PFL experimental team, ICB, Dijon :
All optical measurement and control of molecular alignment

Institut Carnot de Bourgogne, UMR CNRS-UB 5209
BP 47 870, 21 078 DIJON cedex, France

Permanent staff : **O. Faucher, B. Lavorel, E. Hertz, F. Chaussard,**
F. Billard, R. Saint-Loup

PhD : **M. Renard, V. Renard, H. Tran, A. Rouzée**
V. Loriot, R. Tehini, Th. Vieillard

Collaboration with theory group : H. Jauslin, S. Guérin, D. Sugny

ICB
Institut Carnot de Bourgogne
UMR 5209 CNRS - Université de Bourgogne
http://icb.u-bourgogne.fr
Physique - Chimie
CNRS
UB
UNIVERSITÉ DE BOURGOGNE

Research area

- High resolution frequency-domain Raman spectroscopy :

  Rovibrational line frequency/intensity study

  Collisional effects on lineshape (linewidths, lineshifts, line mixing, speed effect, …)

- Time resolved spectroscopy :

  Pure rotational Raman spectroscopy (concentration and temperature measurements)

  Femtosecond CARS (collisional effects)

- Coherent control :

  LICS

  Molecular alignment

Main experimental means

- High resolution frequency-domain Raman spectrometer (0.003 cm^{-1})
- Two repetition rate CPA laser system (100 and 1000 Hz, 10 and 1 mJ, 90 fs)
- Molecular jets : pulsed and CW (in construction)
- Pulse shapers : 128 and 320 pixels LCD masks
- Spider and autocorrelator
- Optical devices for pump-probe experiments :

  Raman induced polarization spectroscopy
  DFWM, CARS
  Cross-defocusing
  FTOP
  TOF spectrometer
  ion/electron imaging spectrometer

Outline

I. Optical techniques for measurement of field-free molecular alignment

II. Control of field-free alignment through polarization and phase modulation

III. One application: calibration of ionization rate

IV. Recent developments: 3-D alignment, alignment and collisional relaxation, optimization of alignment

I. Measurement of field-free molecular alignment

Measurement of $<\cos^2\theta>$

Ion imaging after ionization-dissociation (Stapeldfeldt, Vrakking, …)

Variation of index of refraction due to molecular alignment (Dijon group)

Non-intrusive
High density

$$n_Z - 1 = \frac{\rho}{2\varepsilon_0}\left[\bar{\alpha} + \Delta\alpha\left(\left\langle \cos^2\theta \right\rangle_{(t)} - \frac{1}{3}\right)\right]$$

$$n_Y - 1 = \frac{\rho}{2\varepsilon_0}\left[\bar{\alpha} + \Delta\alpha\left(\left\langle \cos^2\psi \sin^2\theta \right\rangle_{(t)} - \frac{1}{3}\right)\right]$$

Nonlinear part of n_y, n_z

$\Delta\alpha = (\alpha_{//} - \alpha_{\perp}) \rightarrow$ polarizability anisotropy

$\rho \rightarrow$ molecular density

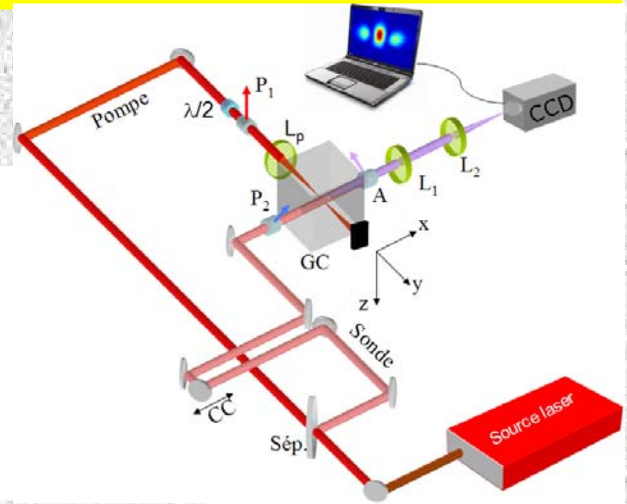
$\bar{\alpha} = \frac{\alpha_{//} + 2\alpha_{\perp}}{3} \rightarrow$ mean polarizability (linear index of refraction)

In isotropic media, all expectation values are 1/3 ---> $\Delta n_{Y,Z}=0$
The interaction induces (time-dependent) expectation values different from 1/3
through Raman ($\Delta J=2$, $\Delta M=0$) transitions ---> efficient alignment with intense laser pulses

First measurements through birefringence → Phys. Rev. Letters. 90, 153601 (2003)
Phys. Rev. A 70, 033420 (2004)

I. Measurement of field-free molecular alignment

$$I_{signal} \propto \left(\left\langle \cos^2\theta \right\rangle - \frac{1}{3} \right) \quad \text{or} \quad I_{signal} \propto \left(\left\langle \cos^2\theta \right\rangle - \frac{1}{3} \right)^2$$



(<cos²θ> is a function of the pump intensity and the time elapsed after the pump shot)

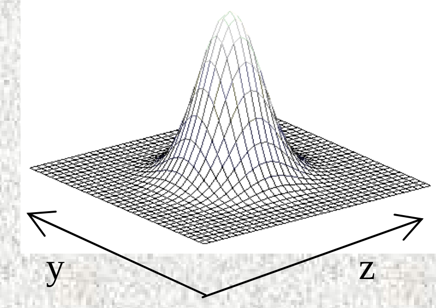
Spatial and time dependence

(<cos²θ>$_{(r,t)}$

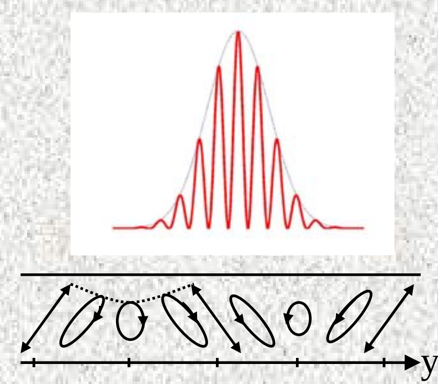
$\Delta n_{y,z}(r,t)$

Imaging of birefringence

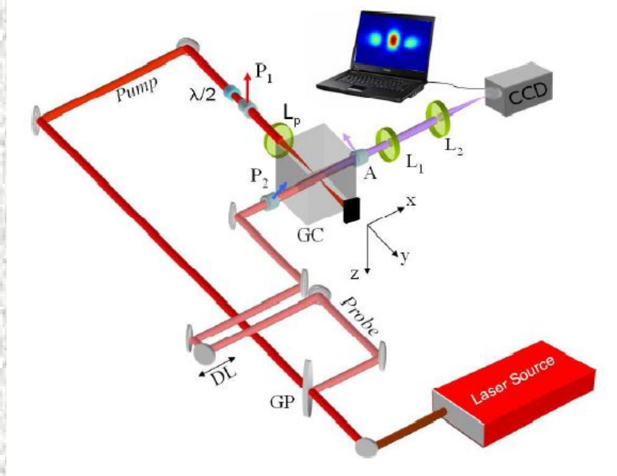
Spatial effect : cross-defocusing (gradient $n_{y,z}(r,t)$)



Spatial effect: transient grating (periodical distribution of $n_{y,z}$)

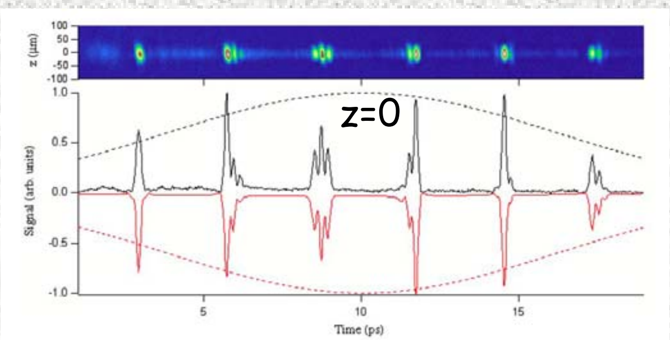


I. Measurement of field-free molecular alignment



Experimental setup

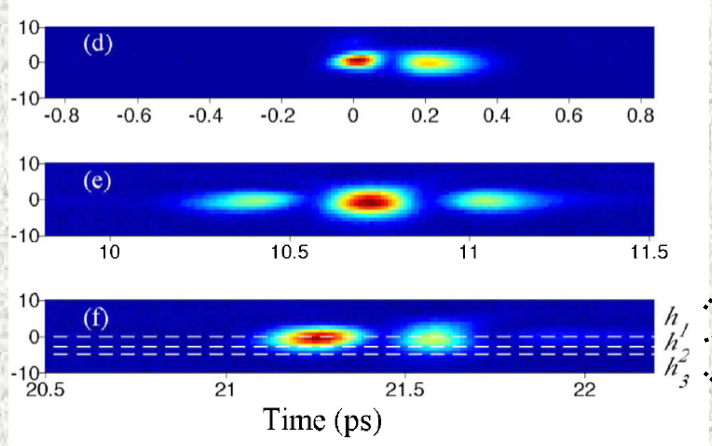
A single shot technique

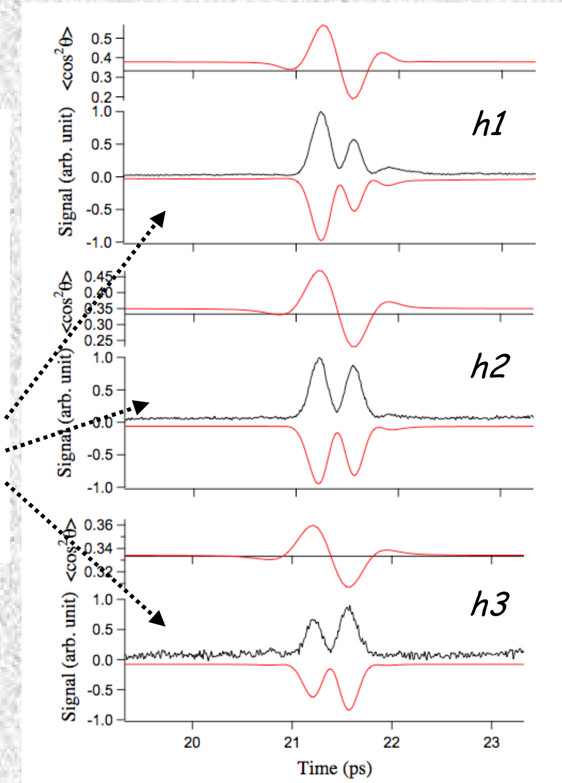


O_2 at 1 atm and 295 K
10 ps pump-probe delay
Intensity 49 TW/cm^2

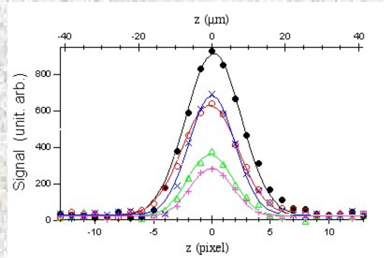
FTOP: Femtosecond time-resolved optical polarigraphy for the measurement of postpulse alignment

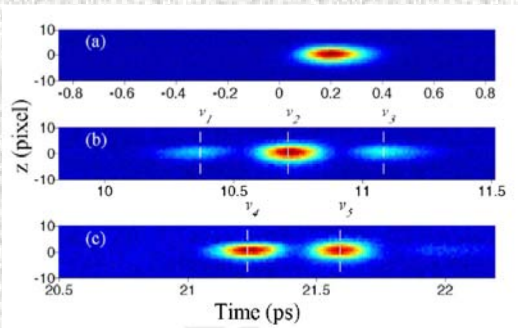
Time and intensity analysis on one image





CO_2
(h_1): z = 0; (h_2): z = -3; (h_3) z = -5 pixels
I = 62, 34, and 7 TW/cm^2





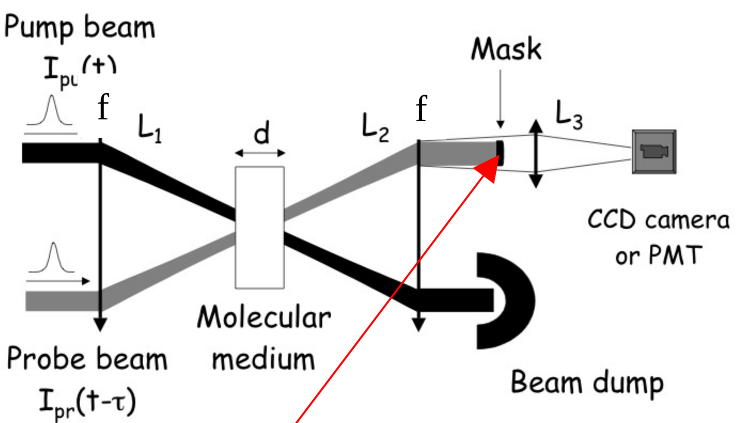
Retrieval of the gaussian vertical profile of the pump

Phys. Rev. A 78, 013412 (2008)

I. Measurement of field-free molecular alignment

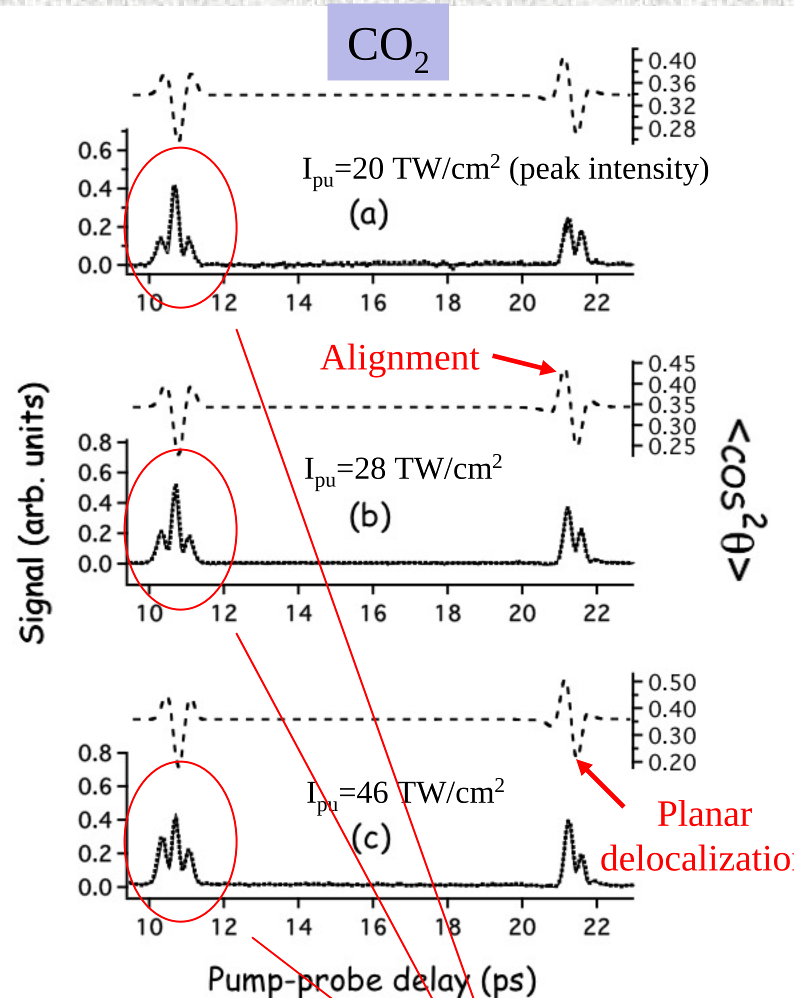
Cross-defocusing at moderate pump intensity: coronography

Optics Lett. 30, 70 (2005)



$(\langle\cos^2\theta\rangle - 1/3)\ \alpha\ I_{pu}$

No plasma, $d < f_{NL}, \rho_0 < f$



Index gradient due to alignment

Beam dimension : $$w^2(z) = w_L^2(z)\left(1 + \frac{16 d^2 \rho_0^2 \Delta n^2}{n_0^2 w_0^4}\right)$$

The medium behaves like a (nonlinear) lens

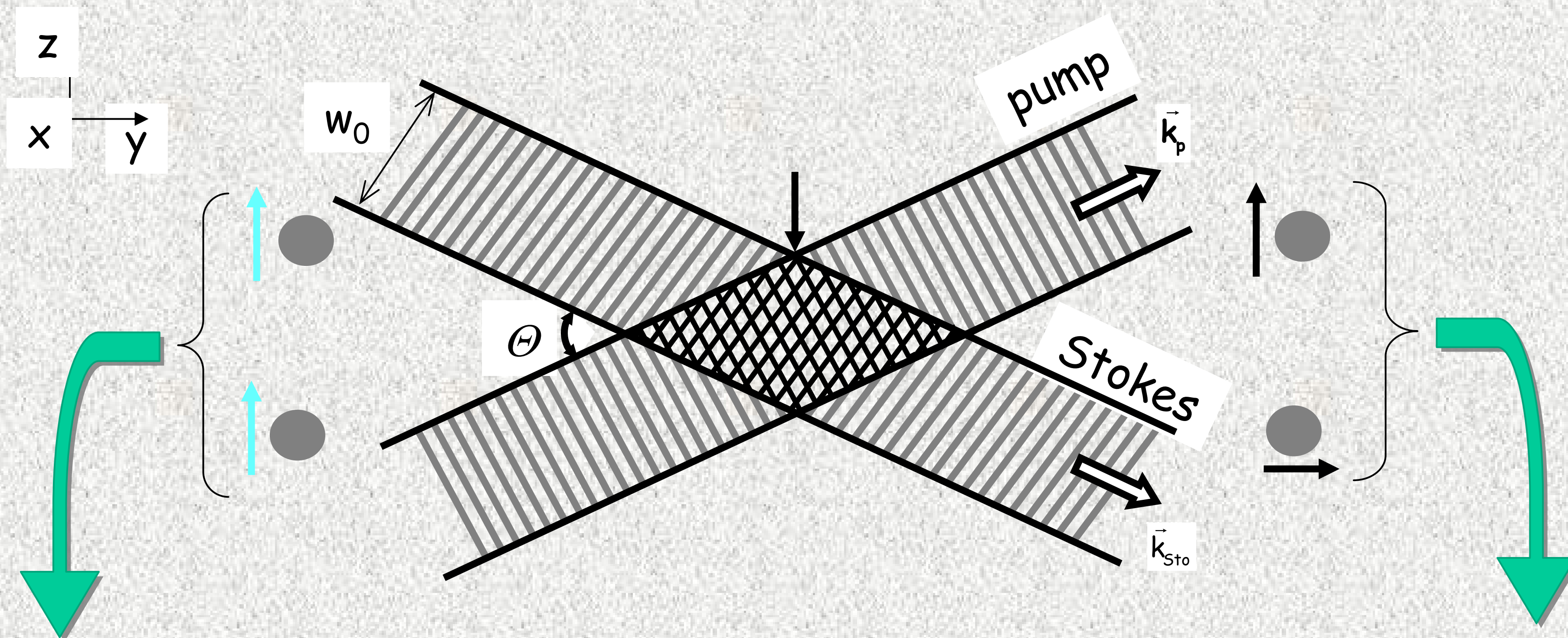
$$I_{signal} \propto \left(\left\langle \cos^2\theta \right\rangle - \frac{1}{3}\right)^2$$

Modification:Interference with the permanent alignment

$$\left\langle \cos^2\theta \right\rangle_{J_0,M_0}(t) = \sum_J \alpha_{J,M_0}\left|C_J^{J_0,M_0}\right|^2 + 2\sum_J \beta_{J,M_0}\left|C_J^{J_0,M_0} C_{J+2}^{J_0,M_0}\right| \cos\left(\omega_J t + \Delta\Theta_J^{J_0,M_0}\right)$$

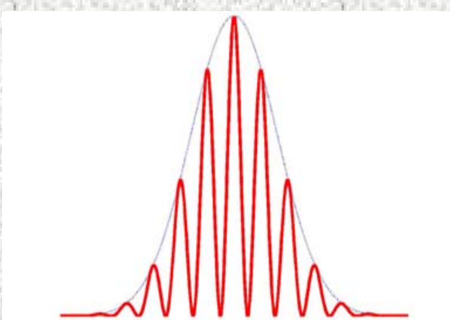
I. Measurement of field-free molecular alignment

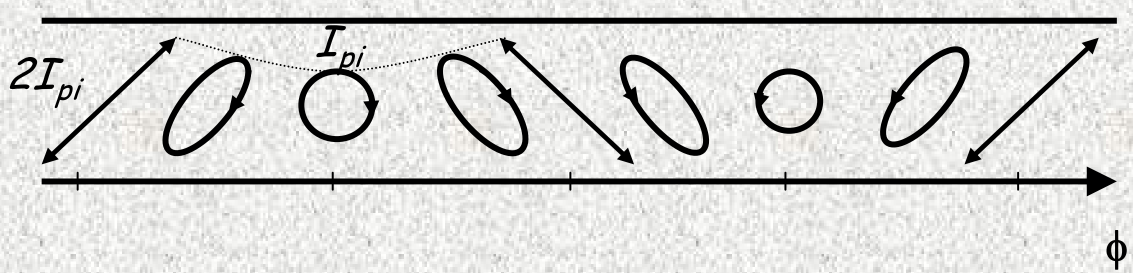
Transient gratings



Intensity grating : $I \propto |E|^2 \propto 4A^2 \cos^2 k_z z$

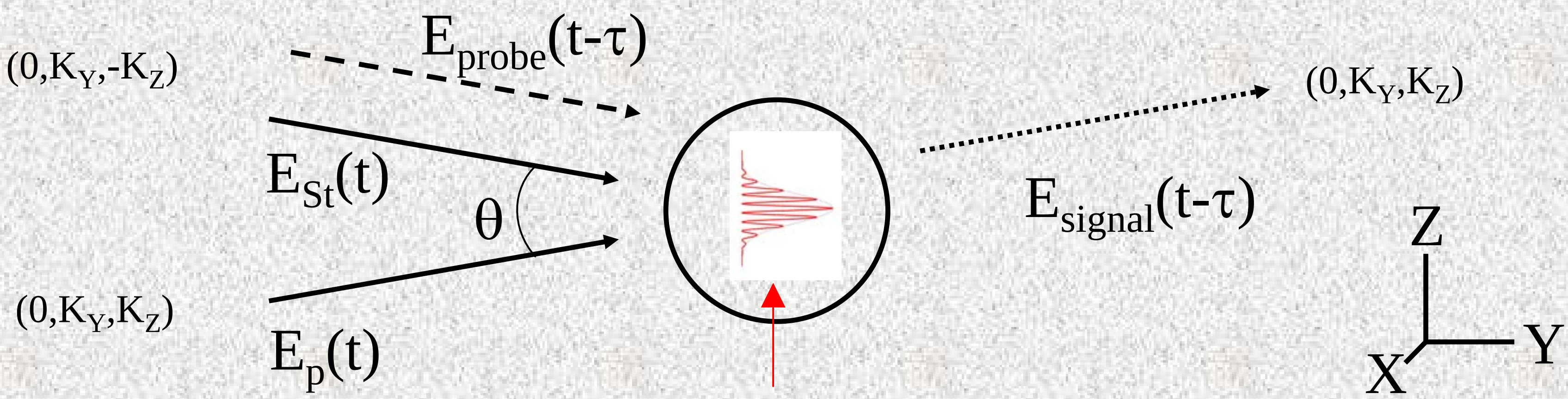
$$\vec{E}_{tot} = A \exp\left[i(\omega t - k_x x - k_y y)\right] \begin{vmatrix} 0 \\ 1 \\ e^{i\phi} \end{vmatrix}$$





I. Measurement of field-free molecular alignment

DFWM-transient grating



Molecular transient grating

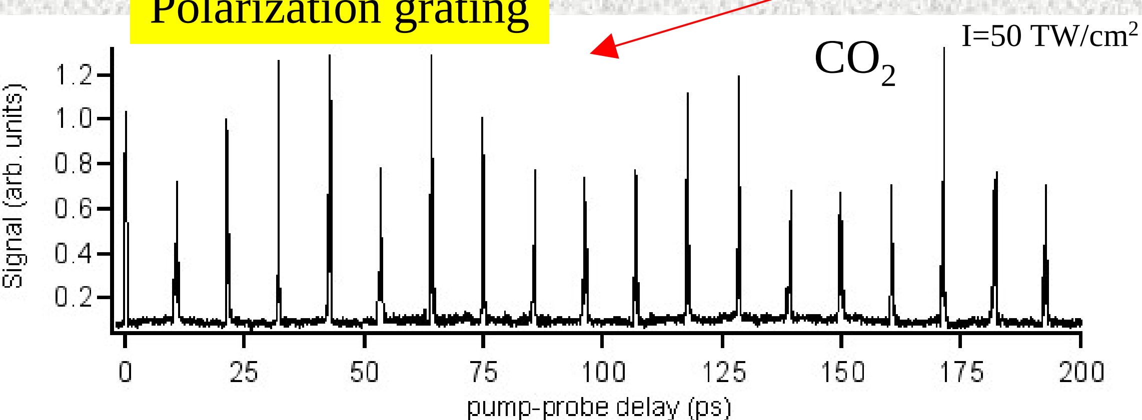
DFWM gives a better sensitivity and allows to work at lower pressure and lower temperature

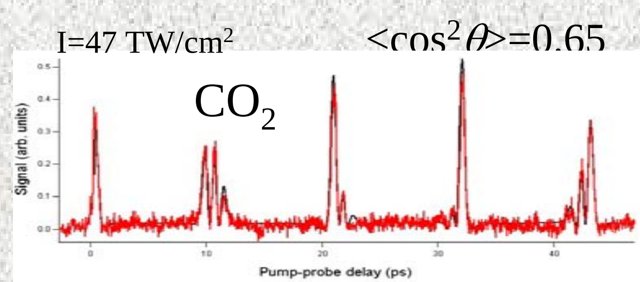
T = 30 K, molecular jet

Ex: T= 296 K, p= 6 mbar

Polarization grating

Better alignment

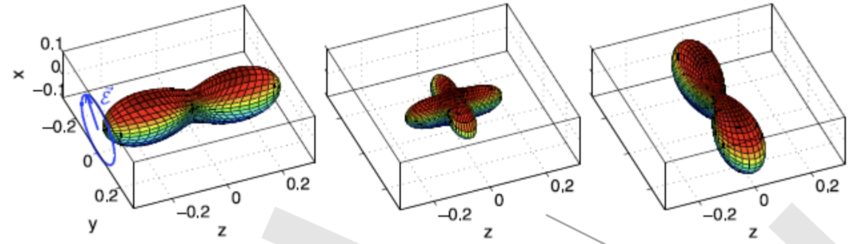




II. Control of field-free molecular alignment

Two-direction alignment alternation with elliptic laser pulses

Theory



$a^2=1/3$
$b^2=2/3$

Representation of the molecular state in spherical coordinates $\{r = |\psi(\theta_z, \phi_z; t)|^2, \theta_z, \phi_z\}$ for $a^2 = 1/3$, $\xi = 11.1$, $\tilde{T} = 20$, at times $t = \tau_{rot}/4$ (left panel), $t \approx 3\tau_{rot}/8$ (middle panel), and $t = 3\tau_{rot}/4$ (right panel). The polarization ellipse of the field $\vec{\mathcal{E}}$ is sketched in the (x, y) plane.

Cross-defocusing experiment in CO_2

(T=296 K, P=4 x10^4 Pa)

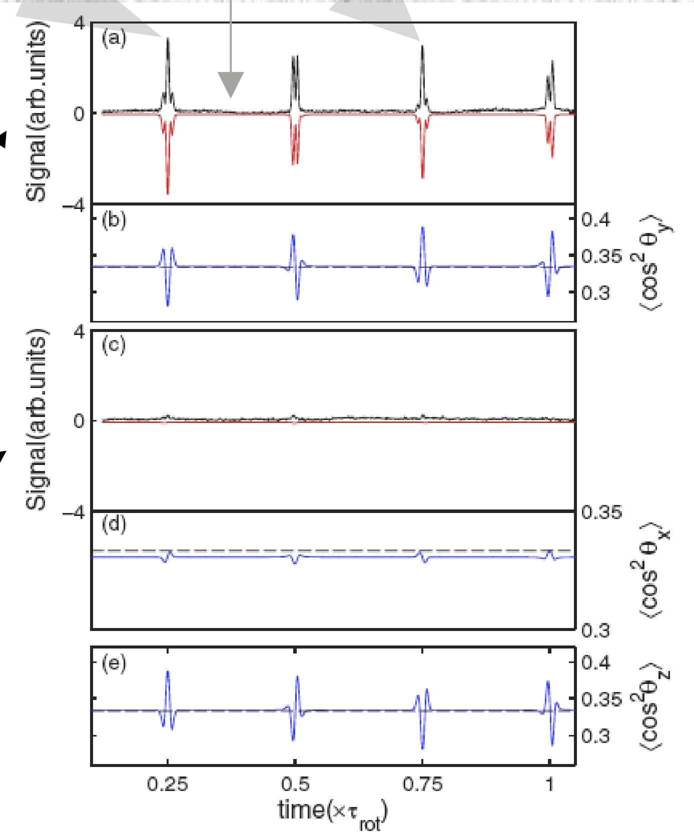
Elliptically polarized pump field ($a^2=1/3$), peak intensity 25 TW/cm^2 and pulse duration 100 fs

Alternation evidenced through measurement

along two orthogonal directions : -*y* axis (a)

-*x* axis (c)

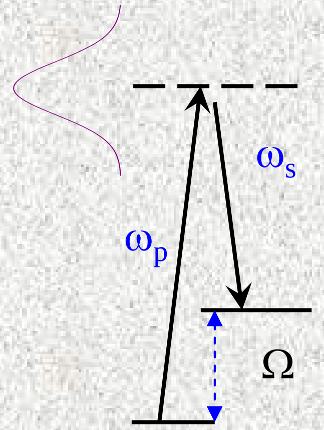
$$\sum_{i=x,y,z} \cos^2 \theta_i = 1$$

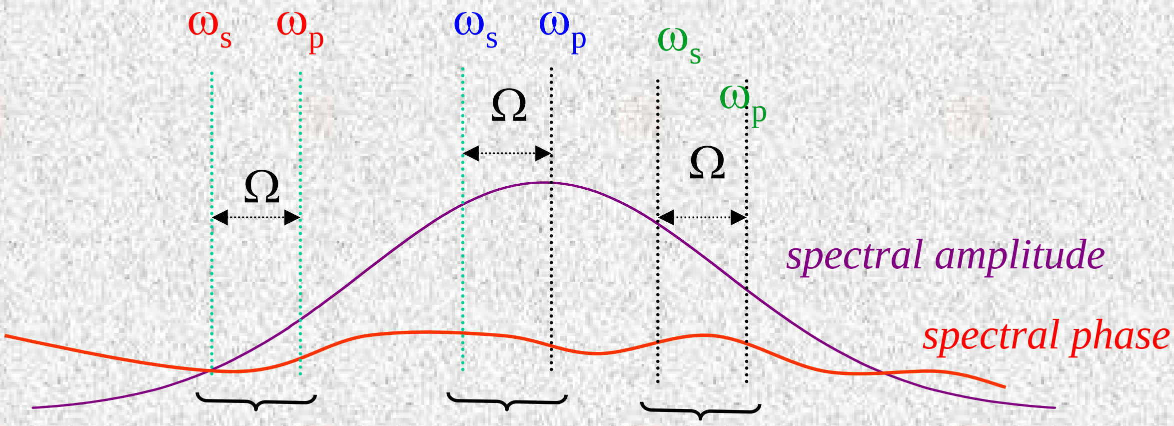


II. Control of field-free molecular alignment

Phase shaping and intrapulse interference

Impulsive Raman process





$$\sum \text{photon pairs with frequencies} \left[\omega', (\omega'-\Omega)\right]$$

Excitation intensity

$$F(\Omega) = \int_{-\infty}^{+\infty} E(\omega')\, E^*(\omega'-\Omega)\, d\omega' = \int_{-\infty}^{+\infty} \varepsilon(\omega')\, \varepsilon(\omega'-\Omega) \exp[i\Delta\phi(\omega')]\, d\omega'$$

$$F(\Omega) = f(\Omega) \exp[i\,\phi_f(\Omega)]$$

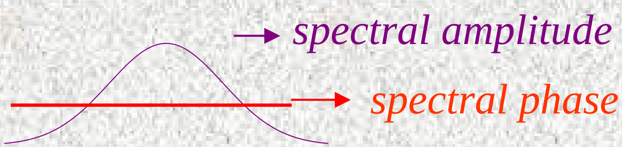
spectral phase modulation ⇨ Control of ***amplitude*** and ***phase*** of the Raman transition excitation

Shaped pulses: Phys. Rev. A 69, 043401 (2004), Phys. Rev. A 72, 025401 (2005)

Two pump pulses: Phys. Rev. A 61,3816 (2000), J. Chem. Phys. 113, 6132 (2000)

Spectral phase modulation

Transformed limited pulse



Gaussian spectral amplitude :

$$\varepsilon(\omega) = A \exp\left[-\frac{\omega^2}{\Delta\omega^2}\right]$$

Spectral phase :

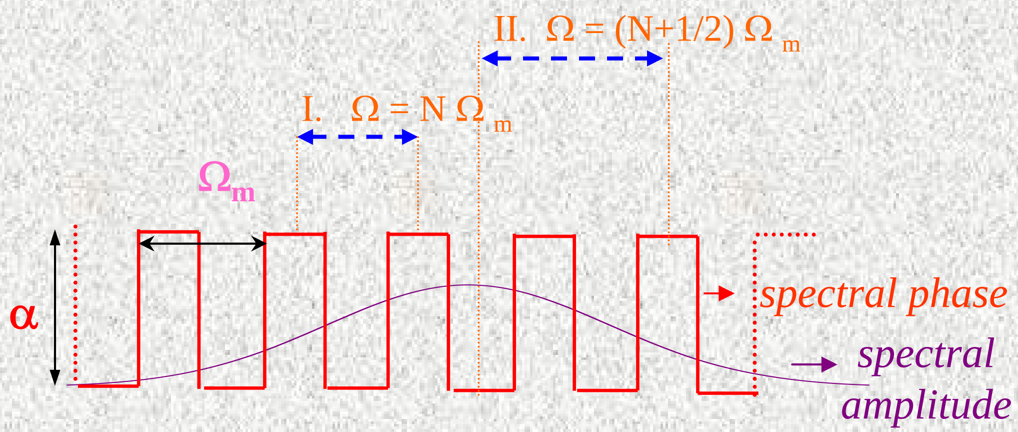
$$\phi(\omega) = 0$$

$$F_{TLP}(\Omega) = A\sqrt{\frac{\pi}{2}}\,\Delta\omega\,\exp\left[-\frac{\Omega^2}{2\Delta\omega^2}\right]$$

Periodic spectral phase

Ω_m modulation period

α modulation amplitude



I. First case: $\Omega = N\,\Omega_m$

$$\forall\omega,\ \Delta\phi(\omega) = 0$$

$$\Downarrow$$

$$\boxed{F(\Omega) = F_{TLP}(\Omega)}$$

II. Second case: $\Omega = (N+1/2)\,\Omega_m$

$$\forall\omega,\ \Delta\phi(\omega) = \pm\alpha$$

$$\Downarrow$$

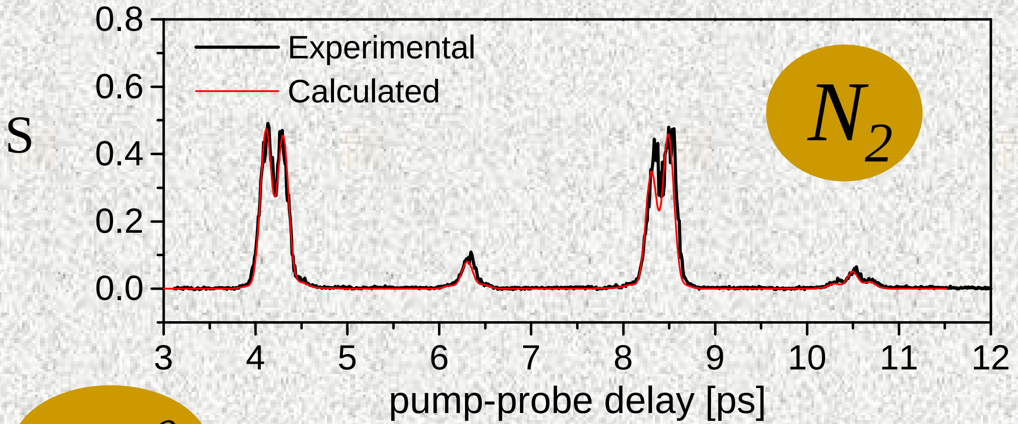
$$\boxed{F(\Omega) = \cos(\alpha)\,F_{TLP}(\Omega)}$$

PRA 69, 043401 (2004)

Liquid cristal spatial light modulator : *Opt. Express 12, 473 (2004)*

II. Control of field-free molecular alignment

Alignment in N_2 : the two different symmetry wavepackets

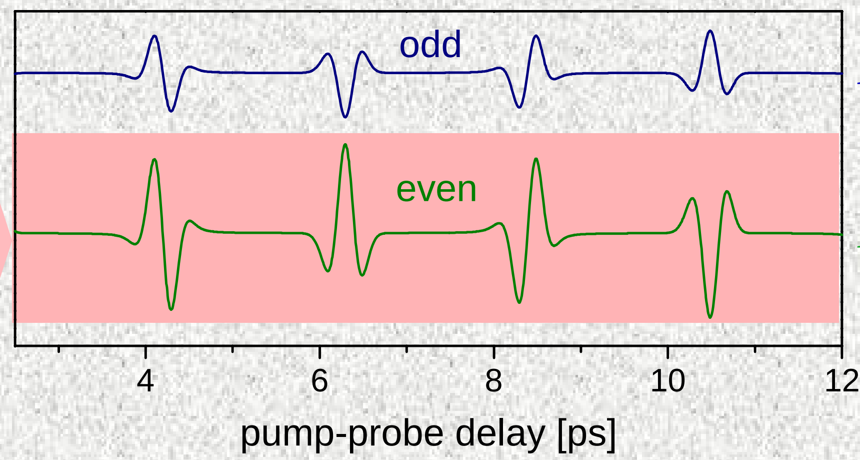


$$S(\tau) = \kappa\left(\Delta n(\tau)\right)^2$$

$$= K\left(E_{odd} + E_{even}\right)^2$$

J even   J odd

$\alpha = 0$



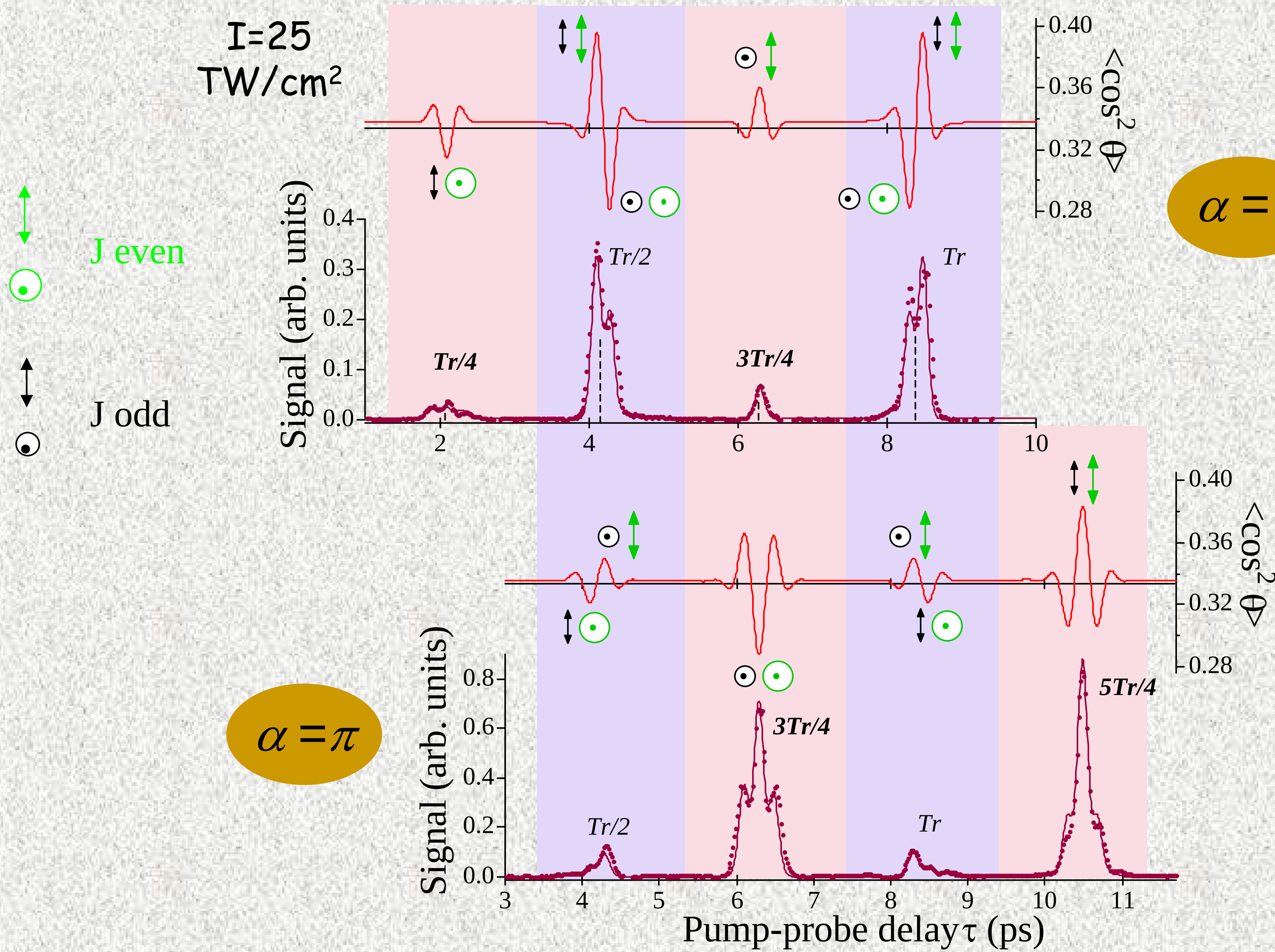
$$E_{odd} = \left\langle \left\langle \cos^2\theta \right\rangle_{J_0 odd, M_0} \right\rangle_T - \frac{1}{3}$$

$$E_{even} = \left\langle \left\langle \cos^2\theta \right\rangle_{J_0 even, M_0} \right\rangle_T - \frac{1}{3}$$

Ω_m adjusted as to only control the even state distribution by applying a $\alpha=\pi$ phase in its excitation

II. Control of field-free molecular alignment

Control of alignment with a shaped spectral phase



III. Applications of field-free molecular alignment

Measurement of ionization probability

The cross-defocusing experiment is sensitive to both molecular alignment and plasma:

$$S(t) \propto I_{pr}(t) \otimes \left[\Delta n_{R0}(t) + N_L \times \Delta n_{P0}\right]^2$$

At high intensity

Molecular alignment

proportional to <cos$^2\theta$>-1/3

Plasma

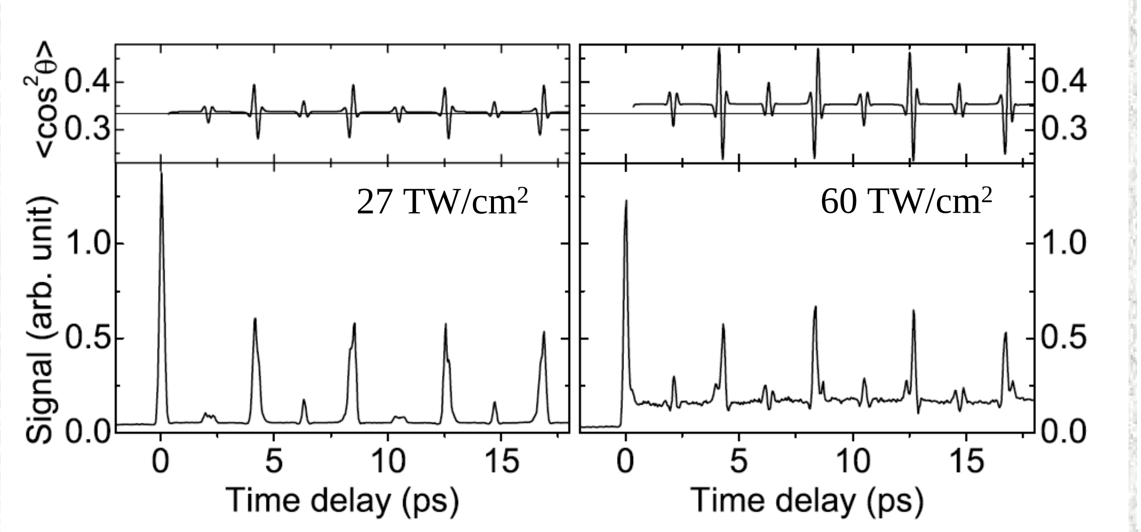
Δn_{P0} : Negative refractive index of free electrons

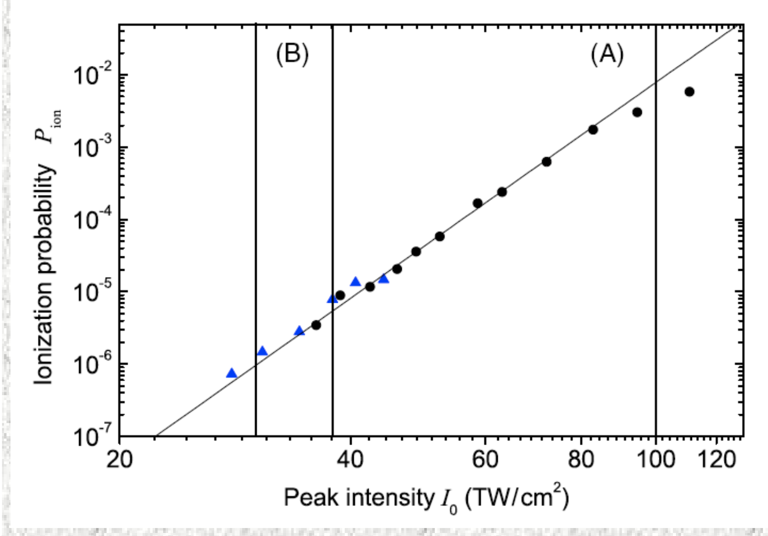
N_L : nonlinearity of ionization

Experiment in N_2

Opt. Lett. 31 2897 (2006)

J. Phys. B 41 015604 (2008)



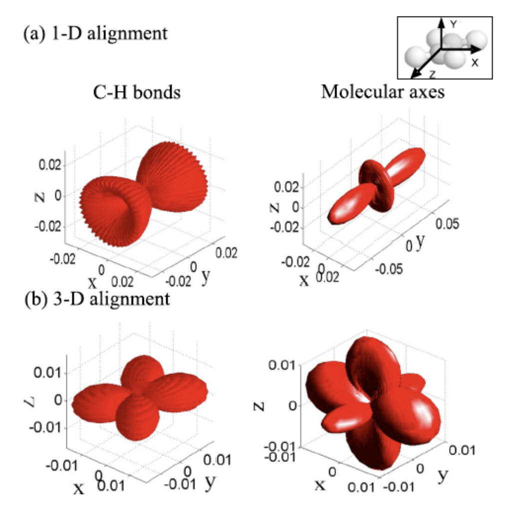


IV. Recent developpments in field-free molecular alignment

Alignment in dissipative media: high pressure gases → See the poster of Thomas Vielliard

J. Raman Spectrosc. 2008

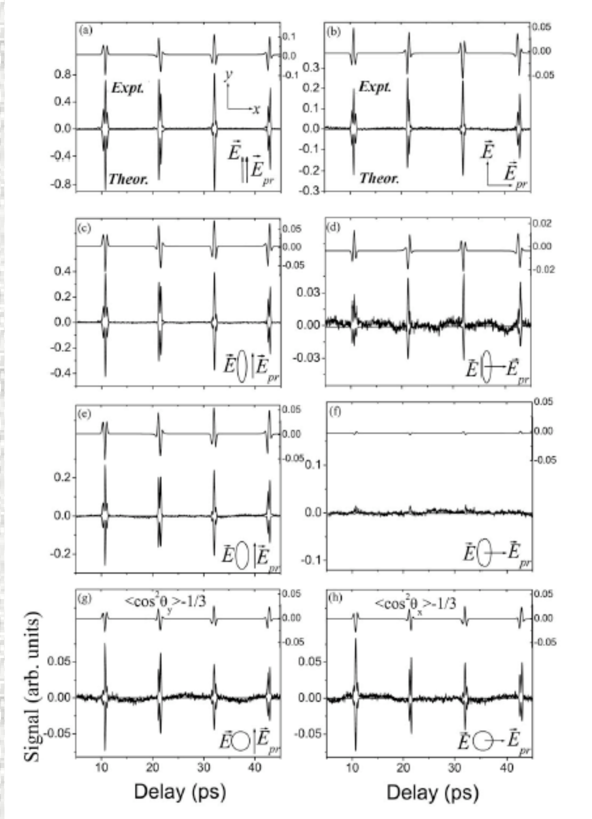
3-D characterization and alignment with elliptically polarized pulses (cross-defocusing measurement)



C_2H_4

PRA 77 043412 (2008)

Experiment: weak 3-D alignment !



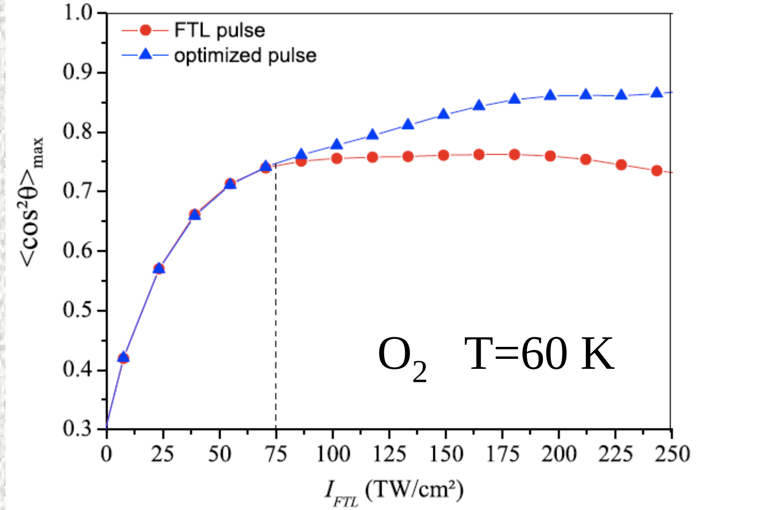
CO_2 PRA 76 043423 (2007)

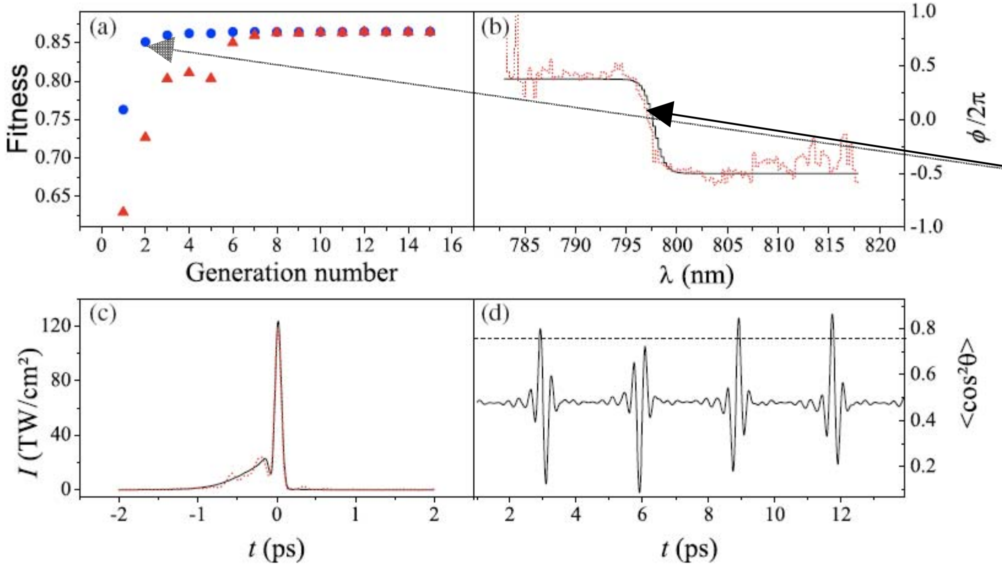
Cross-defocusing

IV. Recent developpments in field-free molecular alignment

Optimization

Theoretical results on optimization with Spectral phase shaping and genetic algorithm





Modelling with a sigmoid-type phase function

$$\phi_n = s\frac{1}{1+e^{a(n-n_0)}} + k$$

Experiment in progress !

PRA 75 031403R (2007)
J. Phys. B 41 074002 (2008)
PRA 77 041404R (2008)