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INTERNATIONAL UNION OF PURE
AND APPLIED CHEMISTRY

ORGANIC AND BIOMOLECULAR CHEMISTRY DIVISION
SUB-COMMITTEE ON PHOTOCHEMISTRY

GLOSSARY OF TERMS USED IN PHOTOCHEMISTRY

3rd Edition, October 2005

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INTRODUCTION TO THE THIRD EDITION

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

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

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

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

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

In this version of the “Glossary” cross links are included to various WEB pages listing quantities relevant to the work of photochemists and other scientists who may consult this document.

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

The Subcommittee on Photochemistry of the IUPAC Division of Organic and Biomolecular Chemistry emphasizes that it is not the purpose of this compilation to impose terms or rules that would hinder the freedom of choice in the use of terminology. Photochemistry being an interdisciplinary area of science which involves, in addition to chemistry, such different fields as laser technology, nanotechnology, spectroscopy, polymer science, solid state physics, biology, and medicine, just to name some of them, it has been necessary to reach compromises and, in some cases, to include alternative definitions used in different areas. It is also important to recognize that this “Glossary” does not intend 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 terms has been: (i) its wide use in the present or past literature and (ii) ambiguity or uncertainty in its usage. With very few exceptions concerning widely accepted terms, name reactions or name equations have been omitted.

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

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

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

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

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

Terms on lasers and laser analytical methods are compiled in [17], on photothermal and photoacoustic methods in [18], and on photochromism in [19]. References are made to original literature in case of name reactions or equations and to some monographies in other cases. This referencing should only serve as a general guide.

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

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

A Note on Units:

SI base units are adopted, with some exceptions, prominently 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.

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

A Note on Symbols:

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

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

Silvia E. Braslavsky

ALPHABETIC LIST OF TERMS AND DEFINITIONS**absorbance (linear A or napierian A_e)**

Logarithm to the base 10 (linear absorbance) of the incident *spectral radiant power*, essentially monochromatic, ($P_\lambda^0 = \int_\lambda I_\lambda \, d\lambda$) 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* in the defined wavelength interval. The terms absorbancy, extinction, and optical density should no longer be used.

When natural logarithms are used, the napierian absorbance is the logarithm to the base e of the incident *spectral radiant power*, essentially monochromatic, 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.

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 1 cm pathlength, 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 in parenthesis may be omitted for P , T , and A defined over a very narrow wavelength range.

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

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

G2/GB

absorptance, a

Fraction of *ultraviolet, visible, or infrared* radiation absorbed, equal to one minus the *transmittance* (T). The use of this term, equivalent to *fraction of light absorbed*, is not recommended.

See *absorbance*.

revG2

absorption (of *electromagnetic radiation*)

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

revG2

absorption coefficient (linear decadic a or linear napierian α)

Absorbance divided by the optical pathlength, l :

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

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} . Common unit is cm^{-1} .

Related terms: *absorptivity, molar absorption coefficient.*

G2/GB

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:

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

where C is the number concentration of molecular entities (number per volume), and l is the optical pathlength.

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

$$\alpha(\lambda) = \ln 10 \varepsilon(\lambda)/N_A$$

with N_A the Avogadro constant. A conversion equation in common units is:

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

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

revG2

absorptivity

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

The use of this term is not recommended.

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

revG2

actinic

Applied or referred to *actinism*.

actinism

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

actinometer

Chemical system for the determination of the number of *photons* integrally or per time interval absorbed into the defined space of a chemical reactor. This name is commonly applied to systems used in the *ultraviolet* and *visible wavelength* ranges.

Note 1: For example, solutions of iron(III) oxalate (among other systems) can be used as a chemical actinometer. Bolometers, thermopiles, and photodiodes are physical devices giving a reading of the radiation hitting them that can be correlated to the number of photons detected as well as to the number of photons entering the chemical reactor.

Note 2: For a list of chemical actinometers and a critical discussion about actinometry see [21].

See *spectral sensitivity*.

revG2

action spectrum

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

Note 1: The action spectrum is sometimes called *spectral responsivity* or sensitivity spectrum. The precise action spectrum is a plot of the *spectral (photon or quantum) effectiveness*. By contrast, a plot of the biological or chemical change or response per absorbed photon (*quantum efficiency*) vs. wavelength is the *efficiency spectrum*.

Note 2: In cases where the fluence dependence of the photoresponse is not linear (as is often the case in biological photoresponses) a plot of the photoresponse vs. fluence should be made at several wavelengths and a standard response should be chosen (e.g., two-lg reduction). A plot of the inverse of the “standard response” level versus wavelength is then the action spectrum of the photoresponse.

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

revG2

adiabatic electron transfer

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

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

Related term: *diabatic electron transfer*.

See [22,23].

G2/GB

adiabatic photoreaction

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

Compare with *diabatic photoreaction*.

See [23].

G2/GB

ADMR

See *ODMR*.

G2/GB

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 anionic species.

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

G2/GB

AM 0 sunlight

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

Related term: *AM 1 sunlight*.

G2/GB

AM 1 sunlight

Solar *irradiance* at sea level traversing the atmosphere when the sun is perpendicular to the earth surface. Also called terrestrial global irradiance.

Related term: *AM 0 sunlight*.

G2/GB

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 length as the standard *low-pressure mercury lamp*.

See [2,15].

anisotropy

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

annihilation

Two atoms or molecular entities both in an *excited state* interact often (usually upon collision) to

produce one atom or molecular entity in an electronically excited state and another in its electronic ground state.

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

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

G2/GB

antimony–xenon lamp (arc)

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

See *lamp* [2,15].

G2/GB

anti–Stokes shift

See *Stokes shift*.

G2/GB

apparent lifetime

See *lifetime*. Same as decay time.

revG2

argon ion laser

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

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

revG2

attenuance, *D*

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

revG2

attenuance filter

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

G2/GB

auxochrome

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

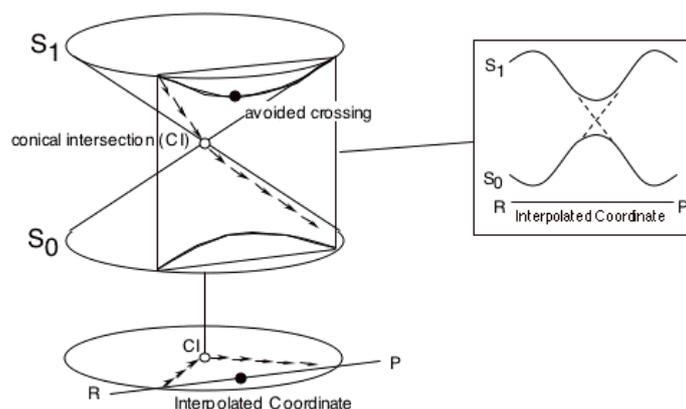
G2/GB

avoided crossing (of potential–energy surfaces)

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

Same as *intended crossing*.

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



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

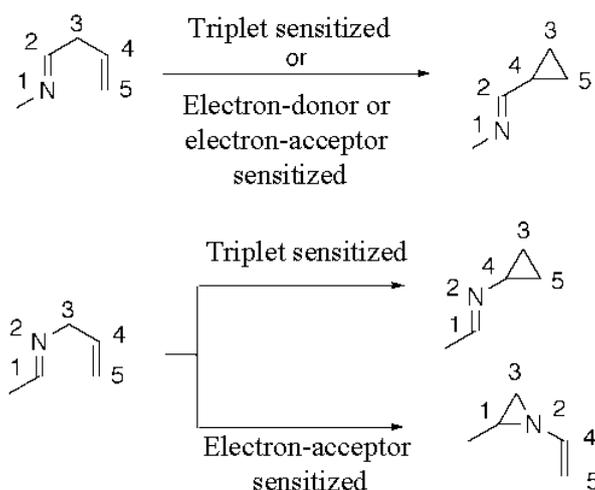
See [6,23].

revG2

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

Related terms: *di– π –methane*, *oxa–di– π –methane rearrangements*.



See [24].

back electron transfer

Term often used to indicate thermal reversal of *excited state electron transfer* restoring the donor and acceptor in their original oxidation state. In using this term one should also specify the resulting electronic state of the donor and acceptor.

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

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 *conduction band*, *Fermi level*.

G2/GB

bandpass filter

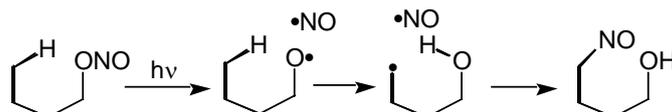
Optical device which permits the transmission of radiation within a specified *wavelength* range and does not permit transmission of radiation at higher or lower wavelengths. It can be an interference *filter*.

Related term: *cut-off filter*.

G2/GB

Barton reaction

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



See [25].

G2/GB

bathochromic shift (effect)

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

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: 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*. 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), which is a commonly used unit. The SI unit of $\varepsilon(\lambda)$ is m² mol⁻¹ (10 dm³ mol⁻¹ cm⁻¹).

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

See *absorbance, attenuation, extinction coefficient, Lambert law*, [35].

G2/GB

bioluminescence

Luminescence produced by living systems.

See *luminescence*.

G2/GB

biphotonic excitation

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

G2/GB

biphotonic process

Resulting from *biphotonic excitation*.

See *multiphoton process*.

G2/GB

bipolarons

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

See *self-localized excitations*.

biradical

An even–electron molecular entity with two (possibly delocalized) radical centres.

Species in which the two radical centres have a weak covalent interaction or have different electronegativities are often referred to as biradicaloids. If the two radical centres are located on the same atom, the term biradical is rarely used, and such species are called carbenes, nitrenes, etc.

Synonymous with *diradical*, which is not recommended.

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

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

See [23].

G2/GB

biradicaloid

Biradical–like. Often used referring to a species in which the two radical centres interact significantly.

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, $\Psi(x, X)$, of a molecular state is written as a product of two factors, i.e., an electronic and a nuclear factor:

$\Psi(q, Q) = \Phi(q, Q)\Theta(Q)$, where q and Q represent the coordinates of all the electrons and all the nuclei, respectively. The electronic wave function $\Phi(q, Q)$ is defined to be the eigenfunction the molecule would have if all its nuclei were clamped in the configuration represented by Q . The corresponding eigenvalue, $E(Q)$, is called the electronic energy. $\Theta(Q)$ 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 ma (where the first label specifies the electronic state and the second the vibrational state) as $\Psi_{ma}(q, Q) = \Phi_m(q, Q)\Theta_a^m(Q)$.

See [6,23].

branching plane

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

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

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

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

Note: The branching plane is also referred to as **g–h** plane. Inspection of x_1 and x_2 provides information on the geometrical deformation imposed to an *excited state* molecular entity immediately after decay at a conical intersection. Consequently, these vectors provide information on the *ground state* species that will be formed after the decay.

See [26].

brightness (of a laser dye)

Product of the *fluorescence quantum yield* (Φ) of a dye and the *molar absorption coefficient* at the excitation *wavelength* λ , i.e., $\Phi \epsilon(\lambda)$.

Cadmium–Helium laser

See *Helium–Cadmium laser*.

G2/GB

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

direction that increases (or decreases) the difference in local charges between donor and acceptor sites. Charge recombination reduces (or increases) the difference.

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

revG2

charge shift

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

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

G2/GB

charge-transfer (CT) absorption

Electronic absorption corresponding to a *charge transfer transition*.

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

revG2

charge-transfer (CT) complex

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

See *charge-transfer transition*.

G2/GB

charge-transfer (CT) state

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

G2/GB

charge-transfer (CT) transition

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

Note: Transition typical for donor–acceptor complexes or multichromophoric molecular entities.

See *charge–transfer absorption*, [35].

G2/GB

charge–transfer transition to solvent, (CTTS)

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

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

revG2

chemical laser

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

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

See [17].

G2/GB

chemiexcitation

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

G2/GB

Related term: *chemiluminescence*.

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.

See [23].

revG2

CIDEP

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

G2/GB

CIDNP

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

See [23].

G2/GB

CIEEL

Acronym for chemically initiated electron exchange luminescence. Type of *luminescence* resulting from a thermal electron-transfer reaction. Also called catalyzed *chemiluminescence*.

G2/GB

circular dichroism

See *dichroism*.

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

CO₂ laser

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

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

G2/GB

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 approximates well 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 [31].

revG2

colourability

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

complete active space self-consistent field, (CASSCF)

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

See *multiconfiguration SCF method*, [6].

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

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

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

computational photochemistry

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

See [26].

concentration depolarization

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

See *energy transfer, photoselection*, [35].

conduction band

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

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

G2/GB

configuration (electronic configuration)

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

Note 1: From one configuration several states with different *multiplicities* may result.

An example is the ground electronic configuration of the oxygen 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.

G2/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 configuration, 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].

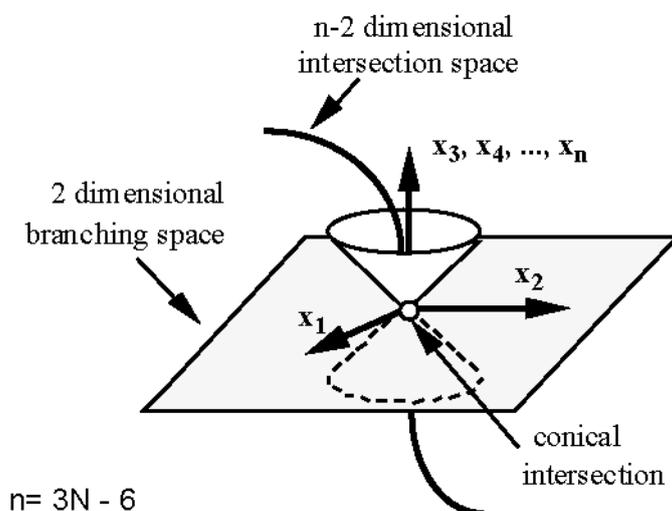
revG2

conical intersection

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

Note: 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 *ground* and *excited state* remain degenerate; movement in the branching plane lifts the degeneracy.

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



See [6,23,26].

contact ion pair

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

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

G2

conversion spectrum

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

Note: For example the conversion cross-section, $\tilde{\nu} \Phi$, has the SI unit m^2 , commonly given in cm^2 .

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

G2/GB

copper vapour laser

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

See *gas lasers*, *laser*.

G2/GB

correlation diagram

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

Note: An example involves the interpolation between the energies obtained for the united atoms and the values for the separated atoms limits.

See [6].

G2/GB

correlation energy

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

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

See [6].

G2/GB

critical quenching radius, R_0

See *Förster resonance energy transfer*.

G2/GB

crystal field splitting

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

Related term: *zero-field splitting*.

G2/GB

CT

Acronym for *charge-transfer*.

G2

current yield

See *photocurrent yield*.

G2/GB

cut-off filter

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

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

See *filter*.

G2/GB

CW

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

G2/GB

cycle (of a photochromic reaction)

See *photochromism*.

dark photochemistry (photochemistry without light)

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

See e.g., [27].

G2/GB

DAS

Acronym for decay associated spectra.

See *global analysis*.

Davydov splitting (factor-group splitting)

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

See [28].

G2/GB

deactivation

Loss of energy by an excited molecular entity.

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

G2/GB

decay associated spectra, (DAS)

See *global analysis*.

decay time

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

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

delayed fluorescence

See *delayed luminescence*.

G2

delayed luminescence

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

Note: The following mechanisms of luminescence provide examples:

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

See [34].

G2/GB

DEDMR

See *ODMR*.

G2/GB

degree of (polarization) anisotropy

See *emission anisotropy*.

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

Inverse of the linear *absorption coefficient*. The SI unit is m.

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 *absorbance, attenuation*.

revG2

Dexter excitation transfer (electron exchange excitation transfer)

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

The transfer rate constant, k_T , is given by

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

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

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

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

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

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

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

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

Related term: *radiative energy transfer*.

See [29,34].

revG2

DFDMR

See *ODMR*.

G2/GB

diabatic electron transfer

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

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

Related term: *adiabatic electron transfer*.

See [23].

G2/GB

diabatic photoreaction

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

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

Compare with *adiabatic photoreaction*.

See [23].

revG2

dichroic ratio

See *linear dichroism*.

dichroism

A sample is said to be dichroic (exhibit dichroism) if its *absorbance* depends on the type of polarization of the measuring beam. This polarization may be linear, corresponding to linear dichroism (LD) in which the difference in absorption for two perpendicularly linearly polarized beams is measured, $\Delta A_l = A_z - A_y$ or circular dichroism (CD) in which the difference in absorption for left minus right circularly polarized beams is measured, $\Delta A_c = A_L - A_R$.

See *light polarization, linear dichroism*, [34,35].

dielectric constant

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

G2/GB

diode lasers

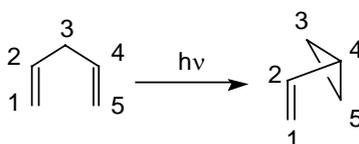
Semiconductor devices of small dimensions serving as sources of *CW* or pulsed *coherent radiation*. These *lasers* are also called semiconductor lasers.

See [30].

G2

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



Related terms: *aza-di- π -methane rearrangement* and *oxa-di- π -methane rearrangement*.

See [24].

G2/GB

dipolar mechanism (of energy transfer)

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

Related term: *energy transfer*.

revG2

dipole-dipole excitation transfer

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

Related term: *energy transfer*.

revG2

diradical

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

G2/GB

dose

Energy or amount of *photons* absorbed per surface area or per volume by an irradiated object during a particular exposure time. The SI units are J m^{-2} or J m^{-3} and mol m^{-2} or mol m^{-3} , respectively. Common units are einstein m^{-2} or einstein m^{-3} , 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 *fluence*, i.e., the energy or amount of photons per surface area (or per volume) received by an irradiated object during a particular exposure time.

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

G2/GB

doublet state

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

Related term: *multiplicity*.

G2/GB

downconversion

Process by which a photon with frequency ν_1 interacts with a non-linear 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 non-linear material. This in turn depends on the power of the incident radiation, the photon frequencies, their indices of refraction in the material, and the non-linear “hyper-susceptibility” of the material.

See *non-linear optical techniques, parametric processes, polarization*, [31].

driving force (for electron transfer)

Term widely used to indicate the negative of the standard Gibbs energy change for outer-sphere *electron transfer* ($\Delta_{\text{ET}}G^0$).

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

Related term: *polar driving force*.

See [22].

revG2

Drude–Nernst equation (for electrostriction)

Equation describing the contraction (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, $\frac{\partial(\ln\epsilon_r)}{\partial p}$, is not known for all media, there are approximations to evaluate this term as a function of ϵ_r and κ_T , the isothermal compressibility of the medium.

See *electrostriction*, [32].

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 molecule (the dye) pumped with a suitable pump laser or with a flash *lamp*.

Note: These lasers can be tuned over a large part of the fluorescence band of the dye.

See [17].

G2/GB

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 involving a species with respect to the sum of the rates of all of the parallel steps which depopulate that species.

Related term: *quantum yield*.

G2/GB

efficiency spectrum

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

See *action spectrum*, *conversion spectrum*.

Compare with *spectral effectiveness*.

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 $E = N_{\text{A}} h \nu$.

revG2

electrochemiluminescence

See *electrogenerated chemiluminescence*.

G2/GB

electrochromic effect

See *Stark effect*.

G2/GB

electrogenerated chemiluminescence, (ECL)

Luminescence produced upon a chemical reaction between species formed in electrode reactions.

Also called *electrochemiluminescence* or (incorrectly) *electroluminescence*.

revG2

electroluminescence

Non-thermal conversion of electrical energy into light.

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

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

Related term: *electrogenerated chemiluminescence*.

revG2

electron correlation

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

Related term: *correlation energy*.

See [6].

G2/GB

electron exchange excitation transfer

Same as *Dexter excitation transfer*.

Related term: *energy transfer*.

G2/GB

electronic configuration

See *configuration*.

G2/GB

electronic energy migration (or hopping)

Movement of electronic excitation energy from one molecular entity to another of the same species, or from one part of a molecular entity to another of the same kind. 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*.

electronically excited state

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

G2/GB

electron transfer

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

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

G2/GB

electron transfer photosensitization

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

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

Related term: *photosensitization*.

G2/GB

electrophotography

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

G2/GB

electrostriction

Contraction of a dielectric in an electric field gradient.

Note 1: For example as taking place around the charged centers created as a consequence of the sudden formation of separated positive and negative charges upon *electron transfer*.

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

See *Drude–Nernst equation*.

El–Sayed rules

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

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

See *multiplicity*, [33].

G2

emission

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

Related terms: *fluorescence*, *luminescence*, *phosphorescence*.

See [34].

G2/GB

emission anisotropy

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

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

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

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

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

For parallel absorbing and emitting transition moments the (theoretical) values are $(r, p) = (1/2, 2/5)$; when the transition moments are perpendicular, the values are $(r, p) = (-1/3, -1/5)$. 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 aligned samples. In the case of a non-isotropic, 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 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 *light polarization, uniaxial sample*, [34,35].

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 [34].

G2/GB

emissivity

Same as *emittance*.

emittance, e

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

Note: Mathematical definition is M/M_{bb} .

See [7].

revG2

encounter complex

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

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

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

G2/GB

energy hypersurface

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

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

See [6].

energy migration

See *electronic energy migration*.

G2/GB

energy pooling

See *annihilation*.

G2/GB

energy storage efficiency, η

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

Related term: *efficiency*.

G2/GB

energy transfer

Term used to describe the process by which a molecular entity absorbs *ultraviolet*, *visible*, or *infrared* radiation and a phenomenon originates from the *excited state* of another molecular entity.

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

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

See [34].

G2/GB

energy transfer plot

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

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

Hammond–Herkstroeter plot.

Related term: *Stern–Volmer kinetic relationships*.

revG2

enhancer (of emission)

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

revG2

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 redissociates in the ground state.

Related term: *exciplex*.

See [34].

revG2

excimer lamp

Incoherent 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 rare gas, halogen, or rare 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 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 I₂ (341) (see Table).

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 up to 1.5 m picture diagonal.

Table. Peak wavelengths (nm) obtained in dielectric-barrier discharges with mixtures of rare gas (Rg) and halogen. Commercially available lamps are in bold

	X₂	Ne	Ar	Kr	Xe
Rg₂			126	146	172
F	157	108	193	249	354
Cl	259		175	222	308
Br	291		165	207	283
I	341			190	253

See [36].

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 domain.

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

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

G2/GB

exciplex

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

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

See [37].

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, only at very low *absorbances* the excitation spectrum of a unique species should be identical to its *absorption spectrum*.

Related term: *emission spectrum*.

See [34].

revG2

excitation transfer

Same as *energy transfer*.

G2/GB

excited state

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

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

G2/GB

exciton

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

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

See *electronic energy migration, self-localized excitations*.

See [31].

revG2

exitance

See *radiant exitance*.

G2/GB

external heavy atom effect

See *heavy atom effect*.

G2/GB

exterplex

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

Related term: *exciplex*.

G2/GB

extinction

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

G2/GB

extinction coefficient

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

See *Beer–Lambert law*.

G2

factor–group splitting

See *Davydov splitting*.

G2/GB

fatigue (of a photochromic system)

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

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

See [3].

Fermi level, E_F

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

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

G2/GB

filter (optical)

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

See [2,15].

G2/GB

flash photolysis

Transient spectroscopy and transient kinetic technique in which a *ultraviolet, visible, or infrared*

radiation pulse is used to produce transient species.

Note: 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).

See [38] for a list of recommended procedures and optical data on transient species. See also [2].

fluence, radiant energy fluence, F_0 , H_0

At a given point in space, the *radiant energy*, Q , incident on an small sphere from all directions divided by the cross-sectional area of that sphere, integrated over time. The 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: The mathematical definition is $F_0 = dQ/dS$, where S is the area of cross-section. If the radiant energy is constant over the area S , then $F_0 = Q/S$.

Note 2: The definition is equivalent to $F_0 = \int_t E_0 dt$ where E_0 is the *fluence rate* and t the duration of the irradiation. If the fluence rate is constant over the time interval, then $F_0 = E_0 t$.

Note 3: Fluence (F_0 , H_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.

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

See [9]

revG2

fluence rate, radiant energy fluence rate, E_0

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

Note 1: The mathematical definition is $E_0 = dP/dS$. If the radiant power is constant over the area S , then $E_0 = P/S$.

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

See *intensity*, *radiance*.

Related term: *photon fluence rate*.

See [9]

revG2

fluorescence

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

See [34].

revG2

fluorescence anisotropy

See *emission anisotropy*, *photoselection*.

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 optical radiation.

fluorogenic

Material in which *fluorescence* is induced by another molecular entity through the mixing of the two.

Note: An example is a non-fluorescent compound consisting of a pyrene connected to a maleimide

group (which quenches the pyrene fluorescence). A reaction with the maleimide moiety producing a succinimide derivative affords the recovery of the pyrene fluorescence.

fluorophore

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

fluxional molecules

Subclass of structurally non-rigid molecules in which all the observable interconverting species are chemically and structurally equivalent.

Note: Classic example of the phenomenon of fluxionality is the rapid “automerization” of tricyclo[3.3.2.0^{2,8}]deca-3,6,9-triene (bullvalene), the rapid interconversion of 1209 600 (10!/3) degenerate isomers.

See *Jahn–Teller effect*, [6].

***f* number**

See *oscillator strength*.

G2/GB

Förster cycle

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

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

Note 2: Foerster is an alternative and acceptable spelling for Förster.

revG2

See [34].

Förster radius

See *Förster resonance energy transfer*, [34].

Förster resonance energy transfer (dipole–dipole excitation transfer)

Non-radiative excitation transfer between two molecular entities separated by distances considerably exceeding the sum of their van der Waals radii. It describes the transfer in terms of the interaction between the *transition dipole moments* of the entities in the very weak dipole–dipole coupling limit. It is 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 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 ($k_T = k_D$).

R_0 is given by

$$R_0^6 = \frac{9000 (\ln 10) \kappa^2 \Phi_D^0}{128 \pi^5 N_A n^4} J$$

where κ is the *orientation factor*, Φ_D^0 is the fluorescence quantum yield of the donor in the absence of transfer, N_A is Avogadro constant, 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 overlapping of the donor emission spectrum with the acceptor absorption spectrum and given by

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

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

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

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

Note 3: A practical expression for R_0 is:

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

The *orientation factor* κ is given by

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

where θ_{DA} is the angle between the donor and acceptor transition 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 (colinear transition moments). When the transition moments are parallel, $\kappa^2 = 1$. For randomly oriented transition dipole moments, e.g., in fluid solutions, $\kappa^2 = 2/3$.

Note 3: The transfer quantum efficiency is defined as

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

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

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

or written in the following form :

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

where τ_D is the donor excited-state lifetime in the presence of acceptor.

Note 4: Foerster is an alternative and acceptable spelling for Förster.

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

See [34,39].

revG2

Fourier transform spectrometer

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

G2/GB

fraction of light absorbed, f

The 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 may be omitted for f , T , and A defined over a very narrow wavelength range.

Note 2: For $A(\lambda) < 0.1$, $f(\lambda) \approx A(\lambda) \ln 10$.

Franck-Condon factor

Square modulus of the overlap integral between the vibrational wave functions (Θ) for the initial (0) and final (e) state of a given electronic transition.

$$\left(\int \Theta_v^e \Theta_v^0 dt \right)^2$$

where the integration is over all nuclear coordinates.

See *Franck–Condon principle*, [34,35].

Franck–Condon principle

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

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

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

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

G2/GB

Franck–Condon state

See *Franck–Condon principle*.

G2/GB

free electron laser

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

See *laser*, [17].

G2/GB

free exciton

See exciton.

free-running laser

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

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. The 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 doubling

See harmonic frequency generation, non-linear optical effects.

G2/GB

FRET

Acronym for *Förster resonance energy transfer*.

Note: Sometimes inappropriately called fluorescence resonance energy transfer.

fundamental emission anisotropy

See emission anisotropy.

FWHM

Acronym for full width at half maximum.

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

G2/GB

gas lasers

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

- neutral atoms (e.g., Ne, Cu, Au, etc.) or molecules (e.g., 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 in many cases may be selected from a single apparatus.

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

See *argon ion-*, *CO₂-*, *excimer*, *copper vapour-*, *helium-neon-*, *krypton-*, *nitrogen-lasers*, [17].

G2

gated photochromism

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

See [3].

gaussian band shape

Band shape described by the Gaussian 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.

Related term: *Lorentzian band shape*.

G2/GB

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 recombination

Recombination reaction of a *geminate pair*.

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

G2

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)

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

where $e = 1.602\,176\,53 \times 10^{-19} \text{ C}$ is the elementary charge, $N_{\text{A}} = 6.022\,1415 \times 10^{23} \text{ mol}^{-1}$ is the Avogadro constant, $E^0(\text{D}^{\bullet+}/\text{D})/\text{V}$ is the standard electrode potential of the donor cation radical

resulting from the electron transfer, $E^0(\text{A}/\text{A}^{-\bullet})/\text{V}$ 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.

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

$$w(\text{D}^+\text{A}^{-\bullet}) / \text{J} = z(\text{D}^+) z(\text{A}^{-\bullet}) e^2 / (4 \pi \varepsilon_0 \varepsilon_r a)$$

$$w(\text{DA}) / \text{J} = z(\text{D}) z(\text{A}) e^2 / (4 \pi \varepsilon_0 \varepsilon_r a)$$

where a is the distance of the charged species after electron transfer, ε_r is the relative medium static permittivity (formerly called dielectric constant), $\varepsilon_0 = 8.854 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$ is the vacuum permittivity, and z_X the charge of the species X.

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

Note 1: Several other approximations are in use for the calculation of the term $w(\text{D}^+\text{A}^{-\bullet})$, depending on the nature of the formed species such as *contact* or *solvent-separated radical ion pairs*, 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 [40] and

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

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

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

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

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

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

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

For a list of electrode potentials see [41] .

See [22].

revG2

global analysis

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

Note: Typical for the analysis of emission (or transient absorption) data. Upon excitation with a particular wavelength, radiant intensity of the emission (or transient absorbance) decays are observed as a function of a variable parameter, e.g., the observation wavelength but otherwise under the same condition. All decays are then analysed together (globally) under the constrain 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.

See [34,38,42,43].

ground state

Lowest energy state of a chemical entity.

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

G2

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

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

See [3].

half-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 band width 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*.

G2/GB

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 non-linear polarizability.

Note: The case $k = 2$ is referred to as frequency doubling, $k = 3$ is frequency tripling, $k = 4$ is

frequency quadrupling. Even higher integer values of k are possible.

See *non-linear optical techniques*, [31].

G2/GB

harpoon mechanism

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

G2/GB

heavy atom effect

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

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

See [23].

G2/GB

heliocromism

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

See [3].

helium-cadmium laser

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

See *gas lasers*.

G2/GB

helium–neon laser

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

See *gas lasers*.

G2/GB

Herkstroeter plot

See *energy transfer plot*.

G2/GB

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 which emits lines over a background continuum between about 200 and 1400 nm.

See *lamp*, [2].

G2/GB

hole burning

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

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

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

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

See [31,44].

revG2

hole transfer

Charge migration process in which the majority of 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 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

Hund rules

(1) Of the different multiplets resulting from different *configurations* of electrons in degenerate

orbitals of an atom those with greatest *multiplicity* have the lowest energy (multiplicity rule).

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

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

Note: Hund rules apply if the “Russell–Saunders” coupling scheme is valid. Sometimes the first rule is applied to molecules.

G2/GB

Hush model

Theory describing an optically induced *electron transfer* process.

Related term: *Marcus–Hush relationship*.

See [45,46].

revG2

hyperchromic effect

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

Related term: *auxochrome*.

G2/GB

hyperfine (interaction)

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

See [6.

revG2

hypochromic effect

Opposite to *hyperchromic effect*.

G2/GB

hypsochromic shift

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

G2/GB

ICT

Acronym for *intramolecular charge transfer*.

See *planar intramolecular charge transfer (PICT)*, *twisted intramolecular charge transfer (TICT)*.

ICT emission

Electronic emission from an *ICT* state.

Related term: *intramolecular charge transfer*.

imaging (photoimaging)

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

G2/GB

incoherent radiation

Not having the properties of the *coherent radiation*.

G2/GB

infrared

Region of the electromagnetic spectrum extending from 700 nm to about 20 000 nm (500 – 14 286 wavenumbers).

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

inner filter effect

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

See *radiative energy transfer*.

G2/GB

inner–sphere electron transfer

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

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

Compare with *outer–sphere electron transfer*.

See [22]

G2/GB

integrating sphere

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

G2/GB

intended crossing (of potential–energy surfaces)

Same as *avoided crossing*.

Note: The term ‘intended’ should not be used in this context since it is an anthropomorphic term.

G2/GB

intensity

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

See [9].

G2/GB

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

Same as *radiant intensity*.

G2

intensity (of a spectral feature)

Describes the magnitude of the particular feature in the spectrum.

G2

interference filter

Optical device which permits the transmission of radiation within a narrow *wavelength* range based on the principle of waves interference. Technically, a thin transparent spacer is placed between two semireflective coatings and multiple reflections and interference are used to select a narrow frequency band, producing an interference filter.

See *filter*.

revG2

interferometer

See *Fourier transform spectrometer*.

G2/GB

internal conversion

A *photophysical process*. Isoenergetic *radiationless transition* between two electronic states of the same *multiplicity*.

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

G2/GB

internal transmittance

See *transmittance*.

G2/GB

intersection space

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

See [26].

intersystem crossing

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

See [23,34,35].

G2/GB

intervalence charge transfer

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

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

G2/GB

intimate ion pair

Same as *contact ion pair*.

G2/GB

intramolecular charge transfer, (ICT)

A process which changes the overall charge separation 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 photoinduced ICT: *planar intramolecular charge transfer (PICT)* or *twisted intramolecular charge transfer (TICT)*. An ICT has been proposed to be responsible for the strongly *Stokes-shifted* additional fluorescence band in dual fluorescent molecules.

inverted region (for electron transfer)

The region where the driving force ($-\Delta_{\text{ET}}G^0$) for *electron transfer* exceeds the total *reorganization energy* (λ), i.e., $-\Delta_{\text{ET}}G^0 > \lambda$ in the *Marcus equation* developed for *outer-sphere electron transfer*.

Note: The behaviour in this region is referred to as *electron transfer* under inverted region conditions because the basic/classical Marcus equation leads to a counter-intuitive prediction that under such conditions the rate of electron transfer should decrease with increasing exergonicity ($\Delta_{\text{ET}}G^0$). It should be noted that experimentally such a decrease in rate is not always observed and, even when it is, a more elaborate theory is required to quantify the actual behaviour in this region.

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

Compare with *normal region*.

See *Gibbs energy of photoinduced electron transfer*, [22,52].

G2/GB

irradiance, E

Radiant power, P , of all wavelengths incident within a parallel beam and perpendicularly on a small element of surface containing the point under consideration divided by the area of the element. The SI unit is W m^{-2} .

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

Note 2: For a beam incident from all directions, *fluence rate* (E_0) is an equivalent term.

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

Related term: *photon irradiance*.

See [9].

revG2

isoabsorption point

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

G2/GB

isoclinic point

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

G2/GB

isoemissive point

Same as *isolampsic* or *isostilbic point*.

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

revG2

isolampsic point

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

Note: The term derives from the Greek words isos: equal and lampein: to emit light or to shine.

Isolampsic is thus symmetric with *isosbestic*.

revG2

isooptoacoustic point

Wavelength, wavenumber, or frequency at which the total energy emitted by a sample as heat does

not change upon a chemical reaction or physical change of the sample. Its position depends on the experimental conditions.

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

See *photoacoustic spectroscopy*, [18].

G2/GB

isosbestic point

Wavelength, wavenumber, or frequency at which the total *absorbance* of a sample does not change during a chemical reaction or a physical change of the sample.

Note 1: A simple example occurs when one molecular entity is converted into another which has the same *molar absorption coefficient* at a given wavelength. As long as the sum of the concentrations of the two molecular entities in the solution is held constant, there will be no change in *absorbance* at this wavelength as the ratio of the 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 reaction occur during the considered time range, since $A_{\lambda} l^{-1} = \sum_{i=1}^n \varepsilon_i(\lambda) c_i$ is invariant. For the reaction $A + B \rightarrow c C + d D + e E$, with c , d , and e the percentages of the products C, D, and E, an isosbestic point will be observed at every wavelength where the condition $\varepsilon_A + \varepsilon_B = c \varepsilon_C + d \varepsilon_D + e \varepsilon_E$, provided that the values of the percentages c , d , and e remain constant during the chemical reaction or the physical change. The use of the term isoabsorption point is not recommended.

revG2

isostilbic point

Same as *isolampsic point*.

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

revG2

Jablonski diagram

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

Note 1: The original Jablonski diagram did not assign a different *multiplicity* to the phosphorescent state. Presently, modified Jablonski diagrams are frequently used and are actually state diagrams in which molecular electronic states, represented by horizontal lines displaced vertically to indicate relative energies, are grouped according to *multiplicity* into horizontally displaced columns. Excitation and *relaxation* processes that interconvert states are indicated in the diagram by arrows. *Radiative transitions* are generally indicated with straight arrows (\rightarrow), while *radiationless transitions* are generally indicated with wavy arrows ()

See [47].

G2/GB

Jahn–Teller effect

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

Note: Effect due to the odd terms in the vibronic perturbation expansion. In the case of molecules with a non-degenerate *ground electronic state*, but with a low lying degenerate *excited state*,

distortions of proper symmetry arise which result in mixing of the ground and excited states, thereby lowering the ground state energy (pseudo Jahn–Teller effect). The pseudo Jahn–Teller effect manifests itself in fluxional behaviour (see *fluxional molecules*) and stereochemical non-rigidity of molecules and ions. The Jahn–Teller effect generates a *surface crossing* (e.g., a *conical intersection*) whereas a pseudo Jahn–Teller effect generates an *avoided crossing*.

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

See [6].

revG2

Kaptein–Closs rules

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

See [48].

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 [49].

revG2

Kasha–Vavilov rule

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

See [50].

G2/GB

Koopmans' theorem

See *photoelectron spectroscopy*, [23].

G2/GB

krypton ion laser

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

See *gas lasers*.

G2/GB

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 *absorbance*, *Beer–Lambert law*.

G2/GB

lamp

Source of *incoherent* radiation.

See *amalgam*, *excimer*, *high–pressure*, *medium–pressure*, and *low–pressure mercury lamp (arc)*, and *antimony–xenon*, *mercury–xenon*, *quartz–iodine*, *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*

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

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 velocity along the reaction coordinate.

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

See [6].

Laporte rule

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

G2/GB

LAS

Acronym for lifetime associated spectra.

See *global analysis*.

laser

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

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

Related term: *lasing*.

See [17].

G2/GB

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

The lifetime of a molecular entity which decays in a first order process is the time needed for a concentration of the entity to decrease to 1/e of its original value. Statistically, it represents the life expectation of the entity. It is equal to the reciprocal of the sum of the first order rate constants of all processes which cause the decay.

Note 1: The mathematical definition is $\tau = 1/k = 1 / (\sum_i k_i)$ with k_i the first-order rate constants for all decay processes of the excited 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 apparent lifetime or *decay time*, instead.

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.

revG2

lifetime associated spectra, (LAS)

See *global analysis*.

ligand field splitting

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

See *crystal field splitting*.

G2/GB

ligand to ligand charge transfer (LLCT) transition

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

G2/GB

ligand to metal charge transfer (LMCT) transition

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

Related term: *metal to ligand charge transfer transition*

G2/GB

light-emitting diode, (LED)

Semiconductor (often a combination of gallium, arsenic and phosphorous) containing an *n* region (where electrons are more numerous than positive charges) separated from a *p* region (where positive charges are more numerous than negative charges). Upon application of a voltage charges move and emission of *ultraviolet*, *visible*, or *infrared* radiation is produced each time a charge recombination takes place. Although a 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 near-*ultraviolet*, *visible* or *infrared*.

Note 3: Organic and polymeric materials are also used for the production of LEDs and are called OLEDs and PLEDs, respectively.

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.

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

See [34,35].

revG2

light source

See *lamp, laser.*

G2/GB

linear dichroism

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

$$\Delta A_l = A_Z - A_Y$$

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

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

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

Thus, ΔA_r is analogous to *emission anisotropy*.

Note 2: the denominator corresponds to three times the absorbance measured in a similar, but isotropic sample.

Note 3: 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 4: 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, which tend to produce *uniaxial* samples. Also crystals may be used as aligned solvents and if the sample forms suitable crystals by itself, they may be used directly. Other alignments techniques include application of electric or magnetic fields. *Photoselection* is a commonly used technique for the production of aligned samples; both the photoselected subset and the set of remaining molecules may be studied.

See *emission anisotropy, photoselection, transition moment*, [34,35].

Lippert–Mataga plot

Correlation of the *Stokes–shift* between the absorption and emission maxima $\Delta\tilde{\nu}$ and the Lippert–Mataga polarity factor $f(\epsilon_r, n)$ of the solvent,

$$\Delta\tilde{\nu} = \frac{(\mu_{\text{exc}} - \mu_{\text{gr}})^2}{2\pi c h \epsilon_0 r^3} f(\epsilon_r, n)$$

with c the speed of light, h the Planck constant, ϵ_0 the vacuum permittivity, and

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

with ϵ_r the static relative permittivity, n the refractive index of the solvent, μ_{exc} and μ_{gr} the dipole moment of *excited* and *ground state*, respectively, and r the effective cavity radius of the excited molecular species in the medium.

Note: The Lippert–Mataga plot is used to calculate the size of the change in charge distribution of

the molecular system, $\frac{(\mu_{\text{exc}} - \mu_{\text{gr}})^2}{r^3}$, upon absorption of a photon.

See [51].

Lippert–Mataga polarity factor

See *Lippert–Mataga plot*.

localized exciton

See *exciton*.

Lorentzian band shape

Band shape described by the function

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

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

Related term: *Gaussian band shape*.

G2/GB

low–pressure mercury lamp (arc)

Resonance lamp which contains mercury vapour at pressures of about 0.1 Pa (0.75×10^{-3} Torr; 1 Torr = 133.3 Pa). At 25 °C, such a lamp emits mainly at 253.7 and 184.9 nm. 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 which emits in the UV–A spectral region (315–400 nm).

See *lamp* [2,15].

revG2

luminescence

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

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

See [34].

G2/GB

luminescence anisotropy

See *emission anisotropy*

lumiphore (luminophore)

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.

G2/GB

magic angle

Upon excitation of an *isotropic* sample (assuming an ultrashort excitation pulse), the relationship between the *fluorescence* intensity detected at a time t and an analyser 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 analyser angle β with respect to the electric *polarization* of the exciting beam, N the excited state population, and R the degree of alignment of the transition dipole moment of the excited molecular entity.

See [34,35].

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 magnitude recorded is given by

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

with $\alpha(\lambda)^+$ and $\alpha(\lambda)^-$ the *absorption coefficients* for right and left circularly polarized light, respectively. The spectra are a representation of Δ vs. *wavelength*. Usually, the MCD signal is recorded as a function of the applied field (up to 10T) and the temperature (1.4 – 300K).

Note 2: The phenomenon is related to magnetically induced optical activity (“Faraday effect”), by the “Kramers–Kronig” transformations which connect optical refraction and absorption, i.e., MCD is observed in optically active materials at wavelengths with non-vanishing absorption. It occurs for diamagnetic, paramagnetic and (anti)–ferromagnetic material and has been observed from IR 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 an optical probe of paramagnetism that permits the identification of the electronic and magnetic properties of the ground states of transition metal ions centers. The wavelength dependence of MCD can be used also to identify and assign optical transitions from metal ion sites.

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

See [35].

Marcus equation (for electron transfer)

Proposed by R.A. Marcus to relate the rate of *outer-sphere electron transfer* with the thermodynamics of this process [52]. 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 *Gibbs energy of photoinduced electron transfer*, [22,23,52].

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 for degenerate electron transfer ($\Delta G^0 = 0$) in, e.g., symmetrical mixed valence systems:

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

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

See *Hush model*, *Gibbs energy of photoinduced electron transfer*, *Marcus equation*, [46]
revG2

Marcus inverted region (for electron transfer)

See *inverted region*, [52].

G2/GB

medium–pressure mercury lamp (arc)

Non–coherent radiation source containing mercury vapour at pressures ranging from 50 to several hundred kPa (1 atm = 101.325 kPa). Emits mostly from 200 to 1000 nm with most intense lines approximately at 218, 248, 254, 266, 280, 289, 297, 303, 313, 334, 366, 406, 408, 436, 546, and 578 nm.

See *lamp* [2,15].

revG2

mercury–xenon lamp (arc)

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

See *lamp* [2,15].

G2/GB

MERP

Acronym for *minimum energy reaction path*.

merry-go-round reactor (turntable reactor)

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

G2/GB

metal to ligand charge transfer (MLCT) transition

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

Compare with *ligand to metal charge transfer transition*

G2/GB

metal to metal charge transfer (MMCT) transition

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

Related term: *intervalence charge transfer*.

G2/GB

minimum energy reaction path, (MERP)

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

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).

Related term: *free-running laser*.

molar absorption coefficient, molar decadic absorption coefficient, ϵ

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

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

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

Note: 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 *absorbance, absorption coefficient, Beer-Lambert law*.

See [7].

G2/GB

molecular alignment

See *linear dichroism*.

molecular orientation

The absorption probability for a molecular transition with its transition moment at an angle u with the electric vector of the light is proportional to $\cos^2 u$. For the whole sample it is proportional to the *orientation factor* $K_u = \langle \cos^2 u \rangle$, 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, it is 1/3 for an isotropic sample and 0 for a sample where all transition moments are perpendicular to the electric vector. The directional cosines provide, especially for *uniaxial* samples, a simple description of exactly those orientational properties of the sample that are relevant for light absorption. With a properly chosen molecular coordinate system (x, y, z), forming angles $u = x, y, z$ with the electric vector, all orientational effects on light absorption are contained in K_u . Since the sum of K_u for 3 perpendicular molecular axes is equal to 1, only two independent parameters are required to describe the orientational effects on light absorption.

Note 1: A related, commonly used description is based on Saupe matrices:

$$S_{uv} = (3 K_u - 1) / 2$$

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

Note 2: Order parameters (Wigner matrices) are an alternative to the directional cosine-based description of molecular alignment. The order parameters-method also work well for non-uniaxial samples, and provide a seemingly more complex, but in other ways convenient, description of molecular orientation distributions. They are used as a basis set for an expansion of the orientational distribution function.

See [34,35].

multiconfiguration SCF (MCSCF) method

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

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

See [6].

multiphoton absorption

See *multiphoton process*.

Related term: *biphotonic excitation*.

G2/GB

multiphoton process

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

See *biphotonic process*, *two-photon process* [31].

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

natural lifetime

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

G2/GB

neodymium laser

CW or pulsed *laser* emitting radiation from excited 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–aluminium garnet, YAG) or in suitable glasses (phosphate, silicate, etc.).

See *solid state lasers*, [17].

G2/GB

neutral–density filter

See *attenuance filter*.

G2/GB

nitrogen laser

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

See *gas lasers*.

G2/GB

non–adiabatic electron transfer

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

non–adiabatic photoreaction

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

Compare with *adiabatic photoreaction*.

G2

non-crossing rule

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

Note: The rule only applies for diatomic molecules and does not apply for polyatomic molecules.

See *conical intersection* [6,23,26].

non-linear optical effect

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

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

See [31].

revG2

non-linear optical techniques

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

Note: Some of these spectroscopies are four-wave mixing, *hole burning, photon echoes*, time-resolved coherent anti-Stokes Raman (CARS), transient grating, 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. Low order non-linear techniques, such as three-wave mixing, are related to the second order *polarization*. For a random isotropic medium with inversion symmetry, the second-order polarization vanishes and then the lowest order optical non-linear techniques, as well as the higher order non-linear techniques are related to the third-order polarization and the corresponding “hyper-susceptibility”.

See [31].

non-radiative decay

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

Same as *radiationless deactivation (decay)*.

revG2

non-vertical energy transfer

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

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

See *Franck-Condon principle*.

See [23].

revG2

See [35].

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 ($\Delta_{\text{ET}}G^0$). This region is predicted by the Marcus theory for *outer-sphere electron transfer* for the case of $\Delta_{\text{ET}}G^0 \leq \lambda$ in the *Marcus equation*.

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

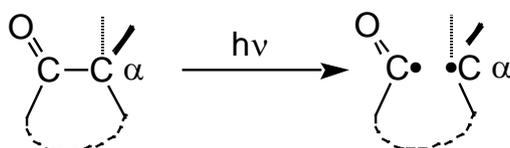
G2/GB

Norrish Type I photoreaction

α -Cleavage of an excited carbonyl compound leading to an acyl-alkyl *radical pair* (from an

acyclic carbonyl compound) or an acyl–alkyl *biradical* (from a cyclic carbonyl compound) as a *primary photoproduct*.

Note: An example is:



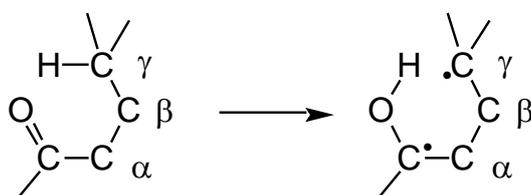
See [53].

G2/GB

Norrish Type II photoreaction

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

Note: An example is:



See [53].

G2/GB

$n \rightarrow \pi^*$ transition

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

G2/GB

$n-\pi^*$ state

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

G2/GB

$n \rightarrow \sigma^*$ transition

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

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

G2/GB

ODMR

Acronym for optically detected magnetic resonance: 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*, non-specified), DFDMR (*delayed fluorescence*), FDMR (*fluorescence*), PDMR (*phosphorescence*). If a reaction yield is monitored the expression RYDMR (reaction yield detected magnetic resonance) is used.

See [35].

G2/GB

OLED

Acronym for organic light-emitting diode.

one-photon photochromism

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

Related term: *two-photon photochromism*.

See [19].

OPO

Acronym for optical parametric oscillator.

optical density

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

G2/GB

optical parametric oscillator, (OPO)

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 1: 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 2: 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*).

Related term: *non-linear optical effect*.

See [54].

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. [18]

revG2

orbital (atomic or molecular)

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

G2/GB

See [6].

order parameters

See *molecular orientation*.

orientation factor

See *Förster resonance energy transfer, molecular orientation*, [35].

oscillator strength, f number

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*, using the equation

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

where $\epsilon(\tilde{\nu})$ is the *molar decadic absorption coefficient* at wavenumber $\tilde{\nu}$ and n 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 2) takes into account line broadening effects.

See [35].

Related term: *transition (dipole) moment*.

revG2

outer–sphere electron transfer

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

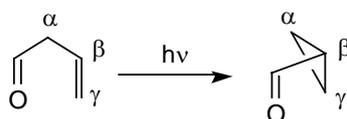
See *Marcus equation*.

Compare with *inner–sphere electron transfer*.

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



Related terms: *aza–di– π –methane rearrangement* and *di– π –methane rearrangement*.

See [24].

G2/GB

parametric processes

Interaction of photons in a non-linear medium satisfying the energy and momentum conservation laws. During the interaction the photon frequencies are mixed and photon(s) with different frequencies are created.

Note: Optical parametric processes of three interacting beams, called frequency mixing processes, are: second-harmonic generation (SHG), sum-frequency generation (SFG), difference-frequency generation (DFG), optical parametric generation and amplification (OPG and OPA), and optical parametric oscillation (OPO).

See *non-linear optical effect*.

See [55].

PAS

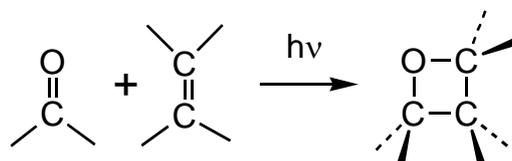
Acronym for *photoacoustic spectroscopy*.

Related term: *optoacoustic spectroscopy*.

See [18].

Paternò-Büchi reaction

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



See [56].

G2/GB

PEC

Acronym for *photoelectrochemistry*.

PDMR

See *ODMR*.

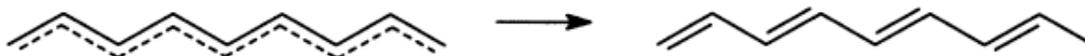
G2/GB

Peierls distortion

Distortion of a regular one-dimensional structure with a partially occupied band to give bond alternation, eventually leading to dimerization or oligomerization. The degree of oligomerization 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 polyacetylene.



See [6].

penetration depth

See *depth of penetration*.

G2/GB

PES

Acronym for *photoelectron spectroscopy*.

Same acronym often used for *potential energy surface*.

G2

PET

Acronym for *photoinduced electron transfer*.

phonon

Elementary excitation in the quantum mechanical treatment of vibrations in a crystal lattice. A quasiparticle which is a quantized sound wave and which can occur in solids and liquid helium II.
revG2

phosphorescence

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

See [34].

G2/GB

phosphorescence anisotropy

See *emission anisotropy*, *photoselection*, [35].

photoacoustic effect

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

See *photoacoustic spectroscopy*, [18].

G2/GB

photoacoustic spectroscopy, (PAS)

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

Related term: *isooptoacoustic point*, *optoacoustic spectroscopy*.

See [18]

G2/GB

photoaffinity labelling

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

G2/GB

photo-assisted catalysis

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

See *photocatalysis*.

G2/GB

photobiology

Branch of biology concerned with the biological and bioenvironmental effects of *ultraviolet*, *visible*, or *infrared* radiation.

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 hole burning

See *hole burning*.

G2/GB

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 [6,26].

photochemical reaction

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

G2/GB

photochemical reaction path

Sequence of geometries adopted by a molecule after initial electronic *excitation*, combined with a specification of the electronic state at each geometry from radiation *absorption* to product formation. Theoretically, this usually involves the computation of the *MERP* connecting the *Franck-Condon* point, located on the *potential-energy surface* of the spectroscopic state, to the final photoproducts located on the *ground state* potential-energy surface. Experimentally, a photochemical reaction path can be probed by detecting transient species or reaction intermediates.

See [23,26]

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 compounds emitted by vegetation.

See [57].

revG2

photochemistry

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

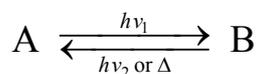
See *photochemical reaction*.

G2/GB

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).



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

Note 1: In a cycle of a *photochromic* system, the initial state A is phototransformed into B, which returns to A either thermally or photochemically; the terms "switch-on" and "switch-off" are used.

Note 2: An important parameter is the "number of cycles" that a photochromic system can undergo under well defined conditions (solution, matrix, concentration, temperature).

See [19].

revG2

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 photo-generation between the two electrodes of a *photovoltaic cell* or a *photoelectrochemical cell*.

G2/GB

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 UV-based processes as well as in the decomposition of polymers by UV-visible based processes which deplete 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 molecular oxygen.

Note: Molecularly, it is the sensitized *photooxidation* involving molecular oxygen.

revG2

photoelectrical effect

Ejection of an electron from a solid or a liquid by a photon.

G2/GB

photoelectrochemical cell

Electrochemical cell in which current and a voltage are simultaneously produced upon *absorption* of *ultraviolet*, *visible*, or *infrared* radiation by one or more of the electrodes. Usually at least one of the electrodes is a semiconductor.

G2/GB

photoelectrochemical etching

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

Note: Method used in the photopatterning of semiconductor surfaces.

G2/GB

photoelectrochemistry, (PEC)

Hybrid field of chemistry employing techniques which combine photochemical and electrochemical methods for the study of the oxidation–reduction chemistry of the ground or *excited states* of molecules or ions. In general, it is the chemistry resulting from the interaction of *ultraviolet*, *visible*, or *infrared* radiation with electrochemical systems.

Related terms: *photoelectrochemical*, *photogalvanic*, *photovoltaic cell*.

See [58].

G2/GB

photoelectron spectroscopy, (PES)

Spectroscopic technique which measures the kinetic energy of electrons emitted upon the ionization of a substance by high energy monochromatic *photons*. A photoelectron spectrum is a plot of the

number of electrons emitted versus their kinetic energy. The spectrum consists of bands due to transitions from the *ground state* of an atom or molecular entity to the ground and *excited states* of the corresponding oxidized atom or molecular entity.

Note: Approximate interpretations are usually based on *Koopmans' theorem* relating ionisation potentials to orbital energies. *UPS* (ultra-violet photoelectron spectroscopy) is the spectroscopy using vacuum ultraviolet sources, while *ESCA* (electron spectroscopy for chemical analysis) and *XPS* use X-ray sources.

For a photoelectron spectroscopy database see [59].

See [60].

G2/GB

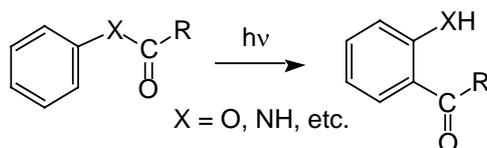
photoexcitation

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 e.g.[61].

G2/GB

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

photoimaging

See *imaging*.

G2/GB

photoinduced electron transfer, (PET)

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

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

Related terms: *driving force*, *Gibbs energy of photoinduced electron transfer*, *Marcus equation*, *polar driving force*, *reorganization energy*, *Weller correlation*.

See [22].

revG2

photoinduced polymerization

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

See *photoinitiation*, [62].

G2/GB

photoinitiation

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

See *photoinduced polymerization*.

revG2

photoionization

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

Related term: *photodetachment*.

G2

photoluminescence

Luminescence arising from direct *photoexcitation* of the emitting species.

Related terms: *fluorescence*, *phosphorescence*.

See [34].

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.

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

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

Note: Technique used for two purposes:

(1) sensitive measurement of low levels of radiation and

(2) recording of emission decays.

See *time-correlated single photon counting*.

revG2

photon echo

Time-resolved optical spectroscopy in which the inhomogeneous broadening of absorbers is eliminated by the proper choice of geometry in a four-wave mixing experiment.

Note 1: Term applied to a group of non-linear optical techniques such as integrated echo, time-gated echo, three-pulse echo peak shift, heterodyne-detected echo, and 2D-echo.

Note 2: Photon echo techniques make use of the third-order optical *polarization* and “hyper-susceptibility”. The main distinguishing feature of photon echo methods from all other third order processes is the time ordering of the field interactions that leads to a rephrasing 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: techniques used, e.g., to probe solvation dynamics upon (ultra-short) pulse excitation of a chromophore.

See [31].

photon emittance

See *photon exitance*.

G2/GB

photon exitance, M_p

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

Note 1: The mathematical definition is dq_p/dS . If q_p is constant over the surface area considered, then $M_p = q_p/S$. Also called specific photon emission.

Note 2: Formerly called photon emittance.

Note 3: This quantity can be expressed on a chemical amount basis by dividing M_p by the Avogadro constant. In this case the symbol is $M_{n,p}$, the name “photon exitance, amount basis”, the SI unit $\text{mol s}^{-1} \text{m}^{-2}$, and the common unit $\text{einstein s}^{-1} \text{m}^{-2}$.

See *spectral photon exitance*.

Related term: *radiant exitance*.

See [8,9].

revG2

photon exposure, H_p

Photon irradiance, E_p , integrated over the time of irradiation for a parallel and perpendicularly incident beam not scattered or reflected by the target or its surroundings. The SI unit is m^{-2} .

Note 1: The mathematical definition is $H_p = \int_t E_p dt$. If the photon irradiance is constant over the time interval, then $H_p = E_p t$.

Note 2: For a beam incident from all directions *photon fluence* ($F_{p,o}$) 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”, the SI unit mol m^{-2} , and the common unit einstein m^{-2} .

Related terms: *fluence, radiant exposure*.

See [9].

revG2

photon fluence, $F_{p,o}$

Amount of photons (quanta of radiation) from all directions incident on a small sphere, divided by the cross-sectional area of that sphere, integrated over time. *Photons* per surface area (quanta m^{-2}). The SI unit is m^{-2} .

Note 1: The mathematical definition is $F_{p,o} = \int_t E_{p,o} dt$, 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, then $F_{p,o} = E_{p,o} t$.

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

Related term: *fluence*.

See [9].

revG2

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

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

Note 1: The mathematical definition is $E_{p,o} = dF_{p,o}/dt$. If $F_{p,o}$ is constant over the time interval, then $E_{p,o} = F_{p,o}/t$.

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”, the SI unit $\text{mol m}^{-2} \text{s}^{-1}$, and the common unit einstein $\text{m}^{-2} \text{s}^{-1}$.

See *photon radiance*.

Related term: *fluence rate*.

See [9].

revG2

photon flux, q_p , Φ_p

Number of *photons* (quanta of radiation, N , Q_p) per time interval. The SI unit is s^{-1} .

Note 1: The mathematical definition is $q_p = dQ_p/dt$. If the number of photons is constant over the time interval, then $q_p = Q_p/t$.

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”, the SI unit mol s^{-1} , and the common unit einstein s^{-1} .

Note 3: Although the symbol recommended by CIE is Φ_p , 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.

See *spectral photon flux*.

Related term: *radiant power*.

See also [9].

revG2

photon irradiance, E_p

Number of *photons* (quanta of radiation, N , Q_p) per time interval (*photon flux*), q_p , incident within a parallel beam and perpendicularly on a small element of surface containing the point under consideration divided by the area of the element. The SI unit is $\text{m}^{-2} \text{s}^{-1}$.

Note 1: The mathematical definition is $E_p = dq_p/dS$. If the photon flux is constant over the surface considered, then $E_p = q_p/S$.

Note 2: 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”, the SI unit $\text{mol m}^{-2} \text{s}^{-1}$, and the common unit einstein $\text{m}^{-2} \text{s}^{-1}$.

See *spectral photon irradiance*.

Related term: *irradiance*.

See [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 Avogadro constant.

Note: The mathematical definition is $N_p = Q/h\nu$ for monochromatic radiation of *frequency* ν , with Q the *radiant energy*.

photon radiance, L_p

Number of *photons* (quanta of radiation, N , Q_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, $dS_{\perp} = dS \cos \theta$.

Note 1: The mathematical definition is

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

for a divergent beam propagating in an elementary cone of the solid angle Ω containing the direction θ . The SI unit is $\text{m}^{-2} \text{s}^{-1} \text{sr}^{-1}$.

Note 2: For a parallel beam it is number of *photons* (quanta of radiation, N , Q_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 . The mathematical definition in this case is $L_p = dq_p / (dS \cos \theta)$. If q_p is constant over the surface area considered, then $L_p = q_p / (S \cos \theta)$ and the 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 the SI unit is $\text{mol m}^{-2} \text{s}^{-1} \text{sr}^{-1}$ and the common unit $\text{einstein m}^{-2} \text{s}^{-1} \text{sr}^{-1}$. For a parallel beam the SI unit is $\text{mol m}^{-2} \text{s}^{-1}$ and the common unit $\text{einstein m}^{-2} \text{s}^{-1}$.

See *spectral photon radiance*.

Related term: *radiance*.

See [9].

revG2

photooxidation

Oxidation reactions induced by *ultraviolet*, *visible*, or *infrared* radiation. Common processes are:

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

Reactions in which neither the substrate nor the oxygen are electronically excited (i.e., *photosensitized* oxidations) are sometimes called photoinitiated oxidations.

Compare with *photoreduction*.

revG2

photooxygenation

Incorporation of molecular oxygen 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 producing radicals by hydrogen atom or electron abstraction. These radicals then react with *triplet* molecular oxygen to produce oxygenated products.

Type II: the photosensitizer reacts with ground state molecular oxygen producing *singlet molecular*

oxygen by energy transfer (the efficiency of this process is controlled by the *spin–statistical factor*). Singlet molecular oxygen then reacts with the substrate producing oxygenated products.

From this point of view, 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 [63]

revG2

photophysical processes

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

G2/GB

photopolymerization

Polymerization processes requiring a *photon* for the propagation step.

Related term: *photoinduced polymerization*.

G2/GB

photoreaction

See *photochemical reaction*.

G2/GB

photoreduction

Reduction reactions induced by *ultraviolet*, *visible*, or *infrared* radiation. Common processes are:

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

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

Compare with *photooxidation*.

G2/GB

photorefractive effect

Photoinduced change in refractive index.

Related term: *photothermal effect*.

See [18].

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 which is useful for the fabrication of microelectronic devices.

Note: Examples are integrated circuits.

G2/GB

photoselection

Selection by an exciting light beam of an aligned subset of sample molecules. The selected subset will have an orientation distribution that is determined by the electric vectors of the beam. If the beam is linearly polarized a *uniaxial* sample with a known orientation distribution will be produced. Also the set of remaining molecules will be aligned, with a known orientation distribution (residual anisotropy).

See *emission anisotropy, linear dichroism, residual anisotropy*, [35].

photosensitization

Photochemical or *photophysical* alteration occurring in one molecular entity as a result of initial *absorption* of radiation by another molecular entity called a *photosensitizer*.

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

See *energy transfer*.

G2/GB

photosensitizer

See *photosensitization*.

G2/GB

photostationary state

Steady state reached by a chemical system undergoing *photochemical* reaction(s) when *ultraviolet*, *visible*, or *infrared* radiation is absorbed by at least one of the components. At this state the rates of formation and disappearance are equal for each of the transient molecular entities formed.

revG2

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 [64].

G2/GB

PICT

Acronym for *planar intramolecular charge transfer*.

Related terms: *TICT*, *twisted intramolecular charge transfer*.

piezoluminescence

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

See *triboluminescence*.

G2/GB

planar intramolecular charge transfer, (PICT)

In a PICT state formed by *intramolecular charge transfer* in an electron donor (D)/acceptor (A) molecule, the D and A subgroups have an overall planar configuration, with substantial electronic coupling of D and A.

Related terms: *TICT state*, *twisted intramolecular charge transfer*.

PLED

Acronym for polymer *light-emitting diode*.

polar driving force

The negative of the standard Gibbs energy change (i.e., $-\Delta G^0$) for *outer-sphere electron transfer* in polar solvents, where the electrostatic work terms in the expression used for the calculation of the *Gibbs energy of photoinduced electron transfer* are in general negligibly small.

Note: The work term might not be negligibly small even in polar solvents for electron transfer in large molecules undergoing a large change in dipole moment upon electron transfer.

Related term: *driving force*.

revG2

polarization, *P*

The relevant material property that couples with the radiation field. May be called optical polarization. Optical spectroscopies may be classified according to their power-law dependence on the external electric field.

Note 1: Mathematically it is defined as the electric dipole moment change per volume resulting from absorption of radiation of optical frequencies, defined as $\mathbf{P} = \mathbf{D} - \varepsilon_0 \mathbf{E}$, where \mathbf{D} is the electric displacement, ε_0 the permittivity of vacuum, and \mathbf{E} the strength of the radiation electric field. A dielectric medium is characterized by the constitutive relation $\mathbf{D} = \varepsilon_0 \chi^{(1)} \mathbf{E}$ where $\chi^{(1)} = \varepsilon_r - 1$ is the linear “susceptibility”, for a transparent singly refracting medium. Depending on the molecular or atomic restoring force on the electron with respect to the displacement \mathbf{D} , the field-induced motion of the electron can introduce other frequency components on the electron motion and this in turn leads to *non-linear optical effects*.

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

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

$$\mathbf{P} = \varepsilon_0 [\chi_e^{(1)} E + (1/2) \chi_e^{(2)} E^2 + (1/6) \chi_e^{(3)} E^3 + \dots] = P^{(1)} + P^{(2)} + P^{(3)} + \dots$$

where $\chi_e^{(n)}$ is the order of the material “susceptibility” and $P^{(n)}$ is the order of the field induced polarization in the material. $\chi_e^{(1)}$ is the linear susceptibility. In an anisotropic medium, $\chi_e^{(1)}$, $\chi_e^{(2)}$, and $\chi_e^{(3)}$ are the medium “hyper-susceptibilities” [7]. $\chi_e^{(1)}$, $\chi_e^{(2)}$, and $\chi_e^{(3)}$ are tensors of increasing order, i.e., of order 2, 3, and 4, respectively.

Linear optical responses such as absorption, light propagation, reflection, and refraction, involving a weak incoming field, are related to $P^{(1)}$. *Non-linear techniques* are connected to the non-linear polarization P_{NL} . Low order non-linear techniques, such as three-wave mixing, are related to the second order *optical polarization* $P^{(2)}$. For a random isotropic medium with inversion symmetry, $P^{(2)}$ vanishes and then the lowest order non-linear techniques, as well as the higher order, are related to the third-order optical polarization $P^{(3)}$ and the corresponding hyper-susceptibility.

See [31].

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 [34,35].

polarization direction

See *transition moment*.

polarization ratio

See *emission anisotropy*.

polarization spectroscopy

In *absorption* experiments, polarization spectroscopy is performed with polarized light on non-isotropic samples.

Note: spectroscopy with natural (unpolarized) light on non-isotropic samples will show directional effects, since the electric vectors of natural light are not isotropic, but are restricted to a plane perpendicular to the beam. In two-photon processes, for example luminescence measured with linear polarizers in both beams, an aligned sample is not required since it will be created by the exciting photon through *photoselection*. However, aligned samples allow a larger number of independent experiments to be recorded and thus contain more information.

See *emission anisotropy*, *linear dichroism*, [35].

polaron

Lattice distortion or polarization caused by *photoexcitation*, and which follows the electron as it moves through the solid.

See *self-localized excitations*.

population inversion

A higher energy state is more populated than a lower energy state.

G2/GB

potential energy surface

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

Note: The acronym PES is often used.

See [6].

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 (photo)process

See *primary photochemical process*.

Note: The term primary (photo)process for *photophysical processes* may lead to inconsistencies, and its use is therefore discouraged.

G2/GB

primary photochemical process (primary photoreaction)

Elementary chemical process undergone by a molecular entity as a result of direct *photoexcitation* and yielding a *primary photoproduct*.

See *primary (photo)process*.

G2/GB

primary (photo)product

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

See *primary (photo)process*.

G2/GB

pseudo Jahn–Teller effect

Same as second order *Jahn–Teller effect*.

See [6].

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 a particular observable. 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 an optical pulse (UV, visible, or infrared) 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 pulse.

Note 1: In the case of an optical probe, this interaction is formally a non–linear optical process that is third order in *polarization* [31]. 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.

revG2

$\pi \rightarrow \pi^*$ 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

π - π^* state

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

G2/GB

 $\pi \rightarrow \sigma^*$ transition

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

Note: Transitions generally involving high transition energies and appearing close to or mixed with *Rydberg transitions*.

G2

QM/MM

Acronym for *quantum mechanics/molecular mechanics*.

Q-switched laser

Laser in which the state of the device introducing important losses in the resonant cavity and preventing *lasing* operation is suddenly switched to a state where the device introduces very low losses. This increases rapidly the Quality factor of the cavity, allowing the build-up of a short and very intense laser pulse.

Note: Typical pulse durations are in the ns range. The Q-switching may be active (a rotating mirror or electro-optic device) or passive (a saturable absorber).

Related term: *free-running laser*, [17].

G2/GB

quantum (of radiation)

Elementary particle of electromagnetic energy in the sense of the wave-particle duality.

See *photon*.

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 also [21].

G2/GB

quantum efficiency

See *efficiency*.

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

G2/GB

quantum yield, Φ

Number of defined events which occur 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 (*photon flux*, amount basis).

Note 1: Φ can be used for *photophysical processes* (such as, e.g., *intersystem crossing*, *fluorescence* and *phosphorescence*) or *photochemical reactions*.

Note 2: Strictly, the term quantum yield applies only for monochromatic excitation.

Related term: *efficiency*.

See [15,34].

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.

quartet state

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

See *multiplicity*.

G2/GB

quartz–iodine lamp

A tungsten (wolfram) filament high–intensity incandescent lamp which contains 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 wolfram atoms to evaporate and combine with the halogen gas. These heavier molecules are then deposited back on

the filament surface. This recycling process increases the life of the wolfram filament and enables the lamp to produce more light per units of energy. Consequently, halogen lamps are used in a variety of applications, including automobile headlights.

Note 2: Other halogens may fill the lamp.

See also *wolfram-lamp*.

See [15].

quencher

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

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

G2/GB

quenching

Deactivation of an excited molecular entity intermolecularly by an external environmental influence (such as a *quencher*) or intramolecularly by a substituent through a *non-radiative process*.

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

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

See *Stern–Volmer kinetic relationships*.

See [34].

G2/GB

quenching constant

See *Stern–Volmer kinetic relationships*. Related terms: *quencher*, *quenching*,

G2

radiance, L

Radiant power, P , leaving or passing through a small transparent element of surface in a given direction from the source about the solid angle 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: The mathematical definition is

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

for a divergent beam propagating in an elementary cone of the solid angle Ω containing the direction θ . The 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 . The mathematical definition in this case is $(dP/(dS \cos \theta))$. If the radiant power is constant over the surface area considered, then $L = P/(S \cos \theta)$. The 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 .

Related terms: *photon flux*, *photon radiance*, *spectral radiance*, *spherical radiance*.

See [9].

revG2

radiant emittance

See *radiant exitance*.

G2/GB

radiant energy, Q

Total energy emitted, transferred or received as radiation of all wavelengths in a defined period of time. The SI unit is J.

Note 1: The mathematical definition is $Q = \int_{\lambda} Q_{\lambda} d\lambda$. If the *radiant power* is constant over the time interval, then $Q = P t$.

Related term: *spectral radiant power*.

See [9].

G2/GB

radiant energy fluence, F_0 , H_0

Same as *fluence*.

radiant (energy) flux, P , Φ

This term is not recommended.

In *photochemistry*, *radiant power*, P is adopted. The SI unit is W.

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

Related terms: *photon flux*, *photon radiance*, *radiant energy*, *spectral radiant flux*.

See [8,9].

revG2

radiant exitance, M

Radiant power, P , emitted at all wavelengths by an element of surface containing the source point under consideration divided by the area of the source. The SI unit is W m^{-2} .

Note 1: The mathematical definition is $M = dP/dS$. If the radiant power is constant over the surface area considered, then $M = P/S$.

Note 2: Equivalent to the integration of the radiant power leaving a source over the solid angle and over the whole *wavelength* range. The mathematical definition is $M = \int_{\lambda} M_{\lambda} d\lambda$, where M_{λ} is the *spectral radiant exitance* at wavelength λ .

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

Related terms: *photon exitance*, *spectral radiant exitance*.

See [8,9].

G2/GB

radiant exposure, H

Radiant energy, Q , incident on an small sphere for a parallel and perpendicularly incident beam not scattered or reflected by the target or its surroundings divided by the cross-sectional area of that sphere. The SI unit is J m^{-2} .

Equivalent definition: *Irradiance, E* , integrated over the time of irradiation for a beam not scattered or reflected by the target or its surroundings. The SI unit is J m^{-2} .

Note 1: The mathematical definition is $H = dQ/dA = \int_t E dt$. If Q is constant over the area, then $H = Q/A$. If E is constant over the time interval, then $H = E t$.

Note 2: For a beam incident from all directions *fluence* (F_0, H_0) is an equivalent term.

See [8,9].

G2/GB

radiant intensity, I

Radiant power, P , at all wavelenghts 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. The SI unit is W sr^{-1} .

Note 1: The mathematical definition is $I = dP/d\Omega$. If the radiant power is constant over the solid angle considered, then $I = P/\Omega$.

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.

Related term: *spectral radiant intensity*.

See [9].

G2/GB

radiant power, P

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

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

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 *spectral radiant power*.

See [7].

revG2

radiationless deactivation (decay)

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

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

G2/GB

radiationless transition

Transition between two states of a molecular entity without *photon* emission or *absorption*.

Compare with *radiative transition*.

G2/GB

radiation trapping

Process by which the *resonance radiation* emitted in a lamp is absorbed and re-emitted many times in the plasma prior to striking the phosphor. This process is called radiation trapping or imprisonment.

Note: This radiation trapping lengthens the effective lifetime of emission as viewed from outside the lamp. The control of this trapping is therefore an important design consideration for low pressure lamps.

See [15].

radiative energy transfer

Transfer of excitation energy by *radiative deactivation* of a donor molecular entity and reabsorption of the emitted radiation by an acceptor molecular entity. It is also called *trivial energy transfer*.

Note 1: Radiative transfer results in a decrease of the donor fluorescence intensity in the region of spectral overlap. Such a distortion of the fluorescence spectrum is called *inner filter effect*.

Note 2: This type of 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 *inner filter effect*.

Related terms: *Dexter energy transfer*, *energy transfer*, *Förster resonance energy transfer*.

See [34].

revG2

radiative lifetime, τ_0

Lifetime of an excited molecular entity in the absence of *radiationless transitions*. The reciprocal of the first-order rate constant for the radiative step, or 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 subindex 0 is used, whereas the superindex 0 is used to indicate a non-quenched lifetime in the *Stern-Volmer kinetic relationships*.

Related term: *Förster resonance energy transfer*.

See [34,35].

revG2

radiative transition

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

See *luminescence*.

Compare with *radiationless deactivation*, *radiationless transition*.

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 geminate radical pair provided that each radical partner is a descendant of the same parental pair.

G2

radioluminescence

Luminescence arising from excitation by high energy particles or radiation.

G2/GB

radiolysis

Bond cleavage induced by high–energy radiation.

Note: Term loosely used for any chemical process brought about by high–energy radiation as well as to refer to the irradiation technique itself (“pulse radiolysis”).

G2/GB

red shift

Informal term for *bathochromic shift*.

G2/GB

reflectance, ρ

Fraction of incident radiation reflected by a surface or discontinuity, $\rho(\lambda) = \frac{P_{\lambda}^{\text{refl}}}{P_{\lambda}^0}$. Same as

reflectivity or reflection factor.

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

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

Reflectance increases as the angle of incidence decreases from 90 degrees.

See [7].

reflectivity

See *reflectance*.

reflection factor

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

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

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 [65] the value $\frac{k_d}{K_d Z} = 0.25$ in acetonitrile was used.

relative spectral responsivity, $\varepsilon(\lambda)$

See *action spectrum*.

G2/GB

relaxation

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

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

G2

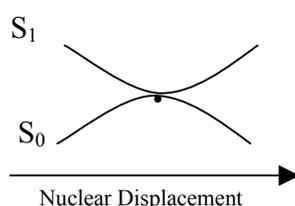
Renner–Teller effect

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

Note 1: The Renner–Teller effect arises from splittings in the vibrational levels of molecular entities due to even terms in the *vibronic* perturbation expansion. This is generally a minor effect for non–linear molecular entities compared to the *Jahn–Teller effect* which is due to the odd terms.

Note 2: For linear molecular entities it is the only possible vibronic effect characteristic of degenerate electronic states.

See [6].



revG2

reorganization energy (in electron transfer)

Gibbs energy dissipated when a system that has undergone “vertical” *electron transfer* (i.e. electron transfer obeying the *Franck Condon principle*) relaxes to the equilibrium state for its new charge

distribution. Commonly the total reorganization energy (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.

See [6,22,52].

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 times. 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 , the decay of emission anisotropy following δ -pulse excitation is given by:

$$r(t) = (r_0 - r_{\infty}) \exp(-t/t_c) + r_{\infty}$$

where r_0 is the *fundamental emission anisotropy*.

Note: The term residual anisotropy is to be preferred to "limiting anisotropy".

See *photoselection, molecular orientation*, [34,35].

resonance absorption technique

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

G2/GB

resonance fluorescence

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

Note: Also used to designate the radiation emitted by an atom of the same wavelength as the longest one capable of exciting its fluorescence, e.g., 122.6 nm in the case of the hydrogen atom, and 253.7 nm in the case of the mercury atom.

Related term: *resonance line*.

G2/GB

resonance fluorescence technique

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

G2/GB

resonance lamp

Lamp emitting *resonance radiation* of atoms and their ions. Depending on the requirements, the lamp is filled either with pure vapour of the element or with a mixture of it and other gases.

Note: Examples are: Hg (253.7 and 184.9 nm), Cd (228.8 and 643.8 nm), Na (589.0 nm), Zn (213.8, 330.3, 334.5, and 636.2 nm), Kr (116.5 and 123.6 nm), Xe (129.6 and 147.0 nm).

For a list of all possible atomic lines see [66]

revG2

resonance line

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

Related term: *resonance fluorescence*.

G2

resonance radiation

Same as *resonance fluorescence*.

G2/GB

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 *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 which 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 which 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].

semiconductor laser

See *diode laser*.

G2/GB

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.

See [63,67].

G2

scintillators

Materials used for the measurement of radioactivity, by recording the *radioluminescence*. They contain compounds (*chromophores*) which combine a high *fluorescence quantum efficiency*, a short *fluorescence lifetime*, and a high solubility.

Note: These compounds are employed as solutes in aromatic liquids and polymers to form organic liquid and plastic scintillators, respectively.

G2/GB

selection rule

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

See [6].

G2/GB

self-absorption

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

G2

self-localized excitations (in conjugated organic polymers)

Physical and chemical properties of conjugated organic polymers with 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 the Table.

excitation	chemical term	charge	spin
positive polaron	radical cation	$+e$	1/2
negative polaron	radical anion	$-e$	1/2
positive bipolaron	dication	$+2e$	0
negative bipolaron	dianion	$-2e$	0
neutral soliton	neutral radical	0	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 [68].

self-quenching

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

Related term: *Stern–Volmer kinetic relationships*.

G2/GB

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, transitions which are spin-forbidden in one of the centres might become spin allowed (spin flip).

See [6].

G2/GB

single photon counting

See *photon counting*.

G2/GB

single photon timing

Technique that permits recovery of the parameters characterizing a *fluorescence* decay after pulse excitation (in particular excited-states lifetimes). It is based on the creation of a time histogram of many stochastic events involving the time delay between the electronic excitation of a molecule or material and its emission of a *photon* from an excited state. A key to the technique is that no more than one photon strike the detector per pulsed excitation. Excitation is commonly achieved with a flash from a repetitive nanosecond *lamp* or *diode laser* or a CW operated *laser* (*mode-locked laser*). The essential components of the hardware are a device to measure the excitation–emission

delay time and another to determine the relative frequency of photons reaching the detector at each delay time. Delay times are usually measured with a time-to-amplitude-converter (TAC) which uses voltage to measure the delay between a start and a stop signal. The frequency of events with each delay is stored in a multi-channel analyzer. This term is preferred to time-correlated single-photon counting

See e.g., [34,42,69].

revG2

singlet molecular oxygen

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 oxygen (i.e., a process of *photosensitization*) is the most common procedure for the production of singlet molecular oxygen in solution. The efficiency of this process is controlled by the *spin-statistical factor*.

For a compilation of singlet molecular oxygen production *quantum yields*, see [70].

Note 3: For a compilation of singlet molecular oxygen *lifetimes* and rate constants of its reaction with several substrates see [71].

revG2

singlet-singlet annihilation

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

G2/GB

singlet-singlet energy transfer

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

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

G2/GB

singlet state

State having a total electron spin quantum number equal to 0.

See *multiplicity*.

G2/GB

singlet–triplet crossing

Point of intersection between the *potential energy surfaces* of states of different *multiplicity*.

Note: The intersection belongs to a $(3N - 7)$ -dimensional subspace of the $(3N - 6)$ -dimensional nuclear coordinate space and therefore appears as a line on a two-dimensional energy surface (N is the number of nuclei). In this case the *branching plane* is one-dimensional and is defined by the gradient difference vector x_1 .

Related term: *conical intersection*.

singlet–triplet energy transfer

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

See *energy transfer*, *spin conservation rule*.

G2/GB

solar conversion efficiency

Gibbs energy gain per time interval per m^2 of surface exposed to the solar *irradiance*, divided by the solar radiance E , integrated over the wavelength range reaching the exposed surface.

G2/GB

solid state lasers

CW or pulsed *lasers* in which the active medium is a solid matrix (crystal or glass) doped with an ion (e.g., Nd^{3+} , Cr^{3+} , Er^{3+}). The emitted *wavelength* depends on the active ion, the selected optical transition, and the matrix.

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].

G2/GB

soliton

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

See *self-localized excitations*.

solvatochromism

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

See [72].

G2

solvent-induced symmetry breaking

Breaking of symmetry of a molecular species by interactions with the solvent that can modify the molecular charge distribution, favouring 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*.

Related term: *contact ion pair*.

G2

solvent shift

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

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

G2/GB

sonoluminescence

Luminescence induced by sound waves.

See *triboluminescence*.

G2/GB

specific photon emission

Same as *photon exitance*.

G2/GB

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

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

Note 1: The mathematical definition at each wavelength interval is $X_\lambda = dX(\lambda)/d\lambda$. The units are $[X] \text{ m}^{-1}$, e.g., W m^{-1} for $X = P$ (radiant power).

Note 2: This term is preferred when dealing with the function $X_\lambda(\lambda)$ over a wide range of wavelengths, such as in the overlap integral in *Dexter* and in *Förster energy transfer*.

spectral (photon) effectiveness

Reciprocal of the *photon fluence rate*, $E_{p,o}$, at *wavelength* λ , causing identical photoresponse, Δy , per time interval ($\Delta y/\Delta t$). The effectiveness spectrum is directly proportional to the *conversion spectrum* of the sensory pigment, if spectral attenuation is negligible.

G2/GB

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

Derivative of *fluence*, F_o , with respect to *wavelength*, λ . The SI unit is J m^{-3} ; commonly used 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, $E_{\lambda,o}$

Derivative of *fluence rate*, E , with respect to *wavelength*, λ . The SI unit is W m^{-3} ; commonly used 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 . The SI unit is W m^{-3} ; commonly used 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

See Dexter excitation transfer, energy transfer, Förster resonance energy transfer, radiative energy transfer.

revG2

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

Derivative of *photon exitance*, M_p , with respect to *wavelength*, λ . The SI unit is $\text{s}^{-1} \text{m}^{-3}$; commonly used unit is $\text{s}^{-1} \text{m}^{-2} \text{nm}^{-1}$.

Note: 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 $M_{np,\lambda}$, the name then being “spectral photon exitance, amount basis”, the SI unit $\text{mol s}^{-1} \text{m}^{-3}$; commonly used unit einstein is $\text{s}^{-1} \text{m}^{-2} \text{nm}^{-1}$.

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 photon flux, $q_{p,\lambda}$, $\Phi_{p,\lambda}$

Derivative of *photon flux*, number basis, q_p , with respect to *wavelength*, λ . The SI unit is $\text{s}^{-1} \text{m}^{-1}$; commonly used unit is $\text{s}^{-1} \text{nm}^{-1}$.

Note: This quantity can be expressed on a chemical amount basis by dividing $q_{p,\lambda}$ by the Avogadro constant, the name then being “spectral photon flux, amount basis”, the SI unit $\text{mol s}^{-1} \text{m}^{-1}$; commonly used unit is einstein $\text{s}^{-1} \text{nm}^{-1}$.

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 photon irradiance, $E_{p,\lambda}$

Derivative of *photon irradiance*, E_p , with respect to *wavelength*, λ . The SI unit is $\text{s}^{-1} \text{m}^{-3}$; commonly used 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 being “spectral photon irradiance, amount basis”, the SI unit $\text{mol s}^{-1} \text{m}^{-3}$; commonly used 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, the SI unit is $\text{s}^{-1} \text{m}^{-3} \text{sr}^{-1}$; commonly used unit is $\text{s}^{-1} \text{m}^{-2} \text{sr}^{-1} \text{nm}^{-1}$.

For a parallel beam the SI unit is $\text{s}^{-1} \text{m}^{-3}$; commonly used unit is $\text{s}^{-1} \text{m}^{-2} \text{nm}^{-1}$.

Note 1: This quantity can be expressed on a chemical amount basis by dividing $L_{p,\lambda}$ by the Avogadro constant, the name then being “spectral photon radiance, amount basis”.

For a divergent beam the SI unit is $\text{mol s}^{-1} \text{m}^{-3} \text{sr}^{-1}$; commonly used unit is $\text{einstein s}^{-1} \text{m}^{-2} \text{sr}^{-1} \text{nm}^{-1}$. For a parallel beam the SI unit is $\text{mol s}^{-1} \text{m}^{-3}$; commonly used 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 the SI unit is $\text{W m}^{-3} \text{sr}^{-1}$; commonly used unit is $\text{W m}^{-2} \text{sr}^{-1} \text{nm}^{-1}$.

For a parallel beam the SI unit is W m^{-3} ; commonly used 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 . The SI unit is J m^{-1} , commonly used unit is J nm^{-1} .

spectral radiant exitance, M_λ

Derivative of *radiant exitance*, M , with respect to *wavelength* λ . The SI unit is W m^{-3} ; commonly used 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 . The SI unit is $\text{W m}^{-1} \text{sr}^{-1}$; commonly used 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 . The SI unit is W m^{-1} ; commonly used 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: The mathematical definition is $s(\lambda) = dY_\lambda/d E_\lambda$. Simplified expression is $s(\lambda) = Y_\lambda/ E_\lambda$ where Y_λ is the magnitude of the output signal for irradiation at *wavelength* λ .

See *action spectrum*.

revG2

spectral sensitivity, $S(\lambda)$

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

Related term: *spectral responsivity*.

revG2

spectral sensitization

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

G2/GB

spherical radiance

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

G2/GB

spherical radiant exposure

Same as *fluence*.

G2/GB

spin-allowed electronic transition

Electronic transition which does not involve 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 other atom or molecular entity in its ground or *excited state*, the overall spin angular momentum of the system, a vector quantity, should not change.

See *annihilation*, [6].

G2

spin-flip method

Quantum mechanical method for the calculation of open shell excited states. The method accurately describes low-lying multi-configurational electronic states of diradicals and triradicals in an efficient and robust single-reference scheme. The target low-spin states (e.g., $S = 0$ or $S = 1/2$) are described as spin-flipping excitations ($S = -1$) from a well-behaved high-spin reference state (e.g., $S = 1$ or $S = 3/4$). By employing theoretical models of increasing complexity for the reference (e.g., SCF, MP2, CCSD), the accuracy in the target states' description can be systematically improved. The SF methods result in multistate single-step computational schemes, e.g., several low-lying states can be computed in a single calculation that includes both dynamical and non-dynamical correlation effects.

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 which conserve 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* by O₂ of *fluorescence* from aromatic hydrocarbons, quenching by O₂ of *triplet states*, and triplet-triplet *annihilation*.

See [73].

spontaneous emission

Emission which occurs in the absence of a perturbing external electromagnetic field.

Note: The transition between states, n and m , is governed by the Einstein coefficient of spontaneous emission, A_{nm} .

Related term: *stimulated emission*.

See [34].

G2/GB

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*.

See [34].

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 the equation (1)

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

K_{SV} is referred to as the Stern–Volmer constant. Eq. (1) applies when a quencher inhibits either a *photochemical reaction* or a *photophysical process* by a single reaction. 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. Eq. (1) can therefore be replaced by the expression (2)

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

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

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

where $\Phi(p)$ is the quantum *efficiency* of product formation, A the formation efficiency of the reactive excited state, B the fraction of reactions of the excited state with substrate S which leads to product, and [S] is the concentration of reactive ground–state substrate. The intercept divided by the slope gives $k_r \times \tau^0$. If [S] = [Q], and if a photophysical process is monitored, plots of equations (2) and (3) should provide independent determinations of the product–forming rate constant k_r . When the lifetime of an excited state is observed as a function of the concentration of S or Q, a linear relationship should be observed according to eq. 4

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

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

Note 2: a superindex 0 is used, whereas the subindex 0 is used for the *radiative lifetime* τ_0 .

Related terms: *self-quenching*, *spin-statistical factor*.

See [34,74].

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} . *CIDNP* emission and *lasing* action are examples of processes which require stimulated emission.

Related term: *spontaneous emission*.

See [34,35].

G2/GB

Stokes shift

Difference (usually in *frequency* units) between the spectral positions of the *Franck-Condon* maxima of the two spectra, i.e., of the lowest energy (highest *wavelength*) band origins of the *absorption* and *luminescence* arising from the same electronic transition (the 0–0 bands).

Note 1: Often used referring to the difference in the respective band maxima.

Note 2: Generally, the luminescence occurring at a longer *wavelength* than the absorption is stronger than the opposite. The latter may be called an anti-Stokes shift.

See [34].

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 [75].

superexchange interaction

Electronic interaction between two molecular entities mediated by one or more molecules or ions.
G2/GB

superradiance

Spontaneous emission amplified by a single pass through a *population inverted* medium.

Note: Distinguished from true *laser* action by its lack of coherence. The term superradiance is frequently used in laser technology.

See *coherent radiation*.

G2/GB

surface crossing

In a diagram of electronic energy versus molecular geometry, the electronic energies of two states of different symmetry may be equal at certain geometrical parameters. At this point (unidimensional representation), line or surface (more than one dimension), the two *potential-energy surfaces* are said to cross one another.

Note: In states of the same spin *multiplicity* the surface crossing is usually $3N - 8$ dimensional. In states with different spin multiplicity the surface crossing is usually $3N - 7$ dimensional (N is the number of nuclei).

See *avoided crossing*, *conical intersection*, *singlet-triplet crossing*, [26].

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: Transitions generally involving high transition energies, and appearing close to or mixed with *Rydberg transitions*.

G2

TD–DFT

Acronym for *time–dependent density functional theory*.

thermal lensing

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

Related term: *photothermal effects*. [18]

G2/GB

thermally activated delayed fluorescence

See *delayed fluorescence*.

G2/GB

thermochromism

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

Related term: *through-space electron transfer*.

G2/GB

through-space electron transfer

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

Related term: *through-bond electron transfer*.

G2/GB

TICT

Acronym for *twisted intramolecular charge transfer*.

See *ICT*, *intramolecular charge transfer*, *twisted intramolecular charge transfer*.

Related terms: *PICT*, *planar intramolecular charge transfer*.

revG2

TICT emission

Electronic emission from a *TICT* state.

Related terms: *PICT*, *planar intramolecular charge transfer*, *twisted intramolecular charge transfer*.

revG2

tight ion pair

Same as *contact ion pair*

G2

time–correlated single photon counting

See *single–photon timing*.

revG2

time–dependent density functional theory, (TD–DFT)

Methods for computing accurate excitation energies at a low computational cost in large molecular species within the time–dependent scheme and the density functional theory. It is the only available DFT–based method for the computing of electronic excitation energies.

See related terms in [6,26].

time–resolved microwave conductivity, (TRMC)

Technique which allows the quantitative and qualitative detection of radiation–induced changes in the real, $\Delta\sigma_R$, and imaginary, $\Delta\sigma_I$, components of the conductivity of a medium by time–resolved measurement of changes in the microwave *absorption* resulting from the formation of mobile charges or from changes in the dipole moment or polarizability of molecules on excitation.

Note: From $\Delta\sigma_R$ (corresponding to a change in the dielectric loss, $\Delta\varepsilon''$) the product of the yield and the mobility of charges carriers or the dipole moment change can be determined. From $\Delta\sigma_I$ (corresponding to a change in the relative permittivity, $\Delta\varepsilon'$) the product of the yield and the change in molecular polarizability can be determined.

See [76].

revG2

time–resolved spectroscopy

Recording of spectra at a series of time intervals after the excitation of the system with a *ultraviolet*, *visible*, or *infrared* radiation pulse (or other perturbation) of appropriately short duration.

G2/GB

Ti-sapphire laser

See *solid state lasers*.

transient spectroscopy

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

Related terms: *flash photolysis*, *time-resolved spectroscopy*.

G2/GB

transition (dipole) moment

An electromagnetic wave may induce an oscillating electric moment in a molecule (possibly leading to *absorption* if the oscillation frequency agrees with the light frequency). The amplitude of this moment is the transition moment between the initial (i) and final (f) states (here assumed to be non-degenerate):

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

where \mathbf{M}_{op} is the electric dipole moment operator, a vector operator that is the sum of the position vectors of all charged particles weighted with their charge. The transition moment \mathbf{M}_{if} is a vector in the molecular framework, characterized both by its direction and its probability.

Note 1: The absorption probability for linearly polarized light is proportional to the cosine square of the angle between the electric vector and \mathbf{M}_{if} ; light absorption will be maximized if they are parallel, if they are perpendicular, no absorption will occur.

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*, [35].

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, t is also used.

See *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 *sonoluminescence*.

G2/GB

triplet state

State having a total electron spin quantum number of 1.

See *multiplicity*.

Note 1: For a list of triplet–triplet absorption spectra see [77]

Note 2: For a critical evaluation of triplet–triplet absorption data see [78].

See [79].

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 ground singlet state.

Note: This process is often, but not always, followed by *delayed fluorescence*.

Related terms: *annihilation, spin conservation rule*.

G2/GB

triplet–triplet energy transfer

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

See *Dexter excitation transfer, spin conservation rule, spin–statistical factor*.

G2/GB

triplet–triplet transitions

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

G2/GB

trivial energy transfer

Same as *radiative energy transfer*.

G2/GB

tungsten–halogen lamp

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

Note: Other halogens may fill the lamp.

tunnelling

Passage of a particle through a potential–energy barrier the height of which is larger than the energy of that particle.

Note: Effect important for some processes involving the transfer of electrons and light atoms, particularly H atoms.

See [6].

G2/GB

turntable reactor

See *merry–go–round reactor*.

G2/GB

twisted intramolecular charge transfer, (TICT)

In a TICT state formed by *intramolecular charge transfer* in an electron donor (D)/acceptor (A) molecule, the D and A subgroups have a mutually perpendicular configuration, that leads to electronic decoupling of D and A.

Related terms: *PICT*, *planar intramolecular charge transfer*.

revG2

two–photon excitation

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

Note: Term used for successive absorption only if some of the excitation energy of the first photon remains in the atom or molecular entity before absorption of the second photon. The simultaneous two–photon absorption can also be called *biphotonic excitation*.

See *two-photon process*.

G2/GB

two-photon photochromism

Photochromic process involving a *two-photon process*. The process might involve the simultaneous or the sequential *absorption* of two photons.

Related term: *one-photon photochromism*.

two-photon process

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

G2/GB

ultraviolet, (UV)

Region of the electromagnetic spectrum extending from about 100 nm to 400 nm. This region is divided into four sub-bands as follows:

Vacuum Ultraviolet	100 – 200 nm
UV-C	200 – 280 nm
UV-B	280 – 315 nm
UV-A	315 – 400 nm.

Note: The notation and the limits of the various regions are as recommended by the International Commission on Illumination (CIE) [80].

uniaxial sample

Sample characterized by a (unique) sample axis *Z* with all directions perpendicular to *Z* being equivalent. In other words, the sample properties are invariant to rotation around *Z*. Uniaxiality exists in many anisotropic samples and simplifies the interpretation of their spectra considerably.

See *linear dichroism*, [35].

upconversion

The process by which two photons with *frequencies* ν_2 and ν_3 combine in a non-linear 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 non-linear material. This in turn depends on the power of the incident radiation, the photon frequencies, their indices of refraction in the material, and the non-linear “hyper-susceptibility” of the material.

See *non-linear optical techniques*, [31,34].

UPS

See *photoelectron spectroscopy*.

UV

Acronym for *ultraviolet*

UV dose

Dose of UV radiation.

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

G2/GB

UV stabilizer

Substance added to a sample to prevent photodeterioration by *ultraviolet* (UV) radiation.

See *photochemical reaction*.

G2/GB

valence band

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

Note 1: The valence band is lower in energy than the *conduction band* and is generally completely full in semi-conductors. When heated, electrons from the valence band jump out of the band across the *band gap* and into the conduction band, making the material conductive. The *Fermi level* separates the valence band from the conduction band.

Note 2: In metals the valence band is the conduction band.

revG2

Vavilov rule

See *Kasha–Vavilov rule*.

G2/GB

vertical transition

See *Franck–Condon principle*.

G2/GB

vibrational redistribution

Intramolecular redistribution of energy among the vibrational modes usually giving a statistical distribution of their populations, characterized by the “vibrational temperature”.

Note: For large molecules, this process does not require collisions.

G2/GB

vibrational relaxation

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

See *relaxation*.

G2/GB

vibronic coupling

Interaction between electronic and vibrational motions in a molecular entity.

See *Jahn–Teller, Renner–Teller effects*, [35].

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 [35].

G2/GB

visible

Region of the electromagnetic spectrum extending from about 400 nm to 760 nm. This is the *wavelength* region that the human eye is sensitive to.

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. The SI unit is m^{-1} ; commonly given in 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 exciplexes* relative to the ground-state in *n*-hexane as a function of the electrochemical one electron standard reduction potential of the cation radical produced upon electron donation and standard reduction potential of the acceptor measured in a polar solvent for the donor (D) and the acceptor (A) involved

$$\Delta H(D^+A^-, \text{hexane})/\text{eV} = e [E^0(D^{\bullet+}/D)/V - E^0(A/A^{\bullet-})/V] + (0.15 \pm 0.10) \text{ eV}$$

Note 1: The third term on the right applies strictly only for diethylaniline as donor and aromatic hydrocarbons as acceptors. This equation assumes a constant Coulomb term and a constant entropy change within a particular series of partners. *e* is the elementary charge.

Note 2: The IUPAC recommendations for the sign and symbols of standard potentials are used in the equation as written [11].

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

$$\Delta H(D^+A^-, \text{hexane})/\text{eV} = e [E_{\text{ox}}^0 - E_{\text{red}}^0] + (0.15 \pm 0.10) \text{ eV}$$

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

Related term: *Gibbs energy of photoinduced electron transfer.*

See [81].

revG2

Wigner matrices

See *molecular orientation*, [6].

Wigner rule

See *spin conservation rule*, [6].

G2/GB

wolfram lamp

Incandescent lamps that generate light by passing an electric current through a thin filament wire (usually of wolfram) until it is extremely hot. The lamps are often filled by an halogen gas such as iodine and bromine that allow filaments to work at higher temperatures and higher efficiencies.

See *quartz–iodine lamp*.

Wood horn

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

G2/GB

Wood lamp

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

See *lamp*.

revG2

xenon lamp

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

Related terms: *antimony–xenon, lamp, mercury–xenon lamp (arc)*.

See [15].

G2/GB

XPS

See *photoelectron spectroscopy*.

G2/GB

YAG

See *neodymium laser*.

G2/GB

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 coloured form of a *photochromic* compound at a specific *wavelength*.

See [3].

QUANTITIES, SYMBOLS, AND TERMS USED IN THIS DOCUMENT

Name	Symbol	Definition	SI Units	Notes
absorbance decadic napierian	A, A_{10} A_e	$A = \lg (P_\lambda^0/P_\lambda) = -\lg T$ $A_e = \ln (P_\lambda^0/P_\lambda) = -\ln T$	1	1
absorption coefficient linear decadic molar decadic linear napierian molar napierian	a ε α κ	$a = A_{10}/l$ $\varepsilon = a/c = A_{10}/c l$ $\alpha = A_e/l$ $\kappa = \alpha/c = A_e/c l$	m^{-1} $\text{m}^2 \text{mol}^{-1}$ m^{-1} $\text{m}^2 \text{mol}^{-1}$	2 3 3
absorption cross-section	$\sigma(\lambda)$	$\sigma(\lambda) = \kappa(\lambda)/N_A = \ln 10 \varepsilon(\lambda)/N_A$	m^2	4
actinometric factor		See spectral sensitivity		
amount of photons	n_p		mol	5
amount concentration	$c, [\text{species}]$	$c = [\text{species}] = n/V$	mol m^{-3}	6
area	S		m^2	
attenuance	D	$D = \lg (P_\lambda^0/P_\lambda) = -\lg T$	1	7
Avogadro constant	N_A	$N_A = 6.022\ 141\ 5 \times 10^{23} \text{ mol}^{-1}$	mol^{-1}	8
bandgap energy	E_g		J mol^{-1}	9
brightness (of a laser dye)		$\Phi \varepsilon(\lambda)$ with Φ the fluorescence quantum yield	1	
circular dichroism	ΔA_C	$\Delta A_C = A_L - A_R$	1	
critical quenching radius (Förster radius)	R_0	distance at which energy transfer from (k_T) and spontaneous decay (k_D) of the excited donor are equally probable, $k_T = k_D$	m	10
degree of polarization	p	$p = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}}$	1	
depth of penetration (of radiation) decadic napierian	β	$1/a$ $\beta = 1/\alpha$	m m	
Dexter transfer rate constant	k_T	$k_T = (1/\hbar) K J \exp(-2r/L)$ with L the average Bohr radius, J the spectral overlap integral (Dexter), r the distance between donor and acceptor, and K a proportionality constant	s^{-1}	
dichroic ratio	$d(\lambda)$	$d(\lambda) = A_Z/A_Y$	1	
dielectric constant see relative permittivity	ε_r		1	
dipole moment	μ		C m	11
driving force (for electron transfer), see		$-\Delta_{ET}G^0$	J mol^{-1}	

Gibbs energy of photoinduced electron transfer				
efficiency (of a reaction step)	η	$\eta = k_i / \sum_i k_i$		
electrical susceptibility	χ_e	$\chi_e = \epsilon_r - 1$	1	
elementary charge	e	$e = 1.602\ 176\ 53 \times 10^{-19}\ \text{C}$	C	8
emission anisotropy	r	$r = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}}$	1	
emission, emissivity	e	$e = M / M_{\text{bb}}$	1	12
excited state <i>lifetime</i> in the absence of quencher (within the <i>Stern–Volmer</i> relationship)	τ^0		s	
$E_{0,0}$ energy	$E_{0,0}$	energy difference between the vibrationally relaxed levels of two electronic states	J mol^{-1}	9
Fermi level	E_{F}		J mol^{-1}	9
fluence, radiant energy fluence	F_o, H_o	$F_o = H_o = \int_t E_o\ dt = dQ/dS$	J m^{-2}	13, 14
fluence rate (see <i>irradiance</i>)	E_o	$E_o = dF_o / dt$	W m^{-2}	14,15
fluorescence polarization (see <i>degree of polarization</i>)				
Förster transfer rate constant	k_{T}	$k_{\text{T}} = k_{\text{D}} \left(\frac{R_0}{r} \right)^6 = \frac{1}{\tau_{\text{D}}^0} \left(\frac{R_0}{r} \right)^6$ k_{D} : emission rate constant of the donor in the absence of energy transfer, r : distance between donor and acceptor, R_0 : critical quenching radius	s^{-1}	
fraction of light absorbed	$f(\lambda)$	$f(\lambda) = 1 - T(\lambda)$	1	
frequency (linear)	ν	$\nu = c/\lambda$	Hz	
frequency (angular)	ω	$2\ \pi\ \nu$	rad s^{-1}	
fundamental emission anisotropy (theoretical value)	r_0	$r_0 = \langle 3 \cos^2 \alpha - 1 \rangle / 5$ α = angle between absorption and emission transition moments	1	
Gibbs energy of photoinduced electron transfer	$\Delta_{\text{ET}}G^0$	$\Delta_{\text{ET}}G^0 = N_{\text{A}} \{ e [E^0(\text{D}^{+\bullet}/\text{D}) - E^0(\text{A}/\text{A}^{-\bullet})] + w(\text{D}^{+\bullet}\text{A}^{-\bullet}) - w(\text{DA}) \} - \Delta E_{0,0}$	J mol^{-1}	16
half-life of a transient entity	$\tau_{1/2}$	$c(t = \tau_{1/2}) = c(t = 0)/2$	s	

half-life of a photochromic system	$T_{1/2}$	$A(t = T_{1/2}) = A(t = 0)/2$	s	
hyper-susceptibility	$\chi_e^{(n)}$	$\chi_e^{(2)} = \partial^2 P / \partial E^2$, 1st hyper-susceptibility $\chi_e^{(3)} = \partial^3 P / \partial E^3$, 2nd hyper-susceptibility with P the polarization and E the electric field strength	$C m J^{-1}$ $C^2 m^2 J^{-2}$	17
irradiance (radiant power received)	E	$E = \int_{\lambda} E_{\lambda} d\lambda = dP/dS$	$W m^{-2}$	18
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	
linear dichroism	ΔA_l	$A_Z - A_Y$	1	
Lippert-Mataga polarity factor	$f(\epsilon_r, n)$	$f(\epsilon_r, n) = \frac{(\epsilon_r - 1)}{(2\epsilon_r + 1)} - \frac{(n^2 - 1)}{(2n^2 + 1)}$	1	
number density of entities number concentration	C	$C = N/V$	m^{-3}	
optical pathlength	l		m	
oscillator strength	f number	theoretical $f_{ij} = \frac{8 \pi^2 m c \tilde{\nu}}{3 e^2 h} G M_{ij}^2$ experimental $f_{ij} = (k/n) \int_{\tilde{\nu}} \epsilon(\tilde{\nu}) d\tilde{\nu}$	1	19
photon exitance (emitted photon flux)	M_p	$M_p = dq_p/dS$	$m^{-2} s^{-1}$	20
photon exposure	H_p	$H_p = \int_t E_p dt$	m^{-2}	20, 21
photon fluence	$F_{p,o}$	$F_{p,o} = dN_p/dS$	m^{-2}	14, 20
photon fluence rate	$E_{p,o}$	$E_{p,o} = dF_{p,o}/dt$	$m^{-2} s^{-1}$	14, 20
photon flux, amount basis	$q_{n,p}$	$q_{n,p} = q_p/N_A = (dN_p/dt) / N_A$	$mol s^{-1}$	22
photon flux, number basis	q_p	dN_p/dt	s^{-1}	20, 23
photon irradiance	E_p	$E_p = dq_p/dS$	$m^{-2} s^{-1}$	20, 24
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 $L_p = dq_p / (dS d\Omega \cos \theta)$	$m^{-2} s^{-1}$ $m^{-2} s^{-1} sr^{-1}$	20

Planck constant	h	$6.626\ 0693(11) \times 10^{-34}$	J s	8
	$\hbar = h/2\pi$	$1.054\ 571\ 68(18) \times 10^{-34}$	J s	8
polarization (optical)	\mathbf{P}	$\mathbf{P} = P^{(1)} + P^{(2)} + P^{(3)} + \dots$ $P = \epsilon_0 [\chi^{(1)} E + (1/2) \chi^{(2)} E^2 + (1/6) \chi^{(3)} E^3 + \dots]$ 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 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	$\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$	25
radiance	L	for a <u>parallel</u> beam $L = (dP/dS) / \cos \theta$	W m^{-2}	
		for a <u>divergent</u> beam $L = d^2P/(d\Omega dS \cos \theta)$	$\text{W m}^{-2} \text{sr}^{-1}$	
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}	26
radiant intensity	I	$I = dP/d\Omega$	W sr^{-1}	
radiant power, radiant energy per time	P	$P = dQ/dt$	W	27
radiative lifetime	τ_0	$\tau_0 = 1/k_r$	s	
rate constant for radiative step	k_r		s^{-1}	
reduced (linear) dichroism	ΔA_r	$\Delta A_r = (A_Z - A_Y)/3 A_{\text{iso}}$	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	28
refractive index	n	$n = c_0 / c$	1	
relative permittivity	ϵ_r	$\epsilon_r = \epsilon / \epsilon_0$	1	29
reorganization energy (for outer-sphere electron transfer,	λ	from $\Delta G^{\ddagger} = (\lambda + \Delta_{\text{ET}} G^0)^2 / 4\lambda$	J	

according to Marcus)				
residual emission anisotropy	r_∞	from $r(t) = (r_0 - r_\infty) \exp(-t/t_c) + r_\infty$		30
sensitivity of a photodiode	S_{pd}	$S_{pd} = I_{pd}/P$	$A W^{-1} = V^{-1}$	31
solid angle	Ω	$\Omega = S/r^2$	sr, 1	32
spectral distribution (of a radiant, luminous or photon quantity)	$X_\lambda(\lambda)$	$X_\lambda(\lambda) = dX(\lambda)/d\lambda$	$[X] m^{-1}$	
spectral fluence (in terms of wavelength)	$F_{\lambda,o}$	$F_{\lambda,o} = dF_o/d\lambda$	$J m^{-3}$	14, 33
spectral fluence rate	$E_{\lambda,o}$	$E_{\lambda,o} = dE_o/d\lambda$	$W m^{-3}$	14, 34
spectral irradiance	E_λ	$E_\lambda = dE/d\lambda$	$W m^{-3}$	35
spectral overlap integral (normalized) Dexter	J	$J = \int_0^\infty I_\lambda^D(\lambda) \varepsilon_A(\lambda) d\lambda$	$m^2 mol^{-1}$	36
Förster	J	$J = \int_0^\infty I_\lambda^D(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda$ with $I_\lambda^D(\lambda)$ the normalized <i>spectral distribution</i> of the <i>spectral radiant intensity</i> of the donor emission	$m^6 mol^{-1}$	37
spectral radiant energy	Q_λ	$dQ/d\lambda$	$J m^{-1}$	38
spectral radiant power	P_λ	$P_\lambda = dP/d\lambda$	$W m^{-1}$	39
spectral responsivity	$s(\lambda)$	$s(\lambda) = dY_\lambda/dE_\lambda$ with Y_λ the spectral output quantity of the system	1	40
spectral sensitivity of an actinometer	S_{ac}	$S_{ac}(\lambda) = \Phi(\lambda) \varepsilon(\lambda_{obs})$ or $S_{ac}(\lambda) = \Phi(\lambda) \Delta\varepsilon(\lambda_{obs})$	$m^2 mol^{-1}$	41
speed of light in vacuum in a medium	c_0 c	$c_0 = 299\,792\,458 m s^{-1}$ $c = c_0/n$	$m s^{-1}$ $m s^{-1}$	
steady-state emission anisotropy	\bar{r}	$\bar{r} = \frac{\int_0^\infty r(t) I(t) dt}{\int_0^\infty I(t) dt}$	1	42
Stern–Volmer constant	K_{SV}	Φ^0/Φ or $M^0/M = 1 + K_{SV} [Q]$ with $[Q]$ the amount concentration of quencher	$dm^3 mol^{-1}$	
Temperature (Celsius)	θ, t	$\theta/^\circ C = T/K - 273.15$	$^\circ C$	
temperature, thermodynamic	T		K	
time	t		s	

transition dipole moment	M_{if}	$M_{if} = \langle f M_{op} i \rangle$ with M_{op} the electric dipole moment operator	C m	11
transmittance	T	$T = P_{\lambda} / P_{\lambda}^0$	1	1
volume	V		m ³	
wavelength	λ		m	
wavenumber in vacuum	$\tilde{\nu}$	$\tilde{\nu} = \nu / c_0 = 1 / n\lambda$	m ⁻¹	
Z ₅₀ number (in photochromic systems)	Z ₅₀	number of cycles needed to lose 50 % of initial absorbance.	1	

Notes

- (1) 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.
- (2) In spectroscopy, usually defined in terms of the spectral radiant power, P_{λ} .
- (3) Numerical values are often quoted in mol⁻¹ dm³ 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 $\epsilon(\nu)$.
- (4) 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 $\sigma/\text{cm}^2 = (3.823\ 6 \times 10^{-21}/\text{mol}) \times (\epsilon/\text{dm}^3\ \text{cm}^{-1}\ \text{mol}^{-1})$.
- (5) Amount of photons is often given in the non-SI unit einstein = mol of photons.
- (6) 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.
- (7) Attenuance reduces to *absorbance* for a not reflected or scattered beam.
- (8) 2002 value [82]
- (9) Common non-SI unit is electronvolt (eV) = 1.602 176 53 (14) × 10⁻¹⁹ J; for one mole of electrons 1 eV = 96.485 kJ mol⁻¹
- (10) Common non-SI unit is ångström (Å) = 10⁻¹⁰ m. Common SI submultiples are nm, pm. Foerster is an alternative and acceptable spelling for Förster.
- (11) Common non-SI unit is debye (D) ≈ 3.335 64 × 10⁻³⁰ C m.
- (12) Relative value with respect to the photon exitance of a black body at the same temperature.
- (13) 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.
- (14) The symbols related to radiant energy incident from all directions have a subindex o (the letter o), not to be confused with 0 (zero) for incident radiation (footnote 1).
- (15) For a parallel and normally incident beam a synonym is *irradiance*. When applied to the total radiant energy incident from all directions the symbol E_o is used.
- (16) For calculations with the equation as given, the terms are quoted with units: $E^0(\text{D}^+/\text{D})/V$: standard electrode potential of the donor cation radical resulting from the electron transfer, $E^0(\text{A}/\text{A}^-)/V$: 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. $w(\text{D}^+\text{A}^-)/J$ and $w(\text{DA})/J$ are electrostatic work terms accounting for the effect of Coulombic attraction in the products and reactants, respectively.
- (17) In an anisotropic medium, $\chi_e^{(1)}$, $\chi_e^{(2)}$, and $\chi_e^{(3)}$ are tensors of rank 2, 3, and 4, respectively. For an isotropic medium (such as a liquid) or for a crystal with a centrosymmetric unit cell, $\chi_e^{(2)} = 0$ by symmetry. These quantities characterize a dielectric medium in the same way that the polarizability and the hyper-polarizabilities characterize a molecule.
- (18) The corresponding term for a beam incident from all directions is *fluence rate* (E_o).
- (19) 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; For $\epsilon(\tilde{\nu})/\text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-1}$ (common units), then $k = 4.32 \times 10^{-9}\ \text{dm}^{-3}\ \text{mol cm}$. The experimental equation takes into account line broadening effects.

- (20) 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.
- (21) The corresponding term for a beam incident from all directions is *photon fluence* ($F_{p,o}$).
- (22) Common unit is einstein s^{-1} . A term not in accordance with the usual definition of flux [7].
- (23) As defined in [4] (see also [20]); called *photon flux* in [8], a term not in accordance with the usual definition of flux [7].
- (24) The corresponding term for a beam incident from all directions is *photon fluence rate*, $E_{p,o}$.
- (25) Superindex 0 indicates *quantum yield* or *radiant intensity*, and *lifetime* in the absence of quencher, no superindex indicates the quantities in the presence of quencher Q. Common units for the quenching rate constant are $dm^3 mol^{-1} s^{-1}$.
- (26) The corresponding term for a beam incident from all directions is *fluence*, F_o .
- (27) Definition from [7]; synonymous *radiant energy power*, *radiant energy flux* defined in [8].
- (28) Superscript 0 indicates incident *radiant power* and refl reflected radiant power.
- (29) Formerly called dielectric constant.
- (30) τ_c is the rotational correlation time and r_0 the *fundamental emission anisotropy*.
- (31) 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.
- (32) The steradian is an SI supplementary unit, but is dimensionless, so has SI unit 1.
- (33) 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.
- (34) Common units are $W m^{-2} nm^{-1}$. Analogous quantities relative to frequency or to wavenumber may also be defined.
- (35) Common units are $W m^{-2} nm^{-1}$. Analogous quantities relative to frequency or to wavenumber may also be defined.
- (36) $I_\lambda^D(\lambda)$ 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 $\int_0^\infty I_\lambda^D(\lambda) d\lambda = \int_0^\infty \epsilon_A(\lambda) d\lambda = 1$.
- (37) $I_\lambda^D(\lambda)$ 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 $dm^3 cm^3 mol^{-1}$.
- (38) Common units are $J nm^{-1}$. Analogous quantity relative to frequency or to wavenumber may also be defined.
- (39) Common units are $W nm^{-1}$. Analogous quantity relative to frequency or to wavenumber may also be defined.
- (40) Relative biological or chemical photoresponse per incident radiant power as a function of *wavelength*.
- (41) 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 units are $dm^3 mol^{-1} cm^{-1}$.
- (42) $r(t)$ is the anisotropy and $I(t)$ is the fluorescence intensity (emission radiant intensity), both at time t following a δ -pulse excitation.

Entries in the table are consistent with terminology, symbols and units given in [7,8,9], and are slightly modified from those in [4], terms from which are included in [20].

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