



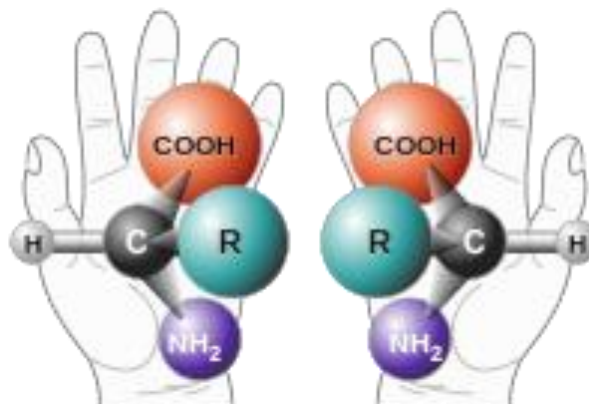
2013 Ghana IGERT Presentation

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Part I: Background

Optical Activity and Chirality

Optical Activity



- Due to Chirality-
Mirror Images not superimposable.
- **Significance:**
 - 3D information of molecules
 - Drugs can be poison if wrong 'handedness'
 - Possible engineering of efficient solar energy cells¹⁻⁵

1. <http://www.ecs.soton.ac.uk/news/679>

2. <http://hdl.handle.net/2142/42174>

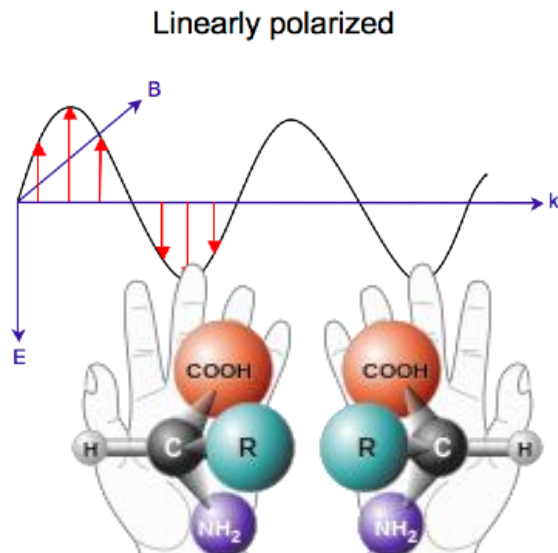
3. Sabah, Uckun, J. Optoelectronics and Adv. Mat., Vol. 8, No. 5, pp.1918-1924, 2006.

4. Srivastava, et al., Science, 2010; 327 (5971): 1355.

5. [Iowa Energy Center](#)

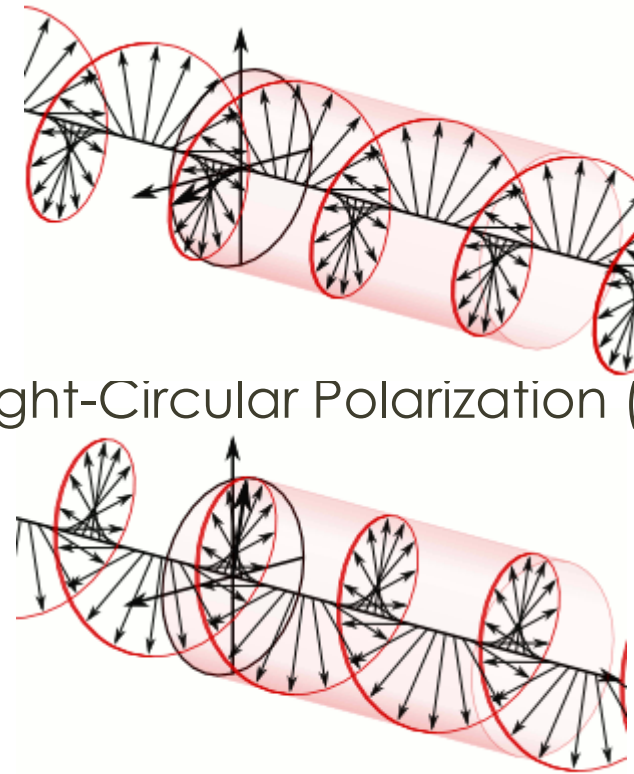
Light = Electric Magnetic (EM) Field

1. Linear Polarization (**LP**)
2. Left-Circular Polarization (**LCP**)



Left-handed or Right-handed molecules interact differently with LCP and RCP light

3. Right-Circular Polarization (**RCP**)

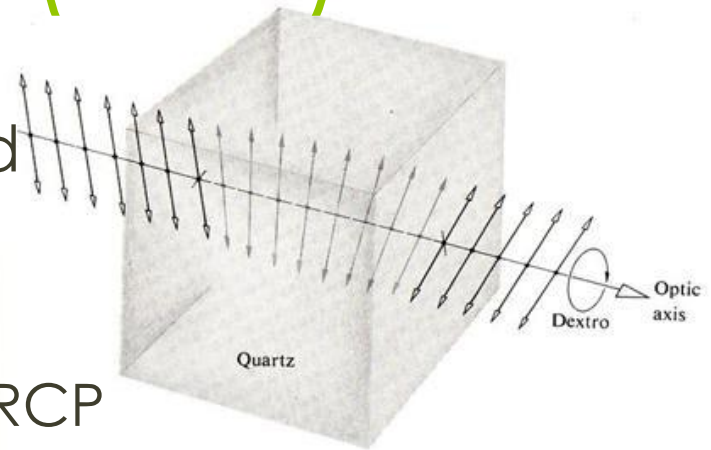


Optical Rotation (ORD)

- Rotation of Linearly Polarized light

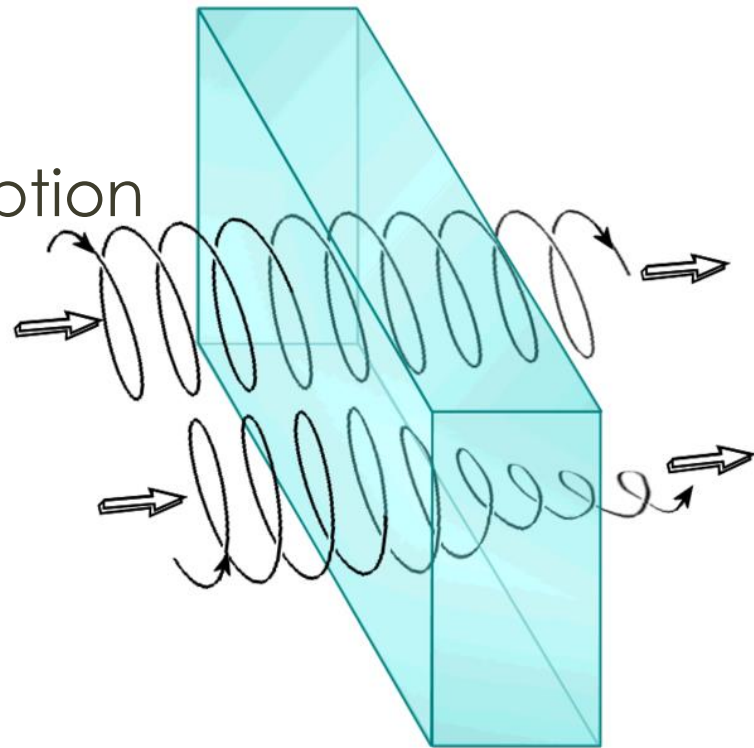
Because:

1. Linear Polarization = LCP + RCP
2. Left- and Right-Circular Polarized light rotate differently in chiral molecules



Circular Dichroism (CD)

- Absorption different for LCP and RCP in chiral medium
- Circular Dichroism = This Differential Absorption



Measuring Optical Activity

- Differential signals for left- vs. right-handed fields and molecules:
 - Very small ($10^{-6} - 10^{-3}$)
 - Difficult
- One measure is Dissymmetry Factor:

$$g = \frac{A^L - A^R}{(A^L + A^R)/2} \sim \frac{\text{Circular Dichroism}}{\text{Average Absorption}}$$

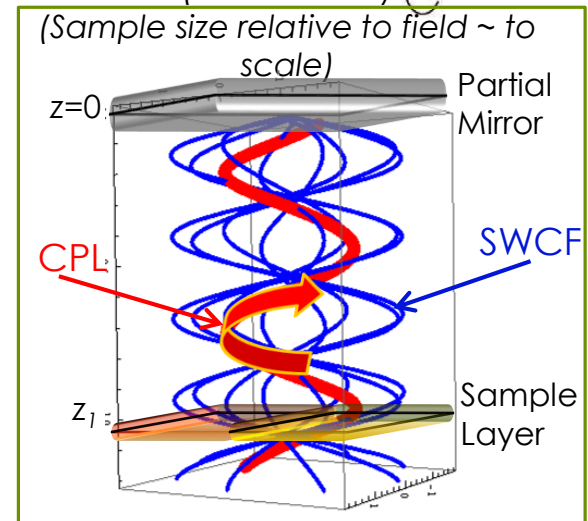
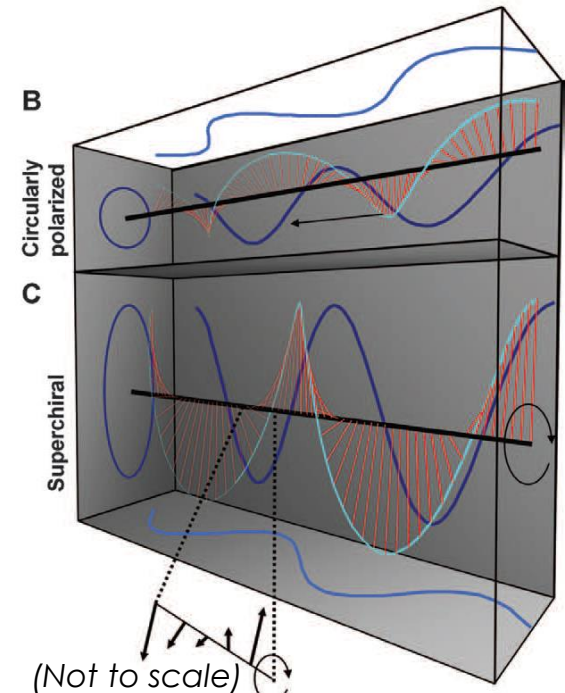
where A^L = LCP Absorption Rate, etc.

Part II: Limitations of a Superchiral Field

Choi, J. S. and Cho, M. *Physical Review A* **86**,063834
(2012)

“Superchiral” Light

- Can we enhance Optical Activity signals dramatically?
- Y. Tang and A. E. Cohen, *Science* **332**, 333 (2011): Engineer light to increase Chirality
- Create Standing Wave of RCPL + LCPL with mirror (**SWCF**)
- Place Chiral sample at Electric Field Energy (U_e) Minimum (node)



Cohen's "Superchirality"- Results

- Enhancement:

$$\frac{g}{g_{\text{CPL}}} = \frac{c C}{2 \omega U_e} \rightarrow \frac{1 + \sqrt{R}}{1 - \sqrt{R}}$$

- R = Reflectivity of mirror
- "Optical Chirality":

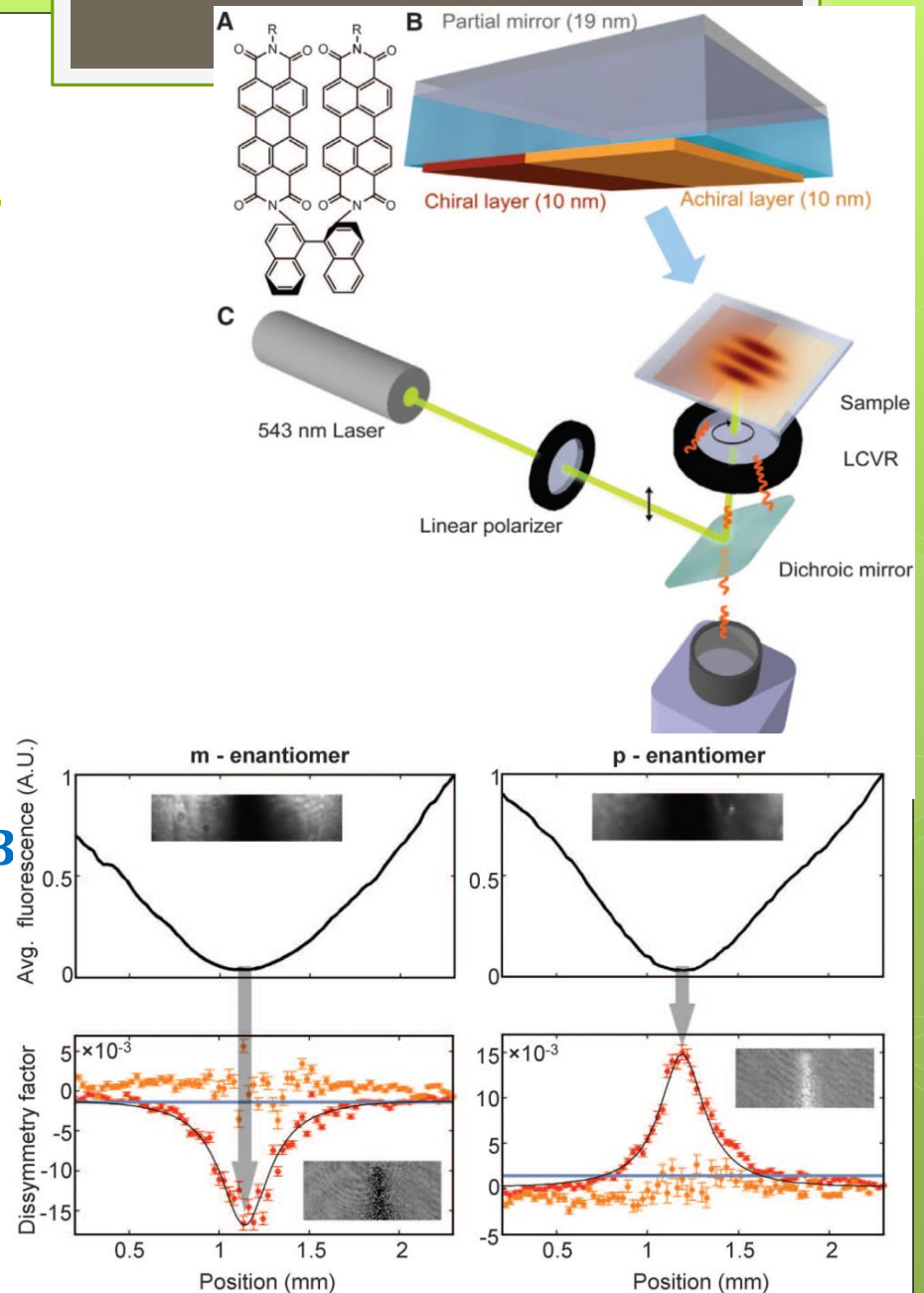
$$C \equiv \frac{\epsilon_0}{2} \mathbf{E} \cdot \nabla \times \mathbf{E} + \frac{1}{2\mu_0} \mathbf{B} \cdot \nabla \times \mathbf{B}$$

- For R=0.72:

11x enhancement

- For R=1:

Infinite enhancement?



WARNING- MATH FUN!

- Induced electric (\mathbf{p}) and magnetic (\mathbf{m}) dipole moments:

$$\tilde{\mathbf{p}} \simeq \tilde{\alpha}\tilde{\mathbf{E}} + \tilde{G}\tilde{\mathbf{B}}, \quad \tilde{\mathbf{m}} \simeq \tilde{\chi}\tilde{\mathbf{B}} - \tilde{G}\tilde{\mathbf{E}}$$

- Work done by EM fields:

$$W_{\text{EM}} = \mathbf{p} \cdot \mathbf{E} + \mathbf{m} \cdot \mathbf{B}$$

- Total absorption rate of molecules:

$$A^{\pm} = \langle \dot{\mathbf{p}} \cdot \mathbf{E} + \dot{\mathbf{m}} \cdot \mathbf{B} \rangle_t$$

Generalized g for SWCF- Final

$$g = \left\{ \frac{(1 - R) \left[4\gamma_{\text{ave}}^{\text{CPL}} \frac{n_{\text{ave}}^0 \Delta n}{(n^2)_{\text{ave}}} + g_{\text{CPL}} \right]}{(1 + R) \left[1 + \gamma_{\text{ave}}^{\text{CPL}} + \frac{1}{2} g_{\text{CPL}} \frac{\Delta n}{n_{\text{ave}}^0} \right] + 2\sqrt{R} \left[\gamma_{\text{ave}}^{\text{CPL}} \frac{n^L n^R}{(n^2)_{\text{ave}}} - 1 - \frac{1}{2} g_{\text{CPL}} \frac{\Delta n}{n_{\text{ave}}^0} \right] \cos(2k_{\text{ave}} z)} \right\}$$

- Combined C_g, U_γ
- Calibrated amplitudes (R)
- Substituted with averaged parameters

$$g_{\text{CPL}} = -4 \frac{G'(g) n_{\text{ave}}^0}{\alpha'' c}$$

$$\gamma_{\text{ave}}^{\text{CPL}} \equiv \frac{\gamma^L + \gamma^R}{2}$$

$$\gamma^{(L/R)} \equiv \frac{(n^{(L/R)})^2 \chi''}{c^2 \alpha''} \geq 0$$

$$R \equiv (E_2/E_1)^2 = (E'_2/E'_1)^2$$

$$n_{\text{ave}}^0 \equiv \frac{1}{2}(n^L + n^R)$$

$$\Delta n \equiv \frac{n^L - n^R}{2} \quad (\Delta n : \text{positive or negative})$$

$$n^L = n_{\text{ave}}^0 + \Delta n$$

$$n^R = n_{\text{ave}}^0 - \Delta n$$

$$(n^2)_{\text{ave}} \equiv \frac{(n^L)^2 + (n^R)^2}{2}$$

$$k_{\text{ave}} \equiv \frac{k^L + k^R}{2} = \frac{\omega}{c} n_{\text{ave}}^0$$

g_0 for SWCF when $\Delta n=0$

(Simpler formula, good approximation)

$$g_0 \equiv g(\Delta n/n_0 = 0)$$

$$= g_{\text{CPL}} \times$$

$$\left\{ \frac{(1 - R)}{(1 + R)(1 + \gamma_0) + 2\sqrt{R}(\gamma_0 - 1) \cos(2k_{\text{ave}}z)} \right\}$$

- Drop γ_0 (10^{-6} - 10^{-4})?
- No, or else same as Tang and Cohen.
- Write denominator differently
→ U_e min $\Rightarrow U_b$ max.

$$\{[\langle U_e \rangle_t] + \gamma_0[\langle U_b \rangle_t]\} \propto$$

$$\begin{aligned} & \left[(1 + R) - 2\sqrt{R} \cos(2k_{\text{ave}}z) \right] \\ & + \gamma_0 \left[(1 + R) + 2\sqrt{R} \cos(2k_{\text{ave}}z) \right] \end{aligned}$$

Correcting Dissymmetry Factor (g)

- ❖ Conservation of Energy:

Electric Energy(U_e) + Magnetic Energy(U_b) = Constant

- ❖ Before (for minimum U_e):

$$\frac{g}{g_{\text{CPL}}} = \frac{c C}{2 \omega U_e} \rightarrow \frac{1 + \sqrt{R}}{1 - \sqrt{R}}$$

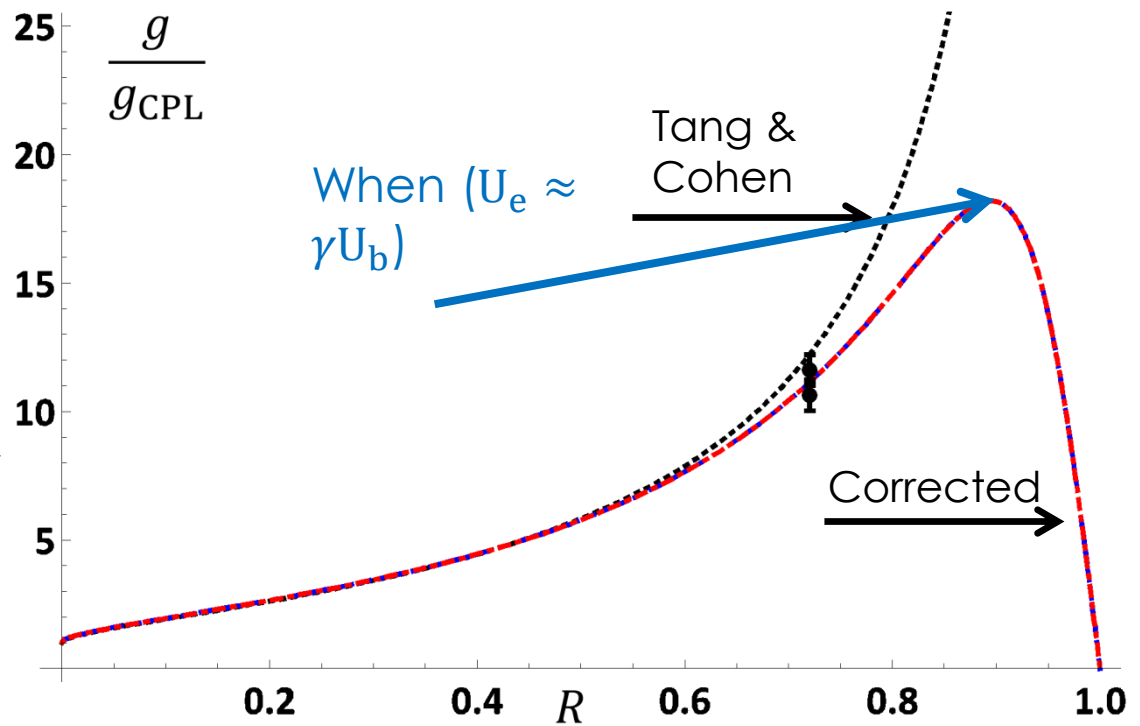
- ❖ Corrected (small $U_e \rightarrow$ large U_b)

$$g/g_{\text{CPL}} = \frac{c C}{2 \omega (U_e + \gamma U_b)} = \frac{1 - R}{(1 - \sqrt{R})^2 + \gamma(1 + \sqrt{R})^2}$$

- ❖ U_b = magnetic field energy density
- ❖ $\gamma \propto$ (magnetic susceptibility) / (electric polarizability)
- ❖ γ = property of material; small; limits enhancement

Plot

1. Material (γ) fixes maximum enhancement (10x - 500x)
2. Find better material?
But signal decreases faster than increase in enhancement



Conclusions 1

- Tang and Cohen:
 - Suggested simple and ingenious method
 - Renewed interest in C as physically useful quantity (discovered originally in 1964)
- We generalized Optical Chirality:
$$C \equiv \frac{\epsilon}{2} \mathbf{E} \cdot \nabla \times \mathbf{E} + \frac{1}{2\mu} \mathbf{B} \cdot \nabla \times \mathbf{B},$$
and analyzed optical rotation effects
- Our correction useful for ongoing discussion and future enhancement search

Acknowledgements 1

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