Electronic structure in high-intensity x-ray fields

Robin Santra

Center for Free-Electron Laser Science, DESY

Department of Physics, University of Hamburg

Nobel Symposium on Free Electron Laser Research
June 14-18, 2015
Sigtunahöjden, Sigtuna, Sweden

HELMHOLTZ
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Grid-based TDCIS
(time-dependent configuration interaction singles)

- Nonperturbative treatment of electron-light interaction
- Takes into consideration coherent electron dynamics
- Restricted to single-ionization processes
- Application presented here:
  Revealing the substructure of a collective excitation

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Grid-based TDCIS

$$|\Psi(t)\rangle = \alpha_0(t)|\Phi_0\rangle + \sum_{i,a} \alpha_i^a(t)\left|\Phi_i^a\right\rangle,$$
$$|\Phi_i^a\rangle = \frac{1}{\sqrt{2}}\{\hat{c}_{a+}^\dagger \hat{c}_{i+} + \hat{c}_{a-}^\dagger \hat{c}_{i-}\}|\Phi_0\rangle,$$

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

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

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

$$i\dot{\alpha}_0(t) = -\sqrt{2}\mathcal{E}(t)\sum_{i,a}\alpha_i^a(t)z_{(i,a)},$$
$$i\dot{\alpha}_i^a(t) = (\varepsilon_a - \varepsilon_i)\alpha_i^a(t) + \sum_{i',a'}\alpha_{i'}^{a'}(t)(2v_{(a,i',i,a')} - v_{(a,i',a',i)})$$
$$- \mathcal{E}(t)\left\{\sqrt{2}\alpha_0(t)z_{(a,i)} + \sum_{a'}\alpha_i^{a'}(t)z_{(a,a')}\right.$$
$$\left. - \sum_{i'}\alpha_{i'}^a(t)z_{(i',i)}\right\}.$$

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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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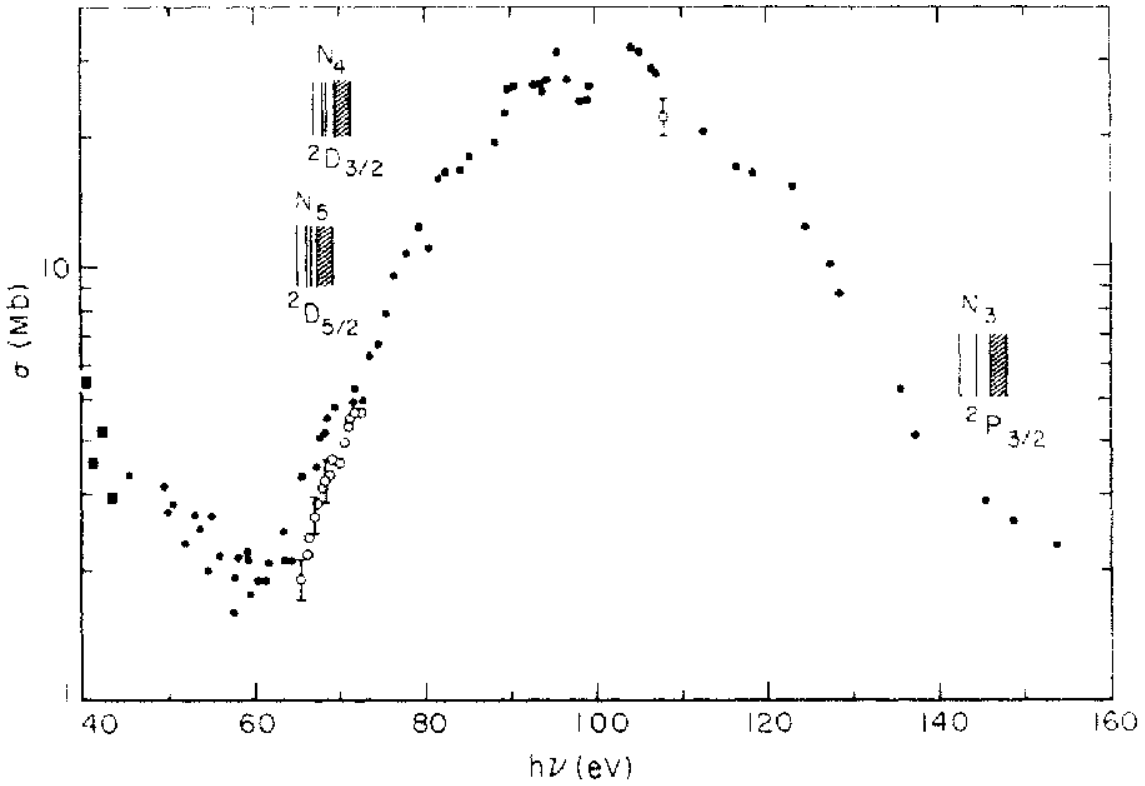
The Xe giant dipole resonance (GDR)

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



D. L. Ederer, Phys. Rev. Lett. **13**, 760 (1964).

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

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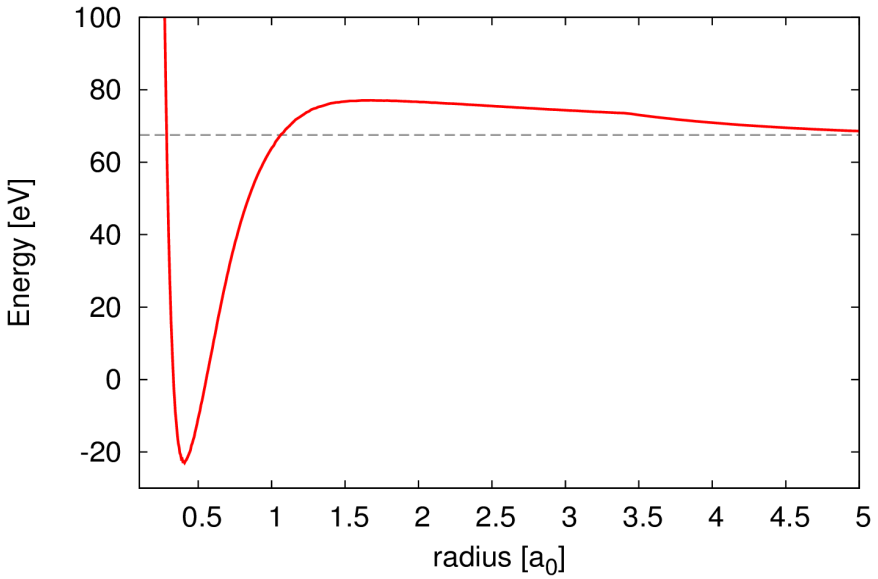
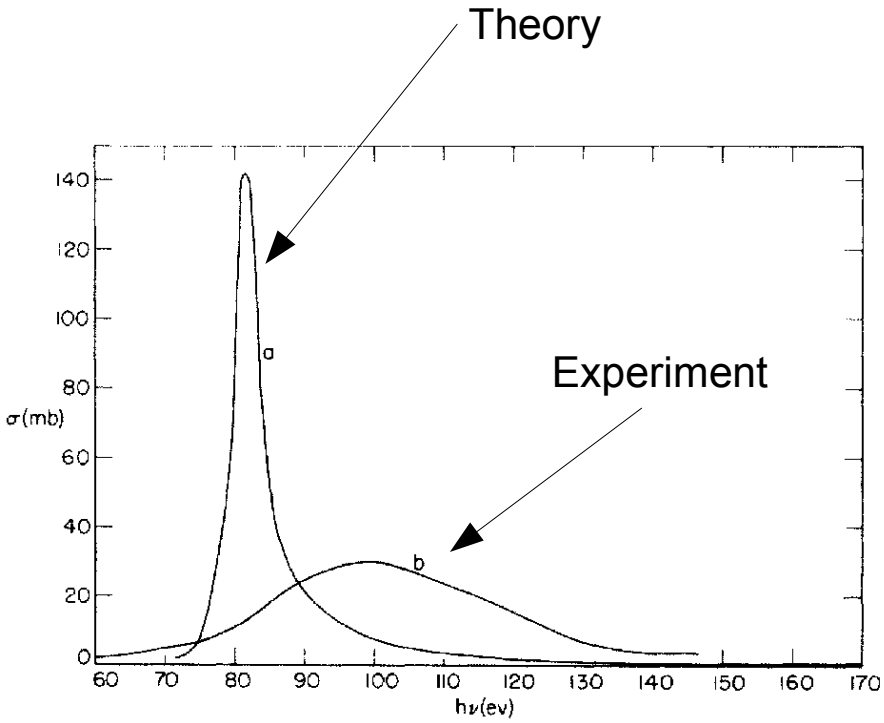
The effective radial potential giving rise to the Xe GDR

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





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

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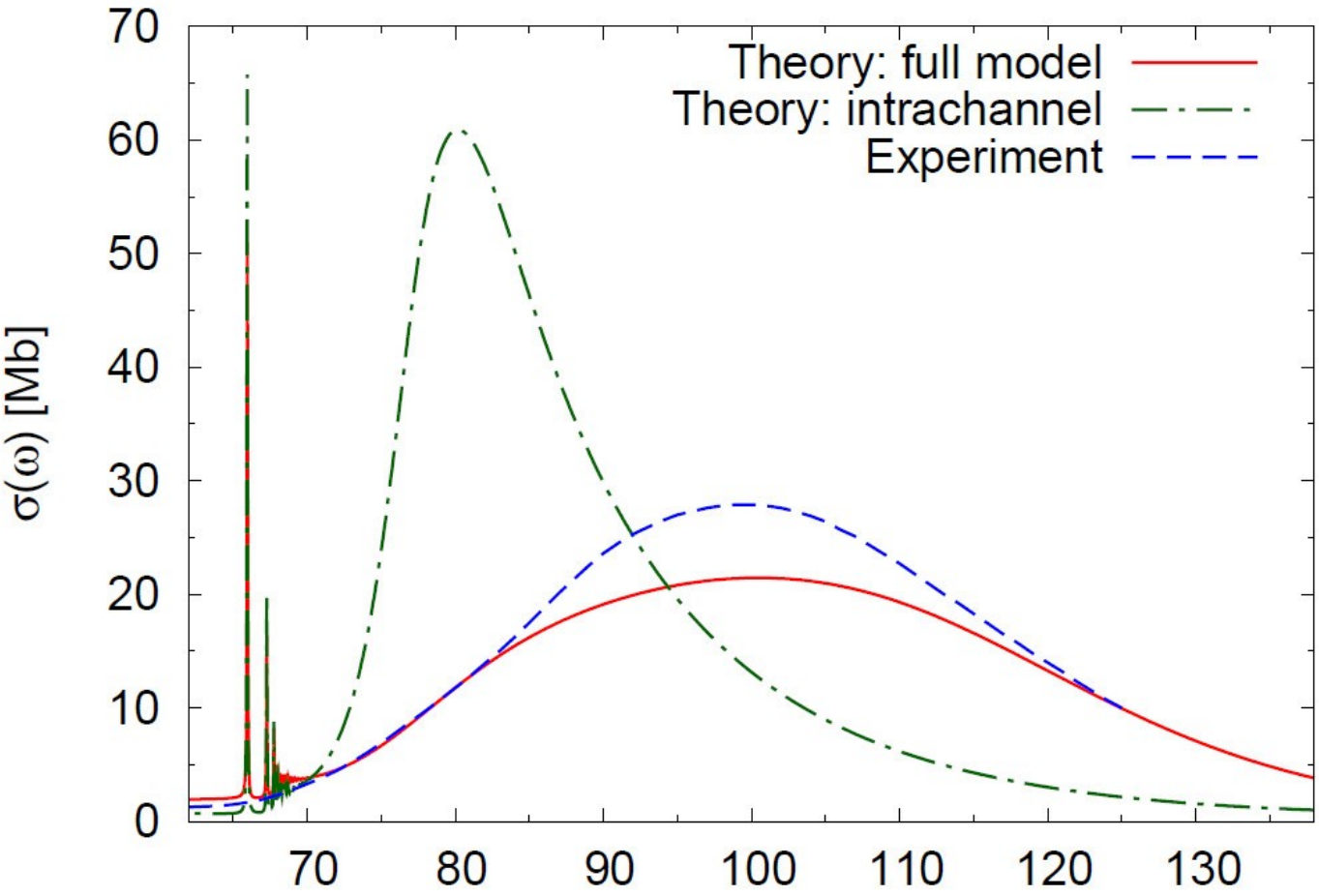
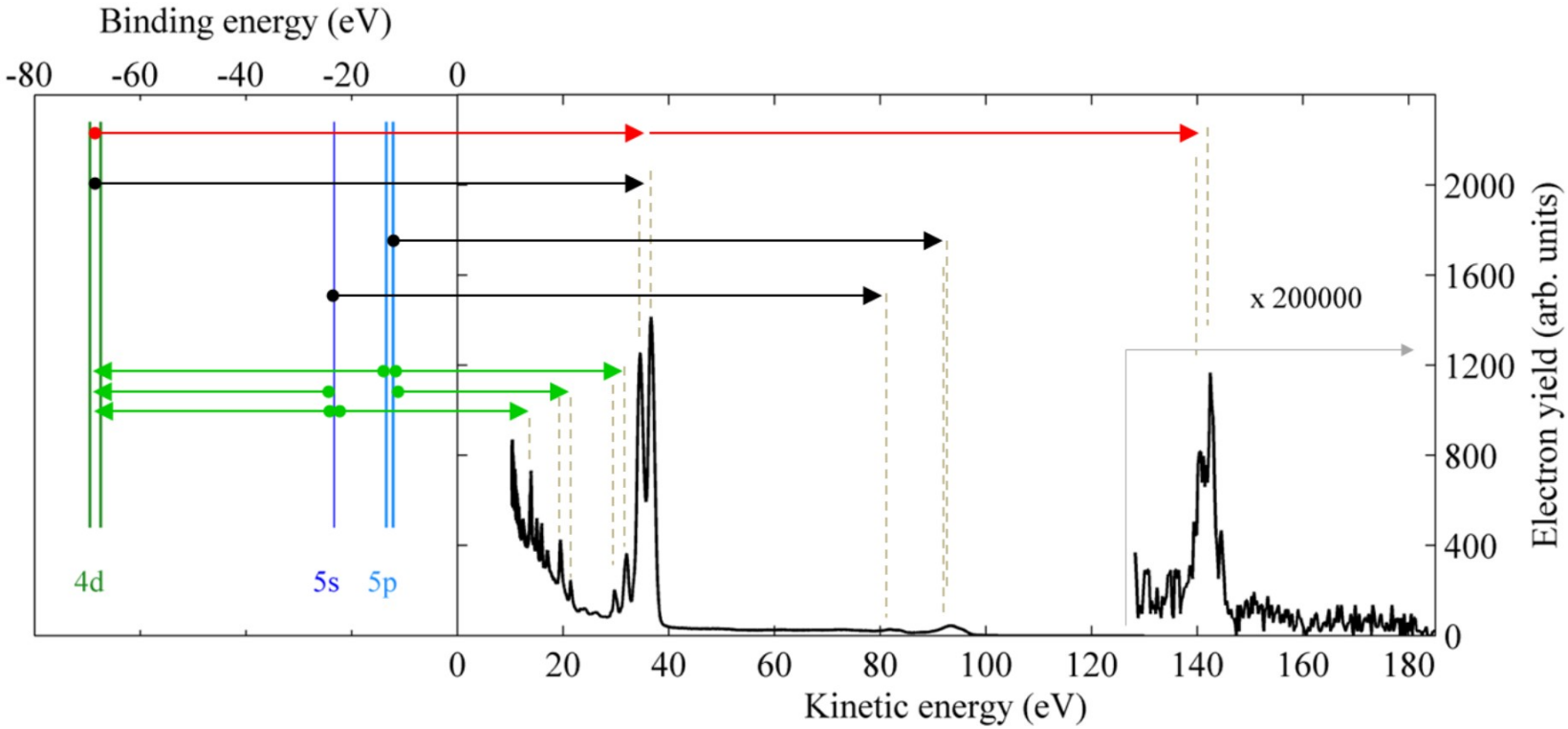
Total photoabsorption cross section of atomic xenon calculated with TDCIS



D. Krebs, S. Pabst, and R. Santra, Am. J. Phys. **82**, 113 (2014).

Xenon ATI in the XUV regime: experimental data

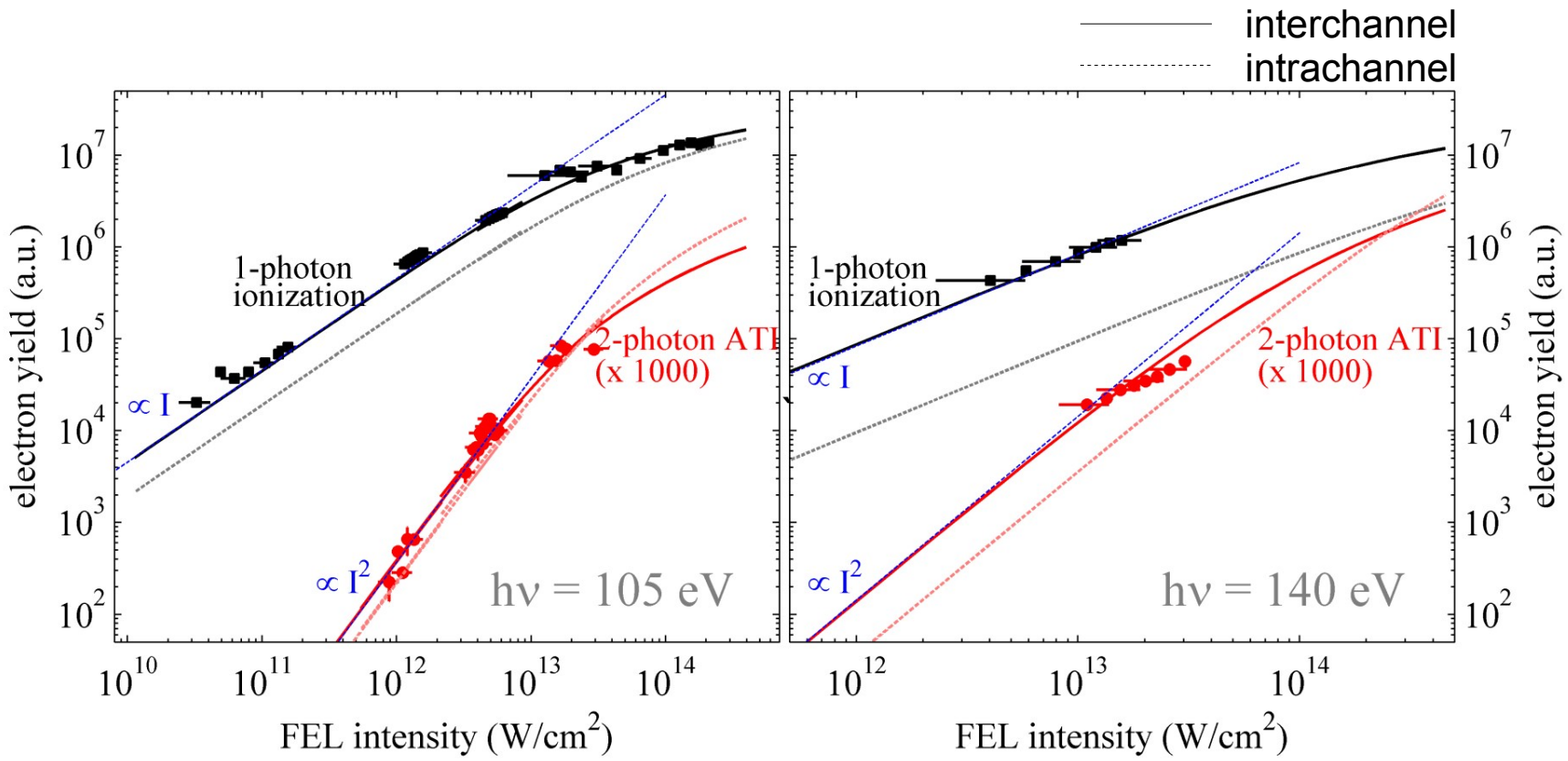
Electronic level scheme and photoelectron spectrum



T. Mazza, A. Karamatskou, *et al.*,
Nature Commun. **6**, 6799 (2015).

Comparison of theory and experiment

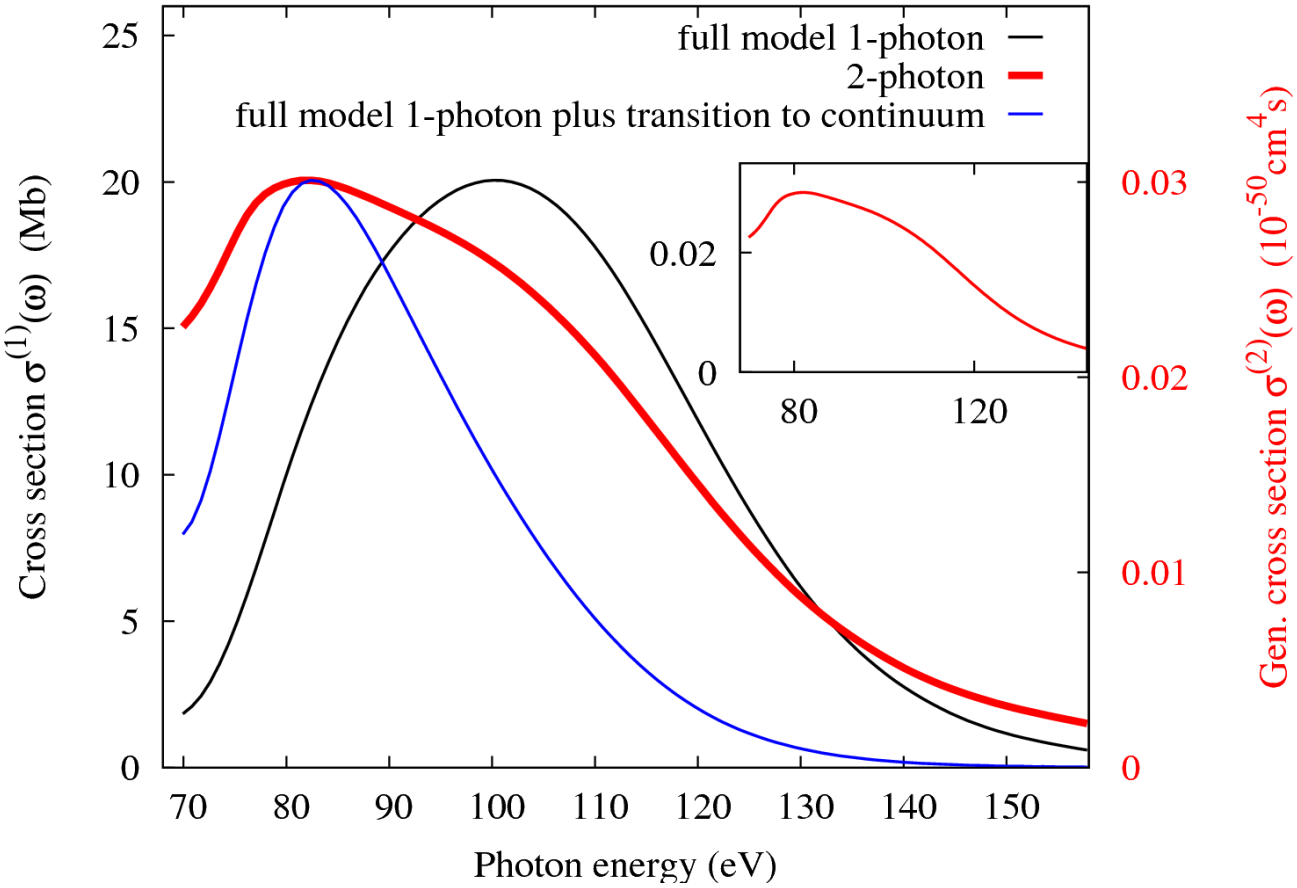
Intensity dependence of photoelectron yields



Full theory (interchannel) coincides with experimental data

T. Mazza, A. Karamatskou, *et al.*, Nature Commun. **6**, 6799 (2015).

Nonlinear process (ATI) uncovers resonance substructure



T. Mazza, A. Karamatskou, *et al.*,
Nature Commun. **6**, 6799 (2015).

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

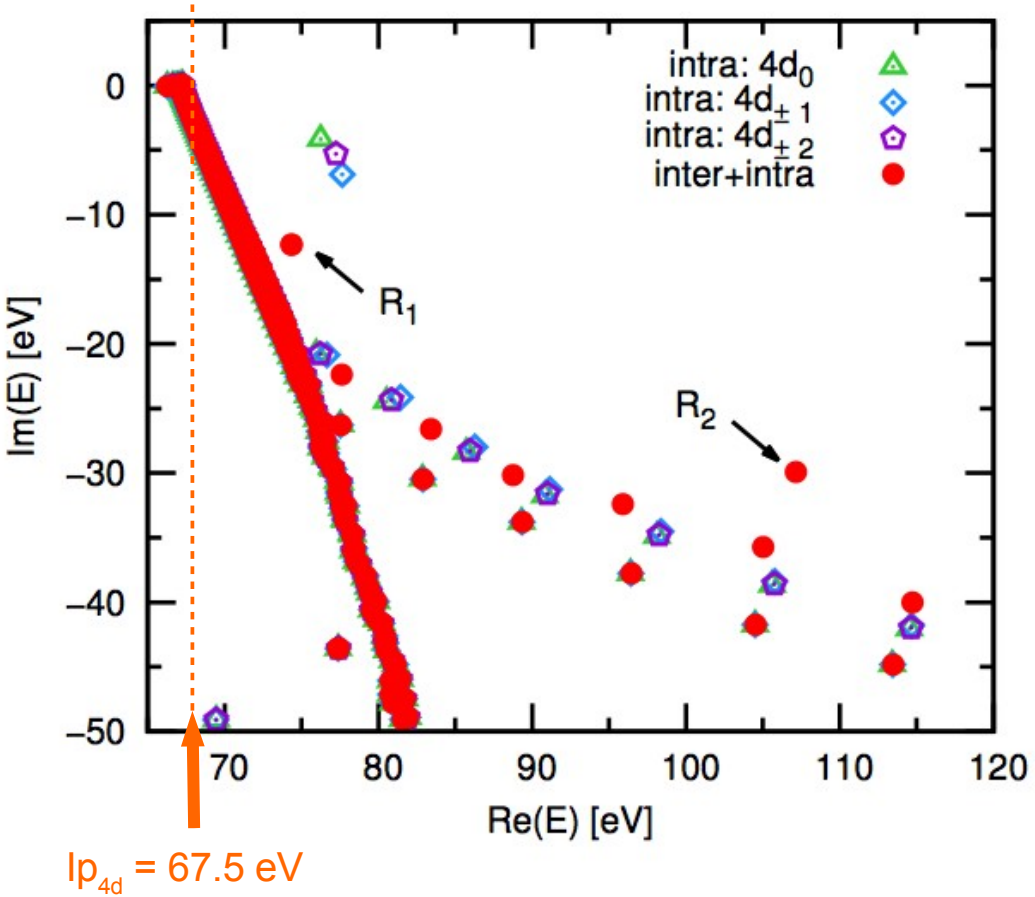
  G. Wendin, Phys. Lett. A **37**, 445 (1971).

- Here: A detailed characterization of the resonance substructure using CIS in combination with smooth exterior complex scaling.

Resonance energies through complex scaling

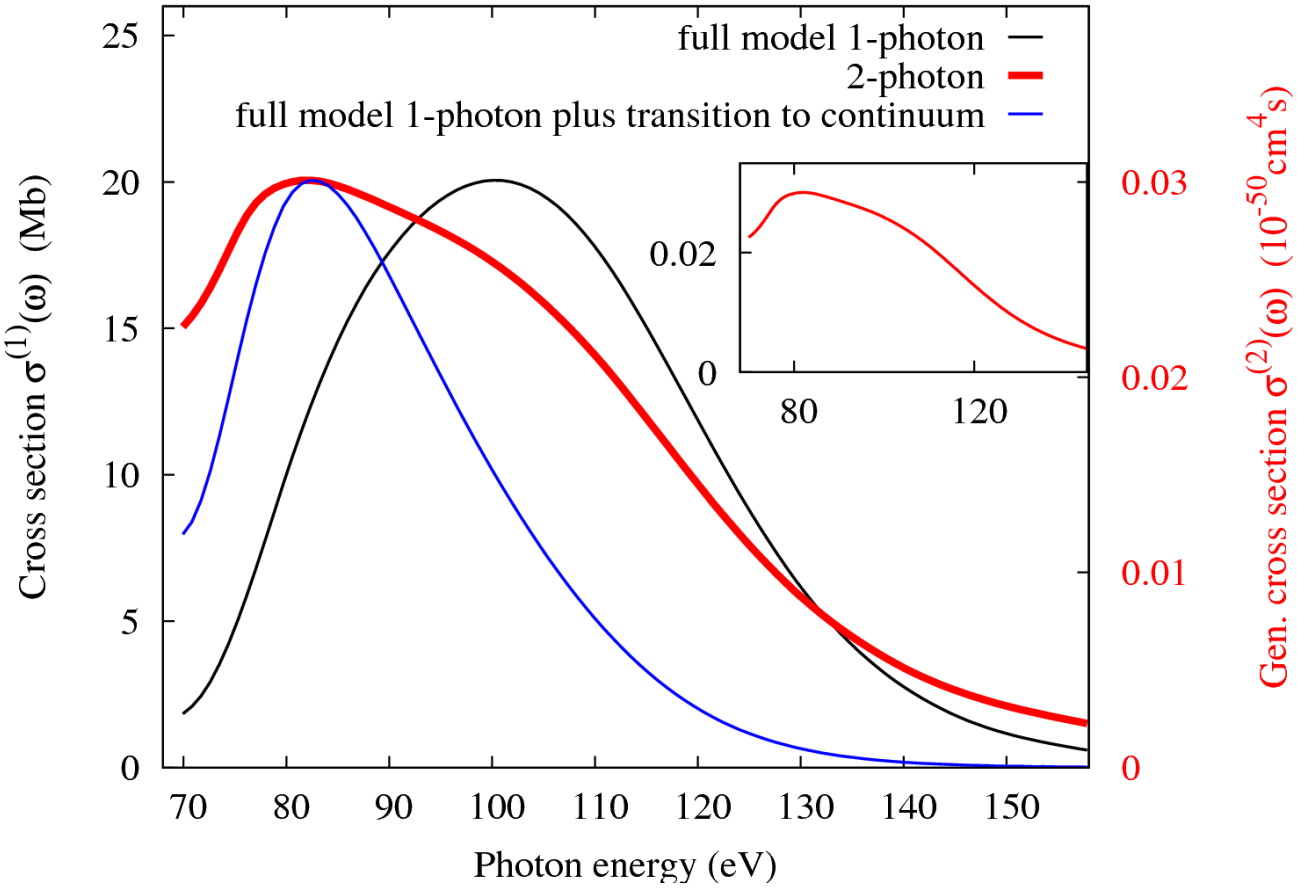
- $(\Xi_1, \Gamma_1) = (74\ \text{eV}, 25\ \text{eV})$,
  $(\Xi_2, \Gamma_2) = (107\ \text{eV}, 60\ \text{eV})$

- 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



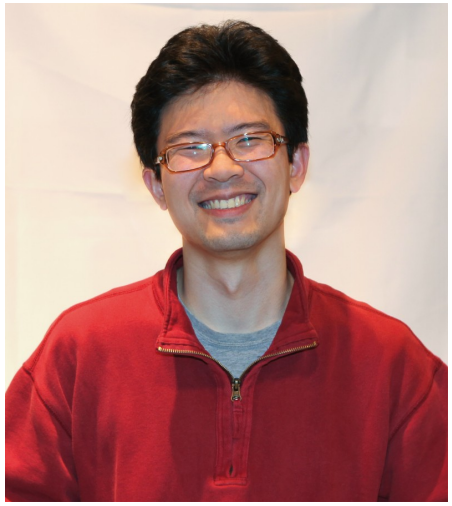
T. Mazza, A. Karamatskou, *et al.*,
Nature Commun. **6**, 6799 (2015).

XATOM / XMDYN / XMOLECULE

- Nonperturbative treatment of sequential multiphoton ionization
- Rate-equation description
- Multiple ionization dynamics (formation of high charge states)

XATOM:
an integrated toolkit for x-ray atomic physics at high intensity

Sang-Kil Son



→ ab initio calculation of atomic parameters (subshell photoionization cross sections, electronic decay rates, x-ray scattering cross sections) for arbitrary electronic configurations

→ description of electronic population dynamics via numerical solution of system of coupled rate equations (one rate equation per electronic configuration)

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X-ray multiphoton ionization of xenon at photon energies of 2 keV

Experiment carried out at the
Linac Coherent Light Source (LCLS) at SLAC

Xe: $[1s^2\ 2s^2\ 2p^6]\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6$

→ ***1,120,581*** coupled rate equations
(excluding ionization from the K and L shells)

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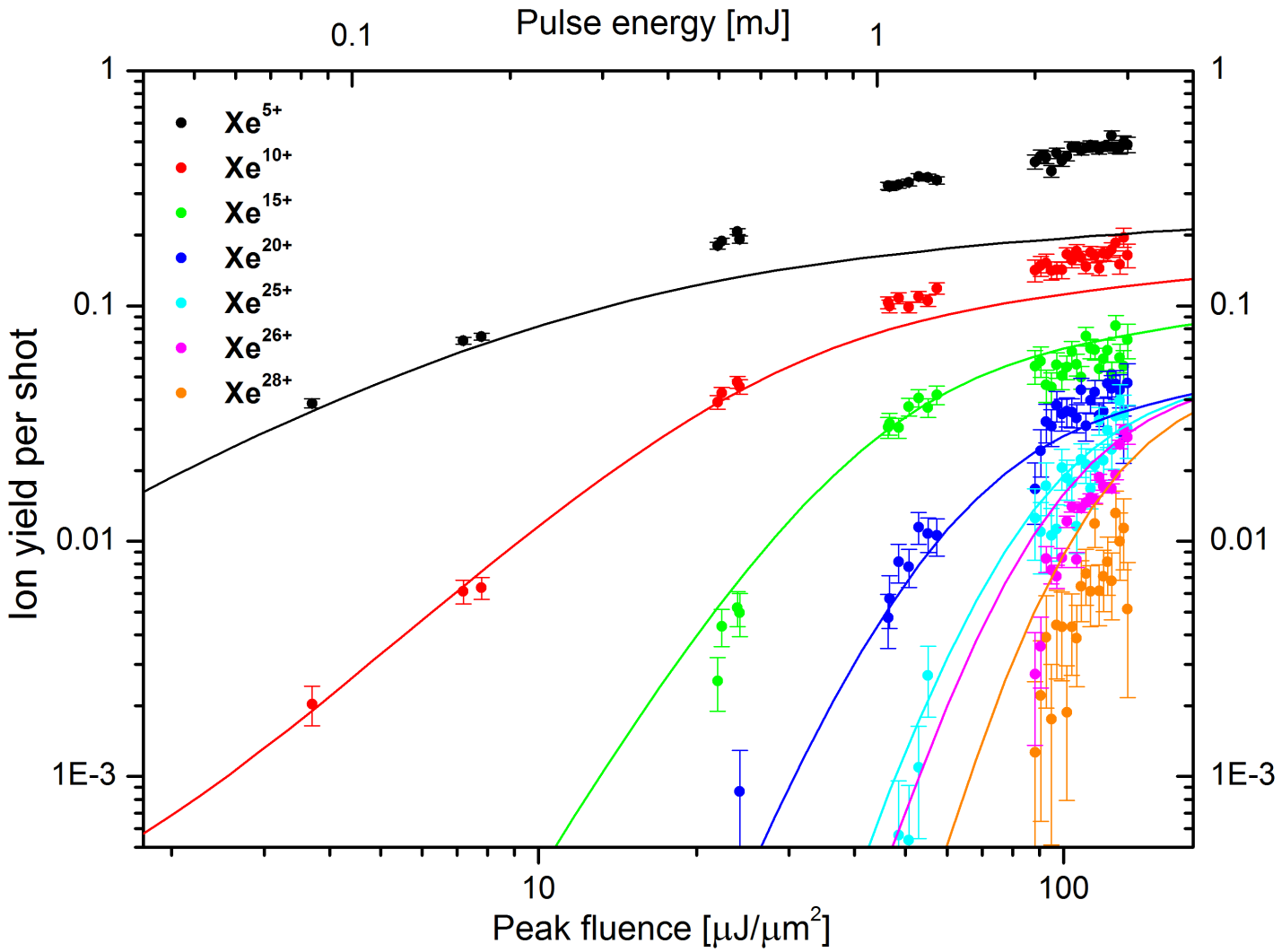
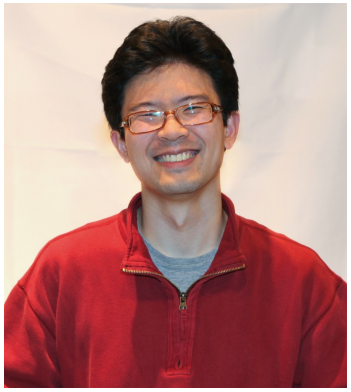
Comparison between experiment and theory at 2 keV



B. Rudek *et al.*, Nature Photonics **6**, 858 (2012).

Towards polyatomic systems: XMDYN

Zoltan Jurek



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Combination of XATOM with a molecular dynamics code (classical dynamics for nuclei and ionized electrons)

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Limitations

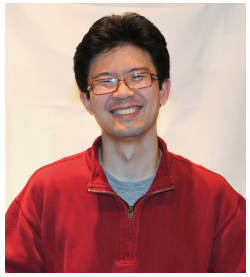
- no rigorous treatment of electronic structure of highly excited, polyatomic systems
- no first-principles treatment of chemical bonds; uses force fields, which are optimized only for the neutral ground state
- no first-principles treatment of influence of molecular environment on decay processes
- no first-principles treatment of charge transfer
- no first-principles treatment of electron impact ionization in molecular environment

XMOLECULE

Yajiang Hao

Ludger Inhester

Kota Hanasaki



Sang-Kil Son

- An ab-initio electronic-structure approach dedicated to ionization dynamics of molecules
- Self-consistent-field calculation for every electronic configuration formed during interaction with intense XFEL pulse
- First results on ionization dynamics

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Molecular multiple-hole state calculation

- Hartree-Fock-Slater method

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_H(\mathbf{r}) + V_X(\mathbf{r})\right]\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

- MO represented by linear combination of AO: $\psi_i(\mathbf{r}) = \sum_\mu C_{\mu i}\phi_\mu(\mathbf{r})$
- Matrix eigenvalue problem: $\mathbf{HC} = \mathbf{SCE}$

$$H_{\mu\nu} = \int d^3r\, \phi_\mu(\mathbf{r})\left[-\frac{1}{2}\nabla^2 + V_{\text{eff}}(\mathbf{r})\right]\phi_\nu(\mathbf{r}), \quad S_{\mu\nu} = \int d^3r\, \phi_\mu(\mathbf{r})\phi_\nu(\mathbf{r})$$

- AO: numerical solutions of corresponding atomic core-hole states

$$\phi_{nlm}(\mathbf{r}) = \frac{u_{nl}(r)}{r}Y_{lm}(\theta,\varphi)$$ calculated by XATOM

- Various numerical techniques employed
  - Multicenter integration on a molecular grid built from atomic grids
  - Multicenter expansion and multipole expansion in direct Coulomb interaction
  - Maximum overlap method to prevent variational collapse

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Y. Hao *et al.*, Structural Dynamics **2**, 041707 (2015).

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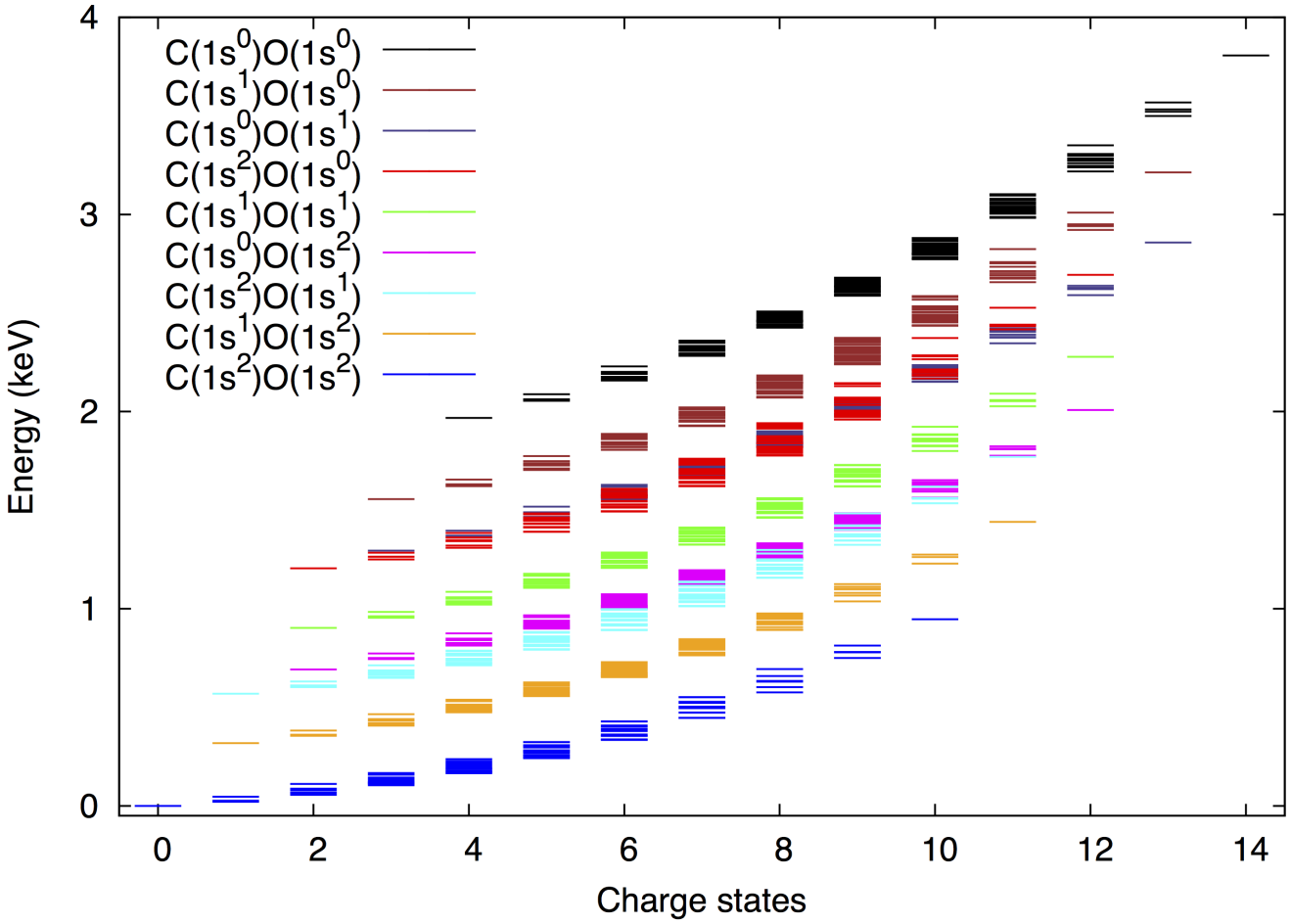
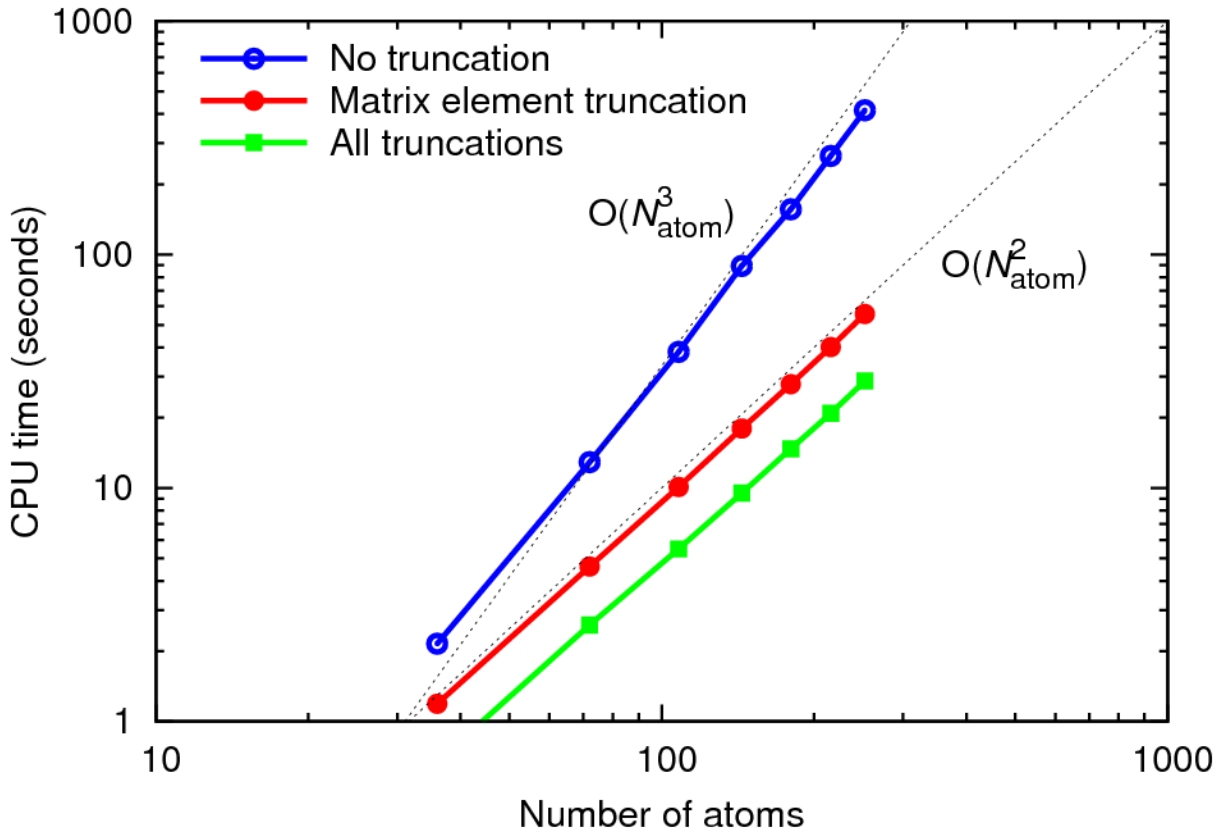
Energy spectrum for various electronic states of CO



All possible multiple-hole configurations formed by x-ray multiphoton ionization

Y. Hao *et al.*, Structural Dynamics **2**, 041707 (2015).

Performance scaling with respect to the molecular size



- Truncation in matrix element evaluations: $O(N_{grid}N_{basis}^2) \rightarrow O(N_{grid}N_{basis}) \sim O(N_{atom}^2)$
- Truncation in direct Coulomb interaction: $O(N_{grid}^2) \rightarrow O(N_{grid}N_{atom}) \sim O(N_{atom}^2)$

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Y. Hao *et al.*, Structural Dynamics **2**, 041707 (2015).

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Conclusions (I)

- 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.

- 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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Conclusions (II)

- XATOM:

  an integrated toolkit for x-ray atomic physics at high intensity

- XMDYN:

  XATOM-based molecular-dynamics/Monte-Carlo code for polyatomic systems

- XMOLECULE:

  XATOM-based electronic-structure and ionization-dynamics code for polyatomic systems

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Conclusions (III)

- Valence electron redistribution on the time scale of a femtosecond or so is not necessarily the result of coherent electron dynamics.

- Relatively small atomic displacements in the vicinity of conical intersections have a dramatic effect on the valence electron distribution.

- The associated charge fluctuations might play a role in x-ray imaging using high-intensity fs pulses.