



# Ellipsometry:

a tool to study single-molecule-  
induced anisotropy?

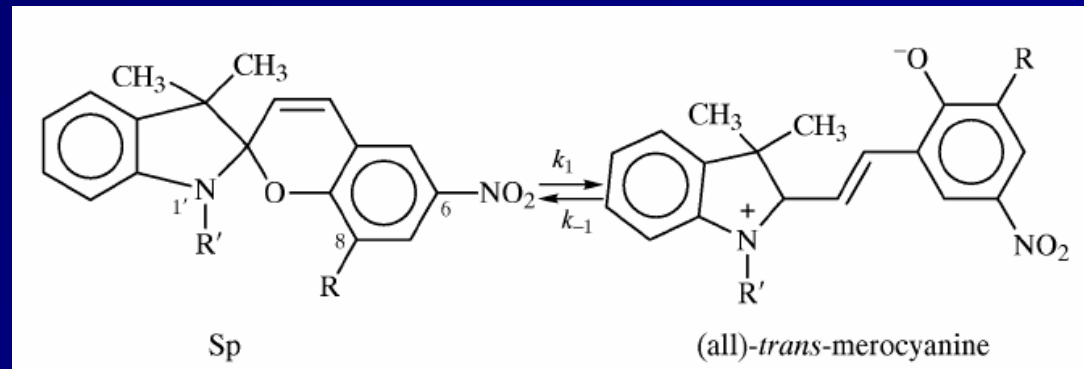
# Outline

- ⇒ *introduction*
- ⇒ *fundamentals of optical properties*
- ⇒ *classification of optical anisotropy*
- ⇒ *introduction to the technique of ellipsometry*
- ⇒ *implications for single molecule spectroscopy*

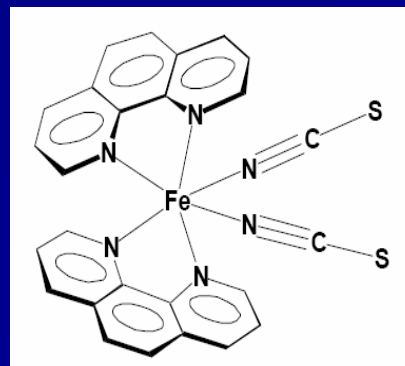
# introduction

goal of project B4 is to investigate the interaction of *switchable magnetic and electric dipoles with well defined surfaces*

➔ *switchable electric dipoles: Spiropyranes*



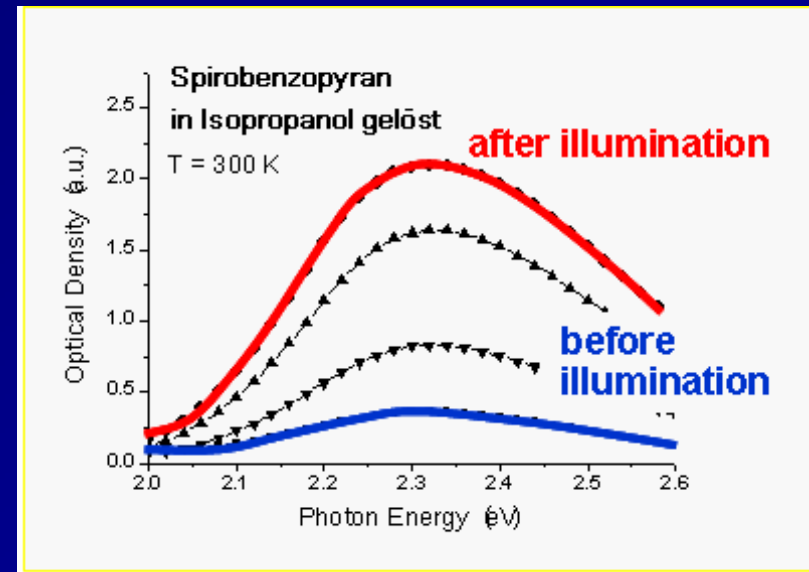
➔ *switchable magnetic dipoles: spin-crossover materials*



# introduction

**Methods:** *optical and magneto-optic spectroscopy in the far field and near-field*

- ➔ *switching of molecules generates structures in the optical spectra which can be used to monitor the conformation change*
- ➔ *monitoring by absorption or reflectivity measurements*
- ➔ *in principle single-molecule sensitivity*



M. Karcher, diploma thesis (2004)

**however: no information on orientation of molecules**

# introduction

**is it possible to determine the orientation of a single molecule by ellipsometry?**

- ➔ *ellipsometry measures the polarization state of light*
- ➔ *the polarization state of light is distorted by optical anisotropy (e.g. birefringence)*
- ➔ *a single molecule induces local optical anisotropy*

***the answer is: in principle yes!***

# fundamentals of optical properties

## Maxwell equations in *vacuum*

$$\vec{\nabla} \cdot \vec{E} = 0$$

$$\vec{\nabla} \cdot \vec{B} = 0$$

$$\vec{\nabla} \times \vec{E} = -\dot{\vec{B}}$$

$$\vec{\nabla} \times \vec{B} = \mu_0 \epsilon_0 \dot{\vec{E}}$$

## Maxwell equations in an *uncharged, polarizable, magnetizable, and conductive material*

$$\vec{\nabla} \cdot \vec{D} = 0$$

$$\vec{\nabla} \cdot \vec{B} = 0$$

$$\vec{\nabla} \times \vec{E} = -\dot{\vec{B}}$$

$$\vec{\nabla} \times \vec{H} = \vec{j} + \dot{\vec{D}}$$

$$\vec{D} = \epsilon_0 \vec{E} + \vec{P}$$

$$\vec{B} = \mu_0 (\vec{H} + \vec{M})$$

$\vec{D}$  = electric displacement

$\vec{H}$  = magnetic field in vacuum

$\vec{P}$  = polarization

$\vec{M}$  = magnetization

# fundamentals of optical properties

## material properties (in linear approximation)

$$\vec{P} = \alpha \vec{E} \quad \rightarrow \quad \vec{D} = \epsilon_0 \vec{E} + \vec{P} = \epsilon \epsilon_0 \vec{E} = \left( 1 + \frac{\alpha}{\epsilon_0} \right) \epsilon_0 \vec{E}$$

$$\vec{M} = \chi_{\text{mag}} \vec{H} \quad \rightarrow \quad \vec{B} = \mu_0 (\vec{H} + \vec{M}) = \mu \mu_0 \vec{H} = \mu_0 (1 + \chi_{\text{mag}}) \vec{H}$$

$$\vec{j} = \sigma \vec{E}$$

$\alpha$  = polarizability

$\epsilon$  = dielectric function

$\chi_{\text{mag}}$  = magnetic susceptibility

$\mu$  = magnetic permeability

$\sigma$  = optical conductivity

*in anisotropic materials:*

**tensors of rank two!**

$$\hat{\sigma} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix}$$

# fundamentals of optical properties

## material properties in *complex notation* (assuming harmonic waves)

$$\vec{E} = \vec{E}_0 e^{i(\omega t - \vec{k} \cdot \vec{r})} \quad \rightarrow \quad \vec{E} = \frac{1}{i\omega} \dot{\vec{E}}$$

$$\vec{\nabla} \times \vec{H} = \vec{j} + \dot{\vec{D}} \quad \rightarrow \quad \vec{\nabla} \times \vec{H} = \vec{j} + \dot{\vec{D}} = \sigma \vec{E} + \epsilon \epsilon_0 \dot{\vec{E}} = \left( \epsilon - i \frac{\sigma}{\epsilon_0 \omega} \right) \epsilon_0 \dot{\vec{E}}$$

$$\rightarrow \quad \tilde{\epsilon} = \left( \epsilon - i \frac{\sigma}{\epsilon_0 \omega} \right) = \epsilon_1 - i \epsilon_2 \quad \text{complex dielectric function}$$

$$\rightarrow \quad \tilde{\epsilon} = 1 - i \frac{\sigma_2}{\epsilon_0 \omega} \quad \tilde{\sigma} = \sigma_1 - i \sigma_2 \quad \text{complex optical conductivity}$$

# fundamentals of optical properties

## Maxwell equations in *complex notation* ( $\mu = 1$ )

$$\vec{\nabla} \cdot \vec{D} = 0$$

$$\vec{\nabla} \cdot \vec{B} = 0$$

$$\vec{\nabla} \times \vec{E} = -\dot{\vec{B}}$$

$$\vec{\nabla} \times \vec{B} = \mu_0 \epsilon_0 \tilde{\epsilon} \dot{\vec{E}} = \frac{\tilde{\epsilon}}{c^2} \dot{\vec{E}}$$

# fundamentals of optical properties

## wave equation in an *isotropic* material

using  $\vec{E} = \vec{E}_0 e^{i(\omega t - \vec{g} \cdot \vec{r})}$  and  $\vec{\nabla} \cdot \vec{D} = \tilde{\epsilon} \vec{\nabla} \cdot \vec{E} = 0$

$$\Delta \vec{E} = \frac{\tilde{\epsilon}}{c^2} \frac{\partial^2 \vec{E}}{\partial t^2} \quad \rightarrow \quad (\vec{g} \cdot \vec{g}) \vec{E} = \tilde{g}^2 \vec{E} = \frac{\omega^2}{c^2} \tilde{\epsilon} \vec{E}$$

$\rightarrow \quad \tilde{g} = (g_1 - ig_2) = \sqrt{\tilde{\epsilon}} \frac{\omega}{c} = \tilde{n} \frac{\omega}{c}$  *complex wave vector*

$\rightarrow \quad \tilde{\epsilon} = \tilde{n}^2 \quad \tilde{n} = n - ik$  *complex index of refraction*

# fundamentals of optical properties

## wave equation in an *anisotropic* material

using  $\vec{E} = \vec{E}_0 e^{i(\omega t - \vec{g} \cdot \vec{r})}$

$$\vec{\nabla} \cdot \vec{D} = \vec{\nabla} \cdot (\vec{\epsilon} \vec{E}) = 0 \quad \rightarrow \quad \vec{\nabla} \cdot \vec{E} \neq 0$$

$$\rightarrow \Delta \vec{E} - \vec{\nabla} (\vec{\nabla} \cdot \vec{E}) = \mu_0 \frac{\partial}{\partial t} \left( \vec{j} + \frac{\partial \vec{D}}{\partial t} \right)$$

$$\rightarrow \left( \vec{g} \cdot \vec{g} \right) \vec{E} - \left( \vec{g} \cdot \vec{E} \right) \vec{g} = \left( \frac{\omega}{c} \right)^2 \vec{\epsilon} \vec{E}$$

***complicated optical behavior!***

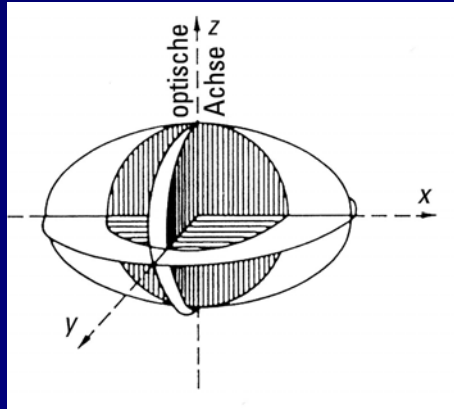
# classification of optical anisotropy: *linear birefringence*

$$\vec{D} = \hat{\epsilon} \vec{E}$$

$$\hat{\epsilon} = \begin{pmatrix} \epsilon_{xx} & \epsilon_{xy} & \epsilon_{xz} \\ \epsilon_{xy} & \epsilon_{yy} & \epsilon_{yz} \\ \epsilon_{xz} & \epsilon_{yz} & \epsilon_{zz} \end{pmatrix}$$

*symmetric tensor*

→ there always exists a coordinate system in which the dielectric tensor is diagonal



→ *principal axes*

→ *Fresnel ellipsoid*

$$\sum_i \sum_k \epsilon_{ik} x_i x_k = \text{const}$$

$$\vec{E} = \hat{\epsilon}^{-1} \vec{D}$$

→ *index ellipsoid*

$$\sum_i \sum_k (\epsilon^{-1})_{ik} x_i x_k = \text{const}$$

$$\hat{\epsilon} = \begin{pmatrix} \epsilon_{xx} & 0 & 0 \\ 0 & \epsilon_{yy} & 0 \\ 0 & 0 & \epsilon_{zz} \end{pmatrix}$$

$$\hat{\epsilon}^{-1} = \begin{pmatrix} n_{xx}^{-2} & 0 & 0 \\ 0 & n_{yy}^{-2} & 0 \\ 0 & 0 & n_{zz}^{-2} \end{pmatrix}$$

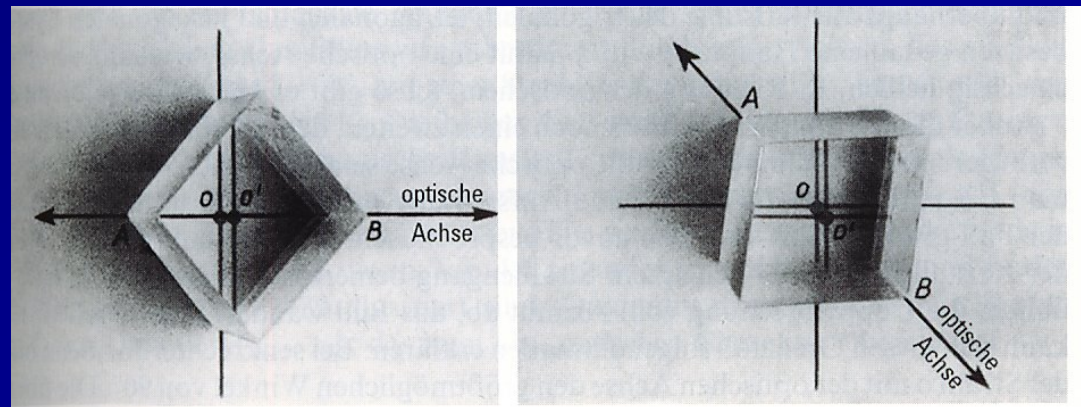
# classification of optical anisotropy: *linear birefringence*

**crystals with a single optical axis**

$$\hat{\epsilon} = \begin{pmatrix} \epsilon_{xx} & 0 & 0 \\ 0 & \epsilon_{xx} & 0 \\ 0 & 0 & \epsilon_{zz} \end{pmatrix}$$

*calcite  $\text{CaCO}_3$ , quartz  $\text{SiO}_2$  or any tetragonal, hexagonal, or rhombohedral crystal*

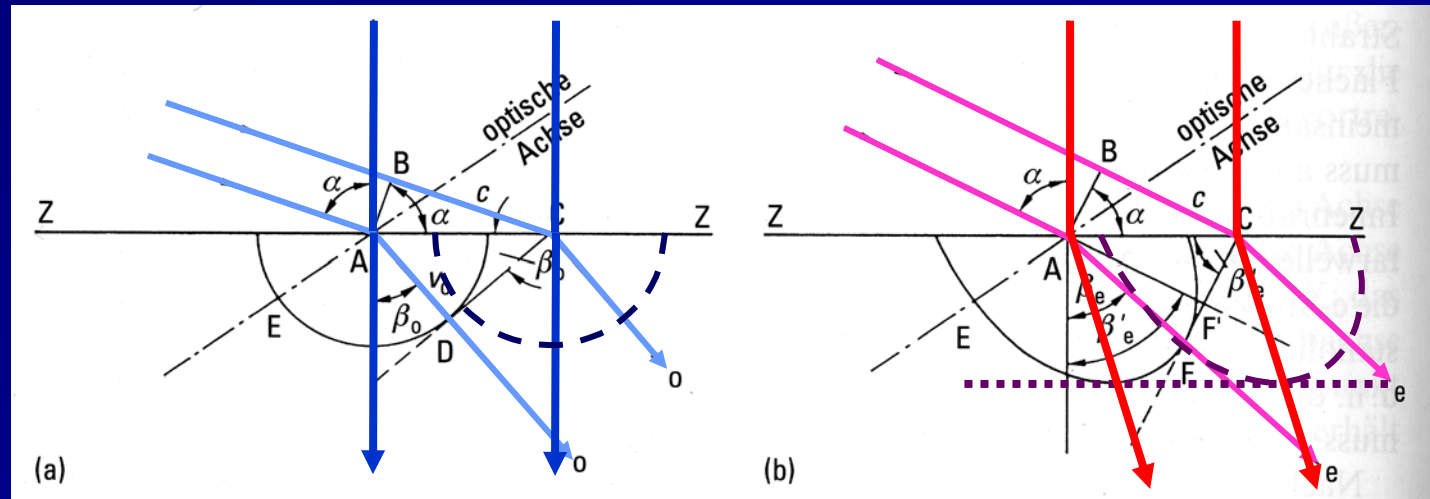
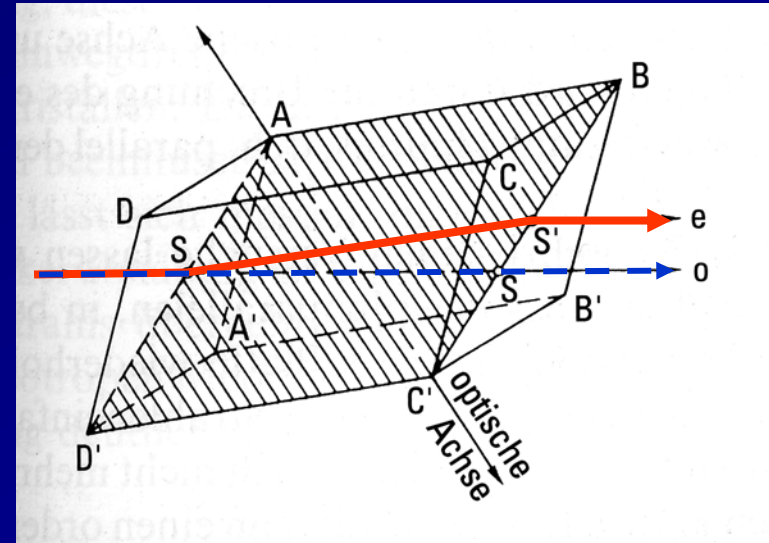
- ➔ *there exists a single direction, where light propagation is isotropic*
  - ➔ *optical axis*
- ➔ *in all other directions, two orthogonally polarized waves with different velocities will propagate*
  - ➔ *ordinary and extraordinary ray*



# classification of optical anisotropy: *linear birefringence*

crystals with a single optical axis

→ extraordinary ray **does not** follow Snellius law



*ordinary ray*

*extraordinary ray*

# classification of optical anisotropy: *optical activity*

$$\hat{\epsilon}^{\dagger} = \begin{pmatrix} \epsilon_{xx} & \epsilon_{xy} & 0 \\ -\epsilon_{xy} & \epsilon_{xx} & 0 \\ 0 & 0 & \epsilon_{zz} \end{pmatrix}$$

***antisymmetric tensor***

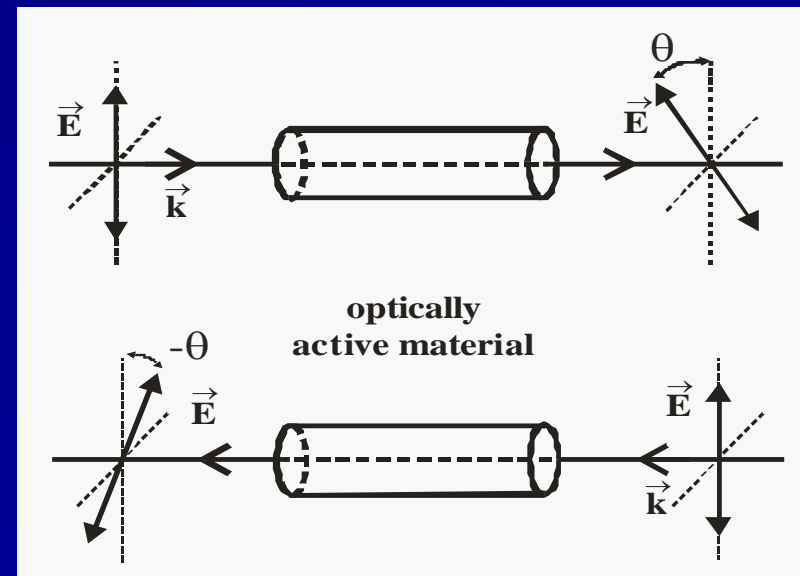
➔ *dielectric tensor is diagonal in a circular coordinate system*

$$\hat{\epsilon}^{\dagger} = \begin{pmatrix} \epsilon_{+} & 0 & 0 \\ 0 & \epsilon_{-} & 0 \\ 0 & 0 & \epsilon_{zz} \end{pmatrix}$$

➔ ***circular dichroism***

➔ *linearly polarized light is rotated along a particular axis*

➔ *the direction of rotation is relative to the direction of the light*



# classification of optical anisotropy: *magneto-optic activity*

$$\hat{\epsilon}^{\dagger} = \begin{pmatrix} \epsilon_{xx} & \epsilon_{xy}(\vec{M}) & 0 \\ -\epsilon_{xy}(\vec{M}) & \epsilon_{xx} & 0 \\ 0 & 0 & \epsilon_{zz} \end{pmatrix}$$

**antisymmetric tensor with magnetic-field-induced off-diagonal elements**

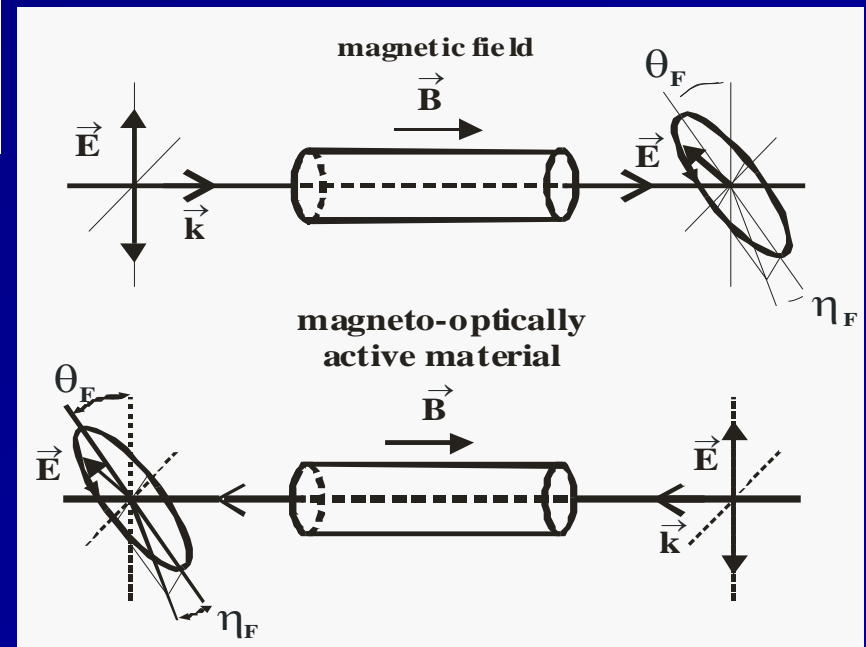
➔ *dielectric tensor is diagonal in a circular coordinate system*

$$\hat{\epsilon}^{\dagger} = \begin{pmatrix} \epsilon_{+}(\vec{M}) & 0 & 0 \\ 0 & \epsilon_{-}(\vec{M}) & 0 \\ 0 & 0 & \epsilon_{zz} \end{pmatrix}$$

➔ *magnetic circular dichroism*

➔ *linearly polarized light is rotated along the direction of magnetization*

➔ *the direction of rotation is relative to the direction of magnetization*



# introduction to the technique of ellipsometry

the optical anisotropy changes the polarization state of the transmitted or reflected light

➔ need an optical technique which is capable to analyze the polarization state of light

➔ ellipsometry

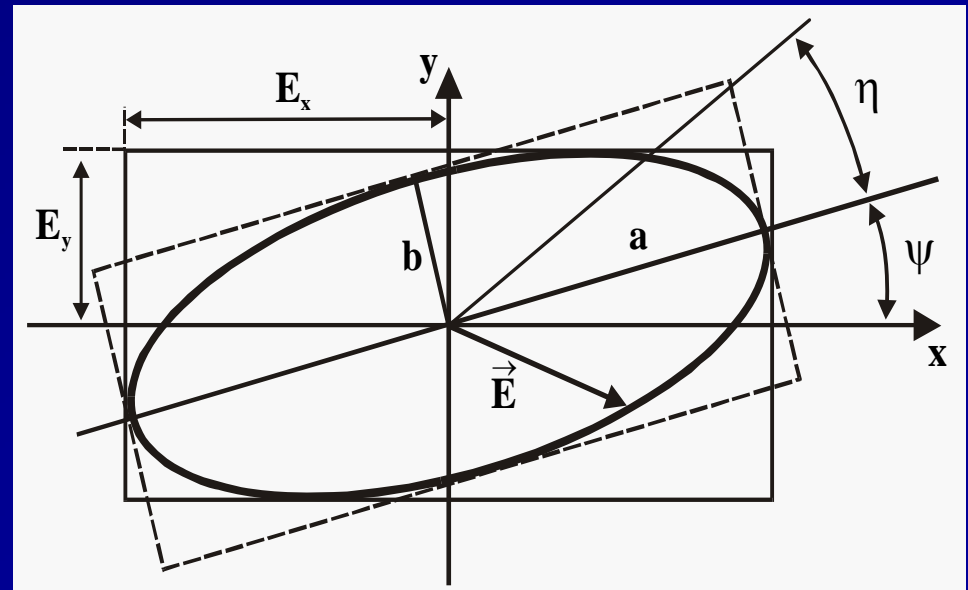
➔ most general polarization state is elliptically polarized light

$$\tan(2\psi) = 2\cos\delta \frac{E_x E_y}{E_x^2 - E_y^2}$$

$$\tan(2\eta) = 2\sin\delta \frac{E_x E_y}{E_x^2 + E_y^2}$$

$$\delta = \delta_y - \delta_x$$

$$\vec{E} = \left( E_x e^{i\delta_x} \hat{e}_x + E_y e^{i\delta_y} \hat{e}_y \right) e^{i(\omega t - \vec{g} \cdot \vec{r})}$$



# introduction to the technique of ellipsometry

it is sufficient to determine the two ellipsometric angles  $\psi$  and  $\eta$

→ *direct measurement of angles*

→ *magneto-optic Kerr spectrometer  
(= null ellipsometer)*

→ *measurement of the complex reflectivity ratio for s- and p-polarized light  $r_p/r_s$*

$$\frac{\tilde{r}_p}{\tilde{r}_s} = \tan(\psi) e^{i\eta}$$

$$\vec{E}_{\text{refl}} = \tilde{r} \vec{E}_0$$

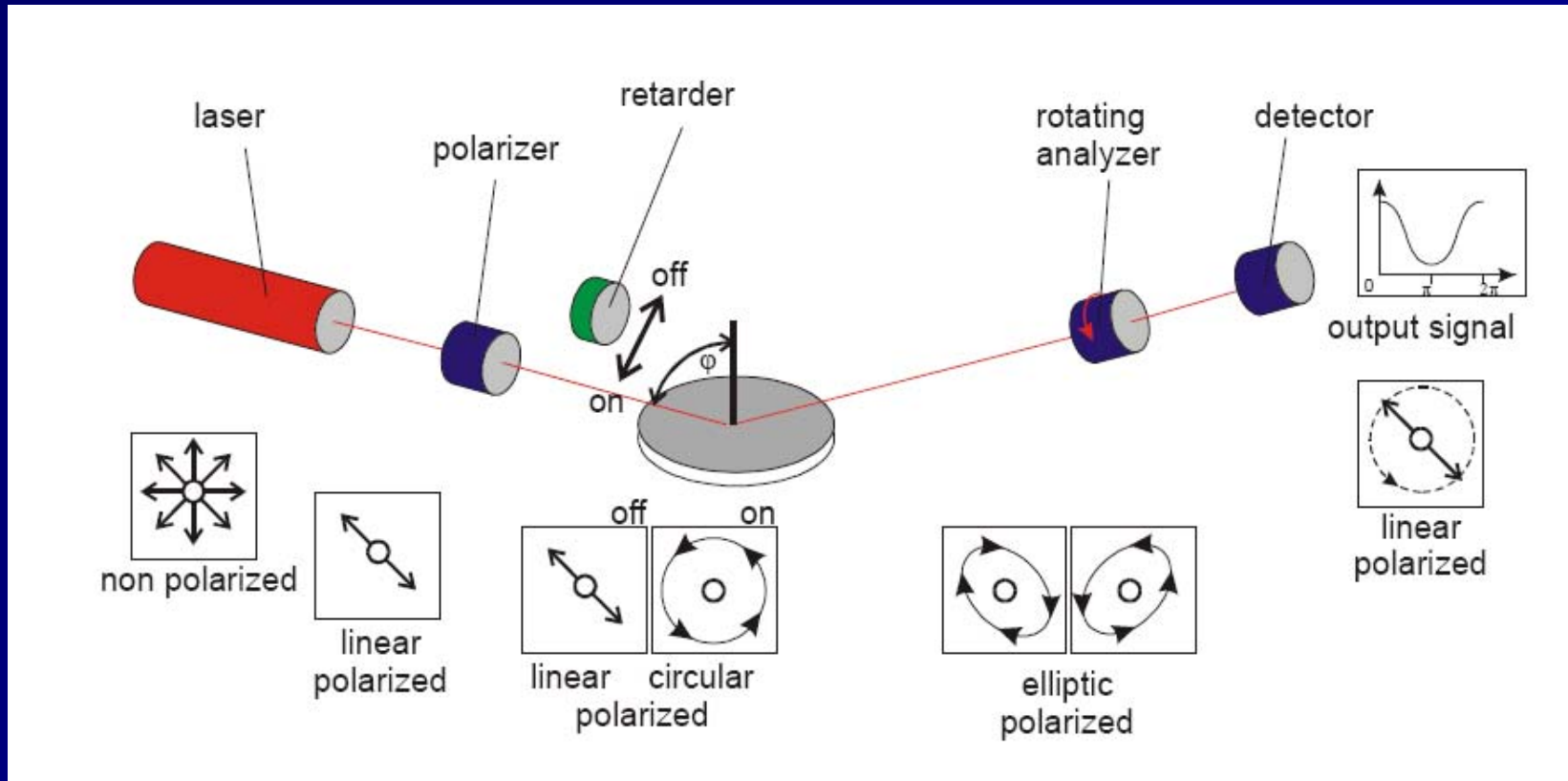
$$\tilde{r} = |\tilde{r}| e^{i\delta_r}$$

→ *rotating analyzer ellipsometer*

→ *phase modulated ellipsometer*

# introduction to the technique of ellipsometry

## rotating analyzer ellipsometer

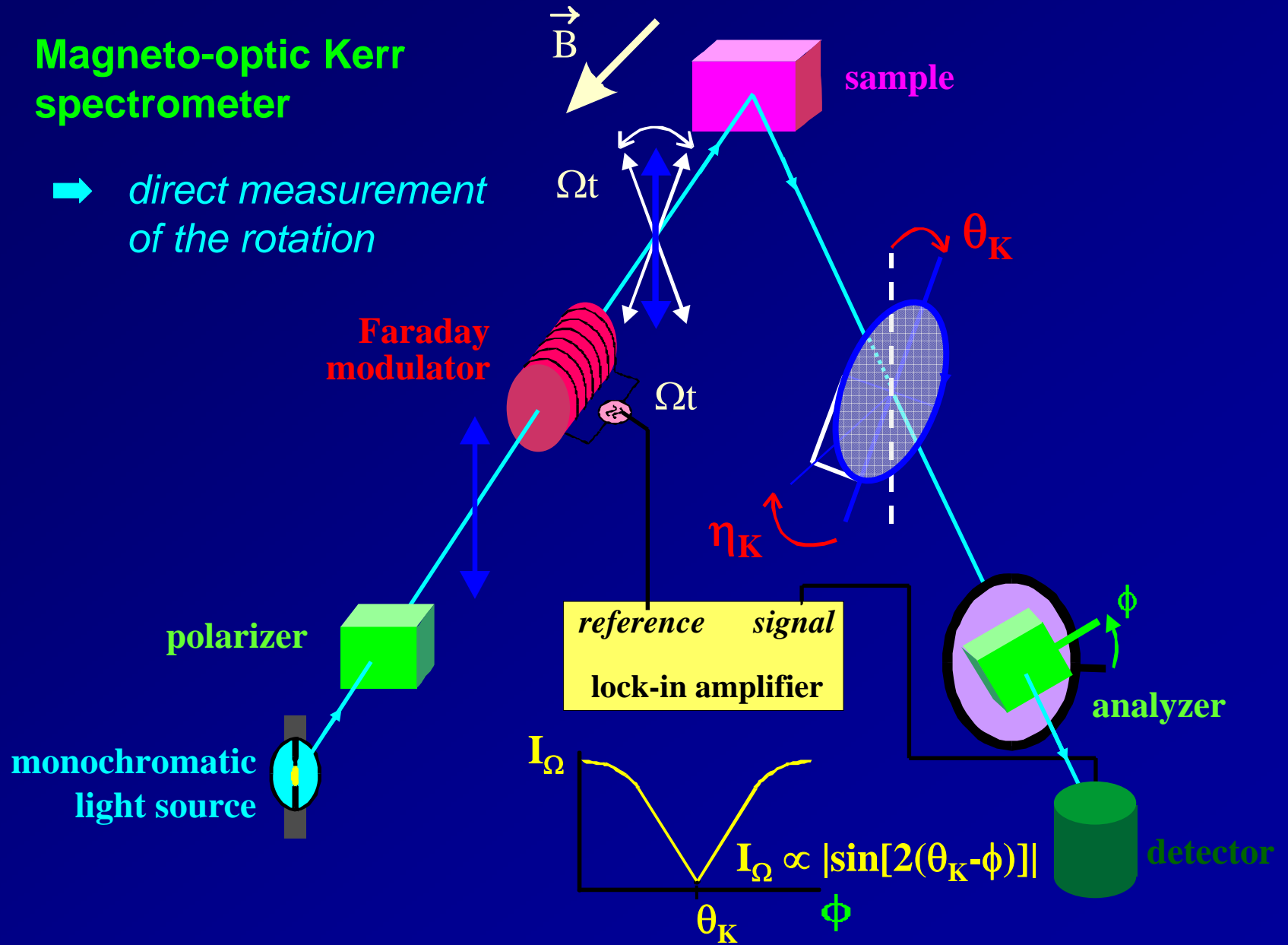


- ➔ *rotating analyzer generates a signal proportional to the projection of the elliptic polarization along the momentary polarizer axis*
- ➔ *sinusoidal intensity curve must be fitted ➔  $\Psi, \eta$*

# introduction to the technique of ellipsometry

## Magneto-optic Kerr spectrometer

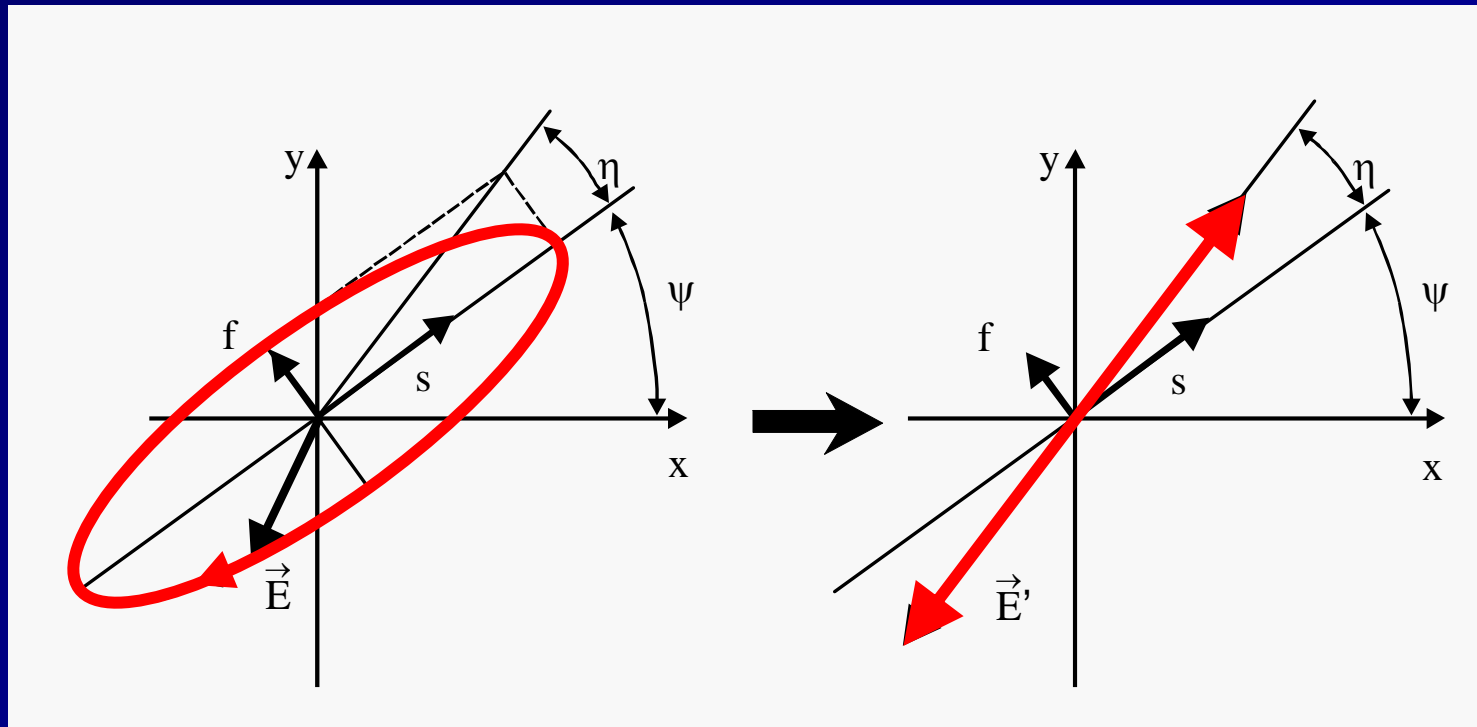
→ direct measurement of the rotation



# introduction to the technique of ellipsometry

## principle of Senarmont

- transforms ellipticity into a rotation using a phase shifter with  $\lambda/4$  retardation between  $f$  (fast) and  $s$  (slow) axis
- direct measurement of the ellipticity



# implications for single-molecule spectroscopy

## single molecule anisotropy

→ *polarization = dipole density*

$$\vec{P} = \frac{1}{V} \sum_N \vec{p}_i$$

→ *single molecule with dipole moment  $\vec{p}_{s.m.}$  induces local polarization*

$$\vec{P}_{local} = \frac{1}{V} \vec{p}_{s.m.}$$

→ *local anisotropy in dielectric function*

$$\vec{D} = \epsilon_0 \vec{E} + \vec{P}_{local} = \vec{\epsilon}_{local} \vec{E}$$

→ *contribution to static part ( $\omega = 0$ ) of dielectric function: electric shielding, Stark effect*

→ *contribution to optical part of dielectric function: Hertz dipole, IR resonance, fluorescence*

→ *increase the local polarization by reduction of volume in the near-field*

$$\vec{P}_{local} = \frac{1}{V_{near-field}} \vec{p}_{s.m.}$$

$$V_{near-field} \ll V$$

## summary

- ⇒ *optical anisotropy changes state of polarization of light*
- ⇒ *ellipsometry is capable of determining any polarization state*
- ⇒ *single molecules induce local anisotropy*
- ⇒ *near-field measurements enhance effect of local anisotropy through reduction of the interaction volume*
- ⇒ *the open question is, at which photon energy this effect is most prominent*