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Winter College on Optics: Trends in Laser Development and Multidisciplinary Applications to Science and Industry

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From Femtosecond to Attosecond Pulses: an overview of science and technology development

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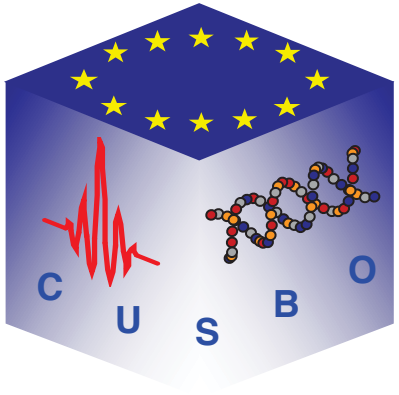
From Femtosecond to Attosecond Pulses: an overview of science and technology development

Sandro De Silvestri

Centre for Ultrafast Science and Biomedical Optics (CUSBO)
Politecnico di Milano - Italy



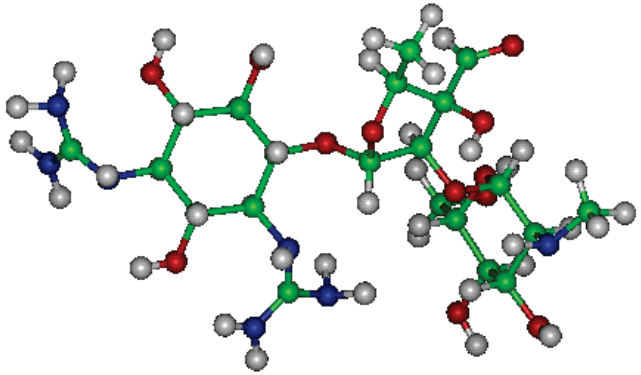
Outline

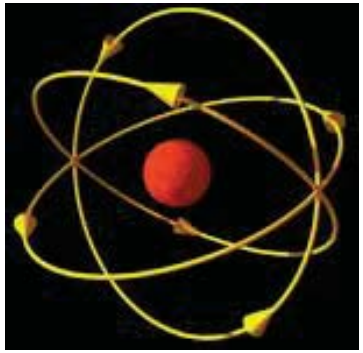
- The tool in ultrafast spectroscopy: Pump-probe
- From dye lasers to solid state lasers: a revolution in femtosecond ultrafast spectroscopy
- Watching the atomic motion in real time: coherent vibrational spectroscopy and molecular dynamics
- Attosecond pulses: generation and measurement
- Watching the electron motion in real time: attosecond science

Space-Time Scale of Matter Dynamics

micron — nanometer — picometer

10^{-6} m — 10^{-9} m — 10^{-12} m



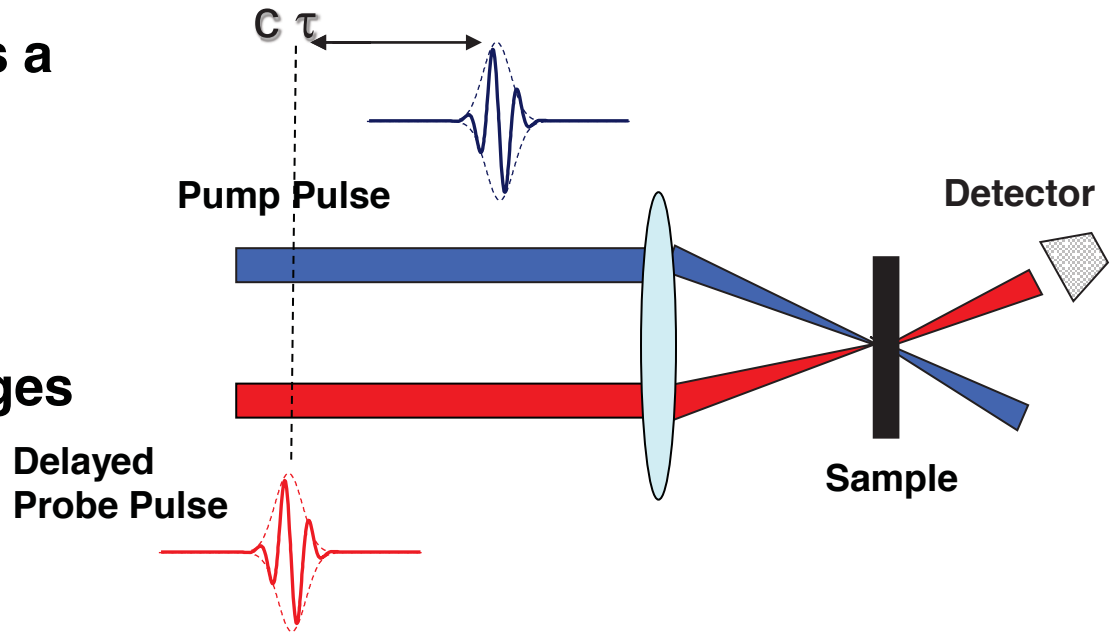


nanosecond — picosecond — femtosecond — attosecond

10^{-9} s — 10^{-12} s — 10^{-15} s — 10^{-18} s

“Pump-Probe” Technique

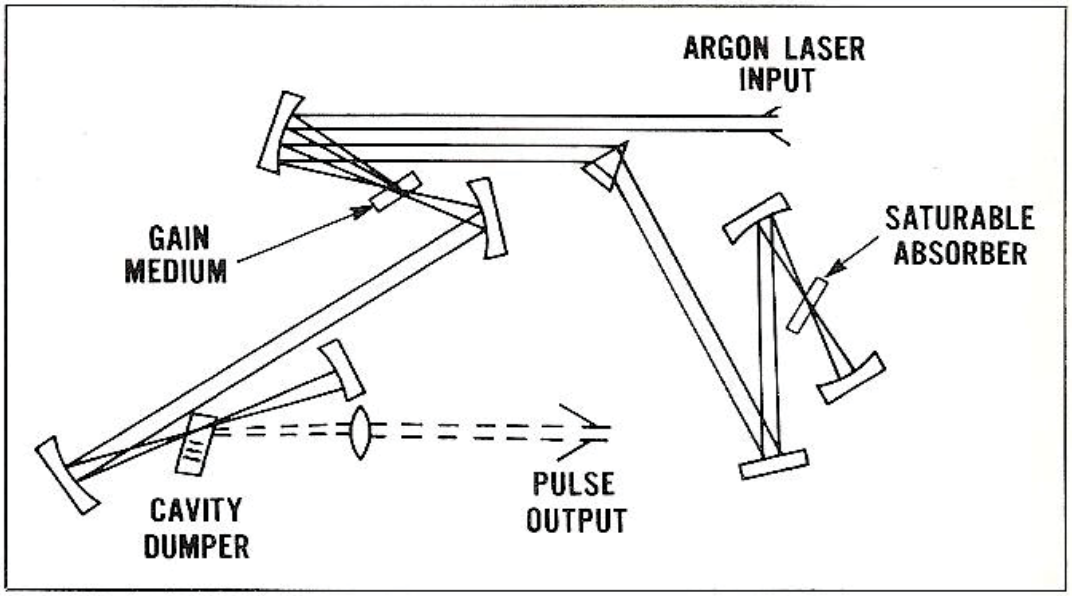
- A first pulse (Pump) triggers a dynamical process
- A second delayed (τ) pulse (Probe) detects the pump-induced transmission changes

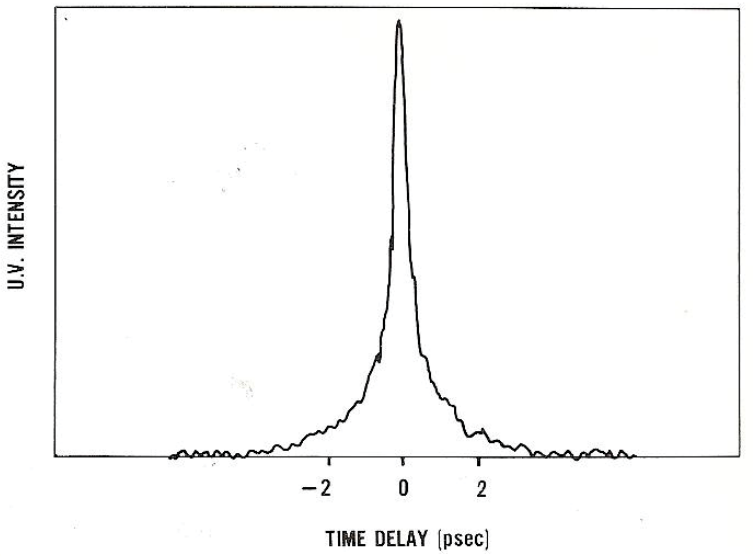


The Golden Rules

- High temporal resolution: short pulses
- Care for sample recovering: moderate pulse repetition rate
- Wide application range: spectrally tunable pump and probe pulses (independently)

Cavity-Dumped Sup-picosecond Dye Laser



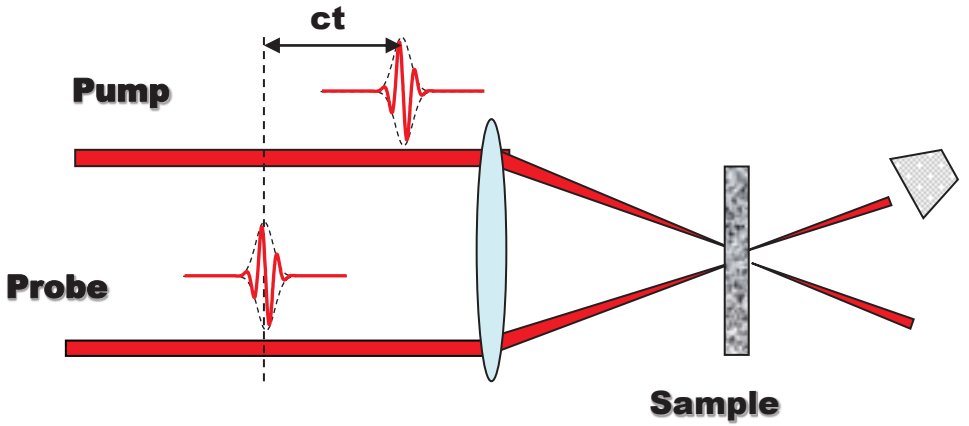


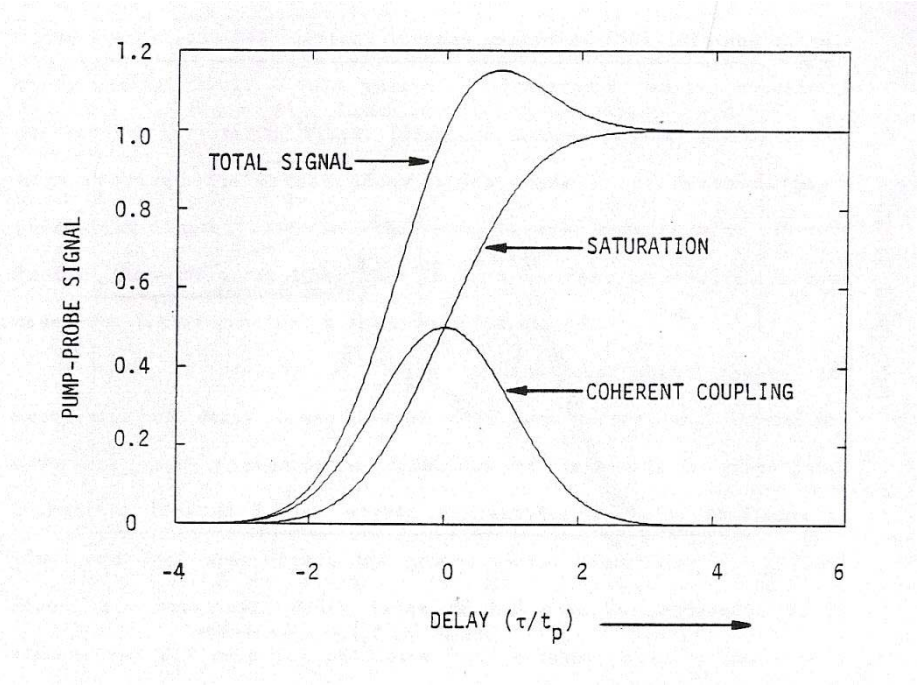
- After grating pair compression and filtering: 300 fs duration at 615 nm
- 100 kHz repetition rate by a cavity dumper insertion (5 nJ pulse energy)
- Option: second harmonic of the output at 307.5 nm

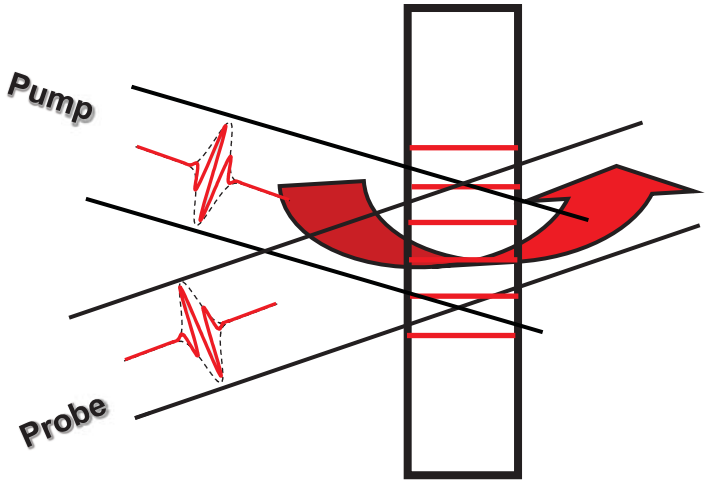
E. Ippen and C.V. Shank, Appl. Phys. Lett. 27, 499 (1975)

Degenerate pump-probe spectroscopy

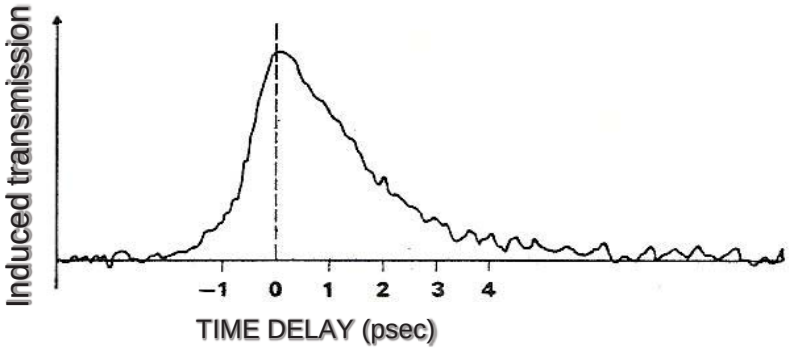
- Time resolution: 300 fs
- Sample recovery: guaranteed by the cavity dumper
- Pump and probe pulses at the same wavelength (coherent coupling problem!)





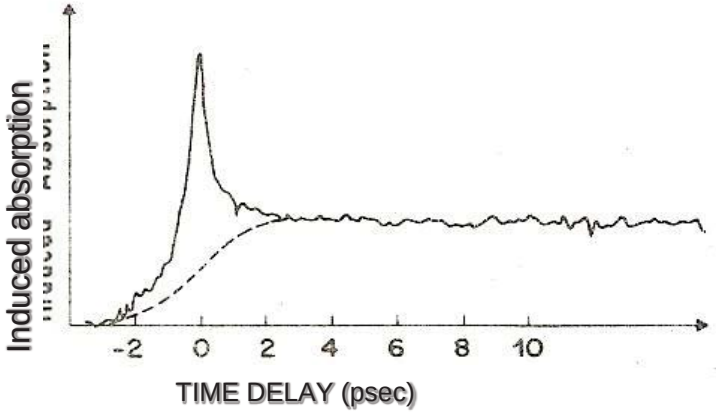


First Applications of Pump-probe Spectroscopy

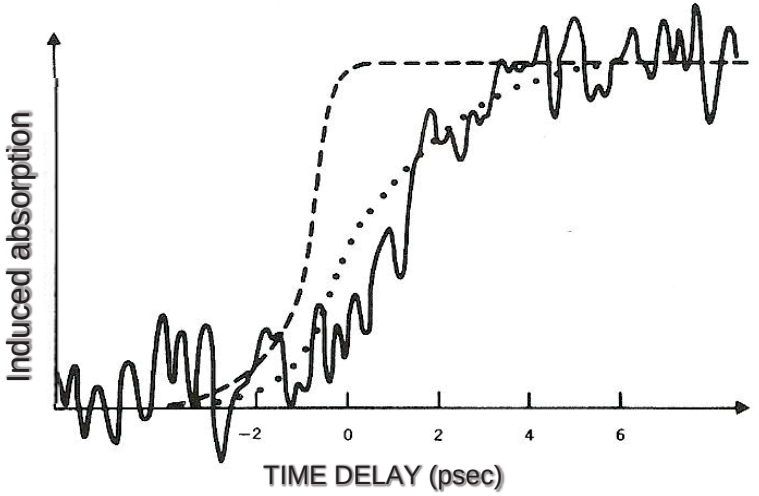


- **Measurement of the recovery time of Malachite Green (2.1 ps):** *E.P.Ippen et al, Chem Phys Lett. 38, 611 (1976)*

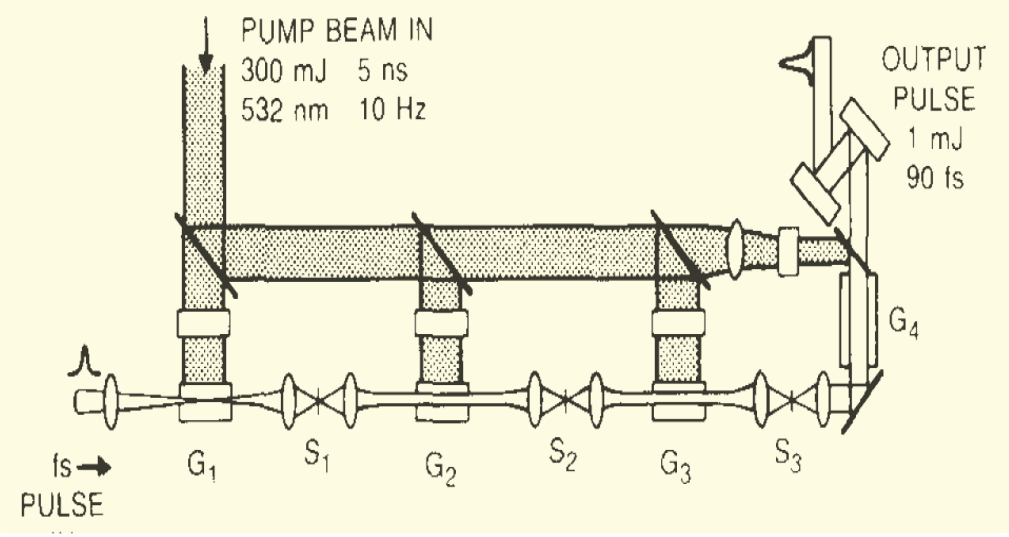
- **Photolysis of carboxyhemoglobin was found to occur in less than 500 fs***: C.V.Shank and E.P.Ippen, Science 193, 50 (1976)*



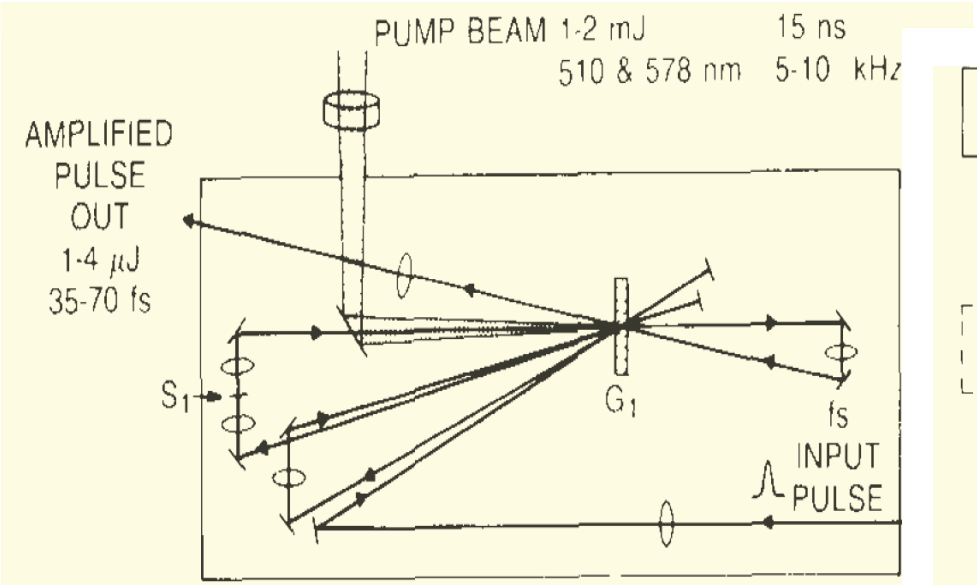
- **Bacteriorhodopsin (converting light into chemical energy) relaxes to its first intermediate in 1 ps:** *E.P.Ippen et al. Science 200, 1279 (1978)*

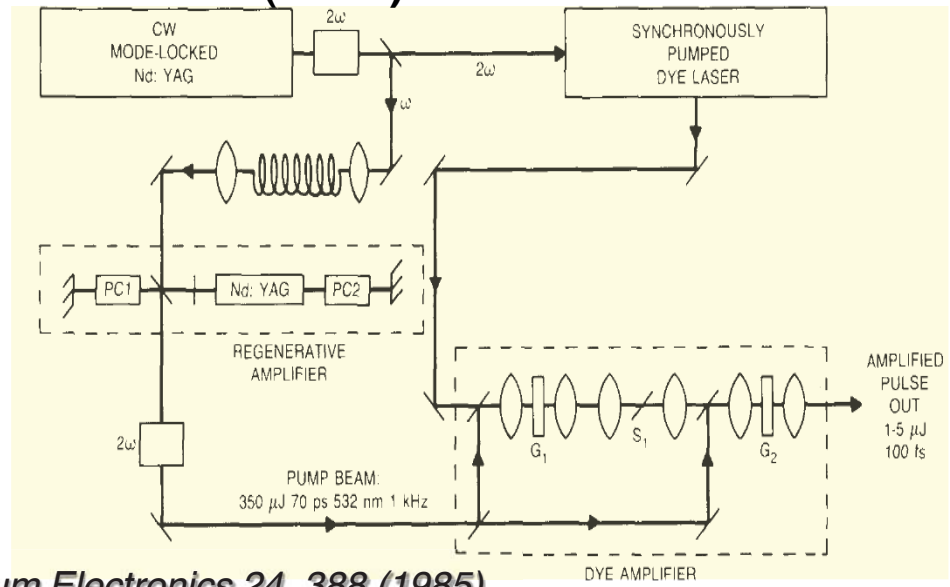


Femtosecond Dye Laser Amplifiers



- Dye cell stages pumped by a Q-switched Nd:YAG (10-20 Hz) – 1978/82
- Multipass dye stream pumped by copper vapor laser (5-10 kHz) - 1984
- CW Nd:YAG/YLF regenerative amplifier as pump source of dye cells (1kHz) - 1985

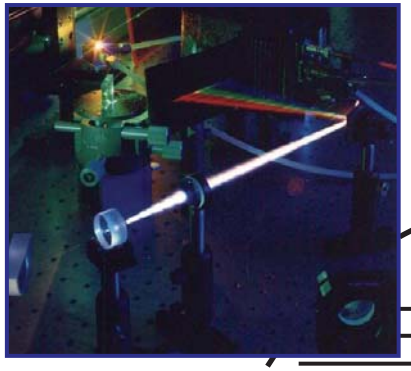


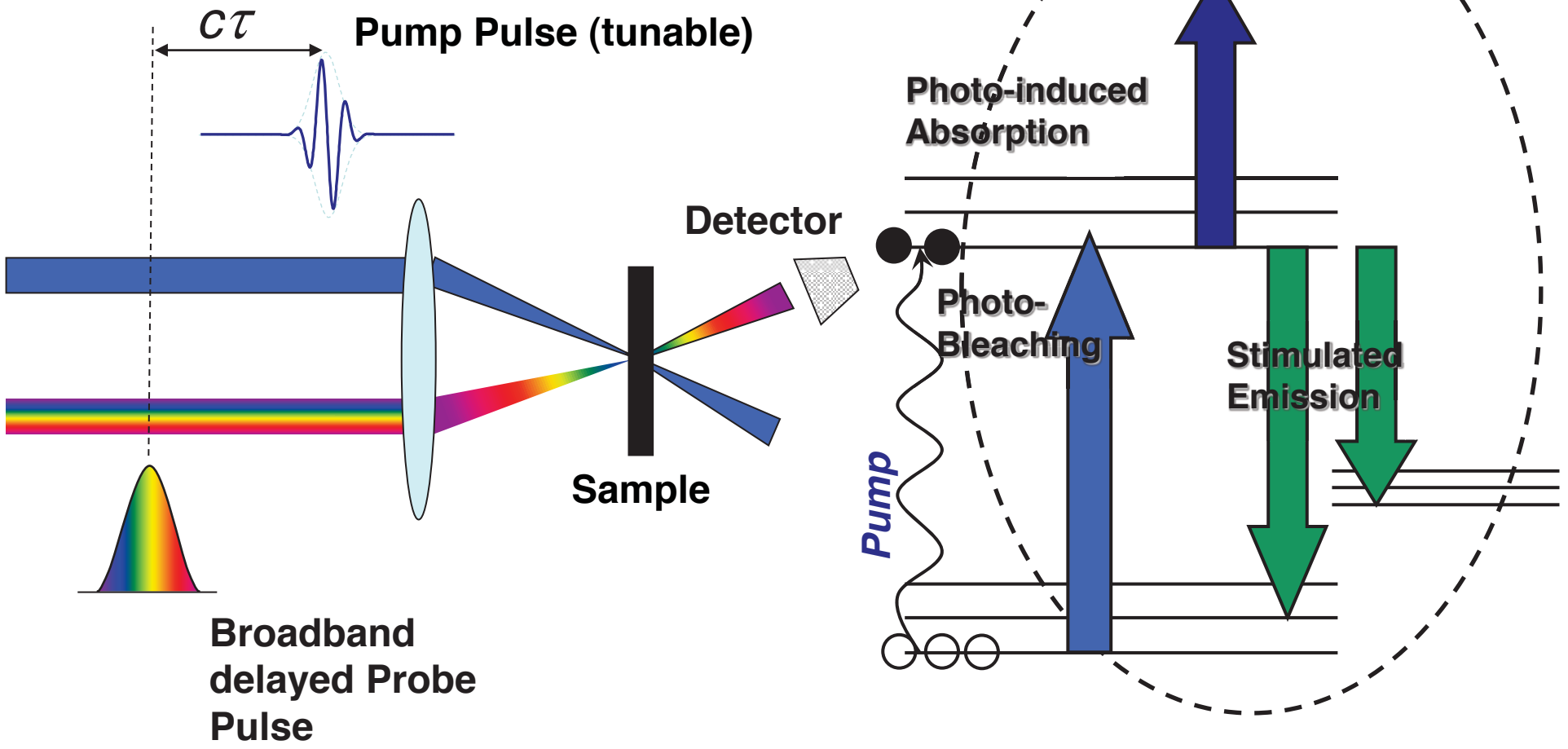


W. H. Knox, IEEE J. of Quantum Electronics 24, 388 (1985)

Tunable Pump-Probe Experiments

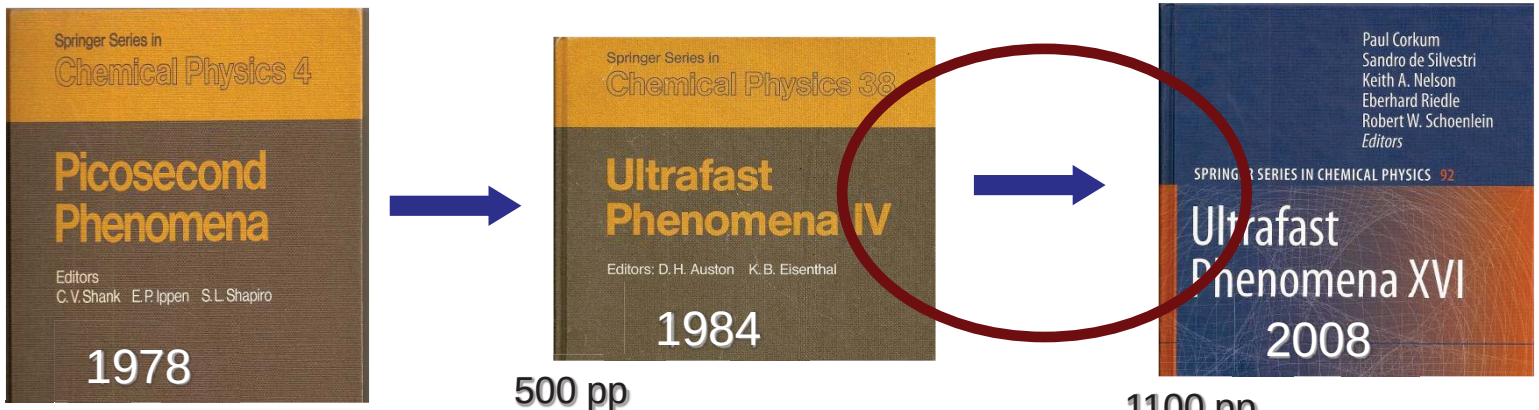
By super-continuum generation tunable radiation can be produced and amplified from near IR to visible (In 1970 Alfano and Shapiro reported the first measurements of frequency broadening in crystals and glasses)





A Landmark Conference

The first conference gathering research groups in ultrashort pulse generation and applications started in 1978 as "Picosecond Phenomena"



360 pp

500 pp

1100 pp

30 years in which we have seen a growing fraction of the proceedings dedicated to applications:

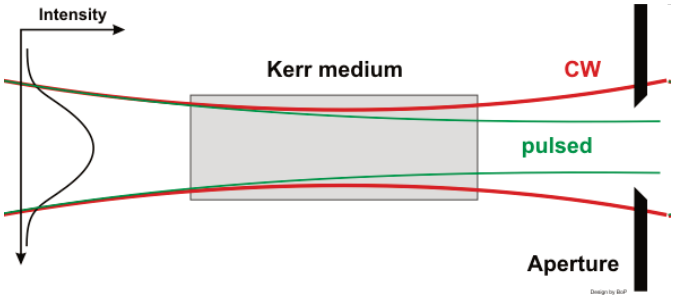
solid state physics, atomic and molecular physics, chemistry, biology, etc…

From dye lasers to solid state lasers:

a revolution in ultrafast spectroscopy

Kerr Lens Mode-locking

Few optical cycle pulses directly from the oscillator !!



Sub-two-cycle pulses from a Kerr-lens mode-locked Ti:sapphire laser

U. Morgner, F. X. Kärtner, S. H. Cho, Y. Chen, H. A. Haus, J. G. Fujimoto, and E. P. Ippen

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V. Scheuer, G. Angelow, and T. Tschudi

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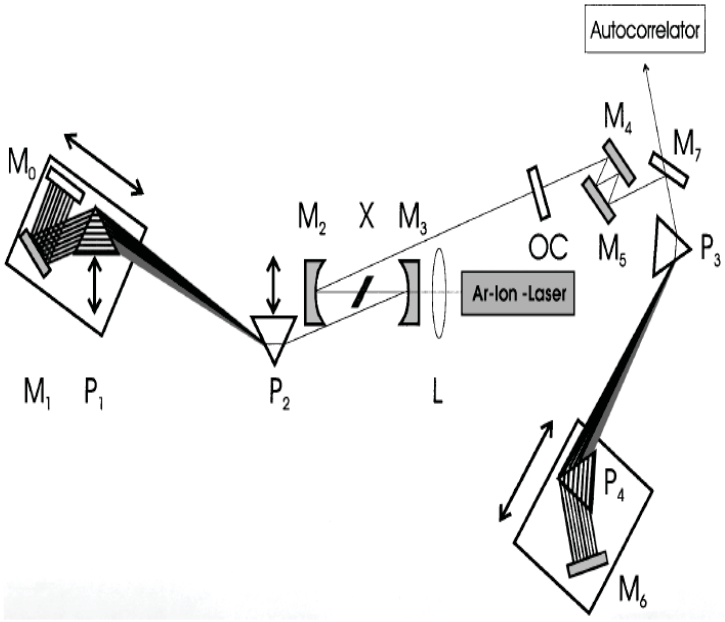
Received October 8, 1998



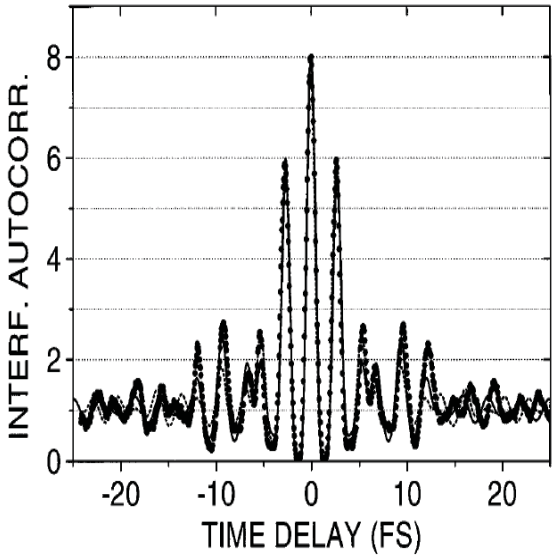
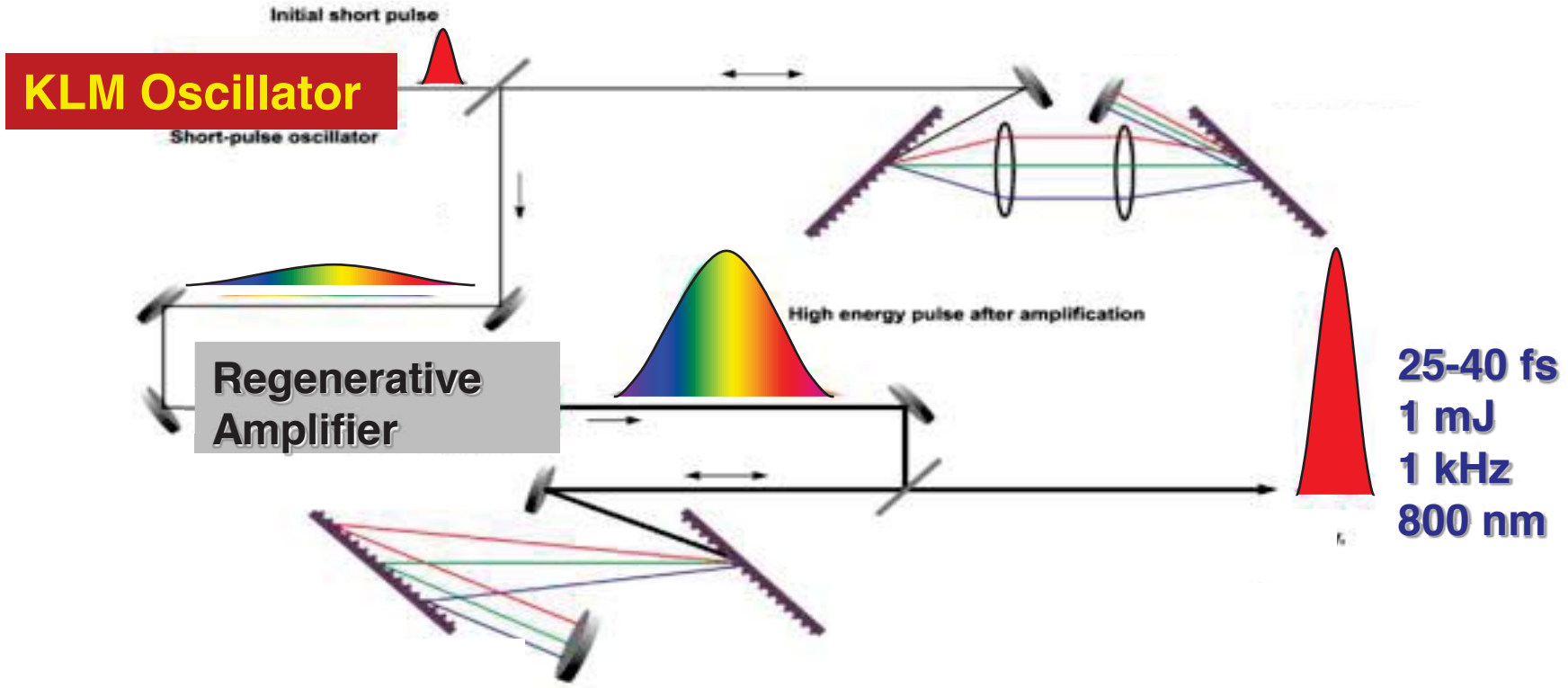


Fig. 4. Measured interferometric autocorrelation of the Ti:sapphire laser. The dashed curve is a fit of a sinc^2 function with a FWHM of 5.4 fs, and the solid curve is the calculation from the spectrum.

Chirped Pulse Amplification (CPA)

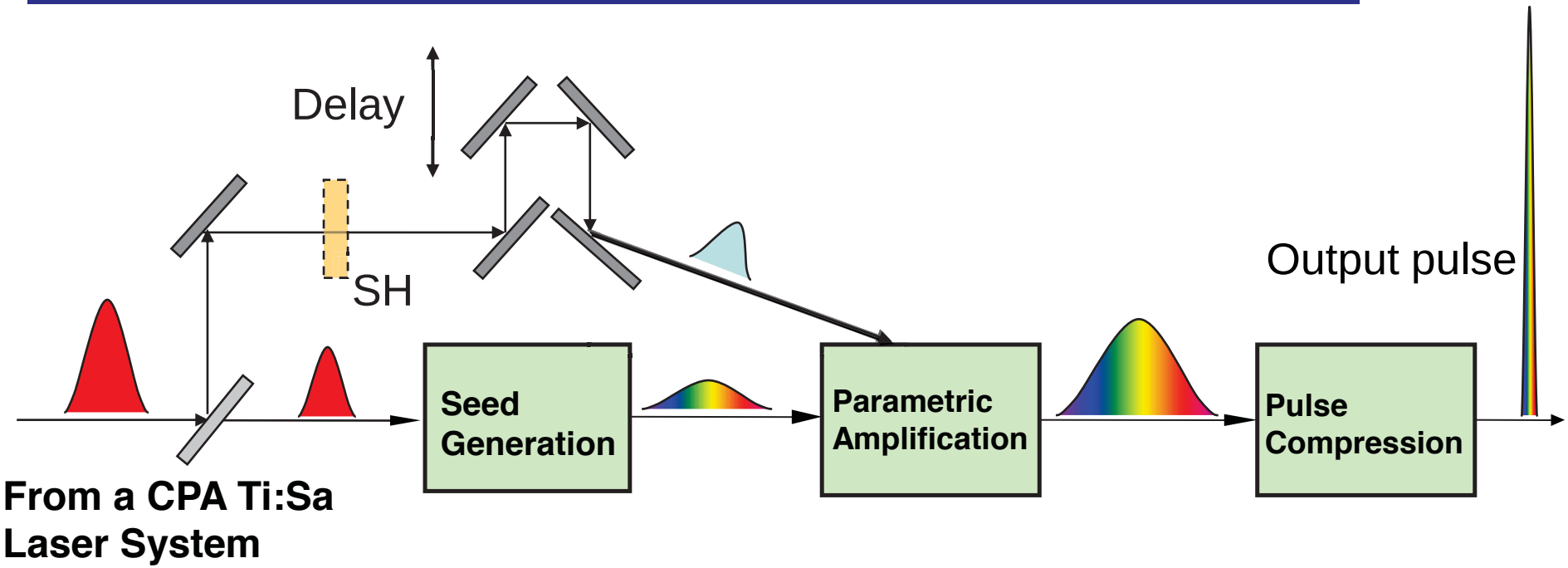


A new powerful tool for ultrafast spectroscopy

- Reliability: very good day to day operation
- Stability: small fluctuations in pulse energy and duration
- High energy pulses at high repetition rate
- Broad dissemination amongst scientists in different fields

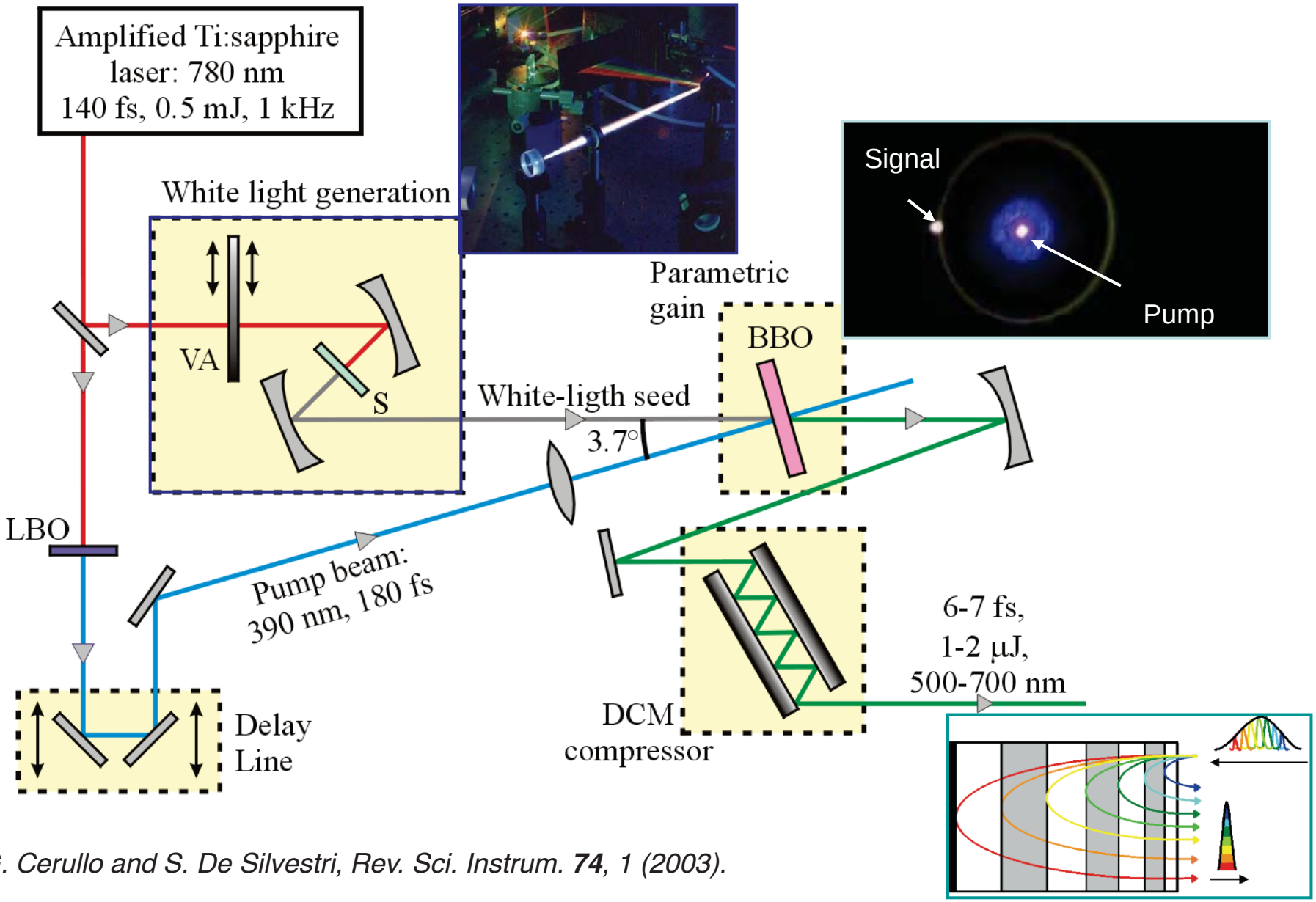
Non Linear Optics for Frequency Tuning

Ultra-broadband Optical Parametric Amplifiers (OPA)



- Broadband seed pulses by white light generation
- Broadband amplification by phase matching over a wide range of seed wavelengths
- Pulse compression by chirped mirrors (or other techniques)

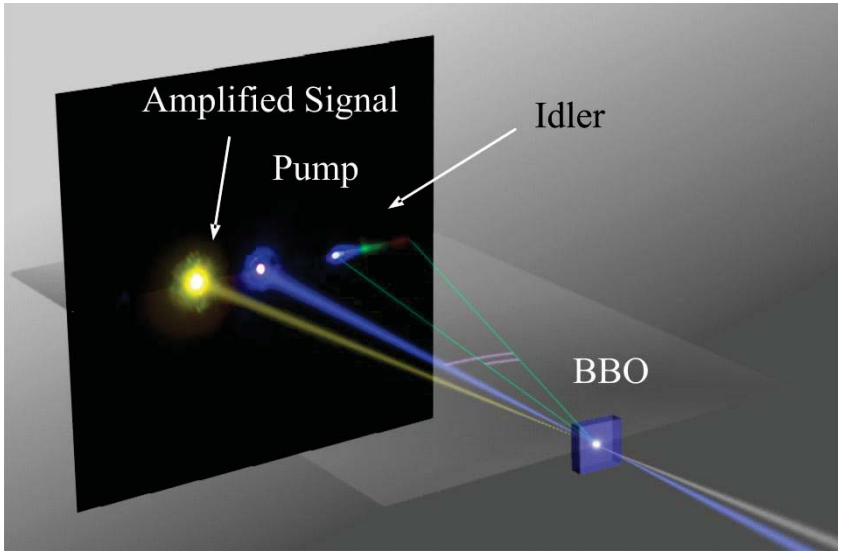
Visible Ultrabroad-band OPA

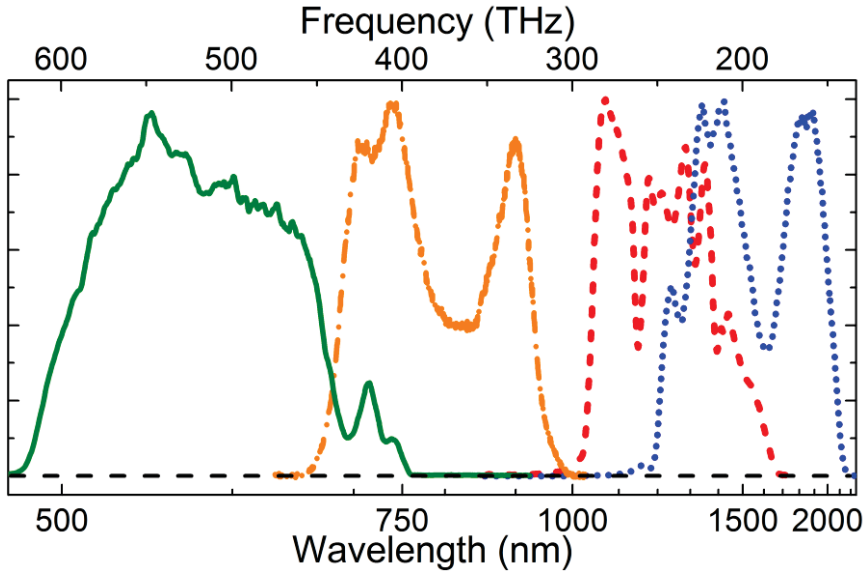


G. Cerullo and S. De Silvestri, Rev. Sci. Instrum. ***74****, 1 (2003).*

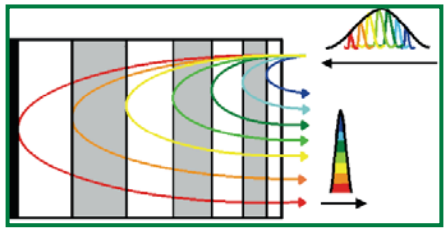
Few Optical Cycle Pulses

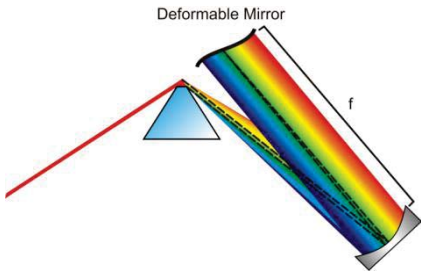
Tunable broad-band OPAs from near-IR to Visible

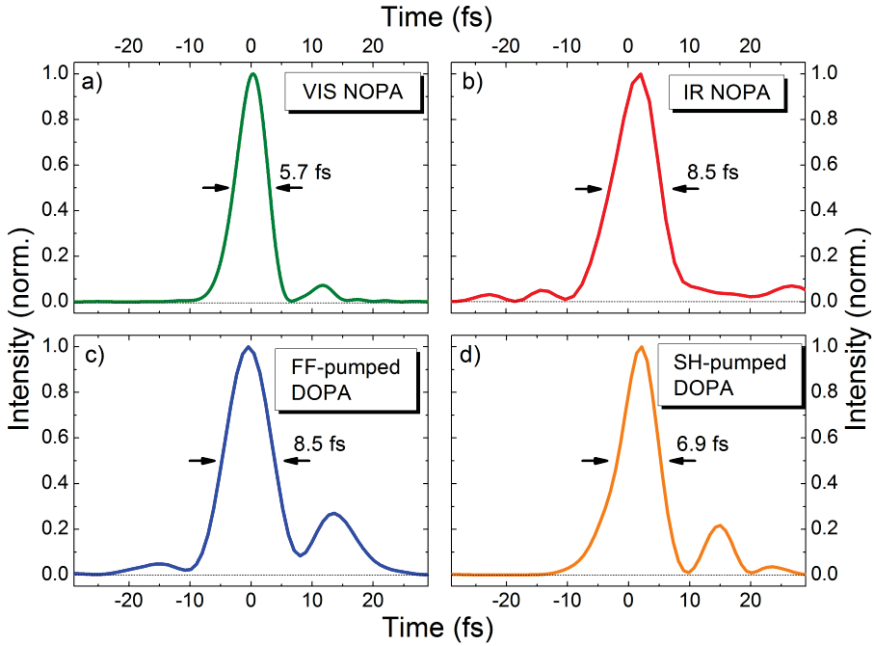




After pulse compression



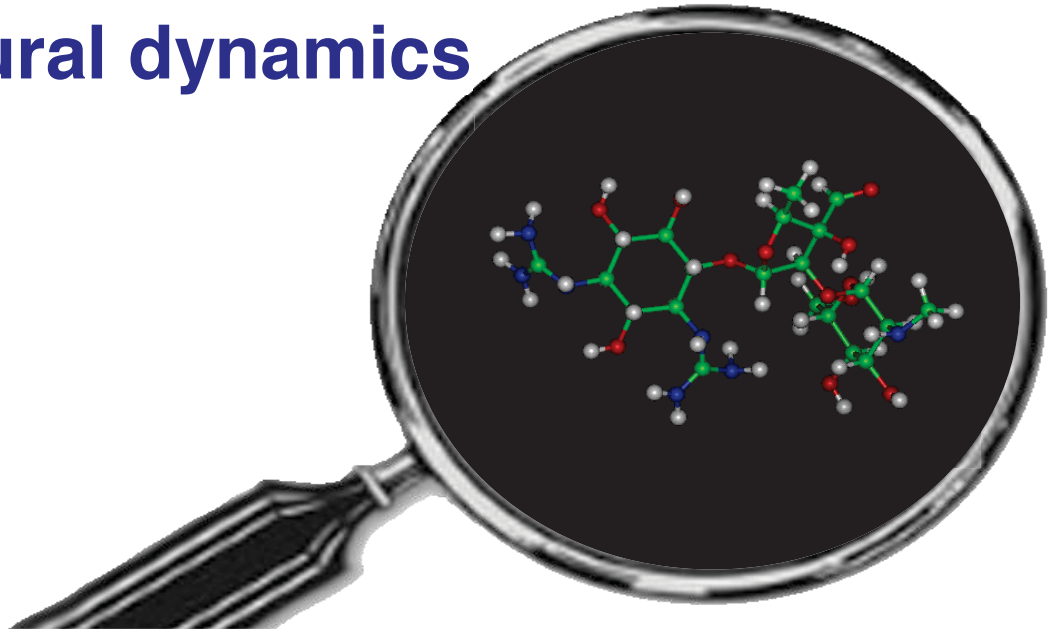




C. Manzoni, D. Polli and G. Cerullo, **Rev. Sci. Instr. 77**, 023103 (2006)
D. Brida et al., **Opt. Lett. 33**, 741-743 (2008)

Watching the atomic motion in real time over a fs time scale provides information on:

- molecular vibrations
- molecular structural dynamics



Non-Resonant Impulsive Raman Scattering

Volume 116, number 2,3 CHEMICAL PHYSICS LETTERS 3 May 1985

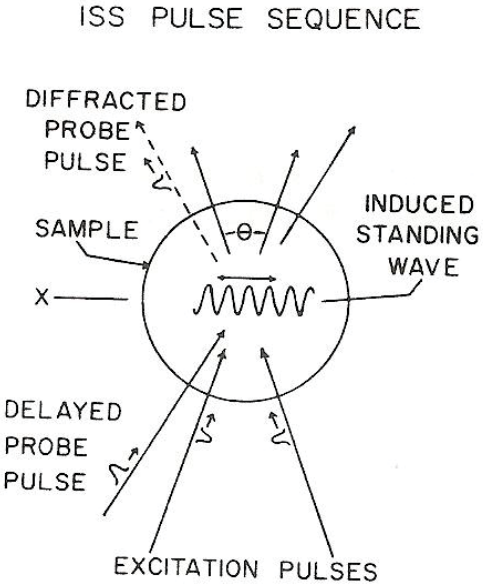
FEMTOSECOND TIME-RESOLVED MEASUREMENTS OF OPTIC PHONON DEPHASING BY IMPULSIVE STIMULATED RAMAN SCATTERING IN α-PERYLENE CRYSTAL FROM 20 TO 300 K

S. DE SILVESTRI [1,2], J.G. FUJIMOTO, E.P. IPPEN

Department of Electrical Engineering and Computer Science and Research Laboratory for Electronics, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

Edward B. GAMBLE Jr. [3], Leah Ruby WILLIAMS [4] and Keith A. NELSON

Department of Chemistry and Research Laboratory for Electronics, Massachusetts Institute of Technology, Cambridge, MA 02139, USA



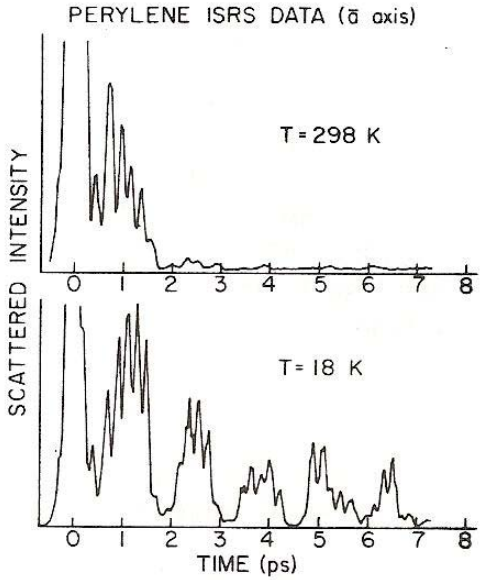
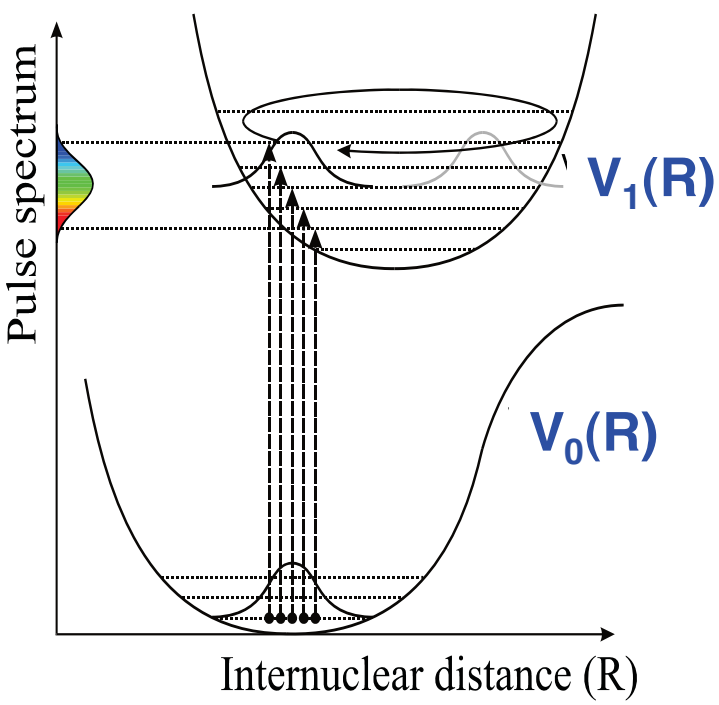


Fig. 3. ISRS data from α-perylene with $k \parallel \bar{a}$. The oscillations in each sweep are due to the 80 and 104 cm^{-1} phonons. The phonon decay rates increase from about 10^{11} s^{-1} at 18 K to 10^{12} s^{-1} at 298 K (see fig. 4).

$$Q(x,t) = \frac{8\pi N(\delta\sigma/\delta Q)I}{\omega_0 nc} e^{-\gamma_0 t}(1+\cos kx)\sin\omega_0 t,$$

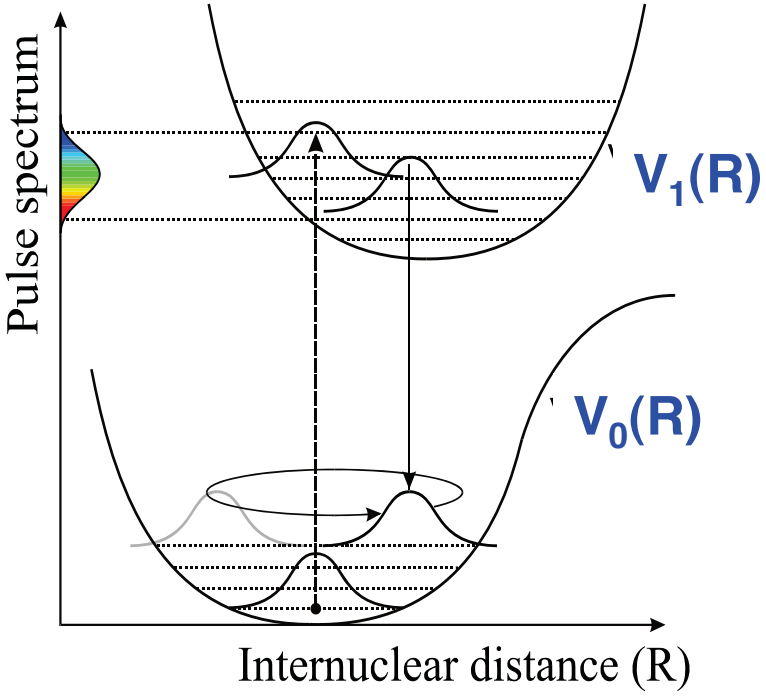
$$\text{Diffraction efficiency} \propto [Q(x,t)]^2$$

Impulsive vibronic excitation



Excited state contribution: wavepacket motion on S_1 energy surface.

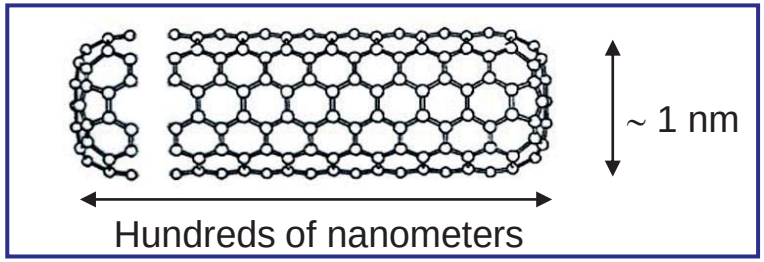
Impulsive resonant Raman scattering



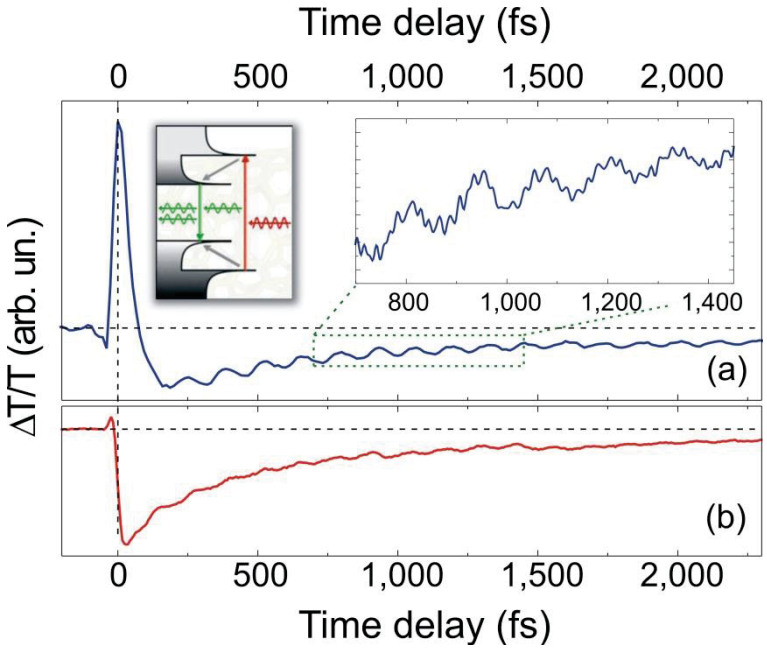
Ground state contribution: wavepacket motion on S_0 energy surface.

Oscillations can come from both **ground** and **excited** state vibrational coherence

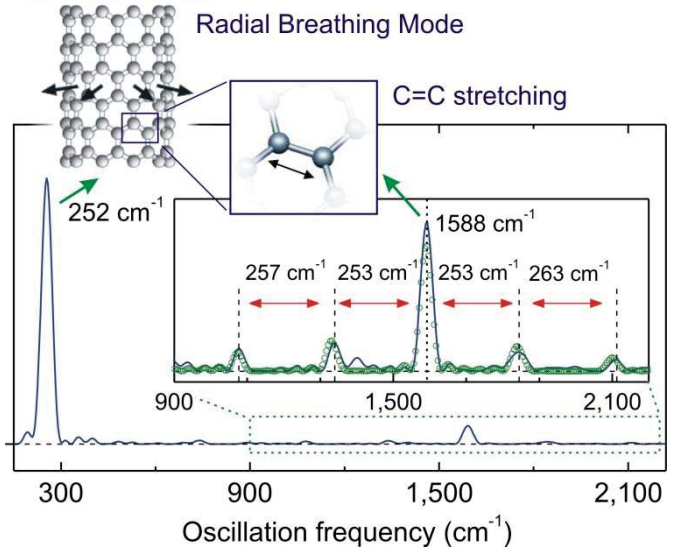
Vibrational Dynamics in Carbon Nanonotubes



- Sub-10 fs pulses in the visible-UV
  - Ultrafast relaxation: inter-subband exciton relaxation time constant of 40 fs



- Vibrational dynamics
  - C=C stretching mode (1588 cm^{-1})
  - Breathing mode (252 cm^{-1})
  - Anharmonic coupling between the two modes (side bands: frequency modulation)



A. Gambetta et al. *"Real-time observation of nonlinear coherent phonon dynamics in single-walled carbon nanotubes"* **Nature Physics 2**, 515 (2006)

cis-trans Direct Observation of the Conical Intersection in Photoisomerization of Rhodopsin

D. Polli,
C. Manzoni,
D. Brida,
G. Cerullo

P. Altoé
G. Tomasello
G. Orlandi
M. Garavelli

O. Weingart

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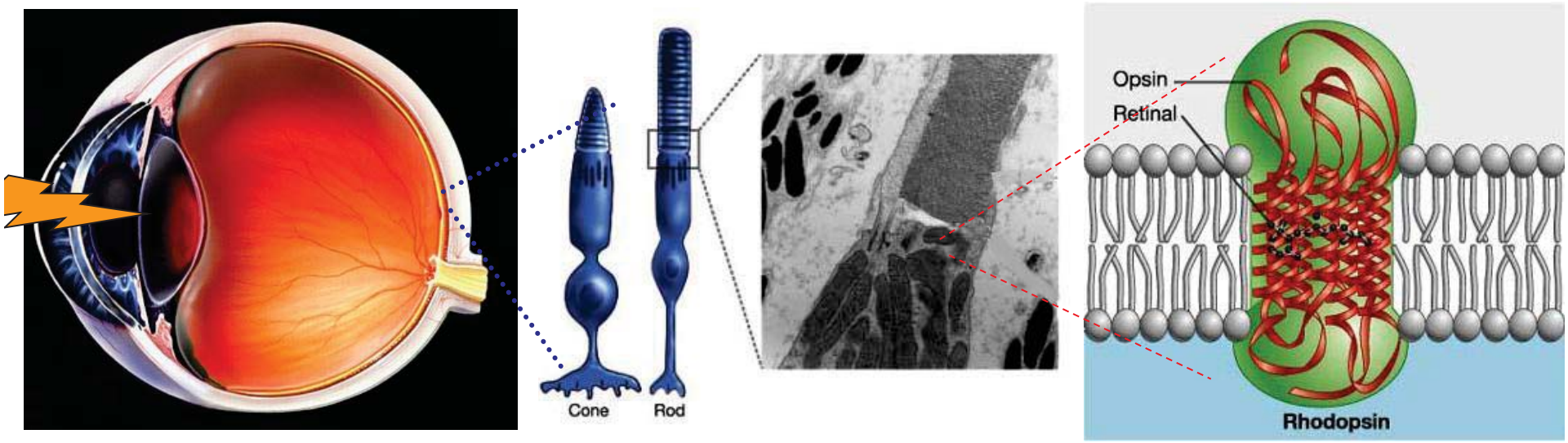
P. Kukura

UNIVERSITY OF OXFORD

K. Spillane,
R. A. Mathies

Berkeley
University of California

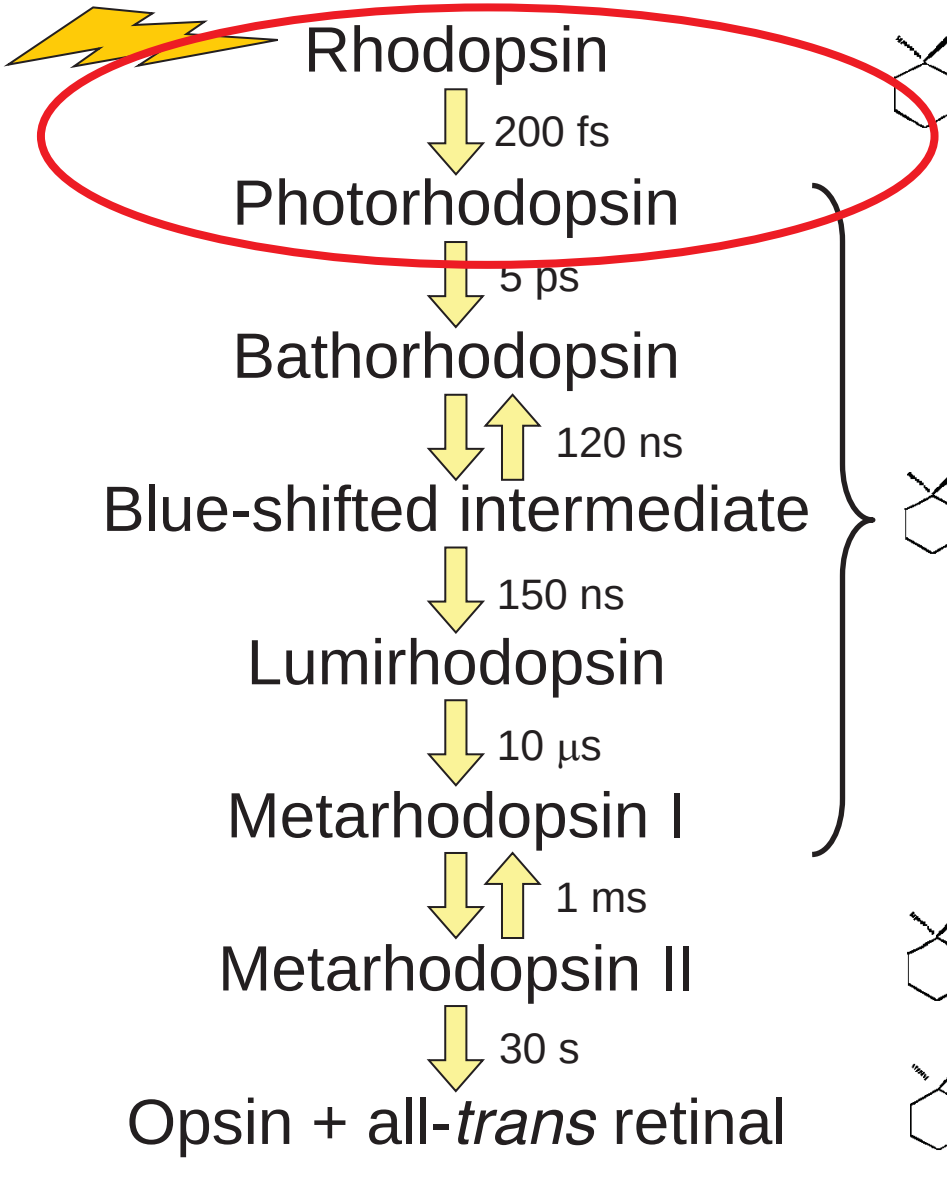
Rhodopsin: Visual Pigment in the Retina

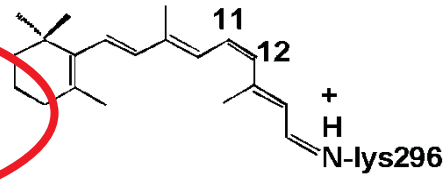


- The photoreceptors in the retina are contained in the **cones** (colour vision) and in the **rods** (night vision)

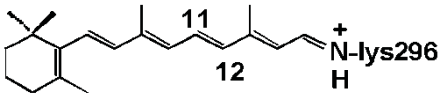
- The **rhodopsin** molecule consists of a protein pocket (**opsin**) containing a light-sensing chromophore (**retinal**)

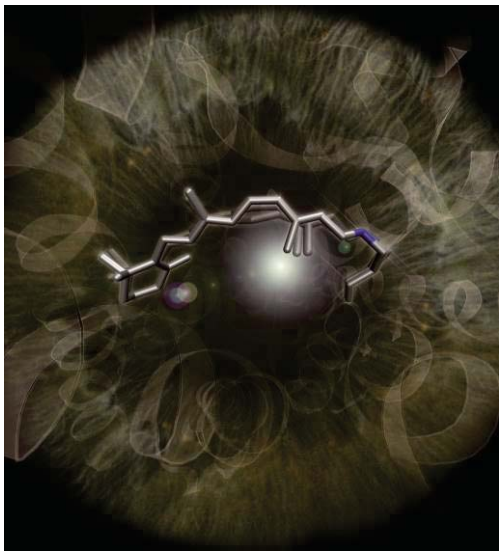
The Visual Photocycle of Rhodopsin

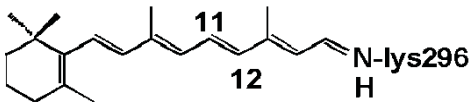


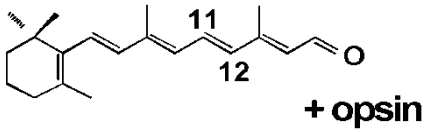


65% quantum yield!



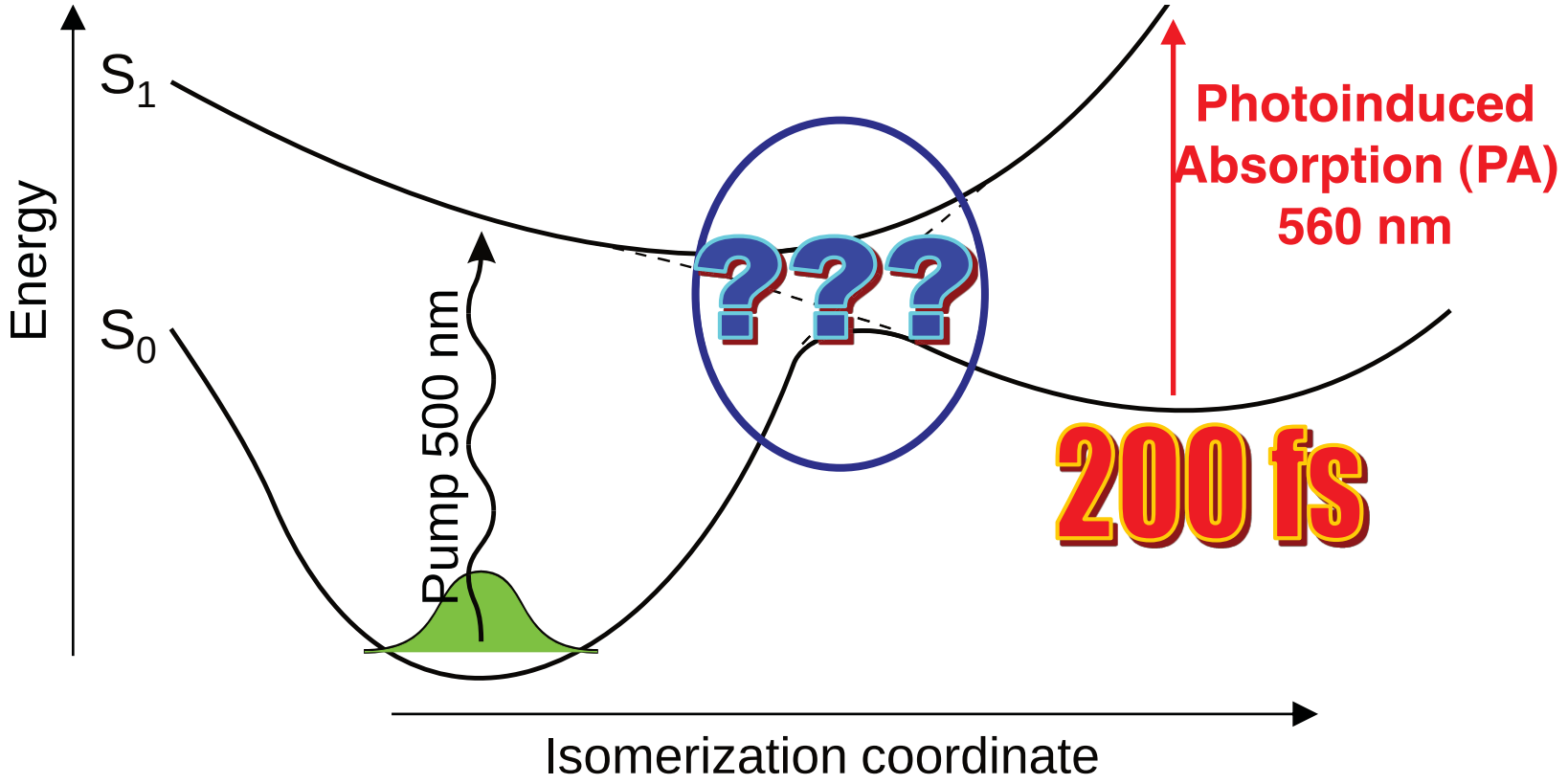






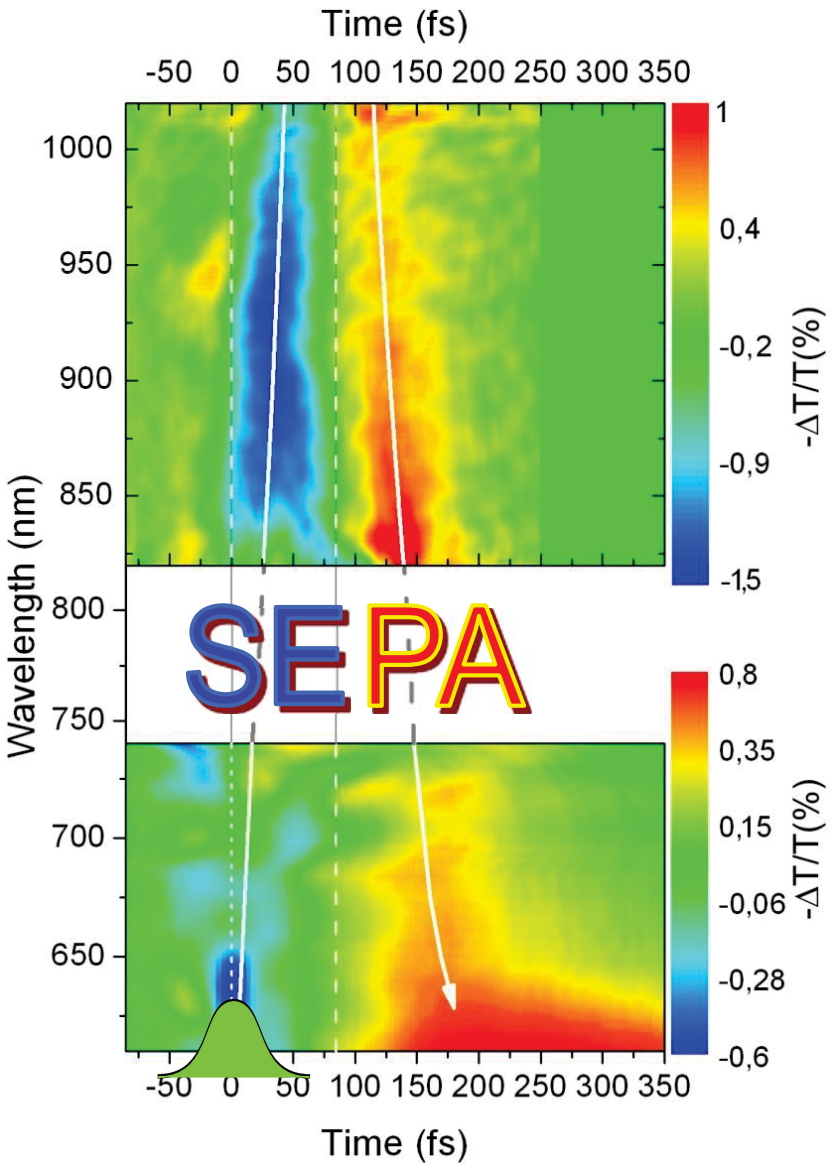
Rhodopsin Isomerization: Primary Event of Vision

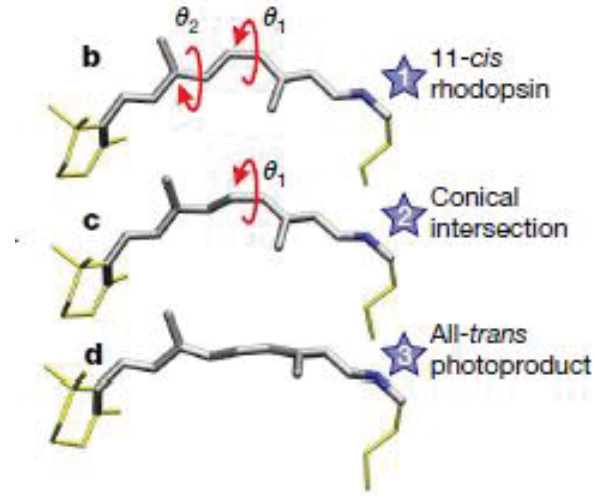
Conical intersections are ubiquitous features in organic photochemistry and photobiology that trigger **radiationless decay** and very efficient **ultrafast conversion of photon energy into chemical energy**

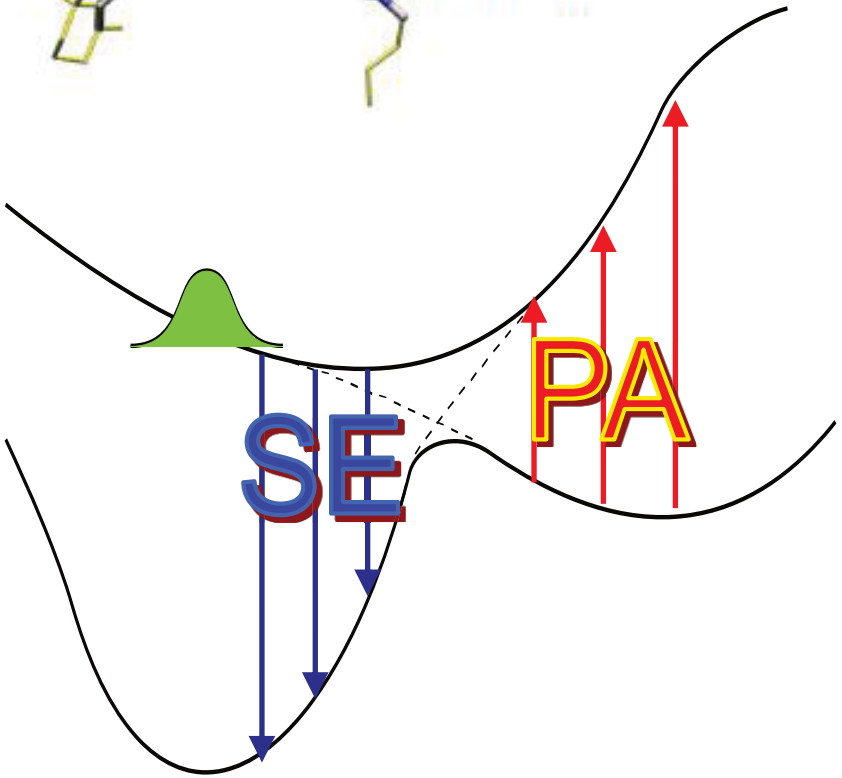


R.Schoenlein et al., **Science** 254, 412 (1991)

Combined Visible-Infrared Measurements



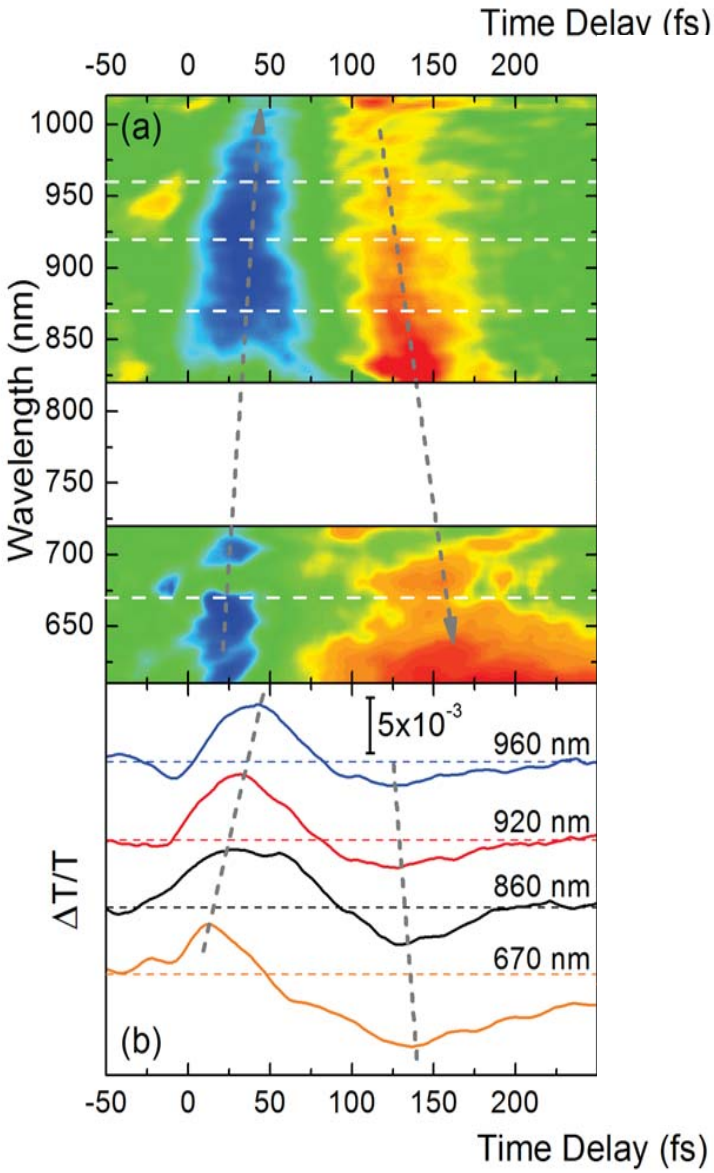




D.Polli et al., **Nature** 467, 440 (2010)

Comparison with Numerical Simulations

Experiments

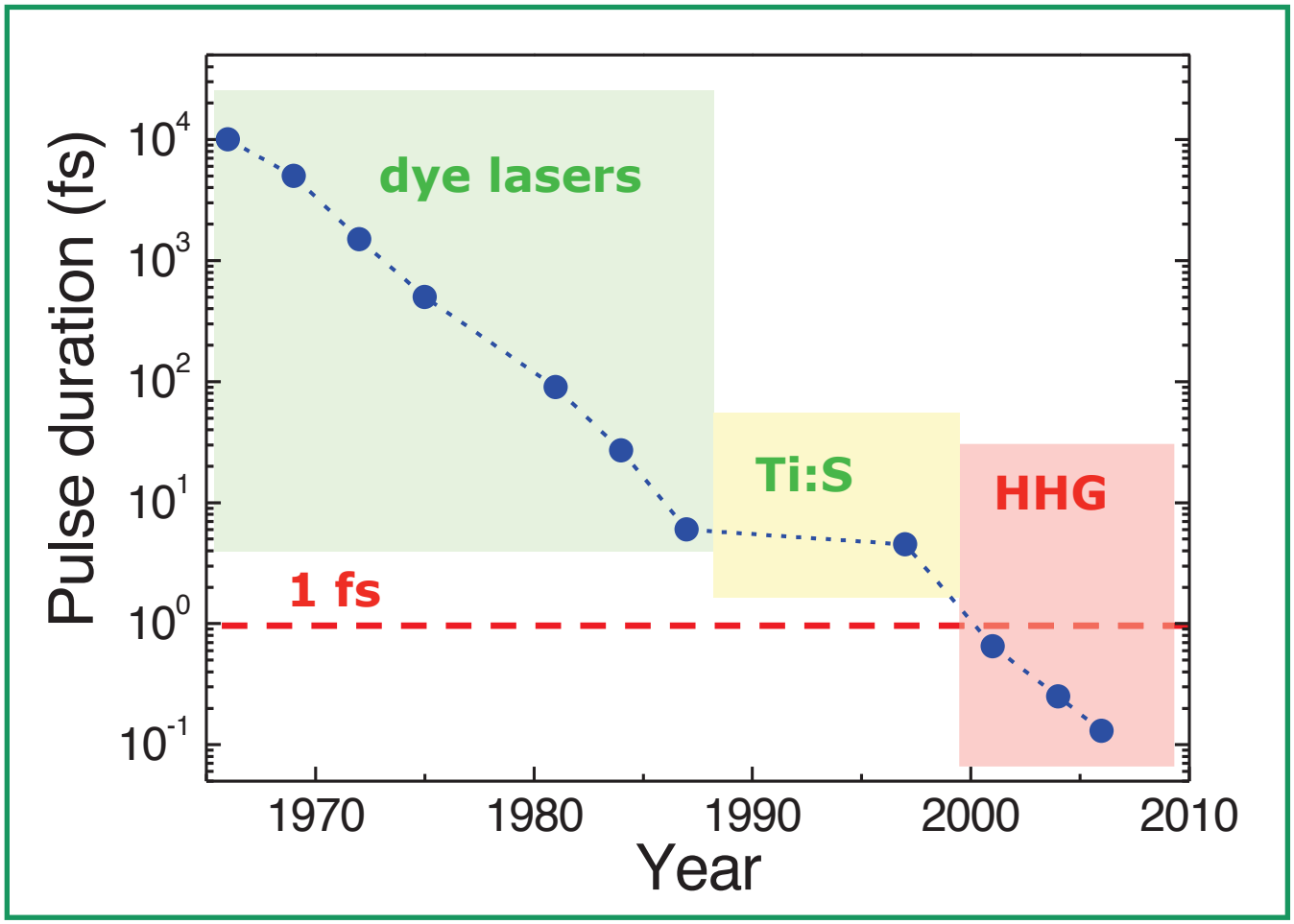


D.Polli et al., **Nature** 467, 440 (2010)

- **QM/MM molecular dynamics**
- **Chromophore** and two neighbouring **water** molecules are **mobile**
- All other atoms are **fixed** at their crystallographic positions
- **38 initial conditions** (vibrational modes sampled at 300 K)

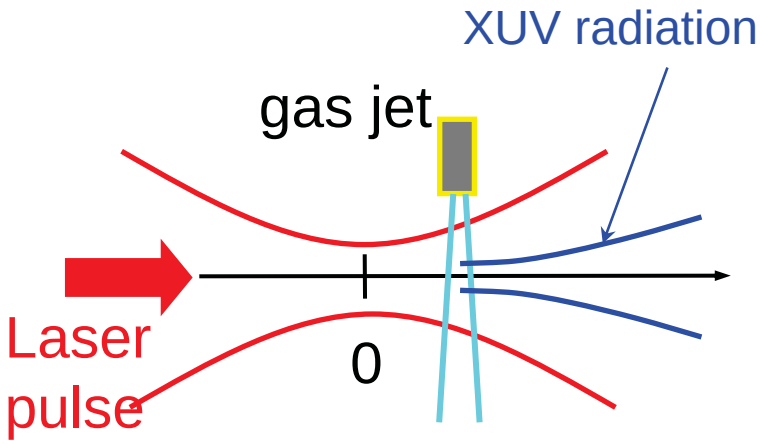
Towards
attosecond pulse generation
and
attosecond physics

Time Line of Ultrafast Optics

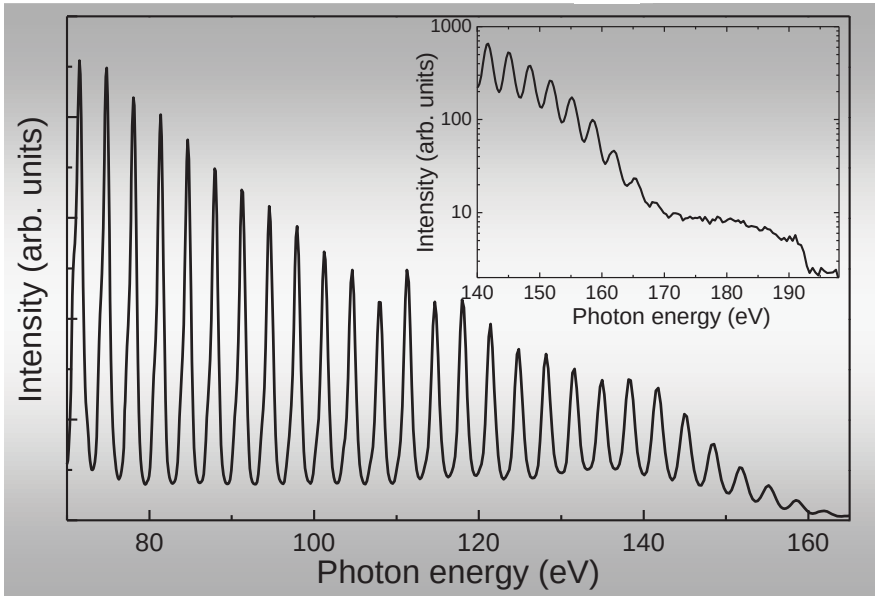


High-order Harmonic Generation

- **An intense light pulse is focused on a gas jet**



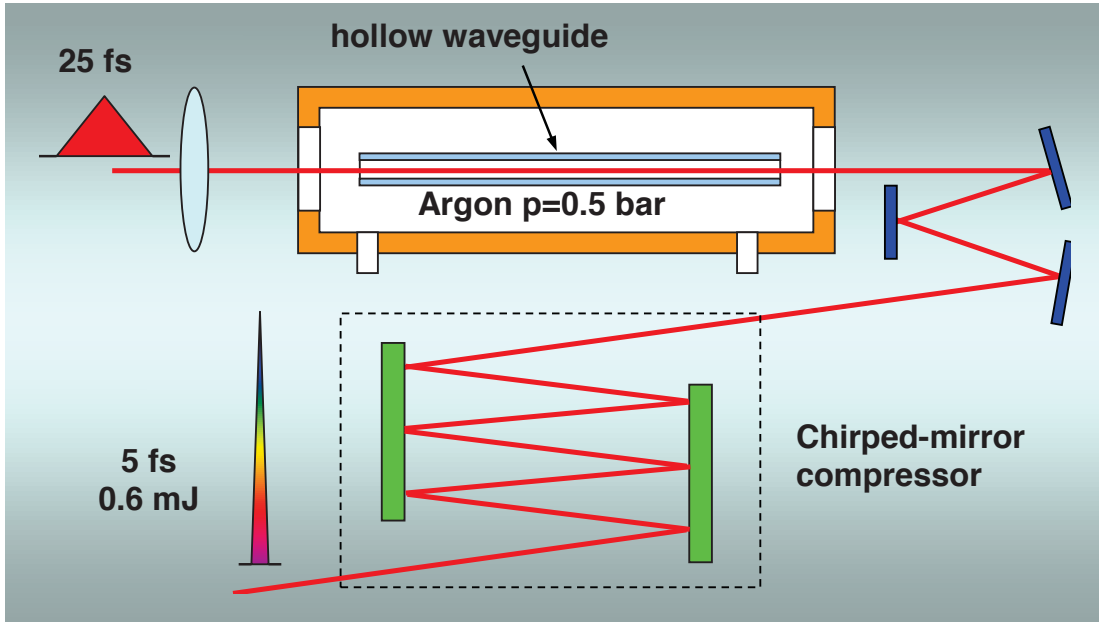
Typical spectrum (Helium)

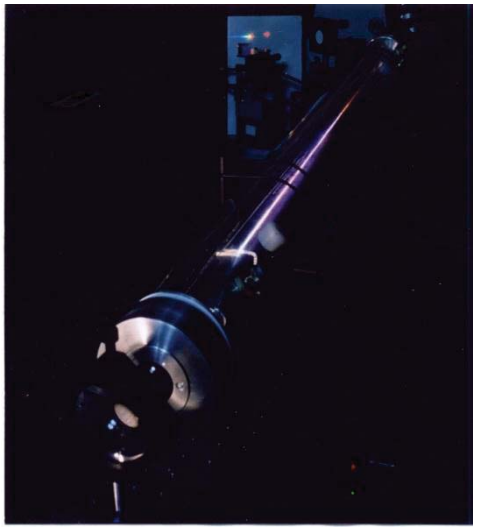


- ➔ **Odd harmonics of the visible light are generated up to the soft-X-ray region**
- ➔ **A periodic spectrum comes from a periodic process in the time domain**

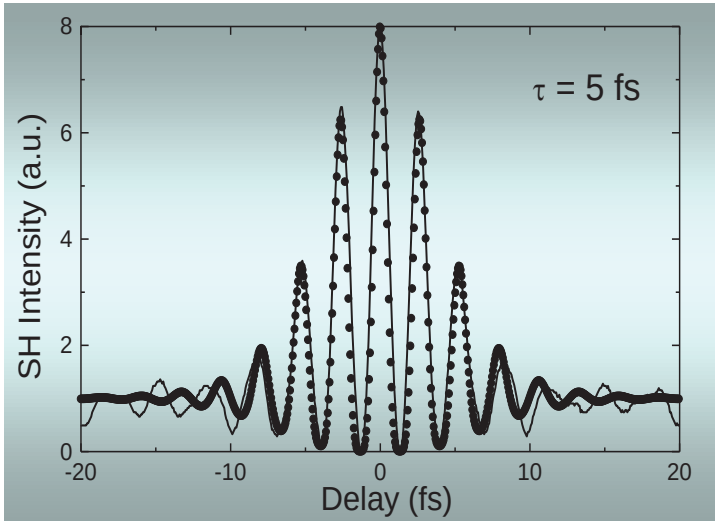
High Energy Sub-10-fs Laser Pulses

CPA Ti:Sapphire Laser 25 fs, 1 mJ, 1 kHz





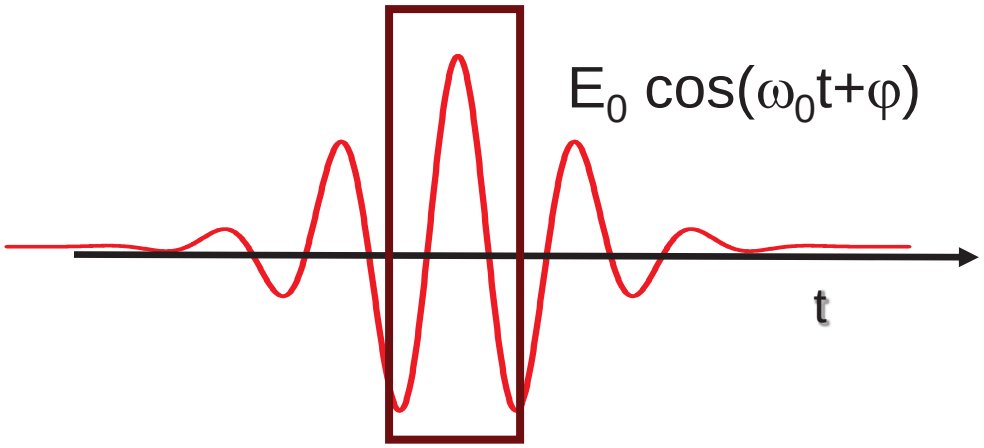
Interferometric
autocorrelator trace

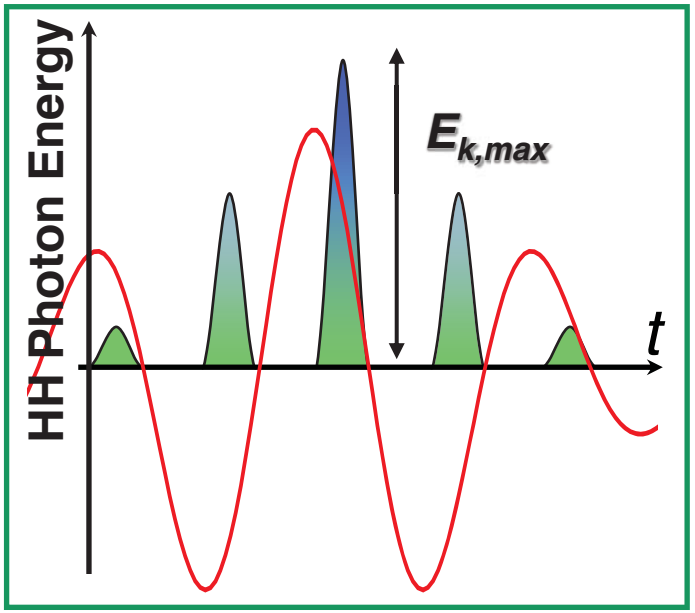


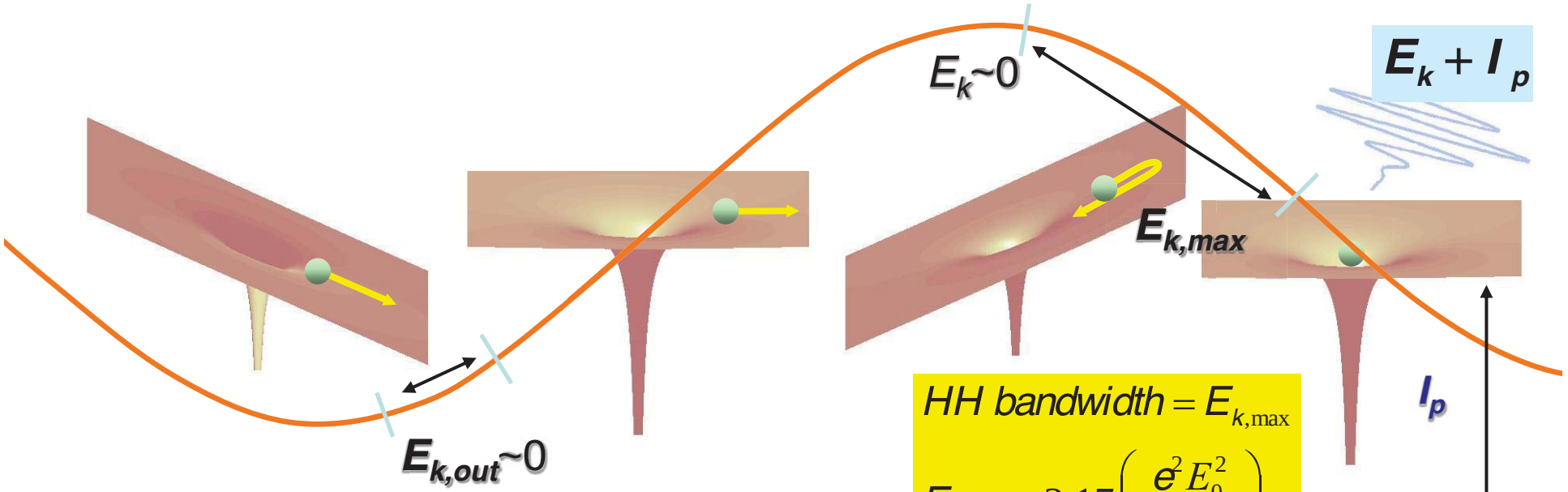
M. Nisoli *et al.*, Appl. Phys. Lett. **68**, 2793 (1996)
M. Nisoli *et al.*, Opt. Lett. **22**, 522 (1997)

Modeling the HHG Process

Few optical cycle pulse on a gas jet





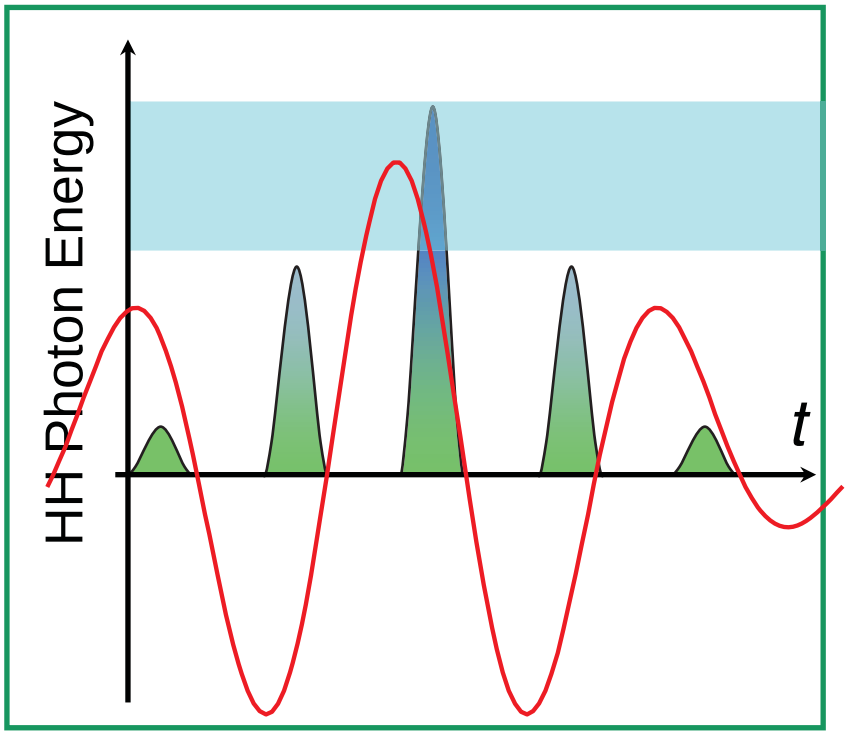


$HH\ bandwidth = E_{k,\max}$

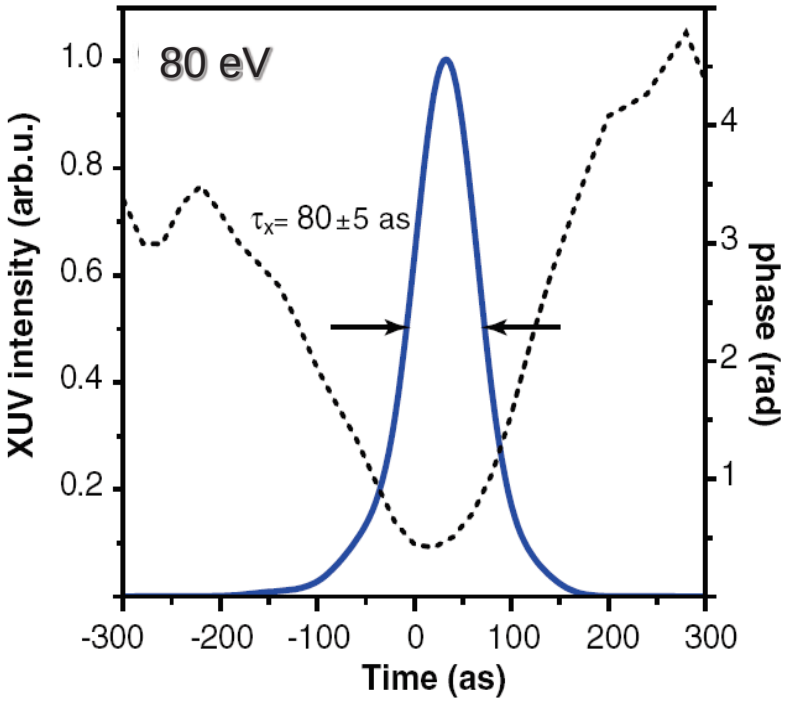
$$E_{k,\max} = 3.17\left(\frac{e^2 E_0^2}{4m\omega_0^2}\right)$$

Isolated Attosecond Pulses (1)

Frequency filtering HHG



Using quasi-monocycle driving pulses: 3.3 fs

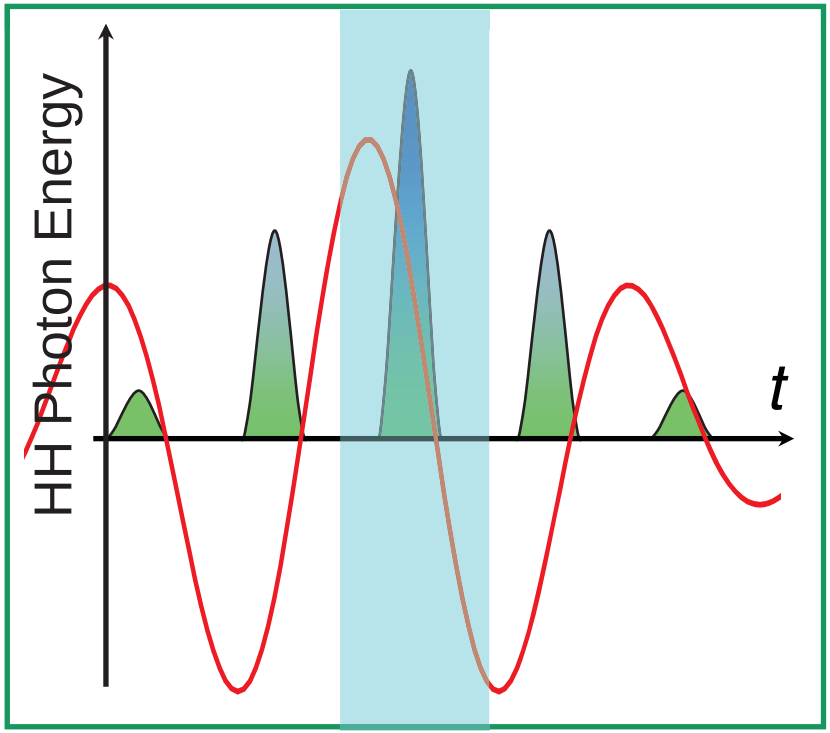


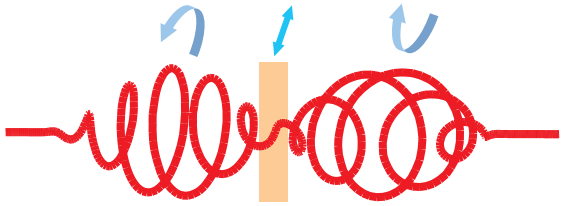
Carrier-envelope phase stabilization

E. Goulielmakis,et al. Science 320, 1614 (2008)

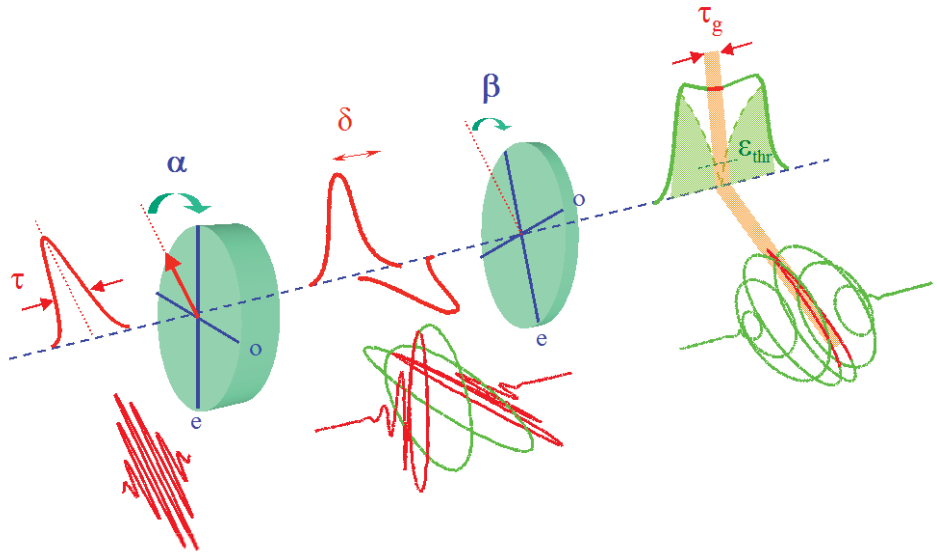
Isolated Attosecond Pulses (2)

Time gating (polarization modulation)

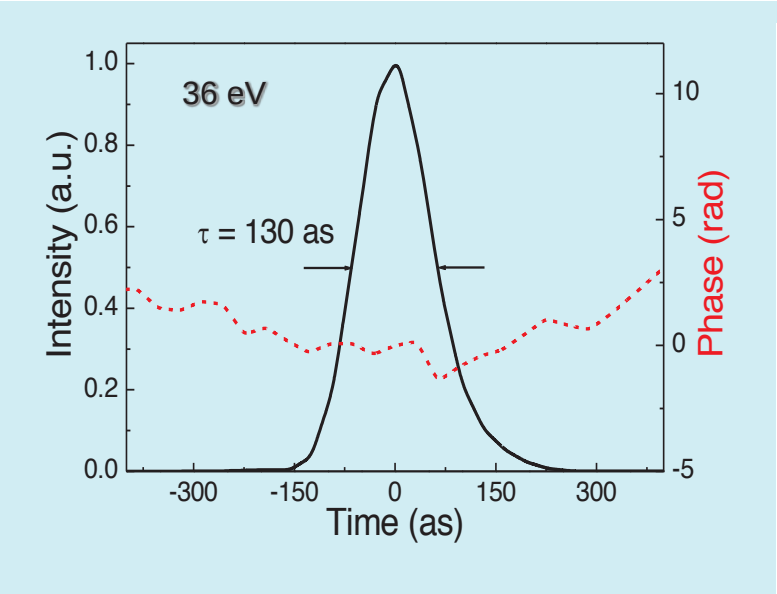




Carrier-envelope phase stabilization

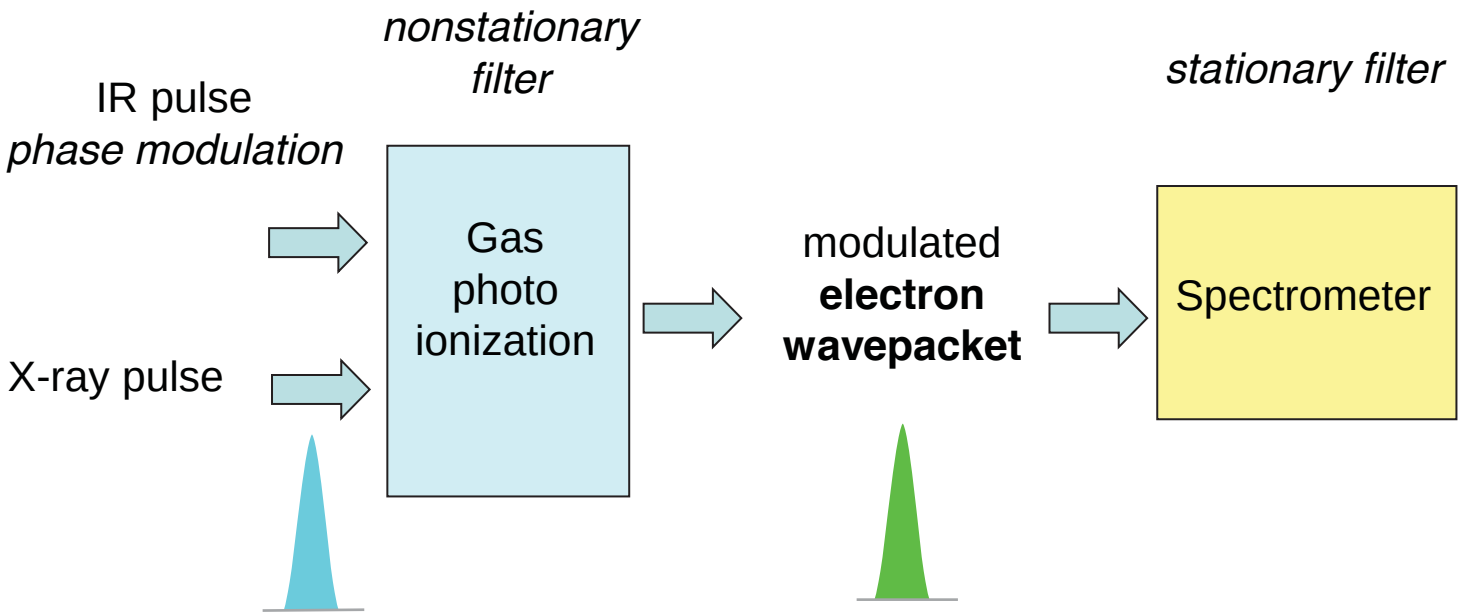


Chirp compensation: 300 nm aluminum foil



*G. Sansone et al., Science **314**, 443 (2006)*

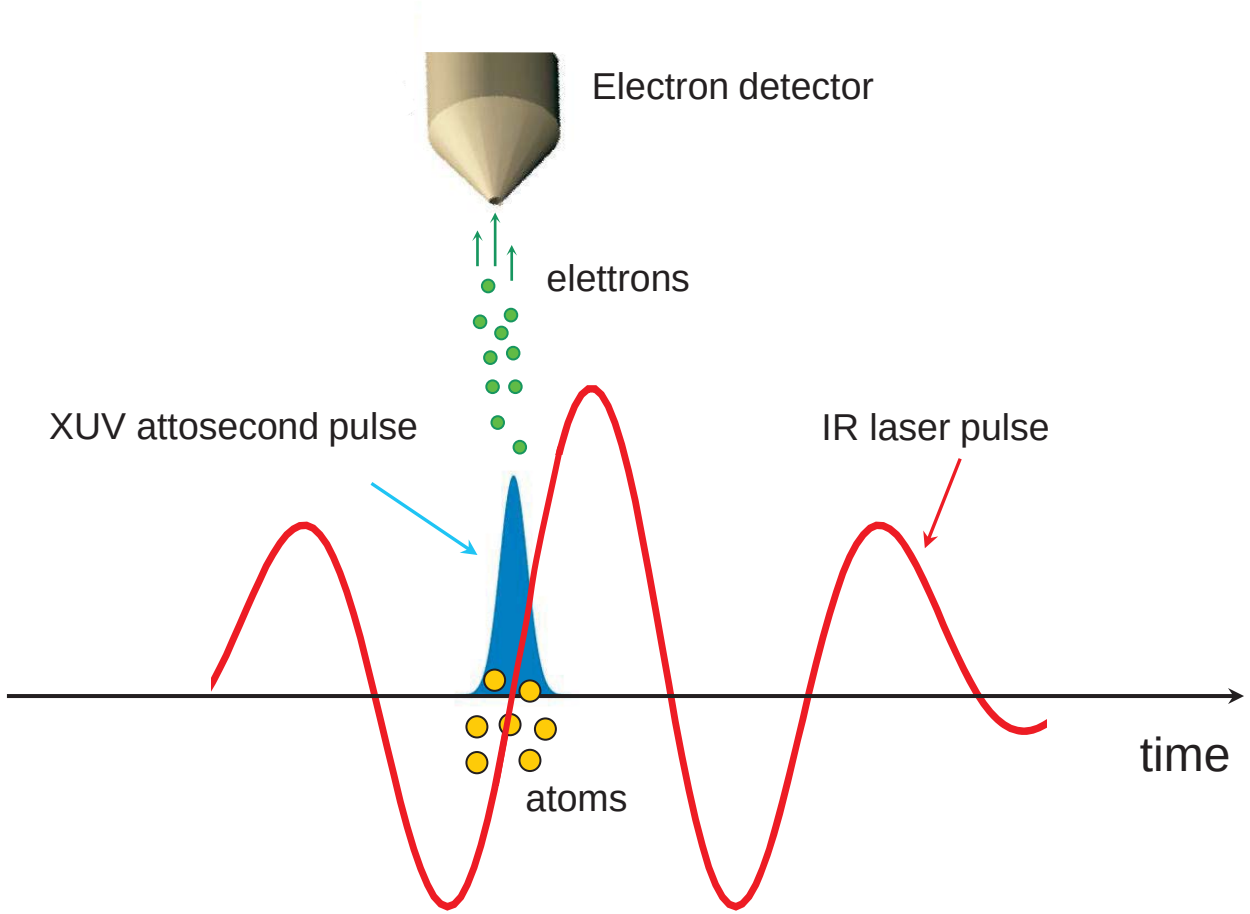
General Scheme of Attosecond Metrology



➔ **Far from any resonance, attosecond electron wavepacket is a replica of the attosecond field**

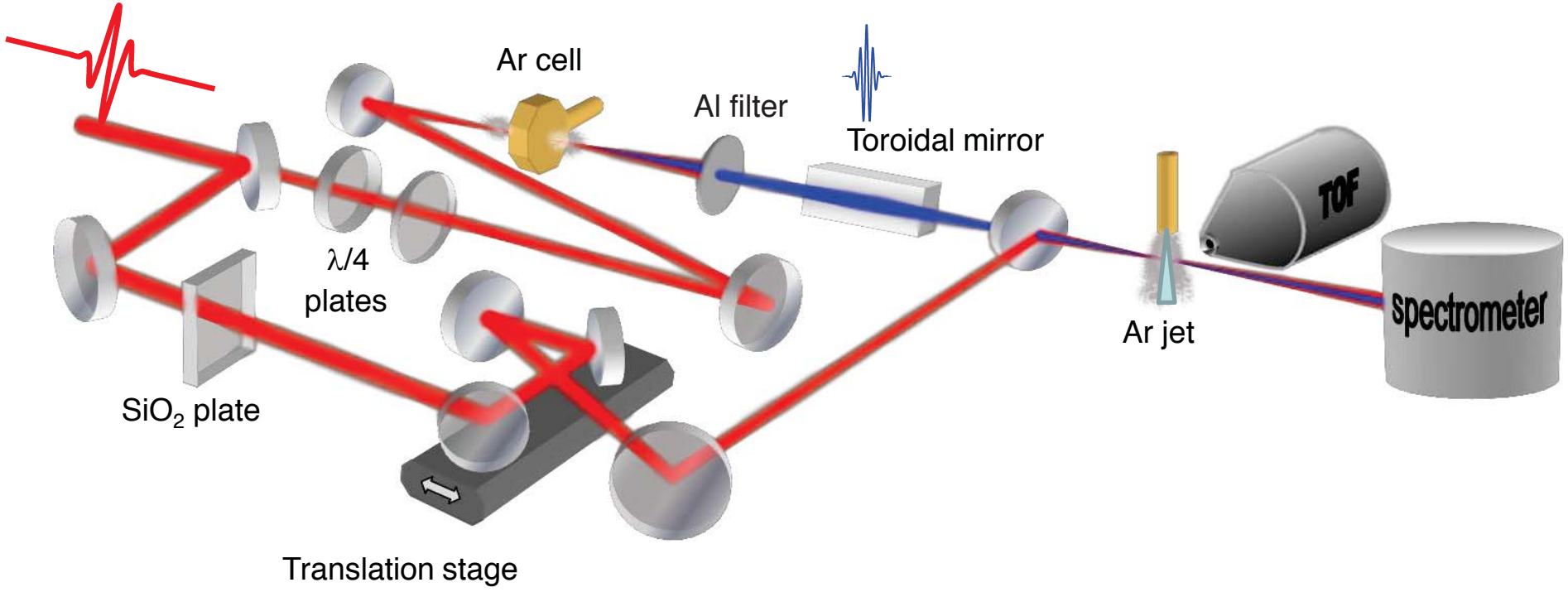
➔ **Characterization of the electron wavepacket**

View of the general scheme of attosecond metrology



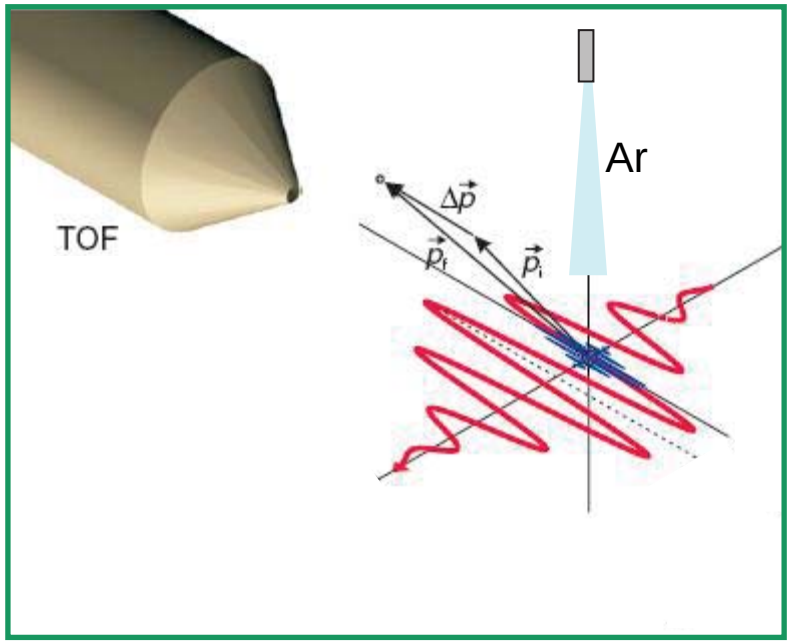
Attosecond Metrology Set-up

- **Cross-correlation of XUV pulse with driving light pulse**



➔ **Photoelectron spectra vs delay**

Attosecond "Streak Camera"



$$p_i = \sqrt{2mW_0} \qquad W_0 = \hbar\omega_{XUV} - I_p$$

Vector potential

$$\Delta\mathbf{p}(t_r) = e\int_{t_r}^{+\infty} \mathbf{E}_{IR}(t')dt' = e\mathbf{A}(t_r)$$

Final electron momentum

$$\mathbf{p}_f(t_r) = \mathbf{p}_i + \Delta\mathbf{p}(t_r)$$

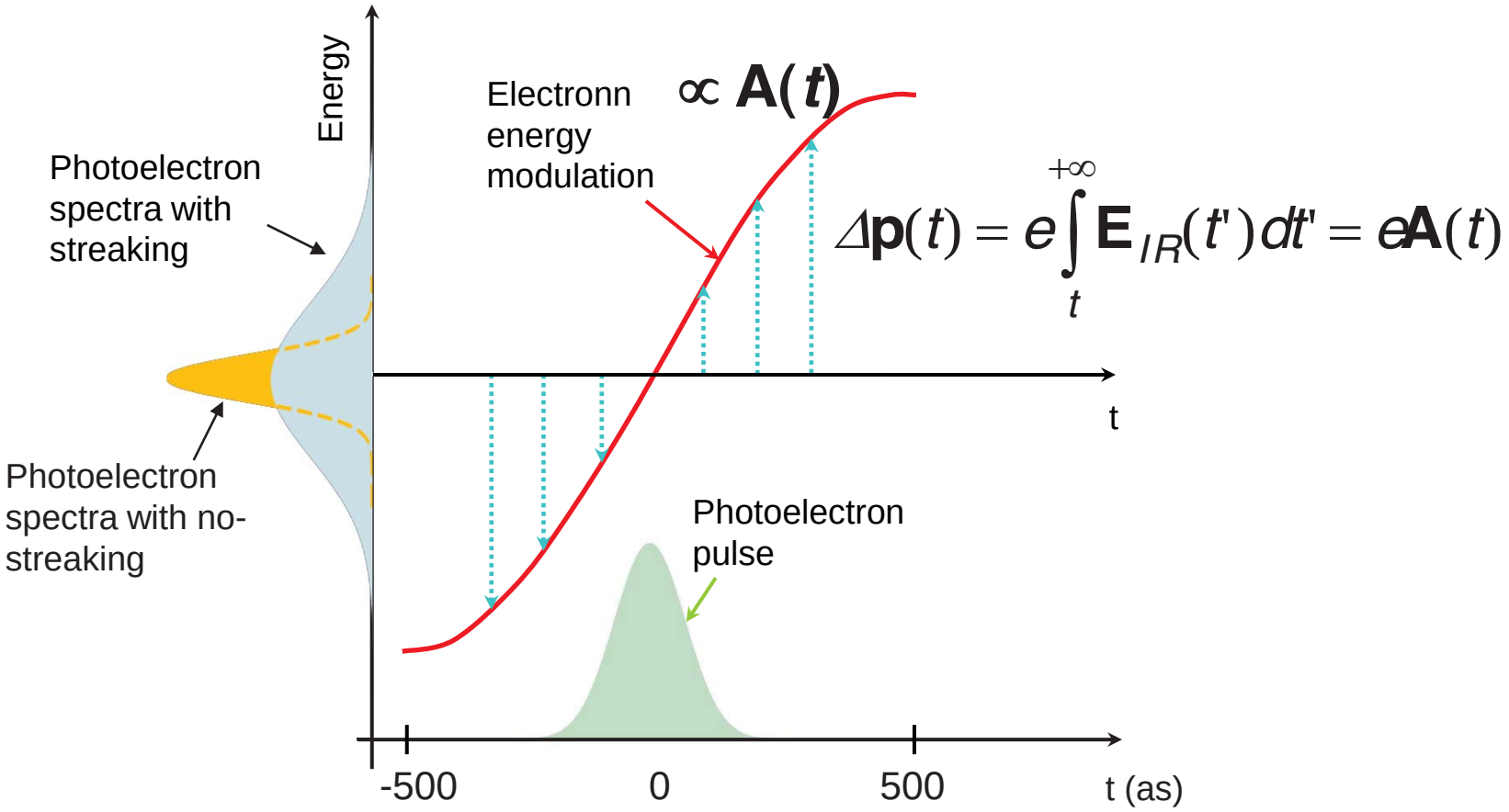
➔ Electron energy:

$$W(t_r) \approx W_0 + \sqrt{8W_0U_p}\sin(\omega_L t_r + \varphi)$$

➔ Time-to-energy mapping permits sampling of electron emission with attosecond resolution

Kitzler et al. PRL **88**,173903 (2002)
Itatani et al. PRL **88**,173904 (2002)

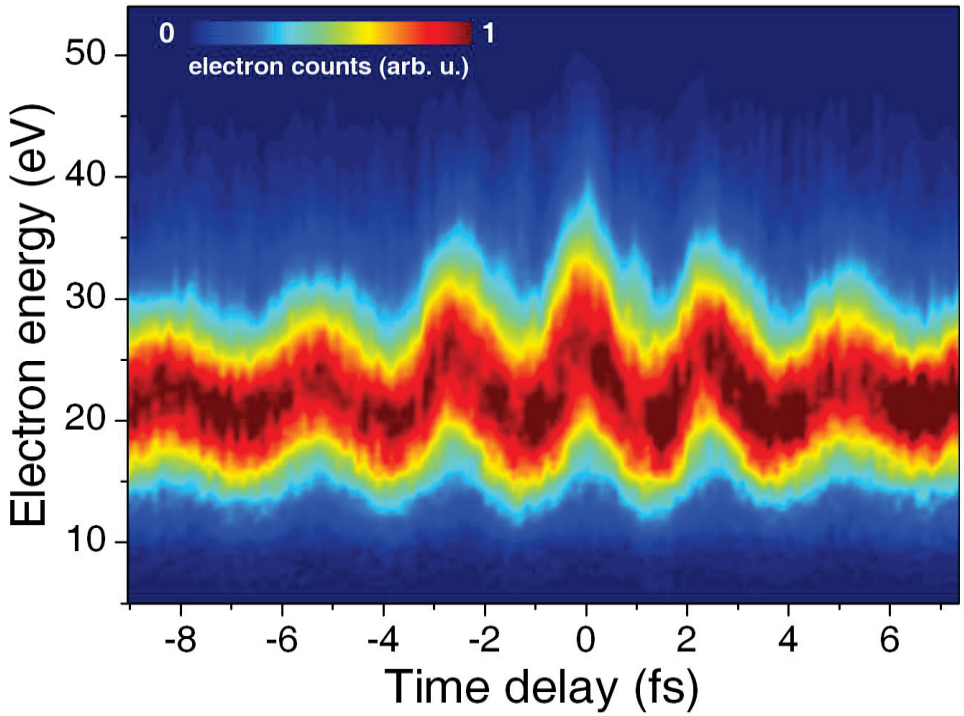
Time-to-energy Mapping



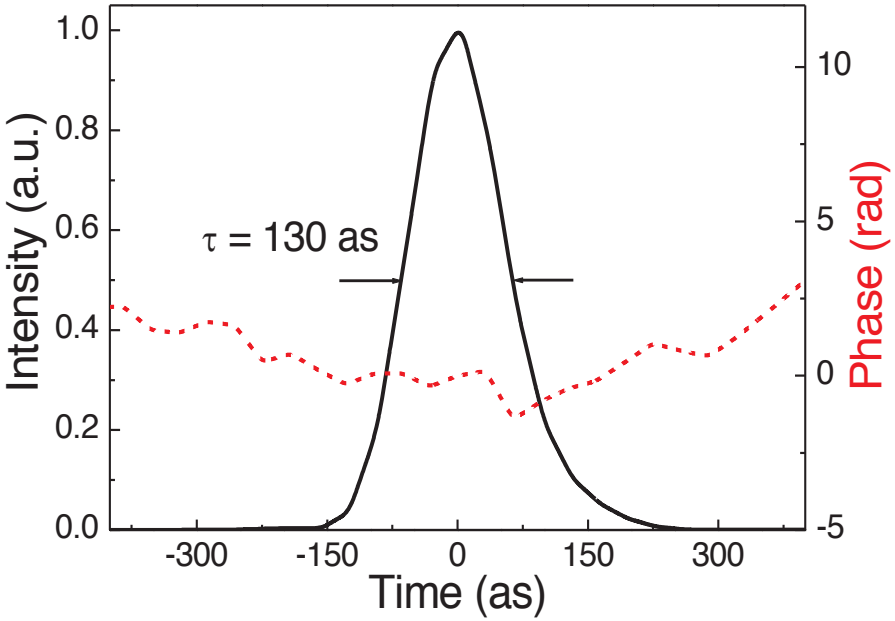
$$\Delta\mathbf{p}(t) = e\int_{t}^{+\infty}\mathbf{E}_{IR}(t')dt' = e\mathbf{A}(t)$$

Temporal characterization

Energy mapping vs. time



Retrieved Intensity profile and phase



- **Dispersion compensation**
  - ➔ **300-nm Aluminum foil**

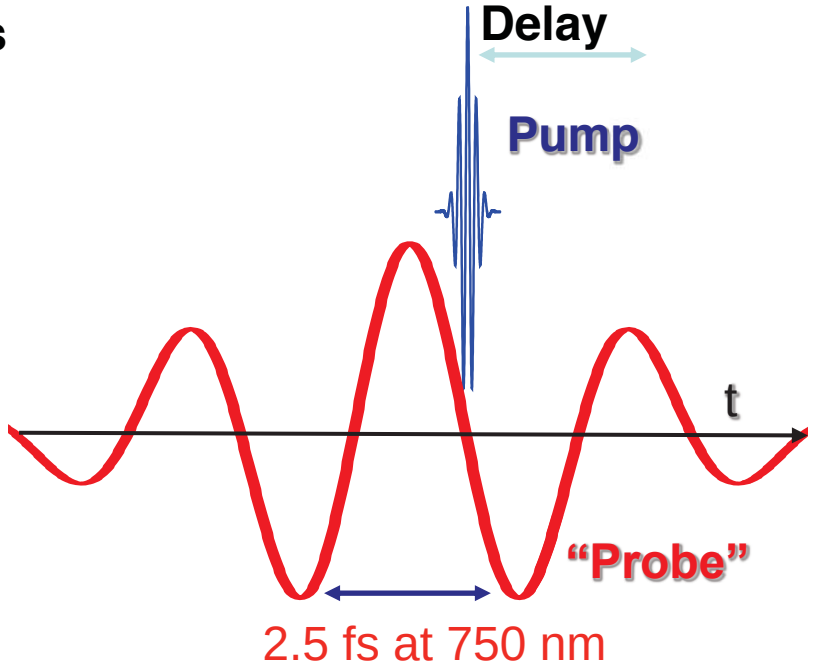
G. Sansone *et al.*, Science **314**, 443 (2006)

Attosecond Spectroscopy

- Attosecond pulse energies of only few hundred pJs are available:
  - Attosecond Pump - Attosecond Probe not yet feasible !

- An attosecond pulse in most cases ionizes the sample:
  - Emission of an electron burst

- The high order harmonic generation process helps:
  - An electric field waveform is always available synchronized on an attosecond time scale: interacting with the electron burst
  - The electron burst is "energy steered" by the electric field and the spectrum detected by a time of flight (TOF)
  - The electron burst can be redirected to the parent atom/molecule for "electron diffraction" studies (resolution close to 1 Å)

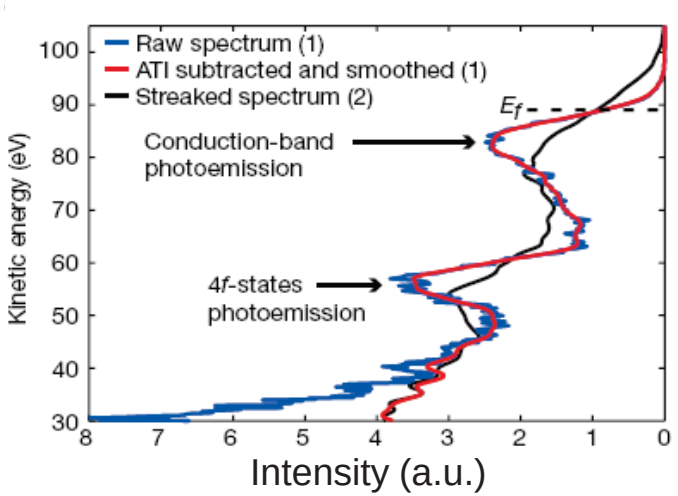


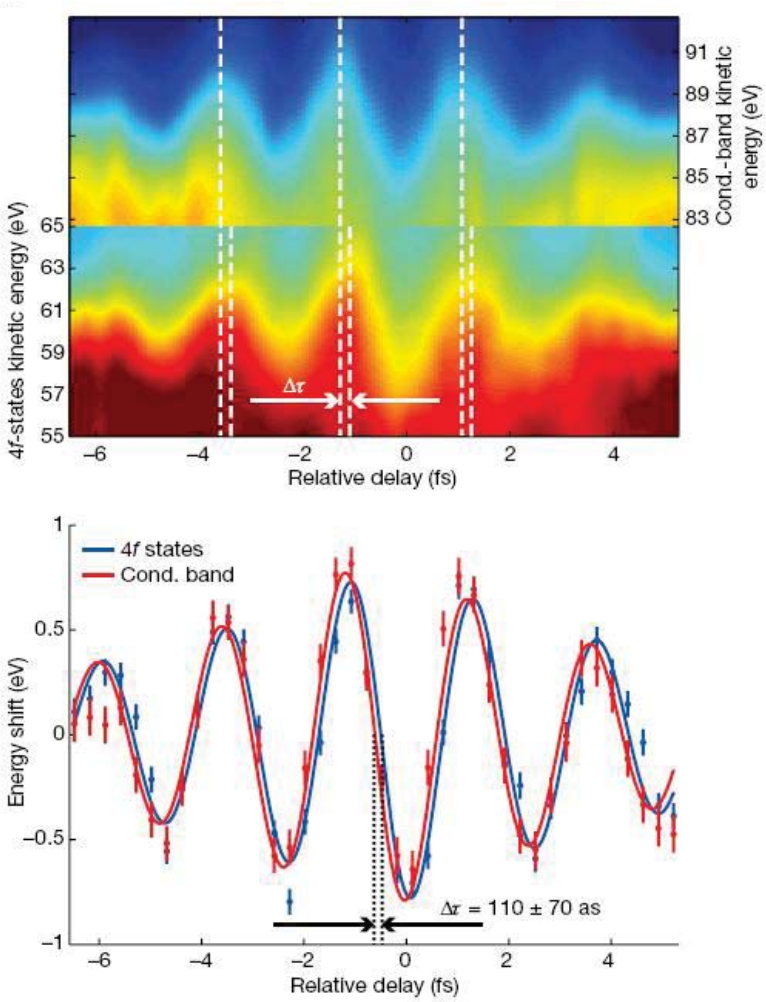
Applications of Attosecond Pulses

- Status and prospects of attosecond spectroscopy and control
  - ➔ condensed matter: example (tungsten crystal)
  - ➔ simple diatomic molecules: example (H_2/ D_2)
  - ➔ molecular tomography: CO_2
  - ➔ complex (bio)molecules and supramolecular assemblies
  - ➔ nanostructures
- Use of synthesized (waveform-controlled) pulses to steer electrons in molecules on the electronic time scale

Attosecond spectroscopy in condensed matter

- **Probing photoelectron emission from single-crystal tungsten**



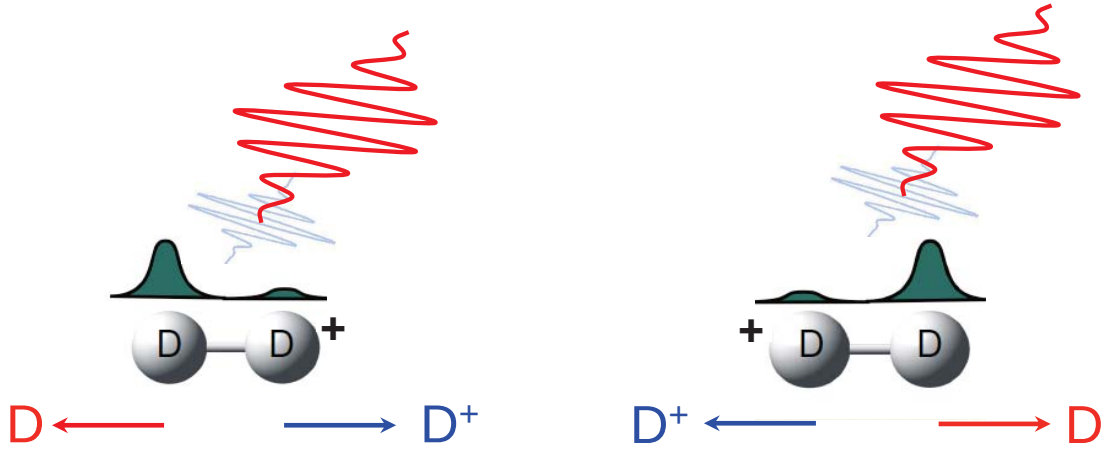


- ➔ Sub-fs photoemission from 4*f* core states and from conduction band
- ➔ Extension of streaking spectroscopy to condensed matter
- ➔ **<u>100-as delay</u>** between photoelectron emission from localized core states and from delocalized conduction-band states

A. Cavalieri *et al.*, Nature **449**, 1029 (2007)

Charge Migration in D_2

- **Method**: measurement of angular asymmetries in momentum distributions of fragments resulting from dissociative ionization
- Excitation of D_2 with attosecond pulses in the presence of few-cycle IR laser field
  - ➔ observation of electron localization following attosecond molecular photoionization

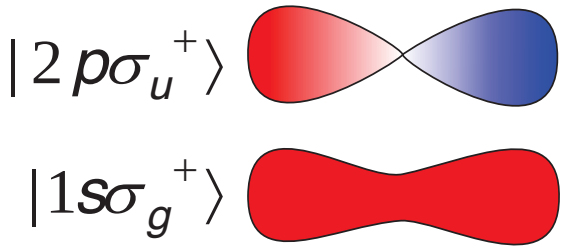


Electron localization in $(D_2)^+$ dissociation

- Charge localization: asymmetry in the dissociation process

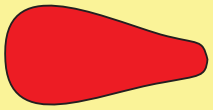
- Left-right asymmetry: <u>induced by coherent superposition of *gerade* and *ungerade* molecular ion states</u>

  ➔ relative phase between the two states leads to left/right electron localization

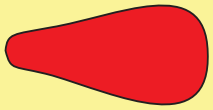


<u>Localized states</u>

$$|\ell\rangle = \frac{1}{\sqrt{2}}(|1s\sigma_u^+\rangle + |2p\sigma_u^+\rangle)$$

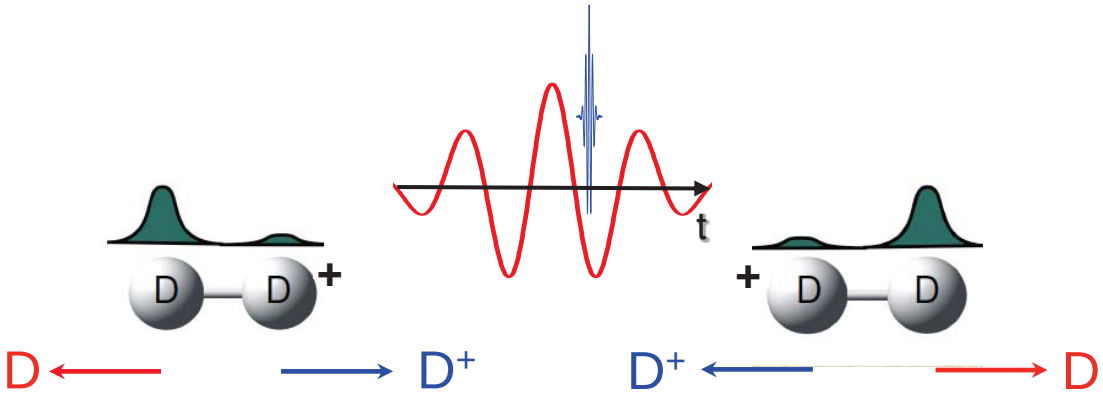


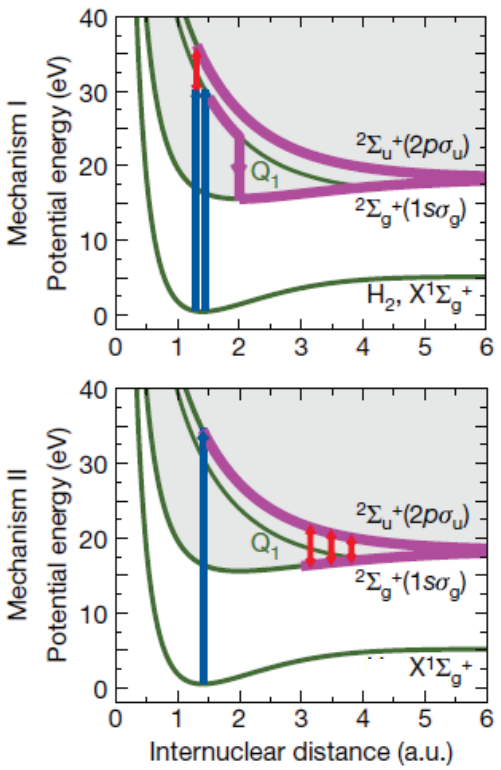
$$|r\rangle = \frac{1}{\sqrt{2}}(|1s\sigma_u^+\rangle - |2p\sigma_u^+\rangle)$$



Electron localization process

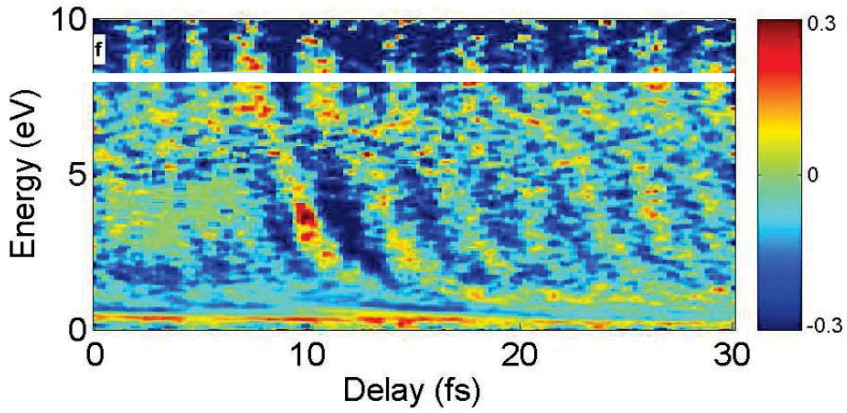
- An **attosecond** pulse ionizes D_2 molecule
- A time-delayed **infrared** pulse couples *gerade* and *ungerade* molecular ion states:





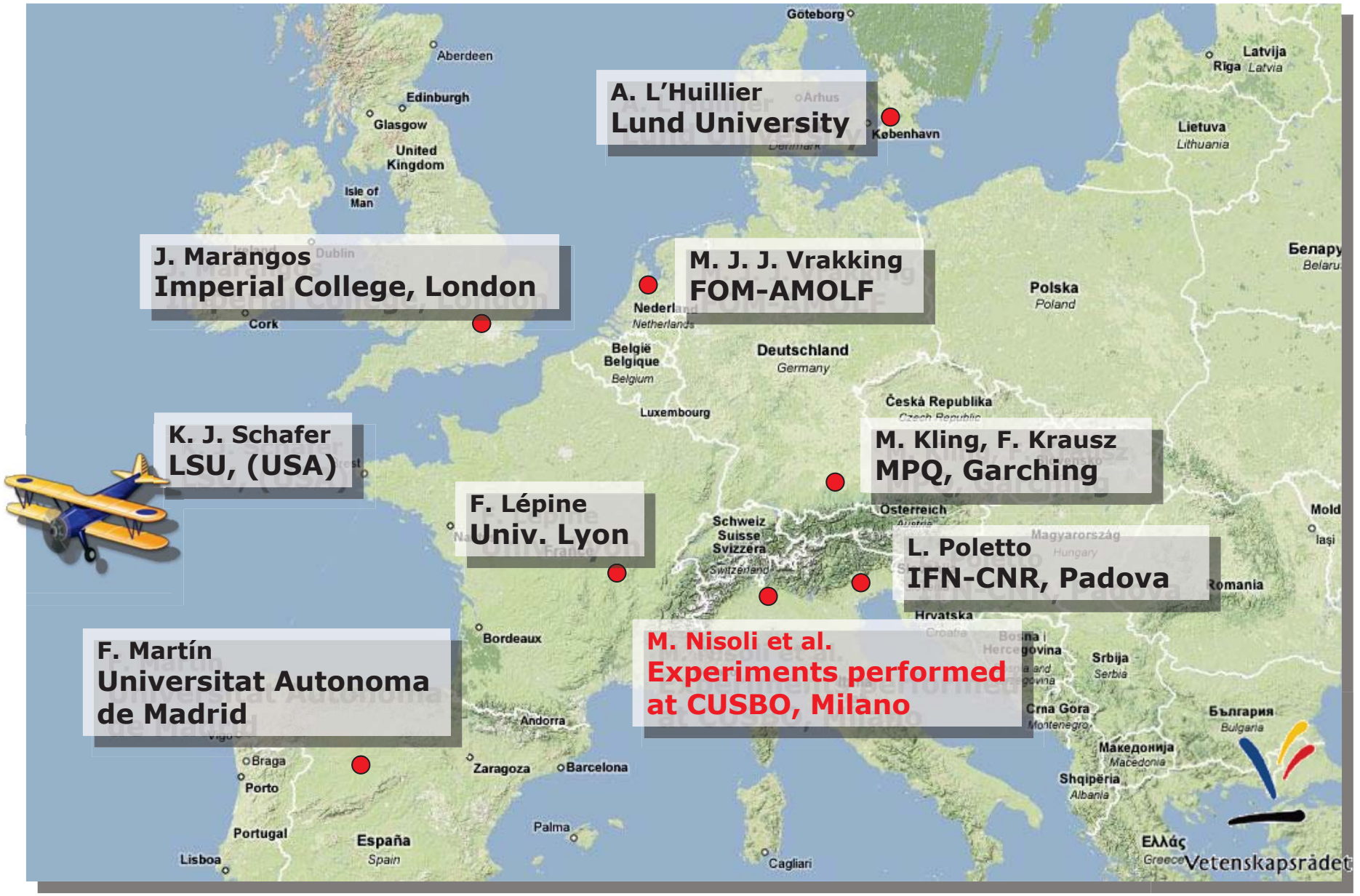
The asymmetry parameter oscillates with the periodicity of the infrared pulse

$$A(E_k,\tau)=\frac{N_L(E_k,\tau)-N_R(E_k,\tau)}{N_L(E_k,\tau)+N_R(E_k,\tau)}$$



*G. Sansone et al., Nature **465**, 763 (2010)*

Wide International Collaboration



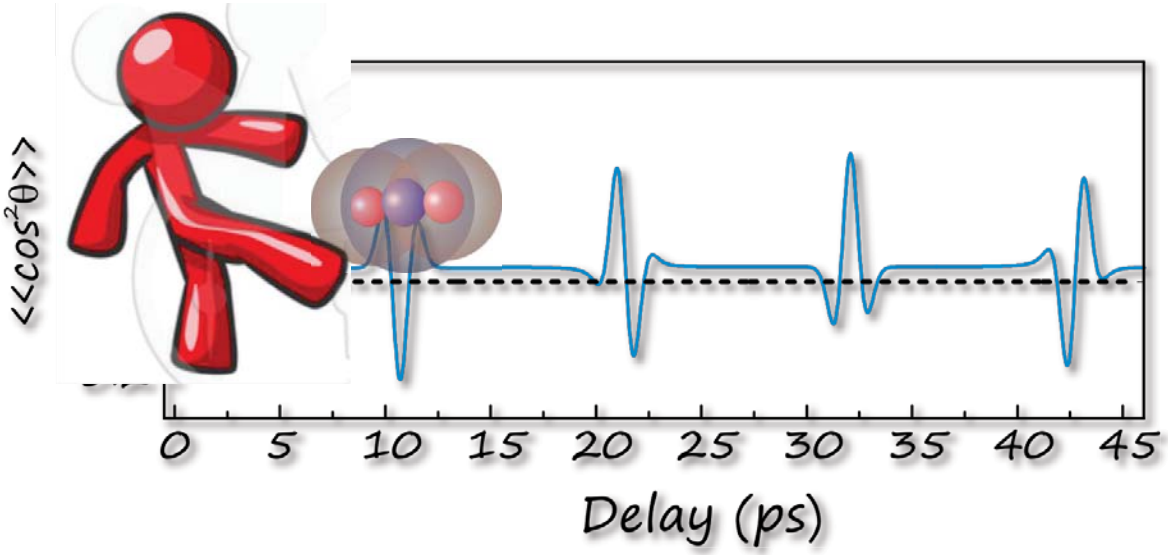
Molecular Orbital Tomography by HHG

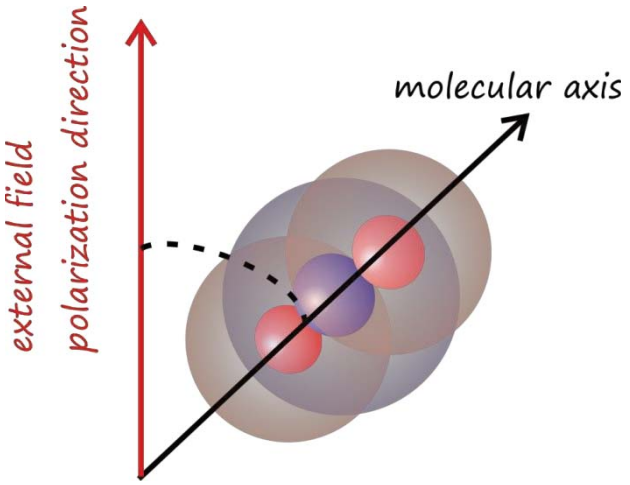
Impulsive Alignment of Molecules

Molecules in intense ultrashort laser pulse:

pulse duration $\tau < T_{rot}$

intensity $I > 10^{12}$ W/cm^2





Coherent excitation of a rotational wave-packet:

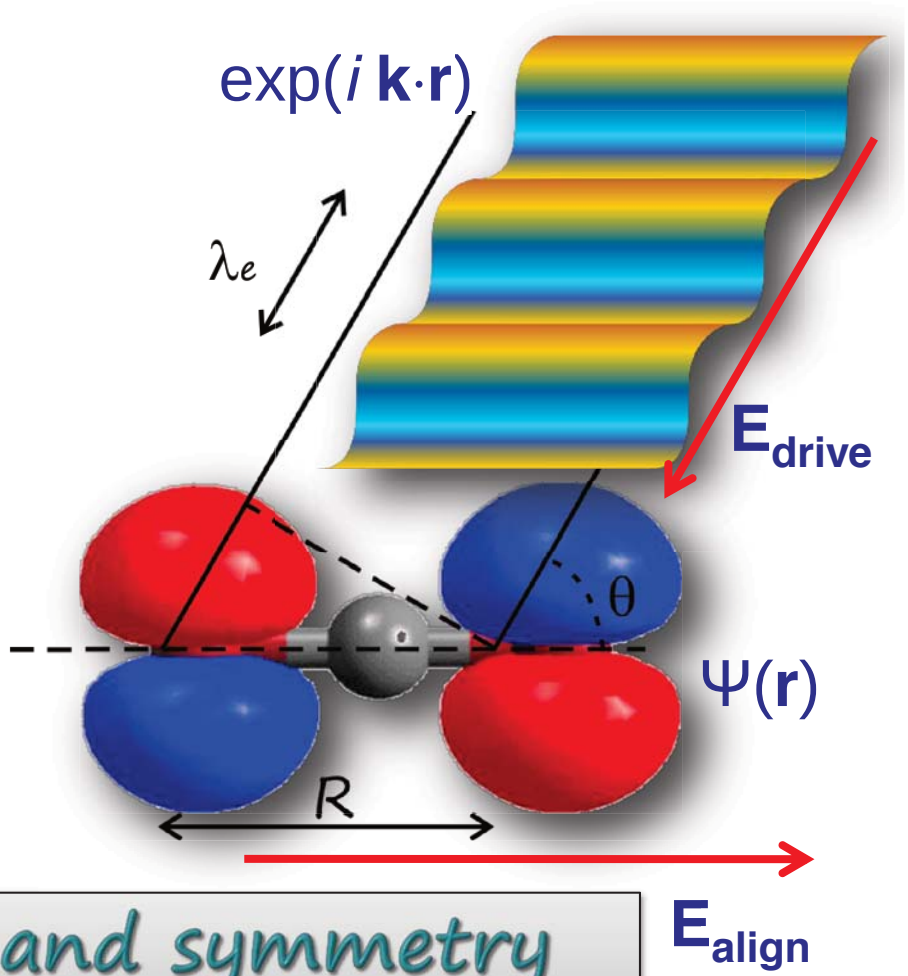
- **rotational revivals**
- **field-free alignment of the molecular sample for certain delays**

Ortigoso et al., J. Chem. Phys. ***110****, 3870 (1999)*

Inferring molecular orbital structure from HHG

1. Align the target molecule
2. Drive the HHG process for different angles θ

The HHG signal depends on the re-colliding wave-packet and the molecular HOMO through the transition dipole moment:
<Ψ(r)| r |exp[ik(ω)·r]>
which is the spatial Fourier transform of **rΨ**



Orbital structure and symmetry are encoded in the HHG spectrum!!

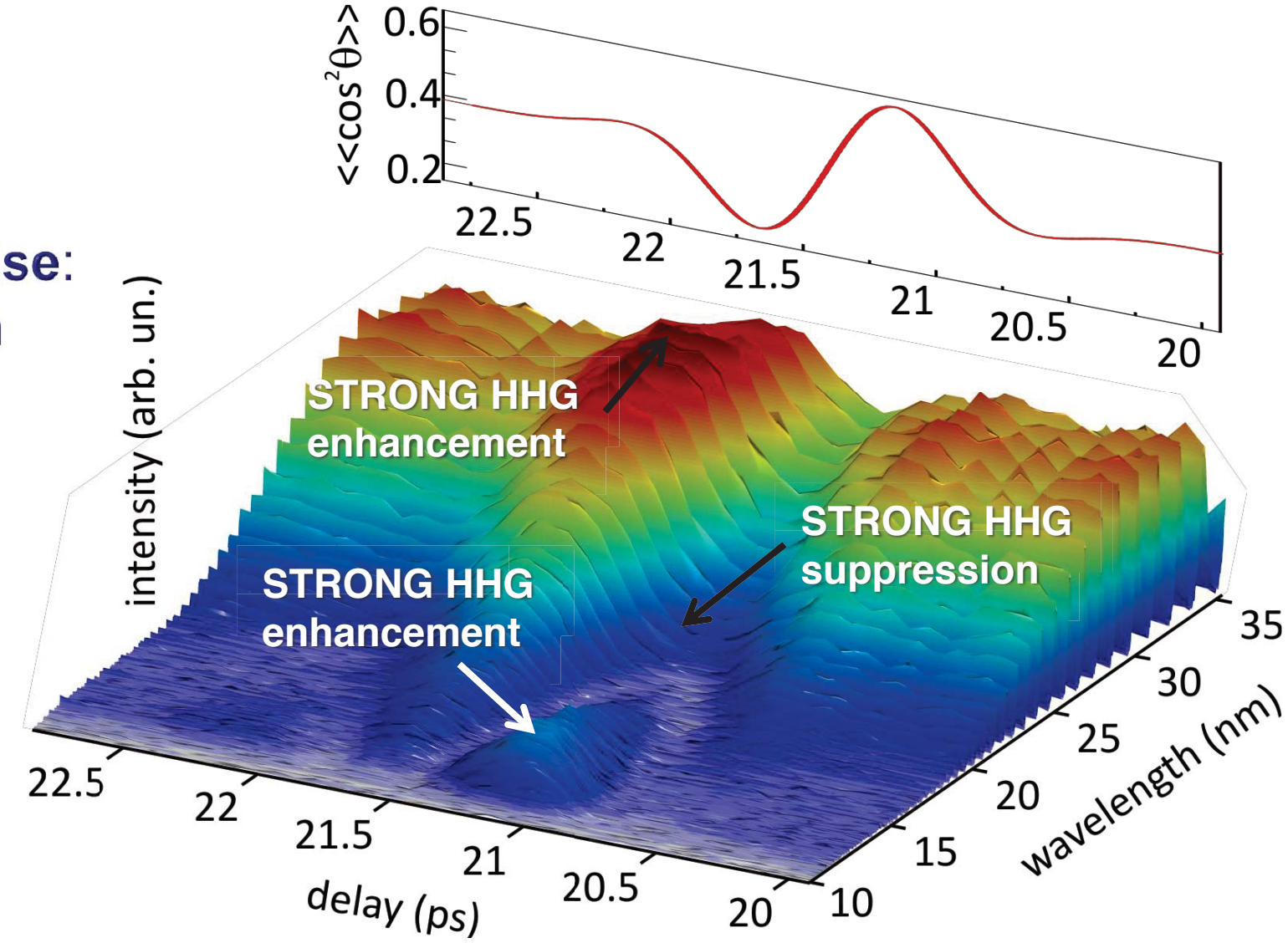
HHG IN ALIGNED CO_2

Experimental results

Aligning pulse:
λ = 800 nm
τ = 100 fs
E = 200 μJ

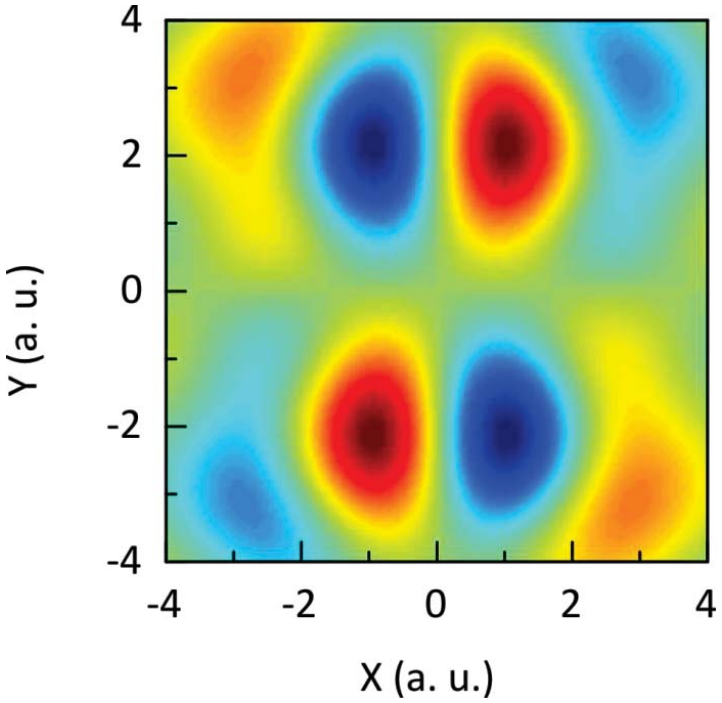
Driving pulse:
λ = 1.45 μm
τ = 20 fs
E = 280 μJ

Parallel polarizations

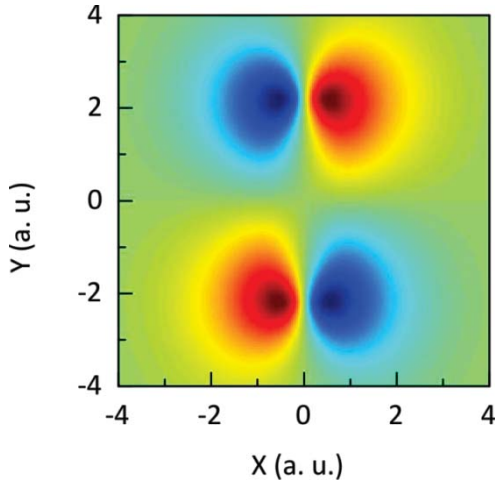


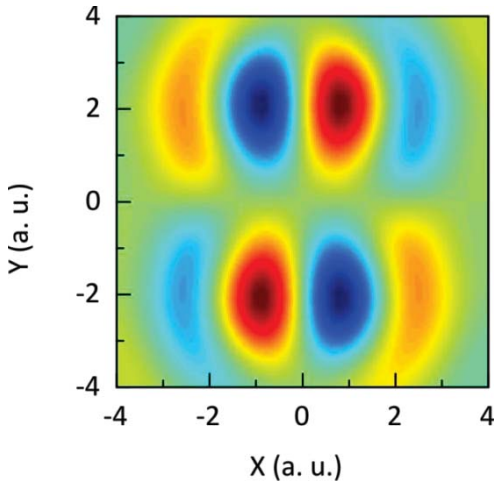
MOLECULAR TOMOGRAPHY OF CO_2

Reconstruction of CO_2 HOMO from HHG spectra



Calculation of CO_2 HOMO with quantum chemistry program





Challenges and Prospects

- Attosecond pump – attosecond probe spectroscopy: this implies the generation of high intensity attosecond pulses
- Attochemistry: steering of chemical/ biochemical reactions by controlling electronic motion on molecular orbitals
- Molecular orbital tomography: from a static to a dynamic orbital reconstruction (time domain tomography)