Processes at high radiation intensity

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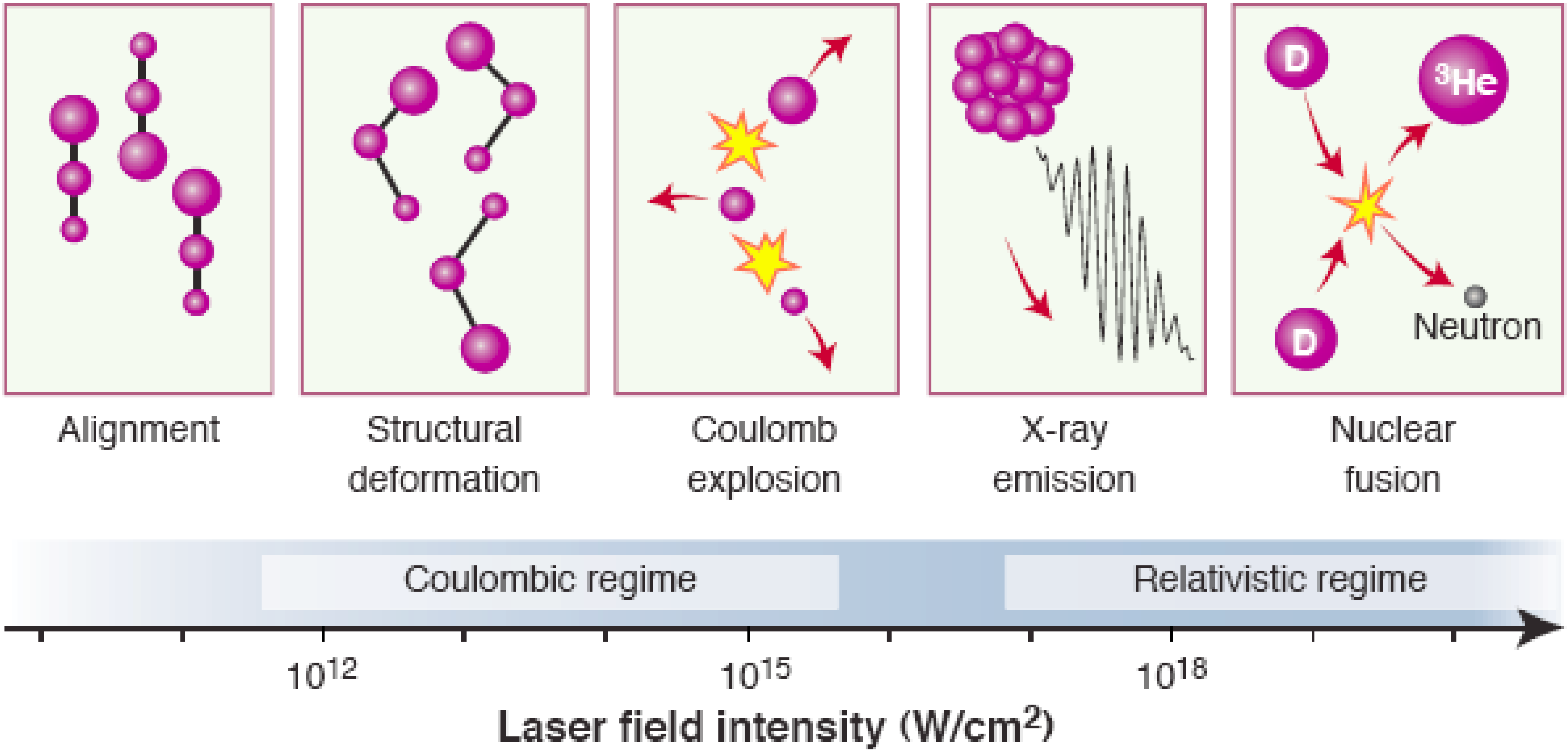
Processes in strong optical fields (~ 800 nm)

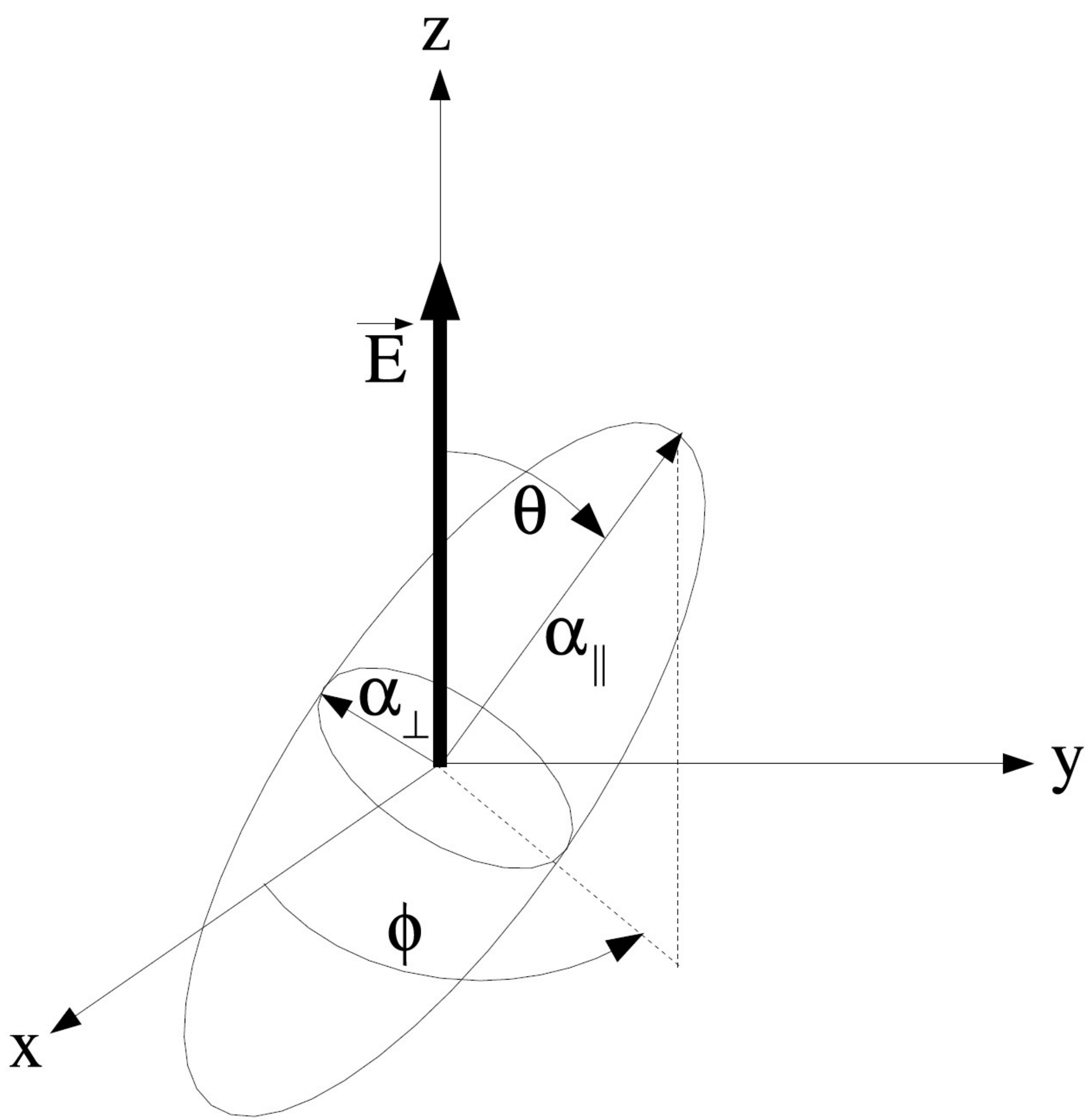


Yamanouchi, Science (2001)

X-ray absorption by laser-aligned molecules

Alignment mechanism

- Exploits dynamic (or AC) Stark effect
- Instantaneous laser electric field induces an electric dipole moment
- The induced dipole moment interacts with the laser electric field
- The resulting potential energy may be averaged over an optical cycle, thus giving rise to an effective Hamiltonian for the rotational degrees of freedom



Stapelfeldt and Seideman, Rev. Mod. Phys. **75**, 543 (2003)

Argonne's Advanced Photon Source (APS) is the brightest source of x-rays for research in the U.S.

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Molecule selected for experimental investigations at the APS: CF_3Br (bromotrifluoromethane, halon-1301)

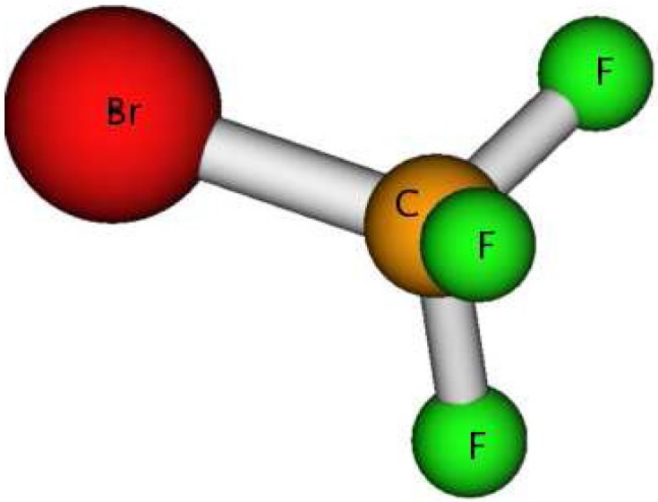

TABLE I: CF_3Br: Mulliken population analysis

C	F	F	F	Br
+0.71	−0.23	−0.23	−0.23	−0.02

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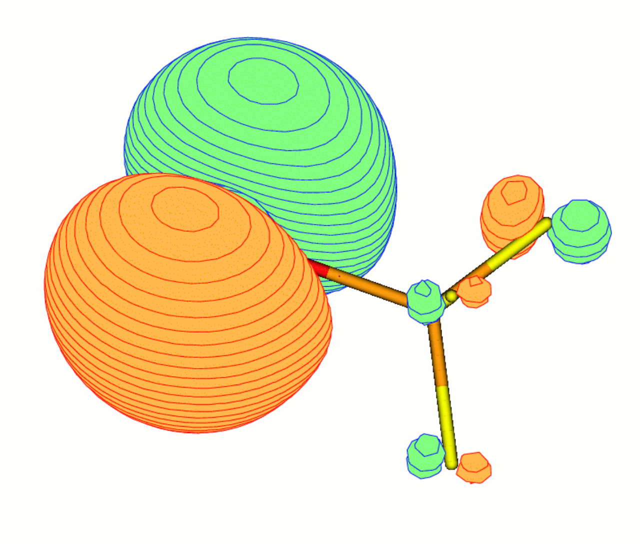
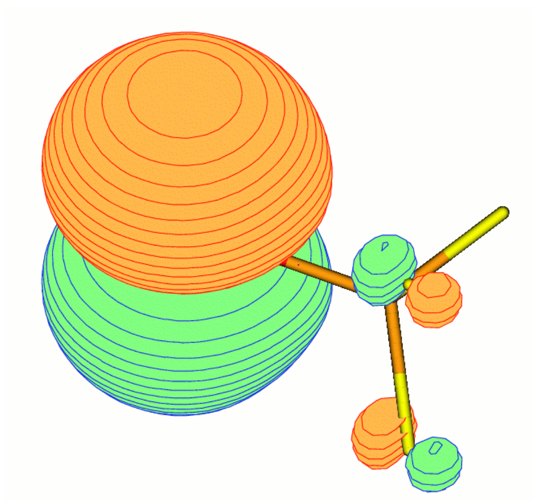
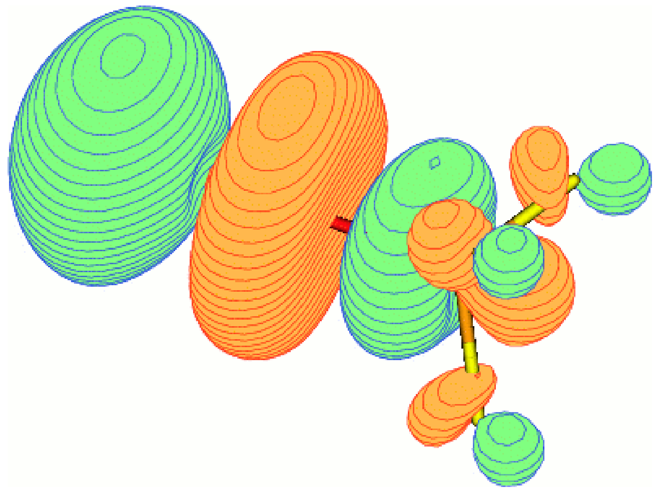
HOMO/LUMO of CF_3Br in Hartree-Fock ground state



HOMO: doubly degenerate π orbital corresponding to Br $4p_x$ and $4p_y$





LUMO: σ^* orbital with large Br $4p_z$ character; resonant x-ray absorption by Br K-shell electron probes only this Br $4p_z$ component

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We can align σ* orbital by aligning the molecule.

This allows us to control x-ray absorption at the Br $1s^{-1}$ σ* resonance.

Theory of laser-induced molecular alignment: Focus on prolate symmetric rotor

$$\hat{H} = \hat{H}_{\text{rot}} + \hat{V}(t)$$

$$\hat{H}_{\text{rot}} = B\hat{J}^2 + (A-B)\hat{J}_A^2$$

$$\hat{V}(t) = -\frac{2\pi}{c} I_L(t) \frac{2}{3}(\alpha_{\parallel} - \alpha_{\perp}) D^{(2)}_{0,0}(\varphi, \vartheta, \chi)$$

$$\langle JKM|\hat{H}_{\text{rot}}|J'K'M'\rangle = \delta_{JJ'}\delta_{KK'}\delta_{MM'}[BJ(J+1) + (A-B)K^2]$$

$$\langle JKM|D^{(2)}_{0,0}|J'K'M'\rangle = \delta_{KK'}\delta_{MM'}\sqrt{\frac{2J'+1}{2J+1}}C(J'2J;M'0M)C(J'2J;K'0K)$$

$$|\psi_{JKM}(t)\rangle = \sum_{J'} e^{-iE_{J',K}t} c^{(KM)}_{J',J}(t)|J'KM\rangle$$

$$\langle\cos^2\vartheta\rangle = \text{tr}[\hat{\rho}(t)\cos^2\vartheta]$$

$$\hat{\rho}(t) = \sum_{JKM} |\psi_{JKM}(t)\rangle \frac{g_I(K)e^{-\beta E_{J,K}}}{Z} \langle\psi_{JKM}(t)|$$

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Buth and Santra, Phys. Rev. A **77**, 013413 (2008).

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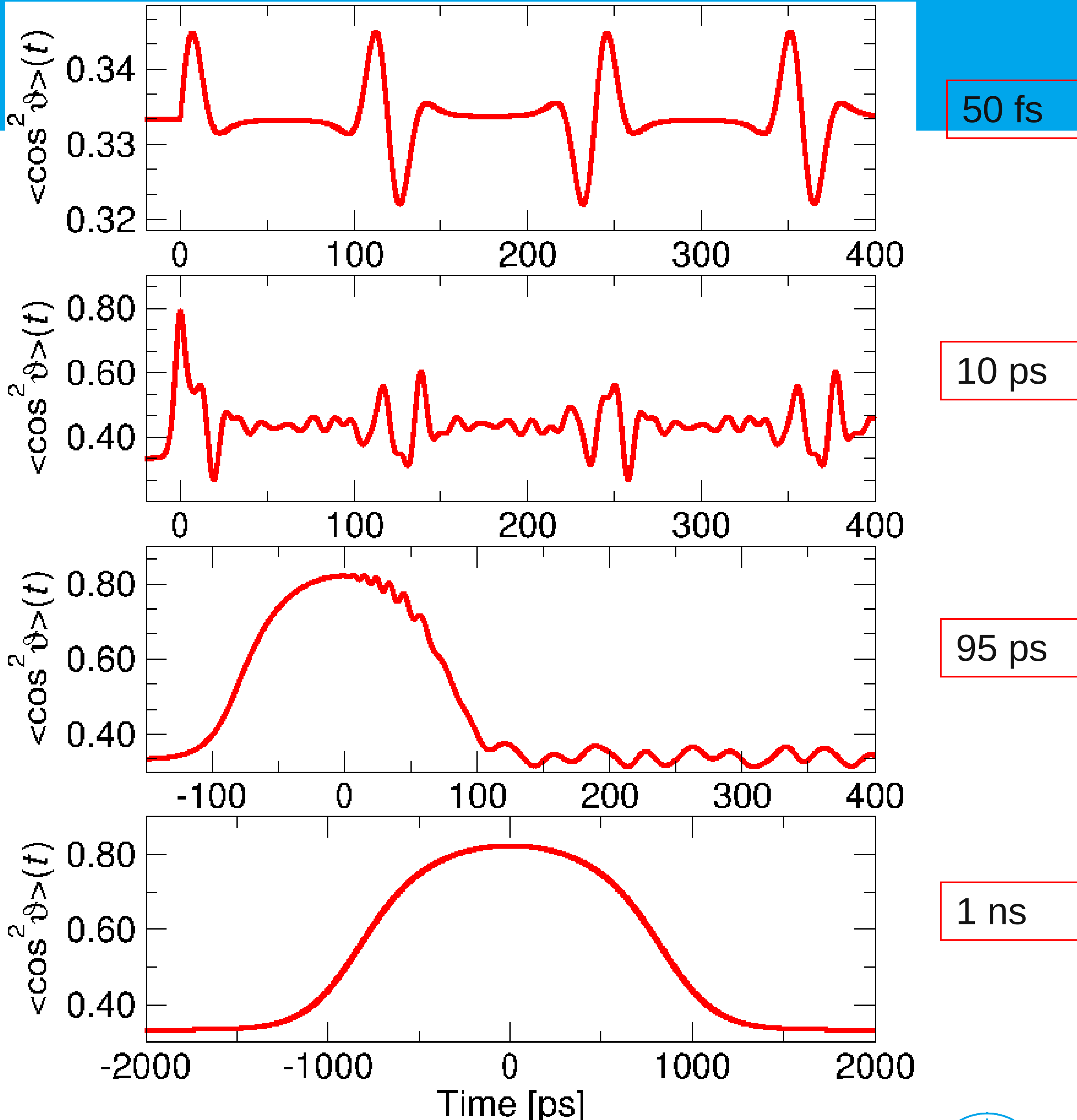
Dependence of alignment on laser pulse duration

Transition from impulsive regime to adiabatic regime

Laser peak intensity fixed at 10^{12} W/cm^2

Temperature = 1 K

Buth and Santra, J. Chem. Phys. **129**, 134312 (2008).



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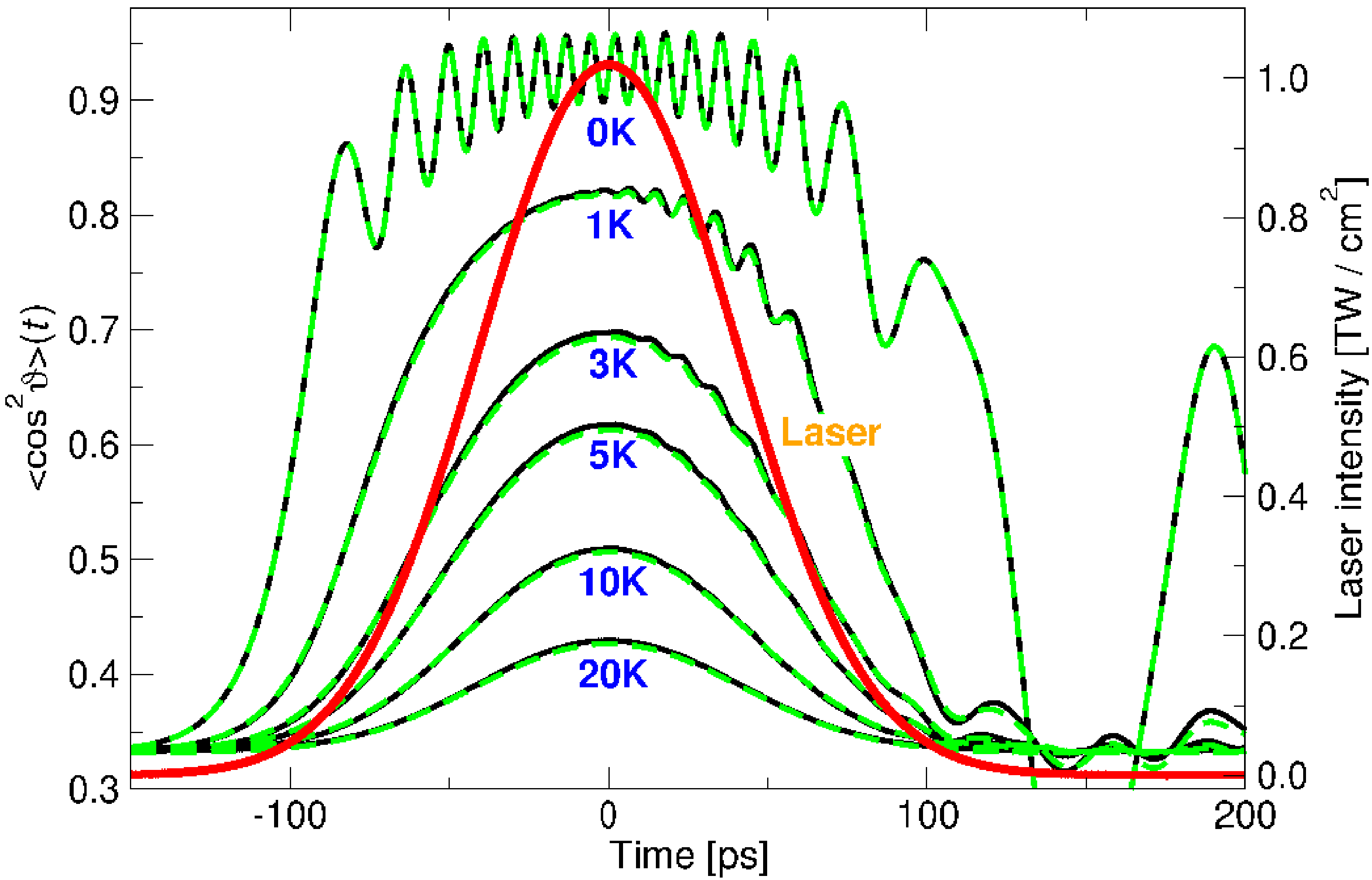
Temperature dependence of alignment in quasi-adiabatic case



Buth and Santra, J. Chem. Phys. **129**, 134312 (2008).

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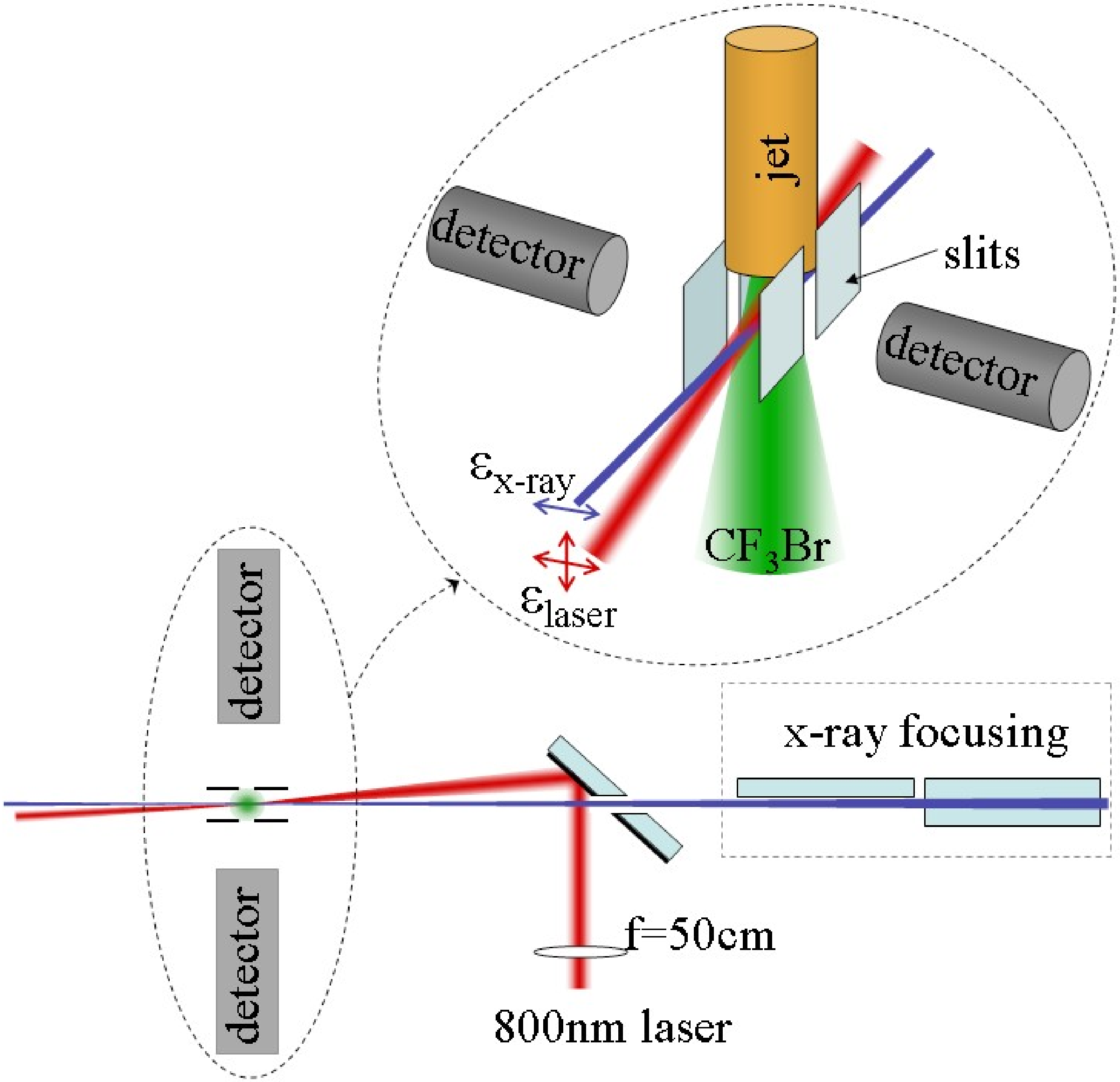
Experimental setup



1.9 mJ, 95 ps, 40 μm laser focus

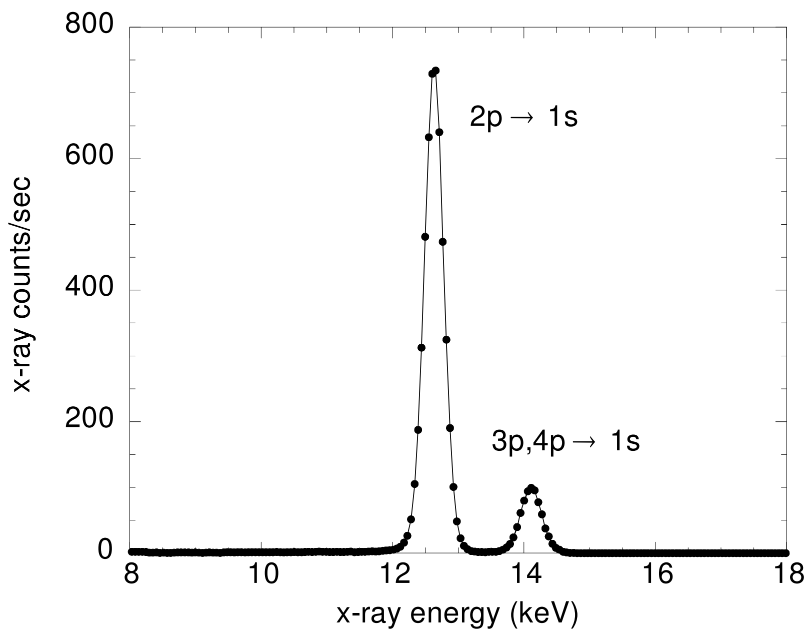
10 μm x-ray focus

1.2 mm viewed overlap region

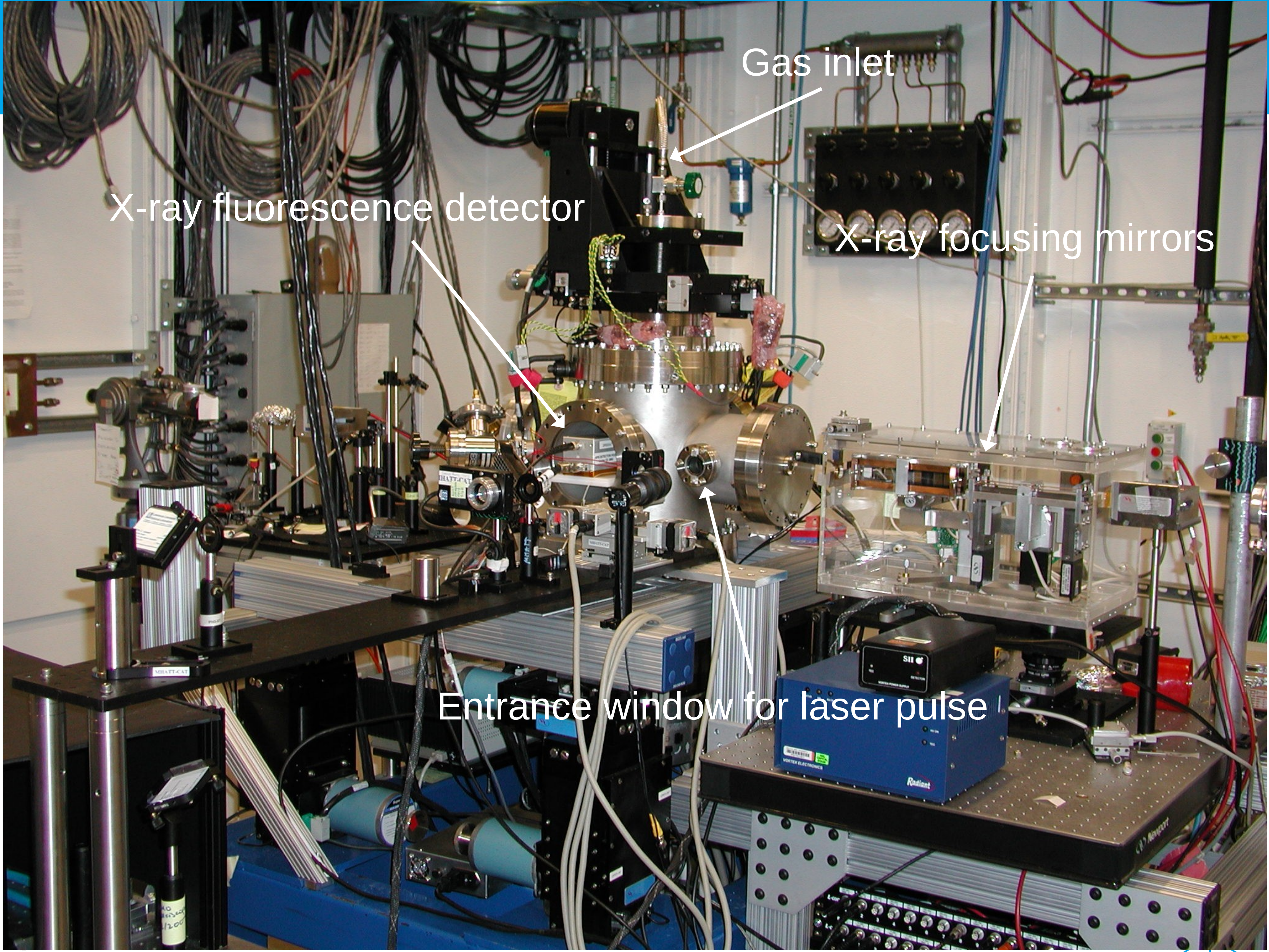
→ 0.85 × 10^{12} W/cm^2 peak intensity

2p → 1s x-ray fluorescence

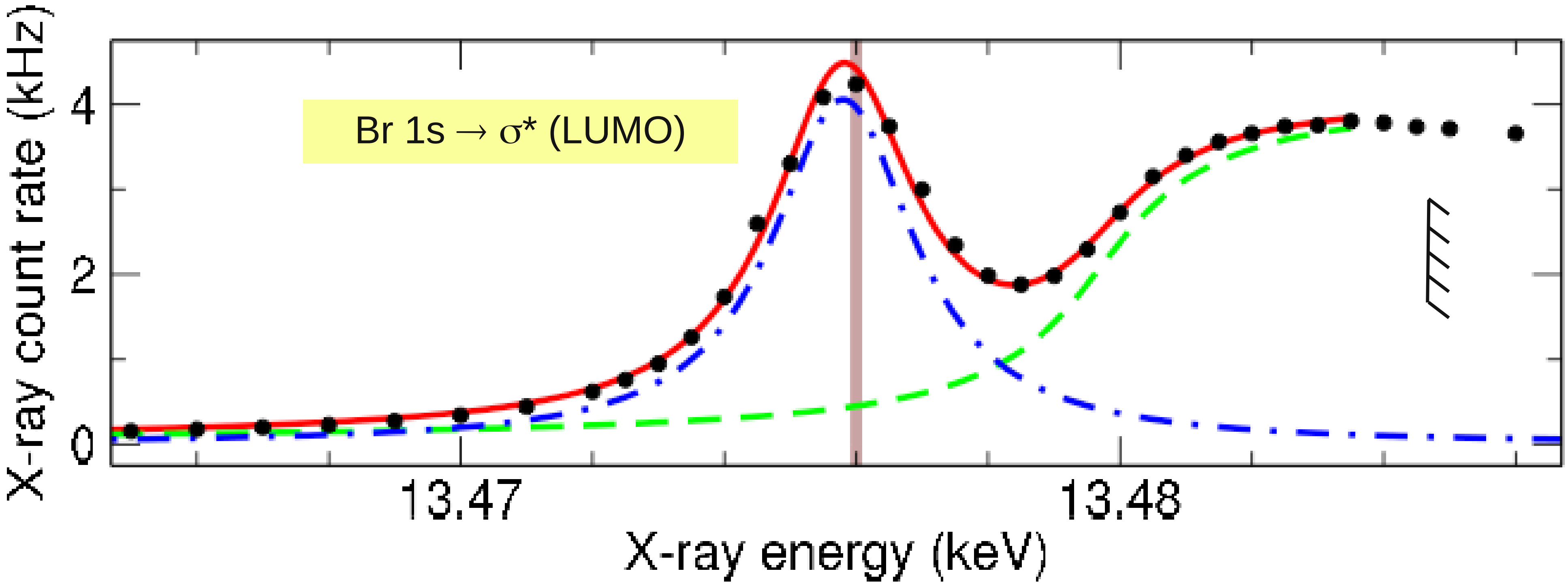
54% yield



E. Peterson *et al.*, Appl. Phys. Lett. **92**, 094106 (2008)


Gas inlet
X-ray fluorescence detector
X-ray focusing mirrors
Entrance window for laser pulse

CF_3Br x-ray absorption at the Br *K* edge



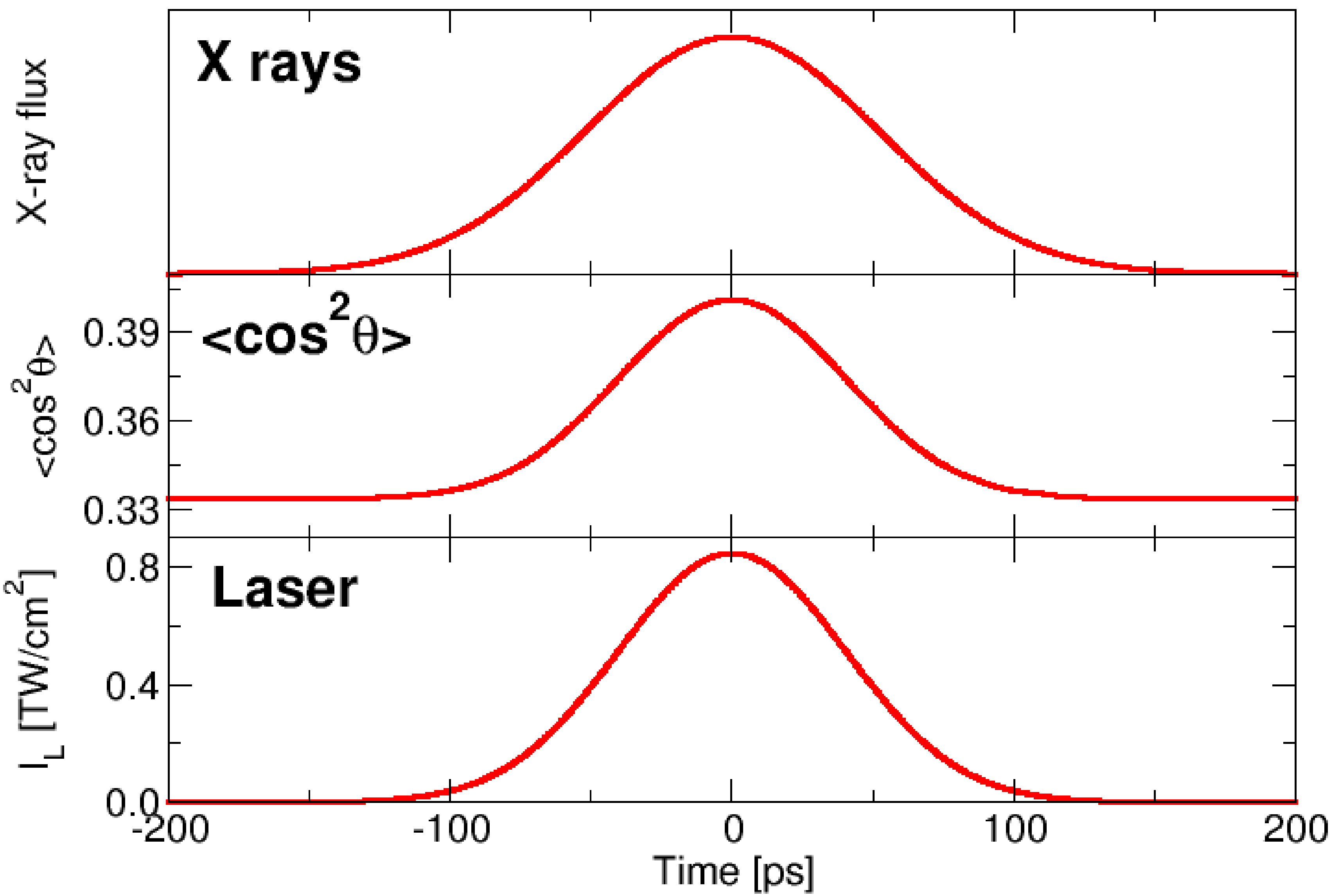
$\Gamma = 2.5$ eV

$\tau = 0.26$ fs

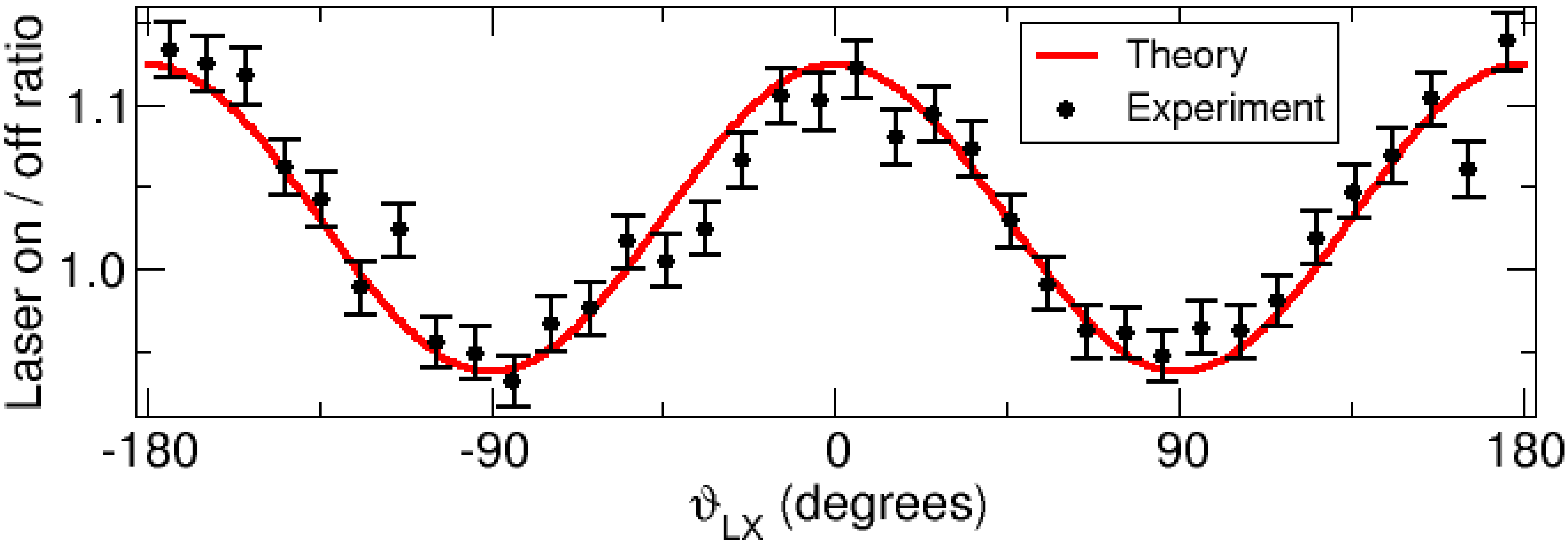
E. Peterson *et al.*, Appl. Phys. Lett. **92**, 094106 (2008)

Laser pulse, x-ray pulse, and $\langle\cos^2\theta\rangle$ for CF_3Br

τ_X=122ps, τ_L=95ps, T=24K



Laser-controlled rotation of symmetry axis of molecules relative to x-ray polarization axis



E. Peterson *et al.*, Appl. Phys. Lett. **92**, 094106 (2008)

X-ray absorption by laser-dressed atoms

or

Controlling x-rays with light: ultrafast transparency

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Ground-state electron configuration of neon

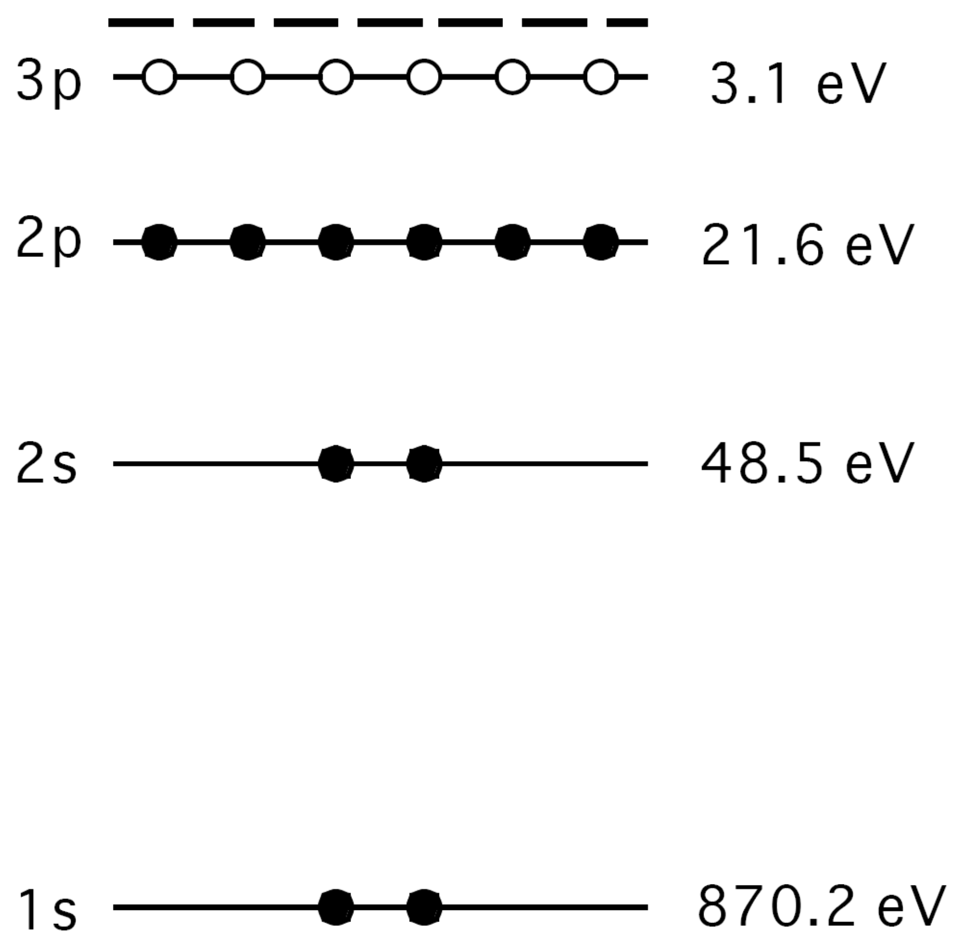
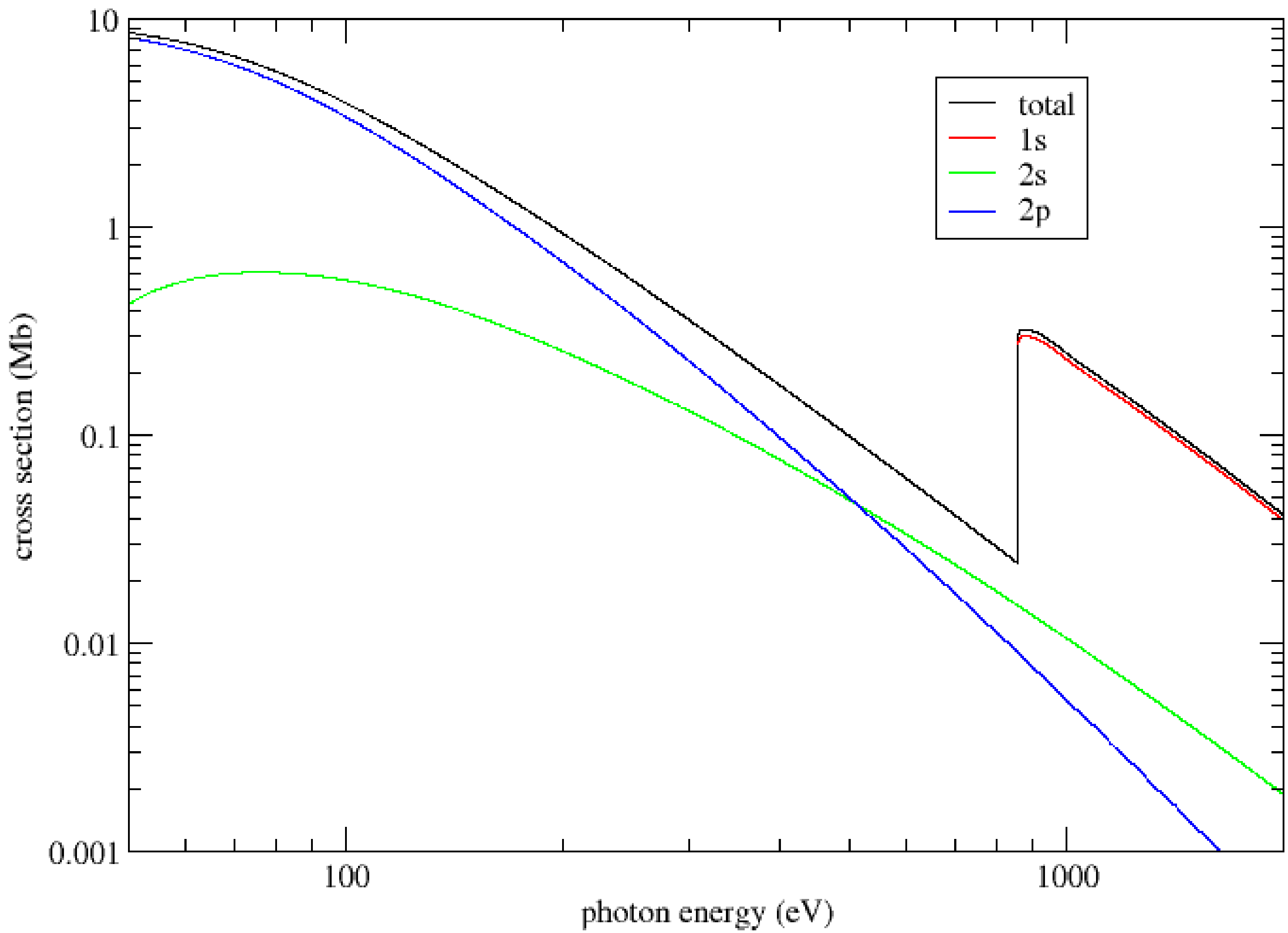


FIG. 1. Orbital configuration and ionization energies of Ne.

Calculated photoemission cross section of neon



Photoabsorption near the Ne K edge

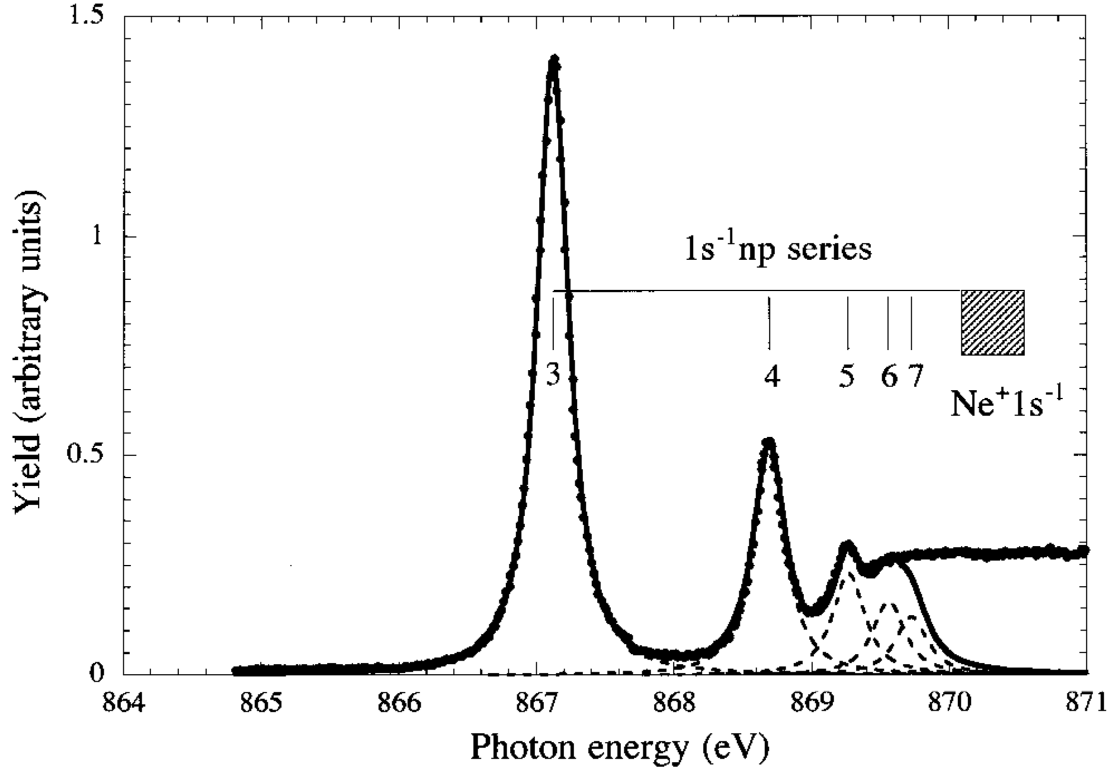


FIG. 1. Ne photoabsorption spectrum in the region of the K edge; the contributions of the different $1s \rightarrow np$ transitions obtained by the best-fit procedure are shown.

M. Coreno *et al.*, Phys. Rev. A **59**, 2492 (1999).

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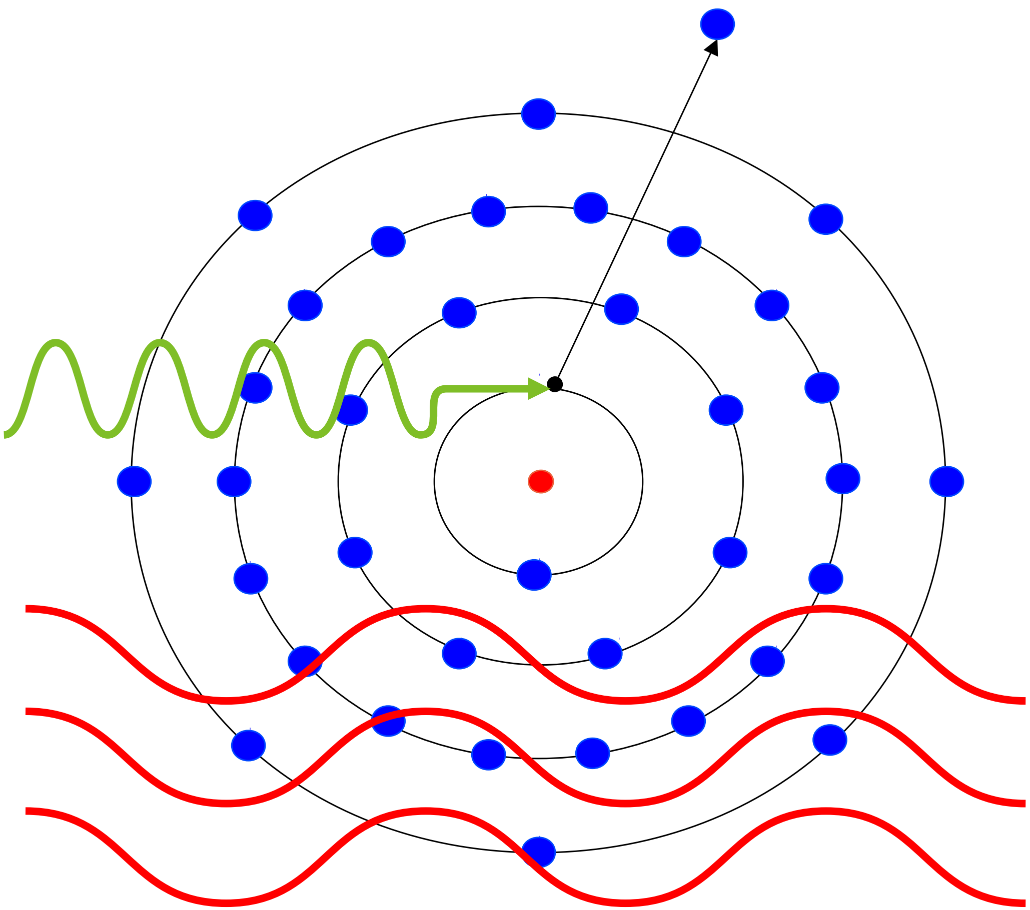
X-ray absorption by laser-dressed atoms

- Atoms are in an optical laser field
- Central assumption: atom in its electronic ground state is not excited by the laser
- X-ray absorption near the *K* edge promotes a 1s electron to a Rydberg or a continuum state
- The Rydberg and continuum states of the excited electron are mixed by the optical laser field



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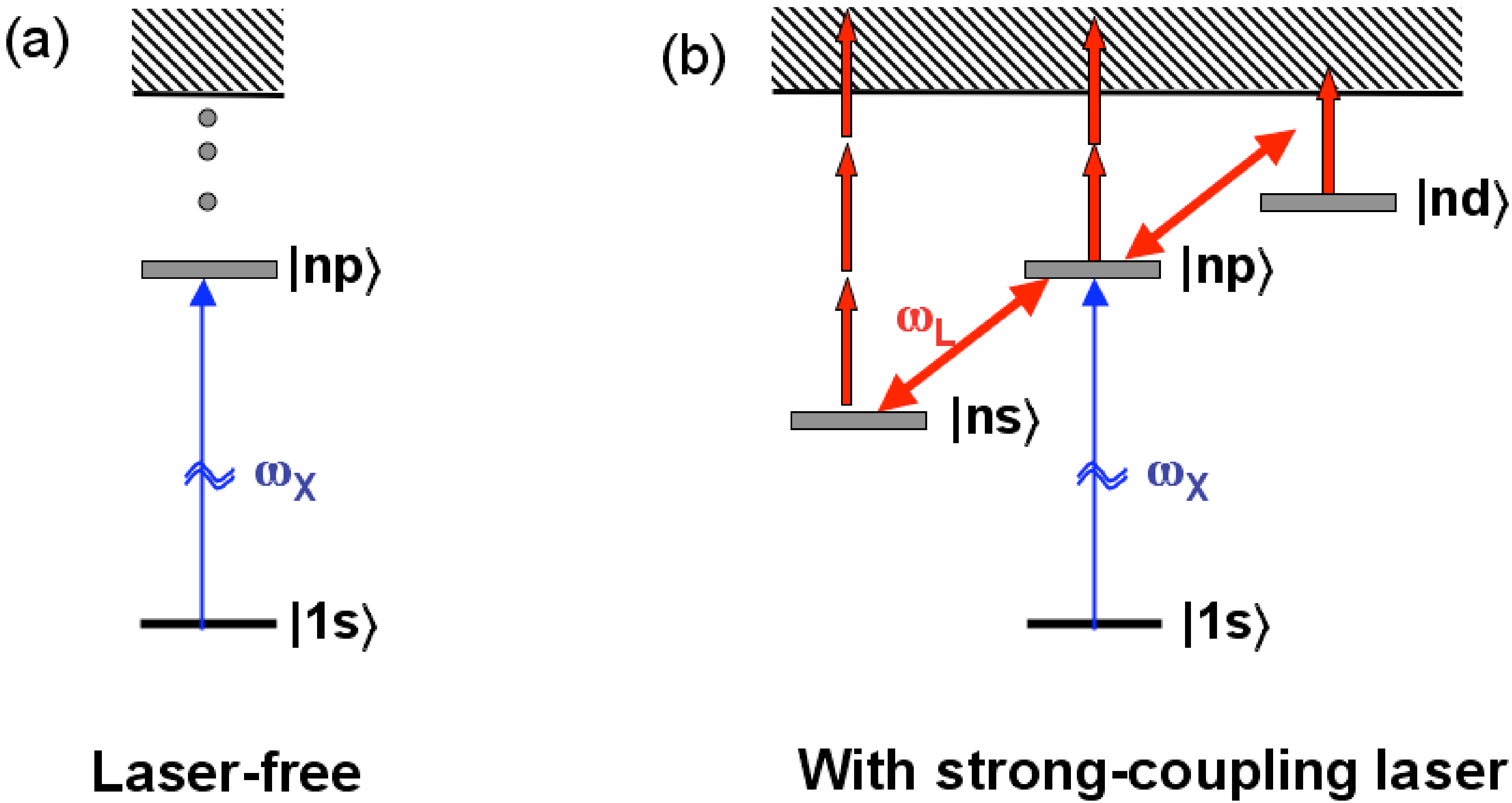
(a)
|np⟩
ω_X
|1s⟩
Laser-free
(b)
|nd⟩
|np⟩
ω_L
|ns⟩
ω_X
|1s⟩
With strong-coupling laser

Theoretical approach

- Hartree-Fock-Slater mean-field model

$$\hat{H}_{\mathrm{AT}} = -\frac{1}{2}\boldsymbol{\nabla}^2 + V_{\mathrm{HFS}}(r).$$

- Free electromagnetic field: laser plus x-ray modes

$$\hat{H}_{\mathrm{EM}} = \omega_L \hat{a}_L^\dagger \hat{a}_L + \omega_X \hat{a}_X^\dagger \hat{a}_X,$$

- Interaction between electrons and photon field

$$\hat{H}_I = \boldsymbol{\chi}^T i\sqrt{\frac{2\pi}{V}\omega_L}[\boldsymbol{e}_L\hat{a}_L - \boldsymbol{e}_L^*\hat{a}_L^\dagger] + \boldsymbol{\chi}^T i\sqrt{\frac{2\pi}{V}\omega_X}[\boldsymbol{e}_X\hat{a}_X - \boldsymbol{e}_X^*\hat{a}_X^\dagger]$$

Buth and Santra, Phys. Rev. A **75**, 033412 (2007).

Laser-atom interaction (Floquet approach)

- Hamiltonian for the atom in the laser field (no x-rays so far)

$$\hat{H}_0 = \hat{H}_{\mathrm{AT}} + \hat{H}_{\mathrm{EM}} + \hat{H}_{I,L} + \hat{W}$$

- Direct product basis set of atomic orbitals and photon Fock states

$$|\Phi_{n,l,m,\mu}\rangle = |\psi_{n,l,m}\rangle|N_L - \mu\rangle|N_X - 1\rangle$$

- Diagonalization of matrix (Floquet matrix) yields laser-dressed atomic energy levels

$$\boldsymbol{H}_0^{(m)}\boldsymbol{c}_F^{(m)} = E_F^{(m)}\boldsymbol{c}_F^{(m)}$$

$$|F^{(m)}\rangle = \sum_{n,l,\mu} c_{n,l,\mu,F}^{(m)}|\psi_{n,l,m}\rangle|N_L - \mu\rangle|N_X - 1\rangle$$

Buth and Santra, Phys. Rev. A **75**, 033412 (2007).

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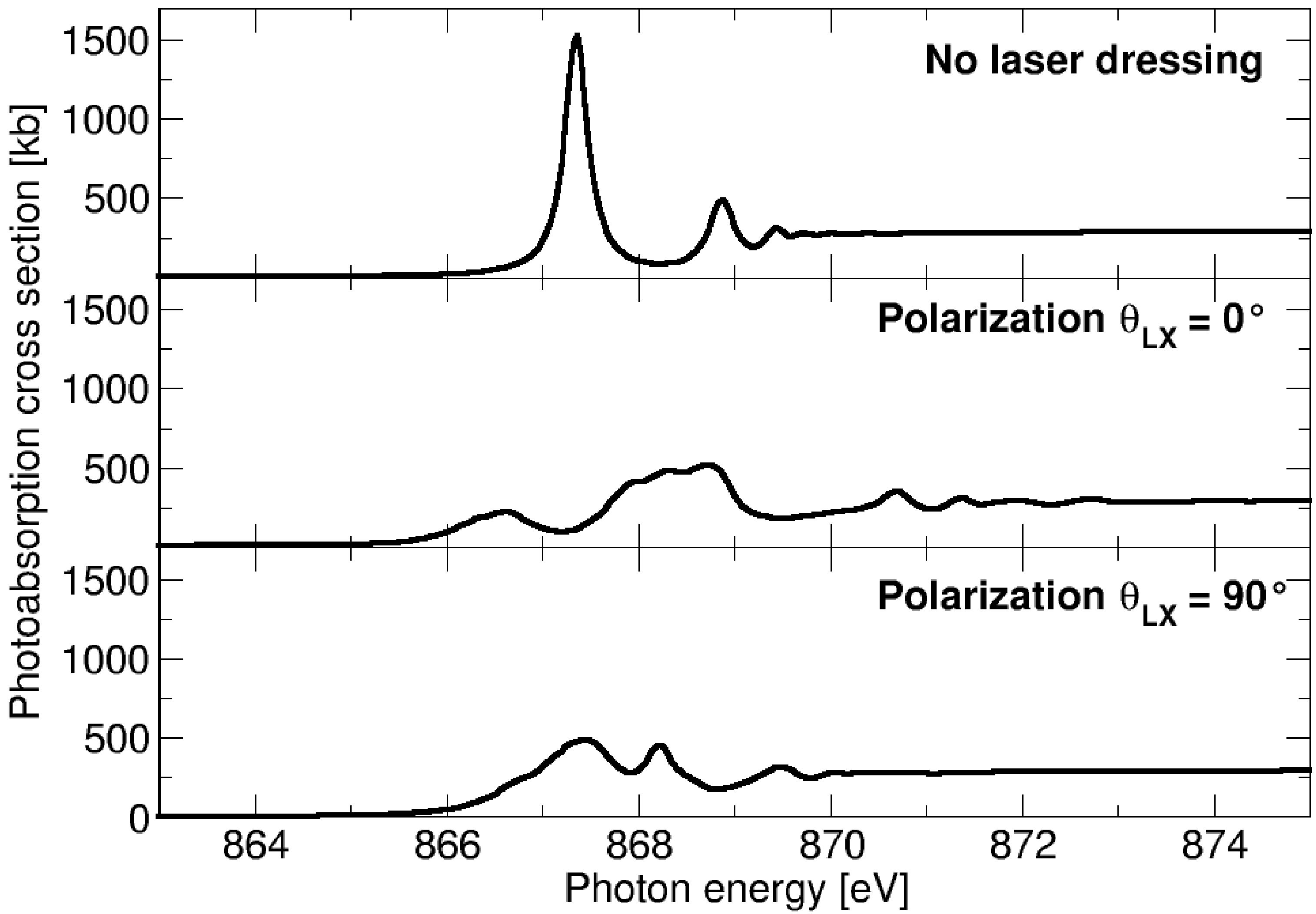
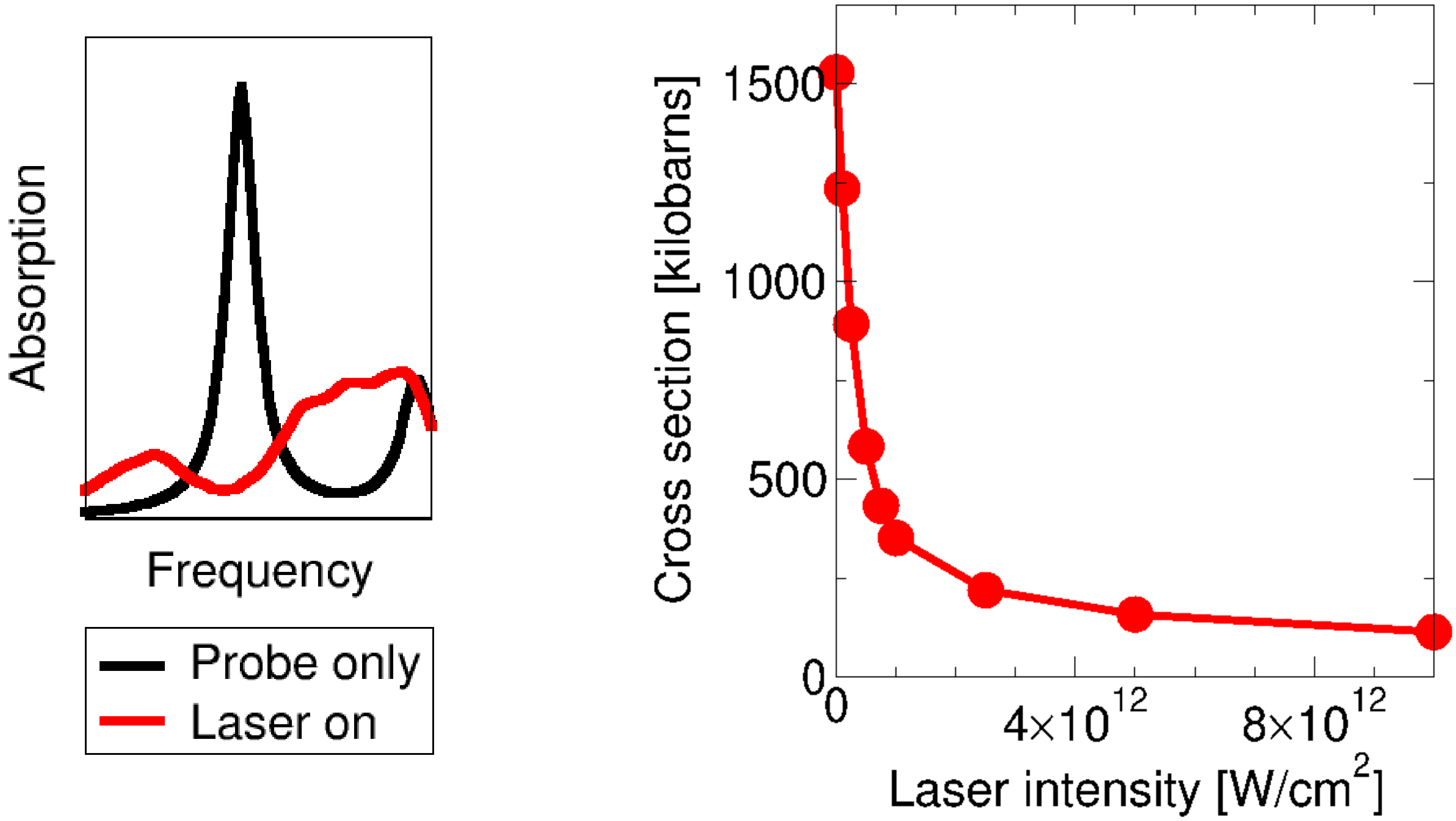
Neon K edge (800 nm, 10^{13} W/cm^2)



Buth, Santra, and Young, Phys. Rev. Lett. **98**, 253001 (2007)

Laser-induced transparency in the x-ray regime



- Neon absorbs strongly at the 1s-3p resonance
- 1s-3p absorption cross section suppressed by a factor of 13 at 10^{13} W/cm^2

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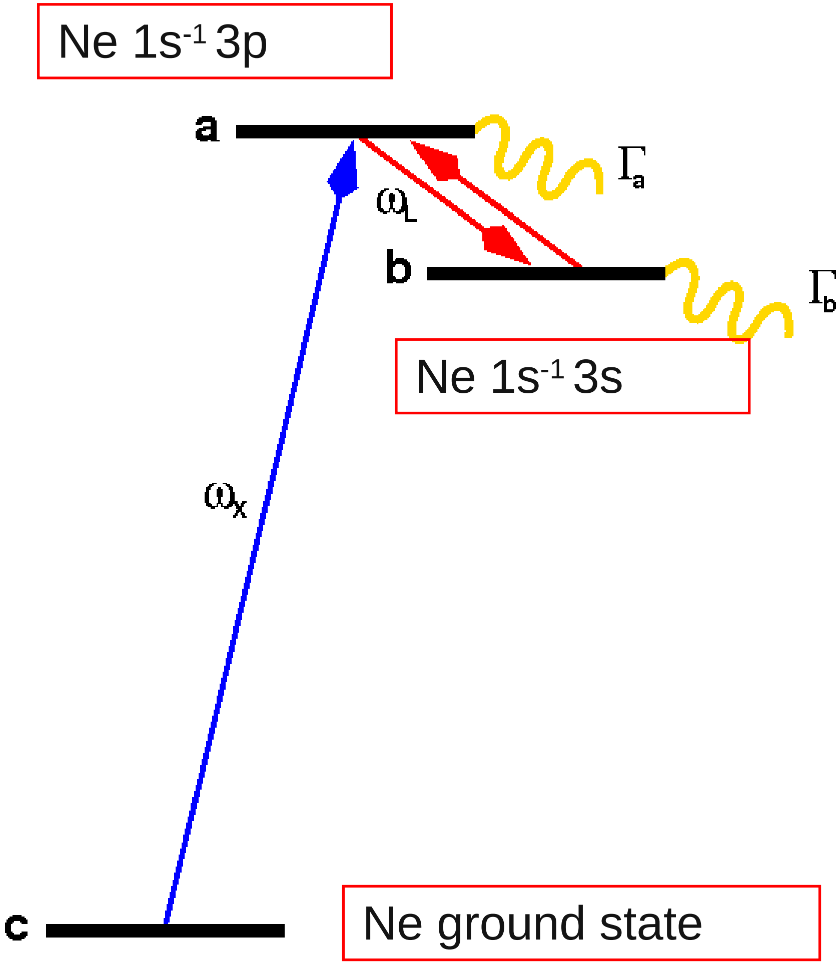
Simplified picture

- Within level widths, the laser is resonant with the transition between $1s^{-1}$ 3s and $1s^{-1}$ 3p
- Formation of Autler-Townes doublet
- Laser must drive Rabi oscillations between levels $1s^{-1}$ 3s and $1s^{-1}$ 3p with a Rabi period of the order of 1 fs
- Intense laser causes coupling to states outside three-level model space
- Laser is so intense that field ionization of the core-excited states is as fast as the Auger decay of the 1s vacancy



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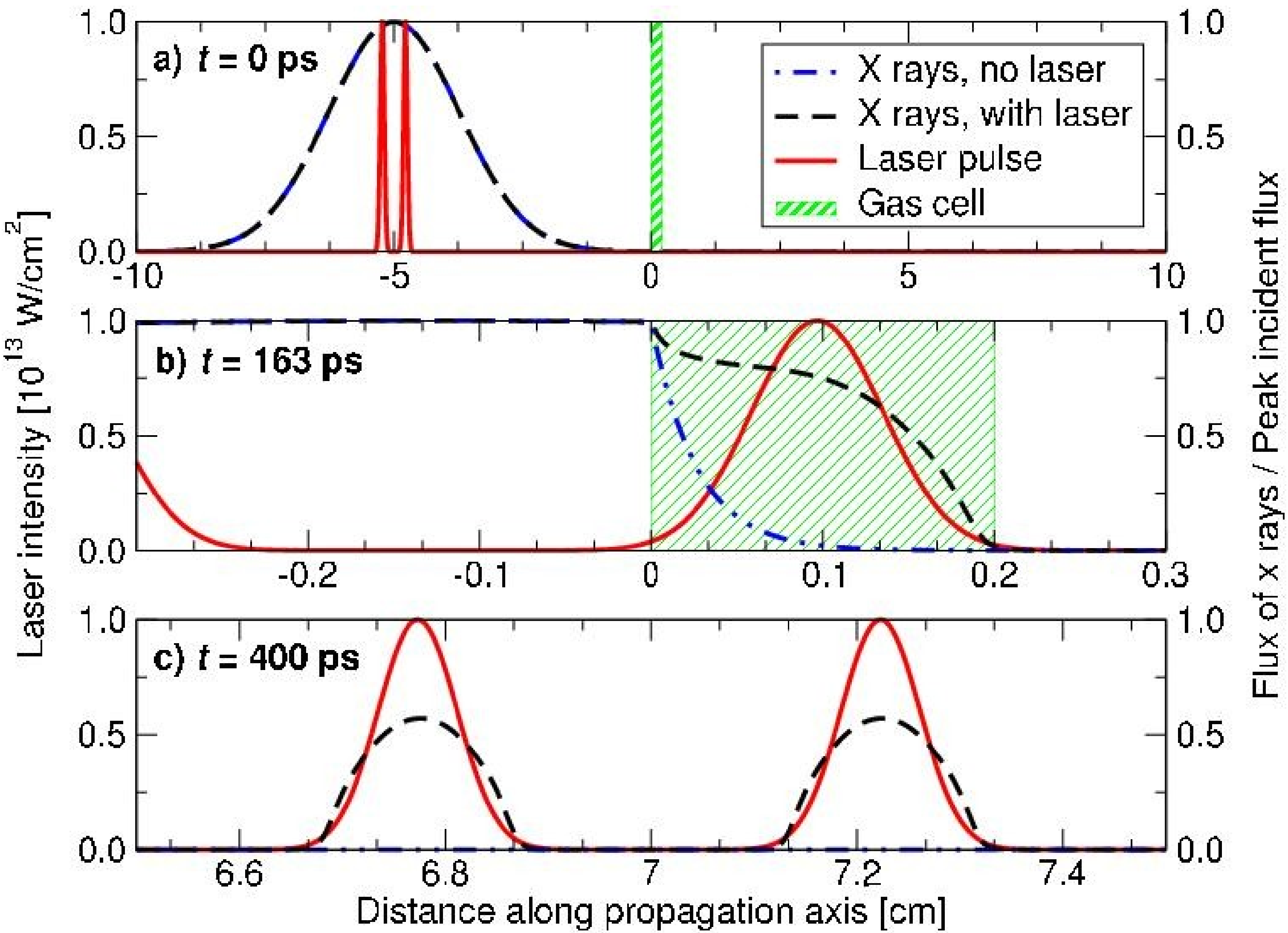
Criterion for observing laser-induced transparency

- Rabi frequency associated with laser coupling between the two upper levels must be greater than the decay width of the core hole.

- Decay width of Ne $1s^{-1}$ is 0.27 eV
  → minimum laser intensity required ~ 10^{12} W/cm^2

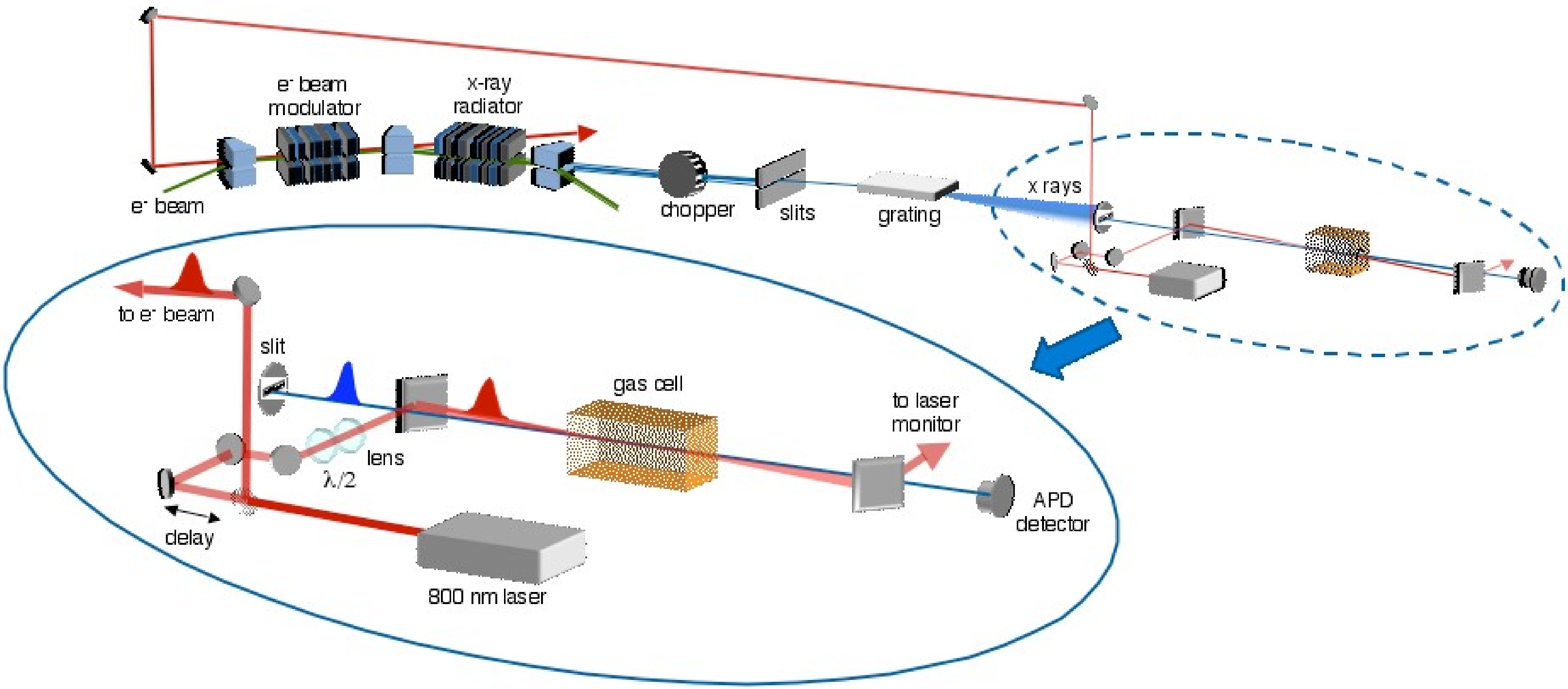
- Decay width of Kr $1s^{-1}$ is 2.7 eV
  → minimum laser intensity required ~ 10^{14} W/cm^2

Use laser-induced transparency to imprint the shape of optical pulses onto an x-ray pulse

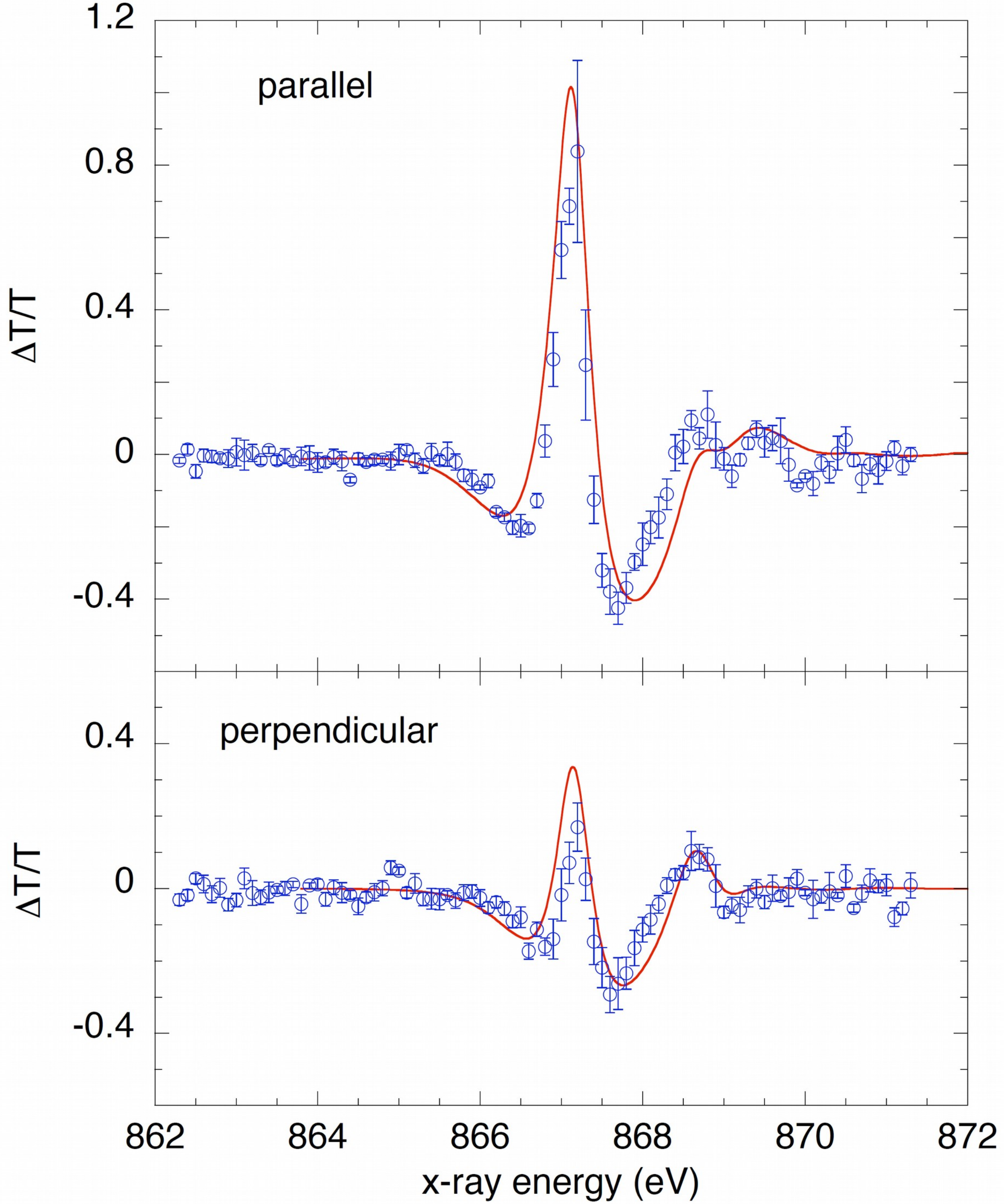


Buth, Santra, and Young, Phys. Rev. Lett. **98**, 253001 (2007)

Experiment carried out at the Advanced Light Source



T. E. Glover *et al.*, Nature Physics **6**, 69 (2009).



First experimental demonstration of laser-induced transparency in the x-ray regime

- The figure shows a comparison between experiment and theory

- The simulated transmission spectra were computed using no adjustable parameters

T. E. Glover *et al.*, Nature Physics **6**, 69 (2009).

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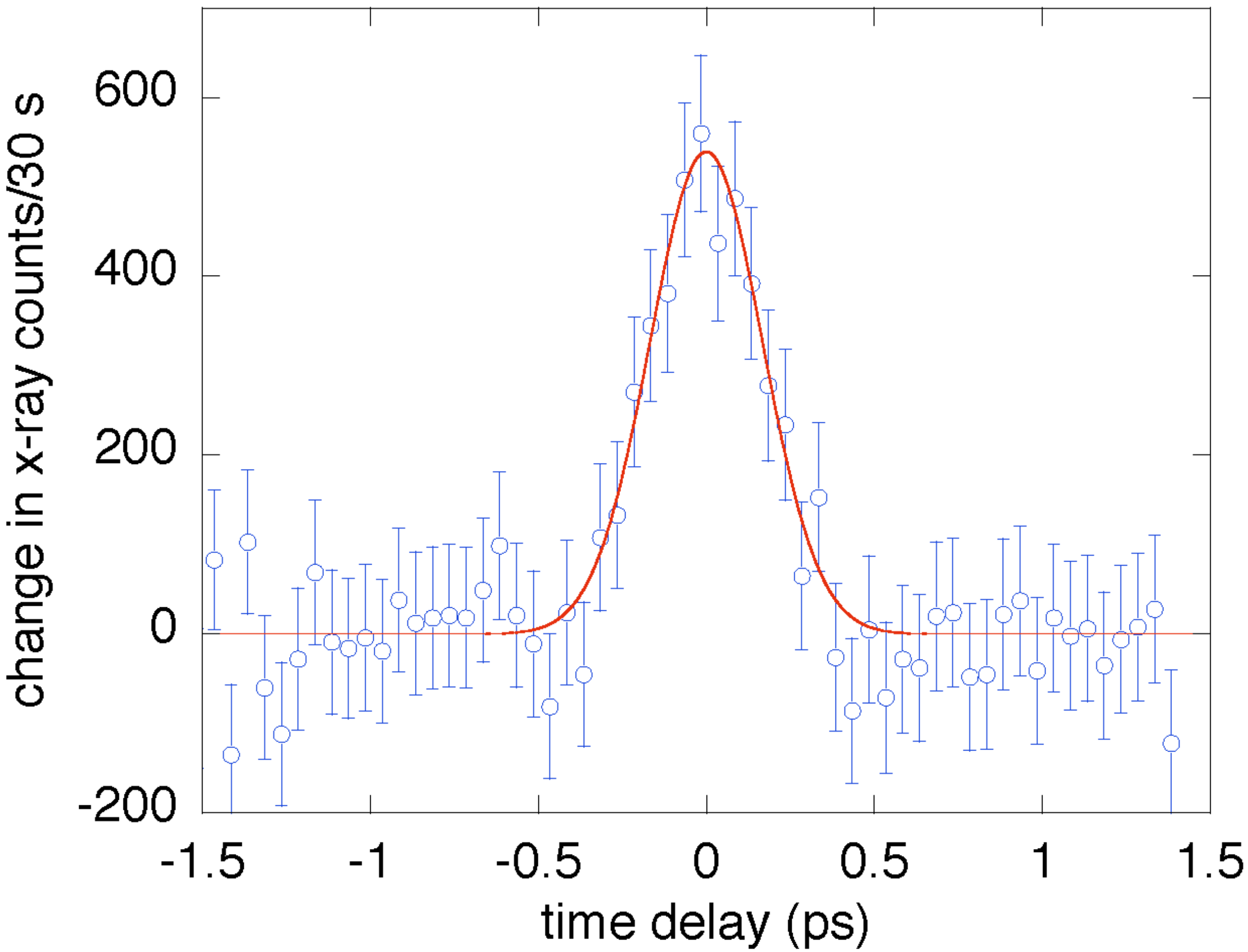
Cross-correlation measurement of the femtosecond x-ray pulse duration from the ALS slicing source



The correlation width (~380 fs) and measured laser duration (~290 fs) indicate an x-ray duration of ~250 fs.

T. E. Glover *et al.*, Nature Physics **6**, 69 (2009).

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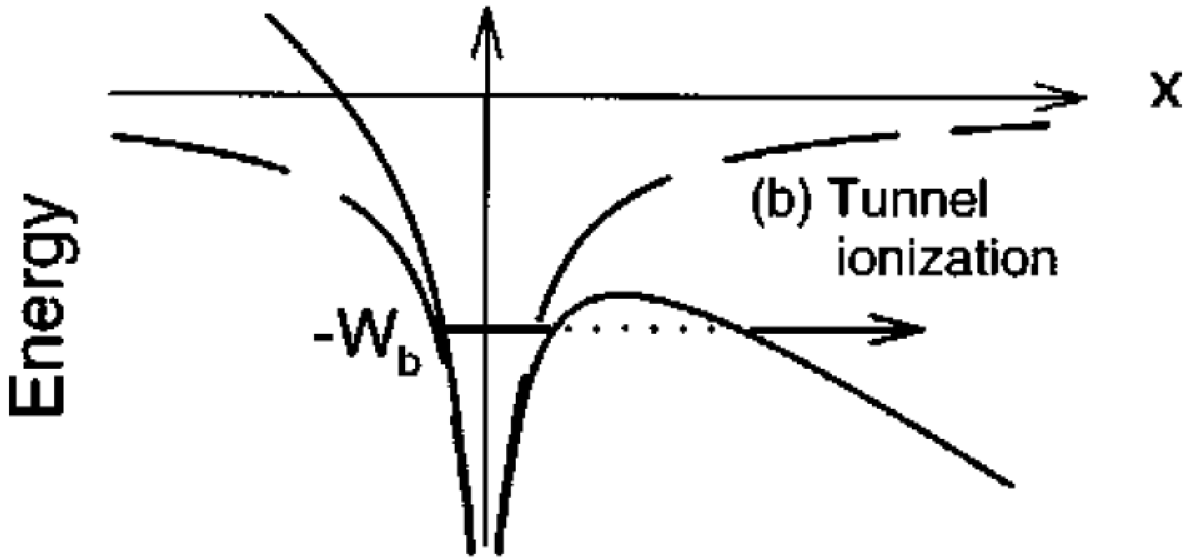
Optical strong-field ionization (tunnel ionization) and hole alignment

Ionization in nonperturbatively strong optical fields

Brabec and Krausz, Rev. Mod. Phys. **72**, 545



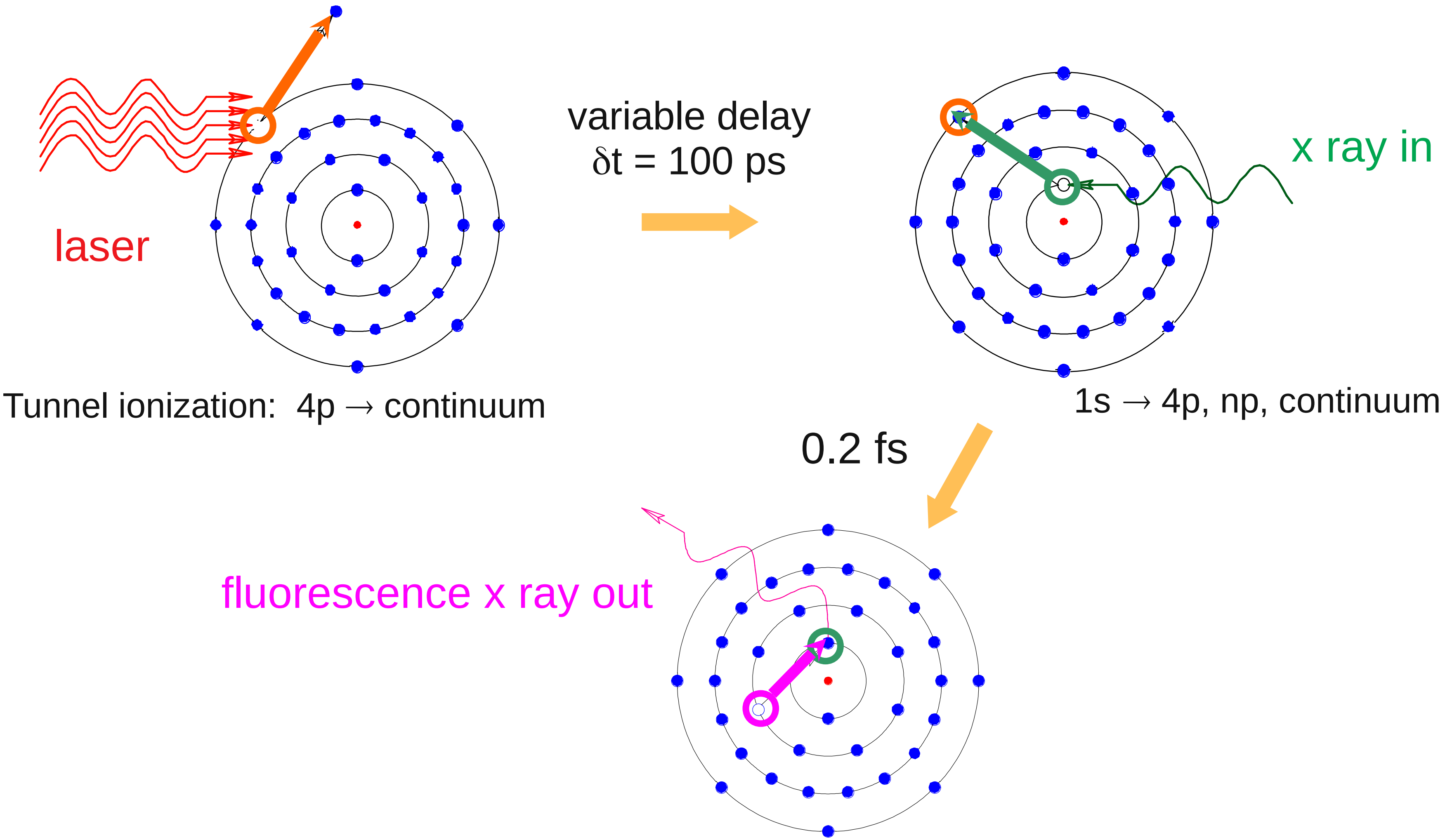
Assumptions:
- the photon energy is much smaller than the electron binding energy
- electric dipole approximation is valid
- multipolar Hamiltonian is used (“length form” or “length gauge”)
- field is so strong that the electronic response at a given time t during the optical cycle is fast in comparison to optical period (2.7 fs at 800 nm).

First observation of hole alignment in linearly polarized laser field

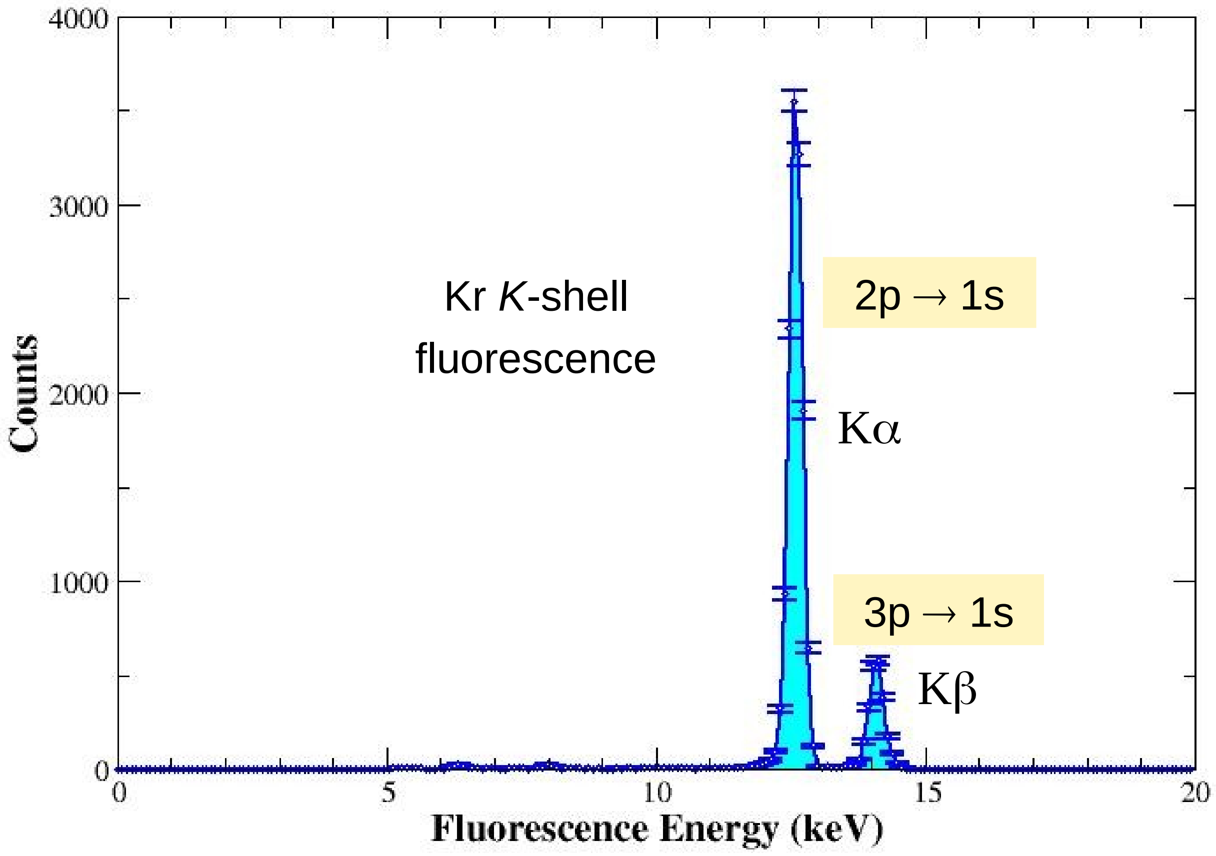
Young *et al.*, PRL **97**, 083601 (2006).

- > Use linearly polarized laser light to ionize Kr atoms
- > Laser polarization axis defines quantization axis
- > Excite Kr ions with linearly polarized x-rays
- > Measure resonant (1s $\rightarrow$ 4p) x-ray absorption rate as function of angle between laser and x-ray polarization axes

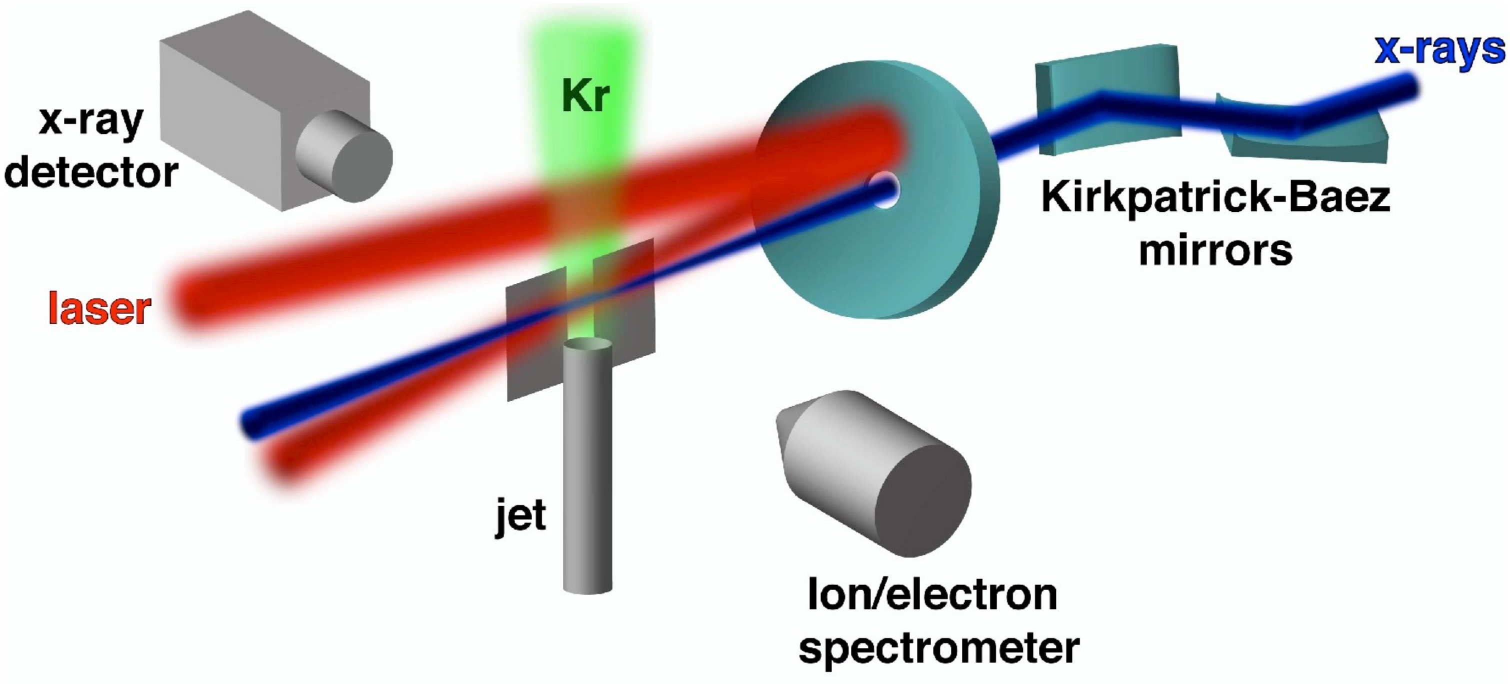
Resonant core excitation of laser-ionized krypton atoms



Detection of x-ray absorption via detection of K-shell x-ray fluorescence

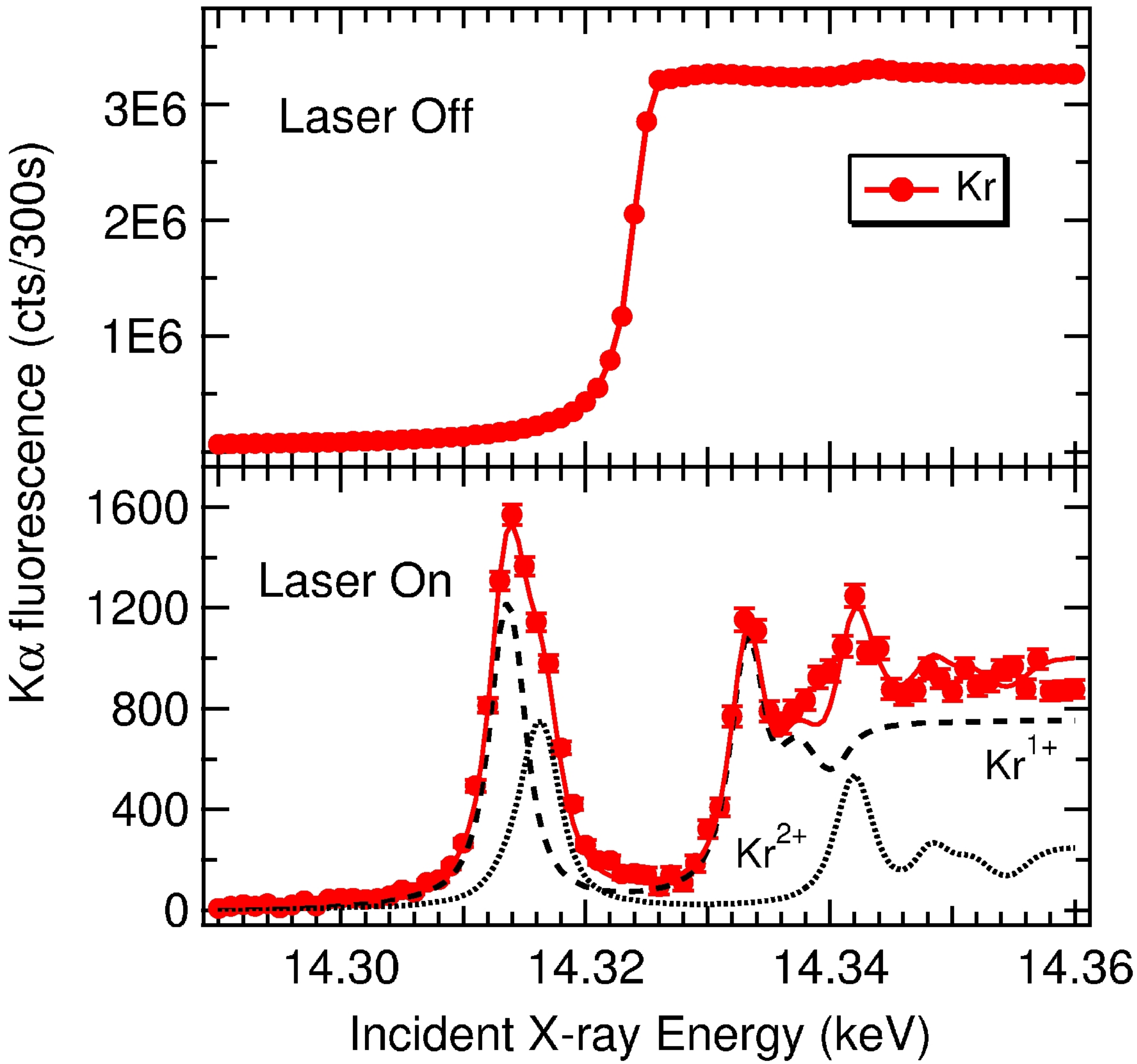


Experimental schematic: laser pump — x-ray probe



Young *et al.*, Phys. Rev. Lett. **97**, 083601 (2006)

Kr near-edge absorption spectrum



Young *et al.*, PRL **97**, 083601 (2006).

Circularly polarized laser!

Fit to experimental data based on *ab initio* calculations by L. Pan, D. R. Beck, and S. M. O'Malley, J. Phys. B **38**, 3721 (2005)

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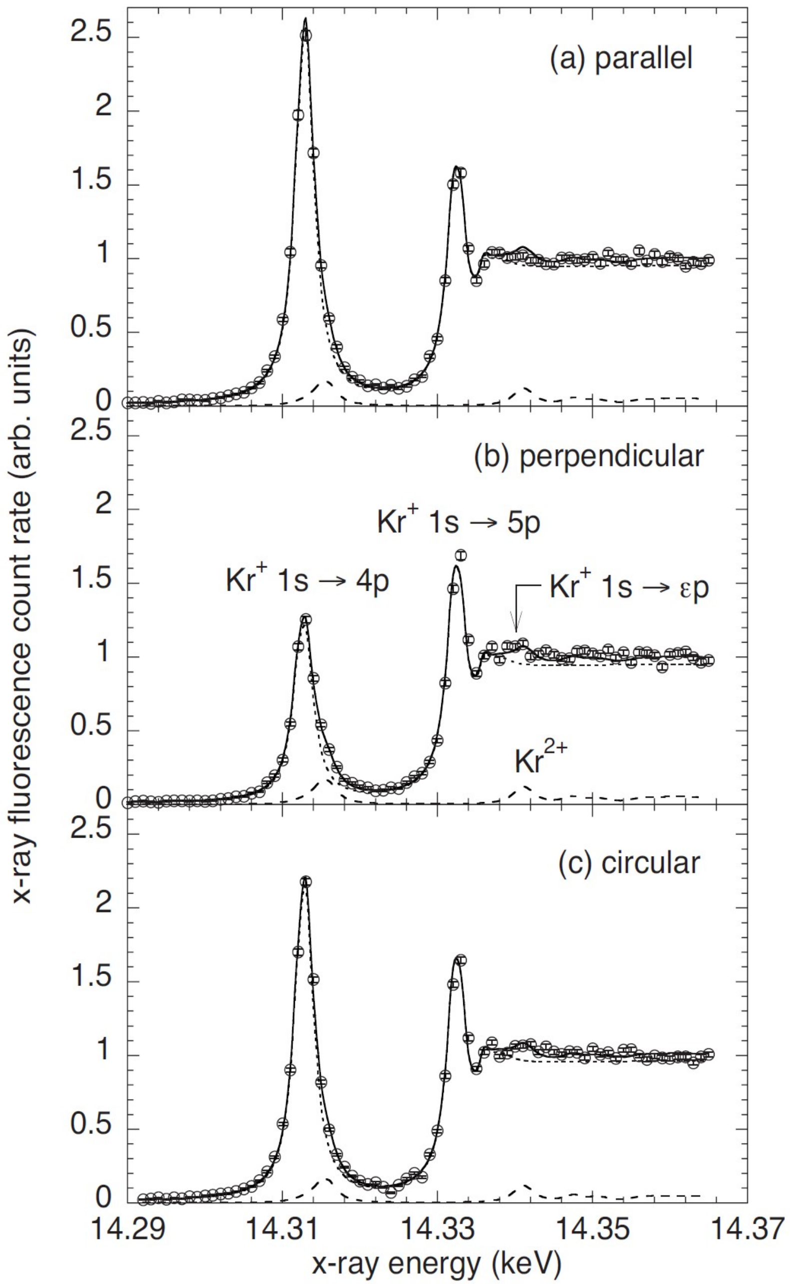

Polarized x-ray absorption probes aligned ion states

observe R = 2 : 1 ratio for || vs. ⊥ (at the 1s → 4p resonance)

Young *et al.*, Phys. Rev. Lett. **97**, 083601 (2006)

Southworth *et al.*, Phys. Rev. A **76**, 043421 (2007)

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Effective one-electron model Hamiltonian

Santra, Dunford, Young, PRA **74**, 043403 (2006).

Coupling to external electric field

Hartree-Slater potential

$$H = -\frac{1}{2}\nabla^2 + V_{\mathrm{HS}}(r) + \frac{1}{2}\alpha^2 \frac{1}{r}\frac{\mathrm{d}V_{\mathrm{HS}}}{\mathrm{d}r}\boldsymbol{l}\cdot\boldsymbol{s} - z\mathcal{E} - \mathrm{i}\eta W(r)$$

Spin-orbit coupling

Complex absorbing potential

Kr⁺ populations at saturation

$$\rho_{3/2,1/2} = 69\%,$$

$$\rho_{1/2,1/2} = 26\%,$$

$$\rho_{3/2,3/2} = 5\%.$$

$\rho_{j,|m|}$ is the probability of finding Kr^+ with a hole in either the $4p_j, m$ or the $4p_j, -m$ orbital

Santra, Dunford, Young, PRA **74**, 043403 (2006).

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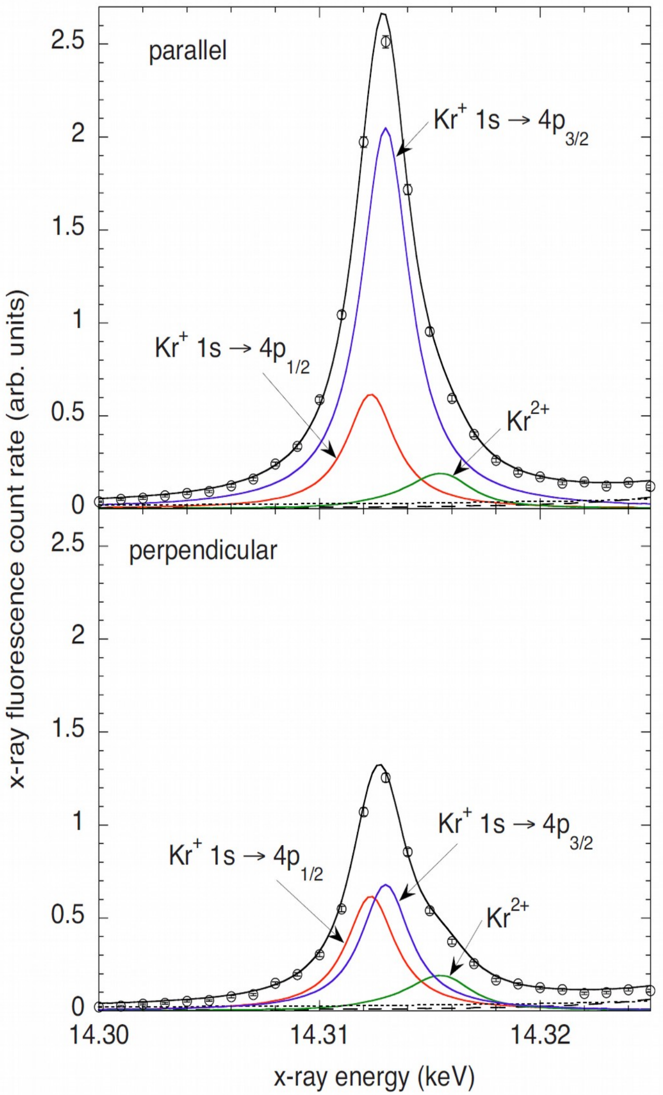
pump and probe pulses are long in comparison to spin-orbit period → insensitive to coherences in ion

Santra, Dunford, Young, PRA **74**, 043403 (2006).

$$R^{[1]} = \frac{P^{[1]}(\vartheta_p = 0^\circ)}{P^{[1]}(\vartheta_p = 90^\circ)} = \frac{2\rho_{1/2,1/2} + 4\rho_{3/2,1/2}}{2\rho_{1/2,1/2} + \rho_{3/2,1/2} + 3\rho_{3/2,3/2}}$$

→ R = 2.4 : 1

Quantum-state populations of strong-field-generated Kr^+



$$\sigma(\omega_x, 0^\circ) = 2\rho_{3/2,1/2}\sigma_{3/2}(\omega_x) + \rho_{1/2,1/2}\sigma_{1/2}(\omega_x)$$

$$\sigma(\omega_x, 90^\circ) = \frac{1}{2}\{\rho_{3/2,1/2} + 3\rho_{3/2,3/2}\}\sigma_{3/2}(\omega_x) + \rho_{1/2,1/2}\sigma_{1/2}(\omega_x)$$

	$\rho_{j,\|m\|}(\%)$	
$\|j,m\rangle$	Experimental	Theoretical
$\|\frac{3}{2}, \pm\frac{1}{2}\rangle$	59±6	71
$\|\frac{1}{2}, \pm\frac{1}{2}\rangle$	35±4	25
$\|\frac{3}{2}, \pm\frac{3}{2}\rangle$	6±6	4

Southworth *et al.*, Phys. Rev. A **76**, 043421 (2007)

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Electronic structure at high x-ray intensity

Some basic questions that become relevant in connection with x-ray free-electron lasers

- Can we produce high charge states in a single pulse?
- Can we photoionize within an inner-shell decay lifetime?
- Can we induce nonsequential (direct) multiphoton processes?
- Can we drive stimulated emission within an inner-shell decay lifetime?

- Questions relevant for understanding radiation damage in matter.
- Relevant for applications such as bioimaging.
- Useful tool for beam diagnostics.

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Our initial model system for studying x-ray–atom interaction processes at high intensity: neon

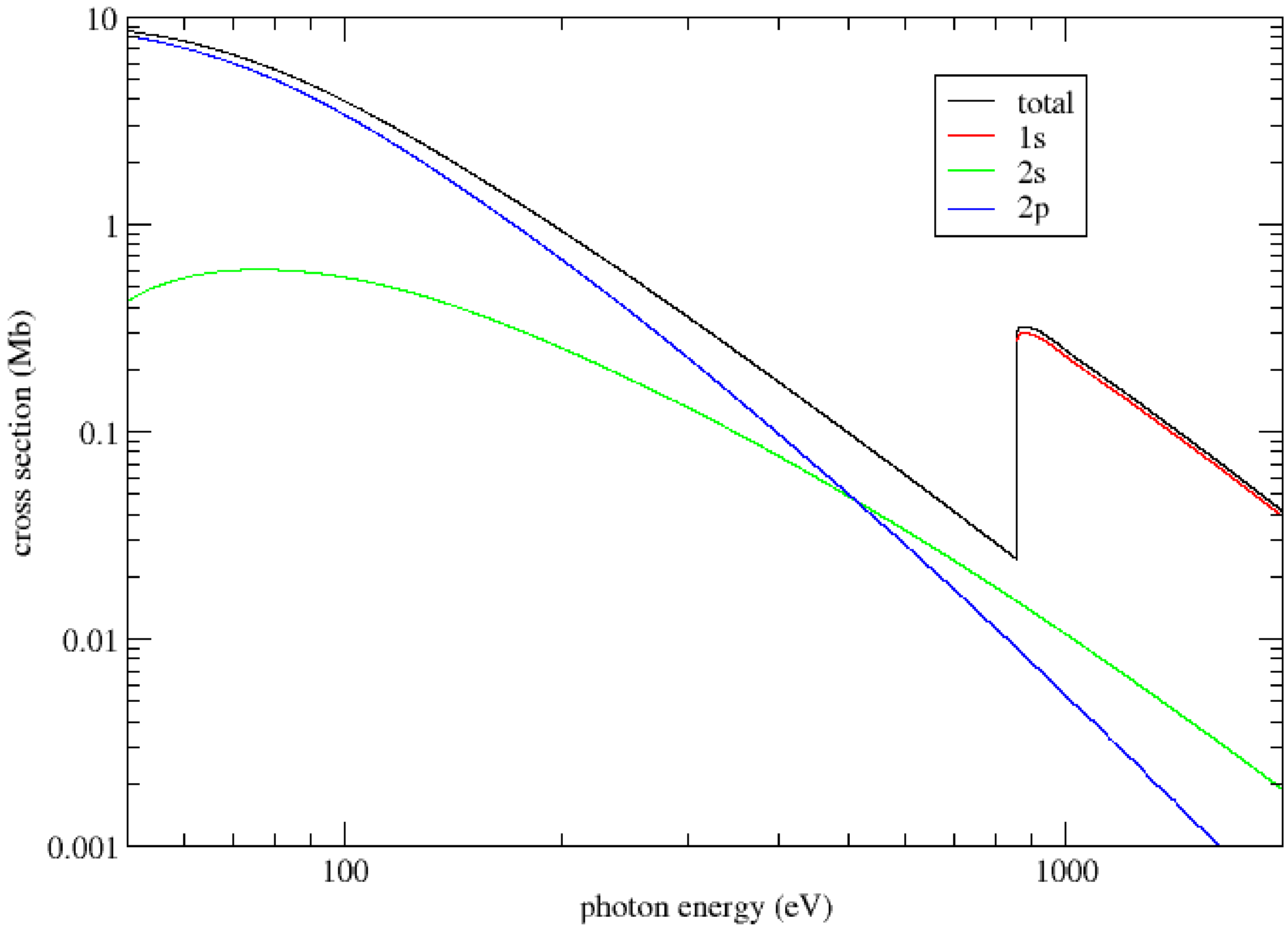
- The photon energies that were available for the first LCLS user experiments in the fall of 2009 were in the range from 800 eV to 2 keV. The Ne K edge lies at 870 eV.

- Neon is a first-row element, which allows one to identify processes relevant for other first-row elements (C, N, O).

- Neon is nontoxic and is easy to handle.

- Neon has been studied in detail at synchrotron radiation sources.

Calculated photoionization cross section of neutral neon (one-photon absorption)



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Strategy

- All electronic shells that may be ionized via one-photon absorption are active.

- The set of all energetically accessible n-hole configurations (n = 0, 1, 2, ...) forms the configuration space.

- For each configuration in this configuration space, a separate self-consistent-field calculation is performed and data for atomic processes are calculated.

- Using these data, the dynamics are described by solving the coupled rate equations

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

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XATOM

→ 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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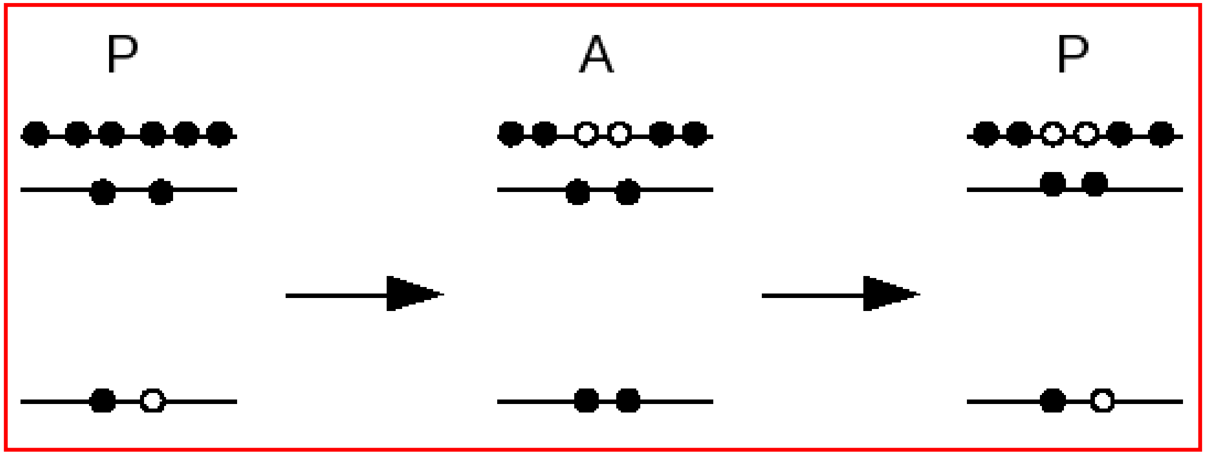
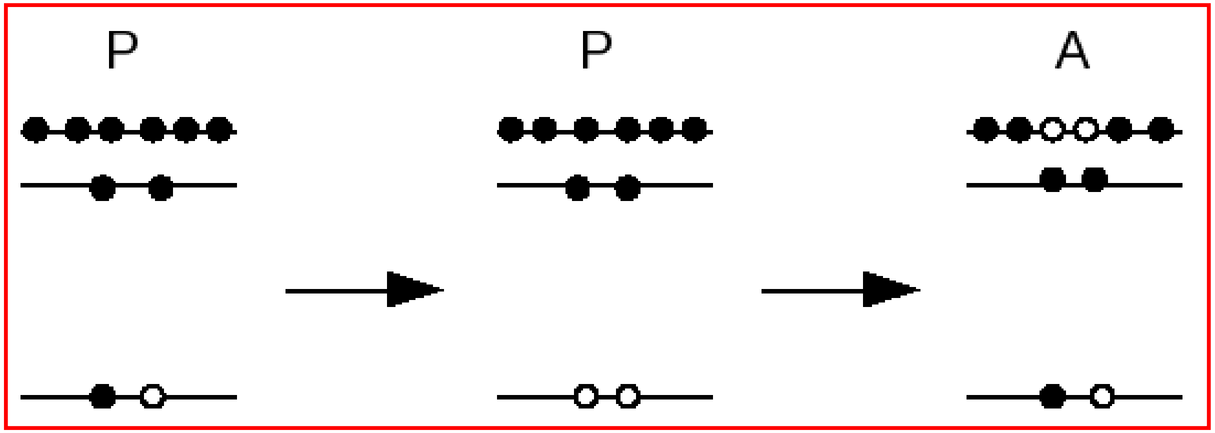
X-ray multiphoton ionization of neon: theoretical predictions

Multiphoton absorption in the x-ray domain: basic "building blocks"





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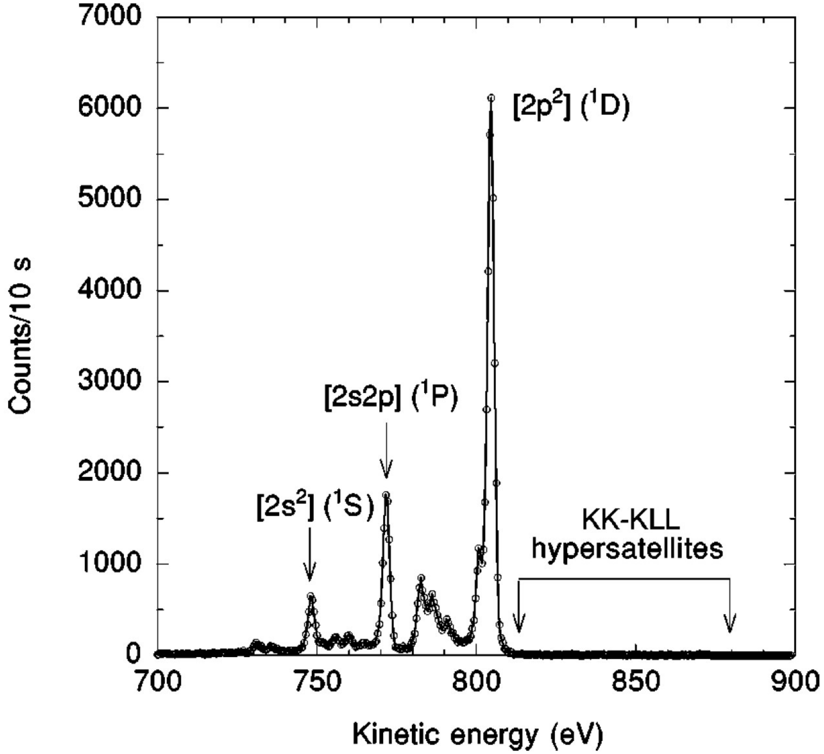
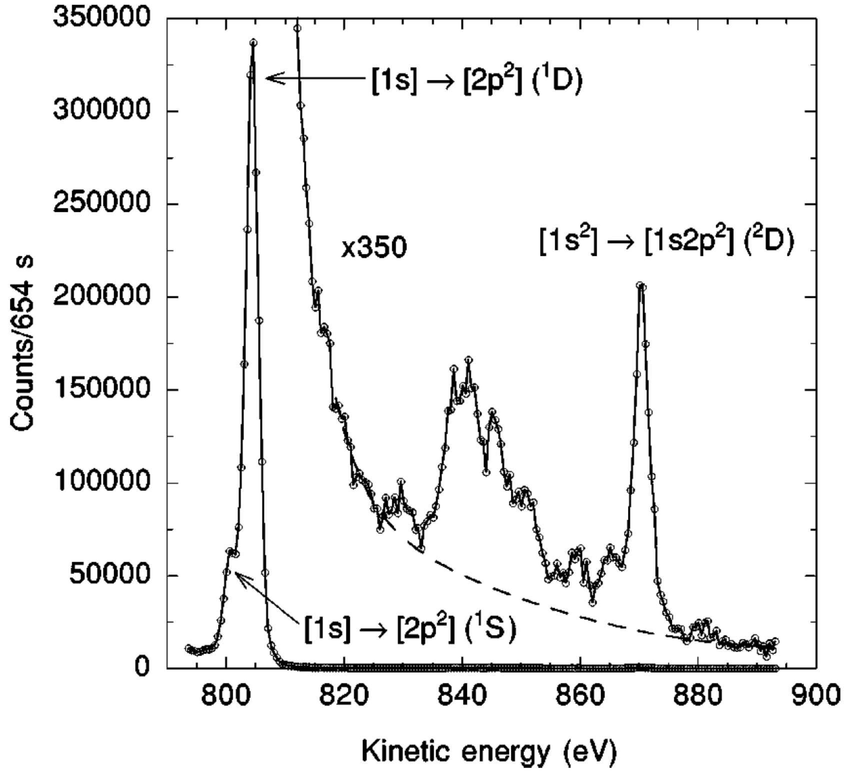
Double-core-hole formation can be monitored by measuring the KK-KLL Auger-electron hypersatellite





Southworth *et al.*, Phys. Rev. A **67**, 062712 (2003)

Dependence of Auger yield on intensity: ensemble average

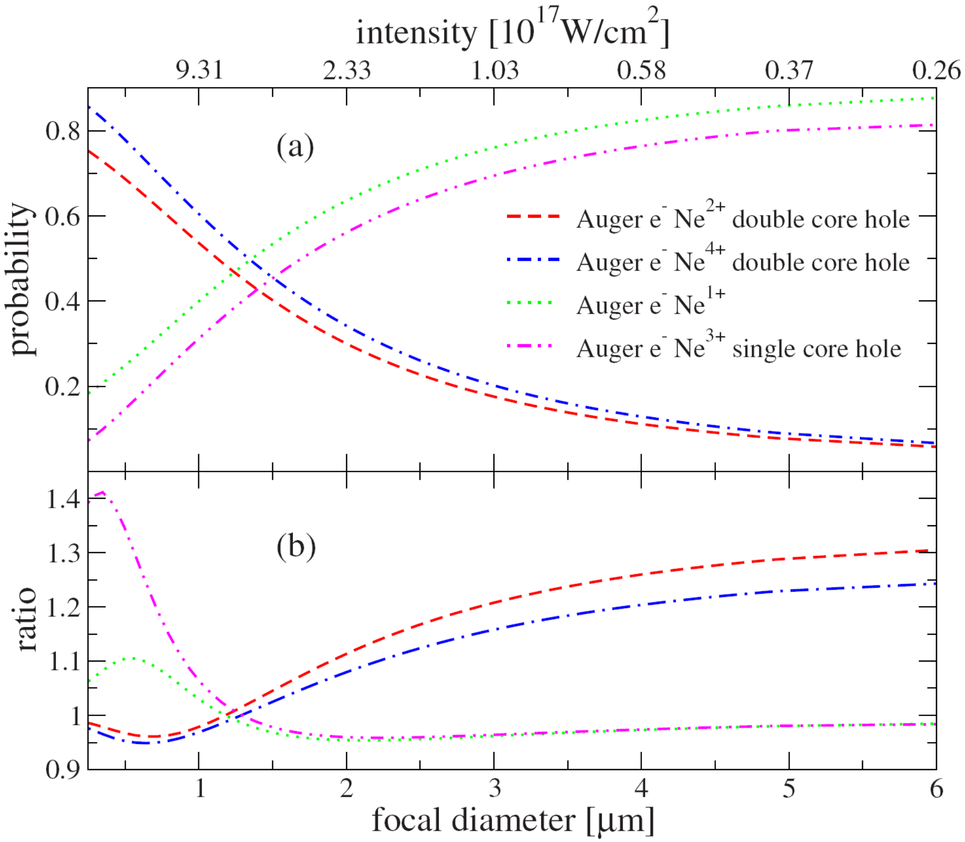


FIG. 3. (Color online) Neon exposed to an ensemble of 10 000 FEL pulses ($\omega_0 = 1050$ eV). (a) Auger electron yields (ensemble average) from the double-core-hole states of Ne^{2+} and Ne^{4+} (PPA process) and from the single-core-hole states of Ne^{1+} and Ne^{3+} (PAP process), as a function of the focal diameter. (b) Ratio of the ensemble average of Auger electron yield and the corresponding yield obtained with the averaged pulse.

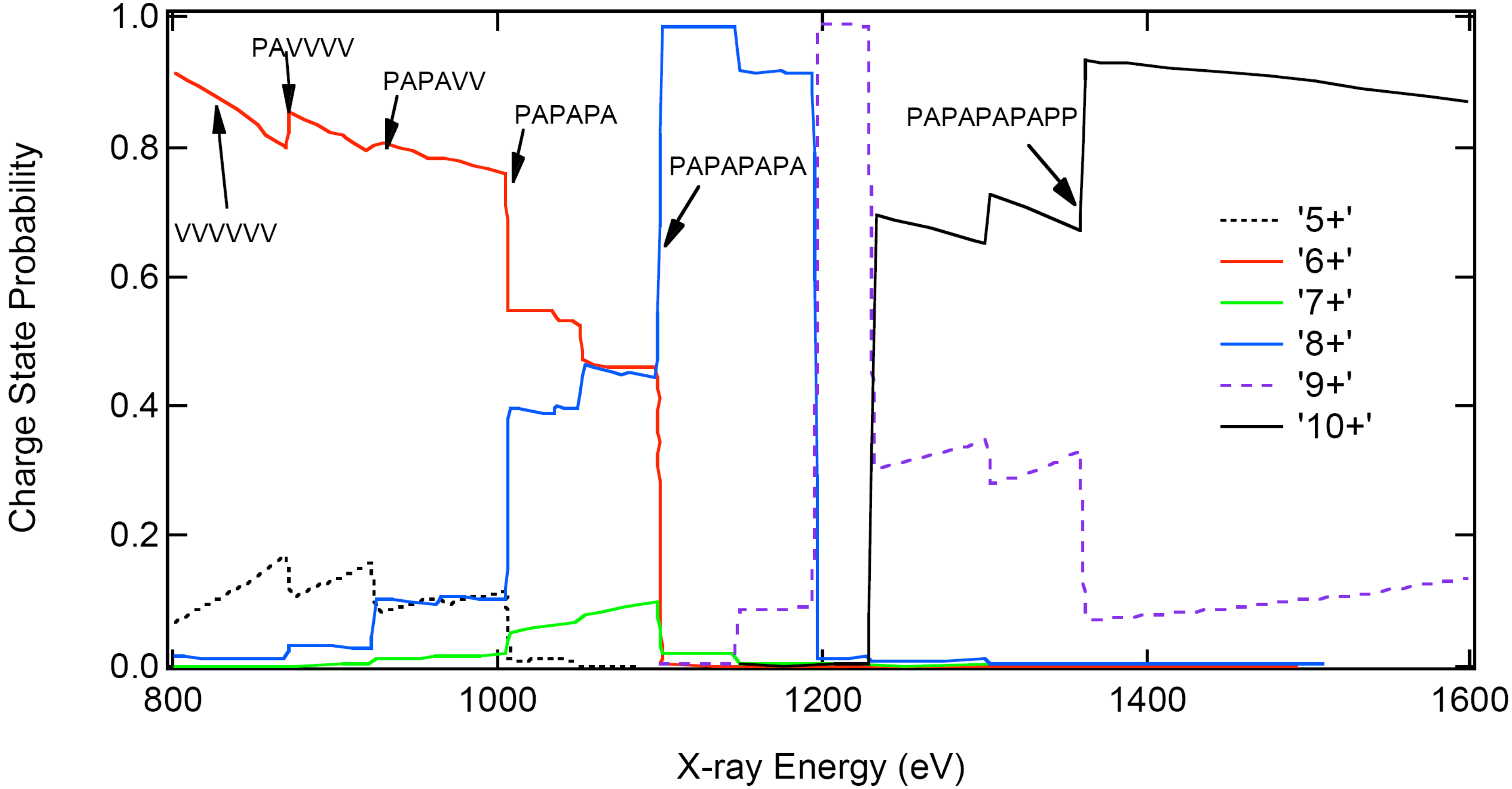
Calculations on neon

Statistical enhancement of double-core-hole formation when SASE FEL is used.

N. Rohringer and R. Santra, Phys. Rev. A **76**, 033416 (2007)

Charge-state distribution of neon as a function of x-ray energy

number of photons 10^{13}, focal width 1 µm, pulse duration 230 fs



N. Rohringer and R. Santra, Phys. Rev. A **76**, 033416 (2007)

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K-shell binding energies

Initial configuration	1s binding energy (eV)	Dominant photoprocess
Ne $1s^2 2s^2 2p^6$	870.2	PAVVVV
Ne^+ $1s^2 2s^2 2p^5$	897.0	
Ne^{2+} $1s^2 2s^2 2p^4$	928.4	PAPAVV
Ne^{3+} $1s^2 2s^2 2p^3$	964.6	
Ne^+ $1s^1 2s^2 2p^6$	993.6	PAPAVV + PPAAVV
Ne^{4+} $1s^2 2s^2 2p^2$	1006	PAPAPA + PPAAPA
Ne^{2+} $1s^1 2s^2 2p^5$	1027	
Ne^{3+} $1s^1 2s^2 2p^4$	1036	PAPAPA + PPAAPA + PPAPAA + PAPPAA
Ne^{5+} $1s^2 2s^2 2p^1$	1051	
Ne^{4+} $1s^1 2s^2 2p^3$	1079	
Ne^{6+} $1s^2 2s^2 2p^0$	1101	PAPAPAPA
Ne^{5+} $1s^1 2s^2 2p^2$	1126	
Ne^{7+} $1s^2 2s^1 2p^0$	1147	
Ne^{6+} $1s^1 2s^2 2p^1$	1176	
Ne^{8+} $1s^2 2s^0 2p^0$	1196	PAPAPAPAP
Ne^{7+} $1s^1 2s^2 2p^0$	1231	PAPAPAPPAA
Ne^{8+} $1s^1 2s^1 2p^0$	1302	PAPAPAPPAA + PPAPAPAPPA +…
Ne^{9+} $1s^1 2s^0 2p^0$	1362	PAPAPAPAPP

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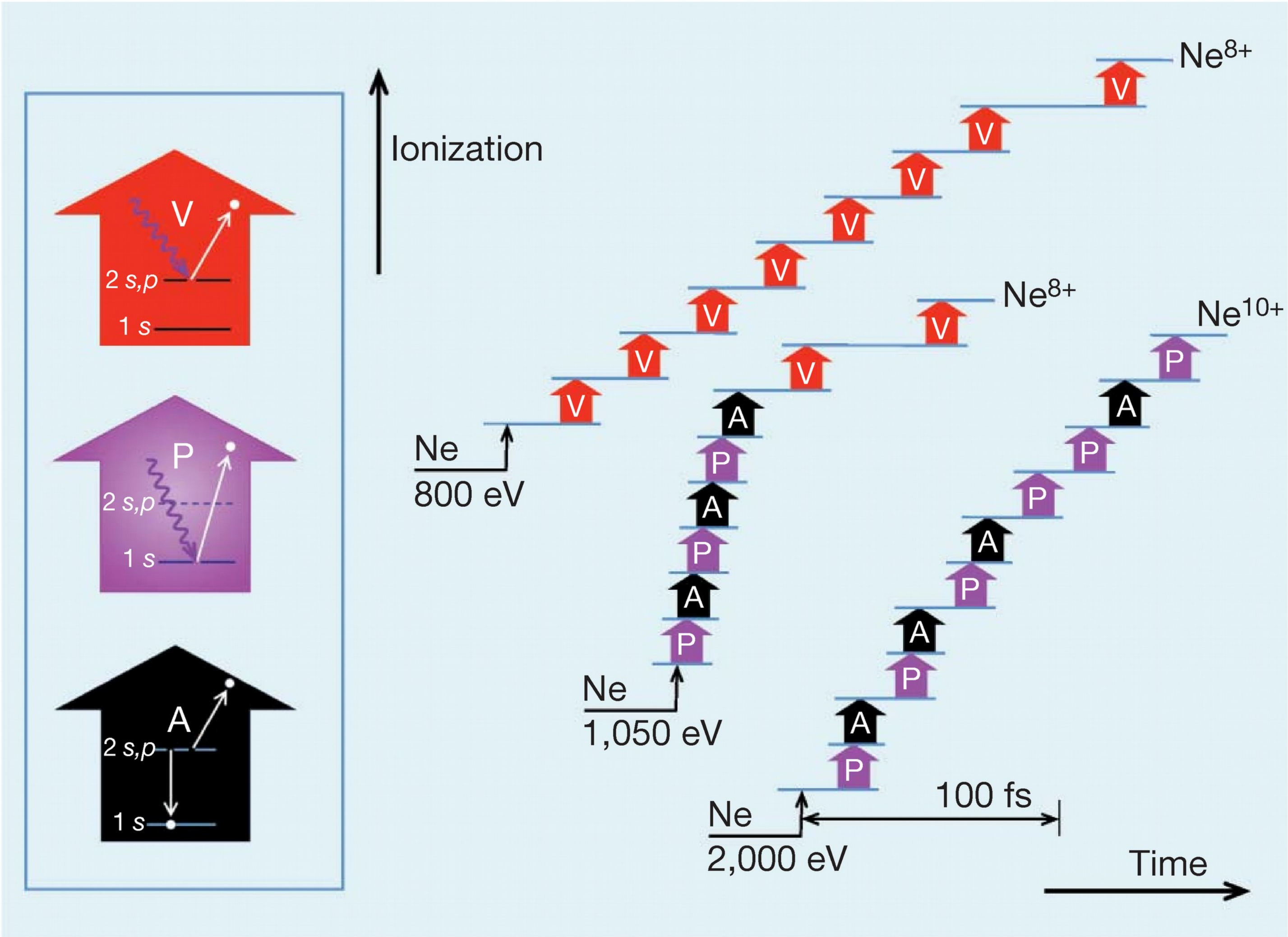
Formation of high charge states in a single pulse

L. Young *et al.*, Nature **466**, 56 (2010)

Photon energy-dependent ionization pathways



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L. Young *et al.*, Nature **466**, 56 (2010)

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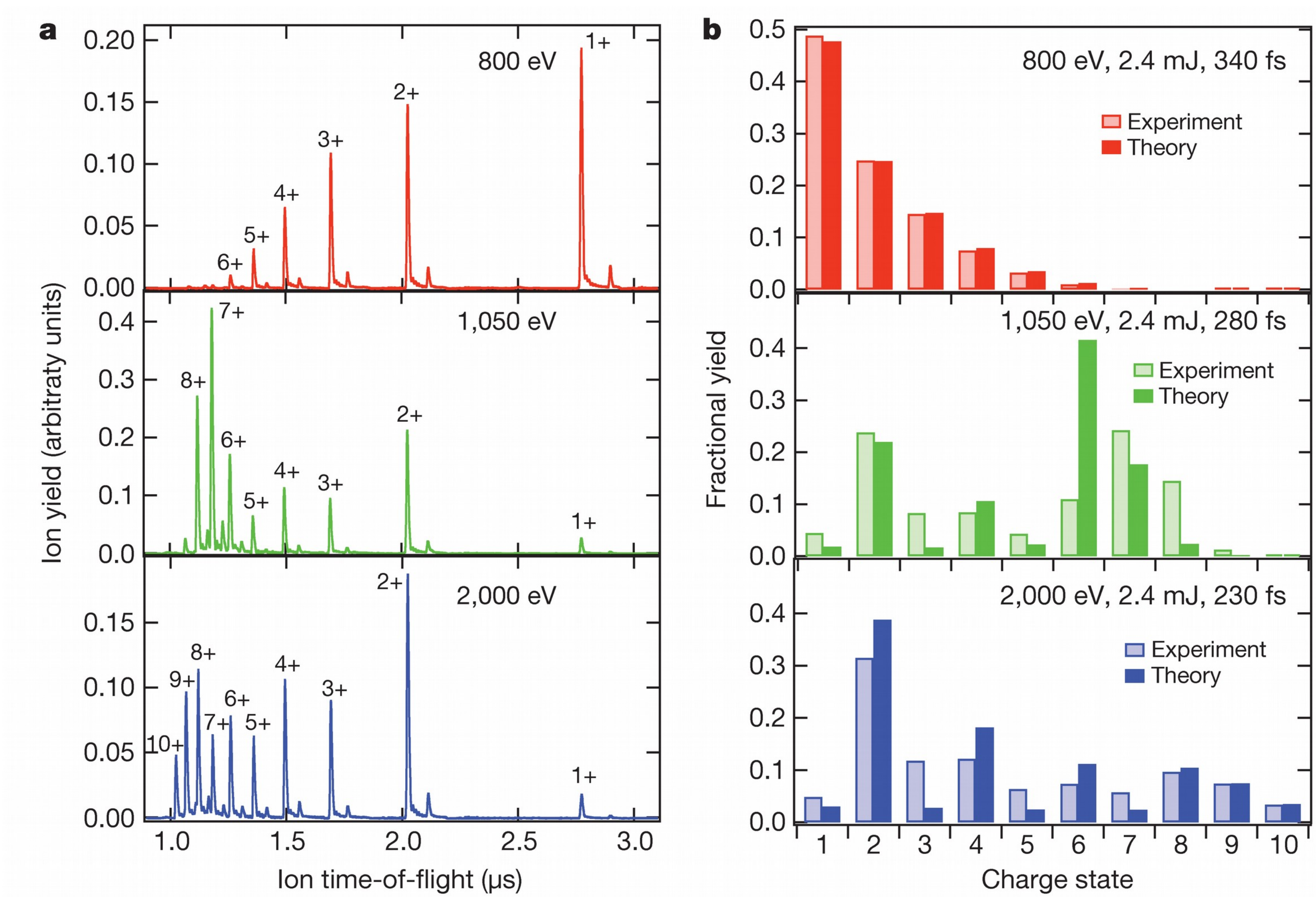
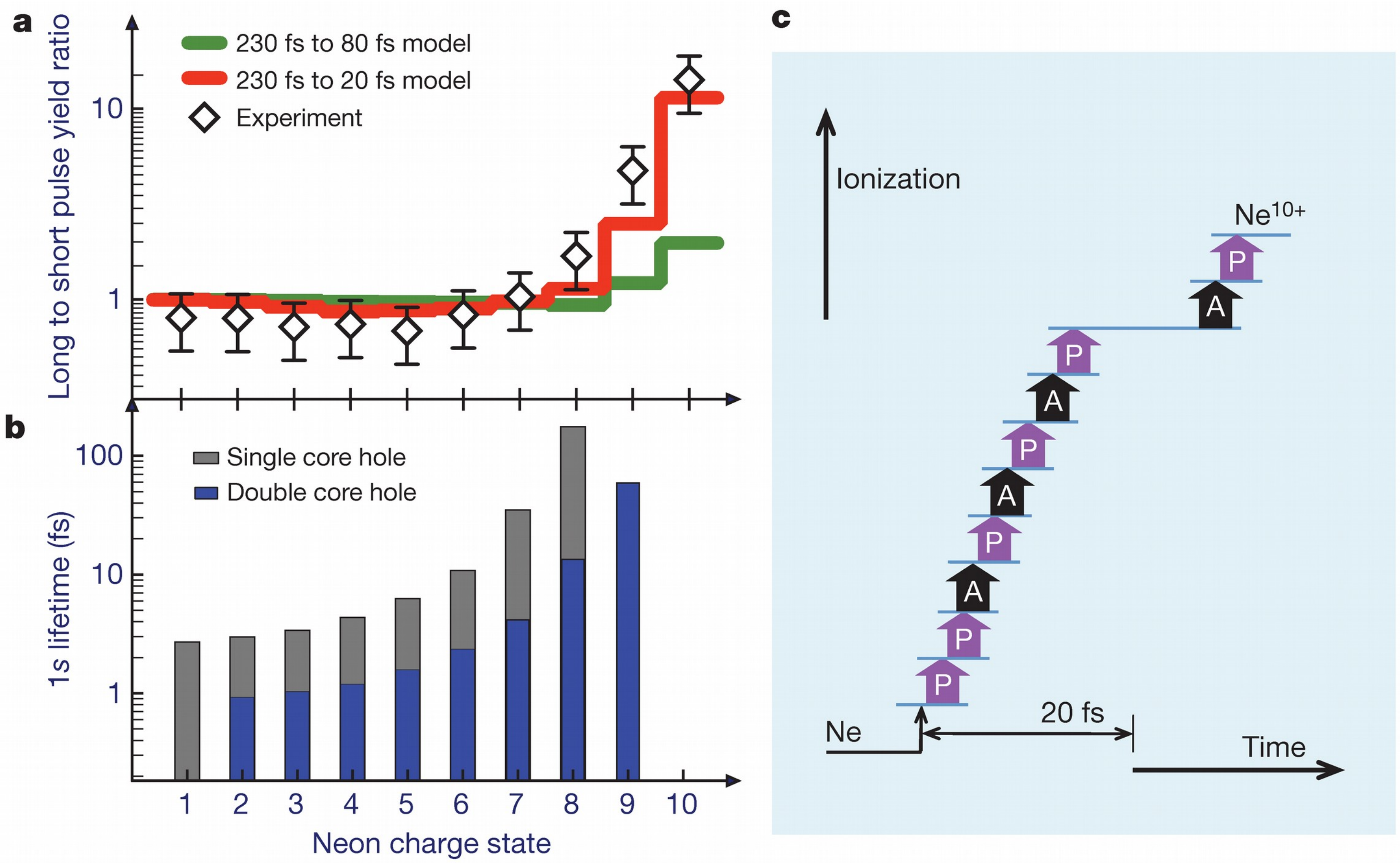
Neon charge states as a function of the photon energy



L. Young *et al.*, Nature **466**, 56 (2010)

Counterintuitive impact of pulse duration

photon energy 2 keV, pulse energy 2 mJ



L. Young *et al.*, Nature **466**, 56 (2010)

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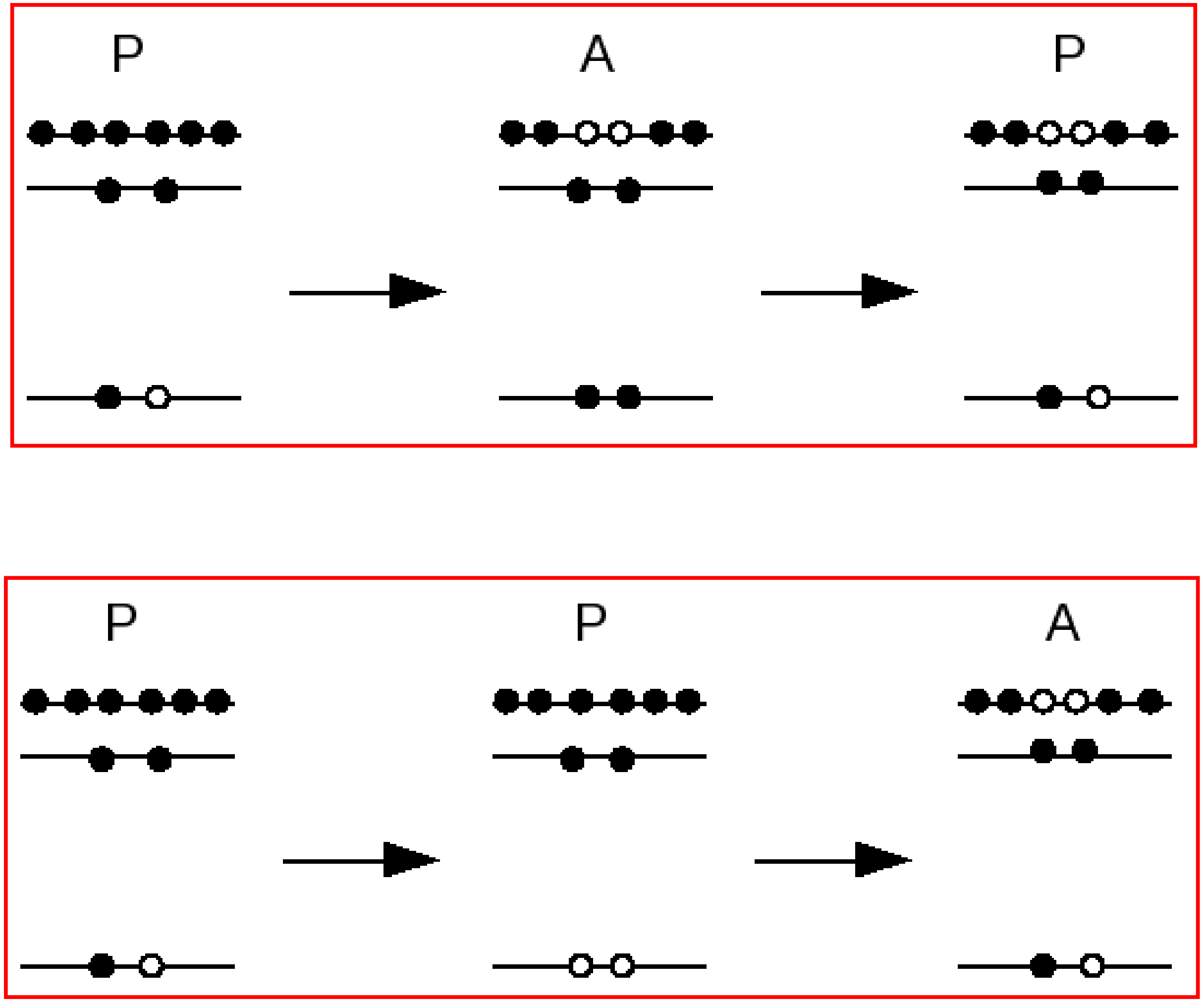
Beating the Auger clock: photoionization within an inner-shell decay lifetime

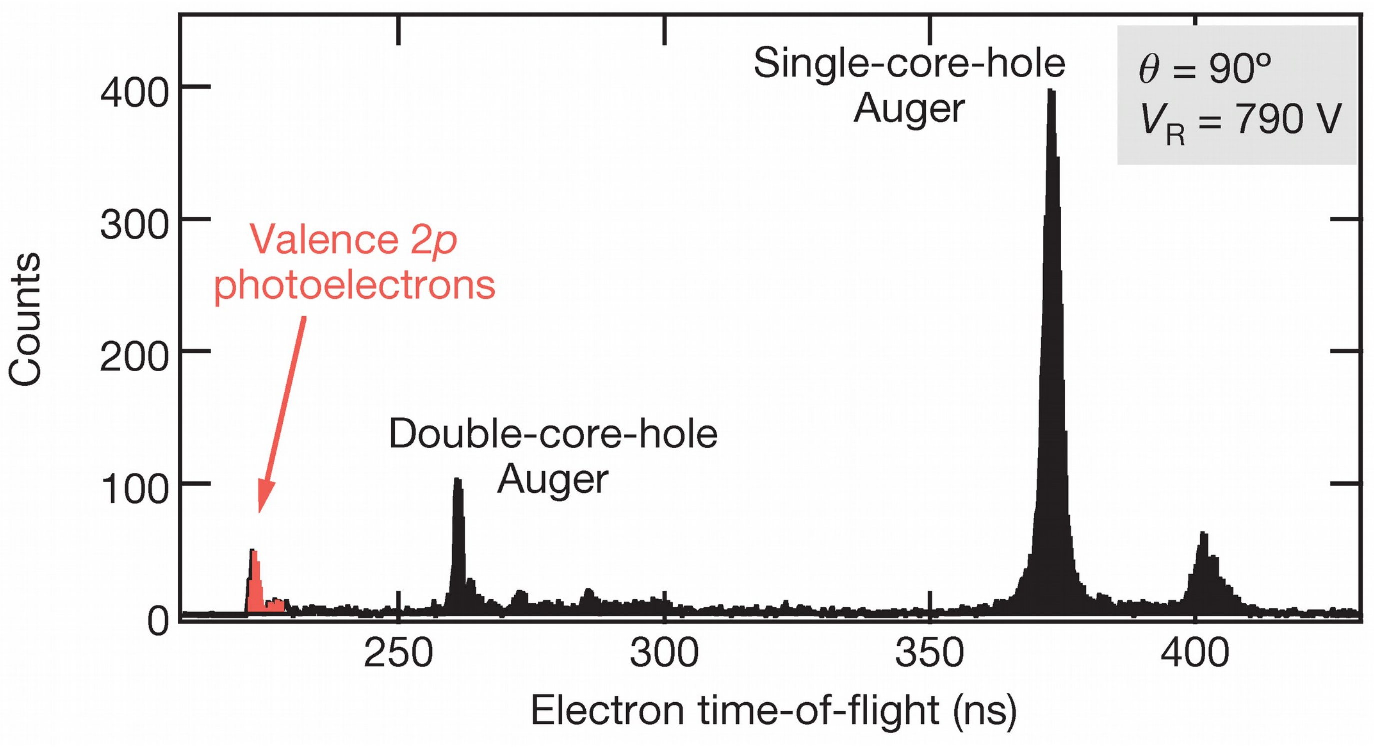
L. Young *et al.*, Nature **466**, 56 (2010)

Basic idea: observe the formation of double-core-hole states via Auger electron spectroscopy



Observation of double-core-hole formation

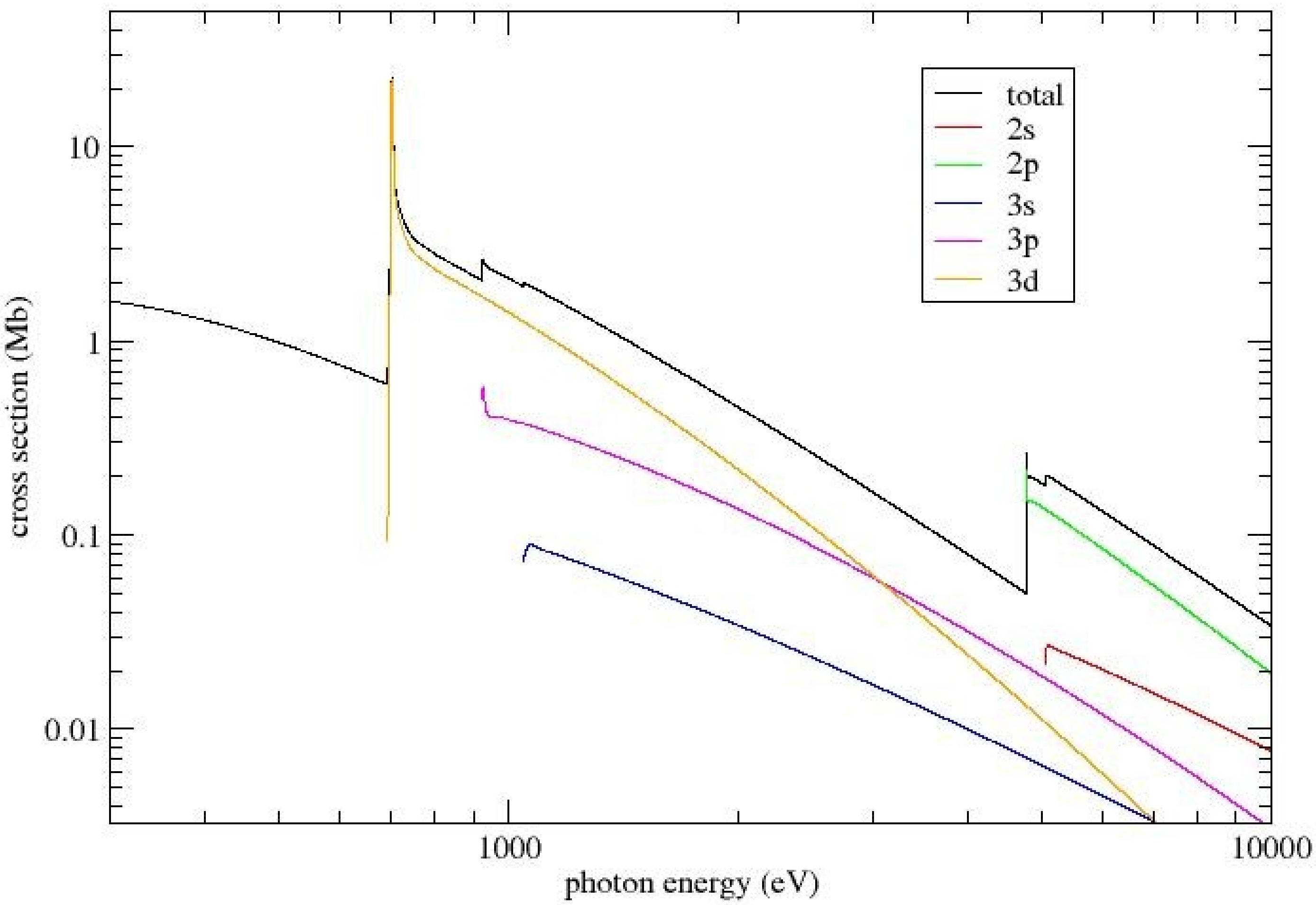
photon energy 1050 eV, pulse energy 2 mJ, nominal pulse duration 80 fs, electrons emitted perpendicular to x-ray polarization axis



L. Young *et al.*, Nature **466**, 56 (2010)

Heavy elements (high *Z*):
the role of Auger cascades

Calculated x-ray photoionization cross section of neutral xenon (one-photon absorption)



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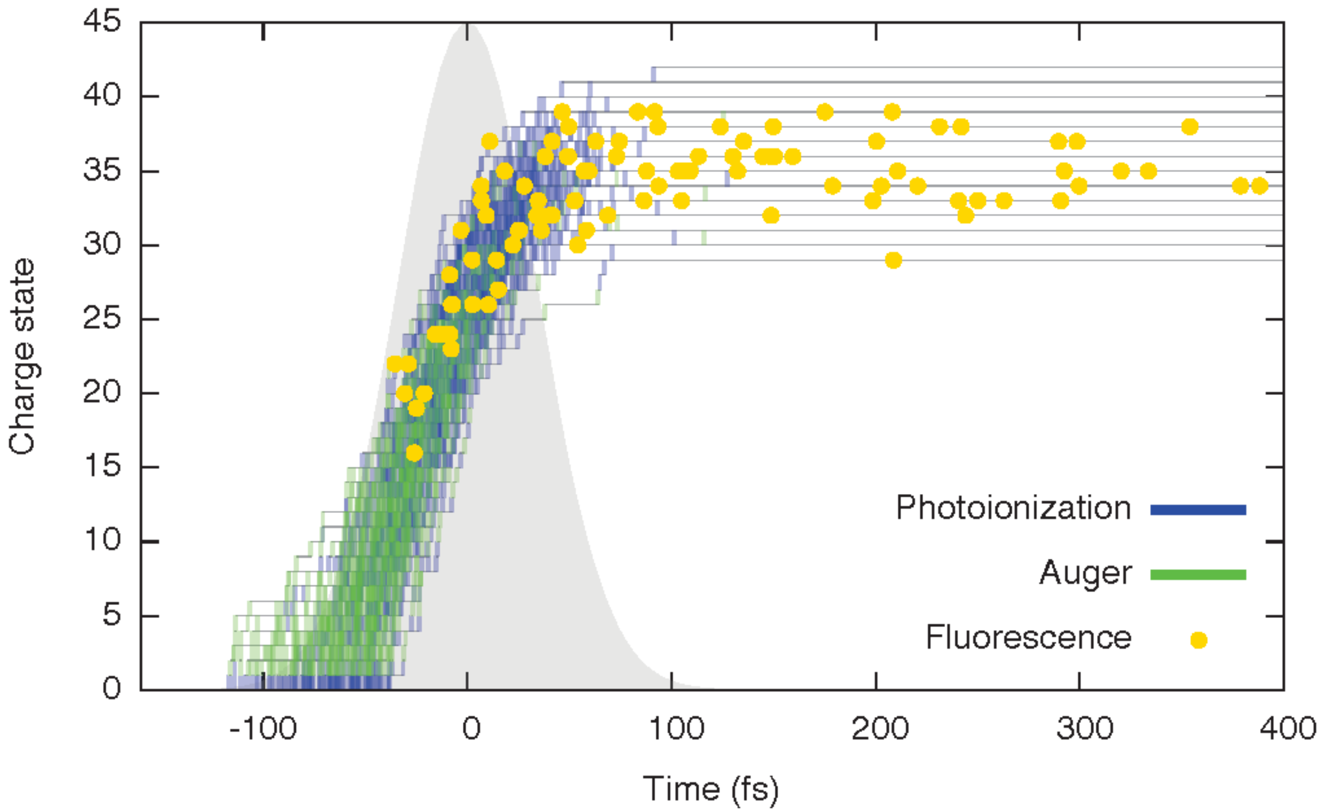
Xe ionization dynamics at high x-ray intensity



- Photon energy: 4.5 keV
- Pulse duration: 80 fs
- Fluence: 5×10^{12} photons/μm^2
- 100 exemplary Monte Carlo trajectories

S.-K. Son and R. Santra, Phys. Rev. A **85**, 063415 (2012).

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X-ray multiphoton ionization of xenon at photon energies of 1.5 keV and 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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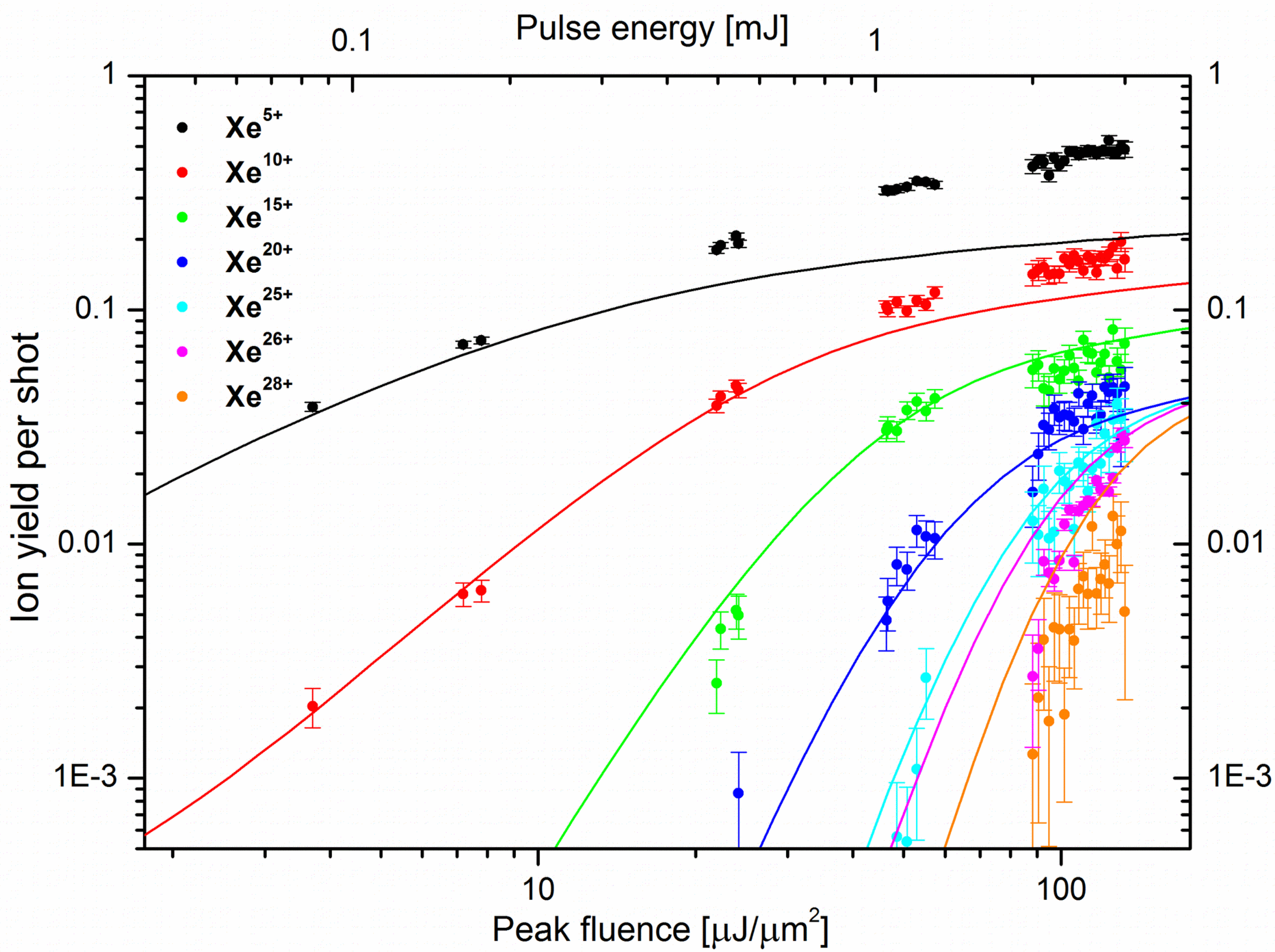
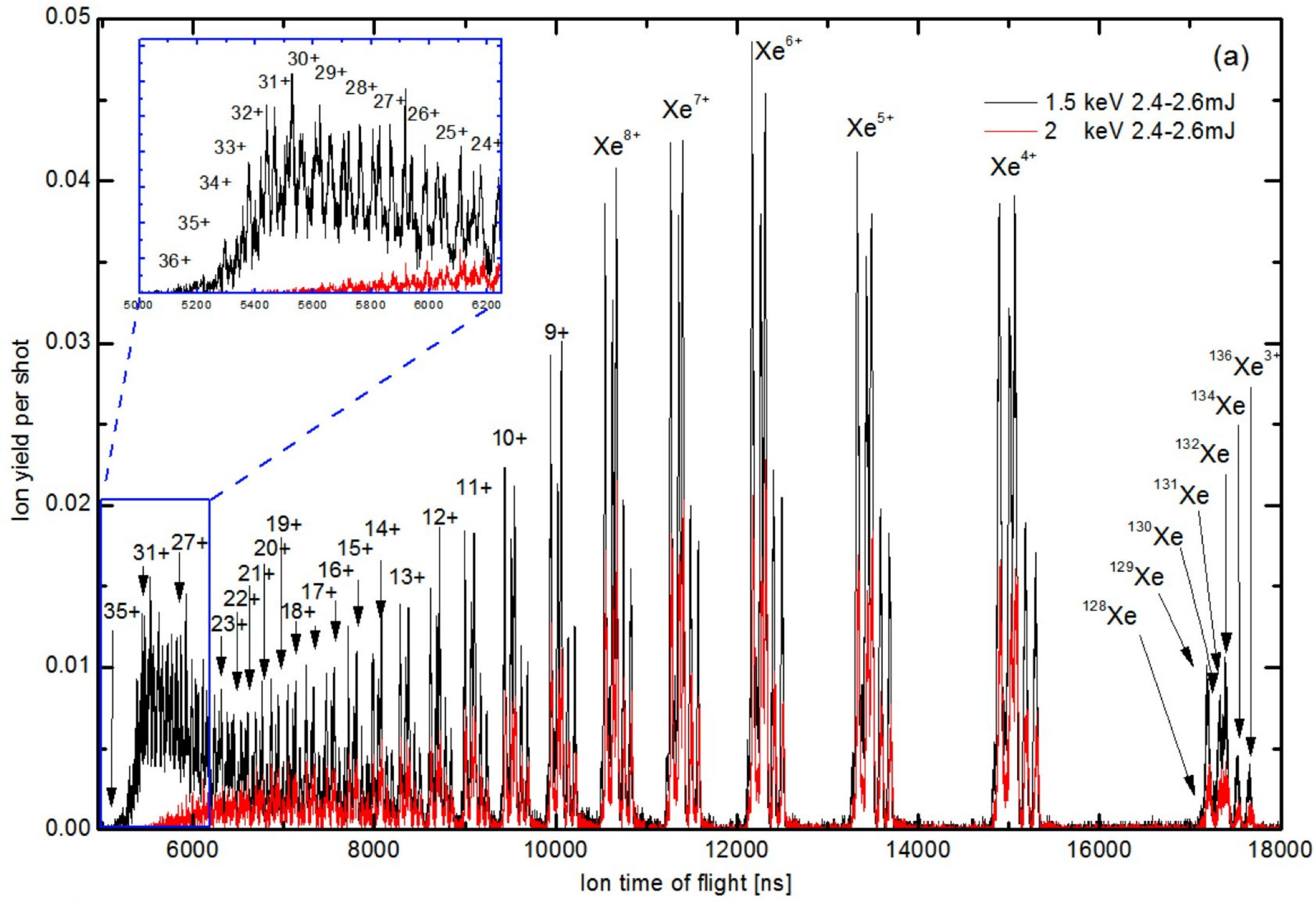
Comparison between experiment and theory at 2 keV



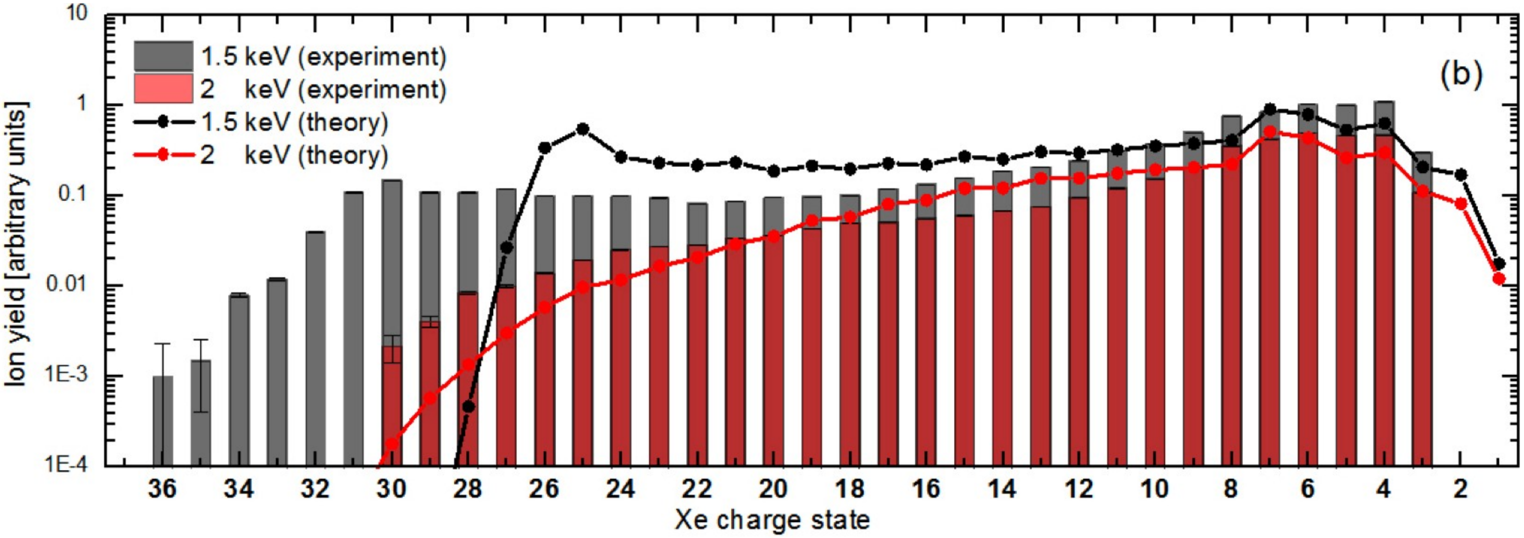
B. Rudek *et al.*, Nature Photonics **6**, 858 (2012).

Experimental charge-state distribution: 2 keV vs 1.5 keV



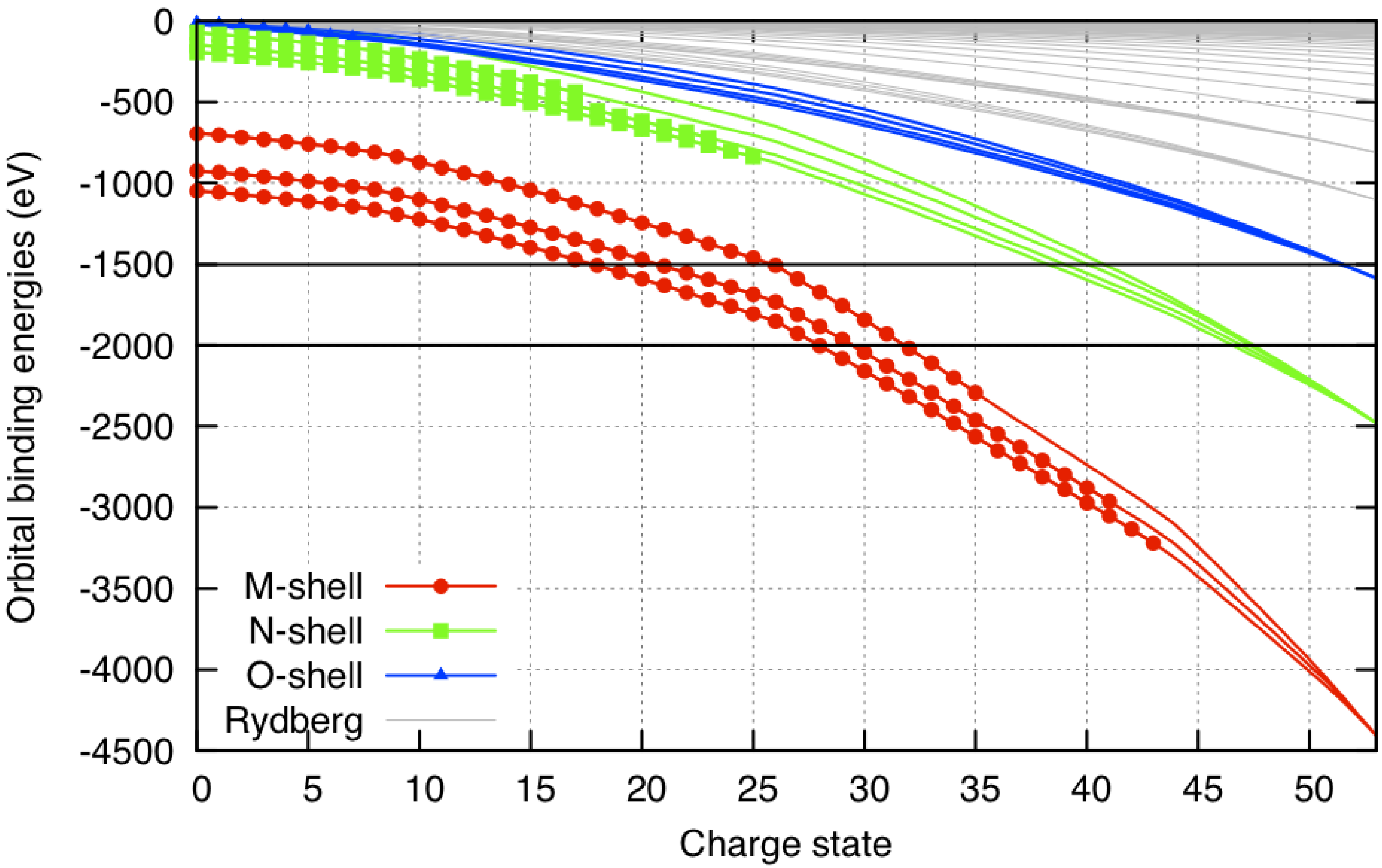
B. Rudek *et al.*, Nature Photonics **6**, 858 (2012).

Enhancement of ionization via resonances



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

Orbital binding energies of the ground configuration of Xe^{q+}



S.-K. Son and R. Santra, Phys. Rev. A **85**, 063415 (2012).

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Ionization dynamics of C_{60} and Ar_{1000}

Towards polyatomic systems: XMDYN

Atomistic Model + Molecular Dynamics (MD) code

[core: Jurek, Faigel, Tegze, Eur. Phys. J. D **29**, 217 (2004)]

> **Atomic processes** (ph.eff./Auger/fluor.): Monte Carlo

Rates and cross sections from **XATOM**

> **Real space dynamics**: MD

– atoms/ions and (quasi-)free electrons: classical particles

– classical force fields, Coulomb; Newton's equations

> Phenomena due to the **molecular environment**

– chemical bonds

– secondary ionizations

– molecular Auger effect

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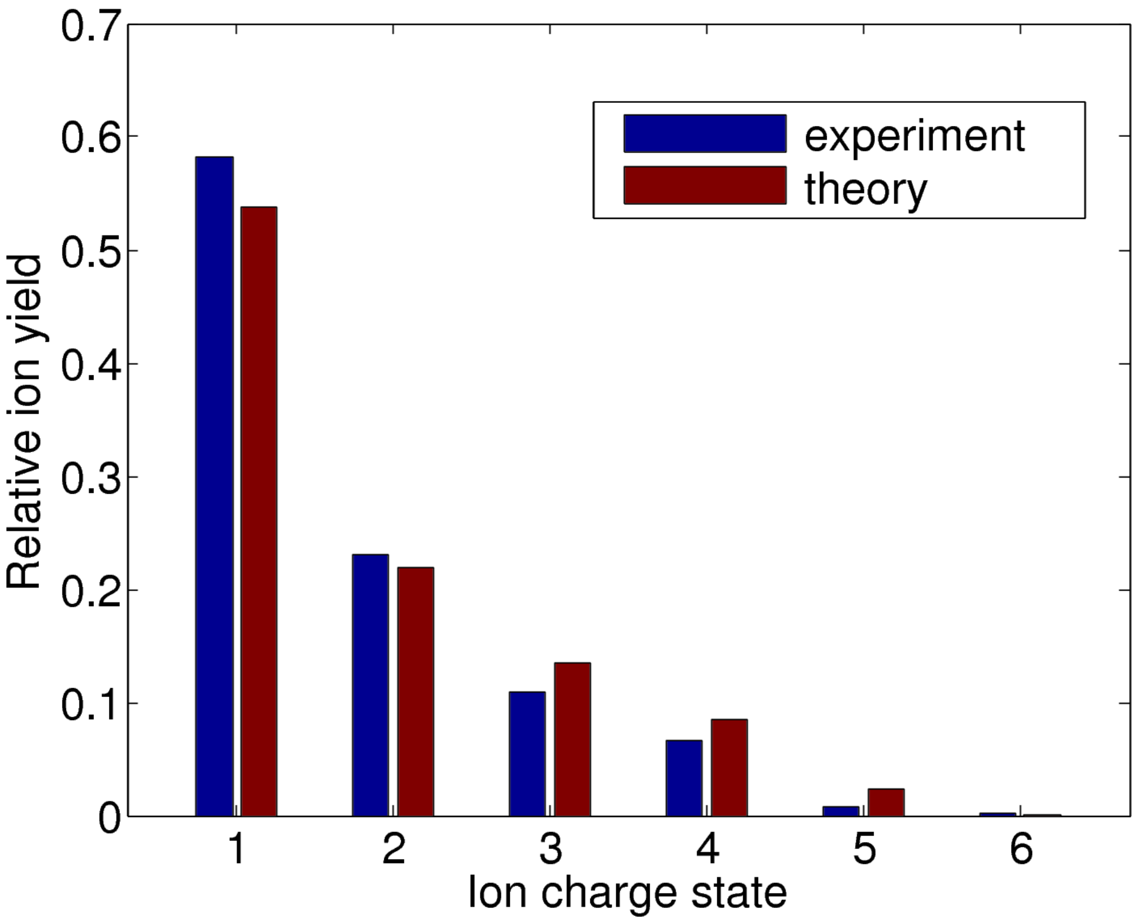
DESY

C_{60} @ LCLS

> **Atomic ions** – experimental and volume integrated theoretical **yields**



Calibration – Ar ion yield

(XATOM, Sang-Kil Son)

Pulse:

60 fs nominal / 30 fs real,

485 eV, 0.345 mJ,

focus = $(1.4\ \mu m)^2$

double Gaussian beam profile

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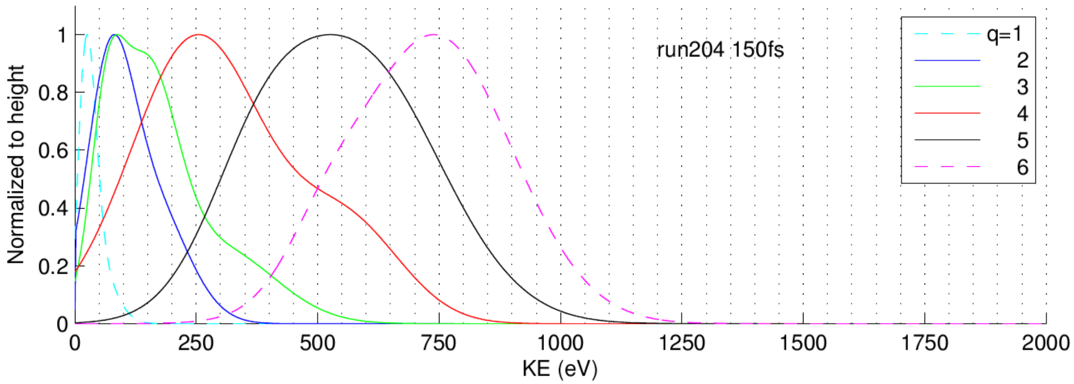
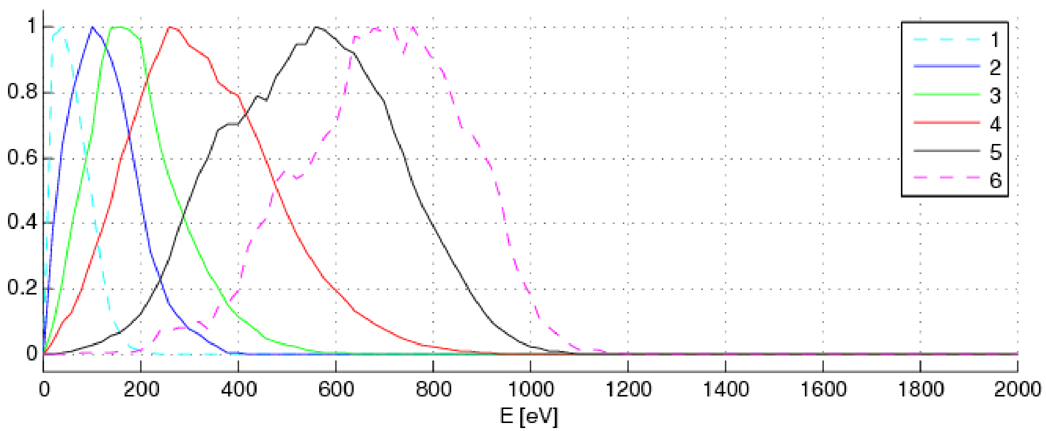
B. F. Murphy *et al.*, Nature Commun. **5**, 4281 (2014).

DESY

C_{60} @ LCLS

> Atomic ions – kinetic energy spectra





Pulse: 150 fs nominal / 90 fs real,

485 eV, 0.91 mJ,

focus = $(1.4\mu m)^2$; 2-Gaussian

– Experiment

– Theory

no parameter fitting!

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B. F. Murphy *et al.*, Nature Commun. **5**, 4281 (2014).

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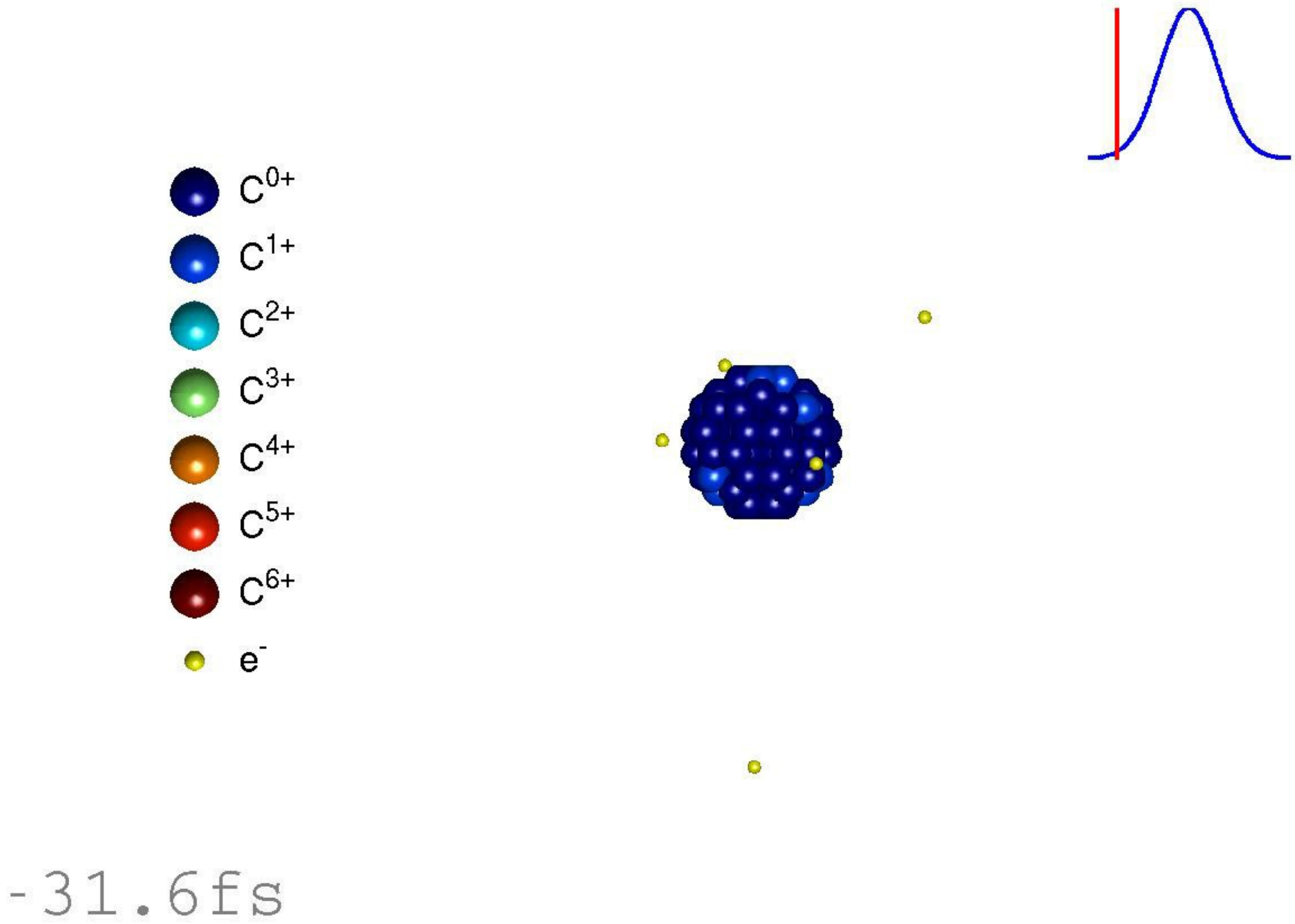
C_{60}: the movie



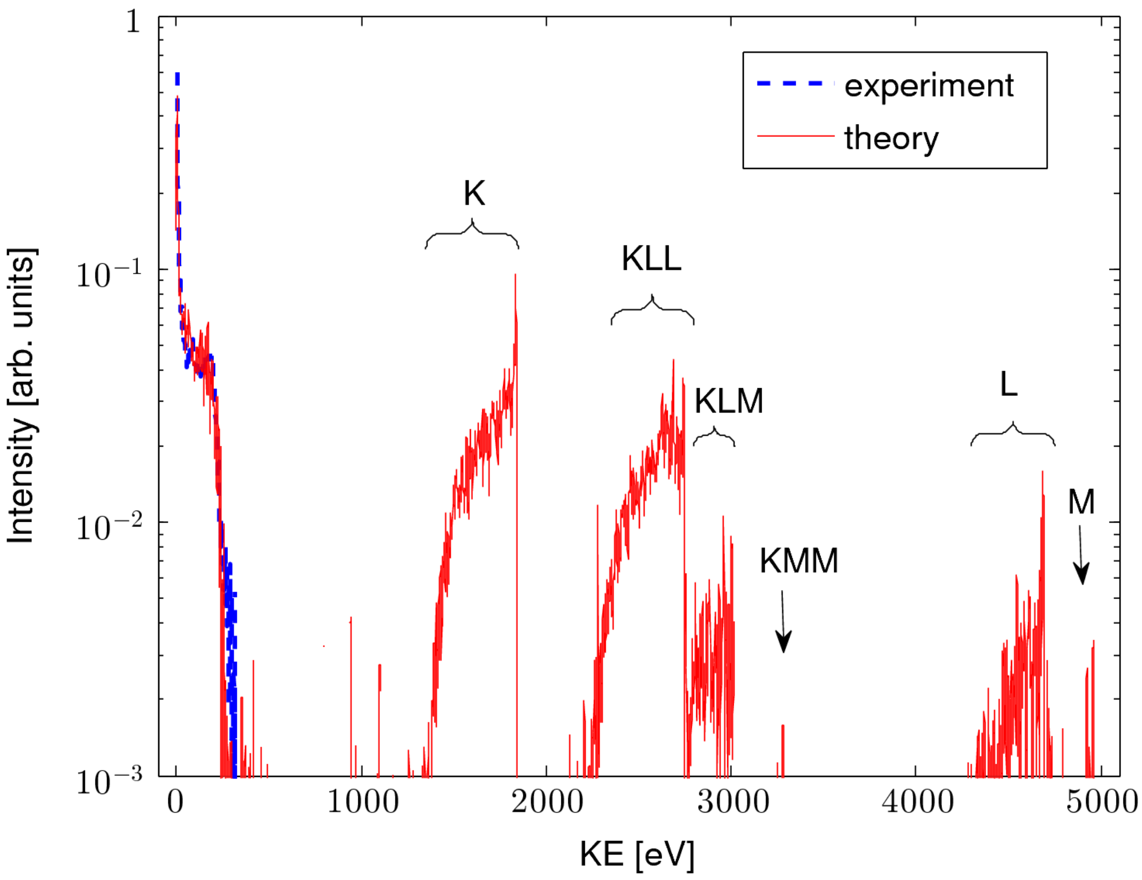
485 eV, 30 fs, 5.4e11 photons/μm^2

Argon clusters @ SACLA

> **Theoretical and experimental electron kinetic energy spectra**,

5 keV, 30 fs

N=1000 atoms



– Experiment

– Theory

no parameter fitting!

T. Tachibana *et al.*, Scientific Reports **5**, 10977 (2015).

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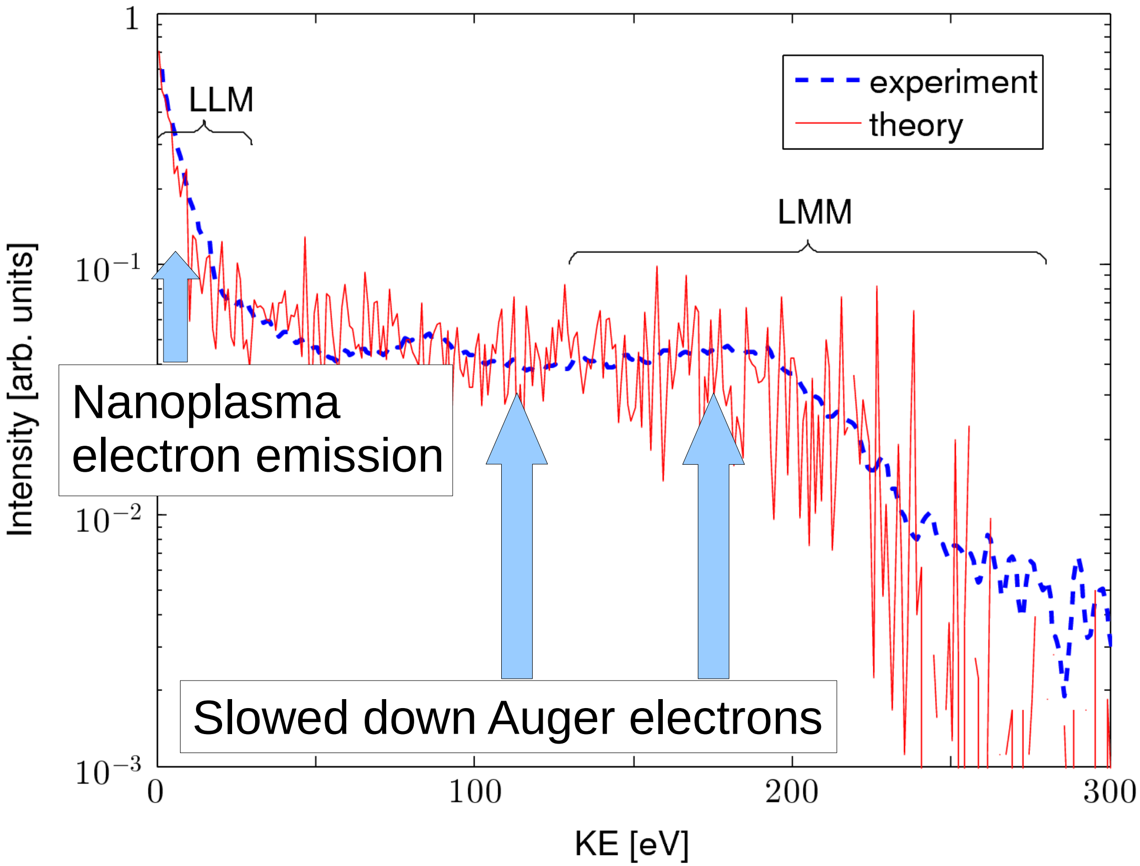
DESY

Argon clusters @ SACLA

> **Theoretical and experimental electron kinetic energy spectra**,

5 keV, 30 fs

N=1000 atoms



– Experiment

– Theory

no parameter fitting!

T. Tachibana *et al.*, Scientific Reports **5**, 10977 (2015).

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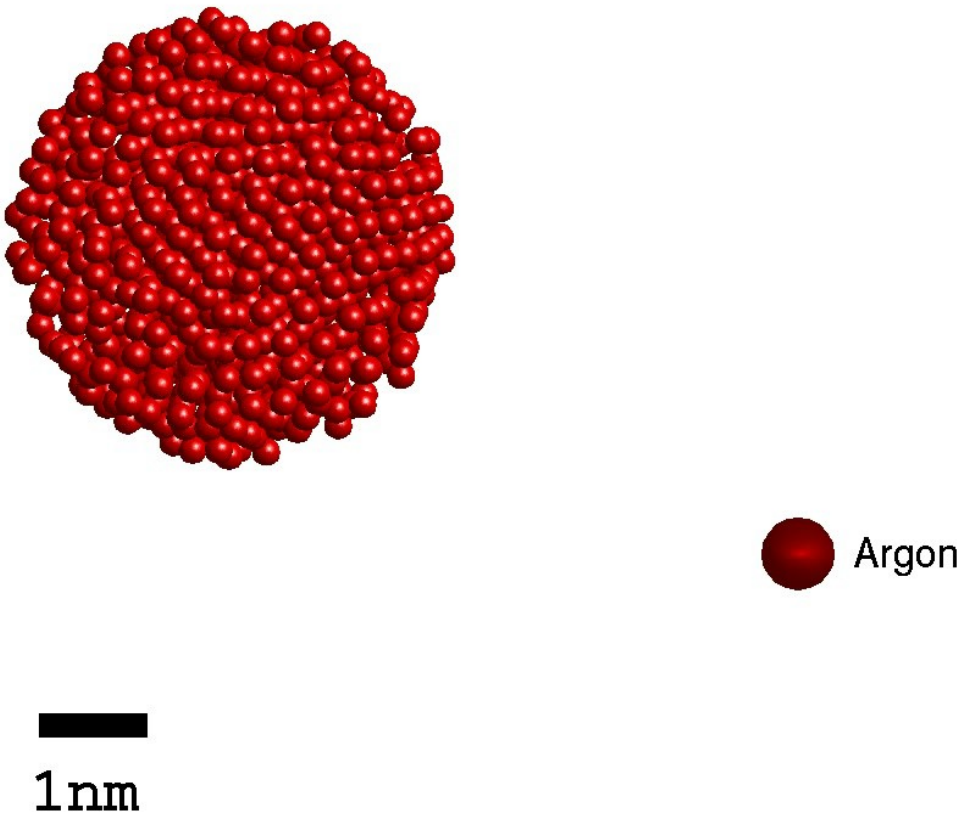
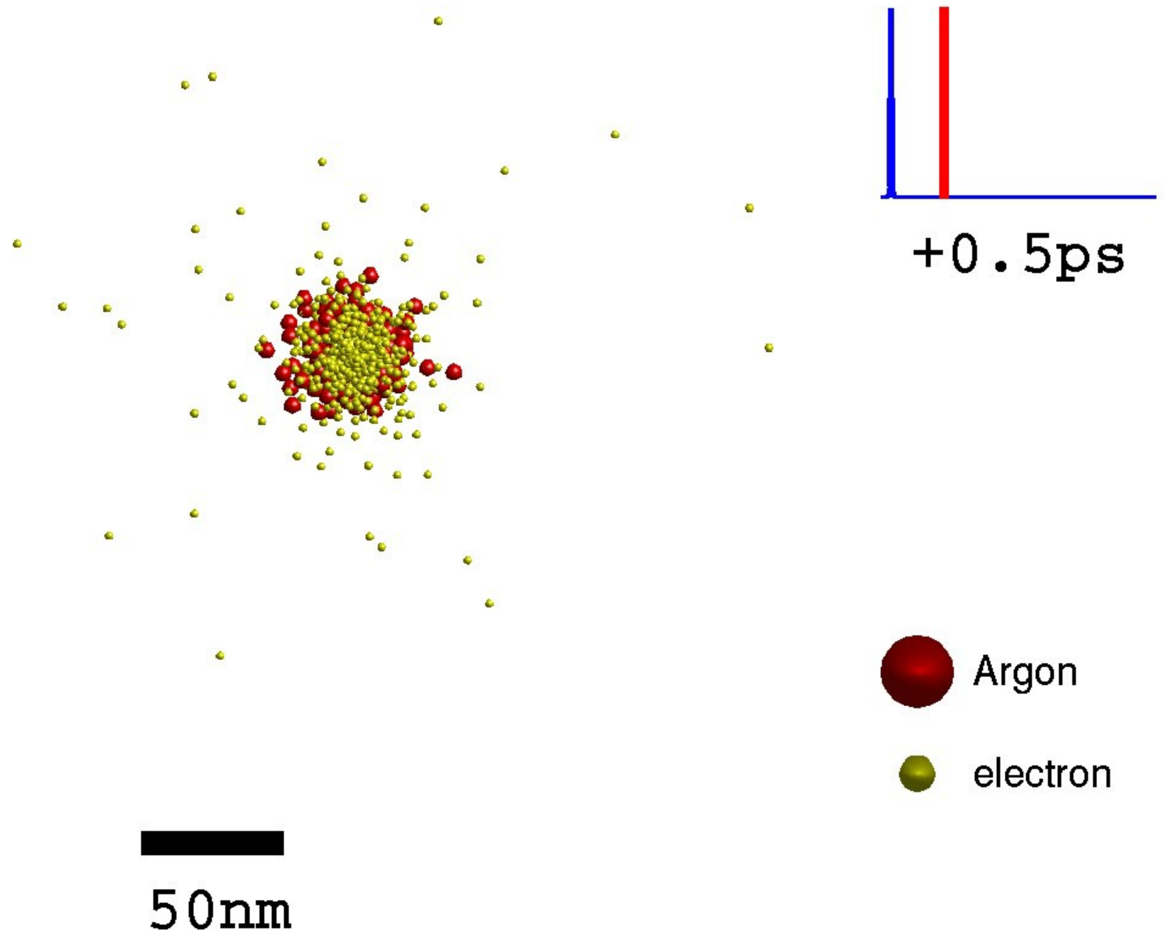
Ar_{1000}: short-term behavior



Ar_{1000}: longer-term behavior



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Limitations

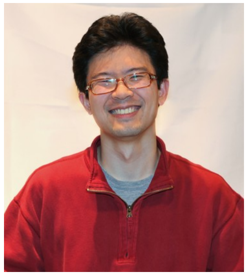
- no rigorous treatment of electronic structure of highly excited, polyatomic systems
- no first-principles treatment of chemical bonds; uses force fields, which are optimized only for the neutral ground state
- no first-principles treatment of influence of molecular environment on decay processes
-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

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 using 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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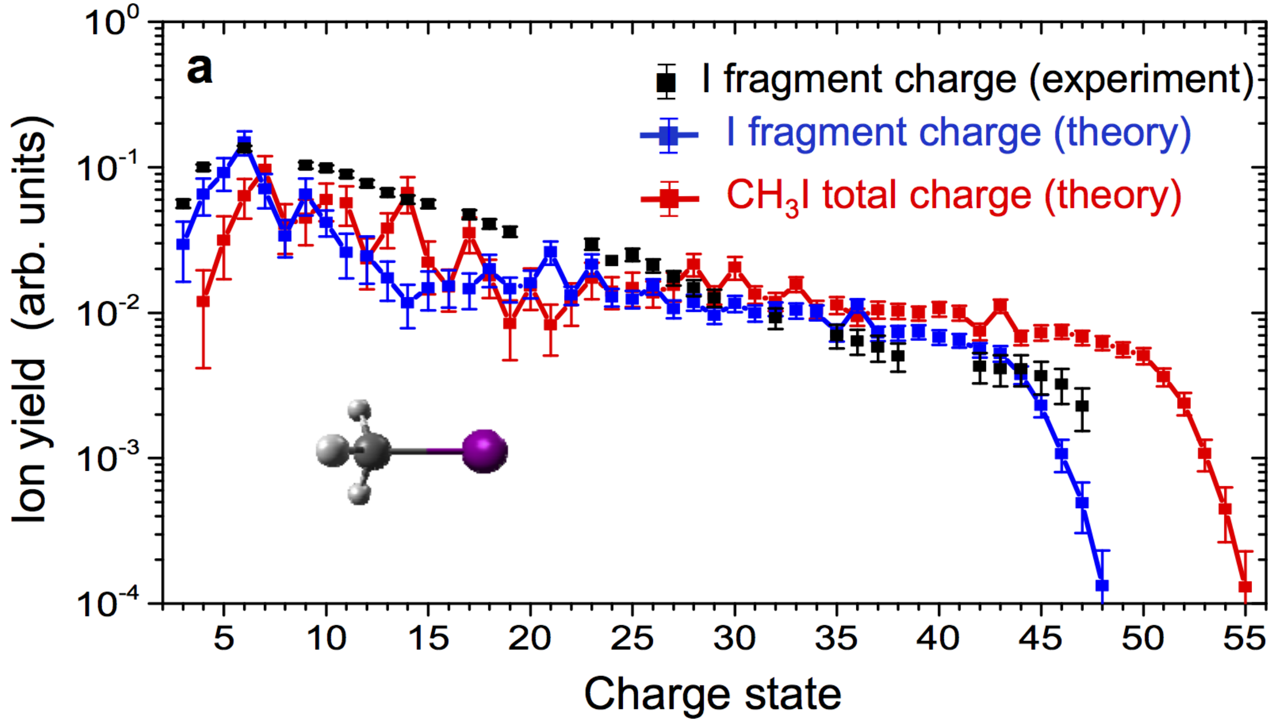
The highest charge states ever produced using light!



Photon energy: 8.3 keV

X-ray intensity: 10^{20} W/cm^2

Experimental data taken by Artem Rudenko, Daniel Rolles, and collaborators

A. Rudenko *et al.*, Nature **546**, 129 (2017).

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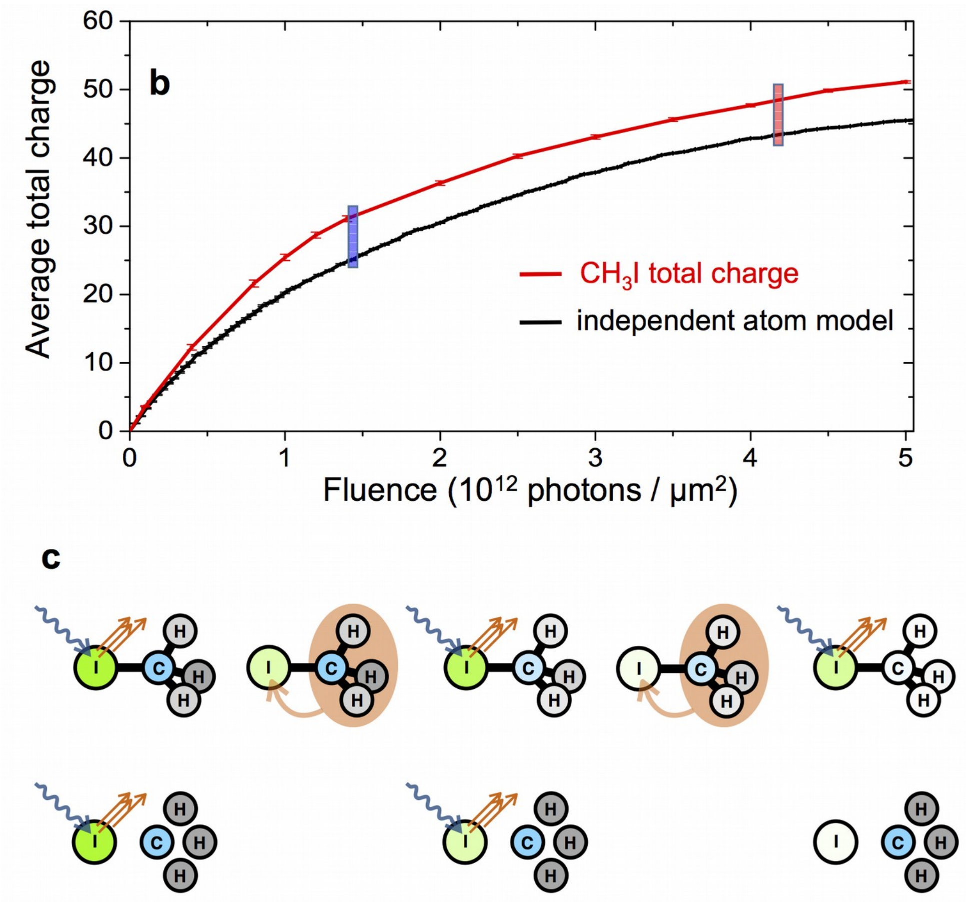
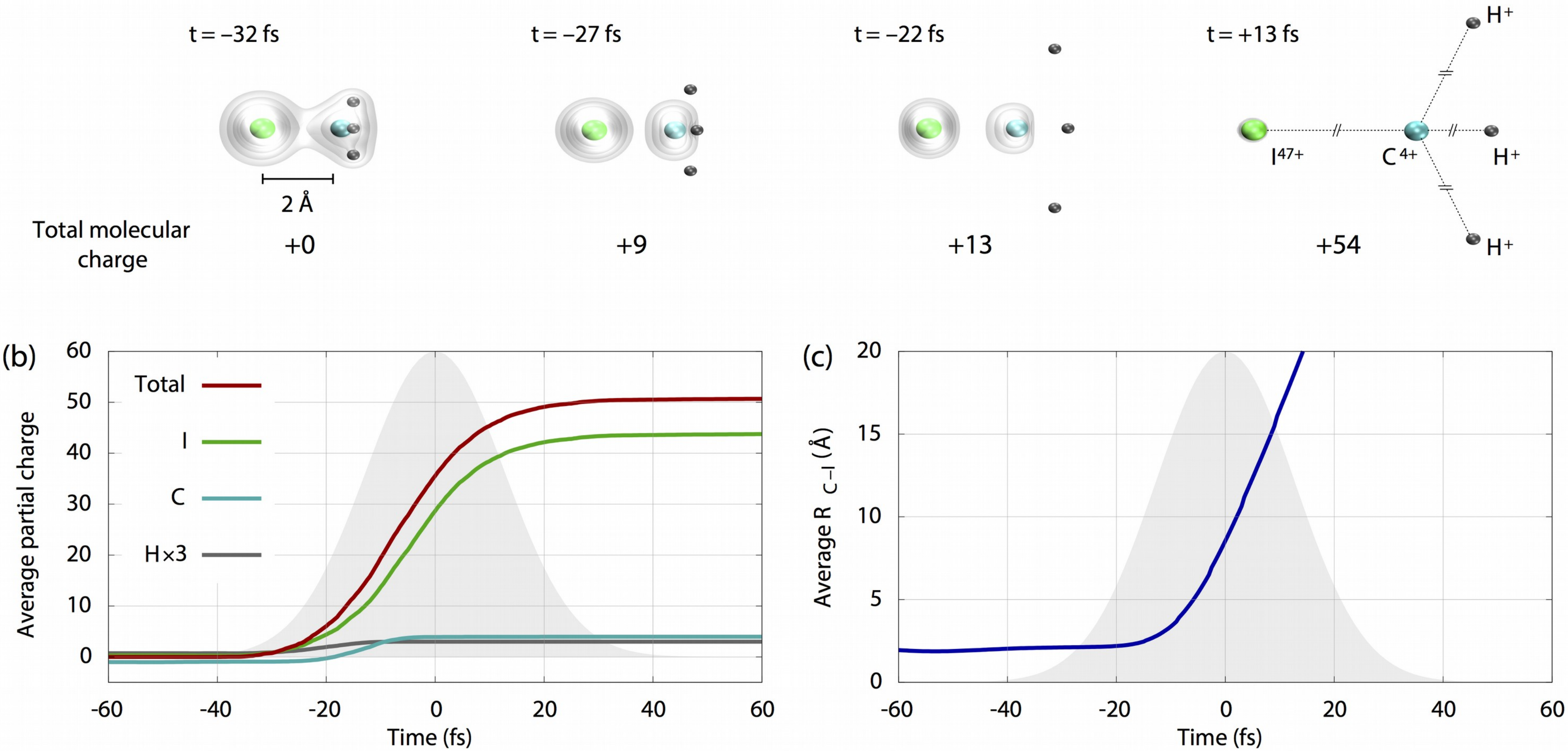
New ionization enhancement mechanism (molecular effect!)



A. Rudenko *et al.*, Nature **546**, 129 (2017).

Time-resolved ionization dynamics (theory)



A. Rudenko *et al.*, Nature **546**, 129 (2017).

Conclusions

- The probability that any given atom absorbs a photon when exposed to a focused x-ray free-electron-laser pulse approaches unity.
- This leads to sequential multiphoton ionization.
- Sequential multiphoton ionization, combined with inner-shell decay and electron impact ionization, leads to the formation of the highest charge states ever produced with light.
- In order to quantitatively describe the associated radiation damage, dedicated software has been, and is being, developed: XATOM, XMDYN, and XMOLECULE.

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http://www.desy.de/~xraypac

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