Interaction of Iron pentacarbonyl with multiply charged ions

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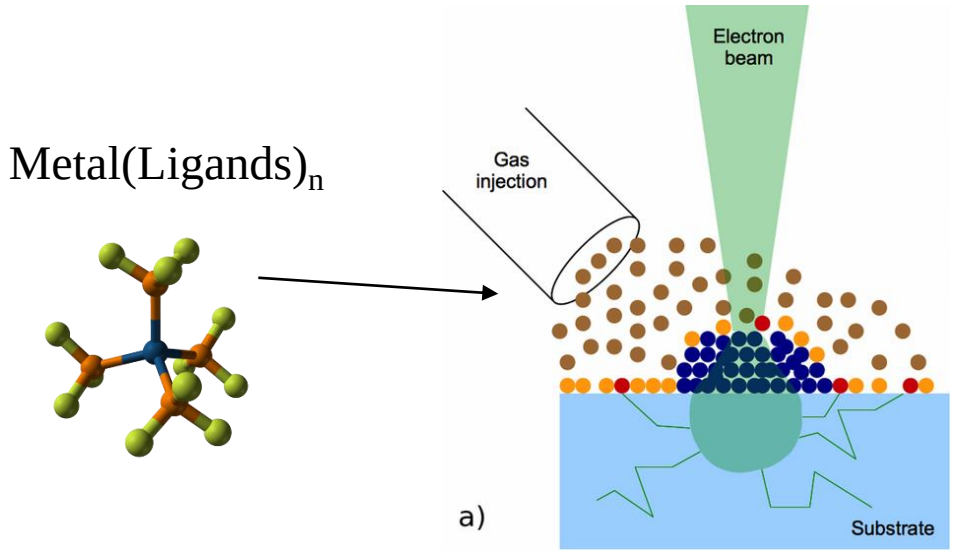
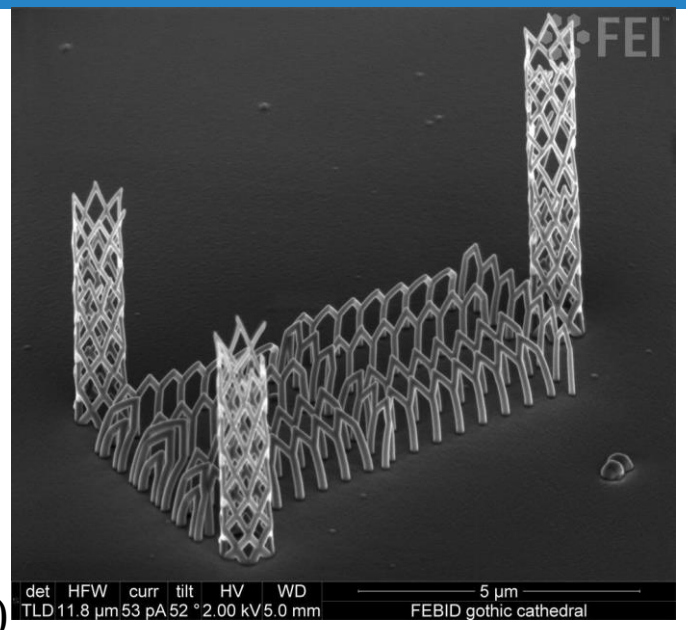
Electron and ion beam induced processes

- Study of electron and ion beam induced dissociation is important from fundamental and application point of view.

- Electron and ion-beam induced deposition – nanofabrication is one of the important applications.

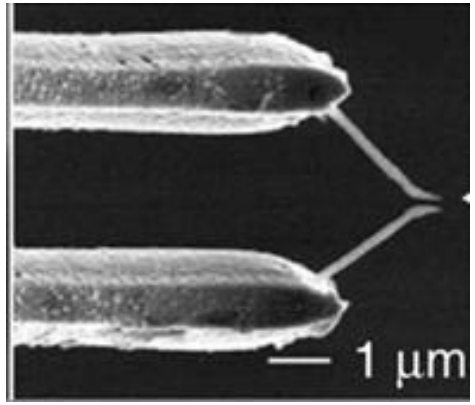
Focused beam nanofabrication





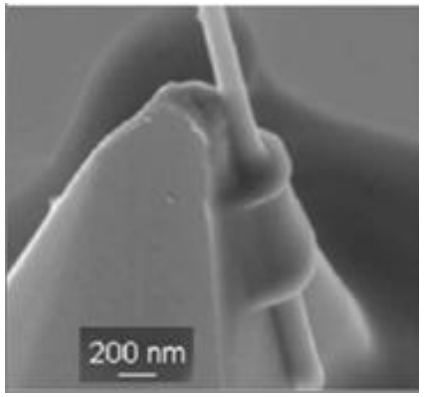
FEBID = focused electron-beam induced deposition (traditional)
FIBID = focused ion-beam induced deposition (emerging field)

Nanotweezers



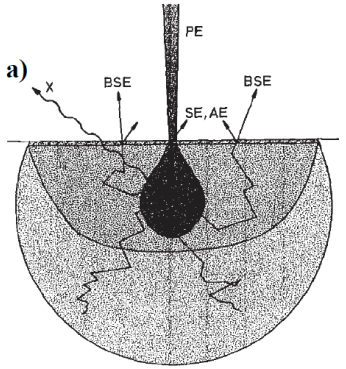
Pyramid connecting four electrode

Clamp to fix nanowires



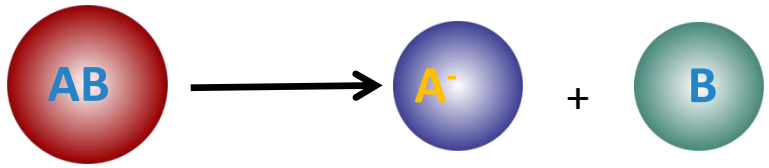
Reviews: Utke et al., *J. Vac. Sci. Technol.* 2008, Thorman et al., *Beilstein J. Nanotechnol.* 2015

Role of secondary low-energy electrons

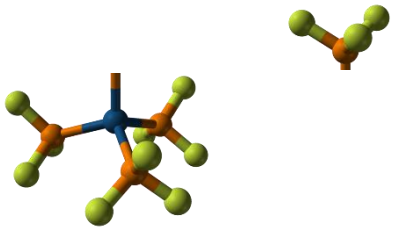


Lau et al. *J. Vac. Sci. Technol*. A, 20, **2002.**

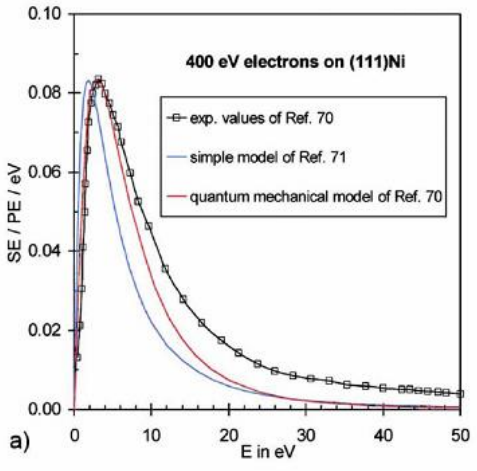
e^-



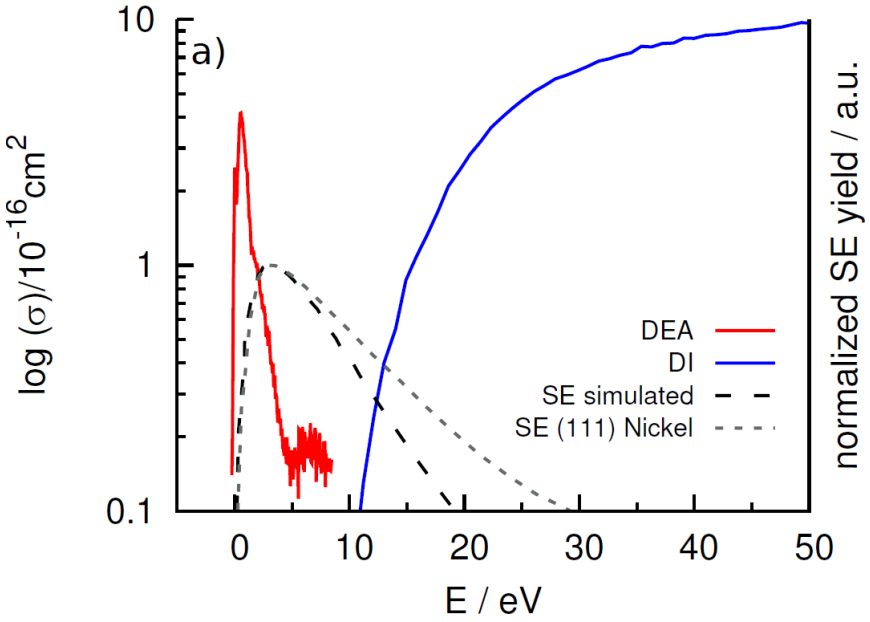
$[Metal(Ligands)_{n-1}]^-$



TNI

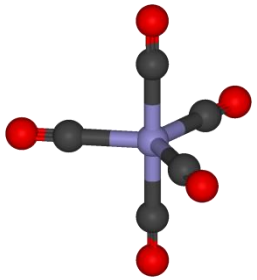


I. Utke et al., J. Vac. Sci. Technol. B 26 (2008) 1197



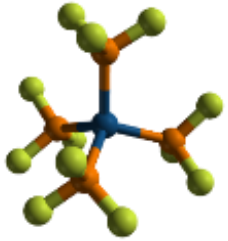
Precursor Molecules

Iron



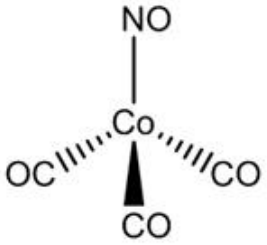
$Fe(CO)_5$

Platinum



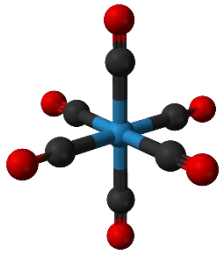
$Pt(PF_3)_4$

Cobalt



$Co(CO)_3NO$

Tungsten

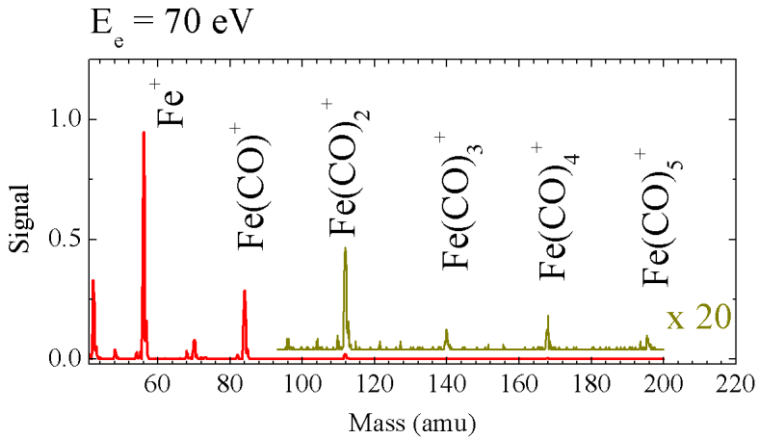


$W(CO)_6$

...

Electron – induced chemistry in $Fe(CO)_5$ (gas phase)

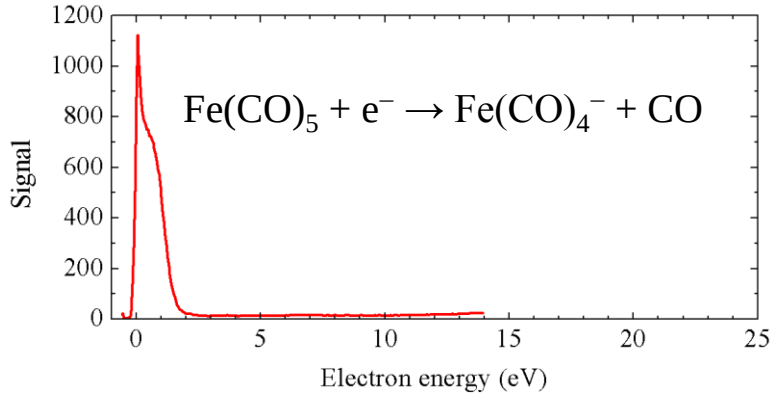
- Electron impact ionization – very fragmentative



J. Lengyel et al.
JPCC 2016

- Dissociative electron attachment

  - Very low electron energies (< 1 eV)
  - Cleaves only one metal-ligand bond
  - Very high cross sections



$Co(CO)_3NO$

S. Engmann et al.,

ACIE 2011

$Pt(PF_3)_4$

O. May et al.,

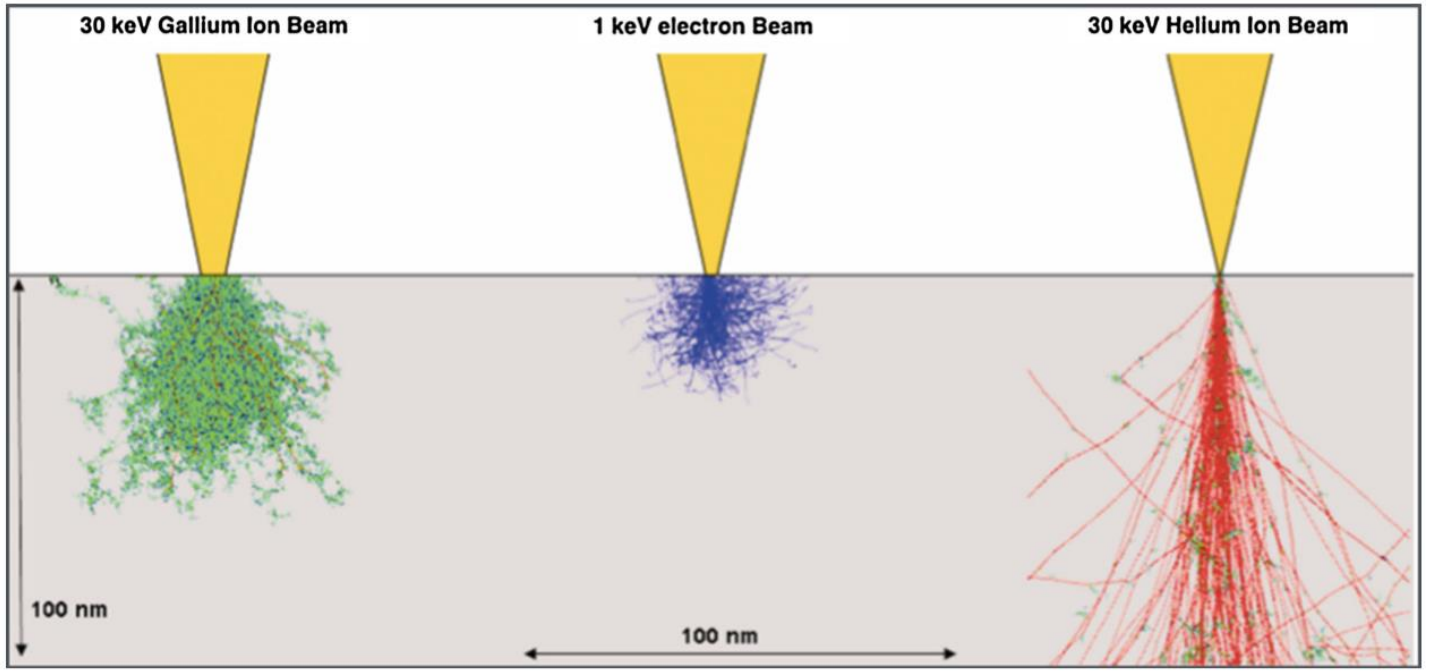
PCCP 2012

Back-draws of FEBID

➢ Problems of FEBID:

- Spatial resolution much worse than it could be
  Deposits – few beam diameters wide –
  low energy secondary electrons

- Purity of the deposits
  Metal content typically 15 to 75 %
  (incomplete dissociation of precursor)



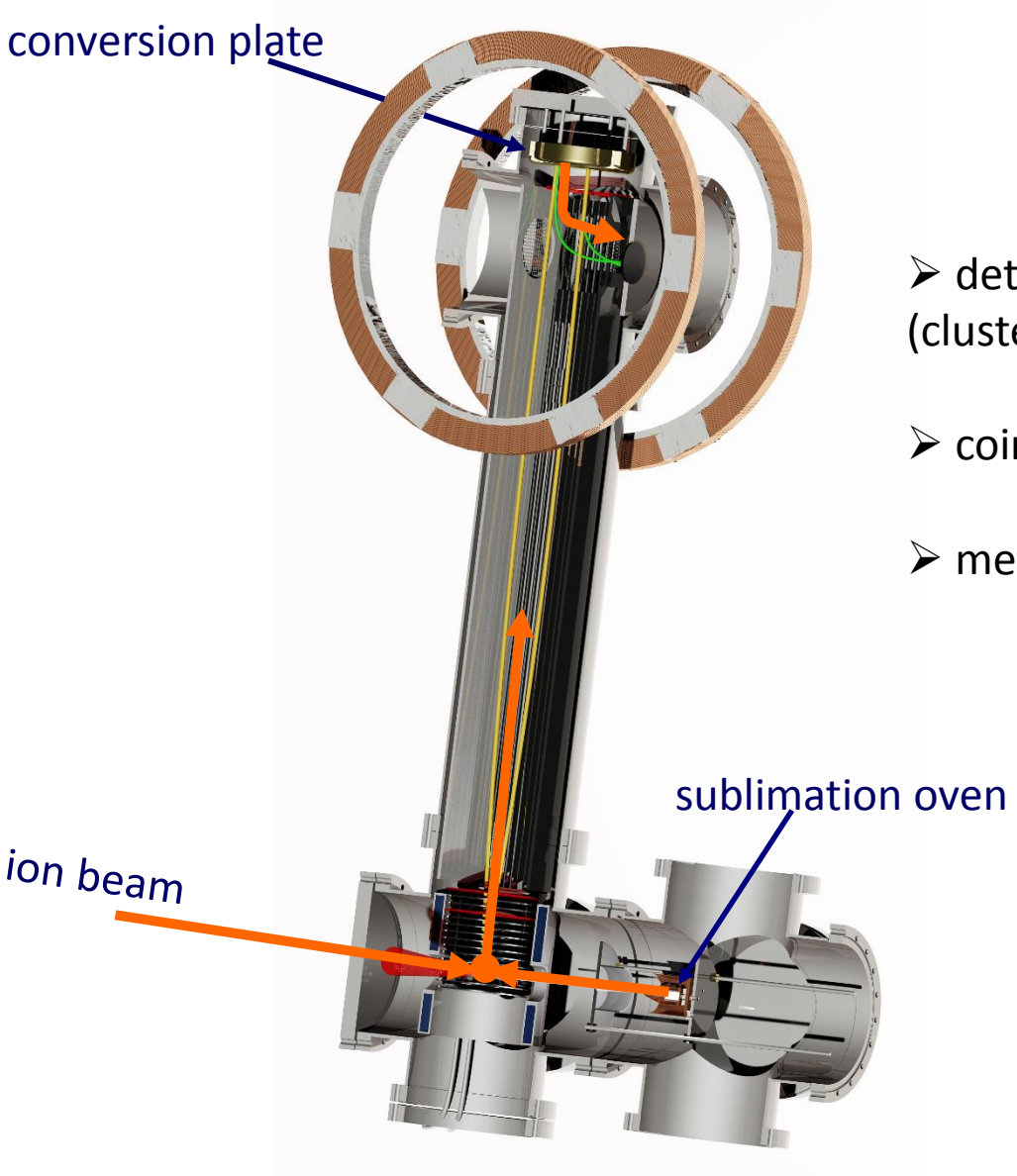
Alkemade and Miro, Appl. Phys. A (2014)

➢ Alternative – use of focused ion beam

- Focused ion beam induced deposition is becoming an important tool.

- Spread of secondary electrons interacting with precursor molecule is low.

COLIMACON TOF mass spectrometer

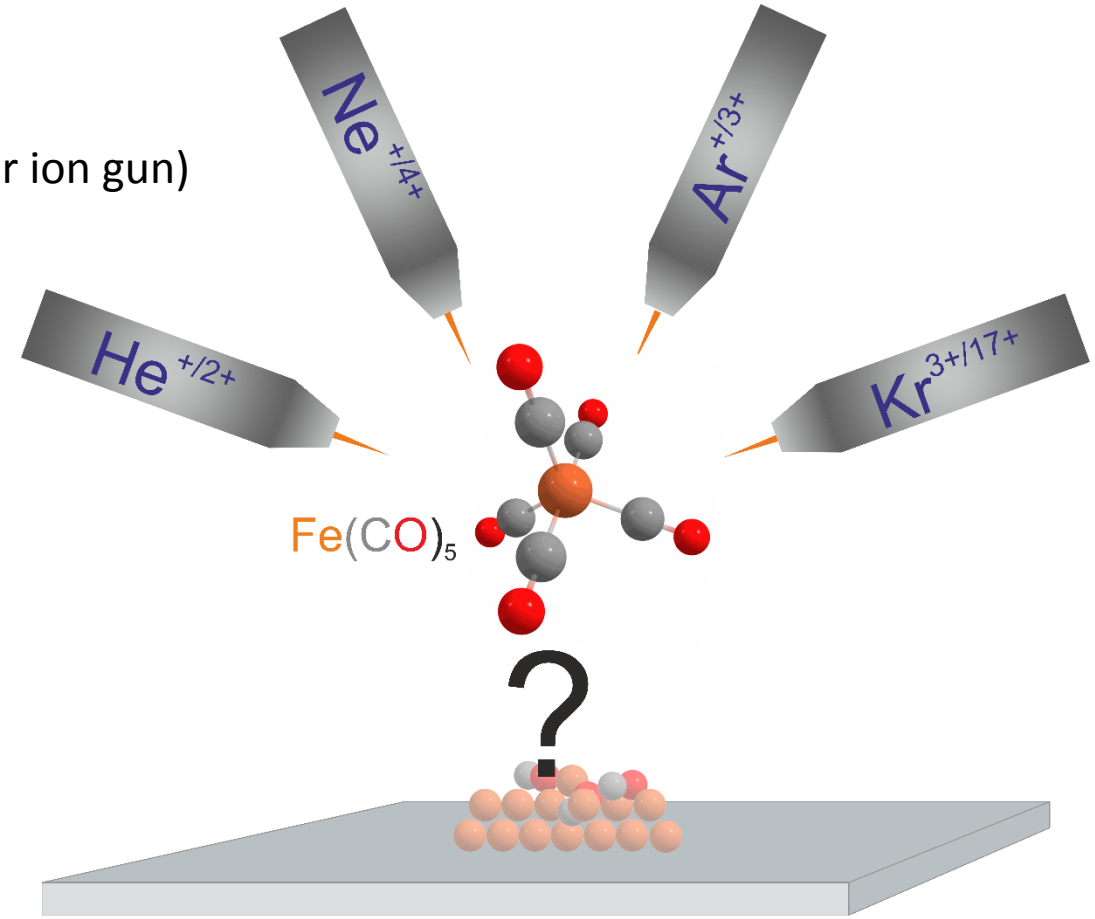


- detection of high mass fragments (clusters)
- coincident detection of fragments
- metastable ion detection

ARIBE low energy ion beamline at GANIL facility in CAEN, Fr

Current study

Single charge:
16 keV $^{4}He^{+}$,
6 keV $^{20}Ne^{+}$
3 keV $^{40}Ar^{+}$ (from Perkin Elmer ion gun)



Multiple charge:
16 keV $^{4}He^{2+}$,
40 keV $^{20}Ne^{4+}$
21 keV $^{40}Ar^{3+}$
12 keV $^{84}Kr^{3+}$
255 keV $^{84}Kr^{17+}$

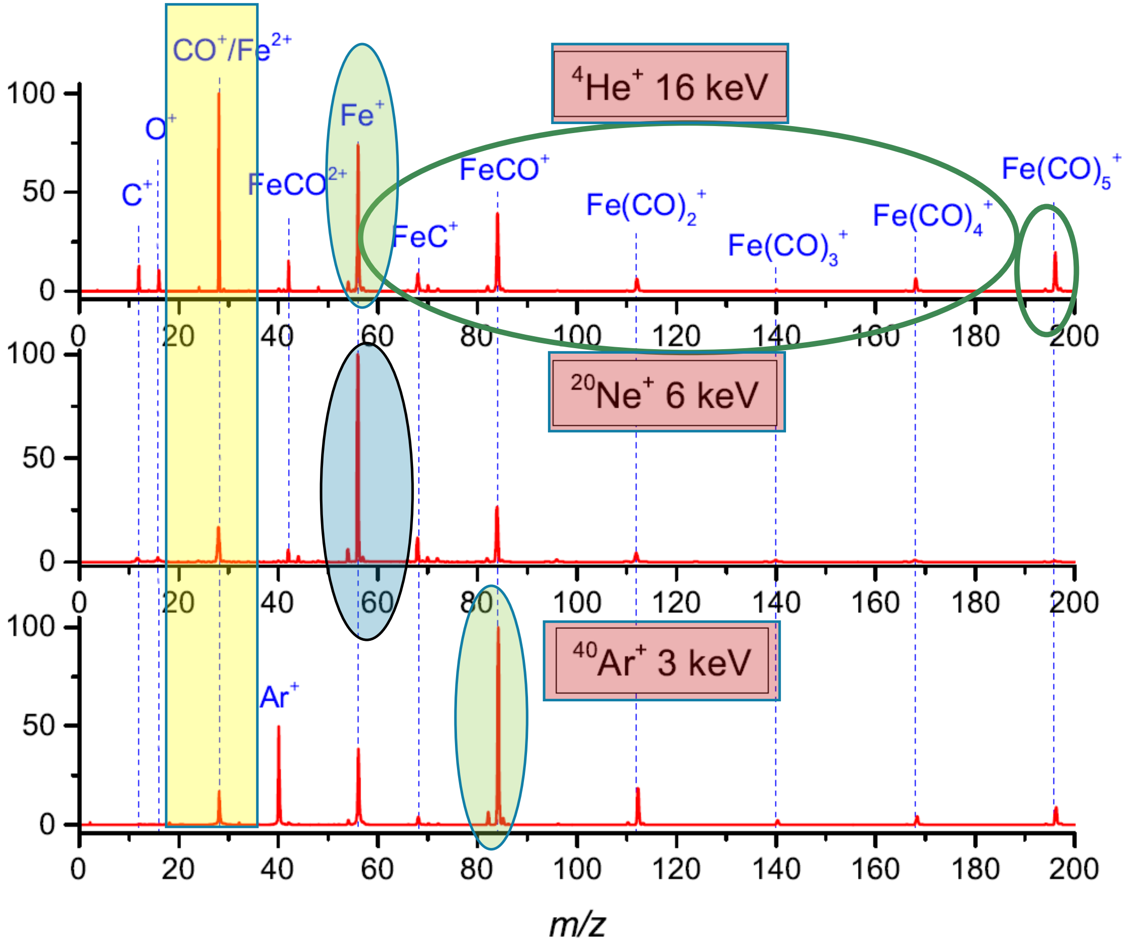
Ion beam-induced fragmentation

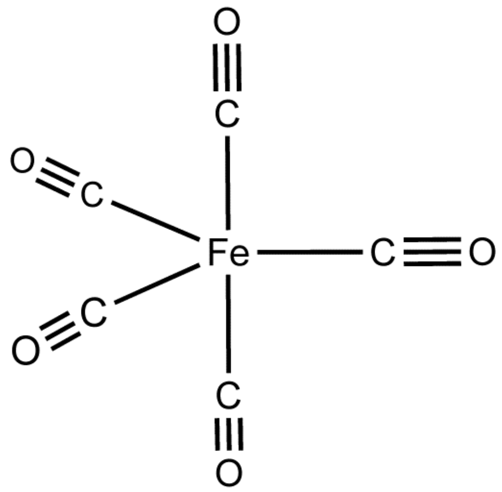
➢ Fragmentation can happen via different processes – depending on ion velocity, mass ratio and charge state

- Ion can interact with electronic cloud of the molecule
  - Electron excitation and electron capture

- Ion can interact with molecular nuclei
  - Vibrational excitation – Sufficient for emission of a nucleus

Interaction with singly charged ions



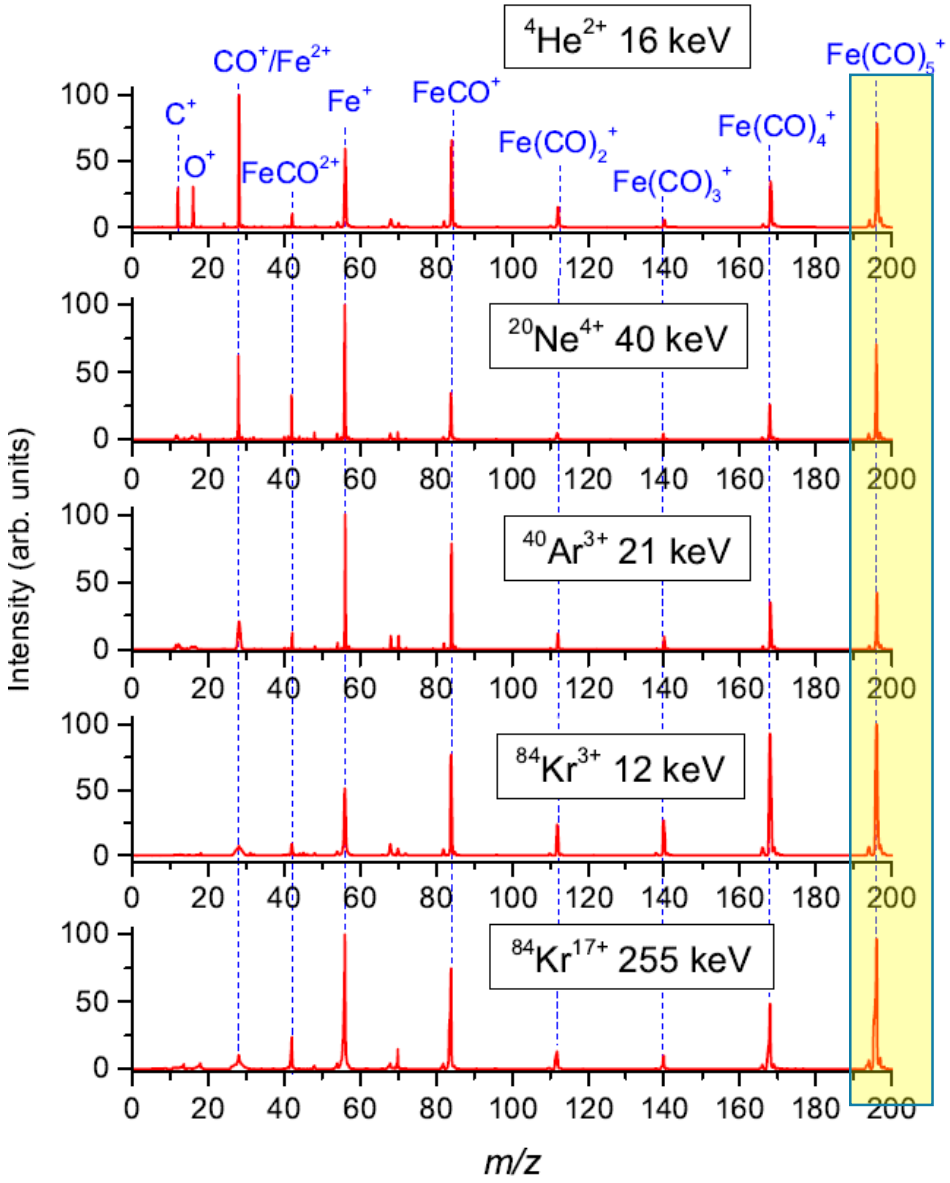


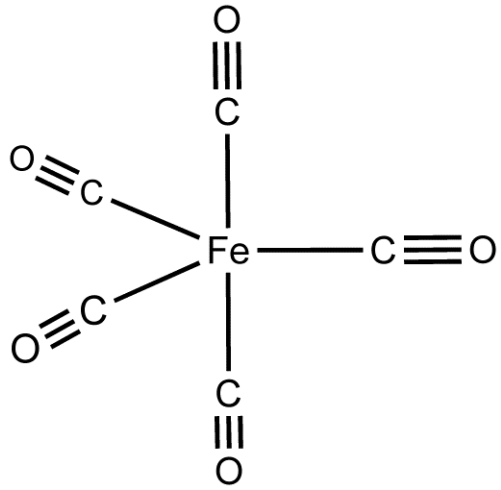
For He^+ projectile the electron capture is dominant process – recombination energy is 24.59 eV

Ne^+ with recombination 21.6 eV is heavier and slower – higher energy transfer – both electron capture and nuclear excitation plays a role

Ar^+ is dominated by nuclear excitation

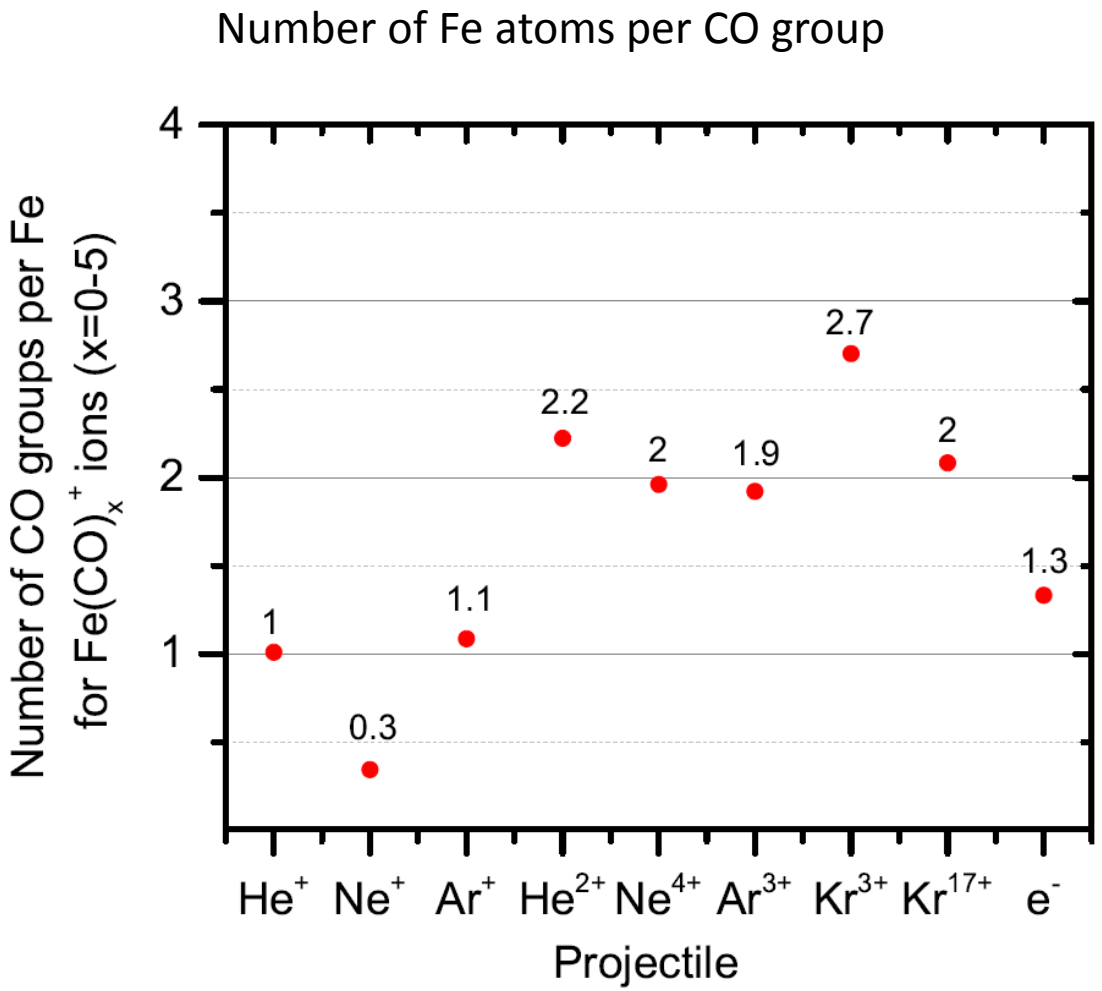
Interaction with multiply charged ions



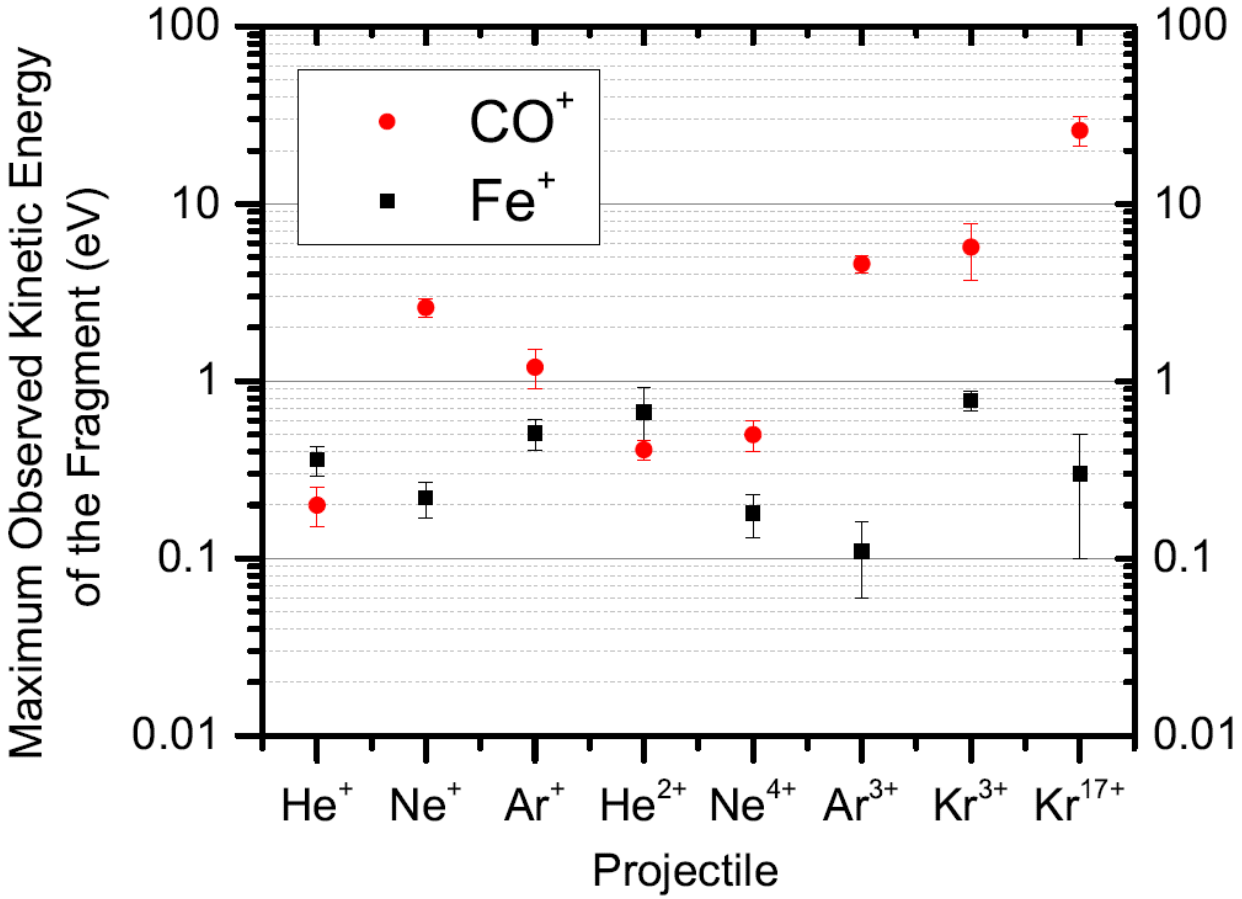


Electron capture at larger inter-nuclear distance – low energy transfer – more intact molecule

Fragmentation efficiency



Maximum kinetic energy of the fragment ions



Conclusion

- The kinetic energy of fragments almost independent of the ion energy – rather depends largely on the precursor molecule – Proper selection of precursor molecule is important
- $Fe(CO)_5$ is a potential precursor molecule to have less spatial spread due to low fragment kinetic energy.
- Singly charged $^{20}Ne^{+}$ ion beam is best projectile to produce purest metal deposition.

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Decomposition of Iron Pentacarbonyl Induced by Singly and Multiply Charged Ions and Implications for Focused Ion Beam-Induced Deposition

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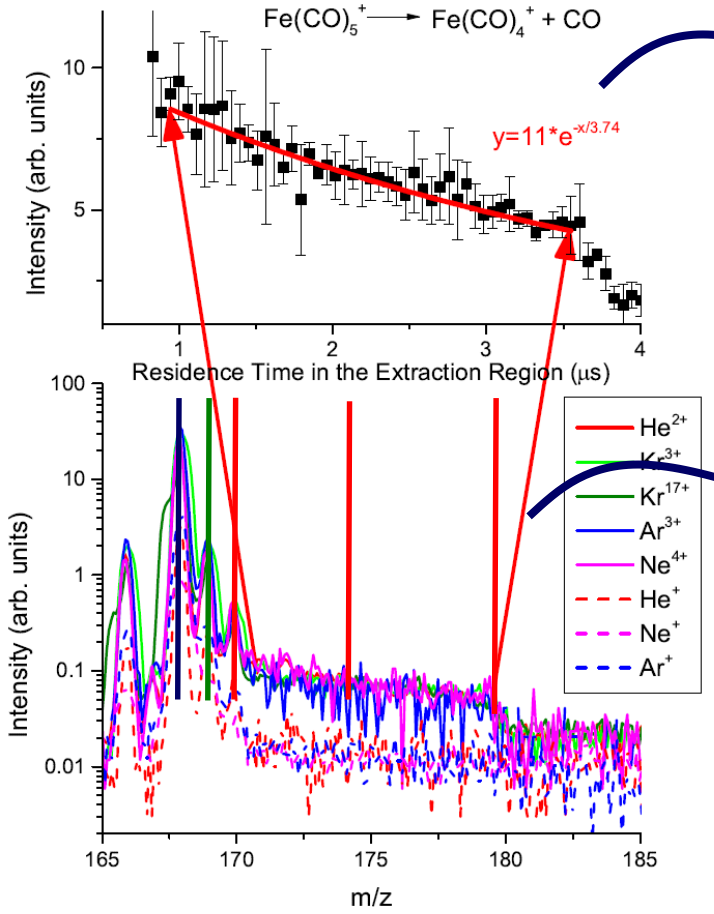
GANIL
laboratoire commun CEA/DRF spiral2 CNRS/IN2P3

French-Czech "Barrande" Nuclear Research Workshop

Thank You

Metastable ion decay

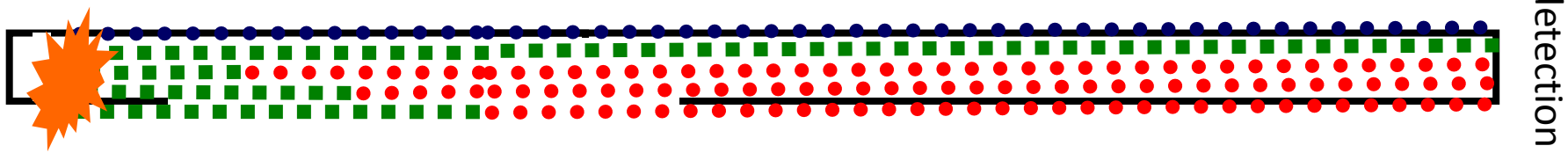


$Fe(CO)_5^+ \rightarrow Fe(CO)_4^+ + CO$

$\tau > 1\mu s$

Requires energetically stable cation!

TOF



E~240 V.cm^{-1}

E=0 V.cm^{-1}