

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION*

STANDARD DEFINITIONS OF TERMS RELATING TO MASS SPECTROMETRY

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Prepared for publication by

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Abstract

This document contains the third draft of recommendations for nomenclature, definitions of terms, and acronyms in mass spectrometry. This draft is currently undergoing review for publication in the IUPAC journal *Pure and Applied Chemistry* and comments during the review process are welcomed. Please direct comments regarding this document to the corresponding author noted above. This document is an update of mass spectrometry nomenclature that goes back over thirty years. In 1974, the IUPAC Commission on Analytical Nomenclature issued recommendations on mass spectrometry terms and definitions. In 1978, the Commission on Molecular Structure and Spectroscopy updated and extended the recommendations and made further recommendations regarding symbols, acronyms and abbreviations. The Physical Chemistry Division Commission on Molecular Structure and Spectroscopy's Subcommittee on Mass Spectroscopy revised the recommended terms in 1991 and appended terms relating to vacuum technology. Some additional terms related to tandem mass spectrometry were added in 1993 and accelerator mass spectrometry in 1994. Due to the rapid expansion of the field, particularly in mass spectrometry of biomolecules, a further revision of the recommendations has become necessary.

Introduction

Mass spectrometry is the study of matter through the formation of gaseous ions that are characterized by their mass and charge. The recommendations in this document pertain to fundamental, technical and experimental aspects of ion formation, mass selection, detection and analysis of mass spectra. Terms that are not specific to the field have been omitted.

In 1991, the IUPAC Physical Chemistry Division Commission on Molecular Structure and Spectroscopy's Subcommittee on Mass Spectroscopy issued recommendations on mass spectrometry nomenclature[1]. These recommendations were supplemented by terms prepared for the Analytical Chemistry Division related to tandem mass spectrometry of organic molecules (Commission on Microchemical Techniques and Trace Analysis and the Working group on Organic Trace Analysis)[2] and accelerator mass spectrometry (Commission on Radiochemistry and Nuclear Techniques)[3] and included as a chapter in the *Compendium of Analytical Nomenclature* "Orange Book".[4]

Over the years, IUPAC has worked with the American Society for Mass Spectrometry in developing mass spectrometry terms and definitions. The ASMS Measurements and Standards Committee published its latest version of Standard Definitions of Terms Related to Mass Spectrometry in 1991.[5] The document represented the compilation of terms and definitions assembled between 1984 and 1990 by the Measurements and Standards Committee and closely paralleled the IUPAC terminology effort. A revised version of these terms was presented at the ASMS Conference in Palm Springs, California in June of 1997 by the Measurements and Standards Committee and was available on the ASMS website between 1998 and 2000[6]. The most recently published compilation of mass spectrometry terms is contained in the book "Mass Spectrometry Desk Reference" by O. David Sparkman.[7]

In the fifteen years since the last recommendations of IUPAC and ASMS, the field of mass spectrometry has changed radically. The introduction of soft ionization methods for the analysis of biological molecules has expanded the scope of mass spectrometry from its early roots in the analysis of inorganic and organic species into other fields such as biology and medicine. The expansion in scope has led to a growth in the number of terms and also in the use of those terms by those not trained in mass spectrometry or in analytical or physical chemistry. As a result, this compilation of terms and definitions represents an extensive revision and expansion of the previous compilation. It is intended that these recommendations replace all earlier publications on the subject.

A Note on the Identification of New and Revised Terms

Terms that can be found in the *Orange Book*[4] and in the *Gold Book*[8] are indicated by OB and GB, respectively. Terms that have been revised are indicated by revOB or revGB. Rewording and additional cross-referencing are not considered as revision in this document. New terms are not identified other than by lack of the above notation.

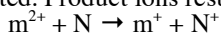
Document Organization

Previous compilations of mass spectrometry terms have been organized alphabetically within sections. This document is organized in glossary format: alphabetically with no sections.

Terms

1 2E mass spectrum

Mass spectrum obtained by setting the electric sector field E to twice the value required to transmit the main ion beam thereby allowing ions with a translational energy-to-charge ratio twice that of the main ion beam to be transmitted. Product ions resulting from partial charge transfer reactions such as



that occur in a collision cell (containing a gas, N) located in a field-free region preceding a magnetic and electric sector combination are detected. When the magnetic sector field B is scanned, a mass spectrum of singly charged product ions of doubly charged precursor ions is obtained. OB.

2 accelerating voltage

Electrical potential used to impart translational energy to ions in a mass spectrometer. See [9].

3 accelerator mass spectrometry, (AMS)

Mass spectrometry technique in which atoms extracted from a sample are ionized, accelerated to MeV energies and separated according to their momentum, charge and energy. See [3].

4 accurate mass

Experimentally determined mass of an ion that is used to determine an elemental formula. Note: *accurate mass* and *exact mass* are not synonymous. The former refers to a measured mass and the latter to a calculated mass. See [10,11].

5 adiabatic ionization

Process whereby an electron is removed from an atom, ion, or molecule in its lowest energy state to produce an ion in its lowest energy state. GB, OB.

6 adduct ion

Ion formed by the interaction of an ion with one or more atoms or molecules to form an ion containing all the constituent atoms of the precursor ion as well as the additional atoms from the associated atoms or molecules. GB, OB.

7 α -cleavage

Homolytic cleavage where the bond fission occurs between the atom adjacent to the atom at the apparent charge site and an atom removed from the apparent charge site by two bonds. GB, OB.

8 a-ion

Fragment ion containing the N-terminus formed upon dissociation of a protonated peptide at a backbone C-C bond. See [12].

9 analog ion

Ions that have similar chemical valence, for example the acetyl cation $\text{CH}_3\text{-CO}^+$ and the thioacetyl cation $\text{CH}_3\text{-CS}^+$. See [13].

10 appearance energy (AE)

Minimum energy that must be imparted to an atom or molecule to produce a detectable amount of a specified ion. In mass spectrometry it is the voltage which corresponds to the minimum electron energy necessary for the production of a given fragment ion. The term *appearance potential* (AP) is deprecated. revGB, OB.

11 array detector

Detector comprising several ion collection elements, arranged in a line or grid where each element is an individual detector. See [14,15].

12 associative ionization

Ionization process in which two atoms or molecules, one or both of which is in an excited state, react to form a single positive ion and an electron. GB, OB.

13 associative ion/molecule reaction

Reaction of an ion with a neutral species in which the reactants combine to form a single ion. See [16].

14 atmospheric pressure ionization (API)

Ionization process in which ions are formed in the gas phase at atmospheric pressure.

revGB, See [17,18].

15 atmospheric pressure chemical ionization (APCI)

Chemical ionization that takes place using a nebulized liquid and atmospheric pressure corona discharge. See [18].

16 atmospheric pressure matrix-assisted laser desorption/ionization (AP MALDI)

Matrix-assisted laser desorption/ionization in which the sample target is at atmospheric pressure. See [19].

17 atmospheric pressure photoionization (APPI)

Atmospheric pressure chemical ionization in which the reactant ions are generated by photoionization. See [20].

18 autodetachment

Formation of a neutral species when a negative ion in a discrete state with an energy greater than the detachment threshold loses an electron spontaneously without further interaction with an energy source. See [21].

19 autoionization

Formation of an ion when an atom or molecule in a discrete state with an internal energy greater than the ionization threshold loses an electron spontaneously without further interaction with an energy source. OB.

20 average mass

Mass of an ion or molecule calculated using the average mass of each element weighted for its natural isotopic abundance. OB, See [22]

21 base peak (BP)

Peak in a mass spectrum that has the greatest intensity. Note: This term may be applied to the spectra of pure substances or mixtures. GB, OB.

22 bath gas

See *buffer gas*. See [23].

23 β -cleavage

Homolytic cleavage where the bond fission occurs between an atom removed from the apparent charge site atom by two bonds and an atom adjacent to that atom and removed from the apparent charge site by three bonds. GB, OB.

24 b-ion

Fragment ion containing the N-terminus formed upon dissociation of a protonated peptide at a backbone C-N bond. See [12].

25 blackbody infrared radiative dissociation (BIRD)

Special case of infrared multiphoton dissociation wherein excitation of the reactant ion is caused by absorption of infrared photons radiating from heated blackbody surroundings, which are usually the walls of a vacuum chamber. Related term: *infrared multiphoton dissociation*. See [24].

26 buffer gas

Inert gas used for collisional deactivation of internally excited ions or of the translational energies of ions confined in an ion trap. See [23].

27 cationized molecule

Ion formed by the association of a cation with a molecule, M, for example $[\text{M} + \text{Na}]^+$ and $[\text{M} + \text{K}]^+$. The terms *quasi-molecular ion* and *pseudo-molecular ion* are deprecated. See [23].

28 centroid acquisition

Procedure of recording mass spectra in which an automated system detects peaks, calculates their centroids, and assigns m/z values based on a calibration file. Only the centroid m/z and the peak intensity are stored. See *continuum acquisition*. See [25].

29 charge exchange ionization

Interaction of an ion with an atom or molecule in which the charge on the ion is transferred to the neutral without the dissociation of either. See *charge transfer ionization*. GB, OB.

30 charge exchange reaction See *charge transfer reaction*. GB, OB.

31 charge inversion mass spectrum

Plot of the relative abundance of ions that result from a charge inversion reaction as a function of m/z . GB, OB.

32 charge inversion reaction

Reaction of an ion with a neutral species in which the charge on the product ion is reversed in sign with respect to the reactant ion. OB.

33 charge mediated fragmentation

Fragmentation of an ion in which the cleaved bond is adjacent to the apparent charge site. See [26].

34 charge number, z

Total charge on an ion, regardless of sign, divided by the magnitude of the electron charge e . GB, OB.

35 charge permutation reaction

Reaction of an ion with a neutral species with a resulting change in the magnitude or sign of the charge on the reactant ion. GB, OB.

36 charge remote fragmentation (CRF)

Fragmentation of an ion in which the cleaved bond is not adjacent to the apparent charge site. See [27,28].

37 charge stripping reaction (CSR)

Reaction of a positive ion with a neutral species in which the positive charge on the product ion is greater than that on the reactant ion. GB, OB.

38 charge transfer reaction

Reaction of an ion with a neutral species in which some or all of the charge of the reactant ion is transferred to the neutral species. revGB, revOB, See [29].

39 chemical ionization (CI)

Formation of a new ion in the gas phase by the reaction of a neutral species with an ion. The process may involve transfer of an electron, a proton or other charged species between the reactants. Note 1: 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 2: this term is not synonymous with *chemi-ionization*. GB, OB.

40 chemi-ionization

Reaction of an atom or molecule with an internally excited atom or molecule to form an ion. Note that this term is not synonymous with *chemical ionization*. GB, OB.

41 c-ion

Fragment ion containing the N-terminus formed upon dissociation of a protonated peptide at a backbone N-C bond. See [12].

42 classical ion

See *non-classical ion*. See [30].

43 cluster ion

Ion formed by a multi-component atomic or molecular assembly of one or more ions with atoms or molecules, such as $[(H_2O)_nH]^+$, $[(NaCl)_nNa]^+$ and $[(H_3PO_3)_nHPO_3]^+$. GB, OB.

44 collisional activation (CA)

See *collisional excitation*. GB, OB.

45 collisional excitation

Reaction of an ion with a neutral species in which all or part of the translational energy of the collision is converted into internal energy of the ion. GB, OB.

46 collision gas

Inert gas used for collisional excitation and ion/molecule reactions. The term *target gas* is deprecated. See [31].

47 collision-induced dissociation (CID)

Dissociation of an ion after collisional excitation. The term *collisionally activated dissociation (CAD)* is deprecated. GB, OB.

48 collision quadrupole

Transmission quadrupole to which an oscillating radio frequency potential is applied so as to focus a beam of ions through a collision gas with no m/z separation. Note: a collision quadrupole is often indicated by a lower case q. See [32,33]

49 collision reaction cell

A transmission hexapole or octapole collision cell to which an oscillating radio frequency potential is applied that is used for charge exchange neutralization of interfering ions in inductively coupled plasma mass spectrometry. See [34].

50 consecutive reaction monitoring (CRM)

MS^n experiment with three or more stages of m/z separation and in which a particular multi-step reaction path is monitored. See [35].

51 constant neutral loss scan

A scan procedure for a tandem mass spectrometer designed to produce a constant neutral loss spectrum of different precursor ions by detection of the corresponding product ions produced by metastable ion fragmentation or collision-induced dissociation.

Synonymous terms are *constant neutral mass loss scan* and *fixed neutral fragment scan*. GB, OB.

52 constant neutral loss spectrum

Spectrum of all precursor ions that have undergone an operator-selected m/z decrement, obtained using a *constant neutral loss scan*. See *constant neutral mass loss spectrum* and *fixed neutral mass loss spectrum*. GB, OB.

53 constant neutral mass gain scan

Scan procedure for a tandem mass spectrometer designed to produce a *constant neutral mass gain spectrum* of different precursor ions by detection of the corresponding product ions of ion/molecule reactions with a gas in a collision cell. GB, OB.

54 constant neutral mass gain spectrum

Spectrum formed of all product ions produced by gain of a pre-selected neutral mass following ion/molecule reactions with the gas in a collision cell, obtained using a *constant neutral mass gain scan*. GB, OB.

55 continuous dynode particle multiplier

An ion-to-electron detector in which the ion strikes the inner surface of the device and induces the production of secondary electrons that in turn impinge on the inner surfaces to produce more secondary electrons. This avalanche effect produces an increase in signal in the final measured current pulse. See [36].

56 continuous flow fast atom bombardment

Variant of fast atom bombardment in which the mixture of analyte and liquid matrix is supplied continuously to the sample probe. See [37,38].

57 conversion dynode

Surface that is held at high potential so that ions striking the surface produce electrons that are subsequently detected. See [39].

58 curved field reflectron

Reflectron in which the retarding field is non-linear. The voltages on the lens elements follow the equation of an arc of a circle according to $R^2 = V^2 + x^2$, where x is the distance from the reflectron inlet, V is the voltage and R is a constant. See [40,41].

59 cyclotron motion

Circular motion of a particle of charge q moving at velocity \mathbf{v} in a magnetic flux density \mathbf{B} that results from the Lorentz force $q\mathbf{v}\times\mathbf{B}$. See [42].

60 dalton, Da

Non-SI unit of mass (symbol Da) that is identical to the unified atomic mass unit. GB, OB.

61 Daly detector

Detector consisting of a conversion dynode, scintillator and photomultiplier. The metal knob at high potential emits secondary electrons when ions impinge on the surface. The secondary electrons are accelerated onto the scintillator that produces light that is then detected by the photomultiplier detector. See [43].

62 delayed extraction (DE)

Application of the accelerating voltage pulse after a time delay in desorption/ionization from a surface. The extraction delay can produce energy focusing in a time-of-flight mass spectrometer. See [41,44]

63 diagnostic ion

Product ion whose formation reveals structural or compositional information of its precursor. For instance, the phenyl cation in an electron ionization mass spectrum is a diagnostic ion for benzene and derivatives. See [45].

64 dimeric ion

An ion formed by ionization of a dimer or by the association of an ion with its neutral counterpart such as $[M_2]^{+}$ or $[M-H-M]^+$. GB.

65 desorption electrospray ionization (DESI)

Production of gaseous ions from material present on a solid surface by directing charged droplets and solvent ions from an electrospray ionization source onto the surface at atmospheric pressure. See [46].

66 desorption ionization (DI)

Formation of ions from a solid or liquid material by the rapid vaporization of that sample. See [47].

67 direct insertion probe

Device for introducing a single sample of a solid or liquid, usually contained in a quartz or other non-reactive sample holder, into a mass spectrometer ion source. See [48].

68 direct liquid introduction (DLI)

Delivery of a liquid sample into a mass spectrometer. See [49].

69 dissociative ionization

Reaction of a gas-phase molecule that results in its decomposition to form products, one of which is an ion. GB, OB.

70 distonic ion

Radical cation or anion arising formally by ionization of diradicals or zwitterionic molecules (including ylides). In these ions the charge site and the unpaired electron spin cannot be both formally located in the same atom or group of atoms as it can be with a *conventional ion*. For example, $^{\bullet}\text{CH}_2\text{-OH}_2^+$ is a distonic ion whereas the radical cation of methanol, $\text{CH}_3\text{OH}^{+\bullet}$ is a conventional ion. This term is also used for multiply charged ions such as the distonic oxonium dication $\text{H}_2\text{O}^+\text{-CH}_2\text{-CH}_2\text{-OH}_2^+$ as opposed to the gitonic (proximal) oxonium dication $\text{HO-CH}_2\text{-CH}_2\text{-OH}_3^{2+}$. See [50].

71 double-focusing mass spectrometer

Mass spectrometer that incorporates a magnetic sector and an electric sector connected in series in such a way that ions with the same m/z but with distributions in both the direction and the translational energy of their motion are brought to a focus at a point. GB, OB.

72 dynamic field mass spectrometer

Mass spectrometer in which m/z separation is achieved using one or more electric fields that vary with time. GB, OB.

73 dynamic reaction cell

Collision cell mounted between a plasma ion source and mass analyzer whose function is to cause collisional dissociation of polyatomic molecules and thereby reduce interferences. See [51].

74 dynamic secondary ionization

Formation of ions by secondary ionization from a surface under conditions so that the intensity and energy of the primary ions are sufficiently high that the material is continuously removed, thus supplying ions derived from increasing depth below the original surface. See [52].

75 einzel lens

Three element charged particle lens in which the first and third elements are held at the same voltage. Such a lens produces focusing without changing the translational energy of the particle. See [52].

76 electric sector

See *electrostatic energy analyzer*. GB, OB.

77 electron affinity, E_{EA}

Electron affinity of a species M is the minimum energy required for the process $M^- \rightarrow M + e$ where M^- and M are in their ground rotational, vibrational and electronic states and the electron has zero translational energy. GB, OB.

78 electron attachment ionization

Ionization of a gaseous atom or molecule by attachment of an electron to form M^+ ions. See [53].

79 electron capture dissociation (ECD)

Process in which multiply protonated molecules interact with low energy electrons. Capture of the electron leads the liberation of energy and a reduction in charge state of the ion with the production of the $[M + nH]^{(n-1)+}$ odd electron ion, which readily fragments. See [54].

80 electron energy

Magnitude of the electron charge multiplied by the potential difference through which electrons are accelerated in order to effect electron ionization. GB, OB.

81 electron ionization

Ionization of an atom or molecule by electrons that are typically accelerated to energies between 10 and 150 eV in order to remove one or more electrons from the molecule. The term *electron impact* is deprecated. GB, OB.

82 electron volt, eV

Non-SI unit of energy (symbol eV) defined as the energy acquired by a particle containing one unit of charge through a potential difference of one volt. An electron volt is equal to $1.602\ 177\ 33(49) \times 10^{-19}$ J. GB.

83 electrospray ionization (ESI)

A process in which ionized species in the gas phase are produced from a solution *via* highly charged fine droplets, by means of spraying the solution from a narrow-bore needle tip at atmospheric pressure in the presence of a high electric field (1,000 to 10,000 V potential). Note: When a pressurized gas is used to aid in the formation of a stable spray, the term *pneumatically-assisted electrospray ionization* is used. The term *ionspray* is deprecated. See [55,56].

84 electrostatic energy analyzer (ESA)

A device consisting of conducting parallel plates, concentric cylinders or concentric spheres that separates charged particles according to their ratio of translational energy to charge by means of a voltage difference applied between the pair. See [57].

85 E/2 mass spectrum

Mass spectrum obtained using a sector mass spectrometer in which the electric sector field E is set to half the value required to transmit the main ion-beam. This spectrum records the signal from doubly charged product ions of *charge-stripping reactions*. GB, OB.

86 even-electron ion

An ion containing no unpaired electrons in its ground electronic state. GB, OB.

87 exact mass

Calculated mass of an ion or molecule containing a single isotope of each atom, most frequently the lightest isotope of each element, calculated from the masses of these isotopes using an appropriate degree of accuracy. See [58].

88 extracted ion chromatogram

Chromatogram created by plotting the intensity of the signal observed at a chosen *m/z* value or series of values in a series of mass spectra recorded as a function of retention time. See *reconstructed ion chromatogram*. See [59,60].

89 faraday cup

A conducting cup or chamber that intercepts a charged particle beam and is electrically connected to a current measuring device. GB, OB.

90 fast atom bombardment (FAB)

Ionization of any species by the interaction of a focused beam of neutral atoms having a translational energy of several thousand eV with a sample that is typically dissolved in a solvent matrix. Related term: *secondary ionization*. See [61].

91 fast ion bombardment (FIB)

Ionization of any species by the interaction of a focused beam of ions having a translational energy of several thousand eV with a solid or liquid sample. For a liquid sample this is the same as *liquid secondary ionization*. GB, OB.

92 field desorption (FD)

Formation of gas-phase ions in the presence of a high electric field from a material deposited on a solid surface. The term *field desorption/ionization* is deprecated. GB, OB.

93 field-free region (FFR)

Section of a mass spectrometer in which there are no electric or magnetic fields. See [62].

94 field ionization (FI)

Removal of electrons from any species, usually in the gas phase, by interaction with a high electric field. GB, OB.

95 first stability region

Region of a Mathieu stability diagram closest to the origin. Ions within this region can traverse the full length of a transmission quadrupole. See [63].

96 fission fragment ionization

See *plasma desorption/ionization*. GB.

97 fixed product ion scan

In a sector instrument, either a high voltage scan or a linked scan at constant B^2/E . Both give a spectrum of all precursor ions that fragment to yield a pre-selected product ion. Note: The term *daughter ion* is deprecated [64,65] OB.

98 focal plane detector

Detector for spatially disperse ion beams in which all ions simultaneously impinge on the detector plane. See [66].

99 forward library search

A procedure of comparing a mass spectrum of an unknown compound with a mass spectral library so that the unknown spectrum is compared in turn with the library spectra, considering only all the m/z peaks observed to have significant intensity in the unknown. See [67].

100 Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR)

A mass spectrometer based on the principle of ion cyclotron resonance in which an ion in a magnetic field moves in a circular orbit at a frequency characteristic of its m/z value. Ions are coherently excited to a larger radius orbit using a pulse of radio frequency energy and their image charge is detected on receiver plates as a time domain signal.

Fourier transformation of the time domain signal results in a frequency domain signal which is converted to a mass spectrum based in the inverse relationship between frequency and m/z . GB, OB.

101 fragment ion

A product ion that results from the dissociation of a *precursor ion*. Note: The term *daughter ion* is deprecated [64,65]. GB, OB.

102 fringe field

Electric or magnetic field that extends from the edge of a sector, lens or other ion optics element. See [68].

103 glow discharge ionization

The formation of ions in the gas phase and from solid samples at the cathode by application of a voltage to a low pressure gas. See [69].

104 gridless reflectron

A reflectron in which ions do not pass through grids in their deceleration and turn-around thereby avoiding ion loss due to collisions with the grid. See [41].

105 hard ionization

Formation of gas-phase ions accompanied by extensive fragmentation. See [9].

106 heterolysis See *heterolytic cleavage*. GB.

107 heterolytic cleavage

Fragmentation of a molecule or ion in which both electrons forming the single bond that is broken remain on one of the atoms that were originally bonded. See *heterolysis*. GB.

108 high-energy collision-induced dissociation

Collision-induced dissociation process wherein the projectile ion has laboratory-frame translational energy higher than 1 keV. See [70,71].

109 high-field asymmetric waveform ion mobility spectrometry

Separation of ions at atmospheric pressure between two electrodes due to simultaneous application of a high voltage asymmetric waveform and a variable DC potential difference whereby ions migrate towards one of the two electrodes depending on the ratio of the high- to low-field mobility of the ion. See [72].

110 homolysis

See *homolytic cleavage*. GB.

111 homolytic cleavage

Fragmentation of an ion or molecule in which the electrons forming the single bond that is broken are shared between the two atoms that were originally bonded. For an odd electron ion, fragmentation results from one of a pair of electrons that form a bond between two atoms moving to form a pair with the odd electron on the atom at the apparent charge site. Fragmentation results in the formation of an even electron ion and a radical. This reaction involves the movement of a single electron and is represented by a single-barbed arrow. See *homolysis*. GB.

112 hydrogen/deuterium exchange

Exchange of hydrogen atoms with deuterium atoms in a molecule or pre-formed ion in solution prior to introduction into a mass spectrometer, or by reaction of an ion with a deuterated collision gas inside a mass spectrometer. See [73,74].

113 hybrid mass spectrometer

A mass spectrometer that combines m/z analyzers of different types to perform tandem mass spectrometry. OB.

114 imaging mass spectrometry

Procedure used to form chemically-selective images of objects based on the mass spectrometric detection of ions desorbed from its surface. See [75].

115 inductive cleavage

A *heterolytic cleavage* of an ion. For an odd electron ion, inductive cleavage results from the pair of electrons that forms a bond to the atom at the apparent charge site moving to that atom while the charge site moves to the adjacent atom. The movement of the electron pair is represented by a double-barbed arrow. See [9].

116 inductively coupled plasma (ICP)

A gas discharge ion source in which the energy to the plasma is supplied by electromagnetic induction. See [76].

117 infrared multiphoton dissociation (IRMPD)

Dissociation of a reactant ion as a result of the absorption of multiple infrared photons. See [77-79].

118 in-source collision-induced dissociation

The dissociation of an ion as a result of collisional excitation during ion transfer from an atmospheric pressure ion source and the mass spectrometer vacuum. This process is similar to *ion desolvation* but uses higher collision energy. See [80].

119 ion

An atomic, molecular or radical species with an unbalanced electrical charge. The corresponding neutral species need not be stable. GB.

120 ion desolvation

The removal of solvent molecules clustered around a gas-phase ion by means of heating and/or collisions with gas molecules. See [80].

121 ion energy loss spectrum

A plot of the relative abundance of a beam or other collection of ions as a function of their loss of translational energy in reactions with neutral species. GB, OB.

122 ion gate

See *mass gate*. See [81].

123 ionic dissociation

The dissociation of an ion into another ion of lower mass and one or more neutral species or ions with a lower charge. GB, OB.

124 ion/ion reaction

The reaction between two ions, typically of opposite polarity. The term *ion-ion* reaction is deprecated. See [82].

125 ionization cross section

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

126 ionization efficiency

Ratio of the number of ions formed to the number of molecules consumed in the ion source.

revGB, revOB, See [83,84].

127 ionizing collision

Reaction of an ion with a neutral species in which one or more electrons are removed from either the ion or neutral. GB, OB.

128 ion kinetic energy spectrometry (IKES)

A procedure of analysis in which a beam of ions is separated according to the ratio of its translational energy to charge. GB, OB.

129 ion mobility spectrometry (IMS)

Separation of ions according to their velocity through a buffer gas under the influence of an electric field. See [85,86].

130 ion/molecule reaction

Reaction of an ion with a molecule. Note: the term *ion-molecule reaction* is deprecated because the hyphen suggests a single species that is both an ion and a molecule. GB, OB.

131 ion/neutral complex

A particular type of transition state that lies between precursor and product ions on the reaction coordinate of some ion reactions. See [86].

132 ion/neutral reaction

Reaction of an ion with an atom or molecule. See [82,87,88].

133 ion/neutral exchange reaction

Reaction of an ion with a neutral species to produce a different neutral species as the product. GB, OB.

134 ion-pair formation

Reaction of a molecule to form both positive ion and negative ion fragments among the products. GB, OB.

135 ion source

Region in a mass spectrometer where ions are produced.

revGB. See [89].

136 ion-to-photon detector

Detector in which ions strike a conversion dynode to produce electrons that in turn strike a phosphor and the resulting photons are detected by a photomultiplier. See [90].

137 ion trap (IT)

Device for spatially confining ions using electric and magnetic fields alone or in combination. revGB, revOB, See [91,92].

138 isotope dilution mass spectrometry

A quantitative mass spectrometry technique in which an isotopically enriched compound is used as an internal standard. See [93].

139 isotope ratio mass spectrometry (IRMS)

The measurement of the relative quantity of the different isotopes of an element in a material using a mass spectrometer. See [94].

140 isotopologue ions

Ions that differ only in the isotopic composition of one or more of the constituent atoms. For example, CH_4^+ and CH_3D^+ , or $^{10}\text{BF}_3$ and $^{11}\text{BF}_3$, or the ions forming an isotope cluster. The term isotopologue is a shortening of isotopic homologue. GB. See [7].

141 isotopomeric ions

Isomeric ion having the same numbers of each isotopic atom but differing in their positions. Isotopomeric ions can be either configurational isomers in which two atomic isotopes exchange positions or isotopic stereoisomers. The term isotopomer is a shortening of isotopic isomer. GB. See [7].

142 kinetic energy release (KER)

Relative translational kinetic energy of fragments resulting from dissociation of a metastable ion measured relative to the center-of-mass. See [95].

143 kinetic energy release distribution (KERD)

Distribution of values of translational kinetic energy release for an ensemble of metastable ions undergoing a specific dissociation reaction. See [95].

144 kinetic method

An approach to determination of ion thermodynamic quantities by a bracketing procedure in which the relative probabilities of competing ion fragmentations are measured *via* the relative abundances of the reaction products. The extended kinetic method takes the associated entropy changes into account. GB.

145 laser desorption (LD)

Formation of gas-phase neutral species by the interaction of photons from a pulsed laser beam with a solid or liquid material. See [96].

146 laser desorption/ionization (LDI)

Formation of gas-phase ions by the interaction of photons from a pulsed laser beam with a solid or liquid material. See [97].

147 laser ionization (LI)

Formation of ions through the interaction of photons from a laser with a material or with gas-phase ions or molecules. GB, OB.

148 laser microprobe mass spectrometry (LMMS)

Laser desorption/ionization mass spectrometry, particularly emphasizing spatially resolved composition information. See [98].

149 linear ion trap (LIT)

A two dimensional Paul ion trap in which ions are confined in the axial dimension by means of an electric field at the ends of the trap. See [99].

150 linked scan

A scan in a *tandem mass spectrometer* with two or more m/z analyzers or in a sector mass spectrometer that incorporates at least one magnetic sector and one electric sector. Two or more of the analyzers are scanned simultaneously so as to preserve a predetermined relationship between scan parameters to produce a product ion, precursor ion or constant neutral loss or gain spectrum. GB, OB.

151 linked scan at constant B/E

A linked scan at constant B/E may be performed on a sector mass spectrometer that incorporates at least one magnetic sector plus one electric sector. The magnetic field B and the electric field E are scanned simultaneously while the accelerating voltage V is held constant, so as to maintain the ratio of the two fields constant. This linked scan may record a product ion spectrum of dissociation or other reactions occurring in a field-free region preceding the two sectors. The term *B/E linked scan* is deprecated. OB.

152 linked scan at constant E^2/V

A linked scan performed on a sector instrument that incorporates 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 the ratio E^2/V at a constant value. This linked scan records a product ion spectrum of dissociation or other reactions occurring in a field-free region preceding the two sectors. The term *E^2/V linked scan* is deprecated. OB.

153 linked scan at constant B^2/E

A linked scan performed on a sector mass spectrometer that incorporates at least one electric sector plus one magnetic sector in either order. The accelerating voltage is fixed and the magnetic field, B, and the electric field, E, are scanned simultaneously so as to maintain the ratio B^2/E at a constant value. This linked scan records a precursor

ion spectrum of dissociation or other reactions occurring in the field-free region preceding the two sectors. The term *B²/E linked scan* is deprecated. OB.

154 linked scan at constant B[1-(E/E₀)]^{1/2}/E

A linked scan performed on a sector instrument that incorporates at least one electric sector plus one magnetic sector placed in either order. The accelerating voltage is fixed while scanning the magnetic field, B, and electric field, E, simultaneously, so as to maintain the quantity B[1-(E/E₀)]^{1/2}/E at a constant value. This linked scan records a constant neutral mass loss (or gain) spectrum of dissociation or other reactions occurring in a field-free region preceding the two sectors. E₀ is the electric field required to transmit the singly charged analog of the desired neutral fragment. The term *B[1-(E/E₀)]^{1/2}/E linked scan* is deprecated. OB.

155 liquid secondary ionization (LSI)

The ionization of any species by the interaction of a focused beam of ions with a sample that is dissolved in a solvent matrix. Related terms: *fast atom bombardment*, *fast ion bombardment*, and *secondary ionization*. See [100].

156 low-energy collision-induced dissociation

A collision-induced dissociation process wherein the precursor ion has laboratory-frame translational energy lower than 1 keV. This process typically requires multiple collisions and the collisional excitation is cumulative. See [101].

157 magnetic sector

A device that produces a magnetic field perpendicular to a charged particle beam that deflects the beam to an extent that is proportional to the particle momentum per unit charge. For a monoenergetic beam, the deflection is proportional to *m/z*. OB.

158 mass-analyzed ion kinetic energy spectrometry (MIKES)

A procedure by which mass spectra are obtained from a sector mass spectrometer that incorporates at least one magnetic sector plus one electric sector in reverse geometry. The accelerating voltage, V, and the magnetic flux density, B, are set at fixed values to *m/z* select the precursor ions, which are then allowed to dissociate or to react in a field-free region between the two sectors. The translational kinetic energy-to-charge ratios of the various product ions are analyzed by scanning the electric sector field E. The width of the product ion spectrum peaks is related to the kinetic energy release distribution for the dissociation process. The term *direct analysis of daughter ions* (DADI) is deprecated. See [102].

159 mass calibration

A means of determining *m/z* values from their times of detection relative to initiation of acquisition of a mass spectrum. Most commonly this is accomplished using a computer-based data system and a calibration file obtained from a mass spectrum of a compound that produces ions whose *m/z* values are known. See [103].

160 mass defect

The difference between the mass number and the monoisotopic mass of a molecule or atom. See [104].

161 mass excess

The negative of the *mass defect*. GB.

162 mass gate

A set of plates or grid of wires in a time-of-flight mass spectrometer that is used to apply a pulsed electric field with the purpose of deflecting charged particles in a given *m/z* range. See [81].

163 mass limit

The *m/z* value above which ions cannot be detected in a mass spectrometer. See [105].

164 mass number, A

Sum of the number of protons and neutrons in an atom, molecule or ion. See *nucleon number*. GB, OB.

165 mass range

Range of *m/z* over which a mass spectrometer can detect ions or is operated to record a mass spectrum. GB.

166 mass resolution

Smallest mass difference Δ*m* between two equal magnitude peaks so that the valley between them is a specified fraction of the peak height. revOB, See [106].

167 mass resolving power

In a mass spectrum, the observed mass divided by the difference between two masses that can be separated: *m*/Δ*m*. The procedure by which Δ*m* was obtained and the mass at which the measurement was made should be reported. GB.

168 mass selective axial ejection

Use of mass selective instability to eject ions of selected *m/z* values from an ion trap. See [107].

169 mass selective instability

A phenomenon observed in a *Paul ion trap* whereby an appropriate combination of oscillating electric fields applied to the body and the end-caps of the trap leads to unstable trajectories for ions within a particular range of *m/z* values and thus to their loss from the trap. See [108].

170 mass spectral library

A collection of mass spectra of different compounds, usually represented as arrays of signal intensity vs. the *m/z* value rounded off to the integral mass number. In some cases the library may consist of *monoisotopic mass spectra*. See [109].

171 mass spectrograph

An instrument that separates a beam of ions according to their *m/z* values in which the ions are directed onto a focal plane detector such as a photographic plate. GB, OB.

172 mass spectrometer

An instrument that measures the m/z values and relative abundances of ions. GB, OB.

173 mass spectrometry

Branch of science that deals with all aspects of mass spectrometers and mass spectrographs and the results obtained with these instruments. The term *mass spectroscopy* is deprecated. GB, OB.

174 mass spectrometry/mass spectrometry (MS/MS)

The acquisition and study of the spectra of the electrically charged products or precursors of m/z selected ion or ions, or of precursor ions of a selected neutral mass loss. MS/MS can be accomplished using beam instruments incorporating more than one analyzer (tandem mass spectrometry in space) or in trap instruments (tandem mass spectrometry in time). See *tandem mass spectrometry*. OB.

175 mass spectrum

A plot of the relative abundances of ions forming a beam or other collection as a function of their m/z values. GB, OB.

176 Mathieu stability diagram

A graphical representation expressed in terms of reduced coordinates that describes the stability or otherwise of charged particle motion in a quadrupole mass filter or quadrupole ion trap mass spectrometer, based on an appropriate form of the Mathieu differential equation. See [110].

177 matrix-assisted laser desorption/ionization (MALDI)

Formation of gas-phase ions from molecules that are present in a solid or liquid matrix that is irradiated with a pulsed laser. Related term: *laser desorption/ionization*. Note 1: MALDI using a liquid plus particulate matrix has been called surface-assisted laser desorption/ionization (SALDI) [111]. Note 2: MALDI using a biochemical affinity target has been called surface-enhanced laser desorption/ionization (SELDI) [112,113]. Note 3: Matrix-assisted laser desorption/ionization in which the matrix is covalently linked to the target surface has been called surface-enhanced neat desorption (SEND) [112]. See [114].

178 Mattauch-Herzog geometry

An arrangement for a double-focusing mass spectrometer in which a deflection of $\pi/(4\sqrt{2})$ radians in a radial electrostatic field is followed by a magnetic deflection of $\pi/2$ radians. GB, OB.

179 McLafferty rearrangement

A dissociation reaction triggered by transfer of a hydrogen atom *via* a 6-member transition state to the formal radical/charge site from a carbon atom four atoms removed from the charge/radical site (the γ -carbon); subsequent rearrangement of electron density leads to expulsion of an olefin molecule. This term was originally applied to ketone ions where the charge/radical site is the carbonyl oxygen, but it is now more widely applied. GB, OB.

180 membrane inlet (MI)

A semi-permeable membrane separator that permits the passage of analytes directly from solutions or ambient air to the mass spectrometer ion source. See [115].

181 metastable ion

An ion that is formed with internal energy higher than the threshold for dissociation but with a lifetime great enough to allow it to exit the ion source and enter the mass analyzer where it dissociates before detection. GB, OB.

182 microchannel plate (MCP)

A thin plate that contains a closely spaced array of channels that each act as a continuous dynode particle multiplier. A charged particle, fast neutral particle, or photon striking the plate causes a cascade of secondary electrons that ultimately exits the opposite side of the plate. See [116].

183 molar mass

Mass of one mole ($6.022\,1415(10) \times 10^{23}$ atoms or molecules) of a compound.

Note: The term molecular weight is deprecated because "weight" is the gravitational force on an object that varies with geographical location. Historically the term has been used to denote the molar mass calculated using isotope-averaged atomic masses for the constituent elements. GB.

184 molecular beam mass spectrometry

A mass spectrometry technique in which the sample is introduced into the ion source of the mass spectrometer as a collimated beam of molecules with a narrow velocity distribution. See [117].

185 molecular ion

An ion formed by the removal of one or more electrons to form a positive ion or the addition of one or more electrons to form a negative ion. GB, OB.

186 momentum transfer collision

See *elastic collision*. See [118].

187 monoisotopic mass

Exact mass of an ion or molecule calculated using the mass of the most abundant isotope of each element. See [22].

188 MSⁿ

This symbol refers to multi-stage MS/MS experiments designed to record product ion spectra where n is the number of product ion stages (progeny ions). For ion traps, sequential MS/MS experiments can be undertaken where $n > 2$ whereas for a simple triple quadrupole system $n = 2$. See *multiple-stage mass spectrometry*. See [119].

189 multiphoton ionization (MPI)

Photoionization of an atom or molecule in which two or more photons are absorbed. GB.

190 multiple-stage mass spectrometry

Multiple stages of precursor ion m/z selection followed by product ion detection for successive progeny ions. See [119].

191 m/z

Three-character symbol m/z is used to denote the dimensionless quantity formed by dividing the mass of an ion in unified atomic mass units by its charge number (regardless of sign). The symbol is written in italicized lower case letters with no spaces. Note 1: The term mass-to-charge-ratio is deprecated. Mass-to-charge-ratio has been used for the abscissa of a mass spectrum, although the quantity measured is not the quotient of the ion's mass to its electric charge. The three-character symbol m/z is recommended for the dimensionless quantity that is the independent variable in a mass spectrum Note 2: The proposed unit *thomson* (*Th*) is deprecated. OB.

192 nanoelectrospray

Electrospray ionization at a flow rate lower than 100 nL/min.

Related term: *electrospray ionization*. Note: the term nanospray is trademarked and its use is recommended only for describing the trademarked product. See [120].

193 negative ion

An atomic or molecular species having a net negative electric charge. GB, OB.

194 negative ion chemical ionization (NICI)

Chemical ionization that results in the formation of negative ions. GB, OB.

195 neutralization reionization mass spectrometry (NRMS)

A procedure by which neutrals are formed from m/z selected ions by charge transfer to a collision gas or by dissociation. The neutrals are separated from the remaining ions and ionized in collisions with a second gas. See [121].

196 neutral loss

Loss of an uncharged species from an ion during either a rearrangement process or direct dissociation. GB, OB.

197 Nier-Johnson geometry

Arrangement for a double-focusing mass spectrometer in which a deflection of $\pi/2$ radians in a radial electrostatic field analyzer is followed by a magnetic deflection of $\pi/3$ radians. GB, OB.

198 nitrogen rule

An organic molecule containing the elements C, H, O, S, P, or a halogen has an odd nominal mass if it contains an odd number of nitrogen atoms. See [9].

199 nominal mass

Mass of an ion or molecule calculated using the mass of the most abundant isotope of each element rounded to the nearest integer value and equivalent to the sum of the *mass numbers* of all constituent atoms. See [22].

200 non-classical ion

Hyper-coordinated carbonium ion such as the penta-coordinated norbornyl cation. Note: Tri-coordinated carbenium ions are termed classical ions. See [30].

201 Nth generation product ion

Serial product ions from dissociation of selected precursor ions where n refers to the number of stages of dissociation. The term *granddaughter ion* is deprecated. Related term: *progeny ion*. See [64,65].

202 Nth generation product ion scan

Specific scan functions or processes that record the appropriate product ion or ions of any m/z selected precursor ions. See [64,65].

203 Nth generation product ion spectrum

Mass spectrum recorded from any mass spectrometer in which the appropriate scan function can be set to record the appropriate generation product ion or ions of m/z selected precursor ions. See [64,65].

204 odd-electron ion

See *radical ion*. GB, OB

205 odd-electron rule

Odd-electron ions may dissociate to form either odd or even-electron ions, whereas even-electron ions generally form even-electron fragment ions. See [122].

206 onium ion

A positively charged hypervalent ion of the nonmetallic elements. Examples are the methonium ion CH_5^+ , the hydrogenonium ion H_3^+ and the hydronium ion H_3O^+ . Other examples are the oxonium, sulfonium, nitronium, diazonium, phosphonium, and halonium ions. Onium ions are not limited to monpositive ions; multiply-charged onium ions exist such as the gitonic (proximal) oxonium dication H_4O^{2+} and the distonic oxonium dication $\text{H}_2\text{O}^+-\text{CH}_2-\text{CH}_2-\text{OH}_2^+$. GB See [123].

207 orbitrap

An ion trapping device that consists of an outer barrel-like electrode and a coaxial inner spindle-like electrode that form an electrostatic field with quadro-logarithmic potential distribution. The frequency of harmonic oscillations of the orbitally trapped ions along the axis of the electrostatic field is independent of the ion velocity and is inversely proportional to the square root of m/z so that the trap can be operated as a mass analyzer using image current detection and Fourier transformation of the time domain signal. See [124].

208 orthogonal extraction

Pulsed acceleration of ions perpendicular to their direction of travel into a time-of-flight mass spectrometer. Ions may be extracted from a directional ion source, drift tube or m/z separation stage. See [125].

209 partial charge exchange reaction

See *partial charge transfer reaction*. GB, OB.

210 partial charge transfer reaction

Reaction of an ion with a neutral species in which some but not all of the ion charge is transferred to the neutral. GB, OB.

211 Paul ion trap

Ion trapping device that permits the ejection of ions with an m/z lower than a prescribed value and retention of those with higher mass. It depends on the application of radio frequency voltages between a ring electrode and two end-cap electrodes to confine the ion motion to a cyclic path described by an appropriate form of the Mathieu equation. The choice of these voltages determines the m/z below which ions are ejected. The term *cylindrical ion trap* is deprecated. See [23].

212 peak (in mass spectrometry)

Localized region of relatively large ion signal in a mass spectrum. Although peaks are often associated with particular ions, the terms peak and ion should not be used interchangeably. See [7].

213 peak intensity

Height or area of a peak in a mass spectrum. GB, OB.

214 peak matching

Procedure for measuring the *accurate mass* of an ion using scanning mass spectrometers, in which the peak corresponding to the unknown ion and that for a reference ion of known m/z are displayed alternately on a display screen and caused to overlap by adjusting appropriate electric fields. See [126].

215 Penning ionization

Ionization that occurs through the interaction of two or more neutral gaseous species, at least one of which is internally excited usually to a high Rydberg state. Note: *Penning ionization* differs from *chemi-ionization* in that no chemical change is involved. OB.

216 photodissociation

Process wherein the reactant ion is dissociated as a result of absorption of one or more photons. See [127].

217 photoionization (PI)

Ionization of an atom or molecule by a photon, written $M + h\nu \rightarrow M^+ + e$. The term *photon impact* is deprecated. GB, OB.

218 plasma desorption/ionization (PDI)

The ionization of material in a solid sample by bombarding it with ionic or neutral atoms formed as a result of the fission of a suitable nuclide, typically ^{252}Cf . See *fission fragment ionization*. GB, OB.

219 pneumatically-assisted electrospray ionization

Electrospray ionization in which the nebulization of the liquid stream is assisted by a concentric stream of gas. See [128].

220 point detector

Detector in which the ion beam is focused onto a point and the individual ions arrive sequentially. See [129].

221 positive ion

Atomic or molecular species having a net positive electric charge. GB, OB.

222 post-acceleration detector

Detector in which a high voltage is applied after m/z separation to accelerate the ions and produce an improved signal. See [130].

223 post-source decay (PSD)

Technique specific to reflectron time-of-flight mass spectrometers where product ions of metastable transitions or collision-induced dissociations generated in the flight tube prior to entering the reflectron are m/z separated to yield product ion spectra. See [131].

224 precursor ion

Ion that reacts to form particular product ions. The reaction can be unimolecular dissociation, ion/molecule reaction, isomerization, or change in charge state. The term *parent ion* is deprecated. revGB, revOB, See [5,132,133].

225 precursor ion scan

Scan function or process that records a precursor ion spectrum. The term *parent ion scan* is deprecated. See [5,132,133].

226 precursor ion spectrum

Mass spectrum recorded from any spectrometer in which the appropriate m/z separation function can be set to record the precursor ion or ions of selected product ions. The term *parent ion spectrum* is deprecated. See [5,132,133].

227 pre-ionization state

Electronic state capable of undergoing autoionization. OB.

228 principal ion

Most abundant ion of an isotope cluster, such as the $^{11}\text{B}^{79}\text{Br}_2^{81}\text{Br}^+$ ion of m/z 250 of the cluster of isotopologue molecular ions of BBr_3 . The term principal ion has also been used to describe ions that have been artificially isotopically enriched in one or more positions such as $\text{CH}_3^{13}\text{CH}_3^+$ or CH_2D_2^+ , but those are best defined as *isotopologue ions*. GB, OB.

229 product ion

An ion formed as the product of a reaction involving a particular precursor ion. The reaction can be unimolecular dissociation to form fragment ions, an ion/molecule reaction, or simply involve a change in the number of charges. The term *fragment ion* is deprecated. The term *daughter ion* is deprecated. revGB, revOB, See [5,132,133].

230 product ion scan

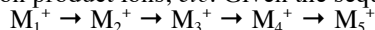
Specific scan function or process that records a product ion spectrum. The terms *fragment ion scan* and *daughter ion scan* are deprecated. See [5,132,133].

231 product ion spectrum

Mass spectrum recorded from any spectrometer in which the appropriate m/z separation scan function is set to record the product ion or ions of selected precursor ions. The terms *fragment ion scan* and *daughter ion scan* are deprecated. Note: The term *MS/MS spectrum* is deprecated; a scan-specific term, e.g. precursor ion spectrum or second-generation product ion spectrum should be used. See [5,132,133].

232 progeny fragment ions

Charged product of a series of consecutive reactions that includes product ions, 1st generation product ions, 2nd generation product ions, *etc.* Given the sequential fragmentation scheme:



M_4^+ is the precursor ion of M_5^+ , a 1st generation product ion of M_3^+ , a 2nd generation product ion of M_2^+ and a 3rd generation product ion of M_1^+ . See [5].

233 prolate trochoidal mass spectrometer

A mass spectrometer in which the ions of different m/z are separated by means of crossed electric and magnetic fields in such a way that the selected ions follow a prolate trochoidal path. The term *cycloidal mass spectrometer* is deprecated. GB, OB.

234 proton affinity

Proton affinity of a species M is the negative of the enthalpy change for the reaction $M + H^+ \rightarrow [M + H]^+$ at 298 K. GB, OB.

235 protonated molecule

An ion formed by interaction of a molecule with a proton, and represented by the symbolism $[M + H]^+$. Note 1: The term *protonated molecular ion* is deprecated; this would correspond to a species carrying two charges Note 2: The terms *pseudo-molecular ion* and *quasi-molecular ion* are deprecated; a specific term such as *protonated molecule*, or a chemical description such as $[M+Na]^+$, $[M-H]^-$, *etc.* should be used. GB, OB.

236 pyrolysis mass spectrometry (PyMS)

A mass spectrometry technique in which the sample is heated to the point of decomposition and the gaseous decomposition products are introduced into the ion source. See [134].

237 quadratic field reflectron

A reflectron in which the electric field varies with the square of the distance from the entrance and compensates for translational kinetic energy spread to all orders. See [135].

238 quadrupole ion storage trap (QUISTOR)

See *Paul ion trap*. GB, OB.

239 quadrupole ion trap (QIT)

See *Paul ion trap*. See [136].

240 quadrupole mass spectrometer (QMS)

See *transmission quadrupole mass spectrometer*. revGB, revOB, See [137].

241 radical ion

An ion, either a cation or anion, containing unpaired electrons in its ground state. The unpaired electron is denoted by a superscript dot alongside the superscript symbol for charge, such as for the molecular ion of a molecule M, that is, $M^{\cdot+}$. Radical ions with more than one charge and/or more than one unpaired electron are denoted such as $M^{(2+)(2\cdot)}$. Unless the positions of the unpaired electron and charge can be associated with specific atoms, superscript charge designation should be placed before the superscript dot designation. GB, OB.

242 reagent ion

An ion produced in large excess in a chemical ionization source that reacts with neutral sample molecules to produce an ionized form of the molecule through an ion/molecule reaction. See [138].

243 recombination energy

Energy released when an electron is added to an ionized molecule or atom, that is, the energy involved in the reverse process to that referred to in the definition of *vertical ionization energy*. See [139].

244 reference ion

Stable ion whose structure is known with certainty. These ions are usually formed by direct ionization of a molecule of known structure, and are used to verify by comparison the structure of an unknown ion. See [140].

245 reflectron

Constituent of a time-of-flight mass spectrometer that uses a static electric field to reverse the direction of travel of the ions entering it. A reflectron improves mass resolution by assuring that ions of the same m/z but different translational kinetic energy arrive at the detector at the same time. See [141].

246 relative molecular mass

Mass of one molecule of a compound, with specified isotopic composition, relative to one-twelfth of the mass of one atom of ^{12}C . revGB See [142].

247 residual gas analyzer (RGA)

Mass spectrometer used to measure the composition and pressure of gases in an evacuated chamber. See [143].

248 resonance-enhanced multiphoton ionization (REMPI)

Multiphoton ionization in which the ionization cross section is significantly enhanced because the energy of the incident photons is resonant with an intermediate excited state of the neutral species. See [144].

249 resonance ion ejection

Mode of ion ejection in a Paul ion trap that relies on an auxiliary radio frequency voltage that is applied to the end-cap electrodes. The voltage is tuned to the secular frequency of a particular ion to eject it. See [145].

250 resonance ionization (RI)

See *resonance-enhanced multiphoton ionization*. See [146].

251 reverse library search

A procedure of comparing a mass spectrum of an unknown compound with a *mass spectral library* so that the unknown spectrum is compared in turn with the library spectra, considering only the m/z peaks observed to have significant intensity in the current library spectrum. See [147].

252 RF-DC ion mobility spectrometry

See *high-field asymmetric waveform ion mobility spectrometry*. See [148].

253 secondary electron

Electrons that are ejected from a sample surface as a result of bombardment by a primary beam of atoms, ions, or photons. See [149].

254 secondary ionization

Process in which ions are ejected from a sample surface as a result of bombardment by a primary beam of atoms or ions. GB.

255 sector mass spectrometer

Mass spectrometer consisting of one or more magnetic sectors for m/z selection in a beam of ions. Such instruments may also have one or more electric sectors for energy dispersion. See [150].

256 selected ion flow tube (SIFT)

Device in which m/z selected ions are entrained in an inert carrier gas and subsequently undergo ion/molecule reactions with molecules introduced into the gas flow. See [151].

257 selected ion monitoring (SIM)

Operation of a mass spectrometer in which the abundances of several ions of specific m/z values are recorded rather than the entire mass spectrum. revGB, revOB, See [152].

258 selected reaction monitoring (SRM)

Data acquired from specific product ions corresponding to m/z selected precursor ions recorded *via* two or more stages of mass spectrometry. Selected reaction monitoring can be performed as tandem mass spectrometry in time or tandem mass spectrometry in space. The term *multiple reaction monitoring* is deprecated. See [153].

259 soft ionization

Formation of gas-phase ions without extensive fragmentation. See [154].

260 space charge effect

Result of mutual repulsion of particles of like charge that limits the current in a charged-particle beam or packet and causes some ion motion in addition to that caused by external fields. See [155].

261 spark ionization

Formation of ions from a solid material by an intermittent electrical discharge. GB, OB.

262 stable ion

Ion with internal energy sufficiently low that it does not rearrange or dissociate prior to detection in a mass spectrometer. GB, OB.

263 stability diagram

See *Mathieu stability diagram*.

264 static field

Electric or magnetic field that does not change in time. See [156].

265 stored waveform inverse Fourier transform (SWIFT)

Technique to create excitation waveforms for ions in FT-ICR mass spectrometer or Paul ion traps. An excitation waveform in the time-domain is generated by taking the inverse Fourier transform of an appropriate frequency-domain programmed excitation spectrum, in which the resonance frequencies of ions to be excited are included. This procedure may be used for selection of precursor ions in MS/MS experiments. See [157].

266 superelastic collision

Collision in which the translational energy of the fast-moving collision partner is increased at the expense of internal energy of one or both collision partners. OB.

267 surface-induced dissociation (SID)

Fragmentation that results from the collision of an ion with a surface. See [158].

268 surface-induced reaction

Process wherein a reactant ion interacts with a surface to produce either chemically different species or a change in the internal energy of the reactant ion. See [159].

269 surface ionization (SI)

Ionization of a neutral species when it interacts with a solid surface with an appropriate work function and temperature. GB, OB.

270 sustained off-resonance irradiation (SORI)

Procedure associated with Fourier transform ion cyclotron resonance mass spectrometry to undertake ion/neutral reactions such as low-energy collision-induced dissociation. A radio-frequency electric field, slightly off-resonance with respect to the cyclotron frequency of the reactant ion, cyclically accelerates and decelerates the reactant ion that is confined in the Penning ion trap. As a consequence the orbit does not exceed the dimensions of the ion trap but maintains a high average translational energy for an extended time that activates an ion/neutral species process. See [160].

271 tandem mass spectrometer

Mass spectrometer designed for mass spectrometry/mass spectrometry. GB, OB.

272 tandem mass spectrometry

See *mass spectrometry/mass spectrometry*.

273 tandem mass spectrometry in time

Tandem mass spectrometry procedure in which product ion spectra are recorded in a single m/z analyzer (such as a Paul Ion Trap or Fourier transform ion cyclotron resonance mass spectrometer) in discrete steps over time. Ions in a specific m/z range are selected, dissociated, and the product ions analyzed sequentially in time. See [161].

274 tandem mass spectrometry in space

Tandem mass spectrometry procedure in which product ion spectra are recorded in m/z analyzers separated in space. Specific m/z separation functions are designed so that in one section of the instrument ions are selected, dissociated in an intermediate region, and the product ions are then transmitted to another analyzer for m/z separation and data acquisition. See [161].

275 thermal ionization (TI)

Ionization of a neutral species through contact with a high temperature surface. GB, OB.

276 time-of-flight mass spectrometer (TOF-MS)

Instrument that separates ions by m/z in a field-free region after acceleration to a fixed acceleration energy. GB, OB.

277 time lag focusing

Energy focusing in a time-of-flight mass spectrometer that is accomplished by introducing a time delay between the formation of the ions and the application of the accelerating voltage pulse. Ion formation may be in the gas phase or at a sample surface. Related term: *delayed extraction*. See [162].

278 total ion current (TIC)

Sum of all the separate ion currents carried by the ions of different m/z contributing to a complete mass spectrum or in a specified m/z range of a mass spectrum. GB, OB.

279 total ion current chromatogram

Chromatogram obtained by plotting the total ion current detected in each of a series of mass spectra recorded as a function of retention time. See [163].

280 transmission

The ratio of the number of ions leaving a region of a mass spectrometer to the number entering that region. GB, OB.

281 transmission quadrupole mass spectrometer

A mass spectrometer that consists of four parallel rods whose centers form the corners of a square and whose opposing poles are connected. The voltage applied to the rods is a superposition of a static potential and a sinusoidal radio frequency potential. The motion of an ion in the x and y dimensions is described by the Mathieu equation whose solutions show that ions in a particular m/z range can be transmitted along the z-axis. See [137].

282 triple quadrupole mass spectrometer

A tandem mass spectrometer comprising two transmission quadrupole mass spectrometers in series, with a non-resolving (RF-only) quadrupole between them to act as a collision cell. See [164].

283 unified atomic mass unit, u

A non-SI unit of mass defined as one twelfth of the mass of one atom of ^{12}C in its ground state and equal to $1.6605402(10) \times 10^{-27}$ kg. The term *atomic mass unit* is deprecated. Note: The term *atomic mass unit (amu)* is ambiguous as it has been used to denote atomic masses measured relative to a single atom of ^{16}O , or to the isotope-averaged mass of an oxygen atom, or to a single atom of ^{12}C .

revGB See [165].

284 unimolecular dissociation

Fragmentation reaction in which the molecularity is treated as one, irrespective of whether the dissociative state is that of a metastable ion produced in the ion source or results from collisional excitation of a stable ion. See [166].

285 unstable ion

Ion with sufficient energy to dissociate within the ion source. GB, OB.

286 vertical ionization

Process in which an electron is removed from or added to a molecule without a change in the positions of the atoms. The resulting ion is typically in an excited vibrational state. GB, OB.

287 x-ion

Fragment ion containing the C-terminus formed upon dissociation of a protonated peptide at a backbone C-C bond. See [12].

288 y-ion

Fragment ion containing the C-terminus formed upon dissociation of a protonated peptide at a backbone C-N bond. See [12].

298 z-ion

Fragment ion containing the C-terminus formed upon dissociation of a protonated peptide at a backbone N-C bond. See [12].

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