



**INSTITUTE OF  
CHEMICAL TECHNOLOGY  
PRAGUE**

Athens: Introduction to Vibrational Spectroscopy

*Vibrational circular dichroism I*

*Marie Urbanová*

## *Schedule*

1. Circular dichroism: What is it?  
How is molecular structure encoded in CD spectra?
2. Experimental: peculiarities
3. Processing of circular dichroism spectra
4. Circular dichroism and molecular structure
5. Utilization of vibrational circular dichroism

# 1 Circular dichroism

## Definition of circular dichroism



$$\Delta A = A_L - A_R$$

$$\Delta A(\nu) = A_L(\nu) - A_R(\nu) \quad A = \varepsilon c l$$



$$\Delta \varepsilon(\nu) = \varepsilon_L(\nu) - \varepsilon_R(\nu)$$

## Other chiroptical methods

Optical rotation

$$\Phi \sim n_L - n_R$$

Optical rotation dispersion

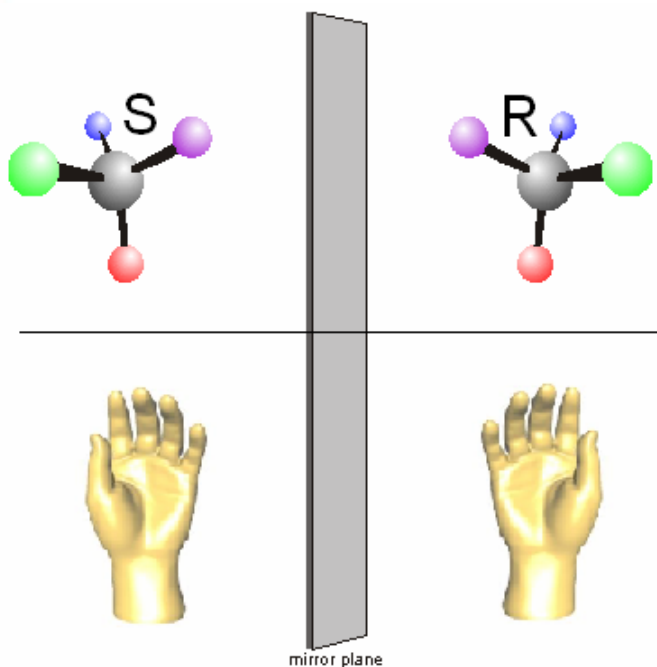
$$\Phi(\nu)$$

Raman optical activity

$$\Delta I(\nu) \sim I_L(\nu) - I_R(\nu)$$

# 1 Circular dichroism

## Definition of chirality



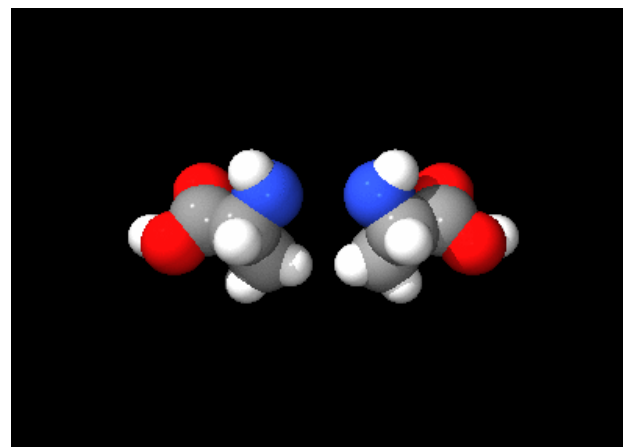
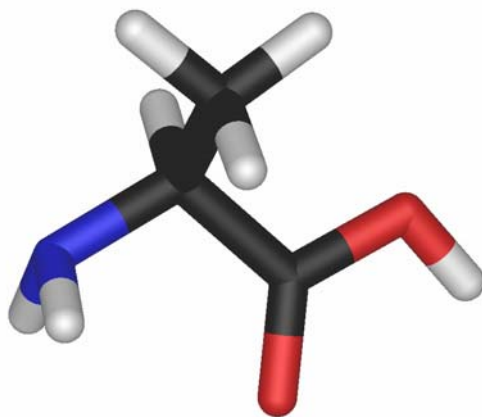
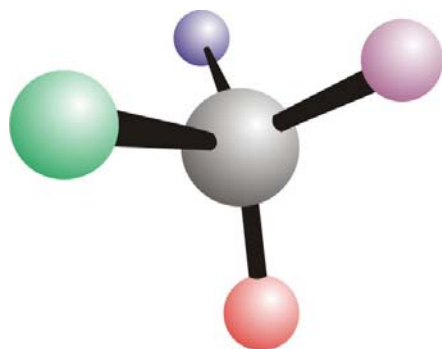
The plane mirror

*"I call any geometrical figure, or group of points, chiral, and say it has chirality, if its image in a plane mirror, ideally realized, cannot be brought to coincide with itself."*

Lord Kelvin, 1904, Baltimore Lectures on Molecular Dynamics and the Wave Theory of Light

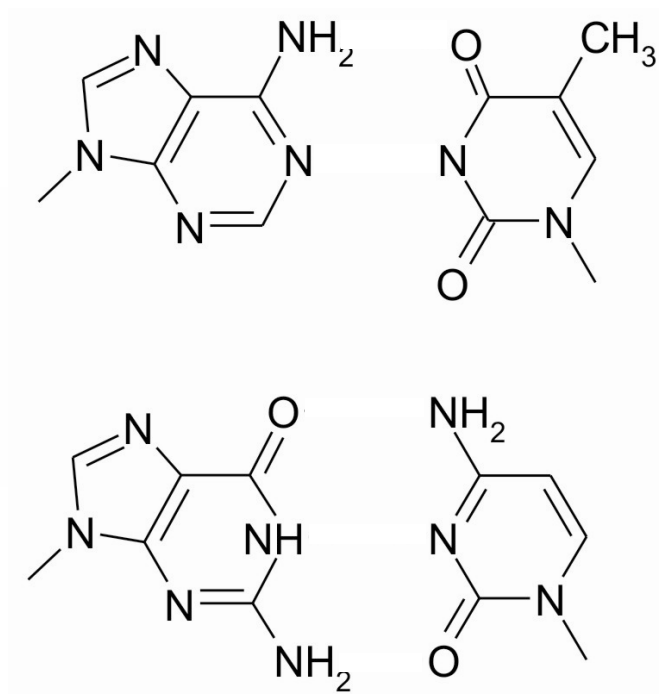
# 1 *Circular dichroism*

Examples of chiral objects



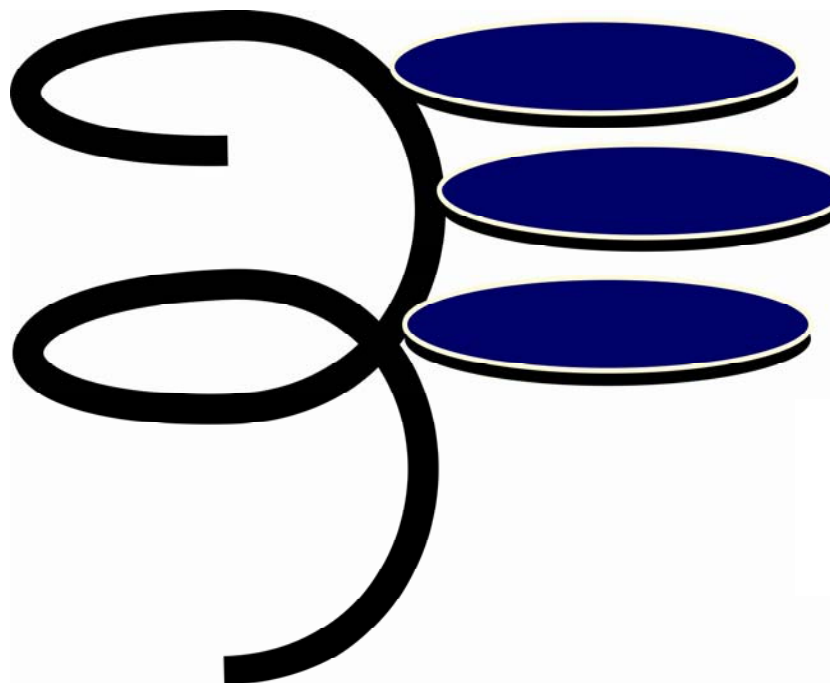
# 1 Circular dichroism

## Examples of chiral objects



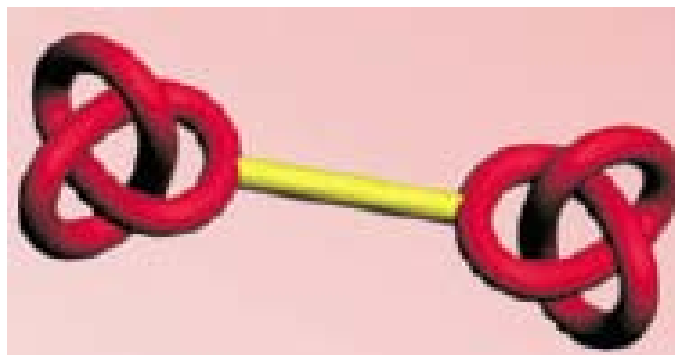
# *1 Circular dichroism*

Examples of chiral objects

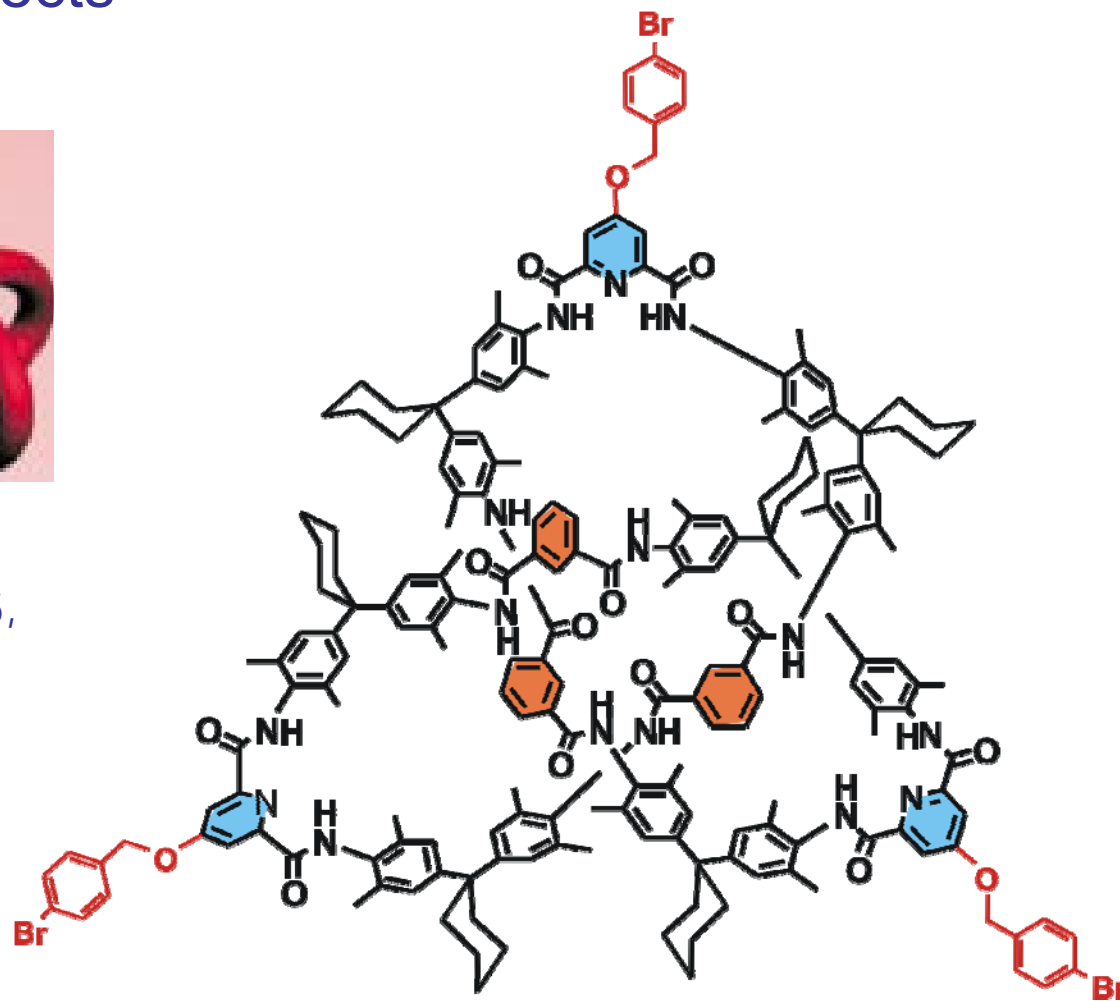


# 1 Circular dichroism

## Examples of chiral objects

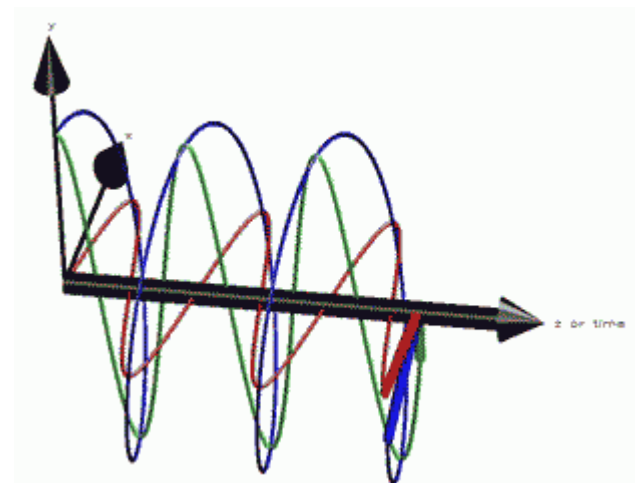


O.Lukin, F. Voegtle  
*Angew. Chem. Int. Ed.* 2005,  
44, 2-23



# 1 Circular dichroism

Circularly polarized radiation (light)



$$\hat{\mathbf{e}}_L = \frac{1}{\sqrt{2}} \{(0, 1, i) \exp(i(kx - \omega t))\}$$

$$\hat{\mathbf{e}}_R = \frac{1}{\sqrt{2}} \{(0, 1, -i) \exp(i(kx - \omega t))\}$$

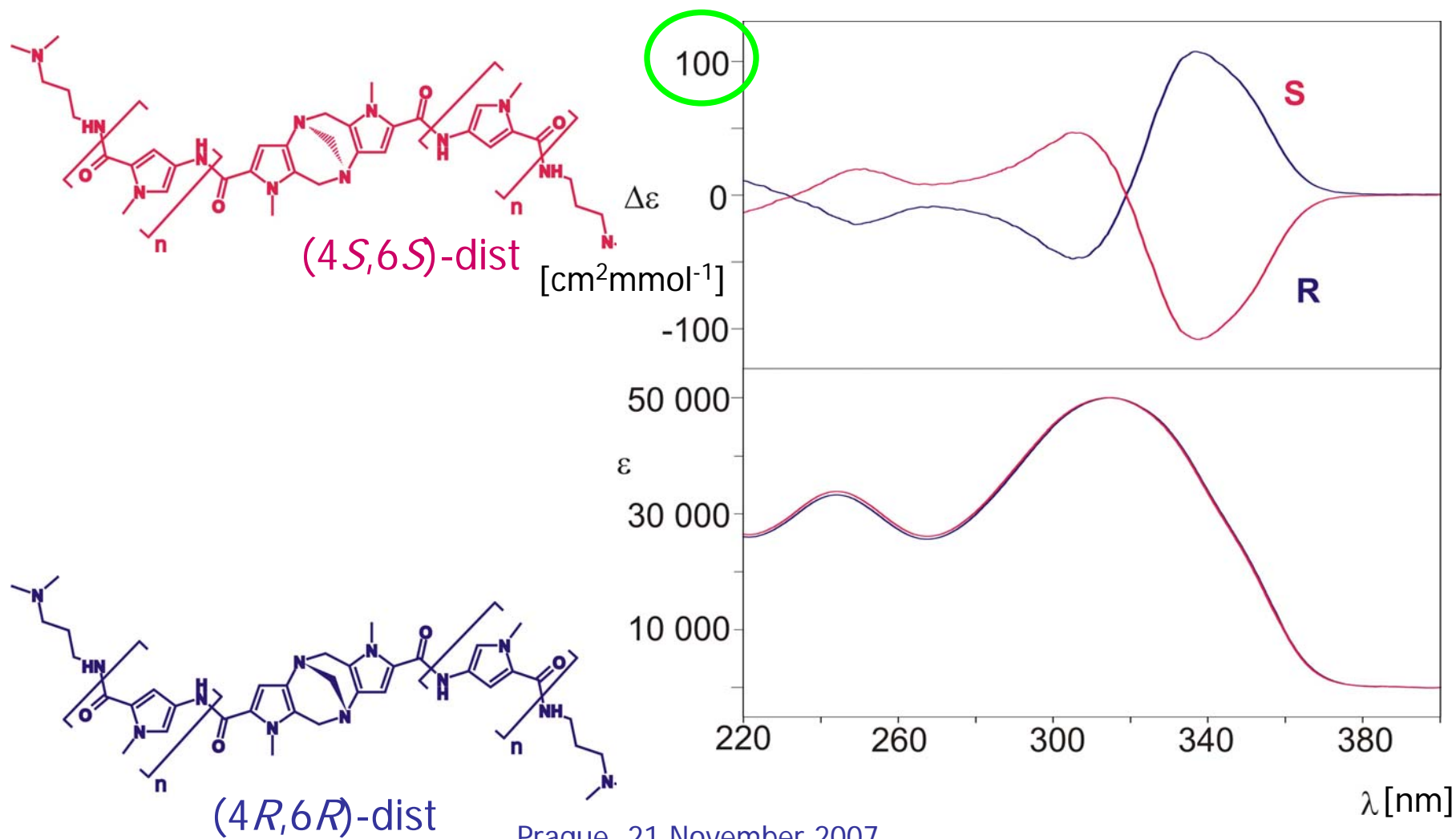
[http://www.chem.ubc.ca/personnel/faculty/straus/C305\\_CD\\_ORD.pdf](http://www.chem.ubc.ca/personnel/faculty/straus/C305_CD_ORD.pdf)

# 1 Circular dichroism

<b>Wavelength</b>	200 nm	400 nm	800 nm	1 μm	10 μm
<b>Wavenumber/cm<sup>-1</sup></b>	5 × 10 <sup>4</sup>			1 × 10 <sup>4</sup>	1 × 10 <sup>3</sup>
<b>Type of radiation</b>	Ultraviolet		Visible		Infrared
<b>Transitions</b>	Electronic			Vibrational	
<b>Spectroscopy</b>	Electronic circular dichroism ECD			Vibrational circular dichroism VCD	
<b>Signal observed for</b>	UV-vis chromophores e.g. aromatic			<u>all</u> compounds	

# 1 Circular dichroism

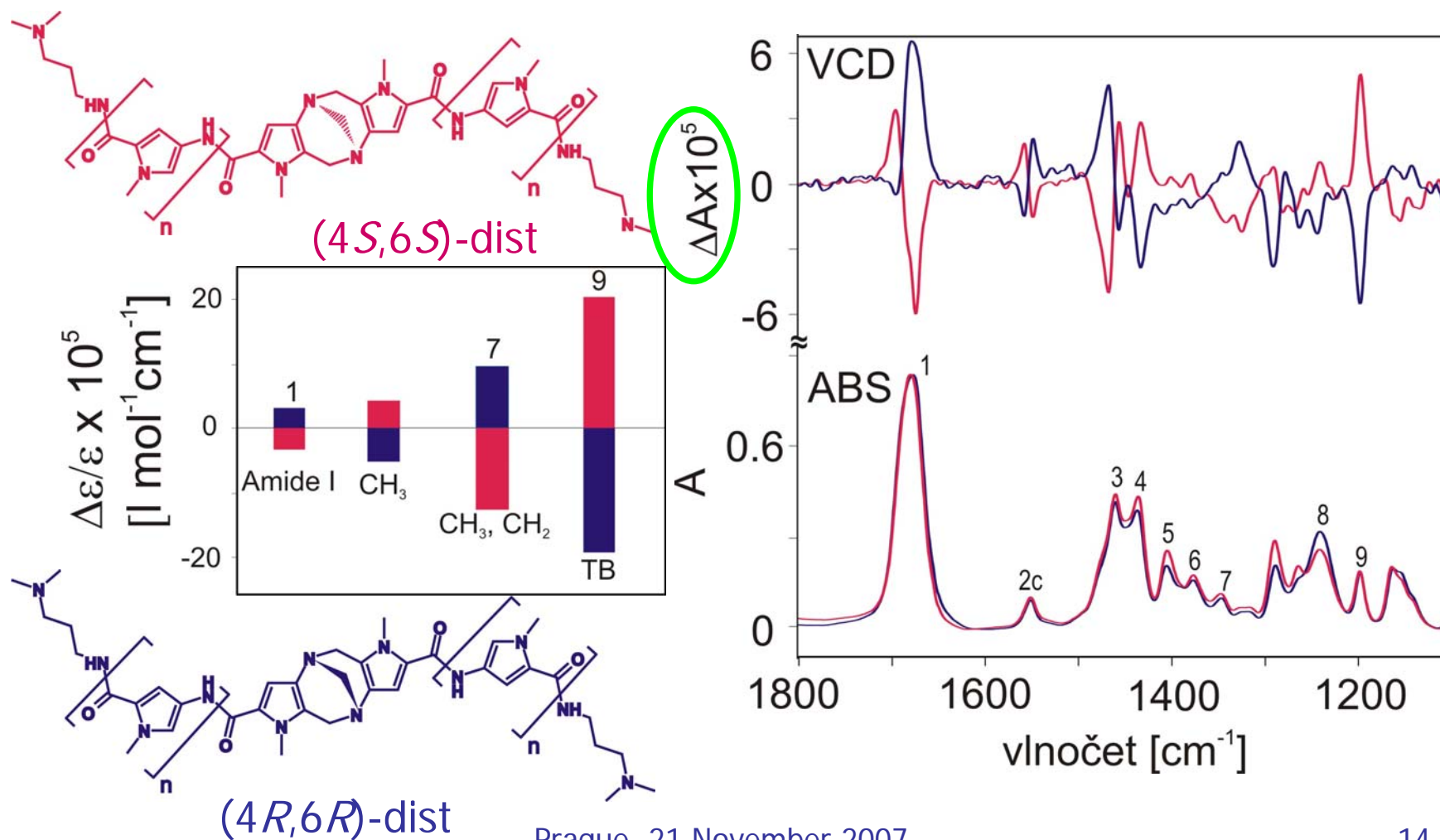
Example of electronic circular dichroism spectra



Prague, 21 November 2007

# 1 Circular dichroism

Example of electronic circular dichroism spectra



## *1 Circular dichroism*

*How is molecular structure encoded  
in CD spectra?*

# 1 Circular dichroism

Spectroscopy – interaction of radiation with molecules

electromagnetic field – intensity of electric field  $\mathbf{E}$  and magnetic induction  $\mathbf{B}$

circularly polarized light – vectors



$$\hat{\mathbf{e}}_L = \frac{1}{\sqrt{2}} \{(0, 1, i) \exp(i(kx - \omega t))\}$$



$$\hat{\mathbf{e}}_R = \frac{1}{\sqrt{2}} \{(0, 1, -i) \exp(i(kx - \omega t))\}$$

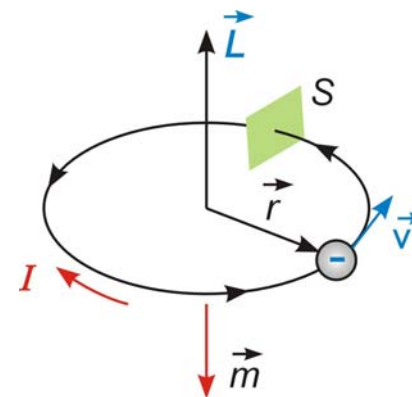
# 1 Circular dichroism

Spectroscopy – interaction of radiation with molecules

electric and magnetic properties of molecule given by  
– electric a magnetic dipol moments

$$\boldsymbol{\mu} = e \sum_i \mathbf{r}_i,$$

$$\mathbf{m} = \frac{e}{2m_e} \sum_i \mathbf{r}_i \times \mathbf{p}_i$$



# 1 Circular dichroism

Interaction of electromagnetic field and a molecule describes quantum mechanics – interaction hamiltonian

$$\hat{H}^{\text{int}} = -\hat{\boldsymbol{\mu}} \cdot \mathbf{E} - \hat{\mathbf{m}} \cdot \mathbf{B} + \text{higher orders}$$

In perturbation theory, absorption is

$$\begin{aligned} A(|i\rangle \rightarrow |f\rangle) &\sim P(|i\rangle \rightarrow |f\rangle) = k |\langle f | \hat{H}^{\text{int}} | i \rangle|^2 \\ &= k' (\boldsymbol{\mu}^{if} \cdot \mathbf{e} + \mathbf{m}^{if} \cdot \mathbf{b})^* (\boldsymbol{\mu}^{if} \cdot \mathbf{e} + \mathbf{m}^{if} \cdot \mathbf{b}) \end{aligned}$$

$$A \sim D^{if} = |\boldsymbol{\mu}^{fi}|^2$$

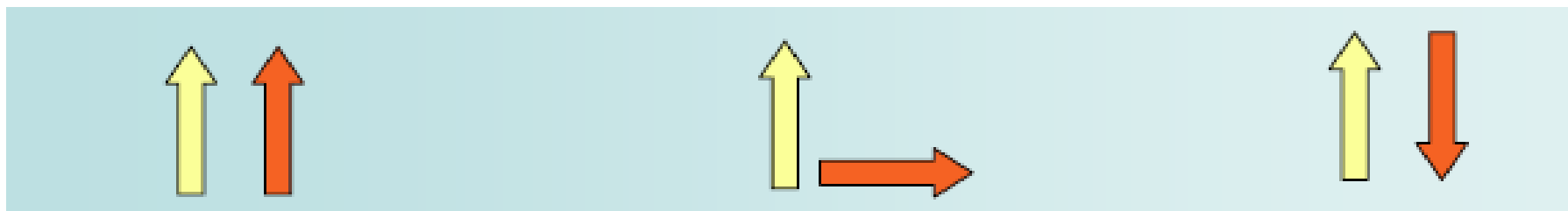
Circular dichroism (CD)

$$\begin{aligned} \Delta A &= A_L - A_R = \\ &= k' (\boldsymbol{\mu}^{if} \cdot \mathbf{e}_L + \mathbf{m}^{if} \cdot \mathbf{b}_L)^* (\boldsymbol{\mu}^{if} \cdot \mathbf{e}_L + \mathbf{m}^{if} \cdot \mathbf{b}_L) \\ &\quad - k' (\boldsymbol{\mu}^{if} \cdot \mathbf{e}_R + \mathbf{m}^{if} \cdot \mathbf{b}_R)^* (\boldsymbol{\mu}^{if} \cdot \mathbf{e}_R + \mathbf{m}^{if} \cdot \mathbf{b}_R) = \dots \end{aligned}$$

# 1 Circular dichroism

Circular dichroism (CD) ~ rotational strength o

$$\Delta A \sim R^{if} = \text{Im}[\boldsymbol{\mu}^{fi} \bullet \boldsymbol{m}^{if}]$$



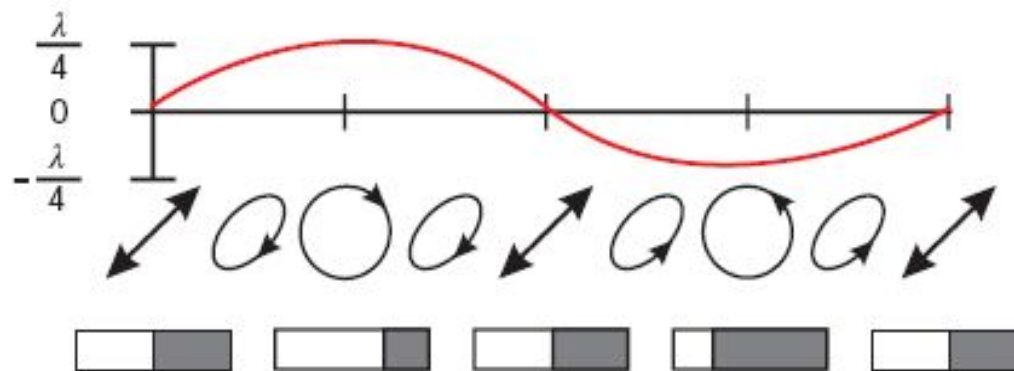
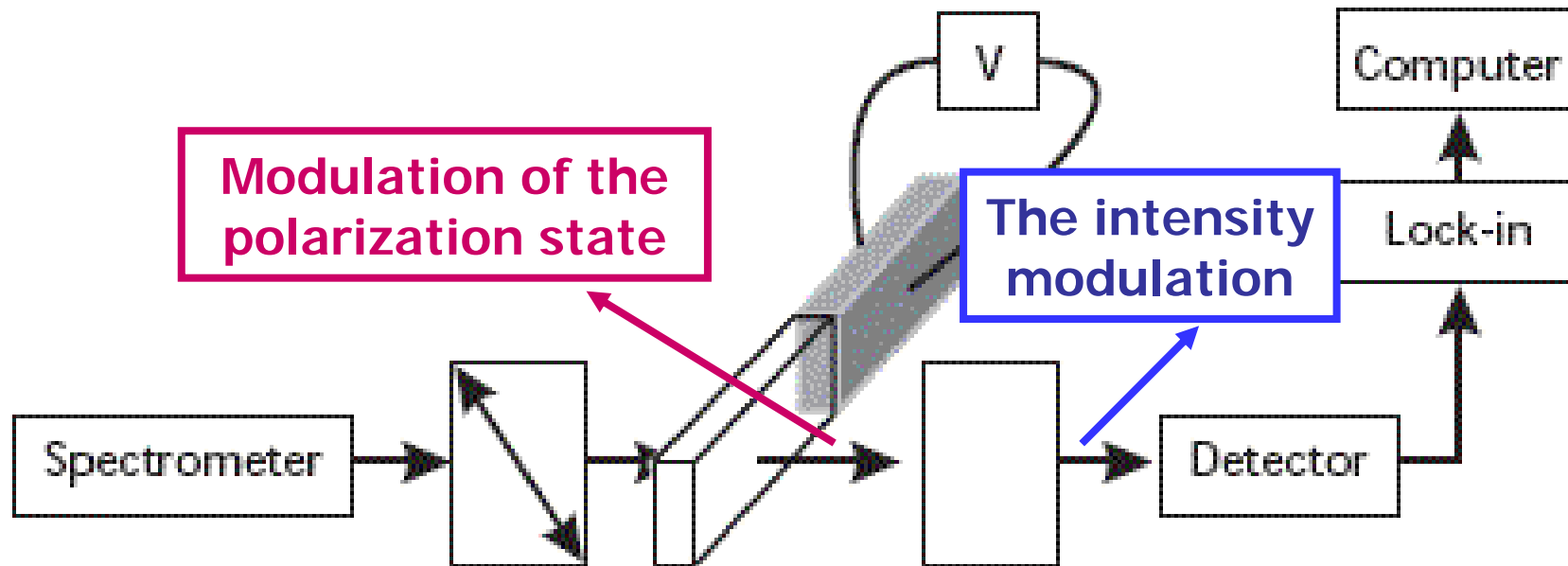
- = > structure gives the quantity and the sign of CD
- = > opposite sign of CD for the enantiomers in the whole spectral region, although non-polarized absorption does not differentiate them

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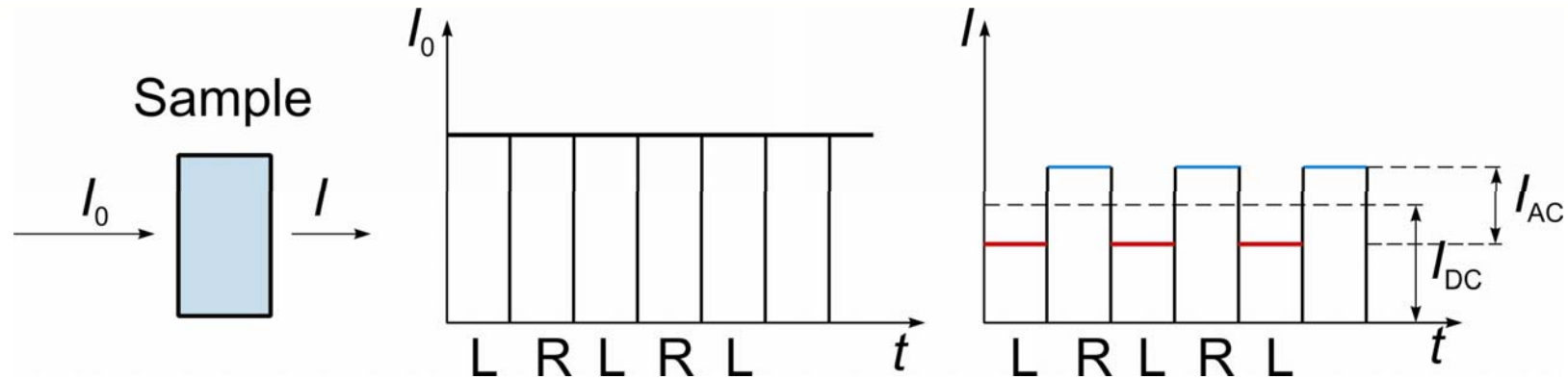
## 2 Experimental

The crucial part of CD spectrometer  
– photoelastic modulator (PEM)



Hinds Instruments

## 2 Experimental



$$I / I_0 = 10^{-A}$$

$$I = I_{0R} 10^{-A_R} + I_{0L} 10^{-A_L}$$

$$I_{0L} = (I_0/2)(1 + \sin \alpha), \quad I_{0R} = (I_0/2)(1 - \sin \alpha)$$

$$I = I_0 \underbrace{\frac{10^{-A_R} + 10^{-A_L}}{2}}_{I_{DC}} + I_0 \underbrace{\frac{10^{-A_R} - 10^{-A_L}}{2} \sin \alpha}_{I_{AC}}$$

## 2 Experimental

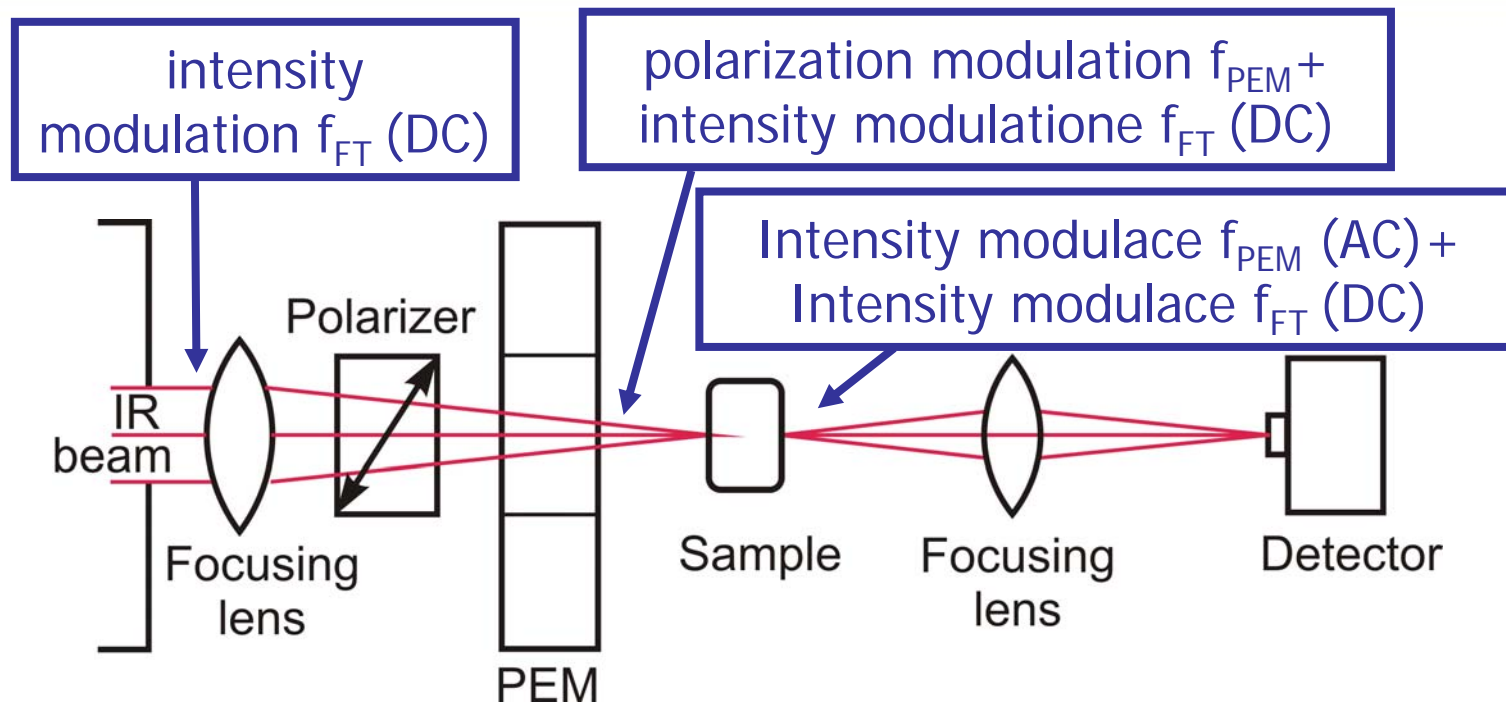
$$I = I_0 \underbrace{\frac{10^{-A_R} + 10^{-A_L}}{2}}_{I_{DC}} + I_0 \underbrace{\frac{10^{-A_R} - 10^{-A_L}}{2}}_{I_{AC}} \sin \alpha$$

$$\frac{I_{AC}}{I_{DC}} = 2J_1(\alpha_0) [1.15(A_L - A_R)] g$$

$$A_L - A_R \sim \frac{I_{AC}}{I_{DC}}$$

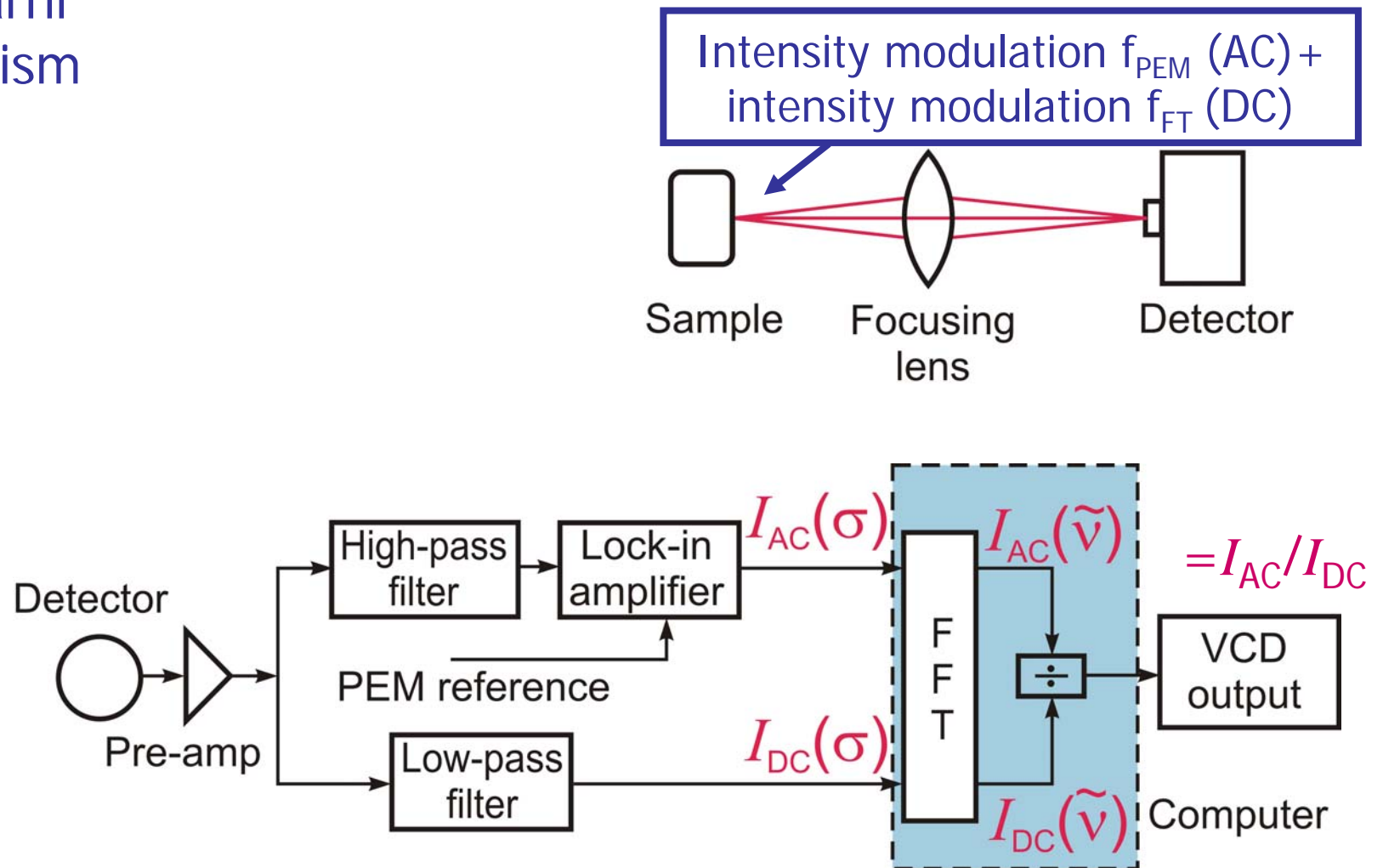
## 2 Experimental

Vibrational  
Circular  
dichroism  
(VCD)



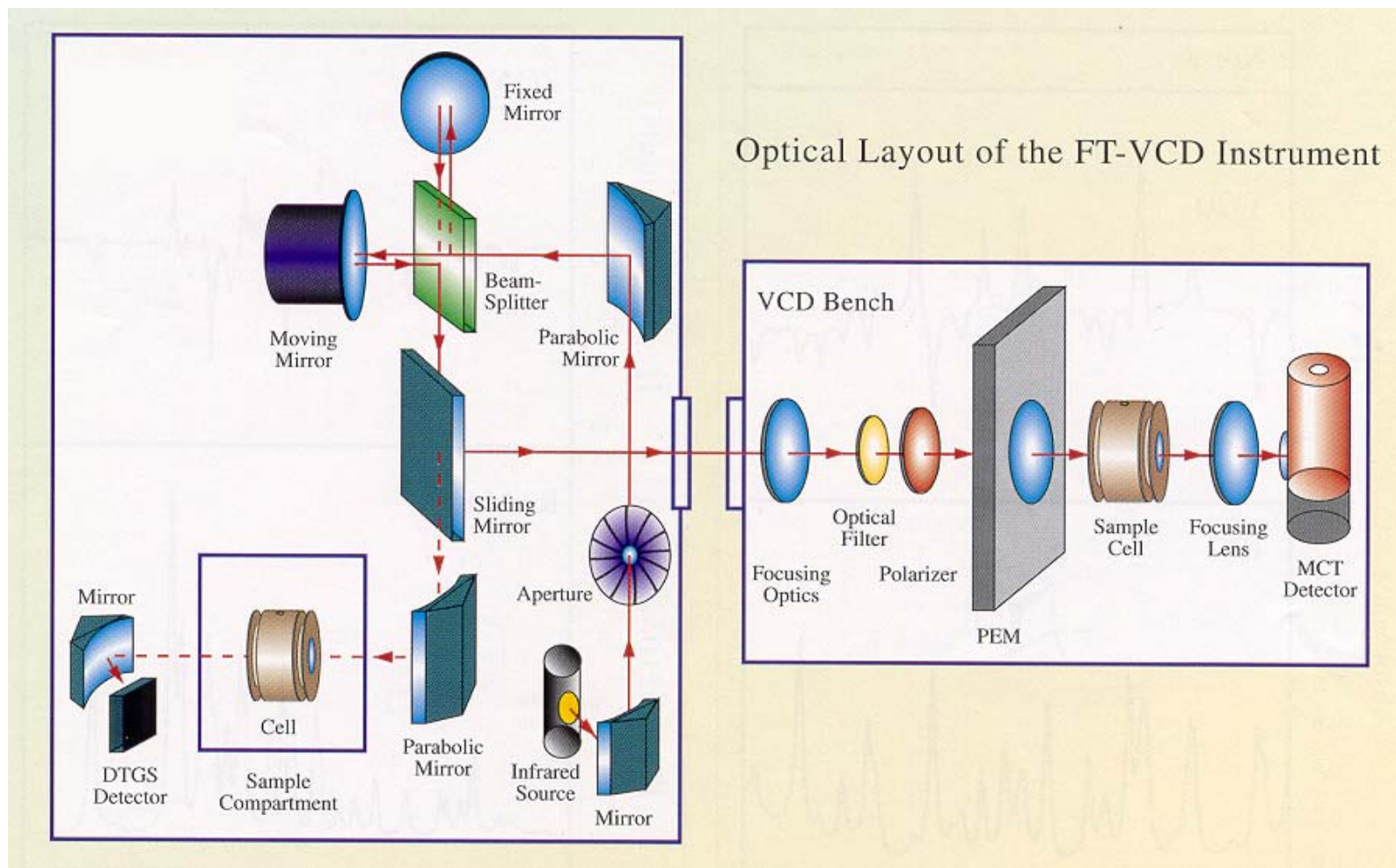
## 2 Experimental

Vibrational  
circular  
dichroism  
(VCD)



## 2 Experimental

### Vibrational circular dichroism (VCD)



Nafie L. A.: *Appl. Spectrosc.* 1996, 50, 14A.

## 2 Experimental

- Experimental conditions in VCD spectroscopy
  - Spectral limitation given
    - by the materials of all optical elements (PEM)
    - Sensitivity of detector
      - 900-1800  $\text{cm}^{-1}$ : MCT, cooled by liquid nitrogen
      - 2000-4000  $\text{cm}^{-1}$ : MCT, thermodynamically cooled
      - 4000-6000  $\text{cm}^{-1}$ : InGaAs, room temperature
      - 5000-9000  $\text{cm}^{-1}$ : Ge, room temperature
    - The most popular region 2000 – 800  $\text{cm}^{-1}$

## *2 Experimental*

- Experimental conditions in VCD spectroscopy
  - Dynamic region 0,1-1, optimal 0,4 - 0,6
    - Combination by appropriate sample concentration, the cell thickness and appropriate solvent
    - Typical concentrations 0,05 – 1 mol l<sup>-1</sup>
    - Typical volume 50 – 100 ml
    - Typical mass of sample 1 – 15 mg

## 2 Experimental

- IR solvents appropriate for VCD spectroscopy in the mid IR region and their spectral windows

Solvent	Spectral window (cm <sup>-1</sup> )	Solvent	Spectral window (cm <sup>-1</sup> )
CCl <sub>4</sub>	2000–850	DMSO- <i>d</i> <sub>6</sub>	2000–1100; 970–700
CS <sub>2</sub>	2000–1640; 1350–700	Methanol- <i>d</i> <sub>4</sub>	2000–1200
CHCl <sub>3</sub>	2000–1260; 1175–700	H <sub>2</sub> O <sup>a</sup>	2000–1770; 1525–1000
CDCl <sub>3</sub>	2000–975	D <sub>2</sub> O	2000–1300; 1100–800 <sup>a</sup>
Propanol	2000–1500	trifluorethanol	2000–1500

<sup>a</sup>only when a short pathlength < 6 μm and higher concentrations are used.

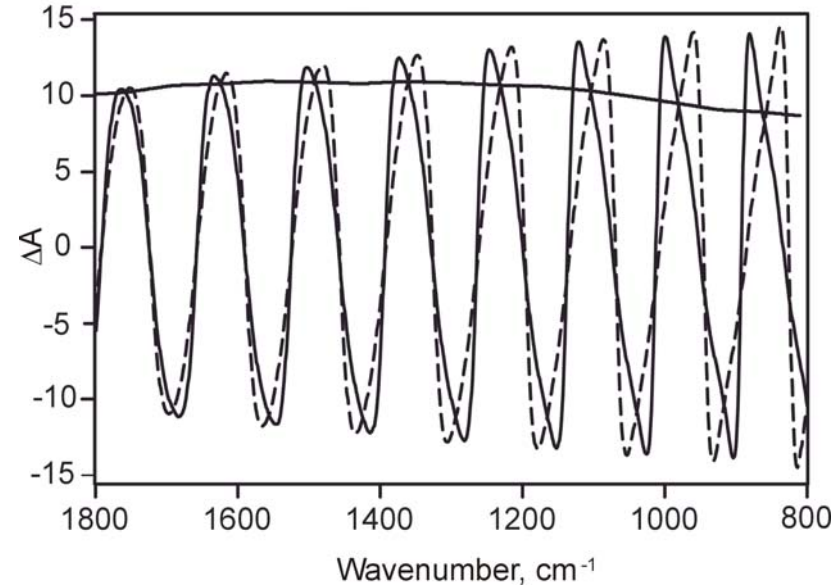
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### 3 Processing of circular dichroism spectra

Single beam measurements → calibration of intensity, the zero line correction

- calibration of intensity done by pseudosample:  
 $\Delta A = \pm 1$  in special points, which give calibration curve :



### *3 Processing of circular dichroism spectra*

- the zero line correction
  - the zero line distortion may be comparable in size to the sample signals and cause artifacts, the sources are:
    - Birefringence in the optical material of optical lenses, filters, cells and other windows,
    - Reflections,
    - Sample absorption: in the region of the absorption band, anomalous dispersion takes place that may distort the equilibrium of the responses to right and left circularly polarized light, primarily in the case of a narrow sharp absorption band

### 3 Processing of circular dichroism spectra

- The corrected spectrum can be obtained when both enantiomers are available:
  - For the same concentrations of the both enantiomers  $R$  and  $S$ :  $A_S(\nu) = A_R(\nu)$       $\Delta A_S(\nu) = -\Delta A_R(\nu)$
  - experimental spectra of the both enantiomers contain the same distortion  $D(\nu)$  :  
$$\Delta A_R^{\text{exp}}(\nu) = \Delta A_R(\nu) + D(\nu)$$
$$\Delta A_S^{\text{exp}}(\nu) = \Delta A_S(\nu) + D(\nu)$$
  - Summation gives twofold distortion and difference twofold spectrum of single enantiomer:

$$N(\nu) = \frac{1}{2} \left( \Delta A_S^{\text{exp}}(\nu) + \Delta A_R^{\text{exp}}(\nu) \right) \quad \Delta A_S(\nu) = \frac{1}{2} \left( \Delta A_S^{\text{exp}}(\nu) - \Delta A_R^{\text{exp}}(\nu) \right)$$

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## 4 *Circular dichroism and molecular structure*

- 1 Structural methods with high (**atomic**) resolution
  - X-ray, electron, neutron diffraction
  - NMR
  - rotation a rotation-vibration spectroscopy (for small molecules in the gas state only)
  - Numerical methods
- 2 Scanning and transition microscopy

## 4 *Circular dichroism and molecular structure*

### 3 Structural methods with **low** resolution – optical spectroscopy

spectral region and further properties of electromagnetic radiation implicate information that can be obtained

- UV-VIS absorption and fluorescence are intensity oriented
- IR absorption and Raman spectroscopy frequency oriented
- CD (ECD or VCD) contains the structural information in the frequency, intensity and the shape of signal
- **in all states, in different physical-chemical conditions, fast, less expensive**

## *4 Circular dichroism and molecular structure*

Vibrational circular dichroism (VCD) – advantages and disadvantages

- higher spectral resolution than UV-VIS
- additional resolution by isotopic substitution
- all molecules possess IR spectrum, no special chromospheres needed
- characteristic vibrations are localized in molecule
- very good theoretical background

## *4 Circular dichroism and molecular structure*

Vibrational circular dichroism (VCD) – **advantages** and disadvantages

- Only chiral objects
- High concentrations needed (single measurement - 2,5 mg of sample)
- Weak signals,  $10^{-4}$  -  $10^{-5}$  A
- Limited IR transmission solvent, deuterated solvents

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## *5 Utilization of vibrational circular dichroism*

### Vibrational circular dichroism

- enantiomeric purity
- absolute configuration of small and middle molecules
- structure of peptides, proteins, oligonucleotides a DNA
- biologically interesting interactions
- structural studies of supramolecular interactions
- transcription of chiral information
- molecular recognition



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*Vibrational circular dichroism II  
Application*

*Marie Urbanová*