Mass spectrometry as an important tool in chemical discovery

Clusters
Fullerenes, rings
Gas phase chemistry
Reaction dynamics
Atmospheric chemistry
Environmental sciences
Biology

Chemical mass spectrometry

Analytical tool   Process of discovery

kDa range, femtomole quantities, newer methods, instrumentation

Miniaturisation, adaptation, absorption of other tools into mass spectrometry

Spectroscopy of the largest to the least
From near to far
Molecules to materials
Atom to biomolecules

Range is infinite

Mass spectrometry: Then

Figure 30.1 Directional focusing of an ion beam that is at right angles to a magnetic sector.
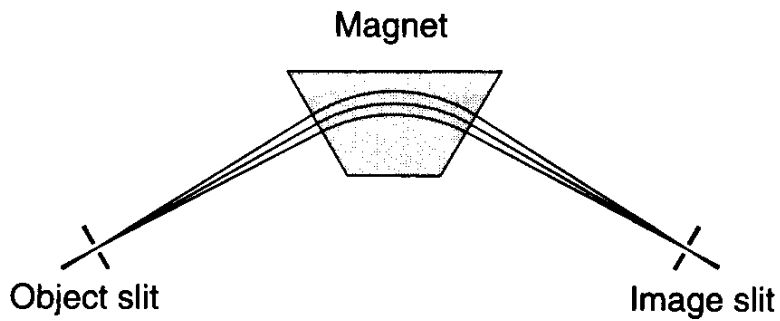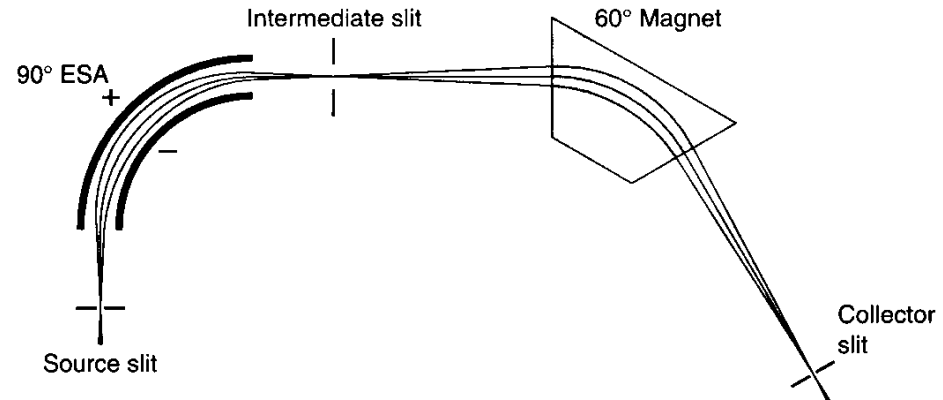
Magnet

Object slit

Image slit

Figure 30.4 Double-focusing mass spectrometer of the Nier–Johnson type.

Intermediate slit

60° Magnet

90° ESA

Source slit

Collector slit

Analysis methods

Electric sector

$mv^2/r = zE$, electric sector is a mass filter for daughter ions

Magnetic sector

$mv^2/r = zvB$ or $mv/z = Br$, $m/z = B^2r^2/2V$, mass to charge ratio of the ion is a function of both accelerating voltage and magnetic field.

Quadrupole

DC, V_1 RF $V_o\cos t$, opposite rods of different polarity
Force on the ions,
$F_y = ma_Y = z(V_1+V_o\cos t)2y/r_o^2)$
$F_z = ma_z = -z(V_1+V_o\cos t)2_z/r_o^2)$
$F_x = ma_x = 0$ x is along the axis of the quadruopole, ion motion is in th
zy plane.

Time of flight

$t = L/v$ or $t = Lm^{1/2} / (2zV)^{1/2}$
Time taken for the ion for a complete revolution inside the cell, $t = 2r/v$
$t = 2(m/zB)$, time is inversely proportional to cyclotron frequency, $f_c = 1/t$
$=Bz/2m$, $m/z = B/2f_c$.

ICR   Each ion has a characteristic f_c. Upon application of rf voltage, parallel to the field, with frequency fc, ions with that fc absorb energy, increase r and finally reach the detector plates. In FT ICR a broad band rf pulse is given exciting all ions and image current as function of time.
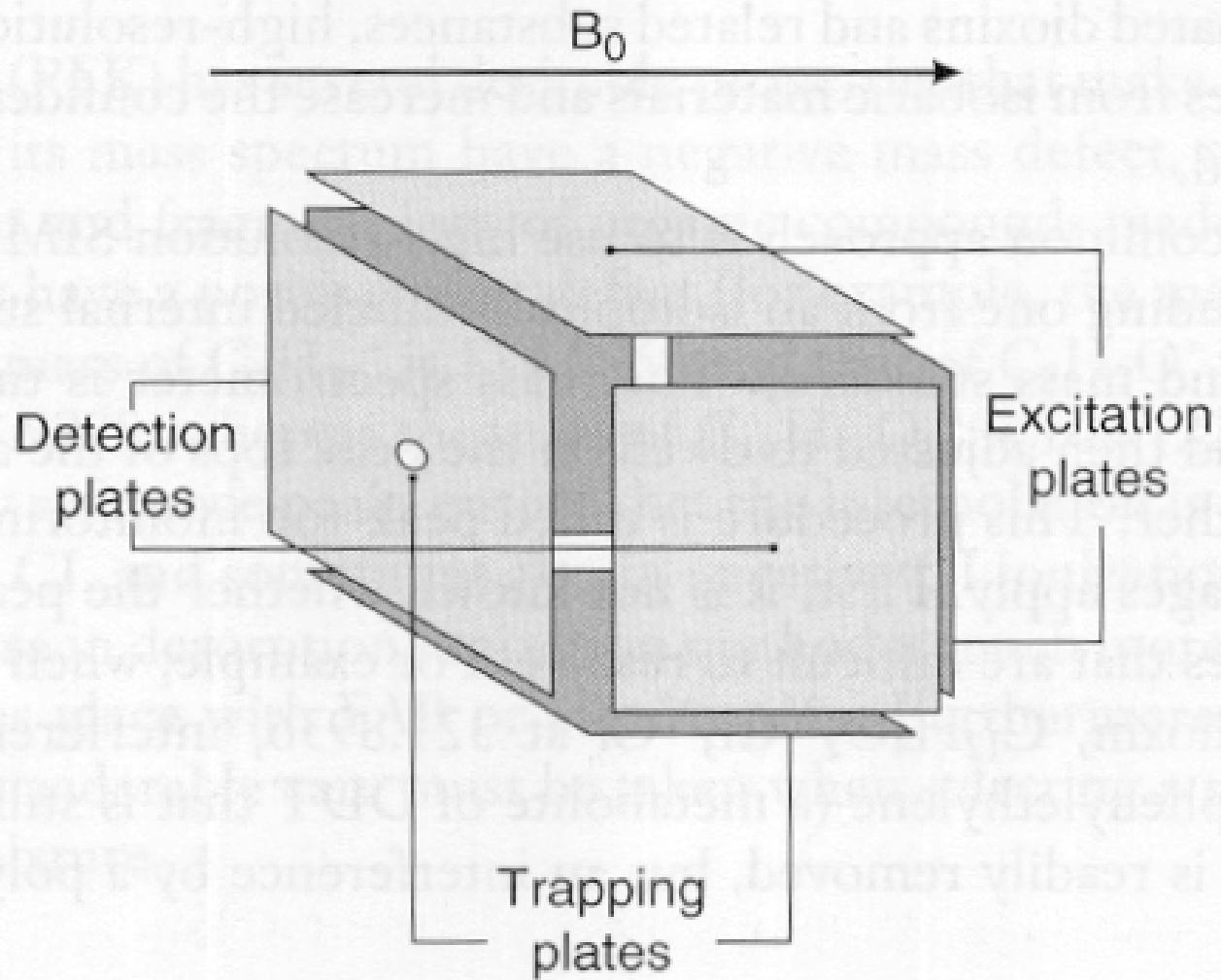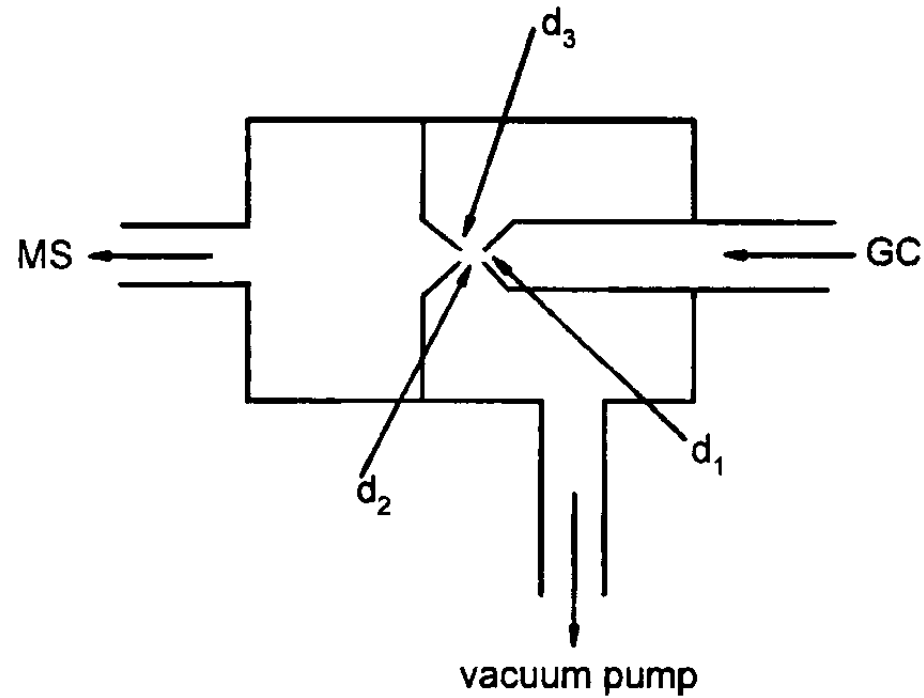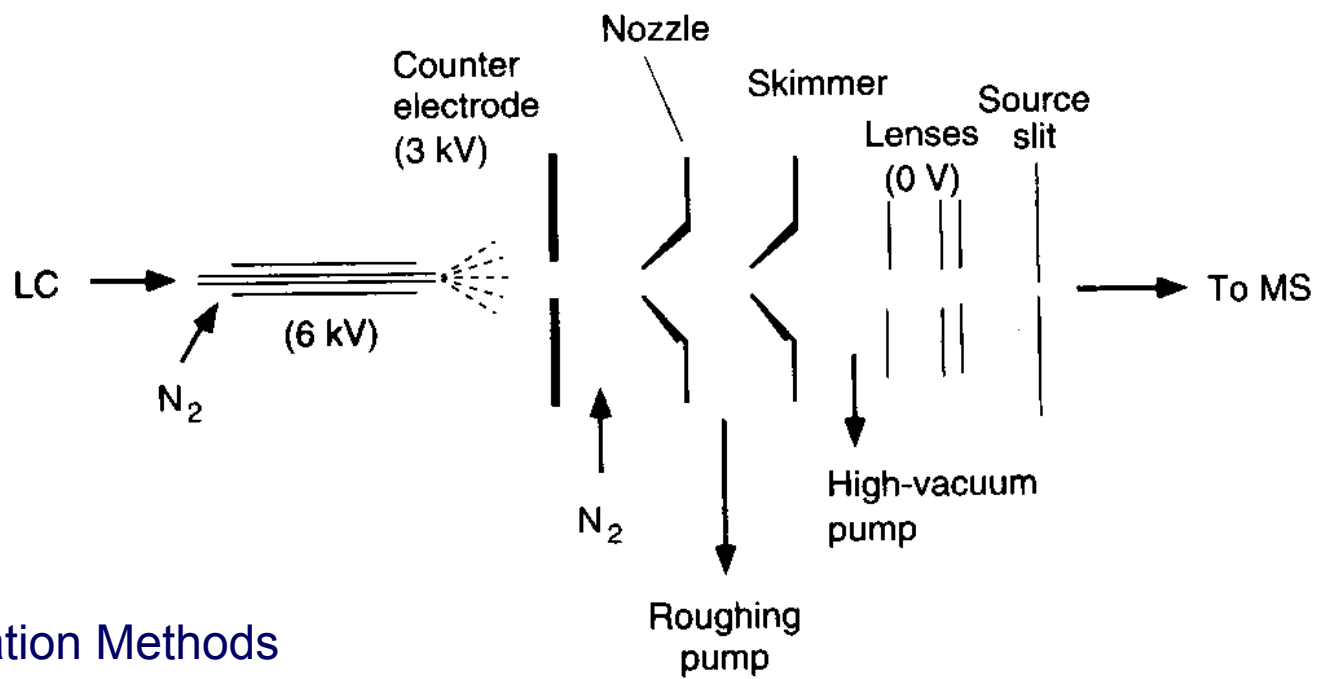
Figure 30.6 FTMS cubic cell.

B_0

Detection
plates

Excitation
plates

Trapping
plates

Figure 31.1 The jet separator, a device for interfacing a packed column GC with an MS. The three distances are typically d_1, 100 μm; d_2, 300 μm; and d_3, 240 μm.
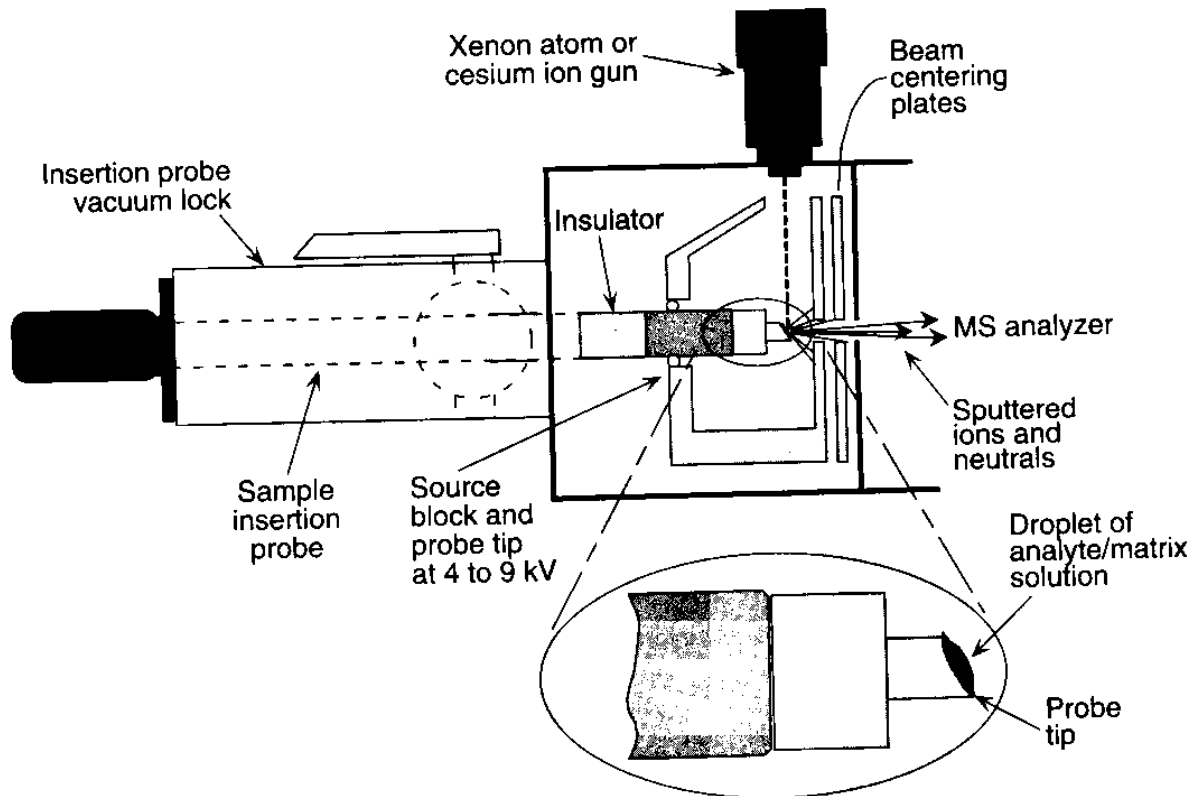

vacuum pump

GC Interface
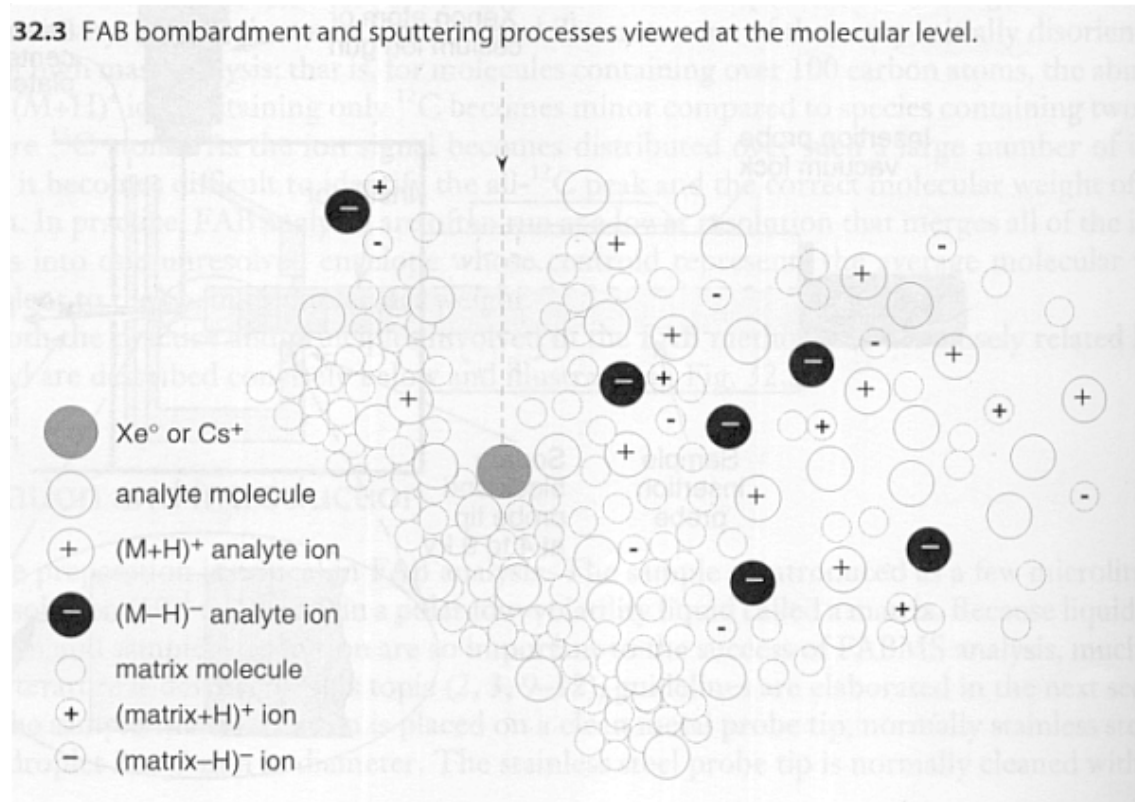
Figure 33.2 Schematic of a typical ESI source.

New Ionization Methods

Figure 32.2 The FAB or LSIMS sample insertion probe, inserted into the ion source of a magnetic mass spectrometer. The sample is bombarded by either Xe^0 atoms or Cs^+ ions.

32.3 FAB bombardment and sputtering processes viewed at the molecular level.

Legend:
- Xe° or Cs⁺
- analyte molecule
- (+) (M+H)⁺ analyte ion
- (−) (M−H)⁻ analyte ion
- matrix molecule
- (+) (matrix+H)⁺ ion
- (−) (matrix−H)⁻ ion

Soft methods

Mass spectrometry and modern advances

New ion activation tools

Collisional activation

Mass spectrometer → Gas cell → Mass spectrometer

Surface activation
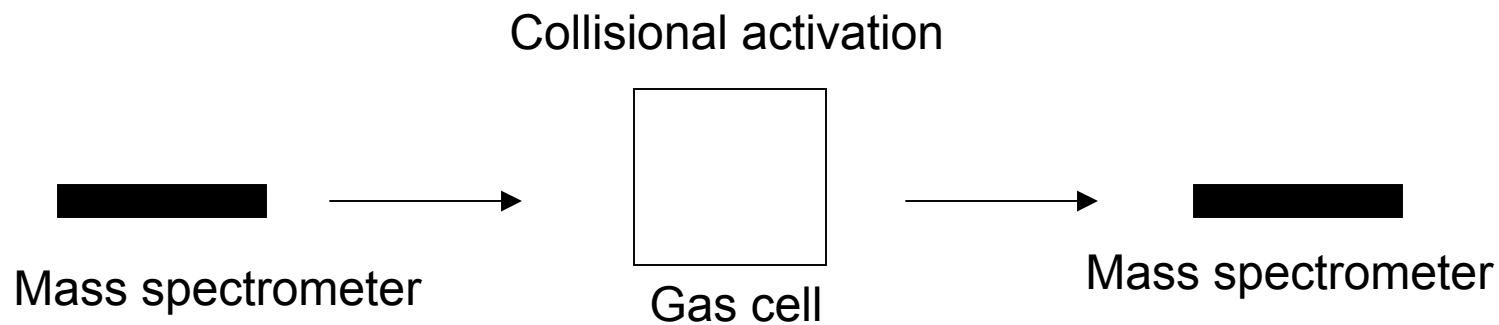
Mass spectrometers → Surface
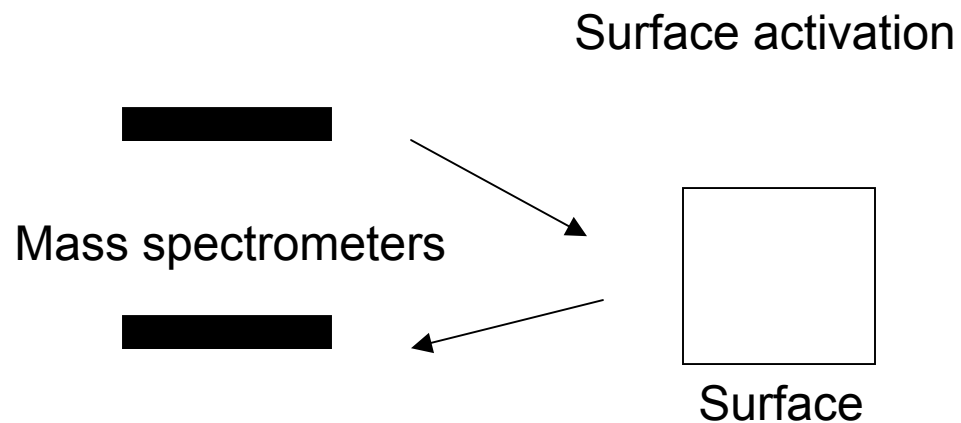
Figure 34.1 The mass spectrum of cascade polymer 48-cascade:benzene[3-1,3,5]:(5-ethynyl-1,3-phen-lylene):5-ethynyl-1,3-di(tert-butyl)benzene, containing 94 phenylacetylene monomer units (D-94) analyzed by UV MALDI-TOF. The measured mass accuracy is 40 ppm using the PEG as an internal mass standard. The spectral resolution of the molecular ion is 1100.
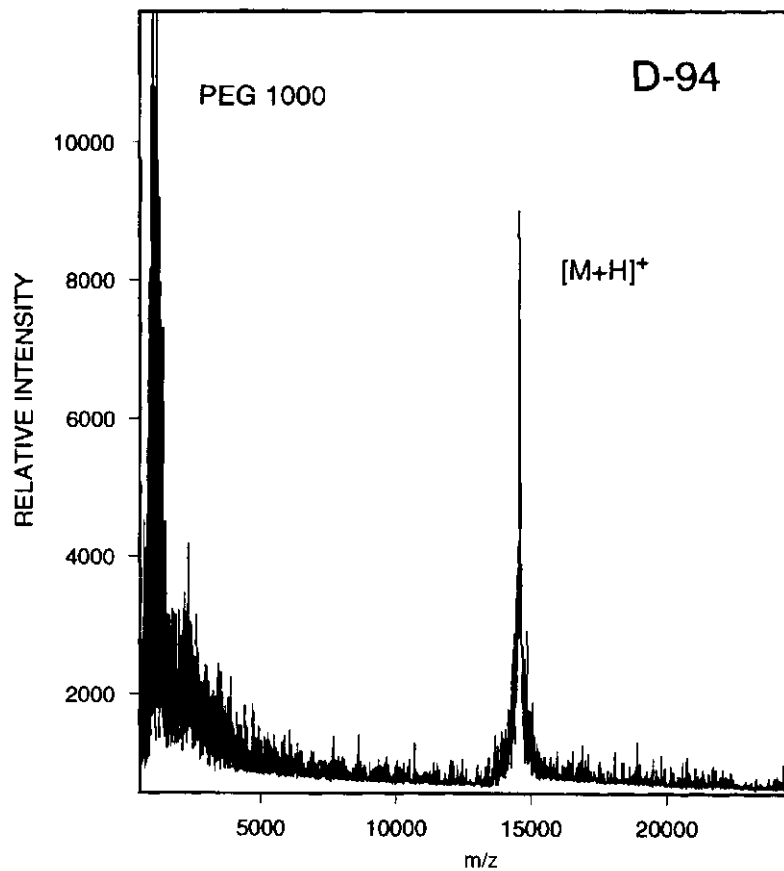
Figure 34.2 The mass spectrum of a substituted fullerene obtained with UV MALDI-FTMS. The mass measurement accuracy was found to agree with that of the proposed structure to within 3.7 ppm, externally calibrated, and the spectral resolution is 10,000.
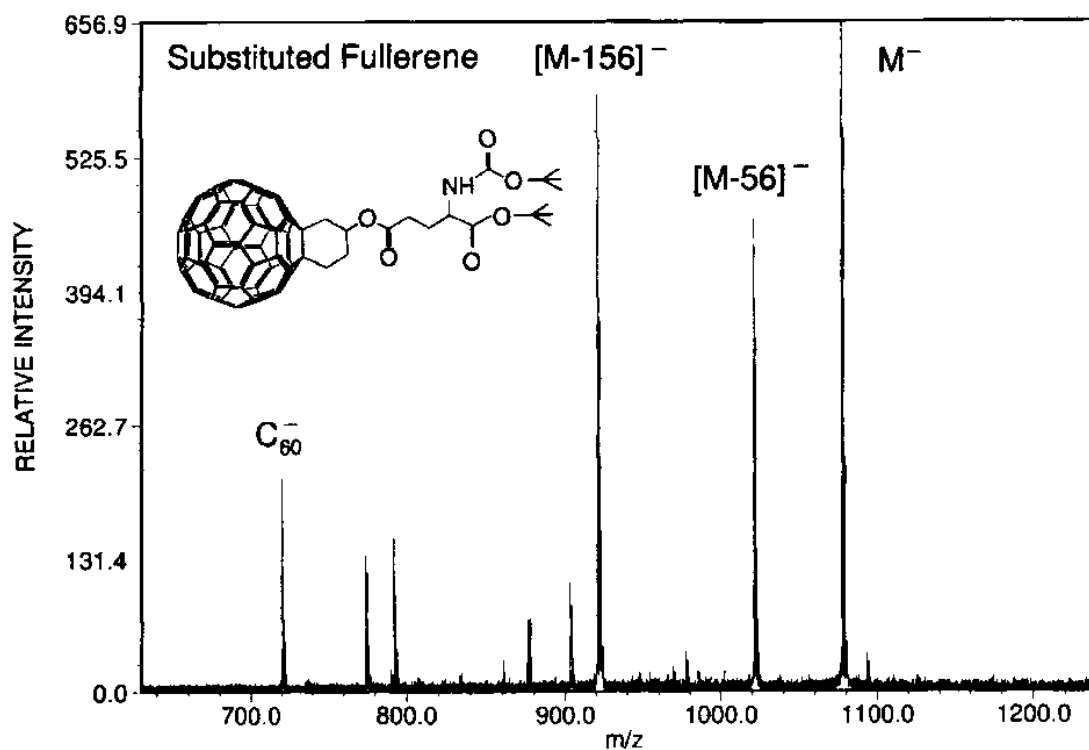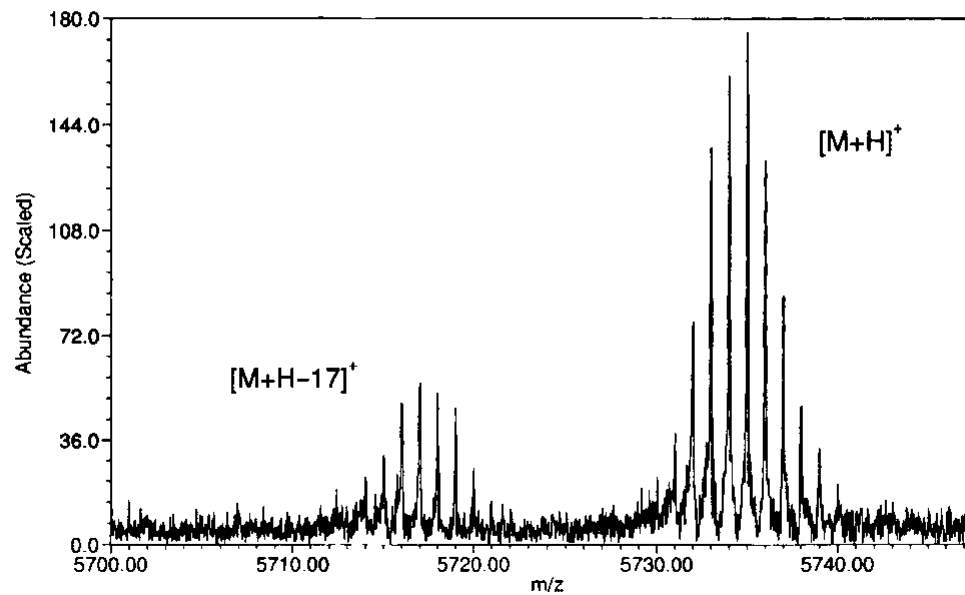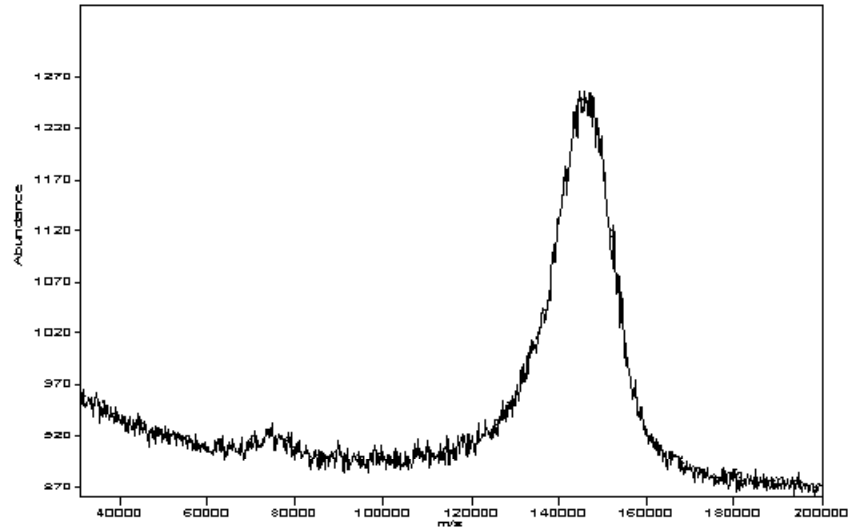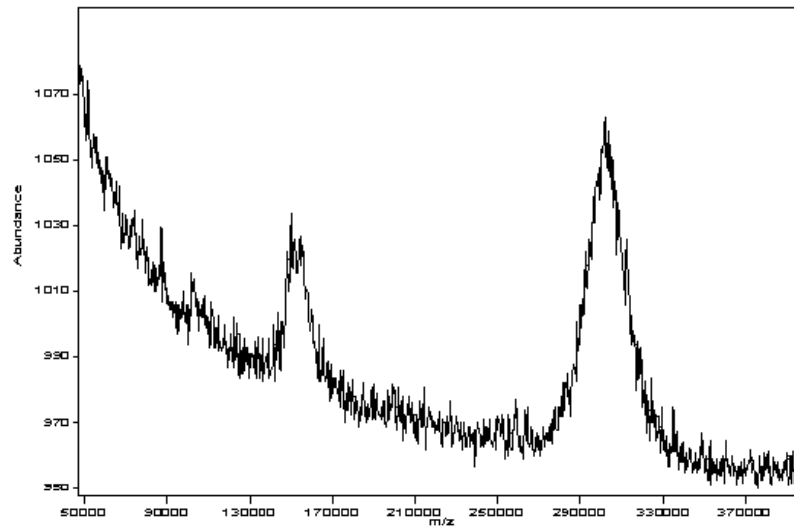
Figure 34.4 A high-resolution UV MALDI-FTMS spectrum of the protein standard bovine insulin. The lower-intensity distribution corresponds to the mass $(M+H)^+ - 17$ Da. The average resolution of the molecular ion peak is 60,000 and the average mass accuracy is 70 ppm, externally calibrated.
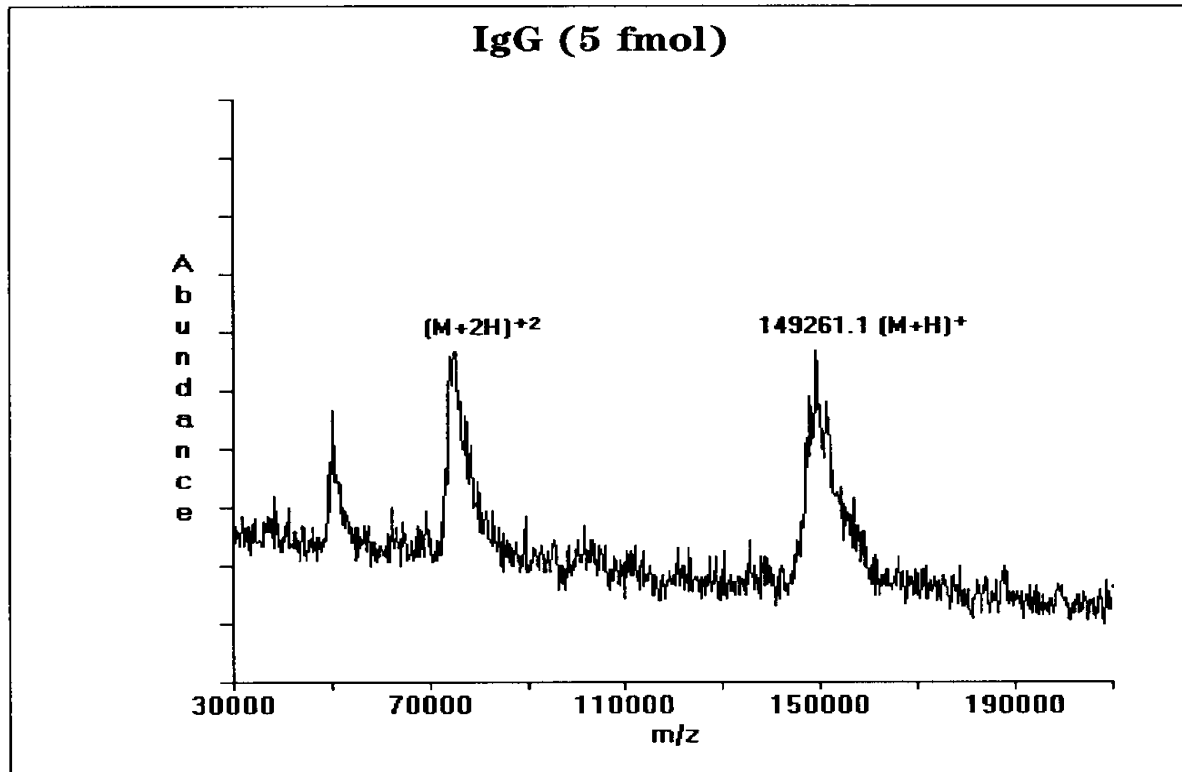
MALDI spectrum o f polystyrene 145000 distribution

MALDI spectrum o f polystyrene 295000 distribution

Immunoglobin (IgG)

IgG (5 fmol)

(M+2H)$^{+2}$

149261.1 (M+H)$^+$

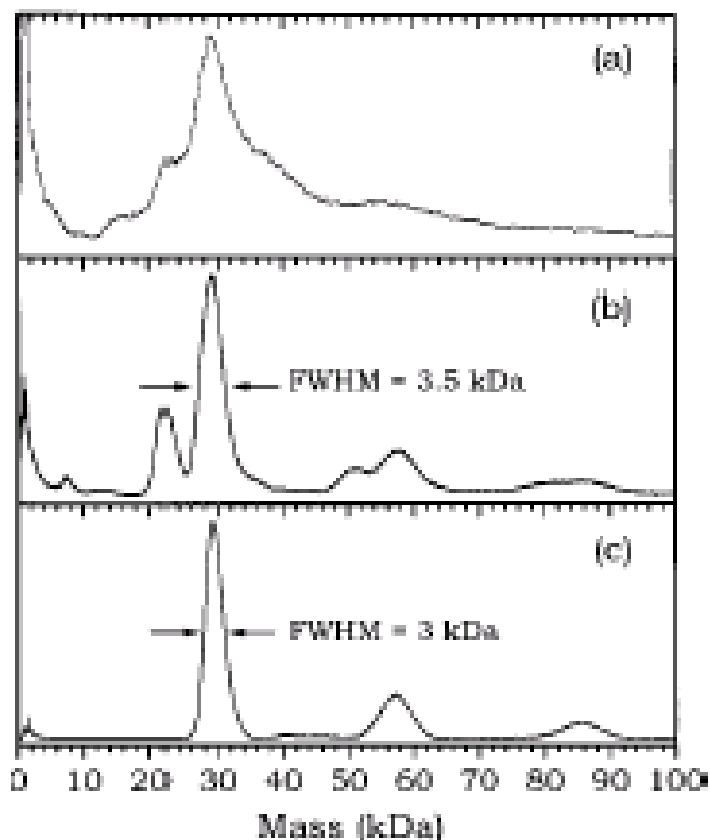Abundance

m/z

30000   70000   110000   150000   190000

Figure 1. (a) Laser desorption ionization mass spectra from the original, as-prepared, cluster compounds (R = C6). (b) LDI-MS of the mixture after heating in neat dodecanethiol for 18 h and (c) the LDI-MS of the final separated cluster compound that produces ions in the 29 kDa range.
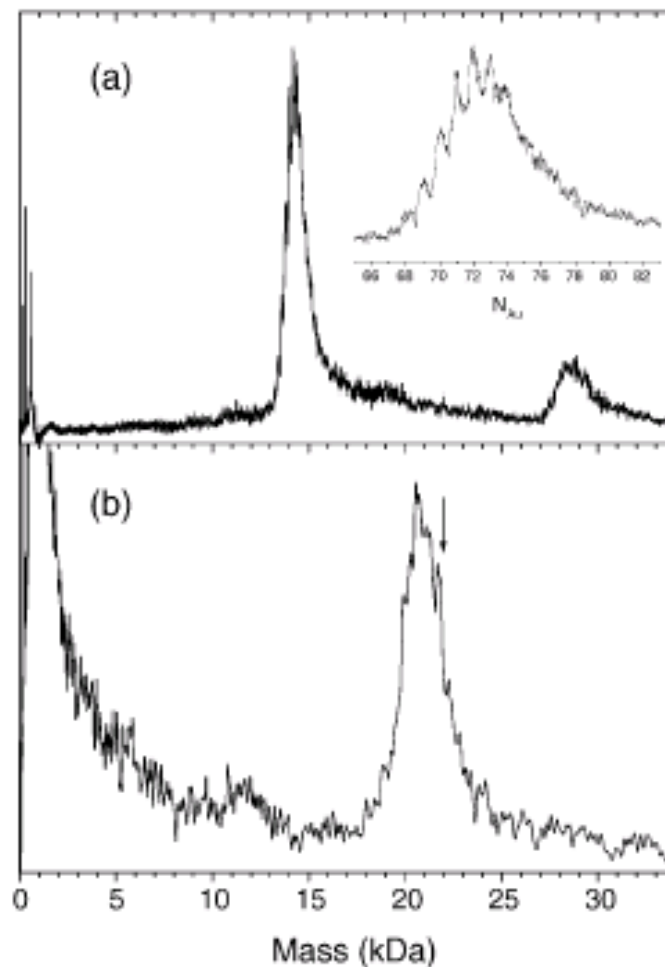
Fig. 3. The negative-ion MALDI mass spectra for Greengold under poor (a) and well (b) co-crystallized conditions [26]. The inset (a) shows an expanded view of the main band, plotted in Au-atom units. The arrow in (b) marks the tentative assignment of the total molecular weight.

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