Chiroptical Spectroscopy
Theory and Applications in Organic Chemistry

Lecture 3: (Crash course in) Theory of optical activity

Masters Level Class (181 041)
Mondays, 8.15-9.45 am, NC 02/99
Wednesdays, 10.15-11.45 am, NC 02/99
Crossed polarizers
Crossed polarizers and optically active sample

- Unpolarized light
- Transmission axis
- Optically active sample
- Rotates plane of polarization by $\theta$
Optical rotation: Difference of refractive indices

Linear polarized light can be expressed as superposition of left and right circular polarized light:

\[ E = E^+ + E^- \]

with

\[ E^+ = E_0 \cdot x \cdot \cos \varphi_+ + E_0 \cdot y \cdot \sin \varphi_+ \]
\[ E^- = E_0 \cdot x \cdot \cos \varphi_- - E_0 \cdot y \cdot \sin \varphi_- \]

respectively

\[ E^\pm = E_0 \cdot x \cdot \cos \varphi_\pm \pm E_0 \cdot y \cdot \sin \varphi_\pm \]

\(x, y\): unit vectors perpendicular to propagation direction
Optical rotation: Difference of refractive indices

\[ E = E^+ + E^- \quad \text{with} \]
\[ E^\pm = E_0 \cdot x \cdot \cos \varphi_\pm \pm E_0 \cdot y \cdot \sin \varphi_\pm \]

Taking into account that LCP and RCP light can have different velocities in a medium:

\[ \varphi_\pm = \omega t - \frac{2\pi z}{\lambda_\pm} \quad \lambda_\pm = \frac{v_\pm}{f} = \frac{c}{n_\pm f} \]

Because \( \omega = 2\pi f \), we can rewrite the equation:

\[ \varphi_\pm = \varphi \mp \frac{\omega t \Delta n}{2c} \quad \left\{ \begin{array}{l}
\varphi = \omega t - n\omega z/c \\
n = \frac{1}{2}(n_+ + n_-) \\
\Delta n = n_+ - n_-
\end{array} \right. \]
If medium is not circularly birefringent (optically active),
then $\Delta n=0$ and

$$E^{\pm} = E_0 \cdot x \cdot \cos \varphi \pm E_0 \cdot y \cdot \sin \varphi$$

Hence, the superposition is

$$E = E^+ + E^- = 2E_0 \cdot x \cdot \cos \varphi$$

… i.e. it still oscillates in the plane of the direction of
propagation and the unit vector $x$. 
Optical rotation: Difference of refractive indices

If the medium shows circular birefringence, we have

$$E^\pm = E_0 \cdot \mathbf{x} \cdot \cos \varphi_\pm \pm E_0 \cdot \mathbf{y} \cdot \sin \varphi_\pm$$

and the superposition becomes

$$E = E^+ + E^- = E_0 \cdot \left\{ \cos \varphi_+ \cos \varphi_- \mathbf{x} + (\sin \varphi_+ - \sin \varphi_-) \mathbf{y} \right\}$$

After some rearrangements, we get

$$E = 2E_0 \left\{ \mathbf{x} \cos \left( \frac{z \omega \Delta n}{2c} \right) - \mathbf{y} \sin \left( \frac{z \omega \Delta n}{2c} \right) \right\} \cos \varphi$$
The exiting ray is still linearly polarized, but its plane is now rotated by the angle $\theta$:

$$\theta = \frac{z \omega \Delta n}{2c}$$

Consequently, we have a *dextrorotatory* sample if $n_+ > n_-$ and a *levorotatory* sample if $n_- > n_+$. 

Details on the following equations can be found in Atkins, Friedman, Molecular Quantum Mechanics, 5th Edition, p. 417.
How does the refractive index depend on molecular properties?

From Maxwell equations, we find a relationship with the relative permittivity $\varepsilon_r$, aka the dielectric constant:

$$n = \left( \frac{\varepsilon}{\varepsilon_0} \right)^\frac{1}{2} = \varepsilon_r^\frac{1}{2}$$

Relative permittivity $\varepsilon_r$ directly relates to electric susceptibility $\chi_e$, which measures how easily a dielectric is polarized in response to an electric field:

$$\chi_e = \varepsilon_r - 1$$

Ok, then:

How does the dielectric constant depend on molecular properties?

For non-polar molecules in a static electric field, it can be shown that

$$\varepsilon_r = \frac{1 + 2\alpha N/(3\varepsilon_0)}{1 - \alpha N/(3\varepsilon_0)}$$

with $\alpha$ as polarizability

$$\alpha = \frac{2}{3} \sum_{n \neq 0} \frac{\hat{\mu}_0 \cdot \hat{\mu}_{n0}}{E_n - E_0}$$

and $N = N/V$.
How does the refractive index depend on a molecular properties?

From Maxwell equations, we find a relationship with the relative permittivity $\varepsilon_r$, aka the dielectric constant:

$$n = \left(\frac{\varepsilon}{\varepsilon_0}\right)^\frac{1}{2} = \varepsilon_r^\frac{1}{2} = \left(\frac{1 + 2\alpha N / (3\varepsilon_0)}{1 - \alpha N / (3\varepsilon_0)}\right)^\frac{1}{2} \approx 1 + \frac{N\alpha}{2\varepsilon_0}$$

But the polarizability is not chiral!?

We made a mistake when deriving $\varepsilon_r$ from the polarizability $\alpha$!

We assumed $P = \alpha NE$

This is fully correct if there is a constant electric field.
**Contribution of the magnetic field**

**Mistake:** We ignored the contribution of the magnetic field to the polarization!

Rewriting our definition of polarization as

\[ P = \alpha N E - \beta N \dot{B} \]

with \( \beta \) being another molecular characteristic and not to be mixed up with the hyperpolarizability!
The problem of static polarization

From this definition of the polarization \( \mathbf{P} \), we get after solving a few equations again

\[
n_{\pm} = 1 + \frac{N \alpha}{2 \varepsilon_0} \pm \frac{N \omega \beta}{2c \varepsilon_0}
\]

and thus the difference of the refractive indices becomes

\[
\Delta n = \frac{N \omega \beta}{c \varepsilon_0}
\]

For the optical rotation angle, it follows that after passing through a sample of length \( l \),

and taking into account that \( \varepsilon_0 \mu_v = c^2 \) with \( \mu_v \) being the vacuum permeability:

\[
\Delta \theta = \frac{z \omega \Delta n}{2c} = \frac{N l \omega^2 \beta}{2c^2 \varepsilon_0} = \frac{1}{2} N l \mu_v \omega^2 \beta
\]
Polarization and quantum mechanics

Polarization $\mathbf{P} = \text{dipole moment density}$

$P = \langle \mu \rangle \cdot \frac{N}{V} = \langle \mu \rangle \cdot N$

- Quantum mechanical calculation of the induced average dipole moment $\langle \mu \rangle$ should lead to expression for $\beta$!
**Schrödinger equation**

The time-independent Schrödinger equation

\[ \hat{H}\psi(\vec{r}) = E\psi(\vec{r}) \]

while the full wavefunction has the form

\[ \Psi(t, \vec{r}) = \psi(\vec{r}) \cdot e^{-iEt/\hbar} \]

It gives us access to observables by evaluating the observables' expectation value

\[ \langle \Omega \rangle = \int \Psi^* \hat{\Omega} \Psi \, d\tau = \langle \Psi | \hat{\Omega} | \Psi \rangle \]
The basic idea of perturbation theory

In perturbation theory, we define a (time-dependent) perturbation in the Hamilton operator:

$$\hat{H}(t) = \hat{H}^0 + \hat{H}^1(t)$$

In presence of a perturbation, the wavefunction is a linear combination of states:

$$\Psi(t) = \psi_0^0 \cdot e^{\left(\frac{-iE_0 t}{\hbar}\right)} + \sum_{n \neq 0} a_n(t) \cdot \psi_n^0 \cdot e^{\left(\frac{-iE_n t}{\hbar}\right)}$$

For $a_n(t)$ it can be shown that

$$a_n(t) = \frac{1}{i\hbar} \int_0^t \hat{H}^1_{n0}(t) \cdot e^{i\omega_{n0} t} dt$$

with $\hbar \omega_{n0} = E_n - E_0$
Evaluating $\langle \mu \rangle$

The expectation value for the average dipole moment (its z-component) is

$$\langle \mu_z \rangle = \langle \Psi | \widehat{\mu}_z | \Psi \rangle$$

Taking into account that $\Psi$ is a perturbed wavefunction with ground state $|0\rangle$ and perturbed states $|n\rangle$, we get

$$\langle \mu_z \rangle = \langle 0 | \widehat{\mu}_z | 0 \rangle + \sum_{n \neq 0} \left\{ \langle 0 | \widehat{\mu}_z | n \rangle \cdot a_n(t) \cdot e^{-i\omega_n t} + \langle n | \widehat{\mu}_z | 0 \rangle \cdot a_n^*(t) \cdot e^{i\omega_n t} \right\}$$

$$= \mu_{0z} + \sum_{n \neq 0} \left\{ \mu_{z,0n} a_n(t) \cdot e^{-i\omega_n t} + \mu_{z,n0} \cdot a_n^*(t) \cdot e^{i\omega_n t} \right\}$$
Perturbation theory: Magnetically induced polarization

In our case, the perturbation to the Hamiltonian is

$$H^1(t) = -\hat{\mu} \cdot \dot{E} - \hat{m} \cdot \dot{B}$$

with

$\hat{\mu}$: electric dipole moment operator
$\hat{m} = \gamma_e \hat{\ell} = \gamma_e (r \times \hat{p})$: magnetic dipole moment operator
$E$: electric field
$B$: magnetic field

More precisely, we also need to take into account the circular polarization states of the electric and magnetic field:

$$H^\perp_{\pm}(t) = -\hat{\mu} \cdot \dot{E}^\pm - \hat{m} \cdot \dot{B}^\pm$$

with

$$E^\pm(t) = E(x \cdot \cos \omega t \pm y \cdot \sin \omega t) \quad \text{and} \quad B^\pm(t) = B(\pm x \cdot \cos \omega t - y \cdot \sin \omega t)$$
Perturbation theory: Magnetically induced polarization

\[ E^{\pm}(t) = E(x \cdot \cos \omega t \pm y \cdot \sin \omega t) \]
\[ B^{\pm}(t) = B(\pm x \cdot \cos \omega t - y \cdot \sin \omega t) \]

\[ H^{1}_{\pm}(t) = -\mu \cdot E^{\pm} - \hat{m} \cdot B^{\pm} \]
\[ = -\mu \cdot E(x \cdot \cos \omega t \pm y \cdot \sin \omega t) - \hat{m} \cdot B(\pm x \cdot \cos \omega t - y \cdot \sin \omega t) \]

As \( \mu_x = \hat{\mu} \cdot x \) and \( m_x = \hat{m} \cdot x \)

\[ = -E(\mu_x \cdot \cos \omega t \pm \mu_y \sin \omega t) - B(\pm m_x \cos \omega t - m_y \sin \omega t) \]

\[ \cos \alpha = \frac{1}{2} (e^{i\alpha} + e^{-i\alpha}) \]
\[ \sin \alpha = -\frac{i}{2} (e^{i\alpha} - e^{-i\alpha}) \]

\[ = -\frac{1}{2} E(\mu_x \cdot (e^{i\omega t} + e^{-i\omega t}) \mp i\mu_y (e^{i\omega t} - e^{-i\omega t})) \]

\[ -\frac{1}{2} B(\mp m_x \cdot (e^{i\omega t} + e^{-i\omega t}) - m_y (e^{i\omega t} - e^{-i\omega t})) \]
Perturbation theory: Magnetically induced polarization

Based on this perturbation Hamiltonian, the coefficients of the perturbed wavefunctions can be determined:

\[ a_n(t) = \frac{1}{i \hbar} \int_0^t \hat{H}_{\pm, n_0}^1(t) \cdot e^{i \omega n_0 t} \, dt \]

with

\[ \hat{H}_{\pm, n_0}^1(t) = -\frac{1}{2} E \left( \mu_x \cdot (e^{i \omega t} + e^{-i \omega t}) \mp i \mu_y (e^{i \omega t} - e^{-i \omega t}) \right) \\
- \frac{1}{2} B \left( \mp m_x \cdot (e^{i \omega t} + e^{-i \omega t}) - m_y (e^{i \omega t} - e^{-i \omega t}) \right) \]

Then, the induced electric dipole moment is the expectation value of the operator using the perturbed wavefunctions:

\[ \langle \mu \pm \rangle = \langle \Psi^* | \hat{\mu} \pm | \Psi \rangle = \mu_0 + \sum_{n \neq 0} \mu_{0n} \cdot a_n^\pm (t) \cdot e^{-i \omega n_0 t} + \mu_{n0} \cdot a_n^{\pm*} (t) \cdot e^{i \omega n_0 t} \]
Perturbation theory: Magnetically induced polarization

Solving the equation for the expectation value

\[ \langle \mu^\pm \rangle = \langle \Psi^* | \mu^\pm | \Psi \rangle = \mu_0 + \sum_{n \neq 0} \mu_{0n} \cdot a_n^\pm (t) \cdot e^{-i\omega_{n0}t} + \mu_{n0} \cdot a_n^{\pm*} (t) \cdot e^{i\omega_{n0}t} \]

leads to the final expression

\[ \langle \mu^\pm \rangle = \frac{2}{\hbar} \text{Re} \left\{ \sum_{n \neq 0} \left( \frac{\omega_{n0}}{\omega_{n0}^2 - \omega^2} \right) \cdot \mu_{0n} \cdot \mu_{n0} \cdot E^\pm (t) \right\} - \frac{2}{\hbar} \text{Im} \left\{ \sum_{n \neq 0} \left( \frac{\omega_{n0}}{\omega_{n0}^2 - \omega^2} \right) \cdot \mu_{0n} \cdot m_{n0} \cdot B^\pm (t) \right\} \]

Comparison with the definition of polarization in an electromagnetic field

\[ \mathbf{P} = \alpha \mathcal{N} \mathbf{E} - \beta \mathcal{N} \mathbf{B} \]

shows that

\[ \beta = \frac{2}{\hbar} \text{Im} \sum_{n \neq 0} \frac{\mu_{0n} \cdot m_{n0}}{\omega_{n0}^2 - \omega^2} \]
The rotational strength

Taking the rotational average \((\beta_{xx}, \beta_{yy}, \beta_{zz})\)

\[
\beta = \frac{2}{3\hbar} \text{Im} \sum_{n \neq 0} \frac{\mu_{0n} \cdot m_{n0}}{\omega_{n0}^2 - \omega^2}
\]

we get

The Rosenfeld equation

\[
\Delta \theta = \frac{N_{\nu} \mu_{\nu}}{3\hbar} \sum_{n \neq 0} \frac{\omega^2 R_{n0}}{\omega_{n0}^2 - \omega^2}
\]

rotational strength of transition \(n \leftrightarrow 0\)

\[
R_{n0} = \text{Im}\{\mu_{0n} \cdot m_{n0}\}
\]

\(\mu\): electric dipole transition moment (EDTM)
\(m\): magnetic dipole transition moment (MDTM)
Symmetry properties of the rotational strength

With respect to reflection:
- EDTM transforms as translation
- MDTM transforms as rotation

Requirement:
Sign of R must be conserved upon action of any symmetry element of the molecule

If a molecule has a mirror plane, reflection changes sign of EDTM but not of MDTM.

Consequence: Rotational strength changes sign $\rightarrow R = 0$
Optical rotatory dispersion (ORD)

The Rosenfeld equation

\[ \Delta \theta = \frac{N \mu_v}{3\hbar} \sum_{n \neq 0} \frac{\omega_n^2 R_{n0}}{\omega_n^2 - \omega^2} \]

where

\[ \omega_n = \frac{(E_n - E_0)}{\hbar} \]

At very high frequencies (\( \omega^2 \gg \omega_{n0}^2 \)) and in the opposite case of \( \omega^2 \ll \omega_{n0}^2 \), the rotational angle is \( \Delta \theta = 0 \) due to the sum rule \( \sum_n (R_{n0}) = 0 \).

OR is close to zero far away from absorption bands, but becomes very large when approaching them: \( \omega_{n0}^2 - \omega^2 \rightarrow 0 \)
Optical rotatory dispersion (ORD)

When $\omega_{n0}^2 - \omega^2 \to 0$, i.e. if the excitation frequency is close to an absorption band, the contribution of that particular transition dominates the OR value:

$$\Delta \theta = \frac{N l \mu \omega^2 R_{10}}{3h(\omega_{10}^2 - \omega^2)}$$

- Observation of Cotton effect

„Normal“ ORD curve:

- First resonances in the UV range
- Appears monosignate in usual range of measurement
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