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IUPAC Standard Definitions of Terms Relating to Mass Spectrometry

Kermit K. Murray,¹ Robert K. Boyd,² Marcos N. Eberlin,³
G. John Langley,⁴ Liang Li,⁵ and Yasuhide Naito,⁶

1. Department of Chemistry, Louisiana State University, Baton Rouge, LA.
2. Institute for National Measurement Standards, National, Research Council, Ottawa, Ontario, Canada.
3. Department of Chemistry, State University of Campinas, Brazil.
4. School of Chemistry, University of Southampton, Southampton, United Kingdom
5. Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada
6. Graduate School for the Creation of New Photonics Industries, Hamamatsu, Japan

Details of IUPAC Project

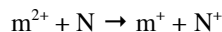
The *Standard Definitions of Terms Relating to Mass Spectrometry* project is sponsored by the International Union of Pure and Applied Chemistry Analytical Chemistry Division (V) and Physical and Biophysical Chemistry Division (I) and the objective is to update and extend the definitions of terms related to the field of mass spectrometry. The project is number: 2003-056-2-500. The leader of the task group is Kermit Murray (USA) and members are Robert Boyd (Canada), Marcos N. Eberlin (Brazil), John Langley (UK), Liang Li (Canada), and Yasuhide Naito (Japan).

Definitions of terms for mass spectrometry are under the purview of IUPAC Analytical Chemistry Division (Division V). The most recent edition of these terms and definitions can be found in Chapter 12 of the "Orange Book" Compendium of Analytical Nomenclature (Todd 1991). The goal of this project is to update these terms and definitions in close conjunction with the mass spectrometry journals, companies, societies, and practitioners worldwide.

Widely accepted standard definitions of terms are necessary for clear communication in the discussion and dissemination of results. This is particularly important for multidisciplinary fields such as mass spectrometry. During the several decades, the field of mass spectrometry has seen a revolutionary change in practice and scope. 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 many other fields such as biology and medicine and related areas. This expansion in scope and length of time since the last update of standard terms and definitions make it important to undertake a revision of these terms at this time.

I. Terms

2E Mass Spectrum – A 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 kinetic 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.

Accelerating Voltage – The electrical potential used to impart kinetic energy to ions in a mass spectrometer.

Accelerator Mass Spectrometry – A 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.

Accurate Mass – An experimentally determined mass of an ion that is used to determine an elemental formula. For ions containing combinations of the elements C, H, N, O, P, S, and the halogens, with mass less than 200 u, a measurement with 5 ppm uncertainty is sufficient to uniquely determine the elemental composition.

Adiabatic Ionization – A 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.

Adduct Ion – An 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.

α -Cleavage – A homolytic cleavage where the bond fission occurs between at the atom adjacent to the atom at the apparent charge site and an atom removed from the apparent charge site by two bonds.

a-Ion – A fragment ion containing the N-terminus formed upon dissociation of a protonated peptide at a backbone C-C bond.

Analog Ion – Ions that have similar chemical valence, for example the acetyl cation $\text{CH}_3\text{-CO}^+$ and the thioacetyl cation $\text{CH}_3\text{-CS}^+$.

Anion – Synonymous with *negative ion*.

Anti-Aromatic Ion – A planar cyclic ion with $4n$ π electrons and is therefore not aromatic. See *aromatic ion*.

Appearance Energy – The minimum energy that must be imparted to an atom or molecule to produce a specified ion. The term *appearance potential* is not recommended.

Aromatic Ion – A planar cyclic ion that obeys the Hückel ($4n + 2$) rule where n is a positive integer representing the number of conjugated π electrons. Charge delocalization leads to greater stability compared to a hypothetical localized structure.

Array Collector – A detector composed of a number of ion collection elements or devices, arranged in a line or grid where each element is an individual detector.

Associative Ionization – An 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.

Associative Ion/Molecule Reaction – The reaction of an ion with a neutral species in which the reactants combine to form a single ion.

Atmospheric Pressure Ionization – Any ionization process in which ions are formed in the gas phase at atmospheric pressure.

Atmospheric Pressure Chemical Ionization – Chemical ionization that takes place at atmospheric pressure as opposed to the reduced pressure that is normally used for chemical ionization.

Atmospheric Pressure Matrix-Assisted Laser Desorption/Ionization – Matrix-assisted laser desorption/ionization in which the sample target is at atmospheric pressure.

Atmospheric Pressure Photoionization – Atmospheric pressure chemical ionization in which the reactant ions are generated by photoionization.

Autodetachment – The 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.

- Autoionization** – The 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.
- Average Mass** – The mass of an ion or molecule calculated using the average mass of each element weighted for its natural isotopic abundance.
- Base Peak** – The peak in a mass spectrum that has the greatest intensity. This term may be applied to the spectra of pure substances or mixtures.
- Bath Gas** – See *buffer gas*.
- β -Cleavage** – A 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.
- b-Ion** – A fragment ion containing the N-terminus formed upon dissociation of a protonated peptide at a backbone C-N bond.
- Blackbody Infrared Radiative Dissociation** – A 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. See also *infrared multiphoton dissociation*.
- Buffer Gas** – An inert gas used for collisional deactivation of internally excited ions or of the translational energies of ions confined in an ion trap.
- Cation** – Synonymous with *positive ion*.
- Cationized Molecule** – An ion formed by the association of a cation with a molecule, M, for example $[M + Na]^+$ and $[M + K]^+$. The terms *quasi-molecular ion* and *pseudo-molecular ion* should not be used.
- Centroid Acquisition** – A method 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*.
- Charge Exchange Ionization** – The 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. Synonymous with *charge transfer ionization*.
- Charge Exchange Reaction** – Synonymous with *charge transfer reaction*.
- Charge Induced Fragmentation** – Fragmentation of an ion in which the cleaved bond is adjacent to the apparent charge site. Synonymous with *charge mediated fragmentation*.
- Charge-Inversion Mass Spectrum** – The measurement of the relative abundance of ions that result from a charge inversion reaction as a function of m/z .
- Charge-Inversion Reaction** – The 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.
- Charge Number** – The total charge on an ion, regardless of sign, divided by the magnitude of the electron charge e , usually denoted by z (italicized).
- Charge Permutation Reaction** – The reaction of an ion with a neutral species with a resulting change in the magnitude or sign of the charge on the reactant ion.
- Charge Remote Fragmentation** – A fragmentation of an ion in which the cleaved bond is not adjacent to the apparent charge site.
- Charge Stripping Reaction** – The 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.
- Charge Transfer Reaction** – The 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.
- Chemical Ionization** – The formation of a new ion 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. 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*.
- Chemi-Ionization** – The 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*.

- c-Ion** – A fragment ion containing the N-terminus formed upon dissociation of a protonated peptide at a backbone N-C bond.
- Classical Ion** – See *non-classical ion*.
- Cluster Ion** – An ion formed by a multi-component atomic or molecular assembly of one or more ions with atoms or molecules, such as $[(\text{H}_2\text{O})_n\text{H}]^+$, $[(\text{NaCl})_n\text{Na}]^+$ and $[(\text{H}_3\text{PO}_3)_n\text{HPO}_3]$.
- Collisional Activation** – Synonymous with *collisional excitation*.
- Collisional Excitation** – The 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.
- Collision Gas** – An inert gas used for collisional excitation and ion/molecule reactions. The term *target gas* is not recommended.
- Collision-Induced Dissociation** – The dissociation of an ion after collisional excitation. The term *collisional-activated dissociation* is not recommended.
- Collision Quadrupole** – A 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.
- Consecutive Reaction Monitoring** – An MS^n experiment with three or more stages of m/z separation and in which a particular multi-step reaction path is monitored.
- Constant Neutral Loss Scan** – A scan method 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*.
- Constant Neutral Loss Spectrum** – A spectrum of all precursor ions that have undergone an operator-selected m/z decrement, obtained using a *constant neutral loss scan*. Synonymous with *constant neutral mass loss spectrum* and *fixed neutral mass loss spectrum*.
- Constant Neutral Mass Gain Scan** – A scan method 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.
- Constant Neutral Mass Gain Spectrum** – A 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*.
- Continuous Dynode Electron 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.
- Continuum Acquisition** – A method of recording mass spectra in which the digitized output from the detector is stored directly without any pre-processing. See *centroid acquisition*. Synonymous with *profile acquisition*.
- Continuous Flow Fast Atom Bombardment** – A variant of fast atom bombardment in which the mixture of analyte and liquid matrix is supplied continuously to the sample probe.
- Conversion Dynode** – A surface that is held at high potential so that ions striking the surface produce electrons that are subsequently detected.
- Curved Field Reflectron** – A 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 entrance, V is the voltage and R is a constant.
- Cyclotron Motion** – The circular motion of a particle of charge q moving at velocity \mathbf{v} in a magnetic flux density \mathbf{B} that results from the force $q\mathbf{v} \times \mathbf{B}$.
- Dalton** – A non-SI unit of mass (symbol Da) that is equal to the unified atomic mass unit: $1.660\,538\,86(28) \times 10^{-27}$ kg.
- Daly Detector** – A metal knob held at high potential that emits secondary electrons when ions impinge on the surface. The secondary electrons are accelerated onto a scintillator that produces light that is then detected by a photomultiplier detector.
- Delayed Extraction** – The 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.

- Diagnostic Ion** – A 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.
- Dimeric Ion** – An ion formed by ionization of a dimer or by the association of an ion with its neutral counterpart such as $[M_2]^{2+}$ or $[M-H-M]^+$.
- Desorption Electrospray Ionization** – The production of gaseous ions from material present on a solid surface by directing charged droplets and solvent ions from an electrospray ionization source on to the surface at atmospheric pressure.
- Desorption Ionization** – The formation of ions from a solid or liquid material by the rapid vaporization of that sample.
- Desorption Ionization on Silicon** – The formation of ions by laser desorption/ionization of a sample deposited on a porous silicon surface.
- Direct Insertion Probe** – A 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.
- Direct Liquid Introduction** – The delivery of a liquid sample into a mass spectrometer.
- Dissociative Ionization** – The reaction of a gas-phase molecule that results in its decomposition to form products, one of which is an ion.
- Distonic Ion** – A 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 $\text{HO-CH}_2\text{-CH}_2\text{-OH}_3^{2+}$.
- Double-Focusing Mass Spectrometer** – A 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 collector*.
- Dynamic Fields Mass Spectrometer** – A mass spectrometer in which m/z separation is achieved using one or more electric fields that vary with time.
- Dynamic Secondary Ionization** – The 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.
- Dynode** – One of a series of electrodes in an electron multiplier tube arranged so that the secondary electron emission amplifies the current emitted by the conversion dynode.
- Einzel Lens** – A 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 kinetic energy of the particle.
- 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 kinetic energy.
- Electron Attachment Ionization** – The ionization of a gaseous atom or molecule by attachment of an electron to form $M^{\cdot-}$ ions.
- Electron Capture Dissociation** – A process in which multiply protonated molecules interact with low energy electrons. Capture of the electron leads to 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.
- Electron Energy** – The magnitude of the electron charge multiplied by the potential difference through which electrons are accelerated in order to effect electron ionization.
- Electron Induced Excitation in Organics** – The reaction of an ion with an electron in which the translational energy of the collision is converted into internal energy of the ion.
- Electron Ionization** – The 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. Usually 70 eV electrons are used to produce positive ions. The term *electron impact* is not recommended.

- Electron Multiplier** – A device to amplify the current of a beam or packet of charged particles or photons by incidence upon the surface of an electrode to produce secondary electrons. The secondary electrons are then accelerated to other electrodes or parts of a continuous electrode to produce further secondary electrons.
- Electron Volt** – A 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 $1.602\ 176\ 53(14) \times 10^{-19}$ J.
- Electrospray Ionization** – A process in which ionized species in the gas phase are produced from an analyte-containing 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. When a pressurized gas is used to aid in the formation of a stable spray, the term *pneumatically-assisted electrospray ionization* is used.
- Electrostatic Energy Analyzer** – A device consisting of conducting parallel plates, concentric cylinders or concentric spheres that separates charged particles according to their ratio of kinetic energy to charge by means of an electric field that is constant in time.
- E/2 Mass Spectrum** – A 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*.
- Even-Electron Ion** – An ion containing no unpaired electrons in its ground electronic state.
- Exact Mass** – The 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 expressed using an appropriate degree of accuracy.
- Extracted Ion Chromatogram** – A 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. Synonymous with *reconstructed ion chromatogram*.
- Faraday Cup** – A conducting cup or chamber that intercepts a charged particle beam and is electrically connected to a current measuring device.
- Fast Atom Bombardment** – The 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. See also *secondary ionization*.
- Fast Ion Bombardment** – The 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*.
- Field Desorption** – The formation of gas-phase ions in the presence of a high electric field from a material deposited on a solid surface.
- Field-Free Region** – A section of a mass spectrometer in which there are no electric or magnetic fields.
- Field Ionization** – The removal of electrons from any species, usually in the gas phase, by interaction with a high electric field.
- First Stability Region** – The region of a Mathieu stability diagram closest to the origin. Ions within this region can traverse the full length of a transmission quadrupole.
- Fission Fragment Ionization** – Synonymous with *plasma desorption/ionization*.
- 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.
- Focal Plane Collector** – A detector for spatially disperse ion beams in which all ions simultaneously impinge on the detector plane.
- Forward Library Search** – A method 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.
- Fourier Transform Ion Cyclotron Resonance Mass Spectrometer** – 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 excited to a coherent 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*.
- Fragment Ion** – A product ion that results from the dissociation of a *precursor ion*.

- Fringing Field** – The electric or magnetic field that extends from the edge of a sector, lens or other ion optics element.
- 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.
- 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.
- Hard Ionization** – The formation of gas-phase ions accompanied by extensive fragmentation.
- Heterolysis** – Synonymous with *heterolytic cleavage*.
- 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. This term is synonymous with *heterolysis*.
- High-Energy Collision-Induced Dissociation** – A collision-induced dissociation process wherein the projectile ion has laboratory-frame translational energy higher than approximately 1000 eV.
- High-field Asymmetric Waveform Ion Mobility Spectrometry** – The separation of ions 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.
- Homolysis** – Synonymous with *homolytic cleavage*.
- Homolytic Cleavage** – In general, 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. Synonymous with *homolysis*.
- Hydrogen/Deuterium Exchange** – The 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.
- Hybrid Mass Spectrometer** – A mass spectrometer that combines m/z analyzers of different types to perform tandem mass spectrometry.
- Imaging Mass Spectrometry** – The technique used to form chemically-selective images of objects based on the mass spectrometric detection of ions desorbed from its surface.
- 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.
- Inductively Coupled Plasma** – A gas discharge ion source in which the energy to the plasma is supplied by electromagnetic induction.
- Infrared Multiphoton Dissociation** – Dissociation of a reactant ion as a result of the absorption of multiple infrared photons.
- 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.
- Ion** – An atomic, molecular or radical species with an unbalanced electrical charge. The corresponding neutral species need not be stable.
- Ion Desolvation** – The removal of solvent molecules clustered around a gas-phase ion by means of heating and/or collisions with gas molecules.
- 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.
- Ion Gate** – See *mass gate*.
- 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.
- Ion/Ion Reaction** – The reaction between two ions, typically of opposite polarity.

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.

Ionization Efficiency – The ratio of the number of ions formed to the number of molecules consumed in the ion source.

Ionizing Collision – The reaction of an ion with a neutral species in which one or more electrons are removed from either the ion or neutral.

Ion Kinetic Energy Spectrometry – A method of analysis in which a beam of ions is separated according to the ratio of its translational energy to charge.

Ion Mobility Spectrometry – The separation of ions according to their velocity through a buffer gas under the influence of an electric field.

Ion/Molecule Reaction – The reaction of an ion with a molecule. The term *ion-molecule reaction* is not recommended because the hyphen suggests a single species that is that is both an ion and a molecule.

Ion/Neutral Complex – A particular type of transition state that lies between precursor and product ions on the reaction coordinate of some ion reactions.

Ion/Neutral Species Reaction – The reaction of an ion with an atom or molecule.

Ion/Neutral Species Exchange Reaction – The reaction of an ion with a neutral species to produce a different neutral species as the product.

Ion-Pair Formation – The reaction of a molecule to form both positive ion and negative ion fragments among the products.

Ion Source – The region in a mass spectrometer where ions are produced.

Ion-to-Photon Detector – A 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.

Ion Trap – A device for spatially confining ions using electric and magnetic fields alone or in combination.

Isotope Dilution Mass Spectrometry – A quantitative mass spectrometry technique in which an isotopically enriched compound is used as an internal standard.

Isotope Ratio Mass Spectrometry – The measurement of the relative quantity of the different isotopes of an element in a material using a mass spectrometer.

Isotopologue Ions – Ions that differs 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.

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.

Kinetic Energy Analyzer – A device for measuring the kinetic energy of charged particles using a retarding field, time-of-flight, the extent of deflection in an electric or magnetic field, or other method.

Kinetic Energy Release – The relative kinetic energy of fragments resulting from dissociation of a metastable ion measured relative to the center-of-mass.

Kinetic Energy Release Distribution – The distribution of values of kinetic energy release for an ensemble of metastable ions undergoing a specific dissociation reaction.

Kinetic Method – An approach to determination of ion thermodynamic quantities by a bracketing method 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.

Laser Desorption – The formation of gas-phase neutral species by the interaction of photons from a pulsed laser with a solid or liquid material.

Laser Desorption/Ionization – The formation of gas-phase ions by the interaction of photons from a pulsed laser with a solid or liquid material.

Laser Ionization – The formation of ions through the interaction of photons from a laser with a material or with gas-phase ions or molecules

Laser Microprobe Mass Spectrometry – *Laser desorption/ionization* mass spectrometry, particularly emphasizing spatially resolved composition information.

- Linear Ion Trap** – 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.
- 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.
- 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.
- 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 not recommended.
- 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 *B^2/E linked scan* is not recommended.
- Linked Scan at Constant $B[1-(E/E_0)]^{1/2}/E$** – 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 $B[1-(E/E_0)]^{1/2}/E$ 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. E_0 is the electric field required to transmit the singly charged analog of the desired neutral fragment. The term *$B[1-(E/E_0)]^{1/2}/E$ linked scan* is not recommended.
- Liquid Secondary Ionization** – The ionization of any species by the interaction of a focused beam of ions with a sample that is dissolved in a solvent matrix. See also *fast atom bombardment*, *fast ion bombardment*, and *secondary ionization*.
- Low-Energy Collision-Induced Dissociation** – A collision-induced dissociation process wherein the precursor ion has laboratory-frame translational energy lower than approximately 1000 eV. This process typically requires multiple collisions and the collisional excitation is cumulative.
- 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 .
- Mass-Analyzed Ion Kinetic Energy Spectrometry** – A technique 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 kinetic energy/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.
- 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.
- Mass Defect** – The difference between the *nominal mass* (or *mass number*) and the *monoisotopic mass* of a molecule or atom.
- Mass Excess** – The negative of the *mass defect*.
- Mass Limit** – The m/z value above which ions cannot be detected in a mass spectrometer.
- Mass Number** – The sum of the number of protons and neutrons in an atom, molecule or ion.
- Mass Range** – The range of m/z over which a mass spectrometer can detect ions or is operated to record a mass spectrum.

- Mass Resolution** – The smallest mass difference Δm between two equal magnitude peaks so that the valley between them is a specified fraction of the peak height
- Mass Resolving Power** – In a mass spectrum, the observed mass divided by the difference between two masses that can be separated: $m/\Delta m$. The method by which Δm was obtained and the mass at which the measurement was made should be reported.
- Mass Selective Axial Ejection** – The use of mass selective instability to eject ions of selected m/z values from a Paul ion trap.
- 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.
- Mass Spectral Library** – A collection of mass spectra of different compounds, usually expressed 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*.
- 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.
- Mass Spectrometer** – An instrument that measures the m/z values and relative abundances of ions.
- Mass Spectrometry** – The branch of science that deals with all aspects of mass spectrometers and mass spectrographs and the results obtained with these instruments.
- Mass Spectrometry/Mass Spectrometry** – 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. Synonymous with *tandem mass spectrometry*. 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*).
- Mass Spectrum** – A plot of the relative abundances of ions forming a beam or other collection as a function of their m/z values.
- 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.
- Matrix-Assisted Laser Desorption/Ionization** – The formation of gas-phase ions from molecules that are present in a solid or liquid matrix that is irradiated with a pulsed laser. See also *laser desorption/ionization*.
- 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.
- 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.
- Membrane Inlet** – A semi-permeable membrane separator that permits the passage of analyte molecules directly from solutions or ambient air to the mass spectrometer ion source.
- 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.
- Microchannel Plate** – 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.
- Microelectrospray** – Electrospray ionization at a solution flow rate less than 1 $\mu\text{L}/\text{min}$.
- Molar Mass** – The mass of one mole ($6.022\,1415(10) \times 10^{23}$ atoms or molecules) of a compound.
- 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.
- 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.
- Momentum Transfer Collision** – Synonymous with elastic collision.

Monoisotopic Mass – The *exact mass* of an ion or molecule calculated using the mass of the most abundant isotope of each element.

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. Synonymous with *multiple-stage mass spectrometry*.

Multiphoton Ionization – Photoionization of an atom or molecule in which in two or more photons are absorbed.

Multiple-Stage Mass Spectrometry – Multiple stages of precursor ion *m/z* selection followed by product ion detection for successive progeny ions.

m/z – The three-character symbol *m/z* is used to denote the dimensionless quantity formed by dividing the mass of an ion by the *unified atomic mass unit* and also by its *charge number* (regardless of sign). The symbol is written in italicized lower case letters with no spaces.

Nanoelectrospray – Electrospray ionization at a flow rate less than 100 nL/min. See also *electrospray ionization* and *microelectrospray*.

Negative Ion – An atomic or molecular species having a net negative electric charge.

Negative Ion Chemical Ionization – Chemical ionization that results in the formation of negative ions.

Neutralization Reionization Mass Spectrometry – A technique 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.

Neutral Loss – The loss of an uncharged species from an ion during either a rearrangement process or direct dissociation.

Nier-Johnson Geometry – An 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.

Nitrogen Rule – The rule stating that 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.

Nominal Mass – The mass of an ion or molecule calculated using the mass of the most abundant isotope of each element rounded to the nearest integer value. It is in effect the sum of the *mass numbers* of all constituent atoms

Non-Classical Ion – A hyper-coordinated carbonium ion such as the penta-coordinated norbornyl cation named non-classical by S. Winstein. The term derives from a cornerstone of the classical theory of structural chemistry since the time of Kekulé in the 1860s that stated that carbon could bind at most four other atoms (tetra-coordination). Tri-coordinated carbenium ions (see Enium Ion) are consequently termed 'Classical Ions'.

Nth Generation Product Ion – The serial product ions from dissociation of selected precursor ions where n refers to the number of stages of dissociation. See also *progeny ion*.

Nth Generation Product Ion Scan – The specific scan functions or processes that record the appropriate generation of product ion or ions of any *m/z* selected precursor ions.

Nth Generation Product Ion Spectrum – The 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.

Odd-Electron Ion – Synonymous with *radical ion*.

Odd-Electron Rule – The rule stating that, upon dissociation, odd-electron ions may form either odd or even-electron ions, whereas even-electron ions generally form even-electron ions.

Onium Ion – A positively charged hypervalent ion of the nonmetallic elements. Examples are the methonium ion CH₅⁺, the hydrogenonium ion H₃⁺ and the hydronium ion H₃O⁺. Other examples are the oxonium, sulfonium, nitronium, diazonium, phosphonium, and halonium ions. Onium ions are not limited to monovalent ions; multiply-charged onium ions exist such as the gitonium (proximal) oxonium dication H₄O²⁺ and the distonic oxonium dication H₂O⁺-CH₂-CH₂-OH₂⁺.

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 used as a mass analyzer.

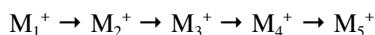
- Orbitrap Mass Spectrometer** – A mass spectrometer based on the *orbitrap* principle in which ions are orbitally trapped and oscillate harmonically along the trap axis. The oscillation frequency is inversely proportional to square root of m/z is measured using image current detection and Fourier transformation of the time domain signal.
- Orthogonal Extraction** – The 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.
- Partial Charge Exchange Reaction** – Synonymous with *partial charge transfer reaction*.
- Partial Charge Transfer Reaction** – The reaction of an ion with a neutral species in which some but not all of the ion charge is transferred to the neutral.
- Paul Ion Trap** – An ion trapping device that permits the ejection of ions with an m/z less 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.
- Peak** – A 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.
- Peak Intensity** – The height or area of a peak in a mass spectrum.
- Peak Matching** – A method 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.
- 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. *Penning ionization* differs from *chemi-ionization* in that no chemical change is involved.
- Photodissociation** – A process wherein the reactant ion is dissociated as a result of absorption of one or more photons.
- Photoionization** – The ionization of an atom or molecule by a photon, written $M + h\nu \rightarrow M^+ + e$. The term *photon impact* is not recommended.
- Plasma Desorption/Ionization** – 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 . Synonymous with *fission fragment ionization*.
- Pneumatically-Assisted Electrospray Ionization** – A modification of electrospray ionization in which the nebulization of the liquid stream is assisted by a concentric stream of gas.
- Point Collector** – A detector in which the ion beam is focused onto a point and the individual ions arrive sequentially.
- Positive Ion** – An atomic or molecular species having a net positive electric charge.
- Post-Acceleration Detector** – A detector in which a high voltage is applied after m/z separation to accelerate the ions and produce an improved signal.
- Post-Source Decay** – A 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.
- Precursor Ion** – An 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 not recommended.
- Precursor Ion Scan** – The specific scan function or process that will record a precursor ion spectrum.
- Precursor Ion Spectrum** – The 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.
- Pre-Ionization State** – An electronic state capable of undergoing autoionization.
- Principal Ion** – The 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*.

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 terms daughter ion and parent ion are not recommended.

Product Ion Scan – The specific scan function or process that records product ion spectrum.

Product Ion Spectrum – A 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.

Progeny Fragment Ions – A 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^+

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 not recommended.

Proton Affinity – The proton affinity of a species M is defined as the negative of the enthalpy change for the reaction $M + H^+ \rightarrow [M+H]^+$, where all species are in their ground rotational, vibrational and electronic states.

Protonated Molecule – An ion formed by interaction of a molecule with a proton, and represented by the symbolism $[M + H]^+$. The terms protonated molecular ion, quasi-molecular ion and pseudo-molecular ion are not recommended.

Pyrolysis Mass Spectrometry – 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.

Quadrupole Ion Storage Trap – See *Paul ion trap*.

Quistor – An abbreviation of quadrupole ion storage trap.

Quadratic Field Reflectron – A reflectron in which the electric field varies with the square of the distance from the entrance and compensates for kinetic energy spread to all orders.

Quadrupole Ion Trap – See *Paul ion trap*.

Quadrupole Mass Spectrometer – See *transmission quadrupole mass spectrometer*.

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^{\bullet} . Radical ions with more than one charge and/or more than one unpaired electron are denoted such as $M^{(2+)(2\bullet)}$. 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.

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.

Recombination Energy – The 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*.

Reference Ion – A 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.

Reflectron – A 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 kinetic energy arrive at the detector at the same time.

Relative Molecular Mass – The mass of one molecule of a compound, with specified isotopic composition, relative to one-twelfth of the mass of one atom of ^{12}C .

Residual Gas Analyzer – A mass spectrometer used to measure the composition and pressure of gasses in an evacuated chamber.

Resonance-Enhanced Multiphoton Ionization – *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.

- Resonance Ion Ejection** – A mode of ion ejection in a quadrupole 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.
- Resonance Ionization** – Synonymous with *resonance-enhanced multiphoton ionization*.
- Reverse Library Search** – A method 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.
- RF-DC Ion Mobility Spectrometry** – Synonymous with *high-field asymmetric waveform ion mobility spectrometry*.
- Secondary Electron** – Electrons that are ejected from a sample surface as a result of bombardment by a primary beam of atoms, ions, or photons.
- Secondary Ionization** – The process in which ions are ejected from a sample surface as a result of bombardment by a primary beam of atoms or ions.
- Sector Mass Spectrometer** – A 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.
- Selected Ion Flow Tube** – A 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.
- Selected Ion Monitoring** – The 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.
- Selected Reaction Monitoring** – 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*.
- Soft Ionization** – The formation of gas-phase ions without extensive fragmentation.
- Space Charge Effect** – The 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.
- Spark Ionization** – The formation of ions from a solid material by an intermittent electrical discharge.
- Stable Ion** – An ion with internal energy sufficiently low that it does not rearrange or dissociate prior to detection in a mass spectrometer.
- Stability Diagram** – See *Mathieu stability diagram*.
- Static Field** – An electric or magnetic field that does not change in time.
- Stored Waveform Inverse Fourier Transform** – A technique to create excitation waveforms for ions in FT-ICR mass spectrometer or Paul ion trap. 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 technique may be used for selection of precursor ions in MS/MS experiments.
- Superelastic Collision** – A 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.
- Surface-Assisted Laser Desorption/Ionization** – The formation of gas-phase ions from molecules deposited on a particular surface substrate that is irradiated with a pulsed laser. See also *matrix-assisted laser desorption/ionization*.
- Surface-Enhanced Laser Desorption/Ionization** – The formation of ionized species in the gas phase from analytes deposited on a particular surface substrate which is irradiated with a laser beam with a wavelength that is absorbed by the surface. See also *desorption/ionization on silicon* and *laser desorption/ionization*.
- Surface-Enhanced Neat Desorption** – Matrix-assisted laser desorption/ionization in which the matrix is covalently linked to the target surface.
- Surface-Induced Dissociation** – Fragmentation that results from the collision of an ion with a surface.
- Surface-Induced Reaction** – A 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.
- Surface Ionization** – The ionization of a neutral species when it interacts with a solid surface with an appropriate work function and temperature.

Sustained Off-Resonance Irradiation – A technique 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 ion's 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.

Tandem Mass Spectrometer – A mass spectrometer designed for *mass spectrometry/mass spectrometry*.

Tandem Mass Spectrometry – See *Mass spectrometry/Mass Spectrometry*.

Tandem Mass Spectrometry in Time – A tandem mass spectrometry method 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.

Tandem Mass Spectrometry in Space – A tandem mass spectrometry method 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.

Thermal Ionization – The ionization of a neutral species through contact with a high temperature surface.

Time-of-flight Mass Spectrometer – An instrument that separates ions by *m/z* in a field-free region after acceleration to a fixed *acceleration energy*.

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.

Total Ion Current – The 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.

Total Ion Current Chromatogram – The chromatogram obtained by plotting the *total ion current* detected in each of a series of mass spectra recorded as a function of retention time.

Transmission – The ratio of the number of ions leaving a region of a mass spectrometer to the number entering that region.

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.

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.

Unified Atomic Mass Unit – A non-SI unit of mass (symbol u) defined as one twelfth of the mass of one atom of ¹²C in its ground state and equal to 1.660 538 86(28) x 10⁻²⁷ kg.

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.

Unstable Ion – An ion with sufficient energy to dissociate within the ion source.

Vertical Ionization – A 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.

x-Ion – A fragment ion containing the C-terminus formed upon dissociation of a protonated peptide at a backbone C-C bond.

y-Ion – A fragment ion containing the C-terminus formed upon dissociation of a protonated peptide at a backbone C-N bond.

z-Ion – A fragment ion containing the C-terminus formed upon dissociation of a protonated peptide at a backbone N-C bond.

II. Acronyms

AE – Appearance Energy
AMS – Accelerator Mass Spectrometry
AP – Appearance Potential; Atmospheric Pressure
AP MALDI – Atmospheric Pressure Matrix-Assisted Laser Desorption/Ionization
APCI – Atmospheric Pressure Chemical Ionization
API – Atmospheric Pressure Ionization
APPI – Atmospheric Pressure Photoionization
B – Magnetic Field
BIRD – Blackbody Infrared Radiative Dissociation
BP – Base Peak
CA – Collisional Activation
CAD – Collisionally Activated Dissociation
CE-MS – Capillary Electrophoresis Mass Spectrometry
CF-FAB – Continuous Flow Fast Atom Bombardment
CI – Chemical Ionization
CID – Collision-Induced Dissociation
CIT – Cylindrical Ion Trap
CRF – Charge Remote Fragmentation
CRM – Consecutive Reaction Monitoring
CS – Charge Stripping
CX – Charge Exchange
Da – Dalton
DE – Delayed Extraction
DESI – Desorption Electrospray Ionization
DI – Desorption/Ionization
DIOS – Desorption/Ionization on Silicon
DIP – Direct Insertion Probe
DLI – Direct Liquid Introduction
DMS – Dynamic Mass Spectrometry
E – Electric Field
EA – Electron Affinity
ECCI – Electron Capture Chemical Ionization
ECD – Electron Capture Dissociation
EE – Even Electron
EI – Electron Ionization
EM – Electron Multiplier
ES – Electrospray
ESA – Electrostatic Energy Analyzer

ESI – Electrospray Ionization
eV – Electron Volt
FA – Flowing Afterglow
FAB – Fast Atom Bombardment
FAIMS – High-Field Asymmetric Waveform Ion Mobility Spectrometry
FD – Field Desorption
FFR – Field-Free Region
FI – Field Ionization
FIB – Fast Ion Bombardment
FPD – Focal Plane Detector
FT-ICR – Fourier Transform Ion Cyclotron Resonance
FT-MS – Fourier Transform Mass Spectrometry
GC/MS – Gas Chromatography Mass Spectrometry
GD-MS – Glow Discharge Mass Spectrometry
HDX – Hydrogen/Deuterium Exchange
HRMS – High Resolution Mass Spectrometry
ICP-MS – Inductively Coupled Plasma Mass Spectrometry
ICR – Ion Cyclotron Resonance
IDMS – Isotope Dilution Mass Spectrometry
IE – Ionization Energy
IKES – Ion Kinetic Energy Spectrometry
IMS – Ion Mobility Spectrometry
IRMPD – Infrared Multiphoton Dissociation
IRMS – Isotope Ratio Mass Spectrometry
ISD – In-Source Decay
IT – Ion Trap
ITD – Ion Trap Detector
ITMS – Ion Trap Mass Spectrometry
KER – Kinetic Energy Release
KERD – Kinetic Energy Release Distribution
LAMMA – Laser Microprobe Mass Analyzer
LCMS – Liquid Chromatography Mass Spectrometry
LD – Laser Desorption
LDI – Laser Desorption/Ionization
LIMS – Laser Ionization Mass Spectrometry
LIT – Linear Ion Trap
LMMS – Laser Microprobe Mass Spectrometry
LSIMS – Liquid Secondary Ion Mass Spectrometry
MALDI – Matrix-assisted Laser Desorption/Ionization
MBMS – Molecular Beam Mass Spectrometry

MCP – Microchannel Plate
MID – Multiple Ion Detection
MIKES – Mass-Analyzed Ion Kinetic Energy Spectrometry
MIMS – Membrane Introduction Mass Spectrometry
MPD – Multiphoton Dissociation
MPI – Multiphoton Ionization
MRM – Multiple Reaction Monitoring
MS – Mass Spectrometry
MS/MS – Mass Spectrometry/Mass Spectrometry
MSⁿ – Multiple Stage Mass Spectrometry
NICI – Negative Ion Chemical Ionization
NRMS – Neutralization Reionization Mass Spectrometry
OE – Odd Electron; Orthogonal Extraction
PA – Proton Affinity
PD – Plasma Desorption
PDMS – Plasma Desorption Mass Spectrometry
PI – Photoionization
PSD – Post-Source Decay
PyMS – Pyrolysis Mass Spectrometry
q – Collision Quadrupole; Quadrupole Lens
Q – Quadrupole Mass Spectrometer
QIT – Quadrupole Ion Trap
QUISTOR – Quadrupole Ion Storage Trap
REMPI – Resonance-Enhanced Multiphoton Ionization
reTOF – Reflectron Time-of-Flight
RGA – Residual Gas Analyzer
RIC – Reconstructed Ion Chromatogram
RIMS – Resonance Ionization Mass Spectrometry
RP – Resolving Power
SALDI – Surface-Assisted Laser desorption/Ionization
SELDI – Surface-Enhanced Laser desorption/Ionization
SEND – Surface-Enhanced Neat Desorption
SFC/MS – Supercritical Fluid Chromatography Mass Spectrometry
SI – Surface Ionization
SID – Surface-Induced Dissociation
SIFT – Selected Ion Flow Tube
SIM – Selected Ion Monitoring
SIMS – Secondary Ion Mass Spectrometry
SORI – Sustained Off-Resonance Irradiation
SRM – Selected Reaction Monitoring

SSMS – Spark Source Mass Spectrometry
SWIFT – Stored Waveform Inverse Fourier Transform
TEL – Translational Energy Loss
TES – Translational Energy Spectrometry
TIC – Total Ion Chromatogram; Total Ion Current
TICC – Total Ion Current Chromatogram
TIMS – Thermal Ionization Mass Spectrometry
TLF – Time Lag Focusing
TOF – Time-of-Flight
TOF-MS – Time-of-Flight Mass Spectrometry
u – Unified Atomic Mass Unit
z – Charge Number

III. Terms Not Recommended

Appearance Potential – Not recommended; use *appearance energy*.

Atomic Mass Unit (amu) – not recommended; this term 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 . See *unified atomic mass unit*.

B/E Linked Scan – Not recommended; see *linked scan at constant B/E*.

B²/E Linked Scan – Not recommended; see *linked scan at constant B²/E*.

B[1-(E/E₀)]^{1/2}/E Linked Scan – Not recommended; see *linked scan at constant B[1-(E/E₀)]^{1/2}/E*.

Collisionally Activated Dissociation (CAD) – Not recommended; see *collision-induced dissociation*.

Cycloidal Mass Spectrometer – Not recommended; see *prolate trochoidal mass spectrometer*.

Cylindrical Ion Trap – Not recommended; synonymous with *Paul ion trap*.

Daughter Ion – Obsolete term, not recommended; see *product ion*.

Daughter Ion Scan – Obsolete term, not recommended; see *product ion scan*.

Daughter Ion Spectrum – Obsolete term, not recommended; see *product ion spectrum*.

Direct Analysis of Daughter Ions (DADI) – Obsolete term; see *mass-analyzed ion kinetic energy spectrometry*.

E²/V Linked Scan – Not recommended; see *linked scan at constant E²/V*.

Electron Impact Ionization – Not recommended; see *electron ionization*.

Field Desorption/Ionization – Not recommended.

Fragment Ion Scan – Not recommended; see *product ion scan*.

Fragment Ion Spectrum – Not recommended; see *product ion spectrum*.

Granddaughter ion – Obsolete term, not recommended; see *Nth generation product ion scan*.

Grandparent ion – Obsolete term, not recommended; see *Nth generation product ion spectrum*.

Ion-Ion Reaction – Not recommended; see *ion/ion reaction*.

Ion-Molecule Reaction – Not recommended; see *ion/molecule reaction*.

Mass Spectroscopy – Not recommended; see *mass spectrometry*.

Mass-to-Charge Ratio – Not recommended. This term 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.

Molecular Weight – Not recommended; since "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.

MS/MS Spectrum – Not recommended. A scan-specific term, *e.g.* precursor ion spectrum or second-generation product ion spectrum should be used.

Multiple Reaction Monitoring – Not recommended; see *selected reaction monitoring*.

Parent Ion – Obsolete term, not recommended; see *precursor ion*.

Parent Ion Scan – Obsolete term, not recommended; see *precursor ion scan*.

Parent Ion Spectrum – Obsolete term, not recommended; see *precursor ion spectrum*.

Photon Impact – Not recommended; see photoionization.

Protonated Molecular Ion – Incorrect term since this would correspond to a species carrying two charges. The recommended term is *protonated molecule*.

Pseudo-Molecular Ion – Not recommended; use a specific term such as *protonated molecule*, or a chemical description such as $[M+Na]^+$, $[M-H]^-$, *etc.*

Quasi-Molecular Ion – Not recommended; use a specific term such as *protonated molecule*, or a chemical description such as $[M+Na]^+$, $[M-H]^-$, *etc.*

Target Gas – Not recommended. See *collision gas*.

Thomson (Th) – Not recommended; use *m/z* unit.

References

Orange Book, "Compendium of Analytical Nomenclature," edited by H M N H Irving, H Freiser and T S West, Pergamon, Oxford, **1978**. [ISBN 0-08-022008-8]; 2nd edition, edited by H Freiser and G H Nancollas, Blackwell Scientific Publications, **1987**. [ISBN 0-632-01907-7]; 3rd edition, edited by J Inczedy, Blackwell Scientific Publications, **1998**. [ISBN 0-86542-615-5]

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