Time-dependent configuration interaction singles on a grid: Applications

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Nordita Program "Control of Ultrafast Quantum Phenomena"
Stockholm, May 19, 2015

Time-dependent configuration interaction singles

TDCIS

Full electronic Hamiltonian (clamped nuclei)

$$\hat{H}(t) = \hat{T} + \hat{V}_{\text{e-n}} + \hat{V}_{\text{e-e}} + \hat{V}_{\text{rel}} - \hat{\boldsymbol{D}} \cdot \mathcal{E}(t)$$

$\hat{T}$: electron kinetic energy

$\hat{V}_{\text{e-n}}$: electron–nucleus interaction

$\hat{V}_{\text{e-e}}$: electron–electron interaction

$\hat{V}_{\text{rel}}$: relativistic corrections

$-\hat{\boldsymbol{D}} \cdot \mathcal{E}(t)$: semiclassical interation of EM field with electrons

introduction of mean-field $\hat{\bar{V}}$:

$$\hat{H}(t) = \underbrace{\hat{T} + \hat{V}_{\text{e-n}} + \hat{\bar{V}}}_{\hat{H}_0} + \underbrace{\hat{V}_{\text{e-e}} - \hat{\bar{V}} + \hat{V}_{\text{rel}}}_{\hat{H}_1} - \hat{\boldsymbol{D}} \cdot \mathcal{E}(t)$$

$\rightarrow$ use one-body operator $\hat{H}_0$ to define spin orbitals:

$$\hat{H}_0 |\varphi_p\rangle = \varepsilon_p |\varphi_p\rangle$$

$$\hat{H}_0 = \sum_p \varepsilon_p \hat{c}_p^\dagger \hat{c}_p$$

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Basis for *N*-electron problem

N-electron ground state at mean-field level

$$|\Phi_0^N\rangle = \prod_{i=1}^{N} \hat{c}_i^\dagger |0\rangle$$

using the N energetically lowest spin orbitals

(unique if $|\Phi_0^N\rangle$ is closed-shell state)

basis for N-electron problem:

$$|\Phi_0^N\rangle \qquad 0\text{p} - 0\text{h}$$

$$|\Phi_i^a\rangle = \hat{c}_a^\dagger \hat{c}_i |\Phi_0^N\rangle \qquad 1\text{p} - 1\text{h}$$

$$|\Phi_{ij}^{ab}\rangle = \hat{c}_a^\dagger \hat{c}_b^\dagger \hat{c}_j \hat{c}_i |\Phi_0^N\rangle \qquad 2\text{p} - 2\text{h}$$

$$\vdots$$

$\rightarrow$ general N-electron solution to TDSE

$$i\frac{\partial}{\partial t}|\Psi^N, t\rangle = \hat{H}(t)|\Psi^N, t\rangle$$

may be written

$$|\Psi^N, t\rangle = \alpha_0(t)|\Phi_0^N\rangle + \sum_{i,a} \alpha_i^a(t)|\Phi_i^a\rangle + \dots$$

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Hartree-Fock mean field for *N*-electron ground state

If and only if

$$\hat{\hat{V}} = \sum_{p,q} \left\{ \sum_i [v_{piqi} - v_{piiq}] \right\} \hat{c}_p^\dagger \hat{c}_q,$$

where

$$v_{pqrs} = \int d^3x_1 \int d^3x_2 \varphi_p^\dagger(\boldsymbol{x}_1)\varphi_q^\dagger(\boldsymbol{x}_2)\frac{1}{|\boldsymbol{x}_1 - \boldsymbol{x}_2|}\varphi_r(\boldsymbol{x}_1)\varphi_s(\boldsymbol{x}_2),$$

then, neglecting $\hat{V}_{\text{rel}}$,

$$\langle \Phi_0^N | \hat{H}_0 + \hat{H}_1 | \Phi_i^a \rangle = 0 \qquad \text{(Brillouin)}$$

and

$$\langle \Phi_i^{N-1} | \hat{H}_0 + \hat{H}_1 | \Phi_j^{N-1} \rangle - \langle \Phi_0^N | \hat{H}_0 + \hat{H}_1 | \Phi_0^N \rangle \delta_{ij} = -\varepsilon_i \delta_{ij}, \qquad \text{(Koopmans)}$$

where

$$|\Phi_i^{N-1}\rangle = \hat{c}_i |\Phi_0^N\rangle.$$

Note that the matrix $\langle \Phi_i^a | \hat{H}_0 + \hat{H}_1 | \Phi_j^b \rangle$ is not diagonal with respect to i, j (or a, b) $\rightarrow$ *interchannel coupling*

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Implementation using a radial grid

$$|\Psi(t)\rangle = \alpha_0(t)|\Phi_0\rangle + \sum_{i,a} \alpha_i^a(t)\left|\Phi_i^a\right\rangle,$$

$$|\Phi_i^a\rangle = \frac{1}{\sqrt{2}}\{\hat{c}_{a+}^\dagger \hat{c}_{i+} + \hat{c}_{a-}^\dagger \hat{c}_{i-}\}|\Phi_0\rangle,$$

$$\hat{H}(t) = \hat{F}_{\mathrm{CAP}} + \hat{V}_C - \hat{V}_{\mathrm{HF}} - E_{\mathrm{HF}} - \mathcal{E}(t)\hat{z},$$

$$\hat{F}_{\mathrm{CAP}} = \hat{F} - i\eta\hat{W},$$

$$i\dot{\alpha}_0(t) = -\sqrt{2}\mathcal{E}(t)\sum_{i,a}\alpha_i^a(t) z_{(i,a)},$$

$$i\dot{\alpha}_i^a(t) = (\varepsilon_a - \varepsilon_i)\alpha_i^a(t) + \sum_{i',a'}\alpha_{i'}^{a'}(t)(2v_{(a,i',i,a')} - v_{(a,i',a',i)}) - \mathcal{E}(t)\left\{\sqrt{2}\alpha_0(t) z_{(a,i)} + \sum_{a'}\alpha_i^{a'}(t) z_{(a,a')} - \sum_{i'}\alpha_{i'}^a(t) z_{(i',i)}\right\}.$$

L. Greenman et al., Phys. Rev. A **82**, 023406 (2010)

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Our papers on grid-based TDCIS

- Methodology

N. Rohringer, A. Gordon, and R. Santra, Phys. Rev. A **74**, 043420 (2006).
L. Greenman *et al.*, Phys. Rev. A **82**, 023406 (2010).
A. Karamatskou *et al.*, Phys. Rev. A **89**, 033415 (2014).

- Optical strong-field physics

A. Wirth *et al.*, Science **334**, 195 (2011).
S. Pabst *et al.*, Phys. Rev. A **85**, 023411 (2012).
S. Pabst *et al.*, Phys. Rev. A **86**, 063411 (2012).
S. Pabst and R. Santra, Phys. Rev. Lett. **111**, 233005 (2013).
A. Karamatskou, S. Pabst, and R. Santra, Phys. Rev. A **87**, 043422 (2013).
S. Pabst and R. Santra, J. Phys. B **47**, 124026 (2014).

- XUV and x-ray physics

S. Pabst *et al.*, Phys. Rev. Lett. **106**, 053003 (2011).
A. Sytcheva *et al.*, Phys. Rev. A **85**, 023414 (2012).
D. Krebs, S. Pabst, and R. Santra, Am. J. Phys. **82**, 113 (2014).
E. Heinrich-Josties, S. Pabst, and R. Santra, Phys. Rev. A **89**, 043415 (2014).
Y.-J. Chen *et al.*, Phys. Rev. A **91**, 032503 (2015).
T. Mazza *et al.*, Nature Commun. **6**, 6799 (2015).

Acknowledgments

Yi-Jen Chen

Antonia Karamatskou

Dietrich Krebs

Stefan Pabst

- T. Mazza, M. Ilchen, S. Bakhtiarzadeh, A.J. Rafipoor, **M. Meyer**
  European XFEL
- P. O'Keeffe
  CNR Istituto di Struttura della Materia
- T.J. Kelly, N. Walsh, J.T. Costello
  Dublin City University

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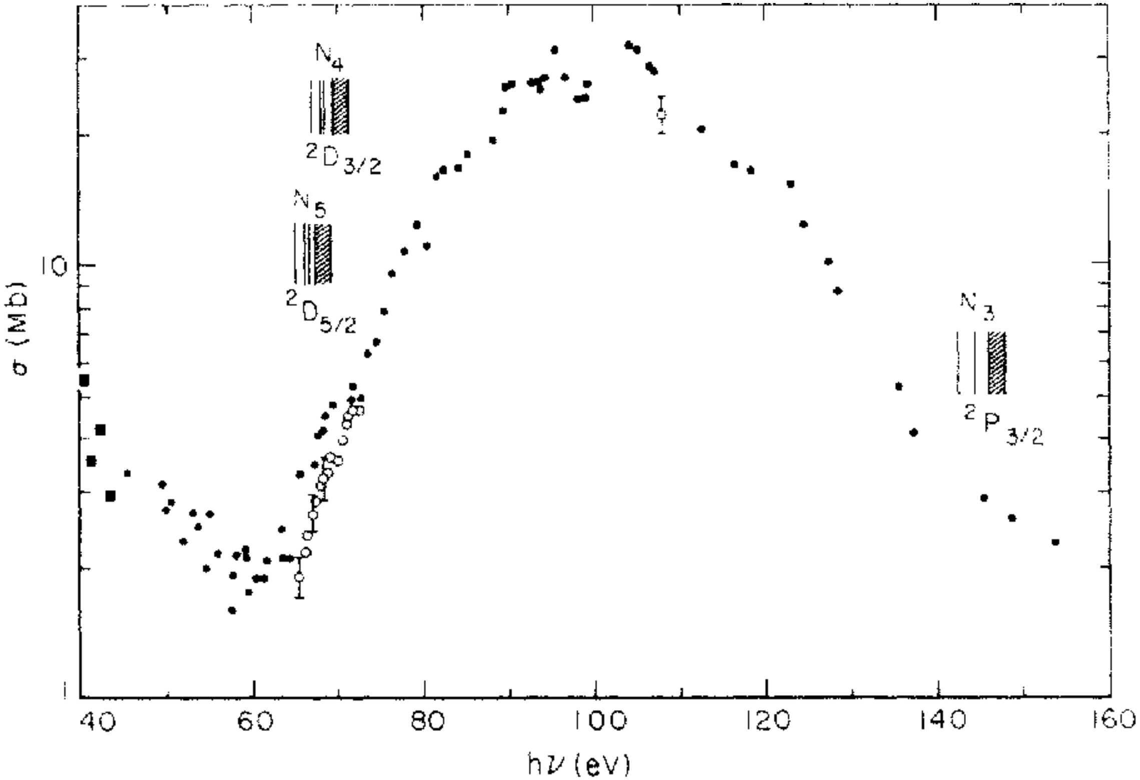
The Xe giant dipole resonance (GDR)

2014 marked the 50th anniversary of the discovery of the giant dipole resonance in the XUV photoabsorption spectrum of atomic xenon.



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A. P. Lukirskii, I. A. Brytov, and T. M. Zimkina, Opt. Spectrosc. **17**, 234 (1964).

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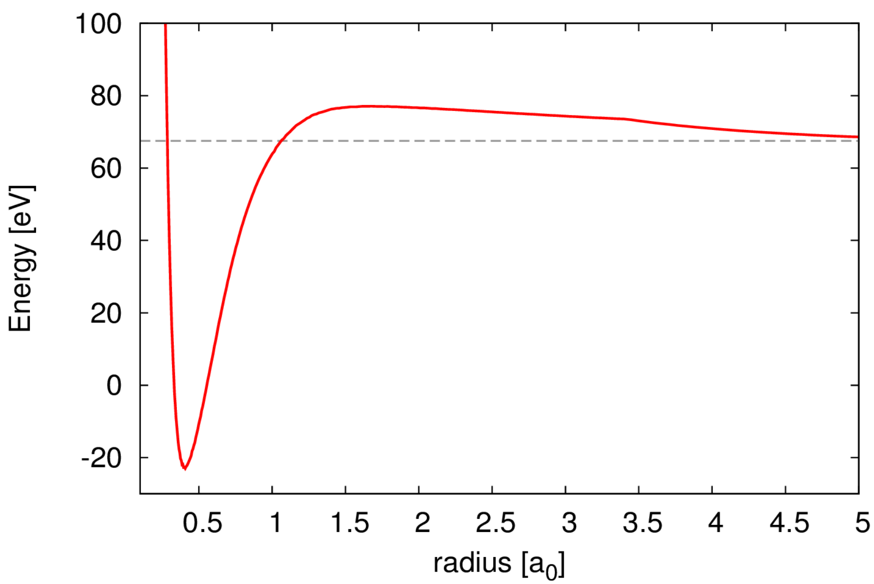
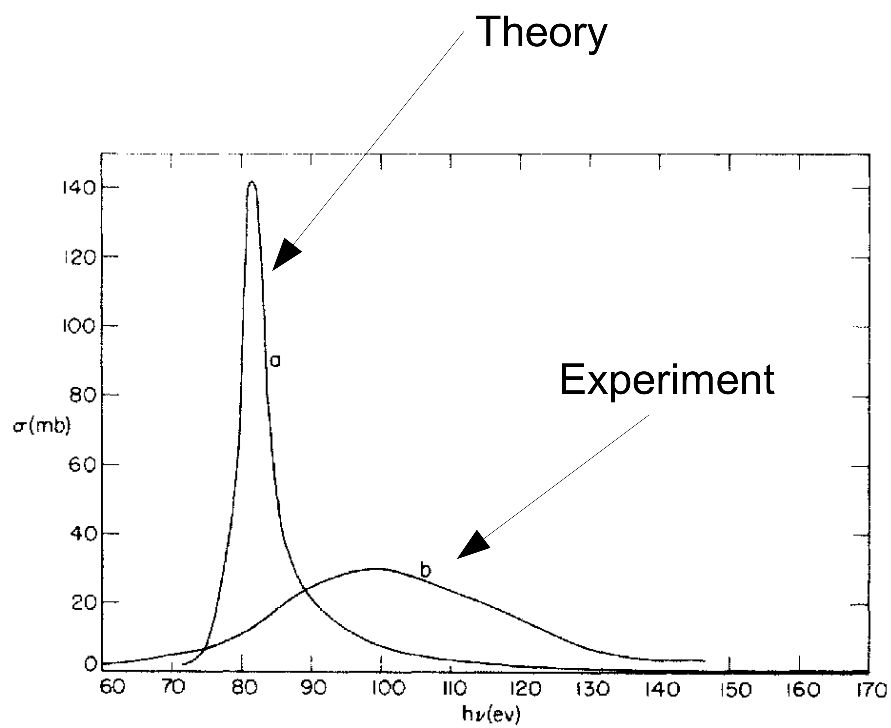
The effective radial potential giving rise to the Xe GDR

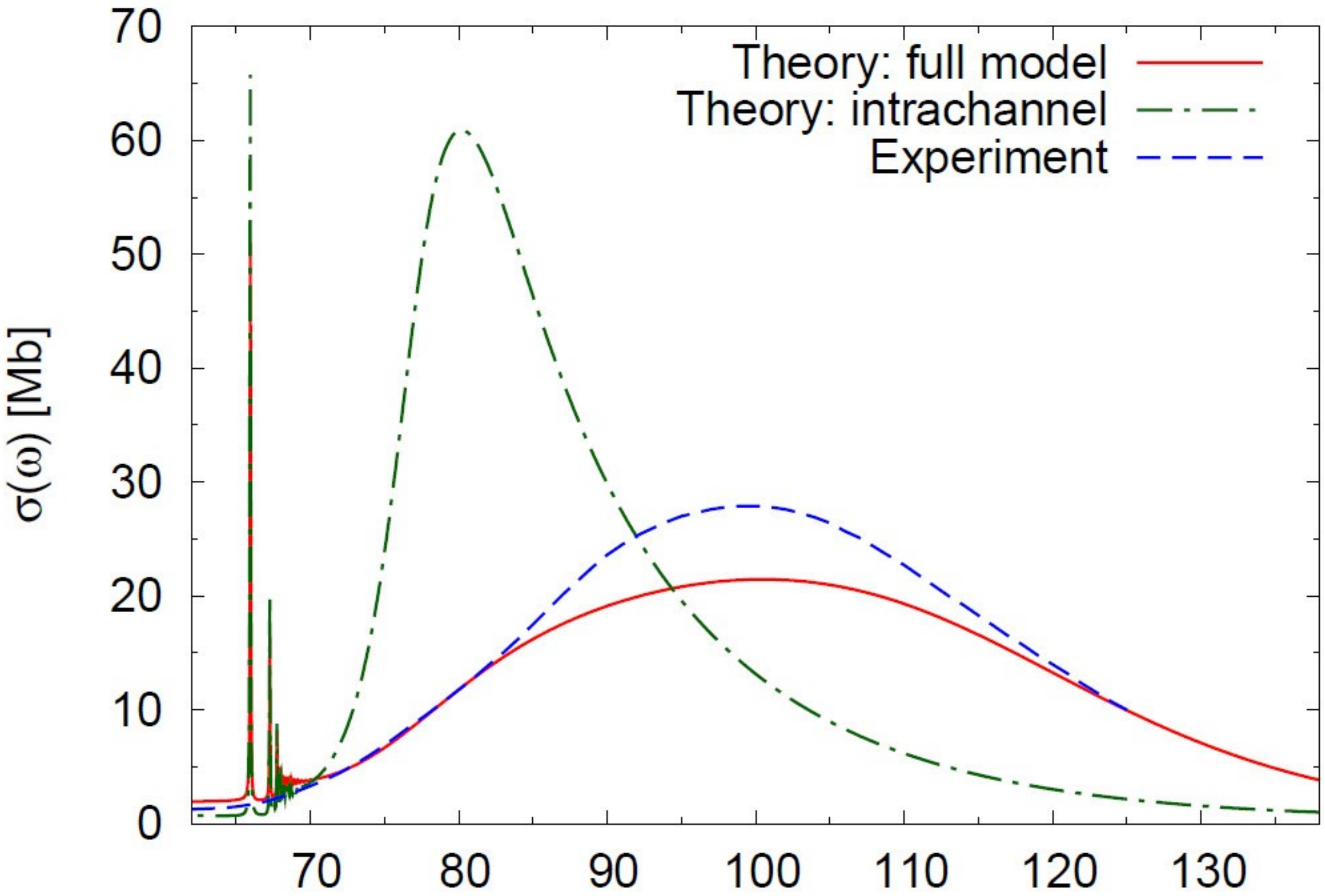
$$V(r) = V_{\mathrm{HS}}(r) + \frac{l(l+1)}{2r^2}, \quad l = 3$$





J. W. Cooper, Phys. Rev. Lett. **13**, 762 (1964).

Total photoabsorption cross section of atomic xenon calculated with TDCIS



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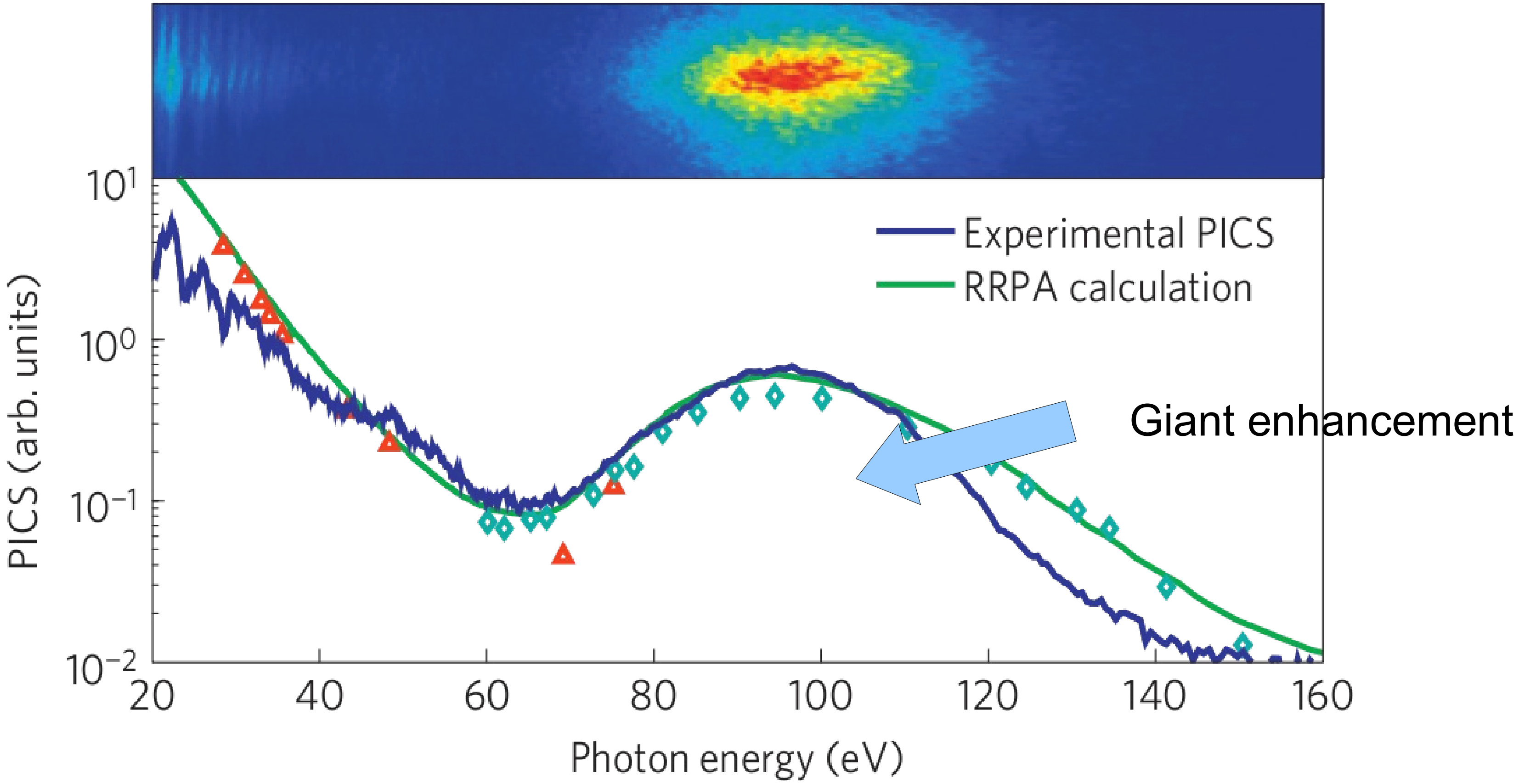
The impact of the GDR on the high-harmonic-generation spectrum of atomic xenon

Experimental observation



Shiner *et al.*, Nature Phys. **6**, 464 (2011).

Predicted by M. V. Frolov *et al.*, Phys. Rev. Lett. **102**, 243901 (2009).

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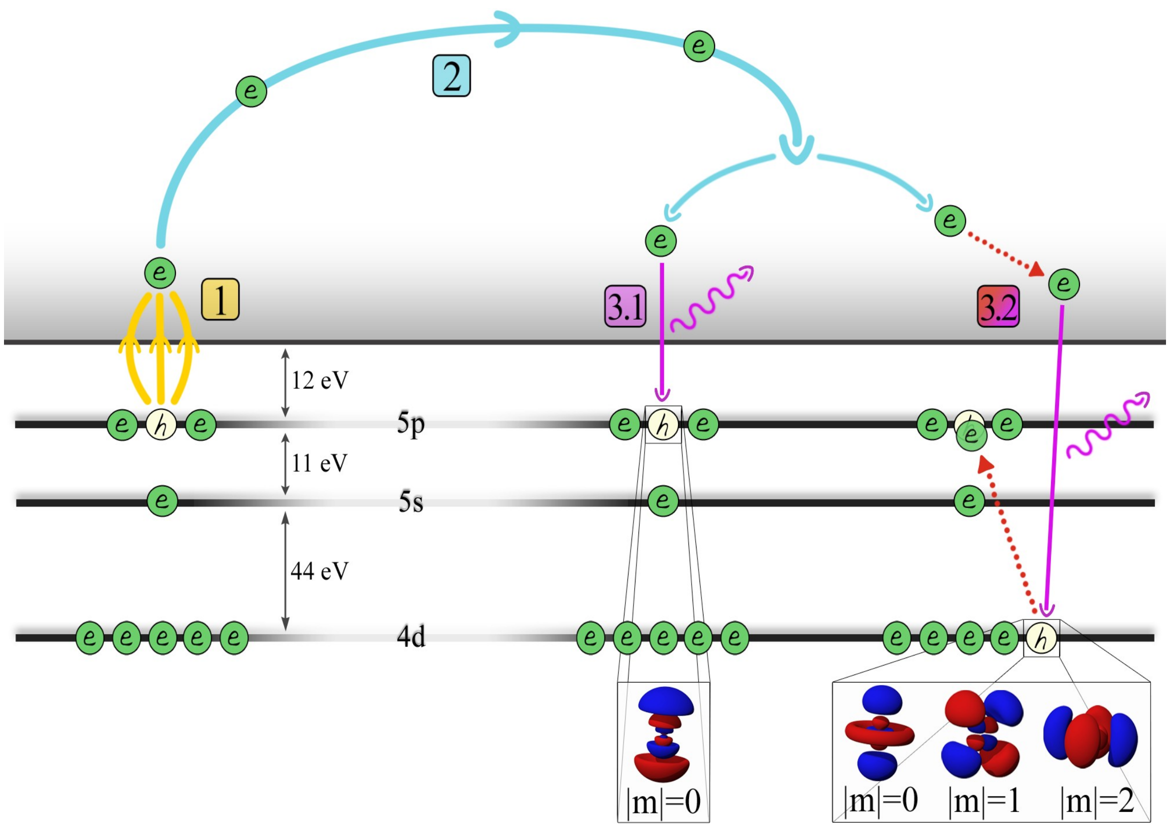
The basic picture

- Giant Dipole Resonance
  - Collective excitation of 4d electrons
  - 5s and 5p electrons are also participating
- HHG
  - GDR opens up new recombination mechanism
  - HHG yield is strongly affected by the GDR



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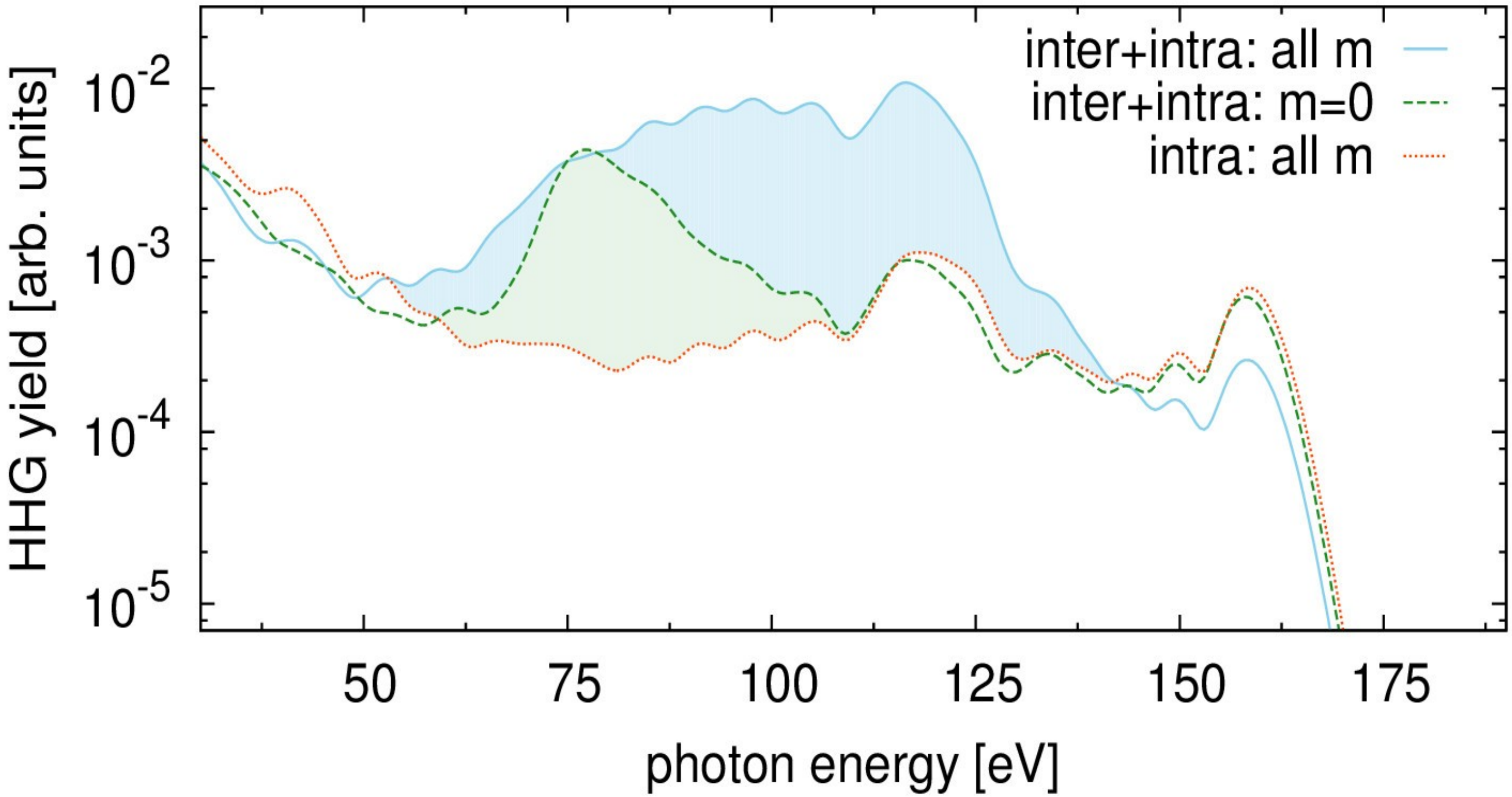
TDCIS calculation of HHG in xenon



Pabst and Santra, Phys. Rev. Lett. **111**, 233005 (2013).

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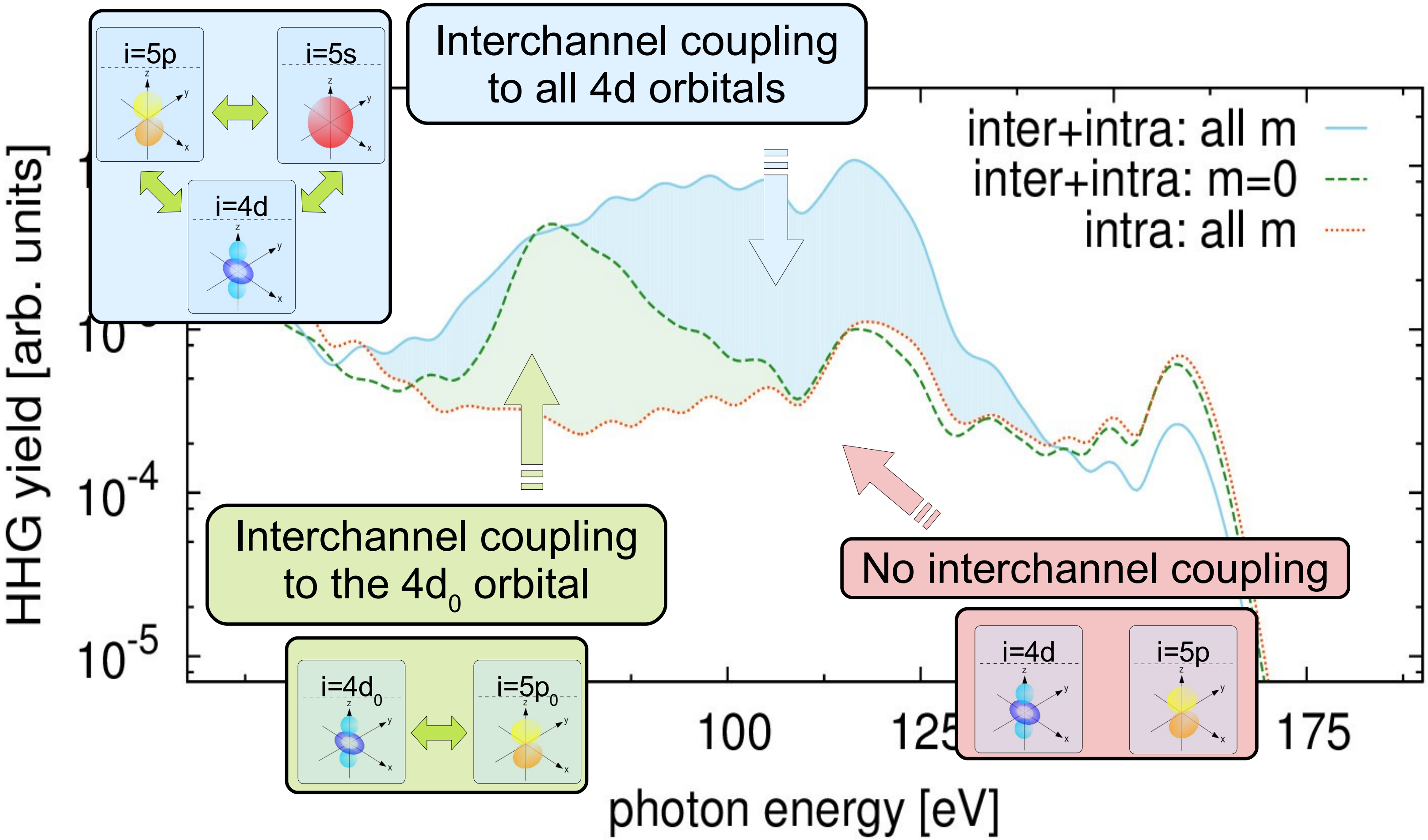

Pabst and Santra, Phys. Rev. Lett. **111**, 233005 (2013).

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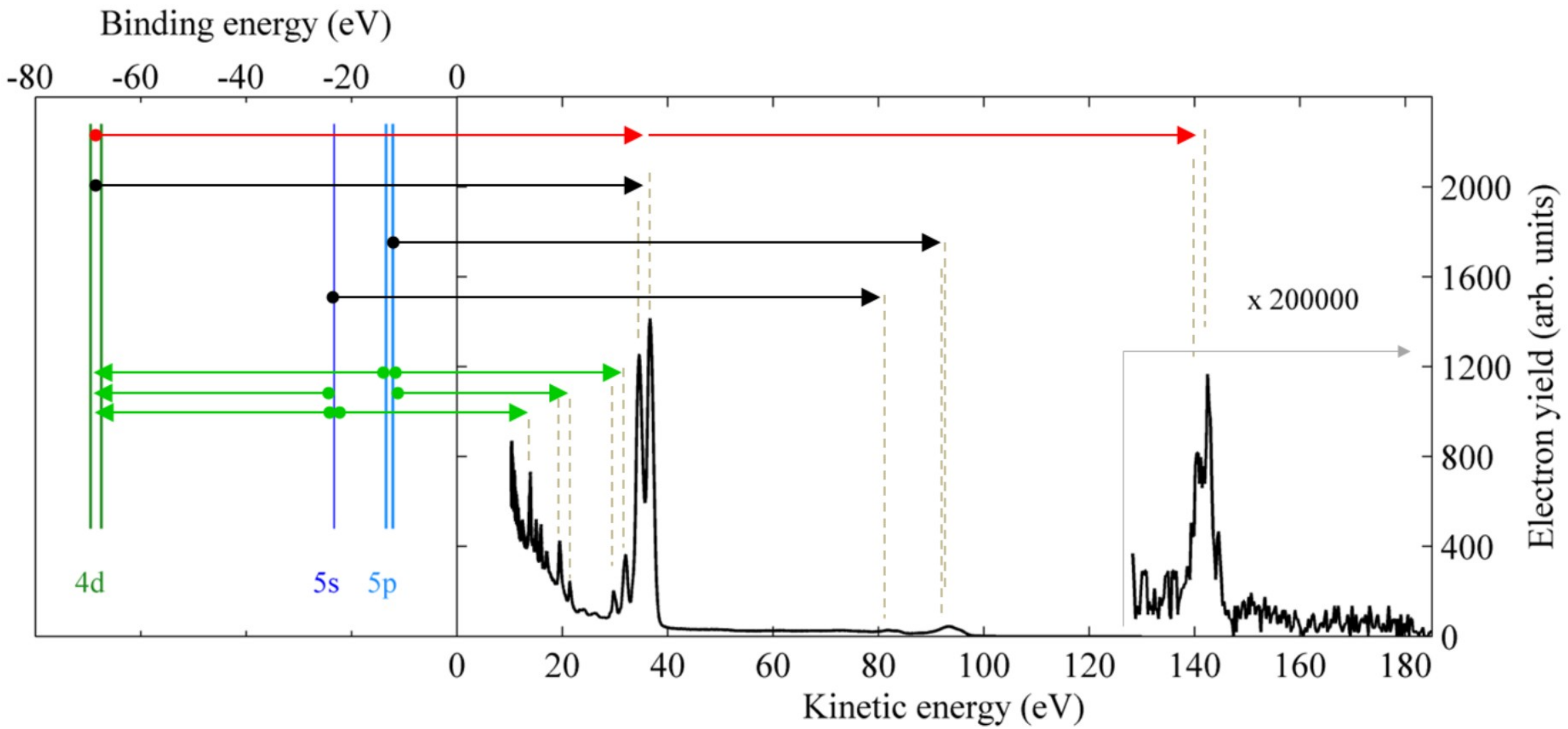
Revealing the substructure of the Xe GDR

Xenon ATI in the XUV regime: experimental data

Electronic level scheme and photoelectron spectrum

$\hbar\omega$ = 105 eV

I = $6{\cdot}10^{12}$ Wcm^{-2}



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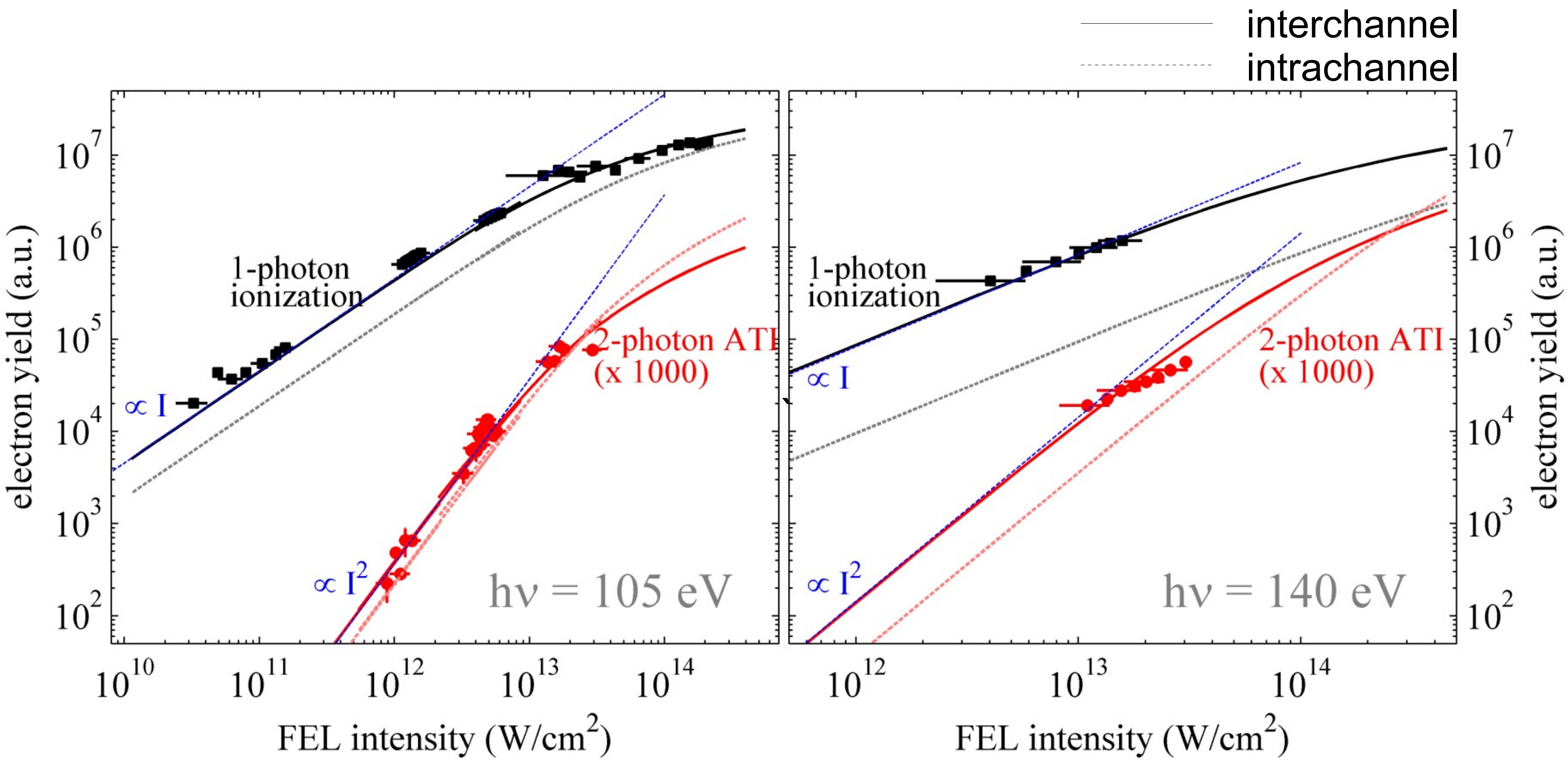
Nature Commun. **6**, 6799 (2015).

Comparison of theory and experiment

Intensity dependence of photoelectron yields



Full theory (interchannel) coincides with experimental data

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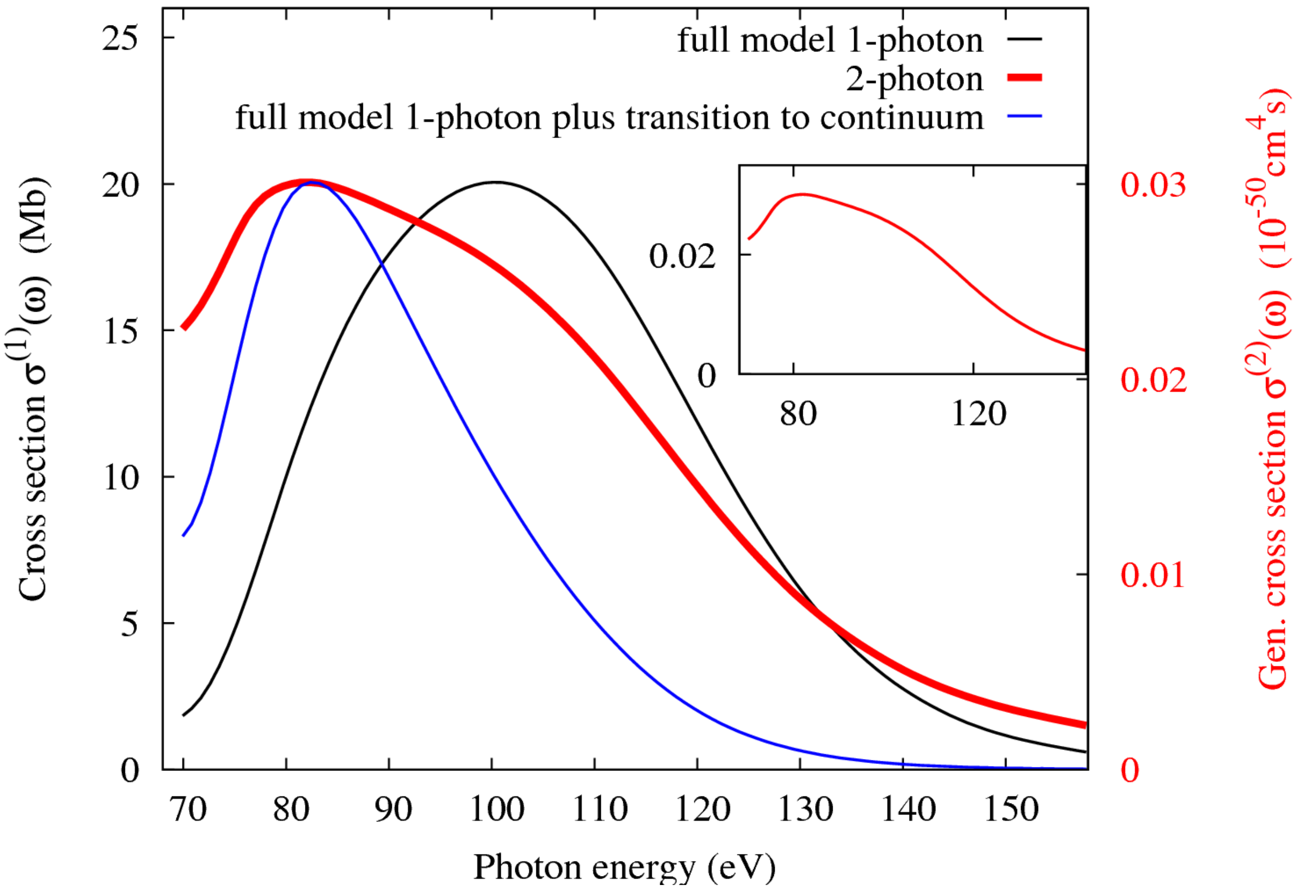
Nonlinear process (ATI) uncovers resonance substructure



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Nature Commun. **6**, 6799 (2015).

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Theoretical characterization of the resonance states underlying the Xe GDR

- A calculation by Göran Wendin in 1971 predicted two resonances and their respective energy positions:

  G. Wendin, Phys. Lett. A **37**, 445 (1971).

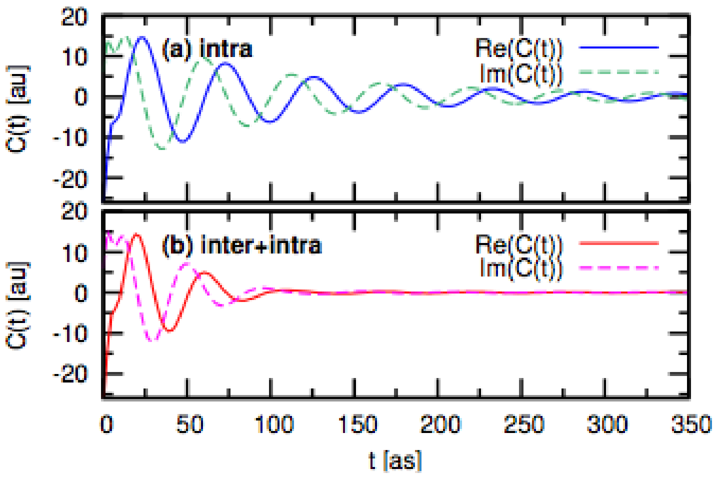
- Here: A detailed characterization of the resonance substructure by two complementary methods within CIS.

Time-dependent technique: Gabor analysis

- Time-dependent autocorrelation function:

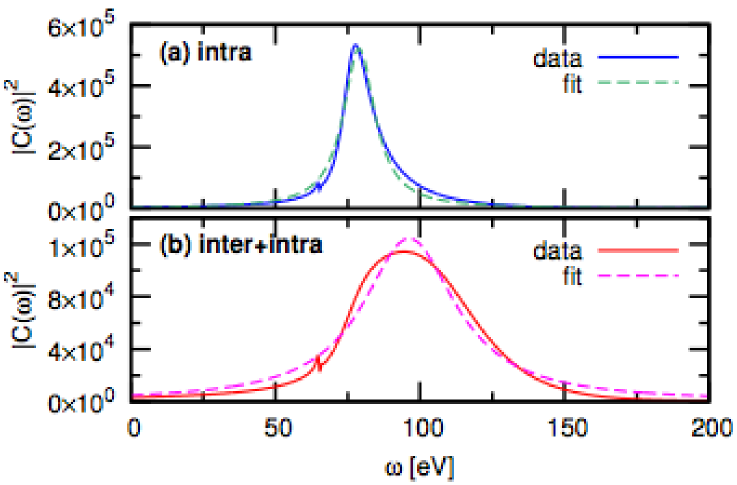
$$C(t) := (\Psi(0)|\Psi(t)) = \sum_n a_n^2 e^{-i\Xi_n t - \frac{\Gamma_n}{2} t}$$

$$|\Psi(0)) = \hat{D}_z \, |\Phi_0^{HF})$$



- Autocorrelation function in frequency domain:

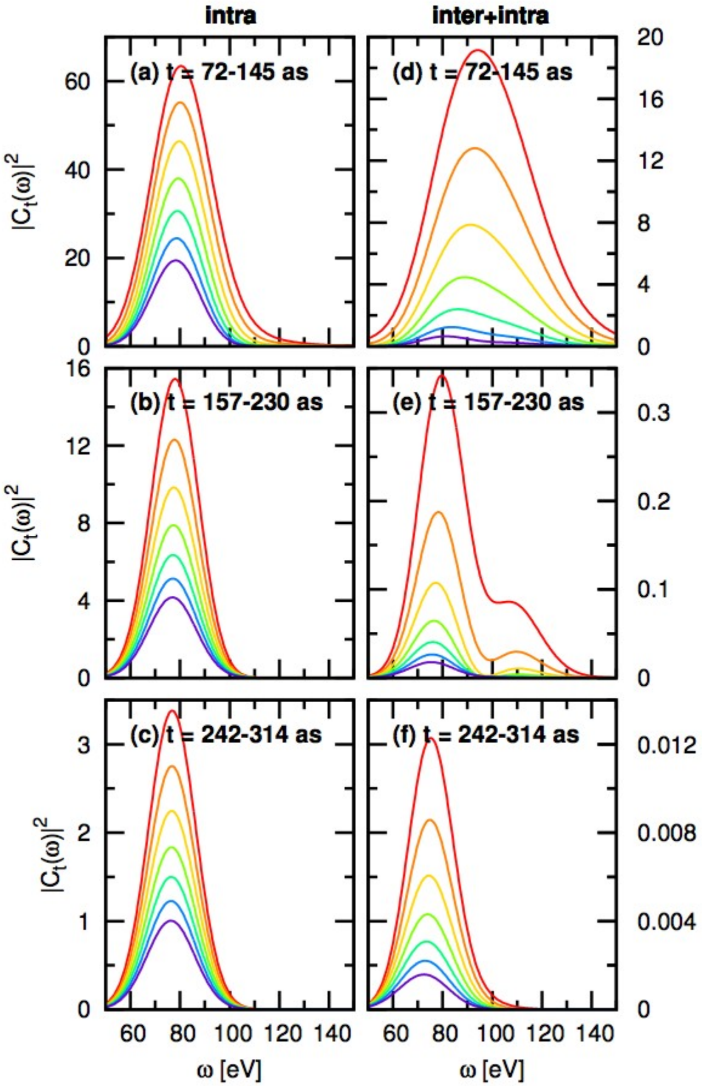
  ⇒ The two resonances cannot be disentangled.



Y.-J. Chen *et al.*, Phys. Rev. A **91**, 032503 (2015).

Autocorrelation function in combined time-frequency domain:

$$C_t(\omega) = \frac{1}{\sigma\sqrt{2\pi}} \int_0^{+\infty} dt' e^{i\omega t'} e^{-\frac{(t'-t)^2}{2\sigma^2}} C(t')$$



Y.-J. Chen *et al.*, Phys. Rev. A **91**, 032503 (2015).

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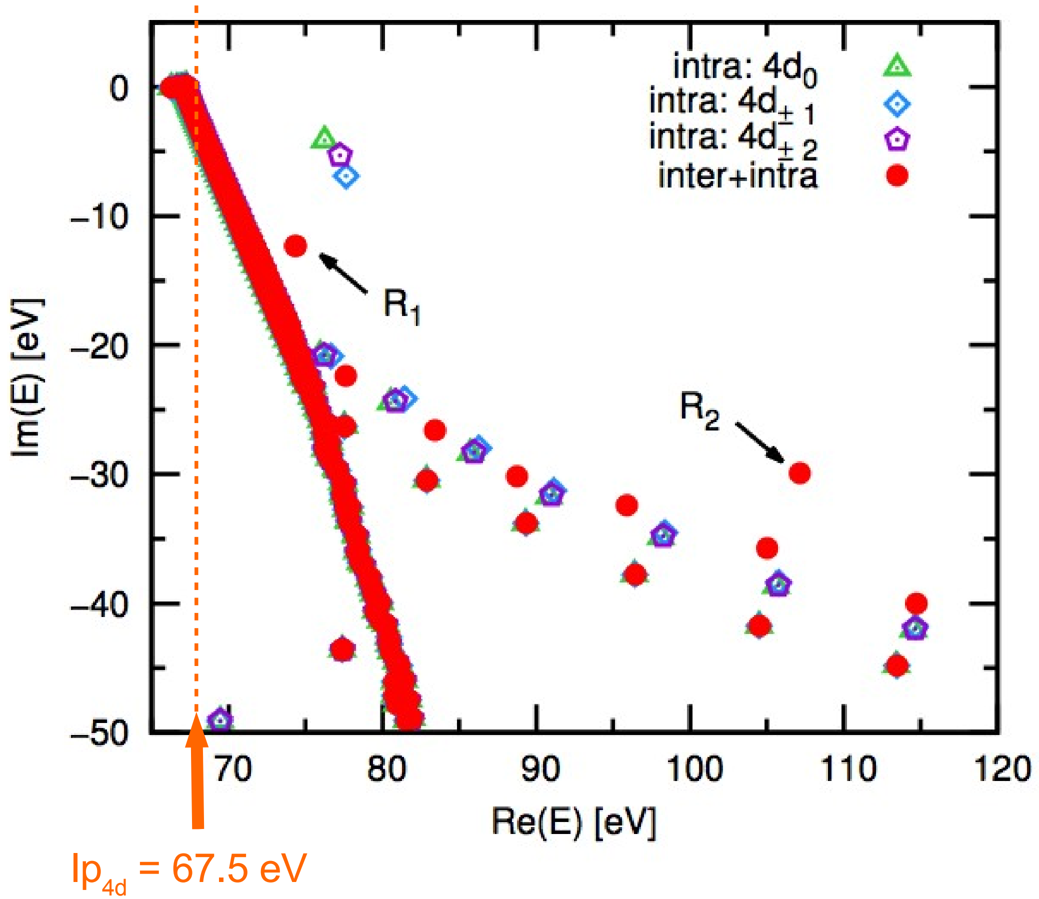
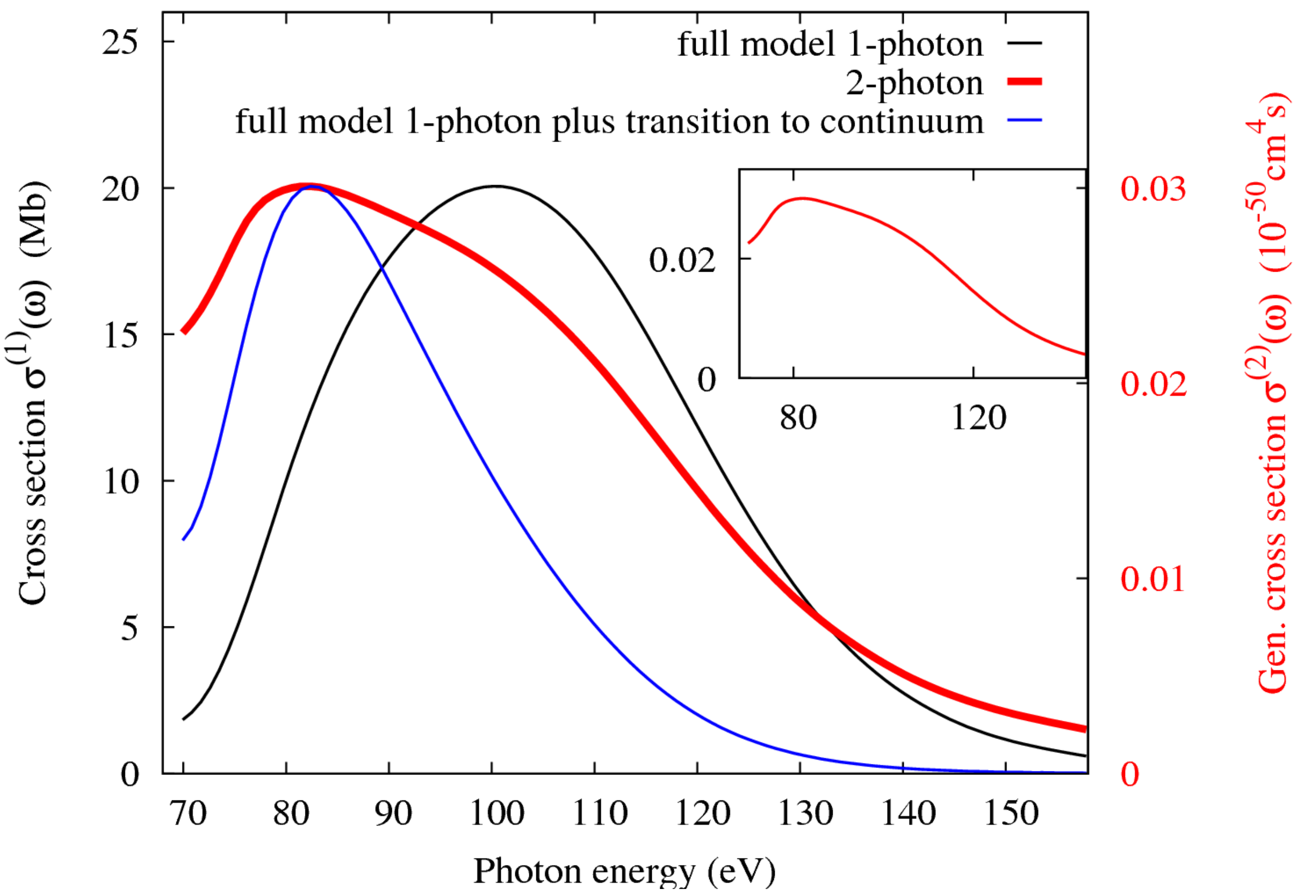
Resonance energies through complex scaling

- (Ξ_1, Γ_1) = (74 eV, 25 eV),
  (Ξ_2, Γ_2) = (107 eV, 60 eV)
- Resonance waves functions cannot be written as a single particle-hole state ⇒ Collective excitations of the 4d shell



Y.-J. Chen *et al.*, Phys. Rev. A **91**, 032503 (2015).

Nonlinear process (ATI) uncovers resonance substructure



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Conclusions

- In the Xe GDR, an electron excited from the 4d shell is temporarily trapped by an angular-momentum barrier in an f-wave resonance state. As a consequence of strong particle-hole interaction, the true resonance states are entangled particle-hole states, i.e., collective electronic states.

- TDCIS is an *ab-initio* electronic-structure model that captures the essential physics associated with the Xe GDR, including the experimentally observed impact of the Xe GDR on the HHG spectrum of atomic xenon.

- TDCIS calculations demonstrate that XUV two-photon ATI is sensitive to the substructure of the Xe GDR.

- This indicates that nonlinear XUV spectroscopy can reveal previously hidden quantum states of matter.

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