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INTERNATIONAL UNION OF PURE
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PHYSICAL CHEMISTRY DIVISION

COMMISSION ON MOLECULAR STRUCTURE AND SPECTROSCOPY

RECOMMENDATIONS FOR SYMBOLISM AND NOMENCLATURE FOR MASS SPECTROSCOPY

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RECOMMENDATIONS FOR SYMBOLISM AND NOMENCLATURE FOR MASS SPECTROSCOPY

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The Commission on Analytical Nomenclature of IUPAC has previously issued recommendations for nomenclature of mass spectrometry [*Pure and Applied Chemistry* (1974) *37*, No.4, 469]. These are in the form of definitions of some of the terms used in this subject. In formulating the definitions, note was taken of the definitions proposed by the Fachnormenausschuss Vakuumtechnik in *Deutschen Normenausschuss* and in the Editorial Review in *Organic Mass Spectrometry* (1969), *2*, 249. The Commission on Molecular Structure and Spectroscopy through its Sub-Commission on Mass Spectroscopy (Chairman, Professor J.H. Beynon) is now up-dating and extending these recommendations and, in addition, making further recommendations concerning the use of symbols, acronyms, abbreviations and newly invented jargon. Some preliminary findings on this topic by Sub-Committee X of Committee E-14 of the American Society for Testing and Materials were published in the proceedings of the 22nd Annual Conference on Mass Spectrometry and Allied Topics of the American Society for Mass Spectrometry held in Philadelphia in 1974 and their help is acknowledged.

The recommendations now presented take note of all the above and represent a summary of the majority views of mass spectroscopists from some 31 countries who were invited to submit their views to the Sub-Commission on Mass Spectroscopy. Because the subject is still growing and continuously changing in emphasis, it was decided to restrict these recommendations either to general matters of presentation of results or to those aspects of the subject that are already well developed and established. It is expected, therefore, that further up-dating will be necessary from time to time but at present it is not considered worthwhile to define all terms, but only those that have been used in a considerable number of papers.

1. An acronym, abbreviation or invented jargon should only be used after a full explanation of its meaning has been given in the text. It is not sufficient merely to give the expression followed by a literature reference. It is only necessary or desirable to use a special term at all if it allows an appreciable saving of space or prevents repetition of a long or clumsy phrase. The only exceptions, relating to mass spectroscopy, should be the following few commonly accepted initials that may be used freely and without amplification:

GC/MS	meaning either the combined techniques of gas chromatography and mass spectroscopy or the combination of a gas chromatograph with a mass spectroscope
ICR	meaning ion cyclotron resonance
m/z	meaning mass-to-charge ratio

[NOTE: Except in the case of GC/MS given above, the initials MS should not be used. They can mean, for example, mass spectrum, mass spectrometer, mass spectroscopy, metastable, magnetic sector, etc., etc., and their use thus leads to considerable confusion.]

2. Terms peculiar to the discipline of mass spectroscopy should be used only when more generally used and understood terms are either inadequate, ambiguous or very inconvenient. Authors should resist the proliferation of invented words; jargon should be minimised to maximise communication with scientists in other areas. Several special terms are already in widespread use. It is recommended that the following list be confirmed as terms of this kind that may be used without explanation.

[NOTE: Other terms can be added to this list from time to time. Comments or additions would be welcomed.]

Omegatron spectrometer

Radio-frequency mass spectrometer

Quadrupole mass spectrometer (or monopole, hexapole, etc.)

Time-of-flight mass spectrometer

Single-focussing mass spectrometer

Double-focussing mass spectrometer

Electron impact ionization

Field ionization

Field desorption

Photoionization

Chemical ionization

Thermal ionization

Auto-ionization

Molecular ion

Fragment ion

Rearrangement ion

Base peak

Metastable peak

Most of these terms are among those defined in the 'Recommendations for Nomenclature of Mass Spectrometry' by the Analytical Chemistry Division of IUPAC (loc. cit.)

The terms *electric sector* (not electrostatic sector or electrostatic analyser) and *magnetic sector* are recommended.

For descriptions of ions in the gas phase, the term *positive ion* is preferred over *cation* and *negative ion* over *anion*.

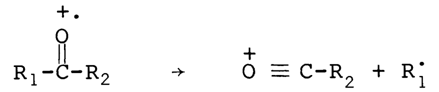
The term *deuterated* is preferred over *deuteriated* to represent replacement of protium by deuterium.

The term *isotopic scrambling* should only be used to denote complete random mixing of isotopes between specified positions in an ion or neutral species.

The term *partial scrambling* has no meaning and should not be used. One can, however, talk about partial or incomplete isotopic or atomic exchange over specified positions.

It is recommended that the term *principal ion* be defined as a molecular or fragment ion made up of the most abundant isotopes of each of its atomic constituents. In the case of compounds that have been artificially isotopically enriched in one or more positions such as $CH_3{}^{13}CH_3$ or CH_2D_2 the principal ion may be defined treating the heavy isotopes as new atomic species. Thus, in the above two examples, the principal ions would be of masses 31 and 18 respectively. A *monoisotopic mass spectrum* is a spectrum containing only principal ions.

It is recommended that the convention used by Budzikiewicz, Djerassi and Williams ['Mass Spectrometry of Organic Compounds', Holden-Day Inc.,(1967) P.2] be followed in referring to *α-cleavage* as "fission of a bond originating at an atom which is adjacent to the one assumed to bear the charge; the definition of β-, γ-, cleavage then follows automatically". The process



$$R_1-\overset{\overset{+\cdot}{O}}{\overset{\|}{C}}-R_2 \rightarrow \overset{+}{O}\equiv C-R_2 + R_1^{\cdot}$$

would thus be described as "*α-fission of a ketone with expulsion of a radical* $R_1^{\cdot}$". The carbon atoms of the radical $R_1^{\cdot}$ are called the α-, β-, γ-, carbons, starting with the atom nearest the functional group.

The term *parent ion* has been defined as the ion precursor of a fragment ion. It must be clear that the term refers to <u>any</u> ion that undergoes fragmentation. The term is not interchangeable with *molecular ion*.

The term *quasi-molecular ion* to represent a protonated molecular ion or an ion formed from a molecular ion by loss of a hydrogen atom is not recommended.

A number of special terms have been invented that are useful in particular areas of mass spectroscopy. For example in GC/MS one has *multiple ion detection* and *mass fragmentography*. Useful though these terms are as a shorthand, they add to the difficulties of scientists from other areas reading this part of the literature. Further, there are objections to many of these terms. Thus, an alternative to the first term given is *multiple peak scanning* to emphasize that monitoring of peaks rather than detection of ions is the important feature. An objection to the second term is that it is often not fragments that are being monitored but peaks from molecular ions. None of the above terms is recommended.

Other terms that have been invented to describe equipment or techniques are often referred to by their initials. This can become confusing when, for example, SID is used regularly to mean *specific ion detector*, *secondary ion detection* and *surface induced dissociation*. This emphasizes another aspect of the general undesirability of a proliferation of new terms and acronyms.

Special terms have also been used to describe particular methods of scanning. For example, one of these has been variously described as *the Barber-Elliott method*, *metastable defocussing*, *metastable refocussing* and *scanning in the metastable mode*. All of these expressions are misleading and undesirable and it is recommended that in all cases, the scanning method should be described by detailing exactly how the scan has been carried out. The above would be described as "*scanning the accelerating voltage with fixed electric sector voltage and fixed magnetic field*".

In some instances, words that have a recognised meaning in everyday conversation are used (sometimes with inverted commas) to have a somewhat different meaning. Thus, the terms "*loose*" and "*tight*" transition complex appear in the literature and the meaning to be ascribed to them is not clear. Such terms should never be used without definition or a reference explaining the meaning. [NOTE: In a preliminary note, definition of these terms was invited, but no-one accepted the invitation. Several senior mass spectroscopists said they did not understand the meaning.]

It is recommended that one should refer to the *abundance* of an ion, to the *intensity* of an ion beam and to the *height* or *area* of a peak.

It is recommended that one should refer to an *ion/molecule reaction* when discussing the reaction between an ion and a molecule. The use of *ion-molecule reaction* is not recommended; the hyphen suggests a reaction of a species that is both an ion and a molecule and this is not the intended meaning.

3. Proper names should only be used as a shorthand method of referring to an instrument, a theory, a rule or a reaction if there is no other convenient and adequate descriptive method available. Proliferation of the use of names should be discouraged on the grounds that their use can lead to subjective thinking, to lack of recognition of simultaneous work in other laboratories and to confusion when a person extends or changes his ideas or equipment. It is recommended that in the few cases where the use of proper names is unavoidable, their use should always be accompanied by a literature reference to the original work. Only in this way can ambiguity of meaning be avoided.

It is recommended that three cases of the use of proper names that have already been defined in the earlier IUPAC recommendations should continue to be used as a convenient shorthand. These are:

Mattauch-Herzog geometry

Nier-Johnson geometry

McLafferty rearrangement

In connection with the use of the above terms, it should be noted that they only refer to the defined arrangements and reaction. Thus, the Nier-Johnson geometry necessarily involves a deflection of $\Pi/3$ radians in the magnetic field and no other. Terms such as *modified Nier-Johnson geometry* or *quasi-McLafferty rearrangement* are meaningless and should not be used.

4. Symbolism used for the representation of ions should be standardised as far as possible.

The superscript symbol $^{+}$ should be used to represent a positive charge and $^{-}$ to represent a negative charge.

The superscript symbol $^{\cdot}$ should be used to represent an odd electron. When used in combination, the above symbols should be written $^{+\cdot}$ and $^{-\cdot}$. The use of $\underset{\cdot}{+}$ and $\underset{\cdot}{-}$ is not recommended. The symbol M should be used exclusively to represent an even electron molecule and $M^{\cdot}$ an odd electron molecule. The symbol $M^{+\cdot}$ represents the odd-electron ion formed from an even electron molecule by the removal of a single electron (the molecular ion).

Capital letters enclosed in parentheses should be used to represent an ion containing different structural features and the charge should be located outside the parentheses. Thus, one should write for example, $(ABC)^{+}$ or $(ABC)^{+\cdot}$ [if it is desired to emphasise that one is dealing with an odd electron species].

An exception to the above is that an ion may be written, for example, $(\overset{+}{A}BC)$ or $(\overset{+\cdot}{A}BC)$ if it is required to discuss structures in which the charge and odd electron are localised.

When it is required to write the empirical formula of a molecular ion, this may be written in 4 ways. Thus, for example, the molecular ion of aniline may be written $(C_6H_7N)^{+\cdot}$ or it may be written $C_6H_5NH_2\rceil^{+\cdot}$ to emphasize that one is discussing an ion formed from a molecule with the structure $C_6H_5NH_2$ by the removal of a single electron, the upper half of a square bracket being used to indicate that the structure of the ion may or may not be the same as that of the molecule from which it was formed. [NOTE: Other special symbols suggested by the members of the IUPAC Molecular Structure and Spectroscopy Commission as alternatives to "$\rceil$" were "$>$" and "$\rbrace$"]. If one wishes to discuss a particular structure, in which an odd electron is localised then one can write, for example, $(C_6H_5\overset{+\cdot}{N}H_2)$.

The ionization process, for example, under electron bombardment, may be written:

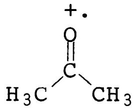
$$C_6H_5NH_2 + e^- \rightarrow C_6H_5NH_2\rceil^{+\cdot} + 2e^-$$

$$\rightarrow (C_6H_7N)^{+\cdot} + 2e^-$$

or (to represent
a particular ion
structure) $\rightarrow \quad (C_6H_5NH_2)^{+\cdot} \quad + \quad 2e^-$

Structural formulae of ions in which it is desired to indicate the localisation of an odd electron may, alternatively, be written without the parentheses. Thus,

$C_6H_5\overset{+\cdot}{N}H_2$ or



Confusion sometimes arises because of the use of a hyphen or of a dash sign in the symbolism. Thus D(R-X) has been used to mean the dissociation energy of the bond between R and X while $(X\text{-}CH_2)^+$ might mean the next higher homologue of X^+ or the ion formed from X^+ by removal of a CH_2 group. To overcome some of this confusion, it is recommended that a dash should not be used to indicate a bond, except in a conventional structural formula such as that for the acetone molecular ion shown above this paragraph. In other cases, the next higher homologue of X^+ should be written $(XCH_2)^+$, without any dash being used.

In the exceptional event that it is necessary to emphasize that a bond is breaking, then it should be represented by two dots with a wavy line between them. Thus we might write

$$[R_1 \cdot \Big\} \cdot CH_2CH_2R_2]^{+\cdot}$$

no other bond than the breaking bond being illustrated. When, in addition to indicating fragmentation of the bond, it is necessary to emphasize the mass numbers of the fragments formed, this is done by writing the mass numbers at the top (right-hand fragment) or the bottom (left-hand fragment) as shown

$$CH_3CH_2 \cdot \underset{29}{\Big\}} \cdot CH_2CH_2 \cdot \overset{47}{\underset{57}{\Big\}}} \cdot CH_2SH\Big]^{+\cdot}$$

Loss of a particular group should be indicated by the use of a minus sign located outside the parentheses or to the right of the $^{+\cdot}$ sign. Spaces should be left on either side of the minus sign to reduce any confusion as to its meaning. Thus one would write

$$(M)^{+\cdot} - CH_2 \qquad \text{or} \qquad C_6H_5CH_3\Big]^{+\cdot} - H^\cdot$$

The symbols m_1, m_2, m_3 etc., may be used to represent the masses of neutral species. Ions carrying a single positive or negative charge and having a mass m_1 may be represented by m_1^+ or m_1^- or by $m_1^{+\cdot}$ or $m_1^{-\cdot}$, if it desired to emphasize the presence of an odd electron. Ions carrying 2, 3 or 4 charges may be represented as m_1^{2+}, m_1^{3+}, m_1^{4+} etc., or m_1^{2-}, m_1^{3-}, m_1^{4-} etc. Alternative symbolism, for example, m_1^{++}, m_1^{+2}, m_1^{---}, m_1^{-3}, is not recommended.

The <u>number</u> of charges carried by an ion should be indicated by the symbol z. The ratio of the mass number of an ion to the number of charges carried (commonly referred to as the mass-to-charge ratio) should be written m_1/z, m_2/z, etc. m/e should not be used to indicate this ratio, e being reserved for the charge upon the electron and e^- for the electron itself when it appears in an equation.

A fragmentation reaction may be written:

$$m_1^+ \rightarrow m_2^+ + m_3$$

The decomposition of a metastable ion of mass-to-charge ratio m_1/z_1 into an ion of mass-to-charge ratio m_2/z_2 after electric acceleration of the metastable ion and before magnetic deflection gives rise to a peak in the mass spectrum at an apparent mass, $m_2^2 z_1/m_1 z_2^2$. The symbol m^* should be used to indicate the apparent mass of the product ions giving rise to this peak. Traditionally, the peak itself has been called a *metastable* peak and it is recommended that this term should be retained. The word *metastable* should never be used as a noun. Its use as an adjective should be limited to such terms as *metastable ion*, where it is used correctly, and to the special case of *metastable peak* discussed above. It should never be used in such terms as *metastable reaction*, *metastable decomposition*, *metastable studies*, *etc*. It should be clear that the metastable ion is the ion that undergoes fragmentation; it is not detected. When a reaction is written with an asterisk above the arrow as shown:

$$m_1^{+} \xrightarrow{*} m_2^{+} + m_3$$

this means that the reaction has been confirmed by the observation of a metastable peak.

It has become general practice to use the terms *ionization potential* of a molecule and *appearance potential* of an ion X^+ in connection with the minimum energies for formation of the molecular and fragment ions respectively and to use the abbreviations IP(M) and AP(X^+) to represent these terms. What is being reported in each case is, however, an energy and not a potential. To overcome this difficulty, it is recommended that the terms be referred to as *ionization energy* and *appearance energy* respectively and that the symbolism I(M) and $A(X)^+$ be used to represent these quantities. [NOTE: Symbols $E_i(M)$ and $E_a(X)^+$ were also considered as alternatives to I(M) and $A(X)^+$.]

The symbol u has been recommended for atomic mass units using the standard that the mass of ^{12}C is 12 u exactly (see, for example, Proc. Chem. Soc. (1960) 97). The symbol amu is no longer recommended - this was the old unit using the standard based on the mass of ^{16}O.

The symbol ↷ is recommended for indicating the movement of one electron.

The symbol ↷ is recommended for indicating the movement of two electrons.

5. The parts of a mass spectrometer should be described clearly according to their position within the instrument or the function that they perform. Thus, one should not refer to the α- or β- slits or to the first or second field-free regions. Rather, one should use terms such as the *source slit*, *the slit limiting the angular divergence*, *the energy resolving slit*, *the field-free region traversed by the ion beam before entering the magnetic sector* or *the ion repeller plate*.

The initials HV or EHT to describe voltages of the order of a few thousand volts should not be used. Rather, one should use the expression *accelerating voltage* without abbreviation.

To describe the performance of mass spectroscopic equipment it is necessary to specify *inter alia* the resolving power and sensitivity.

The resolving power should be given in terms of the mass and the reciprocal of the peak width measured at a given percentage of the peak height. Resolving power measured using a single peak made up of singly-charged ions of mass m should be designated $m/\Delta m$ and it should be stated clearly at what percentage of the peak height the measurement has been made. It is recommended that one of the three values 50%, 5% or 0.5% should always be used. A peak showing the number of ions as a function of their translational energy should be used in the same way to give a value of the energy resolving power.

The definition of mass resolving power in terms of the overlap (or "valley") between two peaks is common and is also acceptable. Thus for two peaks of equal height, masses m_1 and m_2, when there is overlap between the two peaks to a stated percentage of either peak height (10% is recommended), then the resolving power is defined as $m_1/(m_1 - m_2)$. The percentage overlap (or "valley") concerned must always be stated.

Two different measures of sensitivity are recommended. The first, which is suitable for relatively involatile materials as well as gases, depends upon the observed change in ion current for a particular change of flow rate of sample through the ion source. The recommended unit is coulomb per microgram. A second method of stating sensitivity, that is most suitable for gases, depends upon the change of ion current related to the change of partial pressure of the sample in the ion source. The recommended unit is ampere pascal^{-1}.

It is important that the relevant experimental conditions corresponding to sensitivity measurement should always be stated. These include in a typical case details of the bombarding electron current, slit dimensions, angular collimation, gain of the multiplier detector, scan speed and whether the measured signal corresponds to a single mass peak or to the ion beam integrated over all masses. Some indication of the time involved in the determination should be given, e.g. counting time or band width.

The detection limit of an instrument should be differentiated from the sensitivity. The detection limit reflects the smallest flow of sample or the lowest partial pressure that gives a signal that can be distinguished from the background noise. Once again, it is important to specify the experimental conditions used and also to give the value of signal-to-noise ratio corresponding to the detection limit. It is recommended that a signal-to-noise ratio of unity be used.