

Techniques chiroptiques développées au sein du groupe GSM de l'ISM

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Techniques chiroptiques

Polarimétrie

$$[\alpha]_{\lambda, c}^T = \frac{\pi}{\lambda} (n_L - n_R) \ell$$

Dispersion rotatoire optique (ORD)

$$\alpha(\lambda) \propto n_L(\lambda) - n_R(\lambda)$$

Dichroïsme circulaire électronique (ECD)

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

Dichroïsme circulaire vibrationnel (VCD)

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

Activité optique Raman (ROA)

$$\text{ROA} = I_R(\lambda) - I_L(\lambda)$$

Luminescence polarisée circulairement (CPL)

$$\text{CPL} = I_L(\lambda) - I_R(\lambda)$$

Intensités en absorption infrarouge et en VCD

Absorption IR



Force d'oscillateur

$$D_i^{01} = \frac{\hbar}{2\omega_i} \left| \left(\frac{\partial \vec{\mu}}{\partial Q_i} \right)_0 \right|^2$$



moment dipolaire électrique

$$D_i^{01} = \frac{9.2 \cdot 10^{-39}}{\nu_0 \text{cl}} \int^{\text{band}} A(\nu) d\nu$$

VCD



Force rotationnelle

$$R_i^{01} = \frac{\hbar}{2i\omega_i} \left(\frac{\partial \vec{\mu}}{\partial Q_i} \right)_0 \cdot \left(\frac{\partial \vec{m}}{\partial Q_i} \right)_0$$

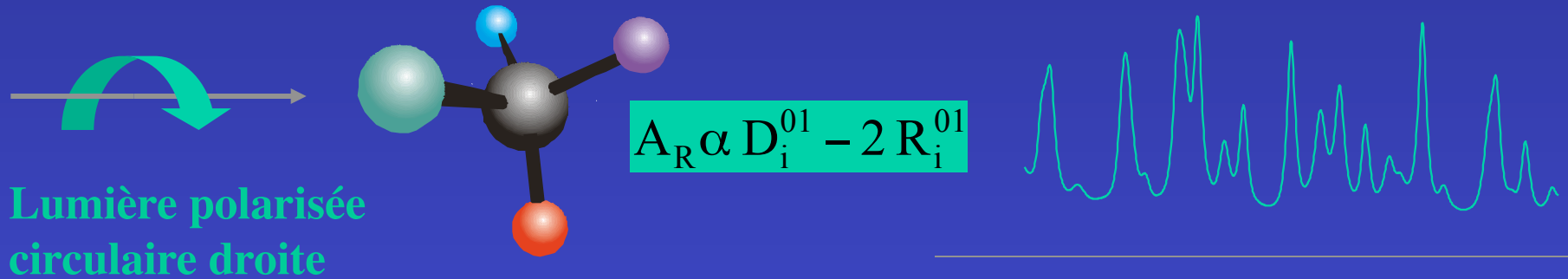
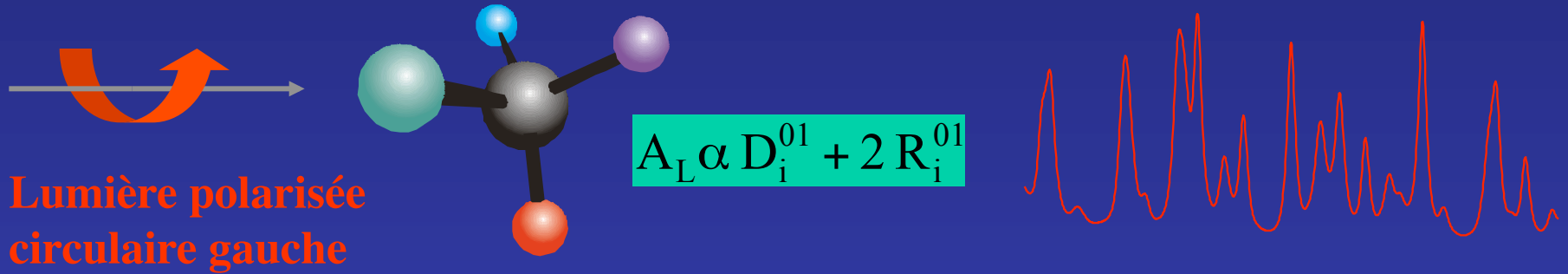


moment dipolaire magnétique

$$R_i^{01} = \frac{2.3 \cdot 10^{-39}}{\nu_0 \text{cl}} \int^{\text{band}} \Delta A(\nu) d\nu$$

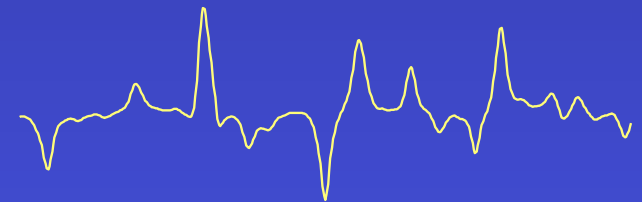
$$\Delta A(\nu) = A_L(\nu) - A_R(\nu)$$

Interaction d'une molécule chirale avec une onde polarisée circulairement

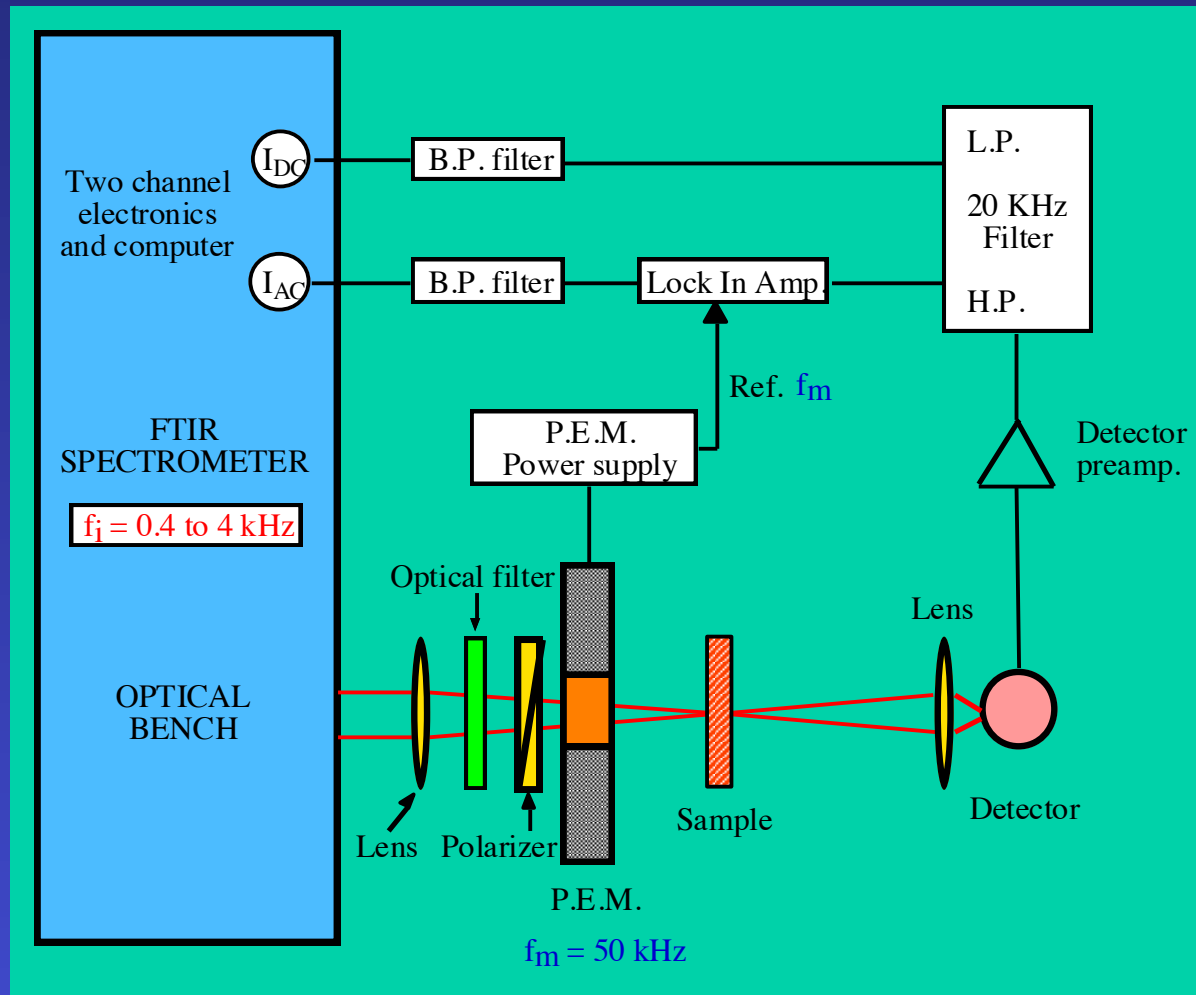


Spectre VCD : $\Delta A = A_L - A_R$

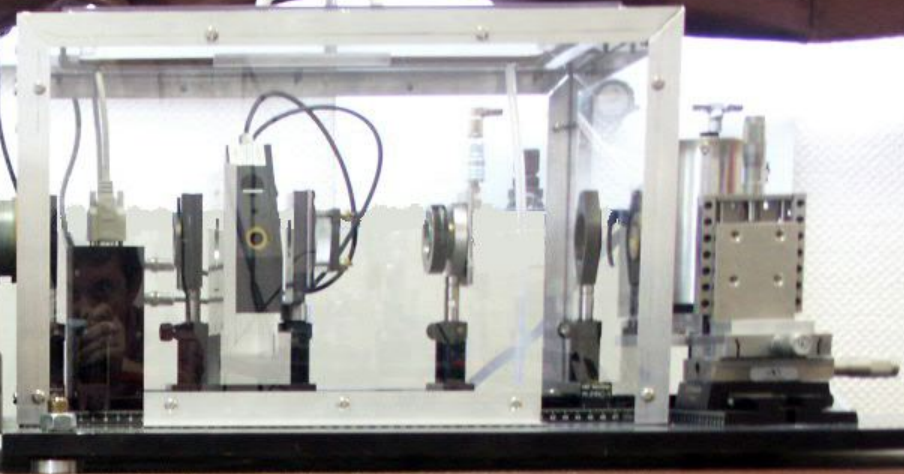
$\Delta A = 10^{-4} - 10^{-6} \text{ AU}$



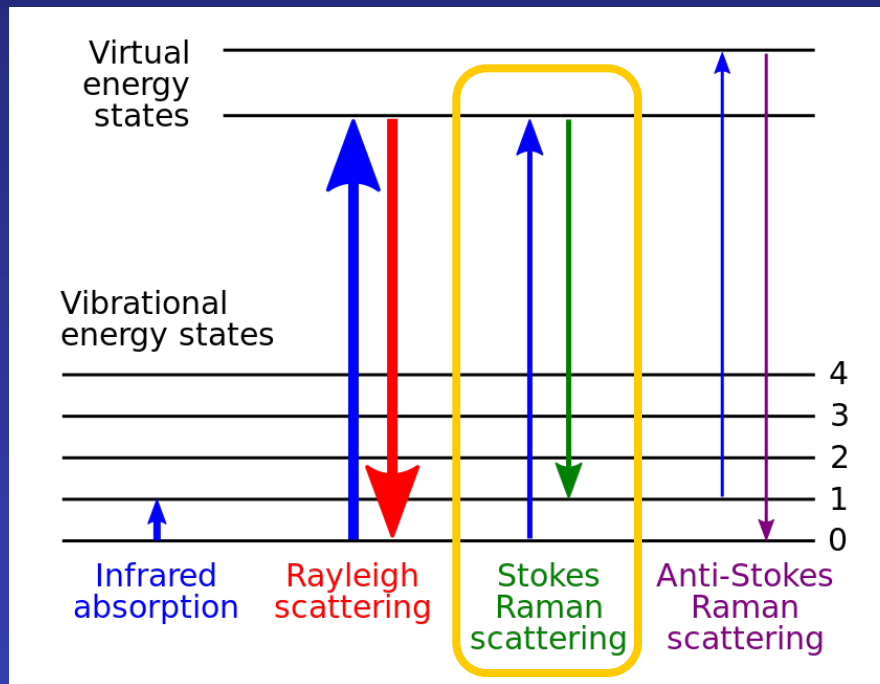
Montage optique, traitement électronique du signal



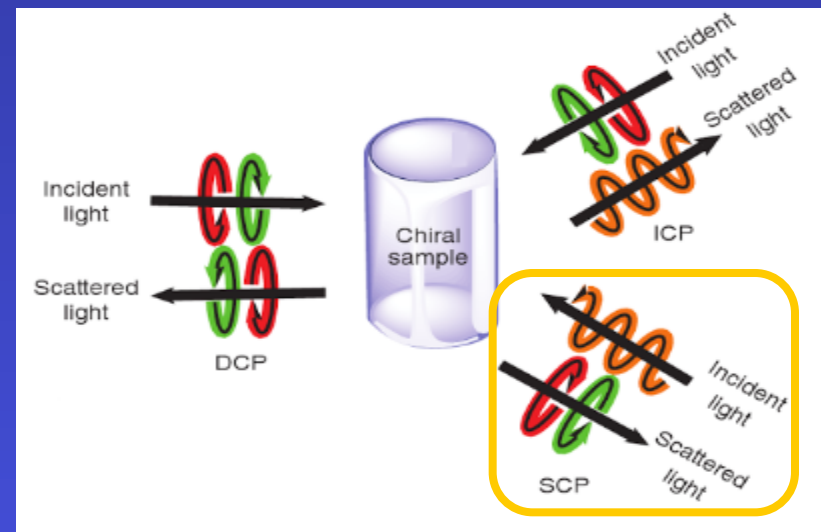
$$\frac{I_{AC}(\bar{\nu})}{I_{DC}(\bar{\nu})} = [J_1[\varphi_0(\bar{\nu})] \exp[-(2V\bar{\nu})\tau] (\text{Ln}(10))] \cdot \Delta A(\bar{\nu})$$



Activité Optique Raman (ROA)



ROA method	Incident polarization	Scattered polarization
ICP	RCP/LCP	linear or unpolarized
SCP	linear or unpolarized	RCP/LCP
DCP I	RCP/LCP	RCP/LCP
DCP II	RCP/LCP	LCP/RCP



Théorie du ROA

Pour expliquer la différence de réponse à une onde incidente polarisée circulairement gauche ou droite, on doit tenir compte de termes supplémentaires du moment dipolaire, dus à l'onde incidente, son champ magnétique oscillant \mathbf{B} et le gradient de son champ électrique \mathbf{E} .

Moment dipolaire induit

Moment magnétique induit

Moment quadripolaire électrique induit

$$\begin{aligned}\mu_\alpha &= \alpha_{\alpha\beta} E_\beta + \frac{1}{\omega} G'_{\alpha\beta} \dot{B}_\beta + \frac{1}{3} A_{\alpha\beta\gamma} \nabla_\beta E_\gamma + \dots, \\ m_\alpha &= -\frac{1}{\omega} G'_{\beta\alpha} \dot{E}_\beta + \dots, \\ \Theta_{\alpha\beta} &= A_{\alpha\beta\gamma} E_\gamma + \dots\end{aligned}$$

Polarisabilité $\mu.\mu$

$$\alpha_{\alpha\beta} = \frac{2}{\hbar} \sum_{j \neq n} \frac{\omega_{jn}}{\omega_{jn}^2 - \omega^2} \text{Re}(\langle n | \mu_\alpha | j \rangle \langle j | \mu_\beta | n \rangle),$$

Activité optique $\mu.m$

$$G'_{\alpha\beta} = -\frac{2}{\hbar} \sum_{j \neq n} \frac{\omega}{\omega_{jn}^2 - \omega^2} \text{Im}(\langle n | \mu_\alpha | j \rangle \langle j | m_\beta | n \rangle),$$

Activité optique $\mu.\Theta$

$$A_{\alpha\beta\gamma} = \frac{2}{\hbar} \sum_{j \neq n} \frac{\omega_{jn}}{\omega_{jn}^2 - \omega^2} \text{Re}(\langle n | \mu_\alpha | j \rangle \langle j | \Theta_{\beta\gamma} | n \rangle).$$

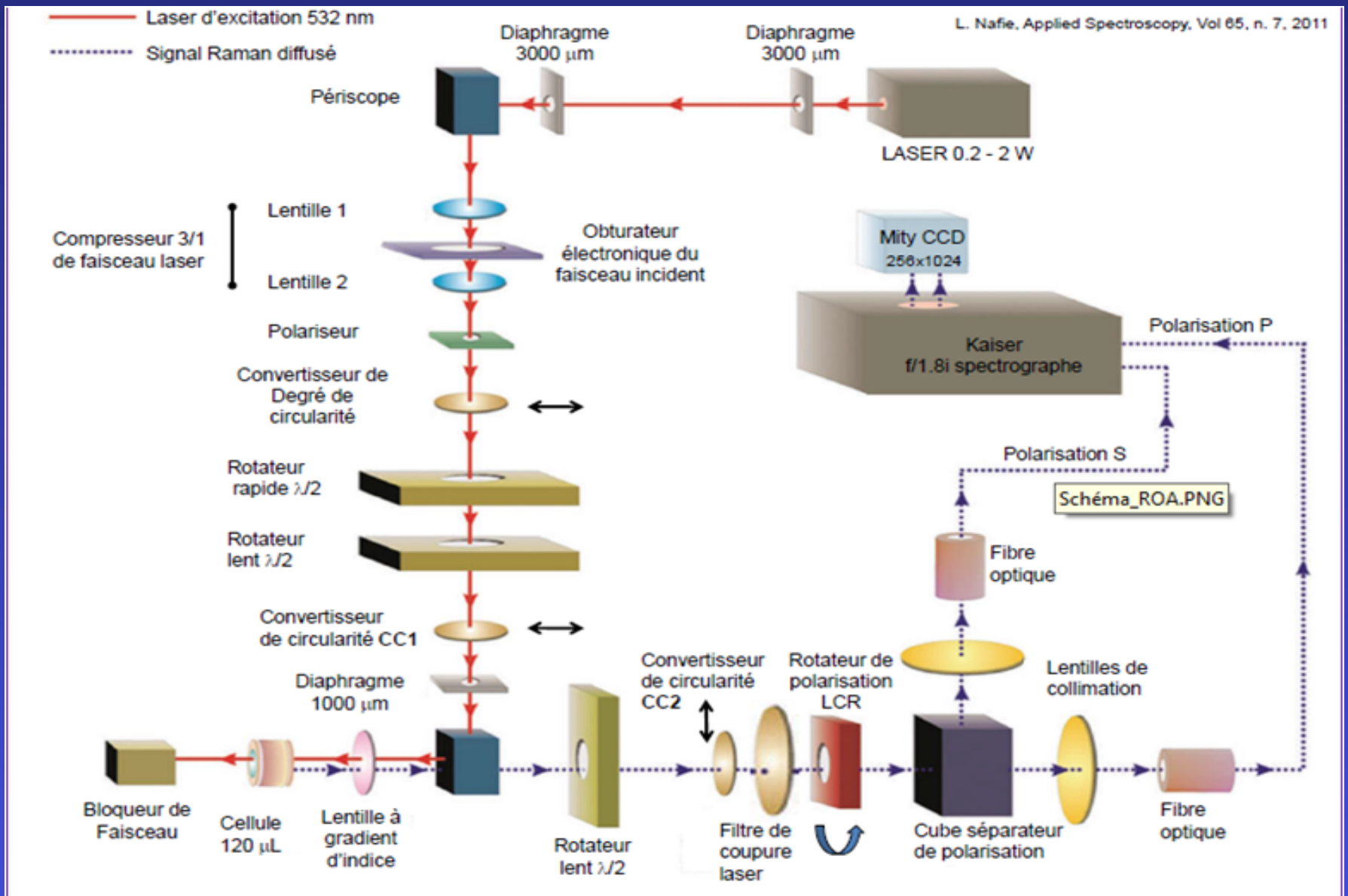
Réduction aux invariants isotropes et anisotropes

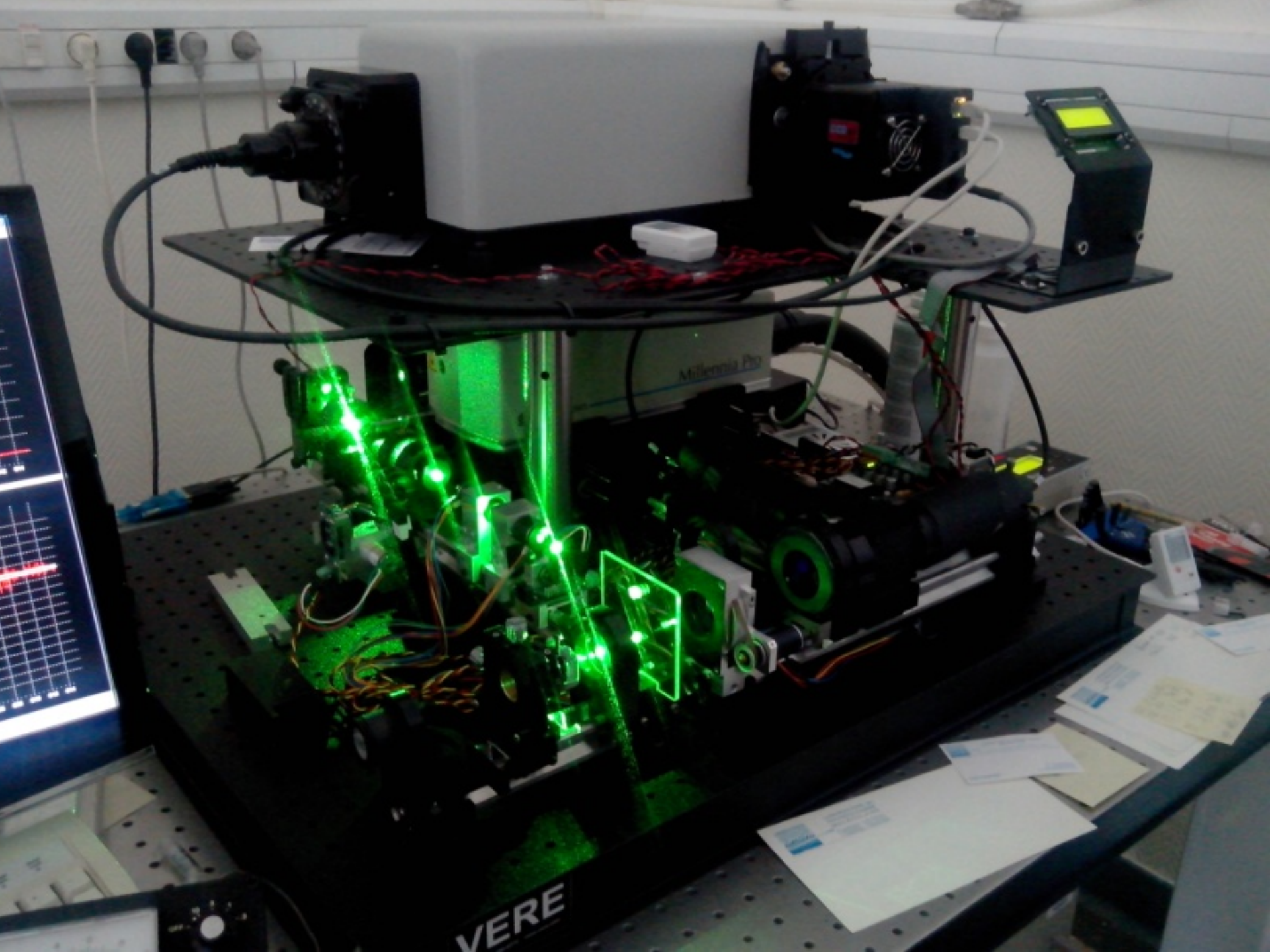
$$\begin{aligned}\alpha &= \frac{1}{3} \alpha_{\alpha\alpha} = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}), \\ G' &= \frac{1}{3} G'_{\alpha\alpha} = \frac{1}{3} (G'_{xx} + G'_{yy} + G'_{zz})\end{aligned}$$

$$\begin{aligned}\beta(\alpha)^2 &= \frac{1}{2} (3\alpha_{\alpha\beta} \alpha_{\alpha\beta} - \alpha_{\alpha\alpha} \alpha_{\beta\beta}), \\ \beta(G')^2 &= \frac{1}{2} (3\alpha_{\alpha\beta} G'_{\alpha\beta} - \alpha_{\alpha\alpha} G'_{\beta\beta}), \\ \beta(A)^2 &= \frac{1}{2} \omega \alpha_{\alpha\beta} \varepsilon_{\alpha\gamma\delta} A_{\gamma\delta\beta},\end{aligned}$$

$$\text{CID} = \frac{\text{ROA(SCP)}}{\text{RAMAN}} = \frac{I_R - I_L}{I_R + I_L} = \frac{24 \left[\beta(G')^2 + \frac{1}{3} \beta(A)^2 \right]}{c \left[45\alpha^2 + 7\beta(\alpha)^2 \right]} < 10^{-3}$$

Schéma optique du ROA





VERE

Millennia Pro

Applications du VCD et du ROA

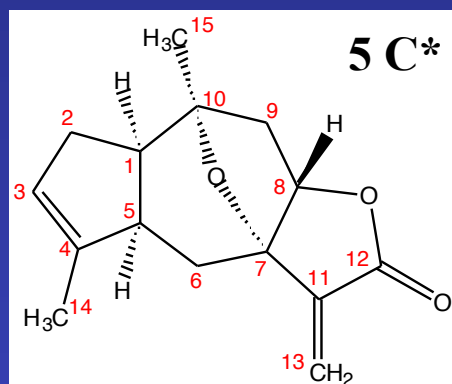
- Détermination de la configuration absolue d'une molécule naturelle chirale (guaianolide)
- Détermination de la conformation absolue d'une molécule chirale (2,2'-bioxirane)
- Induction de chiralité dans des assemblages supramoléculaires (gels bigéminés)
- Détermination de la structure secondaire d'un polypeptide ou d'une protéine
- Dichroïsme circulaire vibrationnel en phase solide

Configuration absolue d'une molécule naturelle chirale de la famille des guaianolide

Molécule extraite d'une Chloranthacée que l'on retrouve dans les caraïbes

Activité biologique intéressante (antitumeur, antiulcère, cardiotonique ...)

Structure chimique de la molécule déterminée par RMN ^1H et ^{13}C



1D NOE et 2D NOESY

H_1 couplé avec H_5

H_1 pas couplé avec H_8

Effet stérique

Pont époxy et C_{15} même côté



Diastéréoisomère A :

H_1 et H_5 du même côté

H_8 , C_{15} et pont époxy
du côté opposé

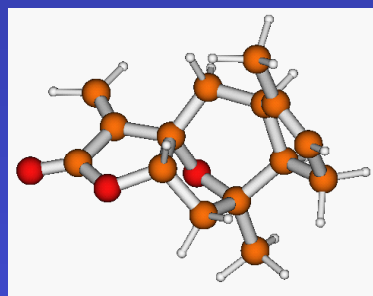
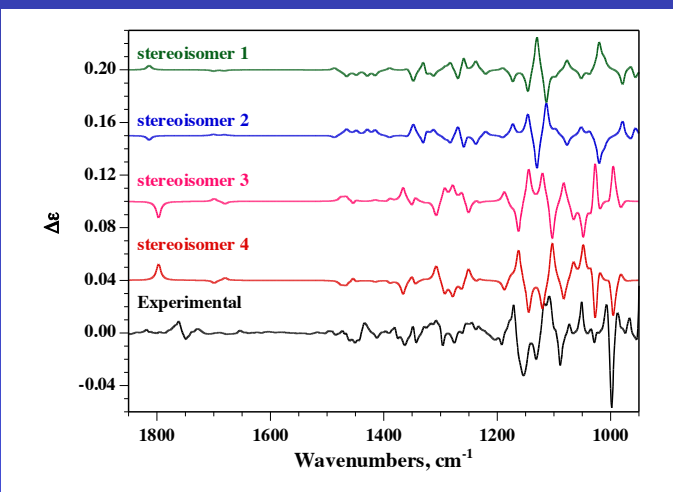
=> Stéréoisomères 1 et 2

Diastéréoisomère B :

H_1 , H_5 , C_{15} et pont époxy
du même côté

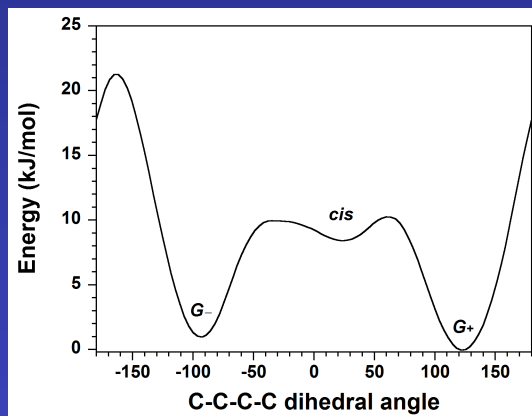
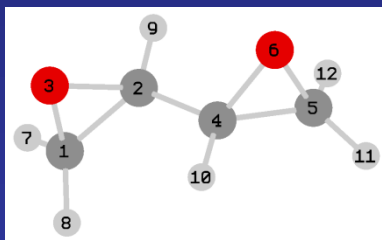
H_8 du côté opposé

=> Stéréoisomères 3 et 4



7R,10R-epoxy-1R,5R-guaia-3,11-dien-8S,12-olide

Détermination de la conformation du 2,2'-bioxirane



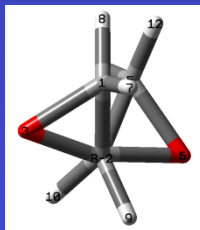
G_-

cis

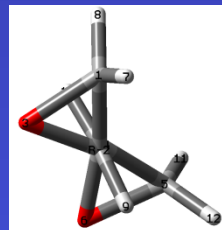
G_+



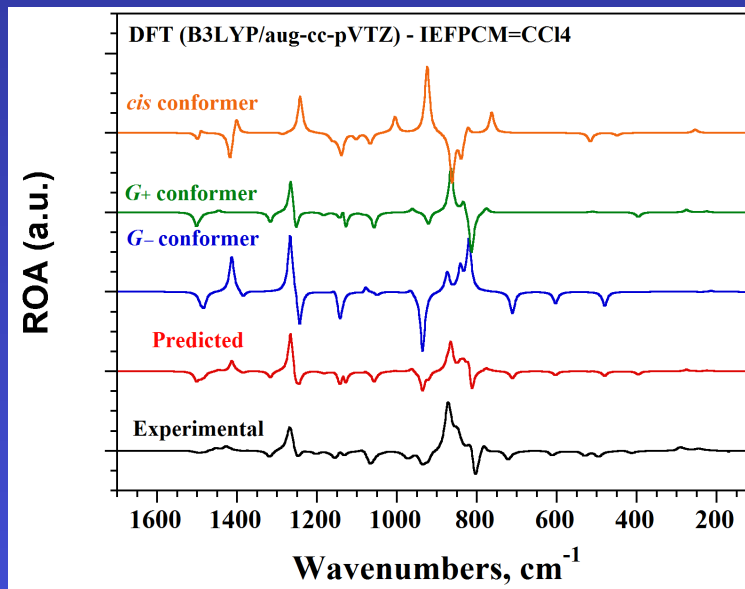
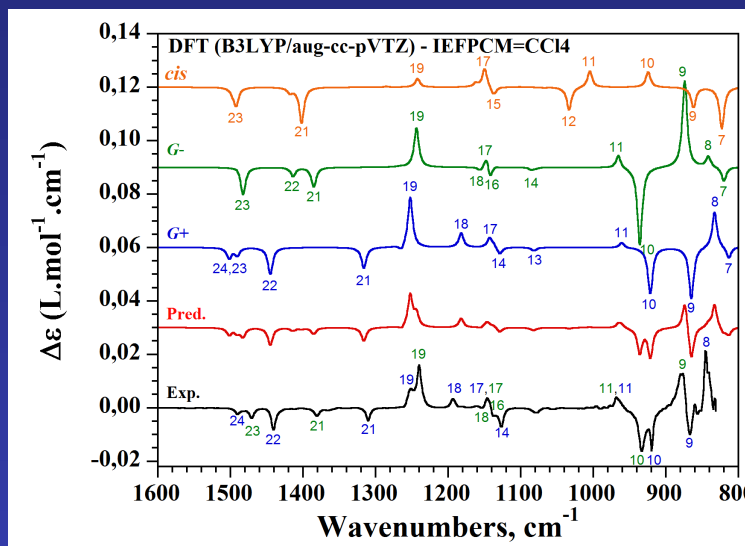
44 %



5 %



51 %



CCl_4

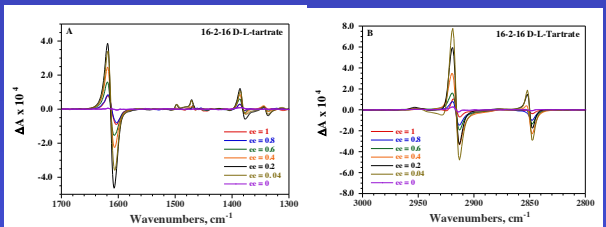
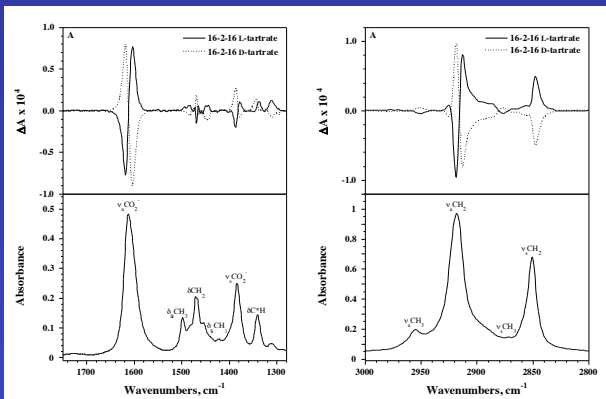
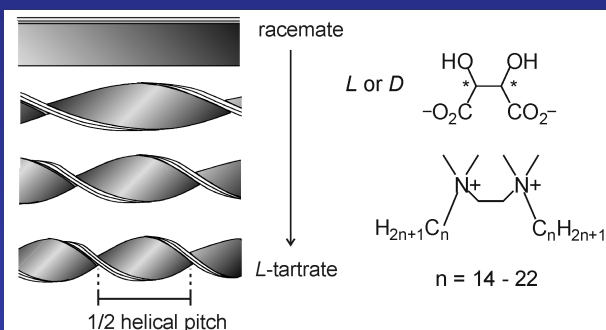
cis : 4%

G_- : 32 %

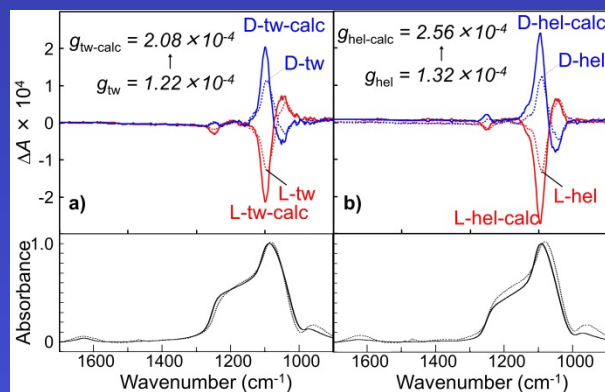
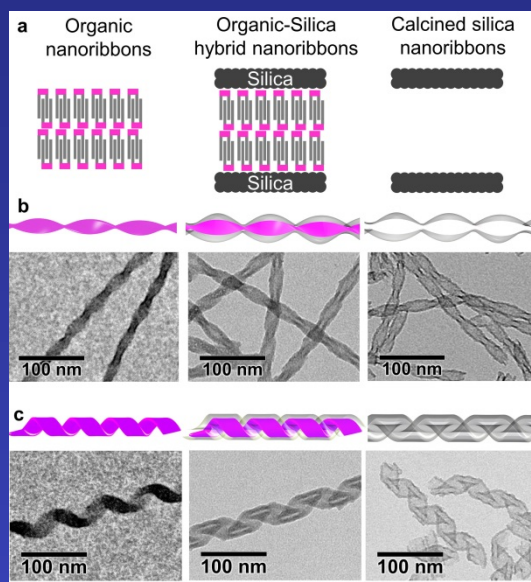
G_+ : 64 %

Chiral induction : molecular and supramolecular chirality in gemini-tartrate amphiphiles

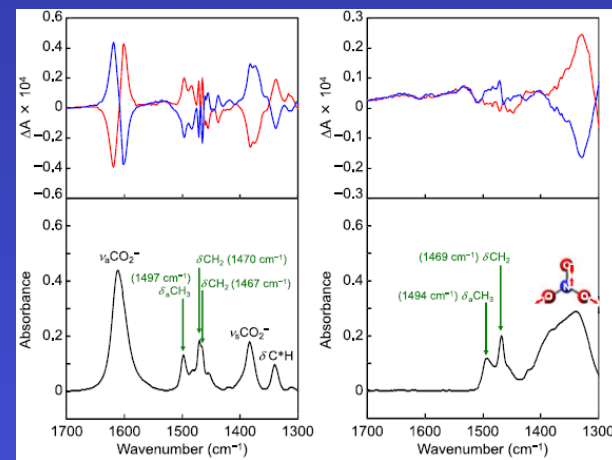
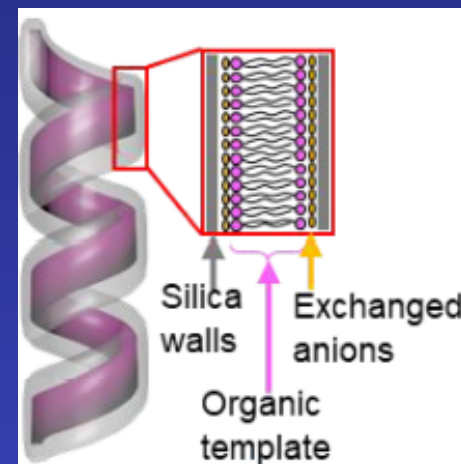
Molecular chirality of tartrate and chiral induction on bilayers



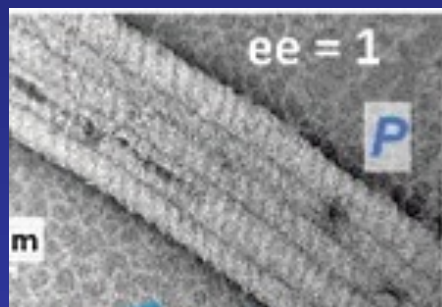
Chiral induction on silica helices



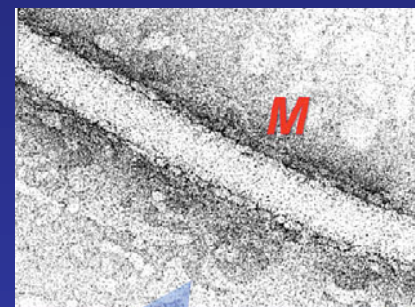
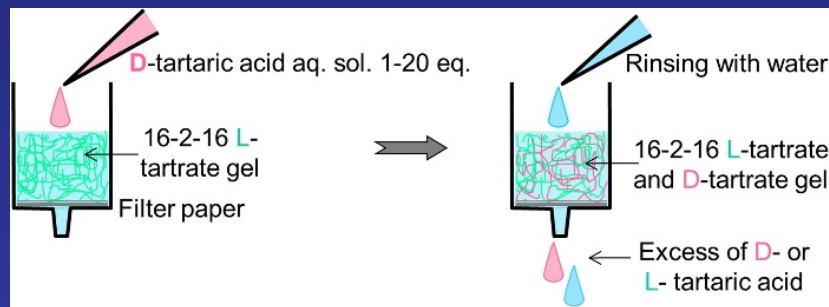
Chiral induction on achiral molecules (NO_3^-)



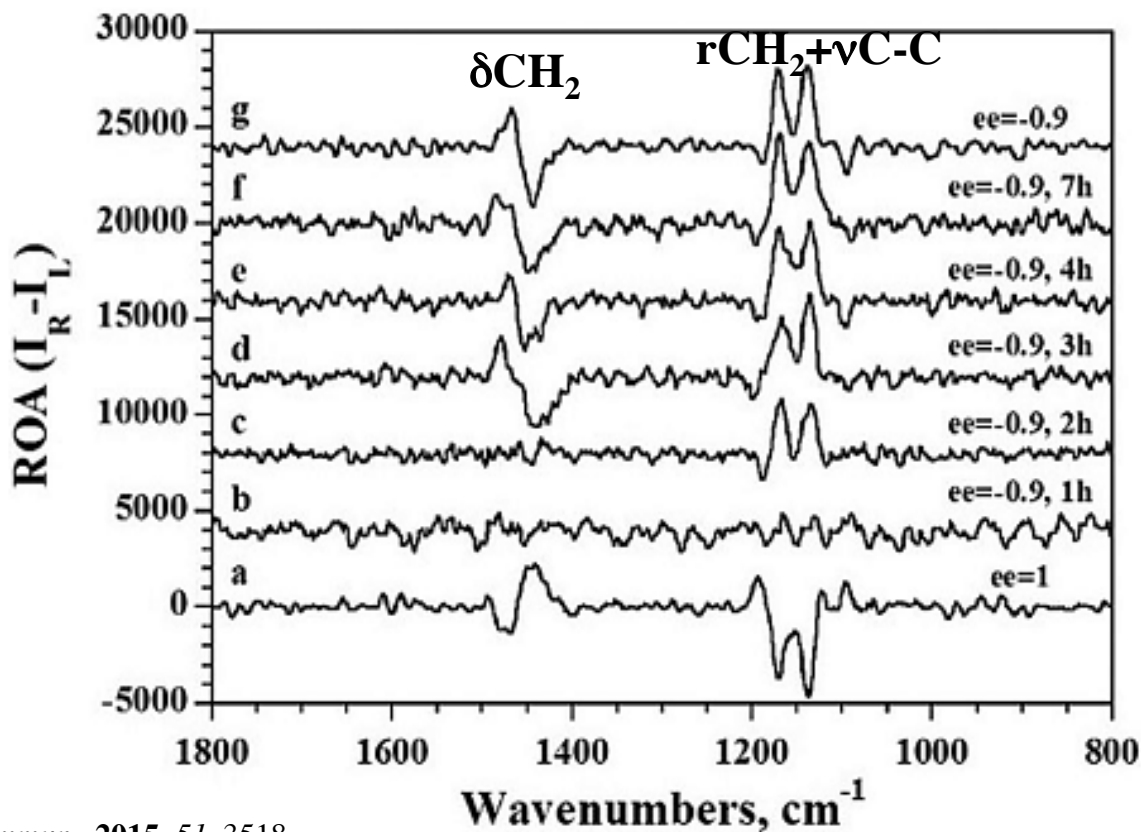
In situ helicity inversion of self-assembled nanohelices monitored by ROA



Right-handed

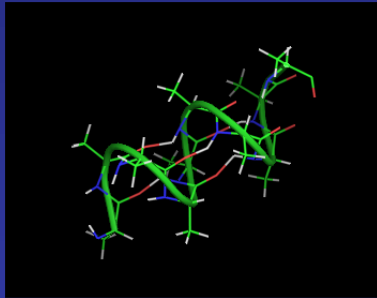


Left-handed

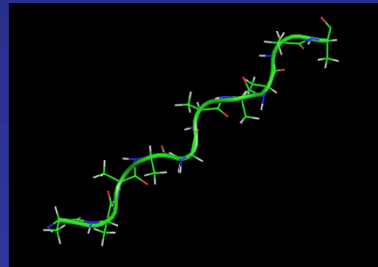


Secondary structure determination of polypeptides

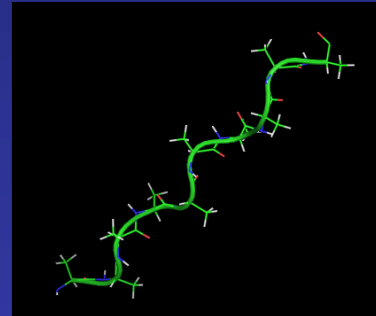
α -helix



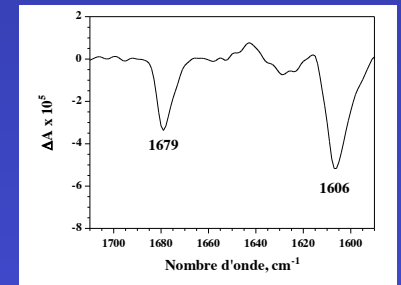
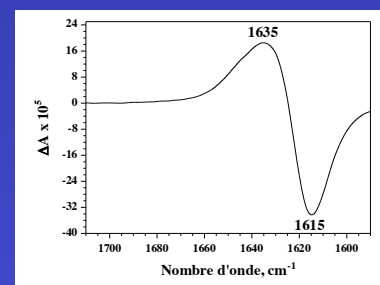
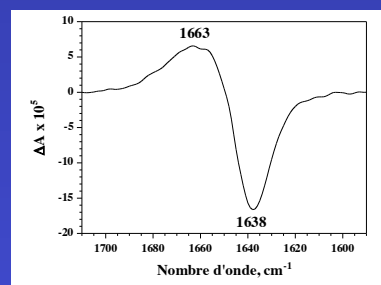
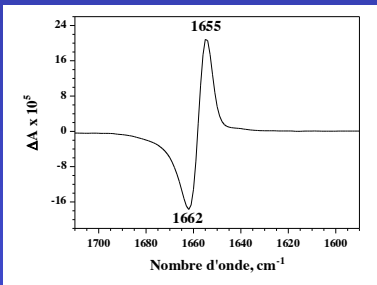
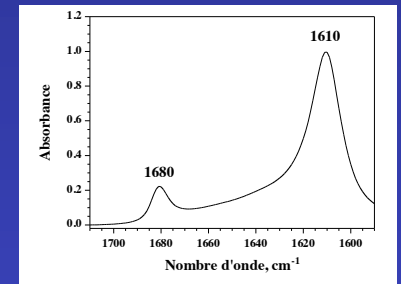
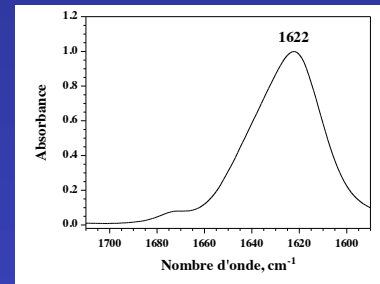
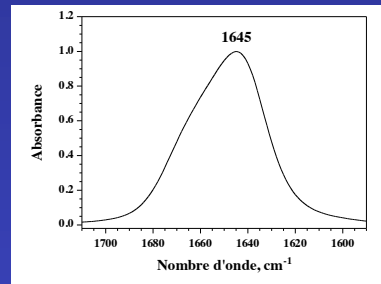
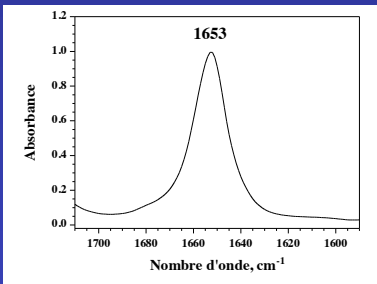
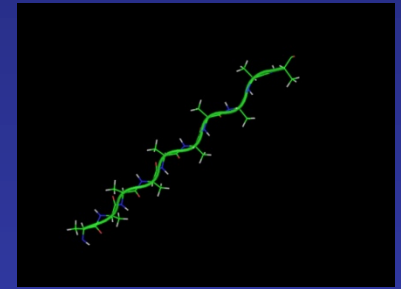
3_1 helix



PPII helix



β -sheet



PBLG/ CDCl_3
 $M_w=22000$

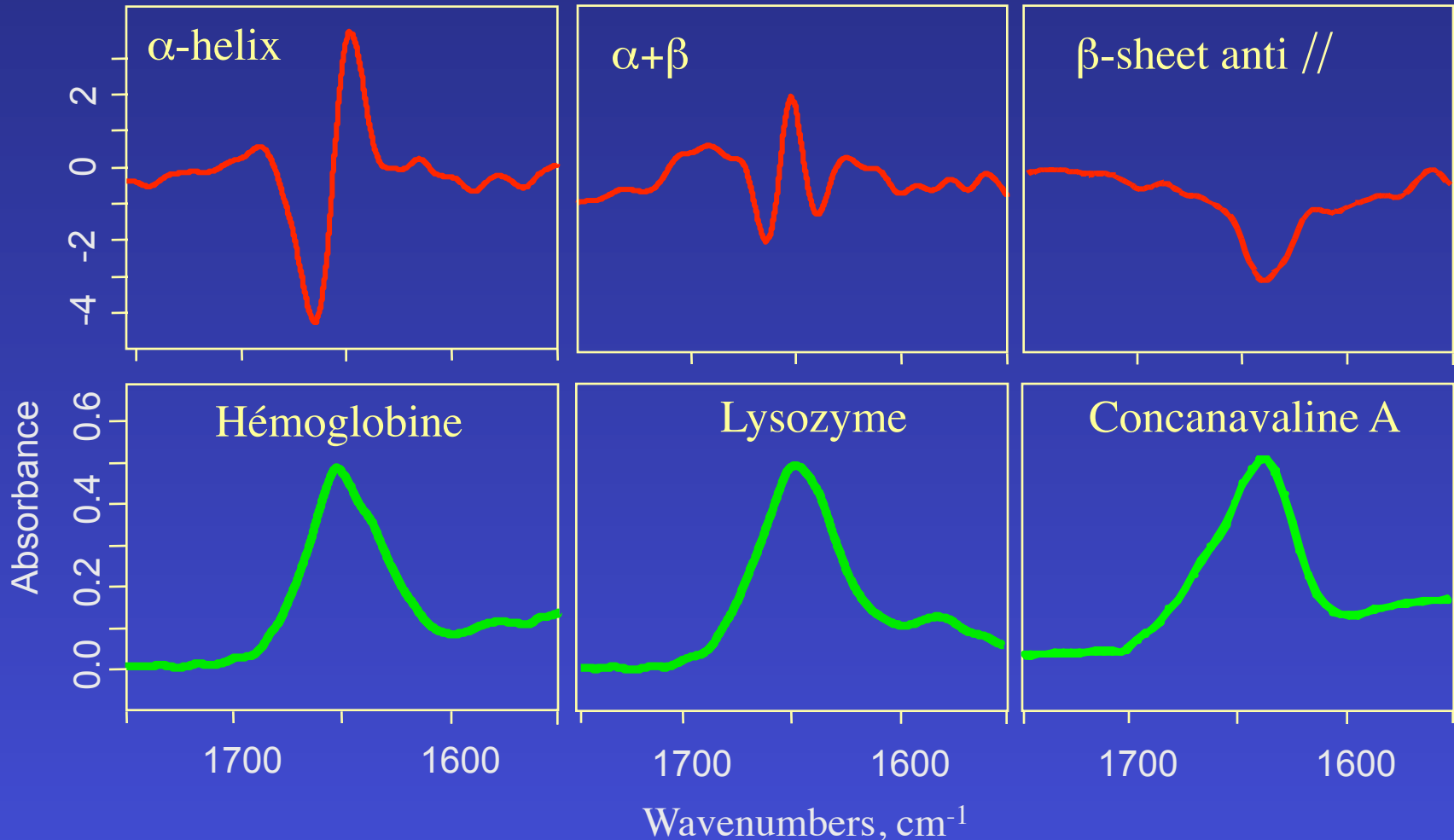
PLL/ D_2O
 $M_w=40000$

PLP/ D_2O
 $M_w=5800$

PLL/ D_2O pH=12
 $M_w=56000$

Secondary structure determination of proteins

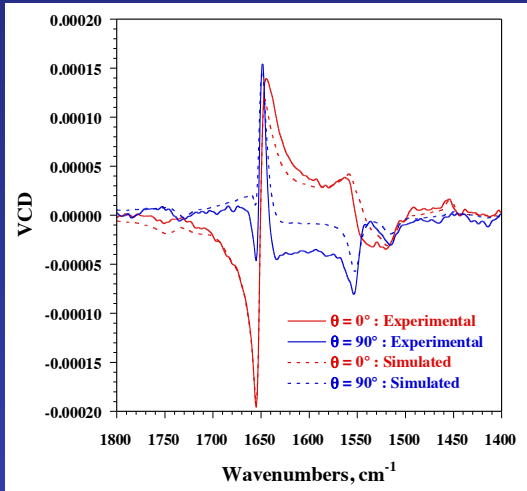
Protein in D₂O : Amide I region - Concentration 4 - 5 mg / 100 μ L



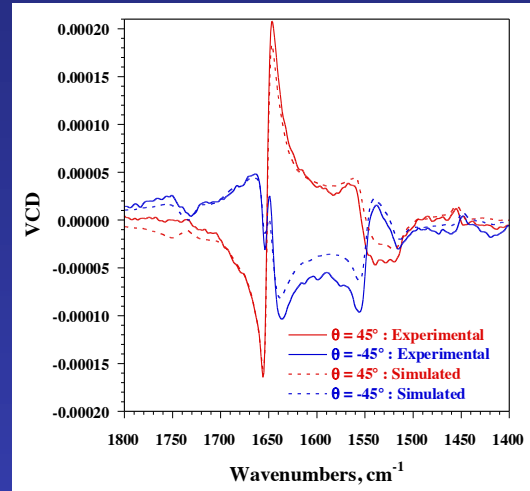
VCD in anisotropic thin solid films :

$$CD = \frac{VCD(\theta) + VCD(\theta \pm 90^\circ)}{2}$$

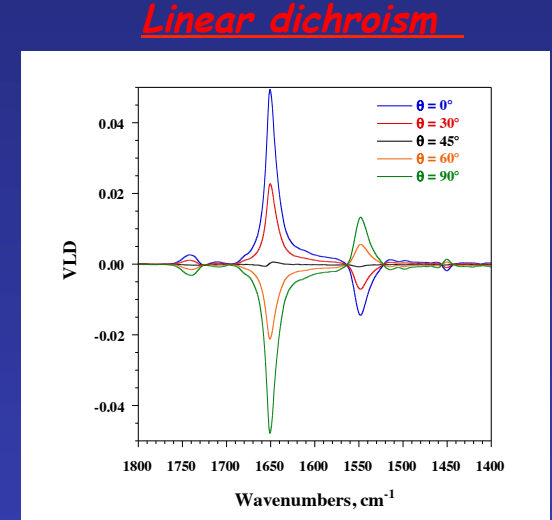
$$S_{VCD} = 2GJ_1(\delta_0) \left\{ [CD \cos \phi_0 - LD \cos 2\theta \sin \phi_0] + \left(\frac{p_X^2 - p_Y^2}{p_X^2 + p_Y^2} \right) LB \cos \phi_0 [\sin 2\theta \cos 2\alpha - \cos 2\theta \sin 2\alpha] \right\}$$



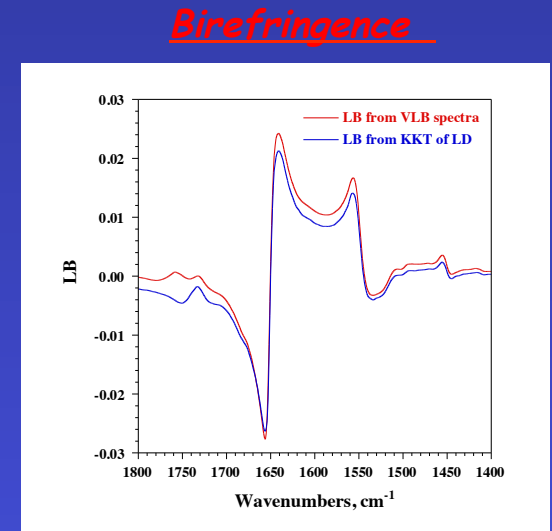
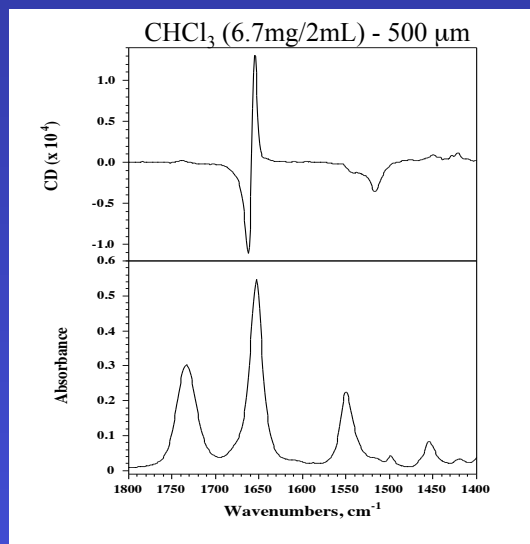
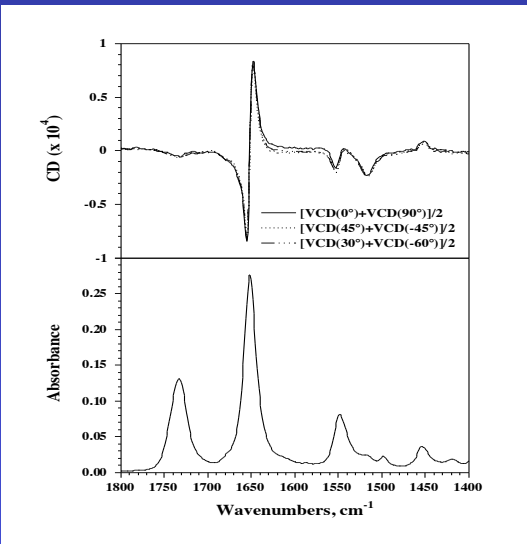
PBLG Thin Film



PBLG Solution

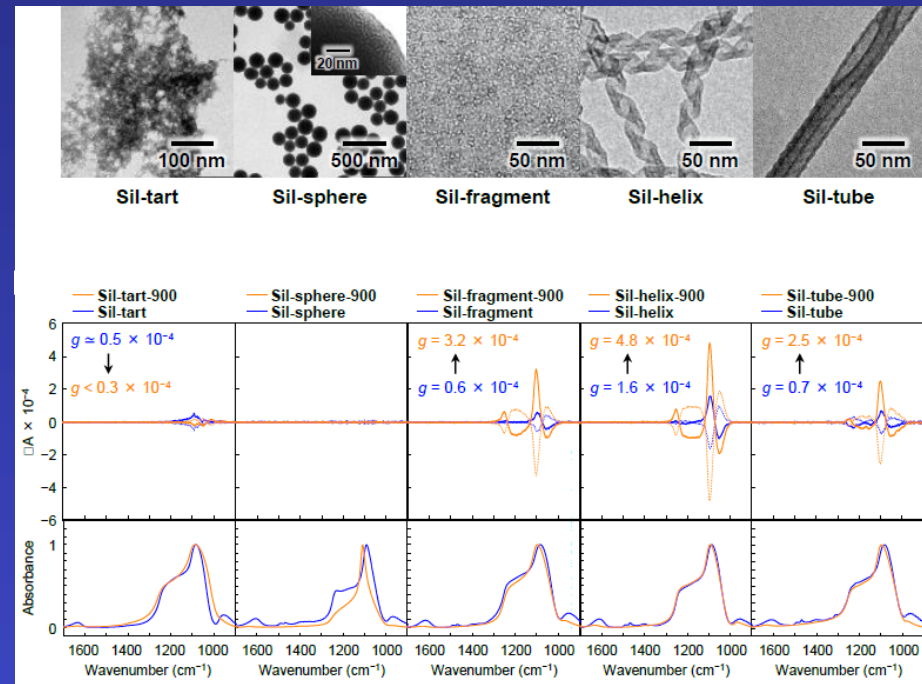
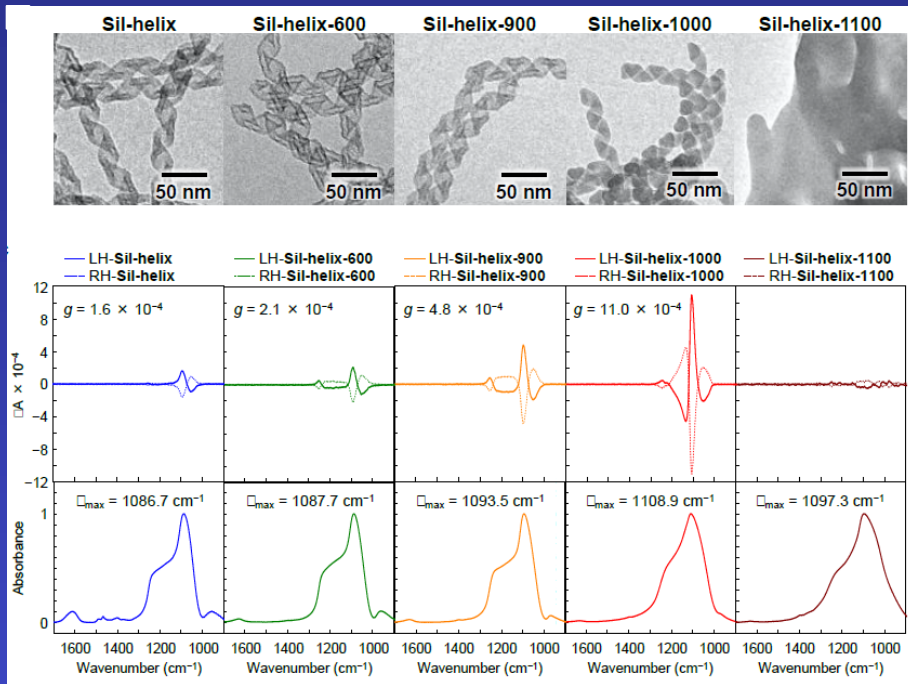


Linear dichroism



Birefringence

VCD spectra of silica helices in KBr pellet



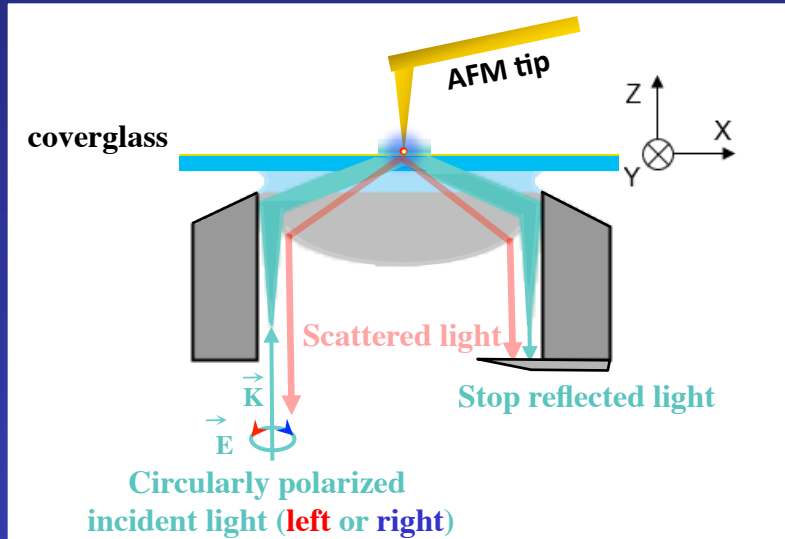
g-factor increases up to 1000°C

Heating above 1000°C leads to destroy the helical morphology : no VCD signal

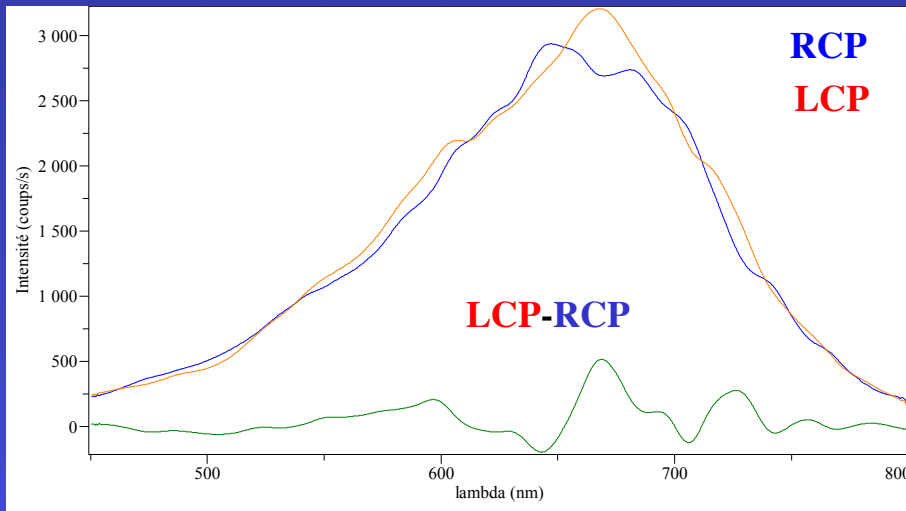
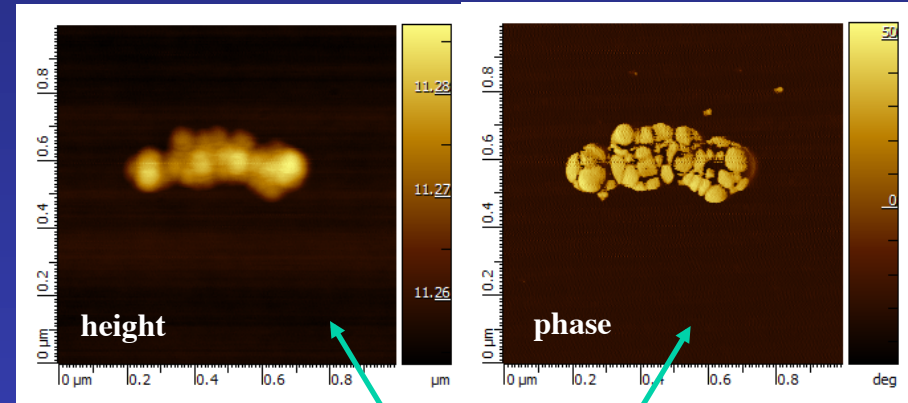
g-factor depends on the morphology of silica

Dark-Field Rayleigh Scattering (DFRS) in TIR

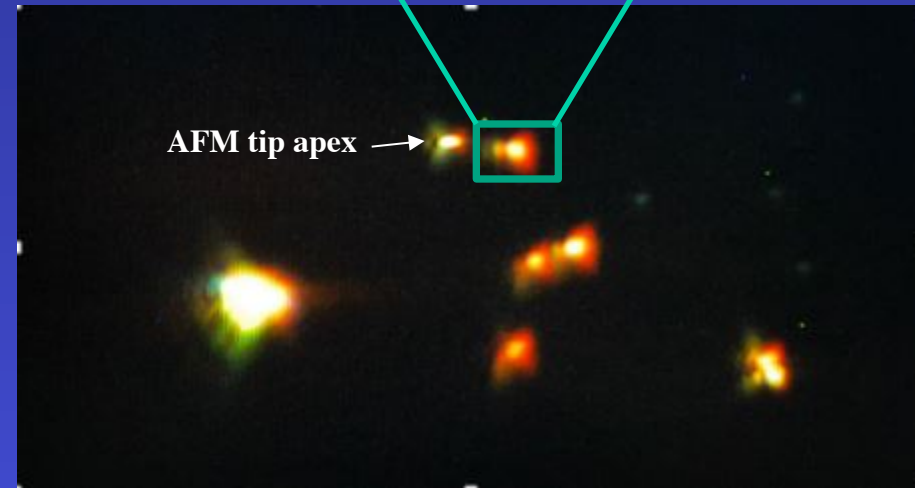
ANR project : CHIMERA



AFM images of silica helix covered by 10 nm gold nanoparticles



Circularly polarized DFRS spectra of silica helix covered by 10 nm gold nanoparticles



Dark field image of silica helix covered by 10 nm gold nanoparticles