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2015 J. Phys.: Conf. Ser. 618 012029

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# Positron annihilation in benzene and cyclohexane: a comparison between gas and liquid phase

**Kamil Fedus**

Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Grudziadzka 5, 87-100 Torun, Poland

E-mail: [kamil@fizyka.umk.pl](mailto:kamil@fizyka.umk.pl)

**Abstract.** A comparative study about positron annihilation in gas and liquid phases of two non-polar ring molecules: benzene ( $C_6H_6$ ) and cyclohexane ( $C_6H_{12}$ ) is presented including the most recent experimental and theoretical achievements. In addition the preliminary results of positron annihilation lifetime measurements in a liquid phase at room temperature for these two molecules are reported.

## 1. Introduction

The problem of linking the gas-phase and the condensed-phase interactions is one of the most fundamental concepts in physics. The goal is to describe how much the mechanisms of individual interactions present in the gas-phase are distorted and/or retained in the condensed phases. In particular this issue has been raised some time ago [1] by community studying behavior of slow electrons at interfaces of the gaseous and the condensed phases of matter. It is well known that the high-energy electrons, whose wavelength is short in comparison with the "diameter" of the elementary constituents of condensed matter, preserve the unique nature of two-body electron-target interaction present in the gas-phase. This concept is no longer valid at low energies, where the electron wavelength is of the order of the interatomic or intermolecular distances. In this case, the electron interacts collectively with many neighboring atoms and/or molecules and thus the mechanisms of interactions are significantly modified when compare to a pure two-body case.

Nowadays the low-energy electron studies in a gas and condensed phases are quite well developed. On the other hand the attempts to find similar links have been rarely undertaken for an antimatter counterpart – the positron (see pages 121-140 in Ref.[1]). The recent progress in studies on slow positron scattering and annihilation in a gas phase matter combined with a very fast development of positron chemistry focused on the behavior of antielectron in condensed matter, makes possible to construct some first conclusive connections between positron interactions in gas and condensed phases. For example, the latest paper by Zubiga et al.[2] shows that a theory for positron interaction with single atoms can be transferable to the condensed phase. Such study is particularly important in the context of numerical modeling of positron behavior in liquids, solids and living tissues [3] where the gas-phase results can serve as an input data.

The main purpose of the present paper is to shortly describe the current state of the art of the research on low-energy positron interaction with two non-polar ring molecules: benzene

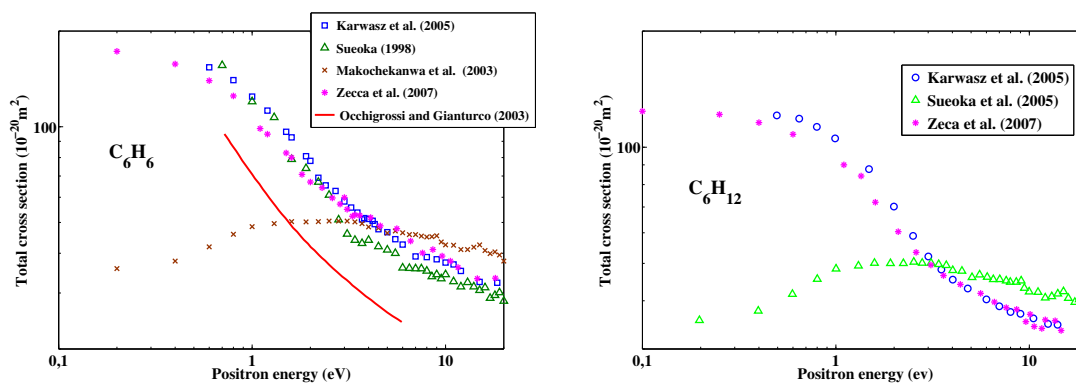


(C<sub>6</sub>H<sub>6</sub>) and cyclohexane (C<sub>6</sub>H<sub>12</sub>) in gas and liquid phases. In addition the preliminary results of positron annihilation lifetime measurements in a liquid phase for these two molecules are reported.

## 2. Gas phase

Recently, a substantial breakthrough in understanding interactions of low-energy positrons with materials in gas phase has been achieved (see for example [4]), where both scattering and annihilation occur. The most recent measurements of total cross sections for positron scattering from atoms and molecules in gas phase show a sharp rise of total cross sections when positron energy goes to zero. This effect has been explained by a dominating long-range polarization interaction at low energies [5]. Furthermore, the increase of the scattering cross sections is accompanied by the enhancement of annihilation rates in the low energy limit. It has been proved by Gribakin [6] that the annihilation rates are directly related to the elastic scattering cross sections in thermal energy range for simple targets such as noble gases and small molecules. However the situation appears to be much more complex for large molecules such as benzene (C<sub>6</sub>H<sub>6</sub>) and cyclohexane (C<sub>6</sub>H<sub>12</sub>).

Fig.1 shows all available experimental and theoretical data of total cross sections (TCS) for positron scattering from C<sub>6</sub>H<sub>6</sub> and C<sub>6</sub>H<sub>12</sub> near and below the positronium formation threshold. The experimental results were obtained using two positron beam systems: from Trento University in Italy (Karwasz et al.[7], Zecca et al.[8]) and from Yamaguchi University in Japan (Sueoka [9], Makochekanwa et al.[10]). Note that the Yamaguchi group reported two completely different datasets for benzene. The older cross-sections (1988) by Sueoka [9], obtained with very low magnetic field applied in scattering region to guide the positron beam, are in quite good agreement with both results from Trento. Whereas a more recent dataset (2003) by Makochekanwa et al.[10], obtained with much higher magnetic field, largely underestimates the cross-sections in the low energy limit. The same effect is also valid for c-hexane data by Sueoka et al.[11]. Both datasets from Trento, Karwasz et al.[7] (2005) and Zecca et al.[8] (2007), are similar - the small difference comes from different energy scaling in both experiments.



**Figure 1.** Total cross-sections for positron scattering on benzene (C<sub>6</sub>H<sub>6</sub>) and cyclohexane (C<sub>6</sub>H<sub>12</sub>). Experimental data are from Karwasz et al. [7], Sueoka et al. [9, 11], Makochekanwa et al. [10] and Zecca et al. [8]. Theory from Occhigrossi and Gianturco [13] is also presented.

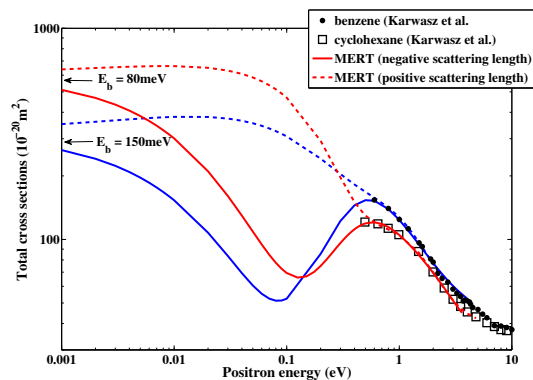
Experimental TCS for benzene are higher by about 20-30% when compare to data for c-hexane at around 1eV. However the measurements of positron binding energies carried out by Surko and co-workers using positron trap techniques [6] show that the zero-energy cross-sections ( $\sigma(E = 0)$ ) are exactly in an opposite relationship. To visualize this reversal of TCS (see Fig.2) in low energy range for both molecules, the experimental cross-sections by

Karwasz et al.[7] have been extrapolated down to zero energy using a simple model based on the Modified Effective Range Theory (MERT, see for more details [5]). Unlike in our previous paper on this subject [12], here both negative and positive scattering lengths  $A = \pm 9.52a_0$  and  $A = \pm 13.04a_0$  are assumed for benzene and c-hexane, respectively. The latter were determined from relation  $E_b = 1/2A^2$  [6] (atomic units) using experimental positron binding energies ( $E_b = 150$  meV and 80 meV for  $C_6H_6$  and  $C_6H_{12}$ , respectively) and they were used to calculate the zero-energy cross sections from  $\sigma(0) = 4\pi A^2$ . The results of extrapolation are shown in Fig.2. It is clear that regardless the sign of the scattering length, the cross sections for c-hexane are larger than for benzene in the thermal energy range,  $E < 100$ meV, where the annihilation process is highly probable. Note however that MERT extrapolation has to be treated as a rough approximation since the model considers only elastic scattering neglecting the contribution of the inelastic processes related to vibrational excitations. Experimentally determined annihilation rates (thermally averaged) at room temperature expressed by a dimensionless quantity  $\langle Z_{eff} \rangle$  [6] indicate higher annihilation rates for positron interaction with c-hexane ( $\approx 20000$ ) than with benzene ( $\approx 15000$ ). This is qualitatively consistent with MERT-derived cross-section in thermal energy range - in analogy to noble gases and small molecules: higher cross-sections are followed by larger annihilation rates [6]. However the measured annihilation rates in hydrocarbones are few order of magnitude larger than the corresponding coefficients in simpler targets. Energy-resolved positron trap [6] experiments show an appearance of numerous resonances in the annihilation at thermal and sub-thermal energies, which are attributed to the Feschbach resonances associated with low vibrational modes of C-H bonds [6]. Hence in the case of large molecules the annihilation rates at room temperature should be a function of both, elastic and vibrational cross-sections. However no *ab initio* calculations have been done so far to prove this prediction.

### 3. Liquid phase

Positrons implanted into the condensed matter are quickly slowed down to the thermal energies by inelastic processes. Then they diffuse through the material interacting with the environment before being eventually annihilated. The main difference when compared to a gas phase is related to the Ps formation. In liquids the mechanisms responsible for this process are much more complicated than in gases where a simple Ore picture is valid [14]. Different theories including the modified Ore, spur and blob models, have been proposed to explain the results of annihilation experiments in condensed matter. The comparison of these models is out of the scope of this paper and it can be found elsewhere (see for example Refs.[14, 15] and references therein).

We measured the positron annihilation lifetime spectra for both  $C_6H_6$  and  $C_6H_{12}$ . The experiments were carried out at room temperature using the fast-fast coincidence ORTEC PLS system described in Ref.[16]. At least  $10^6$  counts of annihilation events were collected in each experimental acquisition. The obtained spectra were analyzed with two methods: (i) the MELT procedure [17] and (ii) the conventional multiexponential model. Both methods give similar results revealing the presence of three lifetime components corresponding to three different



**Figure 2.** MERT extrapolation of experimental total cross-sections [7] for positron scattering from  $C_6H_6$  and  $C_6H_{12}$ . See text for more details.

annihilation events. This is consistent with results reported for other liquid hydrocarbons [14]. The derived averaged lifetimes are summarized in Tab.1 where they are compared with some data from literature [14, 18]. Note that the quantitative agreement between the present data and the literature is relatively poor. This is because our liquid samples were not degassed before the measurements. It has been shown recently by Zgardzinska and Goworek [18] that the presence of air significantly changes the room temperature lifetime spectra of liquid *c*-hexane, giving the longest component  $\tau_3 = 2.40$  ns in non-degassed samples and 3.20 ns in degassed ones. The first results is in good agreement with our present data. The measurements with the air-free samples are in progress. Despite the quantitative inconsistency, all spectra from Tab.1 have a common feature - all lifetimes in  $C_6H_{12}$  are always higher than in  $C_6H_6$ . Hence the positron annihilation rates in liquid *c*-hexane are smaller than in liquid benzene. This results is in direct contradiction to the output from the gas-phase experiments [6]. Note however that a simple three exponential model typically used to analyze PALS data does not take into account the complexity of the Ps formation process occurring in the liquids. Therefore probably a more sophisticated approach is needed to get more accurate annihilation rates in liquids and to do more reliable comparison with a gas phase.

**Table 1.** Positron annihilation lifetimes in  $C_6H_6$  and  $C_6H_{12}$ .

$C_6H_6$	$\tau_1$ (ns)	$\tau_2$ (ns)	$\tau_3$ (ns)
present	0.261	0.542	2.30
Ref.[14]	0.142	0.440	3.18
Ref.[18]	-	-	3.00
$C_6H_{12}$	$\tau_1$ (ns)	$\tau_2$ (ns)	$\tau_3$ (ns)
present	0.284	0.601	2.57
Ref.[14]	0.214	0.469	3.25
Ref.[18]	-	-	3.20

#### 4. Conclusions

The most recent experimental and theoretical results describing the positron interaction with molecules of benzene and cyclohexane at room temperature in gas and liquid phases have been shortly summarized. In particular it was noticed that the gas-phase experiments give higher annihilation rates for  $C_6H_{12}$  when compare to  $C_6H_6$ , while the liquid-phase experiments give an opposite result when analyzing PALS data with the conventional three exponential model. This is confirmed by positron annihilation lifetime measurements in liquid phase presently reported.

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