Fundamentals of X-Ray Excitation and Relaxation in EUV Resists

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Outline

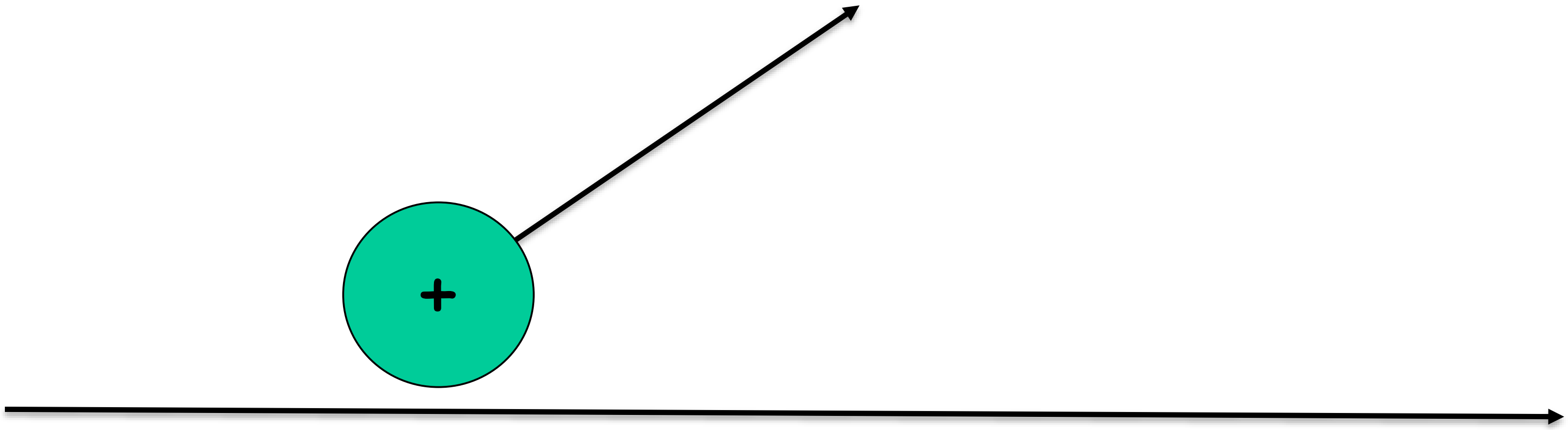
- Basic Interactions: EBL vs EUV

- Strategy to increase sensitivity and understanding
  - Gas phase experiments & theory to detect reaction intermediates
  - EUV absorption and electronic structure

- Photoemission and Relaxation
  - Mechanisms
  - Auger emission in Xe
  - Molecular Fragmentation in H_2O
- Experiments and Theory at LBL

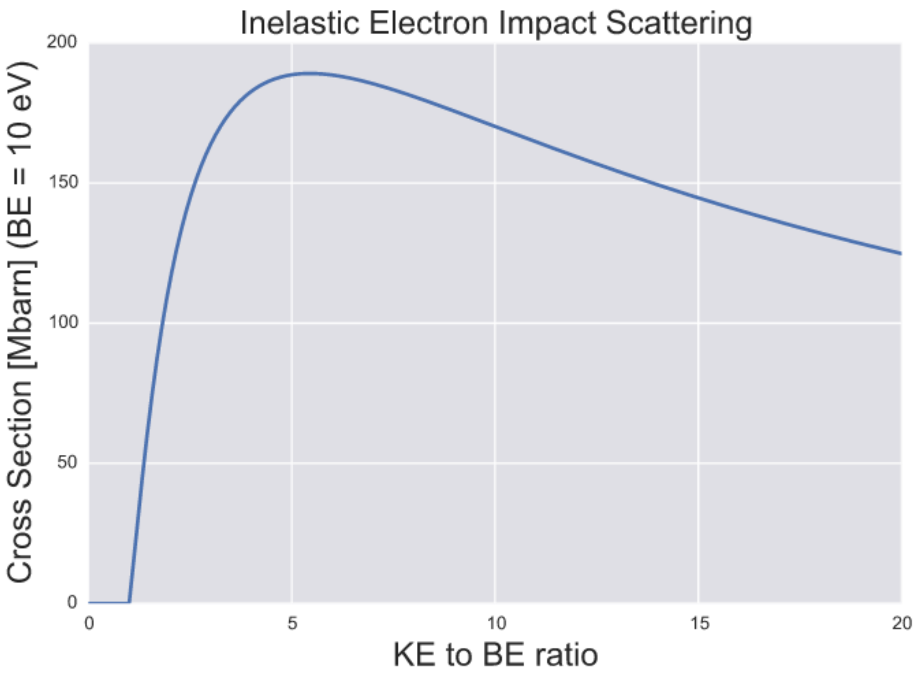
- Connection to condensed resist films

Electron Beam Lithography

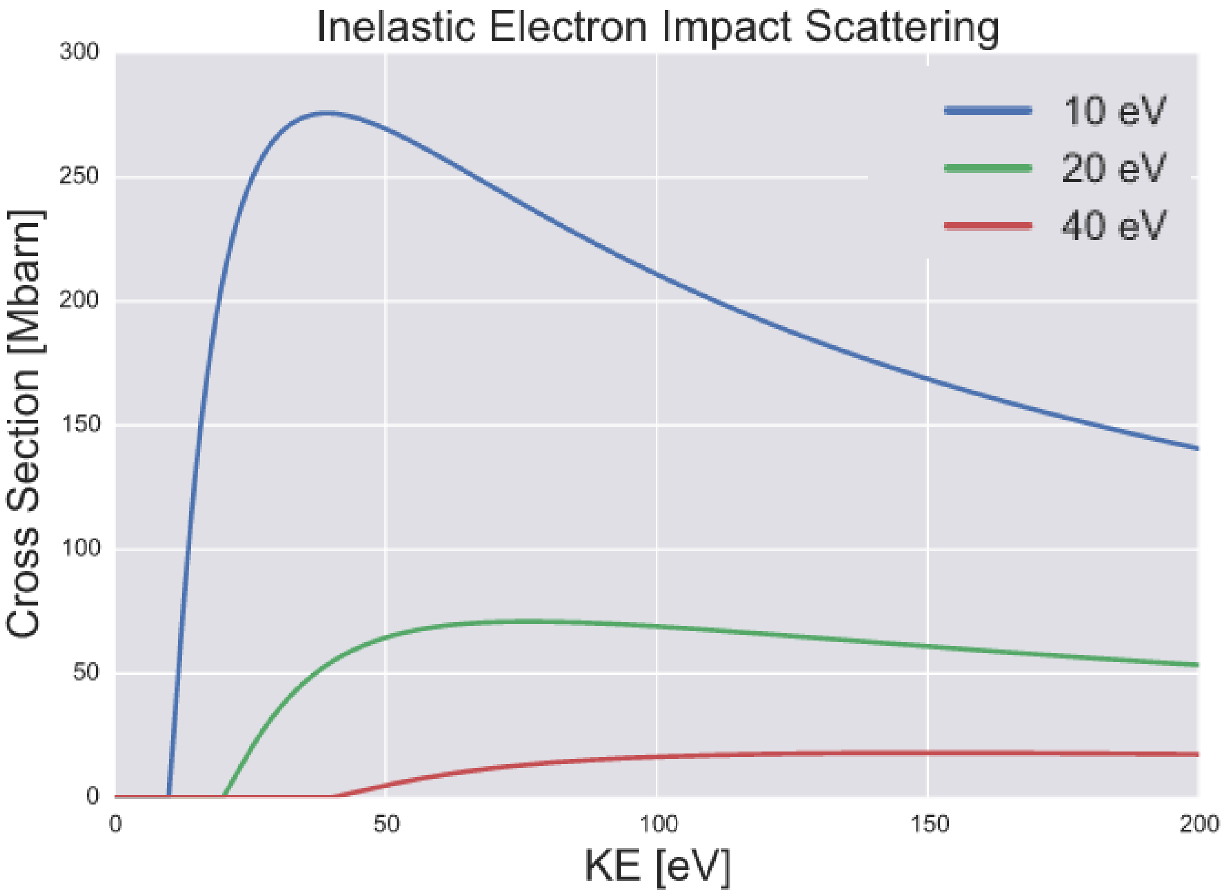


HOMO most likely
to be ionized

Cross Section
scales as $1/BE^2$



Inelastic Electron Scattering



Effect of Increasing Orbital Binding Energy

EUV Lithography

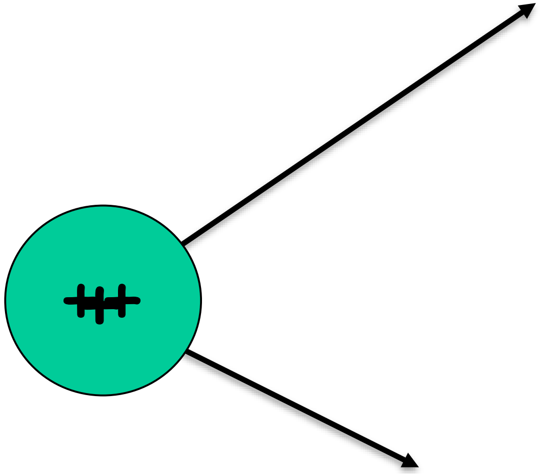
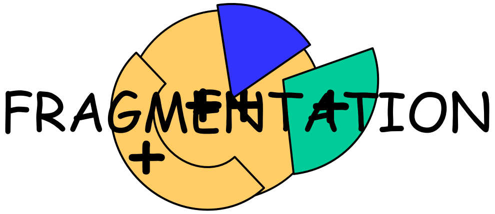


Photo-Electron
Residual Internal
Energy in Molecule

Auger Electron
Molecule Relaxes
Reduced Residual
Energy

EUV Lithography



- DEEPER orbitals most likely to be ionized
- This REDUCES photoelectron energy (relative to HOMO photoionization)
- Molecule is left with Residual Energy
- RELAXATION processes – Auger Emission, Fragmentation

EBL vs EUV

EUV Photo Ionization

- Deeper valence/semi-core ionization more likely than HOMO
- Lots of residual internal energy
- Auger relaxation and fragmentation are likely

EBL Inelastic Electron Scattering

- HOMO ionization is likely
- Stable parent ions are common
- Molecule left with relatively little internal energy

Strategy to Increase Sensitivity

- Incorporate high cross-section atoms into resist systems to absorb more x-rays
  - better for shot noise
- Measure/Understand/Tailor reaction intermediates
  - Photoelectron energy distribution
  - Auger electron energy distribution
  - Molecular fragmentation products: ions, radicals and radical ions
- Make better use of Photo-absorption reaction intermediates to drive pattern generation in resist systems

Strategy to Increase Understanding

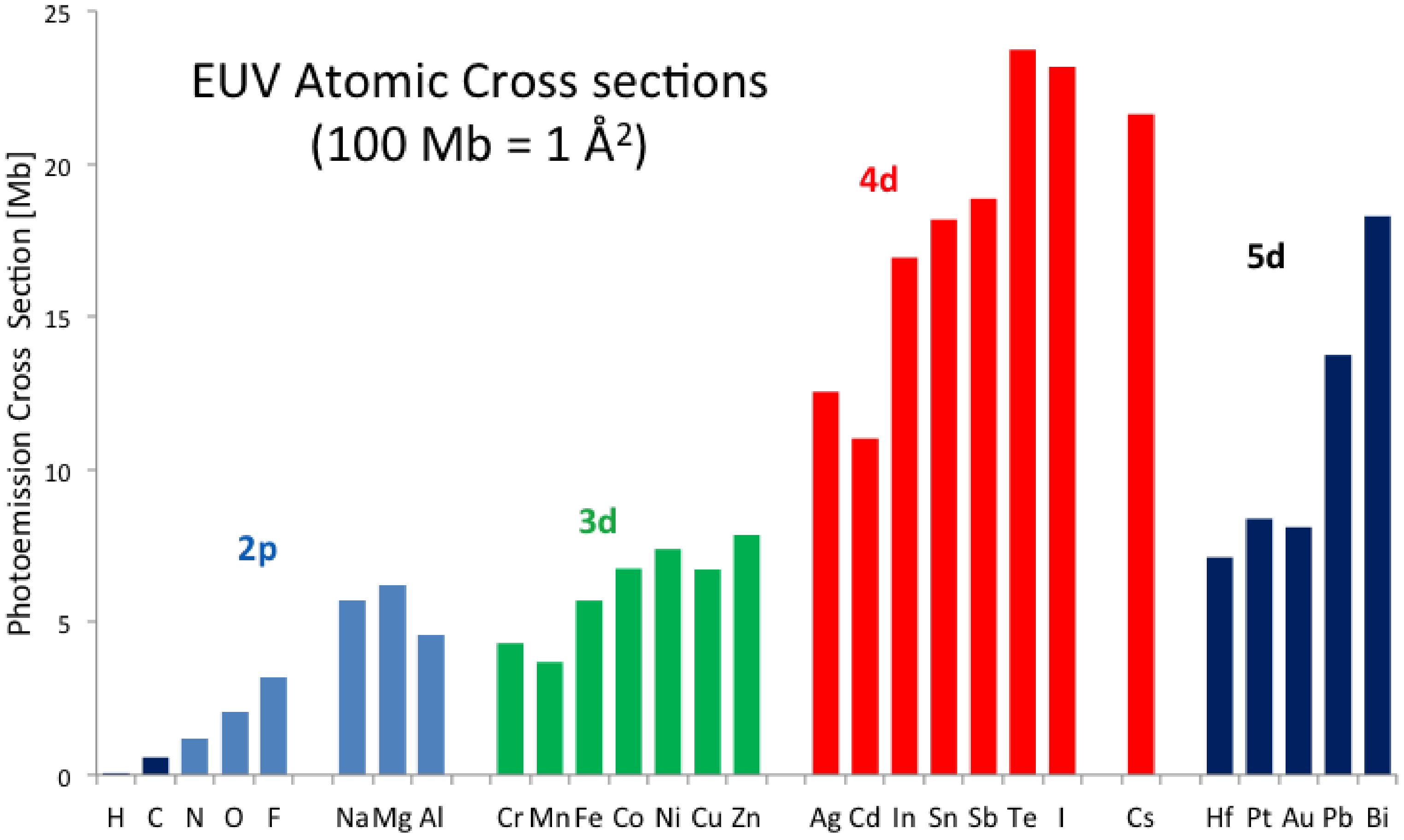
- Gas-phase Synchrotron Experiments to Directly Measure Reaction Intermediates [Oleg Kostko]
  - Photo electron and Auger electron distributions
  - Molecular fragmentation, radical and ion yields
- Gas-phase Electron-Molecule Scattering
  - Secondary electron distributions
  - Molecular fragmentation, radical and ion yields
- Theoretical Simulations e,γ-Molecule [Cristina Klosser]
  - Orbital ionization cross sections
  - Auger relaxation branching ratios
  - Molecular dynamics fragmentation calculations
  - Validate predictive capability with experiments
- Critical inputs for understanding condensed resist system pattern formation mechanisms

The Problem

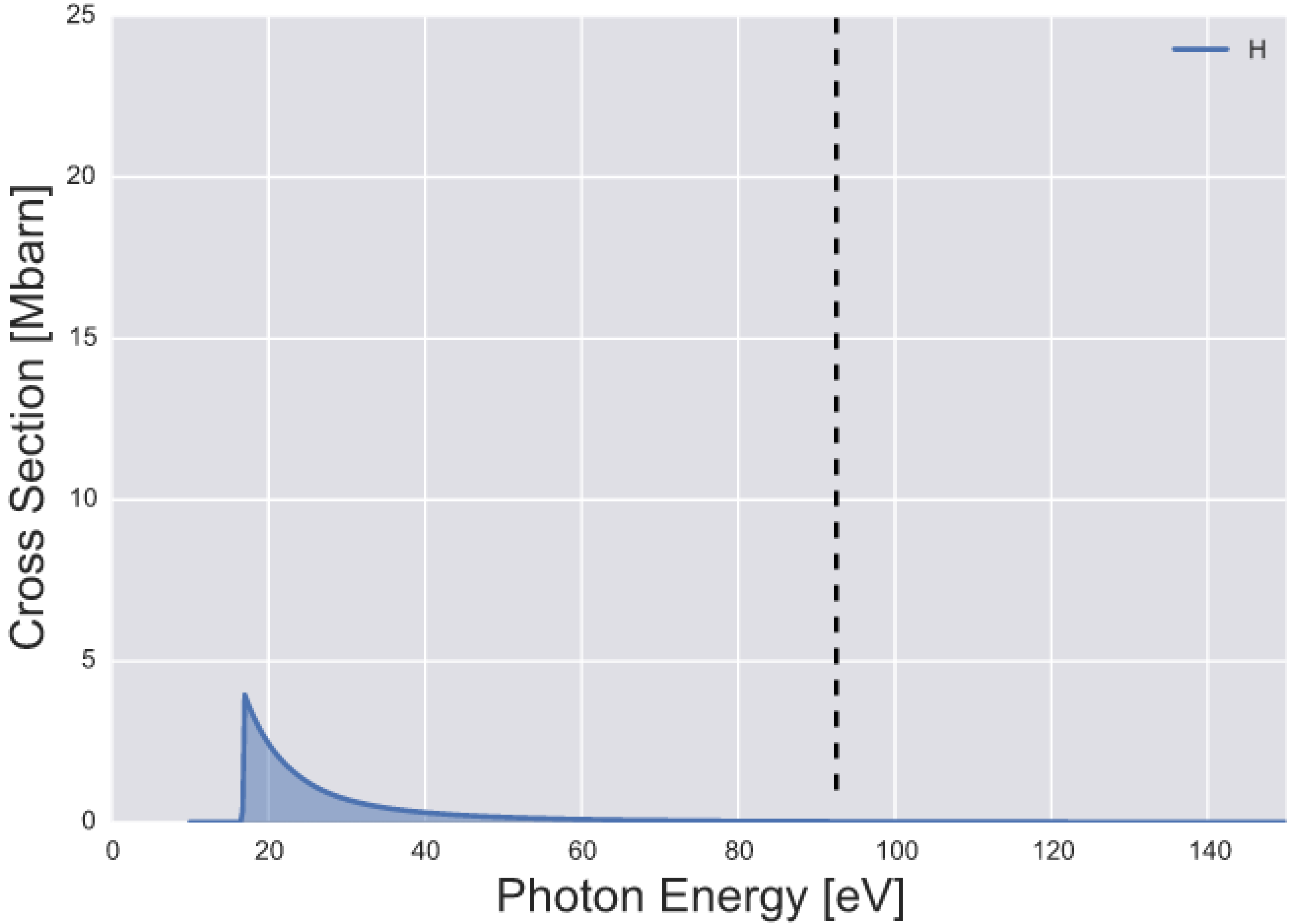
"…it is technically nearly impossible to directly observe the reactions induced in ultrathin resist films by 92.5 EUV radiation…"

Kozawa & Tagawa EUV CAR review
Jpn J Appl Phys 2010

Atomic Cross Sections

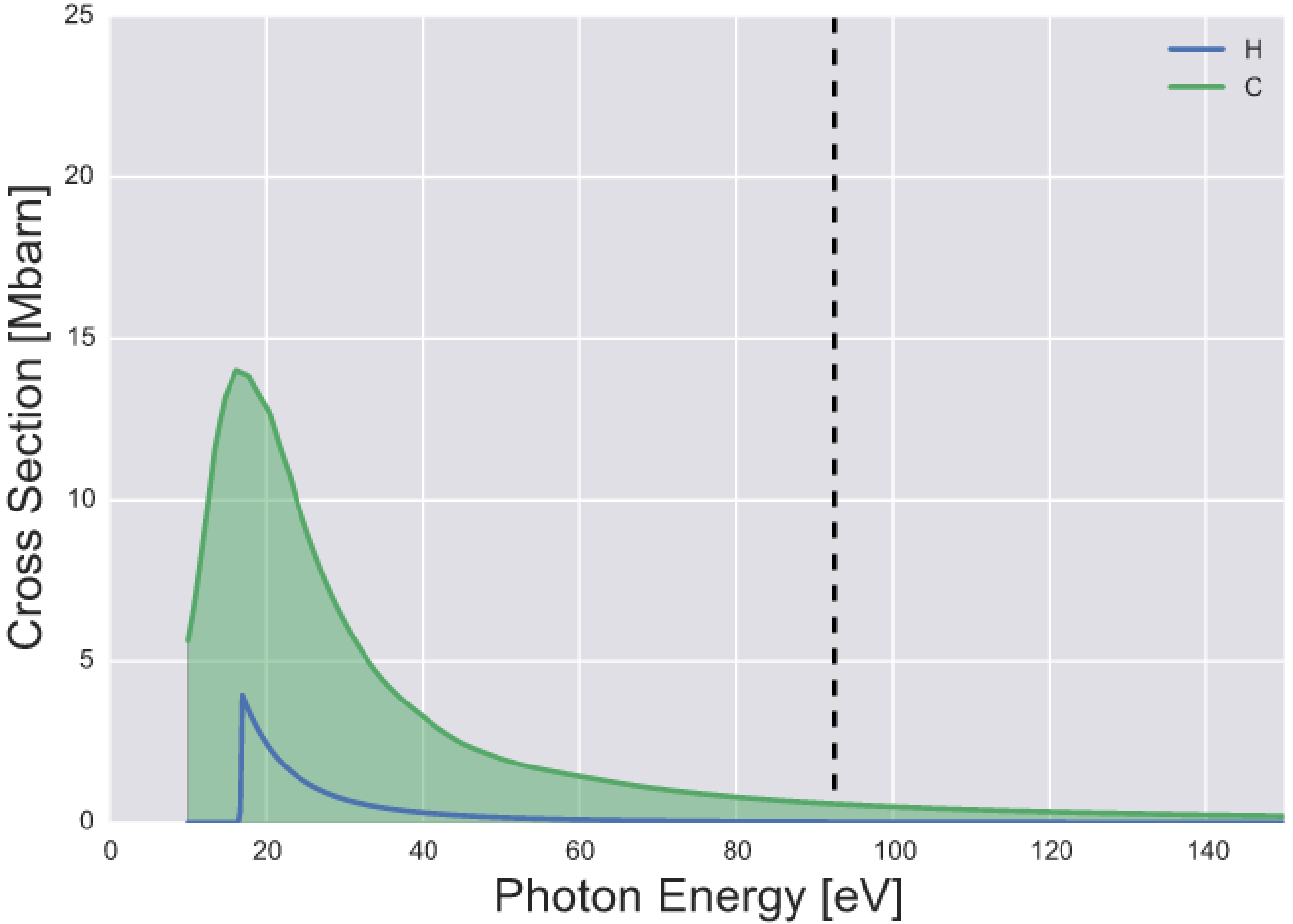


Light Elements - H



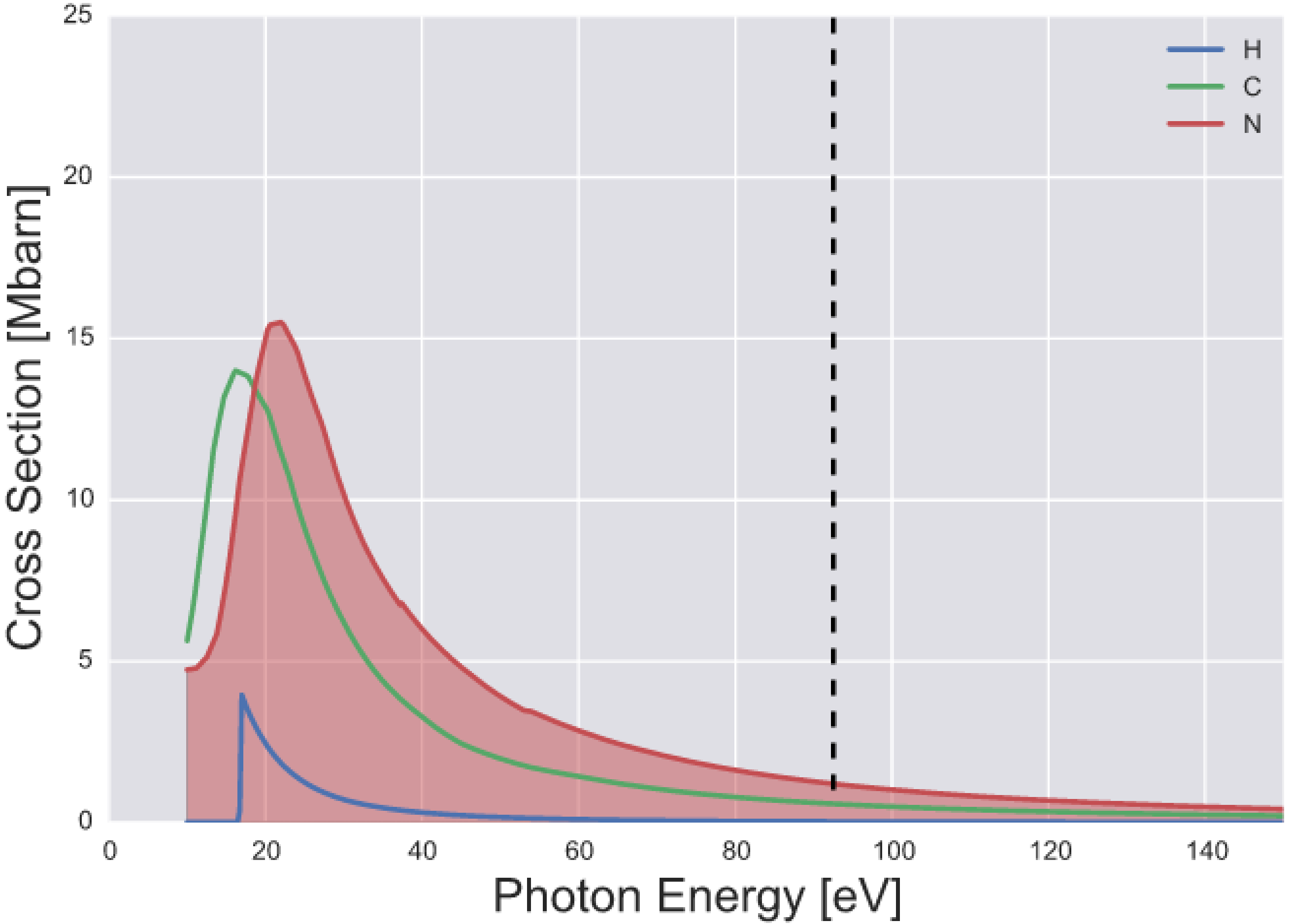
Data from CXRO – 10 eV and up

Light Elements - H, C

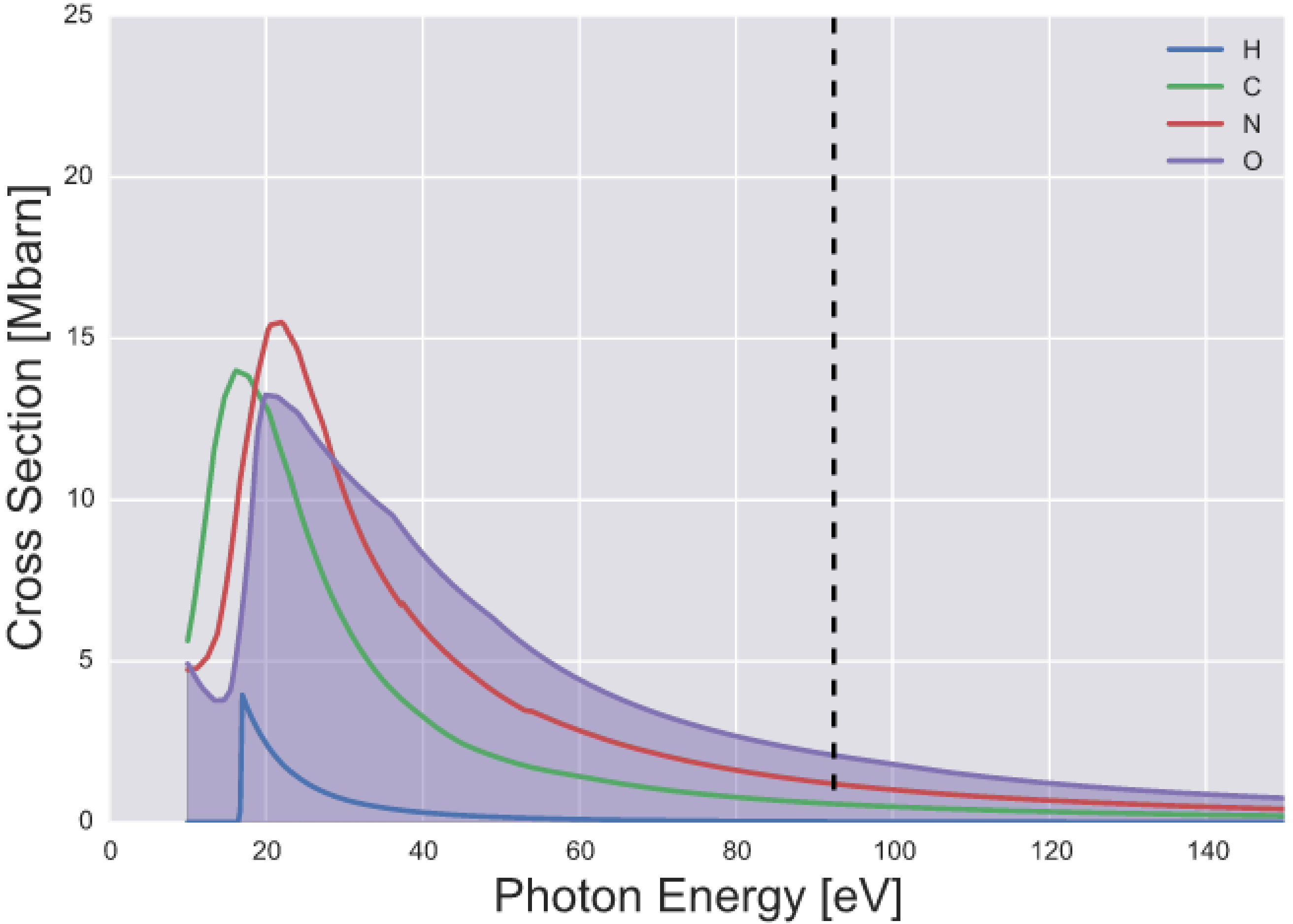


Area under curve proportional to number of electrons in molecule

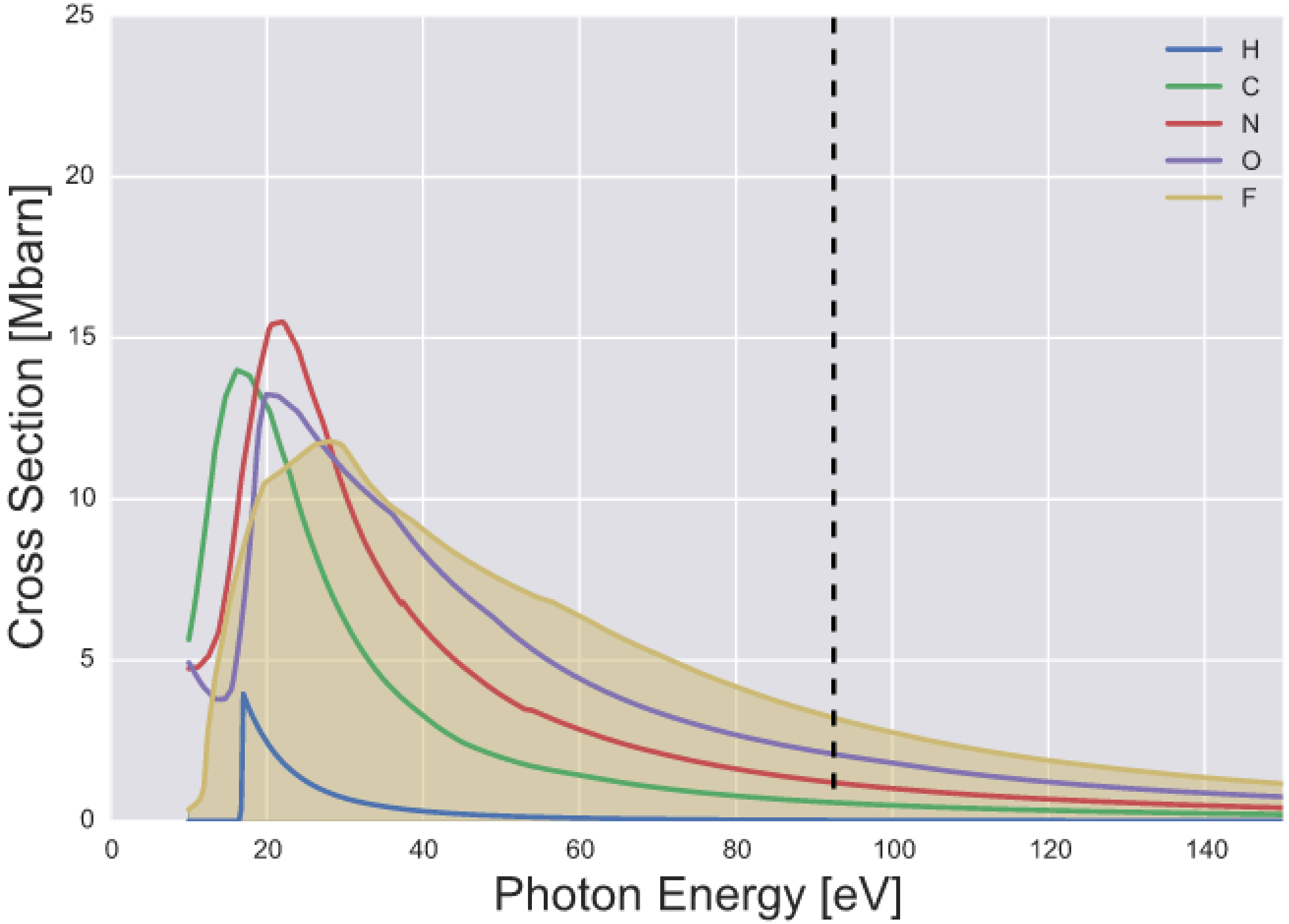
Light Elements - N



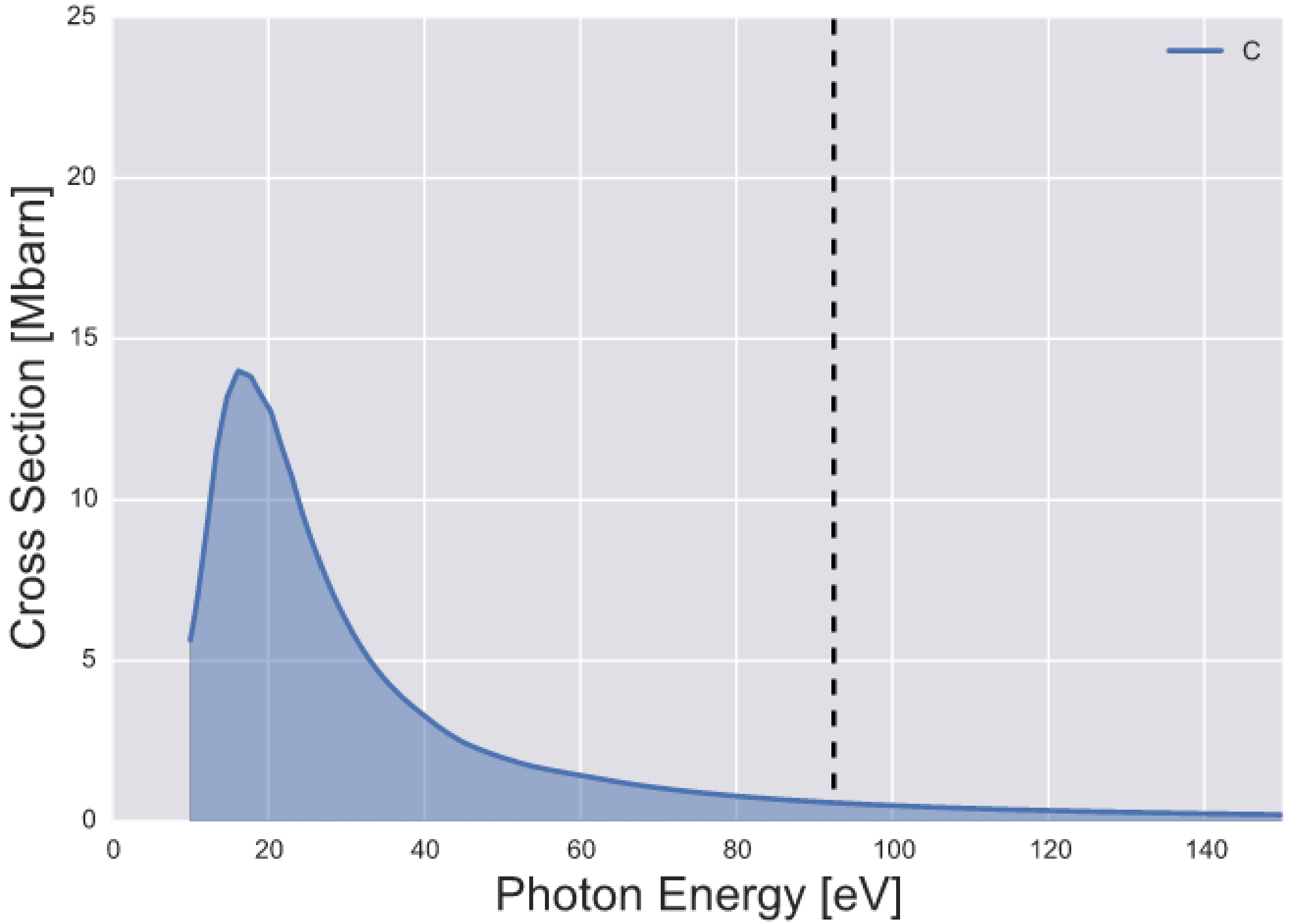
Light Elements - O



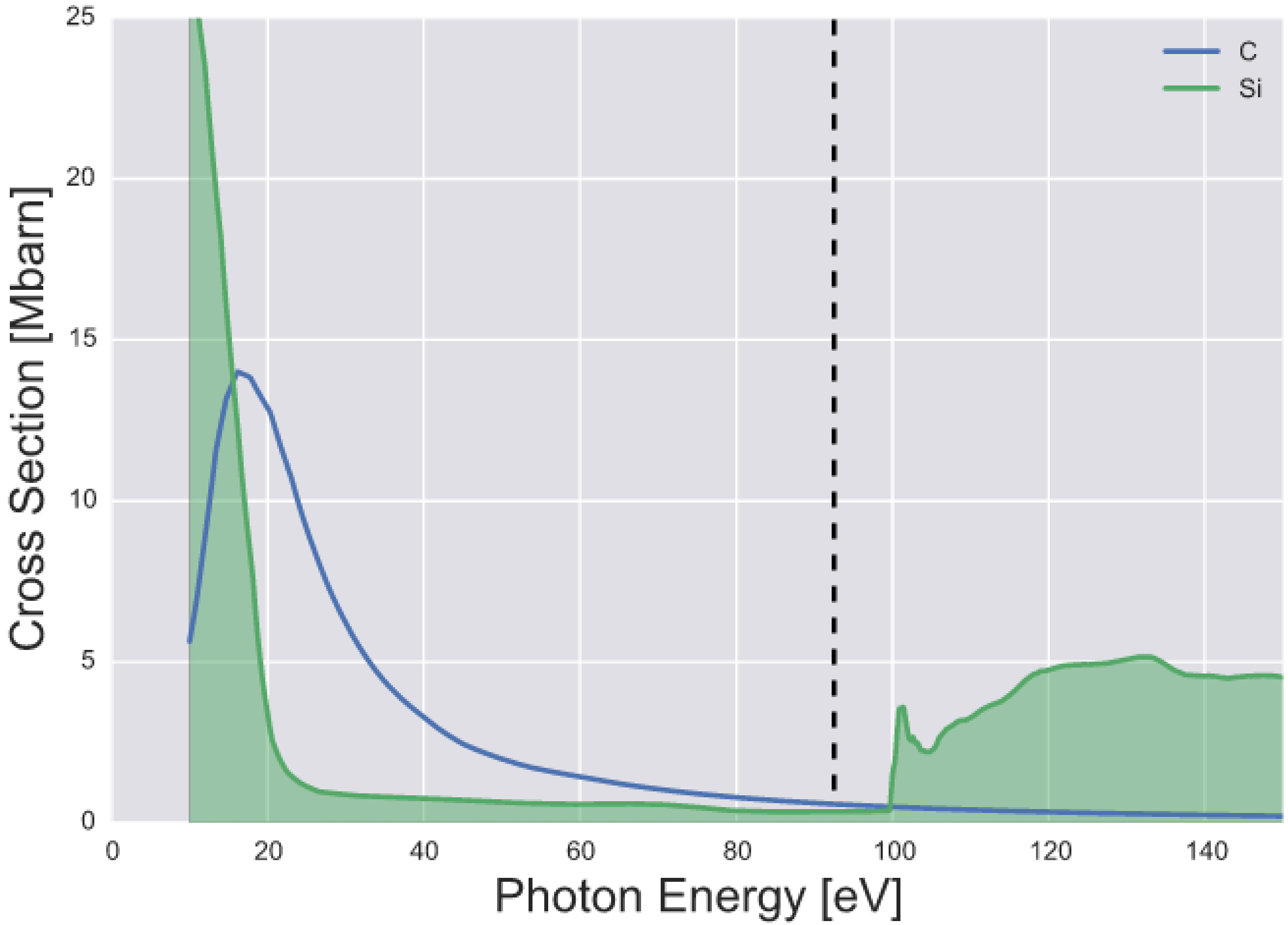
Light Elements - F



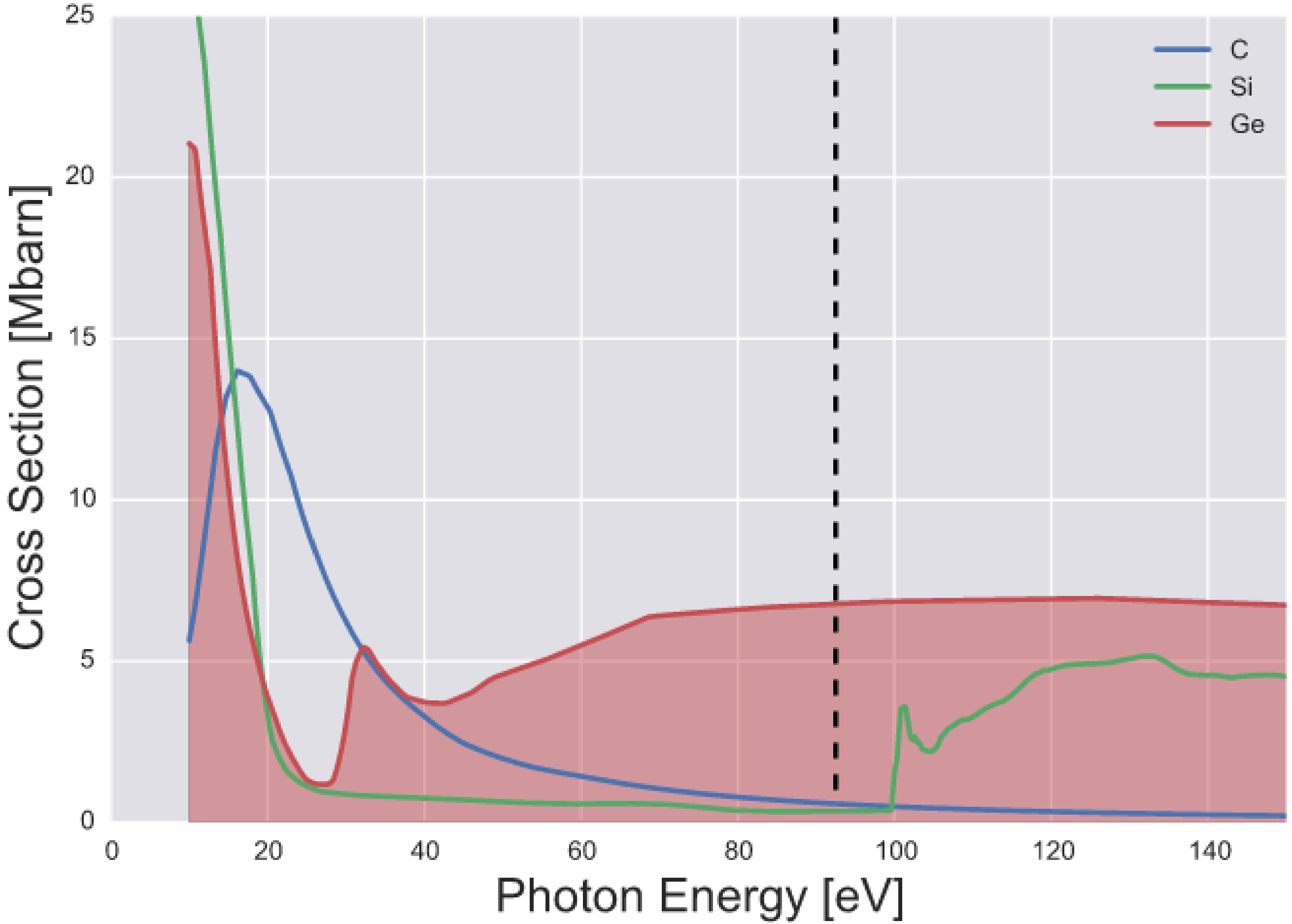
Group IV a Elements - C



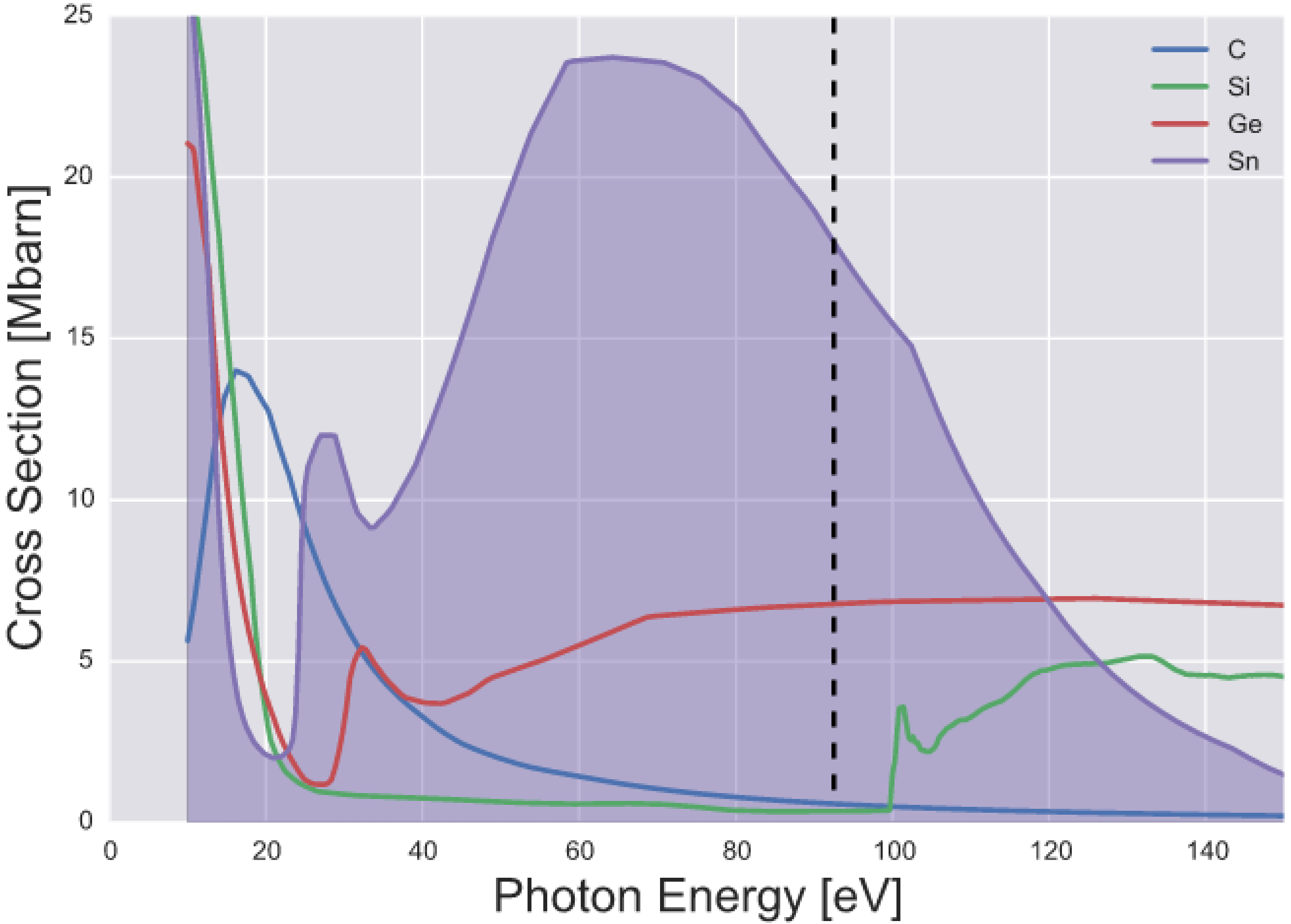
Group IV a Elements - Si



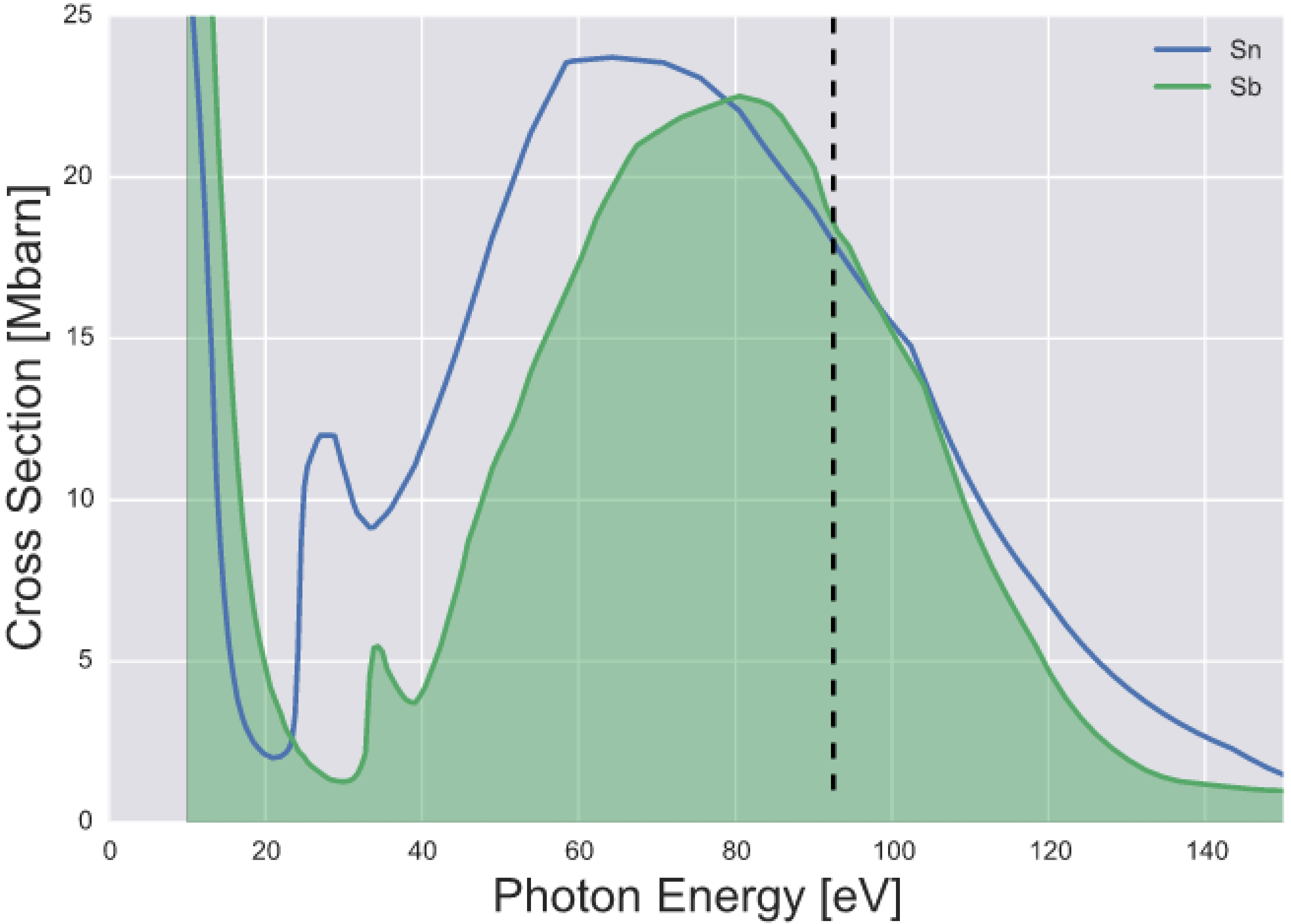
Group IV a Elements - Ge



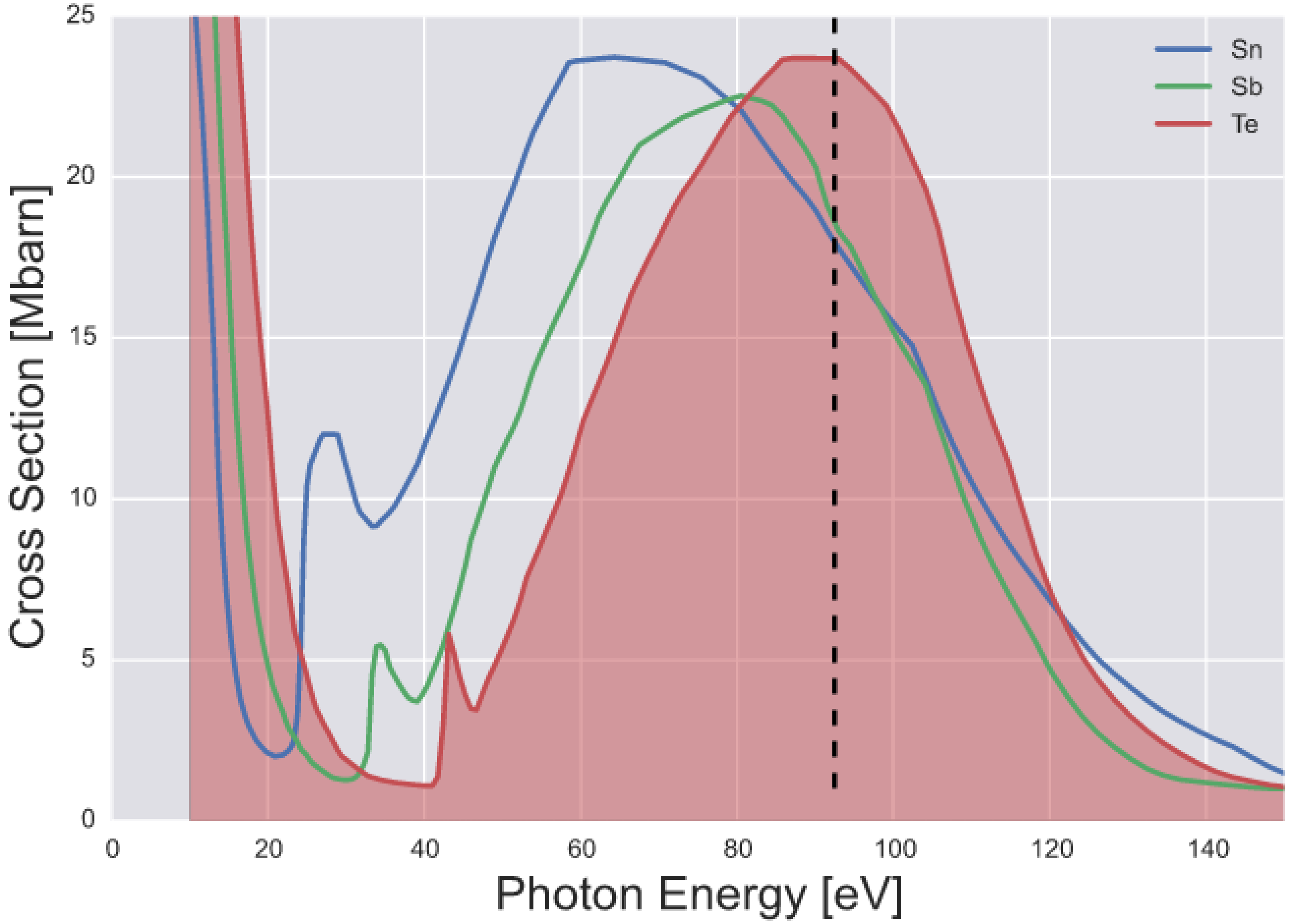
Group IV a Elements - Sn



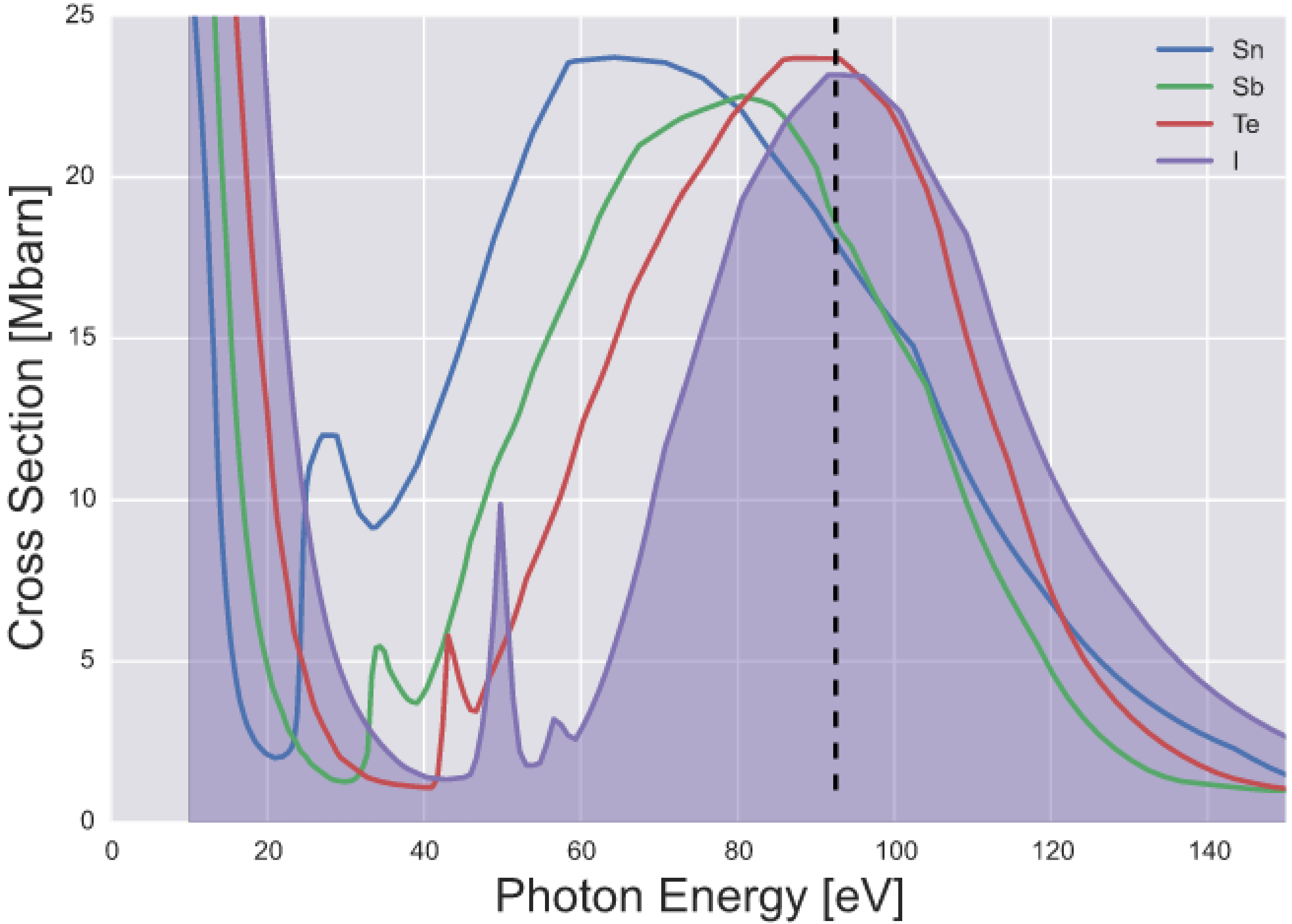
4d Elements - Sb



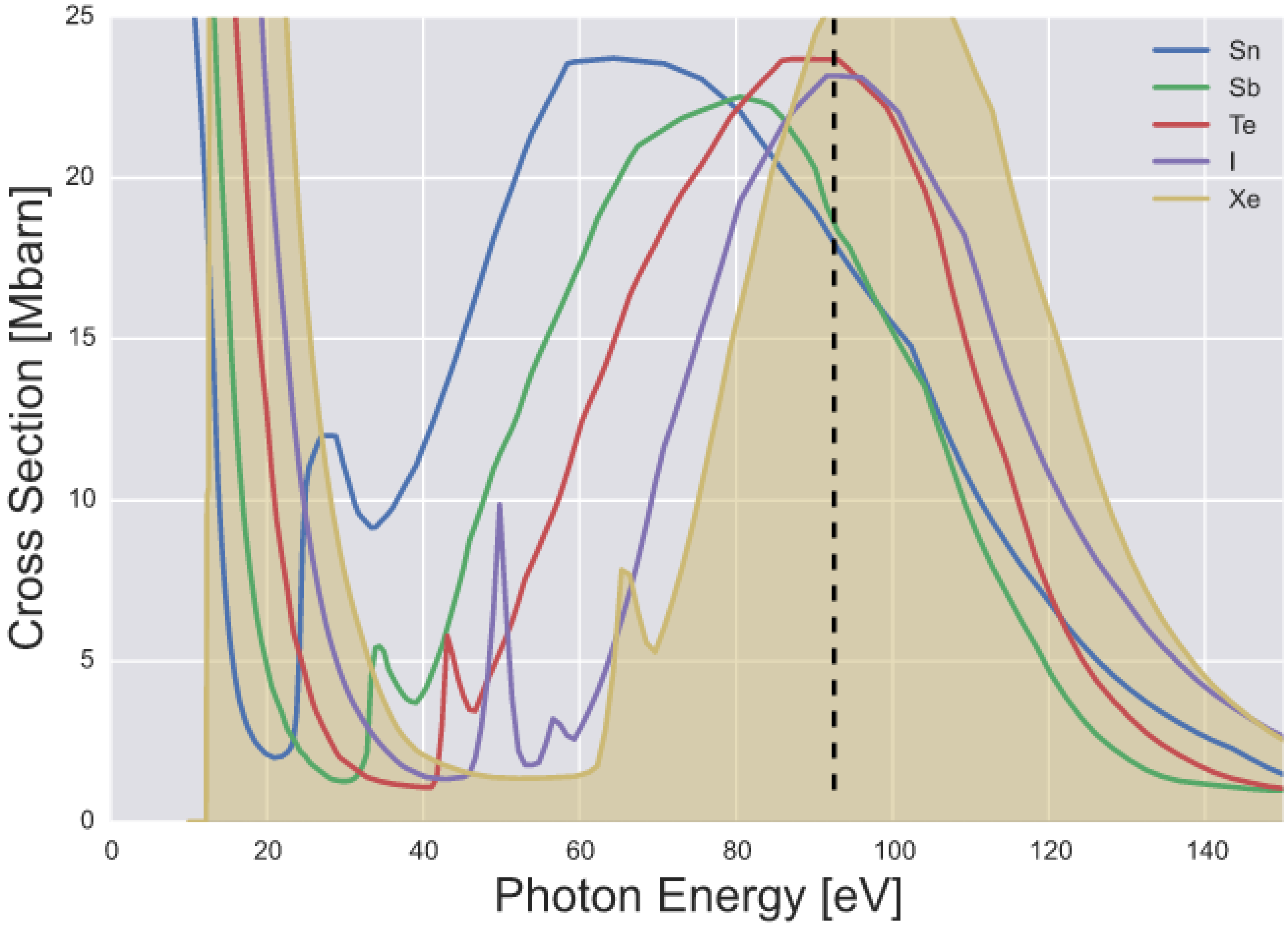
4d Elements - Te



4d Elements - I



4d Elements - Xe



Thin Film EUV Absorption

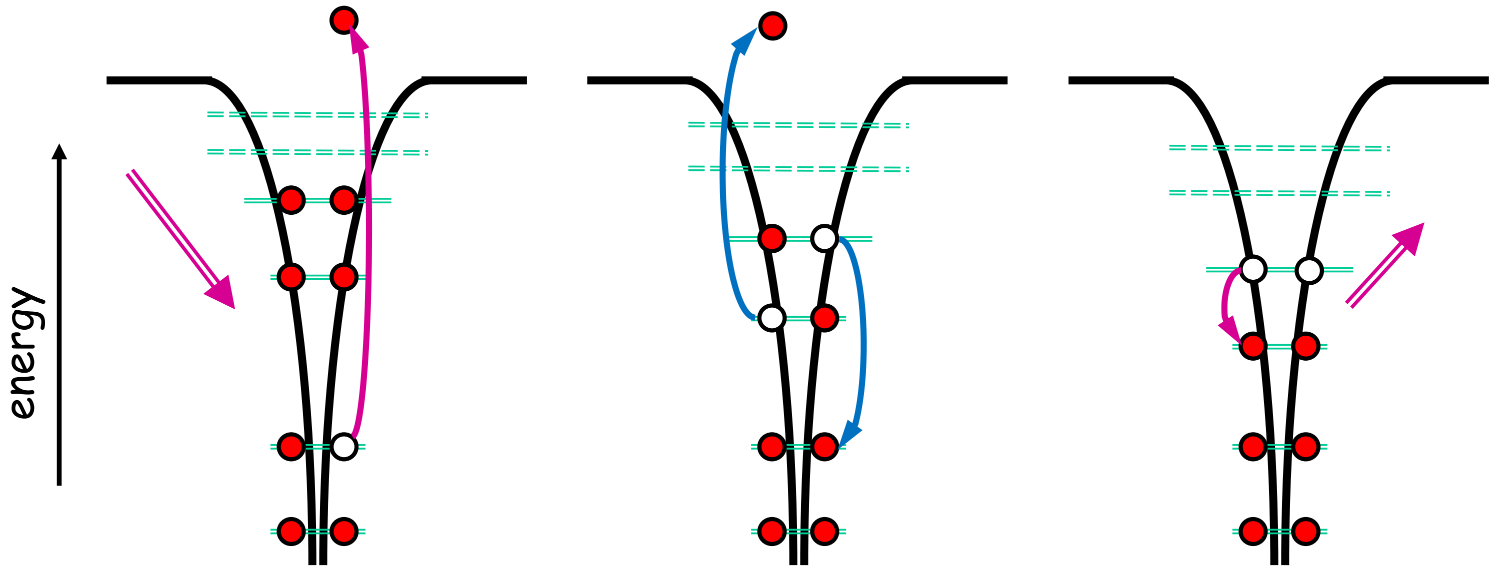
Material	Formula	EUV absorption (50 nm film)
Polypropylene	C_3H_6	11 %
PMMA	$C_5H_8O_2$	24%
Polyimide	$C_{22}H_{10}N_2O_5$	25%
Teflon	C_2F_4	60%
Hafnium Oxide	HfO_2	30%
Tin Oxide	SnO_2	62%

Data[65] from Center for X-Ray Optics "X-Ray Interactions with Matter"

High Cross Sections

- Cross sections are high BECAUSE of deep levels
- This will REDUCE PE Energy and INCREASE residual internal energy
- This will INCREASE the importance of RELAXATION
- More Electrons per Photon - Auger emission
- More Molecular Fragmentation

Atomic Photoemission and Relaxation



(1) $A + \gamma \rightarrow A^{+*} + e$

(2) $A^{*+} \rightarrow A^{*++} + e$

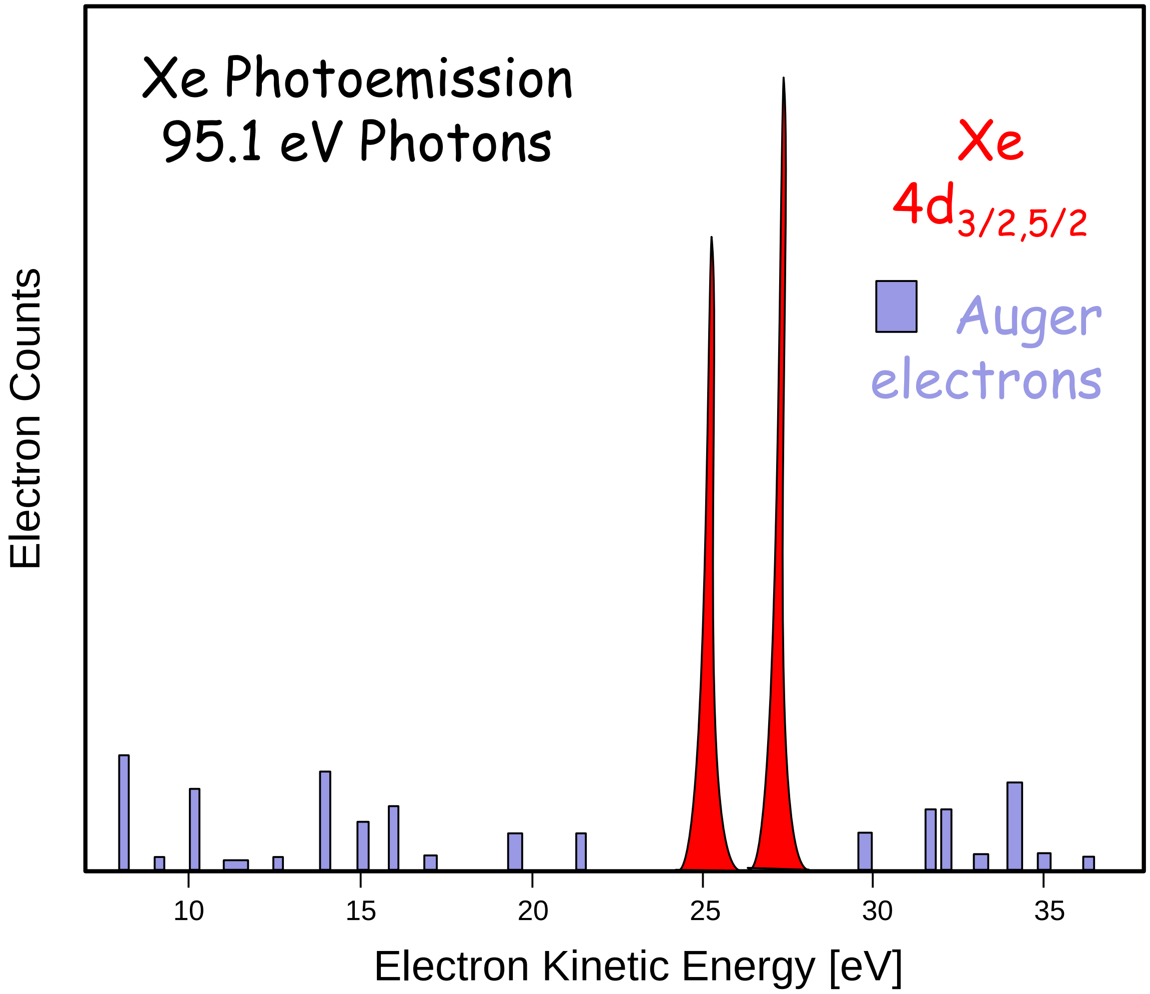
(3) $A^{*++} \rightarrow A^{++} + \gamma$

Photon In

Auger Out

Not enough energy for Auger, Fluorescence or Energy Transfer

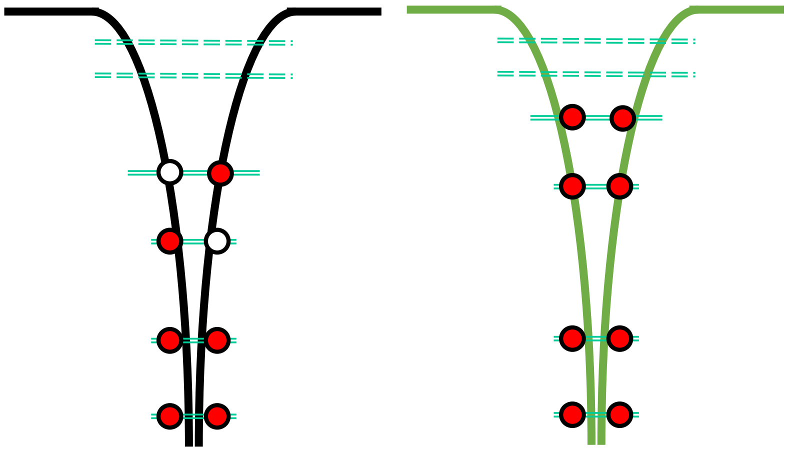
Xe 4d Example



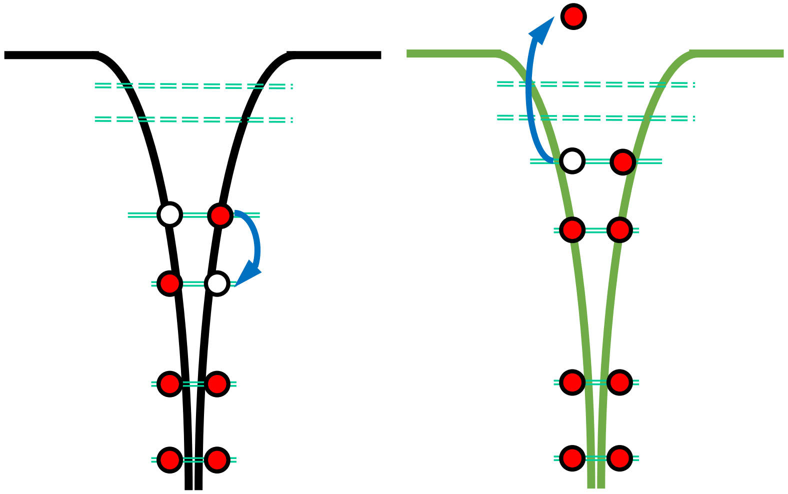
Adapted from P. M. Mishra *et al.*,
Journal of Physics: Conference Series **583** (2015)

- 68 to 70 eV of residual energy in Xe$^+$ after *4d* photoemission
- Xe^{++} 2^{ed} ionization energy 21 eV
- Up to 48 eV available for Auger emission
- 18 Auger peaks detected with KE of 8 to 37 eV
- 1:1 Auger to Photo electron ratio

Inter-Atomic Energy Transfer

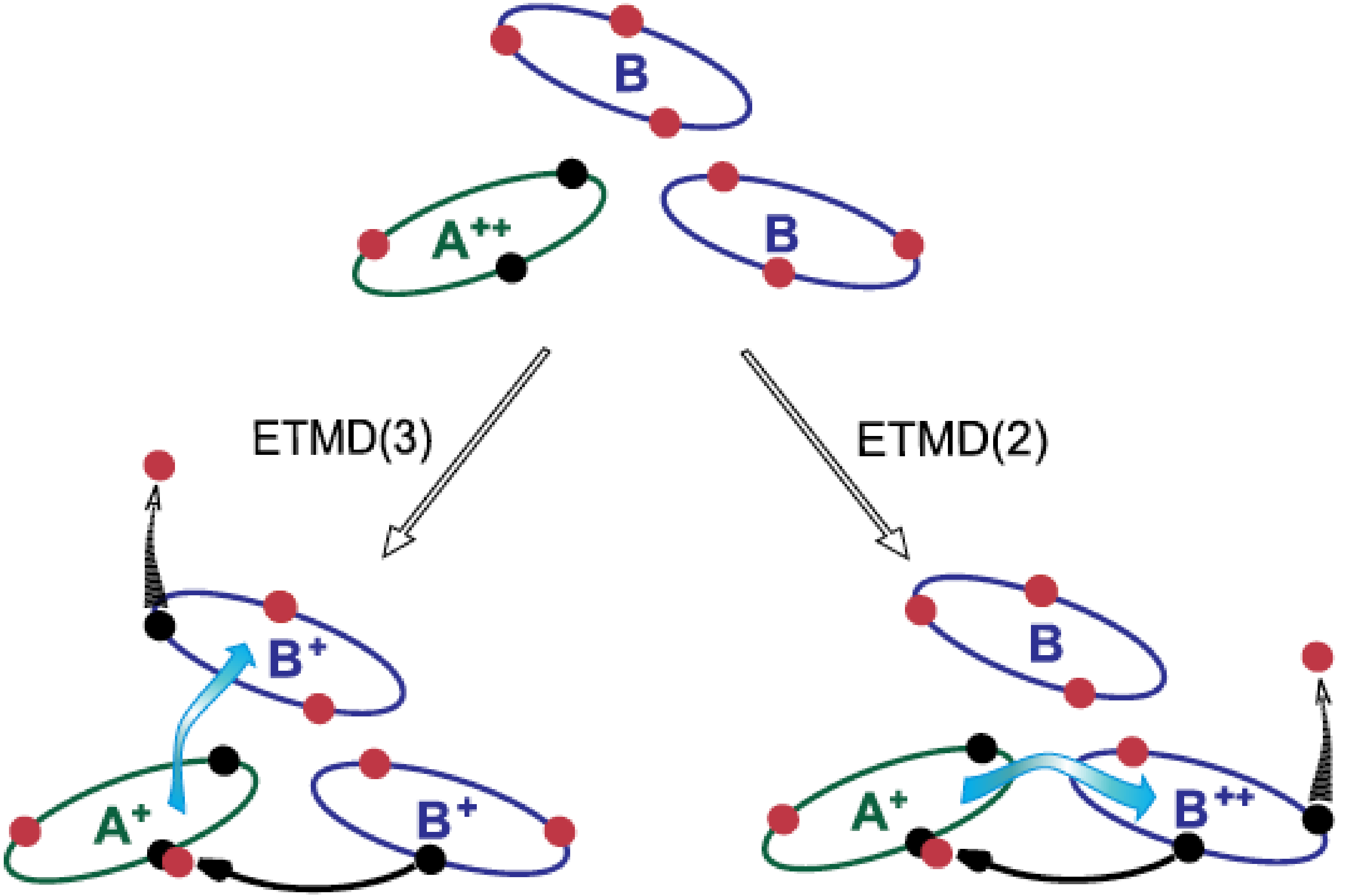


Excited atom near another atom/molecule



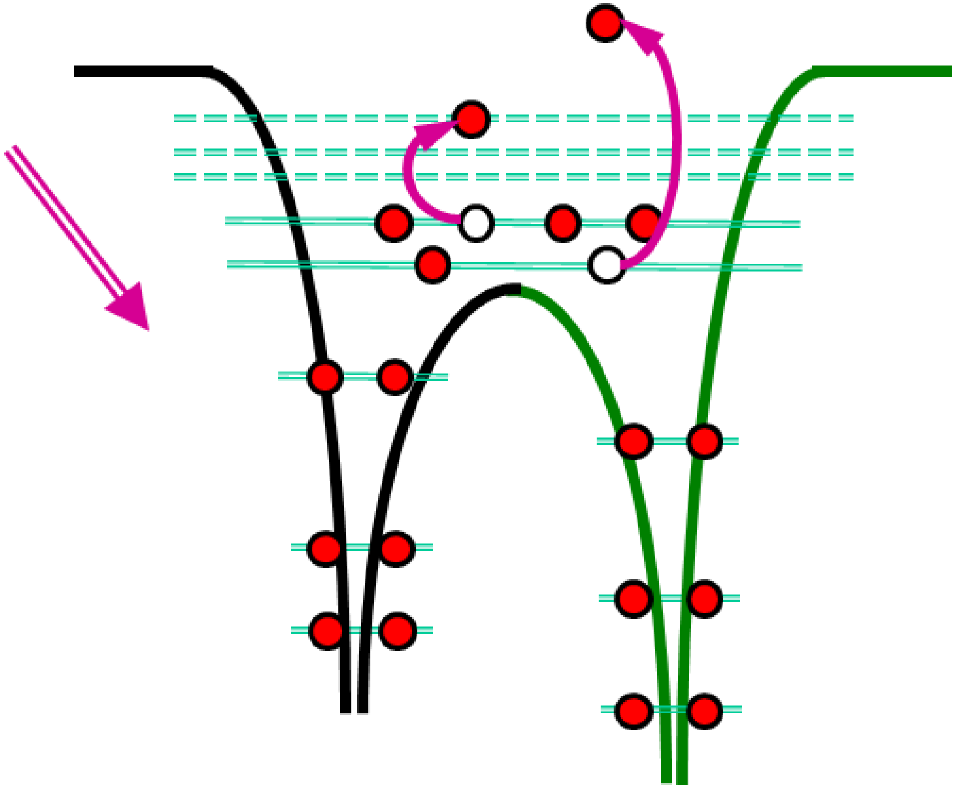
Electrostatic Energy Transfer
"Inter-Coulombic Decay"

Electron Transfer Mediated Decay



Stumpf, Cederbaum *et al.*
Phys Rev Lett **110** (2013)

"Shakeup" Processes



One photon can excite more than one electron in a molecule (the one-electron picture breaks down)

Water Fragmentation

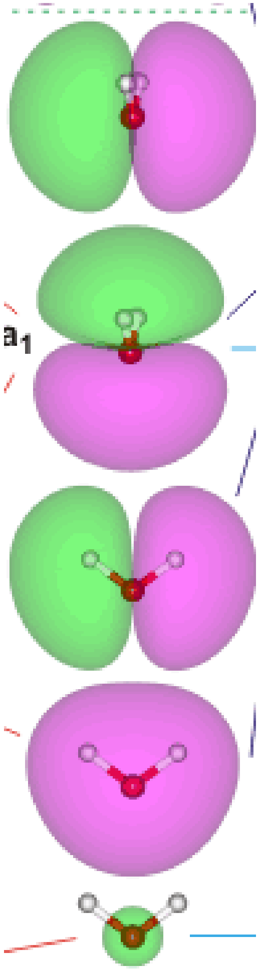
HOMO
$1b_1$ 12.6 eV

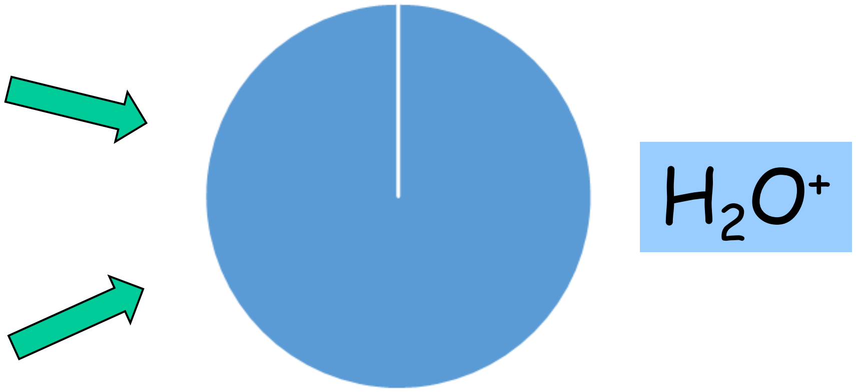
$3a_1$ 15.6 eV

$1b_2$ 15.6 eV

$2a_1$ 36.9 eV

$1a_1$ 512 eV





100% Parent Ion

Scully *et al. Phys Rev A* (2006)
Tan *et al.* Chem Phys (1978)

Water Fragmentation

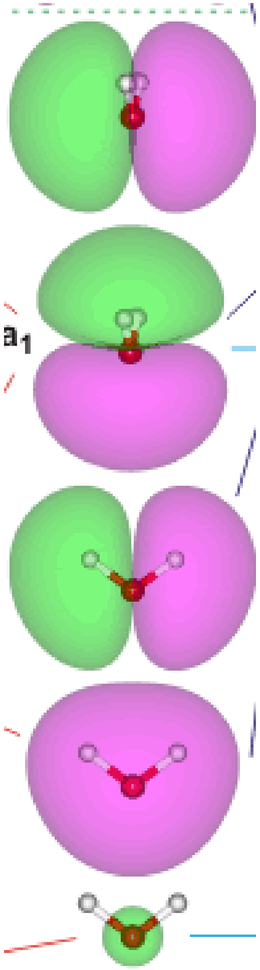
HOMO
$1b_1$ 12.6 eV

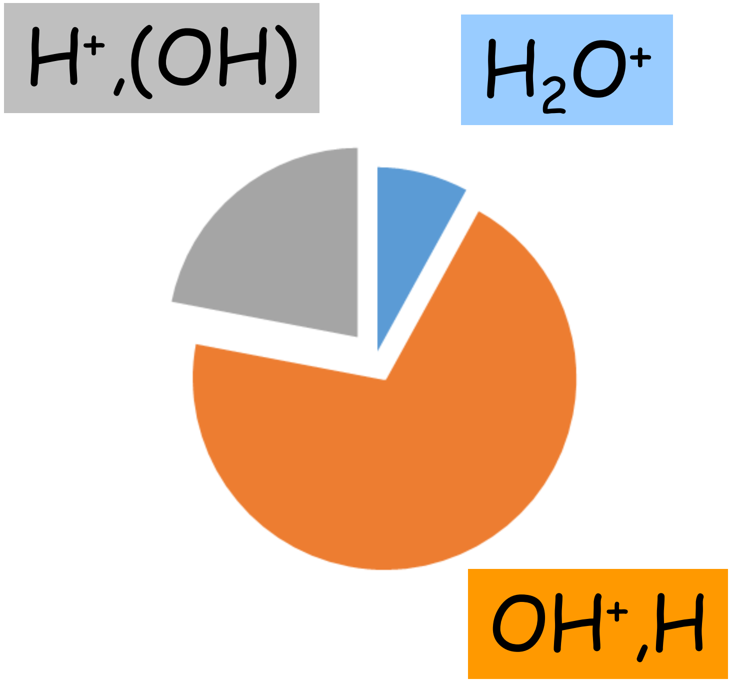
$3a_1$ 14.8 eV

$1b_2$ 18.8 eV

$2a_1$ 32.6 eV

$1a_1$ 512 eV





92% Fragmentation

Water Fragmentation

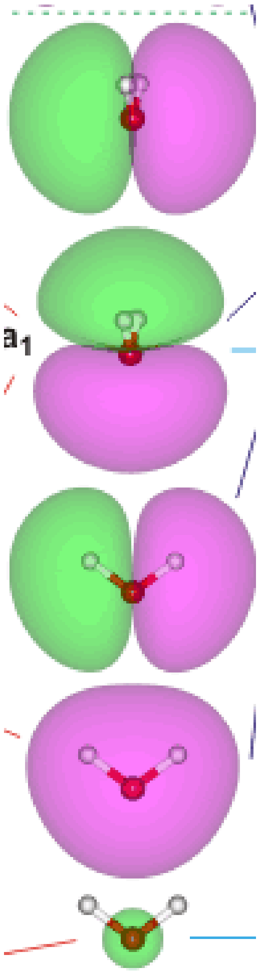
HOMO
$1b_1$ 12.6 eV

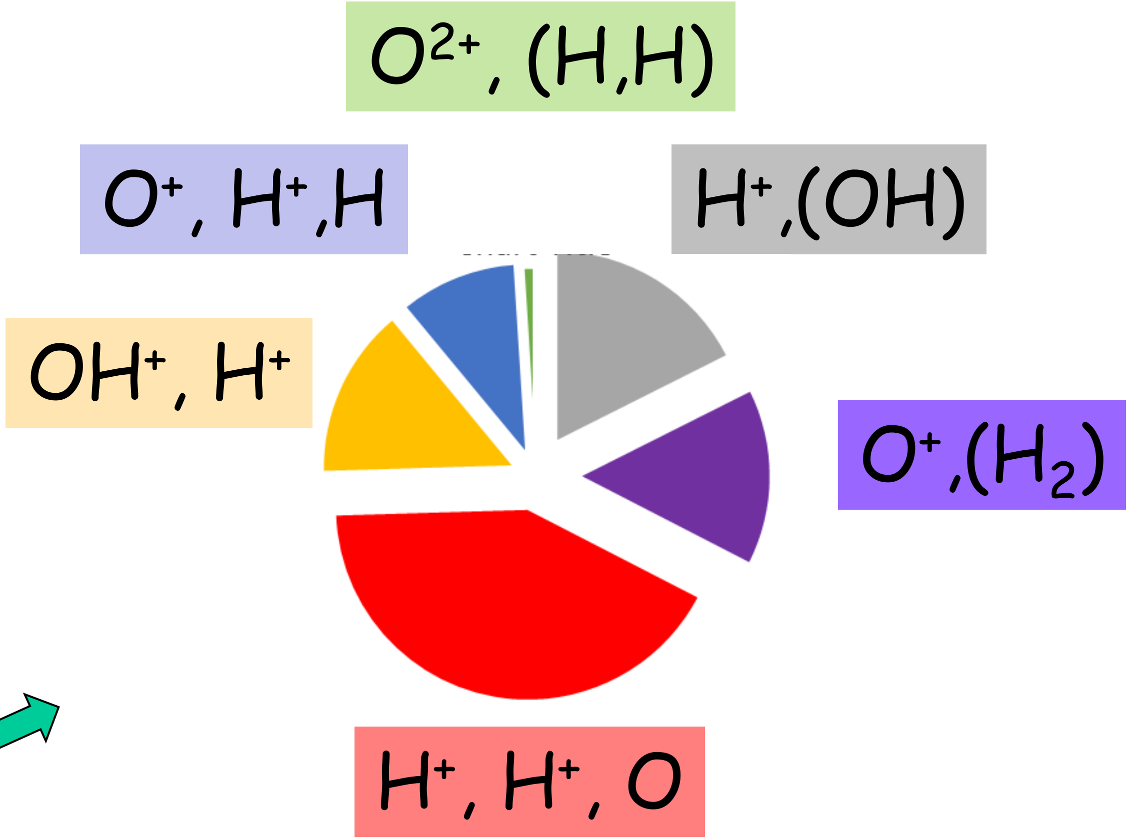
$3a_1$ 14.8 eV

$1b_2$ 18.8 eV

$2a_1$ 32.6 eV

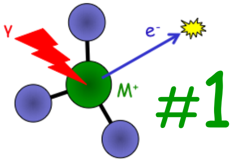
$1a_1$ 512 eV

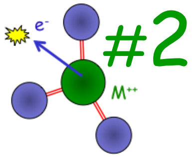




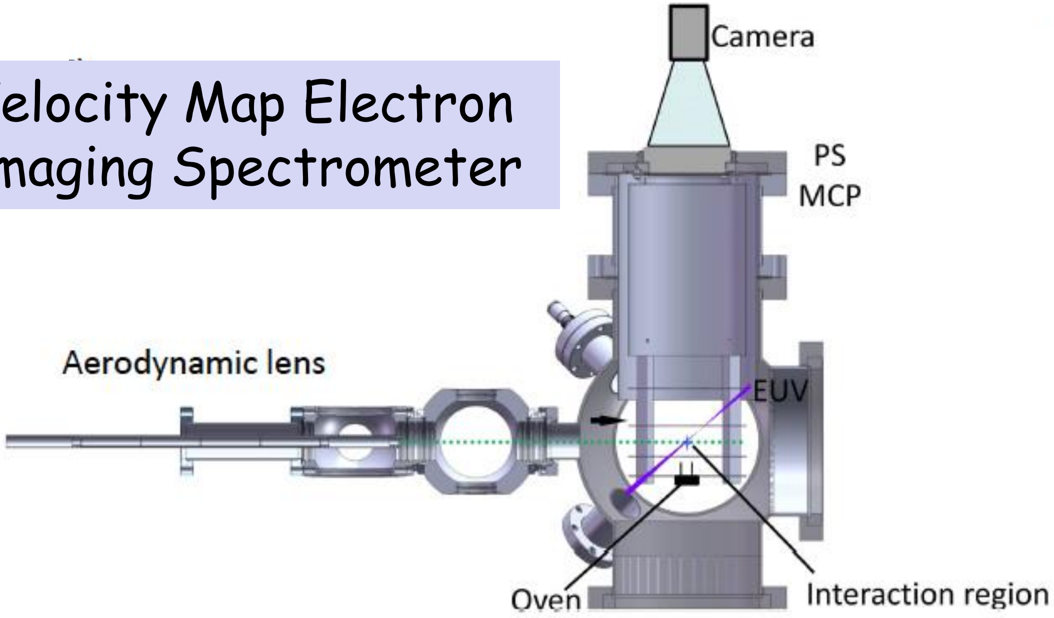
100 % Fragmentation
67% Auger double ionized

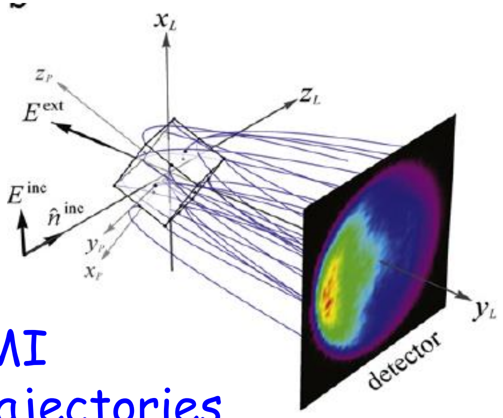
LOOK: Gas-phase Photoemission



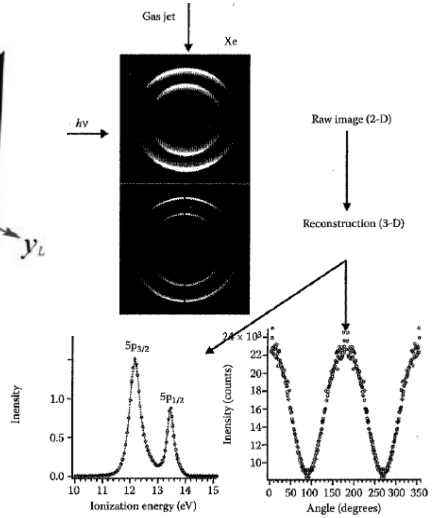


Velocity Map Electron Imaging Spectrometer





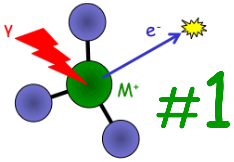
VMI trajectories

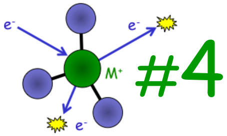


Electron energy and angular distributions calculated from maps

Auger and Photo electrons have different distributions

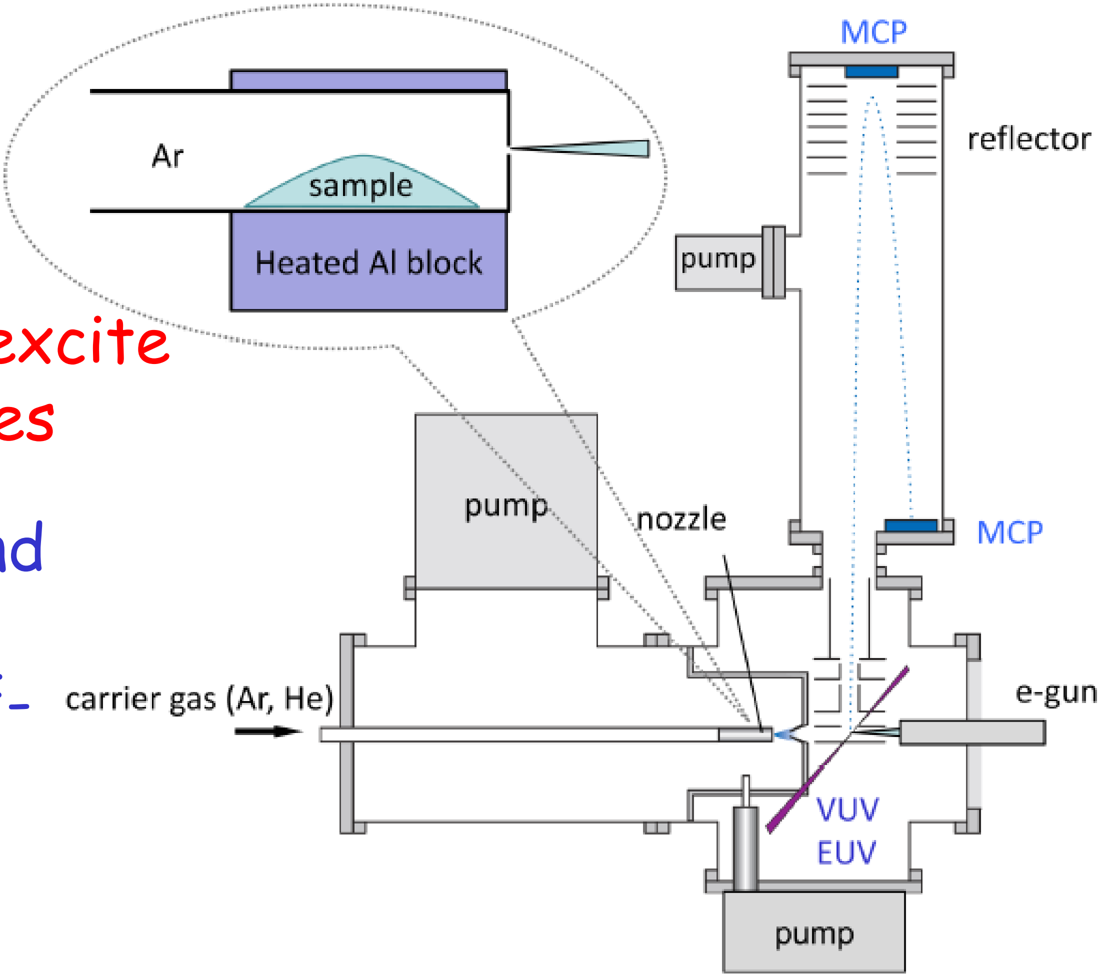
LOOK: Synchrotron Mass Spec



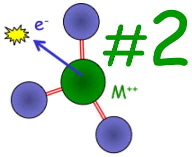


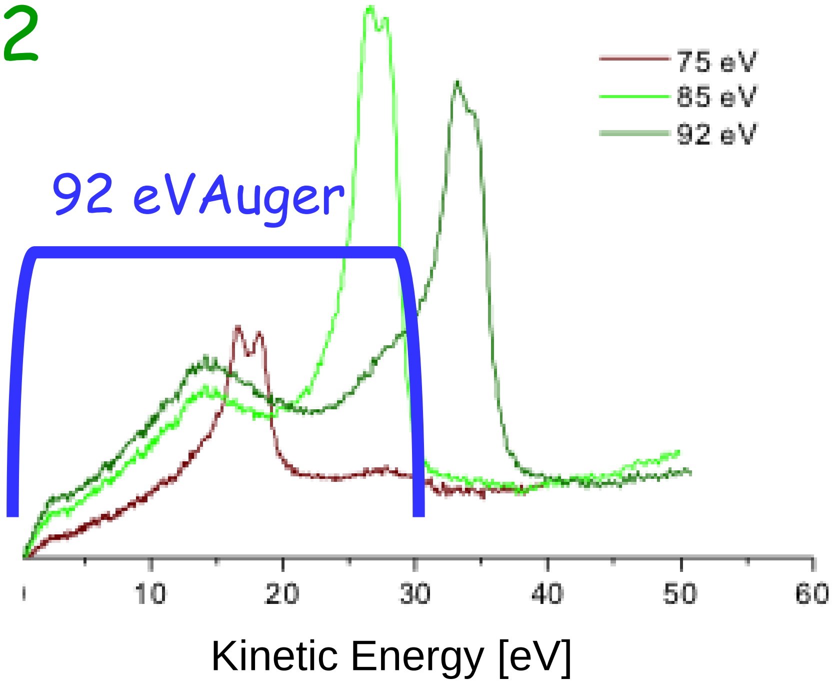
Variable Energy Photons or Electrons excite gas-phase molecules

Ionized Molecules and Fragments are detected by time-of-flight MS

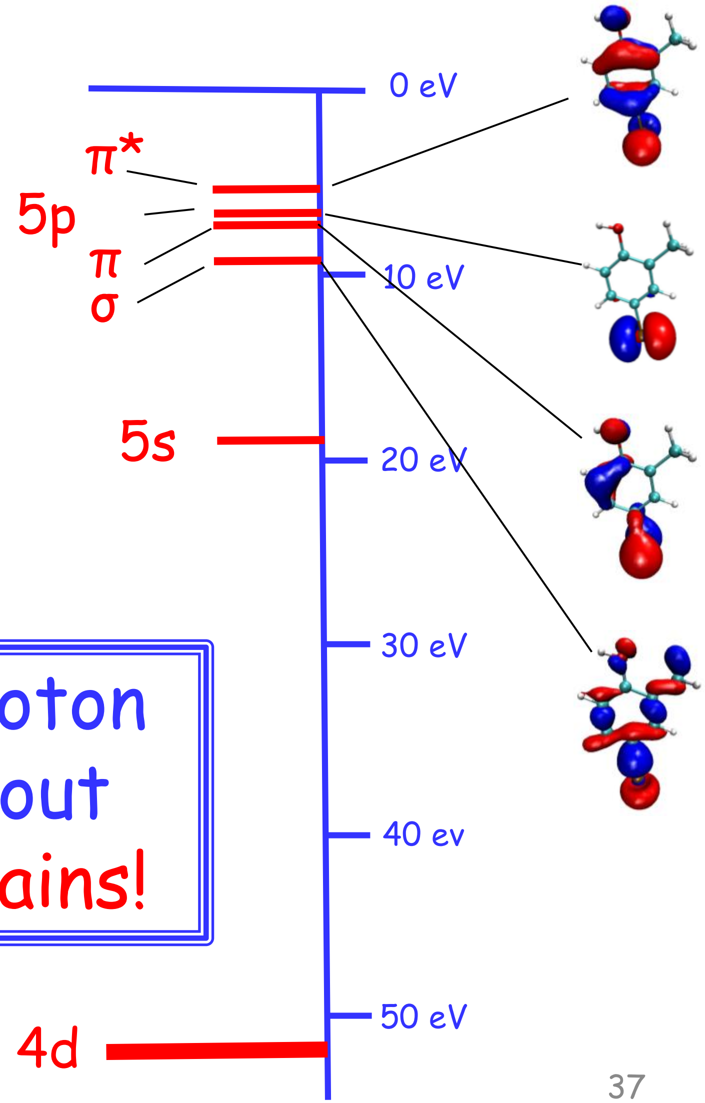


LOOK: VMI Electron Spectra





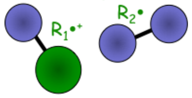
Calculated energies of I-related orbitals (2e⁻ except for 4d with 10)

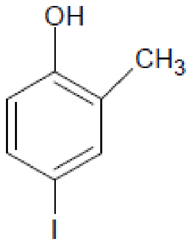


I 4d is excited, one 92 eV photon in, one 35 eV photoelectron out
~ 55 eV potential energy remains!

LOOK: Molecular Fragmentation

#3

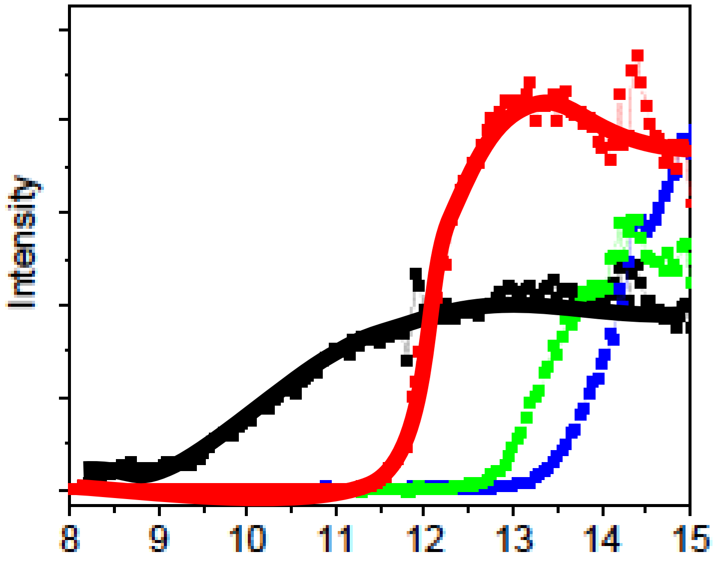




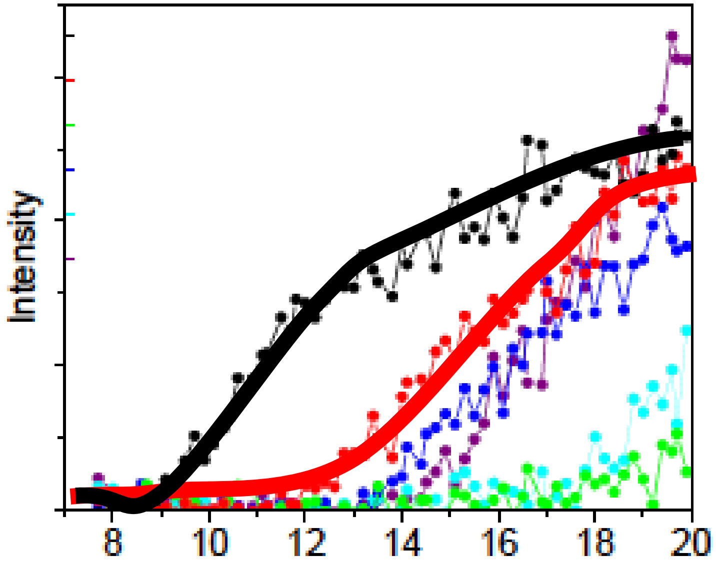
▬ $(\text{I-MePh})^+$

▬ $\text{I}\bullet + (\text{MePh})^+$

▬ ▬ $\text{I}\bullet + \text{R}\bullet + \text{R}^+$ ring-breaking events

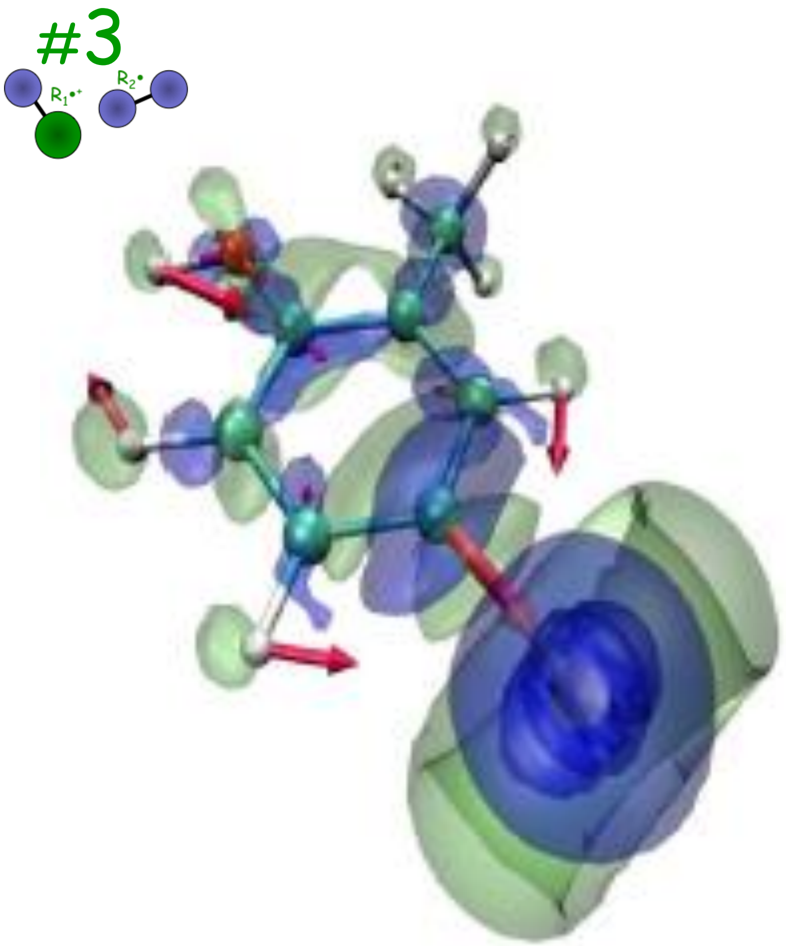


PHOTONS



ELECTRONS

UNDERSTAND: Ionized Molecules



I 4d level is ionized,
Molecular orbital density increases (blue) or decreases (green)

This generates forces on the atoms (red arrows)
and fragmentation, (probable loss of I radical)

other orbitals produce OH radicals or stable ions

Condensed Resist Films?

- Photoemission and Atomic Auger relaxation almost unchanged
  - dielectric environment reduces binding energies ~ 4 eV
  - sharp lines are broadened
- Confined Molecular fragmentation
  - fragments are trapped in polymer matrix, may recombine or generate secondary reactions…
- Intra-Molecular Relaxation Possible

Condensed Resist Films?

- Inelastic electron scattering
  - possible plasmon excitation in condensed films followed by decay to hot electrons
- Elastic electron scattering
  - within the electric field of the photo-ion
  - photoelectrons may be recaptured by primary or other ions
- Nanoparticles?
  - No core fragmentation expected, possible charge trapping, ligand scission, etc

Summary and Outlook

Molecular Relaxation, Auger Emission and Fragmentation are intrinsic to EUVL

One EUV photon generates multiple secondary electrons in the PRIMARY event

Our theoretical and experimental tools can be applied to more realistic resist component molecules

MOLECULAR FOUNDRY

CXRO

BERKELEY LAB

ALS

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