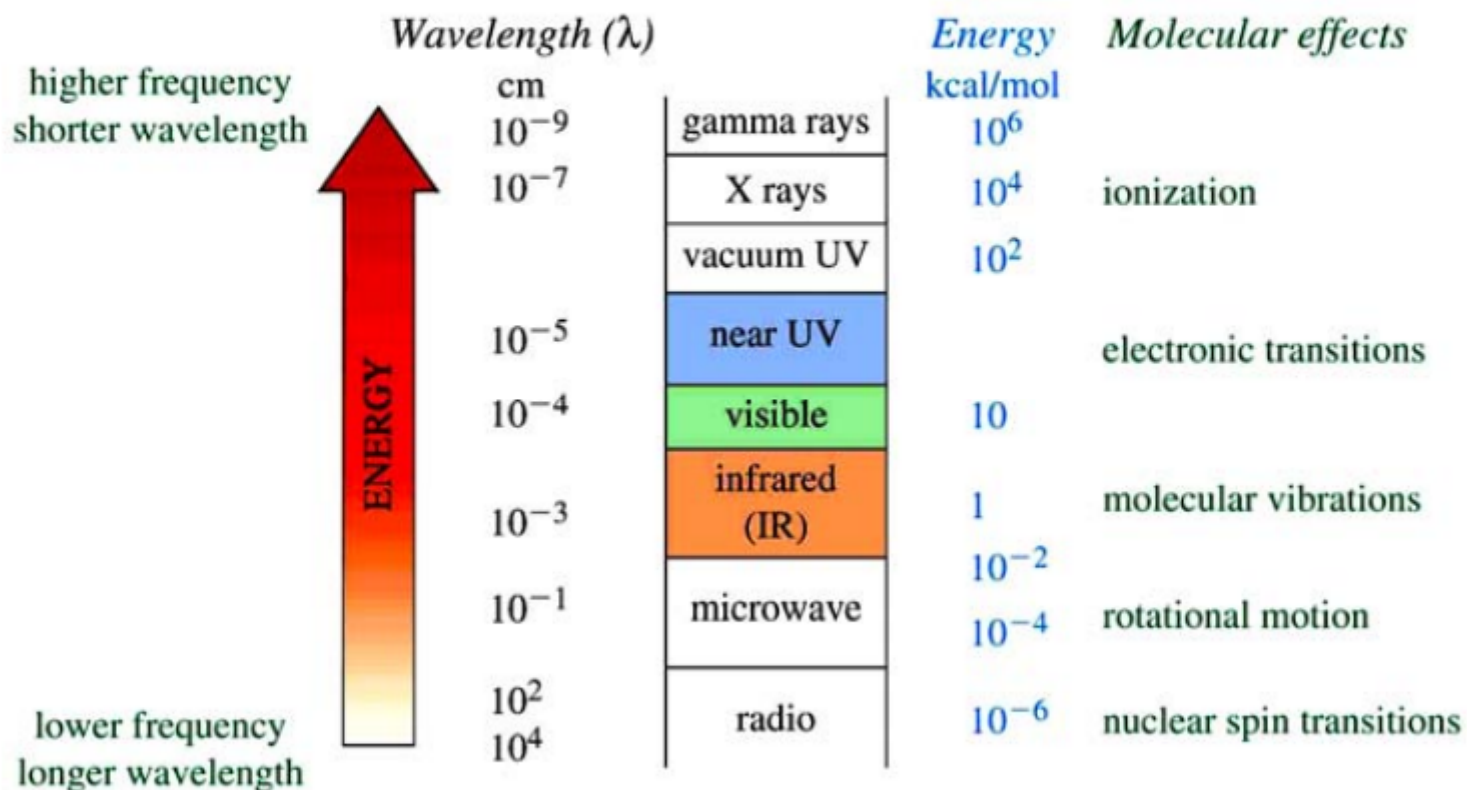


UV-Vis, CD, ORD

Dariusz Witt

EFFECT OF ELECTROMAGNETIC RADIATION ON MOLECULES



Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 5th ed. Pearson Education Inc., 2003

Electronic Spectroscopy

- Ultraviolet (UV) and visible (vis) spectroscopy:
- This is the earliest method of molecular spectroscopy.
- A phenomenon of interaction of molecules with UV and visible lights.
- Absorption of photon results in electronic transition of a molecule, and electrons are promoted from ground state to higher electronic states.

UV and Visible Spectroscopy

- In structure determination : UV-vis spectroscopy is used to detect the presence of chromophores like dienes, aromatics, polyenes, and conjugated ketones, etc.
- Also very useful in quantitative analysis of compounds with chromophores.
- Chiroptical spectroscopy-ORD and CD : the *difference* in the refraction (ORD) or absorption (CD) of left and right circularly polarized light is measured, or absorptivity (CD) between left and right circularly polarized light .

Chiroptical Spectroscopy

- Chiroptical properties reflect stereochemical arrangement of atom in a molecule. Both CD and ORD show sense of handedness in reflecting the handedness of nonsuperimposable mirror-image molecule (enantiomer). So their curves appear as positive or negative peaks of Cotton effects reflecting the difference in chirality of molecule.

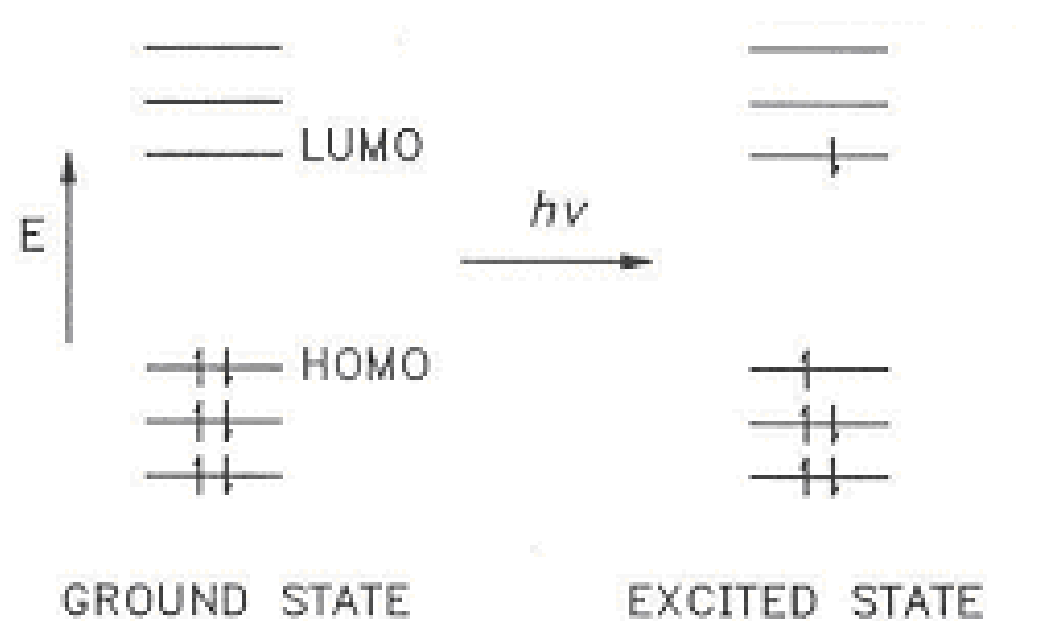
Display of spectra

- Horizontal scale (abscissa): all three methods use wavelength, λ , in nm (nanometer) unit.
- Vertical scale (ordinate):
- UV-vis: absorbance, A , or molar absorptivity, ϵ .
- CD: difference in molar absorptivity, $\Delta \epsilon$, or molar ellipticity, $[\theta]$.
- ORD: molar rotation, $[\varphi]$.

Origin of electronic spectra

- Absorptions of UV-vis light photons by molecule results in electronic excitation of molecule with chromophore.
- The electronic transition involves promotion of electron from a electronic ground state to higher energy state, usually from a molecular orbital called HOMO to LUMO.

UV Spectral Origin

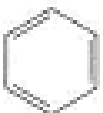



Transition of an electron from HOMO to LUMO
by light photon

UV Absorptions for some isolate chromophores

TABLE 10-1

Electronic Absorption Data for Isolate Chromophores*

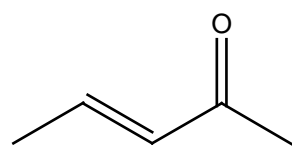
Chromophore	Example	Solvent	λ_{max} (nm) [†]	ϵ (liter mol ⁻¹ cm ⁻¹)
C=C	1-Hexene	Heptane	180	12,500
—C≡C—	1-Butyne	Vapor	172	4,500
	Benzene	Water	254	205
	Toluene	Water	203.5	7,400
			261	225
			206.5	7,000
C=O	Acetaldehyde	Vapor	298	12.5
	Acetone	Cyclohexane	182	10,000
			275	22
	Camphor	Hexane	190	1,000
—COOH	Acetic acid	Hexane	295	14
—COCl	Acetyl chloride	Ethanol	204	41
—COOR	Ethyl acetate	Heptane	240	34
—CONH ₂	Acetamide	Water	204	60
—NO ₂	Nitromethane	Methanol	205	160
		Hexane	279	15.8
$\overset{+}{\text{N}}=\overset{-}{\text{N}}$	Diazomethane		202	4,400
—N=N—	<i>trans</i> -Azomethane	Diethyl ether	417	7
		Water	343	25
	C ₂ H ₅ CH—NC ₄ H ₉	Isooctane	238	200

* From J.B. Lambert, H.F. Shurvell, L. Verbit, R.G. Cooks, and G.H. Stout, *Organic Structural Analysis*, Macmillan Publishing, New York, 1976.

† Chromophores often have more than one absorption band.

Solvents used in UV-Vis measurement

solvent	$\lambda_{\text{cut-off}}$ (nm)
Water	205
Acetonitrile	210
Cyclohexane	210
Diethyl ether	210
Ethanol	210
Hexane	210
Methanol	210
Dioxane	220
THF	220
Dichloromethane	235
Chloroform	245
Carbon tetrachloride	265
Benzene	280
Acetone	300



methanol



Hypsochromic shift

heptane

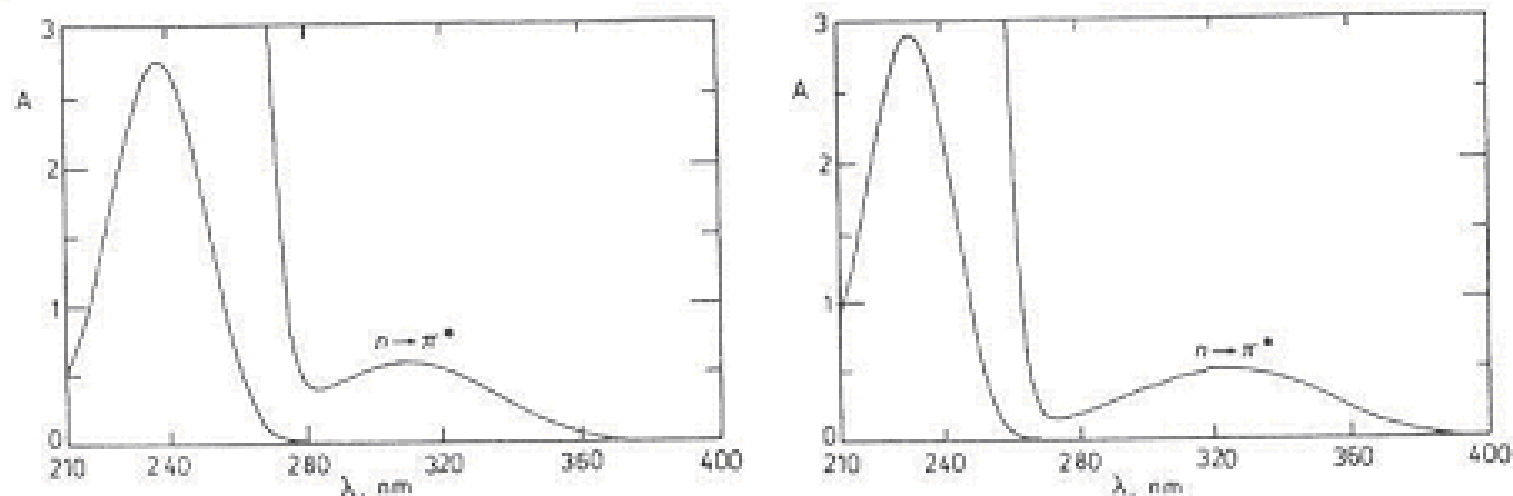


Figure 10-6 UV-vis absorption spectra of 4-methyl-3-penten-2-one (mesityl oxide) in (left) methanol and (right) heptane. Spectra in methanol were run in a 1 cm cuvette at 0.0105 M and 2.63×10^{-4} M concentrations. Spectra in heptane were run at 0.014 M and 2.8×10^{-4} M concentrations. The vertical axis is in absorbance units. The ~320 nm absorption is the $n \rightarrow \pi^*$ transition, the ~240 nm is mainly $\pi \rightarrow \pi^*$. (Spectra run by Portia Mahal Sabido.)

Terms describing UV absorptions

- 1. **Chromophores**: functional groups that give electronic transitions.
- 2. **Auxochromes**: substituents with unshared pair e's like OH, NH, SH ..., when attached to π chromophore they generally move the absorption max. to longer λ .
- 3. **Bathochromic shift**: shift to longer λ , also called red shift.
- 4. **Hysochromic shift**: shift to shorter λ , also called blue shift.
- 5. **Hyperchromism**: increase in ϵ of a band.
- 6. **Hypochromism**: decrease in ϵ of a band.

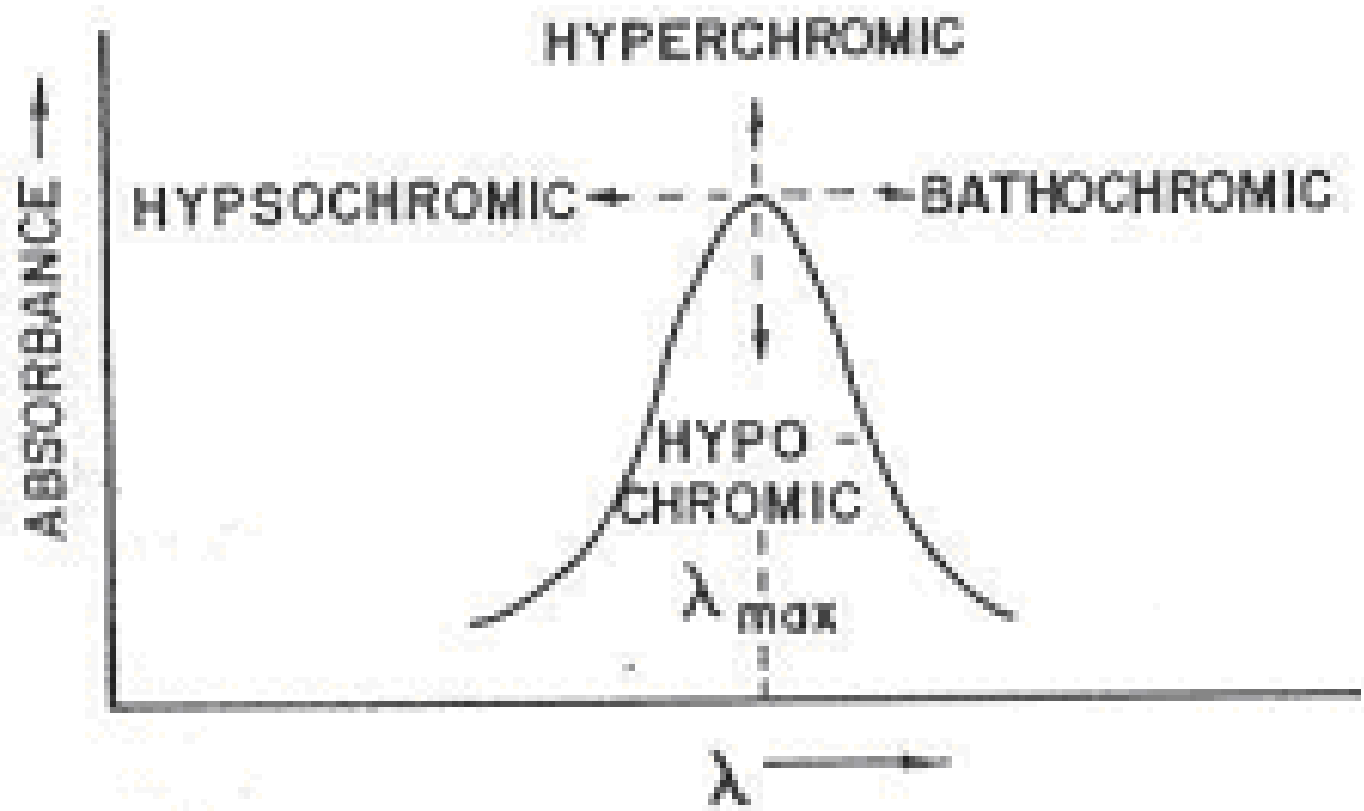
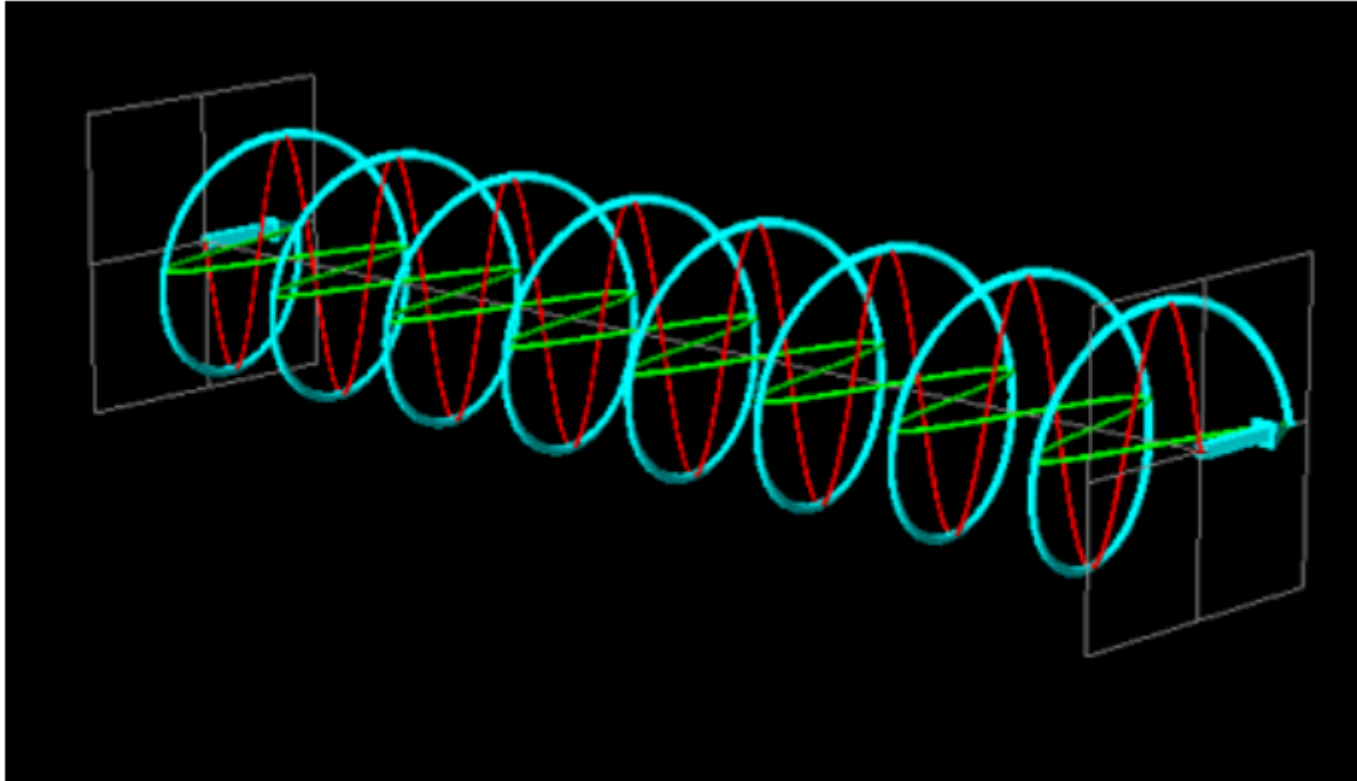


Figure 11-3 Terminology of shifts in the position of an absorption band.

Circular Dichroism - CD

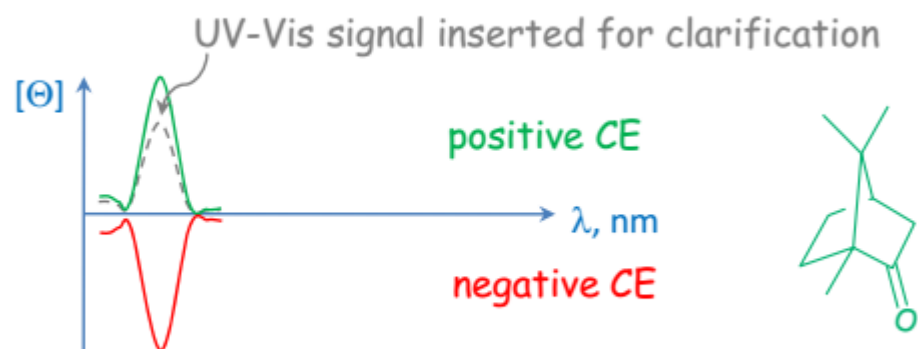
Circular dichroism (CD) is the difference in the absorption of left-handed circularly polarised light (L-CPL) and right-handed circularly polarised light (R-CPL) and occurs when a molecule contains one or more chiral chromophores (light-absorbing groups).

Circular dichroism = $\Delta A(\lambda) = A(\lambda)_{\text{LCPL}} - A(\lambda)_{\text{RCPL}}$, where λ is the wavelength

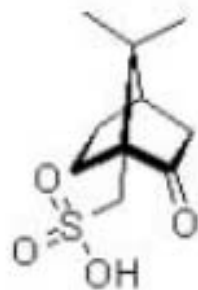
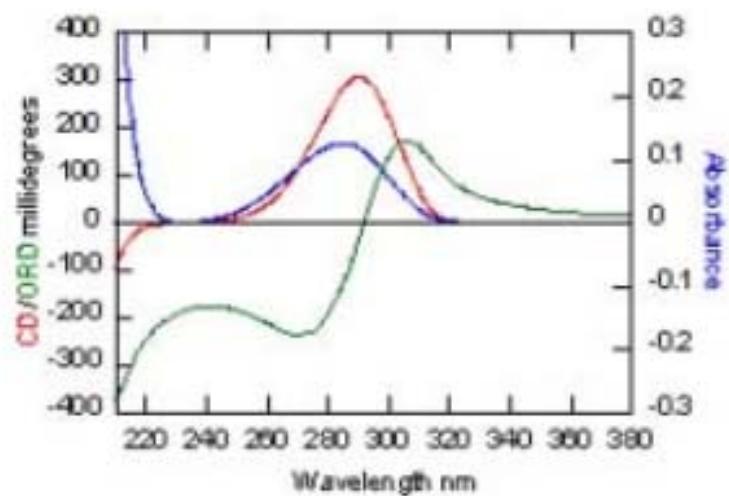


Left Circularly Polarised (LCP) Light

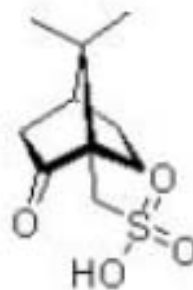
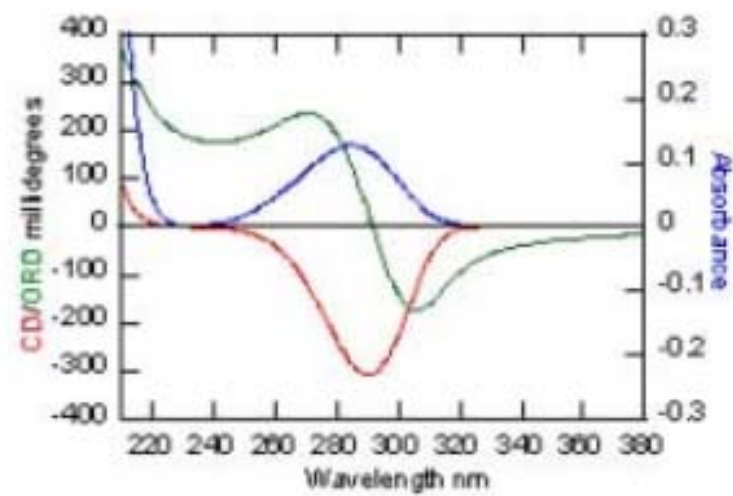
- CD spectrum (for an absorbing compound)



- "Cotton-effect (CE) curve"

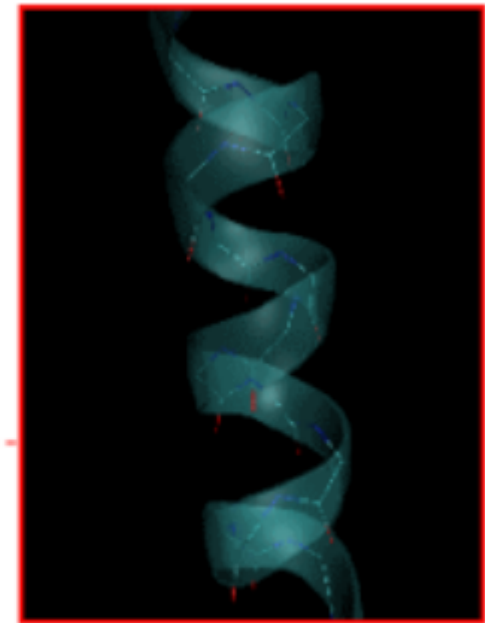
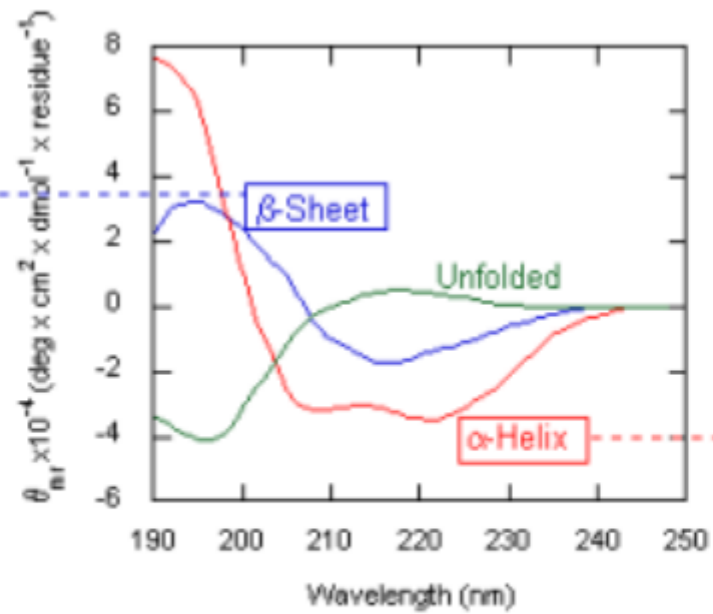
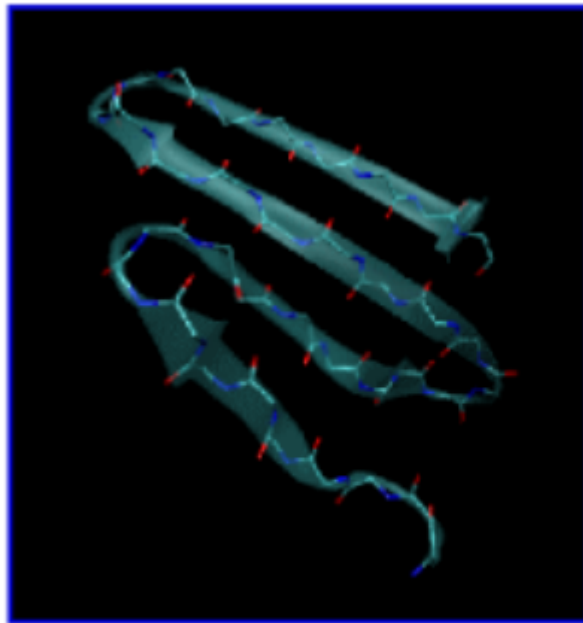


(1S)-(+)-Camphor-10-sulphonic acid



(1R)-(-)-Camphor-10-sulphonic acid

CD, ORD and Absorbance spectra of R and S forms of camphor sulphonic acid

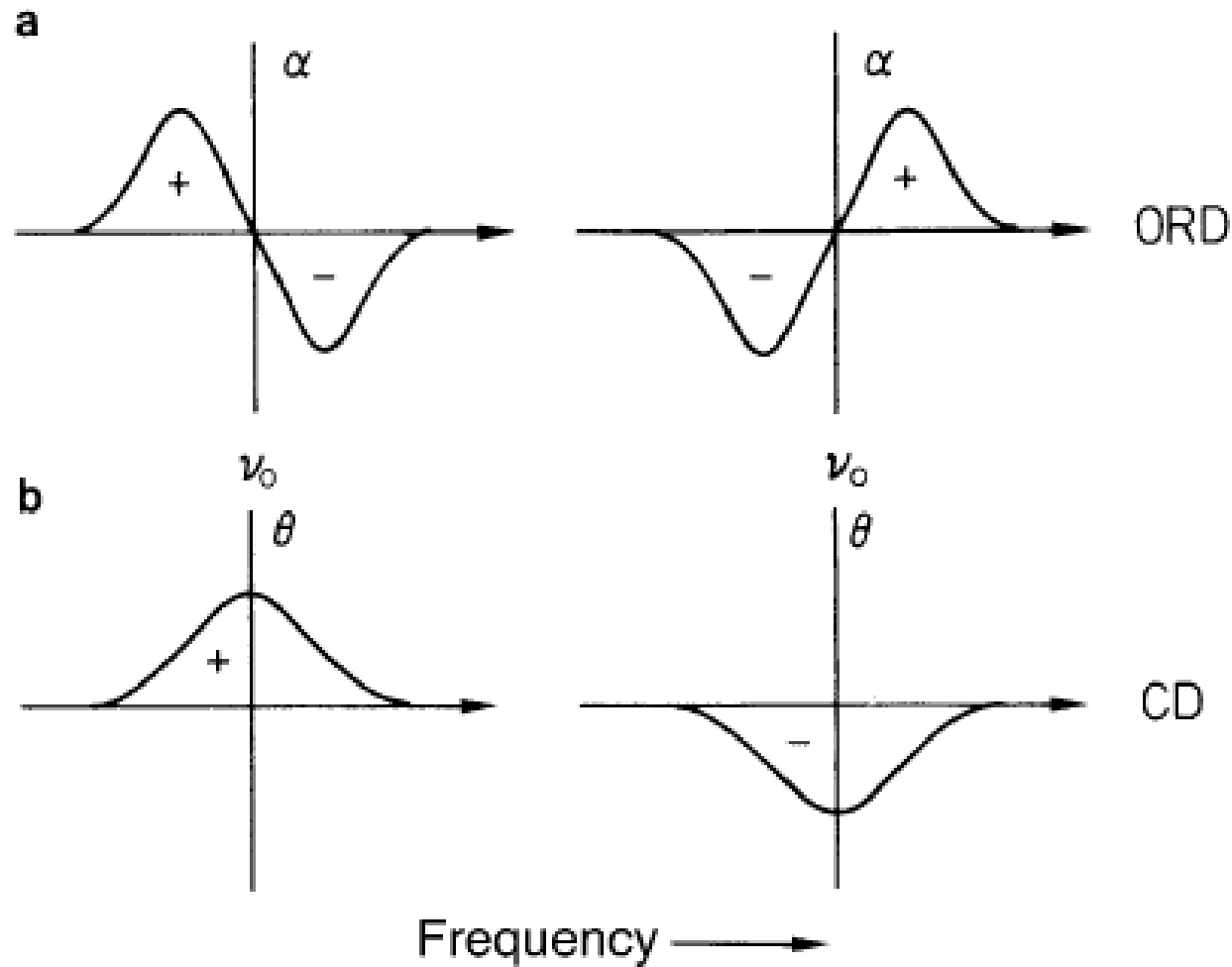


The secondary structure conformation and the CD spectra of protein structural elements. Right is an example of the backbone conformation of a peptide in an α -helix and left is the conformation of a peptide in a β -sheet. In the centre are the associated CD spectra for these different conformations.

ORD and CD

Optical Rotatory Dispersion ORD
involves measurement of a rotation,
whereas **Circular Dichroism CD**
involves measurement of an absorption

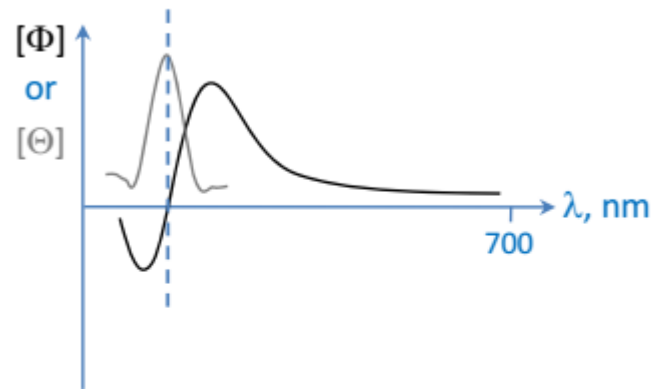
ORD (optical rotatory dispersion)



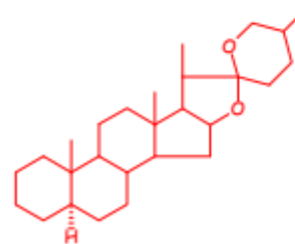
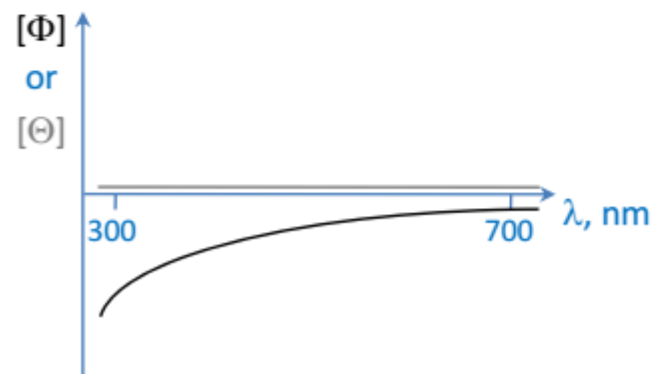
ORD spectra are dispersive (called a *Cotton effect* for a single band) whereas circular dichroism spectra are absorptive. The two phenomena are related by the so-called König-Kramers transforms.

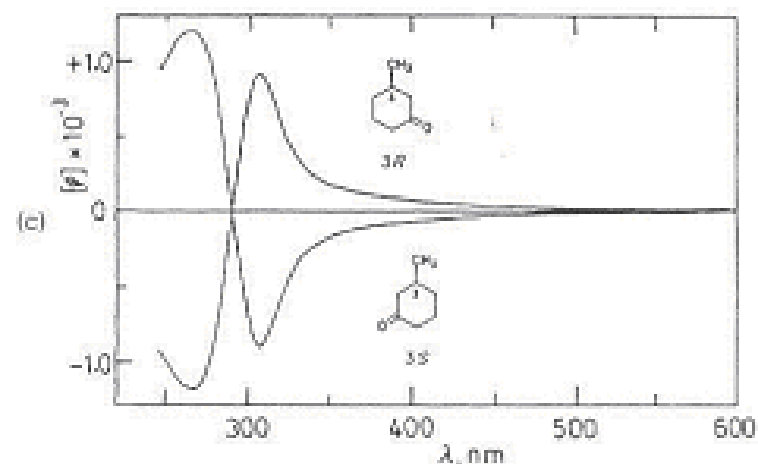
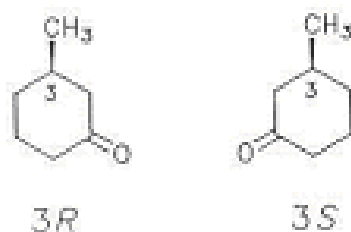
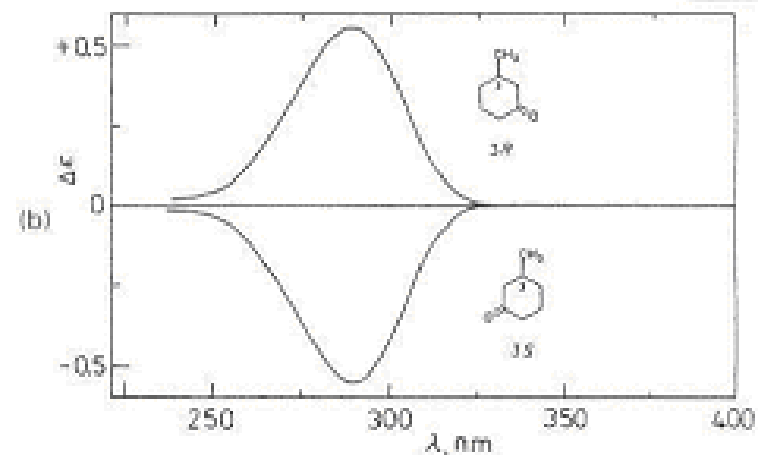
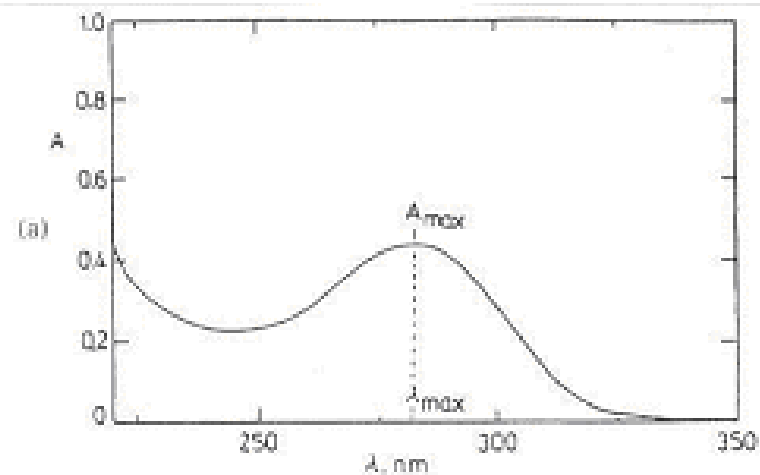
- CD maximum coincides with ORD cross-over

superposition of both spectra (not normally done):



- there might not be a CD spectrum, but there will always be an ORD!





UV: A vs. λ (nm), the same curve for $3R$ -, $3S$ -isomer, and racemate.

CD: $\Delta \epsilon$ vs. λ , + Cotton effect for $3R$ -isomer, and - Cotton effect for $3S$ -isomer.

ORD: $[\varphi]$ (molar rotation) vs. λ , + C. E. for $3R$ -isomer and - C. E. for $3S$ -isomer.

Relative configuration

B. Through chiroptical methods

- **qualitative:** optical activity

(refraction phenomenon, circularly polarized light...)

gives α , which gives $[\alpha]$

- **quantitative**

I. ORD (optical rotatory dispersion)

- measures the **specific rotation** as a function of the wavelength

- in the UV-Vis region, 200-800 nm



- instead of the specific rotation $[\alpha]$, often the molrotation $[\Phi]$ is used

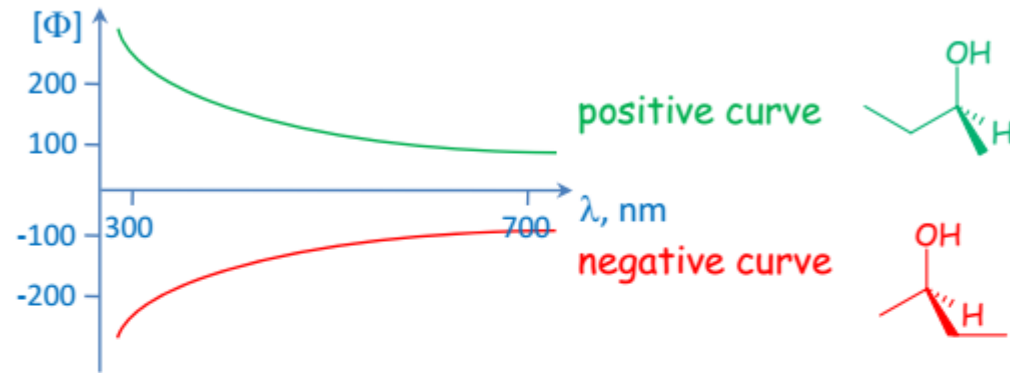
$$[\Phi]_{\lambda}^T = \frac{M}{100} [\alpha]_{\lambda}^T \quad M: \text{molar mass}$$

Molrotation: rotation on a "per mole" basis,
for the comparison of $[\alpha]$ for different compounds.

Relative configuration

- ORD spectrum for a transparent compound

(compound does not absorb in that spectral region)



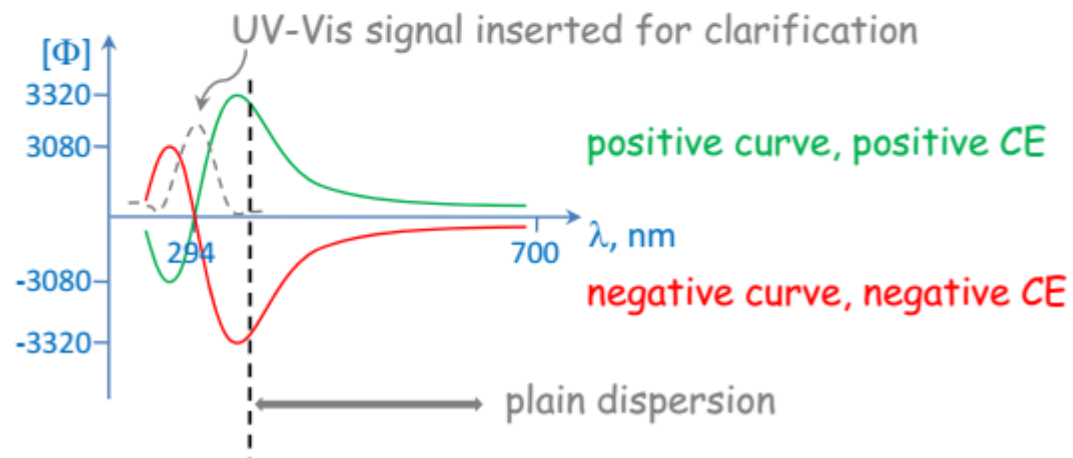
- "plain (dispersion) curve"

- monotonic change

- +: rises towards shorter λ

- -: falls towards shorter λ

- ORD spectrum for an absorbing compound



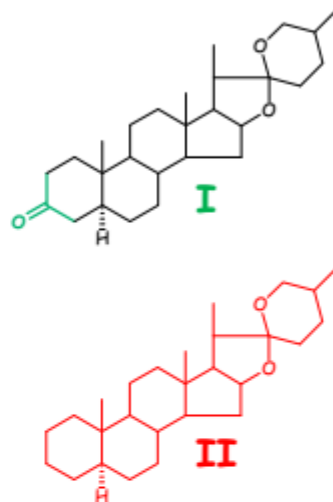
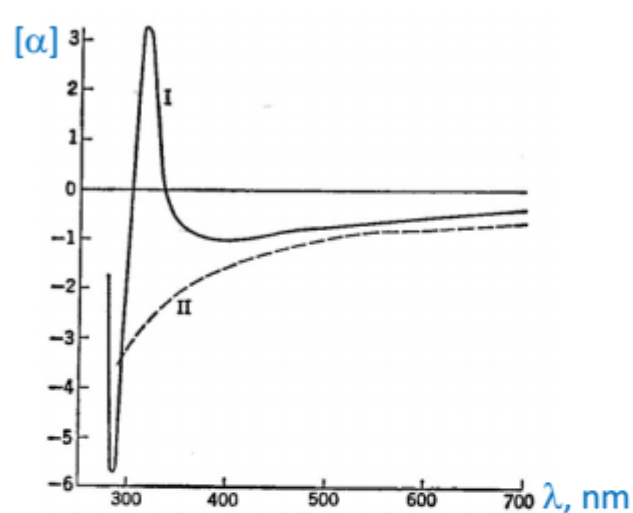
- "Cotton-effect (CE) curve"

- anomalous change

- cross-over point

Relative configuration

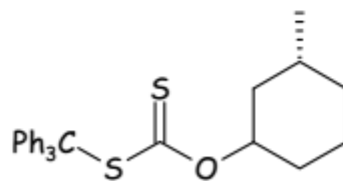
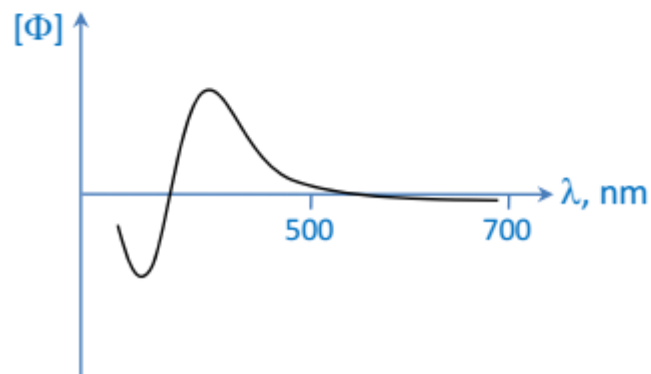
- two more issues on ORD spectra
- negative plain dispersion + positive CE



skeleton of II causes the negative "background curve"

Djerassi, Optical rotatory dispersion, McGraw-Hill, NY, 1960

- importance of second cross-over point



cross-over close to the Na D-line

The octant rule

The octant rule states that substituents lying in the nodal planes make no contributions to $n \rightarrow \pi^*$ Cotton effect. Substituents within an octant contribute the sign of that octant to the overall sign of the Cotton effect. Since most substituents are usually on the same side of the nodal surface as the carbonyl carbon, the octant diagram is simplified by considering only the four rear octants. Relative intensities are determined qualitatively. For example, when both negative rear octants are occupied, the magnitude of the Cotton effect is enhanced.

The octant rule

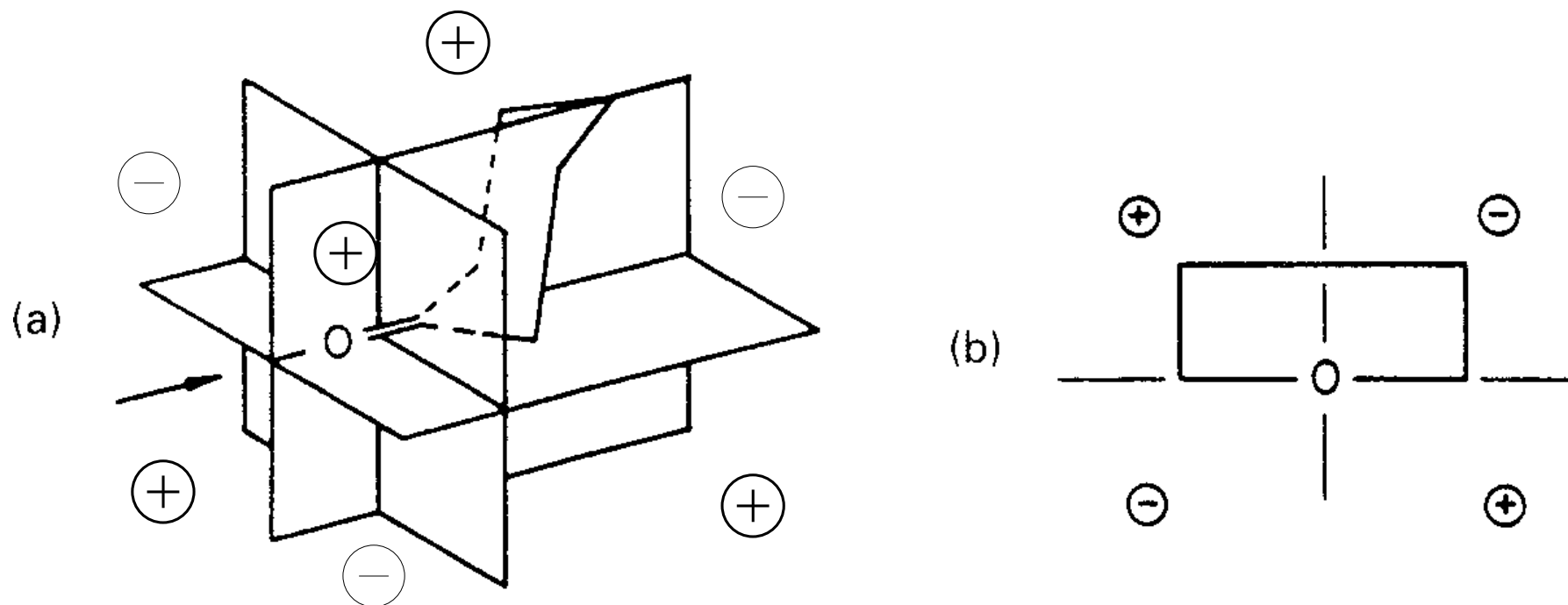


Figure 12-2 (a) Octants for saturated cyclohexanones. (b) Signs of the four rear octants viewed along the carbonyl bond axis from oxygen to carbon. (The front octants have opposite signs.)

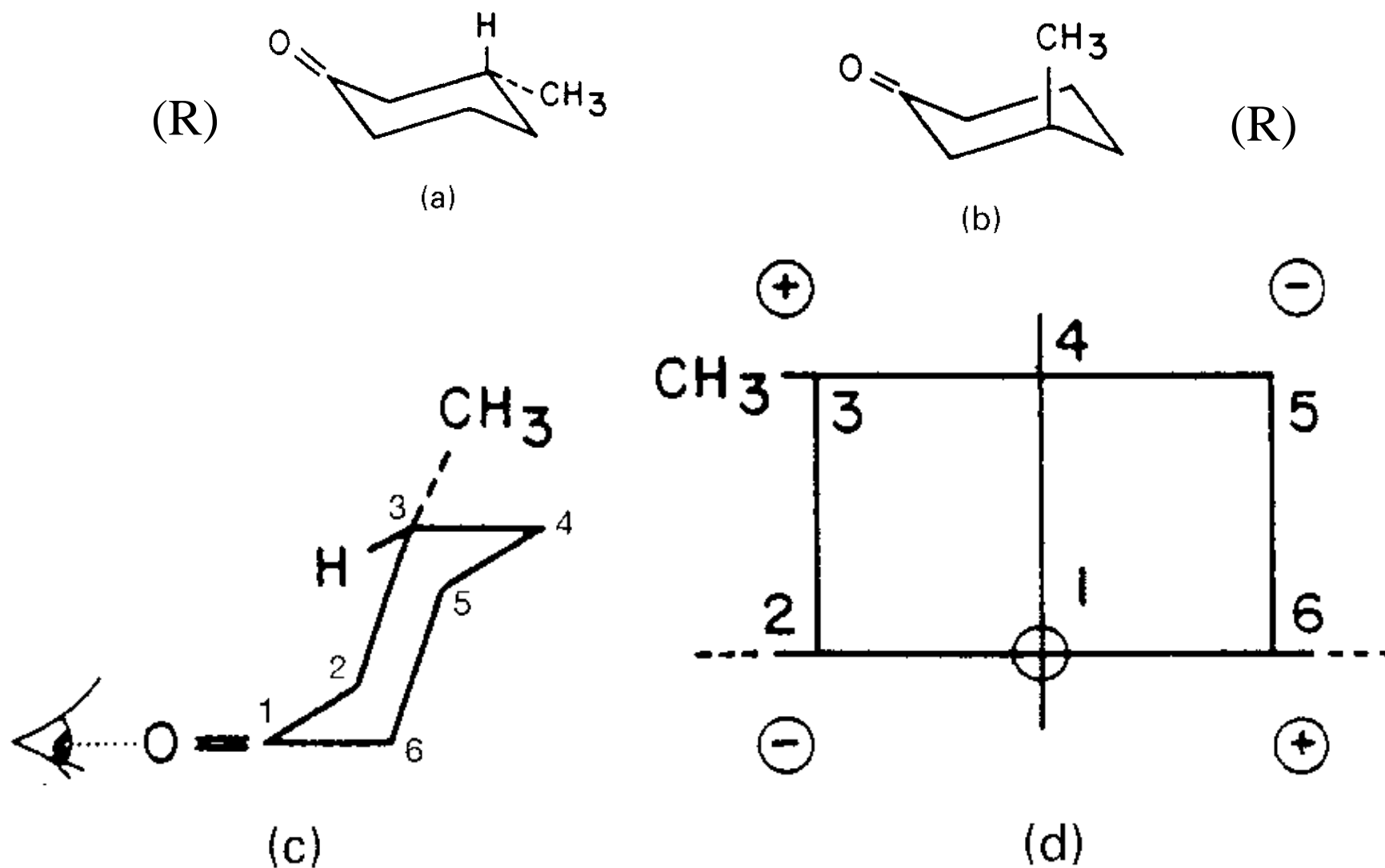
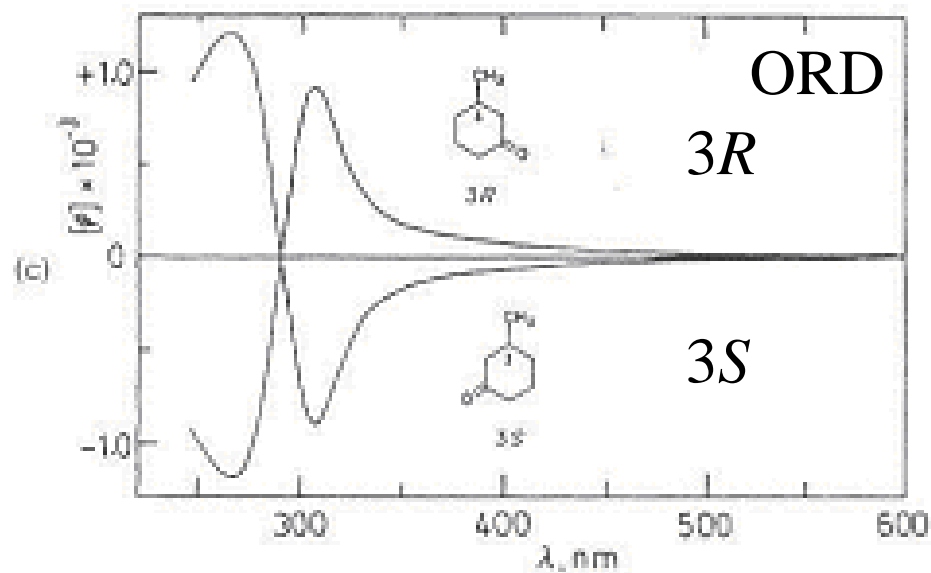
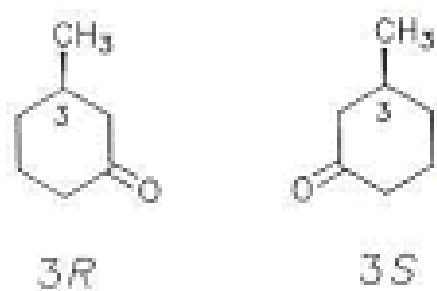
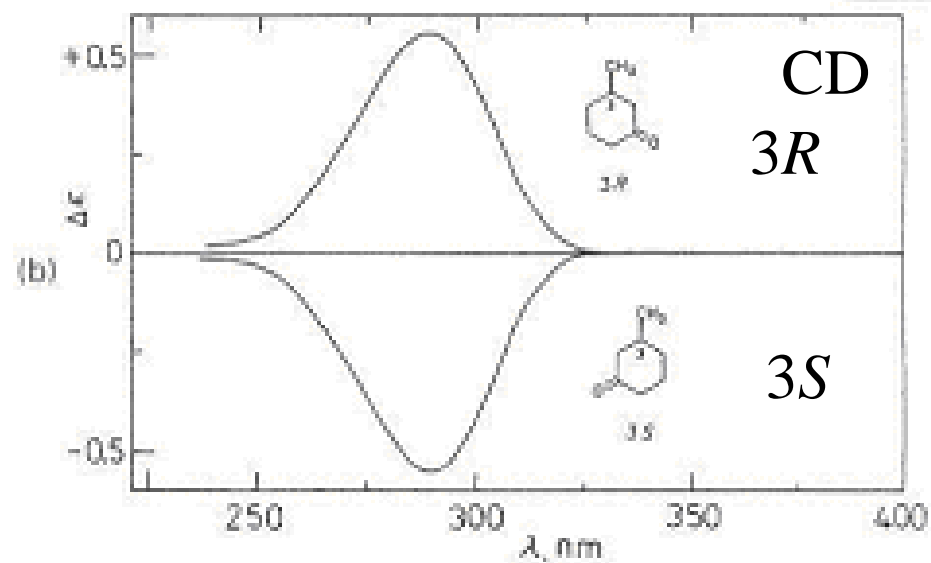
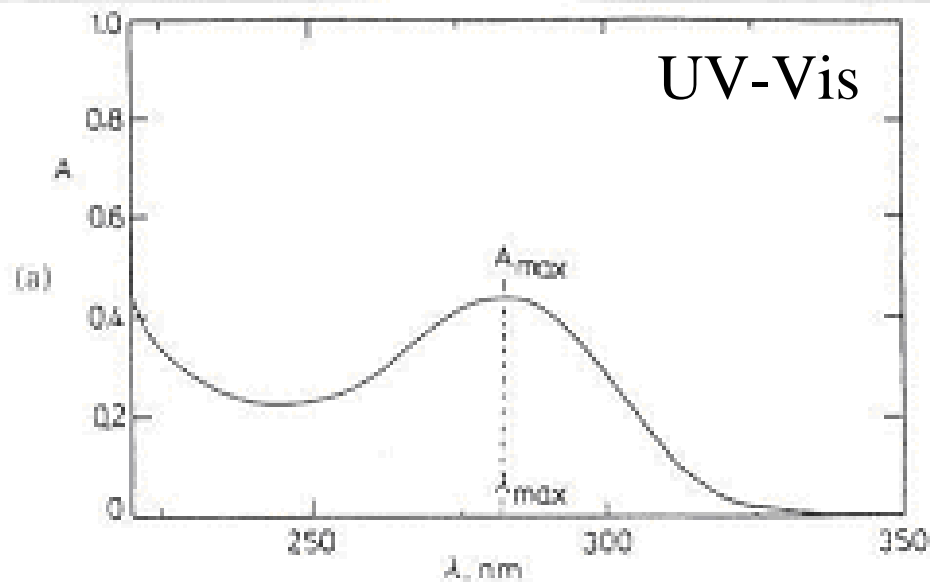


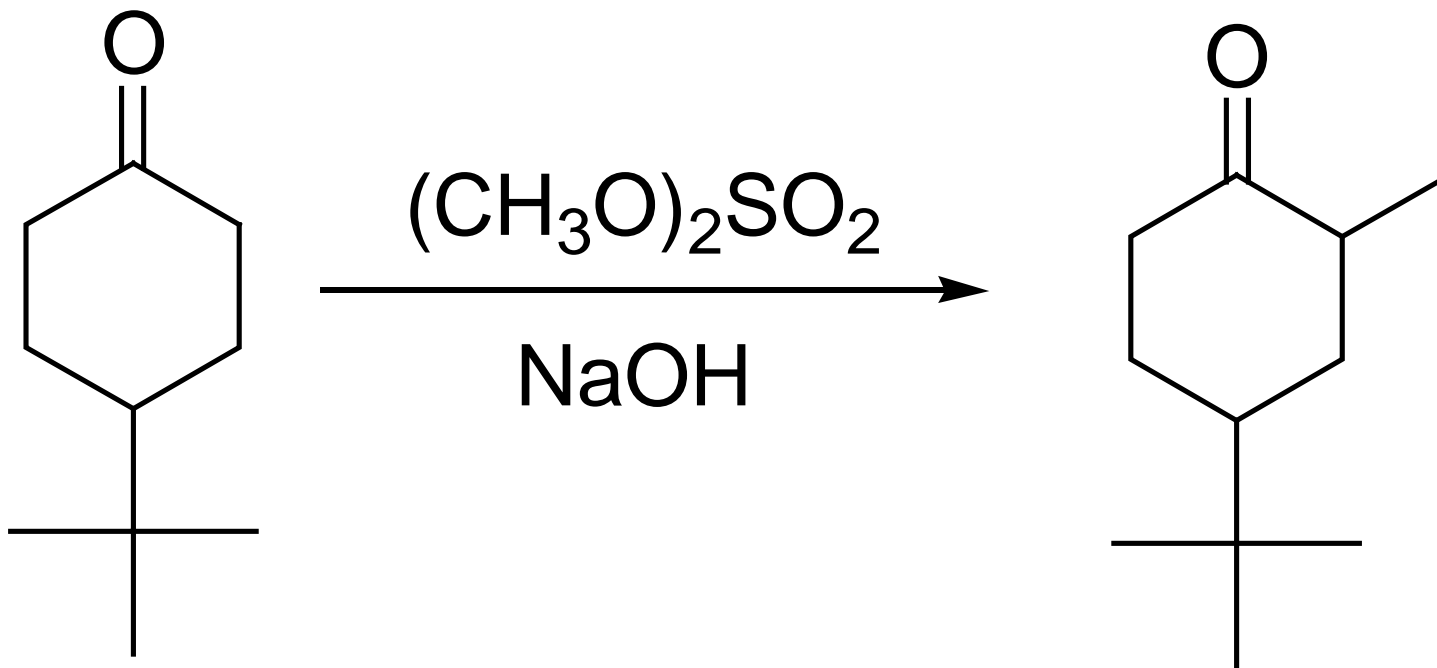
Figure 12-3 Equatorial (a) and axial (b) conformations of (+)-3-methylcyclohexanone and the octant rule, projection of the equatorial conformer (c, d).

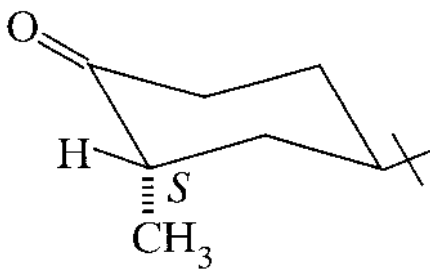
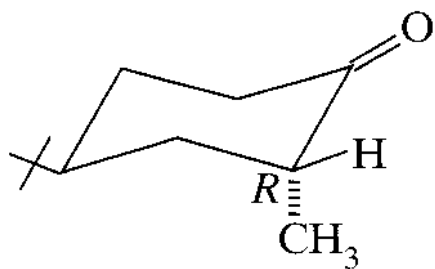


How would look spectrum of racemate like?

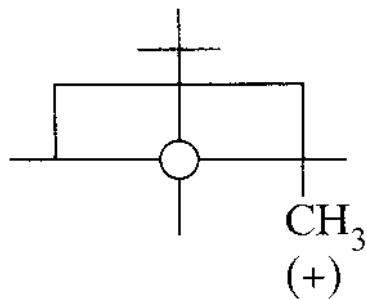
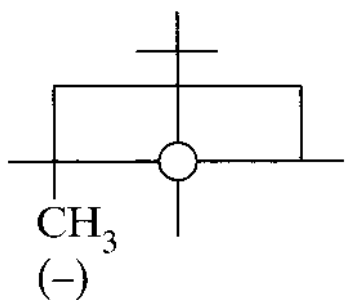
Problem

Two optically active isomeric 2-methyl-4-*tert*-butylcyclohexanone were prepared, and their CD spectra were run. One ketone had an $n \rightarrow \pi^*$ Cotton effect $\Delta\epsilon_{\max} = +1.4$; the other had $\Delta\epsilon_{\max} = -0.3$. Both ketones had the same optical purity. Assign the absolute configuration of each ketone.

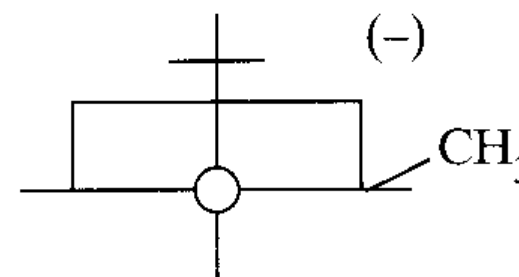
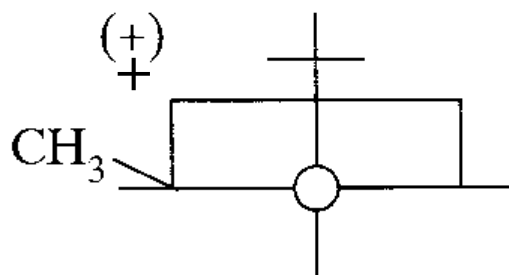
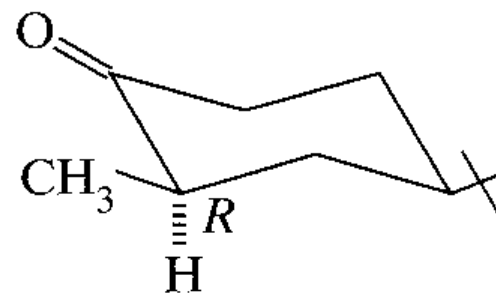
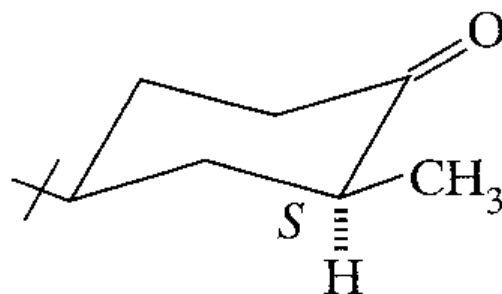




$$\Delta\varepsilon_{\max} = +1.4$$



$$\Delta\varepsilon_{\max} = -0.3$$



Why is the value of the Cotton effect different?