Emergent chiroptical properties in supramolecular and plasmonic assemblies

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1. **Proof:** “Absorbance of unpolarized light equals the average absorbance of left- and right-handed circularly polarized light”

Transmittance $T$ is defined as the ratio between the intensity of the light transmitted by a sample, $I$, divided by the intensity of the incident light, $I_0$

$$ T = \frac{I}{I_0} \quad \text{......... (1)} $$

Similar expressions hold for the transmittance of left- and right-circularly polarized light:

$$ T_R = \frac{I_R}{I_0} \quad \text{and} \quad T_L = \frac{I_L}{I_0} $$

$$ I^0 = I^0_R + I^0_L \quad \text{......... (2)} $$

For non-polarized light,

$$ I^0_R = I^0_L \quad \text{and hence} \quad I^0 = 2I^0_R = 2I^0_L \quad \text{......... (3)} $$

$$ T = \frac{I_L + I_R}{I^0_R + I^0_L} \quad \text{......... (4)} $$

$$ T_L + T_R = \frac{I_L}{I^0} + \frac{I_R}{I^0} \quad \text{......... (5)} $$

Substituting equation (3),

$$ T_L + T_R = \frac{2I_L}{I^0} + \frac{2I_R}{I^0} = 2\left(\frac{I_L + I_R}{I^0}\right) = 2T $$

For very dilute solutions,

$T \approx 1$ or $T = 1 - x$, where $x$ is very small

According to the Taylor series,

$$ \ln(1-x) = -x - \frac{x^2}{2} - \frac{x^3}{3} - \frac{x^4}{4} - ... $$

Then,

$$ \ln(T) = \ln(1-x) \approx -x $$

$$ A = -\log_{10} T = -0.43\ln(1-x) $$

$$ \approx 0.43x = 0.43(1-T) $$

Therefore, $A$ is approximately proportional to $T$ in a very dilute solution.

Since $T_L + T_R = 2T$, we can consider $A_L + A_R = 2A$
2. Light-matter interaction: a primer (see ref. 1)

An electromagnetic wave propagating in vacuum can be described by the propagation of the vector potential:

\[ \vec{A}(\vec{r}, t) = \vec{\epsilon} \left[ A_0 e^{i(\vec{k} \cdot \vec{r} - \omega t)} + A_0^* e^{-i(\vec{k} \cdot \vec{r} - \omega t)} \right] \]  

Where \( \vec{r} = (x, y, z) \) is the vector that identifies each point in space, \( \vec{\epsilon} \) is a vector that defines the direction along which the vector potential oscillates, \( \omega \) is the wave frequency and \( \vec{k} \) is the wave-vector, a vector that defines the direction of propagation of the wave and whose modulus is \( 2\pi/\lambda \) (\( \lambda \) is the wavelength). The electric and magnetic fields can be obtained from the vector potential as follows:

\[ \vec{E} = -\frac{1}{c} \frac{\partial \vec{A}}{\partial t} \]  
\[ \vec{B} = \vec{\nabla} \times \vec{A} \]  

Actually, to define uniquely the fields from the potentials we must introduce an additional condition, called the Coulomb gauge:

\[ \vec{\nabla} \cdot \vec{A} = 0 \]  

The Coulomb gauge imposes that \( \vec{\epsilon} \) is orthogonal to \( \vec{k} \), and, since there are two independent directions perpendicular to \( \vec{k} \), there are two directions of polarization of a wave propagating along \( \vec{k} \).

The above equation describes a vector, \( \vec{A} \), that oscillates in space and time. Specifically, considering a wave that propagates along the z axis (\( \vec{k} \parallel z \)), \( \vec{A} \) oscillates either along x or y with amplitude \( A_0 \). The oscillation occurs in time with a frequency \( \omega \) and propagates along the z direction with a wavelength \( \lambda = 2\pi/|\vec{k}| \). The period, \( T = 2\pi/\omega \) is the time required to span a wavelength, so the velocity of propagation is \( \lambda/T \). In vacuum the light velocity \( (c) \) is constant and this gives a fundamental relation \( c = \omega/|\vec{k}| \).

Coming back to the electric and magnetic fields, the electric field is always parallel to \( \vec{A} \), oscillates in the same direction and with the same phase, with amplitude \( \omega A_0/c \). The magnetic field oscillates with the same amplitude and phase as the electric field, but is orthogonal to both the electric field and to \( \vec{k} \). Summarizing, a plane wave that propagates along z with x polarization describes an electric field that oscillates along x and a magnetic field that oscillates along y (the direction of polarization is conventionally fixed as the direction of the electric field).

The leading term of the light-matter interaction Hamiltonian is:
\[ H_{\text{int}} = -\sum_i \frac{e}{mc} \vec{A} \cdot \vec{p}_i \] (9)

where \(i\) runs on electrons, \(m\) and \(e\) are the electron mass and charge, respectively, and \(\vec{p}_i\) is the linear momentum of the electron.

If we are considering molecular systems excited by visible light, the wavelength is several orders of magnitude larger than the molecular dimensions, so that \(\vec{k} \cdot \vec{r} \ll 1\) and in Eq. 6 the exponentials can be truncated to

\[ e^{\pm i \vec{k} \cdot \vec{r}} \sim 1 \] (10)

In this approximation, the interaction between the radiation and the matter reduces to the interaction between the electric field of the electromagnetic wave and the molecular electric dipole moment. For this reason, the long wavelength approximation is also called the electric dipole approximation.

When the exponential in eqn 6 is expanded to the linear term:

\[ e^{\pm i \vec{k} \cdot \vec{r}} \sim 1 \pm i \vec{k} \cdot \vec{r} \] (11)

other terms appear in the light-matter interaction Hamiltonian accounting for the interaction between the magnetic field and the magnetic dipole moment as well as for quadrupolar terms. However, in molecular systems these interactions, proportional to \(\vec{k} \cdot \vec{r}\), are a few orders of magnitude smaller than the one related to the electric dipole.

3. Reference