Picosecond Absorption Kinetic Spectrometer with a Laser and a Streak Camera

Du-Jeon Jang

Spectroscopy Laboratory
Korea Standards Research Institute, Daejon 305-606

Abstract

A high resolution picosecond absorption kinetic spectrometer utilizing dye emission and a streak camera is presented and compared with other methods of picosecond transient absorption measurements. Typical transient absorption and bleach recovery kinetics measured with this spectrometer are shown. Single wavelength transient absorption or ground state bleach recovery kinetics are determined on the basis of a single laser shot, so that the samples are relatively free from decomposition by irradiation. Excellent kinetics may be obtained from the near UV to the near IR and are not subject to interference from luminescence of samples. The sensitivity of this spectrometer is very high and it is reasonably easy and convenient to set up and use.

Introduction

Transient absorption kinetics studies are of great importance in the understanding of ultrafast photophysical, photochemical, and photobiological processes. Absorption techniques, however, have been less frequently employed than time-resolved emission techniques to understand these processes. One reason for this is that picosecond emission spectroscopic methods are much more sensitive and technically easier than the currently available methods of picosecond absorption kinetic measurements. Another problem of current picosecond absorption kinetics measurements is that samples may be subject to photochemical degradation by the many laser shots required for a complete determination of the kinetics. To solve the main problems of current picosecond absorption kinetics measurements, we have developed a high sensitivity transient absorption spectrometer utilizing dye emission and a streak camera [1 - 3].

Picosecond spectroscopy has been developed following the achievement of extremely short light pulses from mode-locked ruby [4], Nd:glass [5], and Nd:YAG [6] lasers. Initially, most picosecond absorption techniques utilized mode-locked laser pulses [7], or their related harmonics and/or stimulated Raman frequencies [8 - 10] for both sample excitation and probe. Recently mode-locked dye lasers have provided some tunability to these techniques [11 - 14]. One obvious defect of those early methods is that absorption process can be studied only at a single wavelength or a small set of discrete wavelengths. Furthermore, it was necessary to measure the kinetics of absorption process by scanning the pump-probe relative delays, requiring multiple laser shot experiments. A broad picosecond continuum pulse can be generated by the interaction of a monochromatic picosecond laser pulse of high intensity with glass, liquid, or liquid mixtures [9, 15 - 17]. Continuum probe pulses have been widely used as interrogating light since the first application of the continuum to picosecond absorption spectroscopy [16]. Continuum generation provide an excellent wavelength-resolved transient absorption spectrum with a single laser shot experiment. However, the kinetics of any spectral feature may be determined only by scanning the relative delay between pump and probe pulses, requiring multiple laser shot experiments.

Echelon techniques have been used for a single-shot time resolution of picosecond absorption events since 1971 [18]. The use of an echelon along with multichannel detectors permits the simultaneous determination of the transient absorbance at several different relative delay times. The defects of the technique are that

the available total time range is practically only subnanoseconds and that the optical setup is somewhat complicated [16-18].

Picosecond streak cameras have been widely used to measure picosecond events since the early 1970's [19, 20], however, they have been rarely applied to absorption studies. The reason for their uncommon application to absorption studies is that proper probe light sources have not been developed. The probe must have a high intensity and a relatively long (nanosecond) duration, stable amplitude and must be synchronized with the sample excitation. To our knowledge Yoshihara *et al.* [1], for the first time, applied a streak camera for absorption studies in 1979. The probe light was the fluorescence of Rhodamine 6G which provides a quasi-CW source of light. Absorption kinetics were determined by measuring the intensity of R6G emission transmitted through the sample. Recently, Eisenthal *et al.* [21] used a laser-triggered flash lamp and a streak camera to monitor transient absorption. In both of the cases the signal-to-noise (S/N) ratios are rather low even though the transients have high absorbances. Our idea is basically same as that of Yoshihara *et al.*'s. Using the optimum conditions, we have improved the S/N by at least two orders of magnitude.

Experimental Details

Figure 1 shows the optical setup of the absorption kinetic spectrometer. The sample is excited by one of the harmonic frequencies of an actively/passively mode-locked Nd:YAG laser. Other excitation wavelengths may also be generated from stimulated Raman scattering from these harmonics. An organic dye solution is excited by an appropriate harmonic generated from the remaining fundamental frequency. The dye fluorescence is collimated and focused through a 0.5-mm pinhole to define the image size of the fluorescence. The fluorescence is then recollimated at f/2.4 and focused to a 0.8-mm spot in the sample overlapping the excitation beam. The dye fluorescence is then recollimated and focused through a SPEX 0.25 M monochromator with a low resolution grating of 150 grooves/mm. Some experiments have also been done using narrow band interference filters for wavelength selection. The

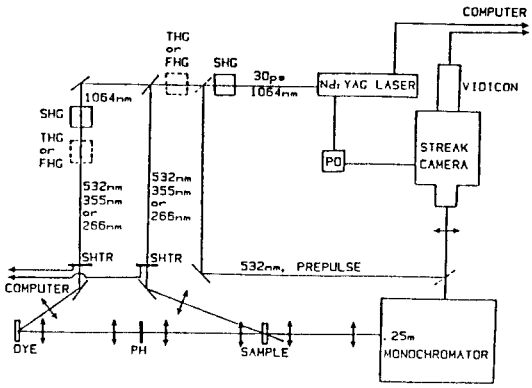

Fig. 1. Optical setup of the high resolution absorption kinetic spectrometer utilizing dye emission and a streak camera. SHG = second harmonic generator; THG = third harmonic generator; FHG = fourth harmonic generator; PH = pinhole; PD = photodiode; SHTR = mechanical shutter; double headed arrow = convex lens; dashed diagonal line = partial refractive mirror.

wavelength-selected dye fluorescence is then focused into a Hamamatsu C979 streak camera which is coupled to PAR 1254E red extended SIT vidicon. Achromatic optics are used throughout the spectrometer. The vidicon controller is interfaced into a DEC LSI 11/02 computer. The repetition rate of the spectrometer is limited by the rate at which the vidicon can be scanned and is about 2 Hz. A transient absorption in the sample alters the apparent kinetics of the dye emission seen by the streak camera. Comparison of these kinetics with and without sample excitation after considering sample luminescence yields very accurate picosecond absorption kinetics of a ~10-nm band. The shot to shot jitter associated with streak camera triggering is about 50-100 ps. The onset of dye luminescence is used as a timing marker to eliminate the effects of streak camera jitter upon signal averaging. In cases where the sample is luminescent at the probing wavelength, this emission must be subtracted off. This requires signal averaging with the sample excitation only, and a prepulse timing marker is used to align each streak.

The materials used to produce the probe light are highly fluorescent organic dyes. The dye solutions most commonly used in this apparatus are ethanol solutions of Nd:YAG pumped laser dyes such as stilbenes, coumarins, rhodamines, DCM, and LDSs. The main

problem with the use of laser dyes is that as the name of laser dye implies, it is difficult to eliminate laser emission. If laser emission from the dye occurs, the range of the probe is close to the pulse width of pump laser pulse. To obtain only the spontaneous fluorescence, we use a special but simple dye cell, as well as adjust the dye concentration and dye excitation intensity to optimum values. The dye cell is a 2-mm deep sandblasted aluminium cell covered with a quartz window. We find that the tendency for laser emission to occur increases with both dye concentration and pump intensity. The typical optimal values (for R6G) are ~10^{-5} M solutions pumped by ~1 mJ of 532-nm laser pulse which is focussed to a 1-mm diameter spot. The intensity of the probe light at the sample cell is dependent on many factors such as the dye, the dye pumping laser pulse, and the associated optical components. It is estimated to be on the order of 10^4 W/cm^2/nm at the sample cell with this spectrometer. The laser dye fluorescence which usually has a lifetime of several nanoseconds serves as an excellent quasi-cw analyzing light in the picosecond time domain upto approximately 20 ns. If proper dyes with longer lifetimes and high fluorescence quantum yields are chosen, the full time range of the streak camera at the slowest streak rate (~100 ns) may be used. The dye fluorescence polarization is the same as that of the pump pulse immediately following excitation, and subsequently randomizes. The time required for the depolarization to occur is tens to hundreds of picoseconds [22]. Experimental artifacts associated with the relaxation of polarization may be avoided by if the dye and sample excitation polarization angles to the probe axis differ by 54.7° ("magic" angle). The spectral region of this technique is limited only by the availability of dyes, and the spectral response (S-20) of the streak camera. Kinetics may therefore be obtained from the near UV throughout the visible and into the near IR.

Careful considerations have been made for the computer programs to average the signals properly against the streak camera jitter, to monitor the intensity fluctuations of laser pulses and to extract time constants from the observed absorption signals which are the convolutions of the absorption signals and the total instrument response functions. The transient absorbance at each channel is calculated as $-\log[(I-I_1)/I_0]$, where I is the measured intensity with the probe and the excitation, I_1 is that with the excitation only, and where I_0 is that with the probe only. The normalized profile of the averaged prepulse is used to determine the temporal instrument response function for the deconvolution of each observed kinetics curve. In the cases where the luminescence from the sample is negligible the transient absorbance at each channel is simply calculated as $-\log(I/I_0)$. The temporal instrument response function is mainly due to the convolution of the temporal profile of the laser pulse (fwhm: ~30 ps) and the temporal response function of the streak camera (fwhm: ~10 ps on the fastest streak rate). When interference filters are employed for the probe wavelength selection, the measured temporal instrument function has a fwhm of ~35 ps on the fastest streak rate. When the monochromator is employed for the probe wavelength selection, the temporal instrument response function is increased to a fwhm of ~40 ps on the fastest streak rate due to the dispersion of the grating [23]. In all cases the streak rate as a function of OMA channel number has been calibrated with etalons.

Discussion

Typical transient absorption decay and ground state repopulation curves taken with the spectrometer presented here are shown in Figs. 2 - 4. The kinetics in Figs. 2 - 4 were taken with 150, 300, 1500 laser shots

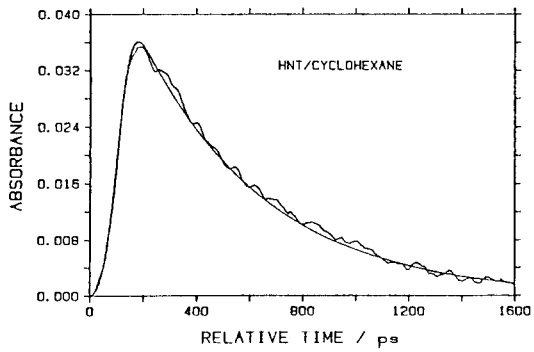

Fig. 2. Transient absorption kinetics of 2-hydroxy-4,5-naphthotropone (HNT) in cyclohexane, excited at 355 nm and probed at 510 nm. The solid curve was generated from a 500-ps exponential decay convoluted with the instrument response function.

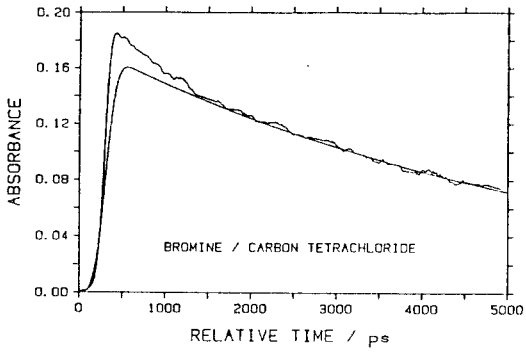

Fig. 3. Kinetics of transient absorption of bromine in carbon tetrachloride, excited at 532 nm and probed at 640 nm. The solid curve was generated from a 5.5 ns exponential decay convoluted with the instrument response function.

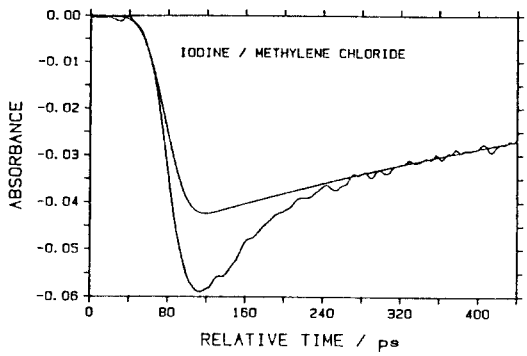

Fig. 4. Kinetics of ground state repopulation of iodine in methylene chloride, excited at 683 nm and probed at 500 nm. The solid curve was generated from a 475-ps exponential recovery convoluted with the instrument response function.

respectively. Figure 2 shows the kinetics of transient absorption, $S_1' \rightarrow S_n'$, of 2-hydroxy-4,5-naphthotropone (HNT) in cyclohexane.The lifetime of this decay is exactly the same as that of the tautomer fluorescence, $S_1' \rightarrow S_0'$, of HNT in cyclohexane reported earlier [24]. This fact shows that because the intensity of the probe is low compared to that of the excitation pulse, the population depletion of the absorbing transient resulted from probing is negligible compared to the total population of the transient, so that the lifetime of the transient absorption is not affected by probing. Figure 2 shows that high S/N ratios are obtained in spite of the very low transient absorbance and the photochemically unstable sample [24]. Figures 3 and 4 show that very good kinetics may be obtained over both long and short time ranges. Both kinetics curves show a short lived transient immediately following excitation with a longer lived absorption or bleach. It may be noticed that the sensitivity in Fig. 3 decreases slightly as the relative time increases. The reason is that as the time increases, the intensity of the probe decreases exponentially. The kinetics in Fig. 4 was measured at 500 nm following 683 nm excitation. The optical densities at these wavelengths were 1.3 and 0.065 respectively. The 500-nm probe was therefore attenuated by a factor of 20 due to the large static absorbance. The 683-nm excitation was generated by stimulated Raman scattering of H_2 from the second harmonic. Figure 4 shows that excellent ground-state repopulation kinetics is obtained even though samples have a very small bleach and a very large static absorbance at the interrogating wavelength. The three kinetics show that high sensitivity absorption kinetics may be obtained in variety of simple compounds as well as large organic molecules.

The spectrometer presented here has several advantages to other common methods introduced earlier. The continuum probe technique [25] can provide excellent transient absorption spectra, however, the kinetics obtained from these spectra are of only moderate quality. One of the reasons is that the intensity fluctuations of the sample excitation pulses result in the fluctuations of transient absorbances measured at different times. Perhaps more importantly, the intensity and spectrum of the continuum are subject to considerable shot-to-shot fluctuations. Another main problem of the continuum probe technique is that samples may be subject to photochemical degradation since many more laser shots are required for the determination of the absorption kinetics. Because the entire kinetics is measured on the basis of a single-shot experiment with the presented spectrometer, these problems are greatly reduced. About 50 laser shots are often enough to average the signals for an excellent absorption kinetics. Clearly, this and continuum probe techniques are quite complementary. The echelon technique [16, 17] with the continuum probe or with picosecond dye laser probe provides a complete kinetics

with a single laser shot. One problem of this technique is that the practically available total time range is quite short. Because a different type or size of echelon is required for a different time resolution, the corresponding alignment has to be changed and the optical setup is somewhat complicated. Also, the observed signal is discontinous because an echelon provides stepwise time delays to the probe.

In conclusion, the spectrometer presented here has greatly improved the sensitivity of transient absorption measurements compared to the other current methods. The sample has less chance to decompose by irradiation because the kinetics are determined by single laser shots. Excellent transient absorption kinetics may be obtained from the near UV to the near IR, and are not subject to interference by the sample luminescence. The available total time range is that of a streak camera if proper dyes are chosen. Furthermore, it is reasonably easy and convenient to set up and use this spectrometer. Picosecond absorption kinetics measurements are sensitive, easy, and relatively free from sample decomposition by irradiation with this spectrometer.

References

1. K. Yoshihara, A. Namiki, M. Sumitani, and N. Nakashima, *J. Chem.Phys.* **71**, 2892 (1979).
2. D. J. Bradley, in Ultrashort Light Pulses, *Springer Topics in Applied Physics*, **Vol. 18**, edited by S. L. Shapiro (Springer, Berin, 1977), pp. 25-36.
3. N. H. Schiller, Y. Tsuchiya, E. Inuzuka, Y. Suzuki, K. Kinoshita, K. Kamiya, H. Iida, and R. R. Alfano, *Opt. Spectra* **14**, 15 (1980).
4. H. W. Mocker and R.J. Collins, *Appl. Phys. Lett.* **7**, 270 (1965).
5. A. J. DeMaria, C. M. Ferrar, and G. E. Davidson, *Appl. Phys. Lett.***8**, 22 (1966); A. J. DeMaria, D. A. Stetser, and H. Heynau, *Appl.Phys. Lett.* **8**, 174 (1966).
6. M. DiDomenico, Jr., J. E. Geusic, H. M. Marcos, and R. G. Smith, *Appl. Phys. Lett.* **8**, 180 (1966).
7. R. I. Scarlet, J. F. Figueira, and H. Mahr, *Appl. Phys. Lett.***13**, 71 (1968).
8. P. M. Rentzepis, *Chem. Phys. Lett.* **2**, 117 (1968); *ibid.* **3**, 717 (1969).
9. R. R. Alfano and S. L. Shaphiro, *Chem. Phys. Lett.* **8**, 631 (1971).
10. D. Rechard, W. H. Lowdermilk, and J. Ducuing, *Chem. Phys. Lett.* **16**, 617 (1972).
11. D. J. Bradley and A. J. F. Durrant, *Phys. Lett.* **27A**, 73 (1968); D. J. Bradley, A.J.F. Durrant, G. M. Gale, M. Morse, and P. D. Smith, *IEEE J. Quant. Electr.* **QE-4**, 707 (1968).
12. W. H. Glenn, M. J. Brienza, and A. G. Memarian, *Appl. Phys. Lett.***12**, 54 (1968).
13. C. V Shank, E. P. Ippen, and O. Teschke, *Chem. Phys. Lett.* **45**, 29 (1977).
14. R. K. Jain and J. P. Heritage, *Appl. Phys. Lett.* **32**, 41 (1978).
15. R. R. Alfano and S. L. Shapiro, *Phys. Rev. Lett.* **24**, 592 (1970); *ibid.* **24**, 1217 (1970); *ibid.* **26**, 1247(1971).
16. G. E. Busch, P. M. Jones, and P. M. Rentzepis, *Chem. Phys. Lett.* **18**, 178 (1973).
17. G. E. Busch and P. M. Rentzepis, *Science* **194**, 276 (1976); P.M. Rentzepis, Methd. *Enzymol.* **54**, 3 (1978).
18. M. M. Malley and P. M. Rentzepis, *Chem. Phys. Lett.* **7**, 57 (1970).
19. D. J. Bradley, J. F. Higgins, and M. H. Key, *Appl. Phys. Lett.* **16**, 53 (1970); D. J. Bradley, B. Liddy, and W. E. Sleat, *Opt. Commun.* **2**, 391 (1971)
20. M. Y. Shelev, M. C. Richardson, and A. J. Alcock, *Appl. Phys. Lett.* **18**, 354 (1971).
21. Y. Wang, M. K. Crawford, M. J. McAuliffe, and K. B. Eisenthal, *Chem.Phys. Lett.* **74**, 160 (1980); Y. Wang and K.B. Eisenthal, *J. Chem.Edu.* **59**, 472 (1982).
22. G. R. Fleming, J. M. Morris, and G. W. Robinson, *Chem. Phys.* **17**, 91 (1976).
23. N. H. Schiller and R. R. Alfano, *Opt. Commun.* **35**, 451 (1980).
24. D.-J. Jang and D. F. Kelley, *J. Phys. Chem.* **89**, 209 (1985).
25. See, for an example, D. F. Kelley, N. A. Abul-Haj, and D.-J. Jang, *J. Chem. Phys.* **80**, 4105 (1984).