

Glossary of Terms used in Photochemistry

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INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

ORGANIC AND BIOMOLECULAR CHEMISTRY DIVISION*
SUBCOMMITTEE ON PHOTOCHEMISTRY

GLOSSARY OF TERMS USED IN PHOTOCHEMISTRY 3rd EDITION

(IUPAC Recommendations 2006)

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Glossary of terms used in photochemistry, 3rd edition

(IUPAC Recommendations 2006)

Abstract: The second 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, nonlinear 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.

Keywords: IUPAC Organic and Biomolecular Chemistry Division; glossary; photochemistry; photobiology; electron transfer; energy transfer; fluorescence; radiation-related units.

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 Organic Chemistry Division 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 home pages.

This third edition both incorporates revisions and enhances the Glossary by introducing additional terms related to organic photochemical reactions, terms in the area of molecular anisotropy; the use of polarized ultraviolet, visible, or infrared radiation; and nonlinear 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 Organic and Biomolecular Chemistry Division 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 IUPAC Physical Organic Chemistry Commission has been followed for the typeface used: *italicized* 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. Where synonymous terms are in common usage, the recommended term (“main term”) is followed on the second line of the glossary entry by the synonym or synonyms in roman type, which are then followed by the definition and notes, if any. The synonyms are also listed separately in their proper alphabetical position, with the annotation “See (main term)”. The annotation “See (term)” may also refer to use of the term within another definition or within notes to that definition. The annotation “See also (term)” refers to a related term.

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]. Cross-checking 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 [7–9]. 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 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 IUPAC “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 revised terms are designated 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 Note on units

SI units are adopted, with some exceptions, prominently in the use of the *molar decadic absorption coefficient*, ϵ , 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 Note on symbols

Functional dependence of a physical quantity f on a variable x is indicated by placing the variable in parentheses following the symbol for the function; e.g., $\epsilon(\lambda)$. Differentiation of a physical quantity f

with respect to a variable x is indicated by a subscript x ; e.g., the typical *spectral radiant power* quantity $P_\lambda = dP/d\lambda$.

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_0 or F_0 for fluence, E_0 for fluence rate, $H_{p,0}$ or $F_{p,0}$ for photon fluence, and $E_{p,0}$ for photon fluence rate; note the letter o as subscript. This has been done primarily to comply with internationally agreed-upon symbols. It is important, however, to avoid confusion with the terms used to designate an amount of energy (or photons) prior to absorption. In these cases, the **superscript 0 (zero)** is used.

1.4 Note on the relationship between spectral, radiometric, and photonic quantities

When a quantity expressed in photonic units (G_p) covers a wavelength range (polychromatic irradiation between λ_1 and λ_2), then G_p is the integral between λ_1 and λ_2 of the corresponding spectral photonic quantity, $G_p(\lambda)$:

$$G_p = \int_{\lambda_1}^{\lambda_2} G_p(\lambda) d\lambda$$

(e.g., spectral photon flux).

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

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

with $E(\lambda) = h c/\lambda$, the energy of a photon of wavelength λ .

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

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

Or, more useful in practice:

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

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

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*, P_λ^0 divided by the transmitted spectral radiant power, P_λ :

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

$T(\lambda)$ is the (internal) *transmittance* at the defined wavelength. The terms *absorbancy*, *extinction*, and *optical density* should no longer be used.

When natural logarithms are used, the *napierian absorbance* is the logarithm to the base e of the incident *spectral radiant power*, P_{λ}^0 divided by the transmitted spectral radiant power, P_{λ} :

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

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_{λ} , was used instead of *spectral radiant power*, P_{λ} , [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. However, the wavelength should be specified for which the value of the particular property is reported.

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

See also *absorption coefficient*, *absorptance*, *attenuance*, *Beer–Lambert law*, *depth of penetration*, *fraction of light absorbed*, *internal transmittance*, *Lambert law*, *molar absorption coefficient*.

revG2

absorbed (spectral) photon flux density

Number of photons of a particular *wavelength*, per time interval (*spectral photon flux*, number basis, $q_{p,\lambda}$, or *spectral photon flux*, amount basis, $q_{n,p,\lambda}$) absorbed by a system per volume, V . On number basis, SI unit is $\text{s}^{-1} \text{m}^{-4}$; common unit is $\text{s}^{-1} \text{cm}^{-3} \text{nm}^{-1}$. On amount basis, SI unit is $\text{mol s}^{-1} \text{m}^{-4}$; common unit is $\text{einstein s}^{-1} \text{cm}^{-3} \text{nm}^{-1}$.

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

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

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

absorbed (spectral) radiant power density

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

Note: Mathematical expression: $\frac{P_{\lambda}^0 [1 - 10^{-A(\lambda)}]}{V}$, where $A(\lambda)$ is the *absorbance* at wavelength λ and superscript 0 (zero) 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 also *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* ν is given by the difference ΔE 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 [21].

revG2

absorption coefficient (linear decadic a or linear napierian α)

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_{λ}^0 and P_{λ} 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 α is the linear napierian absorption coefficient. Since *absorbance* is a dimensionless quantity, the coherent SI unit for a and α is m^{-1} ; the common unit is cm^{-1} .

See also *absorptivity*, *molar absorption coefficient*.

revG2

absorption cross-section, σ

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_{λ}^0 and P_{λ} are, respectively, the incident and transmitted *spectral radiant power*.

SI unit is m^2 , common unit is 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_{A} the Avogadro constant. A conversion equation in common units is:

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

See also *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* λ . This term is preferred to *absorptance*.

Note 1: The wavelength symbol may be omitted for f , T , and A . The wavelength should be specified for which the value of the particular property is reported.

Note 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*, ν , *wavenumber*, $\tilde{\nu}$, or *wavelength*, λ .

absorptivity

Absorbance 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 nonliving 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 potassium oxalatoferrate(III), $K_3[Fe(C_2O_4)_3]$ (among other systems) can be used as a chemical actinometer. Bolometers, thermopiles, and photodiodes are physical devices giving a reading of the radiation impinging on them that can be correlated to the number of photons detected as well as to the number of photons entering the chemical reactor.

Note 2: For a list of chemical actinometers and a critical discussion about actinometry, see [22].

See also *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*, vs. *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 vs. wavelength is then the action spectrum of the photoresponse.

See also *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 also *aza-di- π -methane rearrangement*, *di- π -methane rearrangement*, *di- π -silane rearrangement*, *oxa-di- π -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*).

See also *diabatic electron transfer*.
See [21,23].
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 [21].
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 α,β -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: Geometrical isomerization of a C–C double bond is called a *cis/trans isomerization* in 1,2-disubstituted alkenes. *E/Z isomerization* 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 also *aza-di- π -methane rearrangement*, *di- π -methane rearrangement*, *di- π -silane rearrangement*, *oxa-di- π -methane rearrangement*.

alpha-cleavage, α -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-(α)-elimination*.

alpha-elimination, α -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-(α)-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.

See also *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.

See also *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

energy pooling

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.

See also *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 vapor and xenon under high pressure. Its output in the ultraviolet region is higher than that of the *mercury–xenon arc*.

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

revG2

aromatic photocycloaddition

Inter- and intramolecular *photochemical processes* involving the addition of a C–C double (or triple) bond (i) to 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^{2,8}]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 also *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 also *crystal photochemistry*, *photochirogenesis*, [27–30].

attenuance, D

Logarithm to the base 10 of the incident *spectral radiant power*, P_{λ}^0 , divided by the transmitted spectral radiant power, P_{λ} [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 also *Beer–Lambert law*, *depth of penetration*.

revG2

attenuance filter

neutral-density filter

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

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.

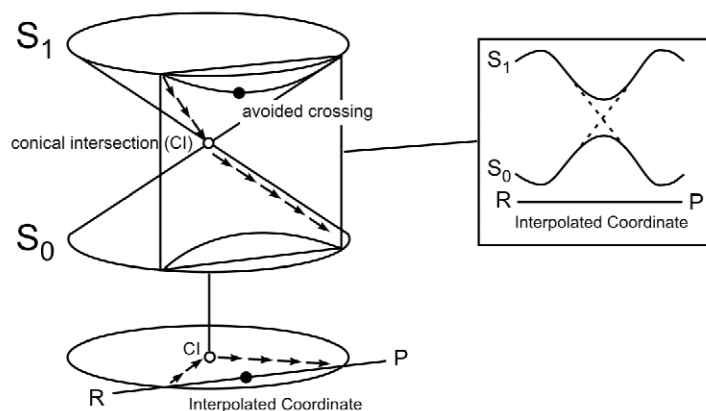
G2/GB

avoided crossing (of potential energy surfaces)

intended crossing

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).

Note: If the electronic states are of the same symmetry, the *surface crossing* is always avoided in diatomic species and usually allowed in polyatomic species. 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.



See also *Born–Oppenheimer approximation*, *conical intersection*, *noncrossing rule*.

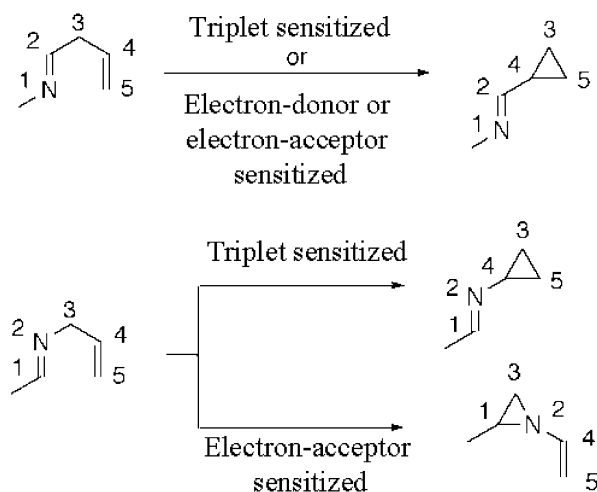
See [6,21].

revG2

aza-di- π -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.

Note: The rearrangement formally amounts to a 1,2-shift of the imino group and “bond formation” between the C(3) and C(5) carbon atoms of the azadiene skeleton. 1-Aza-1,4-dienes also undergo the rearrangement to cyclopropylimines using electron-acceptor and electron-donor *sensitizers* via radical-cation and radical-anion intermediates, respectively. 2-Aza-1,4-dienes rearrange to *N*-vinylaziridines on irradiation using electron-acceptor sensitizers. In this instance the reaction amounts to a 1,2-shift of the alkene unit and “bond formation” between the C(1) and C(3) carbon atoms of the azadiene skeleton.



See also *di- π -methane rearrangement*, *di- π -silane rearrangement*, *oxa-di- π -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. Process better designated as *electron back-transfer*. 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*, electron back-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 also *Fermi level*.

G2/GB

bandpass filter

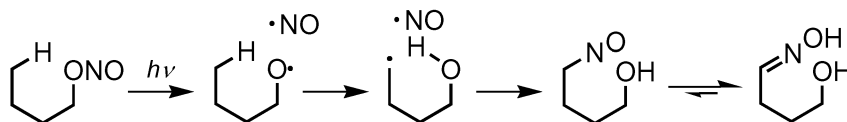
Optical device that permits the transmission of radiation within a specified *wavelength* range and does not permit transmission of radiation at higher or lower wavelengths. It can be an interference or a colored *filter*.

See also *cut-off filter*.

G2/GB

Barton reaction

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

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

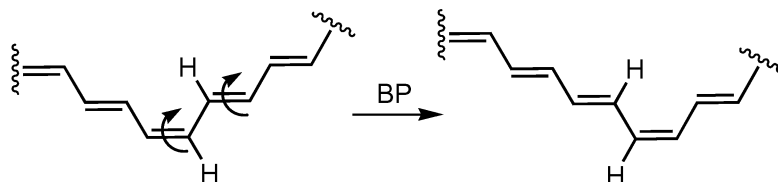
where the proportionality constant, $\varepsilon(\lambda)$, is the *molar (decadic) absorption coefficient*, and P_{λ}^0 and P_{λ} are, respectively, the incident and transmitted *spectral radiant power*. For l in cm and c in mol dm⁻³ (M), $\varepsilon(\lambda)$ will result in dm³ mol⁻¹ cm⁻¹ (M⁻¹ cm⁻¹), a commonly used unit. SI unit of $\varepsilon(\lambda)$ is m² mol⁻¹ (10 dm³ mol⁻¹ cm⁻¹).

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 also *absorbance*, *attenuance*, *extinction coefficient*, *Lambert law*, [34].
revG2

bicycle-pedal (BP) mechanism

Volume-conserving mechanism proposed for the *photoisomerization* of conjugated double bonds. Two alternating double bonds rotate concertedly with only the two CH units turning in and out of the plane of the molecule.

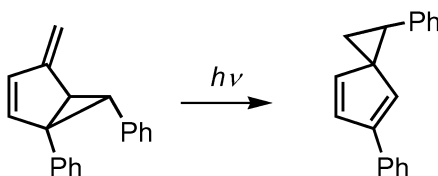


See also *hula-twist mechanism*.
See [35,36].

bicycle rearrangement

Photochemical rearrangement of unsaturated substrates by group migration over a π perimeter following the movement of a bicycle pedal.

An example is [37]:



See also *photoisomerization*, [38].

bioluminescence

Luminescence produced by living systems.

See also *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 also *multiphoton process*.

G2/GB

bipolarons

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

See also *self-localized excitations*.

biradical

See *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: $\Psi(q, Q) \equiv \Phi(q, Q) \Theta(Q)$, 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 [6,21].

branching plane

At a *conical intersection* point, the plane spanned by the gradient difference vector (x_1) and the gradient of the interstate coupling vector (x_2):

$$x_1 = \frac{\partial(E_2 - E_1)}{\partial Q} \mathbf{q}$$

$$x_2 = \left\langle \mathbf{C}_1' \left(\frac{\partial H}{\partial Q} \right) \mathbf{C}_2 \right\rangle \mathbf{q}$$

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 *g-h* plane. Inspection of x_1 and 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 [39].

Brewster angle, θ_B

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

Note 1: Expression for Brewster angle: $\theta_B = \arctan(n_2 / n_1) = \arctan(\epsilon_2 / \epsilon_1)^{1/2}$ where n_2 and n_1 are the refractive indices of the receiving surface and the initial medium, respectively, and ϵ_2 and ϵ_1 are the relative static 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 nonquantitative 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* (Φ_f) of a dye and the *molar decadic absorption coefficient* at the excitation *wavelength* $\epsilon(\lambda)$, i.e., $\Phi_f \epsilon(\lambda)$.

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 also *photoremovable protecting group*, [40].

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 *electron back-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 also *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 also *charge-transfer absorption*, [34].

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.

See also *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.

G2/GB

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 [21].

G2/GB

chemically initiated electron exchange luminescence (CIEEL)

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

G2/GB

chemiexcitation

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

See also *chemiluminescence*, *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: 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 [21].

revG2

CIDEP

Acronym for *chemically induced dynamic electron polarization*.

CIDNP

Acronym for *chemically induced dynamic nuclear polarization*.

CIEEL

Acronym for *chemically initiated electron exchange luminescence*.

circular dichroism (CD)

See *dichroism*.

***cis/trans* photoisomerization**

Photoinduced geometric isomerization about a double bond.

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

Note 2: 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.

Note 3: In a C–C double bond, a geometrical *cis/trans* (or *E/Z*) isomerization implies a 180° rotation (except when modified by steric interactions), whereas in other bonds the mechanism might be different, e.g., in azocompounds, a *cis/trans* photoisomerization may occur through an inversion at a N center.

See [41].

CO₂ laser

Continuous (CW) or pulsed source of *coherent radiation* normally tunable through the CO₂ vibration–rotation band centered near 10.6 μm.

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

G2/GB

coherence 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 Δl 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 [42].
revG2

coherence 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

colorability

Ability of a colorless or slightly colored *photochromic* material to develop color.

color scale

Series of ordered numbers that represents observable gradations of a given attribute or gradations of a combination of attributes of color 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 also *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 nondynamic correlation), whereas the remaining electron correlation (the so-called dynamic correlation) is included through the use of second-order perturbation theory.

See also *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 [39].

concentration depolarization

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

See also *energy transfer*, *photoselection*, [34].

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. Term usually used to describe the properties of metals and semiconductors.

See also *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_2): $1\sigma_g^2$, $1\sigma_u^2$, $2\sigma_g^2$, $2\sigma_u^2$, $1\pi_u^4$, $3\sigma_g^2$, $1\pi_g^2$, 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.

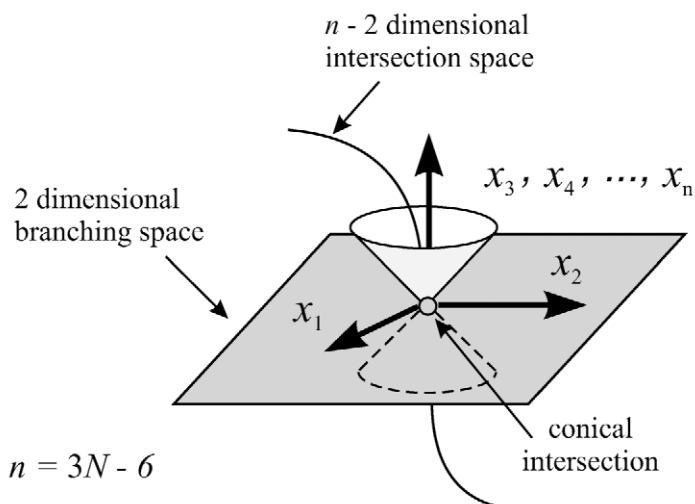
See [6].
revG2

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 [6,21,39].

contact ion pair

tight 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.

See [17].

conversion cross-section

Product of the *quantum yield* by the *absorption cross-section*, $\sigma \Phi$. SI unit is m^2 ; commonly expressed in 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*, ν , *wavenumber*, $\tilde{\nu}$, or *wavelength*, λ .

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

G2/GB

copper vapor laser

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

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

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 nonrelativistic 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*.

See also *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

current yield

See also *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 also *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.
See also *cut-off filter*, *filter*.

CW

Acronym for *continuous wave*. Nonpulsed 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., [43].
G2/GB

dark reaction

Chemical reaction that does not require or depend on the presence of light. Contrasts with a *photochemical reaction*, which is initiated by light absorption by one or more of the reactants [5].

Note: A dark reaction is essentially a thermally activated reaction.

DAS

Acronym for *decay-associated spectra*.
See *global analysis*.

Dauben–Salem–Turro rules

Set of rules proposed in 1975 to classify *photochemical reactions* based on *correlation diagrams* and under the assumption that all photochemical processes are controlled by the generation of *primary products* with characteristics of diradicals, i.e., considering the physical fact that the initial single excitation separates two electrons of a pair into two distinct orbitals. The reactions are classified according to their topicity, i.e., the total number and nature of available radical sites generated in the primary photochemical product.

See [44].

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 [45].
G2/GB

deactivation

Loss of energy by an excited molecular entity.

Note: Examples are decays at a conical intersection and singlet–triplet surface crossing.

See also *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.

DEDMR

See *ODMR*.

G2/GB

degree of (polarization) anisotropy

See *emission anisotropy*.

delayed fluorescence

See *delayed luminescence*.

G2

delayed luminescence

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

Note: The following mechanisms of luminescence provide examples:

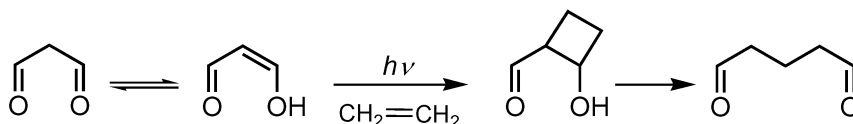
- (1) *triplet–triplet annihilation* to form one molecular entity in its *excited singlet state* and another molecular entity in its electronic *ground state* (sometimes referred to as P type); in diffusion-controlled annihilation, the efficiency of this process is dominated by the *spin-statistical 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 [46].

G2/GB

de Mayo reaction

Photochemical process leading to the formation of cyclobutanols by cycloaddition of an alkene to a 1,3-dicarbonyl-enol. 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 also *photocycloaddition*, [47,48].

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

See also *absorbance*, *attenuance*.

revG2

Dexter excitation transfer (electron-exchange excitation transfer)

Nonradiative 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

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

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 *wavelength* 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* vs. 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.

See also *radiative energy transfer*.

See [46,49].

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. The electronic transmission factor is $\ll 1$ (see *Marcus equation*) for diabatic electron transfer.

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

See also *adiabatic electron transfer*.

See [21].

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 *nonadiabatic 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 [21].

revG2

dichroic filter

See *interference filter*.

Note: The name dichroic arises from the fact that the filter appears one color 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

Dependence of *absorbance* of a sample 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, $\Delta A_{\text{L}} = A_{\text{Z}} - A_{\text{Y}}$, or circular dichroism (CD) in which the difference in absorption for left minus right circularly polarized beams is measured, $\Delta A_{\text{C}} = A_{\text{L}} - A_{\text{R}}$.

See also *light polarization, linear dichroism*, [34,46].

dielectric constant

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

G2/GB

differential quantum yield

See *quantum yield*.

diode laser

semiconductor 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 [50].

G2

dipolar mechanism (of energy transfer)

See *Förster-resonance-energy transfer (FRET)*.

See also *energy transfer*.

revG2

dipole–dipole excitation transfer

See *Förster-resonance-energy transfer (FRET)*.

See also *energy transfer*.

revG2

diradical

biradical

Even-electron molecular entity with two (possibly delocalized) radical centers. Synonymous with biradical. Species in which the two radical centers have a weak covalent interaction or have different

electronegativities are often referred to as *diradicaloids* (or biradicaloids). If the two radical centers 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 centers 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 nonbonding molecular orbitals, two of the natural orbitals have occupancies close to one, etc.

See [21,51].
revG2

diradicaloid

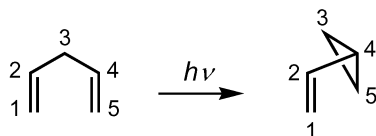
biradicaloid

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

di- π -methane rearrangement

Photochemical reaction of a molecular entity comprising two π -systems, separated by a saturated carbon atom (a 1,4-diene or an allyl-substituted aromatic analog), to form an ene- (or aryl-) substituted cyclopropane.

Note: The rearrangement formally amounts to a 1,2 shift of one ene group (in the diene) or the aryl group (in the allyl-aromatic analog) and “bond formation” between the lateral carbons of the nonmigrating moiety.

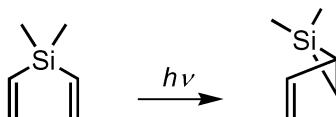


See also *aza-di- π -methane rearrangement*, *di- π -silane rearrangement*, *oxa-di- π -methane rearrangement*.

See [31].
G2/GB

di- π -silane rearrangement

Silicon version of the *di- π -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 J m^{-3} or J g^{-1} and mol m^{-3} or mol g^{-1} , respectively. Common units are einstein m^{-3} or 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.

See also *einstein*, *UV dose*.

G2/GB

doublet state

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

See also *multiplicity*.

G2/GB

downconversion

Process by which a *photon* with *frequency* ν_1 interacts with a nonlinear medium and splits into two simultaneously emitted photons with frequencies ν_2 and ν_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 nonlinear material. This in turn depends on the power of the incident radiation, the photon frequencies, their indices of refraction in the material, and the nonlinear “hyper-susceptibility” of the material.

See also *nonlinear optical techniques*, *parametric processes*, *polarization*, [42].

driving force

The negative of the standard Gibbs energy change (ΔG^0) for a particular reaction, e.g., for *energy transfer* or *electron transfer* ($\Delta_{\text{ET}}G^0$).

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*.

See also *polar driving force*.

See [23].

revG2

Drude–Nernst equation (for electrostriction)

Equation describing the contraction (ΔV_{el}) taking place in a dielectric medium of relative static permittivity ϵ_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, $\partial \ln \epsilon_r / \partial p$, is not known for all media, there are approximations to evaluate this term as a function of ϵ_r and of the “isothermal compressibility” of the medium, κ_T .

See also *electrostriction*, [52].

dual fluorescence (of systems or molecular species)

Systems or molecular species showing two *fluorescence* bands. Several nontrivial 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: 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

effectiveness

See *spectral effectiveness*.

G2/GB

efficiency (of a step), η

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.

See also *quantum yield*.

G2/GB

efficiency spectrum

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

Compare with *spectral effectiveness*; see also *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* ν 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

Nonthermal 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)*.

See also *electrogenerated chemiluminescence*.

revG2

electron back-transfer

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. This term is preferred to *back electron-transfer*.

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*, electron back-transfer will result in *charge recombination*.

electron correlation

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

See also *correlation energy*.

See [6].

G2/GB

electron-exchange excitation transfer

Same as *Dexter excitation transfer*.

See also *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.

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

G2/GB

electron-transfer photosensitization

Photochemical process in which a reaction of a nonabsorbing 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.

See also *photosensitization*.

G2/GB

electronic configuration

See *configuration*.

G2/GB

electronic energy hopping

See *electronic energy migration*.

electronic energy migration

electronic energy hopping
energy migration

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, κ_{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 (*photoconductive* 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 centers 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 also *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 also *multiplicity*, [53].

revG2

emission (of light)

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

See also *fluorescence*, *phosphorescence*.

See [46].

revG2

emission anisotropy

degree of (*polarization*) anisotropy
luminescence 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

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

where $r(t)$ is the anisotropy and $I(t)$ is the *radiant intensity* of the emission, both at time t following a δ -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 α 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 δ -pulse excitation, the theoretical value at time zero is identified with the fundamental emission anisotropy.

See also *light polarization, uniaxial sample*, [34,46].

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*, ν , *wavenumber*, $\tilde{\nu}$, or *wavelength*, λ .

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

See [46].

G2/GB

emissivity

See *emittance*.

emittance, e

emissivity

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

Note: Mathematical expression: M/M_{bb} with M and M_{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*.

See also *contact ion pair*.

G2/GB

energy hypersurface

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, η

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

See also *efficiency*.

revG2

energy transfer

excitation transfer

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.

See also *Dexter-excitation transfer, Förster-resonance-energy transfer, radiative-energy transfer*.

See [46].

revG2

energy-transfer plot

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

Note: Alternatively, plot of the rate constant for the *sensitization* of a reaction vs. 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).

See also *Stern–Volmer kinetic relationships*.

See [54].

revG2

enhancer (of emission)

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 *photostimulated radical nucleophilic substitution* to designate the induction of the reaction of a less reactive (or nonreactive) nucleophile with a substrate by the addition of catalytic amounts of another nucleophile, more reactive at initiation. Often, the nonreactive nucleophile at initiation is, however, quite reactive at propagation [55].

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 [56] and cryptochromes in mammals and insects [57].

ESCA

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 “nonbonding” in the ground state.

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

See also *exciplex*.

See [46].

revG2

excimer lamp

Noncoherent 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 ~ 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 Ar₂, 146 nm with Kr₂, 172 nm with Xe₂, 222 nm with KrCl, and 308 nm with XeCl, obtained with efficiencies of 5–15 %. Pulsed Xe-excimer (Xe₂) 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 (Cl₂), and 341 nm (I₂) (see Table 1).

Table 1 Peak wavelengths (nm) obtained in dielectric-barrier discharges with mixtures of noble gas (Ng) and halogen (X₂). Wavelengths of commercially available lamps are shown in boldface type. The molecular species indicated are excimers or exciplexes.

	X ₂	Ne	Ar	Kr	Xe
Ng ₂			126	146	172
F	157	108	193	249	354
Cl	259		175	222	308
Br	291		165	207	283
I	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 [58].

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 also *gas lasers* [17].

G2/GB

exciplex

Electronically excited complex, of definite stoichiometry, “nonbonding” in the *ground state*. In general, a complex formed by the interaction of an electronically excited molecular entity with a ground-state partner of a different 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 [59].

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*.

See also *emission spectrum*.

See [46].

revG2

excitation transfer

See *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

free 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 also *electronic energy migration*, *self-localized excitations*, [42].

revG2

exitance

See also *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 also *photon exposure*, *radiant exposure*.

external heavy-atom effect

See *heavy-atom effect*.

G2/GB

external quantum efficiency

Efficiency of light *emission* for solid-state light-emitting devices, such as *organic light-emitting devices* (OLEDs). Analogous to *emission quantum yield*.

See [60].

exterplex

Termolecular analog 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 also *Beer–Lambert law*.

G2

E/Z photoisomerization

General designation of a photoinduced geometrical isomerization of a C–C double bond.

Note: Geometrical isomerization of a C–C double bond is called a *cis/trans isomerization* in 1,2-disubstituted alkenes.

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 nondestructive process, side reactions can occur.

See [3].

Fermi level, E_F

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

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

G2/GB

filter (optical)

Device that reduces the spectral range (*bandpass, cut-off, cut-on, and interference filter*) or *radiant power* of incident radiation (*neutral density or attenuance 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 [61] for a list of recommended procedures and optical data on transient species. See also [2].
revG2

fluence, H_0 , F_0

radiant energy fluence

spherical radiant exposure

At a given point in space, the *radiant energy, Q* , incident on a small sphere from all directions divided by the cross-sectional area of that sphere. SI unit is 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: $H_0 = dQ/dS$, where S is the area of cross-section. If the radiant energy is constant over the area S , $H_0 = Q/S$.

Note 3: The definition is equivalent to $H_0 = \int_t E_0 dt$ where E_0 is the *fluence rate* and t the duration of the irradiation. If the fluence rate is constant over the time interval, $H_0 = E_0 t$.

Note 4: Fluence (H_0 , F_0) 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.

See also *dose*, *photon fluence*.

See [9].

revG2

fluence rate, E_o

radiant energy fluence rate

spherical irradiance

Total *radiant power*, P , incident from all directions onto a small sphere divided by the cross-sectional area of that sphere. 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 , $E_o = P/S$. Equivalent definition: $E_o = \int_{4\pi} L d\Omega$, with Ω the solid angle of each beam passing through the given point on the surface and L the *radiance* of the beam at that point.

Note 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.

See also *intensity*, *photon fluence rate*, *radiance*, [9].

revG2

fluorescence

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

See [46].

revG2

fluorescence anisotropy

See *emission anisotropy*, *photoselection*.

fluorescence lifetime

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

See also *lifetime*, [46].

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 nonfluorescent 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 nonrigid 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^{2,8}]deca-3,6,9-triene (bullvalene), the rapid interconversion of 1 209 600 (10!/3) degenerate isomers.

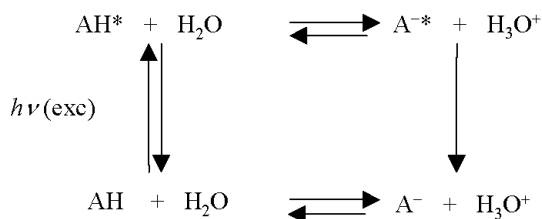
See also *Jahn–Teller effect*, [6].

Förster cycle

Indirect method for 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.

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

Equation 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 ΔH_m^* and ΔH_m , the molar enthalpy difference between the ground and excited states of the protonated and deprotonated species, respectively, and $h\nu_{0-0}(\text{A}^-)$ and $h\nu_{0-0}(\text{AH})$ 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

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

Equation 4 is thus obtained

$$pK_a^* - pK_a = N_A / (\ln 10 RT) [h\nu_{0-0} (A^-) - h\nu_{0-0} (AH)] \quad (4)$$

which permits the calculation of 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 there from are not necessarily established prior to relaxation.

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

See [46].

revG2

Förster radius

See *Förster-resonance-energy transfer*, [46].

Förster-resonance-energy transfer (FRET)

dipole–dipole excitation transfer

Nonradiative 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 τ_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 κ is the *orientation factor*, Φ_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

$$J = \int_{\lambda} I_{\lambda}^{\text{D}}(\lambda) \varepsilon_{\text{A}}(\lambda) \lambda^4 d\lambda$$

where $I_{\lambda}^{\text{D}}(\lambda)$ is the normalized *spectral radiant intensity* of the donor so that $\int_{\lambda} I_{\lambda}^{\text{D}}(\lambda) d\lambda = 1$. $\varepsilon_{\text{A}}(\lambda)$ 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 $\int_{\lambda} I_{\lambda}^{\text{D}}(\lambda) d\lambda$ is the area under the plot of the donor emission intensity versus the emission wavelength.

Note 3: A practical expression for R_0 is:

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

The orientation factor κ is given by

$$\begin{aligned} \kappa &= \cos \theta_{\text{DA}} - 3 \cos \theta_{\text{D}} \cos \theta_{\text{A}} \\ &= \sin \theta_{\text{D}} \sin \theta_{\text{A}} \cos \varphi - 2 \cos \theta_{\text{D}} \cos \theta_{\text{A}} \end{aligned}$$

where θ_{DA} is the angle between the donor and acceptor moments, and θ_{D} and θ_{A} are the angles between these, respectively, and the separation vector; φ is the angle between the projections of the transition moments on a plane perpendicular to the line through the centers. κ^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

$$\Phi_{\text{T}} = \frac{k_{\text{T}}}{k_{\text{D}} + k_{\text{T}}}$$

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

$$\Phi_{\text{T}} = \frac{1}{1 + (r/R_0)^6}$$

or written in the following form:

$$\Phi_{\text{T}} = 1 - \frac{\tau_{\text{D}}}{\tau_{\text{D}}^0}$$

where τ_{D} is the donor excited-state lifetime in the presence of acceptor, and τ_{D}^0 in the absence of acceptor.

Note 5: FRET is sometimes 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.

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

See [46,62].

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

See also *coherent radiation*.
revG2

Fourier-transform spectroscopy

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

Note: 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 also *coherent radiation*.

fraction of light absorbed, f

See *absorption factor*.

Franck–Condon factor

Squared modulus of the overlap integral between the vibrational wave functions (Θ) 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 also *Franck–Condon principle*, [34,46].

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 also *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, λ_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 also *laser*, [17].

G2/GB

free exciton

See *exciton*.

free-radical photosubstitution

See *radical photosubstitution*.

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 μs – 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, ν or ω

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

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

See [7].

G2

frequency-domain fluorometry

Technique that permits recovery of the parameters characterizing a *fluorescence* decay. Instead of using an exciting *visible, UV, or infrared* radiation pulse (see *single-photon timing*), the sample is excited by sinusoidally modulated radiation at high *frequency*. The fluorescence response is sinusoidally modulated at the same frequency as, but delayed in phase and partially demodulated with respect to the excitation.

Note 1: The modulation ratio is defined as the ratio of the modulation depth (AC/DC ratio) of the fluorescence and the modulation depth of the excitation. The phase shift and the modulation ratio characterize the harmonic response of the system. These parameters are measured as a function of the modulation frequency. No deconvolution is necessary because the data are directly analyzed in the frequency domain.

Note 2: Phase and modulation measurements can be done by using either a *CW laser* (or a *xenon lamp*) and an optical modulator (in general a Pockel cell) or the harmonic content of a pulsed laser.

See, e.g., [46].

frequency doubling

See also *harmonic frequency generation, nonlinear 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 also *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 (e.g., He) and an active medium consisting of:

- neutral atoms (e.g., Ne, Cu, Au, etc.) or molecules (e.g., N₂, CO₂, CO, I₂, 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 also *argon ion-*, *CO₂-*, *excimer-*, *copper vapor-*, *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 nonphotochromic 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 ν_0 the frequency at the band maximum.

See also *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 an *electron back-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.

revG2

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, $N_{\text{A}} = 6.022\,141\,5 \times 10^{23}$ mol⁻¹ 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, ϵ_{r} is the relative medium static permittivity (formerly called dielectric constant), $\epsilon_0 \approx 8.854 \times 10^{-12}$ C² J⁻¹ m⁻¹ is the electric constant (vacuum permittivity), and z_{X} the charge of the species X.

In SI units, the factor $e^2/(4 \pi \epsilon_0) = 2.307 \times 10^{-28}$ J m. For the case of neutral species A and D, $z(A) = z(D) = 0$.

Note 1: Several approximations are in use for the calculation of the term $w(\text{D}^{+\bullet}\text{A}^{-\bullet})$, 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 μ in a cavity of radius ρ could be an appropriate model [63] and

$$w(\text{D}^{+\bullet}\text{A}^{-\bullet}) = [N_{\text{A}} (\mu^2)/(4\pi\epsilon_0 \rho^3)] [(\epsilon_{\text{r}} - 1)/(2\epsilon_{\text{r}} + 1)]$$

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:

$$\Delta_{\text{ET}}G^{\circ} = N_{\text{A}} \{ e (E^{\circ}_{\text{ox}} - E^{\circ}_{\text{red}}) + [z(A) - z(D) - 1] e^2 / (4 \pi \epsilon_0 \epsilon_{\text{r}} a) \} - \Delta E_{0,0}$$

with E°_{ox} the standard electrode potential at which the oxidation occurs, and E°_{red} 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. For a list of electrode potentials, see [64].

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*.

See also *driving force, polar driving force*.

See [23].

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 analyzed 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 [46,61,65,66].

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 colored 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 $1/2$ 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 [54,67].

revG2

harmonic frequency generation

Production of *coherent radiation* of frequency $k\nu$ ($k = 2, 3, \dots$) from coherent radiation of frequency ν . In general, this effect is obtained through the interaction of *laser ultraviolet, visible, or infrared* radiation with a suitable optical medium with nonlinear 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 also *nonlinear optical techniques*, [42].

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 [21].

G2/GB

heliochromism

Applied to *photochromic* compounds possessing a high efficiency for coloring 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 also *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 also *gas lasers*.

G2/GB

Herkstroeter plot

See *energy transfer plot*, *Hammond–Herkstroeter plot*, *triplet–triplet energy transfer*.

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 also *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 *nonlinear 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 [42,68].

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.

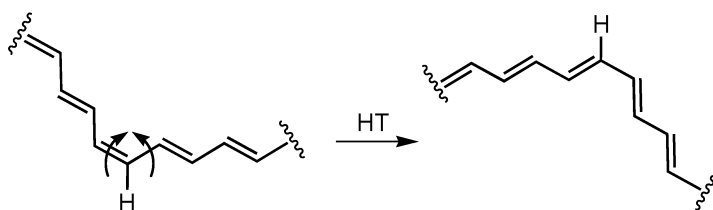
G2/GB

HT

Acronym for *hula-twist mechanism*.

hula-twist (HT) mechanism

Volume-conserving mechanism of *photoisomerization* of a double bond in a conjugated system involving simultaneous configurational and conformational isomerization, e.g., the photoinitiated concerted rotation of two adjacent double and single bonds.



Note: Under unconstrained conditions, the conventional *one-bond-flip* (OBF) process is the dominant process with the hula-twist (HT) being an undetectable higher energy process. It has been proposed that under confined conditions (e.g., a conjugated double bond *chromophore* in a protein cavity or in a solid matrix), the additional viscosity-dependent barriers makes the OBF a less favorable process, allowing the volume-conserving HT to be the dominant process for photoisomerization [69].

See also *bicycle-pedal mechanism*.

See [36].

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.

See also *Marcus–Hush relationship*.

See [70,71].

revG2

hyperchromic effect

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

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

ICT emission

Electronic *emission* from an *ICT* state.

See also *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 *noncoherent radiation*; not having the properties of *coherent radiation*.

G2/GB

infrared

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

According to the CIE, the range between 780 nm and 1 mm is subdivided into [9]:

IR-A 780–1400 nm

IR-B 1.4–3 μm

IR-C 3 μm –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

Term used in two different ways:

- (1) In an *emission* experiment, it refers to (a) an apparent decrease in emission *quantum yield* at high concentration of the emitter due to strong *absorption* of the excitation light and (b) an apparent decrease in emission quantum yield and/or distortion of bands shape as a result of reabsorption of emitted radiation (particularly severe for emitters with small *Stokes shift*).

- (2) During an irradiation experiment, absorption of incident radiation by a species other than the intended primary absorber is also described as an inner-filter effect.

See also *radiative energy transfer*.

See [74].

revG2

inner-sphere electron transfer

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

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

Compare with *outer-sphere electron transfer*.

See [23].

G2/GB

integrating sphere

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

G2/GB

intended crossing (of potential energy surfaces)

See *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 an ultraviolet, visible, or infrared radiation source)

See *radiant intensity*.

G2

intensity (of a spectral feature)

Describes the magnitude of the particular feature in the spectrum.

G2

interference filter

dichroic filter

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

Note: 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 also *filter*.

revG2

interferometer

See *Fourier-transform spectrometer*.

G2/GB

internal conversion (IC)

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

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.

revG2

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 [39].

intersystem crossing (ISC)

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

See [21,34,46].

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 nonequivalent metal centers.

G2/GB

intimate ion pair

See *contact ion pair*, the preferred term.

revG2

intramolecular charge transfer (ICT)

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 based on the molecular structure of the final state reached upon photo-induced 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)

Marcus inverted region (for electron transfer)

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

Note: The behavior 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 behavior 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*, [23,75].

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 W m^{-2} .

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

Note 2: Alternative definition: Integral, taken over the hemisphere visible from the given point, of the expression $L \cos\theta \, d\Omega$, where L is the *radiance* at the given point in the various directions of the incident elementary beams of solid angle Ω and θ 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 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_{λ} is the *spectral irradiance* at wavelength λ .

See also *photon irradiance*.

See [9].

revG2

ISC

Frequently used acronym for *intersystem crossing*.

isoabsorption point

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 nonlinear relationship between the *molar absorption coefficient* and the *photoacoustic* signal.

See also *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 $A_{\lambda} l^{-1} = \sum_{i=1}^n \epsilon_i(\lambda) c_i$ is invariant (A_{λ} is the *absorbance* at *wavelength* λ , l is the optical path, ϵ_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 $\epsilon_A + \epsilon_B = c \epsilon_C + d \epsilon_D + e \epsilon_E$, 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

state diagram

Originally, 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 (\rightsquigarrow).

See [76].
G2/GB

Jahn–Teller effect

Molecular distortions due to an electronically degenerate *ground* state. For nonlinear molecular entities in a geometry described by a point symmetry group possessing degenerate irreducible representations, there always exists at least one 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 nondegenerate *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 behavior (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*.

See also *Renner–Teller effect, vibronic coupling*.
See [6].
revG2

Kaptein–Closs rules

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

See [77].
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 [78].
revG2

Kasha–Vavilov rule

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

See [79].

G2/GB

Koopmans' theorem

See *photoelectron spectroscopy*, [21].

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 also *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_{λ}^0 .

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

See also *absorbance*, *Beer–Lambert law*.

G2/GB

lamp

Source of *incoherent* radiation.

See also *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 ε_{12} is the potential energy gap between the two electronic states at a *surface crossing point*, $|s_1 - s_2|$ is the difference in slopes between the intersecting *potential energy curves* at this point, and v is 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 nonvanishing electric *transition (dipole) moments* are those that connect an even term with an odd term with respect to parity.

See [80].

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

See [17].

G2/GB

laser diode

See *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

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

See [81].

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, τ

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 also *crystal-field splitting*.

G2/GB

ligand-to-ligand charge-transfer (LLCT) 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* 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 center 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 an LED emits incoherent monochromatic light, normally a very narrow *frequency* range is obtained.

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

Note 2: The color 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.

See also *dichroism*, *emission anisotropy*, *linear dichroism*, *magic angle*.

See [34,46].

revG2

light source

See *lamp*, *laser*.

G2/GB

linear dichroism (LD)

For a uniaxial sample with sample axis Z is defined as:

$$\Delta A_1 = A_Z - A_Y$$

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 $\Delta A_1 = 0$.

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_{iso} the isotropic *absorbance*. Thus, ΔA_r is analogous to *emission anisotropy*, and the denominator in the equation 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 molecular 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 also *emission anisotropy*, *molecular orientation*, *photoselection*, *transition (dipole) moment* [34,46].

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 μ_{exc} and μ_{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 ϵ_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 ϵ_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 [46,82].

Lippert plot

See *Lippert–Mataga equation*.

localized exciton

See *exciton*.

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 ν_0 is the mean band position, γ is the half *bandwidth* at half maximum.

See also *Gaussian band shape*.

G2/GB

low-pressure mercury lamp (arc)

Resonance lamp that contains mercury vapor at pressures of about 0.1 Pa (0.75×10^{-3} Torr; 1 Torr = 133.3 Pa). At 25 °C, such a lamp emits mainly at 253.7 and 184.9 nm. 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 also *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.

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

See [46].

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 ultra short excitation pulse), the relationship between the *fluorescence* intensity detected at a time t and through a polarization analyzer oriented at an angle β 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 analyzer angle β 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 [34,46].

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, Δ , is calculated as

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

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

Note 2: Phenomenon 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 nonvanishing 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 centers. The wavelength dependence of MCD can be used also to identify and assign optical transitions from metal ion sites.

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

See [34].

Marcus equation (for electron transfer)

Relation between the rate of *outer-sphere electron transfer* and the thermodynamics of this process [75]. 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 κ_{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 λ 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 also *Gibbs energy of photoinduced electron transfer*, [21,23,75].
revG2

Marcus–Hush relationship

Relationship between the barrier (ΔG^\ddagger) to thermal *electron transfer*, the energy of a corresponding optical *charge-transfer transition* (ΔE_{op}), and the overall change in standard Gibbs energy accompanying thermal electron transfer (ΔG^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 $\Delta G^\ddagger = \Delta E_{\text{op}}/4$, for degenerate electron transfer ($\Delta G^0 = 0$) in, e.g., symmetrical mixed-valence systems.

Note: For the latter situation, the *Marcus equation* reads $\Delta G^\ddagger = \lambda/4$.

See also *Gibbs energy of photoinduced electron transfer*, *Hush model*, *Marcus equation*, [71].
revG2

Marcus inverted region (for electron transfer)

See *inverted region*, [75].
G2/GB

medium-pressure mercury lamp (arc)

Noncoherent radiation source containing mercury vapor at pressures ranging from 50 to several hundred kPa (1 atm = 101.325 kPa). 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.

See also *high-pressure mercury lamp*, *lamp*, [2,15].
revG2

mercury–xenon lamp (arc)

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

See *lamp*, [2,15].
G2/GB

MERP

Acronym for *minimum-energy reaction path*.

merry-go-round reactor

turntable reactor

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 centers has occurred.

See also *intervalence charge transfer*.

G2/GB

meta-photocycloaddition

See *aromatic photocycloaddition*, [25,83].

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*.

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).

See also *free-running laser*.

See *mode locking* in [17].

molar absorption coefficient, ϵ

molar decadic absorption coefficient

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

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

where P_{λ}^0 and P_{λ} 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/cm and $c/\text{mol dm}^{-3}$ (M), $\epsilon(\lambda)$ 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 also *absorbance*, *absorption coefficient*, *Beer–Lambert law*, [7].

revG2

molecular alignment

See *linear dichroism*.

molecular orientation

Absorption probability (referred to electric dipolar absorption) for a molecular transition with its electric *transition (dipole) moment* at an angle θ 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_{θ} for three 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_{θ} are diagonal.

To describe processes involving two 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 nonuniaxial 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 [34,46].

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

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 nondynamic correlation energy than the conventional CIS, CID, and CISD methods.

See [6].

multiphoton absorption

See *multiphoton process*.

G2/GB

multiphoton process

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

See also *biphotonic excitation*, *biphotonic process*, *two-photon process*, [42].

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 $S = 1/2$, $2S + 1 = 2$, 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 also *multiconfiguration SCF method*, *configuration interaction*, [6].

natural lifetime

See *radiative lifetime*. The use of this term is discouraged.

G2/GB

neodymium laser

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

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

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

G2/GB

neutral-density filter

See *attenuance filter*.

G2/GB

nitrogen laser

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

See also *gas lasers*.

G2/GB

nonadiabatic electron transfer

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

nonadiabatic photoreaction

See *diabatic photoreaction*. Use of double negative is discouraged.

G2

noncoherent radiation

Not having the properties of *coherent radiation*.

noncrossing rule

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

Note: Only applies to diatomic molecules and not to polyatomic molecules.

See also *conical intersection*, [6,21,39].

nonlinear optical effect

Effect brought about by electromagnetic radiation and of magnitude not proportional to the *irradiance*.

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

See [42].

revG2

nonlinear optical techniques

Collective name applied to techniques related to *nonlinear 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 nonlinear 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 nonlinear techniques, as well as the higher-order nonlinear techniques are related to the third-order polarization and the corresponding “hyper-susceptibility”.

See [42].

nonradiative decay

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

See *radiationless deactivation (decay)*.

revG2

nonvertical 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 nonvertical 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 also *Franck–Condon principle*, [21,34].

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*.

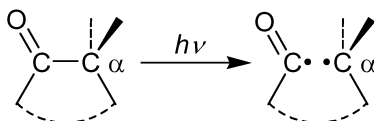
See also *Gibbs energy of photoinduced electron transfer*, [23].

revG2

Norrish Type I photoreaction

α -Cleavage of an excited carbonyl compound leading to an acyl-alkyl *radical pair* (from an acyclic carbonyl compound) or an acyl-alkyl *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., [84].

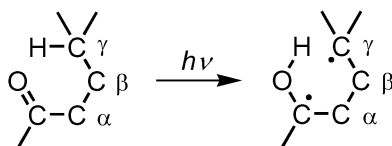
See also *Norrish Type II photoreaction*, *Norrish–Yang reaction*, *Yang photocyclization*, [85,86].

revG2

Norrish Type II photoreaction

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

Note: An example is

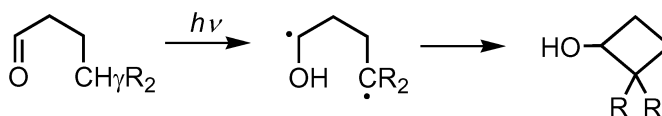


See also *Norrish Type I photoreaction*, *Norrish–Yang reaction*, *Yang photocyclization*, [85].

revG2

Norrish–Yang reaction

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



See also *Norrish Type I photoreaction, Yang photocyclization*.
See [87–89].

nucleophilic aromatic photosubstitution

Photosubstitution in aromatic compounds with the participation of nucleophiles.

Note: While electrophilic substitution is the most common reaction on aromatic compounds in the *ground state*, nucleophilic substitution is typical for the *excited states* of these compounds. Some electrophilic aromatic photosubstitutions (upon excitation of the aromatic substrate) have been reported [90].

See also *photochemical nucleophile-olefin combination, aromatic substitution (photo-NOCAS), [91,92] photostimulated unimolecular radical nucleophilic substitution* [93].

For a classification of nucleophilic aromatic substitution reactions, see [94].

n- π^* state

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

G2/GB

n \rightarrow π^* transition

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

G2/GB

n \rightarrow σ^* transition

Electronic transition described approximately as promotion of an electron from a “nonbonding” (lone-pair) *n orbital* to an “antibonding” σ orbital designated as σ^* .

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

G2/GB

OBF

Acronym for *one-bond-flip*.

ODMR

Acronym for optically detected magnetic resonance: a double *resonance* technique in which transitions between spin sublevels are detected by optical means. Usually, these are sublevels of a *triplet* and the transitions are induced by microwaves.

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

See [34].
G2/GB

OLED

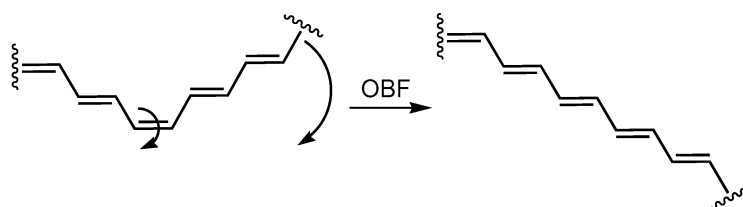
Acronym for *organic light-emitting device*.

OMA

Acronym for *optical multichannel analyzer*.

one-bond-flip (OBF)

Photoisomerization of one double bond in a conjugated double-bond system. It is a regular *E/Z* photoisomerization.



Compare with *bicycle-pedal mechanism*, *hula-twist mechanism*.
See [36,69].

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.

See also *two-photon photochromism*.
See [19].

OPA

Acronym for *optical parametric amplifier*.
See *optical parametric amplification*.

OPO

Acronym for *optical parametric oscillator*.

optical density

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

G2/GB

optical multichannel analyzer (OMA)

Detection system for fast acquisition of spectra. It consists of a “polychromator” fitted with a detector that enables spatial resolution, e.g., a “vidicon tube”, a “charge-coupled device”, or a “silicon photo-diode array”.

See [95].

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 “nonlinear 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 (BaB_2O_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* λ_p , frequency ν_p) is partially converted into two coherent beams, the signal and the idler, with wavelengths (λ_s , λ_i) and frequencies (ν_s , ν_i) such that $(\nu_s + \nu_i) = \nu_p$. By simultaneous rotation of the crystal and adjustment of the optical resonator, the wavelength of the signal beam is continuously tunable, theoretically from λ_p to $2 \times \lambda_p$ and practically over a slightly more reduced range.

Note 2: For example, for $\lambda_p = 355$ nm (3rd harmonic of a Nd:YAG laser), λ_s can be tuned from 400 nm (with $\lambda_i \approx 3.15$ μ) up to 600 nm (with $\lambda_i \approx 870$ nm).

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

See also *nonlinear optical effect*.

See [96].

optical parametric processes

See *parametric processes*.

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*, [34].

orientation polarizability

See *Lippert–Mataga equation*.

ortho-photocycloaddition

See *aromatic photocycloaddition*, [24,97,98].

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.

See also *transition (dipole) moment*.

See [34].

revG2

outer-sphere electron transfer

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

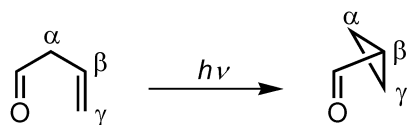
Compare with *inner-sphere electron transfer*; see also *Marcus equation*.

G2

oxa-di- π -methane rearrangement

Photochemical reaction of a β,γ -unsaturated aldehyde or ketone to form the corresponding saturated α -cyclopropyl carbonyl compound.

Note 1: The rearrangement formally amounts to a 1,2-shift of the carbonyl group and “bond formation” between the former α and γ carbon atoms.



Note 2: The 1,2-shift of the carbonyl group as depicted in the figure above should be called 1-oxa-di- π -methane rearrangement, to differentiate it from the possible 3-oxa-di- π -methane rearrangement [99].

See also *aza-di- π -methane rearrangement*, *di- π -methane rearrangement*, *di- π -silane rearrangement*.

See [31].

G2/GB

PAL

Acronym for *photoaffinity labelling*.

parametric amplification

Amplification of a signal based on *parametric processes*.

parametric processes

optical parametric processes

Interaction of *photons* in a nonlinear 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 also *nonlinear optical effect*, [100].

para-photocycloaddition

See *aromatic photocycloaddition*, [24,101].

PAS

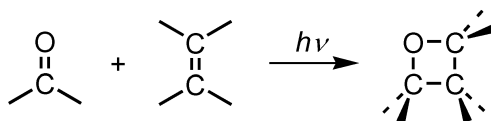
Acronym for *photoacoustic spectroscopy*.

See also *optoacoustic spectroscopy*.

See [18].

Paternò-Büchi reaction

Photocycloaddition of an electronically excited carbonyl group to a *ground-state* olefin yielding an oxetane.



See [102].

G2/GB

PDMR

See *ODMR*.

G2/GB

PEC

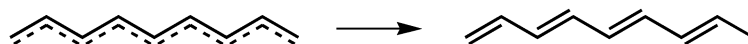
Acronym for *photoelectrochemistry*.

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, λ , 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*.

phase-modulation fluorometry

See *frequency-domain fluorometry*.

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 ν 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”.

See also *photon*.

revG2

phosphorescence

Phenomenologically, term 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 [46].
G2/GB

phosphorescence anisotropy

See *emission anisotropy*, *photoselection*, [34].

phosphorescence lifetime

Parameter describing the time evolution of the decay of the *phosphorescence radiant intensity*.
See also *lifetime*, [46].

photoacoustic effect

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

See also *photoacoustic spectroscopy*, [18].
G2/GB

photoacoustic spectroscopy (PAS)

optoacoustic spectroscopy

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

See also *iso-optoacoustic point*.
See [18].
G2/GB

photoaffinity labelling (PAL)

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: Technique 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, [103].

revG2

photo-assisted catalysis

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

See also *photocatalysis*.
G2/GB

photo-Bergman cyclization

Intramolecular photoinduced cyclization of enediyne leading to aromatic compounds.

Note 1: The solvent plays a key role in the reaction efficiency and product distribution. The reversibility of the initial photoreaction and competing radical vs. ionic pathways dictate product distribution, in stark contrast to the thermal process.

Note 2: This reaction is particularly attractive in molecular biology and molecular medicine. In particular, it permits the expeditious synthesis of core synthones of great diversity.

See [104].

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 also *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*, [94].

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 nonpolar solvents, the reaction follows a different course.

See also *photo-NOCAS*, *photo-ROCAS*.

See [105].

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 [6,39].

photochemical hole burning

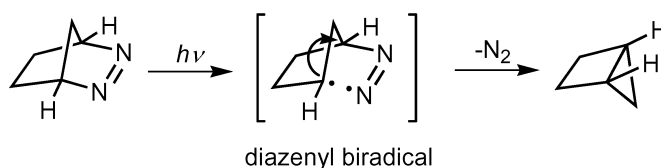
See *hole burning*.

G2/GB

photochemical nitrogen extrusion

Photoinduced dinitrogen (N_2) elimination.

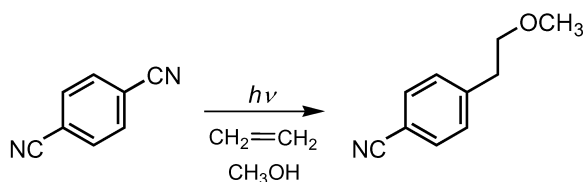
Note: Typical examples are the photoinduced denitrogenation of azoalkanes [106,107]. The following scheme also shows the diazenyl radical intermediate.



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:



See also *photo-EOCAS*, *photo-ROCAS*.

See [108].

photochemical radical-olefin combination, aromatic substitution (photo-ROCAS)

Regioselective combination of a radical, an olefin, and an arene via a *photoinduced electron-transfer* pathway.

See also *photo-EOCAS*, *photo-NOCAS*.

See [109,110].

photochemical reaction

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: Photochemical paths offer the advantage over thermal methods of forming thermodynamically disfavored products, overcome large activation barriers in a short period of time, and allow reactivity otherwise inaccessible by thermal methods.

For a large collection of articles reviewing many photoinduced reactions and their application in organic synthesis, see [111].

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 [21,39].

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 [112].

revG2

photochemistry

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

See also *photochemical reaction*.

G2/GB

photochirogenesis

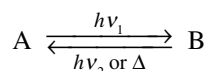
Photochemical induction of molecular chirality.

See also *asymmetric photochemistry*, [113,114].

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* color and is accompanied by differences in other physical properties.

The thermodynamically stable form A is transformed by irradiation into form B. The back reaction can occur thermally (photochromism of type T) or photochemically (photochromism of type P).



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).

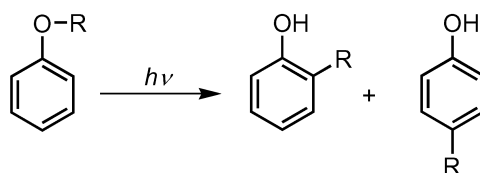
See also *gated photochromism*, *half-life (of a photochromic system)*, *one-photon photochromism*, *two-photon photochromism*, [19].

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.

Note: An example is the photoinduced rearrangement of phenyl ethers to *ortho*- and *para*-alkyl phenols.



See [115–117].

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 [118].

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 also *aromatic photocycloaddition*, *de Mayo reaction*.

See, e.g., [119,120].

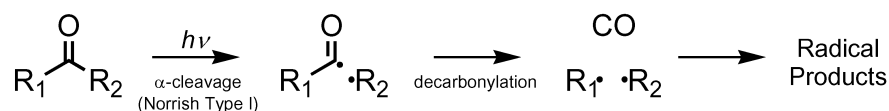
photocycloaddition (aromatic)

See *aromatic photocycloaddition*.

photodecarbonylation

Photoinduced extrusion of carbon monoxide (CO).

Note 1: Typical example is the *Norrish Type I photoreaction*, in which, after production of the *diradical* upon photoinduced α -cleavage, CO is eliminated. This reaction has been widely exploited for the production of radicals in crystals [121], as well as for the synthesis of cyclic compounds [84].

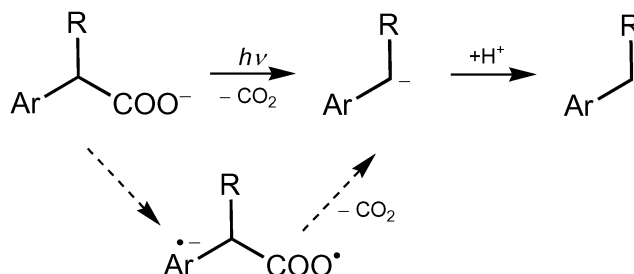


Note 2: Another example is the photodecarbonylation of α -aryl aldehydes [122].

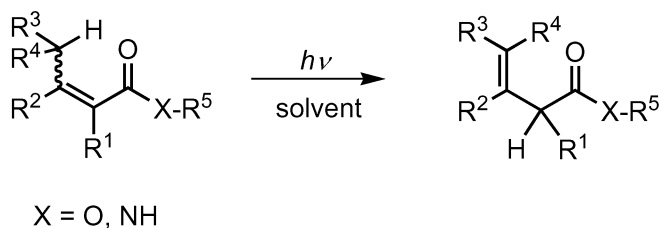
photodecarboxylation

Photoinduced extrusion of carbon dioxide (CO₂).

Note: Typical examples are the CO₂ extrusion upon excitation of anti-inflammatory 2-arylpropionic acids, such as ketoprofen [123].

**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 β,γ -unsaturated carboxylic acids from photoexcitation of α,β -unsaturated carboxylic acid derivatives, excluding the use of strong bases, as required for similar isomerizations performed in the *ground state*.

See [124,125].

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 irradiation as well as in the decomposition of polymers by processes based on UV-visible irradiation, 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 [126].

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.

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

See [127].

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 vs. 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, whereas *ESCA* (electron spectroscopy for chemical analysis) and *XPS* use X-ray sources.

For a photoelectron spectroscopy database, see [128].

See [129].

G2/GB

photoelectron spectrum

See *photoelectron spectroscopy*.

photoenolization

A special case of *phototautomerization*.

photo-EOCAS

Abbreviation for *photochemical electrophile-olefin combination, aromatic substitution*.

See also *photo-NOCAS*, *photo-ROCAS*.

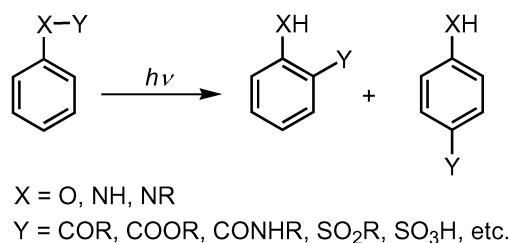
photoexcitation

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 [115] and, e.g., [130].

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 analog) 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.

See also *driving force*, *Gibbs energy of photoinduced electron transfer*, *Marcus equation*, *polar driving force*, *reorganization energy*, *Weller correlation*.

See [23].

revG2

photoinduced polymerization

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

See also *photoinitiation*, [131].

G2/GB

photoinitiation

Photoproduction of a radical or ion capable of initiating a chain reaction such as polymerization, halogenation, nitrosylation, and others.

See also *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.

See also *photodetachment*.

G2

photoisomerization

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

Note 1: Typical examples are *cis/trans photosomerization of alkenes* [41], *polyenes* [132], 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 [133]), phytochromes [134], and the photoactive yellow protein [135].

See also *hula-twist mechanism*.

photoluminescence

Luminescence arising from direct photoexcitation of the emitting species.

See also *fluorescence*, *phosphorescence*.

See [46].

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 also *flash photolysis*.

G2/GB

photon

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

G2/GB

photon counting

single-photon counting

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

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

Note 2: 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 also *time-correlated single-photon counting*, [46].

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 *nonlinear 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 [42].

photon emittance

Former name for *photon exitance*.

G2/GB

photon exitance, M_p

specific photon emission

Photon flux, number basis, q_p , emitted by an element of the surface containing the source point under consideration divided by the area S of that element. SI unit is $s^{-1} m^{-2}$.

Note 1: Mathematical definition: dq_p/dS . If q_p is constant over the surface area considered, $M_p = q_p/S$.

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 $mol s^{-1} m^{-2}$; common unit is $einstein s^{-1} m^{-2}$.

See also *radiant exitance, 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 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 mol m^{-2} ; common unit is einstein m^{-2} .

See also *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 m^{-2}). SI unit is m^{-2} .

Note 1: Mathematical definition: $H_{p,o} = F_{p,o} = dN_p/dS = \int_t E_{p,o} dt$, with $E_{p,o}$ the *photon fluence rate*, integrated over the duration of the irradiation, t . If $E_{p,o}$ is constant over the time interval, $H_{p,o} = F_{p,o} = E_{p,o} t$.

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

See also *fluence*.

See [9].

revG2

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

Rate of *photon fluence*. Total number of photons (N_p) incident from all directions on a small sphere divided by the cross-sectional area of the sphere and per time interval. SI unit is $\text{m}^{-2} \text{s}^{-1}$. Same as photon spherical irradiance.

Note 1: Mathematical definition: $E_{p,o} = dN_p/(dt dS) = dH_{p,o}/dt$. If N_p is constant over the time interval and the surface, $E_{p,o} = N_p/t S$. Equivalent definition: $E_{p,o} = \int_{4\pi} L_p d\Omega$ with L_p the *photon radiance* and Ω the solid angle of the beams passing through the given point on the surface.

Note 2: It reduces to *photon irradiance* E_p for a parallel and normally incident beam not scattered or reflected by the target or its surroundings.

Note 3: This quantity can be used on a chemical amount basis by dividing $E_{p,o}$ by the Avogadro constant, the symbol then being $E_{n,p,o}$, the name “photon fluence rate, amount basis”, SI unit is $\text{mol m}^{-2} \text{s}^{-1}$; common unit is $\text{einstein m}^{-2} \text{s}^{-1}$.

See also *fluence rate, photon radiance*, [9].

revG2

photon flux, q_p , Φ_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 mol s^{-1} ; common unit is einstein s^{-1} .

Note 3: Although the symbol recommended by CEI is Φ_p [9], the symbol q_p is preferred since Φ 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].

See also *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 $\text{m}^{-2} \text{s}^{-1}$. Equivalent definition: Integral, taken over the hemisphere visible from the given point, of the expression $L_p \cos \theta \, \text{d}\Omega$, with L_p the *photon radiance* at the given point in the various directions of the incident beam of solid angle Ω and θ the angle between any of these beams and the normal to the surface at the given point.

Note 1: Mathematical definition: $E_p = dq_p/\text{d}S$. If the photon flux is constant over the surface considered, $E_p = q_p/S$. Equivalent definition: $E_p = \int_{2\pi} L_p \cos \theta \, \text{d}\Omega$.

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 einstein $\text{m}^{-2} \text{s}^{-1}$.

See also *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* ν , 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 Ω , divided by the solid angle and by the orthogonally projected area of the element in a plane normal to the given beam direction, $\text{d}S_{\perp} = \text{d}S \cos \theta$, with θ the angle between the normal to the surface and the direction of the beam. Equivalent definition: Integral taken over the hemisphere visible from the given point, of the expression $L_p \cos \theta \, \text{d}\Omega$, with L_p the *photon radiance* at the given point in the various directions of the incident beam of solid angle Ω and θ the angle between any of these beams and the normal to the surface at the given point.

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 Ω containing the direction θ . SI unit is $\text{m}^{-2} \text{s}^{-1} \text{sr}^{-1}$. $E_p = \int_{2\pi} L_p \cos \theta d\Omega$.

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, θ . 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 einstein $\text{m}^{-2} \text{s}^{-1} \text{sr}^{-1}$. For a parallel beam, SI unit is $\text{mol m}^{-2} \text{s}^{-1}$; common unit is einstein $\text{m}^{-2} \text{s}^{-1}$.

See also *radiance*, *spectral photon radiance*, [9].

revG2

photon spherical irradiance

See *photon fluence rate* [9].

photo-NOCAS

Abbreviation for *photochemical nucleophile-olefin combination, aromatic substitution*.

See also *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 *photo-oxygenation*.

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 also *Schenck-sensitization mechanism*, [136].

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.

See also *photoinduced polymerization*.

G2/GB

photoreaction

See *photochemical reaction*.

G2/GB

photorearrangement

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*) [137], of cyclohex-2-enones [138], of endoperoxides [139], of thioarenes [140], the *di- π -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.

See also *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 [40].

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

Abbreviation for *photochemical radical-olefin combination, aromatic substitution*.

See also *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 also *emission anisotropy, linear dichroism, residual anisotropy*, [34].

photosensitization

sensitization

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 also *energy transfer*.
G2/GB

photosensitizer
sensitizer

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_{RN}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_{RN}1 reactions.

See also *entrainment*.
See [141,142].

photosubstitution

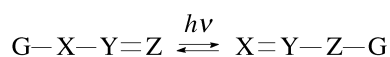
Photochemical process leading to a substitution reaction.

Note: Typical examples are photoinduced substitutions such as *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., [143].

phototautomerization

Photoisomerization of the general form



Note 1: The commonest case, when 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 [144].

G2/GB

PICT

Acronym for *planar intramolecular charge transfer*.

See also *TICT*, *twisted intramolecular charge transfer*.

See [72,73].

piezoluminescence

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

See also *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.

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

See [72,73].

PLED

Acronym for polymer *light-emitting diode*.

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 large molecules undergoing a large change in dipole moment upon electron transfer.

See also *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 the dielectric polarization 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 $P = D - \epsilon_0 E$, where D is the electric displacement, ϵ_0 the electric constant (vacuum permittivity), and E the strength of the radiation electric field. A dielectric medium is characterized by the constitutive relation $D = \epsilon_0 \chi^{(1)} E$ where $\chi^{(1)} = \epsilon_r - 1$ 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 D , the field-induced motion of the electron can introduce other frequency components on the electron motion, and this in turn leads to *nonlinear optical effects*.

Note 2: The polarization component to the n th-order in the field is denoted as $P^{(n)}$. Thus, the following equations apply,

$$P = P^{(1)} + P_{\text{NL}} \quad \text{and} \quad P_{\text{NL}} = P^{(2)} + P^{(3)} + \dots$$

$$P = \epsilon_0 [\chi_e^{(1)} E + (1/2) \chi_e^{(2)} E^2 + (1/6) \chi_e^{(3)} E^3 + \dots] = P^{(1)} + P^{(2)} + P^{(3)} + \dots$$

where E^i is the i -th component of the electric field strength and $\chi_e^{(n)}$ is the usual “susceptibility” $\chi^{(1)} = \epsilon_r - 1$ in the absence of higher terms and $P^{(n)}$ 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 $P^{(1)}$. *Nonlinear techniques* are connected to the nonlinear polarization P_{NL} . Low-order nonlinear techniques, such as three-wave mixing, are related to the second-order *optical polarization* $P^{(2)}$. 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 nonlinear techniques, as well as the higher-order, are related to the third-order optical polarization, $P^{(3)}$, and the corresponding hyper-susceptibility.

See [42].

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 [34,46].

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 also *emission anisotropy*, *light polarization*, *linear dichroism*, [34].

polaron

Lattice distortion or polarization caused by *photoexcitation*.

See also *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) vs. 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)

primary (photo)process

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

revG2

primary (photo)process

See *primary photochemical process*.

Note: For *photophysical processes*, the term 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 also *primary (photo)process*.
G2/GB

pseudo Jahn–Teller effect

See 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 also *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 *nonlinear 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]. Diffractive 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 also *transient spectroscopy*, [42].

revG2

π - π^* state

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

G2/GB

$\pi \rightarrow \pi^*$ transition

Electronic transition described approximately as a promotion of an electron from a “bonding” π orbital to an “antibonding” π orbital designated as π^* .

G2/GB

$\pi \rightarrow \sigma^*$ transition

Electronic transition described approximately as a promotion of an electron from a “bonding” π orbital to an “antibonding” σ orbital designated as σ^* .

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 *QM/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).

See also *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 also *photon* [126,145].

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 [22].

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, Φ

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

Note 2: Φ can be used for *photophysical processes* (such as, e.g., *intersystem crossing*, *fluorescence* and *phosphorescence*) or *photochemical reactions*.

See also *efficiency*.

See [15,46].

revG2/GB

quartet state

State having a total electron spin quantum number $S = 3/2$.

See also *multiplicity*.

revG2

quartz–iodine lamp

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 lifetime 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: Halogens other than iodine 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 also *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 *nonradiative process*.

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

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

See also *Stern–Volmer kinetic relationships*, [46].

revG2

quenching constant

See *Stern–Volmer kinetic relationships*.

See also *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 Ω , 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 Ω containing the direction θ . 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, θ . Mathematical definition in this case: $(dP)/(dS \cos \theta)$. If the radiant power is constant over the surface area considered, $L = P/(S \cos \theta)$. SI unit is W m^{-2} .

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

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

See [9].

revG2

radiant emittance

Former name for *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: Mathematical definition: $Q = \int_{\lambda} Q_{\lambda} d\lambda$. If the *radiant power* P is constant over the time interval, $Q = P t$.

See also *spectral radiant power*.

See [9].

G2/GB

radiant energy fluence, H_0, F_0

See *fluence*.

radiant energy fluence rate

See *fluence rate*.

radiant (energy) flux, P, Φ

This obsolete term is not recommended. In *photochemistry*, *radiant power*, P , is adopted. SI unit is W.

Note: P is preferred, because in *photochemistry*, Φ is reserved for *quantum yield*.

See also *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 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_{λ} is the *spectral radiant exitance* at wavelength λ .

Note 3: Same as *spherical radiant exitance*. Formerly called *radiant emittance*.

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

See [8,9].

G2/GB

radiant exposure, H

Radiant energy, Q , incident from all upward directions on a small sphere divided by the cross-sectional area of that sphere. SI unit is J m^{-2} .

Note 1: Equivalent definition: *Irradiance, E* , integrated over the time of irradiation.

Note 2: 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 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* (H_0, F_0) is an equivalent term.

See [8,9].

revG2

radiant intensity, I
intensity

Radiant power, P , at all *wavelengths* per solid angle, Ω . 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 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_{λ} is the *spectral radiant intensity* at wavelength λ .

Note 3: It is not recommended to abbreviate this term to just intensity because it is confusing.

See also *spectral radiant intensity*.

See [9].

revG2

radiant power, P

Power emitted, transferred, or received as radiation. SI unit is $\text{J s}^{-1} = \text{W}$.

Note 1: Mathematical definition: $P = dQ/dt$. If the radiant energy Q is constant over the time interval, $P = Q/t$.

Note 2: In radiometry, *flux* (Φ) is used with the same units as P . The symbol Φ is reserved for *quantum yield* in photochemistry. Therefore, the use of *flux* (Φ) is not recommended.

See also *spectral radiant power*; [7].

revG2

radiationless deactivation (decay)

Loss of electronic excitation energy without *photon emission* or chemical change. Often, ultrafast radiationless decays are mediated by *conical intersections*.

See also *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

trivial 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.

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, Φ_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.

See also *Dexter-energy transfer*, *energy transfer*, *Förster-resonance-energy transfer*, *inner-filter effect*, [46].

revG2

radiative lifetime, τ_0

natural lifetime

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 τ_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 nonquenched lifetime in the *Stern–Volmer kinetic relationships*.

See also *Förster-resonance-energy transfer*.

See [34,46].

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 also *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 *geminate 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

radical photosubstitution

free-radical photosubstitution

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

See, e.g., [146].

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., γ 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

See *absorbed photon flux density*.

red shift

Informal term for *bathochromic shift*.

G2/GB

reduced dichroism

See *linear dichroism*.

reflectance, ρ

reflectance factor
reflectivity

Fraction of incident radiation reflected by a surface or discontinuity, $\rho(\lambda) = \frac{P_{\lambda}^{\text{refl}}}{P_{\lambda}^0}$, where P_{λ}^0 and $P_{\lambda}^{\text{refl}}$ are, respectively, the incident and reflected *spectral radiant power*.

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°.

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 ($\Delta_{\text{ET}}G^0$):

$$k_q = \frac{k_d}{1 + \frac{k_d}{K_d Z} \left[\exp\left(\frac{\Delta G^{\ddagger}}{RT}\right) + \exp\left(\frac{\Delta_{\text{ET}}G^0}{RT}\right) \right]}$$

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 ΔG^{\ddagger} the activation Gibbs energy of the forward electron-transfer reaction.

Note: In the original formulation of this equation [147], the value $\frac{k_d}{K_d Z} = 0.25$ in acetonitrile was used.

relative spectral responsivity, $s(\lambda)$

See also *action spectrum*.

G2/GB

relaxation

Passage of a system that has been perturbed from equilibrium by radiation excitation or otherwise, toward or into thermal equilibrium with its environment.

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

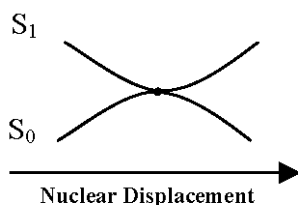
G2

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 nonlinear 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 (λ) is written as the sum of an inner contribution (λ_{in}) and an outer contribution (λ_{out}) attributed to nuclear reorganizations of the redox partners and their environment (solvent), respectively.

Note: Approximations have been proposed to calculate the value of λ_{out} taking into account the “relative permittivity” of the solvent.

See [6,23,75].

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_∞ , called residual emission anisotropy. In the case of a single *rotational correlation time*, τ_c or θ , the decay of emission anisotropy following δ -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 preferred to “limiting anisotropy”.

See also *molecular orientation*, *photoselection*, [34,46].

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.

See also *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 vapor 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 [148].

revG2

resonance line (in fluorescence)

Longest *wavelength* capable of exciting *fluorescence* in an atom.

See also *resonance fluorescence*.

G2

resonance radiation

Same as *resonance fluorescence*.

G2/GB

rotational correlation time, τ_c or θ

Parameter describing the time dependence of the tumbling of a molecular entity in a medium of viscosity η . 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 η (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 [46].

rotational relaxation time, ρ

Parameter describing the time dependence of the tumbling of a molecular entity in a medium of viscosity η , as originally defined by Debye [149], and used by Perrin in the original development of the theories of rotational motion of *fluorophores* [150].

Note: Related to the *rotational correlation time*, τ_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 (Cr^{3+}) in aluminum oxide.

See also *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 Δ the quantum defect that differentiates between s, p, d, etc., orbitals. The notation used is, e.g., $\pi \rightarrow ns$.

See [6].
revG2

RYDMR

See *ODMR*.
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

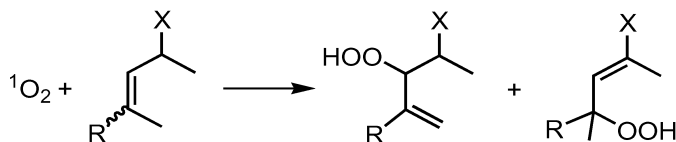
Saupe matrices

See *molecular orientation*, [6].

Schenck reaction

The diastereoselective ene reaction of *singlet molecular dioxygen* with alkenes.

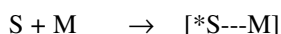
An example is:



See [151,152].

Schenck-sensitization mechanism

Chemical transformation of one molecular entity caused by *photoexcitation* of a *sensitizer*, which undergoes temporary covalent bond formation with the molecular entity (M).



Note 1: This mechanism is the basis of the Type I *photooxygenation*.

Note 2: The reactive molecular entity could be ground-state molecular dioxygen, O₂, in which case *energy transfer* may occur producing *singlet molecular oxygen*, this being the basis of the Type II *photooxygenation*.

See [136,153].

revG2

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 *radiative energy transfer*.

G2

self-localized excitations (in conjugated organic polymers)

Physical and chemical properties of conjugated organic polymers with π -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 Table 2.

Table 2

Excitation	Chemical term	Charge	Spin
positive polaron	radical cation	$+e$	$\frac{1}{2}$
negative polaron	radical anion	$-e$	$\frac{1}{2}$
positive bipolaron	dication	$+2e$	0
negative bipolaron	dianion	$-2e$	0
neutral soliton	neutral radical	0	$\frac{1}{2}$
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 [154].

self-quenching

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

See also *Stern–Volmer kinetic relationships*.

G2/GB

semiconductor laser

See *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 centers 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 multichannel analyzer. This term is preferred to time-correlated single-photon counting.

See e.g., [46,65,155].

revG2

singlet molecular oxygen (singlet molecular dioxygen)

Oxygen molecule (dioxygen), O₂, in an excited *singlet* state. The *ground state* of O₂ is a *triplet* ($^3\Sigma_g^-$). The two metastable singlet states derived from the ground-state *configuration* are $^1\Delta_g$ and $^1\Sigma_g^+$ (the 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* [156].

For a compilation of singlet molecular oxygen production *quantum yields*, see [157].

For a compilation of singlet molecular dioxygen *lifetimes* and rate constants of its reaction with several substrates, see [158].

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 also *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 .

See also *conical intersection*.

singlet–triplet energy transfer

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

See also *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*, and by the solar radiance E , and 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., Nd^{3+} , Cr^{3+} , 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 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 [17,159].
G2/GB

soliton

Localized excitations propagating in a system with constant velocity and colliding with each other without change in their shapes.

See also *self-localized excitations*.

solvatochromism

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

See also *Lippert–Mataga equation*.

See [160].

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 favor 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 spectral band *frequency* of a chemical species, arising from interaction with its solvent environment.

See also *bathochromic shift*, *hypsochromic shift*, *solvatochromism*, [160].

G2/GB

sonoluminescence

Luminescence induced by sound waves.

See also *triboluminescence*.

G2/GB

specific photon emission

See *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., W m^{-1} for $X = [P] = \text{W}$ (unit for 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

effectiveness

Reciprocal of the *photon fluence rate*, $E_{\text{p},0}$, at *wavelength* λ , causing identical photoresponse, Δy , 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*, λ . SI unit is 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*, ν , 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*, λ . SI unit is 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*, ν , or *wavenumber*, $\tilde{\nu}$, and are referred to, when necessary, as in terms of wavelength, or frequency or wavenumber, respectively.

spectral irradiance, E_λ

Derivative of *irradiance*, E , with respect to *wavelength*, λ . SI unit is 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*, ν , 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*, λ . 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 $\text{einstein s}^{-1} \text{m}^{-2} \text{nm}^{-1}$.

Note 2: All *spectral* terms may also be defined as derivatives with respect to *frequency*, ν , 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*, λ . 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 $\text{einstein s}^{-1} \text{nm}^{-1}$.

Note 2: All *spectral* terms may also be defined as derivatives with respect to *frequency*, ν , 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*, λ . 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*, ν , 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*, λ .

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: Spectral photon radiance of a divergent beam is the quantity used when working with large photochemical reactors.

Note 2: 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*, ν , or *wavenumber*, $\tilde{\nu}$, and are referred to, when necessary, as in terms of wavelength, or frequency or wavenumber, respectively.

revG2

spectral radiance, L_λ

Derivative of *radiance*, L , with respect to *wavelength*, λ .

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 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*, ν , 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_λ

Derivative of *radiant energy*, Q , with respect to *wavelength* λ . SI unit is J m^{-1} ; common unit is J nm^{-1} .

spectral radiant exitance, M_λ

Derivative of *radiant exitance*, M , with respect to *wavelength* λ . SI unit is 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*, ν , 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_λ

Derivative of *radiant intensity*, I , with respect to *wavelength*, λ . 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*, ν , 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_λ

Derivative of *radiant power*, P , with respect to *wavelength*, λ . SI unit is W m^{-1} ; common unit is W nm^{-1} .

Note: All *spectral* terms may also be defined as derivatives with respect to *frequency*, ν , 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_λ .

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

See also *action spectrum*.

revG2

spectral sensitivity, $S(\lambda)$

actinometric factor

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

See also *spectral responsivity*.

revG2

spectral sensitization

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

G2/GB

spherical irradiance

See *fluence rate*.

spherical radiance

radiant exitance

Integral of the *radiant power*, P , leaving a source over the total solid angle and over the whole *wavelength* range. SI unit is W m^{-2} .

G2/GB

spherical radiant exposure

See *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 also *annihilation*, [6].

G2

spin-flip method

Quantum mechanical method for the calculation of open-shell *excited states*. The method accurately describes low-lying multiconfigurational 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 nondynamical correlation effects.

See also *correlation energy*.

See [161].

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 O₂, quenching of *triplet states* by O₂, and triplet–triplet *annihilation*.

See [162].

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.

See also *stimulated emission*.

See [46].

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*, [46].

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 Φ^0/Φ (or M^0/M for *emission*) vs. amount concentration of quencher, [Q], is linear, obeying eq. 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. Equation 1 applies when a quencher inhibits either a *photochemical reaction* or a *photophysical process* by a single reaction. Φ^0 and M^0 are the quantum yield and emission intensity (*radiance*), respectively, in the absence of the quencher Q, while Φ and M are the same quantities in the presence of the different concentrations of Q. In the case of *dynamic quenching*, the constant K_{SV} is the product of the true *quenching* constant k_q and the *excited-state lifetime*, τ^0 , in the absence of quencher. The rate constant k_q is the bimolecular reaction rate constant for the elementary reaction of the excited state with the particular quencher Q. Equation 1 can therefore be replaced by 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

$$\frac{1}{\Phi(p)} = 1 + \frac{1}{k_r \tau^0 [S]} \frac{1}{(\eta B)} \quad (3)$$

where $\Phi(p)$ is the quantum *efficiency* of product formation, η the formation efficiency of the reactive excited state, B the fraction of reactions of the excited state with substrate S that leads to the product, and [S] the concentration of the 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 eqs. 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 τ^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* τ_0 .

See also *self-quenching*, *spin-statistical factor*.

See [46,163].

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.

See also *spontaneous emission*.

See [34,46].

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 [46].

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-ylum-1-ide) with one methylene group pyramidalized.

See [164].

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 also *coherent radiation*.

G2/GB

surface crossing

In a diagram of electronic energy vs. 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*, [39].

revG2

 $\sigma \rightarrow \sigma^*$ transition

Electronic transition described approximately as promotion of an electron from a “bonding” σ orbital to an “antibonding” σ orbital designated as σ^* .

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.

See also *photothermal effect*, [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* color.

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.

See also *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.

See also *through-bond electron transfer*.

G2/GB

TICT

Acronym for *twisted intramolecular charge transfer*.

See also *ICT*, *intramolecular charge transfer*, *PICT*, *planar intramolecular charge transfer*, *twisted intramolecular charge transfer*, [72,73].

revG2

TICT emission

Electronic *emission* from a *TICT* state.

See also *PICT*, *planar intramolecular charge transfer*, *twisted intramolecular charge transfer*.

revG2

tight ion pair

See *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 also [6,39].

time-resolved anisotropy, $r(t)$

See *emission anisotropy*.

time-resolved fluorometry

See *frequency-domain fluorometry, single-photon timing*.

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, $\Delta\epsilon''$), 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, $\Delta\epsilon'$), the product of the yield and the change in molecular polarizability can be determined.

See [165].

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-resonance-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.

See also *flash photolysis, pump–dump–probe, pump–probe, time-resolved spectroscopy*.

revG2

transient-stimulated emission pumping (TSEP)

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 also *pump–dump–probe* [166].

transition (dipole) moment

electronic transition 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 nondegenerate):

$$\mathbf{M}_{if} = \langle f | \mathbf{M}_{op} | i \rangle$$

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*, [34].

revG2

transmittance, T

Transmitted *spectral radiant power*, P_{λ} , through a particular pathlength l , divided by the *spectral radiant power* incident on the sample P_{λ}^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 also *absorbance*, *attenuance*, *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 also *sonoluminescence*.

G2/GB

triplet state

State having a total electron spin quantum number of 1.

See *multiplicity* [79,167].

For a list of triplet–triplet absorption spectra, see [168]. For a critical evaluation of triplet–triplet absorption data, see [169].

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*.

See also *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 also *Dexter excitation transfer*, *spin-conservation rule*, *spin-statistical factor*, [54,67].

See also [170].

G2/GB

triplet–triplet transitions

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

G2/GB

trivial energy transfer

See *radiative energy transfer*.

G2/GB

TSEP

Acronym for transient-stimulated emission pumping.

TTET

Acronym for *triplet–triplet energy transfer*.

tungsten-halogen lamp

tungsten lamp

See *quartz–iodine lamp*, *wolfram lamp*.

Note: Halogens other than iodine 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: Important effect 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.

See also *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 also *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.

See also *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 to 400 nm. This region is divided into four sub-bands as follows:

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

Note: The notation and the limits of the various regions are as recommended by the International Commission on Illumination (CIE) [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 also *linear dichroism, molecular orientation*, [34].

upconversion

The process by which two *photons* with frequencies ν_2 and ν_3 combine in a nonlinear medium to produce a higher-energy photon with frequency ν_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 nonlinear material. This in turn depends on the power of the incident radiation, the photon frequencies, their indices of refraction in the material, and the nonlinear “hyper-susceptibility” of the material.

See also *nonlinear optical techniques*, [42,46].

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 also *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 semiconductors. When heated, electrons from the valence band jump out of the band across the *band gap* and into the conduction band, making the material conductive. The *Fermi level* 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 also *relaxation*.

G2/GB

vibronic coupling

Interaction between electronic and vibrational motions in a molecular entity.

See also *Jahn–Teller, Renner–Teller effects*, [34].

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 [34].

G2/GB

visible

Region of the electromagnetic spectrum extending from about 400 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.

VUV

Acronym for vacuum ultraviolet.

See *ultraviolet*.

wavelength, λ

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, $\tilde{\nu}$, σ

Reciprocal of the *wavelength*, λ , or the number of waves per length along the direction of propagation. SI unit is m^{-1} ; common unit is cm^{-1} .

Note: $\tilde{\nu}$ is preferred since σ is used for *absorption cross-section*.

See [7].

G2/GB

Weller correlation

Empirical correlation for the energy of full *charge-transfer exciplex* 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

$$\Delta H(D^+A^-, \text{hexane}) = e [E^{\circ}(D^{+\bullet}/D) - E^{\circ}(A/A^{\bullet-})] + e \Delta E$$

with $E^{\circ}(D^{+\bullet}/D)$ and $E^{\circ}(A/A^{\bullet-})$ the standard electrode potentials of the donor and acceptor, respectively.

Note 1: In the case of 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 above [11].

Note 3: Although not complying with the IUPAC recommended nomenclature for the standard electrode potentials, traditionally the equation has been written as:

$$\Delta H(D^+A^-, \text{hexane}) = e [E^{\circ}_{\text{ox}} - E^{\circ}_{\text{red}}] + (0.15 \pm 0.10) \text{ eV}$$

with E°_{ox} the standard electrode potential at which the oxidation occurs, and E°_{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.

See also *Gibbs energy of photoinduced electron transfer*.

See [171].

revG2

Wigner matrices

See *molecular orientation*, [6].

Wigner rule

See *spin-conservation rule*, [6].

G2/GB

wolfram lamp

tungsten lamp

Incandescent lamp that generates 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 also *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 also *lamp*.

revG2

xenon lamp

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

See also *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 photoreaction*, [172].

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

Z₅₀ (of a photochromic system)

Number of cycles required to reduce by 50 % the initial *absorbance* of the colored form of a *photochromic* compound at a specific *wavelength*.

See [3].

QUANTITIES, SYMBOLS, AND TERMS USED IN THIS GLOSSARY¹

Name	Symbol	Definition	SI unit	Notes
absorbance				
decadic	A, A_{10}	$A = \lg (P_{\lambda}^0/P_{\lambda}) = -\lg T(\lambda)$	1	2
napierian	A_e	$A_e = \ln (P_{\lambda}^0/P_{\lambda}) = -\ln T(\lambda)$		
absorbed (spectral) photon flux density, amount basis		$\frac{q_{n,p,\lambda}^0 [1 - 10^{-A(\lambda)}]}{V}$ with $q_{n,p,\lambda}^0$ the amount of photons <u>incident</u> per time interval and per wavelength interval (<i>spectral photon flux</i> , amount basis)	$\text{mol s}^{-1} \text{m}^{-4}$	3
absorbed (spectral) photon flux density, number basis		$\frac{q_{p,\lambda}^0 [1 - 10^{-A(\lambda)}]}{V}$ with $q_{p,\lambda}^0$ the amount of photons <u>incident</u> per time interval and per wavelength interval (<i>spectral photon flux</i> , number basis)	$\text{s}^{-1} \text{m}^{-4}$	4
absorbed (spectral) radiant power density		$\frac{P_{\lambda}^0 [1 - 10^{-A(\lambda)}]}{V}$	W m^{-4}	5
absorption coefficient				6
linear decadic	a	$a = A_{10}/l$	m^{-1}	
molar decadic	ε	$\varepsilon = a/c = A_{10}/c l$	$\text{m}^2 \text{mol}^{-1}$	7
linear napierian	α	$\alpha = A_e/l$	m^{-1}	
molar napierian	κ	$\kappa = \alpha/c = A_e/c l$	$\text{m}^2 \text{mol}^{-1}$	7
absorption cross-section	$\sigma(\lambda)$	$\sigma(\lambda) = \kappa(\lambda)/N_A = \ln 10 \varepsilon(\lambda)/N_A$	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	$c, [\text{species}]$	$c = [\text{species}] = n/V$	mol m^{-3}	9
amount of entities	n		mol	

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(Continued)

Name	Symbol	Definition	SI unit	Notes
amount of photons	n_p	$n_p = N_p/N_A$	mol	10
area	S		m ²	
attenuance	D	$D = \lg(P_\lambda^0/P_\lambda) = -\lg T$	1	2,11
Avogadro constant	N_A	$N_A = 6.022\ 141\ 5 \times 10^{23} \text{ mol}^{-1}$	mol ⁻¹	12
bandgap energy	E_g		J mol ⁻¹	13
Brewster angle	θ_B	$\theta_B = \arctan(n_2/n_1) = \arctan(\epsilon_2/\epsilon_1)^{1/2}$ with n_2 and n_1 the refractive indices of the receiving surface and the initial medium, respectively, and ϵ_2 and ϵ_1 the respective <i>electric permittivities</i>		
brightness (of a laser dye)		$\Phi_f \epsilon(\lambda)$ with Φ_f the <i>fluorescence quantum yield</i> and $\epsilon(\lambda)$ the <i>molar decadic absorption coefficient</i>	1	
circular dichroism	ΔA_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	Δl	$\Delta l = c \Delta\tau$ 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 Φ the reaction <i>quantum yield</i> and σ the <i>absorption cross-section</i>	m ²	

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(Continued)

Name	Symbol	Definition	SI unit	Notes
critical quenching radius (Förster radius)	R_0	$R_0 = \text{Const.} \left(\frac{\kappa^2 \Phi_D^0 J}{n^4} \right)^{1/6}$ <p>with κ the <i>orientation factor</i>, Φ_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 Förster <i>spectral overlap integral</i></p>	m	14
decay time	τ	$c(t = \tau) = c(t = 0)/e$	s	
degree of emission polarization	p	$p = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}}$ <p>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</p>	1	
depth of penetration (of radiation)				
decadic		$1/a$	m	
napierian	β	$\beta = 1/\alpha$	m	
		with a and α the <i>linear decadic</i> and the <i>linear napierian absorption coefficients</i>		
Dexter transfer rate constant	k_T	$k_T = (1/\hbar) K J \exp(-2 r/L)$ <p>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</p>	s^{-1}	
dichroic ratio	$d(\lambda)$	$d(\lambda) = A_Z/A_Y$ <p>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</p>	1	

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(Continued)

Name	Symbol	Definition	SI unit	Notes
dielectric constant see <i>relative permittivity</i>	ϵ_r		1	
differential quantum yield	Φ	$\Phi(\lambda) = \frac{dx/dt}{q_{n,p,\lambda}^0 [1 - 10^{-A(\lambda)}]}$ <p>with dx/dt the rate of change of a measurable quantity x (amount or number basis), $q_{n,p,\lambda}^0$ the amount of photons <u>incident</u> per time interval and per wavelength interval (<i>spectral photon flux</i>, amount or number basis, resp.), and $A(\lambda)$ the <i>absorbance</i> at the excitation wavelength</p>	1	15
dipole moment	μ	$\mu = q d$	C m	16
driving force		$-\Delta G^0$	J mol ⁻¹	
driving force (for electron transfer), see <i>Gibbs energy of photoinduced electron transfer</i>		$-\Delta_{ET}G^0$	J mol ⁻¹	
Drude–Nernst equation for electrostrictive volume change	ΔV_{el}	$\Delta V_{el} = -\frac{(ze)^2}{2r\epsilon_r} \frac{\partial(\ln\epsilon_r)}{\partial p}$ <p>with ϵ_r the static <i>relative permittivity</i>, r the radius of the ion, e the elementary charge, and z the charge</p>	L mol ⁻¹	
efficiency (of a reaction step)	η	$\eta = k_i / \sum_i k_i$ <p>with k_i the rate constants of all decay processes undergone by the species considered</p>	1	
electric constant	ϵ_0	$\epsilon_0 \approx 8.854 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$	C ² J ⁻¹ m ⁻¹	12
electrical susceptibility	χ_e	$\chi_e = \epsilon_r - 1$ <p>with ϵ_r the <i>relative permittivity</i></p>	1	

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Name	Symbol	Definition	SI unit	Notes
electronic transmission factor (within <i>Marcus electron transfer theory</i>)	κ_{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	$e = M/M_{\text{bb}}$	1	17
energy storage efficiency	η	$\eta = \text{energy out/energy in}$	1	
excited-state lifetime in the absence of quencher (within the <i>Stern–Volmer</i> relationship)	τ^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	J mol^{-1}	13
Fermi level	E_{F}		J mol^{-1}	13
fluence, radiant energy fluence, spherical radiant exposure	H_0, F_0	$H_0 = F_0 = \int_t E_0 \, dt = dQ/dS$	J m^{-2}	18,19
fluence rate, spherical irradiance	E_0	$E_0 = dP/dS = dH_0 \, dt$	W m^{-2}	19,20

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Name	Symbol	Definition	SI unit	Notes
fluorescence polarization (see <i>degree of polarization</i>)				
Förster-transfer rate constant	k_T	$k_T = k_D \left(\frac{R_0}{r} \right)^6 = \frac{1}{\tau_D^0} \left(\frac{R_0}{r} \right)^6$ <p>with k_D the emission rate constant of the donor in the absence of energy transfer, r the distance between donor and acceptor, and R_0 the <i>critical quenching radius</i></p>	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	$a = \frac{1}{\Phi_D^0} \int_{\lambda} I_{\lambda}^D(\lambda) \left[1 - 10^{-\varepsilon_A(\lambda)c_A l} \right] d\lambda$ <p>with c_A the molar concentration of acceptor, Φ_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 $\varepsilon_A(\lambda)$ 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 $\Phi_D^0 = \int_{\lambda} I_{\lambda}^D(\lambda) d\lambda$</p>	1	21
Franck–Condon factor		$\left \int \Theta_v^{(e)} \Theta_v^{(0)} dQ \right ^2$ <p>with Θ the vibrational wave functions for the initial (0) and final (e) states of a given electronic transition. The integral is over all nuclear coordinates.</p>	1	
frequency (angular)	ω	$2 \pi \nu$	rad s^{-1}	
frequency (linear)	ν	$\nu = c/\lambda$	Hz	

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Name	Symbol	Definition	SI unit	Notes
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	
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 ν_0 the frequency at the band maximum	1	
Gibbs energy of photoinduced electron transfer	$\Delta_{\text{ET}}G^\circ$	$\Delta_{\text{ET}}G^\circ = N_{\text{A}} \{ e [E^\circ(\text{D}^{+\bullet}/\text{D}) - E^\circ(\text{A}/\text{A}^{-\bullet})] + w(\text{D}^{+\bullet}\text{A}^{-\bullet}) - w(\text{DA}) \} - \Delta E_{0,0}$ with $w(\text{D}^{+\bullet}\text{A}^{-\bullet})$ and $w(\text{DA})$ the electrostatic work terms accounting for the Coulombic interactions in the products and reactants, respectively	J mol^{-1}	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	$\chi_e^{(n)}$	$\chi_e^{(2)} = \partial^2 \mathbf{P} / \partial \mathbf{E}^2$, 1 st hyper-susceptibility $\chi_e^{(3)} = \partial^3 \mathbf{P} / \partial \mathbf{E}^3$, 2 nd hyper-susceptibility with \mathbf{P} the polarization and \mathbf{E} the electric field strength	$(\text{C m J}^{-1})^n$	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 θ the angle of the beams with the surface and Ω the solid angle of the <u>incident</u> beam	W m^{-2}	24
lifetime	τ	$\tau = 1/k = 1/(\sum_i k_i)$ with k_i the first-order rate constants for all decay processes of the excited state $c(t = \tau) = c(t = 0)/e$	s	

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Name	Symbol	Definition	SI unit	Notes
linear dichroism	ΔA_{\parallel}	$A_Z - A_Y$ 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		$\Delta \tilde{\nu} = 2 \frac{(\mu_{\text{exc}} - \mu_{\text{gr}})^2}{c h r^3} f(\epsilon_r, n) + \text{const.}$ with μ_{exc} and μ_{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, ϵ_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 ν_0 the mean band position, γ the half <i>bandwidth</i> at half maximum, and $F(\nu - \nu_0)$ the <i>frequency distribution function</i>		
magnetic circular dichroism signal	Δ	$\Delta = \frac{[\alpha(\lambda)^- - \alpha(\lambda)^+]}{[\alpha(\lambda)^- + \alpha(\lambda)^+]}$ 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	$C = N/V$	m^{-3}	
number of entities	N		1	

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Name	Symbol	Definition	SI unit	Notes
optical pathlength	l		m	
orientation factor (in Förster energy transfer)	κ	$\kappa = \cos \theta_{DA} - 3 \cos \theta_D \cos \theta_A = \sin \theta_D \sin \theta_A \cos \varphi - 2 \cos \theta_D \cos \theta_A$ <p>with θ_{DA} the angle between the donor and acceptor moments, θ_D and θ_A the angles between these, respectively, and the separation vector, φ the angle between the projections of the transition moments on a plane perpendicular to the line through the centers</p>	1	
orientation polarizability (of a solvent)	$f(\epsilon_r, n)$	$f(\epsilon_r, n) = \frac{(\epsilon_r - 1)}{(2\epsilon_r + 1)} - \frac{(n^2 - 1)}{(2n^2 + 1)}$ <p>with ϵ_r the static <i>relative permittivity</i> and n the refractive index of the medium</p>	1	
oscillator strength	f value	<p>theoretical</p> $f_{ij} = \frac{8}{3} \frac{m^2 c \tilde{\nu}}{e^2 h} G M_{ij}^2$ <p>experimental</p> $f_{ij} = (k/n) \int_{\tilde{\nu}} \epsilon(\tilde{\nu}) d\tilde{\nu}$	1	25
permittivity (see <i>relative permittivity</i>)	ϵ_r		1	
permittivity of vacuum, see <i>electric constant</i>	ϵ_0			12
photon exitance (emitted <i>photon flux</i>)	M_p	$M_p = dq_p/dS$	$m^{-2} s^{-1}$	26
photon exposure	H_p	$H_p = \int_t E_p dt$	m^{-2}	26,27
photon fluence	$H_{p,o}, F_{p,o}$	$H_{p,o} = F_{p,o} = dN_p/dS = \int_t E_{p,o} dt$	m^{-2}	19,26
photon fluence rate	$E_{p,o}$	$E_{p,o} = dH_{p,o}/dt = dN_p/(dS dt)$	$m^{-2} s^{-1}$	19,26

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Name	Symbol	Definition	SI unit	Notes
photon flux, amount basis	$q_{n,p}$	$q_{n,p} = q_p/N_A = (dN_p/dt)/N_A$	mol s^{-1}	28
photon flux, number basis	q_p	dN_p/dt	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 Ω containing the beam direction θ $L_p = d^2q_p/(d\Omega dS \cos \theta)$	$\text{m}^{-2} \text{s}^{-1}$ $\text{m}^{-2} \text{s}^{-1}$ sr^{-1}	26 [7]
Planck constant	h $\hbar = h/2\pi$	$6.626\,0693(11) \times 10^{-34}$ $1.054\,571\,68(18) \times 10^{-34}$	J s J s	12
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	Φ Φ_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 Φ^0/Φ or $M^0/M = 1 + k_q \tau^0 [Q]$ with $[Q]$ the amount concentration of quencher	$\text{m}^3 \text{mol}^{-1}$ s^{-1}	31

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Name	Symbol	Definition	SI unit	Notes
radiance	L	for a <u>parallel</u> beam $L = (dP)/(dS \cos \theta)$	W m^{-2}	
		for a <u>divergent</u> beam $L = d^2P/(d\Omega dS \cos \theta)$	W m^{-2} sr^{-1}	[7]
radiant energy	Q	$Q = \int_{\lambda} Q_{\lambda} d\lambda$	J	
radiant exitance (for emitted <i>radiant power</i>)	M	$M = dP/dS$	W m^{-2}	
radiant exposure	H	$H = \int_t E dt = dQ/dS$	J m^{-2}	32
radiant intensity	I	$I = dP/d\Omega$	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	τ_0	$\tau_0 = 1/k_r$	s	
rate constant for radiative step	k_r		s^{-1}	
reduced (linear) dichroism	ΔA_r	$\Delta A_r = (A_Z - A_Y)/3 A_{\text{iso}}$ 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	ρ	$\rho = P_{\lambda}^{\text{refl}}/P_{\lambda}^0$ $\rho(l) = \frac{(n_1 - n_2)^2}{(n_1 + n_2)^2}$ with n_1 and n_2 the refractive index of each of the media	1	34

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Name	Symbol	Definition	SI unit	Notes
refractive index	n	$n = c_0/c$	1	
Rehm–Weller equation for the quenching rate constant of an electron-transfer process	k_q	$k_q = \frac{k_d}{1 + \frac{k_d}{K_d Z} \left[\exp\left(\frac{\Delta G^\ddagger}{RT}\right) + \exp\left(\frac{\Delta_{ET}G^0}{RT}\right) \right]}$ <p>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 ΔG^\ddagger the activation Gibbs energy of the forward electron-transfer reaction</p>		35
relative permittivity	ϵ_r	$\epsilon_r = \epsilon/\epsilon_0$ with ϵ_0 the <i>electric constant</i>	1	36
reorganization energy (for outer-sphere electron transfer, according to Marcus)	λ	from $\Delta G^\ddagger = (\lambda + \Delta_{ET}G^0)^2/4\lambda$ with ΔG^\ddagger the activation Gibbs energy and λ the reorganization energy (after Marcus)	J	
residual emission anisotropy	r_∞	from $r(t) = r_0 - r_\infty) \exp(-t/\tau_c) + r_\infty$ with r_0 the <i>fundamental emission anisotropy</i> and τ_c the <i>rotational correlation time</i>		37
rotational correlation time	τ_c, θ	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	37
rotational relaxation time	ρ	$\rho = 3\tau_c$ with τ_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

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Name	Symbol	Definition	SI unit	Notes
solid angle	Ω	$\Omega = S/r^2$	sr, 1	39
spectral distribution (of a radiant, luminous or photon quantity)	$X_\lambda(\lambda)$	$X_\lambda(\lambda) = dX(\lambda)/d\lambda$	$[X] \text{ m}^{-1}$	
spectral fluence (in terms of wavelength)	$H_{\lambda,0}$	$H_{\lambda,0} = dH_0/d\lambda$	J m^{-3}	19,40
spectral fluence rate	$E_{\lambda,0}$	$E_{\lambda,0} = dE_0/d\lambda$	W m^{-3}	19,41
spectral irradiance	E_λ	$E_\lambda = dE/d\lambda$	W m^{-3}	41
spectral overlap integral (normalized)				
Dexter	J	$J = \int_0^\infty I_\lambda^D(\lambda) \varepsilon_A(\lambda) d\lambda$	$\text{m}^2 \text{ mol}^{-1}$	42
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	$\text{m}^6 \text{ mol}^{-1}$	43
spectral photon flux	$q_{p,\lambda}$	$dq_p/d\lambda$	$\text{s}^{-1} \text{ m}^{-1}$	26
spectral radiant energy	Q_λ	$dQ/d\lambda$	J m^{-1}	44
spectral radiant power	P_λ	$P_\lambda = dP/d\lambda$	W m^{-1}	45
spectral responsivity	$s(\lambda)$	$s(\lambda) = dY_\lambda/dE_\lambda$ with Y_λ the spectral output quantity of the system	1	46
spectral sensitivity of an actinometer	S_{ac}	$S_{ac}(\lambda) = \Phi(\lambda) \varepsilon(\lambda_{\text{obs}})$ or $S_{ac}(\lambda) = \Phi(\lambda) \Delta\varepsilon(\lambda_{\text{obs}})$ with $\Delta\varepsilon(\lambda_{\text{obs}})$ the difference in <i>molar absorption coefficient</i> between product and reactant at the observation wavelength	$\text{m}^2 \text{ mol}^{-1}$	47

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Name	Symbol	Definition	SI unit	Notes
speed of light in vacuum	c_0	$c_0 = 299\,792\,458\text{ m s}^{-1}$	m s^{-1}	
in a medium	c	$c = c_0/n$	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	48
Stern–Volmer constant (See <i>Stern–Volmer equation</i>)	$K_{SV} = k_q \tau^0$	from Φ^0/Φ or $M^0/M = 1 + K_{SV} [Q]$ with $[Q]$ the amount concentration of quencher	$\text{dm}^3 \text{mol}^{-1}$	31
Stern–Volmer equation	Φ^0/Φ or M^0/M τ^0/τ	Φ^0/Φ 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, τ^0 the <i>lifetime</i> of excited state in the absence of quencher, and τ the lifetime in the presence of quencher	1	31
temperature (Celsius)	θ, 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 resonance energy transfer)	Φ_T	$\Phi_T = 1 - \frac{\tau_D}{\tau_D^0}$ with τ_D the donor excited-state <i>lifetime</i> in the presence of acceptor, and τ_D^0 in its absence	1	
transition (dipole) moment	M_{if}	$M_{if} = \langle f M_{\text{op}} i \rangle$ 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		m^3	

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Name	Symbol	Definition	SI unit	Notes
wavelength	λ		m	
wavenumber in vacuum	$\tilde{\nu}$	$\tilde{\nu} = \nu/c_0 = 1/n\lambda$	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	kJ mol^{-1}	49
Z_{50} number (in photochromic systems)	Z_{50}	number of cycles needed to lose 50 % of initial absorbance	1	

NOTES

- Entries in the table are consistent with terminology, symbols, and units given in [7–9], 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.
- 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.
- Common unit is $\text{einstein s}^{-1} \text{cm}^{-3} \text{nm}^{-1}$, superscript 0 (zero) indicates incident photons.
- Common unit is $\text{s}^{-1} \text{cm}^{-3} \text{nm}^{-1}$, superscript 0 (zero) indicates incident radiation.
- Common unit is $\text{W cm}^{-3} \text{nm}^{-1}$; superscript 0 (zero) indicates incident radiant power.
- In spectroscopy, usually defined in terms of the spectral radiant power, P_λ .
- 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. ϵ depends on wavelength, or wavenumber, or frequency, and may be quoted as $\epsilon(\lambda)$, or as $\epsilon(\tilde{\nu})$, or as $\epsilon(\nu)$.
- 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 $\sigma/\text{cm}^2 = (3.823 6 \times 10^{-21}/\text{mol}) \times (\epsilon/\text{dm}^3 \text{cm}^{-1} \text{mol}^{-1})$.
- Usual units are mol dm^{-3} or mol L^{-1} or submultiples. Commonly, the non-SI unit M (small cap) is used as an abbreviation for mol dm^{-3} .
- Amount of photons is often given in the non-SI unit einstein = mol of photons.
- Attenuance reduces to *absorbance* for a not reflected or scattered beam.
- 2002 value [173].
- Common non-SI unit is electronvolt (eV) = $1.602 176 53 (14) \times 10^{-19}$ J; for one mole of electrons, $1 \text{ eV} = 96.485 \text{ kJ mol}^{-1}$.
- Common non-SI unit is ångström (\AA) = 10^{-10} m. Common SI submultiples are nm, pm. κ^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

$R_0/nm = 2.108 \times 10^{-2} \{ \kappa^2 \Phi_D^0 n^{-4} \int_{\lambda} I_{\lambda}^D(\lambda) [\epsilon_A(\lambda)/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}] (\lambda/nm)^4 d\lambda \}^{1/6}$ with (λ) the normalized *spectral radiant intensity* of the donor so that $\int_{\lambda} I_{\lambda}^D(\lambda) d\lambda = 1$; $\epsilon_A(\lambda)$ is the *molar decadic absorption coefficient* of the acceptor. Foerster is an alternative and acceptable spelling for Förster.

- (15) Strictly, the quantum yield definition applies only for monochromatic irradiation. Thus, the *absorbed spectral photon flux density* (number or amount basis) should be used in the denominator, when x in the equation for the differential quantum yield is either a number concentration, or an amount concentration, respectively.
- (16) Common non-SI unit is debye (D) $\approx 3.335\ 64 \times 10^{-30}$ C m.
- (17) Ratio of the flux emitted by the sample to the flux emitted by a black body (M_{bb}) at the same temperature.
- (18) For a beam not scattered or reflected by the sample, a synonym is *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 1).
- (20) For an incident beam not reflected or scattered by the target or its surroundings, a synonym is *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 $a = \frac{2.3}{\Phi_D^0} c_A l \int_{\lambda} I_{\lambda}^D(\lambda) \epsilon_A(\lambda) d\lambda$ 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: $E^{\circ}(\text{D}^{+\bullet}/\text{D})/\text{V}$: standard electrode potential of the donor cation radical resulting from the electron transfer, $E^{\circ}(\text{A}/\text{A}^{-\bullet})/\text{V}$: 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. $w(\text{D}^{+\bullet}\text{A}^{-\bullet})/\text{J}$ and $w(\text{DA})/\text{J}$ 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 ranks 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, $\epsilon(\tilde{\nu})$ = *molar decadic absorption coefficient* at wavenumber $\tilde{\nu}$, n = average refractive index of the medium, c = speed of light, e = elementary charge, h = Planck constant, m = mass of the electron; for $\epsilon(\tilde{\nu})/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ (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. The relationship between a photonic (e.g., photon flux q_p) and a wavelength-dependent radiometric quantity [e.g., radiant power $P(\lambda)$] integrated over a wavelength range λ_1 – λ_2 is given by $q_p = (1/hc) \int_{\lambda_1}^{\lambda_2} P(\lambda) \lambda d\lambda$. Thus, to calculate a photon flux over a wavelength interval, the spectral distribution of the radiant power is necessary. Note the relationship between spectral, radiometric, and photonic terms as developed in the **Introduction**, Section 1.4.

- (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 s^{-1} . A term not in accordance with the usual definition of flux [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 as given in [7].
- (30) The corresponding term for a beam incident from all directions is *photon fluence rate*, $E_{p,o}$.
- (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 $dm^3 mol^{-1} s^{-1}$.
- (32) The corresponding term for a beam incident from all directions is *fluence*, $H_o = F_o$.
- (33) Definition from [7]; synonymous *radiant energy power*, *radiant energy flux* defined in [8].
- (34) Superscript 0 (zero) indicates incident *radiant power* and refl reflected radiant power.
- (35) In the original formulation of this equation [147], the value $\frac{k_d}{K_d Z} = 0.25$ in acetonitrile was used.
- (36) Formerly called dielectric constant [7].
- (37) τ_c is the rotational correlation time and r_o 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 $W m^{-2} nm^{-1}$. Analogous quantities relative to frequency or to wavenumber may also be defined.
- (42) $I_\lambda^D(\lambda)$ is the normalized spectral distribution of the *spectral radiant intensity* of the donor emission and $\epsilon_A(\lambda)$ is the normalized *molar decadic absorption coefficient* of the acceptor. Common unit of J is $dm^3 cm^{-1} mol^{-1}$. Normalization condition is $\int_0^\infty I_\lambda^D(\lambda) d\lambda = \int_0^\infty \epsilon_A(\lambda) d\lambda = 1$.
- (43) $I_\lambda^D(\lambda)$ is the normalized spectral distribution of the *spectral radiant intensity* of the donor emission normalized so that $\int_0^\infty I_\lambda^D(\lambda) d\lambda = 1$, $\epsilon_A(\lambda)$ is the *molar decadic absorption coefficient* of the acceptor. Common unit of the overlap integral J is $dm^3 cm^3 mol^{-1}$.
- (44) Common unit is $J nm^{-1}$. Analogous quantity relative to frequency or to wavenumber may also be defined.
- (45) Common unit is $W nm^{-1}$. Analogous quantity relative to frequency or to wavenumber may also be defined.
- (46) Relative biological or chemical photoresponse per incident radiant power as a function of *wavelength*.
- (47) λ is the excitation wavelength, and λ_{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 λ_{obs} , whereas the second definition corresponds to the case in which the actinometer absorbs at λ_{obs} . Common unit is $dm^3 mol^{-1} cm^{-1}$.
- (48) $r(t)$ is the *anisotropy*, and $I(t)$ is the fluorescence intensity (*emission radiant intensity*), both at time t following a δ -pulse excitation.
- (49) In the case of 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.

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