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On the influence of electron mobilities on the yields of formation of positronium in liquids: New I_3 measurements and Monte Carlo simulations

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We study the formation of positronium (Ps) at the end of the radiation tracks generated by the passage of energetic positrons in various liquids. We focus particularly on the possible influence of the thermal electron mobility $\mu(e^-)$ on this process. To this end, we present a compilation of experimental data of the probability of ortho-Ps formation I_3 and $\mu(e^-)$ in 51 pure liquids at room temperature. We also present new measurements of I_3 as a function of temperature for *n*-hexane, 2,2-dimethylbutane, tetramethylsilane, and tetramethylstannane from the melting point up to 294 K. Those results are compared to the variation of $\mu(e^-)$ with temperature which can be found in the literature. Finally, we use Monte Carlo simulation techniques to perform a sensitivity study in which we evaluate the relative contributions of various physicochemical properties of the liquids (such as the mean thermalization distances of e^+ and e^- , their thermal mobilities, the dielectric constant, and the temperature) on the values of I_3 . A review of previous works on this question is also given. © 1998 American Institute of Physics. [S0021-9606(98)50206-1]

I. INTRODUCTION

The positron (e^+), the antiparticle of the electron (e^-), when injected with a certain amount of kinetic energy in a liquid, appears to be an ionizing particle in many ways comparable to an electron of the same energy. Indeed, both have the same mass and the same absolute charge. However, positrons present some specific characteristics making a direct transposition of models and experimental results from one particle to another difficult. The opposite electric charge of e^+ and e^- leads, for example, to differences in the potentials experienced by those particles. Moreover, it is clear that, contrary to an electron, a positron cannot recombine with one of the molecules that it has ionized within its track.

It is well known that the ultimate fate of a positron in matter is its annihilation with an e^- of the medium. There is a possibility, however, that the encounter pair (e^+, e^-) forms a transient bound state called “positronium” (Ps). In this way, the formation of Ps can be regarded as a peculiar recombination process. According to a standard convention, the probability of Ps formation consists of two terms, I_1 and I_3 , which correspond to the formation of para-positronium and ortho-positronium, respectively. The remaining probability $I_2 = 1 - (I_1 + I_3)$ is associated to the case where the e^+

does not form Ps but annihilates directly with an electron. The spur model¹⁻³ describing Ps formation is based on the knowledge we have of the primary processes occurring in a liquid, as deduced from radiation chemistry results. It also includes the specific properties of e^+ and Ps. This model essentially states that the electrons involved in the formation of Ps are not those that are bound to molecules, but the quasifree ones that originate from the numerous ionization events of the radiation track. The name “spur” refers to the fact that those electrons tend to belong to more or less isolated clusters associated to neighboring ionization events. On that basis, positrons can hardly be studied on their own because their ionizing properties, as stressed above, lead to the concomitant presence of a large number of electrons. The respective effects of each of these particles are therefore intricately entangled.

Nevertheless, one may take advantage of the specific properties of e^+ to improve our knowledge of the electron spur and more particularly of the radiation track ends where the Ps are formed. When looking for a comprehensive model of primary processes in a liquid, the results derived from positron annihilation techniques should be taken into account.

In this paper, we try to join radiation chemistry interests and positron annihilation data to highlight the possible mutual benefits each of these communities could gain from more work done conjunctively. We decided to center this

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study on the possible influence of the thermal electron mobility $\mu(e^-)$ on Ps formation. First, we gather a wide compilation of I_3 data in a number of pure liquids of known $\mu(e^-)$. Second, we present new experimental results on the variation of I_3 with temperature (between the melting point and 294 K) in four liquids, namely, tetramethylsilane (TMS), 2,2-dimethylbutane (2,2-DMB), *n*-hexane, and tetramethylstannane (TMSn). In the first three of those liquids, the possible correlation between I_3 and $\mu(e^-)$ can be examined since measurements of the temperature dependence of $\mu(e^-)$ exist in the literature. For TMSn, this information is not available and we submit our data as an open challenge for further measurements. Finally, we describe the process of Ps formation with Monte Carlo simulation techniques to get some insight on the conditions in which it can occur. In particular, we investigate the respective roles played by different variables of the problem, such as the mean thermalization distances of e^- and e^+ , the thermal mobilities of those particles, and the dielectric constant of the considered medium.

II. EXPERIMENT

Tetramethylsilane, tetramethylstannane, 2,2-dimethylbutane, and *n*-hexane, reagent grade from Aldrich, were used as received, without further purification. For each sample, an ampule containing approximately 4 cm³ of liquid and a 5.55 Bq ²²Na source (β^+ emitter) deposited on a thin glass foil was prepared by due degassing as previously described.⁴ The percentage of positrons emitted by the ²²Na and annihilating in the glass foil instead of in the liquid was 8%. The glass container was sealed under vacuum to avoid oxygen contamination. The cooling system is composed of a liquid-nitrogen container over which the cryostat is fixed. The temperature adjustment is achieved through gaseous exchange and the whole cooling and temperature control process is monitored by a dedicated computer. The temperature was controlled within 0.1 K over all the investigated range.

The lifetime spectroscopy (LS) apparatus is a classical setup, composed of two photomultipliers and scintillators, connected to a basic electronic device, as extensively described elsewhere.⁵ The emission of a positron in the liquid is monitored via the detection of the 1.28 MeV photon which readily follows the β^+ decay of the ²²Na atom, using a traditional Pilot U scintillator and a XP2020 photomultiplier (Philips). The instant of positron annihilation is determined through the detection of one of the two photons emitted at that time. In this case, a BaF₂ scintillator and a XP2020Q photomultiplier (quartz window) have been used to take advantage of the high-energy selectivity of such a scintillator. The low activity of the source ensures the presence of only one positron at a time in the sample. The temporal resolution of the LS setup was 230 ps, as measured as the full width at half maximum of the ⁶⁰Co prompt curve.

The LS spectra were decomposed in a sum of three exponential decays, of relative intensities I_i (in %) and characteristic decay times τ_i , convoluted by the measured apparatus response. These components are ascribed, with increasing subscript i , to the three considered fates of the positron in a pure solvent: the singlet para-positronium (*p*-Ps), the e^+

remaining free (that is, not having formed Ps), and the triplet ortho-positronium (*o*-Ps, with substates $m = -1, 0, +1$). Owing to the rather low value of τ_1 (≈ 125 ps), the lifetime of singlet Ps, no reliable value of both τ_1 and I_1 can be deduced from a LS fit because of inherent correlation of the two parameters that describe the shortest-lived component. Due to the statistical population of the substates of positronium in the temperature range investigated, the ratio I_3/I_1 should be strictly equal to 3. One should note that, in some cases, a slight deviation to this ratio has been evidenced and attributed to the small influence of the medium on the wave function of Ps.^{6,7} However, previous experiments⁸ showed that, in the case of *n*-hexane, this effect gives a ratio of 3.12 and is independent of temperature over a large range. As a consequence, we will consider throughout this study that the value of I_3 corresponds to 75% of the total amount of Ps formed. The LS data will be presented in terms of I_3 , τ_3 , and τ_2 , obtained in a multiparametric fit in which none of the parameters I_i and τ_i were arbitrarily fixed.

III. RESULTS AND DISCUSSION

A. Compilation of data

Among the physical properties of the liquids that may influence the formation of Ps, Jansen and Mogensen⁹ have suggested that the thermal electron mobility $\mu(e^-)$ could be a determinant one. This assumption relied on a comparison of 12 solvents, for which these authors reported a "strong correlation" between I_3 and $\mu(e^-)$. A priori, the mobility of the electron has to play a role in Ps formation because of the necessity of a $e^+ - e^-$ encounter. However, this correlation might be more intricate than originally envisioned. In this paper, we extend the comparison to a wider range of liquids and point out the difficulties in reaching a clear conclusion on this subject.

Table I presents a new compilation of I_3 and $\mu(e^-)$ obtained at room temperature for 51 pure liquids.⁹⁻³⁰ The same data can be visualized in Fig. 1, along with the values reported by Jansen and Mogensen.⁹ A first glance at Fig. 1 seems to confirm the previously reported correlation. However, if one makes a distinction between low-, intermediate-, and high-mobility solvents, the existence of a universal correlation between I_3 and $\mu(e^-)$ becomes questionable. For e^- mobilities below $\sim 4 \times 10^{-3}$ cm² V⁻¹ s⁻¹, I_3 is approximately constant and equal to $\sim 23\%$. For $\mu(e^-)$ between 4×10^{-3} and 1 cm² V⁻¹ s⁻¹, the values of I_3 are larger ($\sim 40\%$) but remain rather independent of $\mu(e^-)$. A continuous positive correlation between I_3 and $\mu(e^-)$ appears only above 1 cm² V⁻¹ s⁻¹, that is, for high-mobility solvents. This last observation echoes the well-known relation between the free-ion yields and $\mu(e^-)$ in high-mobility solvents.¹⁰

One should note that the absence of correlation in the case of polar solvents can be understood in the framework of the spur model describing Ps formation. In fact, following this model, positronium is formed either with quasifree or with weakly trapped electrons,²⁷ but not with fully solvated electrons.^{31,32} Therefore, there is no reason to observe any correlation between the *solvated* electron mobility (the only

TABLE I. *o*-Ps formation probability I_3 and thermal electron mobility $\mu(e^-)$ in a variety of pure liquids.^a

Liquid	I_3 (%)	$\mu(e^-)$ (cm ² V ⁻¹ s ⁻¹)	References
Tetramethylsilane	59.0 ^b	102	10, 11
Tetramethylstannane	56.5 ^b	75	10, 11
2,2-dimethylpropane (neopentane)	52.5	69.5	10, 12
2,2-dimethylbutane (neohexane)	46.1 ^b	12	10
2,2,4-trimethylpentane (isooctane)	42.4	6.5	10, 12–14
2,3-dimethylbutene-2	43.7	6	10, 15
<i>cis</i> -butene-2	49	2.2	9, 10
2-methylpentane	36.5	0.29	10, 15
Cyclohexane	38.1	0.28	10, 12, 16
3-methylpentane	37.1	0.2	10, 15
1,3,5-trimethylbenzene (mesitylene)	46	0.17	10, 12
<i>n</i> -pentane	41	0.154	10, 12
Benzene	43.5	0.125	10, 12–14, 17
<i>cis</i> -decalin	33.6	0.1	10, 18
Methylbenzene (toluene)	42.6	0.075	10, 12, 13
<i>n</i> -hexane	41.8 ^b	0.074	10
1,3-dimethylbenzene (<i>m</i> -xylene)	45	0.071	10, 12, 19
1,4-dimethylbenzene (<i>p</i> -xylene)	45	0.066	10, 12
Methylcyclohexane	41	0.057	10, 12
<i>n</i> -heptane	41	0.051	10, 20
<i>trans</i> -butene-2	45	0.029	9, 10
<i>n</i> -decane	39.6	0.025	10, 12
1,2-dimethylbenzene (<i>o</i> -xylene)	44	0.021	10, 12, 19
1,2,3,4-tetramethylbenzene	46	0.02	10, 12
<i>n</i> -dodecane	38	0.02	10, 12
<i>n</i> -tetradecane	36	0.016	10, 12
<i>trans</i> -decalin	37.3	0.013	10, 16
Hexafluorobenzene	51	0.011	10, 12
Diethyl ether	32	0.0086	12, 21
Carbon disulfide	44	0.0078	12, 13, 22
Tetrahydrofuran (THF)	29.3	0.0067	21, 23
Triethylamine	42.9	0.0045 ^c	23, 25
<i>n</i> -butylamine	29.9	0.0027	15, 21
<i>N,N</i> -dimethylformamide	18.2	0.0023 ^c	26
Hexamethylphosphoric triamide (HMPT or HMPA)	27.5	0.0021	21, 27
Tributylamine	35.3	0.002	15, 21
<i>N,N</i> -dimethylacetamide	22.6	0.002 ^c	28
Water (H ₂ O)	28	0.001 91	12, 21
Deuterium oxide (D ₂ O)	23	0.001 51	12, 21
Dimethylsulfoxide (DMSO)	14.3	0.0011 ^c	20, 27
1,4-dioxane	53.5	0.0009	12, 14, 21
1-butanol	23.4	0.000 75	12, 21
Methanol	22	0.000 62	21, 29
2-propanol	22.1	0.000 51	15, 21
1-propanol	22.9	0.000 46	12, 21
Ethanol	22	0.000 37	12, 21
1-octanol	24.5	0.000 36 ^c	12
1,2-ethanediol (ethylene glycol)	22.3	0.000 28	21, 29
1,3-propanediol	22.2	0.000 083 ^c	29
Cyclohexanol	26	0.000 063 ^c	9, 21
1,2,3-propanetriol (glycerol)	24	0.000 007 5	21, 30

^aSelected values are for room temperature. The different liquids are listed in the order of decreasing $\mu(e^-)$.

^bPresent work.

^cEstimated from the empirical relation $\mu(e^-)$ (in cm² V⁻¹ s⁻¹) = C/η^p , where η (in centipoise) is the viscosity of the solvent, $C = 1.92 \times 10^{-3}$, and $p = 0.84$ (see Ref. 24).

FIG. 1. Variation of the *o*-Ps formation probability I_3 with the thermal electron mobility $\mu(e^-)$ (in cm² V⁻¹ s⁻¹) in a variety of liquids at ambient temperature. ○: values given in Table I; ■: values reported in Ref. 9 and on which the idea of a I_3 vs $\mu(e^-)$ correlation was originally based. The vertical dotted lines define three ranges of $\mu(e^-)$ in which I_3 has specific behaviors (see text). Those divisions, which are based on a visual inspection of the present compilation, are essentially phenomenological. One can note that the intermediate group [$4 \times 10^{-3} < \mu(e^-) < 1$ cm² V⁻¹ s⁻¹], which consists mainly of nonpolar liquids, also includes some weakly polar solvents that display similar properties as far as Ps formation is concerned.

one to be measured in polar liquids) and the Ps formation yield. As for the absence of correlation between I_3 and $\mu(e^-)$ among the low-mobility nonpolar solvents, it indicates that the factors determining the yields of Ps formation are not necessarily the same for all the considered liquids. It is important to realize here that in comparing the values of I_3 for different liquids at a given temperature, $\mu(e^-)$ is not the only parameter which is varied. Various other physicochemical properties which could influence the formation of Ps are specific for each liquid. One can think, for example, of the dielectric constant of the medium, the related Onsager radius, the solvent density, and the mean thermalization distances of e^- and e^+ .

In order to overcome this intrinsic limitation of solvent-to-solvent comparisons, Mogensen and co-workers³³ also studied the influence of temperature (T) on I_3 in a single solvent, neopentane, to assess more firmly the bases of the foreseen correlation. From their study, ranging from the melting point of neopentane up to its critical temperature, the idea of a I_3 vs $\mu(e^-)$ correlation was reinforced by the fact that the variation with temperature of those two quantities displayed some similarities. However, one should keep in mind that, even in a given liquid, $\mu(e^-)$ is not the only physical property that varies with T . The lack of theoretical background stopped any further attempts of these authors to handle the problem.

At this stage, two remarks are in order:

(i) The dependence of I_3 on the physicochemical parameters of a given liquid is obviously a multiparametric problem, and temperature does not appear to be a “good” parameter, because all other quantities vary along with it. Some variations are small, such as that of the dielectric constant ϵ , and some are important, such as that of the density. Therefore, in such a case, the Ps formation yield in a given liquid might not appear to be dependent on ϵ , whereas density would seem to be strongly correlated to I_3 . Under these

FIG. 2. Variation with temperature of the *o*-Ps formation probability I_3 in tetramethylsilane (TMS), tetramethylstannane (TMSn), 2,2-dimethylbutane (2,2-DMB), and *n*-hexane.

conditions, the joint variation of two parameters with T must be examined with caution before concluding to the existence of any physical correlation. As an example of correlations to be examined with caution, note the work of Gee and Freeman,²² who also mentioned the I_3 vs $\mu(e^-)$ correlation first stated by Mogensen, and added the correlation of τ_3 with $\mu(e^-)$. They pointed out that this observation was offered “without interpretation.” In fact, the annihilation process of *o*-Ps whose characteristic time is τ_3 , is a nuclear phenomena occurring on the nanosecond time scale and sensitive mainly to the electronic density of the medium. This annihilation predominantly occurs with one of the outer electrons of the molecules surrounding Ps (the so-called pick-off process) and there are no basic physical reasons that could explain a direct causal relation between $\mu(e^-)$ and τ_3 .

(ii) In the specific case of neopentane,³³ it can be noted that both I_3 and $\mu(e^-)$ level off a few tens of degrees before the critical point, but the ranges of T values in which these quantities remain constant do not coincide exactly. In our opinion, this is evidence that I_3 does not depend solely on the value of $\mu(e^-)$. Thus in order to get an improvement of our knowledge of the intricate process of Ps formation, one has to handle the whole problem together.

B. New data

Taking into account the previous remark about the multiparametric aspect of the problem, we chose to focus on three liquids (TMS, 2,2-DMB, and *n*-hexane) for which the literature provided a good deal of information on the temperature dependence of density, electron thermalization distance, and $\mu(e^-)$. Figures 2–4 show the variation with T of I_3 , τ_2 , and τ_3 , respectively, in these three liquids and in TMSn, a solvent for which much less information is available. In the case of *n*-hexane, the values of I_3 above 294 K shown in Fig. 2 are taken from a previous study,⁸ where I_3 was measured from 264 K up to 338 K. The two sets of measurements are in agreement in the overlapping temperature range. As can be seen from Fig. 2, the four liquids studied could be separated into two distinct groups. On the one hand, the I_3 values in TMS and TMSn are large and decrease slightly with T . On the other hand, the I_3 values in

FIG. 3. Variation with temperature of the lifetime τ_2 (in ps) of the free positron in tetramethylsilane (TMS), tetramethylstannane (TMSn), 2,2-dimethylbutane (2,2-DMB), and *n*-hexane.

2,2-DMB and *n*-hexane are smaller and increase with T . One can note that the temperature dependence is more pronounced in the second group than in the first one. This distinction between two groups is less clear, but still visible, in the τ_2 values, as illustrated in Fig. 3. In TMS and TMSn, our values of τ_2 are rather high, as compared to those found in most solvents,³⁴ but are in agreement with another determination for TMS.³⁴ In contrast to what was seen in Figs. 2 and 3 concerning a possible classification of the four solvents into two groups, Fig. 4 displays no such grouping of the data. For instance, TMS and TMSn, presenting similar high I_3 and τ_2 values, are the most different of our four liquids in terms of their τ_3 values. In all cases, we find that τ_3 increases monotonically with T , a phenomenon usually observed, which is attributed to a decrease in density.²⁸

When comparing the variation with T of I_3 in *n*-hexane and in 2,2-DMB to that of $\mu(e^-)$ in the same liquids,^{35,36} we find that both I_3 and $\mu(e^-)$ display a rather steady increase.³⁷ This similarity of temperature dependence of those two quantities supports the observation that was made by Jacobsen *et al.*³³ in neopentane. In TMS, however, the situation is quite different. In fact, as can be seen in Fig. 5, $\mu(e^-)$ passes through a minimum around 260 K in this high-mobility liquid,³⁸ whereas I_3 appears to decrease monotonically in the temperature range investigated. This result sug-

FIG. 4. Variation with temperature of the lifetime τ_3 (in ns) of the *o*-Ps in tetramethylsilane (TMS), tetramethylstannane (TMSn), 2,2-dimethylbutane (2,2-DMB), and *n*-hexane.

FIG. 5. Variation with temperature of the *o*-Ps formation probability I_3 and of the thermal electron mobility $\mu(e^-)$ (Ref. 38) in tetramethylsilane.

gests that I_3 does not depend solely on the value of $\mu(e^-)$. In view of the fact that the variations of $\mu(e^-)$ and I_3 involved in this comparison are rather small, it would be useful to extend the measurements of I_3 to higher temperatures in order to further substantiate this conclusion.

C. Monte Carlo simulations

1. General approach

In order to interpret the observed temperature dependence of I_3 and its variation from one solvent to another, we use Monte Carlo simulation techniques to describe the fate of quasifree positrons in the tracks that they generate in a liquid. The reason for resorting to a numerical approach rather than to an analytical one lies mainly in the complexity of the problem at hand. In fact, as was explained above, a number of factors influence the probability that the e^+ encounters one of the quasifree e^- that it creates by ionizing the surrounding medium. Moreover, many of those factors cannot be quantified from direct measurements or from first principles, especially those related to the transport properties of e^+ . We are thus led to conduct a *sensitivity* study that consists of assessing the role played by various physical quantities in the observed temperature dependence of I_3 .

The probability of Ps formation is essentially determined by the competition between three processes: the encounter of e^+ and e^- , the recombination of the geminate pair (e^-, S^+), and the first-order decay of e^+ due to its annihilation with a *bound* electron of the medium. Since Ps formation is thought to occur at the end of the primary e^+ track, it would be quite unrealistic to disregard the relative proximity of the energy deposition events in this region.³⁹ As was done in a similar Monte Carlo simulation study of Ps formation,⁴⁰ we found it important to include more than one (e^-, S^+) pair in our modeled spur. This multi-ionization nature of the spur is determined by a comparison of the most probable thermalization distances b_{e^-} and b_{e^+} to the average distance D between neighboring ionization sites. The parameters of the model are thus: (i) the thermalization distance distribution of both e^+ and e^- , (ii) the average distance D between successive ionizations in the track end, (iii) the thermal mobility $\mu(e^+)$ and $\mu(e^-)$ of those two particles (the mobility of the cation S^+ is generally negligible), (iv) the dielectric constant which

affects the strength of the Coulombic interactions in the medium, and (v) the characteristic decay time τ_2 of the e^+ .

2. Simulations

The first stage of a simulation run consists of generating a set of initial positions for a single thermalized e^+ as well as for the cations S^+ and the thermalized e^- that lie in the e^+ track end. The thermalization of e^- and e^+ does not have to be explicitly simulated here since b_{e^-} and b_{e^+} can be stochastically sampled from the Gaussian distributions that were obtained for e^- from previous free-ion-yield studies.^{41,42} One should note that the trajectories of the thermalizing e^+ and e^- are essentially independent of each other because the average kinetic energy of those "hot" particles (~ 2 eV) is much larger than the potential energy associated to their mutual interaction. Moreover, since many scatterings are involved in the thermalization process, the geometry of the positions of the species is independent of the angle at which the electron is ejected during the ionization of S by e^+ . For simplicity, we fix the geometry of the track end as consisting of a linear string of N_i equidistant ionization sites where the cations S^+ remain immobile and from which the electrons start the random walk that leads to their progressive thermalization. In the model considered here, the thermalization process for the e^+ is assumed to start from the last one of those ionization sites.

In the second stage of the simulation, the Brownian motion and encounters of those thermalized species is followed with a step-by-step procedure^{43,44} until the fate of the e^+ is determined. The simulation of the motion of the particles is performed with a Monte Carlo code that decomposes the trajectory of the N_i electrons and of the e^+ into a series of stochastically sampled relaxation times during which the "free paths" of the particles are determined classically, accounting for the net Coulomb field experienced by the charges. To take into account the dynamic nature of the electric field (since the whole set of charges is continually moving), the relaxation times are subdivided into smaller time intervals of the order of 10^{-15} s. The distribution of relaxation times is exponential and its average value is directly proportional to the mobility of the particle.⁴⁴ The free paths are interrupted by isotropic scatterings during which the scattered particle sees the direction and the module of its velocity redetermined through a sampling procedure that respects Boltzmann's distribution for the temperature of the medium.

The reactions of the pairs (e^+, e^-) and (e^-, S^+) are assumed to be diffusion controlled. The encounters of the reactive species are considered to occur when their separation becomes smaller than a predefined reaction radius of the order of 0.5 nm. The dielectric constant being close to 2 for the solvents studied here, the (negative) energy of the field dominates the thermal kinetic energy for separations up to a few tens of nanometers and one can show that the actual choice of the reaction radius is not critical. The simulations were achieved up to times of ~ 500 ps, after which the probability of Ps formation is negligible. Typically, a thousand runs were necessary to obtain an uncertainty of 1% on the calculated values of I_3 .

As a verification of the validity of our simulation code and its algorithm, we studied the motion of electrons in an external electric field $\mathbf{E}$, as well as the geminate recombination of a single (e^-, S^+) pair. In the former case, the variation of the simulated drift velocity $\mathbf{v}$ of the electrons with $\mu(e^-)$ followed the expected relation $(\mathbf{v} = \mu\mathbf{E})$.⁴⁴ In the latter case, we compared the simulated free-ion yields to those predicted by the Onsager theory⁴⁵ for different initial separations and the agreement was always excellent in the range of applicability of the theory.⁴⁶

3. Results and interpretation

In order to anchor our sensitivity study to the actual measurements of I_3 , we started from the case of ambient 2,2-DMB, a solvent in which $\mu(e^-) \sim 10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ is low enough to avoid problems related to the breakdown of the Onsager recombination theory,⁴⁶ and large enough to ensure that electrons are quasifree and undergo very little transient trapping.⁴⁷ Assuming, for simplicity, that the transport properties of e^+ in 2,2-DMB (which are totally unknown) are the same as those of e^- , we found a good agreement between the simulated I_3 value and the experimental one (46%) at ambient temperature if the mean distance D between successive ionizations in the e^+ track end is $\sim 16.5 \text{ nm}$. The average formation time of Ps was found to be $\sim 18 \text{ ps}$, a value which is compatible with the fast rise of the signal in the γ -emission measurements.

The systematic variation of the parameters of our simulations led to the following main observations.

(i) The multi-ionization nature of the spur is important since only half of the Ps formation could be accounted for by the encounter of e^+ with the last e^- of the track end. Yet the whole positron track structure does not have to be incorporated in the model since 95% of the Ps involved one of the last five electrons out of the twenty $e^- - S^+$ cation pairs considered in our simulations. The values of I_3 increase with decreasing interionization distance D since it provides more possibilities for the $(e^+ - e^-)$ encounters.

(ii) I_3 increases with the mean thermalization distance b . For example, with $\mu(e^+) = \mu(e^-) = 10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, I_3 varies from 43% to 47% when the most probable thermalization distance of e^- and e^+ is brought from 6 to 12 nm. These two b values correspond to those found in the literature for n -hexane⁴² and 2,2-DMB,⁴¹ respectively, and are thus typical. The dependence of I_3 upon b can be attributed to the multi-ionization nature of the studied spur. In fact, an increase in b affects predominantly the $e^- + S^+$ recombination (as opposed to the $e^- + e^+$ encounter) since the initial separation between the e^+ and the various e^- also includes the fixed distance D between the successive ionization sites. Simulations performed on single-ionization spurs ($D \rightarrow \infty$) showed that a change in b affects about equally the two competing processes and does not influence I_3 significantly.

(iii) I_3 increases logarithmically with the thermal electron and positron mobilities. Fixing b at a value of 6 nm, we found that I_3 increases from 35% to 43% when both $\mu(e^-)$ and $\mu(e^+)$ were brought from 0.1 to $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. For the intermediate value of $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, the simulated I_3 was 39%. This variation of I_3 with the mobility can be in-

terpreted in terms of the competition between Ps formation and the first-order decay of the quasifree e^+ . In fact, a change in the mobility does not affect the ultimate probability of recombination of a given pair of charges but modifies its kinetics. At the lowest mobilities considered here, the Ps formation occurs over a few tens of picoseconds and the decay of the e^+ whose characteristic time τ_2 is of the order of 450 ps in n -hexane (see Fig. 3) is sufficiently competitive to reduce I_3 by a few percents. This effect is found to be negligible for mobilities above $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

(iv) The role of the temperature as an explicit variable, as opposed to its influence on μ and b which, in turn, affects I_3 , is mainly to counterbalance the potential energy of the Coulomb field. In this respect, a change in temperature is equivalent to a variation of the dielectric constant of the solvent. A lower temperature therefore leads to a larger recombination probability for a pair of charged reactants. This effect is particularly important for the (e^-, S^+) pairs which are less separated than the (e^-, e^+) pairs. The simulations thus show that I_3 decreases with decreasing T . One must also consider the influence of the temperature on the kinetics of the encounters. In fact, the rate of encounter of the reactants depends on their diffusion coefficients which are related to the product of their mobility with temperature. As was the case when the mobility was reduced (with T kept constant), the sole lowering of T causes a slowing-down of the nonhomogeneous chemistry and, in turn, favors the first-order decay of the e^+ in the liquid. As a consequence of the combination of those two effects, the simulations exhibit a slight reduction (of $\sim 2\%$) of I_3 when T is lowered from 293 to 213 K.

From this discussion, one can grasp the complexity of the factors that cause the variation of I_3 which is observed experimentally when the temperature is lowered for a given liquid. The cooling simultaneously changes many relevant physical parameters, such as b_{e^-} , b_{e^+} , $\mu(e^-)$, $\mu(e^+)$, the dielectric constant, and the decay time τ_2 . Based on the important assumption that the transport properties of e^+ are similar to those of e^- , our simulations suggest that, in 2,2-DMB and in n -hexane, the observed variations of I_3 with T are mainly caused by its dependence on $\mu(e^-)$ and $\mu(e^+)$ that was explained above. The value of b_{e^-} does not vary by more than $\sim 10\%$ for a given liquid; it follows approximately the variation of the inverse of the density with T .⁴¹ As for the variation of I_3 from one liquid to another at room temperature, it seems to result mainly from a change in the thermalization distances of e^- and e^+ (for example, $b_{e^-} = 12.3 \text{ nm}$ in 2,2-DMB and 6.2 nm in n -hexane).^{42,43} The differences in the thermal mobilities of e^- and e^+ in those two liquids also contribute to a change in I_3 .

One should note that our simulations with low mobilities were meant to show the influence of this parameter on I_3 . They may not provide a satisfying description of Ps formation in n -hexane since the e^- transport in this liquid is known to involve transient trapping³⁵ and since very large values of $\mu(e^+)$ (8.5 and $100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) can be found in the literature.^{48,49} A preliminary study of the situation using $\mu(e^+) = 8.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \gg \mu(e^-) = 0.065 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ is underway and suggests that the measured I_3 can be repro-

duced with the simulations if a most probable thermalization distance of ~ 12.5 nm is chosen for e^+ , that is, a value which is twice as large as that of b_{e^-} . This clearly illustrates that the reproduction of the experimental I_3 results does not determine a unique set of physical properties for the composition of the spur and for the transport properties of the positron.

If we consider higher mobility liquids, such as neopentane and TMS, the simulations show that I_3 should again increase due to the longer thermalization distances. The explicit influence of $\mu(e^-)$ and $\mu(e^+)$ were found to be small due to the very short Ps formation time (with which τ_2 cannot compete) and to the breakdown of Onsager's recombination theory⁴⁶ that occurs at high mobilities and restrains the probability of an $e^- - e^+$ encounter. Our simulations did not allow us to reproduce the large values of I_3 ($> 50\%$) which are observed. Perhaps other factors should be included in the simulations, such as the complex structure of the positron track end or a significant difference between the transport properties of e^- and those of e^+ .

Finally, the case of Ps formation in polar liquids is worth mentioning. For those solvents, a very fast process competes with the encounter of e^+ and e^- , namely, the trapping of those two types of particles. We found that the low values of I_3 observed in those liquids ($\sim 23\%$) could be well explained with our model if we take a trapping time of the order of a few hundreds of femtoseconds, in excellent agreement with various experimental determinations of this time.^{50,51} This result supports what was stated in Sec. III A on this issue, that is, the low values of I_3 in polar solvents are not caused by the low mobilities of the solvated e^+ and e^- .

IV. CONCLUSIONS

We have reexamined the proposed correlation between I_3 and $\mu(e^-)$ in liquids along two ways. First, we presented a compilation of I_3 and $\mu(e^-)$ values measured at ambient temperature for 51 different pure liquids. This compilation showed that the (low-mobility) polar liquids constitute a distinct group that displays small values of I_3 . It also showed that, for nonpolar solvents, a positive correlation between I_3 and $\mu(e^-)$ is only apparent among the highest mobility liquids. Second, we measured I_3 as a function of temperature in three solvents (TMS, 2,2-DMB, and *n*-hexane) covering a wide range of e^- mobilities. In *n*-hexane and 2,2-DMB, the temperature dependence of I_3 and $\mu(e^-)$ are found to be similar. The fact that this is not the case for TMS may be related to the very large $\mu(e^-)$ values in this liquid. It remains unclear, however, why its behavior contrasts with that of neopentane.³³ Finally, we used Monte Carlo simulation techniques to perform a sensitivity study on the influence of various physical parameters on Ps formation. In the light of those simulations, the problem clearly appears as being multiparametrical. We find, in particular, that the thermalization distances of e^+ and e^- may constitute the most significant physical parameters influencing Ps formation and that their role relies on the multi-ionization nature of the positron track

end. An extension of this kind of work to higher temperatures (up to the critical point) is expected to bring further insight on this question.

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