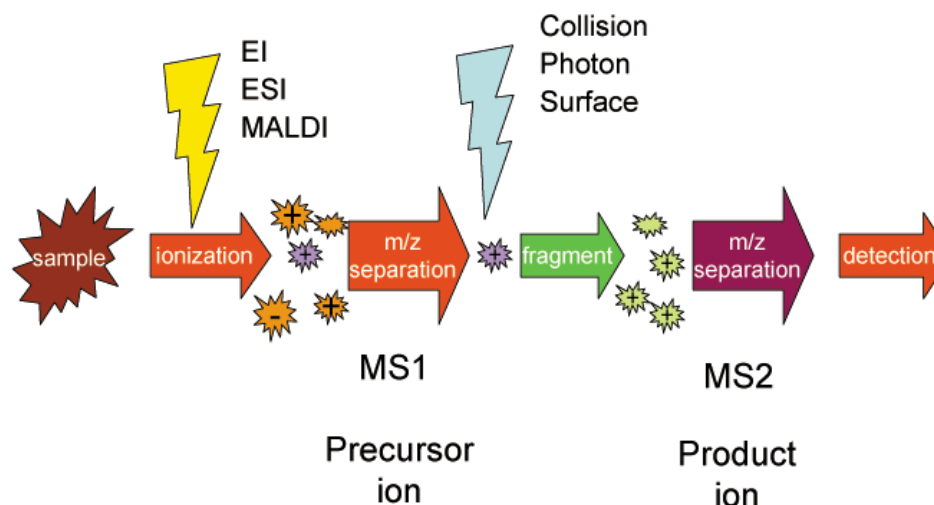




Tandem Mass Spectrometry (MS/MS)

Tandem Mass Spectrometry (MS/MS)

- ❑ **MS/MS:** A method that allows the mass spectrum of preselected & fragmented ions to be obtained.
- ❑ **Precursor ions:** A particular ion selected in the first mass analyzer.
- ❑ **Interaction cell:** The precursor ion is decomposed spontaneously or by the interaction with energy sources.
- ❑ **Products ions:** Fragment ions from the precursor ions.

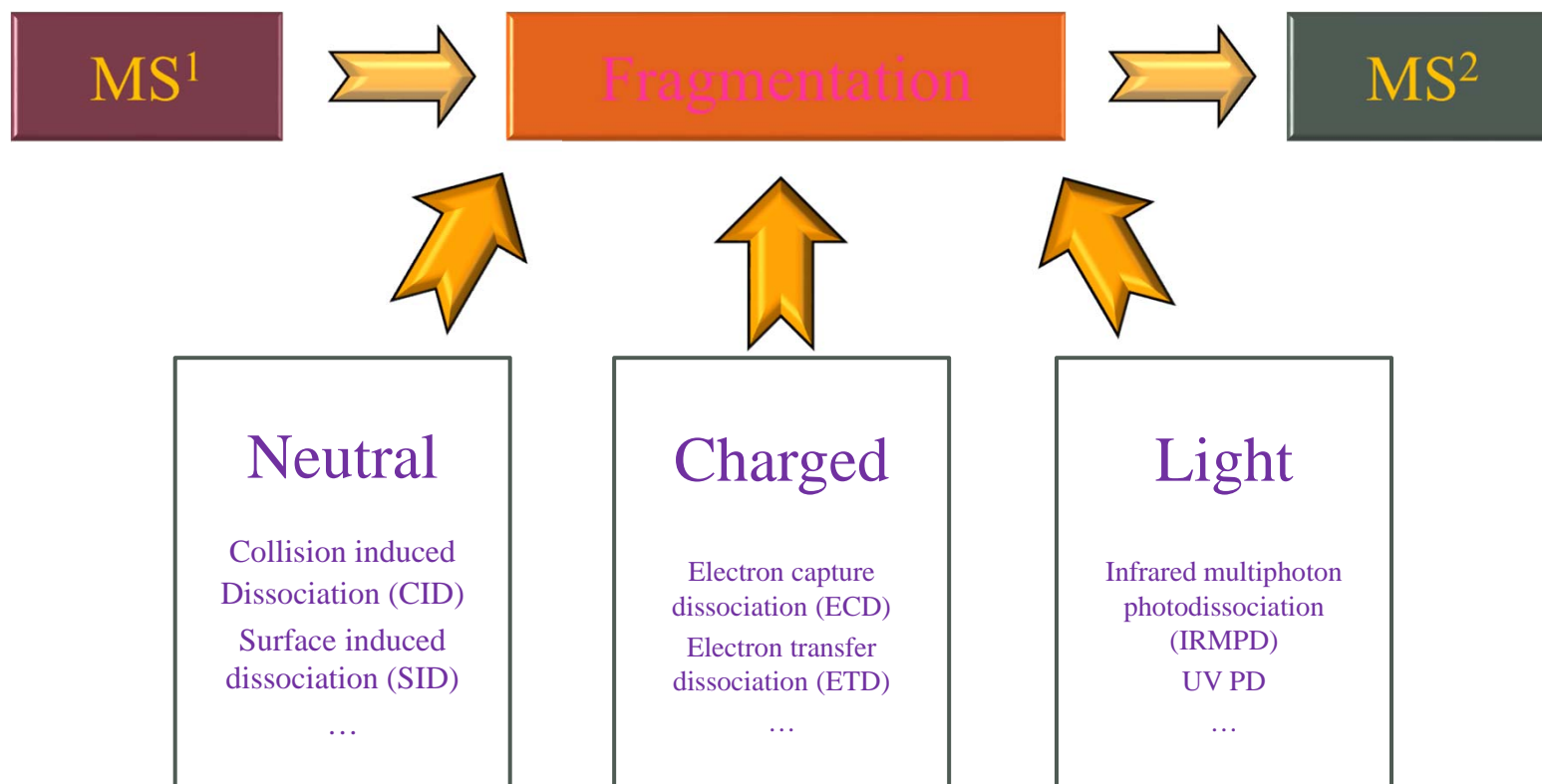


Block diagram of a tandem mass spectrometer.

http://en.wikipedia.org/wiki/Tandem_mass_spectrometry

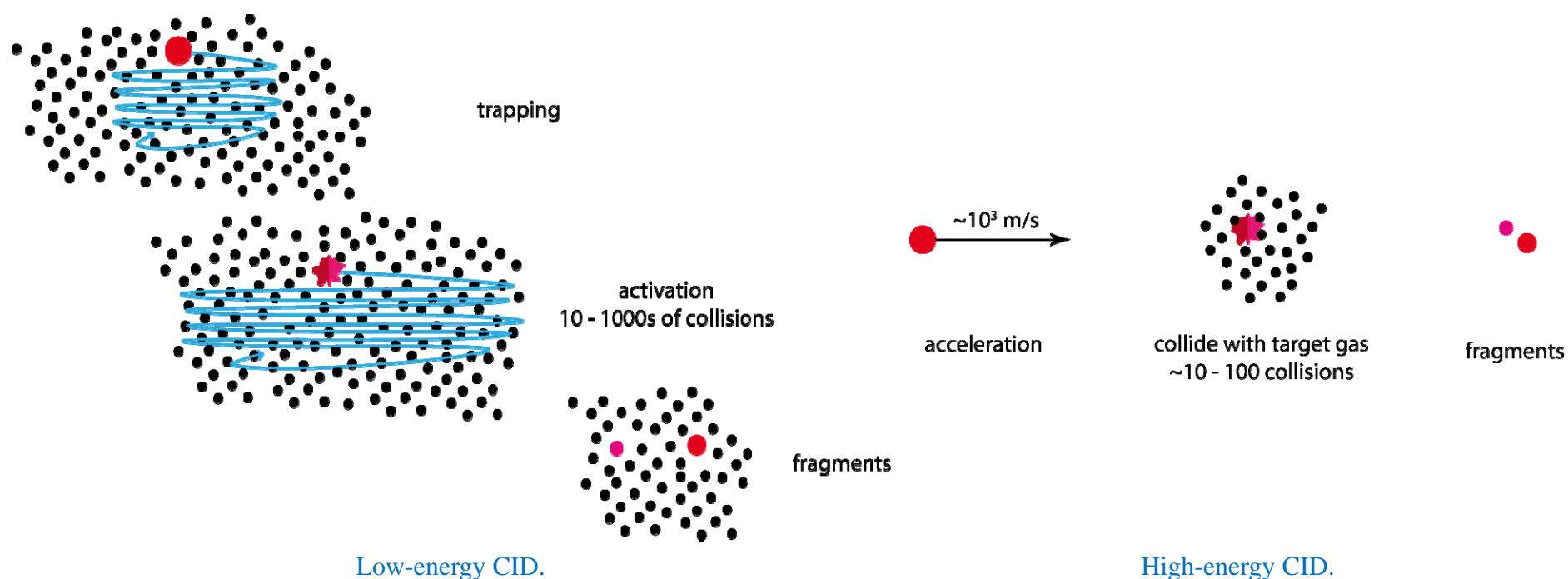
Ion activation methods

: Dissociative interactions in the interaction cell



Neutral

: Low-energy CID vs. high-energy CID



<http://www.lamondlab.com/MSResource/LCMS/MassSpectrometry/collisionalActivationMethods.php>

Three commonly used CID regimes

	HCD in QE		CID in LTQ
Figure of merit	“High-energy” CID (fast activation)	“Low-energy” CID (slow activation)	Trapping CID (very slow activation)
Instruments used	Magnetic/electric sectors, TOF/TOF	Tandem quadrupoles, quadrupole hybrids (e.g., QqTOF)	Quadrupole ion traps, FT-ICR traps
Collision energy	2–10 keV	1–200 eV	1–20 eV
Collision number	1–5	10–100	100 s
Activation time scale	1–10 μ s	0.5–1 ms	10–100 ms
Instrument time scale (kinetic window)/minimum observable reaction rate	10–100 μ s / 10^6 – 10^4 s ⁻¹	0.1–1 ms / 10^4 – 10^3 s ⁻¹	10 ms–1 s / 10^2 –1 s ⁻¹
Distribution of internal energy	Centered at a few electron volts, high-energy tail to tens of electron volts	Centered at few eV, no high energy tail	Centered at a few electron volts, may be Boltzmann or Boltzmann-like
Variability of internal energy	Relatively invariable, scattering angle provides some energy resolved info.	Readily variable with collision energy to obtain energy resolved info.	Some variability with collision energy and number
Efficiency	<10%	5–50%	50–100%
General results	High-energy channels may be accessed together with lower energy processes, sequential dissociation observed	Lower energy processes only, isomerization of precursor may occur, sequential dissociation observed	Low-energy processes only, extensive isomerization of precursor, very slow processes can be observed, typically little sequential dissociation

Charge

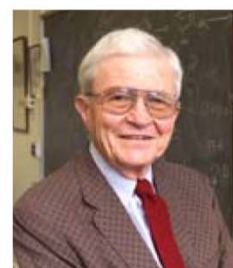
: Electron capture dissociation (ECD)



Roman A. Zubarev



Neil L. Kelleher



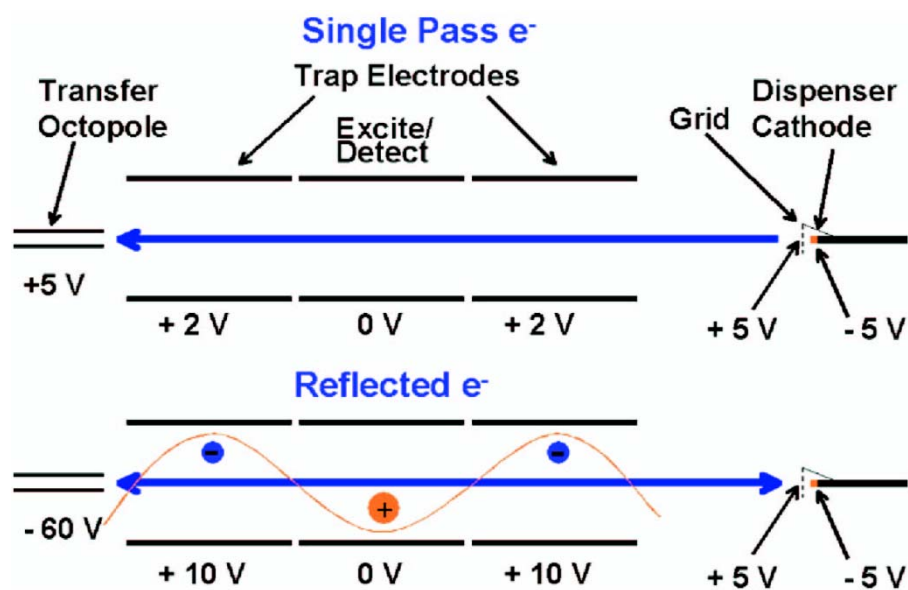
Fred W. McLafferty



Near Thermal Energy Electron

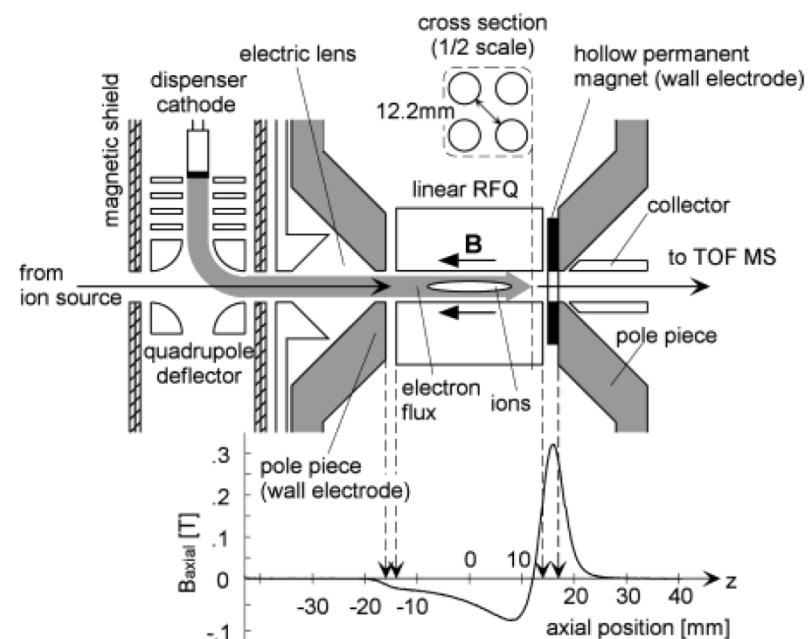
J. Am. Chem. Soc. (1998) **120**, 3265

ECD : Instrumentation



ECD in an FT-ICR cell.

J. Am. Soc. Mass Spectrom. (2005) **16**, 1060



ECD in a RF ion trap.

Anal. Chem. (2004) **76**, 4263

Charge

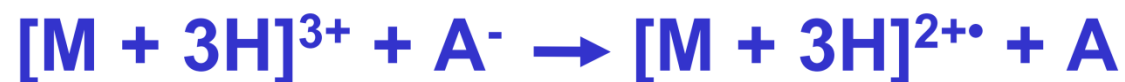
: Electron transfer dissociation (ETD)



Joshua J. Coon



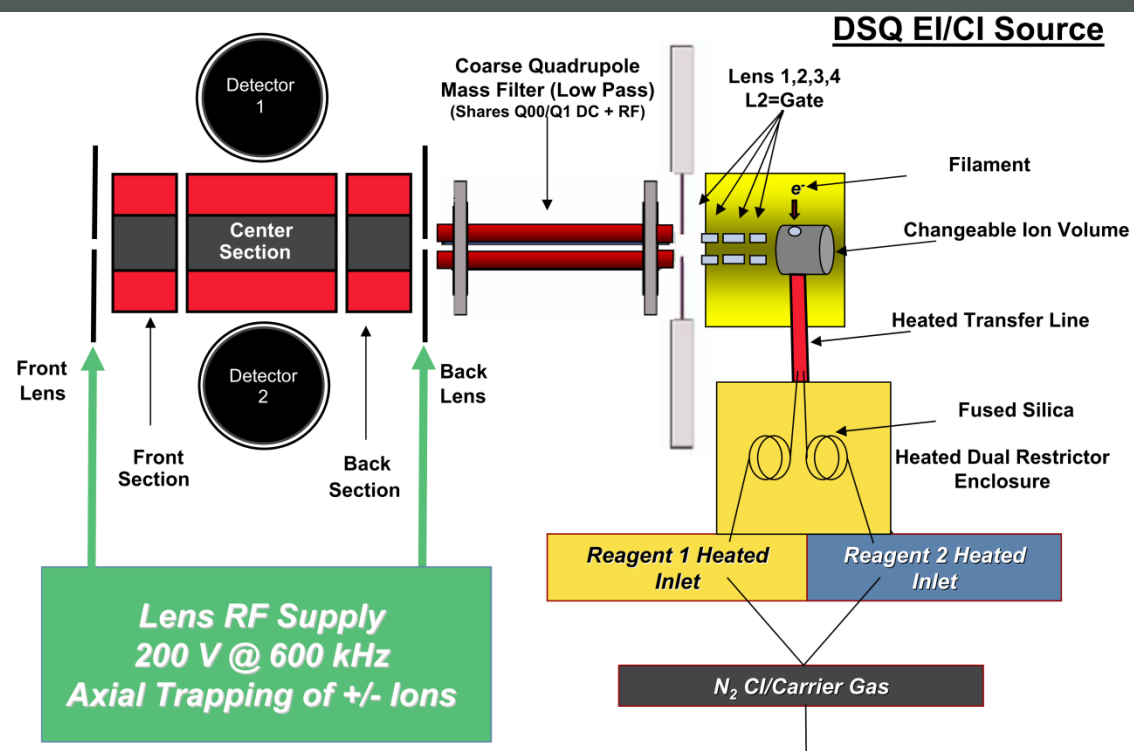
Donald F. Hunt



PNAS. (2004) **101**, 9528

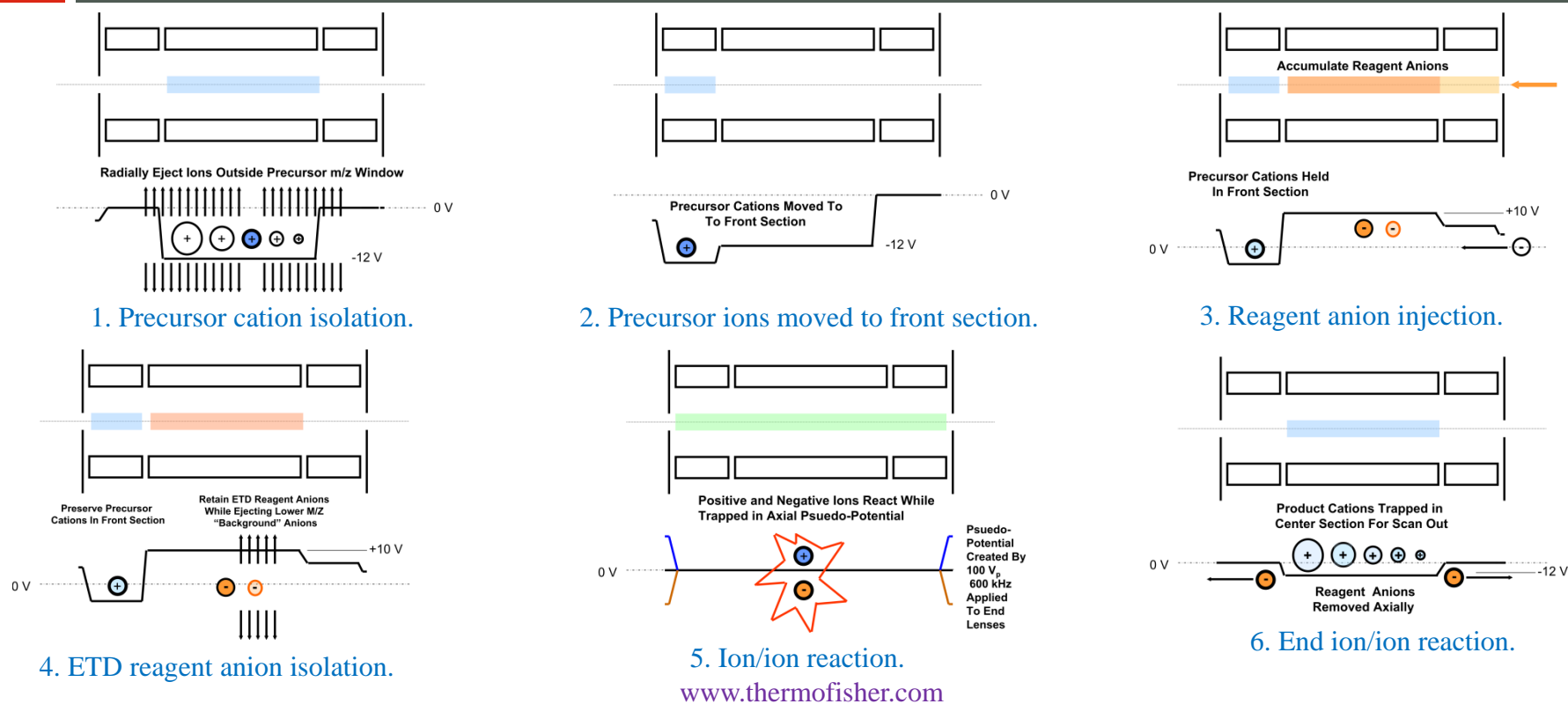
ETD

: Instrumentation in LTQ

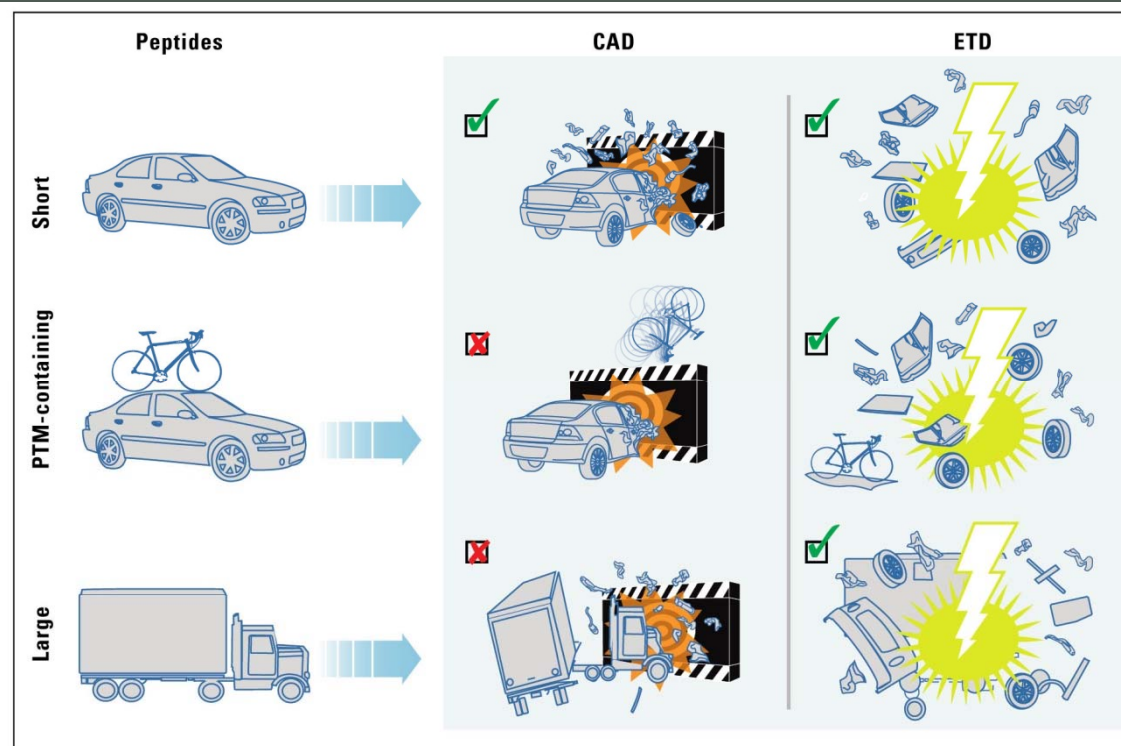


ETD

: Instrumentation in LTQ



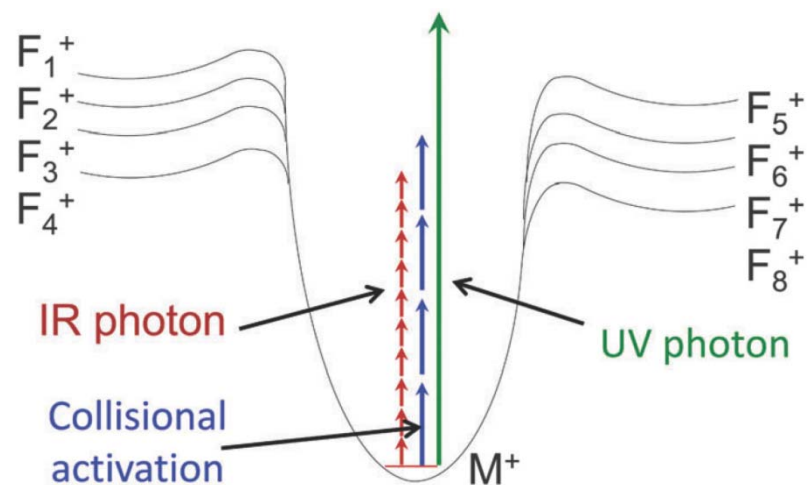
CID vs. ETD



Anal. Chem. (2009) **81**, 3208

Photodissociation

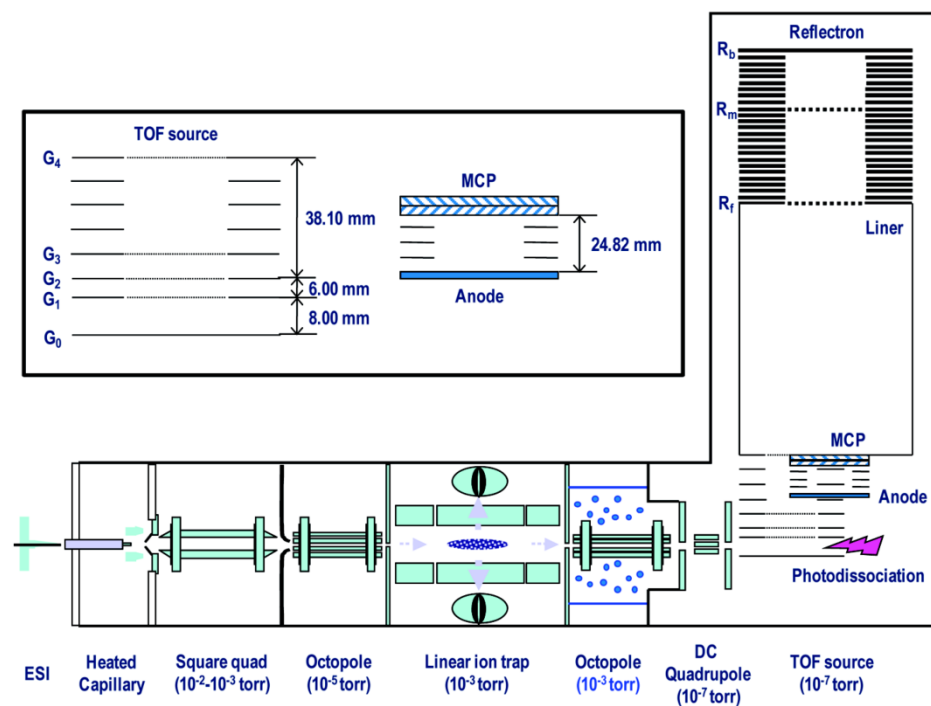
- Compatible with all types of mass analyzers.
- Deposits a well-defined energy into precursor ions.
- Uniform, selective photochemical fragmentation possible.



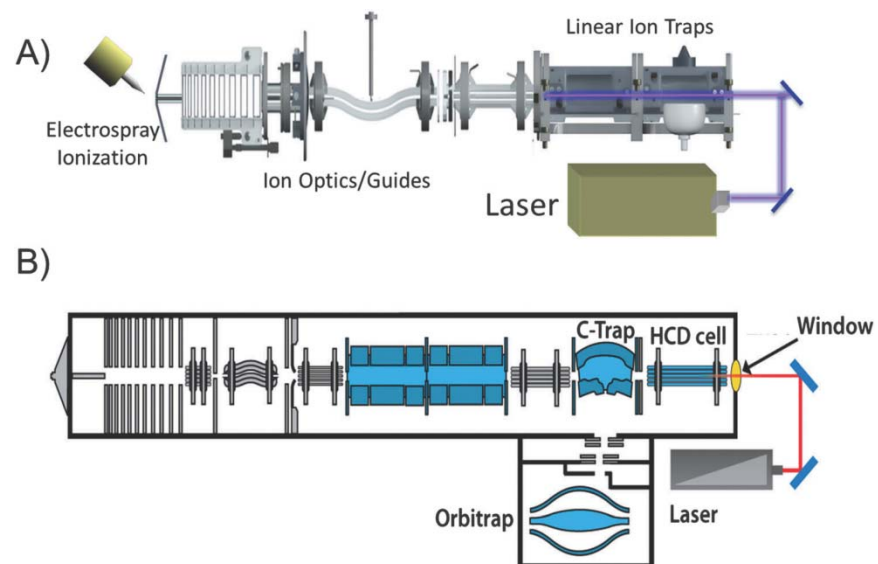
Energy diagram illustrating energy deposition by CID, IR & UV photon.

Chem. Soc. Rev. (2014) **43**, 2757

Photodissociation : Instrumentation



Anal. Chem. (2009) **81**, 8809



Chem. Soc. Rev. (2014) **43**, 2757