Efficient and Quantitative Simulation of Charge-Rearrangement-Enhanced X-Ray Ionization of Molecules

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CFEL SCIENCE

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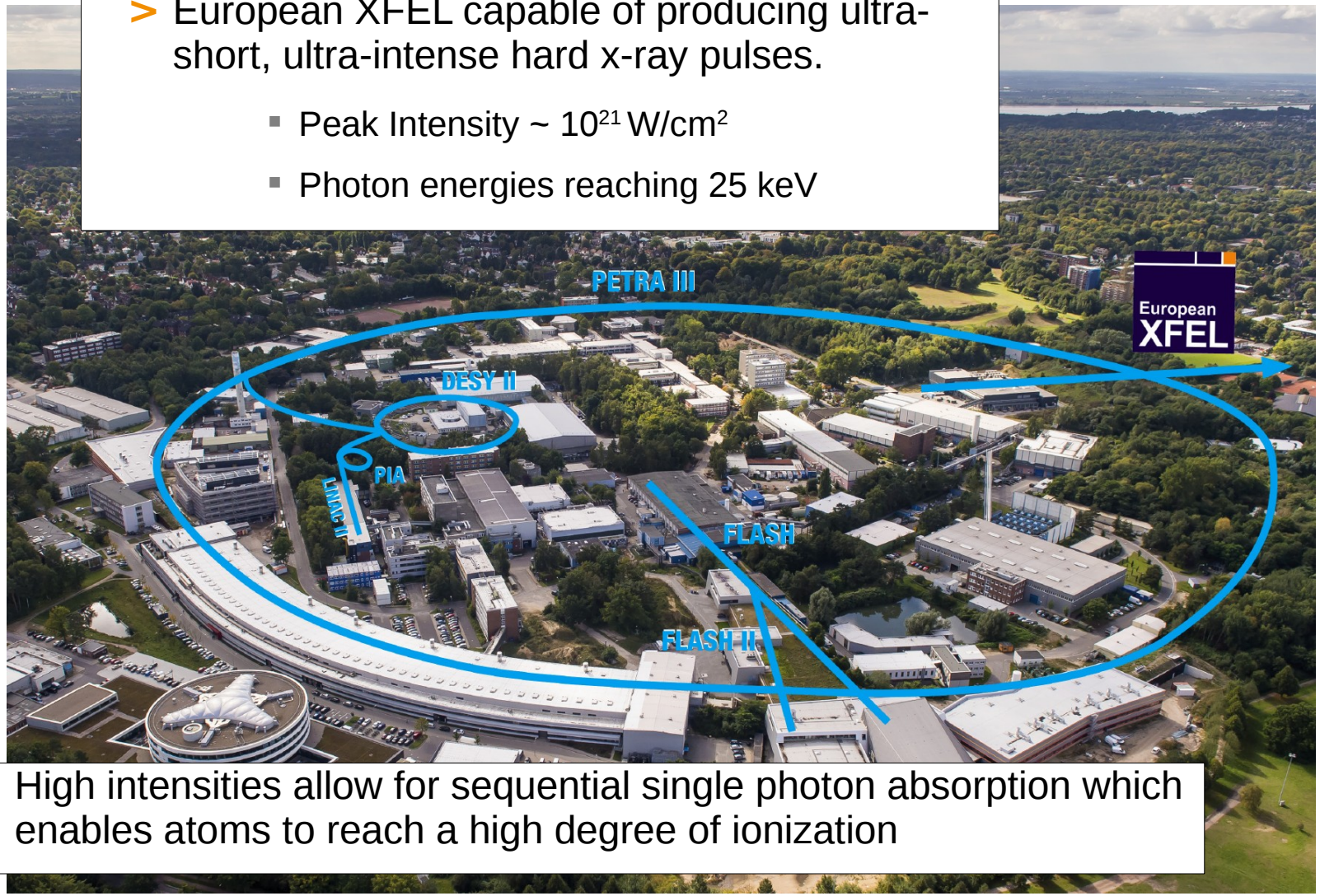
Motivation

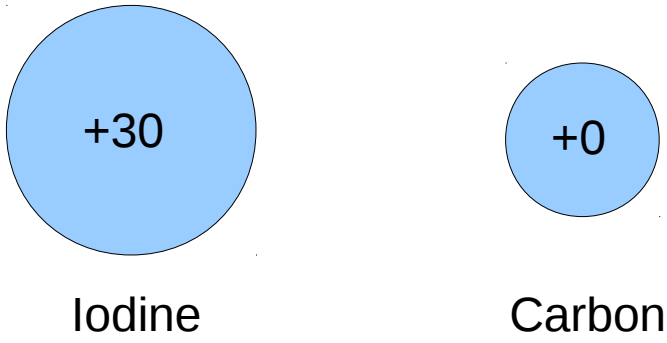
- European XFEL capable of producing ultra-short, ultra-intense hard x-ray pulses.
  - Peak Intensity ~ 10^{21} W/cm^2
  - Photon energies reaching 25 keV



- High intensities allow for sequential single photon absorption which enables atoms to reach a high degree of ionization

Motivation

- What if two atoms in close proximity are ionized very differently?
- What is the effect of possible charge rearrangement on the ionization dynamics?



X-Ray induced Processes in an Atom

> Photoionization

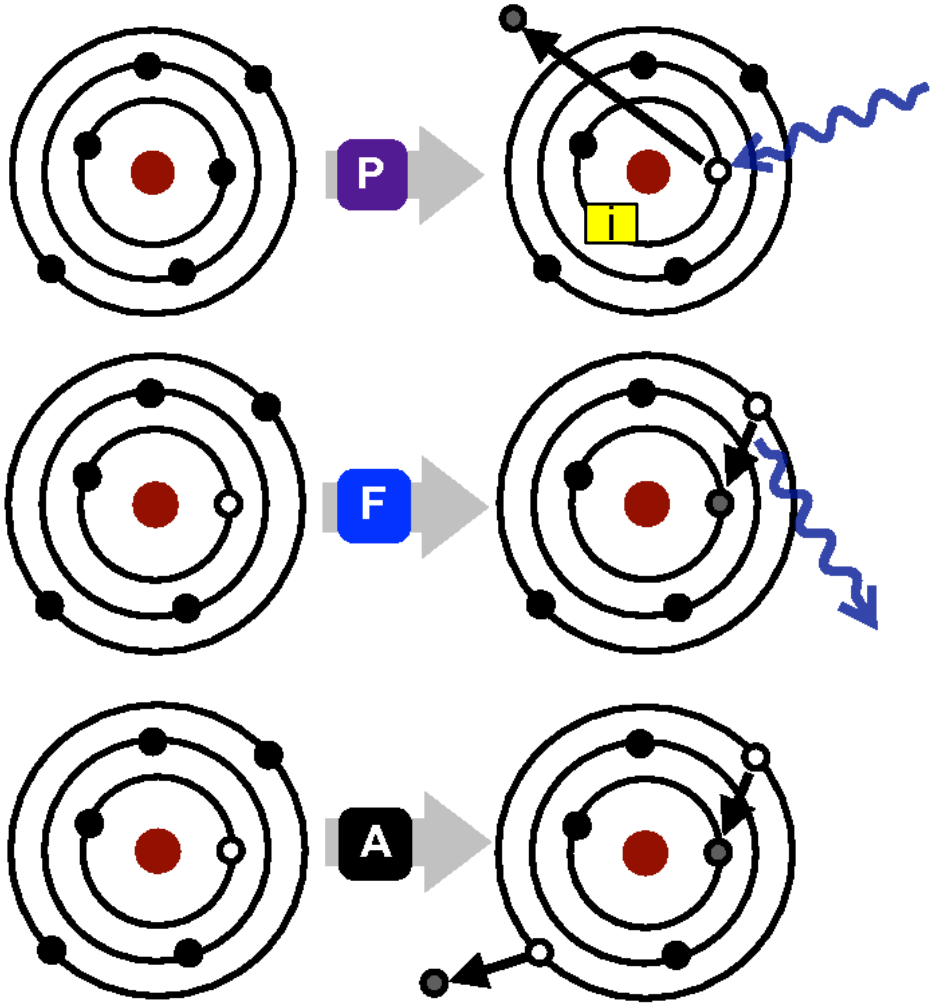
- $E_{out} = \hbar\omega - (E^{(f)}_{atom} - E^{(i)}_{atom})$
- Larger cross sections:
  Core electrons
  Heavy elements

> Fluorescent Decay

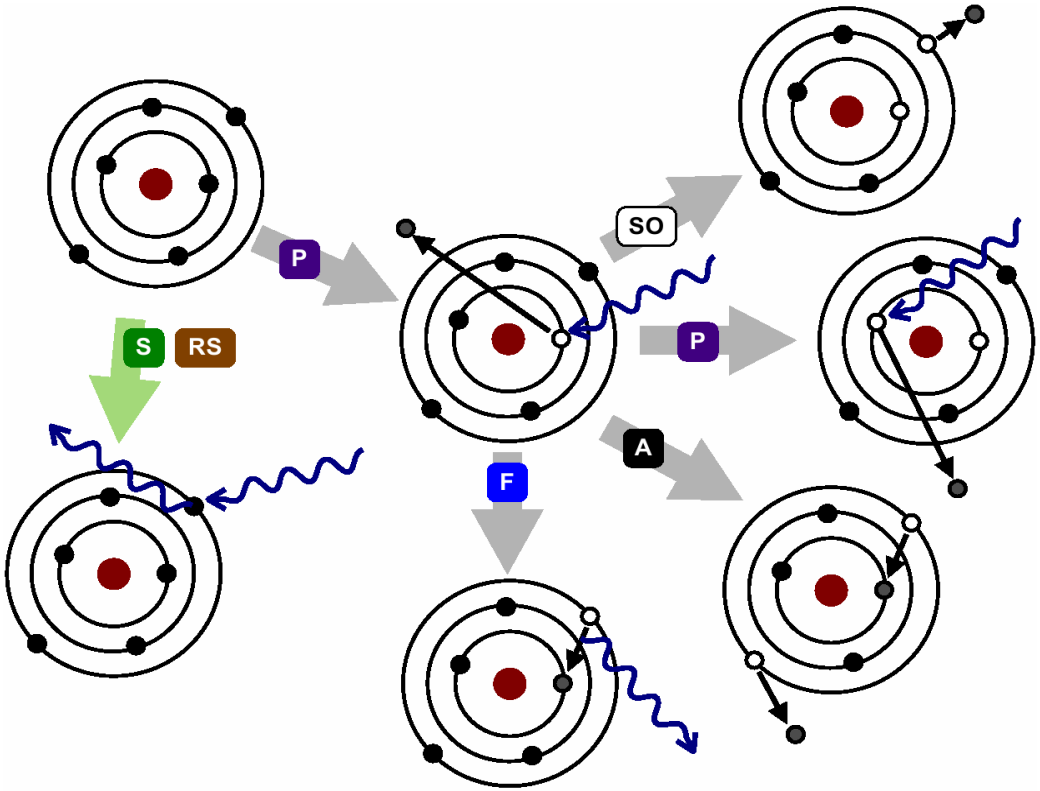
- $\hbar\omega = E^{(f)}_{atom} - E^{(i)}_{atom}$

> Auger Decay

- $E_{Auger} = E^{(f)}_{atom} - E^{(i)}_{atom}$



Software – XATOM: X-ray physics of an atom



- Ab initio code based on the Hartree-Fock-Slater approach
- Calculates atomic orbitals and energies, photoionization cross sections, auger and fluorescent decay rates
- Ionization dynamics described by rate equations

Software – XMOLECULE: X-ray physics of a molecule

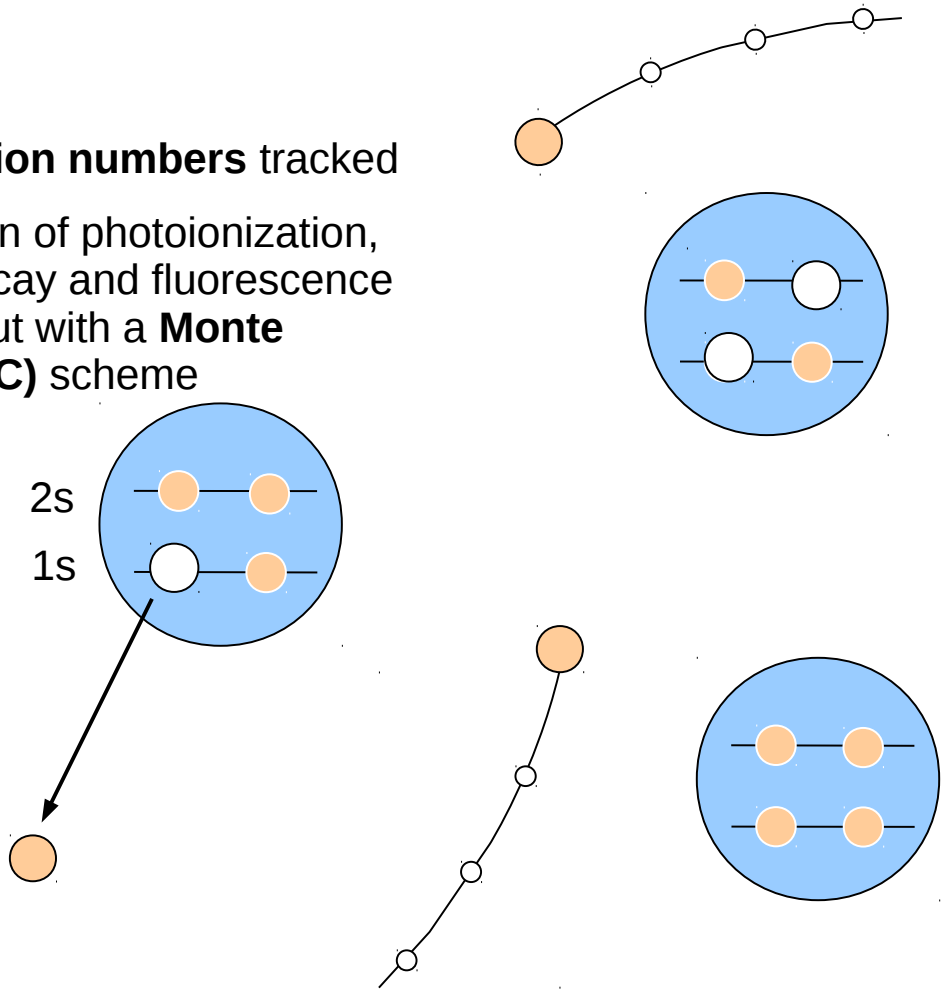
- Basic concept borrowed from XATOM
- Calculates molecular orbitals and energies using atomic orbitals as basis functions
- Cross sections, rates and potential gradients calculated on the fly
- Orbitals continually recalculated as the system evolves

Software – XMDYN: X-ray induced dynamics of matter

> For large systems e.g: clusters, bulk...

> Uses data calculated by XATOM (Orbitals, cross sections, etc...)

- **Occupation numbers** tracked
- Evaluation of photoionization, auger decay and fluorescence carried out with a **Monte Carlo (MC)** scheme



- **Molecular dynamics (MD)** carried out treating the atoms, ions and free electrons as classical particles
- Classical force fields
- Newtons equations

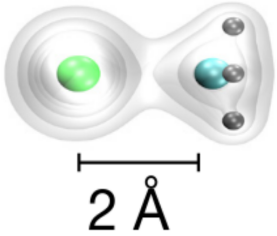
Charge-rearrangement-enhanced Ionization

LETTER

doi:10.1038/nature22373

Femtosecond response of polyatomic molecules to ultra-intense hard X-rays

A. Rudenko[1], L. Inhester[2,3], K. Hanasaki[2,3,4], X. Li[1], S. J. Robatjazi[1], B. Erk[5], R. Boll[5,6], K. Toyota[2,3], Y. Hao[2,3,7], O. Vendrell[2,3,8], C. Bomme[5], E. Savelyev[5], B. Rudek[9], L. Foucar[10], S. H. Southworth[11], C. S. Lehmann[11,12], B. Kraessig[11], T. Marchenko[13], M. Simon[13], K. Ueda[14], K. R. Ferguson[15], M. Bucher[11,15], T. Gorkhover[15,16,17], S. Carron[15], R. Alonso-Mori[15], J. E. Koglin[15], J. Correa[2,5], G. J. Williams[15,18], S. Boutet[15], L. Young[11,19], C. Bostedt[11,20], S.-K. Son[2,3], R. Santra[2,3,21] & D. Rolles[1,5]



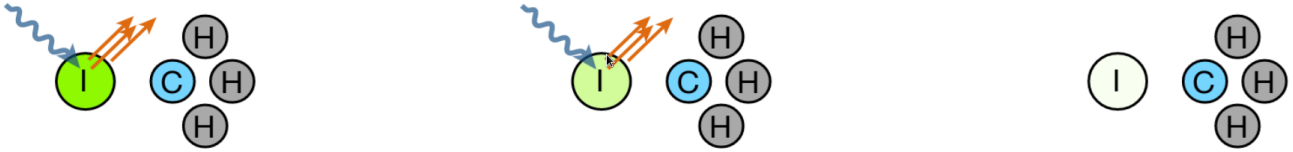
> Investigates CH3I interaction with ultra-intense, hard X-ray pulse

> Compares **XMOLECULE** simulations to experimental results

> Study found that **ultrafast charge transfer** within the molecule plays a key role in shaping it's response

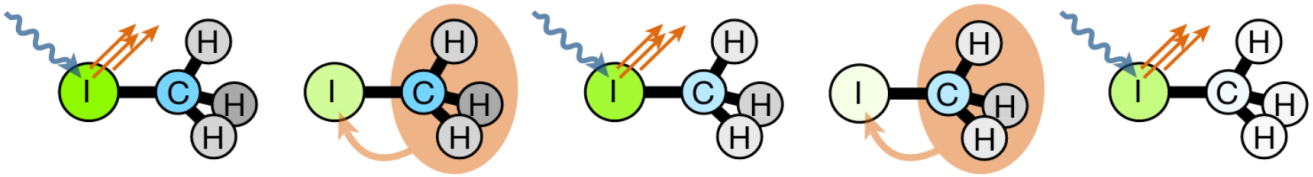
Charge-rearrangement-enhanced Ionization

> Without charge Transfer



- Photoionization cross sections for carbon the hydrogen are negligible
- Only iodine is ionized

> With charge Transfer

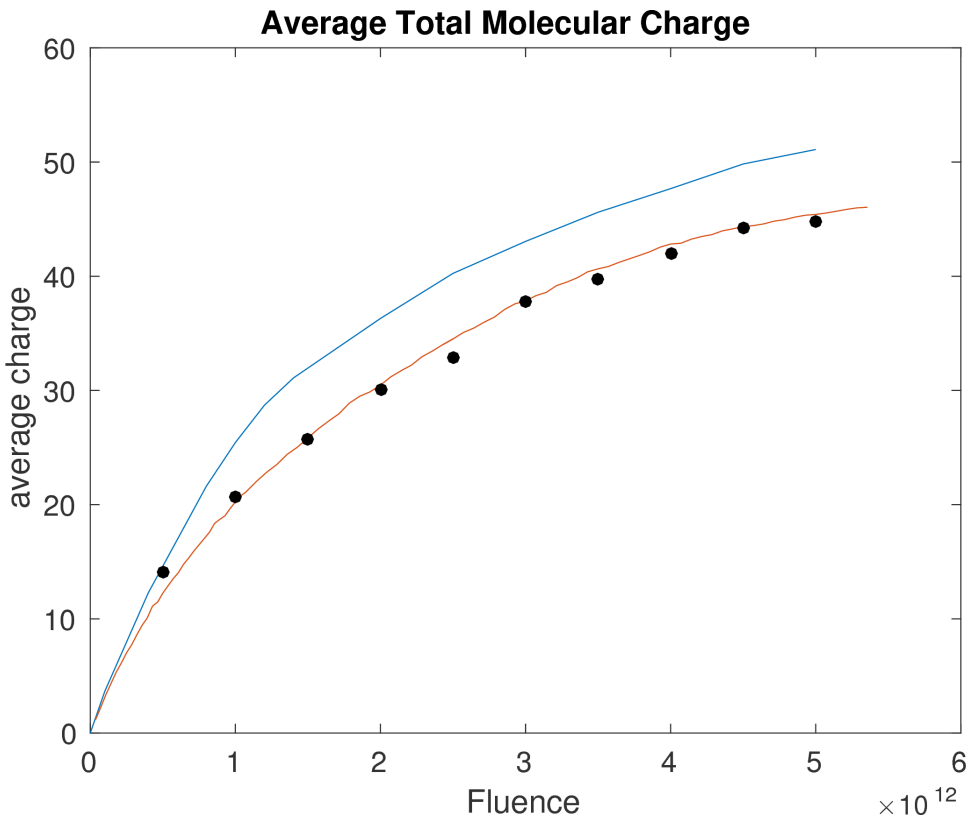


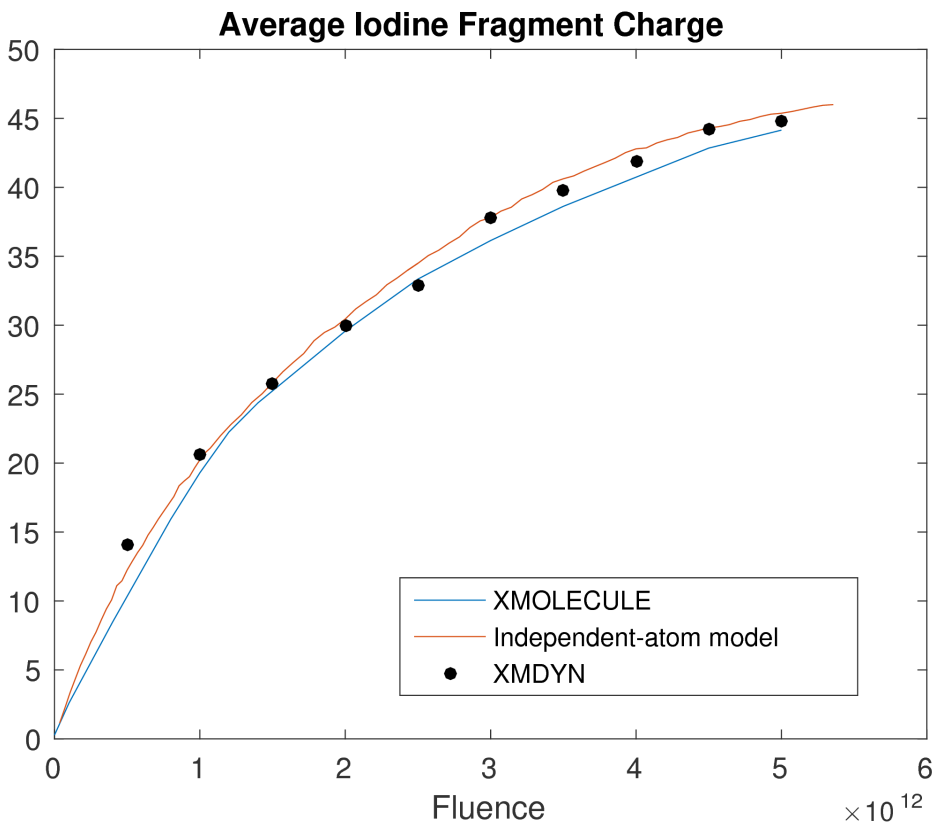
- Electrons from carbon and hydrogen refill iodine core holes
- These electrons can be photoionized from iodine
- **Higher charge** states reached
- Electrostatic repulsion introduced – **Coulomb explosion**

Results

XMDYN	XMOLECULE
> Without Charge Transfer	> Full
> With Charge Transfer	
> MC + MD	> MC + ab initio
> 8 min/run	> Few hours/run

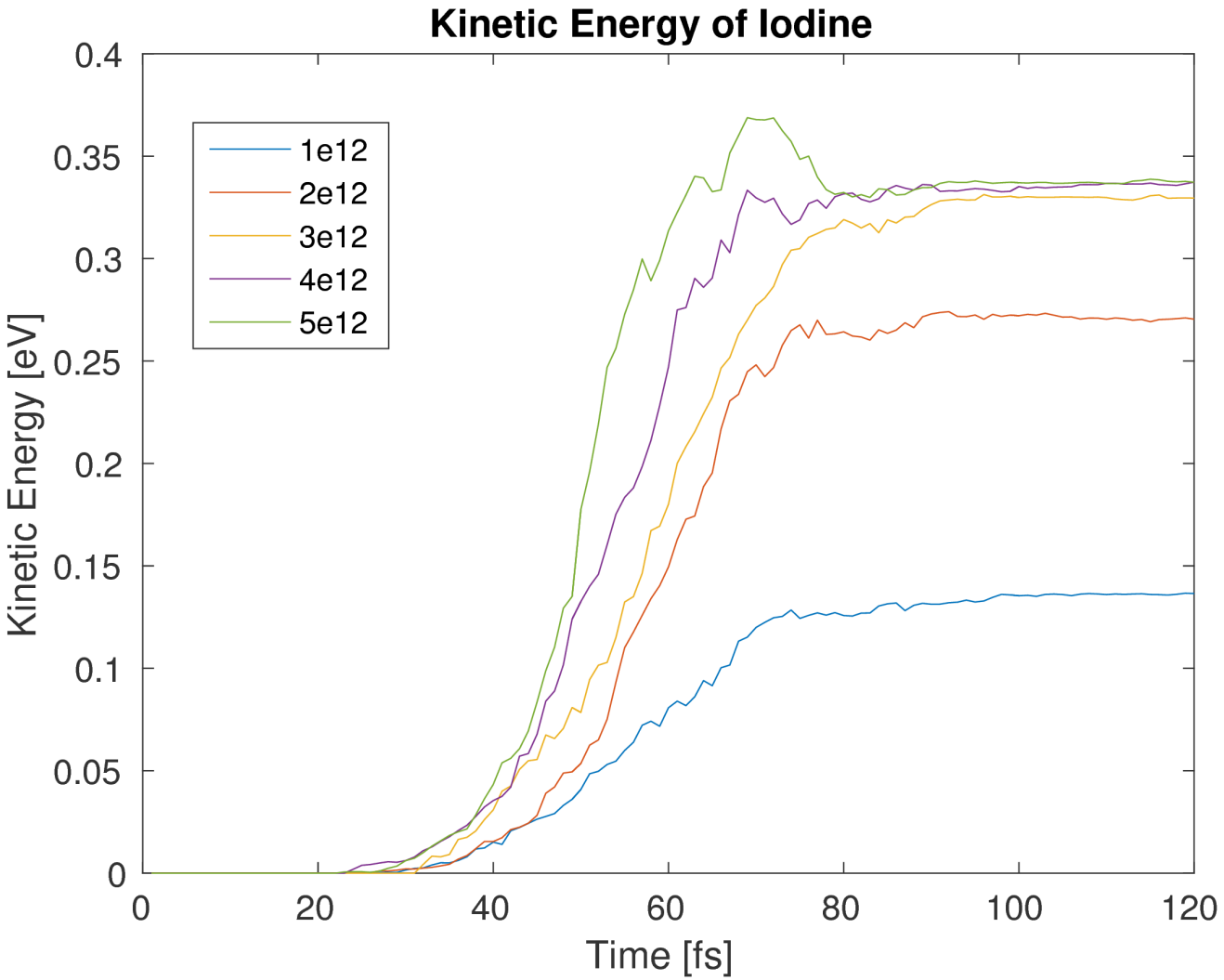
XMDYN without Charge Transfer – Final Charge States





> Consistent with the results from the independent atom model

XMDYN without Charge Transfer – Kinetic Energy



- Significantly smaller than predicted by XMOLECULE (~70 eV)
- No electrostatic repulsion
- KE from conservation of momentum when electrons are emitted.

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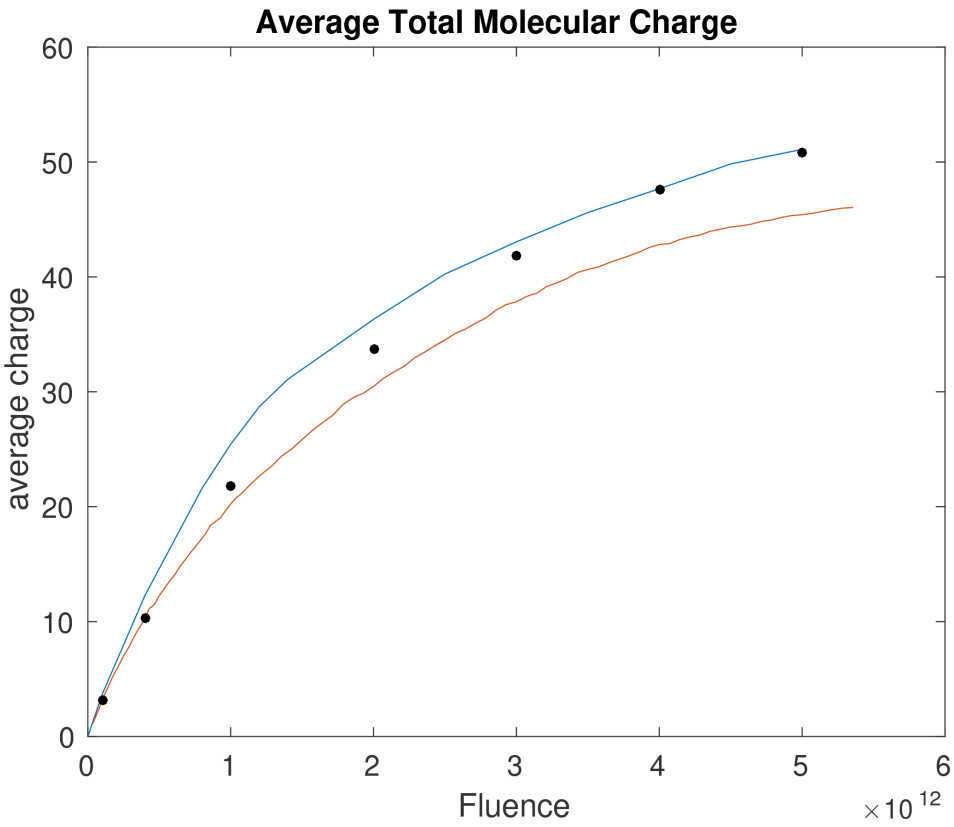
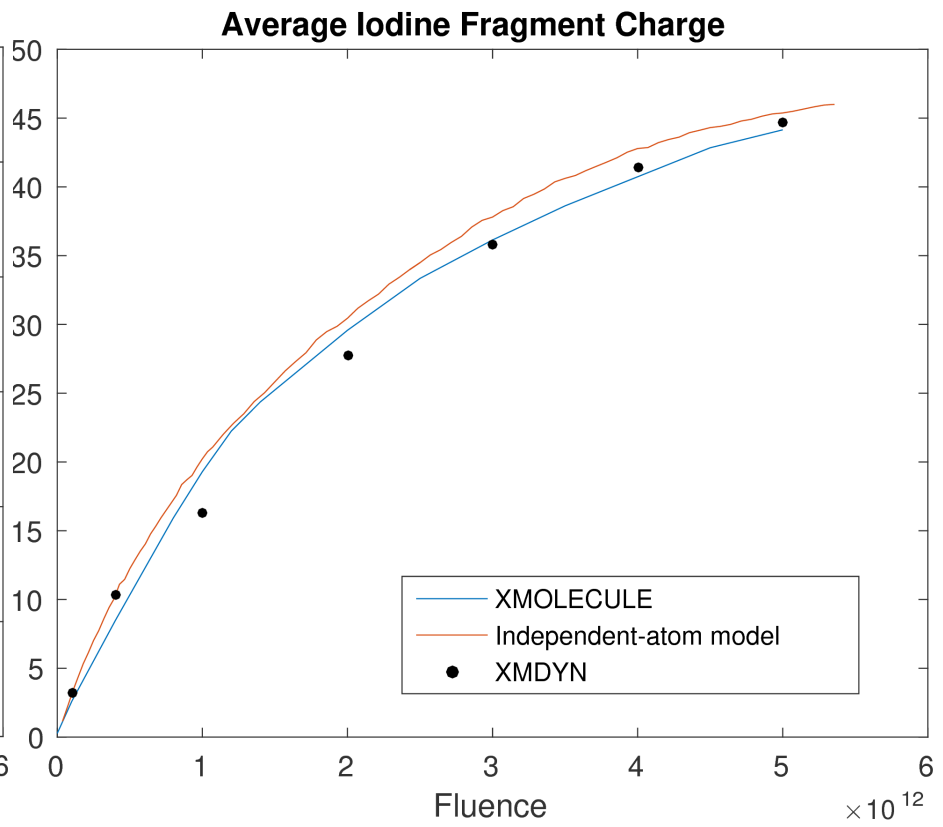
XMDYN with Charge Transfer - Final Charge States





- First two XMDYN points sit directly on the independent-atom model curve
- Charge transfer begins to occur between the fluences 4×10^{11} and 1×10^{12}
- Better agreement between XMDYN and XMOLECULE for higher fluences

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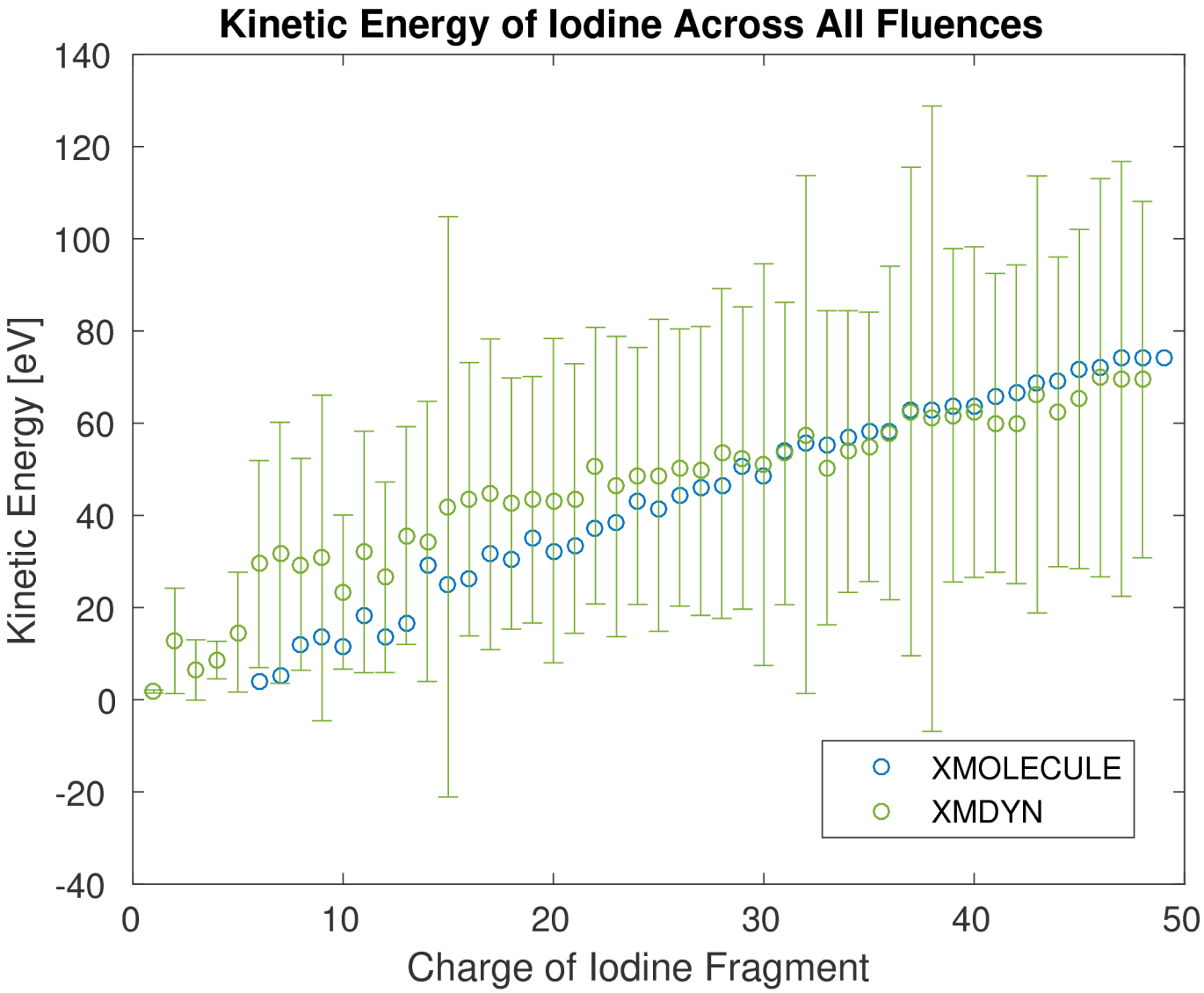
XMDYN with Charge Transfer – Kinetic Energy



- Close agreement between XMDYN and XMOLECULE for mean KE
- Standard deviations
  - Much larger than in XMOLECULE. (~10eV)
  - But closer to experiment. (~50eV)

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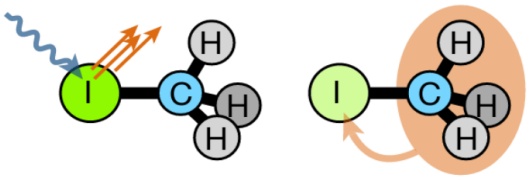
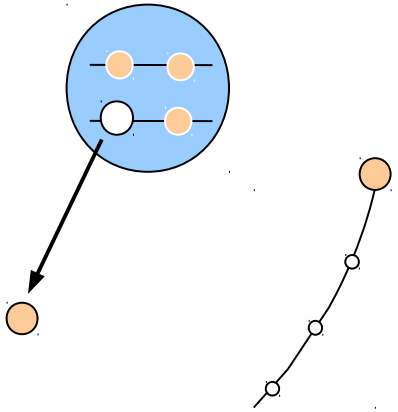
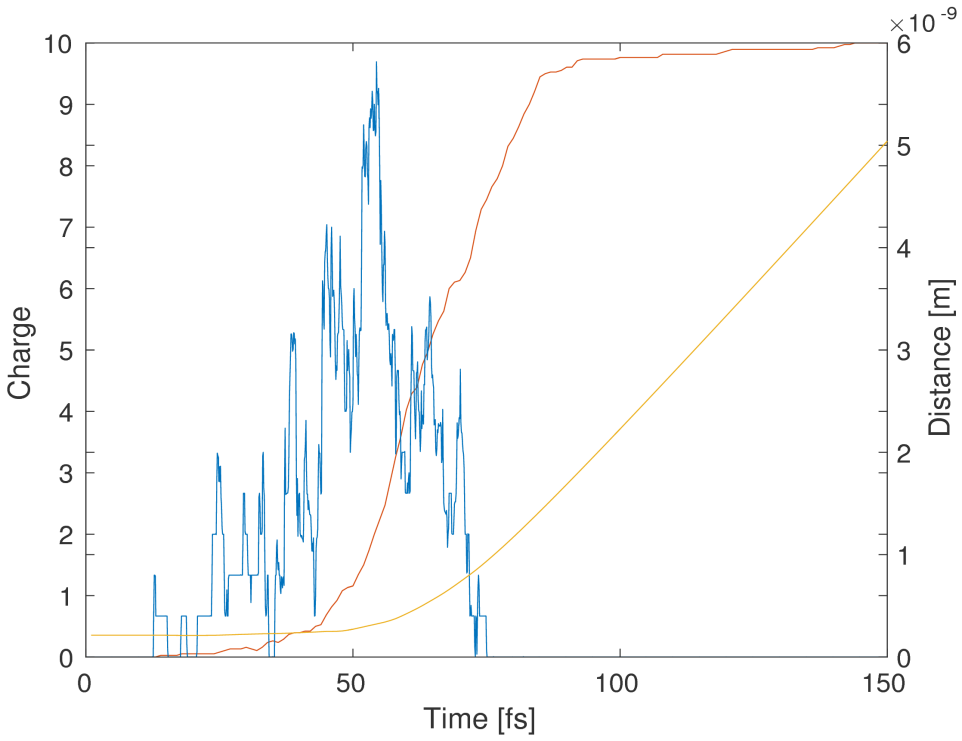
Conclusion

- The presence of a heavy atom enhances the **ionization** in matter **through charge rearrangement**



- With the addition of charge transfer, **XMDYN** provides a **cheap** and **quantitatively accurate** way of simulating x-ray interaction with matter




×10 -9
Charge
Distance [m]
Time [fs]
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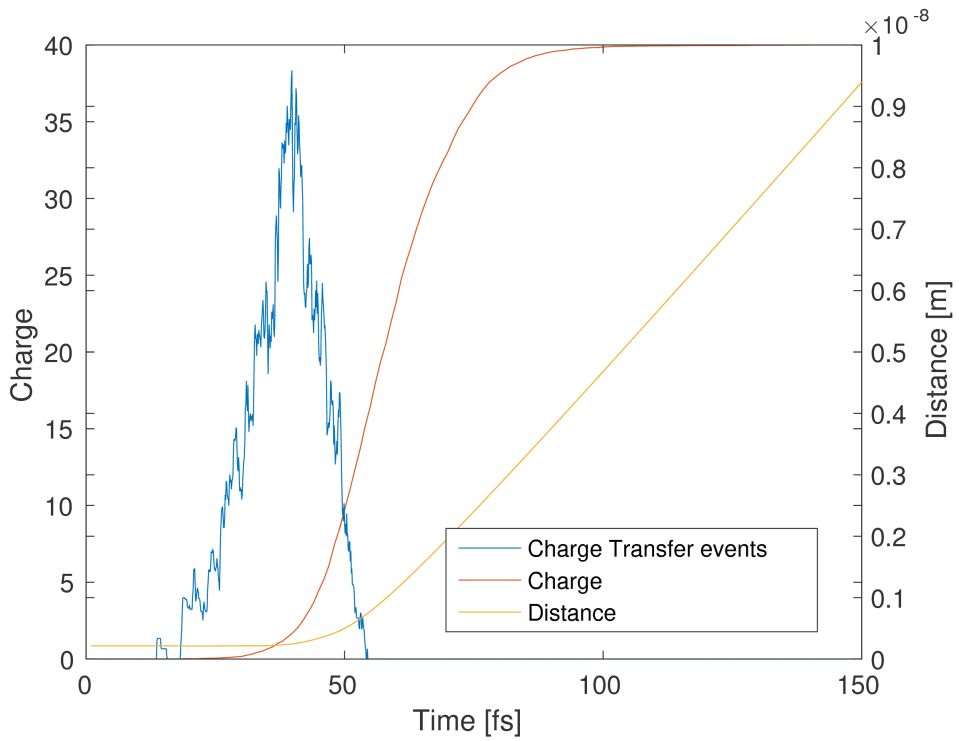
50
100
150


×10 -8
Charge
Distance [m]
Time [fs]
Charge Transfer events
Charge
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