

20 November 2003; C:\TXT\Iupac-Org-Chem Div\reportsandprojects-iupac\Glossary-Photochemistry\Glossary-Photoch3rdVer18-11-03.doc

INTERNATIONAL UNION OF PURE
AND APPLIED CHEMISTRY

ORGANIC AND BIOMOLECULAR CHEMISTRY DIVISION
SUB-COMMITTEE ON PHOTOCHEMISTRY

GLOSSARY OF TERMS USED IN PHOTOCHEMISTRY

3rd Edition, December 2003

Prepared for publication by:

S.E. Braslavsky (1st and 3rd edition)

K.N. Houk (1st edition) and J.W. Verhoeven (2nd edition)

Contributors to the 3rd edition of this Glossary have been:

Ulises Acuña, Diego Armesto, Cornelia Bohne, Jim Bolton, Roland Bonneau, Andre Braun, Marta Litter, Razi Naqvi, Massimo Olivucci, Jan Verhoeven, John Warman, Richard Weiss

INTRODUCTION TO THE 2003 REVISION

The first edition of the "Glossary of Terms Used in Photochemistry" was prepared for publication in the Commission of Photochemistry of the IUPAC Division of Organic Chemistry by S.E. Braslavsky and K.N. Houk, it was published in 1988 [*Pure & Appl. Chem.* (1988) 60, 1055-1106], and has been incorporated in the "Handbook of Organic Photochemistry" Vol. II, J.C. Scaiano Ed., CRC Press Inc., Boca Raton, 1989, and in "Photochromism: Molecules and Systems", H. Dürr and H. Bouas-Laurent Eds., Elsevier Science Publishers, 1990.

The second edition prepared by J. Verhoeven, corrected some minor mistakes of the first one and was expanded especially to incorporate terms related to (photoinduced) electron transfer processes. It was published in 1996 [*Pure & Appl. Chem.* (1996) 12, 2223-2286].

The major Journals in Photochemistry have since adopted the "Glossary" as a guideline. The photochemical Societies have posted the electronic version of the "Glossary" in their homepages.

This third edition incorporates revisions and enhances the Glossary introducing terms related to the use of polarized light and the emerging field of computation of excited species. For the magnitudes implying energy or photons incident on a surface from all directions, we recommend the use of a different set of symbols (*i.e.*, H' for fluence, E' for fluence rate, H'_p for photon fluence, and E'_p for photon fluence rate) than those in previous glossaries (a superscript 0 was used before), in order to avoid confusion with the terms used to designate an amount of energy (or photons) prior to absorption.

We expect that this Glossary will continue to serve its purpose, which is to provide definitions of terms and symbols commonly used in the field of photochemistry in order to achieve consensus on the adoption of some definitions and on the abandonment of inadequate terms.

The Sub-Committee on Photochemistry of the IUPAC Division of Organic and Biomolecular Chemistry re-emphasizes that it is not the purpose of this compilation to impose terms or rules which would hinder the freedom of choice in the use of terminology. Photochemistry being an interdisciplinary area of science which involves, in addition to chemistry, such different fields as laser technology, nanotechnology, spectroscopy, polymer science, solid state physics, biology, and medicine, just to name some of them, it has been necessary to reach compromises and, in some cases, to include alternative definitions used in different areas. The general criterion adopted for the inclusion of a term has been:

- (i) its wide use in the present or past literature, and
- (ii) ambiguity or uncertainty in its usage.

With very few exceptions concerning widely accepted terms, name reactions have been omitted.

The arrangement of entries is alphabetical and the criterion adopted some years ago by the Physical Organic Chemistry Commission of IUPAC has been followed for the type of lettering used: *italicized* words in a definition or at the bottom of it indicate a relevant cross reference, a term in quotation marks indicates that it is not defined in this Glossary (see “Glossary of Terms Used in Physical Organic Chemistry”, *Pure & Appl.Chem.* (1983) 55,1281-1371). In addition, an underlined word marks its importance in the definition under consideration.

It is expected that many of the definitions provided will be subject to change. We welcome all suggestions for improvement and updating of the Glossary and commit ourselves to revise it in the future.

The terms pertaining to Physical Organic Chemistry are defined in the “Glossary of Terms Used in Physical Organic Chemistry” (revision 1994, <http://www.chem.qmul.ac.uk/iupac/gtpoc/>) Cross checking for consistency has been performed with this Glossary. The terms pertaining to Theoretical Organic Chemistry have been taken from the "Glossary of Terms used in Theoretical Organic Chemistry" published in *Pure & Appl. Chem.* (1999) 71, 1919-1981 and also available at: <http://www.iupac.org/reports/1999/7110minkin/>.

Internationally agreed upon terms were taken from:

“Manual of Symbols and Terminology for Physicochemical Quantities and Units”, *Pure & Appl. Chem.* (1979) 51, 1-41. (Latest version: “Quantities, Units and Symbols in Physical Chemistry”, I. Mills, T. Cvitas, K. Homann, N. Kallay and K. Kuchitsu, Blackwell Science Ltd, 1993).

“Quantities and units of light and related electromagnetic radiations” International Standard ISO 31/6 (1980/1992), International Organization for Standardization (ISO).

See also the Recommendations 1983, “Molecular Luminescence Spectroscopy”, *Pure & Appl. Chem.* (1984) 56, 231-245.

Other sources:

“Recommended Standards for Reporting Photochemical Data”, A. Lamola, Wrighton *Pure and Applied Chemistry* (1984) 56, 939-

“The Vocabulary of Photochemistry”, J. N. Pitts, Jr., F. Wilkinson, G. S. Hammond, *Advances in Photochemistry* (1963) 1, 1-22.

“Optical Radiation Physics and Illuminating Engineering; Quantities, Symbols and Units of Radiation Physics”, DIN (Deutsches Institut für Normung) 5031 (1982), F.R.G.

“Radiometric and Photometric Properties of Materials; Definitions Characteristics”, DIN 5036,

Part 1 (1979), F.R.G.

“Radiometric and Photometric Characteristics of Materials and their Measurement”, International Commission on Illumination (CIE) (1977) 38.

“Photochemical Technology” A. M. Braun, M.-T. Maurette, E. Oliveros, Chichester, Wiley, 1991.

Silvia E. Braslavsky
Mülheim an der Ruhr, November 2003

ALPHABETIC LIST OF TERMS AND DEFINITIONS

ABSORBANCE (A)

The logarithm to the base 10 of the ratio of the *spectral radiant power* of incident, essentially monochromatic, radiation ($I = \int_{\lambda} I_{\lambda} d\lambda = P_{\lambda}^0$) to the radiant power of transmitted radiation (P_{λ}):

$$A = \log(P_{\lambda}^0/P_{\lambda}) = -\log T$$

In practice, absorbance is the logarithm to the base 10 of the ratio of the *spectral radiant power* of light transmitted through the reference sample to that of the light transmitted through the solution, both observed in identical cells. T is the (internal) *transmittance*. This definition supposes that all the incident light is either transmitted or absorbed, reflection or scattering being negligible.

Traditionally (*spectral*) *radiant intensity*, I , was used instead of *spectral radiant power*, P_{λ} , which is now the accepted form. (The terms: absorbancy, extinction, and optical density should no longer be used.)

See *absorption coefficient, absorptance, attenuation, Beer-Lambert law, depth of penetration, internal transmittance, Lambert law, molar absorption coefficient.*

ABSORPTANCE

The fraction of light absorbed, equal to one minus the *transmittance* (T).

See *absorbance*.

ABSORPTION (of electromagnetic radiation)

The transfer of energy from an electromagnetic field to a molecular entity.

ABSORPTION ANISOTROPY

Operationally, the uniaxial absorption anisotropy or *linear dichroism* is defined as follows:

$$r = \frac{A_Z - A_Y}{A_Z + 2A_Y} = \frac{\Delta A}{A_{\max}} = \frac{\Delta A}{3A_{\text{iso}}}$$

where A_P ($P = Y$ or Z) stands for the absorbance of the sample for a light beam (travelling along the X -axis) polarized along the P -axis. The measured value of r would have an immediate physical significance only if the absorbance arises from a single transition dipole (μ), and the uniaxial sample under examination is aligned so that its symmetry axis (d) coincides with the Z -axis. If these conditions are met, r can be identified with S , the *order parameter* of μ ; $\Delta A \equiv A_Z - A_Y$ is known as *linear dichroism* (LD), and $A_{\max} \equiv A_Z + 2A_Y$ and A_{iso} are the absorbances corresponding to $S = 1$ and $S = 0$, respectively.

See *polarized absorption spectroscopy, uniaxial systems*

ABSORPTION COEFFICIENT (*decadic- a or Napierian- α*)

Absorbance divided by the optical pathlength, l :

$$a_\lambda = A_\lambda/l = (1/l)\log (P_\lambda^0/P_\lambda)$$

Physicists usually use natural logarithms. In this case:

$$\alpha_\lambda = a_\lambda \ln 10 = (1/l) \ln(P_\lambda^0/P_\lambda)$$

where α is the Napierian absorption coefficient. Since *absorbance* is a dimensionless quantity, the coherent SI unit for a and α is m^{-1} . Also cm^{-1} is often used.

See also *absorptivity, molar absorption coefficient*.

ABSORPTION CROSS SECTION (σ)

Operationally, it can be calculated as the *absorption coefficient* divided by the number of molecular entities contained in a unit volume of the absorbing medium along the light path:

$$\sigma_\lambda = \alpha_\lambda/N = [1/(Nl)] \ln(P_\lambda^0/P_\lambda)$$

where N is the number of molecular entities per unit volume, l is the optical pathlength, and α is the Napierian absorption coefficient.

The relation between the absorption cross section and the *molar (decadic) absorption*

coefficient, ε_λ , (in the common units $\text{M}^{-1}\text{cm}^{-1}$) is

$$\sigma_\lambda = (\varepsilon_\lambda/N_A) \ln 10 = 3.825 \times 10^{-21} \varepsilon_\lambda$$

where σ_λ is in the common unit cm^2 and N_A is the Avogadro constant. For ε_λ in the coherent SI units $\text{m}^2 \text{mol}^{-1}$,

$$\sigma_\lambda = 3.825 \times 10^{-24} \varepsilon_\lambda \text{ and } \sigma_\lambda \text{ is in } \text{m}^2$$

See *attenuance, Beer-Lambert law*.

ABSORPTIVITY

Absorptance divided by the optical pathlength. For very low *attenuance* it approximates the *absorption coefficient* (within the approximation $(1 - e^{-A}) \sim A$). The use of this term is not recommended.

ACTINOMETER

A chemical system which determines the number of *photons* integrally or per unit time emitted into the defined space of a chemical reactor. This name is commonly applied to systems used in the ultraviolet and visible *wavelength* ranges. For example, solutions of iron(III) oxalate can be used as a chemical actinometer. Bolometers, thermopiles, and photodiodes are physical devices giving a reading of the radiation hitting them which can be correlated to the number of photons detected as well as to the number of photons entering the chemical reactor

ACTION SPECTRUM

A plot of a relative biological or chemical photoresponse ($= \Delta y$) per number of incident photons, against *wavelength* or energy of radiation. This form of presentation is frequently used in the studies of biological or solid state systems, where the nature of the absorbing species is unknown. It is advisable to control that the *fluence* dependence of the photoresponse is the same (e.g. linear) for all the wavelengths studied. The action spectrum is sometimes called *spectral responsivity* or sensitivity spectrum. The precise action spectrum is a plot of the *spectral (photon or quantum) effectiveness*. By contrast, a plot of the biological or chemical change or response per absorbed photon (quantum efficiency) versus wavelength is the *efficiency spectrum*.

See also *excitation spectrum, efficiency spectrum*.

ADIABATIC ELECTRON TRANSFER

Electron transfer process in which the reacting system remains on a single electronic surface in passing from reactants to products. For adiabatic electron transfer the electronic transmission factor is close to unity (see *Marcus equation*.)

See also *diabatic electron transfer*.

ADIABATIC PHOTOREACTION

Within the "Born-Oppenheimer approximation", a reaction of an *electronically excited state* species that occurs on a single *potential-energy surface*.

Compare *diabatic photoreaction*.

ADMR

See *ODMR*.

ALPHA-CLEAVAGE (α -Cleavage)

Homolytic cleavage of a bond connecting an atom or group to a specified group or reaction center. Often applied to a bond connected to a carbonyl group, in which case it is called a *Norrish type I photoreaction*. This reaction should be distinguished from an *alpha-(α -)expulsion*.

ALPHA-EXPULSION (α -Expulsion)

A general reaction by which a group attached to the alpha carbon of an excited chromophore is expelled either as an odd electron species or as an anionic species. This reaction should be distinguished from an *alpha-(α -)cleavage*.

AM (0) SUNLIGHT

The solar *irradiance* in space just above the earth atmosphere (air mass, AM, zero). Also called extraterrestrial global irradiance.

AM (1) SUNLIGHT

The solar *irradiance* traversing the atmosphere when the sun is in a position perpendicular to the earth surface. Also called terrestrial global irradiance.

See also *AM (0) sunlight*.

ANISOTROPY

The term may refer to an individual molecule or to matter in bulk; it signifies the dependence of a response (to a stimulus) on the direction along which the response is measured. Intrinsic or molecular anisotropy is best illustrated by considering polarizability. A spherically symmetric (or isotropic) molecule acquires, upon interaction with an electric field \mathbf{E} , an induced dipole moment, $\mathbf{p} = \alpha \mathbf{E}$; the scalar α is known as the polarizability. The corresponding relations for an anisotropic molecule are of the form $p_x = \alpha_{xx}E_x + \alpha_{yy}E_y + \alpha_{zz}E_z$; $\{E_x, E_y, E_z\}$ and $\{p_x, p_y, p_z\}$ are the components of \mathbf{E} and \mathbf{p} in an arbitrary coordinate frame, and $\alpha_{ij} = \alpha_{ji}$; this symmetry implies that there exists a coordinate frame $O-x_1x_2x_3$ such that $p_k = \alpha_k E_k$, where E_k and p_k are the components of \mathbf{E} and \mathbf{p} along the axis Ox_k . A molecule or a molecular assembly is said to be isotropic if $\alpha_1 = \alpha_2 = \alpha_3$; uniaxial, if $\alpha_1 = \alpha_2 \neq \alpha_3$; linear, if only one polarizability is nonzero. Similar considerations apply to *transition dipoles* and *photoselection*, and the measured emission or absorption anisotropy has a direct physical significance only if it pertains to a uniaxial system.

See *absorption anisotropy, dichroism, emission anisotropy*

ANNIHILATION

Two atoms or molecular entities both in an *excited state* interact often (usually upon collision) to produce one atom or molecular entity in an electronic excited state and another in its electronic ground state. This phenomenon is sometimes referred to as energy pooling.

See *singlet-singlet annihilation, spin-conservation rule, triplet-triplet annihilation*.

ANTIMONY-XENON LAMP (Arc)

An intense source of ultraviolet, visible, and near infra-red radiation produced by an electrical discharge in a mixture of antimony vapour and xenon under high pressure. Its output in the ultraviolet region is higher than that of the *mercury-xenon arc*.

See *lamp*.

ANTI-STOKES SHIFT

See *Stokes shift*.

APPARENT LIFETIME

See *lifetime*. Same as decay-time.

ARGON ION LASER

A *CW* or pulsed *laser* emitting lines from 334 to 529 nm from singly ionized argon. Principal emissions are at 488.0 and 514.5 nm.

See *laser, gas lasers*.

ATTENUANCE (D)

The logarithm to the base 10 of the ratio of the radiant power of the incident (P_{λ}^0) and transmitted (P_{λ}) radiation:

$$D = \log(P_{\lambda}^0/P_{\lambda}) = -\log T$$

where T is the *transmittance*. Attenuance reduces to *absorbance* if the incident beam is only either transmitted or absorbed, but not reflected or scattered.

See *Beer-Lambert law, depth of penetration*.

ATTENUANCE FILTER

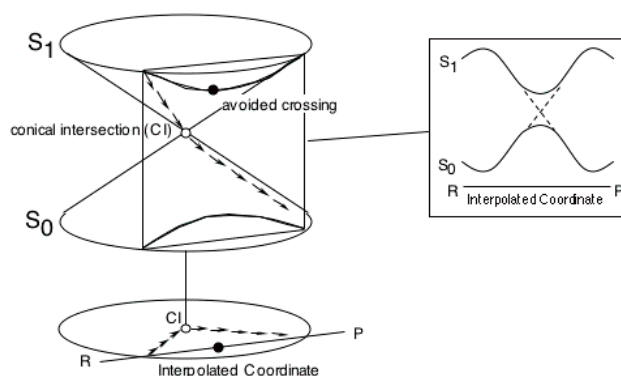
An optical device (*filter*) which reduces the *radiant power* of a light beam by a constant factor over all *wavelengths* within its operating range. Sometimes called attenuator or neutral density filter.

AUXOCHROME

An atom or group which, when added to or introduced into a *chromophore*, causes a *bathochromic* shift and/or a *hyperchromic* effect in a given band of the chromophore, usually in that of lowest *frequency*. This term is obsolete.

AVOIDED CROSSING (of potential-energy surfaces)

Frequently, two Born-Oppenheimer electronic states (R,P) change their energy order as molecular geometry is changed continuously along a path from reactants to products. In the process their energies may become equal at some points (the surfaces are said to cross, dotted lines in the figure), or only come relatively close (the crossing of the surfaces is said to be avoided). If the electronic states are of the same symmetry, the *surface crossing* is always avoided in diatomics and usually avoided in polyatomics. The scheme illustrates the relationship between *conical intersection* and avoided crossing in a polyatomic molecule. Notice that avoided crossing occurs in the vicinity of the conical intersection.

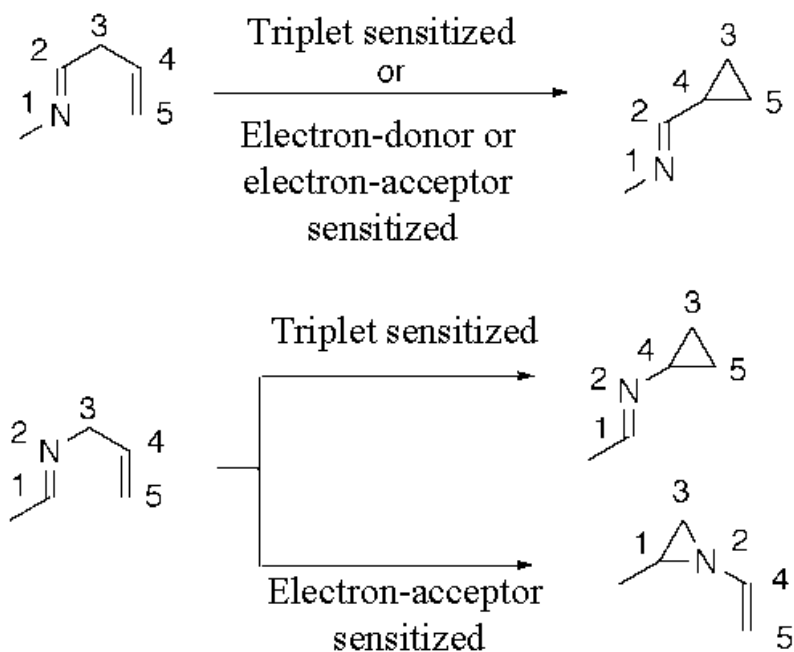


Same as *intended crossing*

See *conical intersection, noncrossing rule*.

AZA-DI-1,4-METHANE REARRANGEMENT

A photochemical reaction of a 1-aza-1,4-diene or a 2-aza-1,4-diene in the *triplet excited state* to form the corresponding cyclopropylimine. The rearrangement formally amounts to a 1,2-shift of the imino group and “bond formation” between the C-3 and C-5 carbon atoms of the azadiene skeleton. 1-Aza-1,4-dienes also undergo the rearrangement to cyclopropylimines using electron-acceptor and electron-donor *sensitizers* via radical-cation and radical-anion intermediates, respectively. 2-Aza-1,4-dienes rearrange to N-vinylaziridines on irradiation using electron-acceptor sensitizers. In this instance the reaction amounts to a 1,2-shift of the alkene unit and “bond formation” between the C-1 and C-3 carbon atoms of the azadiene skeleton.



See also *di- π -methane* and *oxa-di- π -methane* rearrangements

BACK ELECTRON TRANSFER

A term often used to indicate thermal reversal of *excited state electron transfer* restoring the donor and acceptor in their original oxidation state. In using this term one should also specify the resulting electronic state of the donor and acceptor. It is recommended to use this term only for the process restoring the original electronic state of donor and acceptor.

BANDGAP ENERGY (E_g)

The energy difference between the bottom of the conduction band and the top of the valence band in a semiconductor or an insulator.

See *conduction band*, *Fermi level*.

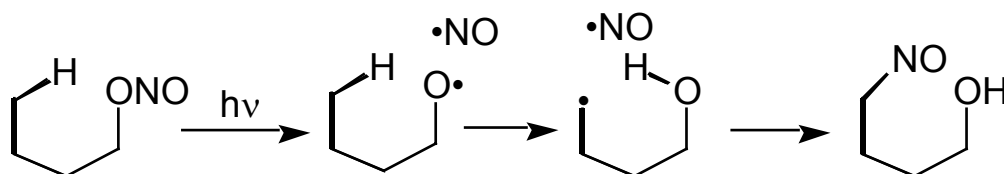
BANDPASS FILTER

An optical device which permits the transmission of radiation within a specified wavelength range and does not permit transmission of radiation at higher or lower wavelengths. It can be an interference *filter*.

See also *cut-off filter*.

BARTON REACTION

Photolysis of a nitrite to form a δ -nitroso alcohol. The mechanism is believed to involve a homolytic RO-NO cleavage, followed by δ -hydrogen abstraction and radical coupling.

BATHOCHROMIC SHIFT (Effect)

Shift of a spectral band to lower frequencies (longer wavelengths) owing to the influence of substitution or a change in environment (e.g., solvent). It is informally referred to as a *red shift* and is opposite to *hypsochromic shift*.

BEER-LAMBERT LAW (or Beer-Lambert-Bouguer Law)

The *absorbance* of a beam of collimated monochromatic radiation in a homogeneous isotropic medium is proportional to the absorption pathlength, l , and to the concentration, c , or - in the gas phase - to the pressure of the absorbing species. This law holds only under the limitations of the *Lambert law* and for absorbing species exhibiting no concentration or pressure dependent aggregation. The law can be expressed as

$$A = \log(P_{\lambda}^0/P_{\lambda}) = \varepsilon c l$$

or

$$P_{\lambda} = P_{\lambda}^0 10^{-\varepsilon c l}$$

where the proportionality constant, ε , is called the *molar (decadic) absorption coefficient*. For l in cm and c in mol dm⁻³ or M, ε will result in dm³ mol⁻¹ cm⁻¹ or M⁻¹ cm⁻¹, which is a commonly used unit. The SI unit of ε is m² mol⁻¹. Note that spectral radiant power must be used because the Beer-Lambert law holds only if the spectral bandwidth of the light is narrow compared to spectral linewidths in the spectrum.

See *absorbance, attenuation, extinction coefficient, Lambert law.*

BIOLUMINESCENCE

Luminescence produced by living systems.

See *luminescence.*

BIPHOTONIC EXCITATION

Also called *two-photon excitation*. The simultaneous (*coherent*) *absorption* of two *photons* (either same or different wavelength) the energy of excitation being the sum of the energies of the two photons.

BIPHOTONIC PROCESS

A process resulting from *biphotonic excitation*.

See *multiphoton process.*

BIRADICAL (Synonymous with *diradical*)

An even-electron molecular entity with two (possibly delocalized) radical centres which act nearly independently of each other.

Species in which the two radical centres interact significantly are often referred to as biradicaloids. If the two radical centres are located on the same atom, they always interact strongly, and such species are called carbenes, nitrenes, etc.

The lowest-energy triplet state of a biradical lies below or at most only a little above its lowest singlet state (usually judged relative to kT , the product of the Boltzmann constant k and the absolute temperature T). The states of those biradicals whose radical centres interact particularly weakly are most easily understood in terms of a pair of local doublets.

Theoretical descriptions of low-energy states of a biradical display the presence of two unsaturated valences (biradicals contain one fewer bond than permitted by the rules of valence): the dominant valence bond structures have two dots, the low energy molecular orbital *configurations* have only two electrons in two approximately nonbonding molecular orbitals, two of the natural orbitals have occupancies close to one, etc.

BIRADICALOID

Biradical-like.

BLEACHING

In *photochemistry* this term refers to the loss of *absorption* or emission intensity.

BLUE SHIFT

Informal expression for *hypsochromic shift*.

BORN-OPPENHEIMER APPROXIMATION

In the Born-Oppenheimer approximation, the wave function, $\Psi(x, X)$, of a molecular state is written as a product of two factors: $\Psi(q, Q) = \Phi(q, Q)\Theta(Q)$, where q and Q represent the coordinates of all the electrons and all the nuclei, respectively. The electronic wave function $\Phi(q, Q)$ is defined to be the eigenfunction the molecule would have if all its nuclei were clamped in the configuration represented by Q . The corresponding eigenvalue, $E(Q)$, is called the electronic energy. The nuclear motion is described by a Hamiltonian in which the $E(Q)$ plays the role of potential energy. A plot of the electronic energy against the nuclear coordinates is called a *potential-energy surface*, or a *potential energy curve* if one is considering a diatomic molecule. Within the framework of this approximation, one associates a set of vibrational states with each electronic state, and writes the wavefunction of a vibronic state ma (where the first label specifies the electronic state and the second the vibrational state) as $\Psi_{ma}(q, Q) = \Phi_m(q, Q)\Theta_a^m(Q)$

BRANCHING PLANE

At a *conical intersection* point, the plane spanned by the gradient difference (\mathbf{x}_1) vector and the gradient of the interstate coupling (\mathbf{x}_2) vector:

$$\mathbf{x}_1 = \frac{\partial(E_1 - E_2)}{\partial \mathbf{Q}}$$

$$\mathbf{x}_2 = \left\langle \mathbf{C}_1 \left(\frac{\partial H}{\partial \mathbf{Q}} \right) \mathbf{C}_2 \right\rangle$$

where \mathbf{C}_1 and \mathbf{C}_2 are the configuration interaction eigenvectors (*i.e.* the excited and ground state *adiabatic* wavefunctions) in a conical intersection problem, H is the conical intersection Hamiltonian, \mathbf{Q} represents the nuclear configuration vector of the system and E_1 and E_2 are the energies of the lower and upper states, respectively. The branching plane is also referred to as **g-h**

plane. Inspection of \mathbf{x}_1 and \mathbf{x}_2 provides information on the geometrical deformation imposed to an *excited state* molecular entity immediately after decay at a conical intersection. Consequently, these vectors provide information on the *ground state* species that will be formed after the decay.

CADMIUM-HELIUM LASER

See *Helium-Cadmium laser*.

CAVITY DUMPING

Periodic removal of *coherent radiation* from a *laser* cavity.

CHARGE HOPPING

Electron or *hole transport* between equivalent sites.

CHARGE RECOMBINATION

Reverse of *charge separation*. In using this term it is important to specify the resulting electronic state of the donor and acceptor.

CHARGE SEPARATION

A process in which, under the influence of a suitable *driving force* (e.g. provided by photoexcitation), electronic charge moves in a direction that increases the difference in local charges between donor and acceptor sites. *Electron transfer* between neutral species is one of the most important examples.

CHARGE SHIFT

A process in which under the influence of a suitable *driving force* (e.g. provided by photoexcitation) electronic charge moves without changing the difference in local charges between donor and acceptor sites. *Electron transfer* reversing the charges in a system composed of a neutral donor and a cationic acceptor or of a neutral acceptor and an anionic donor provide prominent examples.

CHARGE-TRANSFER ABSORPTION

An electronic absorption corresponding to a *charge transfer transition*. In some cases the charge transfer absorption band(s) may be strongly obscured by the local absorptions of the donor and acceptor systems.

CHARGE-TRANSFER COMPLEX

Ground state complex which exhibits *charge-transfer absorption*. Note that the charge-transfer absorption band(s) may be largely obscured by the individual absorptions of the complex partners.

CHARGE-TRANSFER (CT) STATE

A state related to the *ground state* by a *charge transfer transition*.

CHARGE-TRANSFER (CT) TRANSITION

An electronic transition in which a large fraction of an electronic charge is transferred from one region of a molecular entity, called the electron donor, to another, called the electron acceptor (intramolecular CT) or from one molecular entity to another (intermolecular CT). Typical for donor-acceptor complexes or multichromophoric molecular entities.

See *charge-transfer absorption*.

CHARGE-TRANSFER (CT) COMPLEX

A ground-state complex which exhibits an observable charge transfer absorption band.

See *charge-transfer transition*.

CHARGE-TRANSFER TRANSITION TO SOLVENT (CTTS)

Electronic transition which is adequately described by single *electron transfer* between a solute and the solvent, as opposed to excitation followed by *electron transfer* to solvent.

See also *charge-transfer (CT) transition*

CHEMICAL LASER

A *CW* or pulsed *laser* in which the excitation and population inversion of the emitting species results from a chemical reaction. Typical examples are HF and DF lasers emitting many lines in the IR region.

CHEMIEXCITATION

Generation, by a chemical reaction, of *electronically excited* molecular entities from reactants in their ground electronic states.

CHEMILUMINESCENCE

Luminescence arising from chemiexcitation.

CHROMOPHORE

That part of a molecular entity consisting of an atom or group of atoms in which the electronic transition responsible for a given spectral band is approximately localized.

CIDEP (Chemically Induced Dynamic Electron Polarization)

Non-Boltzmann electron spin state population produced in thermal or *photochemical reactions*, either from a combination of radical pairs (called radical-pair mechanism), or directly from the triplet state (called triplet mechanism), and detected by ESR spectroscopy.

CIDNP (Chemically Induced Dynamic Nuclear Polarization)

Non-Boltzmann nuclear spin state distribution produced in thermal or *photochemical reactions*, usually from a combination of radical pairs, and detected by NMR spectroscopy.

CIEEL (Chemically Initiated Electron Exchange Luminescence)

A type of *luminescence* resulting from a thermal electron-transfer reaction.

Also called catalyzed *chemiluminescence*.

COLLISION COMPLEX

An ensemble formed by two reaction partners for which the distance is the sum of their Van der Waals radii. As such it constitutes a subclass of the species indicated as *encounter complex*.

See also *encounter complex*.

CO₂ LASER

A continuous or pulsed source of *coherent radiation* normally tunable through the CO₂ vibration-rotation band centered near 10.6 μm.

See *gas lasers, laser*.

COHERENT RADIATION

A source is said to emit coherent radiation when all the elementary waves emitted have a phase difference constant in space and time.

COMPLETE ACTIVE SPACE SELF-CONSISTENT FIELD (CASSCF)

Computational scheme employed in *multiconfigurational SCF theory* especially suitable for studies of *excited states* reactivity. The wavefunction is defined by selecting the set of active orbitals involved in the excitation or chemical reaction under investigation and is constructed as a linear expansion in the set of configuration functions that can be generated by occupying the active orbitals in all ways consistent with an overall spin and space symmetry (full *configuration interaction, CI*).

COMPLETE ACTIVE SPACE SELF-CONSISTENT FIELD SECOND-ORDER PERTURBATION THEORY (CASPT2)

A theoretical scheme suitable for computations of accurate excitation energies and reaction barriers that in the first step takes electron correlation into account only to a certain extent by using a CASSCF formalism (the so called nondynamic correlation), whereas the remaining electron correlation (the so called dynamic correlation) is included through the use of second-order perturbation theory.

See *multiconfiguration SCF method*

CONCENTRATION DEPOLARIZATION

The loss of photoinduced anisotropy due to transfer of electronic excitation from a photoselected molecule to another molecule with a different orientation; the larger the acceptor concentration the greater is the loss.

See *emission anisotropy, energy transfer, photoselection*

CONDUCTION BAND

A vacant or only partially occupied set of many closely spaced electronic levels resulting from an array of a large number of atoms forming a system in which the electrons can move freely or nearly so. This term is usually used to describe the properties of metals and semiconductors.

See *bandgap energy, Fermi level, valence band*.

CONFIGURATION (Electronic Configuration)

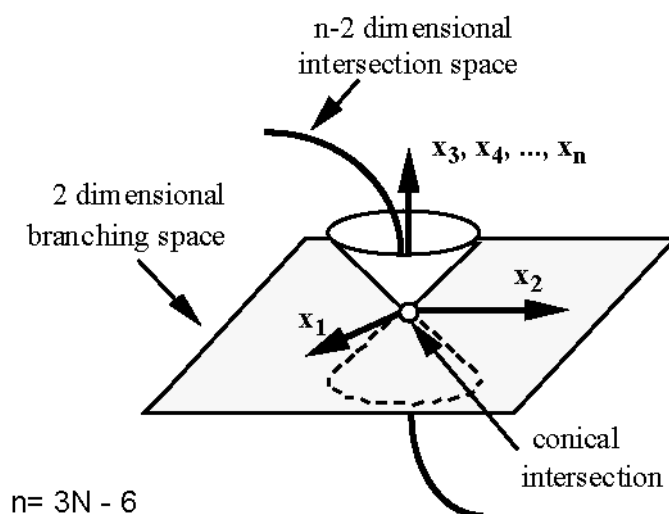
A distribution of the electrons of an atom or a molecular entity over a set of one-electron wavefunctions called *orbitals*, according to the Pauli principle. From one configuration several states with different *multiplicities* may result. For example, the ground electronic configuration of the oxygen molecule (O_2) is $1\sigma_g^2, 1\sigma_u^2, 2\sigma_g^2, 2\sigma_u^2, 1\pi_u^4, 3\sigma_g^2, 1\pi_g^2$, resulting in the $^3\Sigma_g^-, ^1\Delta_g$, and $^1\Sigma_g^+$ states of different energy.

CONFIGURATION INTERACTION (CI)

The mixing of wavefunctions representing different electronic *configurations* to obtain an improved wavefunction for a many-electron state. In the full CI method, an n-electron wavefunction is expanded as a linear combination of Slater determinants describing the *ground state* configuration and all the possible different excited electronic configurations. In practical calculations, CI methods consider only a limited set of configuration, *i.e.*, the CIS method adds only the single excitations, CID adds double excitations, CISD adds single and double excitations, and so on.

CONICAL INTERSECTION

Point of crossing between two electronic states of the same spin *multiplicity* (most commonly *singlet* or *triplet*). In a polyatomic molecule two *potential-energy surfaces* are allowed to cross along a $(3N - 8)$ -dimensional subspace of the $(3N - 6)$ -dimensional nuclear coordinate space (the so-called *intersection space*) even if they have the same spatial/spin symmetry (N is the number of nuclei). Each point of the intersection space corresponds to a conical intersection. If the energy is plotted against two special internal geometrical coordinates, \mathbf{x}_1 and \mathbf{x}_2 , which define the so-called *branching plane*, the potential-energy surface would have the form of a double cone in the region of the degeneracy. In the remaining $(3N - 8)$ directions, the energies of *ground* and *excited state* remain degenerate; movement in the branching plane lifts the degeneracy. From a mechanistic point of view, conical intersections often provide the channel mediating *radiationless deactivation* and *photochemical reaction*.



CONTACT ION PAIR

Pair of ions in direct contact and not separated by an intervening solvent or other neutral molecule. One mode of formation for a (geminate) contact ion pair is *electron transfer* between precursor species in an *encounter complex* (cf. *collision complex*). If one of the precursors in the *encounter complex* is electronically excited the contact ion pair formed by *electron transfer* is equivalent to a polar *exciplex*.

CONVERSION SPECTRUM

A plot of a quantity related to the *absorption* (*absorbance*, *cross section*, etc.) multiplied by the *quantum yield* for the considered process against a suitable measure of photon energy, such as *frequency*, ν , *wavenumber*, σ , or *wavelength*, λ . E.g., the conversion cross section, $\sigma \Phi$, has the SI unit m^2 .

See also *action spectrum*, *efficiency spectrum*, *spectral effectiveness*.

COPPER VAPOUR LASER

A pulsed source of *coherent radiation* emitting at 578.2 and 510.5 nm from excited copper atoms.

See *gas lasers*, *laser*.

CORRELATION DIAGRAM

A diagram which shows the relative energies of *orbitals*, *configurations*, valence bond structures, or states of reactants and products of a reaction, as a function of the molecular geometry, or another suitable parameter. An example involves the interpolation between the energies obtained for the united atoms and the values for the separated atoms limits.

CORRELATION ENERGY

The difference between the Hartree-Fock energy calculated for a system and the exact nonrelativistic energy of that system. The correlation energy arises from the approximate representation of the electron-electron repulsions in the Hartree-Fock method.

CRITICAL QUENCHING RADIUS (r_0)

See *Förster excitation transfer*.

CRYSTAL FIELD SPLITTING

The removal of a degeneracy of the energy levels of molecular entities or ions due to the lower site symmetry created by a crystalline environment. This term is sometimes incorrectly used synonymously with the term *ligand field splitting*.

CT

Abbreviation for *charge-transfer*.

CURRENT YIELD

See *photocurrent yield*.

CUT-OFF FILTER

An optical device which only permits the transmission of radiation of *wavelengths* that are longer than or shorter than a specified wavelength. Usually, the term refers to devices which transmit radiation of wavelengths longer than the specified wavelength.

See *filter*.

CW (Continuous Wave)

Nonpulsed source of electromagnetic radiation.

DARK PHOTOCHEMISTRY (photochemistry without light)

Chemical reactions involving electronically excited molecular entities which are generated thermally rather than by *absorption* of electromagnetic radiation. The use of this term is discouraged.

DAVYDOV SPLITTING (*factor-group splitting*)

The splitting of bands in the electronic or vibrational spectra of crystals due to the presence of more than one (interacting) equivalent molecular entity in the unit cell.

DEACTIVATION

Any loss of energy by an excited molecular entity.

See *emission, energy transfer, internal conversion, radiationless deactivation and transition, radiative transition.*

DECAY-TIME

The time needed for the concentration of an entity to decrease to 1/e of its initial value when this entity does not disappear by a first order process.

See *lifetime*. The same as apparent lifetime.

DELAYED FLUORESCENCE

See *delayed luminescence*.

DELAYED LUMINESCENCE

Luminescence decaying more slowly than that expected from the rate of decay of the emitting state. The following mechanisms of luminescence provide examples:

- (1) *triplet-triplet annihilation* to form one molecular entity in its excited singlet state and another molecular entity in its electronic *ground state* (sometimes referred to as P type),
- (2) thermally activated *delayed fluorescence* involving reversible *intersystem crossing* (sometimes referred to as E type), and
- (3) combination of oppositely charged ions or of an electron and a cation. For *emission* to be referred to in this case as delayed luminescence at least one of the two reaction partners must be generated in a *photochemical process*.

DEDMR

See *ODMR*.

DEPTH OF PENETRATION (of light)

The inverse of the *absorption coefficient*. The SI unit is m. When the decadic absorption coefficient, a , is used, the depth of penetration ($1/a$) is the distance at which the *spectral radiant power*, P_λ decreases to one tenth of its incident value, P_λ^0 . When the Napierian absorption coefficient, α , is used, the depth of penetration ($1/\alpha = \beta$ in this case) is the distance at which the *spectral radiant power* decreases to 1/e of its incident value.

See *absorbance, attenuation*.

DEXTER EXCITATION TRANSFER (Electron Exchange Excitation Transfer)

Excitation transfer occurring as a result of an electron exchange mechanism. It requires an overlap of the wavefunctions of the energy donor and the energy acceptor. It is the dominant mechanism in *triplet-triplet energy transfer*.

The transfer rate constant, k_{ET} , is given by

$$k_{ET} \propto [h/(2\pi)] P^2 J \exp[-2r/L],$$

where r is the distance between donor (D) and acceptor (A), L and P are constants not easily related to experimentally determinable quantities, and J is the *spectral overlap* integral. For this mechanism the *spin conservation rules* are obeyed.

See also *radiative energy transfer*.

DFDMR

See *ODMR*.

DIABATIC ELECTRON TRANSFER

Electron transfer process in which the reacting system has to cross over between different electronic surfaces in passing from reactants to products. For diabatic electron transfer the electronic transmission factor is $\ll 1$ (see *Marcus equation*). The term non-adiabatic electron transfer has also been used and is in fact more widespread, but should be discouraged because it

contains a double negation.

See also *adiabatic electron transfer*.

DIABATIC PHOTOREACTION

Within the Born-Oppenheimer approximation, a reaction beginning on one *excited state potential-energy surface* and ending, as a result of *radiationless transition*, on another surface, usually that of the *ground state*. The term *non-adiabatic* photoreaction has also been used and is in fact more widespread, but should be discouraged because it contains a double negation.

Compare with *adiabatic photoreaction*.

DICHROISM

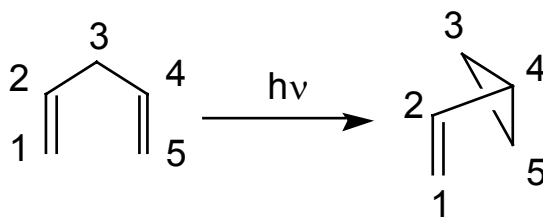
A sample is said to be dichroic (or exhibit dichroism) if its absorbance depends on the state of polarization of the measuring beam. One speaks of circular dichroism if the absorbance for left-circularly polarized light differs from that for right-circularly polarized light, and of linear dichroism if the absorbance is unequal for two orthogonally polarized beams.

DIODE LASERS

Semiconductor devices of small dimensions serving as sources of *CW* or pulsed *coherent radiation*. These *lasers* are also called semiconductor lasers.

DI- π -METHANE REARRANGEMENT

A *photochemical reaction* of a molecular entity comprising two π -systems, separated by a saturated carbon atom (a 1,4-diene or an allyl-substituted aromatic analog), to form an ene- (or aryl-) substituted cyclopropane. The rearrangement formally amounts to a 1,2 shift of one ene group (in the diene) or the aryl group (in the allyl-aromatic analog) and "bond formation" between the lateral carbons of the nonmigrating moiety.



See also *aza-di- π -methane rearrangement* and *oxa-di- π -methane rearrangement*.

DIPOLAR MECHANISM (of energy transfer)

Same as *Förster excitation transfer*.

See also *energy transfer*.

DIPOLE-DIPOLE EXCITATION TRANSFER

Same as *Förster excitation transfer*.

See also *energy transfer*.

DIRADICAL

This term, synonymous with *biradical*, is no longer recommended.

DOSE

The energy or amount of *photons* absorbed per unit area or unit volume by an irradiated object during a particular exposure time.

In medicine and in some other research areas (e.g. photopolymerization and water handling through irradiation) dose is used in the sense of *fluence*, i.e. the energy or amount of photons per unit area or unit volume received by an irradiated object during a particular exposure time. The SI units are J m^{-2} or J m^{-3} and mol m^{-2} (or einstein m^{-2}) mol m^{-3} (or einstein m^{-3}) respectively.

See also *UV-dose*.

DOUBLET STATE

A state having a total electron spin quantum number equal to 1/2.

See *multiplicity*.

DRIVING FORCE (for electron transfer)

Term widely used to indicate the negative of the standard Gibbs energy change (ΔG^0) for (photoinduced) *outer-sphere electron transfer*. This quantity can often be calculated rather accurately from independently determined properties of the donor and acceptor species involved using the *Rehm-Weller equation*.

DYE LASER

A *CW* or pulsed source of *coherent radiation* in which the active medium is usually a solution of a *fluorescent* organic molecule (the dye) pumped with a suitable pump laser or with a flash *lamp*. These lasers can be tuned over a large part of the fluorescence band of the dye.

DYNAMIC QUENCHING

See *quenching*.

EFFECTIVENESS

See *spectral effectiveness*.

EFFICIENCY (of a step; η)

The ratio between the useful energy delivered or bound and the energy supplied, *i.e.*, energy output/energy input. It is also used in the sense of a quantitative measure of the relative rate of a given step involving a species with respect to the sum of the rates of all of the parallel steps which depopulate that species.

See also *quantum yield*.

EFFICIENCY SPECTRUM

A plot of the *efficiency* of a step (η) against *wavelength* or photon energy.

See *action spectrum*, *conversion spectrum*.

Compare *spectral effectiveness*.

EINSTEIN

One mole of *photons*. Widely used, although it is not an IUPAC sanctioned unit.

Einstein sometimes is defined as the energy of one mole of photons. This latter use is discouraged.

ELECTROCHEMILUMINESCENCE

See *electrogenerated chemiluminescence*.

ELECTROCHROMIC EFFECT

See *Stark effect*.

ELECTROGENERATED LUMINESCENCE (ECL)

Luminescence produced by electrode reactions. Also called *electroluminescence* or *electrochemiluminescence*.

ELECTROLUMINESCENCE

See *electrogenerated chemiluminescence*.

ELECTRON CORRELATION

The adjustment of electron motion to the instantaneous (as opposed to time-averaged) positions of all the electrons in a molecular entity.

See also *correlation energy*.

ELECTRON EXCHANGE EXCITATION TRANSFER

Same as *Dexter excitation transfer*.

See also *energy transfer*.

ELECTRONIC CONFIGURATION

See *configuration*.

ELECTRONIC ENERGY MIGRATION (or Hopping)

The movement of electronic excitation energy from one molecular entity to another of the same species, or from one part of a molecular entity to another of the same kind (*e.g.* excitation migration between the chromophores of an aromatic polymer). The migration can happen via *radiative* or *radiationless* processes.

ELECTRONIC TRANSITION MOMENT

If the wave functions appearing in the transition dipole moment are written according to the *Born-Oppenheimer approximation*, the *transition (dipole) moment* for a *vibronic transition* (from the *a*-th vibrational state of the *m*-th electronic state to the *b*-th vibrational state of the *n*-th electronic state, or vice versa) can be written as

$$\vec{M}_{nm,ba} = \int \left[\Theta_b^n(Q) \right]^* \bar{\mu}_{nm}(Q) \Theta_a^m(Q) dQ$$

where $\bar{\mu}_{nm}(Q)$, called the electronic transition moment is the integral defined below:

$$\bar{\mu}_{nm}(Q) = \int \Phi_n^*(q, Q) \bar{\mu} \Phi_m(q, Q) dq .$$

If an additional approximation, due originally to Condon, is made and the Q -dependence of the electronic transition moment ignored in a zero-order approach, the vibronic transition moment

$\vec{M}_{nm,ba}$ becomes a product of a purely *electronic transition moment* (usually evaluated at Q_0 , the

equilibrium configuration of the nuclei) and the vibrational overlap integral $I_{nm} \equiv \int \left[\Theta_n^b \right]^* \Theta_m^a dQ$,

and one is led to the *Franck-Condon principle*. The squared modulus of the overlap integral,

$F_{nm} \equiv |I_{nm}|^2$, is known as the *Franck-Condon factor*.

ELECTRONICALLY EXCITED STATE

A state of an atom or molecular entity which has larger electronic energy than the *ground state* of the same entity.

ELECTRON TRANSFER

The transfer of an electron from one molecular entity to another or between two localized sites in the same molecular entity.

See also *inner-sphere electron transfer*, *outer-sphere electron transfer*, *Marcus equation*.

ELECTRON TRANSFER PHOTOSENSITIZATION

Photochemical process in which a reaction of a nonabsorbing substrate is induced by electron transfer (not energy transfer) with an excited light-absorbing *sensitizer*. The overall process must be such that the sensitizer is recycled. Depending on the action of the excited sensitizer as electron donor or acceptor the sensitization is called reductive or oxidative.

See also *photosensitization*.

ELECTROPHOTOGRAPHY

Processes of *photoimaging* which are based on photo-induced changes of electric fields (*photo-conductive* or *photo-electrostatic* effects).

EL-SAYED RULES

The rate of *intersystem crossing*, e.g. from the lowest *singlet state* to the *triplet manifold*, is relatively large if the *radiationless transition* involves a change of orbital type. E.g., ${}^1\pi,\pi^* \rightarrow n,\pi^*$ is faster than ${}^1\pi,\pi^* \rightarrow \pi,\pi^*$ and ${}^1n,\pi^* \rightarrow \pi,\pi^*$ is faster than ${}^1n,\pi^* \rightarrow n,\pi^*$.

See *multiplicity*.

EMISSION

Radiative *deactivation* of an *excited state*; transfer of energy from a molecular entity to an electromagnetic field.

See also *fluorescence*, *luminescence*, *phosphorescence*.

EMISSION ANISOTROPY (Photo-induced anisotropy)

The uniaxial emission anisotropy (or photoinduced anisotropy) is the anisotropy resulting from photoselection. It is defined as

$$r = \frac{S_Z - S_Y}{S_Z + 2S_Y},$$

where $S = I$ or ΔA , depending on whether the anisotropy refers to emission or absorption; in the former case, I_P ($P = Y$ or Z) is the output of a detector viewing the P -polarized component of the emitted light travelling along the X -axis; in the latter case, ΔA_P is the photo-induced change in the absorbance of the sample for P -polarized light; X, Y and Z refer to a laboratory-based coordinate frame. If the Z -axis is identified with the vertical direction (V), and the other two with the horizontal (H), I_Z and I_Y can be replaced by I_V and I_H , respectively.

See *anisotropy*, *photoselection*, *uniaxial systems*

EMISSION SPECTRUM

Plot of the emitted *spectral radiant power* (*spectral radiant exitance*) or of the emitted *spectral photon irradiance* (*spectral photon exitance*) against a quantity related to photon energy,

such as *frequency*, ν , *wavenumber*, σ , or *wavelength*, λ . When corrected for wavelength dependent variations in the equipment response, it is called a corrected emission spectrum.

EMITTANCE

See *radiant exitance*.

ENCOUNTER COMPLEX

An intermolecular ensemble formed by molecular entities in contact or separated by a distance small compared to the diameter of solvent molecules and surrounded by several shells of solvent molecules; the innermost shell is the solvent "cage". If one of the species is excited, the excitation usually takes place prior to formation of the encounter complex. During the lifetime of the encounter complex the reactants can collide several times to form collision complexes, and then undergo structural and electronic changes. If the interaction between the reactants leads to a minimum in the potential energy and one of the entities is electronically excited, the encounter complex may represent an *exciplex* or *excimer*.

See also *contact ion pair* and *collision complex*.

ENERGY HYPERSURFACE

Synonymous with *potential-energy surface* (PES): The notion of hypersurface is used to stress the multidimensionality of PESs. In a molecular system consisting of N atomic nuclei, the number of the independent coordinates that fully determine the PES is equal to 3N-6 (or 3N-5 if the system is linear).

ENERGY MIGRATION

See *electronic energy migration*.

ENERGY POOLING

See *annihilation*.

ENERGY STORAGE EFFICIENCY (η)

The rate of the Gibbs energy storage in an endothermic photochemical reaction divided by the incident *irradiance*.

See also *efficiency*.

ENERGY TRANSFER

From a phenomenological point of view, the term is used to describe the process by which a molecular entity absorbs light and a phenomenon originates from the *excited state* of another molecular entity. In mechanistic photochemistry the term has been reserved for the *photophysical process* in which an excited state of one molecular entity (the donor) is deactivated to a lower-lying state by transferring energy to a second molecular entity (the acceptor), which is thereby raised to a higher energy state. The excitation may be electronic, vibrational, rotational or translational. The donor and acceptor may be two parts of the same molecular entity, in which case the process is called intramolecular energy transfer.

See also *Dexter excitation transfer*, *Förster excitation transfer*, *radiative energy transfer*, and *spectral overlap*.

ENERGY TRANSFER PLOT

A plot of the *quenching* rate constant of an electronically excited molecular entity by a series of *quenchers* versus the *excited state* energy of the quenchers. Alternatively, a plot of the rate constant for the *sensitization* of a reaction versus the excited state energy of different *sensitizers*. This type of plot is used to estimate the energy of the excited molecular entity quenched (in the former case) or produced (in the latter case). Also known as Hammond-Herkstroeter plot.

See also *Stern-Volmer kinetic relationships*.

ENHANCER (of emission)

A *fluorescent* compound which accepts energy and thus enhances or promotes the emission from a sample containing a chemically or enzymatically generated excited molecular entity.

ESCA

See *photoelectron spectroscopy*.

EXCIMER

An electronically excited dimer, "nonbonding" in the *ground state*. For example, a complex formed by the interaction of an excited molecular entity with a ground state partner of the same structure.

See also *exciplex*.

EXCIMER LASER

A source of pulsed *coherent radiation* obtained from an *exciplex*. The proper name should be *exciplex laser*. Typical lasing species are noble gas halides (XeCl, KrF, etc.) emitting in the UV domain.

See *laser*, *gas lasers*.

EXCIPLEX

An electronically excited complex, of definite stoichiometry, "nonbonding" in the *ground state*. In general, a complex formed by the interaction of an *electronically excited* molecular entity with a *ground state* partner of a different structure. If the partners have the same structure this special case of an exciplex is called an *excimer*.

If the partners have pronounced electron-donor and -acceptor character their exciplex attains ion-pair character. The terms compact exciplex and loose exciplex have sometimes been used to indicate that such polar exciplexes may have structures closely related to a *contact ion pair* or a *solvent-separated ion pair*.

EXCITATION SPECTRUM

Plot of the *spectral radiant exitance* or of the *spectra photon exitance* against the *frequency* (or *wavenumber*, or *wavelength*) of excitation. When corrected for wavelength dependent variations in the excitation *radiant power* this is called a corrected excitation spectrum. Due to the proportionality of the emission intensity with the absorbed radiant power, only at very low *absorbances* the excitation spectrum of a unique species should be identical to its *absorption spectrum*.

See also *emission spectrum*.

EXCITATION TRANSFER

Same as *energy transfer*.

EXCITED STATE

A state of higher energy than the *ground state* of a chemical entity. In photochemistry an *electronically excited state* is usually meant.

EXCITON

In some applications it is useful to consider electronic excitation as if a quasi-particle capable of migrating, were involved. In organic materials two models are used: the band or wave model (low temperature, high crystalline order) and the hopping model (higher temperature, low crystalline order or amorphous state). *Energy transfer* in the hopping limit is identical with *energy migration*. In semiconductors and insulators, a free exciton is a bound electron-hole (neutral quasi-particle) capable of migrating and transferring its energy to the solid lattice. A localized exciton is an exciton trapped by a defect, which leads to the electronically *excited state* of the defect.

See *electronic energy migration*.

EXITANCE

See *radiant exitance*.

EXTERNAL HEAVY ATOM EFFECT

See *heavy atom effect*.

EXTERPLEX

Termolecular analogue of an *exciplex*. Use of this term is discouraged.

See also *exciplex*

EXTINCTION

This term, equivalent to *absorbance*, is no longer recommended.

EXTINCTION COEFFICIENT

This term, equivalent to *molar (decadic) absorption coefficient*, is no longer recommended.

See *Beer-Lambert law*.

FACTOR-GROUP SPLITTING

See *Davydov splitting*.

FERMI LEVEL (E_F)

The chemical potential of electrons in a solid (metals, semiconductors or insulators) or in an electrolyte solution.

See *bandgap energy, conduction band, valence band*.

FILTER (optical)

A device which reduces the spectral range (*bandpass, cut-off, and interference filter*) or *radiant power* of incident radiation (*neutral density or attenuation filter*) upon transmission of radiation.

FLASH PHOTOLYSIS

A technique of *transient spectroscopy* and transient kinetic studies in which a light pulse is used to produce transient species. Commonly, an intense pulse of short duration is used to produce a sufficient concentration of a transient species suitable for spectroscopic observation.

FLUENCE (H')

When applied to energy, it is the total radiant energy incident from all directions on an infinitesimal small sphere of cross-sectional area dS , divided by dS . The product of the *fluence rate* and the duration of the irradiation ($\int E' dt$, simplified expression: $H' = E' t$ when the fluence rate is constant over the time considered). The SI unit is $J m^{-2}$. Energy fluence is identical to spherical radiant exposure and reduces to *radiant exposure (H)* for a parallel and normally incident beam, not scattered or reflected by the target or its surroundings.

See also *dose, photon fluence*.

FLUENCE RATE (E')

The rate of *fluence, H'*. Total *radiant power, P*, incident from all directions onto an infinitesimal small sphere of cross-sectional area dS divided by dS . For energy fluence rate the SI unit is $W m^{-2}$. It reduces to *irradiance, E*, for a parallel and perpendicularly incident beam not scattered or reflected by the target or its surroundings.

See *intensity, radiance*.

See also *photon fluence rate*.

FLUORESCENCE

Spontaneous emission of radiation (*luminescence*) from an excited molecular entity with the formation of a molecular entity of the same spin *multiplicity* .

FLUXIONAL MOLECULES

A subclass of structurally nonrigid molecules in which all the interconverting species that are observable are chemically and structurally equivalent. The classic example of the phenomenon of fluxionality is the rapid "automerization" of tricyclo[3.3.2.0^{2,8}]deca-3,6,9-triene (bullvalene), the rapid interconversion of 1209 600 (10!/3) degenerate isomers.

See *Jahn-Teller effect*.

f NUMBER

See *oscillator strength*.

FÖRSTER EXCITATION TRANSFER (Dipole-Dipole Excitation Transfer)

A mechanism of excitation transfer which can only occur between molecular entities separated by distances considerably exceeding the sum of their van der Waals radii. It is described in terms of an interaction between the *transition dipole moments*, (a dipolar mechanism). The transfer rate constant ($k_{D \rightarrow A}$) is given by

$$k_{D \rightarrow A} = \frac{K^2 J 8.8 \times 10^{-28} \text{ mol}}{n^4 \tau_0 r^6}$$

where K is an orientation factor, n the refractive index of the medium, τ_0 the *radiative lifetime* of the donor, r the distance (cm) between donor (D) and acceptor (A), and J the *spectral overlap* (in coherent units $\text{cm}^6 \text{ mol}^{-1}$) between the absorption spectrum of the acceptor and the *fluorescence spectrum* of the donor. The critical quenching radius, r_0 , is that distance at which $k_{D \rightarrow A}$ is equal to the inverse of the radiative lifetime.

See also *Dexter excitation transfer, energy transfer, radiative energy transfer*.

FÖRSTER CYCLE

Indirect method of determination of *excited state* equilibria, such as $\text{p}K_a^*$ values, based on *ground state* thermodynamics and electronic transition energies. This cycle considers only the

difference in molar enthalpy change ($\Delta\Delta H$) of reaction of ground and excited states, neglecting the difference in molar entropy change of reaction of those states ($\Delta\Delta S$).

FOURIER TRANSFORM SPECTROMETER

A scanning interferometer, containing no principal dispersive element, which first splits a beam into two or more components, then recombines these with a phase difference. The spectrum is obtained by a Fourier transformation of the output of the interferometer.

FRANCK-CONDON FACTOR

See *electronic transition moment*.

FRANCK-CONDON PRINCIPLE

Classically, the Franck-Condon principle is the approximation that an electronic transition is most likely to occur without changes in the positions of the nuclei in the molecular entity and its environment. The resulting state is called a Franck-Condon state, and the transition involved, a *vertical transition*.

The quantum mechanical formulation of this principle is that the *intensity* of a *vibronic transition* is proportional to the square of the overlap integral between the vibrational wavefunctions of the two states that are involved in the transition.

See *electronic transition moment*.

FRANCK-CONDON STATE

See *Franck-Condon principle*.

FREE ELECTRON LASER

Source of *coherent radiation* in which the active medium is an electron beam moving at speeds close to the speed of light in the spatially periodic magnetic field produced by an array of magnets (the wiggler). The emitted wavelength, λ_L , is approximately given by $\lambda_w/(4E^2)$, with λ_w being the wiggler period and E the kinetic energy of the electrons in MeV.

See *laser*.

FREE EXCITON

See *exciton*.

FREE-RUNNING LASER

It applies to a pulsed *laser* and means that the laser emission lasts as long as the pumping process is sufficient to sustain lasing conditions. Typical pulse durations are in the μs - ms range, depending on the pumping source. When the operation mode of a pulsed laser is not specified as *Q-switched*, *mode-locked*, or anything else, it must be considered as free-running.

FREQUENCY (ν or ω)

The number of waveperiods per unit time. The linear frequency, ν , is the number of cycles per unit time. The SI unit is $\text{Hz} = \text{s}^{-1}$. For the angular frequency, the symbol $\omega (= 2\pi\nu)$ is used, with rad s^{-1} as the SI unit.

FREQUENCY DOUBLING

See *harmonic frequency generation, nonlinear optical effects*.

FWHM (Full Width at Half Maximum)

See *half-(band)width*.

GAS LASERS

CW or pulsed *lasers* in which the active medium is a gaseous mixture usually composed of a buffer gas (He for instance) and an active medium consisting of:

- neutral atoms (*e.g.*, Ne, Cu, Au, etc.) or molecules (*e.g.*, N_2 , CO_2 , CO, I_2 , etc.), or
- ionized atoms (*e.g.*, Ar, Kr, Cd, etc.)

These lasers are not tunable but most of them can emit several lines which in many cases may be selected from a single apparatus.

Pulsed lasers may be *free-running*, *Q-switched*, or *mode-locked*. Some CW lasers may be mode-locked.

See *argon ion-, CO₂-, excimer, copper vapour-, helium-neon-, krypton-, nitrogen-lasers*.

GAUSSIAN BAND SHAPE

A band shape described by the Gaussian function

$$F(\nu - \nu_0) = (a/\sqrt{\pi}) \exp [-a^2(\nu - \nu_0)^2].$$

In this equation, a^{-1} is proportional to the width of the band, and ν_0 is the frequency at the band maximum.

See also *Lorentzian band shape*.

GEMINATE ION PAIR

Ion pair, formed from a precursor that constitutes a single kinetic entity, *i.e.*, by *electron transfer* or ion transfer in an *encounter complex* (*cf. collision complex*) or by ionic dissociation of a single molecular entity.

GEMINATE PAIR

Pair of molecular (or atomic) species in close proximity in liquid solution with a solvent cage and resulting from reaction (*e.g.* bond scission, *electron transfer*, group transfer) of a precursor that constitutes a single kinetic entity.

GEMINATE RECOMBINATION

Recombination reaction of a *geminate pair*. The reaction can either be a *back electron transfer* that restores the donor and acceptor species in their ground-state, from which the pair was created via *electron transfer*, or a bond formation or bond reorganization.

GROUND STATE

The lowest energy state of a chemical entity. In photochemistry ground electronic state is usually meant.

HALF-WIDTH (of a band)

The full width of a spectral band at a height equal to half of the height at the band maximum. Also known as *full width at half maximum (FWHM)*. The dimension of band width should be either inverse length (*wavenumbers*) or inverse time (*frequencies*) so that the values give an indication of the energies. Note the hyphen in half-width. Half bandwidth has the meaning of half-width at half maximum.

HAMMOND-HERKSTROETER PLOT

See *energy transfer plot*.

HARMONIC FREQUENCY GENERATION

Production of *coherent radiation* of frequency $k\nu$ ($k = 2, 3, \dots$) from coherent radiation of frequency ν . In general, this effect is obtained through the interaction of *laser* light with a suitable optical medium with nonlinear polarizability. The case $k = 2$ is referred to as frequency doubling, $k = 3$ is frequency tripling, $k = 4$ is frequency quadrupling. Even higher integer values of k are possible.

HARPOON MECHANISM

Reaction sequence (thermal or photoinduced) between neutral molecular or atomic entities in which long-range *electron transfer* is followed by a considerable reduction of the distance between donor and acceptor sites as a result of the electrostatic attraction in the *ion pair* created.

HEAVY ATOM EFFECT

Enhancement of the rate of a spin-forbidden process by the presence of an atom of high atomic number, which is either part of, or external to, the excited molecular entity. Mechanistically, it corresponds to a *spin-orbit coupling* enhancement produced by a heavy atom.

HELIUM-CADMIUM LASER

A *CW laser* emitting mainly at 325.0 and 441.6 nm from singly ionized cadmium.

See *gas lasers*.

HELIUM-NEON LASER

A *CW laser* emitting mainly at 632.8, 1152.3, and 3391.3 nm from excited neutral Ne atoms. See *gas lasers*.

HERKSTROETER PLOT

See *energy transfer plot*.

HETEROEXCIMER

Exciplex in which the partners have a (slightly) different structure. Use of this term is discouraged.

HIGH-PRESSURE MERCURY LAMP (Arc)

Radiation source containing mercury at a pressure of *ca.* 8 MPa (*ca.* 80 bar) or higher which emits lines over a background continuum between about 200 and 1400 nm.

See *lamp*.

HOLE BURNING

The *photobleaching* of a feature, normally a narrow range, within an inhomogeneous broader absorption or emission band. The holes are produced by the disappearance of resonantly excited molecules as a result of *photophysical* or *photochemical processes*. The resulting spectroscopic technique is site-selection spectroscopy.

HOLE TRANSFER

Charge migration process in which the majority carriers are positively charged.

HOT GROUND STATE REACTION

A *hot state reaction* of the ground electronic state.

HOT QUARTZ LAMP

A term sometimes used to describe a *high-pressure mercury lamp*. The use of this term is not recommended.

HOT STATE REACTION

A reaction proceeding from an ensemble of molecular entities possessing a higher average vibrational, rotational or translational energy than they would at thermal equilibrium with the surrounding medium.

HUND RULES

(1) Of the different multiplets resulting from different *configurations* of electrons in degenerate *orbitals* of an atom those with greatest *multiplicity* have the lowest energy (multiplicity rule).

(2) Among multiplets having the same multiplicity, the lowest-energy one is that with the largest total orbital angular momentum (angular momentum rule) (valid if the total orbital angular

momentum is a constant of motion).

(3) In configurations containing shells less than half full of electrons, the term having the lowest total angular momentum J lies lowest in energy, whereas in those with shells more than half filled, the term having the largest value of J lies lowest (fine structure rule).

Hund rules apply if the "Russell-Saunders" coupling scheme is valid. Sometimes the first rule is applied to molecules.

HUSH MODEL

See: *Marcus-Hush relationship*

HYPERCHROMIC EFFECT

Increase in the *intensity* of a spectral band due to substituents or interactions with the molecular environment.

See also *auxochrome*.

HYPERFINE

Due to nuclear spin.

HYPOCHROMIC EFFECT

Opposite of *hyperchromic effect*.

HYPSOCHROMIC SHIFT

Shift of a spectral band to higher *frequency* or shorter *wavelength* upon substitution or change in medium (*e.g.*, solvent). It is informally referred to as a *blue shift*, and is opposite to *bathochromic shift*.

IMAGING (Photoimaging)

The use of a photosensitive system for the capture, recording, and retrieval of information associated with an object using electromagnetic energy.

INCOHERENT RADIATION

Not having the properties of the *coherent radiation*.

INNER FILTER EFFECT

This term is used in two different ways. In an *emission* experiment, it refers to an apparent decrease in emission *quantum yield* and/or distortion of bandshape as a result of reabsorption of emitted radiation. During a light irradiation experiment, absorption of incident radiation by a species other than the intended primary absorber is also described as an inner filter effect.

INNER-SPHERE ELECTRON TRANSFER

Historically an *electron transfer* between two metal centers sharing a ligand or atom in their respective coordination shells. The definition has more recently been extended to any situation in which the interaction between the donor and acceptor centers in the transition state is significant (> 20 kJ mol⁻¹).

Compare *outer-sphere electron transfer*

INTEGRATING SPHERE

A hollow sphere having a highly reflecting inside surface used as a device to collect, with very high efficiency, light scattered or emitted from a sample contained in it or located outside and near one of the ports. Small ports allow the entrance of light and access to a detector.

INTENDED CROSSING (of Potential-Energy Surfaces)

Same as *avoided crossing*. The term 'intended' should not be used in this context since it is an anthropomorphic term.

INTENSITY

Traditional term for *photon flux*, *fluence rate*, *irradiance* or *radiant power*. In terms of an object exposed to radiation, the term should now be used only for qualitative descriptions.

INTENSITY (I) (of a light source)

Same as *radiant intensity*.

INTENSITY (of a spectral feature)

Describes the magnitude of the particular feature in the spectrum.

INTERFERENCE FILTER

See *filter*.

INTERFEROMETER

See *Fourier transform spectrometer*.

INTERNAL CONVERSION

A *photophysical process*. Isoenergetic *radiationless transition* between two electronic states of the same *multiplicity*. When the transition results in a vibrationally excited molecular entity in the lower electronic state, this usually undergoes *deactivation* to its lowest vibrational level, provided the final state is not unstable to dissociation.

INTERNAL TRANSMITTANCE

See *transmittance*.

INTERSECTION SPACE

A $(3N - 8)$ -dimensional subspace of the $(3N - 6)$ -dimensional nuclear coordinate space consisting of an infinite number of *conical intersection* points (N is the number of nuclei).

INTERSYSTEM CROSSING

A *photophysical process*. Isoenergetic *radiationless transition* between two electronic states having different *multiplicities*. It often results in a vibrationally excited molecular entity in the lower electronic state, which then usually deactivates to its lowest vibrational level.

INTERVALENCE CHARGE TRANSFER

Electron transfer (thermal or photoinduced) between two metal sites differing only in oxidation state. Quite often such electron transfer reverses the oxidation states of the sites. The term is frequently extended to the case of *metal-to-metal charge transfer* between nonequivalent metal centers.

INTIMATE ION PAIR

See *contact ion pair*

INVERTED REGION (for electron transfer)

The region where the driving force ($-\Delta G^0$) for *electron transfer* exceeds the total *reorganization energy* (λ), i.e., $-\Delta G^0 > \lambda$ in the *Marcus equation* developed for *outer sphere electron transfer*. The behaviour in this region is referred to as *electron transfer* under inverted region conditions because the basic/classical Marcus equation leads to a counterintuitive prediction

that under such conditions the rate of electron transfer should decrease with increasing exergonicity (ΔG°). It should be noted that experimentally such a decrease in rate is not always observed and, even when it is, a more elaborate theory is required to quantify the actual behaviour in this region.

Note the similarity to the energy gap law for radiationless conversion of an *excited state*.

Compare *normal region*.

IRRADIANCE (E)

The *radiant power*, P , of all wavelengths incident from all upward directions on an infinitesimal element of surface of area dS containing the point under consideration divided by dS . (dP/dS , simplified expression: $E = P/S$ when the radiant power is constant over the surface area considered). The SI unit is W m^{-2} .

Note: $E = \int_{\lambda} E_{\lambda} d\lambda$, where E_{λ} is the spectral irradiance at wavelength λ . For a parallel and

perpendicularly incident beam not scattered or reflected by the target or its surroundings *fluence rate* (E') is an equivalent term.

See also *photon irradiance*, *spectral irradiance*.

ISOABSORPTION POINT

The use of this term, equivalent to *isosbestic point*, is not recommended.

ISOCLINIC POINT

A *wavelength*, *wavenumber*, or *frequency* at which the first derivative of an absorption spectrum of a sample does not change upon a chemical reaction or physical change of the sample.

ISOEMISSIVE POINT

Same as *isostilbic point*.

ISOOPTOACOUSTIC POINT

A *wavelength*, *wavenumber*, or *frequency* at which the total energy emitted by a sample as heat does not change upon a chemical reaction or physical change of the sample. Its position depends on the experimental conditions. The spectral differences between the *isosbestic* points and the isooptoacoustic points are the result of the nonlinear relationship between the *molar absorption coefficient* and the *photoacoustic* signal.

See *photoacoustic spectroscopy*.

ISOSBESTIC POINT


A *wavelength, wavenumber, or frequency* at which the total *absorbance* of a sample does not change during a chemical reaction or a physical change of the sample. The term derives from the Greek word for 'same attenuation'. A simple example occurs when one molecular entity is converted into another which has the same *molar absorption coefficient* at a given wavelength. As long as the sum of the concentrations of the two molecular entities in the solution is held constant, there will be no change in *absorbance* at this wavelength as the ratio of the two entities is varied. In general, the invariant $A(\lambda)l^{-1} (= \sum_n^{i=1} \epsilon_i^\lambda c_i)$ indicates the absence of secondary or side reactions. The use of the term isoabsorption point is not recommended.

ISOSTILBIC POINT

The *wavelength* at which the *intensity of emission* of a sample does not change during a chemical reaction or physical change. The term derives from the Greek word for 'same luminescence'. The terms isoemissive and isolampsic are sometimes used.

See *isosbestic point*.

JABLONSKI DIAGRAM

Originally, a diagram showing that the *fluorescent* state of a molecular entity is the lowest *excited state* from which the transition to the *ground state* is allowed, whereas the *phosphorescent* state is a metastable state below the fluorescent state, which is reached by *radiationless transition*. In the most typical cases the fluorescent state is the lowest *singlet* excited state and the phosphorescent state the lowest *triplet* state, the ground state being a singlet. The original Jablonski diagram did not assign a different *multiplicity* to the phosphorescent state. Presently, modified Jablonski diagrams are frequently used and are actually state diagrams in which molecular electronic states, represented by horizontal lines displaced vertically to indicate relative energies, are grouped according to *multiplicity* into horizontally displaced columns. Excitation and *relaxation* processes that interconvert states are indicated in the diagram by arrows. *Radiative transitions* are generally indicated with straight arrows (\rightarrow), while *radiationless transitions* are generally indicated with wavy arrows ()

JAHN-TELLER EFFECT

Deals with molecular distortions due to an electronically degenerate *ground* state. For nonlinear molecular entities in a geometry described by a point symmetry group possessing degenerate irreducible representations there always exists at least one nontotally symmetric vibration that makes electronically degenerate states unstable at this geometry. The nuclei are displaced to new equilibrium positions of lower symmetry causing a splitting of the originally degenerate states (first order Jahn-Teller effect). This effect is due to the odd terms in the vibronic perturbation expansion. In the case of molecules with a nondegenerate *ground electronic state*, but with a very low lying *excited state*, distortions of proper symmetry arise which result in mixing of the ground and excited states, thereby lowering the ground state energy (pseudo Jahn-Teller effect) the pseudo Jahn-Teller effect manifests itself in fluxional behaviour (see *fluxional molecules*) and stereochemical nonrigidity of molecules and ions. The Jahn-Teller effect generates a *surface crossing* (e.g., a *conical intersection*) whereas a pseudo Jahn-Teller effect generates an *avoided crossing*.

See also *Renner-Teller effect*, *vibronic coupling*

KAPTEIN-CLOSS RULES

Rules used to predict the sign of *CIDNP* effects.

KASHA RULE

Polyatomic molecular entities luminesce with appreciable yield only from the lowest *excited state* of a given *multiplicity*. The concept has been extended to the reaction of excited species, *i.e.*, polyatomic molecular entities react with appreciable yield only from the lowest excited state of a given multiplicity. There are exceptions to this rule.

KASHA-VAVILOV RULE

The *quantum yield of luminescence* is independent of the *wavelength* of exciting radiation. There are exceptions to this rule.

KOOPMANS' THEOREM

See *photoelectron spectroscopy*.

KRYPTON ION LASER

A *CW* or pulsed *laser* emitting lines from 337 to 859 nm from singly ionized krypton.

Principal emissions are at 530.9, 568.2, 647.1, and 752.5 nm.

See *gas lasers*.

LAMBERT LAW

The fraction of light absorbed by a system is independent of the incident *spectral radiant power* (P_λ^0). This law holds only if P_λ^0 is small, scattering is negligible, and *multiphoton* processes, *excited state* populations, and *photochemical reactions* are negligible.

See *absorbance*, *Beer-Lambert law*.

LAMP

A source of *incoherent radiation*.

See *high-pressure*, *medium-pressure*, and *low-pressure mercury lamp (arc)*, and *antimony-xenon*, *mercury-xenon*, *quartz-iodine*, *tungsten-halogen*, *resonance*, and *xenon lamp*.

LANDAU-ZENER MODEL

Within the Born-Oppenheimer approximation, a semiclassical model for the probability, P , of hopping from one electronic state to another of the same spin *multiplicity*

$$P = \exp\left[-(4\pi^2\varepsilon_{12}^2)/hV|s_1 - s_2|\right]$$

where ε_{12} is the potential-energy gap between the two electronic states at a *surface crossing point*, $|s_1 - s_2|$ is the difference in slopes between the intersecting *potential-energy* curves at this point, and V is nuclear velocity along the reaction coordinate.

LAPORTE RULE

For monophotonic *radiative* transitions in centro-symmetric systems, the only nonvanishing electric-dipole transition moments are those which connect an even term (g) with an odd term (u).

LASER

A source of ultraviolet, visible, or infrared radiation which produces light amplification by stimulated emission of radiation from which the acronym is derived. All lasers contain an energized

substance that can increase the intensity of light passing through it. The amplifying medium may be a solid, a liquid or a gas. The light emitted is *coherent* except for *superradiance* emission.

See *argon ion, helium-cadmium, chemical, CO₂ copper vapour, diode, dye, excimer, free electron, free-running, gas, helium-neon, krypton ion, mode-locked, neodymium, nitrogen, Q-switched, solid state, and ruby laser.*

See also *lasing.*

LASING

The process of light amplification by stimulated emission of radiation (*laser*).

LATENT IMAGE

The primary result of radiation *absorption* in a *photo-imaging* system which is susceptible to development.

LED

Light emitting diode.

LIFETIME (τ)

The lifetime of a molecular entity which decays in a first-order process is the time needed for a concentration of the entity to decrease to 1/e of its original value. Statistically, it represents the life expectation of the entity. It is equal to the reciprocal of the sum of the (pseudo)unimolecular rate constants of all processes which cause the decay. Lifetime is used sometimes for processes which are not first order. However, in such cases, the lifetime depends on the initial concentration of the entity, or of a *quencher* and therefore only an initial or a mean lifetime can be defined. In this case it should be called apparent lifetime or decay-time, instead. Occasionally, the term half-life ($\tau_{1/2}$) is used, representing the time needed for the concentration of an entity to decrease to one half of its original value.

LIGAND FIELD SPLITTING

The removal of a degeneracy of atomic or molecular levels in a molecule or ion with a given symmetry induced by the attachment or removal of ligands to produce reduced symmetries.

See *crystal field splitting.*

LIGAND TO LIGAND CHARGE TRANSFER (LLCT) TRANSITION

An electronic transition of a metal complex that corresponds to excitation populating an electronic state in which considerable *electron transfer* between two ligands has occurred.

LIGAND TO METAL CHARGE TRANSFER (LMCT) TRANSITION

An electronic transition in a metal complex that corresponds to excitation populating an electronic state in which considerable *electron transfer* from a ligand to a metal center has occurred.

See also *metal to ligand charge transfer transition*

LIGHT EMITTING DIODE (LED)

A semiconductor (normally a combination of gallium, arsenic and phosphorous) containing an *n* region (where electrons are more numerous than positive charges) separated from a *p* region (where positive charges are more numerous than negative charges). Upon application of a voltage charges move and emission of light is produced each time a charge recombination takes place. Normally a very narrow frequency range is emitted.

LIGHT POLARIZATION

When the end point of the electric vector of a polarized light beam is viewed along the direction of light propagation, it moves along a straight line if the light is linearly polarized, along a circle if it is circularly polarized, and along an ellipse if it is elliptically polarized.

LIGHT SOURCE

See *lamp, laser*.

LINEAR DICHROISM

See *absorption anisotropy*.

LOCALIZED EXCITON

See *exciton*.

LORENTZIAN BAND SHAPE

This band shape is described by the function

$$F(\nu - \nu_0) = (1/\pi) \gamma [(\nu - \nu_0)^2 + \gamma^2]^{-1},$$

where ν_0 is the mean band position, γ is the half *band width* at half maximum, and $F(\nu - \nu_0)$ is the *frequency distribution function*.

See also *Gaussian band shape*.

LOW-PRESSURE MERCURY LAMP (Arc)

A type of *resonance lamp* which contains mercury vapour at pressures of about 0.1 Pa (0.75 x 10⁻³ Torr; 1 Torr = 133.3 Pa). At 25 °C, such a lamp emits mainly at 253.7 and 184.9 nm. These lamps are also called *germicidal*. There are cold and hot cathode as well as cooled electrode-less (excited by microwaves) low-pressure mercury lamps. The *Wood lamp* is a low-pressure mercury arc with an added fluorescent layer which emits in the UV-A spectral region (320-400 nm).

See *lamp*.

LUMINESCENCE

Spontaneous emission of radiation from an electronically or vibrationally excited species not in thermal equilibrium with its environment.

See also *bioluminescence, chemiluminescence, electro-generated chemiluminescence, fluorescence, phosphorescence, photoluminescence, radioluminescence, sono luminescence, thermoluminescence, triboluminescence*.

LUMIPHORE (Luminophore)

A part of a molecular entity (or atom or group of atoms) in which *electronic excitation* associated with a given *emission band* is approximately localized. (Analogous to *chromophore* for absorption spectra.)

MARCUS EQUATION (for electron transfer)

Equation proposed by R.A. Marcus to relate the rate of *outer-sphere electron transfer* with the thermodynamics of this process [see: R.A. Marcus, J. Chem. Phys. 24, 966-978 (1956)].

Essentially the rate constant within the *encounter complex* (or the rate constant of intramolecular transfer) is given by the Eyring equation:

$$k_{\text{et}} = (\kappa_{\text{el}} kT/h) \exp(-\Delta G^\ddagger/RT)$$

where k represents Boltzmann's constant and κ_{el} is the so called electronic transmission factor ($\kappa_{\text{el}} \sim 1$ for adiabatic and $\ll 1$ for diabatic electron transfer). It was shown by Marcus that for *outer-sphere electron transfer* the barrier height can then be expressed as:

$$\Delta G^\ddagger = (\lambda + \Delta G^o)^2 / 4\lambda$$

where ΔG^o represents the standard Gibbs energy change accompanying the reaction and λ the total *reorganization energy*.

It should be noted that whereas the classical Marcus equation has been found to be quite adequate in the *normal region*, it is now generally accepted that in the *inverted region* a more elaborate formulation, taking into account explicitly the Franck-Condon factor due to quantum mechanical vibration modes, should be employed

MARCUS INVERTED REGION (for electron transfer)

See *inverted region*

MARCUS-HUSH RELATIONSHIP

Relationship between the barrier (ΔG^\ddagger) to thermal *electron transfer*, the energy of a corresponding optical *charge transfer transition* (ΔE_{op}), and the overall change in standard Gibbs energy accompanying thermal electron transfer (ΔG^o). Assuming a quadratic relation between the energy of the system and its distortions from equilibrium (harmonic oscillator model) the expression obtained is:

$$\Delta G^\ddagger = \Delta E_{\text{op}}^2 / 4(\Delta E_{\text{op}} - \Delta G^o)$$

The simplest form of this expression obtains for degenerate electron transfer (ΔG^o) in *e.g.* symmetrical mixed valence systems:

$$\Delta G^\ddagger = \Delta E_{\text{op}} / 4$$

Note that for this situation the *Marcus equation* reads $\Delta G^\ddagger = \lambda/4$.

See *Marcus equation*

MEDIUM-PRESSURE MERCURY LAMP (Arc)

Radiation source containing mercury vapour at pressures ranging from 100 to several hundred kPa (1 atm = 101.325 kPa). Emits mostly from 222 to 1000 nm with most intense lines at 253.7, 300, 303, 313, 334, 366, 405, 436, 546, and 578 nm.

See *lamp*.

MERCURY-XENON LAMP (Arc)

An intense source of ultraviolet, visible, and near infrared radiation produced by an electrical discharge in a mixture of mercury vapour and xenon under high pressure.

See *lamp*.

MERP

Minimum energy reaction path.

MERRY-GO-ROUND REACTOR (Turntable Reactor)

An apparatus in which several samples are rotated around a radiation source in order to expose each to equal amounts of radiation.

METAL TO LIGAND CHARGE TRANSFER (MLCT) TRANSITION

An electronic transition of a metal complex that corresponds to excitation populating an electronic state in which considerable *electron transfer* from the metal to a ligand has occurred.

Compare *ligand to metal charge transfer transition*

METAL TO METAL CHARGE TRANSFER (MMCT) TRANSITION

An electronic transition of a bi- or poly-nuclear metal complex that corresponds to

excitation populating an electronic state in which considerable *electron transfer* between two metal centres has occurred.

See also *intervalence charge transfer*.

MINIMUM ENERGY REACTION PATH (MERP)

The path orthogonal to the equipotential contours of a *potential-energy surface*, which connects the energy minima through a saddle point (transition state) from which it slopes downwards along the steepest descent lines in $3N - 6$ configurational space (N is the number of nuclei in the reacting system). MERP calculation allows the investigation of detailed changes in molecular structure describing the transformation of reactants to products.

MLCT

See *metal to ligand charge transfer*.

MODE-LOCKED LASER

A *laser* in which many resonant modes are coupled in phase, to yield a train of very short pulses (*e.g.* fs or ps pulses). The coupling of the modes is obtained by modulation of the gain in the resonator, and can be active (electro-optic modulation of the losses or of the pump intensity), or passive (with a saturable absorber).

See also *free-running laser*.

MOLAR ABSORPTION COEFFICIENT, MOLAR DECADIC ABSORPTION COEFFICIENT

Absorbance divided by the absorption pathlength, l and the concentration, c :

$$\varepsilon = [1/(cl)] \log(P_{\lambda}^0/P_{\lambda}) = A/(cl)$$

In common usage for l in cm and c in mol dm⁻³ or M, ε results in dm³ mol⁻¹ cm⁻¹ or M⁻¹ cm⁻¹ (the most commonly used unit) which equals 0.1 m² mol⁻¹ (coherent SI units). The term *molar absorptivity* for molar absorption coefficient should be avoided.

See *absorbance, absorption coefficient, Beer-Lambert law*.

MULTICONFIGURATION SCF (MCSCF) METHOD

A *configuration interaction* method in which simultaneous optimization of both the shapes of molecular orbitals and contributions from different electronic configurations is carried out by use of the variational method. The MCSCF method with a large enough set of configurations allows better estimation of the *correlation energy* as compared with the conventional CIS, CID, and CISD methods.

MULTIPHOTON ABSORPTION

See *multiphoton process*.

See also *biphotonic excitation*.

MULTIPHOTON PROCESS

A process involving interaction of two or more *photons* with a molecular entity.

See *biphotonic process*, *two-photon process*.

MULTIPLICITY (Spin Multiplicity)

The number of possible orientations, calculated as $2S + 1$, of the spin angular momentum corresponding to a given total spin quantum number (S), for the same spatial electronic wavefunction. A state of *singlet* multiplicity has $S = 0$ and $2S + 1 = 1$. A *doublet* state has $S = 1/2$, $2S + 1 = 2$, etc. Note that when $S > L$ (the total orbital angular momentum quantum number) there are only $2L + 1$ orientations of total angular momentum possible.

MULTIREFERENCE CONFIGURATION INTERACTION (MRCI)

Configuration interaction method in which the configurations are built by excitations out of a wavefunction obtained by using the *multiconfiguration SCF* method.

NONADIABATIC ELECTRON TRANSFER

See *diabatic electron transfer*

NONCROSSING RULE

Electronic states of the same symmetry cannot cross each other along a reaction coordinate. The rule only applies for diatomic molecules and does not apply for polyatomic molecules.

NORMAL REGION (for electron transfer)

In plots relating rate constants for *electron transfer*, or quantities related to it, with the standard Gibbs energy for the reaction (ΔG^o), the region for which the rate constants increase with increasing exergonicity of the reaction is called the normal region. This region is predicted by the Marcus theory for *outer-sphere electron transfer* for the case of $\Delta G^o \leq \lambda$ in the *Marcus equation*.

n → *π** TRANSITION

An electronic transition described approximately as promotion of an electron from a "nonbonding" (lone-pair) *n orbital* to an "antibonding" π orbital designated as π^* .

*n-π** STATE

An *excited state* related to the *ground state* by a $n \rightarrow \pi^*$ transition.

n → *σ** TRANSITION

An electronic transition described approximately as promotion of an electron from a "nonbonding" (lone-pair) *n orbital* to an "antibonding" σ orbital designated as σ^* . Such transitions generally involve high transition energies and appear close to or mixed with *Rydberg transitions*.

NATURAL LIFETIME

Same as *radiative lifetime*. The use of this term is discouraged.

NEODYMIUM LASER

A *CW* or pulsed *laser* emitting radiation from excited Nd^{+3} principally occurring around 1.06 μm (the precise position depends on the matrix). The Nd^{+3} is present as a dopant in suitable crystals (*e.g.*, yttrium-aluminium garnet, YAG) or in suitable glasses (phosphate, silicate, etc.).

See *solid state lasers*.

NEUTRAL-DENSITY FILTER

See *attenuance filter*.

NITROGEN LASER

A source of pulsed semi-coherent *superradiance* mainly around 337 nm. The lasing species is molecular nitrogen.

See *gas lasers*.

NONADIABATIC PHOTOREACTION

Same as *diabatic photoreaction*. Use of double negative is discouraged.

Compare *adiabatic photoreaction*.

NONLINEAR OPTICAL EFFECT

An effect brought about by electromagnetic radiation the magnitude of which is not proportional to the *irradiance*. Nonlinear optical effects of importance to photochemists are *harmonic frequency generation*, *lasers*, Raman shifting, *upconversion*, and others.

NONRADIATIVE DECAY

Disappearance of an excited species due to a *radiationless transition*.

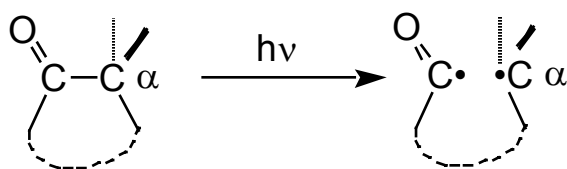
NONVERTICAL ENERGY TRANSFER

An *energy transfer* process which has a low *Franck-Condon* factor.

See *Franck-Condon principle*.

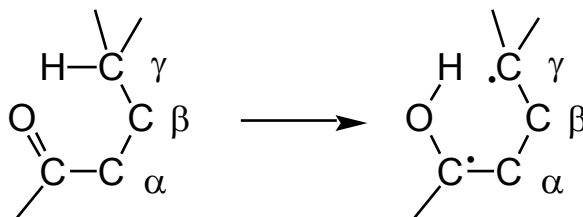
NORRISH TYPE I PHOTOREACTION

α -Cleavage of an excited carbonyl compound leading to an acyl-alkyl *radical pair* (from an acyclic carbonyl compound) or an acyl-alkyl *biradical* (from a cyclic carbonyl compound) as a *primary photoproduct*; e.g.,



NORRISH TYPE II PHOTOREACTION

Intramolecular abstraction of a γ -hydrogen by an excited carbonyl compound to produce a *1,4-biradical* as a *primary photoproduct*; e.g.,



ODMR (Optically Detected Magnetic Resonance)

A double *resonance* technique in which transitions between spin sublevels are detected by optical means. Usually these are sublevels of a *triplet* and the transitions are induced by microwaves. For different types of optical detection (as explained) the following expressions are used: ADMR (*absorption*), DEDMR (*delayed emission*, nonspecified), DFDMR (*delayed fluorescence*), FDMR (*fluorescence*), PDMR (*phosphorescence*). If a reaction yield is monitored the expression RYDMR (reaction yield detected magnetic resonance) is used.

OPO

Optical parametric oscillator.

OPTICAL DENSITY

Synonymous with *absorbance*. The use of the term optical density is discouraged.

OPTICAL PARAMETRIC OSCILLATOR (OPO)

OPO is a powerful solid state source of broadly tunable coherent radiation. It consists of a crystal, usually BBO (beta baryum borate), located inside an optical resonator and pumped by a very intense laser beam (typically provided by a pulsed neodymium laser or a diode laser). The pump beam (wavelength λ_p , frequency ν_p) is partially converted in two coherent beams, the signal and the idler with wavelengths (λ_s, λ_i) and frequencies (ν_s, ν_i) such that $(\nu_s + \nu_i) = \nu_p$. By simultaneous rotation of the crystal and adjustment of the optical resonator, the wavelength of the signal beam is continuously tunable, theoretically from λ_p to $2 \times \lambda_p$ and practically over a slightly more reduced range. For instance, for $\lambda_p = 355$ nm (3rd harmonic of a Nd:YAG laser), λ_s can be tuned from 400 nm (with $\lambda_i \approx 3.15$ μ) up to 600 nm (with $\lambda_i \approx 870$ nm). This "splitting of one photon into two photons" is the reverse of the "sum frequency mixing" used, for instance, to generate the 3rd harmonic of a laser emission by mixing in a convenient crystal the fundamental and the frequency doubled beams (a way to get the 3rd harmonic much more efficient than the pure frequency tripling described under *harmonic frequency generation*).

OPTOACOUSTIC SPECTROSCOPY

Same as *photoacoustic spectroscopy*.

ORBITAL (Atomic or Molecular)

A wavefunction which depends explicitly on the spatial coordinates of only one electron.

ORDER PARAMETER

For a molecular assembly possessing *uniaxial symmetry*, the preferred orientation of a chosen molecular axis towards the unique symmetry axis of the system (or the director) can be defined in terms of average values of certain quantities involving θ , the angle between a molecule-fixed axis and the director. The most pertinent quantities for this purpose are Legendre polynomials, particularly the first three: $P_0(x) = 1$, $P_1(x) = x$, $P_2(x) = (3x^2 - 1)/2$. The average value of $P_2(x)$ at equilibrium is known as the order parameter, and usually denoted by S .

See *uniaxial systems*.

OSCILLATOR STRENGTH (f Number)

A measure of the *intensity* of a spectral band: a classical concept (giving the effective number of electrons taking part in a certain transition) adapted to wave mechanics. For a transition between state i and state j ,

$$f_{ij} = \frac{8\pi^2 m c v}{3h} G R_{ij}^2,$$

where m is the mass of the electron, c the velocity of light, v the *frequency*, h the Planck constant, G the degeneracy of the final state. R_{ij} is the *transition moment* calculated omitting e , the electron charge, in the integral; better called the transition length. Experimentally, f_{ij} is determined by integration of the absorption band, using the equation

$$f_{ij} = (k/n) \int \epsilon(\sigma) d\sigma,$$

where $\epsilon(\sigma)$ is the *molar absorption coefficient* at wavenumber σ and n the average refractive index

of the medium. $k = 4.32 \times 10^{-9} \text{ L}^{-1} \text{ mol cm}$ (for ε in the common units $\text{L mol}^{-1} \text{ cm}^{-1}$); $k = 4.32 \times 10^{-8} \text{ mol m}^{-1}$ (for ε in SI unit $\text{m}^2 \text{ mol}^{-1}$). The oscillator strength, f_{ij} , is a dimensionless quantity.

See also *transition (dipole) moment*.

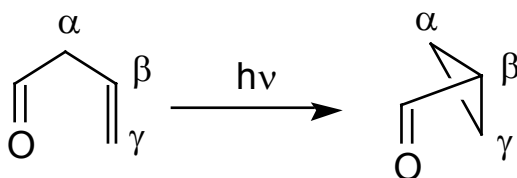
OUTER-SPHERE ELECTRON TRANSFER

Electron transfer between redox centers which do not share a common atom or group, *i.e.*, the interaction between the relevant electronic orbitals of the two centers in the transition state is weak ($< 20 \text{ kJ mol}^{-1}$).

Compare *inner-sphere electron transfer*

OXA-DI-PI-METHANE REARRANGEMENT

A photochemical reaction of a β,γ -unsaturated aldehyde or ketone to form the corresponding saturated α -cyclopropyl carbonyl compound. The rearrangement formally amounts to a 1,2- shift of the carbonyl group and "bond formation" between the former α and γ carbon atoms.



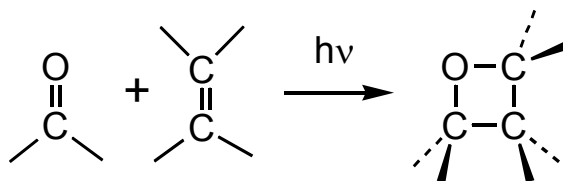
See also *aza-di- π -methane rearrangement* and *di- π -methane rearrangement*.

PARAMETRIC PROCESSES

Photon interactions in an anisotropic medium during which high frequency photons are annihilated and lower frequency photons are created.

PATERNO-BÜCHI REACTION

The *photocycloaddition* of an electronically excited carbonyl group to a *ground state* olefin yielding an oxetane.

PEC

Abbreviation for *photoelectrochemistry*.

PDMR

See *ODMR*.

PEIERLS DISTORTION

The distortion of a regular one-dimensional structure with a partially occupied band to give bond alternation, eventually leading to dimerization or oligomerization. The degree of oligomerization λ depends on the *electronic population* of the conduction band indicated by wave vector of the Fermi level, k_F

$$\lambda = 2\pi/k_F$$

A Peierls distortion opens a gap at the Fermi level, producing a net stabilization of the distorted structure. The Peierls distortion for chain compounds is analogous to the *Jahn-Teller effect* for molecules. The prototypical example of the Peierls distortion in organic chemistry is the bond alternation present in polyacetylene.

PENETRATION DEPTH

See *depth of penetration*.

PES

Abbreviation for *photoelectron spectroscopy*.

PHONON

Elementary excitation in the quantum mechanical treatment of vibrations in a crystal lattice.

PHOSPHORESCENCE

From a phenomenological point of view, the term has been used to describe long-lived *luminescence*. In mechanistic photochemistry, the term designates luminescence involving change in spin *multiplicity*, typically from *triplet* to *singlet* or vice versa. The luminescence from a *quartet state* to a *doublet state* is also phosphorescence.

PHOTOACOUSTIC EFFECT

Generation of a pressure wave after absorption of radiation, due to *radiationless deactivation* and/or chemical reaction.

See also *photoacoustic spectroscopy*.

PHOTOACOUSTIC SPECTROSCOPY

A spectroscopic technique based on the *photoacoustic effect*. A photoacoustic spectrum consists of a plot of the *intensity* of the acoustic signal detected by a microphone or a "piezoelectric" detector, against the excitation *wavelength* or another quantity related to the *photon* energy of the modulated excitation.

See also *isooptoacoustic point*.

PHOTOAFFINITY LABELLING

A technique in which a *photochemically* reactive molecular entity, specifically associated with a biomolecule, is photoexcited in order to covalently attach a label to the biomolecule, usually via intermediates.

PHOTO-ASSISTED CATALYSIS

Catalytic reaction involving production of a catalyst by absorption of light.

See *photocatalysis*.

PHOTOCATALYSIS

A change in the rate of a chemical reaction or its initiation under the action of light in the presence of a substance - the *photocatalyst* - that absorbs light and is involved in the chemical transformation of the reaction partners.

PHOTOCATALYST

A substance that is able to produce, by absorption of light, chemical transformations of the reaction partners. The *excited state* of the photocatalyst repeatedly interacts with the reaction partners forming reaction intermediates and regenerates itself after each cycle of such interactions.

PHOTOCHEMICAL HOLE BURNING

See *hole burning*.

PHOTOCHEMICAL FUNNEL

A molecular structure where the *excited state* reactant or intermediate is delivered to the *ground state* to initiate product formation. For a broad class of organic reactions, the structure of the funnel can take the form of a *conical intersection* or a *singlet-triplet crossing*.

PHOTOCHEMICAL REACTION

This term is generally used to describe a chemical reaction caused by *absorption* of ultraviolet, visible, or infrared radiation. There are many *ground state* reactions which have photochemical counterparts. Among these are photoadditions, photocycloadditions, photoeliminations, photoenolizations, *photo-Fries rearrangements*, photoisomerizations, *photooxidations*, *photoreductions*, photosubstitutions, etc.

PHOTOCHEMICAL REACTION PATH

Description of the behaviour, at a molecular level, from energy absorption to product formation. This involves the computation of the *MERP* connecting the *Franck-Condon* point, located on the *potential-energy surface* of the spectroscopic state, to the final photoproducts located on the ground state potential-energy surface

PHOTOCHEMICAL SMOG

Product of *photochemical reactions* caused by solar radiation and occurring in polluted air.

PHOTOCHEMISTRY

The branch of chemistry concerned with the chemical effects of light (far UV to IR).

See *photochemical reaction*.

PHOTOCHROMISM

A photoinduced transformation of a molecular structure (*e.g.* of a solution), *photochemically* and/or thermally reversible, that produces a spectral change, typically, but not necessarily, of visible color.

PHOTOCONDUCTIVITY

Increase in electrical conductivity resulting from photoproduction of charge carriers.

PHOTOCROSSLINKING

Photoinduced formation of a covalent linkage between two macromolecules or between two different parts of one macromolecule.

PHOTOCURING

Technical expressions for the photoinduced hardening of a monomeric, oligomeric or polymeric substrate normally in the form of a film.

PHOTOCURRENT YIELD

The *quantum efficiency* of charge photo-generation between the two electrodes of a *photovoltaic cell* or a *photoelectrochemical cell*.

PHOTODEGRADATION

The photochemical transformation of a molecule into lower molecular weight fragments, usually in an oxidation process. This term is widely used in the destruction (oxidation) of pollutants by UV-based processes. The term is also widely used in the decomposition of polymers by UV-visible based processes which deplete the characteristic properties of the polymer.

PHOTODETACHMENT (of electrons)

Ejection of an electron from a negative ion upon *photoexcitation*.

PHOTODYNAMIC EFFECT

A term used in photobiology to refer to photoinduced damage requiring the simultaneous presence of light, *photosensitizer* and molecular oxygen. A sensitized *photooxidation* which involves molecular oxygen.

PHOTOELECTRICAL EFFECT

The ejection of an electron from a solid or a liquid by a photon.

PHOTOELECTROCHEMICAL CELL

An electrochemical cell in which current and a voltage are simultaneously produced upon *absorption* of light by one or more of the electrodes. Usually at least one of the electrodes is a semiconductor.

PHOTOELECTROCHEMICAL ETCHING

The dissolution of a semiconductor in an electrolytic solution upon exposure to light. Used in the photopatterning of semiconductor surfaces.

PHOTOELECTROCHEMISTRY

A term applied to a hybrid field of chemistry employing techniques which combine photochemical and electrochemical methods for the study of the oxidation-reduction chemistry of the ground or *excited states* of molecules or ions. In general, it is the chemistry resulting from the interaction of light with electrochemical systems.

See also *photoelectrochemical*, *photogalvanic*, *photovoltaic cell*.

PHOTOELECTRON SPECTROSCOPY (PES)

A spectroscopic technique which measures the kinetic energy of electrons emitted upon the ionization of a substance by high energy monochromatic *photons*. A photoelectron spectrum is a plot of the number of electrons emitted versus their kinetic energy. The spectrum consists of bands due to transitions from the *ground state* of an atom or molecular entity to the ground and *excited states* of the corresponding radical cation. Approximate interpretations are usually based on *Koopmans' theorem* relating ionisation potentials to orbital energies. *UPS* (ultra-violet photoelectron spectroscopy) is the spectroscopy using vacuum ultraviolet sources, while *ESCA* (electron spectroscopy for chemical analysis) and *XPS* use X-ray sources.

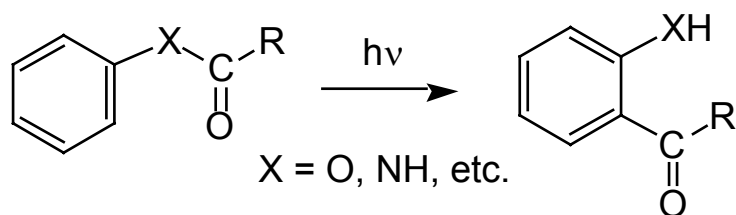
PHOTOEXCITATION

The production of an *excited state* by the absorption of ultraviolet, visible, or infrared radiation.

PHOTO-FRIES REARRANGEMENT

A photorearrangement of O-acyl phenols or N-acyl anilines to give the [1,3]-rearranged

product (as well as the [1,5] rearranged product).



PHOTOGALVANIC CELL

An electrochemical cell in which current or voltage changes result from photochemically generated changes in the relative concentrations of reactants in a solution phase oxidation-reduction couple.

Compare *photovoltaic cell*.

PHOTOIMAGING

See *imaging*.

PHOTOINDUCED ELECTRON TRANSFER

An *electron transfer* resulting from an electronic state produced by the resonant interaction of electromagnetic radiation with matter.

PHOTOINDUCED POLYMERIZATION

Polymerization of a monomer by a free radical or ionic chain reaction initiated by *photoexcitation*.

See *photoinitiation*.

PHOTOINITIATION

Photoproduction of a free radical or ion capable of initiating a chain reaction such as a polymerization.

See *photoinduced polymerization*.

PHOTOIONIZATION

Ejection of an electron into a surrounding medium induced by the absorption of electromagnetic radiation, from a neutral or positively charged molecular entity.

See also *photodetachment*.

PHOTOLUMINESCENCE

Luminescence arising from *photoexcitation*.

PHOTOLYSIS

A light-induced bond cleavage. This term is often used incorrectly to describe irradiation of a sample, although in the combination *flash photolysis* this usage is accepted.

PHOTON

The *quantum* of electromagnetic energy at a given *frequency*. This energy, $E = h\nu$, is the product of the Planck constant (h) and the *frequency* of the radiation (ν).

See also *quantum*.

PHOTON COUNTING

Also called single photon counting. The recording of sequential single *photons* counted by way of recording and counting electron pulses. Each electron pulse consists of $10^5 - 10^6$ electrons resulting from the multiplication, in the "dynode" arrangement (or the microchannel plate) of a photomultiplier, of a single photoelectron emitted by a photosensitive layer, the photocathode of the photomultiplier. This technique is used for two purposes:

- (1) the sensitive measurement of low levels of radiation and
- (2) the recording of emission decays.

See *time-correlated single photon counting*.

PHOTON EMITTANCE

See *photon exitance*.

PHOTON EXITANCE (M_p)

The *photon flow*, N_p , emitted by an element of the surface containing the source point under

consideration divided by the area (S) of that element. ($d\Phi_p/dS$, simplified expression:

$M_p = N_p/S$ when the photon flow is constant over the surface area considered). The SI unit is $s^{-1} m^{-2}$. The term can be used with the amount of photons (mol or its equivalent *einstein*), the SI unit then being $mol s^{-1} m^{-2}$, or $einstein s^{-1} m^{-2}$. Also called specific photon emission. Formerly called photon emittance.

See *spectral photon exitance*.

See also *radiant exitance*.

PHOTON EXPOSURE (H_p)

The *photon irradiance*, E_p , integrated over the time of irradiation ($\int E_p dt$, simplified expression: $H_p = E_p t$ when the photon irradiance is constant over the time considered). The SI unit is m^{-2} . The term can be used with the amount of photons (mol or its equivalent *einstein*), the SI unit then being $mol m^{-2}$ or $einstein m^{-2}$. For a parallel and perpendicularly incident beam not scattered or reflected by the target or its surroundings *photon fluence* (H'_p) is an equivalent term.

See also *fluence*, *radiant exposure*.

PHOTON FLOW (N_p , Φ_p)

The number of *photons* (quanta, N) per unit time. (dN/dt , simplified expression: $N_p = N/t$ when the number of photons is constant over the time considered). The SI unit is s^{-1} . The term can be used with the amount of photons (mol or its equivalent *einstein*), the SI unit then being $mol s^{-1}$ or $einstein s^{-1}$. We prefer the symbol N_p since in photochemistry Φ is reserved for *quantum yield*.

See *spectral photon flow*.

See also *radiant power*.

PHOTON FLUENCE (H'_p)

The amount of photons (quanta) from all directions incident on an infinitesimally small sphere of cross-sectional area S , divided by dS . The *photon fluence rate*, E'_p , integrated over the duration of the irradiation ($\int E'_p dt$, simplified expression: $H'_p = E'_p t$ when E'_p is constant over the

time considered). *Photons* per unit area (quanta m^{-2}). The SI unit is m^{-2} . The term can be used with the amount of photons (mol or its equivalent *einstein*), the SI unit then being mol m^{-2} or einstein m^{-2}

See also *fluence*.

PHOTON FLUENCE RATE (E'_p)

The rate of *photon fluence*. Total number of photons incident per unit time from all directions onto an infinitesimally small sphere of cross-sectional area dS divided by dS . The SI unit is $\text{m}^{-2} \text{s}^{-1}$. The term can be used with the amount of photons (mol or its equivalent *einstein*), the SI unit then being $\text{mol m}^{-2} \text{s}^{-1}$ or $\text{einstein m}^{-2} \text{s}^{-1}$. It reduces to *photon irradiance* for a parallel and normally incident beam not scattered or reflected by the target or its surroundings.

See *photon radiance*.

See also *fluence rate*.

PHOTON FLUX

Same as *photon irradiance*.

PHOTON IRRADIANCE (E_p)

The *photon flow*, N_p , incident on an infinitesimal element of surface of area dS containing the point under consideration divided by dS (dN_p/dS , simplified expression: $E_p = N_p/S$ when the photon flow is constant over the surface considered). The SI unit is $\text{m}^{-2} \text{s}^{-1}$. The term can be used with the amount of photons (mol or its equivalent *einstein*), the SI unit then being $\text{mol m}^{-2} \text{s}^{-1}$ or $\text{einstein m}^{-2} \text{s}^{-1}$. For a parallel and perpendicularly incident beam not scattered or reflected by the target or its surroundings *photon fluence rate* (E'_p) is an equivalent term.

See *spectral photon irradiance*.

See also *irradiance*.

PHOTON RADIANCE (L_p)

For a parallel beam it is the *photon flow*, N_p , leaving or passing through an infinitesimal transparent element of surface in a given direction from the source divided by the orthogonally

projected area of the element in a plane normal to the given direction of the beam, θ , $[(dN_p/dS)/\cos \theta]$, simplified expression: $L_p = N_p/(S \cos \theta)$ when the photon flow is constant over the surface area considered]. The SI unit is $\text{m}^{-2} \text{s}^{-1}$. For a divergent beam propagating in an elementary cone of the solid angle $d\omega$ containing the direction θ , the photon radiance is $d^2N_p/(d\omega dS \cos \theta)$, with SI unit $\text{m}^{-2} \text{s}^{-1} \text{sr}^{-1}$. The term can be used with the amount of photons (mol or its equivalent *einstein*), the SI unit then being $\text{mol m}^{-2} \text{s}^{-1}$ (or *einstein m}^{-2} \text{s}^{-1}*) and $\text{mol m}^{-2} \text{s}^{-1} \text{sr}^{-1}$ (or *einstein m}^{-2} \text{s}^{-1} \text{sr}^{-1}*) respectively.

See *spectral photon radiance*.

See also *radiance*.

PHOTOOXIDATION

Oxidation reactions induced by light. Common processes are:

(1) The loss of one or more electrons from a chemical species as a result of *photoexcitation* of that species;

(2) The reaction of a substance with oxygen under the influence of light. When oxygen remains in the product this latter process is also called *photooxygenation*. Reactions in which neither the substrate nor the oxygen are electronically excited are sometimes called photoinitiated oxidations.

Compare *photoreduction*.

PHOTOOXYGENATION

Incorporation of molecular oxygen into a molecular entity. There are three common mechanisms:

Type I: the reaction of *triplet* molecular oxygen with radicals formed photochemically.

Type II: the reaction of photochemically produced *singlet molecular oxygen* with molecular entities to give rise to oxygen containing molecular entities.

The third mechanism proceeds by electron transfer producing superoxide anion as the reactive species.

Compare *photooxidation*.

PHOTOPHYSICAL PROCESSES

Photoexcitation and subsequent events which lead from one to another state of a molecular entity through *radiation* and *radiationless transitions*. No chemical change results.

PHOTOPOLYMERIZATION

Polymerization processes requiring a photon for the propagation step.

See also *photoinduced polymerization*.

PHOTOREACTION

See *photochemical reaction*.

PHOTOREDUCTION

Reduction reactions induced by light. Common processes are:

- (1) Addition of one or more electrons to a *photoexcited* species;
- (2) The photochemical hydrogenation of a substance.

Reactions in which the substrate is not electronically excited are sometimes called photoinitiated reductions.

Compare *photooxidation*.

PHOTORESIST

A *photoimaging* material, generally applied as a thin film, whose particular properties (usually the local solubility) can be altered *photochemically*. A subsequent development step produces an image which is useful for the fabrication of microelectronic devices (*e.g.*, integrated circuits).

PHOTOSELECTION

The selection by an exciting light beam of a sub-ensemble of molecules oriented preferentially towards \mathbf{E} (the electric vector of the exciting light). If the original (unirradiated) ensemble is isotropic, and the exciting light is plane-polarized, the photoselected sub-ensemble possesses uniaxial symmetry around \mathbf{E} . A two-step photoselection experiment consists of excitation (first step) and detection of the orientational order so created (second step). If the detection entails a measurement of the anisotropy of the resulting emission (fluorescence or phosphorescence), one speaks of polarized luminescence; if it entails the anisotropy of absorption by the excited molecules (or some other photoproduct), the name photoinduced dichroism is used

to emphasize the origin of the anisotropy. The foregoing considerations can be extended in a straightforward manner if the initial ensemble of molecules happens to possess *uniaxial symmetry* and its director is parallel to E ; any other alignment would deprive the photoselected molecules of uniaxial symmetry, and the concept of anisotropy would lose its significance.

See *absorption anisotropy, anisotropy, dichroism, emission anisotropy*

PHOTOSENSITIZATION

The process by which a *photochemical* or *photophysical* alteration occurs in one molecular entity as a result of initial *absorption* of radiation by another molecular entity called a *photosensitizer*. In mechanistic *photochemistry* the term is limited to cases in which the *photosensitizer* is not consumed in the reaction.

See *energy transfer*.

PHOTOSENSITIZER

See *photosensitization*.

PHOTOSTATIONARY STATE

A steady state reached by a reacting chemical system when light is absorbed by at least one of the components. At this state the rates of formation and disappearance are equal for each of the transient molecular entities formed.

PHOTOTHERMAL EFFECT

An effect produced by *photoexcitation* resulting partially or totally in the production of heat.

PHOTOTHERMOGRAPHY

A process utilizing both light and heat, simultaneously or sequentially, for image recording.

PHOTOVOLTAIC CELL

A solid state device, usually a semiconductor, such as silicon, which absorbs *photons* with energies higher than or equal to the *bandgap energy* and simultaneously produces electric power.

Compare *photogalvanic cell*.

PIEZOLUMINESCENCE

Luminescence observed when certain solids are subjected to a change in pressure.

See *triboluminescence*.

POLARIZATION

See *light polarization, transition polarization*.

POLARIZED ABSORPTION SPECTROSCOPY

The traditional statement of the *Beer-Lambert law* tacitly assumes that the measured *absorbance* will be independent of the state of polarization of the beam. If the orientation of the molecules is non-random, the absorbance of the sample for a plane polarized beam will change as the plane of polarization is rotated; such a sample is said to be anisotropic (on the bulk) or dichroic. When dealing with electric dipole transitions in an anisotropic sample, it is advantageous to set $\varepsilon = \varepsilon_0 \cos^2 \theta$, where θ is the angle between the transition moment and the direction of polarization of the measuring beam, and restate the *Beer-Lambert law* in the form shown below:

$$P_\lambda = P_\lambda^0 10^{-\varepsilon_0 \langle \cos^2 \theta \rangle cl},$$

where angular brackets denote an ensemble average. The absorbance attains its maximum value, $\varepsilon_0 cl$, if $\theta = 0$, and vanishes if $\theta = \pi/2$; for random orientation $\langle \cos^2 \theta \rangle = 1/3$.

See *anisotropy*

POLARIZED ELECTRONIC TRANSITIONS

An electronic transition may be spherical, planar or linear depending on the behaviour of the components of the transition moment $\boldsymbol{\mu} = \mu_x \hat{\mathbf{e}}_x + \mu_y \hat{\mathbf{e}}_y + \mu_z \hat{\mathbf{e}}_z$ on the rotation of a molecule-based coordinate frame (O -xyz). A transition, or *absorption* itself, is said to be isotropic (or spherical or unpolarized) if all three components remain equal; planar, if one of the components (say μ_z) vanishes for a particular orientation; linear, if two components can be made to vanish. Planar absorption occurs only in uniaxial molecules (where Oz is an n -fold axis of rotation, with $n \geq 3$); such molecules can also exhibit linear absorption along the z -axis. If its symmetry is lower than uniaxial, a molecule can only exhibit linear absorption.

See *anisotropy, electronic transition moment, uniaxial systems*

POPULATION INVERSION

A situation in which a higher energy state is more populated than a lower energy state.

POTENTIAL-ENERGY SURFACE

Within the Born-Oppheimer approximation, the function of the total energy of a molecular system (minus kinetic energy of the nuclei) versus the coordinates of all nuclei in the system.

PRECURSOR COMPLEX

May either indicate an *encounter complex* or a *collision complex*, but furthermore implies that this complex undergoes a reaction (*e.g. electron transfer*).

PREDISSOCIATION

Dissociation occurring by *tunnelling* from a "bound" to an "unbound" *rovibronic state*. In an absorption spectrum of a molecular entity, the appearance of a diffuse band region within a series of sharp bands, is called predissociation, since irradiation with *frequencies* within the diffuse region leads to effective dissociation. The energy of the band is smaller than that of the dissociation continuum of the bound state.

PRIMARY (PHOTO)PROCESS

See *primary photochemical process*. The term primary (photo)process for *photophysical processes* is apt to lead to inconsistencies, and its use is therefore discouraged.

PRIMARY PHOTOCHEMICAL PROCESS (Primary Photoreaction)

Any elementary chemical process undergone by an electronically excited molecular entity and yielding a *primary photoproduct*.

See *primary (photo)process*.

PRIMARY (PHOTO)PRODUCT

The first observable chemical entity which is produced in the *primary photochemical process* and which is chemically different from the reactant.

See *primary (photo)process*.

PSEUDO JAHN-TELLER EFFECT

Same as second order *Jahn-Teller effect*.

PUMP-PROBE TECHNIQUE

A *flash photolysis* technique involving the use of two light pulses: a high intensity one (pump) for excitation and a low intensity one (probe) for spectral analysis. Often the probe pulse is generated from a portion of the excitation beam, but it can also be an independently generated pulse. A time delay between the pump and probe pulses allows the obtention of kinetic data.

$\pi \rightarrow \pi^*$ TRANSITION

An electronic transition described approximately as a promotion of an electron from a "bonding" π orbital to an "antibonding" π orbital designated as π^* .

π - π^* STATE

An *excited state* related to the *ground state* by a $\pi \rightarrow \pi^*$ transition.

$\pi \rightarrow \sigma^*$ TRANSITION

An electronic transition described approximately as a promotion of an electron from a "bonding" π orbital to an "antibonding" σ orbital designated as σ^* . Such transitions generally involve high transition energies and appear close to or mixed with *Rydberg transitions*.

QM/MM

Quantum Mechanics/Molecular Mechanics.

Q-SWITCHED LASER

A *laser* in which the state of the device introducing important losses in the resonant cavity and preventing *lasing* operation is suddenly switched to a state where the device introduces very low losses. This increases rapidly the Quality factor of the cavity, allowing the build-up of a short and very intense laser pulse. Typical pulse durations are in the ns range. The Q-switching may be active (a rotating mirror or electro-optic device) or passive (a saturable absorber).

See also *free-running laser*.

QUANTUM (of radiation)

An elementary particle of electromagnetic energy in the sense of the wave-particle duality.

See *photon*.

QUANTUM COUNTER

A medium emitting with a *quantum yield* independent of the excitation energy over a defined spectral range (e.g., concentrated rhodamine 6G solutions between 300 and 600 nm). Also used for devices producing an electrical signal proportional to the *photon flux* absorbed in a medium.

QUANTUM EFFICIENCY

See *efficiency*. For a *primary photochemical process*, quantum efficiency is identical to *quantum yield*.

QUANTUM YIELD (Φ)

The number of defined events which occur per photon absorbed by the system. The integral quantum yield is

$$\Phi = \frac{\text{number of events}}{\text{number of photons absorbed}}$$

For a *photochemical reaction*,

$$\Phi = \frac{\text{amount of reactant consumed or product formed}}{\text{amount of photons absorbed}}$$

The differential quantum yield is

$$\Phi = \frac{d[x]/dt}{n},$$

where $d[x]/dt$ is the rate of change of a measurable quantity (spectral or any other property), and n

the amount of *photons* (mol or its equivalent *einstein*) absorbed per unit time. Φ can be used for *photophysical processes* or *photochemical reactions*.

Note: Strictly, the term quantum yield applies only for monochromatic excitation.

See also *efficiency*.

QUANTUM MECHANICS/MOLECULAR MECHANICS (QM/MM)

Hybrid procedure for the treatment of large molecular systems. A crucial part of the system (e.g. the chromophore and its surroundings) is treated explicitly by quantum mechanical (QM) techniques, whereas the rest of the system is approximated by a classical or molecular mechanics (MM) force field treatment.

QUARTET STATE

A state having a total electron spin quantum number equal to 3/2.

See *multiplicity*.

QUARTZ-IODINE LAMP

A tungsten filament high-intensity incandescent lamp which contains iodine in a quartz envelope. Used primarily as a source of visible light.

QUENCHER

A molecular entity that *deactivates* (quenches) an *excited state* of another molecular entity, either by *energy transfer*, electron transfer, or by a chemical mechanism.

See *quenching*, *Stern-Volmer kinetic relationships*.

QUENCHING

The *deactivation* of an excited molecular entity intermolecularly by an external environmental influence (such as a *quencher*) or intramolecularly by a substituent through a *nonradiative process*. When the external environmental influence (quencher) interferes with the behavior of the *excited state* after its formation, the process is referred to as *dynamic quenching*. Common mechanisms include *energy transfer*, charge transfer, etc. When the environmental influence inhibits the excited state formation the process is referred to as *static quenching*.

See *Stern-Volmer kinetic relationships*.

QUENCHING CONSTANT

See *quencher, quenching, Stern-Volmer kinetic relationships*.

RADIANCE (L)

For a parallel beam it is the *radiant power*, P , of all wavelengths leaving or passing through an infinitesimal element of surface in a given direction from the source divided by the orthogonally projected area of the element in a plane normal to the given direction of the beam, θ , $[(dP/dS)/\cos\theta]$, simplified expression: $L = P/(S \cos\theta)$ when the radiant power is constant over the surface area considered]. The SI unit is W m^{-2} . Note that $L = \int_{\lambda} L_{\lambda} d\lambda$, where L_{λ} is the *spectral radiance* at wavelength λ . For a divergent beam propagating in an elementary cone of the solid angle $d\omega$ containing the given direction θ , the radiance is $d^2P/(d\omega dS \cos\theta)$, with SI units $\text{W m}^{-2} \text{sr}^{-1}$.

See also *photon flow, photon radiance, spectral radiance, spherical radiance*.

RADIANT EMITTANCE

See *radiant exitance*.

RADIANT ENERGY (Q)

The total energy emitted, transferred or received as radiation of all wavelengths in a defined period of time ($Q = \int_{\lambda} Q_{\lambda} d\lambda$). It is the product of *radiant power*, P , and time, t : $Q = P t$ when the radiant power is constant over the time considered. The SI unit is J.

See also *spectral radiant power*.

RADIANT (ENERGY) FLUX (P, Φ)

This term is not recommended.

Flux is generally used in the sense of the 'rate of transfer of fluid, particles or energy across a given surface'. We adopt *radiant power*, P . ($P = dQ/d\tau$, simplified expression: $P = Q/t$ when the radiant energy, Q , is constant over the time considered). In *photochemistry* Φ is reserved for *quantum yield*.

See also *photon flow*, *photon radiance*, *radiant energy*, *spectral radiant flux*.

RADIANT EXITANCE (M)

The *radiant power*, P , emitted at all wavelengths by an element of surface containing the source point under consideration of area dS divided by dS . (dP/dS , simplified expression: $M = P/S$ when the radiant power is constant over the surface area considered). It is the integration of the radiant power leaving a source over the solid angle and over the whole *wavelength* range. The SI unit is $W\ m^{-2}$. Note that $M = \int_{\lambda} M_{\lambda} d\lambda$, where M_{λ} is the *spectral radiant exitance* at wavelength λ .

Formerly called radiant emittance. Same as spherical radiant exitance.

See also *photon exitance*, *spectral radiant exitance*.

RADIANT EXPOSURE (H)

The *irradiance*, E , integrated over the time of irradiation ($\int E dt$, simplified expression $H = E t$ when the irradiance is constant over the time considered). The SI unit is $J\ m^{-2}$. For a parallel and perpendicularly incident beam not scattered or reflected by the target or its surroundings *fluence* (H') is an equivalent term.

RADIANT INTENSITY (I)

Radiant power, P , at all wavelengths per unit solid angle, ω . The radiant power emitted in a given direction by a source or an element of the source in an infinitesimal cone containing the given direction divided by the solid angle of the cone ($dP/d\omega$, simplified expression: $I = P/S$ when the radiant power is constant over the surface area considered). The SI unit is $W\ sr^{-1}$. Note that $I = \int_{\lambda} I_{\lambda} d\lambda$, where I_{λ} is the *spectral radiant intensity* at wavelength λ .

See also *spectral radiant intensity*.

RADIANT POWER (P)

Power emitted, transferred or received as radiation. The SI unit is $J\ s^{-1} = W$. In radiometry, *Flux* (Φ) is used with the same units as P . However, this is confusing since in general flux conveys the idea of a quantity per unit surface (see *Photon flux*). In addition, the symbol Φ is reserved for *quantum yield* in photochemistry. Therefore, the use of *Flux* (Φ) is not recommended.

See *spectral radiant power*.

RADIATIONLESS DEACTIVATION (Decay)

Loss of electronic excitation energy without photon emission or chemical change.

See *energy transfer, internal conversion, intersystem crossing*.

RADIATIONLESS TRANSITION

A transition between two states of a system without *photon* emission or absorption.

Compare *radiative transition*.

RADIATION TRAPPING

A process by which the *resonance radiation* emitted in a lamp is absorbed and re-emitted many times in the plasma prior to striking the phosphor. This process is called radiation trapping or imprisonment. This radiation trapping lengthens the effective lifetime of emission as viewed from outside the lamp. The control of this trapping is therefore an important design consideration for low pressure lamps.

RADIATIVE ENERGY TRANSFER

Transfer of excitation energy by *radiative deactivation* of a donor molecular entity and reabsorption of the emitted light by an acceptor molecular entity. The probability of transfer is given approximately by

$$P_{\text{rt}} \propto [A]\chi J,$$

where J is the *spectral overlap integral*, $[A]$ is the concentration of the acceptor, and χ is the specimen thickness. This type of *energy transfer* depends on the shape and size of the vessel utilized. Same as *trivial energy transfer*.

See also *Dexter excitation transfer, energy transfer, Förster excitation transfer*.

RADIATIVE LIFETIME (τ_0)

The *lifetime* of an excited molecular entity in the absence of *radiationless transitions*. It is the reciprocal of the first-order rate constant for the radiative step, or of the sum of these rate constants if there is more than one such step. The equivalent term, natural lifetime, is discouraged. Approximate expressions exist relating τ_0 to the *oscillator strength* of the emitting transition.

RADIATIVE TRANSITION

A transition between two states of a molecular entity, the energy difference being emitted or absorbed as a *photon*.

See *luminescence*.

Compare *radiationless deactivation*, *radiationless transition*.

RADICAL PAIR

Two radicals in close proximity, usually within a solvent "cage" or at least sufficiently close to allow spin correlation. The radicals may be formed simultaneously by some unimolecular process, *e.g.*, photochemical bond breaking, or they may have come together by diffusion. A radical pair is called geminate radical pair provided that each radical partner is a descendant of the same parental pair.

RADIOLUMINESCENCE

Luminescence arising from excitation by high energy particles or radiation.

RADIOLYSIS

Bond cleavage induced by high-energy radiation. The term is also more loosely used for any chemical process brought about by high-energy radiation. The term has also been used to refer to the irradiation technique itself ("pulse radiolysis").

RED SHIFT

Informal term for *bathochromic shift*.

REHM-WELLER EQUATION

For photoinduced electron transfer between a neutral acceptor (A) and a neutral donor (D) (either one of them may be the electronically excited molecular entity) to form an ion pair, the standard Gibbs free energy in a solvent with static dielectric constant ϵ_s can be approximated as

$$\Delta G^{\circ} = e [E^{\circ}(D^{+}/D) - E^{\circ}(A/A^{-})] - e^2/(4\pi\epsilon_0\epsilon_s a) - \Delta E_{0,0}$$

with $E^{\circ}(D^{+}/D)$ the standard reduction potential of the donor cation radical resulting from the electron transfer, $E^{\circ}(A/A^{-})$ the standard reduction potential of the acceptor (both relative to the same reference electrode), $e^2/(4\pi\epsilon_0\epsilon_s a)$ the change in Gibbs energy for bringing the two radical ions of unity charge to an encounter distance a (ϵ_0 is the vacuum permittivity and e the charge of the electron), and $\Delta E_{0,0}$ the vibrational zero electronic energy of the excited partner (provided the *Kasha rule* is obeyed, *i.e.*, that an equilibrated excited state at energy $E_{0,0}$ takes part of the reaction), all data referring to the same solvent. In SI units the Coulomb term is $e^2/(4\pi\epsilon_0) = 2.307 \cdot 10^{-28}$ J m. In the above equation this term is written as stabilizing the species resulting from electron transfer, for the general case in which two neutral species give rise to a positive and a negative charge after electron transfer.

The equation can be applied for electron transfer from the *triplet state* in which case the last term on the right side is the triplet energy E_T .

The equation can also be applied to photoinduced electron transfer involving charged species. In these cases the Coulomb term might destabilize the species resulting from the electron transfer and should be written with a + sign.

See also *driving force*.

RELATIVE SPECTRAL RESPONSIVITY (s_{λ})

See *action spectrum*.

RELAXATION

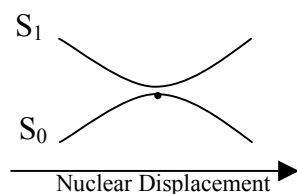
Passage of an excited or otherwise perturbed system towards or into thermal equilibrium with its environment.

See *radiationless deactivation*, *radiationless transition*, *radiative transition*.

RENNER-TELLER EFFECT

The molecular distortion in linear molecular species with degenerate electronic states (*e.g.* belonging to the $C_{\infty v}$ group). The Renner-Teller effect is a particular case of the *Jahn-Teller effect*. From the point of view of the *potential-energy surfaces* the Renner-Teller effect generates a

surface touching (see scheme below).



The Renner-Teller effect arises from splittings in the vibrational levels of molecular entities due to even terms in the *vibronic* perturbation expansion. This is generally a minor effect for nonlinear molecular entities compared to the *Jahn-Teller effect* which is due to the odd terms. For linear molecular entities it is the only possible vibronic effect characteristic of degenerate electronic states.

REORGANIZATION ENERGY (in electron transfer)

Defined as the Gibbs energy dissipated when a system that has undergone "vertical" *electron transfer* (i.e. electron transfer obeying the *Franck Condon principle*) relaxes to the equilibrium state for its new charge distribution. Commonly the total reorganization energy (λ) is written as the sum of an inner contribution (λ_{in}) and an outer contribution (λ_{out}) attributed to nuclear reorganizations of the redox partners and their environment (solvent) respectively.

RESIDUAL ANISOTROPY

The time-dependent anisotropy, $r(t)$, pertaining to a two-step photoselection experiment is defined as follows:

$$r(t) \equiv \langle P_2(\cos\theta_2) \rangle^{\otimes}, \quad P_2(x) \equiv (3x^2 - 1)/2, \quad \cos\theta_2 \equiv \mathbf{E} \cdot \boldsymbol{\mu}_2 / E_Z \mu_2$$

where $\langle \dots \rangle^{\otimes}$ denotes an average over the orientations of the molecules which absorbed a photon (in the first step); \mathbf{E} is the electric vector of the exciting light, and $\boldsymbol{\mu}_k$ the transition moment involved in the k -th step. The asymptotic value $r(t \rightarrow \infty)$, known as residual anisotropy or limiting anisotropy, equals or is proportional to the *order parameter* of the photoselected molecules. Analogous considerations apply to an isotropic assembly of uniaxial subsystems (which retain their orientations), since $\boldsymbol{\mu}_2$ will adopt, in the limit $t \rightarrow \infty$, uniaxial distribution within each subsystem; the limiting anisotropy equals or is proportional to the product of the order parameters of $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$.

See *absorption anisotropy, anisotropy, emission anisotropy, order parameter, photoselection, uniaxial symmetry*

RESONANCE ABSORPTION TECHNIQUE

The monitoring of atoms or radicals generated in the gas phase by observing the attenuation of the radiation from a *lamp* emitting the characteristic *resonance radiation* of the observed species.

RESONANCE FLUORESCENCE

Fluorescence from the primary excited atomic or molecular species at the *wavelength* of the exciting radiation (no relaxation within the excited manifold).

This term is also used to designate the radiation emitted by an atom of the same wavelength as the longest one capable of exciting its fluorescence, *e.g.*, 122.6 nm in the case of the hydrogen atom, and 253.7 nm in the case of the mercury atom.

See also *resonance line*.

RESONANCE FLUORESCENCE TECHNIQUE

The monitoring of atoms or radicals generated in the gas phase by observing the *intensity of fluorescence (exitance)* emitted by the species after excitation with radiation of the same *wavelength*.

RESONANCE LAMP

A *lamp* emitting *resonance radiation* of atoms and their ions. Depending on the requirements the lamp is filled either with pure vapour of the element or with a mixture of it and other gases. *E.g.*, Hg (253.7 and 184.9 nm), Cd (228.8 and 643.8 nm), Na (589.0 nm), Zn (213.8, 330.0, 334.5, and 636.2 nm), Kr (116.5 and 123.6 nm), Xe (129.6 and 147.0 nm).

RESONANCE LINE

The longest *wavelength* capable of exciting *fluorescence* in an atom.

See also *resonance fluorescence*.

RESONANCE RADIATION

Same as *resonance fluorescence*.

ROVIBRONIC STATE

A state corresponding to a particular rotational sublevel of a particular vibrational level of a particular electronic state.

RUBY LASER

A pulsed source of *coherent radiation* emitting mainly at 694.3 nm from chromium ions (Cr⁺³) in aluminum oxide.

See *laser, solid state laser*.

RYDBERG ORBITAL

For an atom, an *orbital* with principal quantum number greater than that of any occupied orbital of the ground state. For a molecular entity, a molecular orbital which correlates with a Rydberg atomic orbital in an atomic fragment produced by dissociation. Typically, the extension of the Rydberg orbital is large compared to the size of the atom or molecular entity.

RYDBERG TRANSITION

An electronic transition described approximately as promotion of an electron from a "bonding" *orbital* to a *Rydberg orbital*. Spectral bands corresponding to Rydberg transitions approximately fit the Rydberg formula

$$\sigma = I - R / (n - \Delta)^2,$$

where σ is the *wavenumber*, I the ionization potential of the atom or molecular entity, n a principal quantum number, R the Rydberg constant, and Δ the quantum defect which differentiates between s, p, d, etc., orbitals. The notation used is, *e.g.*, $\pi \rightarrow ns$.

RYDMR

See *ODMR*.

SACRIFICIAL ACCEPTOR

Molecular entity that acts as the electron acceptor in a *photoinduced electron transfer* process and is not restored in a subsequent oxidation process but is destroyed by irreversible

chemical conversion.

SACRIFICIAL DONOR

Molecular entity that acts as the electron donor in a *photoinduced electron transfer* process and is not restored in a subsequent reduction process but is destroyed by irreversible chemical conversion.

SEMICONDUCTOR LASER

See *diode laser*

SCHENCK SENSITIZATION MECHANISM

The mechanism of chemical transformation of one molecular entity caused by *photoexcitation* of a *sensitizer* which undergoes temporary covalent bond formation with the molecular entity.

SCINTILLATORS

Materials used for the measurement of radioactivity, by recording the *radioluminescence*. They contain compounds (*chromophores*) which combine a high *fluorescence quantum efficiency*, a short *fluorescence lifetime*, and a high solubility. These compounds are employed as solutes in aromatic liquids and polymers to form organic liquid and plastic scintillators, respectively.

SELECTION RULE

A selection rule states whether a given transition is allowed or forbidden, on the basis of the symmetry or spin of the wavefunctions of the initial and final states.

SELF-ABSORPTION

Absorption of part of the *fluorescence* from excited molecular entities by molecular entities of the same species in the *ground state*. The mechanism operating is a *radiative energy transfer*.

SELF-QUENCHING

Quenching of an excited atom or molecular entity by interaction with another atom or molecular entity of the same species in the *ground state*.

See also *Stern-Volmer kinetic relationships*.

SENSITIZER

See *photosensitizer*.

SENSITIZATION

See *photosensitization*.

SIMULTANEOUS PAIR TRANSITIONS

Simultaneous electronic transitions in two coupled absorbers or emitters. Because of the coupling, transitions which are spin-forbidden in one of the centres might become spin allowed (spin flip).

SINGLE PHOTON COUNTING

See *photon counting*.

SINGLE PHOTON TIMING

See *time-correlated single photon counting*.

SINGLET MOLECULAR OXYGEN

The oxygen molecule (dioxygen), O₂, in an excited *singlet* state. The *ground state* of O₂ is a *triplet* ($^3\Sigma_g^-$). The two metastable singlet states derived from the ground state *configuration* are $^1\Delta_g$ and $^1\Sigma_g^-$.

The term singlet oxygen alone, without mention of the chemical species is discouraged since it can also refer to an oxygen atom in a 1S or 1D *excited state*. The oxygen atom ground state is a triplet 3P state and the 1S and 1D states are also derived from the ground state configuration.

SINGLET-SINGLET ANNIHILATION

See *annihilation, spin conservation rule*.

SINGLET-SINGLET ENERGY TRANSFER

Transfer of excitation from an *electronically excited* donor in a *singlet* state to produce an electronically excited acceptor in a singlet state.

See *electron exchange excitation transfer, Förster excitation transfer, radiative energy transfer*.

SINGLET STATE

A state having a total electron spin quantum number equal to 0.

See *multiplicity*.

SINGLET-TRIPLET CROSSING

A point of intersection between states of different *multiplicity* belonging to $(3N - 7)$ -dimensional subspace of the $(3N - 6)$ -dimensional nuclear coordinate space and therefore appears as a line on a two-dimensional energy surface (N is the number of nuclei). In this case the *branching space* is one-dimensional and is defined by the gradient difference vector \mathbf{x}_1

See also *conical intersection*.

SINGLET-TRIPLET ENERGY TRANSFER

Transfer of excitation from an *electronically excited* donor in a *singlet state* to produce an electronically excited acceptor in a *triplet state*.

See *energy transfer, spin conservation rule*.

SOLAR CONVERSION EFFICIENCY

The ratio of the Gibbs energy gain per unit time per m^2 of surface exposed to the sun to and the solar *irradiance*, E , integrated between $\lambda = 0$ and $\lambda = \infty$.

SOLID STATE LASERS

CW or pulsed *lasers* in which the active medium is a solid matrix (crystal or glass) doped with an ion (*e. g.*, Nd^{3+} , Cr^{3+} , Er^{3+}). The emitted *wavelength* depends on the active ion, the selected optical transition, and the matrix. Some of these lasers are tunable within a very broad range (*e. g.*, from 700 to 1000 nm for Ti^{3+} doped sapphire).

Pulsed lasers may be *free-running*, *Q-switched*, or *mode-locked*. Some *CW* lasers may be mode-locked.

SOLVATOCHROMISM

The (pronounced) change in position and sometimes intensity of an electronic absorption or emission band, accompanying a change in solvent polarity.

SOLVENT-SEPARATED ION PAIR

Pair of ions separated by at least one solvent molecule. During electron-transfer processes between neutral molecular species, solvent separated ion pairs may form either directly or via solvation-induced separation of *contact ion pairs*.

See also *contact ion pair*.

SOLVENT SHIFT

A shift in the *frequency* of a spectral band of a chemical species arising from interaction with its solvent environment.

See *bathochromic shift*, *hypsochromic shift*, *solvatochromism*

SONOLUMINESCENCE

Luminescence induced by sound waves.

See *triboluminescence*.

SPECIFIC PHOTON EMISSION

Same as *photon exitance*.

SPECTRAL (PHOTON) EFFECTIVENESS

The reciprocal of the *photon fluence rate*, E'_p , at *wavelength* λ , causing identical photoresponse, Δy , per unit time ($\Delta y/\Delta t$). The effectiveness spectrum is directly proportional to the *conversion spectrum* of the sensory pigment, if spectral attenuation is negligible.

SPECTRAL IRRADIANCE (E_λ)

Irradiance, E , at *wavelength* λ per unit wavelength interval. The SI unit is W m^{-3} , but a commonly used unit is $\text{W m}^{-2} \text{nm}^{-1}$.

SPECTRAL OVERLAP

In the context of *radiative energy transfer*, it is the integral, $J = \int_0^\infty f'_D(\sigma) \varepsilon_A(\sigma) d\sigma$, which measures the overlap of the *emission spectrum* of the excited donor, D, and the absorption spectrum

of the *ground state* acceptor, A. f'_D is the measured normalized emission of D, $f'_D = f_D(\sigma) / \int_0^\infty f_D(\sigma) d\sigma$, $f_D(\sigma)$ is the *photon exitance* of the donor at wavenumber σ , and $\varepsilon_A(\sigma)$ is the *decadic molar absorption coefficient* of A at wavenumber σ .

In the context of *Förster excitation transfer* J is given by:

$$J = \int_0^\infty \frac{f'_D(\sigma) \varepsilon_A(\sigma)}{\sigma^4} d\sigma$$

In the context of *Dexter excitation transfer* J is given by

$$J = \int_0^\infty f_D(\sigma) \varepsilon_A(\sigma) d\sigma$$

In this case f_D and ε_A , the emission spectrum of donor and absorption spectrum of acceptor, respectively, are both normalized to unity, so that the rate constant for energy transfer, k_{ET} , is independent of the *oscillator strength* of both transitions (contrast to Förster mechanism). For the units of J , see the list of symbols.

See *energy transfer*.

SPECTRAL PHOTON EXITANCE ($M_{p\lambda}$)

The *photon exitance*, M_p , at *wavelength* λ per unit wavelength interval. The SI unit is $s^{-1} m^{-3}$, but a commonly used unit is $s^{-1} m^{-2} nm^{-1}$. The term can be used with the amount of photons (mol or its equivalent *einstein*), the SI unit then being $mol s^{-1} m^{-3}$ (or $einstein s^{-1} m^{-3}$) and the common unit $mol s^{-1} m^{-2} nm^{-1}$ (or $einstein s^{-1} m^{-2} nm^{-1}$)

SPECTRAL PHOTON FLOW ($N_{p\lambda}, \Phi_{p\lambda}$)

The *photon flow*, N_p , at *wavelength* λ per unit wavelength interval. The SI unit is $s^{-1} m^{-1}$, but a commonly used unit is $s^{-1} nm^{-1}$. The term can be used with the amount of photons (mol or its equivalent *einstein*), the SI unit then being $mol s^{-1} m^{-1}$ (or $einstein s^{-1} m^{-1}$) and the common unit $mol s^{-1} nm^{-1}$ (or $einstein s^{-1} nm^{-1}$)

SPECTRAL PHOTON FLUX (PHOTON IRRADIANCE) ($E_{p\lambda}$)

The *photon irradiance*, E_p , at wavelength λ per unit wavelength interval. The SI unit is $\text{s}^{-1} \text{m}^{-3}$, but a commonly used unit is $\text{s}^{-1} \text{m}^{-2} \text{nm}^{-1}$. The term can be used with the amount of photons (mol or its equivalent *einstein*), the SI unit then being $\text{mol s}^{-1} \text{m}^{-3}$ (or $\text{einstein s}^{-1} \text{m}^{-3}$) and the common unit $\text{mol s}^{-1} \text{m}^{-2} \text{nm}^{-1}$ (or $\text{einstein s}^{-1} \text{m}^{-2} \text{nm}^{-1}$)

SPECTRAL PHOTON RADIANCE ($L_{p\lambda}$)

The *photon radiance*, L_p , at wavelength λ per unit wavelength interval. The SI unit is $\text{s}^{-1} \text{m}^{-3} \text{sr}^{-1}$, but a commonly used unit is $\text{s}^{-1} \text{m}^{-2} \text{sr}^{-1} \text{nm}^{-1}$. The term can be used with the amount of photons (mol or its equivalent *einstein*), the SI unit then being $\text{mol s}^{-1} \text{m}^{-3} \text{sr}^{-1}$ (or $\text{einstein s}^{-1} \text{m}^{-3} \text{sr}^{-1}$) and the common unit $\text{mol s}^{-1} \text{m}^{-2} \text{sr}^{-1} \text{nm}^{-1}$ ($\text{einstein s}^{-1} \text{m}^{-2} \text{sr}^{-1} \text{nm}^{-1}$)

SPECTRAL RADIANCE (L_λ)

The *radiance*, L , at wavelength λ per unit wavelength interval. The SI unit is $\text{W m}^{-3} \text{sr}^{-1}$, but a commonly used unit is $\text{W m}^{-2} \text{sr}^{-1} \text{nm}^{-1}$.

SPECTRAL RADIANT EXITANCE (M_λ)

The *radiant exitance*, M , at wavelength λ per unit wavelength interval. The SI unit is W m^{-3} , but a commonly used unit is $\text{W m}^{-2} \text{nm}^{-1}$.

SPECTRAL RADIANT INTENSITY (I_λ)

The *radiant intensity*, I , at wavelength λ per unit wavelength interval. The SI unit is $\text{W m}^{-1} \text{sr}^{-1}$, but a commonly used unit is $\text{W nm}^{-1} \text{sr}^{-1}$.

SPECTRAL RADIANT POWER (P_λ)

The *radiant power* at wavelength λ per unit wavelength interval. The SI unit is W m^{-1} , but a commonly used unit is W nm^{-1} .

SPECTRAL RESPONSIVITY

The spectral output quantity of a system such as a photomultiplier, diode array, photoimaging device, or biological unit divided by the *spectral irradiance* $s(\lambda) = \text{d}y(\lambda)/\text{d}E(\lambda)$, simplified expression: $s(\lambda) = Y_\lambda/E_\lambda$, where Y_λ is the magnitude of the output signal for irradiation

at wavelength λ and E_λ is the spectral irradiance of parallel and perpendicular incident beam at the same wavelength.

SPECTRAL SENSITIVITY

See *spectral responsivity*.

SPECTRAL SENSITIZATION

The process of increasing the *spectral responsivity* of a (*photoimaging*) system in a certain wavelength region.

SPHERICAL RADIANCE

Same as *radiant exitance*, M . It is the integration of the *radiant power*, P , leaving a source over the solid angle and over the whole *wavelength range*. The SI unit is W m^{-2} .

SPHERICAL RADIANT EXPOSURE

Same as *fluence*.

SPIN-ALLOWED ELECTRONIC TRANSITION

An electronic transition which does not involve a change in the spin part of the wavefunction.

SPIN CONSERVATION RULE (Wigner rule)

Upon transfer of electronic energy between an excited atom or molecular entity and other atom or molecular entity in its ground or *excited state*, the overall spin angular momentum of the system, a vector quantity, should not change.

See *annihilation*.

SPIN FLIP

See *simultaneous pair transitions*.

SPIN-ORBIT COUPLING

The interaction of the electron spin magnetic moment with the magnetic moment due to the orbital motion of the electron. One consequence of spin-orbit coupling is the mixing of zero-order

states of different *multiplicity*. This effect may result in *fine structure* called *spin-orbit splitting*.

SPIN-ORBIT SPLITTING

Removal of state degeneracy by *spin-orbit coupling*.

SPIN-SPIN COUPLING

The interaction between the spin magnetic moments of different electrons and/or nuclei. It causes, e.g. the multiplet pattern in nuclear magnetic resonance spectra.

SPONTANEOUS EMISSION

That mode of *emission* which occurs even in the absence of a perturbing external electromagnetic field. The transition between states, n and m , is governed by the Einstein coefficient of spontaneous emission, A_{nm} .

See also *stimulated emission*.

STARK EFFECT

Splitting or shifts of spectral lines in an electric field. Also called electrochromic effect.

STATE CROSSING

See *avoided crossing*, *singlet-triplet crossing*, *surface crossing*.

STATE DIAGRAM

See *Jablonski diagram*.

STATIC QUENCHING

See *quenching*.

STERN-VOLMER KINETIC RELATIONSHIPS

This term applies broadly to variations of *quantum yields* of *photophysical processes* (e.g., *fluorescence* or *phosphorescence*) or *photochemical reaction* (usually reaction *quantum yield*) with the concentration of a given reagent which may be a substrate or a *quencher*. In the simplest case, a plot of Φ^0/Φ (or M^0/M for *emission*) vs. concentration of quencher, [Q], is linear, obeying the equation

$$\Phi^0/\Phi \text{ or } M^0/M = 1 + K_{sv} [Q]. \quad (1)$$

In equation (1) K_{sv} is referred to as the Stern-Volmer constant. Equation (1) applies when a quencher inhibits either a *photochemical reaction* or a *photophysical process* by a single reaction. Φ^0 and M^0 are the quantum yield and emission intensity (*radiant exitance*), respectively, in the absence of the quencher Q, while Φ and M are the same quantities in the presence of the different concentrations of Q. In the case of dynamic *quenching* the constant K_{sv} is the product of the true *quenching* constant k_q and the *excited state lifetime*, τ^0 , in the absence of quencher. k_q is the bimolecular reaction rate constant for the elementary reaction of the excited state with the particular quencher Q. Equation (1) can therefore be replaced by the expression (2)

$$\Phi^0/\Phi \text{ or } M^0/M = 1 + k_q \tau^0 [Q]. \quad (2)$$

When an excited state undergoes a bimolecular reaction with rate constant k_r to form a product, a double-reciprocal relationship is observed according to the equation

$$1/\Phi_p = (1 + 1/k_r \tau^0 [S]) [1/(A.B)] \quad (3)$$

where Φ_p is the quantum *efficiency* of product formation, A the formation efficiency of the reactive excited state, B the fraction of reactions of the excited state with substrate S which leads to product, and [S] is the concentration of reactive ground-state substrate. The intercept/slope ratio gives $k_r \tau^0$. If [S] = [Q], and if a photophysical process is monitored, plots of equations (2) and (3) should provide independent determinations of the product-forming rate constant k_r . When the lifetime of an excited state is observed as a function of the concentration of S or Q, a linear relationship should be observed according to the equation

$$\tau^0/\tau = 1 + k_q \tau^0 [Q], \quad (4)$$

where τ^0 is the excited state lifetime in the absence of the quencher Q.

See also *self-quenching*.

STIMULATED EMISSION

That part of the emission which is induced by a resonant perturbing electromagnetic field. The transition between states, n and m , is governed by the Einstein coefficient of stimulated emission, B_{nm} . CIDNP emission and *lasing* action are examples of processes which require stimulated emission.

See also *spontaneous emission*.

STOKES SHIFT

The difference (usually in *frequency* units) between the spectral positions of the band maxima (or the band origins) of the *absorption* and *luminescence* arising from the same electronic transition. Generally, the luminescence occurring at a longer *wavelength* than the absorption is stronger than the opposite. The latter may be called an anti-Stokes shift.

SUDDEN POLARIZATION

The occurrence of a large intramolecular charge separation in the *singlet excited state* of polyenes and their derivatives twisted about a double bond. Unsymmetrical substitution or geometrical distortion is effective in polarizing the system. An example is the stabilization of the zwitterionic structure of 90° twisted ethene (ethan-2-ylum-1-ide) with one methylene group pyramidalized:

SUPEREXCHANGE INTERACTION

Electronic interaction between two molecular entities mediated by one or more different molecules or ions.

SUPERRADIANCE

Spontaneous emission amplified by a single pass through a *population inverted* medium. It is distinguished from true *laser* action by its lack of coherence. The term superradiance is frequently used in laser technology.

See *coherent radiation*.

SURFACE CROSSING

In a diagram of electronic energy versus molecular geometry, the electronic energies of two states of different symmetry may be equal at certain geometrical parameters. At this point

(unidimensional representation), line or surface (more than one dimension), the two *potential-energy surfaces* are said to cross one another. In states of the same spin *multiplicity* the surface crossing is usually $3N - 8$ dimensional. In states with different spin multiplicity the surface crossing is usually $3N - 7$ dimensional (N is the number of nuclei).

See *conical intersection, singlet-triplet crossing*.

See *avoided crossing*.

$\sigma \rightarrow \sigma^*$ TRANSITION

An electronic transition described approximately as promotion of an electron from a "bonding" σ orbital to an "antibonding" σ orbital designated as σ^* . Such transitions generally involve high transition energies, and appear close to or mixed with *Rydberg transitions*.

TD-DFT

Time-dependent density functional theory.

THEORETICAL ANISOTROPY

When applied to a two-step photoselection experiment, the term connotes the uniaxial anisotropy that would be measured if all preventable causes of depolarization (instrumental imperfection, rotational diffusion, concentration depolarization, and non-negligible depopulation of the ground state) could be eliminated. A unique value can be assigned only if each step involves a single transition moment, in which case it can be expressed as:

$$r \equiv \langle P_2(\cos \theta_2) \rangle^{\otimes} = \frac{\langle \cos^2 \theta_1 P_2(\cos \theta_2) \rangle}{\langle \cos^2 \theta_1 \rangle}, \quad P_2(x) \equiv (3x^2 - 1)/2,$$

where $\langle \dots \rangle^{\otimes}$ denotes an average over the orientations of the photoselected molecules and $\langle \dots \rangle$ is an average over the orientations of the molecules prior to the first step; μ_k is the transition moment involved in the k -th step, and θ_k is the angle between μ_k and \mathbf{E} (the electric vector of the exciting light). If the ground-state molecules are randomly oriented, one gets (with $\hat{\mu}_k \equiv \mu_k / \mu_k$)

$$r = \frac{2}{5} P_2(\hat{\boldsymbol{\mu}}_1 \cdot \hat{\boldsymbol{\mu}}_2), \quad -\frac{1}{5} \leq r \leq \frac{2}{5}.$$

In time-resolved measurements with a δ -pulse excitation, the initial value, $r(0+)$, may be identified with the theoretical anisotropy.

See *absorption anisotropy, anisotropy, emission anisotropy, order parameter, photoselection, uniaxial symmetry*

THERMAL LENSING

A technique that determines the alteration in the refractive index of a medium as a result of the temperature rise in the path of a *laser* beam absorbed by the medium. The lens produced (usually divergent) causes a change (usually a decrease) in the *irradiance* measured along the laser beam axis.

See also *photothermal effects*.

THERMALLY ACTIVATED DELAYED FLUORESCENCE

See *delayed fluorescence*.

THERMOCHROMISM

A thermally induced transformation of a molecular structure or of a system (*e.g.* of a solution), thermally reversible, that produces a spectral change, typically, but not necessarily, of visible color.

THERMOLUMINESCENCE

Luminescence arising from a reaction between species trapped in a rigid matrix and released as a result of an increase in temperature.

See *luminescence*.

THROUGH-BOND ELECTRON TRANSFER

Intramolecular *electron transfer* for which the relevant electronic interaction between the donor and acceptor sites is mediated by through-bond interaction, *i.e.* via the covalent bonds interconnecting these sites, as opposed to through-space interaction.

See also *through-space electron transfer*

THROUGH-SPACE ELECTRON TRANSFER

Electron transfer for which the relevant electronic interaction between the donor and acceptor sites is mediated either by direct orbital overlap or by *superexchange interaction* via intervening molecular entities not covalently bound to the donor or acceptor sites.

See also *through-bond electron transfer*

TICT EMISSION

Electronic emission emanating from a *TICT state*.

See also *TICT state, twisted internal charge transfer*.

TICT STATE

The acronym derives from *Twisted Internal Charge Transfer State*, proposed to be responsible for strongly Stokes-shifted fluorescence from certain aromatics, particularly in polar medium.

See *Twisted Internal Charge Transfer*

TIGHT ION PAIR

See: *contact ion pair*

TIME-CORRELATED SINGLE PHOTON COUNTING

A technique for the creation of a time histogram of many stochastic events involving the time delay between the electronic excitation of a molecule or material and its emission of a *photon* from an excited state. A key to the technique is that no more than one photon strike the detector per pulsed excitation. Excitation is commonly achieved with a flash from a repetitive nanosecond *lamp* or *diode laser* or a CW operated *laser (mode-locked laser)*. The essential components of the hardware are a device to measure the excitation-emission delay time and another to determine the relative frequency of each delay time. Delay times are usually measured with a time-to-amplitude-converter (TAC) which uses voltage to measure the delay between a start and a stop signal. The frequency of events with each delay is stored in a multi-channel analyzer.

TIME-DEPENDENT-DENSITY FUNCTIONAL THEORY

Methods for computing accurate excitation energies at a low computational cost in large molecular species within the time-dependent scheme and the density functional theory.

TIME-RESOLVED MICROWAVE CONDUCTIVITY (TRMC)

A technique which allows the quantitative and qualitative detection of radiation-induced changes in the real, $\Delta\sigma_R$, and imaginary, $\Delta\sigma_I$, components of the conductivity of a medium by time-resolved measurement of changes in the microwave absorption resulting from the formation of mobile charges or from changes in the dipole moment or polarizability of molecules on excitation. From $\Delta\sigma_R$ (corresponding to a change in the dielectric loss, $\Delta\varepsilon''$) the product of the yield and the mobility of charges carriers or the dipole moment change can be determined. From $\Delta\sigma_I$ (corresponding to a change in the dielectric constant, $\Delta\varepsilon'$) the product of the yield and the change in molecular polarizability can be determined.

TIME-RESOLVED SPECTROSCOPY

The recording of spectra at a series of time intervals after the excitation of the system with a light pulse (or other perturbation) of appropriately short duration.

TRANSIENT SPECTROSCOPY

A technique for the spectroscopic observation of transient species (excited-state molecular entities or reactive intermediates) generated by a pulse of short duration.

See also *flash photolysis, time-resolved spectroscopy*.

TRANSITION (DIPOLE) MOMENT (M_{nm})

An oscillating electric or magnetic moment can be induced in an atom or molecular entity by an electromagnetic wave. Its interaction with the electromagnetic field is resonant if the *frequency* of the latter corresponds to the energy difference between the initial and final states of a transition ($\Delta E = h\nu$). The amplitude of this moment is referred to as the transition moment. It can be calculated from an integral taken over the product of the wavefunctions of the initial (m) and final (n) states of a spectral transition and the appropriate dipole moment operator (\vec{D}) of the electromagnetic radiation.

$$M_{nm} = e \int \Psi_n^* \sum_i Z_i \vec{r}_i \Psi_m d\tau$$

where the summation is over the coordinates of all charged particles (electrons and nuclei). Its sign is arbitrary, its direction in the molecular framework defines the direction of *transition polarization*, and its square determines the strength of the transition. If e is omitted one obtains R_{nm} in the sense used in *oscillator strength*. The SI unit of the transition dipole moment is C m. The common unit is debye (D).

TRANSITION POLARIZATION

The direction of the *transition moment* in the molecular framework.

TRANSMITTANCE (T)

The ratio of the transmitted *spectral radiant power* (P_λ) to that incident on the sample (P_λ^0):

$$T = P_\lambda / P_\lambda^0$$

Internal transmittance refers to energy loss by absorption, whereas the total transmittance is that due to absorption plus reflection, scatter, etc.

See *absorbance, attenuation, Beer-Lambert law*.

TRIBOLUMINESCENCE

Luminescence resulting from the rubbing together of the surface of certain solids. It can be produced, for example, when solids are crushed.

See *sonoluminescence*.

TRIPLET STATE

A state having a total electron spin quantum number of 1.

See *multiplicity*.

TRIPLET-TRIPLET ANNIHILATION

Two atoms or molecular entities both in a *triplet state* often interact (usually upon collision) to produce one atom or molecular entity in an excited *singlet state* and another in its ground singlet state. This is often, but not always, followed by *delayed fluorescence*.

See also *annihilation*, *spin conservation rule*.

TRIPLET-TRIPLET ENERGY TRANSFER

Energy transfer from an electronically excited triplet donor to produce an electronically excited acceptor in its triplet state.

See *spin conservation rule*.

TRIPLET-TRIPLET TRANSITIONS

Electronic transitions in which both the initial and final states are *triplet states*.

TRIVIAL ENERGY TRANSFER

Same as *radiative energy transfer*.

TUNGSTEN-HALOGEN LAMP

See *quartz-iodine lamp*. Other halogens may fill the lamp.

TUNNELLING

The passage of a particle through a potential-energy barrier the height of which is larger than the energy of that particle. This effect is important for some processes involving the transfer of electrons and light atoms, particularly H atoms.

TURNTABLE REACTOR

See *merry-go-round reactor*.

TWISTED INTERNAL CHARGE TRANSFER (TICT)

Intramolecular, photoinduced *charge transfer* between *chromophores* interconnected by a single bond leading to an *excited state* (a *TICT state*) in which the chromophores interact only weakly because of a considerable twist about the interconnecting bond.

TWO-PHOTON EXCITATION

Excitation resulting from successive or simultaneous absorption of two *photons* by an atom or molecular entity. This term is used for successive absorption only if some of the excitation energy of the first photon remains in the atom or molecular entity before absorption of the second photon. The simultaneous two-photon absorption can also be called *biphotonic excitation*.

See *two-photon process*.

TWO-PHOTON PROCESS

A photophysical or photochemical event triggered by a *two-photon excitation*.

UNIAXIAL SYSTEMS

Among *anisotropic* samples or molecules, the case of greatest interest is that of uniaxial symmetry, where one axis is unique (the other two being equivalent); the unique axis of an isotropic sample is frequently called the director. An isotropic sample may be viewed as a special case of uniaxial symmetry.

UPCONVERSION

A *nonlinear optical effect* in which light *frequency* is increased.

UPS

See *photoelectron spectroscopy*.

UV DOSE

A *dose* of ultraviolet (UV) radiation.

UV STABILIZER

A substance added to a sample to prevent photodeterioration by ultraviolet (UV) light.

See *photochemical reaction*.

VALENCE BAND

The highest energy continuum of energy levels in a semiconductor that is fully occupied by electrons at 0 K.

See *bandgap, conduction band, Fermi level*.

VAVILOV RULE

See *Kasha-Vavilov rule*.

VERTICAL TRANSITION

See *Franck-Condon principle*.

VIBRATIONAL REDISTRIBUTION

Intramolecular redistribution of energy among the vibrational modes usually giving a statistical distribution of their populations, characterized by the "vibrational temperature". For large molecules, this process does not require collisions.

VIBRATIONAL RELAXATION

The loss of vibrational excitation energy by a molecular entity through *energy transfer* to the environment caused by collisions. The molecular entity relaxes into vibrational equilibrium with its environment.

See *relaxation*.

VIBRONIC COUPLING

Interaction between electronic and vibrational motions in a molecular entity.

See *Jahn-Teller* and *Renner-Teller effects*.

VIBRONIC TRANSITIONS

A transition which involves a change in both the electronic and vibrational quantum numbers of a molecular entity, as opposed to purely electronic or purely vibrational transition. The transition occurs between two states, just as in a purely electronic transition, but involves a change in both electronic and vibrational energy.

WAVELENGTH (λ)

The distance, measured along the line of propagation, between two corresponding points on adjacent waves. The wavelength depends on the medium in which the wave propagates.

WAVENUMBER (σ , $\tilde{\nu}$)

The reciprocal of the *wavelength*, λ , or the number of waves per unit length along the direction of propagation. The SI unit is m^{-1} , but a commonly used unit is cm^{-1} .

WELLER CORRELATION

Empirical correlation for the energy of full *charge-transfer exciplexes* relative to the ground-state in n-hexane as a function of the electrochemical one electron oxidation and reduction potentials measured in a polar solvent for the donor (D) and the acceptor (A) involved (see e.g.: A. Weller, in "The Exciplex", Gordon and Ware eds., Academic Press Inc., N. Y., 1975):

$$\Delta H(\text{D}^+\text{A}^-)_{\text{hexane}} = E^0(\text{D}/\text{D}^+) - E^0(\text{A}/\text{A}^-) + (0.15 \pm 0.10) \text{ eV}$$

WIGNER RULE

See *spin conservation rule*.

WOOD HORN

A mechanical device that acts by *absorption* as a perfect *photon* trap.

WOOD LAMP

A term used to describe a *low-pressure mercury arc* possessing a fluorescing layer which emits in the UV-A region.((??)).

See *lamp*.

XENON LAMP

An intense source of ultraviolet, visible and near-infrared light produced by electrical discharge in xenon under high pressure.

See also *antimony-xenon, lamp, mercury-xenon lamp (arc)*.

XPS

See *photoelectron spectroscopy*.

YAG

See *neodymium laser*.

ZEEMAN EFFECT

The splitting or shift of spectral lines due to the presence of external magnetic field.

ZERO FIELD SPLITTING

The separation of multiplet sublevels in the absence of external magnetic field.

ZERO-ZERO (0-0) ABSORPTION OR EMISSION

A purely electronic transition occurring between the lowest vibrational levels of two electronic states.

SYMBOLS DEFINED IN THE GLOSSARY

Common units are mentioned if different from SI units

Symbol	Name	Units	
		SI	common
A	Absorbance	---	a
a	Absorption coefficient (decadic)	m^{-1}	cm^{-1}
α	Absorption coefficient (Napierian)	m^{-1}	cm^{-1}
σ	Absorption cross section	m^2	nm^2, pm^2
D	Attenuance	---	a
E_g	Bandgap energy	J mol^{-1}	eV^b kJ mol^{-1}
r_0	Critical quenching radius	m	nm
β	Depth of penetration (of light, Napierian)	m	nm
η	Efficiency (of a step)	---	a
E_F	Fermi level	J mol^{-1}	eV^b
H	Fluence	J m^{-2}	

E'	Fluence rate	W m^{-2}	
ν	Frequency (linear)	Hz	
ω	Frequency (angular)	rad s^{-1}	
E	Irradiance	W m^{-2}	
τ	Lifetime	s	ms, μs , ns, ps, fs
ε	Molar (decadic) absorption coefficient	$\text{m}^2 \text{mol}^{-1}$	$\text{cm}^{-1} \text{L mol}^{-1}$ or $\text{cm}^{-1} \text{dm}^3 \text{mol}^{-1}$ or $\text{cm}^2 \text{mmol}^{-1}$
f number	Oscillator strength	---	^a
M_p	Photon exitance, Specific photon emission	$\text{s}^{-1} \text{m}^{-2}$ $\text{mol s}^{-1} \text{m}^{-2d}$ or $\text{einstein s}^{-1} \text{m}^{-2d}$	
H_p	Photon exposure	m^{-2} mol m^{-2d} or einstein m^{-2d}	
N_p	Photon flow ^c	s^{-1} mol s^{-1d} or einstein s^{-1d}	
H'_p	Photon fluence	m^{-2} mol m^{-2d} or einstein m^{-2d}	
E'_p	Photon fluence rate	$\text{m}^{-2} \text{s}^{-1}$	

		mol m ⁻² s ^{-1d} or einstein m ⁻² s ^{-1d}	
E_p	Photon irradiance, Photon flux	m ⁻² s ⁻¹ mol m ⁻² s ^{-1d} or einstein m ⁻² s ^{-1d}	
L_p	Photon radiance	s ⁻¹ m ⁻² sr ⁻¹ mol s ⁻¹ m ⁻² sr ^{-1d} or einstein s ⁻¹ m ⁻² sr ^{-1d}	
Φ	Quantum yield	---	<i>a</i>
L	Radiance	W m ⁻² sr ⁻¹	
Q	Radiant energy	J	
M	Radiant exitance, Spherical radiance	W m ⁻²	
H	Radiant exposure	J m ⁻²	
I	Radiant intensity	W sr ⁻¹	
P	Radiant power	W	
τ_0	Radiative lifetime	s	ms, μ s, ns, ps
E_λ	Spectral irradiance	W m ⁻³	W m ⁻² nm ⁻¹
J	Spectral overlap integral(Förster) (Dexter)	m ⁶ mol ⁻¹ m ² mol ⁻¹	dm ³ cm ³ mol ⁻¹ dm ³ cm ⁻¹ mol ⁻¹

$M_{p\lambda}$	Spectral photon exitance	$s^{-1} m^{-3}$ $mol s^{-1} m^{-3d}$ or $einstein s^{-1} m^{-3d}$	$s^{-1} m^{-2} nm^{-1}$ $mol s^{-1} m^{-2} nm^{-1d}$ or $einstein s^{-1} m^{-2} nm^{-1d}$
$N_{p\lambda}, \Phi_{p\lambda}$	Spectral photon flow ^c	$s^{-1} m^{-1}$ $mol s^{-1} m^{-1d}$ or $einstein s^{-1} m^{-1d}$	$s^{-1} nm^{-1}$ $mol s^{-1} nm^{-1d}$ or $einstein s^{-1} nm^{-1d}$
$E_{p\lambda}$	Spectral photon flux, Photon irradiance	$s^{-1} m^{-3}$ $mol s^{-1} m^{-3d}$ or $einstein s^{-1} m^{-3d}$	$s^{-1} m^{-2} nm^{-1}$ $mol s^{-1} m^{-2} nm^{-1d}$ or $einstein s^{-1} m^{-2} nm^{-1d}$
$L_{p\lambda}$	Spectral photon radiance	$s^{-1} m^{-3} sr^{-1}$ $mol s^{-1} m^{-3} sr^{-1d}$ or $einstein s^{-1} m^{-3} sr^{-1d}$	$s^{-1} m^{-2} sr^{-1} nm^{-1}$ $mol s^{-1} m^{-2} sr^{-1} nm^{-1d}$ or $einstein s^{-1} m^{-2} sr^{-1} nm^{-1d}$
L_{λ}	Spectral radiance	$W m^{-3} sr^{-1}$	$W m^{-2} sr^{-1} nm^{-1}$
M_{λ}	Spectral radiant exitance	$W m^{-3}$	$W m^{-2} nm^{-1}$
I_{λ}	Spectral radiant intensity	$W sr^{-1} m^{-1}$	$W sr^{-1} nm^{-1}$
P_{λ}	Spectral radiant power,	$W m^{-1}$	$W nm^{-1}$
s_{λ}	Spectral responsivity	--- ^a	
M_{nm}	Transition dipole moment	C m	D ^b
T	Transmittance	--- ^a	

λ	Wavelength	m	nm, μm
$\sigma, \tilde{\nu}$	Wavenumber	m^{-1}	cm^{-1}

a Dimensionless quantity.

b Recognized unit.

c In photochemistry Φ is reserved for quantum yield.

d If amount of photons is used.