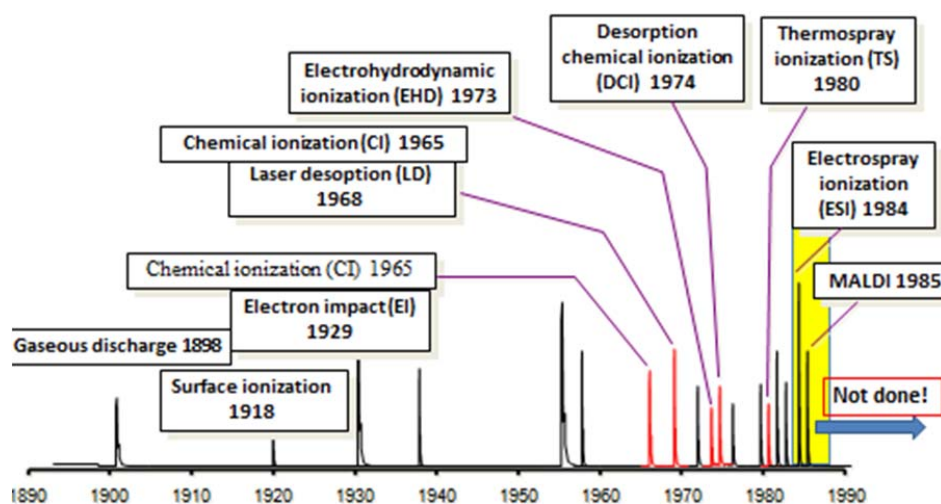


## Lecture 2 Ionization Methods : Electron Ionization

### Ionization Methods : Time Line



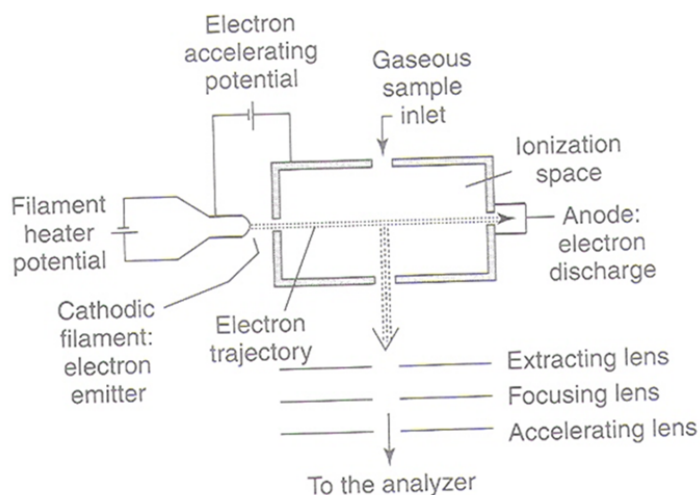
### Four Main Types of Ionization Methods in Molecular Mass Spectrometry

★	<b>EI</b> (Electron Ionization)	Energetic electrons	Vapors	EI	
	<b>CI</b> (Chemical Ionization)	Gas phase ions	Vapors	APCI	
	<b>SI</b> (Spray Ionization)	Electric field, nebulizing gas	Solutions	ESI	
	<b>DI</b> (Desorption Ionization)	Energetic particles, photons	Solids	MALDI SIMS	



## Electron Ionization (EI)

<b><i>Many events possible in an electron-neutral collision</i></b>	
<b>Excitation</b>	$e^{-} + A-B-C = A-B-C^{*} + e^{-}$ (not detected)
<b>Electron capture</b>	$e^{-} + A-B-C = A-B-C^{-}$ (rare, resonance)
<b>Electron ionization</b>	$e^{-} + A-B-C = A-B-C^{+} + 2e^{-}$
<b>Ionization with excitation of ion leading to fragmentation (simple cleavage and/or rearrangement)</b>	$e^{-} + A-B-C \rightarrow A-B-C^{+*} \rightarrow A + B-C^{+}$ $\rightarrow A^{\cdot} + B-C^{+}$ $\rightarrow A^{+} + B-C$ $\rightarrow A-C^{+} + B$ etc.
<b>Multiple Ionization (w/ or w/o excitation, dissociation, rearrangement, etc.)</b>	$e^{-} + A-B-C = A-B-C^{2+} + 3e^{-}$



Electron impact ion source

Gross, J. H. *Mass Spectrometry*, Springer: New York, 2004; de Hoffmann, E.; Stroobant, V. *Mass Spectrometry: Principles and Applications*, 2nd Ed; Wiley: New York, 2004.

### El Source

Developed by Nier in late 1930's

**Filament current:** 1 - 2 A (thermionic electron emission from Rh at 2000K)

**Electron emission current:** 10 - 100 mA

**Trap (anode) current:**  $10^{-4}$  A (control by feedback for quantitation)

**Ion current:**  $10^{-8}$  -  $10^{-9}$  A

**Electron energy:** 70eV (down to 5 eV). Max. efficiency, indep of Eel

**Sample pressure:** ca  $2 \times 10^{-5}$  torr (pressure,  $< 10^{-6}$  torr)

**Filament temperature:** 1800C

**Source temperature:** 200C

(higher or lower if desired)

### Fundamentals of EI

#### Ionization Efficiency (yield)

Typically given in Coulombs/ $\mu$ gram

eg.  $3 \times 10^{-7}$  C/ $\mu$ g methyl stearate MW=300 g/mol

$1 \mu\text{g} = 1/300 \times 10^{-6} \text{ mol} = 3.3 \times 10^{-9} \times 6 \times 10^{23} \text{ molecules} = 1.8 \times 10^{15} \text{ molecules}$

But 1 mol can theoretically give

$1.6 \times 10^{-19}$  C(Faraday) and  $1 \mu\text{g}$  can give

$1.8 \times 10^{15} \times 1.6 \times 10^{-19} \text{ C} = 3 \times 10^{-4} \text{ C}$

**yield is  $3 \times 10^{-7} / 3 \times 10^{-4} = 0.1\%$**

#### Cross section:

Target area per molecule ( $\text{cm}^2/\text{molecule}$ )

Typical value:  $2 \times 10^{-16} \text{ cm}^2/\text{molecule}$

Typical pressure:  $2 \times 10^{-5}$  torr

Pressure: 1 torr = 133 Pascal = 1 mm Hg =

So  $2 \times 10^{-5}$  torr =  $6.4 \times 10^{14}$  molecules/ $\text{cm}^3$

path length is 1 cm

Typical electron current: 10 nA

Total area presented by all molecules in 1

cc volume is:

$2 \times 10^{-16} \times 6.4 \times 10^{14} = 1.28 \times 10^{-1} \text{ cm}^2$

But each electron is randomly placed in a 1  $\text{cm}^2$  area so chance of ionizing collision per  $e^-$  is 12.8%

1 electron  $\text{s}^{-1} = 1.60 \times 10^{-19} \text{ A}$ ,

so 10 nA equals  $1/1.6 \times 10^{11}$  electrons/sec  
=  $6 \times 10^{10}$  electrons/sec

[1.33 mbar =  $3.2 \times 10^{19}$  molecules  $\text{cm}^3$ ]

## Fundamentals of EI cont..

### *Time Scale*

<p>Electrons travel very quickly compared to nuclei (i.e. vibrations)</p> <p>How much faster? Use de Broglie wavelength</p> <ul style="list-style-type: none"> <li>• 70 eV electrons have wavelength of <math>4.6 \times 10^{-9}</math> m</li> <li>• What is wavelength of molecular motion at room temp?             <ul style="list-style-type: none"> <li>– think vibrations: think IR <math>\approx 3000 \text{ cm}^{-1}</math></li> <li>– <math>3.3 \mu\text{m} = 3.3 \times 10^{-6}</math> m (at least <b>three orders of magnitude longer</b>)</li> </ul> </li> <li>• Therefore, quantum mechanics tells us that energy transfer is less probable (energy transfer occurs when waveforms overlap).</li> <li>• Frank-Condon factors will apply » electrons will be excited/ejected must faster than the time frame for molecular rearrangement.</li> <li>• This <i>could</i> impart internal energy into the newly formed ions.</li> </ul>	$\lambda = \frac{h}{(2m_e eV)^{1/2}} = \frac{h}{mv}$ $\lambda = \frac{6.626 \times 10^{-34} \text{ Js}}{(2 \times 9.109 \times 10^{-31} \text{ Kg} \times 1.609 \times 10^{-19} \text{ C} \times 70 \text{ V})^{1/2}}$ <p>1 J = 1 Nm = <math>1 \frac{\text{m}^2 \text{kg}}{\text{s}^2}</math>, 1 C = <math>1 \frac{\text{A}}{\text{s}}</math>, 1 V = <math>\frac{\text{m}^2 \text{kg}}{\text{s}^3 \text{A}}</math></p> $\lambda = 4.6 \times 10^{-9} \frac{\frac{\text{m}^2 \text{kg}}{\text{s}^2} \times \text{s}}{\left(\text{kg} \times \text{A} \times \text{s} \times \frac{\text{m}^2 \text{kg}}{\text{s}^3 \text{A}}\right)^{1/2}} = \frac{\frac{\text{m}^2 \text{kg}}{\text{s}}}{\left(\frac{\text{m}^2 \text{kg}^2}{\text{s}^2}\right)^{1/2}}$ $\lambda = 4.6 \times 10^{-9} \frac{\text{s}}{\frac{\text{mkg}}{\text{s}}} = m$ <p>or <math>2 \times 10^{-17}</math> s              or <math>6 \times 10^{16}</math> Hz</p>
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### Vertical transitions: Franck-Condon Principle

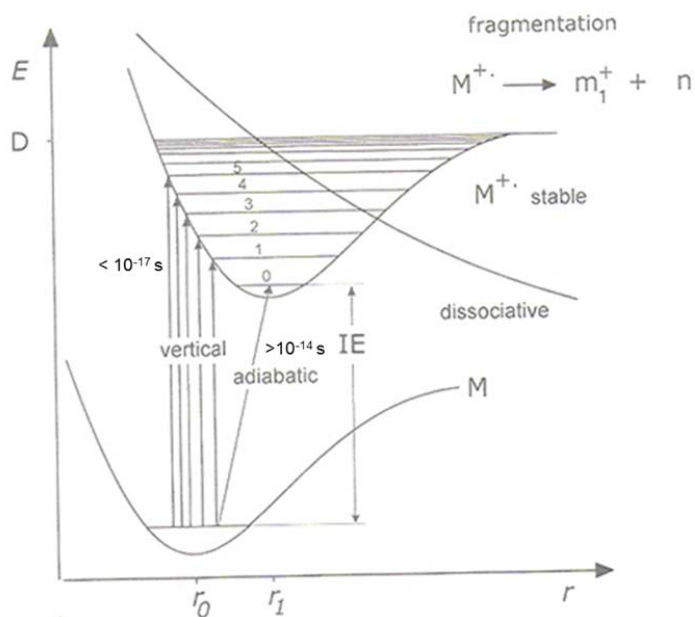
A 70 eV electron has velocity  $5 \times 10^8$  cm/s

Hence a 10 Å molecule is traversed in  $2 \times 10^{-16}$  s

But the vibrational period is  $10^{-11} - 10^{-13}$  s

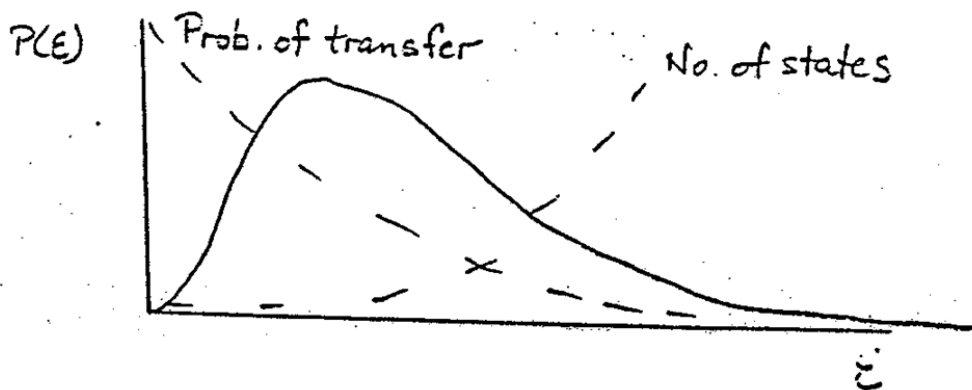
hence EI occurs by vertical, Franck-Condon transitions, nuclear motion is frozen





**Internal energy distributions  $P(\epsilon)$**

Ions do not have thermal (Boltzmann) distributions in EI. IONS ARE ISOLATED – no collisions, no energy loss. The most probable events are the least inelastic. Hence the - probability of transferring energy to the ion decreases with increasing energy. However, the number of states available increases and the net result is an internal energy distribution  $[P(\epsilon)]$  curve of the type shown below:



Lambert et al. Chapter 14 Fragmentation and Ion Chemistry

### Fragmentation in EI Mass Spectra

#### **QET Quasi-equilibrium theory describes unimolecular reactions**

- 1) Energy deposition is faster than intramolecular movement (“vertical ionization”)
- 2) Intermolecular interactions are infrequent compared to intramolecular transitions, and radiationless transitions are favored
- 3) Excess electron energy has time to distribute to other internal modes before fragmentation
- 4) Dissociation rates are related to the probability of random energy localizing in a specific way
- 5) Products containing internal energy may undergo the same steps

What does this mean?

Higher KE electrons can provide

- 1) faster fragmentation rates
- 2) more reaction pathways
- 3) multiple fragmentations

Dissociation rate constants can be determined by QET: **[MORE ON THIS LATER!]**



$$k(E) = \nu [(E - E_0)/E]^{s-1}$$

$k_{(E)}$  = unimolecular (dissociation) rate constant at internal energy E

$\nu$  = frequency factor (number and density of vibrational states)

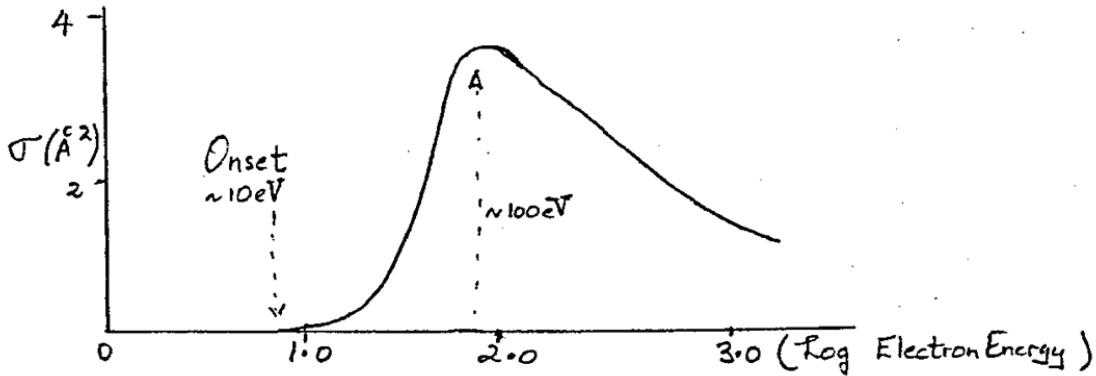
$s$  = number of degrees of freedom (3N-6 where N = number of atoms)

$E_0$  = dissociation energy

**Ionization cross sections**

ref. see Levsen ch 1.

The cross section for EI depends on electron energy (E). It maximizes at a few Å<sup>2</sup> in the region of 70 eV, rises rapidly before this and falls slowly above this value.



Threshold behavior: at the onset of ionization, the cross section ( $\sigma$ ) varies with energy as follows

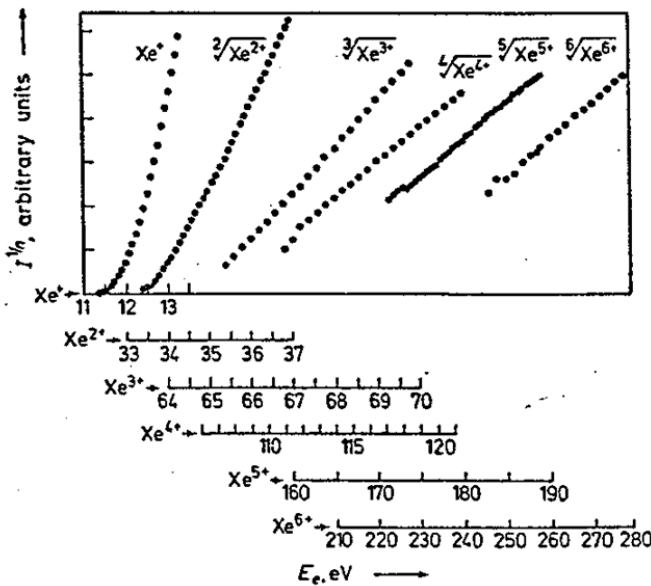
$$\sigma(E) \propto (E-E_0)^{n-1} \text{ ie } \sigma \propto E_{ci} \text{ for EI}$$

$E_0$ =thermochemical threshold

$n$ =no. electrons ejected

$E$ =energy of ionizing agent

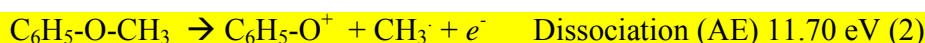
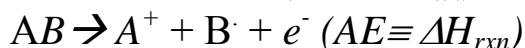
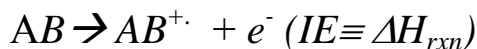
This law applies to electron impact, including multiple ionization, photoionization, etc. It is demonstrated by the ionization of xenon up to  $Xe^{+6}$ :



Threshold functions for multiple ionization processes in xenon111, interpreted in terms of nth root law Hasted p410

## Thermochemical measurements - appearance and ionization energies

Threshold measurements of ionization give Ionization energies and the threshold for a fragment ion gives the appearance energy. By definition these are the minimum energies required for the reactions:



$$\Delta H_{reaction} (2) = \Delta H_f(C_6H_5O^+) + \Delta H_f(CH_3^{\cdot}) - \Delta H_f(C_6H_5OCH_3) = AE - IE \quad [\text{assumes no excess energy}]$$

Knowing IE, AE and knowing  $\Delta H_f(C_6H_5OCH_3) = -17$  kcal/mol from WEBBOOK,

We can determine Heat of formation of neutral radical  $\Delta H_f(CH_3^{\cdot}) = 34$  kcal/mol

[compare standard value, WEBBOOK,  $\Delta H_f^{\circ}_{gas} = 35.1 \pm 2$  kcal/mol]

$$AE(C_6H_5O^+) = \Delta H_f(C_6H_5O^+) + \Delta H_f(CH_3^{\cdot}) - \Delta H_f(C_6H_5OCH_3)$$

$$\therefore \Delta H_f(C_6H_5O^+) = AE(C_6H_5O^+) - \Delta H_f(CH_3^{\cdot}) + \Delta H_f(C_6H_5OCH_3)$$

$$= 11.70 \times 23.06 - (34) + (-17) = 219 \text{ kcal/mol}$$

$$IE(C_6H_5OCH_3) = \Delta H_f(C_6H_5OCH_3^{\cdot+}) - \Delta H_f(C_6H_5OCH_3)$$

$$\therefore \Delta H_f(C_6H_5OCH_3^{\cdot+}) = IE(C_6H_5OCH_3) + \Delta H_f(C_6H_5OCH_3) = 8.30 \times 23.06 + (-17) = 175.6 \text{ kcal/mol}$$

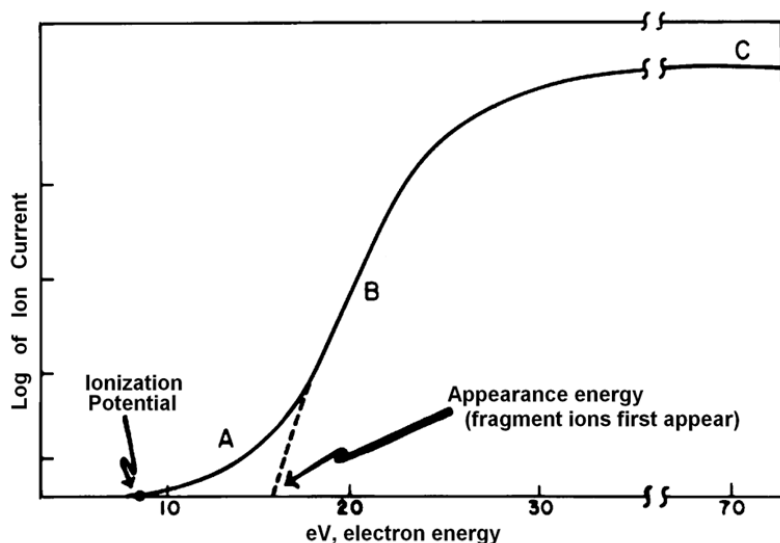
### C – O Bond energy in ion: $C_6H_5OCH_3^{\cdot+}$

$$BE_{ion} = \Delta H_f(C_6H_5O^+) + \Delta H_f(CH_3^{\cdot}) - \Delta H_f(C_6H_5OCH_3^{\cdot+}) = 219 + 34 - 175.6 = 77.4 \text{ kcal/mol} \cong 3.3 \text{ eV}$$

Compare C-O bond energy in neutral,  $C_6H_5OCH_3$  from WEBBOOK,

$$BE_{neutral} = \Delta H_f(C_6H_5O) + \Delta H_f(CH_3) - \Delta H_f(C_6H_5OCH_3) = 13 + 35 - (-17) = 65 \text{ kcal/mol} \cong 2.8 \text{ eV}$$





Adapted from *Interpretation of Mass Spectra*, O. D. Sparkman & J. T. Watson

### Activation/Fragmentation via EI:

Electron Ionization and Excitation:

A)

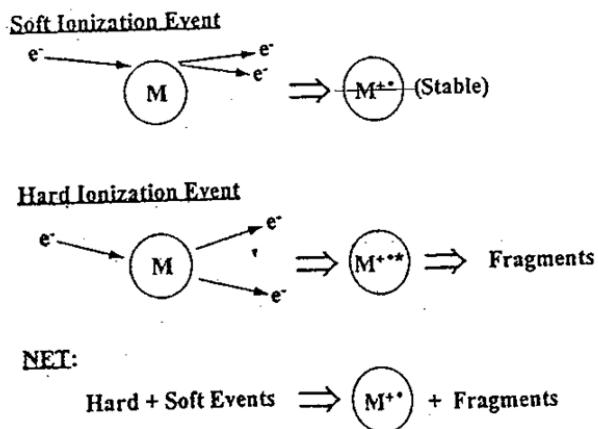


Figure 13-3 Electron ionization accompanied by different degree of excitation of the molecular ion. Soft ionizing events transfer excess energy to the ionized molecule, which is observed. Harder collisions also occur and give rise to the fragment ions frequently seen in EI mass spectra.

B)

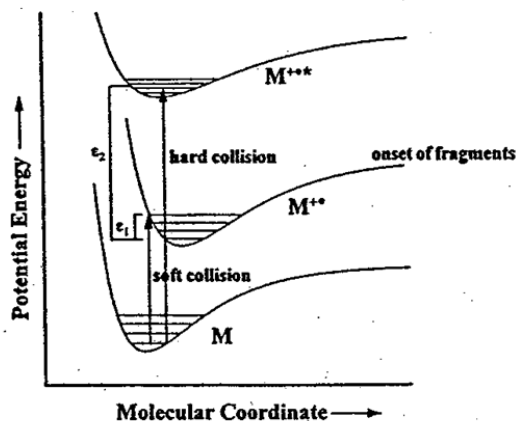


Figure 13-5 Vertical transitions associated with electron ionization ( $M \rightarrow M^+$ ) showing deposition of internal energy in the ion  $M^+$ . Two ionization events are shown, a soft collision leading to stable  $M^+$  of relatively low energy ( $\epsilon_1$ ), and a hard collision leading to high energy molecular ions ( $\epsilon_2$ ), which rapidly fragment.

### Fragmentation: Molecular Effects

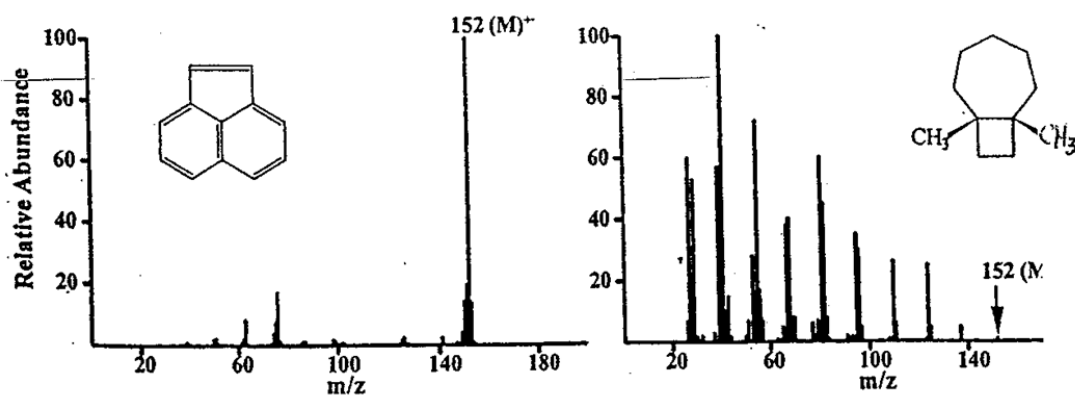


Figure 13-4 Contrasting degrees of fragmentation observed in the EI spectra of an aromatic and an alicyclic compound. The former resists dissociation and gives a molecular ion from which the molecular weight (152 Da) is measured. (From P.J. Ausloos, C. Clifton, O.V. Fateev, A.A. Levitsky, S.G. Lias, W.G. Mallard, A. Shamin, and S.E. Stein, NIST/EPA/NIH Mass Spectral Library—Version 1.5, National Institute of Standards and Technology, Gaithersburg, MD [1996].)

**NOTE: HARD & SOFT IONIZATION METHODS – DEPEND ON COMPOUND**

**Fragmentation: Effect of Electron Energy – attempting to make EI “softer”---  
 succeeds but much intensity lost**

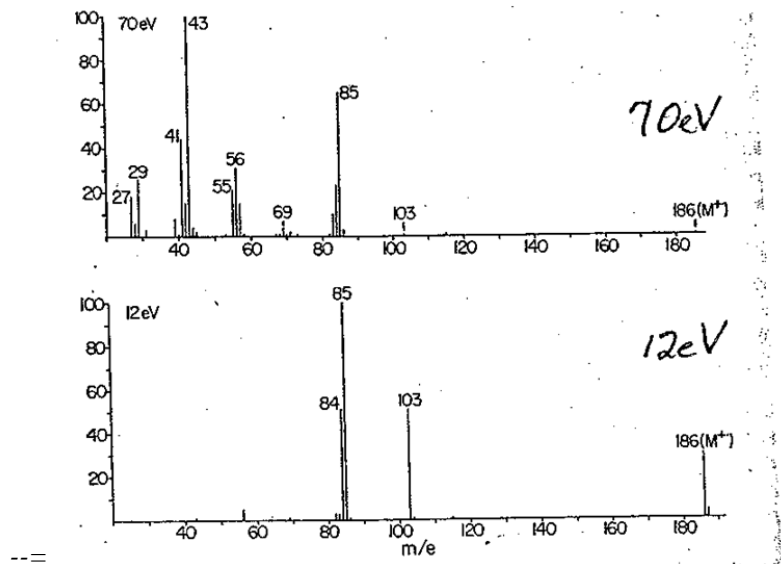
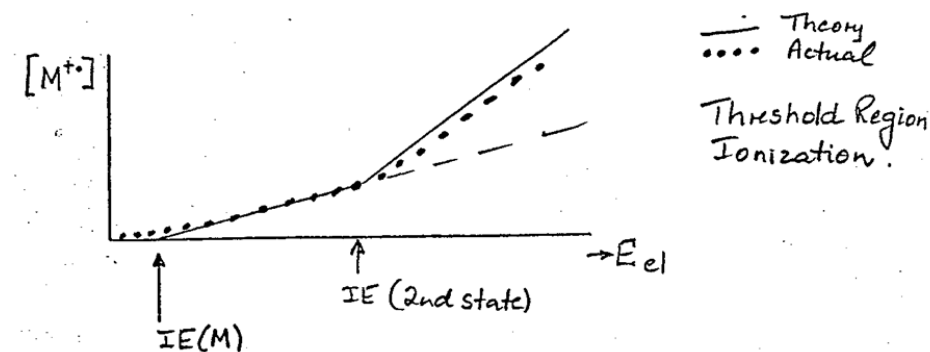


FIGURE 4-8. Mass spectra of di-n-hexyl ether at 70 and 12 eV

In the case of molecules, ionization to form higher electronic states of the ion can sometimes be seen by upward breaks in the ionization efficiency curve, i.e. the plot of ion yield against ionizing electron energy: In the idealized case, one has multiple linear segments. In practice, there are distributions due to the electron energy width, the vibrational energy of the neutral, fragmentation onsets, and the failure of the threshold laws



The fact that breaks in ionization efficiency curves of large molecules are hard, to discern is evident when one considers so simple as a case as CH:

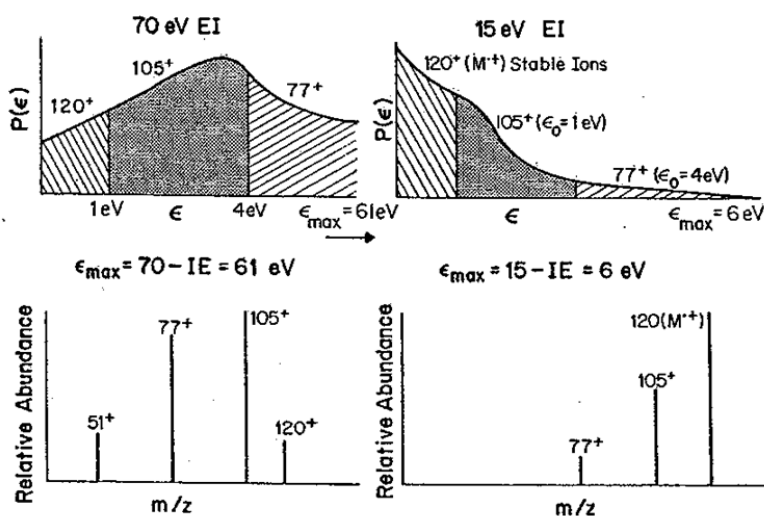
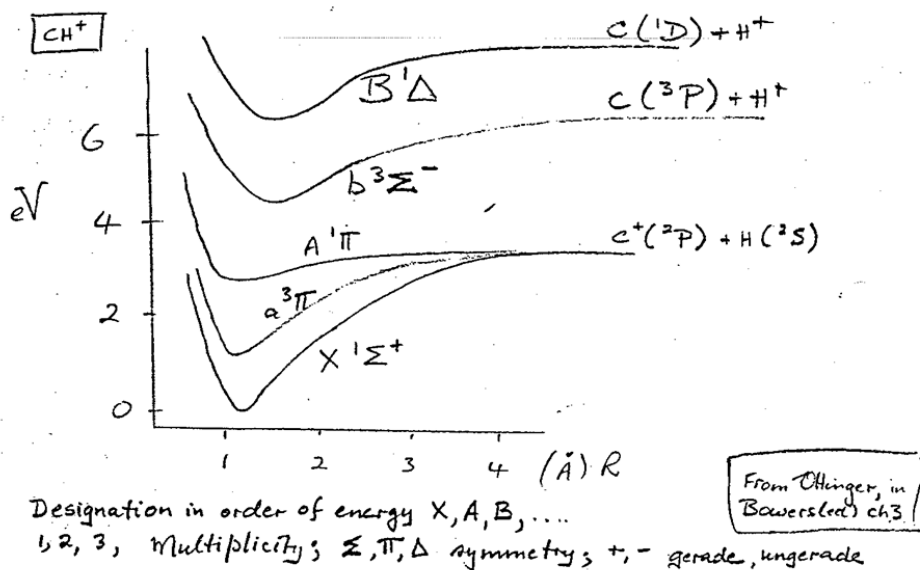


Figure 14-31 Thermochemical factors control EI mass spectrum of acetophenone

**LATER: for certain 'thermometer' ions the internal energy distribution  $P(e)$  can be read from the mass spectrum**

### Negative EI:

Typical negative ion EI spectra don't contain much structural info

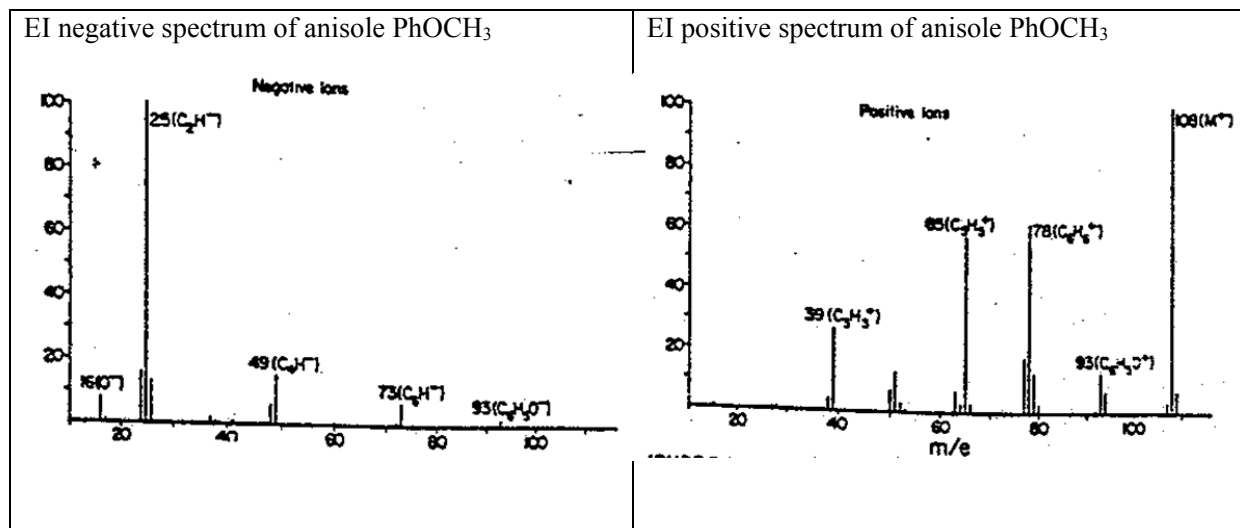


FIGURE 5-8 Negative and positive mass spectra of anisole (upper reproduced with the permission of the American chemical Society from R. T. Aplin, etc JACS 1965, 87, 3180)

### Summary of EI characteristics:

Highly reproducible spectra-- hence libraries of spectra (100,000). No ion/molecule or matrix effects contribute to reproducibility, ie physical rather than chemical processes involved in ionization.

Simple, inexpensive, rugged.

Gas or vapor samples required, otherwise universally applicable. ("in-beam" variant applies to less volatile compounds)

"Hard" ionization method - often does not give molecular ion. (see Table below).

Internal energy distribution broad and poorly characterized, can be reduced by reducing energy of e<sup>-</sup> and this helps recognize molecular ions.

Fragmentation interpretable in terms of structure, but radical cations, M<sup>+</sup>, often fragment by complex rearrangements.

Good ion currents, low absolute efficiencies (10<sup>-3</sup>).

Thermochemical data (AE, IE) by threshold measurements, ie ionization efficiency data.

Poor access to negative ions.

Negligible kinetic energies transferred to ions, hence no loss of mass resolution.

Molecular Ion Abundance in EI spectra<sup>a</sup>

Relative abundance of M <sup>+</sup> (% of base peak)	100-50	49-6	5-1	<1
Fraction of sample (%)	30	32	8	30

<sup>a</sup>A collection of 120 compounds, molecular weight 220. Data from the EPA NIH library of mass spectra

Table 1-3 Characteristics of EI

Characteristic	Consequence
Positive ions formed	Limits applications to some classes of compounds
Sample must be volatile	Limited to compounds, molecular weight <ca.600 Da
Relatively energetic (large internal energy) method	Often extensive fragmentation: limits value in molecular weight determination
Reproducible method	Libraries of EI allow compound identification
Extensive fragmentation occurs	Molecule at structure information can be deduced
Ionization efficiency high	Method is very sensitive in 1000 molecules is ionized
Ionization is non-selective	All vaporized molecules can be ionized

### Glossary of Terms Used in EI

Molecular ion: Ion formed by loss (or, rarely, addition) of an electron by the analyte

Parent ion: Any ion which fragments to yield a product ion

Fragmentation pattern: Set of reactions leading from the molecular ion to fragment ions

Multiply-charged ions: Ions bearing more than a single charge and having correspondingly reduced mass/charge ratios

Radical Ion: (odd-electron ion) Charged open-shell molecule

Even-electron ion: Closed shell or, more rarely, coordinatively unsaturated paired- electron species