Lecture Series Buenos Aires

18-3-2024 until 22-3-2024

Lecture M1 – Time-resolved spectroscopy

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Max-Born-Institut

2023 Physics Nobel Prize

The Nobel Prize in Physics 2023 was awarded jointly to Pierre Agostini, Anne L'Huillier and Ferenc Krausz "for experimental methods that generate attosecond pulses of light for the study of electron dynamics in matter"

1 attosecond = 10^{-18} second

Scope of this lecture series

Powerful new investigations of attosecond electronic and femtosecond structural dynamics have become possible within the last decade, as a result of the development of a number of novel experimental and theoretical tools and methodologies

Within this lecture series an overview will be presented of these new tools and methodologies, and relevant research highlights will be discussed

The plan for this week

	Monday	Tuesday	Wednesday	Thursday	Friday
8.00 – 9.00	Time-resolved spectroscopy (120)	Oscillator including carrier envelope phase (CEP) stability (120)	Generation and characterization of attosecond pulses (120)	Optical parametric chirped pulse amplification (OPCPA) (60/120)	Attosecond atomic physics (120/240)
9.00 – 10.00				Post-compression (120)	
10.00 – 11.00	Mathematical description of laser pulses (60)	Pulse Characterization (60)	Chirped pulse amplification (CPA) (cont.) (60/120)		Attosecond molecular physics (90)
11.00 – 12.00	Non-perturbative physics (120)	High-harmonic generation (120)		Attosecond atomic physics (120/240)	Attosecond condensed phase physics (90)
12.00 – 13.00			Optical parametric chirped pulse amplification (OPCPA) (60/120)		
13.00 – 14.00	Open discussion	Open discussion	Open discussion	Open discussion	Open discussion

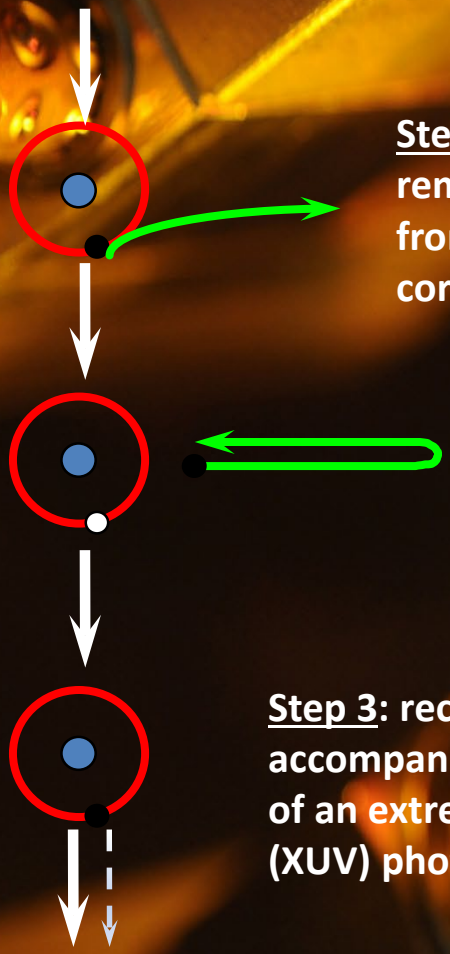
Marc Vrakking Federico Furch

Key ingredients

- We will discuss how materials can be studied by means of pump-probe experiments
- We will discuss the interaction of materials with intense laser light, and see how this can give rise to the formation of extreme ultraviolet (XUV) attosecond laser pulses
- We will discuss how pump-probe experiments can be configured using attosecond laser pulses
- We will learn about key experimental techniques, i.e. how intense lasers are built, sample preparation, detection techniques, etc.
- To understand the lectures, we will understand a basic knowledge of optics and quantum mechanics – if something is not clear, please ask!

The basis of much that we will talk about is the process of High-Harmonic Generation (HHG)

Intense near-infrared femtosecond laser



Step 1: ionization and removal of an electron from the positive ion core

Step 2: acceleration of the electron in the oscillatory laser field

Step 3: recombination, accompanied by the emission of an extreme-ultraviolet (XUV) photon

Intense near-infrared femtosecond laser + XUV or even soft X-ray radiation

HHG produces ultrashort XUV/soft X-ray pulses, with a duration down into the attosecond domain, and ideally synchronized to the infrared driver laser → ideal for pump-probe spectroscopy

The attosecond timescale is the fastest relevant timescale for studying processes that happen outside the atomic nucleus

The use of XUV/soft X-ray radiation implies the possibility to study materials from the viewpoint of indivdual atoms

Selected take home messages that you will understand on Friday

- *The proliferation of attosecond science became possible because of major developments in ultrafast laser technology, and attosecond science drives numerous new developments*
- *High-harmonic generation and the formation of attosecond pulses are best understood in a field picture of the laser-matter interaction*
- *Pump-probe experiments are interference experiments, where time-dependent signals arise through interference between multiple quantum paths that connect the initial state of a system to the final state detected in the experiment*
- *The techniques that were introduced in 2001 for the characterization of attosecond pulse trains and isolated attosecond pulses continue to be workhorses in experiments where attosecond pulses are used to probe electron dynamics*
- *The attosecond pulse structure of High-harmonic radiation is not its only important feature, HHG moreover permits core-level specific time-resolved spectroscopy with enormous impact in atomic, molecular and condensed phase physics*
- *The future of attosecond science looks extremely bright!*

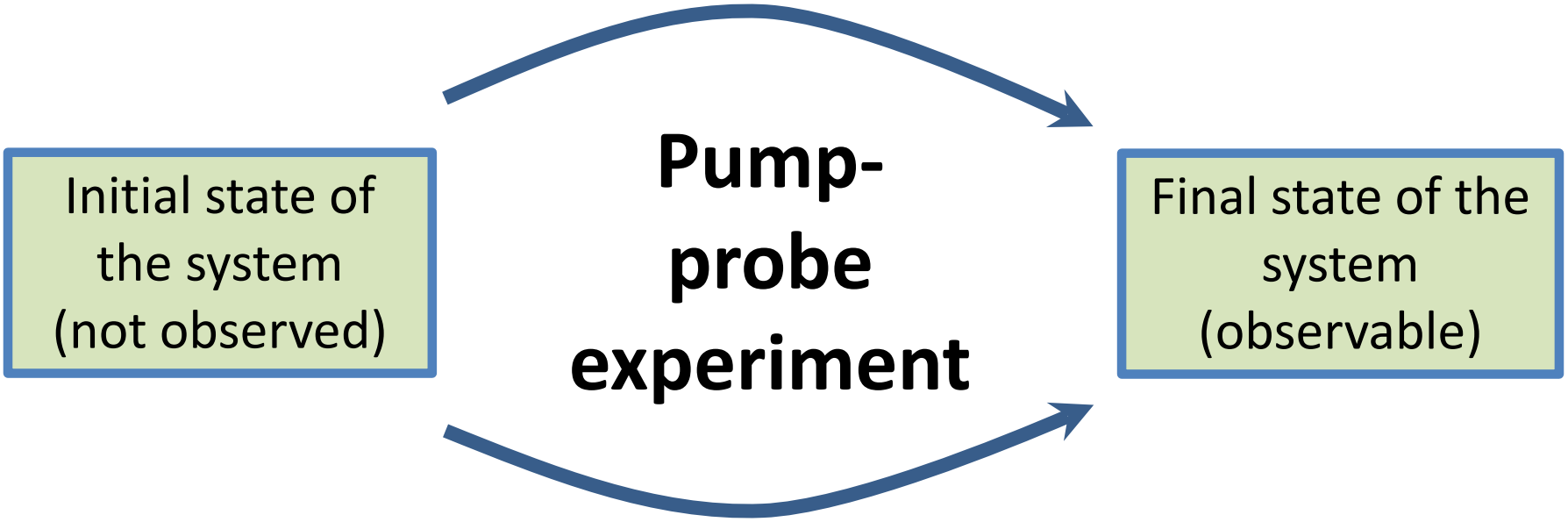
Pump-probe spectroscopy

Before…

After…

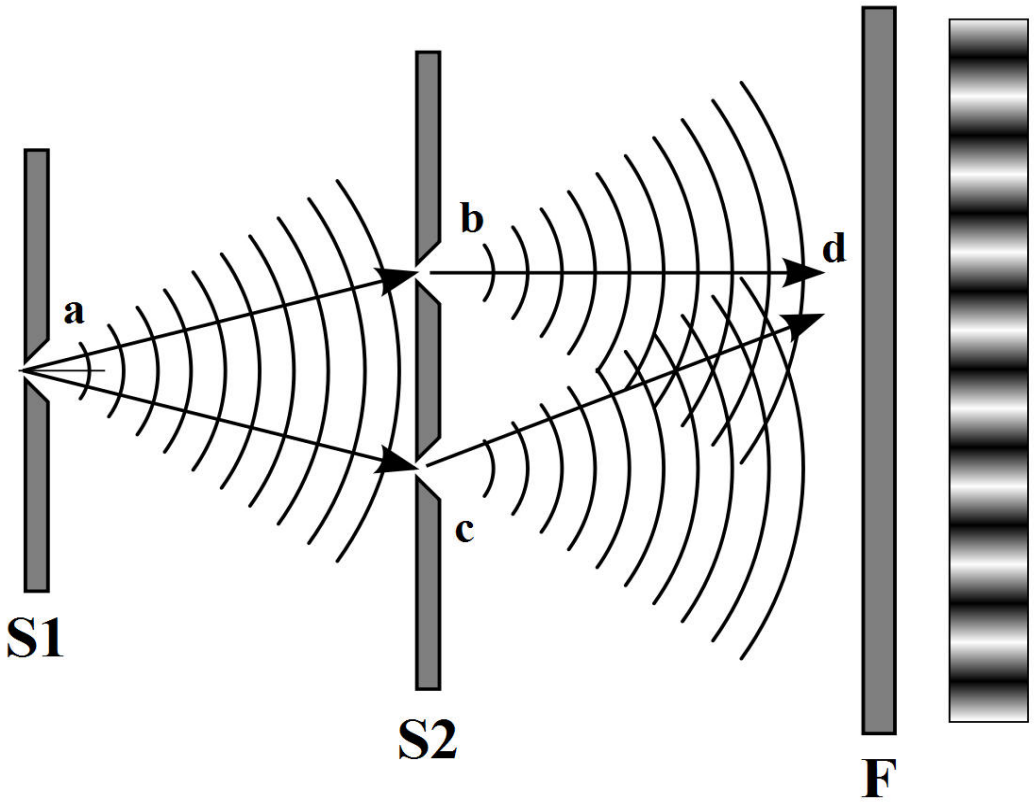

SCORE
0
1
YouTube
FLASHGAMESSHOW

Pump-probe spectroscopy



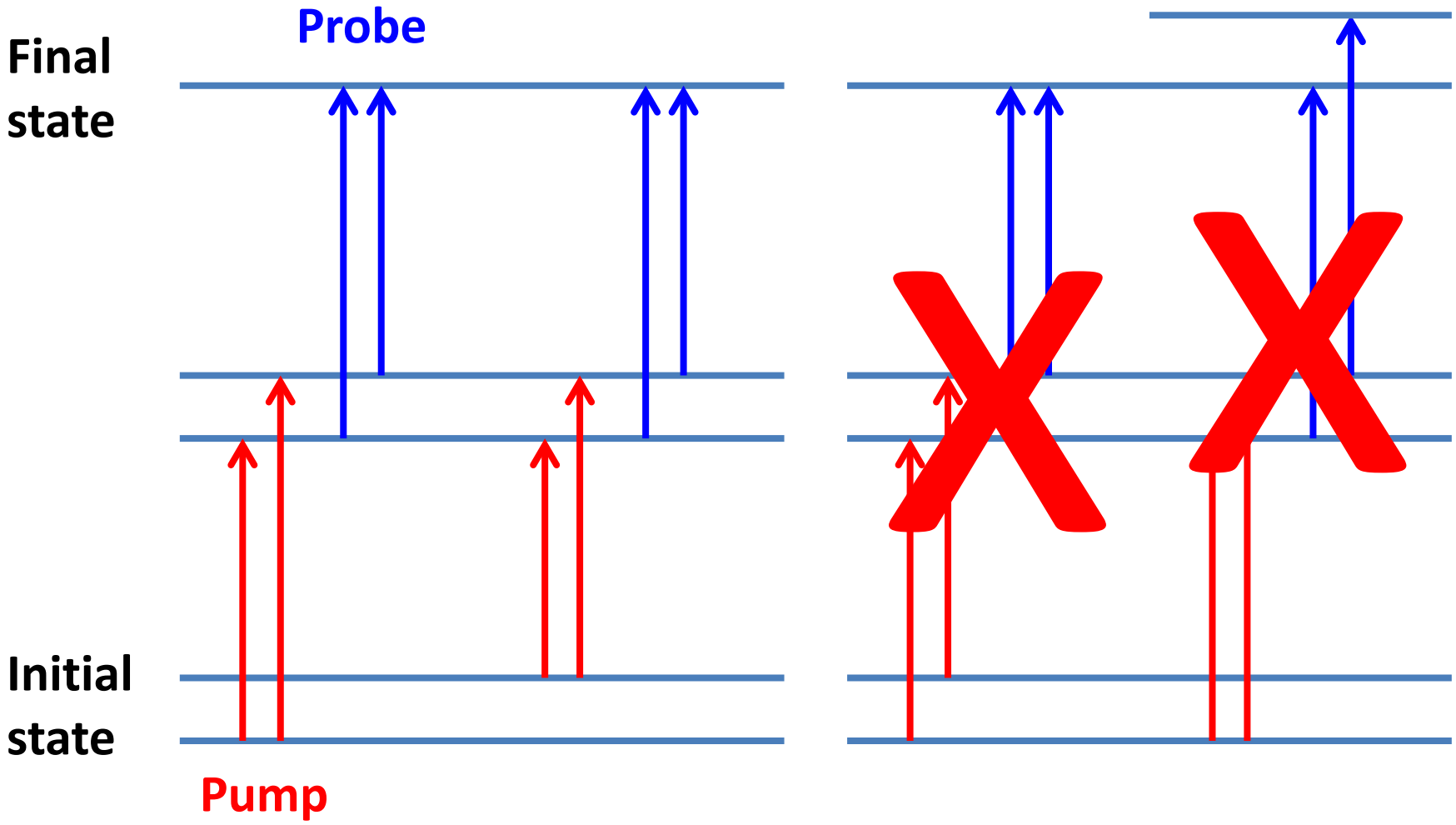
A pump-probe experiment can be thought of as an experiment where a **sequence of interactions** (typically with two laser pulses) by a „pump“ and a „probe“ brings the system from a **unique initial state** to a **unique final state**.

Pump-probe spectroscopy



A pump-probe experiment can be thought of as an interference experiment where we go from an **initial state** to a **final state** by means of **two or more interfering pathways** → similarity to Young´s double-slit experiment

Pump-probe spectroscopy



Quantum-mechanical description

Initially our system is in the ground state, i.e.

$$\Psi(t) = a_0(t)\Psi_0$$

Use the time-dependent Schrödinger equation in order to determine $a_0(t)$

$$i\hbar \frac{d\Psi(t)}{dt} = H\Psi(t)$$

This gives $i\hbar\dot{a}_0(t)\Psi_0 = a_0(t)E_0\Psi_0$, i.e. $\dot{a}_0(t) = (-iE_0/\hbar)a_0(t)$

So $a_o(t) = e^{-iE_0t/\hbar}$ and $\Psi(t) = \Psi_0 e^{-iE_0t/\hbar}$

Quantum-mechanical description

Consider that a **pump laser pulse** excites our system to a coherent superposition of excited states

$$\Psi(t) = a_0\Psi_0 e^{-iE_0 t/\hbar} + \sum_i a_i\,\Psi_i e^{-iE_i t/\hbar}$$

$$= a_0\Psi_0 e^{-iE_0 t/\hbar} + \sum_i b_i\,\Psi_i e^{-i\left(\frac{E_i t}{\hbar}+\varphi_i\right)} \qquad b_i \text{ real}$$

Now consider that a **probe laser pulse** projects our system onto one or more final states

$$\Psi_{final}(t) = \sum_j \Psi_j \left\{ \sum_i b_i \left\langle \Psi_j \middle| \mu.E \middle| \Psi_i \right\rangle e^{-i\left(\frac{E_i t}{\hbar}+\varphi_i\right)} \right\}$$

Quantum-mechanical description

Calculate the signal as – for example - the total population of the final state

$$S(t) = \sum_j \left| \sum_i b_i \langle \Psi_j | \mu . E | \Psi_i \rangle e^{-i\left(\frac{E_i t}{\hbar} + \varphi_i\right)} \right|^2$$

$$= \sum_j \sum_{i,k} b_i b_k \langle \Psi_j | \mu . E | \Psi_i \rangle \langle \Psi_j | \mu . E | \Psi_k \rangle e^{-i\left(\frac{E_i t}{\hbar} + \varphi_i\right)} e^{i\left(\frac{E_k t}{\hbar} + \varphi_k\right)}$$

$$\sim \sum_j \sum_{k \neq i} 2 b_i b_k \langle \Psi_j | \mu . E | \Psi_i \rangle \langle \Psi_j | \mu . E | \Psi_k \rangle \cos\left(\frac{(\boldsymbol{E_i - E_k})\boldsymbol{t}}{\hbar} + \varphi_i - \varphi_k\right)$$

So measured signals are time-dependent because of quantum beats described by energy differences in the states excited by the pump laser

Example: vibrational wavepackets

$$S(t) \sim \sum_j \sum_{k \neq i} 2 b_i b_k \cos\left(\frac{(E_i - E_k)t}{\hbar} + \varphi_i - \varphi_k\right)$$

The molecule has undergone one vibration when the phase-factors $(E_i - E_k)t/\hbar$ in S(t) have advanced by 2π.

Anharmonic oscillator:

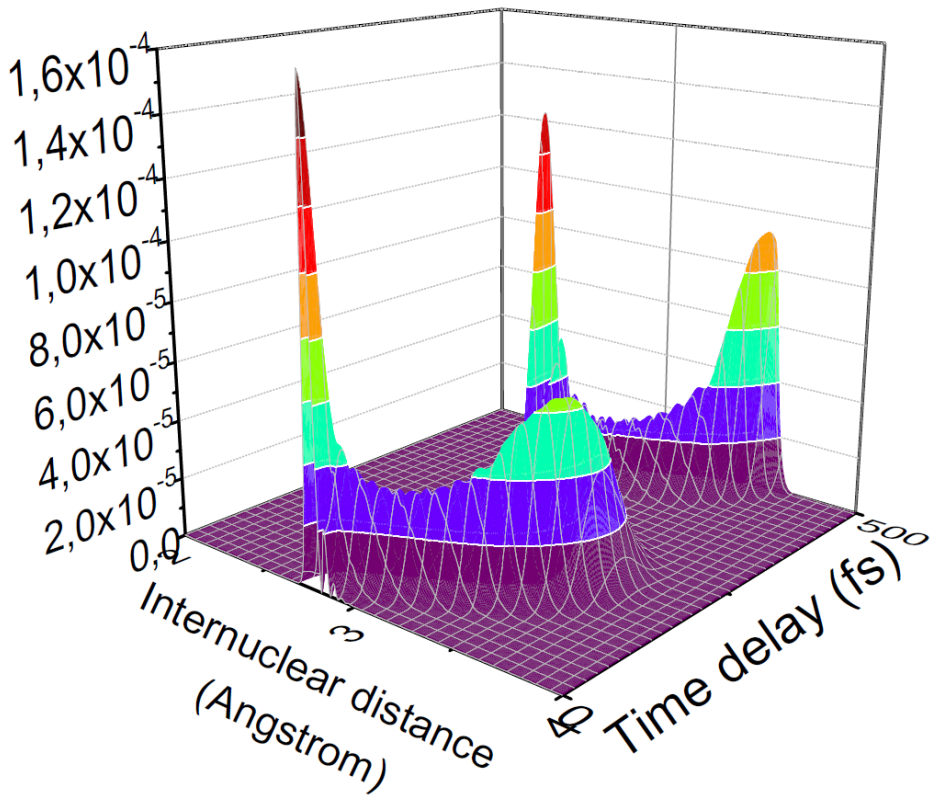
$$E(v) = \hbar\omega_{vib}(v - \alpha v^2) \text{ so } \Delta E(v) = \hbar\omega_{vib}(1 - 2\alpha v)$$

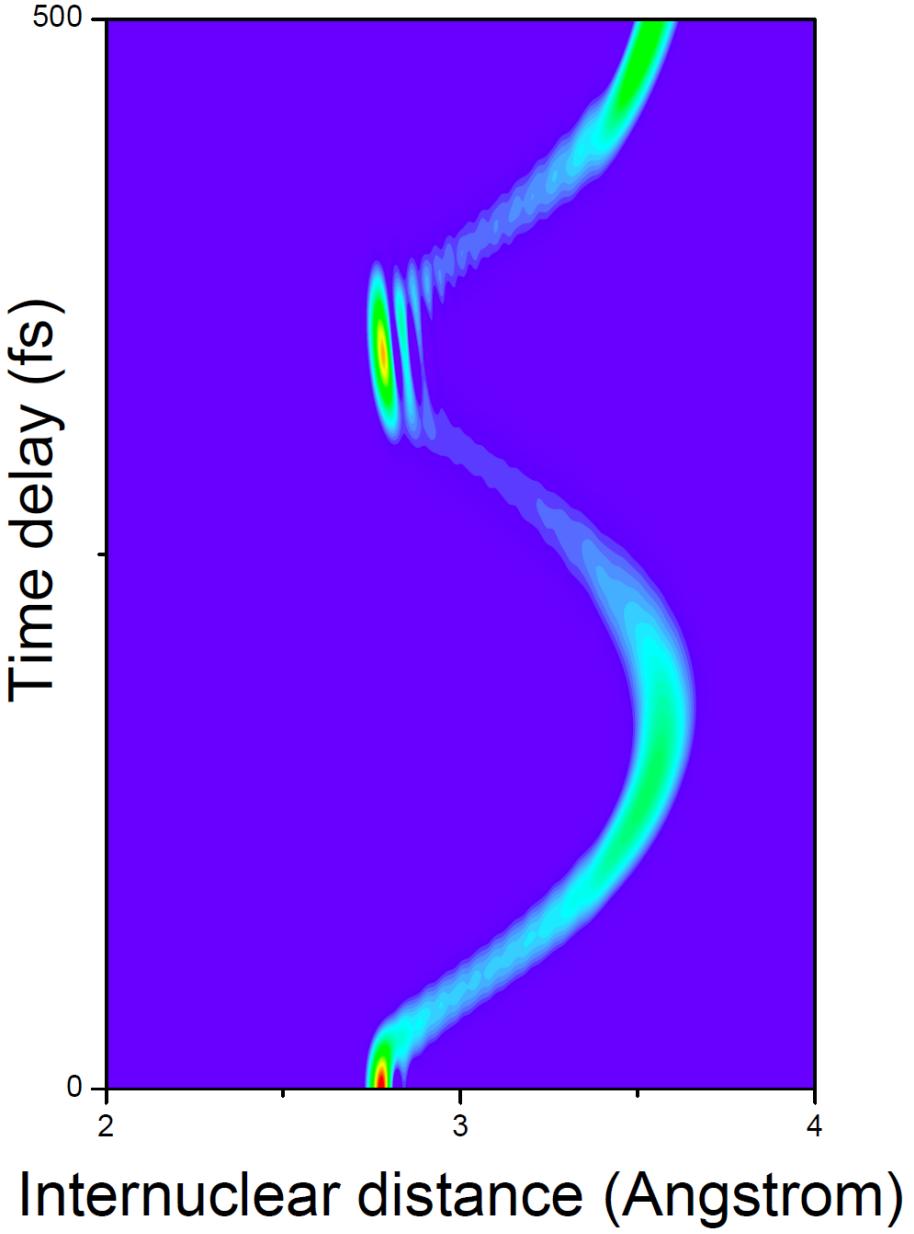
$$\frac{\Delta E \Delta t}{\hbar} = 2\pi, i.e. \omega_{vib}\Delta t = 2\pi$$

In the case of I_2: $\omega_{vib} \cong 100\ cm^{-1} = 4.556\ 33 \times 10^{-4}$ a.u.

$\Delta t = 13789$ a.u. = 333 femtoseconds

Example: vibrational wavepackets





Example: vibrational wavepackets

After a number of vibrations, the wavepacket dephases because the energy difference ΔE between consecutive vibrational levels is not constant.

Anharmonic oscillator: $E(v) = \hbar\omega_{vib}(v - \alpha v^2)$

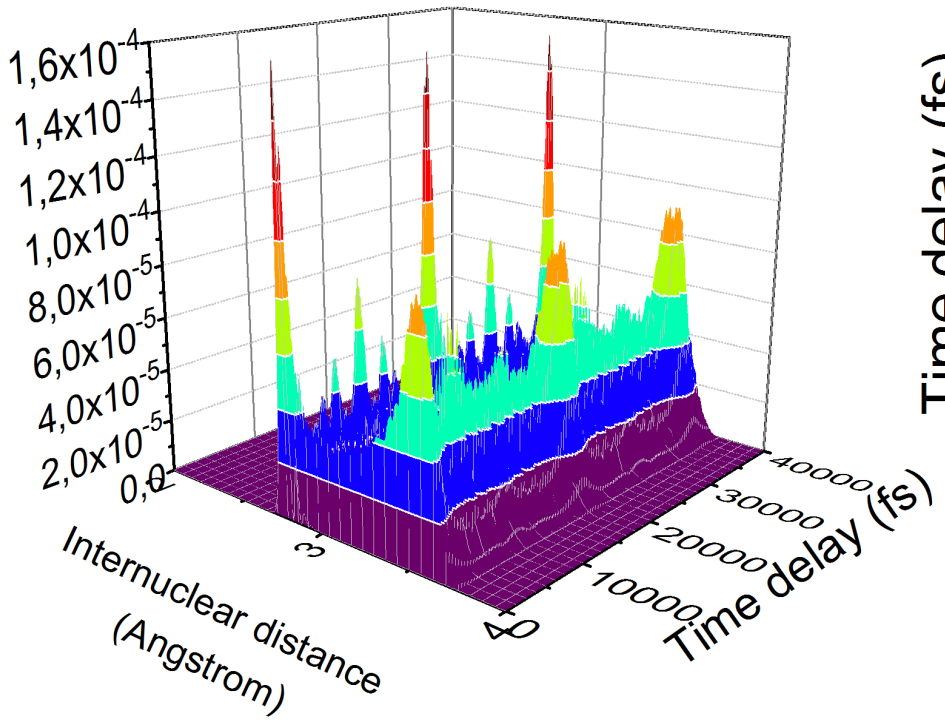
Energy difference between consecutive beat frequencies: $2\hbar\alpha\omega_{vib}$

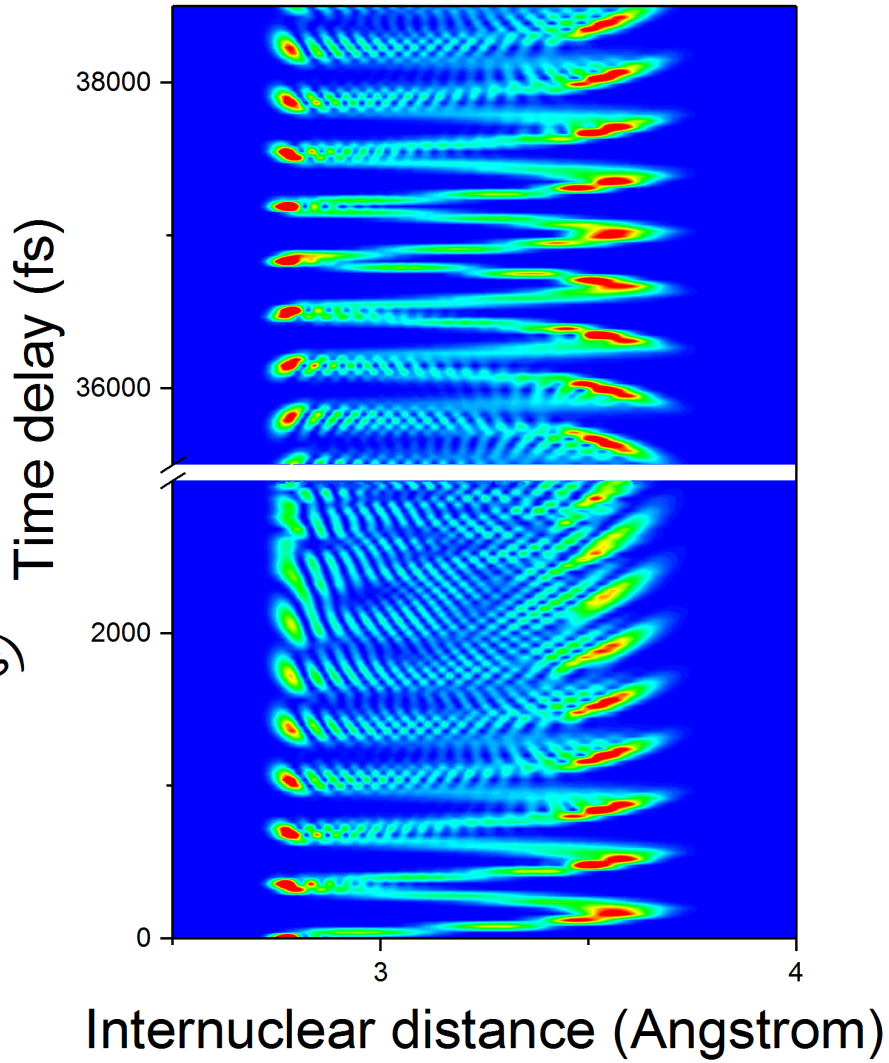
A revival occurs when $2\square_{vib}\Delta t = 2\pi$, i.e. $\Delta T_{revival} = \pi/\square_{vib}$

In the case of I_2: $\omega_{vib} \cong 100$ cm-1 = 4.556 33 x 10^{-4} a.u.
$\alpha \cong 0.01$

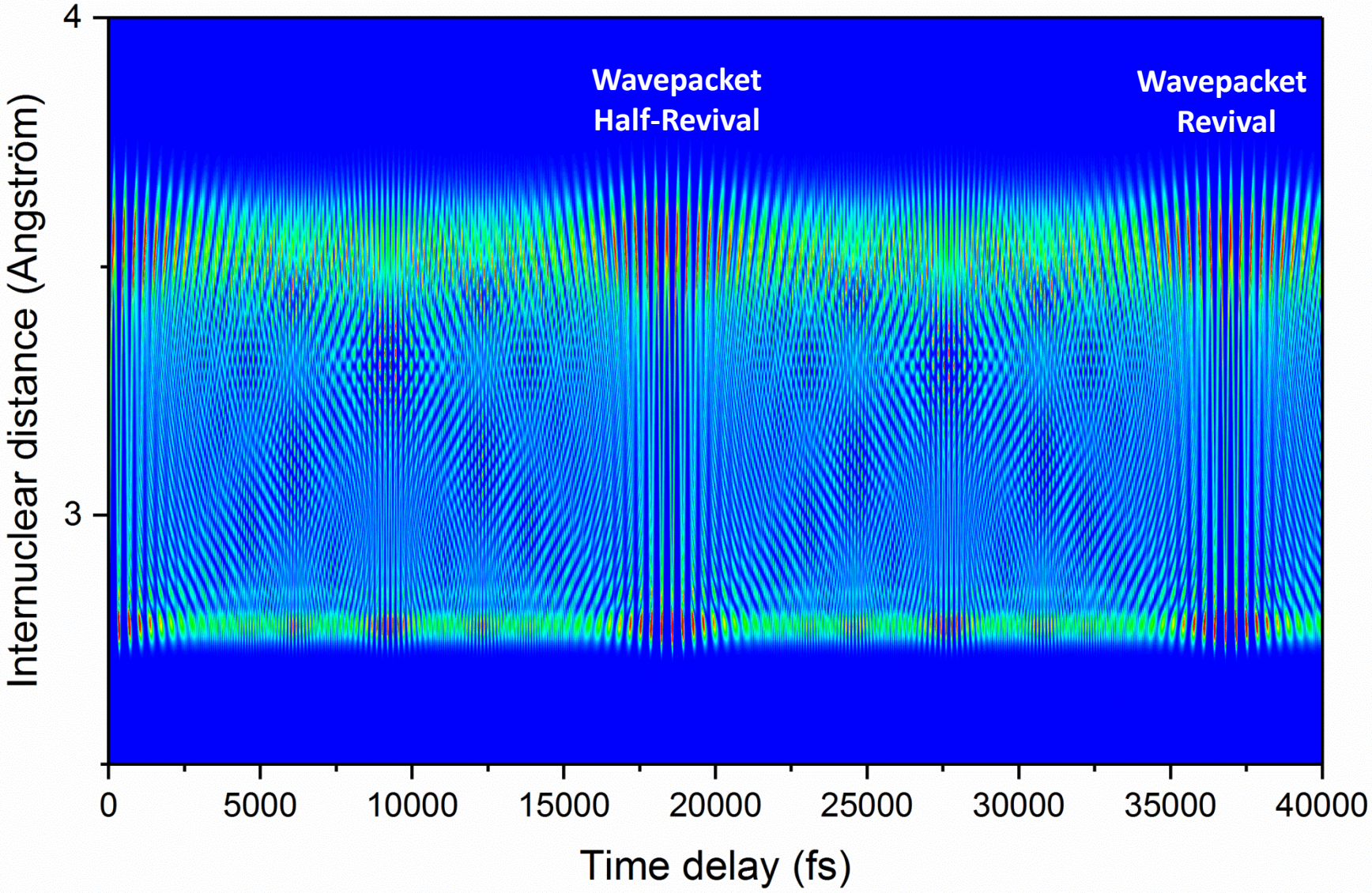
$\Delta t_{revival}$ = 15308 a.u. = 33,3 picoseconds

Example: vibrational wavepackets

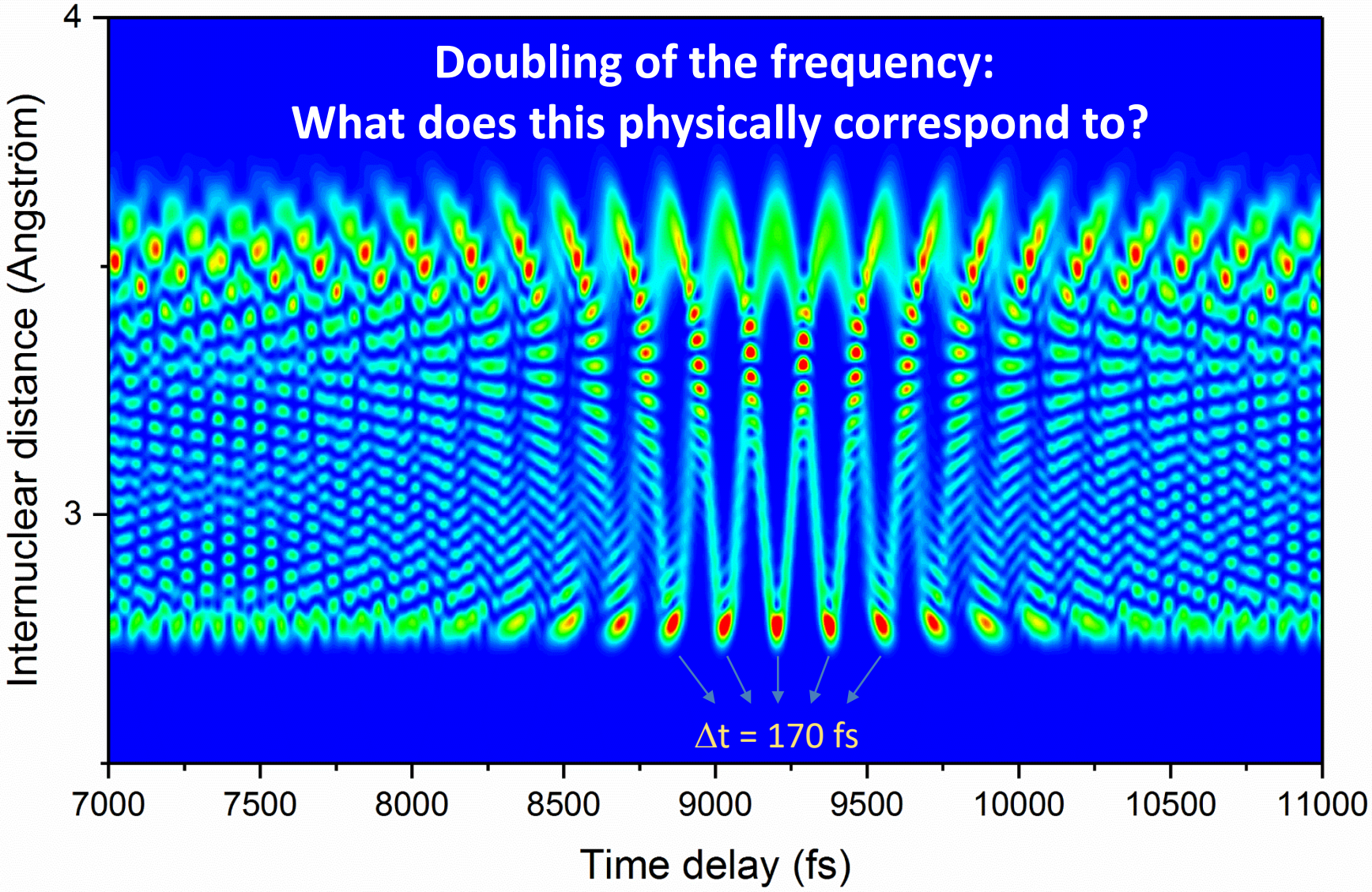




The rephasing after appr. 17 ps corresponds to a half-revival, i.e. consecutive beat frequencies out of phase by π-wavepacket reconstitutes at the outer turning point

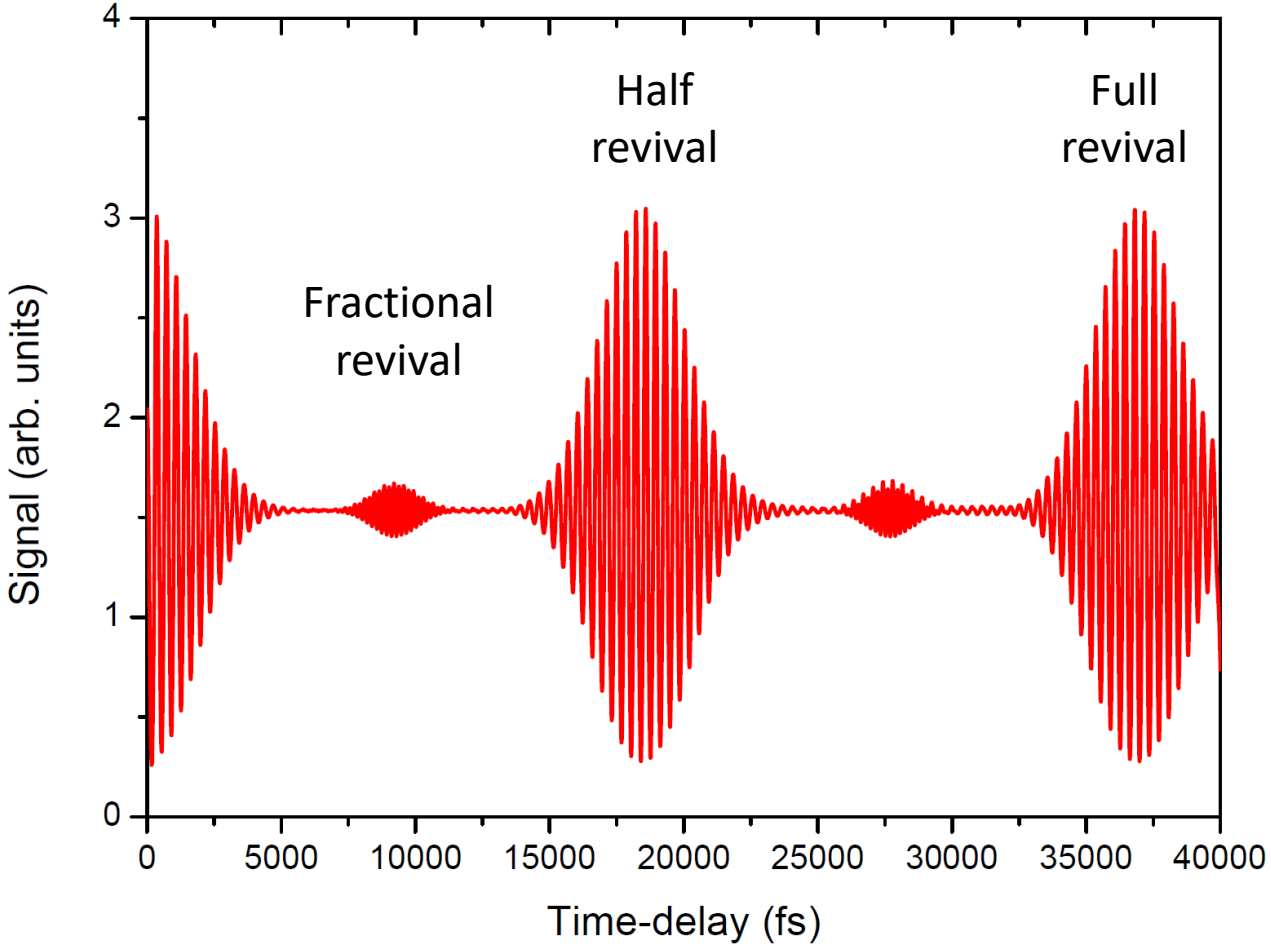


Dephasing and rephasing of the wavepacket


Doubling of the frequency:
What does this physically correspond to?
Δt = 170 fs
Internuclear distance (Angström)
4
3
7000
7500
8000
8500
9000
9500
10000
10500
11000
Time delay (fs)

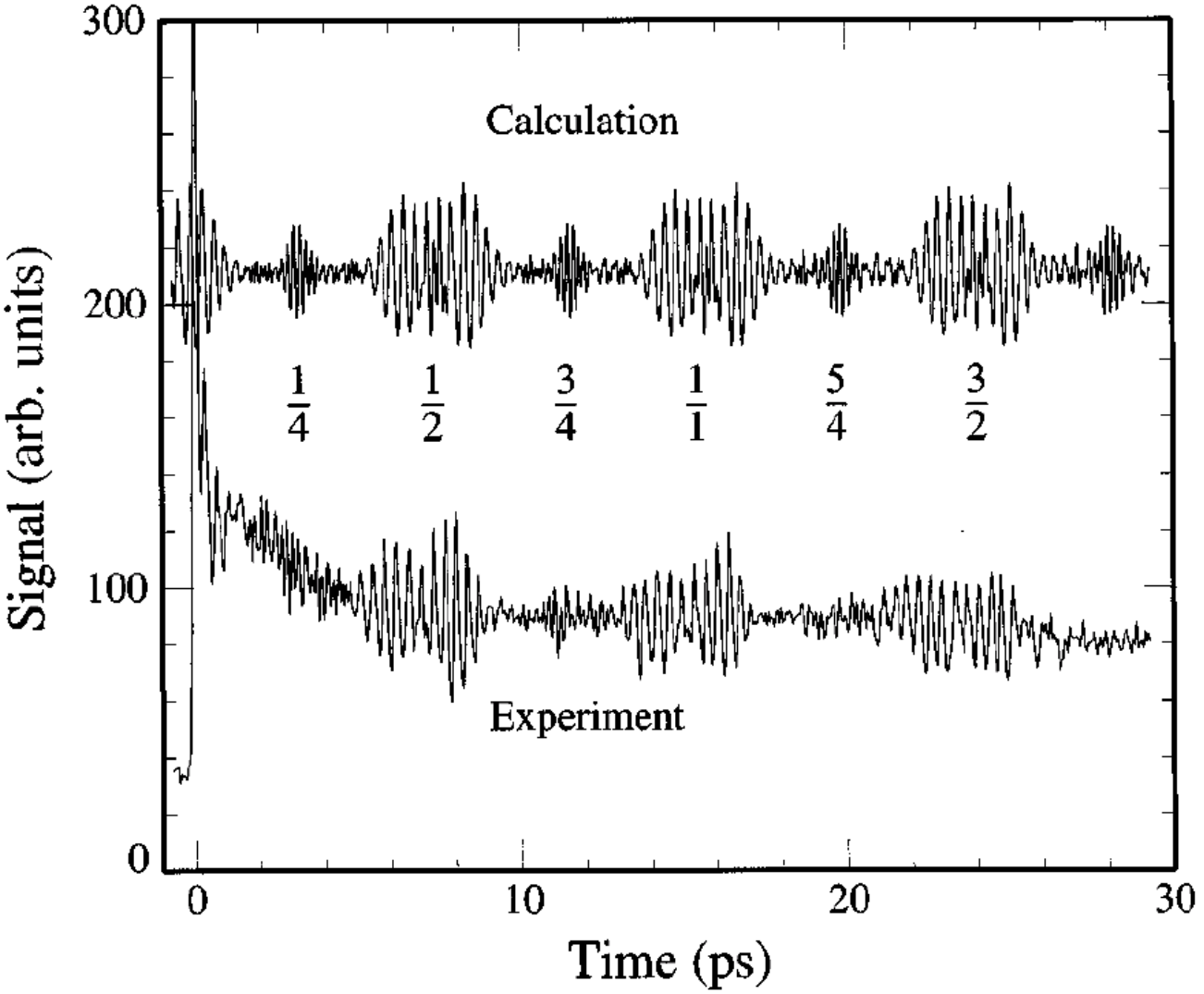
Observation of vibrational wavepackets

$$S(t)=\sum_j \sum_{\substack{i \\ k\neq i}} 2b_i b_k \langle \Psi_j | \mu.E | \Psi_i \rangle \langle \Psi_j | \mu.E | \Psi_k \rangle \cos\left(\frac{(E_i - E_k)t}{\hbar} + \varphi_i - \varphi_k\right)$$



Projection of the wavepacket on the ionization continuum

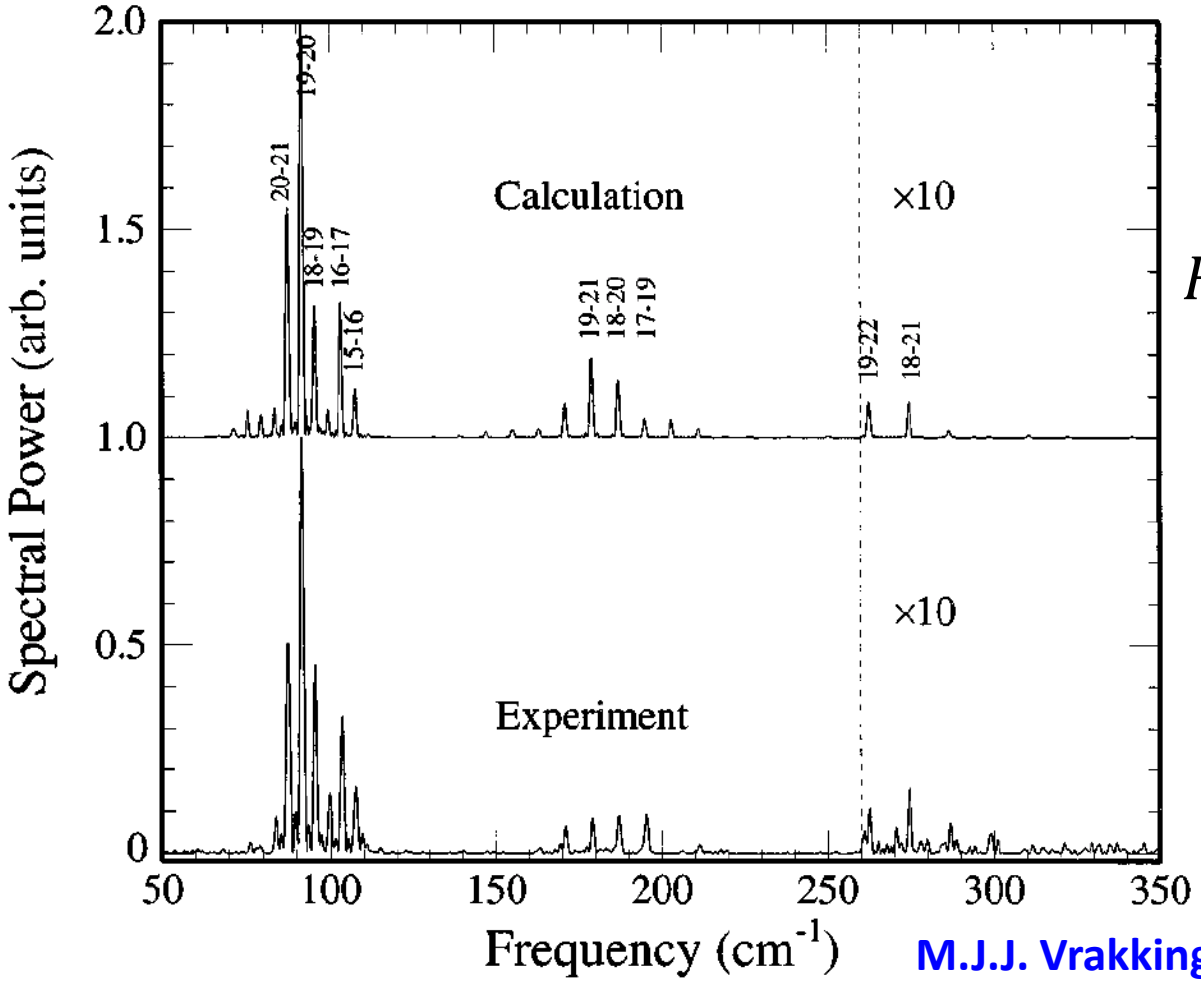
Experimental example: Br_2 wavepackets



M.J.J. Vrakking et.al. Phys. Rev. A 54, R37 (1996)

Experimental example: Br_2 wavepackets

Fourier Analysis



$$F(\omega) = \int_{-\infty}^{\infty} S(t) e^{-i\omega t}\, dt$$

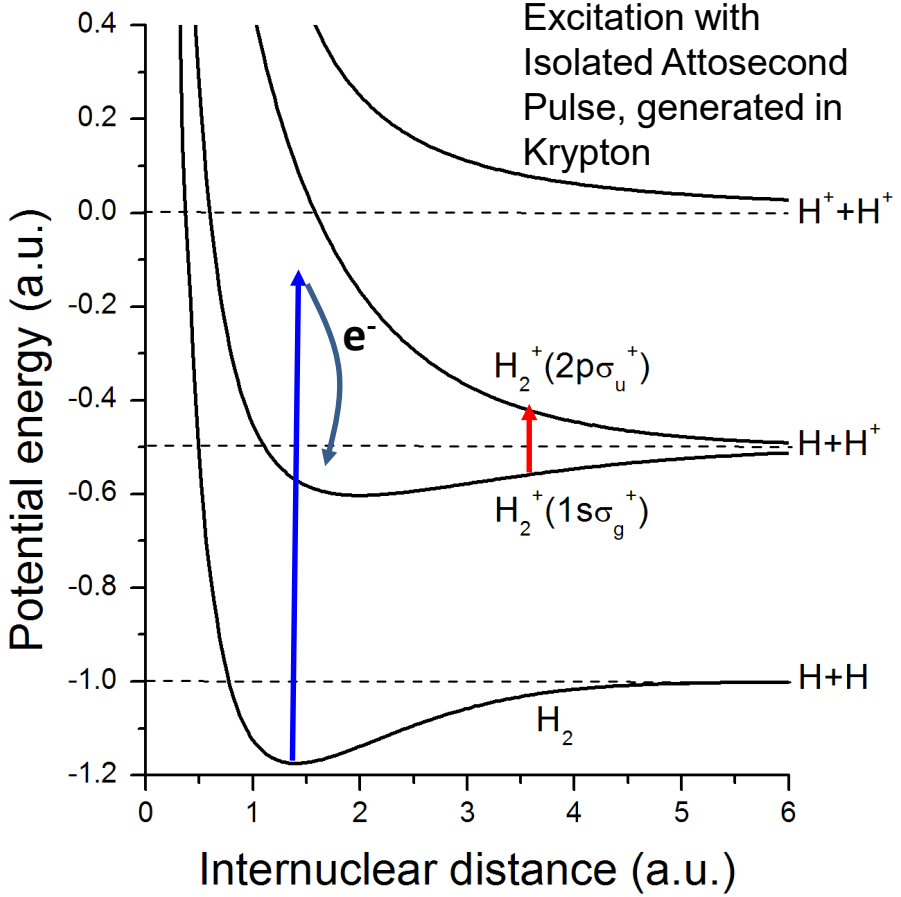
$$S(\omega) = |F(\omega)|^2$$

M.J.J. Vrakking et.al. Phys. Rev. A 54, R37 (1996)

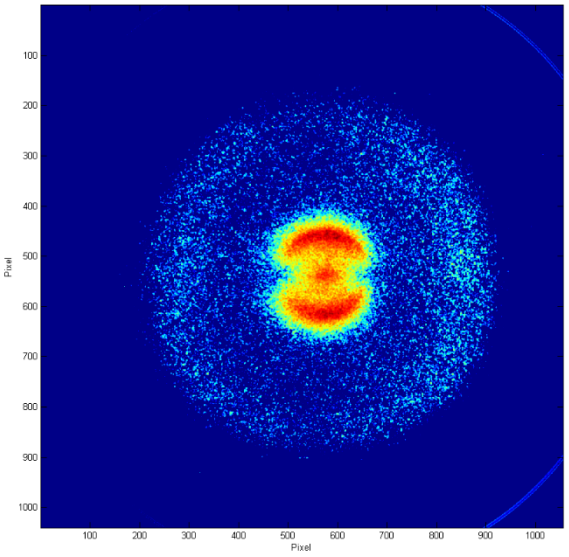
Molecular Dissociative Ionization and Wave-Packet Dynamics Studied Using Two-Color XUV and IR Pump-Probe Spectroscopy

F. Kelkensberg,[1] C. Lefebvre,[2,3] W. Siu,[1] O. Ghafur,[1] T. T. Nguyen-Dang,[2] O. Atabek,[3] A. Keller,[3] V. Serov,[3] P. Johnsson,[1,4] M. Swoboda,[4] T. Remetter,[4] A. L'Huillier,[4] S. Zherebtsov,[7] G. Sansone,[5] E. Benedetti,[5] F. Ferrari,[5] M. Nisoli,[5] F. Lépine,[1,6] M. F. Kling,[1,7] and M. J. J. Vrakking[1]

[1]*FOM Institute for Atomic and Molecular Physics (AMOLF), Science Park 113, 1098 XG Amsterdam, The Netherlands*

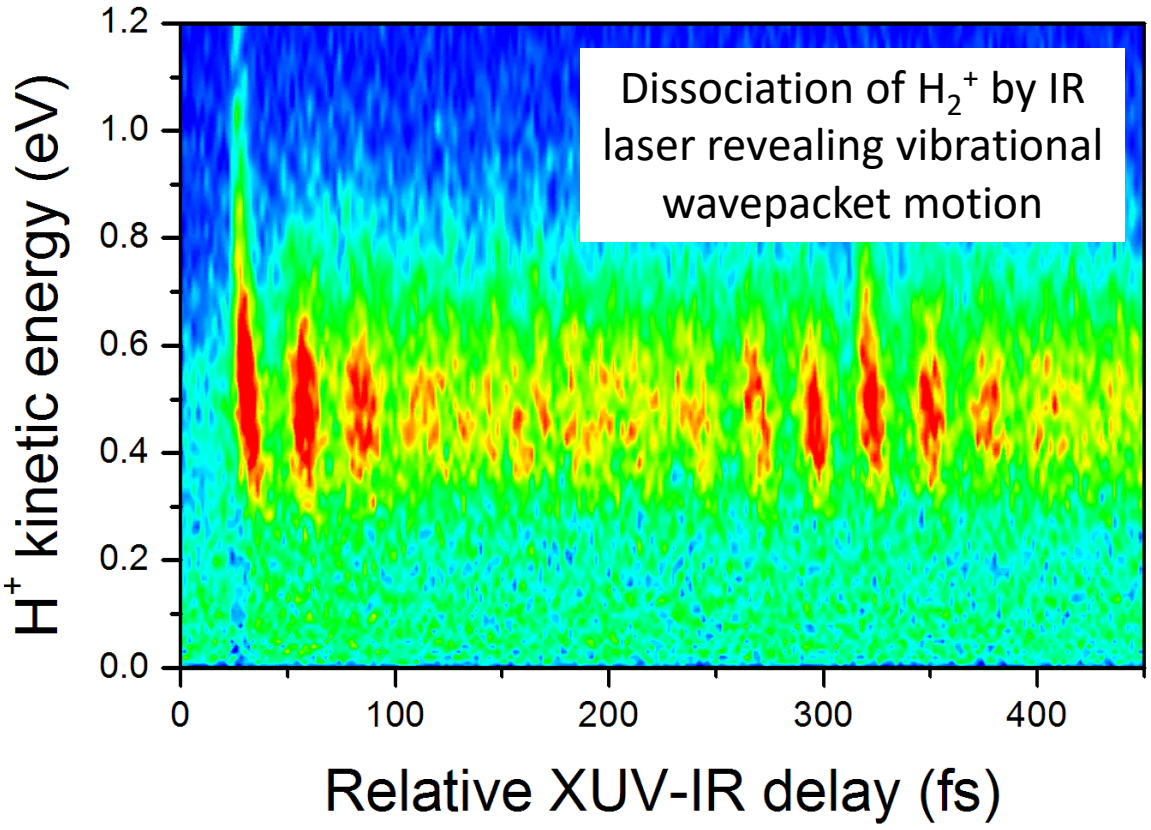


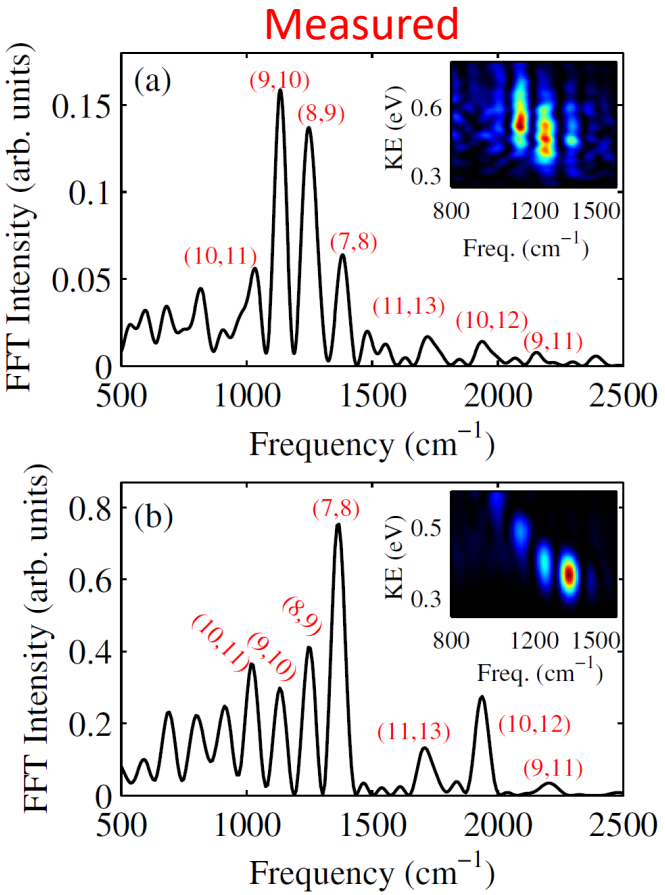
Use isolated attosecond pulse generated in Krypton to launch a wavepacket on the $2p\sigma_u^+$ state or the $1s\sigma_g^+$ state and investigate the subsequent IR interaction



H^+ fragment momentum distribution measured using a velocity map imaging spectrometer

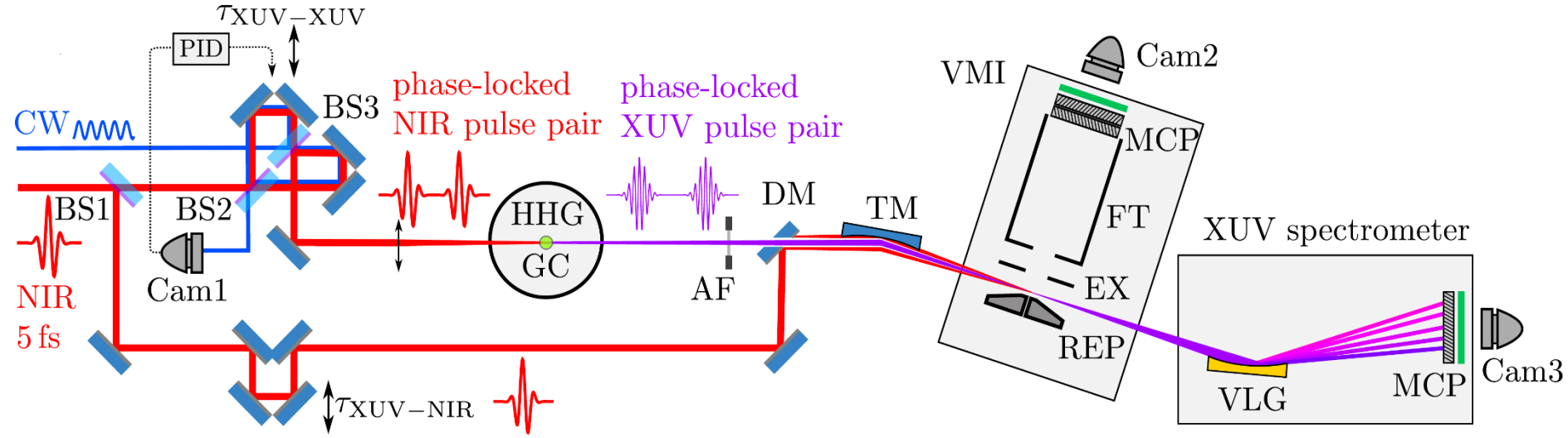
Observation of a vibrational wavepacket in H_2^+

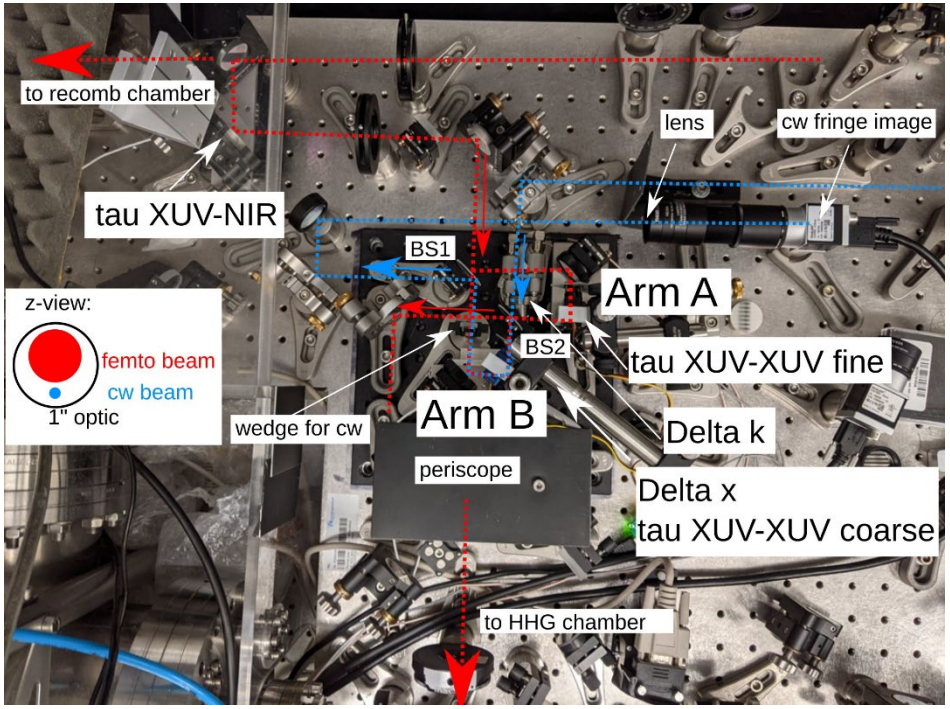


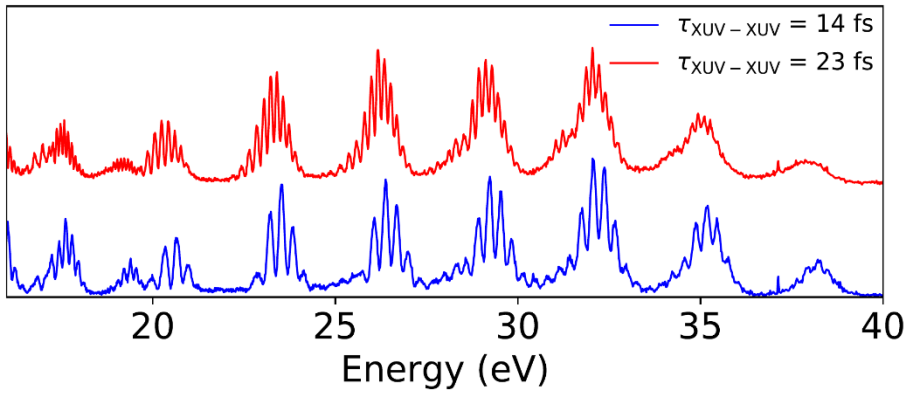


Kelkensberg et al., Phys. Rev. Lett. 103, 123005 (2009)

Freek Kelkensberg & Anne L‘Huillier

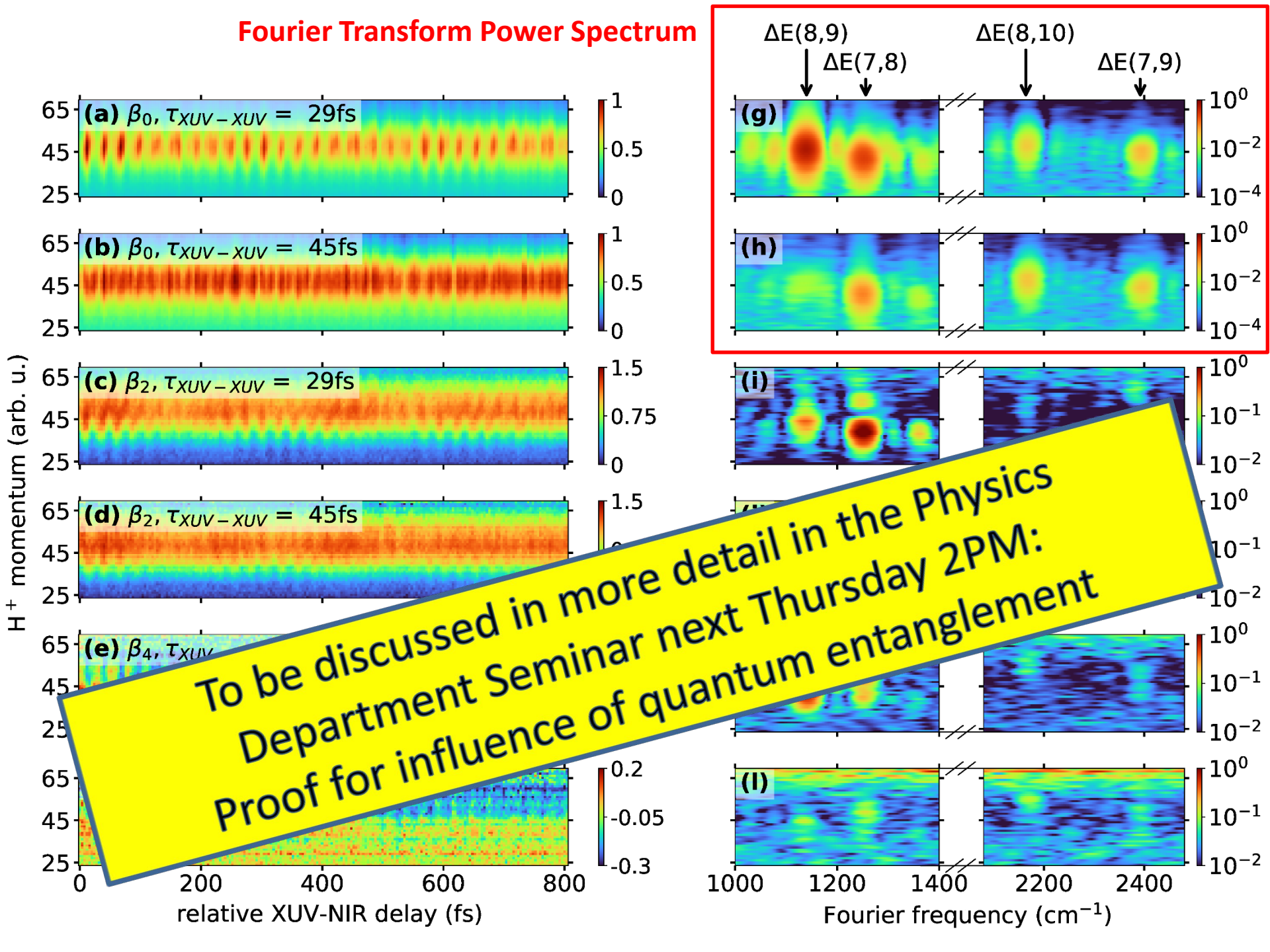






Creation of an XUV pulse pair, in an ultrastable Mach-Zehnder interferometer

Short term stability and long-term stability both 10 as r.m.s.


Fourier Transform Power Spectrum
ΔE(8,9)
ΔE(7,8)
ΔE(8,10)
ΔE(7,9)
(a) $\beta_0, \tau_{XUV-XUV}$ = 29fs
(b) $\beta_0, \tau_{XUV-XUV}$ = 45fs
(c) $\beta_2, \tau_{XUV-XUV}$ = 29fs
(d) $\beta_2, \tau_{XUV-XUV}$ = 45fs
(e) β_4, τ_{XUV}
(g)
(h)
(i)
(l)
To be discussed in more detail in the Physics Department Seminar next Thursday 2PM: Proof for influence of quantum entanglement
H+ momentum (arb. u.)
relative XUV-NIR delay (fs)
Fourier frequency (cm−1)

Intermediate remarks/conclusions

We want to be able to understand how an experiment like the H_2 entanglement experiment works

- What kind of lasers are needed?
- How does the velocity-resolved detection work?
- How were the lasers and detectors combined in the experiment?

We have already seen a first example of an experiment that we can alternatively describe (understand) in the time- and frequency-domain – we will frequently exploit this!

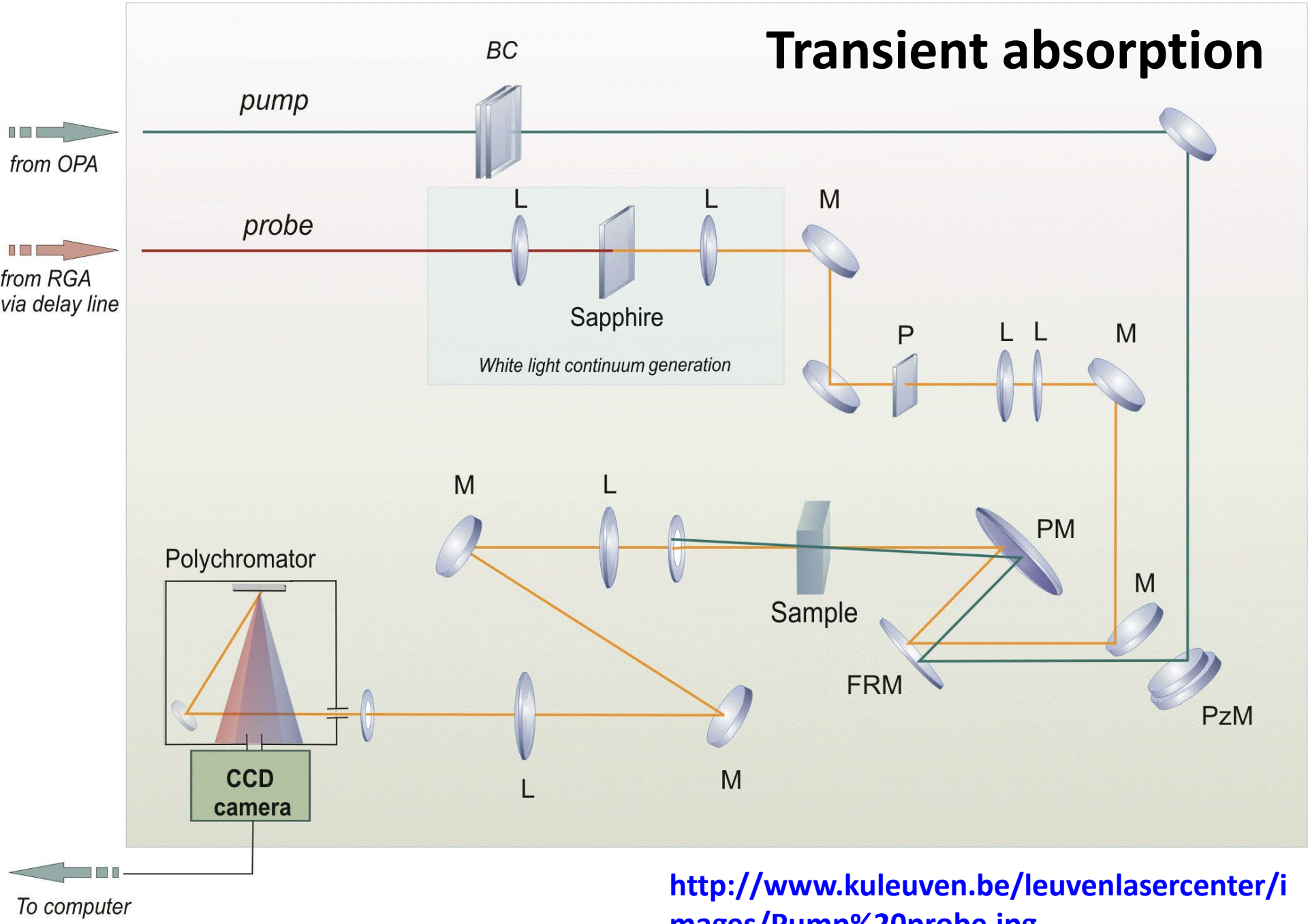
We have already seen a first example of an important emerging research theme within attosecond science, namely investigation of the role of quantum entanglement

Experimental techniques

- Configuration of pump-probe experiments – need laser pulses with appropriate pulse duration, wavelength and intensity to serve as pump and probe pulses in the experiment → Federico

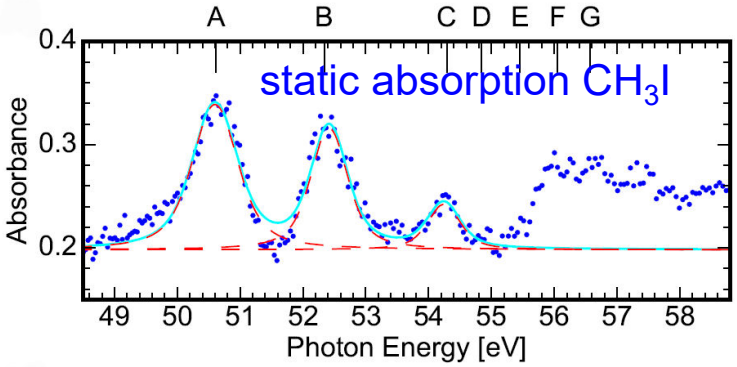
- Implementations of photon, electron and ion detection in pump-probe experiments

Transient absorption

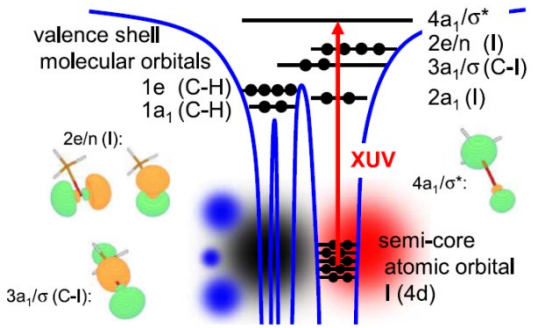


http://www.kuleuven.be/leuvenlasercenter/images/Pump%20probe.jpg

Transient absorption using a XUV high-harmonics xource: molecular photodissociation

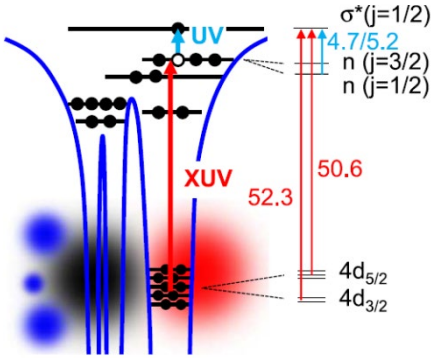


Before dissociation

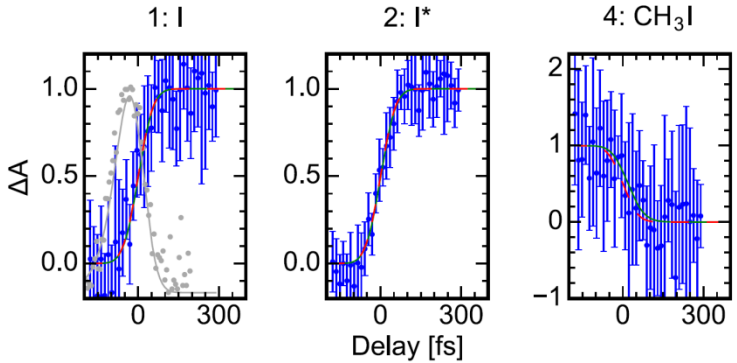


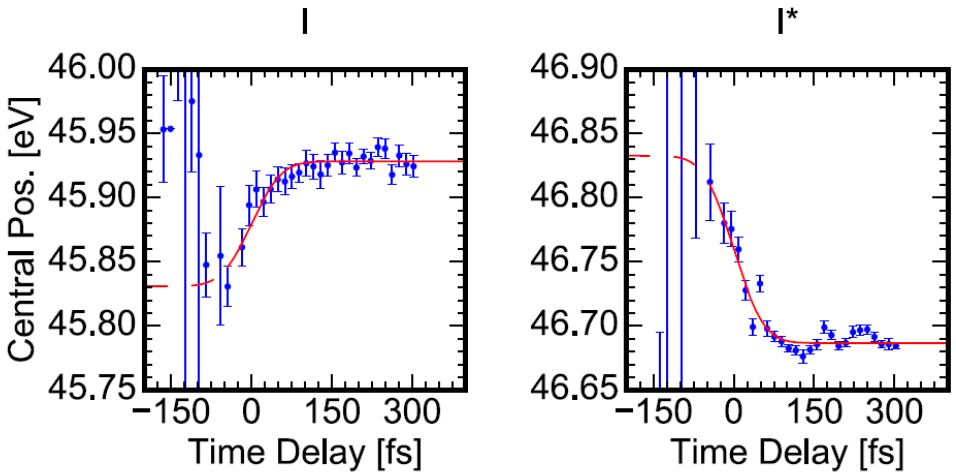
„molecular“

After dissociation



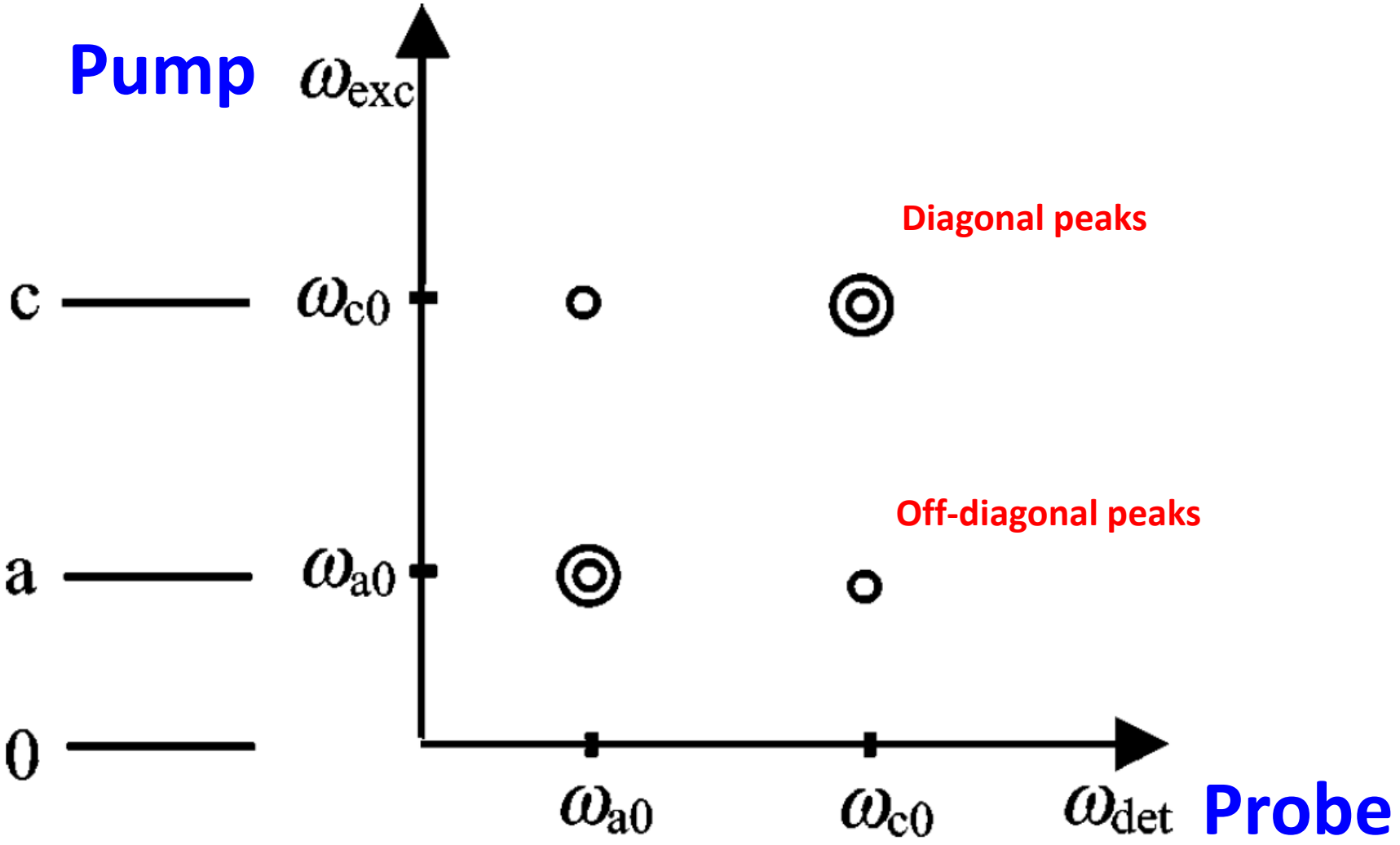
evolve into „atomic“





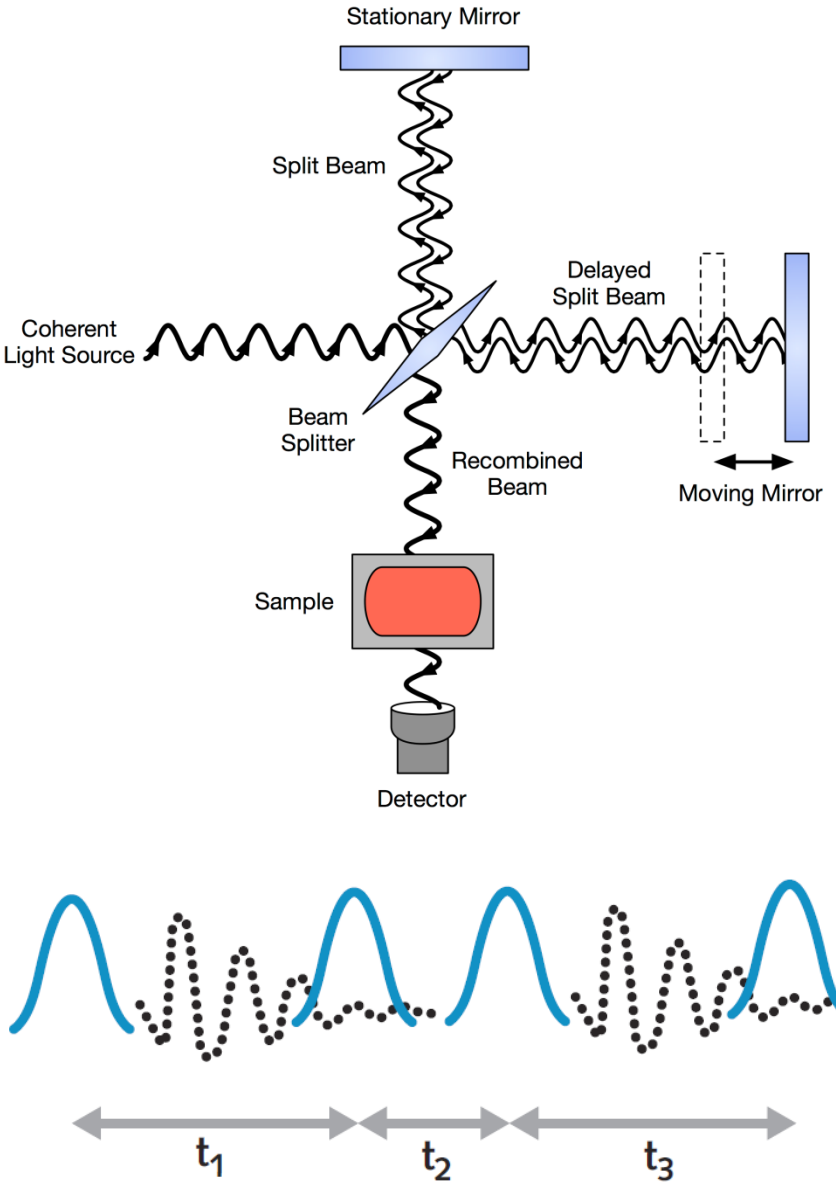
Drescher et al., J. Chem. Phys. 145, 011101 (2016)

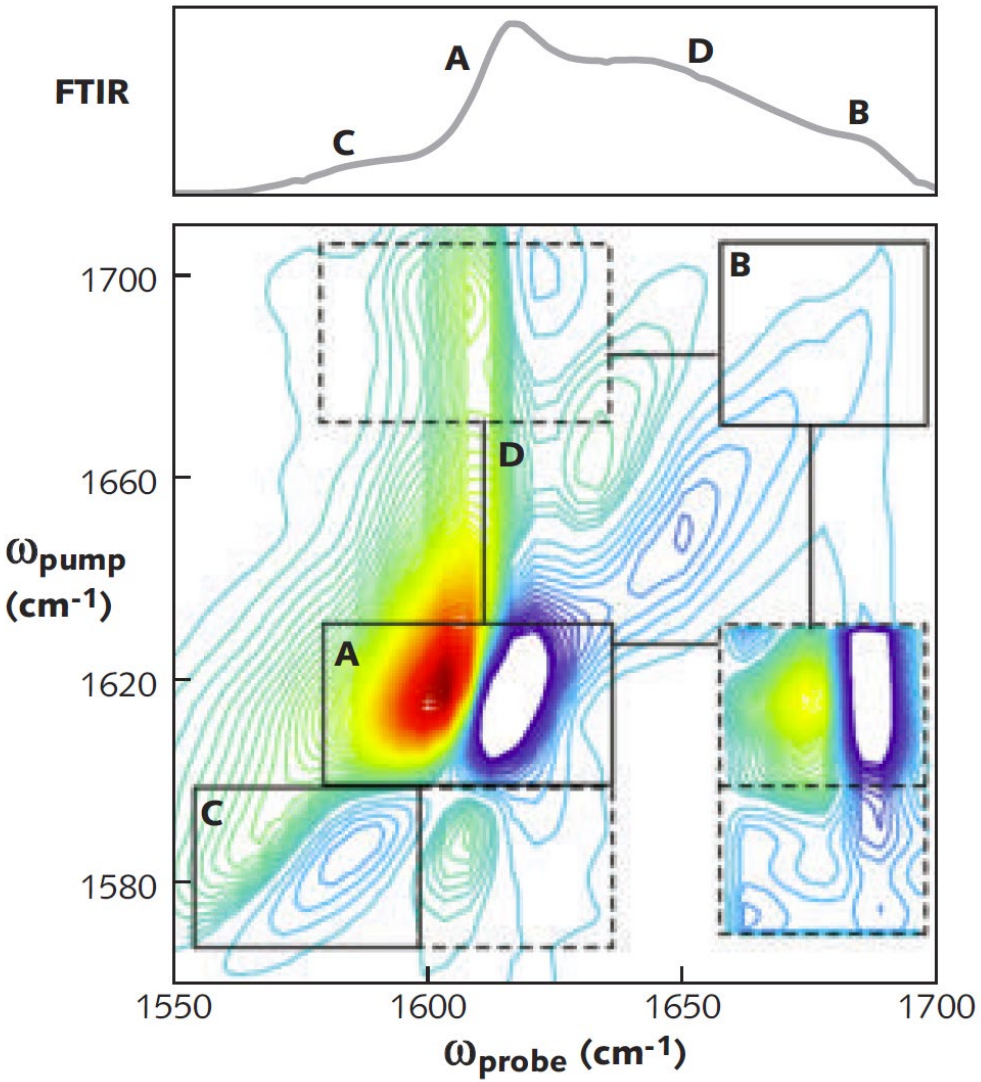
Multi-dimensional absorption spectroscopy



D. Jonas, Ann. Rev. Phys. Chem. 54, 425-465 (2003)

2D FT absorption spectroscopy



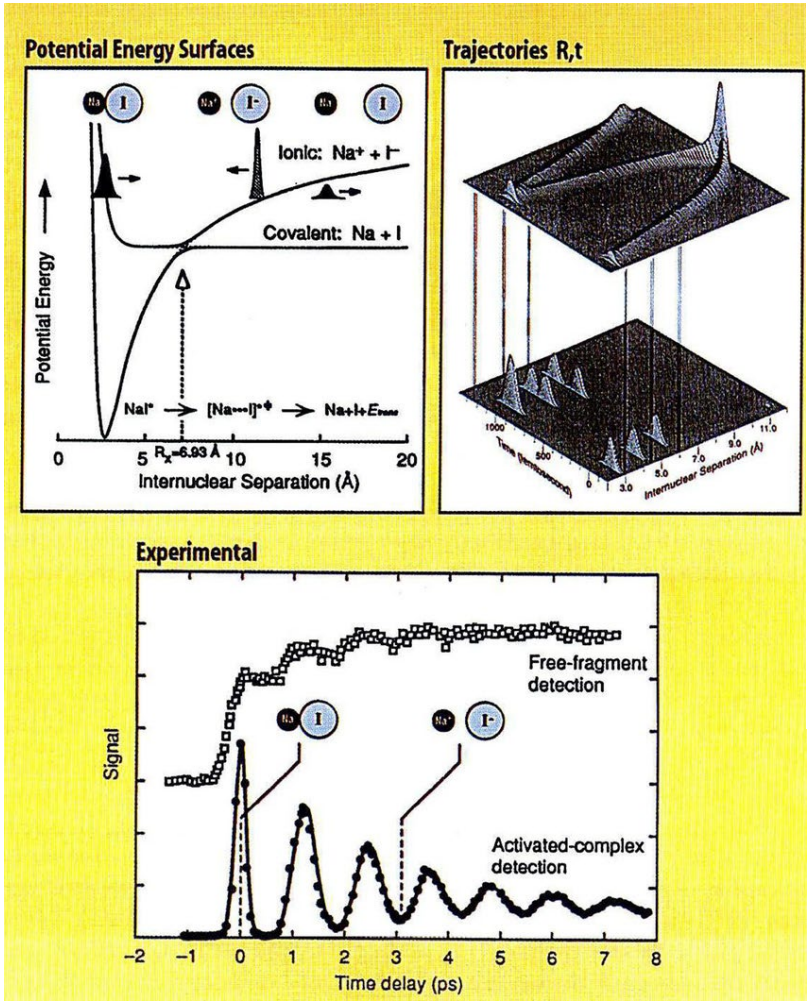


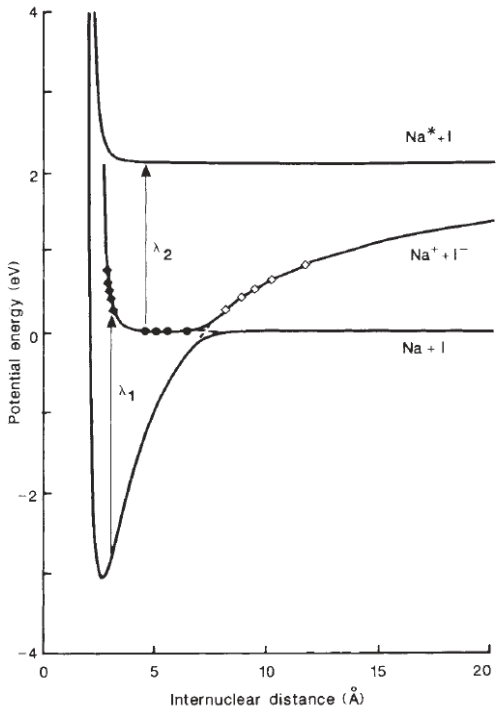
PNAS 2007, themed issue Multidimensional Spectroscopy

Fluorescence detection

Ahmed Zewail (1946-2016)

Nobel Prize in Chemistry 1999 for the development of Femtochemistry





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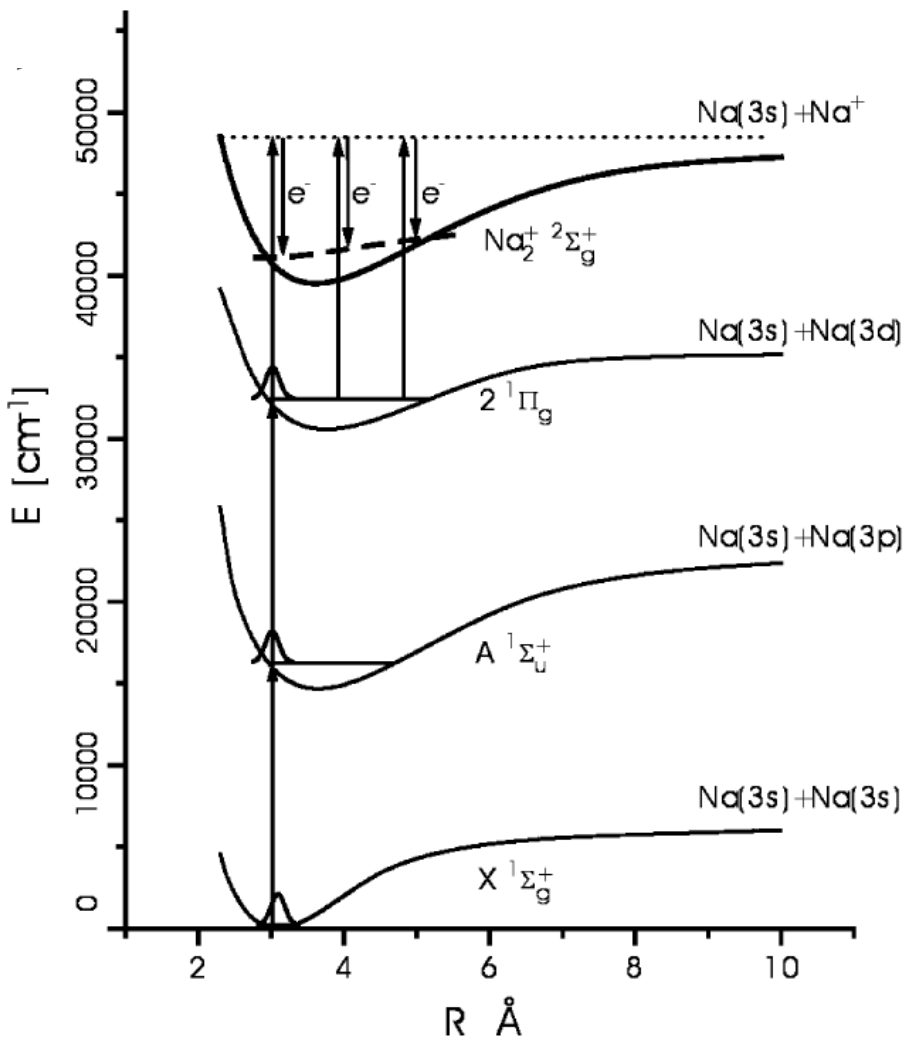
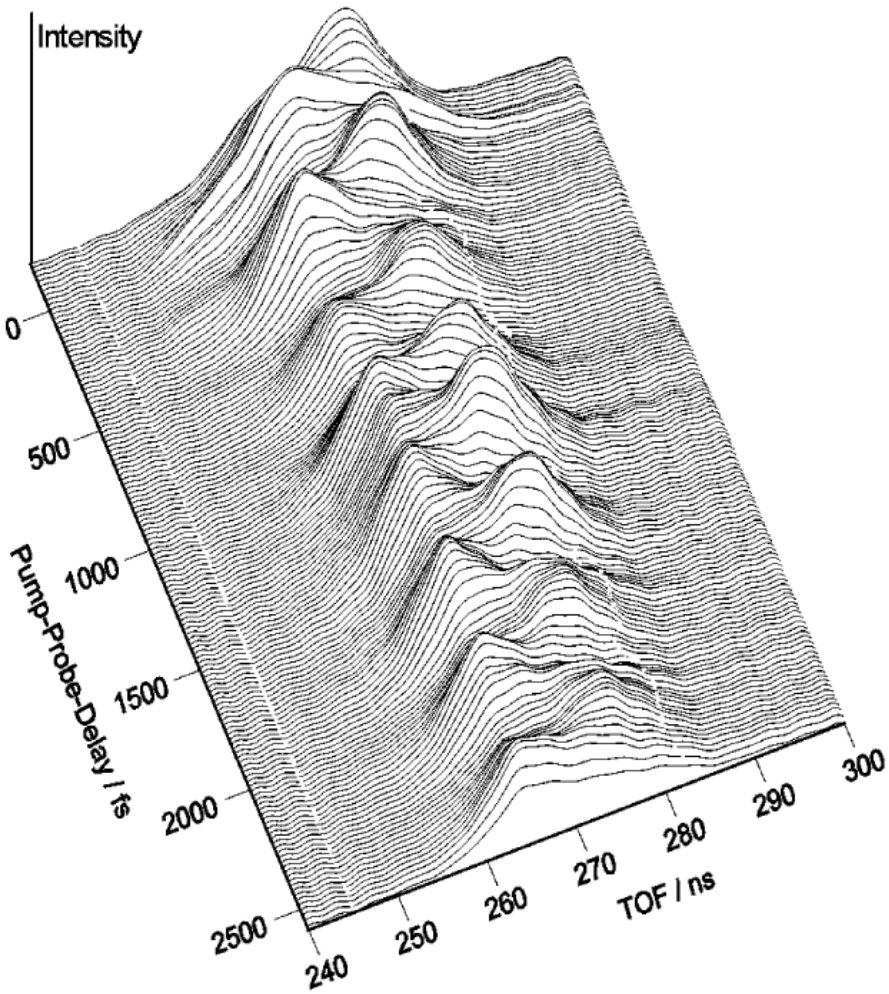
Time-resolved photoelectron spectroscopy





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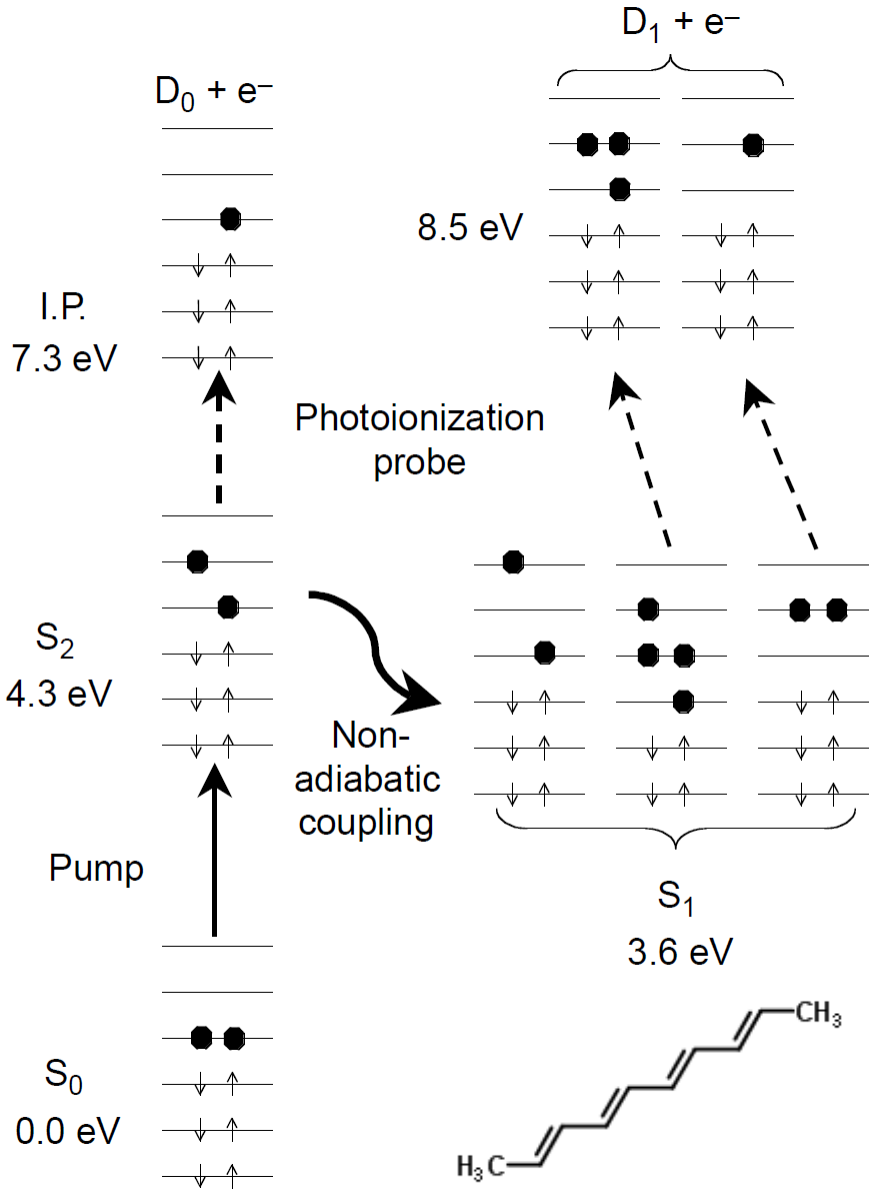
Time-resolved photoelectron spectroscopy



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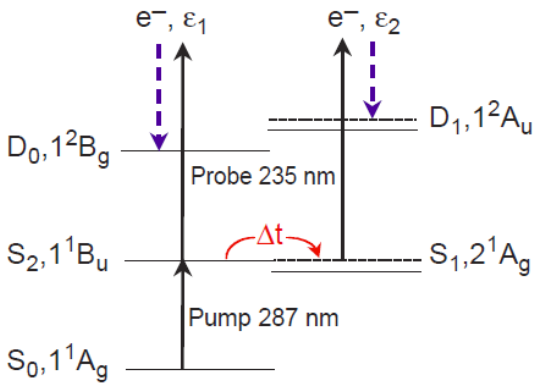

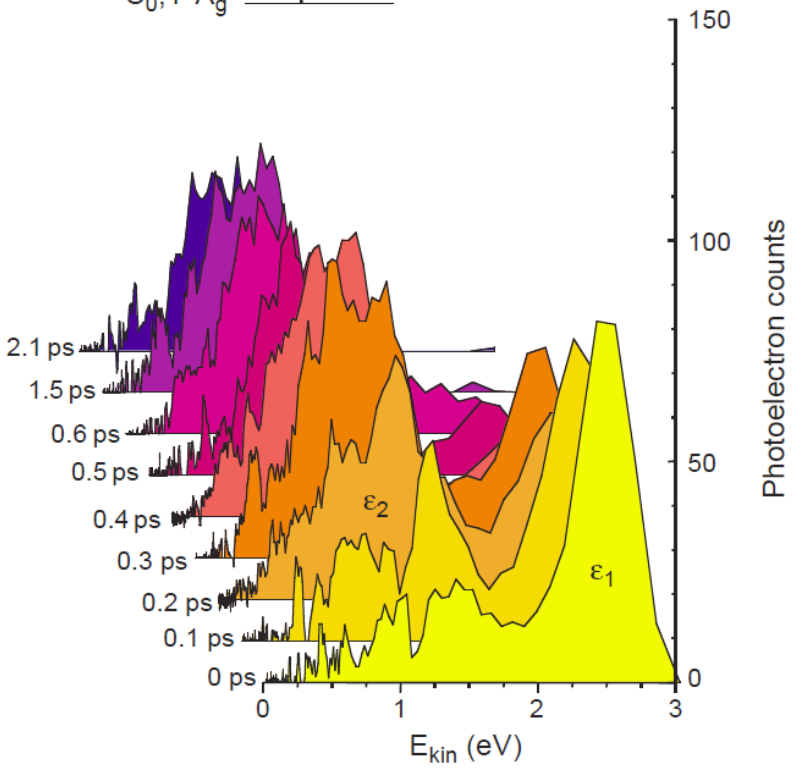

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Useful materials for further reading:

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