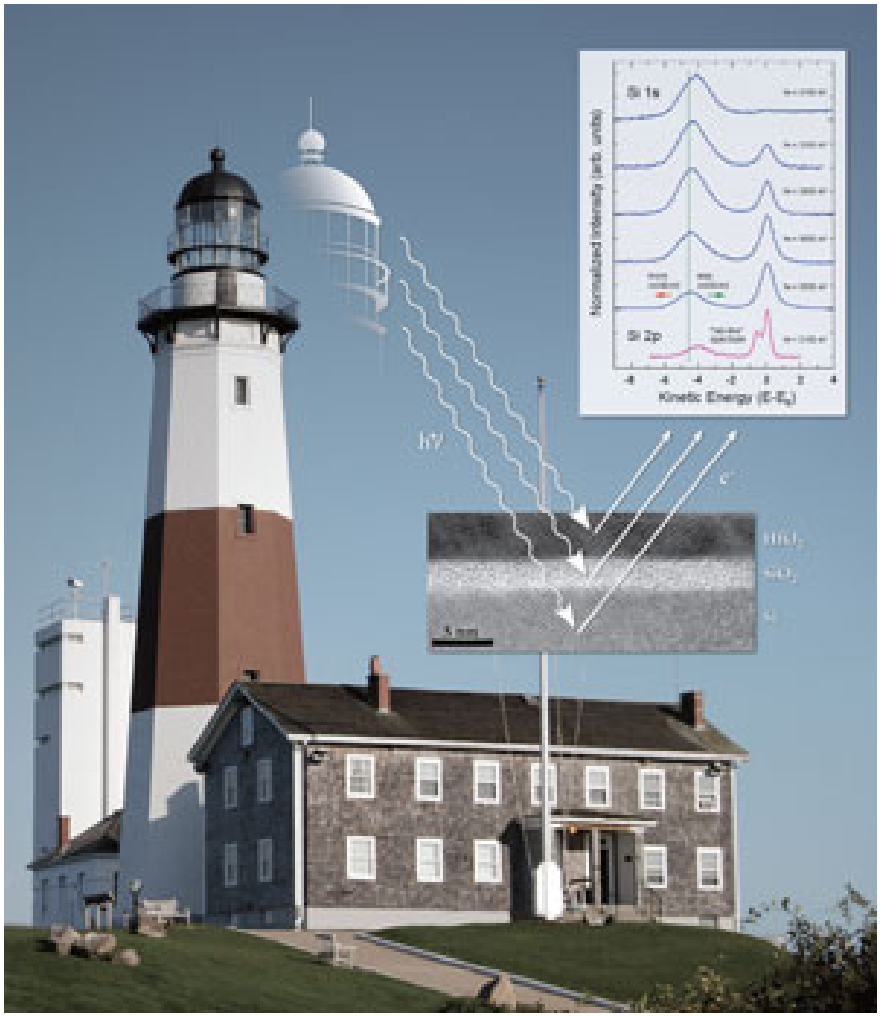
Thank you HAXPES 2009 Organizers



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XPS and HAXPES Studies of Interstellar Chemistry

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Outline

- Introduction
  - Prebiological molecules
  - Chirality
  - Spin-polarized secondary electrons
- Experimental approach
- Chiral selective surface chemistry
- *X-ray induced desorption*
- Conclusions

Prebiological molecules: Miller and Urey (1950's)

- **Based on idea that early Earth had a thick atmosphere of hydrogen, ammonia, methane.**
- **Add a warm ocean, heat for a few million years under a low to medium sun.**
- **Stir with tides and add lightning or UV to get the first microorganisms.**

Actual Experiment

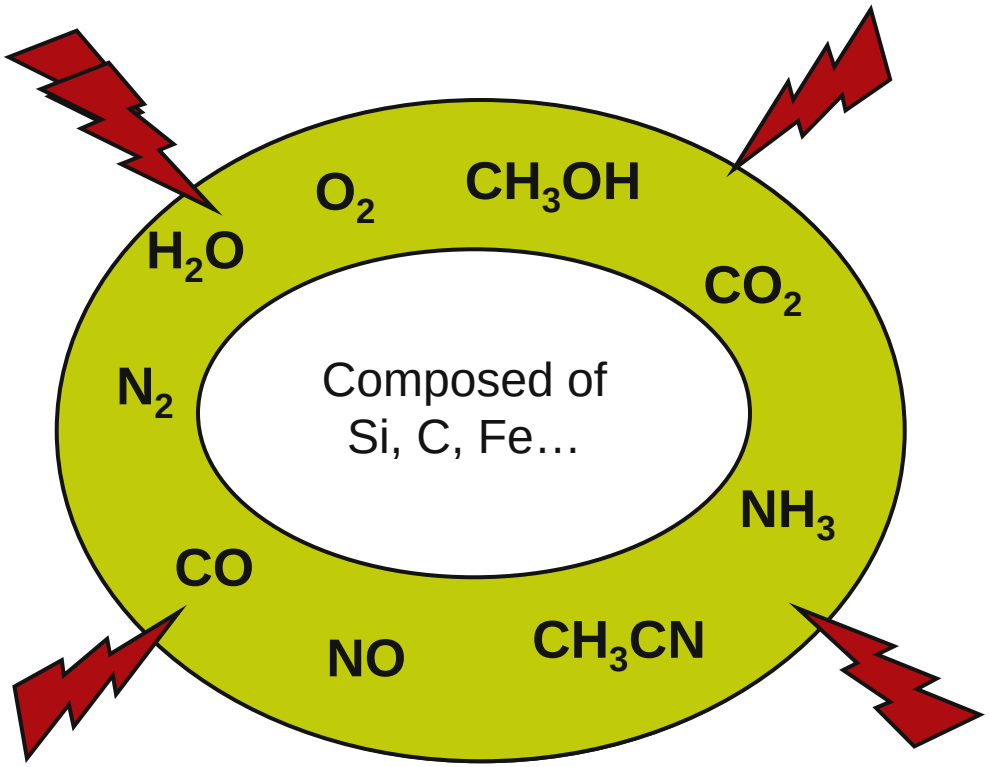
- Shoot sparks (lightning) into a gas/water mixture.
- Astounding results - found they produced, among other things: amino acids (basis for proteins/life and purine bases (steps in the spiral staircase of DNA).
- Mystery solved?

But….

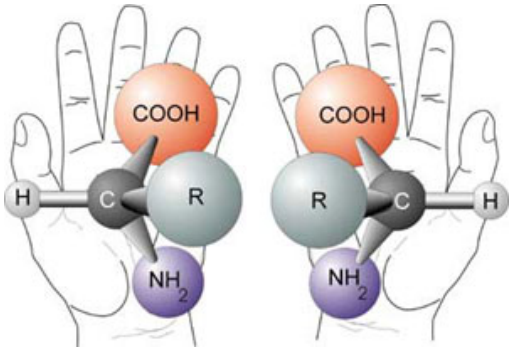
- The early earth was a hot ball of molten rock from which the oceans and atmosphere had been swept away.
- The earth was periodically bombarded by asteroids and comets causing cataclysms that would have aborted any life at that time and causing most of the atmosphere and oceans to boil away.
- The building blocks of life (amino acids) are chiral. Life on earth favors left-handed amino acids, right handed sugars. There is no asymmetry inherent in the “primordial soup” mechanism.
- So, what’s a viable alternative?


Long ago,
in a galaxy far, far away

There was a grain of dust



What about chirality?



- Possible avenues have been investigated since the time of Pasteur.
- No compelling argument has been found for any particular mechanisms.

Circularly polarized UV light and spin-polarized electrons

- Circularly polarized UV light requires light in a narrow band pass and light of a slightly different energy can have an opposite effect

- Spin polarized electrons. Previous mechanisms had postulated the source as high energy beta decay electrons from a radioactive source. Such sources are not widespread and high energy electrons are not effective at promoting chemistry.

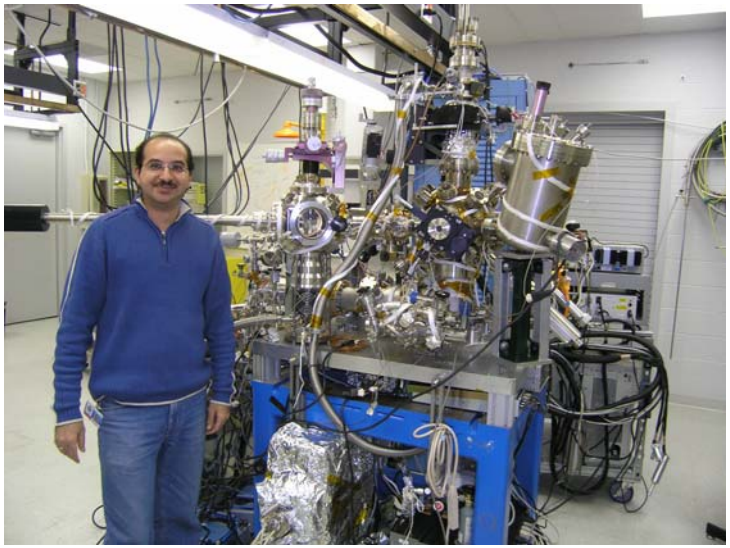
How about spin polarized secondary electrons?

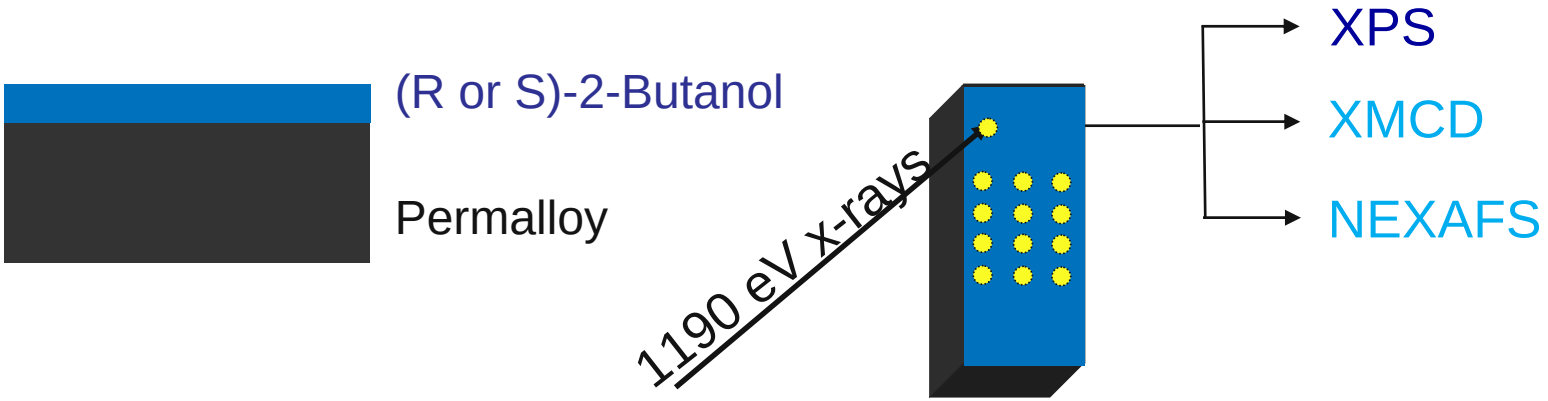
- Low energy electrons have been shown to induce a variety of reactions in condensed molecular films.
  - A.D. Bass and L. Sanche, Low Temp. Phys. **29**, 202 (2003).
  - R. Balog, *et al.*, Int. J. Mass Spec. **233**, 267 (2004).

- Longitudinally spin polarized electron should be effective at promoting chiral-specific chemistry. (M. Avalos *et al.*, Chem. Rev. **98**, 2391 (1998))

- Low energy, spin-polarized secondary electrons are produced by the interaction of ionizing radiation with a magnetic substrate. The polarization is determined by the relative orientation of the propagation vector with the magnetic field direction.

Experiments

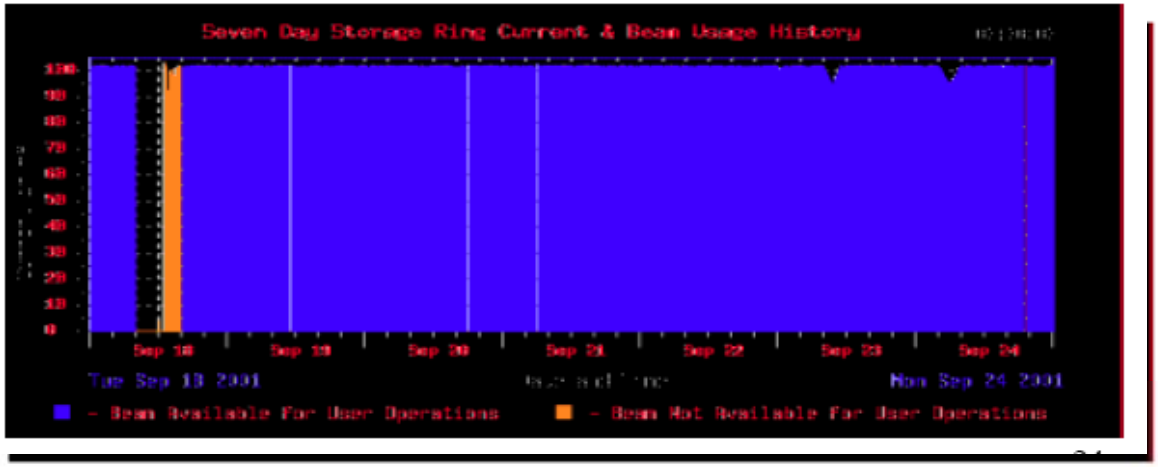




The light source

- The approach relies on determining accurate time constants for the photolysis reaction from [Butanol] = $[\text{Butanol}]_0 \exp(-t/\tau)$
- $\tau = 1/\sigma f$, where σ is the cross section and f is the flux density
- **It is critical to have a constant flux density**.

$$d[\text{Butanol}]/dt = -\sigma f\,[\text{Butanol}]$$



Experimental procedure

1 kV Ar ion sputter clean permalloy film

Dose with (R)- or (S)- 2-butanol @ 9(

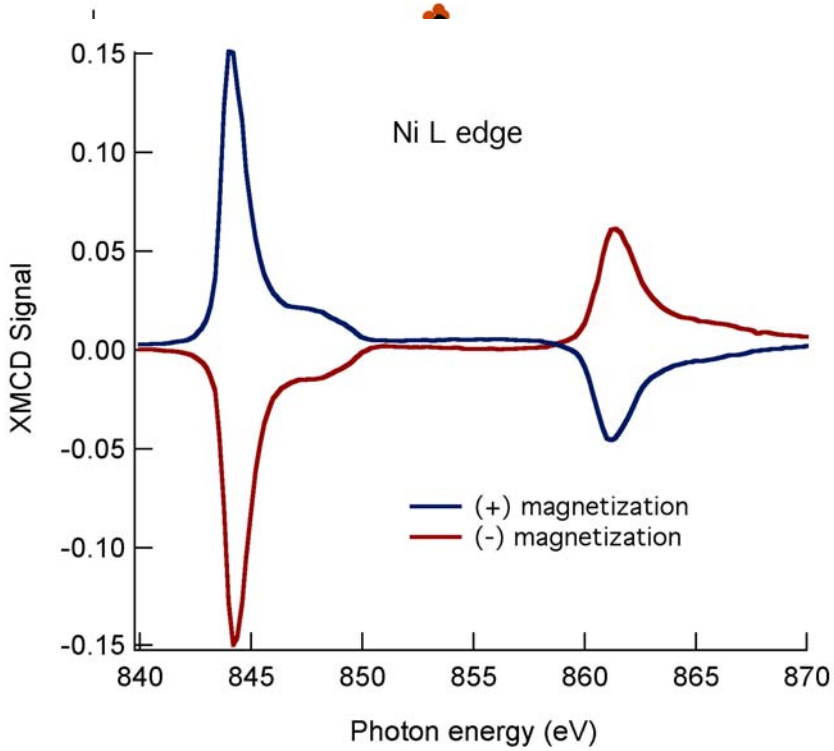
Magnetize in a given direction

Irradiate while recording XPS

Examine different positions

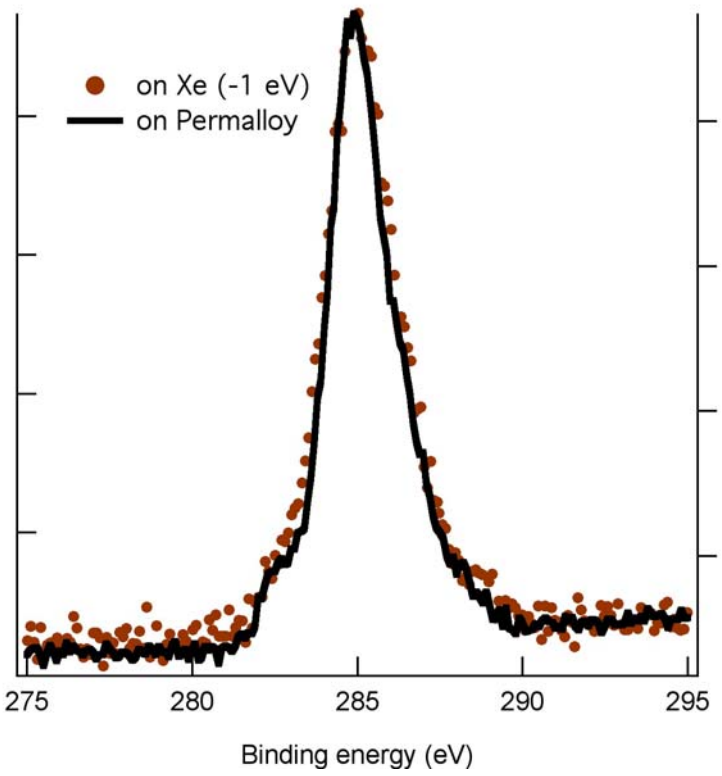
Change magnetizations

2-butanol/Permalloy



Adsorption State

- Molecular adsorption indicated in previous work
  - I. Lee, and F. Zaera, J. Phys. Chem. B **109**, 12920 (2005).
  - A. Mulligan *et al.*, Chem. Commun. **21**, 2492 (2004).
  - C. McFadden, P.S. Cremer, A.J. Gellman, Langmuir **12**, 2483 (1996).
- Molecular adsorption indicated by similarity of XPS spectra of 2-butanol adsorbed on multilayer Xe at 30 K and Permalloy at 90 K.



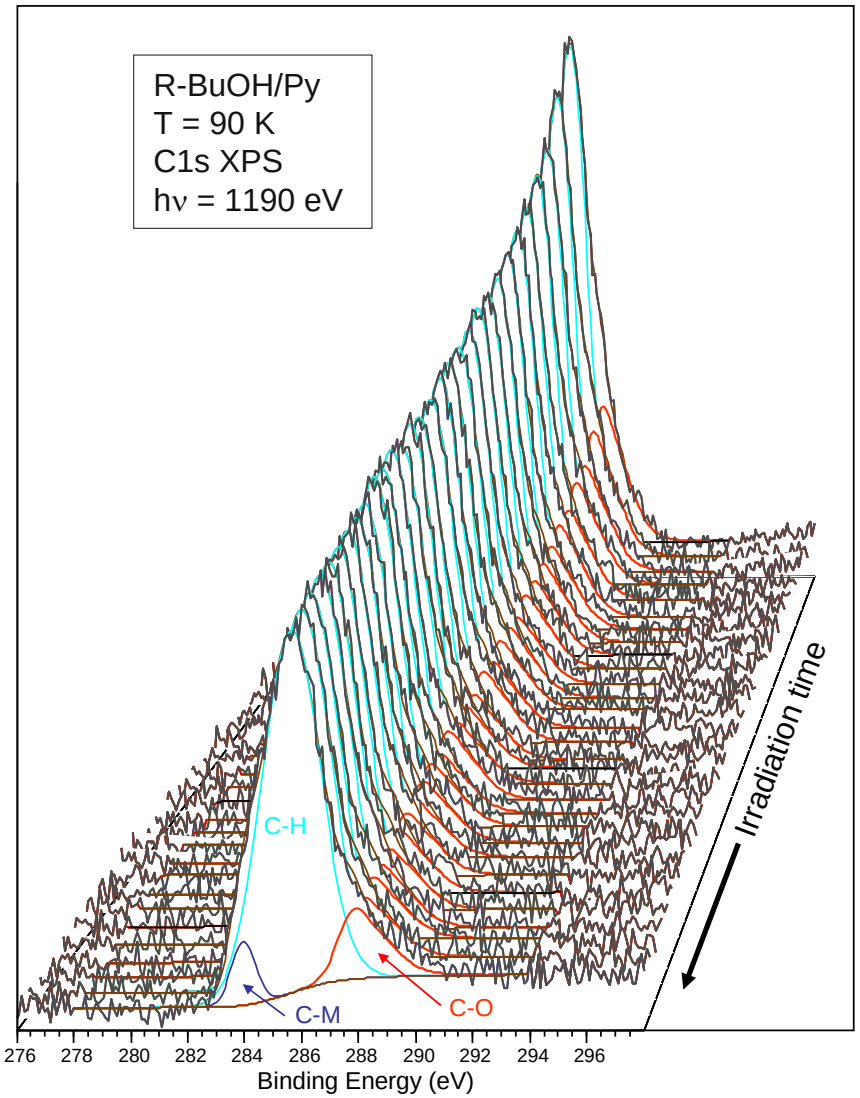
XPS Data

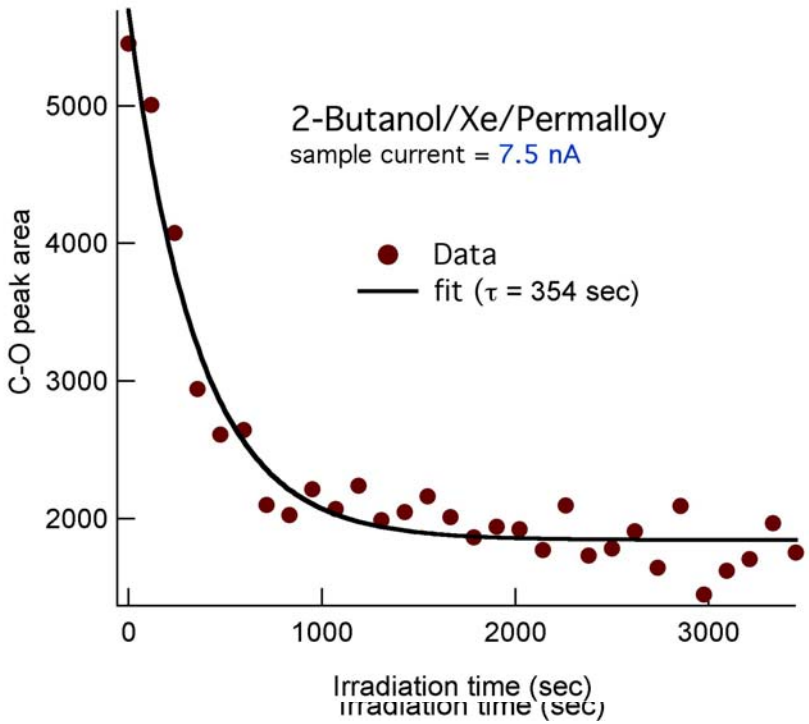
$I = I_0 e^{-t/\tau} + C$

τ = time constant = $1/\sigma f$

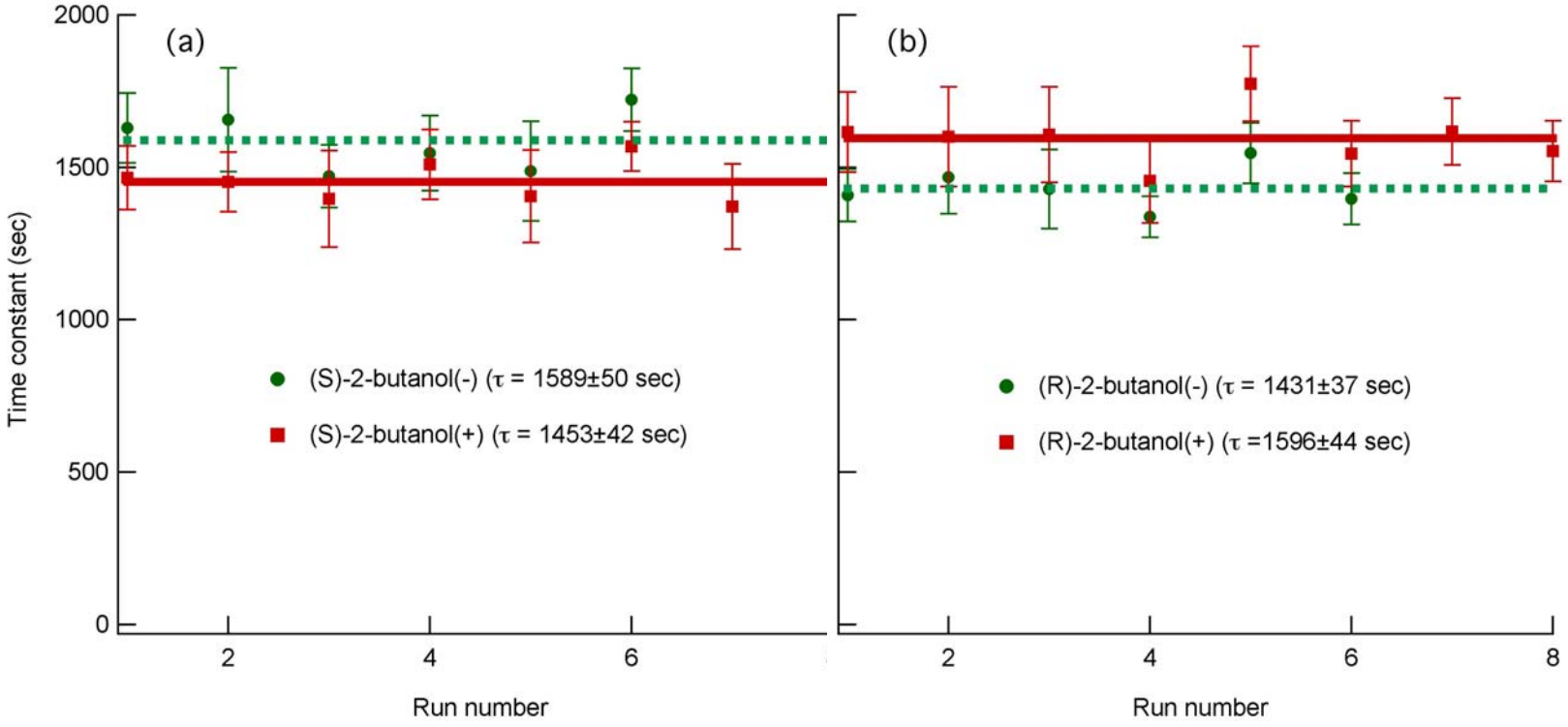
σ = cross section

f = flux density





Results

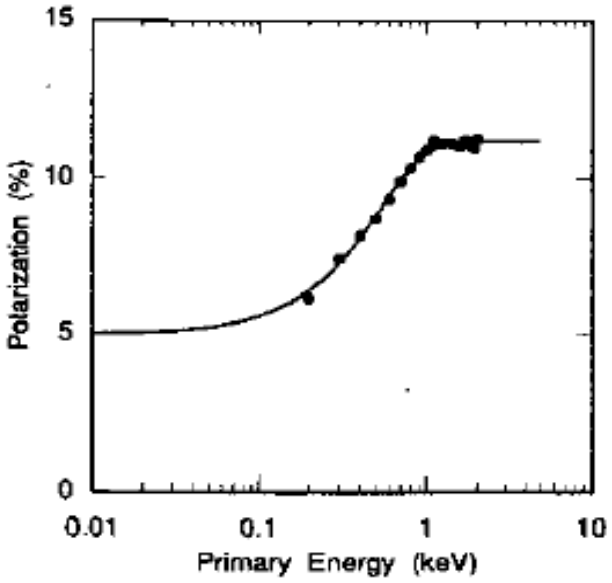

(a)
(b)
Time constant (sec)
2000
1500
1000
500
0
2
4
6
8
Run number
(S)-2-butanol(-) (τ = 1589±50 sec)
(S)-2-butanol(+) (τ = 1453±42 sec)
(R)-2-butanol(-) (τ = 1431±37 sec)
(R)-2-butanol(+) (τ =1596±44 sec)

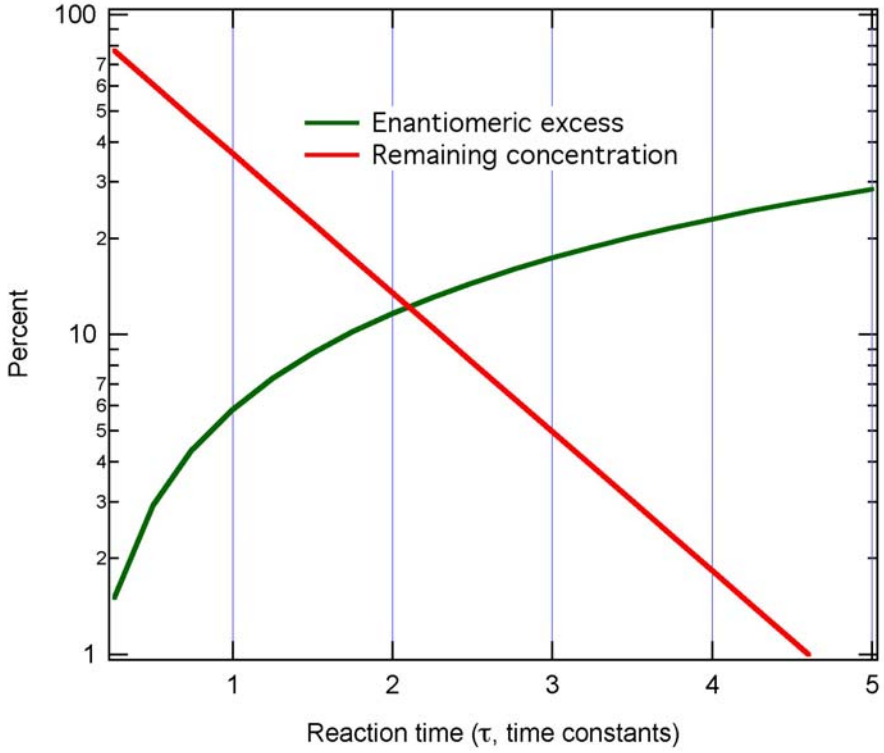
Chiral enhancement

Isomer	τ, % Difference
R-butanol	10.9 ± 3.8
S-butanol	8.9 ± 3.5
Racemic	1.7 ± 4.6

Permalloy, electrons, 58º incident angle

K. Koike and J. Kerschner, J. Phys. D 25, 1139 (1992).





Possible mechanisms

- Recall that τ = time constant = $1/\sigma f$. Using measured sample current and beam size to obtain a total electron flux density of 8 x 10^{13} e/sec cm^2 and a cross section of 9 x 10^{-18} cm^2 (9 Mb).
- This value is close to those reported by Sanche and coworkers for dissociative electron attachment (DEA) cross sections for CO production from condensed films of acetone (9.6 Mb), J. Chem. Phys. **113**, 3602 (2000), or methanol (4.2 Mb), J. Chem. Phys. **107**, 3478 (1997).
- If the orbital occupied during DEA is sufficiently diffuse so as to "sample" the regions of the molecule responsible for the chiral structure then enantomeric specific dissociation will result. (T. M. Stephen, X. Shi, and P. D. Burrow, J. Phys. B, L169 (1988))
- Low energy electrons have wavelength of ~1 nm and thus may interact coherently with many chiral centers (K. Ray *et al*, Science **283** (1999)).
- It has been theorized that two enantiomers will be ionized at different rates by longitudinally spin-polarized electrons. (R. A. Hegstrom, Nature **297**, 643 (1982)) If there are sufficient numbers of higher energy spin-polarized secondary electrons and the final state reached following ionization is dissociative, then this could lead to chiral enhancement.

Conclusions

- Propose a new mechanism for chiral specific chemistry – low energy secondary electrons produced by ionizing (photon, electron, ion) radiation impact with a magnetic substrate.

- Measurements have shown the viability of this mechanism.

- Iron is one of the most common elements and many iron compounds are magnetic where the degree of spin-polarization of the secondary electrons has been shown to reach as high as 70%.

Conclusions (continued)

- It is easy to imagine numerous scenarios where a magnetized iron substrate in an interstellar dust grain, a comet, a meteor, or on primitive Earth or another planet, would have produced spin-polarized secondary electrons as the result of irradiation. Furthermore, low-energy, primary spin-polarized electrons can also be produced directly by the interaction of circularly polarized UV light with a nonmagnetic substrate. Based on the present results, low-energy, spin-polarized electrons interacting with adsorbed chiral molecules could produce a significant enantiomeric excess of a prebiotic molecule.