Coherent multidimensional spectroscopy using femtosecond laser pulses

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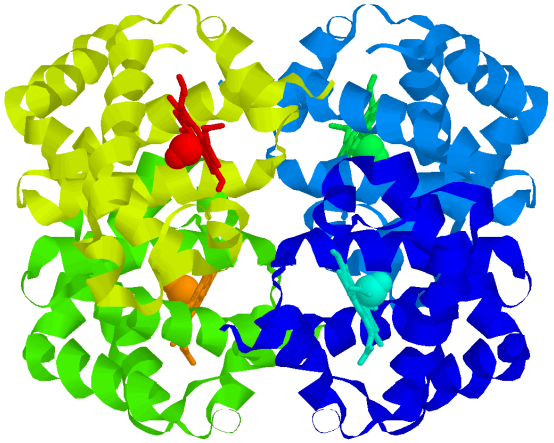
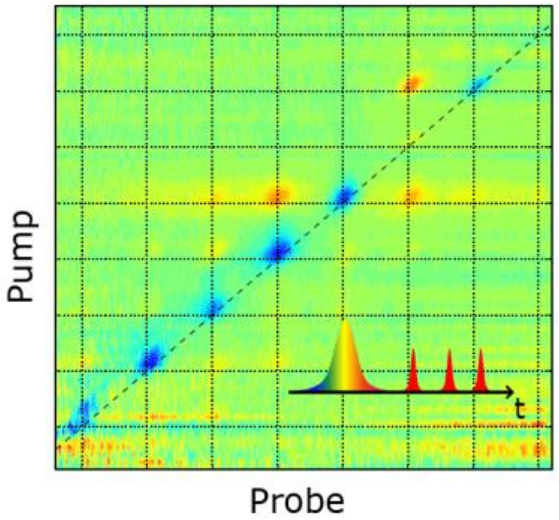
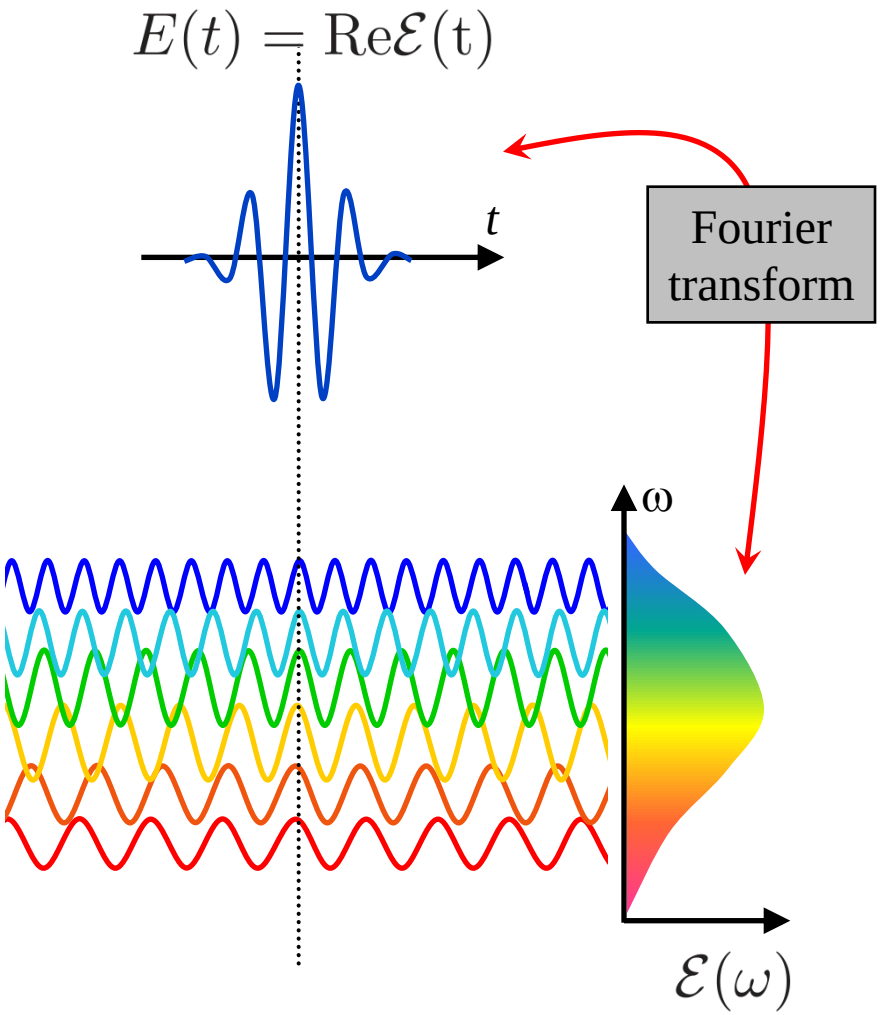
France





2nd Light-Matter Summer School, PALM – NanoSaclay – Université Paris-Saclay (2016)

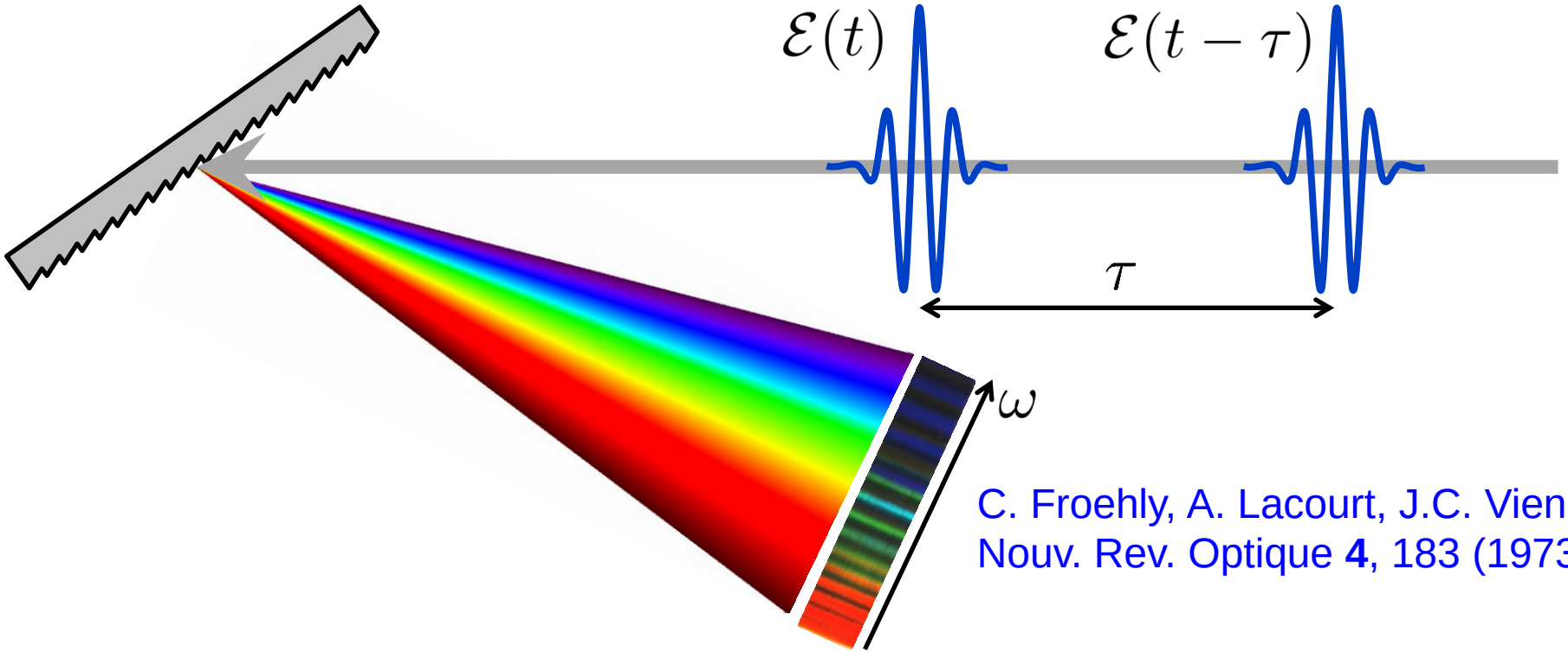
Preamble 1 : time and frequency



$$\mathcal{E}(t) = \int_0^{+\infty} \mathcal{E}(\omega) \exp(-i\omega t) \frac{d\omega}{2\pi}$$

$$\mathcal{E}(\omega) = \int_{-\infty}^{+\infty} \mathcal{E}(t) \exp(i\omega t) dt$$

Preamble 2 : spectral interferometry



C. Froehly, A. Lacourt, J.C. Vienot,
Nouv. Rev. Optique **4**, 183 (1973)

$$\int_{-\infty}^{+\infty} \mathcal{E}(t-\tau)\exp(i\omega t)dt = \int_{-\infty}^{+\infty} \mathcal{E}(t)\exp(i\omega(t+\tau))dt = \mathcal{E}(\omega)\exp(i\omega\tau)$$

$$S(\omega) = \left|\mathcal{E}(\omega) + \mathcal{E}(\omega)e^{i\omega\tau}\right|^2 = \left|\mathcal{E}(\omega)\right|^2\left(1+1+e^{i\omega\tau}+e^{-i\omega\tau}\right)$$

$$= 2\left|\mathcal{E}(\omega)\right|^2(1+\cos\omega\tau)$$

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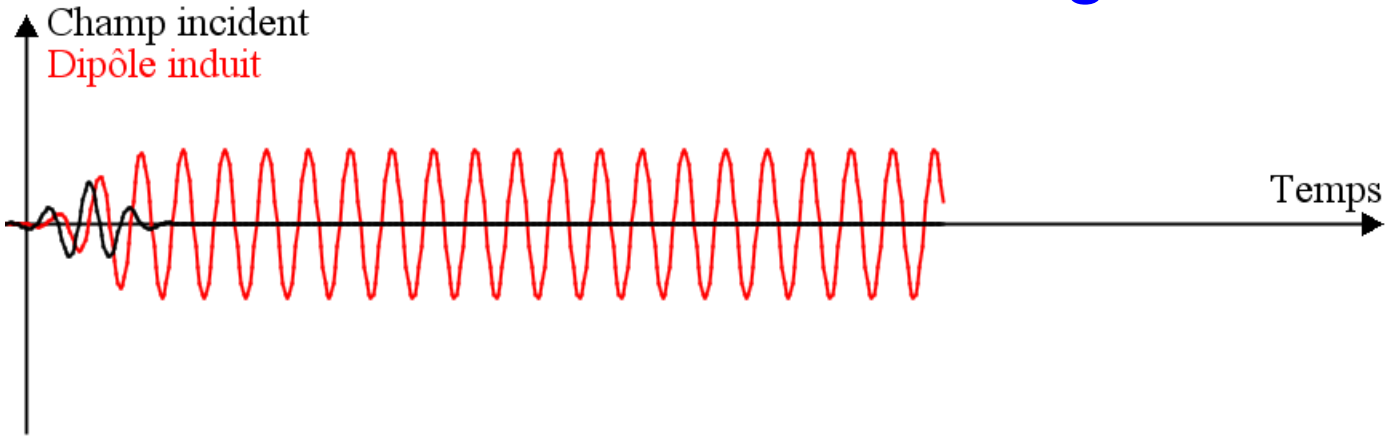
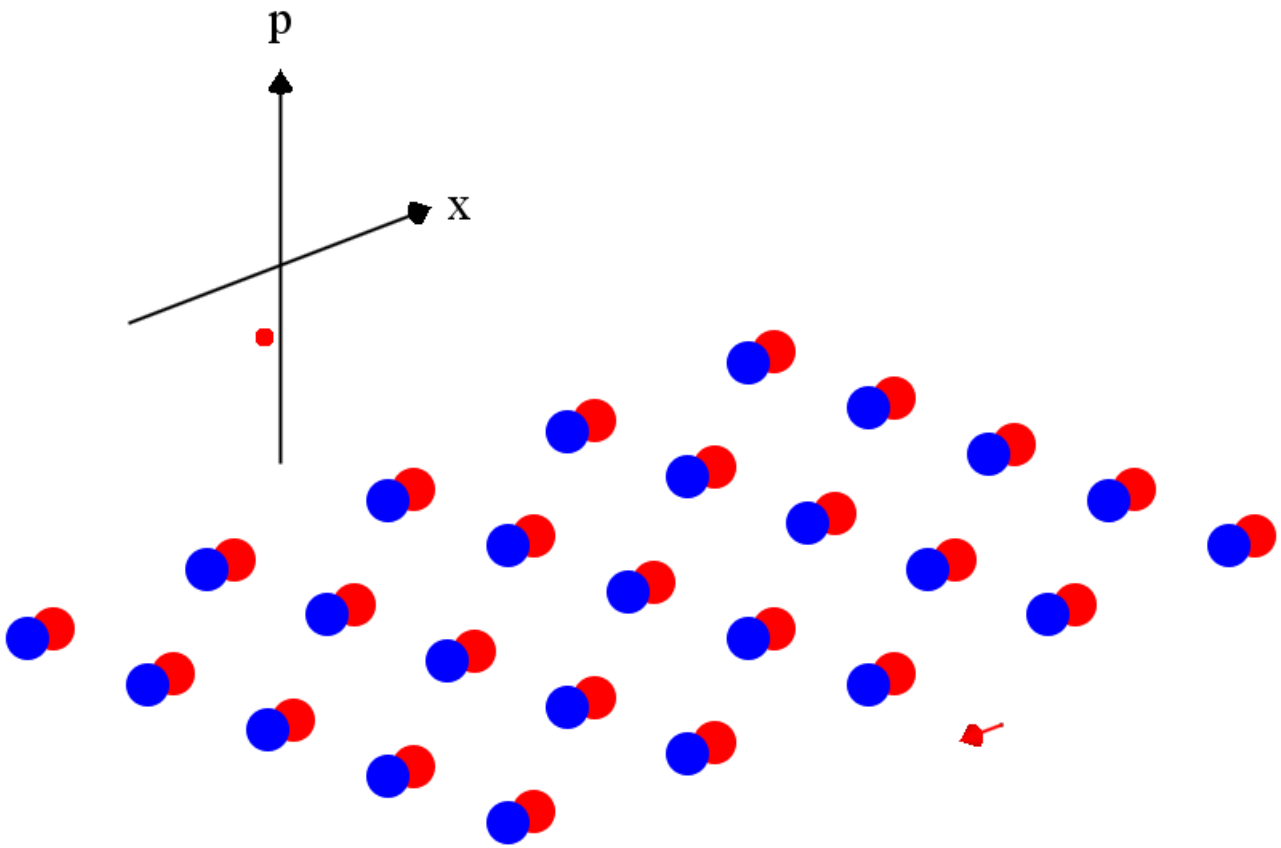
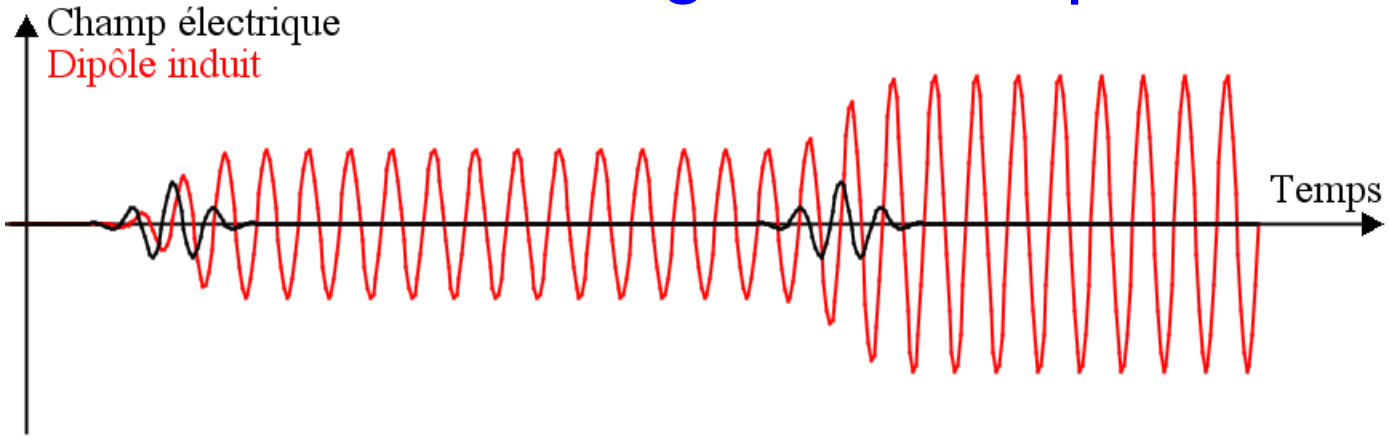
1. Coherence
2. Linear spectroscopy with a broadband source
3. Pump-probe spectroscopy
4. Principle of Multidimensional spectroscopy
5. 2DIR spectroscopy : a few examples

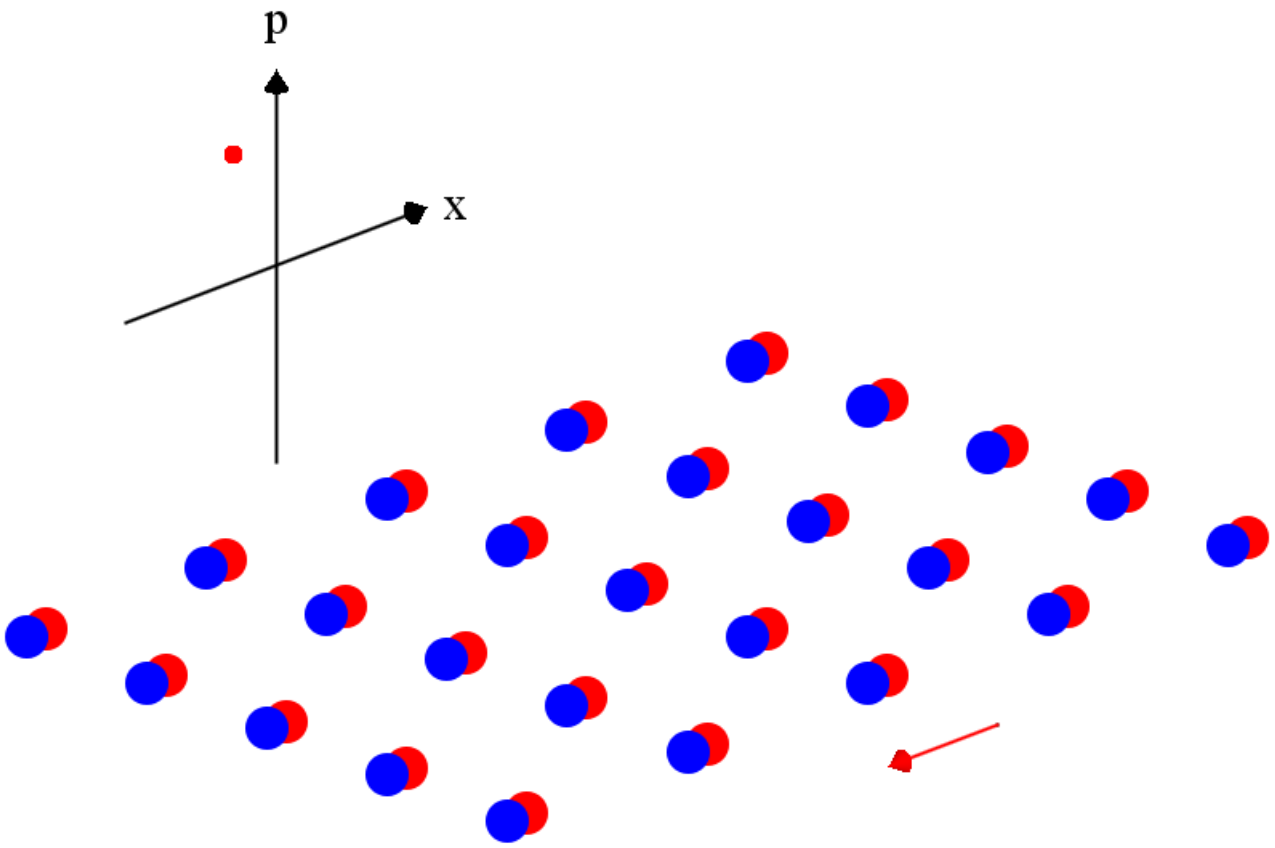
Coherent regime



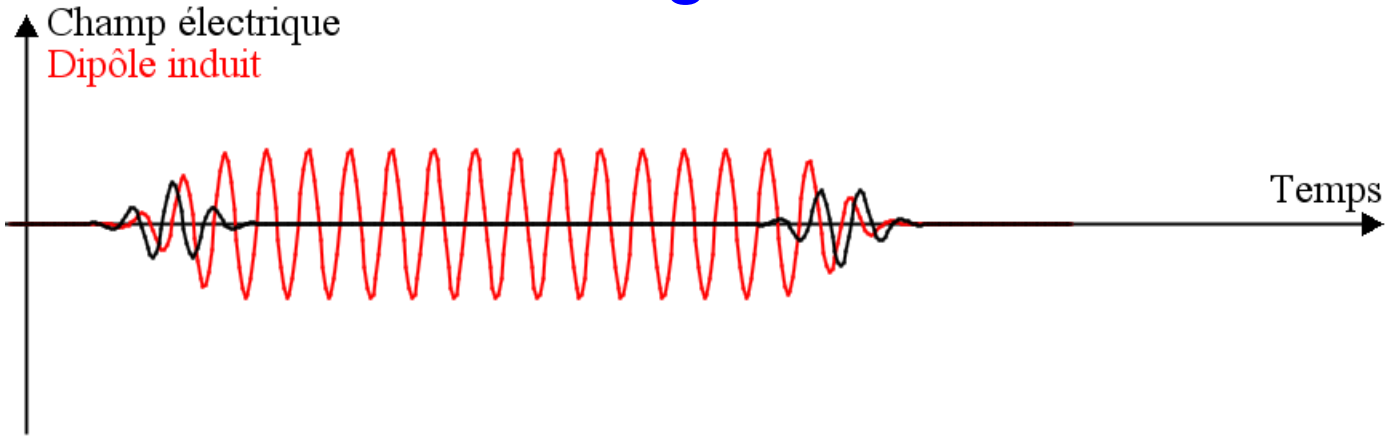


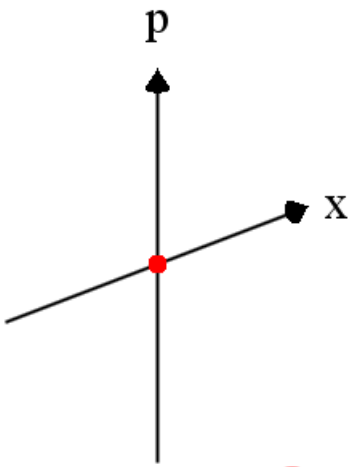
Coherent regime : two-pulse sequence

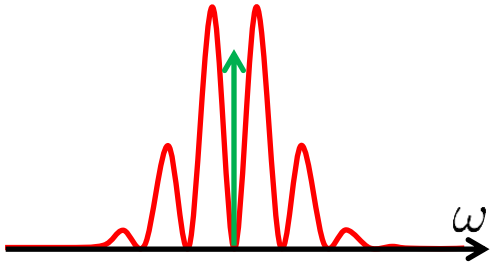


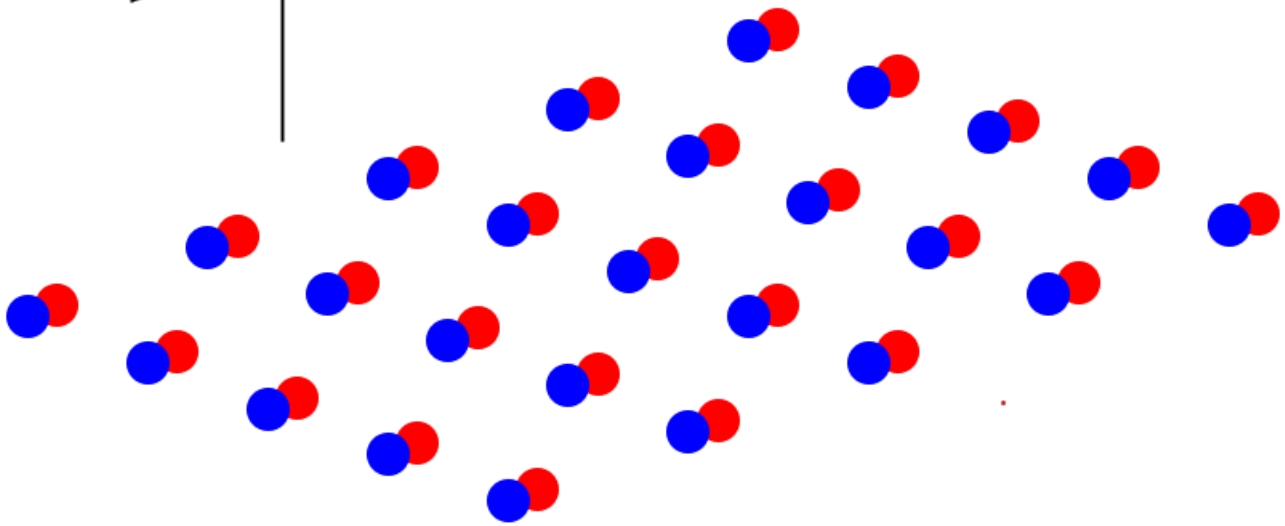


Coherent regime : two π-shifted pulses

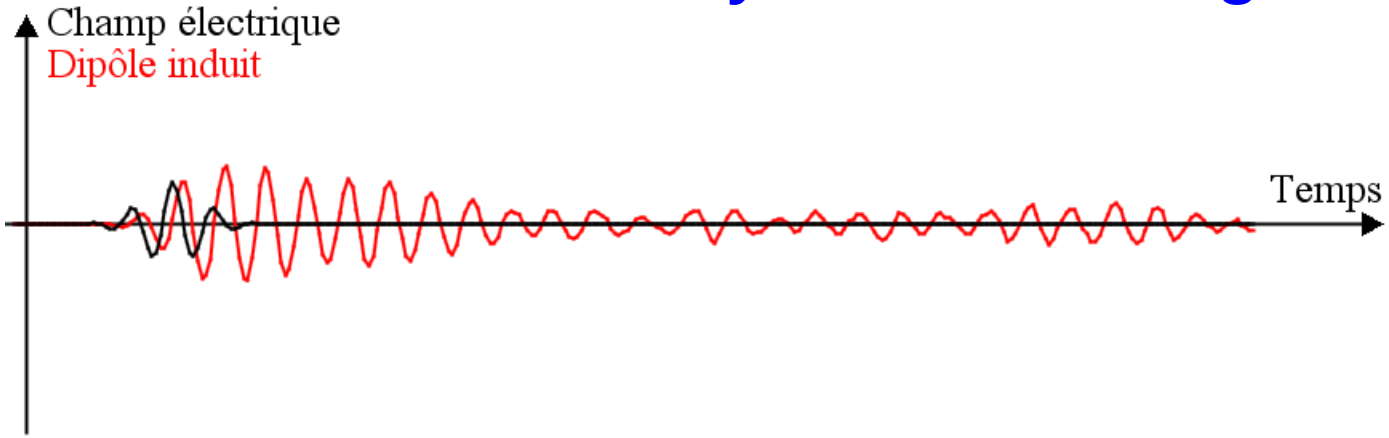


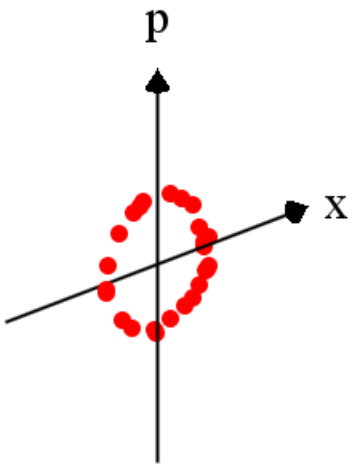


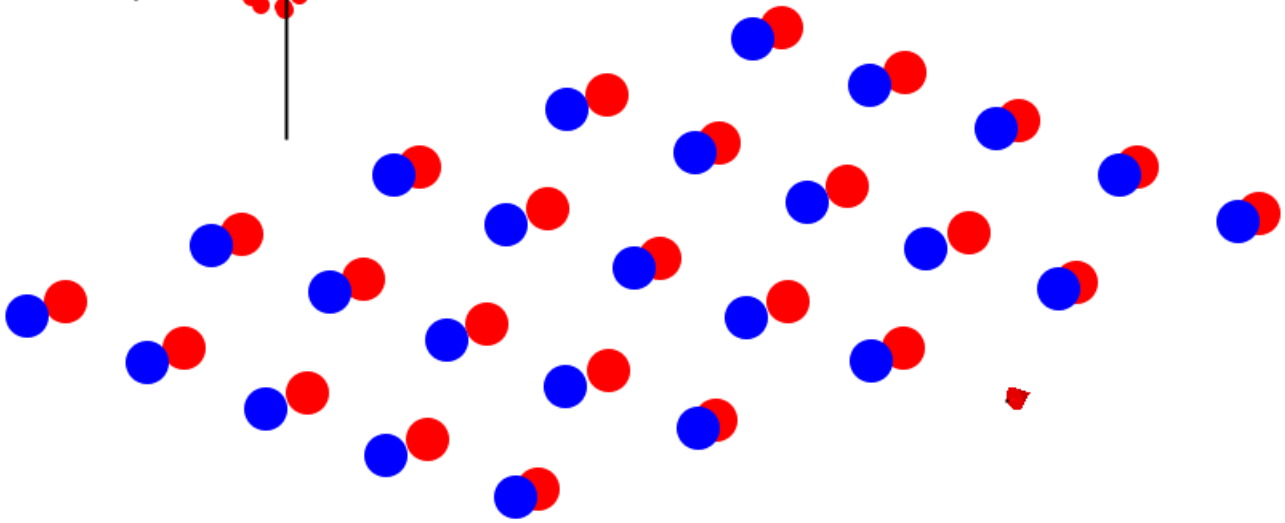




Partially-coherent regime

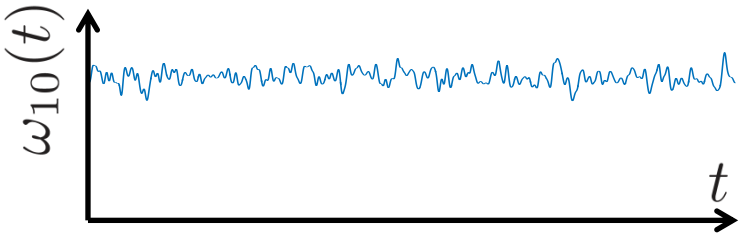




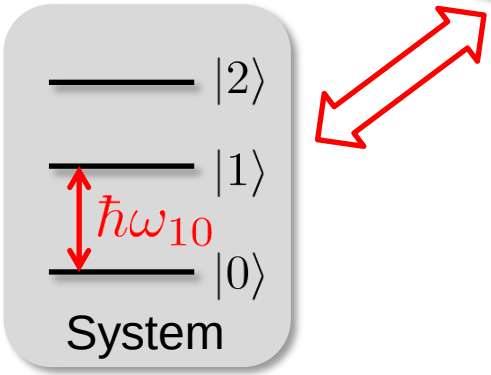


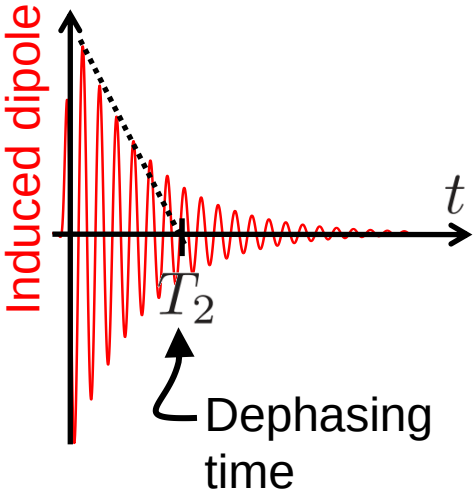
Dephasing processes

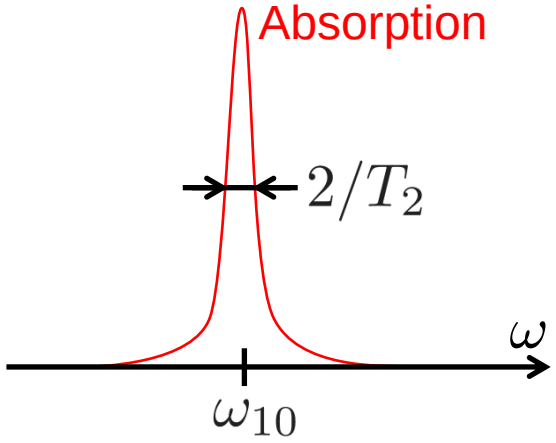
- Homogeneous broadening



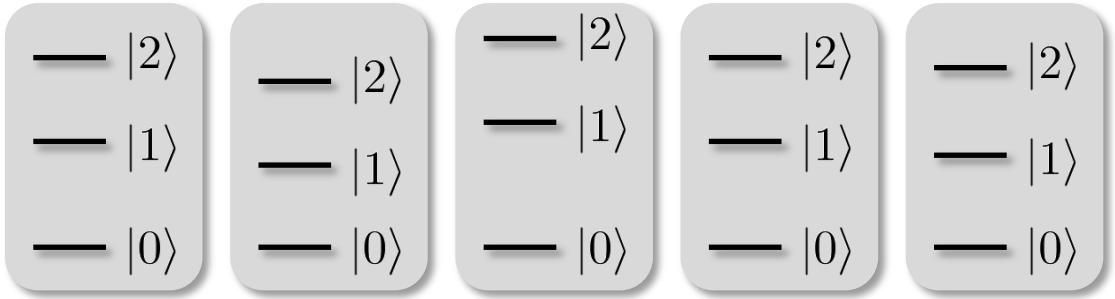
Fluctuating environment

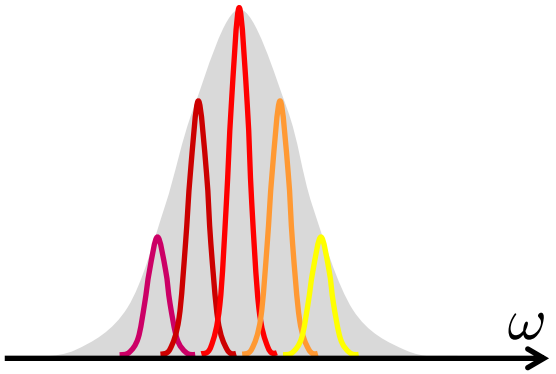




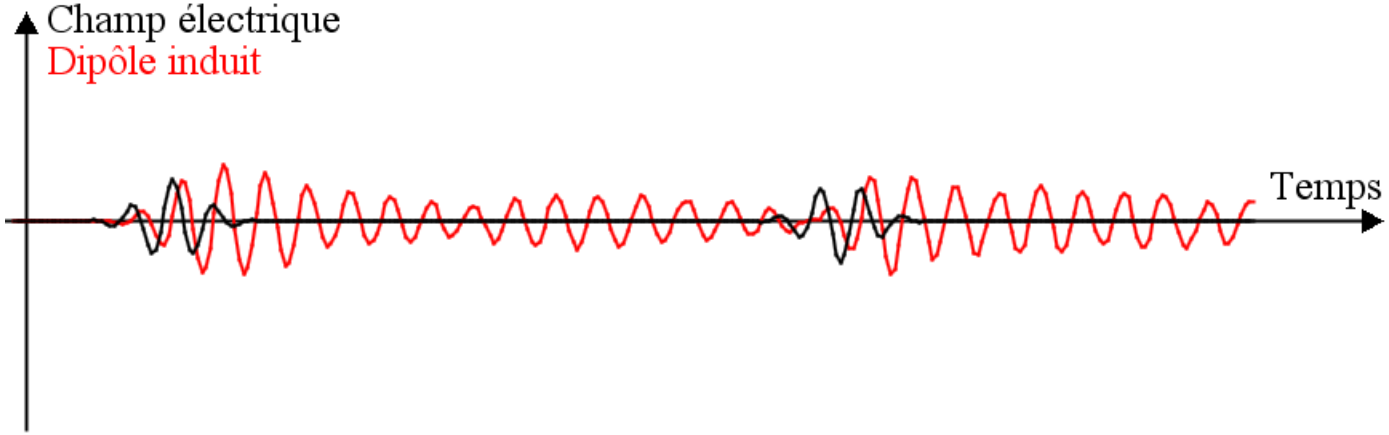


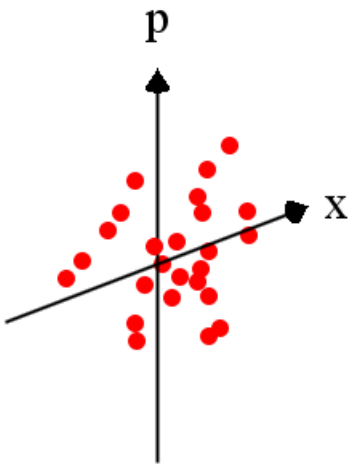
- Inhomogeneous broadening

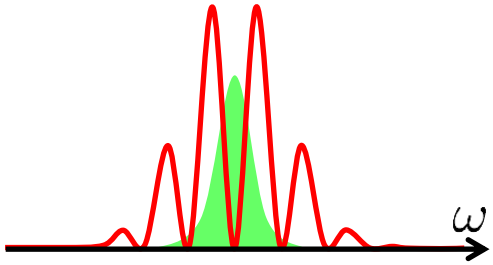


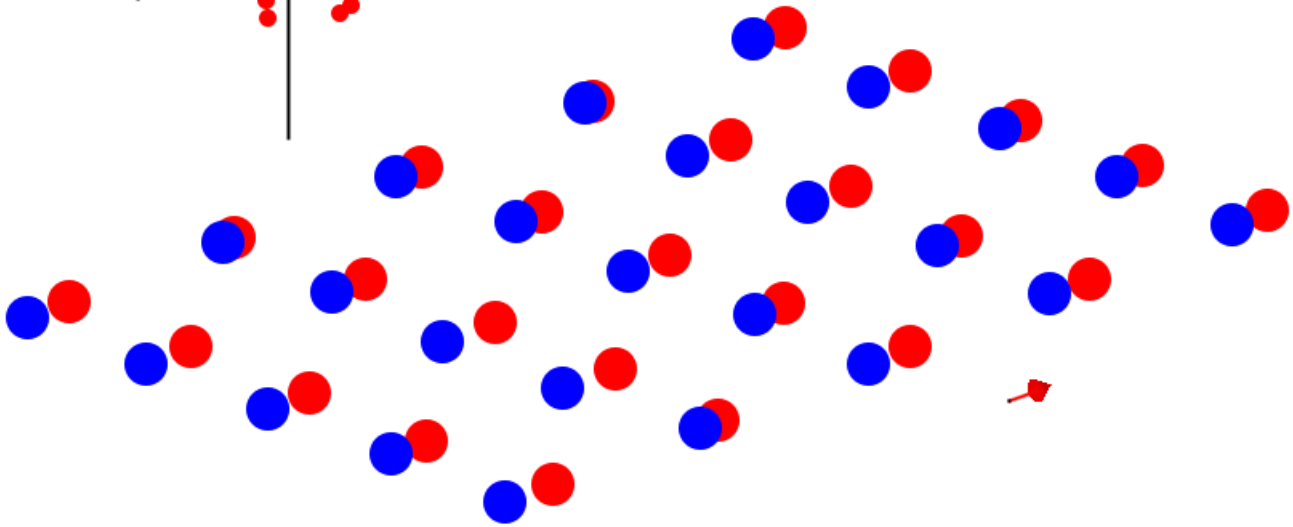


Partially-coherent regime : two π-shifted pulses









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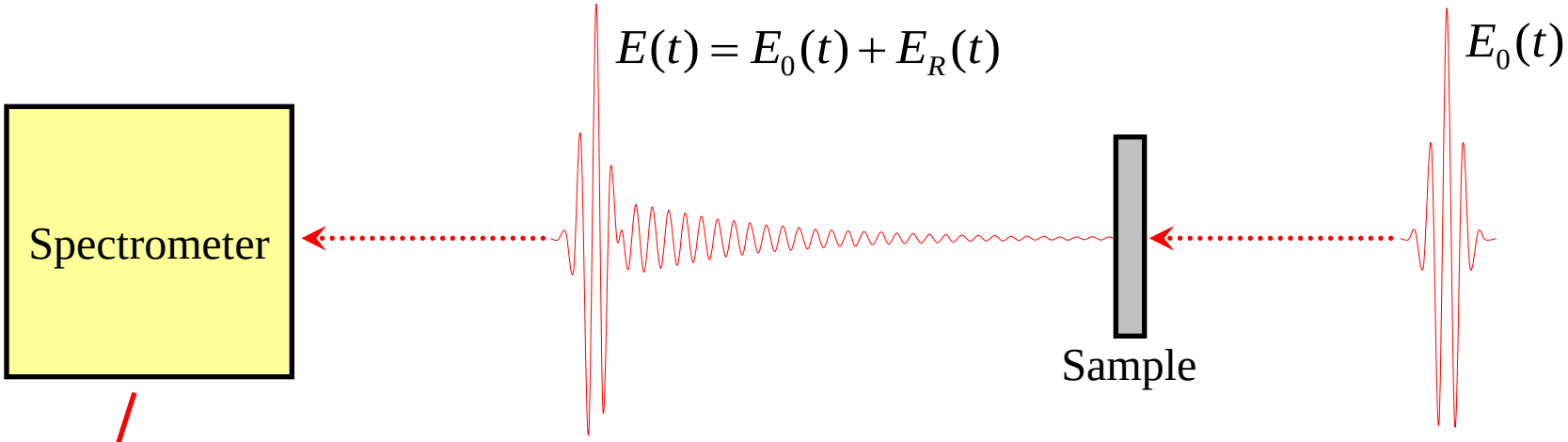
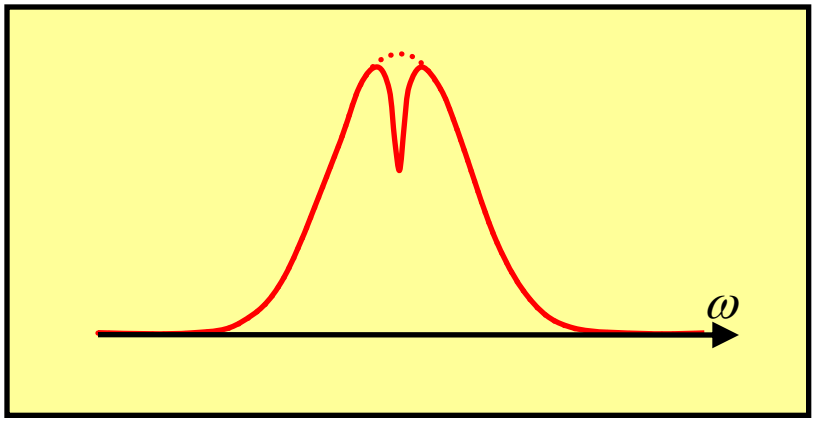
Frequency-domain measurement after impulsive excitation

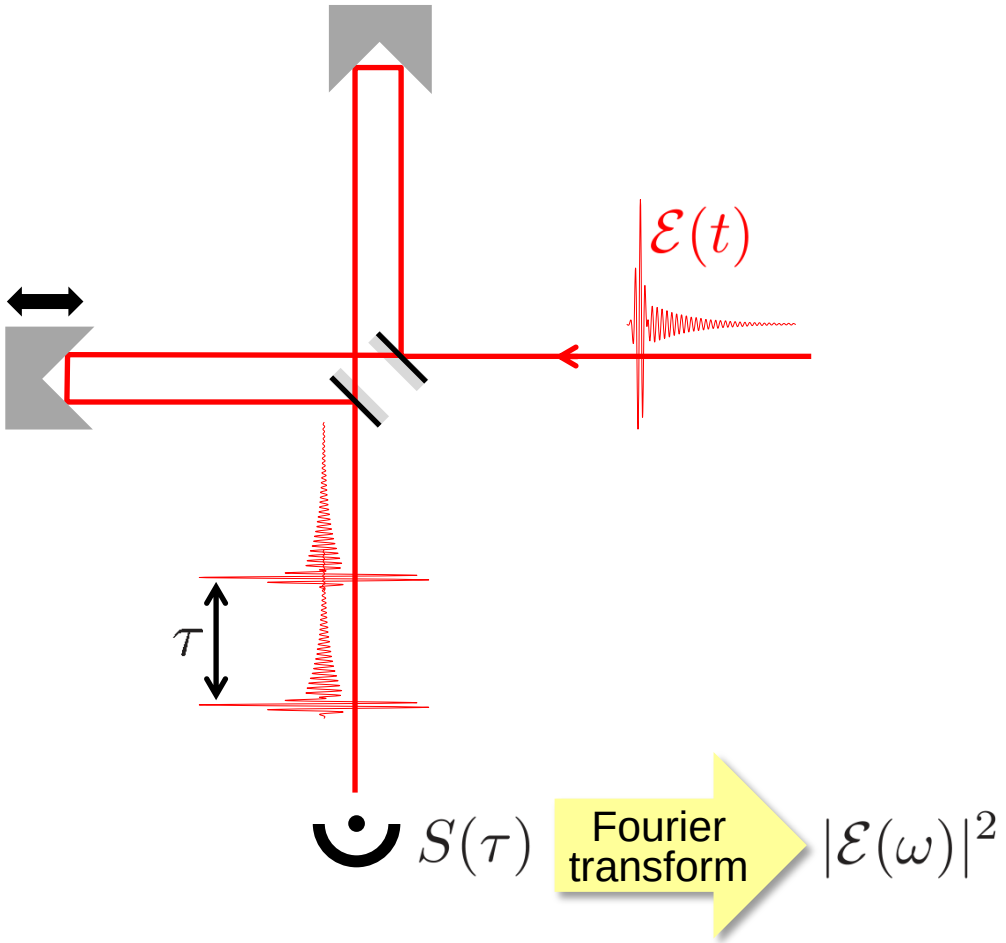
Pulse duration shorter than dephasing time T_2



$$|E(\omega)|^2 = |E_0(\omega) + E_R(\omega)|^2 \approx |E_0(\omega)|^2 + 2\,\mathrm{Re}\,E_0^*(\omega)E_R(\omega)$$



Fourier-transform spectroscopy

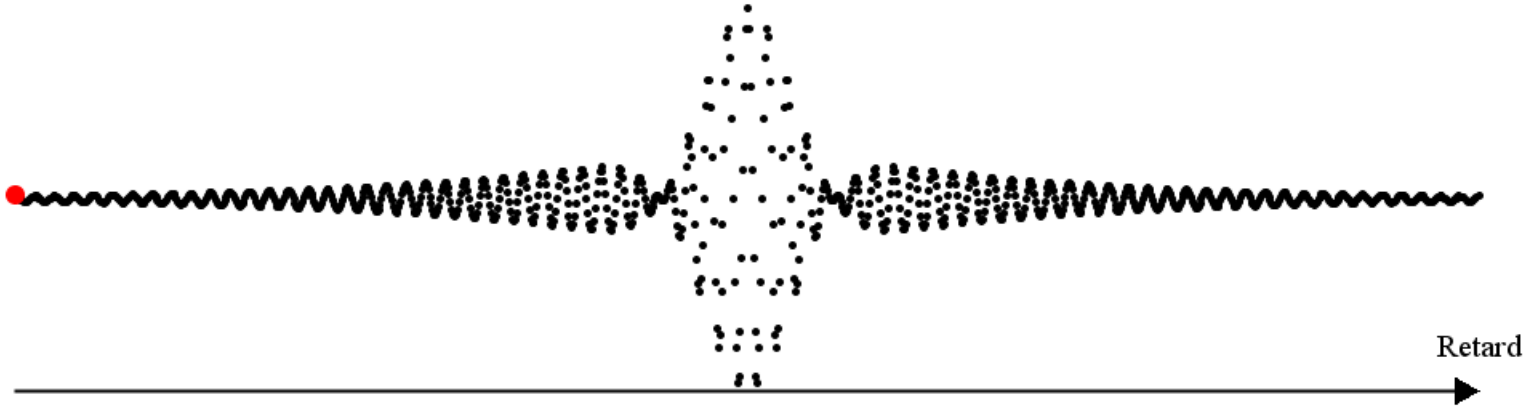


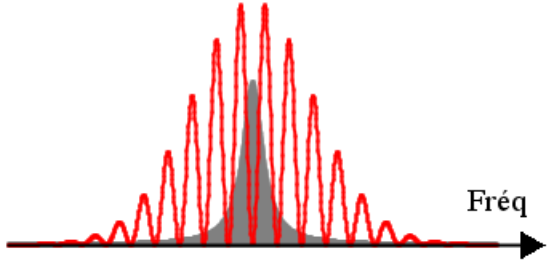
$$S(\tau) = \int |\mathcal{E}_{\rm tot}(\omega)|^2 \frac{d\omega}{2\pi} = \int |\mathcal{E}(\omega)|^2 (1 + \cos\omega\tau) \frac{d\omega}{2\pi}$$

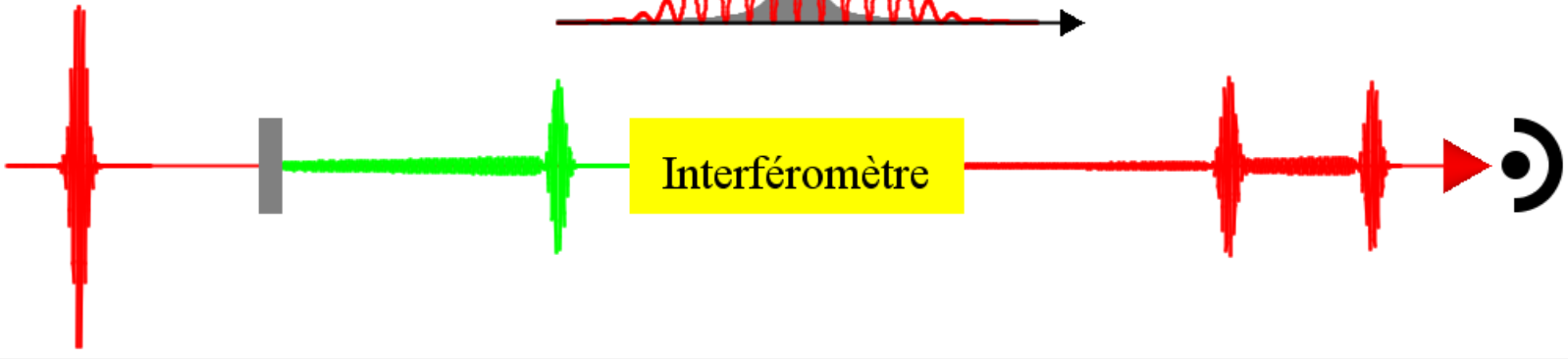
P. R. Griffiths, J. A. de Haseth, *Fourier transform infrared spectrometry*, Chemical Analysis **83** (1986)

Fourier transform spectroscopy

sample before the interferometer

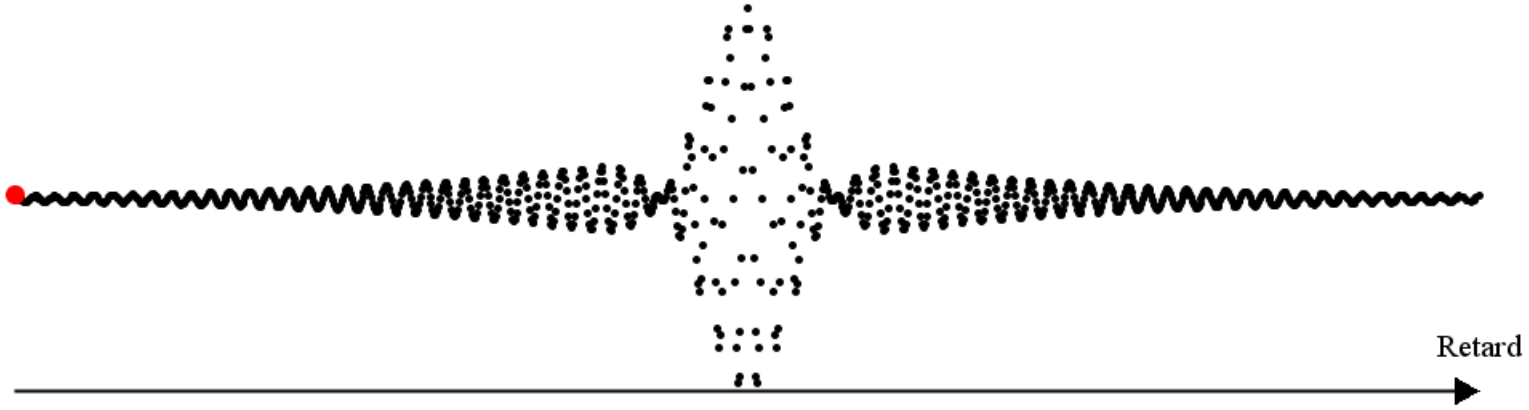


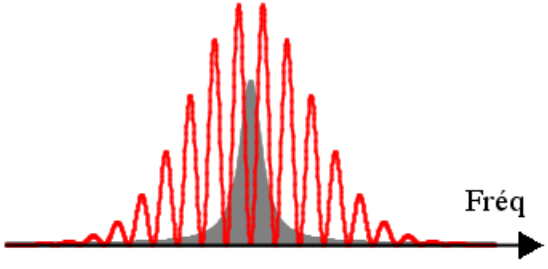


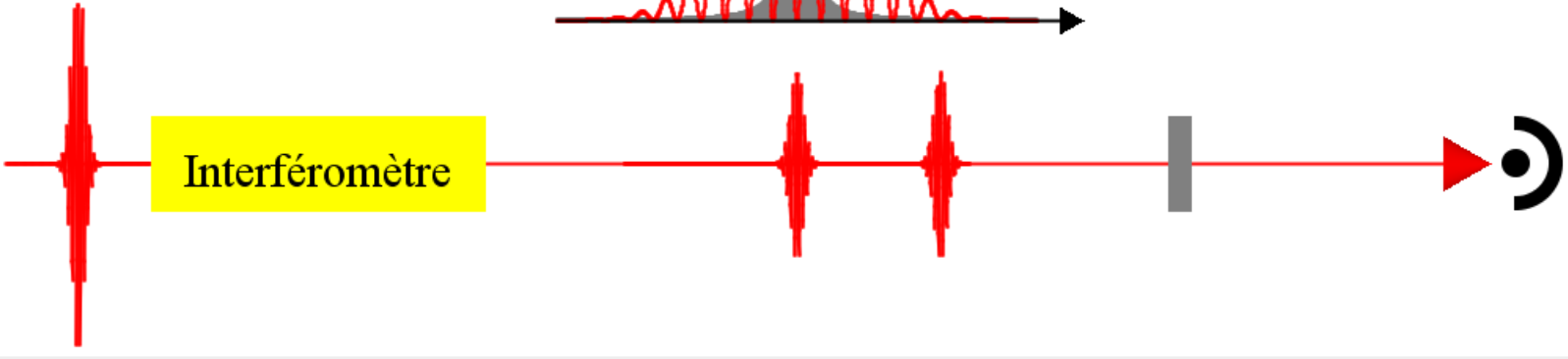


Fourier transform spectroscopy

sample after the interferometer

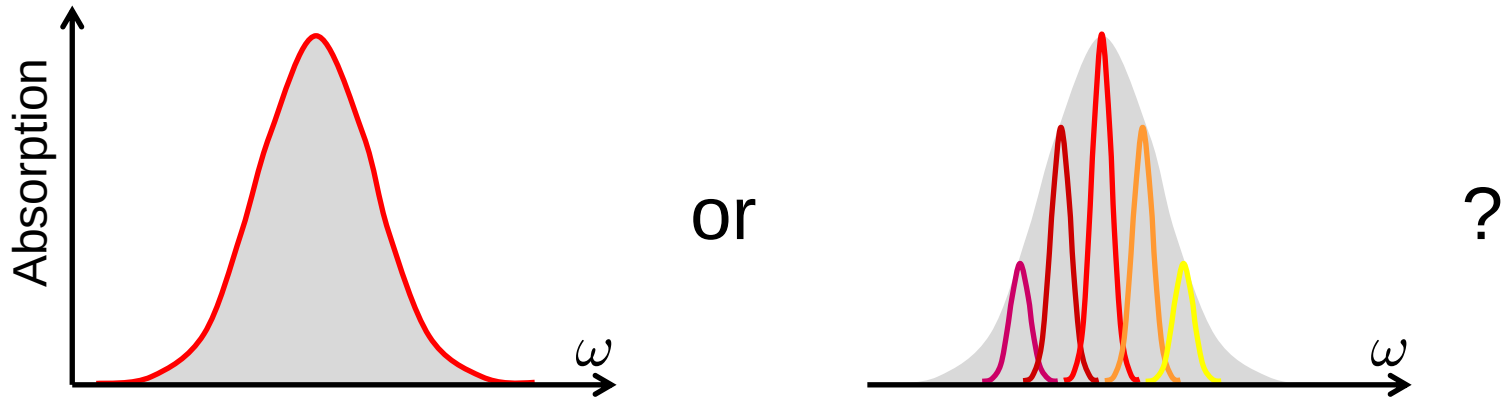




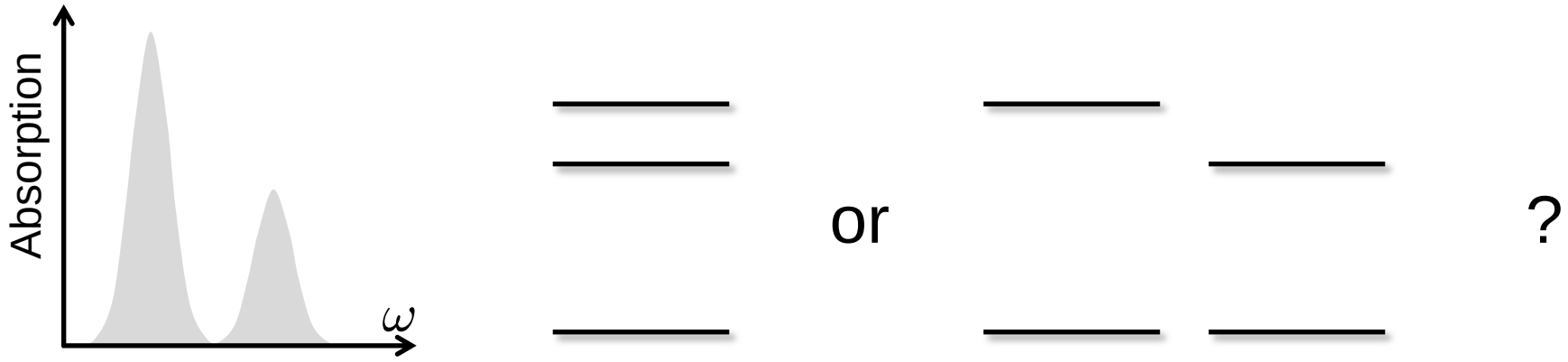


Some limits of linear spectroscopy

✓ Failure to distinguish between homogeneous or inhomogeneous broadening.



✓ Failure to distinguish between a single coupled system or two independent systems.



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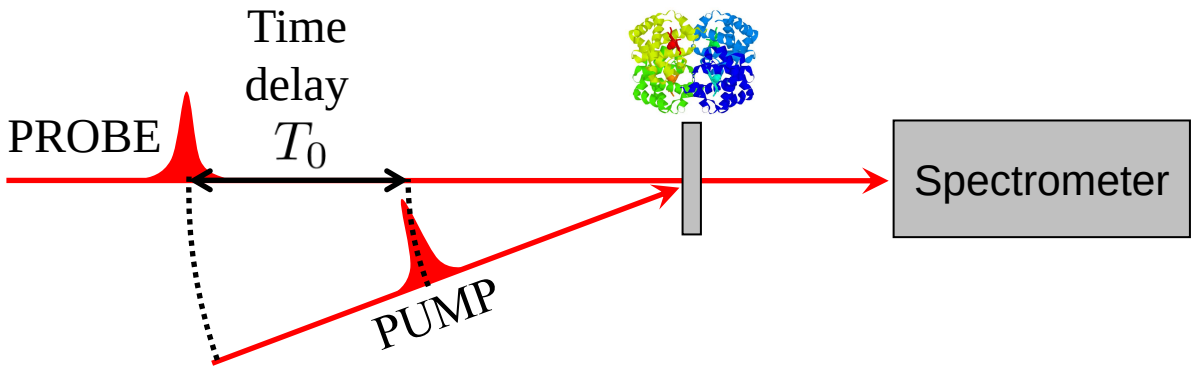
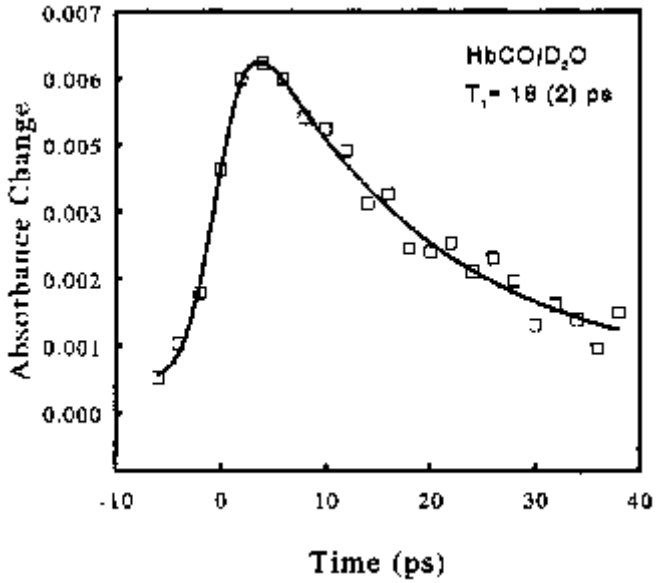
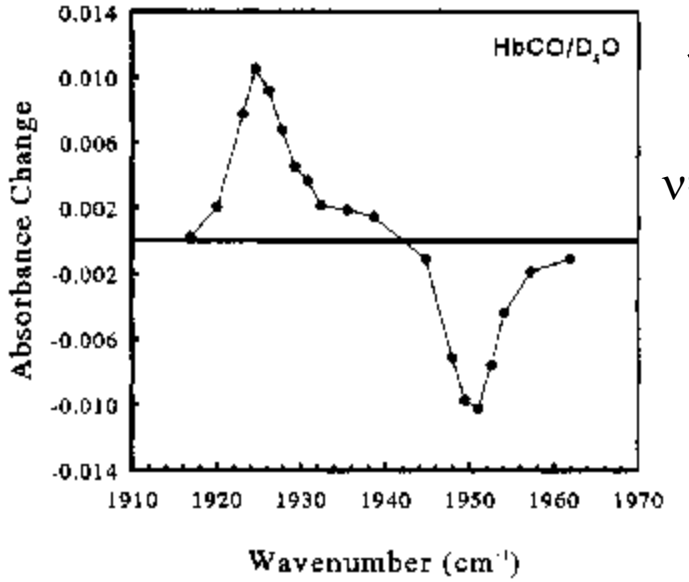
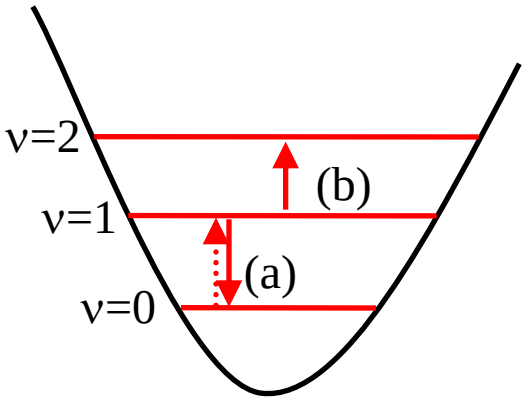
Spectrally-resolved pump-probe spectroscopy



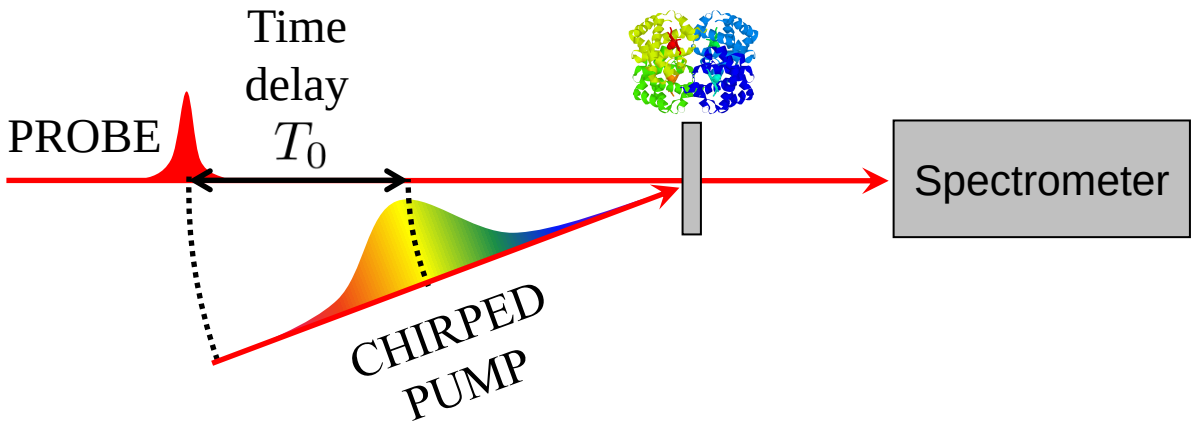


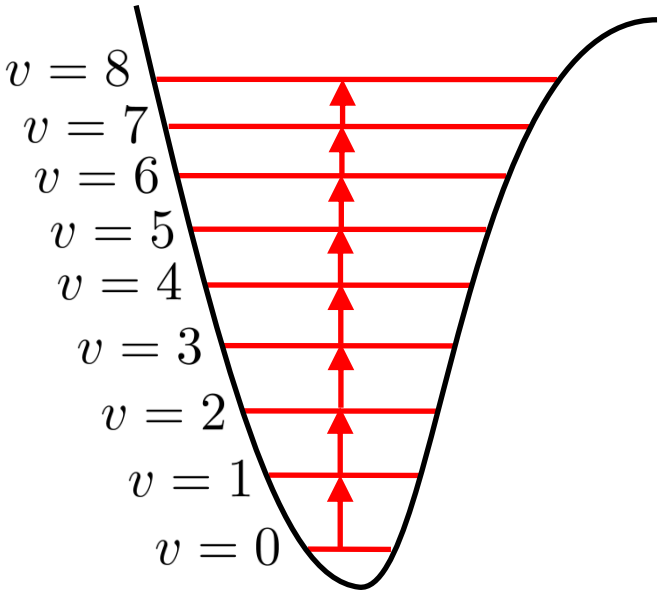


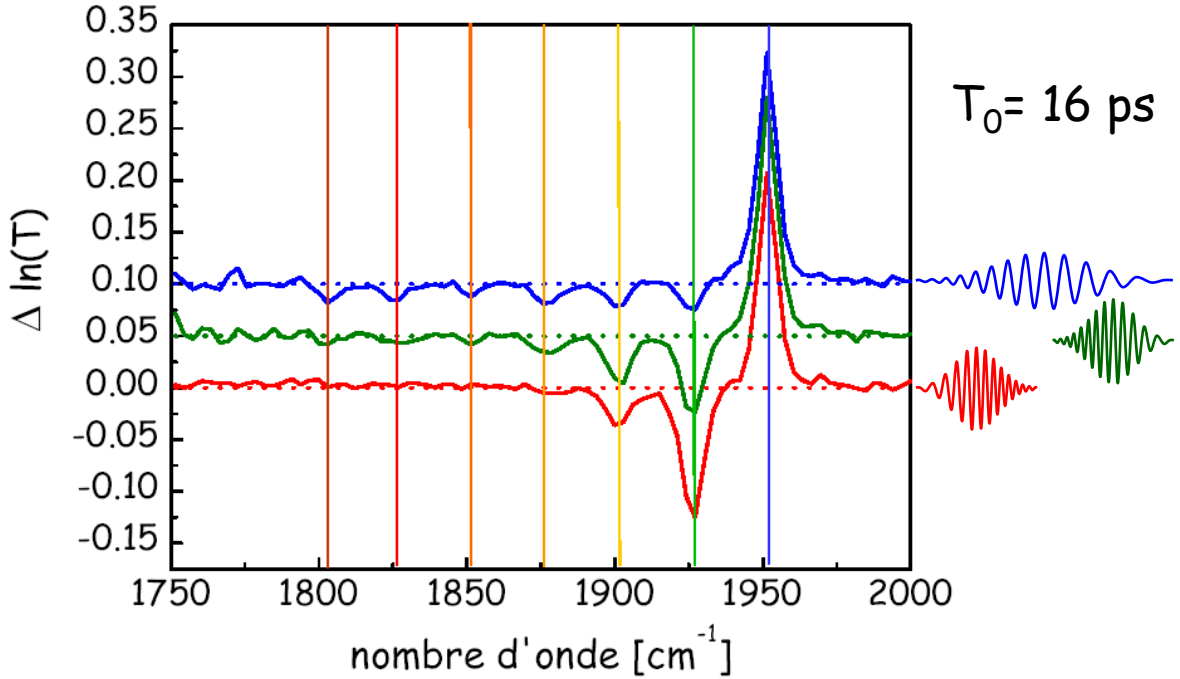


J.C. Owrutsky, M. Li, B. Locke et R.M. Hochstrasser, J. Phys. Chem. **99**, 4842 (1995).

Vibrational ladder climbing in HbCO







C. Ventalon, J.M. Fraser, M.H. Vos, A. Alexandrou, J.L. Martin, M. Joffre, PNAS **101**, 13216 (2004)

1. Coherence
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3. Pump-probe spectroscopy
4. Principle of Multidimensional spectroscopy
5. 2DIR spectroscopy : a few examples

Two-dimensional Nuclear Magnetic Resonance

Two-dimensional spectroscopy. Application to nuclear magnetic resonance

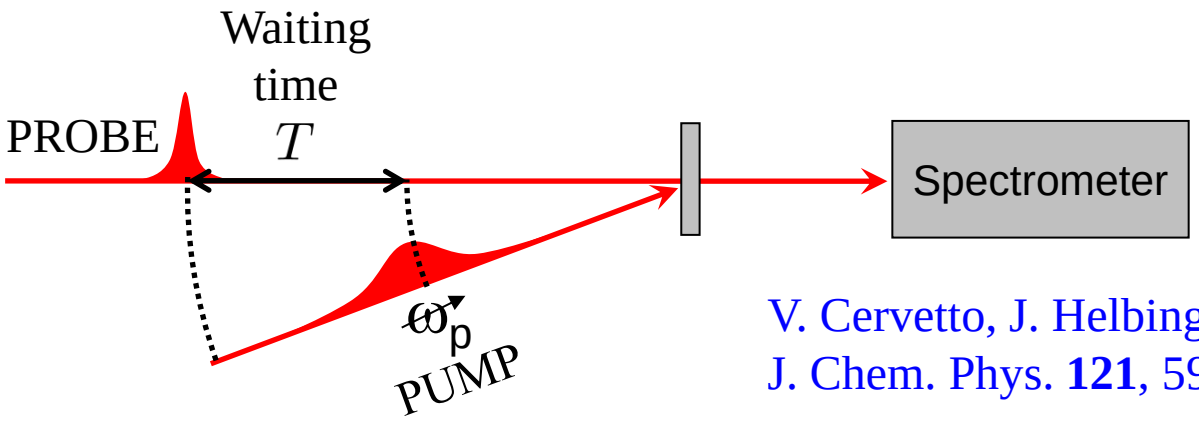
W. P. Aue, E. Bartholdi, and R. R. Ernst
Laboratorium für physikalische Chemie, Eidgenössische Technische Hochschule, 8006 Zürich, Switzerland

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.** »

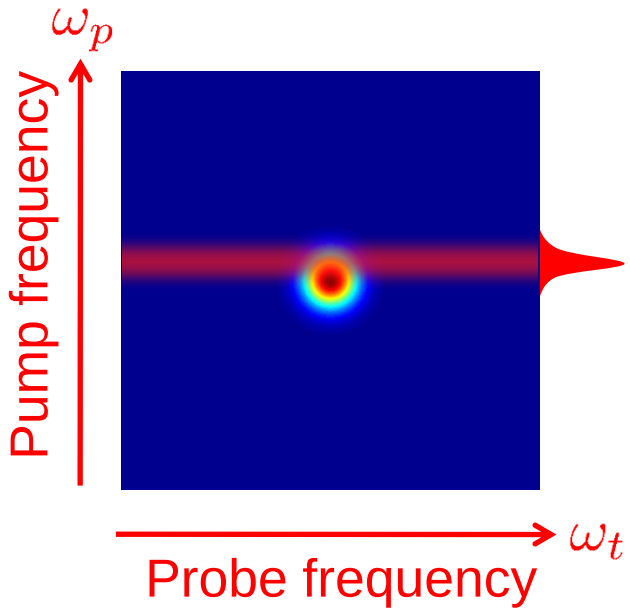
W. P. Aue, E. Bartholdi, R.R. Ernst, J. Chem. Phys. 64, 2229 (1976)

2D spectroscopy in the pump-probe geometry



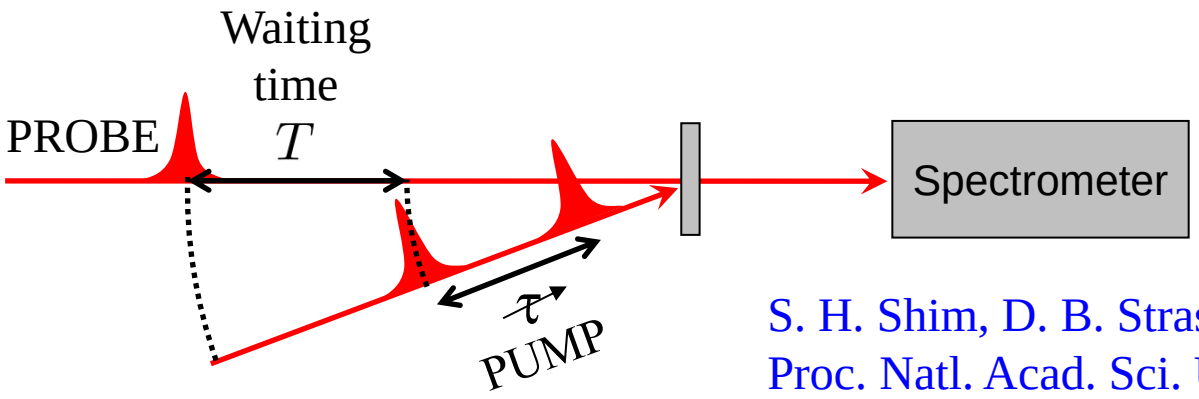
V. Cervetto, J. Helbing, J. Bredenbeck, P. Hamm
J. Chem. Phys. **121**, 5935 (2004)

✓ Frequency space



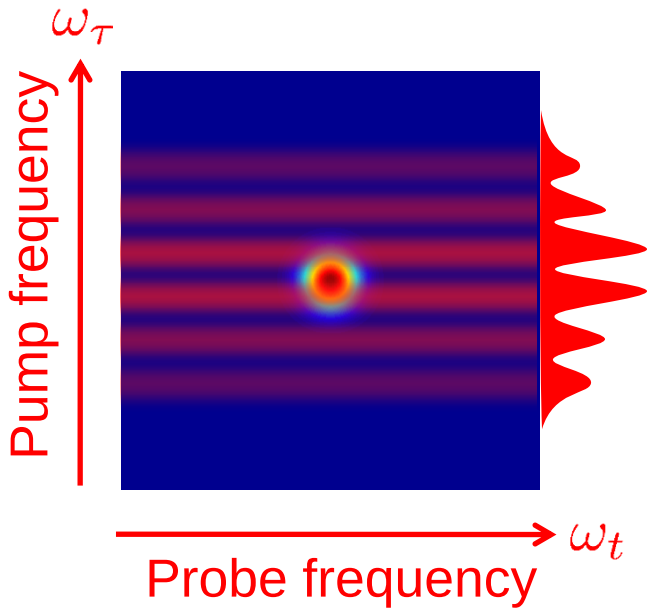
$$S(\omega_t, \omega_p, T)$$

2D spectroscopy in the pump-probe geometry



✓ Fourier space

S. H. Shim, D. B. Strasfeld, Y. L. Ling, M. T. Zanni
Proc. Natl. Acad. Sci. USA **104**, 14197 (2007)
L.P. DeFlores, R.A. Nicodemus, A. Tokmakoff
Opt. Lett. **32**, 2966 (2007)

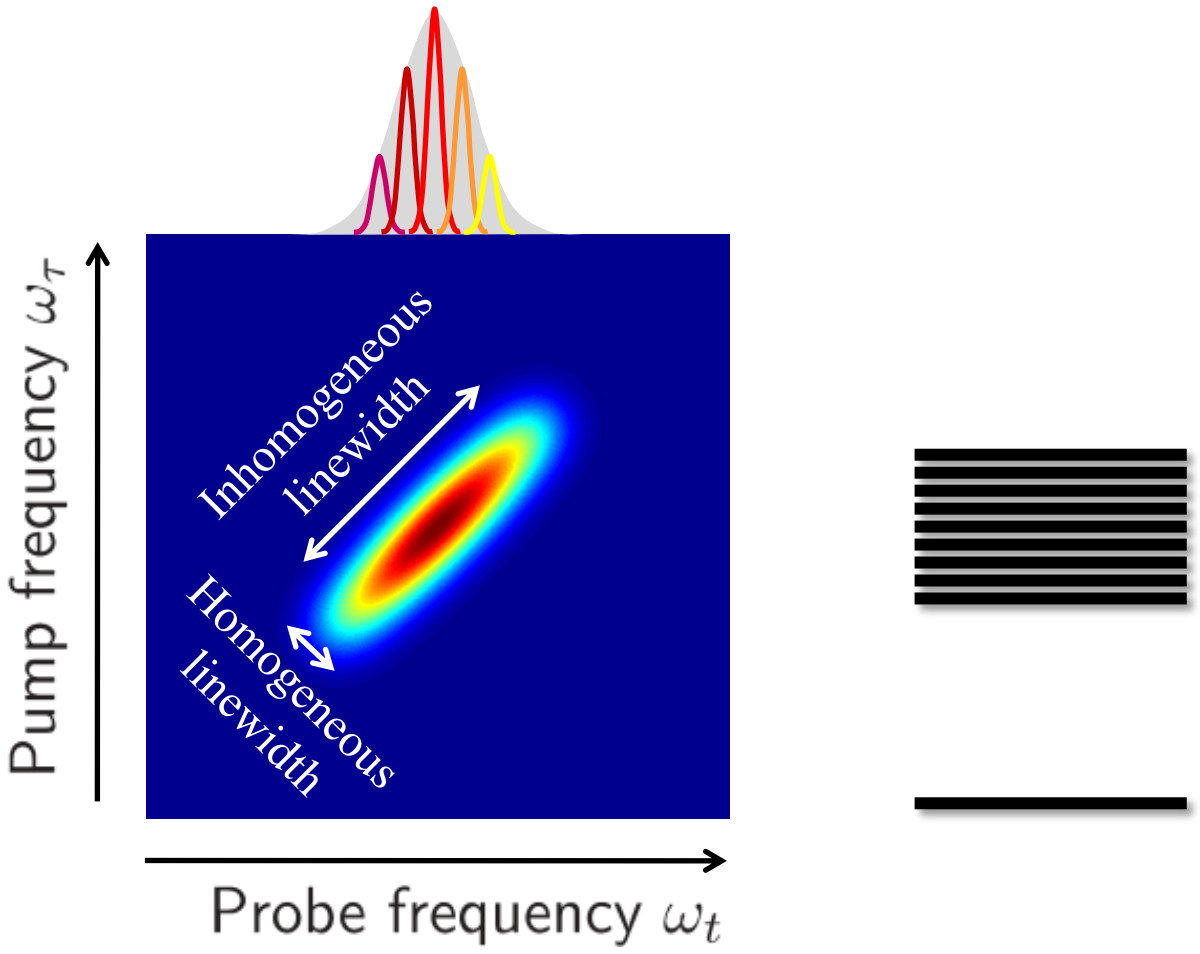


$$S(\omega_t, \tau, T)$$

$$\mathcal{F}$$

$$S(\omega_t, \omega_\tau, T)$$

2D spectrum expected for a 2-level system



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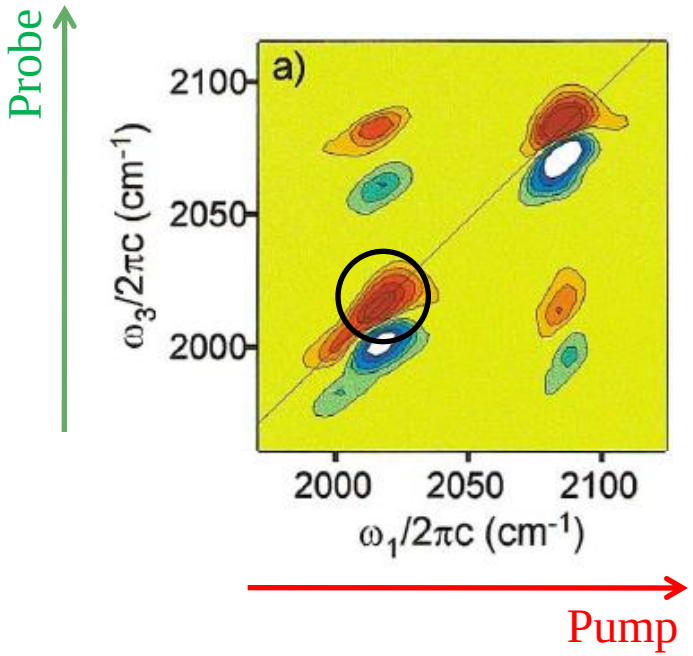
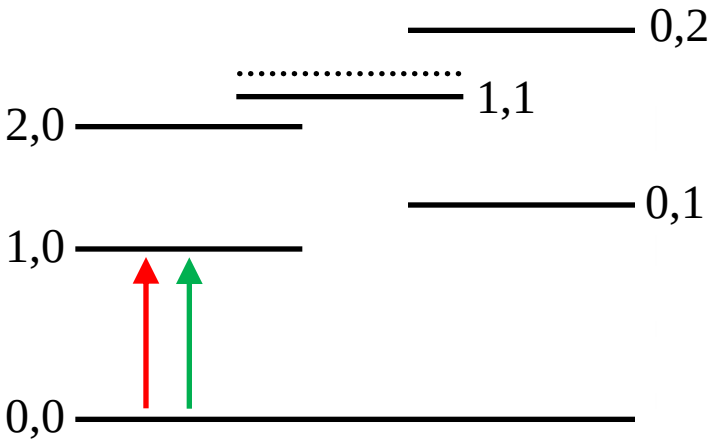
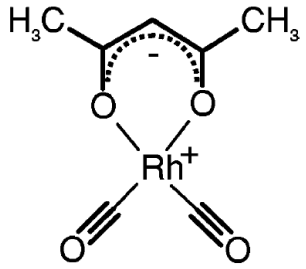
Infrared Two-dimensional Spectroscopy (2DIR)

Example : RDC (acetylacetonato dicarbonyl rhodium(I))





Absorption saturation



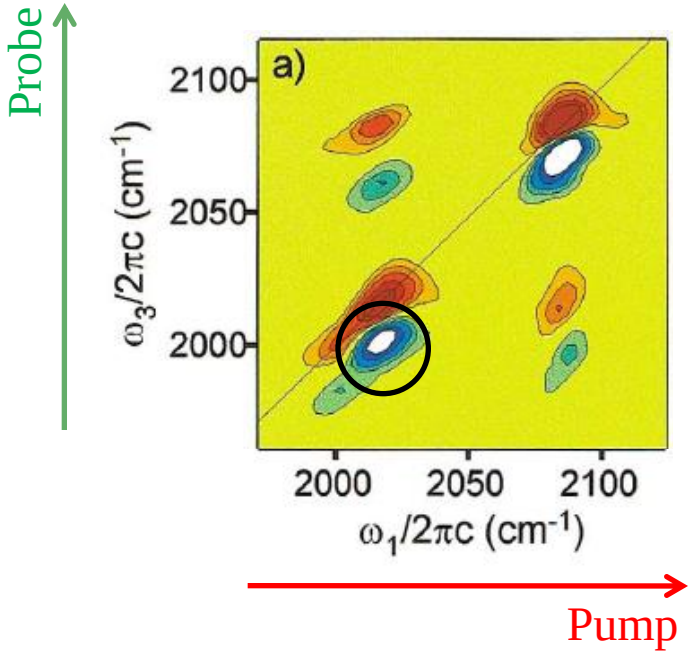
N. Demirdoven, M. Khalil, A. Tokmakoff

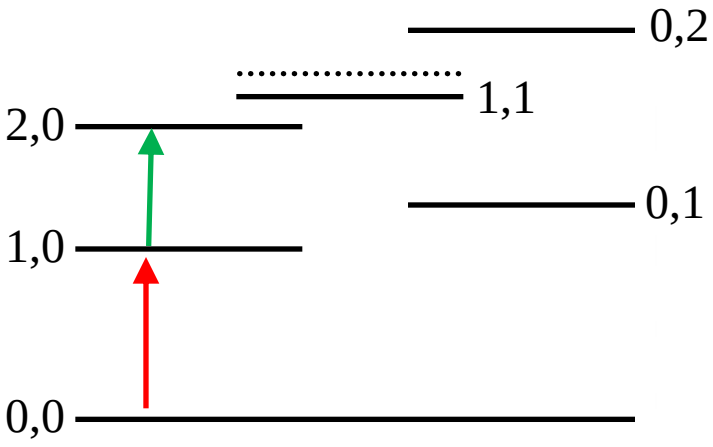
Correlated vibrational dynamics revealed by two-dimensional infrared spectroscopy

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

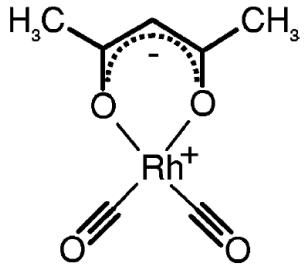
Infrared Two-dimensional Spectroscopy (2DIR)

Example : RDC (acetylacetonato dicarbonyl rhodium(I))





Anharmonicity



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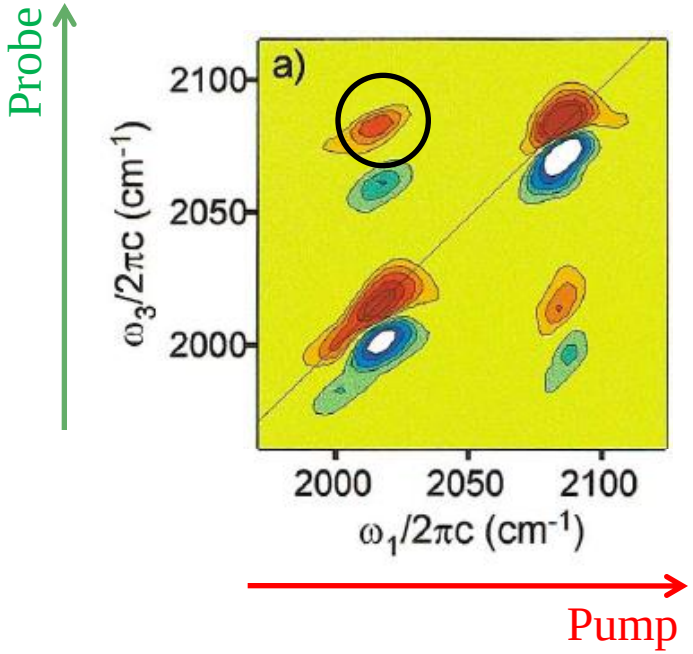

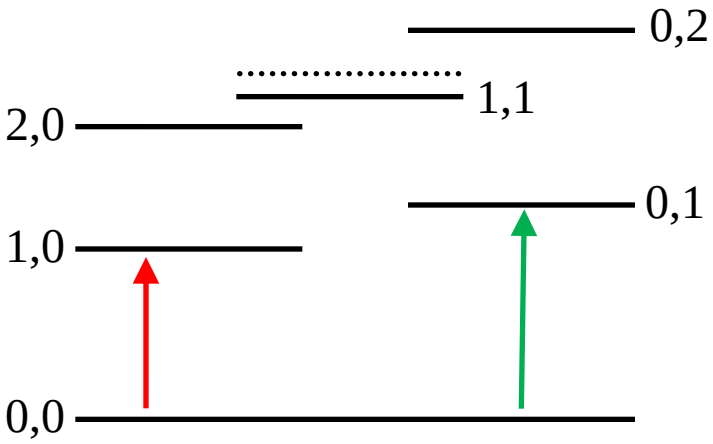

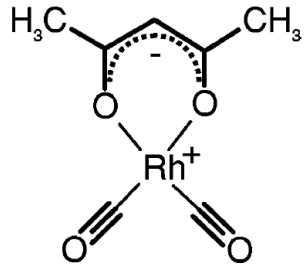

Coupling between two vibrational modes

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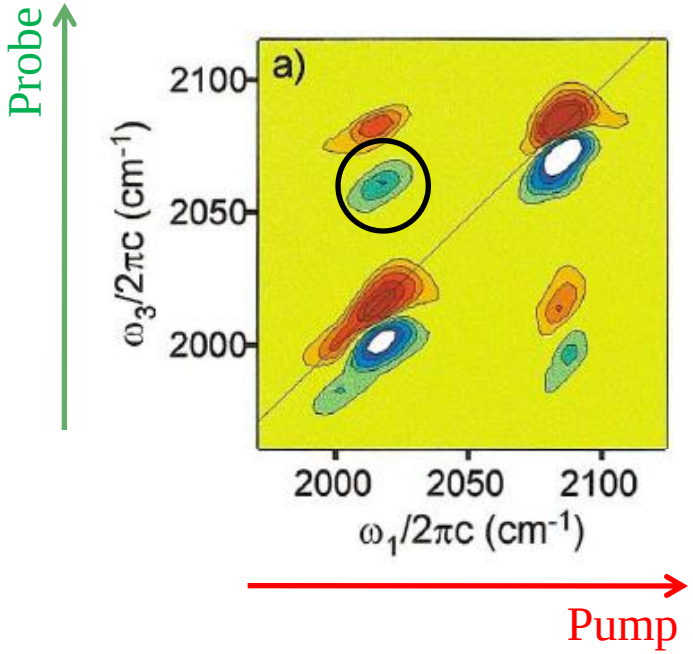
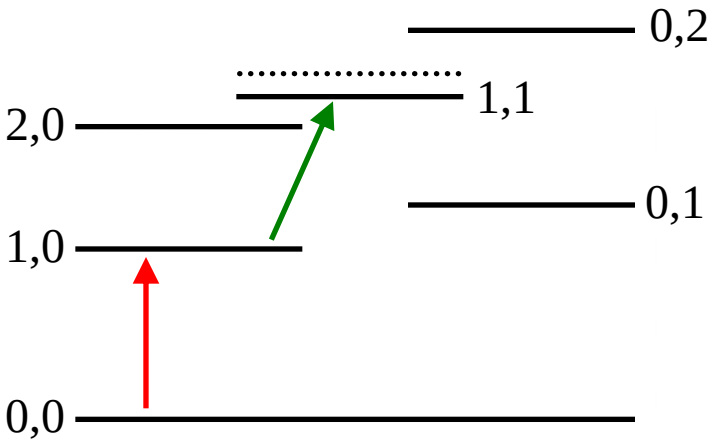
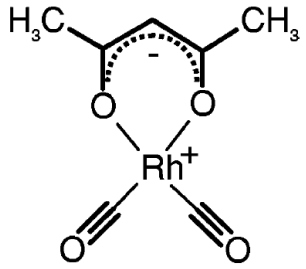




Transitions to combination bands



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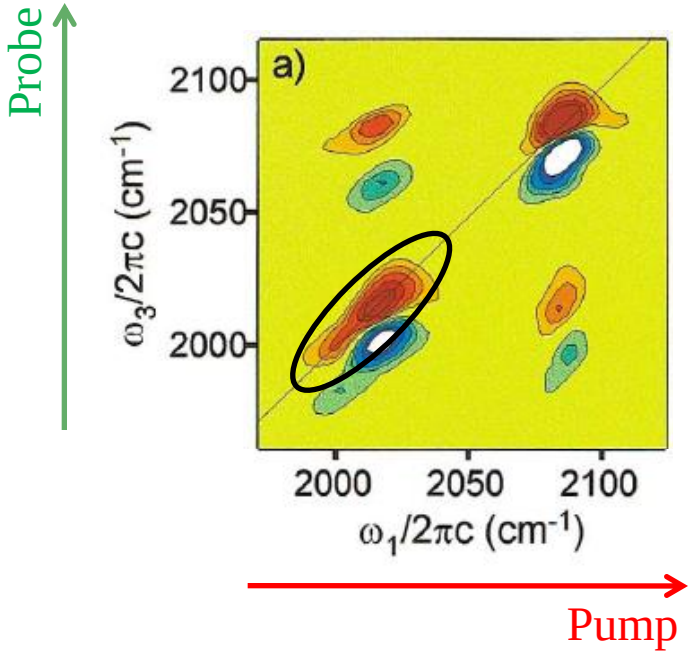
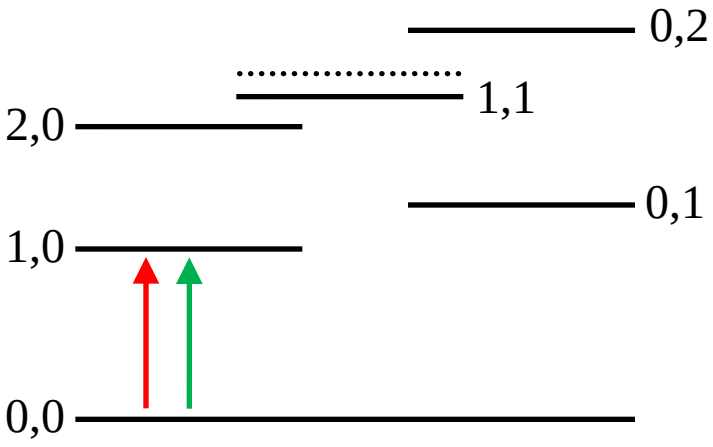
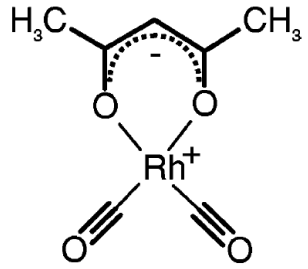




Inhomogeneity



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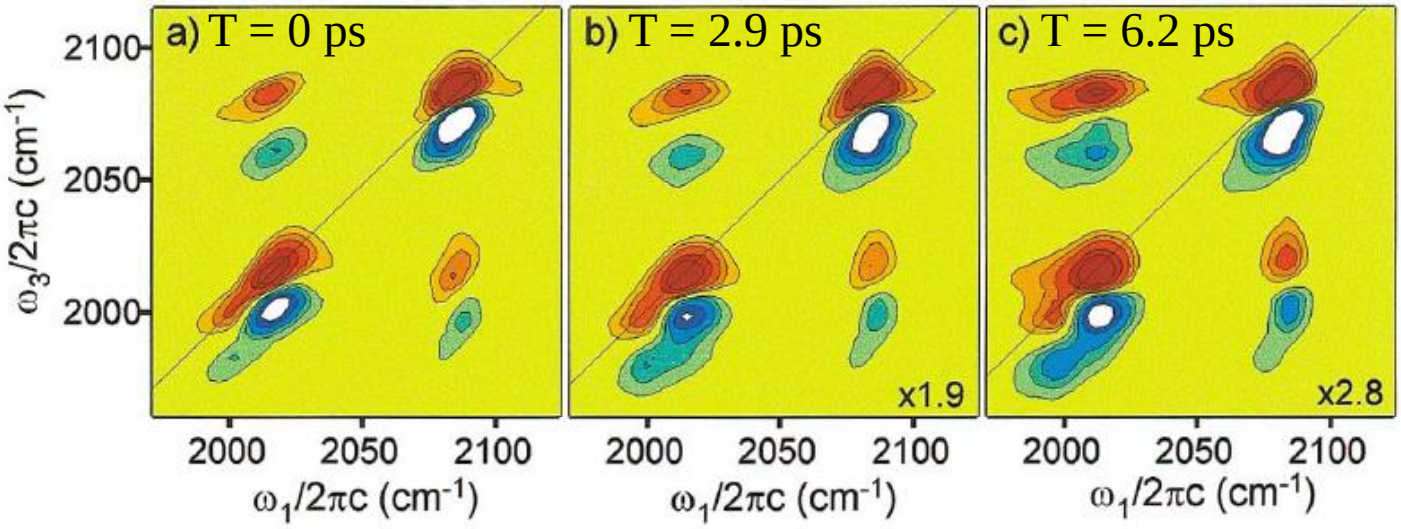

Evolution as a fonction of waiting time T

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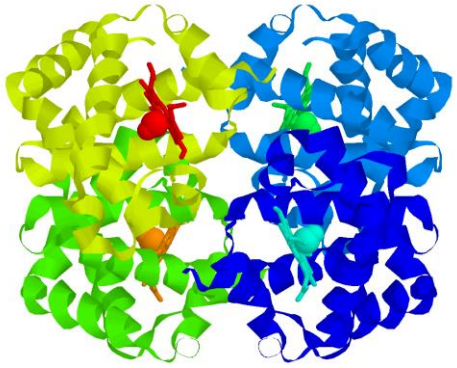
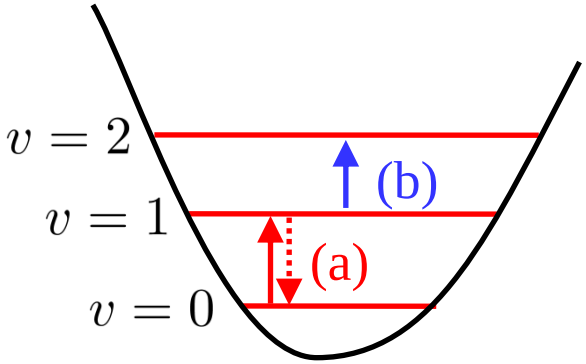
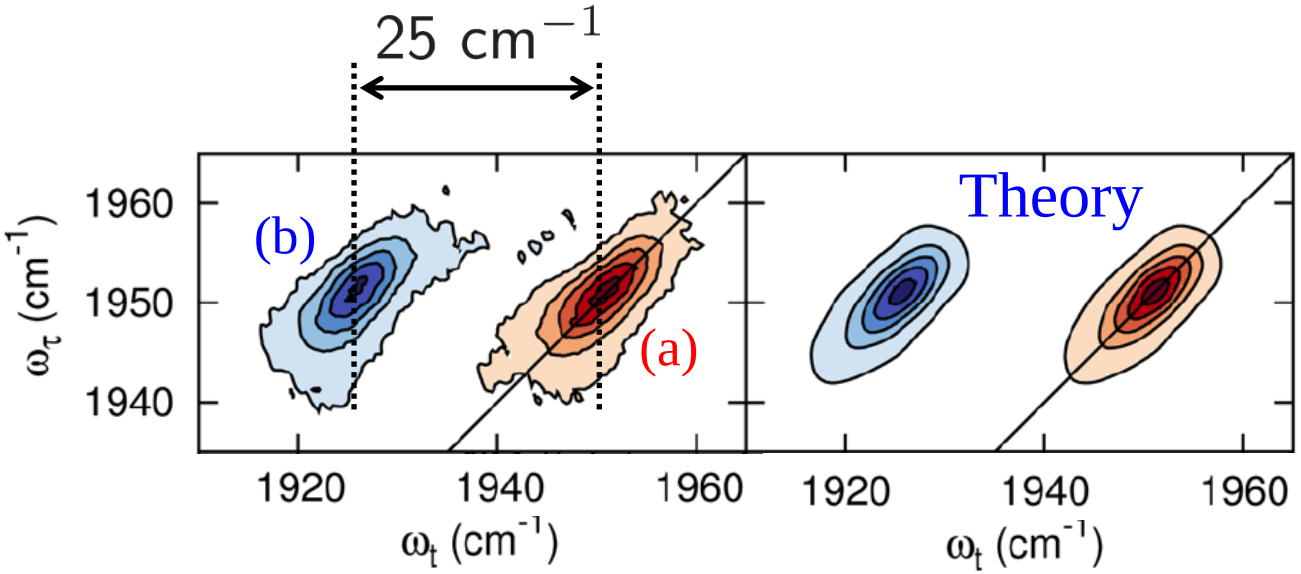
2DIR spectroscopy in carboxy-hemoglobin (HbCO)

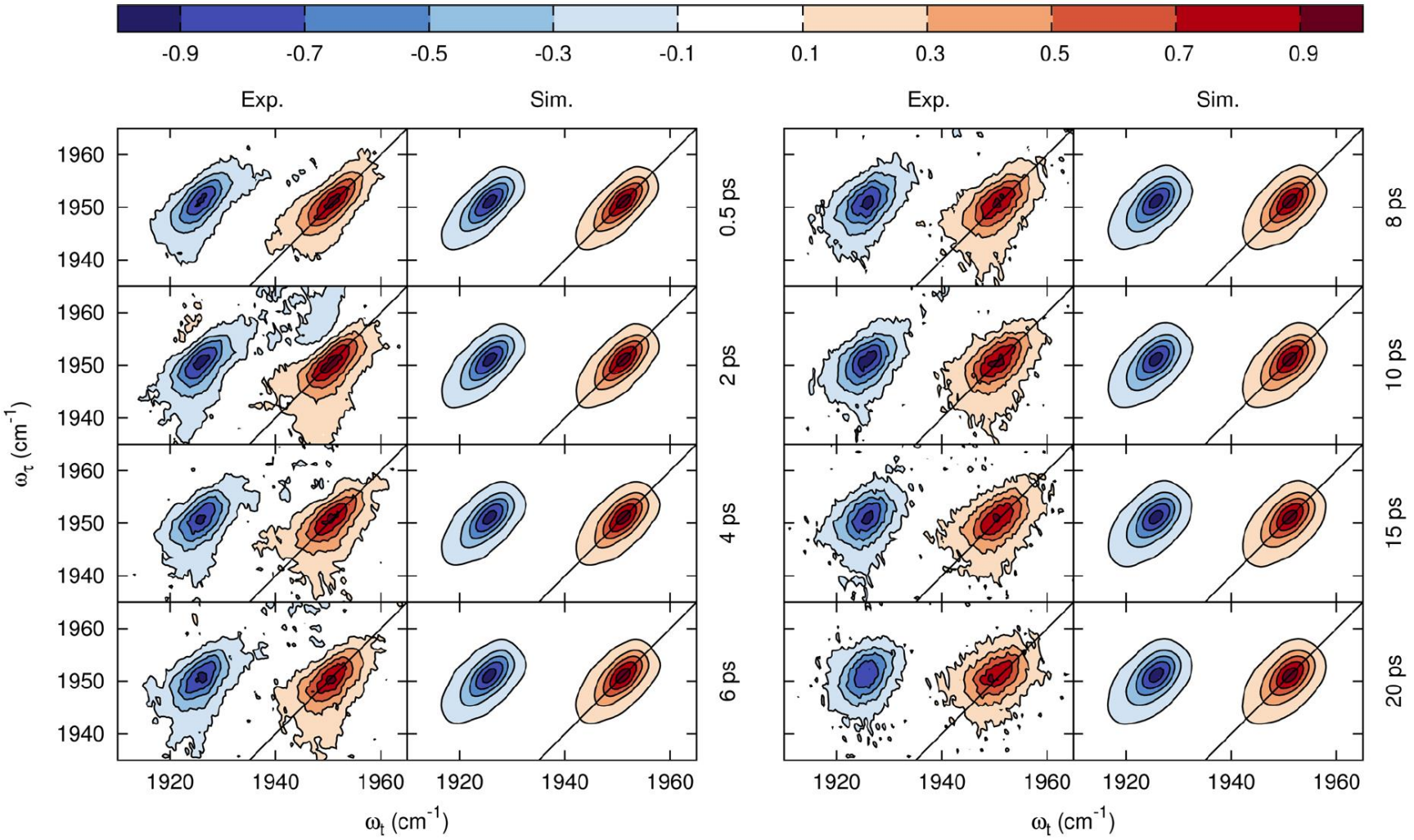






C. Falvo, L. Daniault, T. Vieille, V. Kemlin, J.-C. Lambry, C. Meier, M.H. Vos, A. Bonvalet, M. Joffre, Ultrafast dynamics of carboxy-hemoglobin: 2DIR spectroscopy experiments and simulations
J. Phys. Chem. Lett. ***6****, 2216 (2015)*

Evolution with waiting time



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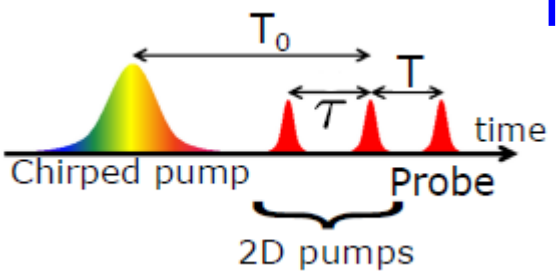
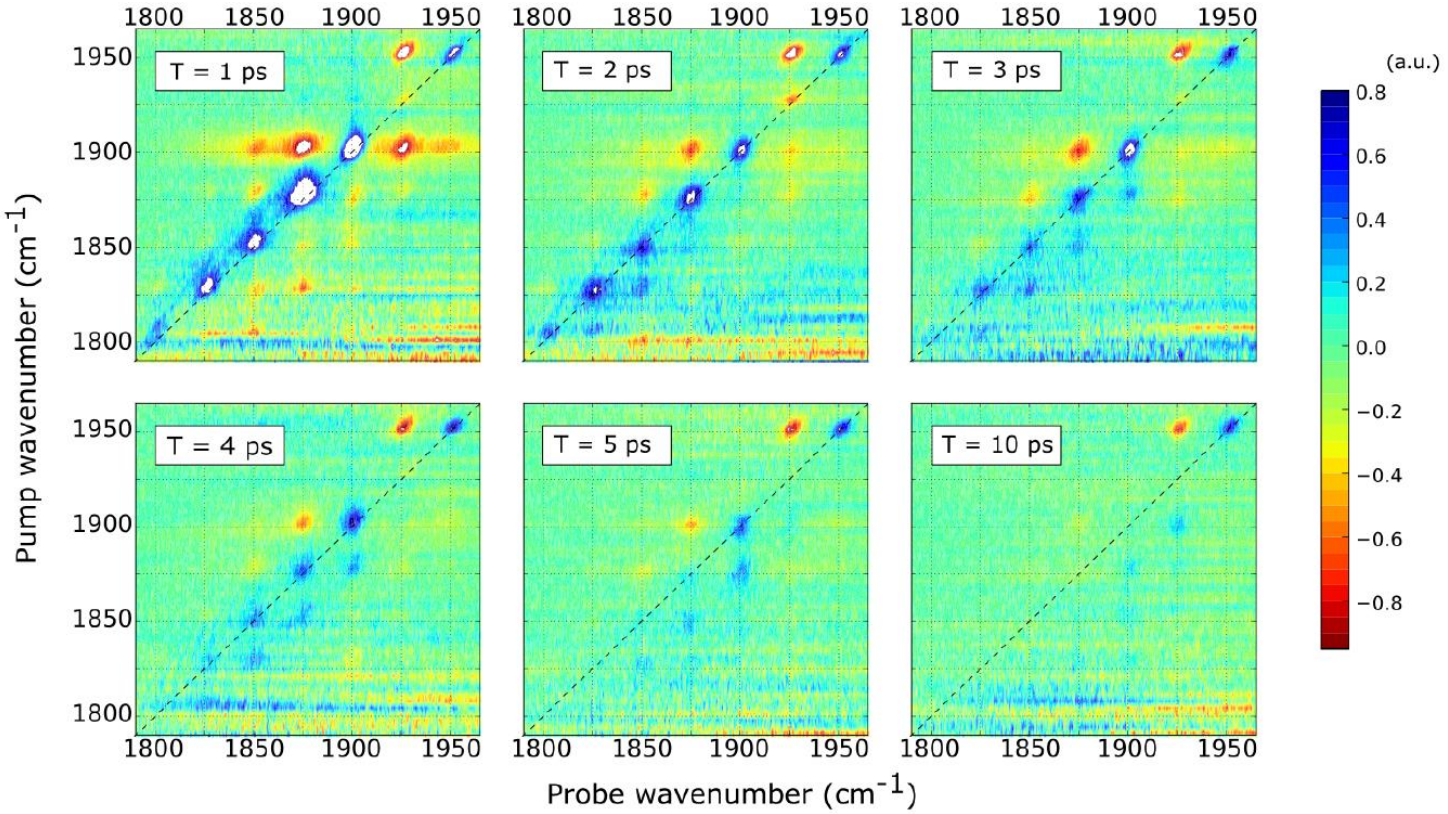
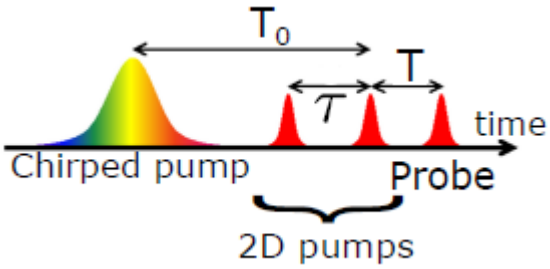
Transient two-dimensional infrared spectroscopy in a vibrational ladder

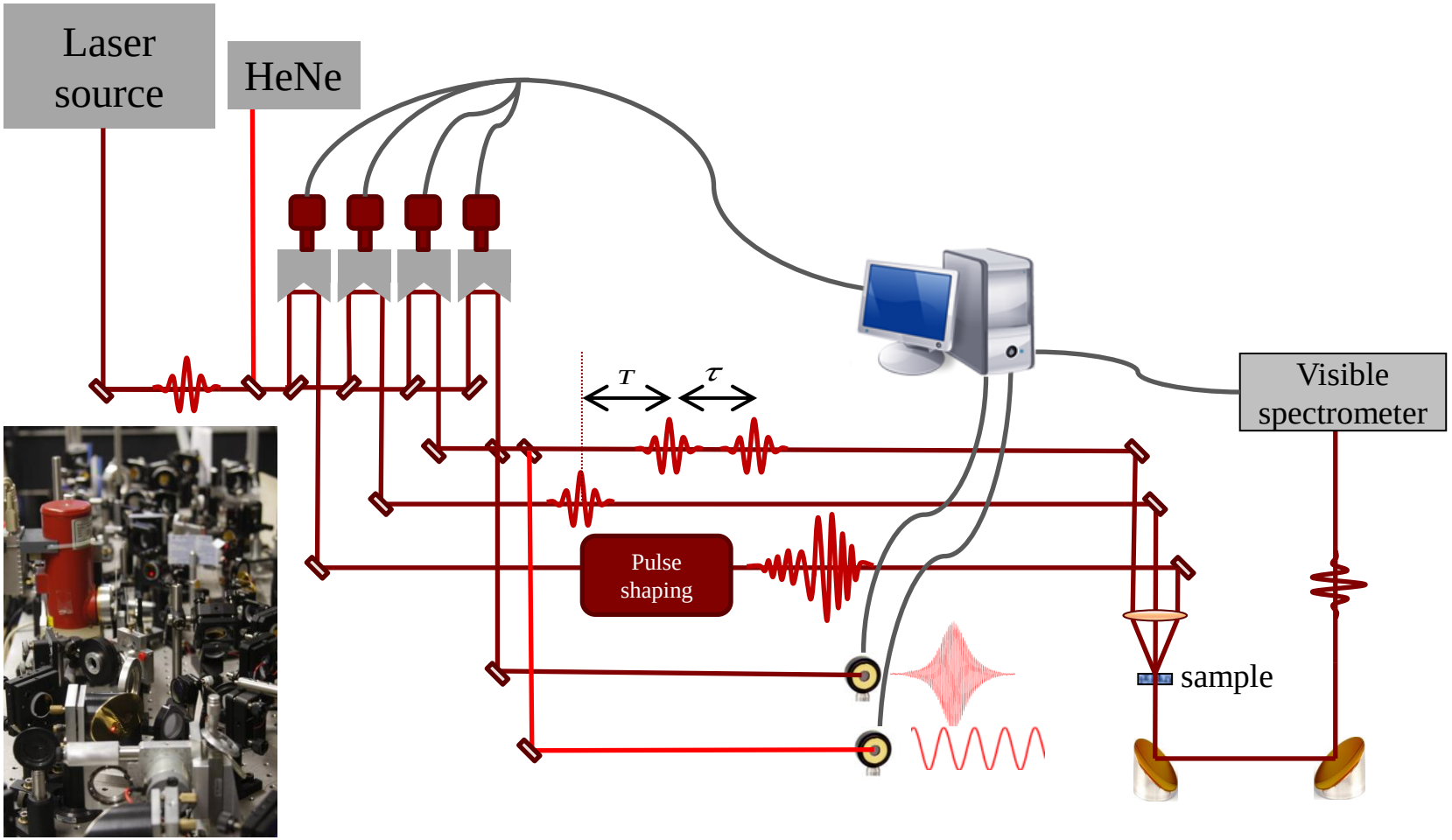


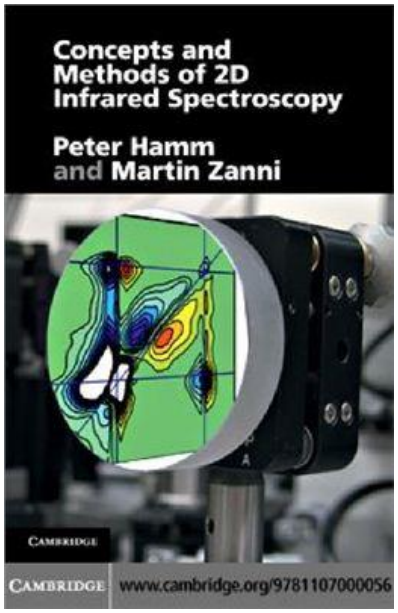


V. Kemlin, L. Daniault, A. Bonvalet, M. Joffre,
Transient two-dimensional infrared spectroscopy in a vibrational ladder
J. Phys. Chem. Lett. ***7****, 3377 (2016)*

The experimental setup







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