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INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY  
ORGANIC AND BIOMOLECULAR CHEMISTRY DIVISION\*  
SUB-COMMITTEE ON PHOTOCHEMISTRY

## GLOSSARY OF TERMS USED IN PHOTOCHEMISTRY

3<sup>rd</sup> Edition

(IUPAC Recommendations 2006)

*Prepared for publication by*

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# Glossary of Terms Used in Photochemistry 3<sup>rd</sup> Edition

## (IUPAC Recommendations 2006)

*Abstract.* The 2<sup>nd</sup> edition of the Glossary of Terms used in Photochemistry (*Pure Appl. Chem.* **68**, 2223–2286 (1996). <http://www.iupac.org/publications/pac/1996/pdf/6812x2223.pdf>) has been both corrected and updated. Terms have been added related to molecular anisotropy, the use of polarized radiation, non-linear optical phenomena, and the emerging field of computation of excited species. Some changes have been introduced in this “Glossary” regarding the terms related to radiation energy to make this collection fully compatible with internationally agreed-upon terms. Many links are included to various WEB pages listing quantities relevant to the work of photochemists and scientists using photochemical tools.

### 1. INTRODUCTION TO THE THIRD EDITION

The first edition of the *Glossary of Terms Used in Photochemistry* (“Glossary”) prepared for publication in the Commission of Photochemistry of the IUPAC Division of Organic Chemistry by S. E. Braslavsky and K. N. Houk was published in 1988 [1] and has been incorporated in the *Handbook of Organic Photochemistry* [2] and in *Photochromism: Molecules and Systems* [3].

The second edition of the “Glossary” prepared by Jan Verhoeven and published in 1996 [4] corrected some minor mistakes in the first one and was expanded especially to incorporate terms related to (photoinduced) electron transfer processes.

Major photochemistry and photobiology journals have since adopted the “Glossary” as a guideline. The Photochemical Societies have posted the electronic version of the “Glossary” on their WEB homepages.

This third edition both incorporates revisions and enhances the “Glossary” by introducing additional terms related to organic photochemical reactions, as well as terms in the area of molecular anisotropy, the use of polarized ultraviolet, visible or infrared radiation, and non-linear optical techniques, as well as the emerging field of computation of excited species.

Some changes have been introduced in this “Glossary” regarding the terms related to radiation energy to make this collection fully compatible with internationally agreed upon terms.

Links are included to various WEB pages listing quantities relevant to the work of photochemists and related to the terms included in this document.

We expect that this “Glossary” will continue to provide definitions of terms and symbols commonly used in the field of photochemistry in order to achieve consensus on the adoption of some definitions and on the abandonment of inadequate terms.

The Subcommittee on Photochemistry of the IUPAC Division of Organic and Biomolecular Chemistry emphasizes that it is not the purpose of this compilation to impose terms or rules that would hinder the freedom of choice in the use of terminology. Photochemistry is an interdisciplinary area of science, which involves, in addition to chemistry, such different fields as laser technology, nanotechnology, spectroscopy, polymer science, solid-state physics, biology, and medicine, among others. For this reason, it has been necessary to reach compromises and, in some cases, to include alternative definitions used in different scientific fields.

It is also important to recognize that this “Glossary” is not intended to replace the textbooks and compilations in which the various complex aspects related to Photochemistry have been handled. The general criterion adopted for the inclusion of a term has been: (i) its wide use in the present or past literature and (ii) ambiguity or uncertainty in its usage.

The arrangement of entries is alphabetical and the criterion adopted some years ago by the Physical Organic Chemistry Commission of IUPAC has been followed for the typeface used: *italicised* words in a definition or following it indicate a relevant cross reference, a term in quotation marks indicates that it is not defined in this Glossary (see *Glossary of Terms Used in Physical Organic Chemistry* [5]). In addition, an underlined word marks its importance in the definitions under consideration.

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

Terms pertaining to Physical Organic Chemistry are defined in [5]. Crosschecking for consistency has been performed with this “Glossary”. Terms pertaining to Theoretical Organic Chemistry have been taken from [6].

Internationally agreed upon terms were taken from [7, 8, 9]. See also [10]. Electrochemical terms and conventions were adopted from [11].

Other sources include: *Recommended Standards for Reporting Photochemical Data* [12], *The Vocabulary of Photochemistry* [13], *Optical Radiation Physics and Illuminating Engineering; Quantities, Symbols and Units of Radiation Physics* [14], and *Photochemical Technology* [15]. Several compilations with data frequently used by photochemists can be found in [16].

Terms on lasers and laser analytical methods are compiled in [17], on photothermal and photoacoustic methods in [18], and on photochromism in [19]. References are made to original

literature for name reactions or equations and to some monographs in other cases. This referencing should serve only as a general guide.

### 1.1 A Note on the Identification of New and/or Revised Terms

Terms that can be found in the previous version of the “Glossary”[4] and in the *Gold Book* [20] are indicated with G2/GB. The designation G2 alone means that the term was not incorporated or differs from the definition in [20], whereas those terms revised have a mark revG2. Minor changes such as better wording or additional cross-referencing are not considered as revisions. New terms are not indicated as such.

### 1.2 A Note on Units

SI units are adopted, with some exceptions, prominently 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. For a fuller explanation see [7].

The symbols and units used in this “Glossary” are compiled at the end of the document.

### 1.3 A 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.,  $\alpha(\lambda)$ . 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  $P_\lambda = \text{d}P/\text{d}\lambda$ .

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) [8] and included in the IUPAC Green Book [7], and by the International Commission on Illumination [9] 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 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.

Silvia E. Braslavsky

## 2. ALPHABETIC LIST OF TERMS AND DEFINITIONS

### absorbance (linear $A$ or napierian $A_e$ )

Logarithm to the base 10 (linear absorbance) of the incident (prior to *absorption*) *spectral radiant power*, essentially monochromatic, ( $P_\lambda^0 = \int_\lambda I_\lambda \, d\lambda$ ) divided by the transmitted spectral radiant power,  $P_\lambda$ :

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

$T(\lambda)$  is the (internal) *transmittance* in the defined wavelength interval. 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*,  $P_\lambda^0$ , essentially monochromatic, divided by the transmitted spectral radiant power,  $P_\lambda$ :

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

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 1: 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 2: In common usage,  $A$  is given for a pathlength of 1 cm, unless otherwise specified.

Note 3: Traditionally (*spectral*) *radiant intensity*,  $I_\lambda$ , was used instead of *spectral radiant power*,  $P_\lambda$ , [7], now the accepted term.

Note 4: The wavelength symbol as a subscript for  $P$  and in parenthesis for  $T$  and  $A$  may be omitted when defined over a very narrow wavelength range.

Note 5: Same as internal optical density, which is a term not recommended.

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

revG2

### **absorbed photon flux density**

Number of photons per time interval (*photon flux*, number basis,  $q_p$ , or *photon flux*, amount basis,  $q_{n,p}$ ) absorbed by a system per volume,  $V$ . On number basis, SI unit is  $s^{-1} m^{-3}$ ; common unit is  $s^{-1} cm^{-3}$ . On amount basis, SI unit is  $mol s^{-1} m^{-3}$ ; common unit is  $einstein s^{-1} cm^{-3}$ .

Note 1: Mathematical expression:  $\frac{q_p^0 [1-10^{-A(\lambda)}]}{V}$  on number basis and  $\frac{q_{n,p}^0 [1-10^{-A(\lambda)}]}{V}$  on

amount basis, where  $A(\lambda)$  is the *absorbance at wavelength  $\lambda$*  and superscript 0 indicates incident photons.

Note 2: Absorbed photon flux density is used in the denominator when calculating a differential *quantum yield* and using in the numerator the rate of change of the number concentration,  $dC/dt$  or the rate of change of the amount concentration,  $dc/dt$ .

Note 3: Sometimes called local volumetric rate of photon absorption.

### **absorbed radiant power density**

*Spectral radiant energy* per time interval (*spectral radiant power*,  $P_\lambda$ ) absorbed by a system per volume,  $V$ . SI unit is  $W m^{-4}$ ; common unit is  $W cm^{-3} nm^{-1}$ .

Note 1: Mathematical expression:  $\frac{P_\lambda^0 [1-10^{-A(\lambda)}]}{V}$ , where  $A(\lambda)$  is the *absorbance at wavelength  $\lambda$*

and superscript 0 indicates incident radiant power.

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

Fraction of *ultraviolet, visible* or *infrared* radiation absorbed, equal to one minus the *transmittance* ( $T$ ), i.e.,  $(1 - T)$ . The use of this obsolete term, equivalent to *absorption factor*, is not recommended.

See *absorbance*.

revG2

### **absorption (of electromagnetic radiation)**

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

Note 1: 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: When energy flows from the material or molecule to the field, stimulated light *emission* occurs.

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

See [23].

revG2

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

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

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

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

Related terms: *absorptivity, molar absorption coefficient.*

revG2

### **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:

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

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*. SI unit is  $\text{m}^2$ , common unit is  $\text{cm}^2$  (see Note).

Note: The relation between the absorption cross-section and the *molar (decadic) absorption coefficient*,  $\varepsilon(\lambda)$ , is

$$\alpha(\lambda) = \ln 10 \varepsilon(\lambda)/N_{\text{A}}$$

with  $N_{\text{A}}$  the Avogadro constant. A conversion equation in common units is:

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

Related terms: *attenuance, Beer-Lambert law.*

revG2

### **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*  $\lambda$ . This term is preferred to *absorptance*.

Note 1: The wavelength symbol may be omitted for  $f$ ,  $T$ , and  $A$ , where these terms are defined over a very narrow wavelength range.

Note 2: For  $A(\lambda) \ll 1/\ln 10$ ,  $f(\lambda) \approx A(\lambda) \ln 10$ .

### **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*,  $\lambda$ .

### **absorptivity**

*Absorptance* divided by the optical pathlength. The unit length must be specified.

The use of this obsolete term is not recommended.

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

revG2

### **actinic**

Applied or referred to *actinism*.

### **actinism**

Chemical changes on living and non-living materials caused by optical radiation.

### **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. This name is commonly applied to systems used in the *ultraviolet* and *visible wavelength* ranges.

Note 1: For example, solutions of iron(III) oxalate (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 2: For a list of chemical actinometers and a critical discussion about actinometry see [21].

See *spectral sensitivity*.

revG2

### **actinometric factor**

See *spectral sensitivity*.

### **action spectrum**

Plot of a relative biological or chemical photoresponse ( $= \Delta y$ ) per number of incident (prior to absorption) *photons*, versus *wavelength*, or energy of radiation, or *frequency* or *wavenumber*. This form of presentation is frequently used in the studies of biological or solid-state systems, where the nature of the absorbing species is unknown. It is advisable to ensure that the *fluence* dependence of the photoresponse is the same (e.g., linear) for all the wavelengths studied.

Note 1: 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 2: 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 (e.g., two-lg reduction). A plot of the inverse of the “standard response” level versus wavelength is then the action spectrum of the photoresponse.

Related terms: *excitation spectrum*, *efficiency spectrum*.

revG2

**acyl shift (1,2-, 1,3-, photochemical)**

*Photochemical process with skeletal isomerization by shift of an acyl group from position 1 to position 2 or 3.*

*See aza-di- $\pi$ -methane rearrangement, di- $\pi$ -methane rearrangement, di- $\pi$ -silane rearrangement, oxa-di- $\pi$ -methane rearrangement, photo-Fries rearrangement.*

**adiabatic electron transfer**

*Electron transfer process in which the reacting system remains on a single electronic surface in passing from reactants to products.*

Note: For adiabatic electron transfer the electronic transmission factor is close to unity (see *Marcus equation*).

Related term: *diabatic electron transfer*.

See [22, 23].

G2/GB

**adiabatic photoreaction**

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

Compare with *diabatic photoreaction*.

See [23].

G2/GB

**ADMR**

See *ODMR*.

G2/GB

**alkene photocycloaddition**

*Photochemical process leading to formation of a cyclobutane upon addition of an electronically excited alkene to another ground-state alkene or of an electronically excited  $\alpha,\beta$ -unsaturated carbonyl compound to a ground-state alkene. The latter is called a *de Mayo reaction*.*

Note: A special case of photocycloaddition is a *photodimerization*.

### **alkene photodimerization**

*Photochemical process* leading to the formation of a cyclobutane from two identical alkenes, i.e., from the *photocycloaddition* of an *electronically excited* alkene to a ground-state alkene.

### **alkene photoisomerization**

*Photochemical process* with geometrical isomerization of a carbon-carbon double bond.

Note 1: the geometrical isomerization of a C-C double bond is called a *cis/trans isomerization* in 1,2-disubstituted alkenes. *E/Z* is a more general designation applying also to higher substituted alkenes.

Note 2: This process leads to a *photostationary state* if both isomers absorb light under the reaction conditions.

### **alkene photorearrangement**

*Photochemical process* leading to the skeletal rearrangement of an alkene.

See *aza-di- $\pi$ -methane rearrangement*, *di- $\pi$ -methane rearrangement*, *di- $\pi$ -silane rearrangement*, *oxa-di- $\pi$ -methane rearrangement*.

### **alpha-cleavage, $\alpha$ -cleavage**

Homolytic cleavage of a bond connecting an atom or group to an *excited chromophore*. Often applied to a bond connected to a carbonyl group, in which case it is called a *Norrish Type I photoreaction*.

Note: This reaction should be distinguished from an *alpha-( $\alpha$ )-elimination*.

### **alpha-elimination, $\alpha$ -elimination**

General term applied to a reaction by which a group attached to the alpha carbon of an *excited chromophore* is expelled either as an odd electron species or as an ionic species.

Note: This reaction should be distinguished from an *alpha*-( $\alpha$ -)cleavage.

G2/GB

### **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). Also called extraterrestrial irradiance.

Related term: *AM 1 sunlight*.

G2/GB

### **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. Also called terrestrial global irradiance.

Related term: *AM 0 sunlight*.

revG2

### **amalgam lamp**

Intense source of *ultraviolet* (185 and 253.7 nm) radiation produced by an electrical discharge in a lamp with the inner side covered by an amalgam of mercury with another element such as indium or gallium to control the vapor pressure of the mercury. These *lamps* have 2 - 3 times the UV output for the same wavelength as the standard *low-pressure mercury lamp*.

See [2, 15].

### **anisotropy**

See *emission anisotropy*, *linear dichroism*, *molecular orientation*.

### **annihilation**

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

Note: This phenomenon is sometimes referred to as energy pooling.

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

G2/GB

### **antimony-xenon lamp (arc)**

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

See *lamp* [2, 15].

G2/GB

### **anti-Stokes shift**

See *Stokes shift*.

G2/GB

### **apparent lifetime**

Same as *decay time*. The use of the expression apparent lifetime is not recommended.

See *lifetime*.

revG2

### **argon ion laser**

Continuous wave (*CW*) or pulsed *laser* emitting lines from 334 to 529 nm from singly ionized argon. Principal *emissions* are at 488.0 and 514.5 nm. Other lines are 351.1, 363.8, 457.9, and 476.5 nm.

See *laser*, *gas lasers*, [17].

revG2

### **aromatic photocycloaddition**

Inter-and intramolecular *photochemical processes* involving the addition of a C-C double (or triple)

bond to (i) the 1,2-positions of an arene in which case it is called an *ortho photocycloaddition*, with formation of a benzocyclobutene (or a benzocyclobutadiene) derivative, (ii) to the 1,3-positions of an arene in which case it is called a *meta photocycloaddition*, with formation of tricyclo[3.3.0.0<sup>2,8</sup>]oct-3-ene (or octa-3,6-dien) derivatives, or (iii) to the 1,4-positions of an arene in which case it is called a *para photocycloaddition*, with formation of bicyclo[2,2,2]oct-2-ene (or octa-2,5-dien) derivatives.

See *photocycloaddition*, [24, 25].

### **asymmetric photochemistry**

*Photochemical process* leading to a chiral substance from an achiral precursor such that one enantiomer predominates over the other.

Note: Asymmetric induction may be achieved by the use of chiral reagents, a chiral environment, or circularly polarized light [26].

See *crystal photochemistry*, *photochirogenesis*, [27, 28, 29, 30].

### **attenuance, $D$**

Logarithm to the base 10 of the incident *spectral radiant power*,  $P_{\lambda}^0$ , divided by the transmitted spectral radiant power,  $P_{\lambda}$  [7]

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

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

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

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

revG2

**attenuance 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. Sometimes called attenuator or neutral density filter.

G2/GB

**auxochrome**

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

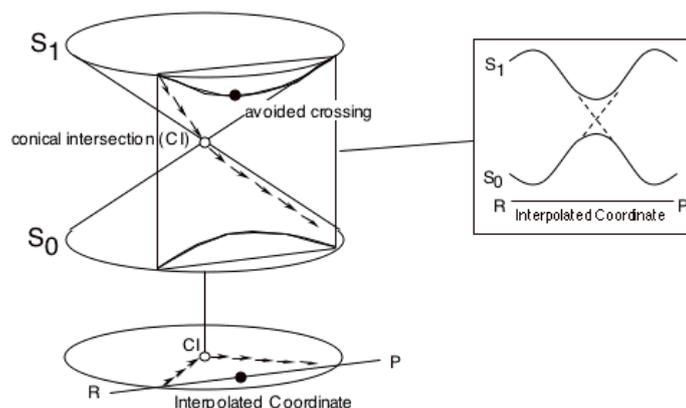
G2/GB

**avoided crossing (of potential energy surfaces)**

Frequently, two Born-Oppenheimer electronic states (e.g.,  $S_1$ ,  $S_0$ ) change their energy order as their molecular geometry is changed continuously along a path from reactants (R) to products (P). In the process their energies may become equal at some point (the surfaces are said to cross, dotted lines in the figure), or only come relatively close (the crossing of the surfaces is said to be avoided).

Same as *intended crossing*.

Note: If the electronic states are of the same symmetry, the *surface crossing* is always avoided in diatomics and usually allowed in polyatomics. The scheme illustrates the relationship between avoided crossing and *conical intersection* in a polyatomic molecule. Notice that avoided crossing usually occurs in the vicinity of the conical intersection.



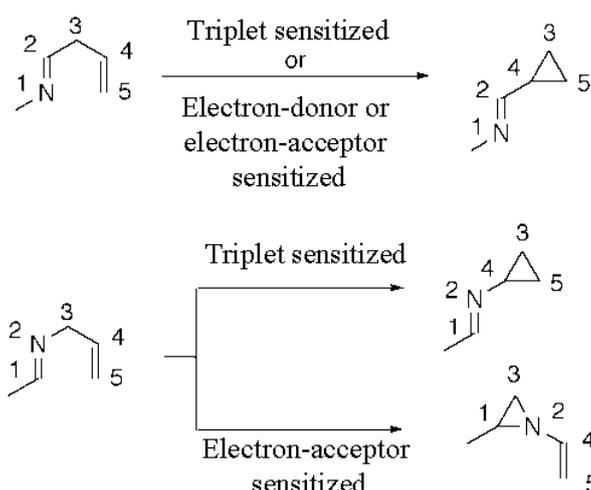
Related terms: *Born-Oppenheimer approximation*, *conical intersection*, *non-crossing rule*.

See [6, 23].

revG2

### aza-di- $\pi$ -methane rearrangement

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



sensitizers. In this instance the reaction amounts to a 1,2-shift of the alkene unit and “bond formation” between the C(1) and C(3) carbon atoms of the azadiene skeleton.

Related terms: *di- $\pi$ -methanerearrangement*, *di- $\pi$ -silane rearrangement*, *oxa-di- $\pi$ -methane rearrangement*.

See [31].

### 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. In using this term one should also specify the resulting electronic state of the donor and acceptor.

Note 1: It is recommended to use this term only for the process restoring the original electronic state of donor and acceptor.

Note 2: Should the forward electron transfer lead to *charge separation*, back electron transfer will result in *charge recombination*.

revG2

### 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.

See *Fermi level*.

G2/GB

### bandpass filter

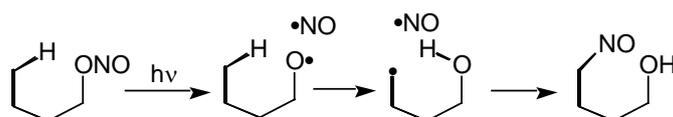
Optical device that permits the transmission of radiation within a specified *wavelength* range and does not permit transmission of radiation at higher or lower wavelengths. It can be an interference or a coloured *filter*.

Related term: *cut-off filter*.

G2/GB

### Barton reaction

*Photolysis* of a nitrite to form a  $\delta$ -nitroso alcohol. The mechanism is believed to involve a homolytic RONO cleavage followed by  $\delta$ -hydrogen abstraction and radical coupling. The  $\delta$ -nitroso alcohol rearranges thermally to give an oxime as the final product.



See [32, 33].

revG2

**bathochromic shift (effect)**

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

G2/GB

**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: 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

$$A(\lambda) = \lg \left( \frac{P_{\lambda}^0}{P_{\lambda}} \right) = \varepsilon(\lambda) c l$$

or

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

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>).

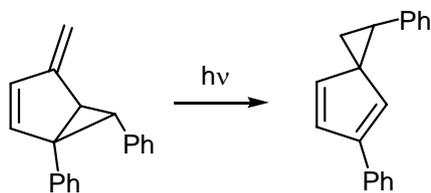
Note 2: *spectral radiant power* must be used because the Beer-Lambert law holds only if the spectral bandwidth of the *ultraviolet*, *visible*, or *infrared* radiation is narrow as compared to spectral linewidths in the spectrum.

See *absorbance*, *attenuance*, *extinction coefficient*, *Lambert law*, [51].

revG2

**bicycle rearrangement**

*Photochemical rearrangement* of unsaturated substrates by group migration over a  $\pi$  perimeter following the movement of a bicycle pedal.



See *photoisomerization*, [34].

**bioluminescence**

*Luminescence* produced by living systems.

See *luminescence*.

G2/GB

**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. Also called *two-photon excitation*.

Note: This term is sometimes also used for a two-step absorption.

revG2

**biphotonic process**

Resulting from *biphotonic excitation*.

See *multiphoton process*.

G2/GB

**bipolarons**

Bound pairs of *polarons* mutually attracted by the lattice distortion in a solid.

See *self-localized excitations*.

**biradical**

Synonymous with *diradical*.

revG2

**biradicaloid**

See *diradicaloid*.

revG2

**bleaching**

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

G2/GB

**blue shift**

Informal expression for *hypsochromic shift*.

G2/GB

**Born-Oppenheimer approximation**

Within the Born-Oppenheimer approximation, the wave function,  $\Psi(q, Q)$ , of a molecular state is written as a product of two factors, i.e., an electronic and a nuclear factor:

$\Psi(q, Q) \cong \Phi(q, Q)\Theta(Q)$ , where  $q$  and  $Q$  represent the coordinates of all the electrons and all the nuclei, respectively. The electronic wave function  $\Phi(q, Q)$  is defined to be the eigenfunction the molecule would have if all its nuclei were clamped in the configuration represented by  $Q$ . The corresponding eigenvalue,  $E(Q)$ , is called the electronic energy.  $\Theta(Q)$  represents the nuclear part of the wave function. The nuclear motion is described by a Hamiltonian in which  $E(Q)$  plays the role of potential energy.

Note: A plot of the electronic energy against the nuclear coordinates is called a *potential energy*

*surface* for the case of polyatomic molecules and a *potential energy curve* for a case of a diatomic molecule. Within the framework of this approximation, one associates a set of vibrational states with each electronic state, and writes the wavefunction of a vibronic state labelled  $ma$  (where the first label specifies the electronic state and the second the vibrational state) as  $\Psi_{ma}(q, Q) \equiv \Phi_m(q, Q) \Theta_a^{(m)}(Q)$ .

See [6, 23].

### branching plane

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

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

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

where  $\mathbf{C}_1$  and  $\mathbf{C}_2$  are the configuration interaction eigenvectors (i.e., the excited and ground-state *adiabatic* wavefunctions) in a conical intersection problem,  $H$  is the conical intersection Hamiltonian,  $\mathbf{Q}$  represents the nuclear configuration vector of the system, and thus  $\mathbf{q}$  is a unit vector in the direction of vector  $\mathbf{Q}$ .  $E_1$  and  $E_2$  are the energies of the lower and upper states, respectively.

Note: The branching plane is also referred to as the  *$\mathbf{g-h}$*  plane. Inspection of  $\mathbf{x}_1$  and  $\mathbf{x}_2$  provides information on the geometrical deformation imposed on an *excited state* molecular entity immediately after decay at a conical intersection. Consequently, these vectors provide information on the *ground-state* species that will be formed after the decay.

See [35].

### 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: The expression for Brewster angle is  $\theta_B = \arctan (n_2 / n_1) = \arctan (\varepsilon_2 / \varepsilon_1)^{1/2}$  where  $n_2$  and  $n_1$  are the refractive indices of the receiving surface and the initial medium, respectively, and  $\varepsilon_2$  and  $\varepsilon_1$  are the respective static electric permittivities (formerly called dielectric constants).

Note 2: 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: 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.

### **brightness**

Obsolete term. This term is reserved for non-quantitative reference to physiological perception of light and is not recommended as a quantitative measure of the *radiance* of an emitting device, e.g., a *lamp*.

See [9].

### **brightness (of a laser dye)**

Product of the *fluorescence quantum yield* ( $\Phi_f$ ) of a dye and the *molar decadic absorption coefficient* at the excitation *wavelength*  $\lambda$ , i.e.,  $\Phi_f \varepsilon(\lambda)$ .

### **cadmium-helium laser**

See *helium-cadmium laser*.

G2/GB

### **caged compound**

Molecular species that can rapidly be converted from inactive into active form by light. Typically, photocaged compounds have a covalently attached group that can be photocleaved by electromagnetic radiation of a specific wavelength.

Note 1: Electromagnetic radiation activated caged compounds (photocages) are widely used in biochemistry for a rapid photoinduced introduction of a variety of compounds to biological systems with spatial and temporal control, allowing the time-resolved study of the ensuing events.

Note 2: An example is the photorelease of nucleotides from their attachment to 1-(4,5-dimethoxy-2-nitrophenyl) ethyl ester.

See *photoremovable protecting group*, [36].

### **CASPT2**

Acronym for *complete active space self-consistent field second-order perturbation theory*.

### **CASSCF**

Acronym for *complete active space self-consistent field*.

### **cavity dumping**

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

See [17].

G2/GB

### **charge hopping**

*Electron* or *hole transport* between equivalent sites.

G2/GB

### **charge recombination**

Reverse of *charge separation*.

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

G2/GB

### **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.

*Charge recombination* reduces (or increases) the difference.

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

revG2

### **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: 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.

G2/GB

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

Electronic absorption corresponding to a *charge-transfer transition*.

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

revG2

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

Ground-state complex that exhibits *charge-transfer absorption*.

See *charge-transfer transition*.

G2/GB

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

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

G2/GB

**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: Transition typical for donor-acceptor complexes or multichromophoric molecular entities.

See *charge-transfer absorption*, [51].

G2/GB

**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.

Related term: *charge-transfer (CT) transition*.

revG2

**chemical laser**

*CW* or pulsed *laser* in which the excitation and *population inversion* of the emitting species results from a chemical reaction.

Note: Typical examples are HF and DF lasers emitting many lines in the IR region.

See [17].

G2/GB

**chemically induced dynamic electron polarization, (CIDEP)**

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

See [37].

**chemically induced dynamic nuclear polarization, (CIDNP)**

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

See [23, 37].

**chemically initiated electron exchange luminescence, (CIEEL)**

Type of *luminescence* resulting from a thermal electron-transfer reaction. Also called catalyzed *chemiluminescence*.

See [38].

**chemiexcitation**

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

Related term: *chemiluminescence*.

See *excited state*, *ground state*.

G2/GB

**chemiluminescence**

*Luminescence* arising from *chemiexcitation*.

G2/GB

**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: 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.

See [23].

revG2

### **CIDEP**

Acronym for *chemically induced dynamic electron polarization*.

revG2

### **CIDNP**

Acronym for *chemically induced dynamic nuclear polarization*.

revG2

### **CIEEL**

Acronym for *chemically initiated electron exchange luminescence*.

revG2

### **circular dichroism**

See *dichroism*.

### ***cis-trans* photoisomerization of alkenes**

A photoinduced geometric isomerization (a 180° rotation except when modified by steric interactions) about a double bond.

Note: Photochemical pathways for *cis-trans* isomerization have the advantage over thermal and catalytic methods of giving equilibrium *cis/trans* mixtures (*photostationary states*) rich in thermodynamically unstable isomers.

See [39].

### **CO<sub>2</sub> laser**

Continuous (CW) or pulsed source of *coherent radiation* normally tunable through the CO<sub>2</sub> vibration-rotation band centred near 10.6 μm.

See *gas lasers, laser*, [17].

G2/GB

### **coherent length**

See *coherent radiation*.

### **coherent radiation**

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

Note 1: The time interval over which the wave is a good approximation to a sinusoid and thus has a well-defined phase is called the coherence time  $\Delta\tau$  and is given by the uncertainty principle:

$$\Delta\tau \Delta\omega \geq 1$$

where  $\Delta\omega$  is the spectral bandwidth. Thus, a perfectly monochromatic light has an infinite coherence time. The coherence length  $\Delta l$  is the distance over which the wave is well-approximated by a sinusoid and is given by:

$$\Delta l = c \Delta\tau$$

where  $c$  is the speed (of light for electromagnetic waves, or sound for acoustic waves).

For a limited (by the observation conditions) interval  $\Delta\tau$ , the radiation can also be coherent within this time interval even if the source is not perfectly monochromatic.

Note 2: One of the great advantages of laser light sources is to produce coherent radiation over useful time and length scales.

See [47].

revG2

**coherent time**

See *coherent radiation*.

**collision complex**

Ensemble formed by two reaction partners, where the distance between them is the sum of their van der Waals radii. It constitutes a subclass of the species indicated as *encounter complex*.

G2/GB

**colourability**

Ability of a colourless or slightly coloured *photochromic* material to develop colour.

**colour scale**

Series of ordered numbers that represents observable gradations of a given attribute or gradations of a combination of attributes of colour perception.

**complete active space self-consistent field, (CASSCF)**

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

See *multiconfiguration SCF method*, [6].

**complete active space self-consistent field second-order perturbation theory, (CASPT2)**

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

See *multiconfiguration SCF method, multireference configuration interaction*, [6].

**computational photochemistry**

Aspects of research that address the study of photochemical events by means of computer simulations using specialized software tools and strategies in order to get an understanding of the process at a microscopic level. The aim is to uncover the mechanism of known photochemical processes, design new photochemical systems, and predict molecular properties that are experimentally inaccessible.

See [35].

**concentration depolarization**

Loss of *emission anisotropy* due to transfer of electronic excitation from photoselected molecules to other molecules with different orientations.

See *energy transfer, photoselection*, [51].

**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. This term is usually used to describe the properties of metals and semiconductors.

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

G2/GB

**configuration (electronic configuration)**

Distribution of the electrons of an atom or a molecular entity over a set of one-electron wavefunctions called *orbitals*, according to the Pauli principle.

Note: From one configuration several states with different *multiplicities* may result.

An example is the ground electronic configuration of the dioxygen molecule (O<sub>2</sub>):  $1\sigma_g^2, 1\sigma_u^2, 2\sigma_g^2, 2\sigma_u^2, 1\pi_u^4, 3\sigma_g^2, 1\pi_g^2$ , resulting in the  $^3\Sigma_g^-, ^1\Delta_g$ , and  $^1\Sigma_g^+$  states of different energy.

revG2/GB

**configuration interaction, (CI)**

Mixing of wavefunctions representing different electronic *configurations* to obtain an improved wavefunction for a many-electron state. In the full CI method, an  $n$ -electron wavefunction is expanded as a linear combination of Slater determinants describing all the possible different electronic configurations within the chosen orbital state.

Note: In practical calculations, CI methods consider only a limited set of configurations, i.e., the CIS method adds only the single excitations, CID adds double excitations, CISD adds single and double excitations, and so on.

See [6].

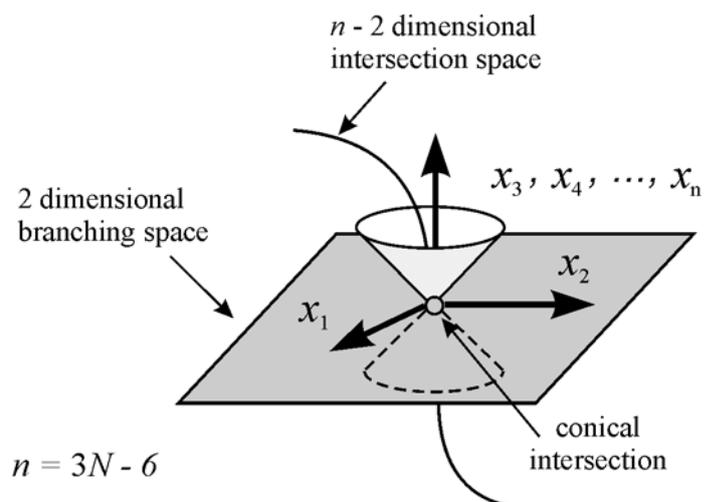
revG2

**conical intersection**

Point of crossing between two electronic states of the same spin *multiplicity* (most commonly *singlets* or *triplets*).

Note 1: In a polyatomic molecule two *potential energy surfaces* are allowed to cross along a  $(3N - 8)$ -dimensional subspace of the  $(3N - 6)$ -dimensional nuclear coordinate space (the *intersection space*) even if they have the same spatial/spin symmetry ( $N$  is the number of nuclei). Each point of the intersection space corresponds to a conical intersection. If the energy is plotted against two special internal geometrical coordinates,  $x_1$  and  $x_2$ , which define the so-called *branching plane*, the potential energy surface would have the form of a double cone in the region surrounding the degeneracy. In the remaining  $(3N - 8)$  directions, the energies of the *ground* and *excited state* remain degenerate; movement in the branching plane lifts the degeneracy.

Note 2: From a mechanistic point of view, conical intersections often provide the channel mediating *radiationless deactivation* and *photochemical reaction*.



See [6, 23, 35].

### contact ion pair

Pair of ions in direct contact and not separated by an intervening solvent or other neutral molecule. One mode of formation for a (geminate) contact ion pair is *electron transfer* between precursor species in an *encounter complex* (cf. *collision complex*).

Note: When one of the precursors in the *encounter complex* is electronically excited, the contact ion pair formed by *electron transfer* is equivalent to a polar *exciplex*.

G2

### continuous wave (CW) laser

CW operation of a *laser* means that the laser is continuously pumped and continuously emits electromagnetic radiation. The *emission* can occur in a single cavity mode or on multiple modes.

Note: Some lasers are called CW mode-locked. This indicates that the pulse average power is constant, i.e., there is no *Q-switched* mode locking.

### conversion cross-section

Product of the *quantum yield* by the *absorption cross section*,  $\sigma \Phi$ . SI unit is  $\text{m}^2$ ; commonly expressed in  $\text{cm}^2$ .

### conversion spectrum

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

Related terms: *action spectrum*, *efficiency spectrum*, *spectral effectiveness*.

G2/GB

### **copper vapour laser**

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

See *gas lasers*, *laser*.

G2/GB

### **correlation diagram**

Diagram showing the relative energies of *orbitals*, *configurations*, valence bond structures or states of reactants and products of a reaction, as a function of the molecular geometry, or another suitable parameter.

Note: An example is a diagram showing the energy levels of separated atoms as horizontal lines in two outer columns, with the energy levels of the united atoms shown as horizontal lines in an inner column. The relations between the levels of separated and united atoms are shown by connecting lines.

See [6].

revG2

### **correlation energy**

Difference between the Hartree-Fock energy calculated for a system and the exact non-relativistic energy of that system.

Note: The correlation energy arises from the approximate representation of the electron-electron repulsions in the Hartree-Fock method.

See [6].

G2/GB

**critical quenching radius,  $R_0$**

See *Förster-resonance-energy transfer*.

G2/GB

**crystal-field splitting**

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

Related term: *zero-field splitting*.

G2/GB

**crystal photochemistry**

*Photochemical process* in the crystal lattice of a photoactive compound or of a chromophore in the crystal lattice of host molecules. Often *asymmetric photochemistry* takes place.

See [29].

**CT**

Acronym for *charge transfer*.

G2

**CTTS**

Acronym for *charge-transfer transition to solvent*.

**current yield**

See *photocurrent yield*.

G2/GB

**cut-off filter**

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

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

See *cut-on filter*, *filter*.

G2/GB

### **cut-on filter**

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

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

### **CW**

Acronym for continuous wave. Non-pulsed source of electromagnetic radiation.

G2/GB

### **cycle (of a photochromic reaction)**

See *photochromism*.

### **dark photochemistry (photochemistry without light)**

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

See e.g., [40].

G2/GB

### **DAS**

Acronym for decay-associated spectra.

See *global analysis*.

**Davydov splitting (factor-group splitting)**

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

See [41].

G2/GB

**deactivation**

Loss of energy by an excited molecular entity.

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

G2/GB

**decay-associated spectra, (DAS)**

See *global analysis.*

**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. Same as “apparent lifetime”. The use of the latter term is not recommended.

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

**delayed fluorescence**

See *delayed luminescence.*

G2

**delayed luminescence**

*Luminescence* decaying more slowly than that expected from the rate of decay of the emitting state.

Note: The following mechanisms of luminescence provide examples:

(1) *triplet-triplet annihilation* to form one molecular entity in its *excited singlet state* and another

molecular entity in its electronic *ground state* (sometimes referred to as P type); in diffusion-controlled annihilation, the efficiency of this process is dominated by the *spin-statistical factor*.  
 (2) thermally activated *delayed fluorescence* involving reversible *intersystem crossing* (sometimes referred to as E type), and  
 (3) combination of oppositely charged ions or of an electron and a cation. For *emission* to be referred to in this case as delayed luminescence at least one of the two reaction partners must be generated in a *photochemical process*.

See [50].

G2/GB

### DEDMR

See *ODMR*.

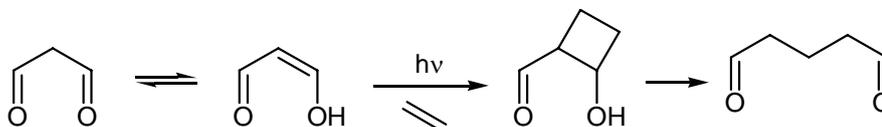
G2/GB

### degree of (polarization) anisotropy

See *emission anisotropy*.

### de Mayo reaction

*Photochemical process* leading to the formation of cyclobutanols by cycloaddition of an alkene to an enol compound. The enol originates in most cases from the tautomerization of a 1,3-dicarbonyl compound. The products of the de Mayo reaction are susceptible to undergo a retro-aldol ring opening resulting in the formation of 1,5-dicarbonyl compounds.



See *photocycloaddition*, [42, 43].

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

Inverse of the linear *absorption coefficient*. SI unit is m; common unit is cm.

Note: 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  $P_\lambda^0 / e$ .

See *absorbance, attenuation*.

revG2

### **Dexter excitation transfer (electron-exchange excitation transfer)**

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

The transfer rate constant,  $k_T$ , is given by

$$k_T = (1 / \hbar) K J \exp (-2 r / L)$$

where  $r$  is the distance between donor (D) and acceptor (A),  $L$  is the average Bohr radius,  $K$  is a constant not easily related to experimentally determinable quantities, and  $J$  is the spectral overlap integral given by

$$J = \int_{\lambda} I_{\lambda}^D(\lambda) \varepsilon_A(\lambda) d\lambda$$

where  $I_{\lambda}^D(\lambda)$  is the normalized *spectral distribution* of the *spectral radiant intensity* of the donor and  $\varepsilon_A(\lambda)$  is the normalized *molar decadic absorption coefficient* of the acceptor. For this mechanism the *spin-conservation rules* are obeyed. The normalization condition is:

$$\int_{\lambda} I_{\lambda}^D(\lambda) d\lambda = \int_{\lambda} \varepsilon_A(\lambda) d\lambda = 1$$

Note 1: The bandpass  $\Delta\lambda$  is a constant in spectrophotometers and spectrofluorometers using gratings. Thus, the scale is linear in wavelength and it is convenient to express and calculate the integrals in wavelengths instead of wavenumbers in order to avoid confusion.

Note 2: In practical terms, the integral  $\int_{\lambda} I_{\lambda}^D(\lambda) d\lambda$  is the area under the plot of the donor *emission* intensity versus the emission wavelength.

Note 3: In the case of Dexter energy transfer the rate constant,  $k_T$ , is independent of the *oscillator strength* of both transitions (in contrast to *Förster-resonance-energy transfer* mechanism), as evidenced by the normalization condition.

Related term: *radiative energy transfer*.

See [44, 50].

revG2

### **DFDMR**

See *ODMR*.

G2/GB

### **diabatic electron transfer**

*Electron-transfer* process in which the reacting system has to cross over between different electronic surfaces in passing from reactants to products. For diabatic electron transfer the electronic transmission factor is  $\ll 1$  (see *Marcus equation*).

Note: The term *non-adiabatic* electron transfer has also been used and is in fact more widespread, but should be discouraged because it contains a double negation.

Related term: *adiabatic electron transfer*.

See [23].

G2/GB

### **diabatic photoreaction**

Within the *Born-Oppenheimer approximation*, a reaction beginning on one *excited state potential energy surface* and ending, as a result of *radiationless transition*, on another surface, usually that of the *ground state*.

Note: The term *non-adiabatic* photoreaction has also been used and is in fact more widespread, but should be discouraged because it contains a double negation.

Compare with *adiabatic photoreaction*.

See [23].

revG2

### **dichroic filter**

Same as *interference filter*.

Note: The name dichroic arises from the fact that the filter appears one colour under illumination with transmitted light and another with reflected light.

### **dichroic mirror**

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

### **dichroic ratio**

See *linear dichroism*.

### **dichroism**

A sample is said to be dichroic (exhibit dichroism) if its *absorbance* depends on the type of *polarization* of the measuring beam. 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,  $\Delta A_C = A_L - A_R$ .

See *light polarization*, *linear dichroism*, [50, 51].

### **dielectric constant**

Obsolete term. Now called “relative static permittivity”[7].

G2/GB

### **differential quantum yield**

See *quantum yield*.

### **diode laser**

Semiconductor device of small dimensions (few hundred microns) serving as source of *CW* or pulsed *coherent radiation*. These *lasers* are also called semiconductor lasers.

Note 1: A device called laser diode generally refers to a combination of the semiconductor chip (the actual lasing unit) along with a monitor photodiode chip (for feedback control of the power output) housed in a package of less than 1 cm.

Note 2: Diode lasers use chips of Gallium-Arsenide or other *semiconductors* to generate *coherent* light in a small package. The *energy gap* between the *conduction* and *valence band* in these semiconductors is the basis of the mechanism for laser action.

See [45].

G2

### **dipolar mechanism (of energy transfer)**

Same as *Förster-resonance-energy transfer (FRET)*.

Related term: *energy transfer*.

revG2

### **dipole-dipole excitation transfer**

Same as *Förster-resonance-energy transfer (FRET)*.

Related term: *energy transfer*.

revG2

### **diradical**

An even-electron molecular entity with two (possibly delocalized) radical centres. Synonymous with biradical. Species in which the two radical centres have a weak covalent interaction or have different electronegativities are often referred to as biradicaloids (or *diradicaloids*). If the two radical centres are located on the same atom, the term biradical is rarely used, and such species are

called carbenes, nitrenes, etc.

Note 1: The lowest-energy triplet state of a diradical lies below or at most only a little above its lowest singlet state (usually judged relative to  $kT$ , the product of the Boltzmann constant  $k$  and the absolute temperature  $T$ ). The states of those diradicals whose radical centres interact particularly weakly are most easily understood in terms of a pair of local doublets.

Note 2: Theoretical descriptions of low-energy states of a diradical display the presence of two unsaturated valences (diradicals contain one fewer bond than permitted by the rules of valence): the dominant valence bond structures have two dots, the low energy molecular orbital *configurations* have only two electrons in two approximately non-bonding molecular orbitals, two of the natural orbitals have occupancies close to one, etc.

Same as biradical.

See [23, 46].

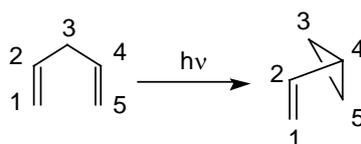
revG2

### **diradicaloid**

*Diradical*-like. Often used to refer to a species in which the two radical centres interact significantly.

### **di- $\pi$ -methane rearrangement**

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



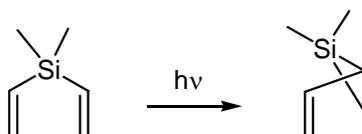
Related terms: *aza-di- $\pi$ -methane rearrangement*, *oxa-di- $\pi$ -methane rearrangement*, *di- $\pi$ -silane rearrangement*.

See [31].

G2/GB

### di- $\pi$ -silane rearrangement

Silicon version of the *di- $\pi$ -methane rearrangement* with a Si atom at position 3 of the basic 1,4-diene chromophore.



### dose

Energy or amount of *photons absorbed* per volume (or per mass) by an irradiated object during a particular exposure time. SI units are  $\text{J m}^{-3}$  or  $\text{J g}^{-1}$  and  $\text{mol m}^{-3}$  or  $\text{mol g}^{-1}$ , respectively. Common units are  $\text{einstein m}^{-3}$  or  $\text{einstein g}^{-1}$ , respectively.

Note: 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.

Related terms: *einstein*, *UV dose*.

G2/GB

### doublet state

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

Related term: *multiplicity*.

G2/GB

### downconversion

Process by which a *photon* with *frequency*  $\nu_1$  interacts with a non-linear medium and splits into two simultaneously emitted photons with frequencies  $\nu_2$  and  $\nu_3$  so that the energy is conserved:

$$\nu_1 = \nu_2 + \nu_3.$$

Note 1: Also known as a parametric downconversion.

Note 2: The efficiency of the conversion process depends on the parametric gain in the non-linear material. This in turn depends on the power of the incident radiation, the photon frequencies, their indices of refraction in the material, and the non-linear “hyper-susceptibility” of the material.

See *non-linear optical techniques, parametric processes, polarization*, [47].

### **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* ( $\Delta_{\text{ET}}G^\circ$ ).

### **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: 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*.

Related term: *polar driving force*.

See [22].

revG2

### **Drude-Nernst equation (for electrostriction)**

Equation describing the contraction ( $\Delta V_{\text{el}}$ ) taking place in a dielectric medium of relative static permittivity  $\epsilon_r$  (formerly called dielectric constant) upon introduction of an ion of charge number  $z$  and radius  $r$ :

$$\Delta V_{\text{el}} = -\frac{(ze)^2}{2r\epsilon_r} \frac{\partial(\ln\epsilon_r)}{\partial p}$$

with  $e$  the elementary charge.

Note: Inasmuch as the derivative of  $\ln\epsilon_r$  with respect to pressure,  $\frac{\partial(\ln\epsilon_r)}{\partial p}$ , is not known for all media, there are approximations to evaluate this term as a function of  $\epsilon_r$  and of the “isothermal compressibility” of the medium,  $\kappa_T$ .

See *electrostriction*, [48].

### **dual fluorescence (of systems or molecular species)**

Systems or molecular species showing two *fluorescence* bands. Several non-trivial molecular properties may be at the basis of a dual fluorescence, such as conformational equilibrium in the *ground state* and a mixture of *excited states*.

Note: A trivial reason for dual fluorescence is the coexistence of two independent *fluorophores*.

### **dual-mode photochromism**

*Photochromism* occurring in complex systems and triggered alternatively by two different external stimuli, such as light and an electric current. In such a case photochromism and "electrochromism" are mutually regulated.

See [19].

### **dye laser**

*CW* or pulsed source of *coherent radiation* in which the active medium is usually a solution of a *fluorescent organic compound* (the *laser dye*) pumped with a suitable pump laser or with a flash *lamp*.

Note 1: These lasers can be tuned to extremely narrow linewidths over a large part of the broad fluorescence band of the dye (50-100 nm).

Note 2: An advantage of dye lasers over *optical parametric oscillators* is the independence of the linewidth of a dye laser on the wavelength, in view of the fact that in general, to select the wavelength, a grating is part of the resonance cavity.

See [17].

revG2

### **dynamic quenching**

See *quenching*.

G2/GB

### **ECL**

Acronym for *electrogenerated chemiluminescence*.

### **effectiveness**

See *spectral effectiveness*.

G2/GB

### **efficiency (of a step), $\eta$**

Useful energy delivered or bound divided by the energy supplied, i.e., energy output/energy input. It is also used in the sense of a quantitative measure of the relative rate of a given step,  $k_i$ , involving a species with respect to the sum of the rates of all of the parallel steps, which depopulate that species.

Note: Mathematical expression:  $\eta = k_i / \sum_i k_i$ , with  $k_i$  the different rate constants for the various deactivation steps of the particular species.

Related term: *quantum yield*.

G2/GB

### **efficiency spectrum**

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

Compare with *spectral effectiveness*.

See *action spectrum*, *conversion spectrum*.

G2/GB

### **einstein**

A mole of *photons*. Widely used, although it is not an SI unit.

Note 1: einstein sometimes is defined as the energy of one mole of photons. This latter use is discouraged.

Note 2: The energy of one einstein of photons of *frequency*  $\nu$  is  $E = N_A h \nu$ , with  $h$  the Planck constant and  $N_A$  the Avogadro constant.

revG2

### **electrochemiluminescence**

See *electrogenerated chemiluminescence*.

G2/GB

### **electrochromic effect**

See *Stark effect*.

G2/GB

### **electrocyclization**

See [20].

### **electrogenerated chemiluminescence, (ECL)**

*Luminescence* produced by a chemical reaction between species generated by electrolysis at an electrode surface. Also called *electrochemiluminescence* or (incorrectly) *electroluminescence*.

Note: ECL is a particular type of electroluminescence.

revG2

**electroluminescence**

Non-thermal conversion of electrical energy into optical radiation.

Note 1: Electroluminescence is distinguished from incandescence, which is a thermal process.

Note 2: An example of electroluminescence is the *photon emission* resulting from electron-hole recombination in a pn junction, as in a *light-emitting diode (LED)*.

Related term: *electrogenerated chemiluminescence*.

revG2

**electron correlation**

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

Related term: *correlation energy*.

See [6].

G2/GB

**electron-exchange excitation transfer**

Same as *Dexter excitation transfer*.

Related term: *energy transfer*.

G2/GB

**electron transfer**

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

Related terms: *inner-sphere electron transfer*, *Marcus equation*, *outer-sphere electron transfer*.

G2/GB

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

Related term: *photosensitization*.

G2/GB

### **electronic configuration**

See *configuration*.

G2/GB

### **electronic energy migration (or hopping)**

Movement of electronic excitation energy from one molecular entity to another of the same species, or from one part of a molecular entity to another of the same kind or of similar electronic excited state energy. The migration can happen via *radiative or radiationless* processes.

Note: An example is excitation migration between the *chromophores* of an aromatic polymer.

G2/GB

### **electronic transition moment**

See *transition (dipole) moment*.

### **electronic transmission factor, $\kappa_{ET}$**

See *Marcus equation*.

### **electronically excited state**

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

G2/GB

### **electrophotography**

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

G2/GB

### **electrostriction**

Contraction of a dielectric in an electric-field gradient.

Note 1: For example, the contraction taking place around the charged centres created as a consequence of the sudden formation of separated positive and negative charges in the process of *electron transfer*.

Note 2: The thermodynamic description of electrostriction was given by Drude and Nernst in 1894 to explain the phenomenon of contraction of a continuum medium, such as an alkane, around charges suddenly produced in that medium.

See *Drude-Nernst equation*.

### **El-Sayed rules**

The rate of *intersystem crossing* is relatively large if the *radiationless transition* involves a change of orbital type.

Note: A typical case is the transition from the lowest *singlet state* to the *triplet manifold*, e.g.,  ${}^1\pi,\pi^* \rightarrow {}^3n,\pi^*$  is faster than  ${}^1\pi,\pi^* \rightarrow {}^3\pi,\pi^*$  and  ${}^1n,\pi^* \rightarrow {}^3\pi,\pi^*$  is faster than  ${}^1n,\pi^* \rightarrow {}^3n,\pi^*$ .

See *multiplicity*, [49].

revG2

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

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

Related terms: *fluorescence, phosphorescence*.

See [50].

revG2

### **emission anisotropy**

Also referred to as degree of (*polarization*) anisotropy. Used to characterize luminescence (*fluorescence, phosphorescence*) polarization resulting from *photoselection*. Defined as:

$$r = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}}$$

where  $I_{\parallel}$  and  $I_{\perp}$  are the intensities measured with the linear polarizer for *emission* parallel and perpendicular, respectively, to the electric vector of linearly polarized incident electromagnetic radiation (which is often vertical). The quantity  $I_{\parallel} + 2I_{\perp}$  is proportional to the total fluorescence intensity  $I$ .

Note 1: Fluorescence polarization may also be characterized by the polarization ratio, also called the degree of polarization  $p$ ,

$$p = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}}$$

For parallel absorbing and emitting transition moments the (theoretical) values are  $(r, p) = (2/5, 1/2)$ ; when the transition moments are perpendicular, the values are  $(r, p) = (-1/5, -1/3)$ . In many cases, it is preferable to use emission anisotropy because it is additive; the overall contribution of  $n$  components  $r_i$ , each contributing to the total fluorescence intensity with a fraction  $f_i = I_i/I$ , is given by:

$$r = \sum_{i=1}^n f_i r_i \quad \text{with} \quad \sum_{i=1}^n f_i = 1$$

Note 2: On continuous illumination, the measured emission anisotropy is called steady-state emission anisotropy ( $\bar{r}$ ) and is related to the time-resolved anisotropy by:

$$r = \frac{\int_0^{\infty} r(t) I(t) dt}{\int_0^{\infty} I(t) dt}$$

where  $r(t)$  is the anisotropy and  $I(t)$  is the *radiant intensity* of the emission, both at time  $t$  following a  $\delta$ -pulse excitation.

Note 3: *Luminescence* polarization spectroscopy, with linear polarizers placed in both beams, is usually performed on isotropic samples, but it may also be performed on oriented anisotropic samples. In the case of an anisotropic, *uniaxial sample*, five linearly independent luminescence spectra, instead of the two available for an isotropic sample, may be recorded by varying the two polarizer settings relative to each other and to the sample axis.

Note 4: The term fundamental emission anisotropy describes a situation in which no depolarizing events occur subsequent to the initial formation of the emitting state, such as those caused by rotational diffusion or *energy transfer*. It also assumes that there is no overlap between differently polarized transitions. The (theoretical) value of the fundamental emission anisotropy,  $r_0$ , depends on the angle  $\alpha$  between the absorption and emission transition moments in the following way:

$$r_0 = \langle 3 \cos^2 \alpha - 1 \rangle / 5$$

where  $\langle \rangle$  denotes an average over the orientations of the photoselected molecules.  $r_0$  can take on values ranging from  $-1/5$  for  $\alpha = 90^\circ$  (perpendicular transition moments) to  $2/5$  for  $\alpha = 0^\circ$  (parallel transition moments). In spite of the severe assumptions, the expression is frequently used to determine relative *transition-moment* angles.

Note 5: In time-resolved fluorescence with  $\delta$ -pulse excitation, the theoretical value at time zero is identified with the fundamental emission anisotropy.

See *light polarization, uniaxial sample*, [50, 51].

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

See [50].

G2/GB

### **emissivity**

Same as *emittance*.

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

*Radiant exitance* emitted by an object relative to that of a black body at the same temperature. It is dimensionless. Same as emissivity.

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

See [7].

revG2

### **encounter complex**

Intermolecular assembly formed by molecular entities in contact or separated by a distance small compared to the diameter of solvent molecules and surrounded by several shells of solvent molecules; the innermost shell is the solvent “cage”.

Note: When one of the species is excited, the excitation usually takes place prior to formation of the encounter complex. During the *lifetime* of the encounter complex the reactants can collide several times to form collision complexes, and then undergo structural and electronic changes. If the interaction between the reactants leads to a minimum in the potential energy and one of the entities is *electronically excited*, the collision complex may represent an *exciplex* or *excimer*.

Related terms: *collision complex*, *contact ion pair*.

G2/GB

### **energy hypersurface**

Synonymous with *potential energy surface* (PES). The notion of hypersurface is used to stress the multidimensionality of PESs.

Note: In a molecular system consisting of  $N$  atomic nuclei, the number of the independent coordinates that fully determine the PES is equal to  $3N - 6$  (or  $3N - 5$  if the molecule is diatomic).

See [6].

### **energy migration**

See *electronic energy migration*.

G2/GB

### **energy pooling**

See *annihilation*.

G2/GB

### **energy storage efficiency, $\eta$**

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

Related term: *efficiency*.

G2/GB

### **energy transfer**

Term used to describe the process by which a molecular entity is excited (e.g., by *absorption* of *ultraviolet*, *visible*, or *infrared* radiation or by *chemiexcitation*) 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: 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.

Related terms: *Dexter-excitation transfer*, *Förster-resonance-energy transfer*, *radiative-energy transfer*.

See [50].

G2/GB

### **energy-transfer plot**

Plot of the rate constant of *quenching* by *energy transfer* of an *electronically excited* molecular entity by a series of *quenchers* versus the *excited-state* energy of the quenchers.

Note: Alternatively, a plot of the rate constant for the *sensitization* of a reaction versus the electronically excited-state energy of different *sensitizers*. This type of plot is used to estimate the energy of the excited molecular entity quenched (in the former case) or produced (in the latter case).

Related term: *Stern-Volmer kinetic relationships*.

See [52].

revG2

### **enhancer (of emission)**

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

revG2

### **entrainment**

Term used in *nucleophilic photosubstitution* to designate the induction of the reaction of a less reactive (or non-reactive) nucleophile with a substrate by the addition of catalytic amounts of another nucleophile, more reactive at initiation. Often, the non-reactive nucleophile at initiation is,

however, quite reactive at propagation [53].

Note: Term also used in *photobiology* in connection with the setting of the circadian clock by biological photosensors such as phytochromes and cryptochromes in plants [54] and cryptochromes in mammals and insects [55].

## ESCA

Acronym for electron spectroscopy for chemical analysis.

See *photoelectron spectroscopy*.

G2/GB

## excimer

Complex formed by the interaction of an *excited* molecular entity with another identical molecular entity in its ground state. The complex dissociates in the ground state because it is “non-bonding” in the ground state.

Note: Typical examples are the noble gas excimers responsible for the emission in *excimer lamps*.

Related term: *exciplex*.

See [50].

revG2

## excimer lamp

Non-coherent source of *ultraviolet* radiation capable of producing quasi-monochromatic radiation from the near *UV* ( $\lambda = 354$  nm) to the vacuum *UV* ( $\lambda = 126$  nm). The operation of the *excimer lamps* relies on the radiative decomposition of *excimers* or *exciplexes* created by various types of discharges.

Note 1: Using noble gas, halogen, or noble gas / halogen mixtures with fill pressure  $\sim 30$  kPa, the radiative decomposition of the *excimer* or the *exciplex* produces nearly monochromatic radiation. Some of the commercially available wavelengths for the particular excimers or exciplexes are 126 nm with  $\text{Ar}_2$ , 146 nm with  $\text{Kr}_2$ , 172 nm with  $\text{Xe}_2$ , 222 nm with  $\text{KrCl}$ , and 308 nm with  $\text{XeCl}$ , obtained with efficiencies of 5–15 %. Pulsed Xe-excimer ( $\text{Xe}_2$ ) lamps may have up to 40 %

efficiency. Good efficiencies are also obtained with XeBr at 291 nm and with XeI at 253 nm. Other wavelengths produced with much less efficiency are 207 nm (KrBr), 253 nm (XeI), 259 nm (Cl<sub>2</sub>), and I<sub>2</sub> (341) (see Table).

Table: Peak wavelengths (nm) obtained in dielectric-barrier discharges with mixtures of noble gas (Ng) and halogen (X<sub>2</sub>). Wavelengths of commercially available lamps are shown in boldface type.

The molecular species indicated are excimers or exciplexes

	<b>X<sub>2</sub></b>	<b>Ne</b>	<b>Ar</b>	<b>Kr</b>	<b>Xe</b>
<b>Ng<sub>2</sub></b>			<b>126</b>	<b>146</b>	<b>172</b>
<b>F</b>	157	108	193	249	354
<b>Cl</b>	259		175	<b>222</b>	<b>308</b>
<b>Br</b>	291		165	207	283
<b>I</b>	341			190	253

Note 2: Phosphors are used to transform the UV radiation into visible radiation. This is the basis of mercury-free fluorescent lamps and of flat plasma-display panels with a large screen.

See [56].

### **excimer laser**

Source of pulsed *coherent radiation* obtained from an *exciplex*.

Note 1: Typical *lasing* species are noble gas halides (XeCl, KrF, etc.) emitting in the *UV* region.

Note 2: The proper name should be *exciplex laser*.

See *gas lasers*, [17].

G2/GB

### **exciplex**

*Electronically excited* complex, of definite stoichiometry, “non-bonding” in the *ground state*. In general, a complex formed by the interaction of an electronically excited molecular entity with a ground-state partner of a different molecular structure. If the partners have the same molecular

structure this special case of an exciplex is called an *excimer*.

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

See [57].

G2

### **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: When corrected for wavelength dependent variations in the excitation *radiant power* this is called a corrected excitation spectrum.

Note 2: 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*.

Related term: *emission spectrum*.

See [50].

revG2

### **excitation transfer**

Same as *energy transfer*.

G2/GB

### **excited state**

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

Note: In photochemistry an *electronically excited state* is usually meant.

G2/GB

**exciton**

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

Note: 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.

See *electronic energy migration, self-localized excitations*, [47].

revG2

**exitance**

See *radiant exitance*.

G2/GB

**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.

See *photon exposure, radiant exposure*.

**external heavy-atom effect**

See *heavy-atom effect*.

G2/GB

**external quantum efficiency**

The *efficiency* of light *emission* for solid-state light emitting devices, such as *organic light-emitting*

*devices* (OLED). Analogous to *emission quantum yield*.

See [58].

**exterplex**

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

G2/GB

**extinction**

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

G2/GB

**extinction coefficient**

This term, equivalent to *molar (decadic) absorption coefficient*, is no longer recommended [7].

See *Beer-Lambert law*.

G2

**factor-group splitting**

See *Davydov splitting*.

G2/GB

**fatigue (of a photochromic system)**

Loss of performance over time, due to chemical degradation. The major cause of fatigue is oxidation.

Note: Although *photochromism* is a non-destructive process, side reactions can occur.

See [3].

**Fermi level,  $E_F$** 

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

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

G2/GB

### **filter (optical)**

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

See [2, 15].

G2/GB

### **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: 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: 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 (the Greek “lysis” means dissolution or decomposition and in general lysis is used to indicate breaking). However, historically the name has been used to describe the technique of pulsed excitation, independently of the process that follows the excitation.

See [59] for a list of recommended procedures and optical data on transient species. See also [2].

revG2

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

At a given point in space, the *radiant energy*,  $Q$ , incident on an small sphere from all directions divided by the cross-sectional area of that sphere. SI unit is  $\text{J m}^{-2}$ .

Note 1: The term is used in photochemistry to specify the energy delivered in a given time interval (e.g., by a *laser* pulse).

Note 2: 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 3: 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 4: 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.

Related terms: *dose*, *photon fluence*.

See [9].

revG2

### **fluence rate, radiant energy fluence rate, $E_o$**

Total *radiant power*,  $P$ , incident from all directions onto a small sphere divided by the cross-sectional area of that sphere. SI unit is  $W m^{-2}$ .

Note 1: Mathematical definition:  $E_o = dP/dS = dH_o/dt$ . If the radiant power is constant over the area  $S$ ,  $E_o = P/S$ .

Note 2: 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.

Related term: *photon fluence rate*.

See *intensity*, *radiance*, [9].

revG2

### **fluorescence**

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

See [50].

revG2

**fluorescence anisotropy**

See *emission anisotropy*, *photoselection*.

**fluorescence lifetime**

Parameter describing the time evolution of the decay of the fluorescent *radiant intensity*.

See *lifetime*, [50].

**fluorescence polarization**

See *emission anisotropy*, *photoselection*.

**fluorescence resonance energy transfer**

Term frequently and inappropriately applied to resonance energy transfer in the sense of *Förster-resonance-energy transfer (FRET)*, which does not involve the *emission* of radiation.

**fluorescence spectrum**

See *emission spectrum*.

**fluorogenic**

Property of a material in which *fluorescence* is induced or enhanced by the addition of another molecular entity.

Note: An example is a non-fluorescent compound consisting of a pyrene connected to a maleimide group (which quenches the pyrene fluorescence). A reaction in which the maleimide moiety is converted to a succinimide derivative results in the recovery of the pyrene fluorescence.

**fluorophore**

Molecular entity (often organic) that emits *fluorescence*.

**fluxional molecules**

Subclass of structurally non-rigid molecules in which all the observable interconverting species are

chemically and structurally equivalent.

Note: Classic example of the phenomenon of fluxionality is the rapid “automerization” of tricyclo[3.3.2.0<sup>2,8</sup>]deca-3,6,9-triene (bullvalene), the rapid interconversion of 1 209 600 (10!/3) degenerate isomers.

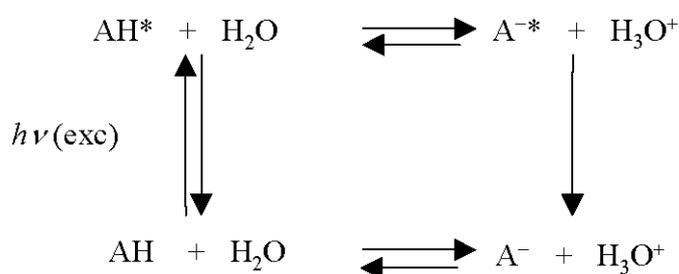
See *Jahn-Teller effect*, [6].

### Förster cycle

Indirect method of determination of *excited-state* equilibria, such as  $pK_a^*$  values, based on *ground-state* thermodynamics and electronic transition energies.

Note 1: This cycle considers only the difference in molar enthalpy change ( $\Delta\Delta H_m$ ) of reaction of ground and excited states, neglecting the difference in molar entropy change of reaction of those states ( $\Delta\Delta S_m$ ).

Note 2: For the following reaction sequence,



eq. 1 holds.

$$N_A h\nu_{0-0}(\text{AH}) + \Delta H_m^* = N_A h\nu_{0-0}(\text{A}^-) + \Delta H_m \quad (1)$$

Eq. 1 affords eq. 2 upon rearrangement

$$\Delta\Delta H_m = \Delta H_m^* - \Delta H_m = N_A [h\nu_{0-0}(\text{A}^-) - h\nu_{0-0}(\text{AH})] \quad (2)$$

with  $\Delta H_m^*$  and  $\Delta H_m$  the molar enthalpy difference between the ground and excited states of the

protonated and deprotonated species, respectively, and  $h\nu_{0-0}(A^-)$  and  $h\nu_{0-0}(AH)$  the 0-0 energy level difference between the excited and ground state deprotonated and protonated species, respectively. The values of  $h\nu_{0-0}(A^-)$  and  $h\nu_{0-0}(AH)$  are usually estimated by using the intersection points of the normalized *absorption* and *emission* spectra for each species. In the case of large *Stokes shifts* it is preferable to take the average of the wavenumbers corresponding to the half-heights of the absorption and emission bands.

Neglecting  $\Delta\Delta S_m$  (see Note 1), eq. 3 results

$$\Delta\Delta G_m = N_A [h\nu_{0-0}(A^-) - h\nu_{0-0}(AH)] \quad (3)$$

Eq. 4 is thus obtained,

$$pK_a^* - pK_a = N_A/2.3 RT [h\nu_{0-0}(A^-) - h\nu_{0-0}(AH)] \quad (4)$$

which permits to calculate the  $pK_a^*$  value from the value of  $pK_a$  together with absorption and emission data. The Förster cycle is a purely thermodynamic concept and excited state equilibria calculated therefrom are not necessarily established prior to deexcitation.

Note 3: Foerster is an alternative and acceptable spelling for Förster.

See [50].

revG2

### **Förster radius**

See *Förster-resonance-energy transfer*, [50].

### **Förster-resonance-energy transfer (dipole-dipole excitation transfer), (FRET)**

Non-radiative excitation transfer between two molecular entities separated by distances considerably exceeding the sum of their van der Waals radii. It describes the transfer in terms of the interaction between the *transition (dipole) moments* of the entities in the very weak dipole-dipole coupling limit. It is a Coulombic interaction frequently called a dipole-dipole coupling. The transfer rate constant from donor to acceptor,  $k_T$ , is given by

$$k_T = k_D \left( \frac{R_0}{r} \right)^6 = \frac{1}{\tau_D^0} \left( \frac{R_0}{r} \right)^6$$

where  $k_D$  and  $\tau_D^0$  are the *emission* rate constant and the *lifetime* of the excited donor in the absence of transfer, respectively,  $r$  is the distance between the donor and the acceptor and  $R_0$  is the critical quenching radius or Förster radius, i.e., the distance at which transfer and spontaneous decay of the excited donor are equally probable ( $k_T = k_D$ ) (see Note 3).

$R_0$  is given by

$$R_0 = \text{Const.} \left( \frac{\kappa^2 \Phi_D^0 J}{n^4} \right)^{1/6}$$

where  $\kappa$  is the *orientation factor*,  $\Phi_D^0$  is the fluorescence quantum yield of the donor in the absence of transfer,  $n$  is the average refractive index of the medium in the wavelength range where spectral overlap is significant,  $J$  is the spectral overlap integral reflecting the degree of overlap of the donor *emission spectrum* with the acceptor *absorption spectrum* and given by

$$J = \int_{\lambda} I_{\lambda}^D(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda$$

where  $I_{\lambda}^D(\lambda)$  is the normalized *spectral radiant intensity* of the donor so that  $\int_{\lambda} I_{\lambda}^D(\lambda) d\lambda = 1$ .  $\varepsilon_A(\lambda)$  is the *molar decadic absorption coefficient* of the acceptor. See Note 3 for the value of *Const.*

Note 1: The bandpass  $\Delta\lambda$  is a constant in spectrophotometers and spectrofluorometers using gratings. Thus, the scale is linear in wavelength and it is convenient to express and calculate the integrals in wavelengths instead of wavenumbers in order to avoid confusion.

Note 2: In practical terms, the integral  $\int_{\lambda} I_{\lambda}^D(\lambda) d\lambda$  is the area under the plot of the donor emission intensity versus the emission wavelength.

Note 3: A practical expression for  $R_0$  is:

$$R_0 / \text{nm} = 2.108 \times 10^{-2} \left\{ \kappa^2 \Phi_D^0 n^{-4} \int_{\lambda} I_{\lambda}^D(\lambda) [\varepsilon_A(\lambda) / \text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}] (\lambda / \text{nm})^4 d\lambda \right\}^{1/6}$$

The *orientation factor*  $\kappa$  is given by

$$\begin{aligned}\kappa &= \cos \theta_{DA} - 3 \cos \theta_D \cos \theta_A \\ &= \sin \theta_D \sin \theta_A \cos \varphi - 2 \cos \theta_D \cos \theta_A\end{aligned}$$

where  $\theta_{DA}$  is the angle between the donor and acceptor moments, and  $\theta_D$  and  $\theta_A$  are the angles between these, respectively, and the separation vector;  $\varphi$  is the angle between the projections of the transition moments on a plane perpendicular to the line through the centres.  $\kappa^2$  can in principle take values from 0 (perpendicular transition moments) to 4 (collinear transition moments). When the transition moments are parallel and perpendicular to the separation vector,  $\kappa^2 = 1$ . When they are in line (i.e., their moments are strictly along the separation vector),  $\kappa^2 = 4$ . For randomly oriented *transition (dipole) moments*, e.g., in fluid solutions,  $\kappa^2 = 2/3$ .

Note 4: The transfer quantum efficiency is defined as

$$\Phi_T = \frac{k_T}{k_D + k_T}$$

and can be related to the ratio  $r/R_0$  as follows:

$$\Phi_T = \frac{1}{1 + (r/R_0)^6}$$

or written in the following form :

$$\Phi_T = 1 - \frac{\tau_D}{\tau_D^0}$$

where  $\tau_D$  is the donor excited-state lifetime in the presence of acceptor, and  $\tau_D^0$  in the absence of acceptor.

Note 5: FRET is some times inappropriately called fluorescence-resonance energy transfer. This is not correct because there is no fluorescence involved in FRET.

Note 6: Foerster is an alternative and acceptable spelling for Förster.

Related terms: *Dexter-excitation transfer, energy transfer, radiative-energy transfer.*

See [50, 60].

revG2

**Fourier-transform spectrometer**

Scanning interferometer (containing no principal 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. The spectrum is obtained by a Fourier transformation of the output of the interferometer.

Note: There are Fourier spectrometers in non-optical-, non-infrared-, 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.

See *coherent radiation*.

revG2

**Fourier-transform spectroscopy**

A 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: 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).

See *coherent radiation*.

**fraction of light absorbed,  $f$** 

See *absorption factor*.

**Franck-Condon factor**

Squared modulus of the overlap integral between the vibrational wave functions ( $\Theta$ ) for the initial (0) and final (e) state of a given electronic transition.

$$\left| \int \Theta_{v'}^{(e)} \Theta_v^{(0)} dQ \right|^2$$

where the integration is over all nuclear coordinates.

See *Franck-Condon principle*, [50, 51].

### **Franck-Condon principle**

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

Note 1: The quantum mechanical formulation of this principle is that the *intensity* of a *vibronic transition* is proportional to the *Franck-Condon factor*, i.e., the square of the overlap integral between the vibrational wavefunctions of the two states that are involved in the transition.

Note 2: Mathematically, the Franck-Condon principle means that the *transition dipole* is independent of nuclear coordinates.

See *transition (dipole) moment*, [6].

G2/GB

### **Franck-Condon state**

See *Franck-Condon principle*.

G2/GB

### **free-electron laser**

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

See *laser*, [17].

G2/GB

### **free exciton**

See *exciton*.

### **free-radical photosubstitution**

*Photoinduced* substitution resulting from the reaction of free radicals produced by *photolysis* of an appropriate reagent, such as, e.g., halogenated compounds.

See, e.g., [61].

### **free-running laser**

It applies to a pulsed *laser* and means that the laser *emission* lasts as long as the pumping process is sufficient to sustain *lasing* conditions.

Note 1: Typical pulse durations are in the  $\mu\text{s}$ -ms range, depending on the pumping source.

Note 2: When the operation mode of a pulsed laser is not specified as *Q-switched*, *mode-locked* or anything else, it must be considered as free-running.

G2

### **frequency, $\nu$ or $\omega$**

The number of waveperiods per time interval. The linear frequency,  $\nu$ , is the number of cycles per time interval. SI unit  $\text{Hz} = \text{s}^{-1}$ .

Note: For the angular frequency the symbol  $\omega (= 2 \pi \nu)$  is used with  $\text{rad s}^{-1}$  as the SI unit.

See [7].

G2

### **frequency doubling**

See *harmonic frequency generation*, *non-linear optical effects*.

G2/GB

### **FRET**

Acronym for *Förster-resonance-energy transfer*.

Note: Sometimes inappropriately called *fluorescence resonance-energy transfer*.

### **fundamental emission anisotropy**

See *emission anisotropy*.

### ***f* value**

See *oscillator strength*.

G2/GB

### **FWHM**

Acronym for *full width at half maximum*.

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

G2/GB

### **gas lasers**

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

- neutral atoms (e.g., Ne, Cu, Au, etc.) or molecules (e.g., N<sub>2</sub>, CO<sub>2</sub>, CO, I<sub>2</sub>, etc.) or
- ionized atoms (e.g., Ar, Kr, Cd, etc.)

Note 1: These lasers are not tunable but most of them can emit several lines, which may be separated by the use of appropriate selection elements.

Note 2: Pulsed lasers may be *free-running*, *Q-switched* or *mode-locked*. Some CW lasers may be mode-locked.

See *argon ion-*, *CO<sub>2</sub>-*, *excimer-*, *copper vapour-*, *helium-neon-*, *krypton-*, *nitrogen-lasers*, [17].

G2

**gated photochromism**

Special form of *photochromism* in which one or both forms of a *photochromic* system are transformed reversibly, either chemically or electrochemically, into a non-photochromic form.

See [3].

**Gaussian band shape**

Band shape described by the Gaussian *frequency* distribution function

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

with  $a^{-1}$  proportional to the width of the band and  $\nu_0$  the frequency at the band maximum.

Related term: *Lorentzian band-shape*.

revG2

**geminate ion pair**

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

G2

**geminate pair**

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

G2/GB

**geminate radical pair**

See *radical pair*.

**geminate recombination**

Recombination reaction of a *geminate pair*.

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

G2

### germicidal lamp

Same as *low-pressure mercury lamp*.

### Gibbs energy of photoinduced electron transfer

For photoinduced *electron transfer* between an acceptor (A) and a donor (D) (either one of them may be the *electronically excited* molecular entity) of any charge type,  $z(A)$  and  $z(D)$ , the change in standard Gibbs energy can be approximated as (the notation is for the case of neutral species D and A)

$$\Delta_{\text{ET}}G^{\circ} = N_{\text{A}} \{ e [ E^{\circ}(\text{D}^{+\bullet}/\text{D}) - E^{\circ}(\text{A}/\text{A}^{-\bullet}) ] + w(\text{D}^{+\bullet}\text{A}^{-\bullet}) - w(\text{DA}) \} - \Delta E_{0,0}$$

where  $e = 1.602\,176\,53 \times 10^{-19}$  C is the elementary charge,  $N_{\text{A}} = 6.022\,1415 \times 10^{23}$  mol<sup>-1</sup> is the Avogadro constant,  $E^{\circ}(\text{D}^{+\bullet}/\text{D})/\text{V}$  is the standard electrode potential of the donor cation radical resulting from the electron transfer,  $E^{\circ}(\text{A}/\text{A}^{-\bullet})/\text{V}$  is the standard electrode potential of the acceptor (both relative to the same reference electrode) and  $\Delta E_{0,0}/\text{J mol}^{-1}$  is the vibrational zero electronic energy of the excited partner (provided that a vibrationally equilibrated excited state at energy  $E_{0,0}$  takes part in the reaction), all data referring to the same solvent.

$w(\text{D}^{+\bullet}\text{A}^{-\bullet})$  and  $w(\text{DA})$  are the electrostatic work terms that account for the effect of Coulombic attraction in the products and reactants, respectively

$$w(\text{D}^{+\bullet}\text{A}^{-\bullet}) / \text{J} = z(\text{D}^{+\bullet}) z(\text{A}^{-\bullet}) e^2 / (4 \pi \epsilon_0 \epsilon_{\text{r}} a)$$

$$w(\text{DA}) / \text{J} = z(\text{D}) z(\text{A}) e^2 / (4 \pi \epsilon_0 \epsilon_{\text{r}} a)$$

where  $a$  is the distance of the charged species after electron transfer,  $\epsilon_{\text{r}}$  is the relative medium static

permittivity (formerly called dielectric constant),  $\varepsilon_0 \approx 8.854 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$  is the electric constant (vacuum permittivity), and  $z_X$  the charge of the species X.

In SI units the factor  $e^2/(4 \pi \varepsilon_0) = 2.307 \times 10^{-28} \text{ J m}$ . For the case of neutral species A and D,  $z(\text{A}) = z(\text{D}) = 0$ .

Note 1: Several approximations are in use for the calculation of the term  $w(\text{D}^+\text{A}^-)$ , depending on the nature of the species formed such as *contact* or *solvent-separated radical ion pairs* or extended and/or linked D and A molecular entities. In the latter case, the stabilization of a dipole  $\mu$  in a cavity of radius  $\rho$  could be an appropriate model [62] and

$$w(\text{D}^+\text{A}^-) = [N_A (\mu^2) / (4 \pi \varepsilon_0 \rho^3)] [(\varepsilon_r - 1) / (2\varepsilon_r + 1)]$$

Note 2: In the above definitions, the IUPAC recommendations for the sign and symbols of standard potentials are used. Although not complying with the IUPAC recommended nomenclature for the standard electrode potentials, traditionally the equation has been written as:

$$\Delta_{\text{ET}}G^0 = N_A \{e (E_{\text{ox}}^0 - E_{\text{red}}^0) + [z(\text{A}) - z(\text{D}) - 1] e^2/(4 \pi \varepsilon_0 \varepsilon_r a)\} - \Delta E_{0,0}$$

with  $E_{\text{ox}}^0$  the standard electrode potential at which the oxidation occurs, and  $E_{\text{red}}^0$  the standard electrode potential at which the reduction occurs. This form of the first term within the brackets is misleading and not recommended.

Note 3: The standard emfs of oxidation and reduction are often called, respectively, “oxidation” and “reduction potential”. These terms are intrinsically confusing and should be avoided altogether, because they conflate the chemical concept of reaction with the physical concept of electrical potential.

Note 4: The equation used for the calculation of the Gibbs energy of photoinduced electron-transfer processes should not be called the *Rehm-Weller equation*.

Related terms: *driving force*, *polar driving force*.

For a list of electrode potentials see [63].

See [22].

revG2

**global analysis**

Method for kinetic analysis of time-resolved *emission* or *absorption* data.

Note: Typical for the analysis of emission (or transient absorption) data. Upon excitation with a particular *wavelength*, *radiant intensity* of the emission (or *transient absorbance* difference) decays are observed as a function of a variable parameter, e.g., the observation wavelength, but otherwise under the same condition. All decays are then analysed together (globally) under the constraint that the *lifetimes* of the transient species do not vary with the variable parameter, e.g., the observation wavelength in the given example. Lifetime-associated spectra (LAS), also called decay-associated spectra (DAS), are thus obtained. In the case of transient absorption data, the resulting spectra are often called lifetime-associated difference spectra (LADS),

See [50, 59, 64, 65].

**ground state**

Lowest energy state of a chemical entity.

Note: In *photochemistry* ground electronic state is usually meant.

G2

**half-life,  $T_{1/2}$ , of a photochromic system**

Time necessary for thermal bleaching to half of the *absorbance* of the coloured form of a *photochromic* compound at a specific *wavelength* during one cycle.

See [3].

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

Time needed for a concentration of the entity to decrease to  $\frac{1}{2}$  of its original value.

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

Full width of a spectral band at a height equal to half of the height at the band maximum. Also known as full width at half maximum (*FWHM*). The dimension of bandwidth should be either

inverse length (*wavenumbers*) or inverse time (*frequencies*) so that the values give an indication of the energies.

Note 1: the hyphen in half-width. Half bandwidth has the meaning of half-width at half maximum.

Note 2: Used widely to specify half-width of transmission bands of optical filters.

G2/GB

### **halogen lamp**

See *quartz-iodine lamp*.

### **Hammond-Herkstroeter plot**

See *energy transfer plot*.

Note: Several authors used similar representations. Therefore, it is not recommended to give an author's name to these plots.

See [52, 66].

revG2

### **harmonic frequency generation**

Production of *coherent radiation* of frequency  $k \nu$  ( $k = 2, 3, \dots$ ) from coherent radiation of frequency  $\nu$ . In general, this effect is obtained through the interaction of *laser ultraviolet, visible or infrared* radiation with a suitable optical medium with non-linear polarizability.

Note: The case  $k = 2$  is referred to as frequency doubling,  $k = 3$  is frequency tripling,  $k = 4$  is frequency quadrupling. Even higher integer values of  $k$  are possible.

See *non-linear optical techniques*, [47].

G2/GB

### **harpoon mechanism**

Reaction sequence (thermal or photoinduced) between neutral molecular or atomic entities in which

long-range *electron transfer* or proton transfer takes place by way of a number of intervening species.

Note: During electron transfer between neutral entities, the process is followed by a considerable reduction of the distance between donor and acceptor sites as a result of the electrostatic attraction in the *ion pair* created.

revG2

### **heavy-atom effect**

Enhancement of the rate of a spin-forbidden process by the presence of an atom of high-atomic number that is either part of, or external to, the excited molecular entity.

Note: Mechanistically, it corresponds to a *spin-orbit coupling* enhancement produced by a heavy atom.

See [23].

G2/GB

### **heliochromism**

Applied to *photochromic* compounds possessing a high efficiency for colouring with near-*ultraviolet* radiation and a low efficiency for *bleaching* with *visible* radiation, but a moderate efficiency for thermal fading at ambient temperature. These compounds are activated by unfiltered sunlight and deactivated under diffuse daylight conditions, therefore being suitable for sun-lens applications.

See [3].

### **helium-cadmium laser**

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

See *gas lasers*.

G2/GB

**helium-neon laser**

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

See *gas lasers*.

G2/GB

**Herkstroeter plot**

See *energy transfer plot, triplet-triplet energy transfer*.

Note: Several authors used similar representations. Therefore, it is not recommended to give an author's name to these plots.

revG2

**heteroexcimer**

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

revG2

**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 and 1400 nm with noticeable peaks.

See *lamp*, [2].

revG2

**hole burning**

*Photobleaching* of a feature, normally over a narrow spectral range, within an inhomogeneously-broadened *absorption* or *emission* band. The holes are produced by irradiation with a narrow-bandwidth light source causing the disappearance of resonantly excited absorbers as a result of *photophysical* or *photochemical* processes.

Note 1: A *pump-probe technique* where the pump-pulse has narrow bandwidth and thus is very long.

Note 2: Hole burning is a *non-linear spectroscopic technique* related to the third order *polarization* and the corresponding “hyper-susceptibility” [7], because it requires the creation of an excited state from which a photophysical or photochemical process displaces the excited molecules from the absorption profile (formally a two-field interaction related to the *radiant power*) plus a third field to probe the change in the ground-state population.

Note 3: The resulting spectroscopic technique is known as a site-selection spectroscopy.

See [47, 67].

revG2

### **hole transfer**

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

G2/GB

### **hot ground-state reaction**

*Hot-state reaction of a ground electronic state.*

G2/GB

### **hot quartz lamp**

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

See [15].

G2/GB

### **hot-state reaction**

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

surrounding medium.

G2/GB

### **hula-twist mechanism**

Mechanism of *photoisomerization* of conjugated systems involving simultaneous configurational and conformational isomerization, e.g., the photoinitiated concerted rotation of two adjacent double and single bonds.

See [68].

### **Hund rules**

- (1) Of the different multiplets resulting from different *configurations* of electrons in degenerate *orbitals* of an atom, those configurations with greatest *multiplicity* have the lowest energy (multiplicity rule).
- (2) Among multiplets having the same multiplicity, the lowest-energy one is that with the largest total orbital angular momentum (angular momentum rule) (valid if the total orbital angular momentum is a constant of motion).
- (3) In configurations containing shells less than half full of electrons, the term having the lowest total angular momentum  $J$  lies lowest in energy, whereas in those with shells more than half filled, the term having the largest value of  $J$  lies lowest (fine structure rule).

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

G2/GB

### **Hush model**

Theory describing an optically-induced *electron-transfer* process.

Related term: *Marcus-Hush relationship*.

See [69, 70].

revG2

**hyperchromic effect**

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

Related term: *auxochrome*.

G2/GB

**hyperfine (interaction)**

Interaction between the electron spin  $S$  and the nuclear spin  $I$ .

See [6].

revG2

**hypochromic effect**

Opposite to *hyperchromic effect*.

G2/GB

**hypsochromic shift**

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

G2/GB

**IC**

Frequently used acronym for *internal conversion*.

**ICT**

Acronym for *intramolecular charge transfer*.

See *planar intramolecular charge transfer (PICT)*, *twisted intramolecular charge transfer (TICT)*, [72, 73].

**ICT emission**

Electronic *emission* from an *ICT* state.

Related term: *intramolecular charge transfer*.

**imaging (photoimaging)**

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

revG2

**incoherent radiation**

Same as *non-coherent radiation*; not having the properties of *coherent radiation*.

G2/GB

**infrared**

Region of the electromagnetic spectrum extending from 780 nm to about 20 000 nm .

According to the CIE (Commission internationale de L'éclairage), the range between 780 nm and 1 mm is subdivided into [9]:

IR-A 780 - 1400 nm

IR-B 1.4 - 3  $\mu\text{m}$

IR-C 3  $\mu\text{m}$  - 1 mm

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

**inner-filter effect**

This term is used in two different ways:

(I) 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 reabsorption of emitted radiation (particularly severe for emitters with small *Stokes shift*).

(II) 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.

See *radiative energy transfer*.

See [71].

revG2

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

Historically, an *electron transfer* between two metal centres sharing a ligand or atom in their respective coordination shells.

Note: The definition has more recently been extended to any situation in which the interaction between the donor and acceptor centres in the transition state is significant ( $> 20 \text{ kJ mol}^{-1}$ ).

Compare with *outer-sphere electron transfer*.

See [22].

G2/GB

### **integrating sphere**

A 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.

G2/GB

### **intended crossing (of potential energy surfaces)**

Same as *avoided crossing*.

Note: "Intended" should not be used in this context since it is an anthropomorphic term.

G2/GB

### **intensity**

Traditional term indiscriminately used for *photon flux*, *fluence rate*, *irradiance* or *radiant power*. In

terms of an object exposed to radiation, the term should now be used only for qualitative descriptions.

See [9].

G2/GB

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

Same as *radiant intensity*.

G2

**intensity (of a spectral feature)**

Describes the magnitude of the particular feature in the spectrum.

G2

**interference filter**

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

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

See *filter*.

revG2

**interferometer**

See *Fourier-transform spectrometer*.

G2/GB

**internal conversion, (IC)**

A *photophysical process*. Isoenergetic (also called horizontal) *radiationless transition* between two electronic states of the same *multiplicity*.

Note: When the transition results in a vibrationally excited molecular entity in the lower electronic state, this usually undergoes *deactivation* to its lowest vibrational level.

G2/GB

**internal transmittance**

See *transmittance*.

G2/GB

**intersection space**

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

See [35].

**intersystem crossing, (ISC)**

*Photophysical process*. Isoenergetic (also called horizontal) *radiationless transition* between two electronic states having different *multiplicities*. It often results in a vibrationally excited molecular entity in the lower electronic state, which then usually undergoes *radiationless deactivation* to its lowest vibrational level.

See [23, 50, 51].

G2/GB

**intervalence charge transfer**

*Electron transfer* (thermal or photoinduced) between two metal sites differing only in oxidation state. Quite often such electron transfer reverses the oxidation states of the sites.

Note: The term is frequently extended to the case of *metal-to-metal charge transfer* between non-equivalent metal centres.

G2/GB

**intimate ion pair**

Same as *contact ion pair*, which is the preferred term

revG2

**intramolecular charge transfer, (ICT)**

A process that changes the overall charge distribution in a molecule.

Note: For intramolecular charge transfer in the *excited state*, several models are discussed in the literature that are based on the molecular structure of the final state reached upon photoinduced ICT: *planar intramolecular charge transfer (PICT)* or *twisted intramolecular charge transfer (TICT)*. For example, an ICT has been proposed to be responsible for the strongly *Stokes-shifted* additional fluorescence band in fluorescent molecules with two fluorescence bands (*dual fluorescent molecules*).

See [72, 73].

**inverted region (for electron transfer)**

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

Note: 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 ( $\Delta_{\text{ET}}G^{\circ}$ ). It should be noted that experimentally such a decrease in rate is not always observed and, even when it is, a more elaborate theory is required to quantify the actual behaviour in this region.

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

Compare with *normal region*.

See *Gibbs energy of photoinduced electron transfer*, [22, 81].

G2/GB

**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. SI unit is  $\text{W m}^{-2}$ .

Note 1: 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 2: Mathematical definition:  $E = dP/dS$ . If the radiant power is constant over the surface area considered,  $E = P/S$ .

Note 3: 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 4:  $E = \int_{\lambda} E_{\lambda} \, d\lambda$ , where  $E_{\lambda}$  is the *spectral irradiance* at wavelength  $\lambda$ .

Related term: *photon irradiance*.

See [9].

revG2

## ISC

Frequently used acronym for *intersystem crossing*.

## isoabsorption point

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

G2/GB

## isoclinic point

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

G2/GB

**isoemissive point**

*Wavelength, wavenumber or frequency* at which the total *intensity* of *emission* of light by a sample does not change during a chemical reaction or physical change. The terms *isolampsic* and *isostilbic* are sometimes used.

Note: This term may be misleading because it does not specifically refer to light emission.

revG2

**isolampsic point**

Same as *isoemissive point*.

Note: The term derives from the Greek words isos: equal and lampein: to emit light or to shine. Isolampsic is thus parallel to *isosbestic*.

revG2

**iso-optoacoustic point**

*Wavelength, wavenumber or frequency* at which the total energy emitted by a sample as heat does not change upon a chemical reaction in or a physical change of the sample. Its position depends on the experimental conditions.

Note: The spectral differences between the *isosbestic* points and the iso-optoacoustic points are the result of the non-linear relationship between the *molar absorption coefficient* and the *photoacoustic* signal.

See *photoacoustic spectroscopy*, [18].

G2/GB

**isosbestic point**

*Wavelength, wavenumber or frequency* at which the total *absorbance* of a sample does not change

during a chemical reaction or a physical change of the sample.

Note 1: A simple example occurs when one molecular entity is converted into another that has the same *molar absorption coefficient* at a given wavelength. As long as the sum of the concentrations of the two molecular entities in the solution is held constant there will be no change in *absorbance* at this wavelength as the ratio of the concentrations of the two entities is varied.

Note 2: The name derives from the Greek words: isos: equal, the same and sbestos: extinguishable.

Note 3: Contrary to a widely accepted idea, the existence of an isosbestic point does not prove that the reaction is a quantitative conversion of one species into a unique other species or that an equilibrium exists between only two species. The observation of isosbestic points only indicates that the stoichiometry of the reaction remains unchanged during the chemical reaction or the physical change of the sample, and that no secondary reactions occur during the considered time range, since  $A_\lambda l^{-1} = \sum_{i=1}^n \varepsilon_i(\lambda) c_i$  is invariant ( $A_\lambda$  is the *absorbance* at wavelength  $\lambda$ ,  $l$  is the optical path,  $\varepsilon_i$  is the *molar decadic absorption coefficient* of the species  $i$  of concentration  $c_i$ ). For the reaction  $A + B \rightarrow c C + d D + e E$ , with  $c$ ,  $d$ , and  $e$  the percentages of the products C, D, and E, an isosbestic point will be observed at every wavelength where the condition  $\varepsilon_A + \varepsilon_B = c \varepsilon_C + d \varepsilon_D + e \varepsilon_E$ , provided that the values of the percentages  $c$ ,  $d$ , and  $e$  remain constant during the chemical reaction or the physical change. The use of the obsolete term isoabsorption point is not recommended.

revG2

### **isostilbic point**

Same as *isoemissive point*.

Note: From the Greek words: isos: equal and stilbein: to shine.

revG2

### **Jablonski diagram**

Originally, a diagram showing that the *fluorescent* state of a molecular entity is the lowest *excited*

*state* from which the transition to the *ground state* is allowed, whereas the *phosphorescent state* is a metastable state below the fluorescent state that is reached by *radiationless transition*. In the most typical cases the fluorescent state is the lowest *singlet* excited state, the phosphorescent state is the lowest *triplet* state and the ground state is a singlet.

Note: The original Jablonski diagram did not assign a different *multiplicity* to the phosphorescent state. At present, modified Jablonski diagrams are frequently used and are actually state diagrams in which molecular electronic states, represented by horizontal lines displaced vertically to indicate relative energies, are grouped according to *multiplicity* into horizontally displaced columns. Excitation and *relaxation* processes that interconvert states are indicated in the diagram by arrows. *Radiative transitions* are generally indicated with straight arrows ( $\rightarrow$ ), while *radiationless transitions* are generally indicated with wavy arrows () .

See [74].

G2/GB

### **Jahn-Teller effect**

Molecular distortions due to an electronically degenerate *ground state*. For non-linear molecular entities in a geometry described by a point symmetry group possessing degenerate irreducible representations there always exists at least one non-totally symmetric vibration that makes electronically degenerate states unstable at this geometry. The nuclei are displaced to new equilibrium positions of lower symmetry causing a splitting of the originally degenerate states (first order Jahn-Teller effect).

Note: Effect due to the odd terms in the vibronic perturbation expansion. In the case of molecules with a non-degenerate *ground electronic state* but with a low-lying degenerate *excited state*, distortions of proper symmetry arise that result in mixing of the ground and excited states, thereby lowering the ground-state energy (pseudo Jahn-Teller effect). The pseudo Jahn-Teller effect manifests itself in fluxional behaviour (see *fluxional molecules*) and stereochemical non-rigidity of molecules and ions. The Jahn-Teller effect generates a *surface crossing* (e.g., a *conical intersection*) whereas a pseudo Jahn-Teller effect generates an *avoided crossing*.

Related terms: *Renner-Teller effect*, *vibronic coupling*.

See [6].

revG2

### **Kaptein-Closs rules**

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

See [75].

G2/GB

### **Kasha rule**

Polyatomic molecular entities luminesce with appreciable yield only from the lowest *excited state* of a given *multiplicity*. There are exceptions to this rule.

Note: The concept has been extended to the reaction of excited species, i.e., polyatomic molecular entities react with appreciable yield only from the lowest excited state of a given multiplicity.

See [76].

revG2

### **Kasha-Vavilov rule**

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

See [77].

G2/GB

### **Koopmans' theorem**

See *photoelectron spectroscopy*, [23].

G2/GB

### **krypton ion laser**

A *CW* or pulsed *laser* emitting lines from 337 to 859 nm from singly ionized krypton. Principal *emissions* are at 530.9, 568.2, 647.1 and 752.5 nm.

See *gas lasers*.

G2/GB

### LADS

Acronym for lifetime-associated difference spectra.

See *global analysis*.

### Lambert-Beer law

See *Beer-Lambert law*.

### Lambert law

The fraction of *ultraviolet, visible or infrared* radiation absorbed by a system is independent of the incident *spectral radiant power*  $P_{\lambda}^0$ .

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

See *absorbance, Beer-Lambert law*.

G2/GB

### lamp

Source of *incoherent* radiation.

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

See [2, 15].

G2/GB

### Landau-Zener model

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

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

where  $\varepsilon_{12}$  is the potential energy gap between the two electronic states at a *surface crossing* point,  $|s_1 - s_2|$  is the difference in slopes between the intersecting *potential energy* curves at this point and  $\nu$  is the nuclear relative velocity with which the system passes the point of closest approach.

Note: The original formalism only considered states of the same spin multiplicity.

See [6].

### Laporte rule

For monophotonic *radiative* transitions, the only non-vanishing electric *transition (dipole) moments* are those that connect an even term with an odd term with respect to parity.

See [78].

G2/GB

### LAS

Acronym for lifetime-associated spectra.

See *global analysis*.

### laser

Source of *ultraviolet, visible* or *infrared* radiation that produces light amplification by stimulated emission of radiation from which the acronym is derived. All lasers contain an energized substance that can increase the intensity of radiation passing through it. The amplifying medium may be a solid, a liquid or a gas. The radiation emitted is *coherent* except for *superradiance* emission.

See *argon ion-, helium-cadmium-, chemical-, CO<sub>2</sub>-, copper vapour-, diode-, dye-, excimer-, free-electron-, free-running-, gas-, helium-neon-, krypton ion-, mode-locked-, neodymium-, nitrogen-, Q-switched-, solid-state- ruby laser*.

Related term: *lasing*.

See [17].

G2/GB

**laser diode**

Same as *diode laser*.

**laser dye**

Organic dyes typically used dissolved in an organic solvent. The dye solution is circulated continuously through the laser chamber of the *dye laser*, in which it is excited (pumped) by flash lamps or by another *laser*.

**laser-jet photochemical technique**

A technique by which high concentrations of *excited states* are generated in a jet, permitting the readily determination of spectroscopic properties of those states.

See [79].

**lasing**

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

G2/GB

**latent image**

Primary result of radiation *absorption* in a *photo-imaging* system susceptible to development.

G2/GB

**LED**

Acronym for *light-emitting diode*.

**lifetime,  $\tau$** 

The 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.,  $c(t = \tau) = c(t = 0)/e$ .

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 1: 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 2: 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 3: 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,  $\tau_{1/2} = \ln 2 \tau$ .

revG2

#### **lifetime-associated difference spectra, (LADS)**

See *global analysis*.

#### **lifetime-associated spectra, (LAS)**

See *global analysis*.

#### **ligand-field splitting**

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

See *crystal-field splitting*.

G2/GB

#### **ligand-to-ligand charge-transfer (LLCT) transition**

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

G2/GB

**ligand-to-metal charge-transfer (LMCT) transition**

Electronic transition in a metal complex that corresponds to excitation populating an electronic state in which considerable displacement of electronic density through partial *electron transfer* from a ligand to a metal centre has occurred.

Compare with *metal-to-ligand charge-transfer transition*.

G2/GB

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

Semiconductor (often a combination of gallium, arsenic and phosphorous or gallium and nitrogen) containing an *n* region (where electrons are more numerous than positive charges) separated from a *p* region (where positive charges are more numerous than negative charges). Upon application of a voltage, charges move and *emission* of *ultraviolet*, *visible* or *infrared* radiation is produced each time a *charge recombination* takes place. Although a LED emits non-*coherent* monochromatic light, normally a very narrow *frequency* range is obtained.

Note 1: This effect is a form of *electroluminescence*.

Note 2: The colour depends on the semiconducting material used, and can be ultraviolet, visible or infrared.

Note 3: Organic light-emitting devices (OLEDs) contain diodes made of small molecules or made of polymeric materials. The latter are sometimes called PLEDs.

**light polarization**

A light beam is said to be linearly polarized if the end point of the electric vector moves in a straight line when viewed along the direction of propagation of the beam. If it moves along a circle the beam is circularly polarized and if it moves along an ellipse the beam is elliptically polarized.

Note: Circular polarization is said to be right-handed if the direction of rotation is clockwise when viewed against the direction of propagation and left-handed if the sense of the rotation is opposite. When the position of the endpoint of the electric vector is viewed at a given time *t* as a function of

distance along  $x$ , it forms a left-handed helix if the light polarization is left-handed and a right-handed helix if it is right-handed.

Related terms: *dichroism, emission anisotropy, linear dichroism, magic angle.*

See [50, 51].

revG2

### **light source**

See *lamp, laser.*

G2/GB

### **linear dichroism**

The linear dichroism (LD) of a uniaxial sample with sample axis  $Z$  is defined as:

$$\Delta A_l = A_Z - A_Y$$

where  $A_Z$  and  $A_Y$  are the *absorption spectra* measured with the electric vector of linearly polarized light along and perpendicular to the sample axis, respectively. For an isotropic sample  $\Delta A_l = 0$ .

Note 1: Sometimes the reduced dichroism is used instead. It is defined as

$$\Delta A_r = (A_Z - A_Y) / (A_Z + 2A_Y) = (A_Z - A_Y) / 3A_{\text{iso}}$$

with  $A_{\text{iso}}$  the isotropic *absorbance*. Thus,  $\Delta A_r$  is analogous to *emission anisotropy* and the denominator in the eq. corresponds to three times the absorbance measured in a similar but isotropic sample.

Note 2: The dichroic ratio  $d(\lambda)$  is also a frequently used function of the wavelength. It is defined as:

$$d(\lambda) = A_Z / A_Y$$

Note 3: Most naturally-occurring solid samples exhibit linear dichroism. It may also be produced in the laboratory by dissolving the sample molecules in anisotropic solvents such as nematic liquid crystals or stretched polymers. This procedure tends to produce *uniaxial* samples. Also crystals may

be used as aligned solvents and if the sample forms suitable crystals by itself these may be used directly. Other alignment techniques include application of electric or magnetic fields.

Note 4: *Photoselection* is a commonly used technique for the production of aligned samples; both the photoselected subset and the set of remaining molecules may be studied.

See *emission anisotropy, light polarization, photoselection, transition(dipole) moment*, [50, 51].

### Lippert equation

See *Lippert-Mataga equation*.

### Lippert-Mataga equation

Correlation of the *Stokes-shift*,  $\Delta\tilde{\nu}$ , between the *absorption* and *emission* maxima, and the orientation polarizability  $f(\epsilon_r, n)$  of the solvent,

$$\Delta\tilde{\nu} = 2 \frac{(\mu_{\text{exc}} - \mu_{\text{gr}})^2}{c h r^3} f(\epsilon_r, n) + \text{const.}$$

with  $\mu_{\text{exc}}$  and  $\mu_{\text{gr}}$  the *excited-* and *ground-state* dipole moments of the dissolved molecule, respectively,  $c$  the speed of light,  $h$  the Planck constant,  $r$  the radius of the cavity in which the solute resides and  $\epsilon_r$  the “relative static permittivity” (formerly called dielectric constant). The expression of the Stokes shift depends only on the absolute magnitude of the difference between dipole moments and not on the angle between the dipoles. The above equation is sometimes called the Lippert equation.

The orientation polarizability is given by

$$f(\epsilon_r, n) = \frac{(\epsilon_r - 1)}{(2\epsilon_r + 1)} - \frac{(n^2 - 1)}{(2n^2 + 1)}$$

with  $\epsilon_r$  the relative static permittivity and  $n$  the refractive index of the solvent,  $f(\epsilon_r, n)$  ranges from 0.001 in cyclohexane to 0.320 in water.

Note 1:  $\Delta\tilde{\nu}$  as a function of  $f(\epsilon_r, n)$  (Lippert plot), is used to determine the difference in dipole moment ( $\mu_{\text{exc}} - \mu_{\text{gr}}$ ) between a molecule in the equilibrated excited state and in the ground state, as a measure of the change in charge distribution brought about by light absorption. In this method it is assumed that the dipole moments do not depend on solvent polarity. A linear variation is not always observed because only dipole-dipole interactions are taken into account and the solute polarizability is neglected.

Note 2: The assumptions made in theories of solvatochromic shifts, together with the uncertainty over the size and shape of the cavity radius  $r$ , explain the inaccuracies in the determined excited-state dipole moments.

See [50, 80].

### **Lippert plot**

See *Lippert-Mataga equation*.

### **localized exciton**

See *exciton*.

### **local volumetric rate of photon absorption**

Same as *absorbed photon flux density*.

### **Lorentzian band shape**

Band shape described by the *frequency* distribution function:

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

where  $\nu_0$  is the mean band position,  $\gamma$  is the half *bandwidth* at half maximum.

Related term: *Gaussian band shape*.

G2/GB

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

*Resonance* lamp that contains mercury vapour at pressures of about 0.1 Pa ( $0.75 \times 10^{-3}$  Torr; 1 Torr = 133.3 Pa). At 25 °C, such a lamp emits mainly at 253.7 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).

See *lamp* [2, 15].

revG2

### **luminescence**

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

Related terms: *bioluminescence*, *chemiluminescence*, *electro-generated chemiluminescence*, *fluorescence*, *phosphorescence*, *photoluminescence*, *radioluminescence*, *sonoluminescence*, *thermoluminescence*, *triboluminescence*.

See [50].

G2/GB

### **luminescence anisotropy**

See *emission anisotropy*.

### **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. Analogous to *chromophore* for absorption spectra.

revG2

### **magic angle**

Upon excitation of an “isotropic” sample (assuming an ultrashort excitation pulse) the relationship between the *fluorescence* intensity detected at a time  $t$  and through a polarization analyser oriented at an angle  $\beta$  with respect to the electric *polarization* of the exciting beam is given by

$$I(t, \beta) \propto N(t) [1 + (3 \cos^2 \beta - 1) R(t)]$$

where  $R(t)$  is the degree of alignment of the emitting transition dipole in the laboratory frame and  $N(t)$  is the excited-state population, both at time  $t$ . For  $\beta = 54.7^\circ$  (the magic angle), the dipole-alignment contribution vanishes and  $I(t, \beta = 54.7^\circ) \propto N(t)$ .

Note 1: This concept also applies for time-resolved absorption measurements in cases in which *photoselection* occurs because the detected species do not freely rotate fast enough to make the measurement isotropic within the time of the experiment.

Note 2: Applies for steady-state measurements on fixed samples. In this case

$$I(\beta) \propto N [1 + (3 \cos^2 \beta - 1) R]$$

with  $I(\beta)$  the intensity of the effect observed at an analyser angle  $\beta$  with respect to the electric *polarization* of the exciting beam,  $N$  the excited-state population at steady-state equilibrium and  $R$  the degree of alignment of the *transition (dipole) moment* of the excited molecular entity.

Note 3: The term magic angle is also used in NMR spectroscopy.

See *light polarization*, [50, 51].

### **magnetic circular dichroism, (MCD)**

Magnetic circular dichroism is observed when a sample differentially absorbs left- and right-circularly polarized light in a magnetic field parallel to the light beam.

Note 1: The MCD signal,  $\Delta$ , is calculated as

$$\Delta = \frac{[\alpha(\lambda)^- - \alpha(\lambda)^+]}{[\alpha(\lambda)^- + \alpha(\lambda)^+]}$$

with  $\alpha(\lambda)^+$  and  $\alpha(\lambda)^-$  the *absorption coefficients* for right and left circularly polarized light, respectively. The spectra are a representation of  $\Delta$  vs. *wavelength*. Often,  $\Delta$  is recorded as a function of the applied field (up to 10 T) and the temperature.

Note 2: The phenomenon is related to “magnetically induced optical activity (Faraday effect)” by the “Kramers-Kronig transformations”, which connect optical refraction and absorption, i.e., MCD is observed in optically active materials at wavelengths with non-vanishing absorption. It occurs for diamagnetic, paramagnetic and (anti)-ferromagnetic material and has been observed from IR (infrared) to X-ray regions. MCD optical transitions in molecular species arise if (i) degenerate electronic states are split in the presence of a magnetic field (first-order-Zeeman effect) or (ii) states are mixed together by the applied magnetic field (second-order-Zeeman effect). This may occur in the initial or the final states.

Note 3: MCD is used as a probe of paramagnetism that permits the identification of the electronic and magnetic properties of the ground states of transition metal ion centres. The wavelength dependence of MCD can be used also to identify and assign optical transitions from metal ion sites.

Note 4: The technique is complementary to both EPR and electronic absorption spectroscopies in facilitating assignment of the ground-state spin and electronic transitions of a molecular entity.

See *light polarization*, [51].

### **Marcus equation (for electron transfer)**

Relation between the rate of *outer-sphere electron transfer* and the thermodynamics of this process [81]. Essentially, the rate constant within the *encounter complex* (or the rate constant of intramolecular transfer) is given by the Eyring equation:

$$k_{\text{ET}} = (\kappa_{\text{ET}} k T / h) \exp(-\Delta G^{\ddagger} / RT)$$

where  $k$  is the Boltzmann constant,  $h$  the Planck constant,  $R$  the gas constant and  $\kappa_{\text{ET}}$  the so-called electronic transmission factor ( $\kappa_{\text{ET}} \sim 1$  for *adiabatic* and  $\ll 1$  for *diabatic electron transfer*). For *outer-sphere electron transfer* the barrier height can be expressed as:

$$\Delta G^{\ddagger} = (\lambda + \Delta_{\text{ET}}G^0)^2 / 4\lambda$$

where  $\Delta_{\text{ET}}G^0$  is the standard Gibbs energy change accompanying the electron-transfer reaction and

$\lambda$  the total *reorganization energy*.

Note: 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.

See *Gibbs energy of photoinduced electron transfer*, [22, 23, 81].

revG2

### **Marcus-Hush relationship**

Relationship between the barrier ( $\Delta G^\ddagger$ ) to thermal *electron transfer*, the energy of a corresponding optical *charge-transfer transition* ( $\Delta E_{\text{op}}$ ), and the overall change in standard Gibbs energy accompanying thermal electron transfer ( $\Delta G^0$ ). Assuming a quadratic relation between the energy of the system and its distortions from equilibrium (harmonic oscillator model) the expression obtained is:

$$\Delta G^\ddagger = \Delta E_{\text{op}}^2 / 4(\Delta E_{\text{op}} - \Delta G^0)$$

The simplest form of this expression yields for degenerate electron transfer ( $\Delta G^0 = 0$ ) in, e.g., symmetrical mixed-valence systems:

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

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

See *Gibbs energy of photoinduced electron transfer, Hush model, Marcus equation*, [70].

revG2

### **Marcus inverted region (for electron transfer)**

See *inverted region*, [81].

G2/GB

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

*Non-coherent* radiation source containing mercury vapour at pressures ranging from 50 to several hundred kPa (1 atm = 101.325 kPa). 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.

Related term: *high-pressure mercury lamp*.

See *lamp* [2, 15].

revG2

**mercury-xenon lamp (arc)**

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

See *lamp* [2, 15].

G2/GB

**MERP**

Acronym for *minimum-energy reaction path*.

**merry-go-round reactor (turntable reactor)**

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

G2/GB

**metal-to-ligand charge-transfer (MLCT) transition**

Electronic transition of a metal complex corresponding to excitation populating an electronic state in which considerable displacement of electronic density through partial *electron transfer* from the metal to a ligand has occurred.

Compare with *ligand-to-metal charge-transfer transition*.

G2/GB

**metal-to-metal charge-transfer (MMCT) transition**

Electronic transition of a binuclear or polynuclear metal complex corresponding to excitation populating an electronic state in which considerable displacement of electronic density through partial *electron transfer* between two metal centres has occurred.

Related term: *intervalence charge transfer*.

G2/GB

**meta-photocycloaddition**

See *aromatic photocycloaddition*, [25, 82].

**MERP**

Acronym for *minimum-energy reaction path*.

**minimum-energy reaction path, (MERP)**

Path orthogonal to the equipotential contours of a *potential energy surface* that connects the energy minima through a saddle point (transition state) from which it slopes downwards along the steepest descending lines in  $3N - 6$  configurational space ( $N$  is the number of nuclei in the reacting system).

Note: MERP calculation allows the investigation of detailed changes in molecular structure describing the transformation of reactants to products.

See [6].

**MLCT**

Acronym for *metal-to-ligand charge transfer*.

**MMCT**

Acronym for *metal-to-metal charge transfer*.

**mode-locked laser**

*Laser* in which many resonant modes are coupled in phase to yield a train of very short pulses (e.g., fs or ps pulses).

Note: The coupling of the modes is obtained by modulation of the gain in the resonator and can be active (electro-optic modulation of the losses or of the pump intensity) or passive (with a saturable absorber).

Related term: *free-running laser*.

See *mode locking* in [17].

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

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

$$\varepsilon(\lambda) = \left( \frac{1}{c l} \right) \lg \left( \frac{P_{\lambda}^0}{P_{\lambda}} \right) = \frac{A(\lambda)}{c l}$$

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

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

Note 2: In common usage for  $l/\text{cm}$  and  $c/\text{mol dm}^{-3}$  (M),  $\varepsilon(\lambda)$  results in  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$  ( $\text{M}^{-1} \text{cm}^{-1}$ , the most commonly used unit), which equals  $0.1 \text{ m}^2 \text{mol}^{-1}$  (coherent SI units).

See *absorbance, absorption coefficient, Beer-Lambert law*, [7].

revG2

### **molecular alignment**

See *linear dichroism*.

### **molecular orientation**

The *absorption probability* (referred to electric dipolar absorption) for a molecular transition with its electric *transition(dipole) moment* at an angle  $\theta$  with the electric vector of the light is proportional to  $\cos^2 \theta$ . For the whole sample it is proportional to the *orientation factor*  $K_{\theta} = \langle \cos^2 \theta \rangle$ , averaged over all sample molecules. This average is 1 for a sample with all transition moments perfectly aligned along the electric vector of the light, 1/3 for an isotropic sample and 0 for a sample where all transition moments are perpendicular to the electric vector.

Note 1: The directional cosines provide, especially for *uniaxial* samples, a simple description of exactly those orientation properties of the sample that are relevant for light absorption. With the principal coordinate system  $(x, y, z)$ , forming angles  $\theta = \alpha, \beta, \gamma$  with the light electric vector in the  $z$  direction, all orientation effects induced by light absorption are contained in  $K_{\theta\theta} = K_{\theta}$ . Since the sum of  $K_{\theta}$  for 3 perpendicular molecular axes is equal to 1, only two independent parameters are required to describe the orientation effects on light absorption.

Note 2: A related, commonly used description is based on diagonalized Saupe matrices:

$$S_{\theta} = (3 K_{\theta} - 1) / 2$$

The principal (molecular) coordinate system  $(x, y, z)$  forming angles  $\theta = \alpha, \beta, \gamma$  with the light electric vector should be chosen such that the matrix  $K$  and the tensor  $S_{\theta}$  are diagonal.

To describe processes involving 2 or more photons, such as luminescence of a uniaxial, aligned sample, an expansion of the directional cosines to the fourth power is required.

Note 3: Order parameters (related to Wigner matrices) are an alternative to the directional cosine-based description of molecular alignment. Order-parameter methods also work well for non-uniaxial samples and provide a seemingly more complex, but in other ways convenient, description of molecular orientation distributions. Wigner matrices are used as a basis set for an expansion of the orientation-distribution function.

See [50, 51].

### **monochromator**

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

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

### **MRCI**

Acronym for *multireference configuration interaction*.

**multiconfiguration SCF (MCSCF) method**

*Configuration-interaction* method in which simultaneous optimization of both the shapes of molecular orbitals and contributions from different electronic configurations is carried out by using the variational method.

Note: The MCSCF method with a large enough set of configurations allows a better estimation of the non-dynamic correlation energy than the conventional CIS, CID, and CISD methods.

See [6].

**multiphoton absorption**

See *multiphoton process*.

Related term: *biphotonic excitation*.

G2/GB

**multiphoton process**

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

See *biphotonic process*, *two-photon process*, [47].

G2/GB

**multiplicity (spin multiplicity)**

Number of possible orientations, calculated as  $2S + 1$ , of the spin angular momentum corresponding to a given total spin quantum number ( $S$ ), for the same spatial electronic wavefunction. A state of *singlet* multiplicity has  $S = 0$  and  $2S + 1 = 1$ . A *doublet* state has  $S = \frac{1}{2}$ ,  $2S + 1 = 2$ , etc.

Note: for  $S > L$  (the total orbital angular-momentum quantum number) there are only  $2L + 1$  orientations of total angular momentum possible.

See [6].

G2

**multireference configuration interaction, (MRCI)**

*Configuration-interaction* method in which the configurations are built by excitation out of a wavefunction obtained by using, e.g., the *multiconfiguration SCF* method.

Note: One of the methods to account for dynamic correlation.

See *configuration interaction, multiconfiguration SCF method*, [6].

**natural lifetime**

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

G2/GB

**neodymium laser**

*CW* or pulsed *laser* emitting radiation from excited  $\text{Nd}^{3+}$  principally occurring around 1.06  $\mu\text{m}$  (the precise position depends on the matrix).

Note:  $\text{Nd}^{3+}$  is present as a dopant in suitable crystals (e.g., yttrium-aluminium garnet, YAG) or in suitable glasses (phosphate, silicate, etc.).

See *solid-state lasers*, [17].

G2/GB

**neutral-density filter**

See *attenuance filter*.

G2/GB

**nitrogen laser**

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

See *gas lasers*.

G2/GB

**non-adiabatic electron transfer**

See *diabatic electron transfer*. Use of double negative is discouraged.

**non-adiabatic photoreaction**

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

Compare with *adiabatic photoreaction*.

G2

**non-coherent radiation**

Not having the properties of *coherent radiation*.

**non-crossing rule**

Electronic states of the same symmetry cannot cross along a reaction coordinate.

Note: The rule only applies to diatomic molecules and not to polyatomic molecules.

See *conical intersection*, [6, 23, 35].

**non-linear optical effect**

Effect brought about by electromagnetic radiation the magnitude of which is not linearly proportional to the *irradiance*.

Note: Non-linear optical effects of importance in photochemistry are *harmonic frequency generation*, *lasers*, *pump-probe* spectroscopy, Raman shifting, *upconversion*, and others.

See [47].

revG2

**non-linear optical techniques**

Collective name applied to techniques related to *non-linear optical effects*.

Note 1: Some of these spectroscopies are four-wave mixing, *hole burning*, *photon echoes*, time-

resolved coherent anti-Stokes Raman (CARS), transient grating and stimulated pumping. These techniques differ in the nature of the pulse sequence, the geometry and the choice of a spatial direction (phase matching), as well as the mode of detection.

Note 2: Low order non-linear techniques, such as three-wave mixing, are related to the second order *polarization*. For a random isotropic medium with inversion symmetry, the second-order polarization vanishes and then the lowest order optical non-linear techniques, as well as the higher order non-linear techniques are related to the third-order polarization and the corresponding “hyper-susceptibility”.

See [47].

### **non-radiative decay**

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

Same as *radiationless deactivation (decay)*.

revG2

### **non-vertical energy transfer**

*Energy transfer* process with a low *Franck-Condon factor* because the nuclear geometries of the minima on the ground- and excited-state *potential energy surfaces* of the donor or of the acceptor are strongly displaced.

Note: A Franck-Condon transition is always vertical. Thus, it is not strictly correct to speak about non-vertical transition. However, the term implies that the projection of all the vibrational wave functions of the donor state onto all the vibrational functions of the acceptor will result in low Franck-Condon factors.

See *Franck-Condon principle*, [23, 51].

revG2

### **normal region (for electron transfer)**

Region for which the rate constants increase with increasing exergonicity of the reaction in plots relating rate constants for *electron transfer*, or quantities related to it, with the standard Gibbs

energy for the reaction ( $\Delta_{\text{ET}}G^{\circ}$ ). This region is predicted by the Marcus theory for *outer-sphere electron transfer* for the case of  $-\Delta_{\text{ET}}G^{\circ} \leq \lambda$  in the *Marcus equation*.

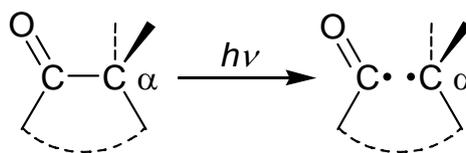
See *Gibbs energy of photoinduced electron transfer*, [22].

revG2

### Norrish Type I photoreaction

$\alpha$ -Cleavage of an excited carbonyl compound leading to an acyl-alkyl *radical pair* (from an acyclic carbonyl compound) or an acyl-alkyl *diradical* (from a cyclic carbonyl compound) as a *primary photoproduct*.

Note 1: An example is:



Note 2: *Decarbonylation* of the primary diradical formed from cyclic carbonyl compounds and subsequent recombination of the biradical afford very interesting cyclic compounds, e.g., [83].

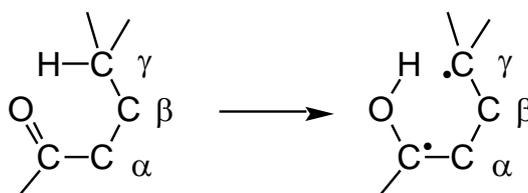
See *Norrish Type II reaction*, *Norrish-Yang reaction*, *Yang photocyclization*, [84, 85].

revG2

### Norrish Type II photoreaction

Intramolecular abstraction of a  $\gamma$ -hydrogen by an excited carbonyl compound to produce a 1,4-*diradical* as a *primary photoproduct*.

Note: An example is:

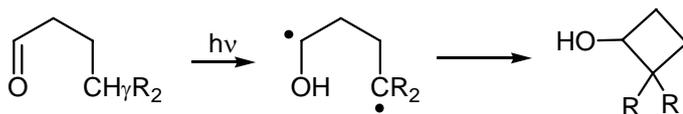


See *Norrish Type I reaction*, *Norrish-Yang reaction*, *Yang photocyclization*, [84].

revG2

**Norrish-Yang reaction**

*Photochemical process* leading to the formation of cyclobutanols from excited carbonyl compounds by intramolecular  $\gamma$ -hydrogen abstraction (*Norrish Type II reaction*) and subsequent 1,4-diradical combination.



See *Norrish Type I, Yang photocyclization*.

See [86, 87, 88].

**nucleophilic photosubstitution**

*Photosubstitution* with the participation of nucleophiles.

See *photostimulated unimolecular radical nucleophilic substitution*.

See, e.g., [89, 90].

 **$n \rightarrow \pi^*$  transition**

Electronic transition described approximately as promotion of an electron from a “non-bonding” (lone-pair)  $n$  orbital to an “antibonding”  $\pi$  orbital designated as  $\pi^*$ .

G2/GB

 **$n-\pi^*$  state**

*Excited state* related to the *ground state* by an  $n \rightarrow \pi^*$  transition.

G2/GB

 **$n \rightarrow \sigma^*$  transition**

Electronic transition described approximately as promotion of an electron from a “non-bonding” (lone-pair)  $n$  orbital to an “antibonding”  $\sigma$  orbital designated as  $\sigma^*$ .

Note: These transitions generally involve high transition energies and appear close to or mixed with *Rydberg transitions*.

G2/GB

### **ODMR**

Acronym for *optically detected magnetic resonance*.

revG2

### **OLED**

Acronym for *organic light-emitting device*.

### **OMA**

Acronym for *optical multichannel analyser*.

### **one-photon photochromism**

*Photochromic* process involving a *one-photon* mechanism. In this case, the photoproduct B is formed from the *singlet* or from the *triplet* state of the thermodynamically stable molecular entity A.

Related term: *two-photon photochromism*.

See [19].

### **OPA**

Acronym for *optical parametric amplifier*.

See *optical parametric amplification*.

### **OPO**

Acronym for *optical parametric oscillator*.

### **optical density**

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

G2/GB

**optical multichannel analyser, (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 “charge-coupled device” or a “silicon photodiode array”.

See [91].

**optical parametric amplification**

Process of signal amplification by a *parametric process* and a pump wave.

**optical parametric oscillator, (OPO)**

Light source similar to a *laser*, but based on “non-linear optical gain” from *parametric amplification* rather than on *stimulated emission*.

Note 1: 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: For example, for  $\lambda_p = 355$  nm ( $3^{\text{rd}}$  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: This “splitting of one photon into two photons” is the reverse of the “sum frequency mixing” used, for instance, to generate the  $3^{\text{rd}}$  harmonic of a laser emission by mixing in a convenient crystal the fundamental and the frequency doubled beams (a way to get the  $3^{\text{rd}}$  harmonic much more efficiently than by pure frequency tripling as described under *harmonic frequency generation*).

Related term: *non-linear optical effect*.

See [92].

### **optical parametric processes**

See *parametric processes*.

### **optically detected magnetic resonance, (ODMR)**

Double *resonance* technique in which transitions between spin sublevels are detected by optical means. Usually these are sublevels of a *triplet* and the transitions are induced by microwaves.

Note: For different types of optical detection (as explained) the following expressions are used: ADMR (*absorption*), DEDMR (*delayed emission*, non-specified), DFDMR (*delayed fluorescence*), FDMR (*fluorescence*), PDMR (*phosphorescence*). If a reaction yield is monitored the expression RYDMR (reaction-yield-detected magnetic resonance) is used.

See [51].

### **optoacoustic spectroscopy**

Same as *photoacoustic spectroscopy*.

Note: 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.

See [18].

revG2

### **orbital (atomic or molecular)**

Wavefunction depending explicitly on the spatial coordinates of only one electron.

See [6].

G2/GB

**order parameters**

See *molecular orientation*.

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

See *light-emitting diode (LED)*.

**orientation factor**

See *Förster-resonance-energy transfer, molecular orientation*, [51].

**orientation polarizability**

See *Lippert-Mataga equation*.

**ortho-photocycloaddition**

See *aromatic photocycloaddition*, [24, 93, 94].

**oscillator strength,  $f$  value**

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

$$f_{ij} = \frac{8\pi^2 m c \tilde{\nu}}{3 e^2 h} G M_{ij}^2$$

where  $m$  is the mass of the electron,  $c$  is the velocity of light,  $\tilde{\nu}$  is the *wavenumber*,  $h$  is the Planck constant,  $G$  is the degeneracy of the final state.  $M_{ij}$  is the *transition (dipole) moment* and  $e$  is the elementary charge.  $f_{ij}$  is a dimensionless quantity.

Note 1: Experimentally,  $f_{ij}$  is determined by integration over the *absorption* bandwidth of the *molar decadic absorption coefficient*,  $\epsilon(\tilde{\nu})$  at *wavenumber*  $\tilde{\nu}$ , using the equation

$$f_{ij} = (k/n) \int_{\tilde{\nu}} \epsilon(\tilde{\nu}) d\tilde{\nu}$$

where  $n$  is the average refractive index of the medium.  $k = 4.32 \times 10^{-9} \text{ dm}^{-3} \text{ mol cm}$  [for  $\epsilon(\tilde{\nu})/\text{dm}^3$ ]

$\text{mol}^{-1} \text{cm}^{-1}$ ];  $k = 4.32 \times 10^{-8} \text{ mol m}^{-1}$  [for  $\epsilon(\tilde{\nu})/\text{m}^2 \text{mol}^{-1}$ ].

Note 2: The experimental equation (Note 1) takes into account line broadening effects.

Related term: *transition (dipole) moment*.

See [51].

revG2

### outer-sphere electron transfer

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

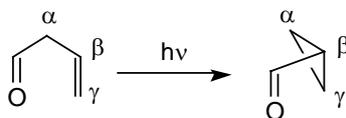
Compare with *inner-sphere electron transfer*.

See *Marcus equation*.

G2

### oxa-di- $\pi$ -methane rearrangement

*Photochemical reaction* of a  $\beta,\gamma$ -unsaturated aldehyde or ketone to form the corresponding saturated  $\alpha$ -cyclopropyl carbonyl compound. The rearrangement formally amounts to a 1,2- shift of the carbonyl group and “bond formation” between the former  $\alpha$  and  $\gamma$  carbon atoms.



Related terms: *aza-di- $\pi$ -methane rearrangement*, *di- $\pi$ -methane rearrangement*, *di- $\pi$ -silane rearrangement*.

See [31].

G2/GB

### PAL

Acronym for *photoaffinity labelling*.

**parametric amplification**

Amplification of a signal based on *parametric processes*.

**parametric processes**

Interaction of *photons* in a non-linear medium satisfying the energy and momentum conservation laws. During the interaction the photon frequencies are mixed and photon(s) with different frequencies are created.

Note: Optical parametric processes of three interacting beams, called *frequency* mixing processes, are: second-harmonic generation (SHG), sum-frequency generation (SFG), difference-frequency generation (DFG), optical parametric generation and amplification (OPG and OPA), and *optical parametric oscillation* (OPO).

See *non-linear optical effect*, [95].

**para-photocycloaddition**

See *aromatic photocycloaddition*, [24, 96].

**PAS**

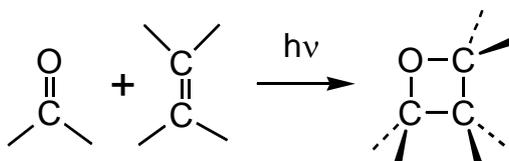
Acronym for *photoacoustic spectroscopy*.

Related term: *optoacoustic spectroscopy*.

See [18].

**Paternò-Büchi reaction**

*Photocycloaddition* of an electronically excited carbonyl group to a *ground-state* olefin yielding an oxetane.



See [97].

G2/GB

**PEC**Acronym for *photoelectrochemistry*.**PDMR**See *ODMR*.

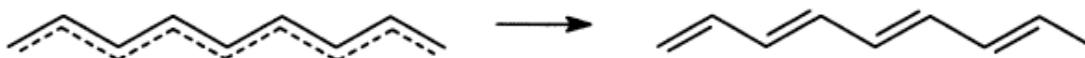
G2/GB

**Peierls distortion**

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

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

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



See [6].

**penetration depth**See *depth of penetration*.

G2/GB

**PES**Acronym for *photoelectron spectroscopy*.Same acronym often used for *potential energy surface*.

revG2

**PET**

Acronym for *photoinduced electron transfer*.

**phonon**

Elementary excitation in the quantum mechanical treatment of vibrations in a crystal lattice. An energy bundle that behaves as a particle of energy  $h\nu$ , with  $\nu$  the vibration frequency and  $h$  the Planck constant.

Note 1: A phonon can be considered as an acoustic mode of thermal vibration of a crystal lattice (or liquid helium II).

Note 2: Every harmonic vibration can be decomposed in phonons, which are the elementary vibrations. The total number of phonons in a system that has internal vibrations (e.g., a crystal) is related to the temperature of the system.

Note 3: The concept of phonons provides a simplification in the theories of thermal and electrical conduction in solids.

Note 4: For example, interactions between phonons and electrons are thought to be responsible for such phenomena as “superconductivity”.

Related term: *photon*.

revG2

**phosphorescence**

Phenomenologically, the term has been used to describe long-lived *luminescence*. In mechanistic photochemistry, the term designates luminescence involving change in spin *multiplicity*, typically from *triplet* to *singlet* or vice versa.

Note: For example, the luminescence from a *quartet state* to a *doublet state* is also phosphorescence.

See [50].

G2/GB

**phosphorescence anisotropy**

See *emission anisotropy*, *photoselection*, [51].

**phosphorescence lifetime**

Parameter describing the time evolution of the decay of the *phosphorescence radiant intensity*.

See *lifetime*, [50].

**photoacoustic effect**

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

See *photoacoustic spectroscopy*, [18].

G2/GB

**photoacoustic spectroscopy, (PAS)**

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

Related term: *iso-optoacoustic point*, *optoacoustic spectroscopy*.

See [18].

G2/GB

**photoaffinity labelling, (PAL)**

A technique by which a *photochemically* reactive molecular entity, specifically associated with a biomolecule, is photoexcited in order to covalently attach a label to the biomolecule, usually via intermediates. Identification of the resulting photo-crosslinked product provides structural information on the protein's binding site.

Note 1: This technique is widely used for identifying in general ligand-receptor interactions in biological macromolecules and in particular the binding site within proteins.

Note 2: Typical examples are nitrenes, carbenes, ketone *excited states*, cations and radicals; [98].

revG2

### **photo-assisted catalysis**

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

See *photocatalysis*.

G2/GB

### **photo-Bergman cyclization**

Intramolecular photoinduced cyclization of diynes leading to aromatic compounds.

Note: The solvent plays a key role in the reaction efficiency and product distribution.

See [99].

### **photobiology**

Branch of biology concerned with the biological and bioenvironmental effects of *ultraviolet*, *visible* or *infrared* radiation.

### **photocage**

See *caged compound*, *photoremovable protecting group*.

### **photocaged fluorescent molecules**

Caged *fluorophores* displaying a high fluorescent enhancement after *photolysis*.

See *caged compound*.

**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.

revG2

**photocatalyst**

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

**photochemical aromatic substitution**

Photoinduced substitution in an aromatic compound.

See also *photochemical electrophile-olefin combination, aromatic substitution (photo-EOCAS)*, *photochemical nucleophile-olefin combination, aromatic substitution (photo-NOCAS)*, *photostimulated unimolecular radical nucleophilic substitution, photosubstitution*, [100].

**photochemical electrophile-olefin combination, aromatic substitution, (photo-EOCAS)**

*Photosubstitution* in electron-rich aromatic compounds, upon reaction with electron-deficient olefins, occurring in polar solvents through an *electron transfer* pathway.

Note: In non-polar solvents the reaction follows a different course.

Related terms: *photo-NOCAS, photo-ROCAS*.

See [101].

**photochemical funnel**

Molecular structure where the *excited-state* reactant or intermediate is delivered to the *ground state* to initiate product formation.

Note: For a broad class of organic reactions, the structure of the funnel can take the form of a *conical intersection* or a *singlet-triplet crossing*.

See [6, 35].

**photochemical hole burning**

See *hole burning*.

G2/GB

**photochemical nitrogen extrusion**

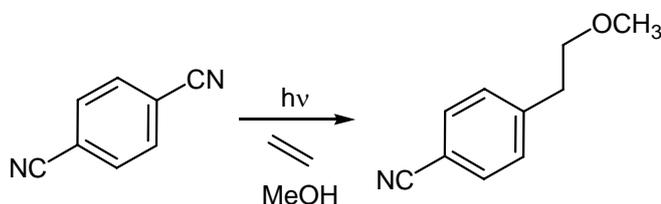
Photoinduced dinitrogen (N<sub>2</sub>) elimination.

Note: Typical examples are the photoinduced denitrogenation of azoalkanes, [102, 103].

**photochemical nucleophile-olefin combination, aromatic substitution, (photo-NOCAS)**

*Photoinduced electron transfer reaction* of an aromatic electron-acceptor in the presence of an olefinic electron donor and a nucleophile, leading to aromatic substitution.

Note: An example is:



Related terms: *photo-EOCAS*, *photo-ROCAS*.

See [104].

**photochemical radical-olefin combination, aromatic substitution, (photo-ROCAS)**

Regioselective combination of a radical, an olefin, and an arene via a *photoinduced electron transfer* pathway.

Related terms: *photo-EOCAS*., *photo-NOCAS*.

See [105, 106].

**photochemical reaction**

Term generally used to describe a chemical reaction caused by *absorption* of *ultraviolet*, *visible* or *infrared* radiation. There are many *ground-state* reactions, which have photochemical counterparts. Among these are *photochemical nitrogen extrusions*, *photocycloadditions*, *photodecarbonylations*, *photodecarboxylations*, *photoenolizations*, *photo-Fries rearrangement*, *photoisomerizations*, *photooxidations*, *photorearrangements*, *photoreductions*, *photosubstitutions*, etc.

Note 1: Photochemical paths offer the advantage over thermal methods of forming thermodynamically disfavoured products, overcome large activation barriers in a short period of time and allow reactivity otherwise inaccessible by thermal methods.

For a large collection on articles reviewing many photoinduced reactions see [107].

revG2

### **photochemical reaction path**

Sequence of geometries adopted by a molecule after initial electronic *excitation*, combined with a specification of the electronic state at each geometry, from radiation *absorption* to product formation. Theoretically, this usually involves the computation of the *MERP* connecting the *Franck-Condon* point, located on the *potential-energy surface* of the spectroscopic state, to the final photoproducts located on the *ground-state* potential energy surface. Experimentally, a photochemical reaction path can be probed by detecting transient species or reaction intermediates.

See [23, 35].

### **photochemical smog**

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

See [108].

revG2

### **photochemistry**

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

See *photochemical reaction*.

G2/GB

### **photochirogenesis**

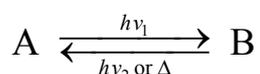
*Photochemical* induction of molecular chirality.

See also *asymmetric photochemistry*, [109, 110].

### **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. The spectral change produced is typically, but not necessarily, of *visible* colour 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).



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

Note: An important parameter is the “number of cycles” that a photochromic system can undergo under well-defined conditions (solution, matrix, concentration, temperature).

See *gated photochromism*, *half-life (of a photochromic system)*, *one-photon photochromism*, *two-photon photochromism*, [19].

revG2

### **photo-Claisen rearrangement**

Rearrangement closely related to the *photo-Fries rearrangement*; it is experienced by aryl ethers (instead of aryl esters) and follows an analogous mechanism.

See [111].

**photoconductivity**

Increase in electrical conductivity resulting from photoproduction of charge carriers.

G2/GB

**photocrosslinking**

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

G2/GB

**photocuring**

Technical expression for the photoinduced hardening of a monomeric, oligomeric or polymeric substrate normally in the form of a film. Also called *UV* curing.

revG2

**photocurrent yield**

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

G2/GB

**photocyclization**

Intramolecular photochemical process leading to carbo- or heterocyclic ring systems by formation of one new single bond, either by a concerted process (e.g., *electrocyclization*) or by multi-step processes such as *Norrish-Yang reaction*, *photoinduced electron transfer* processes, *Yang photocyclization* and others.

See [112].

**photocycloaddition**

Intermolecular *photochemical process* leading to carbo- or heterocyclic ring systems by formation of two new single bonds, either by a concerted process (e.g., a concerted addition) or by multi-step processes (e.g., the *Paternò Büchi reaction*).

Note: *Triplet* state photocycloadditions are two-step processes involving the formation of *diradical* intermediates.

See *aromatic photocycloaddition, de Mayo reaction*.

See, e.g., [113, 114].

**photocycloaddition (aromatic)**

See *aromatic photocycloaddition*.

**photodecarbonylation**

Photoinduced extrusion of carbon monoxide (CO).

Note 1: Typical example is the *Norrish Type I process*, in which, after production of the *diradical* upon photoinduced  $\alpha$ -cleavage, CO is eliminated. This reaction has been widely exploited for the production of radicals in crystals [115], as well as for the synthesis of cyclic compounds [83].

Note 2: Another example is the photodecarbonylation of alpha-aryl aldehydes [116].

**photodecarboxylation**

Photoinduced extrusion of carbon dioxide (CO<sub>2</sub>).

Note: Typical examples are the CO<sub>2</sub> photodetachment upon excitation of anti-inflammatory 2-arylpropionic acids, such as ketoprofen [117].

**photodeconjugation**

Photoinduced reaction of conjugated compounds (e.g., enones and carboxylic acid derivatives) leading to loss of conjugation.

Note: This reaction has important synthetic applications for the synthesis of frameworks of numerous natural products, such as  $\beta,\gamma$ -unsaturated carboxylic acids from photoirradiation of  $\alpha,\beta$ -unsaturated carboxylic acid derivatives, excluding the use of strong bases, as required for similar isomerizations performed in the *ground state*.

See [118].

### **photodegradation**

Photochemical transformation of a molecule into lower molecular weight fragments, usually in an oxidation process.

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

revG2

### **photodetachment (of electrons)**

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

G2/GB

### **photodynamic effect**

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

Note: Molecularly, it is the sensitized *photooxidation* involving dioxygen molecules.

revG2

### **photoelectric effect**

Ejection of an electron from a solid or a liquid by a *photon*.

See [119].

revG2

**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. Usually at least one of the electrodes is a semiconductor.

G2/GB

**photoelectrochemical etching**

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

Note: Method used in the photopatterning of semiconductor surfaces.

G2/GB

**photoelectrochemistry, (PEC)**

Hybrid field of chemistry employing techniques, which combine photochemical and electrochemical methods for the study of the oxidation-reduction chemistry of the *ground* or *excited states* of molecules or ions. In general, it is the chemistry resulting from the interaction of *ultraviolet*, *visible* or *infrared* radiation with electrochemical systems.

Related terms: *photoelectrochemical*, *photogalvanic*, *photovoltaic cell*.

See [120].

G2/GB

**photoelectron spectroscopy, (PES)**

Spectroscopic technique to measure the kinetic energy of electrons emitted upon the ionization of a substance by high-energy monochromatic *photons*.

Note 1: A photoelectron spectrum is a plot of the number of electrons emitted versus their kinetic energy. The spectrum consists of bands due to transitions from the *ground state* of an atom or

molecular entity to the ground and *excited states* of the corresponding oxidized atom or molecular entity.

Note 2: Approximate interpretations are usually based on *Koopmans' theorem* relating ionization potentials to orbital energies. *UPS* (ultra-violet photoelectron spectroscopy) is the spectroscopy using vacuum ultraviolet sources, while *ESCA* (electron spectroscopy for chemical analysis) and *XPS* use X-ray sources.

For a photoelectron spectroscopy database see [121].

See [122].

G2/GB

### **photoelectron spectrum**

See *photoelectron spectroscopy*.

### **photoenolization**

A special case of *phototautomerization*.

### **photo-EOCAS**

Acronym for *photochemical electrophile-olefin combination, aromatic substitution*.

Related terms: *photo-NOCAS, photo-ROCAS*.

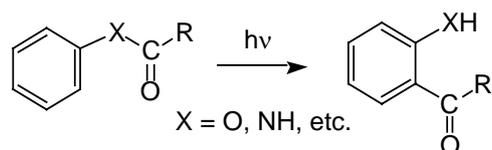
### **photoexcitation**

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

G2/GB

### **photo-Fries rearrangement**

Photorearrangement of O-acyl phenols or N-acyl anilines to give the [1,3]-rearranged product (as well as the [1,5]-rearranged product).



See also *photo-Claisen rearrangement*.

See [111] and, e.g., [123].

revG2

### photogalvanic cell

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

Compare with *photovoltaic cell*.

G2/GB

### photohydration

*Photochemical process* leading to the addition of water across a C-C double (or triple) bond or to a carbonyl (or carbonyl analogue) group.

### photoimaging

See *imaging*.

G2/GB

### photoinduced electron transfer, (PET)

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

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

Related terms: *driving force*, *Gibbs energy of photoinduced electron transfer*, *Marcus equation*, *polar driving force*, *reorganization energy*, *Weller correlation*.

See [22].

revG2

**photoinduced polymerization**

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

See *photoinitiation*, [124].

G2/GB

**photoinitiation**

Photoproduction of a free radical or ion capable of initiating a chain reaction such as polymerisation, halogenation, nitrosylation and others.

See *photoinduced polymerization*.

revG2

**photoionization**

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

Related term: *photodetachment*.

G2

**photoisomerization**

*Photochemical process* leading to an isomerization of the substrate, either by bond rotation, skeletal rearrangement or group transfer.

Note 1: Typical examples are *cis-trans photoisomerization of alkenes* [125] and *phototautomerization*.

Note 2: Photochemical pathways have the advantage over thermal and catalytic methods of giving isomer mixtures (*photostationary states*) rich in thermodynamically unstable isomers.

Note 3: Photoisomerization is the *primary photochemical reaction* of the *chromophore* in several biological photoreceptors such as retinal proteins (e.g., rhodopsin [126]), phytochromes [127], and the photoactive yellow protein [128].

See *hula-twist*.

**photoluminescence**

*Luminescence* arising from direct photoexcitation of the emitting species.

Related terms: *fluorescence*, *phosphorescence*.

See [50].

revG2

**photolysis**

Bond cleavage induced by *ultraviolet*, *visible* or *infrared* radiation.

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

See *flash photolysis*.

G2/GB

**photon**

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

G2/GB

**photon counting**

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

Note 1: 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.

(1) Note 2: 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.

See *time-correlated single-photon counting*.

revG2

### **photon echo**

Time-resolved optical spectroscopy in which the inhomogeneous broadening of absorbers is eliminated by the proper choice of geometry in a four-wave mixing experiment.

Note 1: Term applied to a group of *non-linear optical techniques* such as integrated echo, time-gated echo, three-pulse echo peak shift, heterodyne-detected echo and 2D-echo.

Note 2: Photon echo techniques make use of the third-order optical *polarization* and “hyper-susceptibility”. The main distinguishing feature of photon echo methods from all other third-order processes is the time ordering of the field interactions that leads to a rephasing process in the induced polarization to remove inhomogeneous contributions to the absorption linewidth.

Note 3: In terms of mathematical description, the photon echo is equal to the spin echo (solid-state physics) from which a term “echo” was borrowed.

Note 4: Technique used, e.g., to probe solvation dynamics upon (ultra-short) pulse excitation of a *chromophore*.

See [47].

### **photon emittance**

See *photon exitance*.

G2/GB

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

*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. SI unit is  $s^{-1} m^{-2}$ .

Note 1: Mathematical definition:  $dq_p/dS$ . If  $q_p$  is constant over the surface area considered,  $M_p = q_p/S$ . Also called specific photon emission.

Note 2: Formerly called photon emittance.

Note 3: 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  $\text{mol s}^{-1} \text{m}^{-2}$ ; common unit is  $\text{einstein s}^{-1} \text{m}^{-2}$ .

Related term: *radiant exitance*.

See *spectral photon exitance*, [8, 9].

revG2

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

*Photon irradiance,  $E_p$* , integrated over the time of irradiation for a beam incident from all upward directions. SI unit is  $\text{m}^{-2}$ .

Note 1: 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 2: 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 3: 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  $\text{mol m}^{-2}$ ; common unit is  $\text{einstein m}^{-2}$ .

Related terms: *fluence, radiant exposure*.

See [9].

revG2

### **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. *Photons* per surface area (quanta  $\text{m}^{-2}$ ). SI unit is  $\text{m}^{-2}$ .

Note 1: Mathematical definition:  $H_{\text{p},0} = F_{\text{p},0} = \text{d}N_{\text{p}}/\text{d}S = \int_t E_{\text{p},0} \text{d}t$ , with  $E_{\text{p},0}$  the *photon fluence rate*, integrated over the duration of the irradiation,  $t$ . If  $E_{\text{p},0}$  is constant over the time interval,  $H_{\text{p},0} = F_{\text{p},0} = E_{\text{p},0} t$ .

Note 2: This quantity can be used on a chemical amount basis by dividing  $H_{\text{p},0}$  by the Avogadro constant, the symbol then being  $H_{\text{n,p},0}$ , the name “photon fluence, amount basis”, SI unit is  $\text{mol m}^{-2}$ ; common unit is einstein  $\text{m}^{-2}$ .

Related term: *fluence*.

See [9].

revG2

### **photon fluence rate, $E_{\text{p},0}$**

Rate of *photon fluence*. Total number of photons ( $N_{\text{p}}$ ) incident from all directions on a small sphere divided by the cross-sectional area of the sphere and per time interval. SI unit is  $\text{m}^{-2} \text{s}^{-1}$ .

Note 1: Mathematical definition:  $E_{\text{p},0} = \text{d}N_{\text{p}}/(\text{d}t \text{d}S) = \text{d}H_{\text{p},0}/\text{d}t$ . If  $N_{\text{p}}$  is constant over the time interval and the surface,  $E_{\text{p},0} = N_{\text{p}} / t S$ .

Note 2: It reduces to *photon irradiance*  $E_{\text{p}}$  for a parallel and normally incident beam not scattered or reflected by the target or its surroundings.

Note 3: This quantity can be used on a chemical amount basis by dividing  $E_{\text{p},0}$  by the Avogadro constant, the symbol then being  $E_{\text{n,p},0}$ , the name “photon fluence rate, amount basis”, SI unit is  $\text{mol m}^{-2} \text{s}^{-1}$ ; common unit is einstein  $\text{m}^{-2} \text{s}^{-1}$ .

Related term: *fluence rate*.

See *photon radiance*, [9].

revG2

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

Number of *photons* (quanta of radiation,  $N_p$ ) per time interval. SI unit is  $s^{-1}$ .

Note 1: Mathematical definition:  $q_p = dN_p/dt$ . If the number of photons is constant over the time interval,  $q_p = N_p/t$ .

Note 2: 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  $\text{einstein s}^{-1}$ .

Note 3: Although the symbol recommended by CEI is  $\Phi_p$  [9], the symbol  $q_p$  is preferred since in photochemistry  $\Phi$  is reserved for *quantum yield*.

Note 4: This term is as defined in [8]. It is a term not in accordance with the usual definition of flux as given in [7].

Related term: *radiant power*.

See *spectral photon flux*, [9].

revG2

**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. SI unit is  $\text{m}^{-2} \text{s}^{-1}$ .

Note 1: Mathematical definition:  $E_p = dq_p/dS$ . If the photon flux is constant over the surface considered,  $E_p = q_p/S$ .

Note 2: 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 3: 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  $\text{einstein m}^{-2} \text{s}^{-1}$ .

Related term: *irradiance*.

See *spectral photon irradiance*, [9].

revG2

### **photon number, $N_p$**

Total number of photons calculated as  $N_p = n_p N_A$  with  $n_p$  the amount of photons in *einsteins* and  $N_A$  the Avogadro constant.

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

### **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: Mathematical definition [7]:

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

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

Note 2: 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 3: 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  $\text{einstein m}^{-2} \text{s}^{-1} \text{sr}^{-1}$ . For a parallel beam SI unit is  $\text{mol m}^{-2} \text{s}^{-1}$  and common unit is  $\text{einstein m}^{-2} \text{s}^{-1}$ .

Related term: *radiance*.

See *spectral photon radiance*, [9].

revG2

### **photo-NOCAS**

Abbreviation for *photochemical nucleophile-olefin combination, aromatic substitution*.

Related terms: *photo-EOCAS*, *photo-ROCAS*.

### **photooxidation**

Oxidation reactions induced by *ultraviolet*, *visible* or *infrared* radiation. Common processes are: (i) Loss of one or more electrons from a chemical species as a result of *photoexcitation* of that species; (ii) 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: Photoinduced reactions in which neither substrate nor dioxygen are *electronically excited* (i.e., *photosensitized* oxidations) are sometimes called photoinitiated oxidations.

Compare with *photoreduction*.

revG2

### **photooxygenation**

Photoinduced incorporation of molecular dioxygen into a molecular entity. There are two common mechanisms, depending on the primary interaction of the *photosensitizer*:

Type I: the photosensitizer reacts with the substrate or the solvent to produce radicals by hydrogen atom or electron abstraction or by other mechanism. These radicals then react with *triplet* dioxygen molecules to produce oxygenated products.

Type II: the photosensitizer reacts with ground-state molecular dioxygen producing *singlet molecular oxygen* by energy transfer (for many molecular species the efficiency of this process is controlled by the *spin-statistical factor*). Singlet molecular oxygen then reacts with the substrate

producing oxygenated products.

From the point of view of the partner reacting with the sensitizer, the mechanism involving the production of superoxide anion as the reactive species is also a Type II reaction, although it has occasionally been described as a Type I process in view of the fact that a radical species is formed.

Compare with *photooxidation*.

See [129].

revG2

### **photophysical processes**

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

G2/GB

### **photopolymerization**

Polymerization processes requiring a *photon* for the propagation step.

Related term: *photoinduced polymerization*.

G2/GB

### **photoreaction**

See *photochemical reaction*.

G2/GB

### **photorearrangement**

A *photoisomerization* involving changes in the arrangement of the atoms within the molecular species. It may lead to unstable isomers that react further by, e.g., dehydrogenation, deprotonation, or other reactions.

Note: Examples are photorearrangements of alkenes (other than *cis-trans photoisomerization*)

[130], of cyclohex-2-enones [131], of endoperoxides [132], of thioarenes [133], the *di- $\pi$ -methane rearrangement* and others.

**photoreduction**

Reduction reactions induced by *ultraviolet*, *visible* or *infrared* radiation. Common processes are: (i) Addition of one or more electrons to a *photoexcited* species; (ii) Photochemical hydrogenation of a substance.

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

Compare with *photooxidation*.

G2/GB

**photorefractive effect**

Photoinduced change in refractive index.

Related term: *photothermal effect*.

See [18].

**photoremovable protecting group, (PPG)**

Release of a reactive species by *photolysis* of a molecular entity. The release may be induced by direct excitation, by *triplet sensitization*, or by *photoinduced electron transfer*.

Note 1: Photoremovable protecting groups have numerous applications in synthesis (orthogonal deprotection), biochip production, imaging, time-resolved X-ray crystallography, etc. When excited with pulsed lasers, photoremovable protecting groups that release bioactive molecular species such as neurotransmitters rapidly can provide spatial and temporal control of their concentration, so that physiological response times can be determined.

Note 2: Bioactive molecular species that are inactivated by a photoremovable protecting group are often called *caged compounds* or *photocages* (e.g., ATP).

See [36].

**photoresist**

*Photoimaging* material, generally applied as a thin film, whose particular properties (usually the

local solubility) can be altered *photochemically*. A subsequent development step produces an image useful for the fabrication of microelectronic devices.

Note: Examples are integrated circuits.

G2/GB

### **photo-ROCAS**

Acronym for *photochemical radical-olefin combination, aromatic substitution*.

Related terms: *photo-EOCAS, photo-NOCAS*.

### **photoselection**

Selection of an aligned subset of sample molecules by an exciting light beam. The selected subset will have an orientation distribution that is determined by the electric vector of the beam. If the beam is linearly polarized a *uniaxial* sample with a known orientation distribution will be produced. Also the set of remaining molecules will be aligned with a known orientation distribution (*residual anisotropy*).

See *emission anisotropy, linear dichroism*, [51].

### **photosensitization**

*Photochemical* or *photophysical* alteration occurring in one molecular entity as a result of initial *absorption* of radiation by another molecular entity called a *photosensitizer*.

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

See *energy transfer*.

G2/GB

### **photosensitizer**

See *photosensitization*.

G2/GB

**photostationary state**

Steady state reached by a chemical system undergoing *photochemical* reaction(s) when *ultraviolet*, *visible* or *infrared* radiation is absorbed by at least one of the components. At this state the rates of formation and disappearance are equal for each of the transient molecular entities formed.

revG2

**photostimulated unimolecular radical nucleophilic substitution, S<sub>RN</sub>1**

Nucleophilic substitution in a substrate through processes that involve *electron transfer* steps. The reaction occurs through chain steps. The most extensively used method of initiation is *photoinitiation*.

Note: Many types of compounds, i.e., aliphatic and aromatic species, such as perfluoroalkyl-, cycloalkyl-, neopentyl-, bridgehead-, and alkylmercury halides, as well as carbanions derived from various compounds, are substrates in S<sub>RN</sub>1 reactions.

Related term: *entrainment*.

See [134, 135].

**photosubstitution**

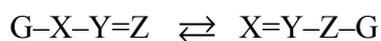
*Photochemical process* leading to a substitution reaction.

Note: Typical examples are photoinduced substitutions such as *free-radical photosubstitution*, *nucleophilic photosubstitution*, *photo-NOCAS*, *photostimulated unimolecular radical nucleophilic substitution*, photosubstitution of aromatic cations and anions. Another example is the photosubstitution of ligands in organometallic complexes.

See, e.g., [136].

**phototautomerization**

*Photoisomerization* of the general form



Note 1: The commonest case, when the  $G = H^+$ , is also known as “prototropy”.

Note 2: A typical example is a photoenolization.

See [20].

### **photothermal effect**

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

See [18].

revG2

### **photothermography**

Process utilizing both *ultraviolet*, *visible* or *infrared* radiation and heat, simultaneously or sequentially, for image recording.

G2/GB

### **photovoltaic cell**

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

Compare with *photogalvanic cell*.

See [137].

G2/GB

### **PICT**

Acronym for *planar intramolecular charge transfer*.

Related terms: *TICT*, *twisted intramolecular charge transfer*.

See [72, 73].

### **piezoluminescence**

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

See *triboluminescence*.

G2/GB

**planar intramolecular charge transfer, (PICT)**

In a PICT state formed by *intramolecular charge transfer* in an electron donor (D)/acceptor (A) molecule, the D and A subgroups have an overall planar configuration, with substantial electronic coupling of D and A.

Related terms: *TICT state*, *twisted intramolecular charge transfer*.

See [72, 73].

**PLED**

Acronym for polymer *light-emitting diode*.

See also *organic light-emitting device*.

**polar driving force**

The negative of the standard Gibbs energy change (i.e.,  $-\Delta G^{\circ}$ ) for *outer-sphere electron transfer* in polar solvents, where the electrostatic work terms in the expression used for the calculation of the *Gibbs energy of photoinduced electron transfer* are in general negligibly small.

Note: The work term might not be negligibly small even in polar solvents for electron transfer in large molecules undergoing a large change in dipole moment upon electron transfer.

Related term: *driving force*.

revG2

**polarization, *P***

The relevant material property that couples with the radiation field. May be called optical or dielectric polarization. Optical spectroscopies may be classified according to their power-law dependence on the external electric field.

Note 1: Mathematically it is defined as the electric dipole moment change per volume resulting from absorption of radiation of optical frequencies, defined as  $\mathbf{P} = \mathbf{D} - \varepsilon_0 \mathbf{E}$ , where  $\mathbf{D}$  is the electric displacement,  $\varepsilon_0$  the electric constant (vacuum permittivity), and  $\mathbf{E}$  the strength of the radiation electric field. A dielectric medium is characterized by the constitutive relation  $\mathbf{D} = \varepsilon_0 \chi^{(1)} \mathbf{E}$  where  $\chi^{(1)} = \varepsilon_r - 1$  is the linear “susceptibility” for a transparent singly refracting medium. Depending on the molecular or atomic restoring force on the electron with respect to the displacement  $\mathbf{D}$ , the field-induced motion of the electron can introduce other frequency components on the electron motion and this in turn leads to *non-linear optical effects*.

Note 2: The polarization component to the  $n$ th-order in the field is denoted as  $\mathbf{P}^{(n)}$ . Thus, the following equations apply,

$$\mathbf{P} = \mathbf{P}^{(1)} + \mathbf{P}_{\text{NL}} \quad \text{and} \quad \mathbf{P}_{\text{NL}} = \mathbf{P}^{(2)} + \mathbf{P}^{(3)} + \dots$$

$$\mathbf{P} = \varepsilon_0 [\chi_e^{(1)} \mathbf{E} + (1/2) \chi_e^{(2)} \mathbf{E}^2 + (1/6) \chi_e^{(3)} \mathbf{E}^3 + \dots] = \mathbf{P}^{(1)} + \mathbf{P}^{(2)} + \mathbf{P}^{(3)} + \dots$$

where  $\mathbf{E}^i$  is the  $i$ -th component of the electric field strength and  $\chi_e^{(n)}$  is the usual “susceptibility”  $\chi^{(1)} = \varepsilon_r - 1$  in the absence of higher terms and  $\mathbf{P}^{(n)}$  is the order of the field-induced polarization in the material.

In an anisotropic medium,  $\chi_e^{(1)}$ ,  $\chi_e^{(2)}$ , and  $\chi_e^{(3)}$  are the medium “hyper-susceptibilities” [7]; they are tensors of rank 2, 3, and 4, respectively.

Linear optical responses such as *absorption*, light propagation, reflection, and refraction, involving a weak incoming field, are related to  $\mathbf{P}^{(1)}$ . *Non-linear techniques* are connected to the non-linear polarization  $\mathbf{P}_{\text{NL}}$ . Low order non-linear techniques, such as three-wave mixing, are related to the second order *optical polarization*  $\mathbf{P}^{(2)}$ . For a random isotropic medium (such as a liquid) or for a crystal with a centrosymmetric unit cell,  $\chi_e^{(2)}$  is zero by symmetry and then the lowest order non-linear techniques, as well as the higher order, are related to the third-order optical polarization,  $\mathbf{P}^{(3)}$ , and the corresponding hyper-susceptibility.

See [47].

### **polarization (of electromagnetic radiation)**

Refers to the orientation of the electric field of the optical radiation, as used in *light polarization* and related terms (see *emission anisotropy*).

See [50, 51].

**polarization direction**

See *transition(dipole) moment*.

**polarization ratio**

See *emission anisotropy*.

**polarization spectroscopy**

In *absorption* experiments, polarization spectroscopy is performed with polarized light on anisotropic samples.

Note: Spectroscopy with natural (unpolarized) light on anisotropic samples will show directional effects, since the electric vectors of natural light are not isotropic, but are restricted to a plane perpendicular to the beam. In two-photon processes, for example *luminescence* measured with linear polarizers in both beams, an aligned sample is not required since it will be created by the exciting *photon* through *photoselection*. However, aligned samples allow a larger number of independent experiments to be recorded and thus contain more information.

See *emission anisotropy, light polarization, linear dichroism*, [51].

**polaron**

Lattice distortion or polarization caused by *photoexcitation*.

See *self-localized excitations*.

**population inversion**

A higher energy state is more populated than a lower energy state.

G2/GB

**potential energy surface**

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

Note: The acronym PES is often used.

See [6].

### **PPG**

Acronym for *photoremovable protecting group*.

### **precursor complex**

*Encounter complex* or *collision complex*, but implies that this complex undergoes a reaction (e.g., *electron transfer*).

G2/GB

### **predissociation**

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

See [6].

G2/GB

### **primary photochemical process (primary photoreaction)**

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

See *primary (photo)process*.

revG2

### **primary (photo)process**

See *primary photochemical process*.

Note: The term primary (photo)process for *photophysical processes* may lead to inconsistencies, and its use is discouraged.

G2/GB

**primary (photo)product**

First observable chemical entity produced in the *primary photochemical process* and that is chemically different from the reactant.

See *primary (photo)process*.

G2/GB

**pseudo Jahn-Teller effect**

Same as second order *Jahn-Teller effect*.

See [6].

**pulsed photoactivation**

See *flash photolysis*.

**pump-dump-probe technique**

Transient absorption spectroscopy using three pulses (a strong pump, a dump pulse that can alter the course of the reaction photoinduced by the first pulse and a weak probe). In general femtosecond *laser* pulses are used.

See *transient-stimulated emission pumping*.

**pump-probe technique**

Transient absorption spectroscopy using two pulses (strong pump and weak probe) and capable of achieving a high temporal resolution. A pump pulse excites the sample and triggers the process under investigation. A second delayed pulse, the probe, monitors an optical property. By varying the time delay between the pump and probe pulses, it is possible to assemble measurements as a function of time. The probe pulse is typically a *UV*, *visible* or *infrared* pulse in which case a snap-

shot spectrum is taken as a function of the delay time. Often the probe pulse is generated from a portion of the excitation beam, but it can also be an independently generated electromagnetic pulse.

Note: In the case of an optical probe, this interaction is formally a *non-linear optical process* that is third order in *polarization*. The excitation intensity to create the *excited state* constitutes a two field interaction and the determination of the change in the time-dependent optical properties involves a third field monitoring the induced time-dependent changes in the “linear susceptibility” [7].

Diffraction probes (e.g., electrons and X-rays) can also be used, in which case one measures a diffraction pattern as a function of time.

See *transient spectroscopy*, [47].

revG2

### **$\pi \rightarrow \pi^*$ transition**

Electronic transition described approximately as a promotion of an electron from a “bonding”  $\pi$  orbital to an “antibonding”  $\pi$  orbital designated as  $\pi^*$ .

G2/GB

### **$\pi$ - $\pi^*$ state**

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

G2/GB

### **$\pi \rightarrow \sigma^*$ transition**

Electronic transition described approximately as a promotion of an electron from a “bonding”  $\pi$  orbital to an “antibonding”  $\sigma$  orbital designated as  $\sigma^*$ .

Note: Transitions generally involving high transition energies and appear close to or mixed with *Rydberg transitions*.

G2

**QC/MM**

Acronym for *quantum chemical/molecular mechanics*, synonymous with *QC/MM*.

**QM/MM**

Acronym for *quantum mechanics/molecular mechanics*.

Note: *QC/MM* is sometimes used.

**Q-switched laser**

*Laser* in which the state of the device introducing important losses in the resonant cavity and preventing *lasing* operation is suddenly switched to a state where the device introduces very low losses. This increases rapidly the Quality factor of the cavity, allowing the build-up of a short and very intense laser pulse.

Note: Typical pulse durations are in the ns range. The Q-switching may be active (a rotating mirror or electro-optic device) or passive (a saturable absorber).

Related terms: *continuous wave laser*, *free-running laser*, [17].

G2/GB

**quantum (of radiation)**

Elementary particle of electromagnetic energy in the sense of the wave-particle duality.

See *photon*, [119, 138].

G2/GB

**quantum counter**

Device emitting with a *quantum yield* independent of the energy of excitation *photons* over a defined spectral range.

Note 1: An example is a concentrated rhodamine 6G solution between 300 and 600 nm.

Note 2: Also used in devices producing an electrical signal proportional to the *photon flux* absorbed in a medium.

See [21].

G2/GB

### quantum efficiency

See *efficiency*.

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

G2/GB

### quantum mechanics/molecular mechanics, (QM/MM)

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

Note: Sometimes called *QC/MM*.

### quantum yield, $\Phi$

Number of defined events occurring per *photon* absorbed by the system.

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), 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 1: When  $x$  in the equation for the differential quantum yield (see above) is either a number concentration, or an amount concentration, it is convenient to use in the denominator the *rate of absorbed photons per volume* (*absorbed photon flux density*) number basis, or amount basis, respectively.

Note 2:  $\Phi$  can be used for *photophysical processes* (such as, e.g., *intersystem crossing*, *fluorescence* and *phosphorescence*) or *photochemical reactions*.

Note 3: Strictly, the term quantum yield applies only for monochromatic excitation.

Related term: *efficiency*.

See [15, 50].

revG2/GB

### **quartet state**

State having a total electron spin quantum number  $S = 3/2$ .

See *multiplicity*.

rev G2

### **quartz-iodine lamp**

A wolfram (tungsten) filament high-intensity incandescent *lamp* containing iodine in a quartz envelope. Used primarily as a source of *visible* radiation.

Note 1: 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 life of the tungsten (wolfram)

filament and enables the lamp to produce more light per unit of input energy. Consequently, halogen lamps are used in a variety of applications, including automobile headlights.

Note 2: Other halogens may be used in these lamps.

See also *tungsten-lamp*, *wolfram-lamp*, [15].

### **quencher**

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

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

G2/GB

### **quenching**

*Deactivation* of an excited molecular entity intermolecularly by an external environmental influence (such as a *quencher*) or intramolecularly by a substituent through a *non-radiative process*.

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

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

See *Stern-Volmer kinetic relationships*, [50].

G2/GB

### **quenching constant**

See *Stern-Volmer kinetic relationships*.

Related terms: *quencher*, *quenching*.

G2

**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: Mathematical definition [7]:

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

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

Note 2: 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  $P$  is constant over the surface area considered,  $L = P/(S \cos \theta)$ . SI unit is  $\text{W m}^{-2}$ .

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

Related terms: *photon flux, photon radiance, spectral radiance, spherical radiance.*

See [9].

revG2

**radiant emittance**

See *radiant exitance*.

G2/GB

**radiant energy,  $Q$** 

Total energy emitted, transferred or received as radiation of all wavelengths in a defined period of time. SI unit is J.

Note 1: Mathematical definition:  $Q = \int_{\lambda} Q_{\lambda} d\lambda$ . If the *radiant power*  $P$  is constant over the time interval,  $Q = P t$ .

Related term: *spectral radiant power*.

See [9].

G2/GB

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

Same as *fluence*.

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

This obsolete term is not recommended.

In *photochemistry*, *radiant power*,  $P$  is adopted. SI unit is W.

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

Related terms: *photon flux*, *photon radiance*, *radiant energy*, *spectral radiant flux*.

See [8, 9].

revG2

**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. SI unit is  $\text{W m}^{-2}$ .

Note 1: Mathematical definition:  $M = dP/dS$ . If the radiant power  $P$  is constant over the surface area considered,  $M = P/S$ .

Note 2: 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 3: Same as *spherical radiant exitance*. Formerly called radiant emittance.

Related terms: *photon exitance*, *spectral radiant exitance*.

See [8, 9].

G2/GB

**radiant exposure,  $H$**

*Radiant energy,  $Q$* , incident from all upward directions on an small sphere divided by the cross-sectional area of that sphere. SI unit is  $\text{J m}^{-2}$ .

Equivalent definition: *Irradiance,  $E$* , integrated over the time of irradiation. SI unit is  $\text{J m}^{-2}$ .

Note 1: 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 2: This term refers to a beam not scattered or reflected by the target or its surroundings. For a beam incident from all directions *fluence* ( $H_0$ ,  $F_0$ ) is an equivalent term.

See [8, 9].

G2/GB

**radiant intensity,  $I$**

*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. SI unit is  $\text{W sr}^{-1}$ .

Note 1: Mathematical definition:  $I = dP/d\Omega$ . If the radiant power is constant over the solid angle considered,  $I = P/\Omega$ .

Note 2: Equivalent to  $I = \int_{\lambda} I_{\lambda} d\lambda$ , where  $I_{\lambda}$  is the *spectral radiant intensity* at wavelength  $\lambda$ .

Note 3: It is not recommended to abbreviate this term to just intensity because it is confusing.

Related term: *spectral radiant intensity*.

See [9].

G2/GB

**radiant power,  $P$**

Power emitted, transferred or received as radiation. SI unit is  $\text{J s}^{-1} = \text{W}$ .

Note 1: Mathematical definition:  $P = \text{d}Q/\text{d}t$ . If the radiant energy  $Q$  is constant over the time interval,  $P = Q/t$ .

Note 2: 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.

See *spectral radiant power*, [7].

revG2

**radiationless deactivation (decay)**

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

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

G2/GB

**radiationless transition**

Transition between two states of a molecular entity without *photon emission* or *absorption*.

Compare with *radiative transition*.

G2/GB

**radiation trapping**

Process by which the *resonance radiation* emitted in a *lamp* is absorbed and re-emitted many times in the plasma prior to striking the phosphor. This process is called radiation trapping or imprisonment.

Note: Radiation trapping lengthens the effective *lifetime* of *emission* as viewed from outside the lamp. The control of this trapping is, therefore, an important design consideration for low pressure lamps.

See [15].

### **radiative energy transfer**

Transfer of excitation energy by *radiative deactivation* of a donor molecular entity and reabsorption of the emitted radiation by an acceptor molecular entity. It is also called *trivial energy transfer*.

Note 1: Radiative transfer results in a decrease of the donor *fluorescence* intensity in the region of *spectral overlap*. Such a distortion of the fluorescence spectrum is called *inner-filter effect*.

Note 2: Radiative energy transfer depends on the shape and size of the vessel utilized and on the configuration of the latter with respect to excitation and observation.

Note 3: The fraction  $a$  of photons emitted by D and absorbed by A is given by

$$a = \frac{1}{\Phi_D^0} \int_{\lambda} I_{\lambda}^D(\lambda) \left[ 1 - 10^{-\varepsilon_A(\lambda)c_A l} \right] d\lambda$$

where  $c_A$  is the molar concentration of acceptor,  $\Phi_D^0$  is the fluorescence *quantum yield* in the absence of acceptor,  $l$  is the thickness of the sample,  $I_{\lambda}^D(\lambda)$  and  $\varepsilon_A(\lambda)$  are the *spectral distribution* of the *spectral radiant intensity* of the donor fluorescence and the *molar decadic absorption coefficient* of the acceptor, respectively, with the normalization condition  $\Phi_D^0 = \int_{\lambda} I_{\lambda}^D(\lambda) d\lambda$ .

For relatively low *absorbance*,  $a$  can be approximated by

$$a = \frac{2.3}{\Phi_D^0} c_A l \int_{\lambda} I_{\lambda}^D(\lambda) \varepsilon_A(\lambda) d\lambda$$

where the integral represents the overlap between the donor fluorescence spectrum and the acceptor *absorption* spectrum.

Related terms: *Dexter-energy transfer*, *energy transfer*, *Förster-resonance-energy transfer*.

See *inner-filter effect*, [50].

revG2

**radiative lifetime**,  $\tau_0$

*Lifetime* of an excited molecular entity in the absence of *radiationless transitions*. The reciprocal of the first-order rate constant for the radiative step, or the reciprocal of the sum of these rate constants if there is more than one such step. The equivalent term, natural lifetime, is discouraged.

Note 1: Approximate expressions exist relating  $\tau_0$  to the *oscillator strength* of the emitting transition.

Note 2: the subscript 0 is used in this definition, whereas the superscript 0 is used to indicate a non-quenched lifetime in the *Stern-Volmer kinetic relationships*.

Related term: *Förster-resonance-energy transfer*.

See [50, 51].

revG2

**radiative transition**

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

Compare with *radiationless deactivation*, *radiationless transition*.

See *luminescence*.

G2/GB

**radical pair**

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

G2

**radioluminescence**

*Luminescence* arising from excitation by high-energy particles or radiation.

G2/GB

**radiolysis**

Bond cleavage induced by high-energy electromagnetic radiation, such as, e.g.,  $\gamma$  radiation.

Note: Term loosely used for any chemical process brought about by high-energy electromagnetic radiation as well as to refer to the irradiation technique itself (“pulse radiolysis”).

G2/GB

**rate of absorbed photons per volume**

Same as absorbed photon flux density.

**red shift**

Informal term for *bathochromic shift*.

G2/GB

**reduced dichroism**

See *linear dichroism*.

**reflectance,  $\rho$** 

Fraction of incident radiation reflected by a surface or discontinuity,  $\rho(\lambda) = \frac{P_{\lambda}^{\text{refl}}}{P_{\lambda}^0}$ , where  $P_{\lambda}^0$  and

$P_{\lambda}^{\text{refl}}$  are, respectively, the incident and reflected *spectral radiant power*. Same as reflectivity or reflection factor.

Note: 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

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

Reflectance increases as the angle of incidence decreases from 90 degrees.

See [7].

### **reflection factor**

See *reflectance*.

### **reflectivity**

See *reflectance*.

### **Rehm-Weller equation**

Empirical correlation found between the observed second-order rate constant,  $k_q$ , for an intermolecular *electron-transfer* reaction and the *Gibbs energy of the photoinduced electron transfer process* within the encounter complex ( $\Delta_{\text{ET}}G^\circ$ ):

$$k_q = \frac{k_d}{1 + \frac{k_d}{K_d Z} \left[ \exp\left(\frac{\Delta G^\ddagger}{RT}\right) + \exp\left(\frac{\Delta_{\text{ET}}G^\circ}{RT}\right) \right]}$$

with  $k_d$  and  $k_{-d}$  the rate constant for the formation and separation, respectively, of the encounter (precursor) complex,  $K_d = k_d / k_{-d}$ ,  $Z$  the universal collision frequency factor,  $R$  the gas constant,  $T$  the absolute temperature and  $\Delta G^\ddagger$  the activation Gibbs energy of the forward electron transfer reaction.

Note: In the original formulation of this equation [139] the value  $\frac{k_d}{K_d Z} = 0.25$  in acetonitrile was used.

**relative spectral responsivity,  $\varepsilon(\lambda)$** 

See *action spectrum*.

G2/GB

**relaxation**

Passage of a system that has been perturbed from equilibrium by radiation excitation or otherwise, towards or into thermal equilibrium with its environment.

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

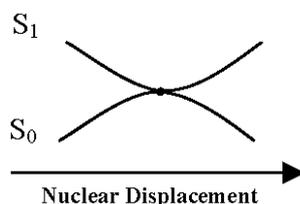
G2

**Renner-Teller effect**

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

Note 1: The Renner-Teller effect arises from splittings in the vibrational levels of molecular entities due to even terms in the *vibronic* perturbation expansion. This is generally a minor effect for non-linear molecular entities compared to the *Jahn-Teller effect*, which is due to the odd terms.

Note 2: For linear molecular entities it is the only possible vibronic effect characteristic of degenerate electronic states.



See [6].

revG2

**reorganization energy (in electron transfer)**

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

Note: Approximations have been proposed to calculate the value of  $\lambda_{\text{out}}$  taking into account the *relative permittivity* of the solvent.

See [6, 22, 81].

G2

### **residual emission anisotropy**

*Photoselected* molecules hindered in their rotation (e.g., in lipid bilayers or liquid crystals) do not become randomly oriented even after long time periods. Thus, the *emission anisotropy* does not decay to zero but to a steady value,  $r_{\infty}$ , called residual emission anisotropy. In the case of a single *rotational correlation time*,  $\tau_c$  or  $\theta$ , the decay of emission anisotropy following  $\delta$ -pulse excitation is given by:

$$r(t) = (r_0 - r_{\infty}) \exp(-t/\tau_c) + r_{\infty}$$

where  $r_0$  is the *fundamental emission anisotropy*.

Note: The term residual anisotropy is to be preferred to “limiting anisotropy”.

See *molecular orientation, photoselection*, [50, 51].

### **resonance-absorption technique**

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

G2/GB

### **resonance fluorescence**

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

Note: Also used to designate the radiation emitted by an atom of the same wavelength as the longest one capable of exciting its fluorescence, e.g., 122.6 nm in the case of the hydrogen atom, and 253.7 nm in the case of the mercury atom.

Related term: *resonance line*.

G2/GB

### **resonance-fluorescence technique**

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

G2/GB

### **resonance lamp**

*Lamp* emitting *resonance radiation* of atoms and their ions. Depending on the requirements, the lamp is filled either with pure vapour of the element or with a mixture of it and other gases.

Note: Examples are: Hg (253.7 and 184.9 nm), Cd (228.8 and 643.8 nm), Na (589.0 nm), Zn (213.8, 330.3, 334.5, and 636.2 nm), Kr (116.5 and 123.6 nm), Xe (129.6 and 147.0 nm).

For a list of all possible atomic lines see [140].

revG2

### **resonance line (in fluorescence)**

Longest *wavelength* capable of exciting *fluorescence* in an atom.

Related term: *resonance fluorescence*.

G2

### **resonance radiation**

Same as *resonance fluorescence*.

G2/GB

### **rotational correlation time, $\tau_c$ or $\theta$**

Parameter describing the time dependence of the tumbling of a molecular entity in a medium of viscosity  $\eta$ . The rotational correlation time can be obtained from the decay of the *fluorescence* or *phosphorescence anisotropy* and is related to the average molecular rotational diffusion coefficient,  $D_r$ , in turn related to the hydrodynamic molecular volume of the *fluorophore*,  $V$ , and to  $\eta$  (see Note 3).

Note 1: Mathematical definition:  $r(t) = r_0 \exp(-t/\tau_c)$ , with  $r(t)$  the *emission anisotropy* at time  $t$  and  $r_0$  the *fundamental emission anisotropy*.

Note 2: In the case of a spherical emitting species reorienting itself in a homogeneous fluid,  $\tau_c = 1/(6D_r)$ .

Note 3: Often, the Stokes-Einstein relationship is used for the calculation of  $D_r$ , i.e.,  $D_r = RT/6V\eta$ , with  $R$  the gas constant,  $T$  the absolute temperature and  $V$  the hydrodynamic molecular volume. However, the use of this relationship at a molecular level is questionable, and  $D_r$  should be independently determined by time-resolved *fluorescence polarization* methods.

Compare with *rotational relaxation time*.

See [50].

### **rotational relaxation time, $\rho$**

Parameter describing the time dependence of the tumbling of a molecular entity in a medium of viscosity  $\eta$ , as originally defined by Debye [141], and used by Perrin in the original development of the theories of rotational motion of *fluorophores* [142].

Note: Related to the *rotational correlation time*,  $\tau_c$ , by  $\rho = 3\tau_c$ . Thus, in the case of a spherically emitting species reorienting itself in a homogeneous fluid,  $\rho = 1/(6D_r)$ , with  $D_r$  the rotational diffusion coefficient.

**rovibronic state**

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

G2/GB

**ruby laser**

Pulsed source of *coherent radiation* emitting mainly at 694.3 nm from chromium ions ( $\text{Cr}^{3+}$ ) in aluminum oxide.

See *laser, solid-state laser*.

G2/GB

**Rydberg orbital**

For an atom, an *orbital* with principal quantum number greater than that of any occupied orbital of the *ground state*. For a molecular entity, a molecular orbital that correlates with a Rydberg atomic orbital in an atomic fragment produced by dissociation.

Note: Typically, the extension of the Rydberg orbital is large compared to the size of the atom or molecular entity.

See [6].

G2/GB

**Rydberg transition**

Electronic transition described approximately as promotion of an electron from a “bonding” *orbital* to a *Rydberg orbital*. Spectral bands corresponding to Rydberg transitions approximately fit the Rydberg formula

$$\tilde{\nu} = I - R / (n - \Delta)^2$$

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

See [6].

revG2

### **RYDMR**

Acronym for reaction-yield-detected magnetic resonance.

See *optically detected magnetic resonance*.

G2/GB

### **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.

G2/GB

### **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.

G2/GB

### **Saupe matrices**

See *molecular orientation*, [6].

### **Schenck-sensitization mechanism**

Chemical transformation of one molecular entity caused by *photoexcitation* of a *sensitizer* undergoing temporary covalent bond formation with the molecular entity.

See [129, 143].

G2

### **scintillators**

Materials used for the measurement of radioactivity by recording the *radioluminescence*. They contain compounds (*chromophores*), which combine a high *fluorescence quantum efficiency*, a short *fluorescence lifetime* and a high solubility.

Note: These compounds are employed as solutes in aromatic liquids and polymers to form organic liquid and plastic scintillators, respectively.

G2/GB

### selection rule

A given transition is allowed or forbidden on the basis of the symmetry or spin of the wavefunctions of the initial and final states.

See [6].

G2/GB

### self-absorption

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

G2

### self-localized excitations (in conjugated organic polymers)

Physical and chemical properties of conjugated organic polymers with  $\pi$ -electrons have been interpreted in terms of self-localized excitations, which are quasi-particles with structural changes over several repeating units. These excitations can be classified into *solitons*, *polarons*, *bipolarons* and *excitons* according to their charge and spin, as shown in the Table.

excitation	chemical term	charge	spin
positive polaron	radical cation	$+e/2$	
negative polaron	radical anion	$-e/2$	
positive bipolaron	dication	$+2e$	0
negative bipolaron	dianion	$-2e$	0
neutral soliton	neutral radical	$0/2$	
positive soliton	cation	$+e$	0
negative soliton	anion	$-e$	0

<i>singlet</i> exciton (neutral bipolaron, exciton polaron)	S	0	0
<i>triplet</i> exciton (neutral bipolaron, exciton polaron)	T	0	1

See [144].

### **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*.

Related term: *Stern-Volmer kinetic relationships*.

G2/GB

### **semiconductor laser**

Same as *diode laser*.

revG2

### **sensitizer**

See *photosensitizer*.

G2/GB

### **sensitization**

See *photosensitization*.

G2/GB

### **simultaneous pair transitions**

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

See [6].

G2/GB

### **single-photon counting**

See *photon counting*.

G2/GB

**single-photon timing**

Technique that permits recovery of the parameters characterizing a *fluorescence* decay after pulse excitation (in particular excited-states lifetimes). It is based on the creation of a time histogram of many stochastic events involving the time delay between the electronic excitation of a molecule or material and its *emission* of a *photon* from an excited state. A key to the technique is that no more than one photon strike the detector per pulsed excitation. Excitation is commonly achieved with a flash from a repetitive nanosecond *lamp* or *diode laser* or a CW operated *laser* (*mode-locked laser*). The essential components of the hardware are a device to measure the excitation-emission delay time and another to determine the relative frequency of photons reaching the detector at each delay time. Delay times are usually measured with a time-to-amplitude-converter (TAC), using voltage to measure the delay between a start and a stop signal. The frequency of events with each delay is stored in a multi-channel analyzer.

This term is preferred to time-correlated single-photon counting.

See e.g., [50, 64, 145].

revG2

**singlet molecular oxygen (singlet molecular dioxygen)**

Oxygen molecule (dioxygen), O<sub>2</sub>, in an excited *singlet* state. The *ground state* of O<sub>2</sub> is a *triplet* ( $^3\Sigma_g^-$ ). The two metastable singlet states derived from the ground-state *configuration* are  $^1\Delta_g$  and  $^1\Sigma_g^+$  (the latter with the higher energy).

Note 1: 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  $^1S$  or  $^1D$  *excited state*. The oxygen atom ground state is a triplet  $^3P$  state and the  $^1S$  and  $^1D$  states are also derived from the ground-state configuration.

Note 2: *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 singlet molecular dioxygen is produced, is controlled by the

*spin-statistical factor* [146].

For a compilation of singlet molecular oxygen production *quantum yields*, see [147].

For a compilation of singlet molecular dioxygen *lifetimes* and rate constants of its reaction with several substrates see [148].

revG2

### **singlet-singlet annihilation**

See *annihilation*, *spin-conservation rule*, *spin-statistical factor*.

G2/GB

### **singlet-singlet energy transfer**

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

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

G2/GB

### **singlet state**

State having a total electron spin quantum number equal to 0.

See *multiplicity*.

G2/GB

### **singlet-triplet crossing**

Point of intersection between the *potential energy surfaces* of states of different *multiplicity*.

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

Related term: *conical intersection*.

**singlet-triplet energy transfer**

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

See *energy transfer*, *spin-conservation rule*.

G2/GB

**solar conversion efficiency**

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

G2/GB

**solid-state lasers**

*CW* or pulsed *lasers* in which the active medium is a solid matrix. The solid matrix can be a) inorganic (crystal or glass) doped with an ion (e.g.,  $\text{Nd}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Er}^{3+}$ ) or an emitting dye or b) organic (polymeric) or hybrid organic (polymeric)-inorganic also doped with a dye. The emitted *wavelength* depends on the active ion, the selected optical transition and the matrix.

Note 1: Some of these lasers are tunable within a very broad range (e.g., from 700 to 1000 nm for  $\text{Ti}^{3+}$ -doped sapphire).

Note 2: Pulsed lasers may be *free-running*, *Q-switched* or *mode-locked*. Some *CW* lasers may be *mode-locked*.

See [17, 149].

G2/GB

**soliton**

Localized excitations propagating in a system with constant velocity and colliding with each other without change in their shapes.

See *self-localized excitations*.

**solvatochromism**

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

Related term: *Lippert-Mataga equation*.

See [150].

G2

**solvent-induced symmetry breaking**

Breaking of symmetry of a molecular species by interactions with the solvent that can modify the molecular charge distribution, to favour asymmetrical configurations.

Note: An example is the stabilization by a polar solvent of a light-induced *charge transfer* state in a symmetric donor-acceptor-donor system.

**solvent-separated ion pair**

Pair of ions separated by at least one solvent molecule.

Note: During *electron-transfer* processes between neutral molecular species, solvent-separated ion pairs may form either directly or via solvation-induced separation of *contact ion pairs*.

G2

**solvent shift**

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

See *bathochromic shift*, *hypsochromic shift*, *solvatochromism*, [150].

G2/GB

**sonoluminescence**

*Luminescence* induced by sound waves.

See *triboluminescence*.

G2/GB

**specific photon emission**

Same as *photon exitance*.

G2/GB

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

Note 2: This term is preferred when dealing with the function  $X_\lambda(\lambda)$  over a wide range of wavelengths, such as in the overlap integral in *Dexter-* and in *Förster-energy transfer*.

**spectral (photon) effectiveness**

Reciprocal of the *photon fluence rate*,  $E_{\text{p},0}$ , at *wavelength*  $\lambda$ , causing identical photoresponse,  $\Delta y$ , per time interval ( $\Delta y/\Delta t$ ) at the different wavelengths. The effectiveness spectrum is directly proportional to the *conversion spectrum* of the sensory pigment under investigation, if spectral *attenuance* is negligible.

revG2

**spectral fluence,  $H_{\lambda,0}$ ,  $F_{\lambda,0}$**

Derivative of *fluence*,  $H_0$ , with respect to *wavelength*,  $\lambda$ . SI unit is  $\text{J m}^{-3}$ ; common unit is  $\text{J m}^{-2} \text{ nm}^{-1}$ .

Note: 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.

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

Derivative of *fluence rate*,  $E_0$ , with respect to *wavelength*,  $\lambda$ . SI unit is  $\text{W m}^{-3}$ ; common unit is  $\text{W m}^{-2} \text{nm}^{-1}$ .

Note: 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.

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

Derivative of *irradiance*,  $E$ , with respect to *wavelength*,  $\lambda$ . SI unit is  $\text{W m}^{-3}$ ; common unit is  $\text{W m}^{-2} \text{nm}^{-1}$ .

Note: 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.

revG2

**spectral overlap**

Degree of superposition of the donor *emission spectrum* with the acceptor *absorption spectrum* in an *energy transfer* process.

Note: The normalization conditions for the calculation of the spectral overlap integral are different for the different mechanisms of *energy transfer*, such as *Dexter-excitation transfer*, *Förster-resonance-energy transfer*, and *radiative-energy transfer*.

revG2

**spectral overlap integral**

See *Dexter-excitation transfer*, *energy transfer*, *Förster-resonance-energy transfer*, *radiative-energy transfer*.

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

Derivative of *photon exitance*,  $M_p$ , with respect to *wavelength*,  $\lambda$ . SI unit is  $\text{s}^{-1} \text{m}^{-3}$ ; common unit is  $\text{s}^{-1} \text{m}^{-2} \text{nm}^{-1}$ .

Note 1: 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 2: 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.

revG2

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

Derivative of *photon flux*, number basis,  $q_p$ , with respect to *wavelength*,  $\lambda$ . SI unit is  $\text{s}^{-1} \text{m}^{-1}$ ; common unit is  $\text{s}^{-1} \text{nm}^{-1}$ .

Note 1: 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 2: 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.

revG2

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

Derivative of *photon irradiance*,  $E_p$ , with respect to *wavelength*,  $\lambda$ . SI unit is  $\text{s}^{-1} \text{m}^{-3}$ ; common unit is  $\text{s}^{-1} \text{m}^{-2} \text{nm}^{-1}$ .

Note 1: 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  $\text{einstein s}^{-1} \text{m}^{-2} \text{nm}^{-1}$ .

Note 2: 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.

revG2

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

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

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

Note 2: 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.

revG2

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

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

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: 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.

revG2

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

Derivative of *radiant energy*,  $Q$ , with respect to *wavelength*  $\lambda$ . SI unit is  $\text{J m}^{-1}$ ; common unit is  $\text{J nm}^{-1}$ .

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

Derivative of *radiant exitance*,  $M$ , with respect to *wavelength*  $\lambda$ . SI unit is  $\text{W m}^{-3}$ ; common unit is  $\text{W m}^{-2} \text{nm}^{-1}$ .

Note: 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.

revG2

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

Derivative of *radiant intensity*,  $I$ , with respect to *wavelength*,  $\lambda$ . SI unit is  $\text{W m}^{-1} \text{sr}^{-1}$ ; common unit is  $\text{W nm}^{-1} \text{sr}^{-1}$ .

Note: 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.

revG2

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

Derivative of *radiant power*,  $P$ , with respect to *wavelength*  $\lambda$ . SI unit is  $\text{W m}^{-1}$ ; common unit is  $\text{W nm}^{-1}$ .

Note: 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.

revG2

**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: 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*  $\lambda$ .

See *action spectrum*.

revG2

**spectral sensitivity (actinometric factor),  $S(\lambda)$**

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.

Related term: *spectral responsivity*.

revG2

**spectral sensitization**

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

G2/GB

**spherical irradiance**

Same as *fluence rate*.

**spherical radiance**

Same as *radiant exitance*,  $M$ . It is the integral of the *radiant power*,  $P$ , leaving a source over the

total solid angle and over the whole *wavelength* range. SI unit is  $\text{W m}^{-2}$ .

G2/GB

**spherical radiant exposure**

Same as *fluence*.

G2/GB

**spin-allowed electronic transition**

Electronic transition not involving a change in the spin part of the wavefunction.

G2/GB

**spin-conservation rule (Wigner rule)**

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

See *annihilation*, [6].

G2

**spin-flip method**

Quantum mechanical method for the calculation of open shell *excited states*. The method accurately describes low-lying multi-configurational electronic states of *diradicals* and triradicals in an efficient and robust single-reference scheme. The target low-spin states (e.g.,  $S = 0$  or  $S = 1/2$ ) are described as spin-flipping excitations ( $S = -1$ ) from a well-behaved high-spin reference state (e.g.,  $S = 1$  or  $S = 3/4$ ). By employing theoretical models of increasing complexity for the reference (e.g., SCF, MP2, CCSD), the accuracy in the target states' description can be systematically improved. The SF methods result in multistate single-step computational schemes, e.g., several low-lying states can be computed in a single calculation that includes both dynamical and non-dynamical correlation effects.

Related term: *correlation energy*.

**spin-flip transition, (SF)**

See *simultaneous pair transitions*.

**spin multiplicity**

See *multiplicity*.

**spin-orbit coupling**

Interaction of the electron spin magnetic moment with the magnetic moment due to the orbital motion of electrons.

Note: One consequence of spin-orbit coupling is the mixing of zero-order states of different *multiplicity*. This effect may result in *fine structure* called *spin-orbit splitting*.

See [6].

G2/GB

**spin-orbit splitting**

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

See [6].

G2/GB

**spin-spin coupling**

Interaction between the spin magnetic moments of different electrons and/or nuclei.

Note: It causes, e.g., the multiplet pattern in nuclear magnetic resonance, NMR, spectra.

See [6].

G2/GB

**spin-statistical factor (in diffusion-controlled reactions)**

From the possible encounter pairs between states of different spin *multiplicity*, only those conserving multiplicity in going to products are expected to react.

Note: This factor determines the efficiency of diffusion-controlled reactions, which have an encounter-controlled rate [5]. Typical examples are *quenching of fluorescence* of aromatic hydrocarbons by O<sub>2</sub> and quenching of *triplet states* and triplet-triplet *annihilation* by O<sub>2</sub>.

See [151].

### **spontaneous emission**

*Emission* occurring in the absence of a perturbing external electromagnetic field.

Note 1: The transition between states,  $n$  and  $m$ , is governed by the “Einstein coefficient” of spontaneous emission,  $A_{nm}$ .

Note 2: No emission is really spontaneous in the sense of absence of perturbation. In a real sample the fluctuations of charges in the environment provide the needed perturbation.

Related term: *stimulated emission*.

See [50].

revG2

### **Stark effect**

Splitting or shifts of spectral lines of atoms, ions or molecules in an electric field. Also called electrochromic effect.

G2/GB

### **state crossing**

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

G2

### **state diagram**

See *Jablonski diagram*.

G2/GB

### **static quenching**

See *quenching*, [50].

G2

### steady-state emission anisotropy

See *emission anisotropy*.

### Stern-Volmer kinetic relationships

Applies broadly to variations of *quantum yields* of *photophysical processes* (e.g., *fluorescence* or *phosphorescence*) or *photochemical reaction* (usually *reaction quantum yield*) with the concentration of a given reagent, which may be a substrate or a *quencher*. In the simplest case, a plot of  $\Phi^0/\Phi$  (or  $M^0/M$  for *emission*) vs. amount concentration of quencher, [Q], is linear, obeying the equation (1)

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

$K_{SV}$  is referred to as the Stern-Volmer constant.

Eq. (1) applies when a quencher inhibits either a *photochemical reaction* or a *photophysical process* by a single reaction.  $\Phi^0$  and  $M^0$  are the quantum yield and emission intensity (*radiance*), respectively, in the absence of the quencher Q, while  $\Phi$  and  $M$  are the same quantities in the presence of the different concentrations of Q. In the case of dynamic *quenching* the constant  $K_{SV}$  is the product of the true *quenching* constant  $k_q$  and the *excited-state lifetime*,  $\tau^0$ , in the absence of quencher. The rate constant  $k_q$  is the bimolecular reaction rate constant for the elementary reaction of the excited state with the particular quencher Q. Eq. (1) can therefore be replaced by eq. (2)

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

Note 1: When an excited state undergoes a bimolecular reaction with rate constant  $k_r$  to form a product, a double-reciprocal relationship is observed according to eq. 3

$$(3) \quad \frac{1}{\Phi(p)} = 1 + \frac{1}{k_r \tau^0 [S]} \frac{1}{(h \text{ B})}$$

where  $\Phi(p)$  is the quantum *efficiency* of product formation,  $\eta$  the formation efficiency of the reactive excited state,  $B$  the fraction of reactions of the excited state with substrate  $S$  that leads to product, and  $[S]$  the concentration of reactive ground-state substrate. The intercept divided by the slope gives  $k_r \times \tau^0$ . If  $[S] = [Q]$ , and if a photophysical process is monitored, plots of equations (2) and (3) should provide independent determinations of the product-forming rate constant  $k_r$ . When the lifetime of an excited state is observed as a function of the concentration of  $S$  or  $Q$ , a linear relationship should be observed according to eq. 4

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

where  $\tau^0$  is the excited-state lifetime in the absence of quencher  $Q$ .

Note 2: A superscript 0 (zero) is used for the excited state lifetime in the absence of a quencher, whereas the subscript 0 is used for the *radiative lifetime*  $\tau_0$ .

Related terms: *self-quenching*, *spin-statistical factor*.

See [50, 152].

revG2

### **stimulated emission**

Part of the *emission* induced by a resonant perturbing electromagnetic field. The transition between states,  $n$  and  $m$ , is governed by the Einstein coefficient of stimulated emission,  $B_{nm}$ .

Note: *CIDNP* emission and *lasing* action are examples of processes, which require stimulated emission.

Related term: *spontaneous emission*.

See [50, 51].

G2/GB

### **Stokes shift**

Difference (usually in *frequency* units) between the spectral positions of the *Franck-Condon* maxima of the lowest energy (highest *wavelength*) *absorption* and the *luminescence* arising from

the same electronic transition (the 0-0 bands).

Note 1: Often used referring to the gap between the respective band maxima.

Note 2: Generally, the luminescence occurring at a longer *wavelength* than the absorption is stronger than that occurring at a shorter wavelength than the absorption. The latter may be called an anti-Stokes shift.

See [50].

revG2

### **sudden polarization**

Large intramolecular charge separation in the *singlet excited state* of polyenes and their derivatives twisted about a double bond. Unsymmetrical substitution or geometrical distortion is effective in polarizing the system.

Note: An example is the stabilization of the zwitterionic structure of 90° twisted ethene (ethan-2-ylidene-1-ide) with one methylene group pyramidalized.

See [153].

### **superexchange interaction**

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

G2/GB

### **superradiance**

*Spontaneous emission* amplified by a single pass through a *population inverted* medium.

Note: Distinguished from true *laser* action by its lack of coherence. The term superradiance is frequently used in laser technology.

See *coherent radiation*.

G2/GB

**surface crossing**

In a diagram of electronic energy versus molecular geometry, the electronic energies of two states of different symmetry may be equal at certain geometrical parameters. At this point (unidimensional representation), line or surface (more than one dimension), the two *potential energy surfaces* are said to cross one another.

Note: In states of the same spin *multiplicity* the surface crossing is usually  $3N - 8$  dimensional. In states with different spin multiplicity the surface crossing is usually  $3N - 7$  dimensional ( $N$  is the number of nuclei).

See *avoided crossing, conical intersection, singlet-triplet crossing*, [35].

revG2

 **$\sigma \rightarrow \sigma^*$  transition**

Electronic transition described approximately as promotion of an electron from a “bonding”  $\sigma$  *orbital* to an “antibonding”  $\sigma$  orbital designated as  $\sigma^*$ .

Note: These transitions generally involve high transition energies and appear close to or mixed with *Rydberg transitions*.

G2

**TD-DFT**

Acronym for *time-dependent density functional theory*.

**thermal lensing**

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

Related term: *photothermal effects*, [18].

G2/GB

**thermally activated delayed fluorescence**

See *delayed fluorescence*.

G2/GB

**thermochromism**

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

G2/GB

**thermoluminescence**

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

G2/GB

**through-bond electron transfer**

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

Related term: *through-space electron transfer*.

G2/GB

**through-space electron transfer**

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

Related term: *through-bond electron transfer*.

G2/GB

**TICT**

Acronym for *twisted intramolecular charge transfer*.

Related terms: *PICT*, *planar intramolecular charge transfer*.

See *ICT*, *intramolecular charge transfer*, *twisted intramolecular charge transfer*, [72, 73].

revG2

**TICT emission**

Electronic *emission* from a *TICT* state.

Related terms: *PICT*, *planar intramolecular charge transfer*, *twisted intramolecular charge transfer*.

revG2

**tight ion pair**

Same as *contact ion pair*.

G2

**time-correlated single-photon counting**

See *single-photon timing*.

revG2

**time-dependent density functional theory, (TD-DFT)**

Methods for computing accurate excitation energies at a low computational cost in large molecular species within the time-dependent scheme and the density functional theory. It is the only available DFT-based method for computing electronic excitation energies.

See related terms in [6, 35].

**time-resolved anisotropy,  $r(t)$** 

See *emission anisotropy*.

**time-resolved microwave conductivity, (TRMC)**

Technique allowing the quantitative and qualitative detection of radiation-induced changes in the real,  $\Delta\text{Re}\sigma$ , and imaginary,  $\Delta\text{Im}\sigma$ , components of the conductivity of a medium by time-resolved measurement of changes in the microwave *absorption* resulting from the formation of mobile charges or from changes in the dipole moment or polarizability of molecules on excitation.

Note: From  $\Delta\text{Re}\sigma$  (corresponding to a change in the dielectric loss,  $\Delta\varepsilon''$ ) the product of the yield and the mobility of charges carriers or the dipole moment change can be determined. From  $\Delta\text{Im}\sigma$  (corresponding to a change in the relative permittivity,  $\Delta\varepsilon'$ ) the product of the yield and the change in molecular polarizability can be determined.

See [154].

revG2

### **time-resolved spectroscopy**

Recording of spectra at a series of time intervals after the excitation of the system with an *ultraviolet, visible or infrared* radiation pulse (or other perturbation) of appropriately short duration.

G2/GB

### **Ti-sapphire laser**

See *solid-state lasers*.

### **transfer quantum efficiency (within the dipole-dipole energy transfer)**

See *Förster energy transfer*.

### **transient spectroscopy**

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

Related terms: *flash photolysis, pump-dump-probe, pump-probe, time-resolved spectroscopy*.

revG2

### **transient-stimulated emission pumping, (TSEP)**

A *transient-spectroscopy* technique in which the excited state dynamics is probed via stimulating

the molecular species from the photoexcited state (produced by a short pump pulse) back to the *ground state* by means of a short dump pulse at various pump-dump time delays.

See *pump-dump-probe*, [155].

### **transition (dipole) moment**

An electromagnetic wave may induce an oscillating electric moment in a molecule (possibly leading to *absorption* if the oscillation frequency is equal to the light *frequency*). The amplitude of this moment is the transition moment between the initial (i) and final (f) states (here assumed to be non-degenerate):

$$\mathbf{M}_{if} = \langle f | \mathbf{M}_{op} | i \rangle$$

where  $\mathbf{M}_{op}$  is the electric dipole moment operator, a vector operator that is the sum of the position vectors of all charged particles weighted with their charge. The transition moment  $\mathbf{M}_{if}$  is a vector in the molecular framework, characterized both by its direction and its probability.

Note 1: The absorption probability for linearly polarized light is proportional to the cosine square of the angle between the electric vector of the electromagnetic wave and  $\mathbf{M}_{if}$ ; light absorption will be maximized if they are parallel, and no absorption will occur if they are perpendicular.

Note 2: It is frequently said that a transition is *polarized* along the direction of its transition moment and this direction is called the *polarization direction* of the transition.

Note 3: In the case of a doubly degenerate final state f, each of the two components at the same energy has a transition moment and the two moments define a plane. The transition is then said to be polarized in that plane, which also defines its polarization direction(s). This is typically the case for some of the transitions in highly symmetrical molecules.

Note 4: In the case of a *vibronic* transition, where both the initial and the final states may be characterized by (different) electronic and vibrational states, the *Franck-Condon principle* is often applied. This approximation separates electronic and nuclear descriptions and allows the transition moment to be written as a product of a purely electronic transition moment and an overlap integral between the two vibrational wavefunctions involved.

See *emission anisotropy, linear dichroism, molecular orientation*, [51].

revG2

### **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: Transmittance depends on the pathlength and this should be specified when giving a transmittance value.

Note 2: 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.

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

revG2

### **triboluminescence**

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

See *sonoluminescence*.

G2/GB

### **triplet state**

State having a total electron spin quantum number of 1.

See *multiplicity*, [156].

For a list of triplet-triplet absorption spectra see [157]. For a critical evaluation of triplet-triplet absorption data see [158].

revG2

**triplet-triplet annihilation**

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

Note: This process is often, but not always, followed by *delayed fluorescence*.

Related terms: *annihilation*, *spin-conservation rule*.

G2/GB

**triplet-triplet energy transfer, (TTET)**

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

See *Dexter excitation transfer*, *spin-conservation rule*, *spin-statistical factor*, [52, 66].

See also [159].

G2/GB

**triplet-triplet transitions**

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

G2/GB

**trivial energy transfer**

Same as *radiative energy transfer*.

G2/GB

**TRMC**

Acronym for *time-resolved microwave conductivity*.

**TTET**

Acronym for *triplet-triplet energy transfer*.

**tungsten-halogen lamp**

See *wolfram lamp*, *quartz-iodine lamp*.

Note: Other halogens may fill the lamp.

**tunnelling**

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

Note: Effect important for some processes involving the transfer of electrons and light atoms, particularly H atoms.

See [6].

G2/GB

**turntable reactor**

See *merry-go-round reactor*.

G2/GB

**twisted intramolecular charge transfer, (TICT)**

In a TICT state formed by *intramolecular charge transfer* in an electron donor (D)/acceptor (A) molecule, the D and A subgroups have a mutually perpendicular configuration that leads to electronic decoupling of D and A.

Related terms: *PICT*, *planar intramolecular charge transfer*.

See [72, 73].

revG2

**two-photon excitation**

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

Note: 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*.

See *two-photon process*.

G2/GB

### **two-photon photochromism**

*Photochromic* process involving a *two-photon process*. The process might involve the simultaneous or the sequential *absorption* of two photons.

Related term: *one-photon photochromism*.

### **two-photon process**

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

G2/GB

### **ultraviolet, (UV)**

Region of the electromagnetic spectrum extending from about 100 nm to 400 nm. This region is divided into four sub-bands as follows:

Vacuum Ultraviolet 100 – 200 nm

UV-C 200 – 280 nm

UV-B 280 – 315 nm

UV-A 315 – 400 nm.

Note: The notation and the limits of the various regions are as recommended by the International Commission on Illumination (CIE, Committee internationale de l'éclairage) [9], with the exception that in these recommendations the UV-C range is 100 – 280 nm, including thus the vacuum UV range.

### **uniaxial sample**

Sample characterized by a (unique) sample axis Z with all directions perpendicular to Z being equivalent. In other words, the sample properties are invariant to rotation around Z. Uniaxiality exists in many anisotropic samples and simplifies the interpretation of their spectra considerably.

See *linear dichroism*, *molecular orientation*, [51].

**upconversion**

The process by which two *photons* with *frequencies*  $\nu_2$  and  $\nu_3$  combine in a non-linear medium to produce a higher energy photon with frequency  $\nu_1$  such that  $\nu_1 = \nu_2 + \nu_3$ .

Note 1: Also known as a parametric upconversion or sum frequency generation. Upconversion is the reverse process of *downconversion*.

Note 2: The efficiency of the conversion process depends on the parametric gain in the non-linear material. This in turn depends on the power of the incident radiation, the photon frequencies, their indices of refraction in the material, and the non-linear “hyper-susceptibility” of the material.

See *non-linear optical techniques, parametric processes* [47, 50].

**UPS**

See *photoelectron spectroscopy*.

**UV**

Acronym for *ultraviolet*

**UV dose**

Dose of *UV* radiation.

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

**G2/GB****UV stabilizer**

Substance added to a sample to prevent photodeterioration by *ultraviolet* (UV) radiation.

See *photochemical reaction*.

**G2/GB**

**valence band**

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

Note 1: The valence band is lower in energy than the *conduction band* and is generally completely full in semi-conductors. 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* separates the valence band from the conduction band.

Note 2: In metals the valence band is the conduction band.

revG2

**Vavilov rule**

See *Kasha-Vavilov rule*.

G2/GB

**vertical transition**

See *Franck-Condon principle*.

G2/GB

**vibrational redistribution**

Intramolecular redistribution of energy among the vibrational modes usually giving a statistical distribution of their populations, characterized by the “vibrational temperature”.

Note: For large molecules, this process does not require collisions.

G2/GB

**vibrational relaxation**

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

See *relaxation*.

G2/GB

**vibronic coupling**

Interaction between electronic and vibrational motions in a molecular entity.

See *Jahn-Teller, Renner-Teller effects*, [51].

G2/GB

**vibronic transitions**

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

See [51].

G2/GB

**visible**

Region of the electromagnetic spectrum extending from about 400 nm to 760 nm. This is the *wavelength* region to which the human eye is sensitive. There are no precise 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.

**wavelength,  $\lambda$**

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

Note: The wavelength depends on the medium in which the wave propagates.

See [7]

G2/GB

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

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

propagation. SI unit is  $\text{m}^{-1}$ ; common unit is  $\text{cm}^{-1}$ .

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

See [7].

G2/GB

### Weller correlation

Empirical correlation for the energy of full *charge-transfer exciplexes* relative to the ground state in *n*-hexane as a function of the electrochemical one electron standard reduction potential of the cation radical produced upon electron donation and standard reduction potential of the acceptor measured in a polar solvent for the donor (D) and the acceptor (A) involved

$$\Delta H(\text{D}^+\text{A}^-, \text{hexane}) = e [E^\circ(\text{D}^{+\bullet}/\text{D}) - E^\circ(\text{A}/\text{A}^-\bullet)] + e \Delta E$$

with  $E^\circ(\text{D}^{+\bullet}/\text{D})$  and  $E^\circ(\text{A}/\text{A}^-\bullet)$  the standard electrode potentials of the donor and acceptor, respectively.

Note 1: In the case diethylaniline as donor and aromatic hydrocarbons as acceptors, the last term on the right, i.e.,  $e \Delta E = (0.15 \pm 0.10)$  eV. This equation assumes a constant Coulomb term and a constant entropy change within a particular series of partners.  $e$  is the elementary charge.

Note 2: The IUPAC recommendations for the sign and symbols of standard potentials are used in the equation as written [11].

Note 3: Although not complying with the IUPAC recommended nomenclature for the standard electrode potentials, traditionally the equation has been written as:

$$\Delta H(\text{D}^+\text{A}^-, \text{hexane}) = e [E^\circ_{\text{ox}} - E^\circ_{\text{red}}] + (0.15 \pm 0.10) \text{ eV}$$

with  $E^\circ_{\text{ox}}$  the standard electrode potential at which the oxidation occurs, and  $E^\circ_{\text{red}}$  the standard electrode potential at which the reduction occurs. This writing of the first term within the square brackets is misleading and not recommended.

Related term: *Gibbs energy of photoinduced electron transfer*.

See [160].

revG2

### **Wigner matrices**

See *molecular orientation*, [6].

### **Wigner rule**

See *spin-conservation rule*, [6].

G2/GB

### **wolfram lamp**

Same as tungsten lamp. Incandescent lamp that generate light by passing an electric current through a thin filament wire (usually of wolfram) until it is extremely hot. The lamps are often filled by a halogen gas such as iodine and bromine that allow filaments to work at higher temperatures and higher efficiencies.

See *quartz-iodine lamp*.

### **Wood horn**

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

G2/GB

### **Wood lamp**

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

See *lamp*.

revG2

### **xenon lamp**

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

Related terms: *antimony-xenon, lamp, mercury-xenon lamp (arc)*.

See [15].

G2/GB

### **XPS**

See *photoelectron spectroscopy*.

G2/GB

### **YAG**

See *neodymium laser*.

G2/GB

### **Yang photocyclization**

Intramolecular coupling of *diradicals* of different sizes (1,4-, 1,5-, 1,6-, 1,7-, 1,8-diradicals, as well as very remote diradicals) formed through intramolecular hydrogen abstraction by an excited ketone, yielding cyclic alcohols of different sizes.

See *Norrish Type II*, [161].

### **Zeeman effect**

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

### **zero-field splitting**

Separation of multiplet sublevels in the absence of external magnetic field.

G2/GB

### **zero-zero (0-0) absorption or emission**

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

G2/GB

**Z<sub>50</sub> (of a photochromic system)**

Number of cycles required to reduce by 50 % the initial *absorbance* of the coloured form of a *photochromic* compound at a specific *wavelength*.

See [3].

QUANTITIES, SYMBOLS, AND TERMS USED IN THIS GLOSSARY<sup>1</sup>

Name	Symbol	Definition	SI Unit	Notes
absorbance decadic napierian	$A, A_{10}$ $A_e$	$A = \lg (P_\lambda^0 / P_\lambda) = -\lg T(\lambda)$ $A_e = \ln (P_\lambda^0 / P_\lambda) = -\ln T(\lambda)$	1	2
absorbed photon flux density, number basis		$\frac{q_p^0 [1 - 10^{-A(\lambda)}]}{V}$ with $q_p^0$ the number of photons <u>incident</u> per time interval ( <i>photon flux</i> , number basis).	$\text{s}^{-1} \text{m}^{-3}$	3
absorbed photon flux density, amount basis		$\frac{q_{n,p}^0 [1 - 10^{-A(\lambda)}]}{V}$ with $q_{n,p}^0$ the amount of photons <u>incident</u> per time interval ( <i>photon flux</i> , amount basis).	$\text{mol s}^{-1}$ $\text{m}^{-3}$	4
absorbed (spectral) radiant power density		$\frac{P_\lambda^0 [1 - 10^{-A(\lambda)}]}{V}$	$\text{W m}^{-4}$	5
absorption coefficient linear decadic molar decadic linear napierian molar napierian	$a$ $\varepsilon$ $\alpha$ $\kappa$	$a = A_{10}/l$ $\varepsilon = a/c = A_{10}/c l$ $\alpha = A_e/l$ $\kappa = \alpha/c = A_e/c l$	$\text{m}^{-1}$ $\text{m}^2 \text{mol}^{-1}$ $\text{m}^{-1}$ $\text{m}^2 \text{mol}^{-1}$	6 7 7
absorption cross- section	$\sigma(\lambda)$	$\sigma(\lambda) = \kappa(\lambda) / N_A = \ln 10 \varepsilon(\lambda) / N_A$	$\text{m}^2$	8
absorption factor (same as fraction of light absorbed)	$f(\lambda)$	$f(\lambda) = 1 - T(\lambda) = 1 - 10^{-A(\lambda)}$	1	
actinometric factor		See <i>spectral sensitivity</i>		
amount concentration	$c, [\text{species}]$	$c = [\text{species}] = n/V$	$\text{mol m}^{-3}$	9
amount of entities	$n$		mol	
amount of photons	$n_p$	$n_p = N_p / N_A$	mol	10
area	$S$		$\text{m}^2$	
attenuance	$D$	$D = \lg (P_\lambda^0 / P_\lambda) = -\lg T$	1	3,11
Avogadro constant	$N_A$	$N_A = 6.022\,141\,5 \times 10^{23} \text{ mol}^{-1}$	$\text{mol}^{-1}$	12
bandgap energy	$E_g$		$\text{J mol}^{-1}$	13
Brewster angle	$\theta_B$	$\theta_B = \arctan (n_2 / n_1) = \arctan (\varepsilon_2 / \varepsilon_1)^{1/2}$ with $n_2$ and $n_1$ the refractive indices of the receiving surface and the initial medium, respectively, and $\varepsilon_2$ and $\varepsilon_1$ the respective <i>electric permittivities</i> .		
brightness (of a laser dye)		$\Phi_f \varepsilon(\lambda)$	1	

		with $\Phi_f$ the <i>fluorescence quantum yield</i> and $\varepsilon(\lambda)$ the <i>molar decadic absorption coefficient</i>		
circular dichroism	$\Delta A_C$	$\Delta A_C = A_L - A_R$ with $A_L$ and $A_R$ the <i>absorbance</i> of left and right circularly polarized beams, respectively	1	
coherence length	$\Delta l$	$\Delta l = c \Delta \tau$ with $c$ the speed of the wave and $\Delta \tau$ (the coherence time) given by $\Delta \tau \Delta \omega \geq 1$ with $\Delta \omega$ the spectral bandwidth.	m	
coherence time	$\Delta \tau$	See <i>coherence length</i>	s	
conversion cross-section		$\Phi \sigma$ with $\Phi$ the <i>reaction quantum yield</i> and $\sigma$ the <i>absorption cross section</i>	m <sup>2</sup>	
critical quenching radius (Förster radius)	$R_0$	$R_0 = \text{Const.} \left( \frac{\kappa^2 \Phi_D^0 J}{n^4} \right)^{1/6}$ with $\kappa$ the <i>orientation factor</i> , $\Phi_D^0$ the <i>fluorescence quantum yield</i> of the donor in the absence of transfer, $n$ the average refractive index of the medium and $J$ the <i>Förster spectral overlap integral</i>	m	14
decay time	$\tau$	$c(t = \tau) = c(t = 0)/e$	s	
degree of emission polarization	$p$	$p = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}}$ with $I_{\parallel}$ and $I_{\perp}$ the intensities of the emission beams parallel and perpendicular, respectively, to the electric vector of linearly polarized incident electromagnetic radiation	1	
depth of penetration (of radiation) decadic napierian	$\beta$	$1/a$ $\beta = 1/\alpha$ with $a$ and $\alpha$ the <i>linear decadic</i> and the <i>linear napierian absorption coefficients</i> .	m m	
Dexter transfer rate constant	$k_T$	$k_T = (1/\hbar) K J \exp(-2r/L)$ with $L$ the average Bohr radius, $J$ the <i>spectral overlap integral</i> (Dexter), $r$ the distance between donor and acceptor, and $K$ a proportionality constant	s <sup>-1</sup>	
dichroic ratio	$d(\lambda)$	$d(\lambda) = A_Z/A_Y$ with $A_Z$ and $A_Y$ the <i>absorbances</i> with the electric vector of linearly polarized light along and perpendicular to the sample axis, respectively.	1	
dielectric constant see relative permittivity	$\varepsilon_r$		1	

differential quantum yield	$\Phi$	$\Phi(\lambda) = \frac{dx/dt}{q_{n,p}^0 [1 - 10^{-A(\lambda)}]}$ <p>with <math>d[x]/dt</math> the rate of change of a measurable quantity <math>x</math>, <math>q_{n,p}^0</math> the amount of photons <u>incident</u> per time interval (<i>photon flux</i>, amount basis), and <math>A(\lambda)</math> the <i>absorbance</i> at the excitation wavelength.</p>	1	15
dipole moment	$\mu$	$\mu = q d$	C m	16
driving force		$-\Delta G^\circ$	J mol <sup>-1</sup>	
driving force (for electron transfer), see <i>Gibbs energy of photoinduced electron transfer</i>		$-\Delta_{ET}G^\circ$	J mol <sup>-1</sup>	
Drude-Nernst equation for electrostrictive volume change	$\Delta V_{el}$	$\Delta V_{el} = -\frac{(ze)^2}{2r\epsilon_r} \frac{\partial(\ln\epsilon_r)}{\partial p}$ <p>with <math>\epsilon_r</math> the static <i>relative permittivity</i>, <math>r</math> the radius of the ion, <math>e</math> the elementary charge, and <math>z</math> the charge.</p>	L mol <sup>-1</sup>	
efficiency (of a reaction step)	$\eta$	$\eta = k_i / \sum_i k_i$ <p>with <math>k_i</math> the rate constants of all decay processes undergone by the species considered.</p>	1	
electric constant	$\epsilon_0$	$\epsilon_0 \approx 8.854 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$	C <sup>2</sup> J <sup>-1</sup> m <sup>-1</sup>	12
electrical susceptibility	$\chi_e$	$\chi_e = \epsilon_r - 1$ <p>with <math>\epsilon_r</math> the <i>relative permittivity</i></p>	1	
electronic transmission factor (within <i>Marcus electron transfer theory</i> )	$\kappa_{ET}$		1	
elementary charge	$e$	$e = 1.602\,176\,53 \times 10^{-19} \text{ C}$	C	12
emission anisotropy	$r$	$r = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}}$	1	
emittance, emissivity	$e$	$e = M / M_{bb}$	1	17
energy storage efficiency	$\eta$	$\eta = \text{energy out/energy in}$	1	
excited-state lifetime in the absence of quencher (within the <i>Stern-Volmer</i> relationship)	$\tau^0$		s	

exposure See <i>photon exposure, radiant exposure</i>				
$E_{0,0}$ energy	$E_{0,0}$	energy difference between the vibrationally relaxed levels of two electronic states	$\text{J mol}^{-1}$	13
Fermi level	$E_F$		$\text{J mol}^{-1}$	13
fluence, radiant energy fluence, spherical radiant exposure	$H_0, F_0$	$H_0 = F_0 = \int_t E_0 dt = dQ/dS$	$\text{J m}^{-2}$	18, 19
fluence rate, spherical irradiance	$E_0$	$E_0 = dP/dS = dH_0/dt$	$\text{W m}^{-2}$	19,20
fluorescence polarization (see <i>degree of polarization</i> )				
Förster-transfer rate constant	$k_T$	$k_T = k_D \left( \frac{R_0}{r} \right)^6 = \frac{1}{\tau_D^0} \left( \frac{R_0}{r} \right)^6$ $k_D$ : emission rate constant of the donor in the absence of energy transfer, $r$ : distance between donor and acceptor, $R_0$ : <i>critical quenching radius</i>	$\text{s}^{-1}$	
fraction of light absorbed	$f(\lambda)$	$f(\lambda) = 1 - T(\lambda)$	1	
fraction of photons emitted by D and absorbed by A (in a radiative energy transfer process)	$a$	$a = \frac{1}{\Phi_D^0} \int_{\lambda} I_{\lambda}^D(\lambda) \left[ 1 - 10^{-\epsilon_A(\lambda)c_A l} \right] d\lambda$ with $c_A$ the molar concentration of acceptor, $\Phi_D^0$ the <i>fluorescence quantum yield</i> of donor in the absence of acceptor, $l$ the thickness of the sample, $I_{\lambda}^D(\lambda)$ and $\epsilon_A(\lambda)$ the spectral distribution of the spectral radiant intensity of the donor fluorescence and the <i>molar decadic absorption coefficient</i> of the acceptor, respectively, with the normalization condition $\Phi_D^0 = \int_{\lambda} I_{\lambda}^D(\lambda) d\lambda$	1	21
Franck-Condon factor		$\left  \int \Theta_{v'}^{(e)} \Theta_v^{(0)} dQ \right ^2$ with $\Theta$ the vibrational wave functions for the initial (0) and final (e) states of a given electronic transition. The integral is over all nuclear coordinates.	1	
frequency (angular)	$\omega$	$2\pi\nu$	$\text{rad s}^{-1}$	
frequency (linear)	$\nu$	$\nu = c/\lambda$	Hz	
fundamental emission anisotropy (theoretical value)	$r_0$	$r_0 = \langle 3 \cos^2 \alpha - 1 \rangle / 5$ $\alpha$ = angle between absorption and emission transition moments	1	

		transition moments		
Gaussian band shape	$F(\nu-\nu_0)$	$F(\nu-\nu_0) = (a/\sqrt{\pi}) \exp[-a^2(\nu-\nu_0)^2]$ with $a^{-1}$ proportional to the width of the band and $\nu_0$ the frequency at the band maximum	1	
Gibbs energy of photoinduced electron transfer	$\Delta_{ET}G^0$	$\Delta_{ET}G^0 = N_A \{e [E^0(D^{+\bullet}/D) - E^0(A/A^{-\bullet})] + w(D^{+\bullet}A^{-\bullet}) - w(DA)\} - \Delta E_{0,0}$ with $w(D^{+\bullet}A^{-\bullet})$ and $w(DA)$ the electrostatic work terms accounting for the Coulombic interactions in the products and reactants, respectively.	J mol <sup>-1</sup>	22
half-life of a transient entity	$\tau_{1/2}$	$c(t = \tau_{1/2}) = c(t = 0)/2$	s	
half-life of a photochromic system	$T_{1/2}$	$A(t = T_{1/2}) = A(t = 0)/2$	s	
hyper-susceptibility	$\chi_e^{(n)}$	$\chi_e^{(2)} = \partial^2 P / \partial E^2$ , 1st hyper-susceptibility $\chi_e^{(3)} = \partial^3 P / \partial E^3$ , 2nd hyper-susceptibility with $P$ the polarization and $E$ the electric field strength.	(C m J <sup>-1</sup> ) <sup>n</sup>	23
irradiance (radiant power received on a surface)	$E$	$E = dP/dS = \int_{2\pi} L \cos\theta \, d\Omega$ $E = \int_{\lambda} E_{\lambda} d\lambda$ with $\theta$ the angle of the beams with the surface and $\Omega$ the solid angle of the <u>incident</u> beam.	W m <sup>-2</sup>	24
lifetime	$\tau$	$\tau = 1/k = 1 / (\sum_i k_i)$ with $k_i$ the first-order rate constants for all decay processes of the excited state. $c(t = \tau) = c(t = 0)/e$	s	
linear dichroism	$\Delta A_l$	$A_z - A_y$ with $A_z$ and $A_y$ the <i>absorbances</i> with the electric vector of linearly polarized light along and perpendicular to the sample axis, respectively.	1	
Lippert-Mataga equation		$\Delta \tilde{\nu} = 2 \frac{(\mu_{exc} - \mu_{gr})^2}{c h r^3} f(\epsilon_r, n) + \text{const.}$ with $\mu_{exc}$ and $\mu_{gr}$ the excited- and ground-state dipole moments of the dissolved molecule, respectively, $c$ the speed of light, $h$ the Planck constant, $r$ the radius of the cavity in which the solute resides, $\epsilon_0$ the electric constant, and $f(\epsilon_r, n)$ the <i>orientation polarizability</i> .		
Lorentzian band shape		$F(\nu-\nu_0) = (1/\pi) \gamma [(\nu-\nu_0)^2 + \gamma^2]^{-1}$ with $\nu_0$ is the mean band position, $\gamma$ the half <i>bandwidth</i> at half maximum and $F(\nu-\nu_0)$ the <i>frequency</i> distribution function.		

magnetic circular dichroism signal	$\Delta$	$\Delta = \frac{[\alpha(\lambda)^- - \alpha(\lambda)^+]}{[\alpha(\lambda)^- + \alpha(\lambda)^+]}$ with $\alpha(\lambda)^+$ and $\alpha(\lambda)^-$ the <i>absorption coefficients</i> for right and left circularly polarized light, respectively.	1	
molar absorption coefficient (See <i>absorption coefficient</i> )				
number density of entities number concentration	$C$	$C = N/V$	$\text{m}^{-3}$	
number of entities	$N$		1	
optical pathlength	$l$		m	
orientation factor (in Förster energy transfer)	$\kappa$	$\kappa = \cos \theta_{DA} - 3 \cos \theta_D \cos \theta_A = \sin \theta_D \sin \theta_A \cos \varphi - 2 \cos \theta_D \cos \theta_A$ with $\theta_{DA}$ the angle between the donor and acceptor moments, $\theta_D$ and $\theta_A$ the angles between these, respectively, and the separation vector, $\varphi$ the angle between the projections of the transition moments on a plane perpendicular to the line through the centres.	1	
orientation polarizability (of a solvent)	$f(\varepsilon_r, n)$	$f(\varepsilon_r, n) = \frac{(\varepsilon_r - 1)}{(2\varepsilon_r + 1)} - \frac{(n^2 - 1)}{(2n^2 + 1)}$ with $\varepsilon_r$ the static <i>relative permittivity</i> and $n$ the refractive index of the medium.	1	
oscillator strength	$f$ value	theoretical $f_{ij} = \frac{8 \pi^2 m c \tilde{\nu}}{3 e^2 h} G M_{ij}^2$ experimental $f_{ij} = (k/n) \int_{\tilde{\nu}} \varepsilon(\tilde{\nu}) d\tilde{\nu}$	1	25
permittivity (see <i>relative permittivity</i> )	$\varepsilon_r$		1	
permittivity of vacuum, see <i>electric constant</i>	$\varepsilon_0$			12
photon exitance (emitted <i>photon flux</i> )	$M_p$	$M_p = dq_p/dS$	$\text{m}^{-2} \text{s}^{-1}$	26
photon exposure	$H_p$	$H_p = \int_t E_p dt$	$\text{m}^{-2}$	26, 27
photon fluence	$H_{p,o}, F_{p,o}$	$H_{p,o} = F_{p,o} = dN_p/dS = \int_t E_{p,o} dt$	$\text{m}^{-2}$	19, 26
photon fluence rate	$E_{p,o}$	$E_{p,o} = dH_{p,o}/dt = dN_p / (dS dt)$	$\text{m}^{-2} \text{s}^{-1}$	19, 26

photon flux, amount basis	$q_{n,p}$	$q_{n,p} = q_p/N_A = (dN_p/dt) / N_A$	$\text{mol s}^{-1}$	28
photon flux, number basis	$q_p$	$dN_p/dt$	$\text{s}^{-1}$	26, 29
photon irradiance	$E_p$	$E_p = dq_p/dS$	$\text{m}^{-2} \text{s}^{-1}$	26, 30
photon number	$N_p$	$N_p = n_p N_A$	1	
photon radiance	$L_p$	for a <u>parallel</u> beam $L_p = (dq_p/dS) / \cos \theta$  for a <u>divergent</u> beam propagating in an elementary cone of solid angle $\Omega$ containing the beam direction $\theta$ . $L_p = d^2q_p / (d\Omega dS \cos \theta)$	$\text{m}^{-2} \text{s}^{-1}$  $\text{m}^{-2} \text{s}^{-1} \text{sr}^{-1}$	26  [7]
Planck constant	$h$	$6.626\ 0693(11) \times 10^{-34}$	J s	12
	$\hbar = h/2\pi$	$1.054\ 571\ 68(18) \times 10^{-34}$	J s	18
polarization (optical)	$\mathbf{P}$	$\mathbf{P} = \mathbf{P}^{(1)} + \mathbf{P}^{(2)} + \mathbf{P}^{(3)} + \dots$ $\mathbf{P} = \varepsilon_0 [\chi^{(1)} \mathbf{E} + (1/2) \chi^{(2)} \mathbf{E}^2 + (1/6) \chi^{(3)} \mathbf{E}^3 + \dots]$ with $\chi^{(n)}$ the hyper-susceptibilities	1	
polarization ratio, see degree of polarization				
pressure	$p$		Pa	
quantum yield of charge carrier formation in a photodiode	$\Phi$  $\Phi_c$	$\Phi = (\text{number of events}) / (\text{number of photons absorbed})$	1	
quenching rate constant, from <i>Stern-Volmer</i> <i>relationship</i>	$k_q$	from $\Phi^0/\Phi$ or $M^0/M = 1 + k_q \tau^0 [Q]$ with $[Q]$ the amount concentration of quencher	$\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$	31
radiance	$L$	for a <u>parallel</u> beam $L = (dP/dS \cos \theta)$  for a <u>divergent</u> beam $L = d^2P / (d\Omega dS \cos \theta)$	$\text{W m}^{-2}$  $\text{W m}^{-2} \text{sr}^{-1}$	[7]
radiant energy	$Q$	$Q = \int_{\lambda} Q_{\lambda} d\lambda$	J	
radiant exitance (for emitted <i>radiant</i> <i>power</i> )	$M$	$M = dP/dS$	$\text{W m}^{-2}$	
radiant exposure	$H$	$H = \int_t E dt = dQ/dS$	$\text{J m}^{-2}$	32
radiant intensity	$I$	$I = dP/d\Omega$	$\text{W sr}^{-1}$	
radiant power, radiant energy per time	$P$	$P = dQ/dt$	W	33

radiative energy transfer (see <i>fraction of photons emitted by D and absorbed by A</i> )				
radiative lifetime	$\tau_0$	$\tau_0 = 1/k_r$	s	
rate constant for radiative step	$k_r$		$s^{-1}$	
reduced (linear) dichroism	$\Delta A_r$	$\Delta A_r = (A_Z - A_Y)/3 A_{iso}$  with $A_Z$ and $A_Y$ the <i>absorbances</i> with the electric vector of linearly polarized light along and perpendicular to the sample axis, respectively, and $A_{iso}$ the isotropic absorbance.	1	
reflectance, reflectivity	$\rho$	$\rho = P_{\lambda}^{refl} / P_{\lambda}^0$ $\rho(l) = \frac{(n_1 - n_2)^2}{(n_1 + n_2)^2}$ with $n_1$ and $n_2$ the refractive index of each of the media.	1	34
refractive index	$n$	$n = c_0 / c$	1	
Rehm-Weller equation for the quenching rate constant of an electron transfer process	$k_q$	$k_q = \frac{k_d}{1 + \frac{k_d}{K_d Z} \left[ \exp\left(\frac{\Delta G^\ddagger}{RT}\right) + \exp\left(\frac{\Delta_{ET}G^0}{RT}\right) \right]}$  with $k_d$ and $k_{-d}$ the rate constant for the formation and separation, respectively, of the encounter complex, $K_d = k_d / k_{-d}$ , $Z$ the universal collision frequency factor, $R$ the gas constant, $T$ the absolute temperature and $\Delta G^\ddagger$ the activation Gibbs energy of the forward electron transfer reaction.		35
relative permittivity	$\epsilon_r$	$\epsilon_r = \epsilon / \epsilon_0$ with $\epsilon_0$ the <i>electric constant</i> .	1	36
reorganization energy (for outer-sphere electron transfer, according to Marcus)	$\lambda$	from $\Delta G^\ddagger = (\lambda + \Delta_{ET}G^0)^2 / 4\lambda$ with $\Delta G^\ddagger$ the activation Gibbs energy and $\lambda$ the reorganization energy (after Marcus).	J	
residual emission anisotropy	$r_\infty$	from $r(t) = (r_0 - r_\infty) \exp(-t/\tau_c) + r_\infty$ with $r_0$ the <i>fundamental emission anisotropy</i> and $\tau_c$ the <i>rotational correlation time</i> .		37
rotational correlation time	$\tau_c, \theta$	from $r(t) = r_0 \exp(-t/\tau_c)$ with $r_0$ the <i>fundamental emission anisotropy</i> and $r(t)$ the <i>emission anisotropy</i> at time $t$	s	

rotational relaxation time	$\rho$	$\rho = 3\tau_c$ with $\tau_c$ the <i>rotational correlation time</i> .	s	
sensitivity of a photodiode	$S_{pd}$	$S_{pd} = I_{pd}/P$	$A W^{-1} = V^{-1}$	38
solid angle	$\Omega$	$\Omega = S/r^2$	sr, 1	39
spectral distribution (of a radiant, luminous or photon quantity)	$X_\lambda(\lambda)$	$X_\lambda(\lambda) = dX(\lambda)/d\lambda$	$[X] m^{-1}$	
spectral fluence (in terms of wavelength)	$H_{\lambda,o}$	$H_{\lambda,o} = dH_o/d\lambda$	$J m^{-3}$	19, 40
spectral fluence rate	$E_{\lambda,o}$	$E_{\lambda,o} = dE_o/d\lambda$	$W m^{-3}$	19, 41
spectral irradiance	$E_\lambda$	$E_\lambda = dE/d\lambda$	$W m^{-3}$	42
spectral overlap integral (normalized) Dexter	$J$	$J = \int_0^\infty I_\lambda^D(\lambda) \varepsilon_A(\lambda) d\lambda$	$m^2 mol^{-1}$	43
Förster	$J$	$J = \int_0^\infty I_\lambda^D(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda$ with $I_\lambda^D(\lambda)$ the normalized <i>spectral distribution</i> of the <i>spectral radiant intensity</i> of the donor emission	$m^6 mol^{-1}$	44
spectral photon flux	$q_{p,\lambda}$	$dq_p/d\lambda$	$s^{-1} m^{-1}$	26
spectral radiant energy	$Q_\lambda$	$dQ/d\lambda$	$J m^{-1}$	45
spectral radiant power	$P_\lambda$	$P_\lambda = dP/d\lambda$	$W m^{-1}$	46
spectral responsivity	$s(\lambda)$	$s(\lambda) = dY_\lambda/dE_\lambda$ with $Y_\lambda$ the spectral output quantity of the system	1	47
spectral sensitivity of an actinometer	$S_{ac}$	$S_{ac}(\lambda) = \Phi(\lambda) \varepsilon(\lambda_{obs})$ or $S_{ac}(\lambda) = \Phi(\lambda) \Delta\varepsilon(\lambda_{obs})$ with $\Delta\varepsilon(\lambda_{obs})$ the difference in <i>molar absorption coefficient</i> between product and reactant at the observation wavelength.	$m^2 mol^{-1}$	48
speed of light in vacuum in a medium	$c_0$ $c$	$c_0 = 299\,792\,458 m s^{-1}$ $c = c_0/n$	$m s^{-1}$ $m s^{-1}$	
steady-state emission anisotropy	$\bar{r}$	$\bar{r} = \frac{\int_0^\infty r(t) I(t) dt}{\int_0^\infty I(t) dt}$	1	49
Stern-Volmer constant  See <i>Stern-Volmer equation</i>	$K_{SV} = k_q \tau^0$	from $\Phi^0/\Phi$ or $M^0/M = 1 + K_{SV} [Q]$ with $[Q]$ the amount concentration of quencher	$dm^3 mol^{-1}$	31

Stern-Volmer equation	$\Phi^0/\Phi$ or $M^0/M$ $\tau^0/\tau$	$\Phi^0/\Phi$ or $M^0/M = 1 + k_q \tau^0 [Q]$ $\tau^0/\tau = 1 + k_q \tau^0 [Q]$ with [Q] the amount concentration of quencher, $\tau^0$ the <i>lifetime</i> of excited state in the absence of quencher and $\tau$ the lifetime in the presence of quencher	1	31
temperature (Celsius)	$\theta, t$	$\theta/^{\circ}\text{C} = T/\text{K} - 273.15$	$^{\circ}\text{C}$	
temperature, thermodynamic	$T$		K	
time	$t$		s	
transfer quantum efficiency (in Förster energy transfer)	$\Phi_T$	$\Phi_T = 1 - \frac{\tau_D}{\tau_D^0}$ with $\tau_D$ the donor excited-state <i>lifetime</i> in the presence of acceptor, and $\tau_D^0$ in its absence.	1	
transition (dipole) moment	$M_{if}$	$M_{if} = \langle f   M_{op}   i \rangle$ with $M_{op}$ the electric dipole moment operator. $\langle \rangle$ indicates a matrix element	C m	16
transmittance	$T$	$T = P_{\lambda} / P_{\lambda}^0$	1	2
volume	$V$		$\text{m}^3$	
wavelength	$\lambda$		m	
wavenumber in vacuum	$\tilde{\nu}$	$\tilde{\nu} = \nu / c_0 = 1 / n\lambda$	$\text{m}^{-1}$	
Weller correlation		$\Delta H(\text{D}^+\text{A}^-, \text{hexane}) = e [E^{\circ}(\text{D}^{+\bullet}/\text{D}) - E^{\circ}(\text{A}/\text{A}^{\bullet-})] + e \Delta E$ with $E^{\circ}(\text{D}^{+\bullet}/\text{D})$ and $E^{\circ}(\text{A}/\text{A}^{\bullet-})$ the standard electrode potentials of the donor and acceptor, respectively.	$\text{kJ mol}^{-1}$	50
$Z_{50}$ number (in photochromic systems)	$Z_{50}$	number of cycles needed to lose 50 % of initial absorbance.	1	

### Notes

- (1) Entries in the table are consistent with terminology, symbols and units given in [7,8,9], and are slightly modified from those in [4], terms from which are included in [20]. Symbols individually listed in the Table may not be explained within a definition.
- (2) If losses from reflection, scattering and luminescence are neglected,  $T = P/P^0 = I/I^0$ , where superscript 0 (zero) indicates incident *radiant power* (or intensity) and no superscript transmitted radiant power (or intensity). *Transmittance* depends on pathlength, which should be specified. In common usage  $A$  is given for 1 cm pathlength unless otherwise specified.
- (3) Superscript 0 (zero) indicates incident radiation.
- (4) Common unit is  $\text{einstein s}^{-1} \text{cm}^{-3}$ ; superscript 0 (zero) indicates incident photons.
- (5) Common unit is  $\text{W cm}^{-3} \text{nm}^{-1}$ ; superscript 0 (zero) indicates incident *radiant power*.
- (6) In spectroscopy, usually defined in terms of the *spectral radiant power*,  $P_{\lambda}$ .

- (7) Numerical values are often quoted in  $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$ . Note the lack of compactness in using two submultiples of length.  $\varepsilon$  depends on wavelength, or wavenumber, or frequency, and may be quoted as  $\varepsilon(\lambda)$ , or as  $\varepsilon(\tilde{\nu})$ , or as  $\varepsilon(\nu)$ .
- (8) In spectroscopy, the net cross-section resulting from the sum of effects due to absorption and induced emission. A conversion equation in common units is  $\sigma/\text{cm}^2 = (3.823\ 6 \times 10^{-21}/\text{mol}) \times (\varepsilon/\text{dm}^3 \text{cm}^{-1} \text{mol}^{-1})$ .
- (9) Usual units are  $\text{mol dm}^{-3}$  or  $\text{mol L}^{-1}$  or submultiples. Commonly the non-SI unit M (small cap) is used as an abbreviation for  $\text{mol dm}^{-3}$ .
- (10) Amount of photons is often given in the non-SI unit *einstein* = mol of photons.
- (11) *Attenuance* reduces to *absorbance* for a not reflected or scattered beam.
- (12) 2002 value [162].
- (13) Common non-SI unit is electronvolt (eV) =  $1.602\ 176\ 53\ (14) \times 10^{-19}$  J; for one mole of electrons  $1 \text{ eV} = 96.485 \text{ kJ mol}^{-1}$ .
- (14) Common non-SI unit is Angström ( $\text{\AA}$ ) =  $10^{-10}$  m. Common SI submultiples are nm, pm.  $\kappa^2$  can take values from 0 (perpendicular transition moments) to 4 (collinear transition moments). When the transition moments are parallel and perpendicular to the separation vector,  $\kappa^2 = 1$ . When they are in line (i.e., their moments are strictly along the separation vector),  $\kappa^2 = 4$ . For randomly oriented *transition (dipole) moments*, e.g., in fluid solutions,  $\kappa^2 = 2/3$ . A practical expression is
- $$R_0 / \text{nm} = 2.108 \times 10^{-2} \left\{ \kappa^2 \Phi_D^0 n^{-4} \int_{\lambda} I_{\lambda}^D(\lambda) [\varepsilon_A(\lambda) / \text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}] (\lambda / \text{nm})^4 d\lambda \right\}^{1/6}$$
- with  $I_{\lambda}^D(\lambda)$  the normalized *spectral radiant intensity* of the donor so that  $\int_{\lambda} I_{\lambda}^D(\lambda) d\lambda = 1$ ;  $\varepsilon_A(\lambda)$  is the *molar decadic absorption coefficient* of the acceptor. Foerster is an alternative and acceptable spelling for Förster.
- (15) When  $x$  in the equation for the differential *quantum yield* is either a number concentration, or an amount concentration, it is convenient to use in the denominator the *rate of absorbed photons per volume (absorbed photon flux density)* number basis, or amount basis, respectively.
- (16) Common non-SI unit is Debye (D)  $\approx 3.335\ 64 \times 10^{-30}$  C m.
- (17) Ratio of the *radiant power* emitted by the sample to that emitted by a black body ( $M_{\text{bb}}$ ) at the same temperature.
- (18) For a beam not scattered or reflected by the sample, same as *radiant exposure*,  $H$ . When applied to the total *radiant energy* incident from all directions the symbol  $H_o$  or  $F_o$  is used.
- (19) The symbols related to *radiant energy* incident from all directions have a subscript o (the letter o), not to be confused with 0 (zero) for incident radiation (prior to absorption, footnote 2).
- (20) For an incident beam not reflected or scattered by the target or its surroundings, same as *irradiance*. When applied to the total radiant energy incident from all directions the symbol  $E_o$  is used.
- (21) For relatively low *absorbance*,  $a$  can be approximated by  $a = \frac{2.3}{\Phi_D^0} c_A l \int_{\lambda} I_{\lambda}^D(\lambda) \varepsilon_A(\lambda) d\lambda$  where the integral represents the overlap between the donor *fluorescence spectrum* and the acceptor *absorption spectrum*.
- (22) For calculations with the equation as given, the terms are quoted with units:  $E^{\circ}(\text{D}^{\bullet+}/\text{D})/V$ : standard electrode potential of the donor cation radical resulting from the electron transfer,  $E^{\circ}(\text{A}/\text{A}^{\bullet-})/V$ : standard electrode potential of the acceptor (both relative to the same reference electrode),  $\Delta E_{0,0}/\text{J mol}^{-1}$ : vibrational zero electronic energy of the excited partner (when a vibrationally equilibrated excited state at energy  $E_{0,0}$  takes part in the reaction), all data referring to the same solvent.  $w(\text{D}^{\bullet+}\text{A}^{\bullet-})/J$  and  $w(\text{DA})/J$  are electrostatic work terms accounting for the effect of Coulombic attraction in the products and reactants, respectively.
- (23) In an anisotropic medium,  $\chi_e^{(1)}$ ,  $\chi_e^{(2)}$ , and  $\chi_e^{(3)}$  are tensors of rank 2, 3, and 4, respectively. For an isotropic medium (such as a liquid) or for a crystal with a centrosymmetric unit cell,  $\chi_e^{(2)} = 0$  by symmetry. These quantities characterize a dielectric medium in the same way that the polarizability and the hyper-polarizabilities characterize a molecule.
- (24) The corresponding term for a beam incident from all directions is *fluence rate* ( $E_o$ ).
- (25)  $G$  = degeneracy of the final state,  $M_{ij}$  = transition (dipole) moment,  $\varepsilon(\tilde{\nu})$  = *molar decadic absorption coefficient* at wavenumber  $\tilde{\nu}$ ,  $n$  = average refractive index of the medium,  $c$  = speed of light,  $e$  = elementary charge,  $h$  = Planck's constant,  $m$  = mass of the electron; For  $\varepsilon(\tilde{\nu})/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$  (common units)  $k = 4.32 \times 10^{-9} \text{ dm}^{-3} \text{mol cm}$ . The experimental equation takes into account line broadening effects.
- (26) These quantities, defined on a number basis, can be expressed on a chemical amount basis by dividing by the Avogadro constant, e.g., *photon flux* (chemical amount basis) =  $q_p/N_A$ . If distinction needs to be made between quantities based on chemical amount and number, then symbols such as  $q_{n,p}$  and  $q_p$  can be used.
- (27) The corresponding term for a beam incident from all directions is *photon fluence* ( $H_{p,o} = F_{p,o}$ ).
- (28) Common unit is einstein  $\text{s}^{-1}$ . A term not in accordance with the usual definition of flux in [7].
- (29) As defined in [4] (see also [20]); called *photon flux* in [8], a term not in accordance with the usual definition of flux in [7].

- (30) The corresponding term for a beam incident from all directions is *photon fluence rate*,  $E_{p,0}$ .
- (31) Superscript 0 (zero) indicates *quantum yield* or *radiant intensity*, and *lifetime* in the absence of quencher, no superscript indicates the quantities in the presence of quencher Q. Common units for the quenching rate constant are  $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ .
- (32) The corresponding term for a beam incident from all directions is *fluence*,  $H_0 = F_0$ .
- (33) Definition from [7]; synonymous with *radiant energy power*, *radiant energy flux* defined in [8].
- (34) Superscript 0 indicates incident *radiant power* and refl reflected radiant power.
- (35) In the original formulation of this equation [139] the value  $\frac{k_d}{K_d Z} = 0.25$  in acetonitrile was used.
- (36) Formerly called dielectric constant, [7].
- (37)  $\tau_c$  is the rotational correlation time and  $r_0$  the *fundamental emission anisotropy*.
- (38) Related to  $q_{n,p}$  by  $q_{n,p} = [\lambda / (N_A h c S_{pd})] i_{pd}$  with  $i_{pd}$  the electric current of the photodiode.
- (39) The steradian is an SI supplementary unit, but is dimensionless, so has SI unit 1.
- (40) Other physical quantities  $X$  such as *irradiance*, *photon flux*, *photon fluence*, *photon fluence rate* and *radiant intensity* may be used to derive the corresponding “spectral” quantity (relative to *wavelength*) by  $X_\lambda = dX/d\lambda$ . Analogous quantities relative to *frequency* or to *wavenumber* may also be defined.
- (41) Common units are  $\text{W m}^{-2} \text{nm}^{-1}$ . Analogous quantities relative to frequency or to wavenumber may also be defined.
- (42) Common units are  $\text{W m}^{-2} \text{nm}^{-1}$ . Analogous quantities relative to frequency or to wavenumber may also be defined.
- (43)  $I_\lambda^D(\lambda)$  is the normalized spectral distribution of the *spectral radiant intensity* of the donor emission and  $\varepsilon_A(\lambda)$  is the normalized *molar decadic absorption coefficient* of the acceptor. Common unit of  $J$  is  $\text{dm}^3 \text{cm}^{-1} \text{mol}^{-1}$ .  
Normalization condition is  $\int_0^\infty I_\lambda^D(\lambda) d\lambda = \int_0^\infty \varepsilon_A(\lambda) d\lambda = 1$ .
- (44)  $I_\lambda^D(\lambda)$  is the normalized spectral distribution of the *spectral radiant intensity* of the donor emission normalized so that  $\int_0^\infty I_\lambda^D(\lambda) d\lambda = 1$ ,  $\varepsilon_A(\lambda)$  is the *molar decadic absorption coefficient* of the acceptor. Common unit of the overlap integral  $J$  is  $\text{dm}^3 \text{cm}^3 \text{mol}^{-1}$ .
- (45) Common units are  $\text{J nm}^{-1}$ . Analogous quantity relative to frequency or to wavenumber may also be defined.
- (46) Common units are  $\text{W nm}^{-1}$ . Analogous quantity relative to frequency or to wavenumber may also be defined.
- (47) Relative biological or chemical photoresponse per incident *radiant power* as a function of *wavelength*.
- (48)  $\lambda$  is the excitation wavelength and  $\lambda_{\text{obs}}$  is the observation wavelength, which may be the same as or differ from the former. The first definition corresponds to the case in which the actinometer does not absorb at  $\lambda_{\text{obs}}$ , whereas the second definition corresponds to the case in which the actinometer absorbs at  $\lambda_{\text{obs}}$ . Common units are  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ .
- (49)  $r(t)$  is the *anisotropy* and  $I(t)$  is the fluorescence intensity (*emission radiant intensity*), both at time  $t$  following a  $\delta$ -pulse excitation.
- (50) In the case diethylaniline as donor and aromatic hydrocarbons as acceptors, the last term on the right, i.e.,  $e \Delta E = (0.15 \pm 0.10) \text{eV}$ . This equation assumes a constant Coulomb term and a constant entropy change within a particular series of partners;  $e$  is the elementary charge.

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