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Chirality Sensitive Effects in Electron Collisions Against Halocamphors

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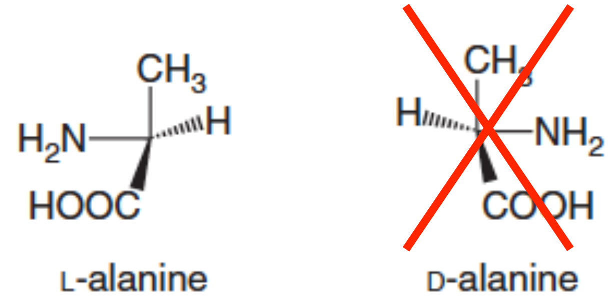
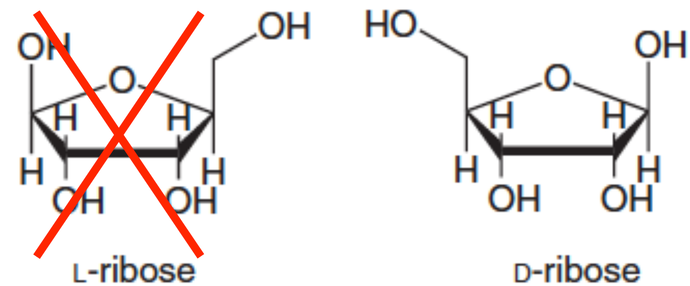
Biological Homochirality

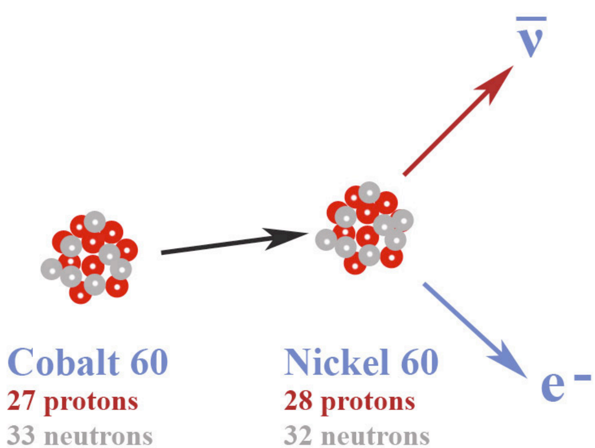
"The biopolymers that characterize life on Earth, and the molecular building blocks from which they are constructed, are both chiral and single-handed (...) they are selectively biosynthesized in only one of the two forms."

D. G. Blackmond, Cold Spring Harb. Perspect. Biol. **11**, a032540 (2019).



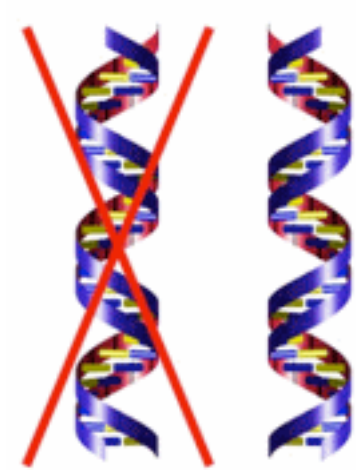


Vester-Ulbrich Hypothesis:
Selective damage to prebiotic molecules.



$$\lambda^{(\pm)} = \mathbf{S} \cdot \mathbf{k}$$

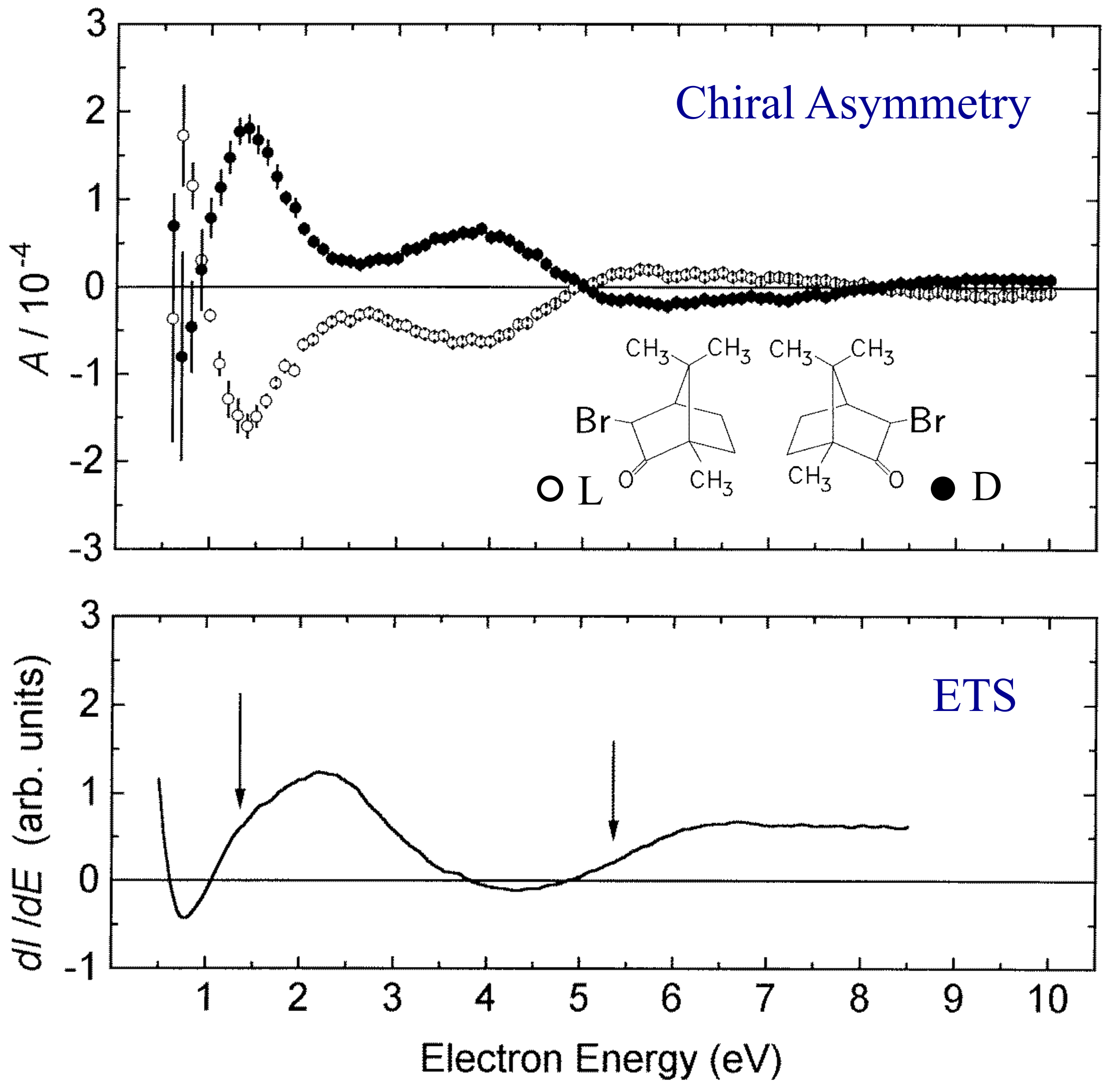
(helicity)



http://www.astronoo.com/en/articles/neutrino.html

Transmission (Scattering) Asymmetry

S Mayer, C Nolting and J Kessler
J. Phys. B: At. Mol. Opt. Phys. 29 (1996) 3497–3511



Incident spin polarization

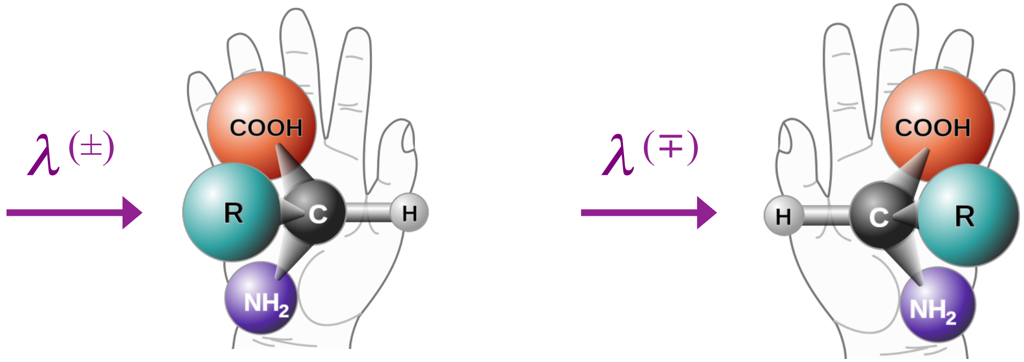
$$P_0 = \frac{N_0^+ - N_0^-}{N_0^+ + N_0^-}$$

Asymmetry

$$a_{\mathrm{tra}} = \frac{N(P_0, \rho d) - N(-P_0, \rho d)}{N(P_0, \rho d) + N(-P_0, \rho d)}$$

Chiral Asymmetry

$$A_{\mathrm{tra}} = [a_{\mathrm{tra}}]_L - [a_{\mathrm{tra}}]_R$$

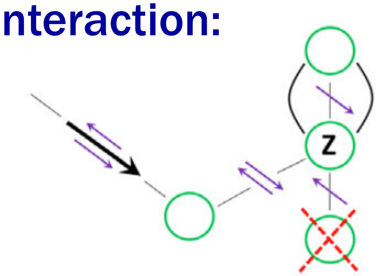


Preferential scattering does not involve symmetry violation*.

– **Chiral effects arise from the spin-orbit interaction:**

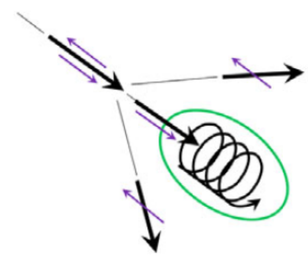
Mott Scattering (spin-same-orbit)

[Kessler, J. Phys. B **15**, L101 (1982)]



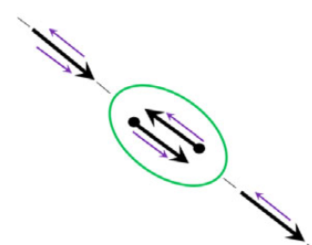
Spin-Other-Orbit

[Walker, J. Phys. B **15**, L289 (1982)]



Helicity Density

[Hegstrom *et al*., PRL, **48** 1341 (1982)]

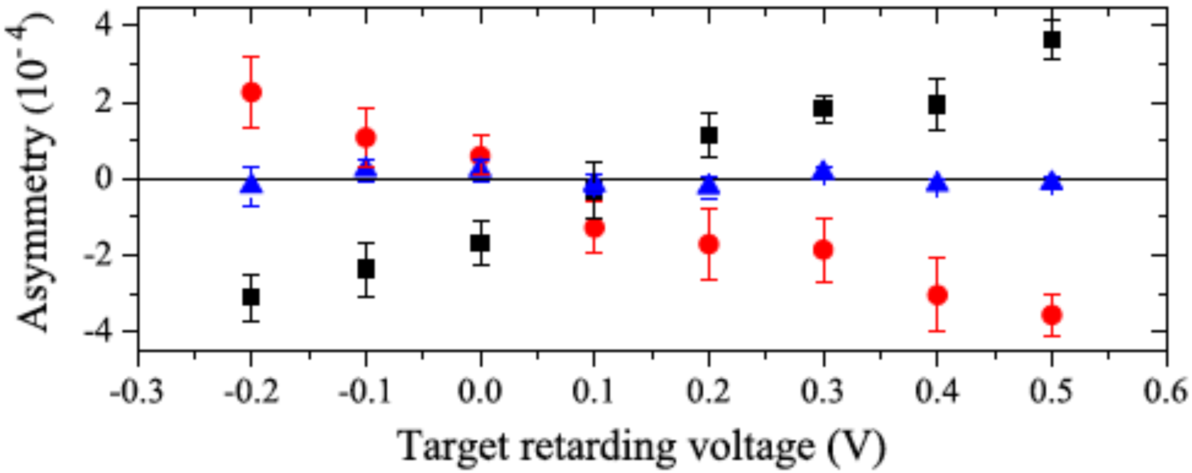


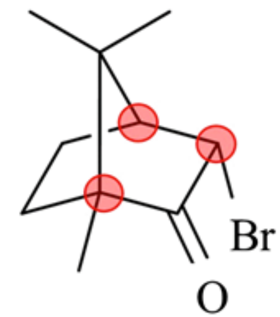
*Symmetry properties: Farago, JPB **13**, L567 (1980); Blum & Thompson, JPB **22**, 1823 (1989)

Chirally Sensitive Electron-Induced Molecular Breakup and the Vester-Ulbricht Hypothesis

J. M. Dreiling* and T. J. Gay

PRL **113,** 118103 (2014)





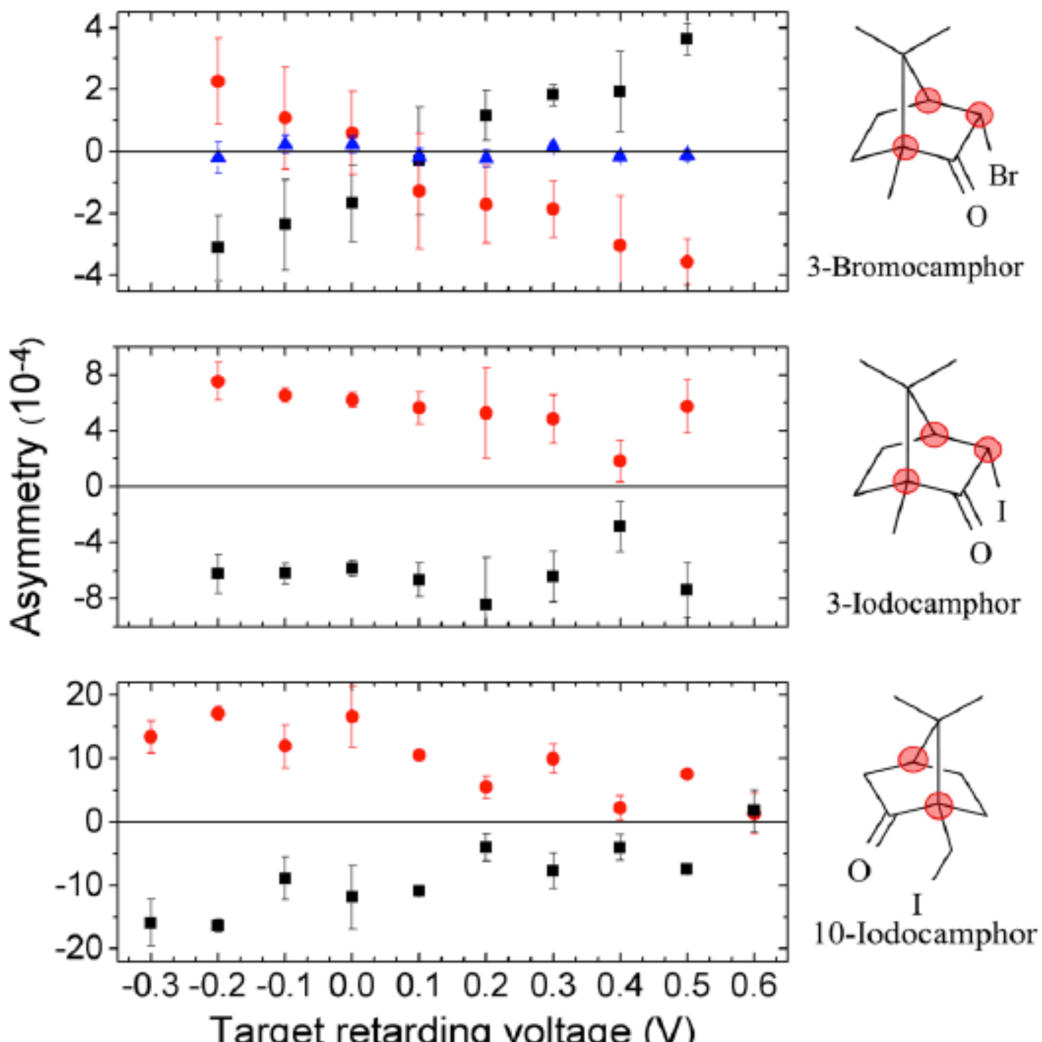
Dissociation (DEA) Chiral Asymmetry

$$a_{\mathrm{DEA}} = \frac{\eta(P_0, \rho d) - \eta(-P_0, \rho d)}{\eta(P_0, \rho d) - \eta(-P_0, \rho d)} \qquad A_{\mathrm{DEA}} = [a_{\mathrm{DEA}}]_L - [a_{\mathrm{DEA}}]_R$$

Anomalously Large Chiral Sensitivity in the Dissociative Electron Attachment of 10-Iodocamphor

J. M. Dreiling, F. W. Lewis, J. D. Mills, and T. J. Gay

PRL **116**, 093201 (2016)



– DEA asymmetries can exceed the transmission conterparts by one order of magnitude.

– Relative DEA asymmetry magnitudes not consistent with Mott Scattering (~Z^2)

– Relative DEA asymmetry magnitudes are not consistent with the helicity densities.

– Lack of knowledge on the collision dynamics.

DEA Asymmetry Theory

$$e^- + AB \rightarrow e^- + AB^* \quad \text{– Elastic and vibrationally inelastic scattering}$$

$$e^- + AB \rightarrow A^- + B^\bullet \quad \text{– Reactive (DEA) scattering}$$

– Transmission asymmetry [Fandreyer *et al*., J. Phys. B. 23, 3031 (1990)]

$$a_{\mathrm{tra}} = \frac{N(P_0,\rho d) - N(-P_0,\rho d)}{N(P_0,\rho d) - N(-P_0,\rho d)} = -P_0 \tanh\left[\frac{1}{2}\left(Q^+_{\mathrm{tot}} - Q^-_{\mathrm{tot}}\right)\rho d\right]$$

– DEA asymmetry:

$$a_{\mathrm{DEA}} = \frac{\eta(P_0,\rho d) - \eta(-P_0,\rho d)}{\eta(P_0,\rho d) - \eta(-P_0,\rho d)} \approx P_0 \left[\alpha_{\mathrm{DEA}} + t(Q^+_{\mathrm{tot}}, Q^-_{\mathrm{tot}}, \rho d)\right]$$

$$t(Q^+_{\mathrm{tot}}, Q^-_{\mathrm{tot}}, \rho d) = \frac{e^{-\frac{1}{2}(Q^+_{\mathrm{tot}}+Q^-_{\mathrm{tot}})\rho d}\sinh\left(\frac{1}{2}(Q^+_{\mathrm{tot}} - Q^-_{\mathrm{tot}})\rho d\right)}{1 - e^{-\frac{1}{2}(Q^+_{\mathrm{tot}}+Q^-_{\mathrm{tot}})\rho d}\cosh\left(\frac{1}{2}(Q^+_{\mathrm{tot}} - Q^-_{\mathrm{tot}})\rho d\right)}$$

Working Approximations

Assumptions:

– ~50% attenuation

– Low-order expansion of hyperbolic trigonometric functions

– $\alpha_{\text{tot}} \lesssim \alpha_{\text{DEA}}$

$$a_{\text{DEA}} \approx P_0 \left[\alpha_{\text{DEA}} + 0.35\alpha_{\text{tot}}\right] \approx P_0\, \alpha_{\text{DEA}}$$

$$\approx P_0 \left[\frac{Q^{+}_{\text{DEA}} - Q^{-}_{\text{DEA}}}{Q^{+}_{\text{DEA}} + Q^{-}_{\text{DEA}}} \right]$$

$$\alpha_{\text{DEA}} = \frac{\left(\frac{Q^{+}_{\text{DEA}}}{Q^{+}_{\text{tot}}} - \frac{Q^{-}_{\text{DEA}}}{Q^{-}_{\text{tot}}} \right)}{\left(\frac{Q^{+}_{\text{DEA}}}{Q^{+}_{\text{tot}}} + \frac{Q^{-}_{\text{DEA}}}{Q^{-}_{\text{tot}}} \right)}$$

$$\alpha_{\text{tot}} = \frac{Q^{+}_{\text{tot}} - Q^{-}_{\text{tot}}}{Q^{+}_{\text{tot}} + Q^{-}_{\text{tot}}}$$

Feshbach Projection Operator Approach

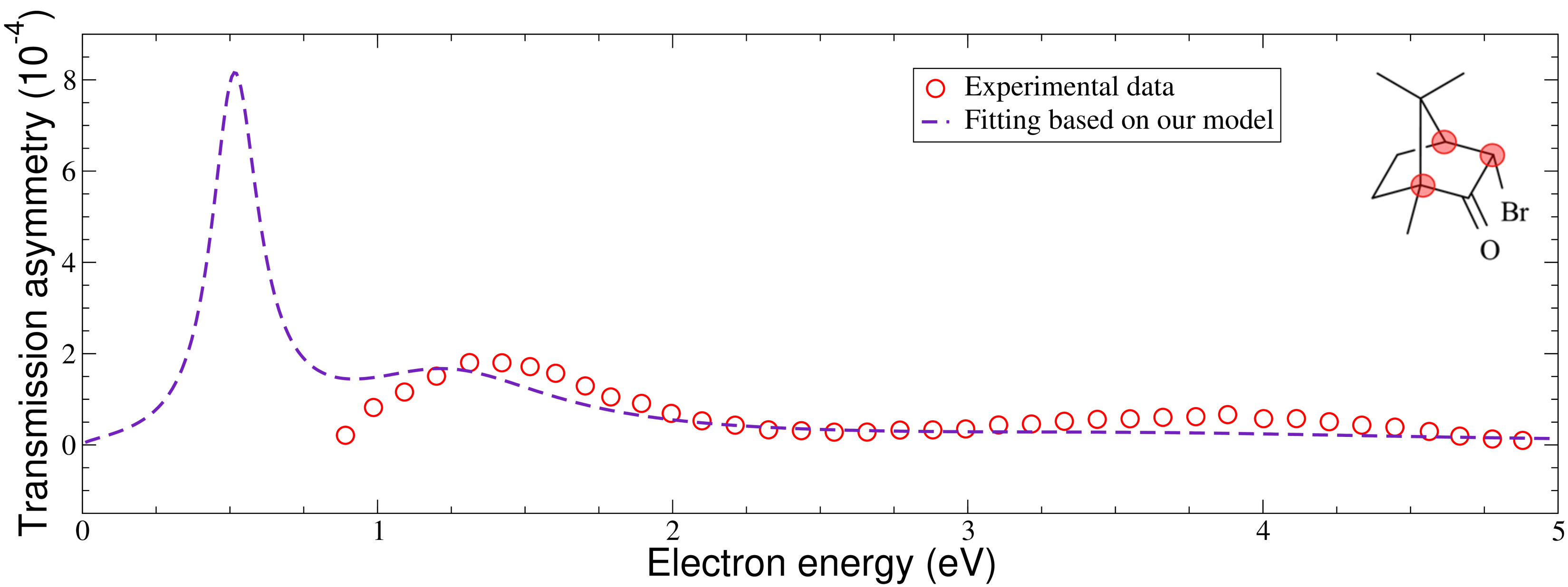
– **Projection operators:**

$$\hat{Q} = |\phi_d+\rangle\langle+\phi_d| \; + \; |\phi_d-\rangle\langle-\phi_d|$$

$$\hat{P} = \int d\mathbf{k}\; |\phi_\mathbf{k}+\rangle\langle+\phi_\mathbf{k}| \; + \; \int d\mathbf{k}\; |\phi_\mathbf{k}-\rangle\langle-\phi_\mathbf{k}|$$

– **Local approximation, purely Coulomb (*U*) complex potential, no background:**

$$A_{\mathrm{tran}}(E;\rho d) \;\approx\; -\rho d P_0 \,\frac{(2\pi)^2}{E}\langle 2\mathrm{Re}[W^{0*}_{\mathbf{k}_i} U_{\mathbf{k}_i}]\rangle \frac{\Gamma_{\mathrm{res}}}{(E-E_{\mathrm{res}})^2 + (\frac{1}{2}\Gamma_{\mathrm{res}})^2}$$



– *T*-Matrix elements for DEA:

Spin-preserving

$$T^{\mathrm{DEA}}_{m_s,m_s} \approx \left(\frac{\mu}{K}\right)^{1/2} \lim_{R\to\infty} e^{-iKR} \left[\langle R| \frac{1}{E - T_{\mathrm{nuc}} - V^{(\pm)}_{\mathrm{opt}}} U_{\mathbf{k}_i} |\eta_{\nu_i}\rangle + \right.$$

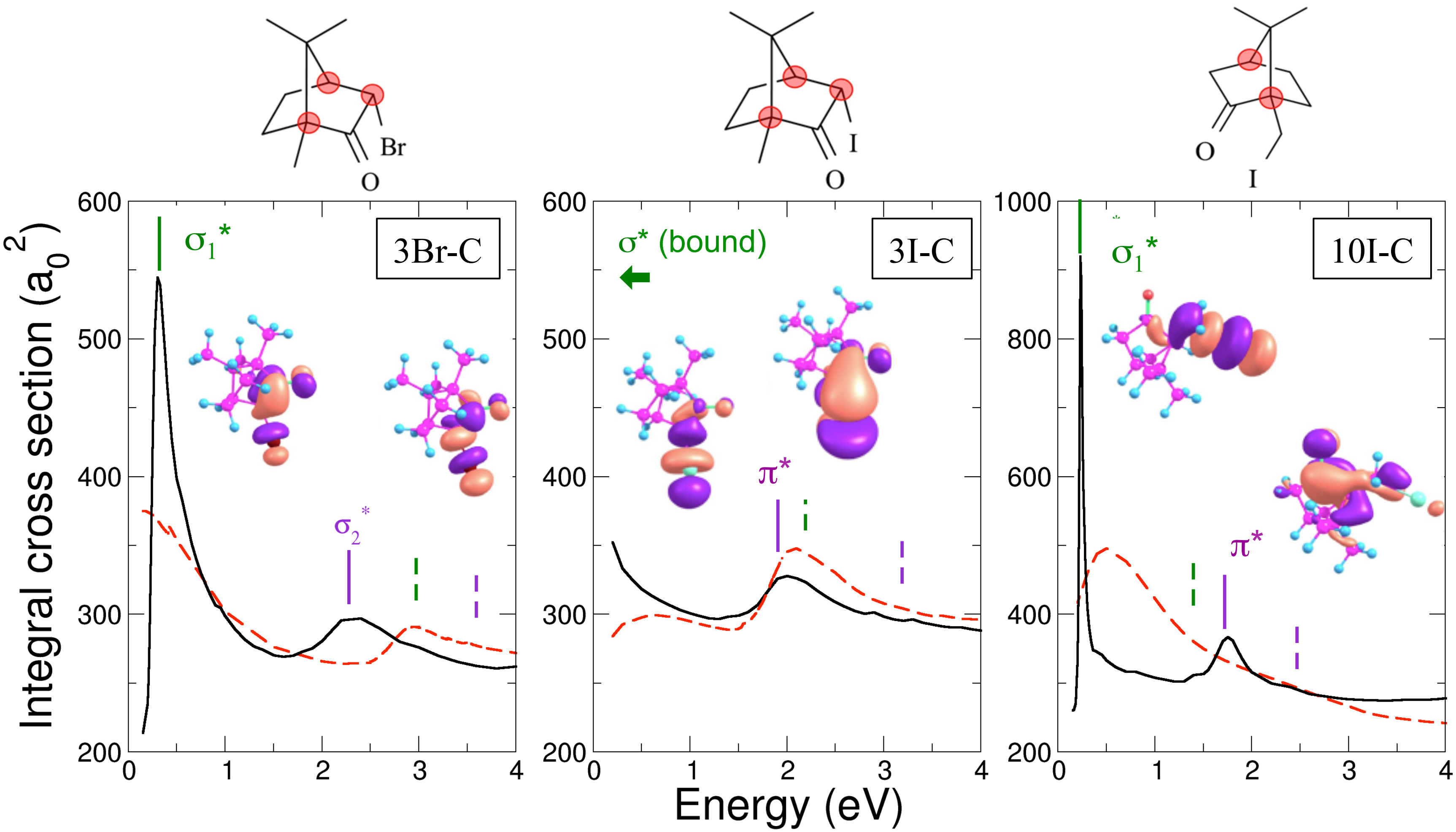
$$\left. + (-1)^{\frac{1}{2}-m_s} \langle R| \frac{1}{E - T_{\mathrm{nuc}} - V^{(\pm)}_{\mathrm{opt}}} W^0_{\mathbf{k}_i} |\eta_{\nu_i}\rangle \right] = T^{\mathrm{DEA}}_0 + (-1)^{\frac{1}{2}-m_s} T^{\mathrm{DEA}}_1$$

Spin-flip

$$T^{\mathrm{DEA}}_{m'_s,m_s} \approx \left(\frac{\mu}{K}\right)^{1/2} \lim_{R\to\infty} e^{-iKR} \left[\delta_{m'_s,m_s+1} \langle R| \frac{1}{E - T_{\mathrm{nuc}} - V^{(\pm)}_{\mathrm{opt}}} W^+_{\mathbf{k}_i} |\eta_{\nu_i}\rangle \right] +$$

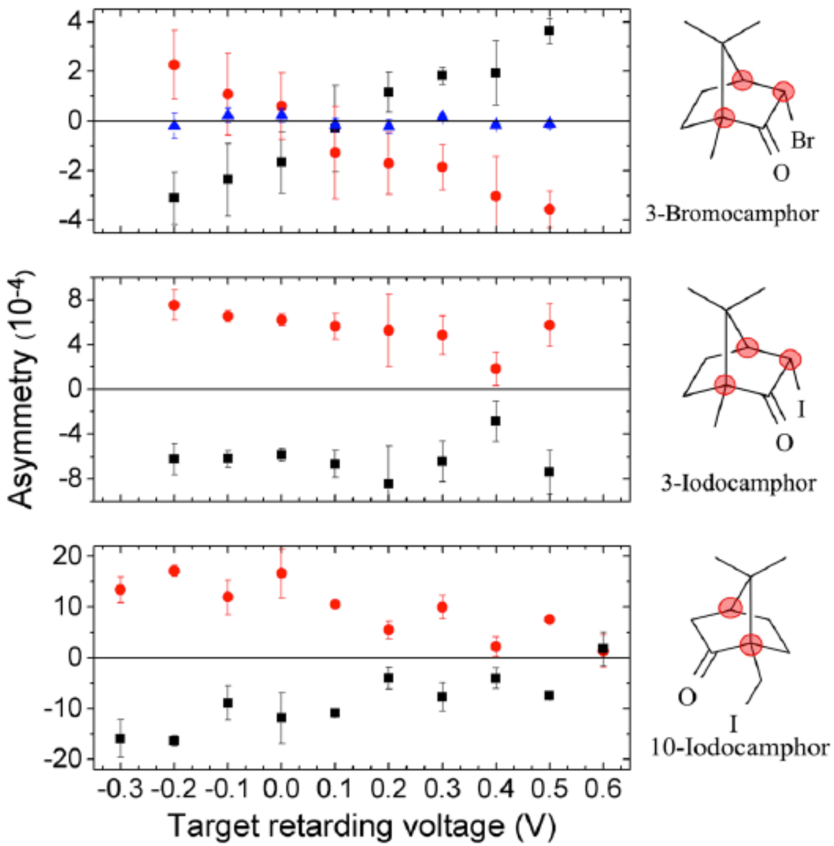
$$+ \left(\frac{\mu}{K}\right)^{1/2} \lim_{R\to\infty} e^{-iKR} \left[\delta_{m'_s,m_s-1} \langle R| \frac{1}{E - T_{\mathrm{nuc}} - V^{(\pm)}_{\mathrm{opt}}} W^-_{\mathbf{k}_i} |\eta_{\nu_i}\rangle \right]$$

Electron Scattering by Halocamphors

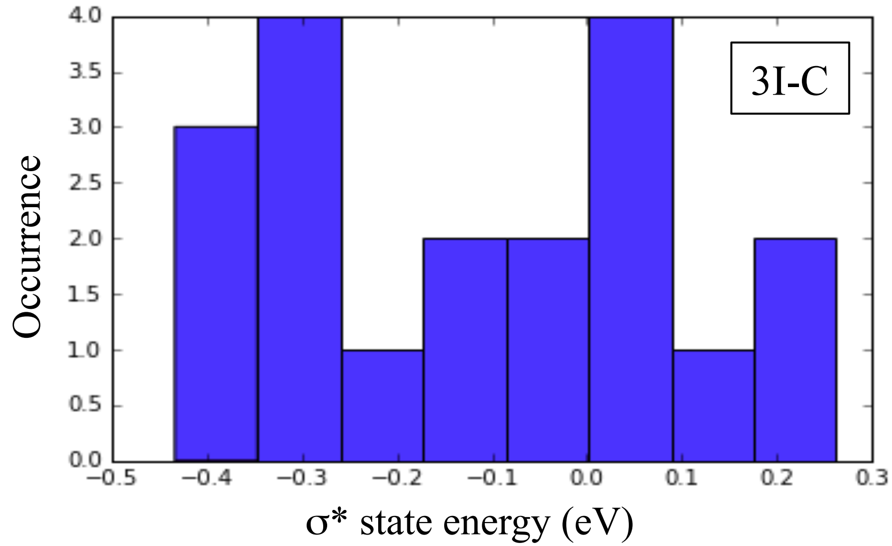


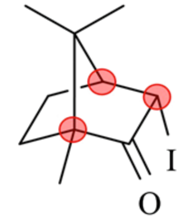
– Fixed-nuclei calculations; only Coulomb interaction
– Static-exchange plus ploarization (SEP) approximation
– SMC implemented in parallel with pseudopotentials [da Costa *et al*., EPJD 69, 159 (2015)]

So, What Do We Learn?

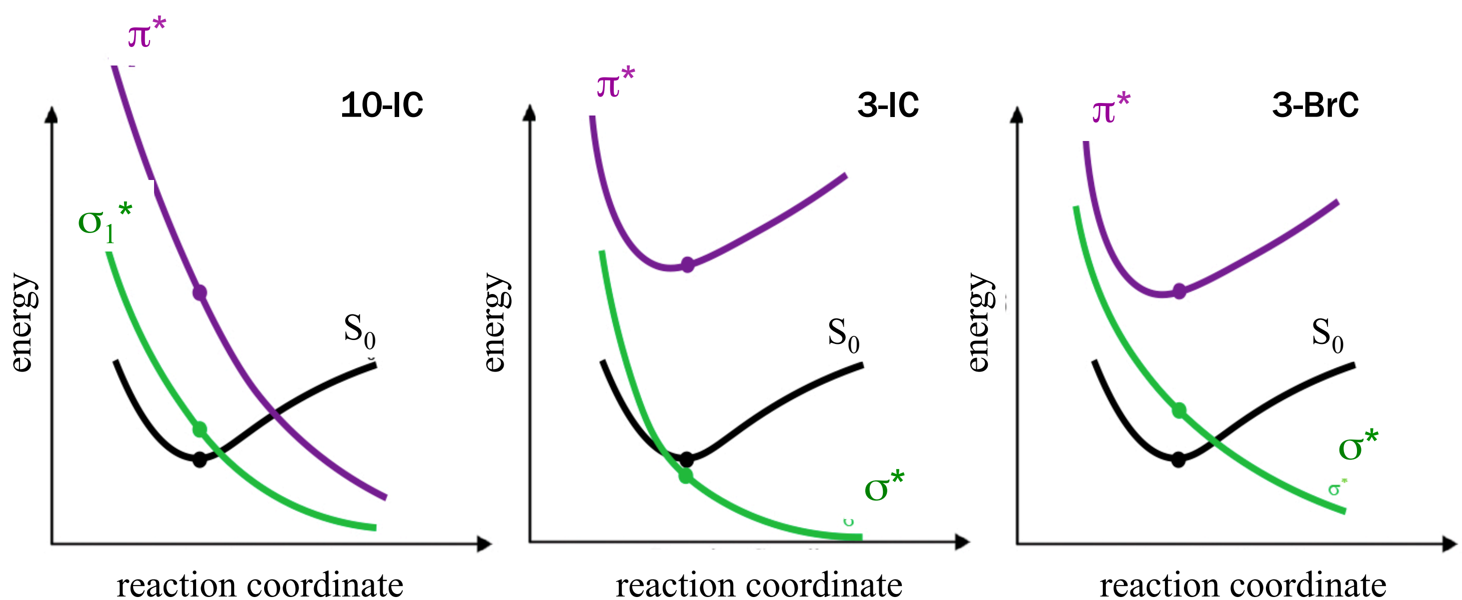


3-bromocamphor	σ_1^*	σ_2^*
SMCPP	0.32 (0.192)	2.34 (0.488)
ETS data	0.53	1.94
Scaled VOEs	0.46	1.82
M06-2X/aug-cc-pVDZ	0.356	
3-iodocamphor	σ^*	π^*
SMCPP	-0.01	2.00 (0.496)
Scaled VOEs	-0.23	1.63
M06-2X/aug-cc-pVDZ	-0.048	
10-iodocamphor	σ^*	π^*
SMCPP	0.25 (0.030)	1.77 (0.194)
Scaled VOEs	0.26	1.52
M06-2X/aug-cc-pVDZ	0.429	



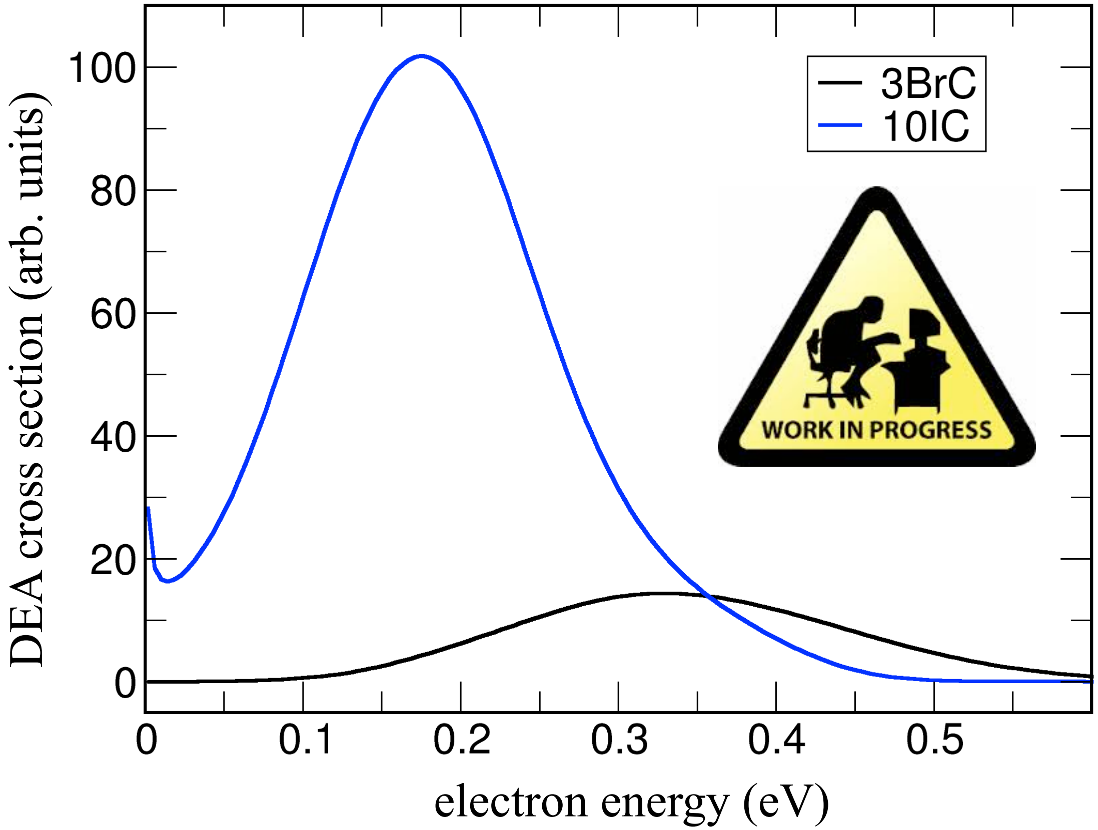


Out of 20 statistically uncorrelated configurations, ~40% show up as resonances.



Molecular dynamics with CP2K: *T* = 353 K, NVT with velocity rescaling for 20ps (after 5-ps thermalization), with DFT/M06-2X/auc-cc-pDZV potentials and gradients.

DEA from Local Pseudo-Diatomic Models
(Coulomb potential)

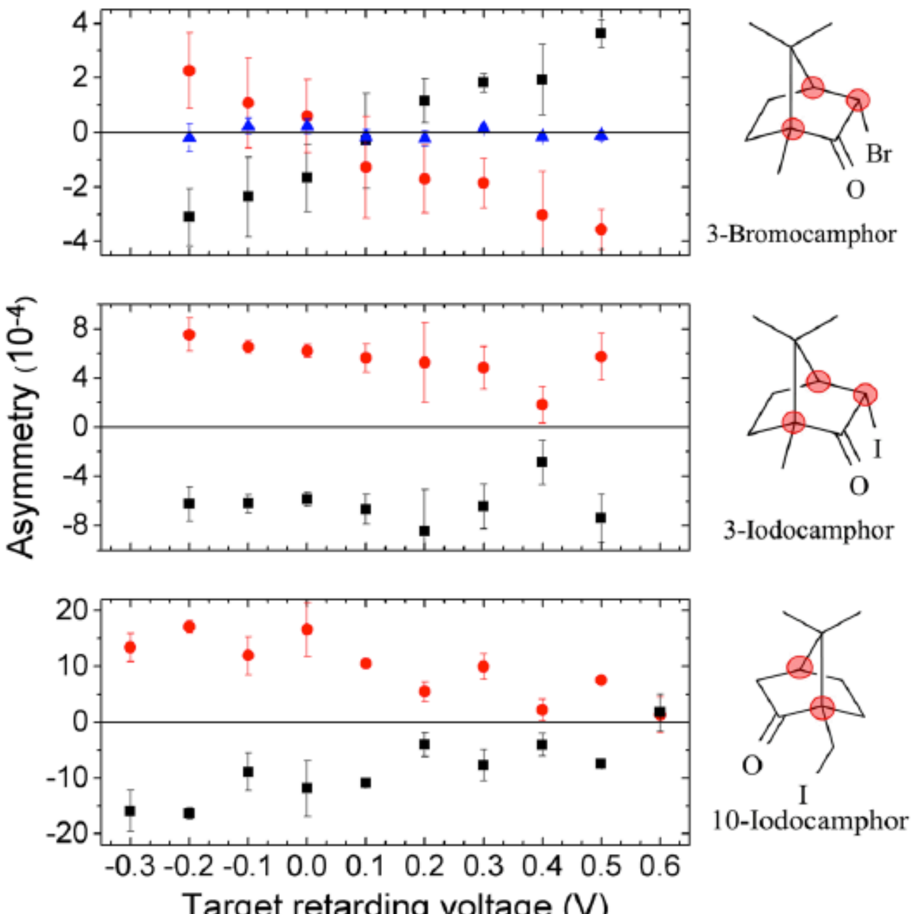


$$a_{\mathrm{DEA}} \approx P_0 \left[\frac{Q^+_{\mathrm{DEA}} - Q^-_{\mathrm{DEA}}}{Q^+_{\mathrm{DEA}} + Q^-_{\mathrm{DEA}}} \right] \qquad T^{\mathrm{DEA}}_{m_s.m_s} = T^{\mathrm{DEA}}_0 + (-1)^{\frac{1}{2}-m_s} T^{\mathrm{DEA}}_1$$

– Geometry-independent attachment amplitudes (Condon approximation):

$$T_0^{\rm DEA} \approx \left(\frac{\mu}{K}\right)^{1/2} \lim_{R\to\infty} e^{-iKR}\, U_{\mathbf{k}_i}(R_0)\, \langle R| \frac{1}{E - T_{\rm nuc} - V_{\rm opt}^{(\pm)}} |\eta_{\nu_i}\rangle$$

$$T_1^{\rm DEA} \approx \left(\frac{\mu}{K}\right)^{1/2} \lim_{R\to\infty} e^{-iKR}\, W^0_{\mathbf{k}_i}(R_0)\, \langle R| \frac{1}{E - T_{\rm nuc} - V_{\rm opt}^{(\pm)}} |\eta_{\nu_i}\rangle$$



$$A_{\rm DEA} \sim \frac{2{\rm Re}(\langle W^{0*}_{\mathbf{k}_i} U_{\mathbf{k}_i}\rangle)}{|\langle U_{\mathbf{k}_i}\rangle|^2 + |\langle W^{0*}_{\mathbf{k}_i}\rangle|^2}$$

or even

$$A_{\rm DEA} \sim \frac{2{\rm Re}(\langle W^{0*}_{\mathbf{k}_i} U_{\mathbf{k}_i}\rangle)}{|\langle U_{\mathbf{k}_i}\rangle|^2}$$

Conclusions and Outlook

– Theory for transmission asymmetries generalized to account for vibrationally inelastic and reactive (DEA) scattering.

– Theory for DEA asymmetries.

– The FPO approach hopefully makes more clear the role of resonances.

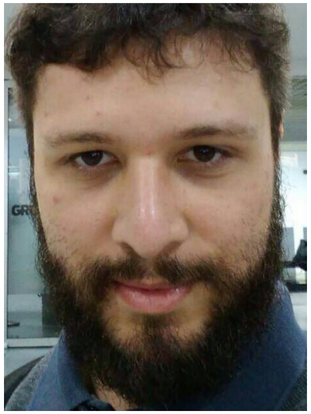
– Low-lying σ* resonances expected to underlie the DEA asymmetries for halocamphors.

– Still working on the DEA models to account for DEA asymmetries, but the Condon approximation seems useful.

– Implementation of SO couplings along with the DWB approximation for the transmission asymmetry:

$$f \approx -\frac{1}{2\pi}\left[\langle S_{\mathbf{k}_f}|U|\Psi^{(+)}_{\mathbf{k}_i}\rangle + \langle\Psi^{(-)}_{\mathbf{k}_f}|W|\Psi^{(+)}_{\mathbf{k}_i}\rangle\right]$$

Many Thanks to



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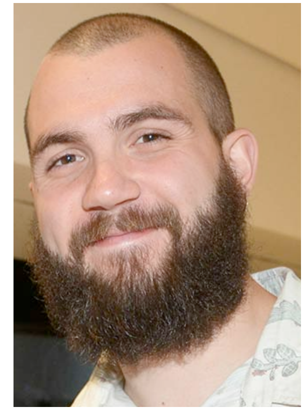

Lucas Cornetta
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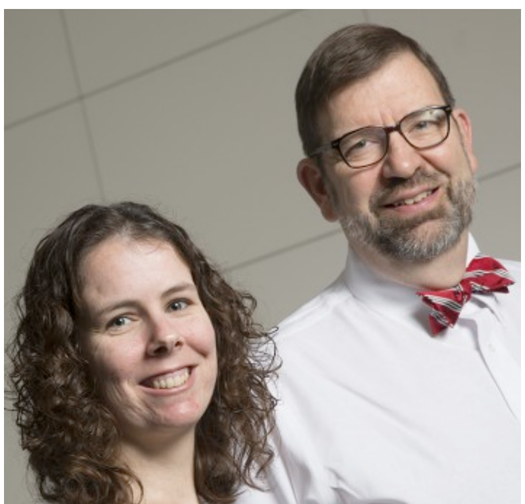

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Thanks for your attention!