Two-Dimensional Infrared (2DIR) spectroscopy as a probe of environment effects

A. Jouan[1], M. Jonušas[1#], W. Chin[1], J. Helbing[2], J. Vincent[1], C. Crépin[1]

[1] *ISMO, UMR 8214, CNRS, Université Paris-Saclay, Orsay*
[#] *current affiliation : LOB, INSERM-CNRS, Institut Polytechnique de Paris, Palaiseau*
[2] *Department of Chemistry, University of Zurich, Zurich*

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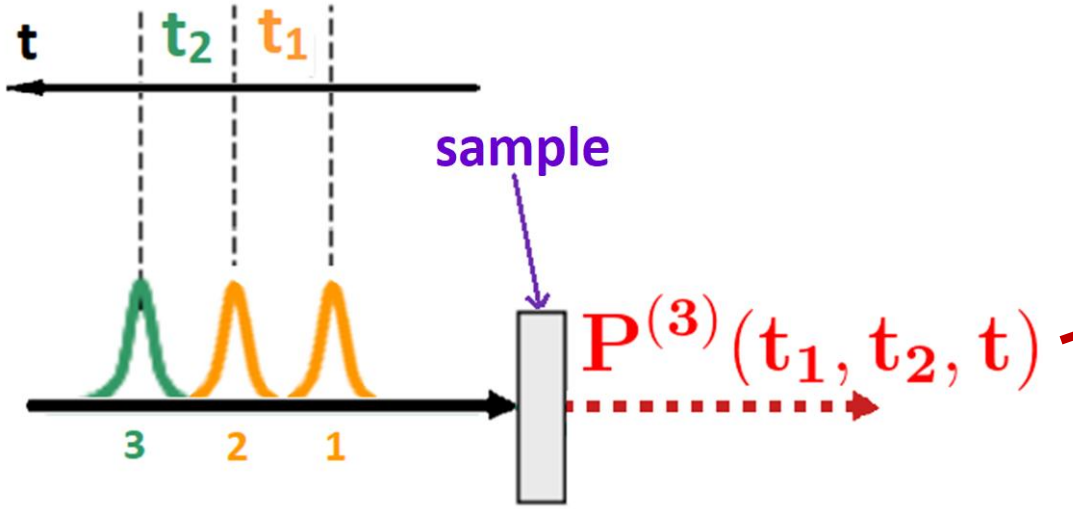
Introduction

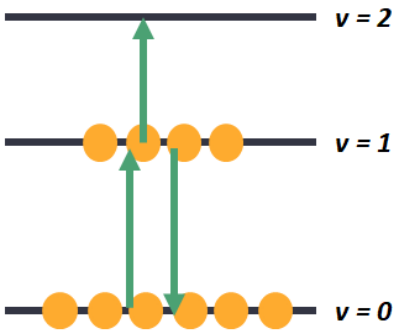
Probing **interactions** and **environment effets** in the condensed phase: **vibrational dynamics** in the ground state

2DIR spectroscopy: non-linear technique



Resonant Degenerate four-wave mixing:

$\omega_1 = \omega_2 = \omega_3 = \omega_{signal}$



3rd order macroscopic polarization:

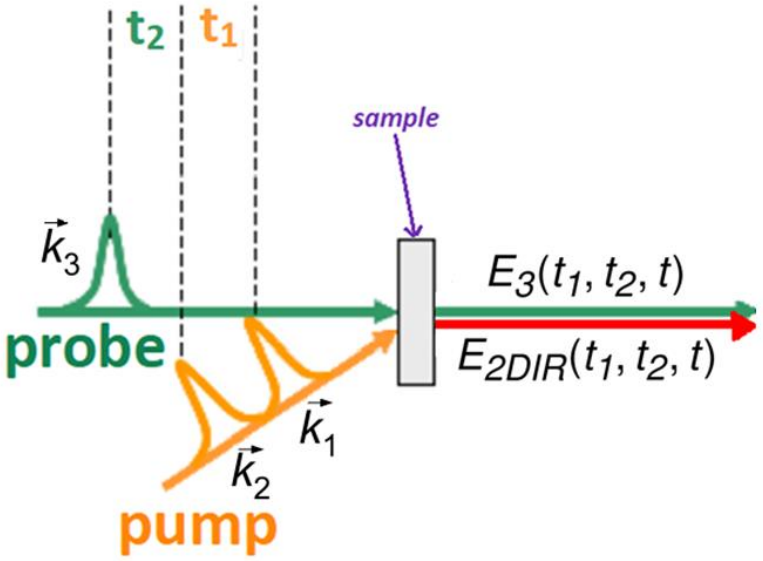
- vibrational structure and anharmonicities;
- populations (T_1) and phase (T_2) dynamics;
- couplings, energy transfers between modes

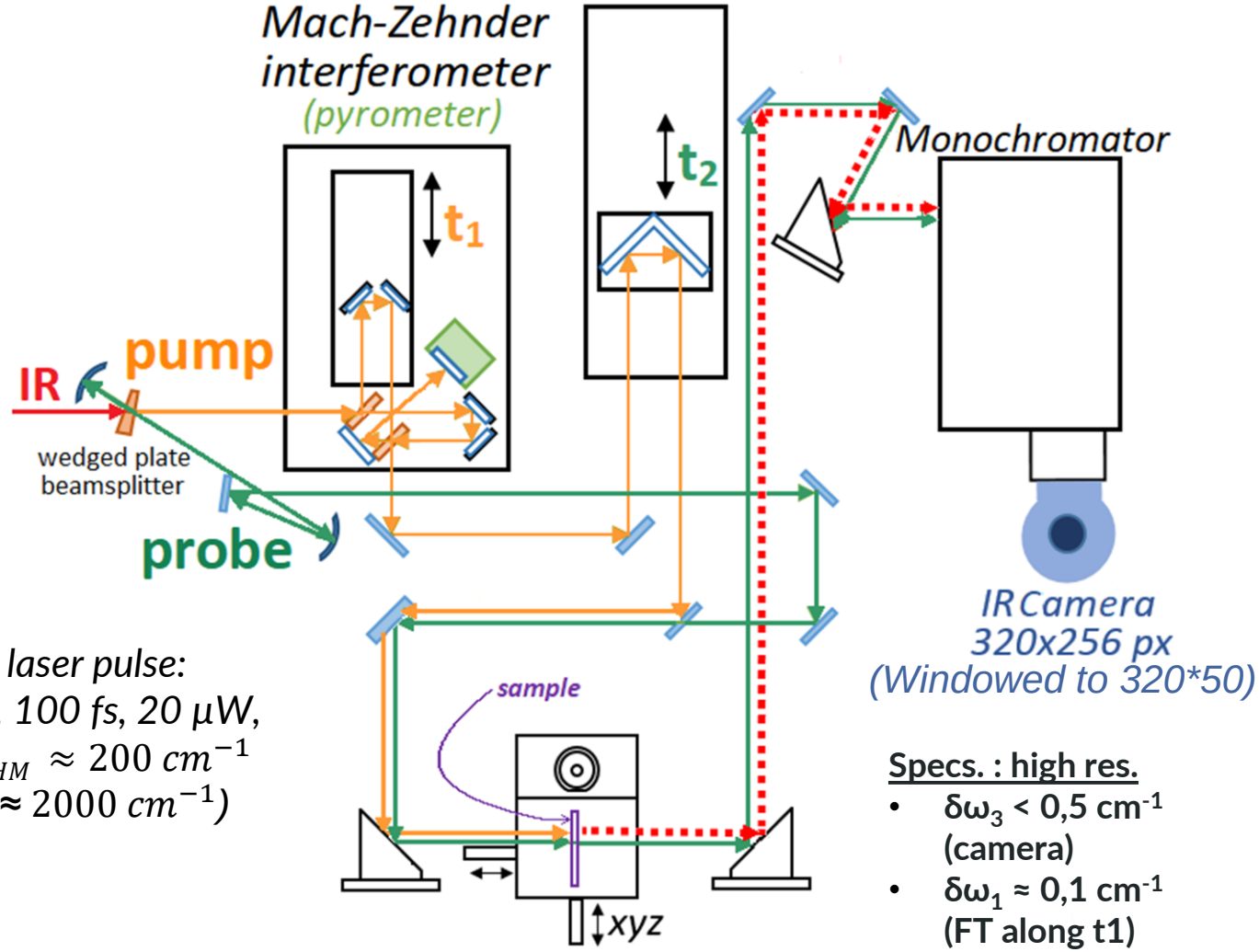
2DIR signal : $\mathbf{S}(\omega_1, \mathbf{t_2}, \omega_3) \propto \int_{-\infty}^{\infty} \mathbf{dt_1} \int_{-\infty}^{\infty} \mathbf{dt}\ \mathbf{P}^{(3)}(\omega_1, \mathbf{t_2}, \omega_3)\mathbf{e}^{\mathbf{i}\omega_1 \mathbf{t_1}}\mathbf{e}^{\mathbf{i}\omega_3 \mathbf{t}}$

Experimental setup

Pump-probe geometry **[1]**

$$\overrightarrow{k_{2DIR}} = \pm\vec{k_1} \mp \vec{k_2} + \vec{k_3} = \vec{k_3}$$





IR laser pulse:
(3 kHz, 100 fs, 20 µW,
$\Delta\nu_{FWHM} \approx 200\ cm^{-1}$
$@\ \nu \approx 2000\ cm^{-1}$*)*

Specs. : high res.

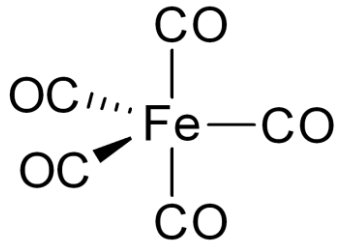
- $\delta\omega_3$ < 0,5 cm^{-1} (camera)
- $\delta\omega_1$ ≈ 0,1 cm^{-1} (FT along t1)

2DIR signal : $\mathbf{S(\omega_1, t_2, \omega_3)}$

excitation freq. — detection freq.

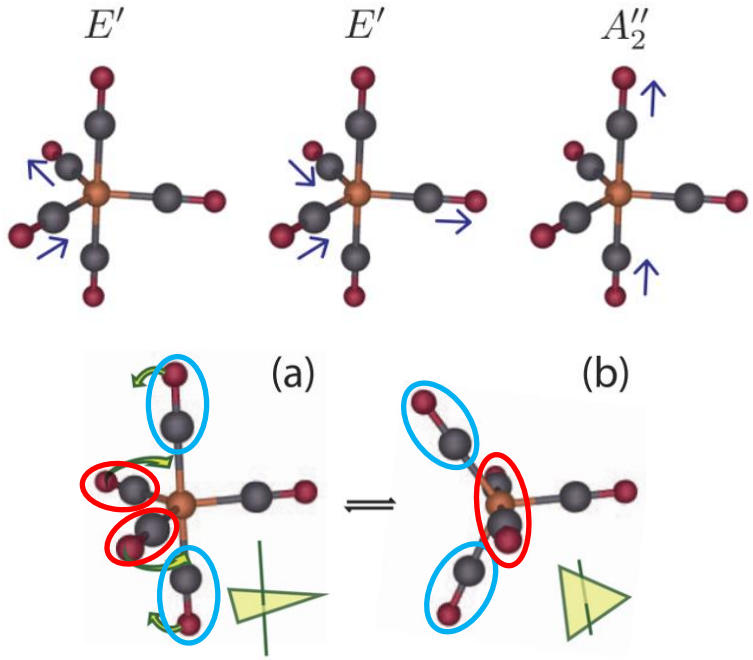
[1] Helbing and Hamm, In: JOSA B 28 (Jan. 2011), pp. 171–178.

$Fe(CO)_5$ vibrational structure and dynamics

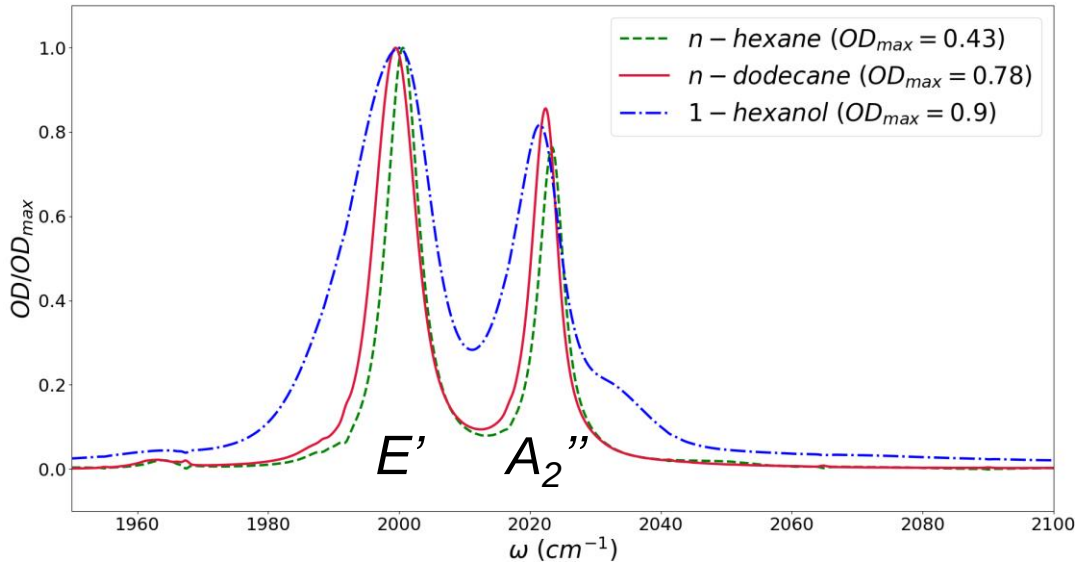


Good « test » molecule:

- Well documented
- High transition dipole
- Interesting dynamics



C≡O stretching modes and Berry pseudo-rotation mechanism ([2], fig. from [3])

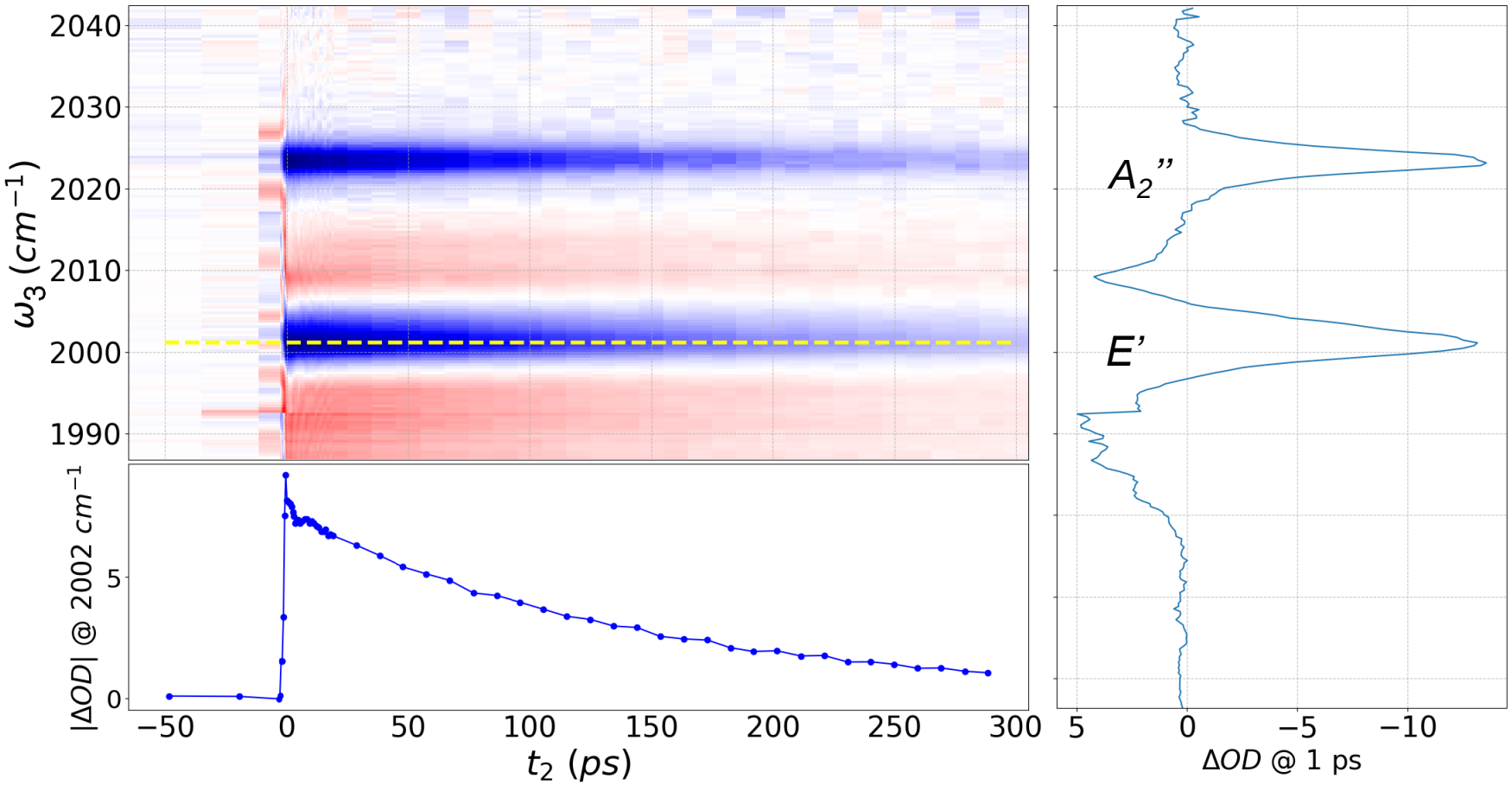


FTIR spectra of $Fe(CO)_5$ in different solvants at room temperature: hexane, dodecane, and 1-hexanol (η = 0.3, 1.3, 4.4 mPa.s, resp.)

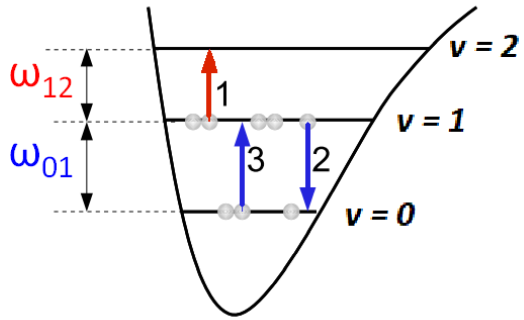
→ **We expect the transfer to happen slower as the viscosity increases**

[2] R. Stephen Berry, *J. Chem. Phys.* 32 (3), pp 933–938 (1960)
[3] Thon et al. *J. Chem. Phys.* 156, 024301 (2022)

Population relaxation dynamics



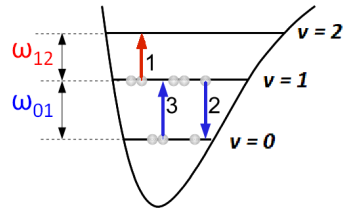
Pump-probe spectrum in hexane



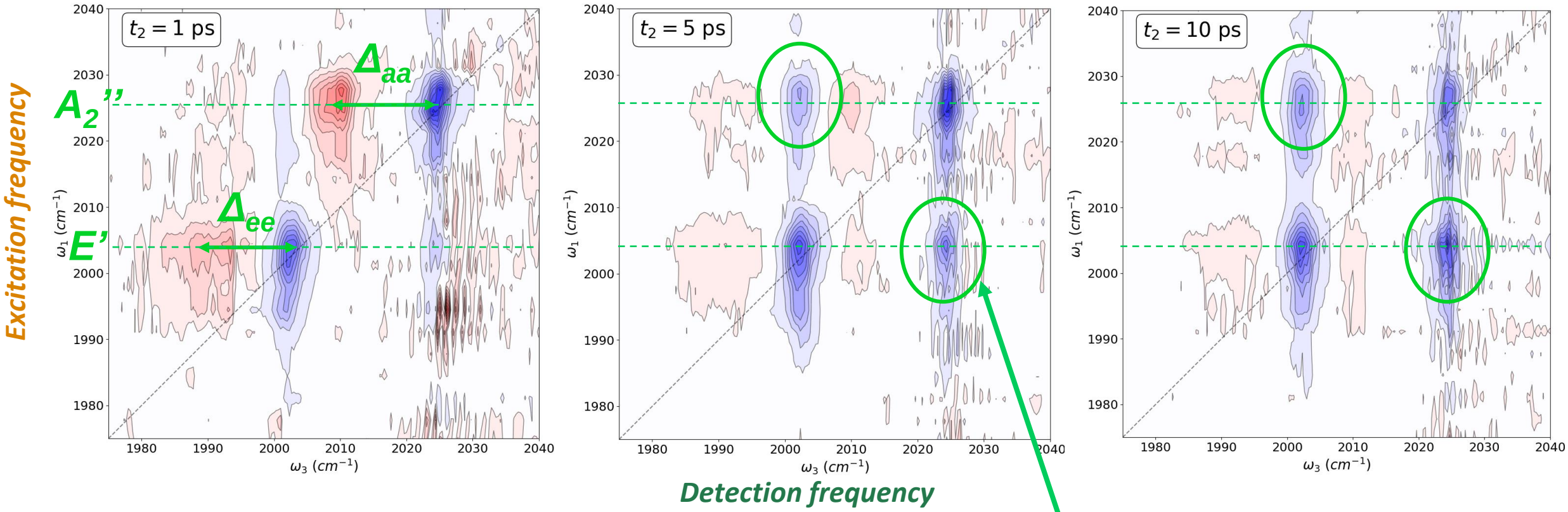
Transitions induced by the probe beam

Solvent	T_1 (ps)
n-hexane	155 ± 10
n-dodecane	145 ± 10
1-hexanol	100 ± 10

2DIR spectra of $Fe(CO)_5$



2DIR spectra for t_2 = 1, 5, and 10 ps in hexane



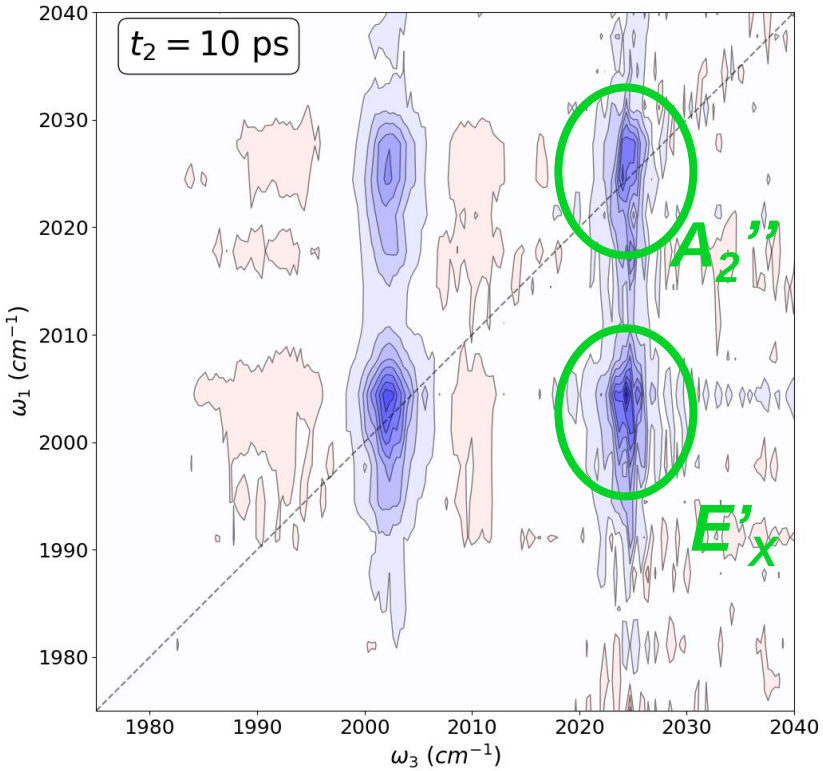
Solvent	Δ_{ee} (cm^{-1})	Δ_{aa} (cm^{-1})
n-hexane	11.5 ± 0.5	16.3 ± 1.0
n-dodecane	13 ± 1	14.4 ± 0.5
1-hexanol	12 ± 1	14 ± 1

Cross-peaks appear as a sign of a transfer occurring between the two modes

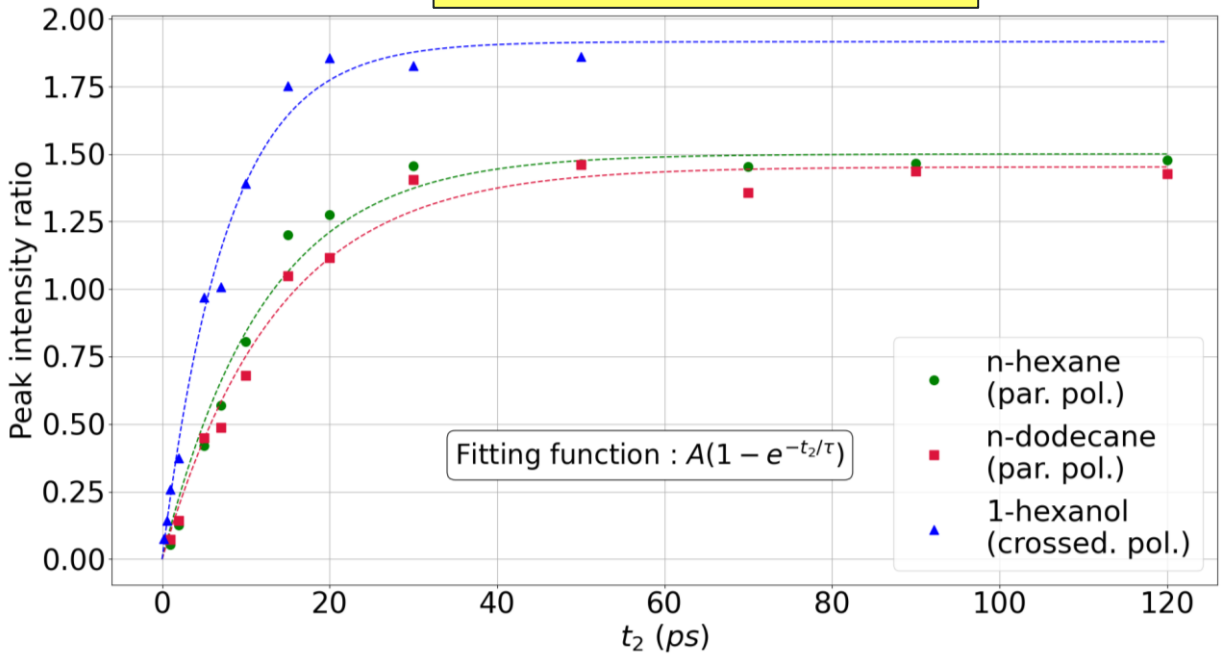
[4] Cahoon et al. *Science* 319, 1820 (2008)

Transfer dynamics

2DIR spectrum for t_2 = 10 ps in hexane

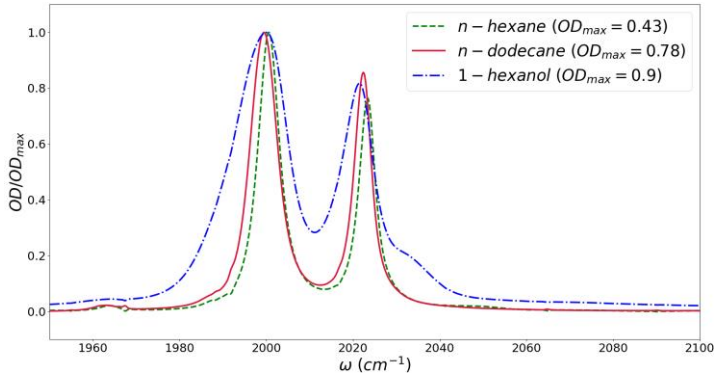


E'_X:A_2'' peak intensity ratio



Solvent	T_1 (ps)	τ (ps)	η (mPa.s)
n-hexane	155 ± 10	12.1 ± 1.1	0.3
n-dodecane	145 ± 10	13.7 ± 1.2	1.3
1-hexanol	100 ± 10	7.7 ± 0.8	4.4

We expected the transfer time to be longer as the viscosity increases : Other phenomena in hexanol ?



[4] Cahoon et al. *Science* 319, 1820 (2008)

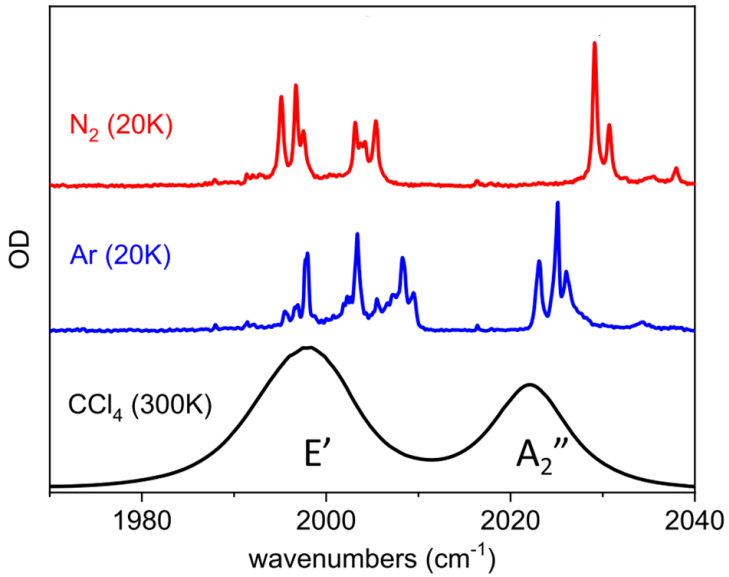
Conclusion

- 2DIR is a **powerful tool** for studying vibrational dynamics
- We observe **solvent effects** on transfer dynamics

Prospects

Studies in cryogenic matrices:

- **T<25K,** Δν~0,2-2 cm^{-1}
- **Site effects** on the structure and dynamics
- **2DIR spectroscopy** to disentangle complex spectral structures



FTIR absorption spectra of $Fe(CO)_5$ in solution and in matrices [3]

[3] Thon et al. *J. Chem. Phys.* 156, 024301 (2022)

Supplements

Bibliography

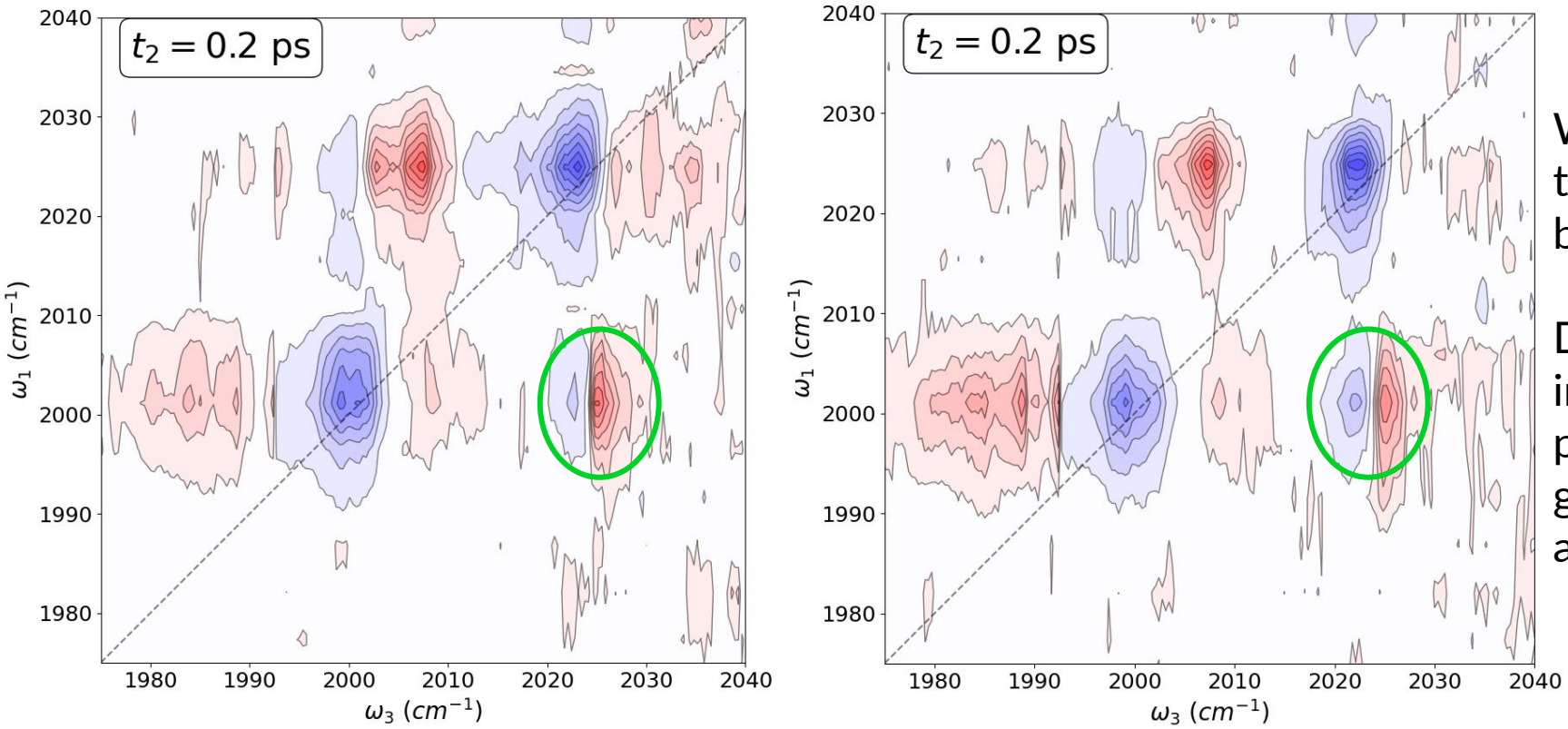
[**1**] Helbing, J. and Hamm, P., J. *Opt. Soc. Am. B* 28, pp 171-178 (2011)

[**2**] R. Stephen Berry, *J. Chem. Phys.* 32 (3), pp 933–938 (1960)

[**3**] Thon et al. *J. Chem. Phys.* 156, 024301 (2022)

[**4**] Cahoon et al. *Science* 319, 1820 (2008)

Coupling between the E' and A_2" modes



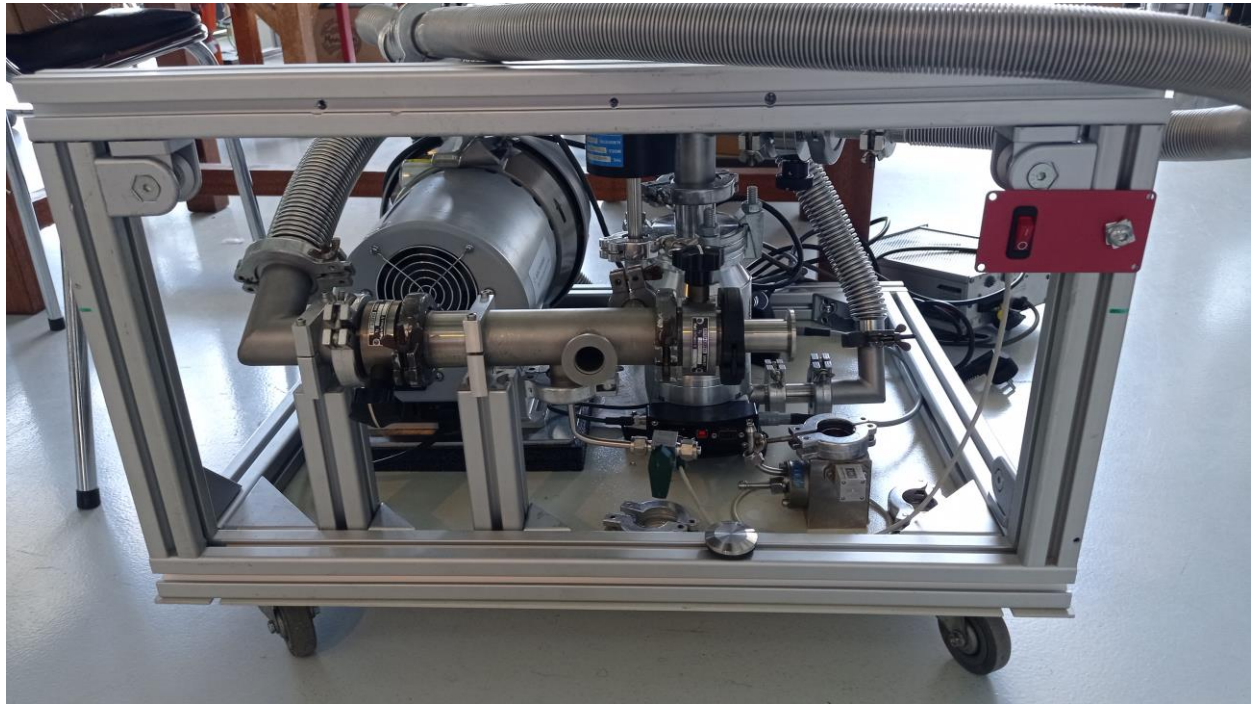
2DIR spectrum for t_2 = 0.2 ps in hexane (left) and dodecane (right) with pump and probe polarizations at a 90° angle

We observed a cross-peak at short times, characteristic of a **coupling** between the modes.

DFT calculations made in [2] predicted in dodecane a crossed anharmonicity parameter of χ = 0.6 cm^{-1}, which is a good match for the experimental anharmonic shift Δ = 3.0 $\pm$ 0.3 cm^{-1}

[4] Cahoon et al. *Science* 319, 1820 (2008)

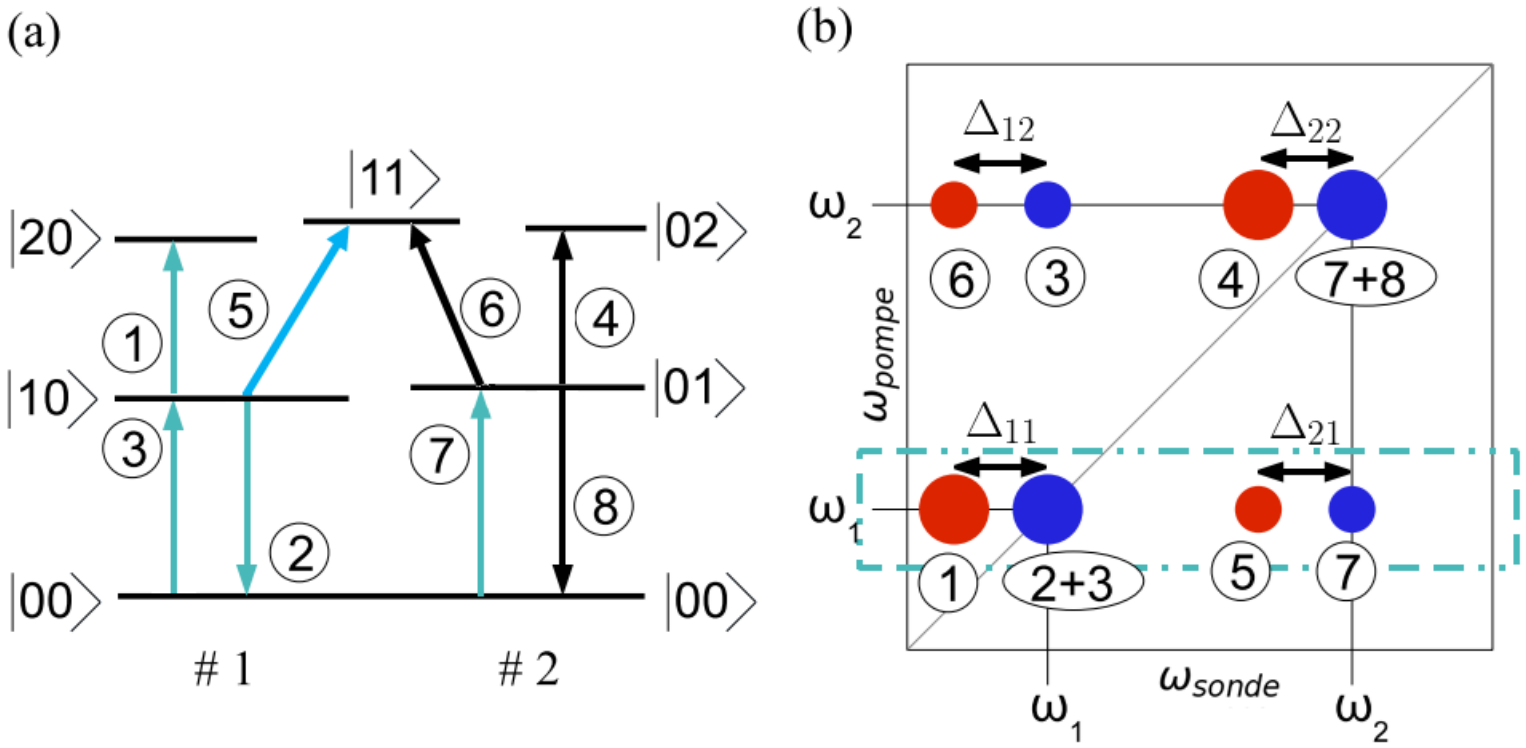
Cryogenic setup



Pumping system

Liquid He bath cryostat

2DIR spectra: case of two coupled oscillators



(a) Level schme of two coupled oscillators
$|ij\rangle$: i quanta in #1 and j quanta in #2.
(b) Corresponding 2DIR spectra **[1]**,**[2]**

Crosspeaks are then indicative of a coupling between modes

$$\omega_{|00\rangle \rightarrow |01\rangle} \neq \omega_{|10\rangle \rightarrow |11\rangle}$$

7 **5**

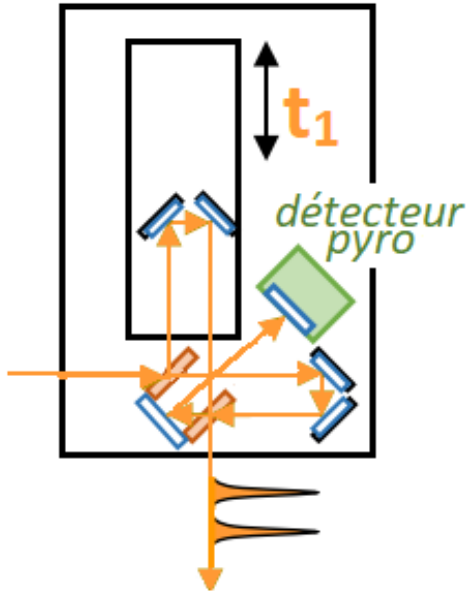
[1] Hamm, Zanni, Cambridge University Press, 2011
[2] Hausherr, Theses, 2013

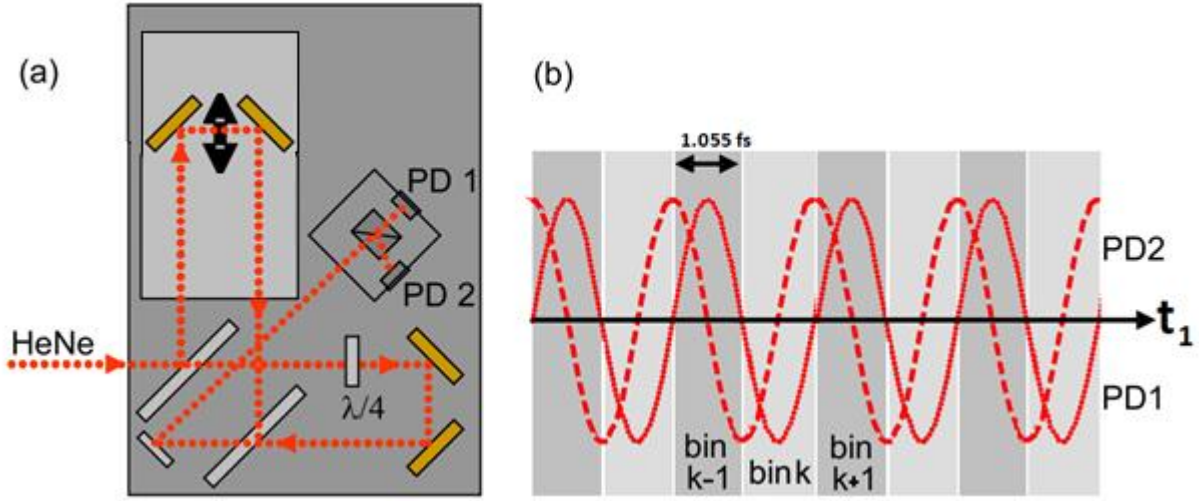
Mach-Zehnder interferometer

Vertically separated beams :

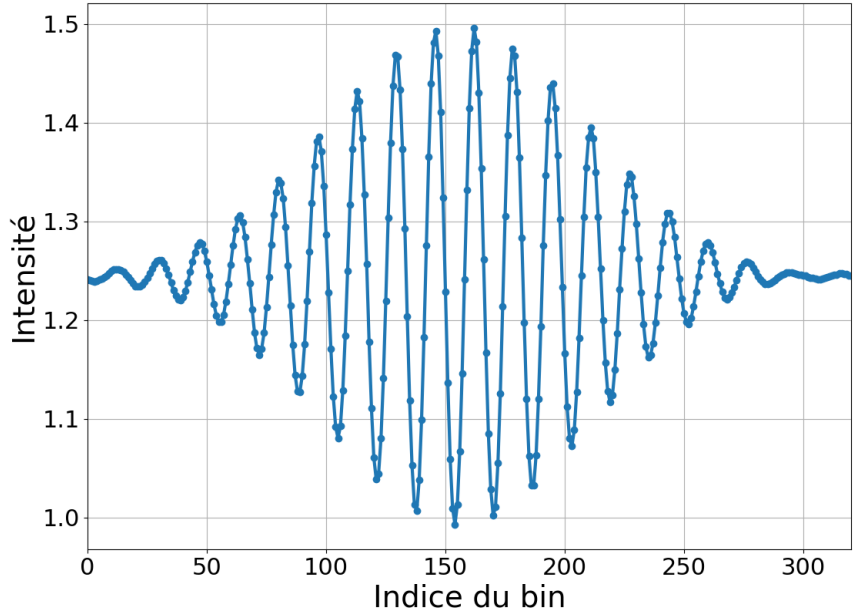
- **IR :** two outputs
  - towards the sample
  - towards the pyrometer
- **HeNe :** quadrature fringe counting to precisely retrieve t_1

IR beam pathway **[3]**





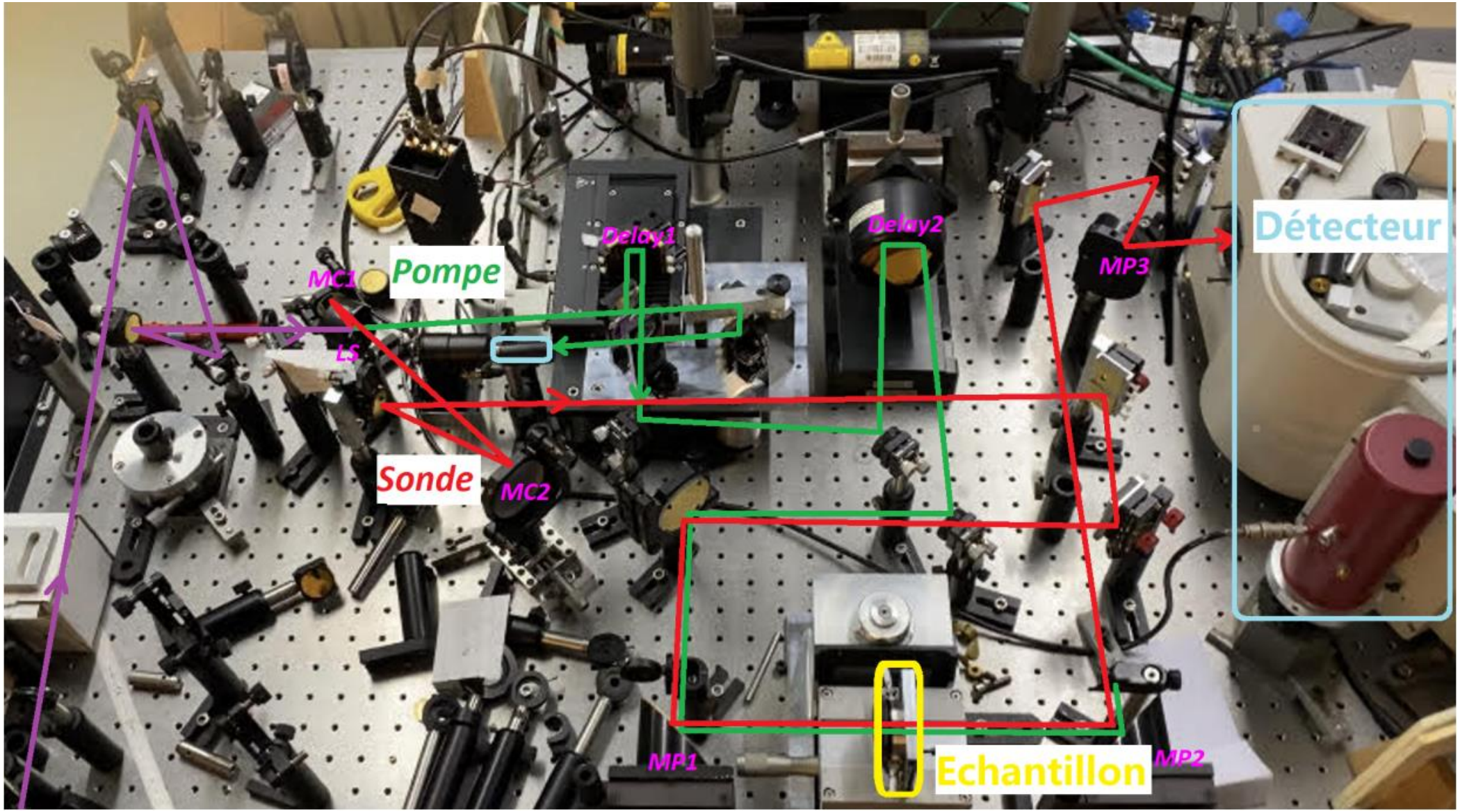
(a) HeNe beam pathway. (b) Quadrature fringe counting with photodiodes PD1 et PD2 **[3]**



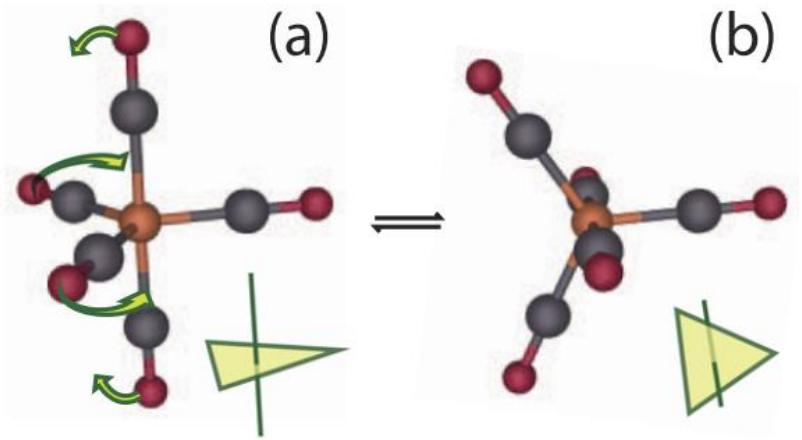
Interferogram of the two pump beams

[3] Helbing and Hamm, In: JOSA B 28 (Jan. 2011), pp. 171–178.

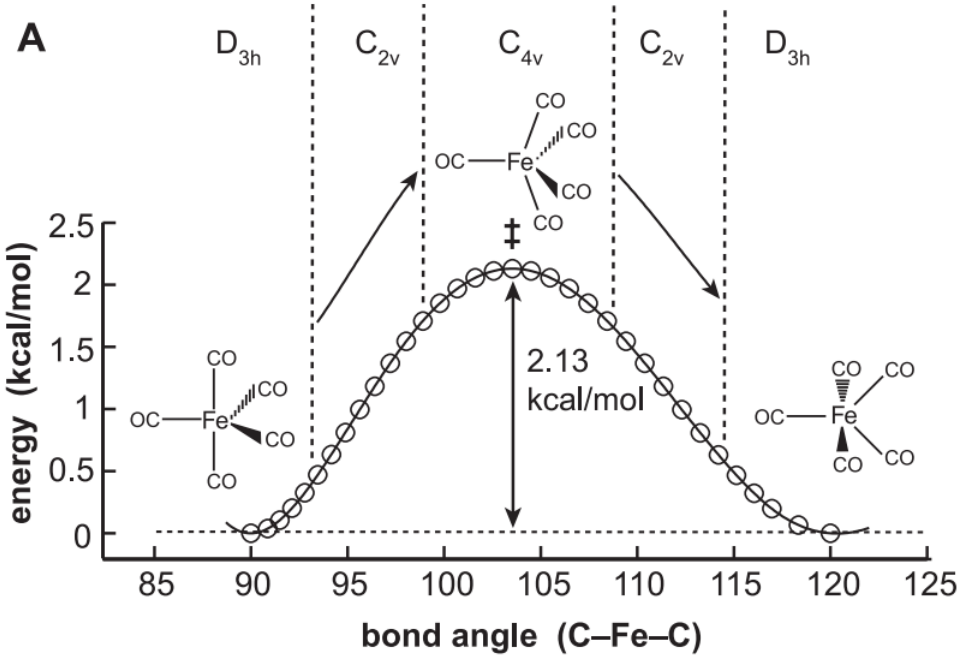
Experimental setup



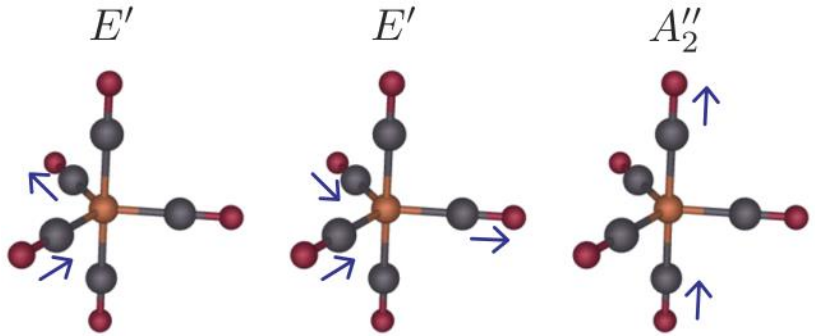
Berry pseudo-rotation



Schematic view of the Berry pseudo-rotation [3]



Mechanism and energy profile [2]



The equatorial plane (yellow triangle) undergoes a 90° roattion from (a) to (b), on a timescale of a few ps [2].
This geometry change allows for transfer between the two modes.

[2] Cahoon et al. *Science* 319, 1820 (2008)