MVSem--Masterseminar
2020-11-10

The sound of the phase: *Atoms*&*molecules* in pulsed light fields

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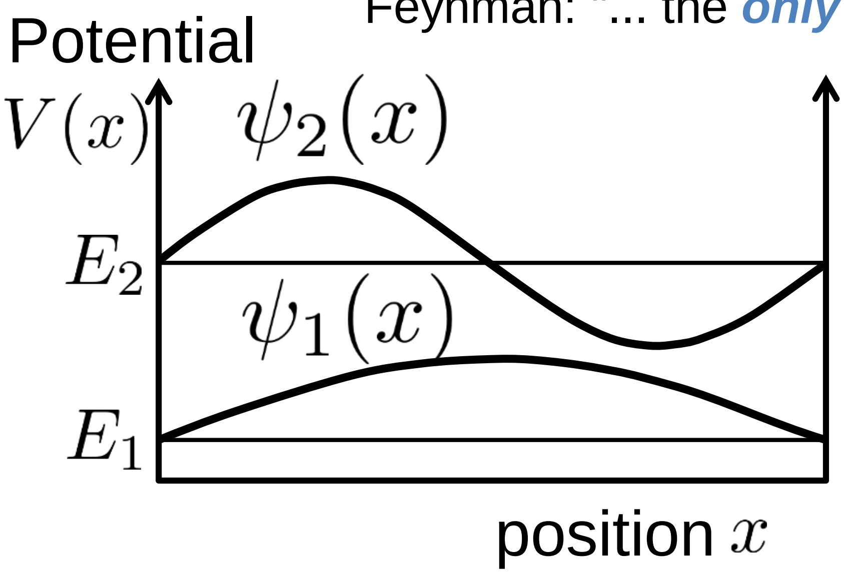
MPIK Heidelberg

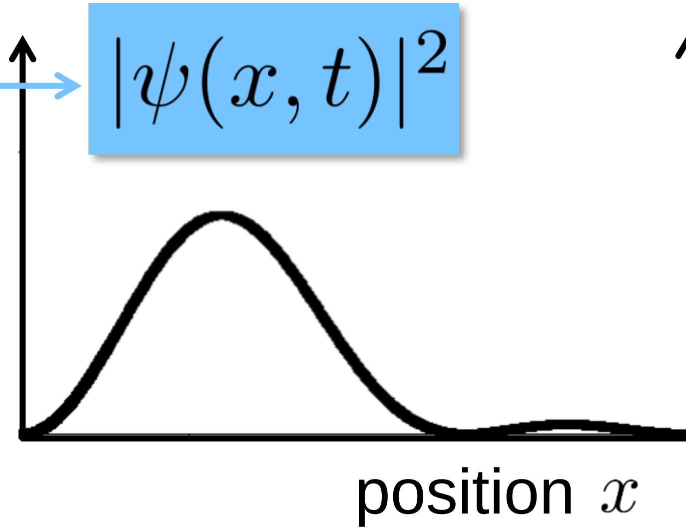
Fundamental Quantum Dynamics

$$i\hbar\frac{\partial}{\partial t}\psi(x,t)=\mathcal{H}\psi(x,t)$$

Interference of quantum states

Feynman: "... the ***only*** mystery [at the heart of quantum mechanics]."





Phase $\varphi 1$ Phase $\varphi 2$

$$\psi(x,t)\propto a_1\psi_1(x)e^{-\frac{i}{\hbar}E_1 t}+a_2\psi_2(x)e^{-\frac{i}{\hbar}E_2 t}$$

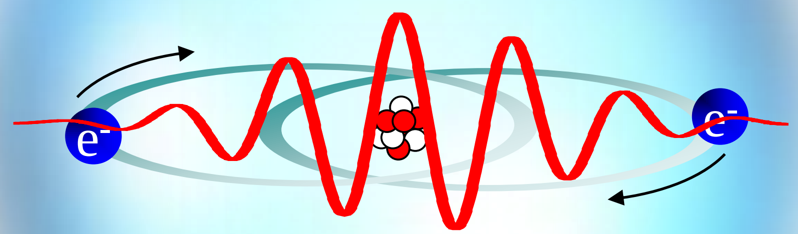
few-body quantum dynamics

a fundamental scientific question:

"how do two or more excited electrons move and interact in atoms and molecules?"

spatial scale
R ~ sub/few Å

temporal scale
T ~ sub/few fs



The
"quantum
few-body
problem"
in strong fields

Science goal:

measure / understand / control
*the **quantum dynamics** of*
small systems
in strong fields

0 as

(x-ray) movies of single molecules

Petahertz-clocked computing

x-ray precision spectroscopy

Laser control of chemical reactions

Electron Facts

- lightest charged elementary particle

- 'chemical glue', holding molecules together

  -> making and breaking of bonds in chemical reactions
- carriers of electric current

  -> electricity generation/conversion/transport
- carriers of information

  -> electronics, computing, data storage
- mediating interactions of matter with light

  -> role in photosynthesis, photovoltaics, vision, ...

...typically more than one electron involved...

What is the problem?

(with two or more electrons)

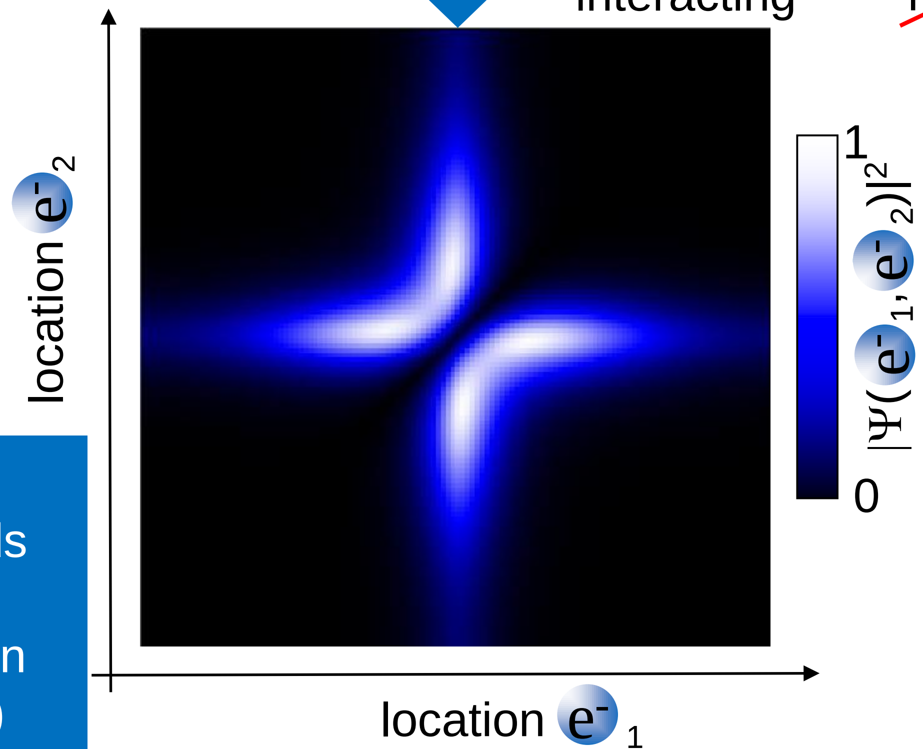
Correlated electron dynamics

interaction (Coulomb)

symmetry (Fermions)

Correlation

$$\underbrace{\Psi(e^-_1, e^-_2)}_{\text{'interacting'}} \neq \underbrace{\Psi(e^-_1) \times \Psi(e^-_2)}_{\text{'non-interacting'}}$$



problem for:

- Hartree–Fock methods
- DFT
  (exchange-correlation potential not known)

Why is it important?

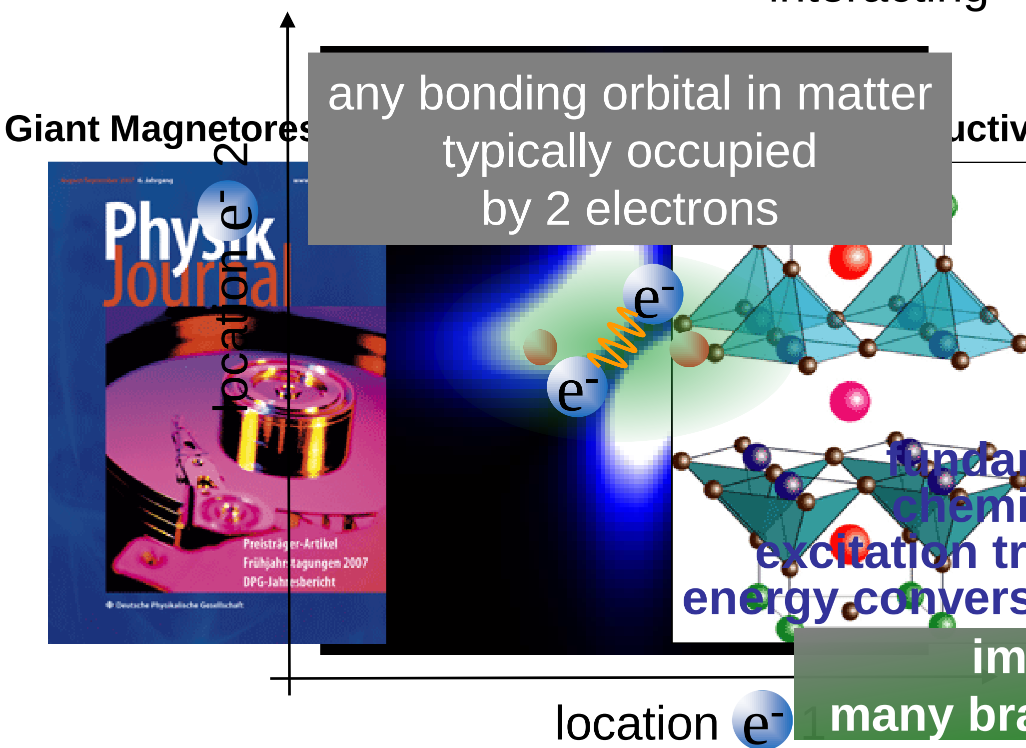
Time-dependent correlated electron dynamics

interaction (Coulomb) →

symmetry (Fermions) →

Correlation

$$\underbrace{\Psi(e^-_1, e^-_2)}_{\text{'interacting'}} \neq \underbrace{\Psi(e^-_1) \times \Psi(e^-_2)}_{\text{'non-interacting'}}$$

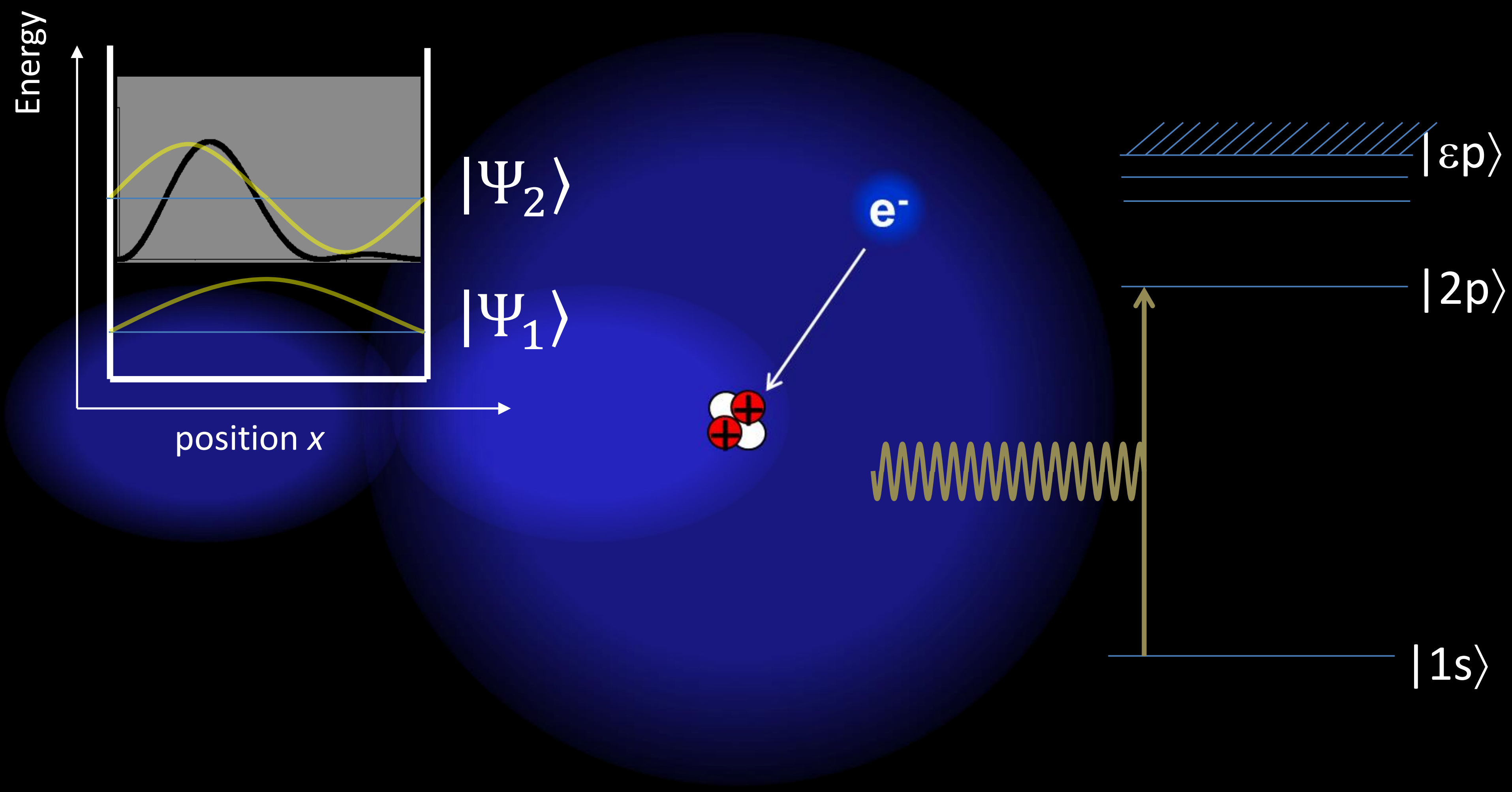


any bonding orbital in matter
typically occupied
by 2 electrons

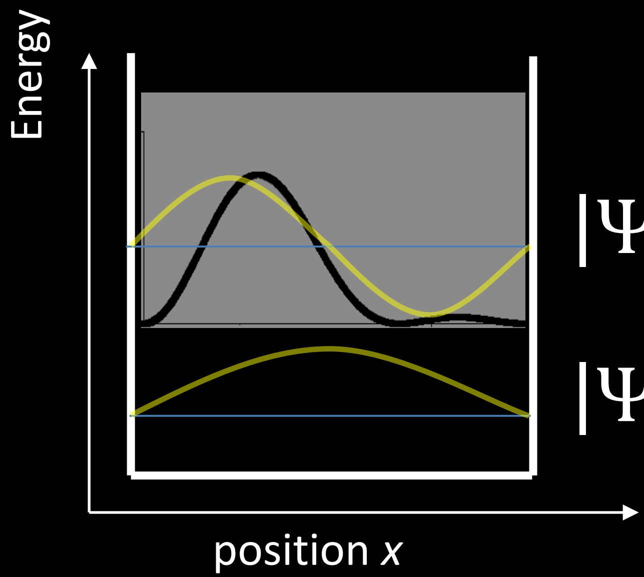
fundamental role in
chemical reactions
excitation transfer, e^- transport
energy conversion, radiation damage

importance in
many branches of science

the language electrons speak ... ... and why is it so fast?



Wavepacket dynamics and observation



Quantum beat period:

$$\Delta T = \frac{\hbar}{\Delta E} \approx 4.1 \text{ fs} / \Delta E[\text{eV}]$$

$$\Psi(t) \sim \Psi_1 e^{\frac{-i}{\hbar}E_1 t} + \Psi_2 e^{\frac{-i}{\hbar}E_2 t}$$

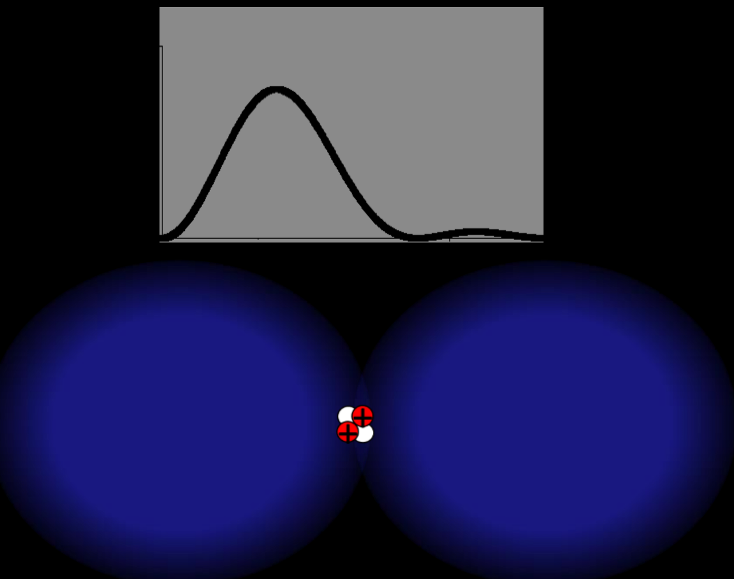
e.g. time-dependent position/dipole:

$$x(t) = \langle \Psi(t) | \hat{x} | \Psi(t) \rangle$$

$$= \frac{1}{2}\left\langle \Psi_1 e^{\frac{-i}{\hbar}E_1 t} + \Psi_2 e^{\frac{-i}{\hbar}E_2 t} \middle| \hat{x} \middle| \Psi_1 e^{\frac{-i}{\hbar}E_1 t} + \Psi_2 e^{\frac{-i}{\hbar}E_2 t} \right\rangle$$

$$= |\langle \Psi_1 | \hat{x} | \Psi_2 \rangle| \cos\left[\frac{(E_1 - E_2)}{\hbar} t + \varphi_0\right] \longrightarrow \varphi(t)$$

the language electrons talk ...
... and why is it so fast?



Quantum beat period:

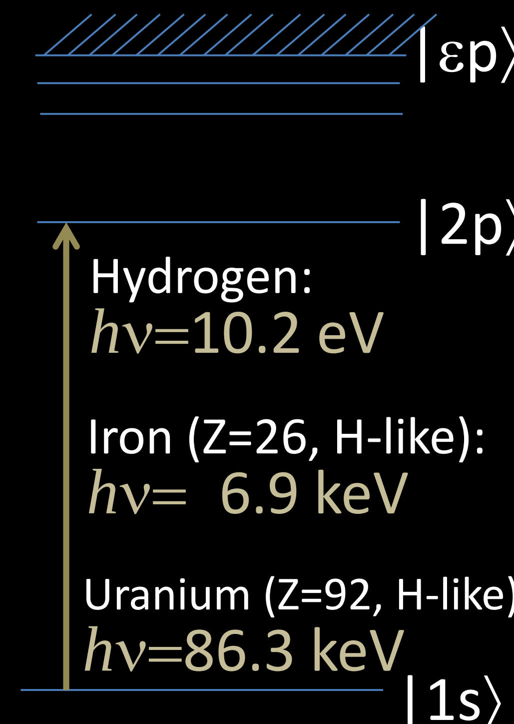
$$\Delta T = \frac{\hbar}{\Delta E} \approx 4.1\ \text{fs} / \Delta E[\text{eV}]$$

Oscillation period:

Hydrogen:
$T = 0.4$ fs (10^{-18} s)

Iron (H-like):
$T = 0.6$ as (10^{-18} s)

Uranium (H-like):
$T = 48.0$ zs (10^{-21} s)

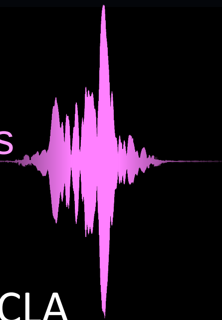


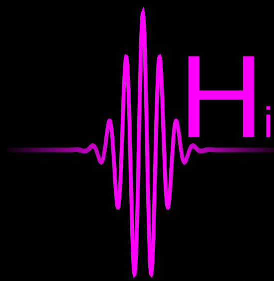
and the way we "listen"...:

Spectroscopy

The light sources: Provided by two parallel revolutions in ultrashort x-ray/XUV laser science

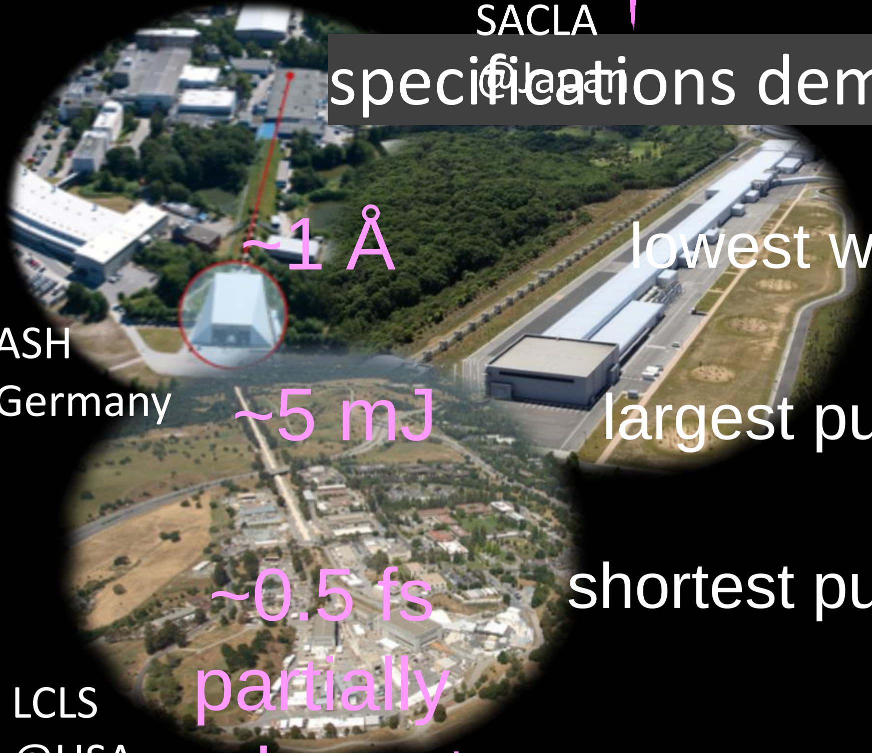
Free Electron Lasers





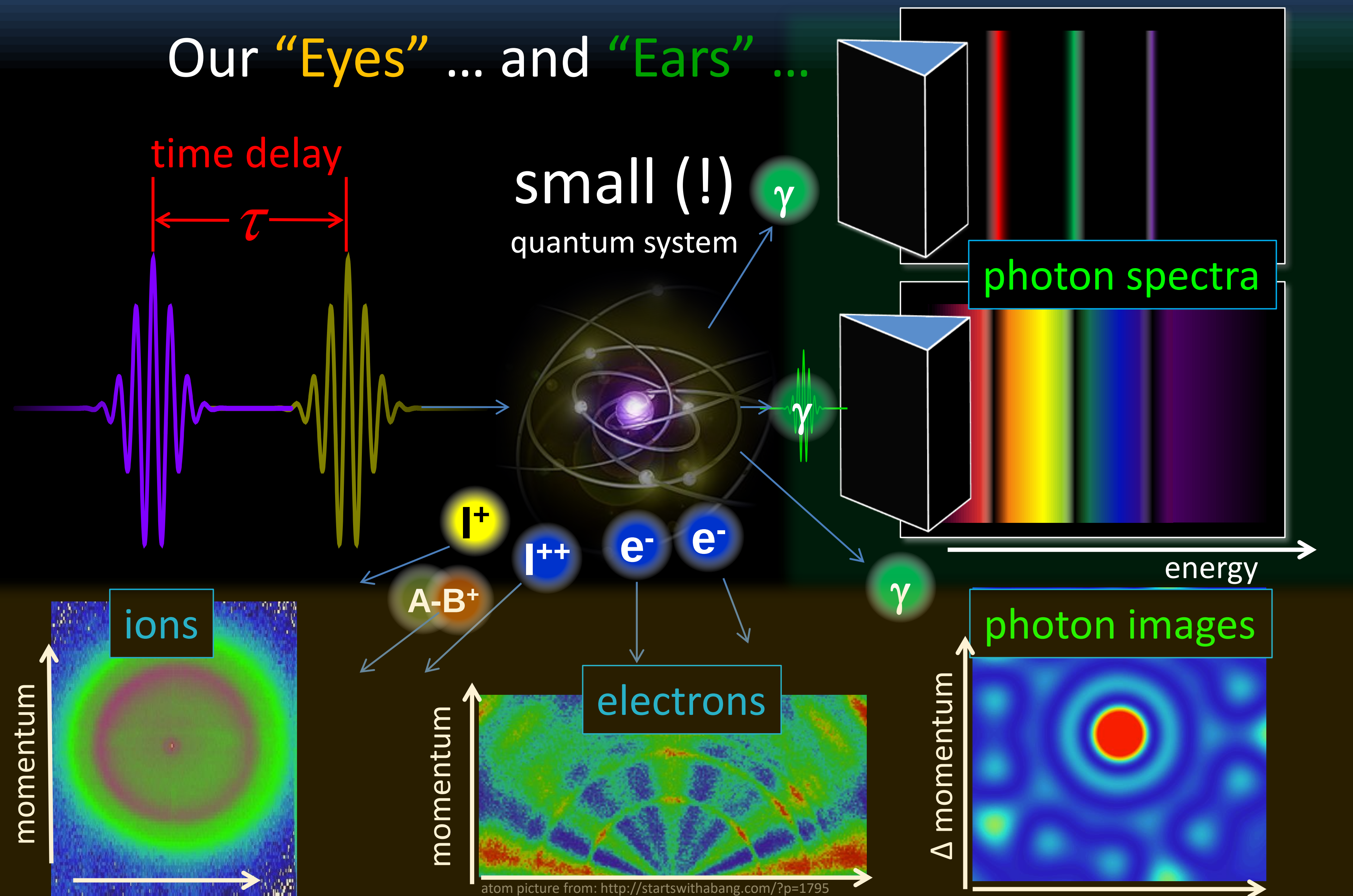
High Harmonic Generation

specifications demonstrated thus far:



~1 Å	lowest wavelength	~1 nm
~5 mJ	largest pulse energy	~1 µJ
~0.5 fs	shortest pulse duration	~50 as
partially coherent		fully coherent

Quantum dynamics imaging and spectroscopy



Our Experimental Focus

(Free Electron) Lasers

Employing **Bright Light**

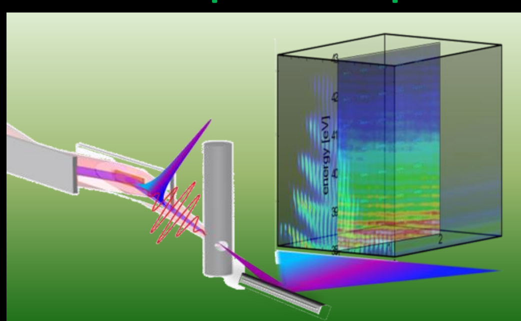
High Harmonic Generation

to understand &control

Atoms, Ions & Molecules

"listening"

Multidim. optical spectroscopy

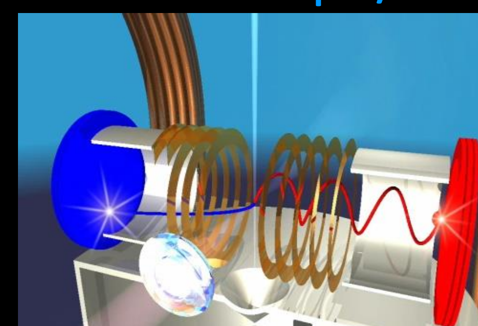


time&energy-resolved detection of **photons**

Goal: extract complete information

"imaging"

Reaction microscope/COLTRIMS



coincidence detection of **electrons/ions**

atom image from: http://startswithabang.com/?p=1795

Our Experimental Focus

(Free Electron) Lasers

Bright Light

High Harmonic Generation

to understand &control

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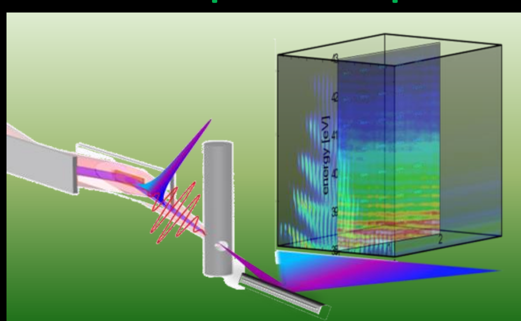
"listening"

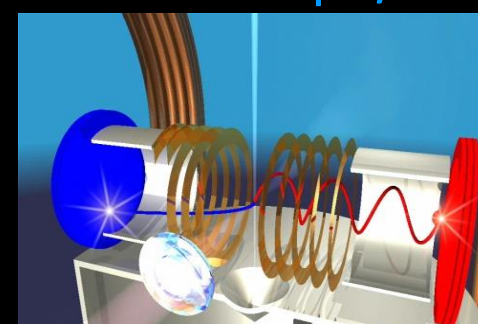
Multidim. optical spectroscopy



time&energy-resolved detection of photons

"imaging"

Reaction microscope/COLTRIMS

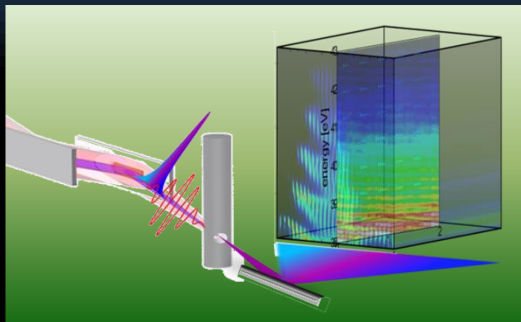


coincidence detection of electrons/ions

Goal: extract complete information

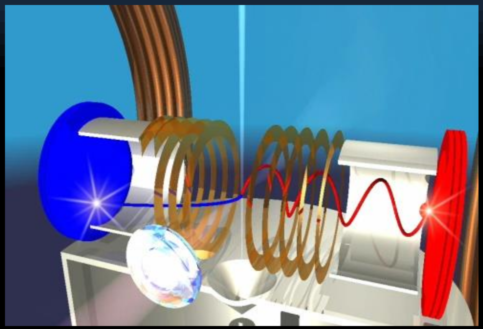
Experimental observation of few-body dynamics

Multidim. optical spectroscopy



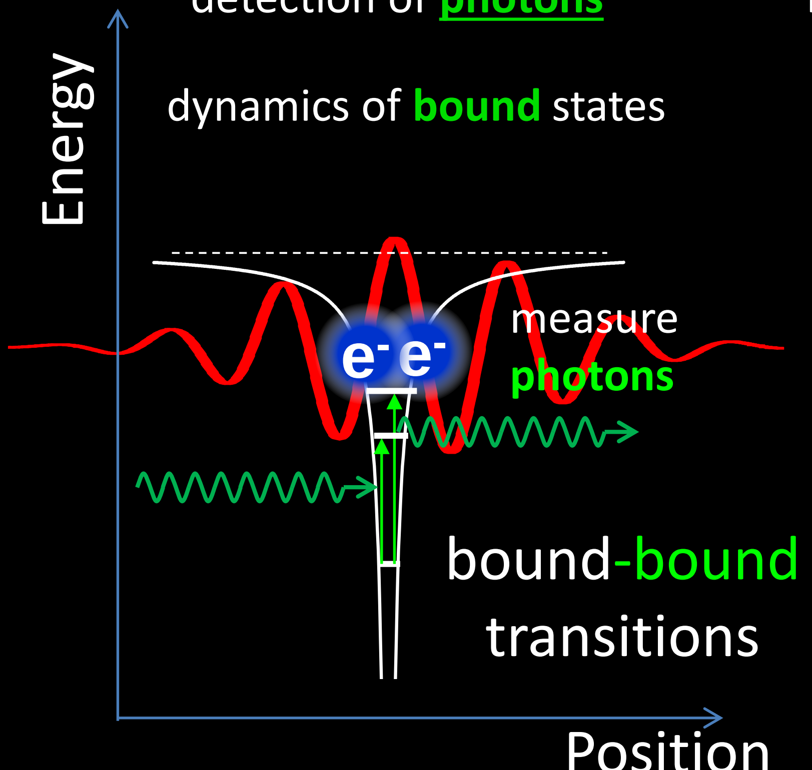
time&energy-resolved
detection of **photons**

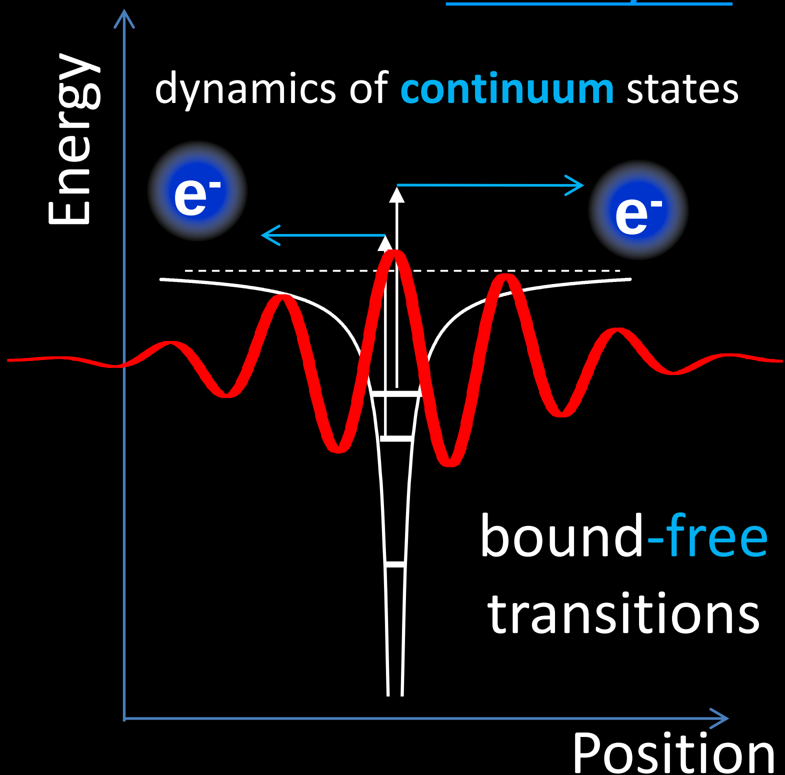
Reaction microscope/COLTRIMS



coincidence
detection of **electrons/ions**

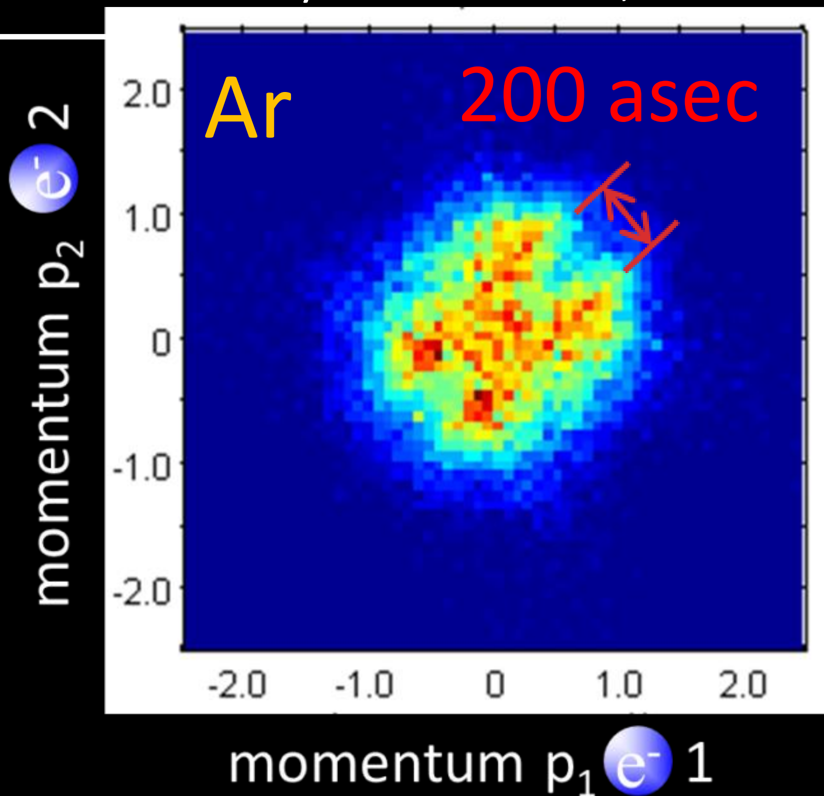
Goal: extract
complete
information





Strong-field Recollision Physics
in "nonsequential" double ionization

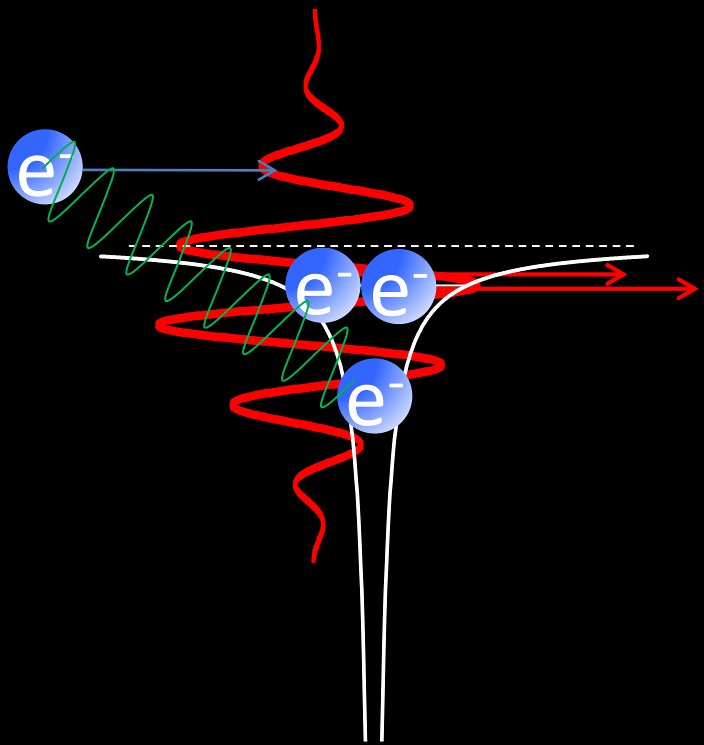
N. Camus *et al.* Phys. Rev. Lett. **108**, 073003



characteristic time delay

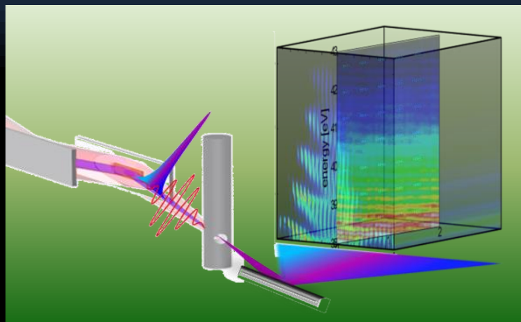
?

low intensity
low recollision energy



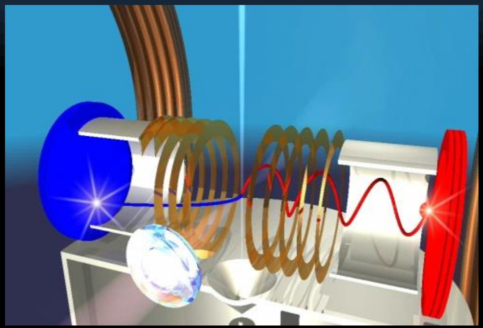
Experimental observation of few-body dynamics

Multidim. optical spectroscopy



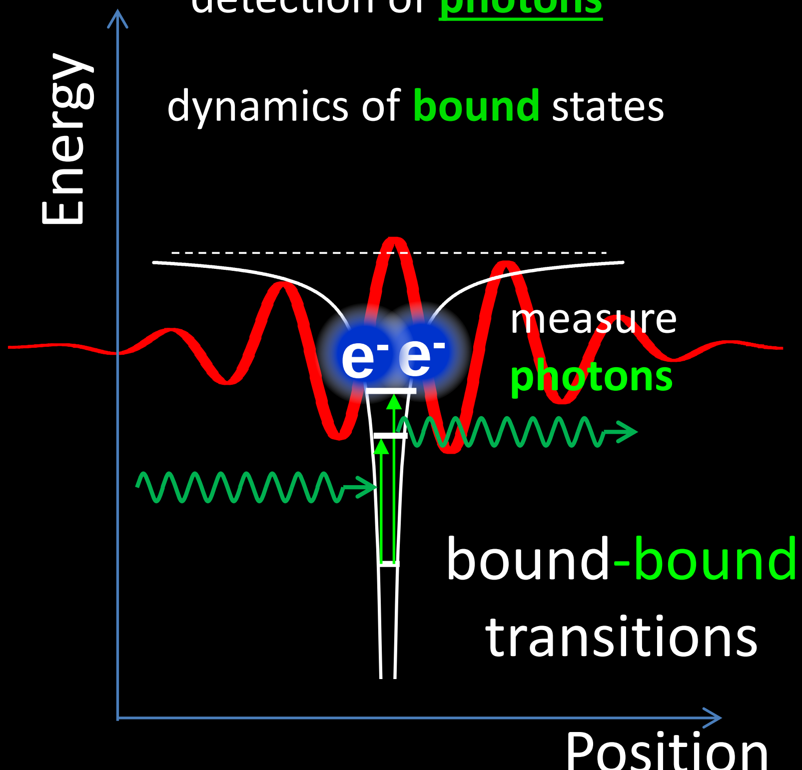
time&energy-resolved
detection of **photons**

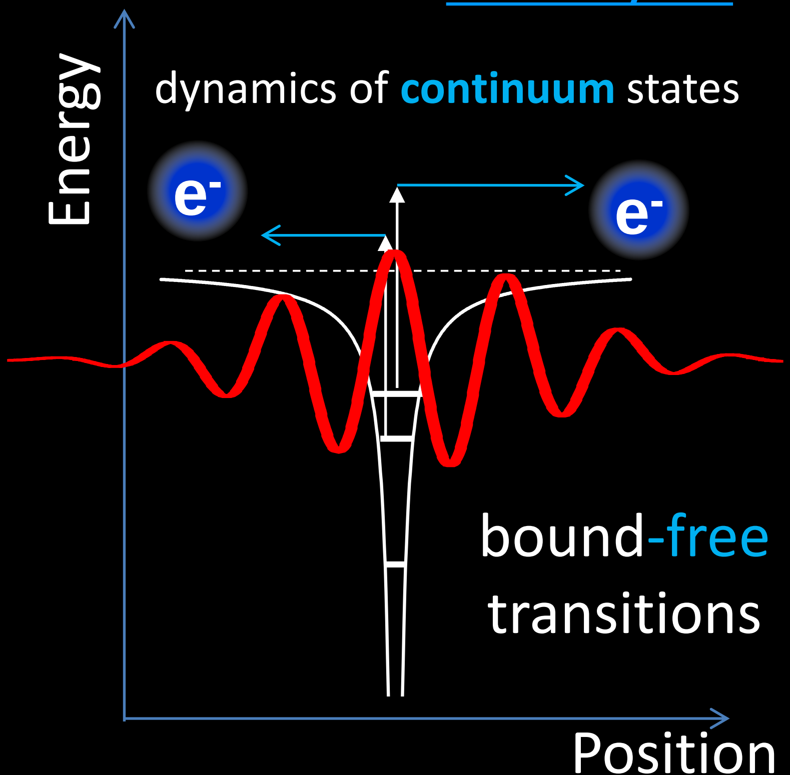
Reaction microscope/COLTRIMS



coincidence
detection of **electrons/ions**

Goal: extract
complete
information

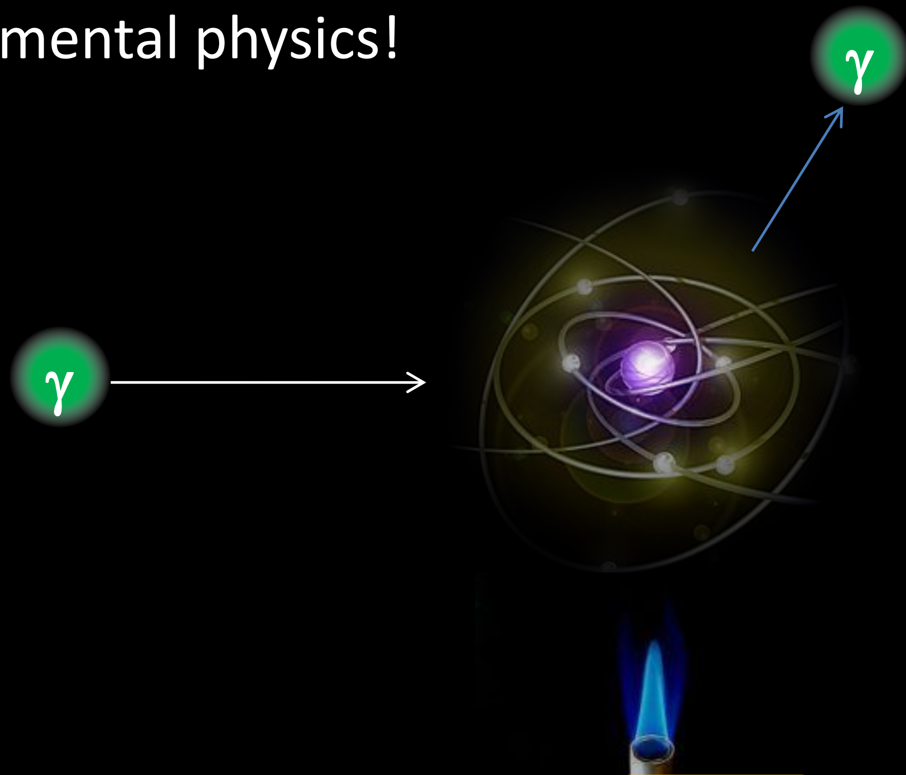


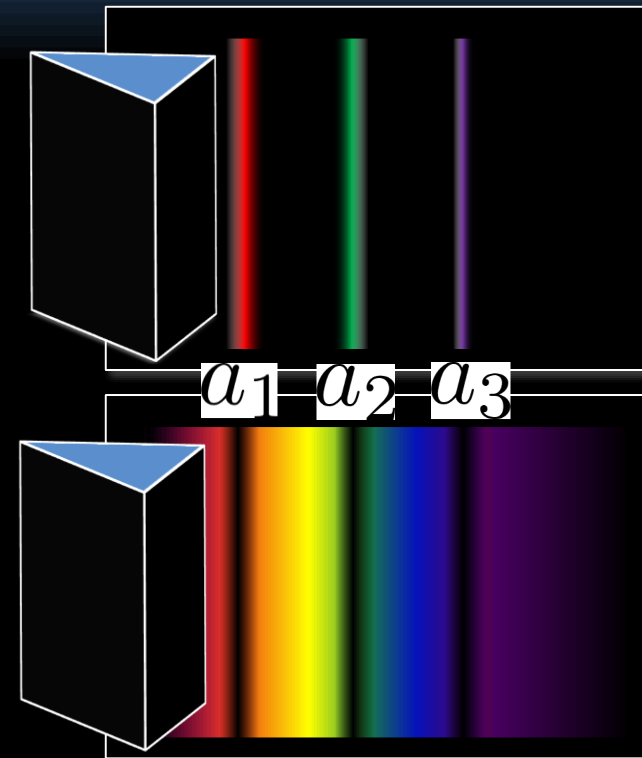


traditional spectroscopy

(Kirchhoff, Bunsen, *et al. @Heidelberg ~1860*)

Electrons in atoms already taught us a lot of fundamental physics!



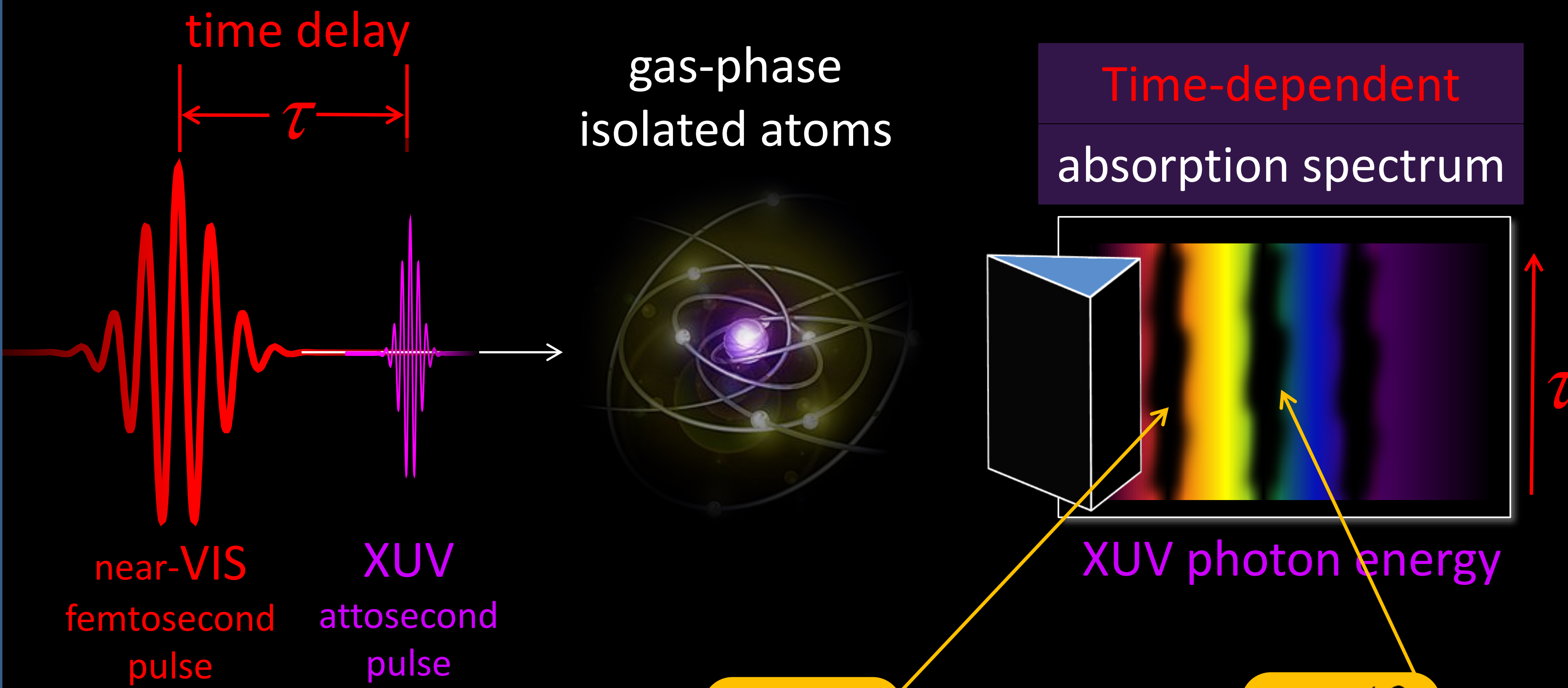


e.g. Fraunhofer *et al.*

Phase φ_1 Phase φ_2

$$\psi(x,t) \propto \boxed{a_1}\,\psi_1(x)\,e^{-\frac{i}{\hbar}E_1 t} + \boxed{a_2}\,\psi_2(x)\,e^{-\frac{i}{\hbar}E_2 t}$$

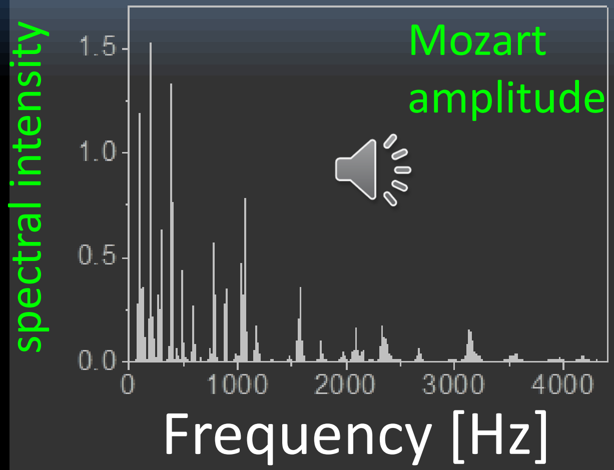
time-dependent absorption spectroscopy

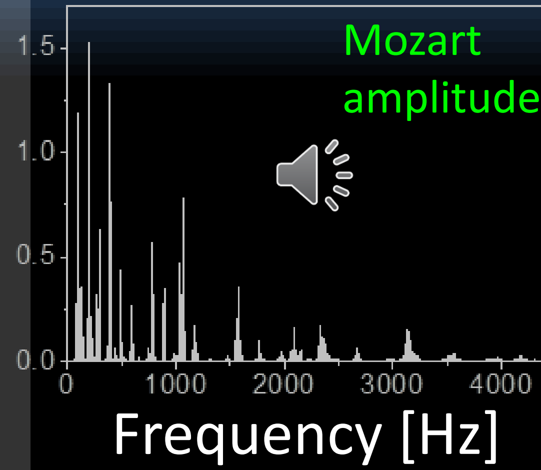


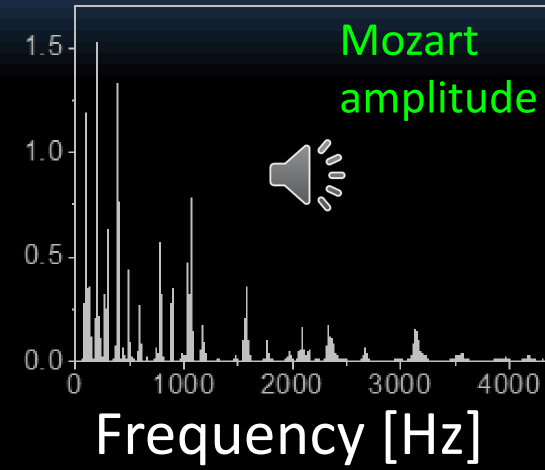
Phase φ_1 Phase φ_2

$$\psi(x,t) \propto a_1\psi_1(x)e^{-\frac{i}{\hbar}E_1 t} + a_2\psi_2(x)e^{-\frac{i}{\hbar}E_2 t}$$

Listening to phases



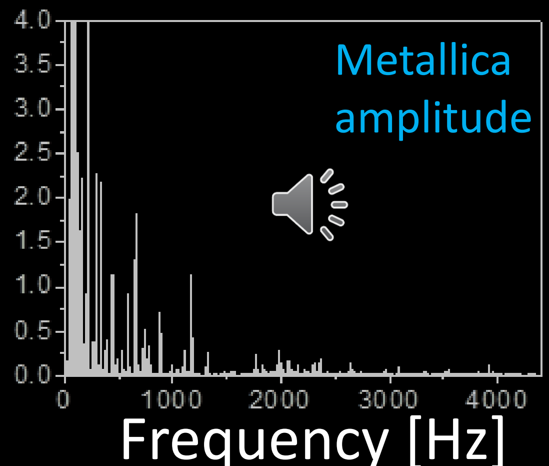


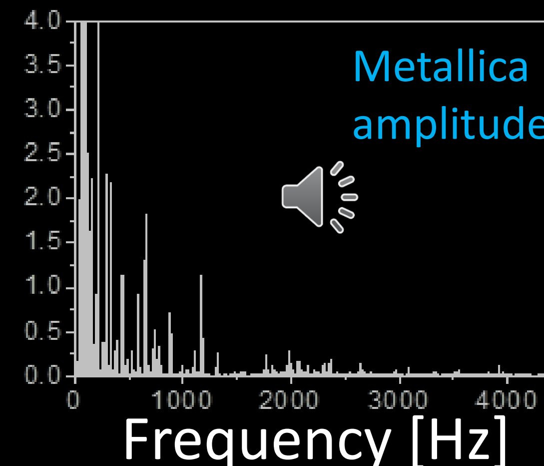


spectral phase by
by W. A. Mozart (1787)
(Eine kleine Nachtmusik)

spectral phase
by Chance
(randomized)

spectral phase
by Metallica (1992)
(Nothing else matters)





Properties of different light sources

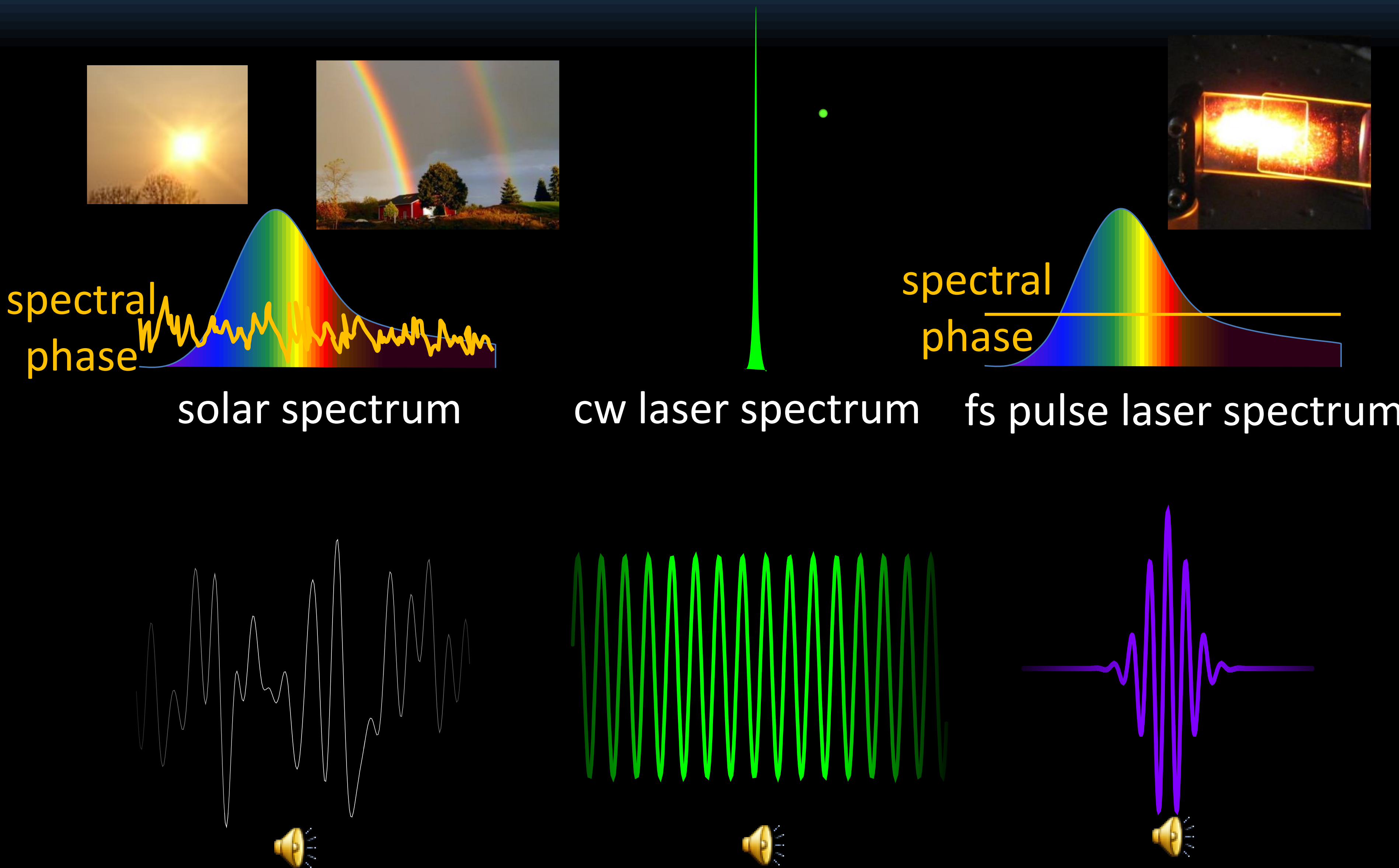
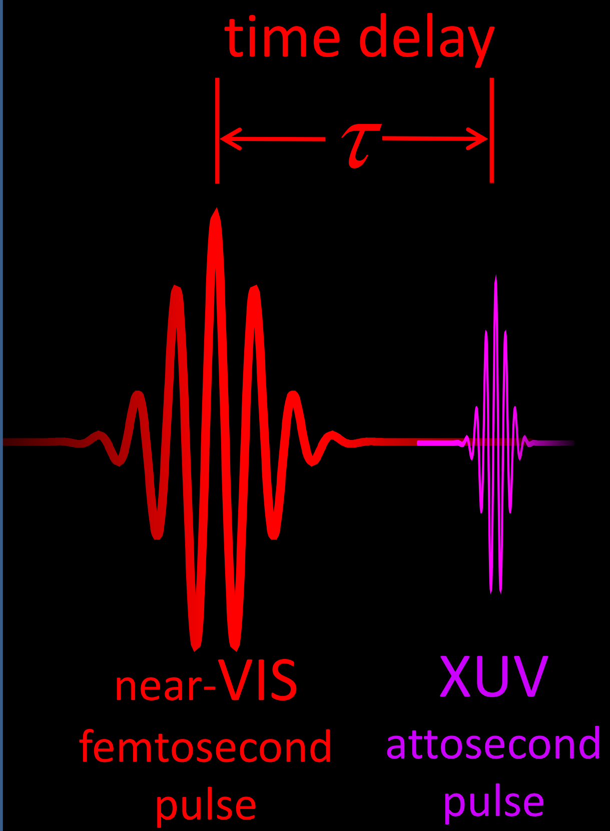
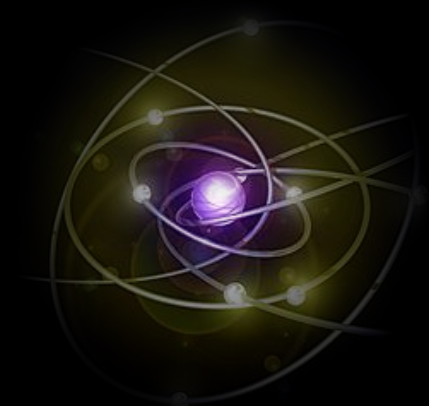


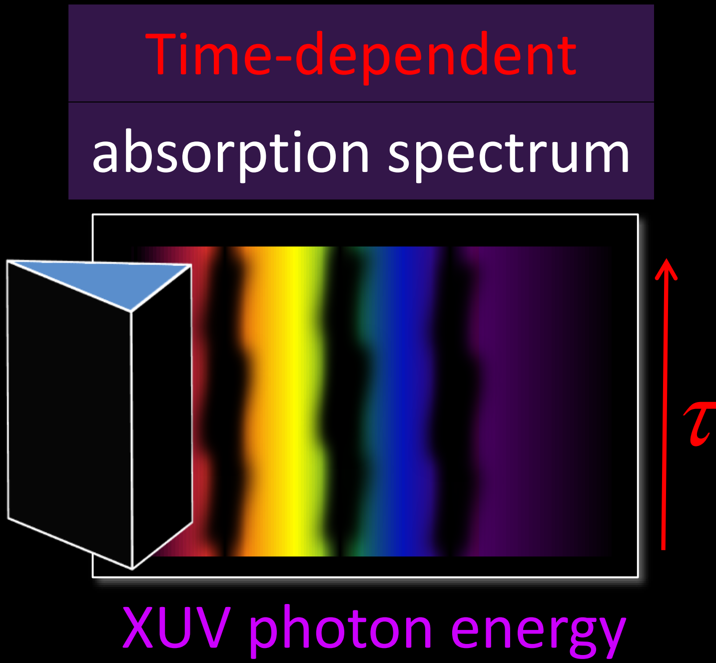
Bild-Quellen: http://www.bhakti-love.com/fotos/sonnenlicht.jpg,
http://climate.met.psu.edu/www_prod/data/frost/images/rainbow.jpg

time-dependent absorption spectroscopy

What's the dynamics of bound states and resonances in *short* and **strong** fields?







Phase $\varphi 1$

Phase $\varphi 2$

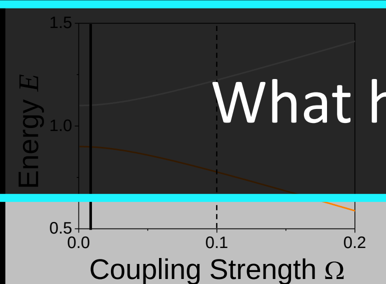
$$\psi(x,t) \propto a_1\psi_1(x)e^{-\frac{i}{\hbar}E_1 t} + a_2\psi_2(x)e^{-\frac{i}{\hbar}E_2 t}$$

General: coupling of states

coupling of **one** to **one other** state	coupling of **one** to **multiple** states	coupling of **one** to a **continuum** of states

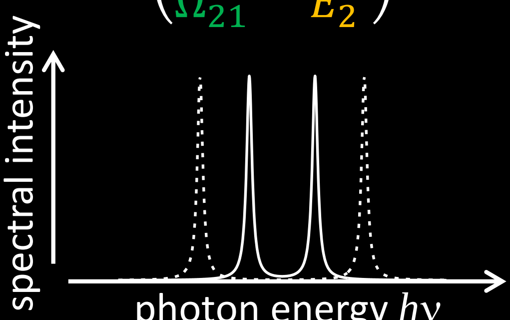
Quite well understood for cases of time-independent (or adiabatic) couplings

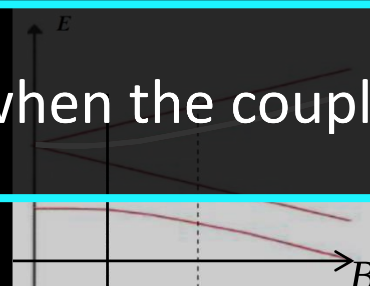
What happens when the coupling is **ultrashort** ?



Rabi oscillation
in strong coupling

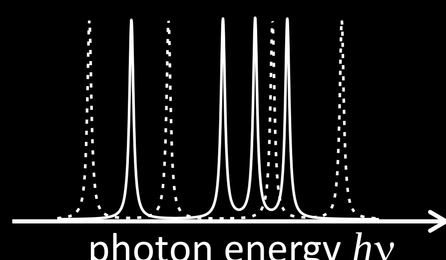
$$\begin{pmatrix} E_1 & \Omega_{12} \\ \Omega_{21} & E_2 \end{pmatrix}$$



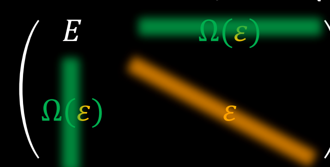


Breit-Rabi
e.g. Paschen-Back regime

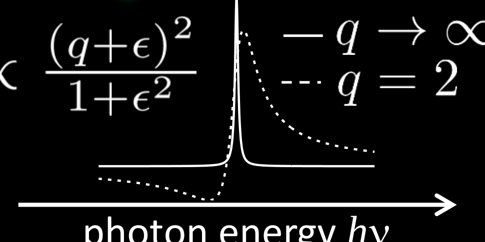
$$\begin{pmatrix} E_1 & \Omega_{12} & \Omega_{13} & \Omega_{14} \\ \Omega_{21} & E_2 & \Omega_{23} & \Omega_{24} \\ \Omega_{31} & \Omega_{32} & E_3 & \Omega_{34} \\ \Omega_{41} & \Omega_{42} & \Omega_{43} & E_4 \end{pmatrix}$$



U. Fano (1935)
Phys. Rev. **124**, 1866 (1961)
Nuovo Cim. 12, 154 (1935)

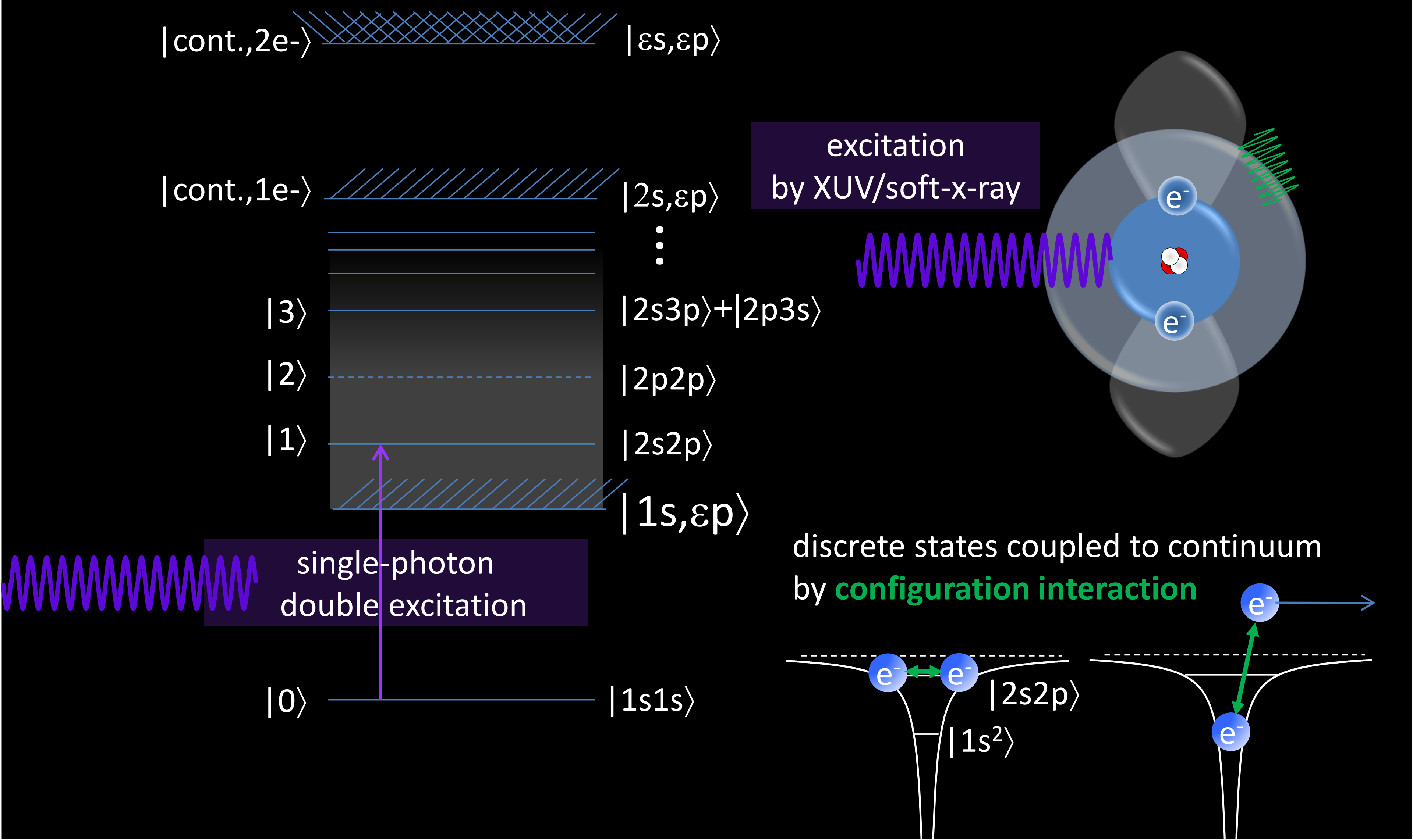


$$\sigma \propto \frac{(q+\epsilon)^2}{1+\epsilon^2}$$



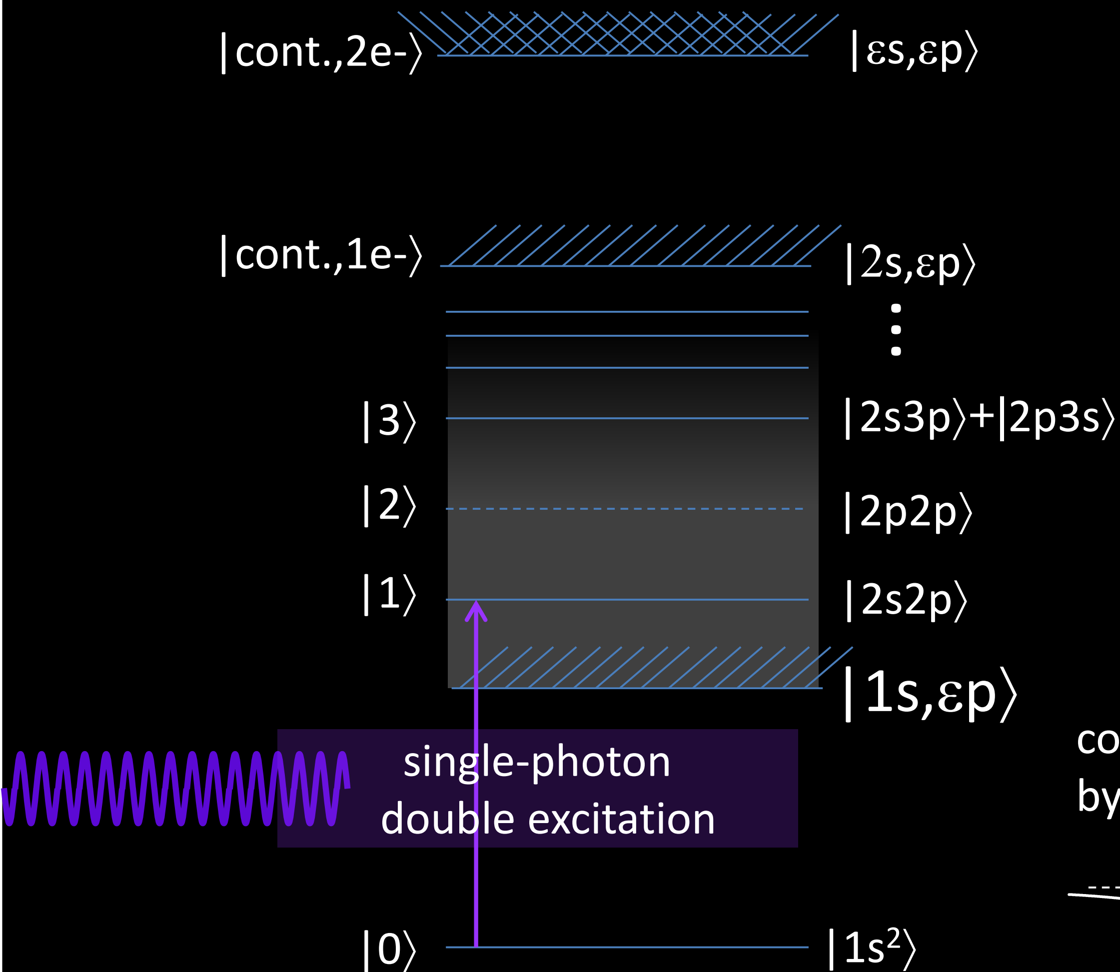
fundamental e⁻–e⁻ correlation in atoms

prototypical target: He atom

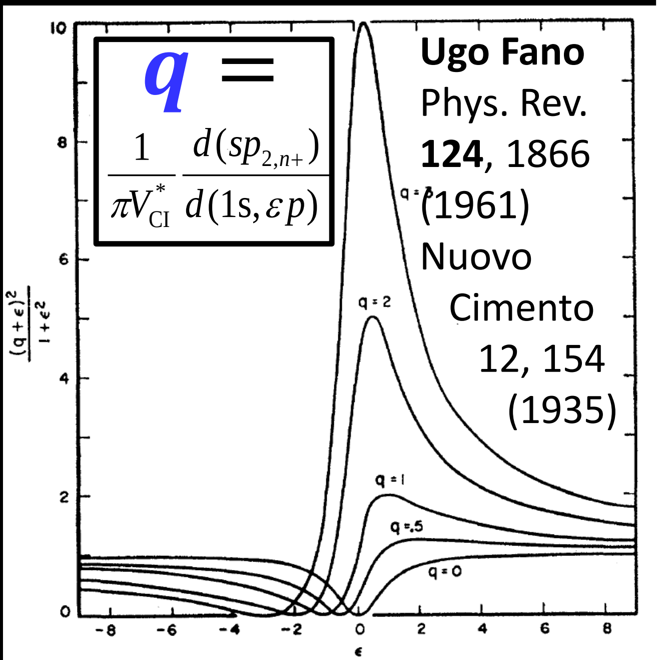


discrete states coupled to continuum by **configuration interaction**

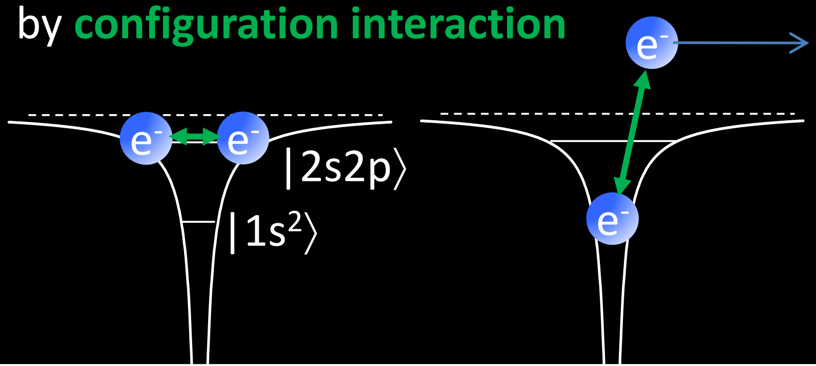
doubly excited helium: Fano resonance



$$\sigma_{Fano} \sim \frac{(q+\varepsilon)^2}{1+\varepsilon^2}$$

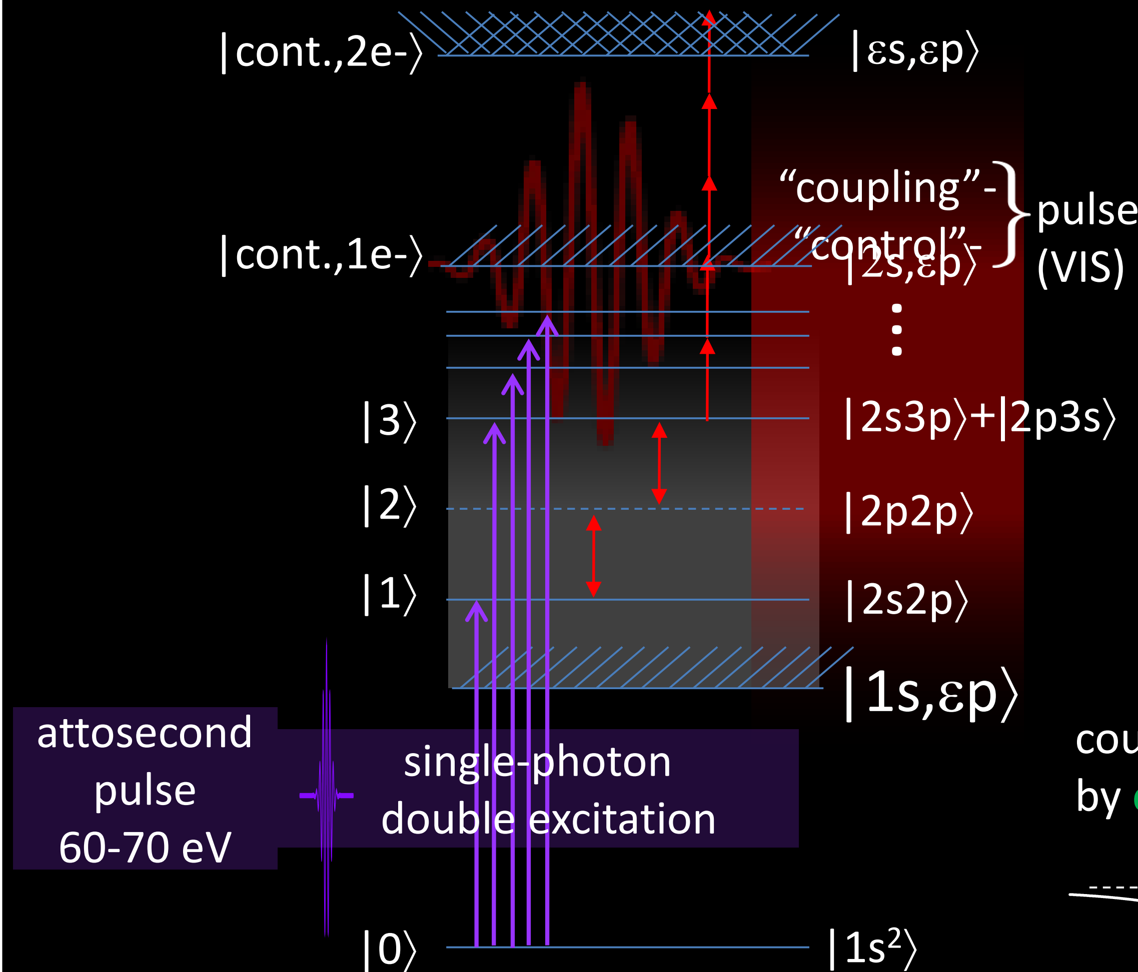


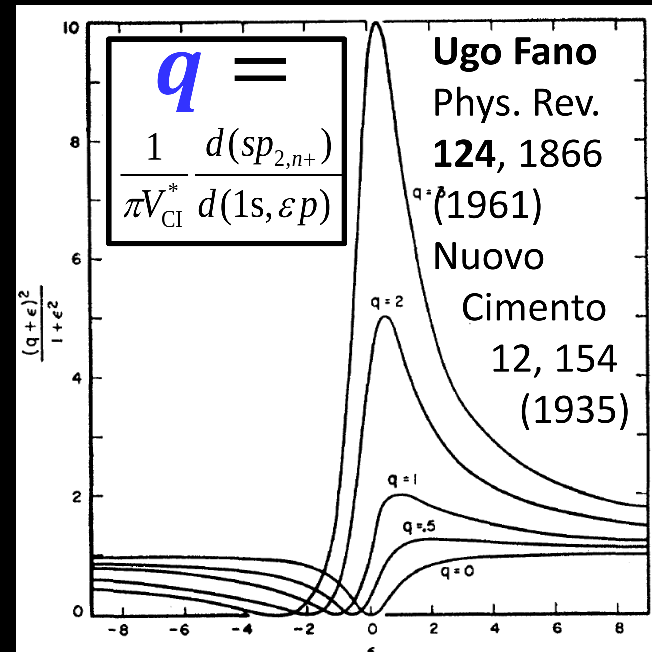
coupled
by **configuration interaction**



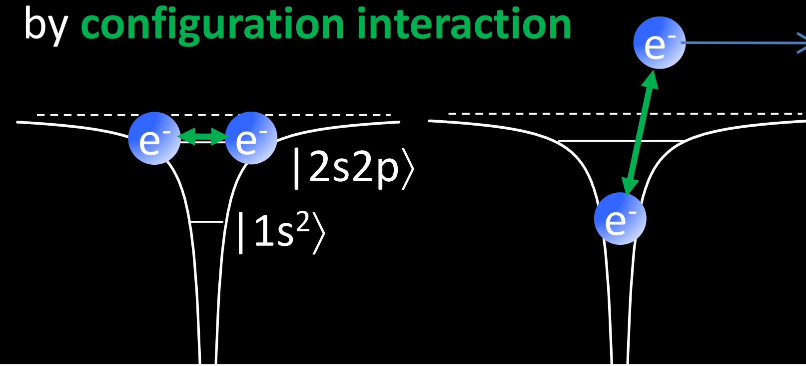
doubly-excited helium, in a strong laser field

$$\sigma_{Fano} \sim \frac{(q+\varepsilon)^2}{1+\varepsilon^2}$$

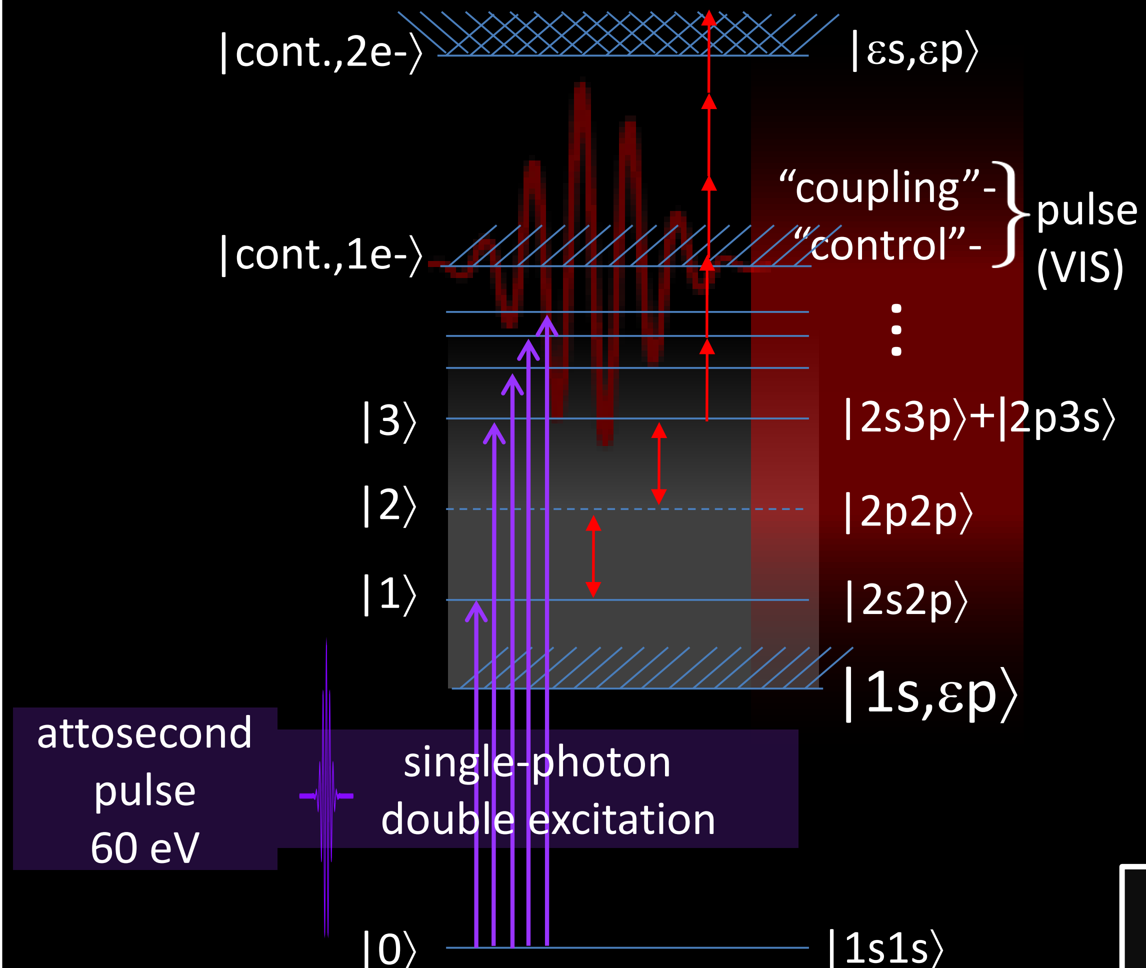




coupled
by **configuration interaction**



doubly-excited helium, in a strong laser field



<u>Previous work</u>
(on laser coupling of doubly-excited helium):

Theory:
- Madsen, Themelis, **Lambropoulos**
- Zhao, Chu, **Lin** et al.

...

Experiment:
- Loh, Greene, **Leone**, et al.
- Gilbertson, **Chang** et al.

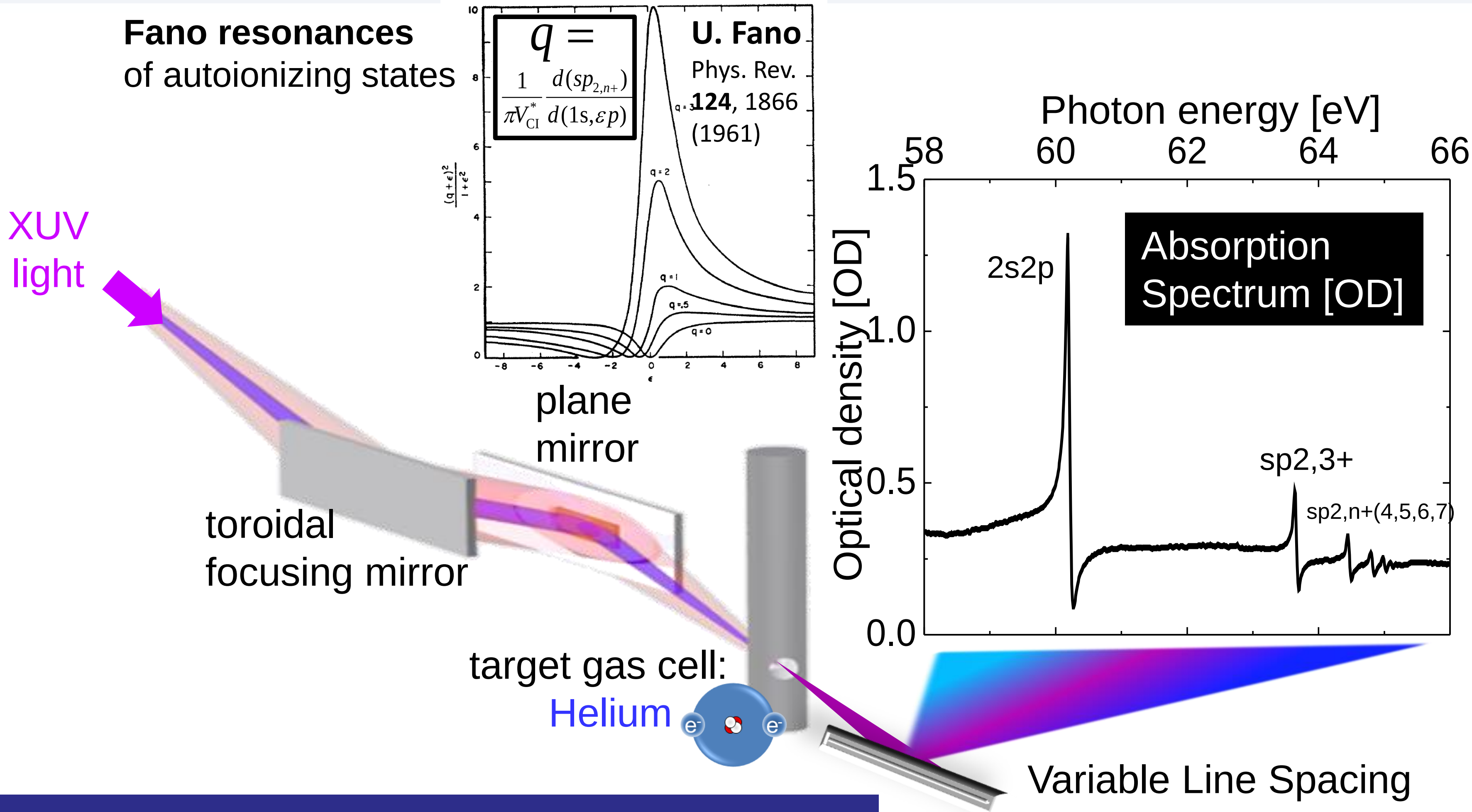
...

Experimental challenge:
- high (asec) temporal and
- high (meV) spectral resolution

required at the same time

Experimental setup

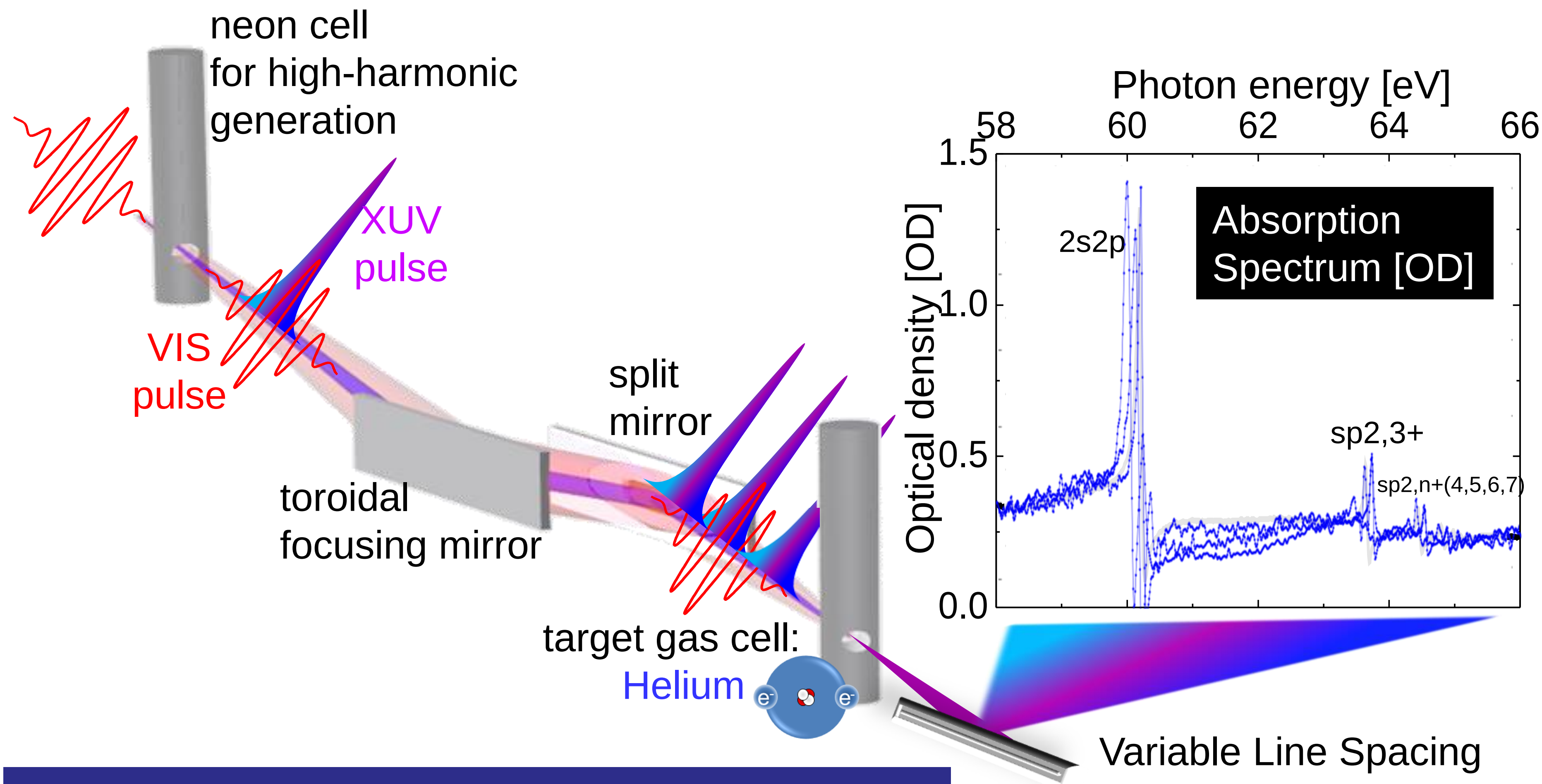
for XUV absorption spectroscopy



Experimental key challenge: **High resolution**
In photon energy ... : **ΔE = 20 meV (@60 eV)**

Experimental setup

for time-resolved XUV absorption spectroscopy

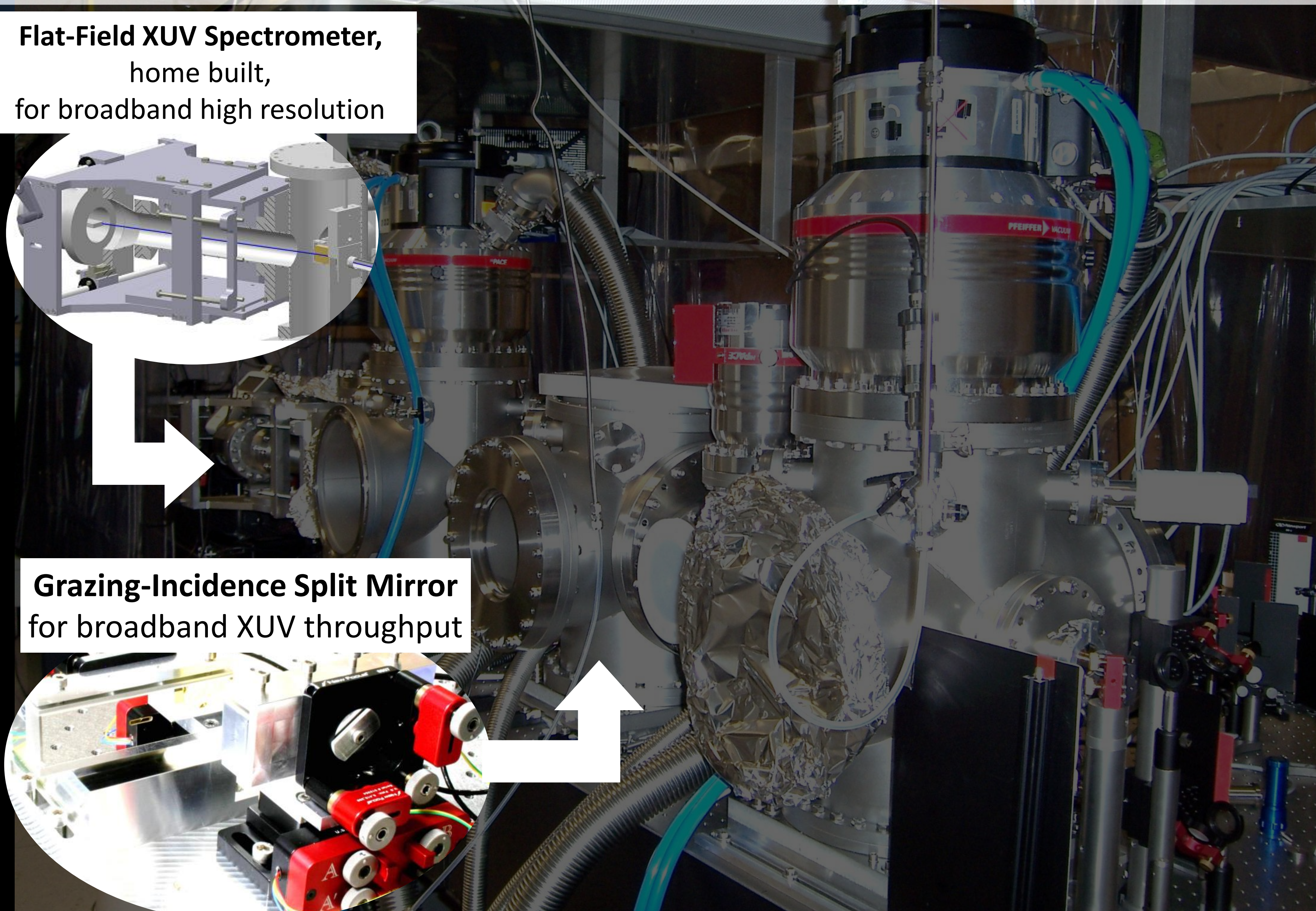


Experimental key challenge: **High resolution**

In photon energy ... : **ΔE = 20 meV (@60 eV)**

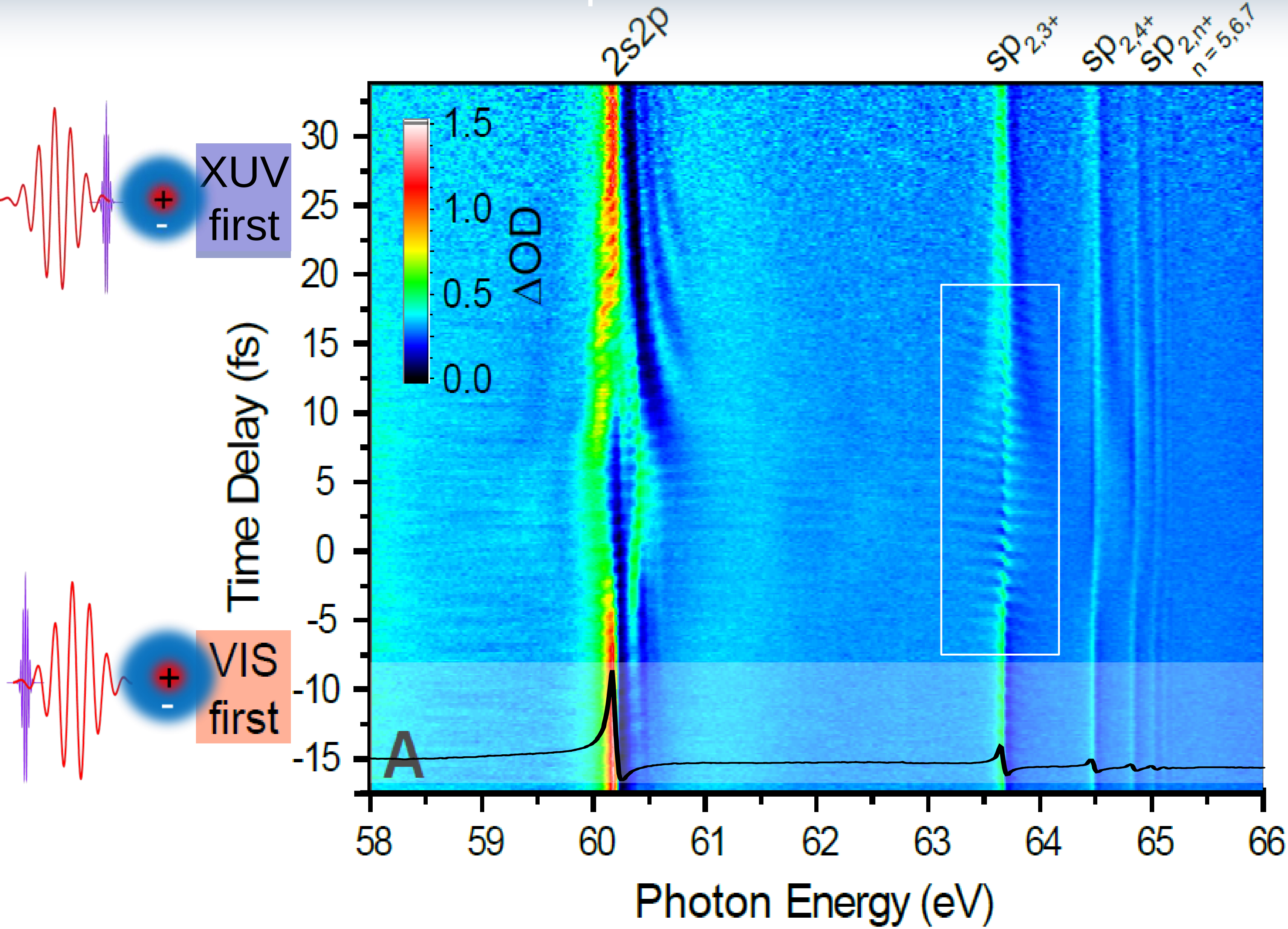
... and time delay : **Δτ = 10 as**

Experimental Setup in the Lab

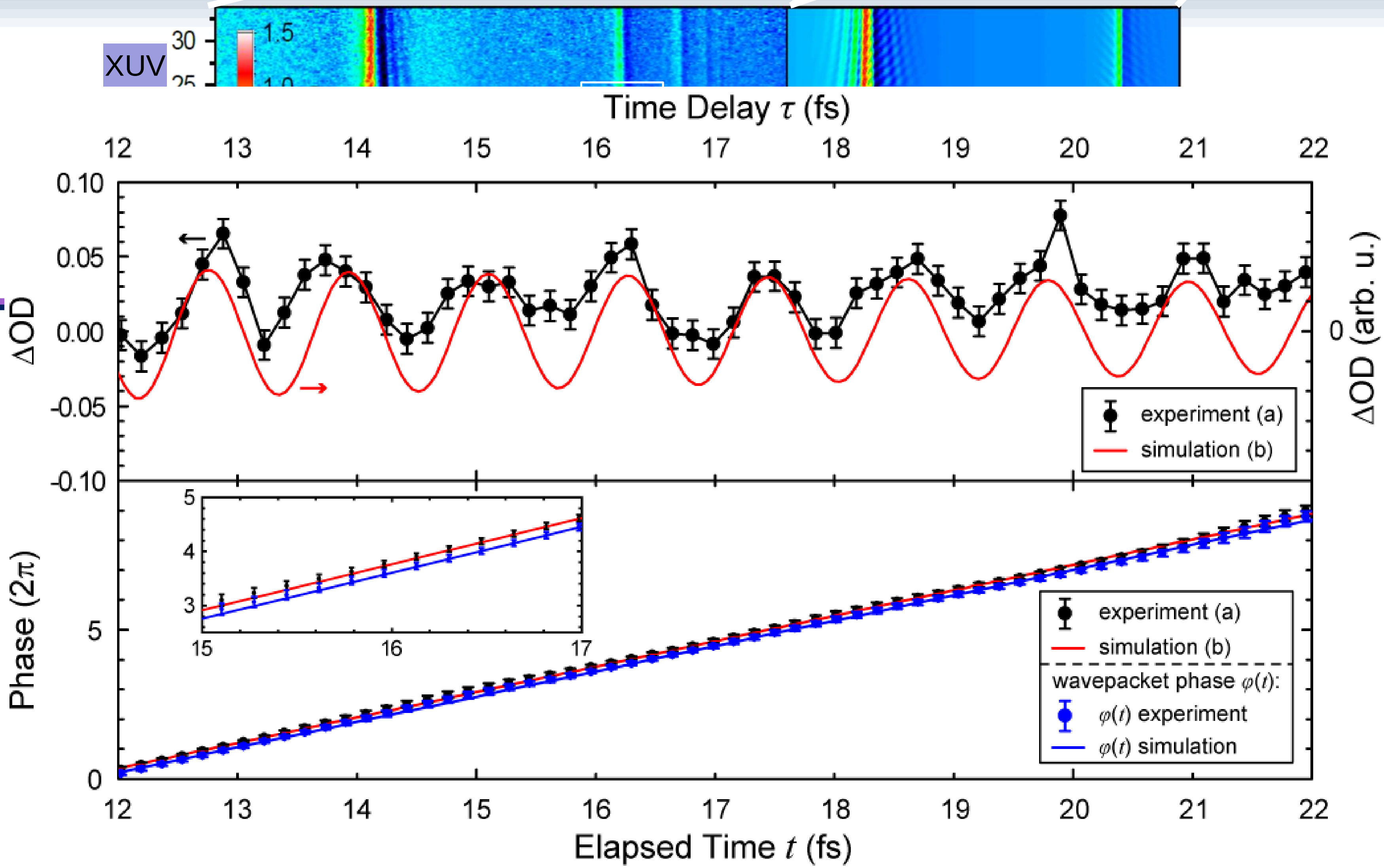


Time-resolved doubly-excited 2e⁻ dynamics in He

Experimental data



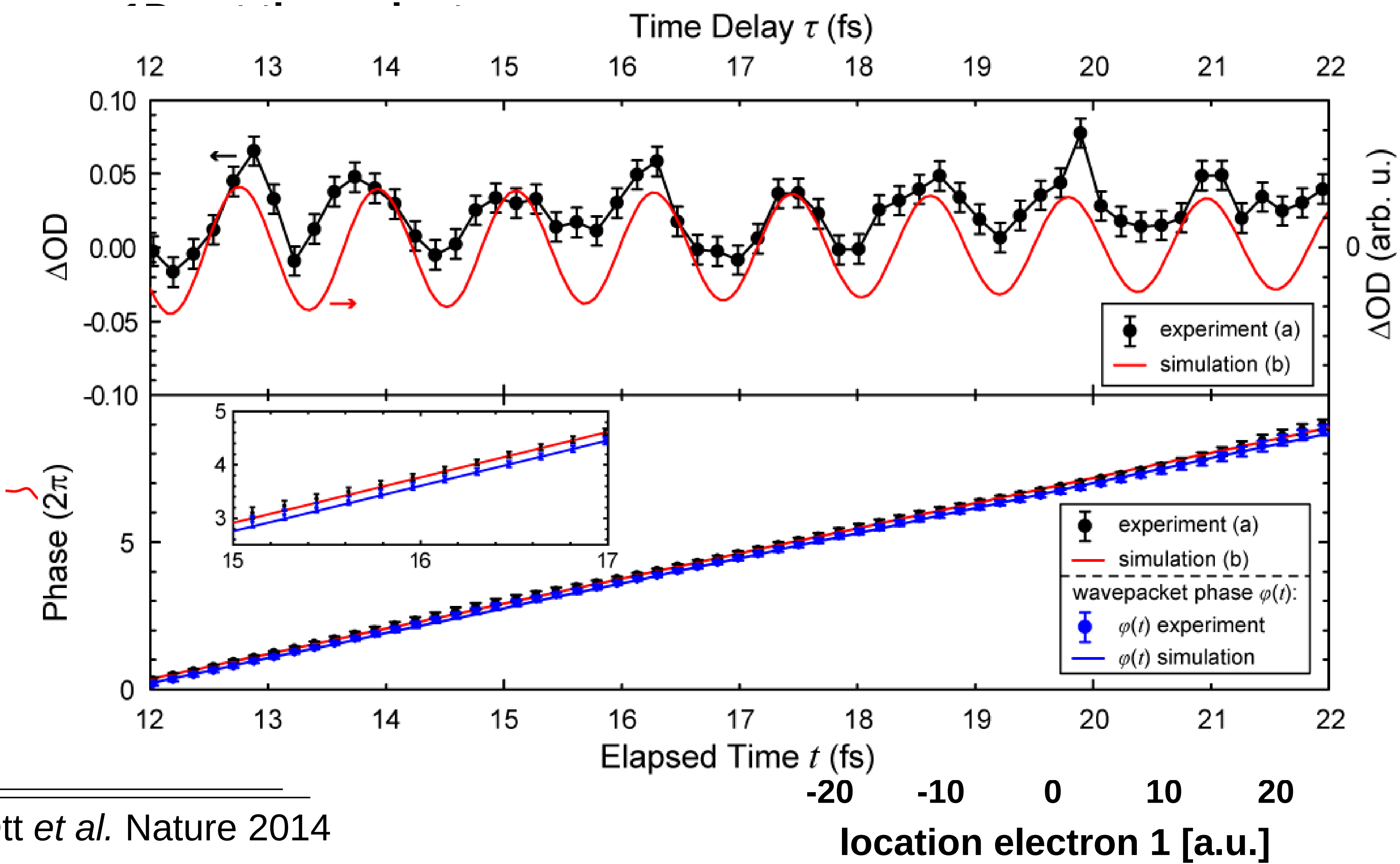
comparison experiment and theory



$\Rightarrow$ Wavepacket

Measuring the time-dependent phase difference of 2s2p and sp_{23+} autoionization states

cooperation with Javier Madroñero (Theory, TU München)

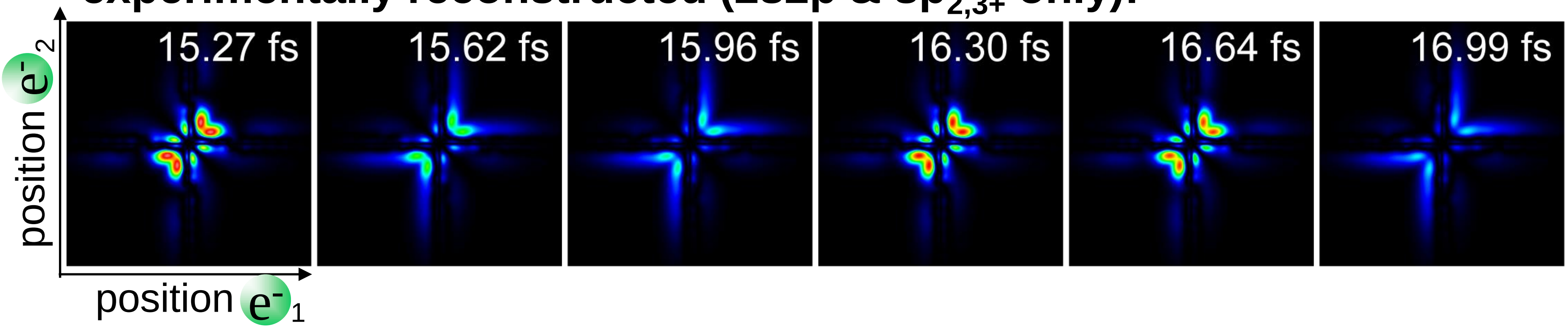


Ott *et al.* Nature 2014

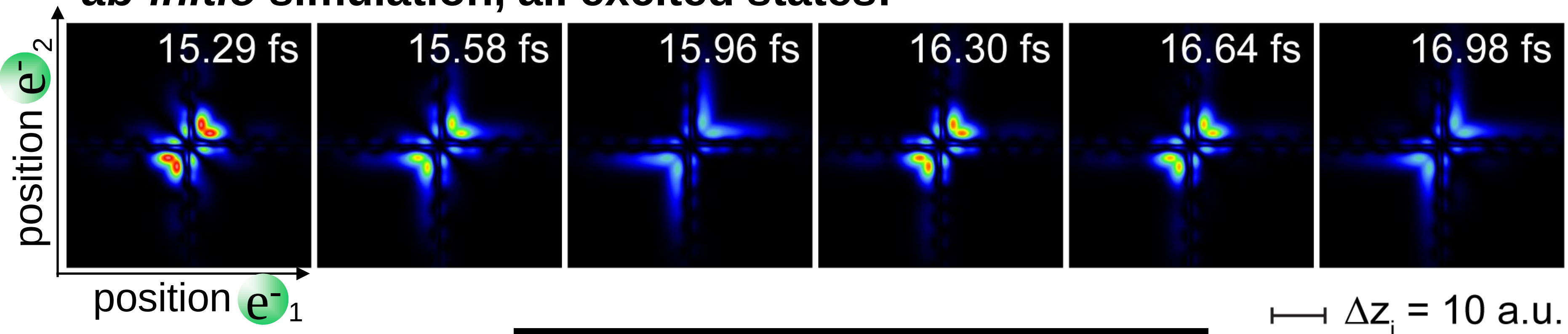
Testing *ab-initio* theory of e^- correlation dynamics

cooperation: Luca Argenti & Fernando Martín (UAM Madrid, Spain)
Javier Madroñero (TU Munich)

experimentally reconstructed (2s2p & $sp_{2,3+}$ only):



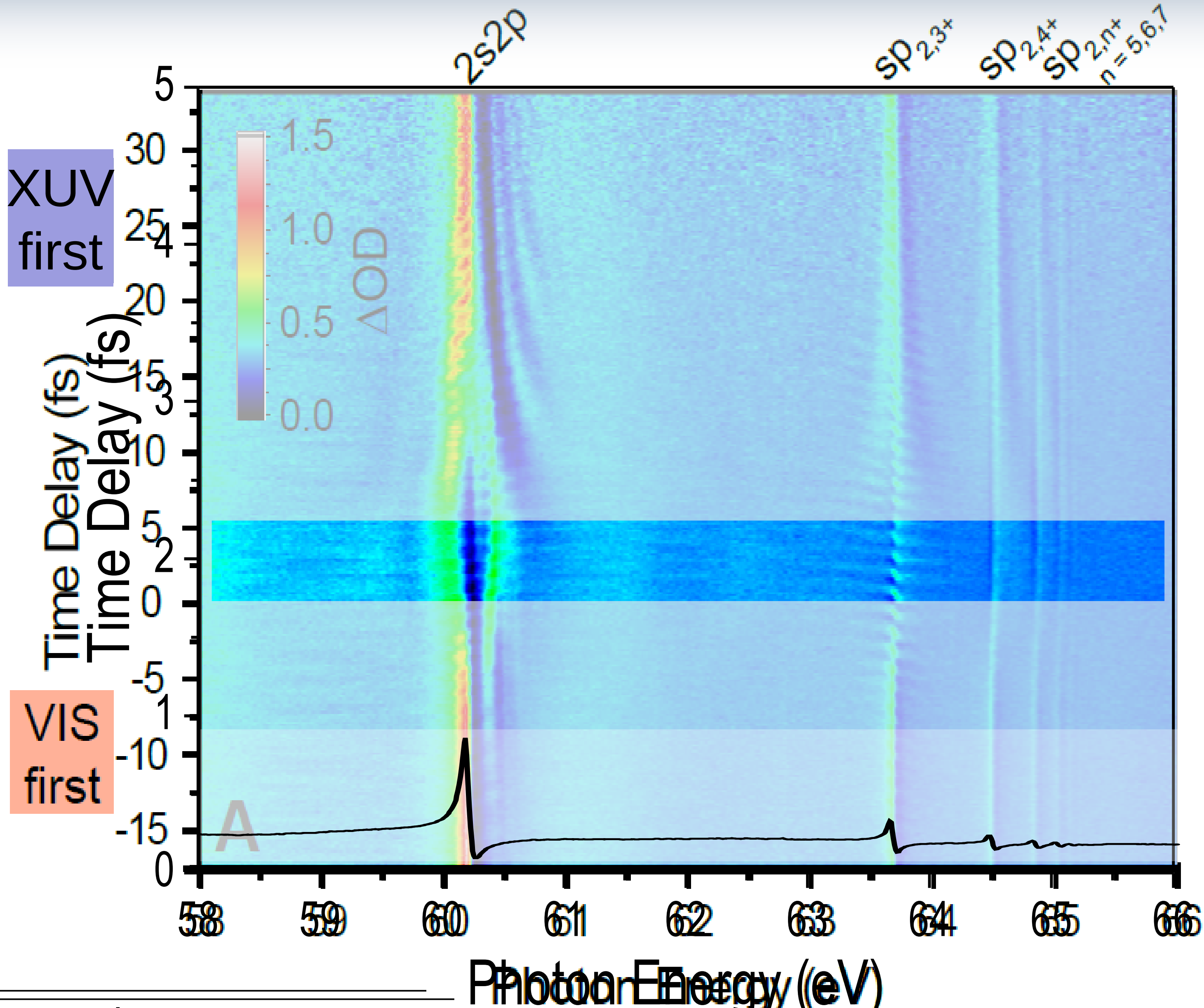
***ab-initio* simulation, all excited states:**



first experimental observation
of **two-electron wavepacket** motion

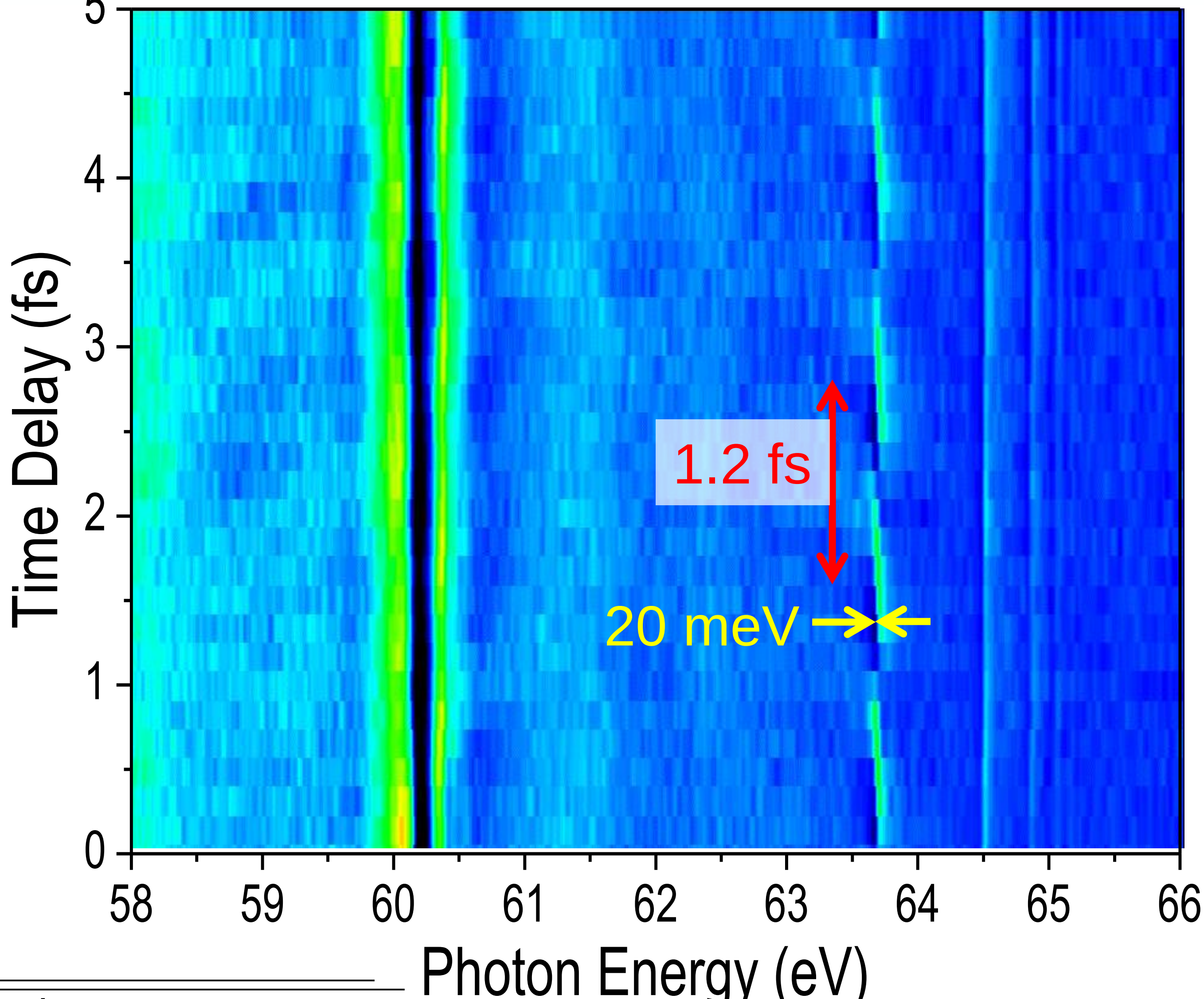
Ott *et al.*
Nature 2014

Time-resolved doubly-excited 2e⁻ dynamics in He



Ott *et al.* Nature 2014

Time-resolved doubly-excited 2e⁻ dynamics in He



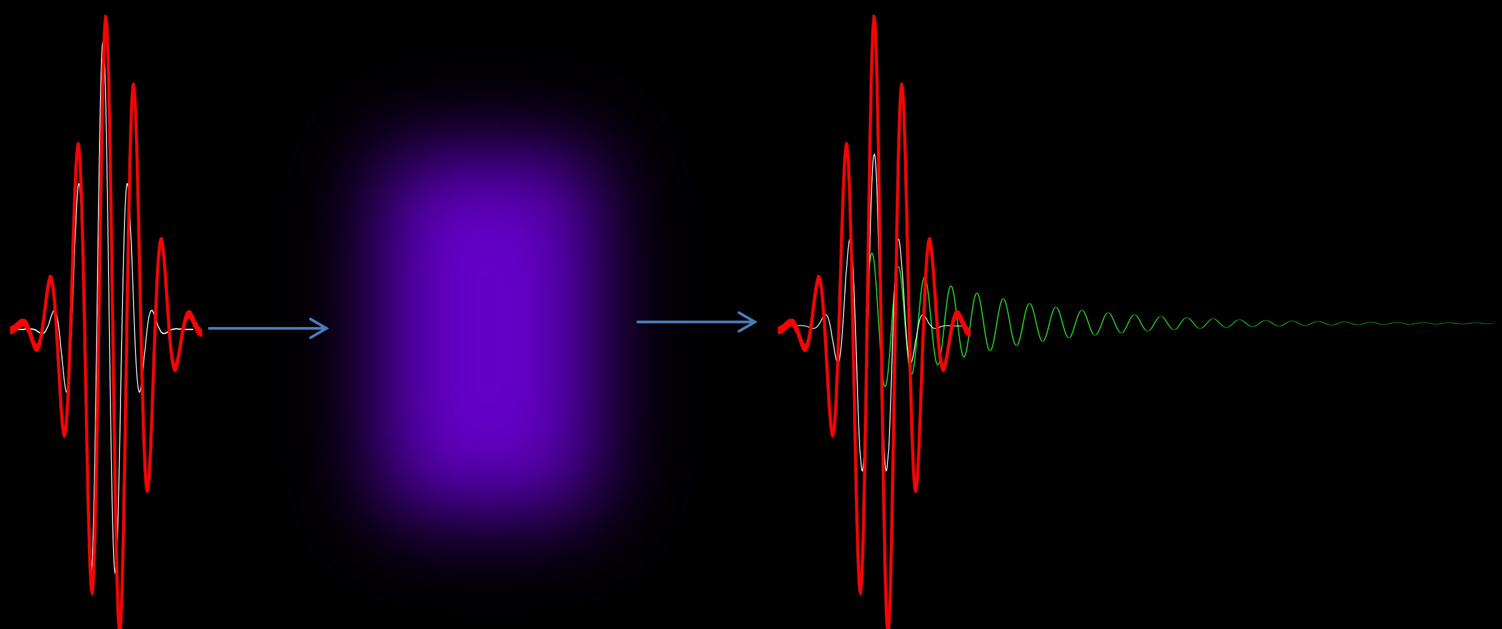
high temporal
and
high spectral
resolution
are
required
simultaneously

Ott *et al.* Nature 2014

Hold on, can I ask you a few questions?

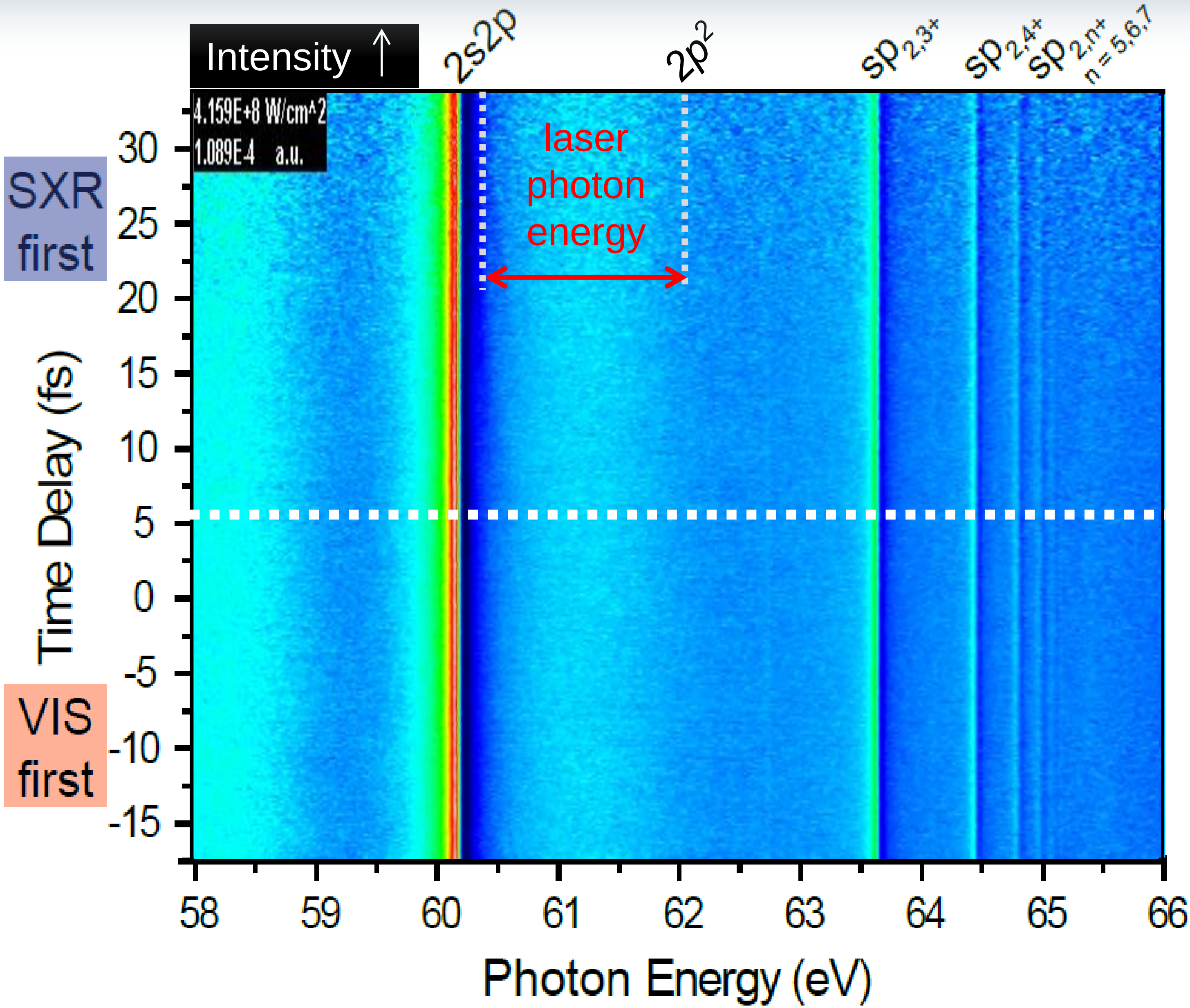
What is absorption?

And how does it respond to intense pulsed light?



Control the electrons, and measure their response

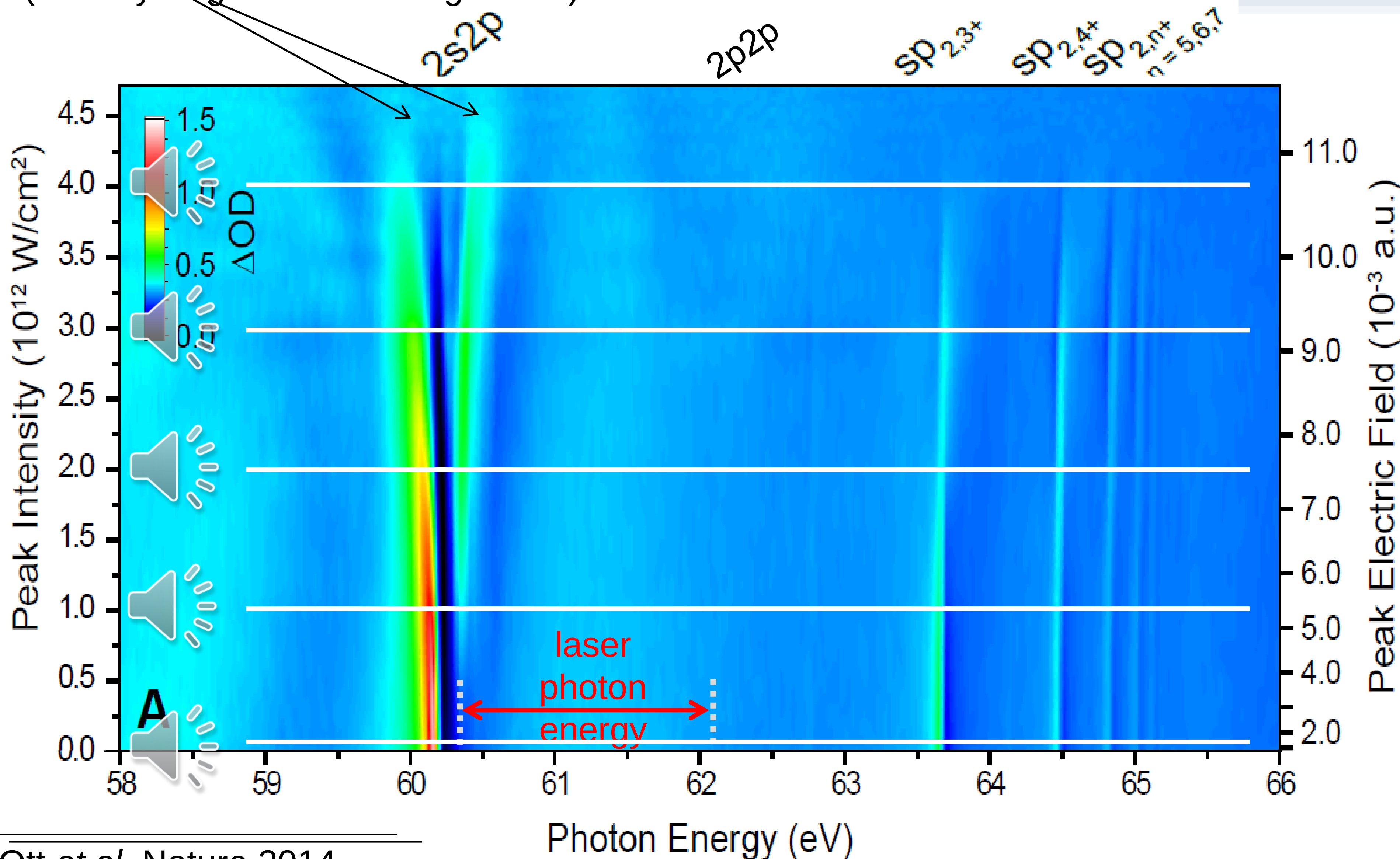
"Ask" "listen"



Intensity, the control knob

Autler-Townes doublet
(Rabi cycling of autoionizing states)

tuning from weak perturbative to strong fields



Ott *et al.* Nature 2014

Intensity, the control knob

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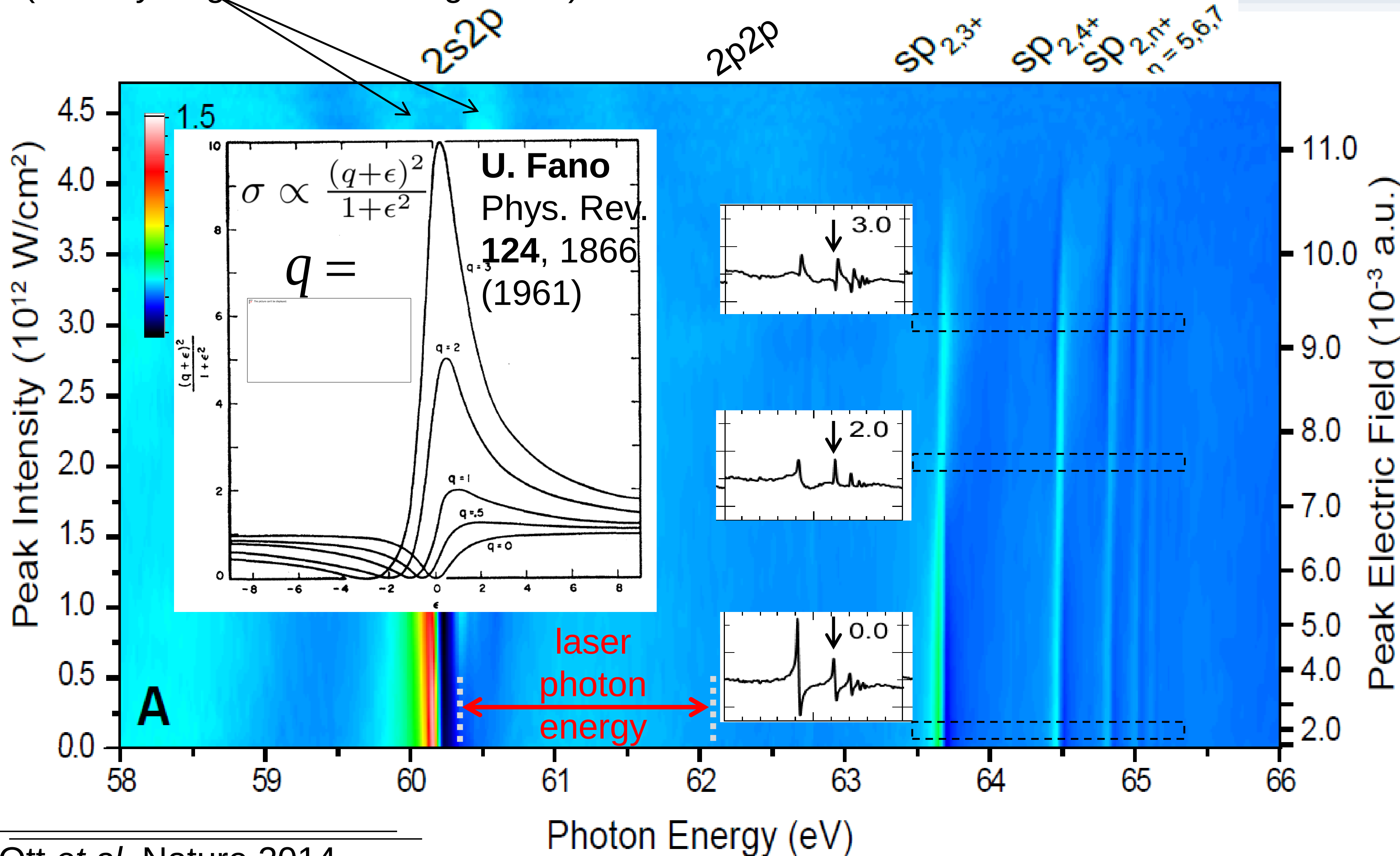


$$\sigma \propto \frac{(q+\epsilon)^2}{1+\epsilon^2}$$

Ott *et al.* Nature 2014

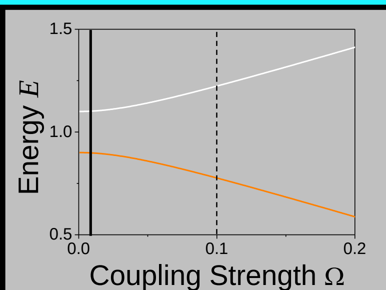
General: coupling of states

coupling of **one** to **one other** state

coupling of **one** to **multiple** states

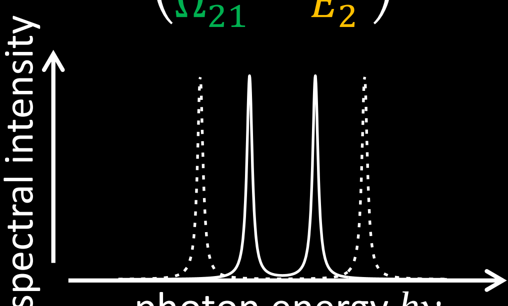
coupling of **one** to a **continuum** of states

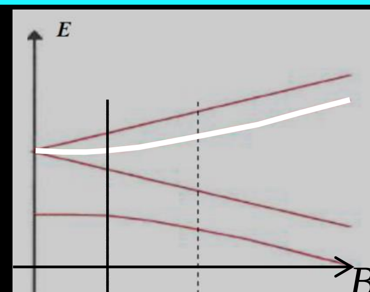
What happens when the coupling is **ultrashort** ?



Rabi oscillation
in strong coupling

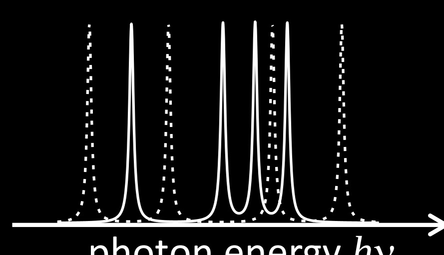
$$\begin{pmatrix} E_1 & \Omega_{12} \\ \Omega_{21} & E_2 \end{pmatrix}$$

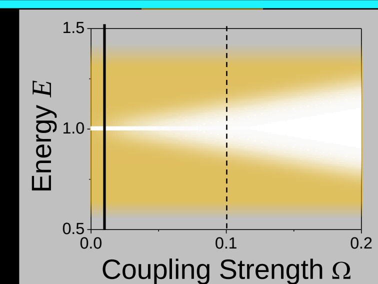




Breit-Rabi
e.g. Paschen-Back regime

$$\begin{pmatrix} E_1 & \Omega_{12} & \Omega_{13} & \Omega_{14} \\ \Omega_{21} & E_2 & \Omega_{23} & \Omega_{24} \\ \Omega_{31} & \Omega_{32} & E_3 & \Omega_{34} \\ \Omega_{41} & \Omega_{42} & \Omega_{43} & E_4 \end{pmatrix}$$

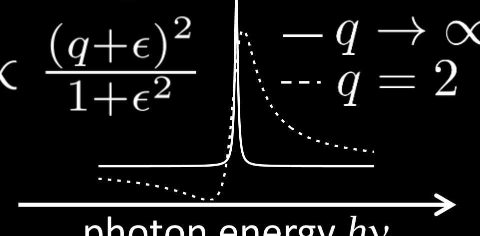




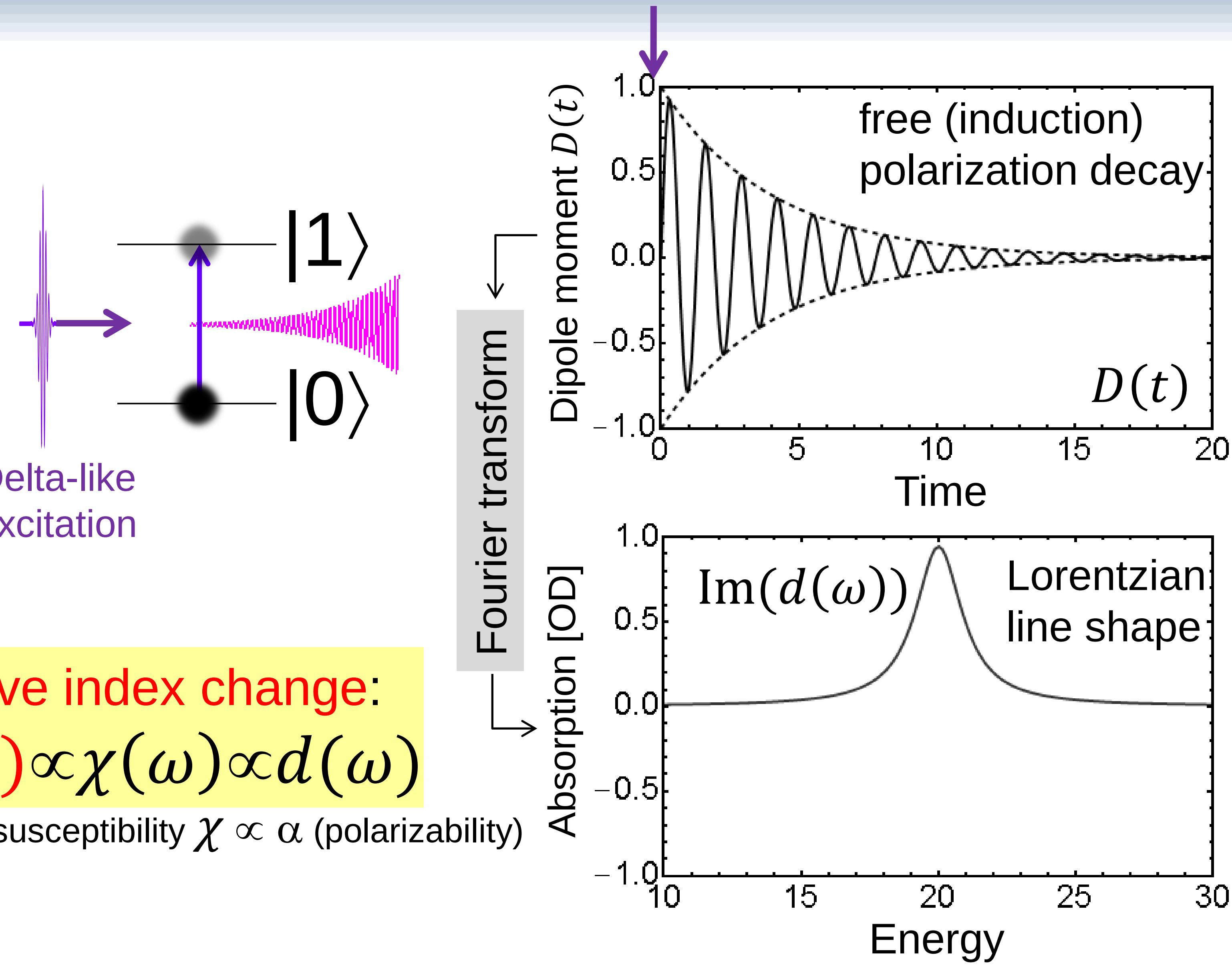
U. Fano (1935)
Phys. Rev. **124**, 1866 (1961)
Nuovo Cim. 12, 154 (1935)

$$\begin{pmatrix} E & \Omega(\varepsilon) \\ \Omega(\varepsilon) & \varepsilon \end{pmatrix}$$

$$\sigma \propto \frac{(q+\epsilon)^2}{1+\epsilon^2}$$



Resonance absorption in the Time Domain



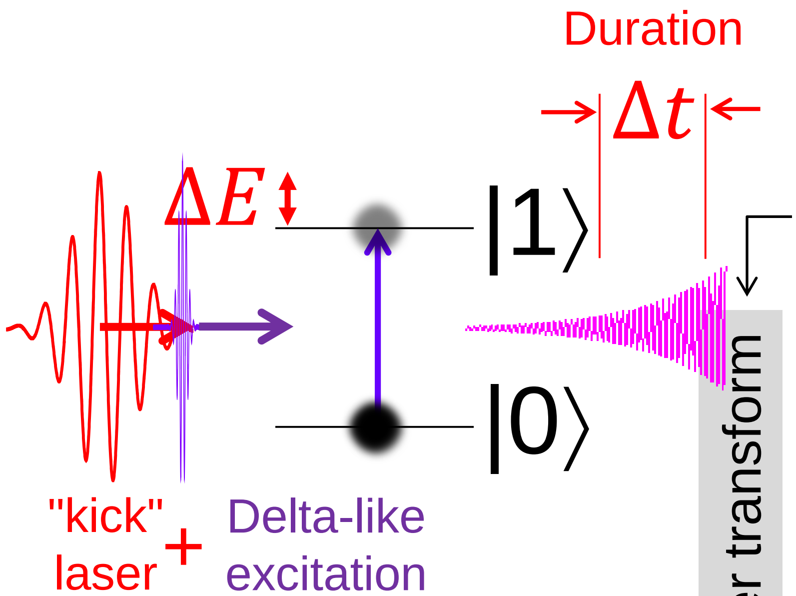
refractive index change:

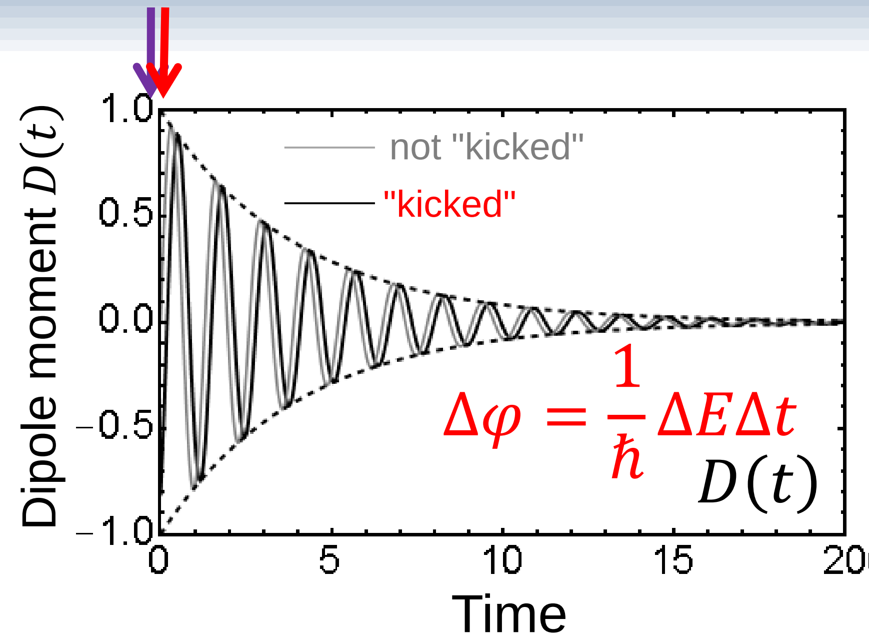
$$\Delta n(\omega) \propto \chi(\omega) \propto d(\omega)$$

susceptibility $\chi \propto \alpha$ (polarizability)

Resonance absorption in the Time Domain

Science **340**, 716 (2013)





...it IS a Fano line shape!

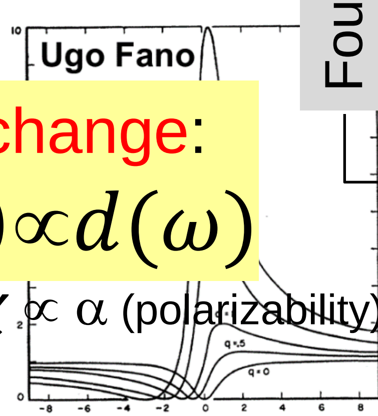
$\varphi(q)$

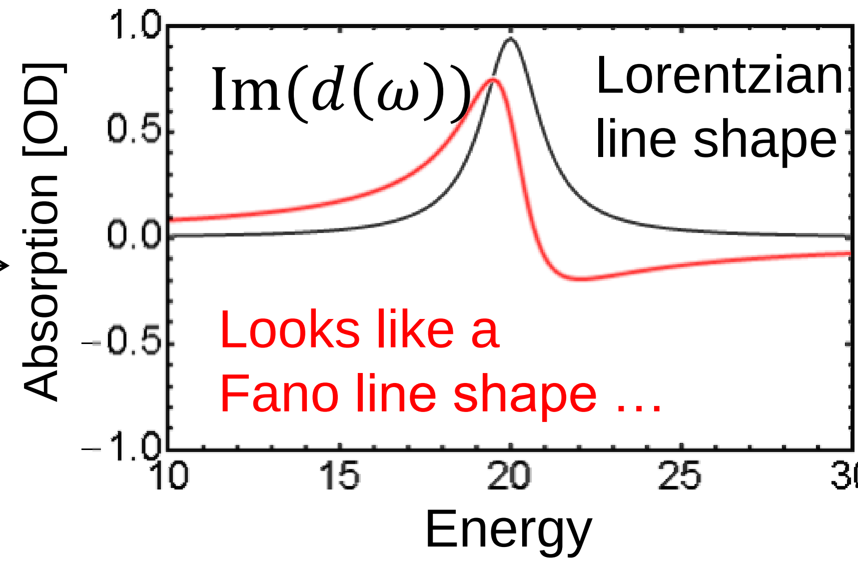
$q(\varphi) = -\cot(\frac{\varphi}{2})$

refractive index change:

$\Delta n(\omega) \propto \chi(\omega) \propto d(\omega)$

susceptibility $\chi \propto \alpha$ (polarizability)





The Fano dipole phase

Exact mapping from Fano q parameter to temporal phase shift φ

cooperation with C. Greene (Purdue), J. Evers and C. Keitel (MPIK)

$$\sigma_{Fano} \sim \frac{(\varepsilon + q)^2}{\varepsilon^2 + 1}$$

$$=$$

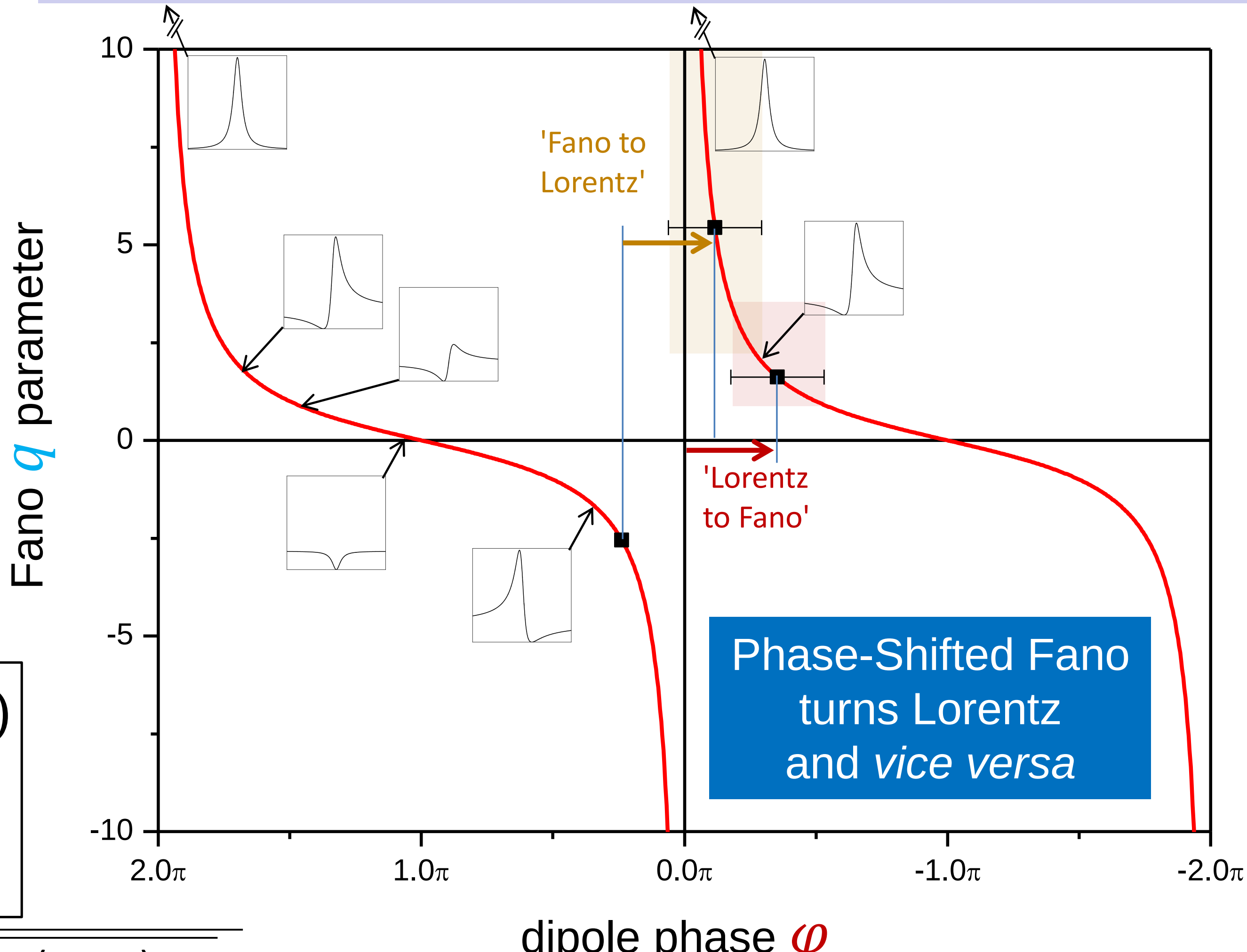
$$\mathrm{Im}\left(\frac{-1}{i+\varepsilon}\exp(i\varphi)\right) + const.$$

Phase-shifted Lorentzian

...it IS a
Fano line shape!

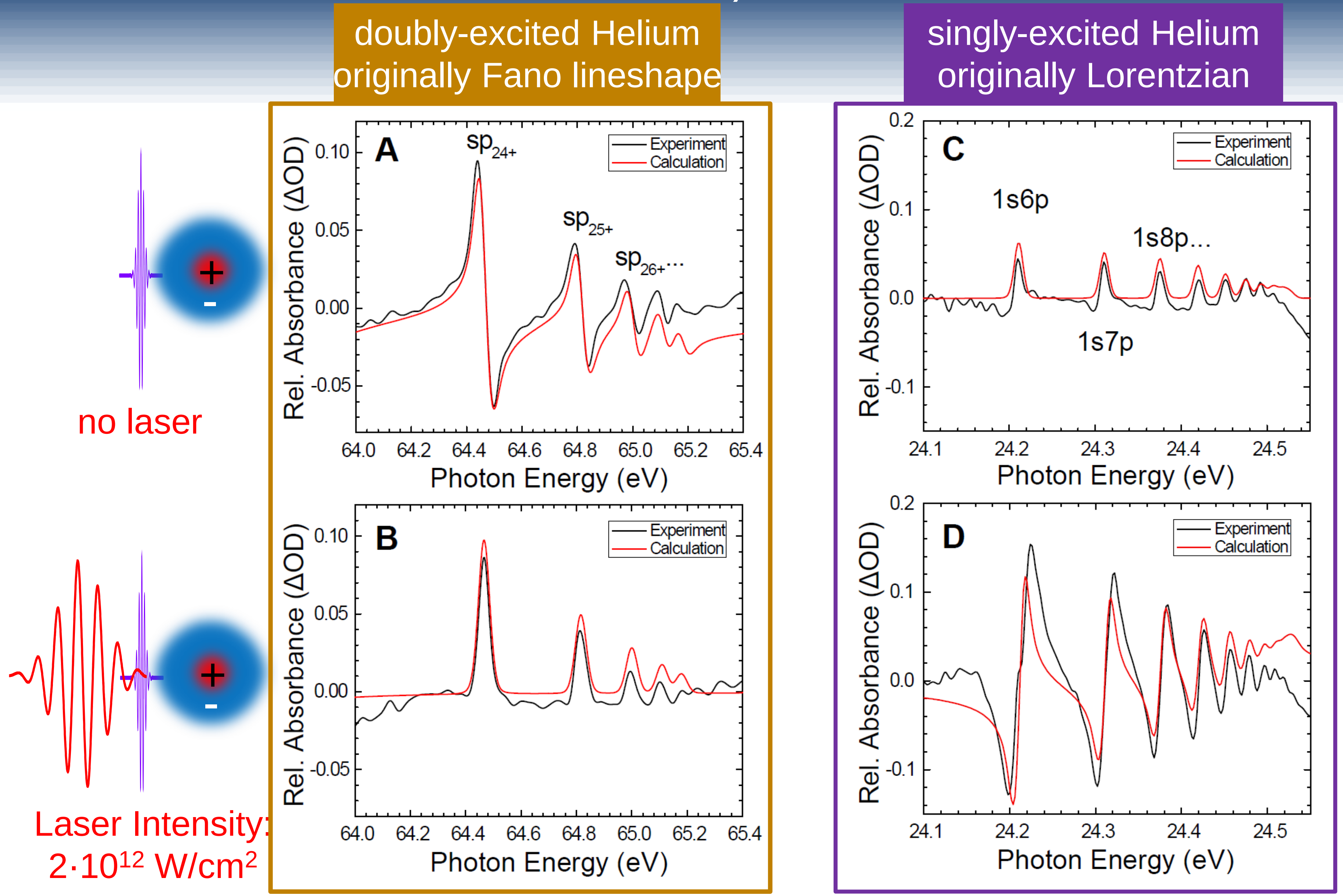
$$\varphi(q) = 2\arg(q - i)$$

$$q(\varphi) = -\cot\left(\frac{\varphi}{2}\right)$$



C. Ott *et al.* Science **340**, 716 (2013)

Fano to Lorentz, and Lorentz to Fano

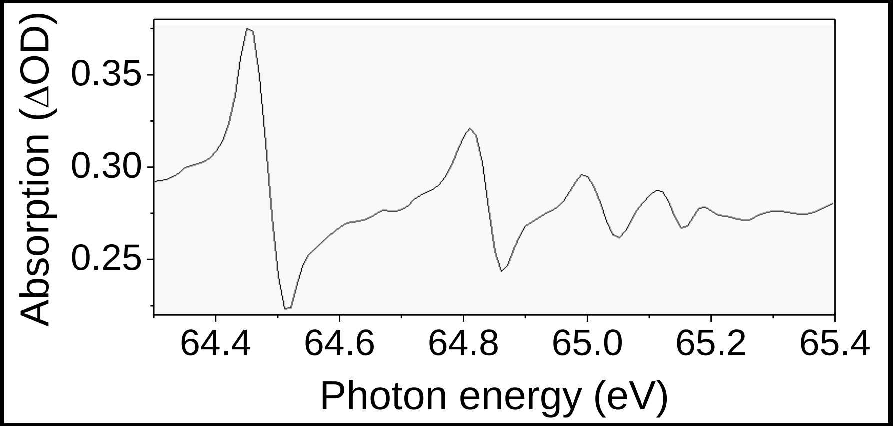


Science **340**, 716 (2013)

Laser Control of Fano and Lorentzian resonances

Helium doubly excited (above the continuum threshold)

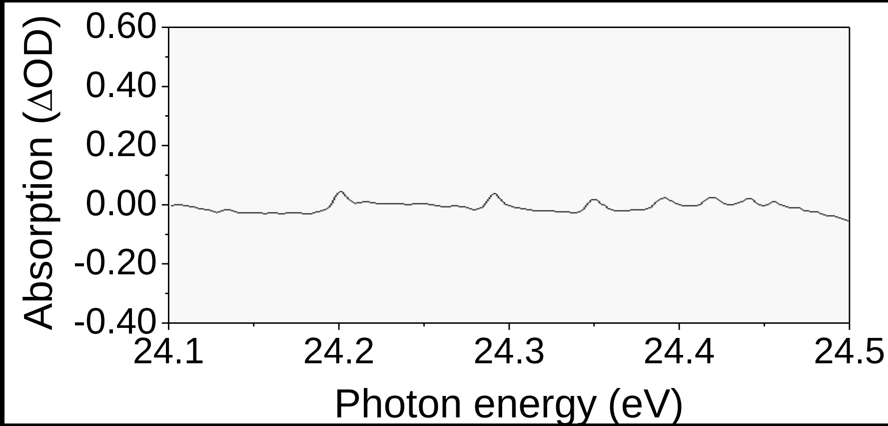
'2s4p' '2s5p' '2s6p' ...



turning original 'Fano' into 'Lorentz'

Helium singly excited (below the continuum threshold)

1s6p 1s7p 1s8p ...



turning original 'Lorentz' into 'Fano'

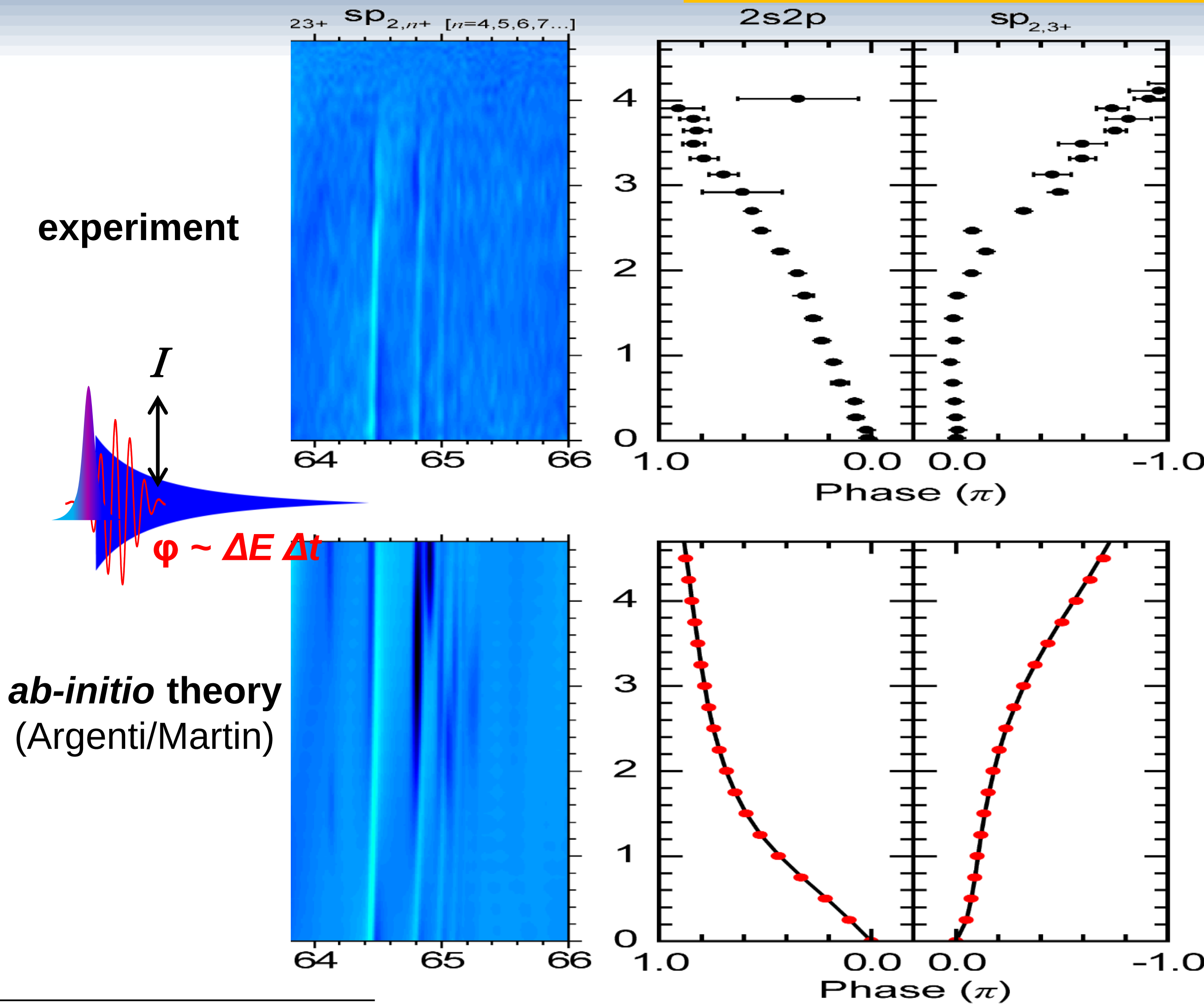
$$q = -\cot\left(\frac{\varphi}{2}\right)$$

$q = -2.55 \Rightarrow \varphi = 0.24\,\pi$

Science **340**, 716 (2013)

Extracting the laser-induced phase shift

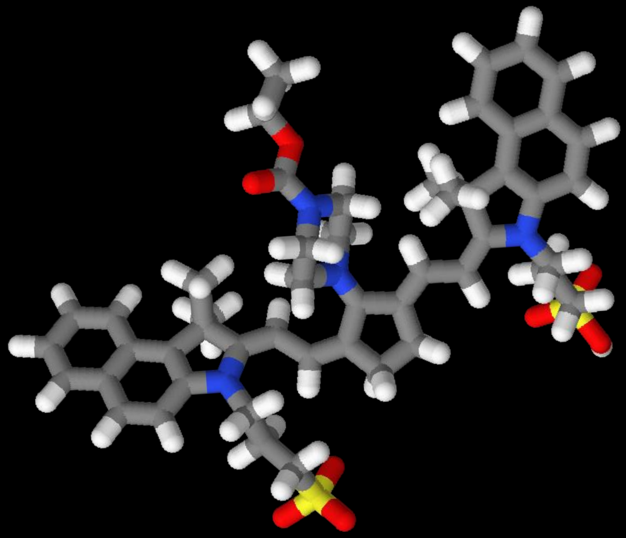
Cooperation with J. Madronero, L. Argenti, F. Martín



C. Ott *et al.* Nature 2014

Phase control of "real molecules"

Can we change the (spectral) shape of complex molecules?

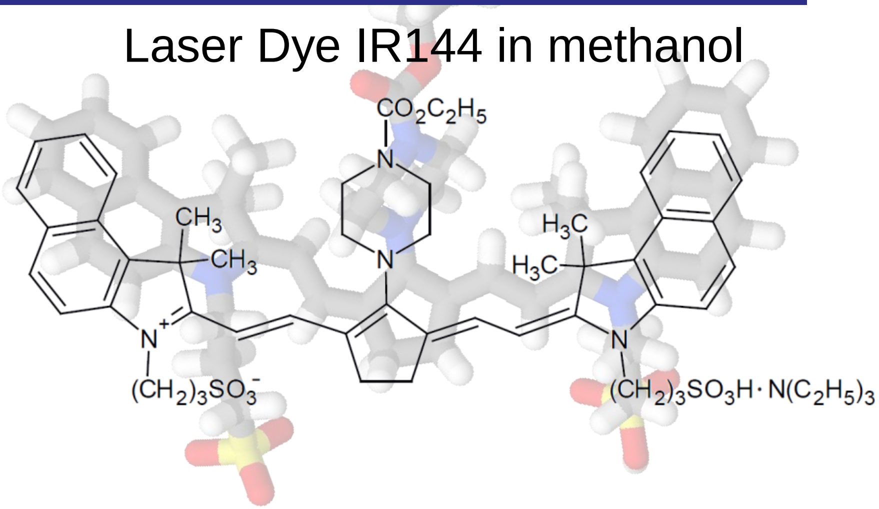


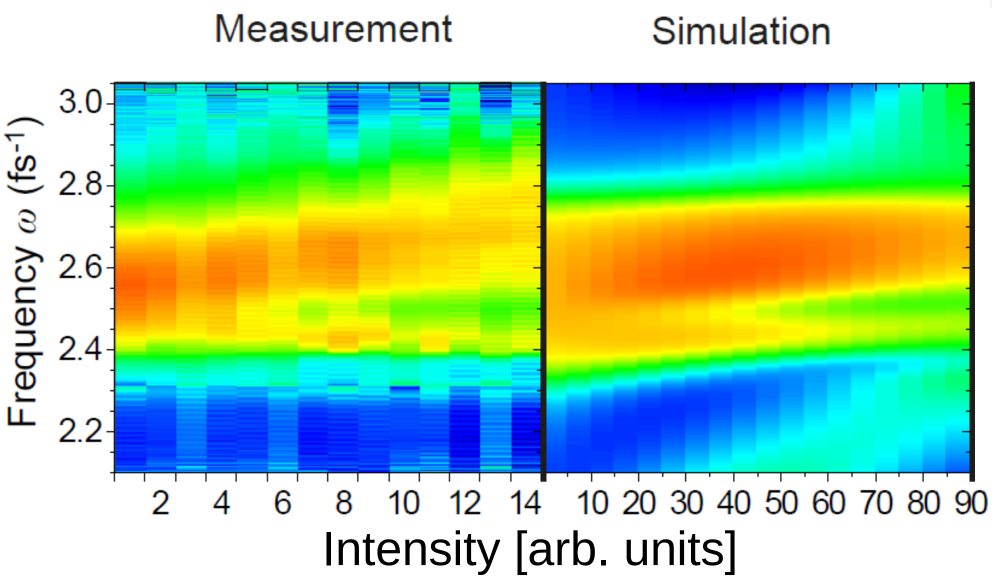
Fano control of molecules in the liquid phase

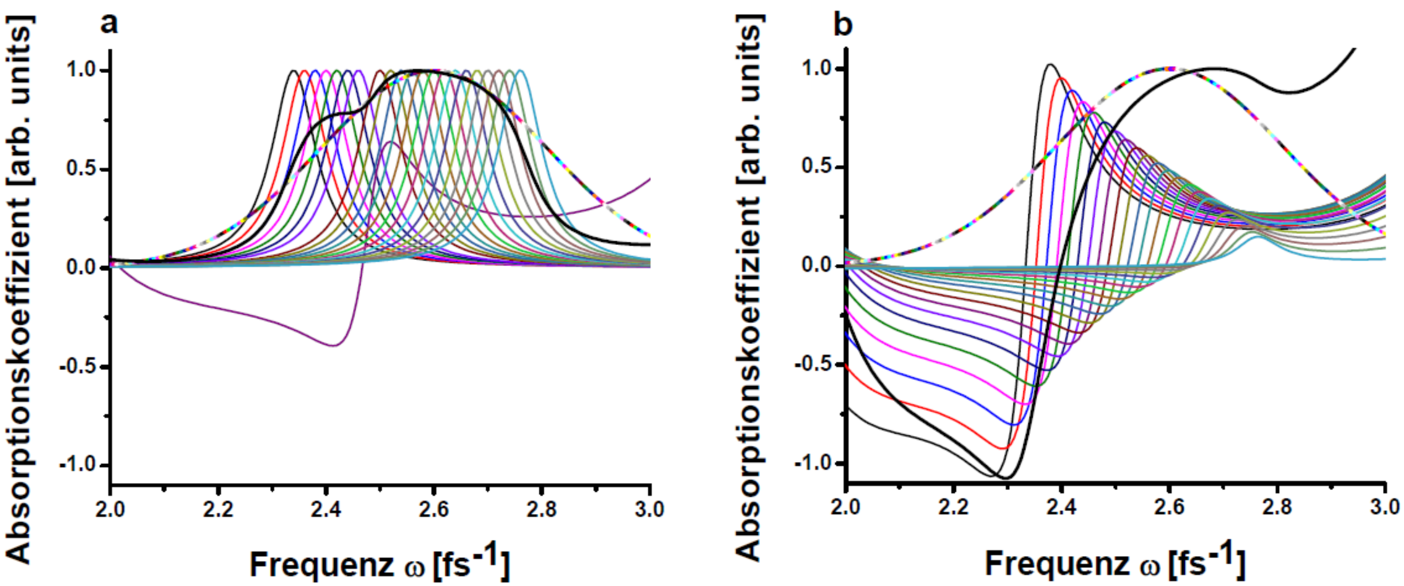
cooperation with J.-M. Mewes, A. Dreuw, T. Buckup, M. Motzkus@Univ. Heidelberg

Kristina Meyer *et al.*, PNAS (2015)

Laser Dye IR144 in methanol

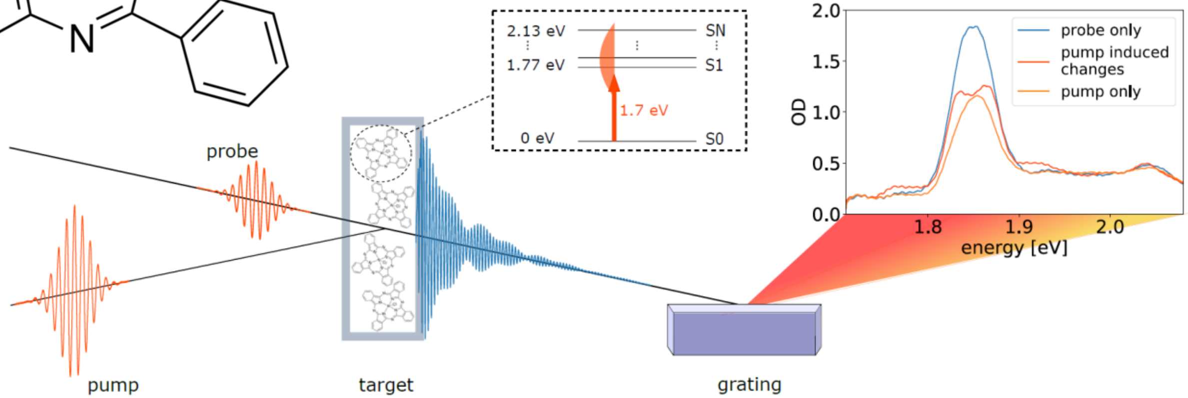


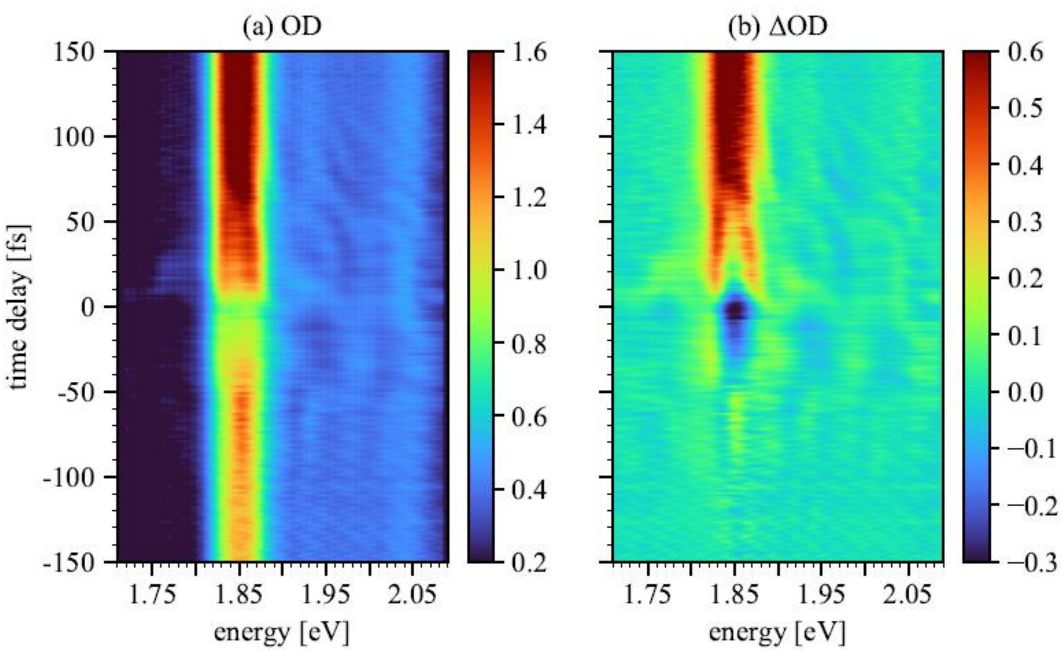


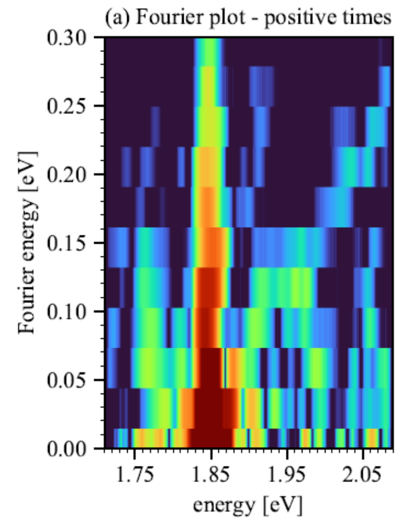


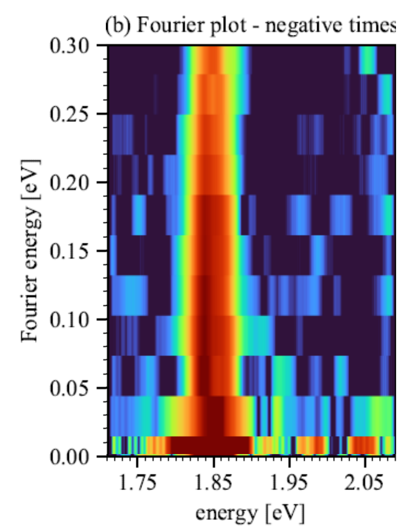
Recent measurements in Aluminum-phthalocyanine-chloride (AlPhCl)

Carina da Costa Castanheira *et al.* (in preparation)

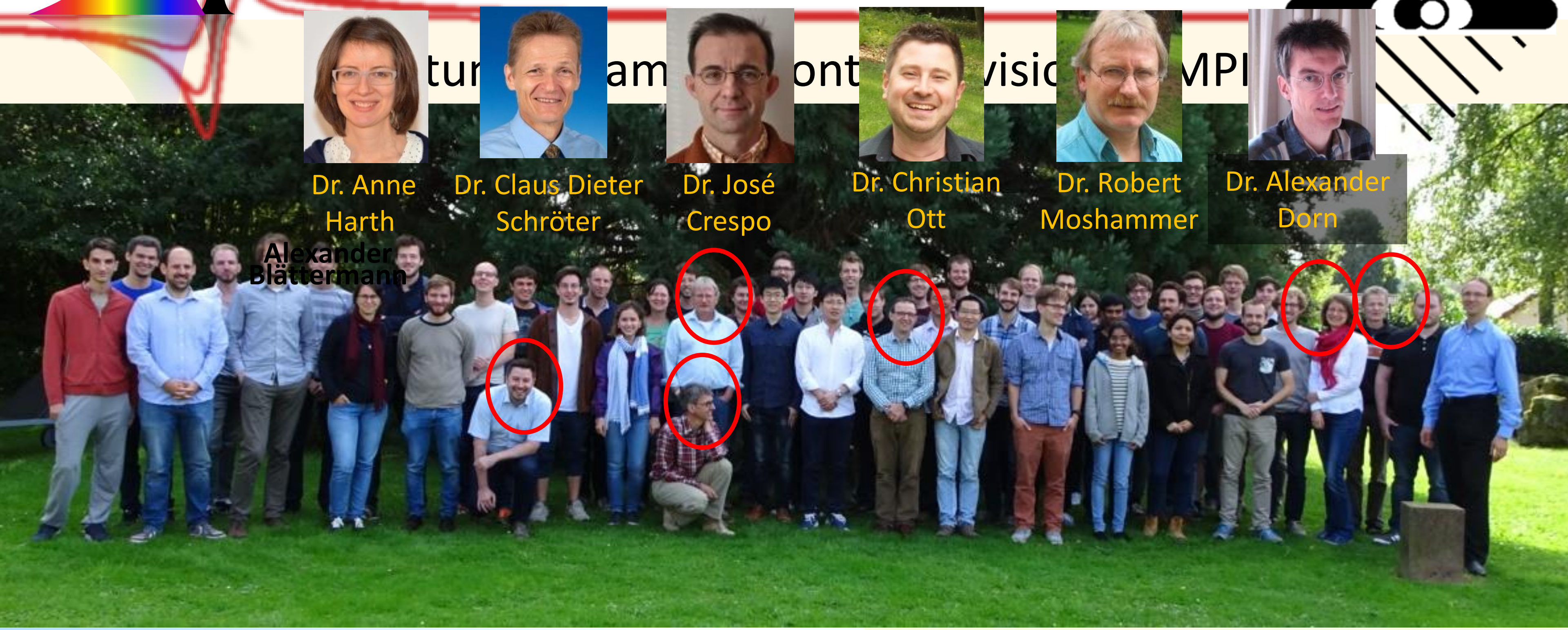








Acknowledgements



Main Cooperators: Thanks to … and many more !

C. Keitel, J. Evers, Z. Harman, S. Cavaletto and groups (MPIK): Fano physics
C. Greene (Purdue Univ., USA): Fano physics
L. Argenti, F. Martín (Univ. A. Madrid, Spain): 2e⁻ WP, 2D spec
J. Madroñero (TUM&Univ. del Valle, Cali, Colombia): 2e⁻ WP
A. Brown, H. Van der Hart (Queens University, Belfast): 2d spec Neon
J. M. Mewes, A . Dreuw, T. Buckup, M. Motzkus (U. Heidelberg): Liquid phase
S. Roling, H. Zacharias (Univ. Münster): FLASH FEL Split and Delay
S. Düsterer, R. Treusch, N. Stojanovich,
G. Brenner, M. Braune (DESY): FLASH FEL exp.
A. Attar (UC Berkeley, USA): FLASH exp.
Z.-H. Loh (NTU, Singapore): FLASH exp.
T. Gaumnitz (ETH Zurich, Switzerland): FLASH exp.

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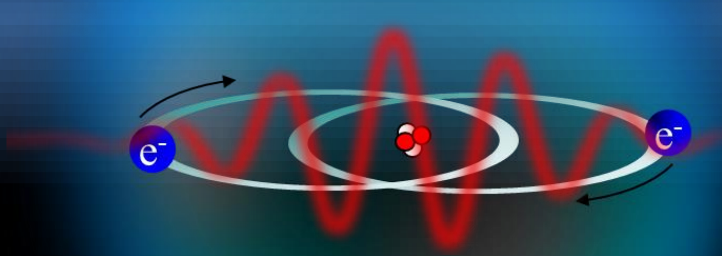
DFG
Grant #PF790

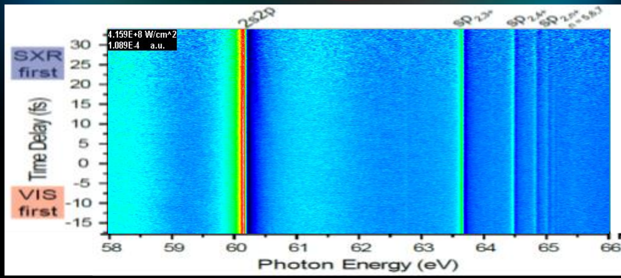
erc
X-MuSiC

Heidelberg Center for Quantum Dynamics

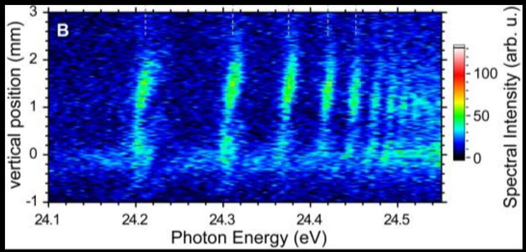
Summary

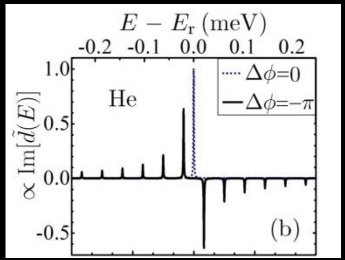


- Ultrafast Laser quantum control of
  small atomic/molecular quantum systems
  (natural, well-defined "Å-labs")
  for fundamental-physics experiments



- Phase information is key to quantum dynamics
  and can be retrieved by time-"resolved" experiments
- qualitatively new insights into fundamental processes
  (e.g. Fano ↔ Lorentz, Absorption ↔ Gain)
  => New ideas…





Understand general mechanisms of time-dependent Quantum Dynamics
Unifying Ultrafast Control and Precision Physics