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Coherence in photoionization

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Frontiers of Physical Sciences with X-ray FELs workshop

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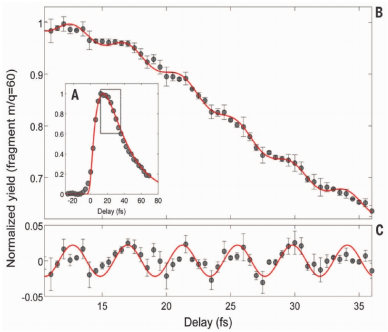
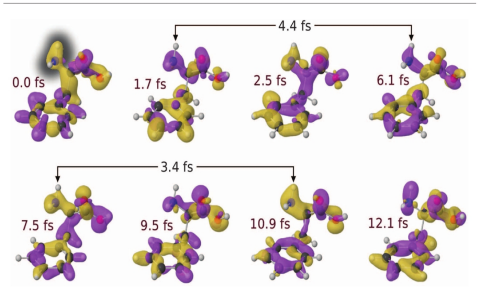
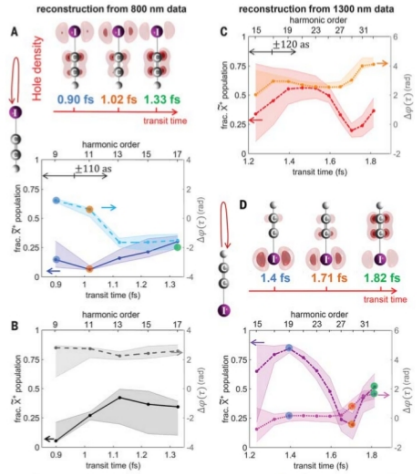
Motivation: ultra-fast hole dynamics following molecular (valence) ionization

- First attempts of time-resolved observation using attoseconf pump – IR probe spectroscopy: Belshaw *et al.*, J. Phys. Chem. Lett. **3**, 3751 (2012); Calegari *et al.*, Science **346**, 336 (2014); using HHG spectroscopy: Kraus *et al.*, Science **350**, 790 (2015).





- using HHG spectroscopy: Kraus *et al.*, Science **350**, 790 (2015).



- Valence photo-ionization can create a non-stationary state of molecular ion
- This leads to oscillations of the electron hole across the molecule that we call hole migration
- Hole migration is purely electronic. Eventually, it is damped by the nuclear motion

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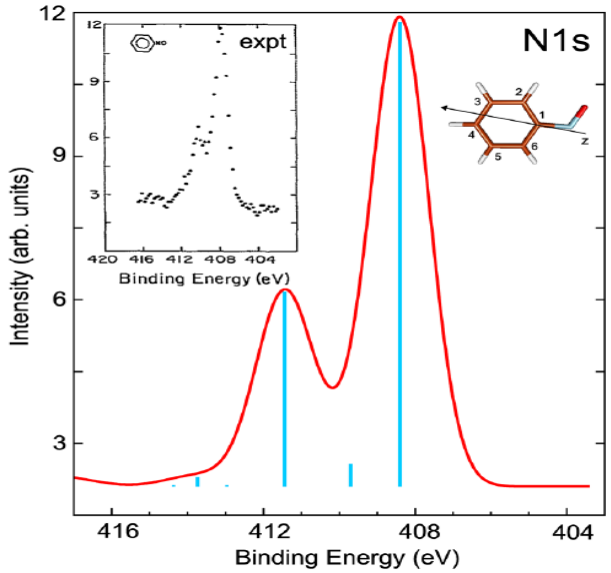
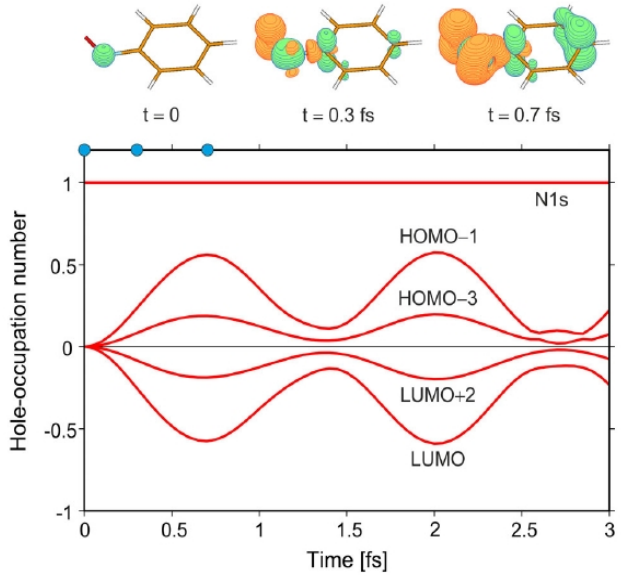
Ultra-fast hole dynamics following molecular (core) ionization

- Core ionization can also initiate sub-femtosecond charge migration in the valence shell of molecules
- Auger decay (femtosecond time scale) –-> coherent (valence) electron dynamics decay





[A. Kuleff et al., Phys. Rev. Lett. **117**, 093002 (2016)]

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Goals

- **Electronic quantum coherence** –> ultrafast (hundreds attoseconds – few femtoseconds) charge dynamics
- Electronic charge dynamics –> (electrons-nuclei couplings) –> rearrengement of the molecular structure, bond breaking, dissociation, **chemical change**
- 1- Prepare **Electronic quantum coherence**
- 2- Probe **Electronic quantum coherence**
- Broadband pump –> high temporal resolution necessary to resolve coherences between electronic states tens of eV apart.
- 3- Control **Electronic quantum coherence**

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“Theoretical” ingredients

- Description of **electron correlation**: shakeup states, correlation satellite states (strong spatial correlations).
- Description of **electronic relaxation**: Relaxation satellite states.
- **Accurate Partial cross-sections** for all the many-electron ionic states of the system as a function of the ionising laser pulse parameters
- Time-dependent description of the ionisation process: ultrafast formation and loss of coherence.
- Description of the **N-electron wavefunction**, ion-photoelectron **entanglement**.
- Effect of the residual **interchannel couplings** between the created ionic system and the **emitted (slow) photoelectron**. **Correlation effects in the continuum**.
- Description of **non-radiative relaxation processes**: Auger decay, Coster-Kronig
- **Coupling to nuclear motion**, multidimensional problem:
  electronic coherences among many different electronic states –> many different potential energy surfaces
  different electronic states might show different coherence decay time-scales (?)
- **Complete knowledge of the many-body state of the system**.

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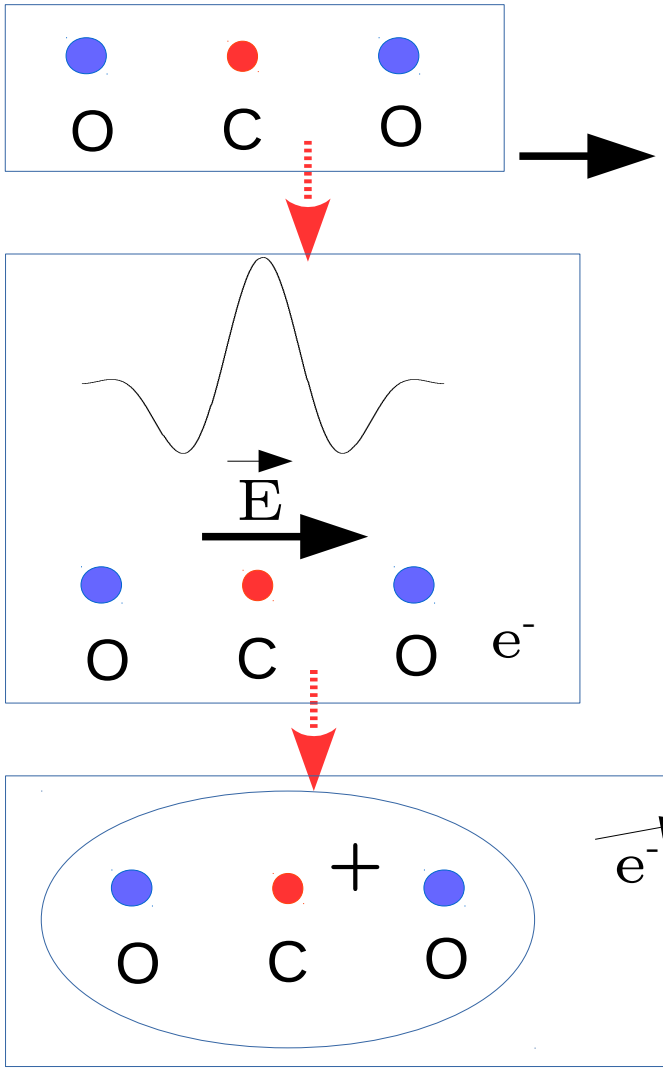
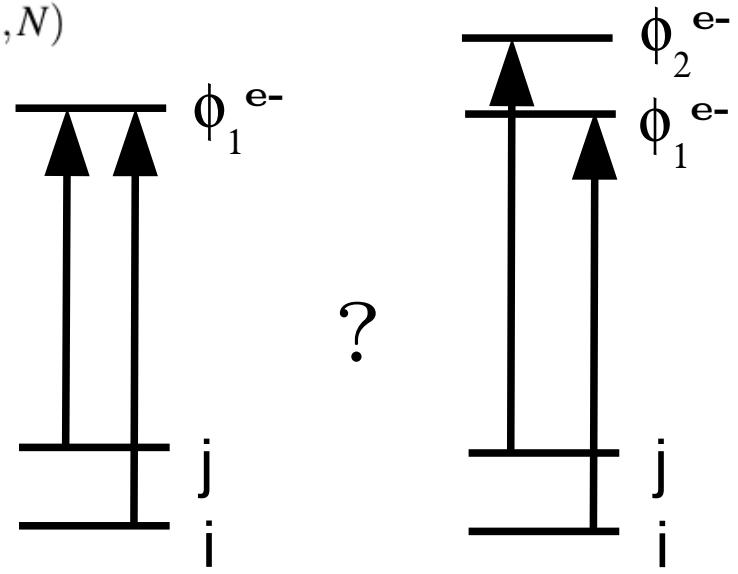
Ionic coherence following ionization?



Is the final wave-function **separable** into the product of an ionic and a photo-electron component? Is the **ionic wave-packet** produced **coherent** and describable in terms of a **pure state**?

$$\Psi^{N}_{Bound}(1,2,3,.....,N)$$



$$\simeq A\left[\sum_{\mathbf{n}}\left(\Phi^{N-1}_{\mathbf{n}}(1,2,3,.....,N-1)\times\phi^{e^-}_{\mathbf{n}}(N)\right)\right]$$

$$\downarrow ?$$

$$\approx A\left[\left(\sum_{\mathbf{n}} c_{\mathbf{n}}\Phi^{N-1}_{\mathbf{n}}(1,2,3,.....,N-1)\right)\times\phi^{e^-}(N)\right]$$

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Ionic wave-function...?

Assuming perfect coherence

$$\Psi^{N}_{Final}(1,2,3,.....,N) \sim A\left[\Psi^{N-1}_{Bound}(1,2,3,.....,N-1)\times\phi^{e^-}(N)\right]$$

$$\Psi^{N-1}_{Bound}(1,2,3,.....,N-1)=\sum_n c_n\Phi^{N-1}_n(1,2,3,.....,N-1) \qquad c_n=c_n\left(E_{field}\right)=?$$

We need a theoretical tool to model molecular photo-ionization beyond the sudden approximation and including electron correlation, and predict to what extent can the resulting ion be described by a Wave-function.

Sudden approximation guess for the initial state (**when is it valid...?**)

$$\{ \quad |\Psi^{N-1}_{initial}\rangle \sim a_i\,|\Psi^{N}_0\rangle$$

Time-dependent Multicentre B-spline restricted correlation space (RCS) -ADC

$$i\hbar\frac{\partial\,|\Psi^N(t)\rangle}{\partial t}=\hat{H}^N(t)\,|\Psi^N(t)\rangle \qquad H^{\hat{N}}(t)=\hat{H}^N_{RCS-ADC(n)}+\hat{D}^N_{RCS-ADC(n)}E(t)-i\hat{W}$$

$$|\Psi^N(t)\rangle=\sum_m\left\{\sum_\mu c_{m\mu}(t)\,\hat{c}^\dagger_\mu\,|\Psi^{(N-1)}_m\rangle^{[n]}\right\}+\sum_{I_{RCS}}c_{I_{RCS}}(t)\,|\tilde{\Psi}^N_{I_{RCS}}\rangle^{[n]}+c_0(t)\,|\Psi^{RCS}_0\rangle^{[n]}$$

$$|\tilde{\Psi}^N_{\mu,n}\rangle=\hat{c}^\dagger_\mu\,|\Psi^{N-1}_n\rangle$$

[M. Ruberti, JCTC **14**, 4991 (2019)]

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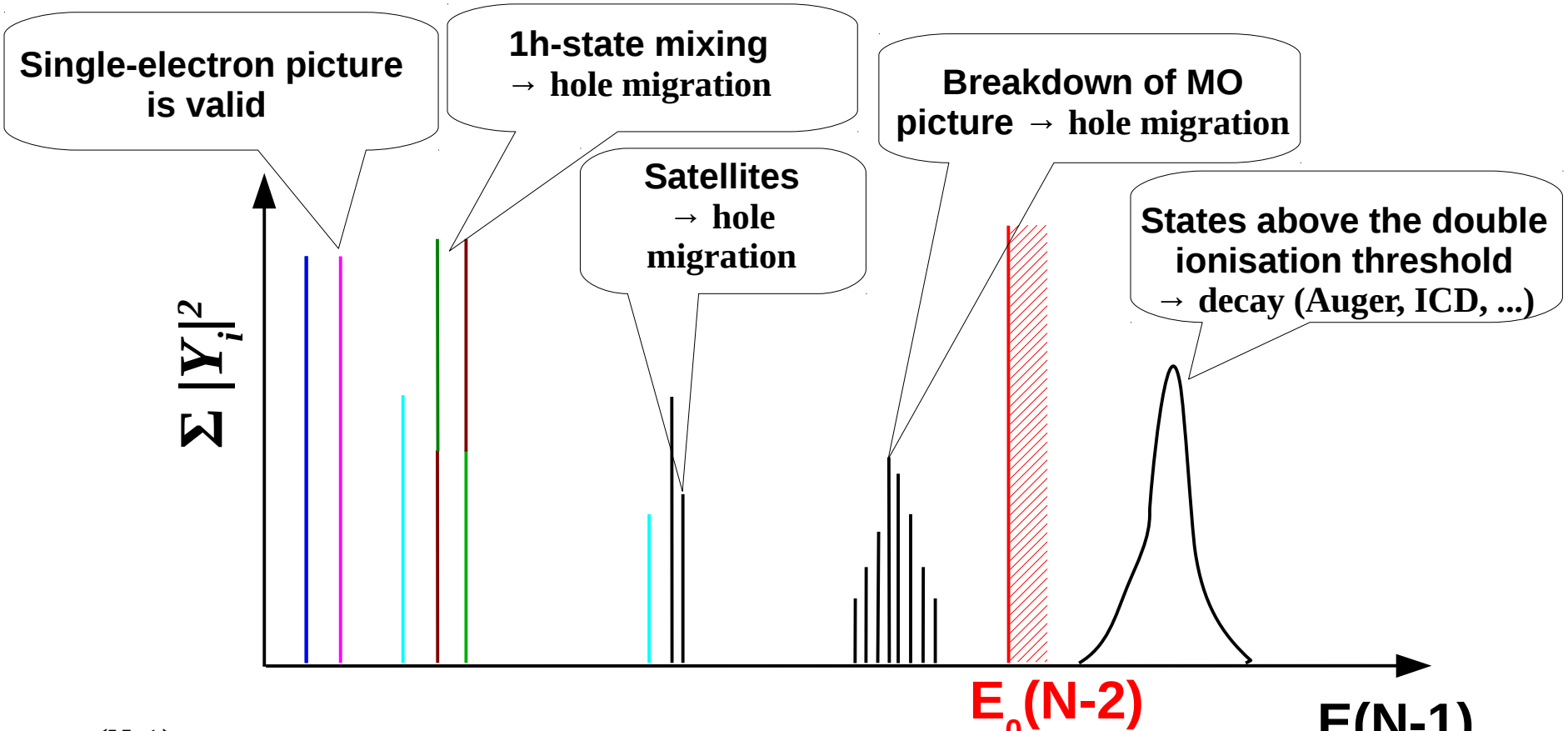
ADC: Electron holes beyond Koopmans



$$\Psi^{(N-1)} = \sum_{1h} Y_i \Psi_i + \sum_{2h1p} Y_{ij}^{\ a} \Psi_{ij}^{\ a} + \sum_{3h2p} Y_{ijk}^{\ ab} \Psi_{ijk}^{\ ab} + \ldots$$

[Cederbaum, Schirmer and co-workers; Using B-splines: Ruberti, Decleva & Averbukh (2014)]

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...no! Reduced ionic density matrix

Reduced ionic density matrix: trace over the **unobserved** photo-electron states

$$\hat{\rho}(t) = |\Psi^N(t)\rangle\langle\Psi^N(t)| \qquad \hat{\rho}^{R-IDM}(t) = Tr_\mu[\hat{\rho}(t)]$$

$$\rho_{mn}^{R-IDM}(t) = \sum_\mu \langle\tilde{\Psi}_{\mu,m}^N \mid \Psi^N(t)\rangle\langle\Psi^N(t) \mid \tilde{\Psi}_{\mu,n}^N\rangle = \sum_\mu c_{m\mu}(t)\, c_{n\mu}^*(t)$$

The degree of coherence between two populated ionic channels $\boldsymbol{i}$ and $\boldsymbol{j}$ is defined as

$$G_{mn}(t) = \frac{|\rho_{mn}(t)|}{\sqrt{P_m(t) * P_n(t)}} \qquad P_n(t) = |\rho_{nn}(t)|$$

Maximum coherence between the two states corresponds to $\boldsymbol{G_{i,j} = 1}$.

$$Tr\left(\hat{\tilde{\rho}}^2(t)\right) \neq Tr\left(\hat{\tilde{\rho}}(t)\right) \leq 1 \quad mixed\ state,$$

$$Tr\left(\hat{\tilde{\rho}}^2(t)\right) = Tr\left(\hat{\tilde{\rho}}(t)\right) = 1 \quad pure\ state.$$

von Neumann entropy

$$s^{Ion}(t) = -ln\left(\frac{1}{N}\right) \quad statistical\ mixture,$$

$$s^{Ion}(t) = 0 \quad pure\ state.$$

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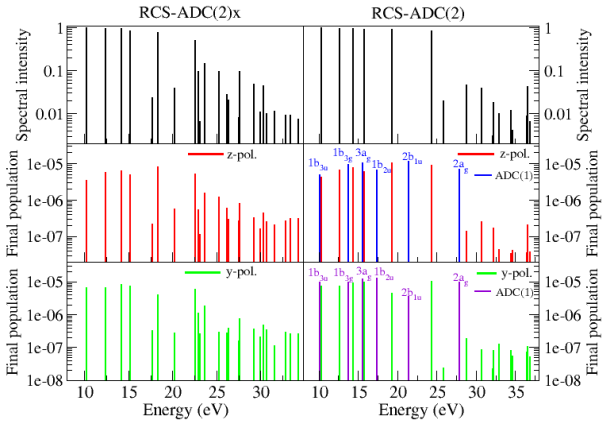
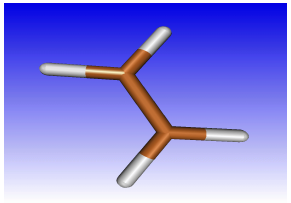
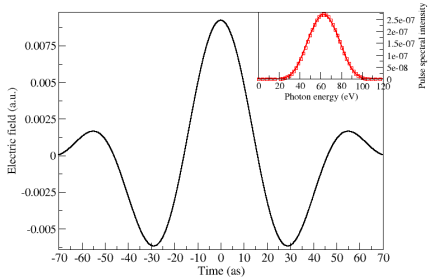
Reduced ionic density matrix after attosecond XUV ionization of C_2H_4

Ionic populations

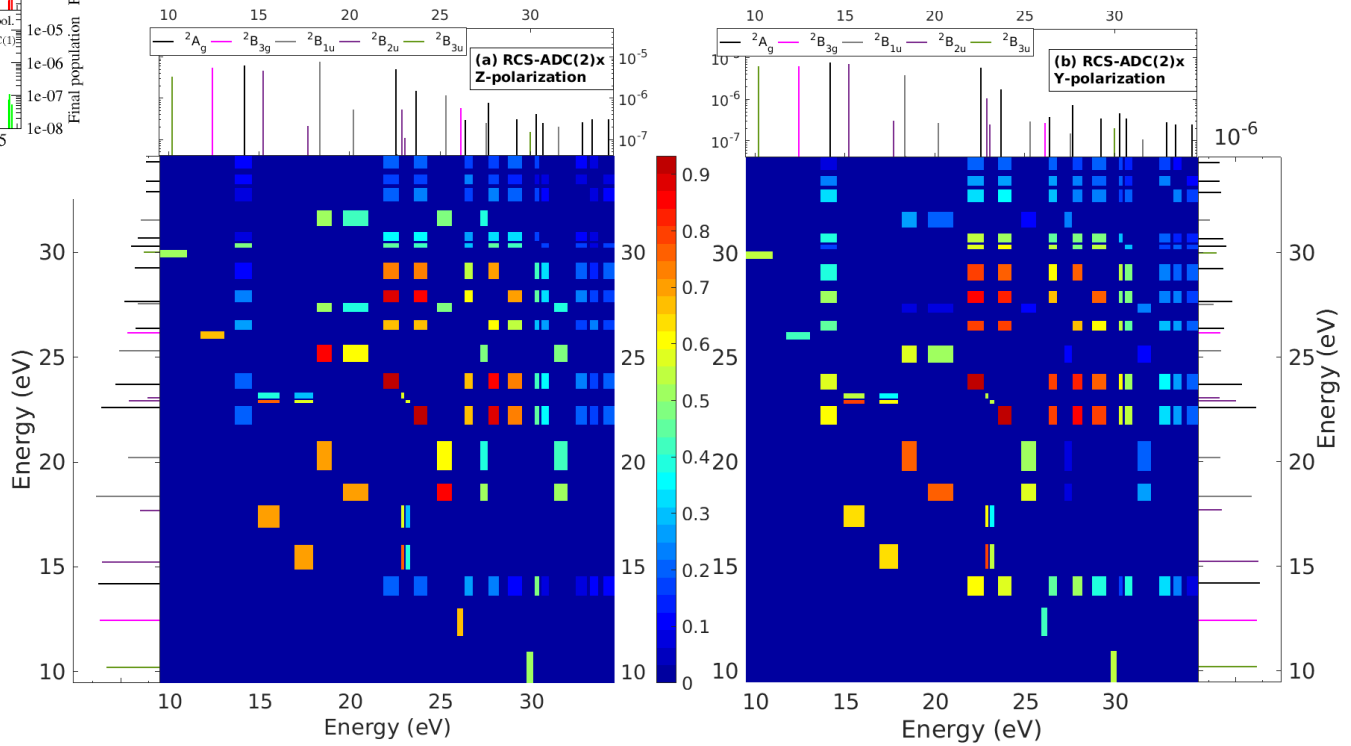






Mean photon energy = 63 eV
Intensity = 3 x 10^{11} W/cm^2

Ionic coherences



[M. Ruberti, Phys. Chem. Chem. Phys., 2019,21, 17584-17604 PCCP HOT Article 2019]

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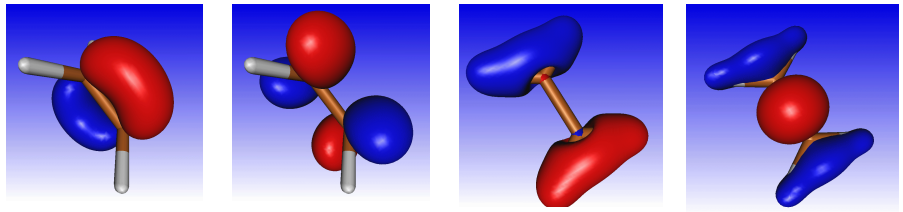
Charge dynamics and ionic coherence evolution after attosecond ionization of C_2H_4

Natural charge orbitals

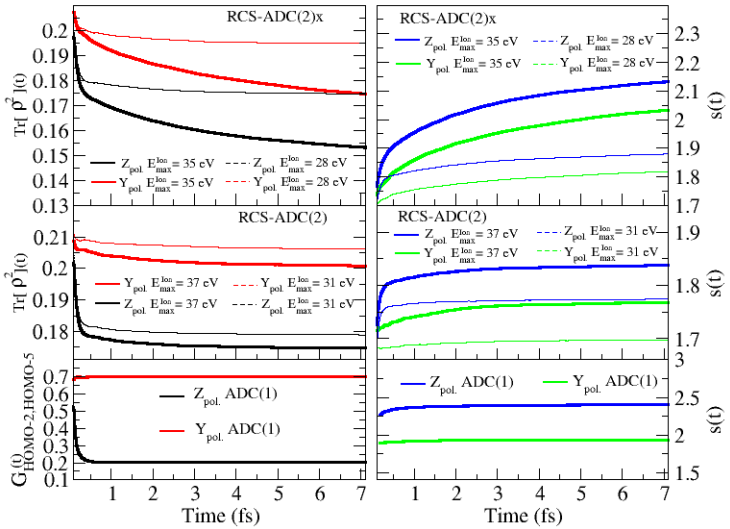


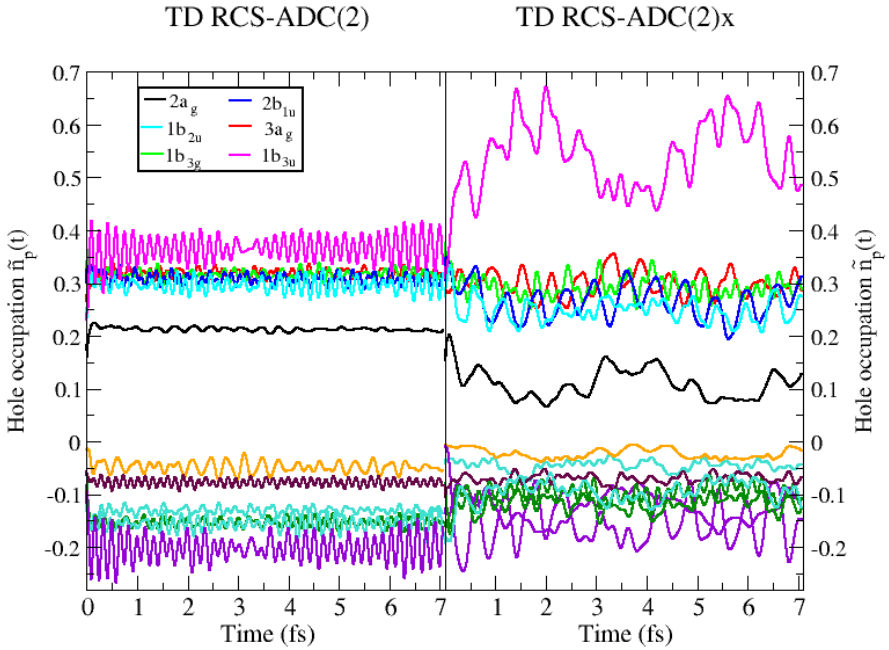
$$\tilde{Q}(r,t) = \langle \Psi_0^N \mid \hat{Q}(r) \mid \Psi_0^N \rangle - Tr\left(\hat{Q}(r)\,\hat{\tilde{\rho}}(t)\right)$$

$$\tilde{Q}(r,t) = \sum_p \mid \tilde{\phi}_p(r) \mid^2 \tilde{n}_p(t)$$

Dominance of correlation-driven charge dynamics

Ionic decoherence due to coupling to the emitted photoelectron





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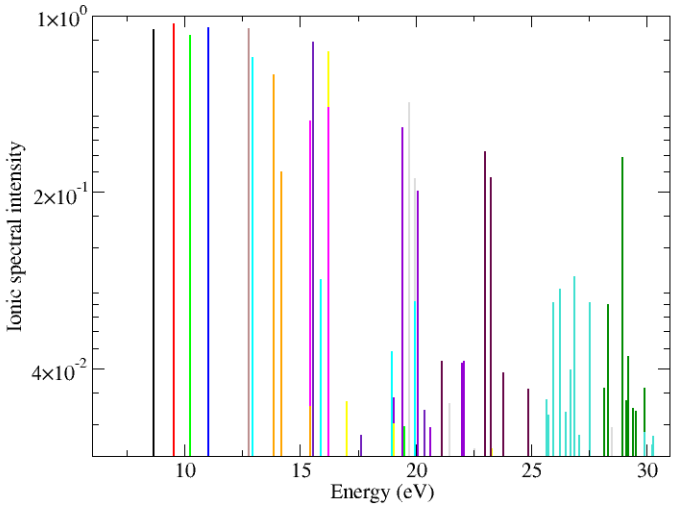
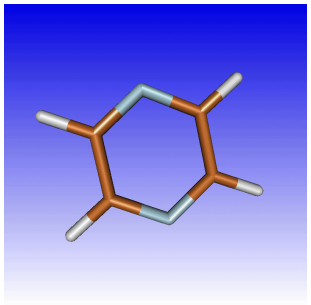
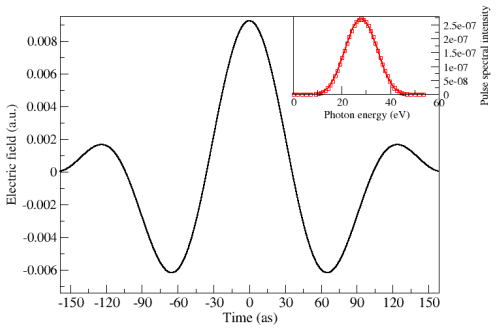
Deviation from sudden approximation: the case of pyrazine





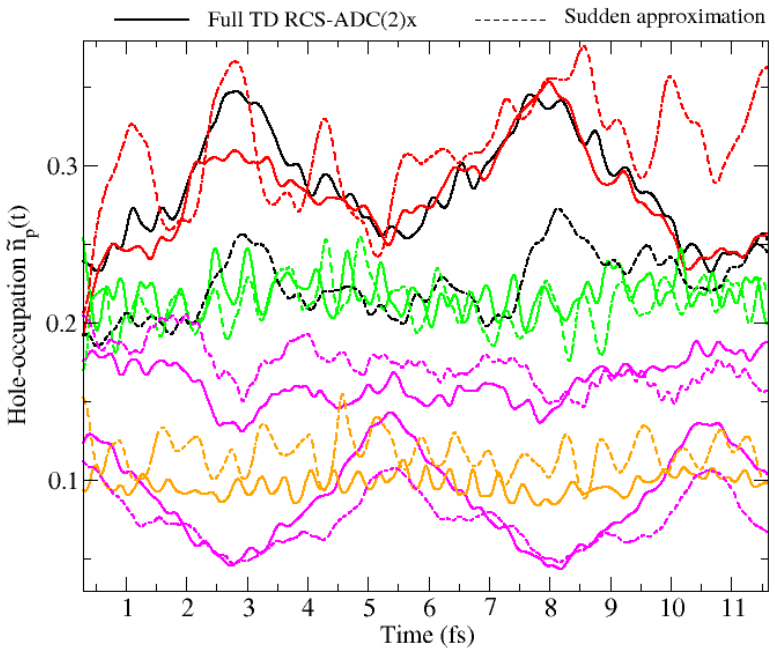


Central photon energy = 25 eV
Intensity = 3 x 10^{11} W/cm^2

Sudden approximation guess for the initial state (**when is it valid...?**)

$$| \Psi^{N-1}_{initial} \rangle \sim a_i \; | \Psi^{N}_{0} \rangle$$

Charge dynamics assuming the initial state to be a coherent superposition of simple holes in orbital i,j lying within the pulse energy bandwidth.



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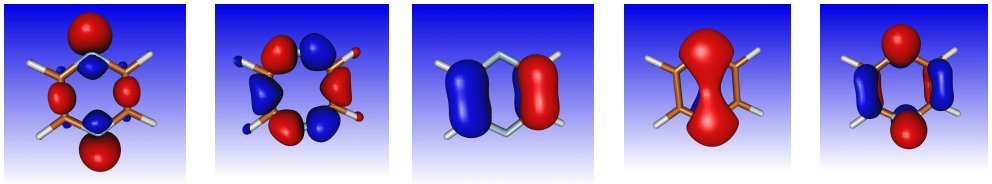
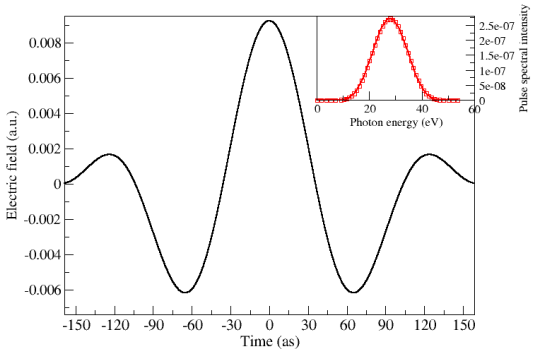
Charge dynamics and ionic coherence evolution after attosecond ionization of pyrazine

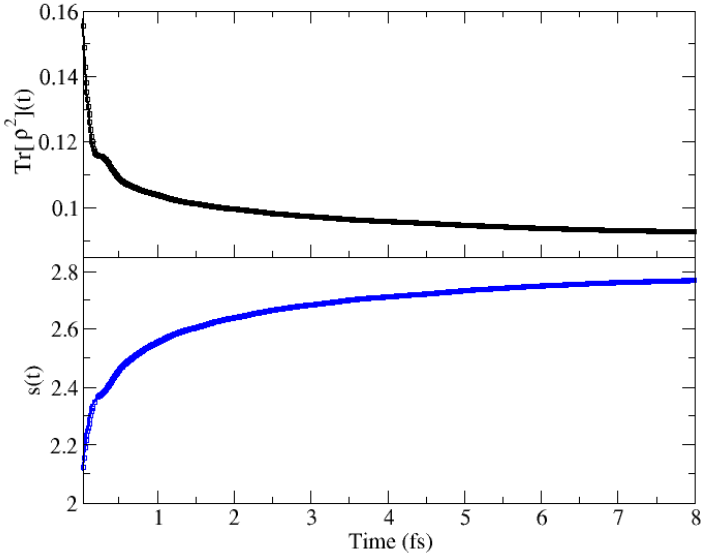
Natural charge orbitals

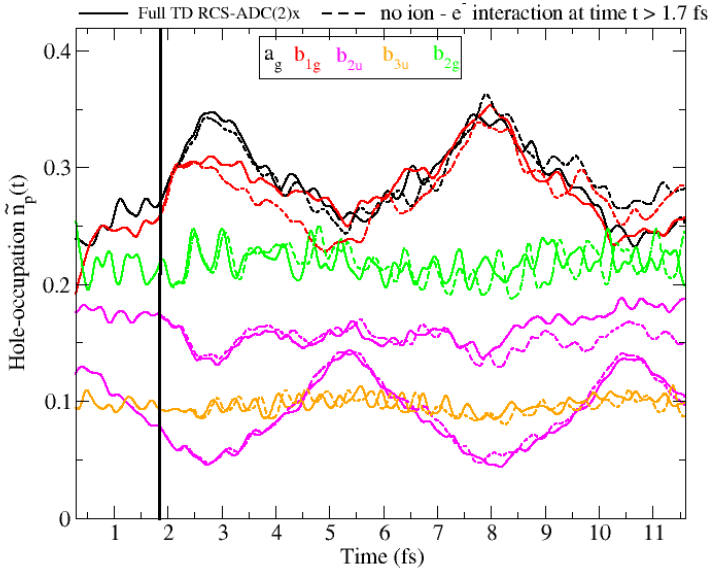




Central photon energy = 25 eV
Intensity = 3 x 10^{11} W/cm^2

Ionic decoherence due to coupling to the emitted (slower) photoelectron





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Attosecond X-ray Transient Absorption probe of charge dynamics and ionic coherence evolution upon XUV attosecond ionization of pyrazine

Attosecond XUV pump -
- attosecond X-ray probe
of charge dynamics.

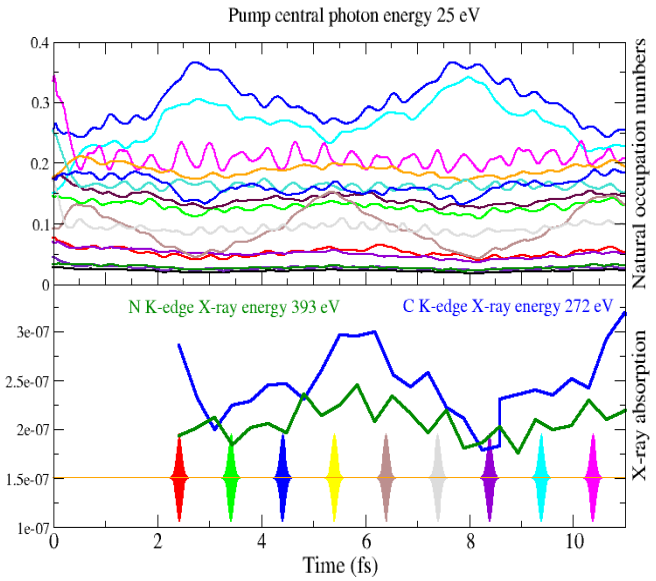
•High temporal resolution.

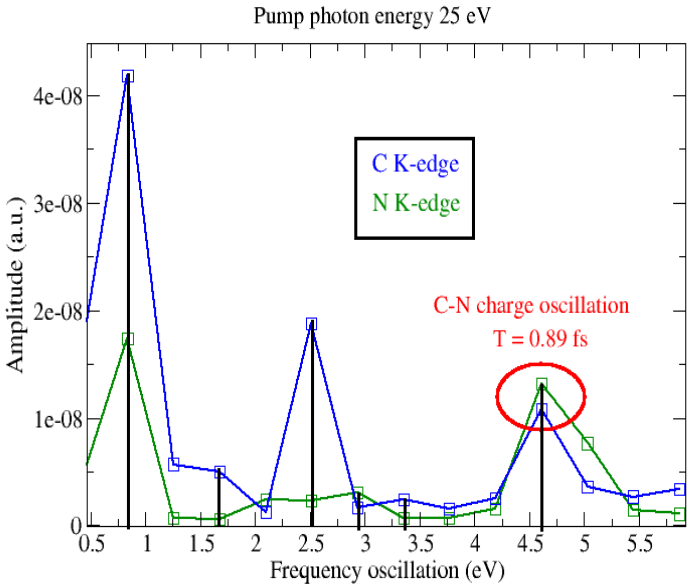
•Core shell:
chemical selectivity,

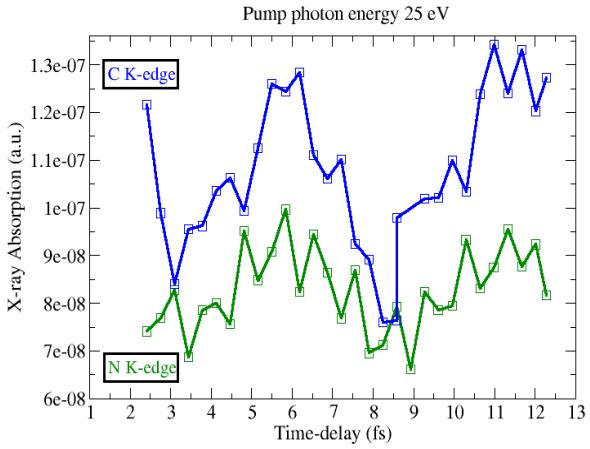
XUV pump photon energy **25 eV**

X-ray probe
Duration = 400 as
Intensity = 10^{12} W/cm^2
C K-edge photon energy = 272 eV

N K-edge photon energy = 393 eV







[M. Ruberti, manuscript in preparation]

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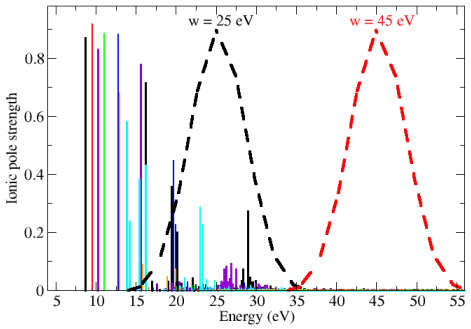
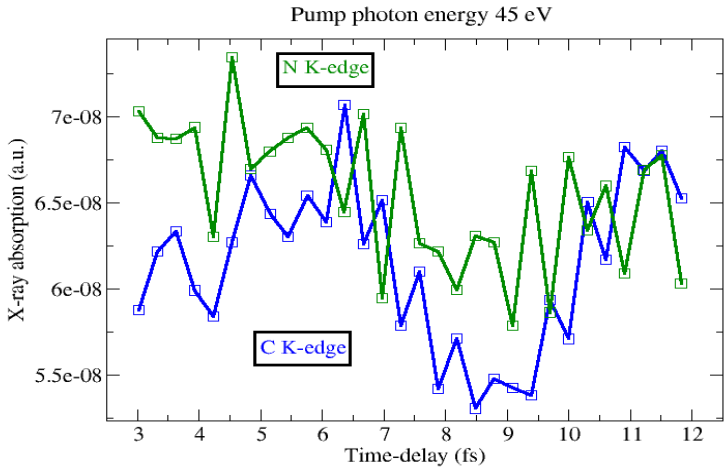
Attosecond X-ray Transient Absorption probe of charge dynamics and ionic coherence evolution upon XUV attosecond ionization of pyrazine

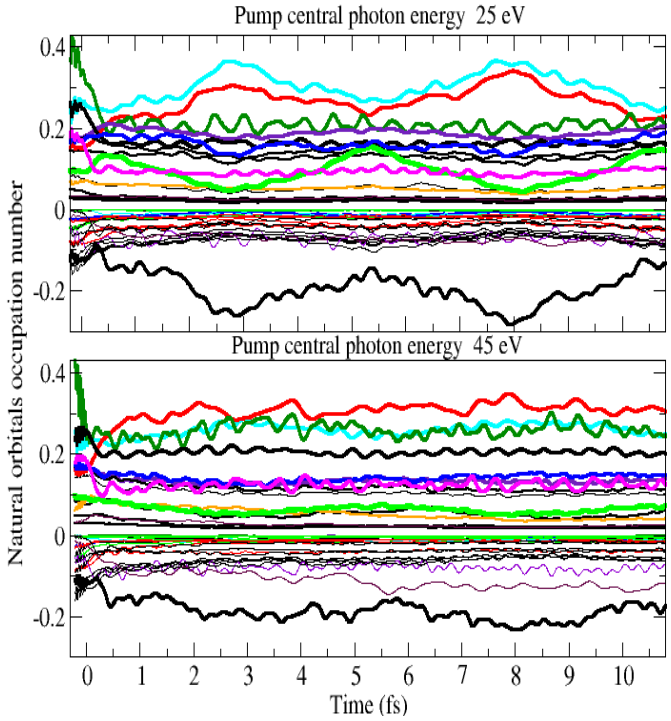


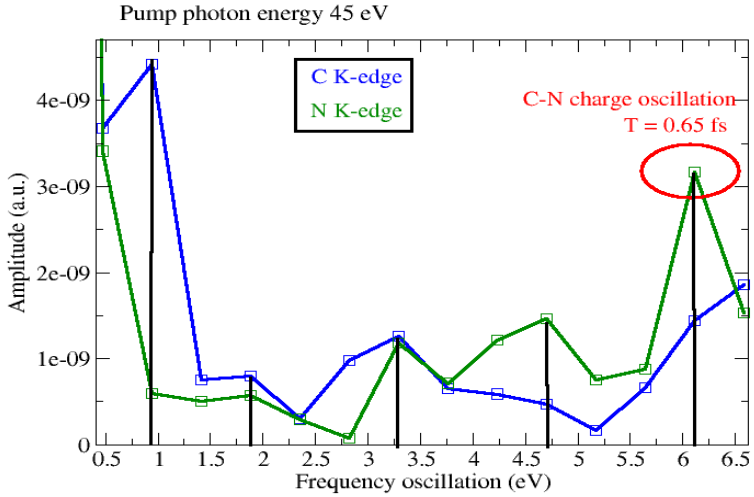
XUV pump photon energy **45 eV**

X-ray probe
Duration = 400 as
Intensity = 10^{12} W/cm^2
C K-edge photon energy = 272 eV

N K-edge photon energy = 393 eV







[M. Ruberti, manuscript in preparation]

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Conclusions

- We have developed a new unique capability: the time dependent B-spline RCS-ADC *ab initio* method, which describes many-electron ionization dynamics in polyatomic molecules beyond the sudden approximation with inclusion of relaxation and correlation effects (such as shake-up) and full description of the photoelectron.

- In particular it allows us to calculate, *ab initio* in the molecular case, electronic coherence/entanglement formation, and the ensuing ultrafast hole dynamics, as a function of the ionizing pulse parameters.

- Going beyond the sudden approximation is necessary in the lower photoelectron energy regime.

- When slow photoelectrons are produced, the onset of the ionic decoherence due to the interchannel coupling with the emitted photoelectron can last long enough (a few femtoseconds) to interplay with the decoherence induced by nuclear motion.

- Attosecond X-rays pulses: high temporal resolution, high spatial resolution, high intensity
  (variety of non-linear spectroscopic techniques possible)

- Quantum coherence decay mechanisms: residual interaction with slow photoelectrons, Auger decay, coupling to nuclear motion, ground vibrational state spread.

- Unravelling the interplay between these mechanisms is the next theoretical (and computational) and experimental challenge...

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Thank you for your attention

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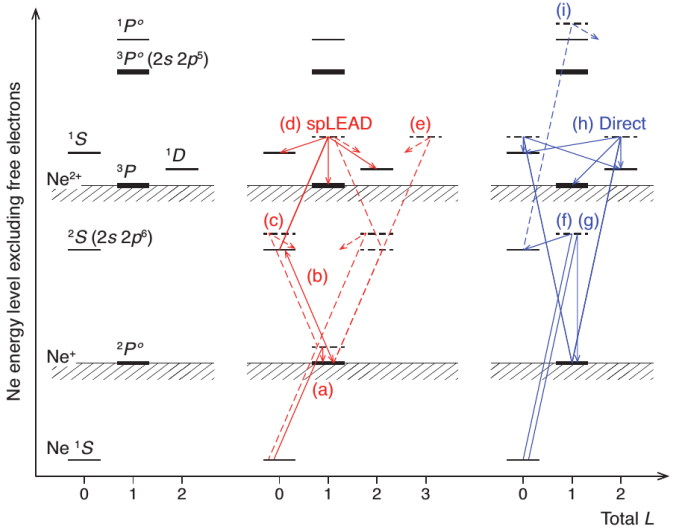
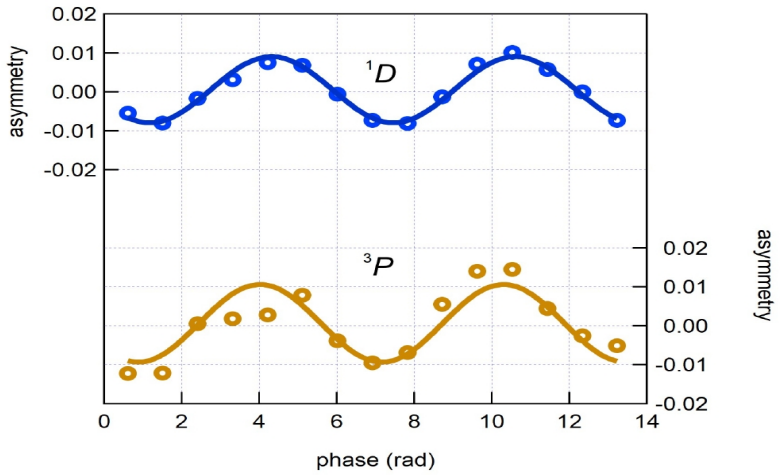
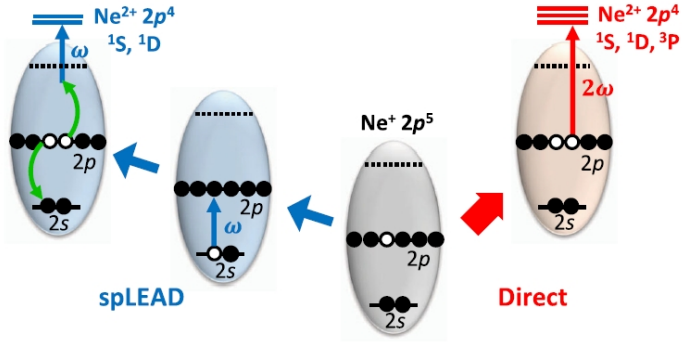
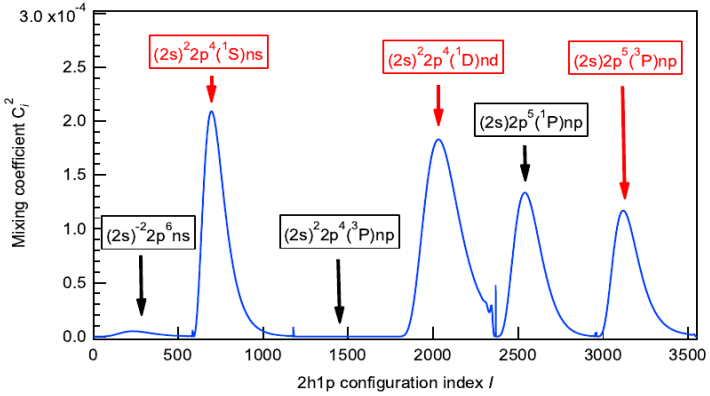
Coherent control interferometric techniques: coherent control of spLEAD photoelectron angular distribution in atoms









$$\mathcal{E} = \mathcal{E}_1 \cos(\omega t) + \mathcal{E}_2 \cos(2\omega t + \phi)$$

collinear linearly-polarised fields with well-controlled relative phase

[D. You, K. Ueda, M. Ruberti et al., 2019 New J. Phys. in press https://doi.org/10.1088/1367-2630/ab520d ; Cooper & Averbukh, PRL **111**, 083004 (2013)]

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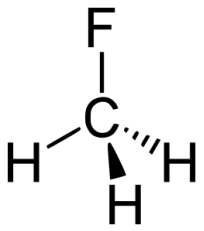
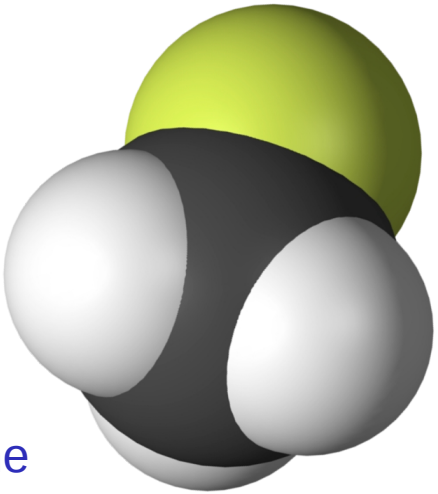
Coherent control interferometric techniques: coherent control of Auger/spLEAD total ionisation yield in molecules

For oriented molecules

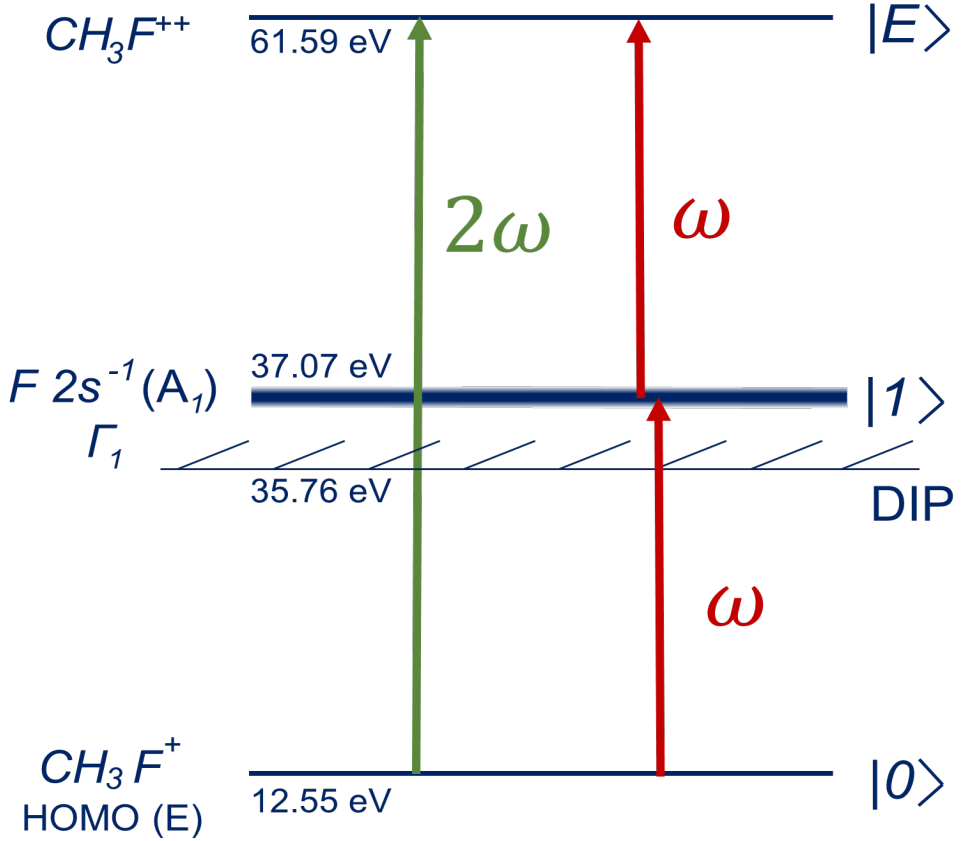
$C_s,\ C_n,\ C_{nv},\ C_{\infty v},\ C_{3h},\ D_3,\ D_{3h},$ and T_d

not merely angular distribution but more fundamentally the total yield of the electrons can be coherently controlled





Fluoromethane



$$\mathcal{E} = \mathcal{E}_1 \cos(\omega t) + \mathcal{E}_2 \cos(2\omega t + \phi)$$

[M. Khokhlova, B. Cooper, K. Ueda, K. C. Prince, P. Kolorenč, M. Yu. Ivanov, and V. Averbukh, Phys. Rev. Lett. **122**, 233001 (2019)]

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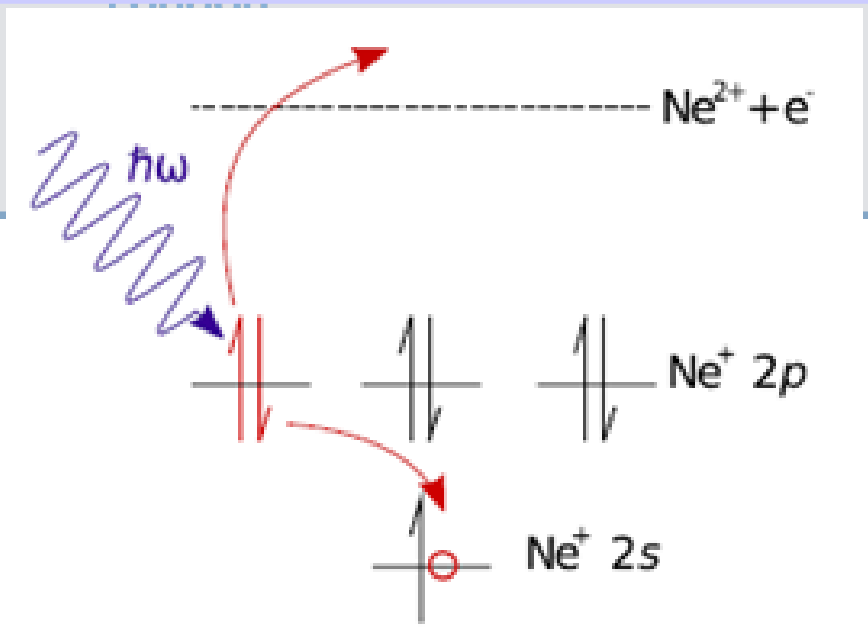
Conclusions

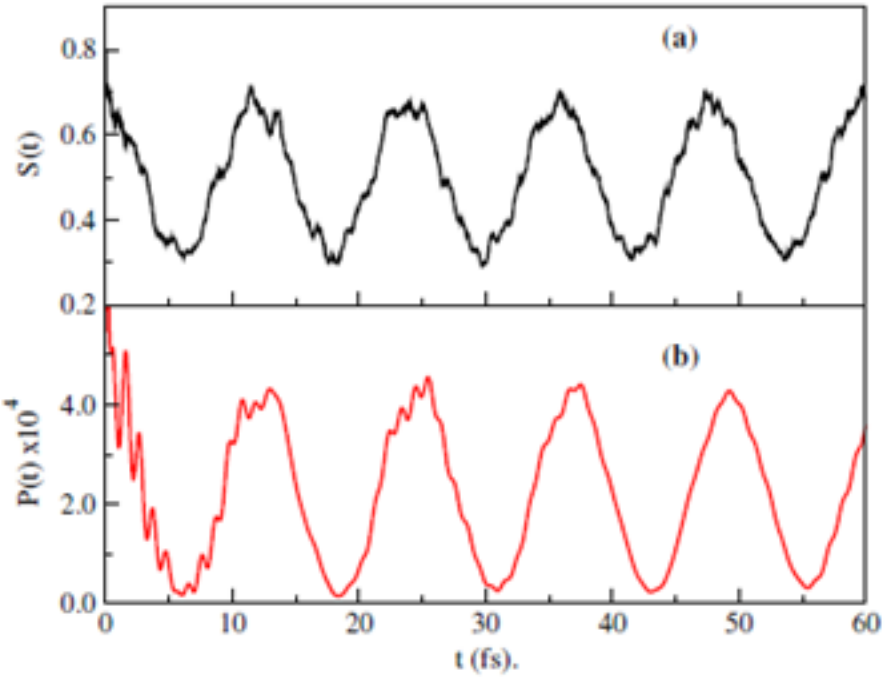
- We have developed a new unique capability: the time dependent B-spline RCS-ADC a*b initio* method, which describes many-electron ionization dynamics in polyatomic molecules beyond the sudden approximation with inclusion of relaxation and correlation effects (such as shake-up) and full description of the photoelectron.
- In particular it allows us to calculate, *ab initio* in the molecular case, electronic coherence/entanglement formation, and the ensuing ultrafast hole dynamics, as a function of the ionizing pulse parameters.
- Going beyond the sudden approximation is necessary in the lower photoelectron energy regime.
- When slow photoelectrons are produced, the onset of the ionic decoherence due to the interchannel coupling with the emitted photoelectron can last long enough (a few femtoseconds) to interplay with the decoherence induced by nuclear motion.
- Timescales discussion + probe feature. Attosecond X-rays pulses: high temporal resolution, high spatial resolution, high intensity (variety of non-linear spectroscopic techniques possible)
- Quantum coherence decay mechanisms: residual interaction with slow photoelectrons, Auger decay, coupling to nuclear motion, ground vibrational state spread.
- Unravelling the interplay between these mechanisms is the next theoretical (and computational) challenge...
- We have developed an analytical theory of coherent control of a normal Auger decay and spLEAD in molecules (Molecular Auger Interferometry)
- Total yield of the photoelectrons or doubly ionised oriented molecules of particular point groups can be controlled and Auger decay lifetime can be reconstructed from the relative ω/2ω phase scan of the photoelectron total yield modulations
- The interference contrast of the total yield can be maximised at any decay width by controlling the ratio of the ω- and 2ω-field intensities. Proposed interferometric measurement is free of the limitations of both high-resolution Auger electron spectroscopy and attosecond time-resolved spectroscopy

Single-photon laser-enabled Auger decay (spLEAD)



Cooper & Averbukh,
"Single-Photon Laser-Enabled Auger Spectroscopy for Measuring Attosecond Electron-Hole Dynamics",
PRL 111, 083004 (2013)

ab initio calculations for inner-valence hole migration in glycine



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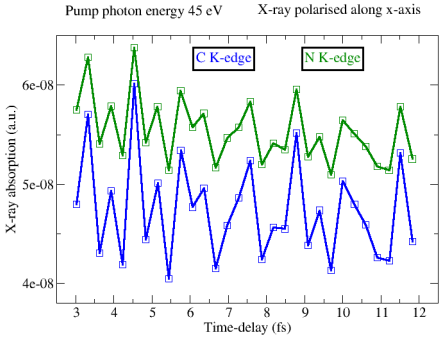
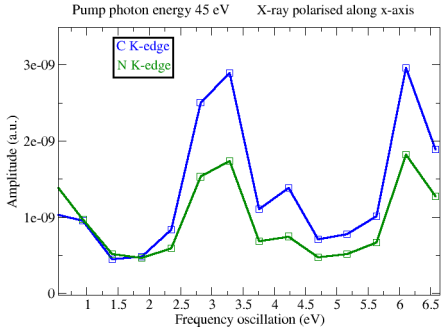
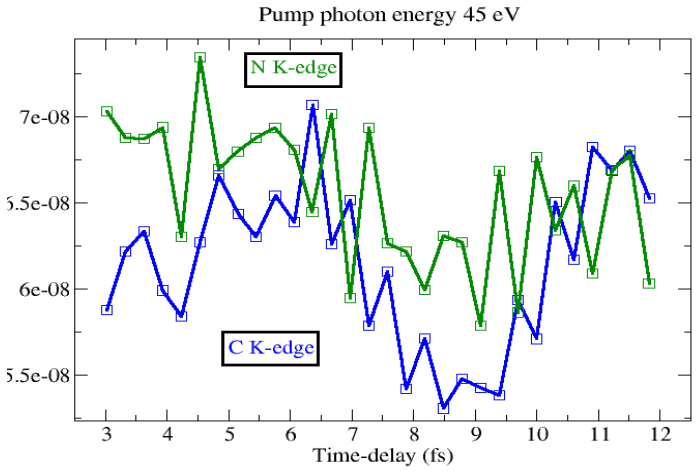
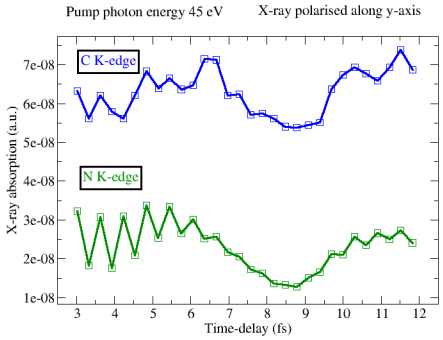
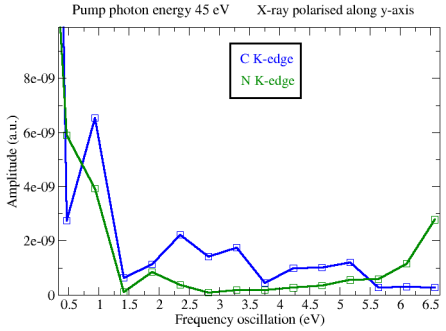
Attosecond X-ray Transient Absorption probe of charge dynamics and ionic coherence evolution upon XUV attosecond ionization of pyrazine

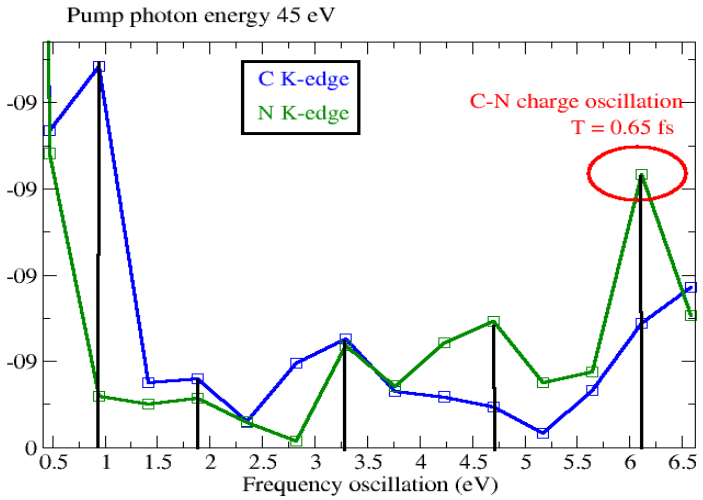


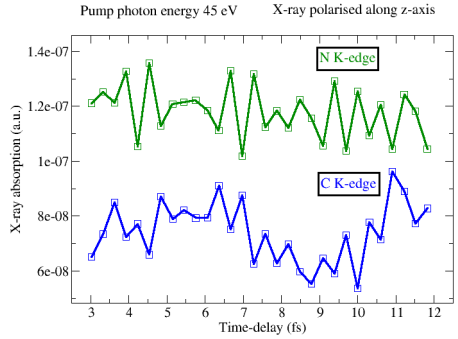


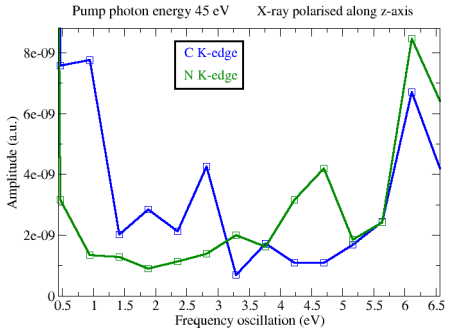












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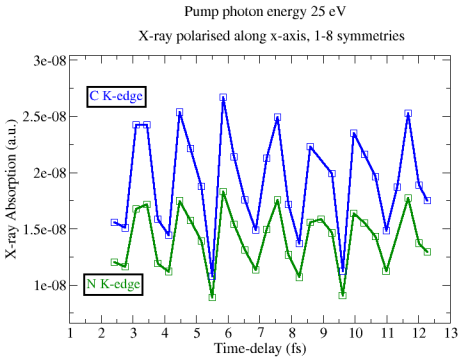
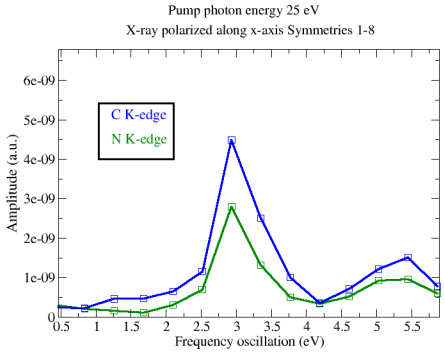
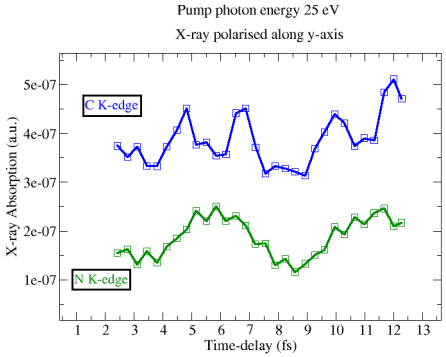
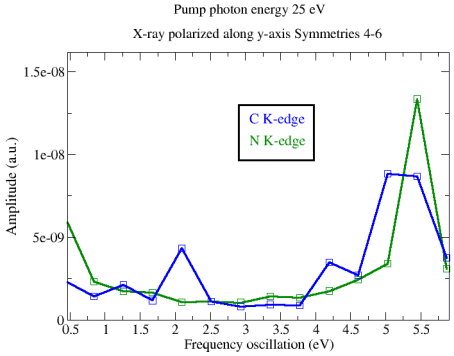
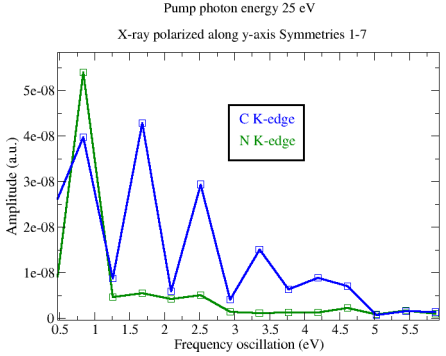
Attosecond X-ray Transient Absorption probe of charge dynamics and ionic coherence evolution upon XUV attosecond ionization of pyrazine

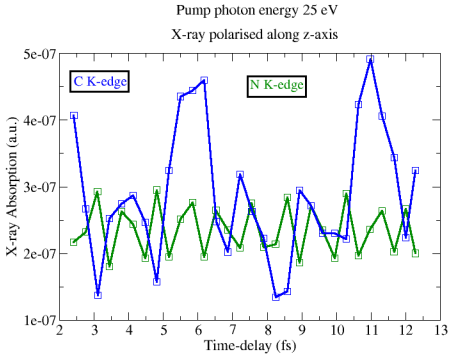


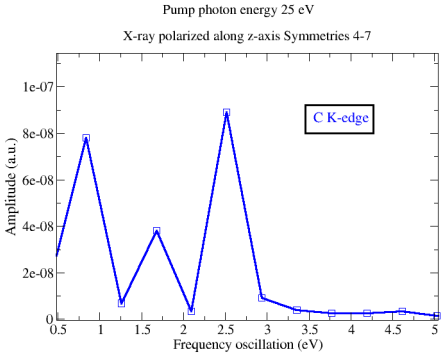


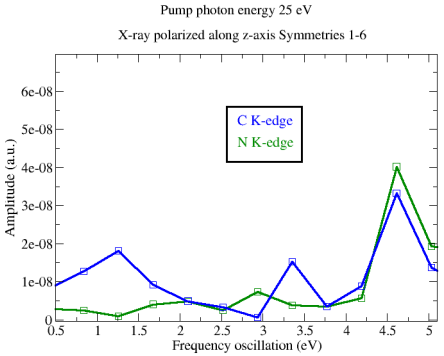












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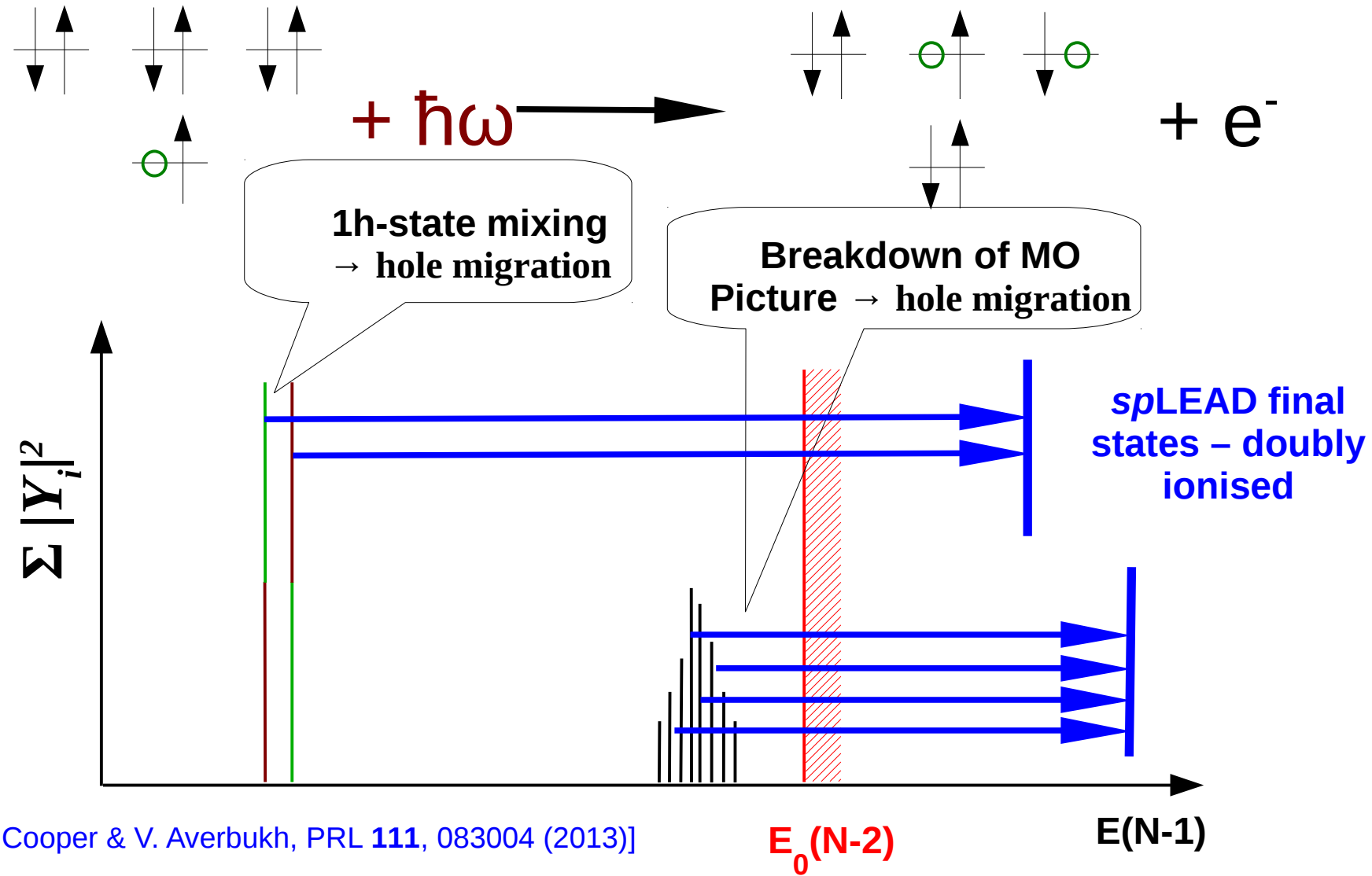
How to probe coherences between principal and shake-up states: Single-photon laser-enabled Auger decay



[B. Cooper & V. Averbukh, PRL **111**, 083004 (2013)]

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Outline

- Ionic coherence after attosecond ionization.
- **Time dependent B-spline restricted correlation space (RCS) ADC** *ab initio* method for molecular ionization.
- Ionic density matrix, decoherence and charge dynamics following attosecond XUV ionization: C_2H_2, C_2H_4 , $C_4H_4N_2$. Deviation from the sudden approximation picture.
- Mechanisms of ionic coherence formation in strong IR field ionization of CO_2.
- Conclusions

Conclusion

We developed an analytical theory of coherent control of a normal Auger decay and spLEAD in molecules (Molecular Auger Interferometry)

- Total yield of the photoelectrons or doubly ionised oriented molecules of particular point groups can be controlled
- Auger decay lifetime can be reconstructed from the relative ω/2ω phase scan of the photoelectron total yield modulations
- The interference contrast of the total yield can be maximised at any decay width by controlling the ratio of the ω- and 2ω-field intensities

Proposed interferometric measurement is free of the limitations of both high-resolution Auger electron spectroscopy and attosecond time-resolved spectroscopy

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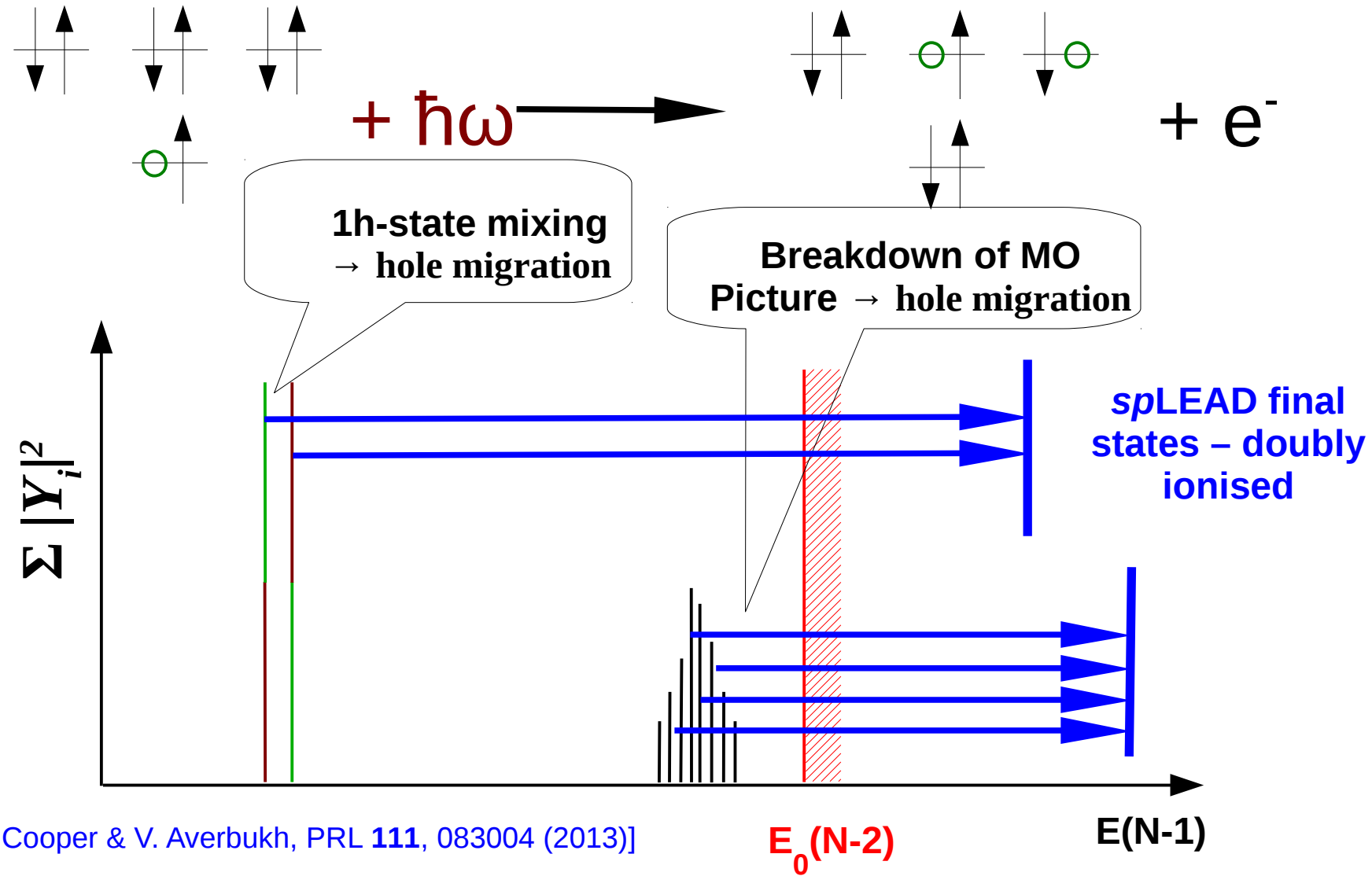
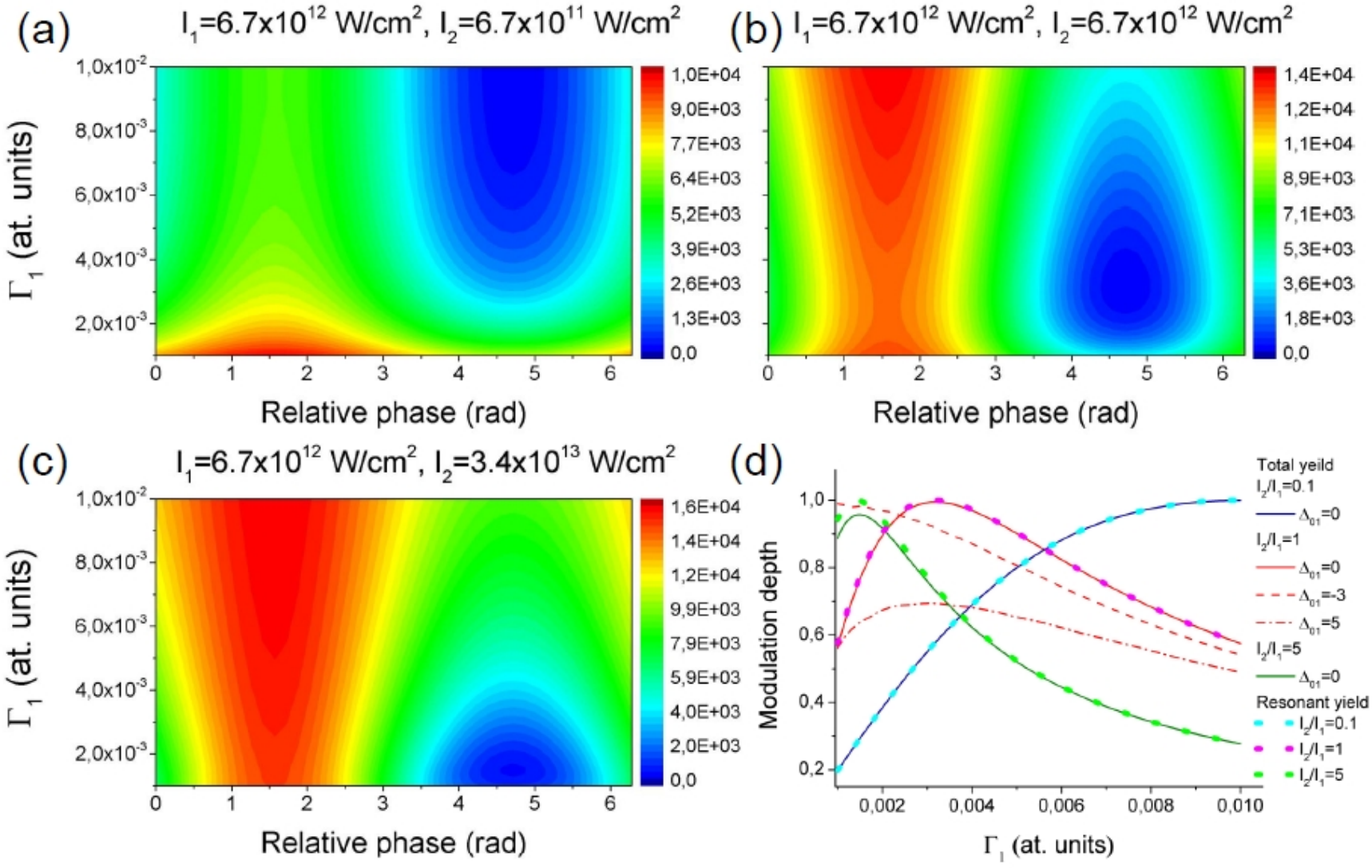
How to probe coherences between principal and shake-up states: Single-photon laser-enabled Auger decay



[B. Cooper & V. Averbukh, PRL **111**, 083004 (2013)]

Molecular Auger interferometry. Mapping



Auger state width can be retrieved from the modulations of the photoelectron (ionic) yield

$$|c_E^r|^2 = 1/(4\pi^2|d_{0E}|^2 I_2) \qquad |c_E^r|^2 = |d_{1E}/d_{01}|^2$$

$$\Gamma_1 = \frac{1-\sqrt{1-\mathcal{M}^2}}{\mathcal{M}} \frac{V_{01}V_{1E}}{V_{0E}}$$

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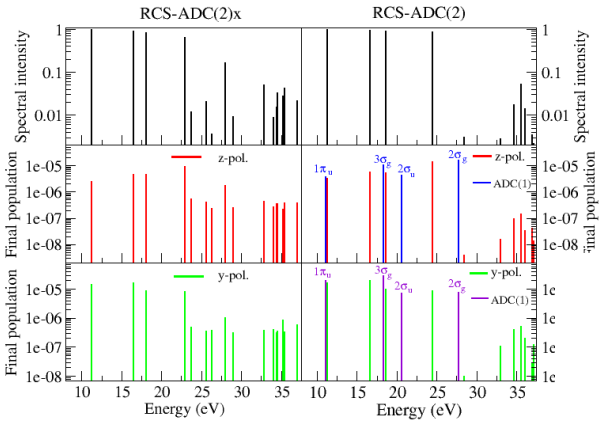
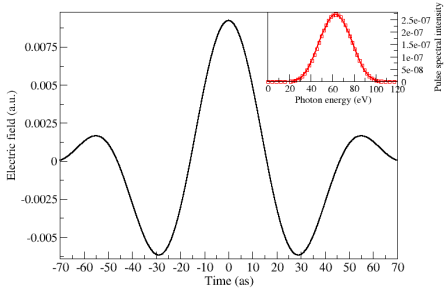
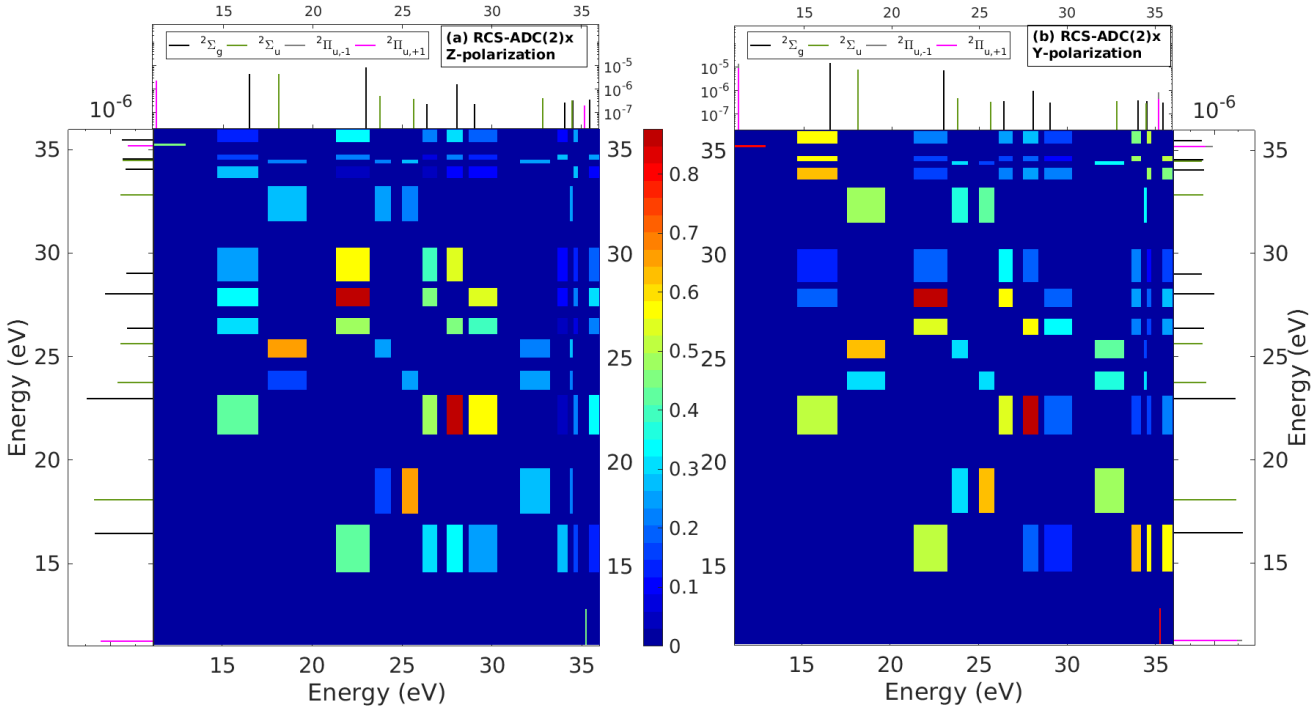
Reduced ionic density matrix after attosecond XUV ionization of C_2H_2

Ionic populations





Ionic coherences



Mean photon energy = 63 eV
Intensity = 3 x 10^{11} W/cm^2

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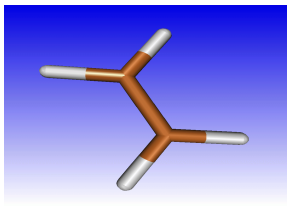
Deviations from the sudden approximation

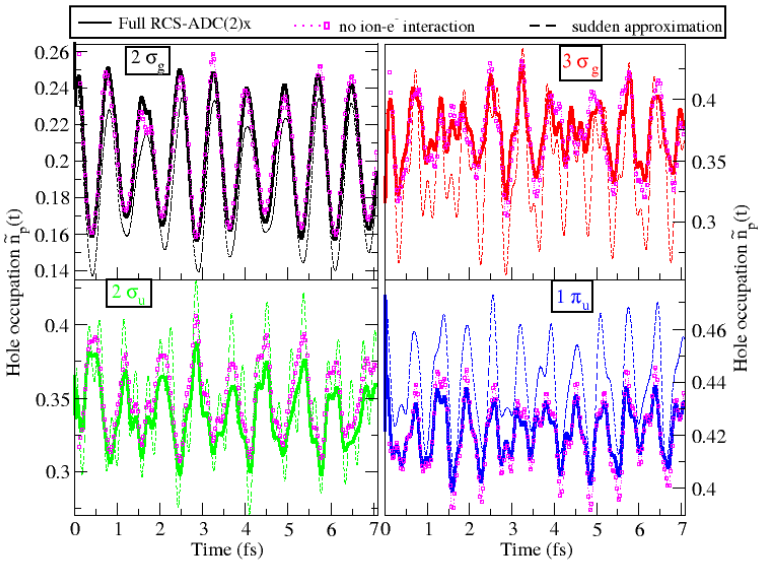
Sudden approximation guess for the initial state (**when is it valid...?**)

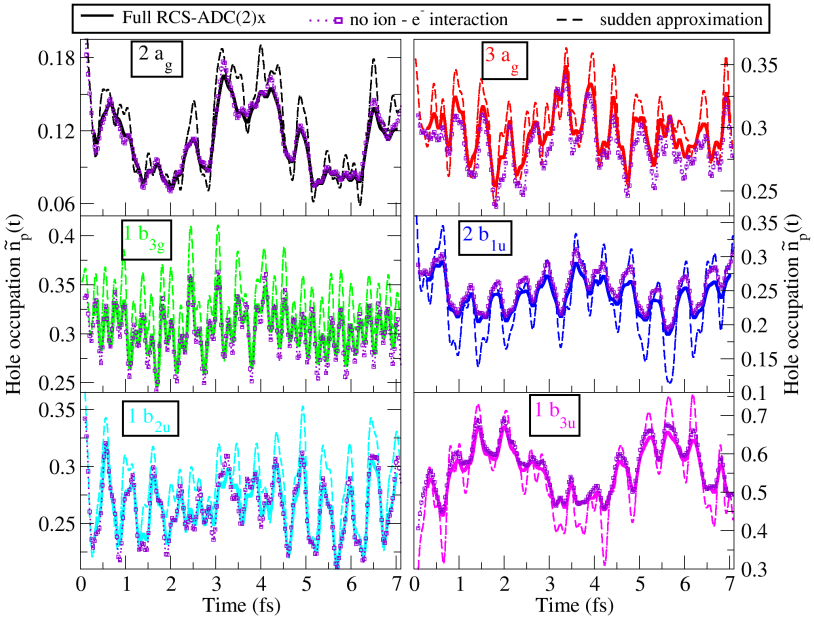
$$\{ \quad |\Psi^{N-1}_{initial}\rangle \sim a_i \; |\Psi^{N}_{0}\rangle$$

Charge dynamics assuming the initial state to be a coherent superposition of simple holes in orbital i,j lying with the pulse energy bandwidth

Mean photon energy = 63 eV
Intensity = 3 x 10^{11} W/cm^2







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Interchannel-couplings: build-up of coherence

$$\rho_{mn}^{R-IDM}(t) = \sum_{\mu} \langle \tilde{\Psi}_{\mu,m}^{N} \mid \Psi^{N}(t) \rangle \langle \Psi^{N}(t) \mid \tilde{\Psi}_{\mu,n}^{N} \rangle = \sum_{\mu} c_{m\mu}(t)\, c_{n\mu}^{*}(t)$$

$$\hat{\rho}(t) = \mid \Psi^{N}(t) \rangle \langle \Psi^{N}(t) \mid$$

$$\hat{\rho}^{R-IDM}(t) = Tr_{\mu}[\hat{\rho}(t)]$$

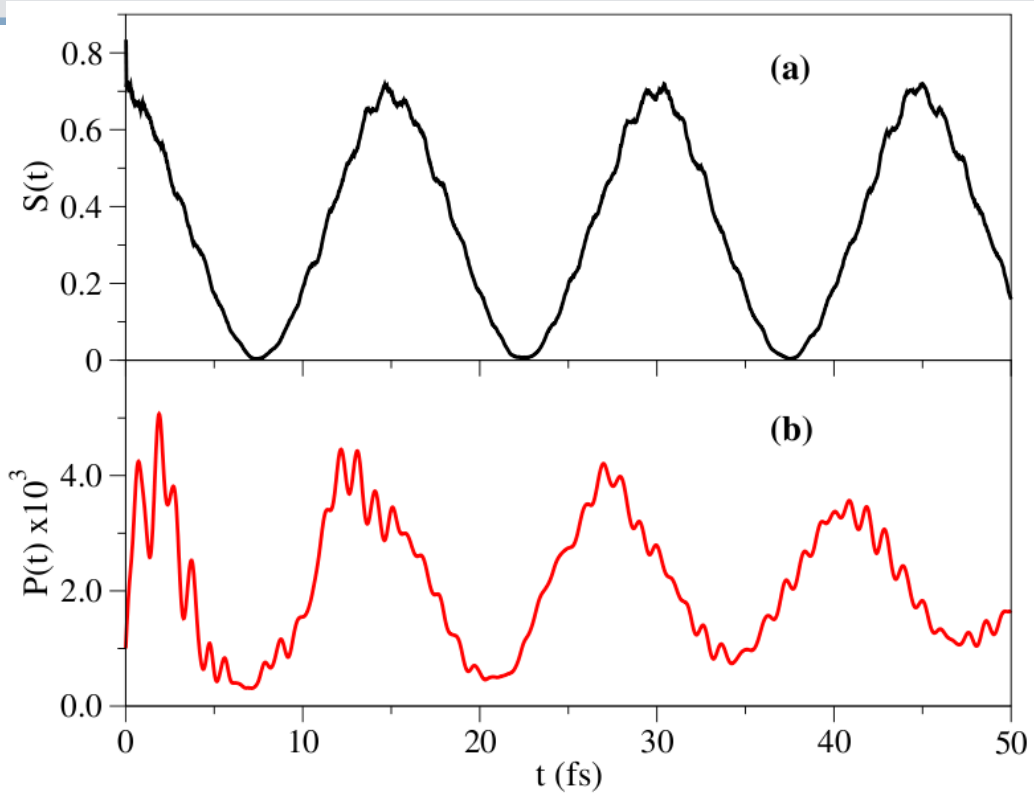
$$\mathbf{H}^{RCS-ADC(n)} = \begin{pmatrix} \mathbf{H}_{RCS}^{ADC(n)} & \left\langle \tilde{\Psi}_{I_{RCS}}^{N} \left| \hat{\tilde{H}} \hat{c}_{\nu}^{\dagger} \right| \Psi_{m}^{N-1} \right\rangle^{ADC(n)} \\ \left\langle \Psi_{m}^{N-1} \left| \hat{c}_{\mu} \hat{\tilde{H}} \right| \tilde{\Psi}_{I_{RCS}}^{N} \right\rangle^{ADC(n)} & \left\langle \Psi_{m}^{N-1} \left| \hat{c}_{\mu} \hat{\tilde{H}} \hat{c}_{\nu}^{\dagger} \right| \Psi_{n}^{N-1} \right\rangle^{ADC(n)} \end{pmatrix}$$

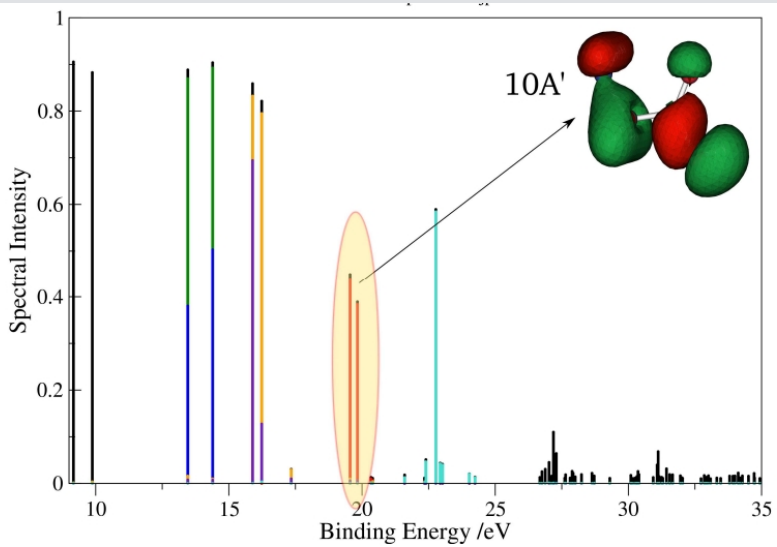
$$\left\langle \Psi_{m}^{N-1} \left| \hat{c}_{\mu} (\hat{H} - E_{0}^{RCS}) \hat{c}_{\nu}^{\dagger} \right| \Psi_{n}^{N-1} \right\rangle^{ADC(2)x} =$$

$$= \delta_{\mu\nu}\delta_{mn} \left\{ E_{m}^{(N-1),ADC(2)x} - E_{0}^{RCS} + \varepsilon_{\mu} \right\} +$$

$$+ \sum_{I_{RCS}} \sum_{J_{RCS}} V_{I_{RCS},m}^{ADC(2)x} V_{J_{RCS},n}^{ADC(2)x} \left\langle \Phi_{\mu,I_{RCS}} \left| \left(\hat{H} - E_{0}^{RCS} \right) \right| \Phi_{\nu,J_{RCS}} \right\rangle$$

*sp*LEAD spectroscopy of hole migration - glycine

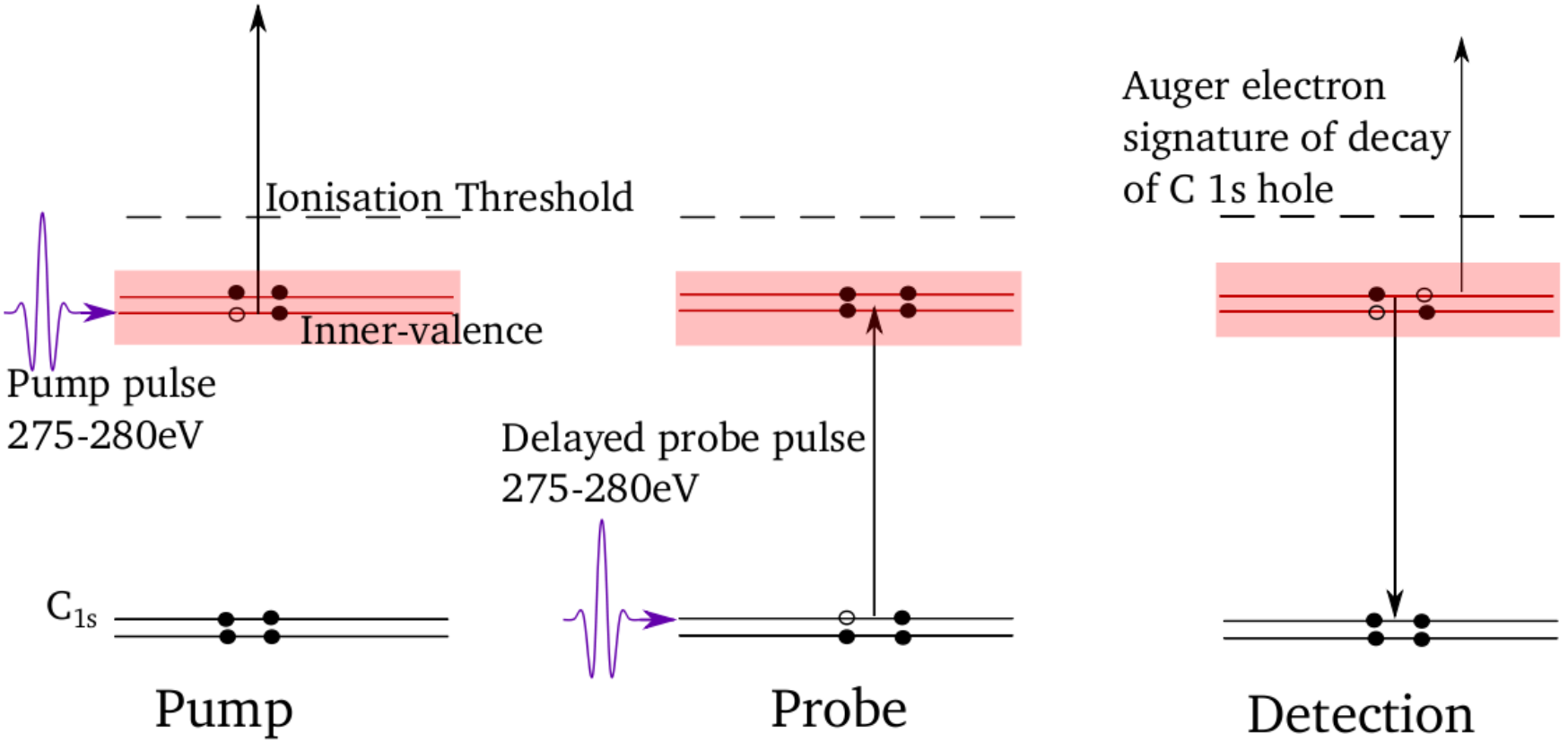




- *sp*LEAD transition probability of the 10A'-ionized state of glycine induced by a single-oscillation, 13 eV VUV pulse mimics the hole survival probability

[B. Cooper & V. Averbukh, PRL **111**, 083004 (2013)]

Time-resolved Auger spectroscopy of hole dynamics: Resonant excitation from the core



[B. Cooper *et al.*, Faraday Discussions **171**, 93 (2014]

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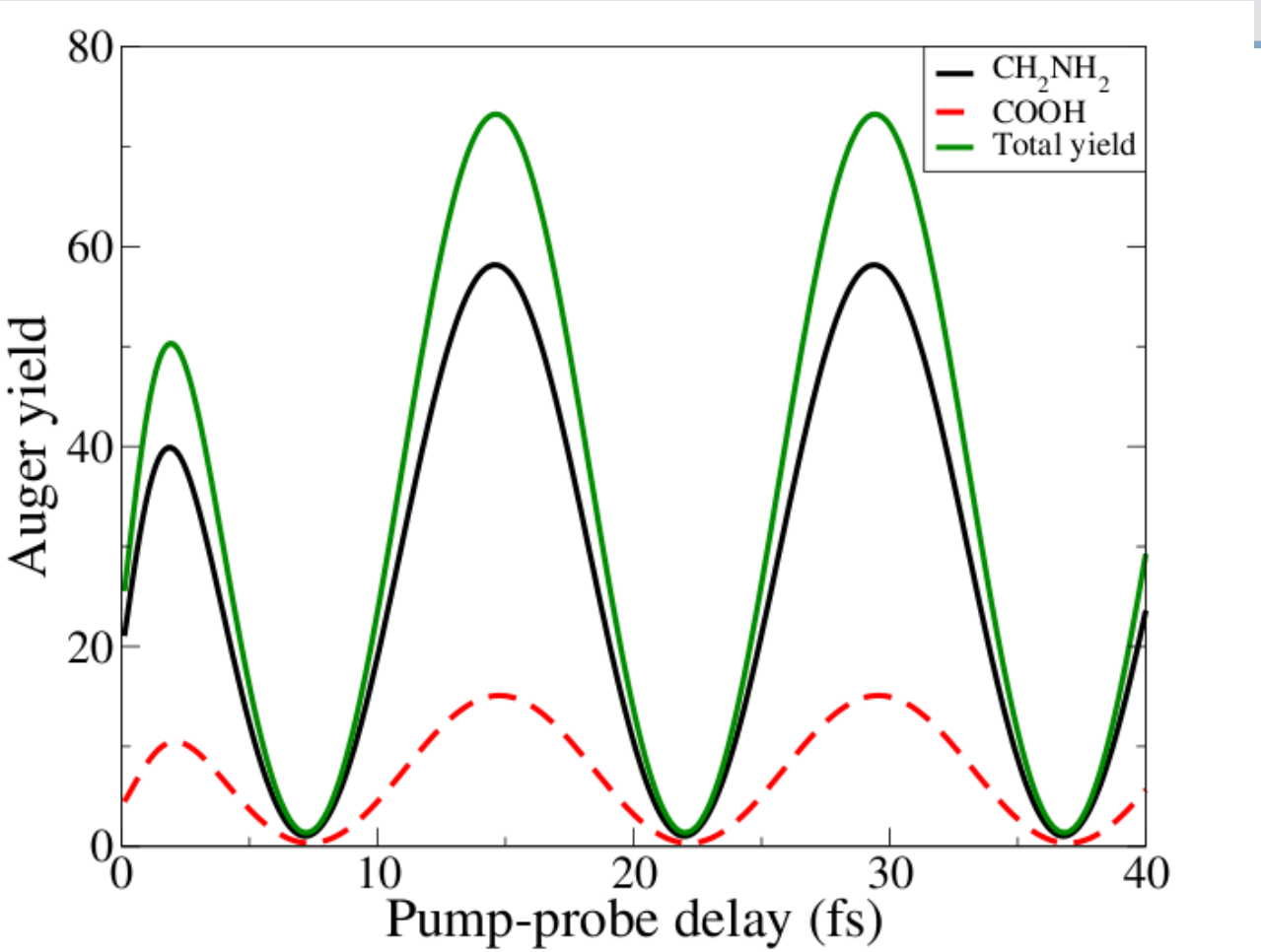
Total C 1s Auger signal follows hole migration dynamics



[B. Cooper *et al.*, Faraday Discussions **171**, 93 (2014]

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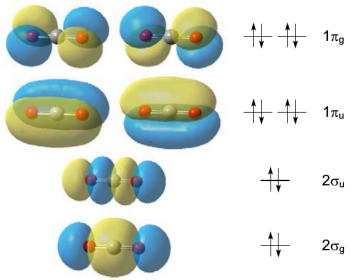
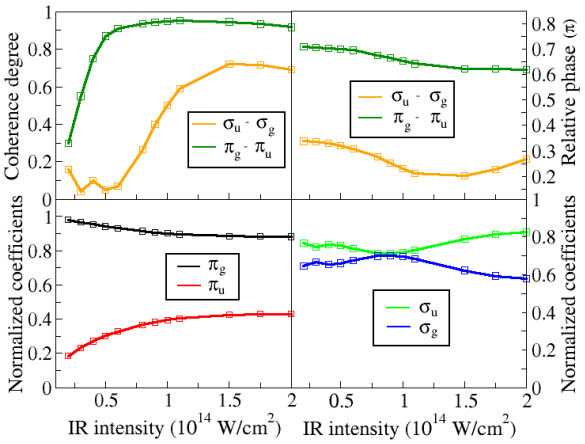
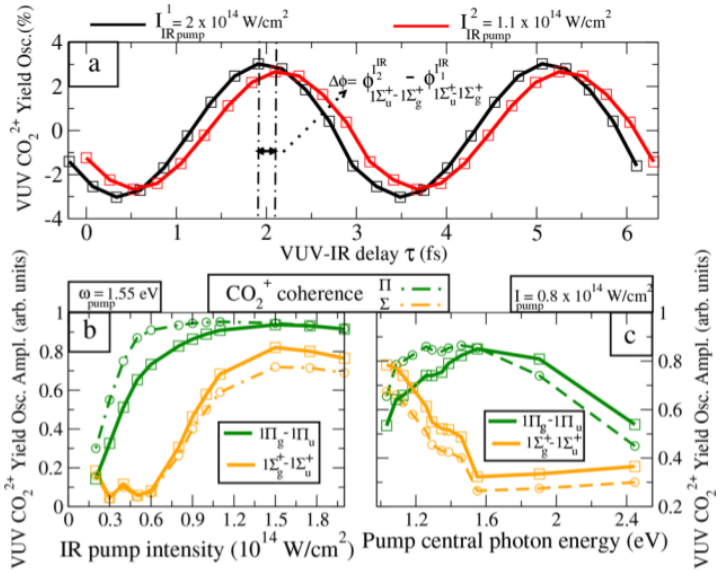
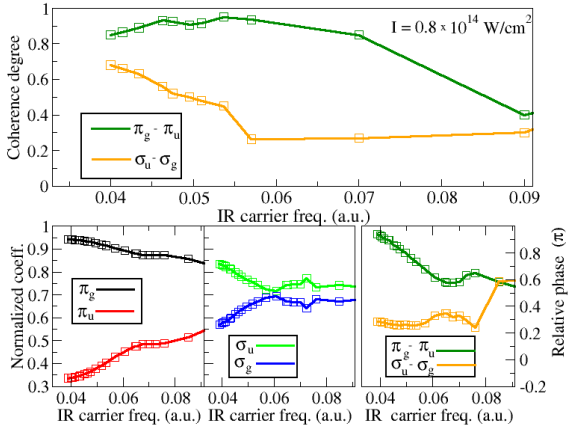
Strong Field Ionization: ADC(1) results on the coherence of CO_2 cation



$$\Psi^{\Sigma}(t) = C_{\Sigma_u} \mid \sigma_u^{-1} \rangle + C_{\Sigma_g} e^{-i(E_{\Sigma_g} - E_{\Sigma_u})t} e^{-i\phi_{\Sigma_u - \Sigma_g}} \mid \sigma_g^{-1} \rangle$$







[M. Ruberti, P. Decleva and V. Averbukh, JCTC **14**, 4991-5000 (2018)]

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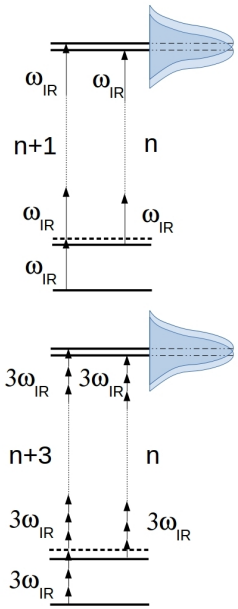
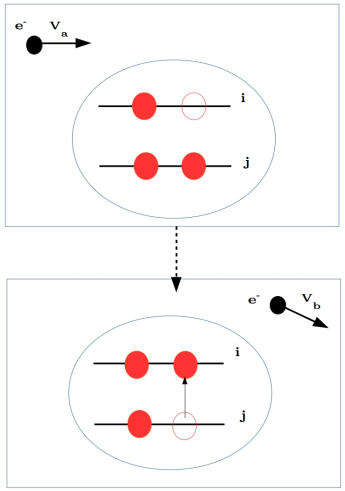
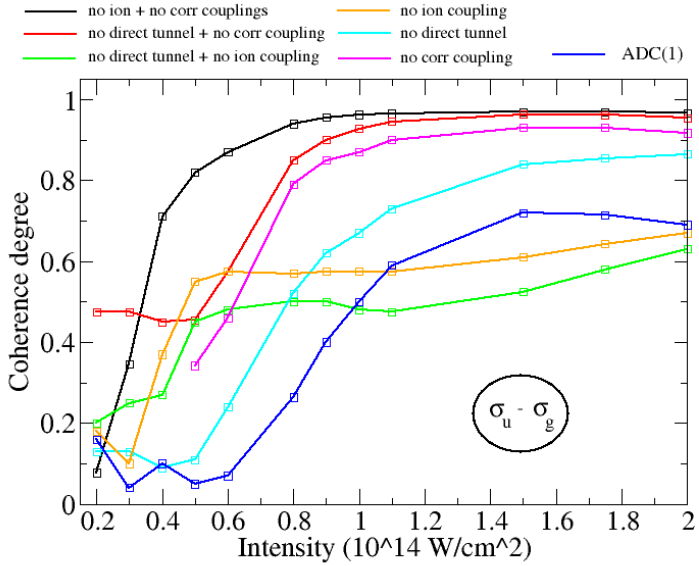
Different mechanisms contributing to the coherence formation in the multi-photon case

Direct ionization of the different ionic states into the same continuum state
(no coupling between different channels)

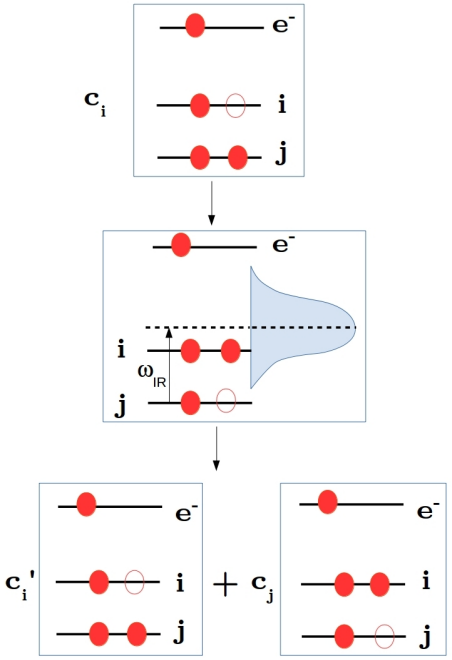


Coupling to the photoelectron





Laser-driven dipole transitions between different ionic states



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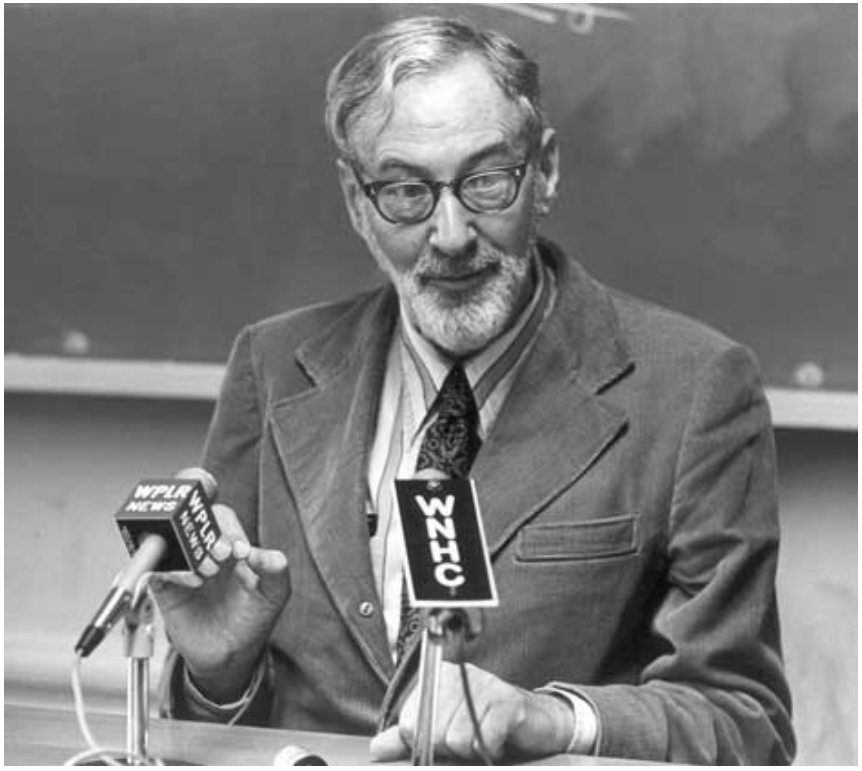
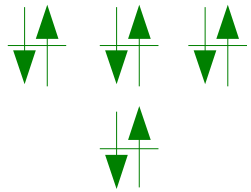
Simple theory of electron holes: Koopmans theorem



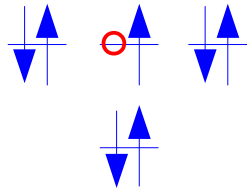
Tjalling C. Koopmans (Nobel prize winner in *economics*, 1975)

If both the ground state of the neutral and the eigenstate of the cation are well approximated by Single HF configurations:

$$\Psi_0^{(N)} = \Phi_0^{HF}$$



$$\Psi_0^{(N-1)} = \hat{a}_i \Phi_0^{HF}$$



then the corresponding ionization potential is given by the HF orbital energy:

$$IP = E_i(N-1) - E_0(N) = -\varepsilon_i$$