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Quantities, Terminology and Symbols in Photothermal and Related Spectroscopies

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1. INTRODUCTION

Interaction of light with matter causes absorption, emission and inelastic scattering of light. Except for emission, the absorbed light energy is converted to heat by various nonradiative processes and induces changes in temperature, pressure, and refractive index of the medium. In photothermal spectroscopy the effects caused by these changes are monitored by various methods. The discovery of the photothermal effect dates back to Bell's discovery of the photoacoustic effect in 1881, but it is after the invention of the laser that the photothermal spectroscopies became popular. In 1964, Gordon et al. found a beam divergence effect from liquid samples that were placed in a gas laser cavity. This phenomenon was correctly interpreted in terms of the 'thermal lens' effect produced by heating induced by the Gaussian laser beam. The thermal lens method soon became a standard technique to detect the thermal energy produced by nonradiative transitions. Since then various types of photothermal spectroscopic methods have been developed and applied to a variety of problems. Today, photothermal spectroscopy is widely used in physics, chemistry, biology and engineering.

Various changes in the medium may be monitored in order to quantify the effects of the temperature rise upon radiationless deactivation in photothermal spectroscopy; temperature rise is measured by laser calorimetry, pressure change by direct and indirect photoacoustic effects, refractive index change by probe beam refraction and diffraction, surface deformation by probe deflection and optical interference, thermal emission by photothermal radiometry, and reflectivity/absorptivity change by transient thermal reflectance, transient piezo-reflectance and transmission monitoring.

The photothermal method has a number of merits compared with other methods. It has a great sensitivity and is applicable to many different types of materials such as gas, liquid, and solid, transparent and opaque, in vacuum and in air, and to samples of any shape. Light of any wavelength may be used such as radio frequency-, microwave, IR, visible, UV, and X-ray. Photothermal detections are nondestructive and noncontact methods. Local properties in very small areas can also be probed. These merits are of great value in analytical applications. By using photothermal spectroscopies it is not only possible to detect photothermal effects but also it is possible to study a variety of processes that give rise to these effects. For example, chemical reactions as well as nonradiative processes from excited states and vibrational relaxations may be analyzed. The dynamic range of the photothermal spectroscopy can be 10^{14} (from seconds to femtoseconds).

Publications in photothermal spectroscopy come from researchers working in the fields of analytical and physical chemistry, physics, optical engineering, and biology. Therefore, there is a wide range of terms used to describe the same method or the same phenomenon in the literature. This causes confusion and hinders proper communication among researchers in different fields. We feel there is a need for reviewing and commenting on the differences and agreements found in the literature.

In the present report we first clarify various origins of the photothermal effects that give rise to signals. The terms are reviewed and a glossary of terms is given. Cross-references refer to the main terms in this section (subsection) unless otherwise stated. Finally, symbols used in photothermal spectroscopy are summarized.

2. ORIGIN OF PHOTOTHERMAL EFFECTS

Photothermal techniques are defined as methodologies detecting the heating effect after photo-excitation. Inasmuch as various temperature-dependent physical parameters (pressure wave, refractive index, absorbance change etc.) are detected, various dynamic processes may be simultaneously monitored.

The pressure wave generated after light excitation contains contributions from various sources, such as radiation pressure, *electrostriction*, thermoelastic expansion (by nonradiative transition or thermal energy of chemical reaction), photoinduced volume change, gas evolution, boiling, *ablation*, and dielectric breakdown. The refractive index change produced upon light absorption may be induced by the pressure wave, a density change, a temperature change (by *radiationless transition* or chemical reaction), molecular alignment, vibrational excitation, rotational excitation, electronic excitation, concentration change, photoinduced volume change, creation of electric field (charge creation), clustering and so on. Absorption changes induced by some of these effects also contribute to the signal. The effects listed above are often connected to each other. For example, the temperature change will induce a concentration change through the *Soret effect* and, in turn, the concentration change may change the temperature by the *Dufour effect*. The thermal energy generally creates stress and pressure, and vice versa.

Since the released energy by *radiationless transitions* in condensed phases will eventually flow into translational freedom, the photothermal effect is generally observed after any type of photoexcitation (resonant condition) and is closely related to the energy dynamics in the system. The changes in refractive index (δn) and absorption index (δk) by the thermal effect may be decomposed as in eqs 1 and 2

$$\delta n = \{(\partial n/\partial \rho)_T(\partial \rho/\partial T) + (\partial n/\partial T)_\rho\}\delta T \quad (1)$$

$$\delta k = \{(\partial k/\partial \rho)_T(\partial \rho/\partial T) + (\partial k/\partial T)_\rho\}\delta T \quad (2)$$

where ρ is the density. The first term in eq 1 represents the refractive index change through the density change and the second term is due to the pure temperature rise without an accompanying density change. Each term in eq 2 has a similar meaning as the corresponding term in eq 1, *i.e.,* the first term is the absorption change induced by a density change and the second one by the temperature change. One prominent example of a temperature-dependent absorption spectrum is the so-called hot band spectrum (see *thermochromism* and *hot band* in section 4). Another example is that of a molecule which has two close lying states and their populations are in thermal equilibrium, *e.g.*, two isomers in equilibrium or equilibrium between hydrogen bonded and non-hydrogen bonded species. In this case, the population of each state and hence the absorption spectrum is temperature dependent. Broadening of the absorption band is frequently observed. These changes in the absorption also cause changes in the refractive index with temperature changes through the Kramers-Kronig relation.

Photothermal effects can be followed not just in the bulk phase, but also in surfaces or interfaces as changes in the reflected light such as intensity, polarization, optical path and reflection angle. The effects are the same as those in the bulk. The intensity and reflectivity depend on the surface temperature

through the absorption and refractive index changes. Unique to the surface photothermal effect is the fact that the reflection angle of reflected light changes when the surface is inhomogeneously deformed. A chart showing the relations among various photothermal effects is shown in Figure 1.For more details of photothermal phenomena and spectroscopies, we list several references at the end of the text.

3. GLOSSARY OF TERMS

The recommended terms are listed as headings. Different terminologies used in the literature are given in parentheses. Commonly used acronyms are also indicated in parentheses.

3.1. GRATING SPECTROSCOPY

transient grating [TG] (dynamic grating, forced light scattering, holographic grating, laser-induced grating, real time holography, time-delayed four wave mixing, two color four wave mixing, see also *degenerate four wave mixing*)

The transient grating (TG) method is a four wave mixing technique. When two coherent light beams cross at a spot within the coherence time, the interference between the beams creates a sinusoidal spatial modulation of light intensity and/or of polarization of the light. The light-matter interaction and subsequent possible photophysical and photochemical processes change the optical properties of the material in the bright region. As a result, spatially modulated refractive index and absorbance patterns are created (*optical grating*). This grating diffracts another probe light beam to a phase matching direction. The intensity of the diffracted light (TG signal) is related to the amplitude of the peak-to-null modulation, wavelength of the probe beam, fringe spacing of the grating, and harmonicity of the spatial modulation. The temporal dependence and the intensity dispersion in the probe wavelength reflect the material response after photo-irradiation.

ACOUSTIC COMPONENT

A grating created by an adiabatic pressure fluctuation which gives rise to a high frequency acoustic wave. Expansion of the refractive index change by two independent parameters, entropy (S) and pressure (p), is expressed by eq 3.

$$\delta n = (\partial n/\partial p)_S \, \delta p + (\partial n/\partial S)_p \, \delta S \qquad (3)$$

The first term on the right hand side gives the acoustic component. The pressure wave is an acoustic standing wave oscillating with a period of $\tau_{ac} = \Lambda/v$ (Λ, fringe length, v, velocity of sound). This component decays by a mechanical acoustic damping or finite geometry effects. In the latter case, if there is a finite number of fringes, the acoustic wave travels out of the optically sampled region and gives rise to a decay in the signal amplitude that is separate from the intrinsic acoustic damping of the medium. After the complete decay of this acoustic component, the isobaric wave appears (*diffusive component*). When the origin of the isobaric component is a density change or purely temperature, 'the acoustic-density grating' or 'the acoustic-temperature grating' may be used, respectively.

See also *thermal grating*

ACOUSTIC GRATING

See *acoustic component*

AMPLITUDE GRATING

A grating that affects the amplitude, and therefore the intensity of the probe light. The source of the grating is the spatial modulation of the absorbance or light scattering efficiency.

ANHARMONIC GRATING

A non-sinusoidal grating created by non-linear processes such as multiphoton absorption or saturation of one photon absorption. This distorted (anharmonic) grating diffracts the probe light not only to the first order angle but also to higher order angles.

BRAGG ANGLE

A special angle at which the scattered light (or sound) waves from various spatial positions of material interfere constructively (in phase). At this angle, the scattered signal field becomes quite intense for *the thick grating*.

BRAGG SCATTERING

See *thick grating*.

CLUSTER GRATING

A spatially sinusoidal light intensity pattern produced by a regular array of particles produced by photoexcitation. Since microparticles strongly scatter the probe light, the spatially modulated particle concentration acts as an amplitude grating (see *amplitude grating*). In this case, the origin of the effect is the light scattering loss by the particles, and not absorption.

COMPLEMENTARY GRATING

A grating formed in the photoproduct species generally formed upon photoexcitation of a photochromic dye or through a chemical reaction, (See also *population grating* and *species gating*). The ground state and product gratings have a spatial phase difference of 180 º.

CONCENTRATION GRATING

A grating formed by a concentration change induced by a temperature change (see *Soret effect* in section 4) without any photochemical reaction. A thermal grating is also created by the reverse effect (see *Dufour effect* in section 4). These effects are generally very small except for mixtures near the critical consolute point. This term is sometimes used to mean a grating similar to the population grating or species grating.

DENSITY GRATING [Dens.G]

A grating due to the first terms of eqs 1 and 2 in **Origin of photothermal effects** in section 2. See also *thermal grating*

DIFFUSIVE COMPONENT

A grating created by an isobaric entropy fluctuation (the second term of the right hand side of eq 3). This component just decays by thermal diffusion.

See *acoustic component*

ELECTRIC FIELD GRATING

A grating signal created by free electric carriers moving and creating space charges either through differential mobilities for the optically generated carriers or differential trapping. The electric field in turn modulates the index of refraction through the electro-optic effect. (This is also called space charge grating)

FORCED RAYLEIGH BRILLOUIN SCATTERING

Scattering of light arising from longitudinal acoustic and density changes (see also *density grating* and *acoustic component*) produced by the thermal expansion. The frequency is determined by the grating fringe spacing and the velocity of sound.

FORCED THERMAL BRILLOUIN SCATTERING (IMPULSIVE STIMULATED-THERMAL SCATTERING, LASER-INDUCED PHONON-SPECTROSCOPY)

Scattering by counterpropagating thermally generated acoustic waves arising from sudden thermal expansion induced by light irradiation.

See also *stimulated light scattering*, *thermal grating*, *acoustic component*.

FREE CARRIER GRATING

A *population grating* involving electrons or holes in solids (semiconductors).

GRATING WAVENUMBER

Wavenumber of the fringe that is created by the light interference. 2π divided by the fringe length.

HIGHER ORDER DIFFRACTION GRATING

See *anharmonic grating*

INTENSITY GRATING

A grating created by light intensity modulation under the condition that two pump beams possess a parallel polarization component.

MOVING GRATING

A grating created by two pump beams of different frequency, $\omega_1 \neq \omega_2$. The interference pattern is not static but shows a spatial wave-like motion governed by the beat frequency, $\omega_1 - \omega_2$. The frequency dependence of the diffracted signal reflects the dynamics of the material which creates the grating.

OPTICAL GRATING

See an introduction of **3.1 GRATING SPECTROSCOPY**

OPTICAL HETERODYNE DETECTION [OHD] (OF A GRATING SIGNAL)

A reference beam (local oscillator field) is coherently overlapped with a diffracted signal beam on a detector. The light intensity produced by the interference between the local oscillator and the signal field is detected. The signal is linearized to the material response and information on the phase of the grating signal can be obtained. This approach enables separation of the index of refraction and absorption terms from the modulated complex index of refraction.

OPTICAL HOMODYNE DETECTION

A direct detection of the grating signal by a photodetector. Inasmuch as a photodetector monitors light intensity, the measured signal contains the modulus squared of both the absorption changes and index of refraction contributions.

OPTICAL KERR GRATING

A transient grating produced by the optical Kerr effect.

See *optical Kerr effect* in section 4.

ORIENTATION GRATING

A grating induced by changes in orientation of molecules or systems that posses an anisotropic optical polarizability. The change in orientation may be induced by the nuclear response of the *optical Kerr effect* or by creation of a photoexcited state, a photochemical change, or a temperature change. One notable example in the liquid phase is the mesophase of liquid crystalline samples. Any perturbation to a molecule in that phase will change the orientation of many molecules through intermolecular interaction and create a pronounced signal. This is a cooperative effect.

PHASE GRATING

A grating that affects the phase of the probe light. The source of the grating is the spatial modulation of the refractive index.

POLARIZATION GRATING

A grating produced by changes in the polarization direction.

POPULATION GRATING

A grating due to changes in the refractive index which is originated from the absorbance changes by the presence of transient species or stable products.

See *species grating.*

RAMAN-NATH SCATTERING

See *thin grating*

REFLECTION GRATING (SURFACE SENSITIVE TRANSIENT GRATING, TRANSIENT REFLECTING GRATING)

A grating signal induced by spatially periodic surface deformations as well as modulation of optical properties (refractive index and absorbance) in the medium on which a probe beam is reflected .

SELF DIFFRACTION

Diffraction of pump light creating the grating.

SPACE CHARGE GRATING

See *electric field grating.*

SPECIES GRATING

A grating due to a spatial concentration modulation of chemical species induced by chemical reactions through eqs 4 and 5 below. The changes in the refractive index and absorbance produced by these species may be written as

$$\delta n = \{(\partial n/\partial \rho)_C(\partial \rho/\partial C) + (\partial n/\partial C)_\rho\}\delta C \quad (4)$$

$$\delta k = \{(\partial k/\partial \rho)_C(\partial \rho/\partial C) + (\partial k/\partial C)_\rho\}\delta C \quad (5)$$

where C is the concentration of the transient or stable product state generated by a chemical reaction. The first term is the refractive index change due to the density change by the presence of the new chemical species. The molecular volume, determined by the intrinsic volume and external volume (such as void volume or electrostriction effect) is changed. The second term on the right side of eq 4 represents the refractive index change due to the different electronic structures of the molecules, relevant to the absorption spectrum. A grating due to this second term is generally called *population grating*. Equation 5 represents the absorption change by the presence of the new species and the depletion of the reactant.

terms of eqs 4 and 5	terminology	
$(\partial n/\partial \rho)_C(\partial \rho/\partial C)$	volume(-phase) grating	species(-phase) grating
$(\partial n/\partial C)_\rho$	population(-phase) grating	
$(\partial k/\partial \rho)_C(\partial \rho/\partial C)$	volume(-amplitude) grating	species(- amplitude) grating
$(\partial k/\partial C)_\rho$	population(- amplitude) grating	

See also *volume grating* and *population grating.*

STATIC GRATING

A grating created by pump beams with $\omega_1 = \omega_2$.

See also *moving grating*

STRAIN GRATING

A grating created by the strain along the direction perpendicular to the grating wave.

STRESS GRATING

A grating created by the stress along the direction perpendicular to the grating wave.

TEMPERATURE GRATING [Temp.G]

Grating due to the second terms of eqs 1 and 2 in **Origin of photothermal effects**.

See also *thermal grating*.

TENSOR GRATING

A grating that depends on the direction of the optical polarization because of tensor nature of the dielectric constant (relative permittivity) and optical susceptibility.

THERMAL GRATING (STIMULATED THERMAL GRATING, PHOTOTHERMAL DIFFRACTION)

A grating created by the thermal effect. In order to specify the origin clearly, the TG signal due to the first term and the second term of eq.1 may be called "density (-phase) grating" and "temperature (-phase) grating", respectively. The first and the second terms of eq 2 represent the absorption change by the change of density and the second one by the temperature change, respectively. They give rise to "density (-amplitude) grating" and "temperature (-amplitude) grating", respectively. The thermal grating indicates these contributions simultaneously. When the origin of the grating (phase or amplitude) is apparent, 'phase' or 'amplitude' may be omitted. Each term can be further decomposed into two components: diffusive and acoustic components. Terminologies of these gratings are summarized as follows.

terms in eqs 1 and 2	Terminology	
$(\partial n/\partial \rho)_T(\partial \rho/\partial T)$	density(-phase) grating	thermal(-phase) grating
$(\partial n/\partial T)_\rho$	temperature(-phase) grating	
$(\partial k/\partial \rho)_T(\partial \rho/\partial T)$	density(-amplitude) grating	thermal(-amplitude) grating
$(\partial k/\partial T)_\rho$	temperature(-amplitude) grating	

THICK GRATING

A grating produced under a condition that the interaction length (sample length) is much longer than the fringe spacing (Λ). The grating wave vector has a spike along the wave vector direction and phase matching considerations become important. It exhibits narrow angular and wavelength selectivity. The scattering by a thick grating is sometimes called *Bragg scattering*. The name is given by analogy to the scattering of x-rays from the atomic planes in a crystal.

THIN GRATING

A grating produced under a condition that the sample length (thickness, L) is much smaller than the fringe spacing (Λ) ($\Lambda / L \geq 10$). The grating vector is not a spike to the wave vector direction but contains a broad distribution of the order L^{-1} along the thickness of the sample. This grating exhibits broad angular and wavelength selectivity. Sometimes, it is called *Raman-Nath scattering*.

TRANSMISSION GRATING SIGNAL

A signal created by the diffraction of a probe beam transmitted through the sample. A diffracted beam propagating in a transmission grating reflected at the second boundary is in this category, even though the propagating direction is opposite to that of the incident beam.

TWO-STEP EXCITATION TRANSIENT GRATING [TSETG]

Two laser beams are used for the excitation of photoexcited states to detect transient absorption processes. The first beam creates excited states and the second one probes the dynamics of the excited states. The grating is read by another probe beam. In TSETG-I, a spatially uniform beam is used to prepare the excited states. The dynamics is probed by a temporally delayed second beam, which induces the grating. In TSETG-II, the sample is first excited by the pulses that create the grating, then, another spatially uniform beam is used to probe the transient absorption.

VOLUME GRATING

A grating due to changes in refractive index induced by changes in molecular volume upon light excitation. Even when only the electronic property such as the dipole moment is changed, the reorientation of the solvated molecule induces a partial molar volume change in the medium. This volume change induces an acoustic wave (*acoustic component*) as well as a diffusive component.

In the field of holography, when the thickness of the recording medium is larger than the distance between fringes, the 'volume effect' of the medium cannot be neglected. Such a grating is called

the volume (or thick) grating.

See also *population grating* and *acoustic grating*.

3.2. LENS SPECTROSCOPY

transient lens [TrL] (photothermal lens, thermal blooming, thermal lens [TL], thermal lensing, time-resolved thermal lens)

When a sample is excited with a pump beam that has a spatially Gaussian form, the profile of the material response to the light should be also Gaussian. If the refractive index or the absorbance is varied by photoexcitation, its behavior may be written as in eq 6.

$$n(r,t) = n_0 - \delta n(t)\exp(-r^2/w^2) \qquad (6)$$

where w is the excitation beam radius and r is the distance from the center of the excitation beam. The energy released by nonradiative transitions from excited states heats up the material and the spatial profile becomes Gaussian. The temperature increase leads to a decrease of the density with corresponding change in the refractive index. The expansion (or focusing) of the light at the central part of the Gaussian profile can be detected as a change of the spatial profile of the beam or the beam density through a pinhole placed in the far (or near) field leading to the transient lens signal. The origin of a transient lensing signal is the refractive index change and the terms are obtained by replacing 'grating' by 'lens' in the above definitions. Absorption contributions (transient absorption and transient bleach) are also included in the transient lens signal, although the main contribution of the transient absorption is to decrease the probe light intensity. The lens signals identified and separated so far are given in the following.

ACOUSTIC COMPONENT (ACOUSTIC LENS)

A lens connected with an adiabatic pressure fluctuation which gives rise to an acoustic wave. The first term on the right side of eq 3 is the origin of this component. This component appears with a rate constant determined by the *acoustic transit time*. After the complete decay of this acoustic component, the isobaric wave remains (*diffusive component*).

CONFOCAL LENGTH

The distance in which the focused beam expands from its minimum size to a radius of $2^{1/2}w_0$ (w_0: focal spot size)

DENSITY LENS [Dens.L]

A lens due to the first terms on the right side of eqs 1 and 2 in **Origin of photothermal effects** in section 2.

See *thermal lens*.

DIFFUSIVE COMPONENT

A lens connected with an isobaric entropy fluctuation due to the second term of the right hand side of eq 3. This wave just decays by the thermal diffusion.

See *acoustic component*

DUAL-BEAM TRANSIENT LENS EFFECT

See *induced defocusing* and *induced focusing*.

INDUCED DEFOCUSING

A defocusing effect of a probe beam by the pump light-induced refractive index change. Induced defocusing has almost the same meaning as the transient lens.

INDUCED FOCUSING

A focusing effect of a probe beam by the pump light-induced refractive index change. Induced focusing has almost the same meaning as the transient lens.

INDUCED PHASE MODULATION

See *induced defocusing* and *induced focusing*.

OPTICAL KERR LENS [OKL]

A lens due to the nuclear and electronic responses based on the *optical Kerr effect* in section 4.

POPULATION LENS [PL]

A lens due to $(\partial n/\partial C)_{\rho}$ and $(\partial k/\partial C)_{\rho}$ of eqs 4 and 5.

SELF DEFOCUSING

A defocusing effect of a pump beam by the refractive index change due to the pump light itself.

SELF FOCUSING

A focusing effect of a pump beam by the refractive index change due to the pump light itself.

SPHERICAL ABERRATION

Interference rings in the transmitted probe beam. This effect arises by a large phase shift of the probe beam that interferes with the probe light itself.

TEMPERATURE LENS [Temp.L]

A transient lens due to the second terms of the right side of eqs 1 and 2 in **Origin of photothermal effects** in section 2.

See *thermal lens*.

THERMAL LENS [TL]

Lens created by the thermal effect. The TrL signal due to the first term and the second term of eq.1 are called "density (-phase) lens" and "temperature (-phase) lens", respectively. The first and the second terms of eq 2 represent the absorption change by the change of density and the second one by the temperature change, respectively. They give rise to "density (-amplitude) lens" and "temperature (-amplitude) lens", respectively. The thermal lens indicates these contributions simultaneously. When the origin of the lens (phase or amplitude) is apparent, 'phase' or 'amplitude' may be omitted. Each term can be further decomposed into two components: diffusive and acoustic components.

TWO-STEP EXCITATION TRANSIENT LENS

Two laser beams are used for the excitation of photoexcited states to detect transient absorption processes. One beam creates the excited states and the second one probes their dynamics by creating the transient lens. In type I configuration, a spatially uniform light is used to prepare the excited states and the dynamics is detected by a temporally delayed lens-creating beam. In type II, the roles of the prepulse and the lens pulses are interchanged. The sample is first excited by a pump pulse for lens creation and a second spatially uniform beam induces the transient absorption.

VOLUME LENS

A lens produced by photoinduced volume changes. This volume change induces an acoustic wave as well as a diffusive component.

See *acoustic component* and *diffusive component* in this section.

3.3. LIGHT-INDUCED ACOUSTIC SPECTROSCOPY

photoacoustic spectroscopy [PAS] (optothermal spectroscopy, photoacoustic calorimetry, thermal-wave spectroscopy,)

time-resolved photoacoustic calorimetry (laser induced optoacoustic spectroscopy, laser induced photoacoustic spectroscopy, photoacoustic laser spectroscopy, pulsed laser resonant photoacoustic, time-resolved photoacoustic)

Detection of photogenerated acoustic waves. The generation may be amplitude-modulated (photoacoustic spectroscopy, PAS) or by a pulse (laser-induced optoacoustic spectroscopy, LIOAS, or photoacoustic calorimetry, PAC). The pressure wave after photo-irradiation is induced not only through the thermal expansion but also through other effects such as radiation pressure, *electrostriction*, thermoelastic expansion, molecular volume change, molecular orientation, gas evolution, boiling, *ablation*, *dielectric breakdown* in section 4. The separation of the thermal contribution from other

sources may be achieved by measuring the pressure wave under different conditions, such as different matrix, temperature, polarization of the excitation light, and excitation wavelength. However, the complete separation is very difficult experimentally and not so many examples have been reported. Therefore, specific names such as volume acoustic, ablation acoustic have not been used so far. This method was previously called optoacoustic spectroscopy, but since this name is confusing (acoustooptic effect), photoacoustic spectroscopy is preferred. Experimentally, there are many versions of this spectroscopy. Designs (resonance condition, shape etc.) of the cell, detectors and excitation methods are subject of modifications. Below, only some terminologies describing the modifications are listed.

ACOUSTIC RINGING

An acoustic signal due to multiple reflection in the cell.

ACOUSTIC TRANSIT TIME

The time required for the acoustic wave to cross the excited region.

AMPLITUDE-MODULATED PHOTOACOUSTICS (CONTINUOUS EXCITATION PHOTO-ACOUSTIC)

The pressure wave induced by a temporally modulated excitation light and detected by a pressure sensitive device (frequently a gas-coupled microphone) with a lock-in amplifier (or boxcar integrator).

CALORIMETRIC REFERENCE

In the absence of multiphoton excitation, the photothermal signal intensity is proportional (not necessarily linearly) to the temperature change in the weak intensity limit. The proportionality constant is determined by using a calorimetric reference, which converts the photon energy to thermal energy with a known efficiency and in a time shorter than the integration time window of the experiment. There are *internal* and *external calorimetric references* (section 4).

DICHROISM PHOTOACOUSTIC SPECTROSCOPY

The polarization of the excitation light is temporally modulated. In this manner, the linear or circular dichroism of a chiral molecule can be detected.

DIRECT COUPLING

An acoustic-wave detection method in which a detector is inserted or attached into or onto the sample without intervention of a gas or other liquids.

FOURIER TRANSFORM PHOTOACOUSTIC SIGNAL

The pressure wave signal created after photoexcitation by infrared light and detected with a

Michelson interferometer. After the Fourier transform of the interferogram, the IR absorption spectrum detected by the pressure wave is reconstructed in the same manner as in the conventional FT-IR spectroscopy.

FRONT-FACE-EXCITATION PHOTOACOUSTIC SIGNAL

The pressure wave signal detected by a device placed perpendicular to the excitation light path. The time resolution is somewhat improved by this configuration.

GAS COUPLING

An acoustic-wave detection method in which the pressure wave created in a photo-illuminated condensed phase sample is detected by a gas phase microphone.

LIQUID COUPLING

An acoustic-wave detection method in which the pressure wave transmitted into liquid from a photo-illuminated sample is detected

OPTICAL ULTRASONICS

A technique of performing high-frequency acoustic measurements using optical means both to generate and to detect the sound waves.

PIEZOELECTRICITY

Production of charges in certain materials (anisotropic crystals or polymeric material) when strained.

PIEZOELECTRIC TRANSDUCER

A device that detects the piezoelectricity. Conversely piezoelectric materials become strained when placed in an electric field. Certain ceramic crystals such as lead zirconate titanate, and lead metaniobate or a certain films are piezoelectric and are frequently used to detect the pressure wave as an electric signal in the photoacoustic spectroscopy.

PHOTOACOUSTIC MICROSCOPY

An imaging technique in which a collimated laser beam is focused on a small spot in a sample and the photoacoustic signal is detected and mapped by scanning the sample or the beam.

PHOTOACOUSTIC RAMAN GAIN SPECTROSCOPY

Stimulated Raman scattering is detected using the acoustic wave. Since a pump photon is of higher energy than a scattered photon in *Stokes Raman scattering*, the energy is deposited in the medium and heats up the medium. This thermal expansion is detected by a pressure sensitive detector.

PUMP-PROBE METHOD OF PHOTOACOUSTIC SPECTROSCOPY

Two laser beams are used for the excitation of photoexcited states to detect transient absorption processes. The first light beam creates excited states and a second beam probes the dynamics of the excited states. The pressure wave created by these heat releasing processes is detected.

TIME-RESOLVED LASER-INDUCED PHOTOACOUSTIC SPECTROSCOPY

Evolution of a pressure pulse resulting from the thermal expansion caused by absorption of pulsed laser light and detected by a piezoelectric pressure transducer. From the waveform of the pressure pulse, kinetics of the system as well as information on medium acoustic properties can be obtained.

WAVELENGTH MODULATED PHOTOACOUSTIC SPECTROSCOPY

Wavelength of the excitation light is temporally modulated and the resulting acoustic wave is processed by a lock-in amplifier.

3.4. PHOTOTHERMAL RADIOMETRY [PTR]

(pulsed) photothermal radiometry (backscattering photothermal radiometry, direct calorimetry, modulated black-body radiation, Planck radiation detection, radiometric spectroscopy, thermometric method, thermal emission detection, thermal radiation detection, transient IR detection, transmission photothermal radiometry)

Infrared radiation associated with sample heating is detected by an IR detector. The source of IR irradiation is treated as a black body emitter. According to the Stefan-Boltzmann law, the emittance (M) is proportional to the fourth power of the temperature (T) over an infinite spectral detection bandwidth;

$$M = \sigma T^4$$

where σ is the Stefan-Boltzmann constant. Hence, the relative change of emission (δM) by the temperature change (δT) induced by the photoirradiation is given by

$$\delta M(T)/M(T) = 4\delta T/T$$

INFRARED [IR] FLUORESCENCE

Emission from an excited vibrational mode. It is sometimes used to reveal the vibrational temperature and vibrational relaxation time.

OPTICAL PYROMETRY

Temperature measurement of a solid or liquid by measuring the radiation it emits.

RADIOMETRIC MICROSCOPY

An imaging technique in which a collimated laser beam is focused on a small spot in a sample and the radiometric signal is detected and mapped by scanning the sample or the beam.

THERMAL RADIATION

Electromagnetic radiation of thermal energy from matter. The energy and spectral distribution are determined by the composition of the matter and the temperature.

3.5. PHOTOTHERMAL CALORIMETRY

photothermal calorimetry, transient thermography

A temperature change after photoexcitation is directly measured by using *thermocouples*, *thermistors*, and *pyroelectric transducers*.

BOLOMETER

A detector of temperature by measuring the electric resistance.

PHOTOPYROELECTRIC SPECTROSCOPY(PPES)

A photothermal detection technique, which uses a pyroelectric thin film as a detector, usually in the transmission mode. Measurement of the temperature increase of a sample due to absorption of radiation by a *pyroelectric transducer* or a *bolometer* in thermal contact with the sample. It can also measure the optical-to-thermal energy conversion coefficient (nonradiative quantum yield) at the excitation wavelength.

PHOTOPYRROELECTRIC SENSORS

Solid-state devices developed to measure thermal/themophysical properties of condensed and gaseous matter after photoirradiation.

See also *pyroelectricity* and *pyroelectric transducer.*

PYROELECTRICITY

Production of charges on the surface of a crystal upon changes in the crystal temperature.

PYROELECTRIC TRANSDUCER

A device for temperature measurement using *pyroelectricity*. Certain crystals, certain thin-films and ferroelectrics are frequently used.

See *pyroelectricity.*

THERMAL-WAVE CAVITIES

A term attributed to photothermal devices exploiting coherent thermal-wave power confinement between two parallel walls, detected by a suitable sensor, such as a pyroelectric thin-film transducer. The thermal analog of acoustic standing-wave cavity resonators, operating on the principle of linear superposition of thermal waves, amplified by confinement.

THERMISTOR

A semiconductor device that has a large temperature dependent electric resistance.

THERMOCOUPLE

A thermometer that uses the *thermoelectromotive force*.

THERMOELECTRIC POWER

Change in *thermoelectromotive force* per unit temperature change in the *thermocouple*.

THERMOELECTROMOTIVE FORCE

Electromotive force generated in an electric circuit when two ends of two different metalic wires are contacted with each other and placed at different temperatures.

THERMOELECTRONIC IMAGING

Imaging contrast from laser-induced photothermal radiometric scans across the surface of electronic semiconductor materials. Thermoelectronic images are generated by the direct recombination of photo-excited electrons and holes, or electrons (or holes) and impurity states in the bandgap of the semiconductor followed by emission of an infrared photon.

3.6. PHOTOTHERMAL INTERFEROMETRY

photothermal interferometry (interferometric photothermal displacement, interferometry, phase fluctuation heterodyne interferometry, phase fluctuation optical heterodyne spectroscopy, phase sensitive optical heterodyne spectrum, photothermal interference, photothermal phase shift spectroscopy, purely-thermal-wave interferometry)

The phase of a monochromatic light beam passing through the light-irradiated region relative to the phase of a light beam passing through the reference arm is detected as a change in power at a light detector. Michelson, Mach-Zehnder, Jamin, and Fabry Perot interferometers are frequently used. The phase difference originates in a refractive index change. The source and the applications are similar to the **Grating spectroscopy** and **Lens spectroscopy**.

INTERFEROMETER

A device that detects the interference of light. Generally, a light beam from one light source is divided into two beams, and the resulting two beams are later recombined and superimposed.

PURELY-THERMAL-WAVE INTERFEROMETRY

An interferometry by the result of coherent thermal flux relationships between two spatially superposed thermal-wave fields generated in the same medium by two modulated and phase-shifted optical sources. It is the diffusion-wave equivalent of a standing wave in freely propagating wave fields.

3.7. PHOTOTHERMAL DEFLECTION

photothermal deflection (acousto-optical beam deflection, mirage detection, mirage effect, optical probing of the acoustic refractive gradient, photothermal beam deflection, transverse mirage effect, probe beam refraction)

Detection of the deflection of a probe beam crossing a non-uniform spatial profile of the refractive index gradient induced by a photothermal excitation. When the temperature change in the medium is non-uniform, it results in a refractive index gradient through the contributions of eq 1 and 2. The temperature change could be also established by the heat diffusion. The spatial gradient in the refractive index changes the direction of the probe beam propagation. The spatially non-uniform refractive index distribution arises from many sources besides the thermal effect as described in section 3.1.

COLLINEAR DEFLECTION METHOD

A photothermal deflection method that uses a probe beam collinear or quasi collinear with the pump beam.

REVERSE MIRAGE EFFECT

A probe beam-deflection for a probe light that passes on the opposite side of the photo-illuminated interface.

SURFACE DEFLECTION

A probe beam deflected from a surface changes direction when heterogeneous expansion occurs on the surface.

TRANSVERSE DEFLECTION METHOD

A photothermal deflection method that uses a probe beam perpendicular to the pump beam.

3.8. PHOTOTHERMAL REFLECTION CHANGE

photothermal reflection change (surface optical reflectance due to the photothermal effect, thermoreflectance detection)

Change of light intensity reflected from the surface due to the photothermal effect. This effect is produced because generally reflectivity of a surface depends on the temperature. Similar to other refractive index sensitive spectroscopies, not only the thermal effect but also other sources of refractive index change and absorbance change can also modify the reflection.

LASER-INDUCED CURVATURE DEFORMATION

A change of a surface flatness of a plate produced by optical irradiation usually on one side only and by usually using a laser beam due to differential surface-stress induced; this can be transient or permanent.

LASER-INDUCED SURFACE BUMP FORMATION

Production of a localized surface feature by a small-spot laser beam incident on the surface; such a surface feature or bump is in the immediate vicinity of the laser spot and can be transient (e.g., due to local thermal expansion) or permanent (e.g., due to plastic flow or due to melting/resolidification).

3.9. RELATED METHODS

The spectroscopies listed in 3.1~3.8 are generally considered to be in the category of the photothermal spectroscopy. There are a number of other methods that can detect the photothermal effect. These methods are summarized in this section in alphabetical order.

FLUORESCENCE EXCITED THROUGH A HOT BAND ABSORPTION

Fluorescence detection after the photoexcitation of a *hot band*. If fluorescence from an excited state is detectable, the fluorescence intensity change with excitation at the red edge of the absorption band can be very sensitive to temperature changes. Hence the heating effect after the photoexcitation can be detected by monitoring the fluorescence intensity change.

See also *hot band*.

HOT BAND ABSORPTION

Detection of enhanced hot band absorption after photoexcitation. The hot band to be monitored can be the band of a photoexcited molecule itself or another molecule in the same sample. In the former case, the molecular cooling process can be detected. In the latter case, the thermal wave from the photoexcited molecule can be measured in the time-resolved manner. The temperature can be determined

by the spectral analysis of the red edge absorption band.

See also *hot band* in section 4.

INFRARED ABSORPTION DETECTION

Infrared absorption detection of molecular vibrational or orientational modes that are sensitive to the temperature. In particular, the IR absorption of water in the OH stretching region is sensitive to the temperature through the temperature dependence of the hydrogen bonding network.

INFRARED EMISSION

See an introduction of **3.4. PHOTOTHERMAL RADIOMETRY**

LASER-INDUCED CAPILLARY VIBRATION

Detection of capillary vibration when a stretched capillary is illuminated. When the substance inside the capillary absorbs the light, the length and the tension of the capillary changes by the photothermal effect. Therefore when the excitation light intensity or the wavelength is temporally modulated, the capillary vibrates.

MOLECULAR THERMOMETER

A molecule which possesses temperature dependent absorbance or luminescence intensity. If two or more states of a molecule are in thermal equilibrium, the absorbance in a variety of wavelength regions (X ray, UV, visible, IR, microwave) or the luminescence spectrum can be sensitive to the temperature. Hence, any such a molecule can be used to monitor the change of the temperature after photoexcitation. A molecule which shows *hot band absorption* can be a molecular thermometer.

See also *thermochromism* and *thermoluminescence* in section 4

NONRADIATIVE QUANTUM YIELD SPECTROSCOPY

The photon-energy dependence of the optical-to-thermal transition probability in an absorbing medium with an excited-state manifold. This spectroscopic mode can be important in identifying thermal transition ranges with low optical (radiative) yield in optical media. It can be performed using some photothermal detection techniques, such as *photopyroelectric spectroscopy*. With this particular spectroscopic technique, the optical absorption spectrum and the nonradiative quantum yield spectrum can be decoupled and measured separately from the spectroscopic data.

RAMAN SCATTERING

A light scattering phenomenon from a material. The wavelength of the scattered light is different from that of the incident light. The Raman scattering on the lower frequency side of the excitation light is called Stokes Raman scattering and that on the higher frequency side is called anti-Stokes Raman scattering. Generally, various excitation or de-excitation processes such as the

rotational excitation, vibrational excitation, electronic excitation, excitation of spin state etc. are involved. The intensity ratio of the anti-Stokes to Stokes scattering depends on the population difference between two states connected by the incident and scattered light fields. Hence, this ratio can be used to monitor the temperature.

See *anti-Stokes shift* and *Stokes shift* in section 4.

4. RELATED TERMS

ABLATION

Material ejection by laser light irradiation due to several mechanisms such as photothermal heating, boiling, optical breakdown, plasma formation, (chain) chemical reaction etc.

ACOUSTIC TRANSIT TIME

The time required for the acoustic wave to cross the excited region:L/v, where L is a characteristic length of the photoirradiation and v is the sound velocity of the medium. For grating spectroscopy, L is the fringe spacing. If a (focused) light beam is used, L is the beam diameter.

ACOUSTO-OPTIC EFFECT

The strain wave produced by a periodic modulation of the refractive index via *photoelasticity*. This provides a phase grating which may diffract part of the incident light into one or more directions.

ANTI-STOKES RAMAN SCATTERING

See *Raman scattering*

ANTI-STOKES SHIFT

See *Stokes shift*

CALORIMETRIC REFERENCE

See *calorimetric reference* in section 3.3

COTTON MOUTON EFFECT

The magnetic field effect on the real part of the dielectric constant. It leads to the linear birefringence.

See *magneto-optical effect*

DC KERR EFFECT

See *electro-optical effect*

DEGENERATE FOUR-WAVE MIXING [DFWM]

A four wave mixing experiment with the same frequency of the four light fields. Generally two antiparallel beams are mixed with a third optical beam having a different propagation direction. The diffracted wave propagates antiparallel to the beams; $\omega_1 = \omega_2 = \omega_3 = \omega_1$, $k_1 = -k_2$, $k_3 = -k_4$.

DELAYED FLUORESCENCE

Fluorescence decaying more slowly than that expected from the rate of decay of the emitting state. 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),

(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.

The thermally activated delayed fluorescence may be used to detect the photothermal effect.

DEPTH OF PENETRATION

The inverse of the absorption coefficient. The SI unit is m. If the decadic absorption coefficient is used, the depth of penetration is the distance at which the spectral radiant power decreases to one tenth of its incident value. If the Napierian absorption coefficient is used, the depth of penetration is the distance at which the spectral radiant power decreases to 1/e of its incident value.

DIFFUSE PHOTON-DENSITY WAVE

An optical oscillation in a scattering (turbid) medium, which is created by the collective motion of coherently driven and randomly scattered and absorbed photons. It creates a diffuse optical field with well-defined spatial phase lags with respect to the source phase and a characteristic diffusion length inversely proportional to the square root of the source modulation frequency. This wave appears at, or above, source modulation frequencies on the order of the inverse effective diffuse photon lifetime, a function of the speed of light and the absorption cross-section in the turbid medium.

DIFFUSION WAVE

A coherent collective oscillation of energy carriers in a medium, which is mathematically a solution to a parabolic (rather than hyperbolic) transport equation. Energy, particles (e.g. photo-excited electrons) or continuous mass is transported subject to Fickian propagation. It exhibits amplitude and phase, but normally lacks wavefronts and obeys accumulation and depletion laws at interfaces between adjoining media, instead of conventional square-law reflection and transmission phenomena. Examples

of such coherent oscillations are thermal waves, diffuse-photon-density waves, electronic-carrier-density waves, mass-density waves, and thermal waves.

DUFOUR EFFECT

A phenomenon where a temperature gradient is formed in a mixture having concentration gradient.

ELASTIC HEAT WAVE

An elastic wave induced by thermal motion.

ELECTROCALORIC EFFECT

Heat induced by *electrostriction* and *optical Kerr effect.* This effect is similar to the usual photothermal effect, with the exception that the source of heat is not that absorbed from the excitation source but rather due to the frictional forces on expansion of a medium constricted by electric field effects.

See *electrostriction* and *optical Kerr effect.*

ELECTRONIC CARRIER DENSITY WAVE

A coherent oscillation of diffusing free electronic carriers in a semiconductor; a result of harmonic optical excitation, e.g. by means of a super-bandgap laser source. This oscillation is also called a "plasma wave". The electron (or hole) diffusion wave appears only at, or above, frequencies on the order of the inverse of the recombination lifetime of the carrier, as a heavily spatially damped concentration oscillation.

ELECTRO-OPTICAL EFFECT

Optical effect caused by an applied dc or low frequency electric field. When the dielectric constant (relative permittivity, ε_r) is expanded into a power series of the amplitude of the electric field (E), the linear term in E is the *Pockel's effect*. The quadratic field-dependent term is known as the *dc Kerr effect*.

ELECTROSTRICTION

Density change of a substance by interaction of the charge or dipole (or change in dipole moment) or polarizability of a molecule created by light absorption and the medium. The molecule moves into (or out of) the higher light intensity region, if it has positive (or negative) polarizability.

EXTERNAL CALORIMETRIC REFERENCE

Molecules that can be used as a *calorimetric reference* in an experiment separated from the measurement of the sample.

See *calorimetric reference* in section 3.3

FARADAY EFFECT

The magnetic field effect on the imaginary part of the dielectric constant. It leads to circular birefringence under a magnetic field.

See *magneto-optical effect.*

FLUORESCENCE

Spontaneous radiation upon transition from an excited molecular entity with the formation of a molecular entity of the same electron spin multiplicity.

FOUR WAVE MIXING [FWM]

The interaction of four waves with four frequencies (ω_1, ω_2, ω_3, ω_4) and propagation directions of k_1 to k_4. The interaction is due to the third order non-linear polarization of the material. In this category are included third harmonic generation, electric-field induced second harmonic generation, coherent Stokes and anti-Stokes Raman scattering, coherent two photon absorption, Raman-induced Kerr effect, optical Kerr effect, photon echo, z scan, self phase modulation, self and induced (de)focusing, transient grating, and transient lens.

HEAT TRANSFER

A transfer of thermal energy. Conduction, convection, and radiation processes are the processes leading to heat transfer. A photothermal signal generally decreases by cooling of the observation region by heat transfer.

HOT BAND

Enhanced absorption owing to the broadening at the red edge of an (generally electronic) absorption band. Main origin of the broadening is the thermal excitation to higher vibrational levels in the ground state.

INTERNAL CALORIMETRIC REFERENCE

A sample that can be a *calorimetric reference* by inhibition of the reactions.

See *calorimetric reference* in section 3.3

INTERNAL CONVERSION [IC]

A photophysical process. Isoenergetic *radiationless transition* between two electronic states having 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. The excess energy generally converts to the translational energy,

i.e. to the thermal energy.

INTERSYSTEM CROSSING [ISC]

A photophysical process. Isoenergetic *radiationless transition* between two electronic states having different multiplicity. It often results in a vibrationally excited molecular entity in the lower electronic state, which then usually deactivates to its lower vibrartional level. The excess energy generally converts to translational energy, i.e. to the thermal energy.

INTRAMOLECULAR VIBRATIONAL REDISTRIBUTION [IVR]

Energy redistribution within the intramolecular vibrational manifold without energy transfer to the medium. It is possible that the energy may not get randomized into all the vibrational modes.

LIGHT-HEAT CONVERSION EFFICIENCY

Thermal energy coming out from the photoirradiated system relative to the input photon energy. Since the energy from the *radiationless transition* ultimately flows into the translational mode of the medium (thermal energy), this conversion efficiency is the same as the *quantum yield* of the radiationless (or nonradiative) transition.

MAGNETO-OPTICAL EFFECT

A magnetic field effect on the dielectric constant.

See *Faraday effect* and *Cotton Mouton effect*.

MASS-DENSITY WAVES

Mass diffusion oscillations resulting in harmonic atomic and molecular diffusion processes, usually through polymers and membranes, by means of pressure oscillations inside a vacuum chamber.

MULTIPHOTON ABSORPTION

Light absorption which occurs as a result of simultaneous absorption of more than one photon. There are coherent and incoherent multiphoton processes.

NONRADIATIVE TRANSITION

See *radiationless transition.*

OPTICAL BREAKDOWN

Catastrophic breakdown in a transparent medium by a strong light field.

OPTICAL KERR EFFECT [OKE]

The electronic cloud deforms by the interaction between the electric field of the light and the

electrons. Reorientation of anisotropic polarizable molecules occurs through the interaction between the electric field and a permanent or induced dipole. The distortion of the electronic cloud and the molecular reorientation induce anisotropic refractive index changes (the linear birefringence), generally called the nuclear and electronic responses of the optical Kerr effect (OKE), respectively. Frequently, molecular librational, vibrational, and orientational redistribution are included.

PENETRATION DEPTH

See *depth of penetration*

PHOSPHORESCENCE

Spontaneous radiation upon transition between two molecular states with different electron spin multiplicity.

PHOTOCARRIER MODULATION

Light-induced temporal variation in electrical carrier concentrations in an optically sensitive semiconductor device.

PHOTOELASTICITY

Changes of optical properties due to a mechanical stress. The strain caused by the application of a stress may change the refractive index.

PHOTOREFRACTIVE EFFECT

A change in the refractive index via the photo-induced electric field modulation in the material. After photoelectrons are generated, they migrate in a lattice and subsequently are trapped at new sites. The resulting space charges give rise to a change of the refractive index via the *electro-optic effect*.

PHOTOTHERMAL BREAKDOWN

Catastrophic breakdown in a medium by heat from the photothermal effect.

PHOTOTHERMAL COOLING

Opposite to the photothermal heating, the (transient) temperature may decrease by photoexcitation in some cases. In many cases, cooling is observed after selective excitation of the Boltzmann distributed ensemble. The kinetic energy is taken from the medium to re-establish the Boltzmann distribution of the molecular system.

PHOTOVOLTAIC EFFECT

Light-induced electric power generation by the photoexcitation of electrons into the charge transfer band with a preferential velocity direction along the polar axis. This effect produces a shift in the

spatial distribution of the electrons and the ionized donors in a manner similar to that produced by as an applied dc field.

POCKEL'S EFFECT

See *electro-optical effect*

QUANTUM YIELD

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

Φ = number of events/number of photons absorbed

QUANTUM YIELD OF FLUORESCENCE

Number of photons emitted by fluorescence per photon absorbed by the system.

RADIATIONLESS TRANSITION

A transition between two states of a system without photon emission or absorption. The energy is transferred to the electronic, vibrational, rotational, translational movements.

SKIN DEPTH

The depth at which the amplitude of electromagnetic field, usually of high frequency, decreases to 1/e of the incident amplitude.

See *depth of penetration*

SORET EFFECT

A phenomenon where a concentration gradient is produced in a mixture possessing a temperature gradient.

STEFAN-BOLTZMANN LAW

See an introduction of section 3.4.

STIMULATED BRILLOUIN SCATTERING

Scattering process due to sound wave that is created by light irradiation.

STIMULATED LIGHT SCATTERING

Scattering process due to material response created by light irradiation. In spontaneous light scattering, the radiation is diffracted as a Fourier component of a spontaneous statistical fluctuation of material response. In analogy to classical light scattering, light can be scattered by temporal and spatial modulation of material response induced by light. When the light scattering is stimulated by an optically

created grating, it is one of the transient grating spectroscopies.

STIMULATED RAMAN SCATTERING

Scattering process due to molecular vibration created by light irradiation.

See *Raman scattering* in section 3.9

STIMULATED RAYLEIGH SCATTERING

Scattering process due to temperature fluctuation of the medium created by light irradiation.

STOKES RAMAN SCATTERING

See *Raman scattering* in section 3.9

STOKES SHIFT

The difference between the spectral position of the band maximum of the absorption and that of the luminescence arising from the same electronic transition. Normally, the luminescence occurring at a longer wavelength than the absorption is stronger than that occurring at wavelength shorter than the absorption wavelength. The latter is referred to as anti-Stokes shift.

THERMAL CONDUCTIVITY

The universal property of matter to conduct thermal energy through interactions and collisions at the molecular and atomic level. Phenomenologically, the ratio of the heat flux per unit time and unit area through an area element arbitrarily located in the medium to the temperature gradient in the direction normal to the area. From a macroscopic or continuum viewpoint, thermal conduction is quantitatively described by Fourier's equation.

THERMAL DIFFUSIVITY

Ratio of thermal conductivity to the product of heat capacity and density.

See *thermal conductivity*

THERMALIZATION TIME

The energy transfer time from a photoexcited molecular species to the translational modes of the medium in a broad sense. Sometimes, this term is used to mean the relaxation time to establish the Boltzmann distribution in the translational mode.

THERMAL STRESS

Stress induced by temperature change.

THERMAL WAVES

Diffusive propagation of thermal energy induced by chopped or repetitive-pulsed excitation. Coherent heat diffusion oscillates in a medium, as a result of harmonic heating (optical, electrical, thermal or otherwise). They are heavily damped in space, where the oscillation penetrates to a depth on the order of one or two thermal diffusion lengths in opaque materials. They penetrate deeper in non-opaque materials and carry information on the optical absorption coefficient at the excitation wavelength.

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 color.

THERMOLUMINESCENCE

Luminescence which arises from a reaction between species trapped in a rigid matrix and released as a result of an increase in temperature. It may be called thermoluminescence when created by the thermal activation from a metastable state.

See also *delayed fluorescence*.

VIBRATIONAL COOLING (VIBRATIONAL RELAXATION)

Population relaxation of a vibrational level accompanied by energy flow to the surrounding medium. The vibrational energy is distributed to lower energy vibrational modes and/or to translational modes.

VIBRATIONAL (ROTATIONAL, TRANSLATIONAL) TEMPERATURE

Temperature within the vibrational, rotational, or translational degrees of freedom. On a fast time scale after the energy is deposited into a molecular system, the energy may not be uniformly distributed in these degrees of freedom. However, for a Boltzmann energy distribution a temperature may be defined within that manifold.

5. Symbols for physical parameters involved in photothermal effects

name	symbols	SI units
absorbance	A	
absorption cross section	σ	m^2
acoustic impedance	Z	kg $m^{-2}s^{-1}$

acoustic resistance	R	
Bragg angle	θ	rad
bulk viscosity	η_b	kg $m^{-1}s^{-1}$
carrier density	N	m^{-3}
carrier diffusivity	D_c,	$m^2 s^{-1}$
carrier lifetime	τ	s
circular frequency	ω	rad s^{-1}
compressibility (isothermal)	κ_T	Pa^{-1}
(adiabatic)	κ_S	Pa^{-1}
conductivity	σ	$\Omega^{-1} m^{-1}$
dielectric constant	ε_r	
diffusion coefficient	D	$m^2 s^{-1}$
electric dipole moment	p, μ	C m
effusivity	J,e	W $s^{1/2}$ K^{-1} m^{-2}
electric polarization	P	C m^{-2}
emittance	ε	
enthalpy	H	J
entropy	S	J K^{-1}
expansion coefficient		
linear	α_l	K^{-1}
volume	α, α_v, γ	K^{-1}
molar absorption coefficient	ε	M^{-1} cm^{-1}
frequency	ν,f	Hz
fringe spacing of grating	Λ	m
grating wavenumber	q	m^{-1}
heat energy	Q	J
heat capacity at constant volume	C_v	J kg^{-1} K^{-1}
heat capacity at constant pressure	C_p	J kg^{-1} K^{-1}
heat capacity ratio	γ=C_p/C_v	
heat flux	J_q	W m^{-2}
heat flow rate	Φ	W
internal energy	U	J
irradiance (radiant flux received)	E	W m^{-2}
isotropic sound speed	v_{ac}	m s^{-1}
light-heat conversion efficiency	ϕ_{nr}	
magnetic permittivity	m	N A^{-2}
mass density	ρ	kg m^{-3}
molar absorption coefficient		

decadic	ε	$m^2\ mol^{-1}$
nepierian	κ	$m^2\ mol^{-1}$
molar volume change	ΔV	$m^3\ mol^{-1}$
nonradiative rate constant	k_{nr}	s^{-1}
n-th order of electric susceptibility	$\chi^{(n)}$	$(m\ V^{-1})n^{-1}$
order of reflection	n	
Peltier coefficient	Π	V
permittivity	ε	$F\ m^{-1}$
pressure	p, P	Pa ($N\ m^{-2}$)
quality factor of cavity	Q	
quantum yield of nonradiative transition	Φ_{nr}	
quantum yield of intersystem crossing	Φ_{isc}	
quantum yield of fluorescence	Φ_f	
quantum yield of phosphorescence	Φ_p	
radiant exitance (emitted radiant flux)	M	$W\ m^{-2}$
radiant flux	Φ	W
radiant energy	Q	J
radiative rate constant	k_r	s^{-1}
rate constant of energy transfer	k_{et}	s^{-1}
rate constant of V-T energy transfer	k_{VT}	s^{-1}
refractive index	n	
reflectance	ρ	
reflectivity	R	
shear viscosity	η_s	$kg\ m^{-1}\ s^{-1}$
sound energy flux	P	W
Stefan-Boltzmann constant	σ	$W\ m^{-2}\ K^{-4}$
surface shear viscosity	η_s	$kg\ s^{-1}$
surface tension	σ	$J\ m^{-2}$
temperature	T	K
thermal conductance	G	$W\ m^{-2}$
thermal conductivity	λ, k	$J\ m^{-1}\ s^{-1}\ K^{-1}$
thermal diffusivity	a, D_{th}	$m^2\ s^{-1}$
thermalization time	τ_{th}	s
thermal resistance	R, Z	$K\ W^{-1}$
transition dipole moment	M	C m
transmittance	T	
wavelength of light	λ	m
wavelength of sound	λ_{ac}	m

6. Cumulative alphabetical list

* on the subsection number indicates that the term is not explained in the Glossary but appears bellow the heading of the subsection.

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optical Kerr lens [OKL]	3.2
optical probing of the acoustic refractive gradient	3.7*
optical pyrometry	3.4
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orientation grating	3.1
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photoacoustic microscopy	3.3
photoacoustic Raman gain spectroscopy	3.3
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Figure caption

A chart showing relations among various photothermal effects. Causes and results are connected by arrows.