11.2 Terms and symbols used in photochemistry and in light scattering

Absorbance (*A*)

The logarithm to the base 10 of the ratio of the radiant power of the incident radiation (P_0) to the radiant power of the transmitted radiation (P). In solution, the absorbance is the logarithm to the base 10 of the radiant power transmitted through the reference sample to that of the light transmitted through the solution.

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

Traditionally radiant intensity, *I*, was used instead of radiant power *P*, which is now the accepted form. The terms absorbancy, extinction and optical density should no longer be used.

Absorptance

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

$$1- (P/P_0).$$

Absorption (of electromagnetic radiation)

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

Absorption Coefficient (decadic - *a* or Naperian - α)

Attenuance divided by the optical pathlength (*l*)

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

or in Naperian terms

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

Absorption cross section (σ_{abs})

It can be calculated as the absorption coefficient divided by the number of molecular entities (or particles) in a unit volume along the lightpath.

$$\sigma_{abs} = [1 / (Nl)] \log_e (P_0 / P) = \alpha/N$$

where N is the number of molecular entities per unit volume, l is the optical pathlength and α is the Naperian absorption coefficient.

Note: In analytical usage the optical pathlength may be given in cm.

Absorption efficiency

The *absorption cross section* divided by the cross sectional area of a particle.

Absorption index

The absorption index (k) is defined by the expression for the complex refractive index ($\hat{n}$)

$$\hat{n} = n + ik$$

where n is the real part of $\hat{n}$ (the *real refractive index*).

Absorptivity

Absorptance divided by the optical pathlength. For very low attenuance it approximates to the *absorption coefficient*. The term is not recommended.

Actinometer

An actinometer is a (usually chemical) device or system which determines the number of photons in a beam integrally or per unit of time.

Action Spectrum

A plot of relative biological or chemical photoresponse per number of incident photons versus wavelength or energy of radiation. By contrast, a plot of the biological or chemical change per absorbed photon versus wavelength is the *efficiency spectrum*.

Adiabatic photoreaction

Within the 'Born-Oppenheimer' approximation, a reaction of an excited state species that occurs on a single "potential energy surface". See *diabatic photoreaction*.

ADMR

See *optically detected magnetic resonance*, (ODMR).

Alpha - cleavage (α - cleavage)

A homolytic cleavage of a bond connecting an atom or group to a specified group. See *Norrish type I photoreaction*.

Alpha - expulsion (α -expulsion)

A general reaction by which a group attached to the alpha carbon of an excited chromophore is expelled as an odd electron species or an anionic species. This should be distinguished from an *alpha-cleavage*.

AM (0) Sunlight

The solar irradiance in space just above the earth's atmosphere (air mass, AM, zero), also termed the extraterrestrial global irradiance.

AM (1) Sunlight.

The solar irradiance traversing the atmosphere when the sun is in a position perpendicular to the earth's surface, also called terrestrial global irradiance.

Annihilation

The interaction of two atoms or molecular entities (both in an excited electronic state), usually by collision, to produce one atom or molecular entity in an excited electronic state and another in its ground electronic state. See *singlet-singlet annihilation*, *spin conservation rule*, *triplet-triplet annihilation*.

Antimony - xenon lamp (arc)

An intense source of ultraviolet, visible and near infrared radiation produced by a discharge in a mixture of antimony vapour and xenon under high pressure. The output in the UV is higher than that of the mercury - xenon lamp.

Anti-stokes shift

See *Stokes shift*.

Apparent lifetime

See *lifetime*.

Argon ion laser

A *cw* or *pulsed lase*r emitting lines from 334 to 529 nm from singly ionised argon. Principal emissions are at 488 and 514.5 nm.

Asymmetry factor for scattering

The asymmetry factor for scattering is defined by

$$\langle \cos\theta \rangle_{sca} = \frac{\int\limits_{-1}^{+1} E_u \cos\theta \cdot d(\cos\theta)}{\int\limits_{-1}^{+1} E_u \cdot d(\cos\theta)}$$

for cylindrically symmetric scattering where E_u is the irradiance of the incident unpolarized light and θ is the *scattering angle*.

Attenuance (D)

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

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

where τ is the *transmittance*.

Attenuance filter

An optical device that reduces the radiant power of a light beam by a constant factor over all wavelengths of its operational range, also called an attenuator or a neutral density filter.

Avoided crossing (of potential energy surfaces)

Frequently, two Born-Oppenheimer electronic states (A,B) change their energy order as molecular geometry is changed continuously along a path. In the process their energies may become equal at some points, the case of *surface crossing,* or only come relatively close when the crossing of surfaces is said to be avoided.

Back scattering

See *scattering plane*.

Bandgap energy (E_g)

The energy difference between the bottom of the conduction band and the top of the valence band in a semiconductor or an insulator. See *conduction band*, *Fermi level*.

Bandpass filter

An optical device that permits the transmission of radiation only within a specified wavelength range.

Barton reaction

Photolysis of a nitrite to form a d-nitroso alcohol.

Bathochromic shift (effect)

Shift of a spectral band to lower frequencies as the result of the influence of substitution or a change in the environment (e.g. solvent). This is informally referred to as a red shift and is opposite to a hypsochromic shift.

Beer-Lambert law (Beer-Lambert-Bouguer law)

The *absorbance*, *A*, 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;

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

where ε is the *molar decadic absorption coefficient*.

Bioluminescence

Chemiluminescence produced by living systems.

Biphotonic excitation (two-photon excitation)

The simultaneous (*coherent*) absorption of two *photons* (of the same or different wavelengths), the energy of excitation being the sum of the energies of the two photons.

Biphotonic process

A process resulting from *biphotonic excitation*.

Biradical (also diradical)

An even-electron molecular entity with two (possibly delocalised) radical centres which act nearly independently.

Bleaching

The loss of absorption or emission intensity.

Blue shift

Informal expression for *hypsochromic shift*.

Cadmium-helium laser

See *helium-cadmium laser*.

Cavity dumping

The periodical removal of *coherent radiation* from a *laser* cavity.

Charge-transfer (CT) state

A state related to the ground state by a charge transfer transition.

Charge-transfer (CT) transition

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

Charge transfer (CT) complex

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

Chemical Laser

A *cw* or *pulsed laser* in which the excitation and *population inversion* of the emitting species result from a chemical reaction.

Chemiexcitation

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

Chemiluminescence

Luminescence arising from *chemiexcitation*.

Chromophore

That part of a molecular entity consisting of an atom or group of atoms in which the electronic transition responsible for a given spectral band is approximately located.

Chemically induced dynamic nuclear polarization (CIDNP)

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

Chemically initiated electron exchange luminescence (CIEEL)

A type of *luminescence* resulting from a thermal electron transfer reaction. Also called catalyzed *chemiluminescence*.

CO_2 laser

A continuous or pulsed source of *coherent radiation* normally tunable through the CO_2 vibration rotation band centred near 10.6 mm.

Coherent radiation

The radiation emitted when all the elementary waves have a phase difference constant in space and time.

Conduction band

A vacant or only partly occupied set of many closely spaced electronic levels resulting from an array of a large number of atoms forming a system in which electrons can move relatively freely. See *bandgap energy*, *Fermi level*, *valence band*.

Configuration (electronic)

A distribution of the electrons of an atom or a molecular entity over a set of one-electron wavefunctions, called *orbitals,* according to the Pauli principle. From one configuration several states with different *multiplicities* may result.

Configuration interaction

The mixing of many-electron wavefunctions constructed from different electronic *configurations* to obtain an improved many-electron state.

Conversion spectrum

A plot of a quantity, related to the *absorption*, *absorbance*, *cross section* etc., multiplied by the quantum yield for the process against a suitable measure of photon energy, such as *wavelength, wavenumber* or *frequency*.

Copper vapour laser

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

Corrected excitation spectrum

See *excitation spectrum*.

Correlation diagram

A diagram that shows the relative energies of *orbitals*, *configurations*, *valence bond* structures or states of reactants or products of a reaction as a function of the molecular geometry, or other suitable parameter.

Correlation distance

See *relative permittivity*.

Correlation energy

The difference between the Hartree-Fock energy calculated for a system and the exact non-relativistic energy of the same system.

Correlation function

See *relative permittivity*.

Critical quenching radius

See *Förster excitation transfer*.

Crystal field splitting

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

Cut-off filter

An optical device that only permits the transmission of radiation of wavelengths that are longer or alternatively shorter than a specified wavelength.

Cw (continuous wave)

Non-pulsed source of electromagnetic radiation.

Davydov splitting

The splitting of bands in the electronic or vibrational spectra of crystals as a result of the presence of more than one (interacting) equivalent molecular entity in the unit cell.

Deactivation

Any loss of energy by an excited molecular entity.

Delayed fluorescence

See *delayed luminescence*.

Delayed luminescence

Luminescence decaying more slowly than expected from the rate of decay of the emitting state. The following mechanisms of luminescence provide examples:

1)   *triplet-triplet* or *singlet-singlet annihilation* to form one molecular entity in its excited *singlet state* and another molecular entity in its electronic *ground state* (sometimes referred to as P type),

2)   thermally activated *delayed fluorescence* involving reversible *intersystem crossing* (sometimes referred to as E type) and

3)   combination of oppositely charged ions or an electron and a cation. For *emission* to be referred to in this case as delayed luminescence at least one of the partners must be generated in a *photochemical process*.

DEDMR

See *optically detected magnetic resonance*.

Depolarization factor

The *Rayleigh ratios* for an ellipsoid whose longest dimension is small compared with the wavelength can be derived by assuming three *polarizabilities* (α) along the axes of the ellipsoid *A, B, C*, e.g.

$$\alpha_A = 4\pi e_0 \frac{v\left(m^2 - 1\right)}{4\pi + \left(m^2 - 1\right)D_A}$$

where *V* is the volume, *m* is the *relative refractive index* and the depolarization factor

$$D_A = \int_0^\infty \frac{2\pi ABCdy}{\left(y + A^2\right)^{3/2}\left(y + B^2\right)^{1/2}\left(Y + C^2\right)^{1/2}}$$

where *y* is an integration constant; similar equations can be written for α_B and α_C.

Depth of penetration

The inverse of the *absorption coefficient*.

Dexter excitation transfer (electron exchange excitation transfer)

Excitation transfer occurring as a result of an electron exchange mechanism. It requires an overlap of the wave functions of the energy donor and the energy acceptor. It is the dominant mechanism in *triplet-triplet energy transfer*.

DFDMR

See *optically detected magnetic resonance (ODMR)*.

Diabatic photoreaction

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

Diode laser

Sources of cw or pulsed *coherent radiation* in the visible and infrared regions, usually tunable over a range of a few nm.

Di-π-methane rearrangement

A photochemical reaction of a molecular entity comprising two p-systems, separated by a saturated carbon atom (a 1,4-diene or an allyl-substituted aromatic analogue) to form an ene- (or aryl-) substituted cyclopropane. See also *oxa-di-π-methane rearrangement*.

Dissymmetry

For the case where the scattering in the half-plane from 0° to 180° is symmetrical with that from 180° to 360°, dissymmetry is defined as the ratio of the scattered irradiance at two scattering angles symmetrical about $\theta = 90°$.

Dose

The energy or amount of *photons* absorbed per unit area or unit volume by an irradiated object during a particular exposure time. In some areas, e.g. medicine, dose is used in the sense of *fluence,* i.e., the energy or amount of photons <u>received</u> by an irradiated object during a particular exposure time.

Doublet state

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

Dye laser

A cw or pulsed source of *coherent radiation* in which the active medium is usually a solution of a fluorescent organic molecule (the dye) pumped with a suitable pump laser or with a flash lamp. These lasers can be tuned over a large part of the fluorescence band of the dye.

Effectiveness

See *spectral (photon) effectiveness*.

Efficiency (of a step)

The ration between the useful energy delivered or bound and the energy supplied, i.e. energy output/energy input.

Efficiency spectrum

A plot of the efficency (of a step) against wavelength or photon energy. See *action spectrum*, *conversion spectrum*.

Elastic scattering

Elastic scattering is *light scattering* with no wavelength shift. See *inelastic scattering*, *quasielastic scattering*.

Electrogenerated chemiluminescence

Luminescence produced by electrode reactions. Also called electroluminescence or electrochemiluminescence.

Electron correlation

The adjustment of electron motion to the instantaneous (as opposed to time-averaged) positions of all the electrons in a molecular entity. See also *correlation energy*.

Electron energy migration

The movement of electronic excitation energy from one molecular entity to another of the same species or from one part of a molecular entity to another of the same kind (e.g. between the chromophores of an aromatic polymer)

Electron exchange excitation transfer

Same as *Dexter excitation transfer*.

Electronically excited state

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

El Sayed rules

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

Emission

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

Emission spectrum

Plot of the emitted *spectral radiant power* (*spectral radiant exitance*) or of the emitted *spectral photon irradiance (spectral photon exitance)* against a quantity related to photon energy such as *frequency, wavenumber* or *wavelength*.

Emittance

See *radiant exitance*.

Energy storage efficiency

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

Energy transfer

This term describes the process by which a molecular entity absorbs light and a phenomenon originates from the *excited state* of another molecular entity. In mechanistic photochemistry the term has been reserved for the *photophysical process* in which an excited state of one molecular entity (the donor) is deactivated to a lower state by the transfer of energy to a second molecular entity (the acceptor) which is thus raised to a higher energy state.

Energy transfer plot

A plot of the *quenching* rate constant of an excited molecular entity by a series of *quenchers* versus the excited state energy of the quenchers. Alternatively a plot of the rate constant for the *sensitization* of a reaction versus the excited state energy of different sensitizers. This type of plot is used to estimate the energy of the excited molecular entity quenched or produced. See also *Stern-Volmer kinetic relationships* .

Enhancer

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

ESCA

See *photoelectron spectroscopy*.

Excimer

An electronically excited dimer, "non-bonding" in the *ground state*, for example a complex formed by the interaction of an excited molecular entity with a ground state partner of the same structure. See also *exciplex*.

Excimer laser

A source of pulsed *coherent* radiation obtained from an *exciplex*. Typical lasing gases are noble gas halides.

Exciplex

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

Excitation spectrum

Plot of the spectral radiant exitance or of the spectral photon exitance against frequency, wavenumber or wavelength of excitation. When corrected for wavelength dependent variations in the excitation *radiant power*, this is called a *corrected excitation spectrum*. See also *emission spectrum*.

Excited State

A state of higher energy than the *ground state*. In photochemistry, excited electronic state is usually meant.

Exciton

It is sometimes useful to consider electronic excitation as if a quasi-particle, capable of migrating, were involved. In organic chemistry two models are used; the band or wave model (low temperature, high crystalline order) and the hopping model (higher temperature, lower crystalline order or amorphous state).

Exitance

See radiant exitance.

External heavy atom effect

See *heavy atom effect*.

Extinction

This term, equivalent to absorbance is not recommended.

Extinction coefficient

This term, equivalent to *molar (decadic) absorption coefficient* is not recommended.

Factor group splitting

See *Davydov splitting*.

Fermi level (E_F)

The chemical potential of electrons in a solid (metals, semiconductors or insulators) or in electrolyte solution. See *bandgap energy, conduction band, valence band*.

Filter (optical)

A device which reduces the spectral range (*bandpass, cut-off* or *interference filter*) or *radiant power* of incident radiation (*neutral density,* or *attenuance filter*) upon transmission of radiation.

Flash photolysis

A technique of *transient spectroscopy* and transient kinetic studies in which a light pulse is used to produce transient species.

Fluence (H_0)

The total energy traversing a small imaginary spherical target, containing the point of interest, divided by the cross section of the target.

$$H_0 = E_0\, t$$

where E_0 is the fluence rate and t is the duration of the irradiation (assuming that fluence rate is constant over the time involved, otherwise $E_0\, t$ is replaced by $\int E_0 \mathrm{d}t$). Energy fluence is identical to spherical radiant exposure and reduces to radiant *exposure* (H) for a parallel and normally incident beam, not scattered or reflected by the target or its surroundings. See also *photon fluence, dose*.

Fluence rate (E_0)

The fluence rate is equal to 4 times the radiant power, P, incident on a small transparent imaginary spherical volume element containing the point of interest, divided by the surface area of that sphere, S_k, when the radiant power is constant over the solid angle considered. It reduces to *irradiance, E,* for a parallel and normally incident beam not scattered or reflected by the target or its surroundings. See also *photon fluence rate*.

Fluorescence

Spontaneous *emission* of radiation (*luminescence*) from an excited molecular entity with the formation of a molecular entity of the same spin *multiplicity*.

Flux

See *radiant energy flux*, *radiant power*.

Förster excitation transfer (dipole-dipole excitation transfer)

A mechanism of excitation transfer that can occur between molecular entities separated by distances considerably exceeding the sum of their van der Waals radii. It is described in terms of *transition dipole moments*. The transfer rate constant is given by

$$k_{D \to A} = \frac{k^2 J \, 8.8 \cdot 10^{-28} \, mol}{n^4 \tau_0 \, r^6}$$

where k is an orientation factor, n the refractive index of the medium, r the distance (cm) between donor and D and acceptor A, τ_0 the radiative lifetime of the donor and J the spectral overlap (in coherent units, $cm^6 \, mol^{-1}$) between the absorption spectrum of the acceptor and the fluorescence spectrum of the donor. See also *Dexter excitation transfer*, energy transfer, *radiative energy transfer*.

Förster cycle

Indirect method of determination of *excited state* equilibria, such as pK_a^* values based on *ground state* thermodynamics and the electronic transition energies. This cycle considers only the difference in molar entropy change of reaction of ground and excited states, neglecting the difference in molar entropy change of reaction of these states.

Forward scattering

The *scattering plane* contains the incident light beam and the line from the centre of the scattering system to the observer, *forward scattering* is at $\theta = 0°$ and *back scattering* is at $\theta = 180°$ where the *scattering angle*, θ, lies in the scattering plane and is measured clockwise viewing in the incident direction. See *scattering plane*.

Fourier transform spectrometer

A scanning interferometer, containing no principle dispersive element, which first splits the

beam into two or more components, then recombines these with a phase difference. The spectrum is obtained by a Fourier transformation of the output of the interferometer.

Franck-Condon principle

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

The quantum mechanical formulation of this principle is that the *intensity* of a *vibronic transition* is proportional to the square of the overlap integral between the vibrational wavefunctions of the two states involved in the transition.

Free electron laser

Source of coherent radiation in which the active medium is an electron beam moving at speeds close to that of light in the spatially periodic magnetic field produced by an array of magnets (the wiggler). The emitted wavelength is approximately given by

$$\lambda_\omega / 4E^2$$

where λ_ω is the wiggler period and E the electron energy in MeV.

Free-running laser

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

Frequency

The number of waveperiods per unit time. The linear frequency, v, is the number of cycles per unit time. For the angular freqency, the symbol $\omega = 2\pi v$ is used.

Frequency doubling

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

FWHM (full width at half maximum)

See *half-width*.

Gas laser

Pulsed or *cw lasers* in which the active medium is a gaseous mixture usually consisting of a buffer gas (e.g. He) and an active medium consisting of:

        neutral atoms (Ne, Cu, Au, etc) or molecules (e.g. N_2, CO_2, CO, I_2 etc),
        or ionised atoms (e.g. Ar, Kr, Cd etc)

Gaussian band shape

A band shape described by the Gaussian function

$$F\left(v - v_0\right) = \left(a/\sqrt{\pi}\right)\exp\left[-a^2\left(v - v_0\right)^2\right]$$

In this equation, a^{-1} is proportional to the width of the band and v_0 is the frequency of the band maximum.

Generalized anisotropy (δ)

This is expressed as

$$\delta^2 = \gamma^2 / 9\left(\bar{\alpha}\right)^2$$

where $\bar{\alpha}$ is the *mean polarizability* and γ is the anisotropy factor. See Pure App. Chem., 55 (1993) 936.

Ground state

The lowest energy state of a chemical entity. In photochemistry the ground electronic state is usually meant.

Half-width (of a band)

The full width of a spectral band at a height equal to half of the height at the absorption band maximum. Also known as *full width at half maximum (FWHM)* expressed in wavenumbers or frequencies.

Harmonic frequency generation

Production of coherent radiation of frequency $k\nu$ (k= 1, 2, 3, ...) from coherent radiation of frequency ν, usually through the interaction of laser light with an optical medium with non-linear polarizability. The case k=2 is *frequency doubling* and k=3, *frequency tripling* etc.

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 an excited molecular entity. Mechanistically it corresponds to a *spin-orbit coupling* enhancement produced by a heavy atom.

Helium-cadmium laser

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

Helium-neon laser

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

High pressure mercury lamp (arc)

Radiation source containing mercury at a pressure of *ca*. 8 MPa or higher which emits lines over a background continuum between about 200 and 1400 nm.

Hole-burning

The photobleaching of a feature, normally a narrow range, within an inhomogeneous broader absorption or emission band. The holes are produced by the disappearance of resonantly excited molecules as a result of *photochemical* or *photophysical processes*.

Hot state reaction

A reaction proceeding from an ensemble of molecular entities possessing a higher average vibrational, rotational or translational energy than they would have at thermal equilibrium with the surrounding medium.

Hot ground state reaction

A *hot state reaction* of the ground electronic state.

Hund rules

1.   Of the different multiplets resulting from the 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 lies lowest in energy, whereas in those shells more than half filled, the term having the largest value of total angular momentum lies lowest (fine structure rule).

Hund rules apply if the Russell-Saunders coupling scheme is valid.

Hyperchromic effect

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

Hypochromic effect

Opposite of *hyperchromic effect*.

Hypsochromic shift

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

Imaging

The use of a photosensitive area for the capture, recording and retrieval of information associated with an object using electromagnetic energy

Incoherent radiation

Not having the properties of *coherent radiation*.

Inelastic scattering

Scattering in which there are wavelength shifts due to molecular transitions (Raman effect, fluorescence). See *elastic scattering*, *quasielastic scattering*.

Inner filter effect

In emission it refers to an apparent decrease in emission *quantum yield* and/or distortion of bandshape as a result of reabsorption of emitted radiation. Alternatively, in light irradiation experiments, absorption of incident radiation by a species other than that intended is also described as an inner filter effect.

Integrating sphere

A hollow sphere with a highly reflecting inner surface used as a device to collect, with very high efficiency, light scattered or emitted from a sample contained in it or located outside and near one of the ports used to allow the entrance of light and access to a detector.

Intensity

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

Intensity (of a light source) (*I*)

Same as *radiant intensity*.

Intensity (of a spectral feature)

Describes the magnitude of the particular feature in the spectrum.

Interference filter

See *Filter*.

Interferometer

See *Fourier transform spectrometer*.

Internal conversion

A *photophysical process*. Isoenergetic *radiationless transition* between two electronic states of the same *multiplicity*. When the transition results in a vibrationally excited molecular entity in the lower electronic state, this usually undergoes *deactivation* to its lowest vibrational level, provided the final state is not unstable to dissociation.

Intersystem crossing

A *photophysical process*. Isoenergetic *radiationless transition* between two electronic states having different *mutiplicities*. It often results in a vibrationally excited molecular entity in the lower electronic state that usually deactivates to its lowest vibrational level.

Irradiance (E)

The *radiant flux* or *radiant power*, P, incident on an infinitesimal element of surface containing the point of interest, divided by the area of the element, (dP /dS, simplified expression: $E = P$ /S, when radiant power is constant over the surface area). For a parallel and perpendicularly incident beam, not scattered or reflected by the target or its surroundings, *fluence rate* (E_0) is an equivalent term. Note that the similar term *radiant exitance* (the radiant flux emitted) differs from *irradiance* only in direction.

Isoclinic point

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

Isooptoacoustic point

A wavelength, wavenumber or frequency at which the total energy emitted by the sample as heat does not change upon chemical reaction or physical change of the sample. The spectral differences between *isobestic points* and isooptoacoustic points are the result of the non-linear relationship between the *molar absorption coefficient* and the *photoacoustic* signal.

Isobestic point

A *wavelength*, *wavenumber* or *frequency* at which *absorption coefficients* of reactants or

chemicals in different modifications are equal. As a consequence the total *absorbance* of a sample at this wavelength does not change during chemical reaction or physical change of the sample. The use of the term isoabsorption point is not recommended.

Isostilbic point

The *wavelength* at which the *intensity of emission* of a sample does not change during chemical reaction or physical change of the sample.

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. Currently, 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 are indicated by arrows. *Radiative transitions* are generally indicated by straight arrows and *radiationless transitions* by wavy arrows.

Jahn-Teller effect

For non-linear molecular entities in a geometry described by a point symmetry group possessing degenerate irreducible representations, there always exists at least one non-totally symmetric vibration that makes electronically degenerate states unstable at this geometry. The nuclei are displaced to new equilibrium positions of lower symmetry causing a splitting of the originally degenerate states. This effect is due to the odd terms in the vibronic perturbation expansion. See also *Renner-Teller effect*.

Kaptein-Closs rules

Rules used to predict the sign of *chemically induced dynamic nuclear polarization* effects. Exceptions exist.

Kasha rule

Polyatomic molecular entities luminesce with appreciable yield only from the lowest *excited state* of a given *multiplicity*.

Kasha-Vavilov rule

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

Koopmans' theorem

See *photoelectron spectroscopy*.

Krishnan's relation

Krishnan's relation is defined as:

$$\rho_u = \frac{1 + \rho_h^{-1}}{1 + \rho_v^{-1}}$$

where ρ_u is the polarization ratio for unpolarized incident light and ρ_h and ρ_v are the polarization ratios for the beam polarized with its electric vector perpendicular and parallel, respectively, to the scattering plane.

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, 647.11 and 752.5 nm.

Lambert law

The fraction of light absorbed by a system is independent of the incident radiant power, provided that radiant power is small, scattering is negligible and that *multiphoton* processes, *excited state* populations and *photochemical* reactions are negligible.

Laporte rule

For monophotonic radiative transitions in centrosymmetric systems, the only non-vanishing electric-dipole transition moments are those which connect an even term with an odd term.

Laser

A source of ultraviolet, visible or infrared radiation which produces light amplification by stimulated emission of radiation from which the acronym laser is derived. The light is *coherent* except for *superradiance* emission.

Laser action

The process of producing light amplification by stimulated emission of radiation. (sometimes referred to as lasing)

Latent image

The primary result of radiation absorption in a *photoimaging* system that is capable of development.

Lifetime (τ)

The lifetime of a molecular entity which decays in a first-order process is the time needed for a concentration of the entity to decrease to 1/e of its original value. Statistically it represents the life expectation of the entity. It is equal to the reciprocal of the sum of the (pseudo)unimolecular rate constants of all processes that cause decay. Lifetime is sometimes used for processes that are not first-order. 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 and the term should be apparent lifetime. Occasionally the term half-life is used, representing the time needed for the concentration of an entity to decrease to half its original value.

Ligand field splitting

The removal of a degeneracy of atomic or molecular levels in a molecule or ion with a given symmetry induced by the attachment or removal of ligands to produce reduced symmetries. See *crystal field splitting*.

Light polarization

When the end point of the electric vector of a polarized light beam is viewed along the direction of light propagation, it moves along a straight line if the light is linearly polarized, along a circle if it is circularly polarized and along an ellipse if it is elliptically polarized.

Light scattering

The deflection of a beam of light by discrete variation in refractive index caused by the presence of particles or by spatial refractive index fluctuations. See also *elastic scattering*, *inelastic scattering* and *quasielastic scattering*.

Lorentzian band shape

This band shape is defined by the function

$$F(v - v_0) = (1/\pi) \; \gamma [\, (v - v_0)^2 + \gamma^2 \,]^{-1}$$

where v_0 is the mean band position, γ the half bandwidth at half maximum and $F(v - v_0)$ is the frequency distribution function.

Low- pressure mercury lamp (arc)

A type of resonance lamp which contains mercury vapour at pressures of about 0.1 Pa, emitting mainly at 253.7 and 184.9 nm at 25° C.

Luminescence

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

Lumiphore

A part of a molecular entity (or atom or group of atoms) in which *electronic excitation* associated with a given emission band is approximately localized. In absorption spectra the analogous term is *chromophore*.

Mean polarizability

The mean polarizability, $\bar{\alpha}$, is defined by the relation

$$\bar{\alpha} = 1/3 \left(\alpha_A + \alpha_B + \alpha_C \right)$$

where α_A, α_B, α_C are respectively the polarizabilities along the three axes A, B, C of the ellipsoid. See *polarizability*.

Medium-pressure mercury lamp (arc)

Radiation source containing mercury vapour at pressures ranging from 100 to several hundred kPa. Emits mainly from 310 to 1000 nm with most intense lines at 300, 303, 313, 334, 366, 405, 436, 546 and 578 nm.

Mercury-xenon lamp (arc)

An intense source of ultraviolet, visible and infrared radiation produced by an electrical discharge in a mixture of mercury vapour and xenon at high pressure.

Mode-locked laser

A laser in which many resonant modes are coupled in phase to yield a train of very short pulses (e.g. ps pulses). The coupling of the modes is obtained by modulation of the gain in the resonator, and can be active (electro-optic modulation of the losses or of the pump intensity) or passive (with a saturable absorber).

Molar absorption coefficient, molar decadic absorption coefficient (ε)

Absorbance (*A*) divided by absorption path length (*l*) and the concentration (*c*).

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

In common usage *l* is in cm and *c* in mol dm^{-3} giving ε in dm^3 mol^{-1} cm^{-1}. The term 'extinction coefficient' equivalent to molar decadic absorption coefficient is not recommended. See *absorbance, Lambert-Beer law*.

Multiphoton absorption

See *multiphoton process*.

Multiphoton process

A process, e.g. absorption, involving interaction of two or more photons with a molecular entity giving rise to e.g. *multiphoton absorption*.

Multiple scattering

In multiple scattering, as opposed to *single scattering*, there are several scattering encounters in which there is successive rescattering of the radiation within the scattering medium.

Multiplicity (spin multiplicity)

The number of possible orientations, calculated as 2S +1, of the spin angular momentum corresponding to a given total spin quantum number (S), for the same spatial electronic wavefunction. A state of *singlet* multiplicity has S = 0 and 2S + 1 = 1. A *doublet* state has S = 1/2, 2S + 1 = 2 etc. Note that when S is greater than the total orbital angular momentum

quantum number, L, there are only 2L + 1 orientations of total angular momentum possible.

n→π* transition

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

n→π* state

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

n→σ* transition

An electronic transition described approximately as promotion of an electron from a "non-bonding" (lone-pair) n orbital to an "antibonding" σ orbital designated as σ*. These generally have high transition energies and appear close to or mixed with "Rydberg transitions".

Neodymium laser

A cw or pulsed laser emitting radiation from excited Nd^{+3} principally occurring around 1.06 nm, the precise wavelength depending on the matrix. The Nd^{+3} is present as a dopant in suitable crystals e.g, yttrium-aluminium garnet (YAG) or in suitable glasses.

Neutral density filter

See *attenuance filter*.

Nitrogen laser

A source of pulsed, semi-coherent *superradiance*, mainly around 337 nm. The laser-active species is molecular nitrogen.

Non-linear optical effect

An effect brought about by electromagnetic radiation the magnitude of which is not proportional to the *irradiance*. They include *harmonic frequency generation*, *Raman shifting*, *upconversion* etc.

Non-radiative decay

Disappearance of an excited species as a result of a *radiationless transition*.

Non-vertical energy transfer

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

Norrish type I photoreaction

-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*.

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*.

Optically detected magnetic resonance (ODMR)

A double resonance technique in which transitions between spin levels are detected by optical means. Usually these are sublevels of a *triplet* and the transitions are induced by microwaves. For different types of optical detection the following expressions are used: *ADMR* (*absorption*), *DEDMR* (*delayed emission*, non-specified), *DFDMR* (*delayed fluorescence*), FDMR (*fluorescence*), *PDMR* (*phosphorescence*.) If a reaction yield is followed the expression *RYDMR* (*reaction yield detected magnetic resonance*) is used.

Optoacoustic spectroscopy

Same as *photoacoustic spectroscopy*.

Orbital

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

Oscillator strength (f number)

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

$$f_{ij} = \frac{8\pi mcv}{3h} GR_{ij}^2$$

where m is the mass of the electron, c is the velocity of light, v the frequency, h the Planck constant, G the degeneracy of the final state, R_{ij} is the transition moment calculated omitting e, the electron charge, in the integral; better called the transition length. Experimentally f_{ij} is determined by integration of the absorption band, using the equation

$$f_{ij} = (k/n)\int \varepsilon(\alpha)d\alpha$$

where ε is the *molar absorption coefficient* at wavenumber α and n the average refractive index of the medium, k = 4.32 · 10^{-9} dm^{-3} mol cm (for ε in the common units dm^3 mol^{-1} cm^{-1}) and = 4.32 · 10^{-8} mol m^{-1} (for SI units m^2 mol^{-1}). Oscillator strength is dimensionless.

Oxa-di-π-methane rearrangement

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

Paterno-Büchi reaction

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

PDMR

See *optically detected magnetic resonance* (*ODMR*).

Phonon

Elementary excitation in the quantum mechanical treatment of vibrations in a crystal lattice.

Phosphorescence

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

Photoacoustic effect

Generation of heat after absorption of radiation due to *radiationless deactivation* or chemical reaction.

Photoacoustic spectroscopy

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

Photoaffinity labelling

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

Photo-assisted catalysis

Catalytic reaction involving production of a catalyst by the absorption of light. See *photocatalysis*.

Photocatalysis

Catalytic reaction involving light absorption by a catalyst or substrate.

Photochemical reaction

This term is generally used to describe a chemical reaction caused by absorption of ultraviolet, visible or infrared radiation. There are many *ground state reactions* which have photochemical counterparts.

Photochemical smog

The product of *photochemical reactions* caused by solar radiation and occurring in polluted air.

Photochemistry

The branch of chemistry concerned with the chemical effects of light (far UV to IR).

Photochromism

A photoinduced transformation of a molecular structure, photochemically or thermally reversible, that produces a spectral change, typically, but not necessarily, of visible colour.

Photoconductivity

Electrical conductivity resulting from photoproduction of charge carriers.

Photocrosslinking

Formation of a covalent linkage between two macromolecules or between two different parts of one macromolecule.

Photocuring

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

Photocurrent yield

The quantum efficiency of electron transport between the two electrodes of a *photovoltaic cell* or a *photochemical cell*.

Photodetachment (of electrons)

Ejection of an electron from a negative ion upon *photoexcitation*.

Photodynamic effect

A term used in photobiology to refer to photoinduced damage requiring the simultaneous presence of light, *photosensitizer* and molecular oxygen. A sensitized *photooxidation* which involves molecular oxygen.

Photoelectric effect

The ejection of an electron from a solid or a liquid by a photon.

Photoelectrochemical cell

An electrochemical cell in which current and a voltage are simultaneously produced upon absorption of light by one or more of the electrodes. Usually at least one of the electrodes is a semiconductor.

Photoelectrochemical etching

The dissolution of a semiconductor in an electrolytic solution on exposure to light. Used in the photopatterning of semiconductor surfaces.

Photoelectrochemistry

A term applied to a hybrid field of chemistry employing techniques that combine photochemical and electrochemical methods for the study of the oxidation-reduction chemistry of the *ground* or *excited states* of molecules or ions. In general it is the chemistry resulting from the interaction of light with electrochemical systems.

Photoelectron spectroscopy

A spectroscopic technique which measures the kinetic energy of electrons emitted upon the ionization of a substance by high energy monochromatic *photons*. A photoelectron spectrum is a plot of the number of electrons emitted versus their kinetic energy. The spectrum consists of bands due to transitions from the *ground state* of an atom or a molecular entity to the ground or *excited states* of the corresponding radical ion. *UPS* uses ultraviolet sources while *ESCA* (*electron spectroscopy for chemical analysis*) and *XPS* use x-ray sources. See 17.2.1.1 and 17.2.1.2.

Photoexcitation

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

Photo-Fries rearrangement

The photorearrangement of aryl or acyl esters to give the [1, 3] - rearranged product.

Photogalvanic cell

An electrochemical cell in which current or voltage changes result from photochemically generated changes in the relative concentrations of reactants in a solution phase oxidation-

reduction couple.

Photoinduced polymerization

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

Photoinitiation

Photoproduction of a free radical or ion capable of initiating a chain reaction such as polymerization. See *photoinduced polymerization*.

Photoionization

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

Photoluminescence

Luminescence arising from *photoexcitation*.

Photolysis

A light-induced bond cleavage. This term is often used incorrectly to describe irradiation of a sample, although in the combination *flash photolysis* this usage is accepted.

Photon

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

Photon counting

The recording of sequential single *photon* pulses counted by way of recording the electron emission events from a photosensitive layer (photocathode) and multiplied by means of a dynode arrangement. This technique is used

(1)   for the sensitive measurement of low levels of radiation and

(2)   for the recording of emission decays.

See *time correlated single photon counting*.

Photon exposure (H_p)

The *photon irradiance*, E_p, integrated over the time of irradiation ($\int E_p dt$, simplified expression: $H_p = E_p t$ when the photon irradiance is constant over the time considered). For a parallel and perpendicularly incident beam, not scattered or reflected by the target or its surroundings, *photon fluence* is an equivalent term. See also *fluence, radiant exposure*.

Photon flow (φ_p)

The number of *photons* (quanta, N) per unit time (dN/dt, simplified expression: $\varphi_p = N/t$ when the number of photons is constant over the time considered). See *spectral photon flow*. See also *radiant power*.

Photon fluence (H_{p0})

The integral of the amount of all *photons* that traverse a small, transparent, imaginary, spherical target divided by the cross-sectional area of this target. The photon fluence rate, E_{p0}, integrated over the duration of irradiation ($\int E_{p0} dt$, simplified expression: $H_{p0} = E_{p0} t$ when E_{p0} is constant over the time considered).

Photon fluence rate (E_{p0})

The rate of *photon fluence*, four times the *photon flow*, φ_p, incident on a small transparent, imaginary, spherical volume element containing the point under consideration divided by the surface of that sphere, S_k. ($\int_{4\pi} L_p dw$, simplified expression: $E_{p0} = 4\varphi_p / S_k$ when the photon flow is constant over the solid angle considered).

Photon flux

Same as *photon irradiance*.

Photon irradiance (E_p)

The photon flow, φ_p, incident on an infinitesimal element of surface containing the point of interest divided by the area, S, of that element. ($d\varphi_p/dS$, simplified expression $E_p = \varphi_p/S$ when the photon flow is constant over the surface considered.) For a parallel and perpendicularly

incident beam not scattered or reflected by the target or its surroundings *photon fluence* (E_{p0}) is an equivalent term.

Photon radiance (L_p)

For a parallel beam it is the *photon flow, φ_p,* leaving or passing through an infinitesimal element of surface in a given direction from the source, divided by the orthogonally projected area of the element in a plane normal to the given direction of the beam, θ, $[(d\varphi_p/dS)/\cos\theta]$, simplified expression:

$$L_p = \varphi_p / (S \cos\theta)$$

when the photon flow is constant over the surface area considered.

For a divergent beam propagating in an elementary cone of solid angle dΩ containing the direction θ, the photon radiance is

$$d^2\varphi_p / (d\Omega \, dS \, \cos\theta).$$

See *spectral photon radiance, radiance.*

Photooxidation

Oxidation reactions induced by light. These include

1)   the loss of one or more electron from a chemical species as a result of *photoexcitation* of that species

2)   the reaction of a substance with oxygen under the influence of light. When oxygen remains in the product the process is also called *photooxygenation.*

Photooxygenation

The incorporation of molecular oxygen into a molecular entity. Common processes include

Type I: reaction of *triplet* molecular oxygen with radicals formed photochemically

Type II: reaction of photochemically produced singlet molecular oxygen with a molecular entity to give rise to oxygen-containing molecular entities, and

a third mechanism proceeding by electron transfer to produce superoxide anion as the reactive species.

Photophysical processes

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

Photopolymerization

Polymerization processes requiring a photon for the propagation step. See also *photoinduced polymerization*.

Photoreduction

Reduction reactions induced by light. These include

1)   addition of one or more electrons to a *photoexcited* species

2)   the photochemical hydrogenation of a substance.

Photoresist

A *photoimaging* material, generally applied as a thin film, whose local solubility properties can be altered photochemically. A subsequent development stage produces an image which is useful for the fabrication of microelectronic devices such as integrated circuits.

Photosensitization

The process by which a *photochemical* or *photophysical* alteration occurs in one molecular entity as a result of initial absorption of radiation by another molecular entity called a *photosensitizer*. In mechanistic *photochemistry* the term is limited to cases where the photosensitizer is not consumed in the reaction.

Photosensitizer

See *photosensitization*.

Photostationary state

A steady state reached by a reacting chemical system when light has been absorbed by at least one of the components. At this state the rates of formation and disappearance are equal for each of the transient molecular entities formed.

Photothermal effect

The effect produced by *photoexcitation* resulting in the production of heat.

Photothermography

A process utilizing both light and heat, simultaneously or sequentially, for image recording.

Photovoltaic cell

A solid state device, usually a semiconductor, which absorbs *photons* with energies higher than or equal to the *bandgap energy* and simultaneously produces electric power.

Piezoluminescence

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

Polarization

See *light polarization*, *transition polarization*, *polarizability*.

Polarization ratio

The polarized components of the *Rayleigh ratio, R*, are defined by

$$R_v = V_v + H_v$$

and

$$R_h = V_h + H_h$$

where subscripts v and h designate the state of polarization of the incident beam (i.e. the electric vector perpendicular or parallel, respectively, to the *scattering plane*) and V and H the polarization states of the scattered beam. Thus H_v is the component of the Rayleigh ratio polarized parallel to the scattering plane when the incident radiation is perpendicularly polarized. The total Rayleigh ratio R_u and its components are related through

$$R_u = V_u + H_u$$

$$V_u = (V_v + V_h) / 2$$

$$H_u = (H_v + H_h) / 2$$

where subscript u denotes unpolarized light.

The polarization ratios (ρ) are then defined by

$$\rho_v = H_v / V_v$$

$$\rho_h = V_h / H_h$$

$$\rho_u = (H_v + H_h) / (V_v + V_h)$$

See *polarization*.

Polarizability

The polarizability (α) of an oscillating dipole is given by

$$\alpha = 4\pi\varepsilon_0 \frac{m^2 - 1}{m^2 + 2} a^2$$

where ε_0 is the permittivity of vacuum, m is the *relative refractive index* ($m = n/n_m$) where n is the refractive index of the scattering particle and n_m that of the immersing medium) and a is the radius of the particle.

Population inversion

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

Predissociation

Dissociation occurring by *tunnelling* from a "bound" to an "unbound" *rovibronic* state. In an absorption spectrum of a molecular entity, the appearence of a diffuse band region within a series of sharp bands, is called predissociation, since irradiation with *frequencies* within the diffuse region leads to effective dissociation. The energy of the band is smaller than that of the dissociation continuum of the bound state.

Primary photochemical process (primary photoreaction)

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

Primary photoproduct

The first observable chemical entity produced in the *primary photochemical process* that is chemically different from the reactant.

Pump-probe technique

A *flash photolysis* technique in which the lightbeam (probe) used for spectral analysis is generated from a portion of the excitation (pump) beam. A time delay in the latter allows kinetic data to be obtained.

$\pi \rightarrow \pi^*$ transition

An electronic transition described approximately as a promotion of an electron from a "bonding" π *orbital* to an "antibonding" π *orbital* designated as π^*.

$\pi \rightarrow \pi^*$ state

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

$\pi \rightarrow \sigma^*$ transition

An electronic transition described approximately as promotion of an electron from a "bonding" π orbital to an "antibonding" σ orbital designated as σ^*. Such transitions generally involve high transition energies and appear close to or mixed with *Rydberg transitions*.

Quasielastic scattering

Quasielastic scattering is *light scattering* in which there are wavelength shifts and line broadening due to time dependent processes.

Q-switched laser

A *laser* in which the state of the device introducing important losses in the resonant cavity and preventing operation is suddenly switched to a state where the device introduces very low losses. This increases very rapidly the Quality factor, Q, of the cavity, allowing the build-up of a short and very intense laser pulse, typically with pulse durations in the nanosecond range. The Q-switching can use an active device (such as a rotating mirror or electro-optic device) or passive one (such as a saturable reactor).

Quantum (of radiation)

An elementary particle of electromagnetic energy in the sense of the wave-particle duality. See *photon*.

Quantum counter

A medium emitting with a *quantum yield* independent of the excitation energy over a defined spectral range (for example concentrated rhodamine 6G solutions between 330 and 600 nm). Also used for devices producing an electrical signal proportional to the *photon flux* absorbed in a medium.

Quantum efficiency

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

Quantum yield (Φ)

The number of defined events which occur per *photon* absorbed by the system. The integral quantum yield is

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

For a photochemical reaction

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

The differential quantum yield is

$$\Phi = \frac{d[x]/dt}{n}$$

Where $d[x]/dt$ is the rate of change of a measurable quantity, and n the amount of photons (mol or its equivalent *einstein*) absorbed per unit time. Φ can also be used for *photophysical processes* or photochemical reactions. See also efficiency.

Quartet state

A state having a total electron spin quantum number equal to 3/2. See *multiplicity*.

Quartz-iodine lamp

A tungsten filament, high-intensity, incandescent *lamp* which contains iodine in a quartz envelope; used mainly as a source of visible light.

Quencher

A molecular entity that *deactivates* (quenches) an *excited state* of another molecular entity, either by energy transfer, electron transfer or by a chemical mechanism. See *quenching, Stern-Volmer kinetic relationship*.

Quenching

The *deactivation* of an excited molecular entity intermolecularly by an external environmental influence (such as a *quencher*) or intramolecularly by a substituent through a *non-radiative process*. When the external environmental influence (quencher) interferes with the behaviour of the *excited state* after its formation, the process is referred to as *dynamic quenching*. When the environmental influence inhibits the excited state formation the process is called *static quenching*.

Radiance (L)

For a parallel beam it is the *radiant power*, P, leaving or passing through an infinitesimal element of surface in a given direction from the source, divided by the orthogonally projected area of the element in a plane normal to the given direction of the beam, θ, [$(\mathrm{d}P/\mathrm{d}S) / \cos\theta$, simplified expression: $L = P/S \cos\theta$ when the radiant power is constant over the surface area considered].

For a divergent beam propagating in an elementary cone of solid angle $\mathrm{d}\Omega$ containing the given direction q, the radiance is

$$\mathrm{d}^2 P / (\mathrm{d}\Omega\ \mathrm{d}S \cos\theta) \text{ with SI units Wm}^{-2}\text{ sr}^{-1}.$$

Radiant energy (Q)

The total energy emitted, transferred or received as radiation in a defined period of time. $\left(Q = \int Q_\lambda d\lambda\right)$. It is the product of radiant power, P, and time (t) when the the radiant power is constant over the time considered. See also spectral radiant power.

Radiant (energy) flux (ϕ)

Although flux is generally used in the sense of the rate of transfer of fluid, particles or energy

across a given surface, the term radiant energy flux has been adopted by IUPAC as equivalent to *radiant power*, *P*. ($P = \phi = dQ /dt$), simplified expression:

$$P = \phi = Q /t$$

when the radiant energy, *Q*, is constant over the time considered. See *spectral radiant flux*, *photon flow*, *photon radiance*, *radiant energy*.

Radiant exposure (*H*)

The irradiance, *E*, integrated over the irradiation time, $\int E dt$, simplified expression:

$$H = E\,t$$

when the irradiance is constant over the time considered). For a parallel and perpendicularly incident beam not scattered or reflected by the target or its surroundings, *fluence*, H_0, is an equivalent term.

Radiant intensity (*I*)

Radiant (energy) flux or *radiant power*, *P*, per unit solid angle, Ω. The radiant power emitted in a given direction by a source or element of the source in an infinitesimal cone containing the given direction divided by the the solid angle of the cone ($dP /d\Omega$, simplified expression:

$$I = P /S$$

when the radiant power is constant over the surface are considered. See also *spectral radiant intensity*.

Radiant power (*P*)

Same as *radiant (energy) flux* (*ϕ*) power emitted, transferred or received as radiation. In *photochemistry*, *ϕ* is reserved for *quantum yield*. See also *spectral radiant power*.

Radiationless deactivation (decay)

Loss of electronic excitation energy without *photon* emission or chemical change. See *energy transfer*, *internal conversion*, *intersystem crossing*.

Radiationless transition

A transition between two states of a system without *photon* emission or absorption.

Radiative energy transfer

The transfer of excitation energy by *radiative deactivation* of a donor molecular entity and reabsorption of the emitted light by an acceptor molecular entity. The probability of transfer, P_{tr} is given approximately by $[A]x\,J$ where J is the spectral overlap integral, $[A]$ is the concentration of the acceptor and x the specimen thickness. See also *Dexter excitation transfer*, *energy transfer*, *Förster excitation transfer*.

Radiative lifetime (τ_0)

The *lifetime* of an excited molecular entity in the absence of *radiationless transitions*. It is the reciprocal of the first-order rate constant for the radiative step, or of the sum of these rate constants if more than one such step. The use of the term 'natural lifetime' is discouraged.

Radiative transition

A transition between two states of a molecular entity, the energy difference being emitted or absorbed as a *photon*. See *luminescence*.

Radioluminescence

Luminescence arising from excitation by high energy particles or radiation.

Radiolysis

Bond cleavage induced by high-energy radiation. It is also more loosely used for any chemical process brought about by high energy radiation.

Rayleigh ratio (R)

The scattered *radiant intensity* in one particular direction divided by the incident *irradiance* and the volume under view.

Rayleigh theory

A theory of scattering by particles that applies when the particle radius is small compared with the wavelength and the *relative refractive index* is not too large. See also *polarizability*.

Real refractive index

See *refractive index*.

Red shift

Informal term for *bathochromic shift*.

Refractive index ($\hat{n}$)

The refractive index or *complex refractive index* of a particle is

$$\hat{n} = n + ik$$

where *n* (sometimes called the *real refractive index*) is the real part of $\hat{n}$ and *k* is the *absorption index*. See also *polarizability*.

Relative permittivity

Scattering in solids can arise because of local variations in the specific electric inductive capacity or relative permittivity, ε_r , where, for a non-absorbing medium of unit specific magnetic inductive capacity, $\varepsilon_r = m^2$, where *m* is the *relative refractive index*.

The mean square of the local deviation of the dielectric constant from $\overline{\varepsilon}_r$ is designated $\overline{\Delta\varepsilon^2}$ and the *correlation distance* $\overline{\Delta\varepsilon(\vec{r_1})\Delta\varepsilon(\vec{r_2})}$ is the average of the indicated product for a *separation distance*, *s*, of $|\vec{r_1} - \vec{r_2}|$. The *correlation function*, $\gamma(s)$, is defined by

$$\overline{\Delta\varepsilon(\vec{r_1})\Delta\varepsilon(\vec{r_2})} = \gamma(s)\overline{\Delta\varepsilon^2}$$

Relative refractive index (*m*)

See *refractive index*. $m = \hat{n}/n_m ; n_m =$ is the refractive index of the nonabsorbing medium in which the particle is immersed.

Relaxation

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

Renner-Teller effect

Splittings in the vibrational levels of molecular entities due to even terms in the *vibronic* perturbation expansions. This is generally a minor effect compared with the *Jahn-Teller effect* due to the odd terms. For linear molecular entities it is the only possible vibronic effect

characteristic of degenerate electronic states.

Resonance absorption technique

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

Resonance fluorescence

Fluorescence from the primary excited atomic or molecular species at the *wavelength* of the exciting radiation (no *relaxation* within the excited manifold). This term is also used to designate the radiation, emitted by an atom, of the same wavelength as the longest one capable of exciting its fluorescence. See also *resonance line*.

Resonance fluorescence technique

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

Resonance lamp

A lamp emitting *resonance radiation* of atoms and their ions. The lamp is filled with pure vapour of the element or a mixture of it and other gases.

Resonance line

The longest wavelength capable of exciting *fluorescence* in an atom. See also resonance fluorescence.

Resonance radiation

Same as *resonance fluorescence*.

Rovibronic state

A state corresponding to a particular rotational sublevel of a particular vibrational level of a particular electronic state.

Ruby laser

A pulsed source of coherent radiation emitting mainly at 694.3 nm from chromium (Cr^{3+}) ions in aluminium oxide.

Rydberg orbital

For an atom, an *orbital* with principal quantum number greater than that of any occupied orbital of the ground state. For a molecular entity, a molecular orbital that correlates with a Rydberg atomic orbital in an atomic fragment produced by dissociation.

Rydberg transition

An electronic transition described approximately as promotion of an electron from a "bonding" *orbital* to a *Rydberg orbital*. Spectral bands corresponding to Rydberg transitions approximately fit the Rydberg formula

$$\sigma = I - R/(n-\Delta)^2$$

where σ is the *wavenumber*, I the ionization potential of the atom or molecular entity, n a principal quantum number, R the Rydberg constant and Δ the quantum defect which differentiates between s, p, d etc orbitals.

RYDMR

See *optically detected magnetic resonance (ODMR)*.

Scattering angle

See scattering plane.

Scattering cross section (of a particle)

The power removed by scattering divided by the irradiance of the beam incident on the particle.

Scattering efficiency

The *scattering cross section* divided by the cross sectional area of the particle.

Scattering plane

The plane containing the incident light beam and the line from the centre of the scattering system to the observer. The *scattering angle*, *q*, lies in the scattering plane and is measured clockwise viewing in the incident direction. *Forward scattering* is at $\theta = 0°$, *back scattering* is at $\theta = 180°$.

Scattering matrix

See *Stokes parameters*.

Schenck sensitization mechanism

The mechanism of chemical transformation of one molecular entity caused by *photoexcitation* of a *sensitizer* which undergoes temporary covalent bond formation with the molecular entity.

Scintillators

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

Selection rule

A selection rule states whether a given transition is allowed or forbidden on the basis of the symmetry or spin of the wave-functions of the initial and final states.

Self-absorption

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

Self-quenching

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

Separation distance

See *relative permittivity*.

Sensitizer

See *photosensitizer*.

Sensitization

See *photosensitization*.

Simultaneous pair transitions

Simultaneous electronic transitions in two coupled absorbers or emitters. Because of the coupling, transitions that are spin-forbidden in one of the centres might become spin-allowed (spin-flip).

Single photon counting

See *photon counting*.

Single photon timing

See *time-correlated single photon counting*.

Singlet molecular oxygen

The oxygen molecule (dioxygen), O_2, in an excited *singlet* state. The ground state of O_2 is a triplet $^3\Sigma_g^-$. The two metastable singlet states derived from the ground state are $^1\Delta_g$ and $^1\Sigma_g^+$. The term singlet oxygen alone, without mention of the chemical species, is discouraged since it can also refer to an oxygen atom in a ^1S or ^1D *excited state*. While the oxygen atom *ground state* is a triplet ^3P state, the ^1S and ^1D states are also derived from the ground state configuration.

Single scattering

See *light scattering*.

Singlet-singlet annihilation

See *annihilation, spin conservation rule*.

Singlet-singlet energy transfer

Transfer of excitation from an *electronically excited* donor in a *singlet* state to produce an electronically excitedacceptor in a singlet state. See *energy transfer, spin conservation rule*.

Singlet state

A state having a total electron spin quantum number equal to 0. See *multiplicity*.

Singlet-triplet energy transfer

Transfer of excitation from an *electronically excited* donor in a singlet state to produce an electronically excited acceptor in a triplet state. See energy transfer, *spin conservation rule*.

Solar conversion efficiency

The ratio of the Gibbs energy gain per unit time and the solar irradiance, E, integrated between $= 0$ and $= \infty$.

Solid state laser

A cw or pulsed *laser* in which the active medium is a solid matrix (crystal or glass). See also *diode laser*.

Solvent shift

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

Sonoluminescence

Luminescence induced by sound waves.

Specific photon emission

Same as *photon exitance*.

Spectral (photon) effectiveness

The reciprocal of the *photon fluence rate*, E_{p0}, at wavelength λ, causing identical photoresponse, per unit time. The *effectiveness spectrum* is directly proportional to the *conversion spectrum* of the sensory pigment, if the spectral attenuance is negligible.

Spectral irradiance (E_λ)

Irradiance, E, at wavelength λ per unit wavelength interval.

Spectral overlap

In the context of *radiative energy transfer*, it is the integral, $J = \int\limits_0^\infty f_D{}'(\sigma)\varepsilon_A(\sigma)\mathrm{d}\sigma$ which measures the overlap of the *emission spectrum* of the excited donor, D, and the absorption spectrum of the *ground state* acceptor, A; f_D' is the measured normalized emission of D,

$f_D' = f_D(\sigma)/\int\limits_0^\infty f_D(\sigma)\mathrm{d}\sigma$, $f_D(\sigma)$ is the *photon irradiance* of the donor at wavenumber σ, and ε_A (σ) is the *decadic molar absorption coefficient* of A at wavenumber σ.

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

$$J = \int\limits_0^\infty \frac{f_D'(\sigma)\varepsilon_A(\sigma)d\sigma}{\sigma^4}$$

In the context of *Dexter excitation transfer*, *J* is given by

$$J = \int\limits_0^\infty f_D(\sigma)\varepsilon_A(\sigma)d\sigma$$

In this case f_D and ε_A the emission spectrum of donor and absorption spectrum of acceptor, respectively, are both normalized to unity so that the rate constant for energy transfer, k_{ET}, is independent of the *oscillator strength* of both transitions.

Spectral photon flow ($\phi_{p\lambda}$)

The photon flow, ϕ_p, at wavelength λ per unit wavelength interval.

Spectral photon flux (photon irradiance) ($E_{p\lambda}$)

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

Spectral photon radiance ($L_{p\lambda}$)

The *photon radiance*, L_p, at wavelength λ per unit wavelength interval.

Spectral radiance (L_λ)

The *radiance*, L, at wavelength λ per unit wavelength interval.

Spectral radiant flux (ϕ_λ)

Same as *spectral radiant power*.

Spectral radiant intensity (I_λ)

The *radiant intensity*, I, at wavelength λ per unit wavelength interval.

Spectral radiant power (P_λ)

The *radiant power* at wavelength λ per unit wavelength interval.

Spectral responsivity (R)

The spectral output quantity of a system such as a photomultiplier, diode array, photoimaging device, or biological unit divided by the *spectral irradiance s* (λ) = d*y* (λ) / d*E* (λ), simplified expression: s (λ) + y_λ/ E_λ, where y_λ is the magnitude of the output signal for irradiation at *wavelength* λ and E_λ is the spectral irradiance of parallel and perpendicular incident beam at the same wavelength.

Spectral sensitivity

See *spectral responsivity*.

Spectral sensitization

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

Spherical radiant exposure

Same as *fluence*.

Spin-allowed electronic transition

An electronic transition which does not involve a change in the spin part of the wavefunction.

Spin conservation rule (Wigner rule)

Upon transfer of electronic energy between an excited atom or molecular entity in its *ground* or *excited state*, the overall spin angular momentum, a vector quantity, should not change.

Spin-flip

See *simultaneous pair transitions*.

Spin-orbit coupling

The interaction of the electron spin magnetic moment with the moment due to the *orbital* motion of the electron. One consequence of spin-orbit coupling is the mixing of zero-order states of different *multiplicity*. This effect may result in fine structure called *spin-orbit splitting*.

Spin-orbit splitting

Removal of state degeneracy by *spin-orbit coupling*.

Spin-spin coupling

The interaction between the spin magnetic moments of different electrons or nuclei. It causes for example the multiplet pattern in nuclear magnetic resonance spectra.

Spontaneous emission

That mode of *emission* that occurs even in the absence of a perturbing external electromagnetic field. The transition between states *n* and *m* is governed by the Einstein coefficient of spontaneous emission, A_{nm}. See also *stimulated emission*.

Stark effect

Splitting or shifts of spectral lines in an electric field.

State crossing

See *avoided crossing, surface crossing*.

State diagram

See *Jablonski diagram*.

Static quenching

See *quenching*.

Stern-Volmer kinetic relationships

This term applies broadly to variations of *quantum yields* of *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, concentration of quencher, [Q], is linear, obeying the equation

$$\varphi_0 / \varphi \ \text{ or } \ M_0 / M \ = \ 1 + K_{sv} \, [Q] \tag{1}$$

Equation (1) applies when a quencher inhibits either a *photochemical reaction* or a *photophysical process* by a single reaction. φ_0 and M_0 are the quantum yields and emission intensity, respectively, while φ and M are the same quantities in the presence of different concentrations of Q. In the case of *dynamic quenching* the constant K_{sv} is the product of the true *quenching* constant k_q and the *excited state lifetime*, τ_0, in the absence of quencher. k_q is the bimolecular reaction rate constant for the elementary reaction of the excited state with the particular quencher Q. Equation 1 can therefore be replaced by the expression (2)

$$\varphi_0 / \varphi \ \text{ or } \ M_0 / M = 1 + k_q \, \tau_0 \, [Q] \tag{2}$$

When an excited state undergoes a bimolecular reaction with rate constant k_r to form a product, a double-reciprocal relationship is observed according to the equation

$$1/\varphi_p = \left(1 + 1/k_r \tau_0 [S]\right)\left[1/(A\,B)\right] \qquad (3)$$

where φ_p is the *quantum efficiency* of product formation, A the efficiency of forming the reactive excited state, B the fraction of reactions of the excited state with substrate S which leads to product, and [S] is the concentration of reactive ground-state substrate. The intercept/slope ratio gives $k_r\,\tau_0$. If [S] = [Q] and if a photophysical process is monitored, plots of equations (2) and (3) should provide independent determinations of the product-forming rate constant k_r.

When the lifetime of an excited state is observed as a function of the concentration of S or Q, a linear relationship should be observed according to the equation

$$\tau_0 / \tau = 1 + k_q\,\tau_0\,[Q]$$

where τ_0 is the lifetime of the excited state in the absence of quencher.

See also *self-quenching*.

Stimulated emission

That part of the emission that is induced by a resonant perturbing electromagnetic field. The transition between states, *n* and *m*, is governed by the Einstein coefficient of stimulated emission, B_{nm}.

Stokes parameters

The Stokes parameters of elliptically polarized incident radiation are given by

$$S_0^0 = E_1^0 + E_2^0$$
$$S_1^0 = E_1^0 - E_2^0$$
$$S_2^0 = 2\left(E_1^0 E_2^0\right)^{1/2} \cos\delta^0$$
$$S_3^0 = 2E\left(E_1^0 E_2^0\right)^{1/2} \sin\delta^0$$

where E_1^0 and E_2^0 specify the irradiances of the incident light polarized with their electric vectors vibrating perpendicular and parallel respectively to the scattering plane and δ^0 the phase difference between these electric vectors. The Stokes parameters of the scattered light are given by the matrix equation

$$(S_0, S_1, S_2, S_3) = F_0 \left(S_0^0, S_1^0, S_2^0, S_3^0 \right)$$

where the 4x4 *scattering matrix*, F_0, is comprised of 16 *scattering matrix elements*.

Stokes shift

The difference (usually in frequency units) between the spectral positions of the band maxima (or band origin) of the *absorption* and *luminescence* arising from the same electronic transition. Generally the luminescence occurring at a wavelength longer than the absorption wavelength is stronger than the opposite case. The latter case is called the *anti-Stokes shift*.

Superradiance

Spontaneous emission amplified by a single pass through a *population inverted* medium. It is distinguished from true laser action by its lack of coherence.

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. See *avoided crossing*.

$\sigma \rightarrow \sigma^*$ transition

An electronic transition described approximately as the promotion of an electron from a "bonding" σ orbital to an "antibonding" σ orbital described as σ^*. Such transitions generally involve high energies and appear close to or mixed with *Rydberg transitions*.

Thermal lensing

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

Thermally activated delayed fluorescence

See *delayed fluorescence*.

Thermochromism

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

Thermoluminescence

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

TICT state

The acronym derives from Twisted Internal Charge Transfer state, proposed to be responsible for strongly Stokes-shifted fluorescence from certain aromatics, particularly in polar medium.

Time-correlated single photon counting

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

Time-resolved spectroscopy

The recording of spectra at a series of time intervals after the excitation of the system with a light pulse (or other perturbation) of appropriately short duration.

Transient spectroscopy

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

Transition (dipole) moment (M_{nm})

An oscillating electric or magnetic moment can be induced in an atom or molecular entity by an electromagnetic wave. Its interaction with the electromagnetic field is resonant if the frequency of the latter corresponds to the energy difference between the initial and final states of a transition ($\Delta E = h\nu$). The amplitude of this moment is referred to as the transition moment. It can be calculated from an integral taken over the product of the wavefunctions of the initial (m) and final (n) states of a spectral transition and the appropriate dipole moment

operator (D) of the electromagnetic radiation.

$$M_{nm} = e \int \Psi_n^* \sum_1 Z_1 \vec{r}_1 \Psi_m d\tau$$

where the summation is over the coordinates of all charged particles (electrons and nuclei). Its sign is arbitrary, its direction in the molecular framework defines the direction of transition polarization, and its square determines the strength of the transition. If e is omitted one obtains R_{nm} in the sense used in *oscillator strength*.

Transition polarization

The direction of the *transition moment* in the molecular framework.

Transmittance (T, τ)

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

$$T = P / P_0$$

Internal transmittance refers to energy loss by absorption, whereas the total transmittance is that due to absorption, reflection, scatter etc. See *absorbance*, *attenuance*, *Beer-Lambert law*.

Triboluminescence

Luminescence caused by pressure effects; usually exhibited during pressurization, squeezing or rubbing together of crystalline materials.

Triplet state

A state having a total electron spin quantum number of 1.

Triplet-triplet annihilation

Two atoms or molecular entities both in a *triplet state* often interact (usually upon collision) to produce one atom or molecular entity in an excited *singlet state* and another in its ground singlet state. This may be followed by *delayed fluorescence*.

Triplet-triplet energy transfer

Energy transfer from an electronically *excited triplet* donor to produce an electronically

excited acceptor in its triplet state.

Trivial energy transfer

Same as *radiative energy transfer*.

Tungsten-halogen lamp

See *quartz-iodine lamp*. Other halogens may fill the lamp.

Tunnelling

The passage of a particle through a potential energy barrier whose height is greater than the energy of that particle. Important for some processes involving the transfer of electrons and of light, particularly hydrogen, atoms.

Turbidity

The turbidity (τ) is the total power of scattered light divided by the incident *irradiance* and the observed volume. The unit is reciprocal length.

Two-photon excitation

Excitation resulting from successive or simultaneous absorption of two *photons* by an atom or molecular entity. The term is used for successive absorption only if some of the excitation energy from the first photon remains in the atom or molecular entity before absorption of the second photon. Simultaneous two-photon absorption can also be called *biphotonic excitation*.

Two-photon process

A photophysical or photochemical event triggered by *two-photon excitation*.

Upconversion

A *non-linear optical effect* in which light frequency is increased.

UPS

See *photoelectron spectroscopy*.

UV Stabilizer

A substance added to a sample to prevent photodeterioration by ultraviolet (UV) light. See *photochemical reaction*.

Valence band

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

Vavilov rule

See *Kasha-Vavilov rule*.

Vertical transition

See *Franck-Condon principle*.

Vibrational redistribution

Intramolecular redistribution of energy among vibrational modes usually giving a statistical distribution of their populations, characterized by the "vibrational temperature". For large molecules this process does not need collisions.

Vibrational relaxation

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

Vibronic coupling

Interaction between electronic and vibrational motions in a molecular entity. See *Jahn-Teller* and *Renner-Teller* effects.

Vibronic transition

A transition which involves a change in both the electronic and vibrational quantum numbers of a molecular entity, as opposed to purely electronic or purely vibrational transition. The

transition occurs between two states just as in a purely electronic transition, but involves a change in both electronic and vibrational energy.

Wavelength (λ)

The distance, measured along the line of propagation, between two corresponding points on adjacent waves. The wavelength depends on the medium in which the wave propagates.

Wavenumber ($\sigma, \tilde{\nu}$)

The reciprocal of the wavelength, λ, or the number of waves per unit length along the direction of propagation.

Wigner rule

See *spin conversion rule*.

Wood horn

A mechanical device that acts by absorption as a perfect photon trap.

Wood lamp

A term used to describe a low pressure mercury arc.

Xenon lamp

An intense source of ultraviolet, visible and near-infrared light produced by electrical discharge in xenon under high pressure.

XPS

See *photoelectron spectroscopy*.

YAG

See *neodynium laser*.

Zeeman effect

The splitting or shift of spectral lines produced by the presence of an external magnetic field.

Zero field effect

The separation of multiplet sublevels in the absence of external magnetic field.

Zero-zero (0-0) absorption or emission

A purely electronic transition occurring between the lowest vibrational levels of two electronic states.