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Two Methods of Two-Step Excitation Thermal Grating Technique for Detection of Transient Absorption and Stimulated Emission

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Two different methods for detection of the transient absorption (TA) and stimulated emission (SE) by using a two-step excitation thermal grating technique are characterized. The sensitivity and the temporal profile of the signals are analyzed in detail. One of them, prepulse−(delay)−grating pulse sequence, provides a very sensitive TA detection with a zero background. The other one, grating pulses−(delay)−boosting pulse sequence, has also a very high sensitivity for the detection of TA and SE together with an easy probe wavelength scanning. The high sensitivity of these methods comes from the cyclic excitation of the excited state and accumulation of the thermal energy. These methods are used to measure the T_1-T_n absorption spectrum of benzophenone, and the T_1-T_n absorption and SE spectra of rhodamine 6G.

1. Introduction

The transient absorption (TA) detection method is very powerful for identification and also studying the dynamics of excited states or transient species. In many cases, TA is detected by observing the decrease of probe light intensity induced by a preexcitation of a sample. One of the difficulties for that conventional method is a rather low sensitivity, which comes from the large background light of the probe. The other limitation of the direct detection method is that the signal is easily disturbed by luminescence from the excited states. Consider fluorescence in monitoring a S_1-S_n absorption for an example, the preexcitation will induce fluorescence and it should have the same time dependence as the S_1-S_n absorption signal. The fluorescence must be subtracted from the observed signal and considerable error can be introduced in the subtraction. To overcome these difficulties, many modifications of the direct detection method have been proposed such as TA detection by monitoring emission or photoinduced ions. One of the attractive ways is the photothermal detection of TA. In this modification, the absorption of light is detected as the thermal energy released by the nonradiative transition from the higher excited states. Thus there should be no interference from the luminescence. For example, the photoacoustic method has been reported for the TA detection with a high sensitivity.[1−3] The thermal lens method is another way for that purpose.[4,5] Here I will show two methods of the two-step excitation transient grating (TSETG) detection technique for the detection of TA, compare both methods each other, and characterize the temporal profiles and sensitivities.

In the transient grating (TG) experiment, two coherent laser beams with a parallel polarization (grating pulses) are crossed at one spot within a coherence time. The interference between the beams creates a sinusoidal modulation of the light intensity, $I(x,t)$ (J/cm^2):

$$I(x,t) = 2h\nu_0 I_0 \delta(t)(1 - \cos(qx)) \qquad (1)$$

where I_0 is the photon number of the grating laser (photons/cm^2), $h\nu_0$ is the photon energy (J/photons), the temporal profile of the laser pulse is assumed to be very short for simplicity reason, the grating is created along the x axis, and q is the grating wavevector. The magnitude of the vector is given by $|q| = 2\pi/\Lambda$ (Λ is the fringe spacing). Due to this periodic photoexcitation, the refractive index and/or absorbance of the sample is periodically modulated by the spatial-dependent concentration of the excited states (population grating), and the spatial modulation diffracts another probe beam to a well-defined direction as the TG signal. When the excited state relaxes nonradiatively, the energy eventually heats the matrix and it produces the refractive index grating (thermal grating). In this sense, this method is one of the photothermal techniques. Since this is a background-free method, even very weak absorption can be detected. Recently, a transient grating (TG) detection method of TA using the population grating contribution has been proposed with probing by a white-light continuum.[6] On the other hand, the two methods, which will be discussed here utilize the thermal grating component. These thermal grating methods have several unique advantages over the conventional direct detection of TA, the population grating technique, or other photothermal methods.

In the first method (TSETG-I), a spatially uniform prepulse is first irradiated to a sample to create excited states. After a temporal delay, the excited state is further excited by the grating pulses. The thermal energy by the relaxation from the upper excited states creates the thermal grating signal. This method was first demonstrated by Miller et al. for detecting excited-state absorption of pentacene in a *p*-terphenyl host very sensitively using the acoustic signal.[7] It has also been applied to a study of the energetic dynamics from a higher excited state previously.[8]

The other one (TSETG-II) uses grating pulses to create the excited states at first. The spatially periodic modulation of the excited states and subsequent thermalization process creates the TG signal. When a spatially uniform probe light is irradiated after some delay (but before the excited states completely relax), TA could occur in the bright region of the interference pattern not in the dark region, because the efficiency of TA depends on the concentration of the excited states, which were created by the grating pulses. In this case, the amplitude of the spatial modulation of the temperature rise increases by the irradiation

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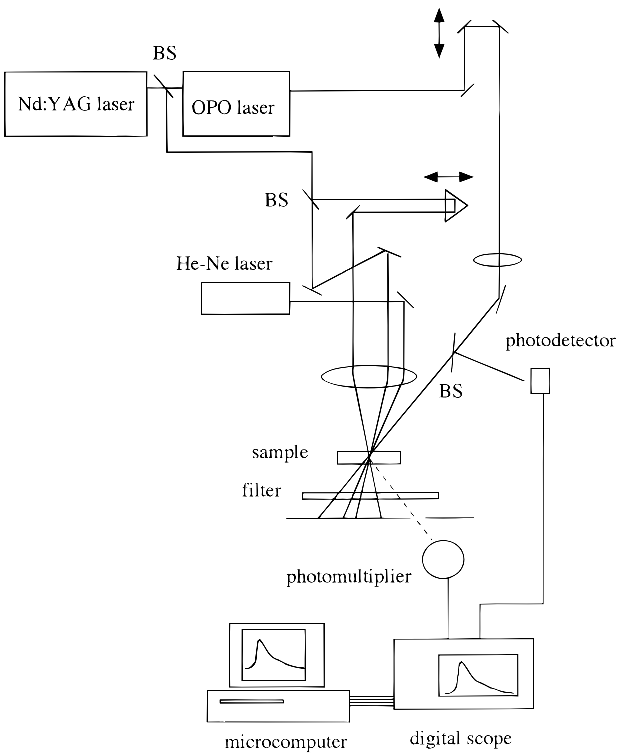


Figure 1. Schematic illustration of the experimental setup for the TSETG-II method (BS: beam splitter).

of the second pulse, and the TG signal, too. If the uniform laser light induces the stimulated emission, the amplitude (and the TG intensity) decreases as described in detail later. The second probe pulse acts as a boosting or suppressing of the TG signal. Although a similar method has been used for studying the photochemical reaction rate from higher excited states by monitoring the population grating in rigid matrix,[9] this method has not been fully characterized as the thermal detection for TA or stimulated emission (SE).

In this paper, these two methods are characterized and investigated as the sensitive TA and SE detection methods. The TSETG-I detection provides a zero background signal with a high sensitivity, but a TA spectrum is difficult to be measured. On the other hand, although the TSETG-II technique gives a background signal, the TA spectrum can be easily recorded. Furthermore, a strong enhancement of the TG signal in the TSETG-II method, which indicates a cyclic excitation of the excited state within a grating pulse width makes this method very sensitive. An excellent sensitivity even for strongly fluorescent dye is demonstrated for a rhodamine 6G sample. These two methods are complemental and provide excellent tools for the TA detection.

2. Experimental Section

Experimental setup for the two step excited TG method (the TSETG-II) is schematically illustrated in Figure 1. The setup for the TSETG-I is similar to that reported previously.[8] For the TSETG-I experiment, a SHG or THG beam of a Nd:YAG laser (Spectra-Physics, GCR-170) was used for creating the excited state (prepulse). After a short delay, an output beam from an OPO laser system, which was pumped by the Nd:YAG laser (MOPO710) was split into two by a beam splitter and introduced to the prepulse-irradiated region. A He−Ne laser was used for probing the transient grating.

For the TSETG-II experiment, the THG or SHG laser beam was irradiated to the sample first under the grating condition. After a short delay, the OPO laser light uniformly illuminated the grating region. Generally the grating pulses in both cases were slightly focused (1 mm o.d.) and the spatially uniform light covered the grating region with a wider beam radius (3 mm o.d.). The laser power of the OPO laser was monitored simultaneously. The TG signal was isolated from scattered light or luminescence by a glass filter, an interference filter, and a pinhole and was detected by a photomultiplier (Hamamatsu R928). The temporal profile was averaged by a digital oscilloscope (Tektronix 2430A). The data were transferred and analyzed by a microcomputer.

3. Two-Step Excitation TG Signal Intensities

Here only thermal effect under an isobaric condition will be considered as the source of the refractive index change (thermal grating).[10] The time dependence of the thermal grating signal is determined by the thermal diffusion among the fringes and can be calculated by solving the thermal diffusion equation. Since the rate constant is $D_{th}q^2$ (D_{th} is the thermal diffusivity of the material), which is in the range of 100 ns−100 μs, the temporal region of the signal can be very different from the time region in which the excited state exists. Therefore the signal is hardly disturbed by luminescence from the sample, which sometimes limits the sensitivity of TA under the direct detection method. There should be no difficulty to extend the treatment to other TG effect such as the population grating or acoustic signal.

(A) TSETG-I Method. The sample is first irradiated uniformly by a prepulse to create the excited states. Then the second grating pulses whose wavelength is tuned to one of a TA band probe the absorption. Under a weak absorption condition, the concentration of the ith excited state ($C^*_i(t)$) created by the prepulse is given by

$$C^*_i(t) = \sigma_0(\lambda = p)I_pC_0f_i(t) \equiv C_0^*f_i(t) \qquad (2)$$

where $\sigma_0(\lambda = p)$ is the cross section of the ground-state molecule at the prepulse wavelength (cm^2), $f_i(t)$ time dependence of the ith excited state ($1 \geq f(t) \geq 0$), I_p photon number of the prepulse (photons/cm^2), C_0 initial concentration of the solute, and C_0^* is defined by an initial concentration of the directly prepared state, which is usually a vibrationally excited state in the singlet manifold. Molecules that is excited from the lowest level of the S_0 state to a vibrationally excited S_n state relax promptly to the lowest level of the S_1 state and the loss of the S_1 state takes place by spontaneous emission, internal conversion (ic), and intersystem crossing (isc) to the T_1 state, if any photochemical reaction is negligible. The spatially uniform-temperature rise by the nonradiative transition from the excited states ($\Delta T_1(t)$) is expressed by

$$\Delta T_1(t) = C_0^*h\nu_pQ(t)/C_p \qquad (3)$$

where $h\nu_p$ is the photon energy of the prepulse, C_p heat capacity of the sample per unit volume (J/cm^3 K), and $Q(t)$ is the time dependence of the heat releasing processes ($1 \geq Q(t) \geq 0$) (Figure 2(A-a)). Here we neglect the thermal diffusion from the light-irradiated region because usually it takes tens of milliseconds before the heat energy flows out completely and we will consider the time dependence in a time region of nano- to microseconds. Even if we neglect a photochemical reaction from the excited states, a part of energy of the excited

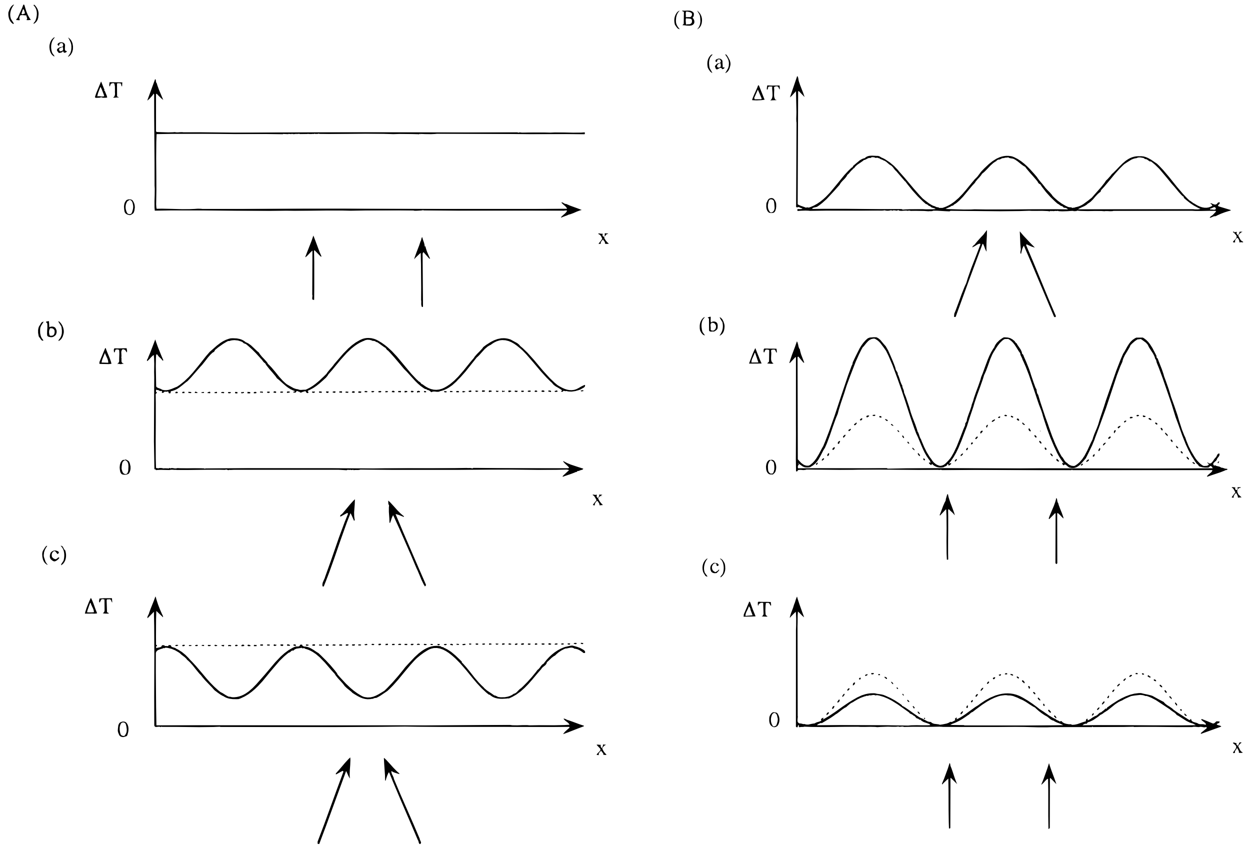


Figure 2. Temperature distributions of a sample for (A) TSETG-I and (B) TSETG-II method. (A) (a) After the prepulse, the temperature rises uniformly by the nonradiative transition from the excited states. (b) The transient absorption by the grating pulses creates the spatially modulated temperature distribution and it produces the TG signal. (c) The stimulated emission decreases the concentration of the excited state and temperature. (B) (a) After the grating pulse, sinusoidally modulated temperature is created. (b) The transient absorption by the boosting laser with a spatially uniform intensity enhances the temperature modulation, and (c) the stimulated emission suppresses the modulation.

states is not converted to the thermal energy but released as luminescence. In solution, generally phosphorescence can be neglected and the fraction of the heat releasing Q(∞) is given by

$$Q(\infty) = (h\nu_p - E_f\phi_f)/h\nu_p \quad (4)$$

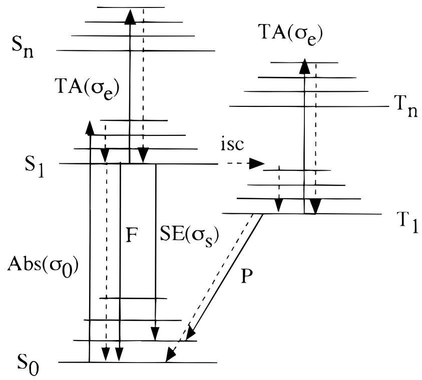
where E_f is the averaged photon energy of fluorescence and ϕ_f is the quantum yield of fluorescence. Applying another light (grating pulses) to the excited-state molecules at $t = t'$ induces TA, stimulated emission, and absorption from the S_0 state depending on the wavelength of the grating light.

(i) Effect of TA (Figure 2(A-b)): When the wavelength of the grating pulses is in the TA region, the excitation from the S_1 (T_1) state occurs to higher state within the singlet (triplet) manifold and the system very rapidly returns to the S_1 (T_1) state via internal conversion and vibrational relaxation within a few picoseconds (Scheme 1). We assume that any photochemical reactions, energy transfer or luminescence from the higher excited state are negligible. That promptly released energy generates heat and it raises the temperature. The temperature rise ($\Delta T_2(t)$) is now given by

$$\Delta T_2(x,t{>}t') = \Delta T_1(t) + \{C^*_i(t')\sigma_e I(x,t')/C_p\}\exp(-D_{th}q^2(t-t')) \quad (5)$$

where σ_e is the TA cross section from the ith excited state at the grating wavelength, and D_{th} is the thermal diffusivity of the medium. Under a weak diffraction condition, the TG signal intensity (I_{TG}) is proportional to the square of the peak-to-null difference of the temperature-induced refractive index change:

SCHEME 1



$$I_{TG}(t{>}t') = A\{(2(dn/dT)C^*_i(t')h\nu_0\sigma_e I_0/C_p)\exp(-D_{th}q^2(t-t'))\}^2 \quad (6)$$

where A is a constant which includes experimental parameters such as the probe laser power, sensitivity of the detector and the geometrical configuration, and dn/dT is the temperature coefficient of the refractive index of the solution.

(ii) Effect of SE (Figure 2(A-c)): When the grating light induces SE from the ith excited state, that excited state is forced down to the S_0 state and it decreases the temperature at the bright region of the interference pattern (reverse thermal grating). This is similar to the case of the thermal lens (TL) detection of

SE; in this TL case, a reverse TL (convex lens) is created as the result of SE instead of concave lens for a usual TL.[5] Since the vibrational relaxation in the ground state is very fast, the temperature rise (ΔT_2) under this condition is given by

$$\Delta T_2(x,t>t') = \Delta T_1(t) - \{C^*_i(t')\sigma_s I(x,t')/C_p\} \exp(-D_{th}q^2(t-t')) \quad (7)$$

where σ_s is the cross section of the SE. In this case, negative TG is created (low temperature in the bright region). The TG signal intensity is

$$I_{TG}(t>t') = A\{2(dn/dT)C^*_i(t')h\nu_0\sigma_s I_0/C_p) \exp(-D_{th}q^2(t-t'))\}^2 \quad (8)$$

(iii) Absorption from the S_0 state: If the wavelength of the grating light is in the region of an absorption band from the S_0 state, unexcited molecules by the prepulse would be excited. The temperature rise is

$$\Delta T_2(x,t>t') = \Delta T_1(t) + \{(C_0 - \sum_i C^*_i(t'))\sigma_0(\lambda=g)I(x,t')Q'(t-t')/C_p\}^*\exp(-D_{th}q^2(t-t')) \quad (9)$$

where * denotes convolution, $Q'(t)$ is the time derivative of Q (dQ/dt), and $\sigma_0(\lambda=g)$ is the absorption cross section of the ground state at the grating wavelength. The TG intensity is then given by

$$I_{TG}(t>t') = A\{2(dn/dT)(C_0 - \sum_i^{?} C^*_i(t'))h\nu_0\sigma_0(\lambda=g)I_0 Q'(t-t')/C_p)^*\exp(-D_{th}q^2(t-t')\}^2 \quad (10)$$

(B) TSETG-II Method. The sample is first excited by the grating pulse $I(x,t)$ to create the excited states. After a delay time, t', another boosting pulse is irradiated to the grating region to monitor TA or SE. Without the boosting laser, the concentration of the excited state (C^*_i) and temperature rise (ΔT_1) are described by

$$C^*_i(x,t) = \sigma_0(\lambda=g)C_0 I(x,t)f_i(t)/h\nu_0 \equiv C_0{}^*f_i(t)(1-\cos(qx)) \quad (11)$$

$$\Delta T_1(x,t) = \{C_0{}^*h\nu_0 Q'(t)(1-\cos(qx))/C_p\}^*\exp(-D_{th}q^2t) \quad (12)$$

The TG intensity (I_{TG}) in this case is expressed by

$$I_{TG}{}^0(t) = A\{2(dn/dT)C_0{}^*h\nu_0 Q'(t)/C_p\}^*\exp(-D_{th}q^2t)\}^2 \quad (13)$$

By applying the boosting pulse at $t = t'$, the TG signal intensity becomes stronger or weaker depending on the direction of the induced transition.

(i) Effect of TA (Figure 2(B-b)): When transient absorptions occur from the *i*th excited state by the boosting laser, the temperature is increased by the nonradiative transition from the higher excited states. This induced temperature rise has the same spatial distribution as the grating pattern.

$$\Delta T_2(x,t>t') = \Delta T_1(x,t) + (C^*_i(t')h\nu_b\sigma_e I_b(1-\cos(qx))/C_p) \exp(-D_{th}q^2(t-t')) \quad (14)$$

where $h\nu_b$ is the photon energy of the boosting light. The TG signal intensity is again given by the square of the peak-to-null refractive index change and expressed by

$$I_{TG}(t>t') = A[2(dn/dT)I_0\sigma_0C_0/C_p\{(h\nu_0Q'(t)^*\exp(-D_{th}q^2t) + f_i(t')h\nu_b\sigma_e I_b \exp(-D_{th}q^2(t-t'))\}]^2 \quad (15)$$

(ii) Effect of SE (Figure 2(B-c)): If the boosting laser induces the stimulated emission from the excited state, the temperature change at the bright region of the grating decreases from that without the boosting laser. Therefore the TG intensity decreases depending on the efficiency of SE, and we have

$$I_{TG}(t>t') = A[2(dn/dT)I_0\sigma_0C_0/C_p\{(h\nu_0Q'(t)^* \exp(-D_{th}q^2t) - f_i(t')h\nu_b\sigma_s I_b \exp(-D_{th}q^2(t-t')))\}]^2 \quad (16)$$

(iii) Absorption from the S_0 state: Due to the photoexcitation by the grating pulse, the concentration of the ground state decreases in proportion to the light intensity. Thus, if the boosting laser induces the ground-state absorption, the temperature rise in the dark region is more pronounced and the TG signal intensity is weakened. The intensity is given by

$$I_{TG}(t>t') = A[2(dn/dT)I_0\sigma_0C_0/C_p\{(h\nu_0Q'(t)^*\exp(-D_{th}q^2t) - (C_0 - \sum_i C^*_i(t'))Q'(t-t')h\nu_b\sigma_0 I_b{}^*\exp(-D_{th}q^2(t-t')))\}]^2 \quad (17)$$

In both the above treatments (TSETG-I and TSETG-II), we assume that the heat releasing from the higher excited state is instantaneous. However, if an energy-transfer process or a photochemical reaction takes place from the higher state, the heat releasing process can be time dependent within the observation time scale. In such a case, the kinetics of that step should be convoluted with the decay of the grating, $\exp(-D_{th}q^2)$, in eqs 6, 8, 12, and 14−16. By monitoring the temporal profile, not only the dynamics of the lowest excited state but also that of the upper state can be studied. This capability of continuous monitoring of the higher excited-state dynamics is one of prominent advantages of this method.

4. Results and Discussion

1. Benzophenone. *(A) TSETG-I.* Benzophenone (BP) in benzene sample (5×10^{-4} M) was irradiated first by the prepulse at 355 nm uniformly. When the second grating pulses are introduced to the previously illuminated region after 30 ns from the prepulse, a strong TG signal is observed (Figure 3). The signal decays with a lifetime of 5.2 μs. This lifetime agrees well with an expected lifetime of the thermal grating $(2D_{th}q^2)^{-1}$ = 5.3 μs, which indicates that the grating signal is originated from the thermal contribution. Since no TG signal is observed without the prepulse, the TG signal comes from the absorption by transient species.

Dynamics of BP after photoexcitation has been well studied, and it has been elucidated that the photoexcited singlet state is quickly relaxed to the T_1 state within 10 ps with a quantum yield of almost unity.[11] Photochemical reaction of BP in benzene is negligible, and there is a T_1−T_n absorption band around 540 nm region as shown later.[12] Therefore the observed TG is assigned to the thermal grating by the nonradiative transition from the higher excited triplet state. The signal rise is determined by the pulse width of the grating laser. This is consistent with the fast deactivation from the higher excited state. Any luminescence from the sample or scattered light of the laser can be eliminated by an appropriate optical filter. (In

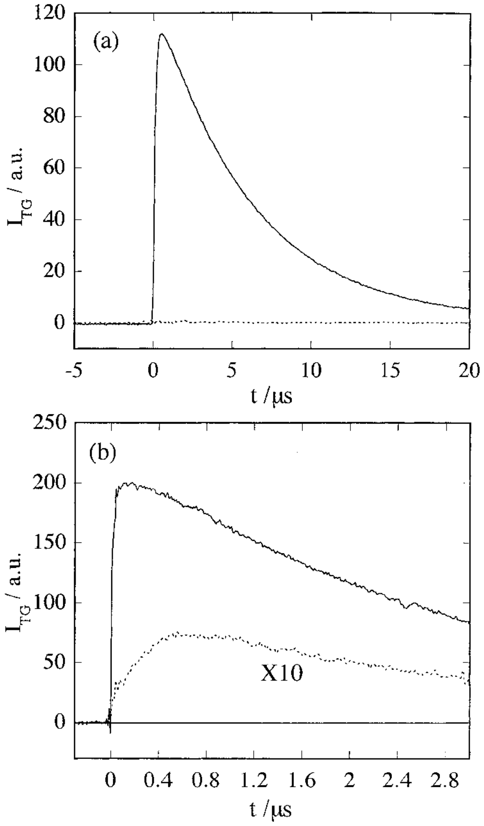


Figure 3. (a) TG signal under the TSETG-I condition of benzophenone in benzene (air saturated). The signal with prepulse is shown by the solid line. Without the prepulse (dotted line), there is no detectable light. (b) The TG signal of benzophenone under the TSETG-II condition. The signal with the boosting light (solid line) is strongly enhanced from that without the boosting light (dotted line).

this BP case, there is no luminescence.) Even unavoidable fluorescence only by the filter cannot disturb the TG signal because of the different time range of the signal from the emission. Therefore, this method is a zero background detection.[7,8] Since the ground-state absorption with an absorbance as small as 10^{-5} can be detected by our TG setup, this small absorbance change should be a detectable lowest limit of TA by this method. Moreover, considering the thermal enhancement by the cyclic excitation as described later, the detection limit of the excited state concentration can be considerably smaller. Assuming that the lifetime of the T_n state is 1 ps, we can have ca. 10^4 enhancement using the 10 ns pulsed laser by the thermal accumulation, and the smallest detection limit by this method can be $10^{-11}-10^{-12}$ M, even neglecting the multiphoton absorption.

(B) TSETG-II. Although the TSETG-I method is completely background free and the sensitivity is excellent, monitoring at various wavelengths requires many adjustments of the experimental configuration. When the wavelength of the grating pulse is changed, the incident angle of the probe light and the position of the detector should be readjusted to satisfy the phase matching condition. Furthermore, diffraction efficiency should vary depending on the wavelength. In the TSETG-II method, any adjustment of the grating pulse is not necessary at different monitor wavelengths.[9] Since, in this case, the grating light is absorbed by the solute (355 nm), the TG signal is observed without the second monitoring light (background signal; Figure 3-b). When the second laser at 540 nm is uniformly irradiated, the TG signal is strongly enhanced, e.g., more than 30 times compared to that without the second light. If we compare the intensity with that slightly before the second laser ($t < t'$), the enhancement is much more drastic (more than 1500 times) because heat releasing process is not complete at this time.

The TG signal after the grating pulse without the boosting laser rises with two steps in ns−μs time range, which represents the radiationless transitions from the excited BP. First, it rises with a time response of the system. This process is due to the vibrational relaxation from the S_1* state to the S_1 state and intersystem crossing from the photoexcited S_1 state to the T_1 state. The other slower rise reflects the heat releasing from the T_1 state and the rate constant is determined by the quenching of the T_1 state by oxygen.[11b] At 30 ns, only 14% of energy is released from the photoexcited molecule, and it is much smaller than the enhanced TG intensity by the boosting laser. The TG signal after the boosting laser rises quickly in ns order, which is expected from the rapid relaxation from the higher excited T_n state.

For a quantitative treatment, the intensity after the boosting light is compared with that without the boosting laser after complete thermalization. Considering the quadratic nature of the grating, we define the enhancement factor (E) by

$$E = \frac{\sqrt{I_{TG}(t')} - \sqrt{I_{TG}{}^{0}(t')}}{\sqrt{I_{TG}{}^{0}/Q(\infty)}} \frac{h\nu_0}{h\nu_b} \tag{18}$$

where $I_{TG}{}^{0}$ is defined by the expected TG intensity after complete relaxation under a negligible thermal diffusion condition ($D_{th} = 0$); $I_{TG}{}^{0} = A\{2(dn/dT)C_0{}^{*}h\nu_0 Q(\infty)/C_p\}\}^2$. From eq 15, E is given by

$$E = f_i(t')\sigma_e I_b \tag{19}$$

for the TA detection case. Physically, this E factor is related to the photon number of the boosting light used for TA (or SE) normalized to the photon number of the grating light for the ground-state absorption. Therefore, if all of the photoexcited states created by the first grating pulse are excited by the boosting laser by the one photon excitation once, E should be unity.

Generally, the normalization constant in eq 18 can be measured two ways. Adding a very efficient excited-state quencher, we measure the TG intensity at $t = 0$ after the complete quenching. Otherwise, we shall wait until the complete relaxation of the excited states and then the TG intensity should be measured. In this BP/benzene case, since the radiative transition and photochemical reaction are negligible ($Q(\infty) = 1$), we conveniently determined $I_{TG}{}^{0}$ by just extrapolating the decay part of the signal to $t = 0$. This simple method is rationalized by a fact that the triplet lifetime under the air saturated condition (~100 ns) is much shorter than the thermal diffusion time ($D_{th}q^2 \geq 10$ μs). By using the thus obtained value, E under a condition of ($I_0 = 6 \times 10^{15}$ photons/cm^2, $I_b = 2 \times 10^{16}$ photons/cm^2) is determined to be 2.4.

It is interesting to note that the enhancement factor E is larger than unity. The observed E larger than unity indicates that the T_1 state of BP is excited by the multiphoton process or is repeatly excited within the laser pulse. The boosting laser power dependence of E is shown in Figure 4. It is concluded from the linear dependence that, after a molecule in the T_1 state is excited, it quickly relaxes to the T_1 state and again is excited by another portion in time of the boosting laser. This excitation−decay−excitation cycle is repeated during the pulse width ~10 ns. After the several cyclic excitations, the thermal energy is accumulated. Since the quantum yield of the triplet state formation of benzophenone is unity, the number of E represents the number of cycle from the T_1 state. Owing to this large

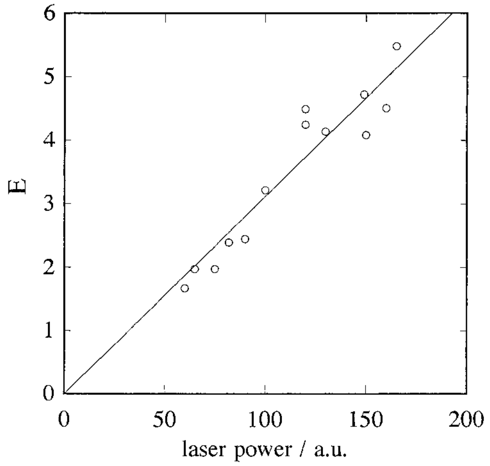


Figure 4. Laser power dependence of the enhancement factor (*E*).

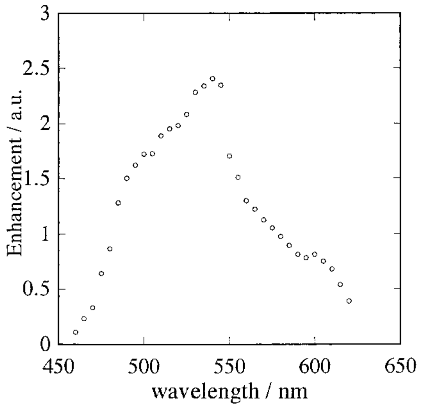


Figure 5. Transient spectrum of *E* for benzophenone in benzene.

enhancement, TA can be detected very sensitively. A similar cyclic excitation from the T_1 state was reported by Rothberg et al. in the photoacoustic detection of TA[2a] and by Fukumura et al. to explain the laser ablation of polymers under a condition that nanosecond pulsed laser was used to excite a sensitizer embedded in the polymer matrix.[13] It would be interesting that we can clearly "count" the number of the excitation cycle from *E* and from the quantum yield of the triplet formation.

When the pulse width is much shorter or the lifetime of the higher excited state is comparable to the pulse width, the enhancement factor cannot exceed much from unity. If the laser power becomes strong, the prepulse laser not only excites the metastable state to the higher states but also induces a transition from the higher states to the T_1 state. Then, the saturation of the TG intensity will be observed. From the light intensity of the saturation curve, the lifetime of the higher excited state, which is usually very difficult to be measured in the condensed phase can be determined.

For measuring the TA spectrum, the wavelength of the boosting pulse is scanned. Since, despite the large enhancement, *E* is proportional to the boosting laser power, *E* measured at various wavelengths can be corrected by the boosting laser power easily. Thus obtained spectrum of *E* (Figure 5) agrees well with the reported T−T absorption spectrum of BP in benzene.[12]

Quantitatively, from eq 19, absolute excited-state absorption coefficients σ_e can be determined from I_b at $E = 1$ or the slope of the power dependence (note that $f_T(30\text{ ns}) = 1$ for BP). The calculated σ_e at 540 nm ($\sigma_e = 1.2 \times 10^{-18}$ cm^2; $\epsilon = 3000$ M^{-1} cm^{-1}) was slightly smaller than the values reported previously ($\epsilon = 4200{-}10300$ M^{-1} cm^{-1}).[12b] We think that this discrepancy comes from a slight misoverlapping of the grating region and the boosting laser region. Modification or improvement for the quantitative measurement of σ_e will be developed. If there is no loss for the excited absorption by the boosting laser, it will be a very convenient and accurate way for measuring σ_e.

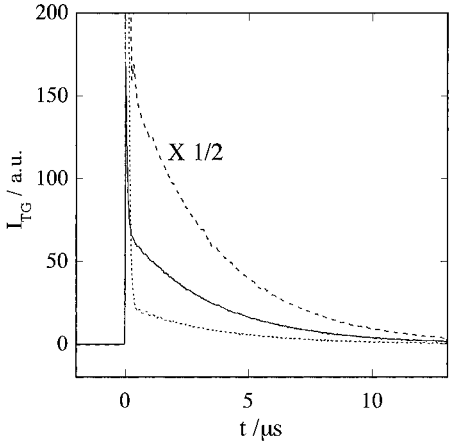


Figure 6. TG signal under the TSETG-I condition for the grating light at 565 nm of R6G in ethanol without the prepulse (solid line). The intensity is reduced (wavelength of the prepulse 532 nm) when the laser power is weak (dotted line), but it increased when it is strong (broken line). The initial strong emission is fluorescence from R6G not the TG signal.

In this study, the thermal grating is used for monitoring TA. Of course, it is possible to use acoustic signal or population grating signal for that purpose. If we use the population grating of the higher excited state or a product of a photochemical reaction from the higher excited states, the enhancement factor of the signal could be much more drastic.[9]

Rhodamine 6G. Next, the two-step TG signal of R6G sample is examined as an example of highly fluorescent sample. R6G is a well-known laser dye with a strong lowest absorption band ($\epsilon_{\text{peak}} = 10\,500$ M^{-1} cm^{-1}).

(A) TSETG-I. The SHG beam (532 nm) from the YAG laser was used as the prepulse for rhodamine 6G (R6G)/ethanol (6×10^{-4} M) solution. When only the grating pulse at 650 nm is irradiated to the solution, there is no detectable signal. After the prepulse is introduced at a zero delay ($t = 0$ ns, i.e., pulses are overlapped), the TG signal is clearly observed despite the strong fluorescence. This signal is monotonously increased with increasing the grating or the prepulse light intensity. From the TA spectrum recorded by the TSETG-II method (vide infra), this signal is attributed to TA from the T_1 state of R6G.

When the wavelength of the grating pulses is shifted to 565 nm, the TG signal is observed even without the prepulse because this wavelength is in the red edge of the absorption spectrum. In this case the TG intensity first decreases and then turns to increase with increasing the prepulse intensity (Figures 6 and 7). This laser power dependence can be explained in terms of the SE and TA processes as follows. In a weak power region, the uniformly created excited state by the prepulse light is forced down to the ground state by the grating pulse through the SE process, and this process creates the negative grating. At the same time, there is a TA contribution from the S_1 and/or T_1 states at the 565 nm. The negative grating by SE is canceled by the (positive) thermal grating created by the TA and also the weak absorption by the grating pulses. Since the cross section of SE is larger than that of TA, the signal decreases with increasing the prepulse intensity. When the prepulse intensity becomes strong, the photoexcitation process is saturated and, as a result, the SE process is saturated. On the other hand, the TA process does not saturate because of the very short

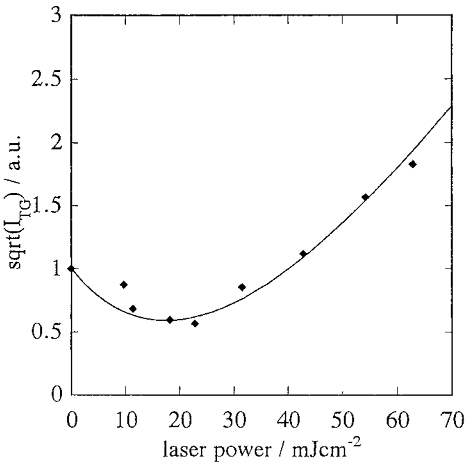


Figure 7. Prepulse laser power dependence of the TG signal of R6G in ethanol (squares). The intensity without the prepulse light is normalized to unity. The calculated power dependence by eq 20 is shown by the solid line.

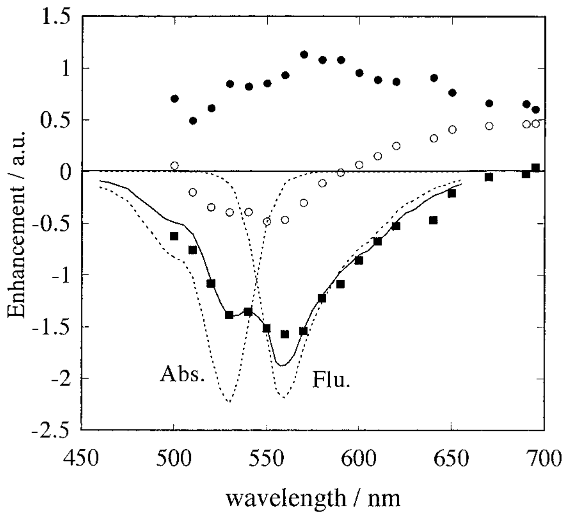


Figure 8. Transient spectra of E for R6G in ethanol at $t = 0$ ns (open circles), at $t = 30$ ns (closed circles) and the difference between these two spectra (squares). Absorption and fluorescence spectra (dotted lines) are taken from ref 18 (intensity is arbitrarily normalized, and the downward of the figure indicates the increase of the intensity). A superposed spectrum of σ_0 and σ_s is shown by the solid line.

lifetime of the higher excited state (cyclic excitation). Therefore the grating intensity then increases as the prepulse intensity increases. Another source of the TG signal is TA by the prepulse. Since the grating pulse itself creates the excited state at this wavelength, the TSETG-II condition is fulfilled at the zero delay time. The TA contribution at 532 nm light should also increase the TG signal linearly with increasing the laser power.

The observed laser power dependence can be reproduced by a superposition of these contributions. The formation of the excited state under steady-state conditions may be expressed by

$$C^* = C_0 I_p \sigma_0 / (2 I_p \sigma_0 + k)$$

where k is a constant relating to the relaxation time. The TA contribution should be just proportional to I_p because of the cyclic excitation. Therefore the TG signal intensity is predicted to be

$$I_{TG}^{1/2} = -A I_p \sigma_0 / (2 I_p \sigma_0 + k) + B I_p + C \qquad (20)$$

where A, B, and C are adjustable parameters, which are physically related to the SE, TA, and ground-state absorption, respectively. The observed laser power dependence of the TG intensity can be fitted by eq 20 well (Figure 7). Again, the used parameter for the fitting is less quantitative because of the imperfect matching of the prepulse and grating light illuminated regions. Another uncertainty for the fitting is the rather long pulse width. During the pulse, SE, TA, and ground-state absorption take place simultaneously, and that makes the quantitative analysis ambiguous. If we can overcome this difficulty by using a shorter pulsed laser (shorter than the S_1 lifetime), we can quantitatively determine the cross section of SE, which is generally difficult to measure.

It may be interesting to note that in the strong laser power region, clearly SE is observed as the increase of the grating light intensity. Therefore the excited state should be forced down to the ground state by the prepulse. Nevertheless, the thermal energy is increased at the expense of the prepulse energy.

(B) TSETG-II. First, the R6G sample (1×10^{-4} M) is excited by the SHG light from the Nd:YAG laser (532 nm). As stated above, R6G is a highly fluorescent dye, and thus the thermal energy by the nonradiative transition is small. If we use $\phi_f = 0.94-0.95$[14] and $E_f = 17\,400$ cm^{-1}, it is calculated that only 12% of the absorbed photon energy is converted to the thermal energy and the TG signal intensity is expected to be weak. Furthermore, the fluorescence is dispersed even at the probe wavelength (633 nm) and the fluorescence is hardly blocked completely only by the optical filter. However, by monitoring the TG signal after 1 μs from the grating pulse, the disturbance from the emission is negligible (cf. Figure 6).

When the second laser pulse is irradiated at about the same timing as the grating pulse ($t \sim 0$ ns), the signal intensity is varied depending on the wavelength (Figure 8). The intensity reduction is observed in 500−600 nm region and the enhancement in 600−700 nm region. When the temporal delay of the boosting pulse after the grating pulse is set to 30 ns, enhancement of the TG intensity is observed in all wavelength region we examined. The spectrum at 30 ns is similar to the reported T−T absorption spectrum.[15] Therefore, in this time range, we conclude that the enhancement is due to the T_1-T_n absorption. It is interesting to note that the TA spectrum in a strong absorption band from the ground state can be easily observed, although observation of a small TA in a strong absorption band is difficult by the direct detection method.

This T_1-T_n absorption can contribute to the spectrum at $t = 0$ because the S_1 lifetime of R6G (ca. 3.8 ns) is shorter than the grating pulse width.[14,16] To remove the T_1-T_n absorption spectrum from the $t = 0$ spectrum, both signals were normalized at the long wavelength region (700 nm) in order to correct a slight misalignment of the boosting laser to the grating region, and the T_1-T_n absorption contribution is just subtracted from the $t = 0$ spectrum. It gives purely "reduced" spectrum. This "reduced" spectrum can be interpreted in terms of the ground-state absorption and SE as shown below.

Theoretically, the cross section of SE, σ_s, at various wavelengths is related to the fluorescence spectrum by[17]

$$\sigma_s = \lambda^4 g(\lambda) / 8 \pi c n^2 \qquad (21)$$

where $g(\lambda)$ is the fluorescence band shape function, which is normalized to unity after the integration with respect to λ. Figure 8 shows the ground-state absorption and fluorescence spectra taken from ref 18. A superposed spectrum of the absorption spectrum and calculated σ_s from the fluorescence spectrum with an appropriate weighting factor is shown in

Figure 8 and compared with the experimental spectrum. The observed spectrum comes reasonably close to the calculated one. An expected S_1-S_n absorption[19] is not observed under this weak excitation condition. Therefore the observed spectrum at $t = 0$ ns is attributed to a superposition of the three effects, ground-state bleach, SE and T_1-T_n absorption.

5. Summary

As a photothermal detection method of transient absorption or stimulated emission, two types of the two-step excitation transient grating (TSETG) method are characterized and analyzed. For the TSETG-I method, prepulse−(delay)−grating pulse sequence, the TG signal is observed under a completely background free condition. Although there is a background signal in the TSETG-II method, grating pulses−(delay)−boosting pulse sequence, the second boosting laser induces a strong TG signal, which makes it very sensitive. The enhancement factor E is found to be far more than unity in the benzophenone/benzene case, and this indicates that the photoexcited triplet state is repeatedly excited due to the very fast relaxation from the higher triplet states within the pulse width. It is interesting to note that the number of the cycle can be counted from the measurement of E. The transient absorption spectrum can be easily measured even from the highly fluorescent dye rhodamine 6G in a strong absorption band from the ground state. The spectrum observed at $t = 0$ ns is explained by a superposition of the ground-state bleach, SE, and T_1-T_n absorption.

Besides the highly sensitive detection of TA and SE, this TSETG method can be used for many unique applications, such as the lifetime measurement of the higher excited states, rates and quantum yields of the energy-transfer processes from the higher excited states,[8] rates of chemical reaction from the higher excited states or biphotonic reactions, and photothermal detection of the stimulated Raman process.[20] Applications of these techniques for photochemical reactions will be presented elsewhere.

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