BİLECİK ŞEYH EDEBALİ ÜNİVERSİTESİ

UMKC UNIVERSITY OF MISSOURI KANSAS CITY

Positron Science Laboratory

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

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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

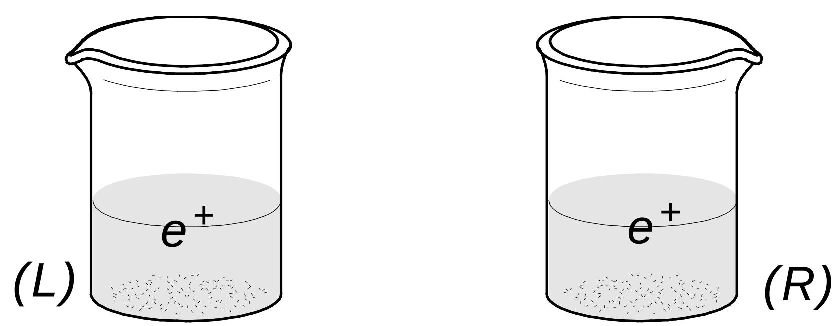
Search for Selectivity between Optical Isomers in the Interactions of Positrons with Chiral Molecules

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

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

Publication costs assisted by the Petroleum Research Fund

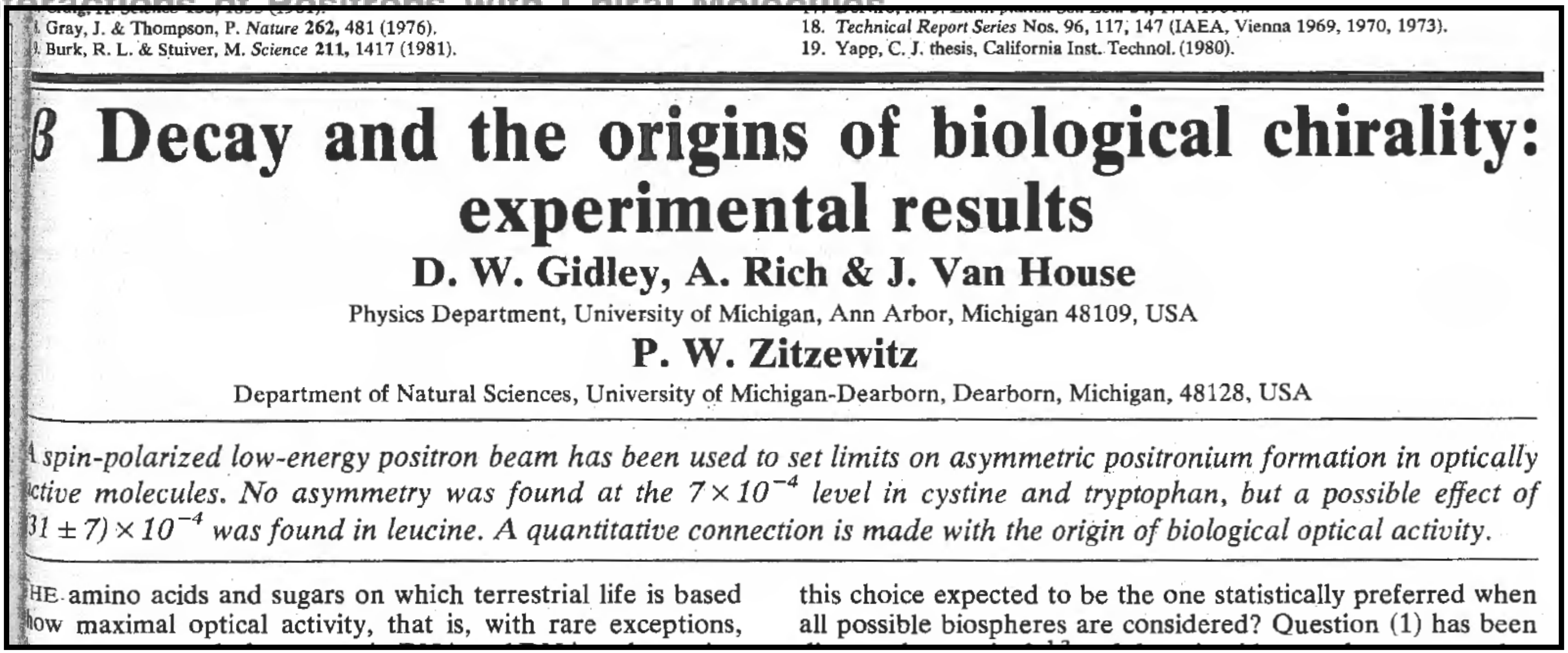
Positron lifetime measurements were performed in the optical isomers of s
as 2-methylbutanol, 2-aminobutanol, octanol-2, α-methylbenzylamine, ca
temperature range from −196 to 100 °C. No significant differences in the lifeti
I_1 and I_2, associated with the short- and long-lived components in the positron
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



(1976)

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

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

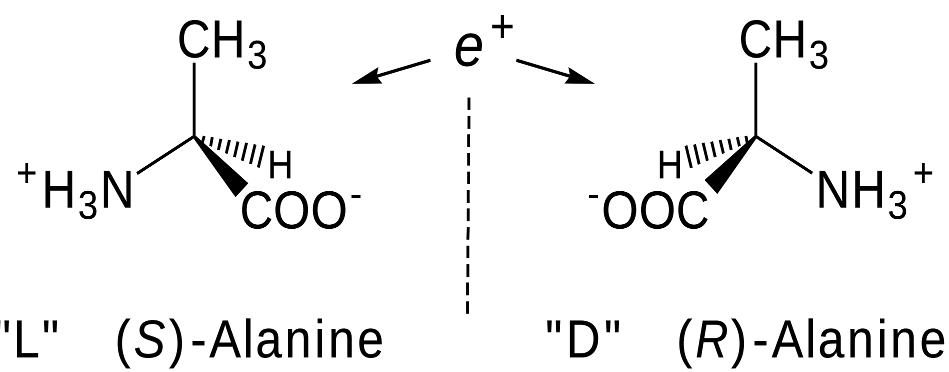

Gray, J. & Thompson, P. *Nature* **262**, 481 (1976).
Burk, R. L. & Stuiver, M. *Science* **211**, 1417 (1981).
18. *Technical Report Series* Nos. 96, 117, 147 (IAEA, Vienna 1969, 1970, 1973).
19. Yapp, C. J. thesis, California Inst. Technol. (1980).

β Decay and the origins of biological chirality: experimental results

D. W. Gidley, A. Rich & J. Van House
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 7×10^{-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 …



(1982)

Differential Reaction by radiolysis or oxidation? (solid-phase)

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).
19. Yapp, C. J. thesis, California Inst. Technol. (1980).

β Decay and the origins of biological chirality: experimental results

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,*]
[1]*ARC Centre for Antimatter-Matter Studies, School of Chemical and Physical Sciences, Flinders University, GPO Box 2100, Adelaide, SA 5001, Australia*
[2]*Department of Physics, University of Trento, Via Sommarive 14, 38123 Povo (TN), Italy*
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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

GAUSSIAN 09 package, were performed as a part of this work in order to assist us in interpreting some aspects of our data.

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

Positron scattering in gas-phase Methyl-2-chloropropionate

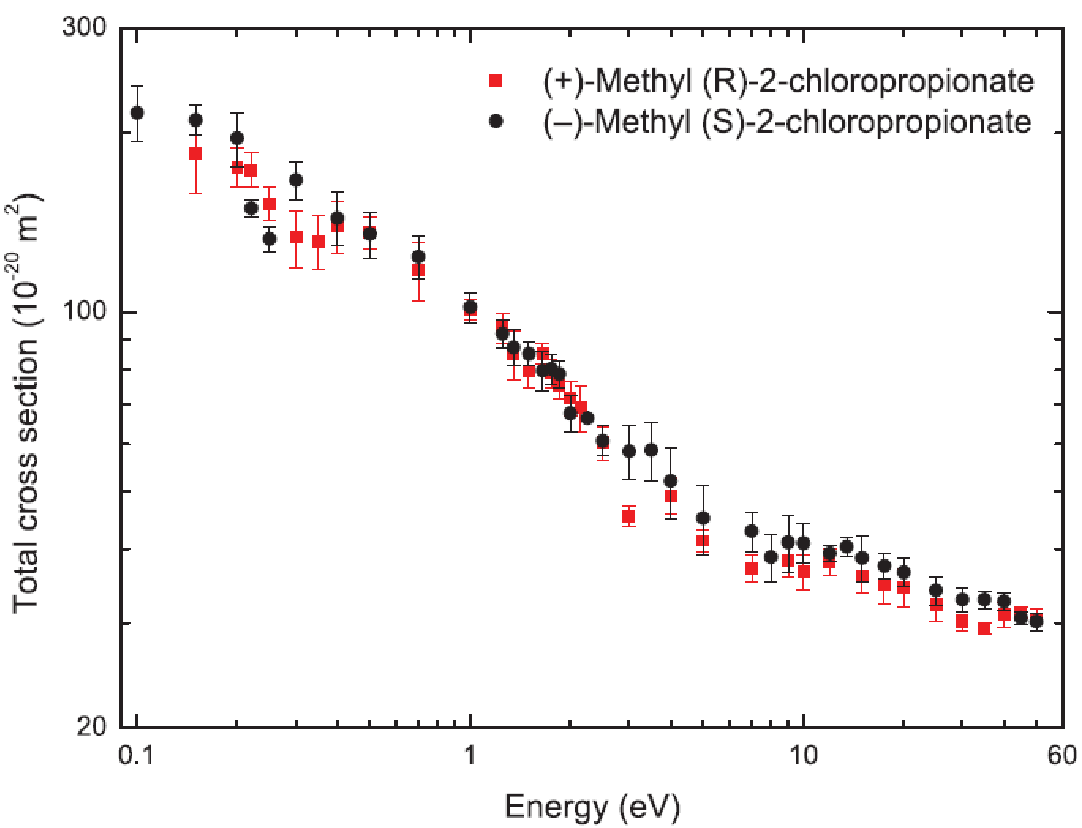
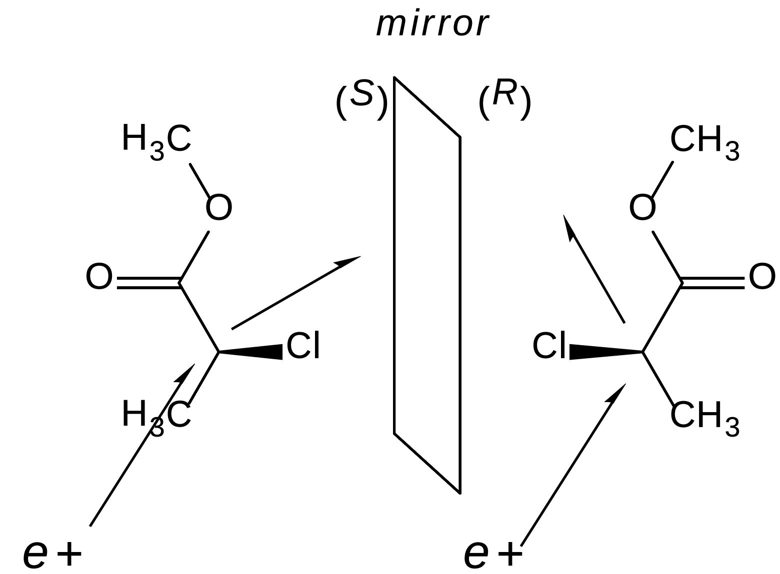


FIG. 2. (Color online) Present measured TCSs ($\times 10^{-20}$ m^2) for positron scattering from (+)-methyl (*R*)-2-chloropropionate (filled squares) and (–)-methyl (*S*)-2-chloropropionate (filled circles). Uncertainties plotted are the statistical errors on the data.

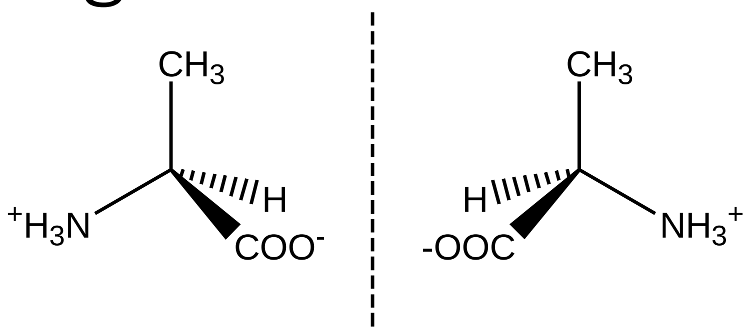


Chirality and Positrons?

Can Positron Techniques Distinguish Stereoisomers?

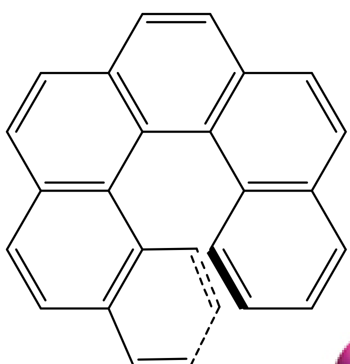
2011 “PSL”

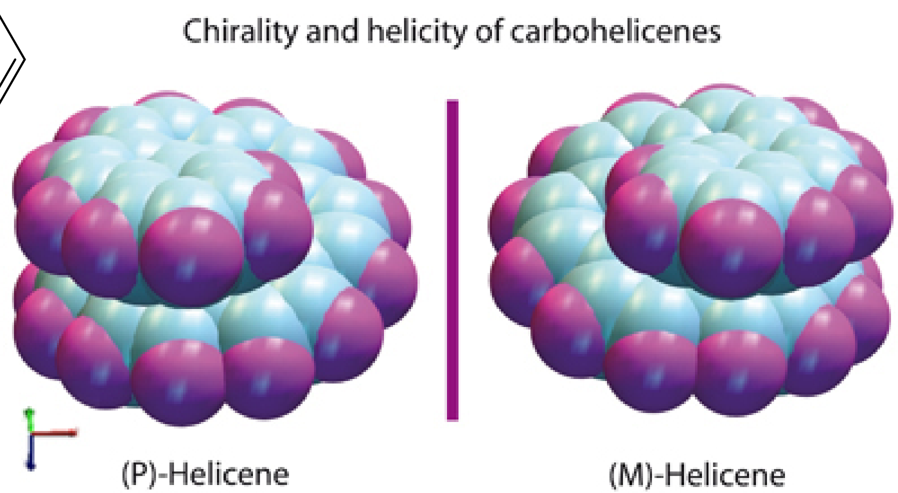
Positron Science Laboratory

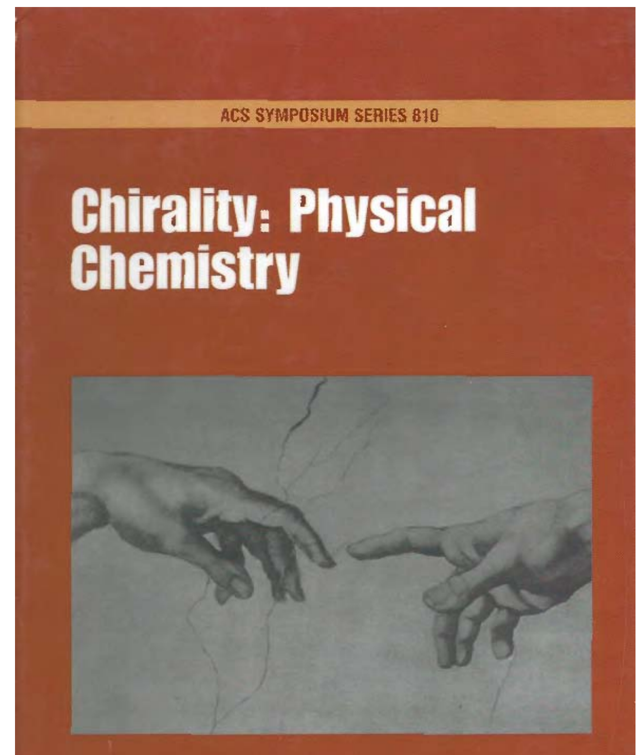


"L"
(*S*)-Alanine

"D"
(*R*)-Alanine







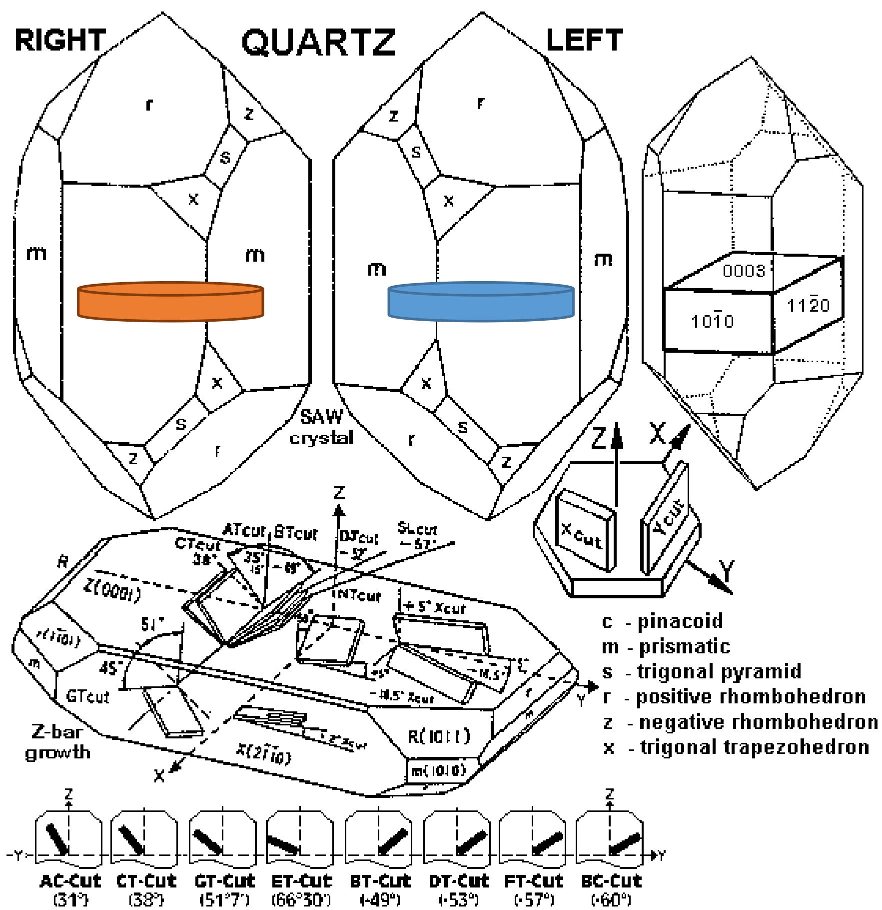
Polarimetry
CD
X-ray
Surface (AFM, SEM)

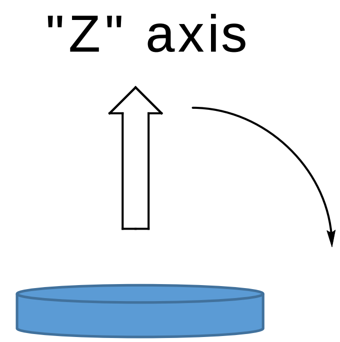
Beta particles with asymmetric matter in different phases?

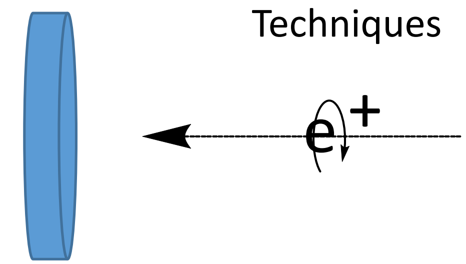
	Gas	Liquid	Solid (amorphous)	Solid (crystalline)
e-	Scattering off asymmetric HOMO; Reaction/Interaction with LUMO	Not expected, solvated electrons→ rapid reaction with oxygen atoms	Not expected.	Electron backscatter/ diffraction; some reaction process [reduction]…
e+ / Ps	Not expected; residence/ interaction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

Positron/Crystalline* Quartz Hypothesis:

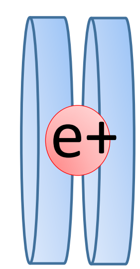
Host-Guest Interactions (e^+ and M*)







Positron Beam Techniques



Bulk Positron Lifetime Analysis

Some Classification of Physical Stereochemistry

- **Stereo-recognition**

  Polarimetry, circular dichroism, optical…

- **Stereo-selection**

  Chiral chromatography, crystallization, chiral resolutions…

- **Stereo-induction**

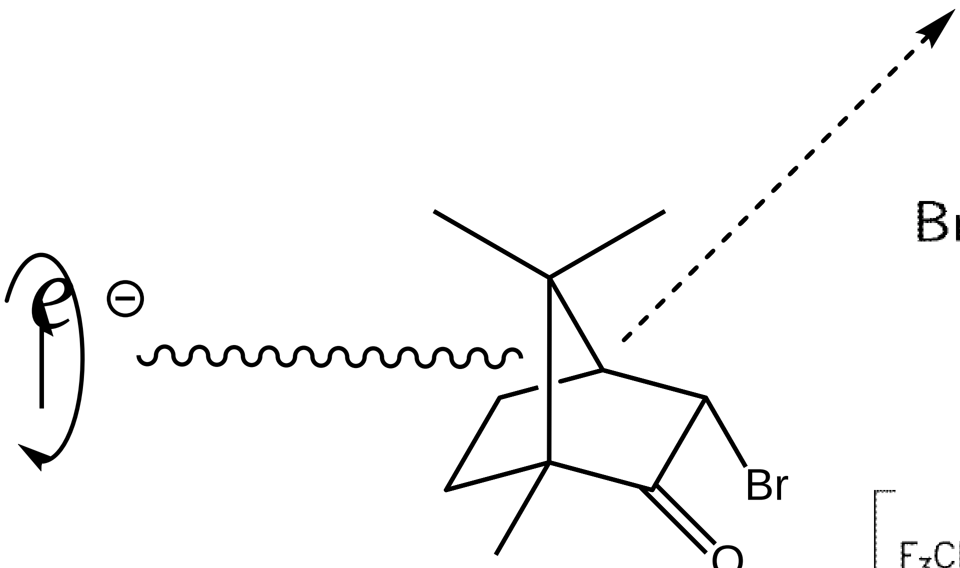
  Chiral catalyst, chiral host,…
  Origin of molecular/biological asymmetry?

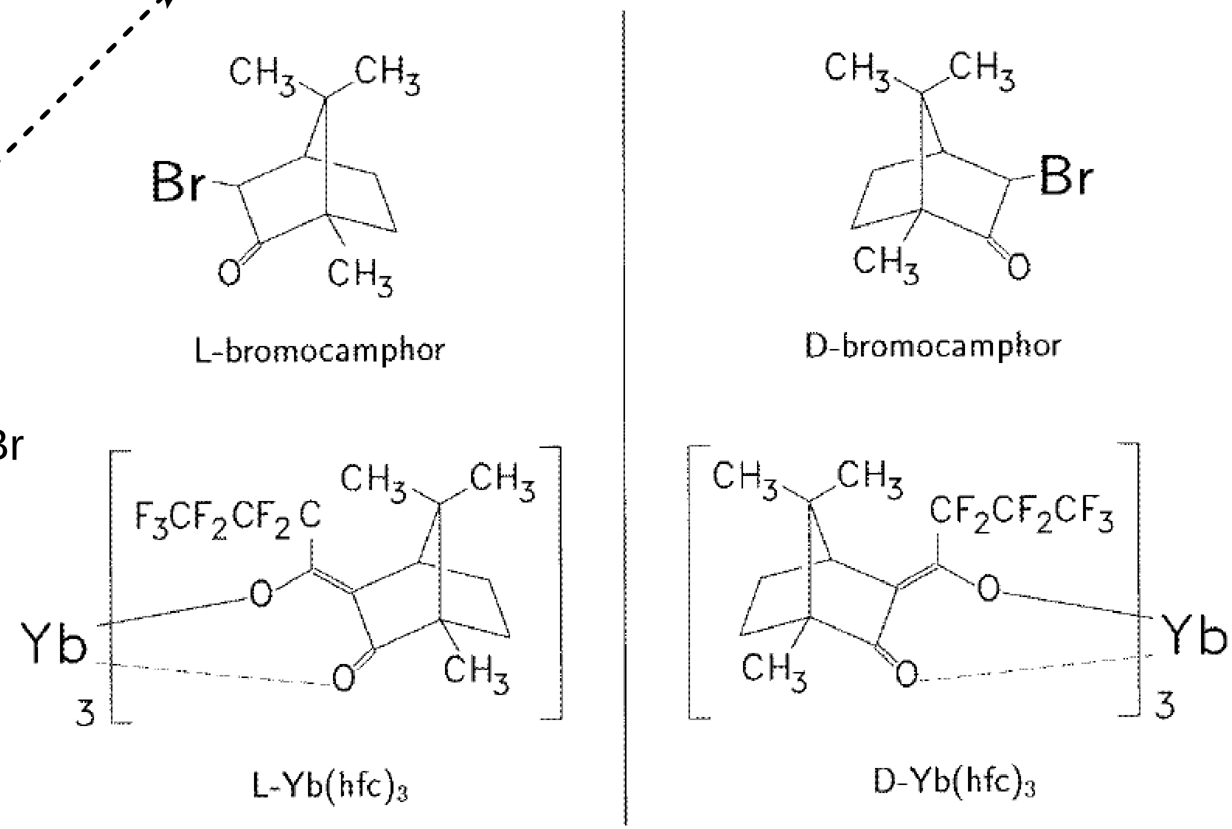
1A. Stereo-*recognition*

- Stereorecognition
- *e.g*. Polarimetry
  - Optical Rotation
  - [α]

1B. Stereo-*recognition*

Polarized *e*– scattering experiments





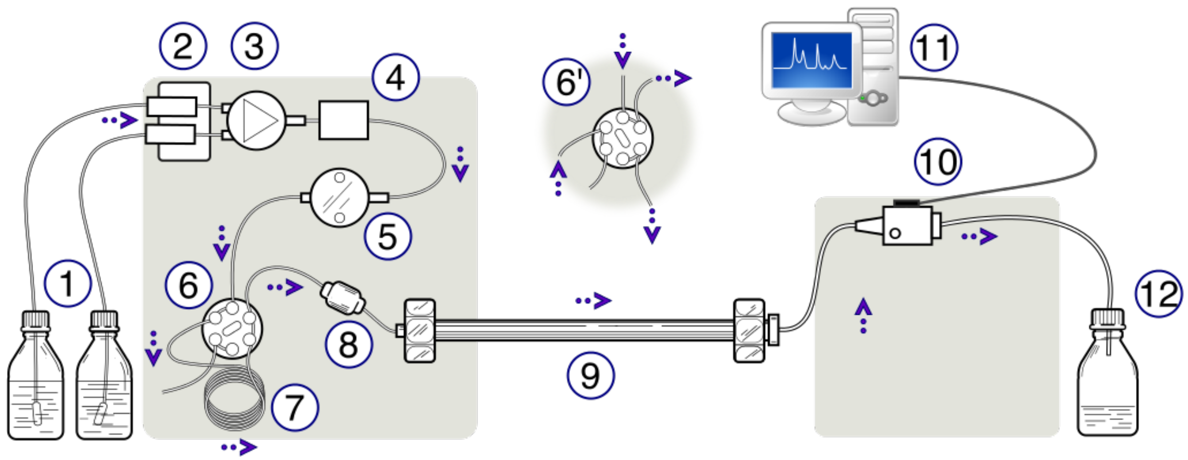
S. Mayer, C. Nolting and J. Kessler, "Electron scattering from chiral molecules." *J. Phys. B: At. Mol. Opt. Phys.* **1996**, *29,* 3497–3511.

AND SEE…

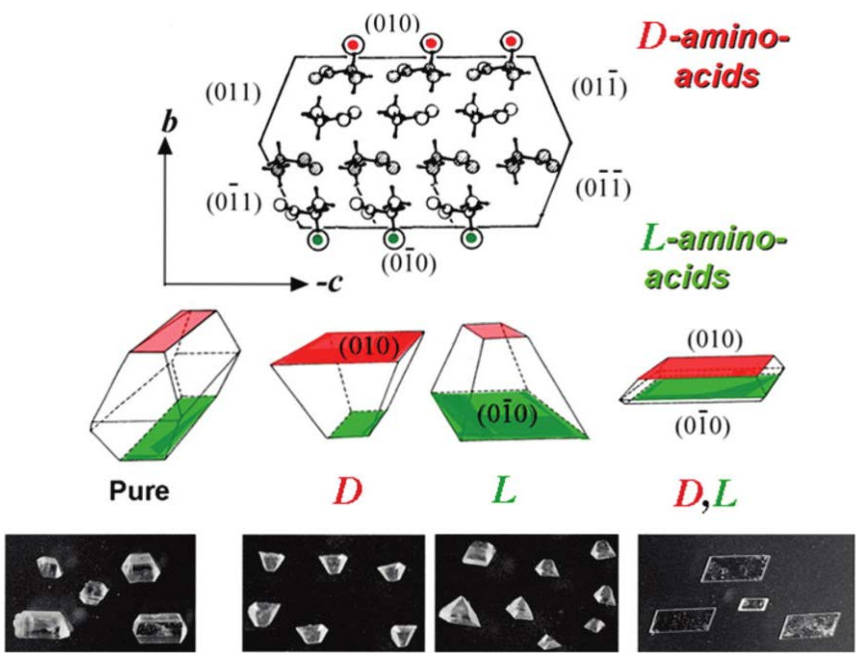
K. Ray, S. P. Ananthavel, D. H. Waldeck and R. Naaman, "Asymmetric Scattering of Polarized Electrons by Organized Organic Films of Chiral Molecules." *Science*, **1999**, *283*, 814-816.

2A. Stereo-*selection*

- *e.g*. Chiral HPLC



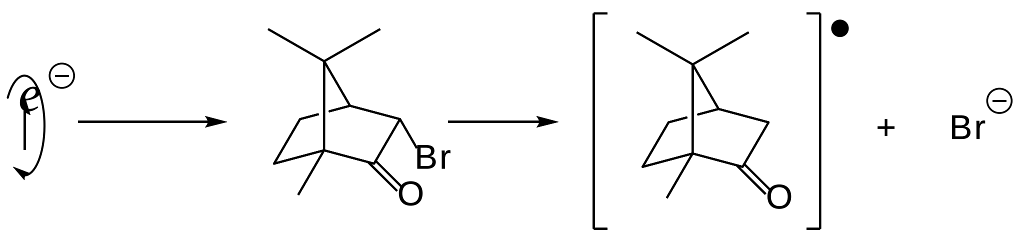
- *e.g*. Selective crystallization/resolution
- *etc*.

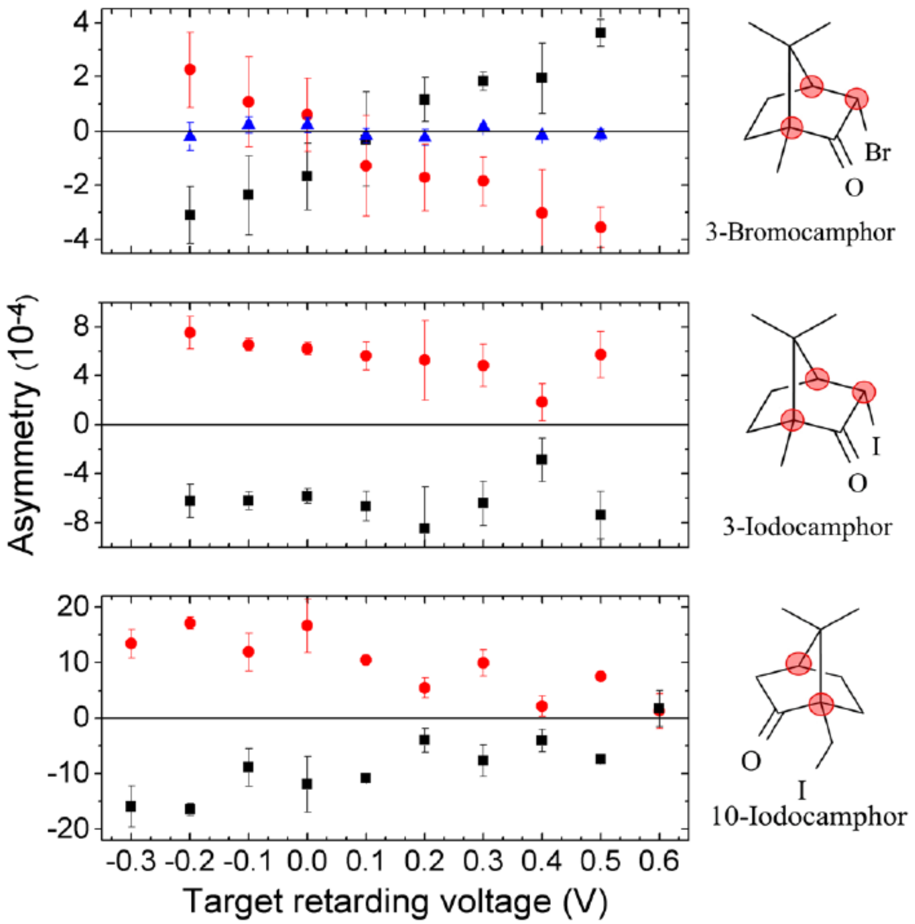


Isabelle Weissbuch and Meir Lahav "Crystalline Architectures as Templates of Relevance to the Origins of Homochirality." *Chem. Rev*. **2011**, *111*, 3236–3267

2B. Stereo-*selection*

Polarized DEA (dissociative *e*– attachment rxn)

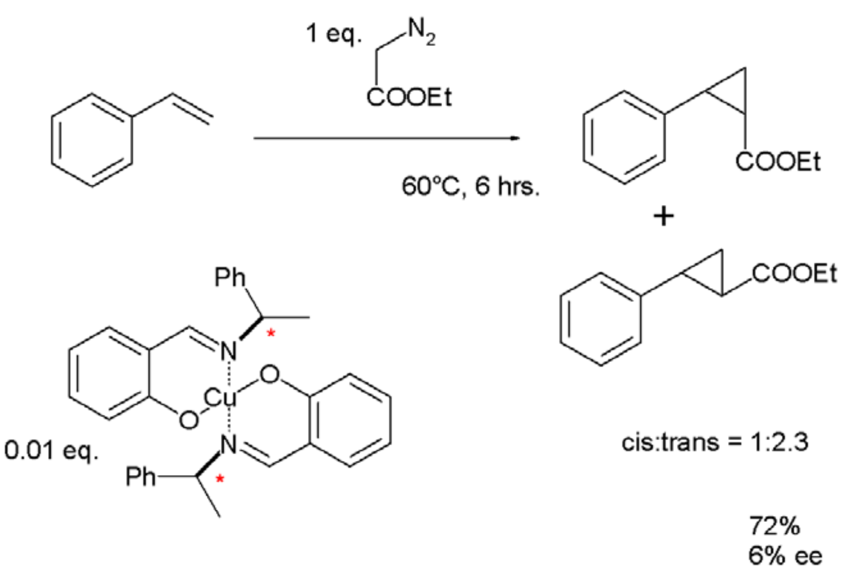


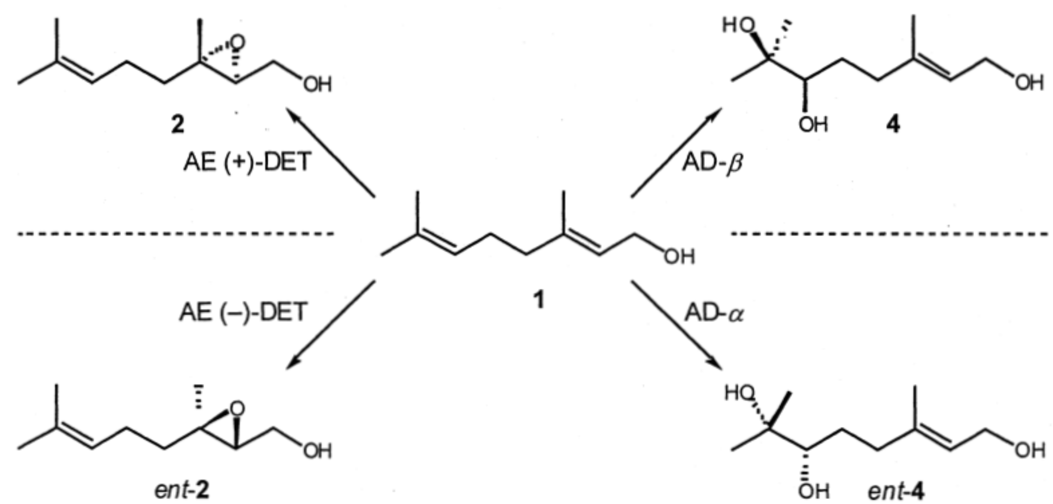


J. M. Dreiling, *et al.*, Phys. Rev. Lett. 116, 093201 (2016).

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".

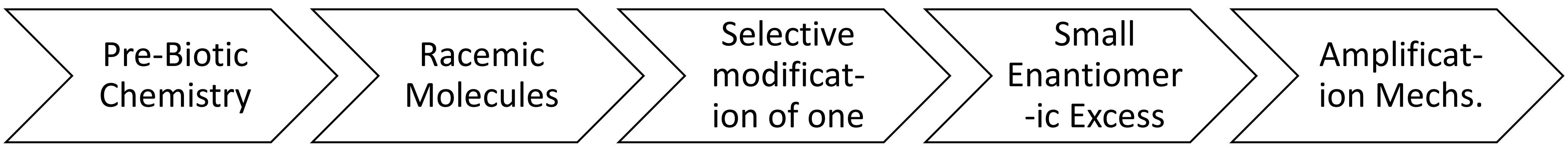




3B. Stereo-*induction*

- 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.

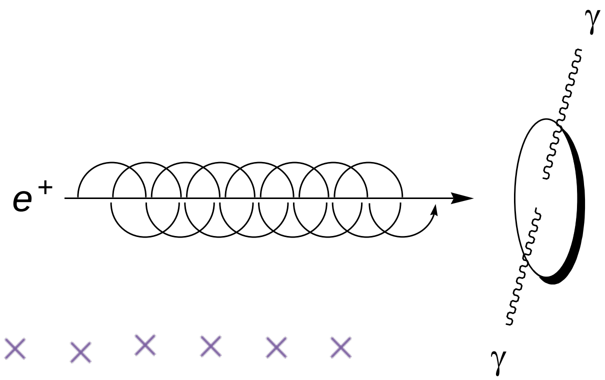
β / Physical Stereochemistry Table

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!]

Quartz results (1)

Positron Stereorecognition of LH and RH Quartz

Slow Beam Experiment ~ 80% polarization



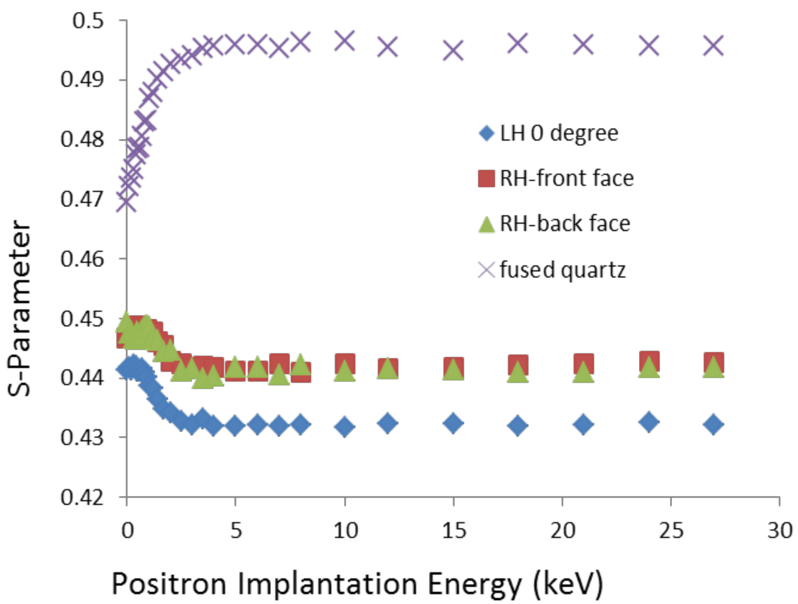


Figure 1. Evaluation of "S-parameter" versus positron implantation energy for fused and crystalline quartz samples in a Doppler-broadening energy spectrum technique.

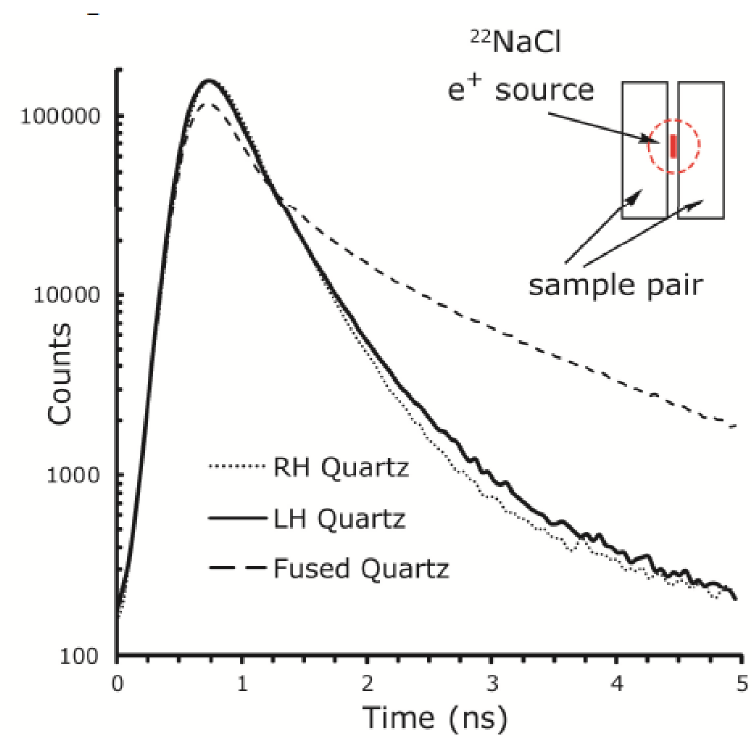


Figure 2. Representative bulk positron lifetime spectra of fused and crystalline quartz samples.

J. David Van Horn, Fei Wu, Gerald Corsiglia, and Y. C. Jean. "Asymmetric Positron Interactions with Chiral Quartz Crystals?" *Defect Diffus. Forum*. **2016**, *373*, 221-226. [DOI: 10.4028/www.scientific.net/DDF.373.221

Representative Data: Bulk Quartz PALS

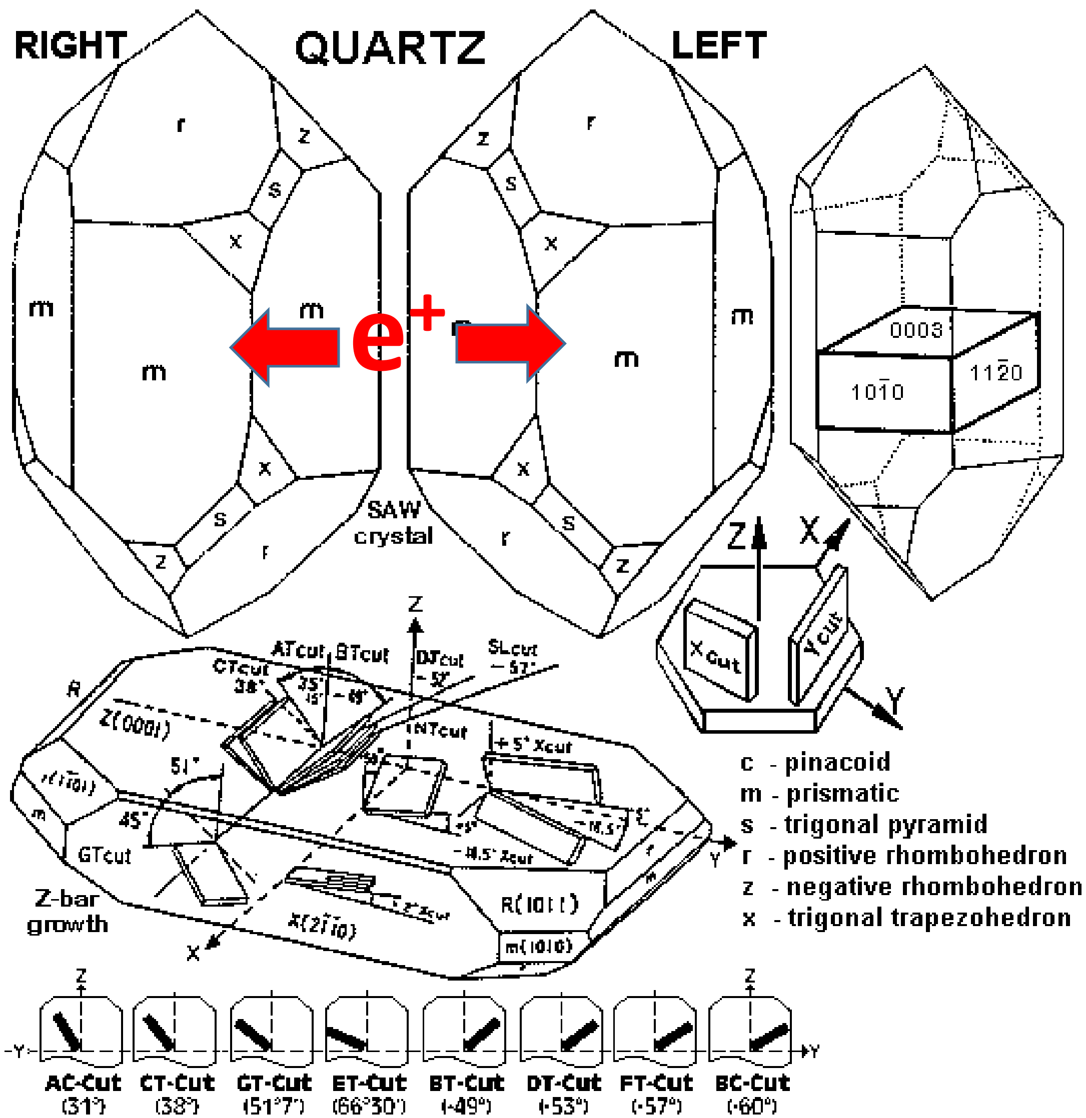
TABLE 1. Positronium lifetimes and intensities in quartz glass and crystal samples, using sealed and open positron sources (2×10^6 counts collected for each exp.).

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. 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 τ_3 lifetime is included in fitting.

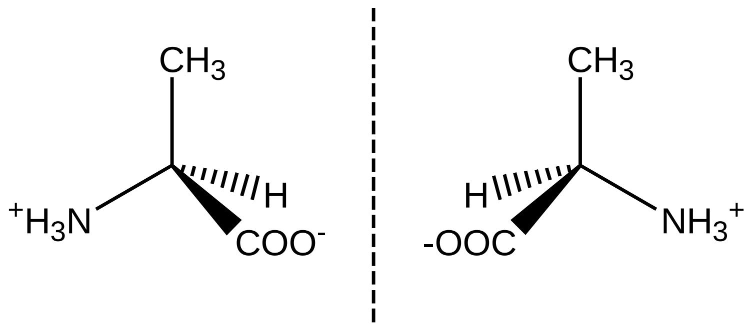
J. D. Van Horn, F. Wu, G. Corsiglia & Y. C. Jean. *Defect Diffus. Forum* , 221-226 (2016).
Saito, H. & Hyodo, T. *Phys. Rev. Lett.* , 193401 (2003).

Quartz (3) Current Work… ‘*x*-cut’ quartz: natural and synthetic. (please see poster)



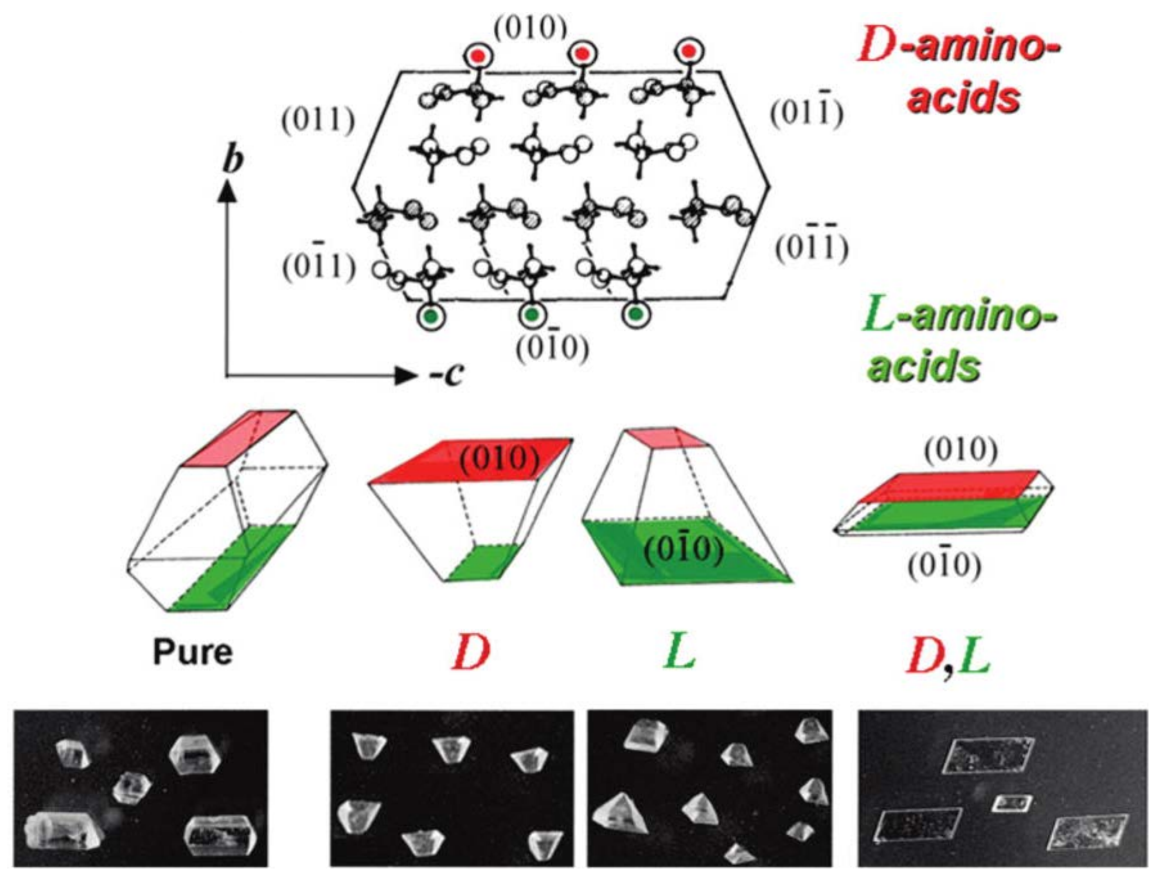
Alanine PALS and a Crystallization Challenge:

- Crystallize large set of D/L crystals?



"L"
(*S*)-Alanine

"D"
(*R*)-Alanine

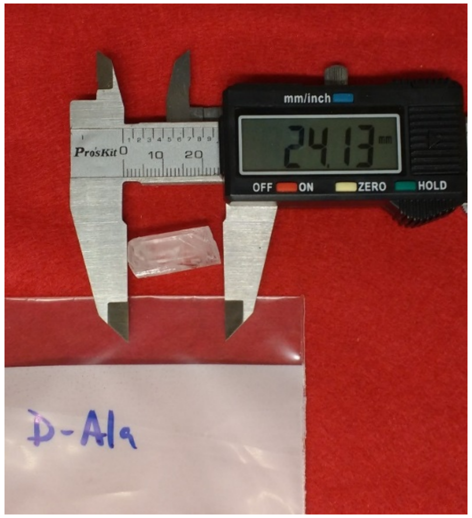


- Future: Obtain a racemic crystal for stereoselection experiment?

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

Alanine Experimental

Figure. Alanine crystals from acetone water mixtures.



- 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

Alanine Results (1): Preliminary 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

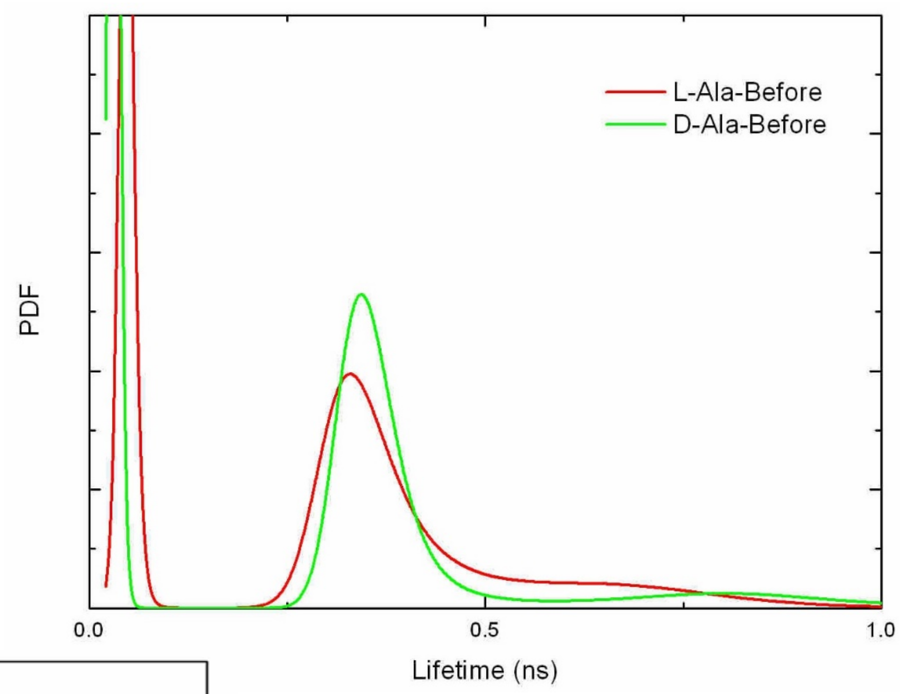
Alanine Results (2): before and after treatment of examined crystal face.

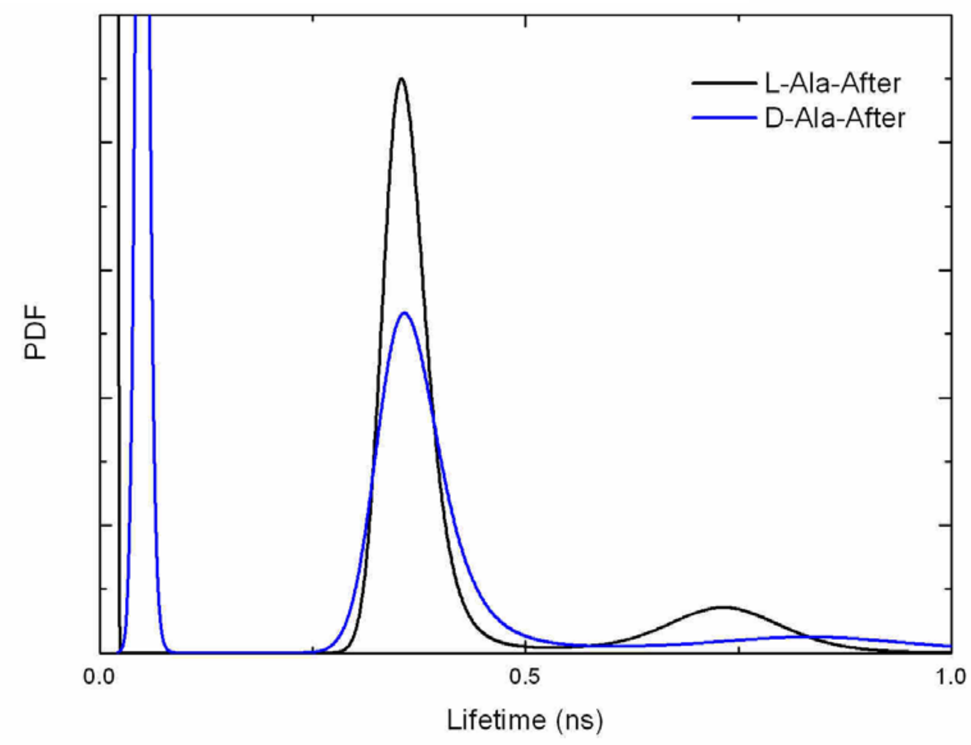
Sample	τ_1 [ns]	τ_2 [ns]	τ_3 [ns]	I_1 [%]	I_2 [%]	I_3 [%]	Variance
L-alanine/before	0.250 (6)	0.526 (12)	1.49 (11)	49.2 (2.4)	48.7 (2.1)	2.1 (0.4)	1.04
L-alanine/after	0.229 (6)	0.496 (14)	1.15 (11)	44.6 (2.6)	52.5 (1.9)	2.9 (0.9)	0.944
D-alanine/before	0.229 (7)	0.476 (12)	1.31 (06)	42.6 (2.8)	53.3 (2.4)	4.1 (0.5)	1.05
D-alanine/after	0.217 (6)	0.478 (11)	1.21 (06)	40.6 (2.4)	55.4 (1.9)	4.0 (0.6)	1.08

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 fo the Zwitterion group may negate any asymmetric interactions
- Additional data point for LH/RH crystal PALS data:

LH/RH Sample	Quartz	Tartaric Acid	Tartrate Salt	Alanine
	Insulator; neutral	Neutral organic	Anionic organic	zwitterion
PALS L/R Δ	Yes	Yes	No	No

- Quartz $\geq$ 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.BİL.04-03.
- Bilge Eren and Erdal Eren.
- We thank James Murowchick (UMKC Geosciences) and Xiaodong Yan (UMKC Chemistry) for assistance with X-ray diffraction measurements.
- 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:
  - Gerald A. Corsiglia, MS Thesis, 2015.
  - Gerald A. Corsiglia, Fei Wu, Y. C. Jean and J. David Van Horn. “Asymmetric Positron Annihilation in Chiral Tartaric Acid Crystals.” **2017**, *in preparation*.
  - 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.

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

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