Mass Spectrometry

Metastable Ions

Some fragment ions, undergo secondary fragmentations in the analyzer tube of the mass spectrometer; the resulting “signals” or peaks represent neither the m/e of the first ion nor that of the second ion; instead, “metastable ion” peaks are observed

For a reaction

$$F_1^+ \rightarrow F_2^+$$

$$(m/e)_1 \qquad (m/e)_2$$

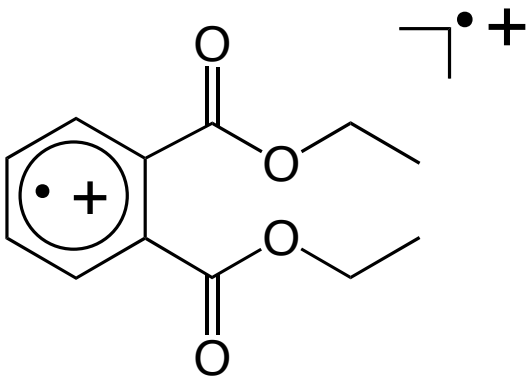
a “metastable ion” peak, m*, is observed

$$m^* = m_2^2/m_1$$

metastable ion peaks require a special type of spectrometer; they give valuable

information about fragmentation patterns of molecular ions.

Example



$M^{\bullet +}$ 222

metastable ion

m* = 125.4

F_1^+ 177 Δ 45 $- \bullet OC_2H_5$

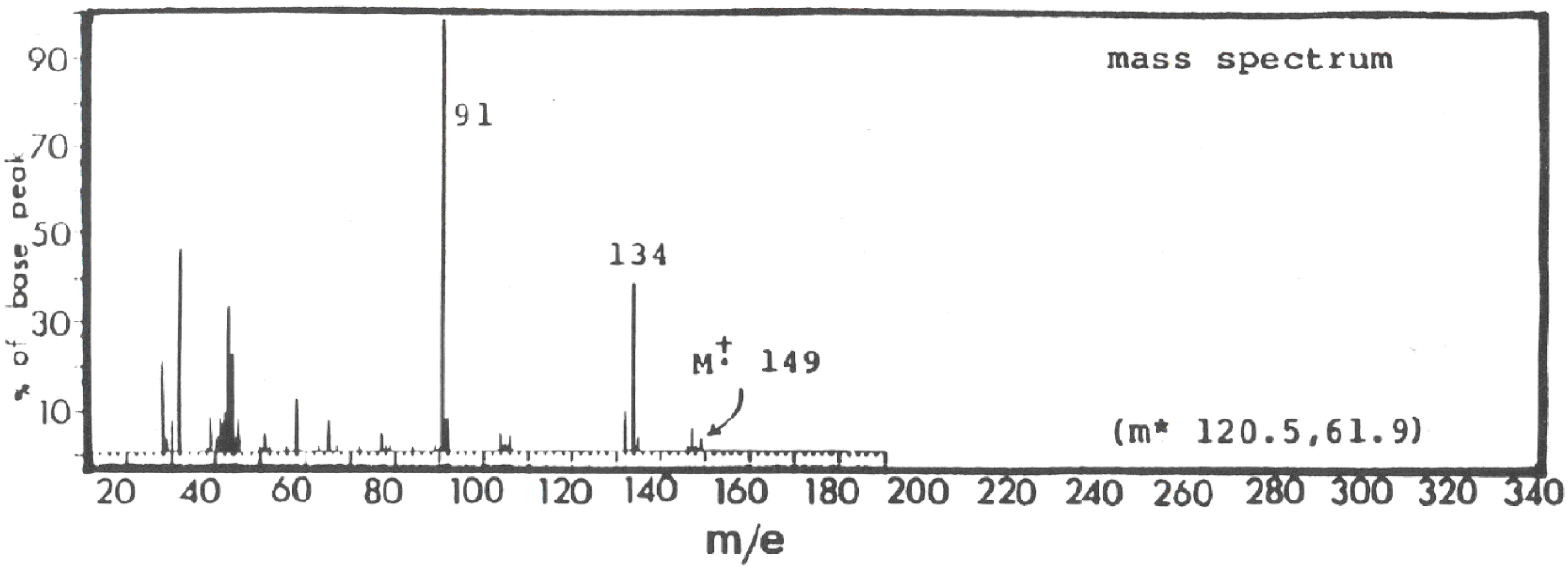
neutral odd electron fragment
not observed

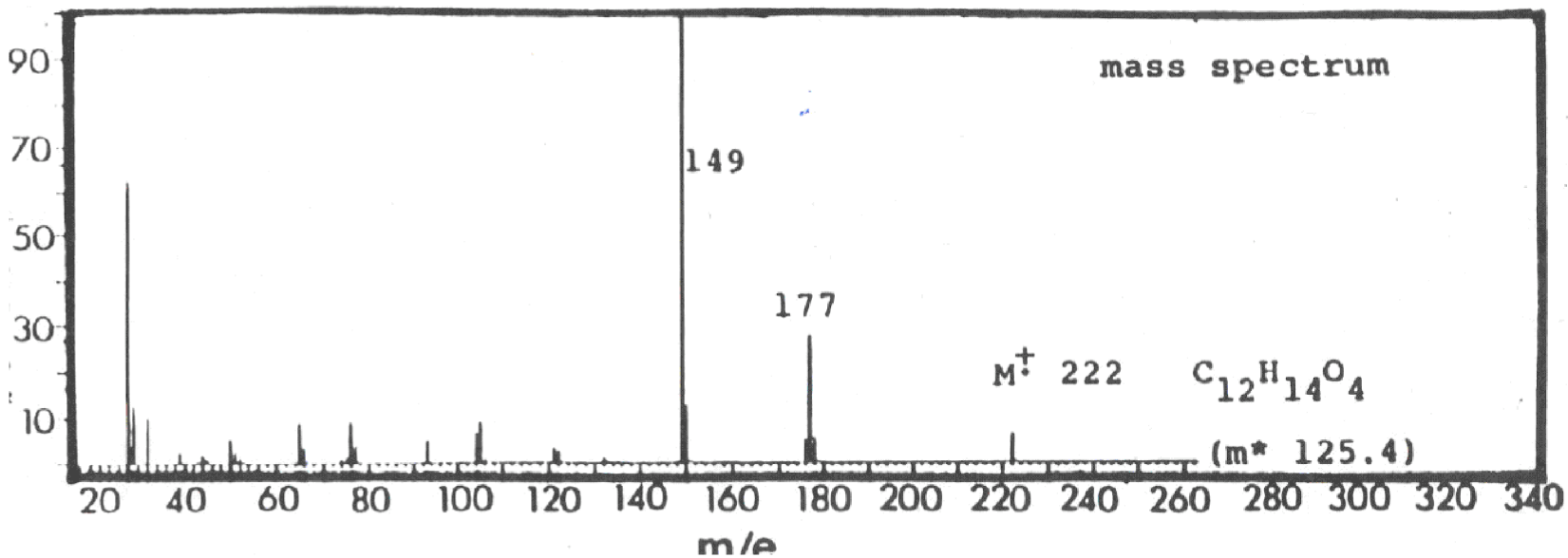
F_2^+ 149 Δ 28 – CO

not observed

metastable ion, $m^* = 149^2 / 177 = 125.4$

The metastable ion peak (125.4) shows that F_1^+ decomposes to F_2^+ plus CO in the analyzer tube.


mass spectrum
91
134
M+ 149
(m* 120.5,61.9)
% of base peak
90
70
50
30
10
20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340
m/e


mass spectrum
149
177
M+ 222
C12H14O4
(m* 125.4)
90
70
50
30
10
20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340
m/e