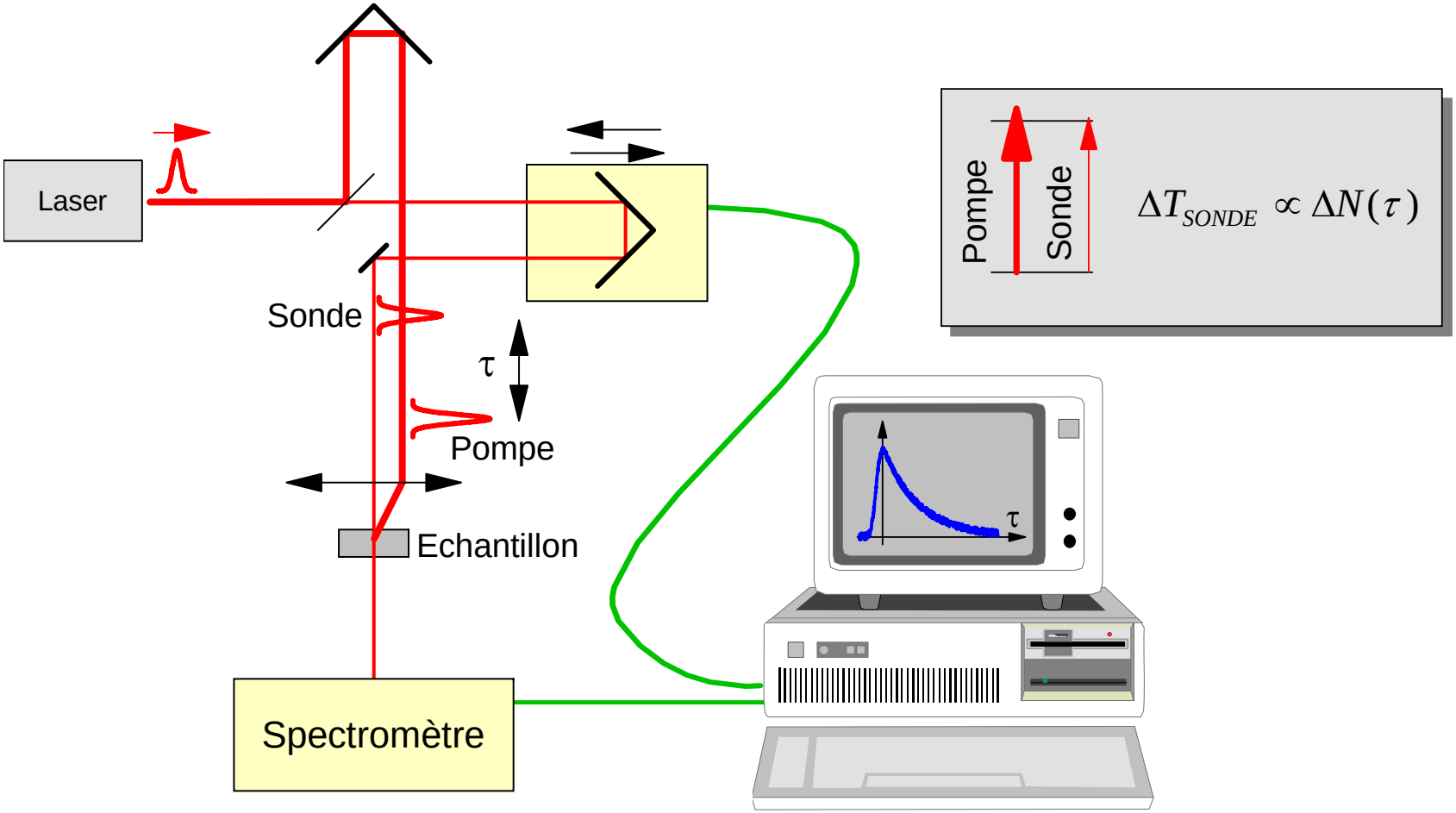
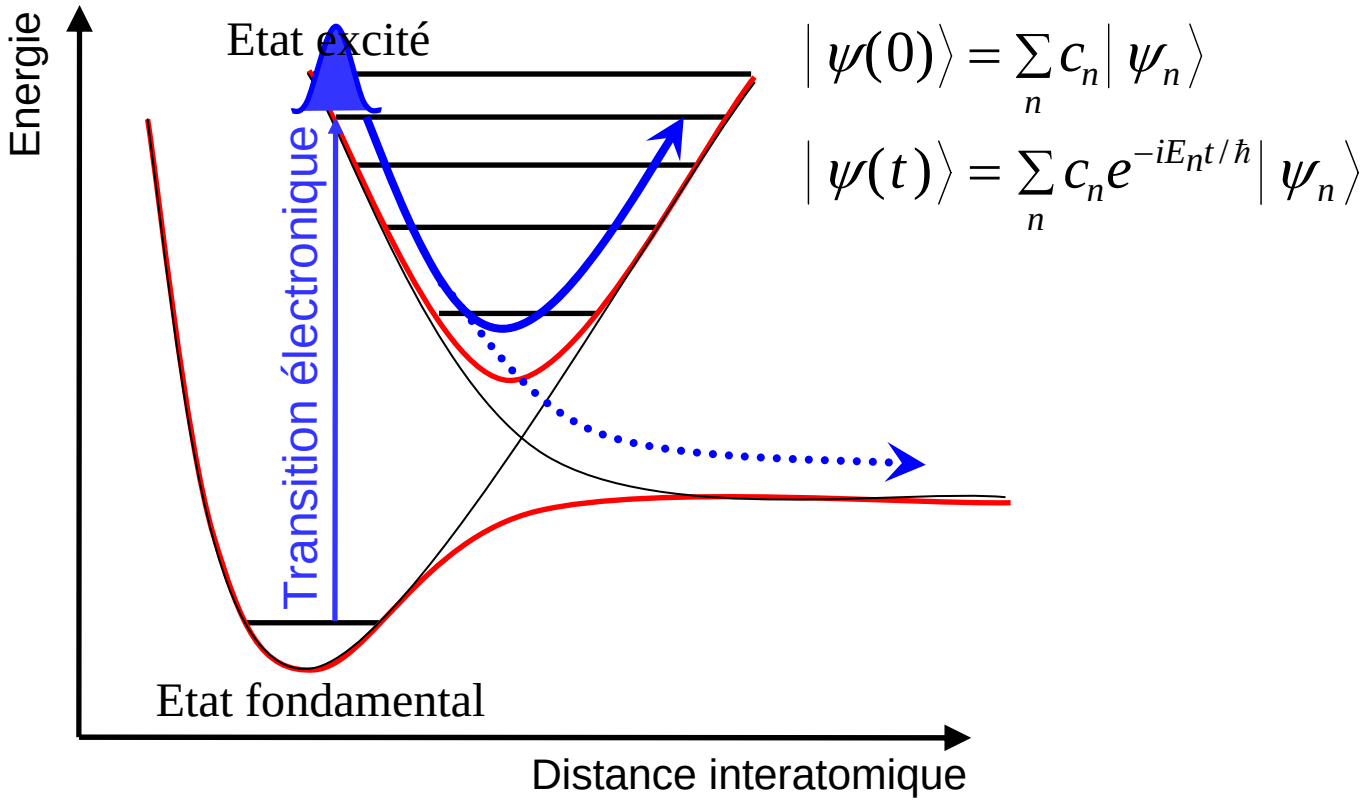
Spectroscopie femtoseconde

1) Expérience pompe – sonde
2) Echo de photon
3) Spectroscopie multidimensionnelle

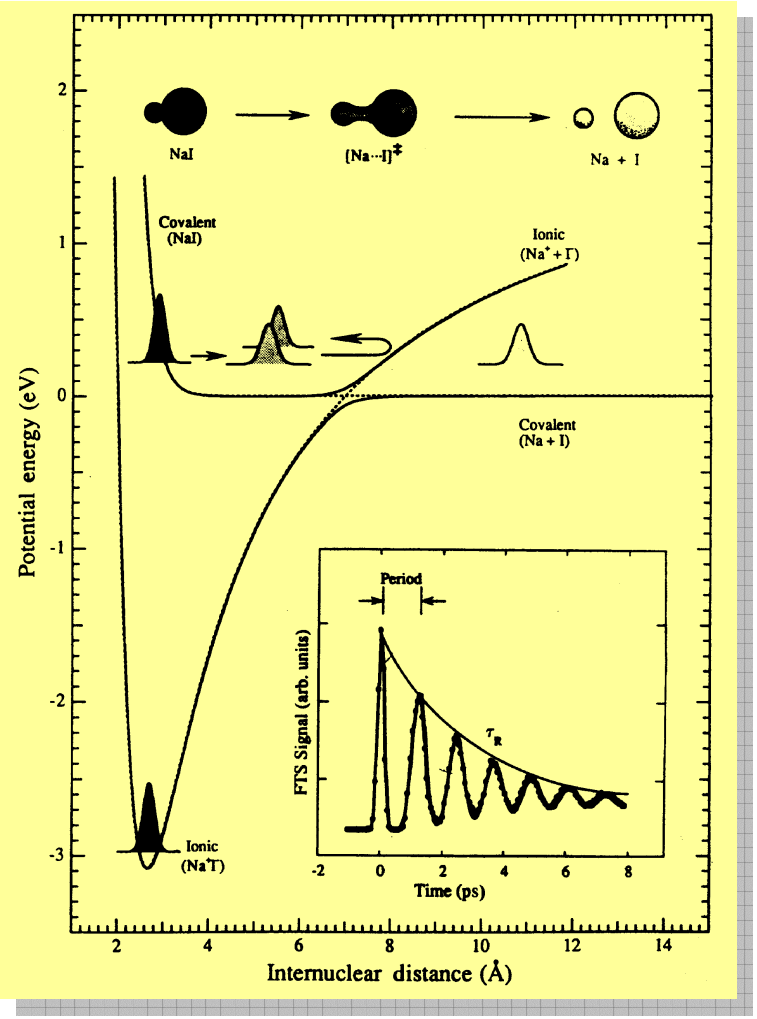
Expérience pompe-sonde : principe



Photodissociation d'une molécule diatomique

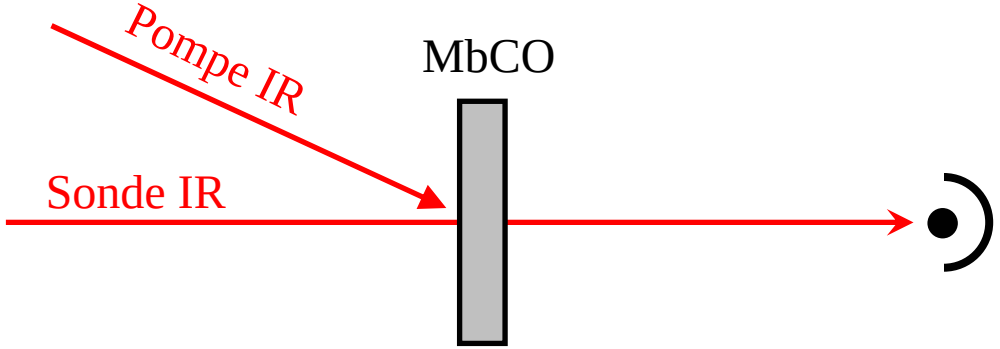


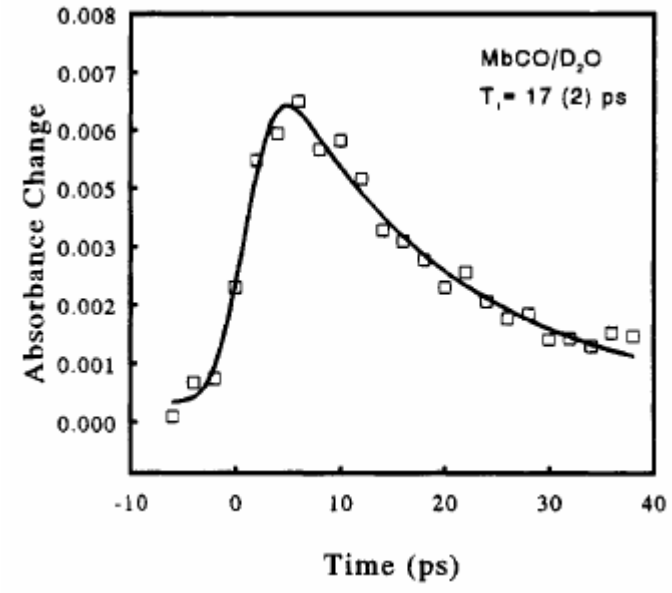
Photodissociation d'une molécule diatomique

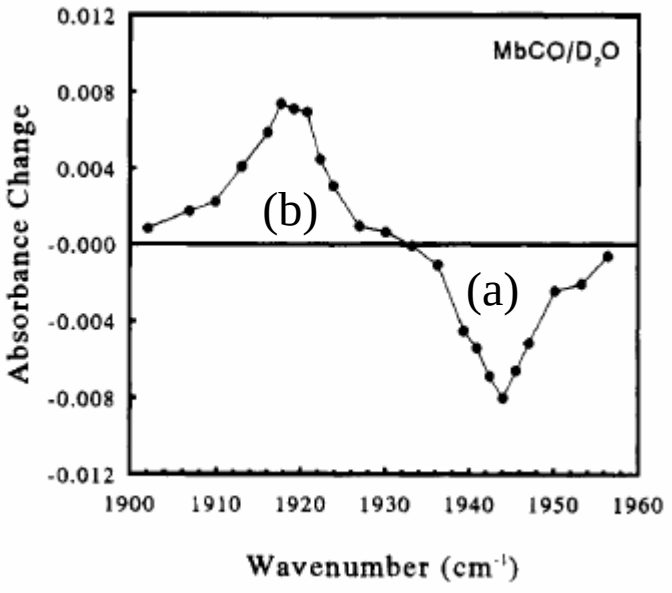


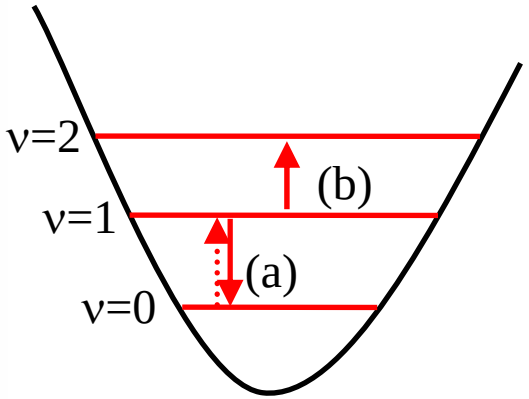
A. Mokhtari, P. Cong, J.L. Herek et A.H. Zewail,
Direct femtosecond mapping of trajectories in a chemical reaction,
Nature **348**, 225 (1990).

Anharmonicité de CO dans la myoglobine
Pompe infrarouge – sonde infrarouge



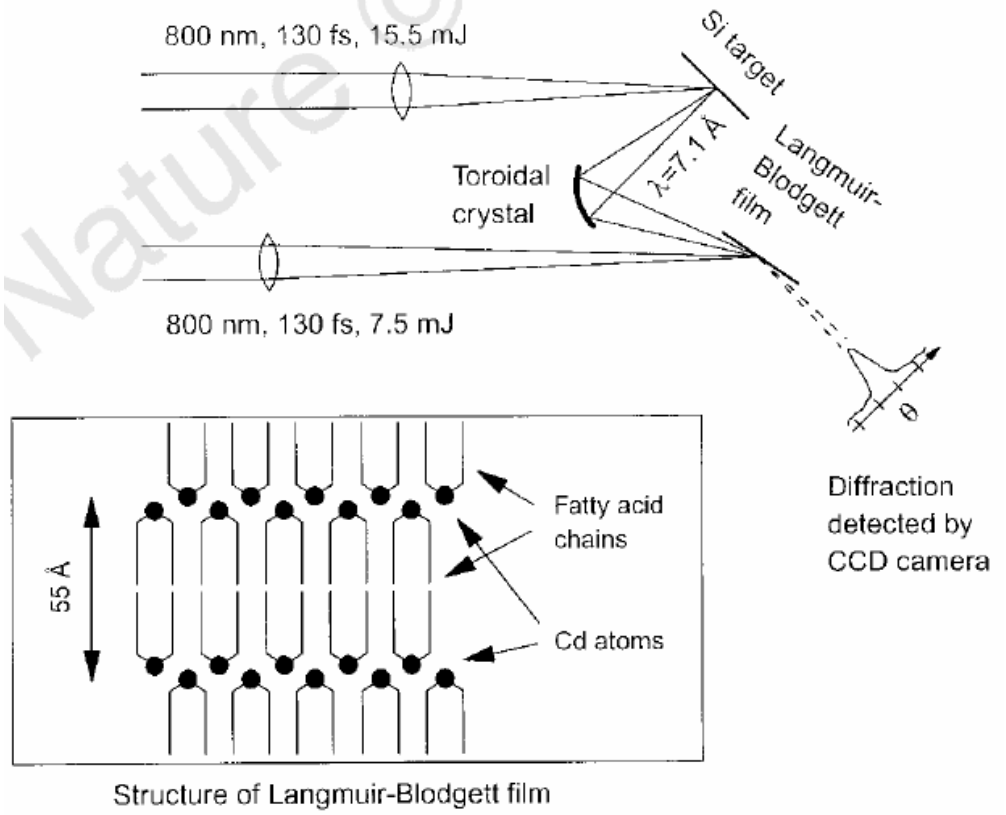




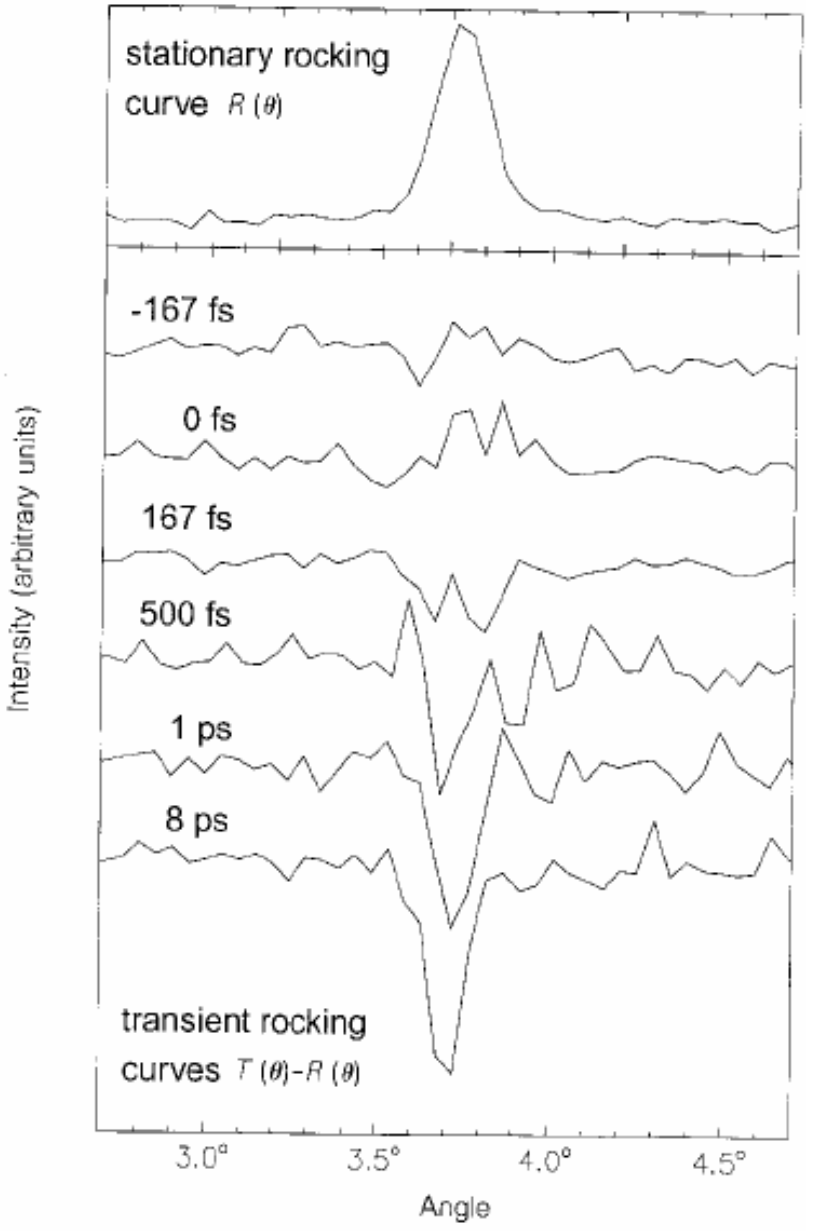


J.C. Owrutsky, M. Li, B. Locke et R.M. Hochstrasser, J. Phys. Chem. **99**, 4842 (1995).

Diffraction X sur une couche de Langmuir-Blodgett

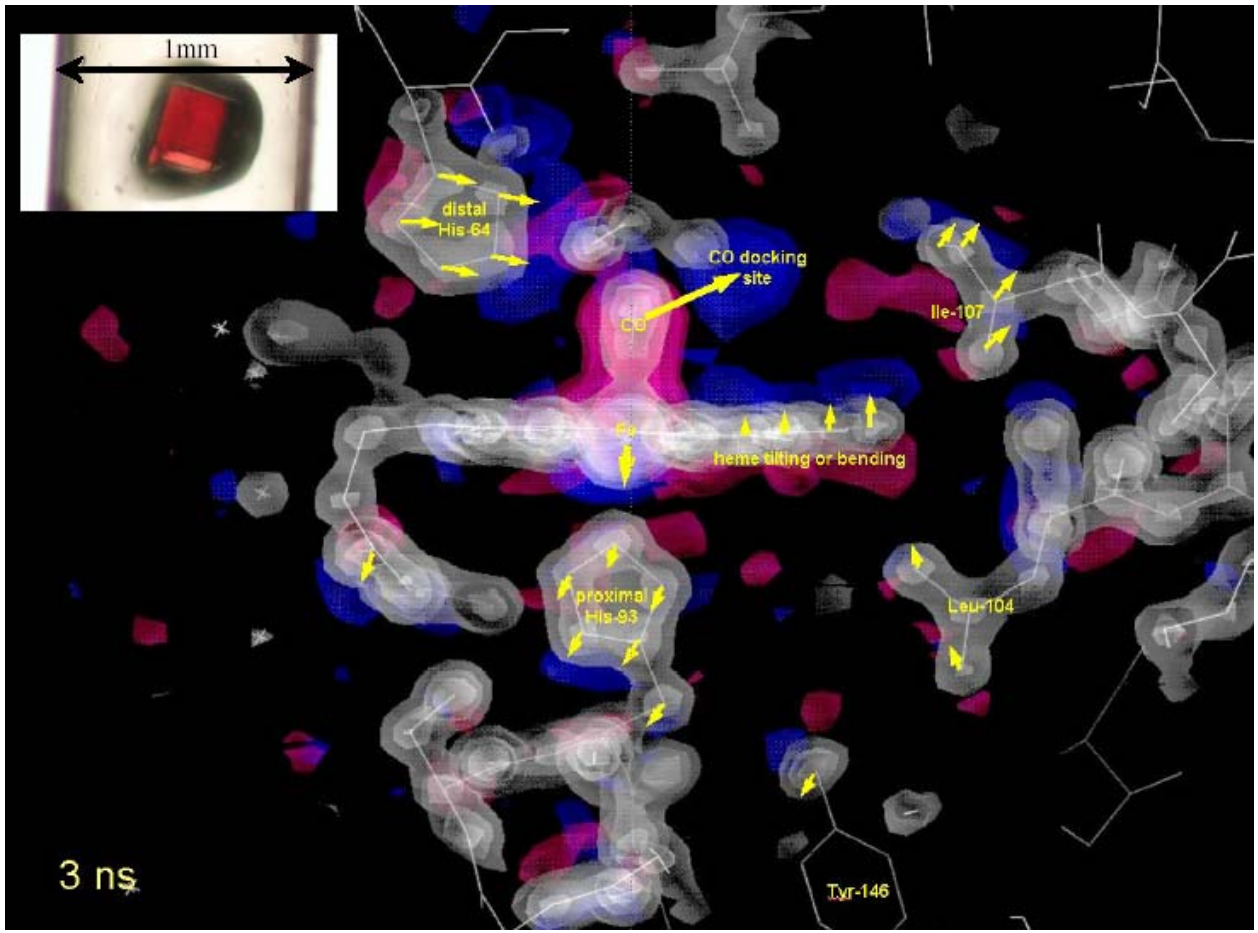


Structure of Langmuir-Blodgett film



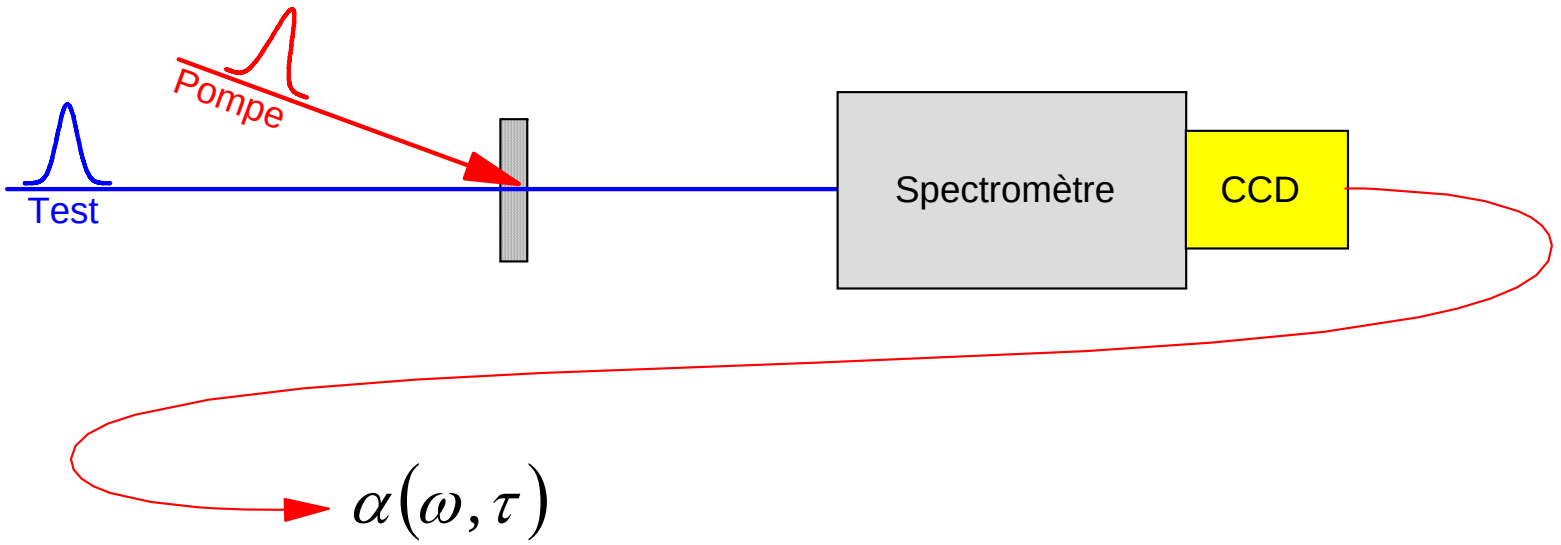
C. Rischel et al., Nature **390**, 490 (1997).

Pompe (400nm) – sonde (RX) dans MbCO



F. Schotte, P.A. Anfinrud et M. Wulff, Ultrafast Phenomena XIII (2002).

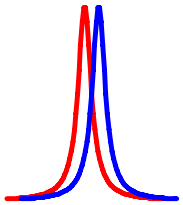
Expérience pompe – sonde résolue spectralement



- Résolution temporelle : limitée par la durée des impulsions
- Résolution spectrale : limitée par le spectromètre

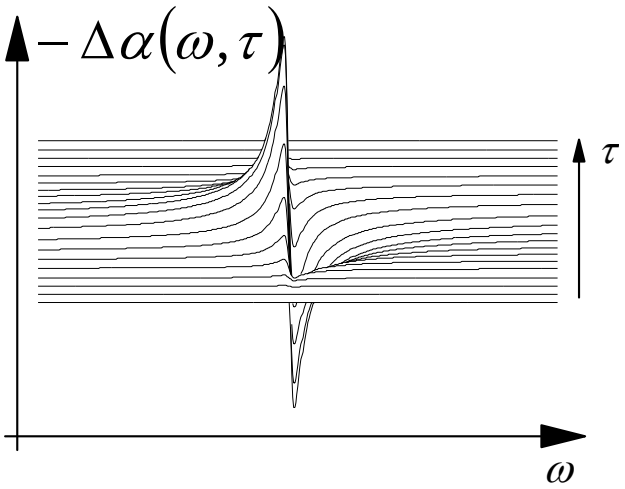
$$\Delta\tau\Delta\omega < \frac{1}{2} \quad ?$$

Limites de l'expérience pompe – sonde résolue spectralement

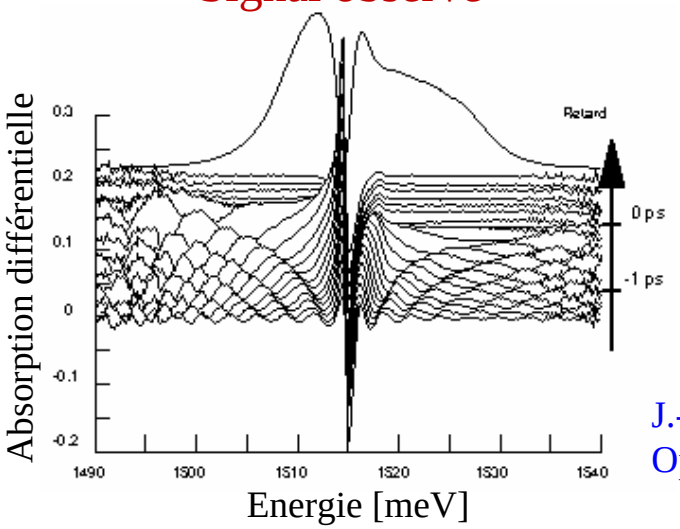


Exemple :
Décalage d'une raie
fine en fonction du temps
(effet Stark optique)

Signal attendu



Signal observé



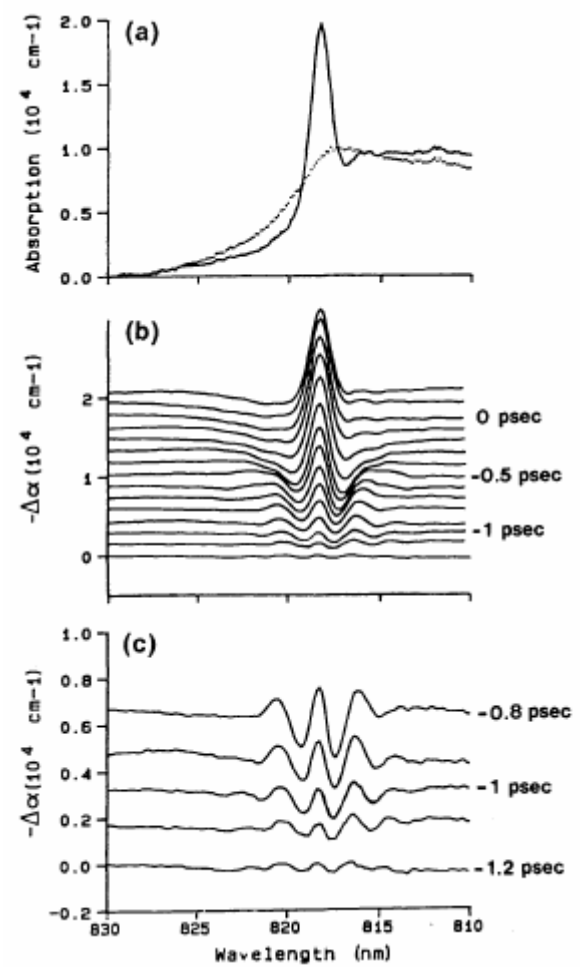
J.-P. Likforman et al.,
Opt. Lett. **20**, 2006 (1995)

Oscillations de cohérence si : $\Delta\tau\Delta\omega < \frac{1}{2}$

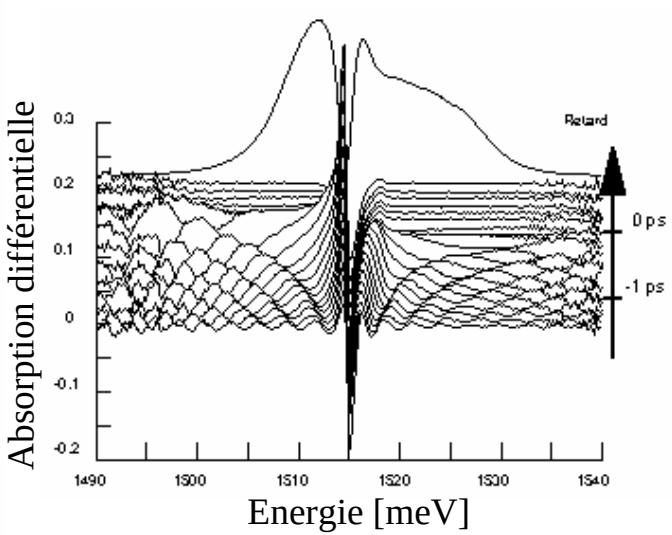
B. Fluegel et al., Phys. Rev. Lett. 59, 2588 (1987)
C. H. Brito-Cruz et al., IEEE J. Quant. Electr. 24, 261 (1988)
M. Joffre et al., Opt. Lett. 13, 276 (1988)

Limites de l'expérience pompe - sonde

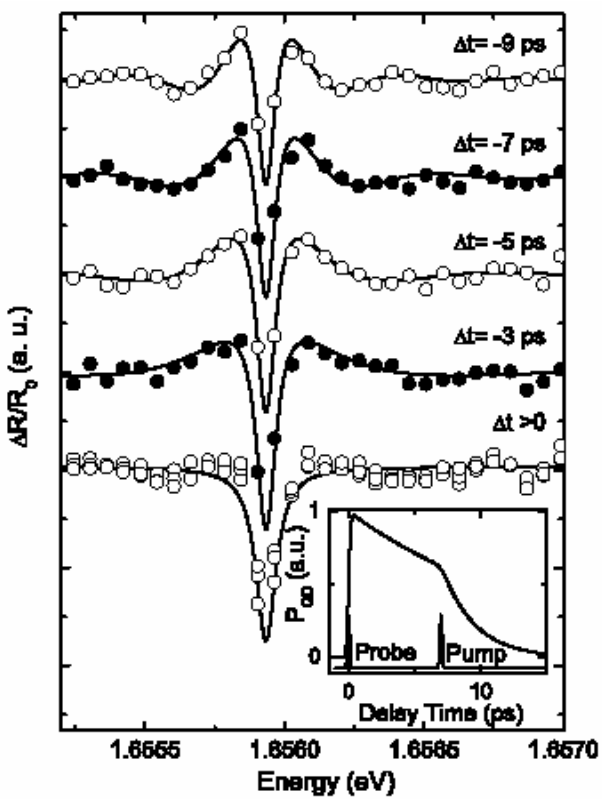
un problème général !



M. Joffre et al.,
Opt. Lett. **13**, 276 (1988)



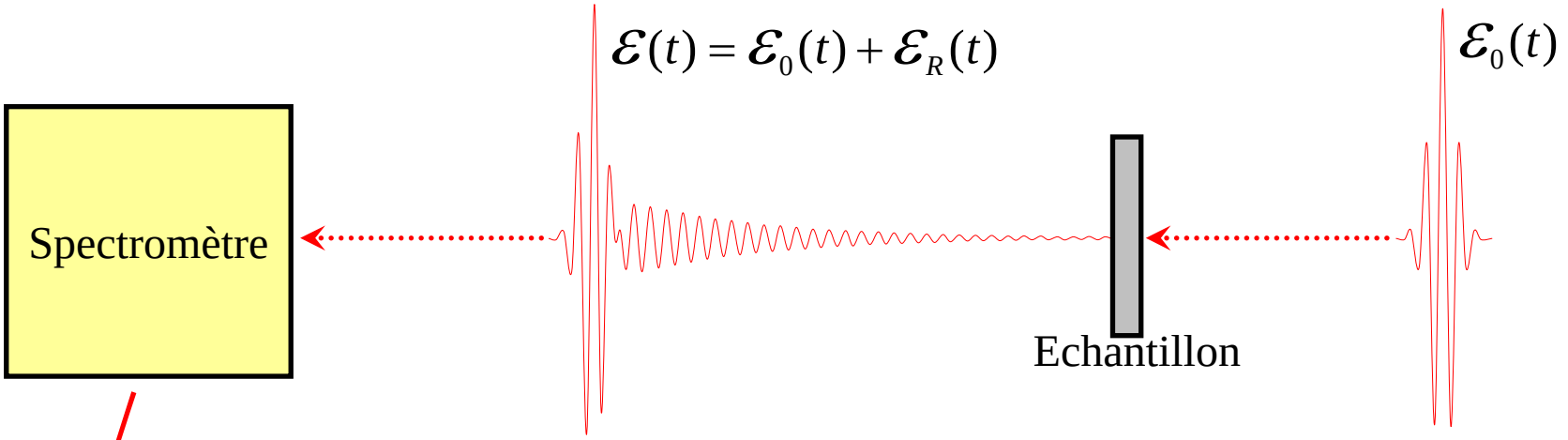
J.-P. Likforman et al.,
Opt. Lett. **20**, 2006 (1995)



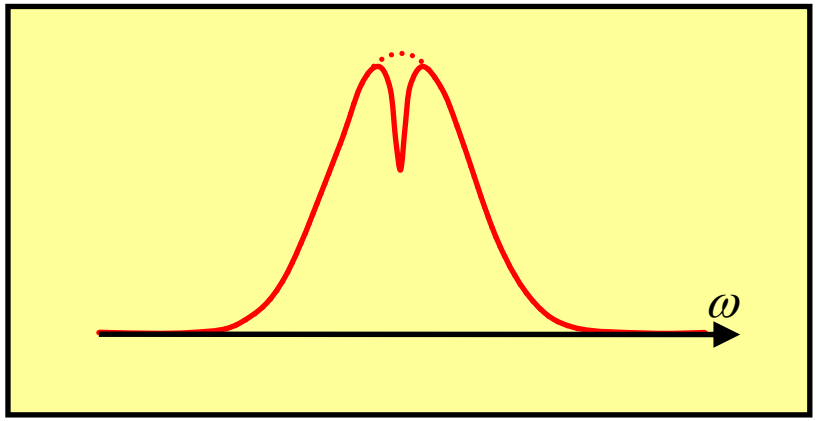
T. Guenther et al.,
Phys. Rev. Lett. **89**, 057401 (2002)

Excitation percusionnelle en régime cohérent

Régime cohérent : Durée d'impulsion inférieure au temps de déphasage T_2



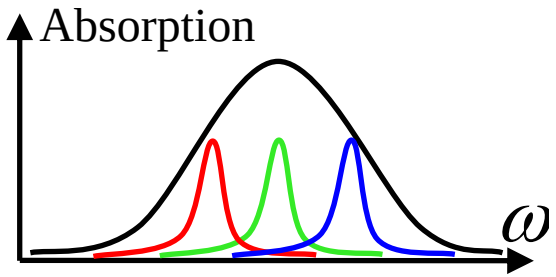
$$\left|\mathcal{E}(\omega)\right|^2 = \left|\mathcal{E}_0(\omega) + \mathcal{E}_R(\omega)\right|^2 \approx \left|\mathcal{E}_0(\omega)\right|^2 + 2\,\mathrm{Re}\,\mathcal{E}_0^*(\omega)\mathcal{E}_R(\omega)$$



2. Echo de photon

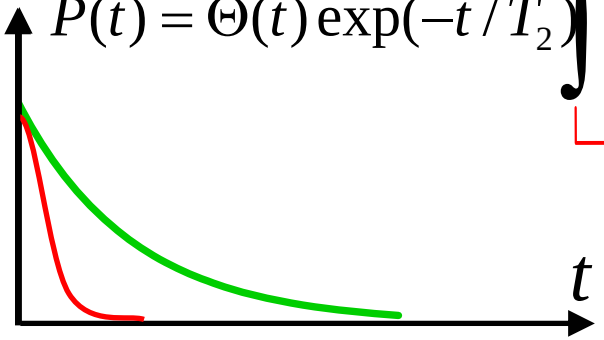
Elargissement inhomogène

• Distribution inhomogène $g(\omega_{eg})$

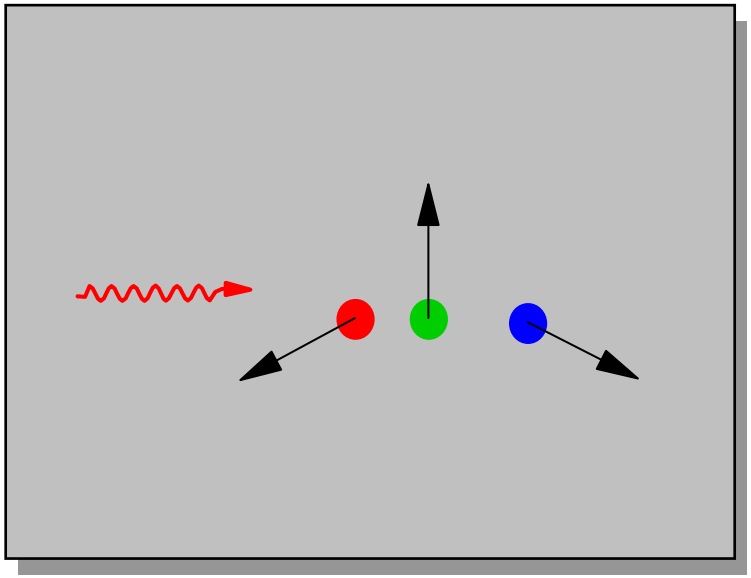


$$P(t) = \Theta(t)\exp(-t/T_2)\int \exp(-i\omega_{eg}t)g(\omega_{eg})d\omega_{eg}$$

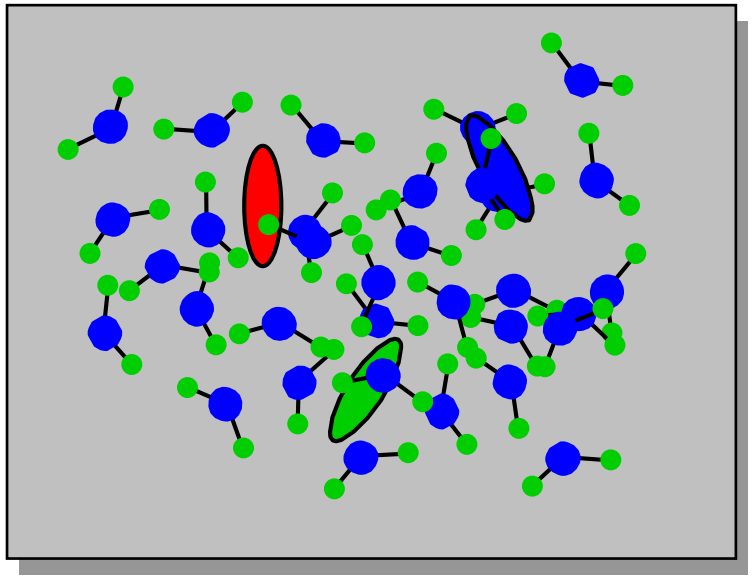
$$g(t)$$



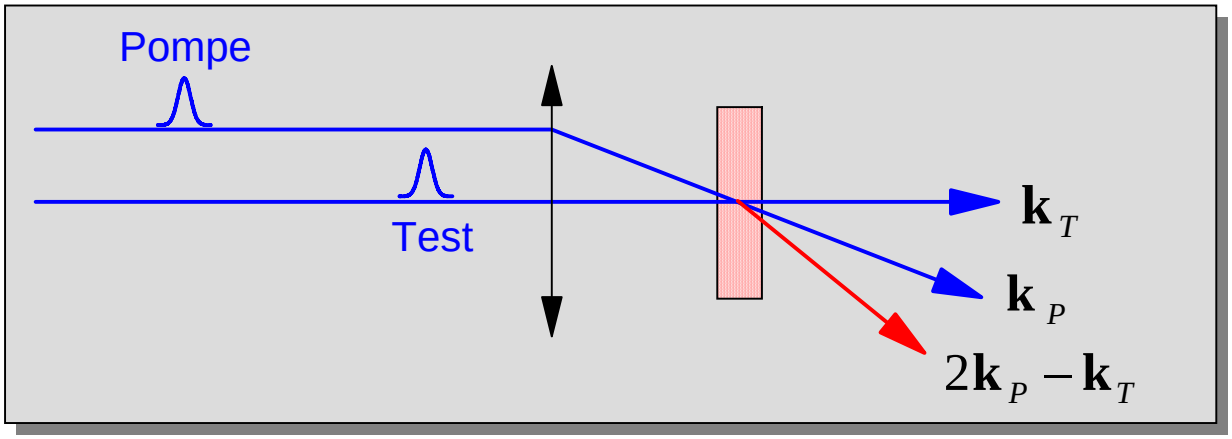
✓ Effet Doppler (gaz)



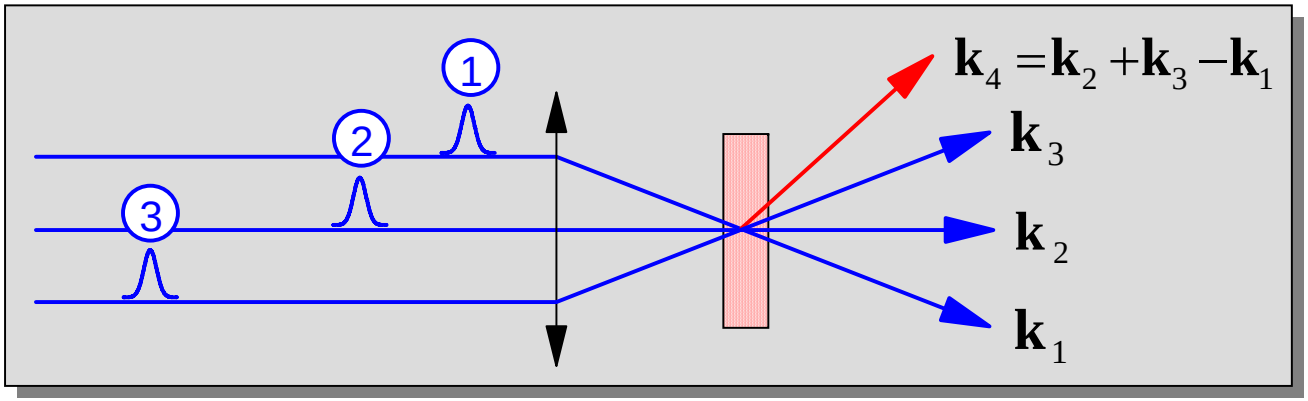
✓ Inhomogénéités de l'environnement (liquide, verre, solide amorphe, …)



Echo de photon : géométries expérimentales



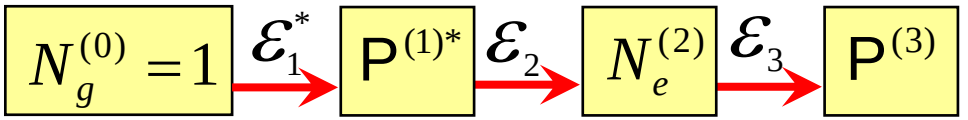
$$\mathbf{k}_2 = \mathbf{k}_3 = \mathbf{k}_P$$
$$\tau_{32} = 0$$

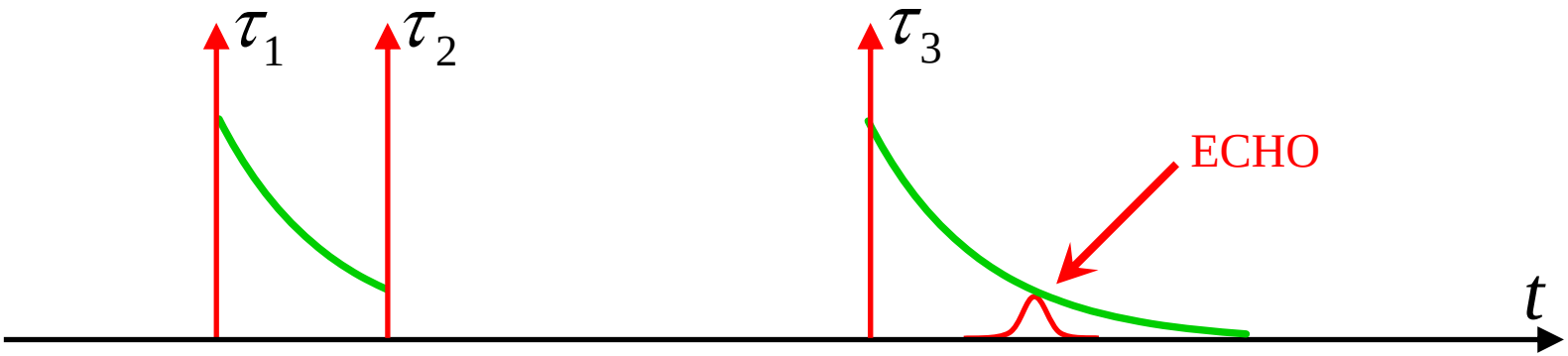


Direction $\mathbf{k}_2 + \mathbf{k}_3 - \mathbf{k}_1 \Rightarrow$ terme en $\mathcal{E}_1^* \, \mathcal{E}_2 \, \mathcal{E}_3$

Echo de photon : théorie

- ✓ Distribution inhomogène $g(\omega_{eg})$
- ✓ Impulsions infiniment brèves

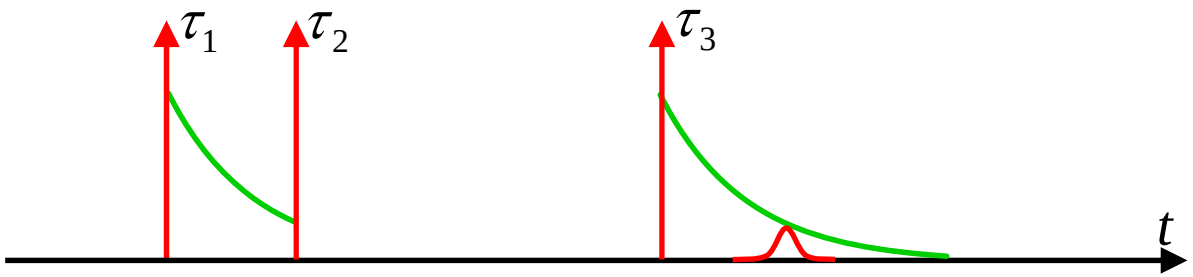




$$P^{(3)}(t) \propto \Theta(t-\tau_3)\Theta(\tau_{32})\Theta(\tau_{21})e^{-\tau_{21}/T_2}e^{-\tau_{32}/T_1}e^{-(t-\tau_3)/T_2}$$
$$\cdot \mathcal{E}_1^*\mathcal{E}_2\mathcal{E}_3 \underbrace{\int \exp\left[-i\omega_{eg}\left(t-\tau_3-\tau_{21}\right)\right] g(\omega_{eg})d\omega_{eg}}_{g(t-\tau_3-\tau_{21})}$$

Echo de photon : deux cas limites

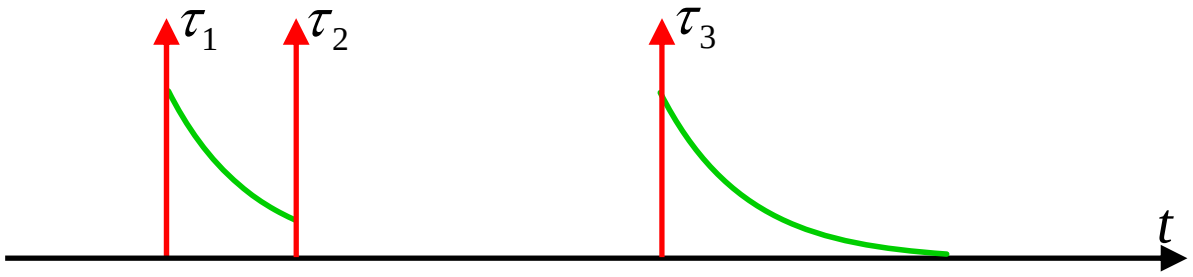
• Cas fortement inhomogène



$$\text{Signal intégré} \propto \int \left| P^{(3)}(t) \right|^2 dt \propto \exp(-4\tau_{21}/T_2)$$

$$T_{echo} = \frac{T_2}{4}$$

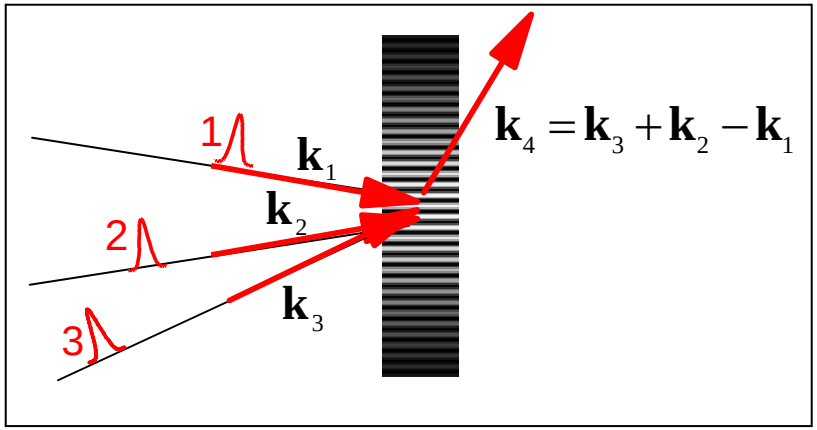
• Cas homogène

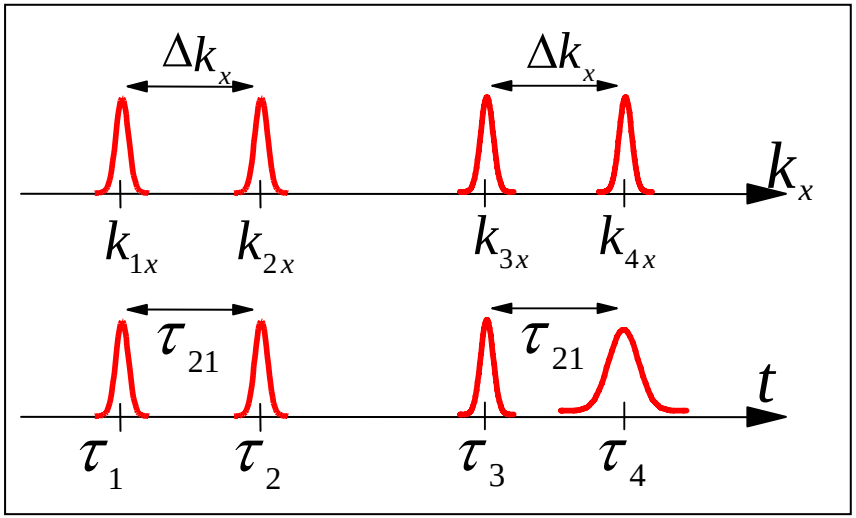


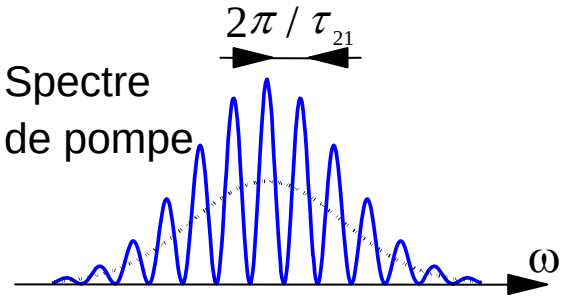
$$\text{Signal intégré} \propto \int \left| P^{(3)}(t) \right|^2 dt \propto \exp(-2\tau_{21}/T_2)$$

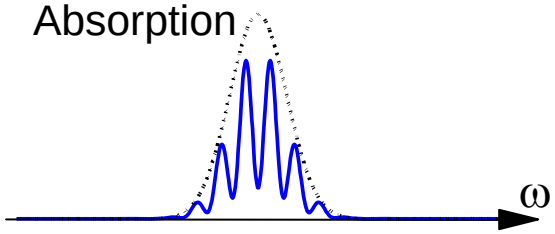
$$T_{FWM} = \frac{T_2}{2}$$

Interprétation spectrale de l'écho de photon









➡ Réseau spectral inscrit dans le matériau

Première observation d'un écho de photon

- ✓ Système étudié : Cristal de rubis (0.005% Cr)
- ✓ Elargissement inhomogène : contraintes

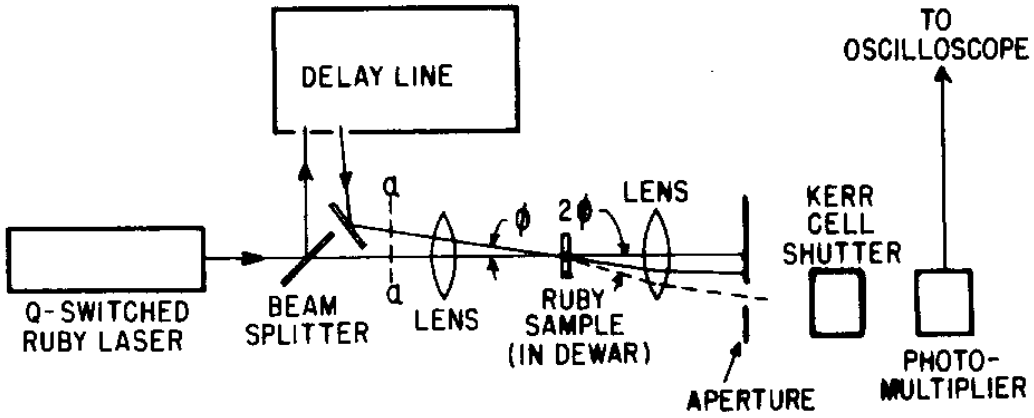
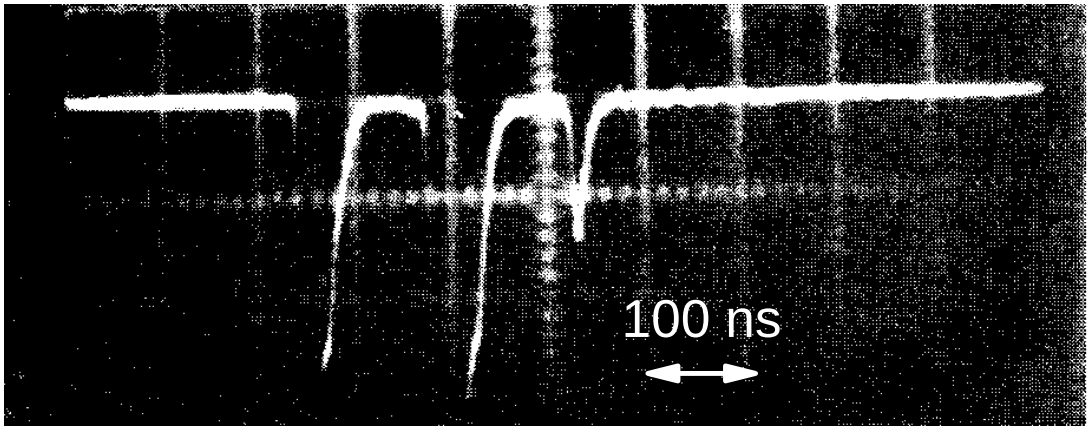


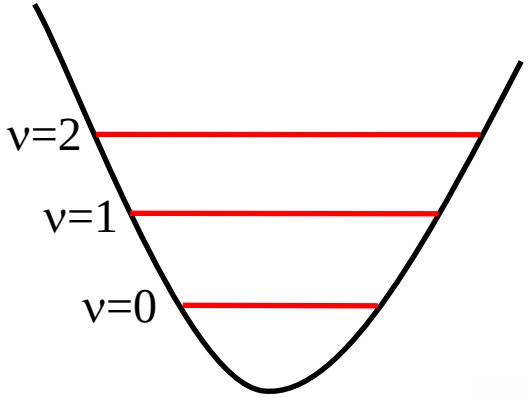
FIG. 2. Schematic experimental arrangement.



N.A. Kurnit, I.D. Abella, S.R. Hartmann, *Observation of a photon echo*, Phys. Rev. Lett. 13, 567 (1964)

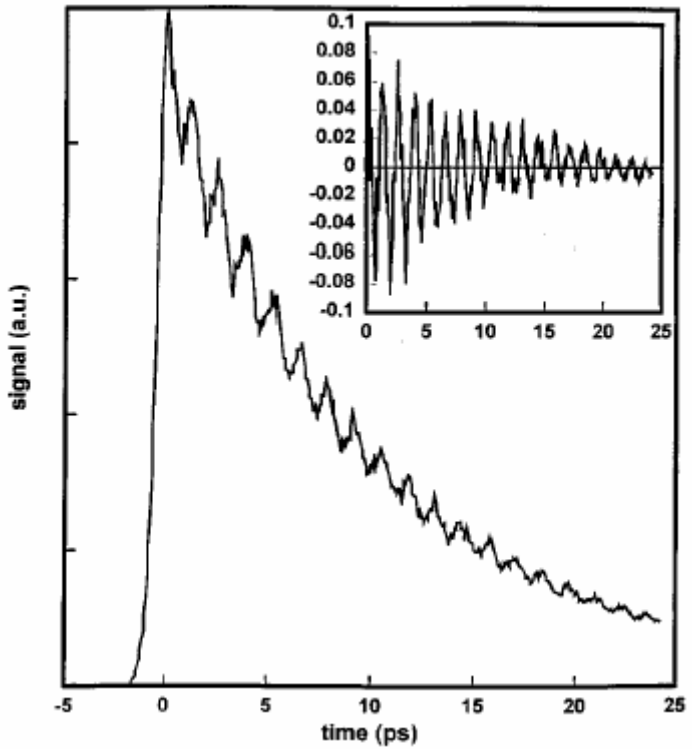
Anharmonicité de CO dans la myoglobine

Echo de photon vibrationnel



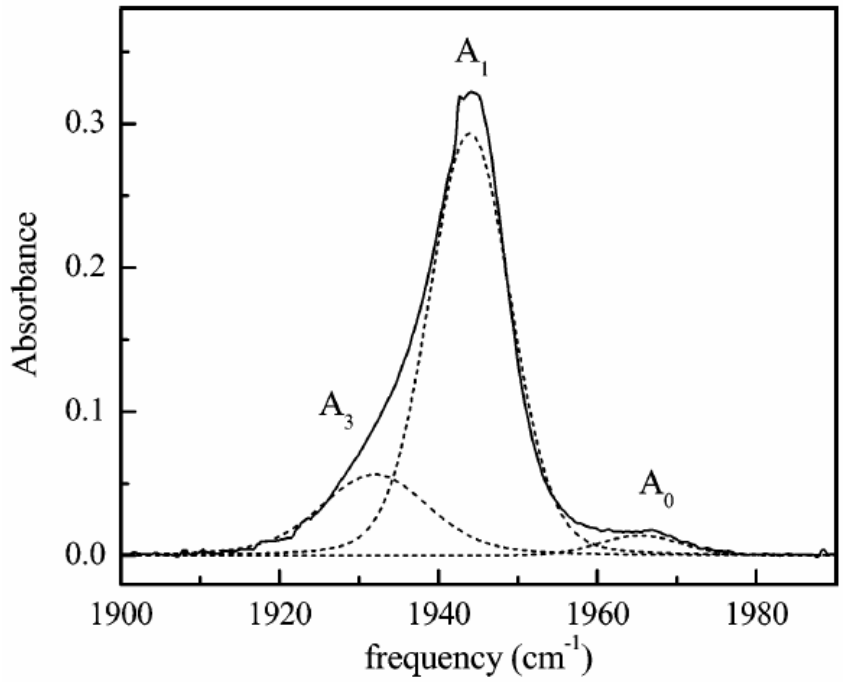
$$\rho_{00}^{(0)}=1 \xrightarrow{\mathcal{E}_1^*} \rho_{01}^{(1)} \xrightarrow{\mathcal{E}_2} \rho_{11}^{(2)} \xrightarrow{\mathcal{E}_3} \rho_{10}^{(3)}$$

$$\rho_{00}^{(0)}=1 \xrightarrow{\mathcal{E}_1^*} \rho_{01}^{(1)} \xrightarrow{\mathcal{E}_2} \rho_{11}^{(2)} \xrightarrow{\mathcal{E}_3} \rho_{21}^{(3)}$$



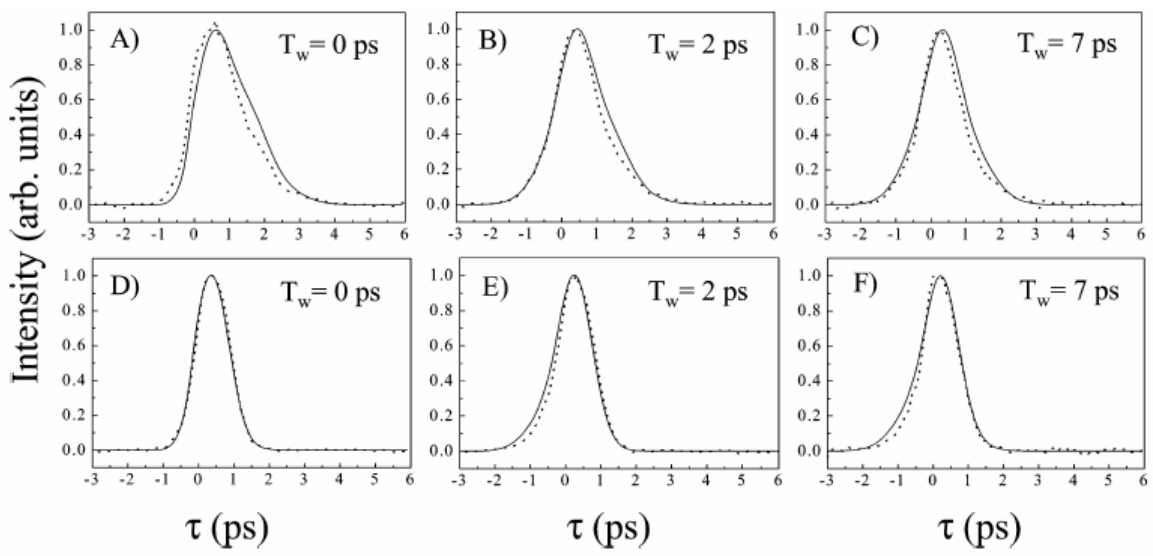
K.D. Rector et al., J. Chem. Phys. **106**, 10027 (1997).

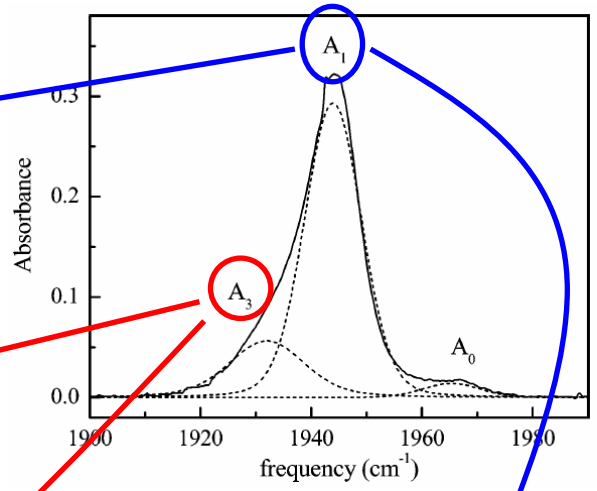
Identification des raies infrarouges dans MbCO

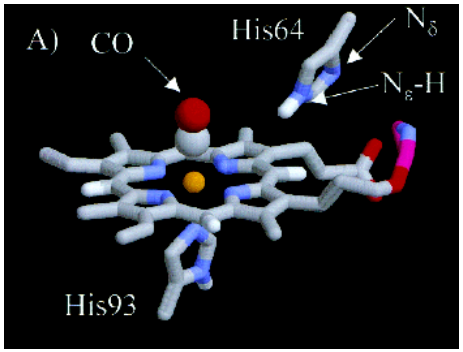


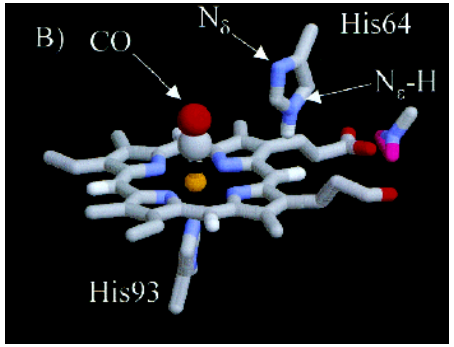
K.A. Merchant et al., J. Phys. Chem. B **107**, 4 (2003).

Echo de photon résolu spectralement dans MbCO



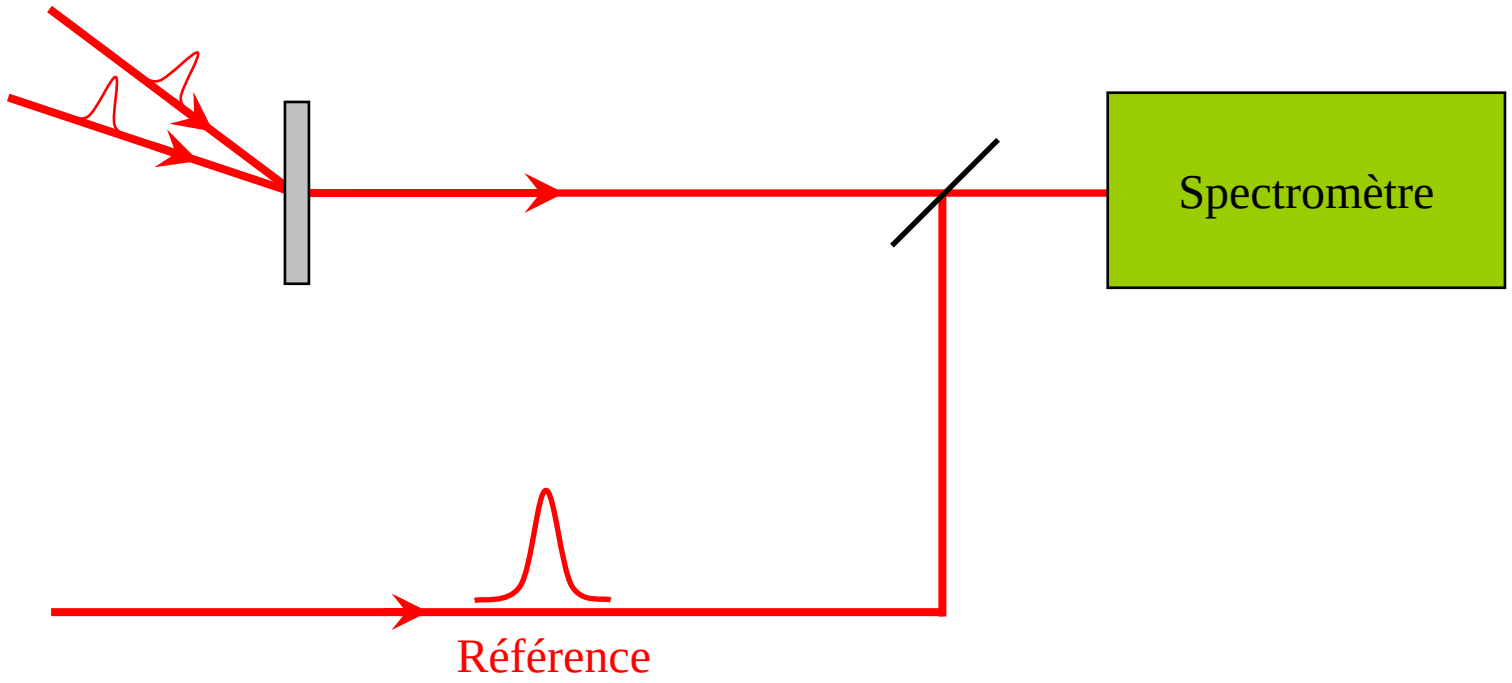






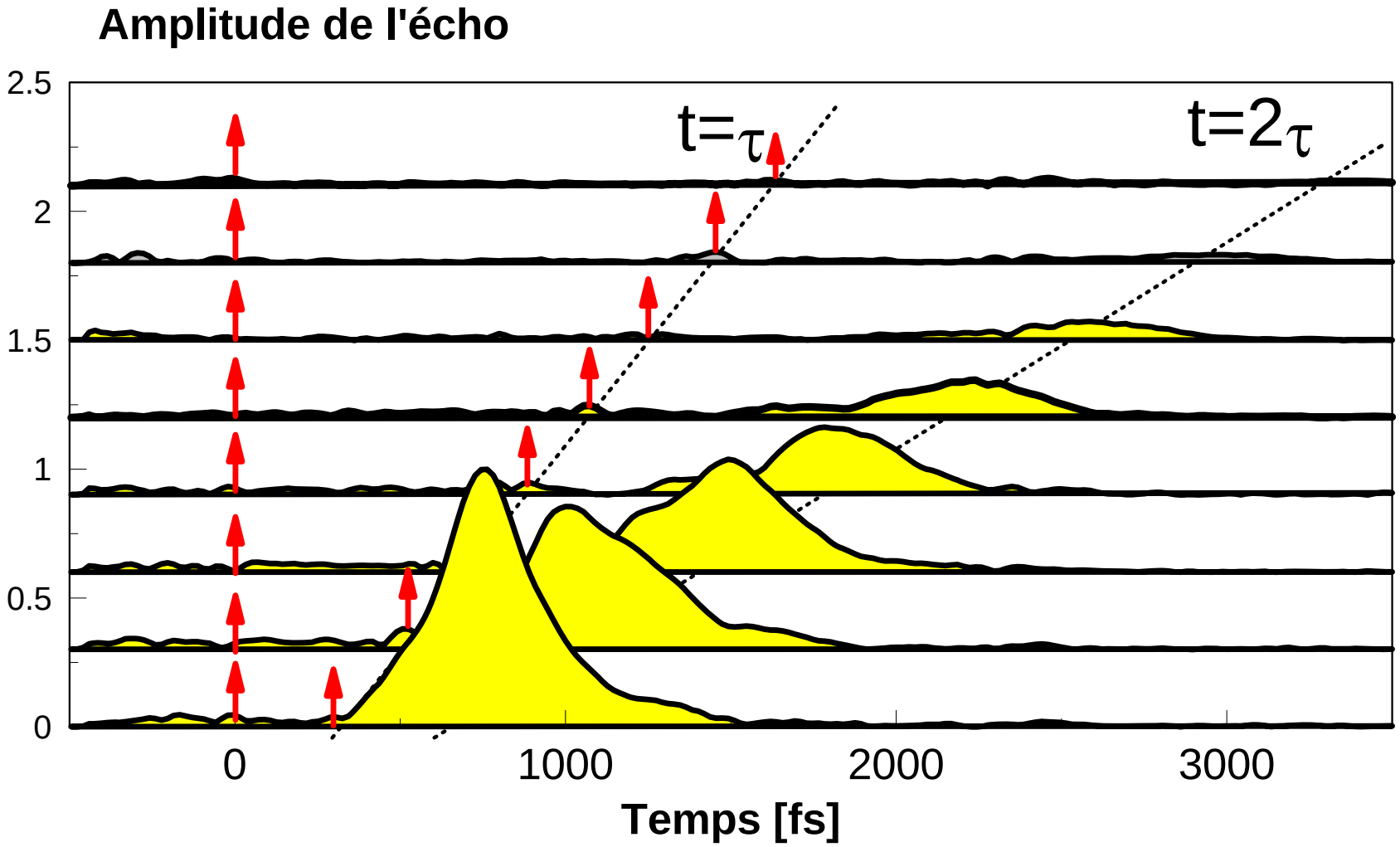
K.A. Merchant et al., J. Phys. Chem. B **107**, 4 (2003).

Echo de photon résolu en temps



Interférométrie spectrale $\longrightarrow \mathcal{E}_0^*(\omega)\mathcal{E}_{echo}(\omega) \longrightarrow \mathcal{E}_{echo}(\omega)\ , \mathcal{E}_{echo}(t)$

Echo de photon résolu en temps



J.-P. Likforman et al., Opt. Lett. **22**, 1104 (1997)

3. Spectroscopie multidimensionnelle

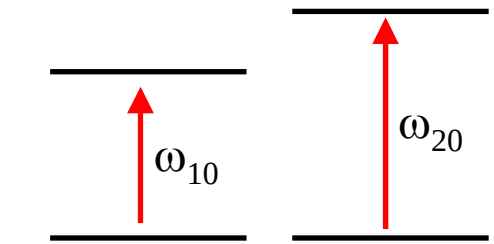
Pourquoi deux dimensions ?

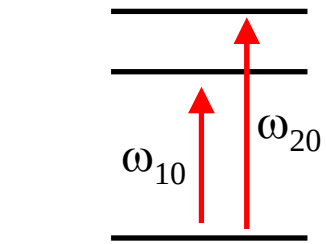
Deux systèmes indépendants

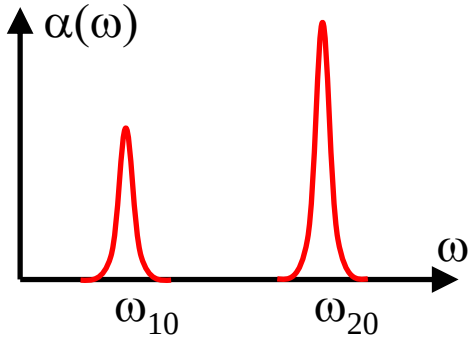
Deux systèmes couplés

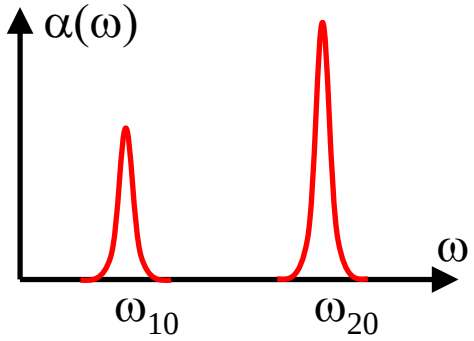
1D

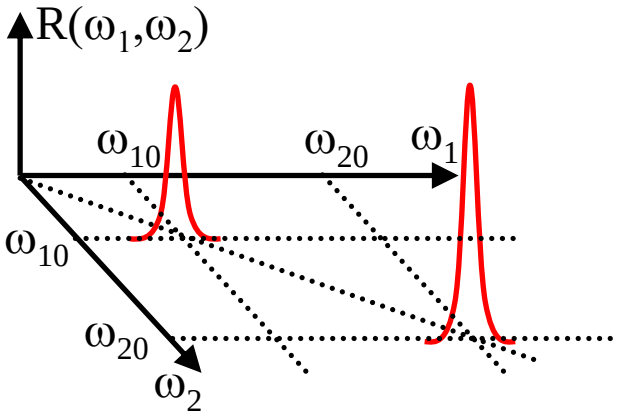
2D

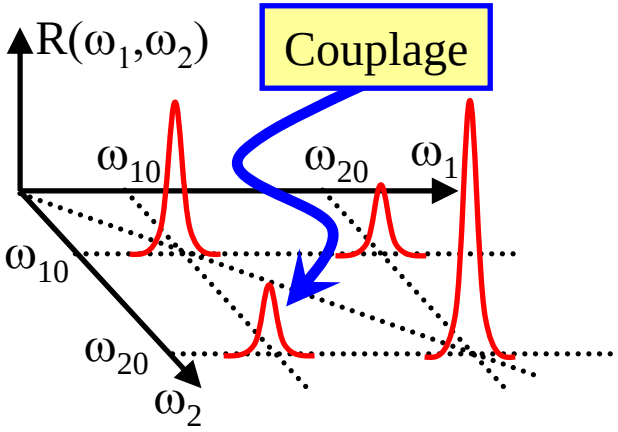






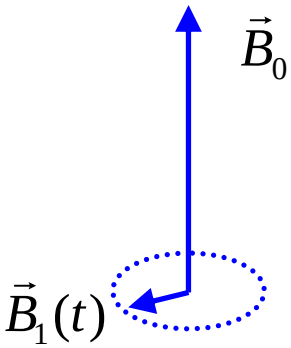




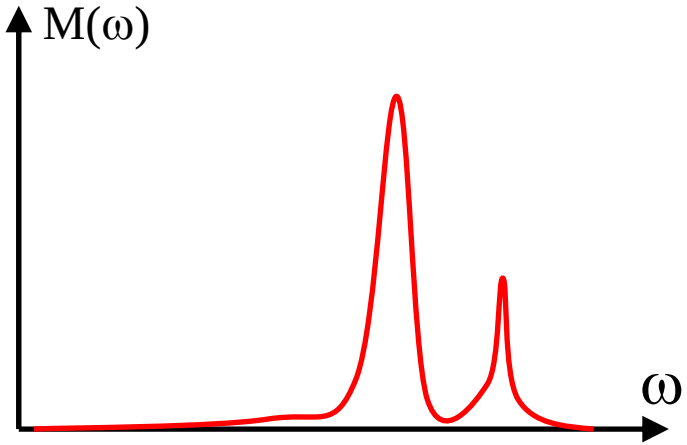


Les deux façons d'enregistrer un spectre RMN

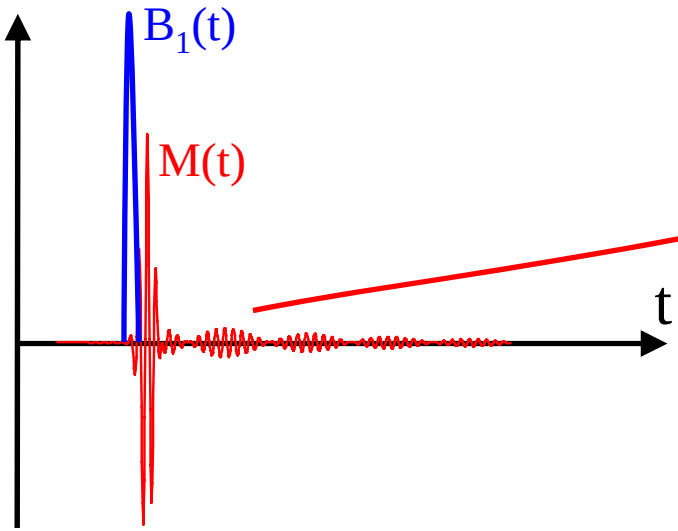
1) Domaine fréquentiel



$$\vec{B}(t) = \begin{vmatrix} B_1 \cos \omega t \\ B_1 \sin \omega t \\ B_0 \end{vmatrix}$$



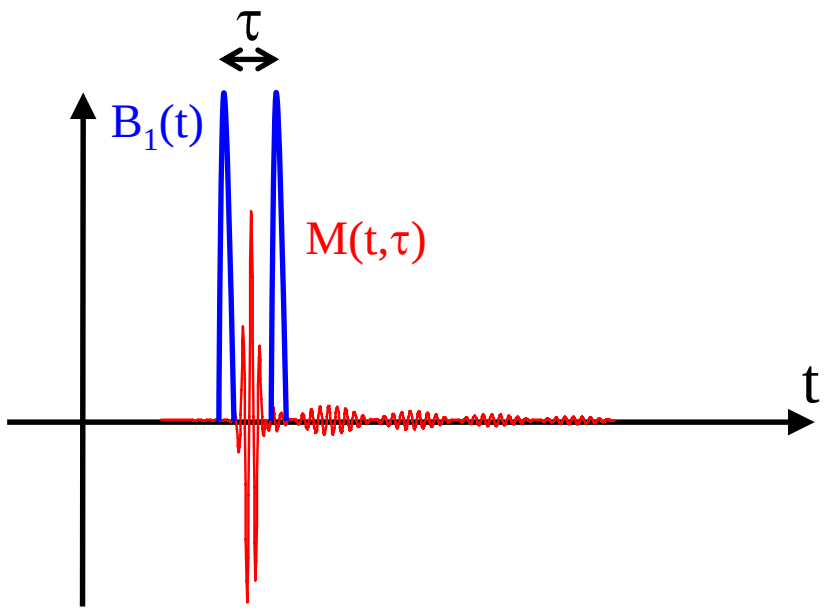
2) Domaine temporel : excitation percussionnelle



Transformation de Fourier

RMN à deux dimensions

1) Application d'une séquence de deux impulsions espacées d'un retard τ
2) Mesure de l'aimantation $M(t,\tau)$
3) Transformée de Fourier à 2D fournit $R(\omega_1,\omega_2)$



W. P. Aue, E. Bartholdi, R.R. Ernst, J. Chem. Phys. 64, 2229 (1976)

RMN à deux dimensions

Two-dimensional spectroscopy. Application to nuclear magnetic resonance

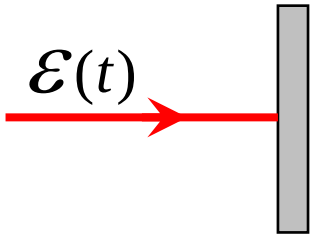
W. P. Aue, E. Bartholdi, and R. R. Ernst
Laboratorium für physikalische Chemie, Eidgenössische Technische Hochschule, 8006 Zürich, Switzerland

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 inhomogenous 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.** »

W. P. Aue, E. Bartholdi, R.R. Ernst, J. Chem. Phys. 64, 2229 (1976)

Optique non-linéaire



$$\mathrm{P}(t) = \mathrm{P}^{(1)}(t) + \mathrm{P}^{(2)}(t) + ...$$

- Réponse instantanée

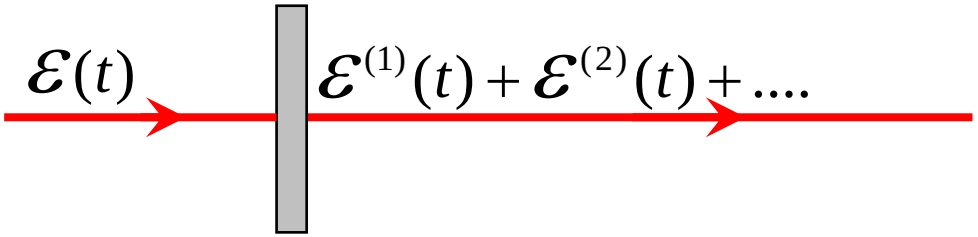
$$\mathrm{P}^{(n)}(t) = \varepsilon_0 \chi^{(n)} \mathcal{E}(t)^n$$

$$\mathrm{P}^{(n)}(t) = \varepsilon_0 \iiint \chi^{(n)} \mathcal{E}(\omega_1)...\mathcal{E}(\omega_n) \exp\left(-i\left(\omega_1 + ... + \omega_n\right)t\right) d\omega_1...d\omega_n$$

- Réponse non instantanée

$$\mathrm{P}^{(n)}(t) = \varepsilon_0 \iiint \chi^{(n)}(\omega_1, \omega_2, ..., \omega_n) \mathcal{E}(\omega_1)...\mathcal{E}(\omega_n) \exp\left(-i\left(\omega_1 + ... + \omega_n\right)t\right) d\omega_1...d\omega_n$$

Réponse non-linéaire d'un échantillon



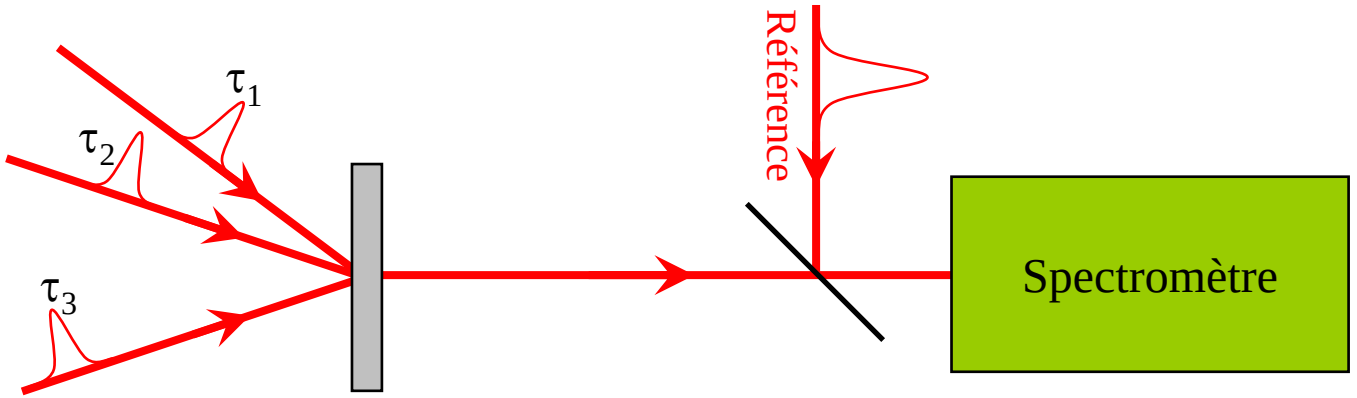
$$\mathcal{E}^{(n)}(t)=\iiint \Xi^{(n)}(\omega_1,\omega_2,...,\omega_n)\mathcal{E}(\omega_1)...\mathcal{E}(\omega_n)\exp\left(-i\left(\omega_1+...+\omega_n\right)t\right)d\omega_1...d\omega_n$$

Exemple : n=2

$$\Xi^{(2)}(\omega_1,\omega_2)\propto\chi^{(2)}(\omega_1,\omega_2)\frac{\exp(i\Delta k(\omega_1,\omega_2)L)-1}{\Delta k(\omega_1,\omega_2)}$$

Spectroscopie multidimensionnelle

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



$$\mathcal{E}^{(n)}(t) = \iiint \Xi^{(n)}(\omega_1,...,\omega_n)\mathcal{E}(\omega_1)\, e^{i\omega_1\tau_1}...\mathcal{E}(\omega_n)\, e^{i\omega_n\tau_n}\; e^{-i(\omega_1+...+\omega_n)t}\; d\omega_1...d\omega_n$$

$$\mathcal{F}_{\tau_2,...,\tau_n,t}$$

$$\Xi^{(n)}(\omega_1,...,\omega_n)\;\mathcal{E}(\omega_1)...\mathcal{E}(\omega_n)$$

- ✓ Y. Tanimura et S. Mukamel, J. Chem. Phys. **99**, 9496 (1993)
- ✓ 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).

Spectroscopies multidimensionnelles

n=2	800 nm 16 fs	KDP	Lepetit et al., Opt. Lett. **21**, 564 (1996)
	800 nm 16 fs	$AgGaS_2$	Belabas et al., Opt. Lett. **27**, 2043 (2002)
n=3	800 nm 22 fs	IR 144 dans du méthanol	Hybl et al., J. Chem. Phys. **115** 6606 (2001)
	4.9 µm 90 fs	RDC dans de l'hexane	Golonzka et al., PRL **86** 2154 (2001)
	6.25 µm 120 fs	1,3-cyclahexanedione Acyl-proline-NH_2 in $CDCl_3$ N-methylacetamide-D	Asplund et al., PNAS **97** 8219 (2000) Zanni et al., J. Phys. Chem. B **105** 6520 (2001) Zanni et al., J. Chem. Phys. **114** 4579 (2001)
	4.9 µm 90 fs	RhCO2acac in PMMA	Merchant et al., PRL **86** 3899 (2001)
n=5	800 nm 42 fs	CCl_4,$CHCl_3$,CS_2	Tokmakoff et al., PRL **79** 2702 (1997) Blank et al., J. Chem. Phys. **113** 771 (2000) Kubarych et al., J. Chem. Phys. **116**, 2016 (2002)
	532 nm, 4.4 µm, 3.2 µm	CH_3CN dans deuterobenzène	Zhao et al., PRL **84** 1411 (2000)

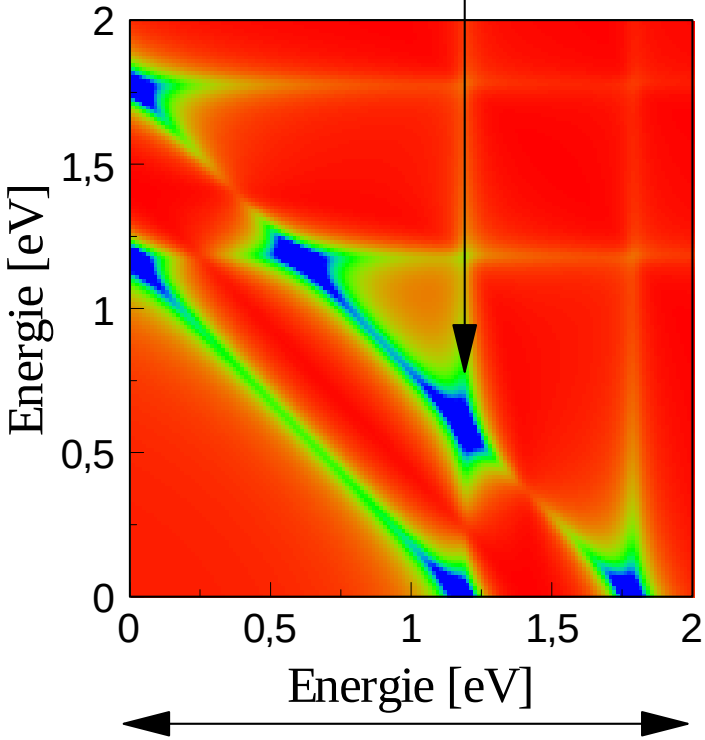
Cf - thèse Nadia Belabas

- David M. Jonas, *two-dimensional femtosecond spectroscopy*, Annual Review of Physical Chemistry

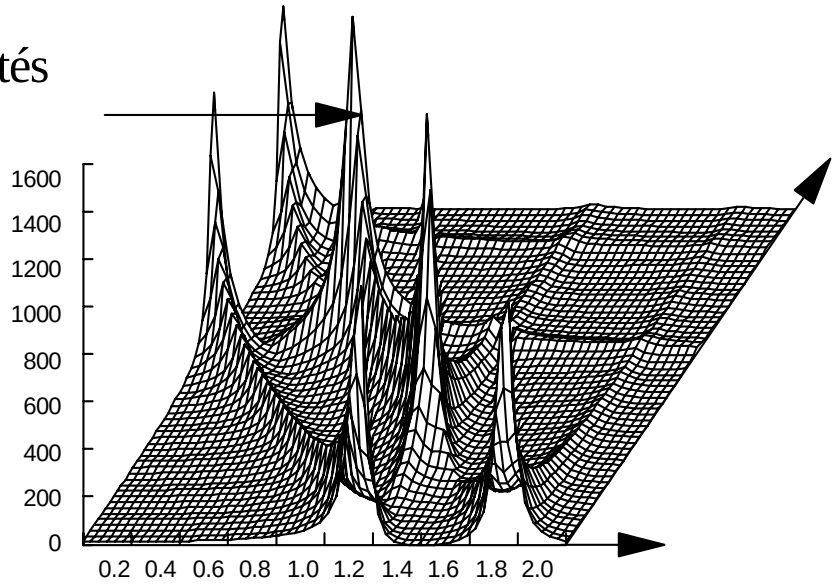
$\chi^{(2)}$

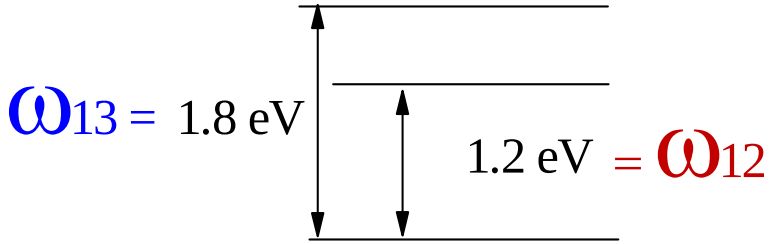
Somme de fréquences $\omega_1+\omega_2 \rightarrow \omega_3$

Couplage entre états excités
(dipôles de transition)



$\left|\chi^{(2)}(\omega_1,\omega_2)\right|$

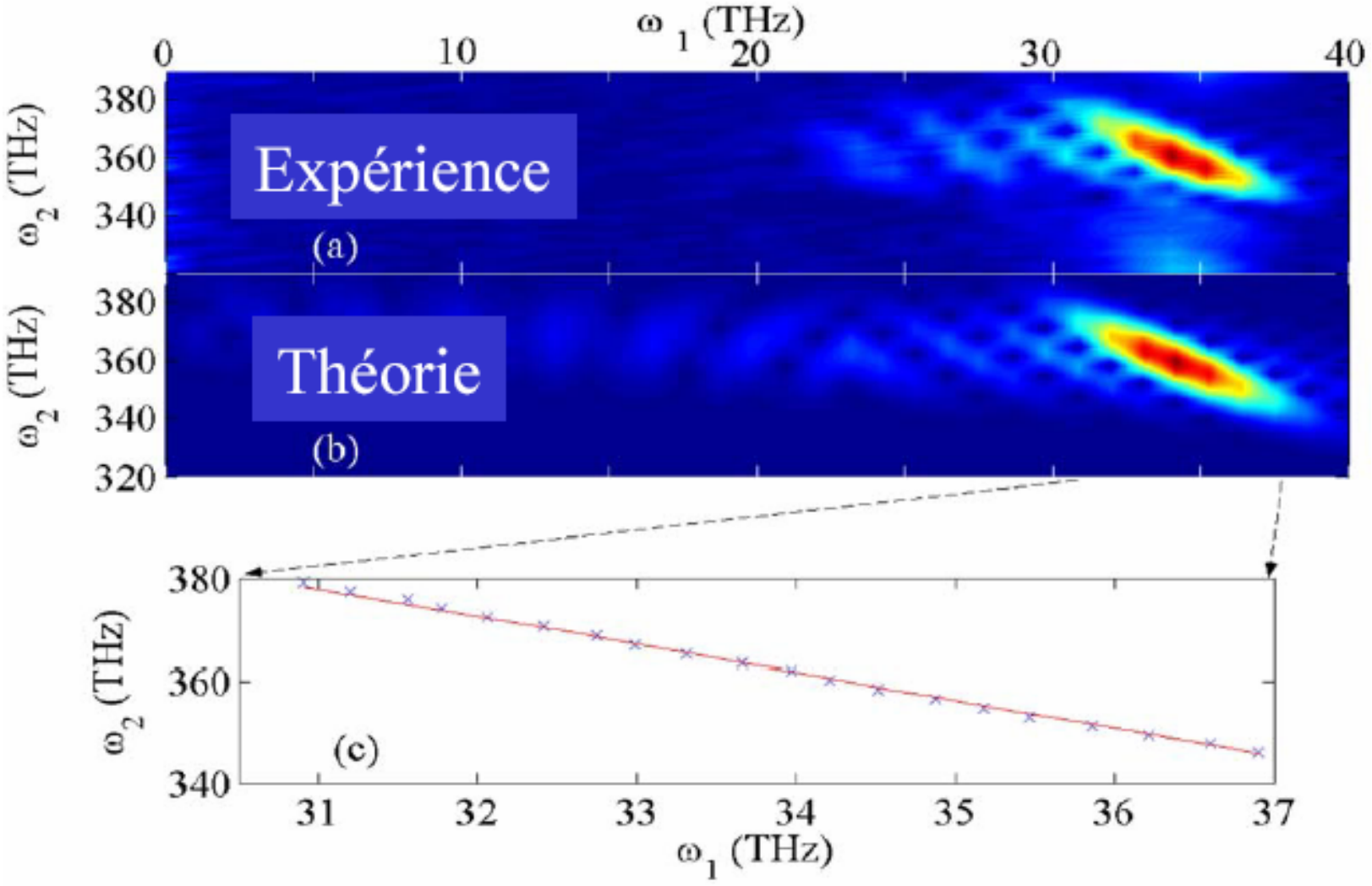




L. Lepetit et M. Joffre, J. nonlin. Opt. Phys. **5**, 465 (1996)

$\Xi^{(2)}$

Carte d'accord de phase dans $AgGaS_2$

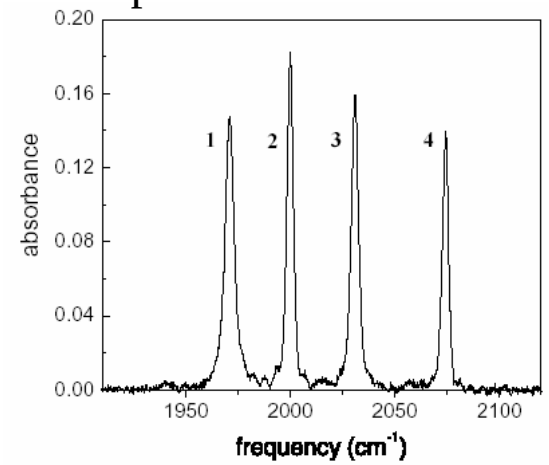


N. Belabas et M. Joffre, Opt. Lett. **27**, 2043(2002)

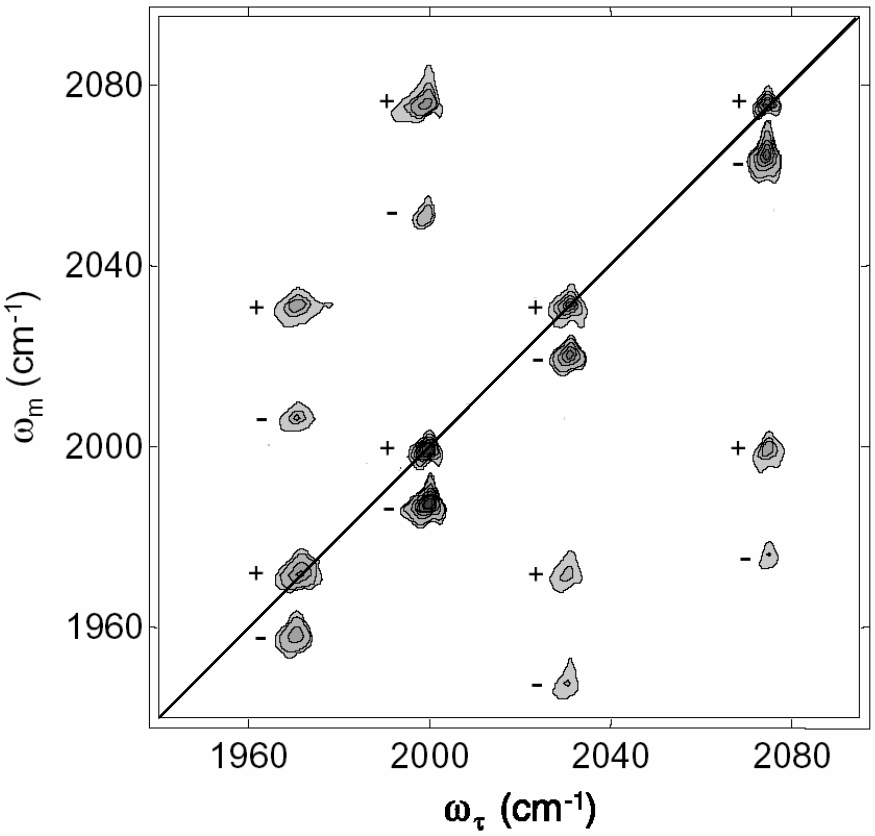
$\chi^{(3)}$

Spectroscopie 2D vibrationnelle

Spectre 1D



Spectre 2D

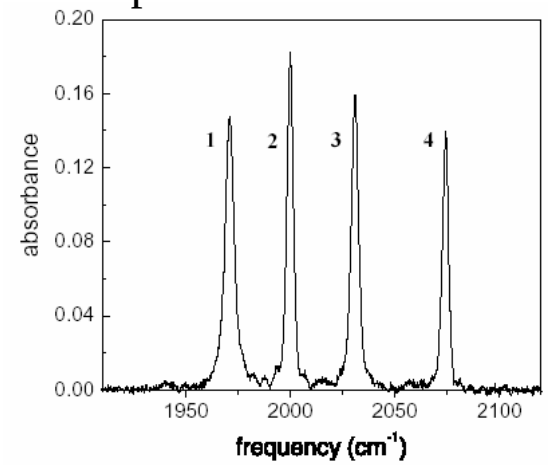


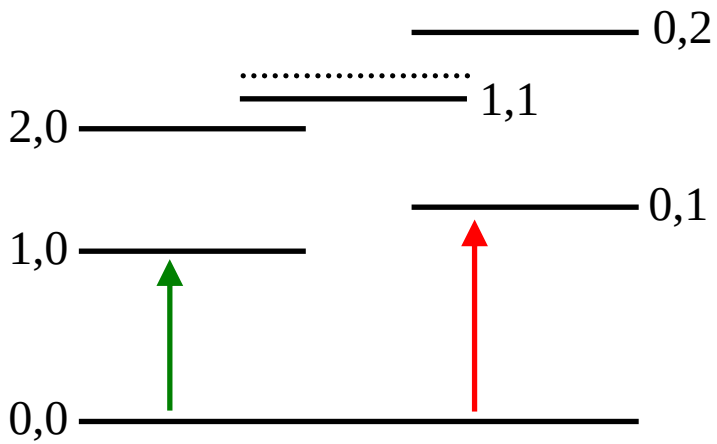
Asbury, Steinel et Fayer, Chem. Phys. Lett. **381**, 139 (2003)

$\chi^{(3)}$

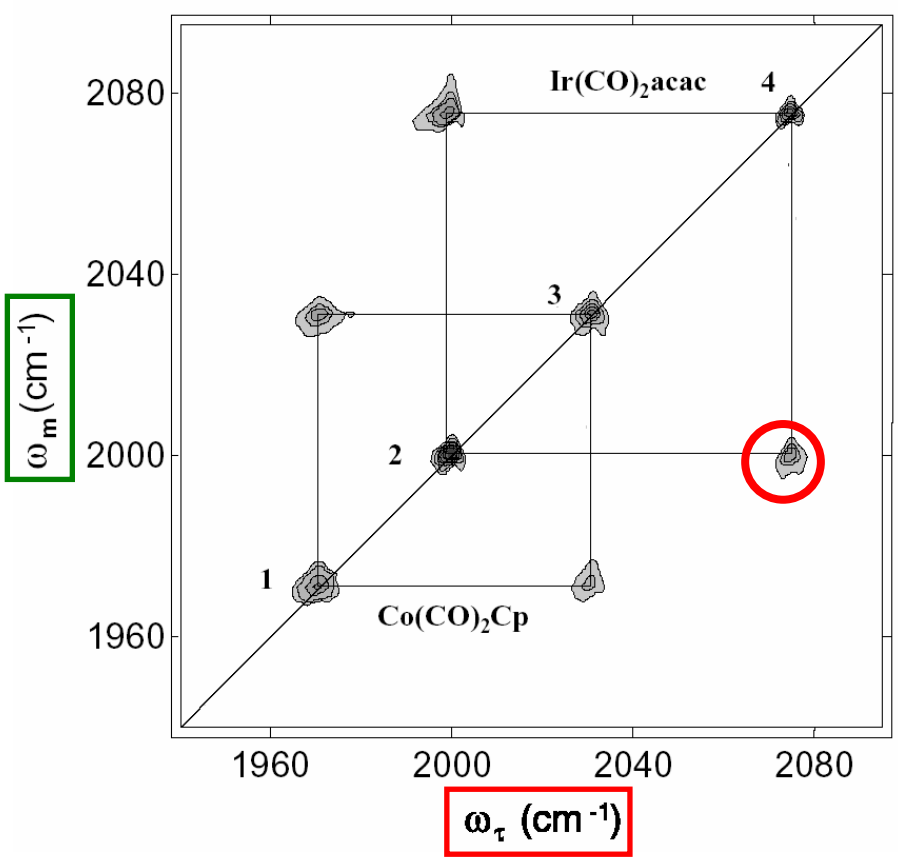
Spectroscopie 2D vibrationnelle

Spectre 1D





Spectre 2D

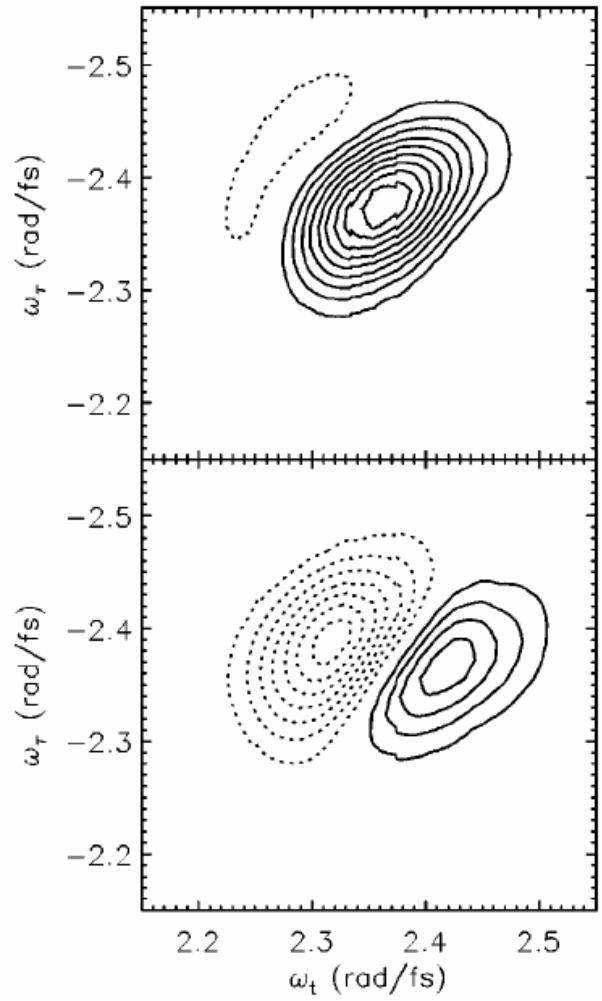


Asbury, Steinel et Fayer, Chem. Phys. Lett. **381**, 139 (2003)

$\chi^{(3)}$

Spectroscopie 2D électronique

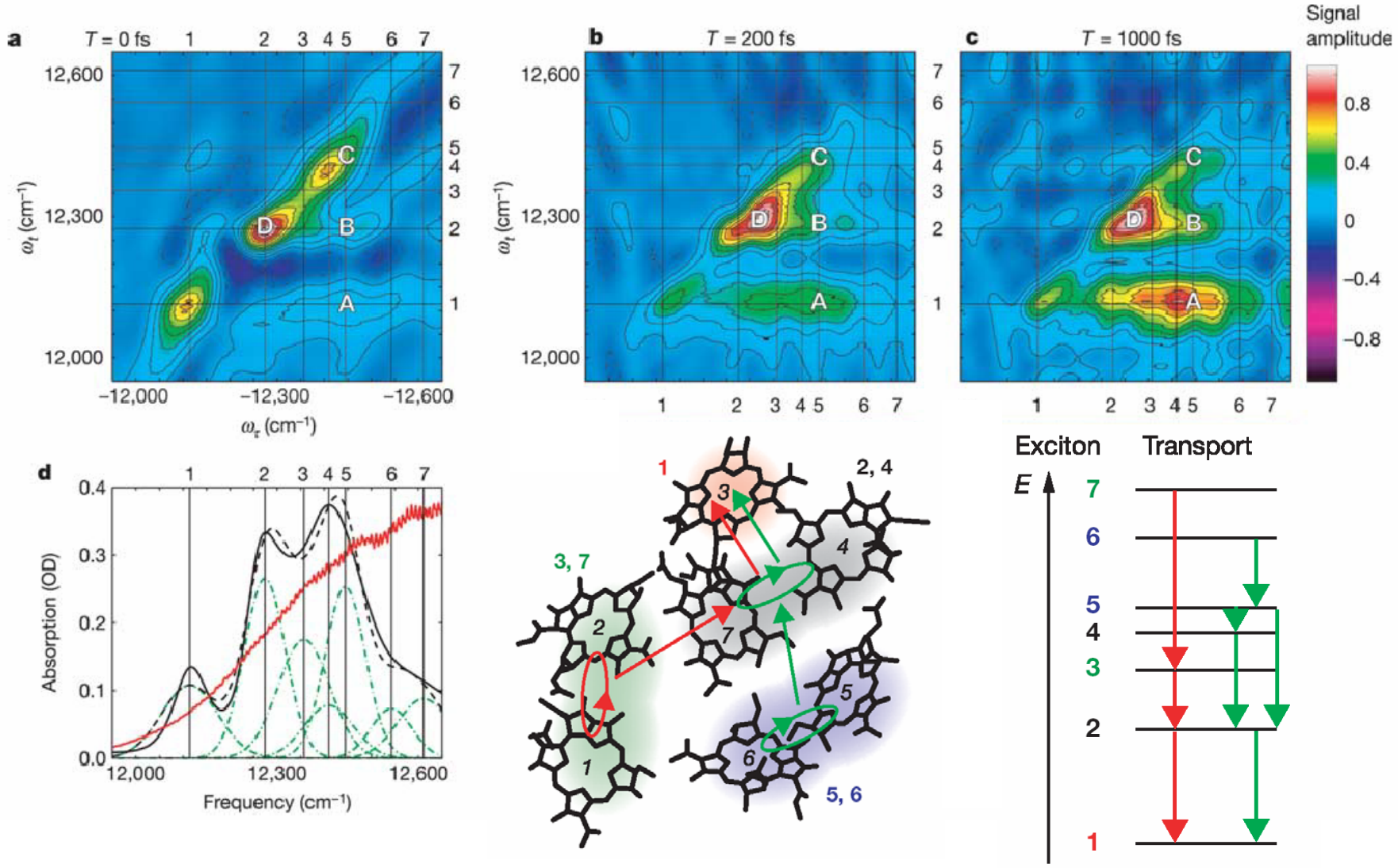
IR 144 in methanol



Hybl, Albrecht et Jonas, J. Chem. Phys. **115**, 6606 (2001)

$\chi^{(3)}$ Couplages électroniques et photosynthèse

Fenna-Matthews-Olson photosynthetic light-harvesting protein



T. Brixner, J. Stenger, H.M. Vaswani, M. Cho, R.E. Blankenship, G.R. Fleming, Nature 434, 625-628 (2005).

Conclusion

- Grande diversité de techniques de spectroscopie femtoseconde : pompe-sonde, écho de photon, spectroscopie multidimensionnelle, etc.
- Grande diversité de processus accessibles selon la longueur d'onde du rayonnement utilisé : visible, infrarouge, X.
- La spectroscopie femtoseconde joue un rôle important dans la compréhension de la dynamique des protéines. Une compréhension plus directe des mouvements structuraux peut être escomptée par l'utilisation d'impulsions infrarouge ou *a fortiori* dans le domaine des rayons X.