Resonances in x-ray multiphoton ionization

Sang-Kil Son
Center for Free-Electron Laser Science, DESY, Hamburg, Germany

Molecular quantum dynamics beyond bound states
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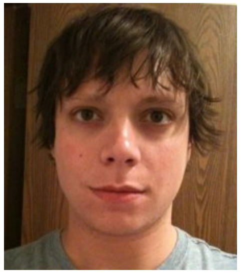
HELMHOLTZ
RESEARCH FOR GRAND CHALLENGES

Center for Free-Electron Laser Science
CFEL is a scientific cooperation of the three organizations:
DESY – Max Planck Society – University of Hamburg

Collaboration

- **REXMI at LCLS**: B. Rudek (PTB), D. Rolles, A. Rudenko (KSU), L. Foucar (MPI-MF), B. Erk, C. Bomme, J. Correa (DESY), R. Boll (EuXFEL), S. Carron, S. Boutet, G. J. Williams, K. R. Ferguson, R. Alonso-Mori, J. E. Koglin, T. Gorkhover, M. Bucher (LCLS), C. S. Lehmann, B. Krässig, S. Southworth, L. Young, Ch. Bostedt (ANL), K. Ueda (Tohoku), T. Marchenko, M. Simon (UPMC)
- **REXMI at European XFEL**: Rebecca Boll, T. Baumann, A. De Fanis, V. Music, D. Rivas, A. Rörig, Ph. Schmidt, S. Usenko, M. Meyer (EuXFEL SQS), J. Laksman (EuXFEL XPD), S. Serkez (EuXFEL SPF), B. Erk (DESY), S. Pathak, D. Rolles (KSU)
- **REMPI at European XFEL**: Aaron LaForge, D. Mishra, S. Duncanson, N. Berrah (UConn), E. Eronen, E. Kukk (U. Turku), P. Walter (LCLS), M. Ilchen, R. Boll, A. De Fanis, M. Meyer, Y. Ovcharenko, D. Rivas, Ph. Schmidt (EuXFEL)
- **CFEL-DESY Theory Division**: Robin Santra, K. Toyota, S. Wirok-Stoletow, D. Kolbasova, Z. Jurek

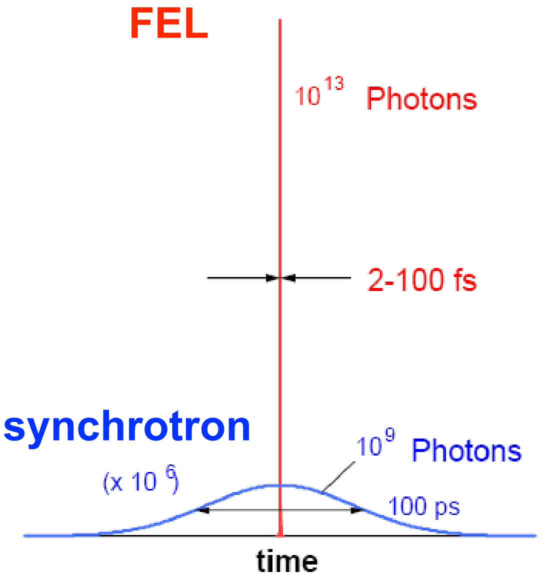

Rebecca Boll


Aaron LaForge

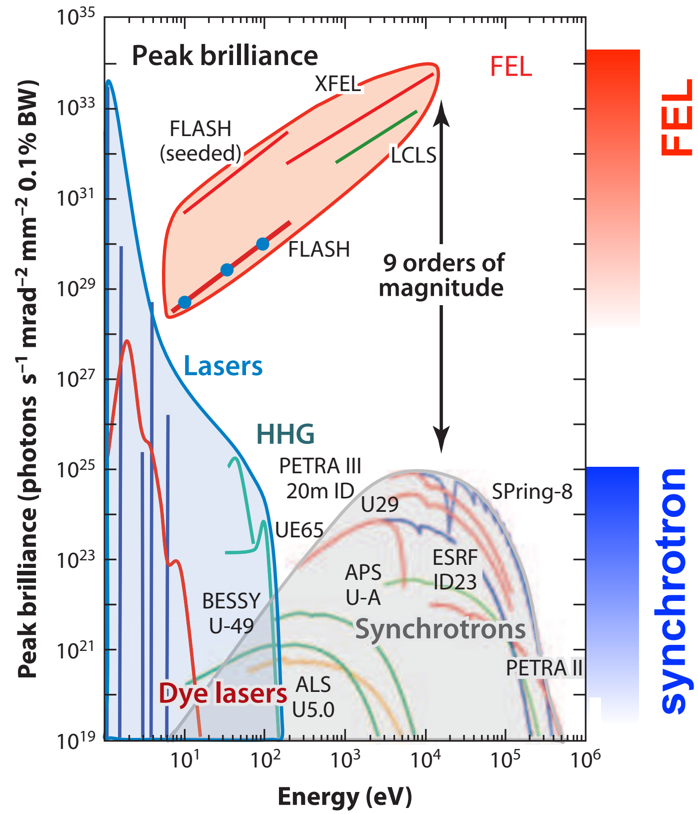

Robin Santra

XFEL: X-ray free-electron laser

- *Ultraintense*: ~10^{13} photons
- *Ultrafast*: ~femtoseconds
  ➔ peak intensity ~ 10^{20} W/cm^2



Schneider, *Rev. Accl. Sci. Tech.* **3**, 13 (2010).

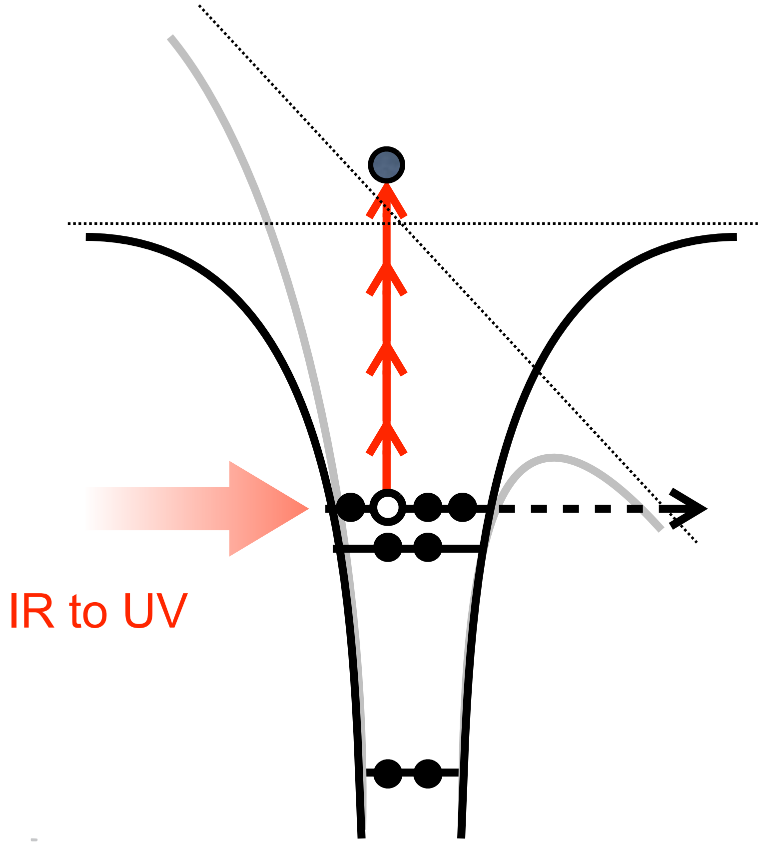


Ullrich *et al.*, *Annu. Rev. Phys. Chem.* **63**, 635 (2012).

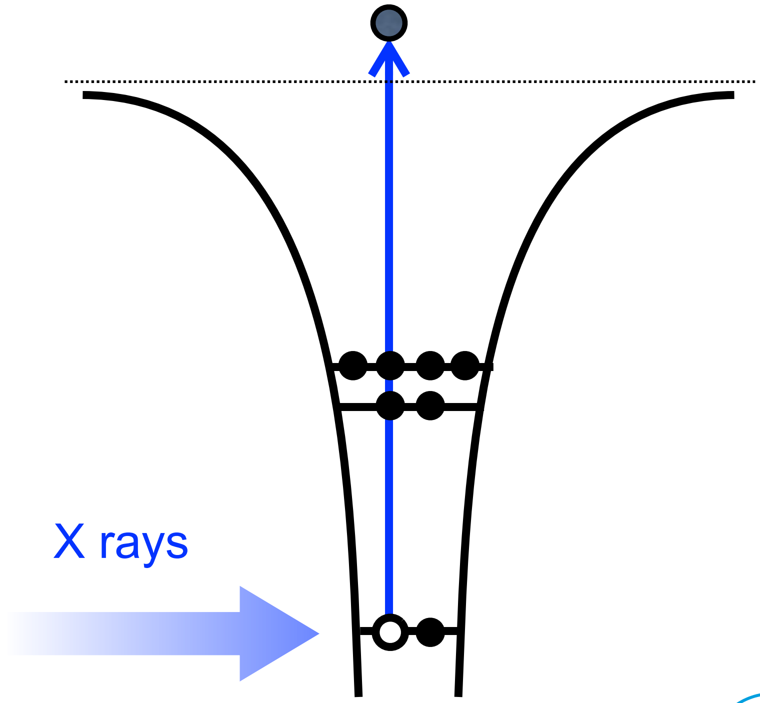
How does matter interact with *ultraintense* and *ultrafast* pulses?

Strong light-matter interaction

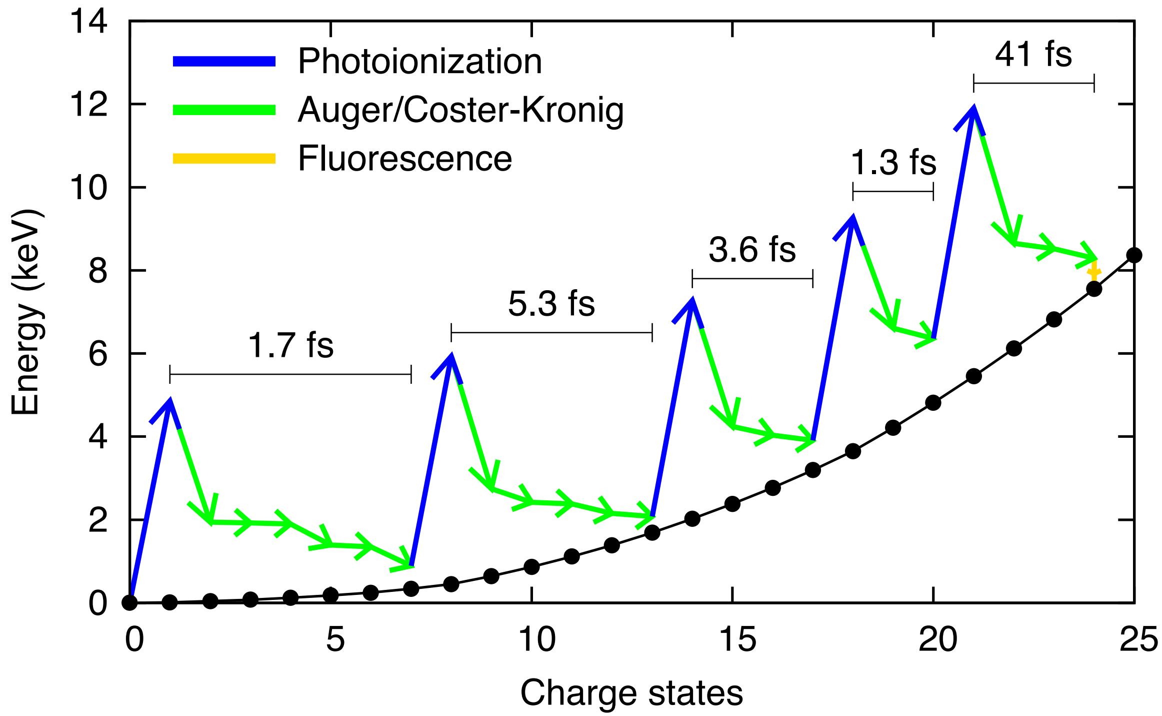
- Strong-field optical regime
  - tunneling or multiphoton processes
  - valence-electron ionization



- Intense X-ray regime
  - mainly one-photon processes
  - core-electron ionization and relaxation
  - multiphoton multiple ionization via a sequence of one-photon processes



X-ray multiphoton ionization



Xe@5.5 keV

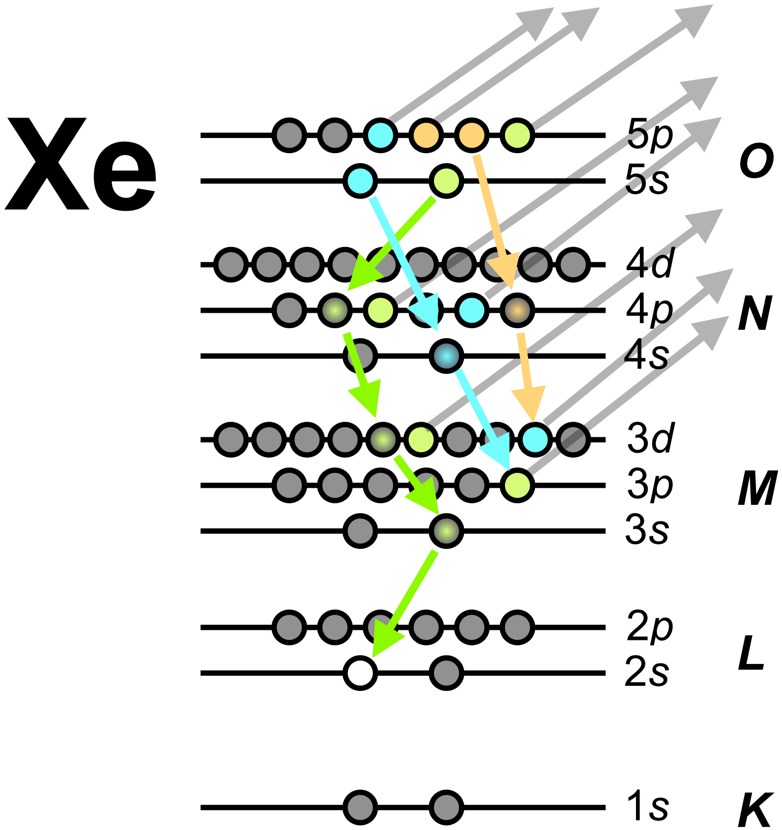
Fukuzawa *et al.*, *Phys. Rev. Lett.* **110**, 173005 (2013).

- A sequence of one-photon absorption and accompanying relaxations
  ➔ sequential multiphoton multiple ionization dynamics
- Direct multiphoton absorption: negligible if one-photon abs. is available

Doumy *et al.*, *Phys. Rev. Lett.* **106**, 083002 (2011).

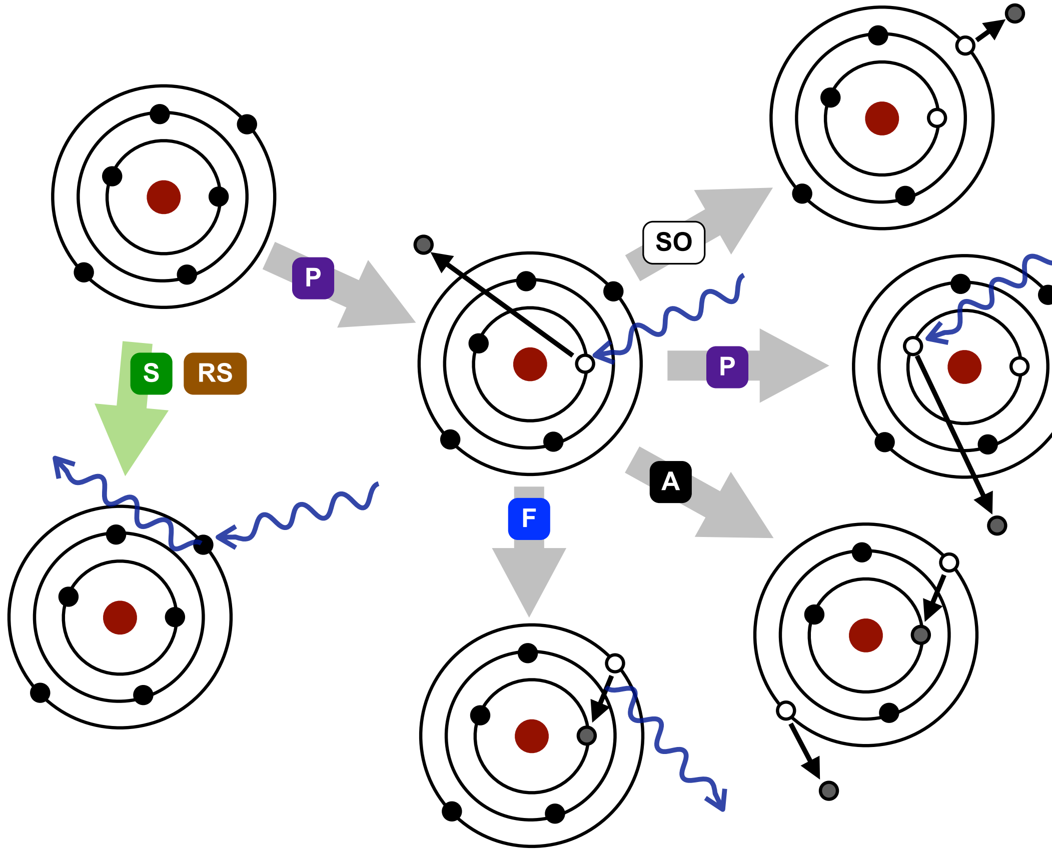
Challenges for x-ray multiphoton ionization

- Theoretical challenges
  - tremendously many hole states by x-ray multiphoton absorption
  - highly excited system far from the ground state
  - electronic continuum states for ionization
  - complex inner-shell ionization dynamics, especially for heavy atoms
- No standard quantum chemistry code available



XATOM: all about x-ray atomic physics

- X-ray-induced atomic processes calculated for any given element and configuration
- Ionization dynamics solved by a rate-equation approach
- Sequential ionization model has been tested by a series of atomic XFEL experiments



Son, Young & Santra, *Phys. Rev. A* **83**, 033402 (2011).
Jurek, Son, Ziaja & Santra, *J. Appl. Cryst.* **49**, 1048 (2016).
Download executables: http://www.desy.de/~xraypac

XATOM: Theoretical details

- Efficient electronic structure calculation required
- Hartree-Fock-Slater (HFS) method

$$\left[-\frac{1}{2}\nabla^2 - \frac{Z}{r} + \int d^3r' \, \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - \frac{3}{2}\left\{\frac{3}{\pi}\rho(\mathbf{r})\right\}^{1/3}\right]\psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r})$$

spherically symmetric: $\psi_{nlm}(\mathbf{r}) = \frac{u_{nl}(r)}{r} Y_{lm}(\theta,\varphi)$

- Bound states ➔ GPS method on *nonuniform* grid
- Continuum states: calculated with the same potential as used in bound states ➔ 4th-order Runge-Kutta method on *uniform* grid
- Calculate all cross sections and rates of x-ray-induced processes based on the perturbation theory

$$\Gamma_{FI} = 2\pi\delta\left(E_F - E_I\right)\left|\langle F|\hat{H}_{\mathrm{int}}|I\rangle\right|^2$$

Son, Young & Santra, *Phys. Rev. A* **83**, 033402 (2011).

XATOM: Coupled rate equations

- Cross sections & rates: (in principle) calculated for every single config.
- Solve coupled rate equations to simulate ionization dynamics

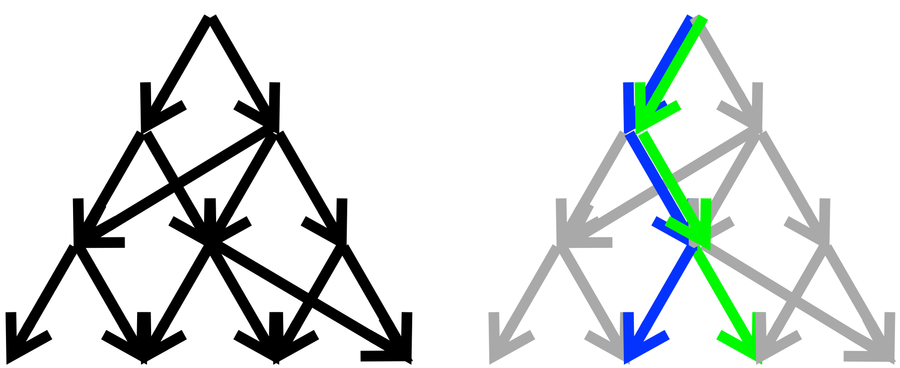
$$\frac{d}{dt}P_I(t) = \sum_{I' \neq I}^{\text{all config.}} \left[\Gamma_{I' \to I} P_{I'}(t) - \Gamma_{I \to I'} P_I(t) \right]$$

- Tremendously large coupled rate equations ➔ solved by Monte Carlo

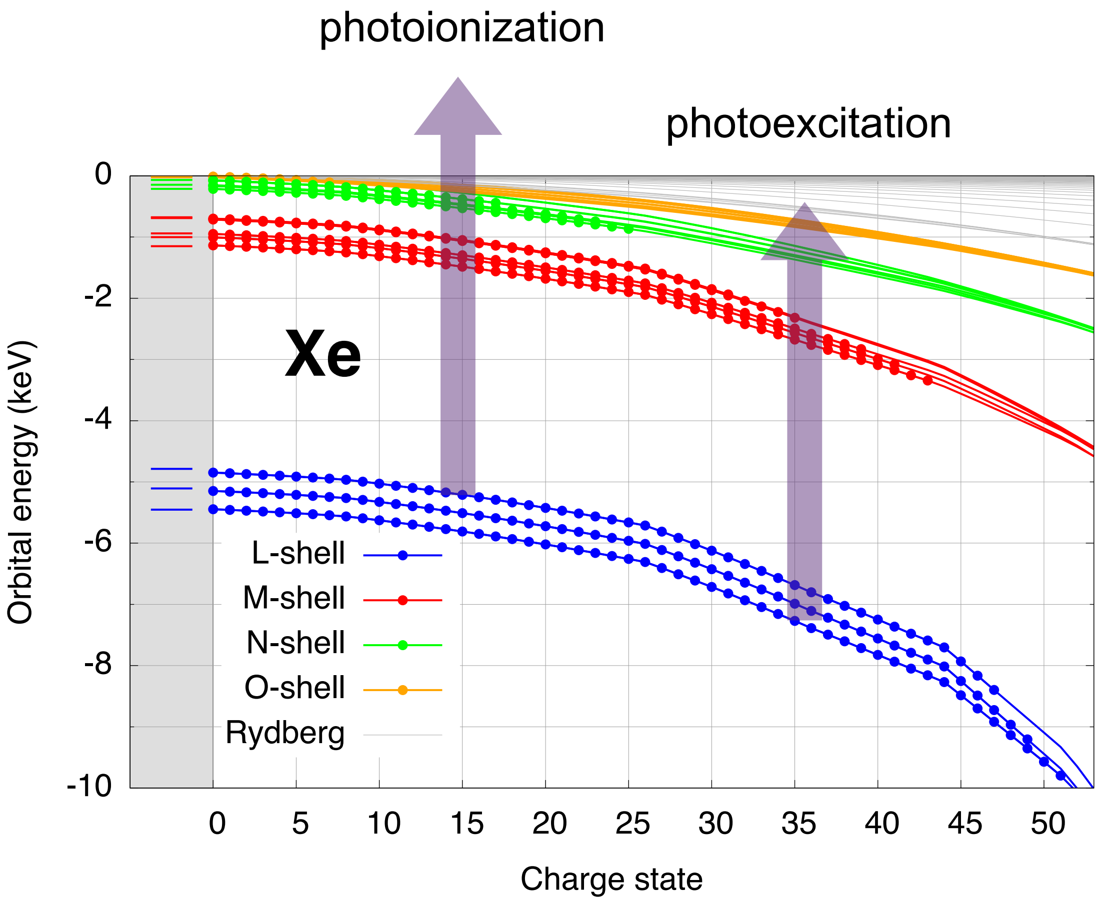
Son & Santra, *Phys. Rev. A* **85**, 063415 (2012).

- Cross sections are rates calculated only for configurations visited during selected pathways ➔ Monte Carlo on-the-fly

Fukuzawa *et al.*, *Phys. Rev. Lett.* **110**, 173005 (2013).



XATOM: Resonant photoexcitation

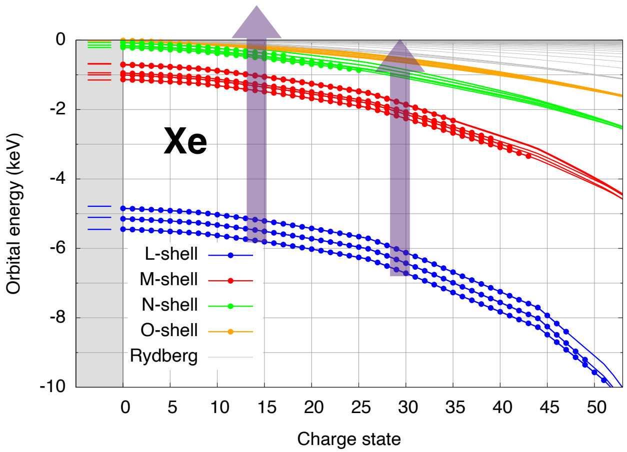


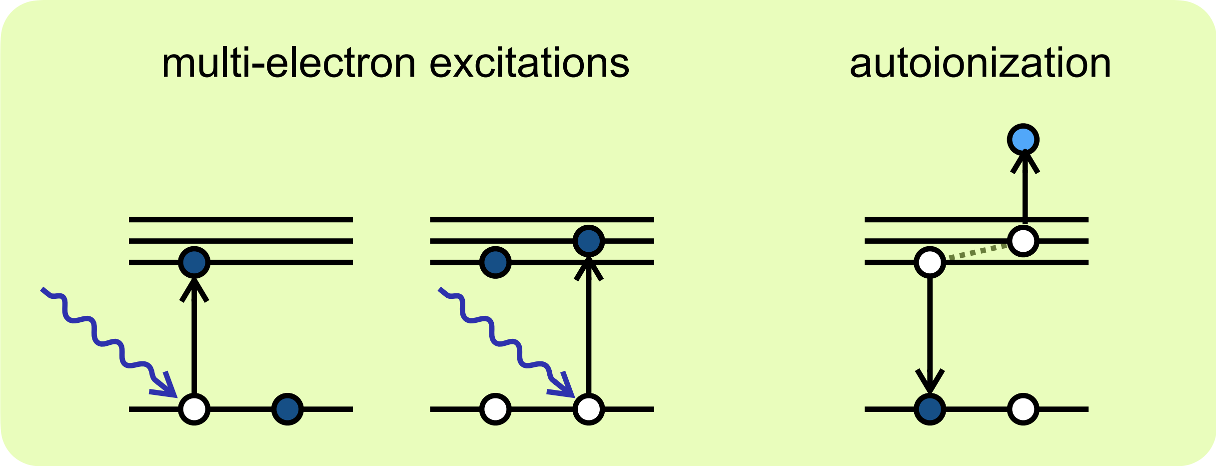
XATOM extended to treat resonant excitation:
Toyota *et al.*, *Phys. Rev. A* **95**, 043412 (2017).

- Resonant photoexcitation to Rydberg states:
  - How many *n* and *l* to be considered?
  - Can we accurately describe these states?
- Number of coupled rate equations explodes
  - For example, Xe *L*-shell
  - non-relativistic, no resonance: *N*=23,532,201
  - relativistic, no resonance: *N*=5,023,265,625
  - relativistic, resonance ($n \leq 30$, $l \leq 7$): ~2.6×10^{68}

REXMI

REXMI mechanism





- REXMI: resonance-enabled or -enhanced x-ray multiple ionization
- Multiple resonant excitations for a range of charge states
- Further ionization via electron-correlation-driven relaxation processes
- Broad energy bandwidth facilitates REXMI
- One of the distinctive phenomena in the field of XFEL–matter interaction

Rudek *et al.*, *Nat. Photon.* **6**, 858 (2012); *Phys. Rev. A* **87**, 023413 (2013); *Nat. Commun.* **9**, 4200 (2018).
Ho *et al.*, *Phys. Rev. Lett.* **113**, 253001 (2014); *Phys. Rev. A* **92**, 063430 (2015).

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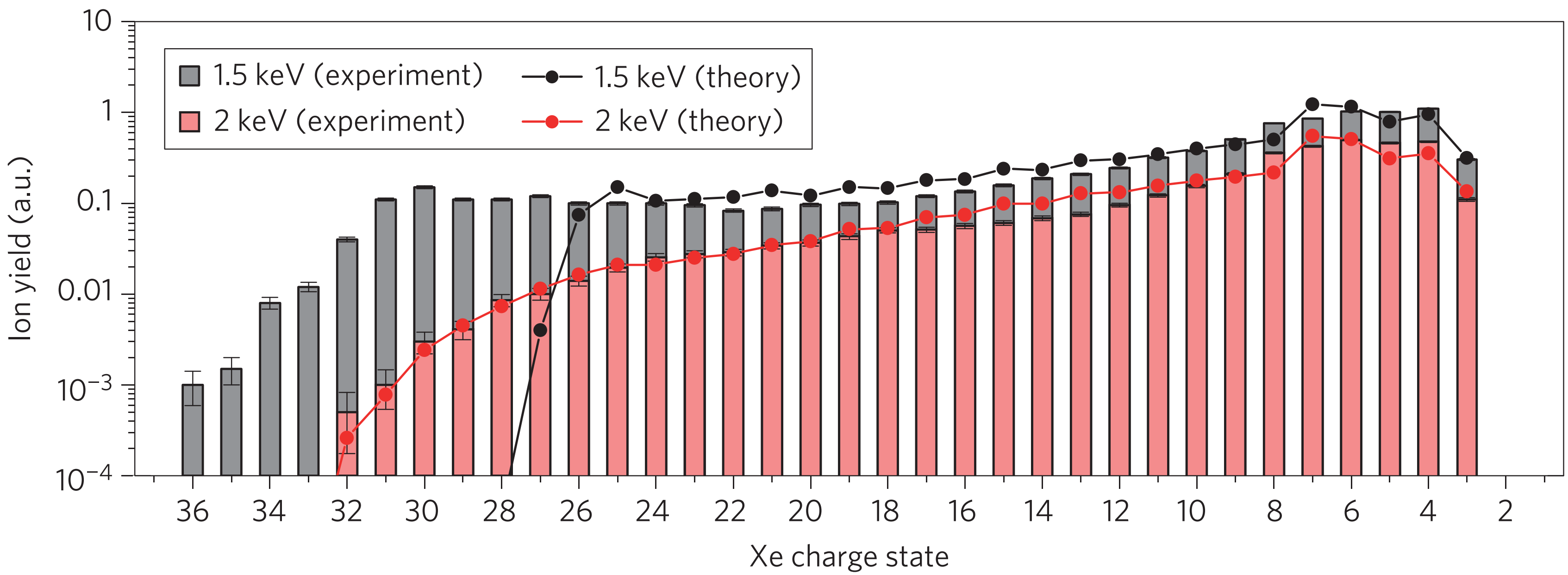
First observation of REXMI



LCLS experiment

Daniel Rolles at KSU

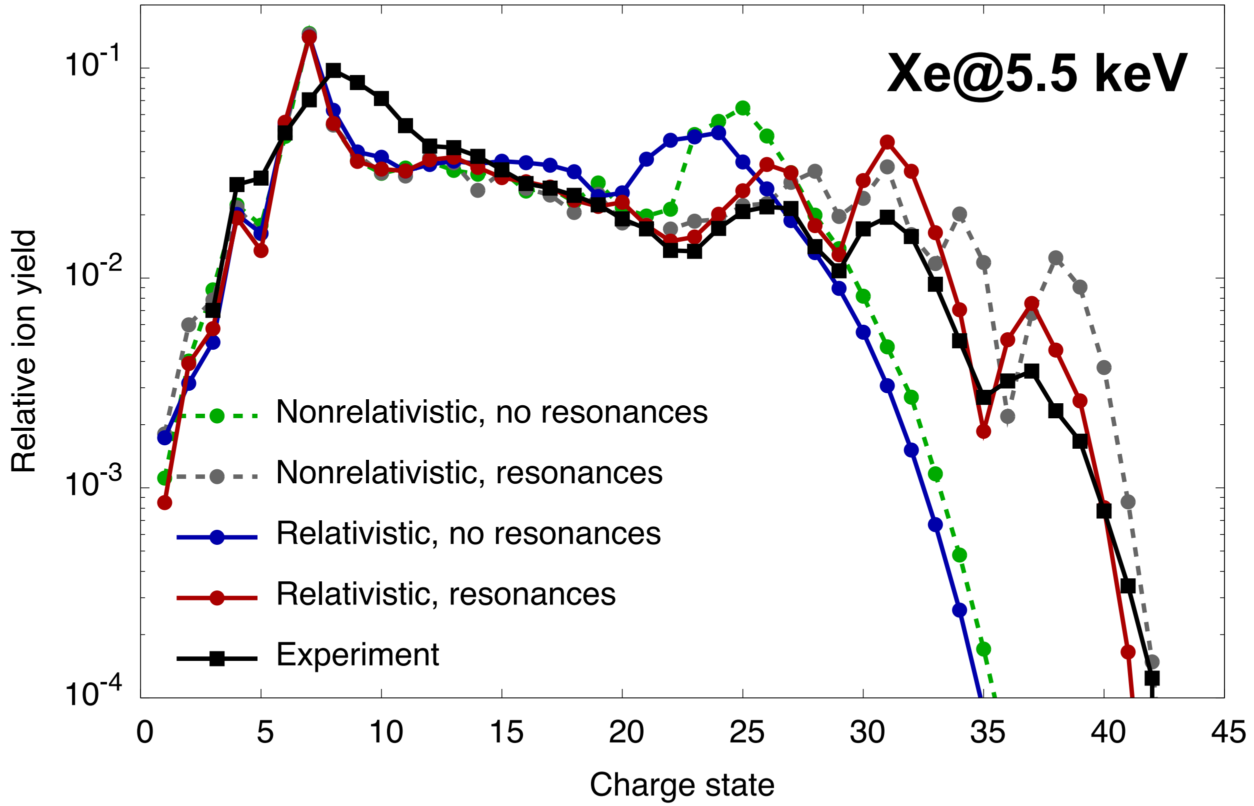
Artem Rudenko at KSU

Benedikt Rudek at PTB

- Xe *M*-shell-initiated ionization
- 2 keV: excellent agreement between theory and experiment
- 1.5 keV: further ionization via resonance

Rudek *et al.*, *Nat. Photon.* **6**, 858 (2012).

Relativistic and resonant effects



XATOM development

Koudai Toyota
at CFEL-DESY Theory

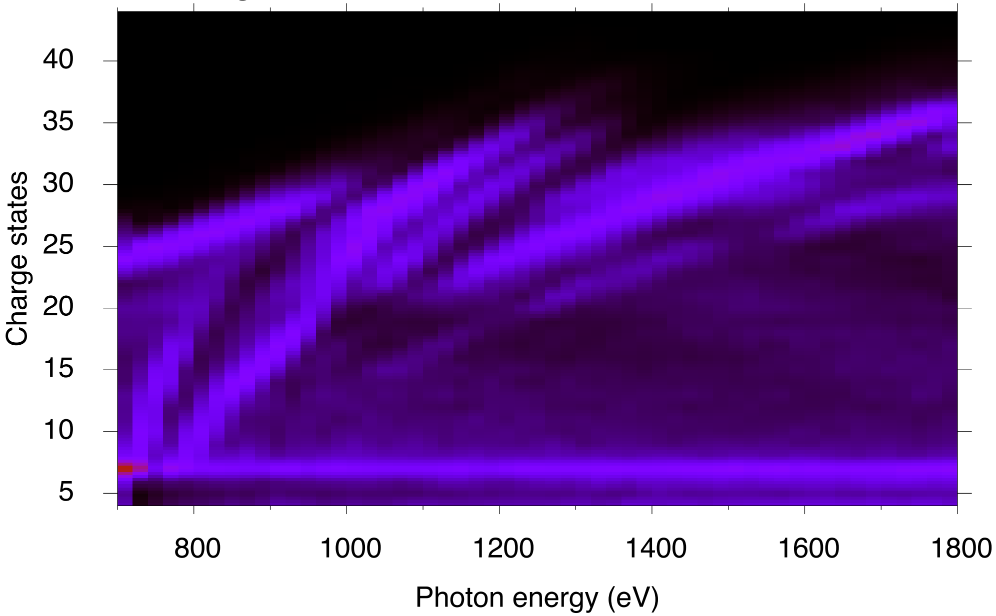
LCLS experiment
Benedikt Rudek
Daniel Rolles
Artem Rudenko

Rudek *et al.*, *Nat. Commun.* **9**, 4200 (2018).

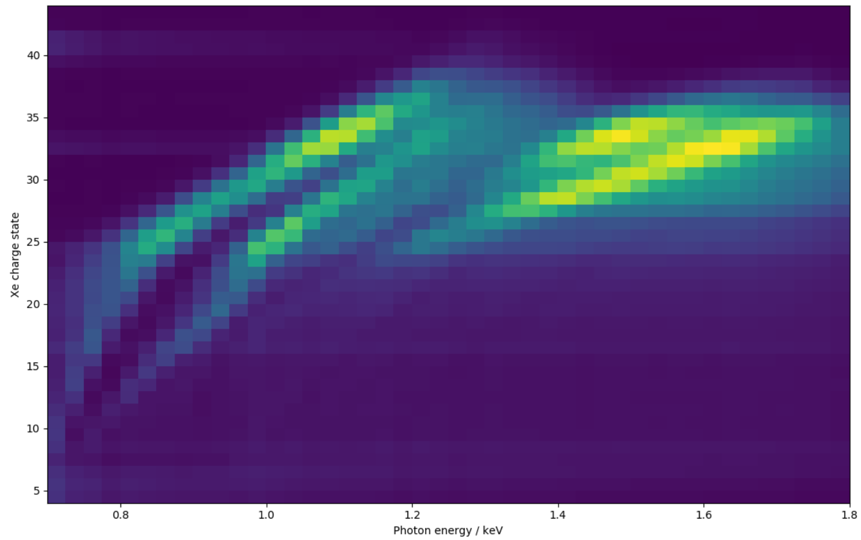
- Xe *L*-shell-initiated ionization: $2p_{1/2}$–$2p_{3/2}$ splitting ~300 eV
- XATOM extended to treat both relativistic and resonant effects
- Structured CSD: interplay of resonance and relativistic effects

Photon-energy scan in soft x-rays

Theory



Experiment (preliminary raw data)



- Overall, good agreement between theory and experiment
- For each slice of photon energy, quantitative comparison could reveal details of ionization dynamics: effects of peak fluence, bandwidth, temporal structure, etc.

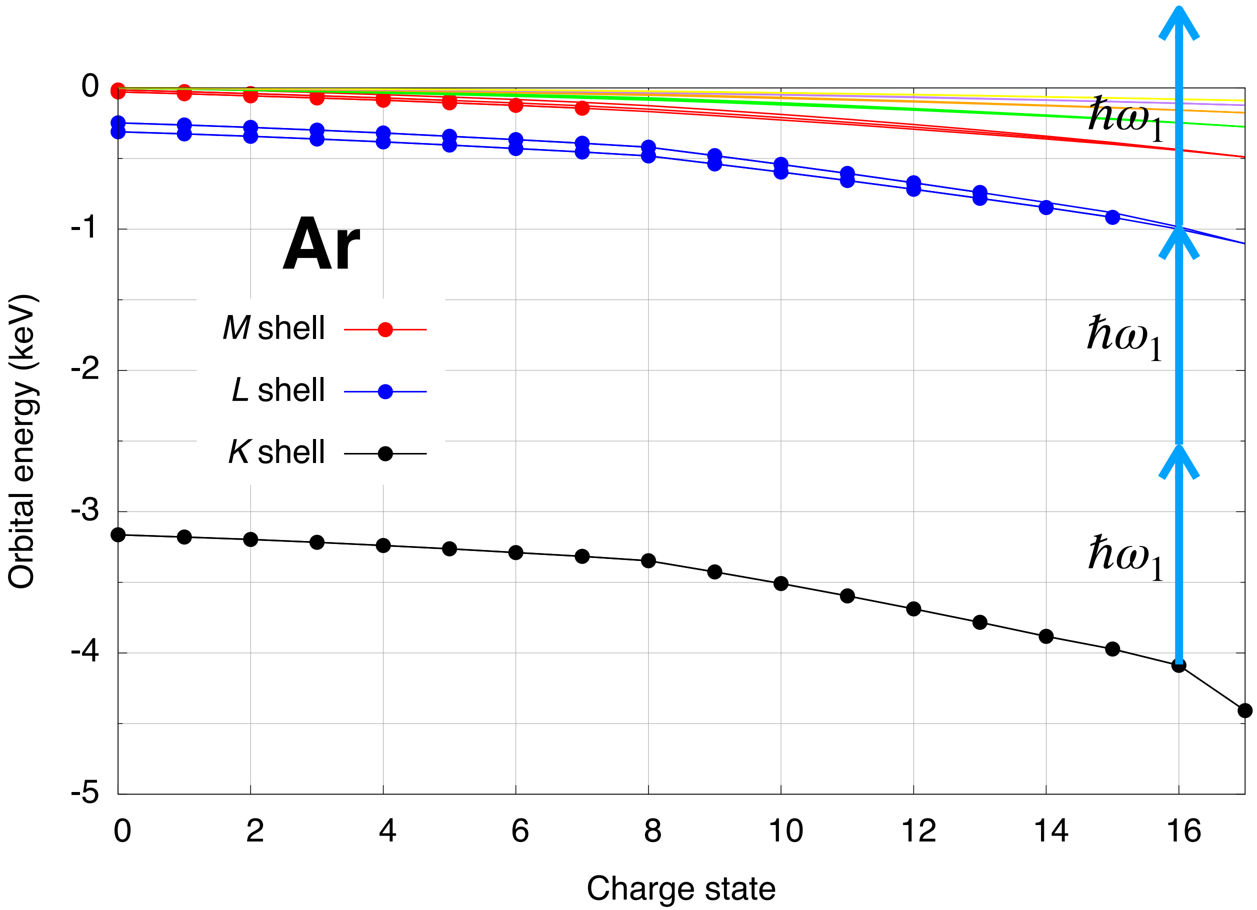
European XFEL SQS experiment

Rebecca Boll
at EuXFEL

Aljoscha Rörig
at EuXFEL

X-ray REMPI

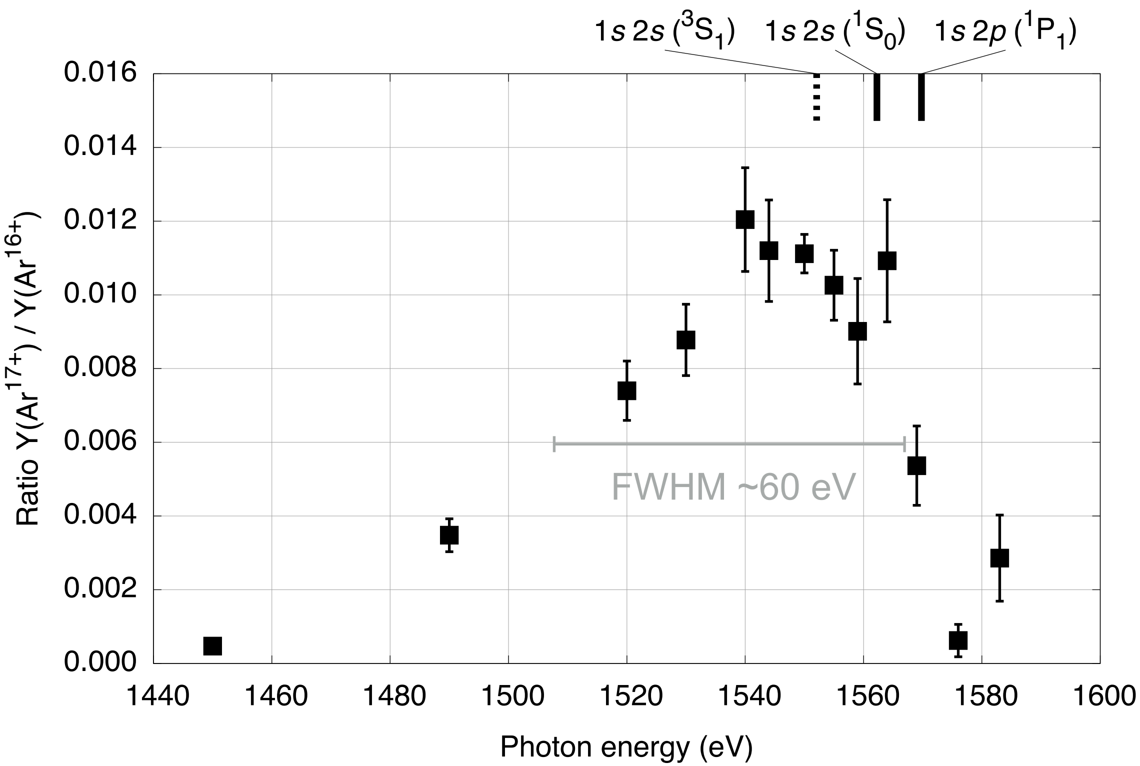
Ar^{17+} measurement



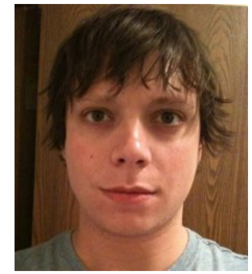
- Ar^{17+} detected: IP=4130 eV, photon energy ~ 1550 eV
- (2+1)-REMPI conceivable
- REXMI cannot create Ar^{17+}
- Any other ionization pathways?

REMPI (resonance-enhanced multiphoton ionization) in the x-ray regime

Experimental resonance profile



European XFEL SQS experiment



Aaron LaForge at UConn

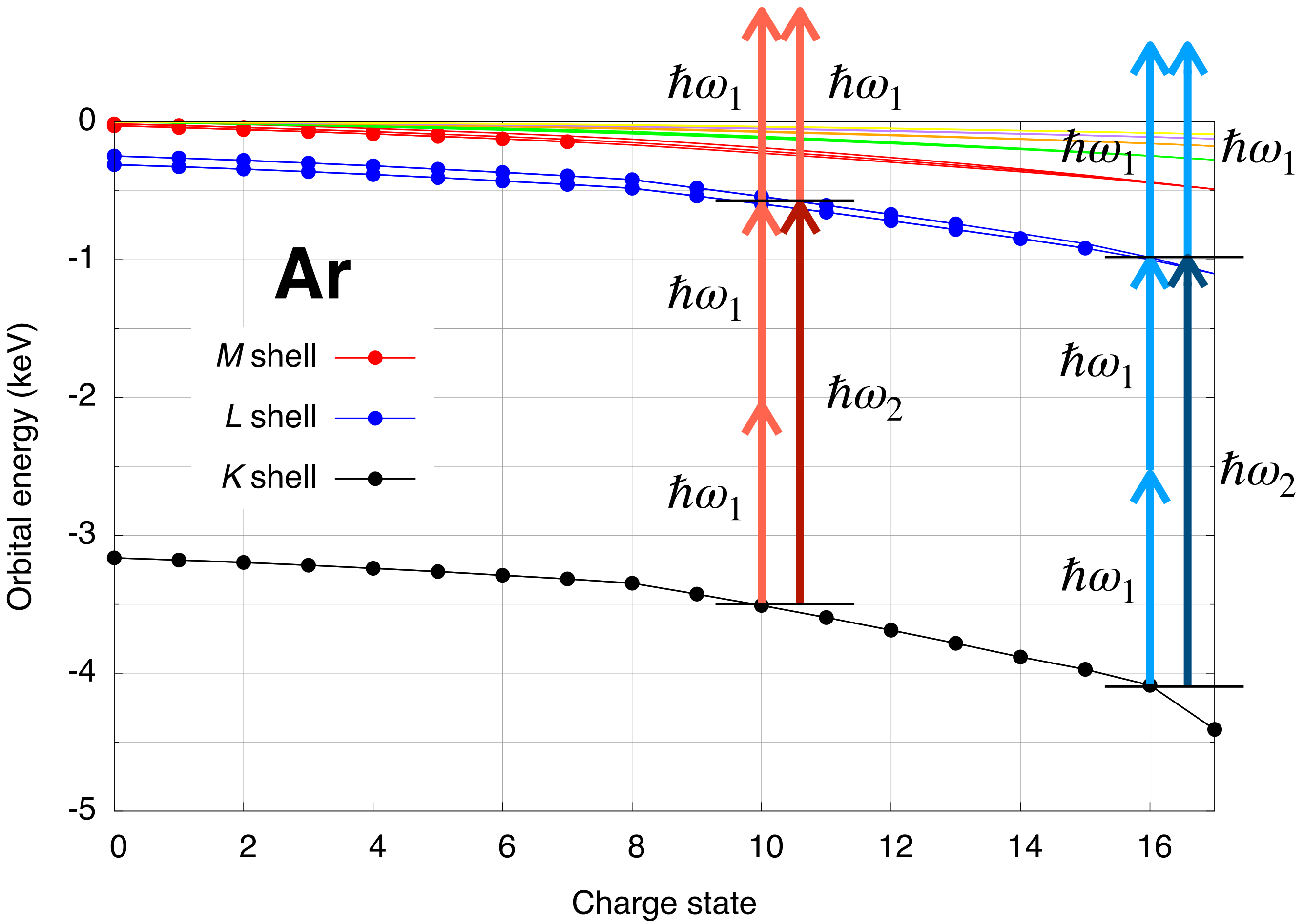
Nora Berrah at UConn

Debadarshini Mishra at UConn

LaForge *et al.*, (submitted).

- Resonance structure: yield ratios of Ar^{17+} to Ar^{16+} as a func. of photon *E*
- X-ray REMPI: broad, red-shifted, asymmetric resonance profile
  ➔ stark contrast to conventional REMPI at longer wavelengths

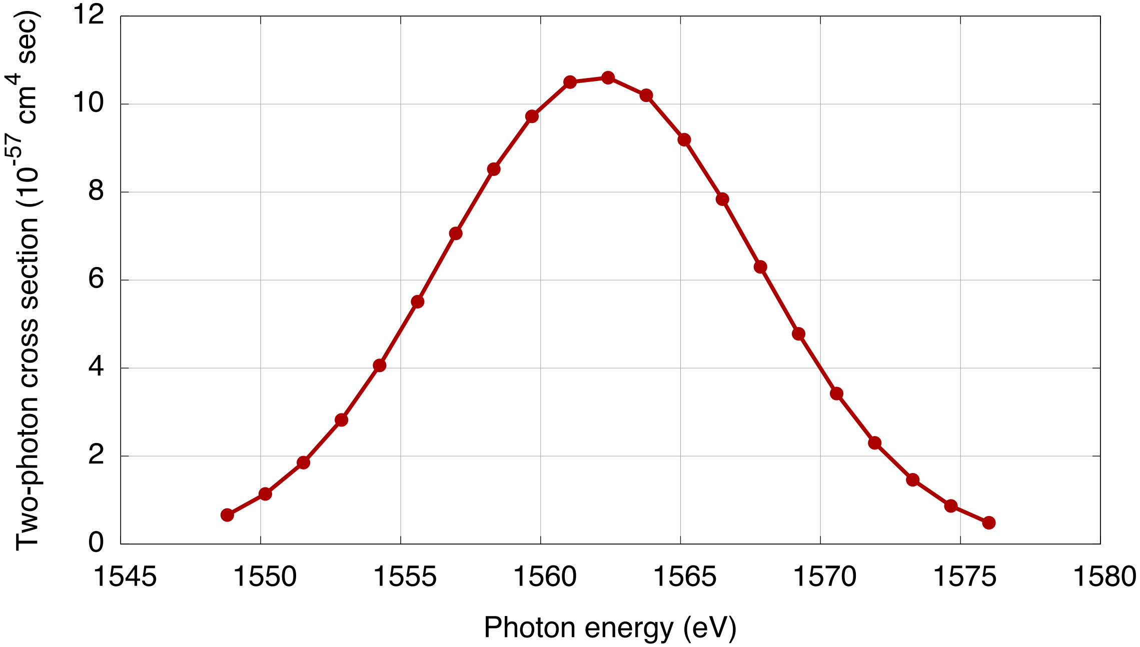
REMPI mechanism



- More ionization channels besides (2+1)-REMPI
- 2nd harmonic (0.2% contrib.): (1′+1)-REMPI
- At low charges: (2+*n*)-REMPI or (1′+*n*)-REMPI

LaForge *et al.*, (submitted).

Direct two-photon resonant excitation



LaForge *et al.*, (submitted).

Stanislaw Wirok-Stoletow at CFEL-DESY Theory

Daria Kolbasova at CFEL-DESY Theory

- XCID: grid-based TDCIS (time-dependent config. interaction singles)
- Calculate direct two-photon $\sigma^{(2)}$ for $1s^2 \rightarrow 1s2s$ of Ar^{16+}
- For other charges, the same σ profile is shifted by Δ in the transition *E*

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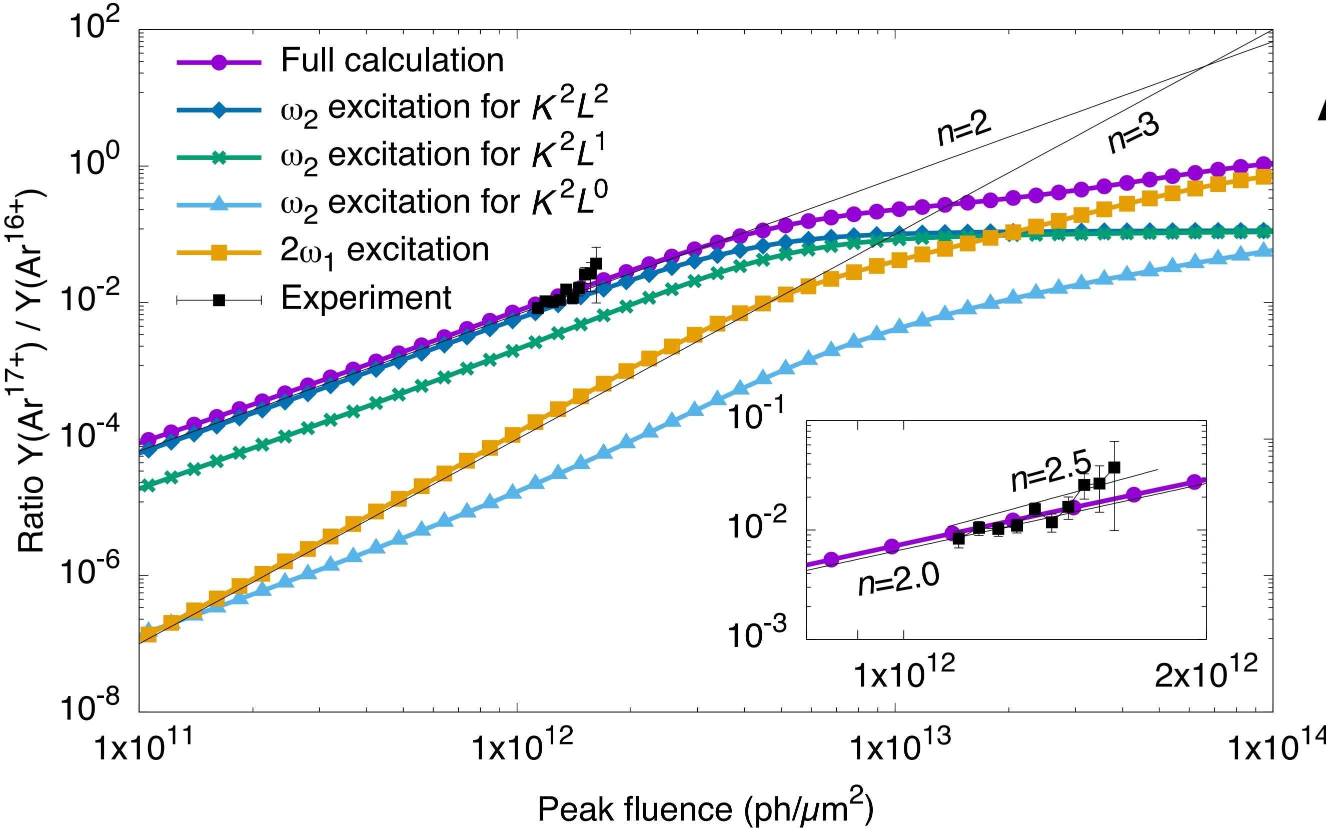
REMPI contribution analysis



Ar@1550 eV

LaForge *et al.*, (submitted).

- Resonant excitation by 2nd harmonic (0.2%) is dominant
- (1′+*n*)-REMPI: resonant excitation by 2nd harmonic at lower charges with lower transition energy ➔ red-shifted and asymmetric broadening

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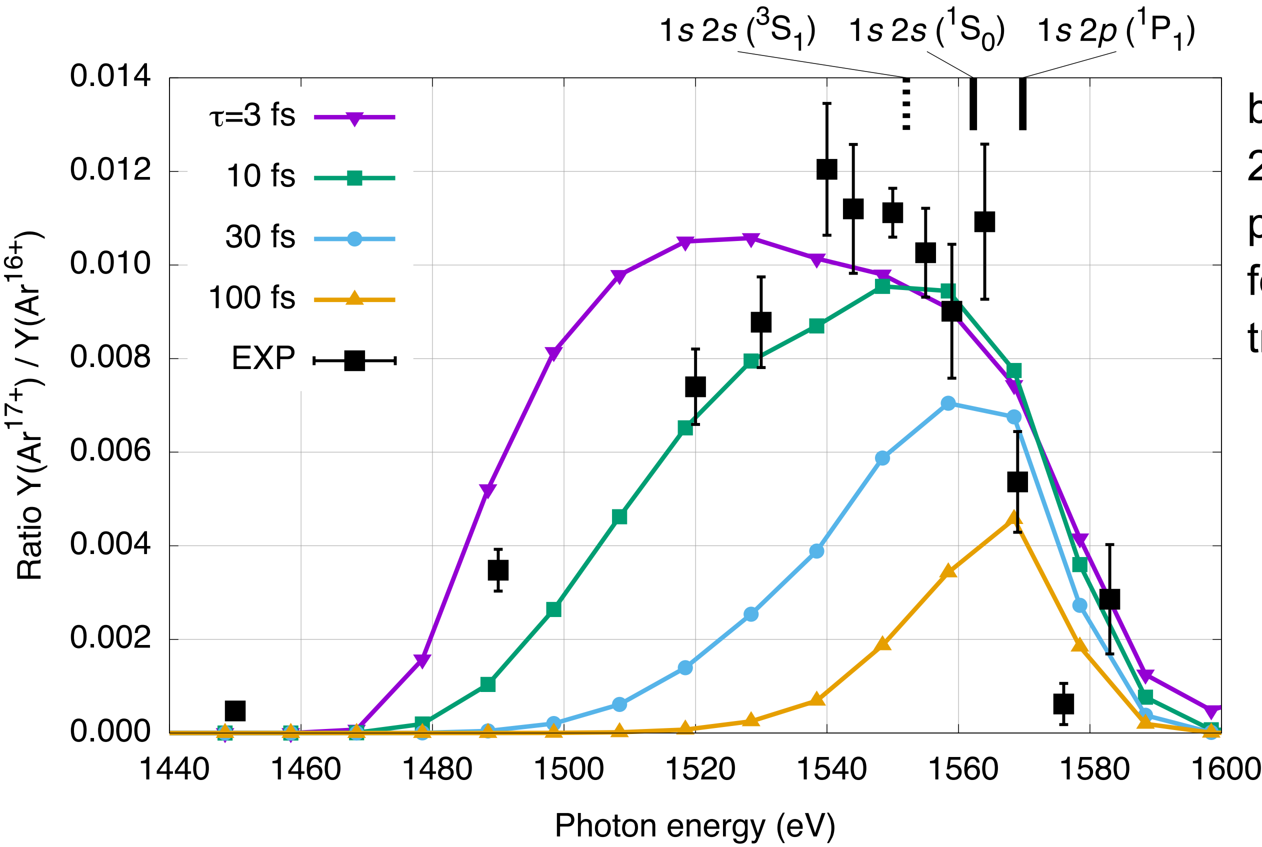
Pulse-duration effects



bandwidth: 1%
2nd harmonic: 0.2%
pusle *E*: 4.2 mJ
focal size: 1.5×1.5 μm²
transmission: 17.1%

LaForge *et al.*, (submitted).

- Calculation with 10-fs matches well with experimental data
- The shorter the pulse length, the more the 1*s* vacancy created at lower charges survives until Ar^{17+} ➔ explains more shifted for shorter pulses

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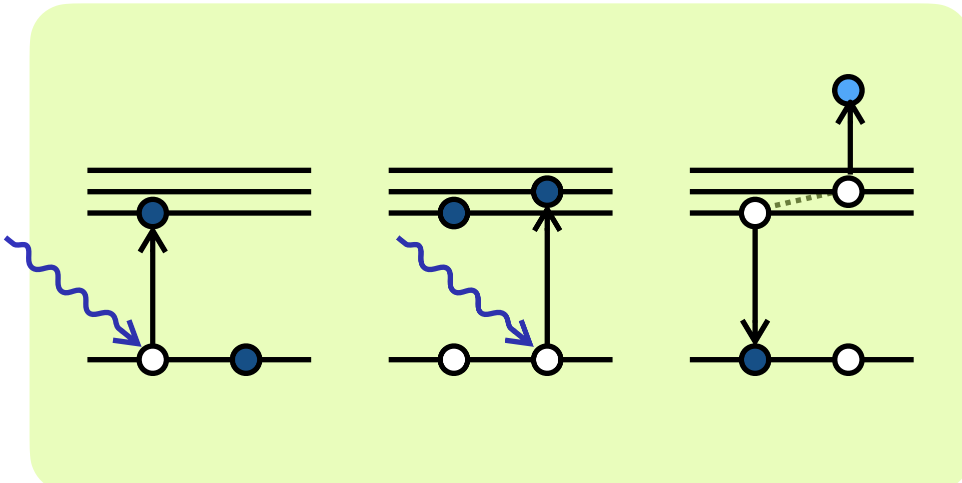
REXMI vs. X-ray REMPI

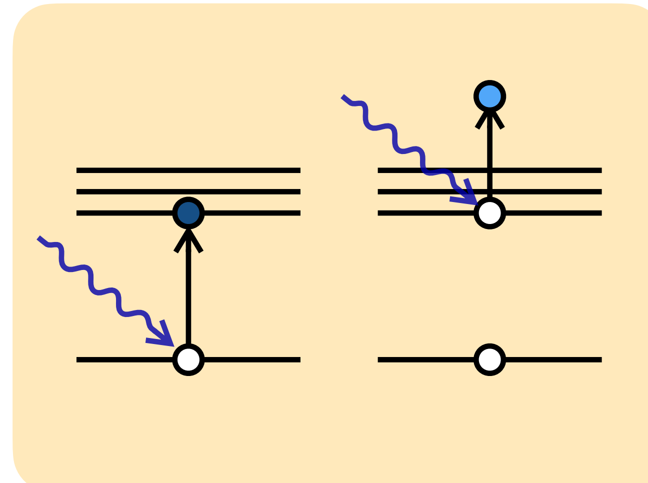
REXMI



- multi-electron excitation
- electron-correlation-driven relaxation
- broad bandwidth

Rudek *et al.*, *Nat. Photon.* **6**, 858 (2012).
Rudek *et al.*, *Nat. Commun.* **9**, 4200 (2018).

X-ray REMPI



- single-electron excitation
- ionization by another photon
- narrow bandwidth
- not necessarily single ionization

LaForge *et al.*, (submitted)

Recent progresses

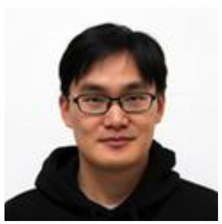
CFEL-DESY Theory Division

Robin Santra

Zoltan Jurek

Julia Schäfer

Zoltan Jurek



Rui Jin

XATOM

XMDYN

Coulomb explosion of iodopyridine molecules

Boll *et al.*, (submitted).

XPOT+XMDYN

Transient IPD in nonthermal dense plasmas

Phys. Rev. E **103**, 023203 (2021).

XMOLECULE

Femtosecond structural dynamics of water molecules

Jahnke *et al.*, (submitted).

Ludger Inhester

Conclusions

- X-ray multiphoton ionization is described by a sequence of one-photon ionization and accompanying relaxation processes
- Resonant excitation plays an important role in x-ray multiphoton ionization via REXMI and REMPI
- REXMI: ultra-efficient ionization mechanism by intense XFEL pulses
- REMPI: first observation in the x-ray regime and its resonance profile with a clear distinction from conventional REMPI
- XATOM: central development for describing XFEL–matter interaction

Thank you for your attention!

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DESY.