

12.3 Processes and techniques

12.3.1 Ionization nomenclature

Adiabatic ionization

A process whereby an electron is either removed from or added to the atom or molecule producing an ion in its ground state.

Appearance energy ($A(X^+)$)

The minimum energy that must be imparted to an atom, molecule or molecular moiety in order to produce a specified ion X^+ . The term 'appearance potential' is not recommended.

Associative ionization

This occurs when two excited gaseous atoms or molecular moieties interact and the sum of their energies is sufficient to produce a single additive ionic product.

Auto-ionization

This occurs when an internally supra-excited atom or molecular moiety (in the *pre-ionization state*) loses an electron spontaneously without further interaction with an energy source.

Charge exchange (charge transfer) ionization

This occurs when an ion/atom or ion/molecule reaction takes place in which the charge on the ion is transferred to the neutral species without any dissociation of either.

Chemi-ionization

A process by means of which gaseous molecules are ionized when they interact with other internally excited gaseous molecules or molecular moieties. See also *associative ionization*. Note that this term is not synonymous with *chemical ionization*.

Chemical ionization

Describes the process whereby new ionized species are formed when gaseous molecules interact with ions. The process may involve transfer of an electron, a proton or other charged species between the reactants. When a positive ion results from chemical ionization the term may be used without qualification. When a negative ion results the term *negative ion chemical ionization* should be used. Note that this term is not synonymous with *chemi-ionization*, nor with negative chemical ionization.

Dissociative ionization

An ionization process in which a gaseous molecule decomposes to form products, one of which is an ion.

Electron affinity

The electron affinity of a species M is defined as the minimum energy required for the process $M^{\cdot -} \rightarrow M + e^{-}$ where $M^{\cdot -}$ and M are in their ground rotational, vibrational and electronic states and the electron has zero potential and kinetic energy.

Electron energy

The potential difference through which electrons are accelerated before they are used to bring about electron ionization.

Fast atom bombardment ionization

This term refers to the ionization of any species by causing interaction of the sample (which may be dissolved in a solvent matrix) and a beam of neutral atoms having a high translational energy. (See also *secondary ionization*).

Field desorption

This term is used to describe the formation of ions in the gas phase from a material deposited on a solid surface (known as an “emitter”) in the presence of an electric field. As this process probably encompasses ionization by *field ionization* as well as other mechanisms of ionization the term “field desorption” is not a precise one, despite its widespread acceptance.

Field ionization

The removal of electrons from any species by interaction with a high electric field. See also *field desorption*.

Ion-pair formation

This involves an ionization process in which a positive fragment ion and a negative fragment ion are among the products.

Ionic dissociation

The dissociation of an ion into another ion of lower mass and one or more neutral species.

Ionization cross section

This is a measure of the probability that a given ionization process will occur when an atom or molecule interacts with a photon.

Ionization efficiency

It is the ratio of the number of ions formed to the number of electrons or photons used.

Ionization energy ($I(M)$)

This is the minimum energy of excitation of an atom, molecule or molecular moiety M required to remove an electron in order to produce a positive ion.

Laser ionization

This occurs when a material is irradiated with a laser beam. In the irradiation of gaseous material ionization takes place by a single- or multi-photon process. For solids the ionization is thermal.

Multi-photon ionization

It occurs when an atom or a molecule and their concomitant ions have energy states whereby the energy in two or more photons is absorbed.

Negative ion chemical ionization

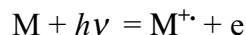
See *chemical ionization*.

Penning ionization

Ionization occurs through the interaction of two or more neutral gaseous species, at least one of which is internally excited.

Photo-ionization

This term is generally used to describe ionization of any species by photons. The process may for example be written



The terms 'photon impact' and 'electron impact' are not recommended.

Plasma desorption (fission fragment) ionization

This term describes the ionization of any species by interacting it with heavy particles (which may be ions or neutral atoms) formed as a result of the fission of a suitable nuclide adjacent to a target supporting the sample.

Pre-ionization state

See *auto-ionization*.

Proton affinity

The proton affinity of a species M is defined as the negative of the enthalpy change for the reaction $M + H^+ \rightarrow MH^+$.

Spark ionization

This occurs when a solid material is vaporized and partially ionized by an intermittent electric discharge. Further ionization occurs in the discharge when gaseous atoms and small molecular moieties interact with energetic electrons in the intermittent discharge.

Surface ionization

This takes place when an atom or molecule is ionized when it interacts with a solid surface. Ionization only occurs when the work function of the surface, the temperature of the surface and the ionization energy of the atom or molecule have an appropriate relationship.

Thermal ionization

This occurs where an atom or molecule interacts with a heated surface or is in a gaseous environment at high temperature. (Examples include a capillary arc plasma, a microwave plasma and an inductively coupled plasma.)

Vertical ionization

This is a process whereby an electron is removed from a molecule in its ground or an excited state so rapidly that a positive ion is produced without change in the positions or momenta of the atoms. The resultant ion is often in an excited state.

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 $[M_2]^+$ 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. CH_2D^+ .

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 CH_3 $^{13}\text{CH}_3$ or CH_2D_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 $SF_6^{\cdot-}$. 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 .

12.3.3 Scanning of spectra

12.3.3.1 General

Accelerating voltage (V) scan

A method of producing a momentum (mass) spectrum in a magnetic deflection instrument by varying the accelerating voltage. This scan can also be used in conjunction with a fixed radial electric field to produce an *ion kinetic energy spectrum*.

Ion kinetic energy spectrum

A spectrum obtained when a beam of ions is separated according to the translational energy-to-charge ratios of the ionic species contained in it. A radial electric field (E) achieves separation of the various ionic species in this way.

Magnetic field (B) scan

The usual method of producing a momentum (mass) spectrum in instruments is by varying the strength of the magnetic field.

Mass spectrum

A spectrum that is obtained when a beam of ions is separated according to the mass/charge (m/z) ratios of the ionic species contained within it.

Momentum spectrum

A spectrum that is obtained when a beam of ions is separated according to the momentum/charge ratios of the ionic species contained within it. A sector magnetic field achieves separation of the various ionic species in this way. If the ion beam is homogeneous in translational energy, as is the case with sector instruments, separation according to the m/z ratios is also achieved and a *mass spectrum* produced.

Selected ion (peak) monitoring

This term is used to describe the operation of the mass spectrometer in which the intensities of several specific ion beams are recorded rather than the entire mass spectrum. An alternative recommended term is *multiple ion (peak) monitoring*. The use of the terms “multiple ion detection” and 'mass fragmentography' is not recommended.

12.3.3.2 Tandem Mass Spectrometers

General

Fixed neutral loss (gain) scan

A scan that determines, in a single instrument, all the parent ion mass/charge ratios which react to the loss or gain of a selected neutral mass.

Fixed neutral loss (gain) spectrum

A spectrum obtained when data are acquired that determine all the parent ion mass/charge ratios that react by the loss (gain) of a selected neutral mass.

Fixed precursor ion scan

A scan that determines, in a single experiment, all the daughter ion mass/charge ratios that are produced by the reaction of a selected parent ion mass-to-charge ratio.

Fixed precursor ion spectrum

A spectrum obtained when data are acquired that determine all the daughter ion mass/charge ratios produced by the reaction of a selected parent mass/charge ratio.

Fixed product ion scan

A scan that determines, in a single experiment, all the parent ion mass/charge ratios that react to produce a selected daughter ion mass/charge ratio.

Fixed product ion spectrum

A spectrum obtained when data are acquired that determine all parent ion mass/charge ratios that react to produce a selected daughter ion mass/charge.

Magnetic Sector Instruments

2E mass spectrum

Processes of the partial charge-transfer type:



occurring in collision cell (containing gas X) located in a field-free region preceding a magnetic and electric sector combination placed in either order, may be detected as follows;

if the instrument slits are wide and if the electric sector field is set to twice the value required to transmit the main ion beam, the only ions transmitted will be those with kinetic energy/charge ratio twice, or almost twice, that of the main ion beam. The product ions of the above charge stripping process fulfil that condition. If the magnetic field, B , is scanned, a mass spectrum of such singly-charged product ions and thus of

their doubly-charged precursors is obtained. Such a spectrum is termed a *2E mass spectrum*.

***B* (magnetic flux density)**

Refers to the *magnetic flux density* within the magnetic sector of a mass spectrometer. See also 1.3.3.

Charge inversion mass spectrum

Charge inversion processes of the types:



respectively, occurring in a collision cell (containing a gas X) located in a field-free zone preceding a magnetic and electric sector combination placed in either order, may be detected as follows:

if the instrument slits are wide and if the connections to the two sectors, appropriate to transmission of either positive or negative main-beam ions, are simply reversed, the negative or positive product ions respectively will be transmitted. If the magnetic field is scanned a spectrum of such ions will be obtained and this is termed a *charge-inversion spectrum*. These are sometimes referred to as *-E* and *+E* spectra.

Note: The terms '*2E*, *E/2*, *-E* or *+E* mass spectrum' should not be used without prior explanation of their meaning.

***E* (electric field strength)**

Refers to the *electric field strength* within the electric sector of a mass spectrometer. See also 1.3.3.

***E* / 2 mass spectrum**

Processes of the charge-stripping type:



occurring in collision cell (containing gas X) located in a field-free region preceding a magnetic and electric sector combination placed in either order, may be detected as follows;-

if the instrument slits are wide and if the electric sector field is set to half the value required to transmit the main ion beam, the only ions transmitted will be those with kinetic energy/charge ratio half, or almost half, that of the main ion beam. The product ions of the above charge stripping process fulfil that condition. If the magnetic field, B , is scanned, a mass spectrum of such doubly-charged product ions and thus of their singly-charged precursors is obtained. Such a spectrum is termed a *E* / 2 mass spectrum.

Linked scan

A scan in an instrument comprising two or more analysers in which two or more of the analyser fields are scanned simultaneously so as to preserve a predetermined relationship between parameters characterizing these fields. While these parameters are commonly field strengths, they may also be frequencies in analysers where alternating fields are employed.

Linked scan at constant B/E

This can be performed with a sector instrument incorporating at least one magnetic sector and one electric sector. The magnetic sector field strength, B , and the electric sector field strength, E , are scanned simultaneously, while holding the accelerating voltage, V , constant, so as to maintain the ratio B/E constant. This constant value is determined by the ratio of the two field strengths required to transmit main-beam ions of predetermined mass/charge ratio. These preselected main-beam ions are the precursor ions whose fragment ion spectrum is required. The term B/E linked scan is not recommended.

Linked scan at constant $B [1 - (E/E_0)]^{1/2} / E$

This can be performed with a sector instrument incorporating at least one electric sector plus one magnetic sector. The magnetic sector field strength, B , and the electric sector field strength, E , are scanned simultaneously, while holding the accelerating voltage, V ,

constant, so as to maintain the ratio $B [1 - (E/E_0)]^{1/2}/E$ constant. This constant value is equal to B_3/E_0 , where E_0 and B_3 are respectively the electric and magnetic sector fields required to transmit M^{3+} ions in the main ion beam; m_3 represents the mass (m_1-m_2) of the selected neutral fragment M_3 whose precursor spectrum is required. The fragmentation reactions thus observed occur in a field-free region traversed before the two sectors scanned in this way. The term ' $B [1 - (E/E_0)]^{1/2}/E$ linked scan' is not recommended.

Linked scan at constant B^2/E

This can be performed with a sector instrument incorporating at least one electric sector plus one magnetic sector. The accelerating voltage is fixed and the magnetic field, B , and the electric field, E , are scanned simultaneously so as to maintain B^2/E constant. This constant value corresponds to the ratio of the two fields which transmits main-beam ions of predetermined mass/charge ratio; these preselected main-beam ions are the fragment ions whose precursor ion spectrum is required. The fragmentation reactions thus observed occur in a field-free region traversed before the two sectors scanned in this way.

The term

' B^2/E linked scan' is not recommended. Note: other examples of linked scan should be defined in a similar way to the examples given here.

Linked scan at constant E^2/V

This may be performed with a sector instrument incorporating at least one electric sector plus one magnetic sector. The electric sector field, E , and the accelerating voltage, V , are scanned simultaneously so as to maintain E^2/V ratio at constant value equal to the value of this ratio that transmits the main beam ions through the electric sector. The magnetic sector field is set at a fixed value such that main-beam ions of a predetermined mass/charge ratio are transmitted by the magnetic sector; these preselected main-beam ions are the precursor ions whose fragment ion spectrum is required. The fragmentation reactions thus observed occur in a field-free region traversed before the two sectors scanned in this way. The term

' E^2/V linked scan' is not recommended.