Multidimensional infrared spectroscopy

Experimental methods and applications

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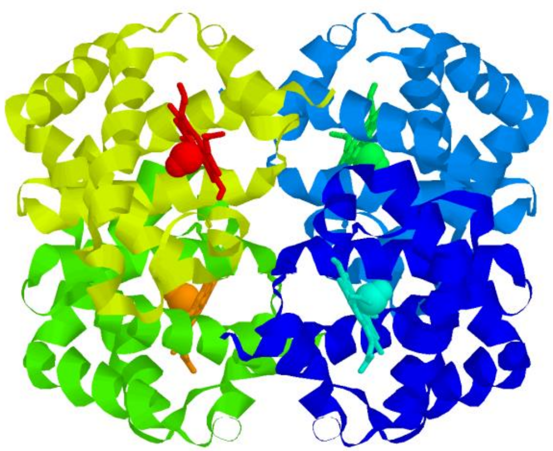
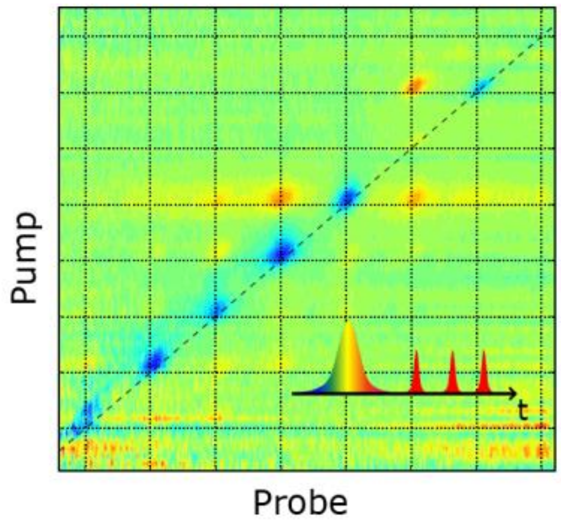
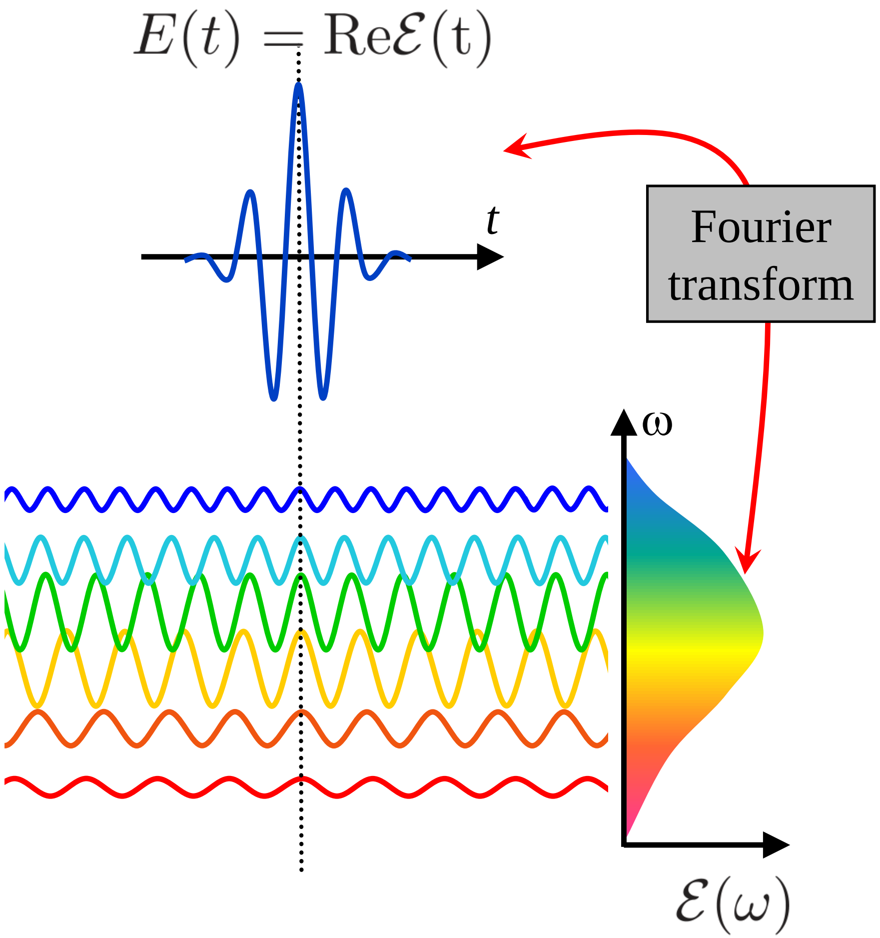




Multiscale Dynamics in Molecular Systems – Les Houches – August 2019

Time-bandwidth product



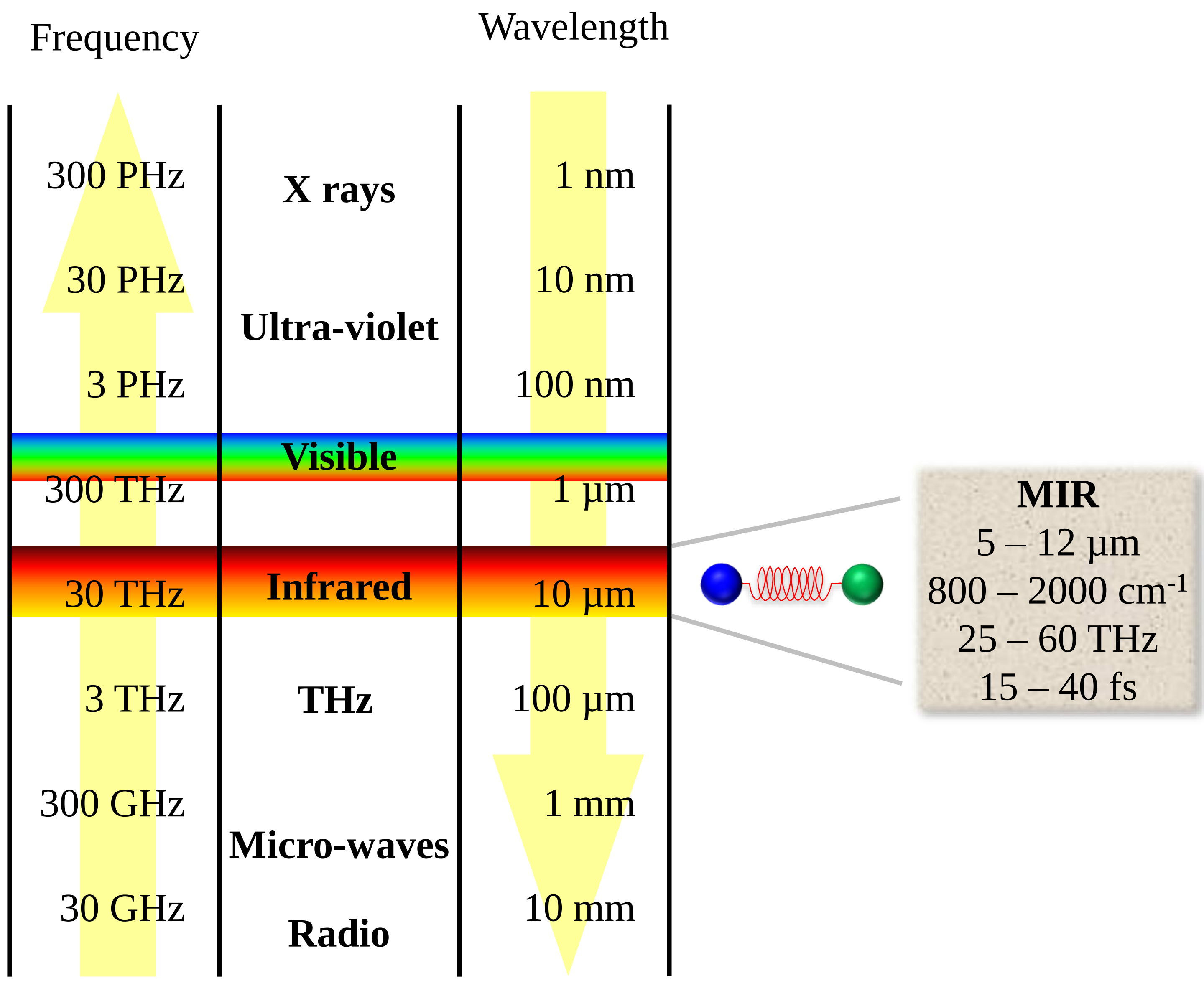
$$\mathcal{E}(t) = \int_0^{+\infty} \mathcal{E}(\omega)\exp(-i\omega t)\frac{d\omega}{2\pi}$$

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

$$\Delta\omega\Delta t \geq \frac{1}{2}$$

➡ An ultrashort pulse provides a broad spectral bandwidth, but the spectral resolution must be provided at the detection level.

The Mid-InfraRed (MIR) spectral domain



1. Generation of MIR femtosecond pulses
2. Shaping of MIR femtosecond pulses
3. 1DIR spectroscopy
4. 2DIR spectroscopy
5. Setting up your own 2DIR spectrometer
6. A few applications

Generation of MIR fs pulses using temporal slicing

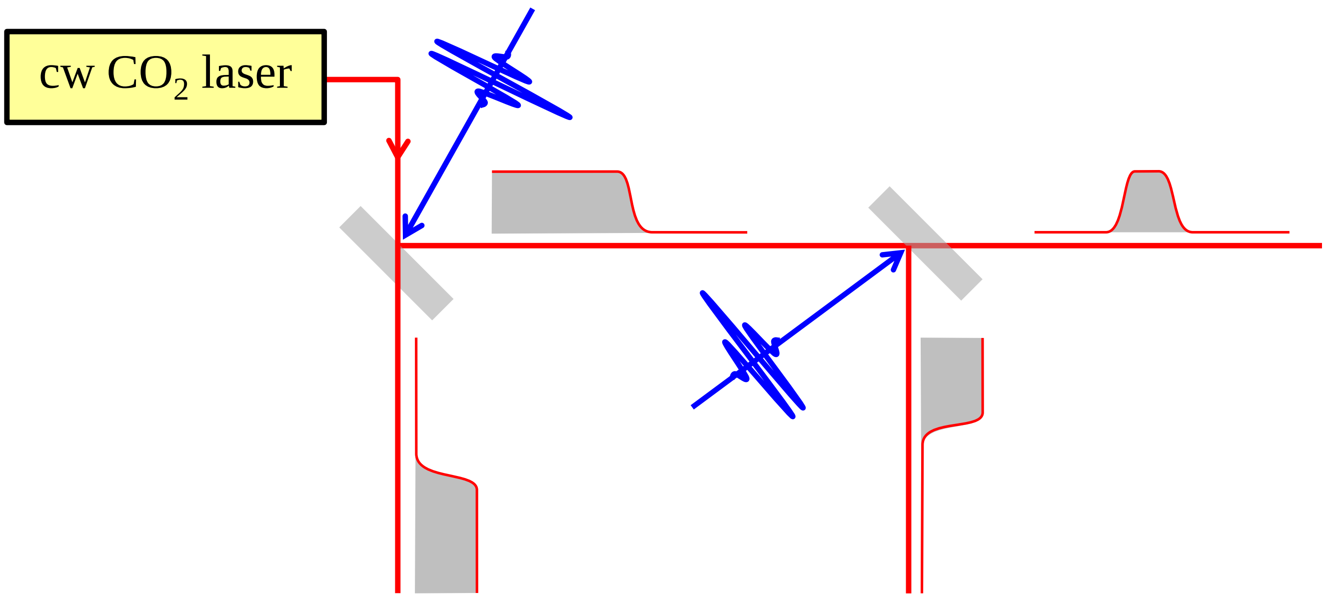
Generation of 130-fsec midinfrared pulses

Claude Rolland and P. B. Corkum

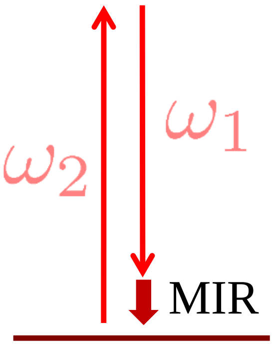
Division of Physics, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada

Received June 16, 1986; accepted July 14, 1986

Infrared (IR) pulses as short as 130 fsec are generated by using semiconductors switching. Such pulses contain only ~4 optical cycles, the shortest ever achieved in the midinfrared. The measured power spectrum (7.5–10.5-μm base width) is consistent with the Fourier transform of the IR pulse.

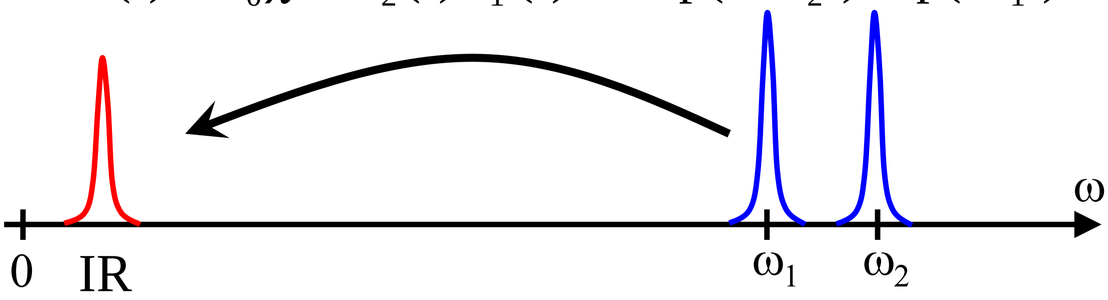


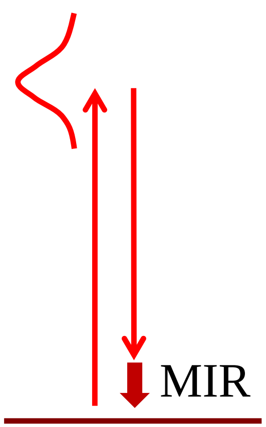
MIR generation using second-order nonlinear optics



a) Difference frequency mixing

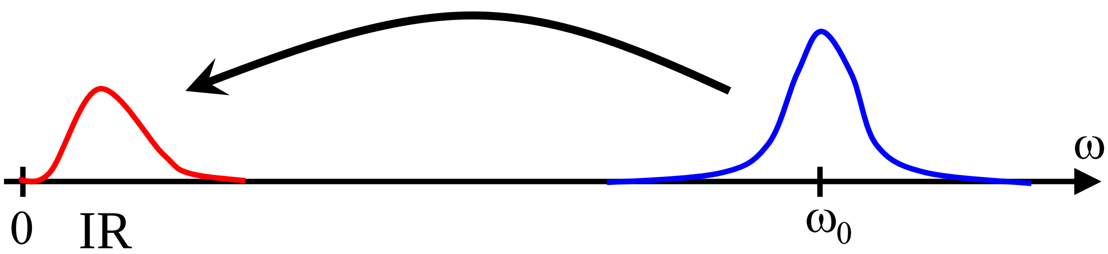
$$P^{(2)}(t) = \varepsilon_0 \chi^{(2)} E_2(t) E_1^*(t) \propto \exp(-i\omega_2 t)\exp(i\omega_1 t) = \exp(-i(\omega_2 - \omega_1)t)$$



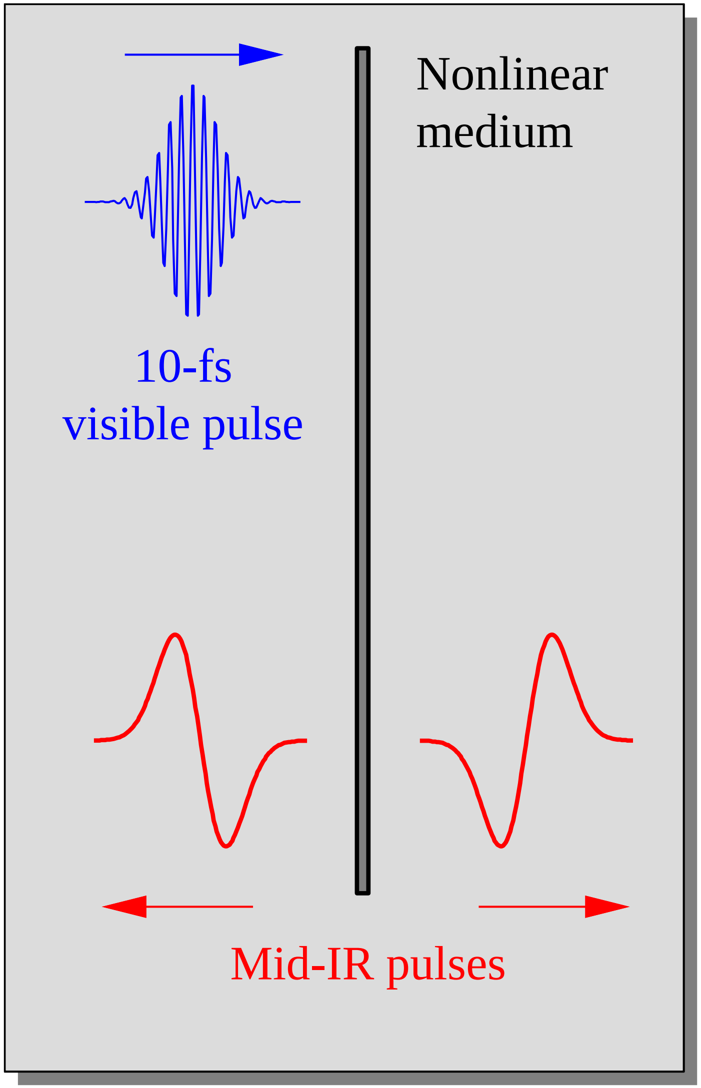


b) Optical rectification (inverse electro-optic effect)

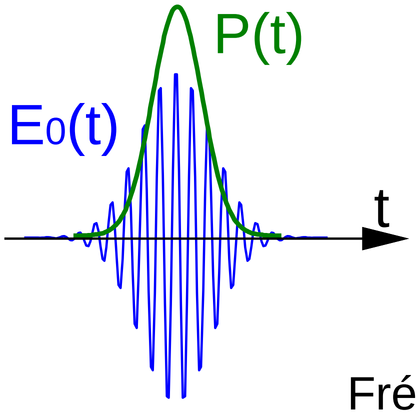
$$P^{(2)}(t) = \varepsilon_0 \chi^{(2)} E(t) E^*(t)$$

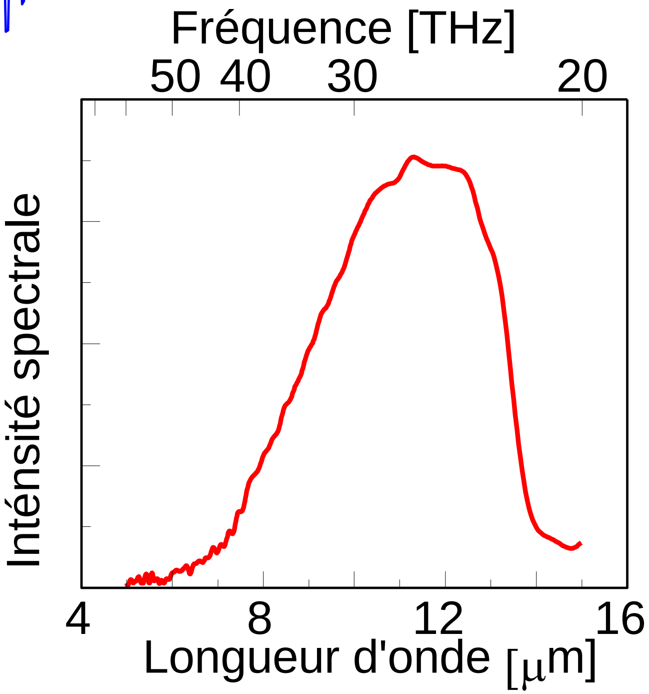


MIR generation using optical rectification



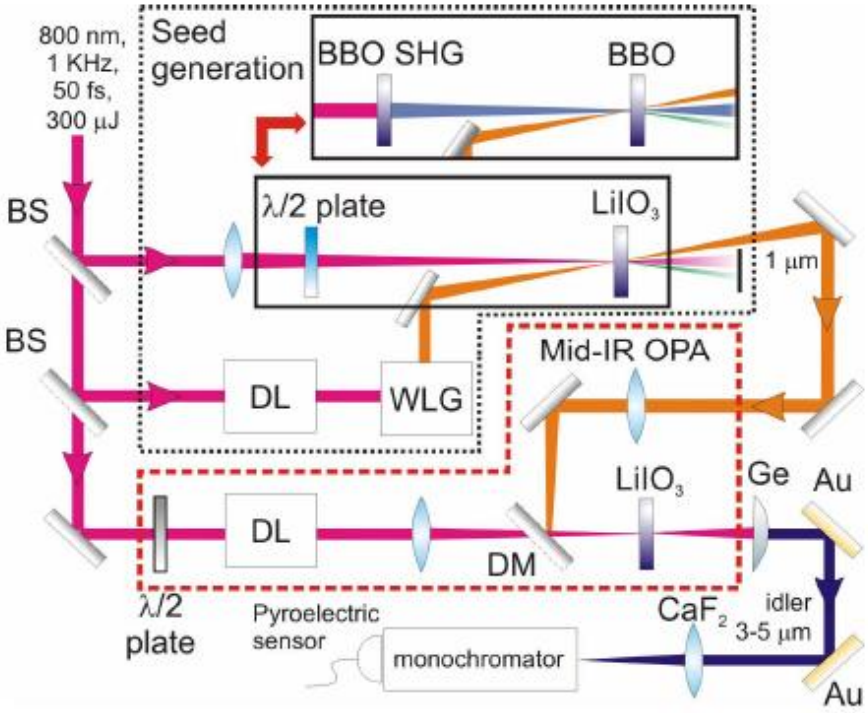
- Optical rectification : $P^{(2)}(t) = \varepsilon_0 \chi^{(2)} \left| E_0(t) \right|^2$

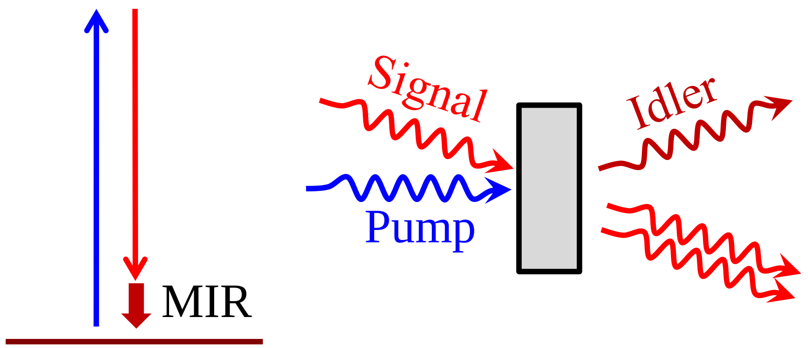


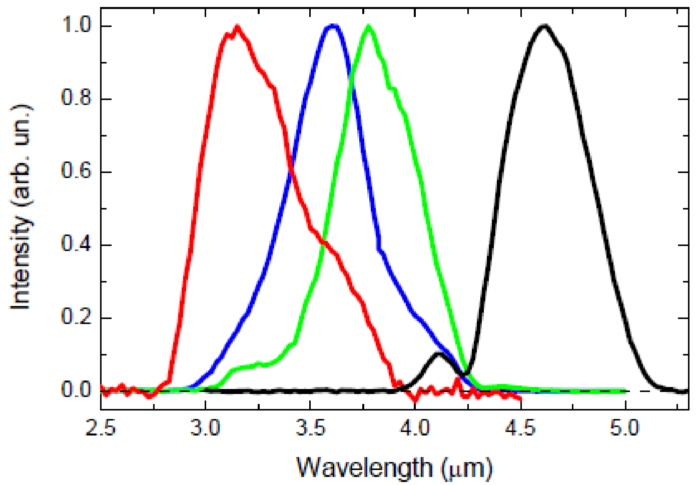


A. Bonvalet, M. Joffre, J.-L. Martin, A. Migus, Appl. Phys. Lett., **67**, 2907 (1995)

Optical parametric amplification



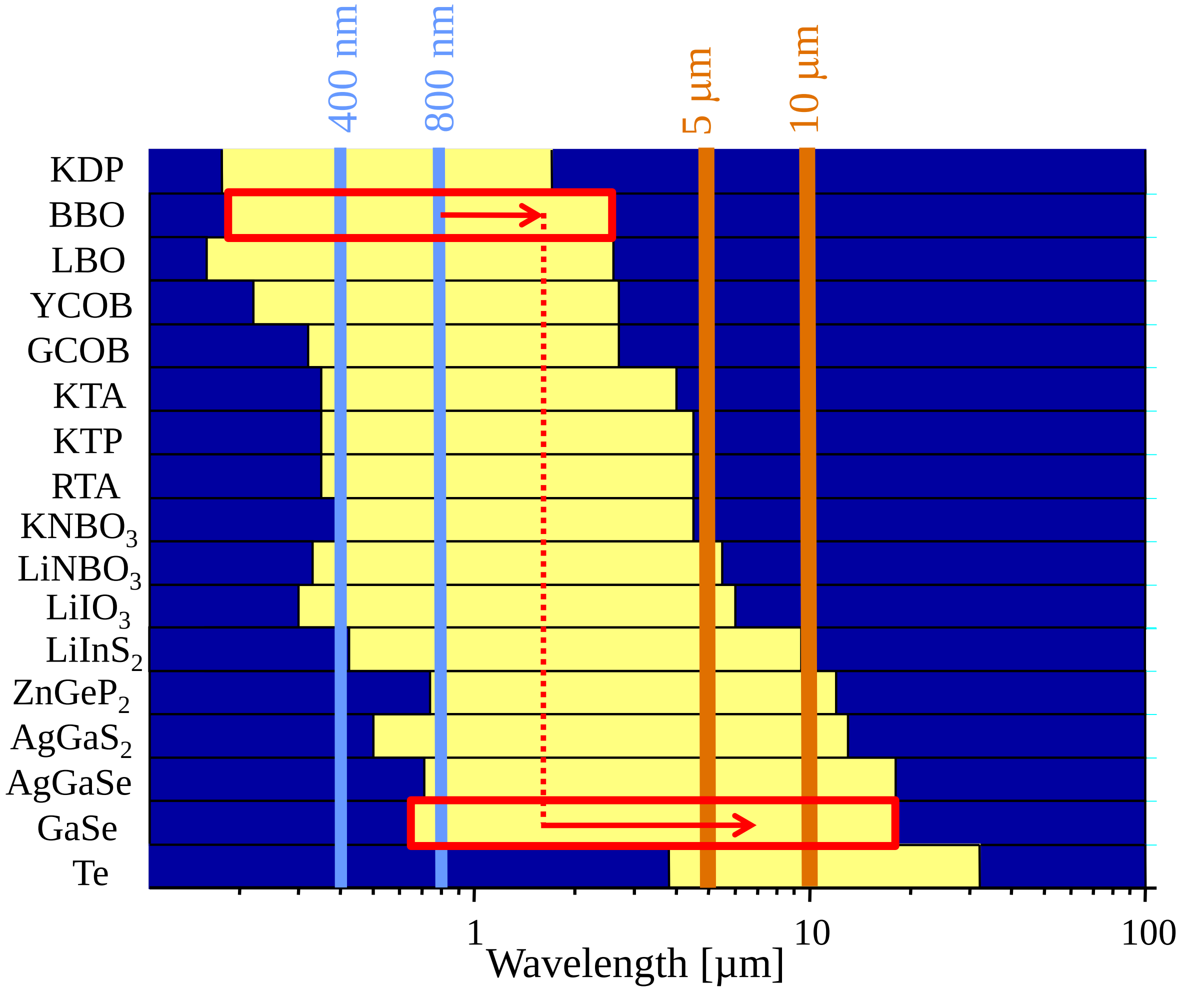




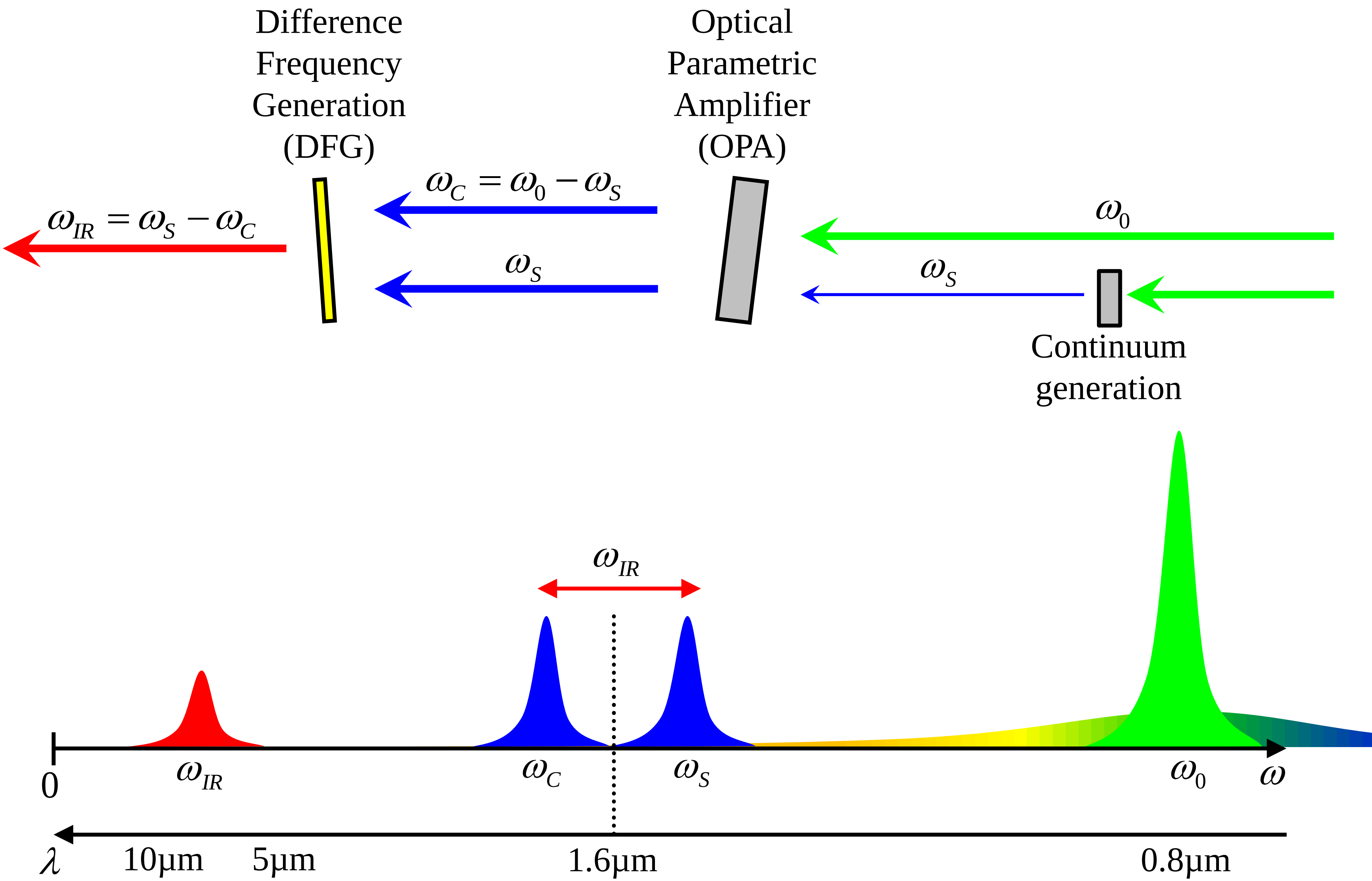
300 μJ → 2 μJ @ λ < 5 μm

D. Brida, C. Manzoni, G. Cirmi, M. Marangoni, S. De Silvestri, G. Cerullo
Generation of broadband mid-infrared pulses from an optical parametric amplifier
Opt. Express **15**, 15035-15040 (2007)

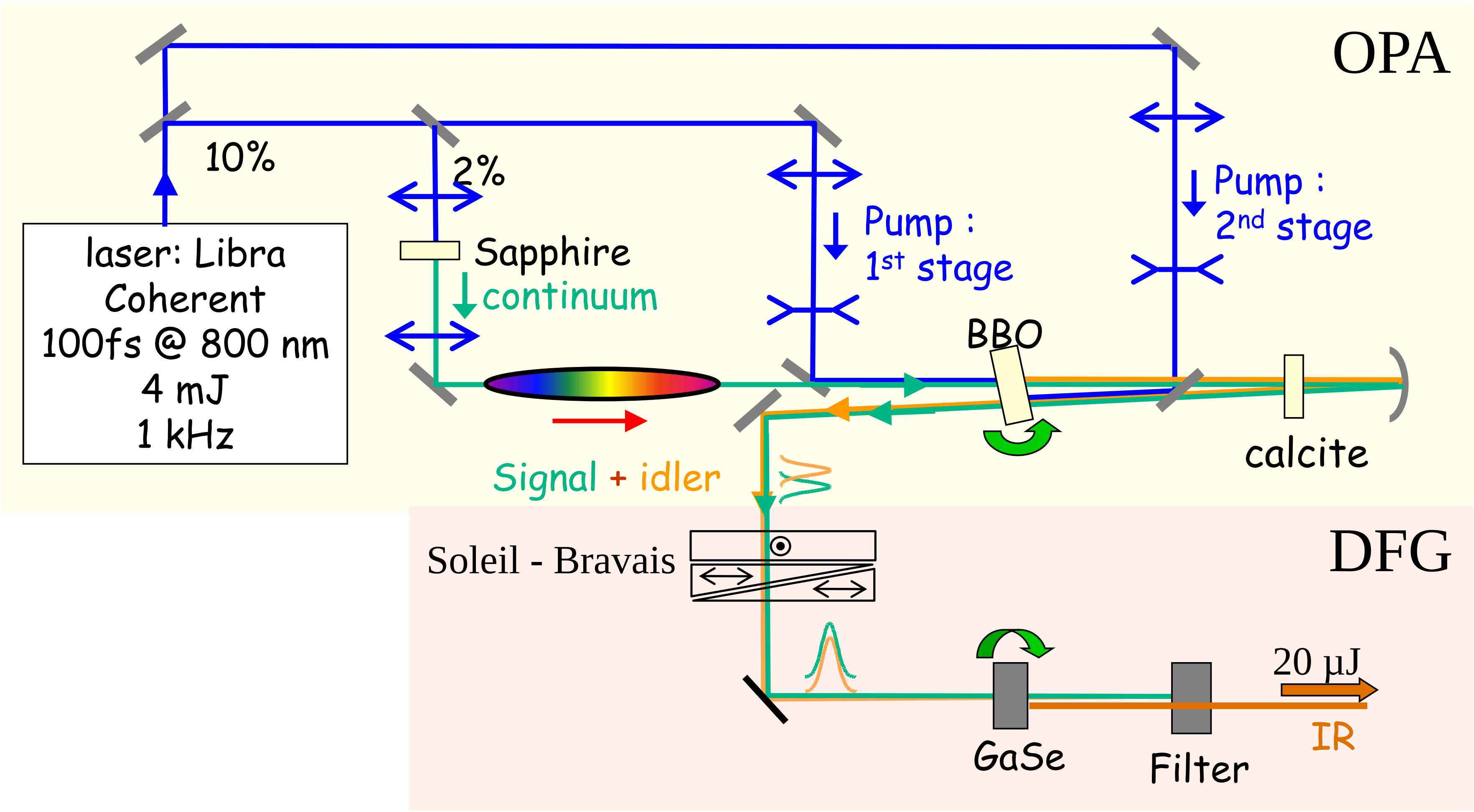
Limiting factor : two-photon absorption



MIR generation using two nonlinear stages

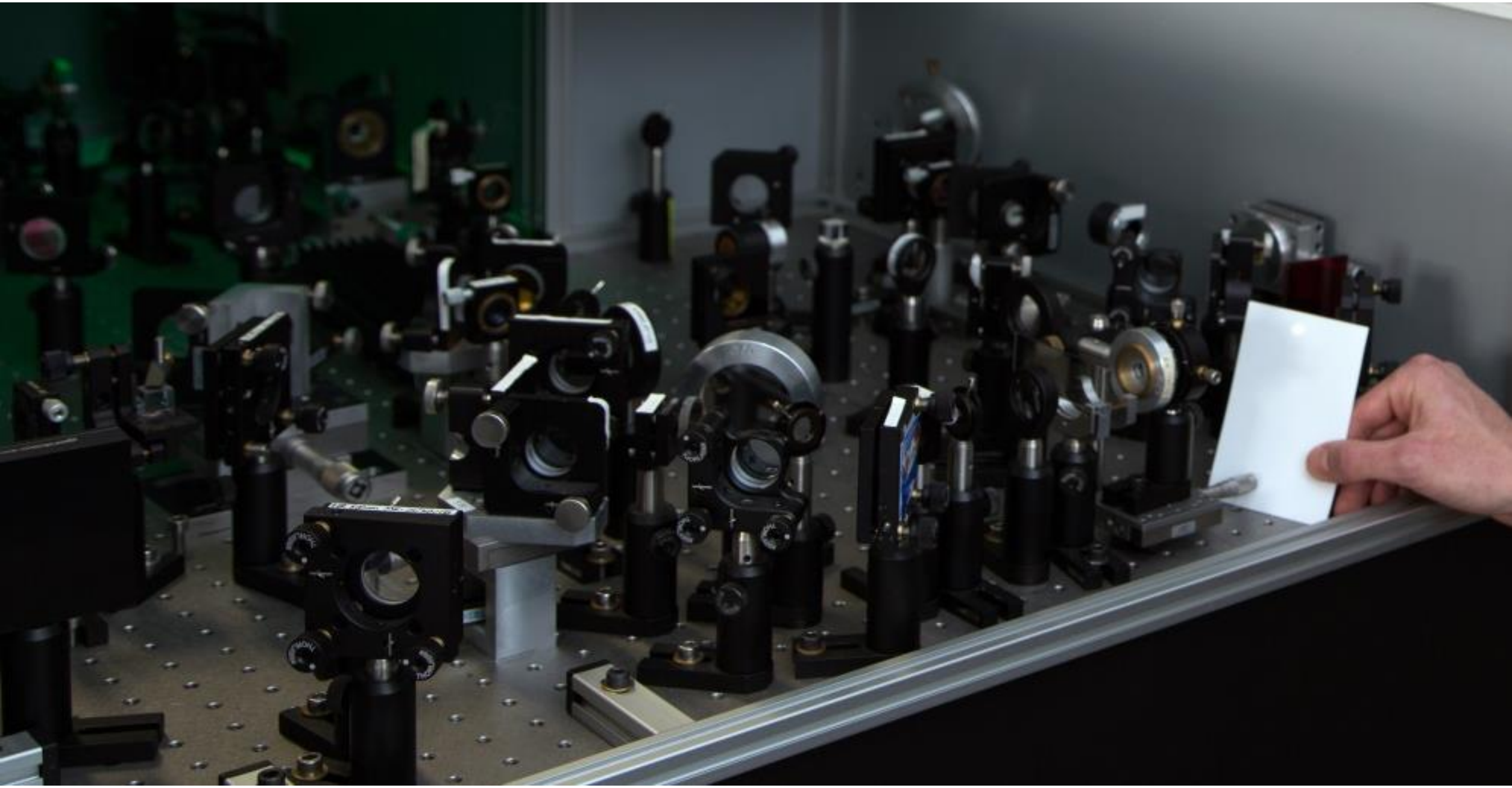


Two-stage MIR generation : experimental setup



R. A. Kaindl, M. Wurm, K. Reimann, P. Hamm, A. M. Weiner, M. Woerner, JOSA B **17**, 2086 (2000)
J.M. Fraser, I.W. Cheung, F. Legare, D.M. Villeneuve, J.P. Likforman, M. Joffre, P.B. Corkum, Appl. Phys. B **74**, S153 (2002)
C. Ventalon, J.M. Fraser, J.P. Likforman, D.M. Villeneuve, P.B. Corkum, M. Joffre, JOSA B **23**, 332 (2006)
A.B. Sugiharto, C.M. Johnson, H.B. De Aguiar, L. Alloatti, S. Roke, Appl. Phys. B **91**, 315 (2008)

Two-stage MIR generation : experimental setup



R. A. Kaindl, M. Wurm, K. Reimann, P. Hamm, A. M. Weiner, M. Woerner, JOSA B **17**, 2086 (2000)
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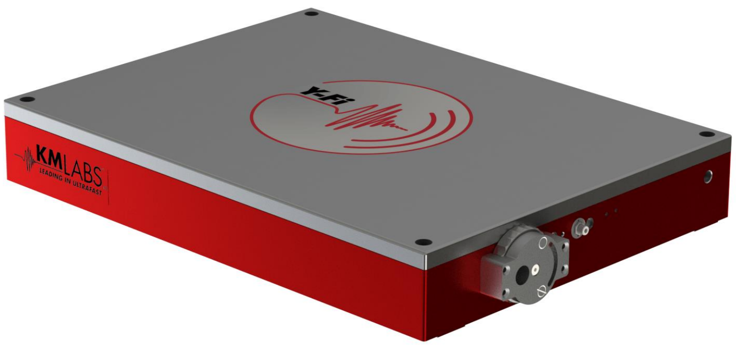
C. Ventalon, J.M. Fraser, J.P. Likforman, D.M. Villeneuve, P.B. Corkum, M. Joffre, JOSA B **23**, 332 (2006)
A.B. Sugiharto, C.M. Johnson, H.B. De Aguiar, L. Alloatti, S. Roke, Appl. Phys. B **91**, 315 (2008)

From 1 to 100-kHz MIR femtosecond sources

1 to 10 kHz Titanium:Sapphire (Ti:S) femtosecond amplifiers are now being replaced with Ytterbium-Doped Fiber Amplifiers (YDFA) laser systems.



https://www.kmlabs.com/product/y-fi/

https://amplitude-laser.com/fr/produit/tangerine/

- ☹ Primary source delivering longer pulses
- ☺ Longer wavelength (less two-photon absorption)
- ☺ Higher repetition rate
- ☺ Better stability

B.M. Luther *et al.*, Opt. Express **24**, 4117 (2016)
K.M. Tracy *et al.*, J. Phys. Chem. Lett. **7**, 4865 (2016)
R. Fritzsch *et al.*, Anal. Chem. **90**, 2732 (2018)
P.M. Donaldson *et al.*, J. Phys. Chem. A **122**, 780 (2018)

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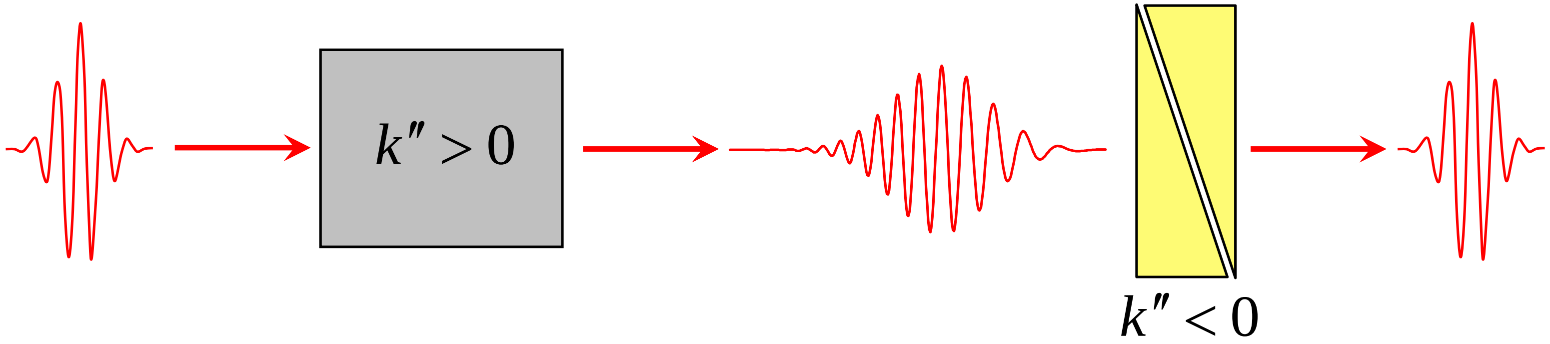
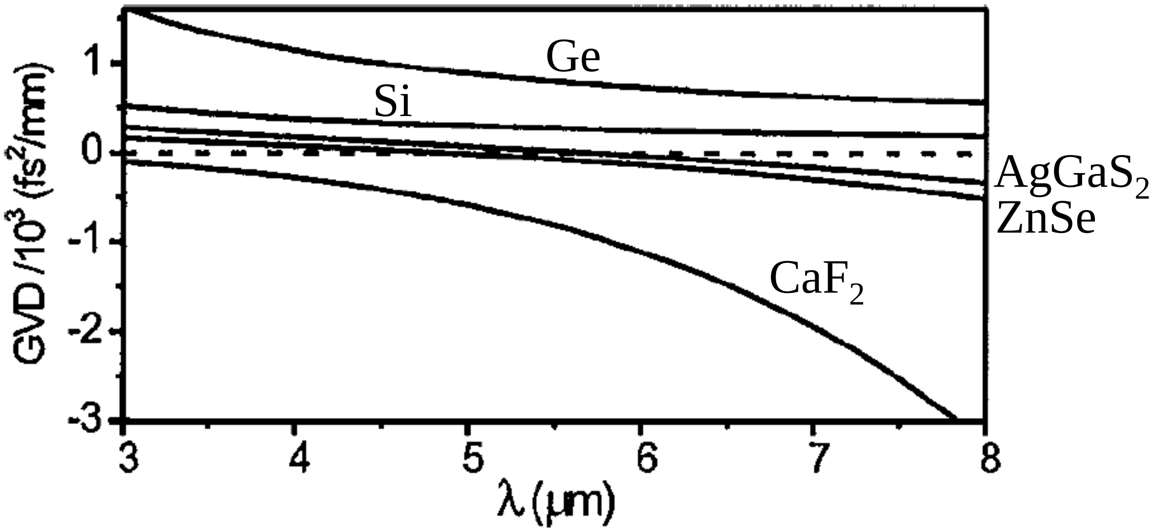
Control of group velocity dispersion

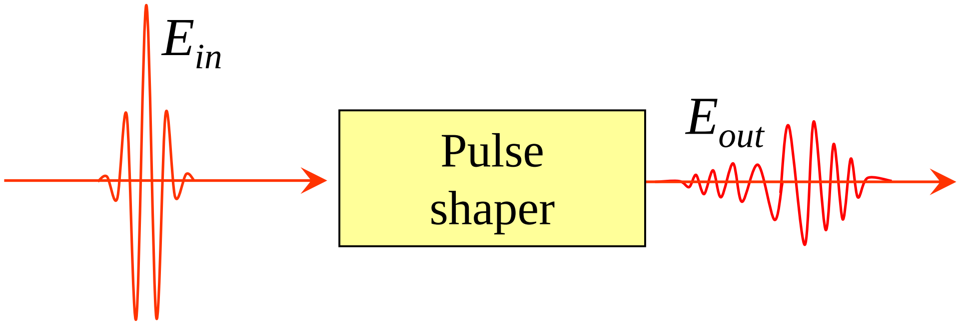
One of the very few things that are easier to achieve in the MIR than in the visible!





N. Demirdöven, M. Khalil, O. Golonzka, A. Tokmakoff, Opt. Lett. **27**, 433 (2002)

Programmable Pulse shaping

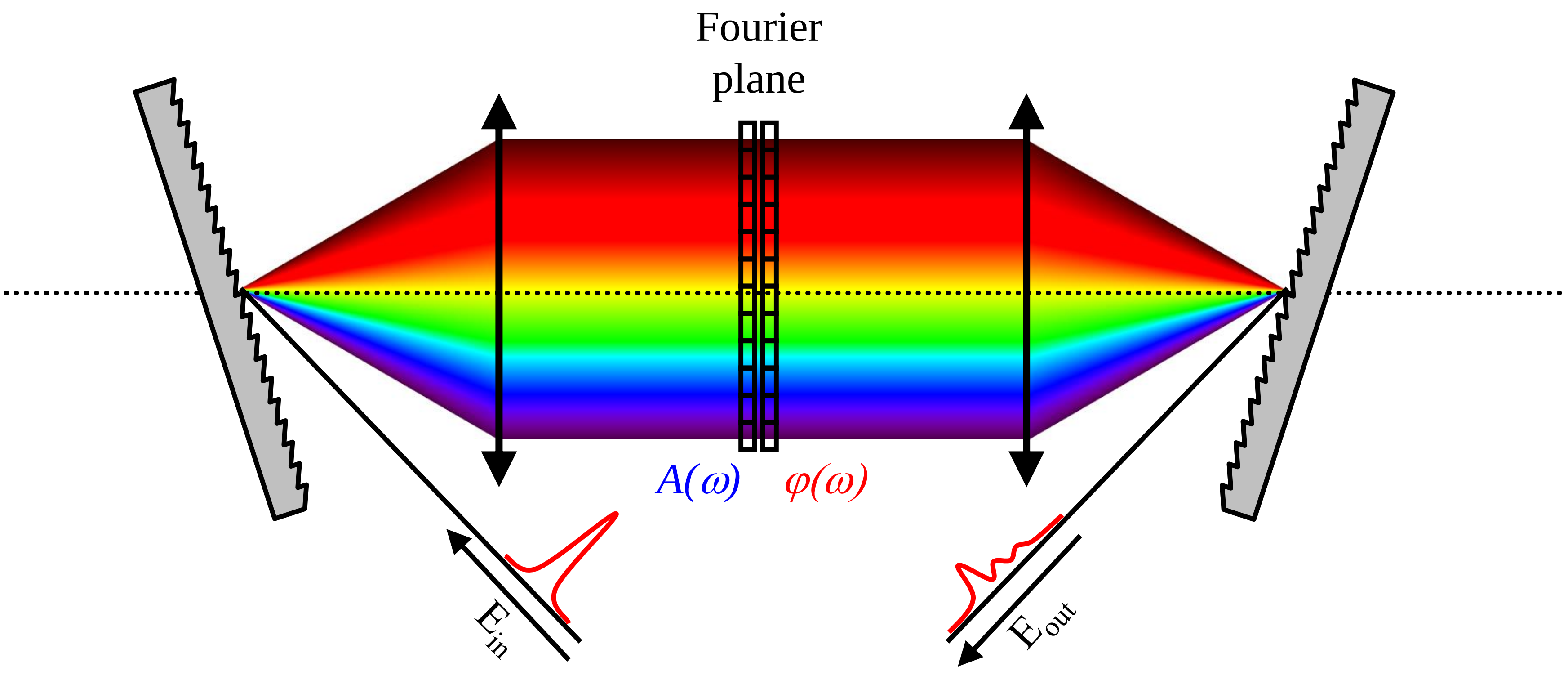


$$E_{out}(t) = R(t) \otimes E_{in}(t)$$

$$E_{out}(\omega) = R(\omega) E_{in}(\omega)$$

$R(\omega)$: complex transfer function of the filter, ideally programmable in amplitude and phase.

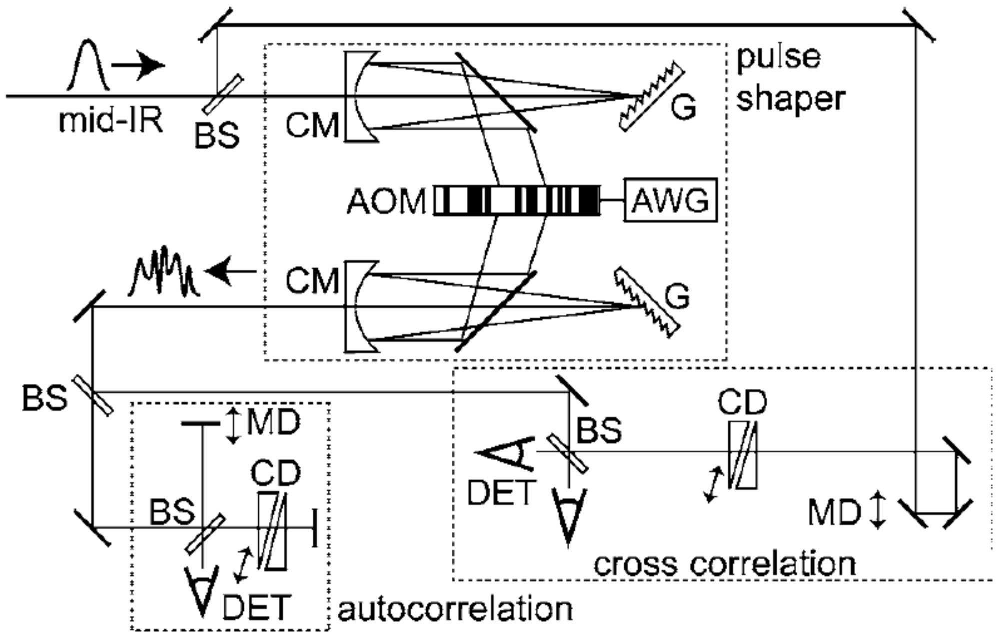
Zero-dispersion line + spatial light modulator

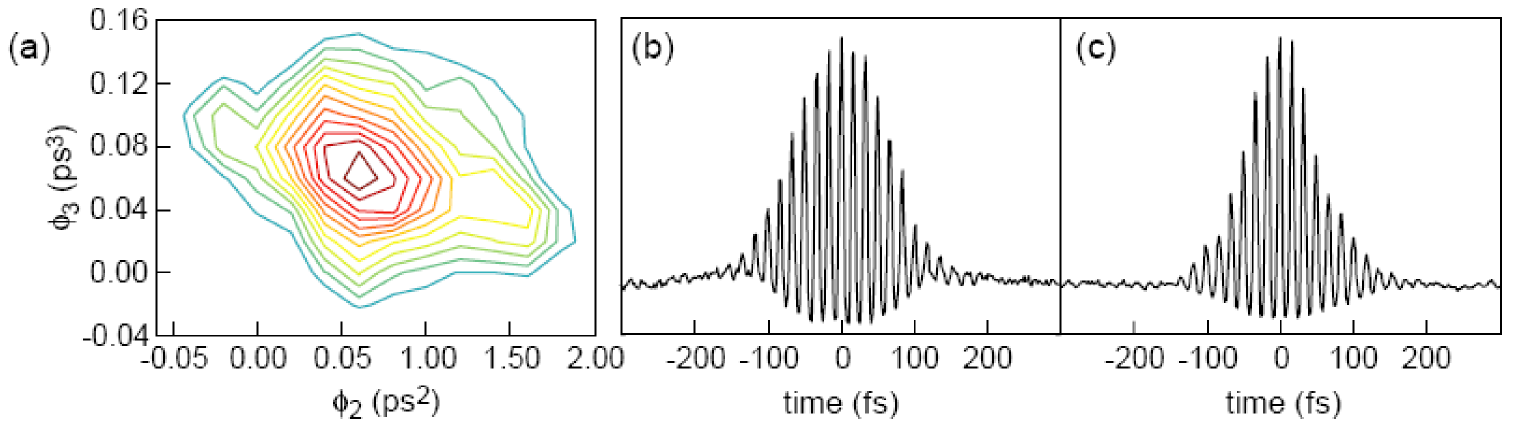


$$E_{out}(\omega) = E_{in}(\omega) A(\omega) \exp(i\varphi(\omega))$$

A.M. Weiner, Rev. Sci. Instr. **71**, 1929 (2000)
A. Monmayrant, B. Chatel, Rev. Sci. Instr. **75**, 2668 (2004)

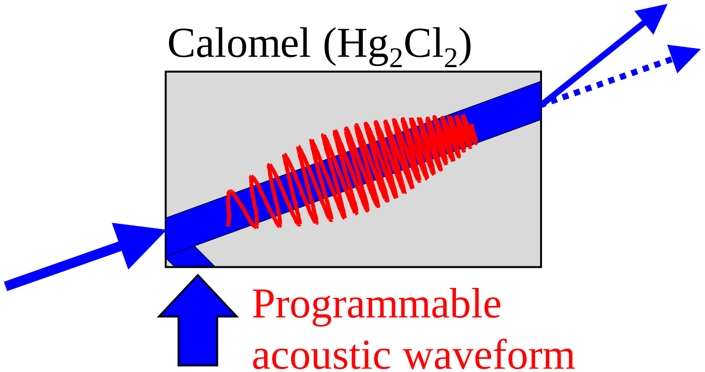
Shaping MIR pulses using a transverse AO modulator



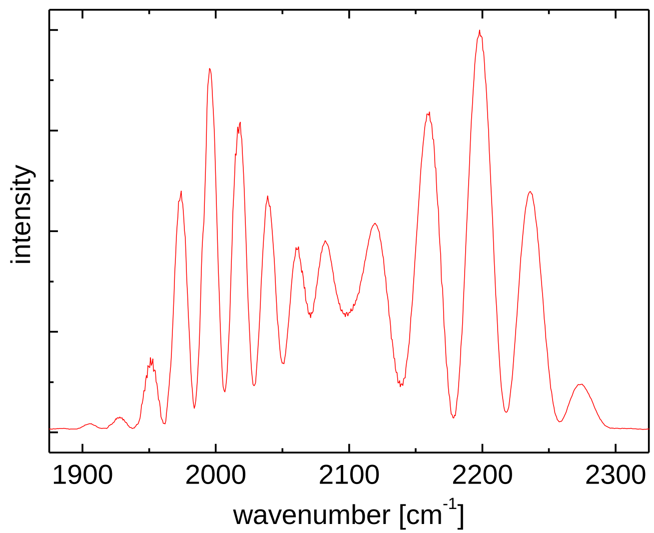


S.-H. Shim, D. B. Strasfeld, E. C. Fulmer, M. T. Zanni, Opt. Lett. **31**, 838 (2006)
S.-H. Shim, D. B. Strasfeld, M. T. Zanni, Opt. Express **14**, 13120 (2006)

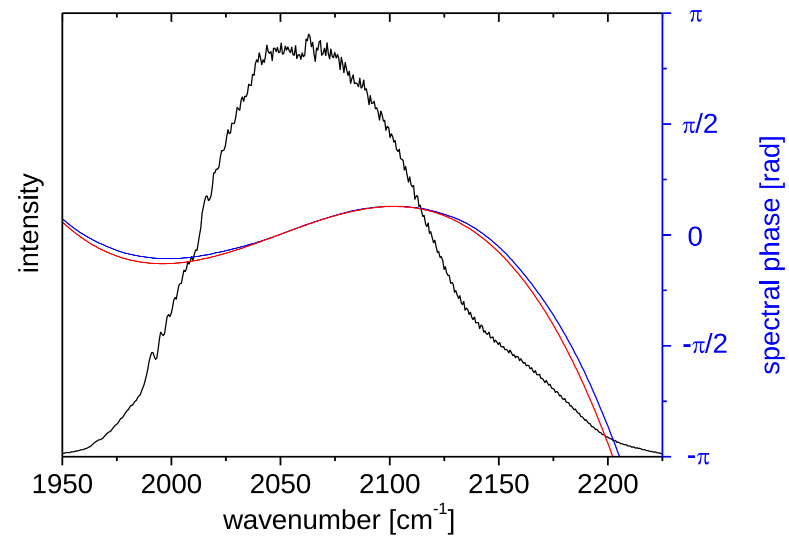
MIR shaping using a Calomel Dazzler



Amplitude shaping



Phase shaping



R. Maksimenka, P. Nuernberger, K.F. Lee, A. Bonvalet, J. Milkiewicz, C. Barta, M. Klima, T. Oksenhendler, P. Tournois, D. Kaplan, M. Joffre, *Direct mid-infrared femtosecond pulse shaping with a calomel acousto-optic programmable dispersive filter*, Opt. Lett. **35**, 3565-3567 (2010)

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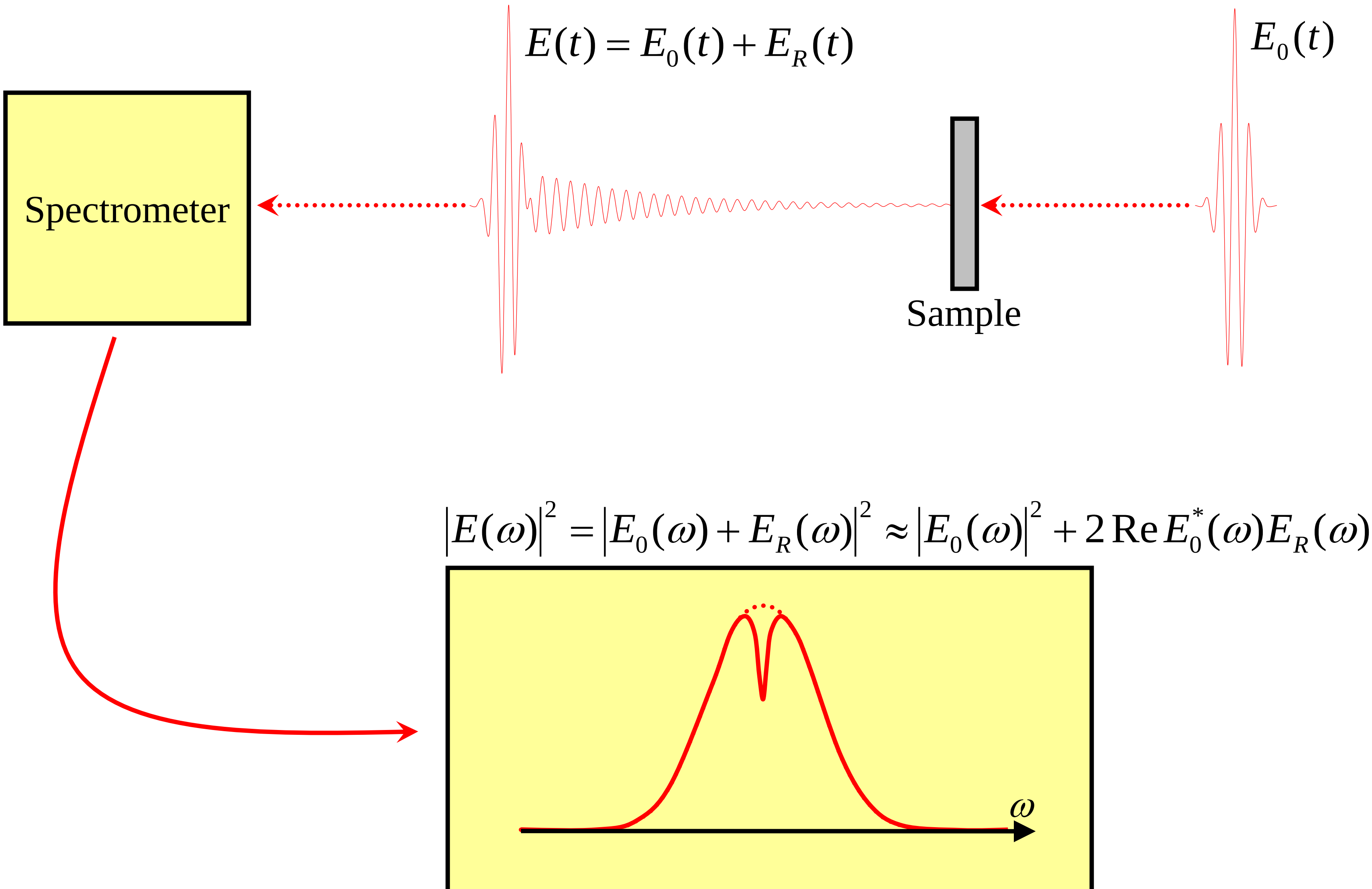
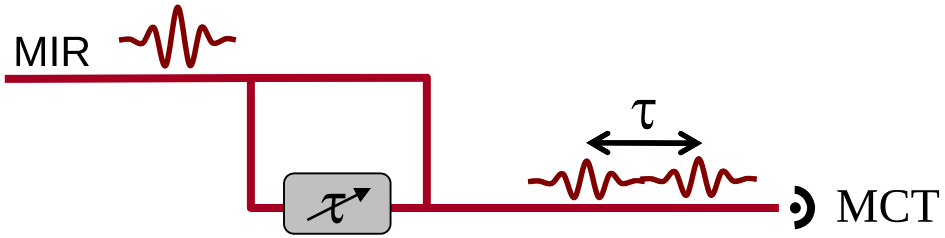
Frequency-domain measurement after impulsive excitation



How shall we measure the MIR spectrum ?

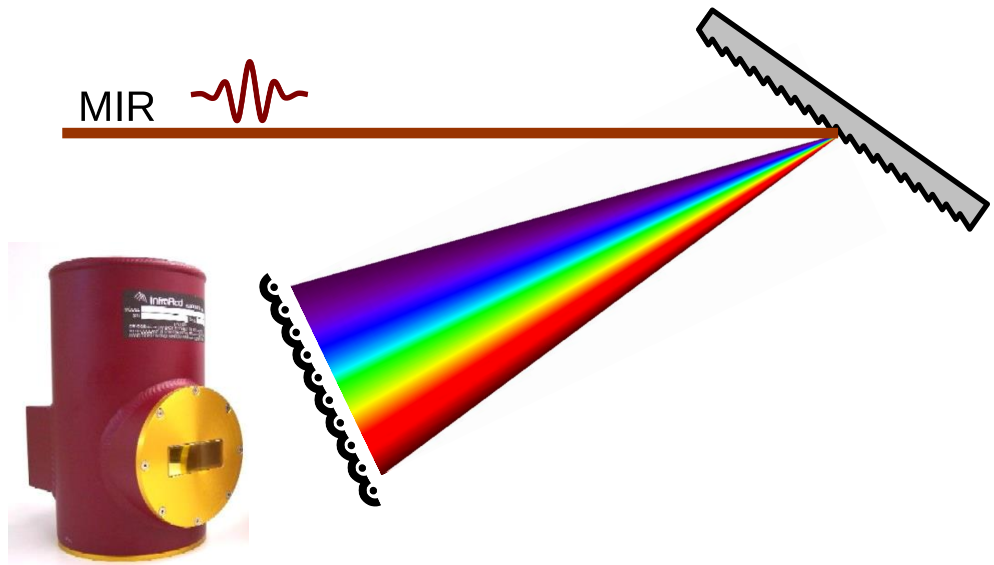
- Fourier-transform spectrometer



$$\mathcal{F}[S(\tau)] \rightarrow |E(\omega)|^2$$

MCT stands for Mercury Cadmium Telluride (HgCdTe)

- Dispersive spectrometer

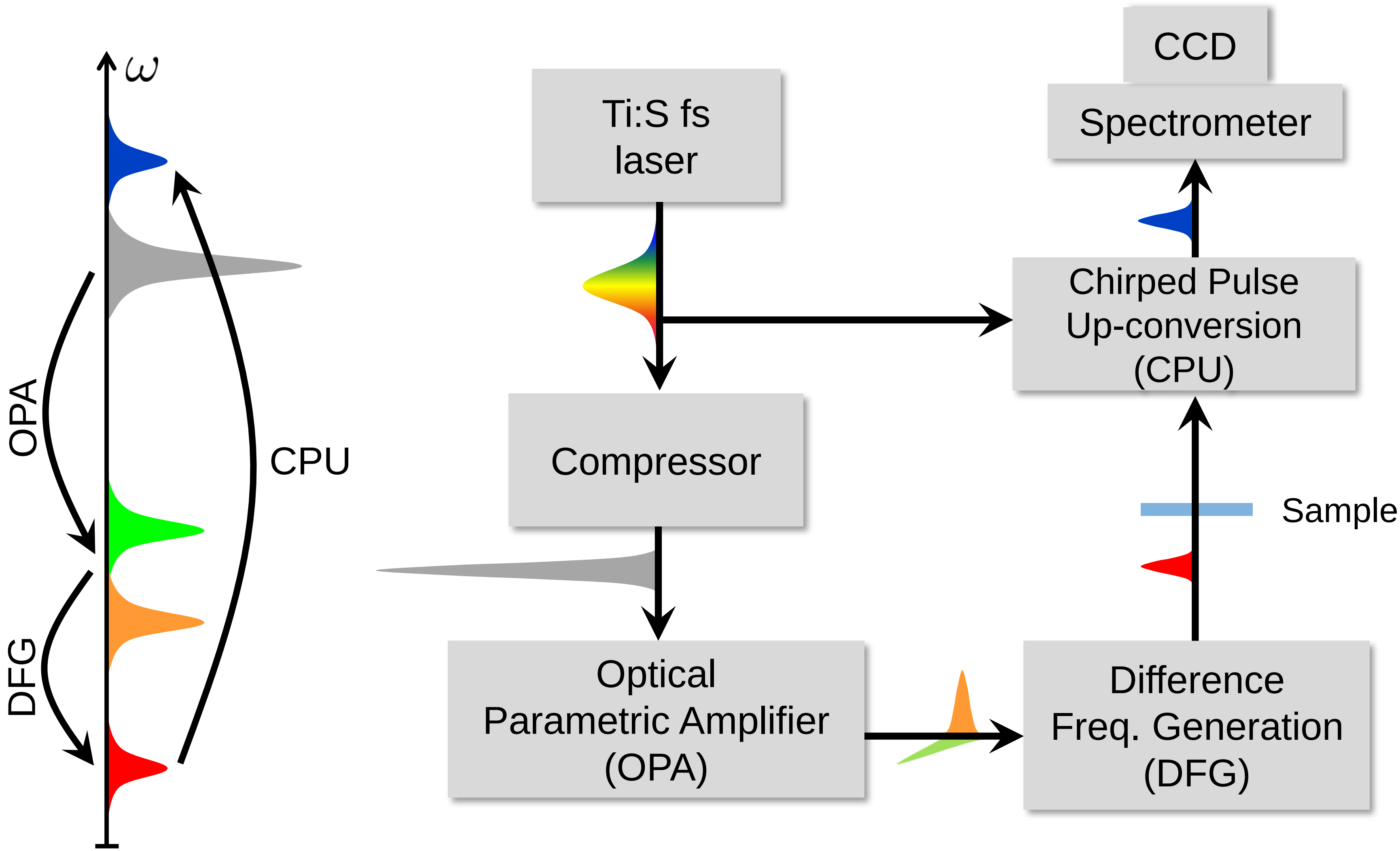


64 pixel MCT array

http://www.irassociates.com/

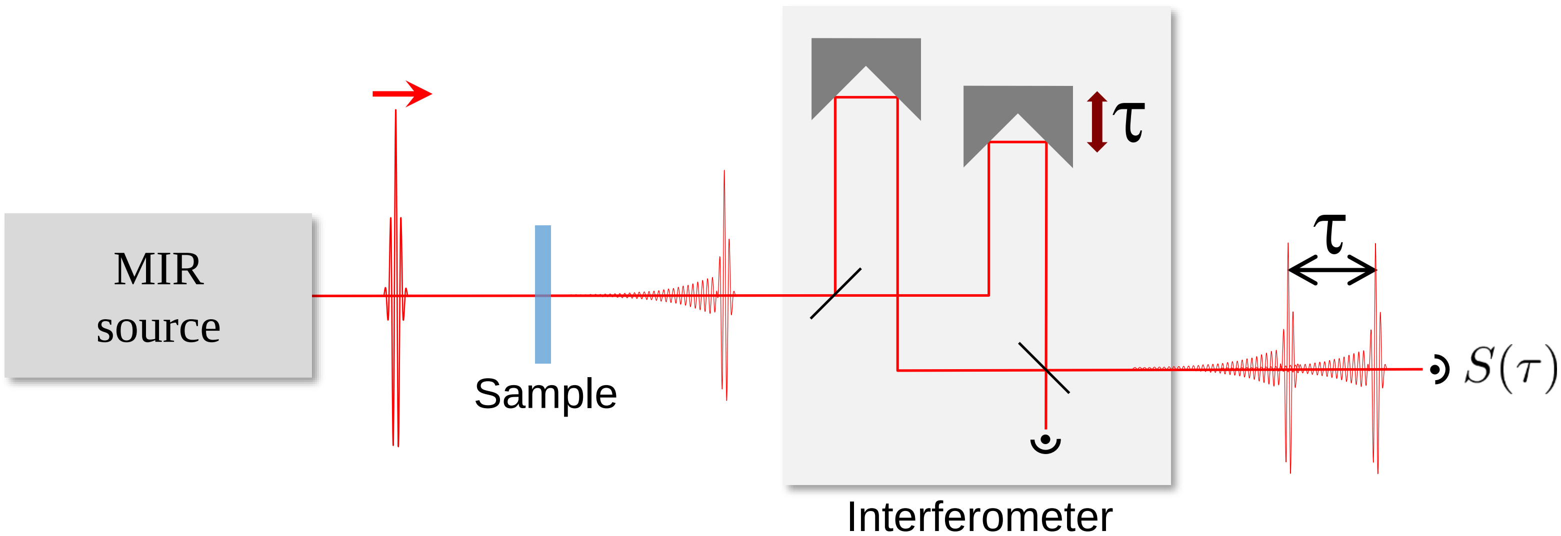
- Chirped Pulse Up-conversion (using a visible detector such as a CCD camera)

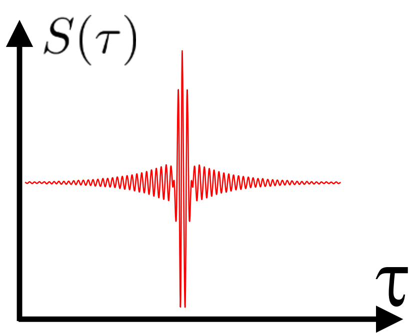
Chirped Pulse Up-conversion

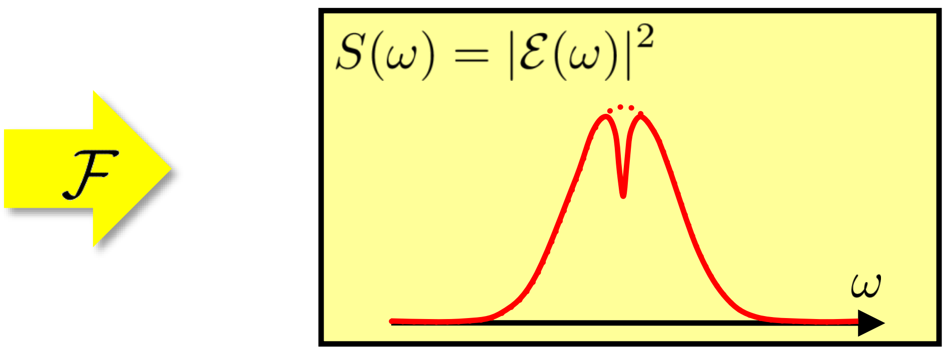


K.J. Kubarych, M. Joffre, A. Moore, N. Belabas, D. Jonasn Opt. Lett. 30, 1228-1230 (2005)
K.F. Lee, P. Nuernberger, A. Bonvalet, M. Joffre, Opt. Express 17, 18738-18744 (2009)

Fourier Transform Infrared Spectroscopy



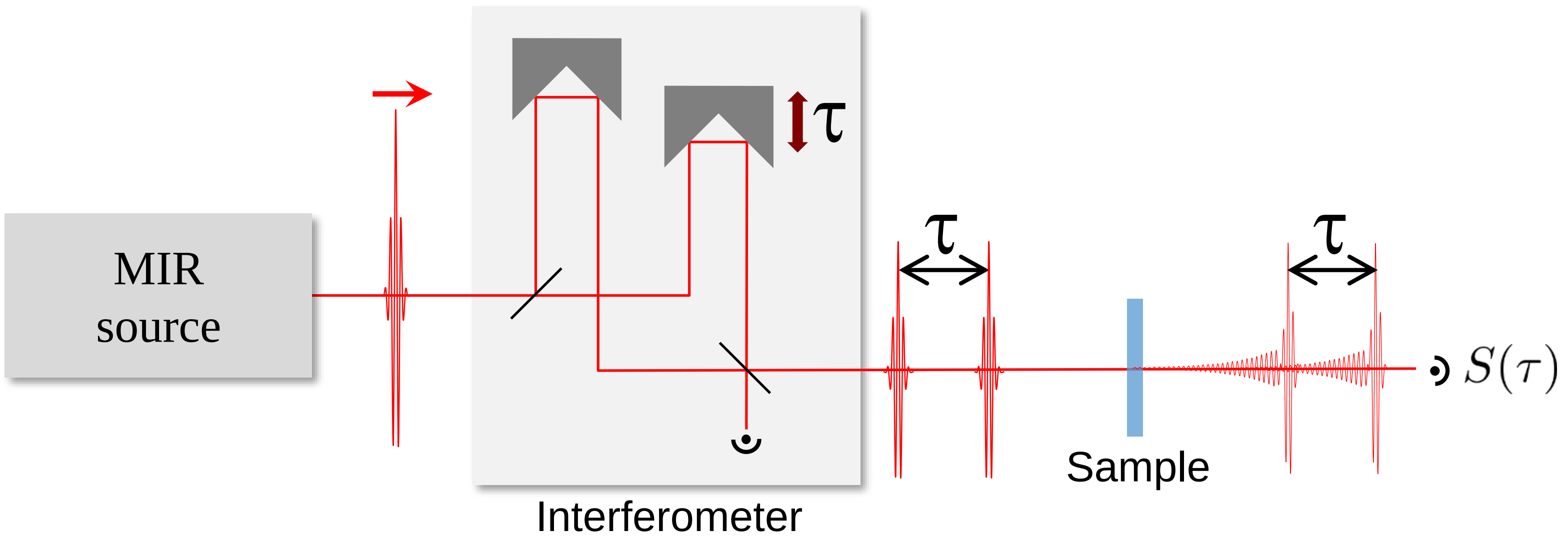


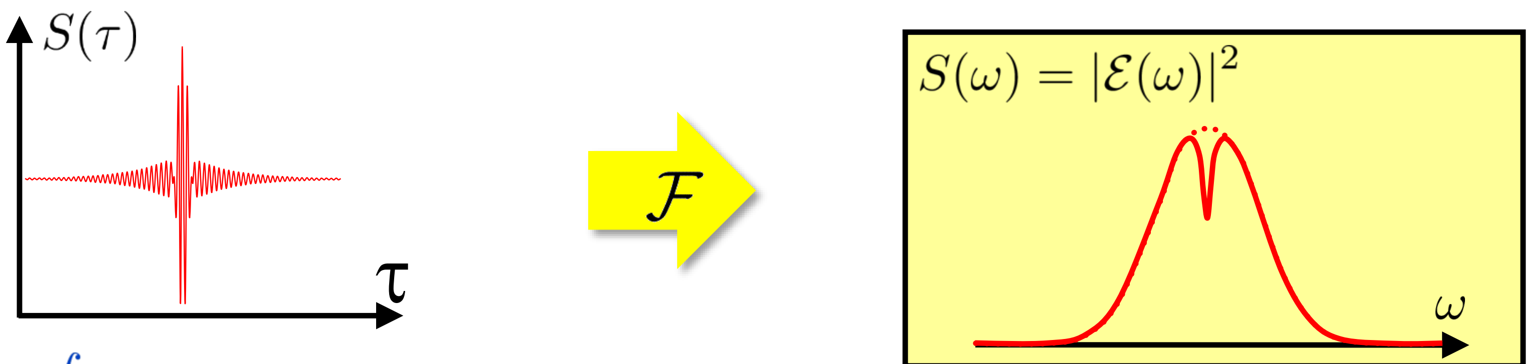


$$S(\tau) = \int |\mathcal{E}(t) + \mathcal{E}(t-\tau)|^2 dt$$

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

Fourier Transform Infrared Spectroscopy





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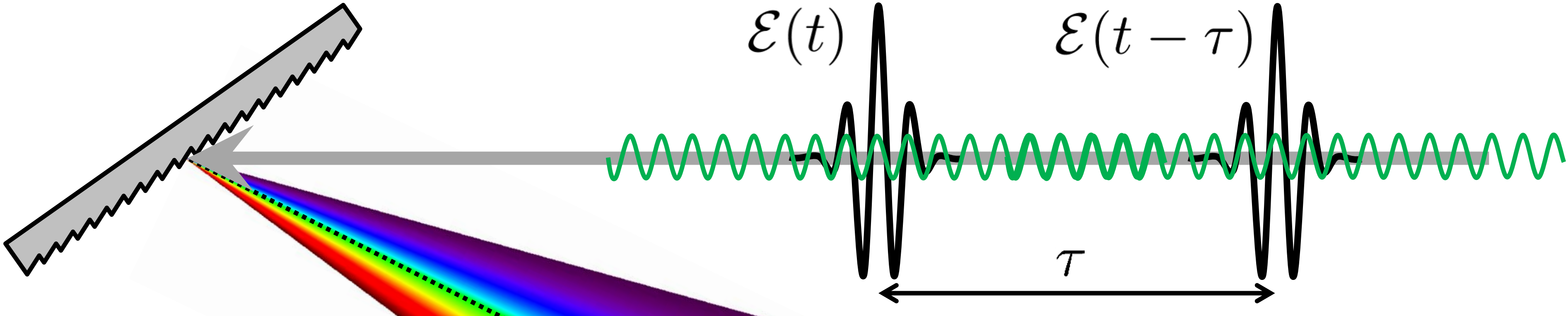
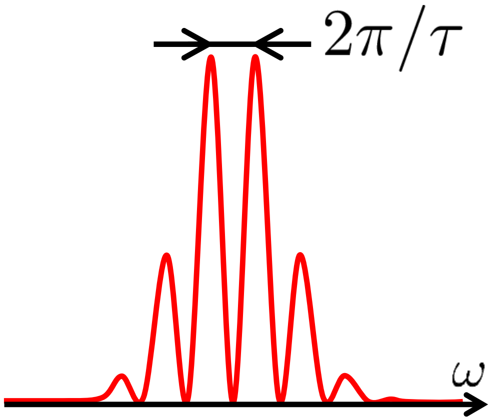
Spectral interferometry





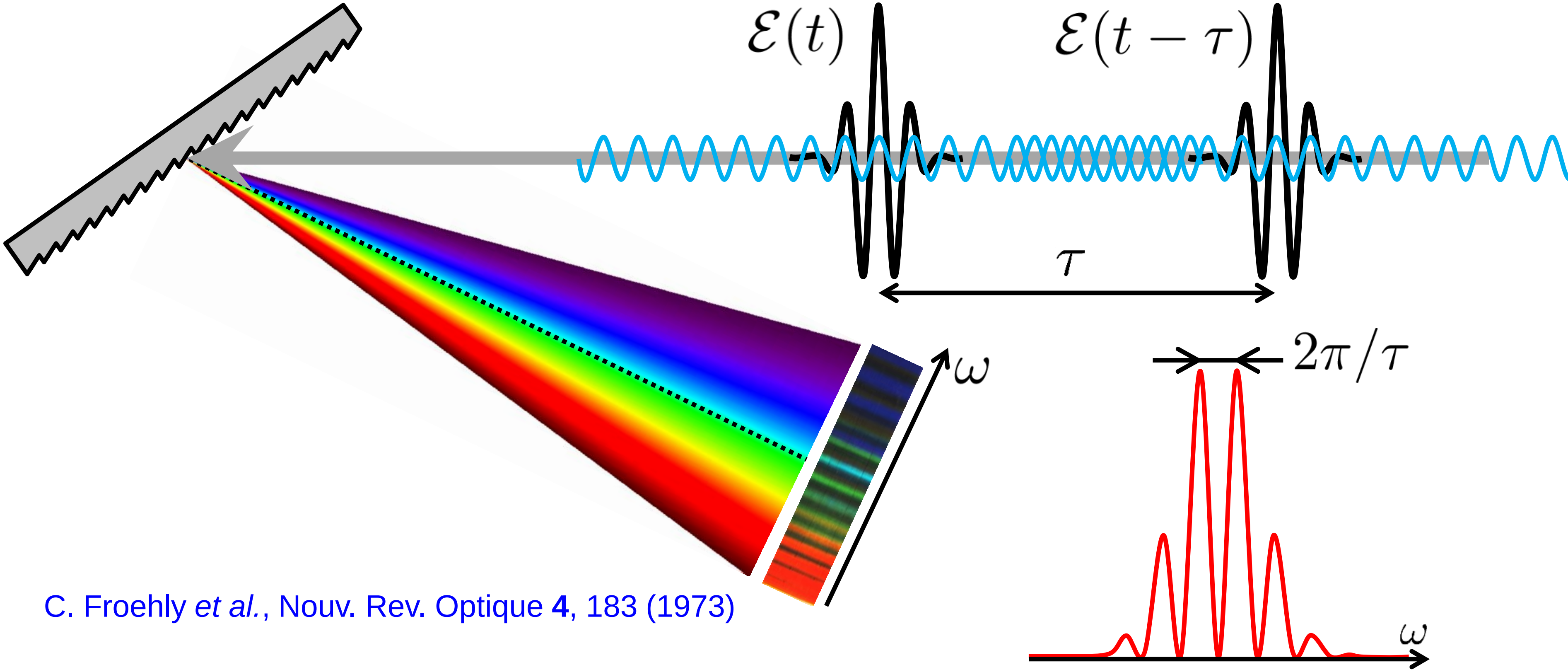
C. Froehly *et al.*, Nouv. Rev. Optique **4**, 183 (1973)

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

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

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

Spectral interferometry



C. Froehly *et al.*, Nouv. Rev. Optique **4**, 183 (1973)

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

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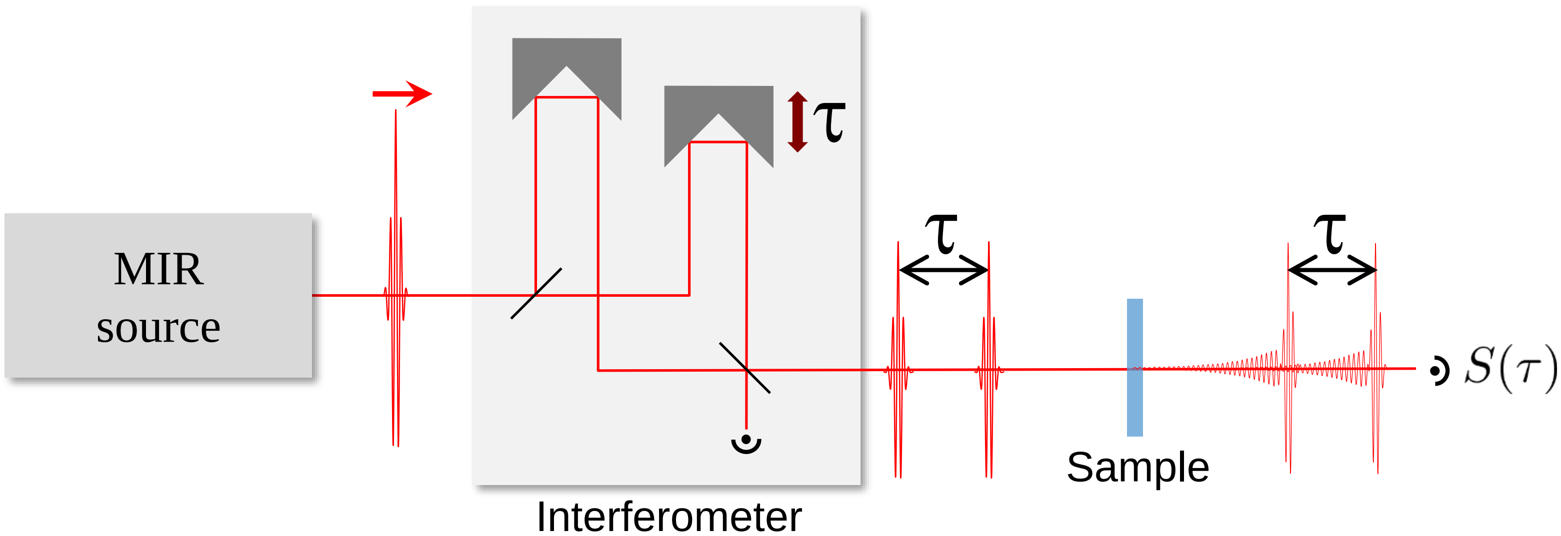
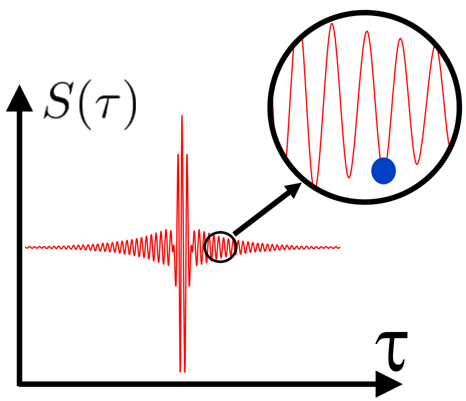
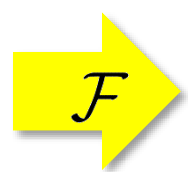
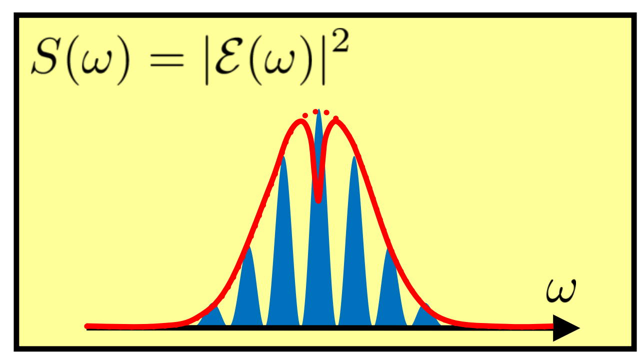
$$= 2\left|\mathcal{E}(\omega)\right|^2 \left(1 + \cos\omega\tau\right)$$

Fourier Transform Infrared Spectroscopy









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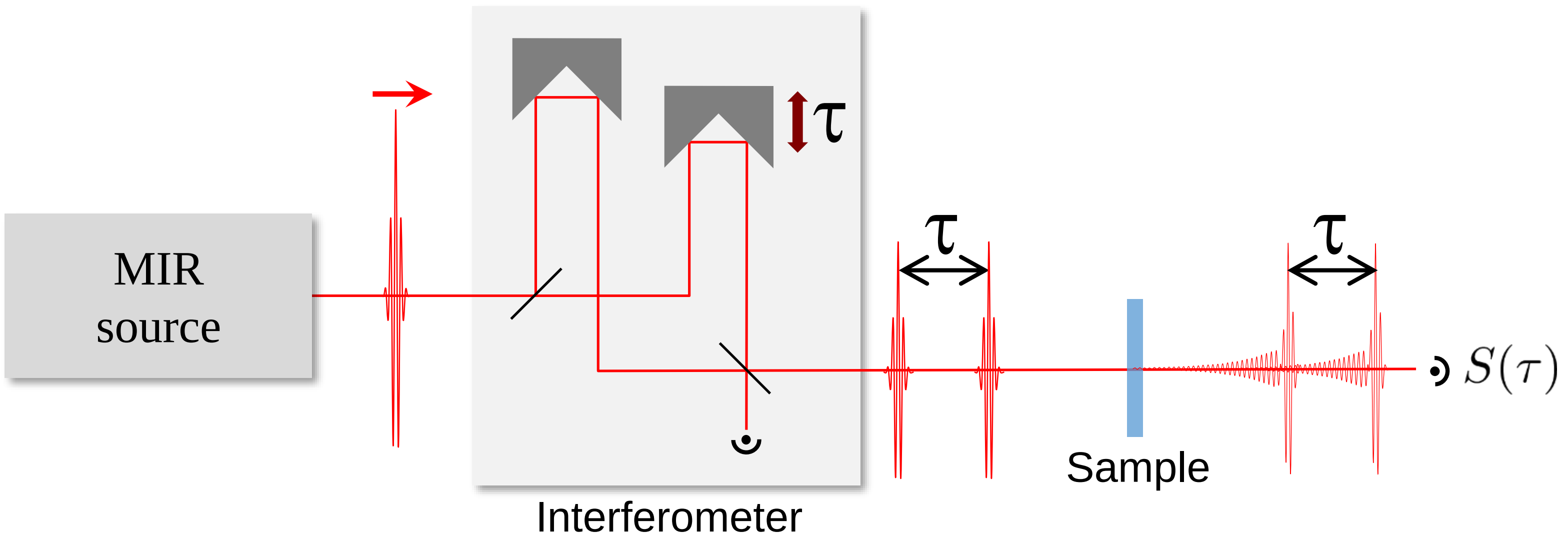
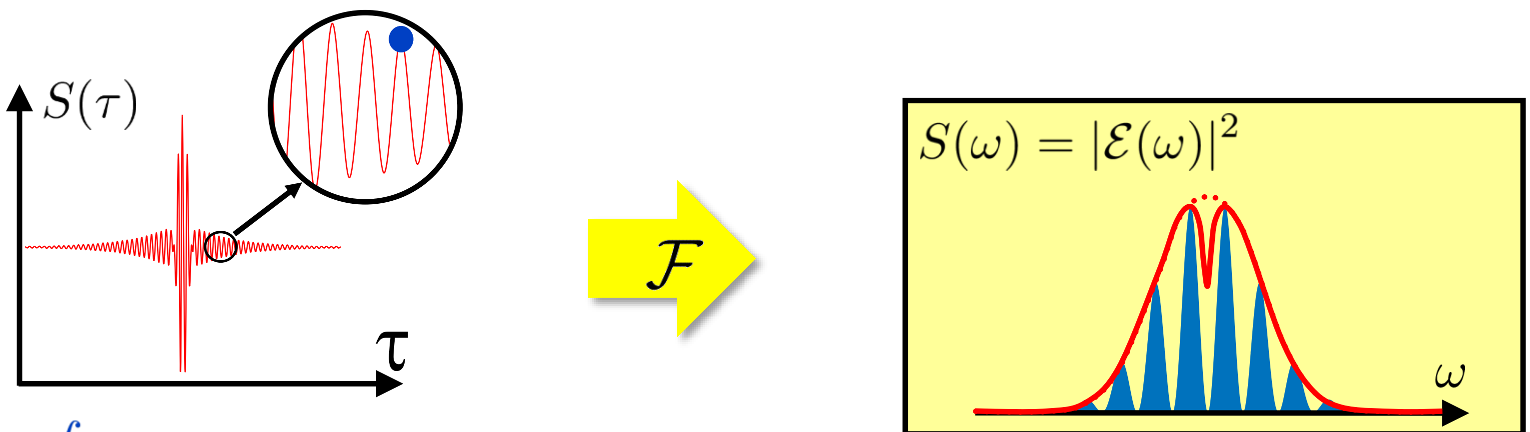


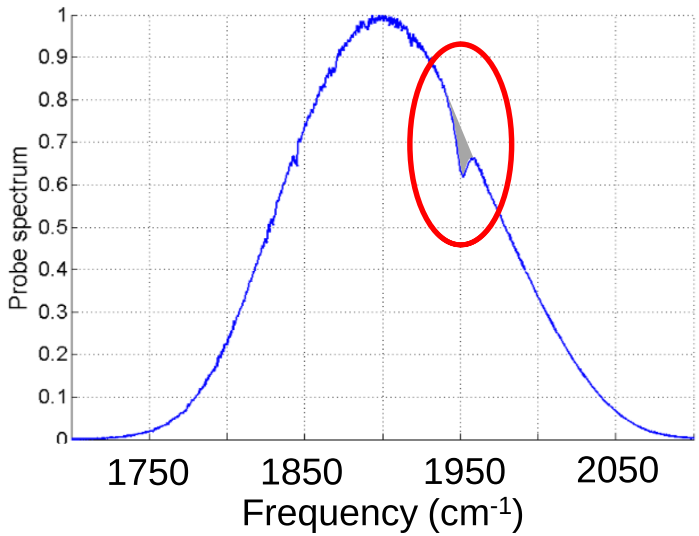


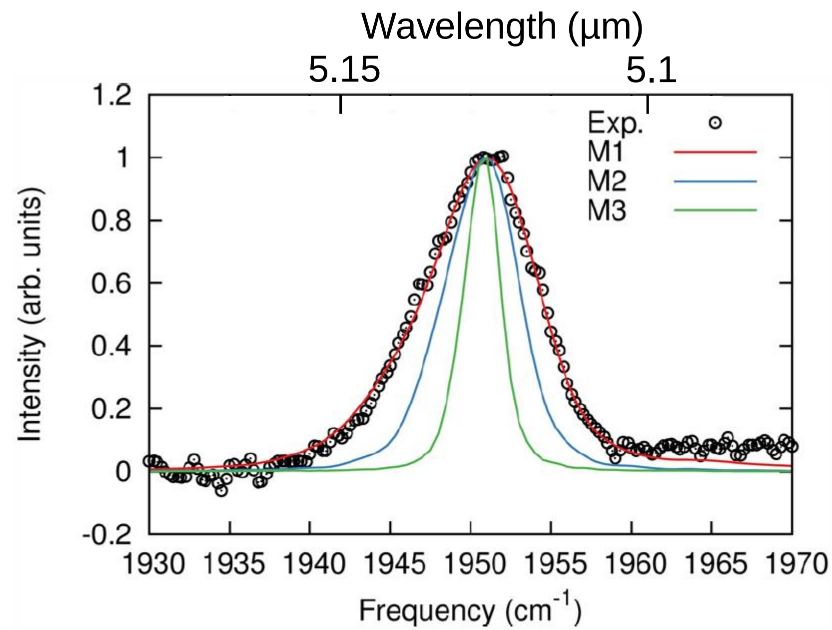
$$S(\tau) = \int |\mathcal{E}(t) + \mathcal{E}(t-\tau)|^2 dt$$

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

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

1DIR spectroscopy in carboxyhemoglobin

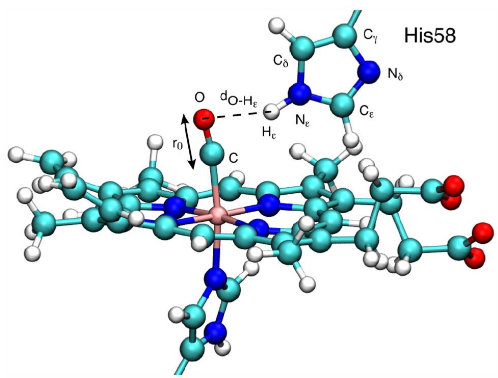




Molecular Dynamics →

$$V(r_0,t) = V(r_0,\{r_i(t)\})$$
$$\mu(r_0,t) = \mu(r_0,\{r_i(t)\})$$

→ 1D Time-dependent Schrödinger equation → Absorption spectrum

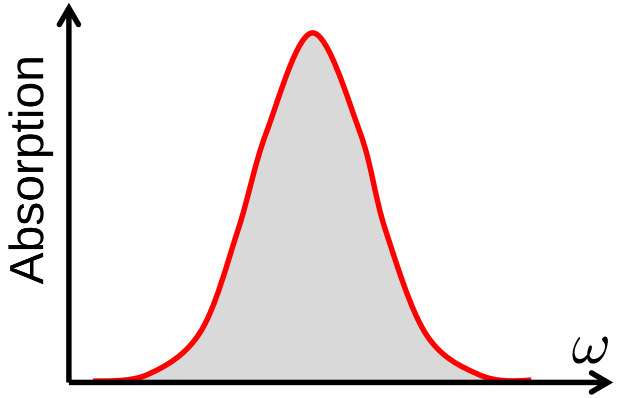


M1 : all contributions
M2 : without distal His58
M3 : heme only

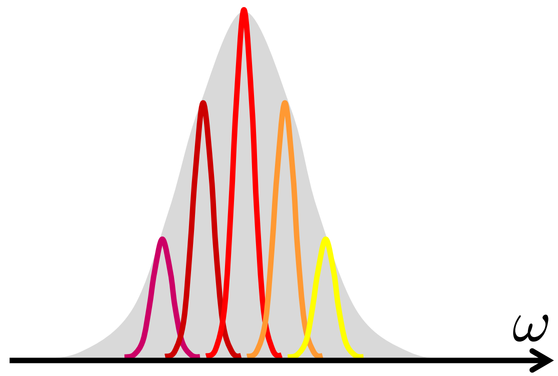
C. Falvo, L. Daniault, T. Vieille, V. Kemlin, J.-C. Lambry, C. Meier, M.H. Vos, A. Bonvalet, M. Joffre, Ultrafast dynamics of carboxy-hemoglobin: 2DIR spectroscopy experiments and simulations J. Phys. Chem. Lett. ***6****, 2216 (2015)*

Limits of linear spectroscopy

✓ Failure to distinguish between homogeneous or inhomogeneous broadening.

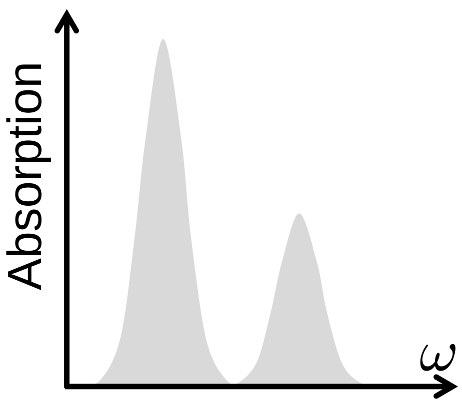


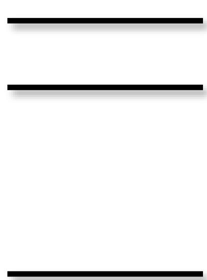
or



?

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





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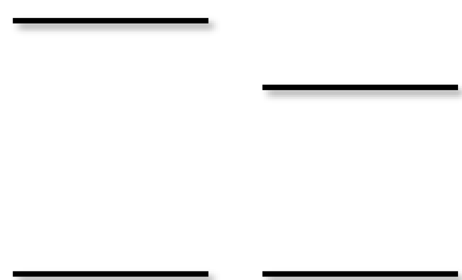


?

1. Generation of MIR femtosecond pulses
2. Shaping of MIR femtosecond pulses
3. 1DIR spectroscopy
4. 2DIR spectroscopy
5. Setting up your own 2DIR spectrometer
6. A few applications

Two-dimensional Nuclear Magnetic Resonance

Two-dimensional spectroscopy. Application to nuclear magnetic resonance

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

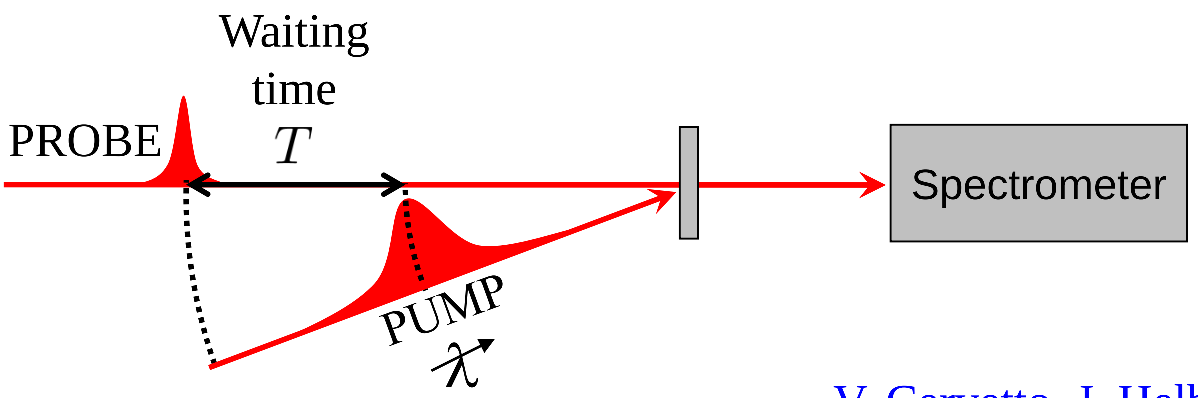
Laboratorium für physikalische Chemie, Eidgenössische Technische Hochschule, 8006 Zürich, Switzerland

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.** »

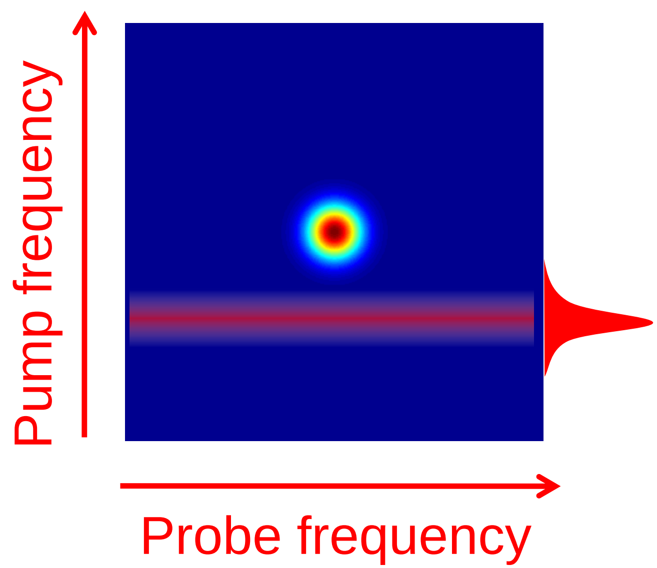
W. P. Aue, E. Bartholdi, R.R. Ernst, J. Chem. Phys. 64, 2229 (1976)

2D spectroscopy in the pump-probe geometry

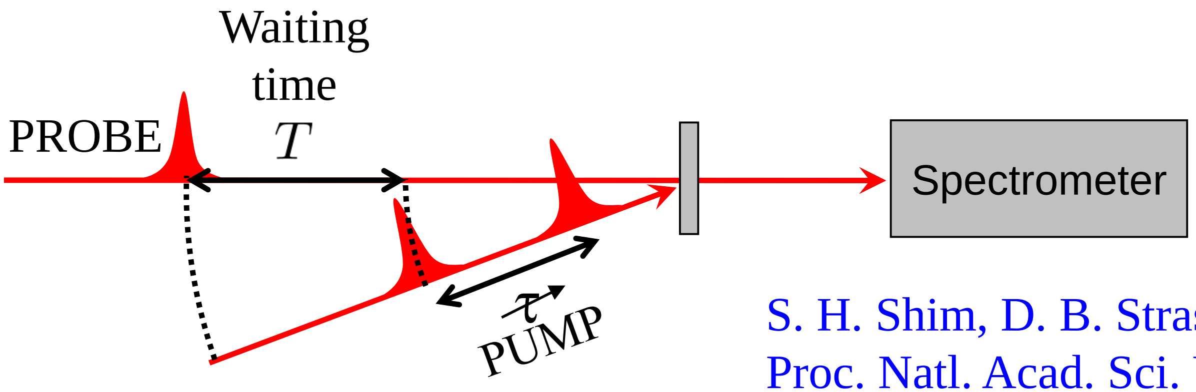


✓ Frequency domain

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

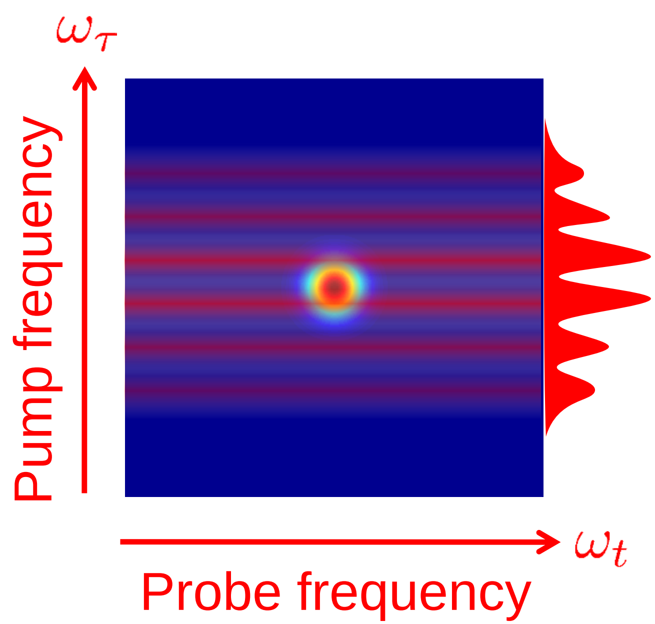


2D spectroscopy in the pump-probe geometry



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)

✓ Fourier domain



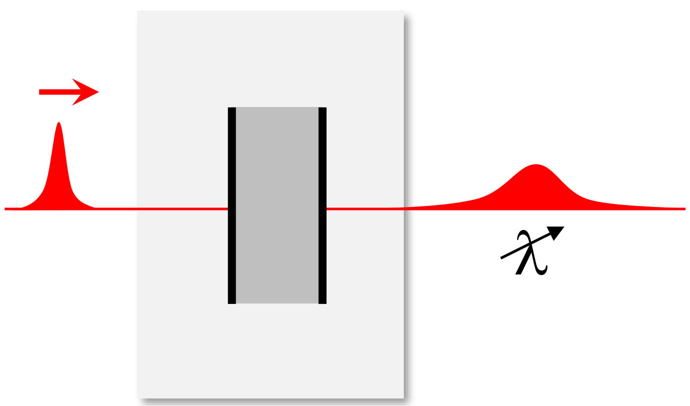
$$S(\omega_t, \tau, T)$$

$$\mathcal{F}$$

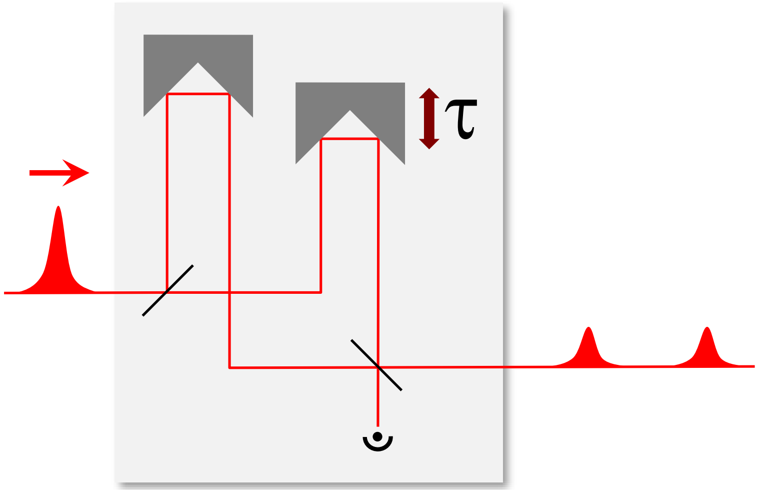
$$S(\omega_t, \omega_\tau, T)$$

Two methods for generating the pump

- ✓ Using an interferometer

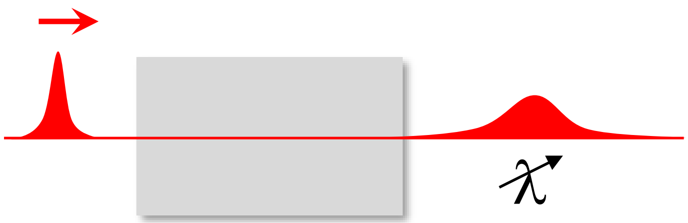


Fabry-Perot

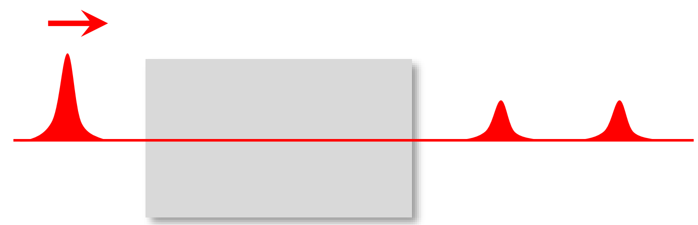


Mach-Zehnder

- ✓ Using a pulse shaper

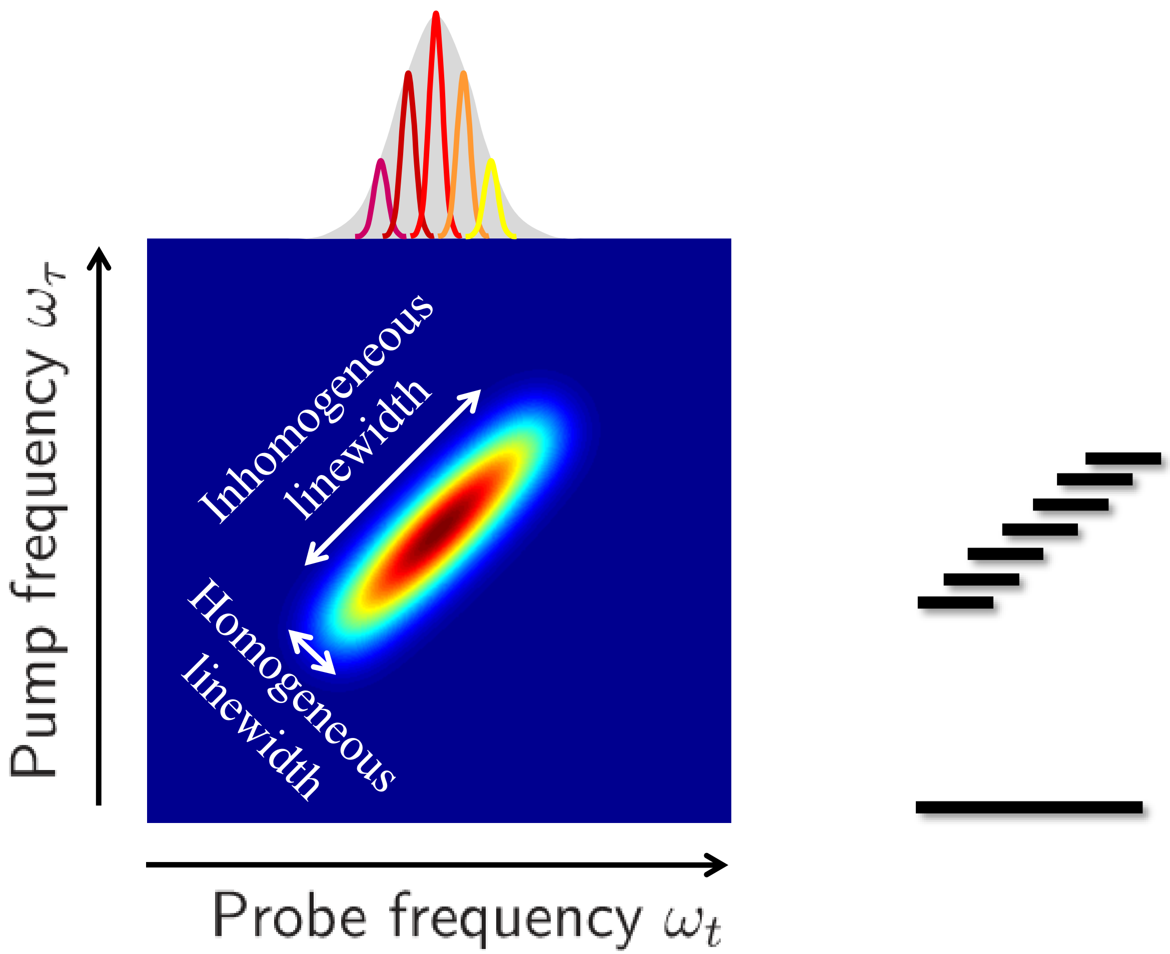


Programmable
linear filter



Programmable
linear filter

2D spectrum expected for a 2-level system



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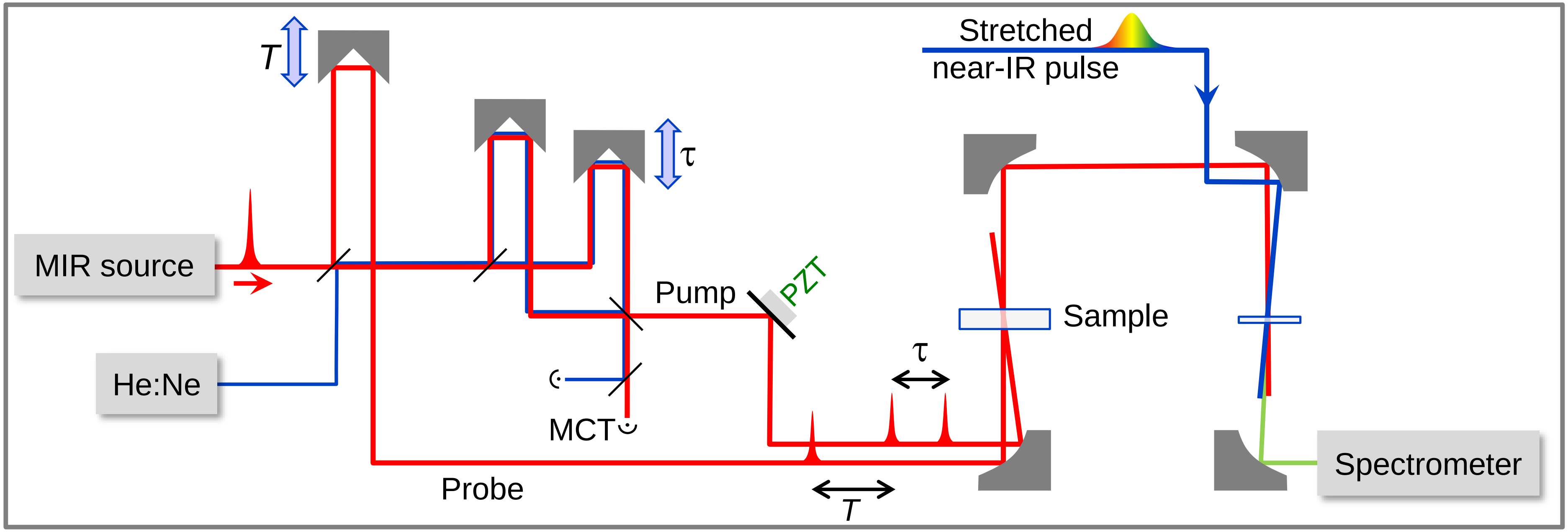
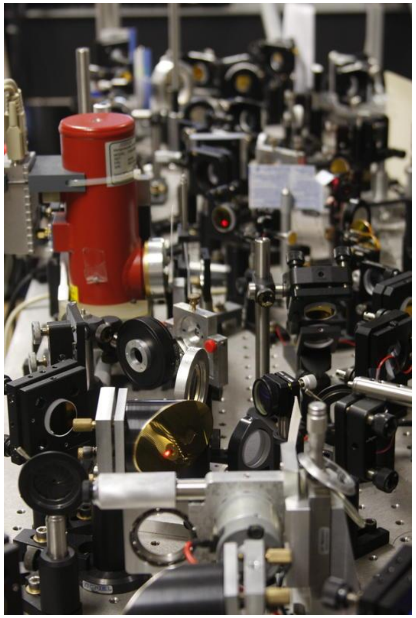
2DIR spectrometer



- ✓ Fourier-domain approach (better time/frequency resolution)
- ✓ Interferometer approach (better spectral resolution)
- ✓ Chirped Pulse Upconversion (with Fourier processing)
- ✓ Optical path tracking using a He:Ne laser
- ✓ Zero determination using MCT detector
- ✓ Pump-probe delay modulation with a PZT (to get rid of pump scattering)
- ✓ Dry-air enclosure (to get rid of water vapor absorption)



1. Generation of MIR femtosecond pulses
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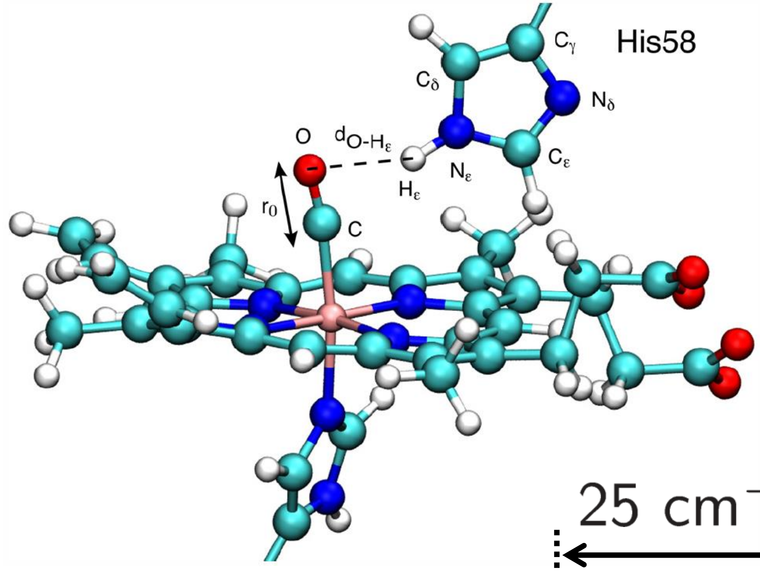
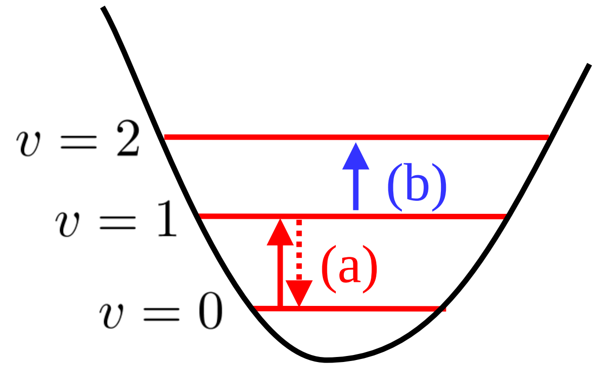
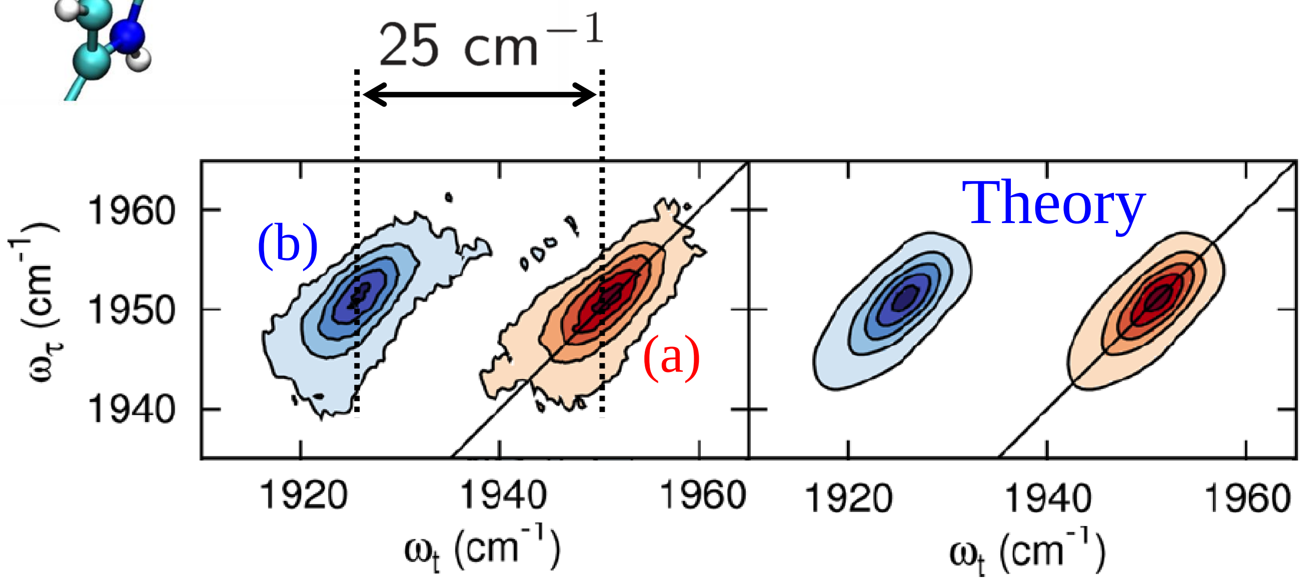
2DIR spectroscopy in carboxy-hemoglobin (HbCO)

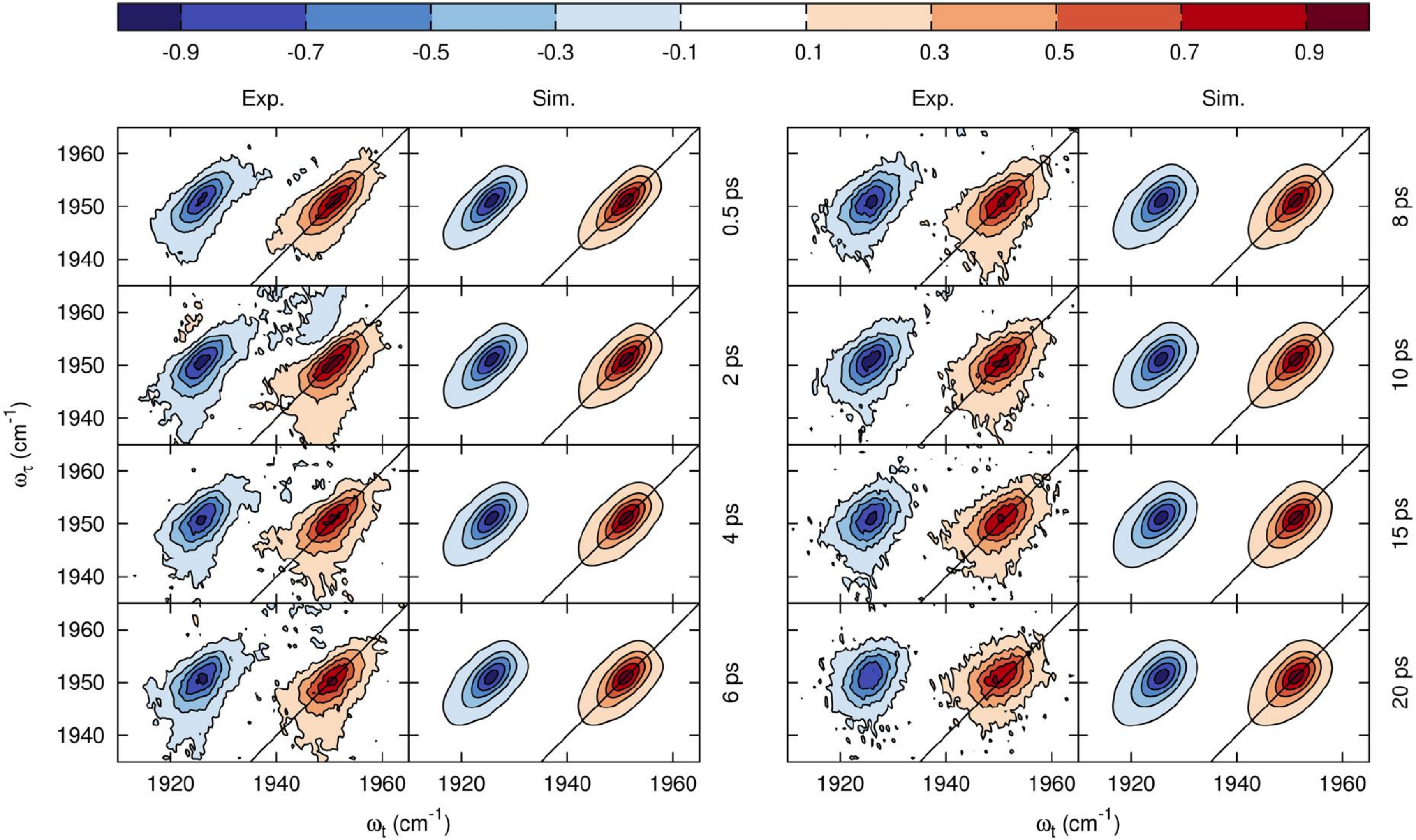






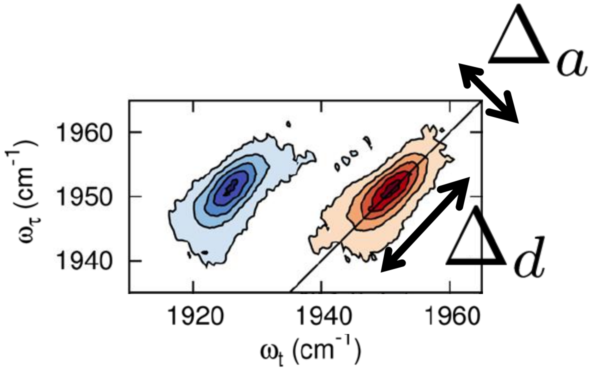
C. Falvo, L. Daniault, T. Vieille, V. Kemlin, J.-C. Lambry, C. Meier, M.H. Vos, A. Bonvalet, M. Joffre,
Ultrafast dynamics of carboxy-hemoglobin: 2DIR spectroscopy experiments and simulations
J. Phys. Chem. Lett. ***6****, 2216 (2015)*

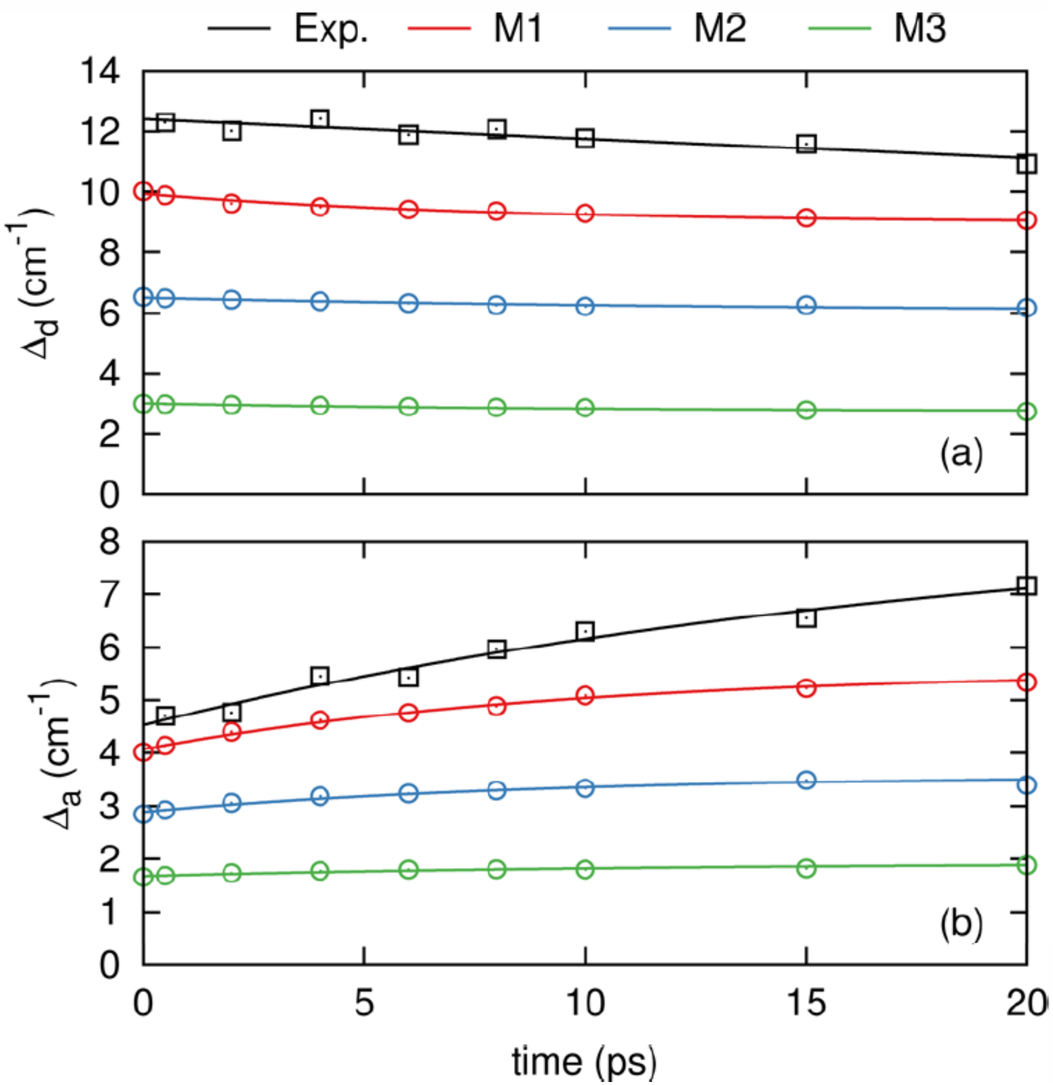
Evolution with waiting time (1)



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 (2)

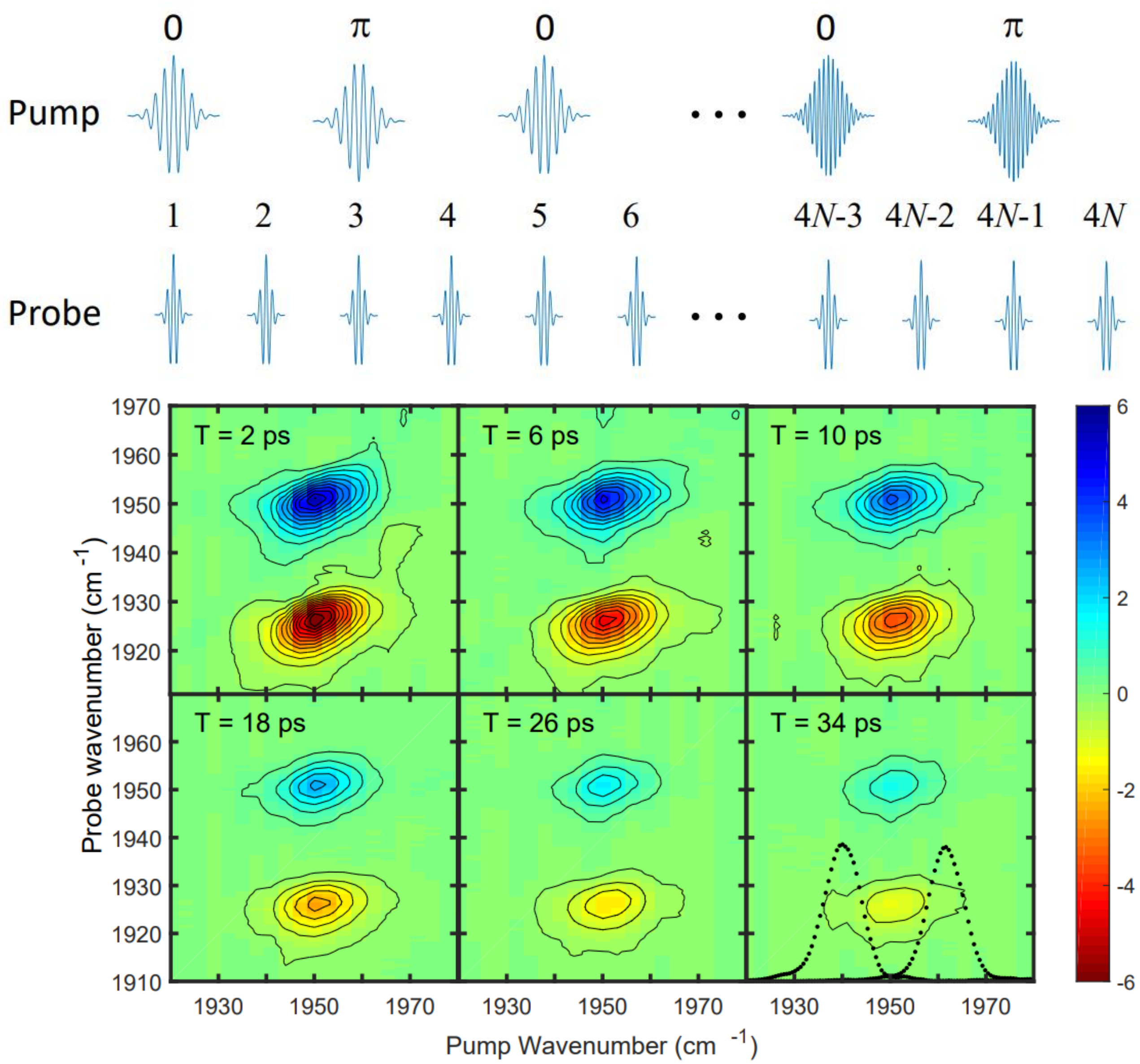




M1 : all contributions
M2 : without distal His58
M3 : heme only

C. Falvo et al., J. Phys. Chem. Lett. ***6****, 2216 (2015)*

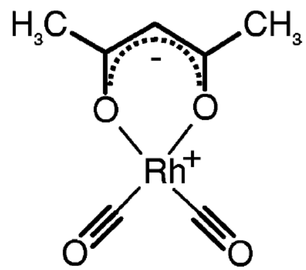
2DIR spectroscopy in HbCO using a pulse shaper

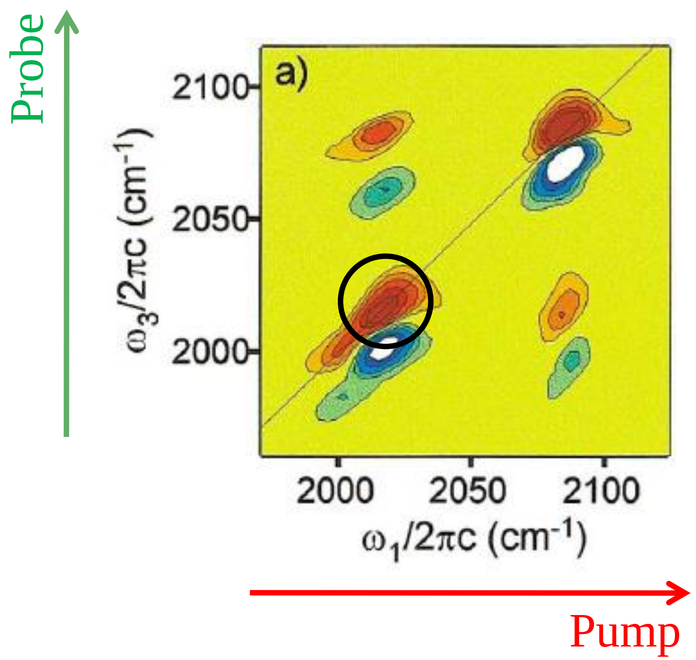


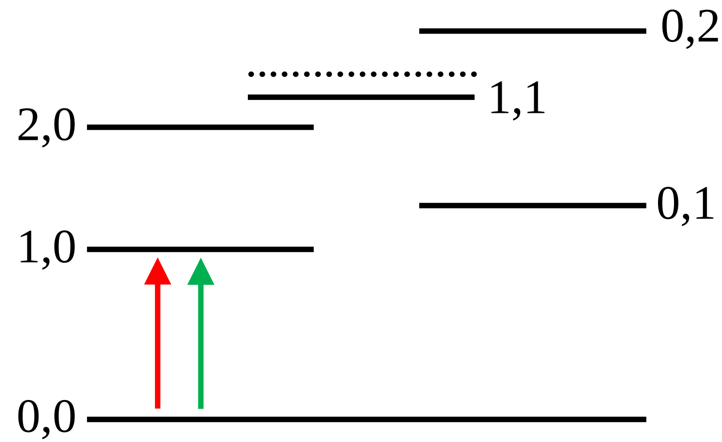
J.A. De La Paz, A. Bonvalet, M. Joffre, Opt. Express **27**, 4140 (2019)

2DIR spectroscopy with two vibrational modes

Example : RDC (acetylacetonato dicarbonyl rhodium(I))





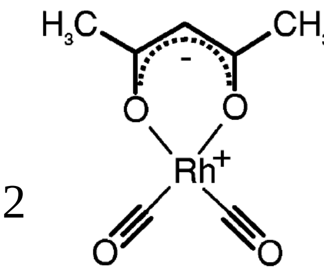


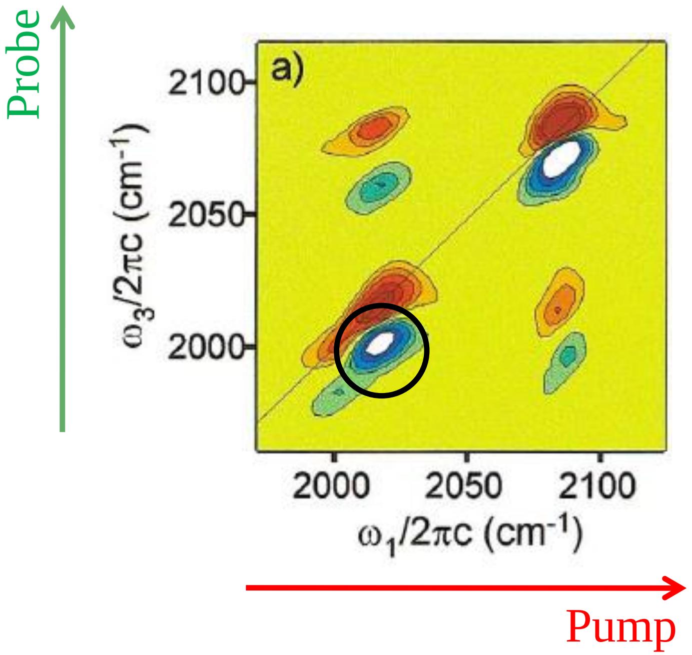
Absorption saturation

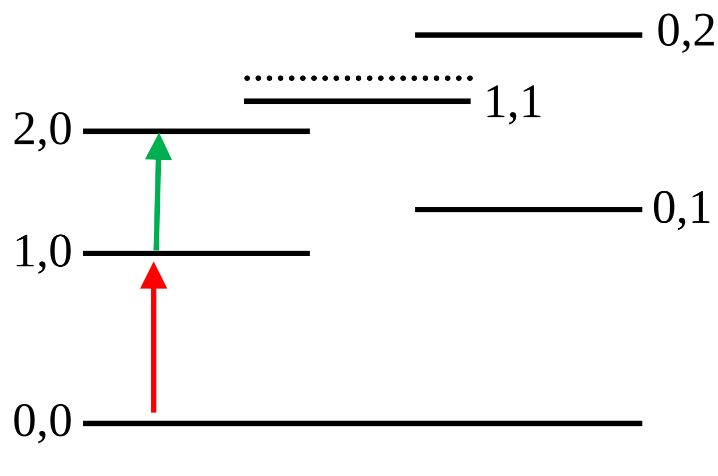
N. Demirdoven, M. Khalil, A. Tokmakoff
Correlated vibrational dynamics revealed by two-dimensional infrared spectroscopy
Phys. Rev. Lett. **89**, 237401 (2002)

2DIR spectroscopy with two vibrational modes

Example : RDC (acetylacetonato dicarbonyl rhodium(I))







Anharmonicity

N. Demirdoven, M. Khalil, A. Tokmakoff

Correlated vibrational dynamics revealed by two-dimensional infrared spectroscopy

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

2DIR spectroscopy with two vibrational modes

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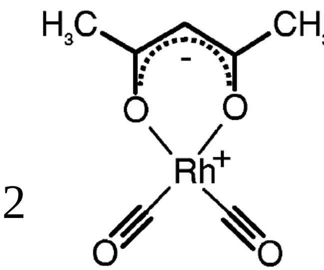

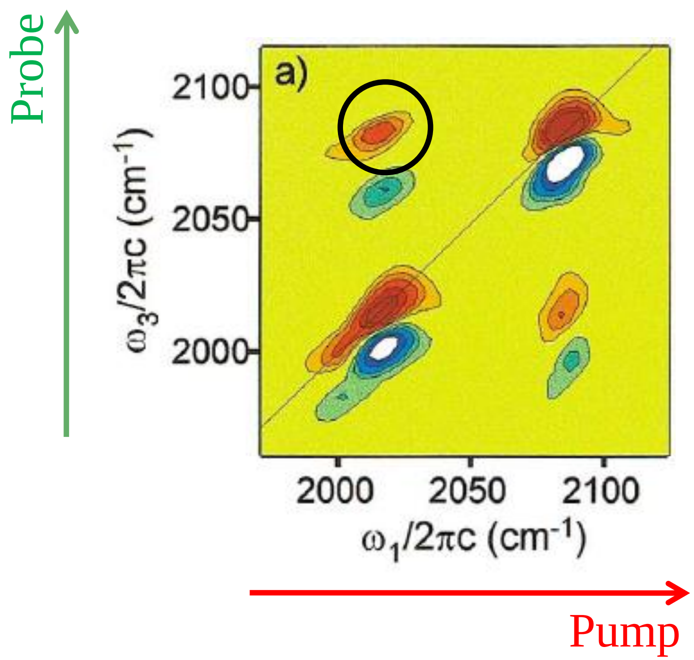

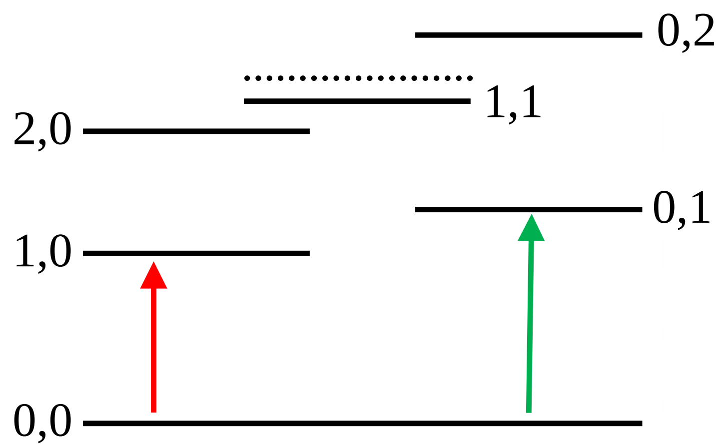

Coupling between two vibrational modes

N. Demirdoven, M. Khalil, A. Tokmakoff
Correlated vibrational dynamics revealed by two-dimensional infrared spectroscopy
Phys. Rev. Lett. **89**, 237401 (2002)

2DIR spectroscopy with two vibrational modes

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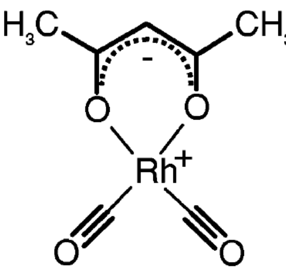

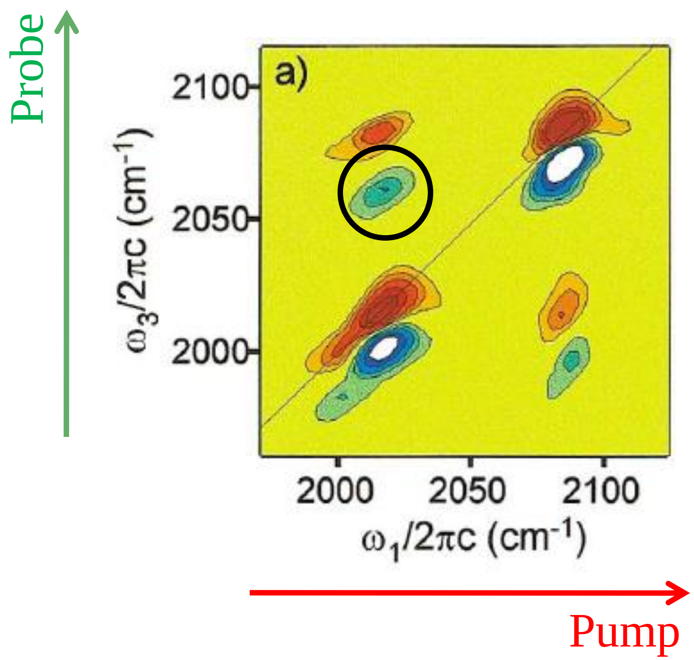

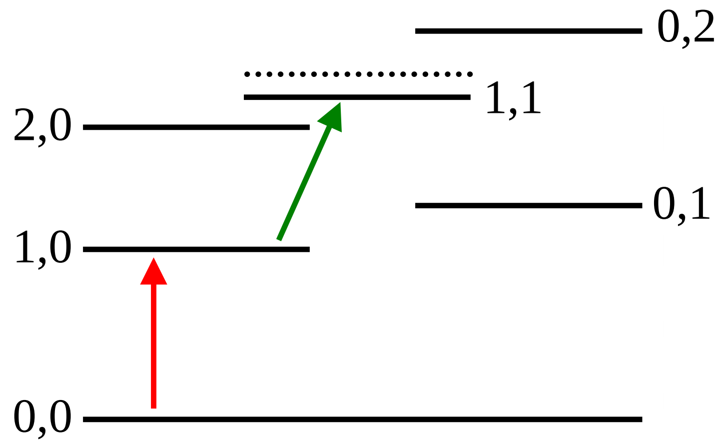

Transitions to combination bands

N. Demirdoven, M. Khalil, A. Tokmakoff
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Phys. Rev. Lett. **89**, 237401 (2002)

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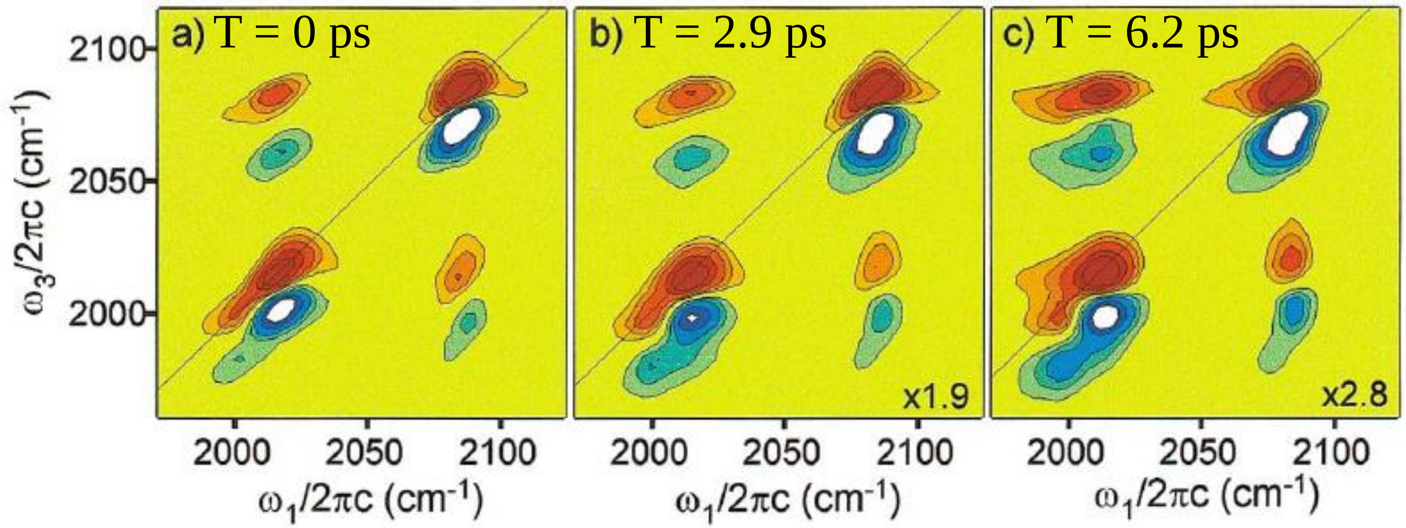
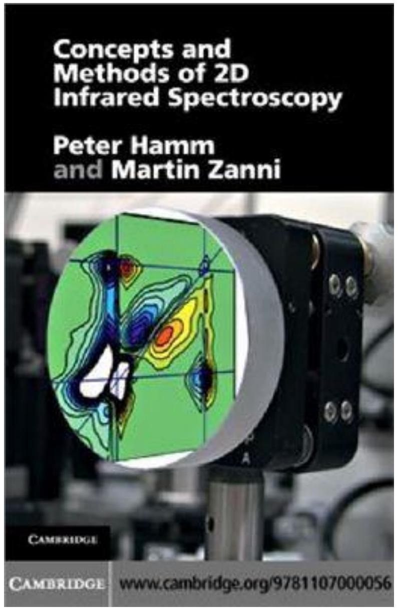


Evolution as a fonction of waiting time T

N. Demirdoven, M. Khalil, A. Tokmakoff
Correlated vibrational dynamics revealed by two-dimensional infrared spectroscopy
Phys. Rev. Lett. **89**, 237401 (2002)

References



P. Hamm and M. Zanni
Concepts and methods of 2D infrared spectroscopy
Cambridge University Press (2011)

M. Cho
Coherent two-dimensional optical spectroscopy
Chem. Rev. **108**, 1331 (2008)

J.P. Ogilvie and K.J. Kubarych
Multidimensional Electronic and Vibrational Spectroscopy: An Ultrafast Probe of Molecular Relaxation and Reaction Dynamics
Adv. At. Mol. Opt. Phys. **57**, 249 (2009)

P. Nuernberger, K.F. Lee, M. Joffre
Femtosecond spectroscopy from the perspective of a global multidimensional response function
Acc. Chem. Res. **42**, 1433 (2009)