[Historical] survey of beta-particle interaction experiments with asymmetric matter.

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JPos17—International Workshop on Physics with Positrons at Jefferson Lab
Thursday, Sept. 14, 2017

JDVH w.r.t. Positrons

- Childhood: fission, fusion and general science.
- BA, PhD: Chemistry
- 1999-2002: Heavy Element Group, UC Berkeley / LBNL
- 2002: Asst. Prof. at UMKC; introduction to positron science for materials studies; Y. C. Jerry Jean group.
- 2002-2011…: Cu, Cr, U and Th bio-inorganic chemistry group at UMKC
- 2010-pres.: re-direction to e^+ studies; leadership of "Positron Science Lab" @ UMKC. (Jean retirement 2012, still assists)
- Ongoing: Various materials science and polymer studies; biomineral, biomaterial, biocompatible, and environmental projects interests.
- Ongoing: Asymmetric e^+ interactions[?]

Overview

- Some Classifications:
  - Physical Stereochemistry: Molecular to Particular
  - Beta particles with asymmetric matter

- Comparisons of recent asymmetric results: quartz, tartaric acid, tartrate salts, alanine.

Some Classification of Physical Stereochemistry

- **Stereo-recognition**

  Polarimetry, circular dichroism, optical…

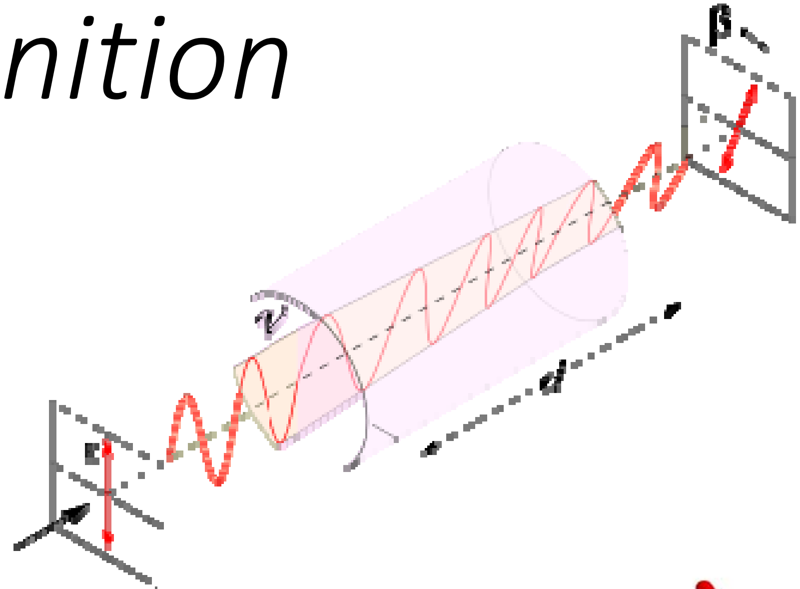
- **Stereo-selection**

  Chiral chromatography, crystallization, chiral resolutions…

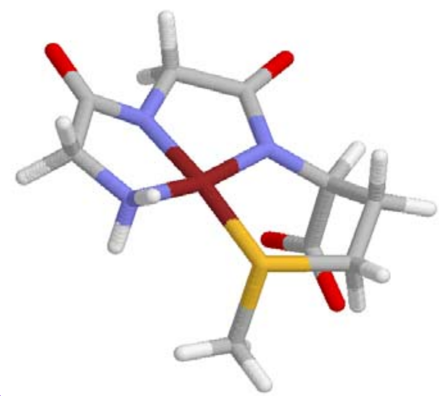
- **Stereo-induction**

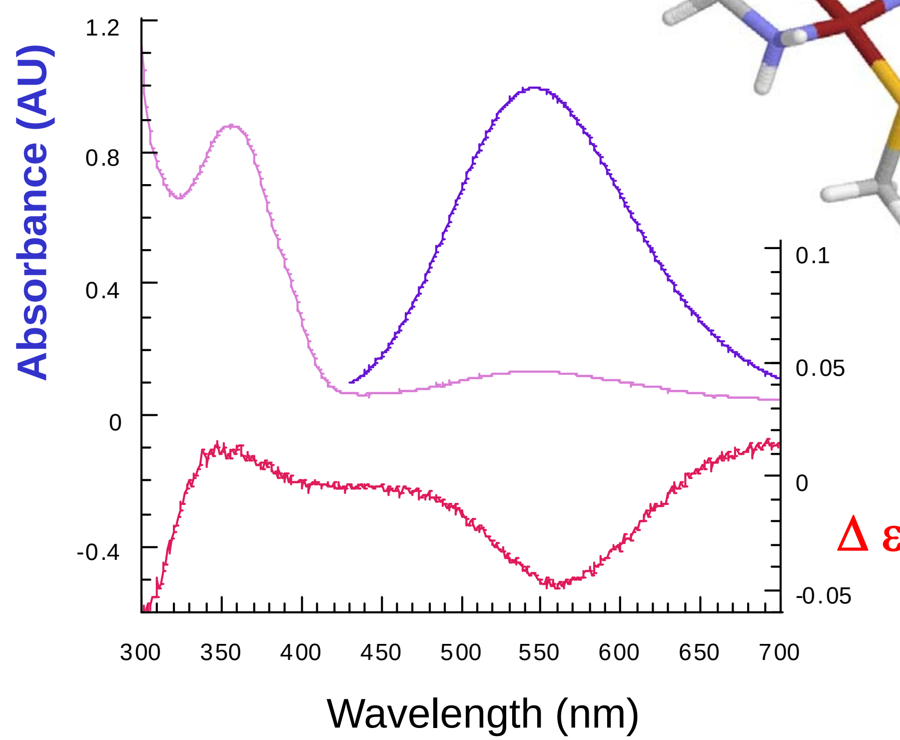
  Chiral catalyst, chiral host,…
  Origin of molecular/biological asymmetry?

1A. Stereo-*recognition*



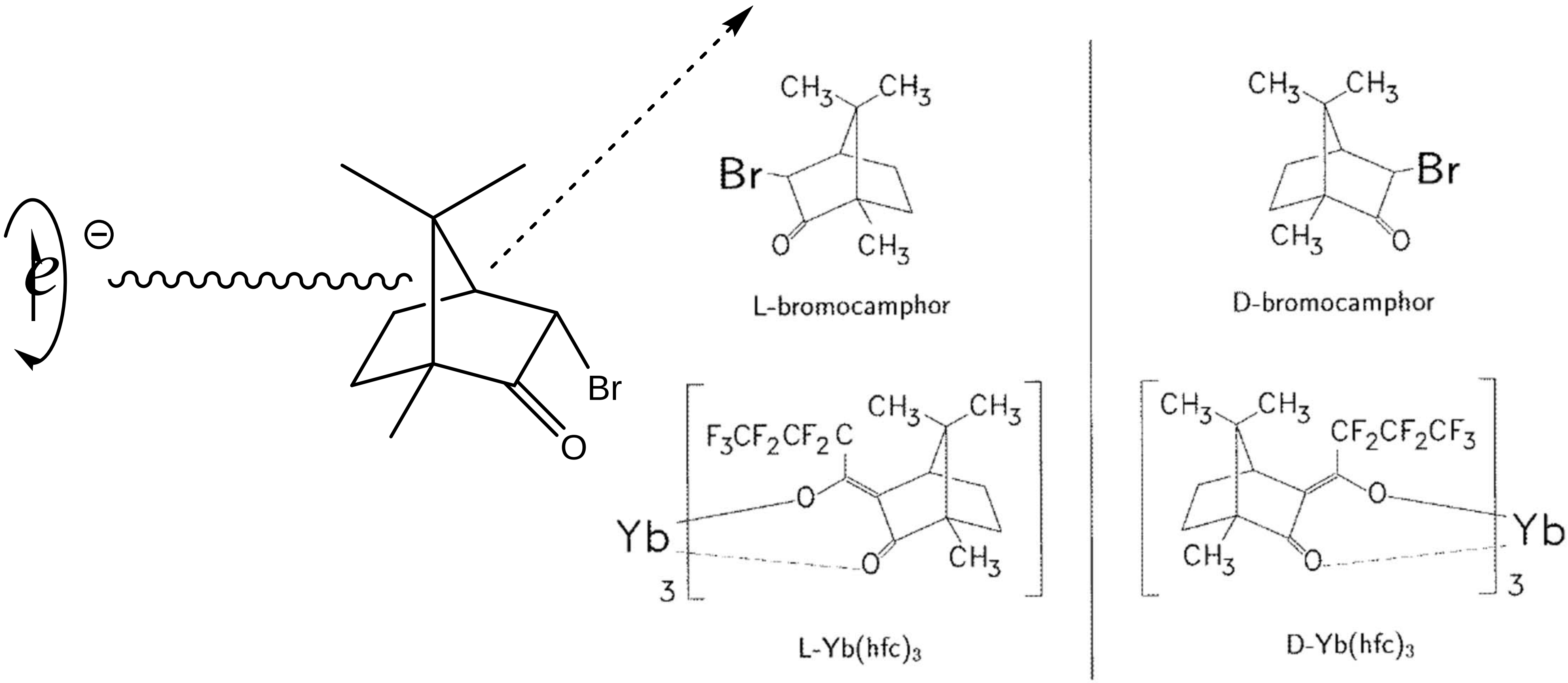
- *e.g.* Polarimetry
  - Optical Rotation
  - $[\alpha]^{T}_{\lambda} = \frac{\alpha}{l \; x \; c}$
- Enantiomeric Excess
  - $ee(\%) = \frac{\alpha_{obs} \times 100}{[\alpha]_{\lambda}}$
- Circular Dichroism





1B. Stereo-*recognition*

Polarized *e*– scattering experiments



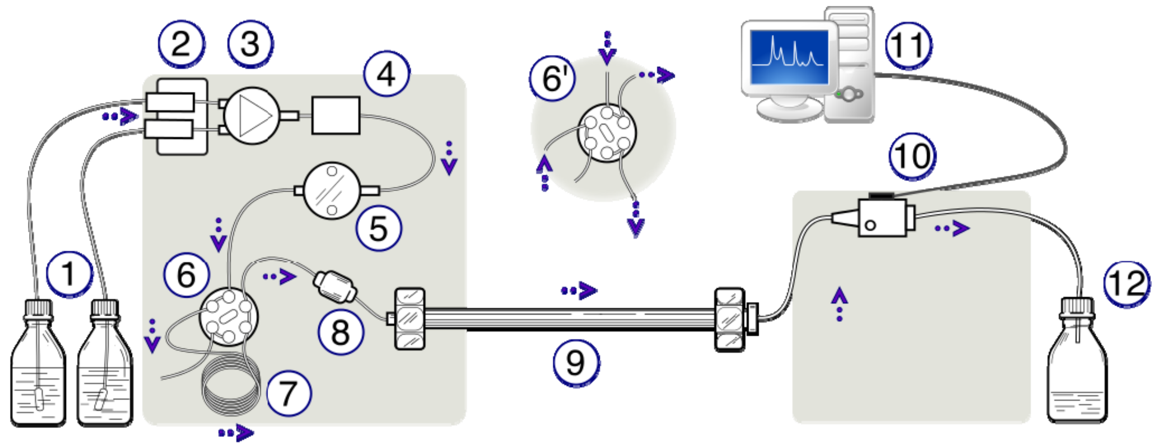
S. Mayer, C. Nolting and J. Kessler, "Electron scattering from chiral molecules." *J. Phys. B: At. Mol. Opt. Phys.* **1996**, *29,* 3497–3511.

AND SEE…

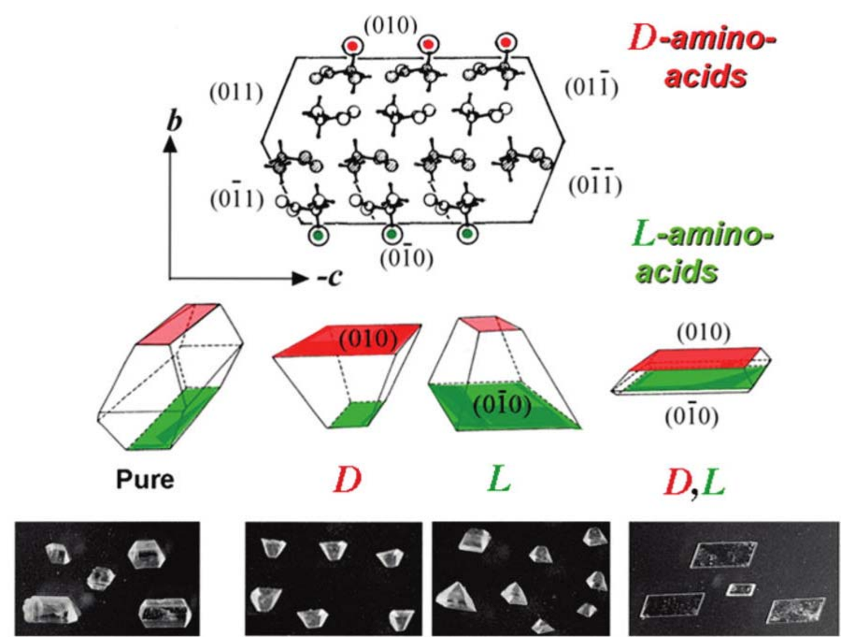
K. Ray, S. P. Ananthavel, D. H. Waldeck and R. Naaman, "Asymmetric Scattering of Polarized Electrons by Organized Organic Films of Chiral Molecules." *Science*, **1999**, *283*, 814-816.

2A. Stereo-*selection*

- *e.g.* Chiral Liquid Chromatography



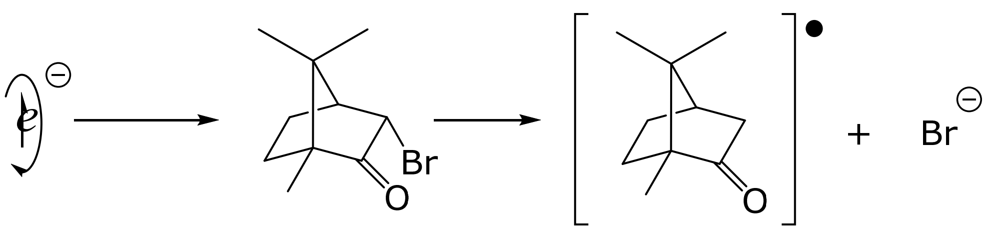
- *e.g.* Selective crystallization/resolution
- *etc.*

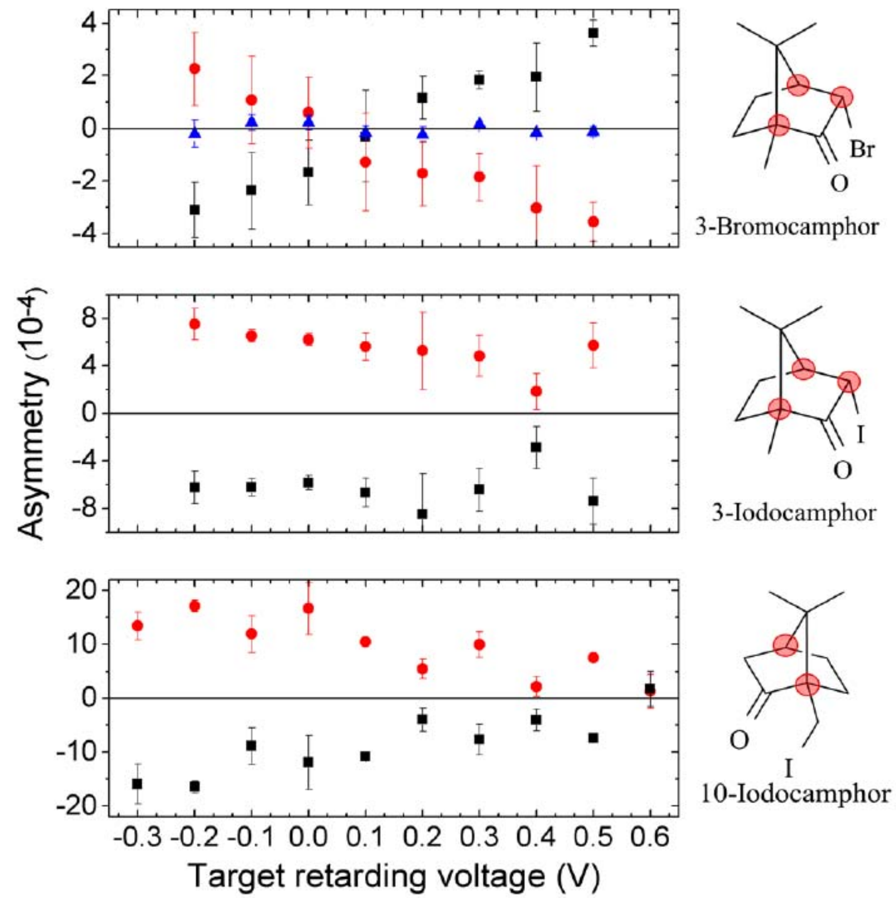


Isabelle Weissbuch and Meir Lahav "Crystalline Architectures as Templates of Relevance to the Origins of Homochirality." *Chem. Rev.* **2011**, *111*, 3236–3267

2B. Stereo-*selection*

Polarized DEA (dissociative *e*– attachment rxn)

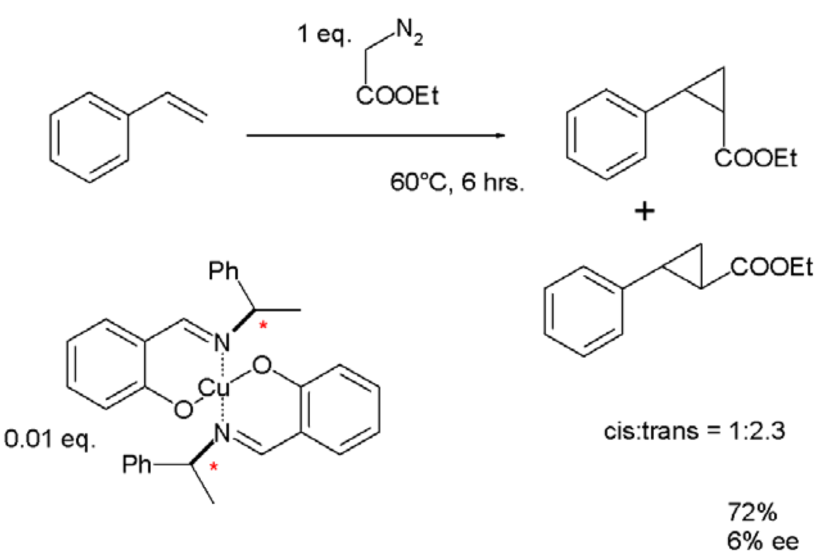


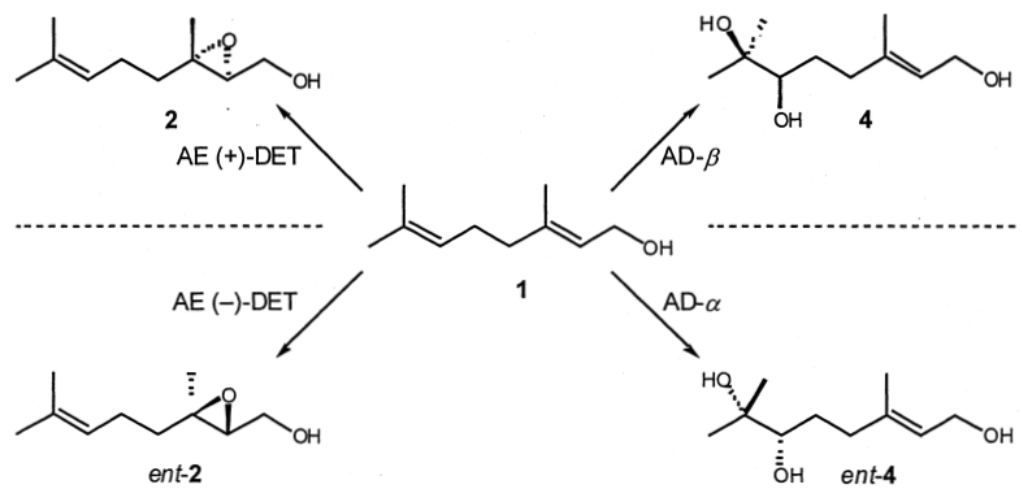


J. M. Dreiling, *et al.*, Phys. Rev. Lett. 116, 093201 (2016).

3A. Stereo-*induction*

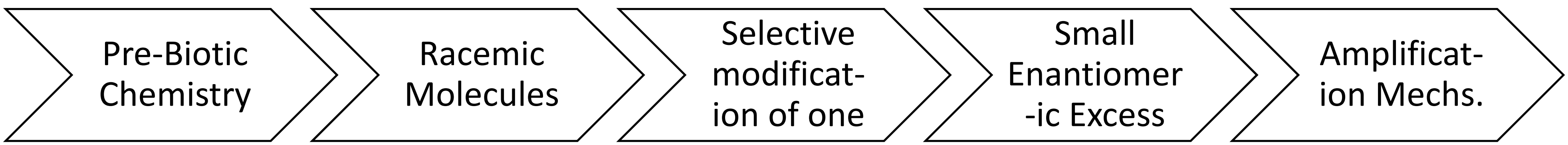
- (Asymmetric Induction)
- *e.g*. The Nobel Prize in Chemistry, 2001, to William S. Knowles and Ryoji Noyori "for their work on chirally catalysed hydrogenation reactions" and to K. Barry Sharpless "for his work on chirally catalysed oxidation reactions".





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.

e^+ with asymmetric matter?

Interactions of Positrons with Chiral Molecules

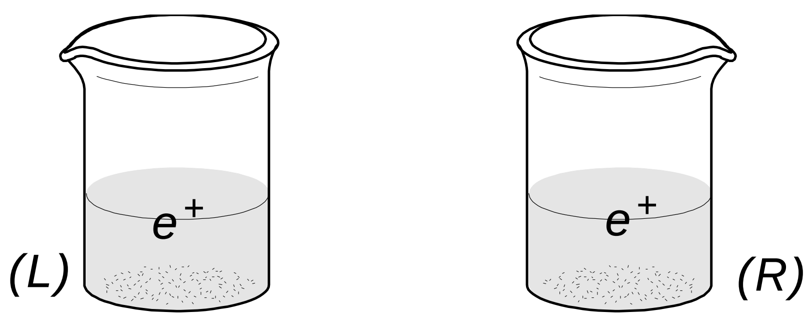
Search for Selectivity between Optical Isomers in the Interactions of Positrons with Chiral Molecules

Yan-ching Jean and Hans J. Ache[*1]

Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virgini

Publication costs assisted by the Petroleum Research Fund

Positron lifetime measurements were performed in the optical isomers of s
as 2-methylbutanol, 2-aminobutanol, octanol-2, α-methylbenzylamine, ca
temperature range from −196 to 100 °C. No significant differences in the lifeti
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 experime
state. Since I_2 is directly related to the (relative) number of orthopositroniu
results provide no evidence for the assumption that optical isomers displ



(1976)

Chirality observation (stereo-recognition) experiment using positron… (liquid and frozen phases)

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

Gray, J. & Thompson, P. *Nature* **262**, 481 (1976).
Burk, R. L. & Stuiver, M. *Science* **211**, 1417 (1981).
18. *Technical Report Series* Nos. 96, 117, 147 (IAEA, Vienna 1969, 1970, 1973).
19. Yapp, C. J. thesis, California Inst. Technol. (1980).

β Decay and the origins of biological chirality: experimental results

D. W. Gidley, A. Rich & J. Van House
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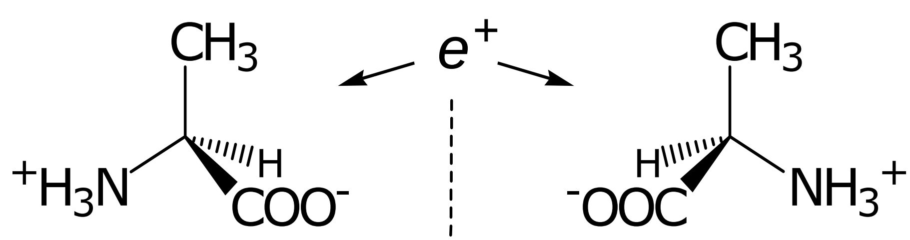
P. W. Zitzewitz
Department of Natural Sciences, University of Michigan-Dearborn, Dearborn, Michigan, 48128, USA

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 7×10^{-4} level in cystine and tryptophan, but a possible effect of $(31\pm7)\times10^{-4}$ 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 show 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



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

(1982)

Differential reaction (stereo-selection) by radiolysis or oxidation? (solid-phase)

Interactions of Positrons with Chiral Molecules

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

(2012)

Gray, J. & Thompson, P. *Nature* **262**, 481 (1976).
Burk, R. L. & Stuiver, M. *Science* **211**, 1417 (1981).
18. *Technical Report Series* Nos. 96, 117, 147 (IAEA, Vienna 1969, 1970, 1973).
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β Decay and the origins of biological chirality: experimental results

D. W. Gidley, A. Rich & J. Van House

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. Brunger[1,5,*]

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[2]*Department of Physics, University of Trento, Via Sommarive 14, 38123 Povo (TN), Italy*

[3]*eChemistry Laboratory, Faculty of Life and Social Sciences, Swinburne University of Technology, Hawthorn, Victoria 3122, Australia*

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[5]*Institute of Mathematical Sciences, University of Malaya, 50603 Kuala Lumpur, Malaysia*

(Received 15 March 2012; published 22 May 2012)

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 moderation, we were particularly interested in probing whether the positron helicity differentiates between the ... Finally, ... in the ... cts of

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

Positron scattering in gas-phase Methyl-2-chloropropionate

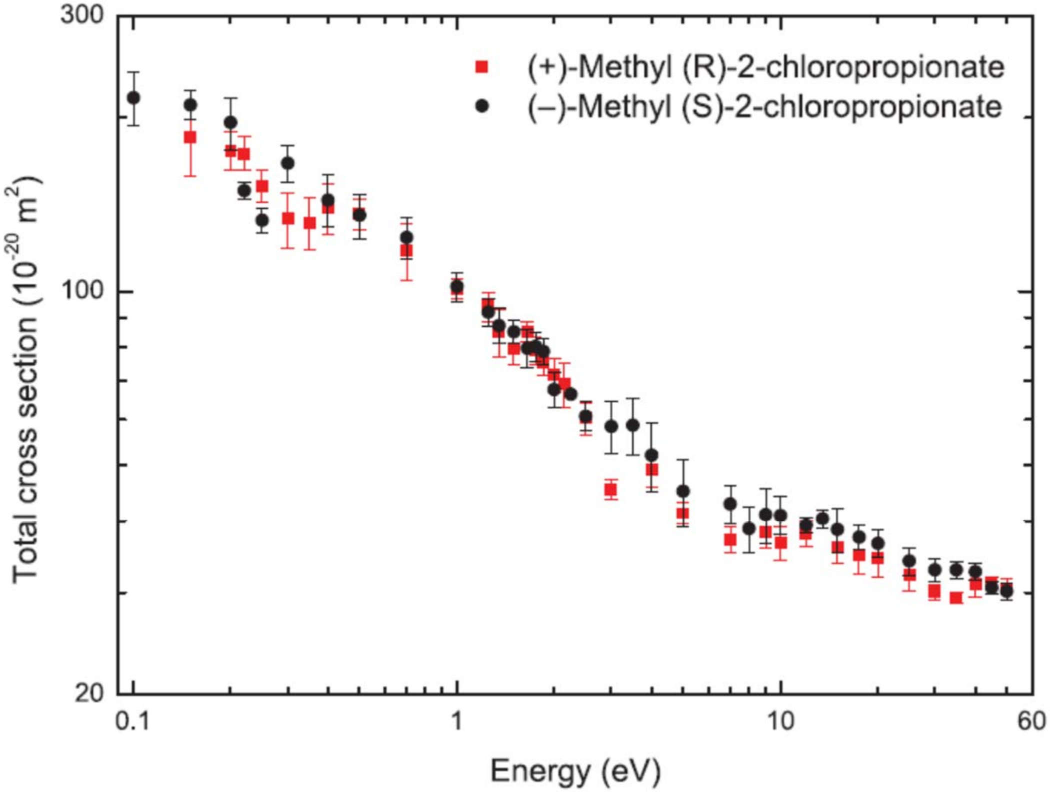
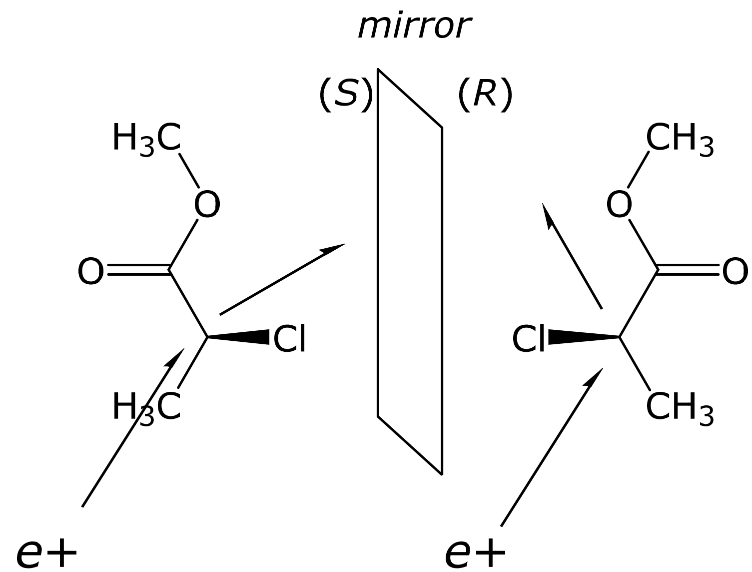


FIG. 2. (Color online) Present measured TCSs ($\times 10^{-20}$ m^2) for positron scattering from (+)-methyl (*R*)-2-chloropropionate (filled squares) and (–)-methyl (*S*)-2-chloropropionate (filled circles). Uncertainties plotted are the statistical errors on the data.



E = ~ 0.1 – 50 eV

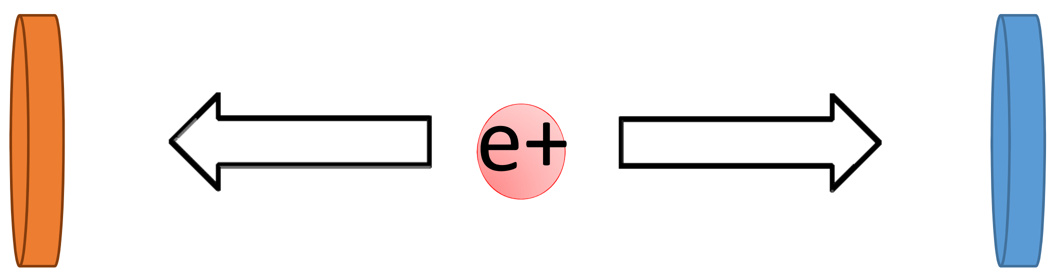
Low-E *beta* particles with asymmetric matter in different phases?

	Gas	Liquid	Solid (amorphous)	Solid (crystalline)
e-	Scattering off asymmetric HOMO; Reaction/Interaction with LUMO	Not expected? solvated electrons→ rapid reaction with oxygen atoms	Not expected.	Electron backscatter/ diffraction; some reaction process [reduction]…
e+ / Ps	Not expected?; residence/ interaction time too small	Not expected? Ps bubble	Not expected, "isotropic" microstructure	Possible? Helical guest in asymmetric host lattice; some reaction process [oxidation]…

β / Physical Stereochemistry Table

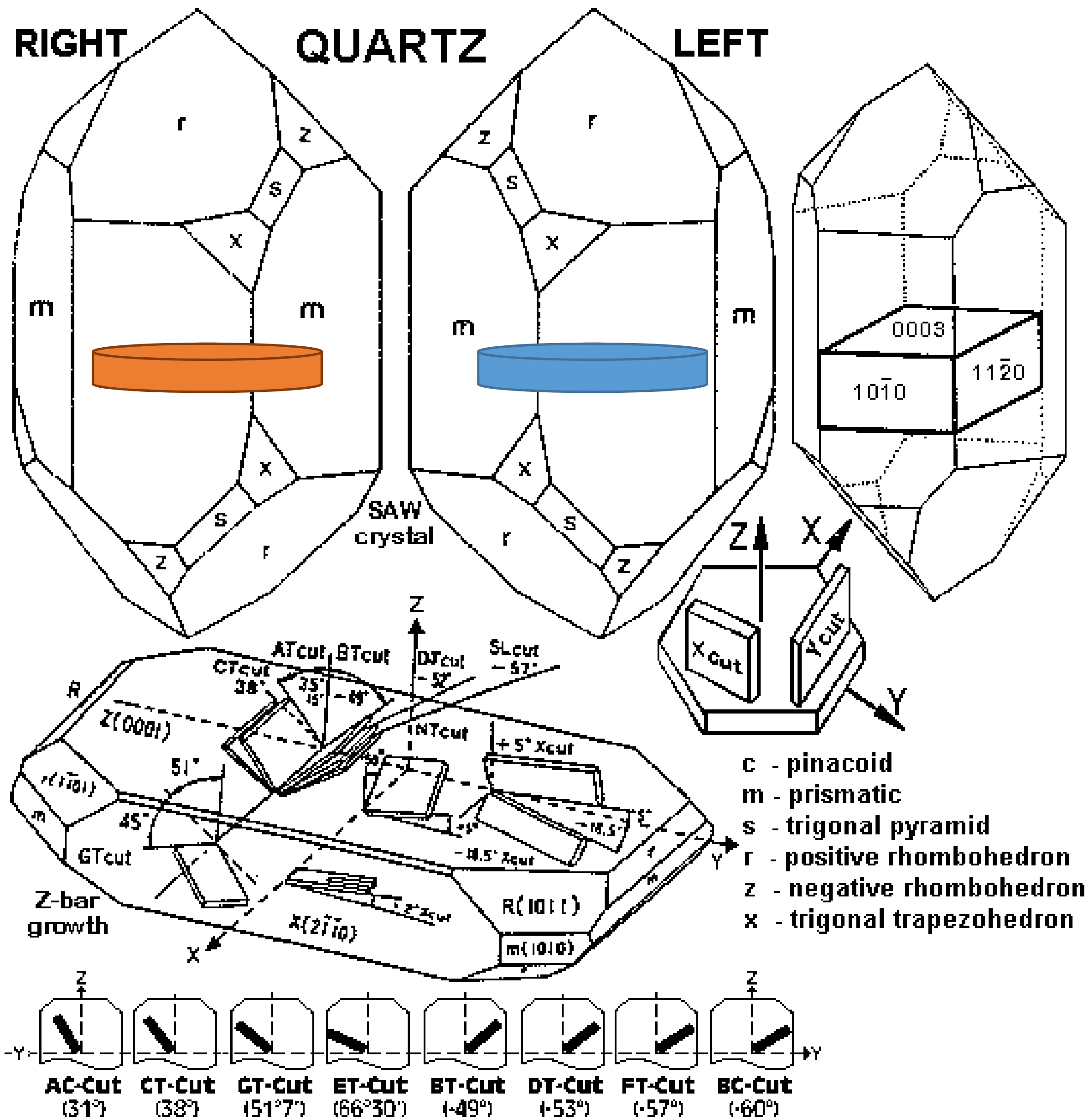
Helical particle	Stereo-recognition	Stereo-selection		Stereo-induction
Electron scattering	e- / HOMO repulsion	?		?
Electron/molecule “reaction”	e- /LUMO interaction →	Selective reaction		Polarized bremsstrahlung; other hypotheses
Positron scattering	Not expected or not presently detectable. e+ / HOMO attraction; Z* interaction	?		?
Positron/molecule “reaction”	Asymmetric single crystal lattices?	Selective Oxidation of one enantiomer? [Some ideas.]		Polarization Transfer? [Crazy schemes!]

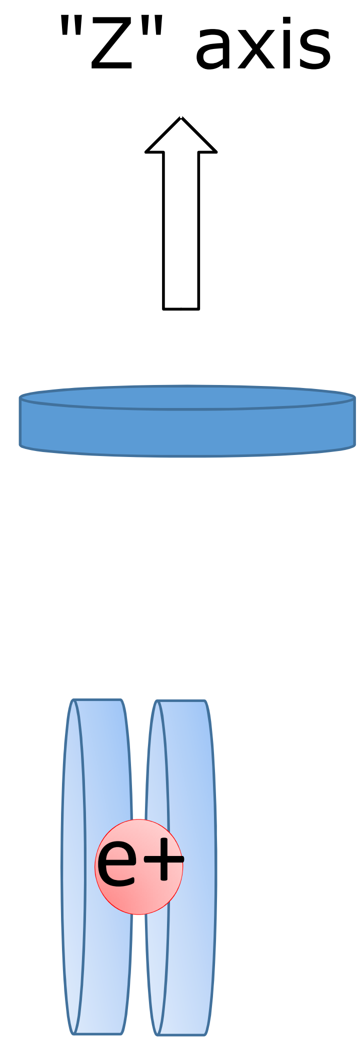
Our Hypothesis: Give the e^+ an asymmetric environment for annihilation.



How? Chiral single crystals. Seems not to be studied...

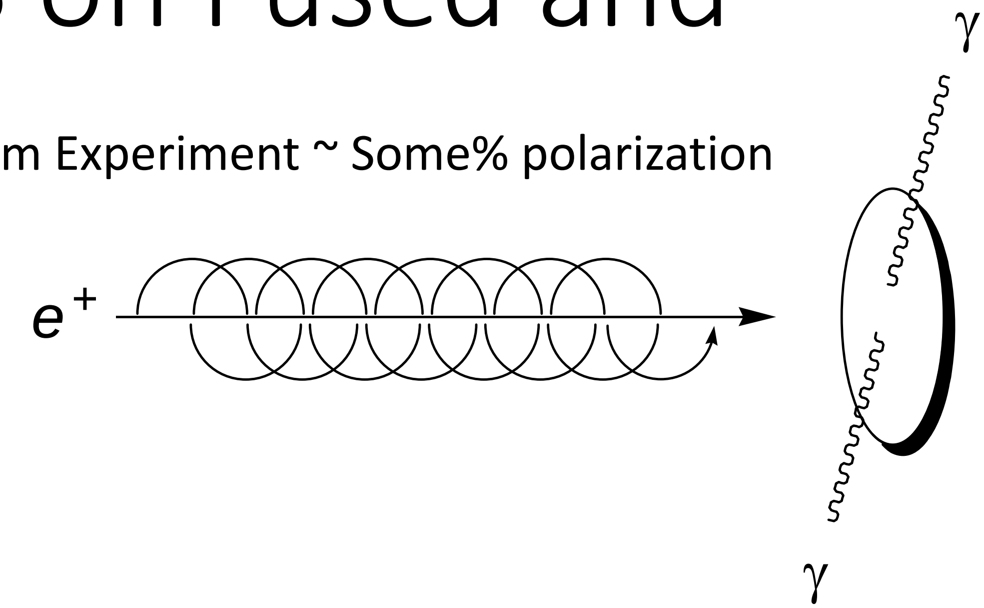
Our Experiment: e^+ with Chiral Crystalline Quartz





PRIOR WORK: DBES on Fused and Crystalline Quartz

Beam Experiment ~ Some% polarization



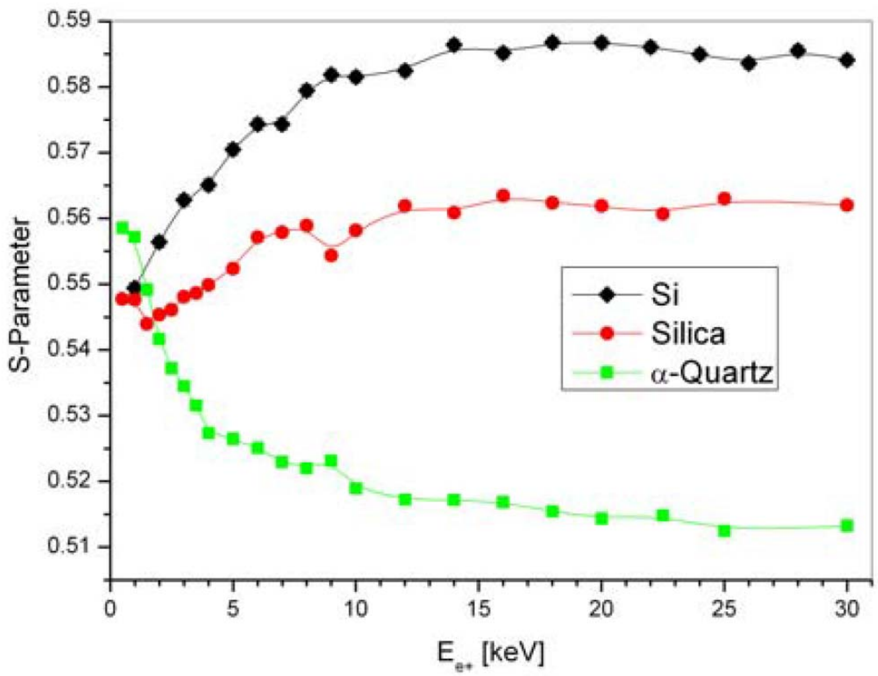
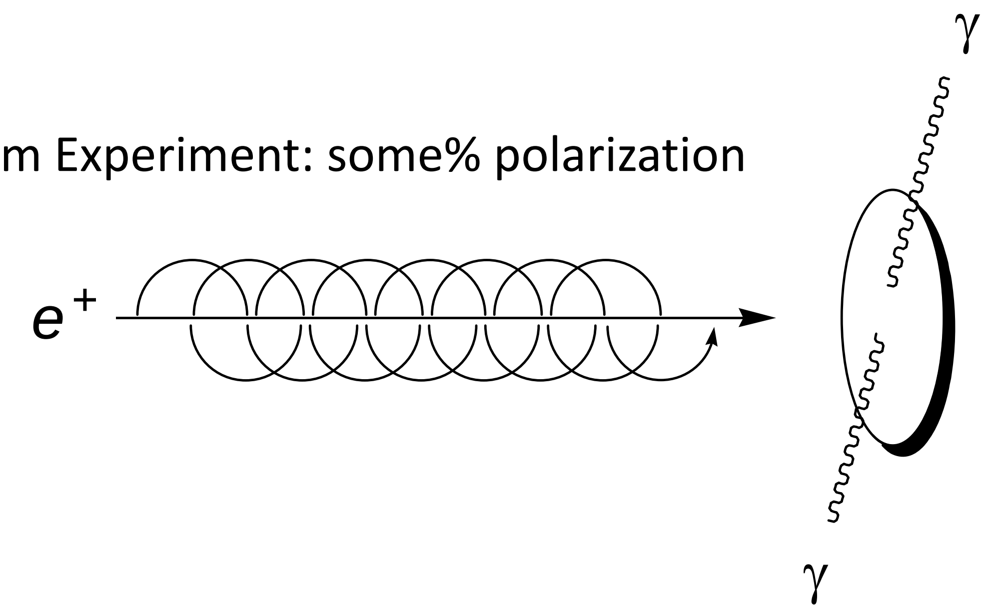


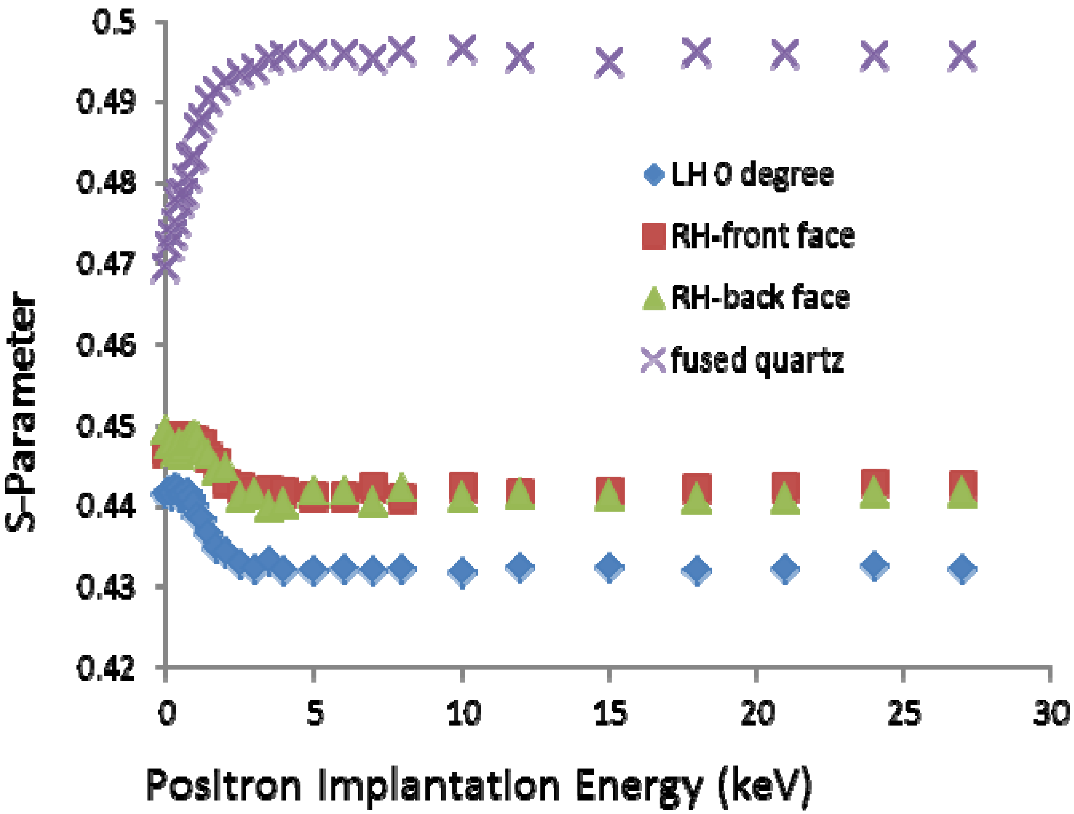
Figure. S-parameter as function of positron implantation energy for silicon, amorphous silica, and crystalline α-quartz. Lines serve as guide to the eye.

From: C. Hugenschmidt, *et al*. "Coincident Doppler-broadening spectroscopy of Si, amorphous SiO_2, and α quartz." *Phys. Status Solidi C* **2009**, *6*, 2459–2461.

PSL: Difference (!) in DBES with Chiral Quartz Crystals

Beam Experiment: some% polarization





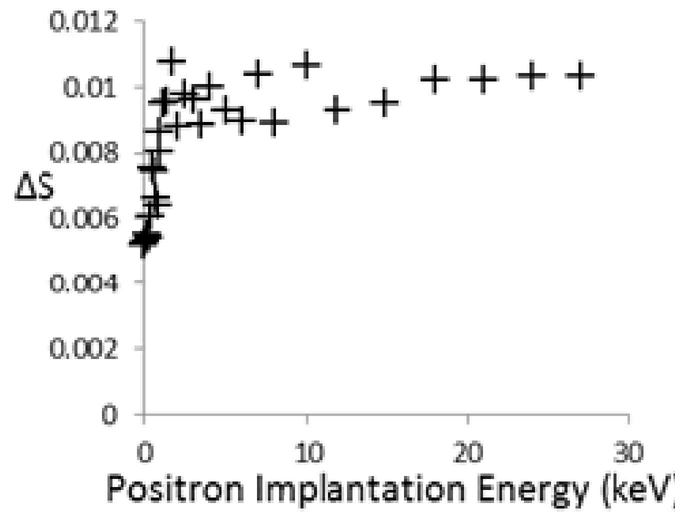


Figure. Evaluation of "S-parameter" versus positron implantation energy for fused and crystalline quartz samples. Inset: difference in RH versus LH quartz "S-parameter" versus positron implantation energy.

DBES on Fused and Chiral Quartz

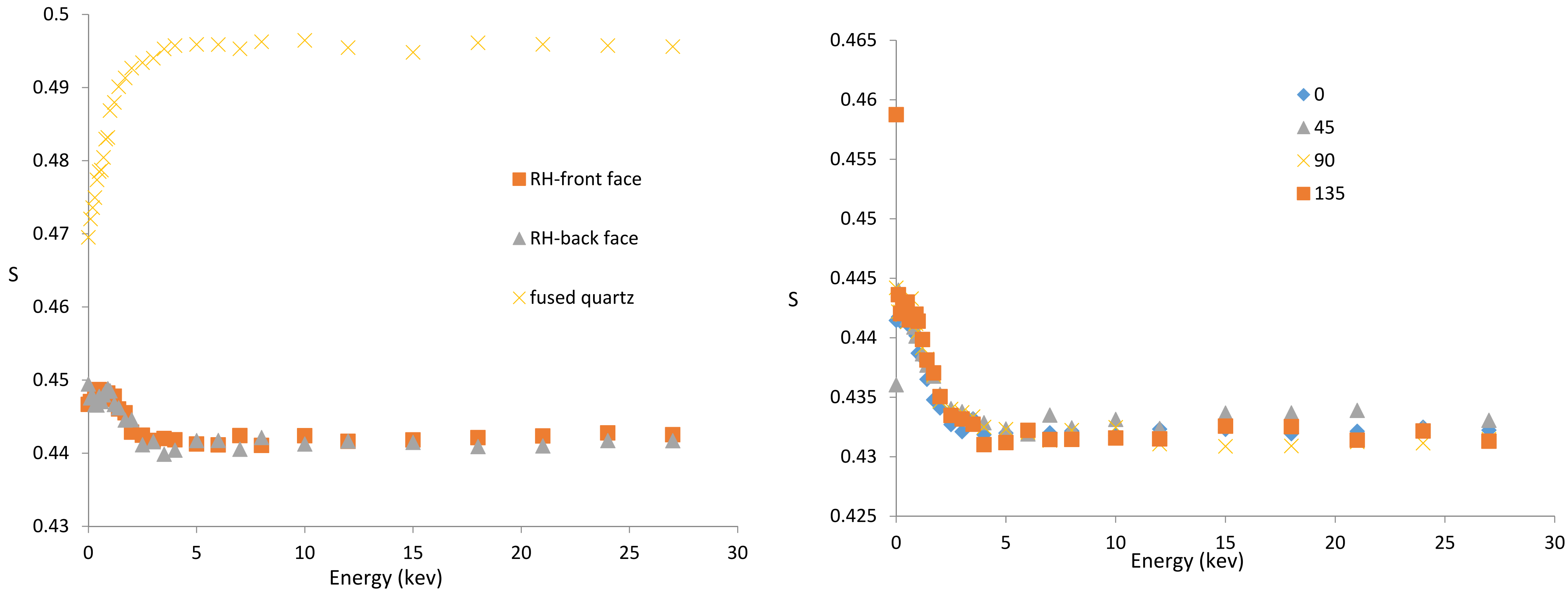
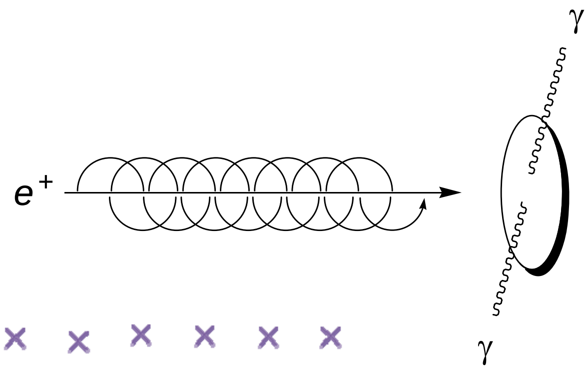


Figure. Evaluation of “S-parameter” versus positron implantation energy for fused and crystalline quartz samples. These experiments explored facial and sample angle dependence.

Quartz results
Positron Stereorecognition of LH and RH Quartz

Slow Beam
Experiment ~ 80%
polarization



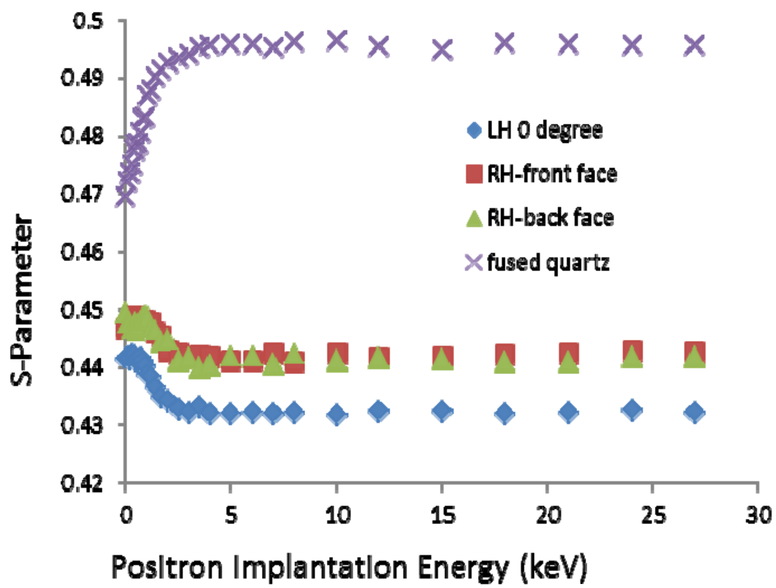


Figure 1. Evaluation of “S-parameter” versus positron implantation energy for fused and crystalline quartz samples in a Doppler-broadening energy spectrum technique.

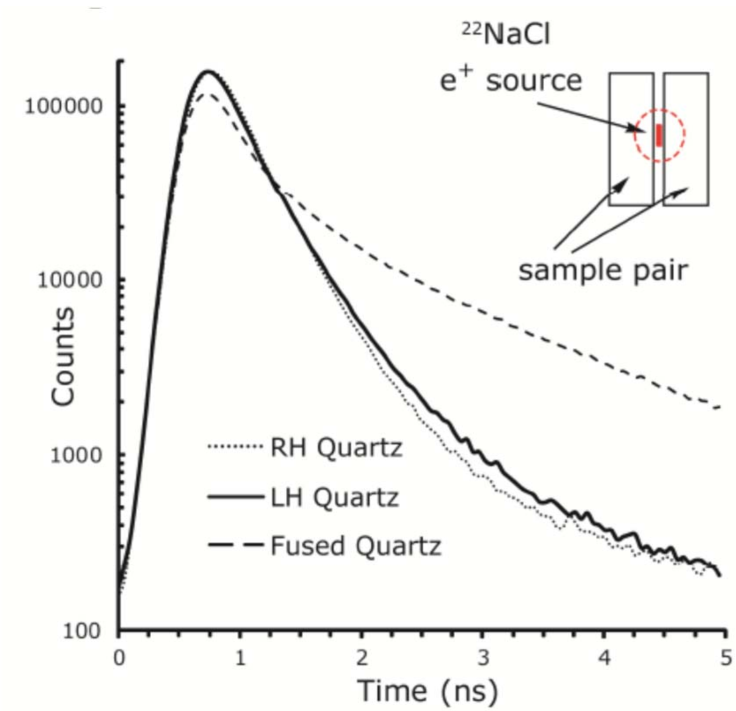


Figure 2. Representative bulk positron lifetime spectra of fused and crystalline quartz samples.

J. David Van Horn, Fei Wu, Gerald Corsiglia, and Y. C. Jean. “Asymmetric Positron Interactions with Chiral Quartz Crystals?” *Defect Diffus. Forum*. **2016**, *373*, 221.

Representative Data: Bulk Quartz PALS

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.).

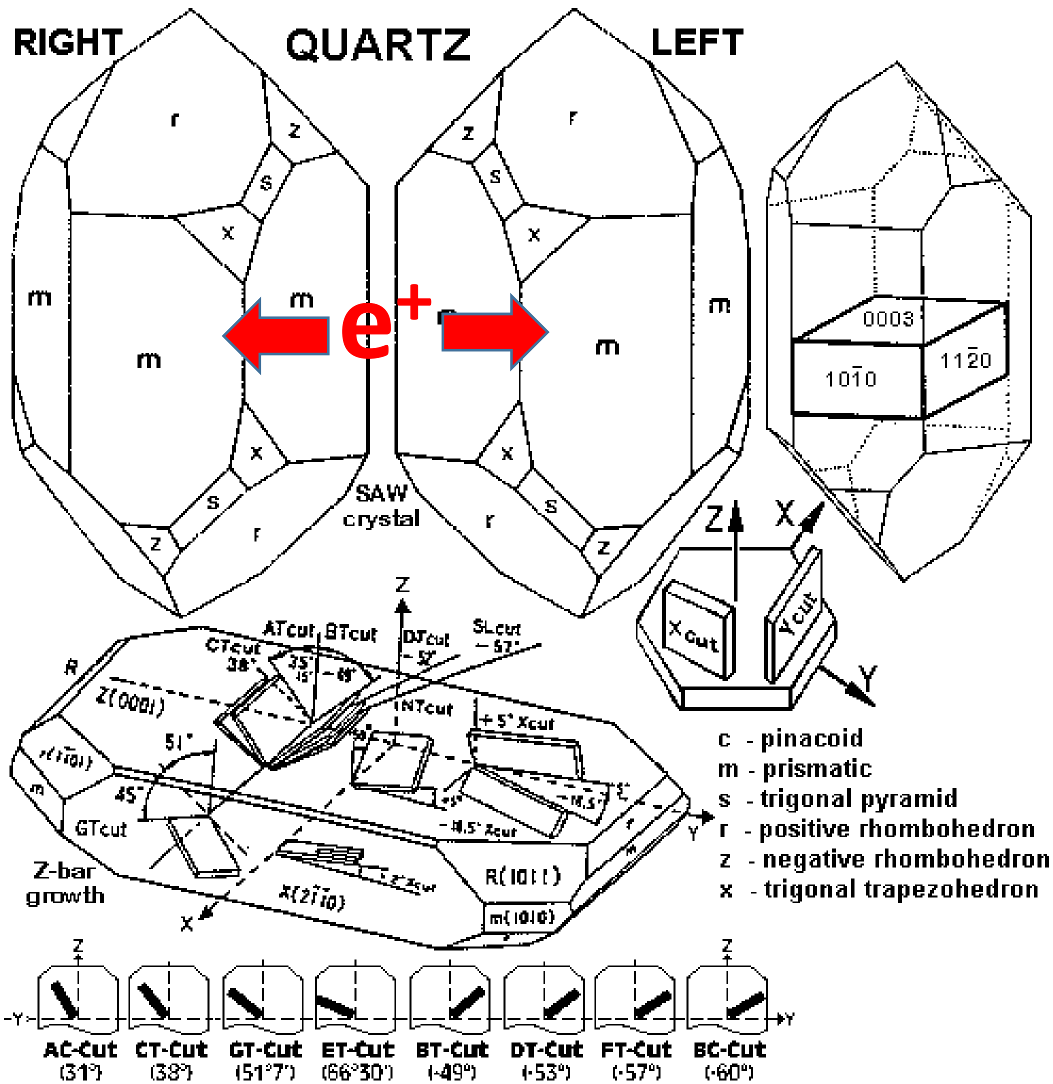
Sample	τ_1 (ps)[a]	I_1(%)	τ_2 (ps)[b]	I_2(%)	τ_3 (ps)[b]	I_3(%)
Fused[c]	156	30.1 ± 0.2	524.0 ± 9.1	24.8 ± 0.3	1607 ± 06	45.6 ± 0.3
LH[c]	156	37.2 ± 0.5	368.1 ± 2.5	57.5 ± 0.4	1304 ± 22	5.3 ± 0.2
RH[c]	156	33.5 ± 0.7	328.7 ± 2.0	62.8 ± 0.6	1498 ± 25	3.7 ± 0.1
DDLH[d]	156	32.8 ± 0.8	319.4 ± 2.2	61.5 ± 0.6	650[a]	5.7 ± 0.2
DDRH[d]	156	23.7 ± 0.8	290.4 ± 1.9	72.7 ± 0.7	650[a]	3.6 ± 0.2
DDLH[d,e]	156	30.3 ± 1.2	304.2 ± 5.9	62.0 ± 0.9	605 ± 29	7.7 ± 1.5
DDRH[d,e]	156	24.0 ± 1.3	293.8 ± 5.0	71.5 ± 0.9	628 ± 51	4.5 ± 1.3

[a] Values fixed following ref. 16. [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 τ_3 lifetime is included in fitting.

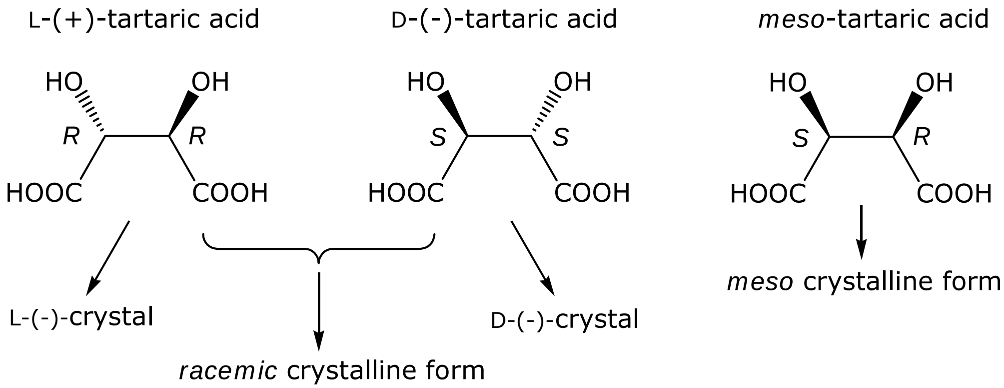
Quartz Reference Lifetimes: Saito, H. & Hyodo, T. *Phys. Rev. Lett*. **90**, 193401 (2003).

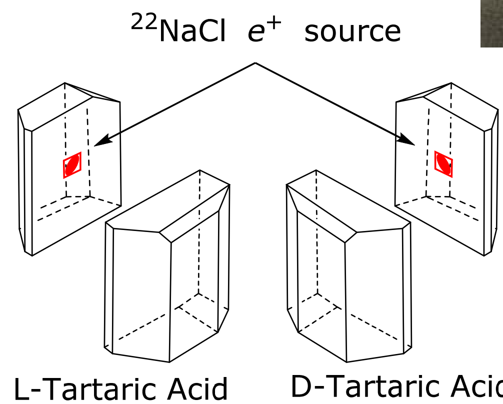
J. David Van Horn, Fei Wu, Gerald Corsiglia, and Y. C. Jean. "Asymmetric Positron Interactions with Chiral Quartz Crystals?" *Defect Diffus. Forum*. **2016**, *373*, 221.

Quartz Current Work… ‘*x*-cut’ quartz: natural and synthetic. (please see poster)



Positron Lifetime Results with Chiral Organics





- Tartaric Acid
  - Yes!
- Tartrate Salts
  - Not so much…

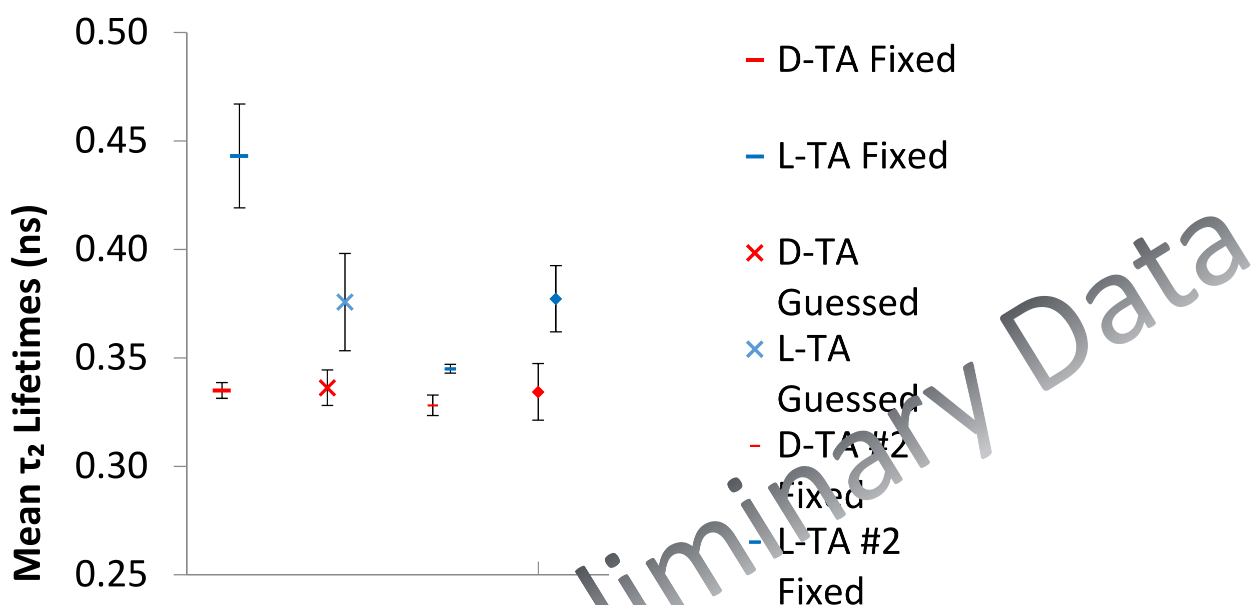
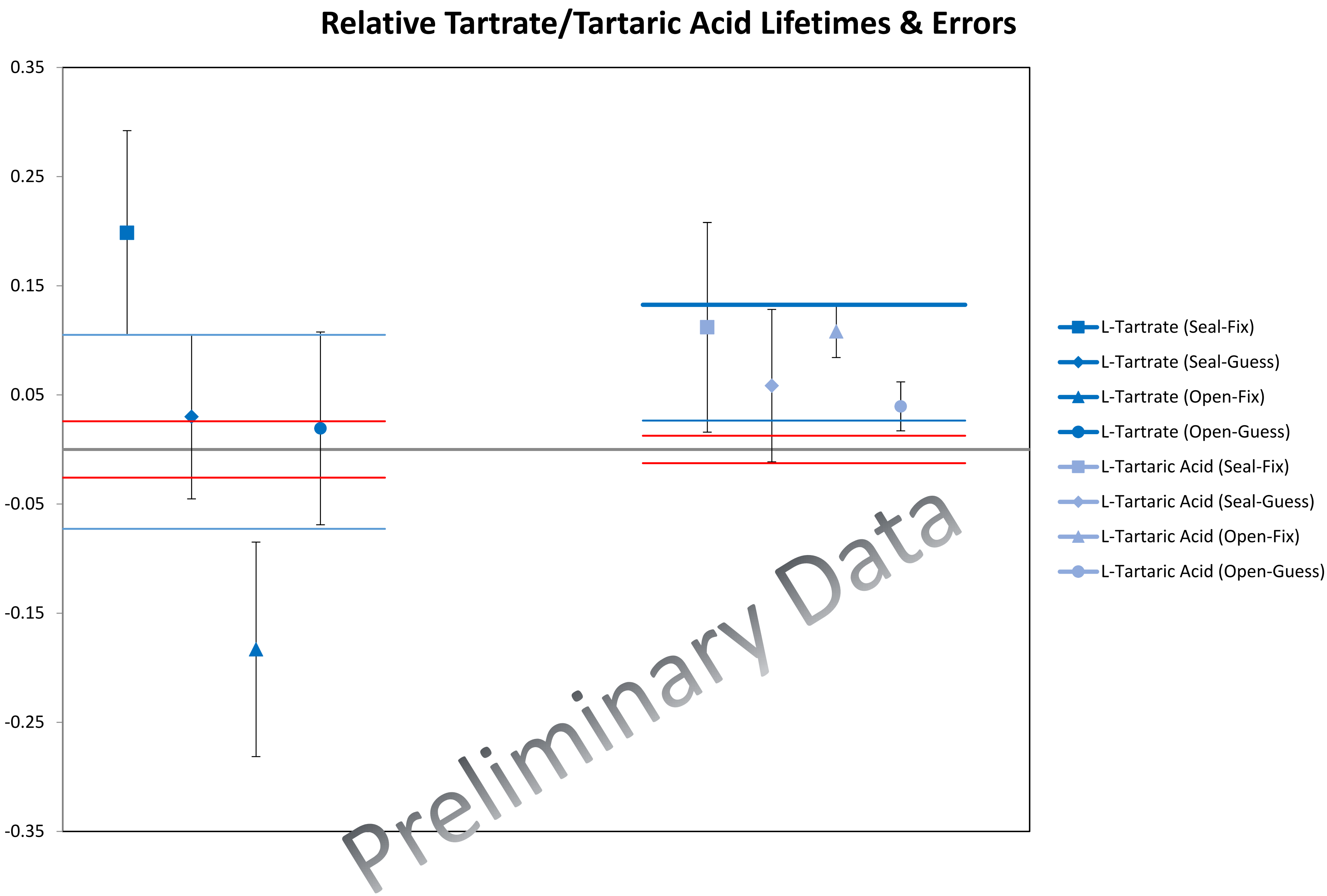


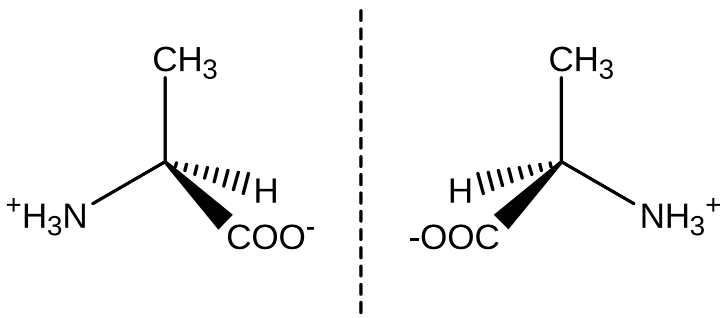
Figure. Relative τ_2 lifetimes for fixed and unfixed data sets. Error bars given as two standard deviations.

Data - Analysis



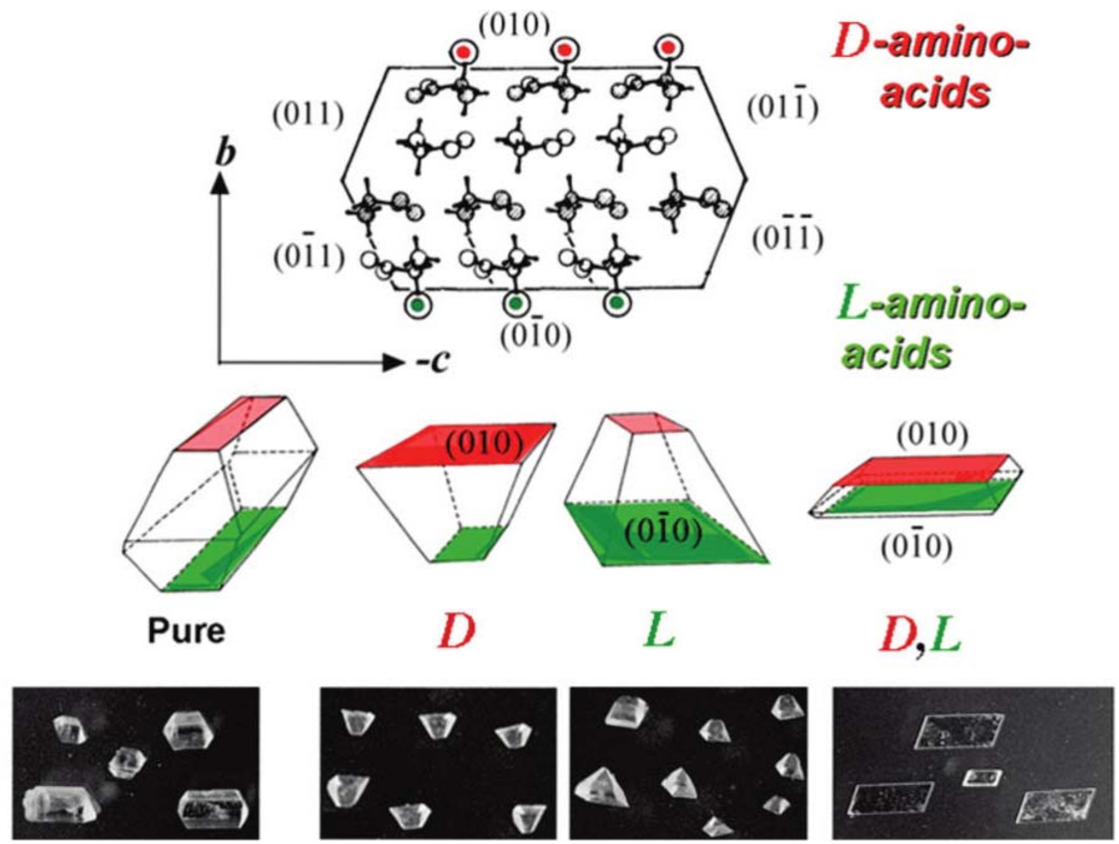
Alanine PALS and a Crystallization Challenge:

- Crystallize large set of D/L crystals?



"L"
(*S*)-Alanine

"D"
(*R*)-Alanine



- Future: Obtain a racemic crystal for stereoselection experiment?

Isabelle Weissbuch and Meir Lahav "Crystalline Architectures as Templates of Relevance to the Origins of Homochirality." *Chem. Rev*. **2011**, *111*, 3236–3267

Alanine Results: Lifetime Data

Table 1. Lifetime and intensity results for D- and L-Alanine. Small crystals (grown from H_2O).

Sample		t1 (ns)	Δt1 (ns)	t2 (ns)	Δt2 (ns)	t3 (ns)	Δt3 (ns)	I1 (%)	ΔI1 (%)	I2 (%)	ΔI2 (%)	I3 (%)	ΔI3 (%)
BE11b	L-ALa	0.2297	0.0059	0.4890	0.007	1.390	0.063	38.83	1.9	58.57	1.6	2.5	0.3
BE12c	D-Ala	0.2309	0.0124	0.4718	0.018	1.250	0.085	42.72	4.7	53.40	4.0	3.8	0.7

Table 2. Lifetime and intensity results for D- and L-Alanine. Large crystals (from H_2O/Acetone).

Sample	t1 (ns)	Δt1 (ns)	t2 (ns)	Δt2 (ns)	t3 (ns)	Δt3 (ns)	I1 (%)	ΔI1 (%)	I2 (%)	ΔI2 (%)	I3 (%)	ΔI3 (%)
BE022b/L	0.170	0.005	0.418	0.006	1.306	0.052	33.3	1.5	63.5	1.3	3.1	0.3
F051ABB/D	0.213	0.006	0.420	0.008	1.682	0.072	47.3	2.8	50.7	2.7	1.9	0.2

PPC-12: International Workshop on Positron and Positronium Chemistry, Lublin, Poland, August 2017
Bilge Eren, Fei Wu, Erdal Eren, Y. C. Jean and J. David Van Horn. "Positron Annihilation Lifetime Analysis of Left- and Right-Handed Alanine Single Crystals." *Acta Phys. Pol. A* **2017,** *submitted*.

Summary, Current & Future Work

- Categorization of beta + asymmetric matter:
  - Review article concept
  - Rxn Type|Energy|Result|etc.
- Asymmetric interactions of e+ with asymmetric single crystals
  - SiO_2 > Tartaric Acid < Tartrate ~ Alanine
  - Further samples
  - Theory
- Asymmetric thin film/positron interactions
- GiPS on single crystal asymmetric quartz

Welcome to your suggestions and potential collaboration.

Acknowledgements

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BİLECİK ŞEYH EDEBALİ ÜNİVERSİTESİ

“Asymmetry is more important than symmetry.” J.D.V.H

Thank you!

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Recent work…

1) Michael B. Larsen, J. David Van Horn, Fei Wu and Marc A. Hillmyer. "Intrinsically **Hierarchical Nanoporous Polymers** via Polymerization-Induced Microphase Separation." *Macromolecules* **2017**, *50*, 4363-4371.
2) J. David Van Horn and Maggie E. McGarry. "**Bibliography of Y. C. Jerry Jean**, Ph.D. Curators' Emeritus Professor of Chemistry and Physics University of Missouri-Kansas City 1976 to present." **2016**.
3) J. David Van Horn, Fei Wu, Gerald Corsiglia, and Y. C. Jean. "Asymmetric Positron Interactions with **Chiral Quartz Crystals**?" *Defect Diffus. Forum*. **2016**, *373*, 221-226.
4) Matthew D. Paul, Jonathan S. Davis, Y. C. Jean and J. David Van Horn. "Application and Evaluation of **3D Printed Materials** with PALS." *Defect Diffus. Forum*. **2016**, *373*, 303-306.
5) J. David Van Horn, Hongmin Chen, Y. C. Jean, Weilong Zhang, Mark R. Jaworowski. "Depth profiles and free volume in **aircraft primer films**." *J. Phys. Conf. Ser.* **2015**, *618*, 012023.
6) Zhiyong Xia, Morgana Trexler, Fei Wu, Y. C. Jean, and J. David Van Horn. "Free Volume Hole Relaxation in **Molecularly Oriented Polymers**." *Phys. Rev. E*, **2014**, *89*, 022603.
7) Y. C. Jean, J. David Van Horn, Wei-Song Hung and Kuier-Rarn Lee. "Perspective of positron annihilation spectroscopy in polymers." *Macromolecules* **2013**, *46*, 7133−7145.
8) Hongmin Chen, J. David Van Horn and Y. C. Jean. "Applications of Positron Annihilation Spectroscopy to Life Science." *Defect Diffus. Forum*. **2012**, *331*, 275-293.

What is Happening?
Theory: Presaged by Arthur Rich[?]

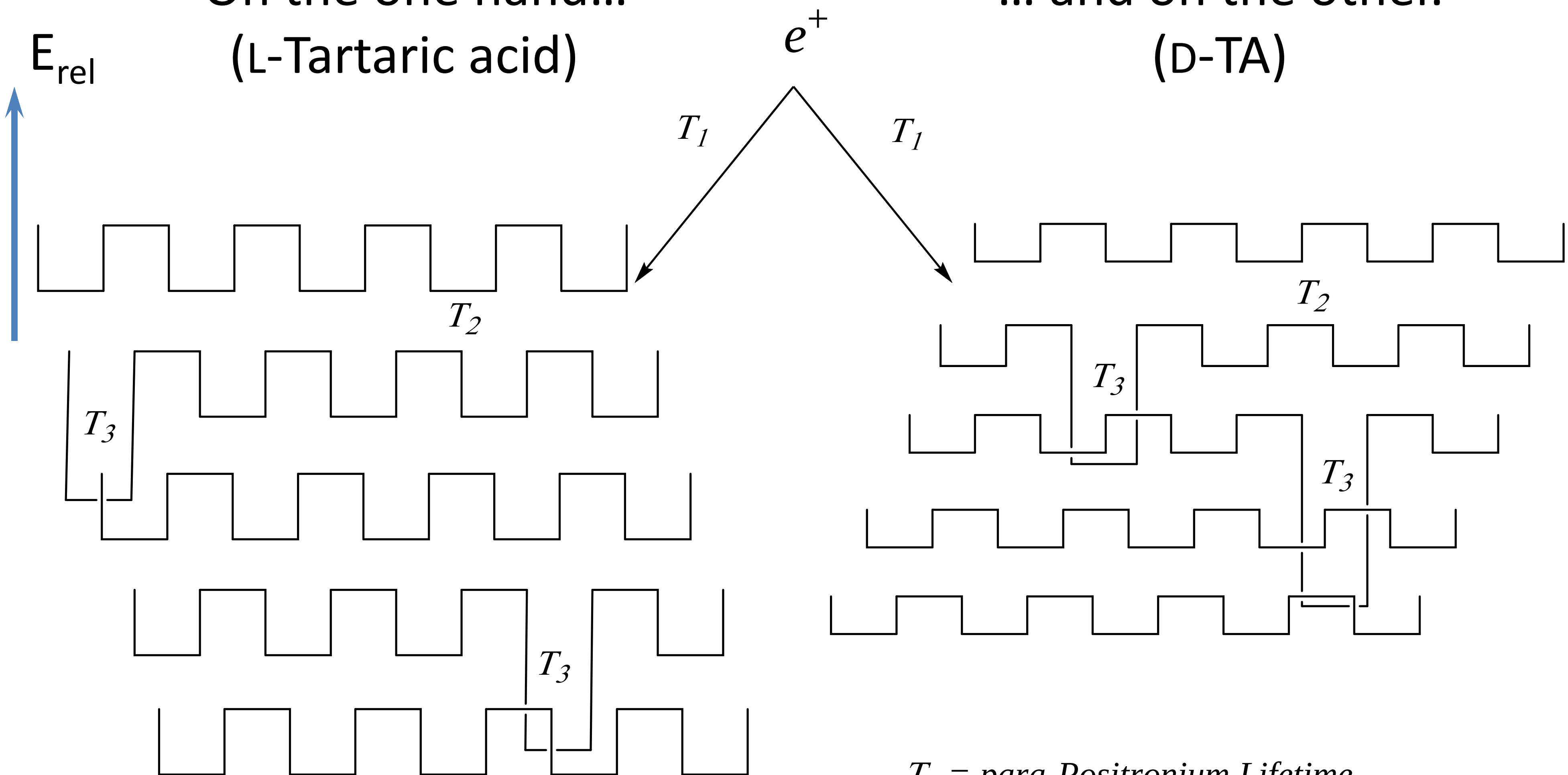
1. Impurities/Difference in crystals' quality? (D- and L-AA microcrystalline samples, Garay, *et al*.)
2. Interaction with positron or electron helicity in enantiomeric forms?
3. Differential Lattice Interactions?

A. Rich *Nature* **1976**, *264*, 482-483.

Relative Energy hypothesis:

On the one hand... (L-Tartaric acid)

... and on the other. (D-TA)

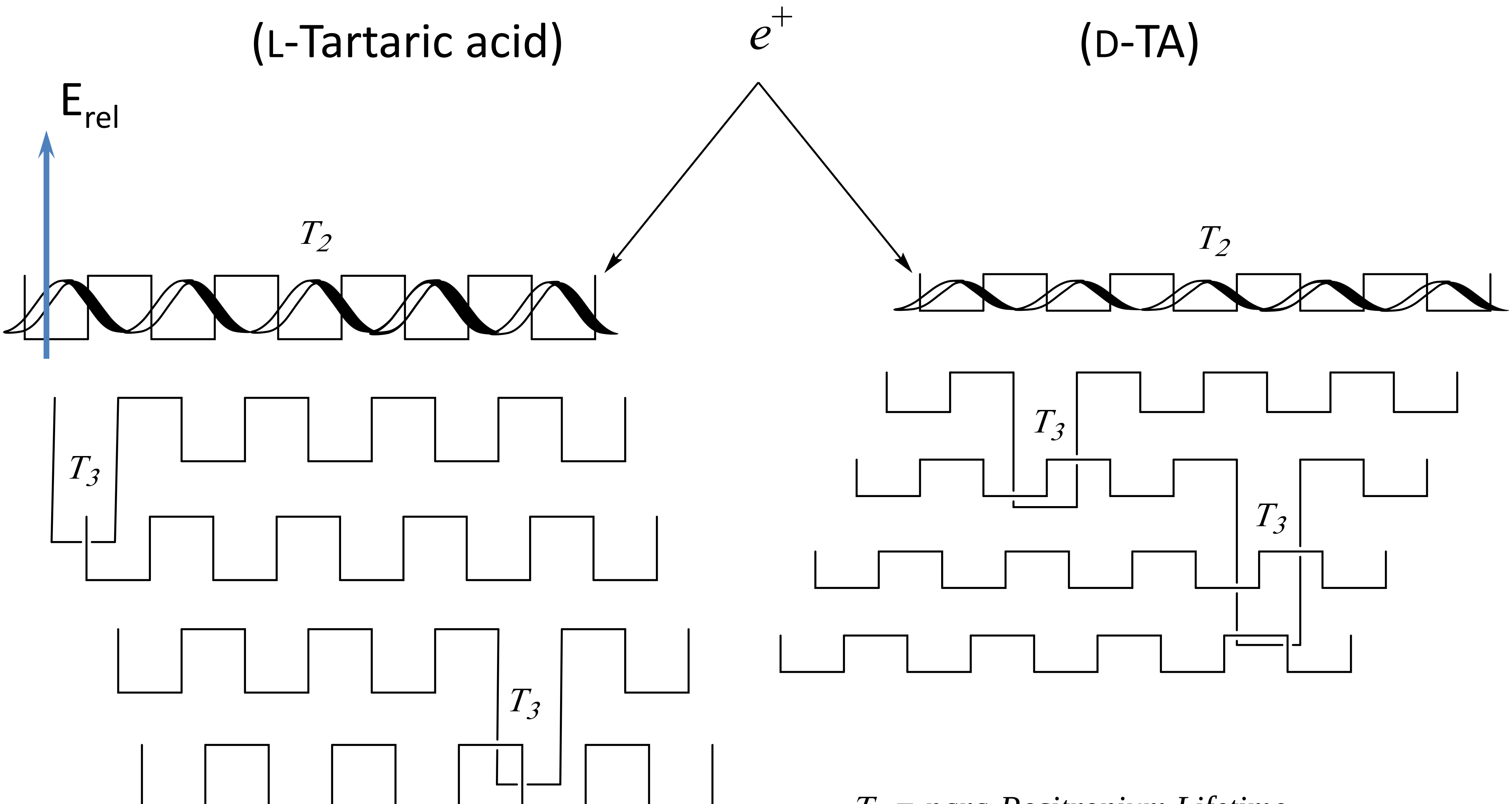


T_1 = *para-Positronium Lifetime*

T_2 = *'free' Positron Lifetime*

T_3 = *Lifetime associated with defects*

Relative Energy hypothesis:

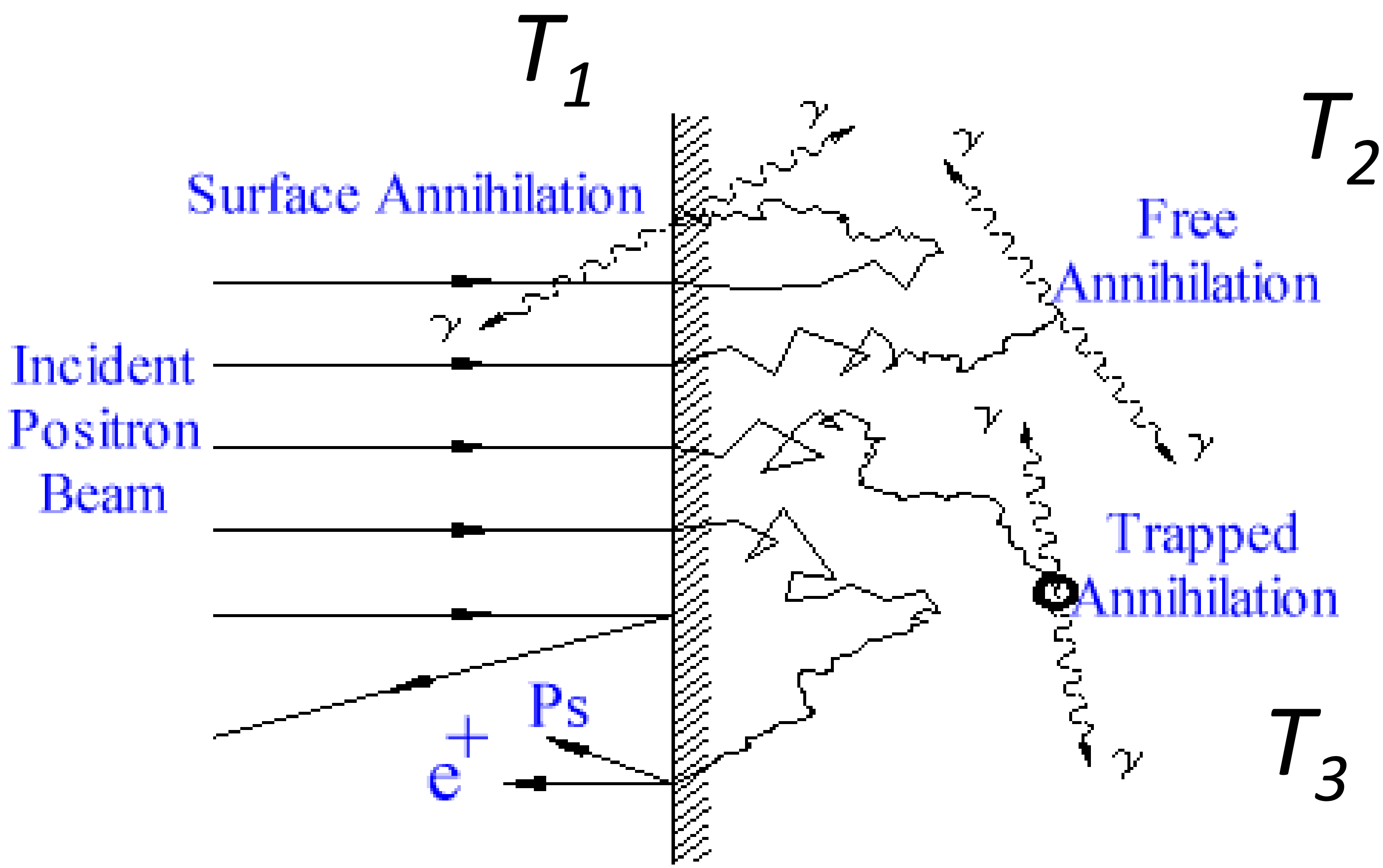


T_1 = para-Positronium Lifetime

T_2 = 'free' Positron Lifetime

T_3 = Lifetime associated with defects

Thermalization Problem.



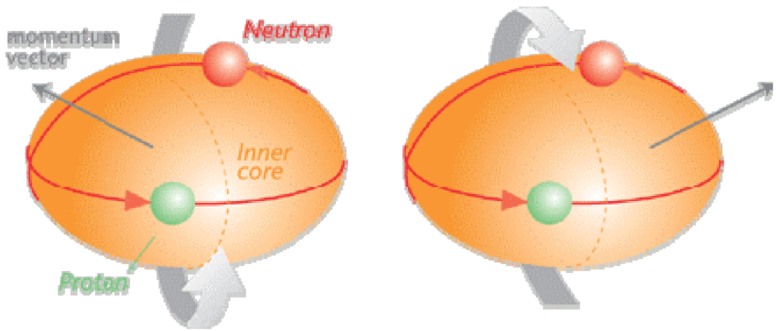
T_1 = *para-Positronium Lifetime*

T_2 = *'free' Positron Lifetime*

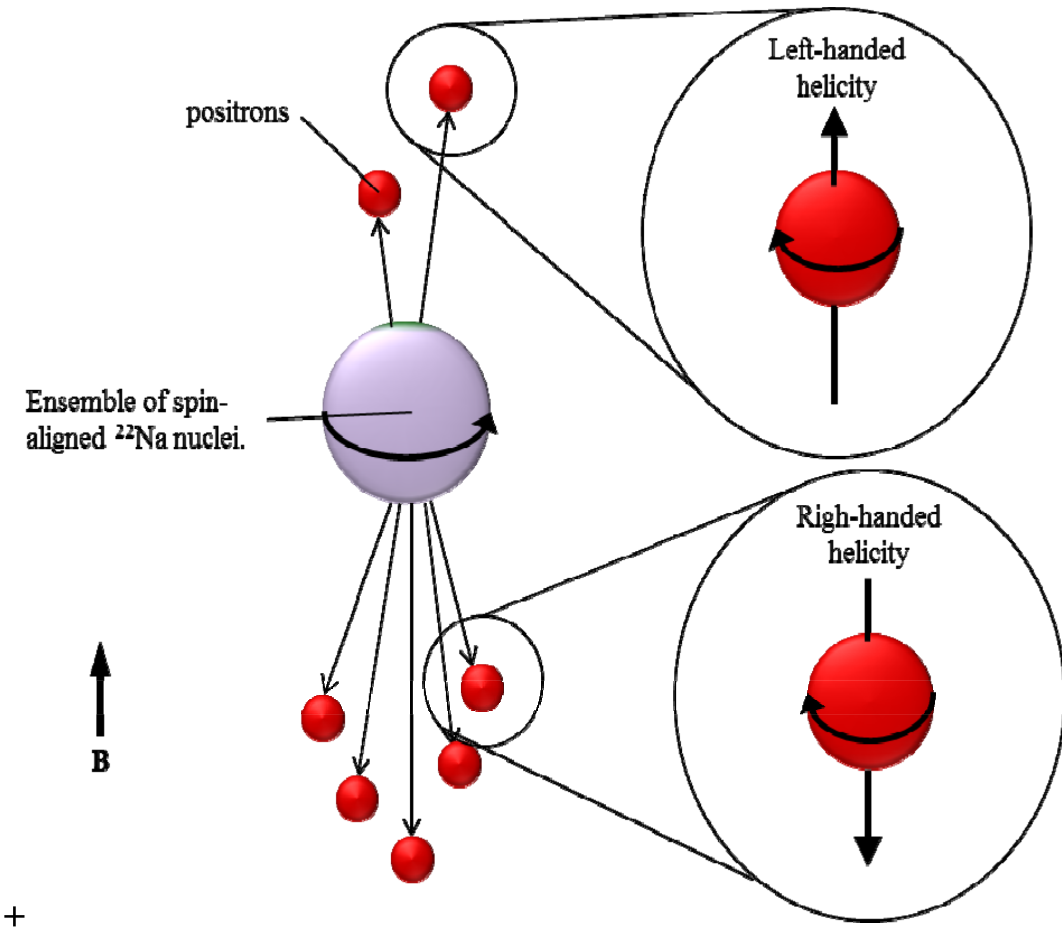
T_3 = *Lifetime associated with defects*

Helicity and Chirality

-Other Chiral Forces in Nature-



- Subatomic Particles
  - Circularly polarized light
  - ½ spin particles (e^-, e^+, muons)
- Atomic Nuclei
- Nuclear Weak Force
  - Parity violation in β decay
    - Net polarization of ejected e^-/e^+
  - Possible effect on biological chirality?



Up to 80% polarized

Chiral nuclei image source: http://ajdubre.tripod.com/