Positron annihilation
in benzene, aniline and cyclohexane

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The primary goal of this study is to find any qualitative or quantitative links between single positron-molecule collisions quantified by *cross sections* measured in a gas phase and *annihilation rates* measured in condensed phase of matter for large molecules.

Experimental data from:
Positron direct annihilation vs scattering cross-section

Two-body interaction with noble gases and simple molecules

\[ Z_{\text{eff}}(k) = F \left( R_t^2 + \frac{\sigma_{el}(k)}{4\pi} + \frac{R_t}{k} \sin\left[ 2\eta_0(k) \right] \right) \]


\[ Z_{\text{eff}} \sim \lambda = 1/\tau \]

- \( \sigma_{el} \) - elastic scattering cross section
- \( \eta_0 \) - s-wave scattering phase-shift

\( R_t \pm \delta R_t \)

spatial region of the effective positron-target interaction
Subjects of present investigation

Methane $\text{C}_6\text{H}_6$

Cyclohexane $\text{C}_6\text{H}_{12}$

Aniline $\text{C}_6\text{H}_5\text{NH}_2$

Dipole polarizabilities:

- $\alpha \approx 70.9 \, [a_0^3]$
- $\alpha \approx 73.8 \, [a_0^3]$
- $\alpha \approx 81.7 \, [a_0^3]$

Permanent dipole moments:

- $M \approx 0 \, [\text{D}]$
- $M \approx 0 \, [\text{D}]$
- $M \approx 1.13 \, [\text{D}]$

CRC Handbook of chemistry and physics, ed. 86 (2005)
Trento low-energy gas-phase positron beam experiments

Total cross-section for positron scattering from benzene, cyclohexane and aniline in a gas phase

Total cross-sections in the literature for $C_6H_6$, $C_6H_{12}$ and $C_6H_5NH_2$

Regarding the literature, there are few reported experimental and no theoretical data for these molecules. In fact, TCS for benzene were measured only by two experimental systems: the one from Trento and the second one from Yamaguchi University in Japan (by Sueoka and co-workers). The results reported by the same Japanese group (Sueoka and Makochekanwa) are completely different due to a different setting in their system. On the other hand, Karwasz measured data in 2005. Two years later a different group (Zecca and co-workers) reported the results for these molecules using the same system. There is no difference between these two sets except the fact that Zecca’s data are shifted by 0.2 eV. Note also a difference between Trento data and Yamaguchi data for cyclohexane.
Extrapolation of total cross-section down to thermal energies by

Modified Effective Range Theory (MERT)


\[
\sigma_{el}(0) = \frac{2\pi}{\varepsilon_b}
\]

G. F. Gribakin, J. A. Young, C. M. Surko, Rev. Mod. Phys, 82, 2557 (2010)

Because the annihilation takes place in thermal energy range which is inaccessible for scattering experiments and there is no reliable theory at low energies. That is why we have developed a model based on the modified… in order to extrapolate…

Here we used MERT to extrapolate our CS for benzene and cyclohexane. MERT can be used only for non-polar targets.

To limit the number of fitting parameters in extrapolation procedure we fixed the value of the CS in the zero energy limit. We used the fact that the large scattering length supports the presence of virtual or bound state for positrons in the limit of zero energy. The latter was estimated using positron binding energies determined experimentally by Surko and co-workers from a shift of vibrational modes. We choose the best fit which provides a continuous change of scattering phase shifts as a function of positron energy. As you can see the CS for CH are higher than for benzene at the thermal energy range. This are cross-sections that we would recommend for these two molecules at thermal energy range.

Following the analogy with noble gases one should expect that annihilation rates should be also larger for C6H12, at least for single molecule collisions that is in low pressure gas phase.
Anomalous annihilation rates for large molecules in a gas phase

TABLE VI. Measured values of $Z_{\text{eff}}$ for ring molecules, aromatics, and other organic molecules.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Formula</th>
<th>$Z$</th>
<th>$Z_{\text{eff}}$</th>
<th>$Z_{\text{eff}}/Z$</th>
<th>DM (D) $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ring hydrocarbons</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>C$_6$H$_6$</td>
<td>42</td>
<td>15 000$^\dagger$</td>
<td>360</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>18 000$^\dagger$</td>
<td>430</td>
<td>0.00</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>C$<em>6$H$</em>{12}$</td>
<td>48</td>
<td>20 000$^\dagger$</td>
<td>420</td>
<td>0.00</td>
</tr>
<tr>
<td>Cyclodecane</td>
<td>C$<em>{10}$H$</em>{20}$</td>
<td>80</td>
<td>369 000$^\dagger$</td>
<td>4 600</td>
<td>0.00</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>C$_{10}$H$_8$</td>
<td>68</td>
<td>494 000$^\dagger$</td>
<td>7 300</td>
<td>0.00</td>
</tr>
<tr>
<td>Decahydonaphthalene</td>
<td>C$<em>{10}$H$</em>{18}$</td>
<td>78</td>
<td>389 000$^\dagger$</td>
<td>5 000</td>
<td>0.00</td>
</tr>
<tr>
<td>Anthracene</td>
<td>C$<em>{14}$H$</em>{10}$</td>
<td>94</td>
<td>4 330 000$^\dagger$</td>
<td>46 000</td>
<td>0.00</td>
</tr>
</tbody>
</table>


thermally averaged $<Z_{\text{eff}}>$ at 300K:

$C_6H_6 \sim 15000 \ < \ C_6H_{12} \sim 20000$
Positron Annihilation Lifetime (PALS) Measurements in liquid phase at room temperature

- $^{22}\text{Na}$ source in 7$\mu$m thick kapton foil with 10$\mu$Ci activity
- 180$\text{ps}$ system resolution
- 3 acquisitions per sample
- $>10^6$ counts per acquisition
PALS results for liquid $C_6H_6$, $C_6H_{12}$ and $C_6H_5NH_2$

The obtained spectra were analysed by two methods: MELT which is a deconvolution method using Bayesian algorithms with maximum entropy principle as regularization factor. The second method is well-known LT10 software fitting a conventional multieponential model to experimental data. Both methods give results which are qualitatively in good agreement with each other.

Three lifetime components were recognized.

$\tau_1$ - para-positronium
$\tau_2$ – direct annihilation
$\tau_3$ - ortho-positronium

and other fast intrinsic processes

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\tau_1$ (ns)</th>
<th>$I_1$ (%)</th>
<th>$\tau_2$ (ns)</th>
<th>$I_2$ (%)</th>
<th>$\tau_3$ (ns)</th>
<th>$I_3$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.284</td>
<td>50</td>
<td>0.442</td>
<td>48</td>
<td>2.30</td>
<td>18</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>0.261</td>
<td>39</td>
<td>0.542</td>
<td>43</td>
<td>2.37</td>
<td>25</td>
</tr>
<tr>
<td>Aniline</td>
<td>0.179</td>
<td>27</td>
<td>0.601</td>
<td>28</td>
<td>2.30</td>
<td>18</td>
</tr>
</tbody>
</table>

MELT and LT10 analysis

normalized intensity

- benzene
- cyclohexane
- aniline

lifetime [ps]
PALS results for liquid $C_6H_6$, $C_6H_{12}$ and $C_6H_5NH_2$

When compared with the literature, there is a little quantitative agreement with the three lifetime components reported by Mogensen. Nevertheless, both results indicate that cyclohexane lifetimes are longer than lifetimes for benzene. Interestingly, the ortho-positronium annihilation lifetimes of Mogensen scale in the same way as positronium formation threshold from Ore-gap model. So we should expect that the annihilation rates are higher for liquid benzene than for liquid cyclohexane. This is against the trend observed between cross section and annihilation rates in simple targets like noble gases. This is also in contradiction to what we generally observe in gas phase annihilation experiments.

$\tau_1$ - para-positronium
$\tau_2$ – direct annihilation
$\tau_3$ - ortho-positronium

and other fast intrinsic processes

New advanced positron chemistry models are needed in order to describe how the multi-body interaction in condensed matter distorts the character of single positron – molecule interaction.
Thank you for your attention

Toruń, Poland
Extrapolation of total cross-section down to thermal energies by Modified Effective Range Theory (MERT)

\[ -\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} - \frac{\alpha}{2r^4} - V_s(r) - E \begin{cases} rR_l(k,r) = 0 \end{cases} \]

For these purposes we developed a model based on the so-called Modified Effective Range Theory. In this approach we divide the interaction potential between charge particles and electron clouds for a long-range polarization potential and unknown short-range potential. Then we solve the radial Schrödinger equation within the partial wave formalism by supposing that the long-range interaction is dominant…
Scattering on polarization potential

Mathieu differential equation:

\[
\left[ \frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + \frac{(R^*)^2}{r^4} + k^2 \right] \Phi_l(r) = 0
\]

\[ R^* = \sqrt{\alpha} \quad \text{- characteristic range of } r^4 \text{ interaction} \]


Behavior of the solution at large \( r \)

\[ \Phi_l(r) \sim \sin \left( kr - \frac{1}{2} l\pi + \eta_l \right) \]

total phase shift: \( \eta_l \)

Behavior of the solution at small \( r \)

\[ \Phi_l(r) \sim r \sin \left( R^*/r + \phi_l \right) \]

short-range phase: \( \phi_l \)

Scattering phase shift

\[
\tan \eta_i = \frac{m_i^2 - \tan^2 \delta_i + \tan (\phi_i + l \pi/2) \tan \delta_i \left(m_i^2 - 1\right)}{\tan \delta_i \left(1 - m_i^2\right) + \tan (\phi_i + l \pi/2) \left(1 - m_i^2 \tan^2 \delta_i\right)}
\]

\[
m_i = m_i(E, \alpha)
\]
\[
\delta_i = \delta_i(E, \alpha)
\]
determined from analytical properties of Mathieu functions (tabulated)


Short-range contribution:

\[
\tan (\phi_i + l \pi/2) \approx B_i + R_i R^* k^2 / 2 + ...
\]

the effective range expansions

\[B_i\] – the zero energy contribution of short-range effects

\[R_i\] – the effective range of short-range effects
Extrapolation of total cross-section down to thermal energies by Modified Effective Range Theory (MERT)

\[ \sigma(k) = \frac{4\pi}{k^2} \sum_l (2l + 1) \sin^2 \eta_l(k) \]

Fit to $Z_{\text{eff}}$ data

\[ Z_{\text{eff}}(k) = F \left( R_t^2 + \frac{\sigma_{el}(k)}{4\pi} + \frac{R_t}{k} \sin \left[ 2\eta_0(k) \right] \right) \]

$Z_{\text{eff}}$ from D. G. Green, J. A. Ludlow, and G. F. Gribakin, Phys. Rev. A 90, 032712 (2014)
Positron direct annihilation vs elastic scattering cross-section

Simple molecular target: N$_2$

FIG. 1. (a) $Z_{\text{eff}}$ spectrum [5]; and (b) infrared absorption spectrum (log scale, arbitrary units) [12] for hexane. Note that, when the 80 meV downshift of the $Z_{\text{eff}}$ spectrum due to the positron-hexane binding energy is taken into account, the strong peaks in the two spectra occur at the same energy.