The Interaction of Chiral Electrons with Molecules and Surfaces – A Progress Report

Timothy Gay, Joan Dreiling – University of Nebraska
Frank Lewis – Northumbria University
Jeff Mills – Air Force Research Laboratory

Northumbria University
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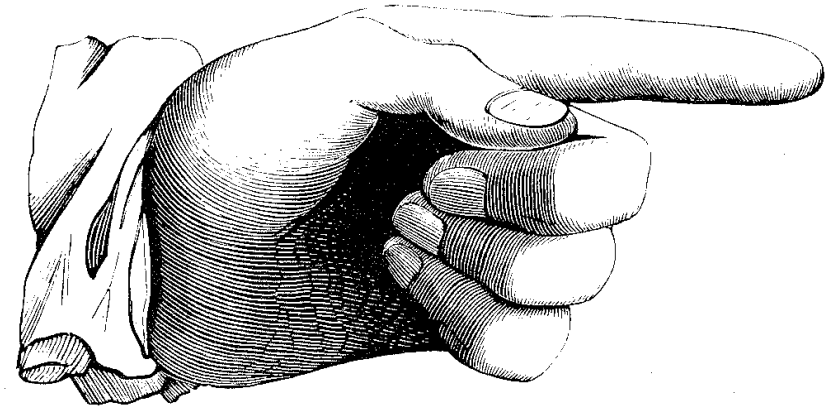

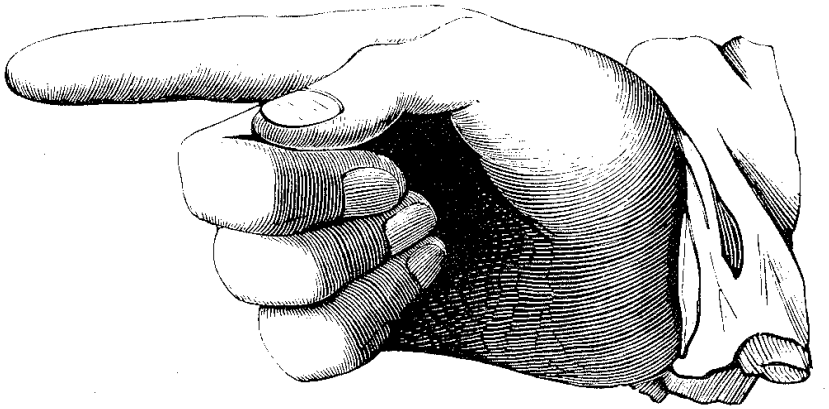

Plane of Mirror Symmetry

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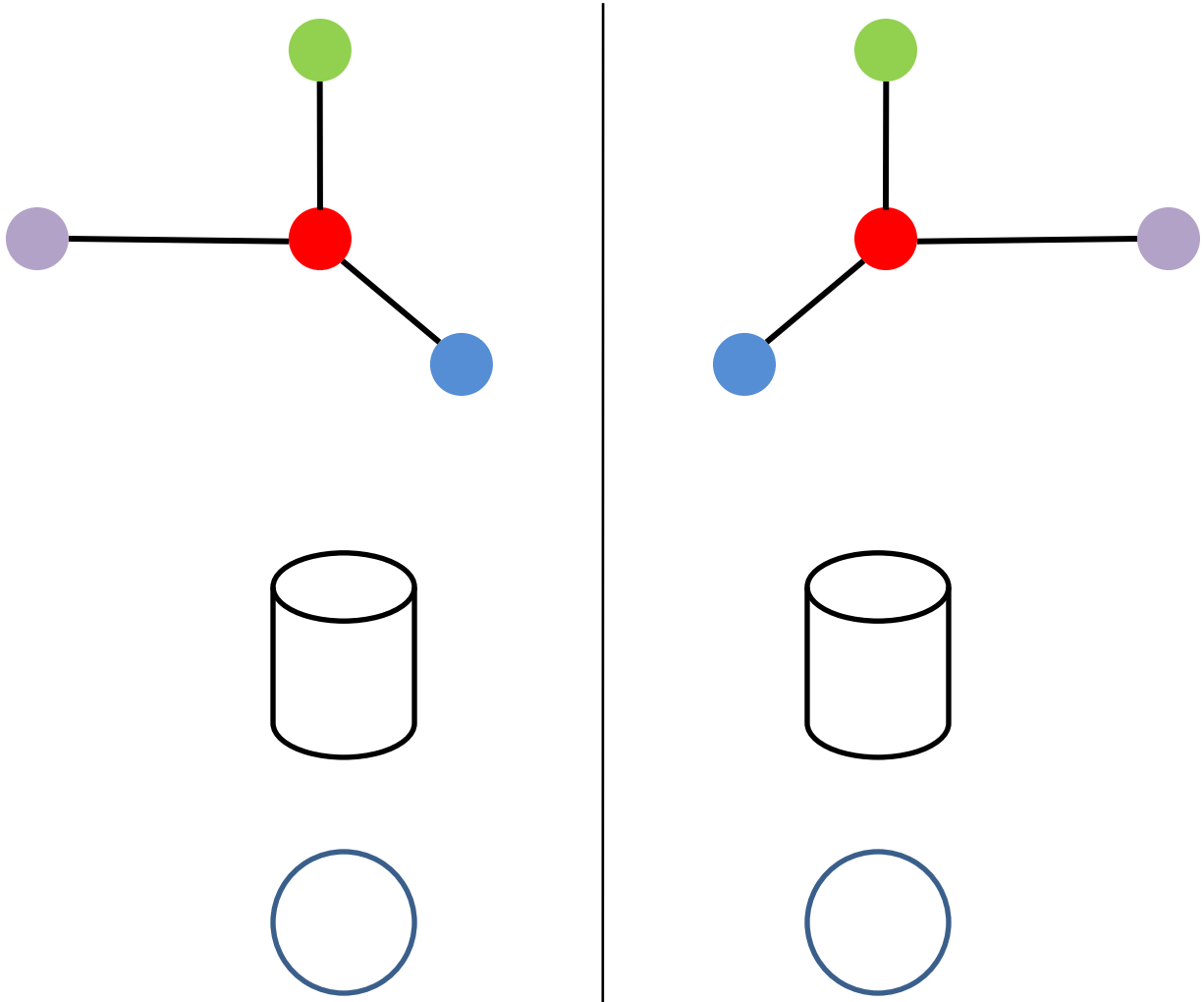

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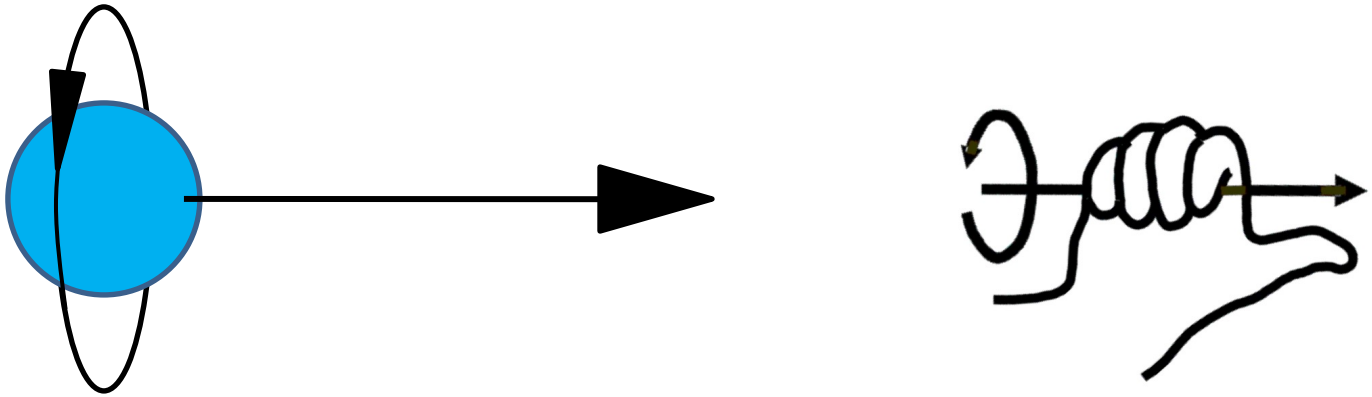
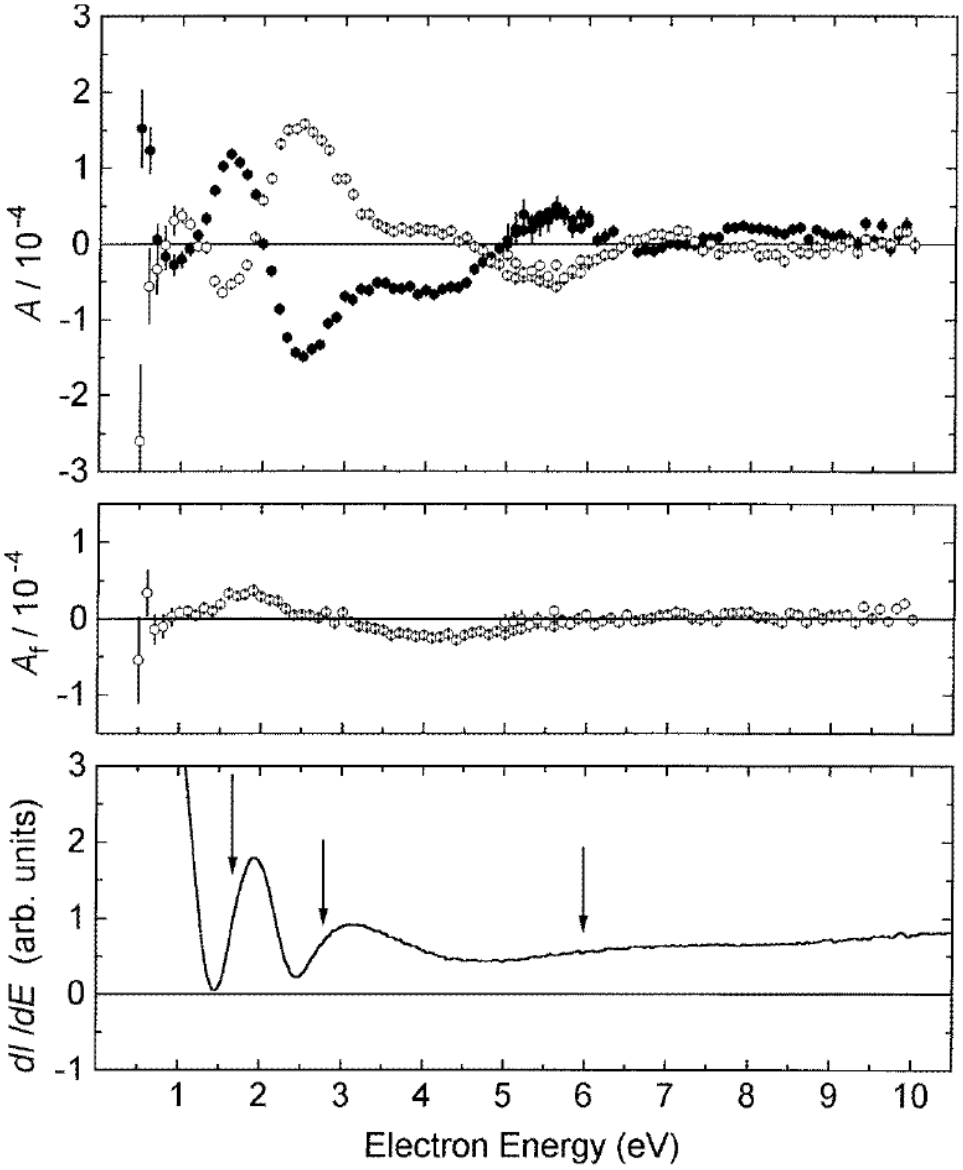


¡electrons can be chiral!

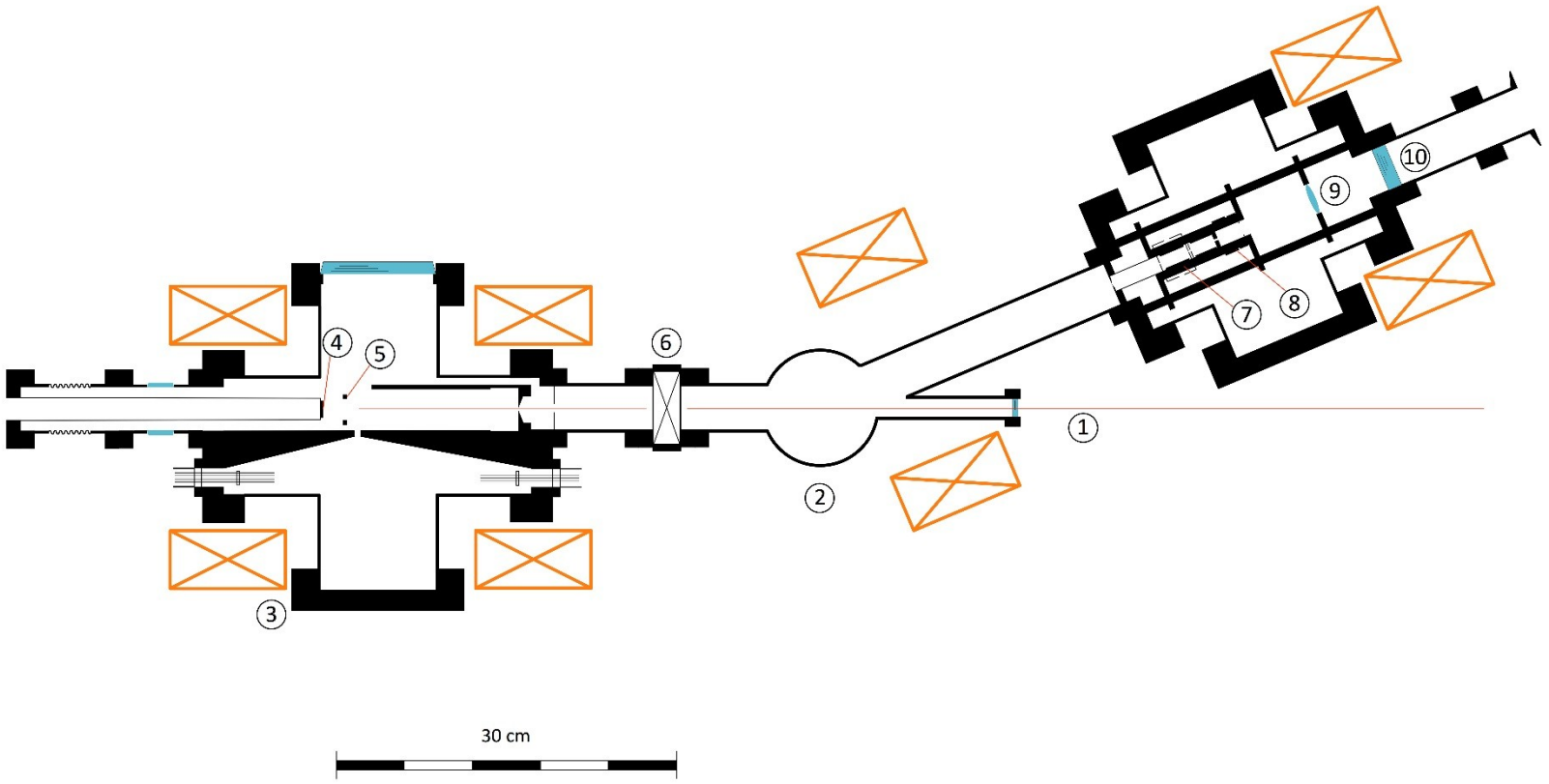
Quasi-elastic Electron Circular Dichroism in Molecules Containg Heavy Atoms (1996)



tris[3-(heptafluorpropylhydroxymethylene)camphorato] Ytterbium!

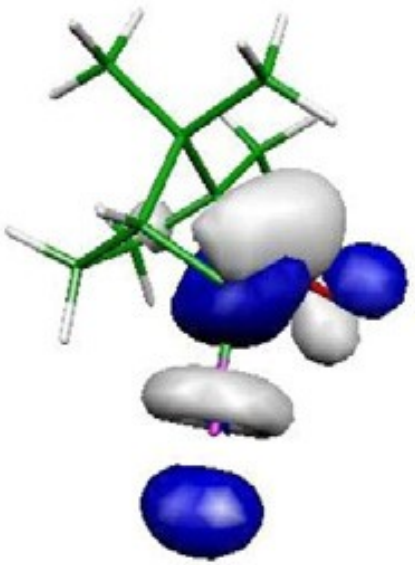
S. Mayer, C.Nolting, u J. Keβler, J. Phys. B **29**, 3497 (1996)

Our Apparatus

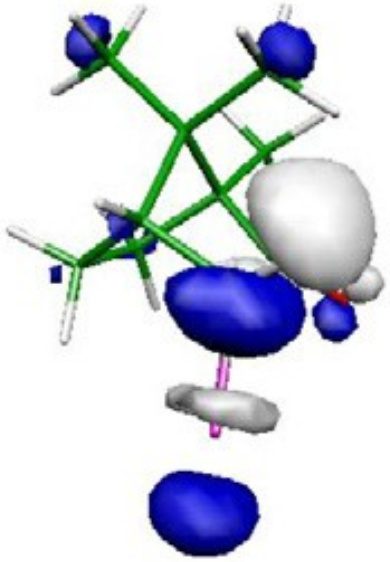


1) laser beam; 2) differential pumping chamber; 3) guiding magnets;
4) GaAs photocathode; 5) cesiators; 6) gate valve; 7) chiral target cell;
8) optical polarimeter target cell; 9) collimating lens; 10) window to optical polarimeter

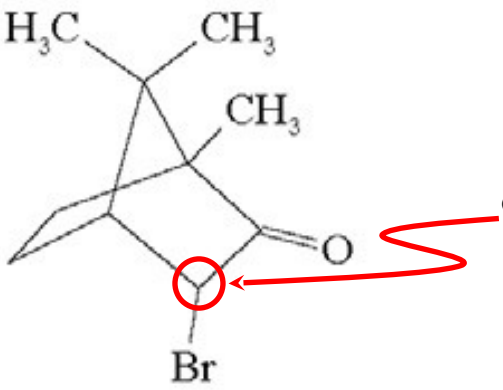
Bromocamphor



LUMO (σ_1*)



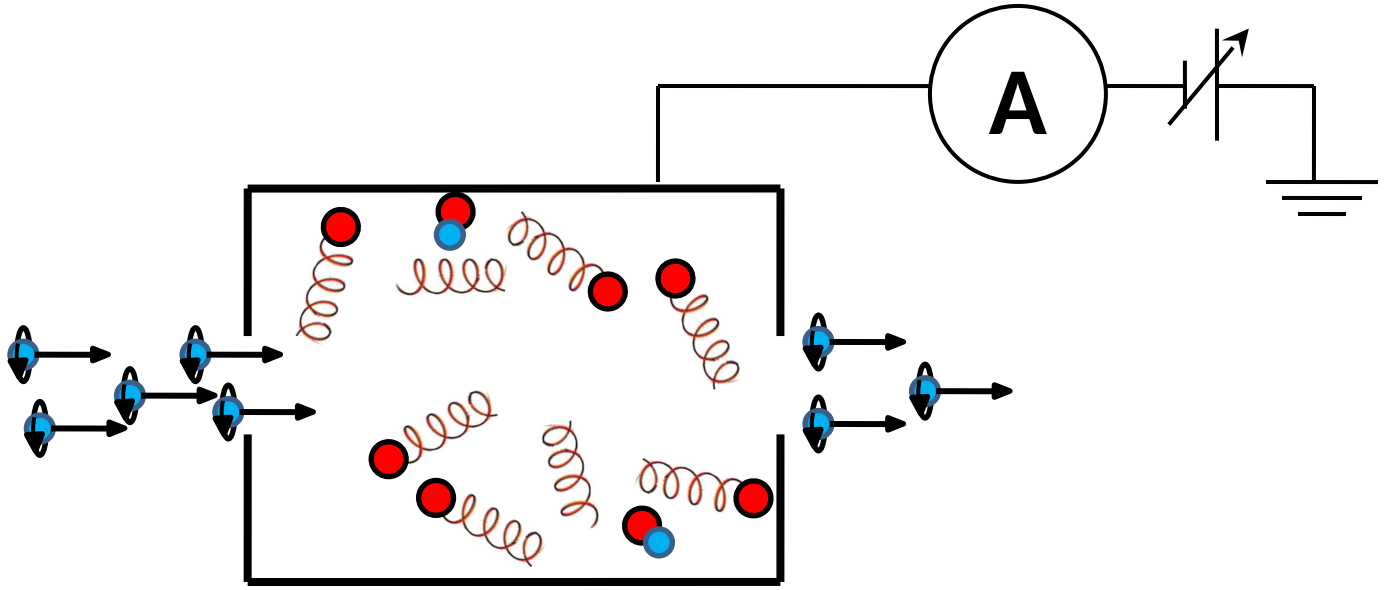
LUMO + 1 (σ_2*)



"chiral center"

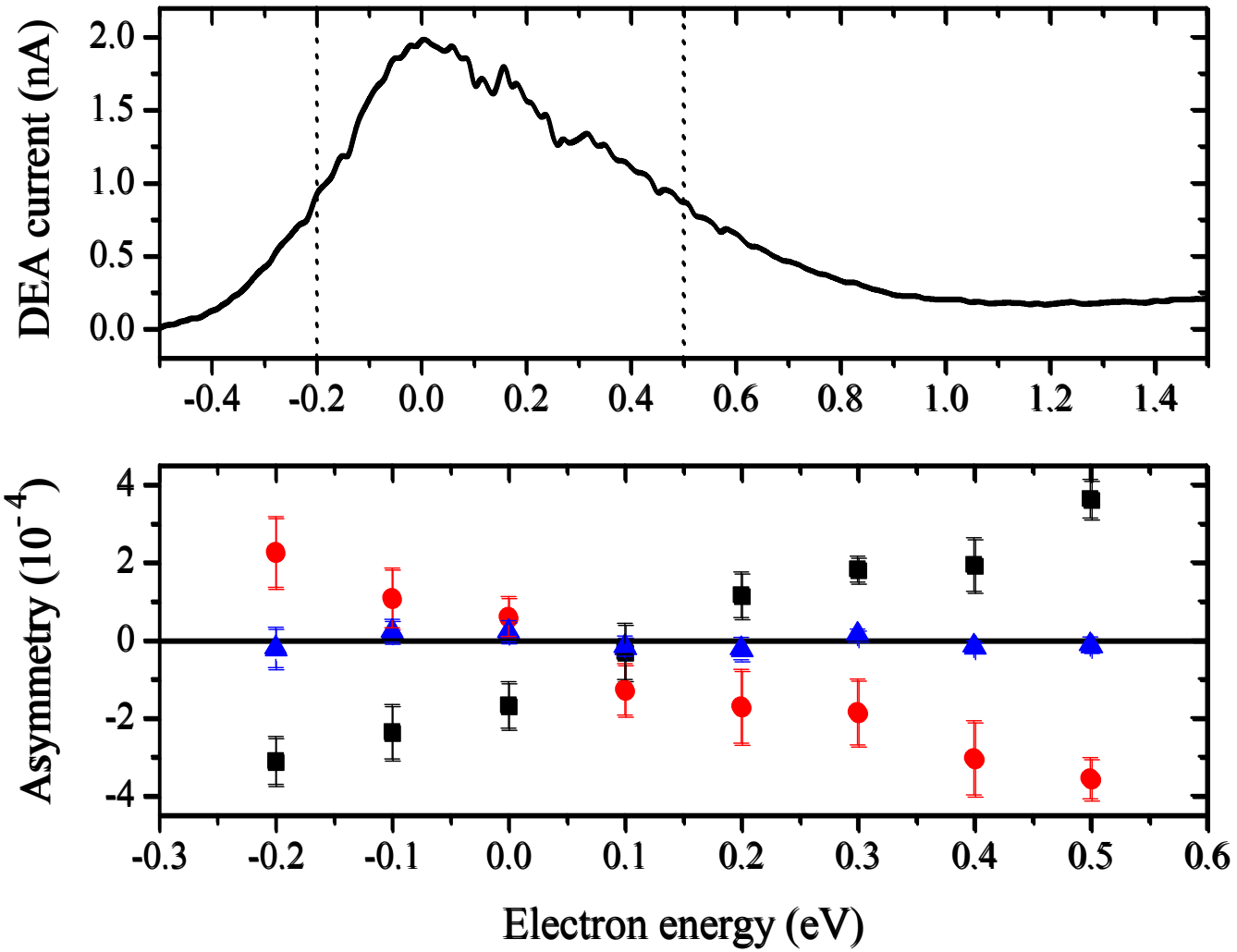
Electron Circular Dichroism

Dissociative Attachment: $e^- + AB \rightarrow A^- + B$



10^{-4}

DEA: $e^- + AB \rightarrow A^- + B$



J.M.Dreiling and T.J.Gay, PRL **113**, 118103 (2014)

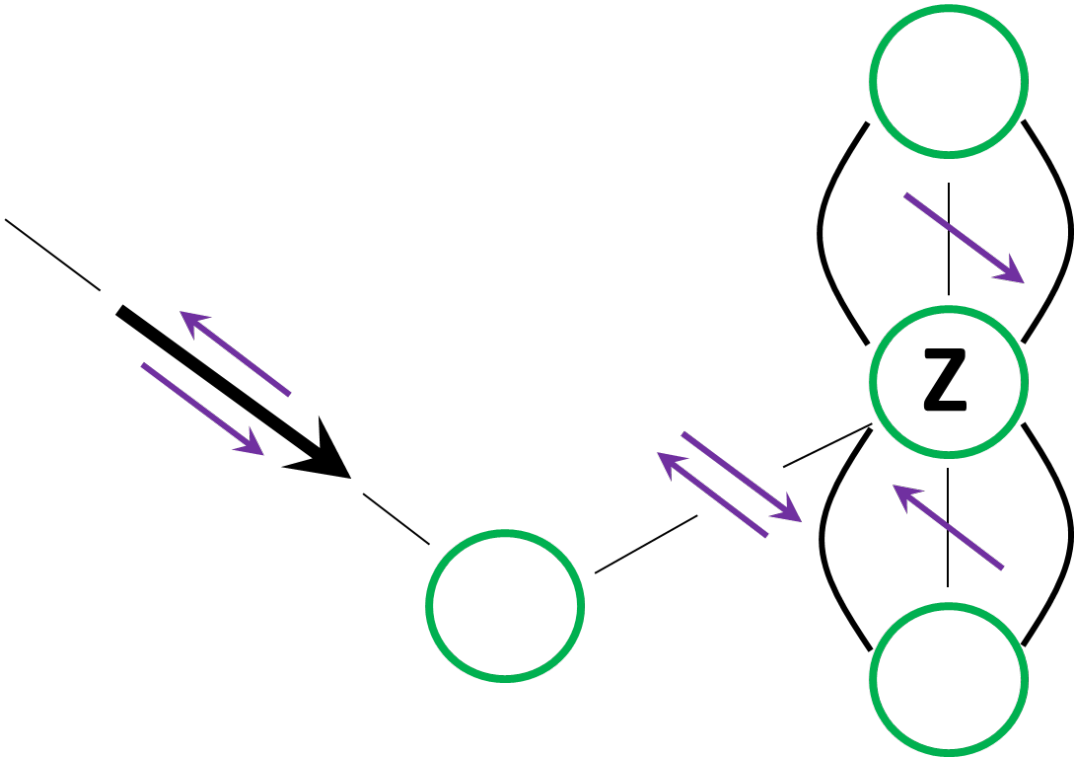
The Dynamic Origins of the Asymmetry

- Our results are permitted by symmetry, but what are the dynamics responsible?

- Three different models
  - Mott/plural scattering (~Z^2)
  - Spin-other-orbit coupling (~Z^0)
  - “Helicity-density” dynamics (~Z^2)

Mott scattering

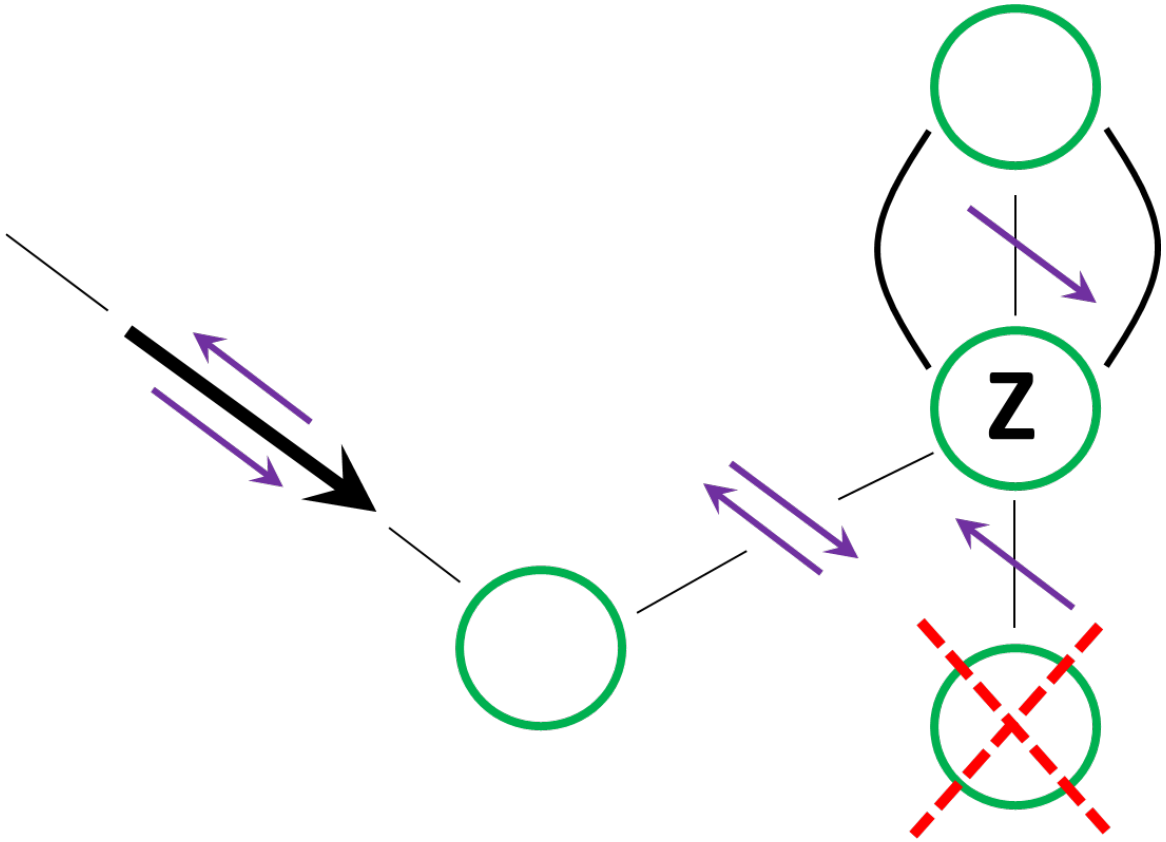
achiral molecule



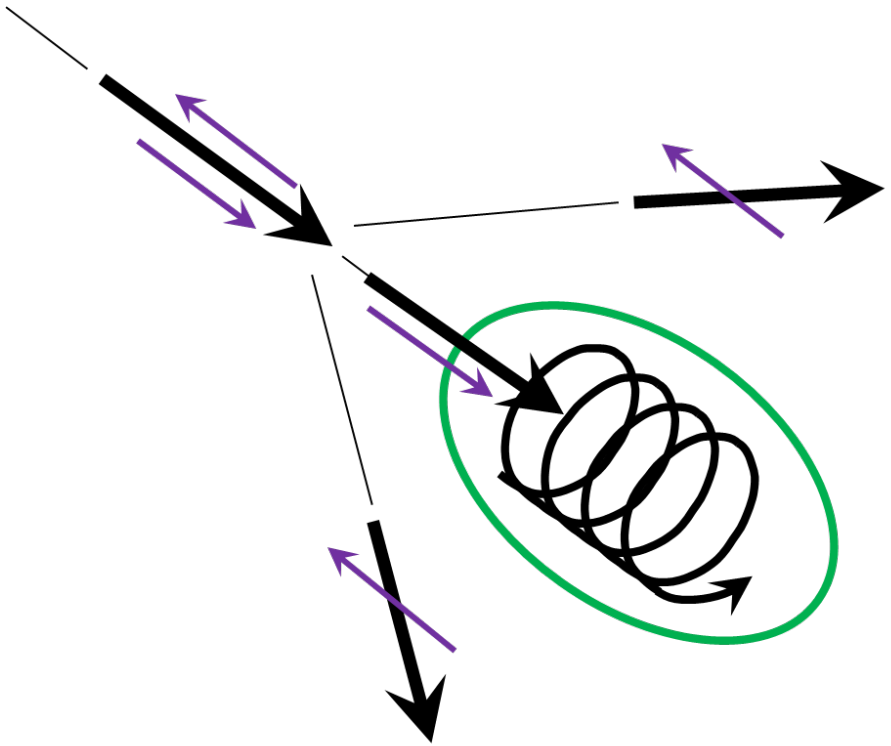
J. Kessler, J. Phys. B **15**, L101 (1982).
R.A. Hegstrom, Nature **297**, 643 (1982).

Mott scattering II

chiral molecule



Spin-other-orbit coupling



D.W. Walker, J. Phys. B **15**, L289-L292 (1982).
T.J. Gay, in *Advances in Atomic, Molecular, and Optical Physics*, **57,** 157–247 (Academic, 2009).

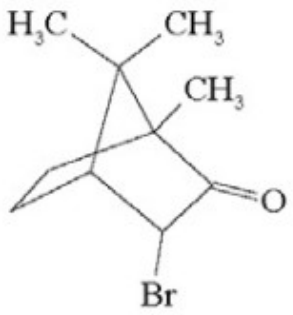
Helicity density I

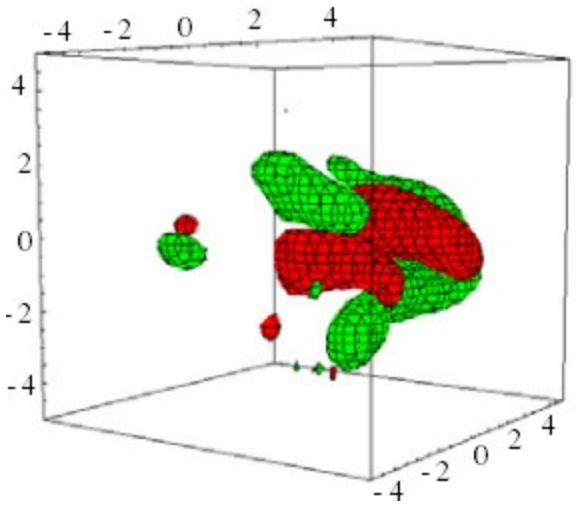
Chiral stereochemistry → Chiral Electrons

$$\sum_{i=1}^{N} \vec{p}_{ei} = 0$$

$$\sum_{i=1}^{N} \vec{\sigma}_{ei} = 0$$

$$\sum_{i=1}^{N} \left(\vec{\sigma}_e \cdot \vec{p}_e \right)_i \neq 0$$





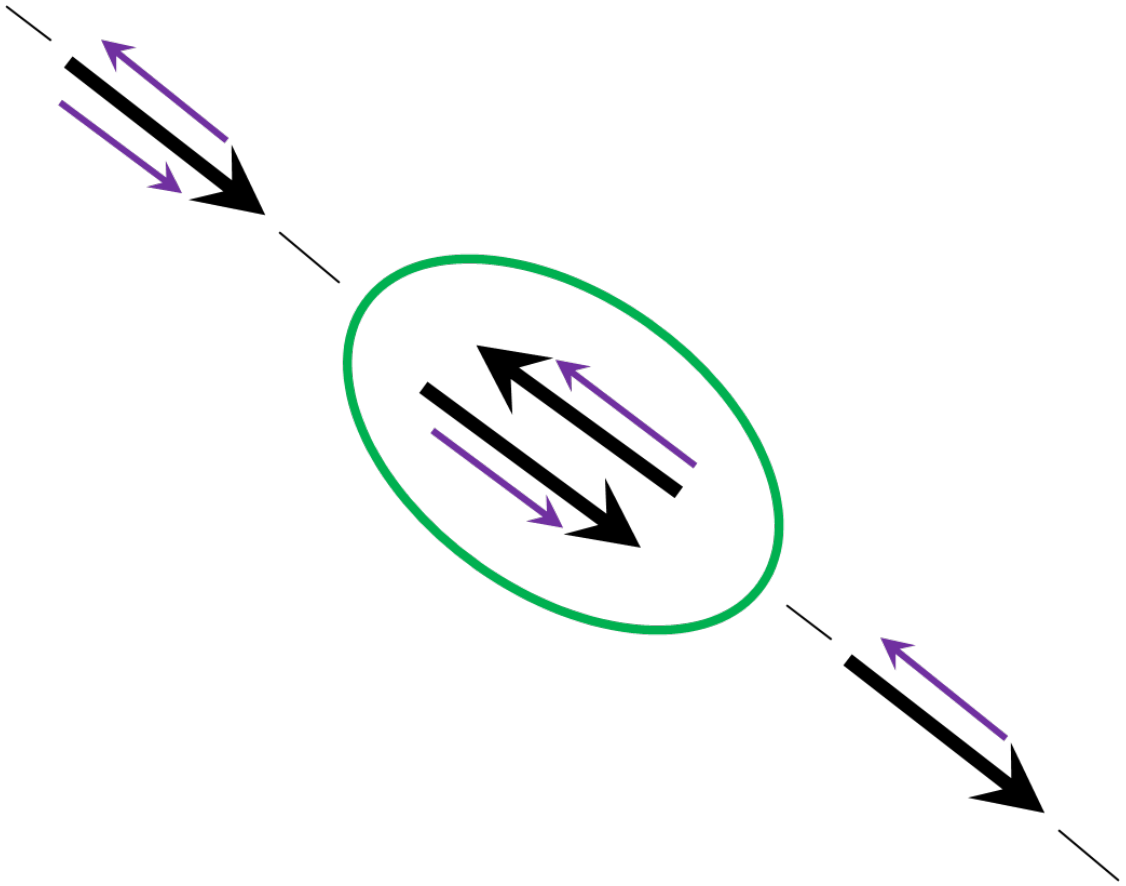
Contour plots of the calculated helicity density

Red lobes indicate regions of positive helicity density

Green lobes indicate regions of negative helicity density

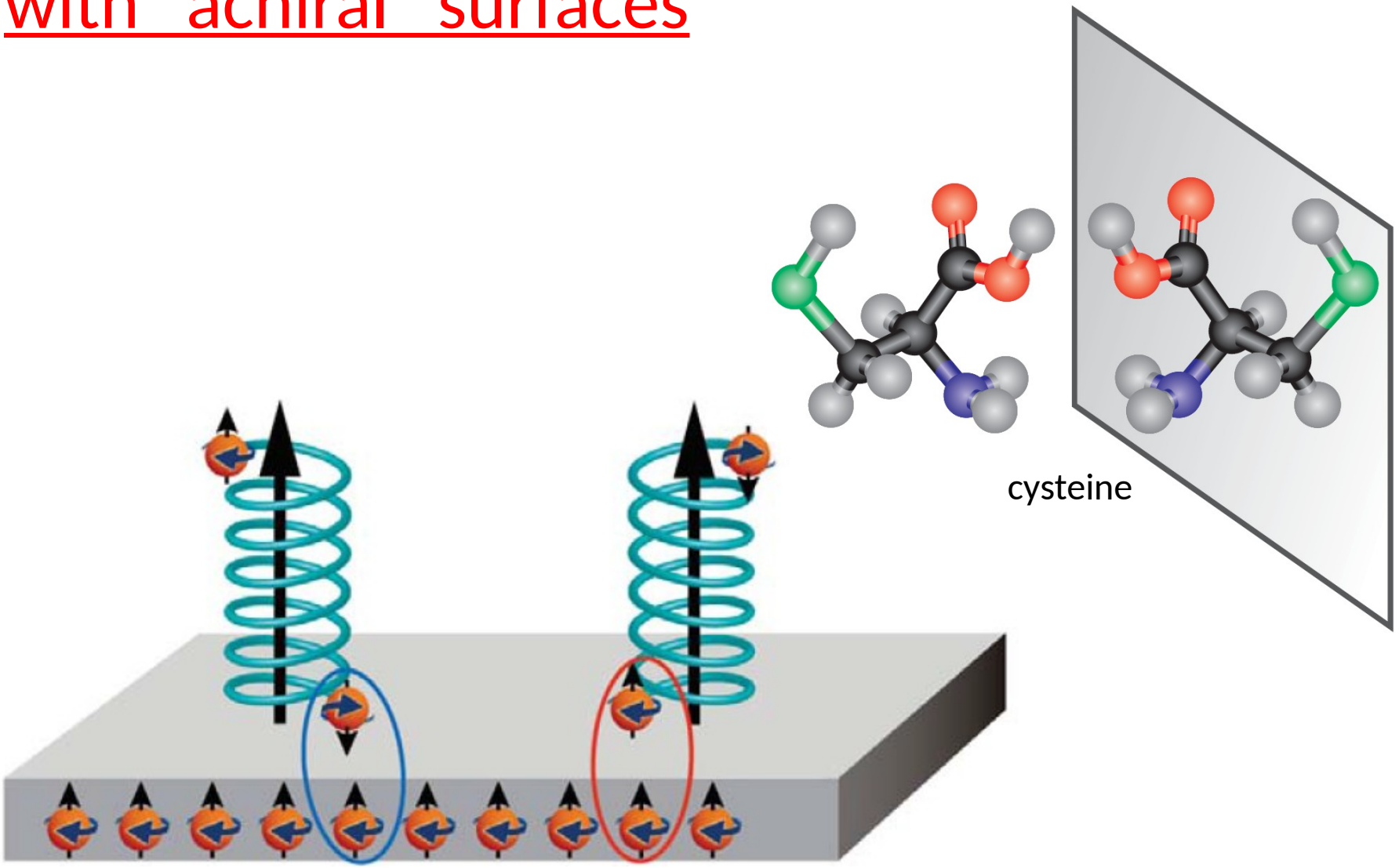
A. D. Scheer, G. A. Gallup and T. J. Gay, J. Phys. B **39**, 2169 (2006)

“Helicity-density” dynamics



V.A. Onishchuk, Sov. Phys. JETP **55**, 412 (1982).
T.J. Gay, M. E. Johnston, K.W. Trantham, and G.A. Gallup, in *Selected Topics in Electron Physics* (Plenum 1996).
A.D. Scheer, G.A. Gallup and T.J. Gay, J. Phys. B **39**, 2169 (2006).

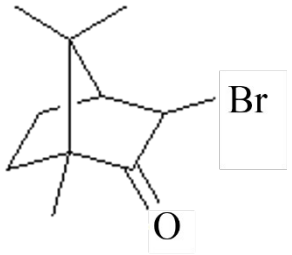
Interaction of left-vs. right handed molecules with “achiral” surfaces



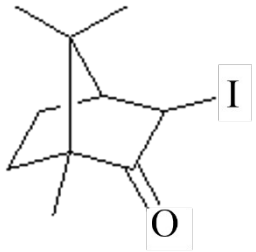
Bannerjee-Ghosh, *et al.*, Science **360**, 1331 (2018)

Investigate collisional dynamics

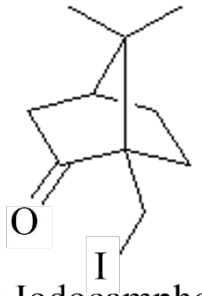
- Theories explaining asymmetry disagree on dependence on Z
- Vary Z
  - Bromocamphor, $Z_{Br} = 35$
  - Iodocamphor, $Z_{I} = 53$
- Vary location of highest Z
  - 3-Iodocamphor
  - 10-Iodocamphor



3-Bromocamphor

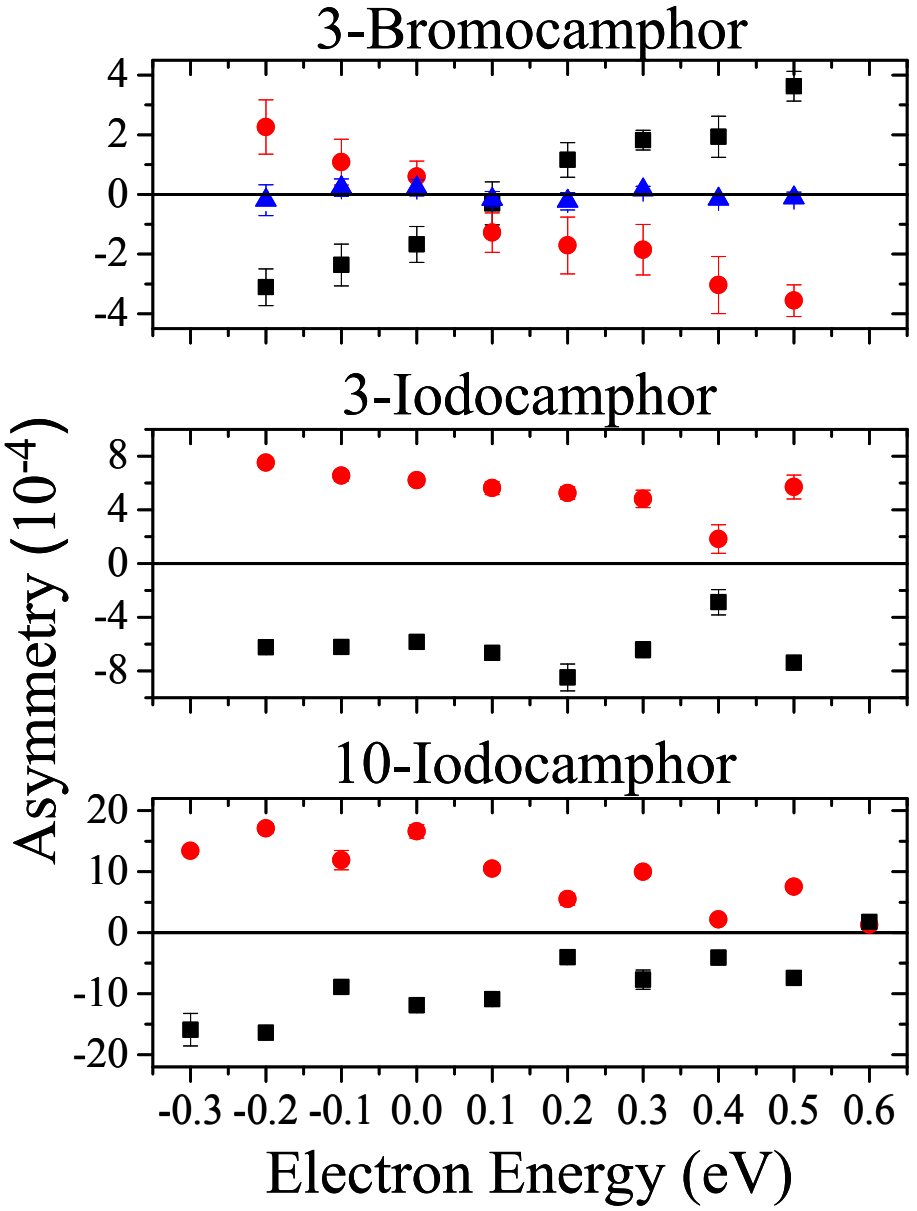


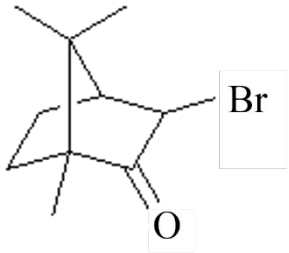
3-Iodocamphor



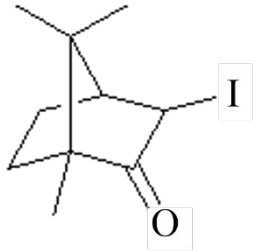
10-Iodocamphor

DEA Asymmetry Data

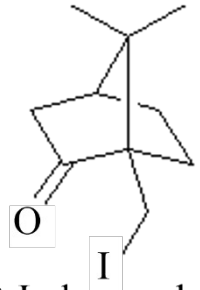




3-Bromocamphor



3-Iodocamphor



10-Iodocamphor

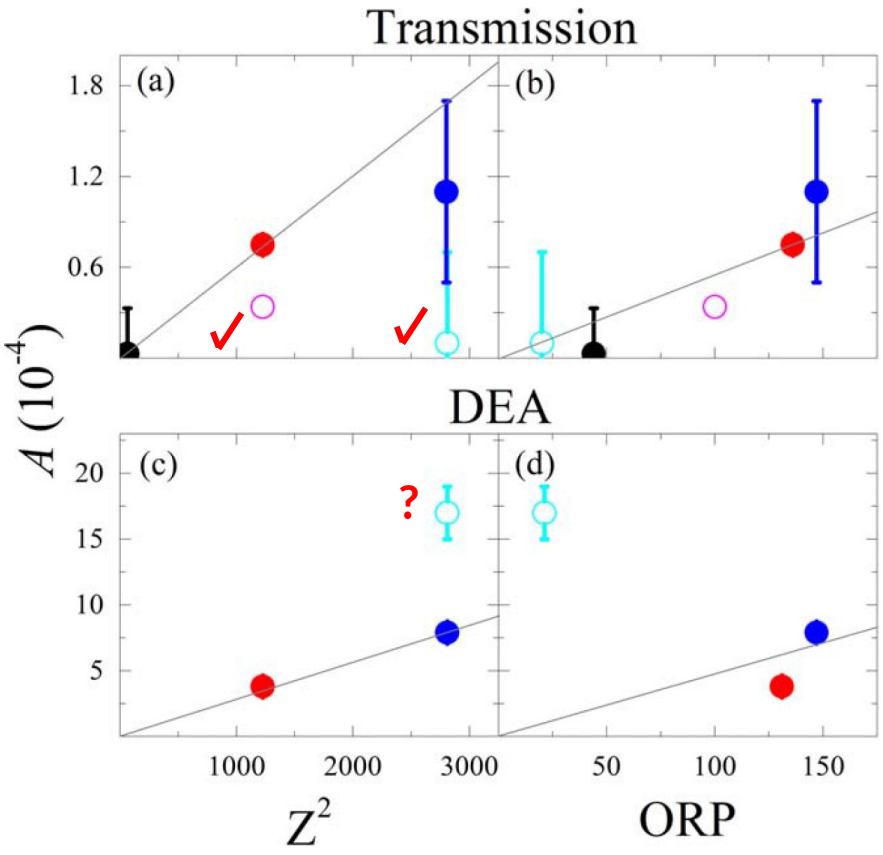
J.M.Dreiling, F.W.Lewis, J.D.Mills, and T.J.Gay, Phys. Rev. Lett. **116**, 093201 (2016)

¿Which mechanism is responsible for A?

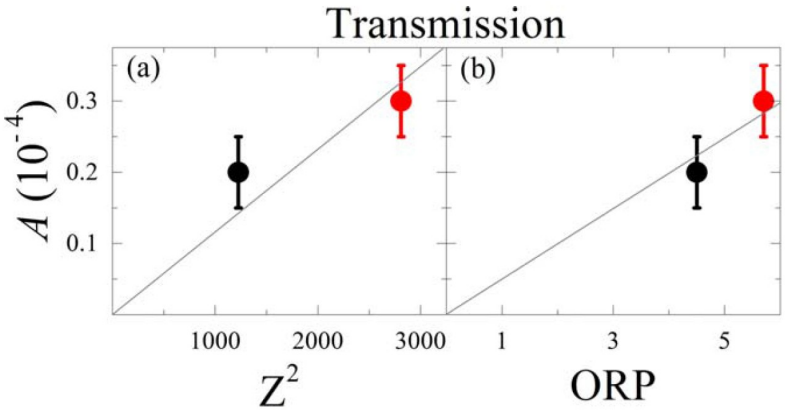
- Energy dependence and sign of A at a specific energy exhibits broad variations.
- The largest asymmetries scale precisely a Z^2 between bromine and iodine for the 3-iodocamphors. This would appear to rule out the spin-other-orbit mechanism.
- Moving the heavy atom (I) away from the chiral center enhances (!) the chiral asymmetry. A simple Mott scattering picture fails to explain this; does this point to a helicity-density mechanism?
- No reasonable helicity-density calculations we can do (isolated at the halogen bond or integrated over the entire molecule) support the large 10-iodocamphor asymmetry.
- We do note a correlation between the maximum A and the mean incident electron energy where the DEA signal peaks. This hints at the possibility that a more thorough *ab initio* DEA calculation *might* explain the 10-iodocamphor anomaly; higher attachment energy implies longer resonant lifetime implies enhanced chiral "sampling."

TABLE I. Calculated helicity density parameters: electronic helicity, H; bond helicity, H_b; LUMO-weighted bond helicity, H_L; LUMO + 1-weighted bond helicity, H_{L+1}; and maximum observed asymmetry A_{max}. All helicity values are reported in units of $\alpha^2/2$.

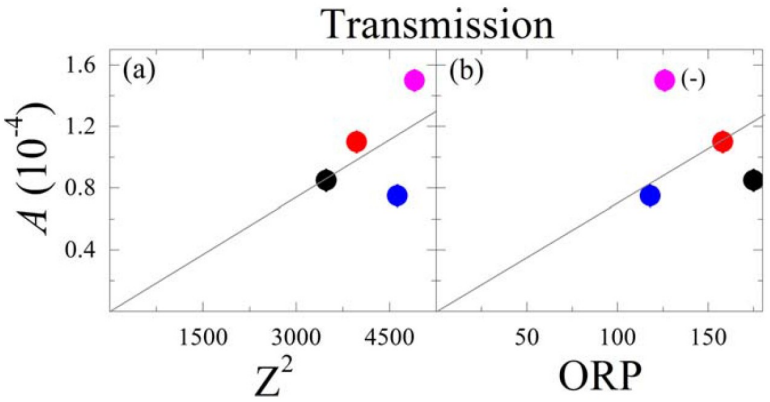
Molecule	H	H_b	H_L	H_{L+1}	$A_{max}(10^{-4})$
3Br	−15.6	1.48	0.05	0.14	4
3I	−19.9	5.32	0.23	0.22	8
10I	−1.9	−0.44	−0.01	N/A	16



camphor derivatives



halometylbutanes



lanthanoid propellers
(chiral blades; achiral propeller)

¿Which mechanism is responsible for A?

- *Halocamphors* – Transmission data is consistent with both Mott and helicity density (HD) models, with some quantitative theoretical support HD. The transmission results are also consistent with a spin-other-orbit model.
- *Halocamphors* – DEA has no clear interpretation, but hints at a HD model.

- *Halomethylbutane derivatives* – All data scale linearly with all three models – no obvious conclusions to be drawn.

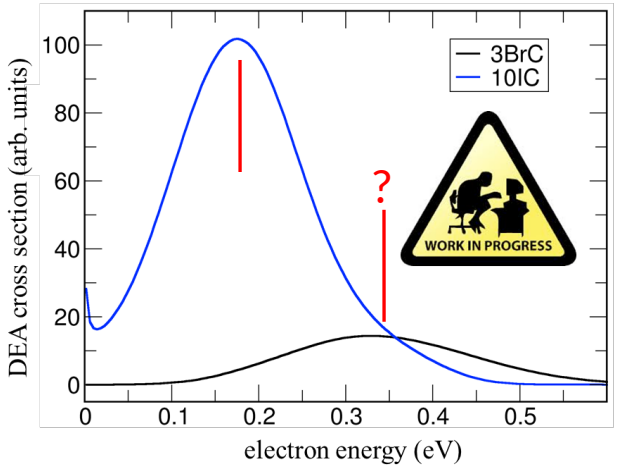
- *Rare earth complexes* – No data correlate withn any model – no obvious conclusions to be drawn.

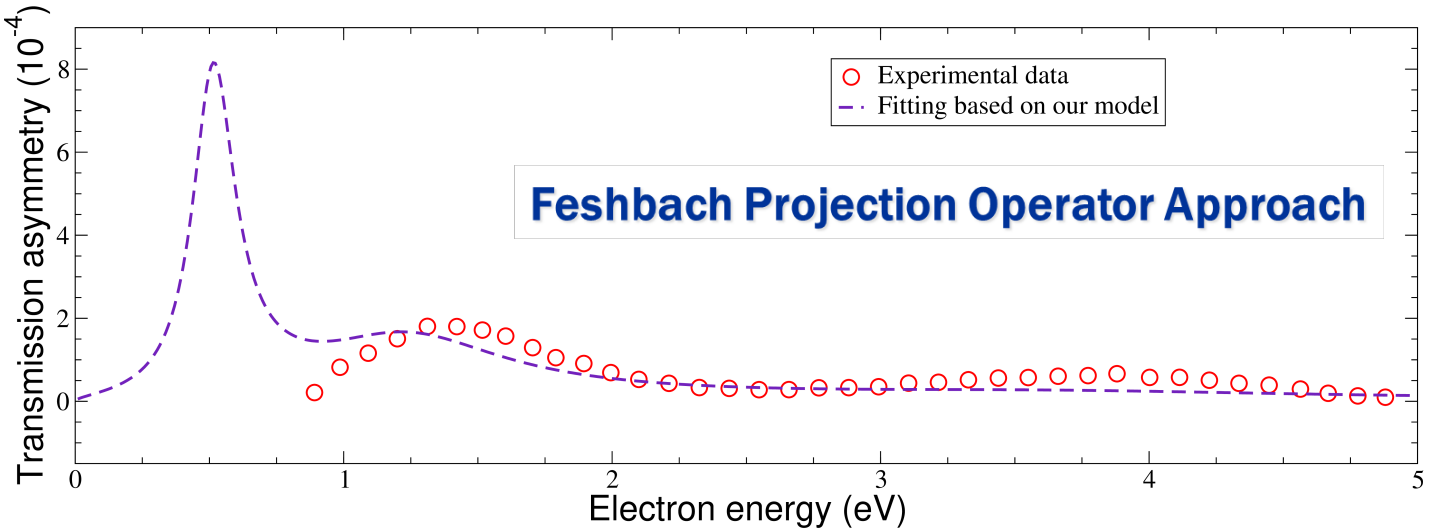
Chirality Sensitive Effects in Electron Collisions against Halocamphors

J. C. Ruivo[1], F. Kossoski[2], L. M. Cornetta[1], M. T. do N. Varella[1]
[1]Institute of Physics, University of São Paulo, São Paulo, SP, Brazil
[2]Aix-Marseille University, CNRS, ICR, Marseille, France
mvarella@if.usp.br

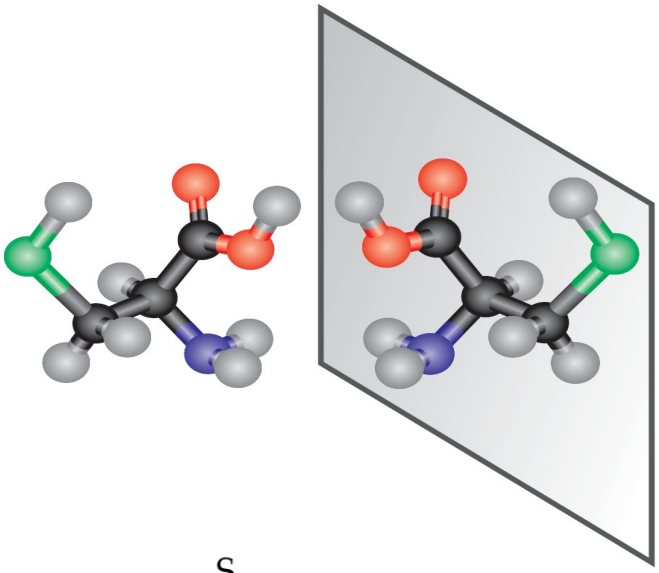
DEA from Local Pseudo-Diatomic Models
(Coulomb potential)

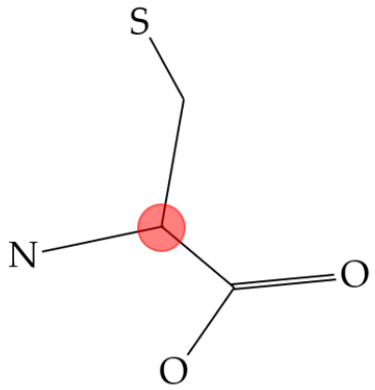
¡encouraging first steps!

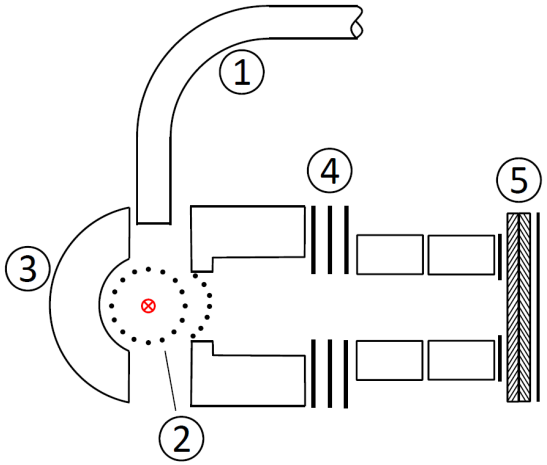




Dissociative Electron Attachment of Cysteine



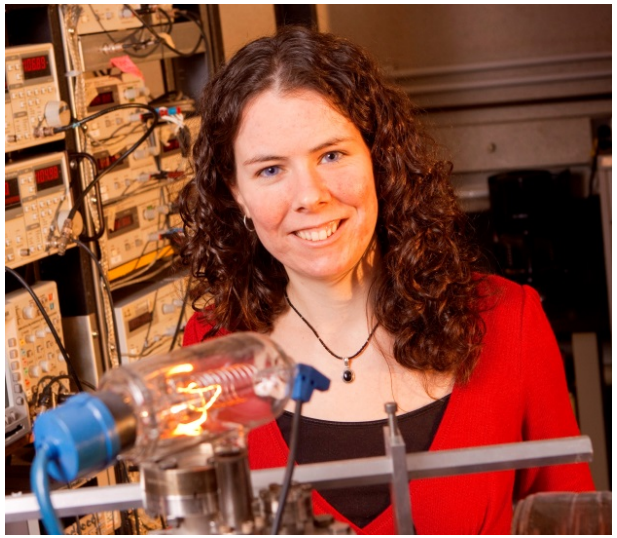


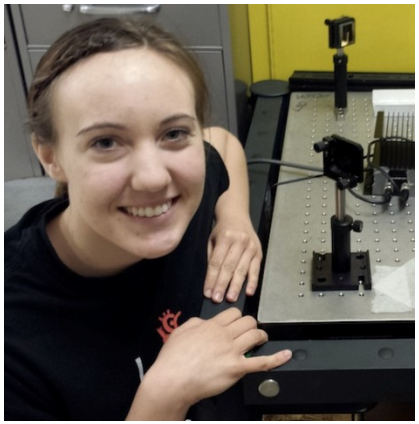


DEA vapor target with incident electron beam heading into the page showing: (1) target vapor feedline; (2) wires to establish the target scattering potential; (3) electrostatic "pusher" electrode; (4) electrostatic lens system to guide anions to (5) a microchannel detector array.

Perpetrators

Joan Dreiling



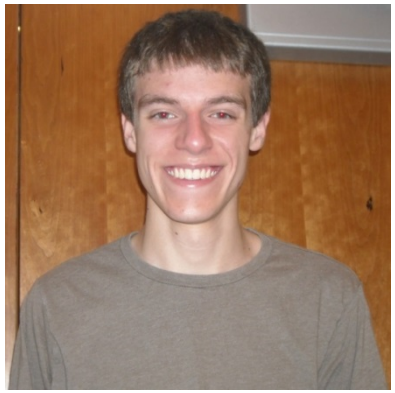


Samantha Burtwistle

Paul Burrow

Ken Trantham

Eric Litaker



Nick Ryan

the GAY Group

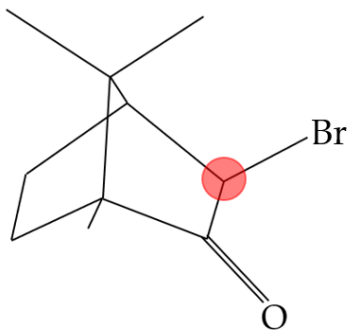
Frank Lewis,
synthetic chemist extraordinaire

Northumbria University
NEWCASTLE

AIR FORCE RESEARCH LABORATORY

…and Jeff Mills, for whom apparently no photos exist…

a)



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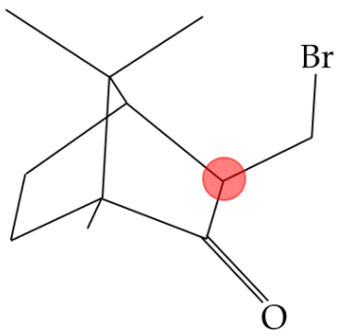

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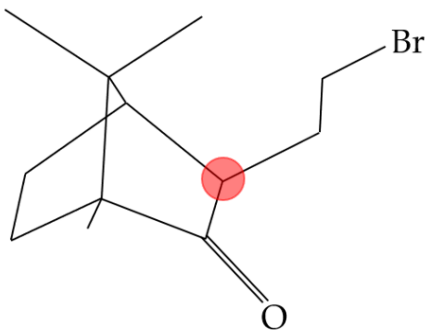

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