POSITRON SCATTERING AND ANNIHILATION IN ORGANIC MOLECULES*

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In this paper, we address the problem of connecting positron lifetimes in liquids with collision cross sections in gases. We present the analyses of annihilation lifetime spectra of positrons in the liquid benzene, c-hexane, n-hexane, methanol and ethanol and calculations of scattering cross sections of positrons with benzene and c-hexane in the gas phase.

1. Introduction

Medical applications of positrons, particularly in the view of rapid all-body PET scans [1, 2], require a deeper knowledge of positron annihilation in liquid media. Formerly performed measurements [3] of 167 organic liquids were focused on the third, *i.e.* the longest lifetime component, in the range of few ns, that is attributed to the annihilation of ortho-Ps (o-Ps). Apart from understanding the fall of lifetimes with rising the dipole moment in polar solvents, *cf.* [4], annihilation in liquids still requires more detailed research. It is also a well-known phenomenon that the presence of air (and to a greater extent the saturation by oxygen [5, 6]) leads to quenching of the o-Ps lifetime. Experiments [7] on magnetic quenching of τ_3 in liquids proved to be a method for deriving the contact density between a positron bound

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in o-Ps and electrons of the medium. A very recent theoretical approach [8] opened new perspectives for the analysis of lifetimes in liquids: the contact density can be obtained directly from lifetime measurements, without the use of the magnetic quenching method. The new theories for positron interaction with molecules in gas phase [9] make the understanding more clear by bridging the gap between annihilation and scattering cross sections. In this paper, we follow the research line presented in [10].

2. Lifetime measurements

The positron annihilation lifetime spectra (PALS) were measured using the fast–fast coincidence ORTEC PLS system equipped with plastic scintillators (St. Gobain BC418) and RCA 8850 photomultipliers [11]. The prompt time resolution of the system was 180 ps in full width at half maximum (FWHM). The positron source ^{22}Na with activity 5 μCi was tightly sealed in 7 μm thick envelope made of Kapton foil. The source was immersed in studied liquids placed inside the vacuum chamber pumped by Varian DS 42 Dual Stage Rotary Vane Pump. The temperature of the chamber was controlled by a Peltier cooler.

The analysis of lifetime spectra was done with the LT-9 program [12]. In all samples, we assumed three lifetime components: the short one of about 125–200 ps attributed to para-Ps (p-Ps) formation (τ_1), the second due to the annihilation of free positrons τ_2 (like in solids), and the third one due to o-Ps formation τ_3 decay. The source correction due to the positron absorption in the Kapton envelope was $I_s = 10\%$ and $\tau_s = 380$ ps.

3. Theory for elastic cross sections

Very few calculations of cross sections for collisions of positrons with organic molecules (in the gas phase) have been published. In this paper, we present computations of elastic cross sections based on positron collisions with two different solvent molecules, benzene and c-hexane. For positron collisions with benzene, elastic cross sections have been calculated previously by Occhigrossi and Gianturco [13], and recently by Franz and Franz [9]. Furthermore, Fedus [14] employed the MERT method to analyse the cross sections for these two compounds.

In the present study, we also used the molecular R-matrix method for positron scattering [15]. The impinging positron and the bound electrons are strongly correlated due to their mutual attraction. It is computationally very demanding to solve the many-particle Schrödinger equation for strongly correlated systems with *ab initio* methods. An alternative is provided by semi-empirical methods. According to the study by Franz *et al.* [16], a

semi-empirical scaling factor f can be introduced, which scales the electron–positron attraction integrals inside of the R-matrix sphere. Franz and Franz [9] obtained good agreement between the computed and experimental cross sections for positron scattering from benzene by adjusting the scaling factor in such a way that the lowest R-matrix pole matches the energy of the Feshbach resonance, which has been observed in annihilation experiments by group in San Diego [17]. In the present study, the lowest R-matrix pole for benzene is shifted to 150 meV (using $f = 1.003688$) and for c-hexane to 80 meV (using $f = 1.003262$) in accordance with values for the Feshbach resonances given by Gribakin *et al.* [17]. All scattering calculations were done with the UK molecular R-matrix codes of Gillan *et al.* [18], using the modifications described in Franz and Tennyson [15] and Franz *et al.* [16]. The R-matrix box is a sphere with a radius of 13 Bohr. The electronic wave functions of the target molecules are computed with the Hartree–Fock method using the DZP basis set of Dunning and Hay [19].

4. Positron lifetimes

In our previous analysis [6] for benzene, c-hexane and methanol, we fixed the p-Ps lifetime τ_1 at 125 ps and the $I_3 : I_1$ ratio at 3 : 1. That choice influenced quite little τ_3 and I_3: obtained results were close to those from comprehensive comparisons in Ref. [4].

The recent theory by Marlotti Tanzi *et al.* [8] predicts that in the presence of matter, the p-Ps lifetime rises with shortening o-Ps lifetime, being in some sense, for a constant electron density, in the inverse proportion to o-Ps lifetime (see Fig. 4.9 in Ref. [20]). In other words, this theory allows to obtain the contact density directly from lifetime experiment, once both the τ_1 and τ_3 are determined. So, in the present analysis, we did not make any constraints either on τ_1 or on the $I_3 : I_1$ ratio.

Results of the present analysis (at a chosen temperature of 20°C) are summarized in Table I. In all five solvents, the third lifetime were similar. Differently from non-polar molecules, in alcohols, the intensities of positronium formation (and decay) are much smaller: the summed intensity $I_1 + I_3$ is about 40% in alcohols and about 66% in the studied hydrocarbons.

In the hydrocarbons, the second lifetime components τ_2 were about 0.49 ns and in alcohols about 0.45 ns, see Table I. Large differences in the lifetime τ_1 can be found among the three hydrocarbons, which are changing from 0.144 ns in benzene to 0.210 ns in c-hexane. Combined with the values of τ_3, this difference in τ_1 indicates different electron densities in the virtual cavities around Ps: a rough evaluation from Fig. 4.9 of Ref. [20] gives the electron density of about $\rho_e = 0.1k_0$ for c-hexane and $\rho_e = 0.5k_0$ for benzene. We will compare these values with total cross sections in the gas phase.

TABLE I

Positron lifetimes in various organic liquids. For n-hexane, methanol and ethanol, the lifetime τ_1 has been kept fixed in the analysis.

Molecule	τ_1 [ns]	I_1 [%]	τ_2 [ns]	I_2 [%]	τ_3 [ns]	I_3 [%]	$I_1 + I_3$ [%]
benzene	0.144 ±0.009	26.6 ±0.8	0.490 ±0.010	33.7 ±0.8	3.17 ±0.2	39.7 ±0.7	66.3 ±1.5
c-hexane	0.210 ±0.009	27.7 ±0.7	0.499 ±0.008	36.1 ±0.7	3.25 ±0.2	36.3 ±0.6	64.0 ±1.3
n-hexane	0.290 fixed	54.7 ±0.5	0.903 ±0.013	11.8 ±0.5	3.61 ±0.02	33.5 ±0.5	88.2 ±1.0
methanol	0.150 fixed	17.7 ±0.5	0.448 ±0.007	61.5 ±0.5	3.28 ±0.02	20.8 ±0.4	38.5 ±0.9
ethanol	0.150 fixed	22.3 ±0.4	0.448 ±0.006	57.2 ±0.4	3.00 ±0.02	20.6 ±0.6	42.9 ±1.0

5. Total cross sections

Results of present calculations of total cross sections for positron scattering in gas phase in benzene and c-hexane are shown in Fig. 1.

Experiments on total cross sections in benzene and c-hexane come from two laboratories: Trento, Italy (Karwasz *et al.* [10] and Zecca *et al.* [21]) and Tokyo (Sueoka [22], Makochekanwa *et al.* [23], and Sueoka *et al.* [24]).
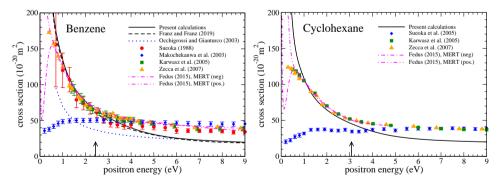

Fig. 1. Present calculations of total cross sections for positron scattering on benzene (left panel) and c-hexane (right panel). Also shown: theory from Franz and Franz [9], Occhigrossi and Gianturco [13], and MERT calculations from Fedus [14]; experiments: from Trento (Karwasz *et al.* [10] and Zecca *et al.* [21]) and from Tokyo (Sueoka [22], Makochekanwa *et al.* [23] and Sueoka *et al.* [24]). The thresholds for Ps-formation are marked with an arrow (in benzene: $E_{\mathrm{Ps}} = 2.45$ eV, in c-hexane. $E_{\mathrm{Ps}} = 3.08$ eV, using the ionization energies from Bieri *et al.* [25]).

The calculations present in this study regarding both molecules, benzene and c-hexane, agree well with the former experiment from Trento [10, 21] in the range between 1 eV and the threshold for positronium formation (see arrow in the figures). For benzene, our calculation agrees also with the earlier experiment from Tokyo [22]. The upper limit of the convergence between the theory and experiment is clear: the total cross sections comprise the free-Ps formation channel, so it is higher than the present calculations which is only the elastic cross section. The lower limit of the agreement between the theoretical modelling and experimental data is more complex. Moreover, different theoretical approaches diverge below 1 eV. Fedus [14] applied Modified-Effective Range Theory [26] which allows to extrapolate experimental data down to zero energy.

Present calculation (of the elastic cross section) allows to estimate the cross sections for the positronium formation (as the difference from the experimental cross section). At 4 eV, such a difference (see [9]) is about $13 \times 10^{-20}\,\mathrm{m}^2$ in a surprising agreement with the experimental evaluation (about $14 \times 10^{-20}\,\mathrm{m}^2$) by Sueoka [22], who used a high (23 G) magnetic field to confine the scattered positrons. A benzene molecule, as indicated both by the experimental data and the theoretical approach, shows a higher cross sections than c-hexane in the whole energy range considered and, in particular, at low energies: at 1 eV $130 \times 10^{-20}\,\mathrm{m}^2$ and $110 \times 10^{-20}\,\mathrm{m}^2$, respectively, see Fig. 1. The Tokyo measurements [24] were subject to a heavy angular resolution error, as described above. At 5 eV, *i.e.* the lowest-energy point in which two sets [22, 23] from Tokyo start to diverge (see left panel in Fig. 1), n-hexane would have slightly higher cross section ($38.5 \times 10^{-20}\,\mathrm{m}^2$) than c-hexane ($36.1 \times 10^{-20}\,\mathrm{m}^2$), see [24].

6. Conclusions

Present measurements of all three lifetime components in polar and non-polar solvents, combined with the recent theoretical approach [8, 20], gave a rather unexpected result: this may be the first lifetime component that brings the information on the electron density in the virtual void in which Ps is formed ("spur", using the terminology of Mogensen [4]). The electron density in the spur is higher in benzene than in c-hexane. The long-studied third component, τ_3, indicates radii of the spurs in all studied molecules, alcohols included. Following the model by Quasso *et al.* [7], the "cavity" radius would be about 0.4 nm.

The present comparison with cross sections for positron scattering in gas phase suggests that higher contact densities are observed in molecules with higher cross sections. This would be reasonable: the interaction inside the spur is dynamic. Positrons injected into the liquid are first cooled to thermal energies (or at least to energies below the threshold for the positronium

formation) and only then form Ps. In spite of the fragmentary experimental data (and open questions of the theories), benzene shows a higher cross section than c-hexane [10], and ethanol higher than methanol [27]. This dependence is reflected in different contact densities in annihilation, as it results from present comparison of τ_1 and τ_3 values.

More precise experiments, both for positron annihilation in polar and non-polar solvents and for positron scattering in gases, are needed to find a more consistent model in further data analysis.

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