Separation of molecules by chirality using circularly polarized light

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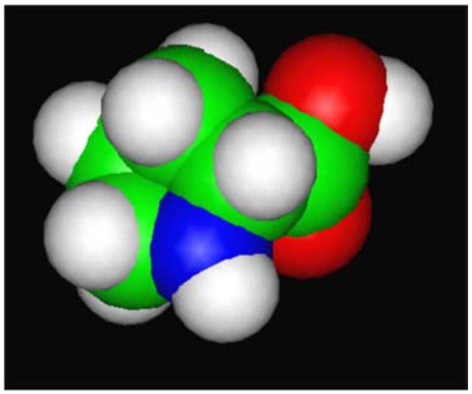
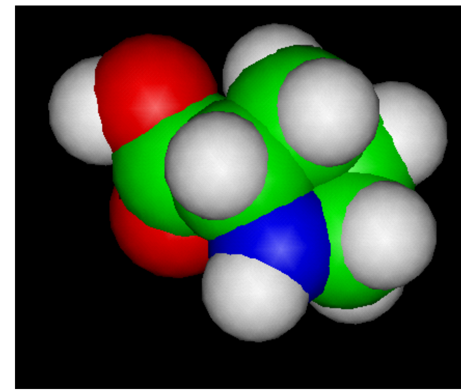
Chiral Molecules

Many molecules exist as right- and left- handed isomers (enantiomers)

Proline molecule: $C_5H_9NO_2$ Molecular Weight: 115.13



R



L

Characteristic time of conversion (by tunneling or thermal activation) may be extremely long

Enantiomers – distinct stable molecules

Often one needs to extract specific enantiomers from a *racemic* (50/50) mixture

1) Conversion L $\rightarrow$ R

2) Spatial separation

Chiral separation with light

Chiral current density: $\mathbf{j}_C = \mathbf{j}_R - \mathbf{j}_L$

Inversion: $R \leftrightarrow L \quad \Rightarrow \quad \mathbf{j}_C$ – pseudovector

Time reversal: $\mathbf{j}_C \to -\mathbf{j}_C$

In an ac electric field: $\mathbf{E}$

by symmetry: $\mathbf{j}_C \sim \langle \mathbf{E} \times \dot{\mathbf{E}} \rangle, \quad \langle \ldots \rangle$ - time average

$$\mathbf{E} = \mathrm{Re}[(\hat{x} + i\hat{y})e^{-i\omega t}]$$

Circularly polarized light
has handedness (photon spin)
and can produce chiral current

What are the mechanisms and magnitude of the effect?

Chiral separation due to torque

Circularly polarized light exerts *torque* τ on a particle

Baranova, Zel'dovich
Chem. Phys. Lett. '78

For *chiral* objects torque induces *rotation* and *drift*

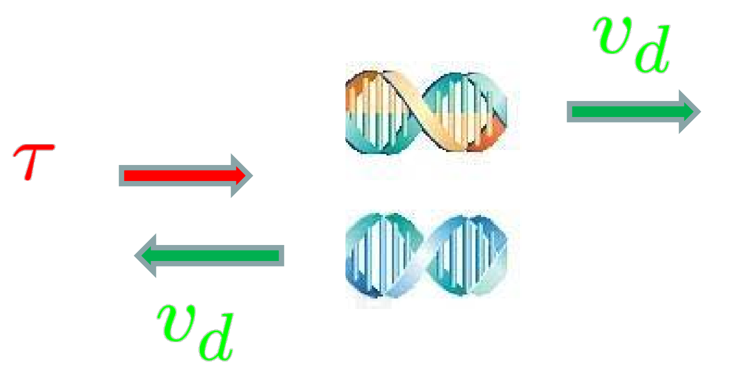
Hydrodynamic regime (chiral particles in a liquid)

Drift velocity: $v_d \sim \frac{\chi}{\eta R^2} \tau$

R – particle size

η – fluid viscosity

χ – measure of chirality



propeller effect

angular momentum per photon is small: $\hbar$

Torque: $\tau = \hbar \frac{dN_{\text{ph}}}{dt}$

Is chiral separation possible in the absence of torque?

Chiral separation in gases

Molecules: mass - m , size - d

Light: frequency - ω , wavelength - $\lambda \gg d$

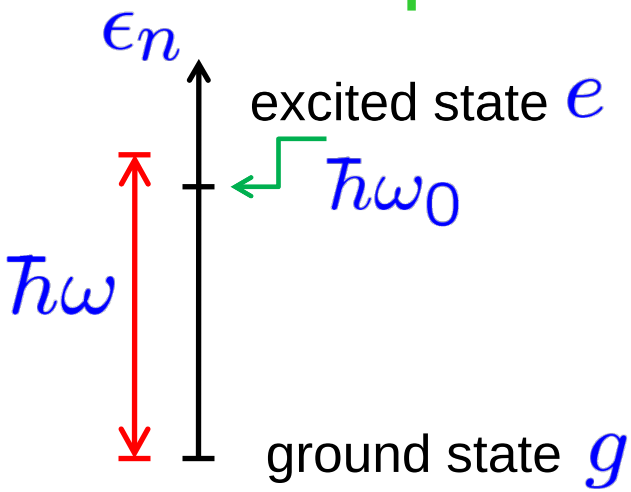
molecule momentum: $p_T \sim \sqrt{mT} \gg \hbar/\lambda$

Rotational motion is classical

angular momentum: $M_T \sim \sqrt{mT}d \gg \hbar$

Neglect transfer of linear and angular momentum from light to molecules

Simplified model: uniaxial rotation

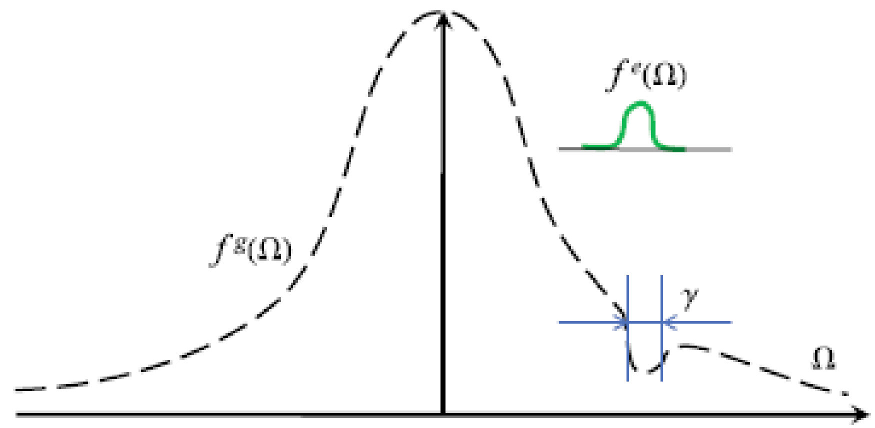


Resonant absorption at

$$\omega - \Omega = \omega_0$$

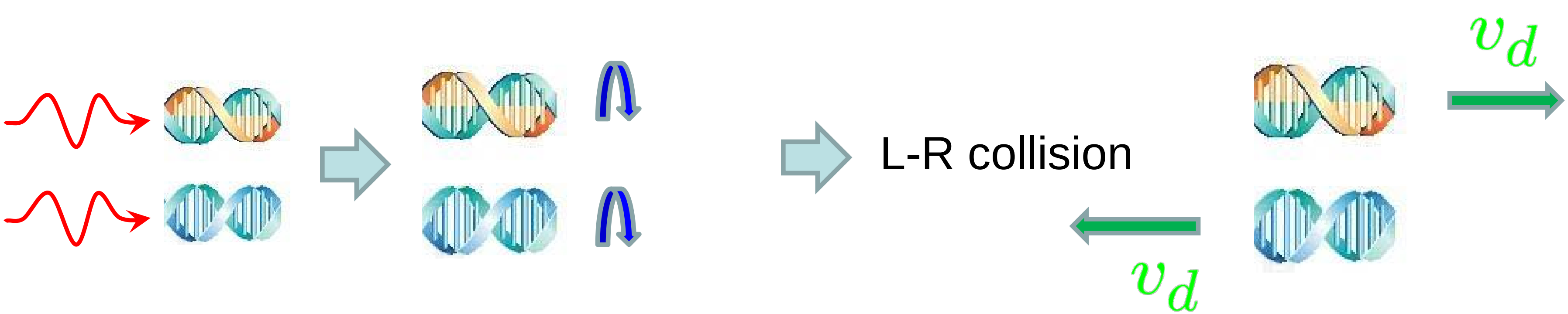
$\Omega -$ molecule angular velocity

Doppler shift: $v_T/\lambda \ll \Omega$



L- and R- molecules absorb light equally
(dipole approximation)

Light absorption changes
collision cross-section

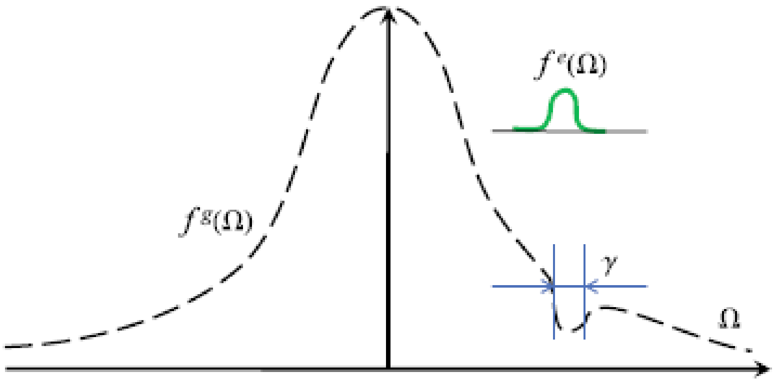


Mechanism comparison

Let's assume:

$$\omega - \omega_0 \sim v_T/d$$

$$\gamma \ll v_T/d$$



Momentum transfer from L to R upon collision

From cross-section change

$$\delta p \sim \frac{M_T}{d}\delta\chi = p_T \delta\chi$$

$$\delta\chi = \chi^e - \chi^g$$

From photon torque

$$\delta p \sim \chi\hbar/d$$

Ratio: $$\frac{\delta\chi}{\chi}\frac{M_T}{\hbar} \sim \frac{\delta\chi}{\chi}\sqrt{\frac{Tmd^2}{\hbar^2}}$$

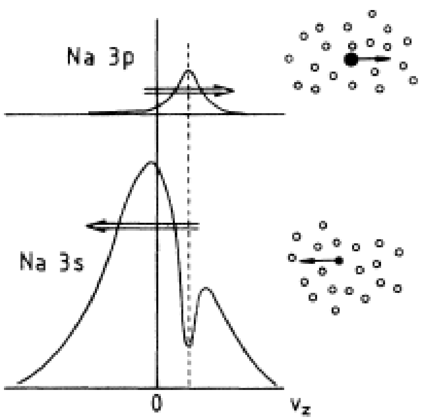
Similarity to optical piston effect

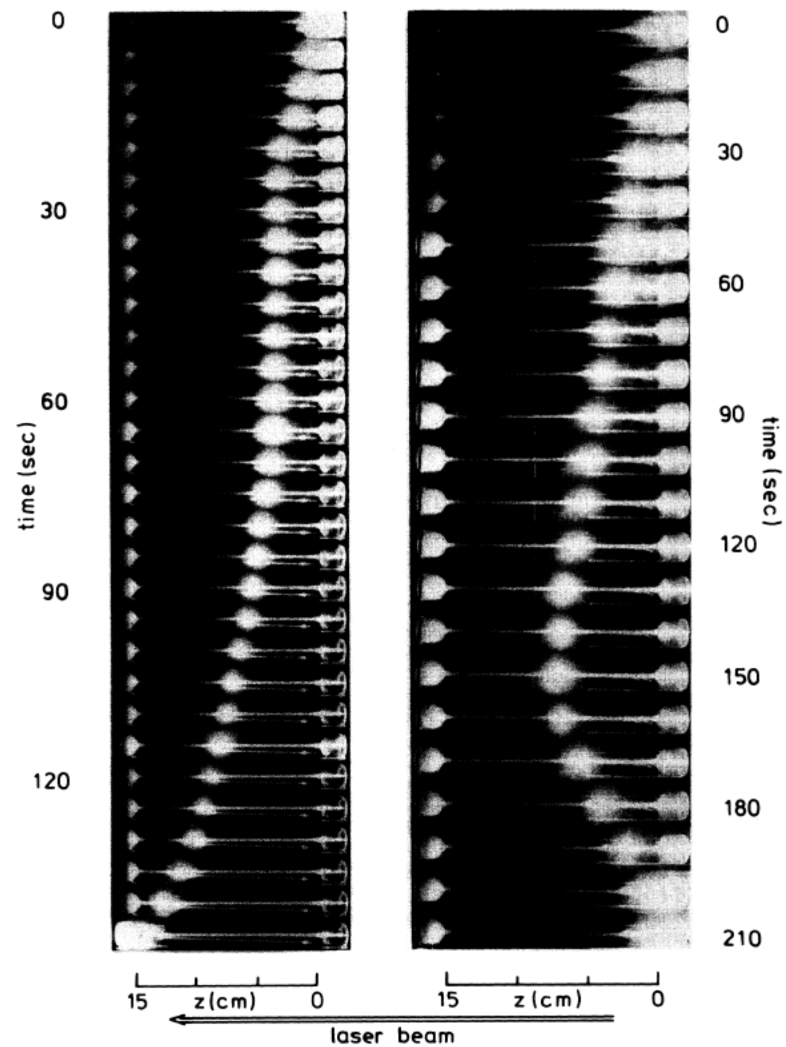
Resonantly absorbing atoms in a buffer gas

Gel'mukhanov, Shalagin
JETP 1980

Doppler shift: $\omega - qv_z = \omega_0$

No momentum transfer
from light to atoms





Experimental observation:
Werij, Heverkort, Woerdman,
Phys. Rev. A, **33**, 3270 (1986)

Drift velocities: $v_d \sim 0.1 cm/s$

Boltzmann equation

Spatially homogeneous case

$$\partial_t \tilde{f}^a_r(\Gamma) = I^a_r\{\tilde{f}(\Gamma)\} + I^a_{ph}(\Gamma)$$

$\tilde{f}^{e/g}_r(\Gamma)$ – distribution function (nonequilibrium part)

$r = \pm 1$ represents R and L chirality

$\Gamma = \{\mathbf{p}, \mathbf{M}, \ldots\}$ – quantities conserved in free motion

$I^a_r\{\tilde{f}(\Gamma)\}$ - collision integral

Equilibrium distribution

$$I^e_{ph}(\Gamma) = f_0(\Gamma)\,\Upsilon(\Gamma)\,\mathcal{I}$$

$$I^g_{ph}(\Gamma) = -f_0(\Gamma)\,\Upsilon(\Gamma)\,\mathcal{I}$$

Photo-excitation (independent of chirality)

absorption probability

light intensity

Symmetry considerations

Inversion: $P \quad \begin{cases} L \leftrightarrow R \, (r \to -r), \\ \Gamma = \{\mathbf{p}, \mathbf{M}\} \to \Gamma^P = \{-\mathbf{p}, \mathbf{M}\} \end{cases}$

Optical excitations are independent of: r

Stationary Boltzmann equation: $0 = I_r^a\{\tilde{f}(\Gamma)\} + I_{ph}^a(\Gamma)$

if collision cross-section were chirality-independent we would have

$$\tilde{f}_r(\mathbf{p}, \mathbf{M}) = \tilde{f}_{-r}(\mathbf{p}, \mathbf{M})$$

Then chiral current would vanish

For chirality-dependent collisions $\tilde{f}_r(\mathbf{p}, \mathbf{M}) \neq \tilde{f}_{-r}(\mathbf{p}, \mathbf{M})$

$\mathbf{j}_C$ arises due to chirality-dependence of collision cross-section

Solution outline

$$0 = I_r^a\{\tilde{f}(\Gamma)\} + I_{ph}^a(\Gamma)$$

To find chiral current:
1. Determine absorption rate $I_{ph}^a(\Gamma)$
2. Solve kinetic equation

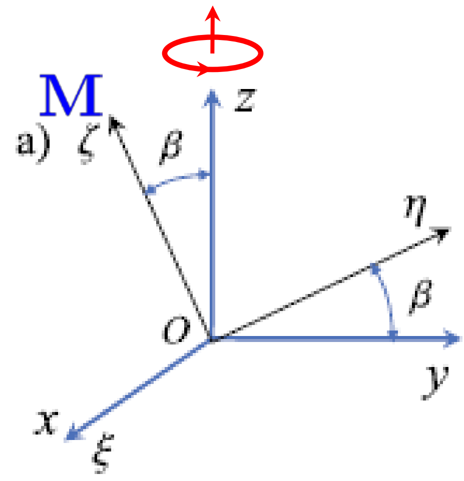
Absorption probability is obtained by transforming electric field to reference frame co-rotating with the molecule

Model:
- Dipole approximation
- Monochromatic light: $\mathbf{E} = \mathrm{Re}[(\hat{x} + i\hat{y})e^{-i\omega t}]$

Absorption cross-section, $\sigma(\omega)$, for stationary molecule is assumed known

Light absoption probability

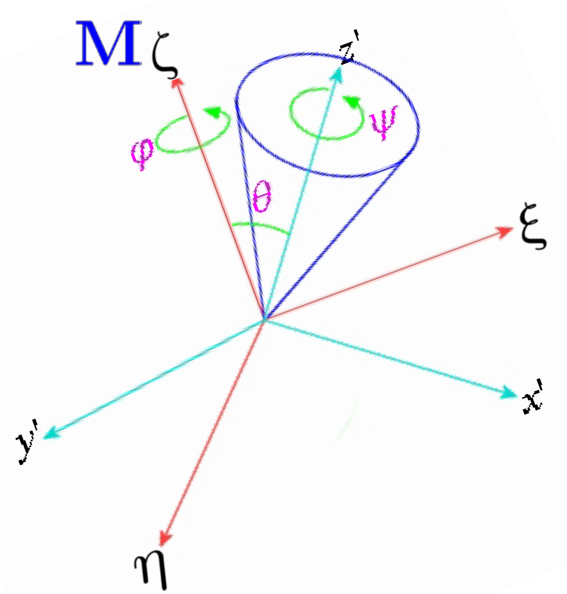
Circular polarization along z
Angular momentum $\mathbf{M}$ along ζ



β – angle between z and $\mathbf{M}$

x', y', z' - body frame

Euler angles



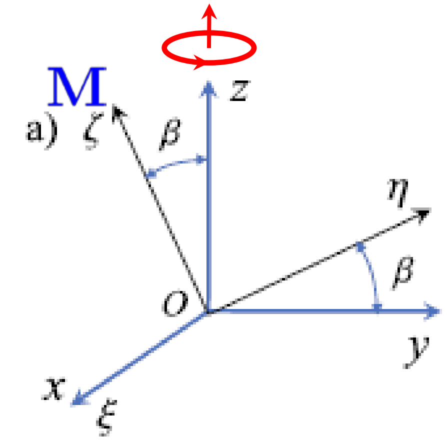
Assume symmetric top molecule:

$$\theta, \dot{\phi}, \dot{\psi} = const$$

In body frame $\mathbf{E}$ has several frequencies

$$\omega_{pq} \equiv \omega - p\dot{\psi} - q\dot{\phi}, \quad p, q = 0, \pm 1$$

Absorption probability $\Upsilon(\Gamma)$



Need absorption asymmetric in $\cos\beta$

Photo-excitation rate: $I^{e}_{ph}(\Gamma) = f_0(\Gamma)\,\Upsilon(\Gamma)\,\mathcal{I}$

Absorption probability (non-symmetric in $\cos\beta$)

$$\Upsilon(\Gamma) = \frac{1}{\hbar\omega}\left[\frac{\sin^2\theta}{8}\sum_{q=\pm1}(1+q\cos\beta)^2\sigma(\omega_{0\,q}) + \frac{\cos^2\theta\sin^2\beta}{2}\,\sigma(\omega_{0\,0})\right]$$

$$\omega_{pq} \equiv \omega - p\dot{\psi} - q\dot{\phi}, \quad p,q = 0,\pm1$$

Collision integral

For simplicity: *dilute* recemic mixture in a buffer gas

Collisions mostly with buffer gas. Buffer gas in equilibrium.

$w^{a'a}(\Gamma';\Gamma)$ - scattering rate from state a,Γ to a',Γ'

Collision integral:

$$
\begin{aligned}
I^g\{\tilde{f}(\Gamma)\} &= \int w^{gg}(\Gamma;\Gamma')\tilde{f}^g(\Gamma')\,d\Gamma' - \tilde{f}^g(\Gamma)\int w^{gg}(\Gamma';\Gamma)\,d\Gamma' \\
&+ \int w^{ge}(\Gamma;\Gamma')\tilde{f}^e(\Gamma')d\Gamma', \\
I^e\{\tilde{f}(\Gamma)\} &= -\tilde{f}^e(\Gamma)\int w^{ge}(\Gamma';\Gamma)\,d\Gamma'.
\end{aligned}
$$

100% de-excitation upon collision

Boltzmann equation

$$\frac{1}{\tau^{ge}(\Gamma)} = \int w^{ge}(\Gamma';\Gamma)\, d\Gamma'.$$

$$\tilde{f}^{e}(\Gamma) = \tau^{ge}(\Gamma)\mathcal{I}\Upsilon(\Gamma) f_0^{g}(\Gamma)$$

$$\tilde{f}^{g}(\Gamma)\int d\Gamma' w^{gg}(\Gamma';\Gamma) - \int d\Gamma' w^{gg}(\Gamma;\Gamma')\tilde{f}^{g}(\Gamma') =$$

$$\mathcal{I}\left[-\Upsilon(\Gamma) f_0^{g}(\Gamma) + \int d\Gamma' w^{ge}(\Gamma;\Gamma')\tau^{ge}(\Gamma')\Upsilon(\Gamma') f_0^{g}(\Gamma')\right].$$

Order of magnitude estimate

Chiral drift velocity: $v_{ch} \sim v_T \tau_p \delta\chi \frac{dN_{ph}}{dt}$

τ_p – momentum relaxation time

$\frac{dN_{ph}}{dt}$ – photon absorption rate per molecule

Summary

- Novel mechanism of separation of enantiomers by circularly polarized light
- No transfer of linear or angular momentum from light to molecules
- Similar to the (experimentally observed) optical piston effect
- Analogous mechanism should exist in liquids
- Need for experiments