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: $\text{C}_5\text{H}_9\text{NO}_2$  Molecular Weight: 115.13

Enantiomers – distinct stable molecules

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

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

1) Conversion $\text{L} \rightarrow \text{R}$  2) Spatial separation
Chiral separation with light

Chiral current density: \( j_c = j_R - j_L \)

Inversion: \( R \leftrightarrow L \) \( \Rightarrow \) \( j_c \) - pseudovector

Time reversal: \( j_c \rightarrow -j_c \)

In an ac electric field: \( E \)

by symmetry: \( j_c \sim \langle E \times \dot{E} \rangle, \langle \ldots \rangle \) - time average

\[ E = \text{Re}\left[(\hat{x} + i\hat{y})e^{-i\omega t}\right] \]

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 $\tau$ on a particle

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
- $\eta$ – fluid viscosity
- $\chi$ – measure of chirality

angular momentum per photon is small: $\hbar$

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

Is chiral separation possible in the absence of torque?

Baranova, Zel’dovich
Chem. Phys. Lett. ’78
Chiral separation in gases

Molecules: mass - $m$, size - $d$

Light: frequency - $\omega$, 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

\[ \omega - \Omega = \omega_0 \]

\( \Omega \) — molecule angular velocity

Resonant absorption at ground state

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

Light absorption changes collision cross-section

Doppler shift: \( \nu_T/\lambda \ll \Omega \)

\[ f^e(\Omega) \]

\[ f^g(\Omega) \]

L-R collision

\[ \nu_d \]
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

\[ \delta p \sim \frac{M_T}{d} \delta \chi = p_T \delta \chi \]
\[ \delta \chi = \chi^e - \chi^g \]

Ratio:

\[ \frac{\delta \chi M_T}{\chi \hbar} \sim \frac{\delta \chi}{\chi} \sqrt{\frac{T m d^2}{\hbar^2}} \]

From photon torque

\[ \delta p \sim \chi \hbar / d \]
Similarity to optical piston effect

Resonantly absorbing atoms in a buffer gas

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

No momentum transfer from light to atoms

Experimental observation:
Werij, Heverkort, Woerdman,

Drift velocities: $v_d \sim 0.1 \text{cm/s}$

Gel'mukhanov, Shalagin
JETP 1980
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
\( \Gamma = \{p, M, \ldots\} \) – quantities conserved in free motion

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

Equilibrium distribution

\[ I^e_{ph}(\Gamma) = f_0(\Gamma) \gamma(\Gamma) \mathcal{I} \]
\[ I^g_{ph}(\Gamma) = -f_0(\Gamma) \gamma(\Gamma) \mathcal{I} \]

Photo-excitation (independent of chirality)

absorption probability  light intensity
Symmetry considerations

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

Optical excitations are independent of: \( \mathcal{R} \)

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

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

\[ \tilde{f}_r (p, M) = \tilde{f}_{-r} (p, M) \]

Then chiral current would vanish

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

\( j_c \) 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:

\[ \begin{align*} 
\text{• Dipole approximation} \\
\text{• Monochromatic light: } E &= \text{Re}[(\hat{x} + i\hat{y})e^{-i\omega t}] 
\end{align*} \]

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

Circular polarization along $\mathcal{Z}$
Angular momentum $\mathbf{M}$ along $\zeta$

$\beta$ – angle between $z$ and $\mathbf{M}$

$x', y', z'$ - body frame

Euler angles

Assume symmetric top molecule:

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

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

$$\omega_{pq} \equiv \omega - p\psi - q\phi,$$  \( p, q = 0, \pm 1 \)
Absorption probability $\Upsilon(\Gamma)$

Need absorption asymmetric in $\cos \beta$

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

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

\[
\Upsilon(\Gamma) = \frac{1}{\hbar \omega} \left[ \frac{\sin^2 \theta}{8} \sum_{q=\pm 1} (1 + q \cos \beta)^2 \sigma(\omega_{0q}) + \frac{\cos^2 \theta \sin^2 \beta}{2} \sigma(\omega_{00}) \right]
\]

$\omega_{pq} \equiv \omega - p\dot{\psi} - q\dot{\phi}, \quad p, q = 0, \pm 1$
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 \( a, \Gamma \) to \( a', \Gamma' \)

Collision integral:

\[
I^g \{ \tilde{f}(\Gamma) \} = \int w^{gg}(\Gamma; \Gamma') \tilde{f}^g(\Gamma') \, d\Gamma' - \tilde{f}^g(\Gamma) \int w^{gg}(\Gamma'; \Gamma) \, d\Gamma'
+ \int w^{ge}(\Gamma; \Gamma') \tilde{f}^e(\Gamma') \, d\Gamma',
\]

\[
I^e \{ \tilde{f}(\Gamma) \} = -\tilde{f}^e(\Gamma) \int w^{ge}(\Gamma'; \Gamma) \, d\Gamma'.
\]

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:

\[
\nu_{ch} \sim \nu_{T} \tau_{p} \delta \chi \frac{dN_{ph}}{dt}
\]

\(\tau_{p}\) – 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