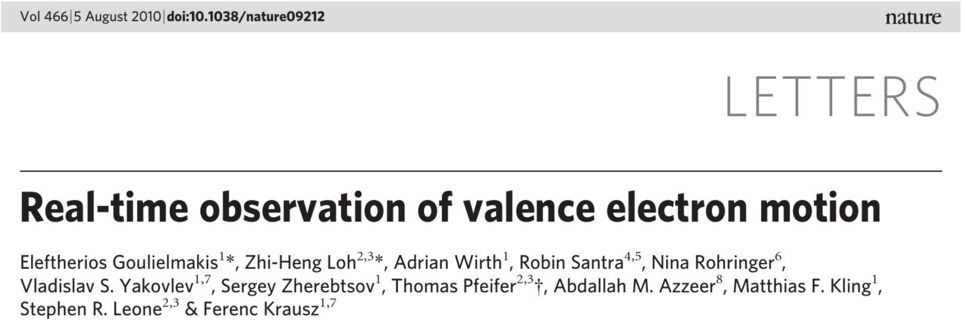
# Attosecond Transient Absorption Spectroscopy

Lauren B Drescher

# Transient Absorption Spectroscopy on Attosecond Timescales

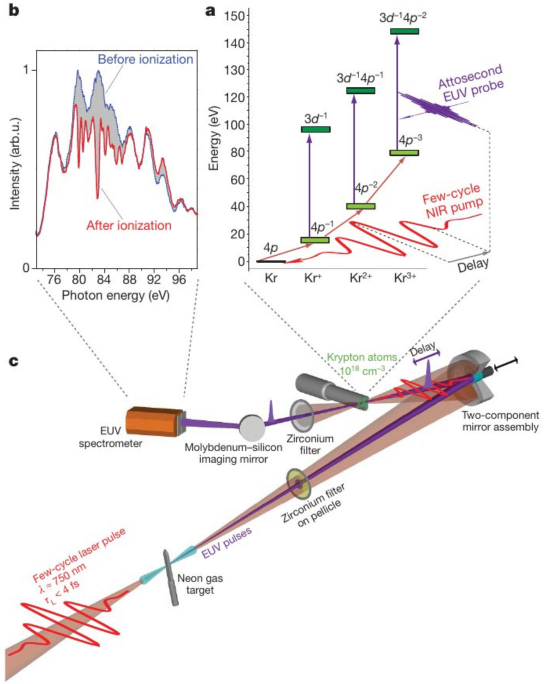

Vol 466|5 August 2010|doi:10.1038/nature09212 nature

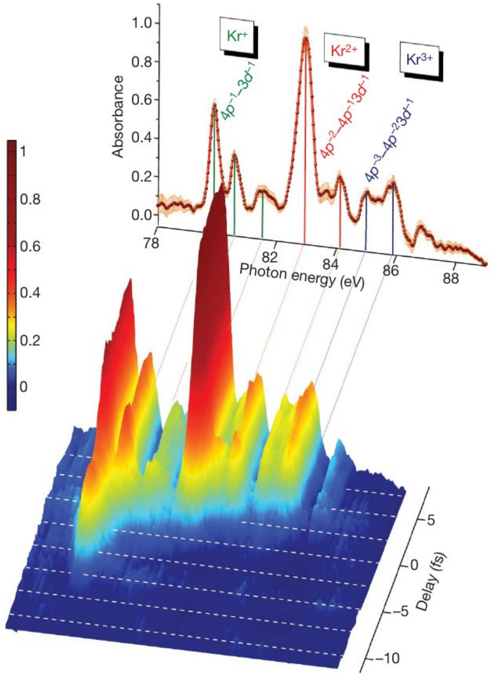
LETTERS

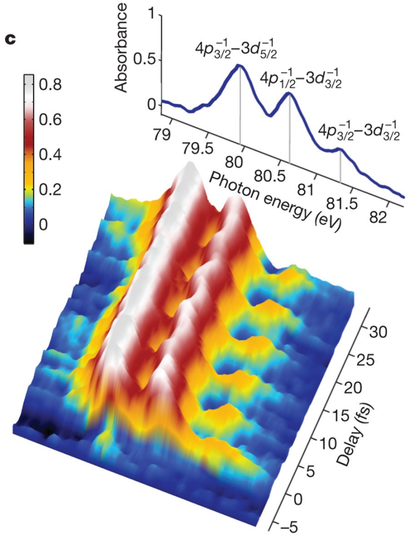
**Real-time observation of valence electron motion**

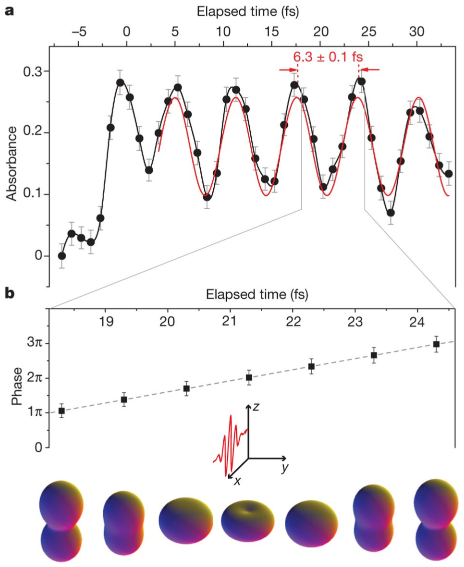
Eleftherios Goulielmakis[1]*, Zhi-Heng Loh[2,3]*, Adrian Wirth[1], Robin Santra[4,5], Nina Rohringer[6], Vladislav S. Yakovlev[1,7], Sergey Zherebtsov[1], Thomas Pfeifer[2,3]†, Abdallah M. Azzeer[8], Matthias F. Kling[1], Stephen R. Leone[2,3] & Ferenc Krausz[1,7]

- Broad XUV Pulses from High Harmonic Generation used for Transient Absorption
- Attosecond Temporal Resolution, High Spectral Resolution
- Core-Level Spectral Region: Element Specific View into Valence Dynamic

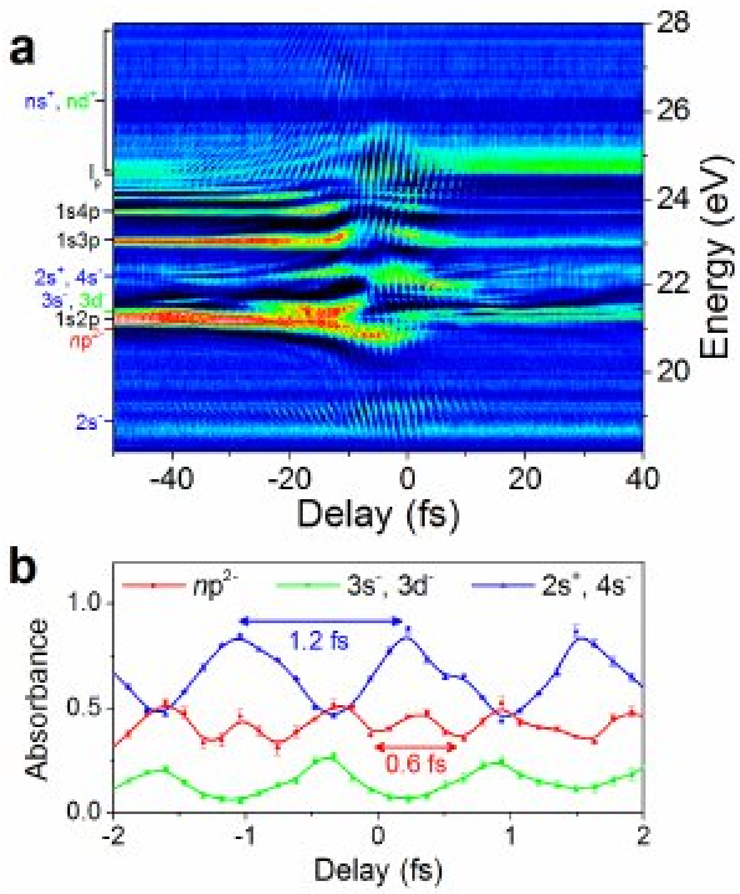


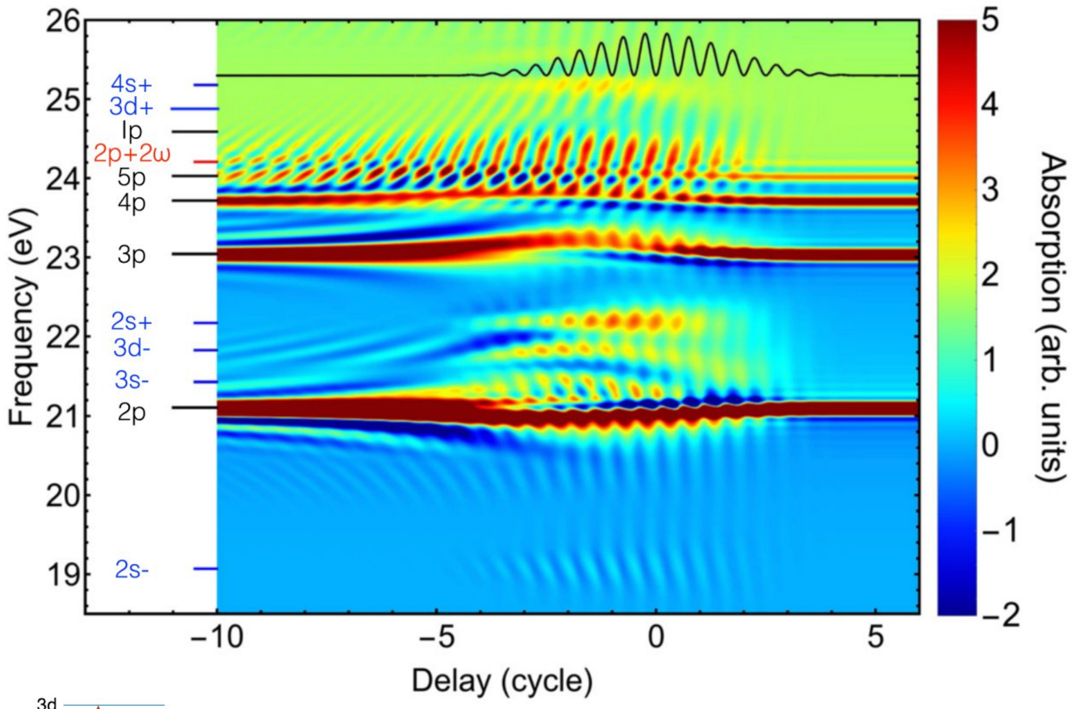



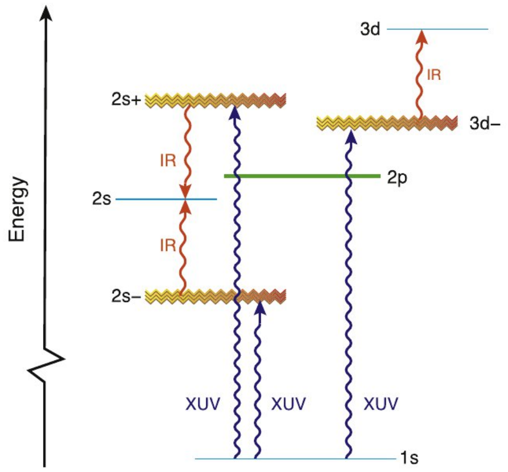



# Transient Absorption of Electron Coherences




SCIENTIFIC REPORTS | 3 : 1105 | DOI: 10.1038/srep01105



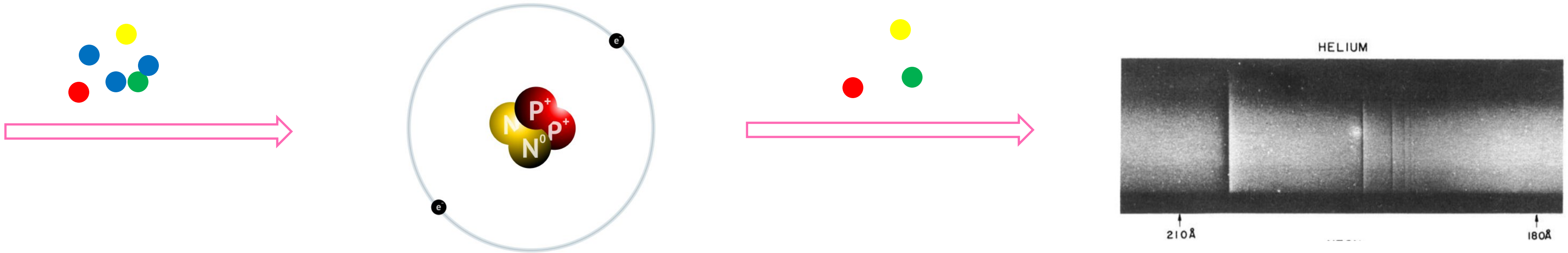




Wu et al., JPB 49 (2016) 062003

# First We Have To Ask: What is Absorption?

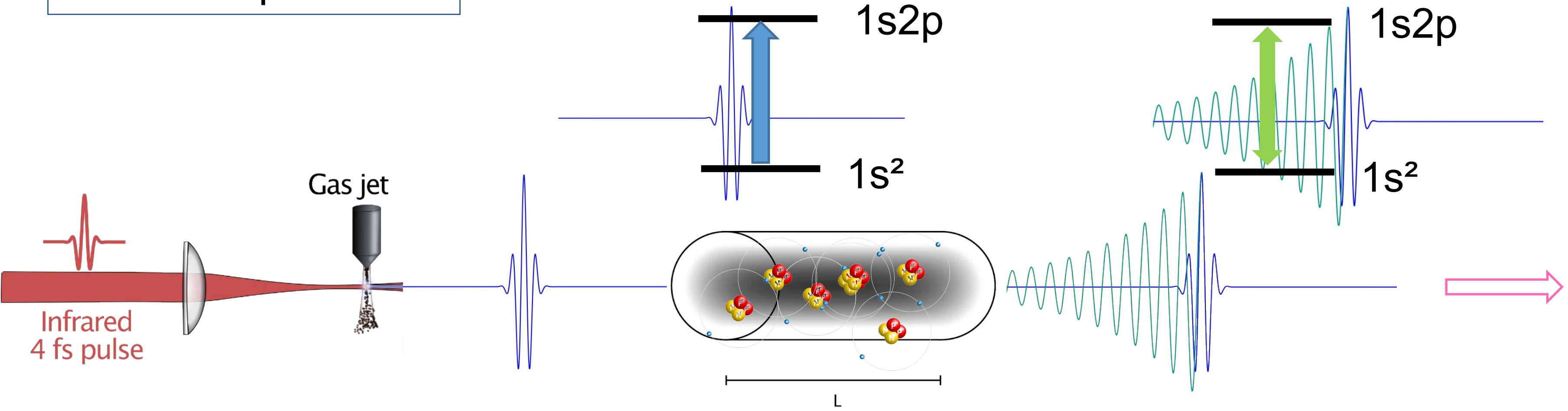
Particle-like picture:

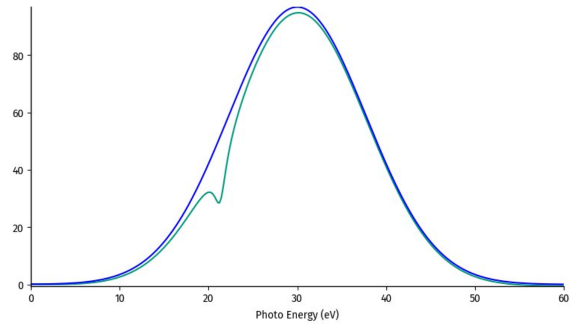
[1]




R. P. Madden and K. Codling, New autoionizing atomic energy levels in He, Ne, and Ar, Phys. Rev. Lett. 10, 516-518 (1963).

Wave-like picture:



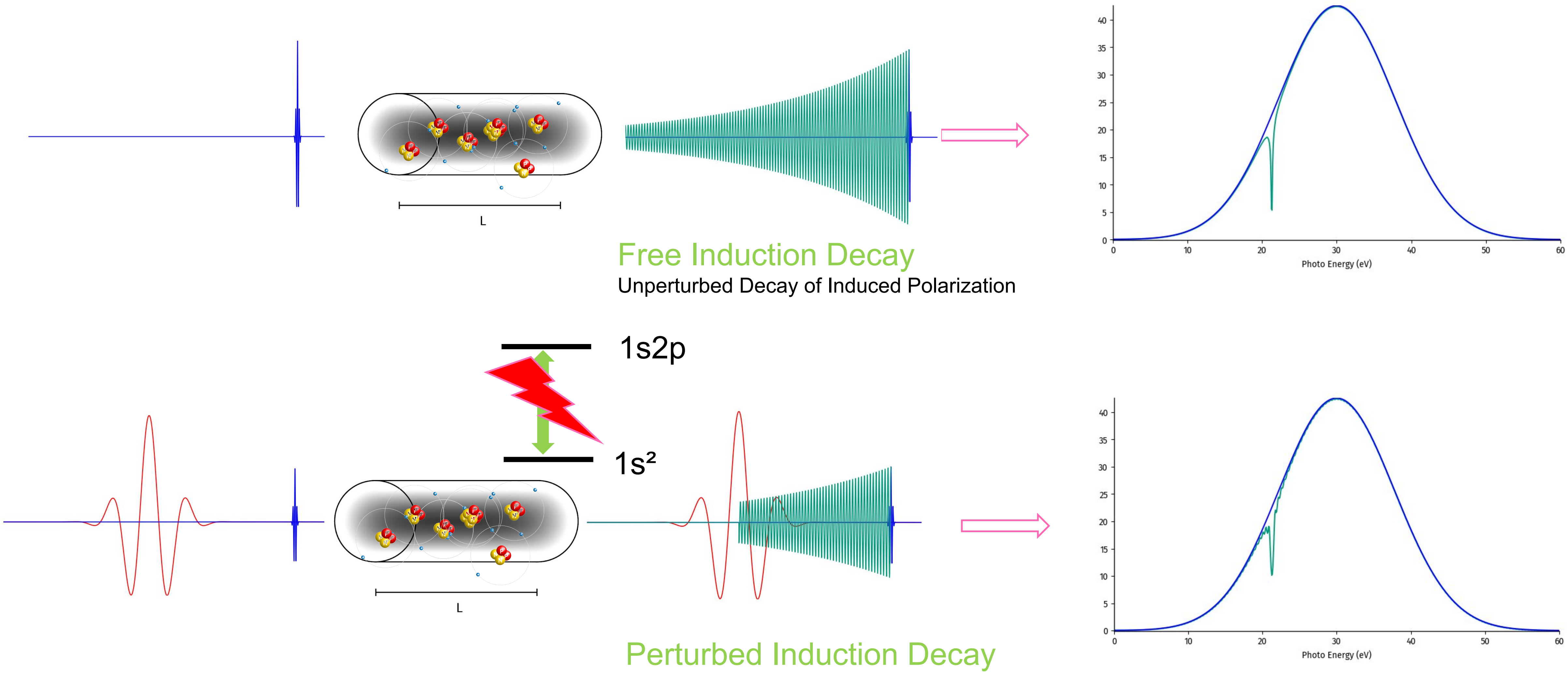




Free Induction Decay

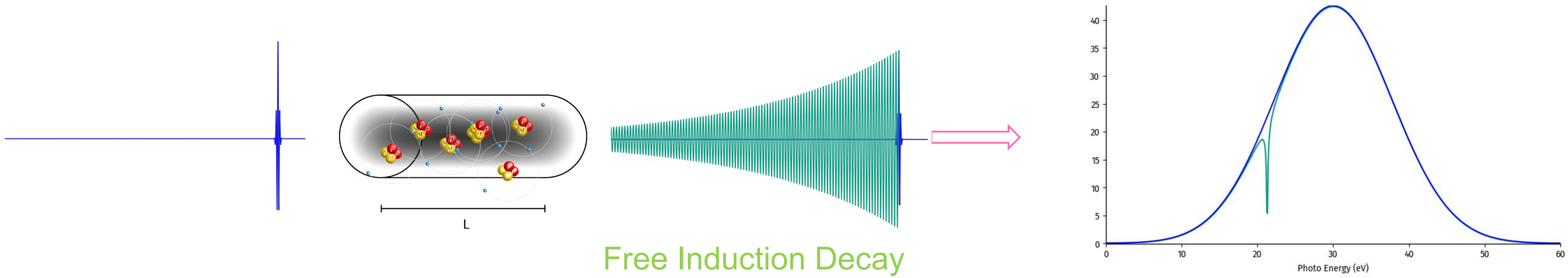
Unperturbed Decay of Induced Polarization

[1]KMJ (https://commons.wikimedia.org/wiki/File:Gluehlampe_01_KMJ.jpg), „Gluehlampe 01 KMJ“, https://creativecommons.org/licenses/by-sa/3.0/legalcode

# What is Attosecond Transient Absorption



# What is Attosecond Transient Absorption




Free Induction Decay

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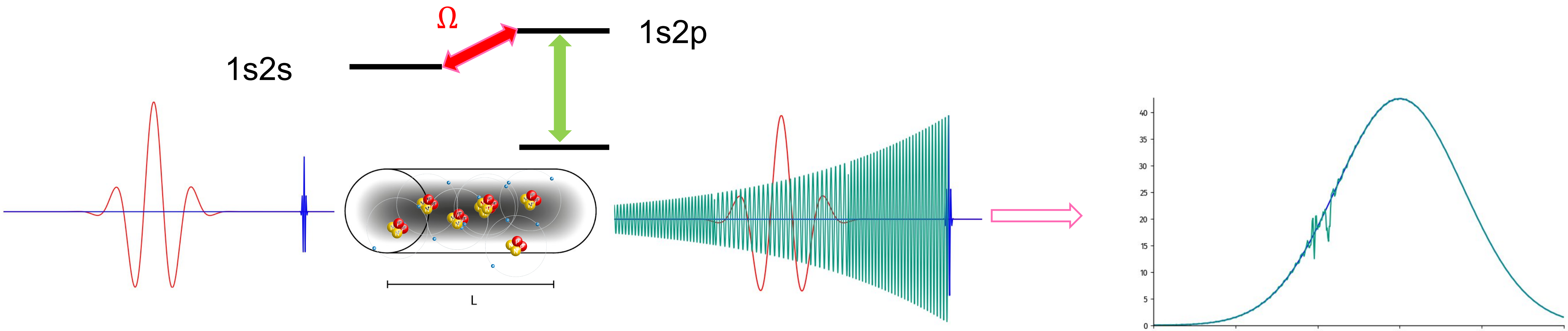
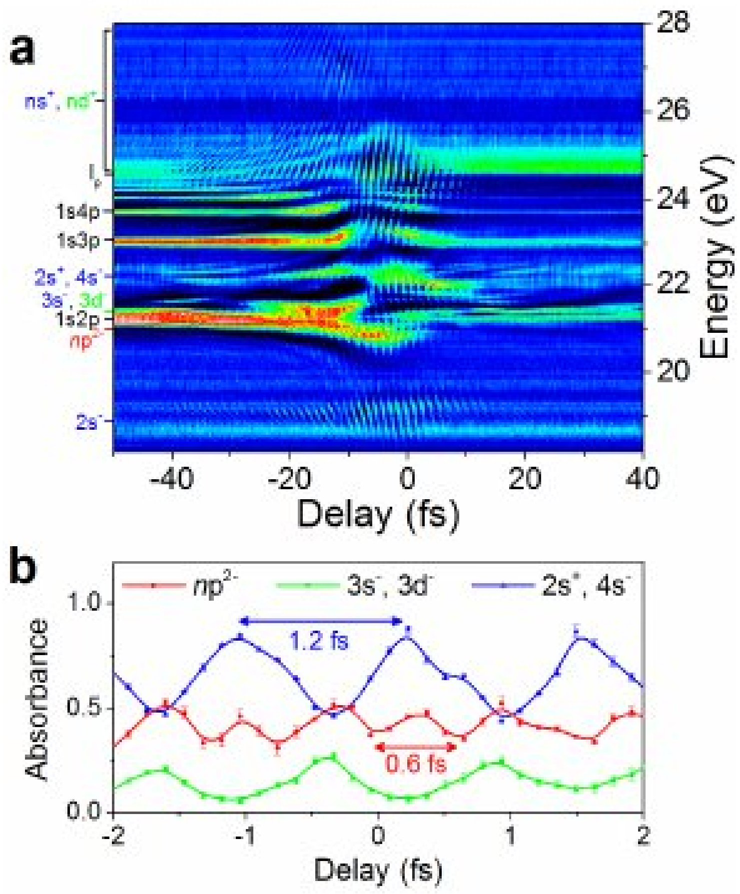



Light Induced Features

# Transient Absorption of Electron Coherences

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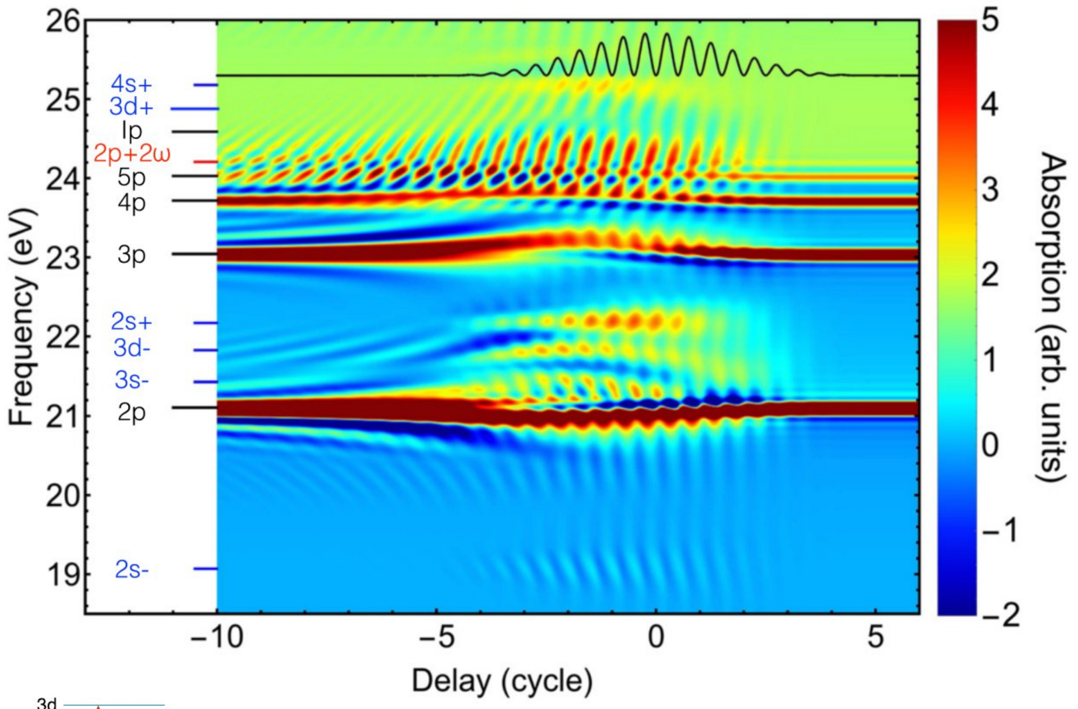
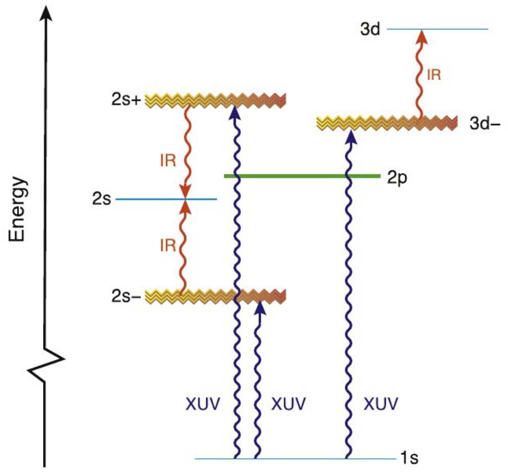


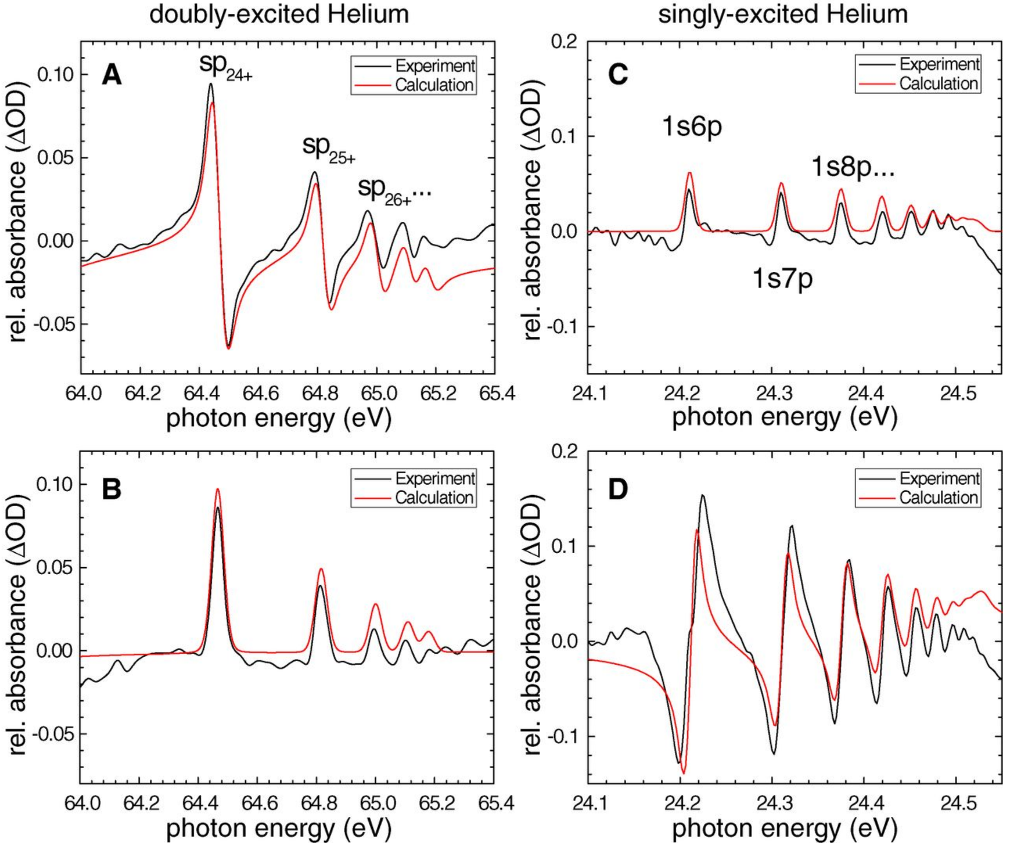

Wu et al., JPB 49 (2016) 062003

# Line Shape Control and Helium Doubly Excited

REPORTS

## Lorentz Meets Fano in Spectral Line Shapes: A Universal Phase and Its Laser Control

Christian Ott,[1] Andreas Kaldun,[1] Philipp Raith,[1] Kristina Meyer,[1] Martin Laux,[1] Jörg Evers,[1] Christoph H. Keitel,[1] Chris H. Greene,[3] Thomas Pfeifer[1,2]*

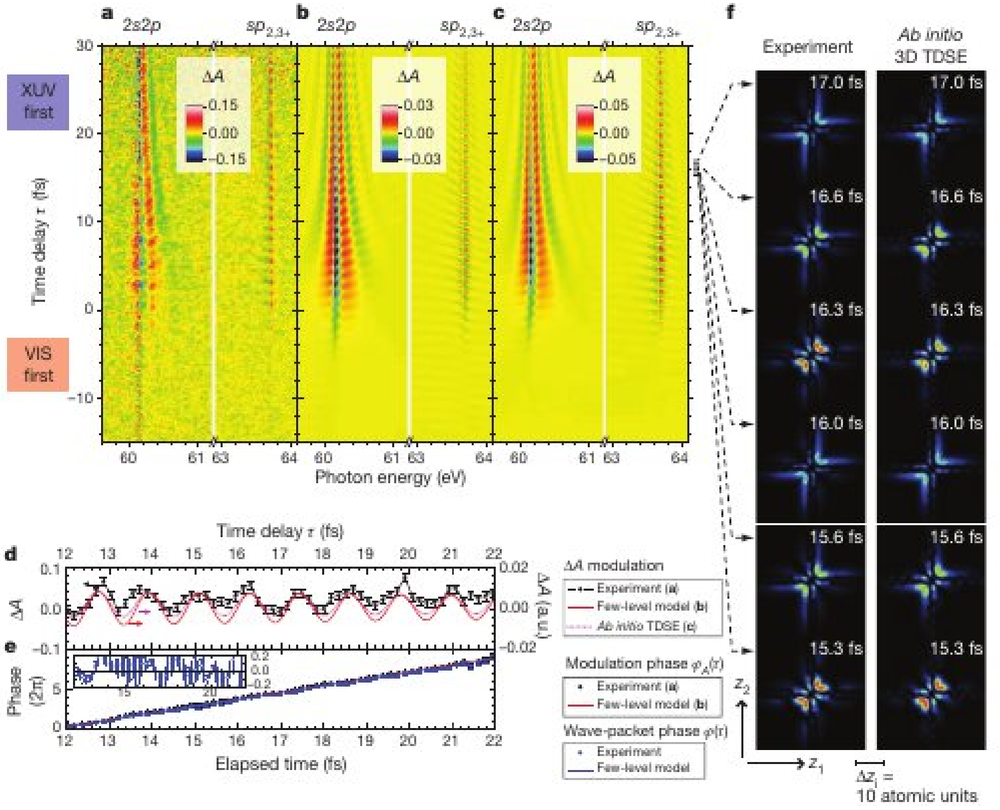



LETTER

doi:10.1038/nature14026

## Reconstruction and control of a time-dependent two-electron wave packet

Christian Ott[1]†, Andreas Kaldun[1], Luca Argenti[2], Philipp Raith[1], Kristina Meyer[1], Martin Laux[1], Yizhu Zhang[1], Alexander Blättermann[1], Steffen Hagstotz[1], Thomas Ding[1], Robert Heck[1], Javier Madroñero[3]†, Fernando Martín[2,4] & Thomas Pfeifer[1,5]



# The Two Coins of Attosecond Transient Absorption

(NIR) Pump Initiates Dynamic

temporal evolution

(XUV) Probe Takes Snapshot

XUV Transient Absorption Spectroscopy on Attosecond Timescales

NIR+XUV Pump-Probe Spectroscopy: What is pump and what is probe?

= Probe?

Attosecond XUV Pulse Induces Polarization

temporal evolution

= Pump?

NIR Pulse Induces Perturbation

Coherent Attosecond Transient Absorption Spectroscopy

# Theoretical Basics

Time-Dependent Schrödinger Equation

$$i\frac{\partial}{\partial t}|\psi(t)> \; = \hat{H}|\psi(t)>$$

Wavefunction of n-levels: $|\psi(t)> \; = \sum_n C_n(t)e^{-i\omega_n t}|n>$

Hamiltonian

$$\hat{H}(t) \; = \widehat{H_0} + (E_{XUV}(t) + E_{NIR}(t))\hat{X}$$

Expectation value of dipole operator

$$\left\langle \Psi(t) \middle| \hat{d} \middle| \Psi(t) \right\rangle = \sum \left\langle 0 \middle| \hat{X} \middle| n \right\rangle \; = d_{0n} c_0^*(t) c_n(t) e^{-i\omega_n t} + c.c.$$

transition dipole moment

Evolution of state amplitudes

decay/dephasing (empirical)

$$i\frac{\partial}{\partial t}C_n(t) \; = \sum_n E_{XUV}(t)d_{0n}e^{-i\omega_n t} + E_{NIR}(t)d_{nm}e^{-i\omega_{nm} t}C_m + i\Gamma_n C_n + c.c.$$

Can be solved by numerical integration or analytically with some approximation

Wu et al., JPB 49 (2016) 062003

# Theoretical Basics: Light Induced Phase

In Atoms:

- Perturbation during Free Induction Decay (FID) modifies absorption

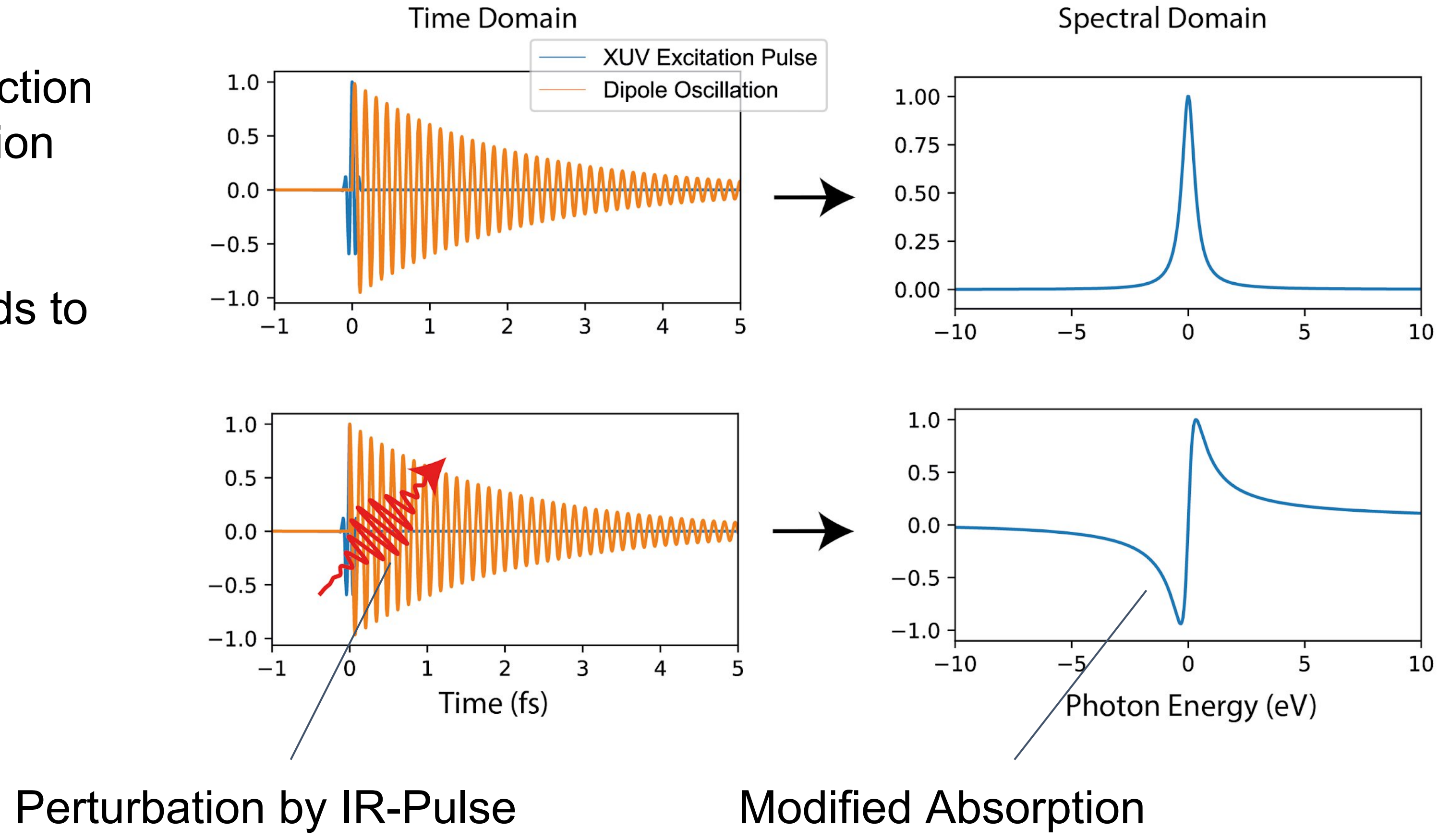
Light Induced Phase:

- Energy shift during decay leads to phase in FID

$$\varphi \propto \int_0^\infty \Delta E(t)dt$$

- e.g. due to AC Stark shift:

$$\Delta E(t) \propto [d_{nm}\varepsilon_{\mathrm{IR}}(t,\tau)]^2$$



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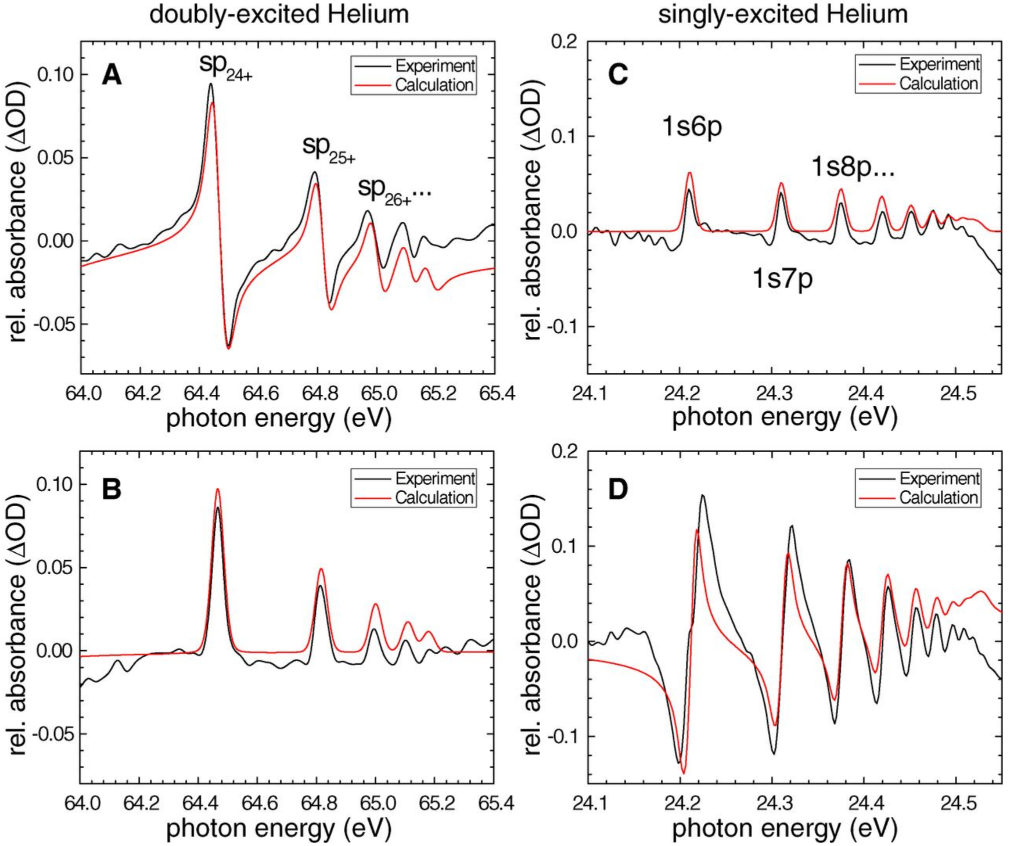


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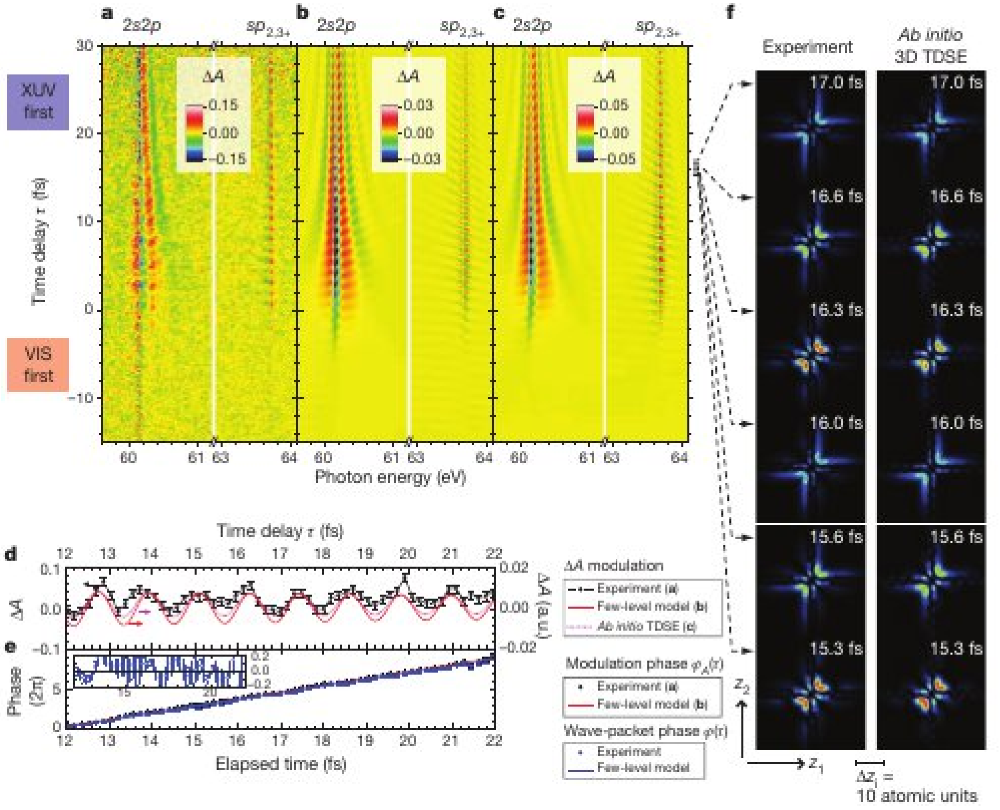
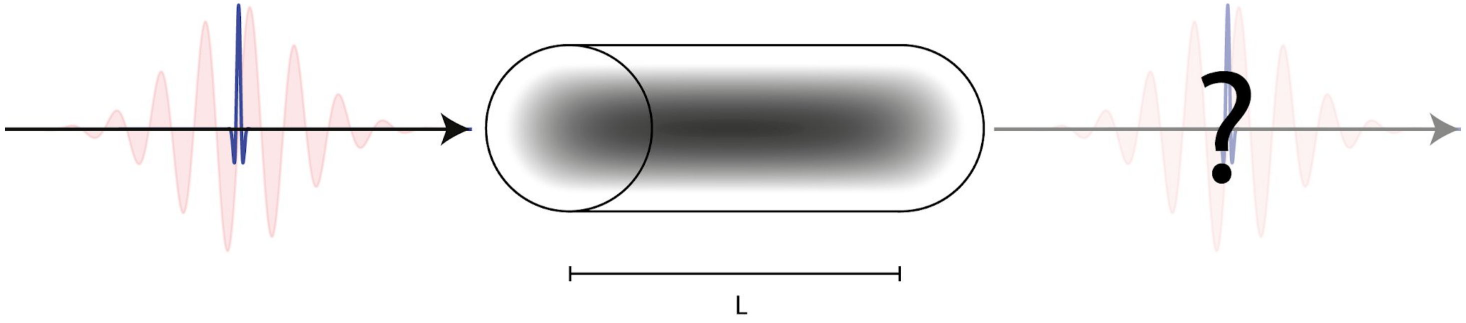


# Connection To Experiment




From Time-Dependent Schrödinger Eq.: $\langle \Psi(t) | \hat{d} | \Psi(t) \rangle$

From Maxwell Wave Eq.: $\frac{\partial}{\partial z}\varepsilon(\omega) = \frac{i\omega\rho}{2\epsilon_0 c} d(\omega)$

$$\varepsilon(\omega, L) = \varepsilon(\omega, 0)\; e^{-A(\omega)L}\; e^{i\Delta n(\omega) L \frac{\omega}{c}}$$

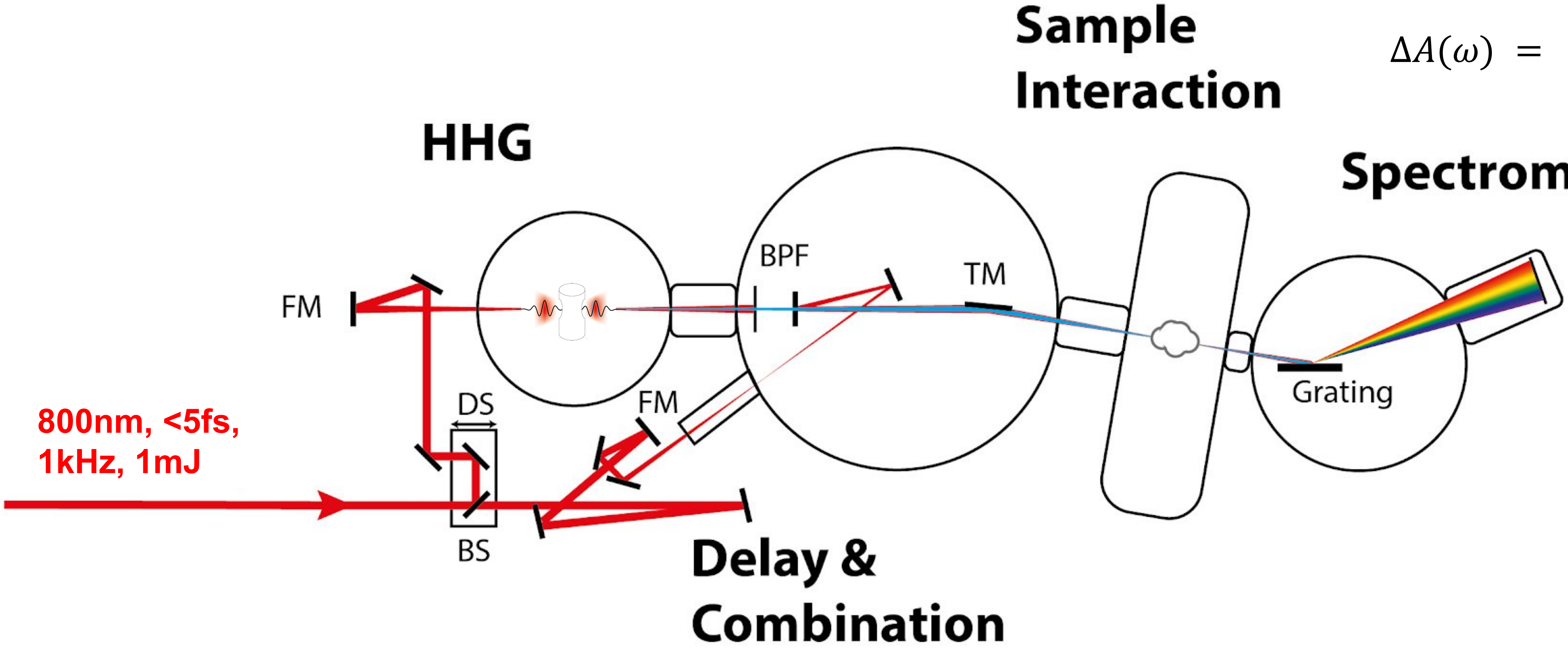
$$A(\omega) \propto \mathrm{Im}[d(\omega)/\varepsilon_{XUV}(\omega)]$$

$$\Delta n(\omega) \propto \mathrm{Re}[d(\omega)/\varepsilon_{XUV}(\omega)]$$

# Experimental Setup

$$A(\omega) = -\log \frac{I_{after}(\omega)}{I_{before}(\omega)}$$

$$\Delta A(\omega) = -\log \frac{I_{w/\ NIR}(\omega)}{I_{w/o\ NIR}(\omega)}$$




Legend:
FM - Focusing Mirror
BS - Beam Splitter
TM - Toroidal Mirror
BPF - Bandpass Filter (200nm Al)
DS - Delay Stage

# Experimental Basics: Detectors

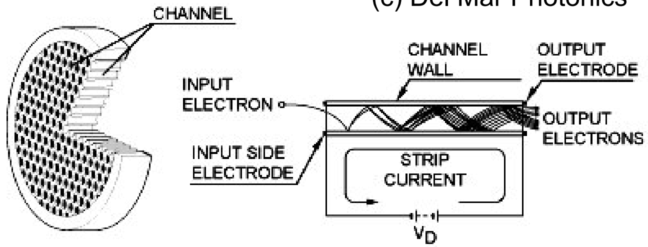
XUV is absorbed in air, the spectra therefore need to be detected under high vacuum conditions

## Direct Detection: In-vacuum cameras


- Old: CCD, New: sCMOS
- High sensitivity, high resolution, small area
- Sensitive to NIR, need second metal filter, cooling
- Very expensive, inflexible electronics, CCDs are slow

## Indirect Detection: MCP + Phosphor + external camera

(c) Del Mar Photonics

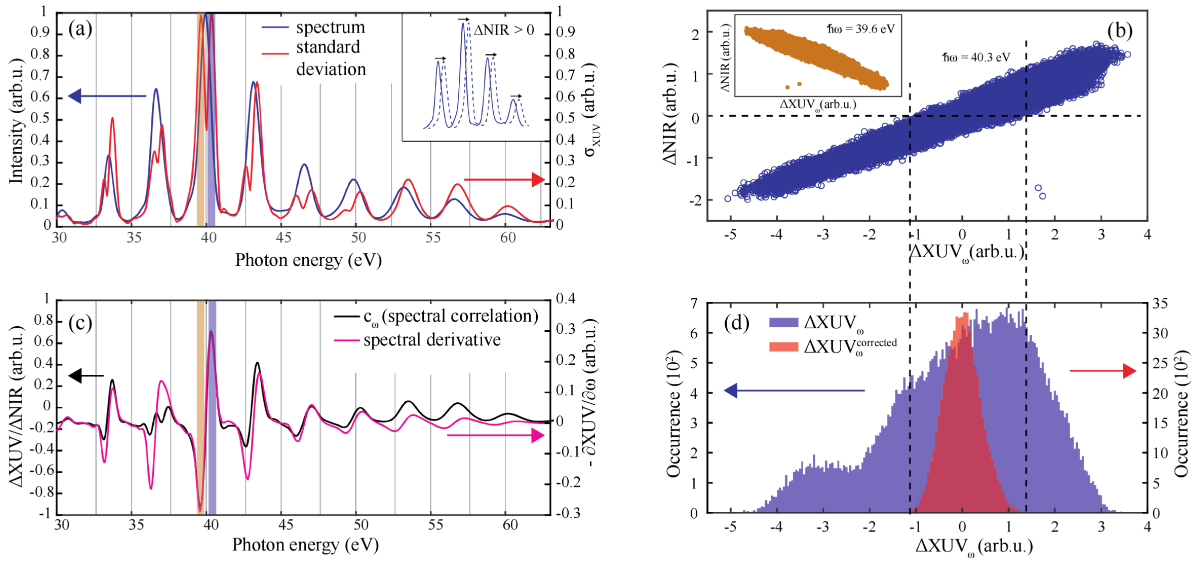



- Larger area, external camera are fast and more flexible
- Needs high voltage supply
- Not sensitive to NIR, less XUV sensitivity and/or resolution
- Less expensive but consumable

# Experimental Basics: Drifts and Noise

The signal to noise conditions are generally pretty poor, experiments generally need to be averaged

- Besides artifacts from drifts in NIR intensity and spatial overlap, we are especially sensitive to changes in the **XUV spectra** and **temporal overlap**




XUV spectra fluctuations are on the order of ~100ms, take spectra faster to track them

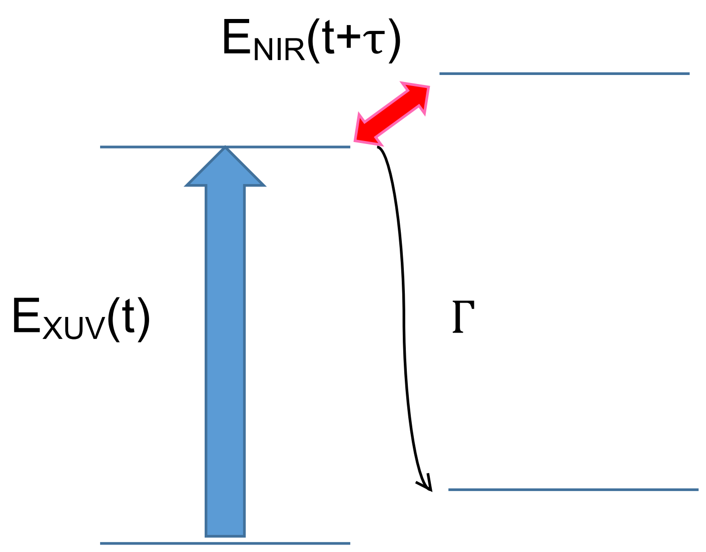
- Slow temporal drifts: Take several scans of delay and correct drift afterwards
- Fast temporal drifts: Active stabilization of the interferometer

M. Volkov, et al. Opt. Express **27**, 7886-7895 (2019)

# Extracting Dynamics: Kinetics

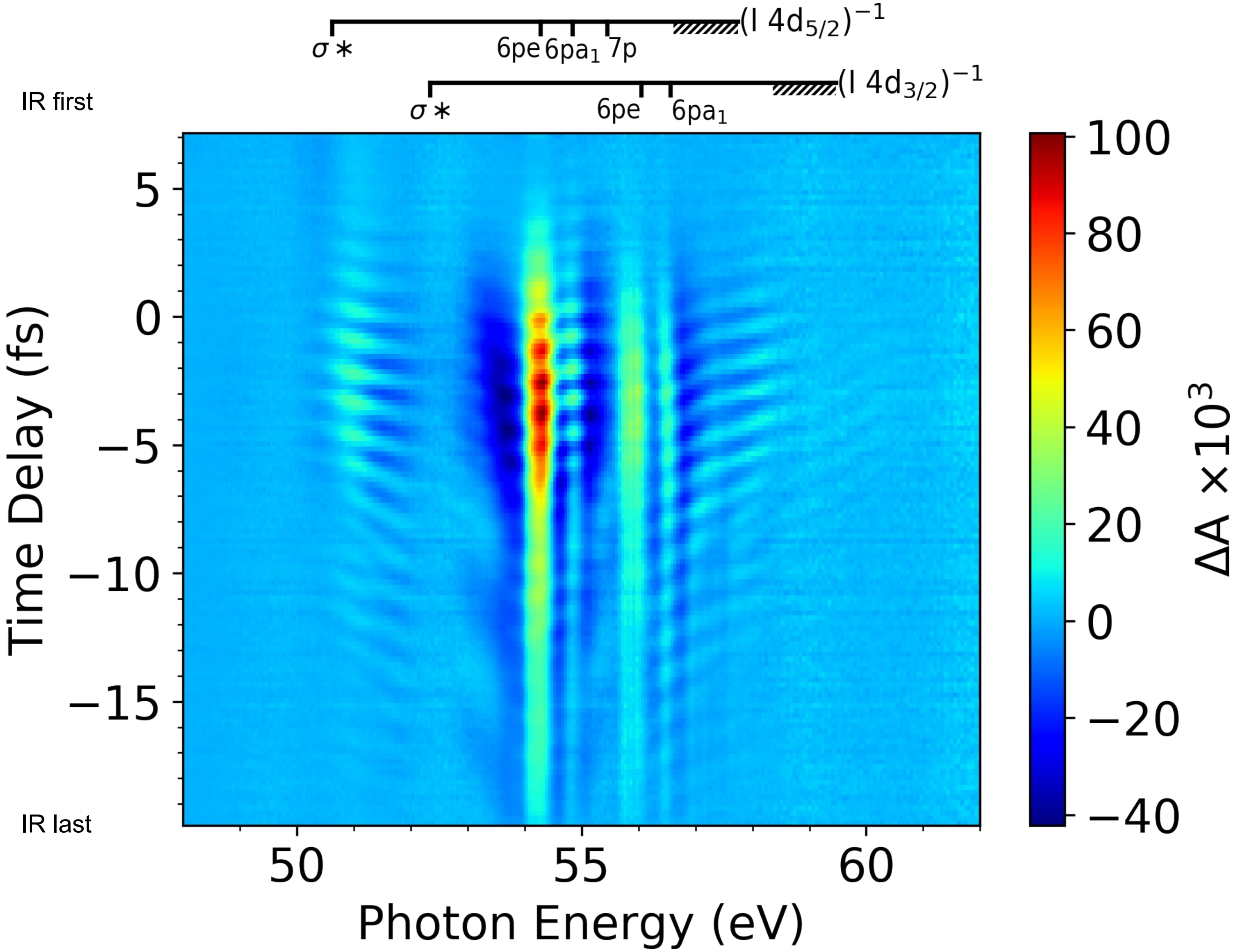
How can we extract dynamics from temporal features?

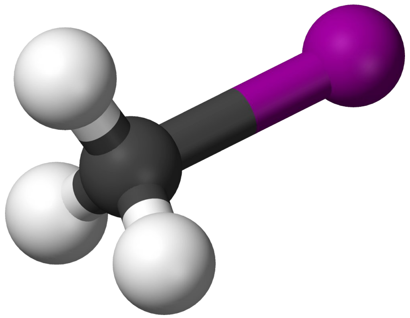
- Consider the dynamics, their dependence on the laser pulses and what you observe

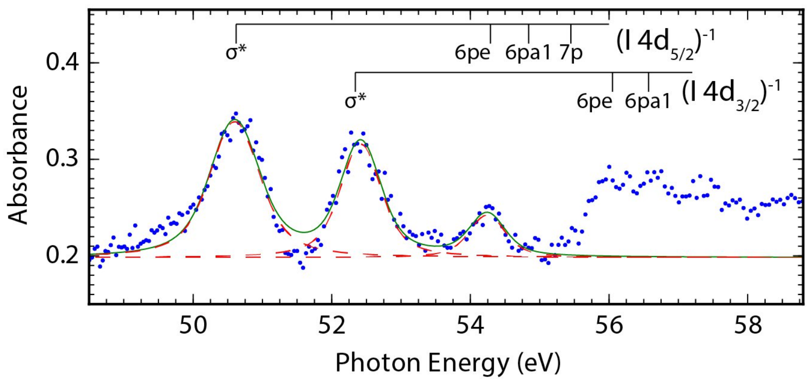



- Field driven processes follow square of field (sub-cycle if you have the resolution)
- Field-free processes typically exponential rate
- Observation if the convolution of all processes that get you to the observed channel.
- i.e. often Gaussian (laser pulse) convoluted with exponential decay (lifetime decay) -> Exp. Modified Gaussian

# Attosecond Transient Absorption Spectroscopy of $CH_3I$ Core-Excited States



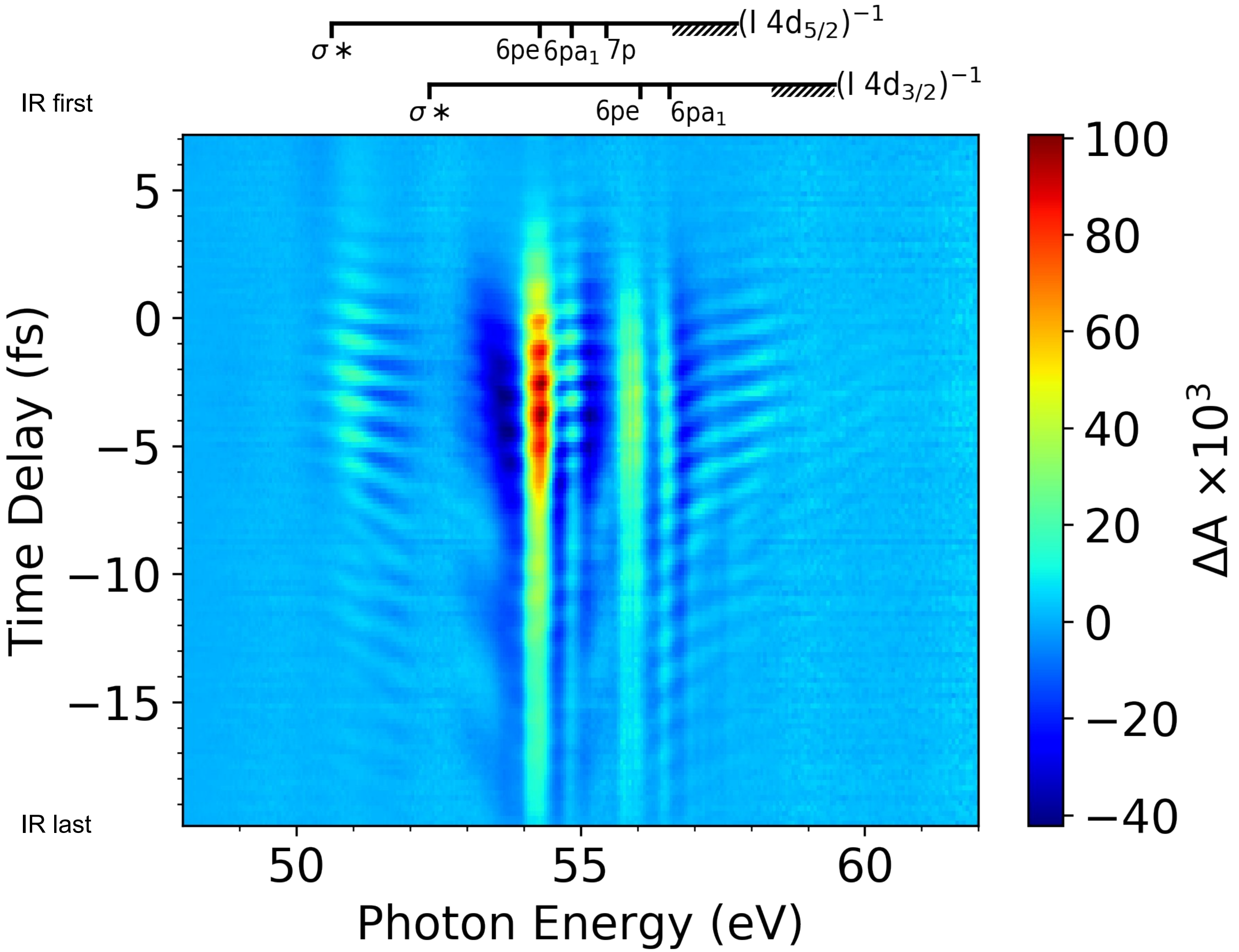


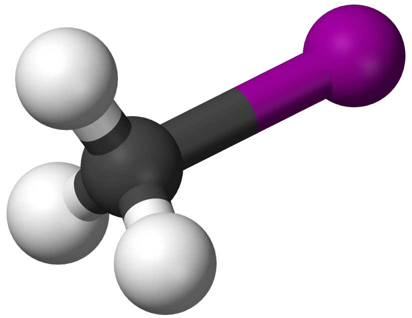

*Static XUV Absorption of $CH_3I$*

- Strong change for *n*p-excited states
- Weak for σ*-excited states - although stronger populated by XUV pulse

LD et al., JPhysChemLett 10 (2), 265-269 (2018)

# Attosecond Transient Absorption Spectroscopy of $CH_3I$ Core-Excited States



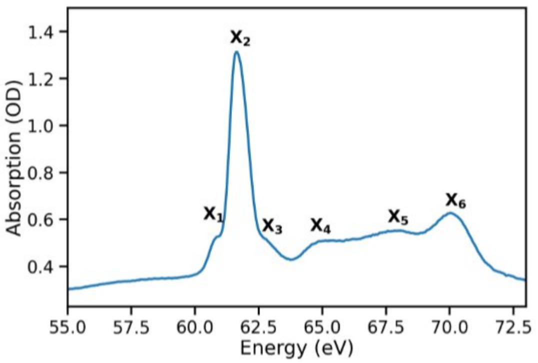



- Change of lineshape due to light-induced coupling (AC Stark) to nearby states
- Reveals strong coupling of Rydberg states

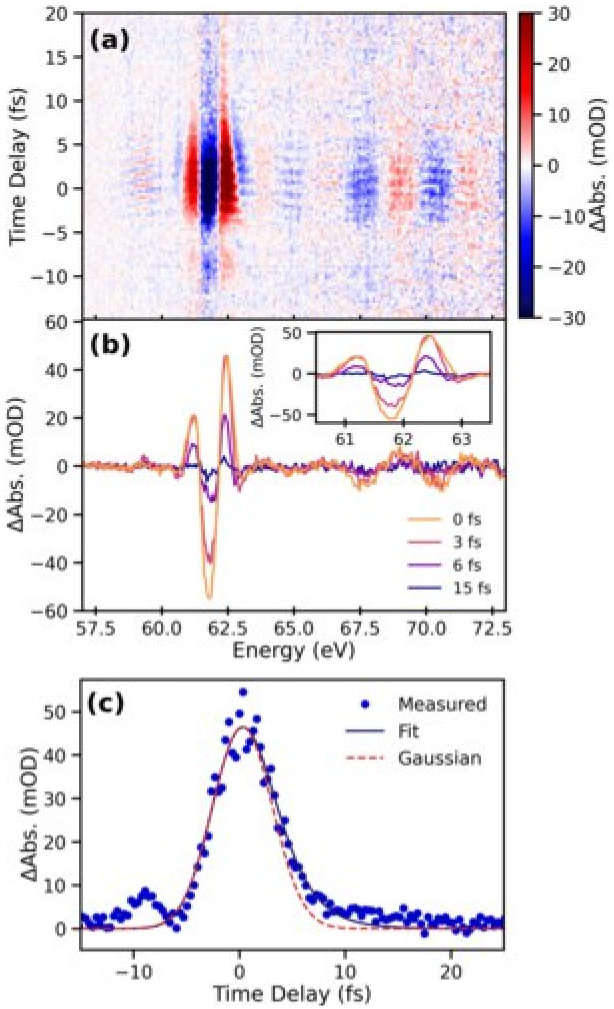
$$\Delta E(t) \propto [d_{nm}\varepsilon_{\mathrm{IR}}(t,\tau)]^2$$

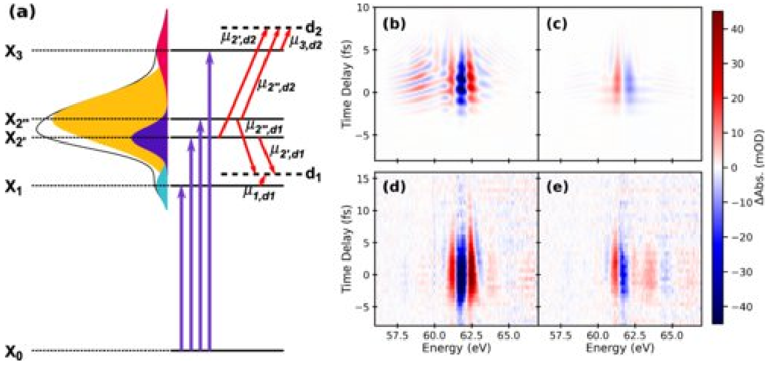
LD et al., JPhysChemLett 10 (2), 265-269 (2018)

# Core-Exciton Lifetimes: LiF




- Core-excitons in solid couple to dark states similar to atoms
- Lifetime limited due to core-hole decay and dephasing due to phonon coupling
- In LiF: Coupling to dark exciton, lifetime of bright exciton <2.4 fs





PHYSICAL REVIEW B **111**, 134306 (2025)

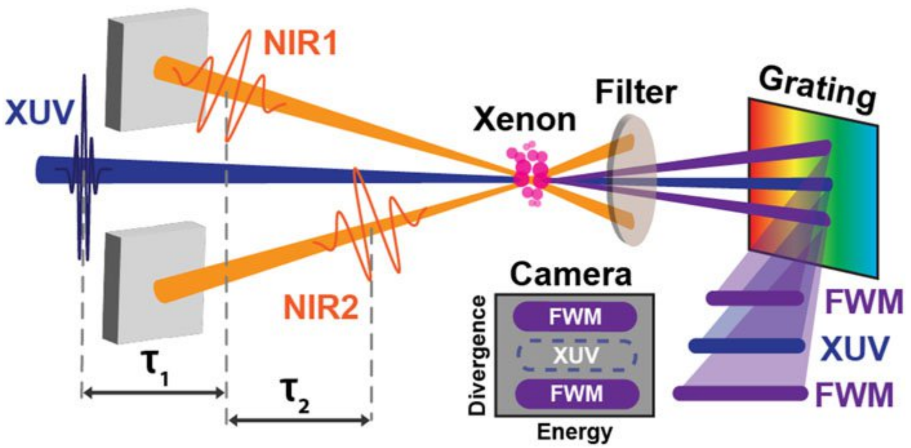
Editors' Suggestion


**Polarization-resolved core exciton dynamics in LiF using attosecond transient absorption spectroscopy**

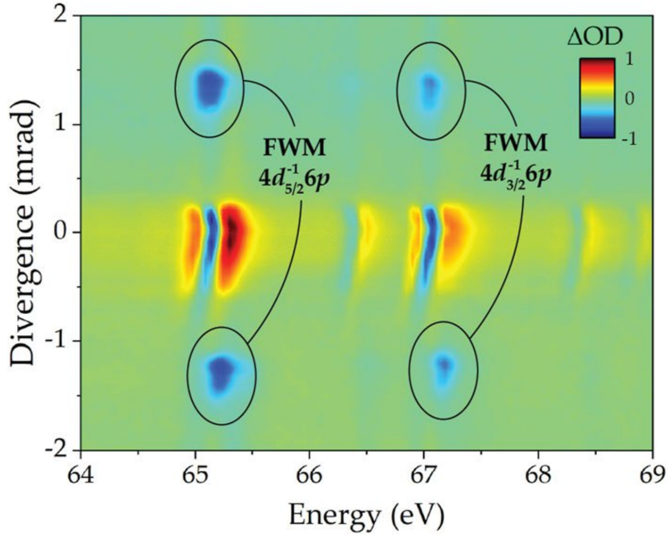

Kylie J. Gannan,[1,*] Lauren B. Drescher,[1,†] Rafael Quintero-Bermudez,[1] Navdeep Rana,[2] Chengye Huang,[1] Kenneth Schafer,[2] Mette B. Gaarde,[2] and Stephen R. Leone[1,3,4,‡]

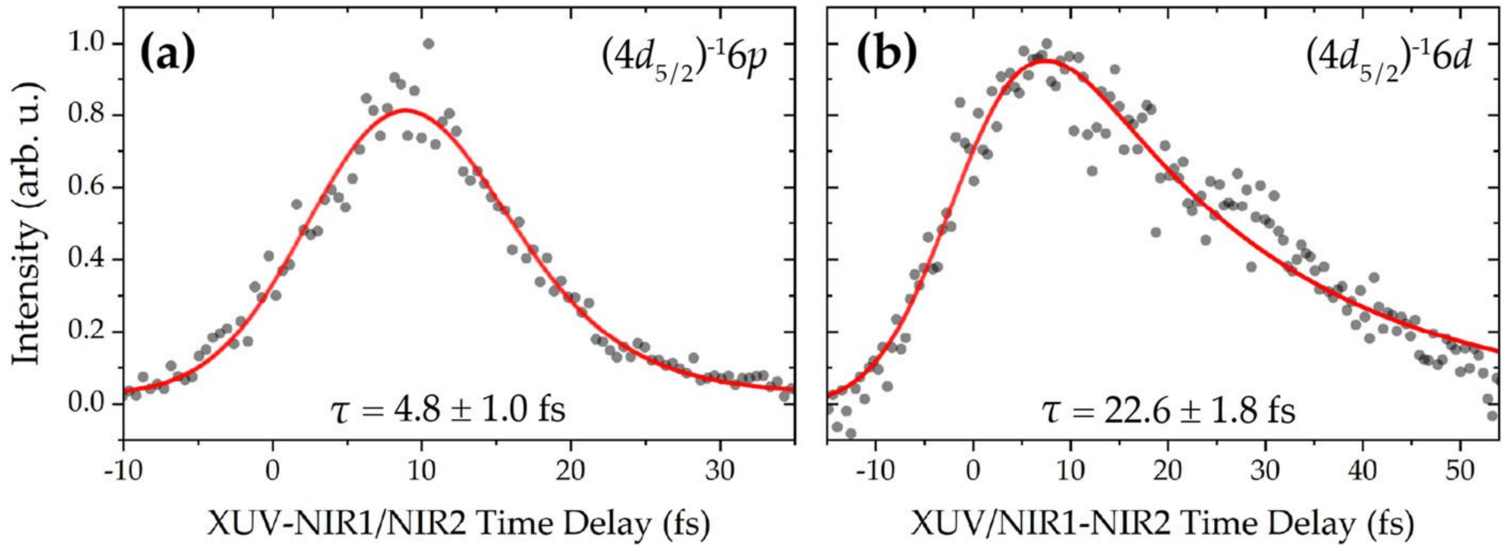
# New Approaches: Non-Collinear Four Wave Mixing

- Allows background-free detection of light-induced features
- Photon Order encoded in divergence
- NIR-NIR delay allows to differentiate dark and bright states
- Light-Induced phase is lost (No interference)
- Temporal Resolution slightly smeared out due to crossing angle

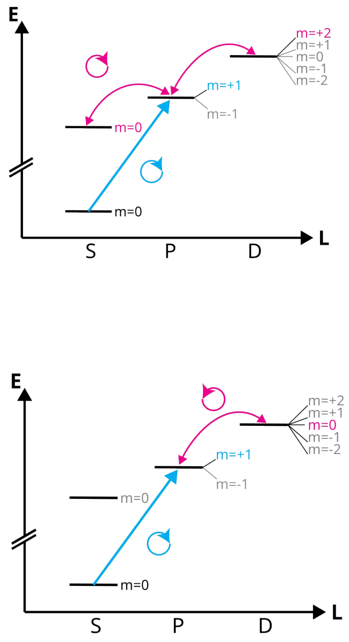


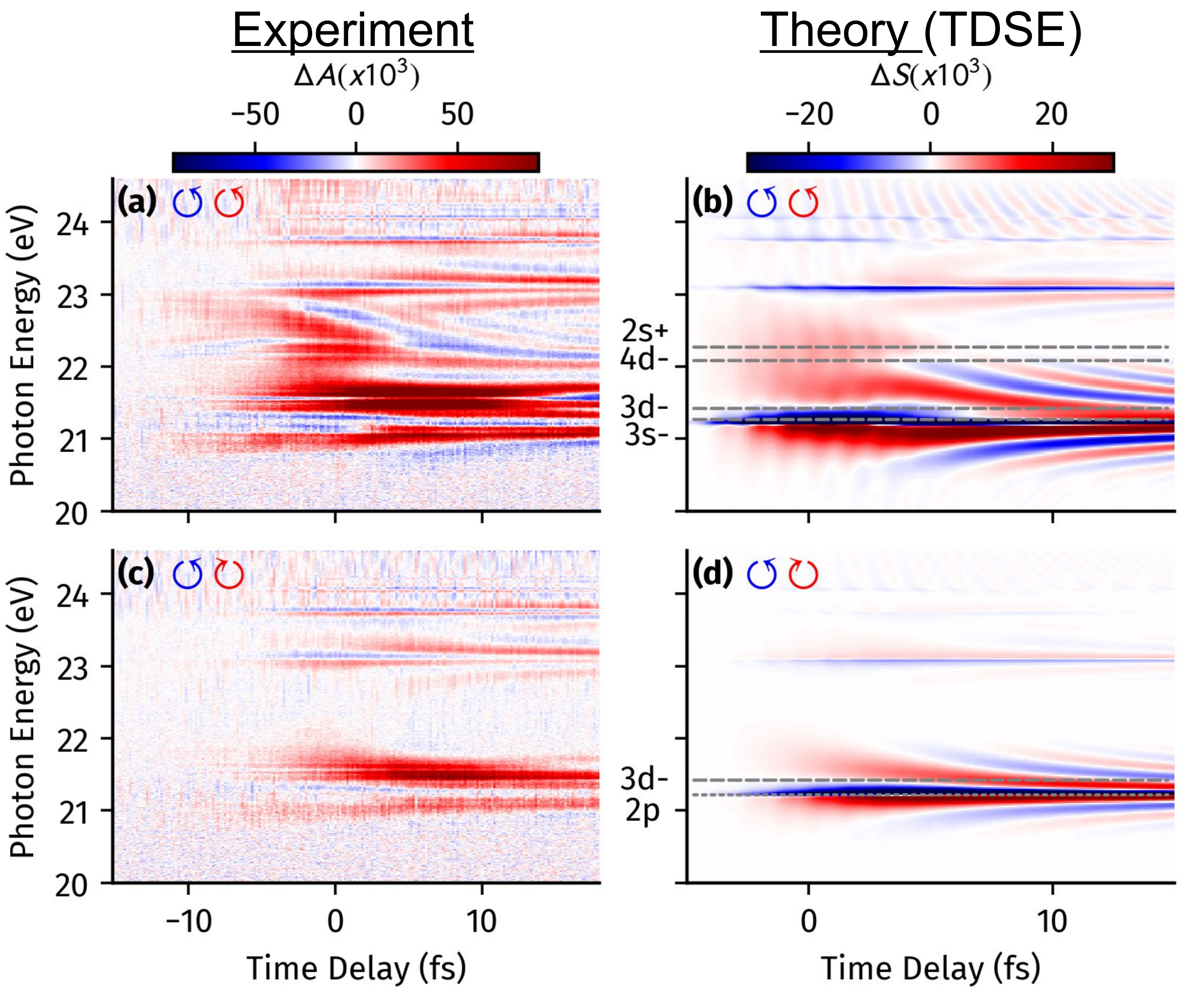

e.g. Puskar *et al.*, J. Chem. Phys. 163, 184302 (2025)

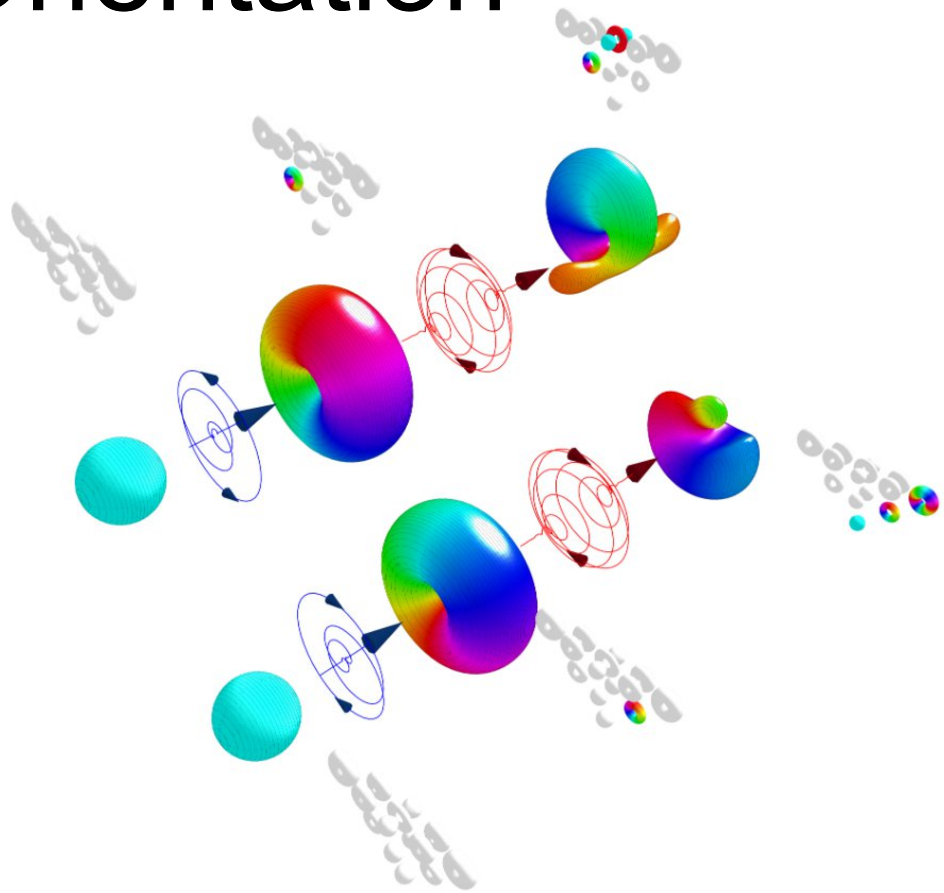


# New Approaches: Optical Orientation



- Using Circularly Polarized XUV and NIR pulses shows Circular Dichroism, reveals m-dependent pathways
- Insight into Spin-Orbit Coupling and Spin-Polarization

LBD *et al.* PRL 135 (16), 163201 (2025)

# What ~~they don't~~ I didn't tell you about ATAS

- Skipped out on all the great work using NIR pump, XUV probe TAS
  - Quantum Beats, Photodissociation Dynamics, Conical Intersections
  - Coherent Phonon Dynamics, Ultrafast Carrier Thermalization, Bandgap Dynamics, Carrier Injection, Charge Density Waves, Spin-Momentum Transfer in Solid State Materials
- Soft X-Ray Transient Absorption (Carbon K-edge)
- Transient Reflection Spectroscopy
- Advanced Theoretical Methods (TDSE, RT-TDDFT, ...)
- Advanced Data Evaluation, Edge-Noise Suppression, Principle-Component Analysis, ...
- Lots and lots of little details