X-Rays, Electrons and Lithography:
Fundamental Processes in Molecular Radiation Chemistry

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EUV Lithography and Pattern Transfer

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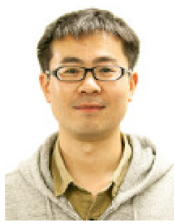

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Theory

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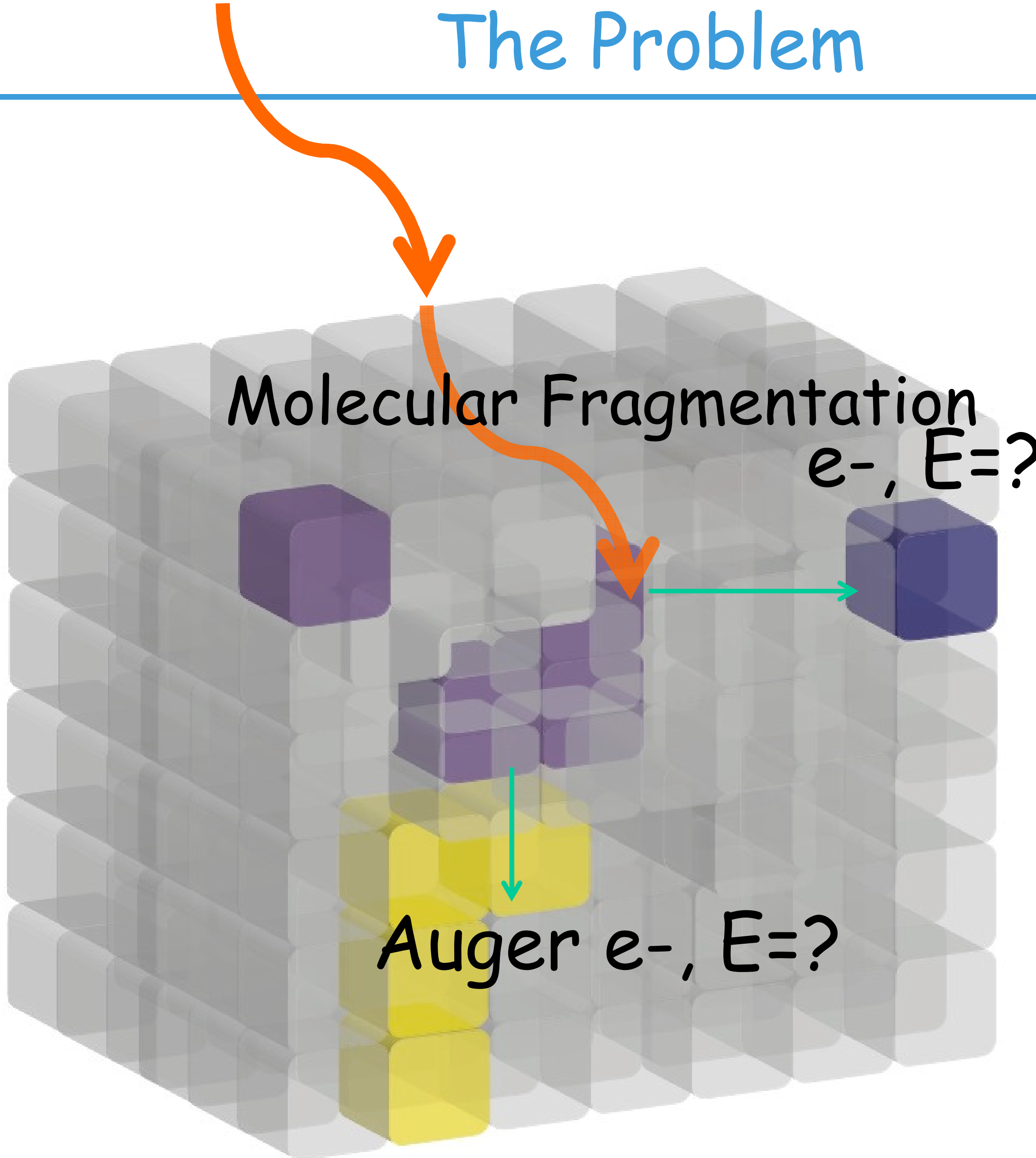
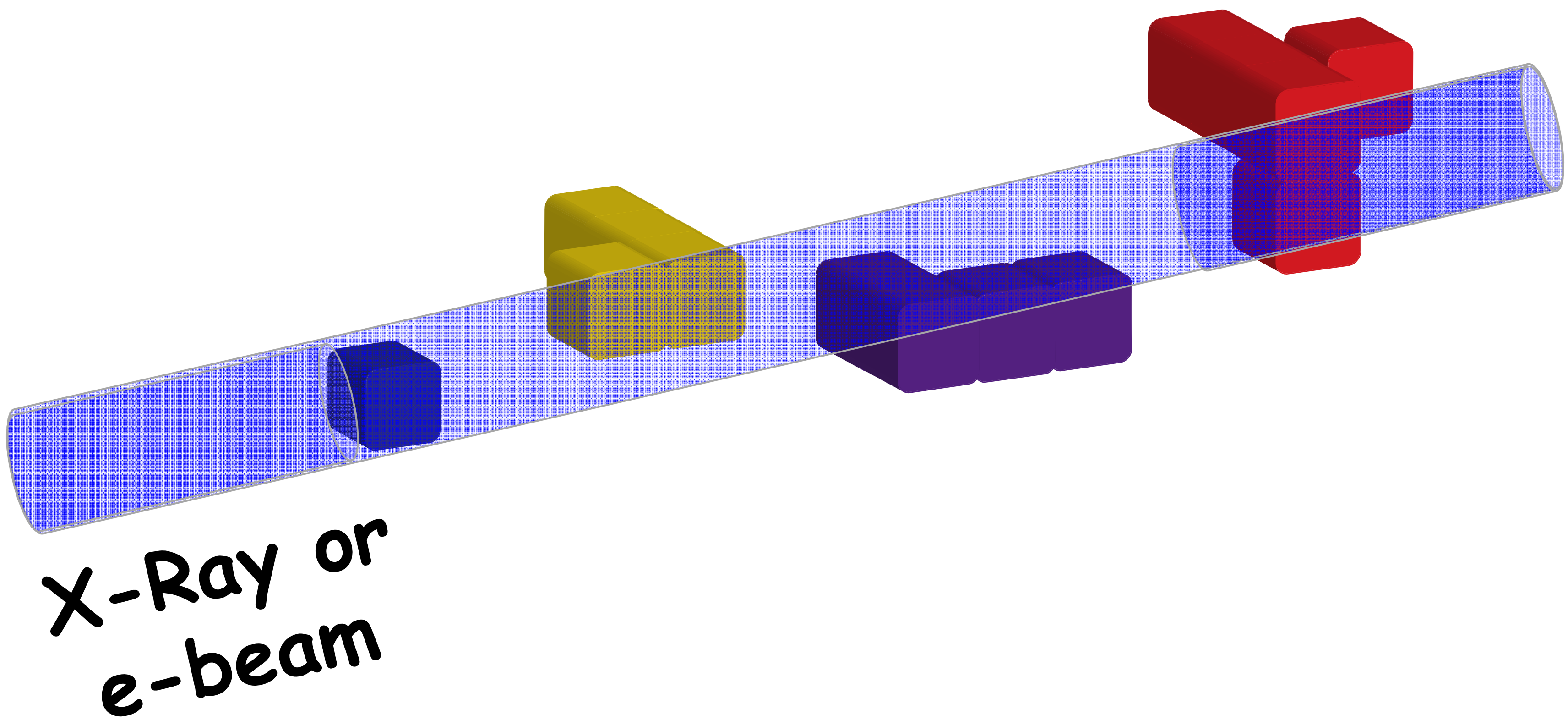
The Problem



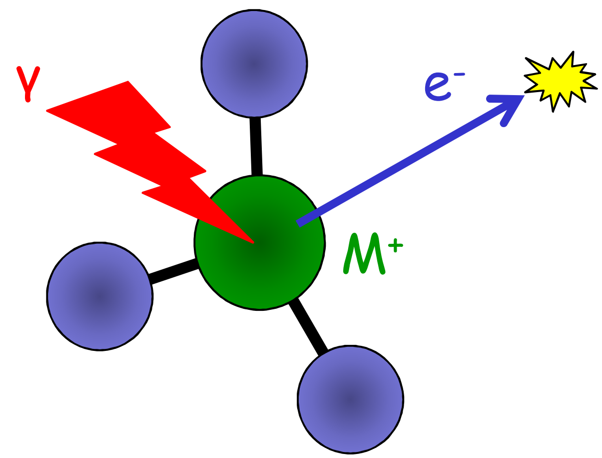
Bulk vs Gas Phase



EUV "Standard Model"

Photoionization

$M + h\nu \rightarrow M^{+} + e^{-}$



92 eV x-ray in

ionization energy ~ 10 eV

~80 eV secondary electron out

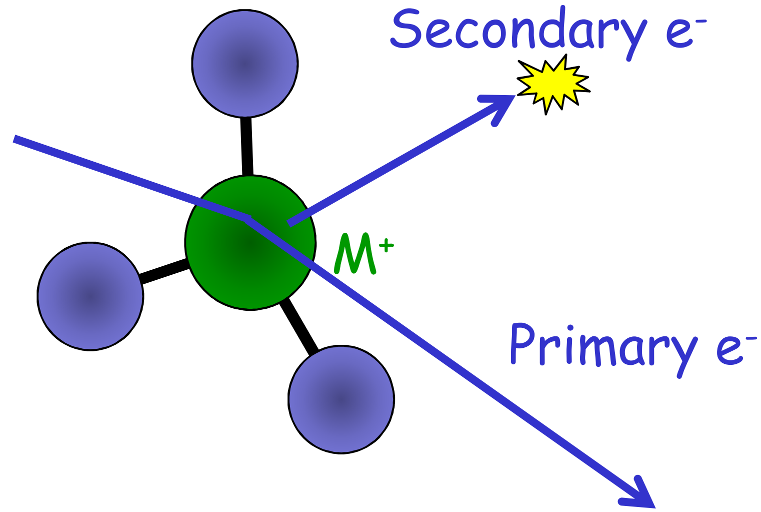
Stable parent ion left behind

The electron does the work!

EBL "Standard Model"

Impact Ionization

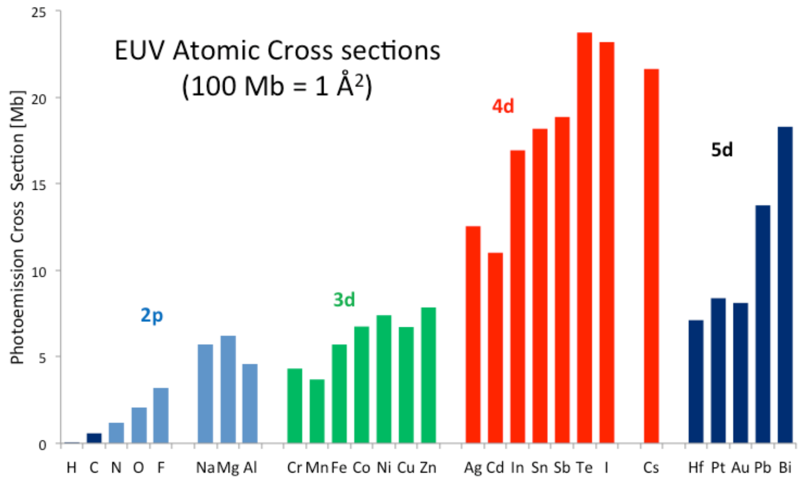
$M + e^- \rightarrow M^+ + 2e^-$

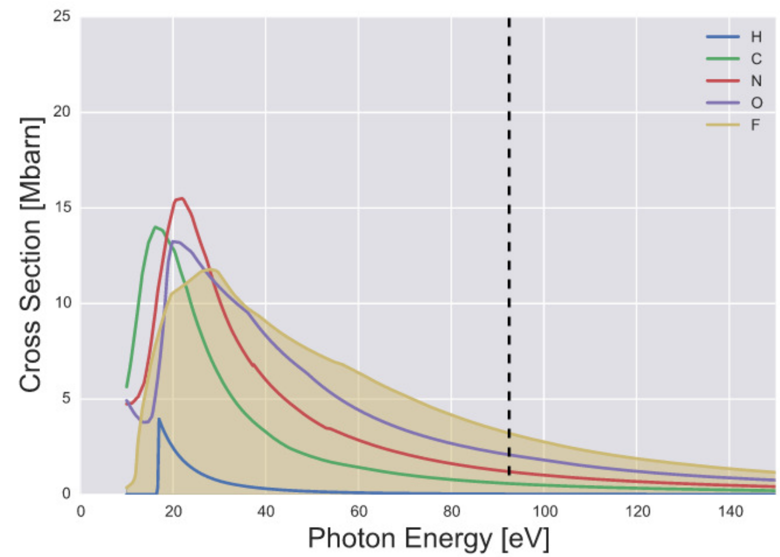


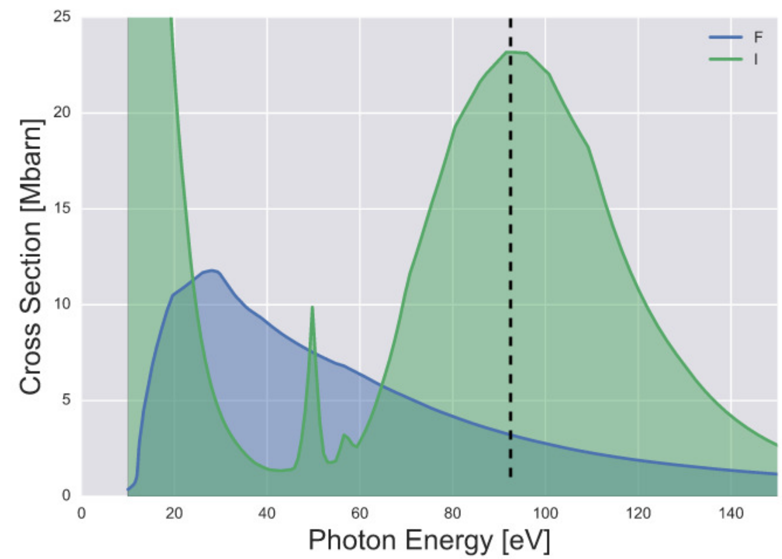
Fast primary electron in
ionization energy ~ 10 eV
~10-30 eV secondary electron out
20-40 eV energy transfer
Stable parent ion left behind

The SE does the work!

EUV Atomic Cross Sections







A molecule has *many* cross sections, one for each orbital

Orbitals closer to the photon energy have *higher* EUV cross sections

Photoemission from deeper levels leaves significant *residual energy* in the ionized molecule

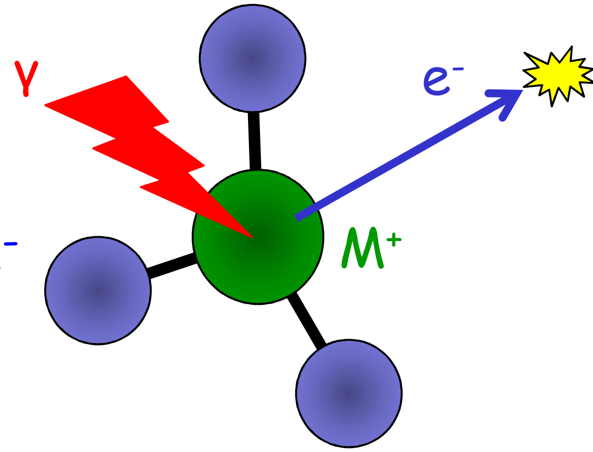
Cross section data cxro.lbl.gov

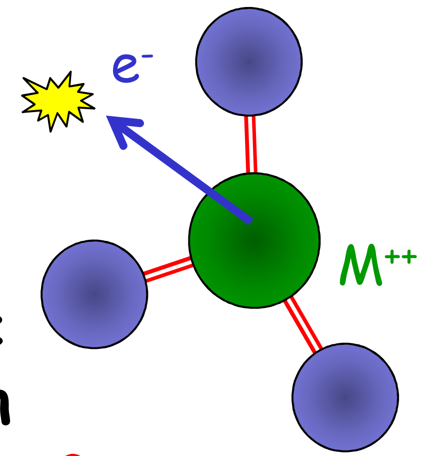
Excitation and Relaxation

Step 1

Photoionization

$M + h\nu \rightarrow M^+ + e^-$





Step 2

Electronic Relaxation

Auger process ?

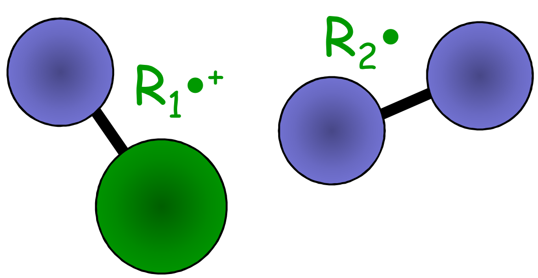
$M^+ \rightarrow M^{++} + e^-$

Step 3

Atomic Relaxation

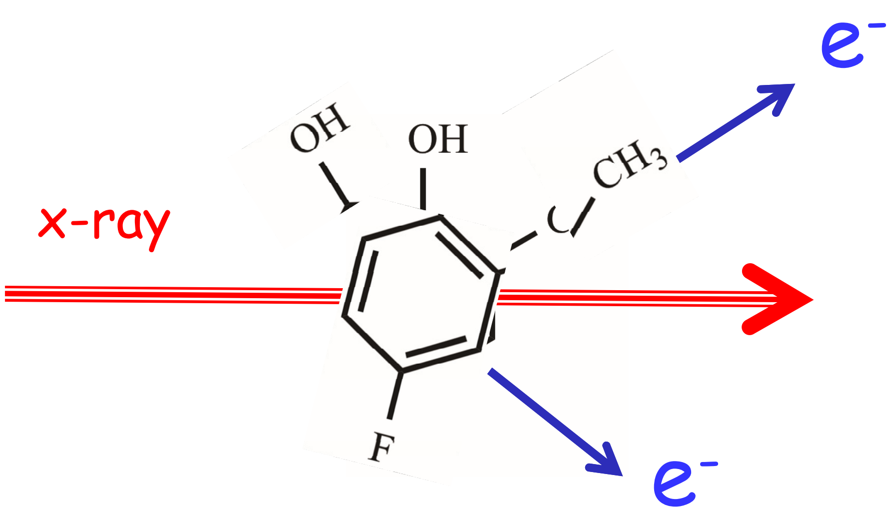
Fragmentation?

$M^+ \rightarrow R_1\bullet^+ + R_2\bullet$



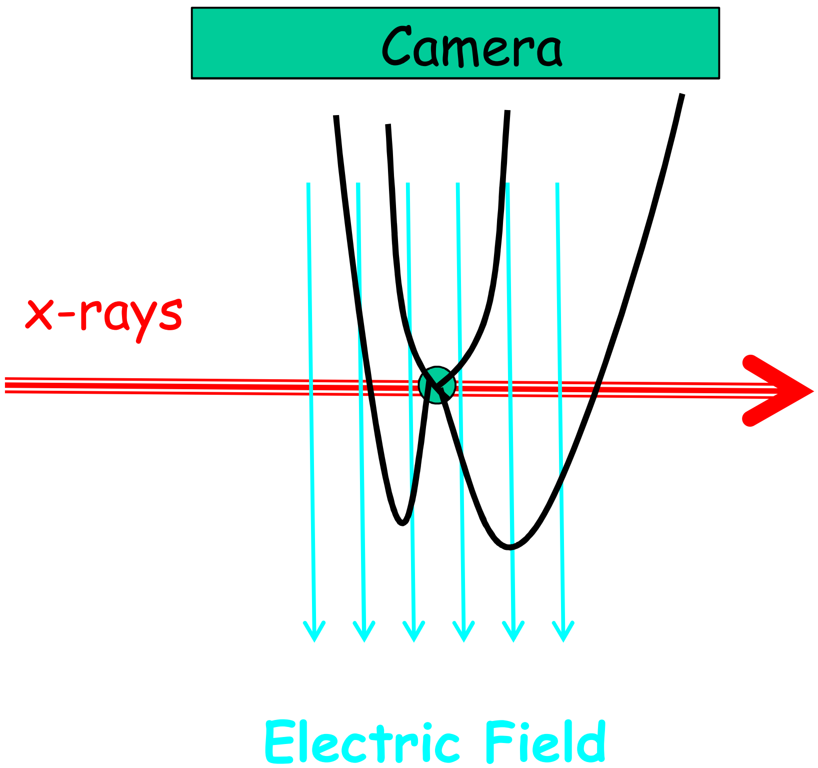
D. F. Ogletree, *Molecular Excitation and Relaxation of Extreme Ultraviolet Lithography Photoresists*. In Frontiers of Nanoscience: Materials and Processes for Next Generation Lithography, Eds. A. P. G. Robinson and R. A. Lawson, Elsivier 2016

Gas Phase Chemical Dynamics



- Count electrons, energy distribution
- Count ions and ionized fragments
- Branching ratios for different processes
- Cross sections
- Photon energy dependence

Experiment Concept

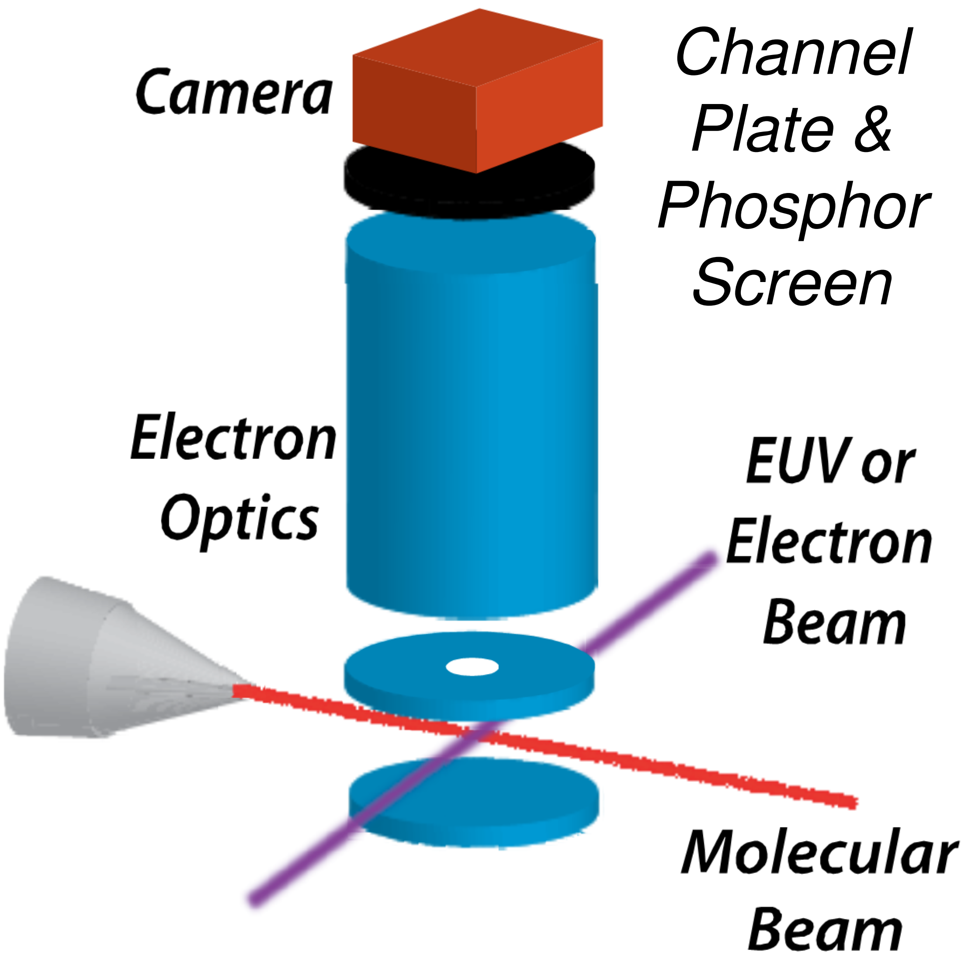


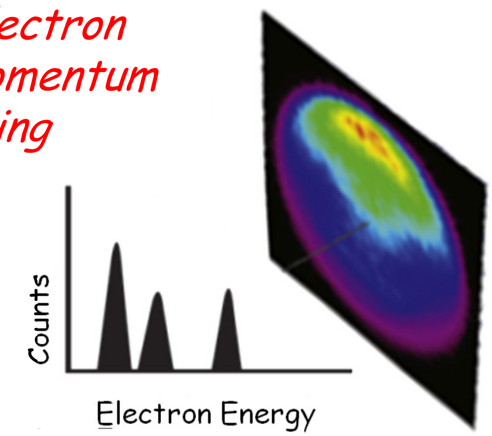
All electrons pushed into imaging detector (4π collection)

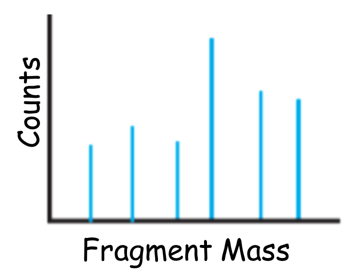
Radial position depends on emission energy and angle

Positive ions detected with reversed field (Time of Flight)

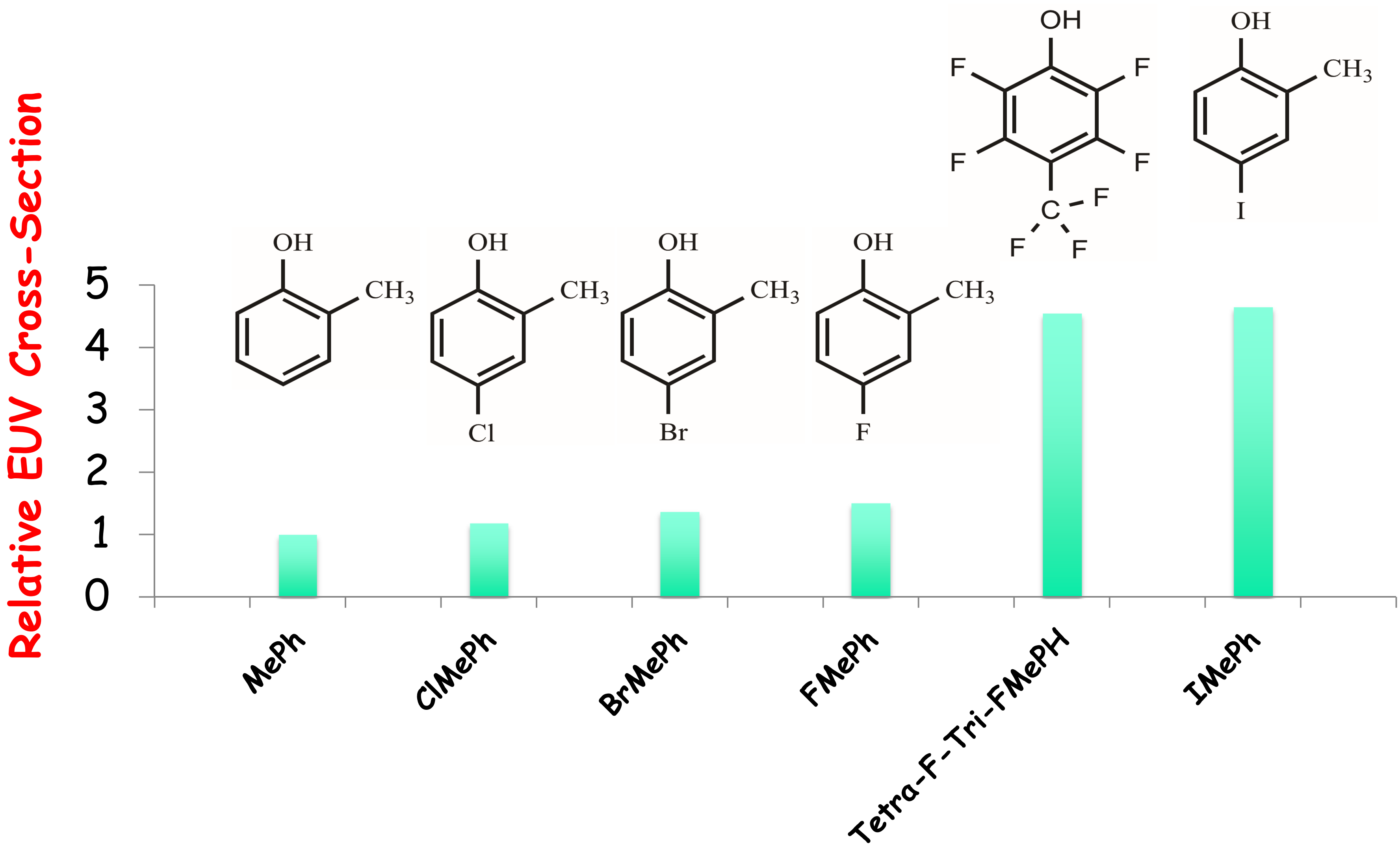
Gas Phase Instrumentation







Methylphenol Model Compounds

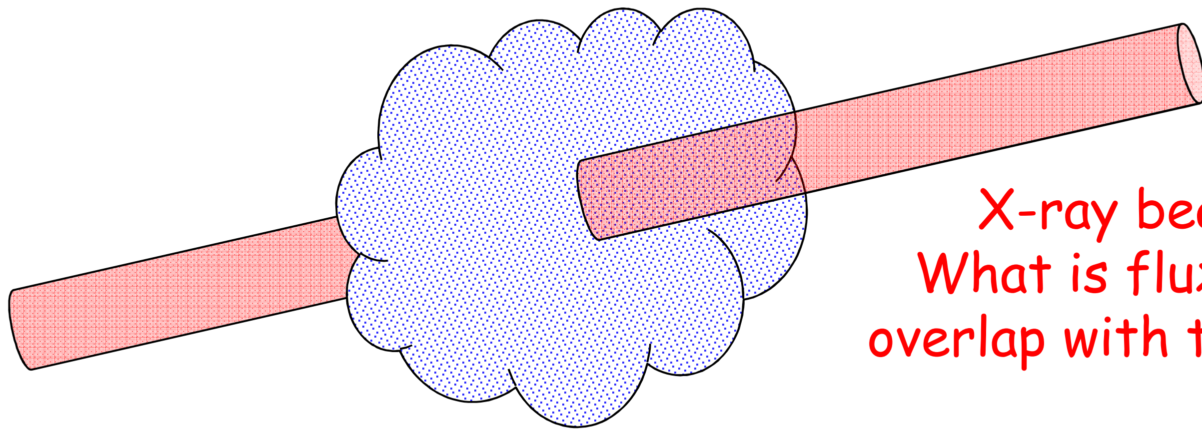


Cross section data cxro.lbl.gov

EUVL Berkeley, June 2017
D. Frank Ogletree LBNL

How to Quantify?

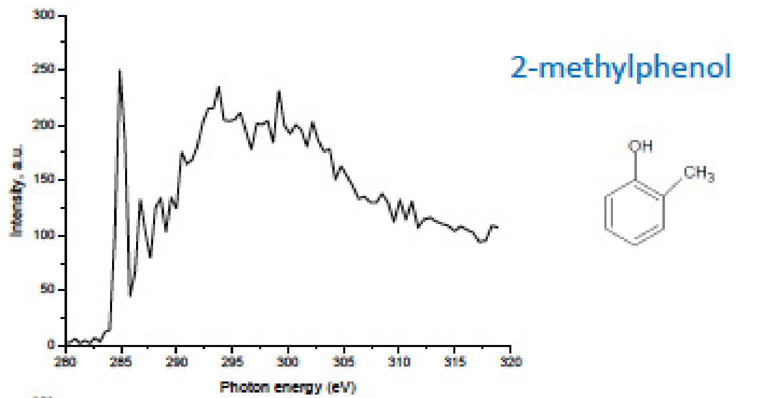
Cloud or molecular beam of gas
What is density and distribution?

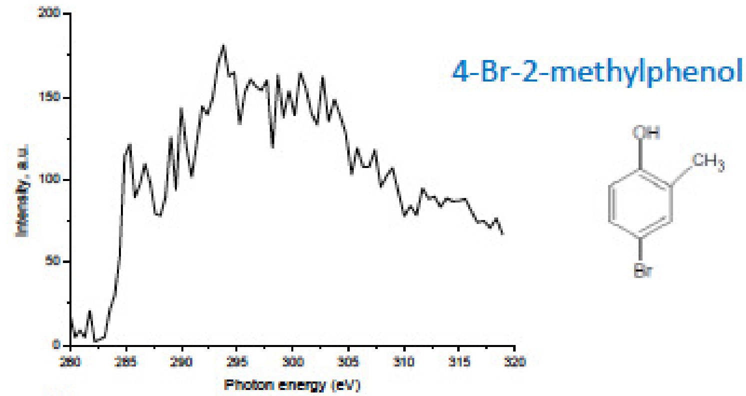


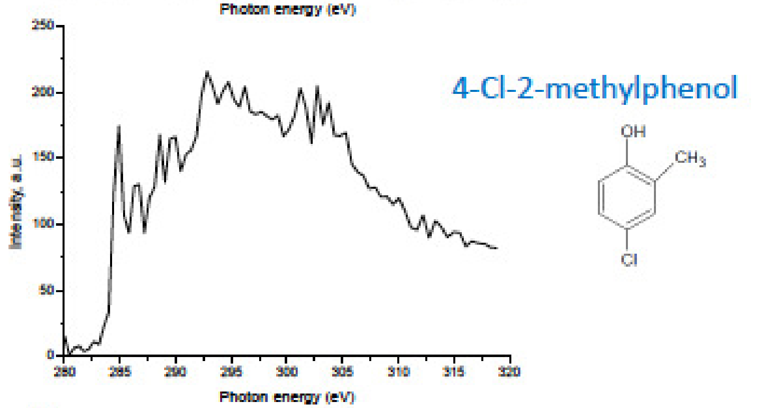
X-ray beam
What is flux and
overlap with target?

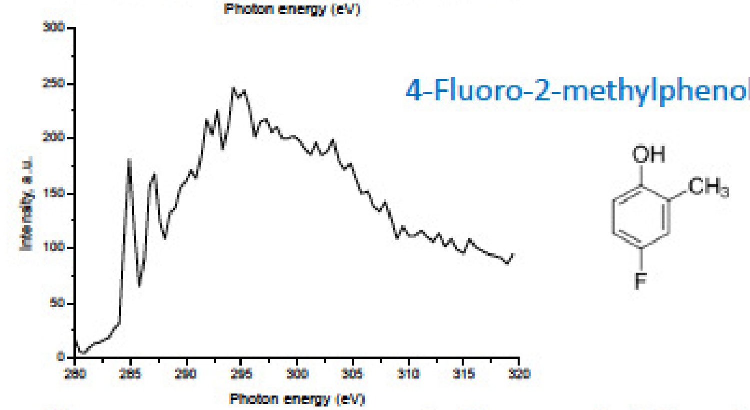
All the molecules have 7 carbon atoms
Scan the photon energy through the carbon 1s edge (XAS) and measure the ion yield
The "edge jump" ~ 50 eV above threshold is proportional to the gas pressure
All the photoemission spectra are normalized to the same number of phenol molecules

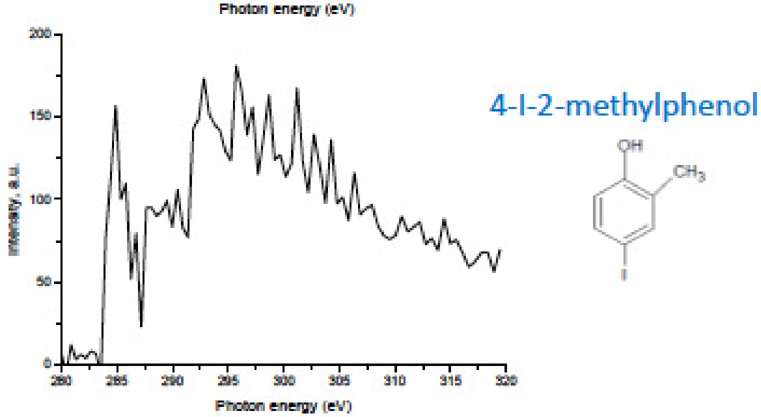
Carbon 1s Ion-Yield NEXAFS

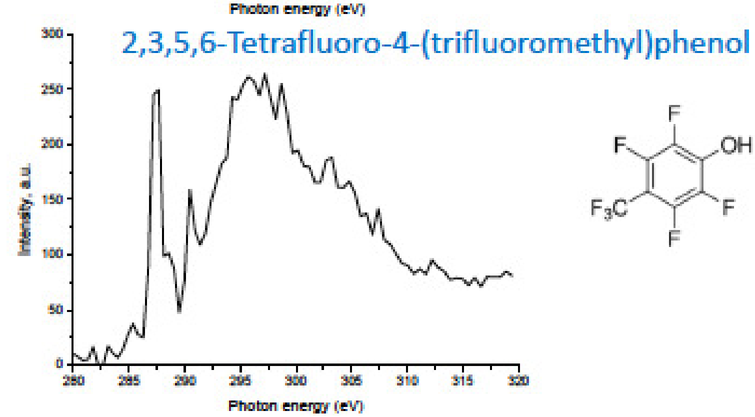




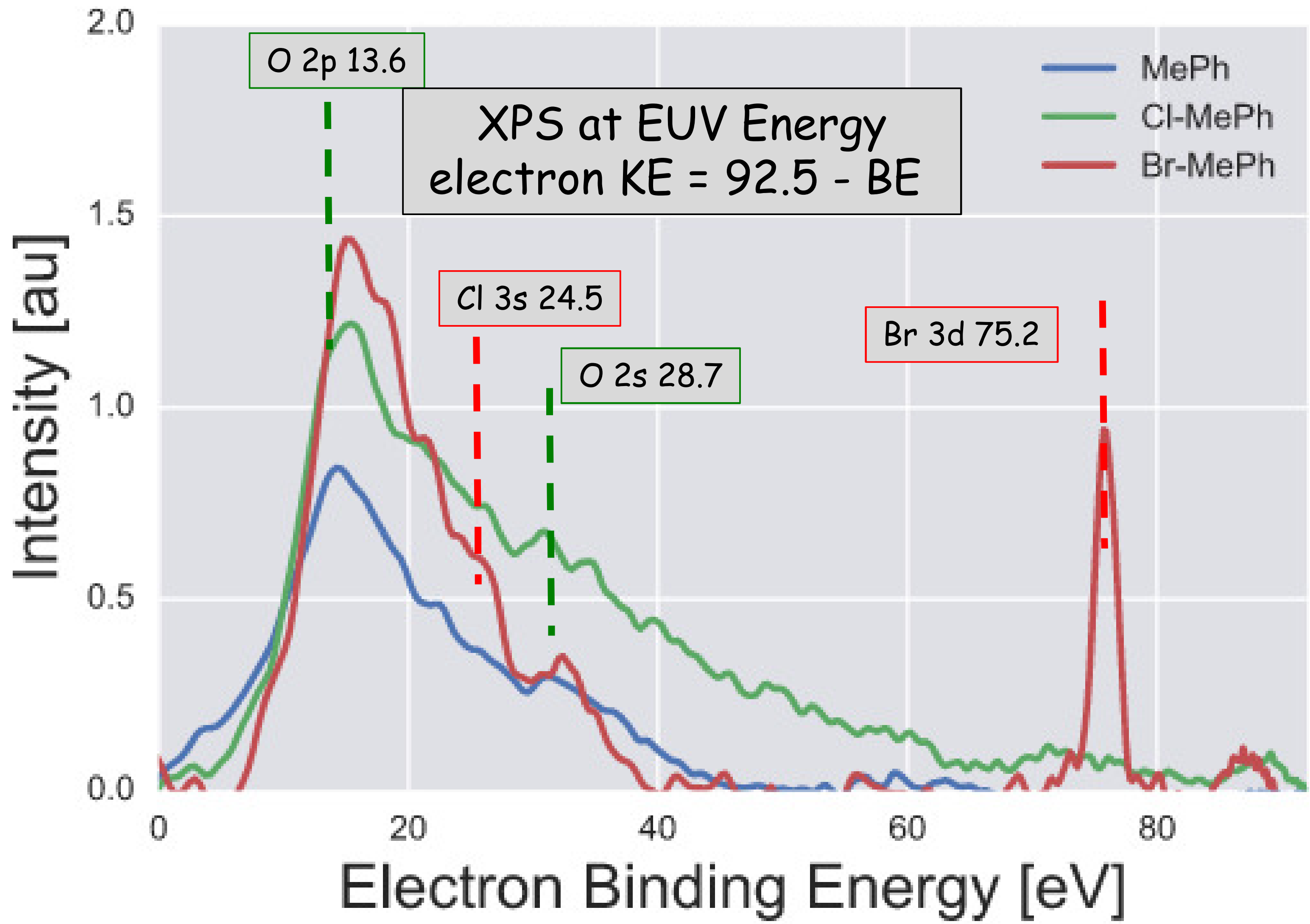




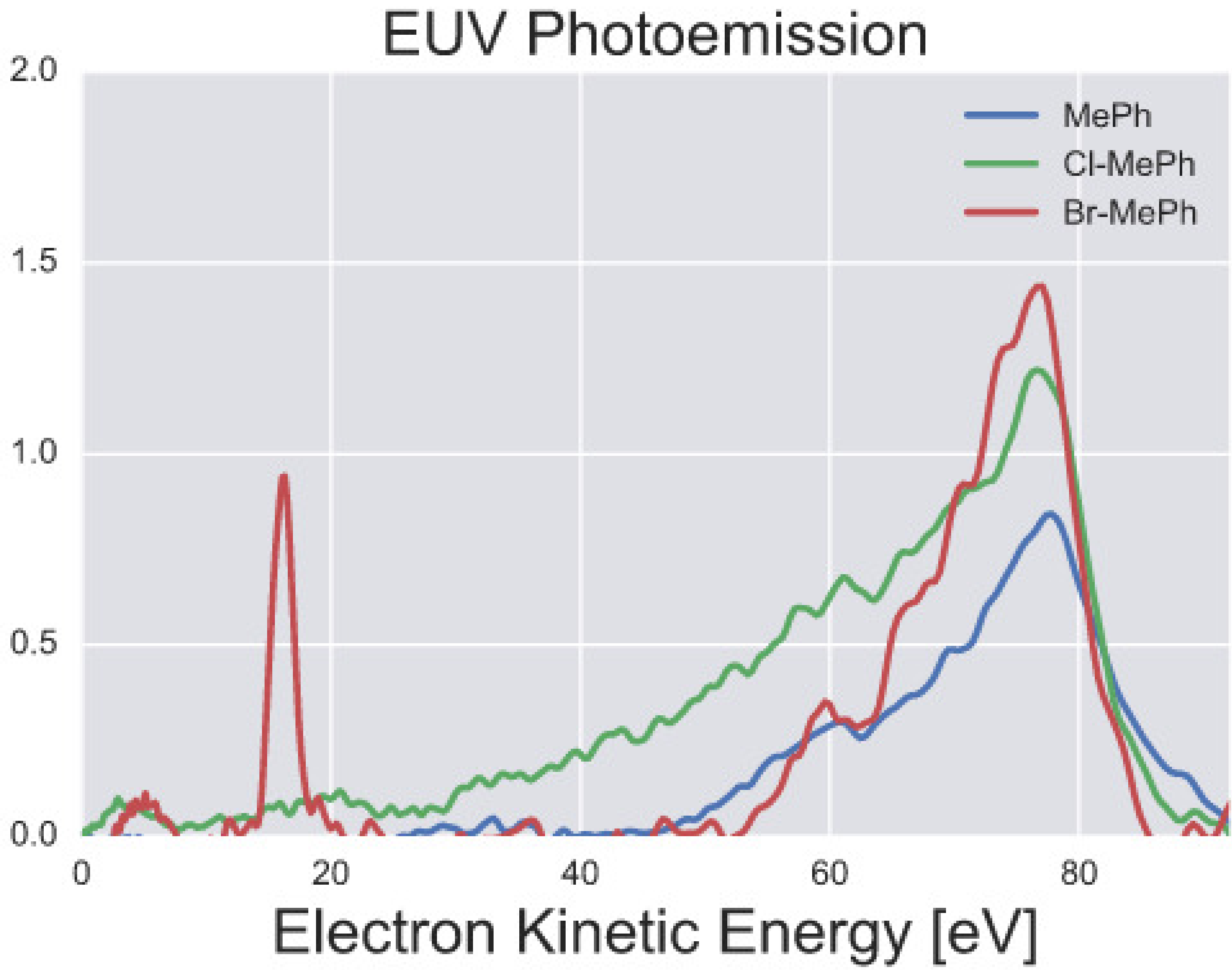




Methyl Phenol Photoemission

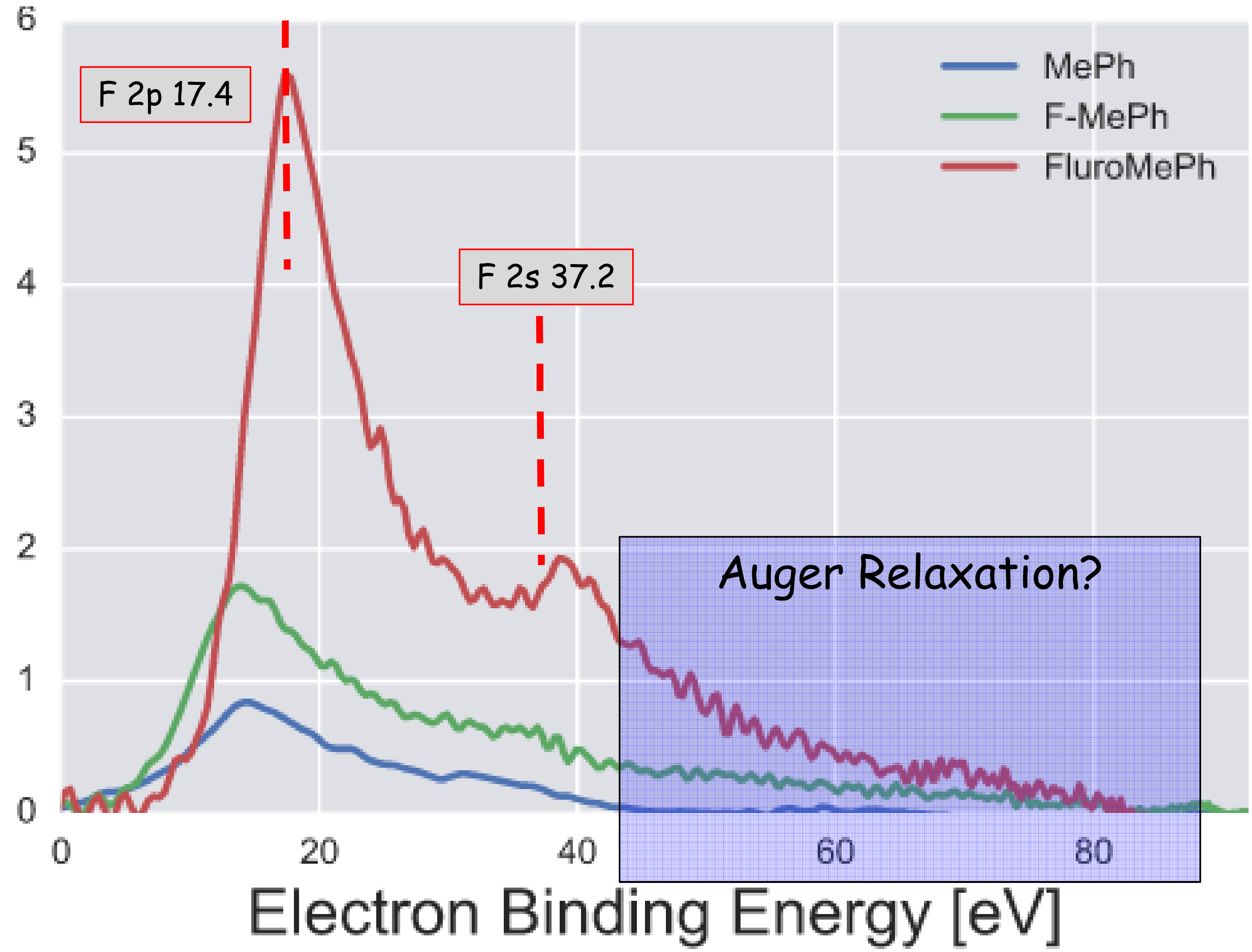


Kinetic Energy Plot



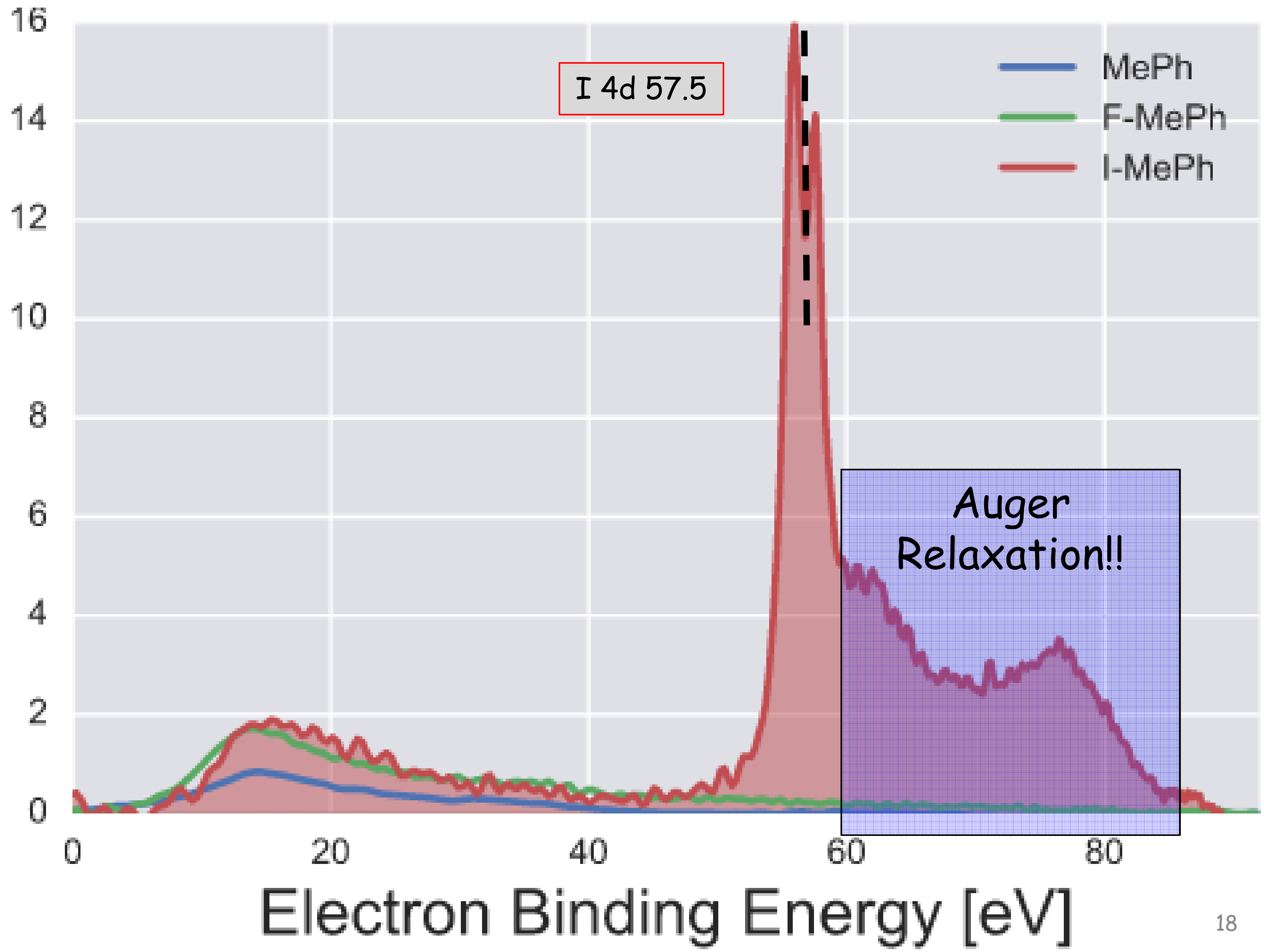
Effects of Fluorine

3x

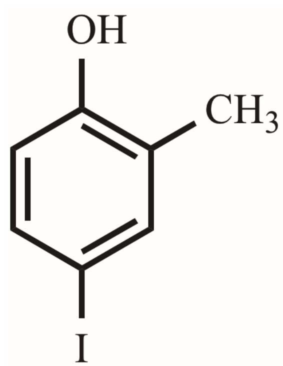


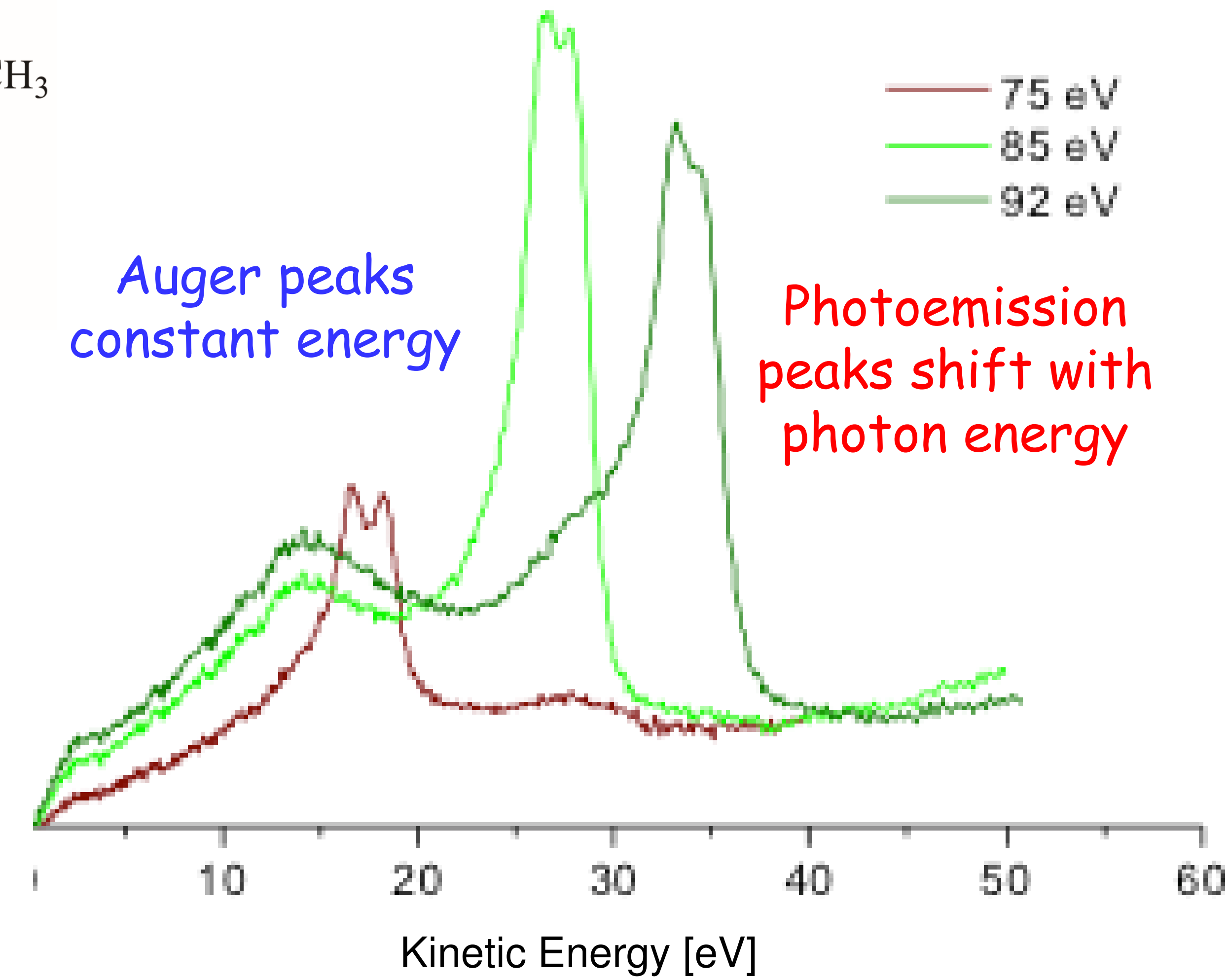
Effects of Iodine

8x

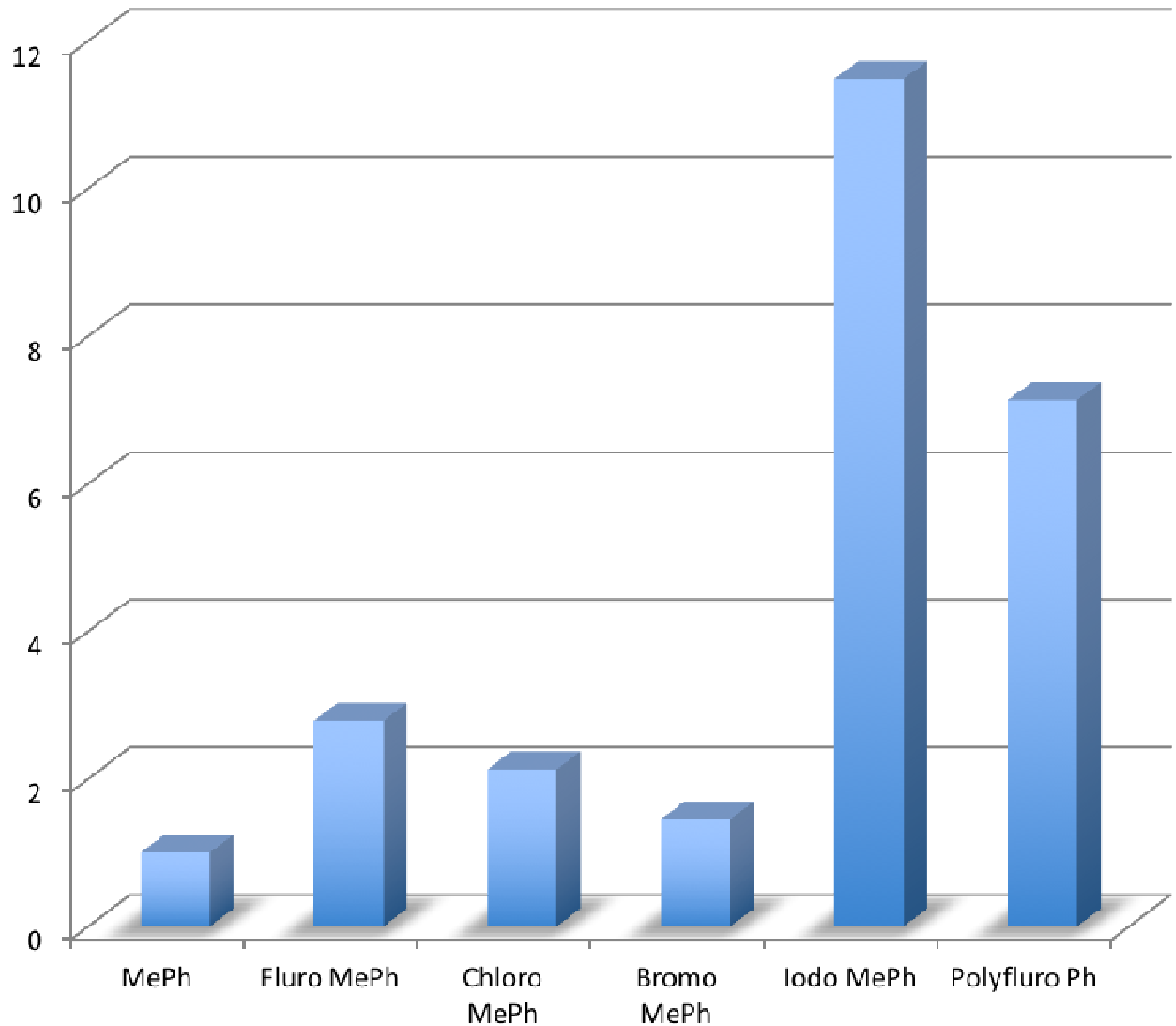


Variable Photon Energy

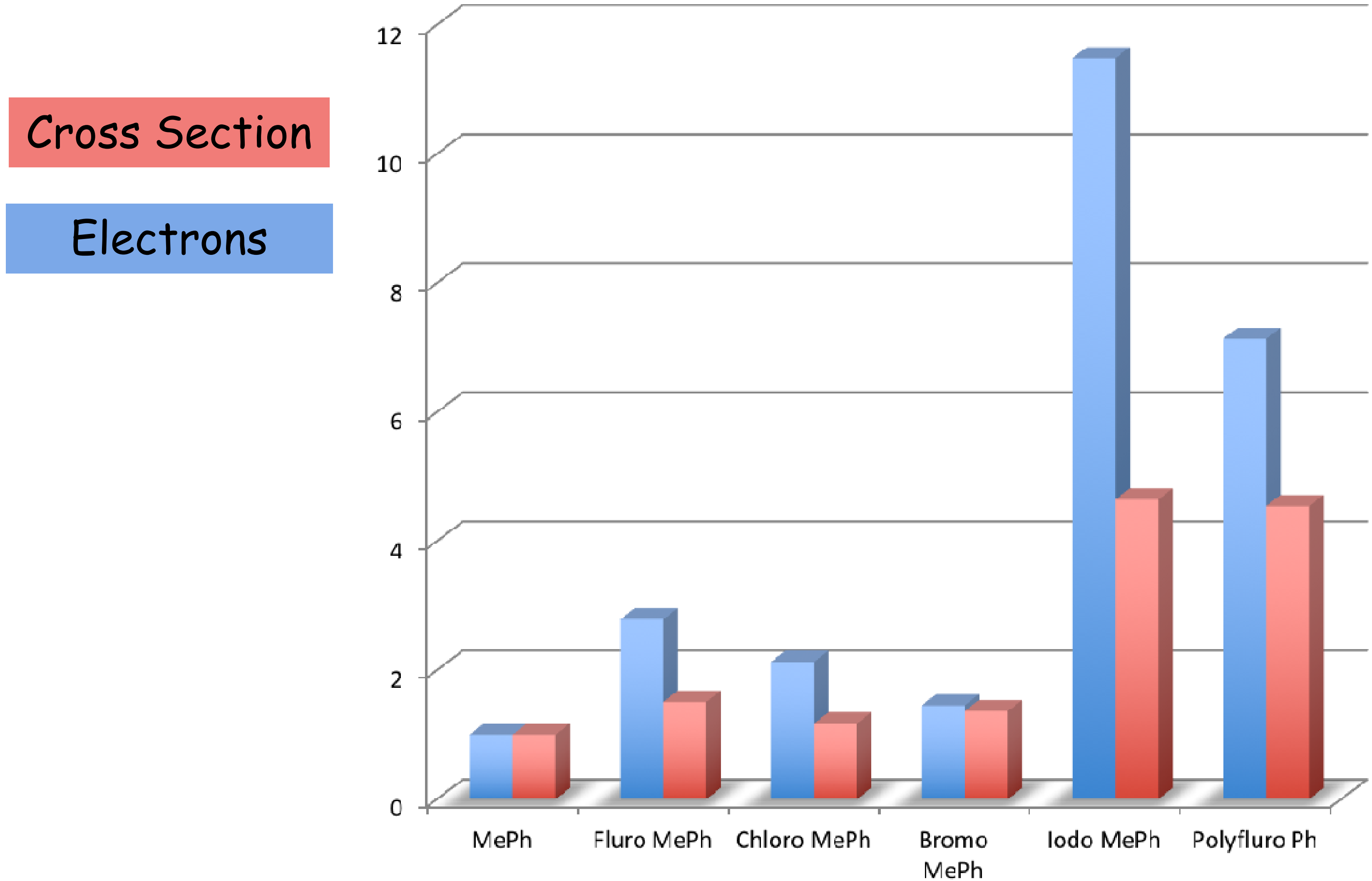




Per-Molecule Electron Yield



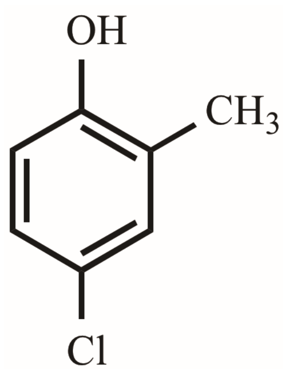
Yield and Cross Section

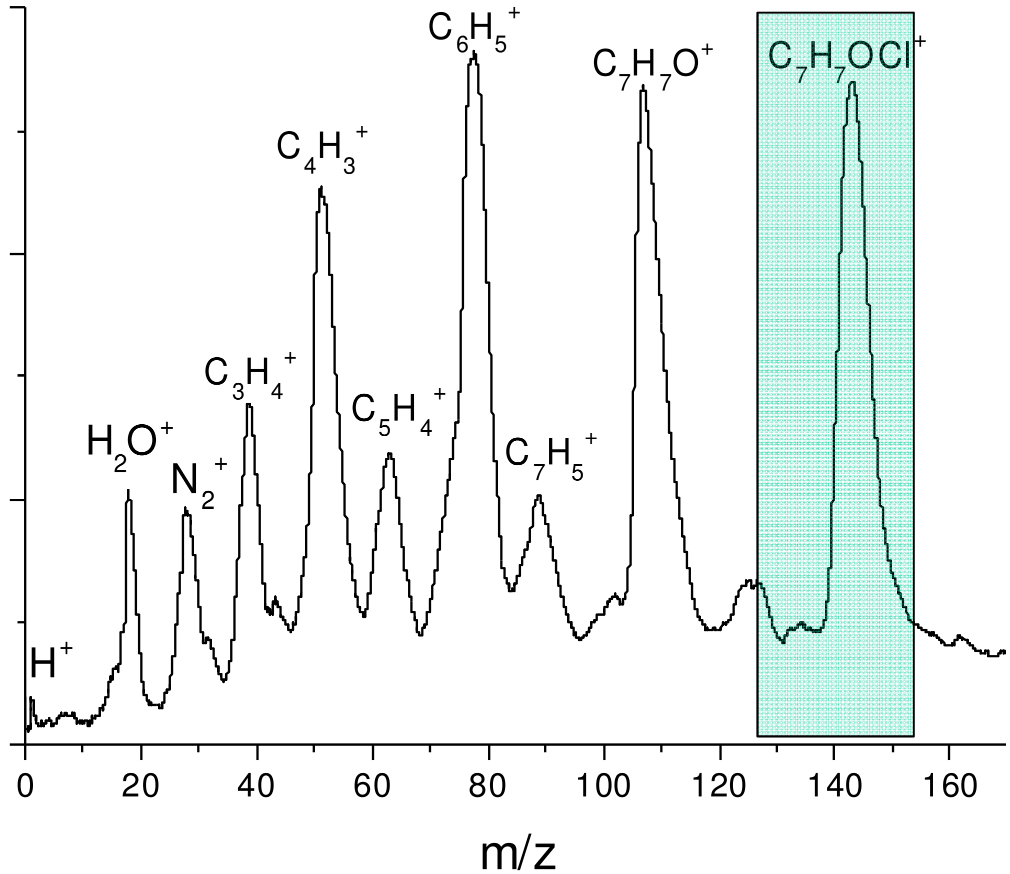


Summary: Electrons

- Electron yield per molecule can be significantly ***increased*** by incorporating high cross-section atoms
  - Iodo-methyl Phenol ~ 10x
  - Fluro-methyl Phenol ~ 1.5 x
- Photoemission can create ***more than 2 electrons*** per molecule through Auger relaxation
  - Energy distribution is changed, can be two ~ 35 eV electrons instead of one ~ 80 eV electron
- Is this better or worse for pattern transfer ??
  - Better photon statistics
  - Can lower energy SEs reduce electron blur ?
  - Can multiple electrons drive "multi spur" chemistry ??
  - Can resist chemistries be tailored to exploit EUV photoemission?

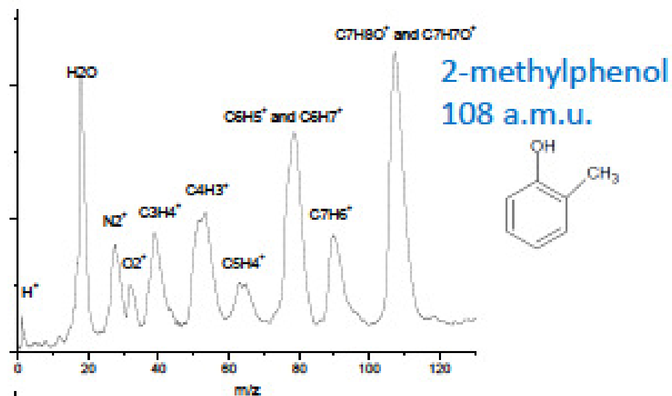
VMI Mass Spec

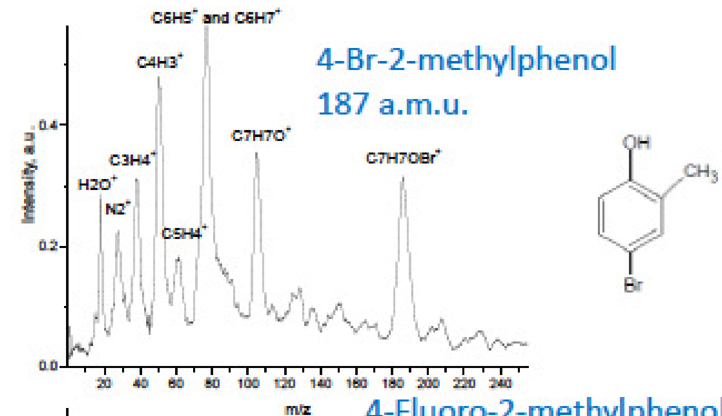


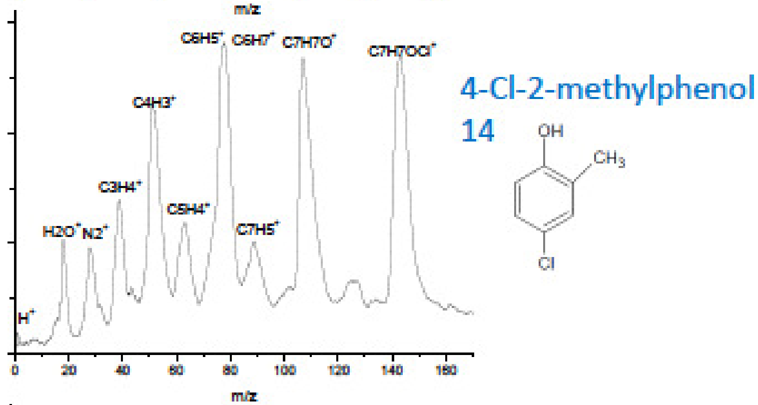


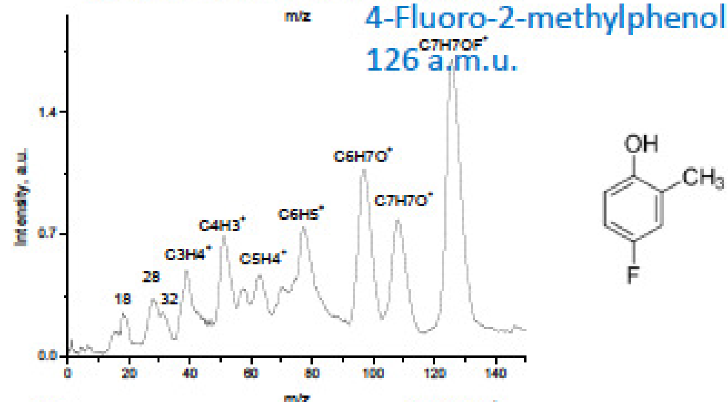
Chloro-Methyl Phenol Fragmentation by EUV photons

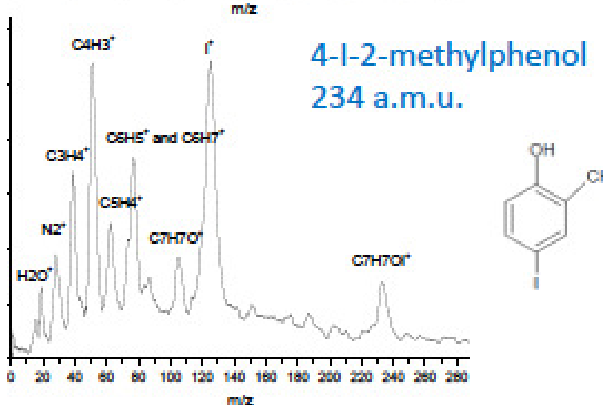
EUV Fragmentation Patterns

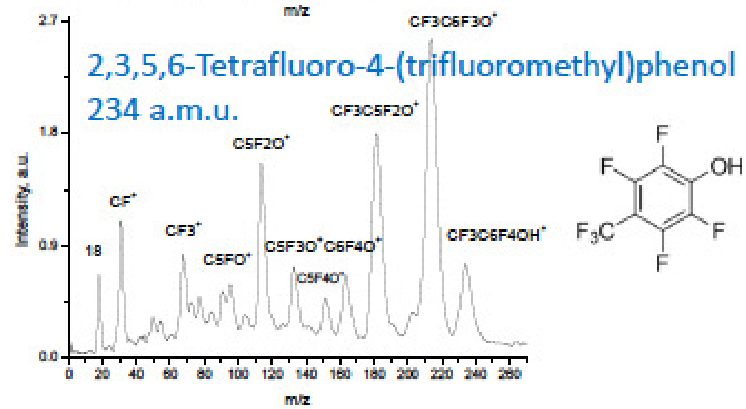




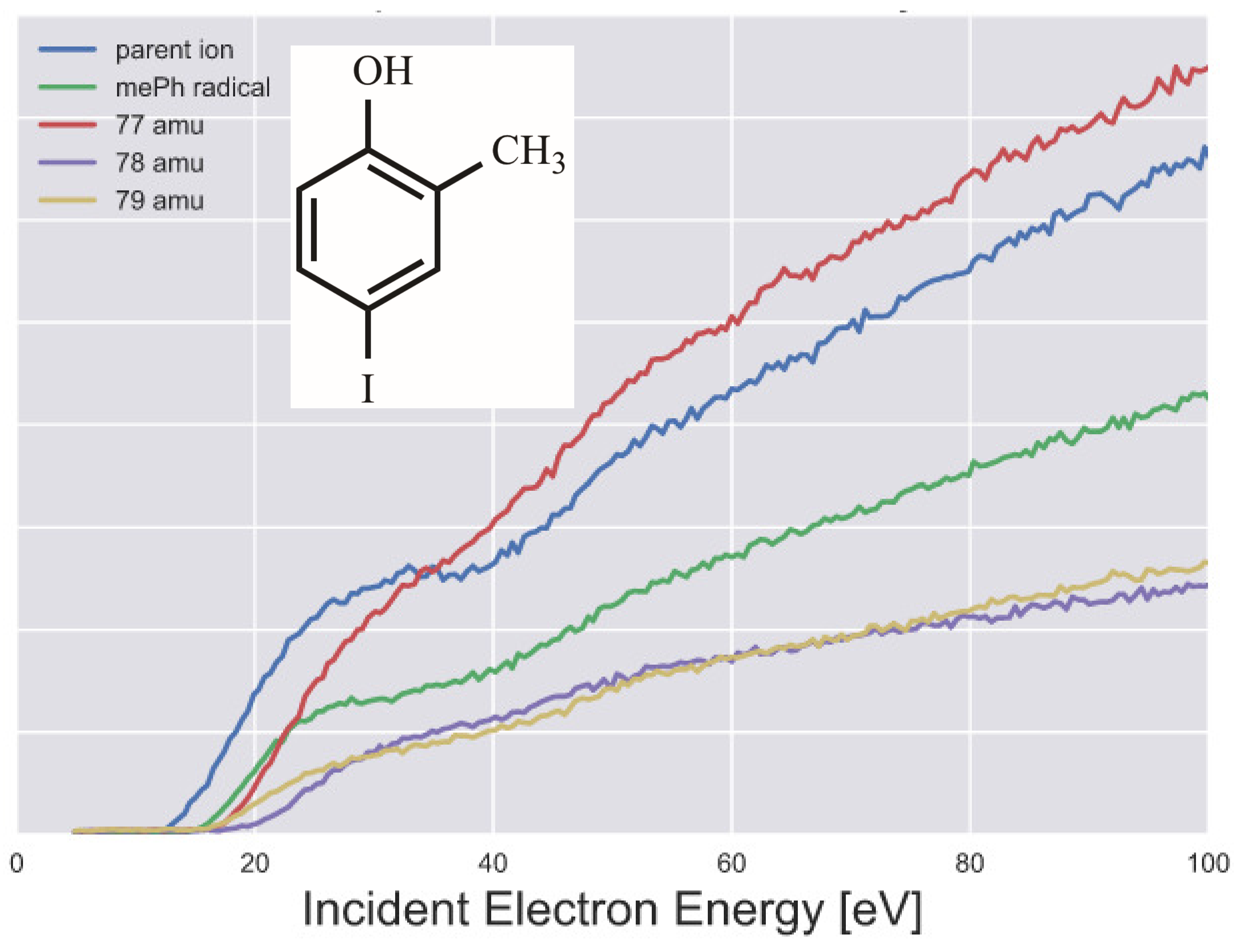






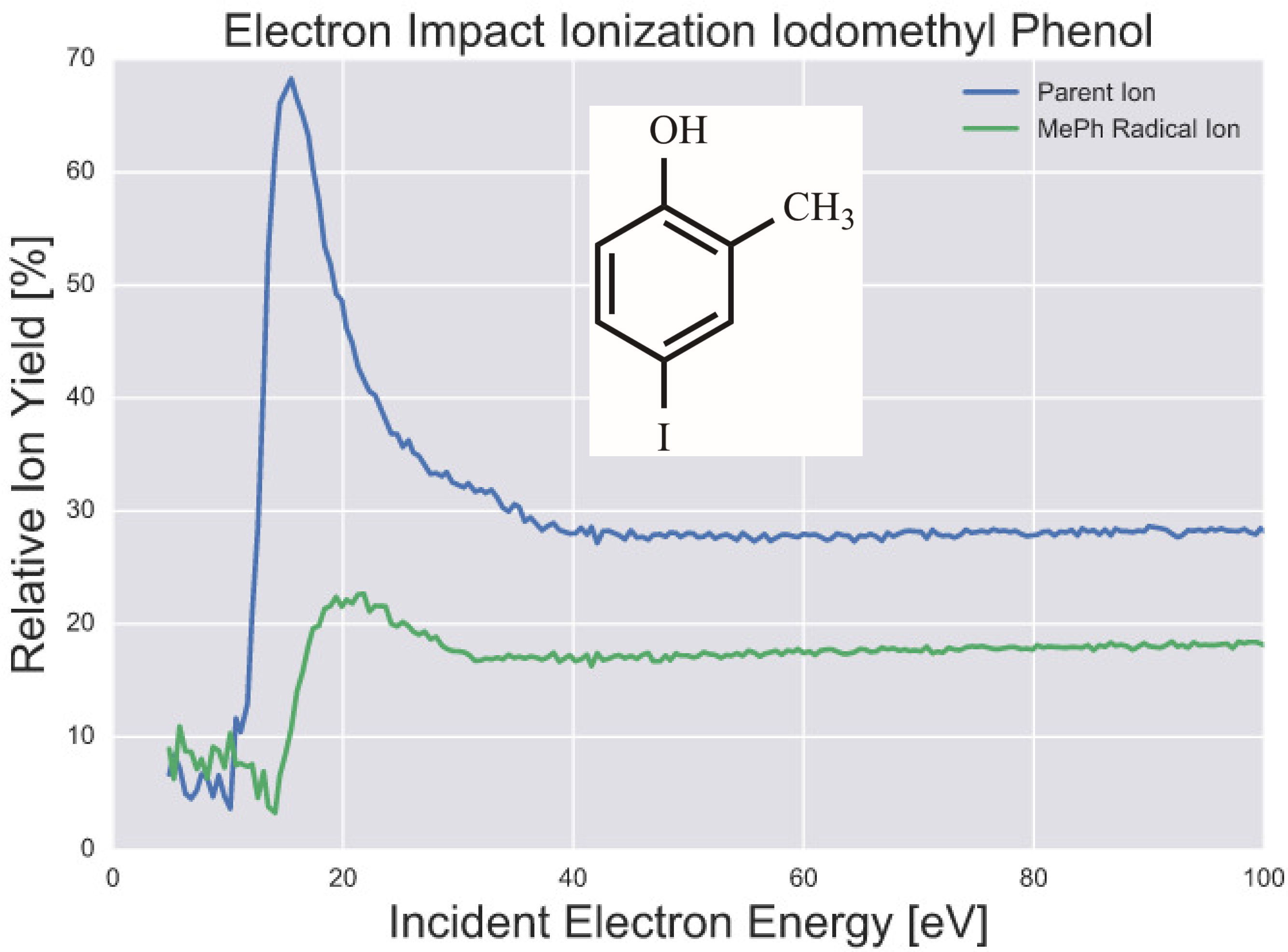


Electron Impact Ionization



MOLECULAR FOUNDRY

Relative Ion Yield



Summary: **Ions**

- EUV photoabsorption ***fragments*** molecules
  - Parent ion generation less than ~ 10%
  - Radicals, excited-state ions and small molecules are generated
- Auger relaxation will ***always*** fragment molecules

- Can Secondary Ions be exploited to drive pattern formation?
- H^+ can be directly generated in the ***primary*** event
  - Should with think about "XAG", x-ray acid generators?
  - Is there a way to provide solvating anions for acid catalysis?
- Can the simultaneous, localized generation of electrons and ions be exploited?

Gas vs Solid Experiments ?

Gas Phase Molecules

- Quantitative photoemission and absorption cross sections for each molecular component
- Electron yield and energy spectrum, Auger relaxation
- Ion yield and mass spectrum, fragmentation patterns

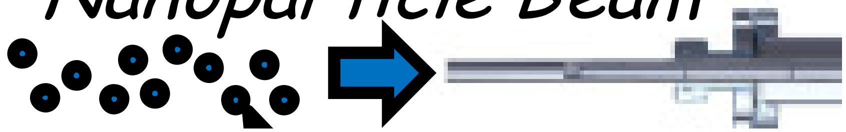
- Variable photon energy photoemission at the synchrotron
- Electron-molecule interactions, dissociative electron attachment

Condensed Films

- Molecular structure and bonding almost unchanged
- Photoemission lines broadened, dielectric film reduces energies ~ 5 eV
- Film photoemission mixed with inelastic losses, all molecules contribute, only near-surface region detected
- Reaction cascade, transient electrons/ions/radicals decay or react in fs to ns to us, very hard to detect
- Some reaction products stable (latent image)

Outlook: Beyond Small Molecules

Nanoparticle Beam

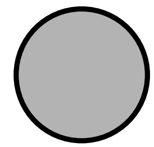


Aerodynamic lens for larger particles

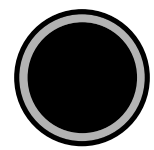
Nebulizer or Electrospray Ionization for smaller particles and large molecules

Nanoparticles:

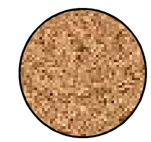
uniform



core-shell



50-500nm



polymer resist particle

Continuous change from small molecule to condensed phase, add complexity

Damage free characterization with molecular or aerodynamic beam

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