Pure Appl. Chem., Vol. 76, No. 6, pp. 1083–1118, 2004.
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INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

PHYSICAL AND BIOPHYSICAL CHEMISTRY DIVISION*

QUANTITIES, TERMINOLOGY, AND SYMBOLS IN PHOTOTHERMAL AND RELATED SPECTROSCOPIES

(IUPAC Recommendations 2004)

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Quantities, terminology, and symbols in photothermal and related spectroscopies

(IUPAC Recommendations 2004)

Abstract: This paper presents quantities, terminology, and symbols of terms related to photothermal phenomena and used in photothermal and related spectroscopies. The terms used in the literature to describe photothermal phenomena and methods are reviewed, and a glossary of terms is given. The origins of photothermal phenomena, as well as the relations among various photothermal effects, are summarized. The listed terms cover the terminology in transient grating, transient lens, photoacoustic spectroscopy, photothermal radiometry, calorimetry, interferometry, deflection, reflection, and other related spectroscopies, which use or are related to photothermal effects.

1. INTRODUCTION

The interaction of electromagnetic radiation with matter causes absorption, emission, and scattering of radiation. Except for emission and scattering, the absorbed electromagnetic 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 [1–11]. The discovery of the photothermal effect dates back to Bell's discovery of the photoacoustic effect in 1880 [12], 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 [13]. 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 methods have been developed and applied to a variety of problems. Today, photothermal spectroscopy is widely used in physics, chemistry, biology, and engineering [1–11].

Various changes in the medium can be monitored by photothermal methods in order to quantify the effects of the temperature rise upon radiationless deactivation [3,5,7–9]; the temperature rise is measured by laser calorimetry, pressure change is sensed by direct and indirect photoacoustic effects, changes of refractive index are detected by probe beam refraction and diffraction, and surface deformation is quantified by probe beam deflection and optical interference. Furthermore, thermal emission is detected by photothermal radiometry, while reflectivity/absorptivity change is sensed by transient thermal reflectance, transient piezo-reflectance, and transmission measurement.

The photothermal method has a number of merits compared with other methods [3,5,7–9]. It is highly sensitive and applicable to different types of materials (gas, liquid, liquid crystal, and solid), transparent and opaque. It can be used in vacuum and in air, and with samples of arbitrary shape. Radiation of any wavelength can be used (radio frequency, microwave, IR, visible, UV, and X-ray, etc.). Photothermal detections are often nondestructive and noncontact methods and can be used to probe optical and thermal local properties in very small areas; these merits are of great value in analytical applications. Photothermal methods also enable studying of various processes giving rise to these effects. For example, chemical reactions and phase transitions as well as nonradiative processes from excited states and vibrational relaxations may be analyzed. The dynamic range for the photothermal methods is wide and extends over 14 orders of magnitude (from seconds to femtoseconds).

Publications in photothermal methods come from researchers working in the fields of analytical and physical chemistry, physics, optical engineering, and biology. Therefore, a wide range of terms is used in the literature to describe the same method or the same phenomenon. 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 within each respective section unless otherwise stated. Finally, symbols used in photothermal spectroscopy are summarized. A cumulative alphabetical list of terms is also provided.

2. ORIGIN OF PHOTOTHERMAL EFFECTS [1–11]

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

The photoacoustic effect is defined by a common effect producing a medium density change, which may be either detected acoustically or optically. The pressure wave generated after photoexcitation 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 changes produced upon photoabsorption 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 effect that directly modifies the absorbance or refractive index upon photoexcitation is generally referred as photo-optical effect. The effects listed above are often connected to each other (Fig. 1). 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.

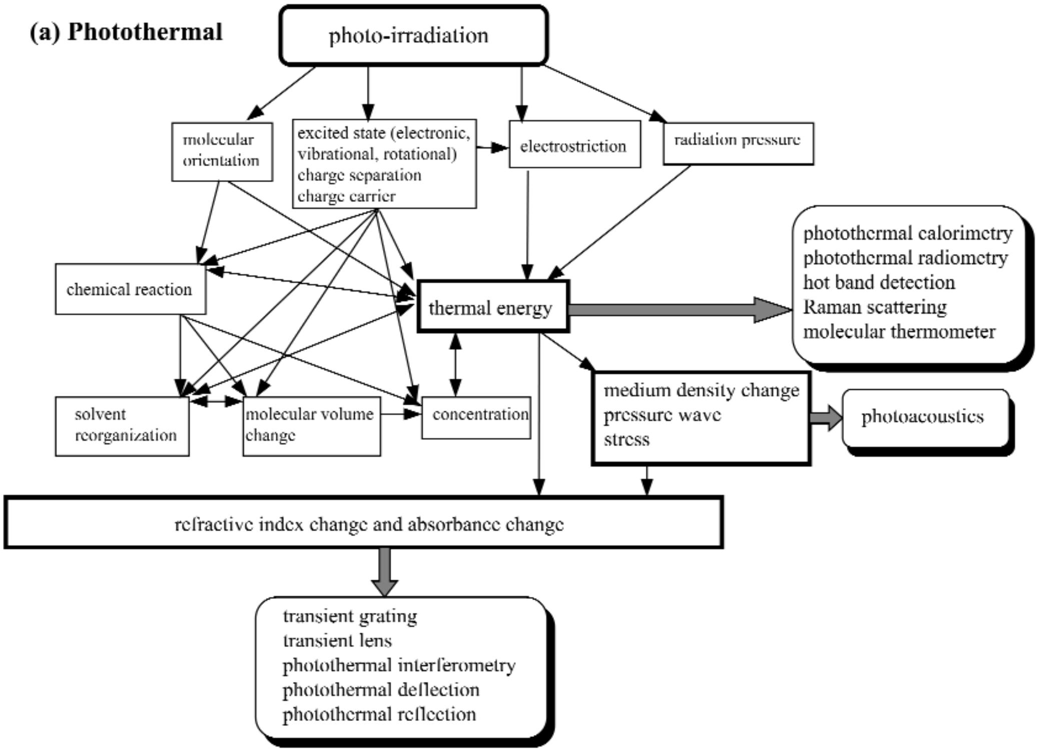
Since the energy released by *radiationless transitions* in condensed phases will eventually flow into translational freedom, the photothermal effect is generally observed after any type of photoexcitation (resonant condition) and is closely related to the energy dynamics in the system. The changes in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

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

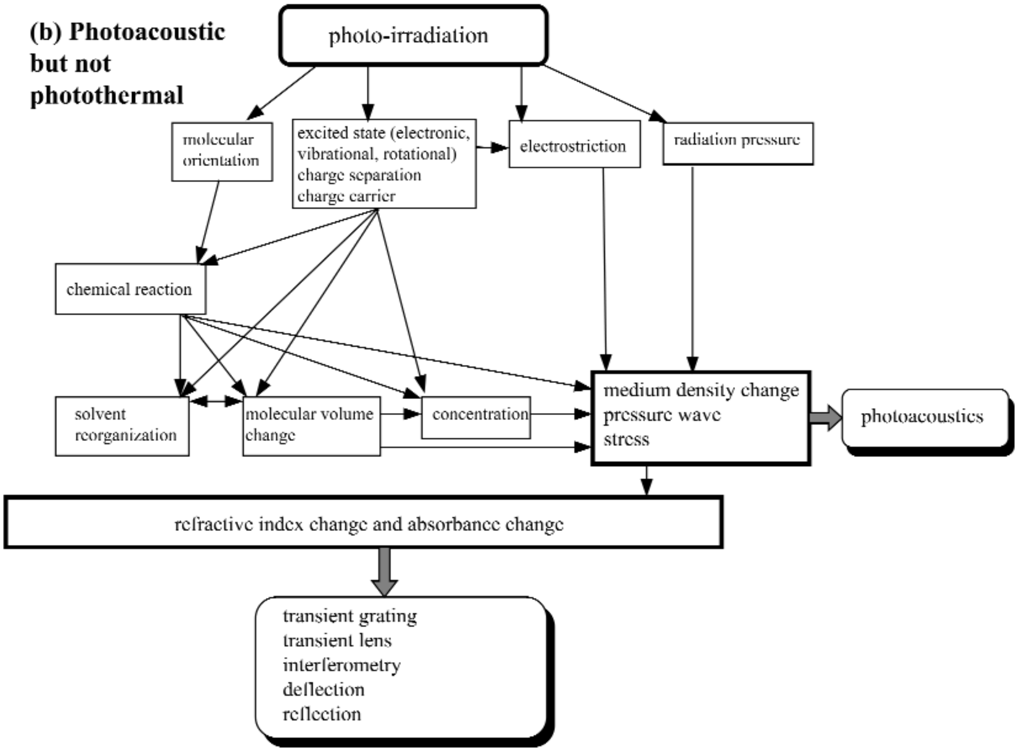
$$\delta k = \{(\partial k/\partial \rho)_T(\partial \rho/\partial T) + (\partial k/\partial T)_\rho\}\delta T \qquad (2)$$

where ρ is the mass 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 that has two closely 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.

(a) Photothermal



(b) Photoacoustic but not photothermal



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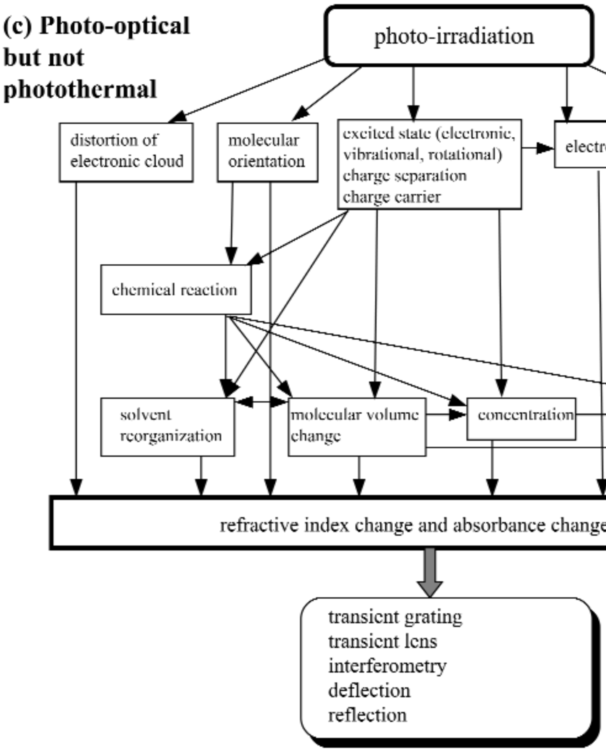

Fig. 1 Charts showing relations among various photothermal effects. Causes and effects are connected by arrows. (a) Origins and detection methods of photothermal effects, which are caused by the heating effect after photoirradiation. (b) Origins and detection methods of acoustic effects induced by photoirradiation, but not by the photothermal effects. (c) Origins and detection methods of photo-optical effects induced by photoirradiation, but not by the photothermal effects.

Photothermal effects can be probed not only in the bulk phase, but also at surfaces or interfaces as changes in such as intensity, polarization, optical path, and reflection angle of the reflected optical radiation. 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 radiation changes when the surface is deformed.

Charts showing the relations among various photothermal effects are shown in Fig. 1.

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 brackets. Some definitions have been taken from the "Gold Book" [14]. These are labeled "GB page number" after the respective definition, with additional notes as necessary. We have also consulted the definitions recommended by photochemists [15,16].

3.1 Grating spectroscopy [3,7,9,11]

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* in Section 4.)

The 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 optical radiation–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*). Such a grating diffracts another probe light beam into 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 photoirradiation.

acoustic component
Grating created by an adiabatic pressure fluctuation, which gives rise to a high-frequency acoustic wave. Expansion of the refractive index change as a function of the two independent variables, entropy (S) and pressure (p), is expressed by eq. 3:

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

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 spacing, v, velocity of sound). A decay of this component is governed 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 decreasing the signal amplitude that is different from the intrinsic acoustic damping of the medium. The isobaric wave appears (*diffusive component*) after the complete decay of this acoustic 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
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
Nonsinusoidal grating created by nonlinear 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, θ
Specific angle at which the light (or sound) waves scattered 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
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 the absorption.

complementary grating
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 spatial phase difference between ground state and product gratings is 180º.

concentration grating
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). This term is sometimes used to refer to a grating similar to the population grating or species grating.

density grating
Grating due to the first terms of eqs. 1 and 2 in Section 2.

diffusive component
In grating spectroscopy, grating created by an isobaric entropy fluctuation (the second term of the right-hand side of eq. 3). This component is attenuated only by thermal diffusion.

See *acoustic component*.

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

evanescent grating
Grating due to the interference of two evanescent waves formed upon total internal reflection at an interface.

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 photoirradiation.

See also *stimulated light scattering* in Section 4, *thermal grating*, *acoustic component* in Section 3.2.

free carrier grating
Population grating involving electrons or holes in solids (semiconductors).

grating wavenumber, q
Wavenumber of the fringe created by the light interference and defined as 2π divided by the fringe length.

higher-order diffraction grating
See *anharmonic grating*.

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

moving grating
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 the introduction of Section 3.2.

optical heterodyne detection, OHD (of a grating signal)
A reference beam (local oscillator field) is coherently overlapped with a diffracted signal beam at 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
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
Transient grating produced by the optical Kerr effect.

See *optical Kerr effect* in Section 4.

orientation grating
Grating induced by changes in orientation of molecules or systems that possess 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. Notable examples in the liquid phase are the mesophases 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
Grating that affects the phase of the probe light. The source of the grating is the spatial modulation of the refractive index.

polarization grating
Grating produced by changes in the polarization direction.

population grating
Grating arising from the refractive index change due to the different electronic structures of molecules (*phase grating*) and the absorbance change by the presence of new species and the depletion of reactants (*amplitude grating*) induced by a chemical reaction.

See *species grating.*

Raman–Nath scattering
See *thin grating*.

reflection grating (surface-sensitive transient grating, transient reflecting grating)
Grating signal induced by spatially periodic surface deformations as well as modulation of optical properties (refractive index and absorbance) in the medium in which the probe beam is being reflected.

self-diffraction
Diffraction of pump light creating the grating.

space charge grating
See *electric field grating.*

species grating
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

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

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

where C is the number 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-hand 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	
$(\partial n/\partial \rho)_C(\partial r/\partial C)$	Volume(-phase) grating	Species(-phase) grating
$(\partial n/\partial C)_r$	Population(-phase) grating	
$(\partial k/\partial \rho)_C(\partial r/\partial C)$	Volume(-amplitude) grating	Species(-amplitude) grating
$(\partial k/\partial C)_r$	Population(-amplitude) grating	

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

static grating
Grating generated by pump beams with $\omega_1 = \omega_2$.
See also *moving grating*.

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

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

temperature grating
Grating due to the second terms of eqs. 1 and 2 in Section 2.
See also *thermal grating*.

tensor grating
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)
Grating created by the thermal effect. In order to specify the origin clearly, the transient grating signal due to the first and the second terms of eq. 1 may be called “density (-phase) grating” and “temperature (-phase) grating”, respectively. The first and second terms of eq. 2 represent the absorption change by the change of density and the second one by the temperature change, respectively. These 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 (i.e., diffusive and acoustic components). Terminologies of these gratings are summarized as follows:

Terms in eqs. 1 and 2	Terminology	
$(\partial n/\partial r)_T(\partial r/\partial T)$	Density(-phase) grating	Thermal(-phase) grating
$(\partial n/\partial T)_r$	Temperature(-phase) grating	
$(\partial k/\partial r)_T(\partial r/\partial T)$	Density(-amplitude) grating	Thermal(-amplitude) grating
$(\partial k/\partial T)_r$	Temperature(-amplitude) grating	

thick grating
Grating produced when 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*: analogy with the scattering of X-rays from the atomic planes in a crystal.

thin grating

Grating produced when 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 a broad angular and wavelength selectivity. Sometimes it is called *Raman–Nath scattering*.

transmission grating signal

Signal created by the diffraction of a probe beam transmitted through the sample. To this category belongs a diffracted beam propagating in a transmission grating reflected at the second boundary, even though its 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 the TSETG-I method, 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 the TSETG-II method, 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

Grating due to changes in refractive index induced by changes in molecular volume upon photoexcitation. 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 [4,5,7,9,11]

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 also be Gaussian. If the refractive index or the absorbance is varied by photoexcitation, its behavior may be written as in eq. 6:

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

where w is the radius of the excitation beam and r is the distance from the excitation beam axis. 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 in the density with corresponding change of the refractive index [12]. A similar shape of temperature distribution in a cylindrical sample tube can be achieved even by uniform illumination of the sample because of the heat flow to the sample wall (similar to *photothermal deflection*). The expansion (or focusing) of the light at the central portion 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 lens 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)
Lens associated with an adiabatic pressure fluctuation that gives rise to an acoustic wave. The first term on the right-hand side of eq. 3 is the origin of this component that appears with a rate constant determined by the *acoustic transit time*. After the complete decay of this acoustic component, it is the isobaric wave that remains (*diffusive component*).

confocal length
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
Lens due to the first terms on the right side of eqs. 1 and 2 in Section 2.
See *thermal lens*.

diffusive component
In lens spectroscopy, a lens related to an isobaric entropy fluctuation due to the second term of the right-hand side of eq. 3. This wave decays only by the thermal diffusion.
See *acoustic component*.

dual-beam transient lens effect
See *induced defocusing* and *induced focusing*.

induced defocusing
Defocusing effect of a probe beam by the pump photoinduced refractive index change. This effect is induced by the spatially inhomogeneous phase modulation of the probe light. Induced defocusing has almost the same meaning as the transient lens.

induced focusing
Focusing effect of a probe beam by the pump photoinduced refractive index change. This effect is induced by the spatially inhomogeneous phase modulation of the probe light. Induced focusing has almost the same meaning as the transient lens.

induced phase modulation
Phase change of (probe) optical radiation field by another (pump) optical radiation.
See *induced defocusing* and *induced focusing*.

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

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

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

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

spherical aberration
Departure of the thermally induced refractive index profile from the idealized quadratic dependence which characterizes an ideal thin lens.

temperature lens
Transient lens due to the second terms of the right side of eqs. 1 and 2 in Section 2.

See *thermal lens*.

thermal lens, TL
Lens created by the thermal effect. The transient lens signal due to the first and second terms of eq. 1 are called “density (-phase) lens” and “temperature (-phase) lens”, respectively. The first and 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 (see also GB 416, *thermal lensing*).

thermal lens microscopy
Transient lens experiment under a microcopy, in which pump and probe laser light beams are focused on a small spot in a sample. The image could be mapped by scanning the sample or the beam.

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, while the second one probes their dynamics by creating the transient lens. In the 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 the type II configuration, the roles of the prepulse and the lens pulses are interchanged. The sample is initially excited by a pump pulse to generate the lens while the second spatially uniform beam induces the transient absorption.

volume lens
Lens produced by photoinduced volume changes. Such a volume change produces an acoustic wave as well as a diffusive component.

See *acoustic component* and *diffusive component*.

3.3 Photoinduced acoustic spectroscopy [1,4,5,7,10]

Photoacoustic spectroscopy [PAS] (optothermal spectroscopy, photoacoustic calorimetry, thermal-wave spectroscopy, resonant laser photoacoustics).
Time-resolved photoacoustic calorimetry (laser-induced optoacoustic spectroscopy, laser-induced photoacoustic spectroscopy, laser photoacoustic spectroscopy, pulsed laser photoacoustics, time-resolved photoacoustics).

Detection of photogenerated acoustic waves. The generation is achieved either by amplitude-modulation (photoacoustic spectroscopy, PAS) or by a pulse (laser-induced optoacoustic spectroscopy, LIOAS, or photoacoustic calorimetry, PAC). The pressure wave after photoirradiation 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*, *optical 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 a different matrix, temperature, polarization of the excitation light, and excitation wavelength. However, the complete separation is very difficult to obtain experimentally and only few examples have been reported thus far. 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 (acousto-optic effect), photoacoustic spectroscopy is preferred. A photoacoustic spectrum consists of a plot of the intensity of the acoustic signal detected by a microphone or a "piezoelectric" detector, against the excitation wavelength or another quantity related to the photon energy of the modulated excitation. Experimentally, there are many versions of this spectroscopy. Designs (resonance condition, shape, etc.) of the cell, detectors, and excitation methods are subject of modifications. Only some terminologies describing the modifications are listed below. See also GB 301-2.

acoustic resonator
Chamber (e.g., cylinder) to store energy by a standing acoustic wave. The corresponding amplification of the photoacoustic signal is characterized by the quality (Q) factor.

acoustic ringing
Acoustic signal due to multiple reflection in the cell.

acoustic transit time
Time required for the acoustic wave to cross the excited region.

amplitude-modulated photoacoustics (continuous excitation photoacoustic)
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 to the n-th (n: integer) power of 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).

cell constant
Quantity of a gas cell that reflects the sensitivity of the photoacoustic signal mainly used in photoacoustic trace gas analysis.

See *set-up constant.*

composite piston effect
Generation of acoustic waves through a combination of the *thermal piston effect* and a contribution of modulated surface thermoelastic expansion, which acts as an acoustic driver on a contacting column of gas.

dichroism photoacoustic spectroscopy
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
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 infrared (FTIR) acoustic signal
Pressure-wave signal created after photoexcitation by infrared radiation and detected with a Michelson interferometer. After taking 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 FTIR spectroscopy.

front-face-excitation photoacoustic signal
Pressure-wave signal detected by a device with front-face irradiation, where the transducer is behind a mirror in the path of the laser beam and the sample solution is placed there in a cell. The time resolution is somewhat improved by this configuration compared with the conventional *perpendicular excitation acoustic signal.*

gas coupling
Acoustic-wave detection method in which the pressure wave created in a photoilluminated condensed phase sample is detected by a gas-phase microphone.

gas microphone photoacoustic effect
Effect caused by the acoustic pressure wave that arises from the thermal piston effect or the composite piston effect in a photothermally heated material and detected by means of a gas microphone.

high-*Q* resonator
Highly optimized acoustic cell (low surface losses, small openings, small microphone, etc.) having a quality factor (Q) near the theoretical value (spheres: $Q \sim 2000–10\,000$, cylinders: $Q \sim 1000$) for measurements in metrology.

intermodulated photoacoustic Stark spectroscopy
Experimental concept proposed to enhance the selectivity in the gas-phase PA measurements by using an intensity-modulated (f_1) laser radiation source and a periodically modulated (f_2) electric field that is applied in a direction perpendicular to the propagation of the laser beam. This causes the molecular energy levels to shift by the interaction between a dipole moment of the molecule and the applied electric field. The PA cell is designed to resonate at frequency f_{res} that is equal to that of either a sum frequency ($f_1 + f_2$) or a difference-frequency ($f_1 - f_2$) sideband. The lock-in detection is performed at the frequency $f_{\mathrm{de}} = f_{\mathrm{res}}$.

laser intracavity photoacoustic spectroscopy
Experimental concept that implies placing of the resonant PA cell within the optical cavity of the laser. This increases the effective power incident on the gaseous sample in the PA cell and therefore enhances the sensitivity.

laser ultrasonics
Excitation and detection of ultrasonic waves with laser radiation.

liquid coupling
Acoustic-wave detection method in which the pressure wave transmitted into liquid from a photoilluminated sample is detected.

low-*Q* resonator
Resonator with low-quality factor (Q) (e.g., $Q < 50$ in cylindrical cells). This is often used in trace gas detection, to avoid a sharp acoustic resonance profile that requires a high stability of the modulation frequency.

open photoacoustic cell
Photoacoustic cell design, in which the radiation absorbing material is attached directly to the miniature microphone. It is the small volume of air adjacent to the metallized diaphragm, which acts as the traditional PA cell.

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

optothermal window
Photoacoustic cell in which the gas inside a normal sample cell has been replaced by a thin plate of solid material (e.g., sapphire) characterized by a large thermal expansion coefficient in the radial direction. The expansion/contraction of the plate that carries the sample are usually detected either by means of the ring formed piezoelectric crystal glued to the irradiated side of the plate crystal or by a thermistor. The strength of the photothermal signal depends on the absorption of radiation taking place within one thermal diffusion length beyond the surface of the sample.

perpendicular excitation acoustic signal
Pressure-wave signal detected by a device in which the transducer is located perpendicular to the excitation light path.

See *front-face-excitation photoacoustic signal*.

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

piezoelectric transducer (piezoelectric detector)
Device that detects the electric field produced when strained. Conversely, piezoelectric materials become strained when placed in an electric field. Certain ceramic crystals such as lead zirconate titanate, and lead metaniobate or certain films (e.g., polyvinylidene difluoride film) are piezoelectric and are frequently used to detect the pressure wave as an electric signal in the photoacoustic spectroscopy.

photoacoustic microscopy
Imaging technique in which a light beam such as a collimated laser beam is focused on a small spot in a sample. 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, 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.

set-up constant
This term should be used instead of the misleading term “cell constant” because this quantity used in photoacoustic trace gas analysis depends not only on the properties of the gas cell, but on the complete set-up, such as the type of laser used for excitation and the laser beam-cell configuration controlling the acoustic modes excited (e.g., laser beam along cylinder axes or different arrangement).

Stark modulation of photoacoustic spectroscopy
Modulation of the electric field in a photoacoustic cell in order to modulate the absorbance of molecules exhibiting a permanent dipole moment. Pressure wave induced by this modulation is detected by the photoacoustic method.

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, it is possible to obtain kinetics of the system as well as information on medium acoustic properties.

thermal piston effect
Modulated heat flow from a heated condensed phase into an adjacent gas layer, causing thermally modulated expansion and contraction of the gas layer over a thickness approximately equal to the thermal diffusion length. The modulated gas layer expansion acts as a piston that drives acoustic waves into the gas column.

ultrasonics
Investigation of acoustic waves (surface and bulk) with frequencies between 2×10^4 Hz (audible sound) and 10^{10} Hz (hypersound).

wavelength-modulated photoacoustic spectroscopy
Wavelength of the excitation radiation is temporally modulated, and the resulting acoustic wave processed by a lock-in amplifier.

3.4 Photothermal radiometry [4,7,8]

(Pulsed) photothermal radiometry (back-scattering 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 (IR) 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 radiant excitance (or emitted radiant flux) of a black body, M_{bb}, is proportional to the fourth power of the temperature, T, over an infinite spectral detection bandwidth:

$$M_{\mathrm{bb}} = \sigma T^4$$

where $\sigma = 2\,\pi^5 k^4 / 15 h^3 c_0^{\,2} = 5.670\,51\,(19) \times 10^{-8}\ \mathrm{W\,m^{-2}\,K^{-4}}$ is the Stefan–Boltzmann constant. In real IR emitters, this equation is replaced by:

$$M = \varepsilon \sigma T^4$$

where ε is the emittance, a material property. Hence the relative change in radiant excitance, δM, arising from a temperature change δT induced by photoirradiation is, for emittance,

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

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 those samples emit.

optothermal transient emission radiometry
Technique that uses pulsed optical excitation and thermal infrared detection for nondestructive and noncontact inspection of the condensed-phase materials.

radiometric microscopy
Imaging technique in which a collimated laser beam is focused on a small spot in a sample and the radiometric signal 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 [4,5,7,8]

Photothermal calorimetry, transient thermography.

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

bolometer
Detector constructed from a material having a large temperature coefficient of resistance. Absorption of radiation gives rise to a change in resistance. A bolometer is named according to its active component, e.g., thermistor bolometer, semiconductor bolometer, superconductor bolometer (GB 45).

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

See also *pyroelectricity* and *pyroelectric detector.*

photopyroelectric spectroscopy
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.

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

pyroelectric detector
Detector (based on the temperature dependence of ferroelectricity in some crystals), which produces an electrical signal proportional to the energy flux on the collector surface (GB 327).

See also *pyroelectricity.*

thermal-wave cavities
Term attributed to photothermal devices exploiting coherent thermal-wave power confinement between two parallel walls, detected by a suitable sensor, such as a thin-film pyroelectric transducer or the other

photothermal methods such as *photothermal deflection*. The thermal analog of acoustic standing-wave cavity resonators, operating on the principle of linear superposition of thermal waves, amplified by confinement.

thermistor
Semiconductor device that has a large temperature-dependent electric resistance.

thermocouple
Device based on the thermoelectric effect, by which two junctions between dissimilar conductors (metallic or heavily doped semiconductors) kept at different temperatures generate an electric potential (GB 417).

thermoelectric power, Thomson coefficient
Thermoelectric force divided by temperature difference causing the force.

thermoelectromotive force, E
The electric potential generated by a *thermocouple*.

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 photoexcited 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 [4,7,8]

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).

The phase of a monochromatic radiation 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
Device that detects the interference of light. Generally, a light beam from one light source is divided into two beams. The resulting two beams are later recombined and superimposed (see also GB 204).

3.7 Photothermal deflection [4,7,8]

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

The photothermal deflection method is defined by a detection of the deflection of a probe beam induced by photoirradiation of a sample. There are two sources of the photothermal deflection effect. One is induced by crossing a nonuniform spatial profile of the refractive index gradient after a photothermal excitation, which is often referred as mirage effect or optical probing of the acoustic refractive gradient. When the temperature change in the medium is nonuniform, it results in a refractive index gradient through the contributions of eqs. 1 and 2. The temperature change could be also established by thermal diffusion. The spatial gradient in the refractive index changes the propagation direction of the probe beam. Spatially nonuniform refractive index distribution arises from many sources besides the thermal effect as described in Section 3.1. The other source comes from topographical deformation of the surface, on which the probe beam is deflected. This effect may be called (surface) photothermo-elastic effect or surface photothermal deflection.

collinear deflection method
Photothermal deflection method that uses a probe beam that is collinear or quasi-collinear with the pump beam.

(direct) mirage effect
Probe-beam deflection for a probe light that passes on the same side of the photoilluminated interface, which is induced by a nonuniform spatial profile of the refractive index gradient.

reverse mirage effect
Probe-beam deflection for a probe light that passes on the opposite side of the photoilluminated interface.

surface (photothermal) deflection
Probe beam deflected from a surface changes direction when heterogeneous expansion occurs on the surface.

transverse deflection method
Photothermal deflection method in which the probe-beam propagation direction is perpendicular to that of the pump beam.

3.8 Photothermal reflection change [7,8]

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. Similar to *photothermal deflection*, there are two types of signal sources. One effect is produced by the temperature-dependent reflectivity of a surface. 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 affect the reflection. The other source comes from topographical deformation of the surface, on which the probe beam is deflected. This effect may be called “(surface) photothermal topographical deflection” or photothermal surface reflection.

laser-induced curvature deformation
Change of flatness of a plate (usually on one side only) produced by optical irradiation (usually by a laser beam), which induces differential surface stress. The effect can be transient or permanent.

laser-induced surface displacement (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).

reflectivity
Ratio of the intensity of the reflected light from a surface to that of the incident light.

3.9 Related methods [2,3,6]

The spectroscopies listed in Sections 3.1~3.8 are generally considered to be in the category of the photothermal spectroscopy. There are other methods that are capable of detecting the photothermal effect; these are summarized in alphabetical order in this section.

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 changes of fluorescence intensity.

See also *hot band* in Section 4.

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 Section 3.4.

laser-induced capillary vibration
Detection of capillary vibration as a result of illumination of a stretched capillary. If the substance in the capillary absorbs the optical radiation, 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
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
Photon-energy dependence of the optical-to-thermal transition probability in an absorbing medium with an excited-state manifold. This spectroscopic mode, important in identifying thermal transition ranges with low optical (radiative) yield in optical media, can be performed using some photothermal detec-

tion 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
Inelastic light-scattering phenomenon from a material, in which the wavelength of the scattered light differs from that of the incident light by the excitation. In classical Raman scattering, excitation occurs off resonance, but resonance Raman excitation takes place with population of excited electronic states. The Raman scattering on the lower-frequency side of the excitation line is called Stokes Raman scattering and that on the higher-frequency side is called anti-Stokes Raman scattering. The principal scattering mechanism involves energy loss (or gain) to an active mode having a change in polarizability with intensity. Generally, various excitation or de-excitation processes such as the rotational excitation, vibrational excitation, electronic excitation, excitation of spin state, etc. are involved. Because 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, this ratio can be used to monitor the temperature.

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

4. RELATED TERMS [1–11,14–16]

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
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
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
Magnetic field effect on the real part of the relative permittivity. It leads to linear birefringence.

See *magneto-optical effect.*

dc Kerr effect
See *electro-optical effect.*

degenerate four-wave mixing, DFWM
Four-wave mixing experiment with the same frequency of the four optical radiation 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: $\omega_1 = \omega_2 = \omega_3 = \omega_4$, $k_1 = -k_2$, $k_3 = -k_4$.

delayed fluorescence
Three types of delayed fluorescence are known:

1. E-type delayed fluorescence: Process in which the first excited singlet state becomes populated by a thermally activated *radiationless transition* from the first excited triplet state. Since in this case the populations of the singlet and triplet states are in thermal equilibrium, the lifetimes of delayed fluorescence and the concomitant *phosphorescence* are equal.
2. P-type delayed fluorescence: Process in which the first excited singlet state is populated by interaction of two molecules in the triplet state (triplet-triplet *annihilation*) thus producing one molecule in the excited singlet state. In this biphotonic process the lifetime of delayed fluorescence is half the value of the concomitant phosphorescence.
3. Recombination fluorescence: The first excited singlet state becomes populated by recombination of *radical ions* with electrons or by recombination of radical ions of opposite charge (GB 105).

depth of penetration
Inverse of the linear absorption coefficient. 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 (GB 107, where linear absorption coefficient is not clearly specified).

depth profiling
Sensing or determining the depth variation of a material's thermal and/or optical properties by photothermal measurements, which vary the thermal diffusion length of thermal waves used to probe a material.

diffuse photon-density wave
Optical oscillation in a scattering (turbid) medium 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.

diffusion wave
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., photoexcited electrons) or continuous mass are 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, which are analogous but not identical to conventional square-law reflection and transmission phenomena. Examples of such coherent oscillations are thermal waves, diffuse photon density waves, and electronic carrier density waves.

Dufour effect
Temperature gradient induced by presence of a concentration gradient.

See also *Soret effect*.

elastic heat wave
Elastic wave induced by the thermal motion.

electrocaloric effect
Heat induced by *electrostriction* and *optical Kerr effect.* This effect is similar to the conventional 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
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 the frequencies that are of the order of the inverse of the recombination lifetime of the carrier, as a spatially heavily damped concentration oscillation.

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

electrostriction
Decrease in dimension of a substance in an electric field. In photothermal spectroscopy, it is used to mean a density change of a substance due to the interaction of the charge or dipole (or change in dipole moment) or polarizability of a molecule created by photoabsorption and the medium.

external calorimetric reference
Molecules that can be used as a *calorimetric reference* in an experiment in place of the sample itself.

See *calorimetric reference* in Section 3.3.

Faraday effect
Magnetic field effect on the imaginary part of the dielectric constant (relative permittivity) that leads to a circular birefringence. The plane of polarization of a linearly polarized optical radiation is rotated upon longitudinal propagation through a magnetic field.

See *magneto-optical effect.*

flow rate (of a quantity), q_X
Quantity X (e.g., heat, amount, mass, volume, etc.) transferred in a time interval divided by that time interval (GB 159).

fluorescence
Spontaneously emitted radiation that ceases immediately after the exciting radiation is removed.

Note: Fluorescence is interpreted in molecular terms as spontaneous emission arising from a transition between two molecular states with the same electron multiplicity (compare GB 159).

flux (of a quantity), J_X
Flow rate of X through a cross-section perpendicular to the flow divided by the cross-sectional area (GB 160).

four-wave mixing, FWM
Interaction of four waves having 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 nonlinear polarization of the material. This category includes 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, transient lens, and transient absorption.

heat flux, J_q
Heat transferred through a cross-section perpendicular to the flow in a small time interval divided by that time interval and the cross-sectional area (GB 182).

See also *flux.*

heat transfer
Transfer of thermal energy through the processes of conduction, convection, and radiation. These processes may occur singly or in conjunction.

Note: A photothermal signal decreases with time owing to cooling of the sample by heat transfer to the surroundings.

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

internal calorimetric reference
Sample that can serve as a *calorimetric reference* by itself.

See *calorimetric reference* in Section 3.3.

internal conversion
A photophysical process. An 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, it usually undergoes deactivation to its lowest vibrational level, provided the final state is not unstable to dissociation. The excess energy is generally converted to the translational energy, i.e., to the thermal energy (GB 104).

intersystem crossing, ISC
A photophysical process. An isoenergetic *radiationless transition* between two electronic states of different multiplicities. It often results in a vibrationally excited molecular entity in the lower electronic state, which then usually deactivates to its lower vibrational level. The excess energy is generally converted to the translational energy, i.e., to the thermal energy (GB 104).

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.

inverse problem
Reconstruction of an unknown depth or spatial profile of optical and/or thermal properties of a sample by application of a mathematical model to the photothermal measurement data, typically with minimal prior information and/or assumptions about the profile structure.

light-heat conversion efficiency, ϕ_{nr}
Thermal energy emitted by the photoirradiated system divided by the input photon energy.

Note: Thermal energy from a *radiationless transition* flows ultimately into the translational modes of the medium. Therefore, this conversion efficiency is the same as the quantum yield for the radiationless transition.

magneto-optical effect
Magnetic field effect on the dielectric constant (relative permittivity).

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
Absorption process involving interaction of two or more photons with a molecular entity. The interaction may be coherent or incoherent.

See *multiphoton process* (GB 267).

nonradiative rate constant, k_{nr}
First-order rate constant for disappearance of an excited species due to a nonradiative transition or the sum of these rate constants if there are more than one nonradiative transitions.

nonradiative transition
See *radiationless transition.*

optical breakdown
Catastrophic breakdown in a transparent medium by a strong electromagnetic field.

optical Kerr effect, OKE
Double refraction (birefringence) in liquids or solids induced by an electric field of radiation.

Note: The difference in refractive index is proportional to the square of the field. In liquids, both the electron distribution and the orientation of a polarizable, anisotropic molecule are affected through interaction between a permanent or induced dipole and the electric field contributions to the OKE. The contribution from distortion of the electron distribution is called the electronic response of the OKE, while the contribution from molecular reorientation is called the nuclear response of the OKE. Frequently, molecular, librational, and orientational redistribution are included as other contributions to the OKE.

See *electro-optical effect* and *Pockels effect.*

penetration depth
See *depth of penetration.*

phosphorescence
Spontaneously emitted radiation that may persist for long periods, typically from seconds to milliseconds.

Note: In molecular terms the term designates luminescence involving a change in electron spin multiplicity, typically from triplet to singlet or vice versa. The luminescence from a quartet state to a doublet state is also phosphorescence (compare GB 301).

photocarrier modulation
Light-induced temporal variation of electrical carrier concentration in an optically sensitive semiconductor device.

photoelasticity
Change of optical properties owing to a mechanical stress. The strain caused by the application of a stress may change the refractive index.

photorefractive effect
Change in the refractive index via the photoinduced electric field modulation in the material. After being generated, photoelectrons migrate in a lattice and are subsequently trapped at new sites. The resulting space charges give rise to a change of the refractive index via the *electro-optical effect*.

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

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

photovoltaic effect
Generation of an electric potential in a substance on absorption of light.

Pockels effect
See *electro-optical effect* and *optical Kerr effect*.

purely thermal-wave interferometry
Interferometry as 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.

quantum yield
Number of defined events divided by the number of photons absorbed by a system. The integral quantum yield is:

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

For a photochemical reaction:

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

The differential quantum yield is:

$$\Phi = \mathrm{d}[x]/\mathrm{d}t/n$$

where $\mathrm{d}[x]/\mathrm{d}t$ 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 be used for photophysical processes or photochemical reactions (GB 330).

quantum yield of fluorescence, Φ_f
Number of photons emitted by fluorescence divided by number of photons absorbed by the system.

radiationless transition
Transition between two states of a system without photon emission or absorption (GB 335).

Note: Energy is transferred in the transition to translational, rotational, vibrational, and electronic degrees of freedom.

radiative rate constant, k_r
First-order rate constant for a radiative decay process of an excited species or the sum of these rate constants if there are more than one radiative decay processes.

skin depth
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
Production of a gradient of concentration when a gradient of temperature is imposed on a mixture.

Stefan–Boltzmann law
See introduction of Section 3.4.

stimulated Brillouin scattering
Scattering process due to the sound wave generated by photoirradiation.

stimulated light scattering
Scattering process due to material response created by light irradiation. In spontaneous light scattering, radiation is diffracted as a Fourier component of a spontaneous statistical fluctuation of material response. In analogy with 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 produced by light irradiation.

See *Raman scattering* in Section 3.9.

stimulated Rayleigh scattering
Scattering process due to temperature fluctuation of the medium generated by light irradiation.

Stokes Raman scattering
See *Raman scattering* in Section 3.9.

Stokes shift
Difference (usually in frequency units) between the spectral positions of the band maxima (or the band origin) of the absorption and luminescence arising from the same electronic transition. Generally, the luminescence occurring at a longer wavelength than the absorption is stronger than the opposite. The latter may be called an anti-Stokes shift (GB 399).

thermal conductance, G
Heat *flow rate* divided by the temperature difference.
See *flow rate*.

thermal conductivity, λ
Tensor quantity relating the *heat flux*, $\boldsymbol{J}_q$, to the temperature gradient, $\boldsymbol{J}_q = -\lambda \operatorname{grad} T$ (GB 416).

thermal diffusion length
Distance over which thermal waves damp or diffuse away from a heat source (which may be either periodically modulated or pulsed). In the case of a periodically modulated heat source, the thermal diffusion length is given by $(2a/\omega)^{1/2}$, where a is the thermal diffusivity; ω is the angular modulation frequency and describes a damping distance away from the source. In the case of a pulsed heat source, the thermal diffusion length describes a diffusion distance away from the source that is $(4at)^{1/2}$, where t is the observation time past application of an impulse.

thermal diffusivity, a
Thermal conductivity divided by the product of specific heat capacity at constant pressure and density.
See *thermal conductivity*.

thermal effusivity
Formally defined as $(\lambda\rho c_p)^{1/2}$ where λ is the thermal conductivity, ρ the mass density, and c_p the specific capacity at constant pressure. At an interface between materials of dissimilar thermal properties, this quantity behaves analogously to a refractive index ratio for thermal waves, controlling processes of accumulation (reflection) and depletion (damping) of diffusion waves.

thermalization time, τ_{th}
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 indicate the relaxation time needed to establish the Boltzmann distribution in the translational mode.

thermally activated delayed fluorescence
See *delayed fluorescence*.

thermal stress
Stress induced by temperature change.

thermal wave
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. Penetration is deeper in nonopaque materials.

thermochromism
Thermally induced transformation of a molecular structure or of a system (e.g., of a solution), thermally reversible, that produces a spectral change, typically, but not necessarily, of visible color (GB 417).

thermoluminescence

Luminescence arising 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 generated by the thermal activation from a metastable state (GB 418).

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. After the energy is deposited into a molecular system, the energy on a fast scale 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 QUANTITIES INVOLVED IN PHOTOTHERMAL EFFECTS

See the IUPAC Green Book [17] for definitions of many of these quantities.

Name	Symbols	SI unit
absorbance	A	1
absorption coefficient		
(linear) decadic	a	m^{-1}
(linear) napierian	α	m^{-1}
absorption cross-section	σ	m^2
absorption index	k	1
Boltzmann constant	k, k_B	$J\ K^{-1}$
Bragg angle	θ	rad
circular frequency	ω	s^{-1}, rad s^{-1}
coefficient of heat transfer	h	$W\ m^{-2}\ K^{-1}$
compressibility (isothermal)	κ_T	Pa^{-1}
(isoentropic)	κ_S	Pa^{-1}
conductivity	σ	$S\ m^{-1}$
density	ρ	kg/m^3
diffusion coefficient	D	$m^2\ s^{-1}$
electric dipole moment	$\boldsymbol{p}$, μ	C m
electric polarization	$\boldsymbol{P}$	$C\ m^{-2}$
emittance	ε	1
enthalpy	H	J
entropy	S	$J\ K^{-1}$
expansion coefficient		
linear	α_l	K^{-1}
cubic	α, α_v, γ	K^{-1}
frequency	ν, f	Hz
fringe spacing of grating	Λ	m
grating wavenumber	q	m^{-1}
heat	Q	J
heat flow rate	$\boldsymbol{\Phi}$	W
heat flux	J_q	$W\ m^{-2}$
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}	1
magnetic permeability	m	$N\ A^{-2}$
mass density	ρ	$kg\ m^{-3}$
molar volume change	ΔV_m	$m^3\ mol^{-1}$
nonradiative rate constant	k_{nr}	s^{-1}
n-th hyper-susceptibility	$\chi^{(n)}$	$(m\ V^{-1})^n$
number concentration	C	m^{-3}
order of reflection	n	1
Peltier coefficient	Π	V
permittivity	ε	$F\ m^{-1}$
Planck constant	h	J s
pressure	p, P	Pa ($N\ m^{-2}$)
quality factor of cavity	Q	1

Name	Symbols	SI unit
quantum yield	Φ	1
quantum yield of fluorescence	Φ_f	1
quantum yield of intersystem crossing	Φ_{isc}	1
quantum yield of nonradiative transition	Φ_{nr}	1
quantum yield of phosphorescence	Φ_p	1
radiant energy	Q	J
radiant exitance (emitted radiant flux)	M	W m^{-2}
radiant power	Φ	W
radiative rate constant	k_r	s^{-1}
refractive index	n	1
reflectance	ρ	1
relative permittivity	ε_r	1
shear viscosity	η_s	kg m^{-1} s^{-1}
specific heat capacity at constant volume	c_v	J K^{-1}
specific heat capacity at constant pressure	c_p	J K^{-1}
specific heat capacity ratio	$\gamma = c_p/c_v$	1
speed of light	c_o	m s^{-1}
Stefan–Boltzmann constant	σ	W m^{-2} K^{-4}
surface shear viscosity	η_s	kg s^{-1}
surface tension	γ, σ	N m^{-1}
temperature	T	K
thermal conductance	G	W K^{-1}
thermal conductivity	λ, k	J m^{-1} s^{-1} K^{-1}
thermal diffusivity	a	m^2 s^{-1}
thermal effusivity	J, e	W $s^{1/2}$ K^{-1} m^{-2}
thermalization time	τ_{th}	s
thermal resistance	R, Z	K W^{-1}
transition dipole moment	$\boldsymbol{M}$	C m
transmittance	T	1
thermoelectric force, Thomson coefficient	μ	V K^{-1}
velocity	v	m s^{-1}
wavelength of light	λ	m
wavelength of sound	λ_{ac}	m

6. CUMULATIVE ALPHABETICAL LIST

*Indicates that the term is not explained in the Glossary, but appears below the heading of the subsection.

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