

Cours n°6

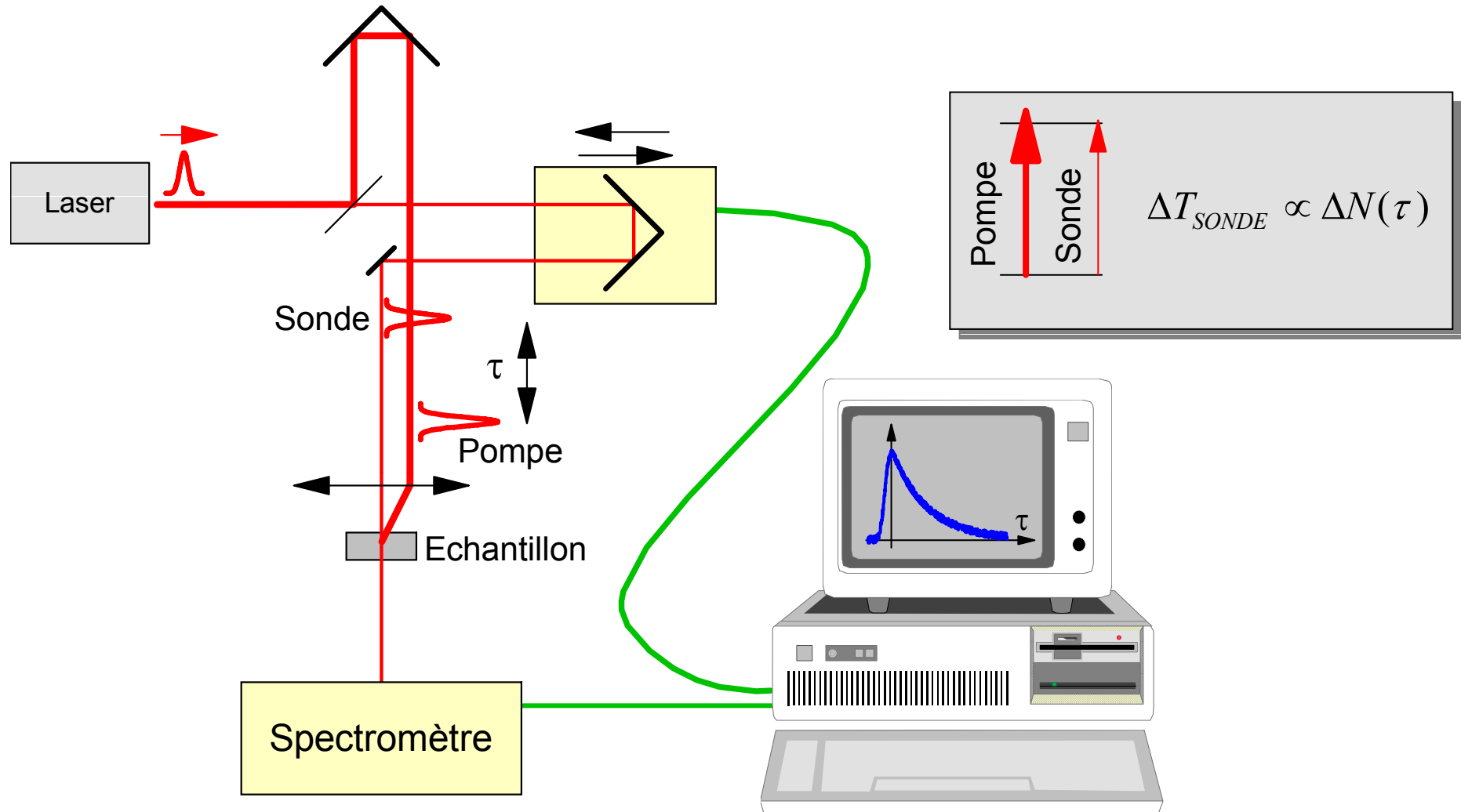
Applications des lasers femtosecondes

Manuel Joffre

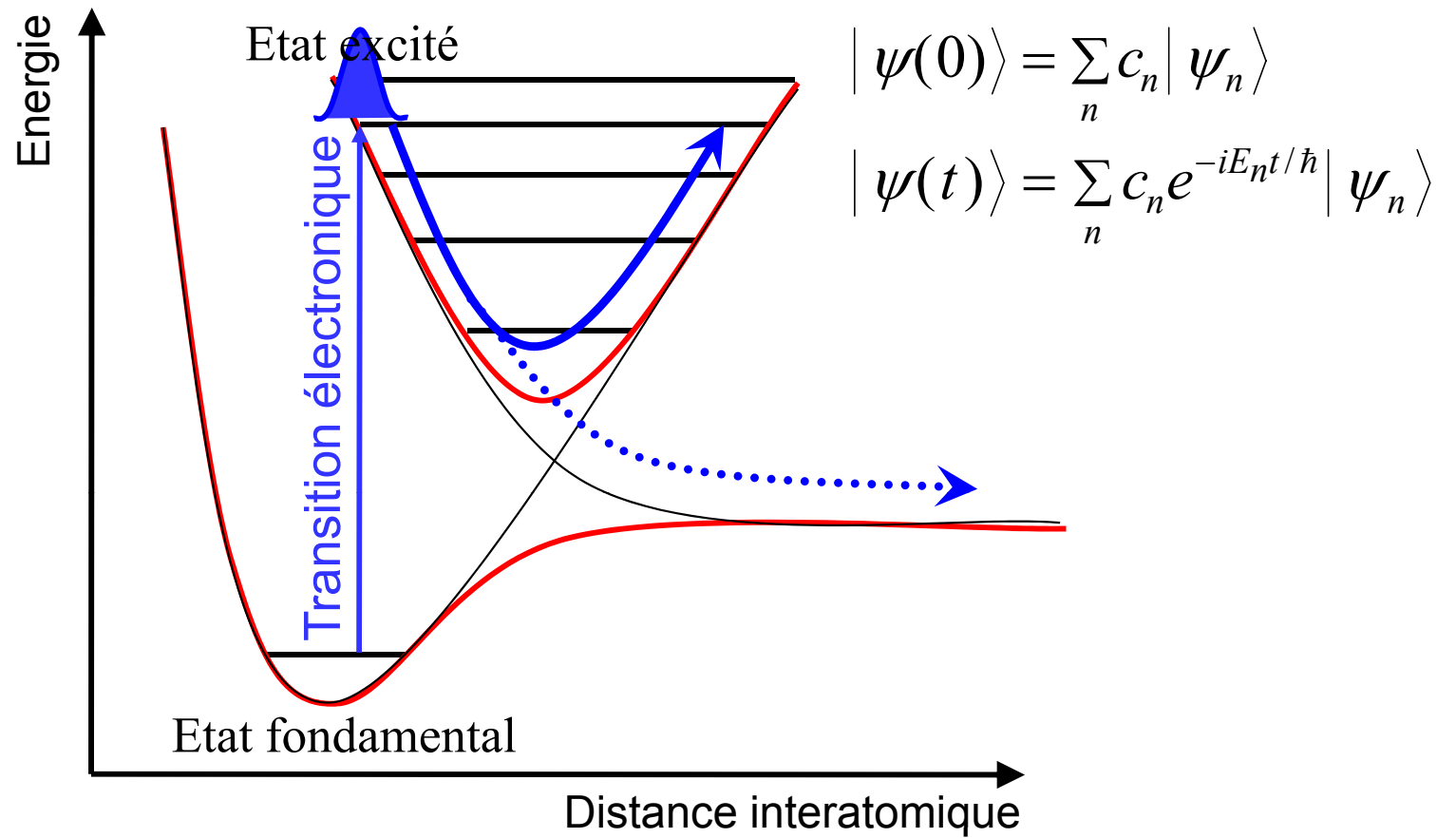
www.enseignement.polytechnique.fr/profs/physique/Manuel.Joffre/dea/

1. Expérience pompe-sonde
2. Spectroscopie multidimensionnelle
3. Contrôle cohérent
4. Microscopie non-linéaire

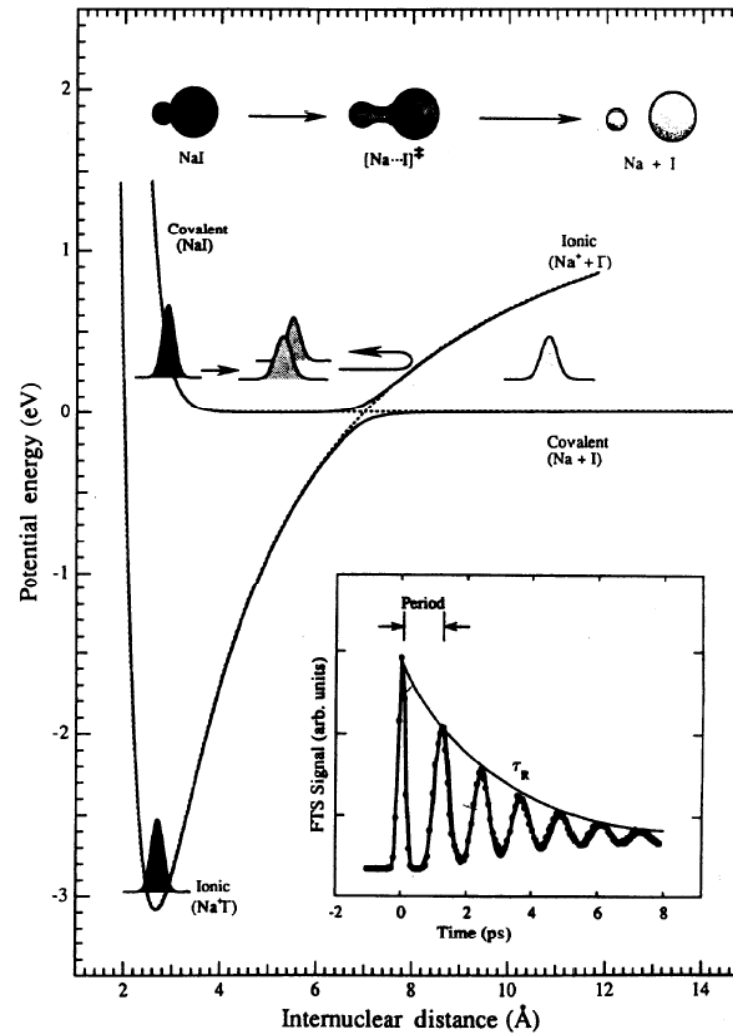
Expérience pompe-sonde



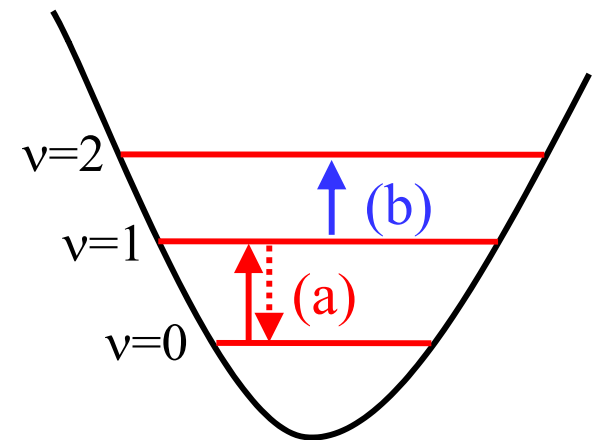
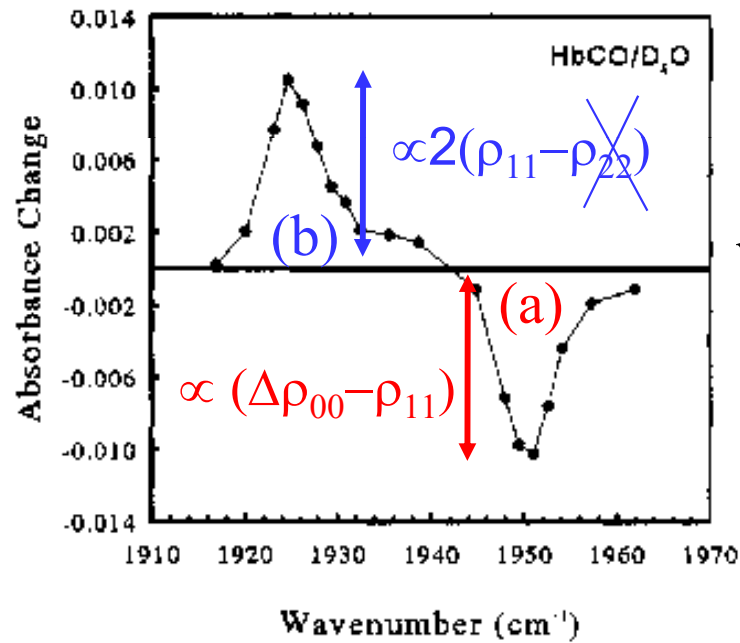
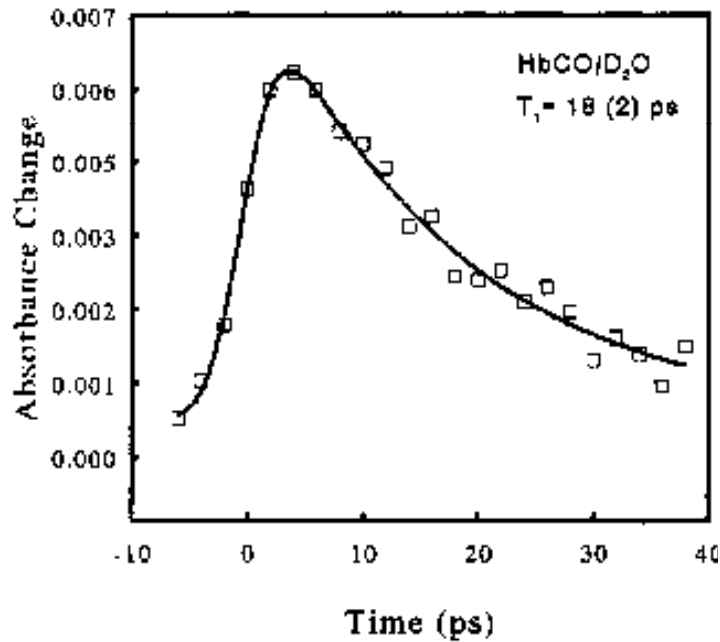
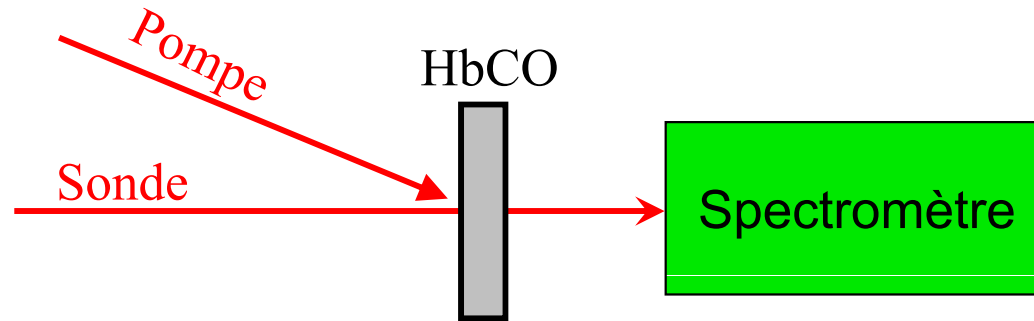
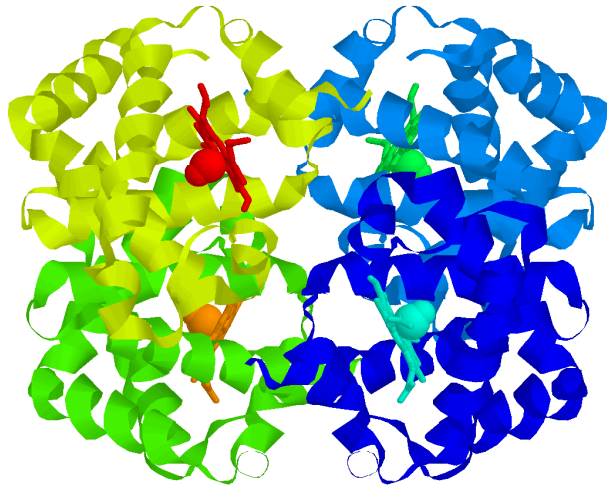
Photodissociation d'une molécule diatomique



Photodissociation d'une molécule diatomique



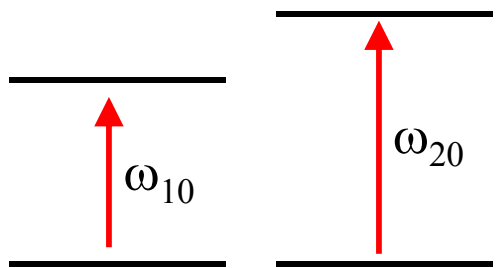
Relaxation vibrationnelle dans l'hémoglobine



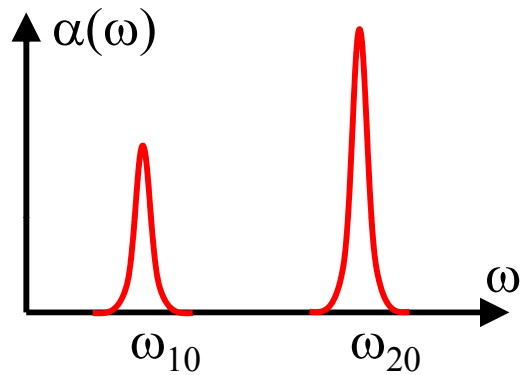
2. Spectroscopie multidimensionnelle

Pourquoi deux dimensions ?

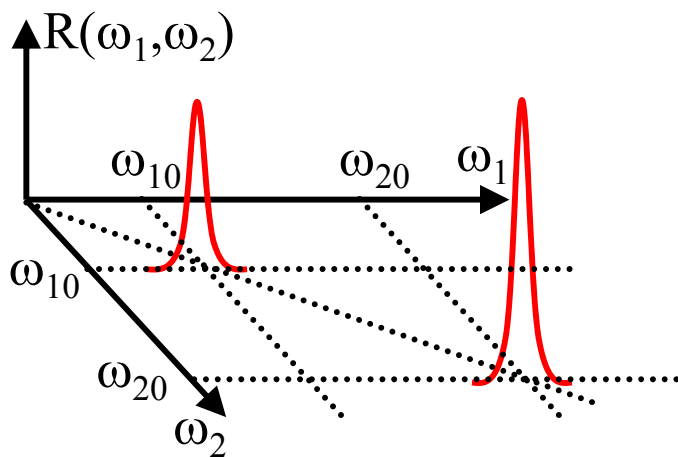
Deux systèmes indépendants



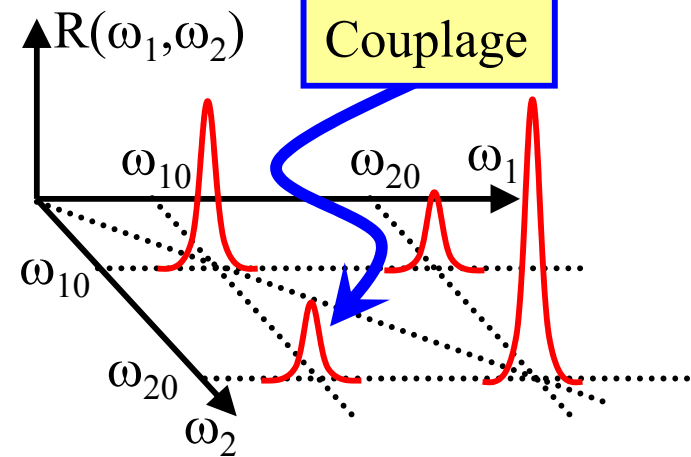
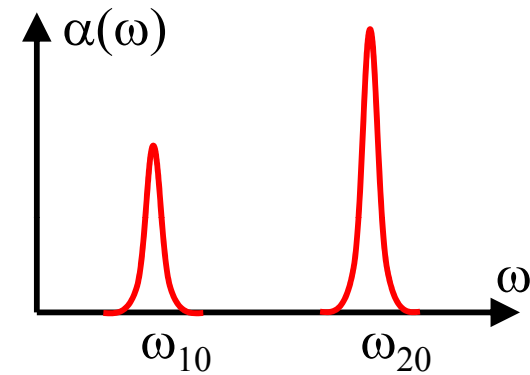
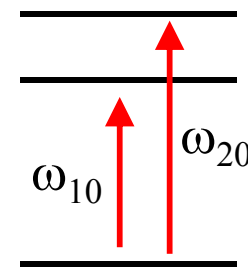
1D



2D



Deux systèmes couplés



RMN à deux dimensions

Two-dimensional spectroscopy. Application to nuclear magnetic resonance

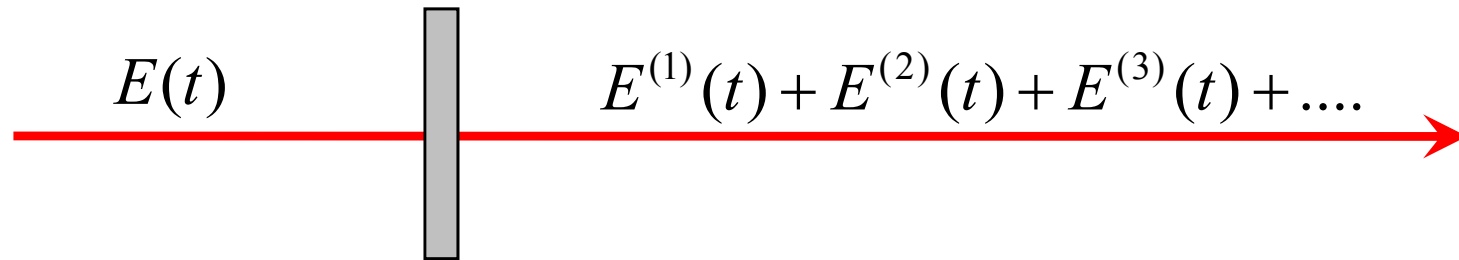
W. P. Aue, E. Bartholdi, and R. R. Ernst

*Laboratorium für physikalische Chemie, Eidgenössische Technische
Hochschule, 8006 Zürich, Switzerland*

The possibilities for the extension of spectroscopy to two dimensions are discussed. Applications to nuclear magnetic resonance are described. The basic theory of two-dimensional spectroscopy is developed. Numerous possible applications are mentioned and some of them treated in detail, including the elucidation of energy level diagrams, the observation of multiple quantum transitions, and the recording of high-resolution spectra in inhomogeneous magnetic fields. Experimental results are presented for some simple spin systems.

« The basic principles which have been exploited are very general and can be applied to other coherent spectroscopies as well. Applications are conceivable in electron spin resonance, nuclear quadrupole resonance, in microwave rotational spectroscopy, **and possibly in laser infrared spectroscopy.** »

Réponse multidimensionnelle

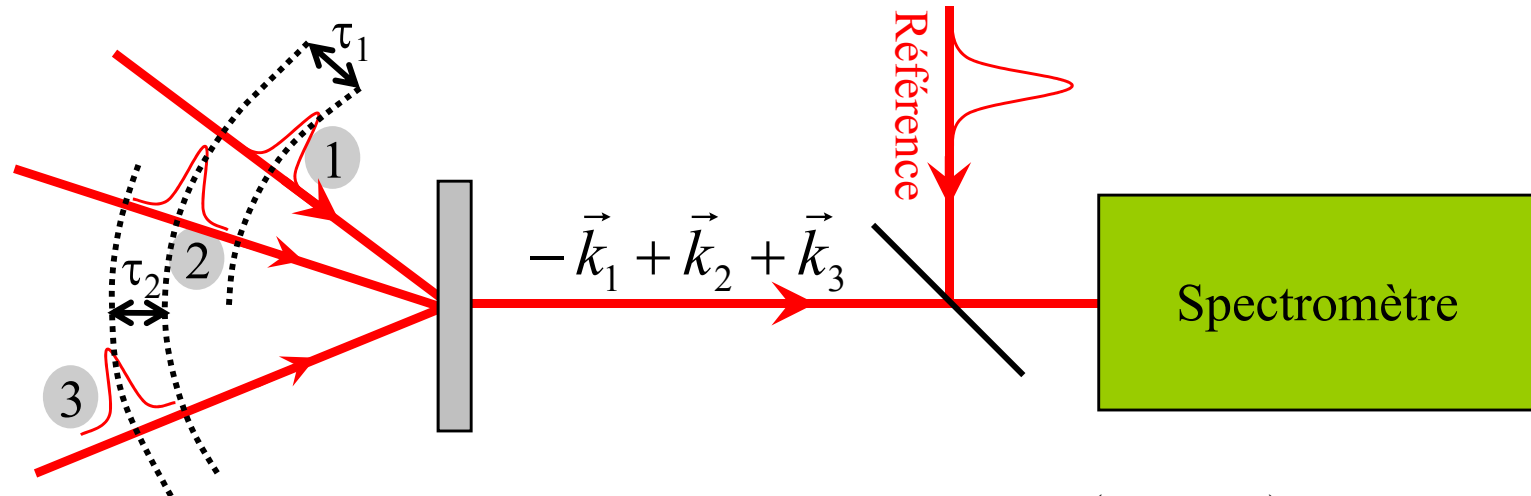


$$\begin{aligned} E^{(3)}(t) &= \iiint \Xi^{(3)}(t_1, t_2, t_3) E(t-t_1) E(t-t_2) E(t-t_3) dt_1 dt_2 dt_3 \\ &= \iiint \Xi^{(3)}(\omega_1, \omega_2, \omega_3) E(\omega_1) E(\omega_2) E(\omega_3) \exp(-i(\omega_1 + \omega_2 + \omega_3)t) \frac{d\omega_1}{2\pi} \frac{d\omega_2}{2\pi} \frac{d\omega_3}{2\pi} \end{aligned}$$

- ✓ La connaissance de $\Xi^{(3)}(\omega_1, \omega_2, \omega_3)$ détermine le résultat de toute expérience non-linéaire du troisième ordre : pompe-sonde, mélange à 4 ondes, écho de photon à 2 ou 3 impulsions, effet Kerr, etc.
- ✓ $\Xi^{(3)}(\omega_1, \omega_2, \omega_3)$ est directement reliée à la réponse microscopique de l'échantillon, $\chi^{(3)}(\omega_1, \omega_2, \omega_3)$.

Spectroscopie multidimensionnelle

Transposition de la RMN impulsionnelle au domaine de l'optique non-linéaire



$$E^{(3)}(t) = \iiint \Xi^{(3)}(\omega_1, \omega_2, \omega_3) E(\omega_1) E(\omega_2) e^{i\omega_2 \tau_1} E(\omega_3) e^{i\omega_3 \tau_2} e^{-i(\omega_1 + \omega_2 + \omega_3)t} d\omega_1 d\omega_2 d\omega_3$$

$\mathcal{F}_{\tau_1, \tau_2, t}$

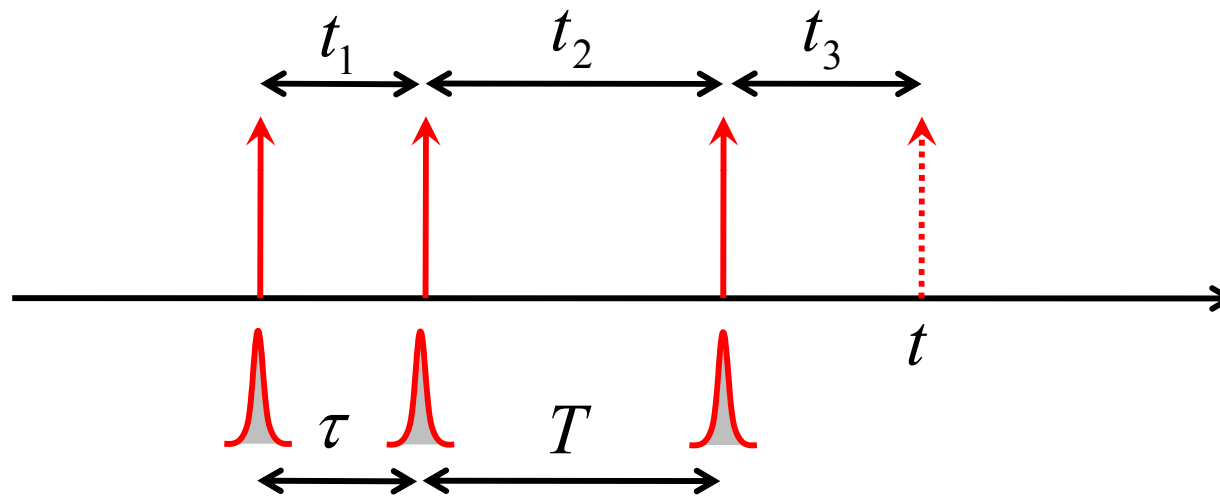
$$\Xi^{(3)}(\omega_1, \omega_2, \omega_3) E(\omega_1) E(\omega_2) E(\omega_3)$$

- ✓ L. Lepetit et M. Joffre, Opt. Lett. **21**, 564 (1996)
- ✓ M.C. Asplund, M.T. Zanni et R.M. Hochstrasser, PNAS **97**, 8129 (2000)
- ✓ J.D. Hybl, A. Albrecht Ferro et D.M. Jonas, J. Chem. Phys. **115**, 6606 (2001)
- ✓ N. Belabas et M. Joffre, Opt. Lett. **27**, 2043 (2002)
- ✓ M. Cho, Chem. Rev. **108**, 1331 (2008)

Spectroscopie 2D pour la réponse du troisième ordre

$$E^{(3)}(t) = \iiint \Xi^{(3)}(t_1, t_2, t_3) E(t-t_1) E(t-t_2) E(t-t_3) dt_1 dt_2 dt_3$$
$$= \iiint R^{(3)}(t_3, t_2, t_1) E(t-t_3) E(t-t_3-t_2) E(t-t_3-t_2-t_1) dt_1 dt_2 dt_3$$

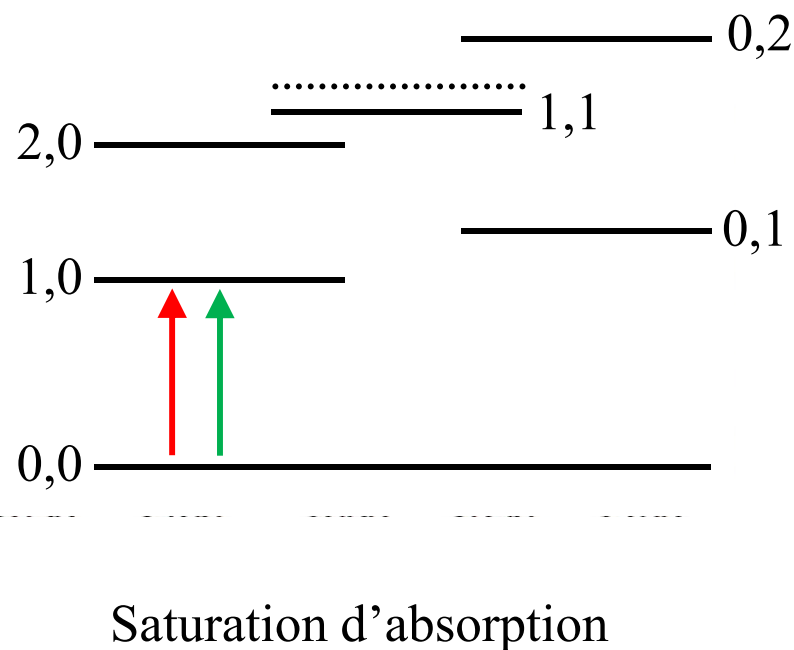
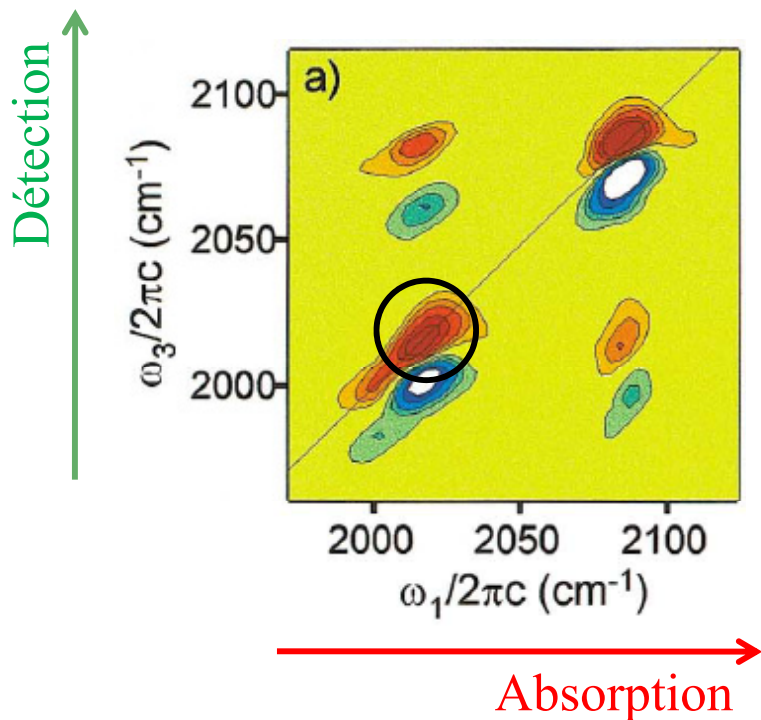
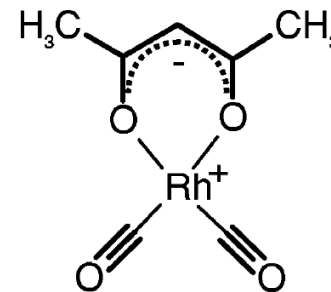
Shaul Mukamel, Principles of Nonlinear Optical Spectroscopy (1995)



Impulsion très courte $\rightarrow R(\tau, T, \omega_t) \xrightarrow{\mathcal{F}_\tau} R(\omega_\tau, T, \omega_t)$

Spectroscopie bidimensionnelle infrarouge

Exemple : RDC (acetylacetonato dicarbonyl rhodium(I))



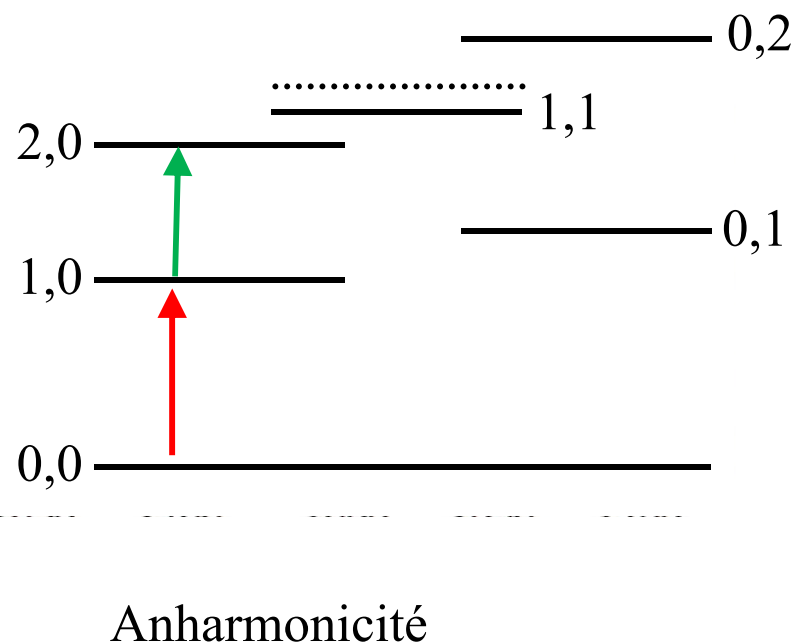
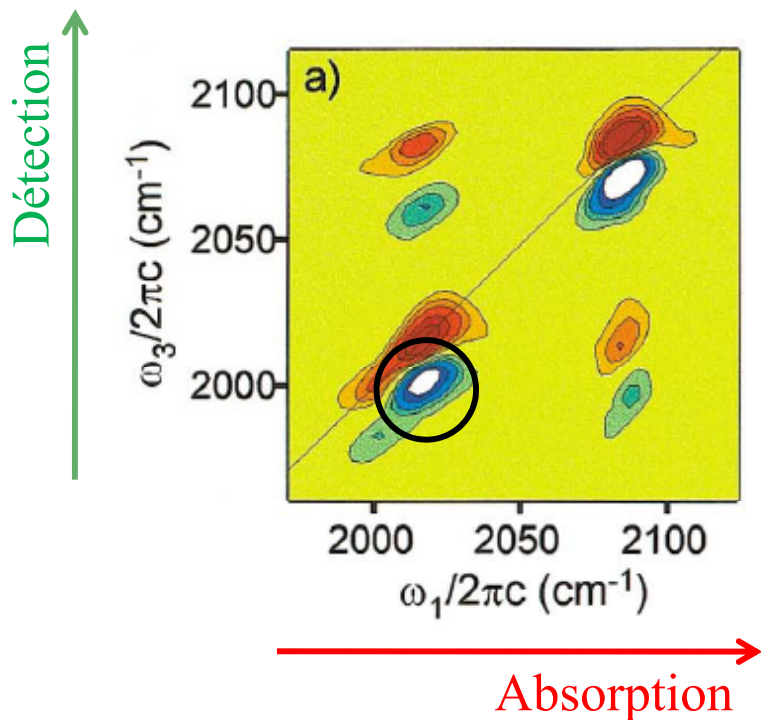
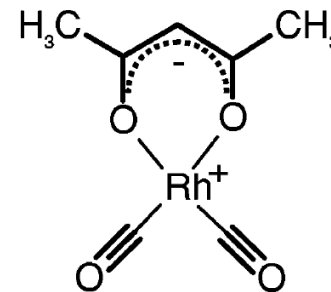
N. Demirdoven, M. Khalil, A. Tokmakoff

Correlated vibrational dynamics revealed by two-dimensional infrared spectroscopy

Phys. Rev. Lett. **89**, 237401 (2002)

Spectroscopie bidimensionnelle infrarouge

Exemple : RDC (acetylacetonato dicarbonyl rhodium(I))



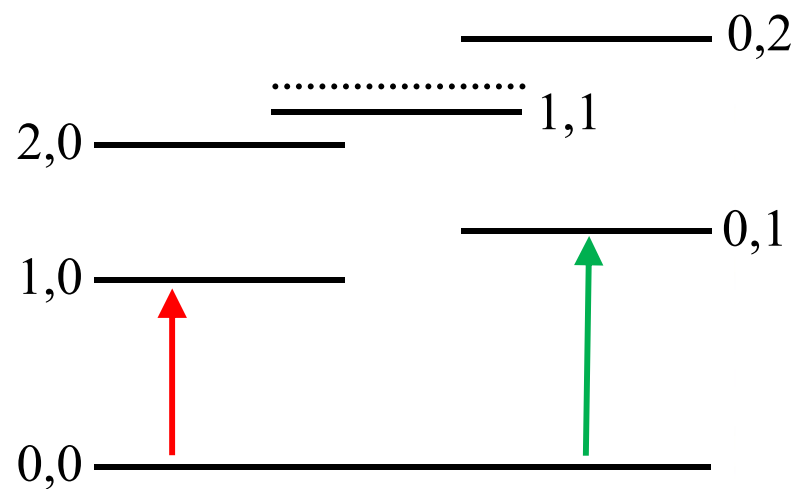
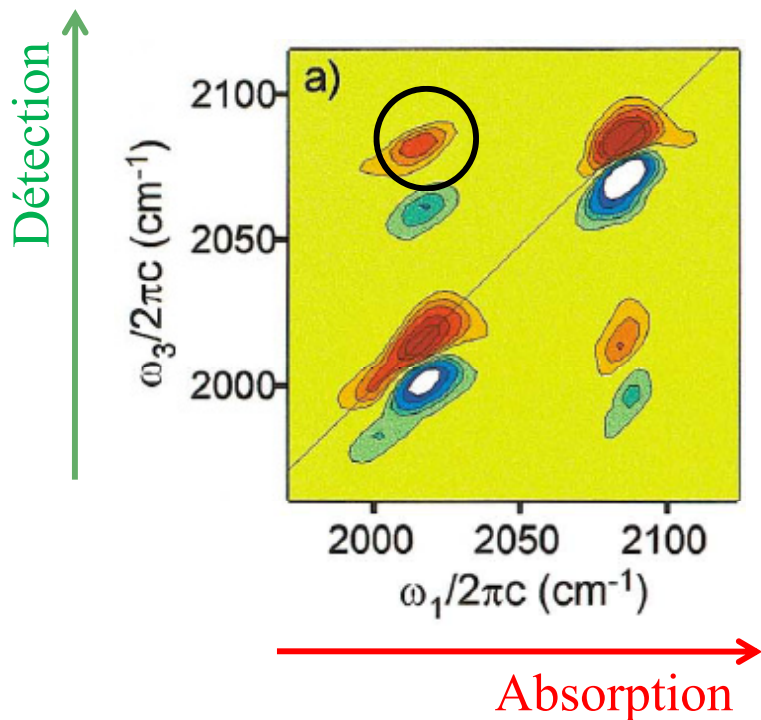
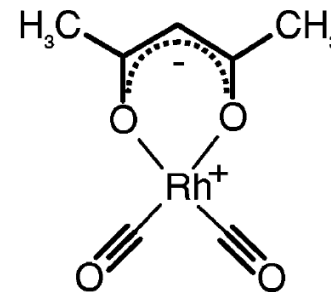
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Couplage entre deux modes vibrationnels

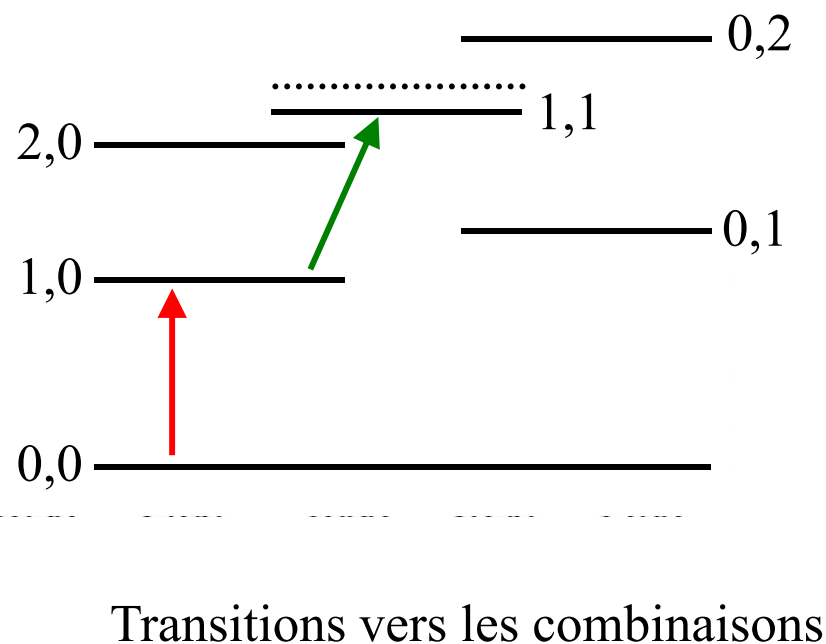
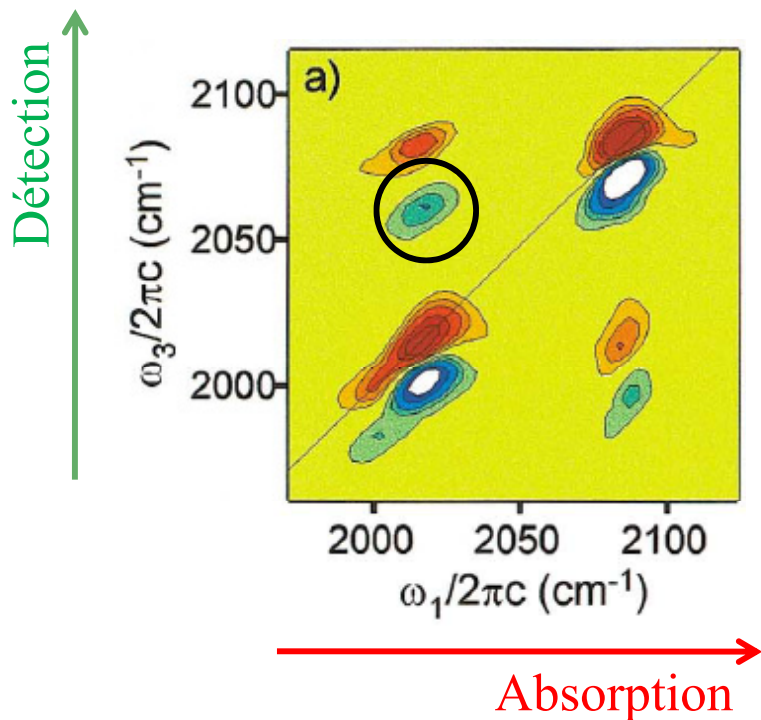
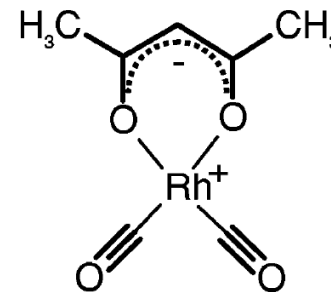
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Spectroscopie bidimensionnelle infrarouge

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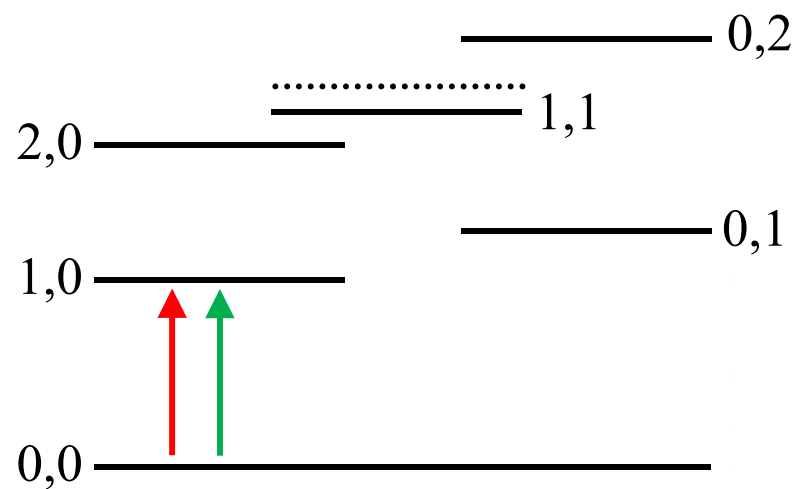
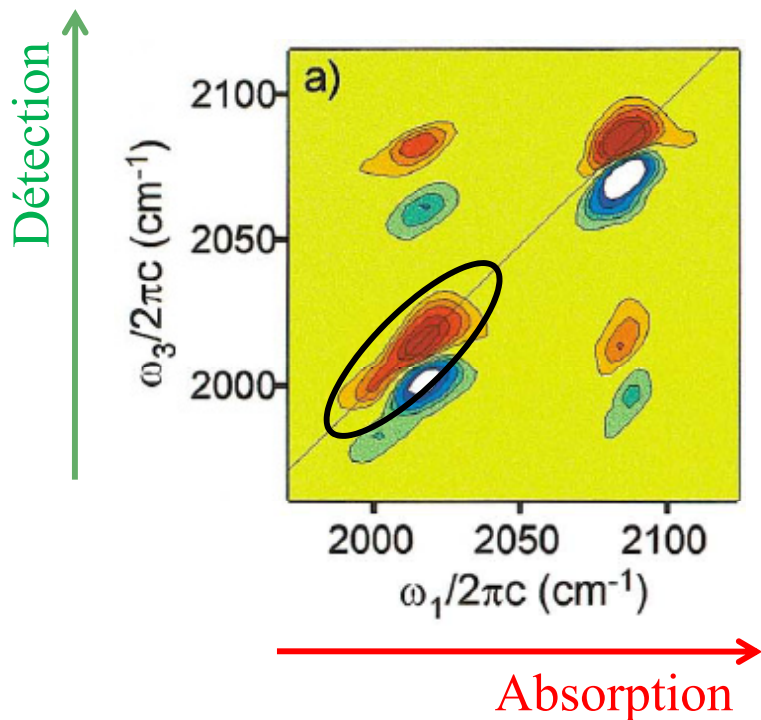
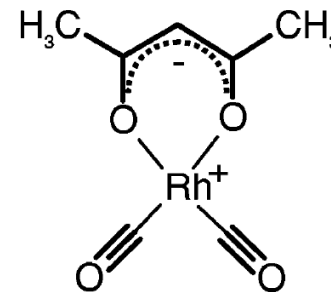
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Inhomogénéité

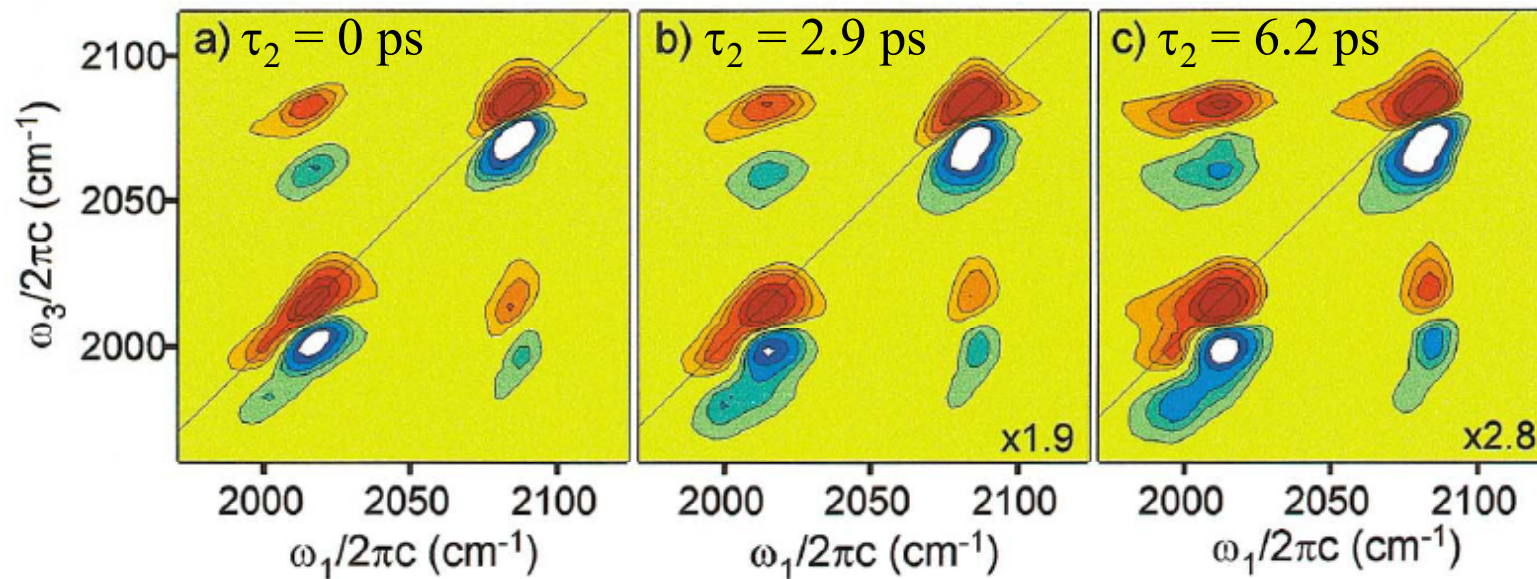
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Correlated vibrational dynamics revealed by two-dimensional infrared spectroscopy

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Evolution en fonction de τ_2

N. Demirdoven, M. Khalil, A. Tokmakoff

Correlated vibrational dynamics revealed by two-dimensional infrared spectroscopy

Phys. Rev. Lett. **89**, 237401 (2002)

3. Contrôle cohérent

Manipuler directement l'état quantique d'un système sous l'action d'une impulsion brève de forme temporelle appropriée

Conditions :

➡ Etre plus rapide que les processus de déphasage

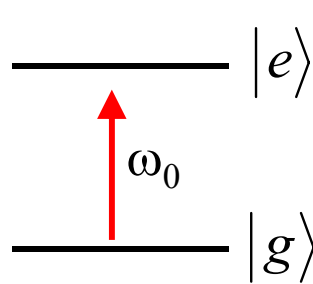
➡ Disposer d'une énergie suffisante

➡ Façonner de façon arbitraire le profil temporel d'une impulsion

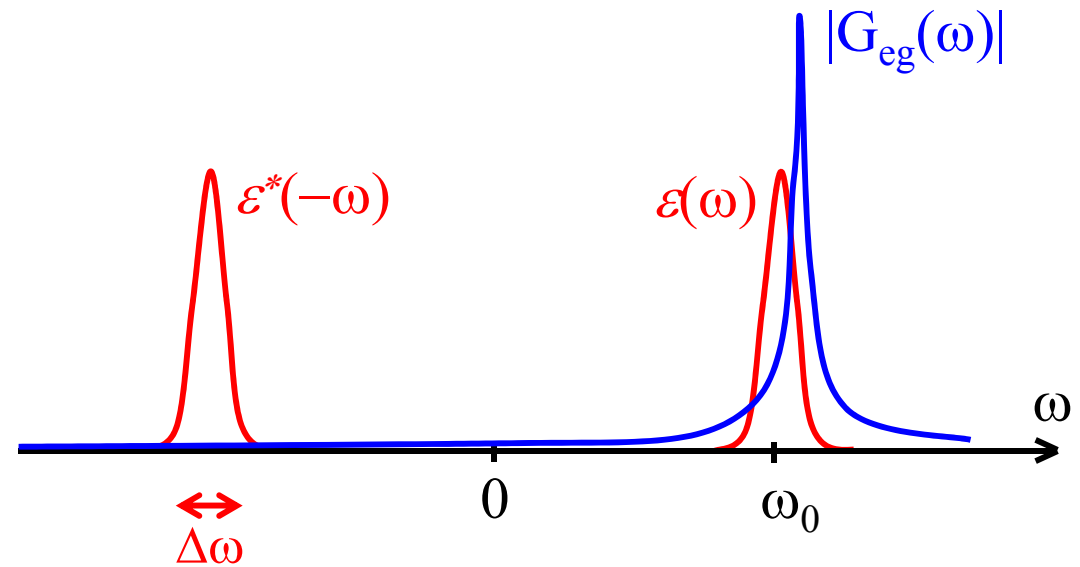
↙ Régime fort : oscillations de Rabi, ascension vibrationnelle, etc.

↘ Régime perturbatif : gouverné par la fonction réponse multilinéaire

Systeme à deux niveaux en régime perturbatif



Régime quasi-résonnant :
 $|\omega_{eg} - \omega_0| \ll \Gamma_{eg}$



$$G_{eg}(t) = \frac{i}{\hbar} \Theta(t) \exp(-i\omega_{eg}t - \Gamma_{eg}t)$$

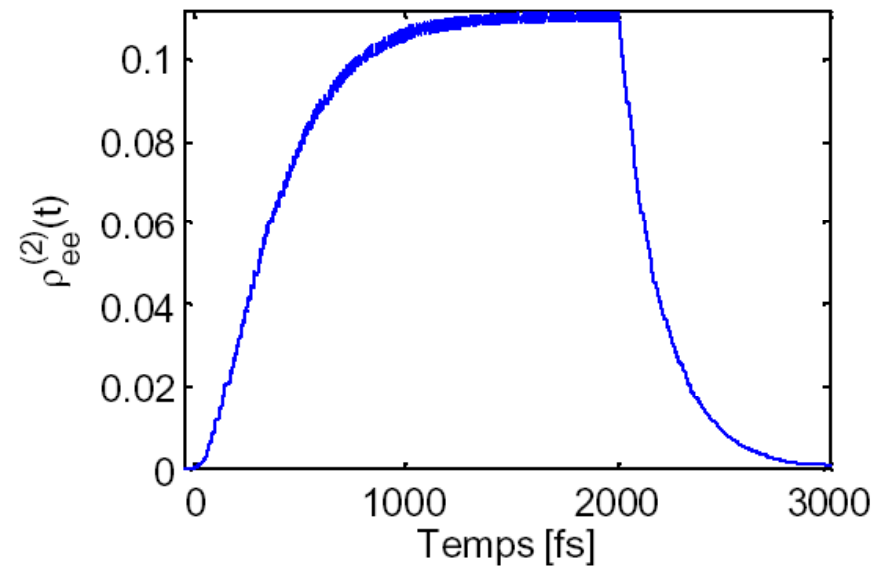
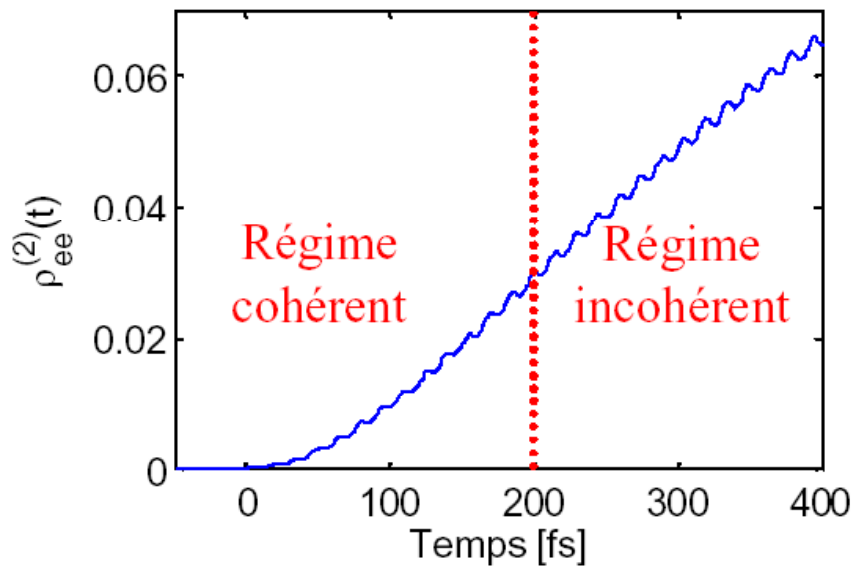
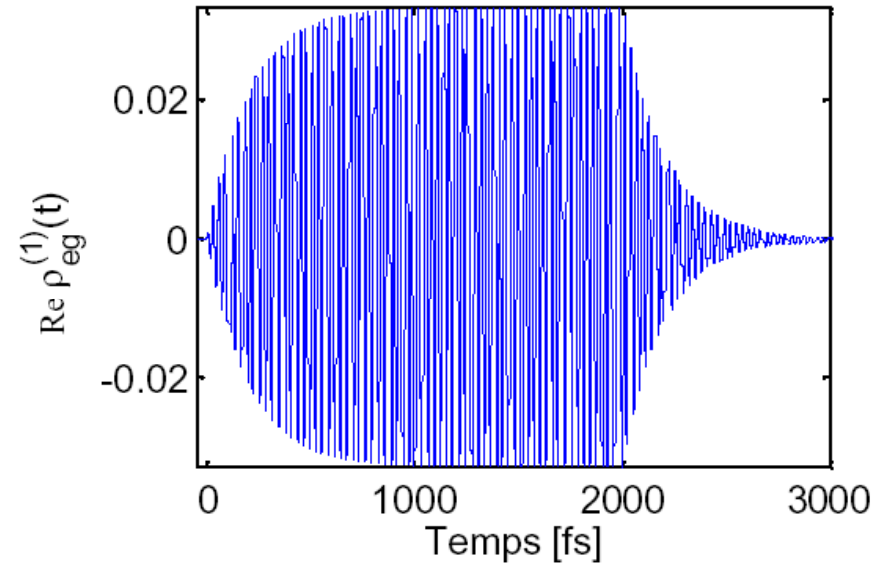
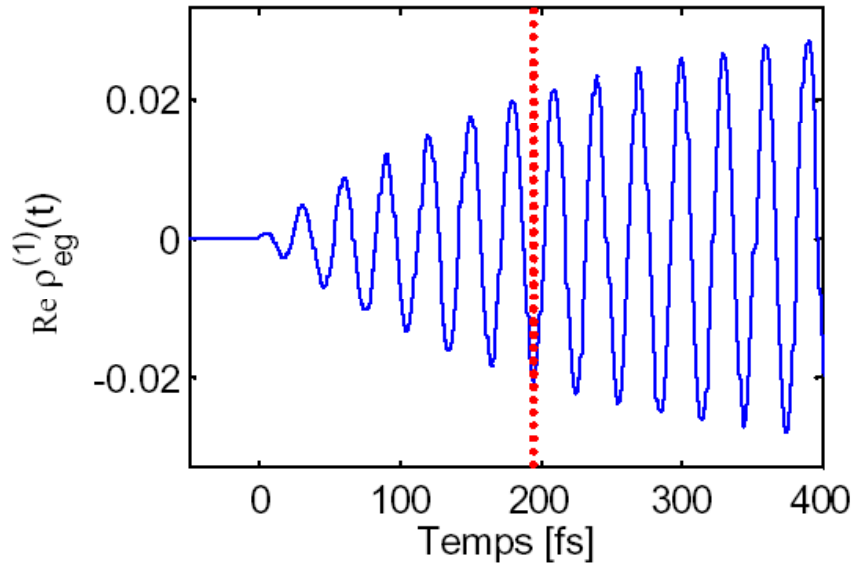
$$G_{ee}(t) = \frac{i}{\hbar} \Theta(t) \exp(-\Gamma_{ee}t)$$

$T_2 = 1/\Gamma_{eg}$: temps de déphasage

$T_1 = 1/\Gamma_{ee}$: temps de relaxation de la population

$$\rho_{nm}^{(p+1)}(t) = G_{nm}(t) \otimes \left(E_i(t) \sum_l (\mu_{nl}^i \rho_{lm}^{(p)}(t) - \rho_{nl}^{(p)}(t) \mu_{lm}^i) \right)$$

Du régime cohérent au régime incohérent

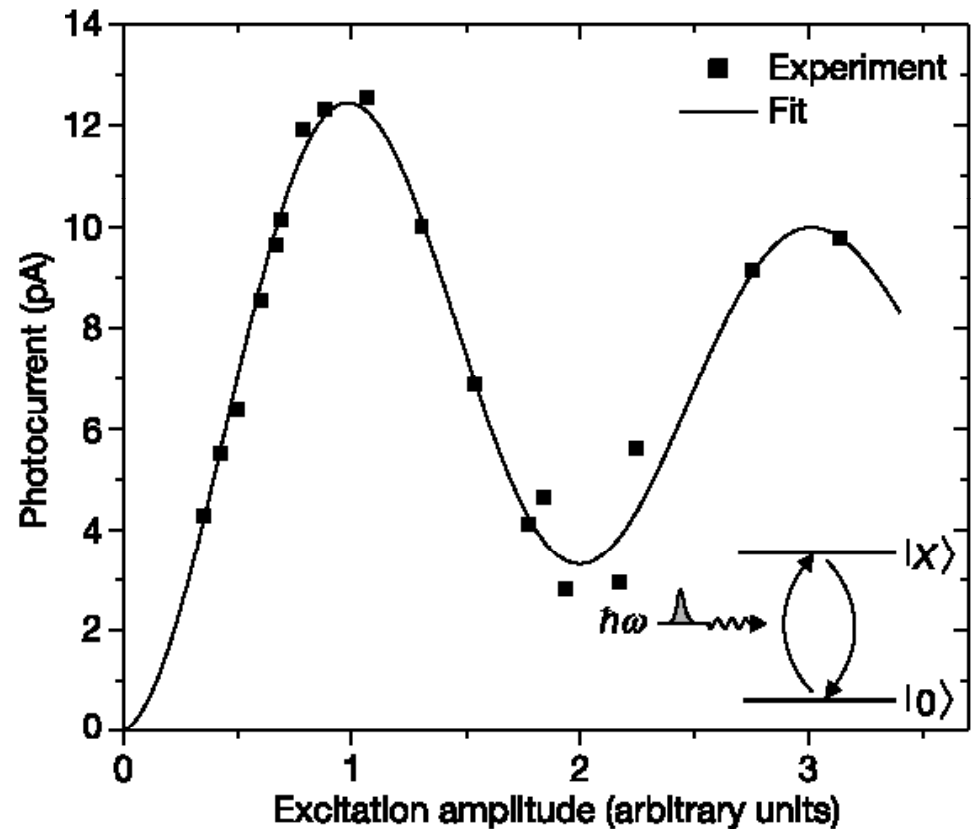
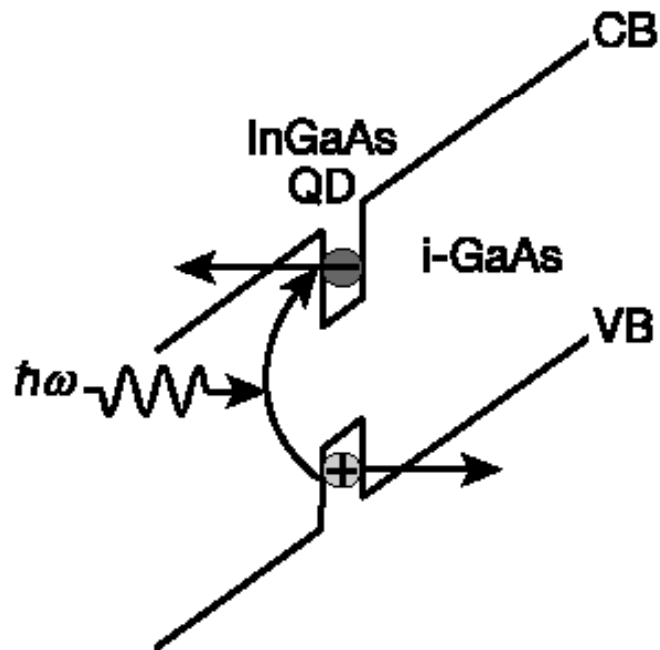


$$T_1 = 200\text{fs}; T_2 = 200\text{fs}; \frac{2\pi}{\omega_{eg}} = 30\text{fs}$$

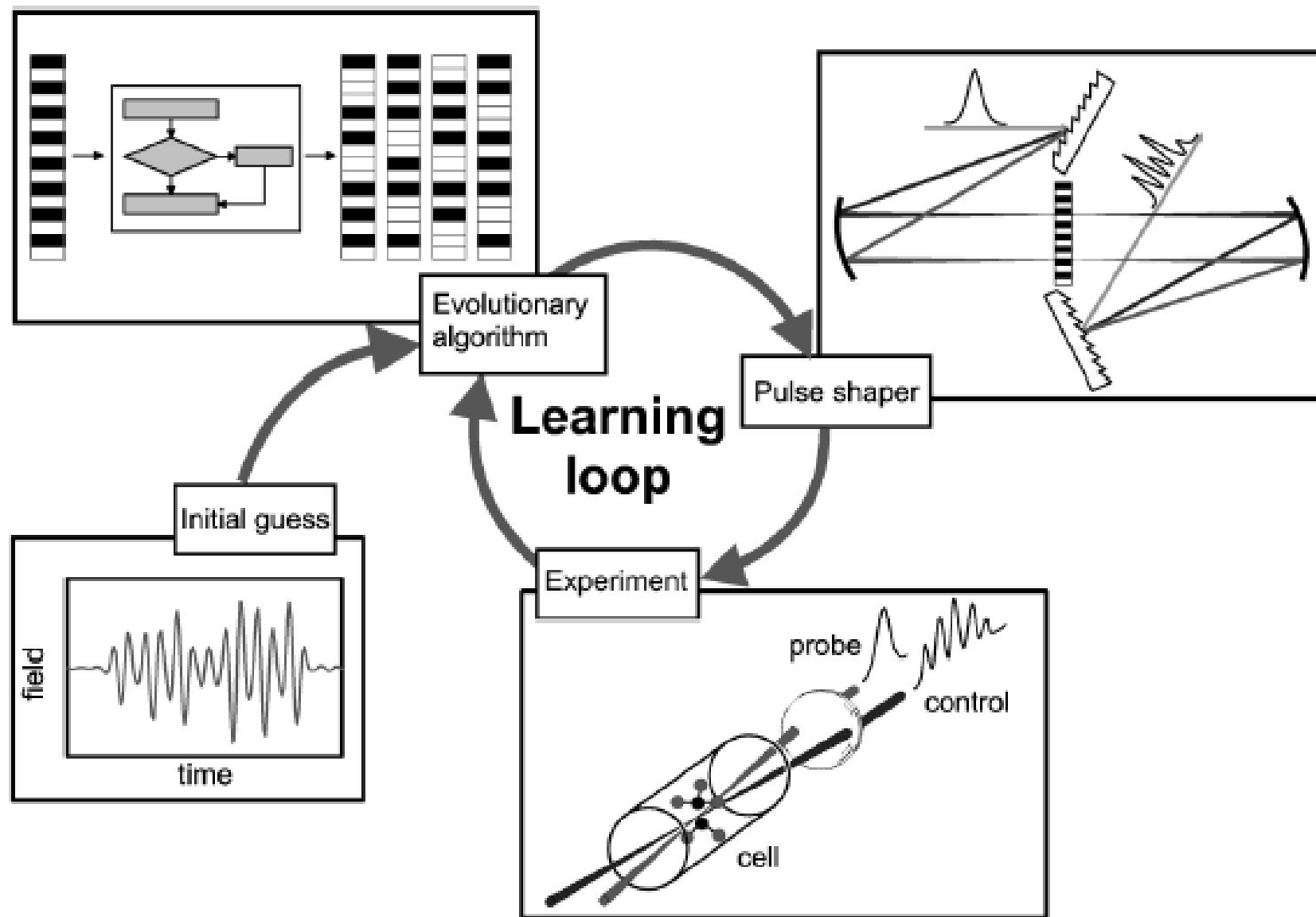
Coherent properties of a two-level system based on a quantum-dot photodiode

A. Zrenner*†, E. Beham*, S. Stufler*†, F. Findeis*, M. Bichler* & G. Abstreiter*

* Walter Schottky Institut, Technische Universität München, Am Coulombwall, D-85748 Garching, Germany



Boucle d'apprentissage avec algorithme génétique



4. Microscopie non-linéaire

Fluorescence par excitation à deux photons

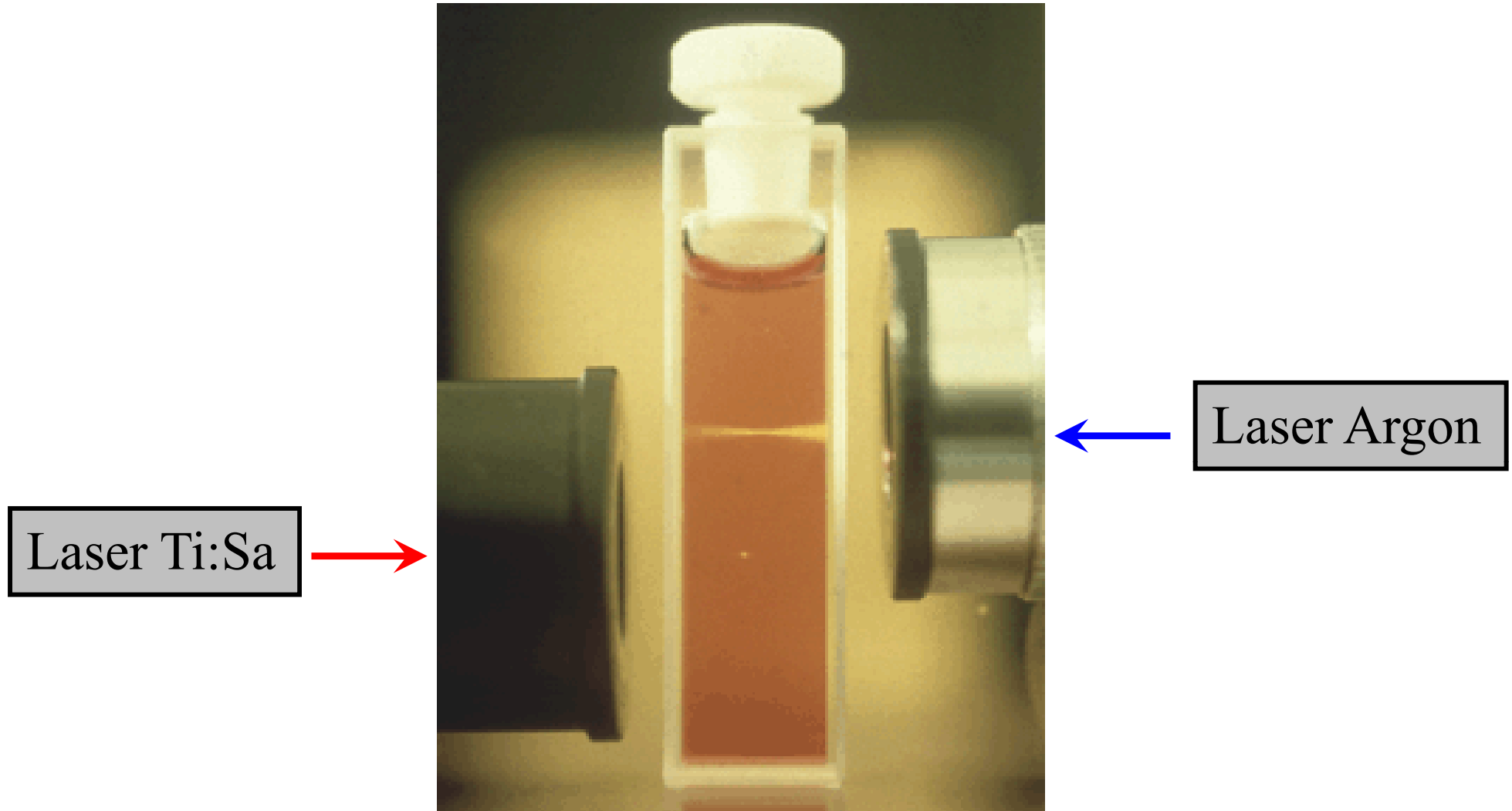
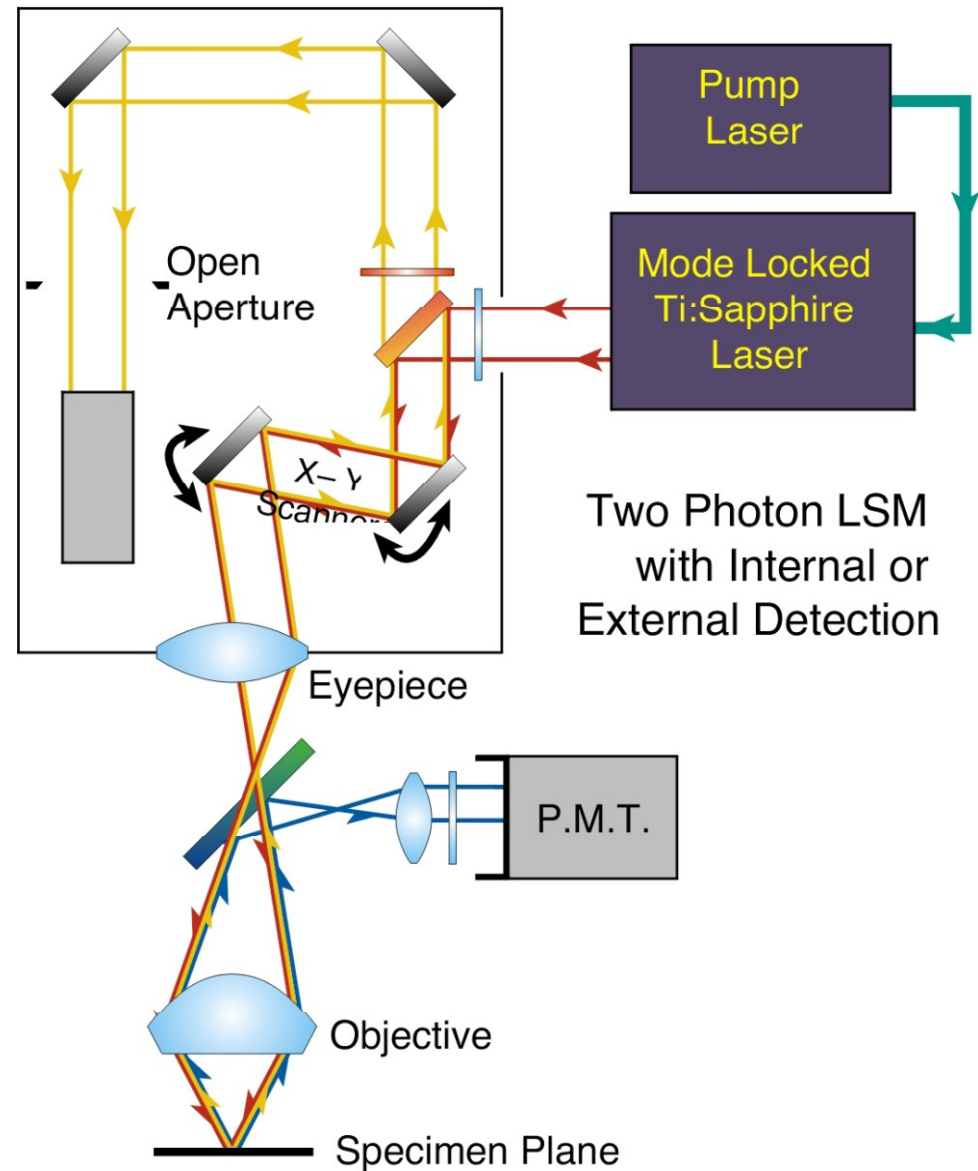


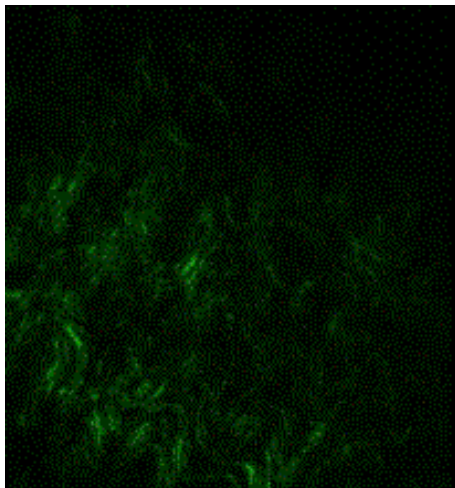
Photo: Brad Amos, MRC, Cambridge

Microscopie à deux photons : schéma de principe

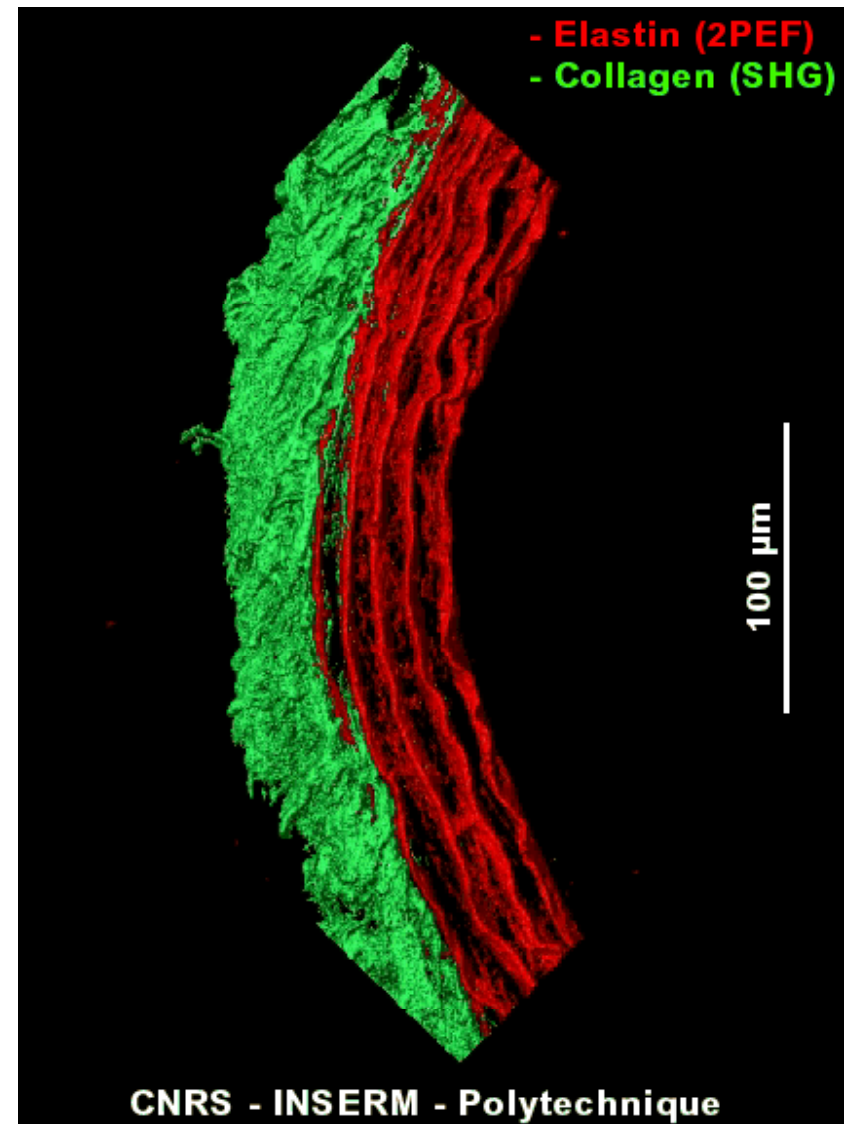


W. Denk, J. H. Strickler, and W. W. Webb, *Science* **248**, 73 (1990)

Reconstruction 3D d'un objet biologique



Empilement de tranches 2D



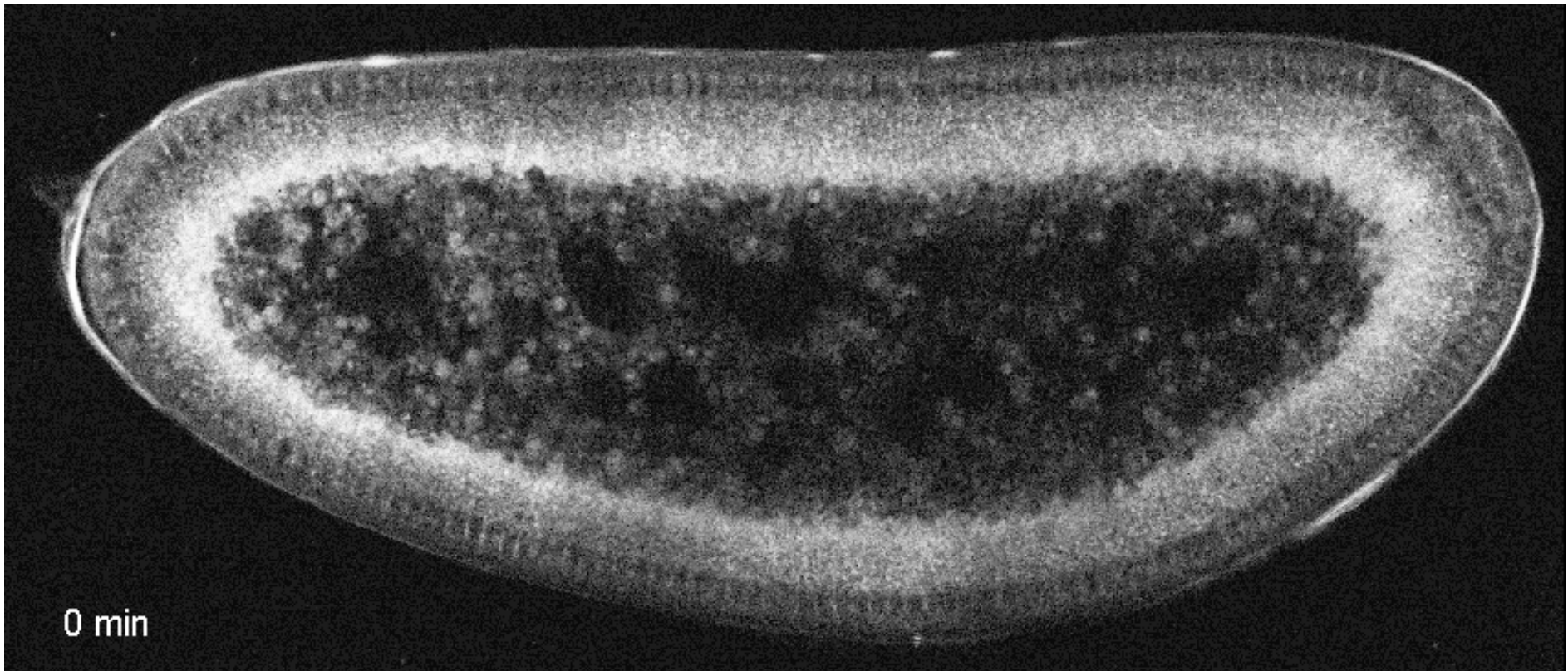
Paroi d'artère de Rat non marquée

E. Beaurepaire, T. Boulesteix, A.-M. Pena, M.-P. Sauviat, M.-C. Schanne-Klein

<http://www.lob.polytechnique.fr>

Morphogénèse dans un embryon de drosophile

Microscopie par génération de troisième harmonique

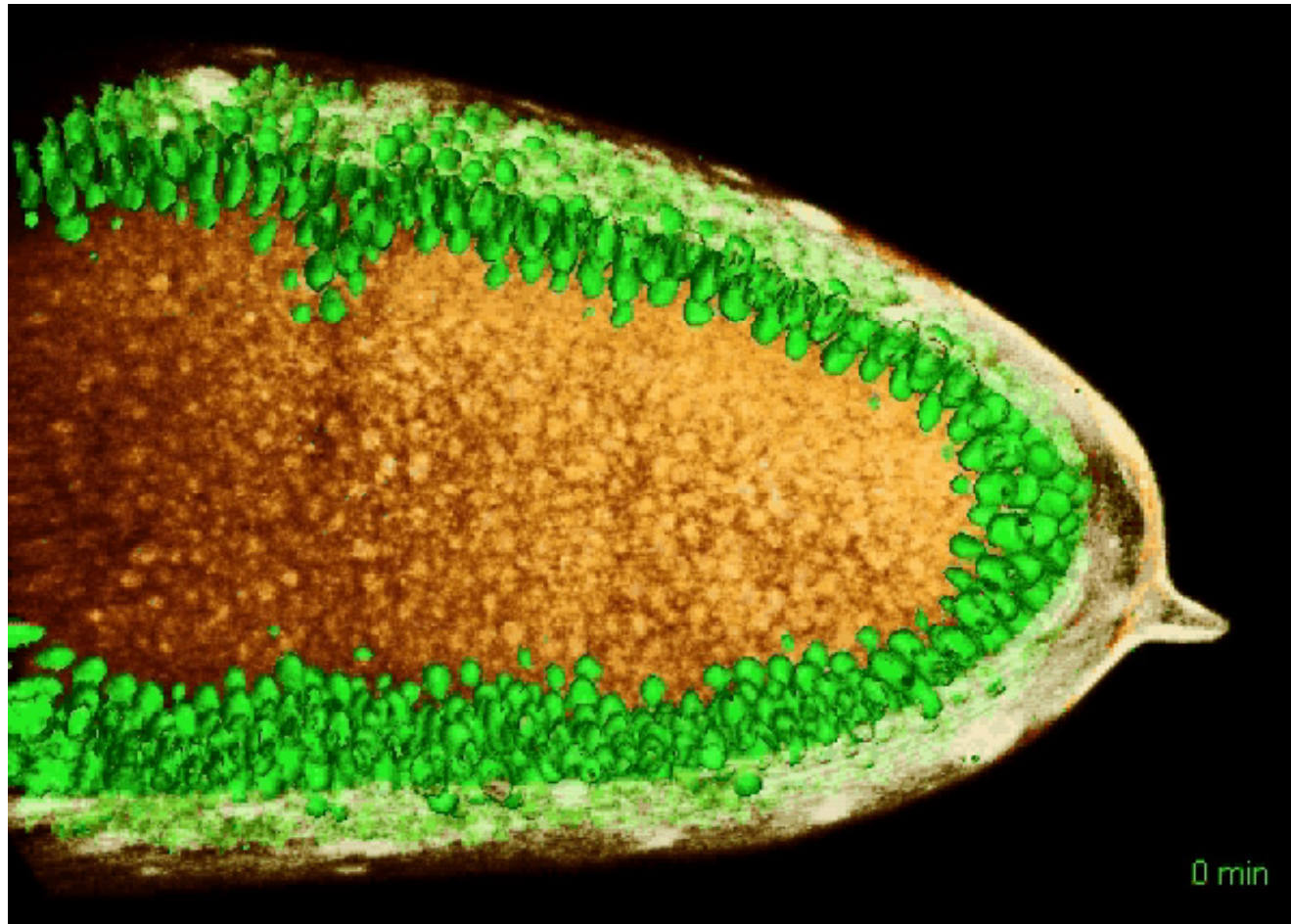


→ Voir problème 2004

W. Supatto, D. Débarre, B. Mouliia, E. Brouzés, J.-L. Martin, E. Farge, E. Beaurepaire
In vivo modulation of morphogenetic movements in Drosophila embryos with femtosecond laser pulses
Proc. Natl. Acad. Sci. USA **102**, 1047 (2005)

Microscopie multi-modale dans un embryon de drosophile (reconstruction 3D)

Génération de troisième harmonique + fluorescence par absorption à deux photons



Nicolas Olivier, Emmanuel Beaurepaire (LOB)
Collaboration Emmanuel Farge (Institut Curie)