Positron analysis of right- and left-handed alanine single crystals

Bilge Eren,¹ Erdal Eren,¹ Fei Wu,² Y. C. Jean,² J. David Van Horn²

¹ Bilecik Seyh Edebali University, Faculty of Science and Arts, Department of Chemistry, 11210 Bilecik, Turkey
² University of Missouri-Kansas City, Department of Chemistry, Kansas City, MO 64110, USA
Overview

• Stories: my introductions to Prof. Y.C. Jerry Jean and positron science; asymmetric PALS.

• Classifications:
  • Beta particles with asymmetric matter
  • Physical Stereochemistry

• Preliminary asymmetric results: quartz and tartaric acid

• Alanine PALS study

• Conclusion
2002 Arrival at UMKC; Jerry Jean, Chair of Department

Interactions of Positrons with Chiral Molecules

Search for Selectivity between Optical Isomers in the Interactions of Positrons with Chiral Molecules

Yan-ching Jean and Hans J. Ache*1

Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia
Publication costs assisted by the Petroleum Research Fund

Positron lifetime measurements were performed in the optical isomers of such as 2-methylbutanol, 2-aminobutanol, octanol-2, α-methylbenzylamine, carbon temperature range from −196 to 100 °C. No significant differences in the lifetime $I_1$ and $I_2$, associated with the short- and long-lived components in the positron between the D and L enantiomers of these chiral molecules if the experimental state. Since $I_2$ is directly related to the (relative) number of orthopositronium results provide no evidence for the assumption that optical isomers display...

(1976)

Chirality observation experiment using positron... (liquid and frozen phases)
β Decay and the origins of biological chirality: experimental results

D. W. Gidley, A. Rich & J. Van House
Physics Department, University of Michigan, Ann Arbor, Michigan 48109, USA

P. W. Zitzewitz
Department of Natural Sciences, University of Michigan-Dearborn, Dearborn, Michigan, 48128, USA

A spin-polarized low-energy positron beam has been used to set limits on asymmetric positronium formation in optically active molecules. No asymmetry was found at the $7 \times 10^{-4}$ level in cystine and tryptophan, but a possible effect of $(0.7 \pm 0.1) \times 10^{-4}$ was found in leucine. A quantitative connection is made with the origin of biological optical activity.

The amino acids and sugars on which terrestrial life is based have maximal optical activity, that is, with rare exceptions, this choice expected to be the one statistically preferred when all possible biospheres are considered? Question (1) has been

![Diagram](1982)

"L" (S)-Alanine

"D" (R)-Alanine

Differential Reaction by radiolysis or oxidation? (solid-phase)
β Decay and the origins of biological chirality: experimental results

D. W. Cidler, A. Rich & I. van Hove

PHYSICAL REVIEW A 85, 052711 (2012)

Positron scattering from chiral enantiomers

L. Chiari,1,2 A. Zecca,2 S. Girardi,2 A. Defant,2 F. Wang,3 X. G. Ma,3 M. V. Perkins,4 and M. J. Brunger1,5,*

1ARC Centre for Antimatter-Matter Studies, School of Chemical and Physical Sciences, Flinders University, GPO Box 2100, Adelaide, SA 5001, Australia
2Department of Physics, University of Trento, Via Sommarive 14, 38123 Povo (TN), Italy
3eChemistry Laboratory, Faculty of Life and Social Sciences, Swinburne University of Technology, Hawthorn, Victoria 3122, Australia
4School of Chemical and Physical Sciences, Flinders University, GPO Box 2100, Adelaide, SA 5001, Australia
5Institute of Mathematical Sciences, University of Malaya, 50603 Kuala Lumpur, Malaysia

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We report on total cross section measurements for positron scattering from the chiral enantiomers (+)-methyl (R)-2-chloropropionate and (−)-methyl (S)-2-chloropropionate. The energy range of the present study was 0.1–50 eV, while the energy resolution of our incident positron beam was ~0.25 eV (FWHM). As positrons emanating from β decay in radioactive nuclei have a high degree of spin polarization, which persists after

**Distinction of (R) and (S) Methyl Esters (gas-phase).**

GAUSSIAN 09 package, were performed as a part of this work in order to assist us in interpreting some aspects of our data.
FIG. 2. (Color online) Present measured TCSs ($\times 10^{-20}$ m$^2$) for positron scattering from (+)-methyl (R)-2-chloropropionate (filled squares) and (−)-methyl (S)-2-chloropropionate (filled circles). Uncertainties plotted are the statistical errors on the data.
Chirality and Positrons? Can Positron Techniques Distinguish Stereoisomers?

"L" (S)-Alanine  
"D" (R)-Alanine  

Chirality and helicity of carbohelicenes

(P)-Helicene  (M)-Helicene

Polarimetry  
CD  
X-ray  
Surface (AFM, SEM)
# Beta particles with asymmetric matter in different phases?

<table>
<thead>
<tr>
<th>Ion</th>
<th>Gas</th>
<th>Liquid</th>
<th>Solid (amorphous)</th>
<th>Solid (crystalline)</th>
</tr>
</thead>
<tbody>
<tr>
<td>e-</td>
<td>Scattering off asymmetric HOMO; Reaction/Interaction with LUMO</td>
<td>Not expected, solvated electrons $\rightarrow$ rapid reaction with oxygen atoms</td>
<td>Not expected.</td>
<td>Electron backscatter/diffraction; some reaction process [reduction]...</td>
</tr>
<tr>
<td>e+ / Ps</td>
<td>Not expected; residence/interaction time too small</td>
<td>Not expected, Ps bubble</td>
<td>Not expected, “isotropic” microstructure</td>
<td>Possible? Helical guest in asymmetric host lattice; some reaction process [oxidation]...</td>
</tr>
</tbody>
</table>
Positron/Crystalline* Quartz Hypothesis:
Host-Guest Interactions ($e^+$ and $M^*$)
Some Classification of Physical Stereochemistry

- **Stereo-recognition**
  
Polarimetry, circular dichroism, optical...

- **Stereo-selection**
  
Chiral chromatography, crystallization, chiral resolutions...

- **Stereo-induction**
  
Chiral catalyst, chiral host,...
Origin of molecular/biological asymmetry?
1A. Stereo-recognition

• Stereorecognition
• *e.g.* Polarimetry
  • Optical Rotation
  • $[\alpha]$
1B. Stereo-recognition
Polarized e- scattering experiments


AND SEE...
2A. Stereo-selection

- *e.g.* Chiral HPLC

- *e.g.* Selective crystallization/resolution

- etc.

2B. Stereo-selection

Polarized DEA (dissociative e-attachment rxn)

3A. Stereo-induction

• (Asymmetric Induction)

• *e.g.* The Nobel Prize in Chemistry, 2001, to William S. Knowles and Ryoji Noyori "for their work on chirally catalysed hydrogenation reactions" and to K. Barry Sharpless "for his work on chirally catalysed oxidation reactions".

![Chemical Reaction Diagram]
3B. Stereo-induction

- Spontaneous absolute asymmetric synthesis?
- Origin of Biological Homochirality?
- Vester-Ulbricht Hypothesis with circularly polarized Bremsstrahlung radiation (or other polarized radiation?)
- Other Hypotheses?
  - Chance versus deterministic.
  - Spontaneous symmetry breaking.
  - Local stereo-enrichment.
  - Light Initiation
  - Chiral induction on clays
  - Etc.

Pre-Biotic Chemistry → Racemic Molecules → Selective modification of one → Small Enantiomer-ic Excess → Amplification Mechs.
<table>
<thead>
<tr>
<th>Helical particle</th>
<th>Stereo-recognition</th>
<th>Stereo-selection</th>
<th>Stereo-induction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron scattering</td>
<td>e- / HOMO repulsion</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>Electron/molecule “reaction”</td>
<td>e- /LUMO interaction →</td>
<td>Selective reaction</td>
<td>Polarized bremsstrahlung; other hypotheses</td>
</tr>
<tr>
<td>Positron scattering</td>
<td>Not expected or not presently detectable. e+ / HOMO attraction; Z* interaction</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>Positron/molecule “reaction”</td>
<td>Asymmetric single crystal lattices?</td>
<td>Selective Oxidation of one enantiomer? [Some ideas.]</td>
<td>Polarization Transfer? [Crazy schemes!]</td>
</tr>
</tbody>
</table>
**Quartz results (1)**

**Positron Stereorecognition of LH and RH Quartz**

- Slow Beam Experiment ~ 80% polarization

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**Figure 1.** Evaluation of “S-parameter” versus positron implantation energy for fused and crystalline quartz samples in a Doppler-broadening energy spectrum technique.

**Figure 2.** Representative bulk positron lifetime spectra of fused and crystalline quartz samples.

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TABLE 1. Positronium lifetimes and intensities in quartz glass and crystal samples, using sealed and open positron sources (2 × 10^6 counts collected for each exp.).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\tau_1$ (ps)$^a$</th>
<th>$I_1$ (%)</th>
<th>$\tau_2$ (ps)$^b$</th>
<th>$I_2$ (%)</th>
<th>$\tau_3$ (ps)$^b$</th>
<th>$I_3$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fused$^c$</td>
<td>156</td>
<td>30.1 ± 0.2</td>
<td>524.0 ± 9.1</td>
<td>24.8 ± 0.3</td>
<td>1607 ± 06</td>
<td>45.6 ± 0.3</td>
</tr>
<tr>
<td>LH$^c$</td>
<td>156</td>
<td>37.2 ± 0.5</td>
<td>368.1 ± 2.5</td>
<td>57.5 ± 0.4</td>
<td>1304 ± 22</td>
<td>5.3 ± 0.2</td>
</tr>
<tr>
<td>RH$^c$</td>
<td>156</td>
<td>33.5 ± 0.7</td>
<td>328.7 ± 2.0</td>
<td>62.8 ± 0.6</td>
<td>1498 ± 25</td>
<td>3.7 ± 0.1</td>
</tr>
<tr>
<td>DDLH$^d$</td>
<td>156</td>
<td>32.8 ± 0.8</td>
<td>319.4 ± 2.2</td>
<td>61.5 ± 0.6</td>
<td>650$^a$</td>
<td>5.7 ± 0.2</td>
</tr>
<tr>
<td>DDRH$^d$</td>
<td>156</td>
<td>23.7 ± 0.8</td>
<td>290.4 ± 1.9</td>
<td>72.7 ± 0.7</td>
<td>650$^a$</td>
<td>3.6 ± 0.2</td>
</tr>
<tr>
<td>DDLH$^{d,e}$</td>
<td>156</td>
<td>30.3 ± 1.2</td>
<td>304.2 ± 5.9</td>
<td>62.0 ± 0.9</td>
<td>605 ± 29</td>
<td>7.7 ± 1.5</td>
</tr>
<tr>
<td>DDRH$^{d,e}$</td>
<td>156</td>
<td>24.0 ± 1.3</td>
<td>293.8 ± 5.0</td>
<td>71.5 ± 0.9</td>
<td>628 ± 51</td>
<td>4.5 ± 1.3</td>
</tr>
</tbody>
</table>

$^a$ Values fixed following ref. below.  $^b$ The last digit need not be considered significant, but is included for comparison.  $^c$ Using Kapton® sealed Na-22 source.  $^d$ Using open source $^{22}$NaCl, directly deposited.  $^e$ The $\tau_3$ lifetime is included in fitting.

Quartz (3) Current Work... ‘x-cut’ quartz: natural and synthetic. (please see poster)
Alanine PALS and a Crystallization Challenge:

- Crystallize large set of D/L crystals?

- Future: Obtain a racemic crystal for stereoselection experiment?

Alanine Experimental

- Water
  - DDI water
  - Crystallization took place within 1-3 weeks in Dewar or oven
  - Small crystal sizes & defects

- Water/Acetone
  - 50:50 mixture of DDI water and acetone
  - Heated then Gravity filtered
  - Initial mixtures used to grow seed crystals
  - Additions of water to prevent oversaturation/nucleation/twinning
  - Growth time of 3-6 weeks in centrifuge tubes in oven

- Inherent difficulties in chiral crystallizations
  - No inversion symmetry (phenyl groups help)
  - Amino Acids take longer; aqueous crystallization may be longer.
  - Lack of viable solvents
  - Slower is better

Figure. Alanine crystals from acetone water mixtures.
## Alanine Results (1): Preliminary Lifetime Data

**Table 1.** Lifetime and intensity results for D- and L-Alanine. Small crystals (grown from H₂O).

<table>
<thead>
<tr>
<th>Sample</th>
<th>t₁ (ns)</th>
<th>Δt₁ (ns)</th>
<th>t₂ (ns)</th>
<th>Δt₂ (ns)</th>
<th>t₃ (ns)</th>
<th>Δt₃ (ns)</th>
<th>I₁ (%)</th>
<th>ΔI₁ (%)</th>
<th>I₂ (%)</th>
<th>ΔI₂ (%)</th>
<th>I₃ (%)</th>
<th>ΔI₃ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BE11b</td>
<td>0.2297</td>
<td>0.0059</td>
<td>0.4890</td>
<td>0.007</td>
<td>1.390</td>
<td>0.063</td>
<td>38.83</td>
<td>1.9</td>
<td>58.57</td>
<td>1.6</td>
<td>2.5</td>
<td>0.3</td>
</tr>
<tr>
<td>BE12c</td>
<td>0.2309</td>
<td>0.0124</td>
<td>0.4718</td>
<td>0.018</td>
<td>1.250</td>
<td>0.085</td>
<td>42.72</td>
<td>4.7</td>
<td>53.40</td>
<td>4.0</td>
<td>3.8</td>
<td>0.7</td>
</tr>
</tbody>
</table>

**Table 2.** Lifetime and intensity results for D- and L-Alanine. Large crystals (from H₂O/Acetone).

<table>
<thead>
<tr>
<th>Sample</th>
<th>t₁ (ns)</th>
<th>Δt₁ (ns)</th>
<th>t₂ (ns)</th>
<th>Δt₂ (ns)</th>
<th>t₃ (ns)</th>
<th>Δt₃ (ns)</th>
<th>I₁ (%)</th>
<th>ΔI₁ (%)</th>
<th>I₂ (%)</th>
<th>ΔI₂ (%)</th>
<th>I₃ (%)</th>
<th>ΔI₃ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BE022b/L</td>
<td>0.170</td>
<td>0.005</td>
<td>0.418</td>
<td>0.006</td>
<td>1.306</td>
<td>0.052</td>
<td>33.3</td>
<td>1.5</td>
<td>63.5</td>
<td>1.3</td>
<td>3.1</td>
<td>0.3</td>
</tr>
<tr>
<td>F051ABB/D</td>
<td>0.213</td>
<td>0.006</td>
<td>0.420</td>
<td>0.008</td>
<td>1.682</td>
<td>0.072</td>
<td>47.3</td>
<td>2.8</td>
<td>50.7</td>
<td>2.7</td>
<td>1.9</td>
<td>0.2</td>
</tr>
</tbody>
</table>
Alanine Results (2): before and after treatment of examined crystal face.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\tau_1$ [ns]</th>
<th>$\tau_2$ [ns]</th>
<th>$\tau_3$ [ns]</th>
<th>$I_1$ [%]</th>
<th>$I_2$ [%]</th>
<th>$I_3$ [%]</th>
<th>Variance</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-alanine/before</td>
<td>0.250 (6)</td>
<td>0.526 (12)</td>
<td>1.49 (11)</td>
<td>49.2 (2.4)</td>
<td>48.7 (2.1)</td>
<td>2.1 (0.4)</td>
<td>1.04</td>
</tr>
<tr>
<td>L-alanine/after</td>
<td>0.229 (6)</td>
<td>0.496 (14)</td>
<td>1.15 (11)</td>
<td>44.6 (2.6)</td>
<td>52.5 (1.9)</td>
<td>2.9 (0.9)</td>
<td>0.944</td>
</tr>
<tr>
<td>D-alanine/before</td>
<td>0.229 (7)</td>
<td>0.476 (12)</td>
<td>1.31 (06)</td>
<td>42.6 (2.8)</td>
<td>53.3 (2.4)</td>
<td>4.1 (0.5)</td>
<td>1.05</td>
</tr>
<tr>
<td>D-alanine/after</td>
<td>0.217 (6)</td>
<td>0.478 (11)</td>
<td>1.21 (06)</td>
<td>40.6 (2.4)</td>
<td>55.4 (1.9)</td>
<td>4.0 (0.6)</td>
<td>1.08</td>
</tr>
</tbody>
</table>

Calculated errors in last digit(s) in round brackets ( ).
Alanine Results (3) MELT

- MELT Analysis of LH and RH Alanine positron lifetime data.
- MELT (Maximum Entropy LifeTime) a statistical analytical evaluation to PALS data, using a Bayesian approach.
- PDF = Probability distribution function.
Conclusions

• We obtained alanine crystals via two methods. Completed PALS on LH or RH alanine crystals; varied sample set-up.

• A low chiral density or the presence of the Zwitterion group may negate any asymmetric interactions.

• Additional data point for LH/RH crystal PALS data:

<table>
<thead>
<tr>
<th>LH/RH Sample</th>
<th>Quartz</th>
<th>Tartaric Acid</th>
<th>Tartrate Salt</th>
<th>Alanine</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Insulator; neutral</td>
<td>Neutral organic</td>
<td>Anionic organic</td>
<td>zwitterion</td>
</tr>
<tr>
<td>PALS L/R Δ</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
</tr>
</tbody>
</table>

• Quartz ≥ Tartaric Acid > Tartrate Salt ~ Alanine

• Amino acid microcrystalline/powder work before; what about neutral chiral organics?

• May inform stereo-*selection* experiments with positron.
Acknowledgements

• The authors thank Bilecik Seyh Edebali University Department of Scientific Research Project Unit for supporting this study as a part of the project 2013-02.İL.04-03.

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• The isotopes used were supplied by the U. S. Department of Energy Office of Science by the Isotope Program in the Office of Nuclear Physics.

• Other References:
“Asymmetry is more important than symmetry.” J.D.V.H

Thank you!