

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

ORGANIC CHEMISTRY DIVISION
COMMISSION ON PHOTOCHEMISTRY*

GLOSSARY OF TERMS USED IN PHOTOCHEMISTRY

(Recommendations 1988)

Prepared for publication by

S. E. BRASLAVSKY¹ and K. N. HOUK²

¹Max-Planck-Institut für Strahlenchemie, D-4330 Mülheim a.d. Ruhr, FRG

²University of California, Los Angeles, CA 90024, USA

*Membership of the Commission during the period 1976–1987 in which the report was prepared was as follows:

Chairman: 1976–81 K. Schaffner (FRG); 1981–85 F. C. De Schryver (Belgium); 1985–87 J. Michl (USA); *Secretary:* 1976–81 F. C. De Schryver (Belgium); 1981–83 A. A. Lamola (USA); 1983–87 S. E. Braslavsky (FRG); *Members:* C. Bradley Moore (USA, Assoc. 1985–87); R. Bonneau (France, Assoc. 1985–87); S. E. Braslavsky (FRG, Assoc. 1981–83); D. F. Eaton (USA, Assoc. 1981–85, Tit. 85–87); Z. R. Grabowski (Poland, Tit. 1979–81); C. Hélène (France, Assoc. 1979–83); A. Heller (USA, Assoc. 1983–87); G. J. Hoytink (UK, Tit. 1976–77); K. N. Houk (USA, Tit. 1979–85); H. Iwamura (Japan, Assoc. 1979–83, Tit. 83–87); M. G. Kuzmin (USSR, Assoc. 1981–85, Tit. 85–87); A. A. Lamola (USA, Tit. 1976–77); J. Michl (USA, Assoc. 1979–81, Tit. 81–85); T. Mukai (Japan, Tit. 1976–77); M. Ottolenghi (Israel, Assoc. 1979–81); G. Quinkert (FRG, Tit. 1976–77); C. Sandorfy (Canada, Assoc. 1979–85); K. Tokumaru (Japan, Tit. 1979–87); D. W. Turner (UK, Assoc. 1976–83); J. W. Verhoeven (Netherlands, Assoc. 1985–87); A. Weller (FRG, Tit. 1976–79); D. G. Whitten (USA, Assoc. 1979–81); U. P. Wild (Switzerland, Assoc. 1979–81); F. Wilkinson (UK, Assoc. 1981–87); M. A. Winnik (Canada, Assoc. 1985–87); M. S. Wrighton (USA, Tit. 1976–83); *National Representatives:* I. Abdullah (Malaysia); E. Fanghänel (GDR); E. Fischer (Israel); M. V. George and P. Natarajan (India); K. Lempert and T. Bérczes (Hungary); A. M. Osman (Arab Rep. of Egypt); E. San Roman (Argentina); O. P. Strausz (Canada); J. W. Verhoeven (Netherlands).

Republication of this report is permitted without the need for formal IUPAC permission on condition that an acknowledgement, with full reference together with IUPAC copyright symbol (© 1988 IUPAC), is printed. Publication of a translation into another language is subject to the additional condition of prior approval from the relevant IUPAC National Adhering Organization.

Glossary of terms used in photochemistry (Recommendations 1988)

CONTENTS

Contributors to the Glossary	1055-56
Introduction	1057
Alphabetic list of terms and definitions	1058
Symbols defined in the Glossary	1104

ADDITIONAL CONTRIBUTORS TO THE GLOSSARY

(those additional to Commission Members listed on p. 1055)

Balzani, V., Italy	Kurreck, H., F.R.G.
Bard, A.J., U.S.A.	Laidler, K.J., Canada
Benson, S., U.S.A.	Lee, J., U.K.
Bergman, B., U.S.A.	Leitich, J., F.R.G.
Berson, J., U.S.A.	Lippert, E., F.R.G.
Birks, J.B. (the late), U.K.	Lissi, E.A., Chile
Blondeel, G., Belgium	Matsuura, T., Japan
Bolton, J.R., Canada	Mark, F., F.R.G.
Borden, W.T., U.S.A.	McBride, J.M., U.S.A.
Bouas-Laurent, H.C.M., France	McGlynn, S., U.S.A.
Breslow, R., U.S.A.	McNaught, A.D., U.K.
Camassei, S., Italy	Mohr, H., F.R.G.
Chanon, M., France	Olbrich, G., F.R.G.
Cilento, G., Brasil	Padwa, A., U.S.A.
Cram, D., U.S.A.	Perkins, M.J., U.K.
Davidson, E.R., U.S.A.	Peyerimhoff, S., F.R.G.
Demuth, M., F.R.G.	Platz, M., U.S.A.
Dervan, P.B., U.S.A.	Porter, G.S. Sir, U.K.
Dewar, M., U.S.A.	Rigg, J.C., Canada
Doering, W., U.S.A.	Roth, W., F.R.G.
Dougherty, D.A., U.S.A.	Sager, J., U.S.A.
Dowd, P., U.S.A.	Salem, L., France
El-Sayed, M.A., U.S.A.	Salahub, D.R., Canada
Fox, M.A., U.S.A.	Saltiel, J., U.S.A.
Frey, H., U.K.	Schaefer, F., U.S.A.
Gajewski, J., U.S.A.	Schuster, D., U.S.A.
Gauglitz, G., F.R.G.	Schenck, G.O., F.R.G.
Getoff, N., Austria	Schneider, S., F.R.G.
Gold, V. (the late), U.K.	Schwetlick, K., D.R.G.
Goldstein, M., U.S.A.	Serpone, N., Canada
Halevi, E.A., Israel	Shropshire, W. Jr., U.S.A.
Hammond, G., U.S.A.	Suter, G., Switzerland
Hartmann, K.M., F.R.G.	Tegmo-Larsson, I.-M., U.S.A.
Heilbronner, E., Switzerland	Thrush, B.A., U.K.
Hoffman, R., U.S.A.	Turro, N.J., U.S.A.
Holmes, G., U.S.A.	Usui, Y., Japan
Holmström, B., Sweden	Whiffen, D.H., U.K.
Holzwarth, A.R., F.R.G.	Willingen, H. van, U.S.A.
Jones, B., U.S.A.	Wirz, J., Switzerland
Keukeleire, D. De, Belgium	Wolf, H.C., F.R.G.
Kimura, K., Japan	Wubbels, G.G., U.S.A.
Kisch, H., F.R.G.	Zare, D., U.S.A.
Klöpffer, W., F.R.G.	Zimmerman, H.E., U.S.A.
Krochmann, J., F.R.G.	

INTRODUCTION

This Glossary was prepared by the Photochemistry Commission of the Organic Chemistry Division of the International Union of Pure and Applied Chemistry during the period 1978-1985. The purpose of the Glossary is to provide definitions of terms and symbols commonly used in the field in order to achieve consensus on the adoption of some definitions and on the abandonment of inadequate terms. The Commission wants to emphasize, however, 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.

An early version of this Glossary was published in the period 1983-1984 in the Newsletters of the European Photochemical Association, the Interamerican Photochemical Society, and the Japanese Photochemical Society with the purpose of gathering the comments of the photochemical community. Many researchers provided valuable criticisms to the Glossary and the present version includes the comments of more than seventy scientists from sixteen different Countries. The Commission, however, takes full responsibility for the content and for any inadvertent mistakes.

Photochemistry being an interdisciplinary area of science which involves, in addition to chemistry, such different fields as laser technology, 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. With very few exceptions concerning widely accepted terms, name reactions have been omitted.

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.

The arrangement of entries is alphabetical and the criterion adopted by the Physical Organic Chemistry Commission has been followed for the type of lettering used: *italicized* words in a definition or at the end 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. The Commission welcomes all suggestions for improvement and updating of the Glossary and commits itself 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", *Pure Appl. Chem.* (1983) 55, 1281-1371.

Internationally agreed upon terms were taken from:

"Manual of Symbols and Terminology for Physicochemical Quantities and Units", *Pure Appl. Chem.* (1979) 51, 1-41.

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

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

Other sources:

"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.

Silvia E. Braslavsky

ALPHABETIC LIST OF TERMS AND DEFINITIONS

ABSORBANCE (A)

The logarithm to the base 10 of the ratio of the radiant power of incident radiation (P_0) to the radiant power of transmitted radiation (P):

$$A = \log_{10} (P_0/P) = \log_{10} T^{-1},$$

In solution, absorbance is the logarithm to the base 10 of the ratio of the 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, radiant intensity, I , was used instead of radiant power, P , which is now the accepted form. (The terms: absorbancy, extinction, and optical density should no longer be used.)

See *absorption coefficient, attenuation, Beer-Lambert law, internal transmittance, Lambert law, molar absorption coefficient.*

ABSORPTANCE

One minus the ratio of the radiant power of transmitted radiation (P) to the radiant power of incident radiation (P_0):

$$1 - (P/P_0)$$

See *absorbance, Beer-Lambert law.*

ABSORPTION (of electromagnetic radiation)

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

ABSORPTION COEFFICIENT (decadic- a or Napierian- α)

Attenuance divided by the optical pathlength, l :

$$a = (1/l) \log_{10} (P_0/P) = A/l$$

Physicists usually use natural logarithms. In this case:

$$\alpha = (1/l) \log_e (P_0/P) = a \log_e 10$$

where α is the Napierian absorption coefficient. Since attenuation 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:

$$\sigma = [1/(Nl)] \log_e (P_0/P) = \alpha/N,$$

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 , is

$$\sigma = (\epsilon/N_A) \cdot \log_e n 10 = \epsilon \cdot 3.825 \times 10^{-24} \text{ mol}^{-1},$$

where N_A is Avogadro constant.

See *attenuance, Beer-Lambert law.*

ABSORPTIVITY

Absorptance divided by the optical path length. For very low attenuation it approximates the absorption coefficient (within the approximation $(1 - 10^{-A}) \approx A$). The use of this term is not recommended.

ACTINOMETER

A chemical system or physical device which determines the number of photons in a beam integrally or per unit time. This name is commonly applied to devices used in the ultraviolet and visible wavelength ranges. For example, solutions of iron(III) oxalate can be used as a chemical actinometer, while bolometers, thermopiles, and photodiodes are physical devices giving a reading that can be correlated to the number of photons detected.

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. This type of action spectrum is sometimes called spectral responsivity or spectral sensitivity spectrum. A precise action spectrum, instead, 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*.

ADIABATIC PHOTOREACTION

Within the "Born-Oppenheimer approximation", a reaction of an 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. 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*.

ANNIHILATION

Two atoms or molecular entities both in an excited electronic state interact often (usually upon collision) to produce one atom or molecular entity in an excited electronic state and another in its ground electronic 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*.

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 *gas lasers*.

ATTENUANCE (D)

The logarithm to the base 10 of the ratio of the *radiant powers* of the incident (P_0) and transmitted (P) radiation:

$$D = \log_{10} (P_0/P) = -\log_{10} T,$$

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

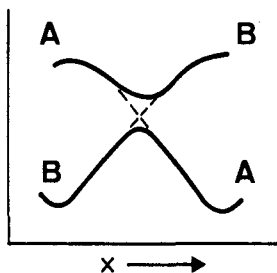
See *Beer-Lambert law*.

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 (A,B) change their energy order as molecular geometry (x) is changed continuously along a path. 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.

Same as *intended crossing*.

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.

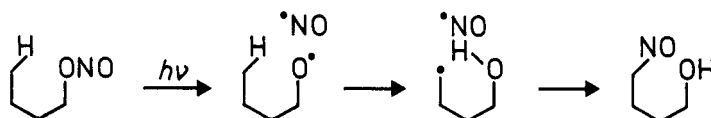
BANDPASS FILTER

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. The law can be expressed as

$$A = \log_{10} (P_0/P) = \epsilon cl$$

or

$$P = P_0 10^{-\epsilon cl},$$

where the proportionality constant, ϵ , is called the molar (decadic) absorption coefficient. For l in cm and c in mol dm⁻³, ϵ will result in dm³ mol⁻¹ cm⁻¹, which is a commonly used unit. The SI unit of ϵ is m² mol⁻¹.

See absorbance, extinction coefficient, Lambert law.

BIOLUMINESCENCE

Chemiluminescence 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.

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 non-bonding 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*.

CADMIUM-HELIUM LASER

See *Helium-Cadmium laser*

CAVITY DUMPING

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

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. In some cases the charge transfer absorption band may be obscured by the absorption of the partners.

CHARGE-TRANSFER (CT) COMPLEX

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

See *charge-transfer transition*.

CHEMICAL LASER

A *CW* or pulsed laser in which the excitation and population inversion of the emitting species result 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.

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.

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 (O₂) 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 many-electron wavefunctions constructed from different electronic configurations to obtain an improved many-electron state.

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 m².

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 non-relativistic 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)

Non-pulsed source of electromagnetic radiation.

DARK PHOTOCHEMISTRY (photochemistry without light)

Excited state reaction not initiated by the *absorption* of electromagnetic radiation. They are often *photochemical processes* undergone by chemically or enzymatically generated excited states. 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*.

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 or singlet-singlet 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. If the decadic absorption coefficient, a , is used, the depth of penetration ($1/a$) is the distance at which the *radiant power*, P decreases to one tenth of its incident value, P_0 . If the Napierian absorption coefficient, α , is used, the depth of penetration ($1/\alpha = \beta$ in this case) is the distance at which the radiant power decreases to $1/e$ of its incident value.

See *absorbance*, *attenuance*.

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 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*. Also called *non-adiabatic*.

Compare with *adiabatic photoreaction*.

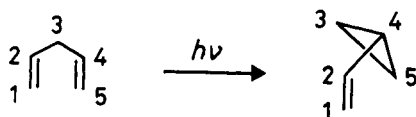
DIODE LASERS

Sources of *CW* or pulsed *coherent radiation* in the visible and infrared regions and usually tunable on a few nm range. These lasers are semiconductor devices of small dimensions. 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 *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 mol m^{-3} , respectively.

See also *UV-dose*.

DOUBLET STATE

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

See *multiplicity*.

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. Although widely used, it is not an IUPAC sanctioned unit. It is sometimes defined as the energy of one mole of photons. This use is discouraged.

ELECTROCHEMILUMINESCENCE

See *electrogenerated chemiluminescence.*

ELECTROCHROMIC EFFECT

See *Stark effect.*

ELECTROGENERATED CHEMILUMINESCENCE (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.

ELECTRONICALLY EXCITED STATE

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

ELECTROPHOTOGRAPHY

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

EL-SAYED RULES

During the radiationless transition from the lowest singlet state to the triplet state manifold (*intersystem crossing*) the change of orbital type enhances the rate of the process.

E.g. $^1\pi, \pi^* \rightsquigarrow ^3n, \pi^*$ is faster than $^1\pi, \pi^* \rightsquigarrow ^3\pi, \pi^*$
 and $^1n, \pi^* \rightsquigarrow ^3\pi, \pi^*$ is faster than $^1n, \pi^* \rightsquigarrow ^3n, \pi^*$.

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 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*.

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, Förster excitation, and radiative energy transfer, and spectral overlap*.

ENERGY TRANSFER PLOT

A plot of the *quenching* rate constant of an 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). A "diffusional" quenching rate constant limit is found for exothermic *energy transfer*, while for endothermic energy transfer the energy deficiency must be supplied as activation energy and an "Arrhenius" type plot can be obtained. Also known as *Hammond-Herkstroeter plot*.

See also *Stern-Volmer kinetic relationships*.

ENHANCER

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.

See also *dark photochemistry*.

ESCA

See *photoelectron spectroscopy*.

EXCIMER

An electronically excited dimer, "non-bonding" 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 *gas lasers*.

EXCIPLEX

An electronically excited complex, of definite stoichiometry, "non-bonding" in the *ground state*. For example, a complex formed by the interaction of an excited molecular entity with a ground state partner of a different structure.

EXCITATION SPECTRUM

Plot of the *spectral radiant exitance* or of the *spectral 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*.

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 excited electronic 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*.

See *electronic energy migration*.

EXITANCE

See *radiant exitance*.

EXTERNAL HEAVY ATOM EFFECT

See *heavy atom effect*.

EXTINCTION

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

EXTINCTION COEFFICIENT

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

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 attenuance 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_0)

When applied to energy, it is the total radiant energy traversing a small transparent imaginary spherical target containing the point under consideration, divided by the cross section of this target. The product of the *fluence rate* and the duration of the irradiation ($\int E_0 dt$, simplified expression: $H_0 = E_0 \cdot t$ 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_0)

The rate of *fluence*, H_0 . Four times the ratio of the *radiant power*, P , incident on a small transparent imaginary spherical volume element containing the point under consideration, divided by the surface area of that sphere, S_k . ($\int_{\Omega} L \cdot d\omega$, simplified expression: $E_0 = 4 P/S_k$ when the *radiant power* is constant over the solid angle considered). 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 having.

FLUX (energy flux, Φ)

See *radiant energy flux, radiant power*.

f NUMBER

See oscillator strength.

FÖRSTER EXCITATION TRANSFER (Dipole-Dipole Excitation Transfer)

A mechanism of excitation transfer which can 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

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

where κ 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 pK^* 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 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.

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_1 , is approximately given by $\lambda_w / (4E^2)$, with λ_w being the wiggler period and E the electrons energy in MeV.

See laser.

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 mode-

locked, Q-switched, 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 $\text{Hz} \equiv \text{s}^{-1}$. For the angular frequency, the symbol ω ($= 2\pi\nu$) is used, with rad s^{-1} as the SI unit.

FREQUENCY DOUBLING

See *harmonic frequency generation, non-linear 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 laser 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.

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 of the band maximum.

See also *Lorentzian band shape*.

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 absorption 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 non-linear 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.

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 responds 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

Same as exciplex.

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.

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 with questionable validity to molecules.

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.

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 (radiant flux)*. 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*.

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.

IRRADIANCE (E)

The *radiant flux* or *radiant power*, P , *incident* on an infinitesimal element of surface containing the point under consideration divided by the area of the element (dP/dS , simplified expression: $E = P/S$ when the *radiant power* is constant over the surface area considered). The SI unit is $W\ m^{-2}$. For a parallel and perpendicularly incident beam not scattered or reflected by the target or its surroundings *fluence rate* (E_0) 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 non-linear relationship between the *molar absorption coefficient* and the *photoacoustic signal*.

ISOSBESTIC POINT

A *wavelength*, *wavenumber*, or *frequency* at which *absorption coefficients* are equal is known as an *isosbestic point*. As a consequence the total *absorbance* of a sample at this wavelength does not change during a chemical reaction or 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, $A(\lambda)l^{-1}$ ($= \sum_{i=1}^n \epsilon_i \lambda^i c_i$) must remain constant during the reaction or physical change in order to observe an isosbestic point. 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 irradiation'. 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. 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 (\rightsquigarrow).

JAHN-TELLER EFFECT

For non-linear molecular entities in a geometry described by a point symmetry group possessing degenerate irreducible representations there always exists at least one non-totally 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. This effect is due to the odd terms in the vibronic perturbation expansion.

See also Renner-Teller effect.

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. 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 radiant power (P_0). This law holds only if P_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.

LAPORTE RULE

For monophotonic radiative transitions in centrosymmetric systems, the only non-vanishing 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. The light emitted is coherent except for superradiance emission.

See argon ion, helium-cadmium, chemical, CO_2 , 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 photoimaging system which is susceptible to development.

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, 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.

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.

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 (0.75×10^{-3} Torr; 1 Torr = 133.3 Pa). At 25 °C, such a lamp emits mainly at 253.7 and 184.9 nm. Other terms used for such a lamp are germicidal, cold and hot cathode, Wood 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, radio-luminescence, sonoluminescence, 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.)

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 310 to 1000 nm with most intense lines at 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.

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.

MLCT

Abbreviation for 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. 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 path length, l and the concentration, c :

$$\epsilon = [1/(cl)] \log_{10} (P_0/P) = A/(cl)$$

In common usage for l is cm and c in mol dm⁻³, ϵ result in dm³ mol⁻¹ cm⁻¹, which equals 0.1 m² mol⁻¹ (coherent SI units) = 10³ cm² mol⁻¹ = cm² mmol⁻¹ = dm³ cm⁻¹ mol⁻¹. The term molar absorptivity for molar absorption coefficient should be avoided.

See absorbance, Beer-Lambert law.

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.

 $n \rightarrow \pi^*$ TRANSITION

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

 $n-\pi^*$ STATE

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

 $n \rightarrow \sigma^*$ TRANSITION

An electronic transition described approximately as promotion of an electron from a "non-bonding" (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-aluminum 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.

NON-ADIABATIC PHOTOREACTION

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

Compare *adiabatic photoreaction*.

NON-LINEAR OPTICAL EFFECT

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

NON-RADIATIVE DECAY

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

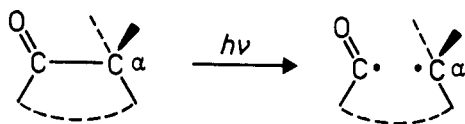
NON-VERTICAL ENERGY TRANSFER

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

See *Franck-Condon principle*.

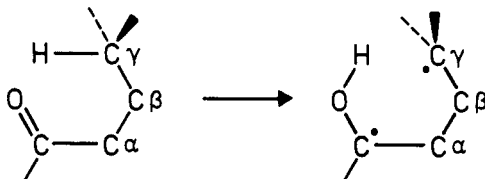
NORRISH TYPE I PHOTOREACTION

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.,



QDMR (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, non-specified), DFDMR (delayed fluorescence), FDMR (fluorescence), PDMR (phosphorescence). If a reaction yield is followed the expression RYDMR (reaction yield detected magnetic resonance) is used.

OPTICAL DENSITY

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

OPTOACOUSTIC SPECTROSCOPY

Same as *photoacoustic spectroscopy*.

ORBITAL (Atomic or Molecular)

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

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*,

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

where *m* is the mass of the electron, *c* the velocity of light, *ν* 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

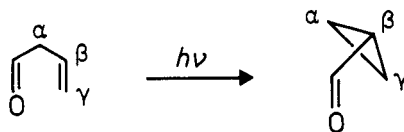
$$f_{ij} = (k/n) \cdot \int \epsilon(\sigma) d\sigma,$$

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*.

OXA-DI-π-METHANE REARRANGEMENT

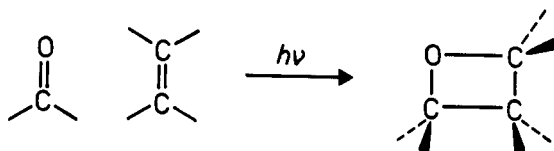
A photochemical reaction of a β,γ-unsaturated ketone to form a saturated α-cyclopropyl ketone. The rearrangement formally amounts to a 1,2-acyl shift and "bond formation" between the former α and γ carbon atoms.



See also *di-π-methane rearrangement*.

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*.

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 heat after absorption of radiation, due to *radiationless deactivation* 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

Catalytic reaction involving light absorption by a catalyst or by a substrate.

PHOTOCHEMICAL HOLE BURNING

See hole burning.

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 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, photochemically or thermally reversible, that produces a spectral change, typically, but not necessarily, of visible colour.

PHOTOCONDUCTIVITY

Electrical conductivity resulting from photoproduction of charge carriers.

PHOTOCROSSLINKING

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 electron transport between the two electrodes of a photovoltaic cell or a photoelectrochemical cell.

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)

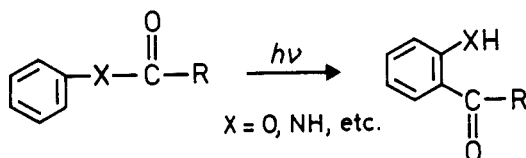
A spectroscopic technique which measures the kinetic energy of electrons emitted upon the ionization of a substance by high energy monochromatic photons. A photoelectron spectrum is a plot of the number of electrons emitted versus their kinetic energy. The spectrum consists of bands due to transitions 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" and yield orbital energies. PES and UPS 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 aryl or acyl esters to give the [1,3]-rearranged product

PHOTO GALVANIC 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 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 *photon* pulses counted by way of recording the electron emission events from a photosensitive layer (photocathode) and multiplied by means of a "dynode" arrangement (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, Φ , emitted by an element of the surface containing the source point under consideration divided by the area (S) of that element. ($d\Phi/dS$, simplified expression: $M_p = \Phi_p/S$ when the photon flow is constant over the surface area considered). The SI unit is $s^{-1} m^{-2}$. Alternatively, the term can be used with the amount of photons (mol or its equivalent *einstein*), the SI unit then being $mol s^{-1} m^{-2}$. 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} . Alternatively, the term can be used with the amount of photons (mol or its equivalent *einstein*), the SI unit then being $mol m^{-2}$. For a parallel and perpendicularly incident beam not scattered or reflected by the target or its surroundings *photon fluence* (H_{p0}) is an equivalent term.

See also *fluence*, *radiant exposure*.

PHOTON FLOW (Φ_p)

The number of photons (quanta, N) per unit time. (dN/dt , simplified expression: $\Phi_p = N/t$ when the number of photons is constant over the time considered). The SI unit is s^{-1} . Alternatively, the term can be used with the amount of photons (mol or its equivalent *einstein*), the SI unit then being mol s^{-1} .

See *spectral photon flow*.

See also *radiant power*.

PHOTON FLUENCE (H_{p0})

The integral of the amount of all photons (quanta) which traverse a small, transparent, imaginary spherical target, divided by the cross-sectional area of this target. The photon fluence rate, E_{p0} , integrated over the duration of the irradiation ($\int E_{p0} dt$, simplified expression: $H_{p0} = E_{p0} t$ when E_{p0} is constant over the time considered). Photons per unit area (quanta m^{-2}). The SI unit is m^{-2} . Alternatively, the term can be used with the amount of photons (mol or its equivalent *einstein*), the SI unit then being mol m^{-2} .

See also *fluence*.

PHOTON FLUENCE RATE (E_{p0})

The rate of photon fluence. Four times the ratio of the photon flow, Φ , incident on a small, transparent, imaginary spherical volume element containing the point under consideration divided by the surface of that sphere, S_K . ($\int_{4\pi} L_p d\omega$, simplified expression: $E_{p0} = 4 \Phi_p / S_K$ when the photon flow is constant over the solid angle considered). The SI unit is $\text{m}^{-2} \text{s}^{-1}$. Alternatively, the term can be used with the amount of photons (mol or its equivalent *einstein*), the SI unit then being $\text{mol m}^{-2} \text{s}^{-1}$. 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, Φ , incident on an infinitesimal element of surface containing the point under consideration divided by the area (S) of that element ($d\Phi_p/dS$, simplified expression: $E_p = \Phi_p/S$ when the photon flow is constant over the surface considered). The SI unit is $\text{m}^{-2} \text{s}^{-1}$. Alternatively, the term can be used with the amount of photons (mol or its equivalent *einstein*), the SI unit then being $\text{mol m}^{-2} \text{s}^{-1}$. For a parallel and perpendicularly incident beam not scattered or reflected by the target or its surroundings photon fluence rate (E_{p0}) is an equivalent term.

See *spectral photon irradiance*.

See also *irradiance*.

PHOTON RADIANCE (L_p)

For a parallel beam it is the photon flow, Φ , leaving or passing through an infinitesimal transparent element of surface^P 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 , $[(d\Phi_p/dS)/\cos \theta]$, simplified expression: $L_p = \Phi_p/(S \cos \theta)$ 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 $d^2\Phi_p / (d\Omega dS \cos \theta)$, with SI unit $\text{m}^{-2} \text{s}^{-1} \text{sr}^{-1}$. Alternatively, the term can be used with the amount₂ of photons (mol or its equivalent *einstein*), the SI unit then being $\text{mol m}^{-2} \text{s}^{-1}$ and $\text{mol m}^{-2} \text{s}^{-1} \text{sr}^{-1}$, 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*.

PHOTOXYGENATION

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 local solubility properties can be altered *photochemically*. A subsequent development step produces an image which is useful for the fabrication of microelectronic devices (e.g., integrated circuits).

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 has been 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*.

POPULATION INVERSION

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

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*.

PUMP-PROBE TECHNIQUE

A flash photolysis technique in which the light beam (probe) used for spectral analysis is generated from a portion of the excitation (pump) beam. A time delay in the latter 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.

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, γ)

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, 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.

See also *efficiency*.

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 *non-radiative process*. When the external environmental influence (*quencher*) interferes with the behaviour 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 , 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} .

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 $W m^{-2} sr^{-1}$.

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

RADIANT EMITTANCE

See *radiant exitance.*

RADIANT ENERGY (Q)

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

See also *spectral radiant energy.*

RADIANT (ENERGY) FLUX (Φ)

Although flux is generally used in the sense of the 'rate of transfer of fluid, particles or energy across a given surface', the radiant energy flux has been adopted by IUPAC as equivalent to *radiant power*, P . ($P = \Phi = dQ/dt$, simplified expression: $P = \Phi = Q/t$ when the radiant energy, Q , is constant over the time considered).

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

RADIANT EXITANCE (M)

The *radiant power*, P , emitted by an element of the surface containing the source point under consideration divided by the surface area (S) of that element. (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 $W m^{-2}$. 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_0) is an equivalent term.

RADIANT INTENSITY (I)

Radiant (energy) flux or *radiant power*, P , 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 $W sr^{-1}$.

See also *spectral radiant intensity.*

RADIANT POWER (P)

Same as *radiant (energy) flux*, Φ . Power emitted, transferred or received as radiation. In *photochemistry* Φ is reserved for *quantum yield*. The SI unit is $J s^{-1} = W$.

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.*

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

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

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.*

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.*

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

Splittings in the vibrational levels of molecular entities due to even terms in the *vibronic* perturbation expansion. This is generally a minor effect for non-linear 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.

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 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 lasers*.

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.

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), O_2 , in an excited singlet state. The ground state of O_2 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. While the oxygen atom ground state is a triplet 3P state, 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 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 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.

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*.

SONOLUMINESCENCE

Luminescence induced by sound waves.

SPECIFIC PHOTON EMISSION

Same as photon exitance.

SPECTRAL (PHOTON) EFFECTIVENESS

The reciprocal of the photon fluence rate, E_{p0} , 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, $J = \int_0^\infty f'_D(\sigma) \epsilon_A(\sigma) d\sigma$, 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 $\epsilon_A(\sigma)$ is the decadic molar absorption coefficient of A at wavenumber σ .

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

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

In the context of Dexter excitation transfer J is given by

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

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 $\text{s}^{-1} \text{m}^{-3}$, but a commonly used unit is $\text{s}^{-1} \text{m}^{-2} \text{nm}^{-1}$. Alternatively, the term can be used with the amount of photons (mol or its equivalent, $\frac{1}{2} \text{einstein}$), the SI unit then being $\text{mol s}^{-1} \text{m}^{-3}$ and the common unit $\text{mol s}^{-1} \text{m}^{-2} \text{nm}^{-1}$.

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

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

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 $\text{s}^{-1} \text{m}^{-2} \text{nm}^{-1}$. Alternatively, the term can be used with the amount of photons (mol or its equivalent, $\frac{1}{2} \text{einstein}$), the SI unit then being $\text{mol s}^{-1} \text{m}^{-3}$ and the common unit $\text{mol s}^{-1} \text{m}^{-2} \text{nm}^{-1}$.

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

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

SPECTRAL RADIANCE (L_λ)

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

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 $W m^{-2} nm^{-1}$.

SPECTRAL RADIANT FLUX (Φ_λ)

Same as spectral radiant power.

SPECTRAL RADIANT INTENSITY (I_λ)

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

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 $s(\lambda) = dy(\lambda)/dE(\lambda)$, 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.

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, 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 *photo-physical 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

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

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 Q 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

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

where Φ_p is the quantum efficiency of product formation, A the efficiency of forming^p 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 lifetime of the excited state 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 origin) 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.

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.

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.

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 colour.

THERMOLUMINESCENCE

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

See *luminescence*.

ICT 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 *charge transfer*.

TIME-CORRELATED SINGLE PHOTON COUNTING

A technique for the measurement of the time histogram of a sequence of photons with respect to a periodic event, e.g. a flash from a repetitive nanosecond lamp or a CW operated laser (*mode locked laser*). The essential part is a time-to-amplitude-converter (TAC) which transforms the arrival time between a start and a stop pulse into a voltage. Sometimes called single photon timing.

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.

$$M_{nm} = e \int \psi_n^* \sum_i Z_i \vec{r}_i \psi_m dt$$

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 nm 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, τ)

The ratio of the transmitted radiant power (P) to that incident on the sample (P_0):

$$T = P/P_0$$

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

See *absorbance*, *attenuance*, *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.

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*.

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*.

UPCONVERSION

A *non-linear 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 TRANSITION

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 unit is commonly cm^{-1} . The SI unit is m^{-1} .

It is common practice to use $\tilde{\nu} = 1/\lambda = \nu/c$ with ν = frequency and c = speed of light in vacuum. For propagation^{vac} in other media $\sigma = 1/\lambda$.

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.

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	Unit ^a	
		SI	common
A	Absorbance	----	
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	----	
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)	----	
E _F	Fermi level	J mol ⁻¹	eV ^b
H ₀	Fluence	J m ⁻²	
E ₀	Fluence rate	W m ⁻²	
Φ ^C	Flux (Energy)	W	
ν	Frequency (linear)	Hz	
ω	Frequency (angular)	rad s ⁻¹	
E	Irradiance	W m ⁻²	
τ	Lifetime	s	ms, μs, ns, ps
ε	Molar (decadic) absorption coefficient	m ² mol ⁻¹	cm ⁻¹ dm ³ mol ⁻¹ or cm ² mol ⁻¹
f number	Oscillator strength	----	
M _p	Photon exitance, Specific photon emission	s ⁻¹ m ⁻² s ⁻¹ mol m ^{-2d}	

Symbol	Name	Unit ^a	
		SI	common
H_p	Photon exposure	m^{-2} $mol\ m^{-2}d$	
ψ_p	Photon flow	s^{-1} $mol\ s^{-1}d$	
H_{p0}	Photon fluence	m^{-2} $mol\ m^{-2}d$	
E_{p0}	Photon fluence rate	$m^{-2}\ s^{-1}$ $mol\ m^{-2}\ s^{-1}d$	
E_p	Photon irradiance, Photon flux	$m^{-2}\ s^{-1}$ $mol\ m^{-2}\ s^{-1}d$	
L_p	Photon radiance	$s^{-1}\ m^{-2}\ sr^{-1}$ $mol\ s^{-1}\ m^{-2}\ sr^{-1}d$	
ϕ, γ	Quantum yield	----	
L	Radiance	$W\ m^{-2}\ sr^{-1}$	
Q	Radiant energy	J	
ϕ^C	Radiant energy flux	W	
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)	$m^6\ mol^{-1}$	$dm^3\ cm^3\ mol^{-1}$
	(Dexter)	$m^2\ mol^{-1}$	$dm^3\ cm^{-1}\ mol^{-1}$
$M_{p\lambda}$	Spectral photon exitance	$s^{-1}\ m^{-3}$ $mol\ s^{-1}\ m^{-3}d$	$s^{-1}\ m^{-2}\ nm^{-1}$ $mol\ s^{-1}\ m^{-2}\ nm^{-1}d$

Symbol	Name	Unit ^a	
		SI	common
$\Phi_{p\lambda}$	Spectral photon flow	$s^{-1} m^{-1}$ $mol^{-1} s^{-1} m^{-1d}$	$s^{-1} nm^{-1}$ $mol s^{-1} nm^{-1d}$
$E_{p\lambda}$	Spectral photon flux, Photon irradiance	$s^{-1} m^{-3}$ $mol s^{-1} m^{-3d}$	$s^{-1} m^{-2} nm^{-1}$ $mol s^{-1} m^{-2} nm^{-1d}$
$L_{p\lambda}$	Spectral photon radiance	$s^{-1} m^{-3} sr^{-1}$ $mol s^{-1} m^{-3} sr^{-1d}$	$s^{-1} m^{-2} sr^{-1} nm^{-1}$ $mol s^{-1} m^{-2} sr^{-1} nm^{-1d}$
I_{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, Spectral radiant flux	$W m^{-1}$	$W nm^{-1}$
s_{λ}	Spectral responsivity	---	
M_{nm}	Transition dipole moment	C m	D ^b
T, τ	Transmittance	---	
λ	Wavelength	m	nm
$\sigma, \tilde{\nu}$	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