Electron Ionisation:

Basic equation for electron ionisation: $M + e \longrightarrow M^{+\cdot} + 2e$

The molecular ions thus formed are odd-electron RADICAL CATIONS.

The ionisation process provides an excess of energy above that required for ionisation; this can result in one or more bonds being broken, resulting in fragmentation of the ion.

Radical cations can fragment by a) elimination of a neutral radical $M^{+\cdot} \longrightarrow A^{+} + B^{\cdot}$
           or by b) elimination of an even-electron molecule $M^{+\cdot} \longrightarrow C^{+\cdot} + D$

The minimum energy required to ionise a given molecule is known as the Ionisation Energy (IE).

Typical ionisation energies lie in the range 6-12 eV.   (1eV = 96.485 kJ mol^{-1})

Energy transfer and distribution accompanying ionisation.

Ionisation of a molecule occurs very fast; the bond lengths in the molecule are assumed not the change during the ionisation process. This means that the ionisation process obeys the *Franck-Condon principle*, which states that electronic transitions occur with no change in nuclear configuration. This corresponds to vertical transitions in the following diagram:
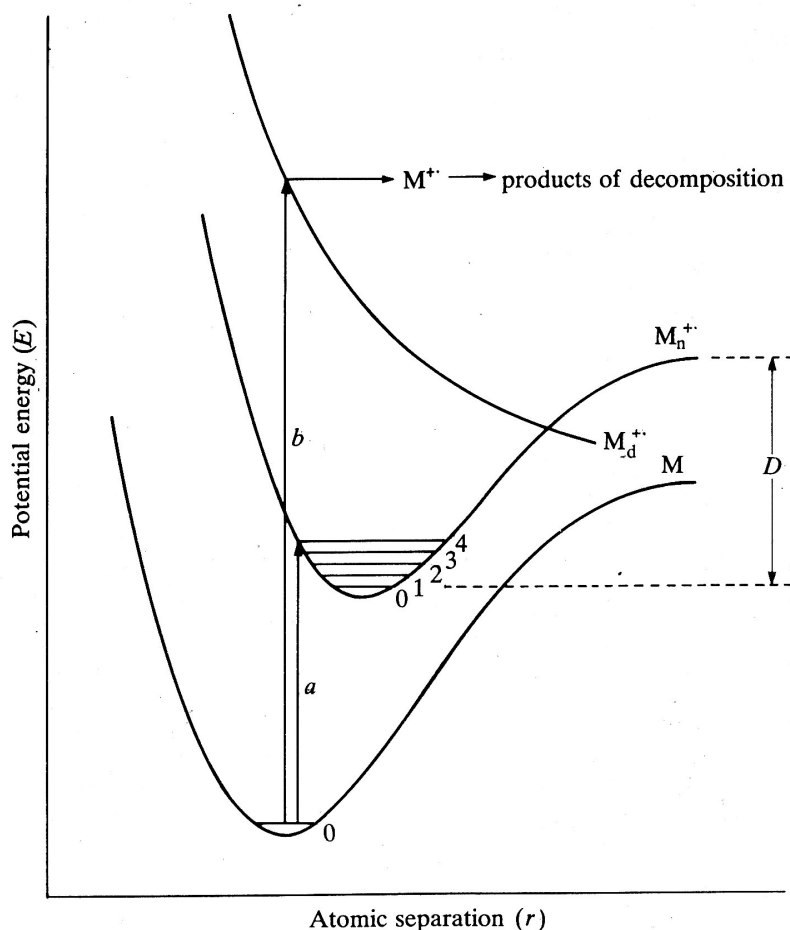
Transition A shows ionisation from the ground state of the molecule to a higher vibrational state of the ion.

If the transition occurs to a state higher than the dissociation energy (D), then the ion will fragment. In the case of curve C the ground state of the ion is dissociative, so no intact meolcular ion will be formed.
This example is for diatomic molecules; for polyatomic molecules, the curves are replaced by surfaces.

Unimolecular Reactions.

Reactions in an electron ionisation source assumed to be unimolecular, since the pressures are too low for significant interaction between molecules and ions.

3 types of ion are detected by the mass spectrometer:

1) Molecular ions - reach the detector without fragmentation
2) Daughter ions - fragment by decomposition reactions in the source
3) Metastable ions - fragment by decomposition reactions after leaving the source

2 factors dictate the extent of the various types of fragmentation and hence the appearance of the spectrum; the internal energy available in the molecular ion (discussed earlier) and the time taken for the ion to be transmitted through the instrument from the source to the detector.

The time factor needs to be considered since different reactions occur with different time scales or rate constants; we need to consider the rate constants for various types of reaction in relation to the time spent by ions in the source and analyser regions of the spectrometer.

Time scales:

Residence time of ions in the source are in the region of 10^{-6} s - 5×10^{-6} s, depending on source parameters and accelerating voltage.

The time taken for an ion to traverse the mass analyser region is of the order of 10^{-5} s.

Decomposition times are expressed in terms of a rate constant, which can be expressed as the reciprocal of the ion lifetime. e.g. the rate constant for a decomposition of an ion with a lifetime of 10μs is 10^5 s^{-1} .
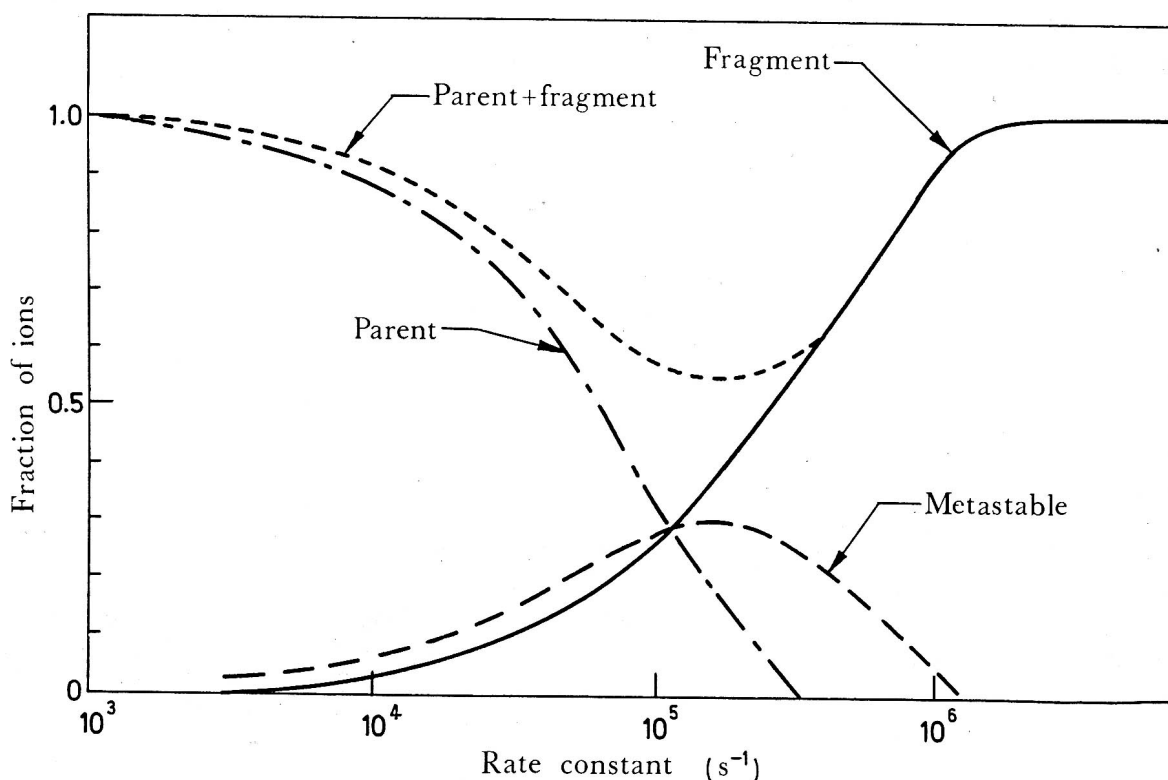
Conclusions of above discussion & diagram:

1) Fragment ions will only be detected if they possess sufficient energy for decomposition **and** the rate constant for decomposition is > ~10^4 s^{-1} (cf. molecular bond vibration times are ~10^{14} s^{-1}).
2) Parent ions will only be detected if the rate constant for decomposition is <~10^4 s^{-1}.
3) In the region of 10^5 s^{-1}, metastable decompositions occur between the source and detector.
4) For rate constants of 10^6 s^{-1} or greater, decompositions occur in the source, giving rise to fragment ions.