Positron Annihilation Rates on Organic Molecules in Dense Liquids and in Gases

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POSITRON ANNIHILATION RATES ON ORGANIC MOLECULES IN DENSE LIQUIDS AND IN GASES

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Positron lifetime data are now available for annihilation on organic molecules over a wide density range from dense liquids to dilute gases. The aim of the present work is to compare and contrast the interpretation of these experimental data in liquid and gaseous phases. Therefore, some regularities in the triplet positronium lifetimes in dense fluids are first noted. Two specific points considered are (i) the remarkable constancy of the product $\tau_2 d = (2.7 \pm 0.2) \, 10^{-6}$ s·kg/m³ in many liquid hydrocarbons at 299 K, where τ_2 is the annihilation half-life of triplet positronium while d is the density, and (ii) an approximate density dependence of $d^{-3/2}$ of τ_2 when d is varied over a wide range from the dense liquid to the critical density: neopentane being taken as the protypical example. Such behaviour, controlled largely by the macroscopic density, is contrasted with the extensive dilute gas data obtained recently by Murphy and Surko on 23 different organic molecules. Here, it is shown that one is concerned (a) with direct annihilation or a singlet positronium, and (b) with properties related to electronic structure·of the organic molecules and in particular with ionization potential and polarizability.

KEY WORDS: Positronium lifetime, liquid hydrocarbons, organic gases, ionization potential, polarizability.

1 INTRODUCTION

Though many aspects of the interaction of positrons with matter are by now well understood, a body of experimental measurements which has built up on positron liftetimes for annihilation on organic molecules is still lacking detailed analysis and theoretical interpretation. Therefore a start will be made in the present paper by considering these data over a wide density range which will embrace organic liquids, dense fluids near critical conditions and also dilute gases.

Beginning with dense liquids, it is relevant to note that many disordered materials, embracing also amorphous solids, exhibit a complex time decay curve which has two distinct components of similar intensity with different mean lives[1]. Roughly speaking, in such complex time decay, about 2/3 of the positrons annihilate with a mean life (τ_1) of about 0.1 ns, while the remaining 1/3 exhibit a mean life (τ_2) of 0.5–3.5 ns, depending on

the substance[1,2]. The longest lifetime is found to decrease, in general, as the sample is cooled, which increases the liquid density. Bell and Graham[2] propose that the τ_2 component is due to the formation of triplet positronium, which is converted to the singlet state by collision before annihilation.

Turning from such dense systems, which will be treated in detail, we shall consider the recent positron experiments of Murphy and Surko[3] who worked with organic molecules in the dilute gas phase. Briefly, their experiments were performed with room temperature positrons confined in a Penning trap. For the molecules these workers studied, such thermal energy is from 0.11 to 1.54 aJ (0.7 to 9.6 eV) below the positron energy required for the formation of free positronium, which therefore eliminates this process as a channel for positron annihilation.

Because of the interest aroused by these new data on the dilute gaseous phase of organics[4], we have re-examined also some older data in which positron half-lives have been studied over a wide range of density, ranging from normal liquid densities down to the critical density. This analysis will be presented in Section 2 immediately below, after a summary of some early work by Freeman and Dodelet[5]. In Section 3, the data on dense fluids will be compared and contrasted with the interpretation of the dilute phase positron results of Murphy and Surko[3] already referred to. Section 4 constitutes a summary, together with some proposals for possible future studies, both by experiment and from theoretical investigation.

2 ORGANIC LIQUIDS AND DENSITY VARIATION

More than twenty years ago, Freeman and Dodelet[5] were concerned with the annihilation half-life τ_2 for triplet positronium (Ps) in liquid hydrocarbons. From then available experimental data for fourteen such molecules, they exposed a remarkable constancy of the product $\tau_2 d$, with d the liquid density, their finding being that

$$\tau_2 d = (2.7 \pm 0.02)10^{-6} \, \text{s} \cdot \text{kg/m}^3. \tag{1}$$

However, Eq. (1) is applicable, as these workers recognised, only for a fairly restricted range of densities. To demonstrate this, data of Mogensen and coworkers[6] for neopentane have been plotted as a function of density in Figure 1. This plot was motivated by a correlation noted by Mogensen et al.[7] between Ps yield and electron mobility in the liquid. In particular, the hump in the o-Ps curve reminded Mogensen et al. of the hump found by Dodelet and Freeman[8] in the electron mobility curve for liquid neopentane. Since DF found that this change of electron mobility in neopentane is primarily due to a change of density, it seemed natural enough to plot Figure 1. The result there can be usefully represented by the approximate relation that the lifetime of o-Ps, $\tau(o\text{-Ps})$ varies inversely as the 3/2 power of the density:

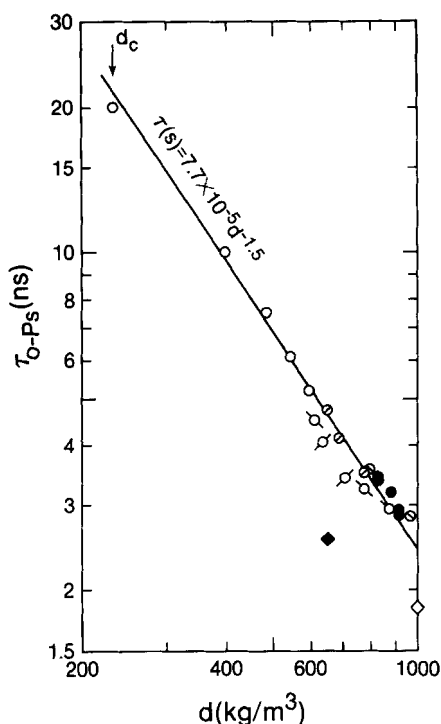$$\tau(o\text{-Ps}) = 7.7 \times 10^{-5} \, d^{-3/2} \tag{2}$$

Figure 1 Mean decay times τ of o-Ps in organic (circles) and inorganic (diamonds) liquids at different densities. ○, tetramethylmethane, 293–463 K, Ref. 6; ⊘, tetramethylsilane, iso-octane, decalin, 293 K. Ref. 10; ◔, cyclopropane, cyclohexane, decalin, 293 K. Ref. 9; ◌, n-hexane, 243–318 K, Ref. 11; ●, benzene, toluene, xylenes, mesitylene, 243–340 K, Ref. 11; ◑, methanol, ethanol, cyclohexanol, 293 K. Ref. 10; ◇, water, 293 K, Ref. 12; ◆, ammonia, ~ 273 K, Ref. 13.

with τ in seconds and d in kg/m^3. The uppermost point in Figure 1 corresponds to the critical density, and τ is independent of temperature in the supercritical gas at this density[6].

We have examined in some detail the addition of data for numerous other organic compounds to this plot: cyclopropane, cyclohexane and $trans$-decalin by Wikander $et\ al.$[9], tetramethylsilane, iso-octane and methylcyclohexane from the work of Jansen and Mogensen[10], n-hexane, toluene, m-xylene and mesitylene by Wikander $et\ al.$[11], and several alcohols studied by Jansen and Mogensen[10]. All fall close, as Figure 1 shows, to an extrapolation of the neopentane line. Figure 1 also shows that lifetimes in the inorganic liquids water[12] and ammonia[13] are shorter than in organic liquids of the same density. (Some comments on positrons as probes in radiation chemistry are relevant and are summarized in Appendix 1).

Having discussed some striking regularities in dense organic liquids, summarized in Eq. (1) over a limited density range, and by Eq. (2) over a wider regime of density

change, let us turn to consider more briefly the recent data of Murphy and Surko[3] on the annihilation of positrons on organic molecules in the dilute gas regime.

3   POSITRON ANNIHILATION ON ORGANIC MOLECULES IN DILUTE GASEOUS PHASE

Let us return then to the Penning trap data of Murphy and Surko[3]. To make some contact with the regularity in Eq. (1) for dense hydrocarbons, we have taken the pressure data of these workers, and using the ideal gas equation of state, we have formed the product of positron half-life and the gaseous density. The values are about four orders of magnitude smaller than those from the dense phase result in Eq. (1). This makes it clear that the Murphy-Surko data, in contrast to the triplet state lifetimes in liquids discussed above, are about a singlet Ps state. Having established this major difference from the above discussion of dense phases, we note two correlations established by Murphy and Surko: namely (i) a relation between positron annihilation rate and molecular polarizability α, and (ii) that the rate correlates with $(I - I_0)^{-1}$, where I is the ionization potential of the organic molecule considered while I_0 is the positronium binding energy, namely 1.09 aJ (6.8 eV).

To press these correlations a little further, we present Murphy and Surko's data in Figure 2 in the $(I - I_0)^{-1}$ against α plane, each of the molecules on the plot being characterized by the log of its positron annihilation rate constant k_a (m^3/mol·s). We prefer not to use the conventional notation of an effective charge[3], because the values
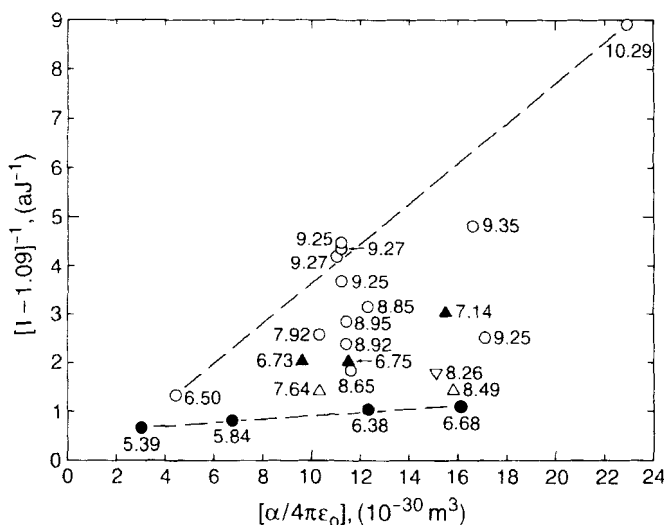
Figure 2   Three-dimensional graph of data for the 23 compounds studied by Murphy and Surko[3]. Each point is labelled with the value of $\log(k_a/\text{m}^3 \, \text{mol}^{-1}\text{s}^{-1})$. $\bigcirc$, all kinds of saturated and unsaturated hydrocarbons; $\bullet$, perfluoroalkanes; $\blacktriangle$, perfluoroaromatics; $\triangle$, CCl$_4$ and C$_2$Cl$_6$; ∇, CBr$_4$. 1 aJ = 6.24 eV; the unperturbed binding energy of Ps is 1.09 aJ = 6.8 eV; in SI the polarizability α(C·m^2/V) is divided by $4\pi\varepsilon_0$(C/V·m) to obtain units of m^3. The lower dashed line passes through the perfluoroalkanes; the upper line passes from ethane to anthracene.

are so high for organic molecules that no simple chemical or physical interpretation as an effective charge seems helpful. The concept of the Dirac annihilation rate of positrons, and hence of an effective charge Z_{eff}, applies to a gas of quasifree, uncorrelated electrons[3], whereas the problem of positrons interacting with electrons in chemical systems usually involves strong correlation. Values of the second order rate constants for positron annihilation with electrons bound to molecules were calculated from the tabulated[3] values of Z_{eff} using the relation

$$k_a = \pi a_0^2 c (e^4/\hbar^2 c^2)^2 \, N_A Z_{\text{eff}} = 4.51 \times 10^3 \, Z_{\text{eff}} \, (\text{m}^3/\text{mol·s}) \tag{3}$$

where a_0 is the Bohr radius $\hbar^2/me^2$, c is the speed of light, and N_A is Avogadro's constant.

Figure 2 contains data for n-alkanes, simple alkenes, conjugated di- and tri-enes, simple aromatics and fused ring aromatics, perfluoroalkanes, perfluoroaromatics, CCl_4, C_2Cl_6 and CBr_4. Careful inspection of the data in Figure 2, assisted by various two-dimensional plots, reveals that the annihilation rate constants k_a on hydrocarbons are determined mainly by the molecular polarizability, whereas k_a on perfluoroalkanes is smaller than on the analogous alkane and is determined mainly by the value of $(I - I_0)$. As suggested by Murphy and Surko[3], the positron before annihilation appears to form a Ps atom that is complexed with the remaining organic positive ion. The various types of hydrocarbon molecule apparently act mainly as a polarizable electron source in which Ps is embedded more easily when α of the resulting ion is larger; there is a limited extra contribution of π bonds. By contrast the Ps is apparently attached to an F ion on a perfluoroalkane, the strength of attachment increasing as I decreases. For perfluoroaromatics, positron annihilation slightly involves the π-bonds, which would be somewhat diminished by electron withdrawal to the fluorines. For the perchloro- and perbromocarbons the values of k_a are mainly determined by α, but are somewhat reduced toward those of the fluorocarbons.

Pressing this point a little further, if we view the singlet Ps as formed by pickup of an electron from the charge cloud of the organic molecule, then one can view this Ps complexed with the remaining positive ion as being perturbed by the charge of the ion. If the distance R between the centers of the Ps and molecular ion is asssumed large, we expect a perturbation interaction energy E_{int} of the gross form

$$E_{\text{int}} \propto \frac{e^2}{4\pi\varepsilon_0 R} \cdot \frac{\alpha_{\text{Ps}}}{4\pi\varepsilon_0 R^3} \tag{4}$$

$$\propto R^{-4}.$$

It is then tempting to evaluate E_{int} at a distance R related to the cube root of the molecular volume. That polarizability $\alpha' = \alpha/4\pi\varepsilon_0$ correlates with molecular volume has been known for a long time. This correlation has been pressed quite recently by Brinck et al.[14], who showed that an improved correlation can be obtained by including an 'average ionization potential'. However, without utilizing this refinement the above discussion suggests that I_0, the 'free' binding energy, should be affected by inclusion of the interaction energy E_{int} roughly characterized by Eq. (4). With α' proportional to the

molecular volume V_m, the 'contact distance' $R_m \propto (V_m)^{1/3}$ inserted in Eq. (4) suggests an inverse 4/3 power of the polarizability, and this has motivated the plot shown in Figure 3. Hydrocarbon molecules of increasing size approach an upper limit of $k_a \approx 10^{11}$ m^3/mol·s, while the limit for perfluoroalkanes is $\sim 10^8$ m^3/mol·s. The sphere like molecules CH_4 and CF_4 provide the lower limits in these series at $10^{5.8}$ and $10^{5.4}$ m^3/mol·s, respectively.

4   SUMMARY AND FUTURE DIRECTIONS

In liquid hydrocarbons in particular, and in dense organic fluids more generally, there is an inverse correlation of o-Ps half-life τ_2 with density d. While, in accord with Eq. (1), it is to be expected that τ_2 will vary roughly with the inverse of a 'mean electron density', which in turn in liquid hydrocarbons is proportional to the mass density d, the approximate $d^{-3/2}$ dependence exposed in Figure 1 has not yet been given a theoretical interpretation.

Although the $d^{-3/2}$ dependence in Eq. (2) is valid for dense fluid hydrocarbons over a wide density range embracing the critical density, it bears no relation to the positron annihilation half-lives observed in the Penning trap experiments of Murphy and Surko[3] on dilute gaseous organic molecules. This in turn makes it clear that their experiments are observations on singlet positronium. Furthermore, the electronic structure of the organic molecules now have a profound influence on the positron annihilation rate constant k_a, this latter quantity correlating with both molecular ionization potential I and polarizability α in a complex manner.

For the future, it will be of interest to attempt to relate k_a more directly not only to the electronic structure but also to liquid correlation functions. At first sight, one might suppose that the change in the fluid pair correlation function $g(r)$ in going from dense

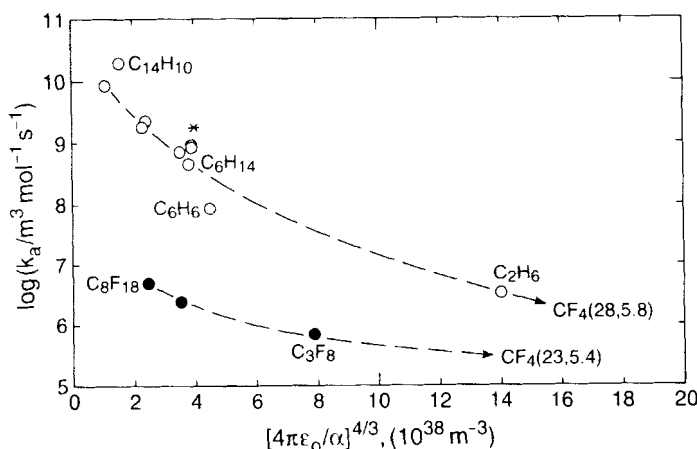**Figure 3**   Log k_a for hydrocarbons (○) and perfluoroalkanes (●) correlated with $\alpha^{-4/3}$. Data from Ref. 3. * represents the cluster of four points for 1,3-hexadiene, *cis* and *trans* isomers of 2,4-hexadiene, and 1,3,5-hexatriene. $C_{14}H_{10}$ is anthracene.

phases through to the gaseous state will be a major factor. However, we have little doubt that while the basic annihilation process in the dilute gas phase studied by Murphy and Surko is with an individual organic molecule, in dense fluids one is dealing, at very least, with a process involving substantial molecular clusters. This convinces us that, in the dense phases, our growing understanding of higher-order correlation functions will need to be invoked to yield a full theoretical interpretation, and in particular a basis for the empirical $d^{-3/2}$ dependence of τ_2 over a wide density range, though still in the dense fluid regime. In contrast, in dilute gases, it still remains to uncover a further, chemical, parameter to supplement the already established dependence of the annihilation rate constant on molecular ionization potential and on polarizability. It would also be fruitful to determine the *molecular shape* effect on the positron-molecule interactions by measuring decay rates in dilute gases of the three isomers of pentane, namely, *n*-pentane, isopentane and neopentane. *n*-Pentane is a floppy chain, neopentane is spherelike and relatively rigid, and isopentane is of intermediate structure.

APPENDIX 1   CHEMICAL REACTIONS OF POSITRONS IN CONDENSED MATTER AND DENSE GASES

The purpose of this Appendix is to summarize briefly what can be said about the reactions of the positrons themselves in condensed matter and dense gases.

Positrons begin their lives in high kinetic energy states. When they penetrate matter, they lose energy by collisions. Towards the end of their flight path, a certain fraction of them pick up electrons to form neutral positronium atoms (perturbed somewhat by their local environment). Ultimately, all of them transform to γ rays by annihilation. The average lifetime before transformation in dense matter is a few ns for triplet positronium (*o*-Ps). The chemical reactions that they undergo must occur before the transformation. This time scale is intermediate in the range of time scales of radiation chemical reactions, which are typically 10^{-14} s to 1 s for processes considered usually to be chemical rather than physical or biological.

The possibility of using positrons as probes of some of the fast processes in radiolysis systems (compare Ref. 5) lies in the fact that only a fraction of the positrons acquire electrons to form (perturbed) *o*-Ps. This fraction is accessible to experiment and depends on the chemical and physical states of the system.

When the velocity of the projectile positron is much greater than those of the valence electrons in the molecular fluid under investigation, the main reaction is the ionization of molecules

$$e^+(\gtrsim 10^2 \, \text{aJ}) + M \longrightarrow e^+(\gtrsim 10^2 \, \text{aJ minus} \sim 10 \, \text{aJ}) + M^+ + e^- . \qquad \text{(A1)}$$
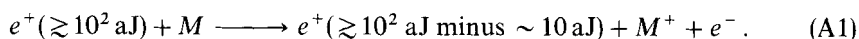
However, when the velocity of the positron is reduced to the order of magnitude of that of the valence electrons in the molecules, another possibility is that the positron sticks to an electron and carries it off. This means that a Ps atom has formed, and it possesses

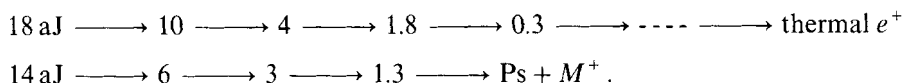most of the kinetic energy that the positron had before the collision:

$$e^+(\lesssim 10\,\text{aJ}) + M \longrightarrow \text{Ps}(\lesssim 10\,\text{aJ}) + M^+. \tag{A2}$$
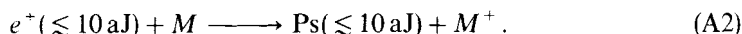
This energetic Ps can be broken apart in a subsequent collision:

$$\text{Ps}(\lesssim 10\,\text{aJ}) + M \longrightarrow e^{+*} + e^{-*} + M. \tag{A3}$$
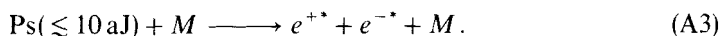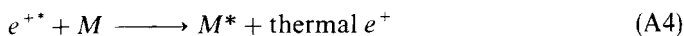
The positron and electron on average would each carry off half the energy. The average decrease in total kinetic energy due to reactions (A2) and (A3) is not much more than equal to the ionization potential of the molecule, but the average positron energy has been reduced by 50%.

Electron pickup and loss might occur more than once, and each time the positron energy becomes roughly half what it was the step before. The energy of the positron might cascade down to near thermal, after which further collisions would reduce it to thermal. However, if its energy happens to fall in the Ore gap, which is the energy gap between the ionization potential of the molecule and 1.09 aJ below that energy (1.09 aJ is IP of Ps), the positron might capture an electron to form Ps and then not have enough energy to break up again. If the ionization potential of the molecules is, for example, 1.68 aJ, the Ore gap would be from 1.68 to 0.59 aJ. Two example energy cascades might be:

$$18\,\text{aJ} \longrightarrow 10 \longrightarrow 4 \longrightarrow 1.8 \longrightarrow 0.3 \longrightarrow \cdots \cdots \longrightarrow \text{thermal } e^+$$
$$14\,\text{aJ} \longrightarrow 6 \longrightarrow 3 \longrightarrow 1.3 \longrightarrow \text{Ps} + M^+.$$

Thus we can write

$$e^{+*} + M \longrightarrow M^* + \text{thermal } e^+ \tag{A4}$$
$$e^{+*} + M \longrightarrow \text{Ps} + M^+ \tag{A5}$$

The fraction of positrons that forms Ps is then the fraction that undergoes reaction (A5) instead of (A4).

The Ore gap model applies mainly to low density gases. In liquids or solids a fraction of the positrons also forms Ps, but a more probable mechanism of Ps formation in dense phases is combination of the positron with one of the electrons generated in the dense ionization zone at the end of the positron track[5]. The mechanism of formation of Ps is not relevant to the present article; the net result is that in dense phases one obtains from the initial, high energy positrons certain fractions of p-Ps, o-Ps, and solvated thermalized e_s^+.

The ultimate tranformation of e^+ occurs in combination with an electron in a molecule

$$e^+ + M \longrightarrow 2\gamma + M^{+*} \tag{A6}$$

with a mean e^+ lifetime of about 0.5 ns in a liquid or solid. The transformation of Ps into γ's occurs at times shorter (0.1 ns for p-Ps) or longer (1–20 ns for o-Ps) than 0.5 ns, so measurement of lifetime spectra distinguishes between reactions (A4), (A5), and (A6).

APPENDIX 2   CONTRAST OF ORGANIC LIQUIDS WITH BEHAVIOUR OF NH_3, H_2O AND SF_6

The inorganic liquids water and ammonia gave shorter o-Ps lifetimes than did an organic liquid at the same density (Fig. 1). Electron exchange between o-Ps and water or ammonia is apparently faster than with an organic liquid at the same density. This indicates that the Ps atom in an alcohol is associated with the alkyl groups rather than with the hydroxy groups. By contrast, a solvated electron in an alcohol is associated more with the hydroxy than with the alkyl groups.

In liquid SF_6 at densities from 730 to 1900 kg/m^3 the lifetimes[7] of o-Ps follow the relation

$$\tau(o\text{-Ps}) = 4.7 \times 10^{-4}\, d^{-3/2}. \qquad (A7)$$

The actual lifetimes are nearly the same as those shown for neopentane in Figure 1 at the same d/d_c; the different values of the coefficients in Eqs. (2) and (A7) are due simply to the greater value of d_c for SF_6 than for $C(CH_3)_4$.

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