Time-resolved photoionization: CS_2 and 1,3-cyclohexadiene

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Glasgow

Photoionization: introduction

Aim:

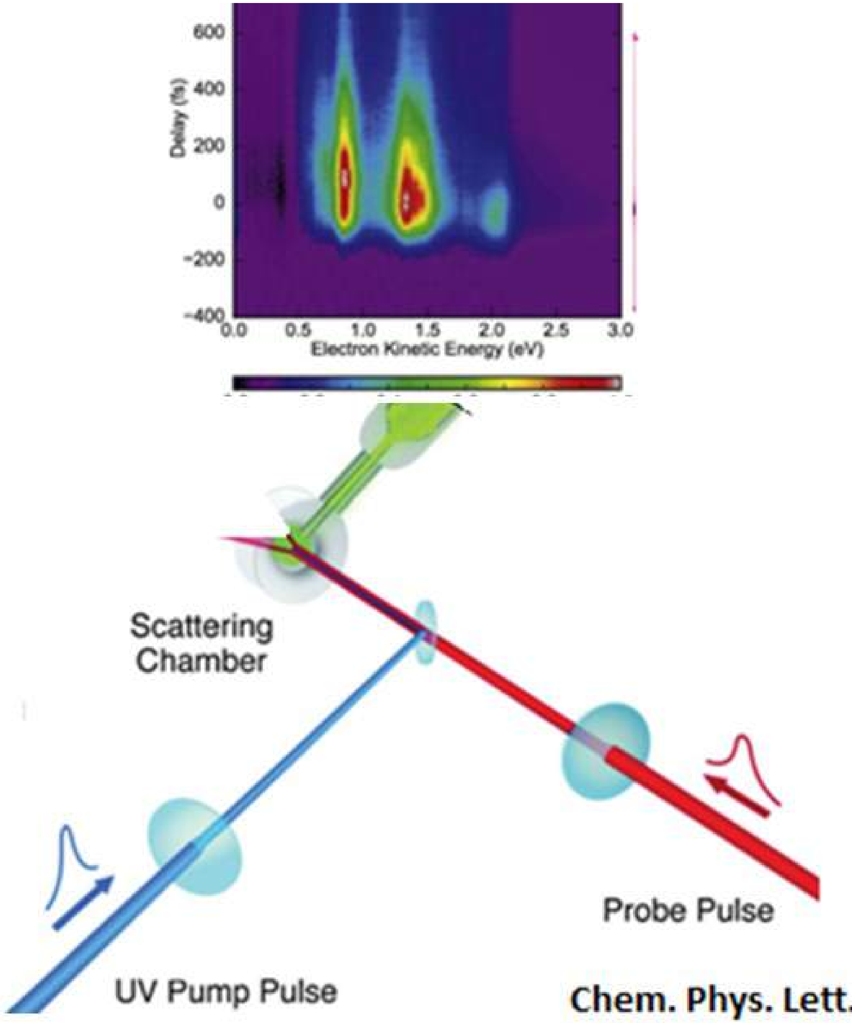
Pump-probe experiments in photochemistry

⬇

Simulation tool for
time-dependent photoionization!

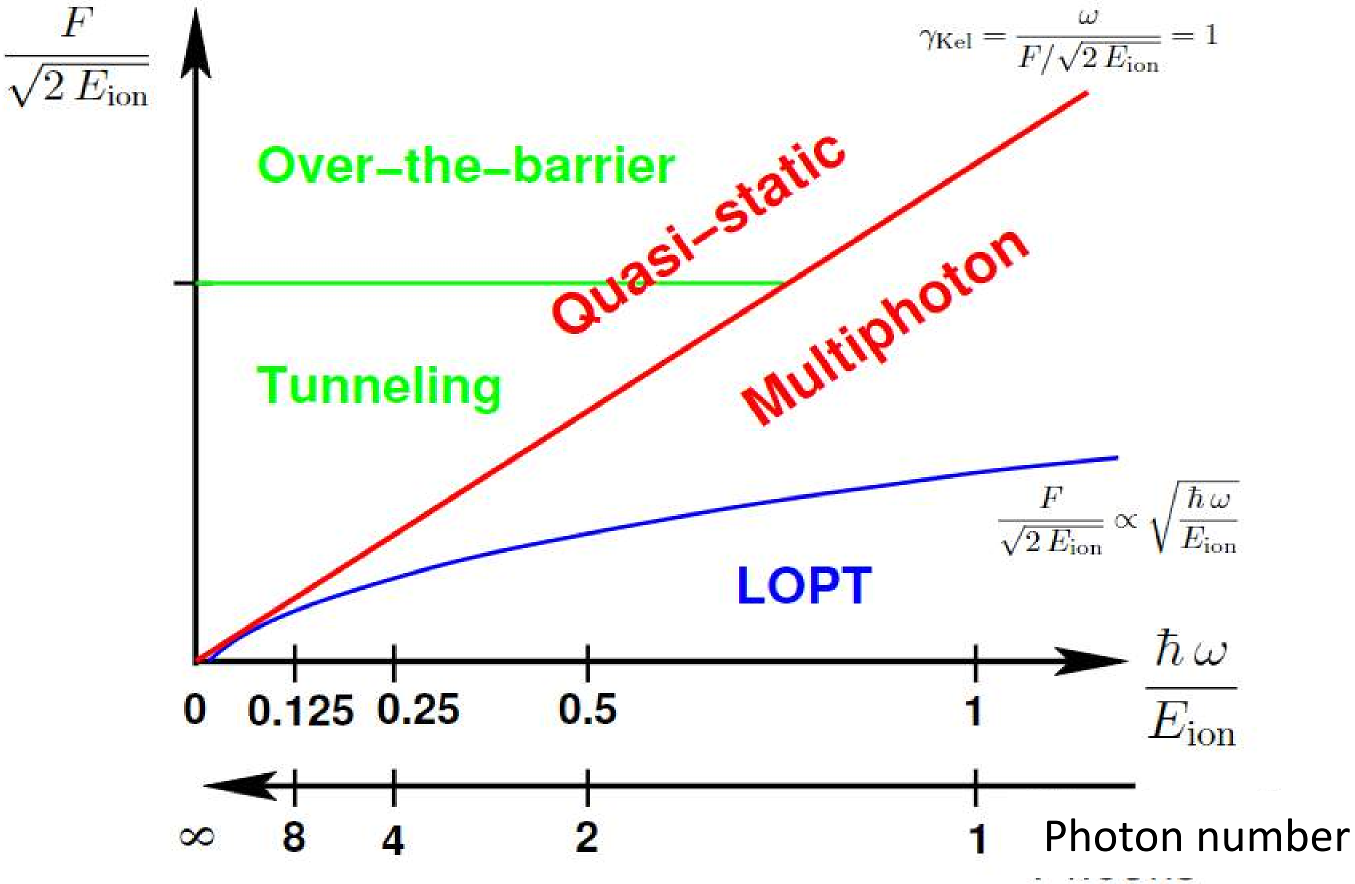
Outline:

- ✓ What is the photoionization rate?
- ✓ Methods
- ✓ CHD: channel-resolved photoionization
- ✓ CS_2: “average trajectory” approach
- ✓ Next steps



Chem. Phys. Lett., Bellshaw, D. *et al.* 2017

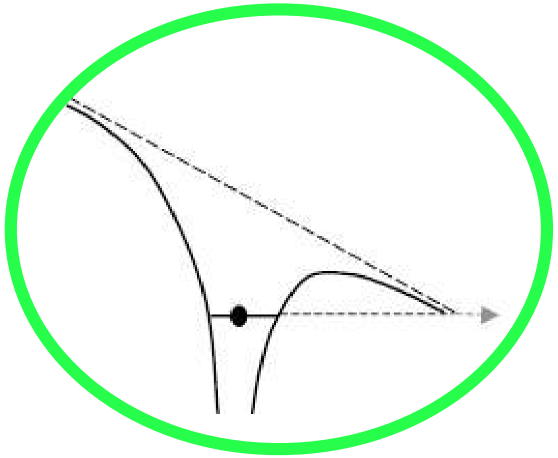
Photoionization regimes

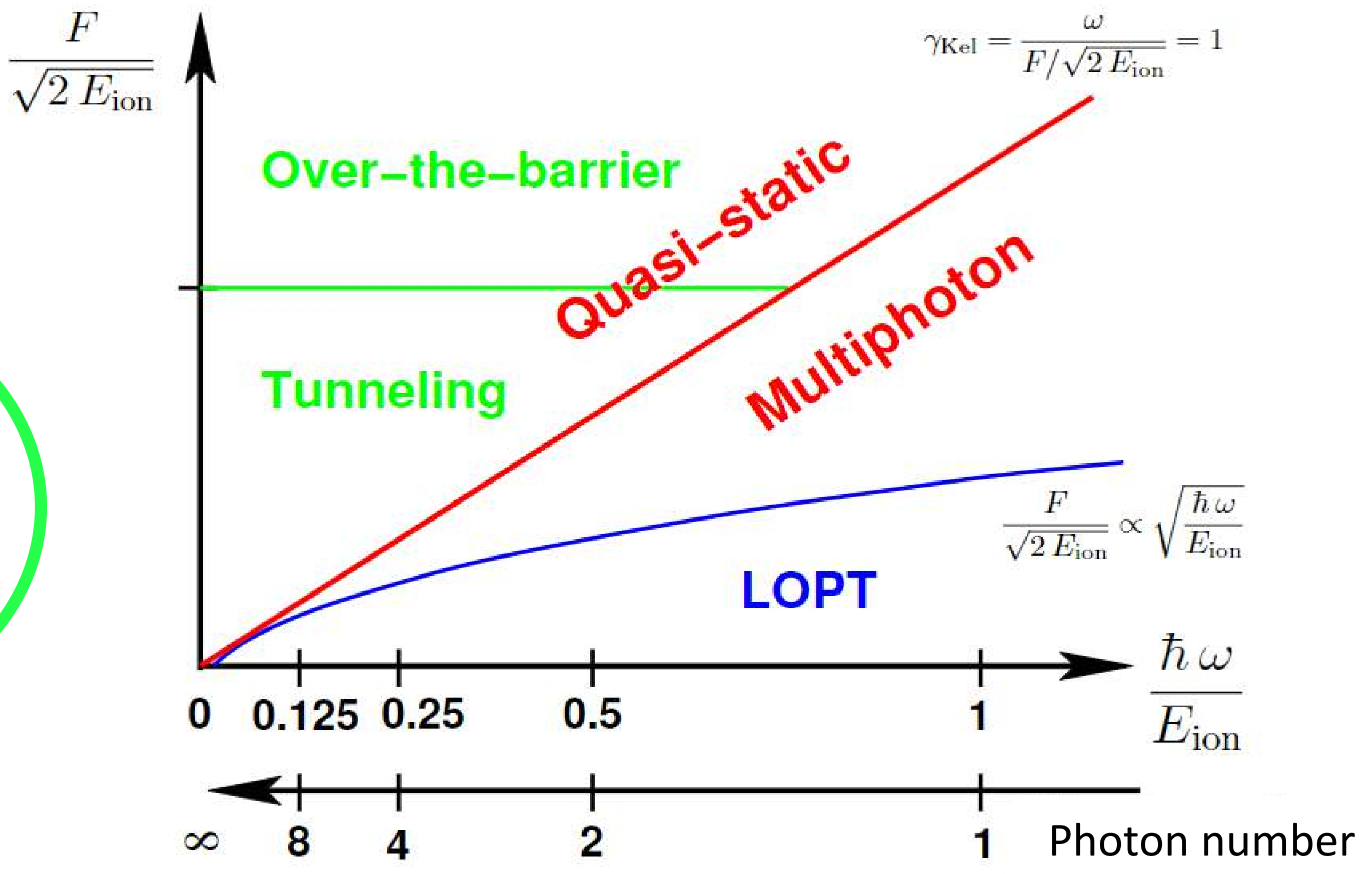


A. Saenz: Atoms and Molecules in
B. Intense Laser Fields, Berlin 2014

$\mathbf{F}$, $\boldsymbol{\omega}$ (field strength & frequency); $\mathbf{E_{ion}}$ (ionization energy)

Photoionization regimes





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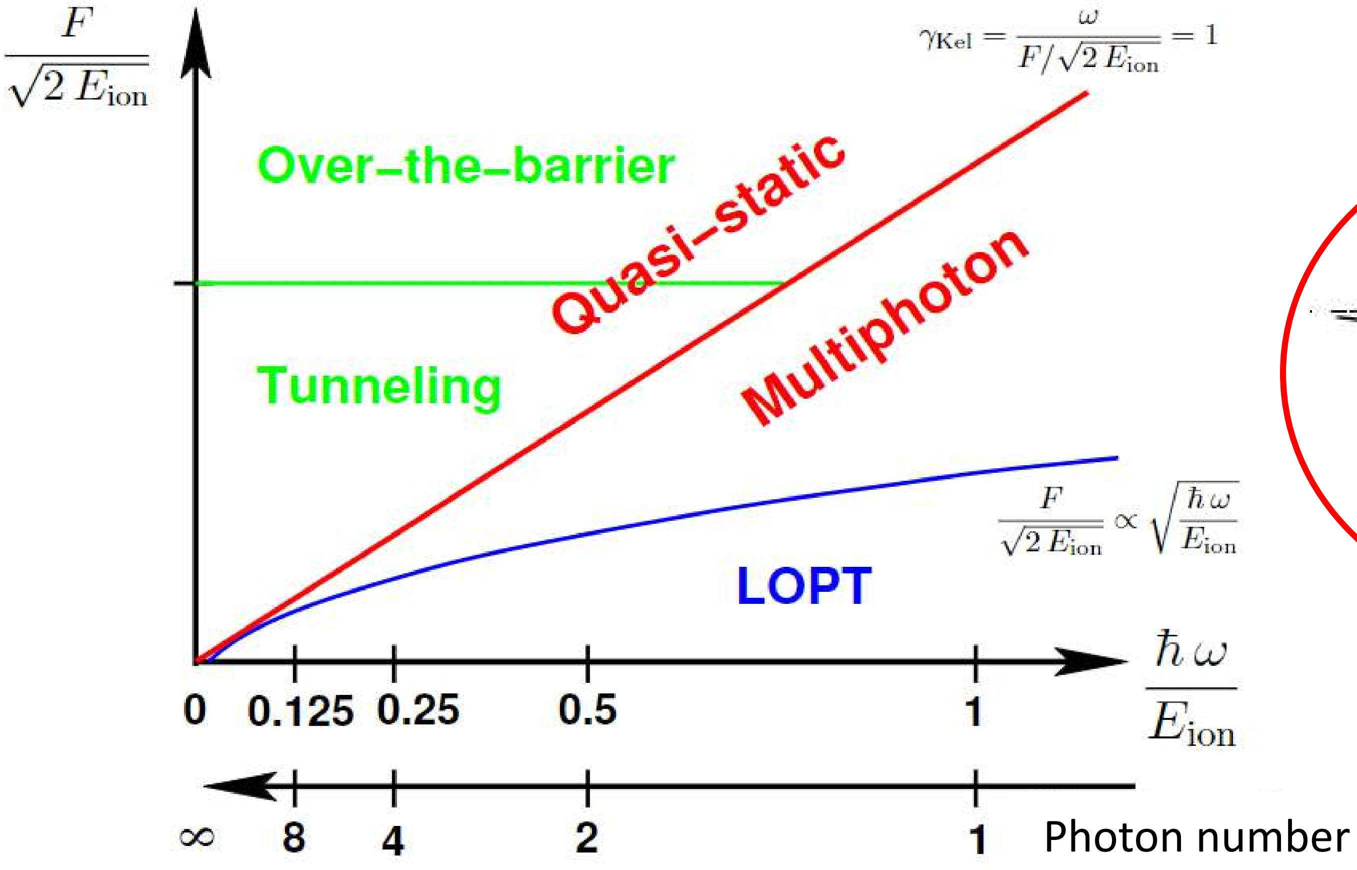
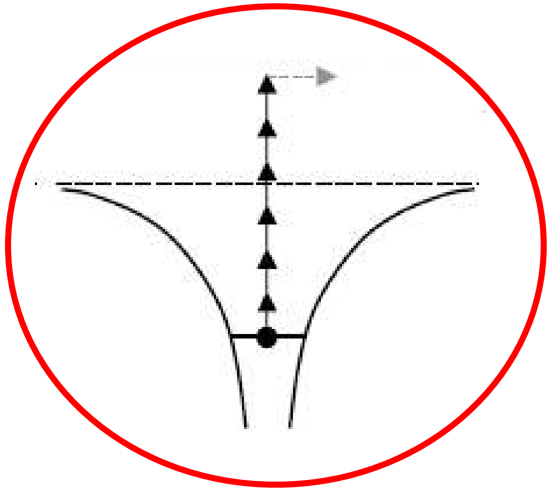
F↑ , ω↓ - tunneling

Photoionization regimes





A. Saenz: Atoms and Molecules in
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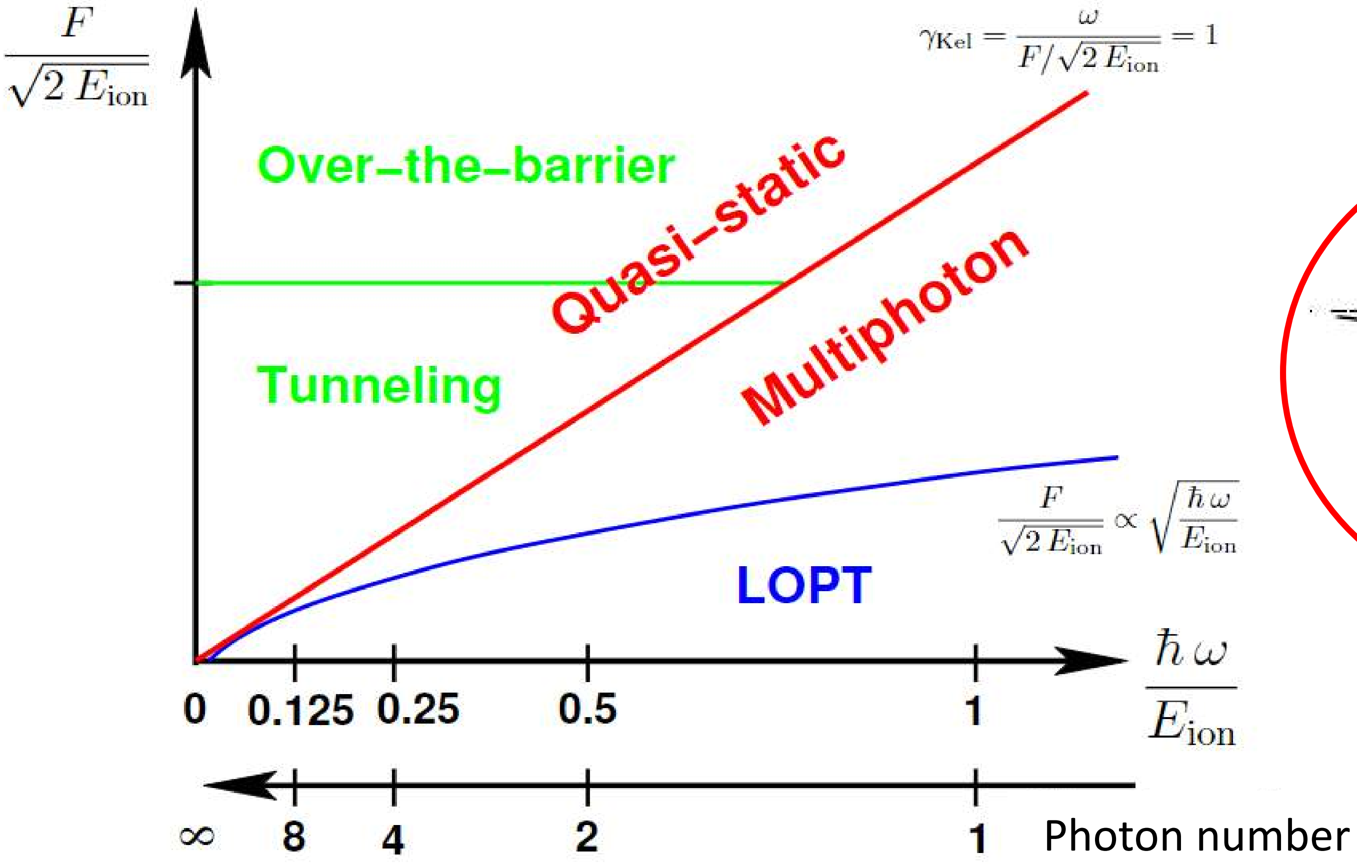
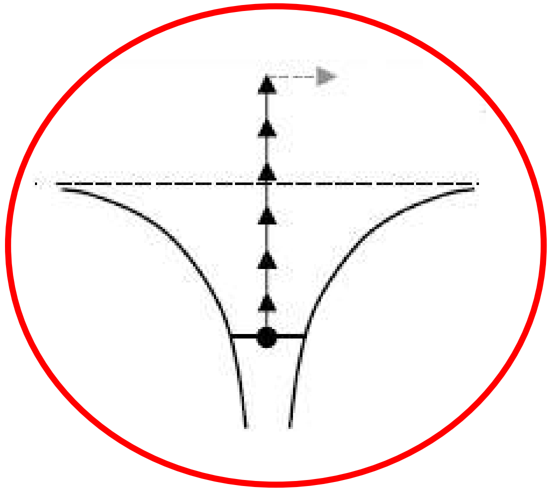
F ↓, ω ↑ - multiphoton

Photoionization regimes





A. Saenz: Atoms and Molecules in
B. Intense Laser Fields, Berlin 2014

$$\Gamma_{\rm LOPT} \propto I^N \left| \sum_{\nu,\mu\ldots\zeta} \frac{\langle\Psi_f|\hat{D}|\Psi_\nu\rangle\langle\Psi_\nu|\hat{D}|\Psi_\mu\rangle\cdots\langle\Psi_\zeta|\hat{D}|\Psi_i\rangle}{[E_\nu - E_i - (N-1)\omega]\,[E_\mu - E_i - (N-2)\omega]\cdots[E_\zeta - E_i - \omega]} \right|^2$$

Theoretical assumptions

- M(i) → $M^+(j)$, no inter-channel interaction
- No resonances
- Upon ionization: Coulomb field of the core only

  field is neglected;

  no e^- – e^- interaction;

- Wave functions: M(i) orthogonal to e^-
- Photoionzation threshold law: $E_\omega = I_p + k^2/2$ (one photon)

  vs. strong-field regime: peaks at $nE_\omega = I_p + k^2/2$

Dyson orbitals: the concept

Rate of n-photon ionization: $\Gamma_n = I^n \sigma$

Electron momentum

Photon energy

$$\sigma_{IF} = 4\pi^2 k\omega |D^k_{IF}|^2,$$

$$D^k_{IF} = \mathbf{u}\langle \phi^d_{IF} | \mathbf{r} | \Psi^k_{el} \rangle$$

From *ab initio* (Q-CHEM)

$$\phi^d_{IF}(1)(\mathbf{r}) = \sqrt{N} \int \Psi^N_I(1,\ldots n)\Psi^{N-1}_F(2,\ldots n) d2\ldots dn$$

Initial state

Final state

Free e⁻ w.f. expansion truncated numerically:

$$\Psi^{\mathrm{el}}_{kf}(x,y,z) = \Psi^{\mathrm{el}}_{kf}(r,\theta,\phi) = \sum_{lm}^{L} C_{klm} R_{kl}(r) Y_{lm}(\theta,\phi),$$

Coulomb/plane wave

Implementation: QCHEM + ezDyson

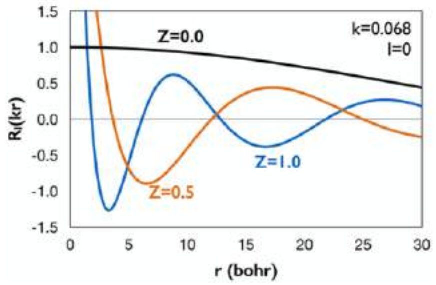
TIME-DEPENDENT INPUT!

QCHEM Input:

- ✓ Geometry (QMD)
- ✓ method eom-ccsd
- ✓ basis
- ✓ M/M$^+$ number of states

EZDYSON Input:

- ✓Free e parameters (l, Q)
- ✓Rotational average +/-



QCHEM Output:

(*Ab initio*)

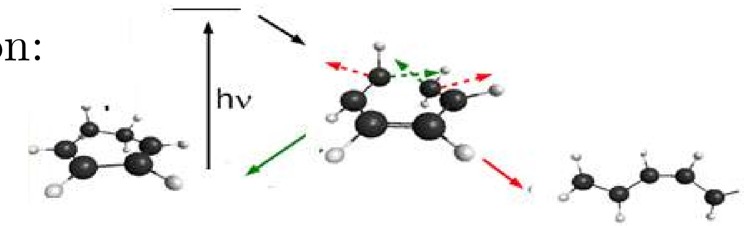
- ✓ Ionization/excitation energies

EZDYSON Output:

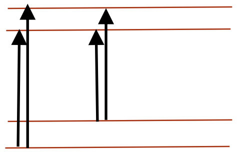
- ✓ Dyson orbitals (**r**) (+plots)
- ✓ Cross section expansion coefficients C_{klm}
- ✓ Cross sections (on the photon energy)
- ✓ Asymmetry parameters

Photoiniozation of 1,3-Cyclohexadiene (CHD)

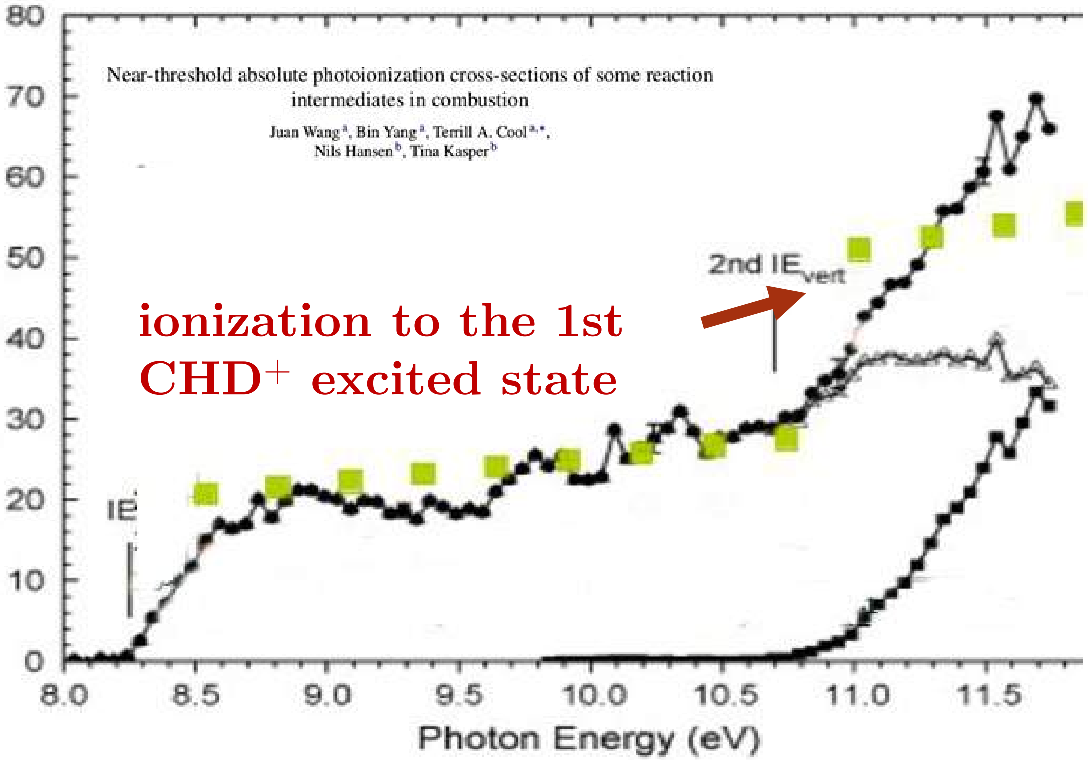
Ring-opening reaction:



Ground-state photoionzation



- 4 Dyson orbitals
- Free electron: $l_{max}=5$
- Orientation-averaged
- Linearly polarized field



CHD: Time-dependent photoionization cross section

QMD:

Trajectory	Weight (%)	Comment
16	20	Direct to
1	19	Closed
2	18	Rapid open
65	14	Closed
66	10	Closed

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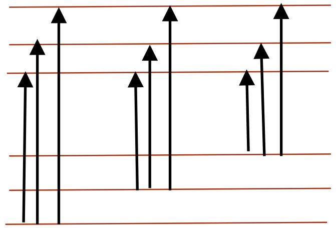
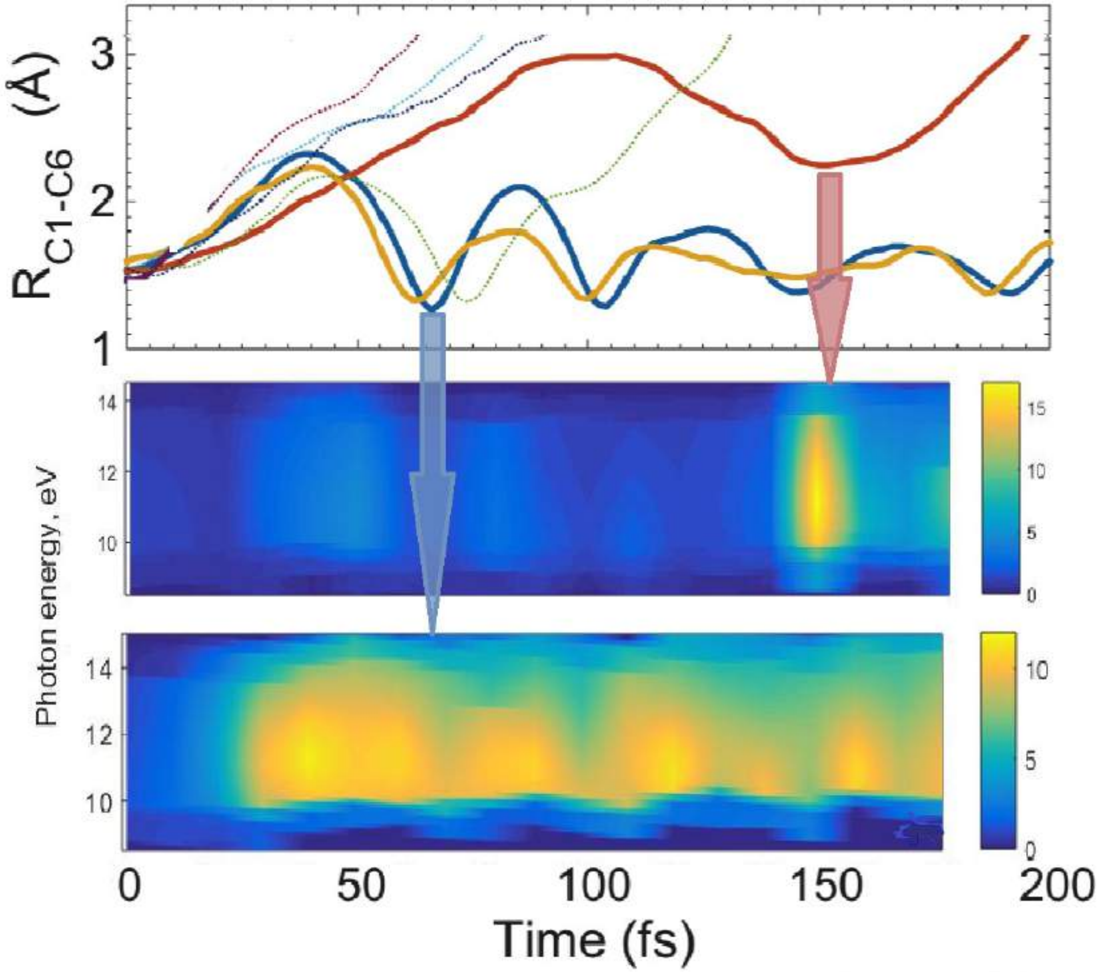
Imaging Molecular Motion: Femtosecond X-Ray Scattering of an Electrocyclic Chemical Reaction

M. P. Minitti,[1,*] J. M. Budarz,[1,2] A. Kirrander,[3] J. S. Robinson,[1] D. Ratner,[1] T. J. Lane,[1,4] D. Zhu,[1] J. M. Glownia,[1] M. Kozina,[1] H. T. Lemke,[1] M. Sikorski,[1] Y. Feng,[1] S. Nelson,[1] K. Saita,[3] B. Stankus,[2] T. Northey,[3] J. B. Hastings,[1,†] and P. M. Weber[2,‡]

9 Dyson orbitals



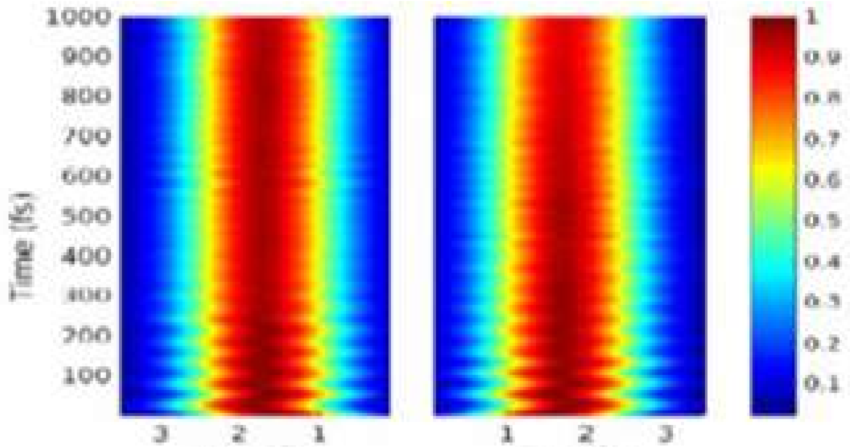


Intensity oscillations reflect the geometry changes!

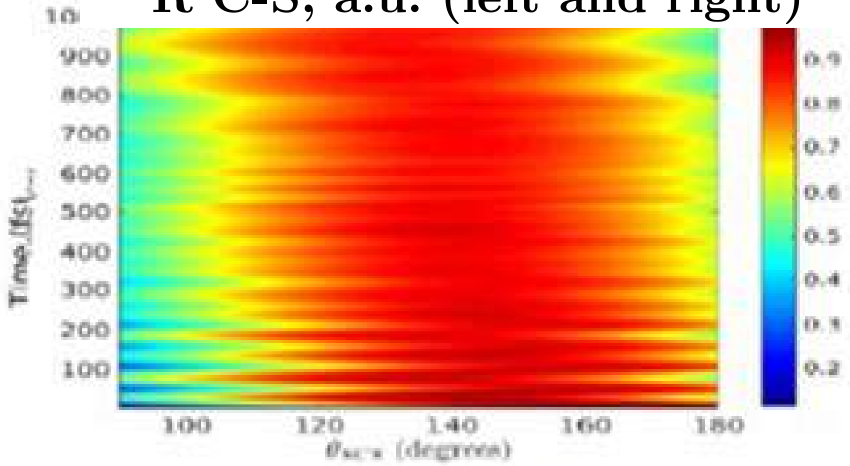
CS2: dynamics upon excitation

(Credit: Darren Bellshaw)

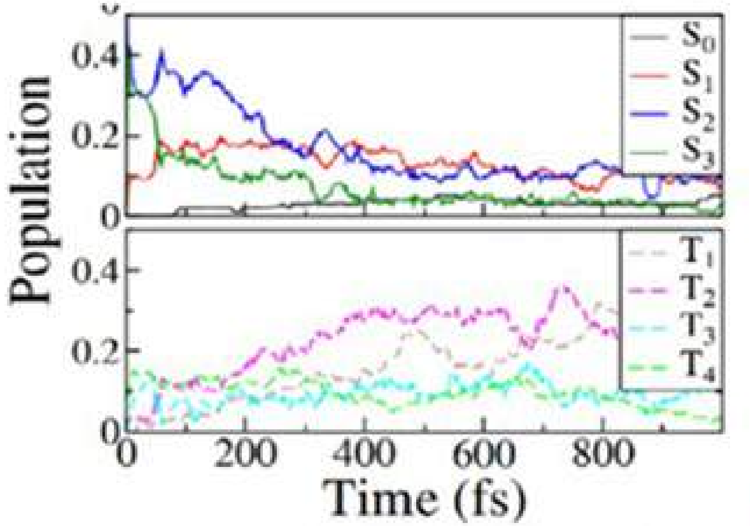
100 classical trajectories | **"average trajectory" concept** | **Total population distribution**



R C-S, a.u. (left and right)



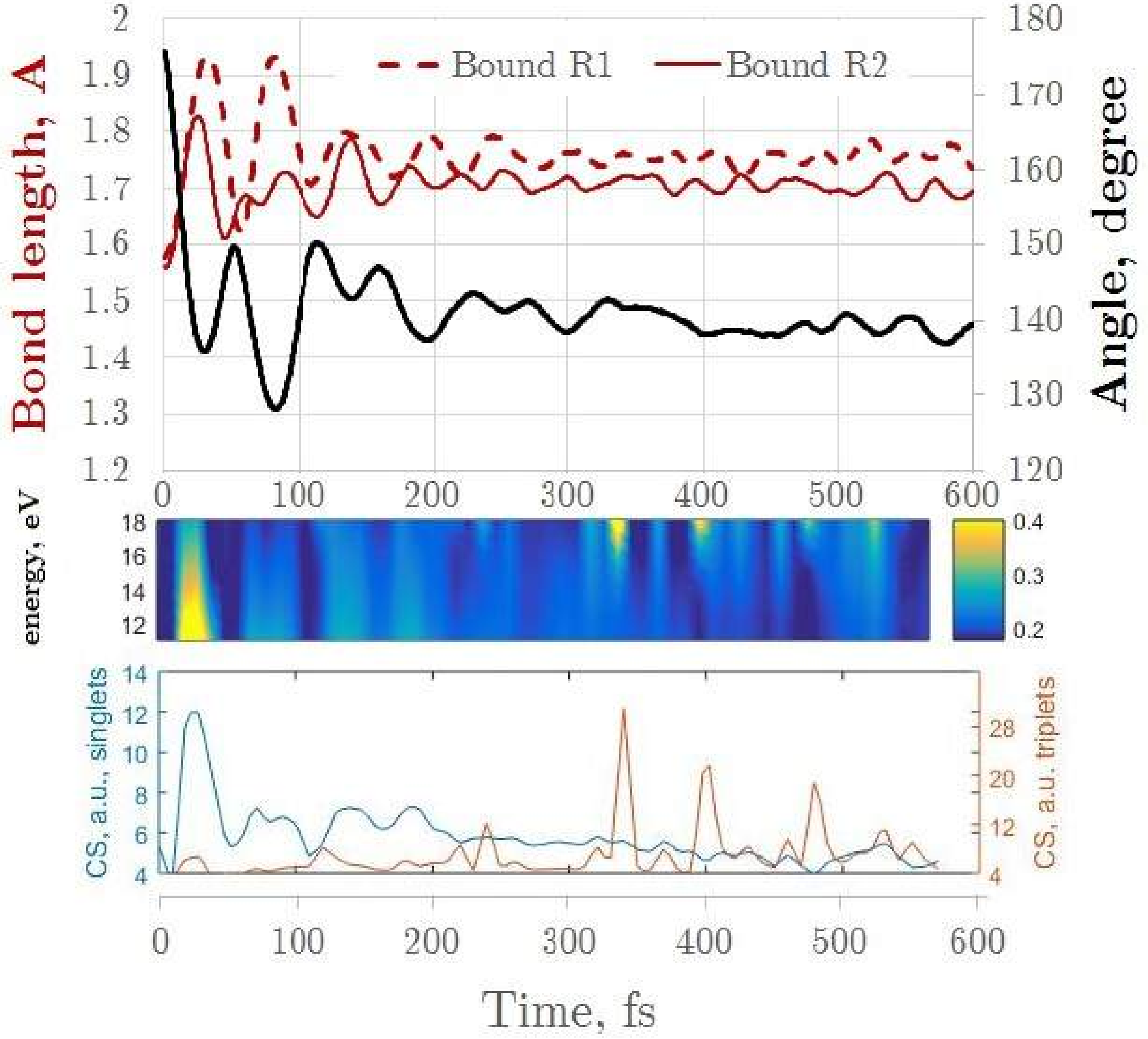
The bond angle, degree



- 8 CS_2 states are involved (4 singlets, 4 triplets)
- N ionic states can be included => N*8 transitions
- Total S ↓, total T ↑

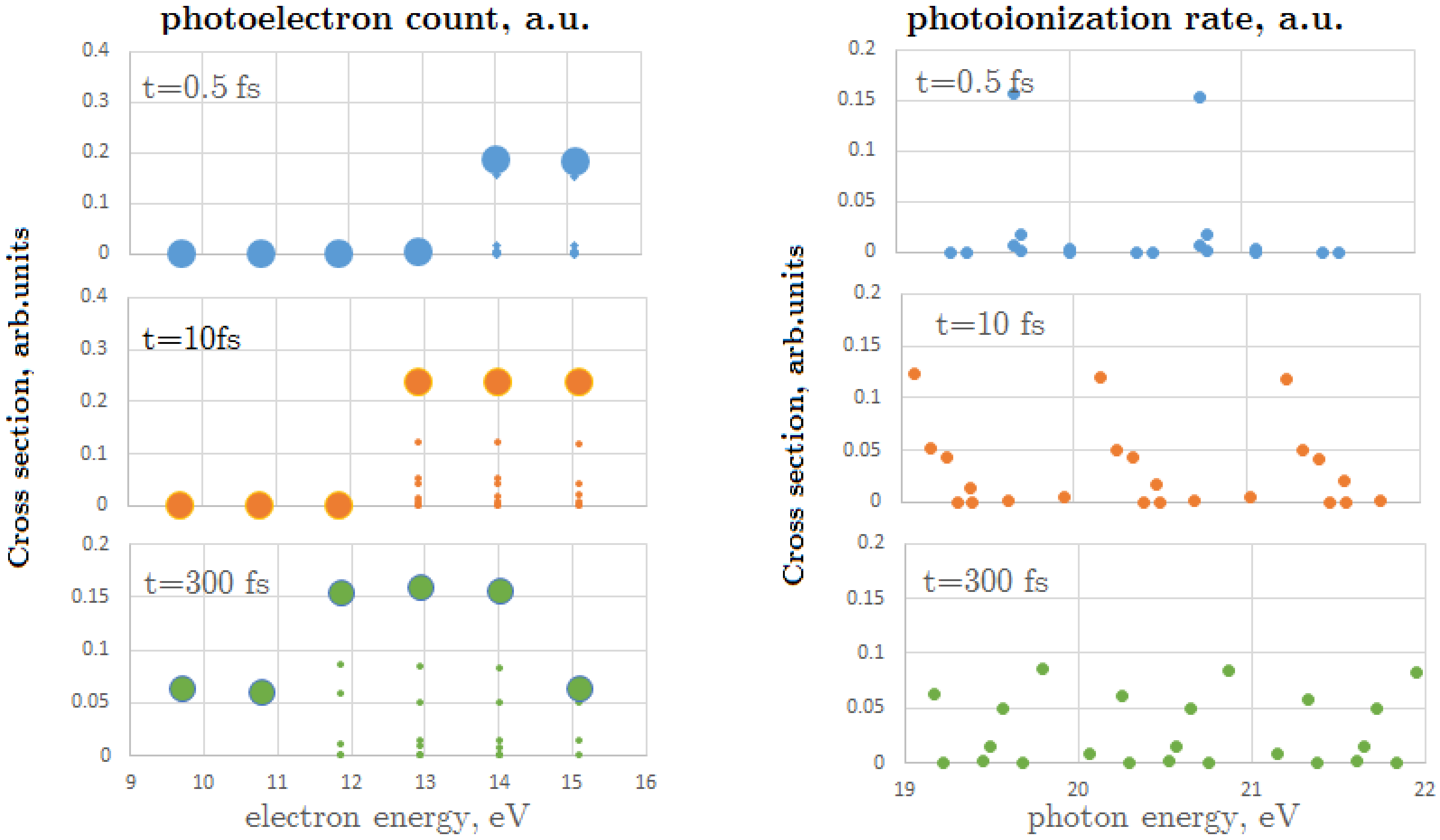
CS_2: time-dependent photoionization

Geometry oscillations along the **“average” trajectory:**

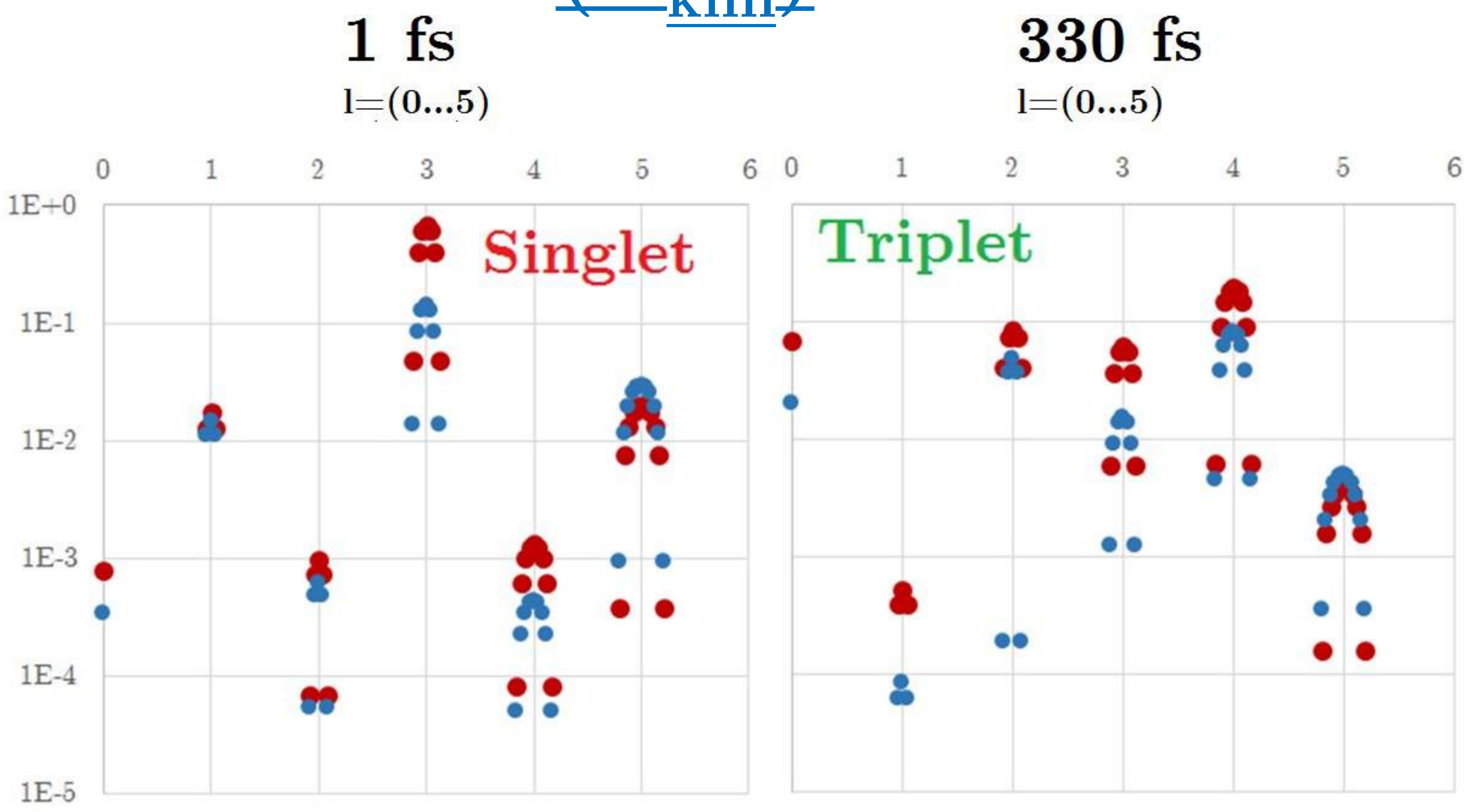


CS_2: channel-resolved photoelectron spectrum

$$E_\omega = I_p + k^2/2$$



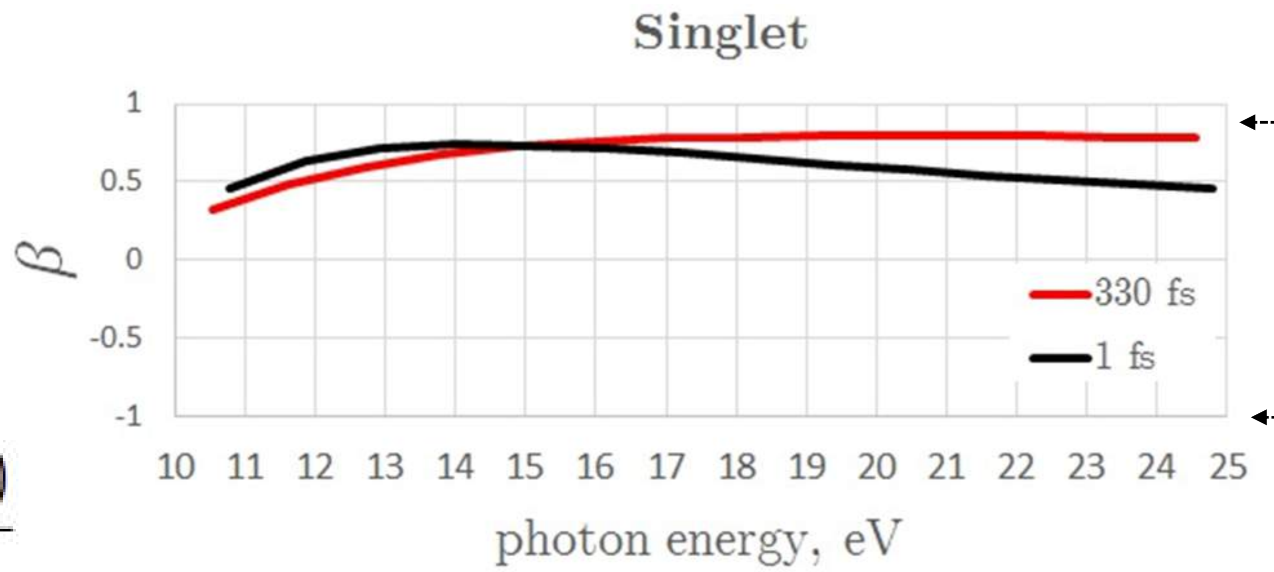
CS_2: free e⁻ angular momentum distribution (C_{klm})



E_k=6.6eV
E_k=13.6eV

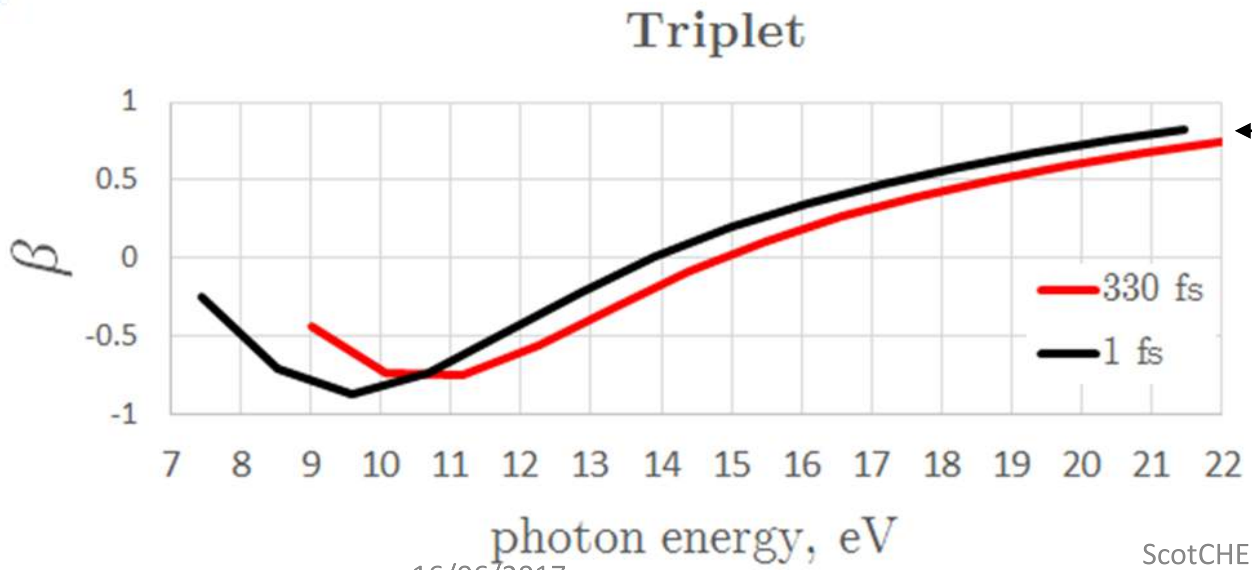
CS_2: anisotropy parameter

$$\beta = \frac{2(\sigma_{par} - \sigma_{perp})}{\sigma_{par} + 2\sigma_{perp}}$$



Anisotropic

No parallel ionization



Anisotropic

No parallel ionization

Conclusions + Next steps:

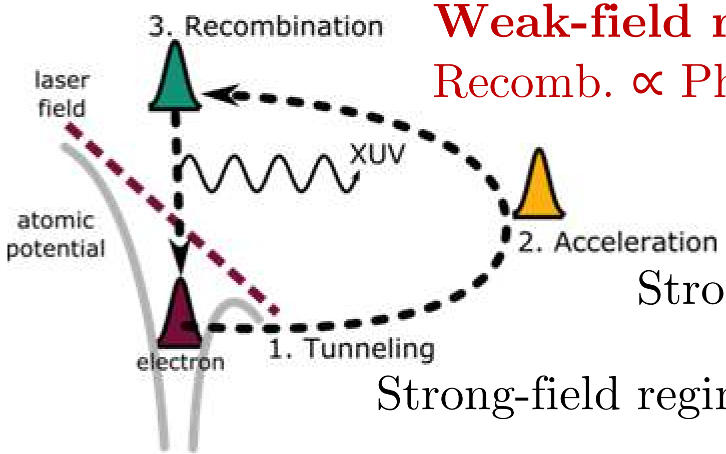
Photoionization:

✓ **Tool to analyse pump-probe experiments**

✓ **Photoionization signal reflects structural changes!**

- **CS_2** : photoelectron spectra vs. experiment
- **CHD:** full ring opening reaction of 1,3-cyclohexadiene

High-harmonic generation (HHG)

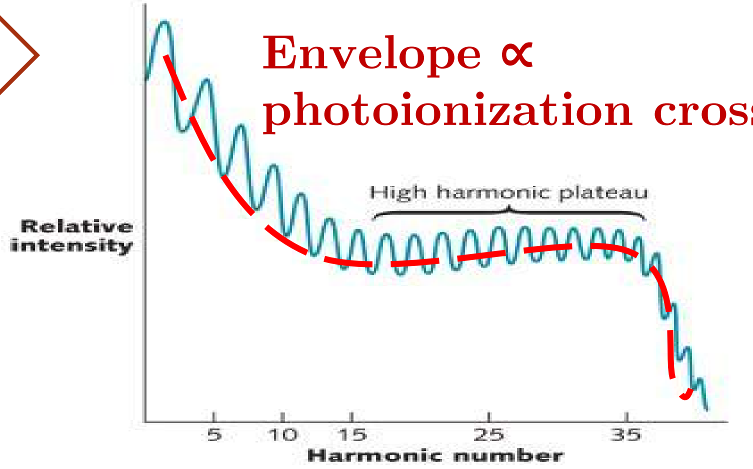


Weak-field regime!

Recomb. ∝ Photoion.

Strong-field regime

Strong-field regime



Envelope ∝ photoionization cross section

Acknowledgements

- Edinburgh: Adam Kirrander, Darren Bellshaw
- Southampton: Russell Minns (experimental group)
- Hokkaido, Japan: Kenichiro Saita
- ezDyson team: Samer Gozem

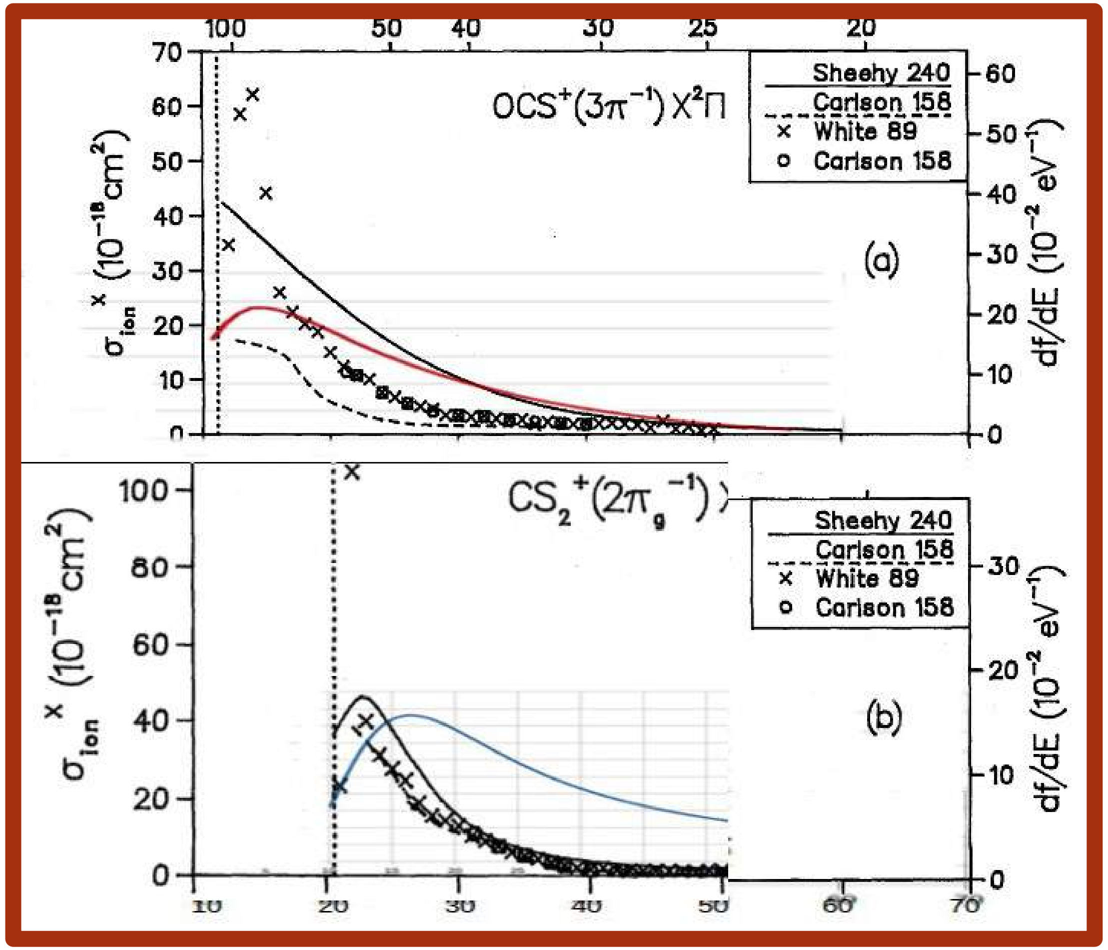
&

Thank you!

CS_2: photoioniozation from the ground state

- Cooper minimum – due to the shape of the orbital and the continuum state;
- Should be visible in the HHG spectrum

CS_2 vs. OCS



J.J. Yeh and I. Lindau. At. Data Nucl. Data Tables 1985, 21, 1.

Next steps: Photoionization and HHG

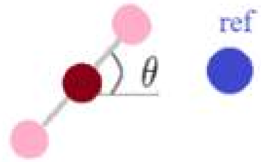
- Saddle-point approximation:

High-Harmonic Generation: Ionization + Free electron acceleration + Electron Photorecombination

I_p (R(t)) — F(t) — I_p (R(t)) ; Energy (R(t))

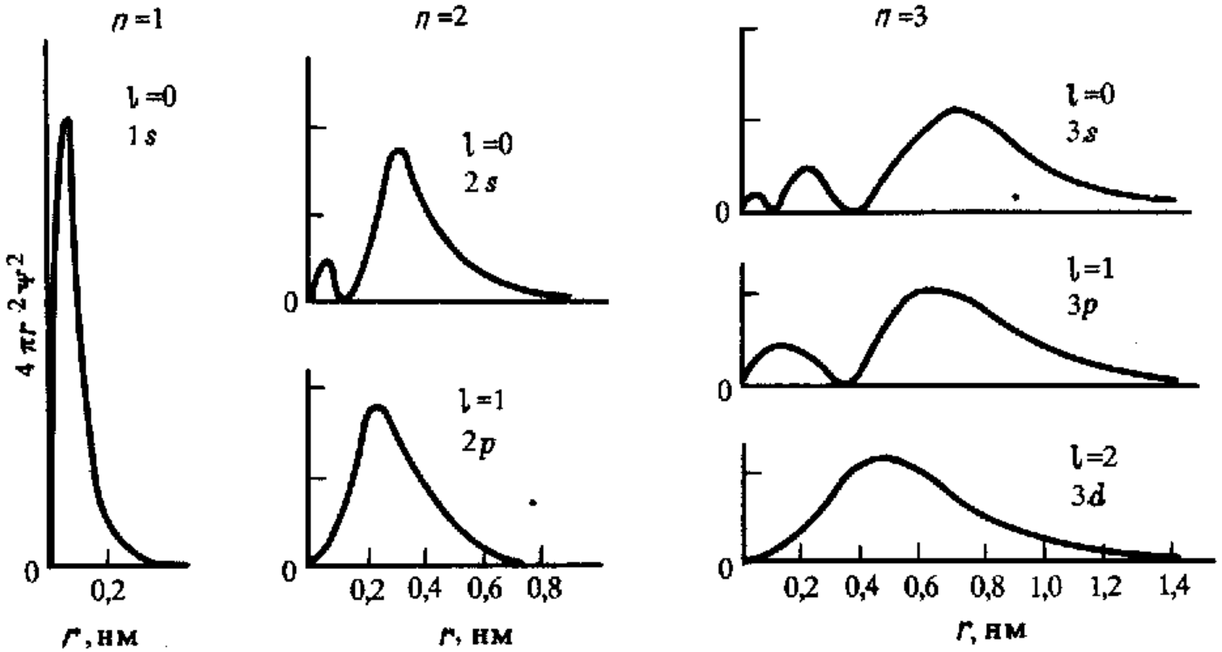
Quantitative Rescattering Theory (Le et. al):

$$S^{QRS}(\omega, \theta) = \frac{N(\theta)}{N^{ref}} \frac{\sigma(\omega, \theta)}{\sigma^{ref}(\omega)} S^{ref}(\omega)$$



- Photorecombination at the low field intensity: multiphoton regime ⇨ DO approach!

Radial part of atomic orbitals



Occurrence of Cooper minimum
In atoms

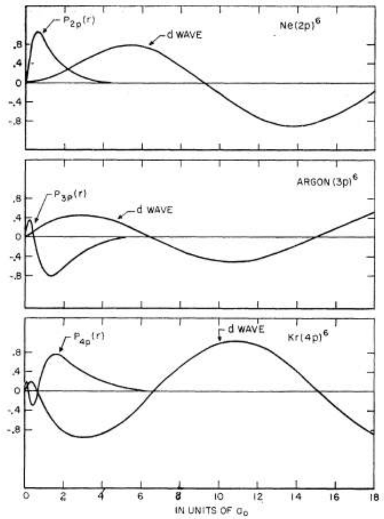


FIG. 2. Outer subshell radial wave functions and d waves for $\epsilon=0$ for Ne, Ar, and Kr.