

12.3 Processes and techniques

12.3.1 Ionization nomenclature

Adiabatic ionization

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

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

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

Associative ionization

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

Auto-ionization

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

Charge exchange (charge transfer) ionization

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

Chemi-ionization

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

Chemical ionization

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

Dissociative ionization

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

Electron affinity

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

Electron energy

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

Fast atom bombardment ionization

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

Field desorption

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

Field ionization

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

Ion-pair formation

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

Ionic dissociation

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

Ionization cross section

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

Ionization efficiency

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

Ionization energy ($I(M)$)

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

Laser ionization

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

Multi-photon ionization

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

Negative ion chemical ionization

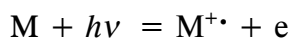
See *chemical ionization*.

Penning ionization

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

Photo-ionization

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



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

Plasma desorption (fission fragment) ionization

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

Pre-ionization state

See *auto-ionization*.

Proton affinity

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

Spark ionization

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

Surface ionization

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

Thermal ionization

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

Vertical ionization

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