Controlling the Rotational Motion of a Single Molecule

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Outline

Photo-induced molecular rotation mechanism and applications

Single molecule approach

Prospect studies

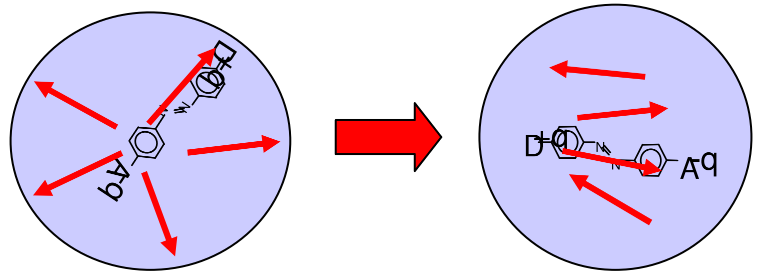
Motivation: optical properties control

Photo-induced linear birefringence by molecular orientation ($\chi^{(1)}$) - Weigert effect

Diffraction gratings / Holography

Polarization gratings

Optical data storage



M. Dumont et al. (2000)

Non linear effects : SHG, and THG symmetry breaking

Photo-induced nonlinear order ($\chi^{(2)}$)

Nonlinear polarization control

Photonic and multifunctional devices

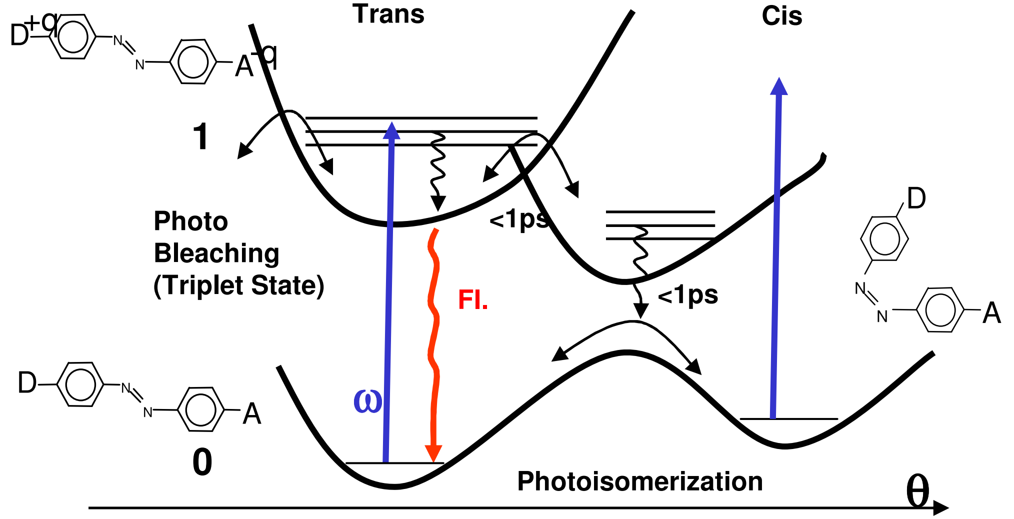
C. Fiorini, JM Nunzi, JOSA B (1996)
S. Brasselet , J. Zyss JOSA B (1998)

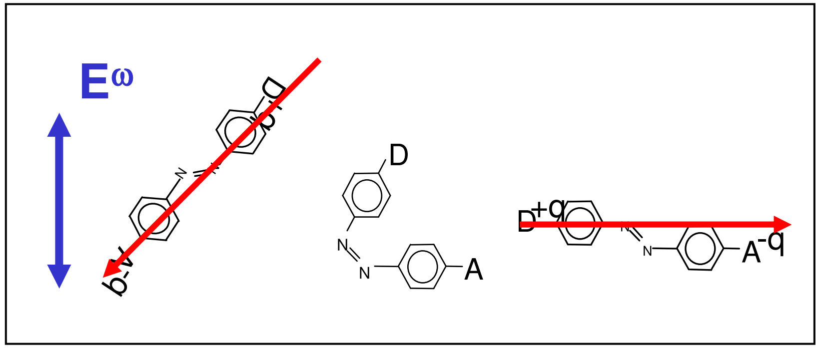
Photo-induced translational motion

Relief gratings (grafted polymers)

L. Kumar et al (1998)

Photo-induced molecular orientation



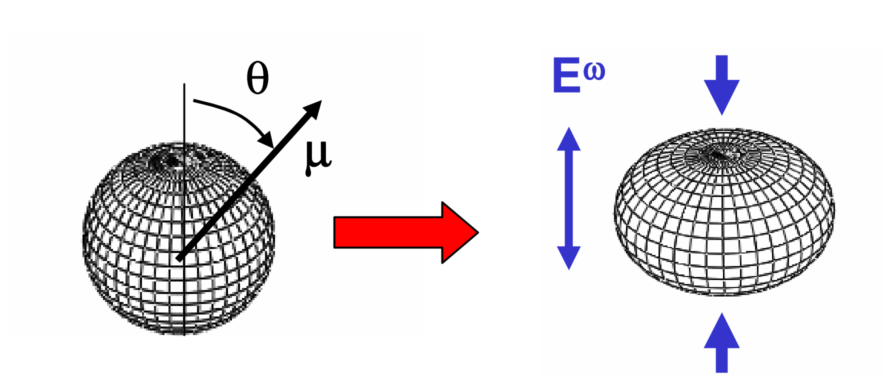


Angular photo-selection:

$$P_{01}(\theta) = \left|\vec{\mu}_{01}(\theta)\cdot\vec{E}^{\omega}\right|^2 \propto \alpha(\theta)\cdot\left(E^{\omega}\otimes E^{\omega *}\right)$$

Orientational hole burning:

$$f(\theta) \propto 1 - P_{01}(\theta)$$



Probing the photo-induced orientation

$$\frac{\partial f(\theta,t)}{\partial t} = D \cdot \Delta f(\theta,t) \qquad \tau_D = \frac{1}{D} = \frac{6V\eta}{kT}$$

Brownian angular motion

$$\frac{\partial f(\theta,t)}{\partial t} = D \cdot \Delta[f(\theta,t) - P_{01}(\theta)f(\theta,t)] + R \cdot \Delta[P_{01}(\theta)f(\theta,t)]$$

Non-excited molecules diffusion — Excited molecules diffusion

$$\tau_D >> \tau_R$$

M. Dumont, Synthetic Metals 115 (2000)

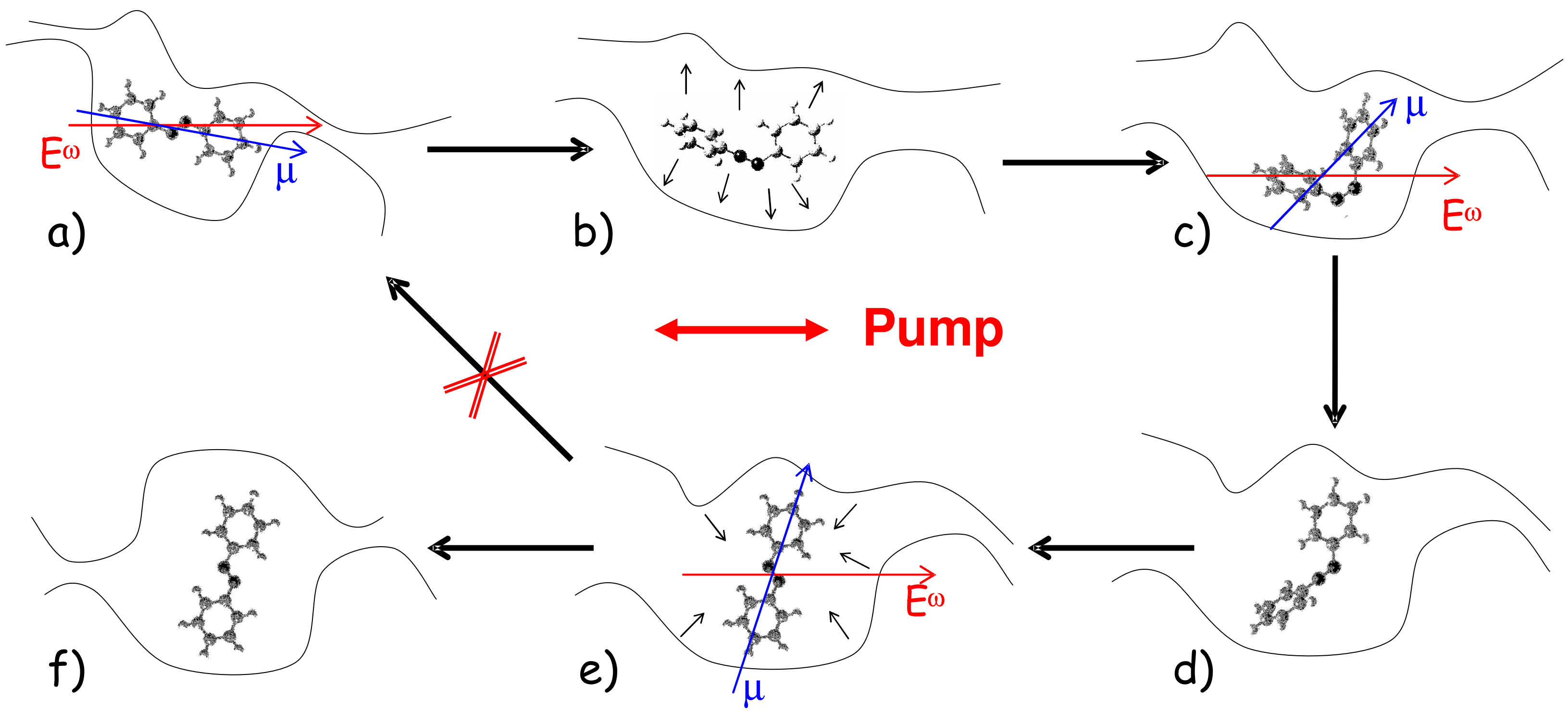
S. Bidault, PhD thesis LPQM (2004)

Competition between Brownian and photo-induced motions

➡ Polymer re-organization effect

Photoisomerization QY: depends on viscosity, polarity, plasticity

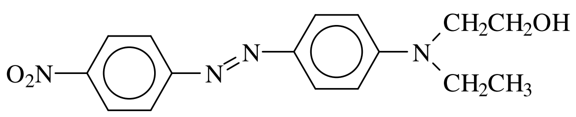
Orientation - stabilization mechanism

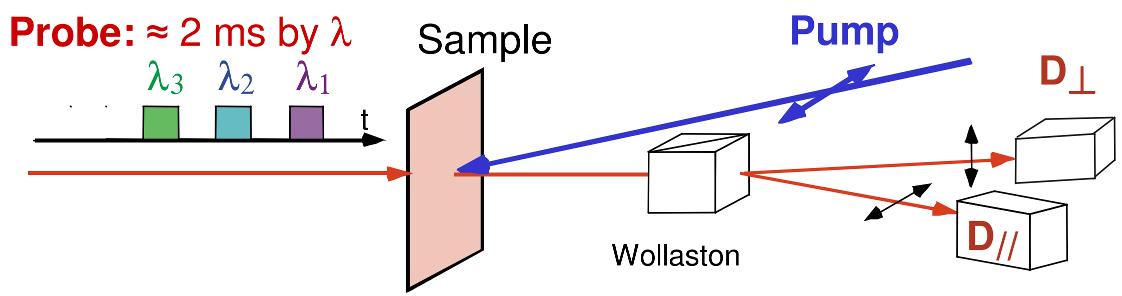


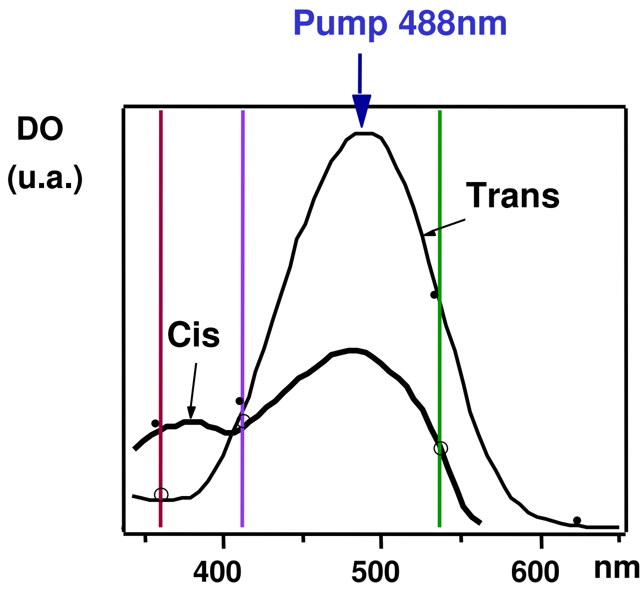
Linear anisotropy in photoisomerizable media

M. Dumont, N. Nguyen (LPQM)

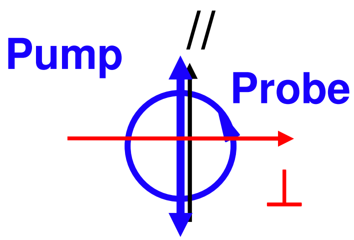
DR1

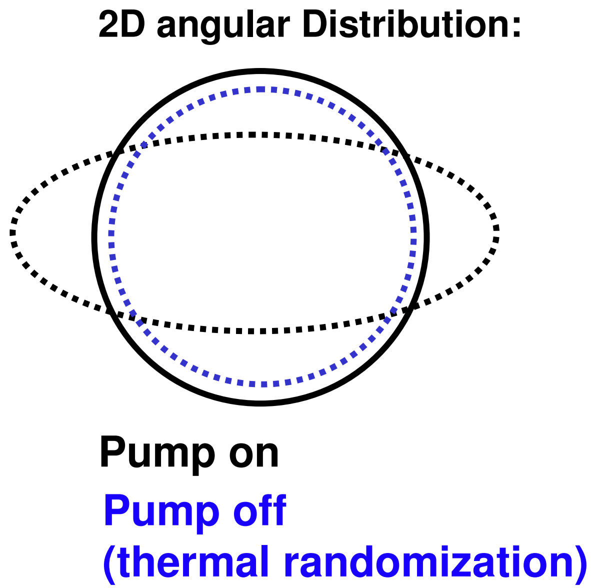






DR1 : absorption spectrum





Linear anisotropy in photoisomerizable media

M. Dumont, N. Nguyen (LPQM)

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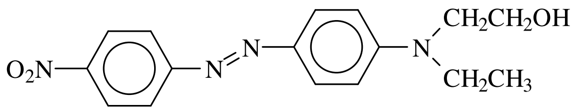
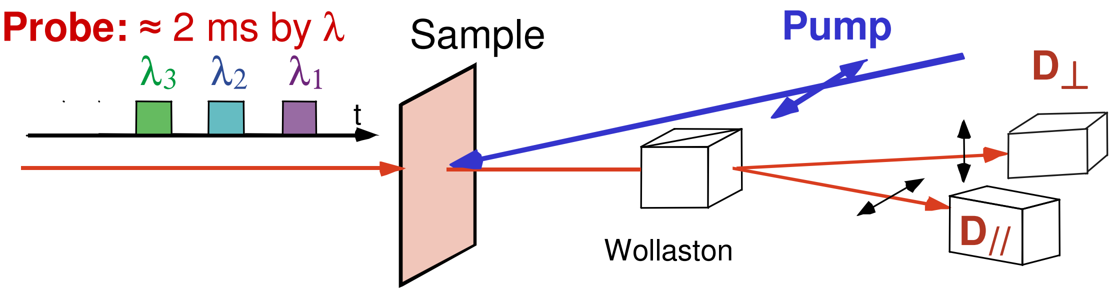
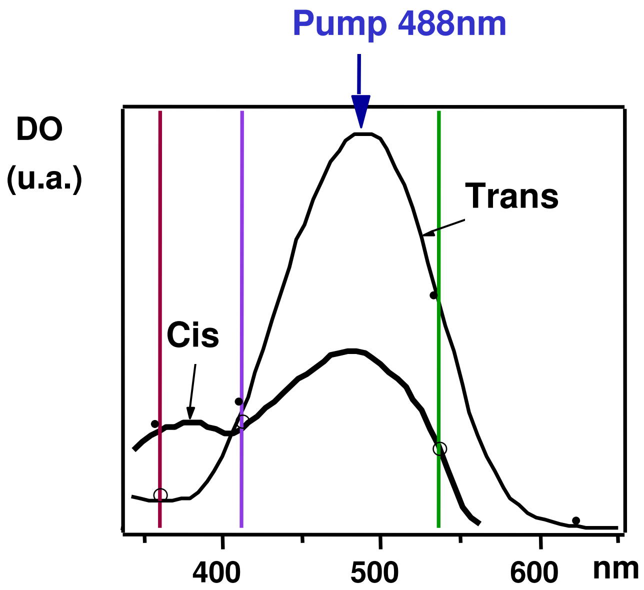
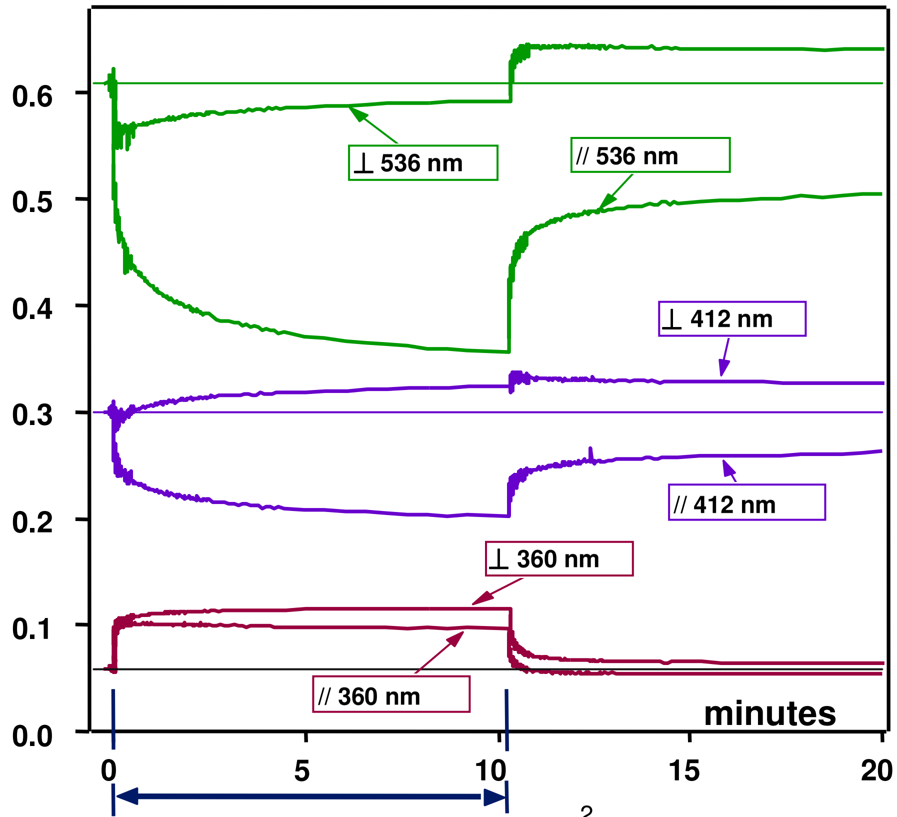






DR1 : absorption spectrum

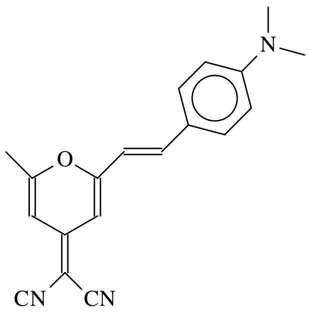


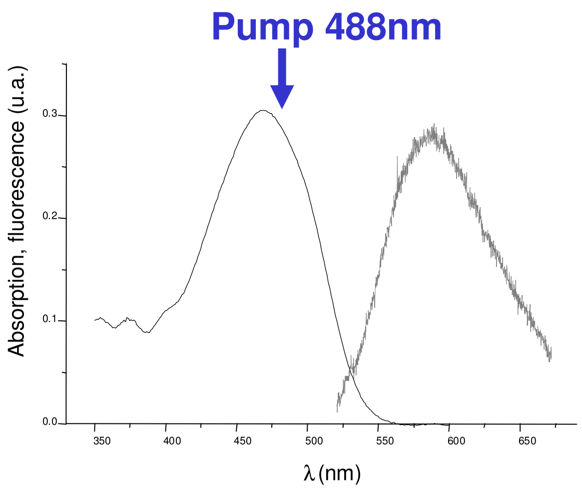
Pump: 488 nm 20mW/cm^2

M. Dumont, Synthetic Metals 115 (2000)

Anisotropy control in photoisomerizable and fluorescent media

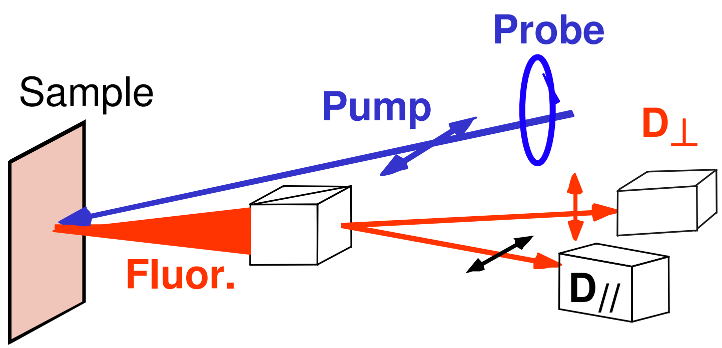
DCM





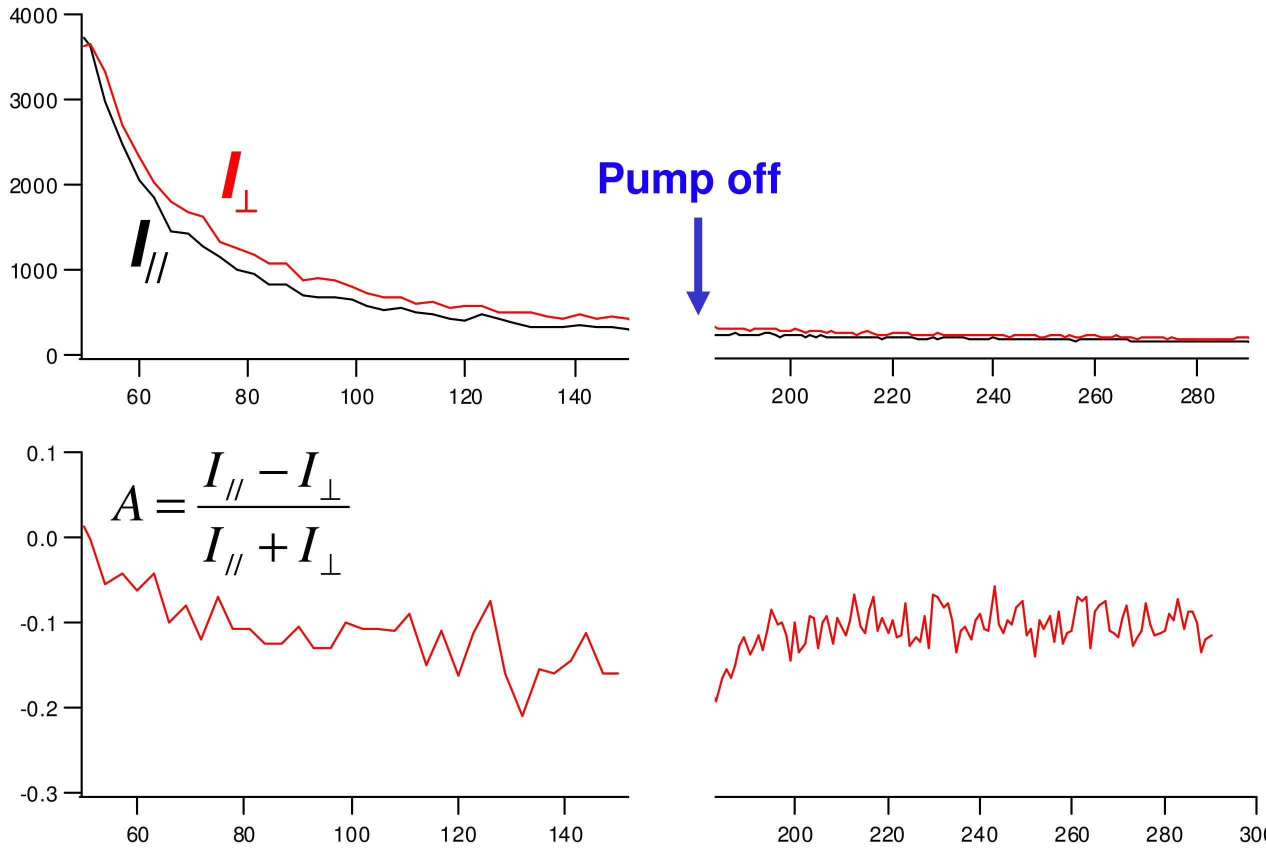
$\Phi_f = 0.3$ in CH_2Cl_2

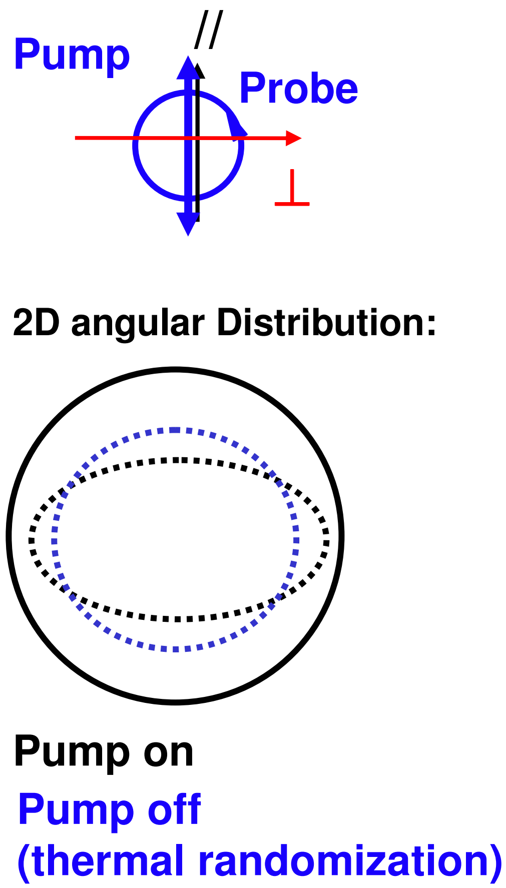
$\Phi_{photoisomerization} = 0.15$



Anisotropy control in photoisomerizable and fluorescent media

Low Tg polymer matrix: PMA (Tg=8℃)



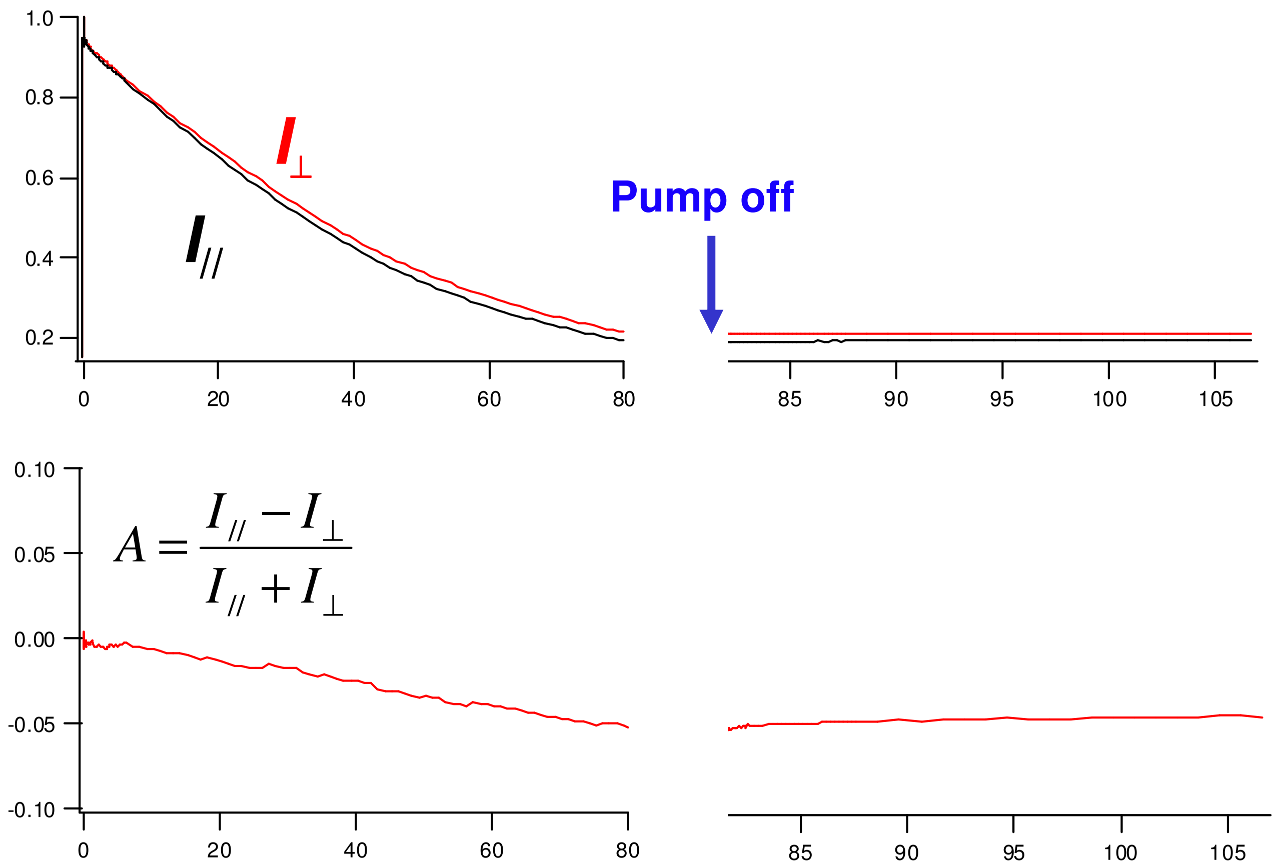


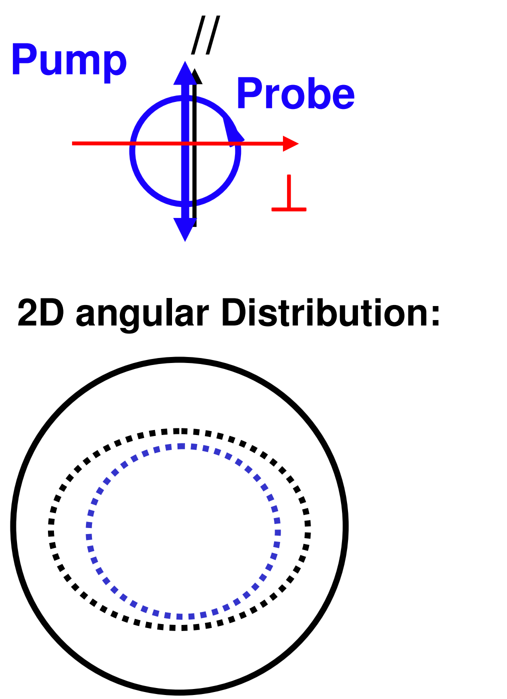
Multi-exponential behavior

Angularly selective photobleaching + Photo-orientation

Anisotropy control in photoisomerizable and fluorescent media

High Tg polymer matrix: PMMA (Tg=120℃)





➡ **Angularly selective photobleaching**

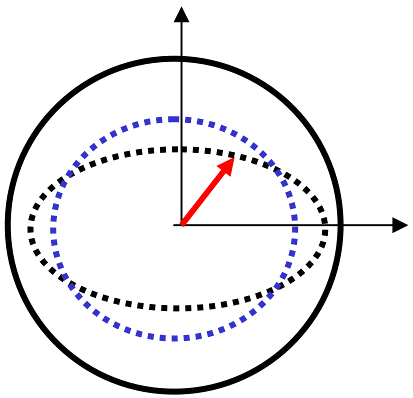
The single molecule approach

Overcome photoselective bleaching

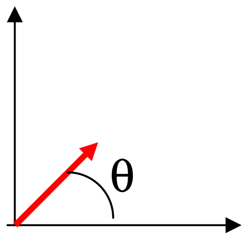
Overcome stastistical effect and reveals heterogeneity

Multiple time-scales behaviors: ensemble or individual?

Dynamic behavior (time jumps, time scales...)



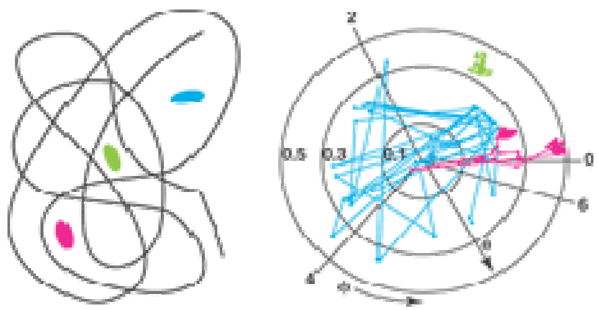
$$\int_{\theta} \alpha(\theta)\cdot f(\theta,t)\sin\theta d\theta$$



$$\alpha(\theta)\cdot f(\theta,t)$$

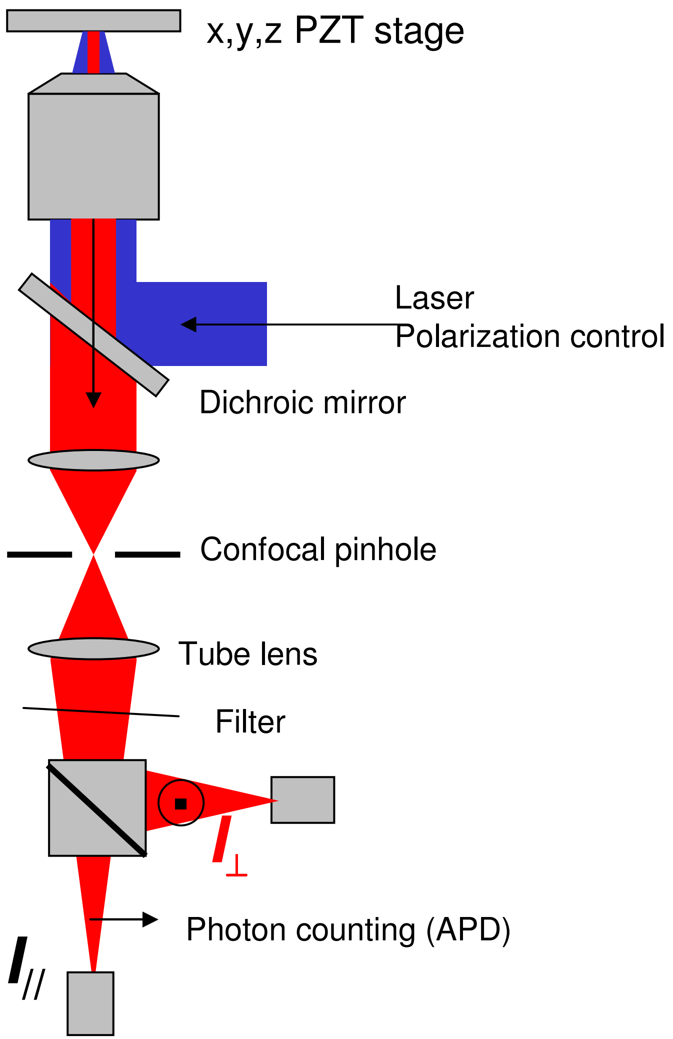
Probability of orientation at time t

Environnement effects

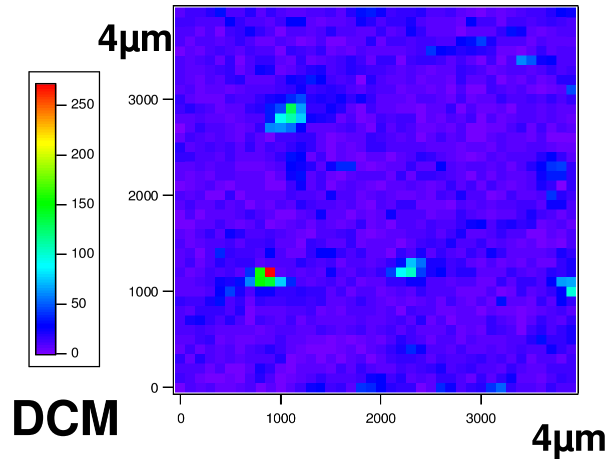


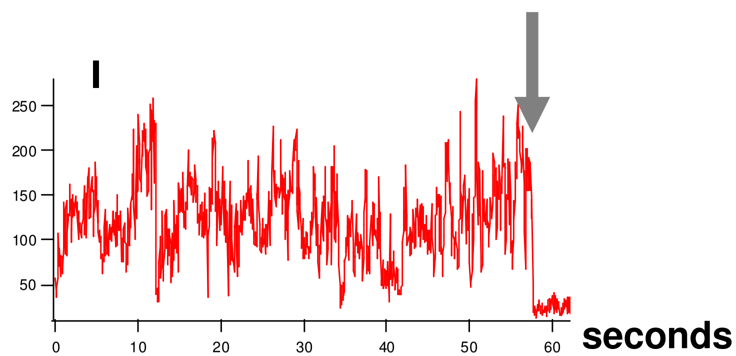
Bartko, Xu and Dickson, PRL (2002)

Experimental Set-up

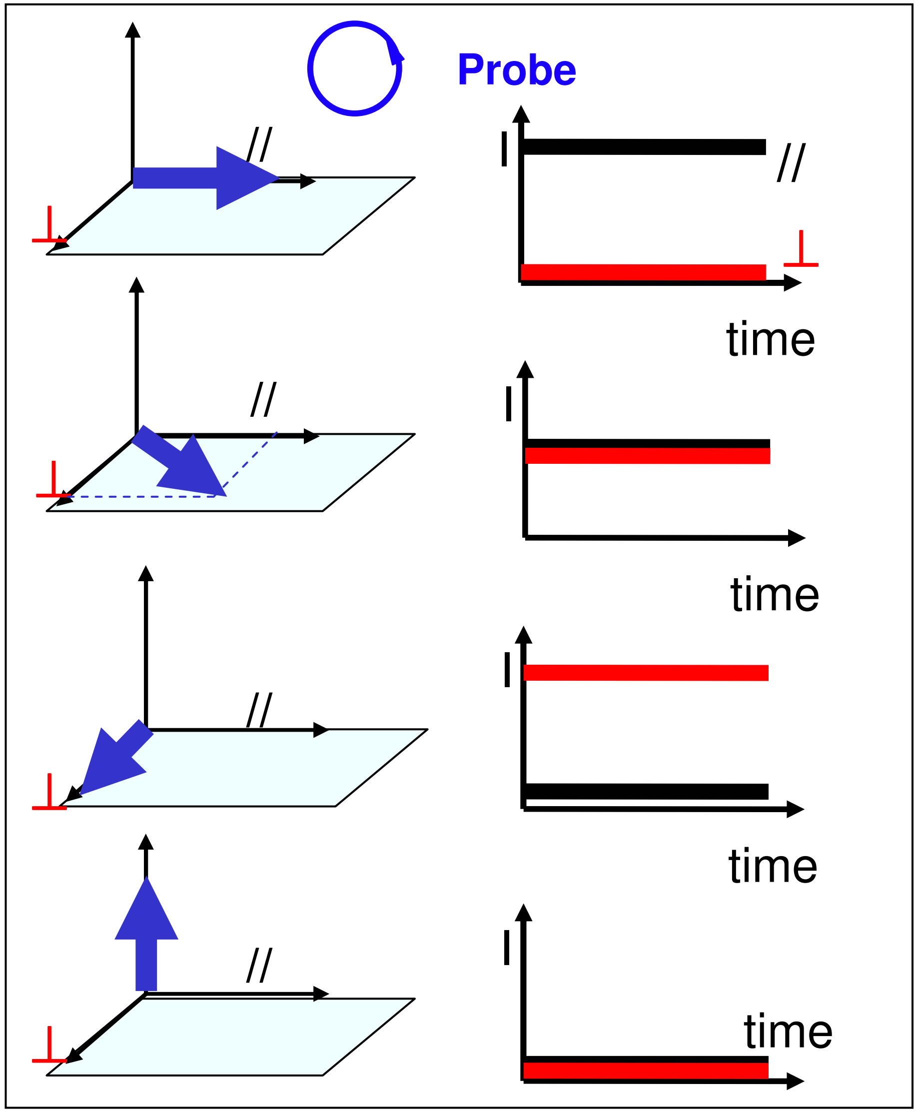


- Constant Nitrogen flow on the sample
- Acid pre-treatment (coverslips)
- UV pre-treatment (polymer solutions)





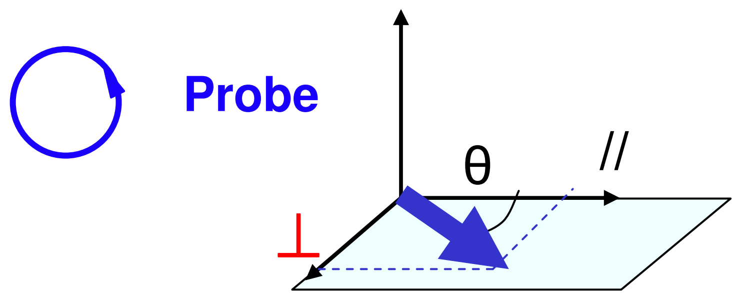
Optical response of a single molecular dipole



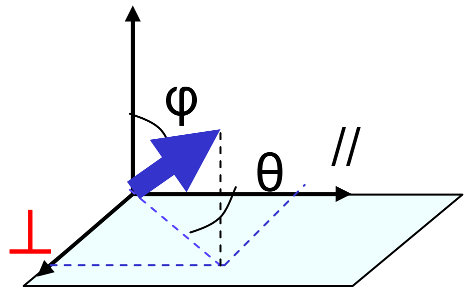
$$I_{K=//,\perp}(\theta,\varphi) = \left|\vec{\mu}_{01}\cdot\vec{E}^{\omega}\right|^2 \left|\vec{\mu}_e\cdot\vec{K}\right|^2$$

$$K = //, \perp$$

Single molecules 3D orientation



$$A = \frac{I_{//} - I_{\perp}}{I_{//} + I_{\perp}} \qquad A = \cos(2\theta)$$



$$Sum = \frac{I_{//} + I_{\perp}}{Max(I_{//} + I_{\perp})} \qquad Sum = \sin^4 \varphi$$

$\pi/2$ indetermination for θ

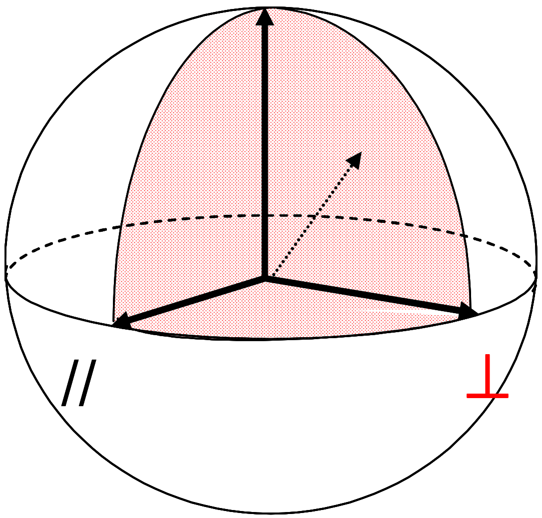
π indetermination for φ

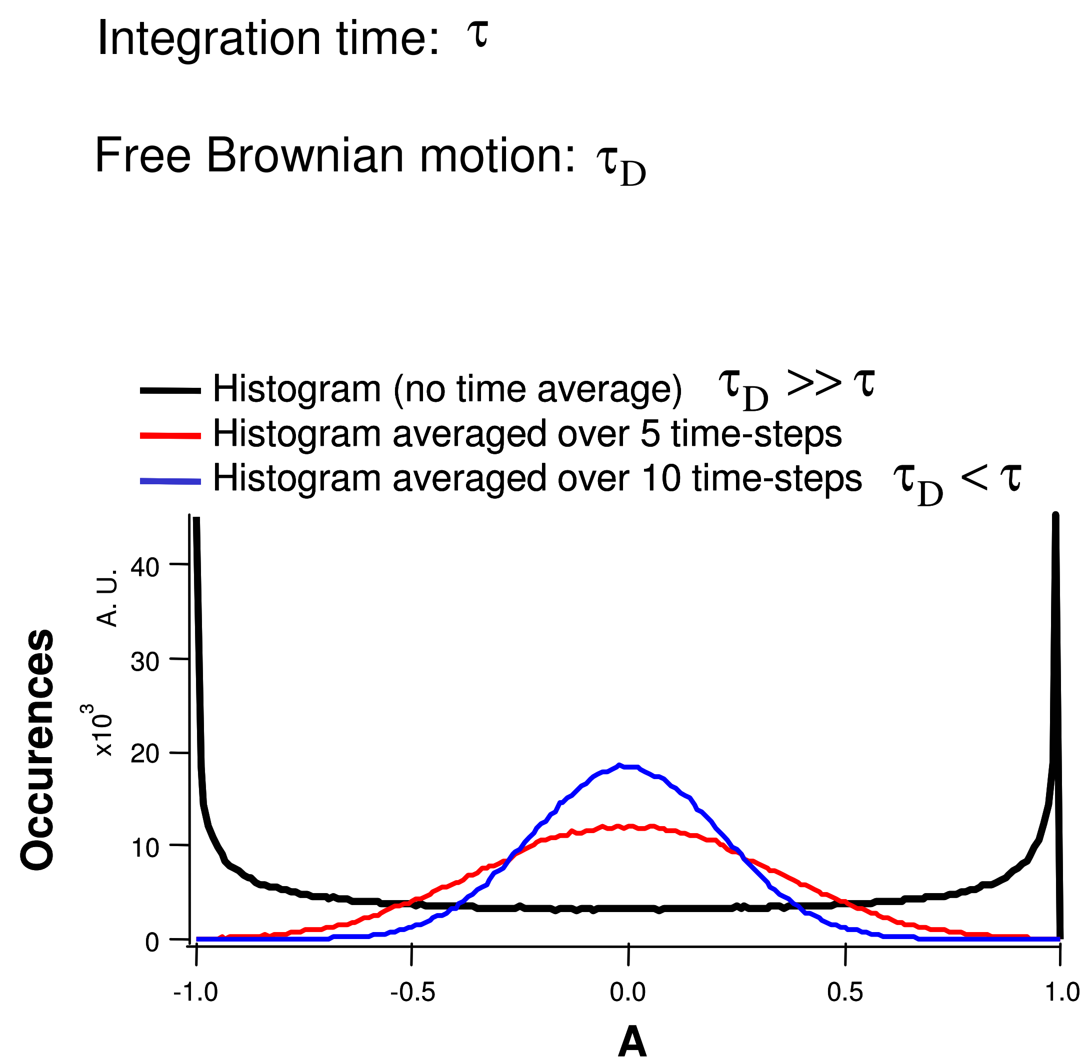
⇨ 3D angle determination

Possible corrections for:

- intensity fluctuations (triplet state transitions (blinking), spectral fluct.)
- out-of plane angular motions
- out-of focus translational motions

Single molecules orientation behavior

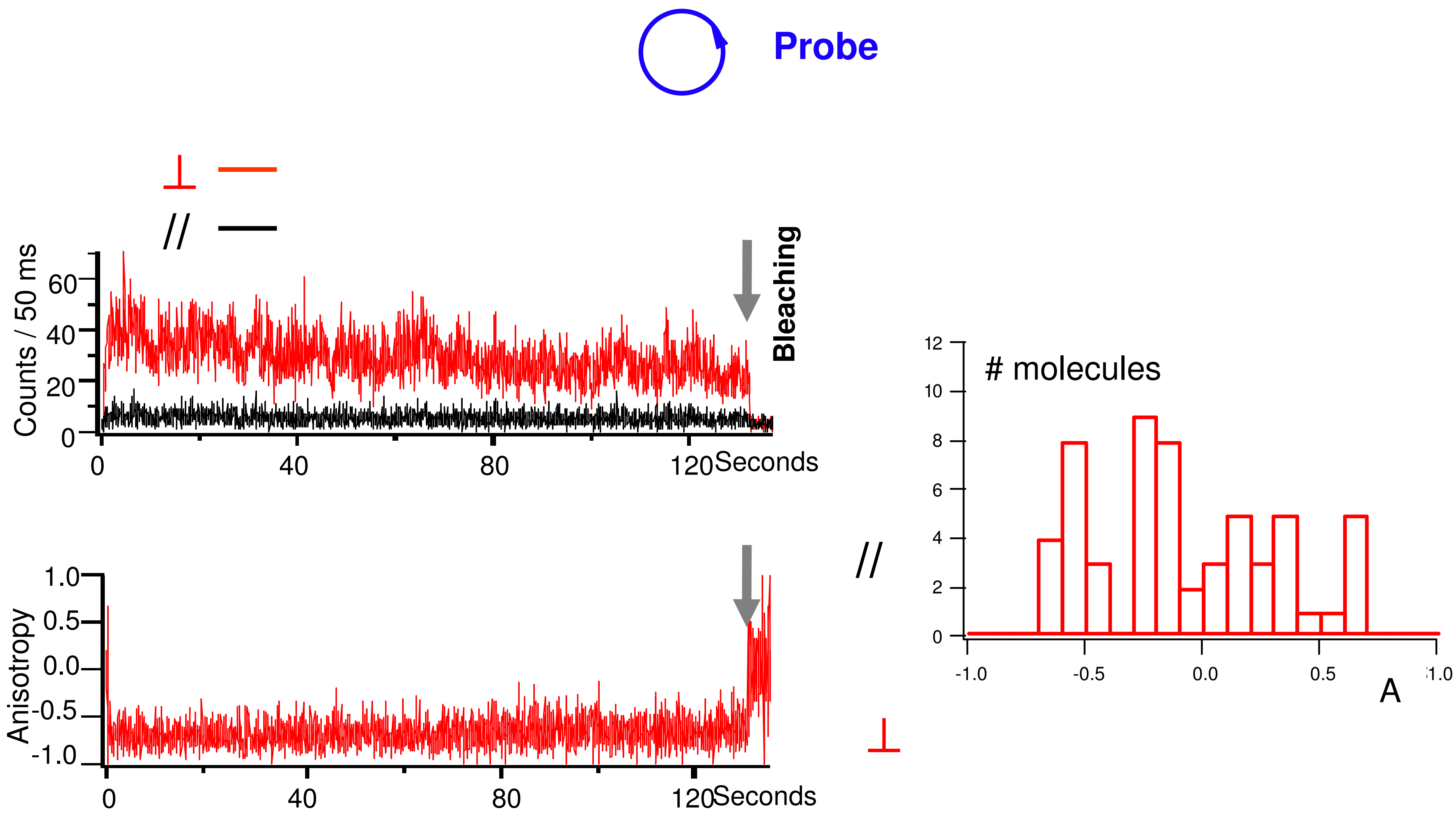




Integration time: τ
Free Brownian motion: τD
Histogram (no time average) τD >> τ
Histogram averaged over 5 time-steps
Histogram averaged over 10 time-steps τD < τ
Occurences
x10^3 A. U.
0
10
20
30
40
-1.0
-0.5
0.0
0.5
1.0
A

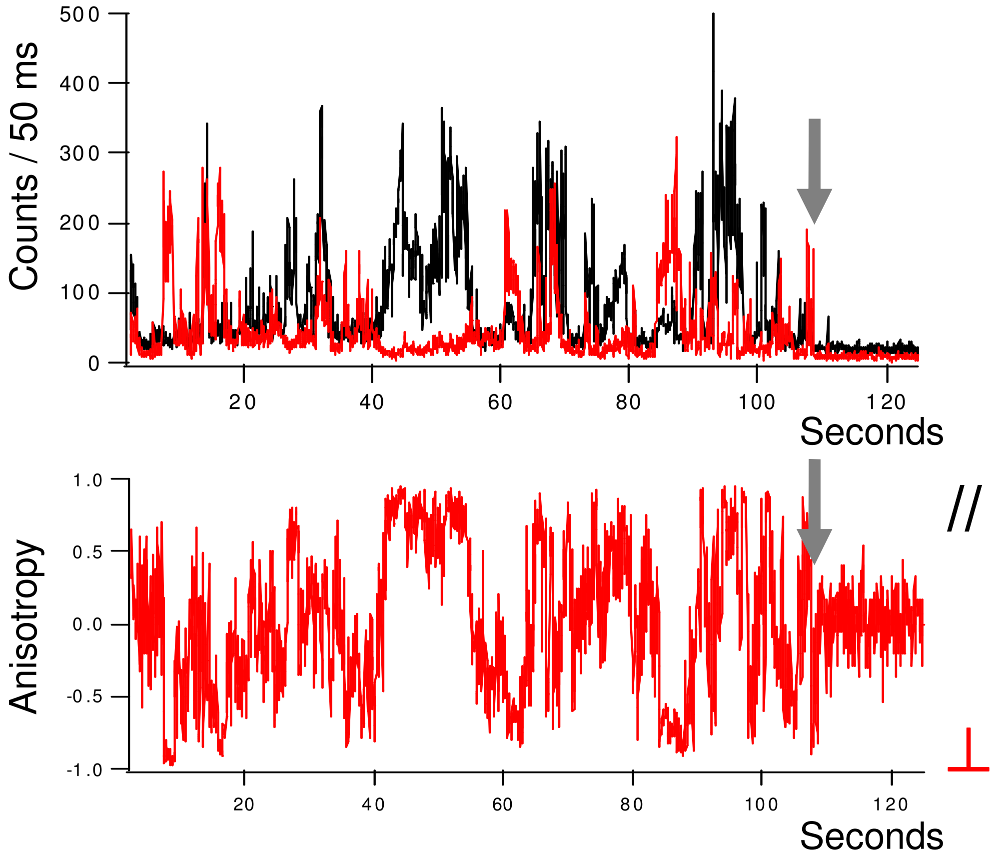
Stable orientation

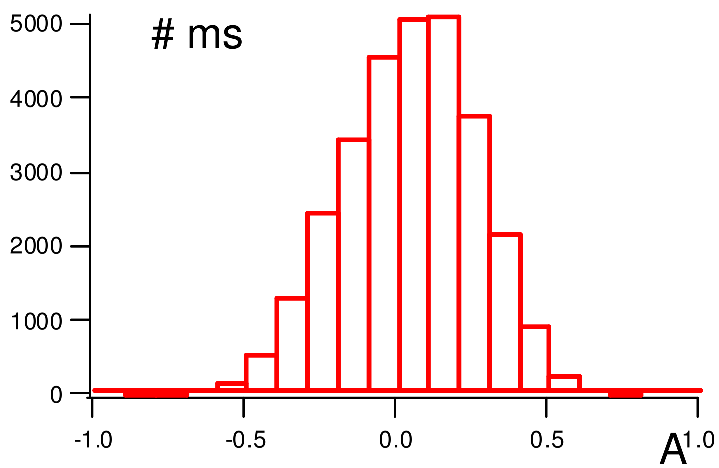
High-Tg polymer matrix: PMMA (Tg=120℃)



Thermal Rotation

Low Tg polymer matrix: PMA (Tg=8 ℃)



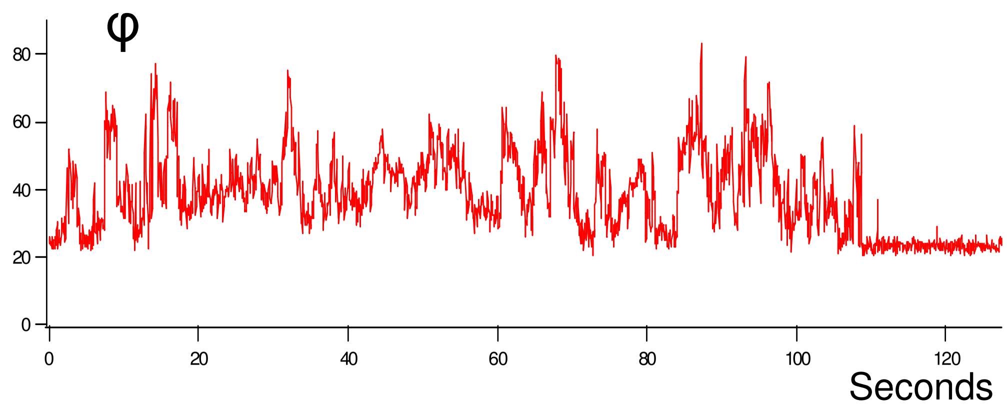


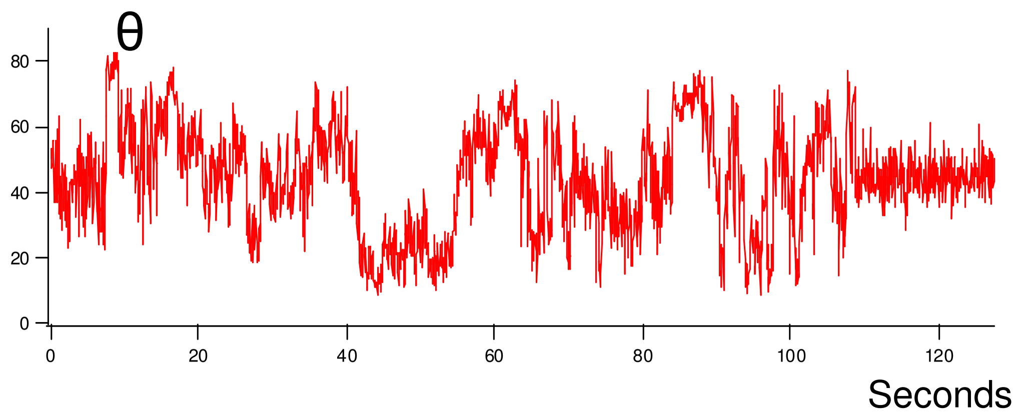
3D Thermal Rotation

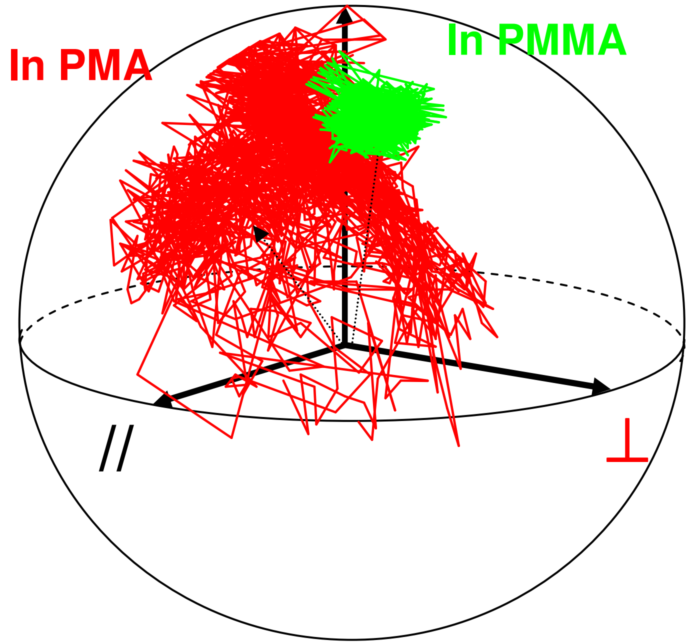
Low Tg polymer matrix: PMA (Tg=8℃)

$$A = \cos(2\theta)$$

$$Sum = \sin^4 \varphi$$

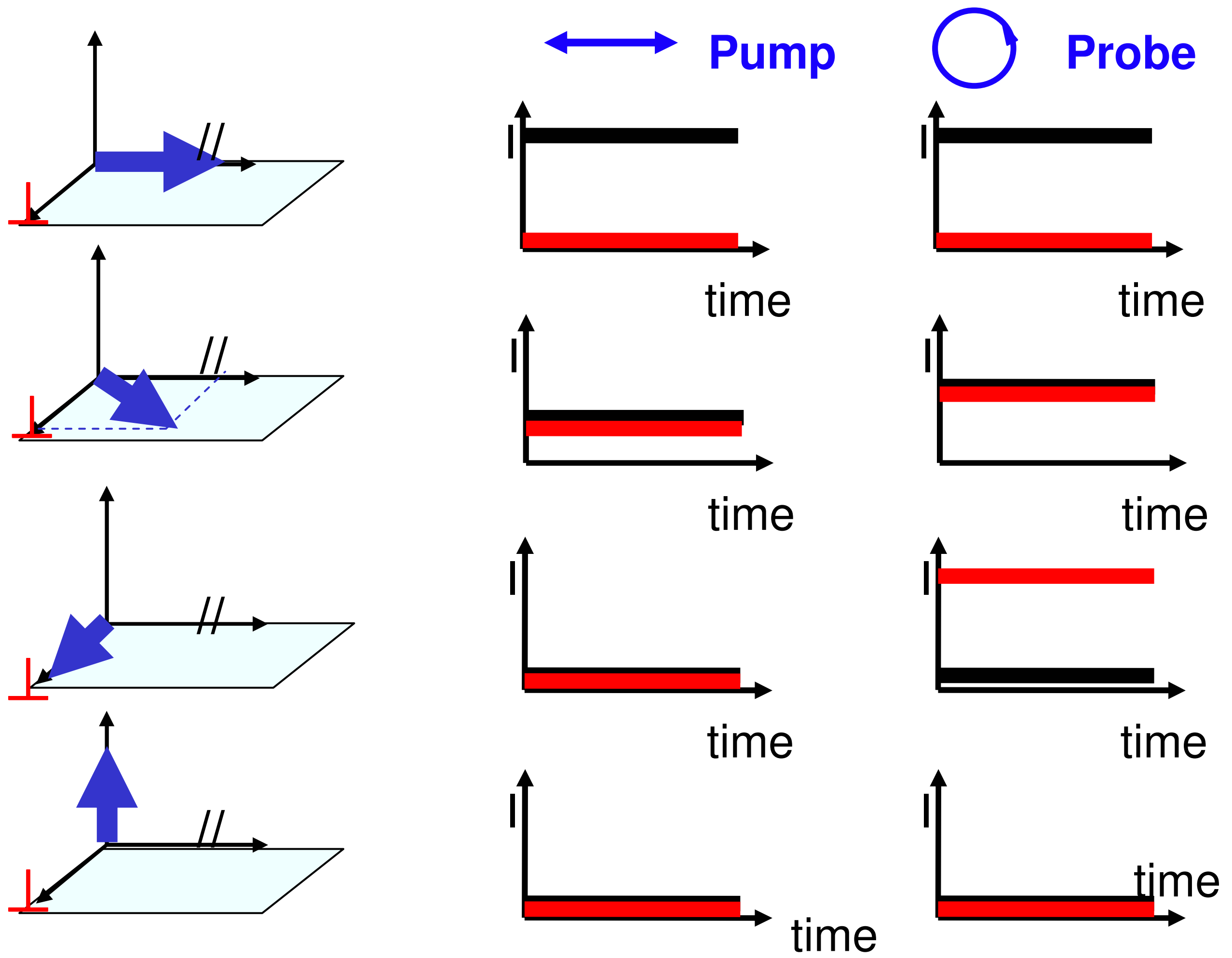




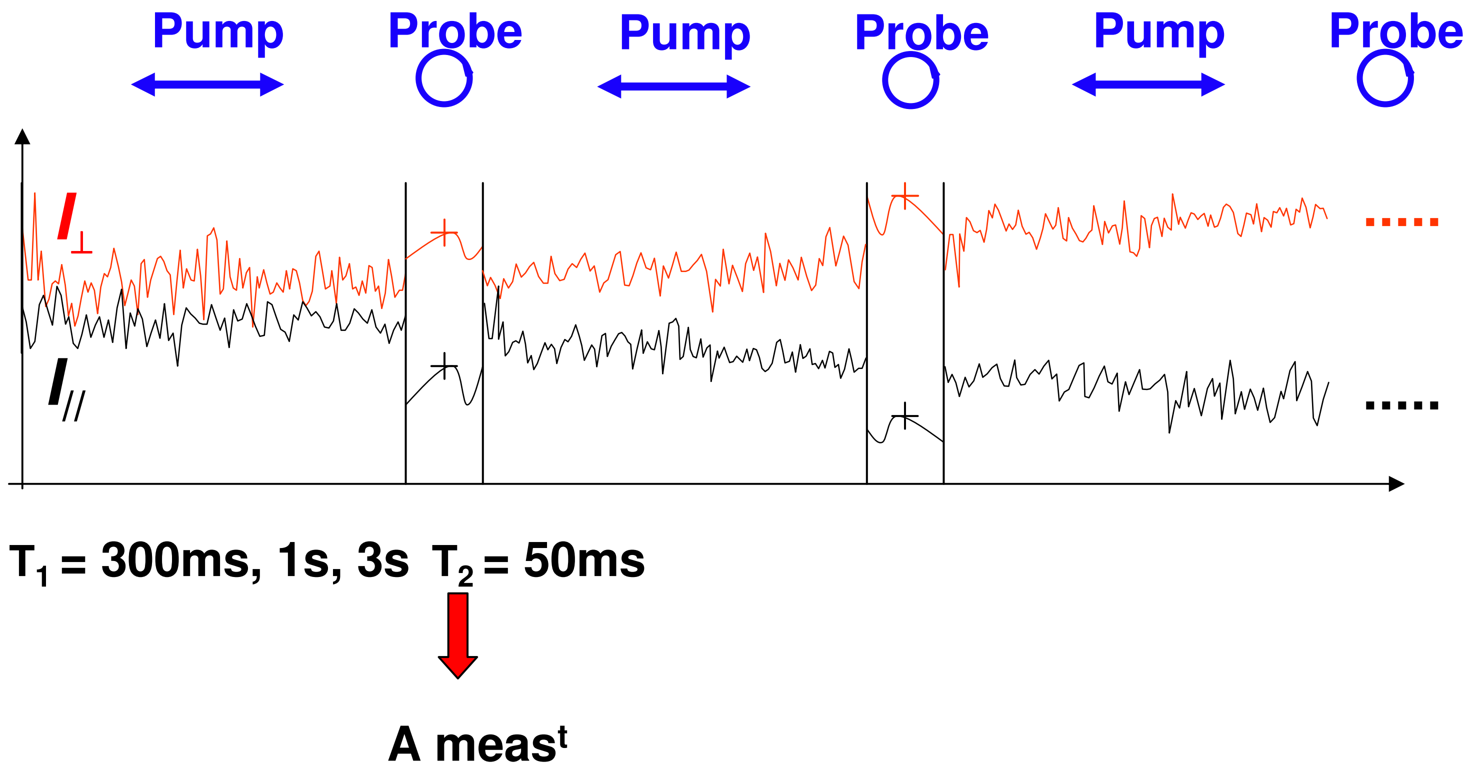


Fast thermal motion in PMA (τ_D~ 5-10ms @ 21℃)

Optical pumping of a single molecular dipole



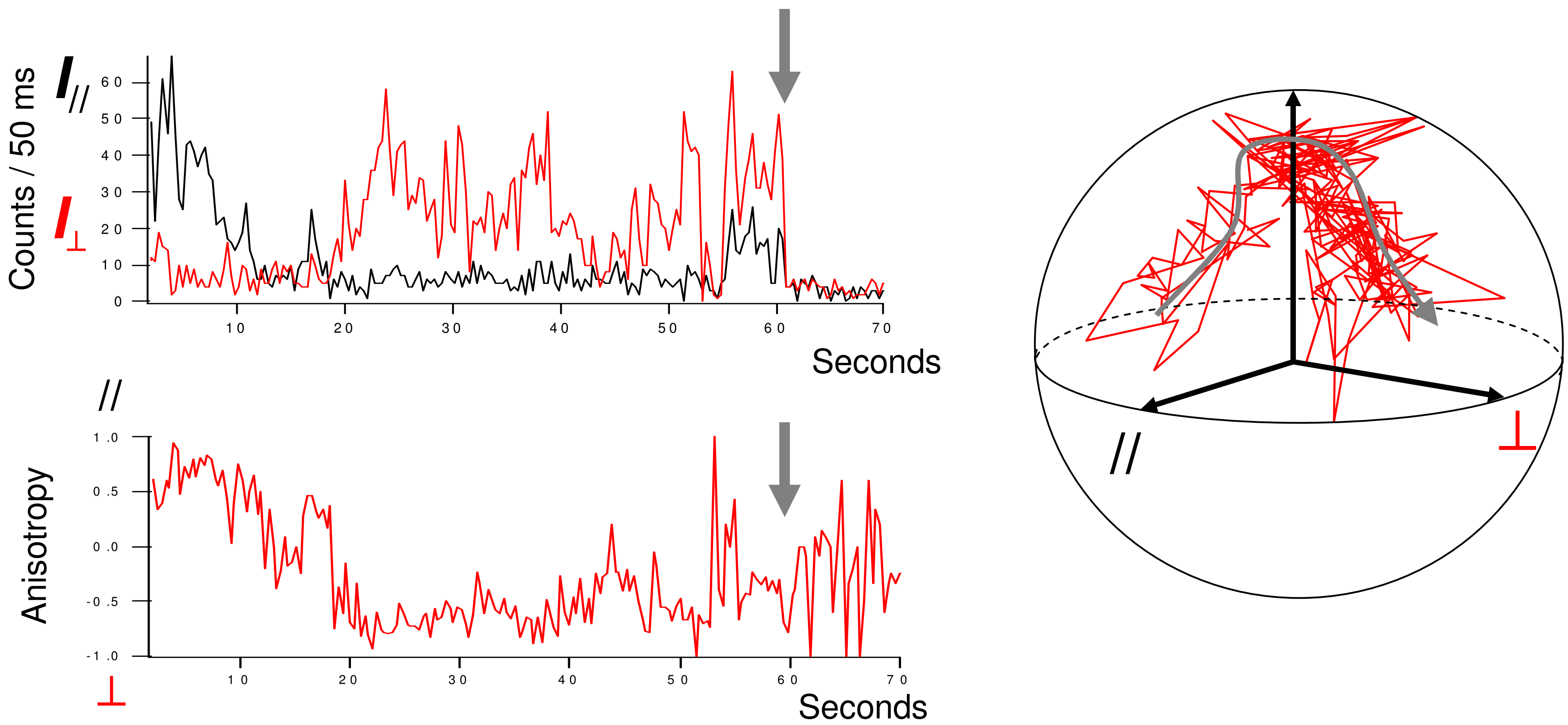
Optical pumping of a single molecular dipole



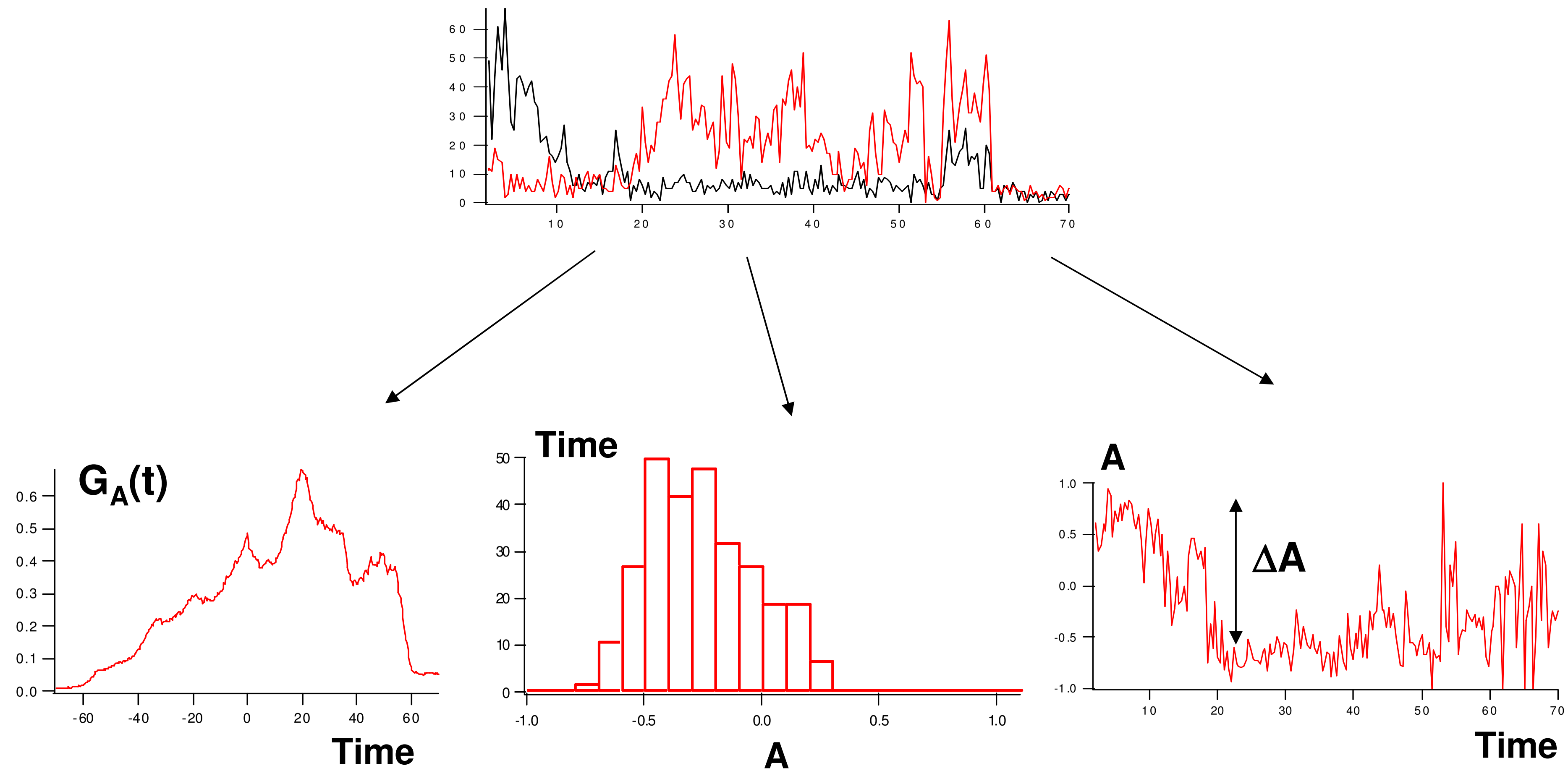
Dynamics of the photoinduced Rotation in PMA

T_1 = 300ms — **Pump**

T_2 = 50ms — **Probe**



Dynamic behavior



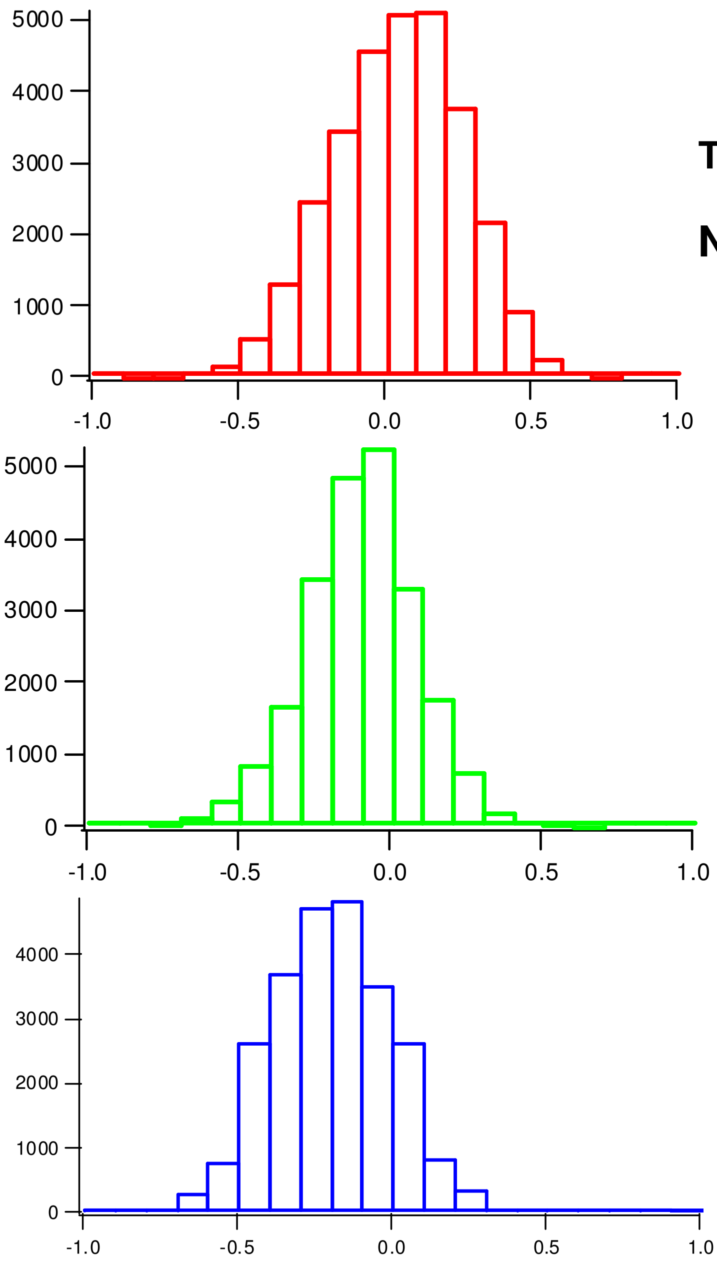
Cross-correlations of A(t): time scales, directional motion

Orientation Histrograms : T_{pump}-dependence

ΔA : large time scales

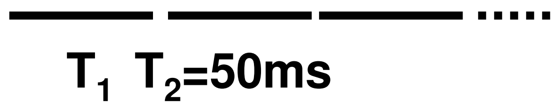
Deschesnes & Vanden Bout, Science (2001)

Orientation – Histrograms: dependence on the pump time

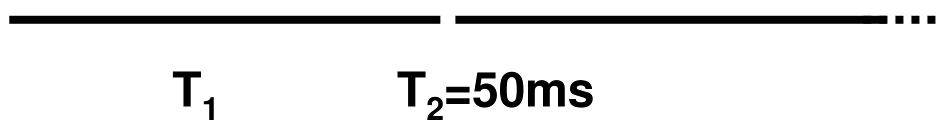


T_1 = 300ms

No pump



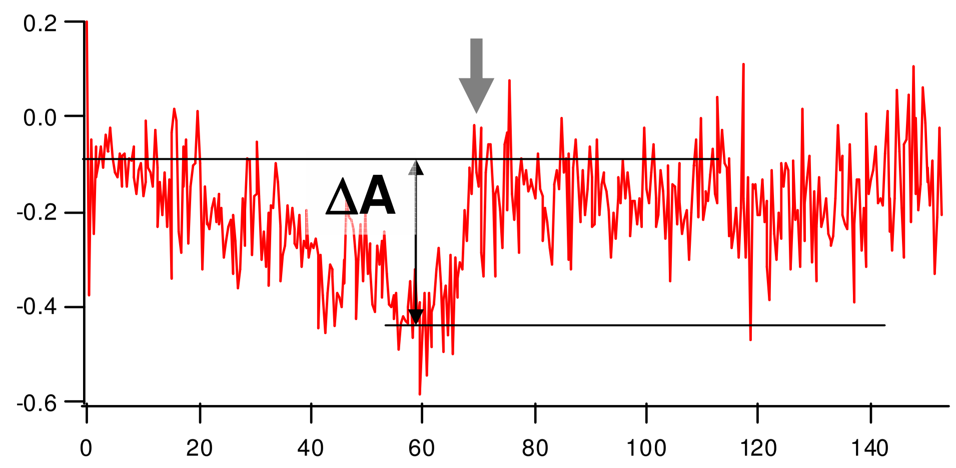
T_1 = 1s

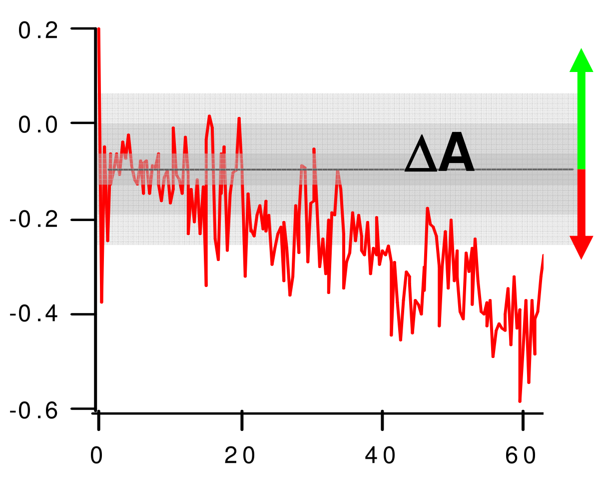


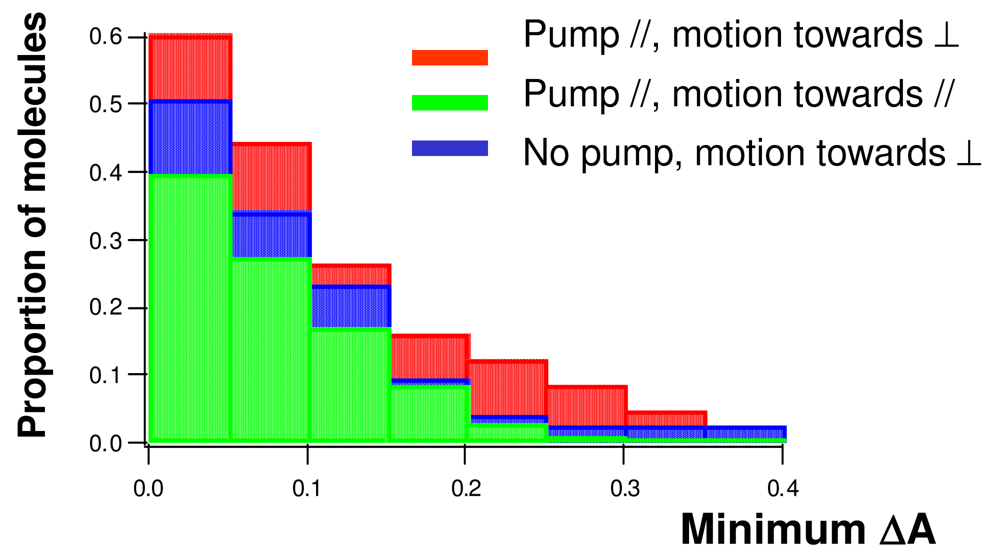
T_1 = 3s

- Photo-induced orientation occurs at time scale <1s
- Another slower time-scale occurs

ΔA asymptotic behavior (times > 10s)

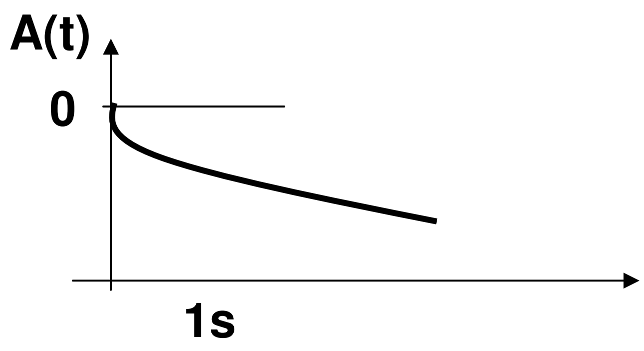




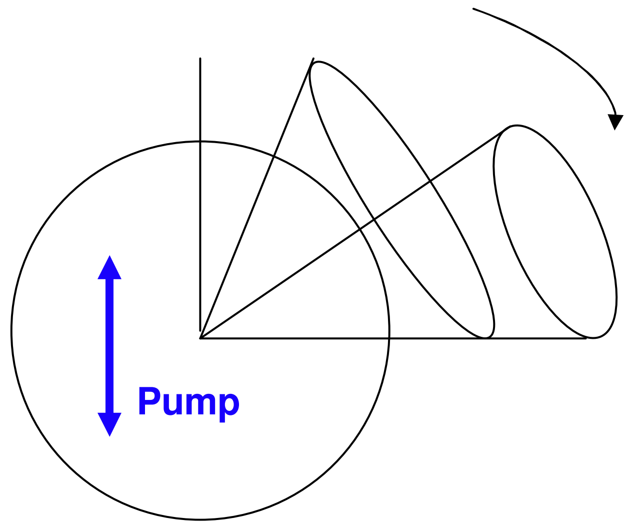


Molecular orientation in PMA

Multi-exponential motion

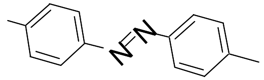


« Hindered » Thermal motion



Prospects

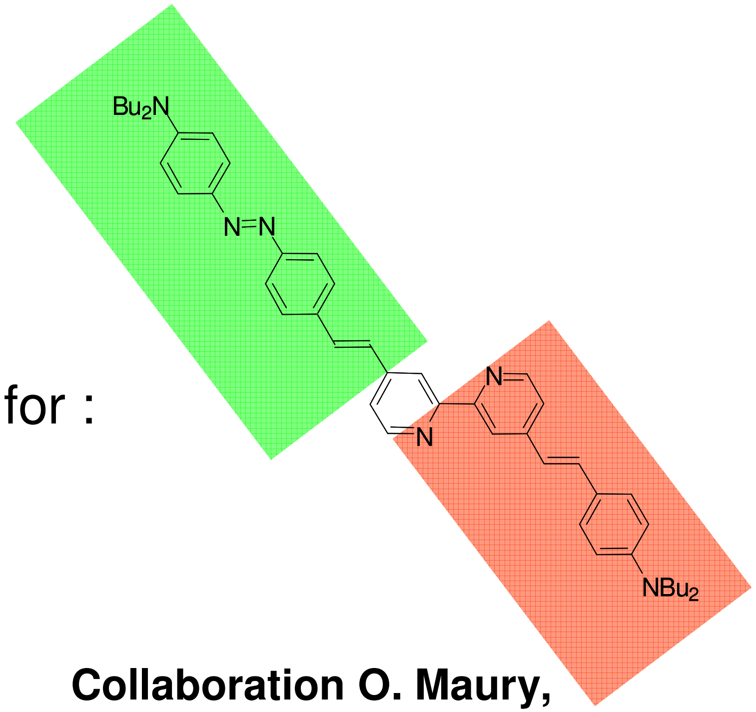
Multi-function molecular structures



Efficient photoisomerization: azobenzene

Fluorophore

Stability, high fluorescence QY

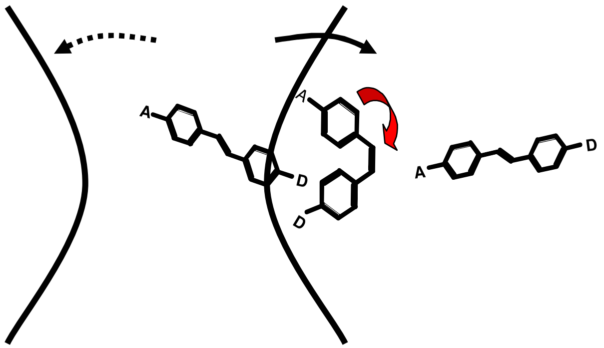


2 different wavelenghts excitation for :

- fluorescence (probe) at λ_1
- photoisomerization (pump) at λ_2

Collaboration O. Maury, Chemistry dept. ENS Lyon

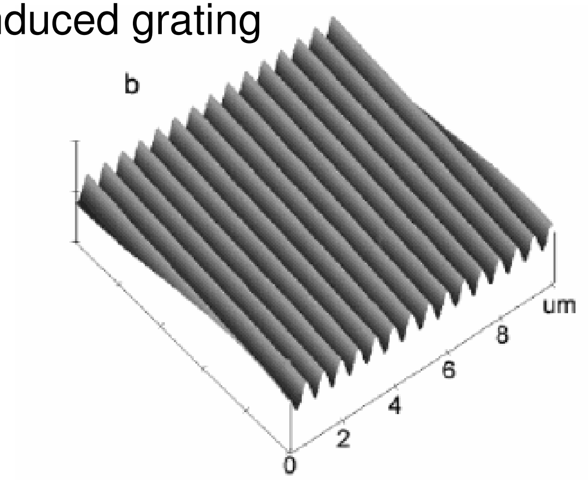
Single molecule translational motions



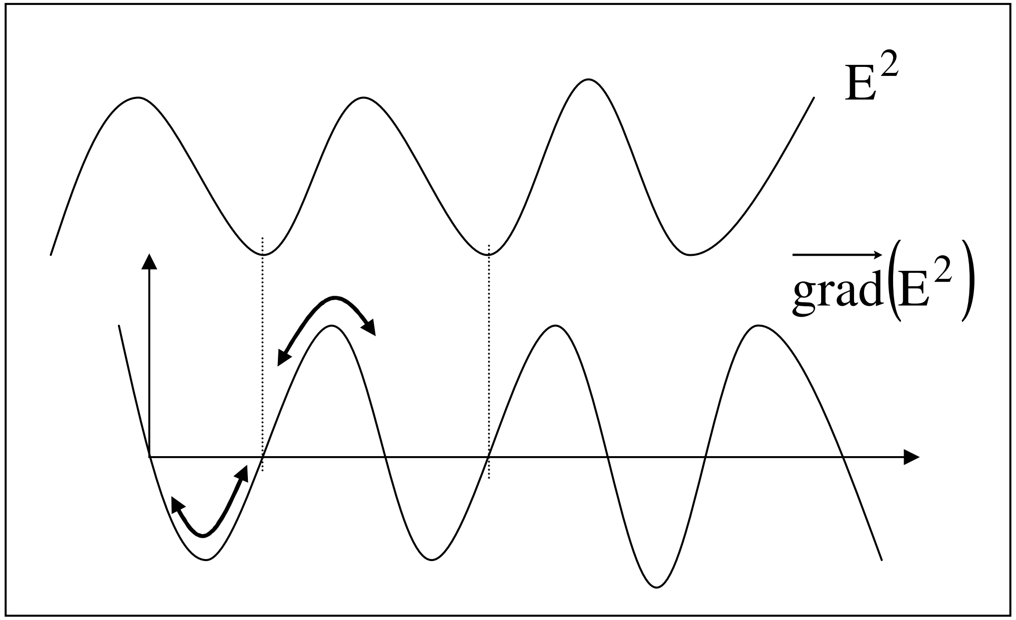
$$\vec{F} \propto \alpha \cdot \overrightarrow{grad}\left(E^2\right)$$

L. Kumar et al., Appl. Phys. Lett. 72 17 (1998)

Optically-induced grating



Wang et al., Macromolecules 37 (2004)



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LPQM

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O. Maury (ENS Lyon)

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