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# Photocatalysis — Glossary of terms

### **National foreword**

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## Photocatalysis - Glossary of terms

Photokatalyse - Glossar der Begriffe

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## **European foreword**

This document (CEN/TS 16981:2016) has been prepared by Technical Committee CEN/TC 386 “Photocatalyse”, the secretariat of which is held by AFNOR.

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## Introduction

Photocatalysis is a very efficient advanced oxidation technique which enables the production of active species following light absorption by the photocatalyst, such as bound/free hydroxyl radicals ( $\cdot\text{OH}$ ), perhydroxyl radicals ( $\cdot\text{OOH}$ ), conduction band electrons and valence band holes, capable of partly or completely mineralising/oxidising the majority of organic compounds. The most commonly used photocatalyst is titanium dioxide ( $\text{TiO}_2$ ), the latter being thermodynamically stable, non-toxic and economical. It can be used in powder form or deposited on a substrate (glass fibre, fabrics, plates/sheets, etc.). The objective is to introduce performance standards for photo-induced effects (including photocatalysis). These standards will mainly concern test and analysis methods.

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## 1 Scope

A common language for standards, disclosed to a wide audience and referring only to the operational protocols and to their outcomes, is needed both for a consistent set of standards and the connection with the scientific literature. This glossary will take into account existing glossary of terms used in *photocatalysis* and *photochemistry*. Because in *photocatalysis* numerous properties are difficult to be evaluated, it is strongly recommended in standard norms to avoid reporting properties depending on number of active sites, the mechanisms of adsorption or kinetic mechanisms of photocatalytic reactions. For the same reason instead of the *quantum yield* and related quantities it is easier to report the *photonic efficiency*.

Most of the definitions reported in this Technical Specification are a sub-set of the IUPAC definitions in *photocatalysis* and radiocatalysis [1]. Some other definitions, in particular for the *photocatalytic rate* and reactors are taken from a dedicated work [2]. The use and many technical specifications on the physical values suggested for irradiation conditions in the standards are reported in a separate Technical Specification [3].

The arrangement of entries is alphabetical, and the criterion adopted by the IUPAC has been followed for the typeface used: *italicized words* in a definition or following it indicate a cross-reference in the Glossary.

## 2 Generalities

### 2.1 Note on units

SI units are adopted, with some exceptions, prominently in the use of the *molar decadic absorption coefficient*,  $\epsilon$ , with common units  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$  and a mole of photons denoted as an *einstein*. Note that “amount concentration” is the preferred term for what has been known as “molar concentration”, and is complementary to the terms “mass concentration” and “number concentration”.

### 2.2 Note on symbols

Functional dependence of a physical quantity  $f$  on a variable  $x$  is indicated by placing the variable in parentheses following the symbol for the function; e.g.,  $\epsilon(\lambda)$ . Differentiation of a physical quantity  $f$  with respect to a variable  $x$  is indicated by a subscript  $x$ ; e.g., the typical *spectral radiant power* quantity  $P_\lambda = dP/d\lambda$ . The natural logarithm is indicated with  $\ln$ , and the logarithm to base 10 with  $\log$ .

For the magnitudes implying energy or photons incident on a surface from all directions, the set of symbols recommended by the International Organization for Standardization (ISO) [4] and included in the IUPAC “Green Book”, and by the International Commission on Illumination [5] are adopted, i.e.,  $H_o$  or  $F_o$  for *fluence*,  $E_o$  for *fluence rate*,  $H_{p,o}$  or  $F_{p,o}$  for *photon fluence*, and  $E_{p,o}$  for *photon fluence rate*, note the letter o as subscript. This has been done primarily to comply with internationally agreed-upon symbols. It is important, however, to avoid confusion with the terms used to designate an amount of energy (or photons) prior to *absorption*. In these cases, the superscript 0 (zero) is used.

### 2.3 Note on the relationship between spectral, radiometric, and photonic quantities

When a quantity expressed in photonic units ( $G_p$ ) covers a *wavelength* range (polychromatic irradiation between  $\lambda_1$  and  $\lambda_2$ ), then  $G_p$  is the integral between  $\lambda_1$  and  $\lambda_2$  of the corresponding spectral photonic quantity,  $G_p(\lambda)$ :

$$G_p = \int_{\lambda_1}^{\lambda_2} G_p(\lambda) d\lambda \text{ (e.g., spectral photon flux).}$$

Since a spectral radiometric or energetic quantity at a given *wavelength*  $\lambda$  ( $G_{e,\lambda}$ , e.g., *spectral radiant power*,  $P_{\lambda/W}$  nm<sup>-1</sup>), is related to the corresponding photonic quantity at the same *wavelength* ( $G_{p,\lambda}$ , e.g., *spectral photon flux* / s<sup>-1</sup> nm<sup>-1</sup>) by the relation:

$$G_{e,\lambda} = E(\lambda) G_{p,\lambda}$$

with

$$E(\lambda) = h c / \lambda, \text{ the energy of a photon of wavelength } \lambda.$$

The relation between photonic ( $G_p$ ) and corresponding radiometric (or energetic,  $G_e$ ) quantity is given by:

$$G_e = h c \int_{\lambda_1}^{\lambda_2} G_p(\lambda) 1/\lambda d\lambda$$

or, more useful in practice:

$$G_p = (1/h c) \int_{\lambda_1}^{\lambda_2} G_e(\lambda) \lambda d\lambda$$

Therefore, for example, to calculate a *photon flux* over a *wavelength* interval, the *spectral distribution* of the *radiant power* is necessary. Note that in the Glossary no sub-index e has been used for the radiometric quantities. Radiometric quantities ( $G_e$ , as above, *radiant power* and others) are needed because *lamp* providers usually give the *spectral distribution* of the *lamps* in these units, and not in photonic units ( $G_p$ , *photon flux* and other photonic quantities) and because of quantification of radiation using, e.g., radiometers.

### 3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

#### 3.1

##### **absorbance, $A_e$**

logarithm to the base 10 (linear *absorbance*) of the incident (prior to *absorption*) *spectral radiant power*,  $P_\lambda^0$  divided by the transmitted *spectral radiant power*,  $P_\lambda$ :

$$A(\lambda) = \log \left( \frac{P_\lambda^0}{P_\lambda} \right) = -\log T(\lambda)$$

Note 1 to entry:  $T(\lambda)$  is the (internal) *transmittance* at the defined *wavelength*. The terms *absorbancy*, *extinction*, and *optical density* should no longer be used. When natural logarithms are used, the napierian *absorbance* is the logarithm to the base e of the incident *spectral radiant power*,  $P_\lambda^0$  divided by the transmitted *spectral radiant power*,  $P_\lambda$ :

$$A_e(\lambda) = \ln \left( \frac{P_\lambda^0}{P_\lambda} \right) = -\ln T(\lambda)$$

Note 2 to entry: These definitions suppose that all the incident *ultraviolet*, *visible*, or *infrared* radiation is either transmitted or absorbed, reflection or scattering being negligible. *Attenuance* should be used when this supposition cannot be made.



Note 3 to entry: In practice,  $A$  is the logarithm to the base 10 of the *spectral radiant power* of *ultraviolet, visible, or infrared* radiation transmitted through a reference sample divided by that transmitted through the investigated sample, both observed in identical cells.

Note 4 to entry: In common usage,  $A$  is given for a path length of 1 cm, unless otherwise specified.

Note 5 to entry: Traditionally, (spectral) *radiant intensity*,  $I_\lambda$ , was used instead of *spectral radiant power*,  $P_\lambda$ , now the accepted term.

Note 6 to entry: The *wavelength* symbol as a subscript for  $P$  and in parenthesis for  $T$  and  $A$  may be omitted. However, the *wavelength* should be specified for which the value of the particular property is reported.

Note 7 to entry: Same as internal *optical density*, which is a term not recommended.

Note 8 to entry: See also *absorption coefficient, absorptance, attenuation, Beer–Lambert law, Lambert law, molar absorption coefficient*.

### 3.2

#### **absorbed (spectral) photon flux density**

number of photons of a particular *wavelength*, per time interval (*spectral photon flux*, number basis,  $q_{p,\lambda}$  or *spectral photon flux*, amount basis,  $q_{n,p,\lambda}$ ) absorbed by a system per volume,  $V$

Note 1 to entry: On number basis, SI unit is  $\text{s}^{-1} \text{m}^{-4}$ ; common unit is  $\text{s}^{-1} \text{cm}^{-3} \text{nm}^{-1}$ . On amount basis, SI unit is  $\text{mol s}^{-1} \text{m}^{-4}$ ; common unit is *einstein*  $\text{s}^{-1} \text{cm}^{-3} \text{nm}^{-1}$

Note 2 to entry: Mathematical expression:  $\frac{q_{p,\lambda}^0 [1 - 10^{-A(\lambda)}]}{V}$  on number basis,  $\frac{q_{n,p,\lambda}^0 [1 - 10^{-A(\lambda)}]}{V}$  on amount basis, where  $A(\lambda)$  is the *absorbance* at *wavelength*  $\lambda$  and superscript 0 (zero) indicates incident photons.

Note 3 to entry: Absorbed (spectral) *photon flux* density (number basis or amount basis) is used in the denominator when calculating a differential *quantum yield* and using in the numerator the rate of change of the number,  $dC/dt$ , or the rate of change of the amount concentration,  $dc/dt$ , respectively.

### 3.3

#### **absorbed (spectral) radiant power density**

*spectral radiant energy* per time interval (*spectral radiant power*,  $P_\lambda$ ) absorbed by a system per volume,  $V$

Note 1 to entry: SI unit is  $\text{W m}^{-4}$ ; common unit is  $\text{W cm}^{-3} \text{nm}^{-1}$ .

Note 2 to entry: Mathematical expression:  $\frac{P_\lambda^0 [1 - 10^{-A(\lambda)}]}{V}$  where  $A(\lambda)$  is the *absorbance* at *wavelength*  $\lambda$  and superscript 0 (zero) indicates incident *radiant power*.

### 3.4

#### **absorptance, $a$**

fraction of *ultraviolet, visible, or infrared* radiation absorbed, equal to one minus the *transmittance* ( $T$ ), i.e.,  $(1 - T)$

Note 1 to entry: The use of this obsolete term, equivalent to *absorption factor*, is not recommended.

Note 2 to entry: See also *absorbance*.

### 3.5 absorption (of electromagnetic radiation)

transfer of energy from an electromagnetic field to a material or a molecular entity

Note 1 to entry: In a semiclassical fashion, this transfer of energy can be described as being due to an interaction of the electric field of the wave with an oscillating electric dipole moment set up in the material or molecular entity. This dipole moment is the result of the perturbation by the outside field, and its oscillation frequency  $\nu$  is given by the difference  $\Delta E$  of the energies of the lower and upper state in the absorbing material or molecular entity,  $\Delta E = h\nu$ . When the frequency of the oscillating dipole moment and the frequency of the field agree, a resonance occurs and energy can flow from the field into the material or molecule (an *absorption* occurs).

Note 2 to entry: When energy flows from the material or molecule to the field, stimulated light *emission* occurs.

Note 3 to entry: The oscillating electric dipole moment produced in the material or molecular entity has an amplitude and direction determined by a vector  $M_{if}$ , known as the electric transition (dipole) moment. The amplitude of this moment is the transition moment between the initial (i) and final states (f).

### 3.6 absorption coefficient (linear decadic $a$ or linear napierian $\alpha$ )

*absorbance*,  $A(\lambda)$ , divided by the optical pathlength,  $l$ :

$$a(\lambda) = \frac{A(\lambda)}{l} = \left(\frac{1}{l}\right) \log \left( \frac{P_{\lambda}^0}{P_{\lambda}} \right)$$

where

$P_{\lambda}^0$  and  $P_{\lambda}$  are, respectively, the incident and transmitted *spectral radiant power*. When napierian logarithms are used

$$\alpha(\lambda) = a(\lambda) \ln 10 = \left(\frac{1}{l}\right) \ln \left( \frac{P_{\lambda}^0}{P_{\lambda}} \right)$$

where

$\alpha$  is the linear napierian *absorption coefficient*.

Note 1 to entry: Since *absorbance* is a dimensionless quantity, the coherent SI unit for  $a$  and  $\alpha$  is  $\text{m}^{-1}$ ; the common unit is  $\text{cm}^{-1}$ .

Note 2 to entry: See also *absorptivity*, *molar absorption coefficient*.

### 3.7 absorption cross-section, $\sigma$

linear napierian *absorption coefficient*,  $\alpha(\lambda)$ , divided by the number of molecular entities contained in a volume of the absorbing medium along the *ultraviolet*, *visible*, or *infrared* radiation path:

$$\sigma(\lambda) = \frac{a(\lambda)}{C} = \frac{1}{Cl} \ln \left( \frac{P_{\lambda}^0}{P_{\lambda}} \right)$$

where

$C$  is the number concentration of molecular entities (number per volume),  $l$  is the optical pathlength, and  $P_{\lambda}^0$  and  $P_{\lambda}$  are, respectively, the incident and transmitted *spectral radiant power*.

Note 1 to entry: SI unit is  $\text{m}^2$ , common unit is  $\text{cm}^2$ .

Note 2 to entry: The relation between the *absorption cross-section* and the *molar (decadic) absorption coefficient*,  $\varepsilon(\lambda)$ , is  $\alpha(\lambda) = \ln 10 \varepsilon(\lambda) / N_A$  with  $N_A$  the Avogadro constant. A conversion equation in common units is:

$$\sigma(\lambda) / \text{cm}^2 = (3.8236 \times 10^{-21} / \text{mol}) \times [\varepsilon(\lambda) / \text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}].$$

Note 3 to entry: See also *attenuance*, *Beer-Lambert law*.

### 3.8

#### **absorption factor**

fraction of *ultraviolet*, *visible*, or *infrared* radiation absorbed by a system

$$f(\lambda) = 1 - T(\lambda) = 1 - 10^{-A(\lambda)}$$

with

$T(\lambda)$  the *transmittance* and  $A(\lambda)$  the *absorbance* at a particular *wavelength*  $\lambda$ .

Note 1 to entry: This term is preferred to *absorptance*.

Note 2 to entry: The *wavelength* symbol may be omitted for  $f$ ,  $T$ , and  $A$ . The *wavelength* should be specified for which the value of the particular property is reported.

Note 3 to entry: For  $A(\lambda) \ll 1 / \ln 10$ ,  $f(\lambda) \approx A(\lambda) \ln 10$ .

### 3.9

#### **absorption spectrum**

plot of the *absorbance* or of the *absorption coefficient* against a quantity related to *photon* energy, such as *frequency*  $\nu$ , *wavenumber*  $\tilde{\nu}$ , or *wavelength*  $\lambda$

### 3.10

#### **absorptivity**

*absorptance* divided by the optical pathlength

Note 1 to entry: The unit length shall be specified.

Note 2 to entry: The use of this obsolete term is not recommended.

Note 3 to entry: For very low *attenuance*, i.e., for  $A(\lambda) \ll 1 / \ln 10$ , it approximates the linear *absorption coefficient*, within the approximation  $[1 - 10^{-A(\lambda)}] \approx A(\lambda) \ln 10$ .

### 3.11

#### **actinic**

applied or referred to *actinism*. Relating to, resulting from, or exhibiting chemical changes produced by radiant energy especially in the *visible* and *ultraviolet* parts of the spectrum

### 3.12

#### **actinism**

chemical changes on living and nonliving materials caused by optical radiation

### 3.13

#### **actinometer**

chemical system for the determination of the number of *photons* integrally or per time interval absorbed into the defined space of a chemical reactor

Note 1 to entry: This name is commonly applied to systems used in the *ultraviolet* and *visible wavelength* ranges.

Note 2 to entry: For example, solutions of potassium oxalatoferate(III),  $K_3[Fe(C_2O_4)_3]$  (among other systems) can be used as a chemical *actinometer*. Bolometers, thermopiles, and photodiodes are physical devices giving a reading of the radiation impinging on them that can be correlated to the number of photons detected as well as to the number of photons entering the chemical reactor.

Note 3 to entry: *See also spectral sensitivity.*

### 3.14

#### **action spectrum**

plot of a relative biological or chemical photoresponse ( $=\Delta y$ ) per number of incident (prior to *absorption*) *photons*, vs. *wavelength*, or energy of radiation, or *frequency* or *wavenumber*

Note 1 to entry: 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.

Note 2 to entry: It is advisable to ensure that the *fluence* dependence of the photoresponse is the same (e.g., linear) for all the *wavelengths* studied.

Note 3 to entry: The *action spectrum* is sometimes called *spectral responsivity* or sensitivity spectrum. The precise *action spectrum* is a plot of the spectral (*photon* or quantum) effectiveness. By contrast, a plot of the biological or chemical change or response per absorbed *photon* (quantum efficiency) vs. *wavelength* is the *efficiency spectrum*.

Note 4 to entry: In cases where the *fluence* dependence of the photoresponse is not linear (as is often the case in biological photoresponses), a plot of the photoresponse vs. *fluence* should be made at several *wavelengths* and a standard response should be chosen. A plot of the inverse of the "standard response" level vs. *wavelength* is then the *action spectrum* of the photoresponse.

Note 5 to entry: *See also excitation spectrum, efficiency spectrum.*

### 3.15

#### **AM 0 sunlight**

solar *irradiance* in space just above the atmosphere of the earth on a plane perpendicular to the direction of the sun (air mass, AM, zero)

Note 1 to entry: Also called extraterrestrial *irradiance*.

Note 2 to entry: *See also AM 1 sunlight.*

### 3.16

#### **AM 1 sunlight**

solar *irradiance* at sea level, i.e., traversing the atmosphere, when the direction of the sun is perpendicular to the surface of the earth

Note 1 to entry: Also called terrestrial global *irradiance*.

Note 2 to entry: *See also AM 0 sunlight.*

**3.17  
 amalgam lamp**

see *mercury lamp*

**3.18  
 attenuance,  $D$**

logarithm to the base 10 of the incident *spectral radiant power*,  $P_{\lambda}^0$ , divided by the transmitted *spectral radiant power*,  $P_{\lambda}$

$$D(\lambda) = \log \left( \frac{P_{\lambda}^0}{P_{\lambda}} \right) = -\log T(\lambda)$$

where

$T(\lambda)$  is the *transmittance*

Note 1 to entry: *Attenuance* reduces to *absorbance* if the incident beam is only either transmitted or absorbed, but not reflected or scattered.

Note 2 to entry: See also *Beer–Lambert law*, *depth of penetration*.

**3.19  
 attenuance filter**

(better use: *neutral-density filter*)

**3.20  
 back electron-transfer**

term often used to indicate thermal inversion of *excited-state electron transfer* restoring the donor and acceptor in their original oxidation state

Note 1 to entry: Process better designated as *electron back-transfer*.

Note 2 to entry: In using this term, one should also specify the resulting electronic state of the donor and acceptor.

Note 3 to entry: It is recommended to use this term only for the process restoring the original electronic state of donor and acceptor.

Note 4 to entry: Should the forward *electron transfer* lead to *charge separation*, *electron back-transfer* will result in *charge recombination*.

**3.21  
 bandgap energy,  $E_g$**

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

Note 1 to entry: See also *Fermi level*.

**3.22  
 bandpass filter**

optical device that permits the transmission of radiation within a specified *wavelength* range and does not permit transmission of radiation at higher or lower *wavelengths*

Note 1 to entry: It can be an interference or a colored *filter*.

Note 2 to entry: See also *filter*.

### 3.23

#### **bathochromic shift (effect)**

shift of a spectral band to lower *frequency* (longer *wavelengths*) owing to the *influence* of substitution or a change in environment (e.g., solvent)

Note 1 to entry: It is informally referred to as a *red shift* and is opposite to a *hypsochromic shift*.

### 3.24

#### **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

Note 1 to entry: This law holds only under the limitations of the *Lambert law* and for absorbing species exhibiting no concentration or pressure dependent aggregation. The law can be expressed as

$$A(\lambda) = \log\left(\frac{P_{\lambda}^0}{P_{\lambda}}\right) = \varepsilon(\lambda)cl$$

or

$$P_{\lambda} = P_{\lambda}^0 10^{-A(\lambda)} = P_{\lambda}^0 10^{-\varepsilon(\lambda)cl}$$

where the proportionality constant,  $\varepsilon(\lambda)$ , is the molar (decadic) *absorption coefficient*, and  $P_{\lambda}^0$  and  $P_{\lambda}$  are, respectively, the incident and transmitted *spectral radiant power*. For *l* in cm and *c* in mol dm<sup>-3</sup> (M),  $\varepsilon(\lambda)$  will result in dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> (M<sup>-1</sup> cm<sup>-1</sup>), a commonly used unit. SI unit of  $\varepsilon(\lambda)$  is m<sup>2</sup> mol<sup>-1</sup> (10 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>).

Note 2 to entry: *Spectral radiant power* shall be used because the *Beer-Lambert law* holds only if the spectral bandwidth of the *ultraviolet*, *visible*, or *infrared* radiation is narrow as compared to spectral linewidths in the spectrum.

Note 3 to entry: See also *absorbance*, *attenuance*, *extinction coefficient*, *Lambert law*.

### 3.25

#### **bioluminescence**

*luminescence* produced by living systems

Note 1 to entry: See also *luminescence*.

### 3.26

#### **biphotonic excitation**

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

Note 1 to entry: Also called *two-photon excitation*.

Note 2 to entry: This term is sometimes also used for a two-step *absorption* when the *absorption* is no longer simultaneous.

### 3.27

#### **biphotonic process**

resulting from *biphotonic excitation*

Note 1 to entry: See also *multiphoton process*.

### 3.28

#### **bleaching**

in *photochemistry*, this term refers to the loss of *absorption* or *emission intensity*

### 3.29

#### **blue shift**

informal expression for *hypsochromic shift*

### 3.30

#### **Brewster angle, $\theta_B$**

when an unpolarized planar electromagnetic wavefront impinges on a flat dielectric surface, there is a unique angle ( $\theta_B$ ), commonly referred to as *Brewster angle*, at which the reflected waves are all polarized into a single plane

Note 1 to entry: Expression for *Brewster angle*:  $\theta_B = \arctan(n_2 / n_1) = \arctan(\epsilon_2 / \epsilon_1)^{1/2}$  where  $n_2$  and  $n_1$  are the refractive indices of the receiving surface and the initial medium, respectively, and  $\epsilon_2$  and  $\epsilon_1$  are the relative static permittivities (formerly called *dielectric constants*).

Note 2 to entry: For a randomly polarized beam incident at *Brewster angle*, the electric fields of the reflected and refracted waves are perpendicular to each other.

Note 3 to entry: For a wave incident from air on water ( $n = 1,333$ ), glass ( $n = 1,515$ ), and diamond ( $n = 2,417$ ), the *Brewster angles* are 53, 57, and 67,5 degrees, respectively.

### 3.31

#### **charge hopping**

electron or hole transport between equivalent sites

### 3.32

#### **charge recombination**

reverse of *charge separation*

Note 1 to entry: In using this term, it is important to specify the resulting electronic state of the donor and acceptor.

### 3.33

#### **charge separation**

process in which, under a suitable *influence* (e.g., *photoexcitation*), electronic charge moves in a way that increases (or decreases) the difference in local charges between donor and acceptor sites

Note 1 to entry: *Charge recombination* reduces (or increases) the difference.

Note 2 to entry: *Electron transfer* between neutral species is the most common example of *charge separation*. The most important example of *charge recombination* is electron backtransfer occurring after photoinduced *charge separation*.

### 3.34

#### **charge shift**

under a suitable *influence* (e.g., *photoexcitation*), electronic charge moves without changing the absolute value of the difference in local charges between the original donor and acceptor sites

Note 1 to entry: Prominent examples are the *electron transfer* reversing the charges in a system composed of a neutral donor and a cationic acceptor or of a neutral acceptor and an anionic donor.

### 3.35

#### **charge-transfer (CT) absorption**

electronic *absorption* corresponding to a *charge-transfer transition*

Note 1 to entry: In some cases, the *charge-transfer absorption* band(s) may be strongly obscured by the local *absorptions* of the donor and acceptor systems.

### 3.36

#### **charge-transfer (CT) complex**

ground-state complex that exhibits *charge-transfer absorption*

Note 1 to entry: See also *charge-transfer transition*.

### 3.37

#### **charge-transfer (CT) state**

state related to the *ground state* by a *charge-transfer transition*

### 3.38

#### **charge-transfer (CT) transition**

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)

Note 1 to entry: Transition typical for donor-acceptor complexes or multichromophoric molecular entities.

Note 2 to entry: See also *charge-transfer absorption*.

### 3.39

#### **charge-transfer transition to solvent (CTTS)**

electronic transition adequately described by single *electron transfer* between a solute and the solvent, different from excitation followed by *electron transfer* to solvent

Note 1 to entry: See also *charge-transfer (CT) transition*.

### 3.40

#### **chemiluminescence**

*luminescence* arising from generation by a chemical reaction of electronically excited molecular entities from reactants in their ground electronic states

### 3.41

#### **chromophore**

part of a molecular entity consisting of an atom or moiety in which the electronic transition responsible for a given spectral band above 200 nm is approximately localized

Note 1 to entry: In practice, this definition is extended to a part of a molecular entity in which an electronic transition responsible for *absorption* in the *ultraviolet* region of the spectrum is approximately localized as well as



to a part of a molecular entity in which a vibrational, rotational, or bending transition responsible for *absorption* in the *infrared* region of the spectrum is approximately localized.

### 3.42

#### **CIELAB**

a Lab color space is a color-opponent space with dimension L for lightness and a and b for the color-opponent dimensions, based on nonlinearly compressed CIE XYZ color space coordinates

Note 1 to entry: Lab is now more often used as an informal abbreviation for the CIE 1976 (L\*, a\*, b\*) color space (or CIELAB).

Note 2 to entry: Unlike the *RGB* and *CMYK* color models, Lab color is designed to approximate human vision.

Note 3 to entry: See also *RGB*.

### 3.43

#### **circular dichroism (CD)**

see *dichroism*

### 3.44

#### **color scale**

see *CIELAB*, *RGB*

### 3.45

#### **conduction band**

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

Note 1 to entry: Term usually used to describe the properties of metals and semiconductors.

Note 2 to entry: See also *bandgap energy*, *Fermi level*, *valence band*.

### 3.46

#### **conversion spectrum**

plot of a quantity related to the *absorption* (*absorbance*, etc.) multiplied by the *quantum yield* for the considered process, against a suitable measure of *photon energy*, such as *frequency*  $\nu$ , *wavenumber*  $\tilde{\nu}$ , or *wavelength*  $\lambda$

Note 1 to entry: See also *action spectrum*, *efficiency spectrum*, *spectral effectiveness*.

### 3.47

#### **conversion (chemical)**

symbols are arbitrary, often  $\eta$  or  $X$  are used

$$\eta = \frac{N_0 - N}{N_0} = \frac{c_0 - c}{c_0}$$

where

$N$  is the number of molecules or on a chemical basis the moles and  $c$  is the concentration entering in (subscript o) and flowing out the reactor. In a batch reactor, for a reactant  $A$  that is converted according to a first order rate  $r = k \times c$ , the *conversion*  $\eta = 1 - \exp(-kt)$ . Typically the *conversion* is evaluated under steady state in CSTR or PFR reactors (see *Reactor*)

### 3.48

#### CT

acronym for charge transfer

### 3.49

#### current yield

see *photocurrent yield*

### 3.50

#### cut-off filter

optical device that only permits the transmission of radiation of *wavelengths* longer or shorter than a specified *wavelength*

Note 1 to entry: Usually, the term refers to devices that transmit radiation of *wavelengths* longer than the specified *wavelength*.

Note 2 to entry: See also *cut-on filter*, *filter*.

### 3.51

#### cut-on filter

optical device that only permits the transmission of radiation of *wavelengths* shorter than a specified *wavelength*

Note 1 to entry: Although more rare than the *cut-off filters*, there are a few *cut-on filters* on the market.

Note 2 to entry: See also *cut-off filter*, *filter*.

### 3.52

#### dark reaction

chemical reaction that does not require or depend on the presence of light

Note 1 to entry: Contrasts with a *photochemical reaction*, which is initiated by light *absorption* by one or more of the reactants.

Note 2 to entry: A *dark reaction* is essentially a thermally activated reaction.

### 3.53

#### deactivation (of the catalyst)

reduced efficiency of the catalyst due to many possible reasons like poisoning, change of the surface texture, chemical migration of species

### 3.54

#### decay time

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

Note 1 to entry: Same as "apparent *lifetime*". The use of the latter term is not recommended.

Note 2 to entry: Should the entity disappear by a first-order process, the term *lifetime* is preferred.

### 3.55

depth of penetration (of *ultraviolet*, *visible*, or *infrared* radiation)

inverse of the linear *absorption coefficient*

Note 1 to entry: SI unit is m; common unit is cm.

Note 2 to entry: When the linear decadic *absorption coefficient*,  $a$ , is used, the *depth of penetration* ( $1/a$ ) is the distance at which the *spectral radiant power*,  $P_\lambda$ , decreases to one-tenth of its incident value, i.e., to  $P_\lambda^0/10$ . When the linear napierian *absorption coefficient*,  $\alpha$ , is used, the *depth of penetration* ( $1/\alpha = \beta$  in this case) is the distance at which the *spectral radiant power* decreases to  $1/e$  of its incident value, i.e., to  $P_\lambda^0/e$ .

Note 3 to entry: See also *absorbance, attenuation*.

### 3.56

#### **dichroic filter**

see *interference filter*

Note 1 to entry: The name dichroic arises from the fact that the *filter* appears one color under illumination with transmitted light and another with reflected light.

### 3.57

#### **dichroic mirror**

mirror used to reflect light selectively according to its *wavelength*

### 3.58

#### **dichroism**

dependence of *absorbance* of a sample on the type of *polarization* of the measuring beam

Note 1 to entry: This polarization may be linear, corresponding to linear *dichroism* (LD) in which the difference in *absorption* for two perpendicularly linearly polarized beams is measured,  $\Delta A_l = A_z - A_y$ , or *circular dichroism* (CD) in which the difference in *absorption* for left minus right circularly polarized beams is measured,  $\Delta A_c = A_L - A_R$ .

### 3.59

#### **dielectric constant**

obsolete term. Now called “relative (static) permittivity”

### 3.60

#### **differential quantum yield**

see *quantum yield*

### 3.61

#### **diode light emitting (LED)**

see *light-emitting diode*

### 3.62

#### **dose**

energy or amount of *photons* absorbed per volume (or per mass) by an irradiated object during a particular *exposure* time

Note 1 to entry: SI units are  $\text{J m}^{-3}$  or  $\text{J g}^{-1}$  and  $\text{mol m}^{-3}$  or  $\text{mol g}^{-1}$ , respectively.

Note 2 to entry: Common units are *einstein m*<sup>-3</sup> or *einstein g*<sup>-1</sup>, respectively.

Note 3 to entry: In medicine and in some other research areas (e.g., *photopolymerization* and water purification through irradiation) *dose* is used in the sense of *exposure*, i.e., the energy or amount of photons per surface area (or per volume) impinging upon an irradiated object during a particular *exposure* time. This use is not recommended. The terms *photon exposure* and *radiant exposure* are preferred. See also *einstein, UV dose*.

### 3.63

#### **driving force**

the negative of the standard Gibbs energy change ( $\Delta G^\circ$ ) for a particular reaction, e.g., for *energy transfer* or *electron transfer* ( $\Delta_{\text{ET}}G^\circ$ )

### 3.64

#### **driving force (for electron transfer)**

term widely used to indicate the negative of the standard Gibbs energy change for *outer-sphere electron transfer* ( $\Delta_{\text{ET}}G^\circ$ )

Note 1 to entry: For photoinduced processes, this quantity can often be estimated from independently determined properties of the donor and acceptor species involved using the equation for the calculation of the Gibbs energy of photoinduced *electron transfer*.

### 3.65

#### **efficiency spectrum**

plot of the efficiency of a step ( $\eta$ ) against *wavelength* or *photon energy*

Note 1 to entry: Compare with *spectral effectiveness*; see also *action spectrum*, *conversion spectrum*.

### 3.66

#### **einstein**

mole of *photons*

Note 1 to entry: Widely used, although it is not an SI unit.

Note 2 to entry: The energy of one *einstein* of photons of *frequency*  $\nu$  is  $E = N_{\text{A}}h\nu$ , with  $h$  the Planck constant and  $N_{\text{A}}$  the Avogadro constant.

### 3.67

#### **electron back-transfer**

thermal inversion of *excited-state electron transfer* restoring the donor and acceptor in their original oxidation state

Note 1 to entry: In using this term, one should also specify the resulting electronic state of the donor and acceptor.

Note 2 to entry: This term is preferred to *back electron-transfer*.

Note 3 to entry: It is recommended to use this term only for the process restoring the original electronic state of donor and acceptor.

Note 4 to entry: Should the forward *electron transfer* lead to *charge separation*, *electron back-transfer* will result in *charge recombination*.

### 3.68

#### **electron transfer**

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

Note 1 to entry: See also *Marcus equation*, *outer-sphere electron transfer*, *inner-sphere electron transfer*.

### 3.69

#### **electron-transfer photosensitization**

photochemical process in which a reaction of a non-absorbing substrate is induced by *electron transfer* (not *energy transfer*) to or from an *ultraviolet, visible, or infrared radiation-absorbing sensitizer*

Note 1 to entry: The overall process shall be such that the *sensitizer* is recycled. Depending on the action of the excited *sensitizer* as electron donor or acceptor the *sensitization* is called, respectively, reductive or oxidative.

Note 2 to entry: See also *photosensitization*.

### 3.70

#### **electronically excited state**

state of an atom or molecular entity that has higher electronic energy than the *ground state* of the same entity

Note 1 to entry: See also *excited state*.

### 3.71

#### **emission (of light)**

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

Note 1 to entry: Same as *luminescence*.

Note 2 to entry: See also *fluorescence, phosphorescence*.

### 3.72

#### **emission spectrum**

plot of the emitted *spectral radiant power* or of the emitted *spectral photon irradiance (spectral photon exitance)* against a quantity related to *photon energy*, such as *frequency,  $\nu$ , wavenumber,  $\tilde{\nu}$ , or wavelength,  $\lambda$*

Note 1 to entry: When corrected for *wavelength*-dependent variations in the equipment response, it is called a corrected *emission spectrum*.

### 3.73

#### **emissivity**

see *emittance*

### 3.74

#### **emittance, $e$**

*radiant exitance* emitted by an object relative to that of a black body at the same temperature

Note 1 to entry: It is dimensionless.

Note 2 to entry: Mathematical expression:  $M/M_{bb}$  with  $M$  and  $M_{bb}$  the *radiant exitance* of the object and of a black body, respectively.

### 3.75

#### **energy transfer**

*excitation transfer*. Process by which a molecular entity is excited (e.g., by *absorption of ultraviolet, visible, or infrared radiation* or by a chemical reaction that generates electronically excited molecular entities from reactants in their ground electronic states) and a phenomenon (a physical or a chemical process) originates from the *excited state* of another molecular entity, which has interacted with the originally absorbing entity

Note 1 to entry: In mechanistic *photochemistry*, the term has been reserved for the process in which an *excited state* (produced by *absorption* of radiation) 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*.

### 3.76 excitation spectrum

for a particular *luminescence wavelength* or *wavenumber*, a plot of the *spectral radiant power* or of the *spectral radiant exitance* or of the *spectral photon exitance* against the *frequency* (or *wavenumber* or *wavelength*) of excitation

Note 1 to entry: When corrected for *wavelength*-dependent variations in the excitation *radiant power*, this is called a corrected *excitation spectrum*.

Note 2 to entry: Due to the proportionality of the *emission* intensity with the absorbed *radiant power*, the *excitation spectrum* of a unique species should be identical to its *absorption spectrum* only at very low *absorbances*.

Note 3 to entry: See also *emission spectrum*.

### 3.77 excitation transfer

see *energy transfer*

### 3.78 excited state

state of higher energy than the *ground state* of a chemical entity

Note 1 to entry: In *photochemistry*, an *electronically excited state* is usually meant.

### 3.79 exciton

free exciton. In some applications, it is useful to consider electronic excitation as a quasi-particle that is capable of migrating

Note 1 to entry: In organic materials, two models are used: the band or wave model (low temperature, high crystalline order) and the hopping model (higher temperature, low crystalline order or amorphous state). *Energy transfer* in the hopping limit is identical with energy migration. In semiconductors and insulators, a free *exciton* is a bound electron-hole (neutral quasi-particle) capable of migrating and transferring its energy to the solid lattice. A localized *exciton* is an *exciton* trapped by a defect, which leads to the *electronically excited state* of the defect. In electroluminescent materials, *excitons* are the emissive entities produced by recombination of bipolarons.

### 3.80 exposure

term generally applied to the time-integrated radiation incident from all upward directions on a small sphere divided by the cross-sectional area of that sphere

Note 1 to entry: See also *photon exposure*, *radiant exposure*.

### 3.81 extinction

this term, equivalent to *absorbance*, is no longer recommended

### 3.82

#### **extinction coefficient**

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

Note 1 to entry: See also *Beer-Lambert law*.

### 3.83

#### **Fermi level, $E_F$**

highest energy level occupied with electrons in the *ground state* of a solid (metal, semiconductor, or insulator) or in an electrolyte solution

Note 1 to entry: See also *bandgap energy, conduction band, valence band*.

### 3.84

#### **filter (optical)**

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

### 3.85

#### **flash photolysis**

*transient-spectroscopy* and transient kinetic technique in which an *ultraviolet, visible, or infrared* radiation pulse is used to produce transient species

Note 1 to entry: Commonly, an intense pulse of short duration is used to produce a sufficient concentration of transient species suitable for spectroscopic observation. The most common use is for the observation of *absorption* of transient species (*transient absorption spectroscopy*).

Note 2 to entry: If only photophysical processes are involved, a more appropriate term would be “pulsed photoactivation”. The term “*flash photolysis*” would only be correct if chemical bonds are broken. However, historically, the name has been used to describe the technique of pulsed excitation, independently of the process that follows the excitation.

### 3.86

#### **fluence, $H_o$ , $F_o$**

*radiant energy fluence, spherical radiant exposure*. At a given point in space, the *radiant energy,  $Q$* , incident on a small sphere from all directions divided by the cross-sectional area of that sphere

Note 1 to entry: SI unit is  $\text{J m}^{-2}$ .

Note 2 to entry: The term is used in *photochemistry* to specify the energy delivered in a given time interval (e.g., by a laser pulse).

Note 3 to entry: Mathematical definition:  $H_o = dQ/dS$ , where  $S$  is the area of cross-section. If the *radiant energy* is constant over the area  $S$ ,  $H_o = Q/S$ .

Note 4 to entry: The definition is equivalent to  $H_o = \int t E_o dt$  where  $E_o$  is the *fluence rate* and  $t$  the duration of the irradiation. If the *fluence rate* is constant over the time interval,  $H_o = E_o t$ .

Note 5 to entry: *Fluence ( $H_o, F_o$ )* is identical to *spherical radiant exposure* and reduces to *radiant exposure,  $H$* , for a beam not scattered or reflected by the target or its surroundings.

Note 6 to entry: See also *dose, photon fluence*.

### 3.87

#### **fluence rate, $E_0$**

*radiant energy fluence rate, spherical irradiance.* Total *radiant power*,  $P$ , incident from all directions onto a small sphere divided by the cross-sectional area of that sphere

Note 1 to entry: SI unit is  $\text{W m}^{-2}$ .

Note 2 to entry: Mathematical definition:  $E_0 = dP/dS = dH_0/dt$ . If the *radiant power* is constant over the area  $S$ ,  $E_0 = P/S$ . Equivalent definition:  $E_0 = \int_{4\pi} L d\Omega$  with  $\Omega$  the solid angle of each beam passing through the given point on

the surface and  $L$  the *radiance* of the beam at that point.

Note 3 to entry: *Fluence rate* is identical to *spherical irradiance* and reduces to *irradiance*,  $E$ , for a parallel and perpendicularly incident beam not scattered or reflected by the target or its surroundings.

Note 4 to entry: See also *intensity, photon fluence rate, radiance*.

### 3.88

#### **fluorescence**

spontaneous *emission* of radiation (*luminescence*) from an excited molecular entity with retention of spin multiplicity

### 3.89

#### **fluorescence lifetime**

parameter describing the time evolution of the decay of the fluorescent *radiant intensity*

Note 1 to entry: See also *lifetime*.

### 3.90

#### **fluorescence spectrum**

see *emission spectrum*

### 3.91

#### **fluorophore**

molecular entity (often organic) that emits *fluorescence*

### 3.92

#### **Fourier-transform spectrometer**

scanning *interferometer* (containing no dispersive element) that first splits a beam into two or more components, then recombines these with a phase difference, thereby measuring the dephasing of the two beams

Note 1 to entry: The spectrum is obtained by a Fourier transformation of the output of the *interferometer*.

Note 2 to entry: There are Fourier spectrometers in nonoptical-, noninfrared-, such as nuclear magnetic resonance- and electron spin-resonance spectroscopies. In these cases, the decay over time of the signal resulting after applying a short pulse of the desired *frequency* is transformed from the time domain into a *frequency*-domain signal by a Fourier transformation.

### 3.93

#### **Fourier-transform spectroscopy**

measurement technique whereby spectra are collected based on measurements of the temporal coherence of a radiative source, using time-domain measurements of the electromagnetic radiation or other type of radiation



Note 1 to entry: This procedure can be applied to a variety of spectroscopies including optical-, *infrared*- (FTIR), nuclear magnetic resonance-, and electron spin-resonance spectroscopy. There are several methods for measuring the temporal coherence of the light, including the CW Michelson or *Fourier-transform spectrometer* and the pulsed Fourier-transform spectrograph (which is more sensitive and has a much shorter sampling time than conventional spectroscopic techniques).

### 3.94

frequency,  $\nu$  or  $\omega$

number of waveperiods per time interval

Note 1 to entry: The linear frequency,  $\nu$ , is the number of cycles per time interval. SI unit is Hz = s<sup>-1</sup>.

Note 2 to entry: For the angular frequency, the symbol  $\omega$  (= 2  $\pi$   $\nu$ ) is used with rad s<sup>-1</sup> as the SI unit.

### 3.95

**FWHM**

acronym for full width at half maximum

Note 1 to entry: See also *half-width (of a band)*

### 3.96

**Gaussian (band) shape**

(band) shape described by the Gaussian distribution function

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

with

$a^{-1}$  is proportional to the width of the band and  $\nu_0$  the value of the independent variable (e.g. *frequency* for band) at the maximum  $F(0)$

### 3.97

**germicidal lamp**

see *low-pressure mercury lamp*

Note 1 to entry: See also *lamp*.

### 3.98

**ground state**

lowest energy state of a chemical entity

Note 1 to entry: In *photochemistry*, ground electronic state is usually meant.

### 3.99

**half-life,  $\tau_{1/2}$ , of a transient entity**

time needed for a concentration of the entity to decrease to 1/2 of its original value

Note 1 to entry: See *lifetime*.

### 3.100

**half-width (of a band)**

full width of a spectral band at a height equal to half of the height at the band maximum

Note 1 to entry: Also known as full width at half maximum (*FWHM*).

Note 2 to entry: The dimension of bandwidth should be either inverse length (*wavenumbers*) or inverse time (*frequencies*) so that the values give an indication of the energies.

Note 3 to entry: The hyphen in *half-width*. Half-bandwidth has the meaning of *half-width* at half maximum.

Note 4 to entry: Used widely to specify *half-width* of transmission bands of optical filters.

### 3.101

#### **halogen lamp**

incandescent *lamp* that has a small amount of a halogen such as iodine or bromine added in the bulb

Note 1 to entry: A halogen cycle chemical reaction redeposits evaporated tungsten back onto the filament, increasing its life and maintaining the clarity of the envelope.

Note 2 to entry: *Halogen lamps* can be operated at a higher temperature than a standard incandescent *lamp*, producing light of a higher luminous efficacy and color temperature.

Note 3 to entry: The small size of *halogen lamps* permits their use in compact optical systems for projectors and illumination.

Note 4 to entry: See also *lamp*.

Note 5 to entry: In *halogen lamps*, the quartz envelope is closer to the filament than the glass used in conventional light bulbs. Heating the filament to a high temperature causes the tungsten (wolfram) atoms to evaporate and combine with the halogen gas. These heavier molecules are then deposited back on the filament surface. This recycling process increases the *lifetime* of the tungsten (wolfram) filament and enables the *lamp* to produce more light per unit of input energy.

Note 6 to entry: See also *tungsten lamp*, *wolfram lamp*.

### 3.102

#### **high-pressure mercury lamp (arc)**

radiation source containing mercury at a pressure of ca. 8 MPa (ca. 80 bar) or higher and emitting a background continuum between about 200 nm and 1400 nm with noticeable peaks

Note 1 to entry: See also *mercury lamp*.

### 3.103

#### **hypsochromic shift**

shift of a spectral band to higher *frequency* (shorter *wavelength*) upon substitution or change in medium (e.g., solvent)

Note 1 to entry: It is informally referred to as a *blue shift* and is opposite to a *bathochromic shift*.

### 3.104

#### **hole transfer**

charge migration process in which the majority carriers are positively charged

### 3.105

#### **infrared**

region of the electromagnetic spectrum extending from 780 to about 20000 nm

Note 1 to entry: According to the CIE, the range between 780 nm and 1 mm is subdivided into:

— IR-A 780–1400 nm, commonly referred to as near infrared (NIR);

- IR-B 1,4–3  $\mu\text{m}$ ;
- IR-C 3  $\mu\text{m}$  –1 mm

Note 2 to entry: This is the *wavelength* region in which *absorption* by a molecular entity causes excitation of its vibrational, rotational, and bending modes.

### 3.106

#### **inner-filter effect**

term used in two different ways:

- 1) in an *emission* experiment, it refers to (a) an apparent decrease in emission *quantum yield* at high concentration of the emitter due to strong *absorption* of the excitation light and (b) an apparent decrease in emission *quantum yield* and/or distortion of bandshape as a result of re-*absorption* of emitted radiation (particularly severe for emitters with small *Stokes shift*);
- 2) during an irradiation experiment, *absorption* of incident radiation by a species other than the intended primary absorber is also described as an *inner-filter effect*

### 3.107

#### **inner-sphere electron transfer**

historically, an *electron transfer* between two metal centers sharing a ligand or atom in their respective coordination shells

Note 1 to entry: See also *electron transfer*.

Note 2 to entry: Definition more recently been extended to any situation in which the interaction between the donor and acceptor centers in the transition state is significant ( $> 20 \text{ kJ mol}^{-1}$ ). Compare with *outer-sphere electron transfer*.

### 3.108

#### **integrating sphere**

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

### 3.109

#### **intensity**

traditional term indiscriminately used for *photon flux*, *fluence rate*, *irradiance*, or *radiant power*

Note 1 to entry: In terms of an object exposed to radiation, the term should now be used only for qualitative descriptions.

### 3.110

#### **intensity, $I$ (of an ultraviolet, visible, or infrared radiation source)**

see *radiant intensity*

### 3.111

#### **intensity (of a spectral feature)**

describes the magnitude of the particular feature in the spectrum

### 3.112 interference filter

*dichroic filter*. Optical device that permits the transmission of radiation within a certain *wavelength* range based on the principle of waves interference

Note 1 to entry: Technically, a thin transparent spacer is placed between two semi-reflective coatings and multiple reflections and interference are used to select a *frequency* band (it may be relatively narrow) to produce an *interference filter*.

### 3.113 interferometer

see *Fourier-transform spectrometer*

### 3.114 inverted region (for electron transfer)

Marcus inverted region (for *electron transfer*). Region where the *driving force* ( $-\Delta_{ET}G^{\circ}$ ) for *electron transfer* exceeds the total reorganization energy ( $\lambda$ ), i.e.,  $-\Delta_{ET}G^{\circ} > \lambda$  in the *Marcus equation* developed for *outer-sphere electron transfer*

Note 1 to entry: The behaviour in this region is referred to as *electron transfer* under *inverted region* conditions because the basic/classical *Marcus equation* leads to a counter-intuitive prediction that under such conditions the rate of *electron transfer* should decrease with increasing exergonicity ( $\Delta_{ET}G^{\circ}$ ).

### 3.115 irradiance (at a point of a surface), *E*

*radiant power*, *P*, of all *wavelengths* incident from all upward directions on a small element of surface containing the point under consideration divided by the area of the element

Note 1 to entry: SI unit is  $W\ m^{-2}$ .

Note 2 to entry: Mathematical definition:  $E = dP/dS$ . If the *radiant power* is constant over the surface area considered,  $E = P/S$ .

Note 3 to entry: Alternative definition: Integral, taken over the hemisphere *visible* from the given point, of the expression  $L \cos\theta\ d\Omega$ , where *L* is the *radiance* at the given point in the various directions of the incident elementary beams of solid angle  $\Omega$  and  $\theta$  is the angle between any of the beams and the normal to the surface at the given point.  $E = \int_{2\pi} L \cos\theta\ d\Omega$

Note 4 to entry: This term refers to a beam not scattered or reflected by the target or its surroundings. For a beam incident from all directions, *fluence rate* ( $E_0$ ) is an equivalent term.

Note 5 to entry:  $E = \int_{\lambda} E\lambda\ d\lambda$ , where  $E\lambda$  is the *spectral irradiance* at *wavelength*  $\lambda$ .

Note 6 to entry: See also *photon irradiance*.

### 3.116 Lambert-Beer law see *Beer-Lambert law*

### 3.117 Lambert law

the fraction of *ultraviolet*, *visible*, or *infrared* radiation absorbed by a system is independent of the incident *spectral radiant power*

Note 1 to entry: This law holds only if  $P_{0\lambda}$  is small, scattering is negligible, and *multiphoton processes*, *excited state populations*, and *photochemical reactions* are negligible.

Note 2 to entry: See also *absorbance*, *Beer–Lambert law*.

### 3.118

#### **lamp**

source of *incoherent* radiation

### 3.119

#### **LED**

acronym for *light-emitting diode*

### 3.120

#### **lifetime, $\tau$**

lifetime of a molecular entity, which decays by first-order kinetics, is the time needed for a concentration of the entity to decrease to  $1/e$  of its original value, i.e.,  $c(t = \tau) = c(t = 0)/e$

Note 1 to entry: Statistically, it represents the life expectation of the entity. It is equal to the reciprocal of the sum of the first-order rate constants of all processes causing the decay of the molecular entity.

Note 2 to entry: Mathematical definition:  $\tau = 1/k = 1 / (\sum_i k_i)$  with  $k_i$  the first-order rate constants for all decay processes of the decaying state.

Note 3 to entry: *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 *decay time*.

Note 4 to entry: 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, i.e.,  $c(t = \tau_{1/2}) = c(t = 0)/2$ . For first-order reactions,  $\tau_{1/2} = \ln 2 \tau$ .

### 3.121

#### **light-emitting diode (LED)**

semiconductor (often a combination of gallium, arsenic, and phosphorous or gallium and nitrogen) containing a *n* region (where electrons are more numerous than positive charges) separated from a *p* region (where positive charges are more numerous than negative charges)

Note 1 to entry: Upon application of a voltage, charges move and *emission of ultraviolet, visible, or infrared* radiation is produced each time a *charge recombination* takes place. Although an LED emits incoherent monochromatic light, normally a very narrow *frequency* range is obtained.

Note 2 to entry: This effect is a form of *electroluminescence*.

Note 3 to entry: The color depends on the semiconducting material used, and can be *ultraviolet, visible, or infrared*.

Note 4 to entry: *Organic light-emitting devices* (OLEDs) contain diodes made of small molecules or made of polymeric materials. The latter are sometimes called PLEDs.

### 3.122

#### **light source**

body able to emit light

### 3.123

#### low-pressure mercury lamp (arc)

*resonance lamp* that contains mercury vapor at pressures of about 0,1 Pa ( $0,75 \times 10^{-3}$  Torr; 1 Torr = 133,3 Pa)

Note 1 to entry: At 25 °C, such a *lamp* emits mainly at 253,7 nm and 184,9 nm. They are also called *germicidal lamps*. There are cold- and hot-cathode as well as cooled electrode-less (excited by microwaves) low pressure *mercury lamps*. The *Wood lamp* is a low-pressure mercury arc with an added fluorescent layer that emits in the UV-A spectral region (315–400 nm).

### 3.124

#### luminescence

*spontaneous emission* of radiation from an *electronically excited state* or from a *vibrationally excited state* of a species not in thermal equilibrium with its environment

Note 1 to entry: See also *bioluminescence*, *chemiluminescence*, *fluorescence*, *phosphorescence*, *photoluminescence*.

### 3.125

#### lumiphore (luminophore)

molecular entity that displays *luminescence* or part of a molecular entity (or atom or group of atoms) in which electronic excitation associated with a given *emission* band is approximately localized

Note 1 to entry: Analogous to *chromophore* for *absorption* spectra.

### 3.126

#### Marcus equation (for electron transfer)

relation between the rate of *outer-sphere electron transfer* and the thermodynamics of this process

Note 1 to entry: Essentially, the rate constant within the encounter complex (or the rate constant of intramolecular transfer) is given by the Eyring equation  $k_{ET} = (\kappa_{ET} k T/h) \exp(-\Delta G^\ddagger/RT)$ .

where  $k$  is the Boltzmann constant,  $h$  the Planck constant,  $R$  the gas constant, and  $\kappa_{ET}$  the so-called electronic transmission factor ( $\kappa_{ET} \sim 1$  for adiabatic and  $\ll 1$  for diabatic *electron transfer*). For *outer sphere electron transfer*, the barrier height can be expressed as  $\Delta G^\ddagger = (\lambda + \Delta_{ET}G^0)^2/(4\lambda)$ , where  $\Delta_{ET}G^0$  is the standard Gibbs energy change accompanying the electron-transfer reaction and  $\lambda$  the total reorganization energy.

Note 2 to entry: Whereas the classical *Marcus equation* has been found to be quite adequate in the normal region, it is now generally accepted that in the *inverted region* a more elaborate formulation, taking into account explicitly the Franck-Condon factor due to quantum mechanical vibration modes, should be employed.

### 3.127

#### medium-pressure mercury lamp (arc)

*noncoherent* radiation source containing mercury vapor at pressures ranging from 50 to several hundred kPa (1 atm = 101,325 kPa)

Note 1 to entry: Emits mostly from 200 to 1000 nm with the most intense lines approximately at 218, 248, 254, 266, 280, 289, 297, 303, 313, 334, 366, 406, 408, 436, 546, and 578 nm.

Note 2 to entry: See also *mercury lamp*.

### 3.128

#### mercury lamp

see *low-pressure mercury lamp*, *medium-pressure mercury lamp*, *high-pressure mercury lamp*

### 3.129

#### mercury-xenon lamp (arc)

*noncoherent* 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

Note 1 to entry: See also *xenon lamp*.

### 3.130

#### molar absorption coefficient, $\varepsilon$

molar decadic *absorption* coefficient. *Absorbance* divided by the *absorption* pathlength,  $l$ , and the amount concentration,  $c$ :

$$\varepsilon(\lambda) = \left( \frac{1}{cl} \right) \log \left( \frac{P_{\lambda}^0}{P_{\lambda}} \right) = \frac{A(\lambda)}{cl}$$

where

$P_{\lambda}^0$  and  $P_{\lambda}$  are, respectively, the incident and transmitted *spectral radiant power*

Note 1 to entry: The term molar *absorptivity* for *molar absorption coefficient* should be avoided.

Note 2 to entry: In common usage for l/cm and c/mol dm<sup>-3</sup> ( $M$ ),  $\varepsilon(\lambda)$  results in dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> ( $M^{-1}$  cm<sup>-1</sup>, the most commonly used unit), which equals 0,1 m<sup>2</sup> mol<sup>-1</sup> (coherent SI units).

Note 3 to entry: See also *absorbance*, *absorption* coefficient, *Beer-Lambert law*.

### 3.131

#### monochromator

optical device that transmits a selectable narrow band of *wavelengths* of electromagnetic radiation chosen from a wider range of *wavelengths* available at the input

Note 1 to entry: It is an energy dispersive element.

Note 2 to entry: To spatially separate the *wavelengths*, a *monochromator* can use either the phenomenon of optical dispersion in a prism, or that of diffraction using a grating.

### 3.132

#### multiphoton process

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

Note 1 to entry: See also *biphotonic excitation*, *biphotonic process*, *two-photon excitation*.

### 3.133

#### neutral-density filter

optical device (*filter*) reducing the *radiant power* of an *ultraviolet*, *visible*, or *infrared* radiation beam by a constant factor over all *wavelengths* within its operating range

Note 1 to entry: Sometimes called attenuator or *attenuance filter*.

### 3.134

#### nonradiative decay

disappearance of an excited species due to a radiationless transition

### 3.135

#### **OLED**

acronym for *organic light-emitting device*

### 3.136

#### **OMA**

acronym for *optical multichannel analyzer*

### 3.137

#### **OPA**

acronym for optical parametric amplifier

Note 1 to entry: See *optical parametric amplification*.

### 3.138

#### **OPO**

acronym for *optical parametric oscillator*

### 3.139

#### **optical density**

see *absorbance*

Note 1 to entry: The use of the term *optical density* is discouraged.

### 3.140

#### **optical multichannel analyzer (OMA)**

detection system for fast acquisition of spectra. It consists of a “polychromator” fitted with a detector that enables spatial resolution, e.g., a “vidicon tube”, a “silicon photodiode array”

### 3.141

#### **optical parametric amplification**

process of signal amplification by a parametric process and a pump wave

### 3.142

#### **optical parametric oscillator (OPO)**

*light source* similar to a *laser*, but based on “nonlinear optical gain” from parametric amplification rather than on stimulated emission

Note 1 to entry: The device is a powerful solid-state source of broadly tunable coherent radiation. It consists of a crystal, usually BBO ( $\text{BaB}_2\text{O}_4$ ), located inside an optical resonator and pumped by a very intense laser beam (typically provided by a pulsed neodymium laser or a diode laser). The pump beam (*wavelength*  $\lambda_p$ , *frequency*  $\nu_p$ ) is partially converted into two coherent beams, the signal and the idler, with *wavelengths* ( $\lambda_s$ ,  $\lambda_i$ ) and frequencies ( $\nu_s$ ,  $\nu_i$ ) such that  $(\nu_s + \nu_i) = \nu_p$ . By simultaneous rotation of the crystal and adjustment of the optical resonator, the *wavelength* of the signal beam is continuously tunable, theoretically from  $\lambda_p$  to  $2 \times \lambda_p$  and practically over a slightly more reduced range.

Note 2 to entry: For example, for  $\lambda_p = 355$  nm (3rd harmonic of a Nd:YAG laser),  $\lambda_s$  can be tuned from 400 nm (with  $\lambda_i \approx 3,15 \mu$ ) up to 600 nm (with  $\lambda_i \approx 870$  nm).

Note 3 to entry: This “splitting of one *photon* into two photons” is the reverse of the “sum *frequency* mixing” used, for instance, to generate the 3rd harmonic of a laser emission by mixing in a convenient crystal the fundamental and the *frequency* doubled beams (a way to get the 3rd harmonic much more efficiently than by pure *frequency* tripling as described under harmonic *frequency* generation).



**3.143**

**optoacoustic spectroscopy**

same as *photoacoustic spectroscopy*

Note 1 to entry: Frequently used to denominate the laser-induced production of acoustic waves combined with a piezoelectric detector and distinguish it from the amplitude-modulated excitation combined with a gas-coupled microphone as detector.

**3.144**

**organic light-emitting device (OLED)**

see *light-emitting diode* (LED)

**3.145**

**outer-sphere electron transfer**

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

Note 1 to entry: Compare with *inner-sphere electron transfer*; see also *Marcus equation*.

**3.146**

**phosphorescence**

phenomenologically, term used to describe long-lived *luminescence*

Note 1 to entry: In mechanistic *photochemistry*, the term designates *luminescence* involving change in spin multiplicity, typically from *triplet* to *singlet* or vice versa.

**3.147**

**photoacoustic spectroscopy (PAS)**

*optoacoustic spectroscopy*. Spectroscopic technique based on the photoacoustic effect

Note 1 to entry: 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.

**3.148**

**photo-assisted catalysis**

catalytic reaction involving production of a catalyst by *absorption* of *ultraviolet*, *visible*, or *infrared* radiation

Note 1 to entry: See also *photocatalysis*.

**3.149**

**photocatalysis**

change in the rate of a chemical reaction or its initiation under the action of *ultraviolet*, *visible*, or *infrared* radiation in the presence of a substance—the *photocatalyst*—that absorbs light and is involved in the chemical transformation of the reaction partners

**3.150**

**photocatalyst**

catalyst able to produce, upon *absorption* of light, chemical transformations of the reaction partners both exoergonic or endoergonic

Note 1 to entry: The *excited state* of the *photocatalyst* repeatedly interacts with the reaction partners forming reaction intermediates and regenerates itself after each cycle of such interactions.

### 3.151

#### **photocatalytic rate**

the *reaction rate* of a given chemical reaction that is affected by the presence of a *photocatalyst*

Note 1 to entry: Careful measurements on the effect of light alone shall be checked, as well as that the photocatalyst is stable (see *photocatalyst*).

### 3.152

#### **photocatalytic reactor**

the apparatus used for carrying out the photocatalytic reaction

Note 1 to entry: It usually refers to the apparatus used to evaluate the *photocatalytic rate*, and the related performance of the materials or photocatalytic specimens.

Note 2 to entry: Different type of reactors can be used, giving different *conversion* depending on the experimental conditions (see *conversion*, *reactor batch*, *reactor CSTR*, *reactor PFR*).

### 3.153

#### **photochemical reaction**

generally used to describe a chemical reaction caused by *absorption* of *ultraviolet*, *visible*, or *infrared* radiation

Note 1 to entry: There are many ground-state reactions, which have photochemical counterparts. Among these are photochemical nitrogen extrusions, photocycloadditions, photodecarbonylations, photodecarboxylations, photoenolizations, photo-Fries rearrangement, *photoisomerizations*, *photooxidations*, photorearrangements, *photoreductions*, photosubstitutions, etc.

### 3.154

#### **photochemical smog**

product of *photochemical reactions* caused by solar radiation and occurring in polluted air as well as in air containing compounds emitted by natural sources, such as those emitted by vegetation

### 3.155

#### **photochemistry**

branch of chemistry concerned with the chemical effects of *ultraviolet*, *visible*, or *infrared* radiation

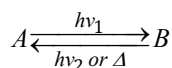
Note 1 to entry: See also *photochemical reaction*.

### 3.156

#### **photochromism**

reversible transformation of a molecular entity between two forms, A and B, having different *absorption* spectra, induced in one or both directions by *absorption* of electromagnetic radiation

Note 1 to entry: The spectral change produced is typically, but not necessarily, of *visible* color and is accompanied by differences in other physical properties. The thermodynamically stable form A is transformed by irradiation into form B. The back reaction can occur thermally (*photochromism* of type T) or photochemically (*photochromism* of type P).



Note 2 to entry: The terms “switch-on” and “switch-off” are sometimes used to denote the two directions of the photochromic reaction.

**3.157**

**photoconductivity**

increase in electrical conductivity resulting from photoproduction of charge carriers

**3.158**

**photocuring**

technical expression for the photoinduced hardening of a monomeric, oligomeric, or polymeric substrate normally in the form of a film

Note 1 to entry: Also called UV curing.

**3.159**

**photocurrent yield**

*quantum efficiency* of charge photogeneration between the two electrodes of a photovoltaic cell or a *photoelectrochemical cell*

**3.160**

**photodegradation**

photochemical transformation of an organic molecule into lower molecular weight molecules, both in an oxidation or reduction process

Note 1 to entry: Term widely used in the destruction (oxidation) of pollutants by processes based on UV irradiation and on *photocatalysis* as well as in the decomposition of polymers by processes based on UV-visible irradiation, which change the characteristic properties of the polymer.

**3.161**

**photodynamic effect**

term used in *photobiology* to refer to photoinduced effect requiring the simultaneous presence of *ultraviolet, visible, or infrared* radiation, a *photosensitizer*, and dioxygen molecules

**3.162**

**photoelectric effect**

ejection of an electron from a solid or a liquid by a *photon*

**3.163**

**photoelectrochemical cell**

electrochemical cell in which current and a voltage are simultaneously produced upon *absorption* of *ultraviolet, visible, or infrared* radiation by one or more of the electrodes

Note 1 to entry: Usually, at least one of the electrodes is a semiconductor.

**3.164**

**photoelectrochemical etching**

dissolution of a semiconductor in an electrolytic solution upon *exposure* to *ultraviolet, visible, or infrared* radiation

**3.165**

**photoexcitation**

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

**3.166**

**photohydration**

*photochemical reaction* leading to the addition of water across a C-C double (or triple) bond or to a carbonyl (or carbonyl analog) group

### 3.167

#### **photoinduced electron transfer (PET)**

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

Note 1 to entry: *Photoinduced electron transfer* is a thermal *electron transfer* subsequent to *photoexcitation* of one of the reactants or the *photocatalyst*.

### 3.168

#### **photoionization**

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

### 3.169

#### **photoisomerization**

*photochemical process* leading to an isomerization of the substrate, either by bond rotation, skeletal rearrangement, or atom- or group transfer

Note 1 to entry: Typical examples are cis/trans photo-isomerization of alkenes, polyenes, and photo-tautomerization.

Note 2 to entry: Photochemical pathways have the advantage over thermal and catalytic methods of giving isomer mixtures (photo-stationary states) rich in thermodynamically unstable isomers.

Note 3 to entry: *Photoisomerization* is the primary *photochemical reaction* of the *chromophore* in several biological photoreceptors such as retinal proteins and the photoactive yellow protein.

### 3.170

#### **photoluminescence**

*luminescence* arising from direct *photoexcitation* of the emitting species

Note 1 to entry: See also *fluorescence*, *phosphorescence*.

### 3.171

#### **photolysis**

bond cleavage induced by *absorption* of *ultraviolet*, *visible*, or *infrared* radiation

Note 1 to entry: Term often used incorrectly to describe irradiation of a sample, although in the combination *flash photolysis* this usage is accepted. See also *flash photolysis*.

### 3.172

#### **photon**

*quantum* of electromagnetic energy at a given *frequency*

Note 1 to entry: This energy,  $E = h\nu$ , is the product of the Planck constant ( $h$ ) and the *frequency* of the radiation ( $\nu$ ).

### 3.173

#### **photon counting**

*single-photon counting*. Recording of sequential single *photons* counted by way of recording and counting sequential electron pulses at the anode of the photomultiplier

Note 1 to entry: Each electron pulse consists of  $10^5$ – $10^6$  electrons resulting from the multiplication, in the “dynode” arrangement (or the microchannel plate) of a photomultiplier, of a single photoelectron emitted by a photosensitive layer (the photocathode of the photomultiplier) upon arrival of a single photon.

Note 2 to entry: Technique used for two purposes: (i) sensitive measurement of low levels of radiation such as those originating from a luminophore and (ii) recording of emission decays.

### 3.174

#### **photon emittance**

former name for *photon exitance*

### 3.175

#### **photon exitance, $M_p$**

specific *photon emission*. *Photon flux, number basis,  $q_p$* , emitted by an element of the surface containing the source point under consideration divided by the area  $S$  of that element

Note 1 to entry: SI unit is  $s^{-1} m^2$ .

Note 2 to entry: Mathematical definition:  $dq_p/dS$ . If  $q_p$  is constant over the surface area considered,  $M_p = q_p/S$ .

Note 3 to entry: Formerly called *photon emittance*.

Note 4 to entry: This quantity can be expressed on a chemical amount basis by dividing  $M_p$  by the Avogadro constant. In this case, the symbol is  $M_{n,p}$ , the name "*photon exitance, amount basis*", SI unit is  $mol s^{-1} m^{-2}$ ; common unit is *einstein*  $s^{-1} m^{-2}$ .

### 3.176

#### **photon exposure, $H_p$**

*photon irradiance,  $E_p$* , integrated over the time of irradiation for a beam incident from all upward directions

Note 1 to entry: SI unit is  $m^{-2}$ .

Note 2 to entry: Mathematical definition:  $H_p = \int_t E_p dt$ . If the *photon irradiance* is constant over the time interval,  $H_p = E_p t$ .

Note 3 to entry: This term refers to a beam not scattered or reflected by the target or its surroundings. For a beam incident from all directions, *photon fluence* ( $H_{p,o}$ ,  $F_{p,o}$ ) is an equivalent term.

Note 4 to entry: This quantity can be used on a chemical amount basis by dividing  $H_p$  by the Avogadro constant, the symbol then being  $H_{n,p}$ , the name "*photon exposure, amount basis*", SI unit is  $mol m^{-2}$ ; common unit is *einstein*  $m^{-2}$ .

Note 5 to entry: See also *fluence, radiant exposure*.

### 3.177

#### **photon fluence, $H_{p,o}$ , $F_{p,o}$**

amount of photons (quanta of radiation) incident on a small sphere from all directions, divided by the cross-sectional area of that sphere and integrated over time

Note 1 to entry: *Photons* per surface area (quanta  $m^{-2}$ ).

Note 2 to entry: SI unit is  $m^{-2}$ .

Note 3 to entry: Mathematical definition:  $H_{p,o} = F_{p,o} = dNp/dS = \int_t E_{p,o} dt$ , with  $E_{p,o}$  the *photon fluence rate*, integrated over the duration of the irradiation,  $t$ . If  $E_{p,o}$  is constant over the time interval,  $H_{p,o} = F_{p,o} = E_{p,o} t$ .

Note 4 to entry: This quantity can be used on a chemical amount basis by dividing  $H_{p,o}$  by the Avogadro constant, the symbol then being  $H_{n,p,o}$ , the name “*photon fluence, amount basis*”, SI unit is  $\text{mol m}^{-2}$ ; common unit is *einstein m}^{-2}*.

Note 5 to entry: See also *fluence*.

### 3.178

#### **photon fluence rate, $E_{p,o}$**

rate of *photon fluence*. Total number of photons ( $N_p$ ) incident from all directions on a small sphere divided by the cross-sectional area of the sphere and per time interval

Note 1 to entry: SI unit is  $\text{m}^{-2} \text{s}^{-1}$ .

Note 2 to entry: Same as *photon spherical irradiance*.

Note 3 to entry: Mathematical definition:  $E_{p,o} = dN_p/(dt dS) = d H_{p,o}/dt$ . If  $N_p$  is constant over the time interval and the surface,  $E_{p,o} = N_p/t S$ . Equivalent definition:  $E_{p,o} = \int_{4\pi} L_p d\Omega$  with  $L_p$  the *photon radiance* and  $\Omega$  the solid angle of the beams passing through the given point on the surface.

Note 4 to entry: It reduces to *photon irradiance*  $E_p$  for a parallel and normally incident beam not scattered or reflected by the target or its surroundings.

Note 5 to entry: This quantity can be used on a chemical amount basis by dividing  $E_{p,o}$  by the Avogadro constant, the symbol then being  $E_{n,p,o}$ , the name “*photon fluence rate, amount basis*”, SI unit is  $\text{mol m}^{-2} \text{s}^{-1}$ ; common unit is *einstein m}^{-2} \text{s}^{-1}*.

Note 6 to entry: See also *fluence rate, photon radiance*.

### 3.179

#### **photon flux, $q_p$ , $\Phi_p$**

number of *photons* (quanta of radiation,  $N_p$ ) per time interval

Note 1 to entry: SI unit is  $\text{s}^{-1}$ .

Note 2 to entry: Mathematical definition:  $q_p = dN_p/dt$ . If the number of photons is constant over the time interval,  $q_p = N_p/t$ .

Note 3 to entry: This quantity can be used on a chemical amount basis by dividing the *photon flux*, number basis,  $q_p$ , by the Avogadro constant, the symbol then being  $q_{n,p}$ , the name “*photon flux, amount basis*”, SI unit is  $\text{mol s}^{-1}$ ; common unit is *einstein s}^{-1}*.

Note 4 to entry: Although the symbol recommended by CEI is  $\Phi_p$ , the symbol  $q_p$  is preferred since  $\Phi$  is reserved for *quantum yield*.

### 3.180

#### **photon irradiance, $E_p$**

number of *photons* (quanta of radiation,  $N_p$ ) per time interval (*photon flux*),  $q_p$ , incident from all upward directions on a small element of surface containing the point under consideration divided by the area of the element

Note 1 to entry: SI unit is  $\text{m}^{-2} \text{s}^{-1}$ .

Note 2 to entry: Equivalent definition: Integral, taken over the hemisphere *visible* from the given point, of the expression  $L_p \cos \theta d\Omega$ , with  $L_p$  the *photon radiance* at the given point in the various directions of the incident beam of solid angle  $\Omega$  and  $\theta$  the angle between any of these beams and the normal to the surface at the given point.

Note 3 to entry: Mathematical definition:  $E_p = dq_p/dS$ . If the *photon flux* is constant over the surface considered,  $E_p = q_p / S$ . Equivalent definition:  $E_p = \int_{2\pi} L_p \cos \theta d\Omega$ .

Note 4 to entry: This term refers to a beam not scattered or reflected by the target or its surroundings. For a beam incident from all directions, *photon fluence rate* ( $E_{p,o}$ ) is an equivalent term.

Note 5 to entry: This quantity can be used on a chemical amount basis by dividing  $E_p$  by the Avogadro constant, the symbol then being  $E_{n,p}$ , the name "*photon irradiance, amount basis*", SI unit is  $\text{mol m}^{-2} \text{s}^{-1}$ ; common unit is *einstein*  $\text{m}^{-2} \text{s}^{-1}$ .

Note 6 to entry: See also *irradiance, spectral photon irradiance*.

### 3.181

#### photon number, $N_p$

total number of photons calculated as  $N_p = n_p N_A$  with  $n_p$  the amount of photons in *einstein* and  $N_A$  the Avogadro constant

Note 1 to entry: Mathematical definition:  $N_p = Q/h\nu$ . for monochromatic radiation of *frequency*  $\nu$ , with  $Q$  the *radiant energy*.

### 3.182

#### photon radiance, $L_p$

number of *photons* (quanta of radiation,  $N_p$ ) per time interval (*photon flux*),  $q_p$ , leaving or passing through a small transparent element of surface in a given direction from the source about the solid angle  $\Omega$ , divided by the solid angle and by the orthogonally projected area of the element in a plane normal to the given beam direction,  $dS_{\perp} = dS \cos \theta$ , with  $\theta$  the angle between the normal to the surface and the direction of the beam.

Note 1 to entry: Equivalent definition: Integral taken over the hemisphere *visible* from the given point, of the expression  $L_p \cos \theta d\Omega$ , with  $L_p$  the *photon radiance* at the given point in the various directions of the incident beam of solid angle  $\Omega$  and  $\theta$  the angle between any of these beams and the normal to the surface at the given point.

Note 2 to entry: Mathematical definition:

$$L_p = \frac{d^2 q_p}{d\Omega dS_{\perp}} = \frac{d^2 q_p}{d\Omega dS \cos \theta}$$

for a divergent beam propagating in an elementary cone of the solid angle  $\Omega$  containing the direction  $\theta$ . SI unit is  $\text{m}^{-2} \text{s}^{-1} \text{sr}^{-1}$ .  $E_p = \int_{2\pi} L_p \cos \theta d\Omega$ .

Note 3 to entry: For a parallel beam, it is the number of photons (quanta of radiation,  $N_p$ ) per time interval (*photon flux*),  $q_p$ , leaving or passing through a small 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,  $\theta$ . Mathematical definition in this case:  $L_p = dq_p/(dS \cos \theta)$ . If  $q_p$  is constant over the surface area considered,  $L_p = q_p/(S \cos \theta)$ , SI unit is  $\text{m}^{-2} \text{s}^{-1}$ .

Note 4 to entry: This quantity can be used on a chemical amount basis by dividing  $L_p$  by the Avogadro constant, the symbol then being  $L_{n,p}$ , the name "*photon radiance, amount basis*". For a divergent beam, SI unit is  $\text{mol m}^{-2} \text{s}^{-1} \text{sr}^{-1}$ ; common unit is *einstein*  $\text{m}^{-2} \text{s}^{-1} \text{sr}^{-1}$ . For a parallel beam, SI unit is  $\text{mol m}^{-2} \text{s}^{-1}$ ; common unit is *einstein*  $\text{m}^{-2} \text{s}^{-1}$ .

Note 5 to entry: See also *radiance*.

### 3.183

#### **photonic efficiency**

efficiency of a photo(cata)lytic reaction given by the ratio of the *reaction rate / photon flux* of incident radiation or light on the sample or solution

Note 1 to entry: *SI unit is mol s<sup>-1</sup> for the rate and einstein s<sup>-1</sup> for the incident light flux.*

Note 2 to entry: See also quantum efficiency.

### 3.184

#### **photooxidation**

oxidation reactions induced by *ultraviolet, visible, or infrared* radiation

Note 1 to entry: Common processes are:

- a) loss of one or more electrons from a chemical species as a result of *photoexcitation* of that species;
- b) reaction of a substance with dioxygen molecules under the *influence of ultraviolet, visible, or infrared* radiation. When oxygen remains in the product, this latter process is also called *photooxygenation*

Note 2 to entry: Photoinduced reactions in which neither substrate nor dioxygen are electronically excited (i.e., photosensitized oxidations) are sometimes called photoinitiated oxidations. Compare with *photoreduction*.

### 3.185

#### **photopolymerization**

polymerization processes requiring a *photon* for the propagation step

### 3.186

#### **photoproduct (primary)**

first observable chemical entity produced in the primary *photochemical reaction* and that is chemically different from the reactant

### 3.187

#### **photoreaction**

see *photochemical reaction*

### 3.188

#### **photoreduction**

reduction reactions induced by *ultraviolet, visible, or infrared* radiation

Note 1 to entry: Common processes are:

- a) addition of one or more electrons to a *photoexcited* species;
- b) photochemical hydrogenation of a substance

Note 2 to entry: Reactions in which the substrate is not electronically excited are sometimes called photoinitiated reductions. Compare with *photooxidation*.

### 3.189

#### **photosensitization**

*sensitization*. Photochemical or photophysical alteration occurring in one molecular entity or in a semiconductor, for example for *electron transfer*, as a result of initial *absorption* of radiation by another molecular entity called a *photosensitizer*



Note 1 to entry: In mechanistic *photochemistry*, the term is limited to cases in which the *photosensitizer* is not consumed in the reaction.

Note 2 to entry: See also *energy transfer*.

### 3.190 photosensitizer sensitizer

Note 1 to entry: See *photosensitization*.

### 3.191 photostationary state

steady state reached by a chemical system undergoing *photochemical reaction(s)* when continuous wave *ultraviolet, visible, or infrared* radiation is absorbed by at least one of the components

Note 1 to entry: At this state, the rates of formation and disappearance are equal for each of the transient molecular entities formed.

### 3.192 quantum efficiency (photocatalytic)

efficiency of a photocatalytic reaction given by the ratio of the *reaction rate* / absorbed (by the *photocatalyst*) *photon flux*

Note 1 to entry: It differs from *photonic efficiency*, and it is more difficult to be evaluated, as scattering effects are often difficult to be quantified. The same as differential *quantum yield*.

Note 2 to entry: See *quantum yield, photonic efficiency*.

### 3.193 quantum yield, $\Phi$

number of defined events occurring per *photon* absorbed by the system

Note 1 to entry: The integral *quantum yield* is

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

For a *photochemical reaction*,

$$\phi(\lambda) = \frac{\text{amount of reactant consumed or product formed}}{\text{amount of photons absorbed}}$$

The differential *quantum yield* is

$$\Phi(\lambda) = \frac{dx/dt}{q_{n,p}^0 [1 - 10^{-A(\lambda)}]}$$

where

$dx/dt$  is the rate of change of a measurable quantity (spectral or any other property, like the rate of consumption of reactants or the rate of product formed), and  $q_{n,p}^0$  the amount of *photons* (mol or its equivalent *einstein*) incident (prior to *absorption*) per time interval (*photon flux*, amount basis).  $A(\lambda)$  is the *absorbance* at the excitation *wavelength*.

Note 2 to entry: Strictly, the term *quantum yield* applies only for monochromatic excitation. Thus, for the differential *quantum yield*, the *absorbed spectral photon flux density* (number basis or amount basis) should be used in the denominator of the equation above when  $x$  is either the number concentration ( $C = N/V$ ) or the amount concentration ( $c$ ), respectively.

Note 3 to entry:  $\Phi$  can be used for photophysical processes (such as, e.g., intersystem crossing, *fluorescence* and *phosphorescence*) or *photochemical reactions*.

Note 4 to entry: See also *quantum efficiency*.

### 3.194 quartz-iodine lamp

Wolfram (tungsten) filament high-*intensity* incandescent *lamp* containing iodine in a quartz envelope

Note 1 to entry: Used primarily as a source of *visible* radiation.

Note 2 to entry: See also *halogen lamp*.

### 3.195 quencher

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

Note 1 to entry: See also *quenching*.

### 3.196 quenching

deactivation of an excited molecular entity intermolecularly by an external environmental *influence* such as a *quencher*) or intramolecularly by a substituent through a *nonradiative decay*

Note 1 to entry: When the external environmental *influence* (*quencher*) interferes with the behavior of the *excited state* after its formation, the process is referred to as dynamic *quenching*. Common mechanisms include *energy transfer*, *electron transfer*, etc.

Note 2 to entry: When the environmental *influence* inhibits the excited-state formation, the process is referred to as static *quenching*.

### 3.197 radiance, $L$

*radiant power*,  $P$ , leaving or passing through a small transparent element of surface in a given direction from the source about the solid angle  $\Omega$ , divided by the solid angle and by the orthogonally projected area of the element in a plane normal to the given beam direction,  $dS_{\perp} = dS \cos \theta$

Note 1 to entry: Mathematical definition:

$$L = \frac{d^2P}{d\Omega dS_{\perp}} = \frac{d^2P}{d\Omega dS \cos \theta}$$

for a divergent beam propagating in an elementary cone of the solid angle  $\Omega$  containing the direction  $\theta$ . SI unit is  $W m^{-2} sr^{-1}$ .

Note 2 to entry: For a parallel beam, it is the *radiant power*,  $P$ , of all *wavelengths* leaving or passing through a small 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,  $\theta$ . Mathematical definition in this case:  $(dP)/(dS \cos \theta)$ . If the *radiant power* is constant over the surface area considered,  $L = P/(S \cos \theta)$ . SI unit is  $W m^{-2}$ .

Note 3 to entry: Equivalent to  $L = \int_{\lambda} L_{\lambda} d\lambda$ , where  $L_{\lambda}$  is the *spectral radiance* at wavelength  $\lambda$ .

Note 4 to entry: See also *photon flux, photon radiance, spectral radiance*.

### 3.198

#### **radiant emittance**

former name for *radiant exitance*

### 3.199

#### **radiant energy, $Q$**

total energy emitted, transferred or received as radiation of all *wavelengths* in a defined period of time

Note 1 to entry: SI unit is J.

Note 2 to entry: Mathematical definition:  $Q = \int_{\lambda} Q_{\lambda} d\lambda$ . If the *radiant power*  $P$  is constant over the time interval,  $Q = P t$ .

Note 3 to entry: See also *spectral radiant power*.

### 3.200

#### **radiant energy fluence, $H_0, F_0$**

see *fluence*

### 3.201

#### **radiant energy fluence rate**

see *fluence rate*

### 3.202

#### **radiant (energy) flux, $P, \Phi$**

this obsolete term is not recommended

Note 1 to entry: In *photochemistry*, *radiant power*,  $P$ , is adopted.

Note 2 to entry: SI unit is W.

Note 3 to entry:  $P$  is preferred, because in *photochemistry*,  $\Phi$  is reserved for *quantum yield*.

Note 4 to entry: See also *photon flux, photon radiance, radiant energy*.

### 3.203

#### **radiant exitance, $M$**

*radiant power*,  $P$ , emitted at all *wavelengths* by an element of surface containing the source point under consideration divided by the area of the source

Note 1 to entry: SI unit is  $W m^{-2}$ .

Note 2 to entry: Mathematical definition:  $M = dP/dS$ . If the *radiant power*  $P$  is constant over the surface area considered,  $M = P/S$ .

Note 3 to entry: Equivalent to the integration of the *radiant power* leaving a source over the solid angle and over the whole *wavelength* range. Mathematical definition:  $M = \int_{\lambda} M_{\lambda} d\lambda$ , where  $M_{\lambda}$  is the *spectral radiant exitance* at wavelength  $\lambda$ .

Note 4 to entry: Same as spherical *radiant exitance*. Formerly called *radiant emittance*.

Note 5 to entry: See also *photon exitance*, *spectral radiant exitance*.

### 3.204

#### **radiant exposure, $H$**

*radiant energy,  $Q$* , incident from all upward directions on a small sphere divided by the cross sectional area of that sphere

Note 1 to entry: SI unit is  $\text{J m}^{-2}$ .

Note 2 to entry: Equivalent definition: *Irradiance,  $E$* , integrated over the time of irradiation.

Note 3 to entry: Mathematical definition:  $H = dQ/dS = \int_t E dt$ . If  $Q$  is constant over the area,  $H = Q/S$ . If  $E$  is constant over the time interval,  $H = E t$ .

Note 4 to entry: This term refers to a beam not scattered or reflected by the target or its surroundings. For a beam incident from all directions, *fluence ( $H_o, F_o$ )* is an equivalent term.

### 3.205

#### **radiant intensity, $I$**

*intensity. Radiant power,  $P$* , at all *wavelengths* per solid angle,  $\Omega$ . The *radiant power* emitted in a given direction by a source or an element of the source in a small cone containing the given direction divided by the solid angle of the cone

Note 1 to entry: SI unit is  $\text{W sr}^{-1}$ .

Note 2 to entry: Mathematical definition:  $I = dP/d\Omega$ . If the *radiant power* is constant over the solid angle considered,  $I = P/\Omega$ .

Note 3 to entry: Equivalent to  $I = \int_{\lambda} I_{\lambda} d\lambda$ , where  $I_{\lambda}$  is the *spectral radiant intensity at wavelength  $\lambda$* .

Note 4 to entry: It is not recommended to abbreviate this term to just *intensity* because it is confusing.

Note 5 to entry: See also *spectral radiant intensity*.

### 3.206

#### **radiant power, $P$**

power emitted, transferred, or received as radiation

Note 1 to entry: SI unit is  $\text{J s}^{-1} = \text{W}$ .

Note 2 to entry: Mathematical definition:  $P = dQ/dt$ . If the *radiant energy  $Q$*  is constant over the time interval,  $P = Q/t$ .

Note 3 to entry: In radiometry, flux ( $\Phi$ ) is used with the same units as  $P$ . The symbol  $\Phi$  is reserved for *quantum yield in photochemistry*. Therefore, the use of flux ( $\Phi$ ) is not recommended.

Note 4 to entry: See also *spectral radiant power*.

### 3.207

#### **rate of absorbed photons**

see *absorbed photon flux density*

**3.208**  
**reaction rate (photocatalytic)**

see reactor batch, reactor CSTR, reactor PFR

**3.209**  
**reactor batch (photocatalytic)**

batch reactor

Note 1 to entry: The reactor is a vessel, charged via two holes of the tank; while reaction is carried out, nothing else is put in or taken out until the reaction is done except stirring, that favour perfect mixing and easy modelling. The tank is easily heated or cooled by jacket. The volume could be arbitrarily chosen. The reactor is never at steady-state as long as a chemical reaction takes place. The inside concentration decrease with time, assuming a first order rate equation, by

$$c = c_0 \exp(-k_{\text{obs}}t)$$

from which it is evident that the initial concentration  $c_0$  decays exponentially with  $k_{\text{obs}} = k_{\text{R}} S / V_{\text{R}}$ , where  $k_{\text{R}}$  is the linear photocatalytic intrinsic rate of degradation,  $S$  is the illuminated sample surface, and  $V_{\text{R}}$  is the reactor volume. The value of  $k_{\text{obs}}$  can be obtained from a fit on a set of data points  $(c(t), t)$  using the above equation or its log linearized form, and observing if the hypothesis of a first order reaction is obeyed, or, for practical and cost reasons, using a single point at time  $t$  where  $k_{\text{obs}} = -\ln(c(t)/c_0)/t$ . This last procedure is more risky as statistical uncertainty is not assessed

The *reaction rate* normalized per surface area and extrapolated at  $t = 0$  to have  $r(c_0) = k_{\text{R}} c_0$ , for a batch experiment is experimentally obtained by:

$$r_{\text{b}}(c_0) = \frac{c_0 k_{\text{obs}} V_{\text{R}}}{S}$$

where the (net) volume of the reactor shall be accounted for. The standardized protocols and good laboratory practice shall explicitly fix that the rate  $r(c_0)$  or  $k_{\text{R}} = r(c_0)/c_0$  shall be calculated using the above equation.

**3.210**  
**reactor CSTR**

continuous Stirred-Tank Reactor (CSTR)

Note 1 to entry: The reactor is a vessel in which a continuous flow of reagents enter in and flow out, while reaction takes place inside on the surface of the *photocatalyst*. It can reach a steady state in which the concentrations in the output flow are constant. The behaviour of a CSTR is often approximated or modelled by that of a Continuous Ideally Stirred-Tank Reactor (CISTR), which assumes perfect mixing in all directions. In a perfectly mixed reactor, the output composition is identical to composition inside the reactor, which is a function of residence time and rate of reaction. If the residence time is 5-10 times the mixing time, this approximation is valid for engineering purposes. The CISTR model is often used to simplify engineering calculations and can be used to describe reactors used for the measure of the rate. Assuming a first order reaction and negligible adsorption of reactants onto the catalyst, at steady state the *conversion* is constant

$$\eta_{\infty} = \frac{Da}{1 + Da}$$

where the dimensionless Damköhler number  $Da = k_{\text{R}}S/F$  and  $\eta_{\infty}$  is the *conversion* at steady state

The rate  $r(c_0) = k_{\text{R}} c_0$  is:

$$r_{(c_0)} = \frac{c_0 \eta_{\infty} F}{S(1 - \eta_{\infty})}$$

where

$c_0$  is the input concentration,  $F$  is the flow of reactant,  $S$  is the illuminated sample area. Using the above equation the rate  $r(c_0)$  (or  $k_R=r(c_0)/c_0$ ) is evaluated at the input concentration and should be independent on the experimentally used flow.

### 3.211

#### reactor PFR (photocatalytic)

plug flow reactor (PFR)

Note 1 to entry: The reactor is a tube or vessel in which a continuous flow enter in and flow out, while reaction takes place inside on the *photocatalyst* surface. The fluid going through a PFR may be modelled as flowing through the reactor as a series of infinitely thin coherent "plugs", each with a uniform composition, traveling in the axial direction of the reactor, with each plug having a different composition from the ones before and after it. The key assumption is that as a plug flows through a PFR, the fluid is perfectly mixed in the radial direction but not in the axial direction (forwards or backwards). Each plug of differential volume is considered as a separate entity, effectively an infinitesimally small continuous stirred tank reactor, limiting to zero volume. When inside the reactor there is a laminar flow, there is no radial and no axial (along the flow path) mixing and governing equations are different. Assuming a first order reaction and negligible adsorption of reactants onto the catalyst, the *conversion* at steady state is

$$\eta_{\infty} = 1 - \exp(-Da)$$

where the dimensionless Damköhler number  $Da = k_R S / F$ , and  $\eta_{\infty}$  is the *conversion* at steady state

The rate normalized for the surface area, evaluated at the input concentration by a PFR for a first order reaction, is given by

$$r_{(c_0)} = \frac{c_0 F}{S} \ln \left( \frac{1}{1 - \eta_{\infty}} \right)$$

where

$c_0$  is the input concentration,  $F$  is the flow of reactant,  $S$  is the illuminated sample area. The rate  $r(c_0)$  or  $k_R=r(c_0)/c_0$  should be independent on flow.

### 3.212

#### red shift

informal term for *bathochromic shift*

### 3.213

#### reflectance, $\rho$

*reflectance* factor, *reflectivity*. Fraction of incident radiation reflected by a surface or discontinuity

$$\rho(\lambda) = \frac{P_{\lambda}^{refl}}{P_{\lambda}^0}$$

where

$P_{\lambda}^0$  and  $P_{\lambda}^{refl}$  are, respectively, the incident and reflected *spectral radiant power*

Note 1 to entry: The *reflectance* for a beam of light normally incident on a surface separating two materials of refractive indices  $n_1$  and  $n_2$  is given by

$$\rho(\lambda) = \frac{(n_1 - n_2)^2}{(n_1 + n_2)^2}$$

Note 2 to entry: *Reflectance increases as the angle of incidence decreases from 90°.*

**3.214**  
**reflection factor**

see *reflectance*

**3.215**  
**reflectivity**

see *reflectance*

**3.216**  
**RGB**

the *RGB* color model is an additive color model in which red, green, and blue light are added together in various ways to reproduce a broad array of colors

Note 1 to entry: The name of the model comes from the initials of the three additive primary colors, red, green, and blue.

Note 2 to entry: See also *CIELAB*.

**3.217**  
**sacrificial acceptor**

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

**3.218**  
**sacrificial donor**

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

**3.219**  
**self-absorption**

*absorption* of part of the *fluorescence* from excited molecular entities by molecular entities of the same species in the *ground state*

Note 1 to entry: The mechanism operating is radiative *energy transfer*.

**3.220**  
**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*

**3.221**  
**sensitizer**

see *photosensitizer*

**3.222**  
**sensitization**

see *photosensitization*

### 3.223

#### **singlet oxygen (singlet molecular oxygen, singlet molecular dioxygen)**

oxygen molecule (dioxygen), O<sub>2</sub>, in an excited *singlet state*

Note 1 to entry: The *ground state* of O<sub>2</sub> is a *triplet* (<sup>3</sup>Σ<sup>-g</sup>). The two metastable *singlet states* derived from the ground-state *configuration* are <sup>1</sup>Δ<sub>g</sub> and <sup>1</sup>Σ<sup>+</sup><sub>g</sub> (the latter with the higher energy)

Note 2 to entry: Use of the term “*singlet oxygen*” alone, without mention of the chemical species is discouraged since it can also refer to an oxygen atom in a <sup>1</sup>S or <sup>1</sup>D *excited state*. The oxygen atom *ground state* is a triplet <sup>3</sup>P state, and the <sup>1</sup>S and <sup>1</sup>D states are also derived from the ground-state configuration.

Note 3 to entry: *Triplet state quenching* by triplet dioxygen (i.e., a process of *photosensitization*) is the most common procedure for the production of singlet molecular dioxygen in solution. For many chemical species, the efficiency with which the *triplet state* is quenched by triplet dioxygen and, independently, the efficiency with which singlet molecular dioxygen is produced, is controlled by the spin-statistical factor.

### 3.224

#### **singlet state**

state having a total electron spin quantum number equal to 0

### 3.225

#### **solar conversion efficiency**

Gibbs energy gain per time interval divided by area of surface exposed to the solar *irradiance*, and by the solar *radiance* *E*, and integrated over the *wavelength* range reaching the exposed surface

### 3.226

#### **solvent shift**

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

Note 1 to entry: See also *bathochromic shift*, *hypsochromic shift*.

### 3.227

spectral distribution (of radiant, luminous, or **photon** quantity),  $X_{\lambda}(\lambda)$

*wavelength*-dependent derivative of the radiant, luminous, or *photon* quantity (denominated *X* in this definition) with respect to *wavelength*

Note 1 to entry: Mathematical definition at each *wavelength* interval:  $X_{\lambda} = dX(\lambda)/d\lambda$ . Unit is  $[X] \text{ m}^{-1}$ , e.g.,  $W \text{ m}^{-1}$  for  $X = [P] = W$  (unit for *P*, *radiant power*).

Note 2 to entry: This term is preferred when dealing with the function  $X_{\lambda}(\lambda)$  over a wide range of *wavelengths*.

### 3.228

#### **spectral (photon) effectiveness**

effectiveness. Reciprocal of the *photon fluence rate*,  $E_{p,o}$ , at *wavelength*  $\lambda$ , causing identical photoresponse,  $\Delta y$ , per time interval ( $\Delta y/\Delta t$ ) at the different *wavelengths*

Note 1 to entry: The effectiveness spectrum is directly proportional to the *conversion spectrum* of the sensory pigment under investigation, if spectral *attenuance* is negligible.

### 3.229

#### **spectral fluence, $H_{\lambda,o}$ , $F_{\lambda,o}$**

derivative of *fluence*,  $H_o$ , with respect to *wavelength*,  $\lambda$

Note 1 to entry: SI unit is  $J \text{ m}^{-3}$ ; common unit is  $J \text{ m}^{-2} \text{ nm}^{-1}$



Note 2 to entry: All spectral terms may also be defined as derivatives with respect to *frequency*,  $\nu$ , or *wavenumber*,  $\tilde{\nu}$ , and are referred to, when necessary, as in terms of *wavelength* or *frequency* or *wavenumber*, respectively.

### 3.230

#### **spectral fluence rate, $E_{\lambda,0}$**

derivative of *fluence rate*,  $E_0$ , with respect to *wavelength*,  $\lambda$

Note 1 to entry: SI unit is  $\text{W m}^{-3}$ ; common unit is  $\text{W m}^{-2} \text{nm}^{-1}$ .

Note 2 to entry: All spectral terms may also be defined as derivatives with respect to *frequency*,  $\nu$ , or *wavenumber*,  $\tilde{\nu}$ , and are referred to, when necessary, as in terms of *wavelength*, or *frequency* or *wavenumber*, respectively.

### 3.231

#### **spectral irradiance, $E_\lambda$**

derivative of *irradiance*,  $E$ , with respect to *wavelength*,  $\lambda$

Note 1 to entry: SI unit is  $\text{W m}^{-3}$ ; common unit is  $\text{W m}^{-2} \text{nm}^{-1}$ .

Note 2 to entry: All spectral terms may also be defined as derivatives with respect to *frequency*,  $\nu$ , or *wavenumber*,  $\tilde{\nu}$ , and are referred to, when necessary, as in terms of *wavelength*, or *frequency* or *wavenumber*, respectively.

### 3.232

#### **spectral overlap**

degree of superposition of the donor *emission spectrum* with the acceptor *absorption spectrum* in an *energy-transfer process*

Note 1 to entry: The normalization conditions for the calculation of the *spectral overlap* integral are different for the different mechanisms of *energy transfer*.

### 3.233

#### **spectral photon exitance, $M_{p,\lambda}$**

derivative of *photon exitance*,  $M_p$ , with respect to *wavelength*,  $\lambda$

Note 1 to entry: SI unit is  $\text{s}^{-1} \text{m}^{-3}$ ; common unit is  $\text{s}^{-1} \text{m}^{-2} \text{nm}^{-1}$ .

Note 2 to entry: This quantity can be expressed on a chemical amount basis by dividing  $M_{p,\lambda}$  by the Avogadro constant. In this case, the symbol is  $M_{n,p,\lambda}$ , the name then is "*spectral photon exitance*, amount basis", SI unit is  $\text{mol s}^{-1} \text{m}^{-3}$ ; common unit is *einstein*  $\text{s}^{-1} \text{m}^{-2} \text{nm}^{-1}$ .

Note 3 to entry: All spectral terms may also be defined as derivatives with respect to *frequency*,  $\nu$ , or *wavenumber*,  $\tilde{\nu}$ , and are referred to, when necessary, as in terms of *wavelength*, or *frequency* or *wavenumber*, respectively.

### 3.234

#### **spectral photon flux, $q_{p,\lambda}$ , $\Phi_{p,\lambda}$**

derivative of *photon flux*, number basis,  $q_p$ , with respect to *wavelength*,  $\lambda$

Note 1 to entry: SI unit is  $\text{s}^{-1} \text{m}^{-1}$ ; common unit is  $\text{s}^{-1} \text{nm}^{-1}$ .

Note 2 to entry: This quantity can be expressed on a chemical amount basis by dividing  $q_{p,\lambda}$  by the Avogadro constant, the name then is "*spectral photon flux*, amount basis", the symbol  $q_{n,p,\lambda}$ , and the SI unit is  $\text{mol s}^{-1} \text{m}^{-1}$ ; common unit is *einstein*  $\text{s}^{-1} \text{nm}^{-1}$ .

Note 3 to entry: All spectral terms may also be defined as derivatives with respect to *frequency*,  $\nu$ , or *wavenumber*,  $\tilde{\nu}$ , and are referred to, when necessary, as in terms of *wavelength*, or *frequency* or *wavenumber*, respectively.

### 3.235

#### **spectral photon irradiance, $E_{p,\lambda}$**

derivative of *photon irradiance*,  $E_p$ , with respect to *wavelength*,  $\lambda$

Note 1 to entry: SI unit is  $\text{s}^{-1} \text{m}^{-3}$ ; common unit is  $\text{s}^{-1} \text{m}^{-2} \text{nm}^{-1}$ .

Note 2 to entry: This quantity can be expressed on a chemical amount basis by dividing  $E_{p,\lambda}$  by the Avogadro constant, the name then is "*spectral photon irradiance, amount basis*", the symbol  $E_{n,p,\lambda}$ , and the SI unit is  $\text{mol s}^{-1} \text{m}^{-3}$ ; common unit is *einstein*  $\text{s}^{-1} \text{m}^{-2} \text{nm}^{-1}$ .

Note 3 to entry: All spectral terms may also be defined as derivatives with respect to *frequency*,  $\nu$ , or *wavenumber*,  $\tilde{\nu}$ , and are referred to, when necessary, as in terms of *wavelength*, or *frequency* or *wavenumber*, respectively.

### 3.236

#### **spectral photon radiance, $L_{p,\lambda}$**

derivative of *photon radiance*,  $L_p$ , with respect to *wavelength*,  $\lambda$

Note 1 to entry: For a divergent beam, SI unit is  $\text{s}^{-1} \text{m}^{-3} \text{sr}^{-1}$ ; common unit is  $\text{s}^{-1} \text{m}^{-2} \text{sr}^{-1} \text{nm}^{-1}$ . For a parallel beam, SI unit is  $\text{s}^{-1} \text{m}^{-3}$ ; common unit is  $\text{s}^{-1} \text{m}^{-2} \text{nm}^{-1}$ .

Note 2 to entry: *Spectral photon radiance* of a divergent beam is the quantity used when working with large photochemical reactors.

Note 3 to entry: This quantity can be expressed on a chemical amount basis by dividing  $L_{p,\lambda}$  by the Avogadro constant, the name then is "*spectral photon radiance, amount basis*". For a divergent beam, SI unit is  $\text{mol s}^{-1} \text{m}^{-3} \text{sr}^{-1}$ ; common unit is *einstein*  $\text{s}^{-1} \text{m}^{-2} \text{sr}^{-1} \text{nm}^{-1}$ . For a parallel beam, SI unit is  $\text{mol s}^{-1} \text{m}^{-3}$ ; common unit is *einstein*  $\text{s}^{-1} \text{m}^{-2} \text{nm}^{-1}$ .

Note 4 to entry: All spectral terms may also be defined as derivatives with respect to *frequency*,  $\nu$ , or *wavenumber*,  $\tilde{\nu}$ , and are referred to, when necessary, as in terms of *wavelength*, or *frequency* or *wavenumber*, respectively.

### 3.237

#### **spectral radiance, $L_\lambda$**

derivative of *radiance*,  $L$ , with respect to *wavelength*,  $\lambda$

Note 1 to entry: For a divergent beam, SI unit is  $\text{W m}^{-3} \text{sr}^{-1}$ ; common unit is  $\text{W m}^{-2} \text{sr}^{-1} \text{nm}^{-1}$ . For a parallel beam, SI unit is  $\text{W m}^{-3}$ ; common unit is  $\text{W m}^{-2} \text{nm}^{-1}$ .

Note 2 to entry: All spectral terms may also be defined as derivatives with respect to *frequency*,  $\nu$ , or *wavenumber*,  $\tilde{\nu}$ , and are referred to, when necessary, as in terms of *wavelength*, or *frequency* or *wavenumber*, respectively.

### 3.238

#### **spectral radiant energy, $Q_\lambda$**

derivative of *radiant energy*,  $Q$ , with respect to *wavelength*  $\lambda$

Note 1 to entry: SI unit is  $\text{J m}^{-1}$ ; common unit is  $\text{J nm}^{-1}$ .

### 3.239

#### **spectral radiant exitance, $M_\lambda$**

derivative of *radiant exitance*,  $M$ , with respect to *wavelength*  $\lambda$

Note 1 to entry: SI unit is  $\text{W m}^{-3}$ ; common unit is  $\text{W m}^{-2} \text{nm}^{-1}$ .

Note 2 to entry: All spectral terms may also be defined as derivatives with respect to *frequency*,  $\nu$ , or *wavenumber*,  $\tilde{\nu}$ , and are referred to, when necessary, as in terms of *wavelength*, or *frequency* or *wavenumber*, respectively.

### 3.240

#### **spectral radiant intensity, $I_\lambda$**

derivative of *radiant intensity*,  $I$ , with respect to *wavelength*,  $\lambda$

Note 1 to entry: SI unit is  $\text{W m}^{-1} \text{sr}^{-1}$ ; common unit is  $\text{W nm}^{-1} \text{sr}^{-1}$ .

Note 2 to entry: All spectral terms may also be defined as derivatives with respect to *frequency*,  $\nu$ , or *wavenumber*,  $\tilde{\nu}$ , and are referred to, when necessary, as in terms of *wavelength*, or *frequency* or *wavenumber*, respectively.

### 3.241

#### **spectral radiant power, $P_\lambda$**

derivative of *radiant power*,  $P$ , with respect to *wavelength*,  $\lambda$

Note 1 to entry: SI unit is  $\text{W m}^{-1}$ ; common unit is  $\text{W nm}^{-1}$ .

Note 2 to entry: All spectral terms may also be defined as derivatives with respect to *frequency*,  $\nu$ , or *wavenumber*,  $\tilde{\nu}$ , and are referred to, when necessary, as in terms of *wavelength*, or *frequency* or *wavenumber*, respectively.

### 3.242

#### **spectral responsivity, $s(\lambda)$**

spectral output quantity of a system such as a photomultiplier, diode array, photoimaging device, or biological, unit divided by the *spectral irradiance*,  $E_\lambda$

Note 1 to entry: Mathematical definition:  $s(\lambda) = dY_\lambda/d E_\lambda$ . Simplified expression:  $s(\lambda) = Y_\lambda/E_\lambda$  where  $Y_\lambda$  is the magnitude of the output signal for irradiation at *wavelength*,  $\lambda$ .

Note 2 to entry: See also *action spectrum*.

### 3.243

#### **spectral sensitivity, $S(\lambda)$**

actinometric factor

Note 1 to entry: Referred to *actinometers* based on spectrophotometric measurements,  $S_{ac}(\lambda) = \Phi(\lambda) \varepsilon(\lambda_{obs}) =$  sensitivity or actinometric factor.  $\Phi(\lambda)$  is the *quantum yield* of the *actinometer* at the excitation *wavelength*, and  $\lambda_{obs}$  is the observation *wavelength*, which may be the same as or differ from the former. Note 2 to entry: See also *spectral responsivity*.

### 3.244

#### **spectral sensitization**

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

### 3.245

#### **transmittance, $T$**

transmitted *spectral radiant power*,  $P_\lambda$ , through a particular pathlength  $l$ , divided by the *spectral radiant power* incident on the sample  $P_\lambda^0$

$$T(l) = \frac{P_\lambda}{P_\lambda^0}$$

Note 1 to entry: *Transmittance* depends on the pathlength and this should be specified when giving a *transmittance* value.

Note 2 to entry: Internal *transmittance* refers to energy loss by *absorption*, whereas the total *transmittance* is that due to *absorption* plus reflection, scatter, etc.  $T$  is the preferred symbol, but  $t$  is also used.

Note 3 to entry: See also *absorbance*, *attenuance*, *Beer–Lambert law*.

### 3.246

#### **triplet state**

state having a total electron spin quantum number of 1

### 3.247

#### **tungsten lamp**

incandescent *lamp* that generates light by passing an electric current through a thin filament wire (usually of wolfram) in an inert gas until it is extremely hot

Note 1 to entry: See also *halogen lamp*, *quartz–iodine lamp*.

### 3.248

#### **tungsten-halogen lamp**

tungsten lamp

Note 1 to entry: See *halogen lamp*, *quartz–iodine lamp*, *wolfram lamp*.

Note 2 to entry: Halogens other than iodine may fill the *lamp*.

### 3.249

#### **tunnelling**

passage of a particle through a potential energy barrier the height of which is larger than the energy of that particle

Note 1 to entry: Important effect for some processes involving the transfer of electrons and light atoms, particularly H atoms.

### 3.250

#### **two-photon excitation**

excitation resulting from successive or simultaneous *absorption* of two *photons* by an atom or molecular entity

Note 1 to entry: Term 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*.

Note 2 to entry: See also *two-photon process*.

### 3.251

#### ultraviolet (UV)

region of the electromagnetic spectrum extending from about 100 nm to 300 nm

Note 1 to entry: This region is divided into four sub-bands as follows:

- Vacuum ultraviolet (VUV) 100–200 nm;
- UV-C 200–280 nm;
- UV-B 280–315 nm;
- UV-A 315–400 nm.

Note 2 to entry: The notation and the limits of the various regions are as recommended by the International Commission on Illumination (CIE), with the exception that in these recommendations the UV-C range is 100–280 nm, including thus the vacuum UV range.

### 3.252

#### UV

acronym for *ultraviolet*

### 3.253

#### UV dose

*dose of UV radiation*

Note 1 to entry: This term is also used widely in UV disinfection applications having the same meaning as *fluence*. This latter use is discouraged.

### 3.254

#### valence band

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

Note 1 to entry: The *valence band* is lower in energy than the *conduction band* and is generally completely full in semiconductors. When heated, electrons from the *valence band* jump out of the band across the band gap and into the *conduction band*, making the material conductive. The *Fermi level* lies in between the *valence band* and the *conduction band*. In metals, the *valence band* is the *conduction band*.

### 3.255

#### visible

region of the electromagnetic spectrum extending from 400 nm to 780 nm

Note 1 to entry: This is the *wavelength* region to which the human eye is sensitive. There are no precise physiological limits for the spectral range of *visible* radiation since they depend upon the amount of *radiant power* reaching the retina and on the responsivity of the observer. For the scope of standardization the above *wavelength* range is considered for Vis radiation.

Note 2 to entry: A careful check of the radiation in the above range, excluding UV or IR with both the *lamp* and *filter* used, is necessary to define a photocatalytic reaction *visible*-activated.

### 3.256

#### VUV

acronym for vacuum ultraviolet

Note 1 to entry: See *ultraviolet*.

**3.257**

**wavelength,  $\lambda$**

distance, measured along the line of propagation, between two corresponding points on adjacent waves

Note 1 to entry: The *wavelength* depends on the medium in which the wave of a given *frequency* propagates.

**3.258**

**wavenumber,  $\tilde{\nu}$ ,  $\sigma$**

reciprocal of the *wavelength*,  $\lambda$ , or the number of waves per length along the direction of propagation

Note 1 to entry: SI unit is  $\text{m}^{-1}$ ; common unit is  $\text{cm}^{-1}$ .

Note 2 to entry:  $\tilde{\nu}$  is preferred since  $\sigma$  is used for *absorption cross-section*.

**3.259**

**wolfram lamp**

see *tungsten lamp*

**3.260**

**wood lamp**

term used to describe a *low pressure mercury arc* possessing a fluorescing layer, which emits in the UV-A region (from 315 nm to 400 nm)

**3.261**

**xenon lamp**

intense source of *ultraviolet*, *visible*, and *near-infrared* radiation produced by electrical discharge in xenon under high pressure

Note 1 to entry: See also *mercury xenon lamp (arc)*.

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