degree of the transition. In comparison τ_4 exhibits a much more gradual increase over several degrees. The hysteresis of the transition is clearly defined. Rather surprisingly the total intensity ($I_3 + I_4$) increases at the transition (brittle \rightarrow plastic). For other plastic crystals so far examined [5, 7, 14] the total intensity decreases.

After cooling through the transition in the second temperature scan some variation with time was observed, especially for τ_4 and I_4 . This is indicated by the dotted line connecting the filled triangles at 275 K at which temperature measurements were repeated over a period of 7 days (only a few points representative of the 7 measurements are shown).

In the plastic range ($T > 280$ K) the param-

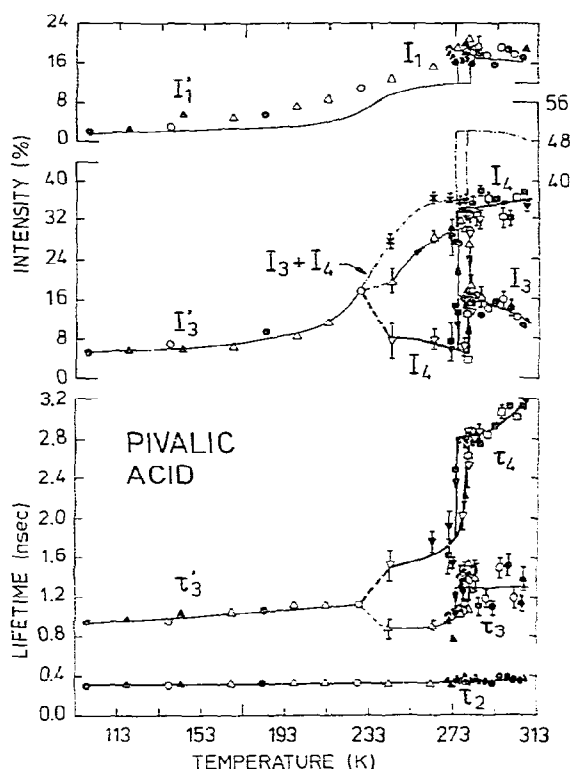


Fig. 1. Lifetimes and relative intensities as a function of temperature. Circles and squares are for the first temperature scan, triangles for the second scan. Open symbols are for increasing and closed ones for decreasing temperatures. The crosses show a few of the points for the sum of the two intensities $I_3 + I_4$ for which the dash-dotted curve is drawn. Below 230 K the parameters result from a three-term analysis (marked with a prime), above 230 K from a four-term analysis (no prime). τ_1 (τ'_1) has been fixed at 0.125 ns at all temperatures. The curve drawn for I_1 (I'_1) is equal to 1/3 of the curve for $I_3 + I_4$ and I'_3 . All other curves are drawn to give the best visual fit to the experimental points.

eters apparently do not vary in the same manner as observed for succinonitrile [5], adamantane [6] and camphene [7]. In particular, when a three-term analysis (not illustrated) is made above the phase transformation the longest, average, ortho-Ps lifetime increases linearly with temperature and shows no sign of the sigmoidal

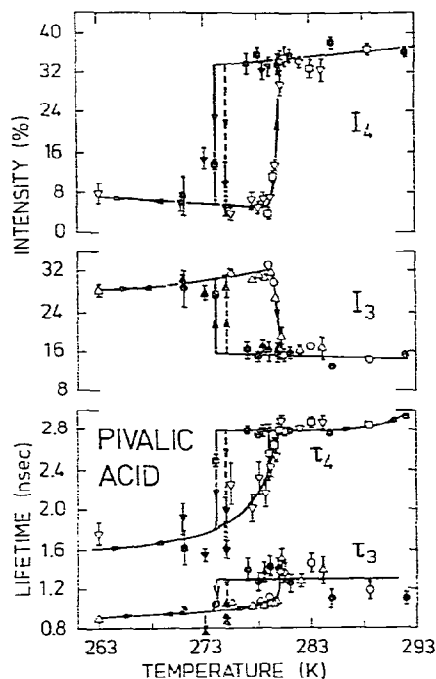


Fig. 2. An expanded view of the phase transition region. The symbols have the same meaning as in fig. 1.

variation observed for the above noted crystals. This apparent distinction is attributable to the high temperature of the transformation which limits observation to $>0.9 T_m$, a range in which the sigmoidal variation tends to saturate.

The lifetime τ_2 (τ'_2), which we associate with the annihilation of free positrons increases slowly with temperature from 0.30 to 0.36 ns showing little or no change across the transition.

Finally, the presence in both phases of a component with lifetime roughly equal to 1 ns (τ'_3 or τ_3) is particularly worthy of note. We have observed such a component in the brittle phases of other plastic crystals so far examined [5–7, 14] but more rarely in the plastic phase. In some cases τ_3 falls with increasing temperature [5–7] in the plastic phase. This has been taken to imply a transfer of ortho-Ps from the bulk to a (predominantly) defect state. However, in the present results τ_3 seems to be constant in the

plastic phase. A similar (1 ns) lifetime component has been observed for a number of other brittle organic crystals [15] and for some polymers [16, 17]. Currently the source of this component and whether or not it is the same source in both types of phase is not defined or understood. Further examination is required.

4. Discussion

4.1. Positronium formation

If Ps is formed in a condensed molecular substance, one would expect a positron lifetime spectrum for that substance to comprise a component with lifetime $\tau_1 \approx 0.125$ ns from the annihilation of para-Ps. (In most experiments this component is not resolved from the “free” positron lifetime $\tau_2 \approx 0.3$ – 0.4 ns.) Additionally the pick-off annihilation of ortho-Ps will normally give rise to one or more (if Ps can exist in more than one state) components with lifetimes ranging from somewhat less than one to several nanoseconds (τ'_3 or τ_3 , τ_4). It is also generally assumed that three times as much ortho-Ps as para-Ps is formed [3] ($3I_1 = I'_3$ or $I_3 + I_4$).

In the present case the measured lifetimes (i.e. 0.1–0.2 ns and 1–3 ns) are consistent with this expectation. The apparent ortho-Ps/para-Ps ratio is however not 3 at all temperatures. Fig. 1 shows the values of I_1 compared with $\frac{1}{3}(I_3 + I_4)$ (or at low temperatures $\frac{1}{3}I'_3$). If the two long-lived components are both due to ortho-Ps the two intensity terms should be in agreement. In the plastic phase there is good agreement within experimental error. However, in the brittle phase, although the points follow the same sigmoidal behaviour as does the curve, they are clearly higher. Previously we have found similar (or better) agreement between these two parameters in other plastic phases [5, 6] whilst in the brittle phase of succinonitrile [5] and cyclohexane [14] I'_1 does tend to be higher than $\frac{1}{3}I'_3$. Recently a similar inequality has been observed for teflon [17].

The question has been raised as to whether or not long lifetime components alone can be

taken as sufficient evidence to confirm the presence of positronium in molecular crystals and polymers [16, 18, 19]. However, we conclude that the present lifetime data are sufficiently indicative of Ps formation in both phases of pivalic acid.

The variation of the ortho-Ps yield (I'_3 or $I_3 + I_4$) in the brittle phase, i.e. the sigmoid increase commencing at circa 200 K may be compared with similar variations which have been observed by Weclawik et al. [20] in the "non-plastic" solids *p*-terphenyl and pyrene. They find that the intensity of the long-lived component (which they associate with ortho-Ps [21]) rises from zero in a sigmoidal manner as function of temperature, starting at 0.75–0.8 T_m . The longest lifetime is about 0.6–0.7 ns, but starts to rise just before the intensity saturates. For pivalic acid, τ'_3 (or above 230 K an average lifetime of τ_3 and τ_4) shows only a weak linear temperature dependence until close to the phase transition where the lifetime starts to rise above linearity. The authors of ref. [20] propose that temperature created defects are responsible for the increase in Ps yield. A similar interpretation can be proposed for pivalic acid.

However, like in ref. [20] the nature of these proposed defects and the way in which they influence the Ps formation is not clear. The ortho-Ps lifetime (≤ 1 ns) is too short to be due to ortho-Ps trapped in vacancies (see sections 4.2 and 4.3). Thus the process cannot be Ps formation directly in vacancies, but maybe in some other (unknown) defects. Alternatively (or in addition) the presence of defects (vacancies or others) may influence Ps formation in the bulk crystal. It is likely that pivalic acid is monotropic in which case the melting point of the low temperature phase will lie between the transition temperature and the melting point of the plastic phase. Thus, the sigmoid intensity increase starts at roughly 0.7 T_m (T_m is here the brittle phase melting point), i.e. about the same as found in ref. [20]. It should be added though that the onset temperature for sigmoid intensity increases is not always found at 0.7–0.8 T_m . In naphthalene it is only 0.5 T_m (T. Goworek, private communication). A sigmoid intensity

behaviour has so far not been observed in the brittle phases of other plastic crystals, although in succinonitrile I'_3 increases with temperature.

4.2. Trapping of Ps at defects

In our other studies of plastic crystals we have found strong evidence for the trapping of Ps at vacancies in the plastic phase. Vacancy formation energies have been derived [5–7]. In all cases two characteristic ortho-Ps lifetime components could be extracted. The longer lifetime, τ_4 , was associated with ortho-Ps trapped at thermally generated vacancies. In general its intensity, I_4 , increases with temperature as the probability of trapping increases. The shorter lifetime, τ_3 , of ortho-Ps in the bulk and its intensity, I_3 , usually decrease with increasing temperature. These parameter variations are in accord with the simple "trapping model" [2]. These changes become apparent at $\approx 0.7 T_m$ [5–7], T_m being the melting temperature.

In pivalic acid a similar analysis of trapping in the plastic phase is probably prohibited by the high transition temperature (0.9 T_m). This reduces the range of observation to temperatures at which all ortho-Ps might be trapped in defects. Thus we observe no preliminary sigmoid change. Our strongest evidence for assigning the τ_4 component in this material to the decay of ortho-Ps from a point defect trapped state is based upon its magnitude (see section 4.3).

In the event that our assignment of τ_4 and I_4 in the plastic phase is correct i.e. ortho-Ps totally trapped from the bulk state into defects, then from its behaviour the τ_3 , I_3 component must either be due to positrons or to ortho-Ps in a state from which it can only slowly make transition to the defect state, if at all.

4.3. Correlation between τ_4 and molecular volume

In previous studies [5–7, 14] an interesting relationship has been observed between the lifetime τ_4 at – or extrapolated to – the melting point (τ_4^M) and the molecular volume Ω , i.e. the

average volume per molecule. This relationship is shown in fig. 3. (For the point for ice at $\Omega = 3.3 \times 10^{-29} \text{ m}^3$ the lifetime is taken to be that of ortho-Ps trapped at a vacancy [4].)

If we make the reasonable assumption that Ω is representative of the vacancy volume and that τ_4^M represents the lifetime of ortho-Ps trapped at vacancies (except for pivalic acid and hexamethylethane, see below) the increase of τ_4^M in fig. 3 is explained as an effect of the size of the free vacancy volume. The lifetime of ortho-Ps trapped in a vacancy is expected to increase with increasing volume of the vacancy since the overlap between the positron and the surrounding molecular electrons decreases and therefore also the pick-off annihilation rate decreases. A very simple model illustrates this trend qualitatively. We represent the vacancy by a spherical potential for Ps. The potential is zero for the radius, r , less than a certain value R_0 and infinite for larger r . For $r < R_1 < R_0$ the electron density is zero, whereas it is assumed

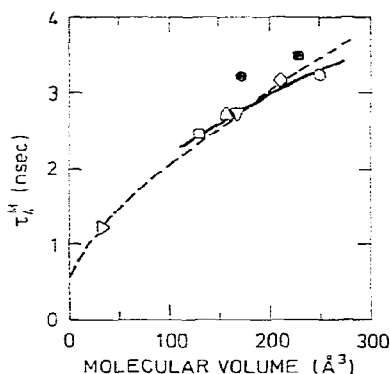


Fig. 3. The correlation between the longest lifetime at – or extrapolated to – the melting point, τ_4^M , and molecular volume, Ω . The open symbols are associated with the lifetime of ortho-Ps trapped in a vacancy of volume Ω . The closed symbols represent materials where also trapping into divacancies apparently takes place. The full curve is drawn through the open symbols (apart from the point for ice) to guide the eye. The dashed curve is the result of a simple model calculation. The symbols are for the following materials: \triangleright ice (hexagonal) [4], see text; \square succinonitrile (bbc) [5, 25]; \triangle norbornylene (hcp) [14, 28]; ∇ cyclohexane (fcc) [14, 25]; \diamond adamantane (fcc) [6, 29]; \circ dl-camphene (bcc) [7, 25]; \blacksquare hexamethylethane (bcc) [14, 25]; \bullet pivalic acid (fcc) [25].

constant in the layer between R_1 and R_0 . For the Ps ground state in this potential the probability of Ps being inside the electron layer is $P = 1 - R_1/R_0 + \sin(2\pi R_1/R_0)/2\pi$. Assuming an ortho-Ps pick-off annihilation rate in this layer of 2 ns^{-1} (that of Ps^- [22] or the spin averaged annihilation rate of Ps) and keeping the layer thickness constant (at about 0.17 nm to normalize τ_4 to 3.0 ns for $\Omega = 2 \times 10^{-28} \text{ m}^3$) we obtain the dotted curve in fig. 3 for $\Omega = 4\pi R_1^3/3$. Such a simplified model should of course not be taken too seriously, but it indicates that the trend of the experimental points is about what one would expect.

This is further strongly supported by a comparison with results obtained for Ps in molecular liquids. It is generally believed that Ps exists localized in a “bubble” in molecular liquids (or maybe in two different bubble states; see ref. [23] and references therein). With increasing size of the bubble, the ortho-Ps lifetime increases. In ref. [23] results for liquid SF_6 were shown. The lifetime of ortho-Ps in the bubble state increases with temperature from about 6 ns up to about 20 ns. This is associated with an increase in bubble radius by about 50% caused mainly by a decrease of surface tension with increasing temperature. A semi-empirical formula was derived which gave a very good fit to the experimental bubble lifetime over the whole temperature range. This formula with the constants derived for SF_6 also give lifetimes in good agreement with the open symbols in fig. 3 (the point for ice deviates 12%, the others less).

We have previously found convincing evidence that Ps does form in the crystals of succinonitrile, adamantane, and camphene [5–7] and the long lifetime τ_4 in these materials can therefore safely be associated with ortho-Ps. Furthermore the results strongly suggested that trapping of ortho-Ps in thermally generated defects takes place leading to saturation trapping close to the melting point. From self-diffusion measurements it is known that vacancies are the dominant defect type in the above materials [1]. We therefore conclude that the full curve drawn through the open symbols in fig. 3 approximately represents the lifetime of

ortho-Ps trapped in a vacancy in a van der Waals molecular crystal as function of vacancy volume.

As one would expect, parameters like the crystal structure, and packing density do not influence the relationship appreciably. It also appears that it is insensitive to molecular shape. Self-diffusion measurements in hexamethylethane [1, 24, 25] indicate that divacancies or strong lattice relaxation around vacancies play an important role, especially at the highest temperatures. The activation volumes for diffusion are unusually high and increase with temperature [1, 25]. This seems to be in good agreement with the fact that τ_4^M in hexamethylethane is higher than expected from the curve in fig. 3. Assuming that the effect is mainly a result of the presence of divacancies which seems most likely [1] a rough estimate of the relative divacancy concentration can be made from fig. 3. τ_4^M for hexamethylethane is equivalent to an effective defect volume of roughly $2.9 \times 10^{-28} \text{ m}^3$. Assuming that the trapping rate of Ps into divacancies is 1–2 times the rate into vacancies and taking into account reasonable uncertainties on the solid curve in fig. 3 we obtain an estimated ratio between the divacancy and vacancy concentrations at the melting point in the range 15–50%. This range covers Lockhardt and Sherwood's estimate of 20% divacancy contribution to self-diffusion [24].

Recent radiotracer self-diffusion isotope mass effect measurements [26] have shown that in the plastic phase of pivalic acid also divacancies make an important contribution to this process at temperatures close to the melting point. This is supported by the fact that τ_4^M for this phase is well above the vacancy curve (fig. 3). On this basis, the continuous increase in τ_4 in this phase could well reflect mainly the temperature dependence of the vacancy/divacancy equilibrium. With the assumptions used for hexamethylethane a rough estimate can be made as above of the relative divacancy concentration in pivalic acid at the melting point. It results in the range 25–80% of the vacancy concentration.

Finally we note that the rise of τ_4 in the brittle phase close to the transition temperature may be a result of trapping of ortho-Ps into defects in the brittle phase. These defects may be vacancies the concentration of which increases towards the phase transition where saturation trapping takes place ($\tau_4 = 2.8 \text{ ns}$). This lifetime value does in fact lie on the vacancy curve in fig. 3. This is further evidence to confirm our conclusions. Since τ_3 , I_3 and I_4 hardly change in this temperature range ortho-Ps in the short-lived state (τ_3 , I_3) is apparently not being trapped into vacancies, but only ortho-Ps in the long-lived state is being trapped. (This is similar to the situation in the plastic phase; see last paragraph of section 4.2.) Just below the transition temperature τ_4 is therefore believed to be an average of trapped (2.8 ns) and untrapped ($\approx 1.6 \text{ ns}$) ortho-Ps lifetimes.

5. Conclusion

In the present work a positron lifetime investigation has been carried out in solid pivalic acid both its brittle and its plastic phase. In contrast to previous investigations of plastic crystals [5–7] we find no transition in the plastic phase with increasing temperatures from a bulk to a vacancy-trapped ortho-Ps state. Instead two long lifetime components are observed, both probably arising from ortho-Ps decay. The longer one of about 3 ns is interpreted as ortho-Ps trapped in mono- and divacancies, while the origin of the shorter one of about 1 ns is less clear. It is pointed out that components with lifetimes of about 1 ns are observed in many molecular solids. The expected ratio of 1/3 between the intensities ascribed to para-Ps and to ortho-Ps is observed in the plastic phase, but not in the brittle phase where the ratio is higher. Similar observations have been made also in other molecular solids. This problem together with the apparent lack of narrow para-Ps components in angular correlation curves for certain molecular crystals seems to be central in obtaining a detailed understanding of Ps characteristics in molecular solids. Further progress

towards their solution requires both angular correlation, 3γ annihilation [27], and lifetime measurements on a variety of materials.

The important conclusion that divacancies are present in pivalic acid in higher concentrations than in other plastic crystals was partly reached through the establishment of the relationship between the lifetime of ortho-Ps in a vacancy and the vacancy volume.

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