Ellipsometry:

a tool to study single-molecule-induced anisotropy?

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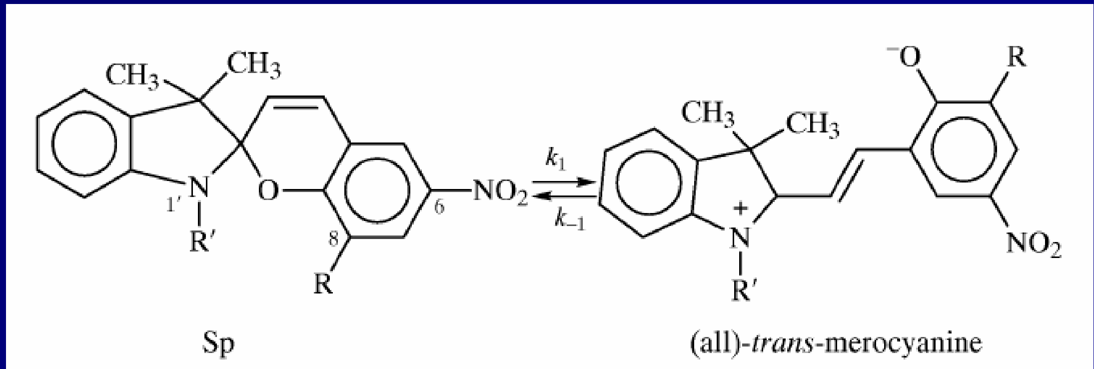
Outline

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

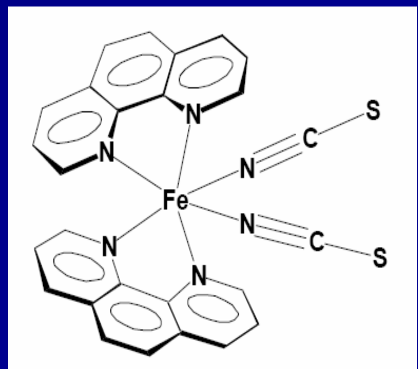
introduction

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*

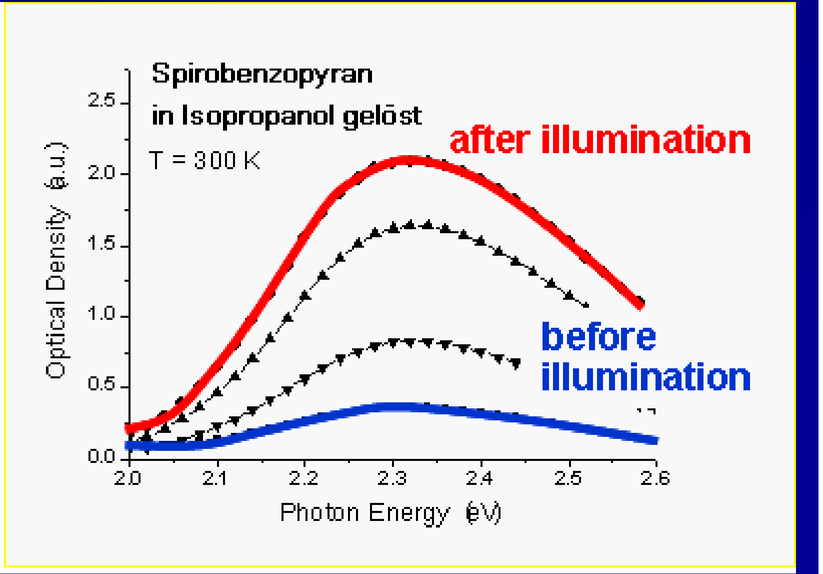


$Fe(phenanthroline)_2(NCS)_2$

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*

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

$$\vec{\nabla} \times \vec{E} = -\dot{\vec{B}} \qquad \vec{\nabla} \times \vec{B} = \mu_0 \varepsilon_0 \dot{\vec{E}}$$

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

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

$$\vec{\nabla} \times \vec{E} = -\dot{\vec{B}} \qquad \vec{\nabla} \times \vec{H} = \vec{j} + \dot{\vec{D}}$$

$$\vec{D} = \varepsilon_0 \vec{E} + \vec{P} \qquad \vec{B} = \mu_0 \left(\vec{H} + \vec{M}\right)$$

$\vec{D}$ = electric displacement *$\vec{H}$ = magnetic field in vacuum*

$\vec{P}$ = polarization *$\vec{M}$ = magnetization*

fundamentals of optical properties

material properties *(in linear approximation)*

$$\vec{P} = \alpha \vec{E} \quad \Rightarrow \quad \vec{D} = \varepsilon_0 \vec{E} + \vec{P} = \varepsilon\varepsilon_0 \vec{E} = \left(1 + \frac{\alpha}{\varepsilon_0}\right)\varepsilon_0 \vec{E}$$

$$\vec{M} = \chi_{mag} \vec{H} \quad \Rightarrow \quad \vec{B} = \mu_0\left(\vec{H} + \vec{M}\right) = \mu\mu_0 \vec{H} = \mu_0\left(1 + \chi_{mag}\right)\vec{H}$$

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

α = polarizability

ε = dielectric function

χ_{mag} = magnetic susceptibility

μ = magnetic permeability

σ = optical conductivity

in anisotropic materials:

tensors of rank two!

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

fundamentals of optical properties

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

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

$$\vec{\nabla}\times\vec{H} = \vec{j} + \dot{\vec{D}} \quad \Rightarrow \quad \vec{\nabla}\times\vec{H} = \vec{j} + \dot{\vec{D}} = \sigma\vec{E} + \varepsilon\varepsilon_0\dot{\vec{E}} = \left(\varepsilon - i\frac{\sigma}{\varepsilon_0\omega}\right)\varepsilon_0\dot{\vec{E}}$$

$$\Rightarrow \quad \tilde{\varepsilon} = \left(\varepsilon - i\frac{\sigma}{\varepsilon_0\omega}\right) = \varepsilon_1 - i\varepsilon_2$$

complex dielectric function

$$\Rightarrow \quad \tilde{\varepsilon} = 1 - i\frac{\tilde{\sigma}}{\varepsilon_0\omega} \qquad \tilde{\sigma} = \sigma_1 - i\sigma_2$$

complex optical conductivity

fundamentals of optical properties

Maxwell equations in *complex notation* (μ = 1)

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

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

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

$$\vec{\nabla} \times \vec{B} = \mu_0 \varepsilon_0 \tilde{\varepsilon} \dot{\vec{E}} = \frac{\tilde{\varepsilon}}{c^2} \dot{\vec{E}}$$

fundamentals of optical properties

wave equation in an *isotropic* material

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

$$\Delta \vec{E} = \frac{\tilde{\varepsilon}}{c^2} \frac{\partial^2 \vec{E}}{\partial t^2} \;\Rightarrow\; (\tilde{\vec{g}} \cdot \tilde{\vec{g}}) \vec{E} = \tilde{g}^2 \, \vec{E} = \frac{\omega^2}{c^2} \tilde{\varepsilon} \, \vec{E}$$

$\Rightarrow$ $\tilde{g} = (g_1 - i g_2) = \sqrt{\tilde{\varepsilon}} \, \frac{\omega}{c} = \tilde{n} \, \frac{\omega}{c}$ *complex wave vector*

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

fundamentals of optical properties

wave equation in an *anisotropic* material

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

$\vec{\nabla} \cdot \vec{D} = \vec{\nabla} \cdot (\tilde{\overleftrightarrow{\varepsilon}} \vec{E}) = 0$ ➡ $\vec{\nabla} \cdot \vec{E} \neq 0$

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

➡ $$(\tilde{\vec{g}} \cdot \tilde{\vec{g}})\vec{E} - (\tilde{\vec{g}} \cdot \vec{E})\tilde{\vec{g}} = \left(\frac{\omega}{c}\right)^2 \tilde{\overleftrightarrow{\varepsilon}} \vec{E}$$

complicated optical behavior!

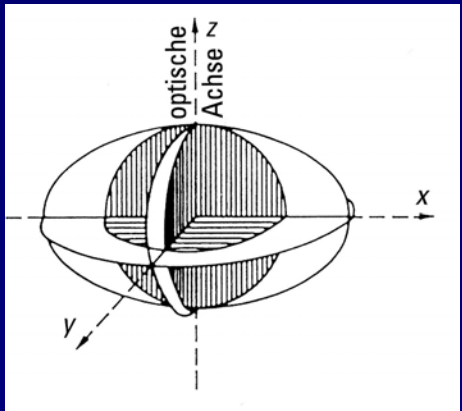
classification of optical anisotropy: *linear birefringence*

$\vec{D} = \overleftrightarrow{\varepsilon}\,\vec{E}$

$$\overleftrightarrow{\varepsilon} = \begin{pmatrix} \varepsilon_{xx} & \varepsilon_{xy} & \varepsilon_{xz} \\ \varepsilon_{xy} & \varepsilon_{yy} & \varepsilon_{yz} \\ \varepsilon_{xz} & \varepsilon_{yz} & \varepsilon_{zz} \end{pmatrix}$$

symmetric tensor

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



➡ *principal axes*

$$\overleftrightarrow{\tilde{\varepsilon}} = \begin{pmatrix} \varepsilon_{xx} & 0 & 0 \\ 0 & \varepsilon_{yy} & 0 \\ 0 & 0 & \varepsilon_{zz} \end{pmatrix}$$

➡ *Fresnel ellipsoid*

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

$\vec{E} = \overleftrightarrow{\varepsilon}^{-1}\vec{D}$ ➡ *index ellipsoid*

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

$$\overleftrightarrow{\tilde{\varepsilon}}^{-1} = \begin{pmatrix} n_{xx}^{-2} & 0 & 0 \\ 0 & n_{yy}^{-2} & 0 \\ 0 & 0 & n_{zz}^{-2} \end{pmatrix}$$

classification of optical anisotropy:
linear birefringence

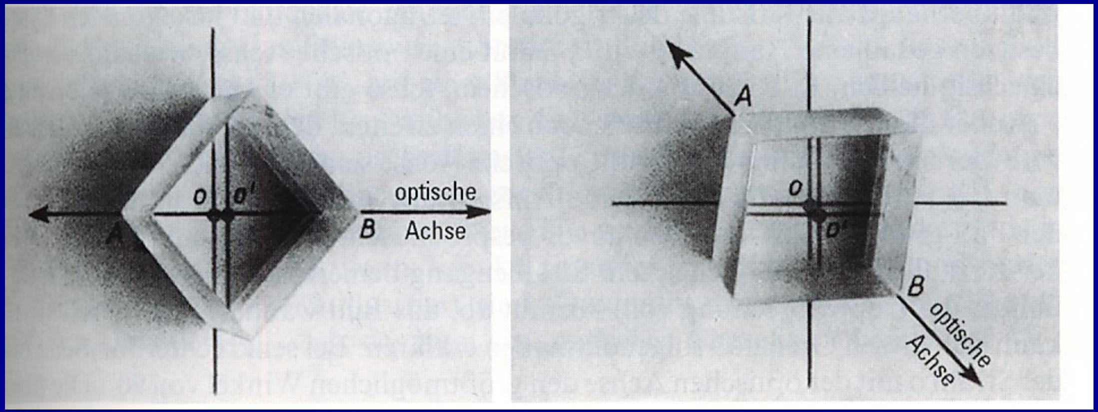
crystals with a single optical axis

$$\overleftrightarrow{\varepsilon} = \begin{pmatrix} \varepsilon_{xx} & 0 & 0 \\ 0 & \varepsilon_{xx} & 0 \\ 0 & 0 & \varepsilon_{zz} \end{pmatrix}$$

calcite $CaCo_3$, quartz SiO_2 or any tetragonal, hexagonal, or rhombohedral crystal

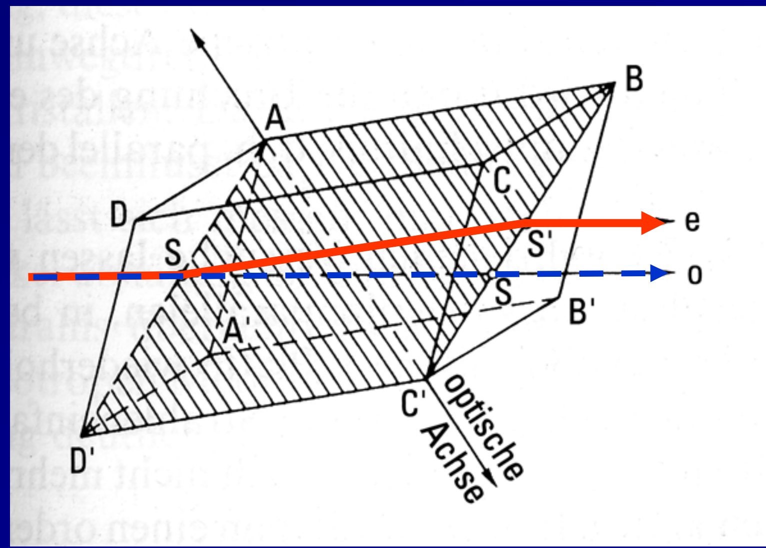
➡ *there exists a single direction, where light propagation is isotropic*
   ➡ *optical axis*

➡ *in all other directions, two orthogonally polarized waves with different velocities will propagate*
   ➡ *ordinary and extraordinary ray*

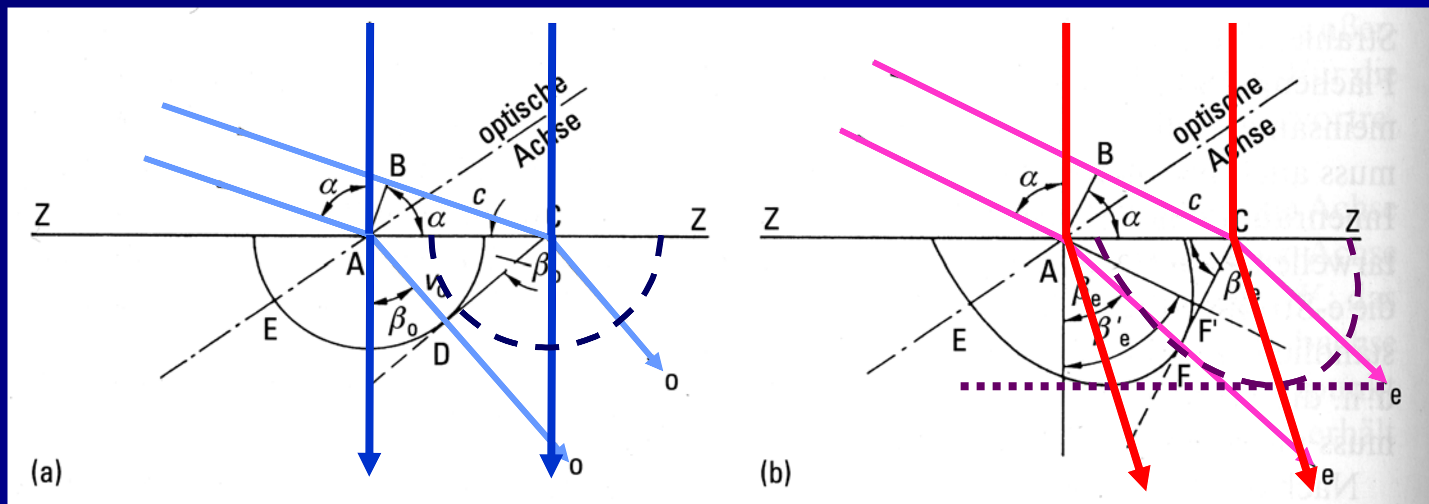


classification of optical anisotropy: *linear birefringence*

crystals with a single optical axis



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



ordinary ray *extraordinary ray*

classification of optical anisotropy: *optical activity*

$$\overleftrightarrow{\varepsilon} = \begin{pmatrix} \varepsilon_{xx} & \varepsilon_{xy} & 0 \\ -\varepsilon_{xy} & \varepsilon_{xx} & 0 \\ 0 & 0 & \varepsilon_{zz} \end{pmatrix}$$

antisymmetric tensor

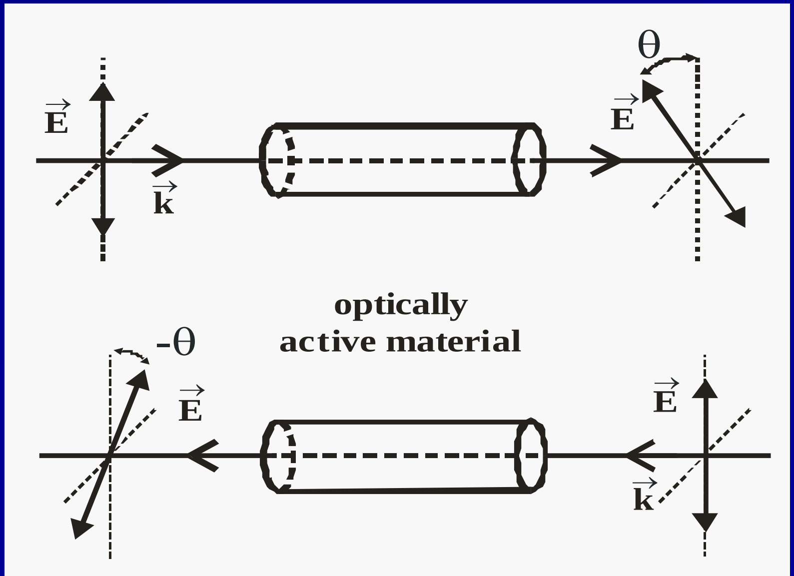
➡ *dielectric tensor is diagonal in a circular coordinate system*

$$\overleftrightarrow{\varepsilon} = \begin{pmatrix} \varepsilon_{+} & 0 & 0 \\ 0 & \varepsilon_{-} & 0 \\ 0 & 0 & \varepsilon_{zz} \end{pmatrix}$$

➡ *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*

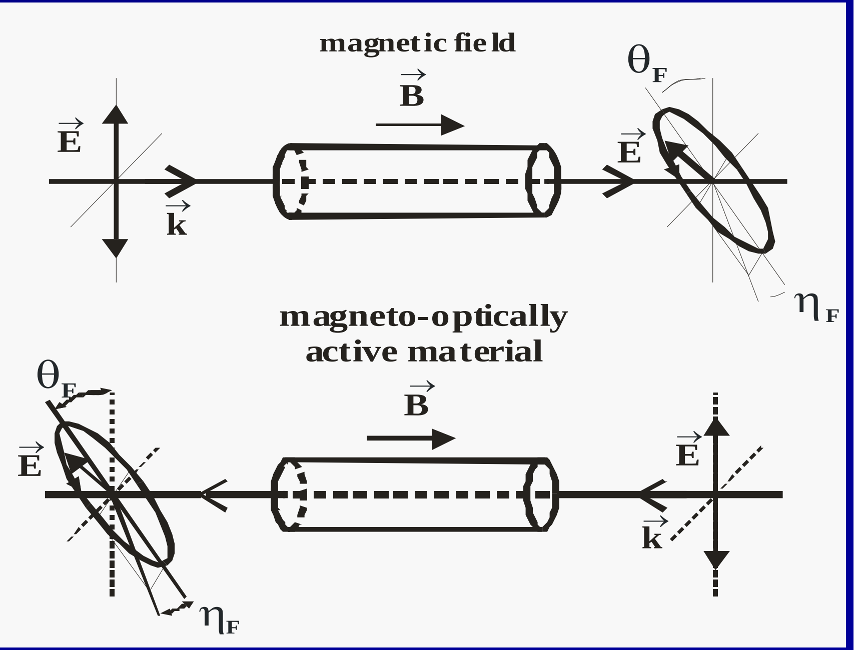
$$\overleftrightarrow{\varepsilon} = \begin{pmatrix} \varepsilon_{xx} & \varepsilon_{xy}(\vec{M}) & 0 \\ -\varepsilon_{xy}(\vec{M}) & \varepsilon_{xx} & 0 \\ 0 & 0 & \varepsilon_{zz} \end{pmatrix}$$

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

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

$$\overleftrightarrow{\varepsilon} = \begin{pmatrix} \varepsilon_{+}(\vec{M}) & 0 & 0 \\ 0 & \varepsilon_{-}(\vec{M}) & 0 \\ 0 & 0 & \varepsilon_{zz} \end{pmatrix}$$

➡ *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*

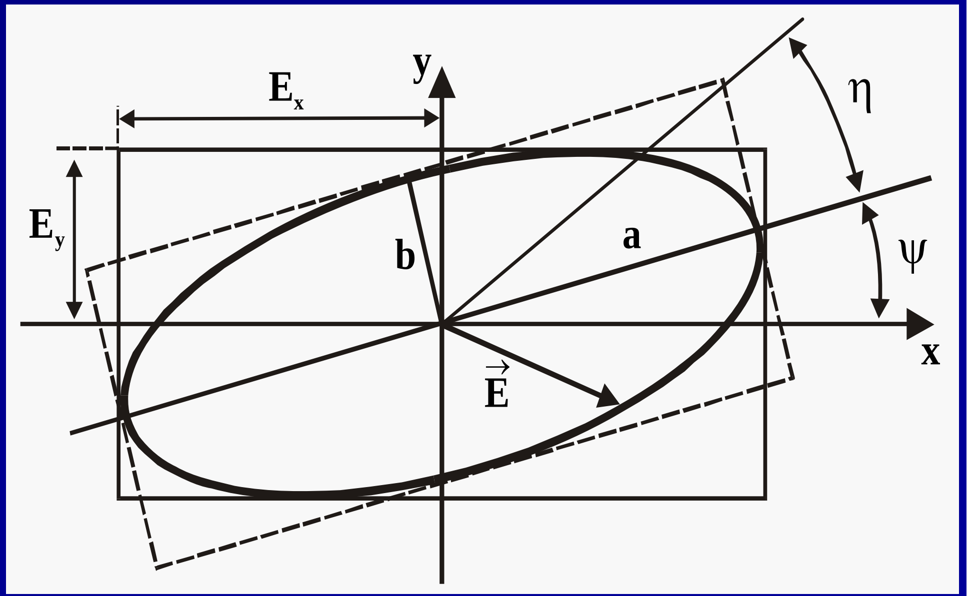
➡ *most general polarization state is elliptically polarized light*

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

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

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

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



introduction to the technique of ellipsometry

it is sufficient to determine the two ellipsometric angles ψ and η

➡ *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

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

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

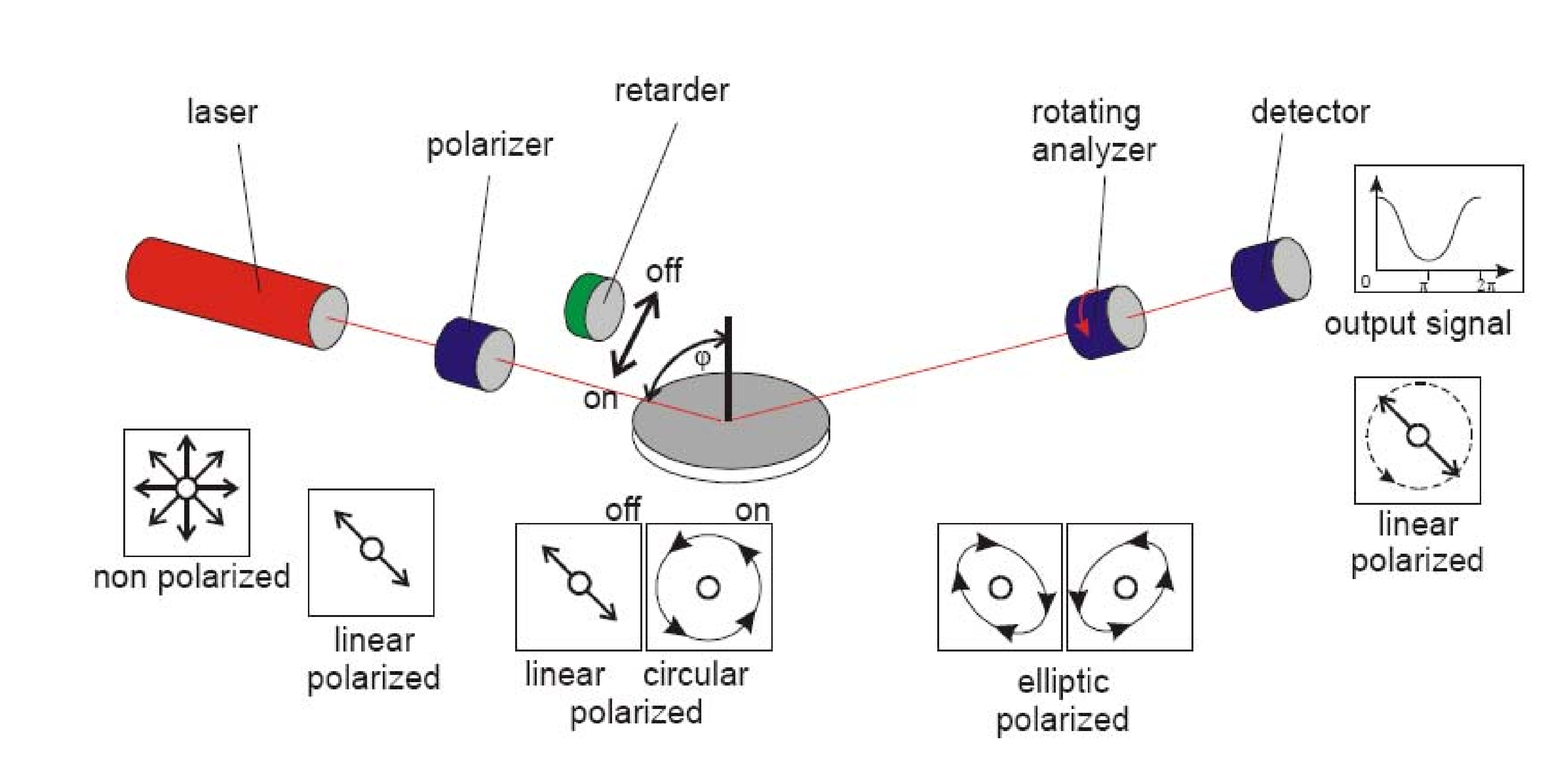
$$\tilde{r} = |\tilde{r}|\, e^{i\delta_r}$$

➡ *rotating analyzer ellipsometer*

➡ *phase modulated ellipsometer*

introduction to the technique of ellipsometry

rotating analyzer ellipsometer



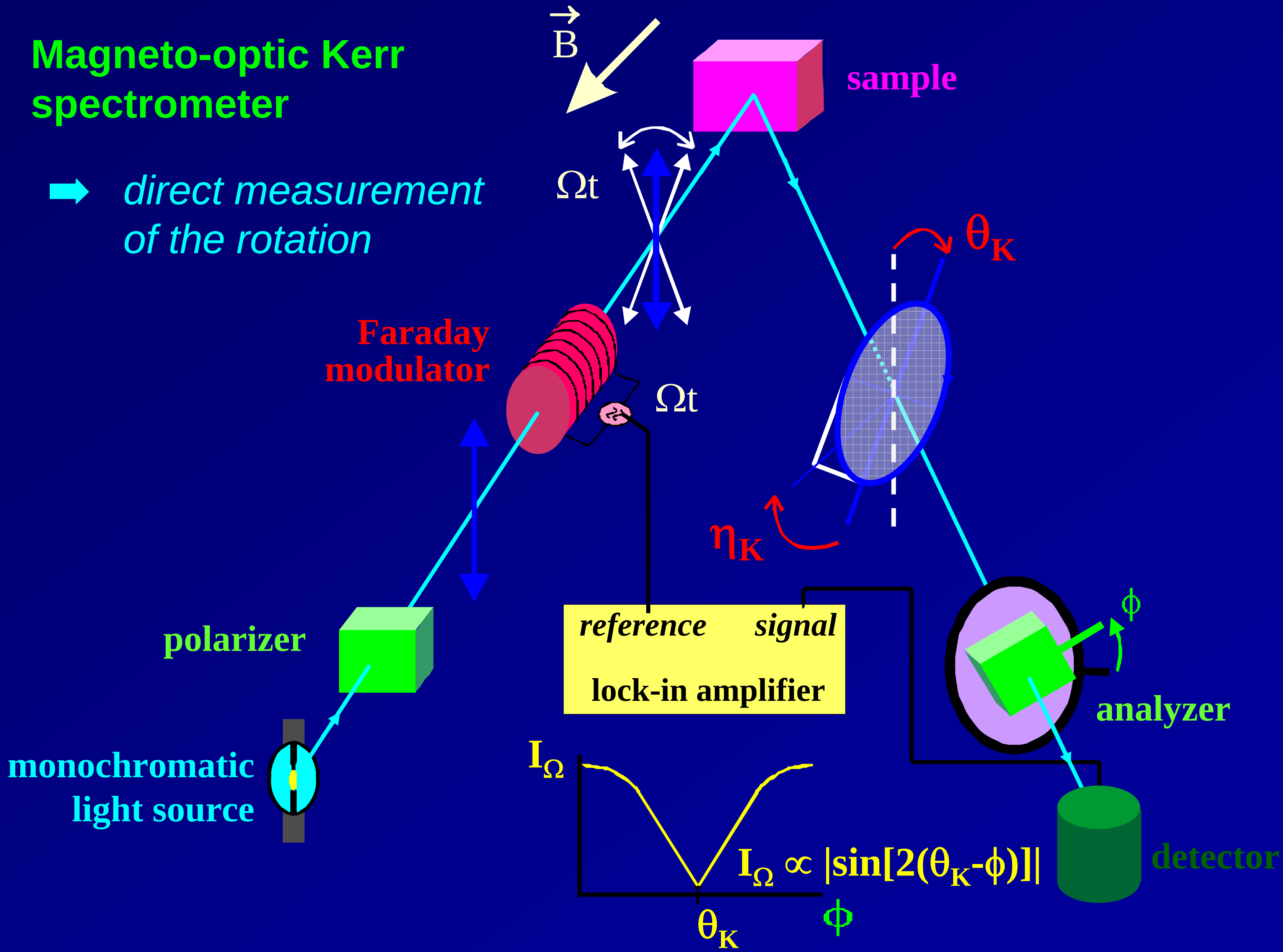
➡ *rotating analyzer generates a signal proportional to the projection of the elliptic polarization along the momentary polarizer axis*

➡ *sinusoidal intensity curve must be fitted* ➡ Ψ, η

introduction to the technique of ellipsometry

Magneto-optic Kerr spectrometer

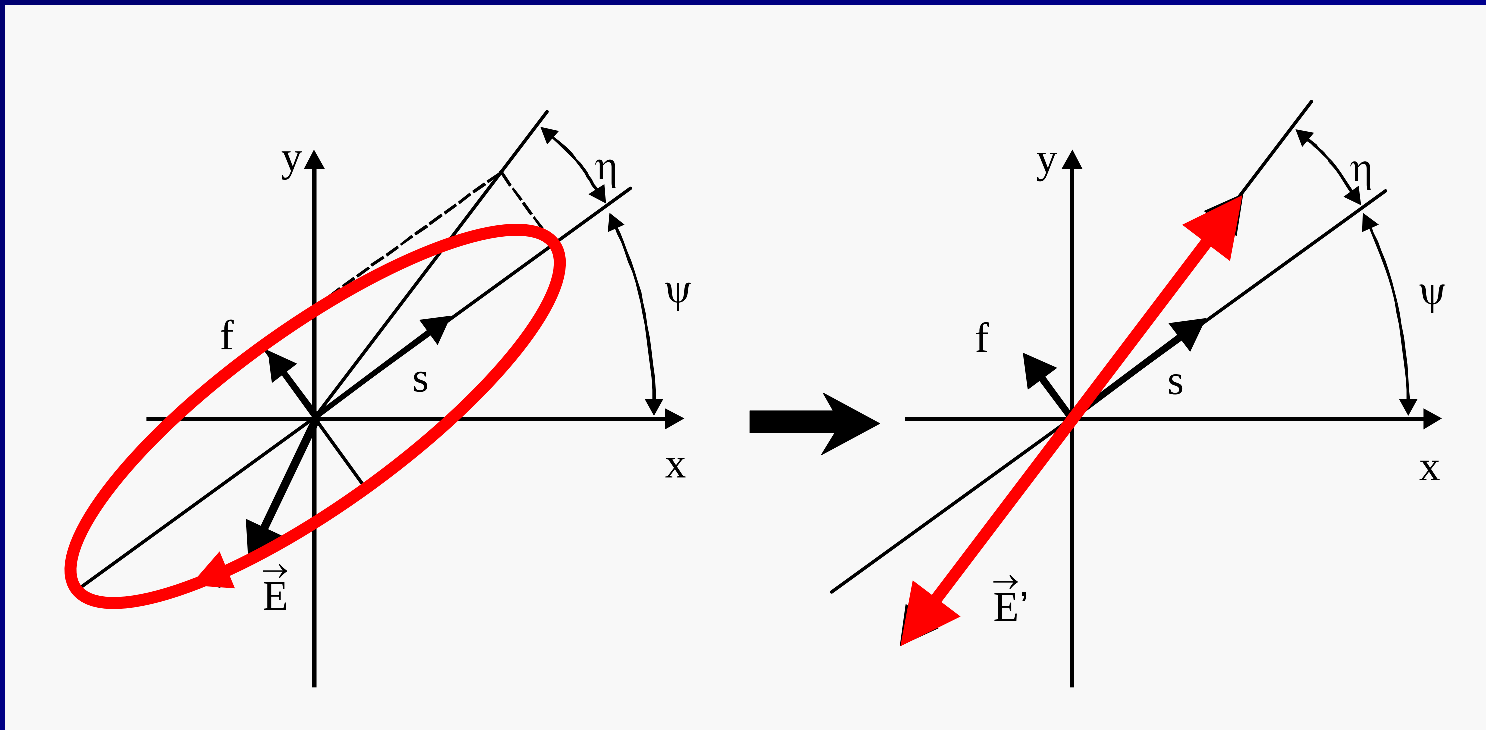
➡ *direct measurement of the rotation*



introduction to the technique of ellipsometry

principle of Senarmont

- ➡ *transforms ellipticity into a rotation using a phase shifter with λ/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*

$$\vec{D} = \varepsilon_0\vec{E} + \vec{P}_{local} = \overleftrightarrow{\varepsilon}_{local}\vec{E}$$

➡ *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*

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

$V_{near-field} << V$

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*