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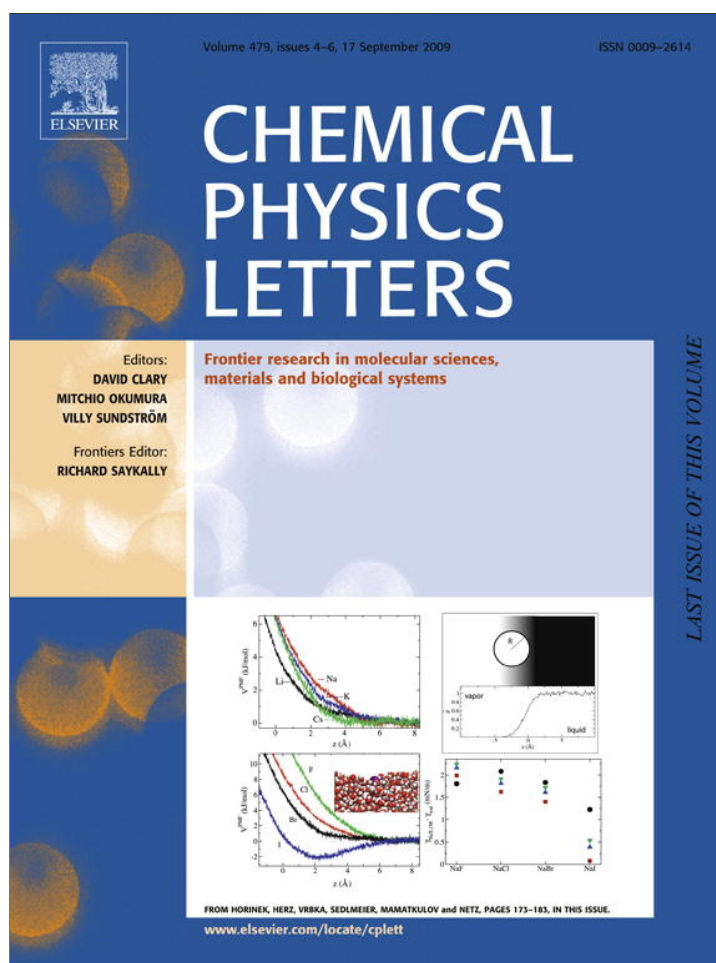


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## Near-field heterodyne transient grating spectroscopy

Kenji Katayama\*, Kazuo Sato, Hisashi Sugiyama, Takafumi Shoji

Department of Applied Chemistry, Faculty of Science and Technology, Chuo University, 1-13-27 Kasuga, Bunkyo, Tokyo 112-8551, Japan

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## ABSTRACT

The recently developed near-field heterodyne transient grating method is a powerful tool for detecting photochemical dynamics by observing the photo-induced temporal response of the refractive index change. We improved this method such that spectroscopic information could be obtained by using a white light source as a probe light. The spectra of the refractive index change were successfully observed for an anthracene solution, and these spectra were compared with the transient absorption spectra for the same sample. This improvement enables not only assessment of transient dynamics but also qualitative analysis of the photoexcited state.

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## 1. Introduction

The transient grating (TG) technique is a versatile tool for understanding nonradiative dynamics in photochemical and photothermal processes [1–3]. In this technique, two crossed pump beams are impinged on a sample, and species gratings (chemical species generated by the interference pattern of the pump light and the grating pattern formed by the concentration profile of the species) and photothermally generated gratings (thermal grating, acoustic grating, etc.) are observed [4]. The dynamics of such gratings are detected by the diffraction of a probe beam. For photochemical applications, the dynamics of photo-induced intermediate states (excited states, radicals, etc.) are measured and analyzed to obtain the lifetime and diffusion coefficient of each species, the reaction enthalpy, and the molar volume of the product species [5].

Since most processes in chemical reactions are nonradiative in nature, TG provides a variety of information on the dynamics of such processes. However, the drawback of this technique lies in the selectivity of the dynamic information since the dynamics of chemical processes overlap in a single transient response. One approach to overcome this drawback is to use heterodyne detection of a TG signal [6–10], and the real and imaginary parts of the refractive index change ( $\Delta n(t)$  and  $\Delta k(t)$ , respectively) are selectively detected by controlling the optical phase of the signal and reference light fields [11,12]. Another approach is to obtain spectroscopic information by using white light as a probe light [13–15], but this approach is rarely utilized because of the complicated optical setup.

We have recently developed the near-field heterodyne transient grating (NF-HD-TG) method [16–18], which features a simple optical setup and a heterodyne detection. Okamoto et al. developed a similar technique [19,20]. In the NF-HD-TG technique, the long-term phase stability is improved by using almost similar optical paths for the reference and signal fields, and the phase difference between the two fields can be easily controlled and the separation between  $\Delta n(t)$  and  $\Delta k(t)$  was demonstrated. This method has been used to study several photochemical reaction dynamics such as photodimerization of anthracene [21], photocatalytic reactions [22,23], and gold nanoparticle formation triggered by photoreduction [24].

In this Letter, we applied a white light source as a probe light in the NF-HD-TG method to give spectroscopic information on photo-induced dynamics. We indicated that the spectroscopic information derived from our method would not only improve the selectivity but also give qualitative information on transient chemical species.

## 2. Principle of the NF-HD-TG method

This section describes the principle of the NF-HD-TG method [16,18,21]. When a pump beam is incident on a transmission grating, the light intensity profile close to the grating on the side opposite to that on which the light is incident shows striped patterns at specific distances from the transmission grating; this phenomenon is called the Talbot effect [25]. The electromagnetic field is reproduced at distances that are integral multiples of the so-called Talbot distance. This distance is given by

$$d_{\text{Talbot}} = 2\Lambda^2/\lambda, \quad (1)$$

where  $\Lambda$  and  $\lambda$  represent the grating spacing and the wavelength of the pump light, respectively. When a liquid sample is placed close

\* Corresponding author. Fax: +81 3 3817 1913.

E-mail address: [kkata@kc.chuo-u.ac.jp](mailto:kkata@kc.chuo-u.ac.jp) (K. Katayama).

to the transmission grating, the sample is illuminated by the striped pattern from the pump light and photochemical and photothermal processes occur in the liquid. The refractive index of the liquid changes according to the intensity profile of the pump light, and the pattern of the refractive index change functions as different types of transiently generated gratings (thermal, acoustic, and species gratings) [4].

There are two methods for detection, as is shown in Fig. 1a. In the first method (Fig. 1a, left), a probe beam is incident in a manner similar to that of the pump beam; it is diffracted both by the transmission grating (reference) and the transiently generated grating (signal). In principle, the two diffractions progress along the same direction; therefore, a combination of these two diffractions is detected by a detector positioned at the first diffraction spot. In the second method (Fig. 1a, right), the probe light is incident, and the transmission light is used. The probe beam that is diffracted by the transmission grating is bent again by the transiently generated grating and it propagates in the original direction (signal). The transmission light (0th order diffraction) is used as a reference in this case, and the signal and the reference are detected at the position of the transmission light.

For measurements that use various probe wavelengths, the latter configuration is superior to the former because the detector position does not have to be changed each time the probe wavelength is changed; therefore, we selected the latter configuration for our

studies. In both cases, the heterodyne signal intensity is expressed as follows [18,21]:

$$I(t) \propto 2E_{\text{ref}}E_{\text{pr}}(\Delta n(t) \cos(\phi + \phi_0) + \Delta k(t) \sin(\phi + \phi_0)), \quad (2)$$

where  $I_{\text{ref}}$  and  $I_{\text{pr}}$  represent the intensities of the reference and probe, respectively;  $E_{\text{ref}}$  and  $E_{\text{pr}}$  are the electric fields of the reference and probe, respectively;  $\phi$  is the phase difference between the signal and the reference, where the signal field is expressed as  $E_s = (\Delta n(t) + i\Delta k(t))E_{\text{pr}}$ ; and  $\phi_0$  is the initial phase difference.  $\phi$  originates from the optical path difference between the signal and reference fields, which can be continuously varied by the distance between the transmission grating and the sample.  $\phi$  is given by [18,21]

$$\phi = (2\pi/\lambda)\Delta l = d(1/\cos\theta - 1)(2\pi/\lambda), \quad (3)$$

where  $\Delta l$  is the optical path difference between the signal and reference fields;  $d$  is the grating-sample distance; and  $\theta$  is the diffraction angle of the 1st order diffraction given by  $\theta = \text{Arc sin}(\lambda/\Lambda)$  ( $\lambda$  = probe wavelength,  $\Lambda$  = grating spacing).

### 3. Experimental

The pump light used was the third harmonic of an Nd:YAG laser (Surelite, Continuum) with a wavelength of 355 nm, repetition rate of 0.01–10 Hz, pulse width of 4 ns, and pulse energy of 160 mJ/pulse; it was used after attenuation to less than 1 mJ/pulse. The probe light was a xenon flash lamp with a wavelength range, 185–2000 nm with a pulse width less than 1  $\mu$ s. The incident timing of the pump and probe pulses were controlled by a 2ch function generator (WF1973, NF Instruments). The optical setup is shown in Fig. 1b. The probe beam was collimated around the sample by a lens. The pump beam was in level with the optical bench and the probe beam was tilted upward to overlap the pump beam in the sample cell with an internal thickness of 1 mm. A transmission grating was made of a Pyrex® glass plate with a grating spacing of 60  $\mu$ m, and it was placed between the cylindrical lens and the sample cell. After the pump and probe beams passed through the sample cell, the pump beam was blocked by a high-pass filter and the 0th order diffraction of the probe beam was detected by a CCD built-in spectrometer (PMA-11, Hamamatsu). In actuality, a part of the probe beam spot was detected because the tip of the optical fiber connected to the spectrometer has a diameter of 1 mm.

An anthracene/cyclohexane solution (2 mM) was used as a test sample. This solution is known to have a triplet–triplet absorption band around 400 nm within a few microseconds by transient absorption (TA) measurements [26,27]. In our setup, TA measurements were made by simply removing the transmission grating, and thus, the TA and NF-HD-TG spectra could be easily compared.

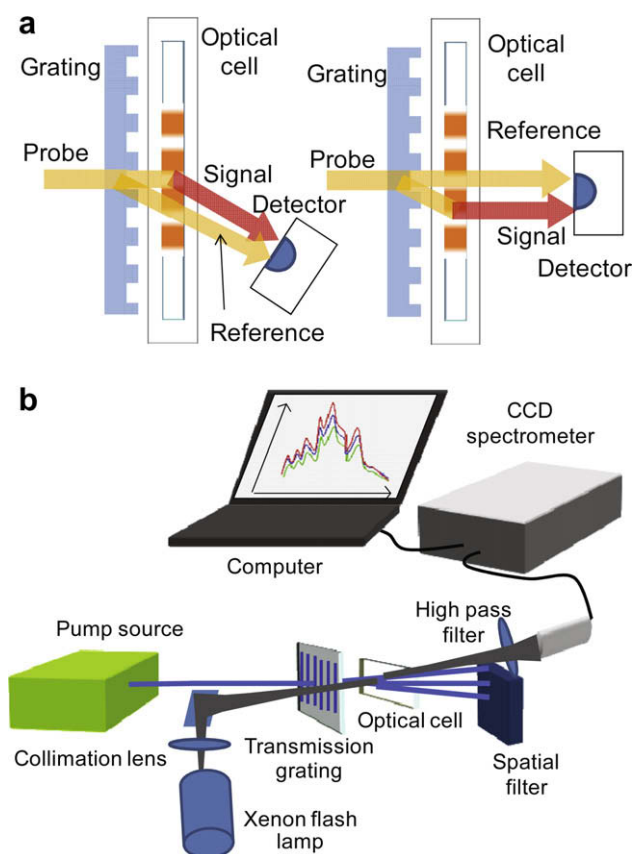
In every measurement of transient grating measurements, the thermal grating (the refractive index change due to thermal energy release) is observed, and the signal decays due to thermal diffusion in the direction perpendicular to the grating stripe. The thermal decay time is theoretically given by [21]

$$\tau = \frac{1}{D} \left( \frac{\Lambda}{2\pi} \right)^2, \quad (4)$$

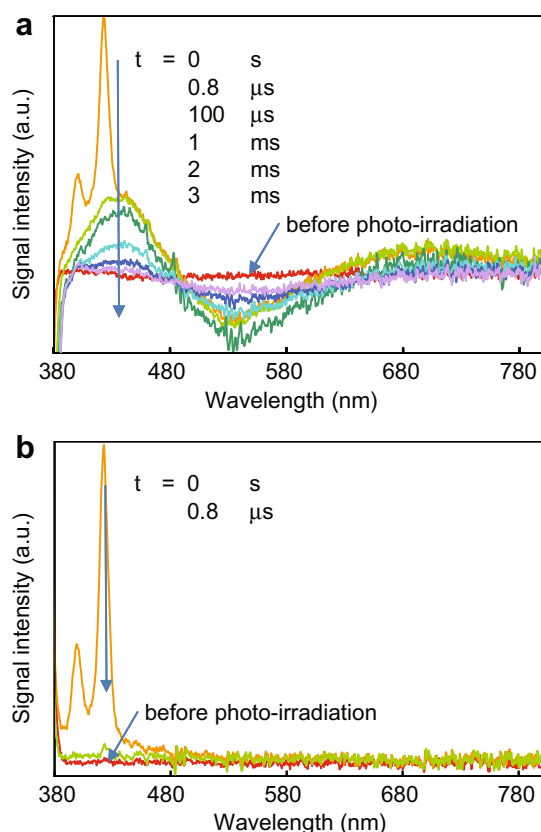
where  $D$  is the thermal diffusion coefficient. The thermal grating is formed as a result of the temperature rise of the solvent, which causes a change only in the real part of the refractive index for most solvents.

### 4. Results and discussion

The measured NF-HD-TG spectra for various times after pump irradiation are shown in Fig. 2a, and the TA spectra observed just by removing the transmission grating are shown in Fig. 2b. The



**Fig. 1.** (a) Schematic picture of the two kinds of heterodyne detection methods for the transient grating signal in the NF-HD-TG method. The picture on the left shows signal detection by using the first order diffraction light, and the right one shows the detection by using the 0th order diffraction light. (b) Schematic representation of the optical setup of the NF-HD-TG method. The pump beam is level with the optical bench and the probe light is tilted upward to overlap the probe light in the sample cell after passing through a transmission grating. The glass plate grating is motion-controlled to change the grating-sample distance. The diffraction of the probe beam is detected by a CCD detector with a built-in spectrometer.

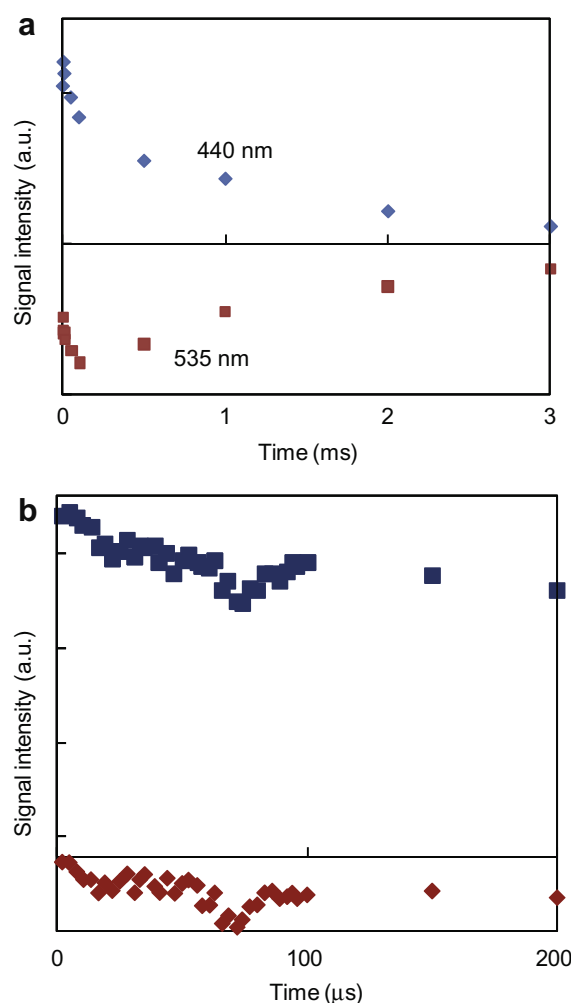


**Fig. 2.** (a) NF-HD-TG spectra of an anthracene/cyclohexane (2 mM) solution for various times. (b) TA spectra of the same sample.

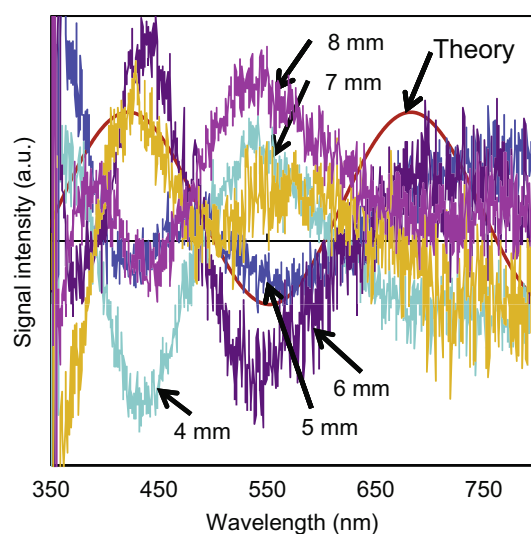
grating–sample distance was 6 mm. The TA spectrum just after photo-excitation showed two peaks at 399 and 422 nm, and they completely decayed after 0.6  $\mu$ s. No other TA spectra were observed at the later times. The NF-HD-TG spectra showed the same peaks as the TA spectra just after photo-excitation, but the NF-HD-TG spectra exhibited a positive–negative shape that decayed within a few milliseconds. The observed TA spectra corresponded to the triplet–triplet absorption of anthracene [26,27].

To investigate the origin of the slower signal observed in the NF-HD-TG spectra, the decay time was obtained by plotting the temporal profile at two different wavelengths (440 and 535 nm) in Fig. 3. The decay times were roughly 2 ms for both wavelengths, which agreed with the decay time of the thermal grating as calculated from Eq. (4) (1.96 ms; thermal diffusion coefficient for cyclohexane:  $4.7 \times 10^{-8} \text{ m}^2/\text{s}$ ). That is, we can safely say that the slower dynamics observed in the NF-HD-TG spectra is due to the thermal grating and originates from the refractive index change of the solvent (cyclohexane) due to the temperature rise.

To verify that these spectra originated from the heterodyne signal, the dependence of the spectral shape on the grating–sample distance ( $d$ ) was assessed. The signal should reverse when the heterodyne phase changes, as shown in Eq. (2). (Note that only the real part of the refractive index change is observed for the thermal grating.) Fig. 4 clearly shows that the signal intensity reversed when  $d$  was changed. The spectrum of the refractive index change for a normal solvent due to a temperature rise does not have a positive–negative shape like the observed NF-HD-TG spectra, it is considered that the shape seen here is because the heterodyne phase depends on the wavelength in Eq. (3) and then the signal intensity also depends on the wavelength as shown in Eq. (2). The oscillating profile was calculated for  $d = 6 \text{ mm}$ , assuming that the refractive index change does not depend on wavelength,



**Fig. 3.** (a) Temporal profiles at 440 and 535 nm of the NF-HD-TG spectra. (b) The expanded figure of (a) within 200  $\mu$ s.



**Fig. 4.** Dependence of the NF-HD-TG spectra at 1 ms on the grating–sample distance.

the oscillating tendency was roughly reproduced. (Only the oscillation period was checked; the amplitude was not adjusted.) However, a discrepancy exists between the theoretical spectrum and



the NF-HD-TG spectrum in the shorter and longer wavelength region. In actual, the refractive index change due to temperature rise of a solvent decreases with increase in wavelength because the refractive index is proportional to the optical path length divided by the wavelength; the density change due to temperature rise is proportional to the change in the optical path length and it is constant for all the wavelength. The amplitude decrease in the longer wavelength in Fig. 4 reflects the above-explained tendency.

Since the phase difference in Eq. (3) depends on the wavelength, it is difficult to get a waveform of pure  $\Delta n(\lambda)$  or  $\Delta k(\lambda)$  at any  $d$  positions as shown in Eq. (2); namely the waveforms are mixed. This fact may make the signal analysis difficult when this technique is applied to more complicated systems. The solution for it is described here; the  $\Delta k(\lambda)$  waveform can be obtained from the TA measurement, which is an easy operation because we just need to remove the transmission rating used in the NF-HD-TG method; The cosine and sine terms in Eq. (2) can be obtained because the phase difference can be calculated using Eq. (3) in theory; The actual waveform is fitted with Eq. (2) as a parameter of  $\Delta n(\lambda)$ . However, the oscillation period did not agree with the theory in the shorter and longer wavelength region in Fig. 4, and we need to clarify the compensation method in future.

Carefully looking at Figs. 2 and 3, another decay and rise component can be found around the positive and negative peaks, respectively. The expanded figure at 440 and 535 nm is shown in Fig. 3b. Although it was difficult to obtain the exact decay times due to the scattered data, both times were on the temporal order of several tens of microseconds. If the data will be taken with better S/N ratio in future, the component can be exactly extracted because the thermal grating decay overlapped with this component can be removed because the decay time is exactly obtained from Eq. (4) and the solvent property. The triplet excited state of anthracene is already decayed; therefore, these observations might possibly reflect the dynamics of a triplet excimer. Under our experimental conditions, anthracene underwent a photodimerization reaction, and it is generally known that an excimer generated from the singlet excited state is involved in this reaction [21,28], but another reaction channel by way of a triplet excimer has also been proposed [29]. If the assignment is correct, there is a question why the component is not observed in the TA signal. It is probably because of the difference between the refractive index change and the absorption change. From the Kramers–Kronig relation, the former extended into broader wavelength region than the latter. In this observation, even if the absorption change may lie in the UV region, the refractive index change could be observed in the visible region. Actually, the singlet excimer was observed by the NF-HD-TG method in the previous paper [21], although it has not been detected by TA method. However, these observations should be clarified in more detail in the near future.

## 5. Conclusion

We have developed an NF-HD-TG spectroscopic method that is an improvement on the original NF-HD-TG technique by adopting white light as the probe light. We successfully obtained a heterodyne signal, even when using an incoherent lamp light, possibly because a coherent component was still evident in the lamp light, and the component gave an heterodyne interference. In our setup, the TA and NF-HD-TG techniques can be interchanged simply by inserting or removing a transmission grating. Our method has the benefit of being able to observe both absorption and refractive index changes under the same experimental conditions, and it will help understand photochemical reaction dynamics and intermediate species in future experiments.

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