

### 12.3.2 Types of ions

#### **Adduct ion**

An ion formed by interaction of two species, usually an ion and a molecule, and often within an ion source, to form an ion containing all the constituent atoms of one species as well as an additional atom or atoms.

#### **Cluster ion**

An ion formed by the combination of two or more atoms, ions or molecules of a chemical species, often in association with a second species.

#### **Daughter ion**

An electrically charged product of reaction of a particular parent (precursor) ion. In general such ions have a direct relationship with a particular precursor ion and may relate to a unique state of the precursor ion. The reaction need not involve fragmentation, but could, for example involve a change in the number of charges carried. Thus a fragment ion is a daughter ion but not all daughter ions are fragment ions.

#### **Dimeric ion**

An ion formed when a chemical species exists in the vapour as a dimer and can be detected as such, or when a molecular ion can attach to a neutral molecule within the ion source to form an ion such as  $[M_2]^{+\bullet}$  where M represents the molecule.

#### **Even-electron ion**

An ion containing no unpaired electrons, e.g.  $CH_3^+$  in its ground state.

#### **Fragment ion**

An electrically charged dissociation product of an ionic fragmentation. Such an ion may dissociate further to produce other electrically charged molecular or atomic moieties of successively lower formula weight. See also *daughter ion*.

### **Isotopic ion**

Any ion containing one or more of the less abundant naturally occurring isotopes of the elements that make up its structure, e.g.  $\text{CH}_2\text{D}^+$ .

### **Isotopic molecular ion**

A molecular ion containing one or more of the naturally occurring isotopes of the atoms that make up the molecular structure. Thus for ethyl bromide there are isotopic molecular ions such as  $^{13}\text{CCH}_5\text{Br}^+$ ,  $\text{C}_2\text{H}_4\text{DBr}^+$ ,  $\text{C}_2\text{H}_5\text{}^{81}\text{Br}^+$ ,  $^{13}\text{C}_2\text{H}_5\text{}^{81}\text{Br}^+$  etc.

### **Isotopically enriched ion**

When the abundance of a particular nuclide is increased above the abundance at which it occurs in nature and this is incorporated in a molecule, the term *isotopically enriched ion* is used to describe any ion enriched in the isotope.

### **Metastable ion**

An ion which is formed with sufficient excitation to dissociate spontaneously during its flight from the ion source to the detector.

### **Molecular ion**

An ion formed by the removal from (positive ions) or addition to (negative ions) a molecule of one or more electrons without fragmentation of the molecular structure. The mass of this ion corresponds to the sum of the masses of the most abundant naturally occurring isotopes of the various atoms that make up the molecule, with a correction for the masses of the electrons lost or gain.

### **Multiply-charged ion**

See *singly-charged ion*.

### **Negative ion**

An atom, radical, molecule or molecular moiety in the vapour phase which has gained one or more electrons, acquiring thereby a negative charge. The term anion is not recommended because of its connotations in solution chemistry.

### **Odd-electron ion**

This term is synonymous with *radical ion*.

### **Parent ion**

An electrically charged molecular moiety which may dissociate to form fragments, one or more of which may be electrically charged, and one or more neutral species. A parent ion may be a molecular ion or an electrically charged fragment of a molecular ion. Synonymous with *precursor ion*.

### **Positive ion**

This is an electrically charged atom, radical, molecule or molecular moiety which has lost one or more electrons, thereby acquiring a positive charge. The term 'cation' is not recommended because of its use in solution chemistry. The use of the term 'mass ion' is not recommended.

### **Precursor ion**

Synonymous with *parent ion*. Instead of the use of *parent ion* and *daughter ion* terms the *precursor* and *product ion* terms are preferred respectively.

### **Principal ion**

This is defined as a molecular or fragment ion which is made up of the most abundant isotopes of each of its atomic constituents. In the case of compounds that have been artificially enriched in one or more positions such as  $\text{CH}_3$   $^{13}\text{CH}_3$  or  $\text{CH}_2\text{D}_2$  the principal ion may be defined by treating the heavy isotopes as new atomic species. Thus in the two above example the principal ions would be of masses 13 and 18, respectively.

### **Product ion**

Synonymous with *daughter ion*. Instead of the use of *parent ion* and *daughter ion* terms the *precursor* and *product ion* terms are preferred respectively.

### **Protonated molecule**

An ion formed by interaction of a molecule with a proton abstracted from an ion, as often happens in *chemical ionization* according to the reaction  $M + XH^+ \rightarrow MH^+ + X$ . The symbolism  $(M+H)^+$  may also be used. The widely used term 'protonated molecular ion' is not recommended as it suggests an association product of a proton with a molecular ion.

### **Quasi-molecular ion**

A term used to represent a protonated molecule or an ion formed from a molecular ion by loss of a hydrogen atom.

### **Radical ion**

This is an ion containing an unpaired electron, which is thus both an ion and a radical. In mass spectroscopy an unpaired electron is denoted by a superscript dot alongside the superscript symbol for charge, thus  $C_2H_6^{+\cdot}$  or  $SF_6^{\bar{\cdot}}$ . An alternative form (IUPAC Compendium of Chemical Terminology, 1987) used in inorganic and organic chemistry literature uses the symbolism as in  $X^{\cdot+}$ . For species with more than one charge and/or more than one unpaired electron the styles  $X^{(2+)(2\cdot)}$  or  $X^{(2\cdot)(2+)}$  are recommended.

### **Rearrangement ion**

An electrically charged species, involving a molecule or parent ion, in which atoms or groups of atoms have transferred from one part of a molecule or molecular moiety to another in the ionization fragmentation process.

### **Singly-, doubly-, triply-, etc. charged ion**

These terms describe an atom molecule or molecular moiety which has gained or lost respectively one, two, three or more electrons. The term *multiply-charged* ion refers to ions that have gained or lost more than one electron where the number of electrons lost or gained is not specified.

### **Stable ion**

An ion which is not sufficiently excited to dissociate spontaneously into a daughter ion and associated neutral fragment(s) or to react further before reaching the detector.

**Unstable ion**

An ion that is sufficiently excited to dissociate within the ion source .