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Development of kinetic analysis system in pump–probe measurement based on femtosecond chromium: forsterite laser and its application to S_1–S_0 relaxation dynamics of azulene

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Abstract

Ultrafast transient absorption measurement system with cavity-dumped chromium:forsterite (Cr:F) laser as a light source was developed. The second harmonic of the Cr:F laser can cover the immeasurable region of the titanium:sapphire laser which is nowadays the most popular light source for the ultrafast spectroscopy. The second harmonic of the Cr:F laser was tunable from 620 to 640 nm and the shortest pulse duration attained in the present condition was ∼25 fs. The sensitivity of this laser to ultrafast spectroscopy was evaluated by the measurement of S_0 and S_1 state dynamics of azulene. In spite of extremely small molar extinction coefficient of the $S_1 \leftarrow S_0$ transition, i.e. 300 $M^{-1}\,cm^{-1}$, the ultrafast dynamics of azulene after photo-excitation to S_1 state was clearly observed with high S/N ratio and ≤30 fs time resolution. Although the small molar extinction coefficient value of 300 $M^{-1}\,cm^{-1}$, pump-and-probe measurement clearly resolved the multi-exponential recovery profile with a very weak oscillation of 160 cm^{-1}.

Keywords: Chromium:forsterite laser; Femtosecond spectroscopy; Azulene; Ultrafast dynamics

1. Introduction

Since the pioneering work of the flash photolysis by Norrish and Porter in 1949 [1], time-resolved detection of transient states has become one of the essential methods to understand the mechanisms of various chemical reactions and physical processes. By the virtue of cutting-edge ultrashort pulse laser technology, we can now access to femtosecond time region by the time-resolved resolutions of conventional spectroscopic methods, such as UV-Vis absorption, emission, IR absorption, and Raman spectroscopy [2]. Moreover, not only shortening of the laser pulse resulted in better time resolution, but also the intense concentration of coherent photons in the pulse led to the development of new types of nonlinear coherent spectroscopy such as CARS, RIKES, four-wave mixing, and photon echo measurement, etc. [3].

Among these various detection methods, time-resolved transient absorption measurement has been utilized as a principle tool to investigate photo-induced dynamical behaviors. Time-resolved spectra can specify transient species involved in the process and their time-evolution. On the other hand, time profile at single wavelength can provide precise dynamical information of the transient species that absorb or emit light in the wavelength monitored. In special, application of ultrashort laser pulse with duration of ≤50 fs allows us to observe oscillating behaviors in the pump–probe signals, which is induced by the intra- and/or intermolecular vibrations. In the present study, we have developed a femtosecond time-resolved transient absorption measurement system with ≤30 fs time resolution leading to acquire the detailed information of the coupling between molecular vibrations and chemical reactions [4].

In the present paper, we represent a femtosecond detection system based on a cavity-dumped Kerr-lens mode-locked chromium:forsterite (Cr^{4+}:Mg_2SiO_4, Cr:F) laser. The center wavelengths of the fundamental and second harmonic of Cr:F laser are ∼1260 and ∼630 nm, respectively. These wavelengths are not readily accessible by titanium:sapphire (Ti:S) laser, i.e. the most popular light source for ultrafast spectroscopy. To evaluate the system, we applied it to transient absorption measurement of azulene in cyclohexane. Since the molar extinction coefficient of $S_1 \leftarrow S_0$ transition of azulene is extremely small, i.e. 300 $M^{-1}\,cm^{-1}$, we can evaluate the limit of our measurement setup.

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2. Femtosecond pump-and-probe system

2.1. Light source

Kerr-lens mode-locked Ti:S laser is known as the most stable ultrashort pulse laser system with the fundamental wavelength coverage of 750–900 nm [5]. However, stable oscillation with ≤30 fs pulse duration is limited in the wavelength region around 800 nm. Although, the SHG can expand the wavelength region, it is still restricted in the wavelength around 400 nm. One of the methods to expand the wavelength coverage is an application of optical parametric generation (OPG) or amplification (OPA) with regenerative amplifier. However, it usually requires rather large laser system with appropriate amplifiers to obtain a stable operation of the parametric devices and the system including these devices is very expensive.

The center wavelengths of the fundamental and the SHG of Cr:F laser are 1260 and 630 nm, respectively [6]. These wavelengths are not readily accessible by Ti:S laser. In addition, generation of ultrashort pulses in near IR region is not seriously affected by group-velocity dispersion arising from the optical devices in the system. Therefore, we have adapted Cr:F laser as the light source.

The composition of the femtosecond home-made cavity-dumped Kerr-lens mode-locked Cr:F laser is illustrated in Fig. 1. It is essentially identical to the one in our previous report [7]. The cavity was constructed by six mirrors, four of which were curved mirrors with radius of 10 cm. One of the flat mirrors was a 4% output coupler to get the information of the energy stored in the laser cavity. It also contained 19 mm Cr:F crystal as the laser medium, SF6 Brewster prism pair for compensation of the group velocity dispersion, and a Bragg cell for cavity-dumping. The Cr:F crystal was cooled to −10 °C and pumped by a continuously emitted diode-pumped Nd:YVO_4 laser (Millennia IR, Spectra Physics) with output of 7 W at 1064 nm. The distance between the prisms was 21 cm. The cavity-dumping efficiency of the Bragg cell was about 30% and the output pulse energy was 10–15 nJ at the dumping rate of 100 kHz. The cavity-dumping was introduced for two reasons: (i) to lower the repetition rate to avoid undesirable multiple excitations of the sample, and (ii) to achieve high peak power to generate efficient nonlinear effects such as SHG. The output pulse was focused into a 4 mm LBO crystal for the SHG. The cavity mirrors and the Cr:F crystal were purchased from Laser for Photochemistry Ltd. and the cavity-dumping system was from Camac Systems Inc.

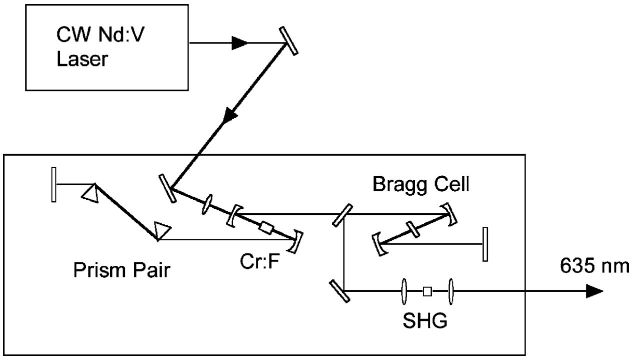

Fig. 1. Block diagram of home-made Cr:F laser.

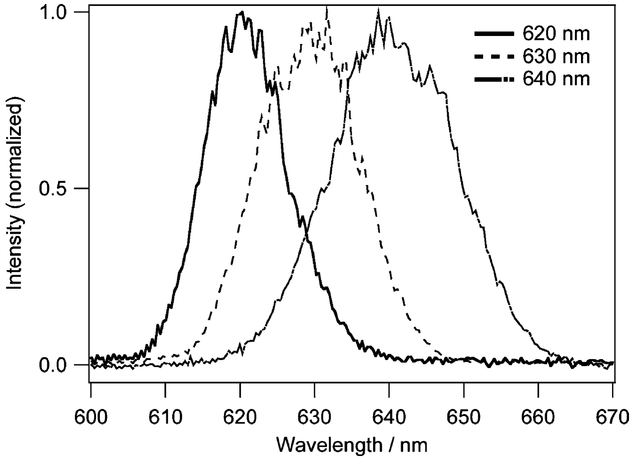

Fig. 2. Spectra of the second harmonics of the Cr:F laser centered at 620, 630, and 640 nm.

Cr:F laser is known as a wavelength-tunable IR laser and the fundamental wavelength can be tuned around 1260 nm, as mentioned above. In the present experiment, the tuning was achieved by moving one of the intracavity prisms in and out of the beam and changing the incident angle of the SHG crystal. The SHG can be tuned from 620 to 640 nm as shown in Fig. 2, which indicates that the fundamental could be tuned at least from 1240 to 1280 nm. The reflectance of the cavity mirrors were >99.5% for 1210–1360 nm except for the 4% output coupler. The limited tunability in this wavelength region may be related to the reflectance of the mirrors, emission spectra, and the pump energy.

The pulse energy and the duration are dependent on the lasing wavelength. The highest pulse energy of 6 nJ can be achieved when the wavelength was tuned to 630 nm in the present optical system. However, the pulse duration became as long as 50 fs at the 630 nm operation. The shortest pulse duration was attained with center frequency of 635 nm (fundamental light at 1270 nm). The autocorrelation trace of the second harmonic and the spectrum at FWHM-optimized-condition are shown in Fig. 3. The closed circles and the solid line in Fig. 3a are respectively the experimentally obtained autocorrelation trace and the curve calculated on the assumption of a Gaussian envelope of the laser pulse with a FWHM of 24.7 fs. The optical set up for the autocorrelation trace is shown in Figs. 4 and 5 and will be explained in later. At the FWHM-optimized condition, the laser spectrum centered at 635 nm with FWHM of about 31 nm, as shown in Fig. 3b. The spectral width and the pulse duration yielded a time–bandwidth product ($\Delta\nu \times \Delta t$) of

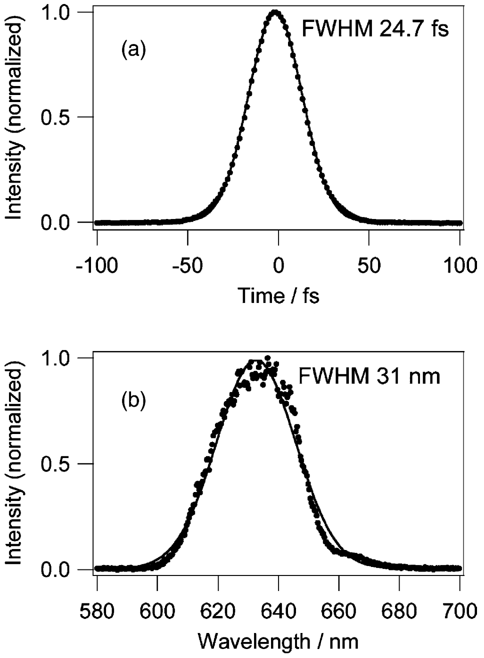

Fig. 3. (a) Autocorrelation trace (closed circles) and the fitting curve (solid line), (b) spectrum of the second harmonic of Cr:F laser for the shortest pulse in the present condition (closed circles) and the fitting curve (solid line). Assuming a Gaussian function, FWHMs of the pulse and the lasing spectrum are 24.7 fs and 31 nm in (a) and (b), respectively.

0.57, which is ca. 1.3 times that of the transform-limited relation. This indicates that the pulse compensation is nearly in ideal condition. The pulse energy of the second harmonic at this condition was ∼4 nJ.

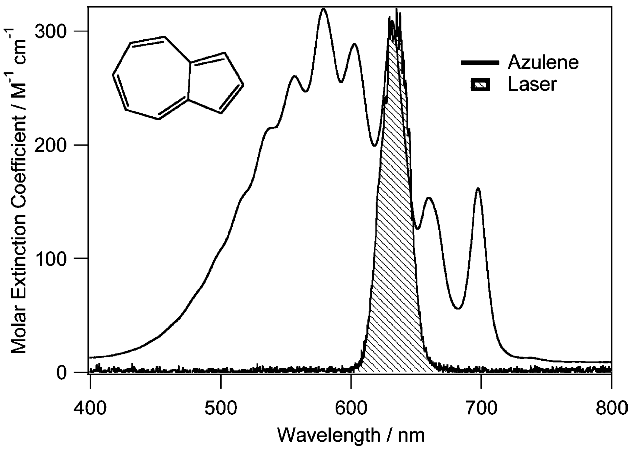

Fig. 5. Absorption spectrum of azulene in cyclohexane, compared with the second-harmonic spectrum of the Cr:F laser and molecular structure of azulene.

The shortest pulse ever generated from a Cr:F oscillator up-to-date is FWHM of 14 fs at 1300 nm [8]. The spectral width of this laser was about 250 nm. However, very few investigations have been reported for cavity-dumped Cr:F laser [6,7], and the shortest pulse width under cavity-dumped operation was reported to be 30 fs by our own group [7]. In the present study, we have achieved the 25 fs pulse duration with the oscillator setup identical with the previous report, by introducing the new pumping CW laser (Millennia IR). The spatial mode of Millennia IR seems to be better than the previous pumping laser; less pumping power was necessary to obtain similar output of the Cr:F laser. Restriction of the

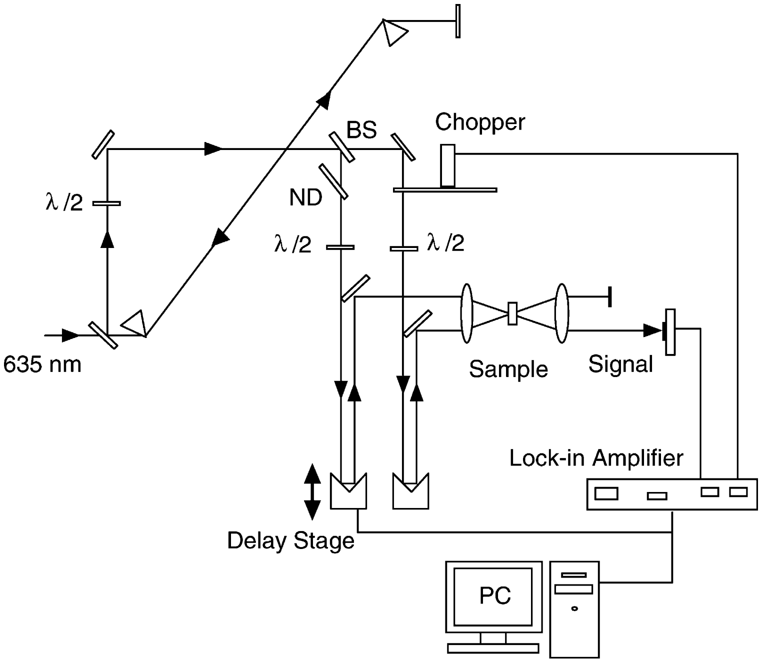

Fig. 4. Optical set-up for the single-wavelength transient absorption measurement: λ/2, halfwave plate; BS, beam splitter; ND, neutral density filter; and PD, photodiode.

pulse duration in the present laser system may be the length of Cr:F crystal, i.e. 19 mm [9] which was only commercially available when we started the construction. Introducing shorter crystal may be effective for further improvement of the pulse duration in the present system. We are planning to change the crystal with length of 7 mm which can result in 20 fs pulse duration [10]. For the 14 fs pulse duration, not only the crystal length needs to be shortened to 5 mm but also specially designed and fabricated double-chirped mirrors in combination with high-index PBH71 prisms are necessary [8].

2.2. The optical setup and the detection system

Fig. 4 shows experimental set-up for measurement of autocorrelation function of the second harmonic pulse as well as the pump-and-probe signal. The second harmonic pulse was divided into pump-and-probe pulses with an intensity ratio of 1:1 by a beam splitter. The probe pulse intensity was reduced to 1/10 for the detection of transient signal by a tunable ND filter. The arrival time of the probe pulse was varied relative to the pump pulse by introducing a computer-controlled optical delay stage (nanomover, Melles Griot) in the optical path of the probe pulse. The minimum step and the maximum length of the delay stage is 100 nm (0.67 fs) and 25 mm (167 ps), respectively. For the transient absorption measurement, photodiode (Model 2031, New Focus) with a lock-in amplifier (Model 5210, EG&G Instrument) was used. The chopper synchronized to the lock-in amplifier modulated the pump pulse with a frequency of 2349 Hz. Both pump-and-probe pulses were focused into the sample by a lens with 10-cm focal length. These pulses were recollimated after passing through the sample and then directed towards an aperture that allows only the probe pulse to be guided to the detector. This system was previously utilized to the pump–probe measurements of triphenylmethane dyes [11] with molar extinction coefficient of ∼80,000 $M^{-1}\,cm^{-1}$ and a blue copper protein, plastocyanin [12], with molar extinction coefficient of ∼5000 $M^{-1}\,cm^{-1}$. Ultrafast dynamics of the X-B band absorption of iodine with molar extinction coefficient of 200 $M^{-1}\,cm^{-1}$ have been measured with dye lasers, Nd^{3+}:YAG lasers and glass lasers [13a–d]. However, measurement with such a low molar extinction coefficient has never been reported for Cr:F laser and will be challenging.

To avoid multi-photon absorption process of azulene molecule, appropriate ND filters were introduced into the beam pathways. Intensities of the pump-and-probe pulses were attenuated to be 760 pJ per pulse (ca. 2.4×10^9 photons per pulse) and 70 pJ per pulse, respectively. Azulene (Aldrich) and spectral-grade cyclohexane (Kanto Chemicals) were used as received. The sample was placed into a home-made high-speed rotating cuvette to avoid optical degradation and multiple excitation of the sample. The optical path length of the sample cuvette was 0.5 mm and absorbance of the sample was ∼1.0 at the peak wavelength of the $S_1 \leftarrow S_0$ absorption.

3. Direct detection of the S_1 state dynamics of azulene

Azulene is a famous molecule that does not obey Kasha's rule [14]. In 1955, Beer and Longuet-Higgins reported an anomalous fluorescence of azulene [15]. The fluorescence of azulene from the S_1 state was much weaker than that from the S_2 state. This characteristic behavior has been interpreted as due to the large energy gap between the S_2 and the S_1 states of azulene and extraordinary fast internal conversion from the S_1 to the S_0 because of the low energy level of the S_1 state. Much attention has been focused on these characteristic behaviors [16–19] and detection of azulene in the S_1 state [20–27] has been attempted by many researchers. The first accurate measurement of the S_1 state lifetime of azulene was performed by Ippen et al. with two-photon absorption fluorescence measurement and they presented a value of 1.9 ± 0.2 ps [22]. With a short optical pulse at 615 nm, azulene molecules were first excited up to the S_1 state. A second delayed pulse excited these molecules into the S_2 state which emits the easily detectable $S_2 \rightarrow S_0$ fluorescence. Thus, the number of molecules in the S_1 state as a function of time can be determined by measuring the amount of the $S_2 \rightarrow S_0$ fluorescence as a function of delay between the two pulses. Recently, similar experiment was carried out with sub-20 fs optical pulse by Wurzer et al. [20,21]. The S_1 state lifetime of 1.7 ps decreased to 400 fs with excess vibrational energy of 1300 cm^{-1}. They also observed oscillatory behavior in their signal with frequencies of ∼160 and ∼200 cm^{-1} and they were assigned to S_1 state vibrations.

However, to the best of our knowledge, direct measurement of $S_n \leftarrow S_1$ absorption have never been reported for azulene and there are very few reports on S_0 state absorption recovery [23,24]. Shank and colleagues reported that the recovery time of the ground state was 1.9 ± 0.5 ps which matched very well with the S_1 state lifetime [23]. Their result suggests that the $S_1 \rightarrow T_1$ intersystem crossing is a minor effect on the short S_1 state lifetime. Sukowski et al. studied vibrational cooling in the ground state by monitoring the red-edge of $S_1 \leftarrow S_0$ absorption after photo-excitation to S_1 state [24]. They observed that the cooling takes place on a time scale of several tens of picoseconds in various solvents. They concluded that energy transfer occurs from azulene molecule to the surrounding solvent shell by binary collisions and the energy transferred per collision lies in the range of several hundred wavenumbers depending on the vibrational excess energy. The energy flowing from the solute to the solvent heats the immediate surrounding of the solute and the transport of energy within the solvent is described by the conduction of heat.

The difficulty of measuring ground state recovery arises from the small molar extinction coefficient of the $S_1 \leftarrow S_0$

transition, i.e. $\sim$300 M^{-1} cm^{-1}. In addition, the small $S_n \leftarrow S_1$ molar extinction coefficient also may make it difficult to measure the S_1 state absorption. Transient absorption signal, ΔAbs, is usually given by

$$\Delta\text{Abs} = (\varepsilon_e - \varepsilon_g) C_e, \quad (1)$$

where ε_e and ε_g are the molar extinction coefficients of the excited state and that of the ground state molecule, respectively. C_e is the concentration of the excited species and is a function of delay time after excitation. Only if $\varepsilon_e > \varepsilon_g$ at the probe wavelength, excited state absorption will appear as positive signal. In the case when $\varepsilon_e \cong 0$ and $\varepsilon_g > 0$, the signal intensity is negative and it can be regarded as the bleach of ground state absorption. If $\varepsilon_e \cong \varepsilon_g$, both the excited state absorption and ground state bleach would be hard to detect, because $\Delta\text{Abs} \cong 0$ in Eq. (1). As will shown in Fig. 6, the ε_e is smaller than the small ε_g, which has been preventing the detection of $S_1 \rightarrow S_0$ recovery by transient detection of the ground state bleaching.

Fig. 6 shows the time profile of the absorption change of azulene in cyclohexane excited with the Cr:F laser centered at 635 nm. We chose this wavelength because of the stability of the laser system. This signal was accumulated over 20 h of operation. The original ordinate is given as difference of transmittance of the probe pulse with and without the pump pulse and converted into ΔAbs as will be shown in Appendix A. The negative ΔAbs indicates that ε_e in the monitoring wavelength region is much less than ε_g. The strong negative signal around time origin is followed by rather slow rise of the signal accompanied with oscillations that vanishes in a several picosecond timescale. The strong signal around the time origin was previously attributed to the "coherent artifact". This coherent signal was attributed to the nonresonant two-photon absorption to the S_2 state [20]. However, this assignment does not seem to be the case for the present experiment, because the long time recovery of the S_2 state with a lifetime of 1.33 ns [28] was not detected in our signal and only the short decay within a few picoseconds was observed. Coherent interaction of the probe pulse with nonresonantly scattered pump pulse could be the plausible candidate to the present signal around the time origin. Such an effect is often observed for samples with small molar extinction coefficients [29]. The signal following the coherent spike gradually decreases in a multi-exponential fashion with weak coherent vibrations and completely diminishes within several picoseconds.

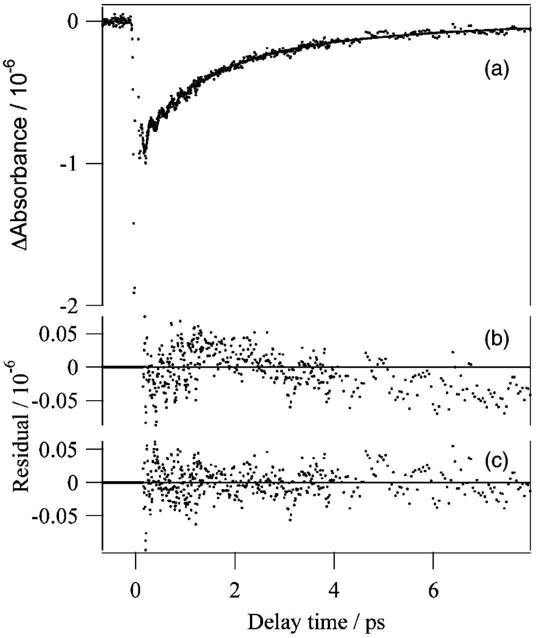

Fig. 6. (a) Transient absorption signal of azulene at 635 nm and the fitting curve after 150 fs with double exponential function and an oscillation of 160 cm^{-1}. The ordinate is in the ΔAbs estimated by Eq. (A.1). Residual of the fitting with (b) single exponential function and (c) double exponential function with an oscillation of 160 cm^{-1}.

To elucidate the time profile, the signal was analyzed by assuming a fitting function, $f(t)$, which was a sum of exponentials and an exponentially damped cosine function:

$$f(t) = -\sum_{i=1}^{n} A_i \exp\left(-\frac{t}{\tau_i}\right) - A_\nu \exp\left(-\frac{t}{\tau_\nu}\right) \cos(\nu t + \phi). \quad (2)$$

Here, A, τ, ν, and ϕ are amplitude, lifetime, vibrational frequency, and phase shift, respectively. To exclude the effect of the coherent artifact, the fitting was performed at and after 150 fs following the time origin. The results of the analysis are summarized in Table 1 and the calculated curve and residuals are shown in Fig. 6. Analysis based on the single exponential function gave a lifetime of 2.1 ps, which agreed with the result of Shank et al. [23]. However, the residual signal shown in Fig. 6b and c indicates that the analysis with double exponential function with the lifetimes of 1.0 and 3.9 ps gives better reproducibility (Table 1). The better experimental time resolution and higher S/N ratio may resolve the multi-exponential feature of the ground state recovery. The longer time constant of 3.9 ps may be due to the vibrational cooling of the ground state. Sukowski et al. obtained a cooling time of 15 ± 5 ps in benzene with picosecond transient absorption measurement with excitation at 527 nm and probed at 735 nm [24]. Since our excitation was at 635 nm, excess energy was smaller and the cooling time might have shortened.

Table 1
Fitting parameters for the transient absorption signal of azulene

	A_1	τ_1 (ps)	A_2	τ_2 (ps)
Decays				
Single exponential function	0.87	2.1		
Double exponential function	0.51	1.0	0.36	3.9
	A_ν	ν (cm^{-1})	ϕ (°)	τ_ν (ps)
Vibration	0.13	161	14	0.41

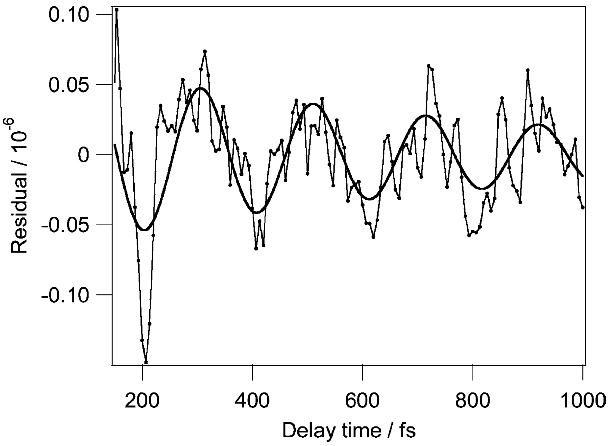

Fig. 7. Oscillatory contribution to the experimentally obtained signal. The solid line represents the damped cosine function with frequency of 160 cm^{-1}.

In addition to the exponential decay process, a weak oscillation with frequency of 160 cm^{-1} appeared in the residual shown in Fig. 7. Two vibrations at ∼160 and ∼200 cm^{-1} were detected in the two-photon absorption fluorescence measurement [20,21], and these two frequencies were assigned to the S_1 state vibrations. However, in our case, contribution from the excited state absorption ($S_n \leftarrow S_1$ transition) was estimated to be very small since the intensity of ΔAbs shown in Fig. 6 was negative. Hence, the present 160 cm^{-1} oscillation may be attributed to the ground state vibration. Such a low frequency mode was observed in the far-infrared and Raman spectra of the ground state of azulene, which was assigned to the out-of-plane mode by the normal mode analysis [30–35].

4. Conclusion

A transient absorption measurement system was developed with a home-made femtosecond chromium:forsterite laser as light source. This system can cover the immeasurable wavelength of Ti:S laser. The shortest second harmonic pulse duration we have obtained was 24.7 fs and the spectrum was centered at 635 nm with FWHM of 31 nm. To the best of our knowledge, this is the shortest second harmonic pulse ever generated from a cavity-dumped Cr:F laser. The performance of the laser system was examined by measuring $S_1 \rightarrow S_0$ recovery dynamics of azulene. Although the small molar extinction coefficient value of 300 M^{-1} cm^{-1}, pump-and-probe measurement clearly resolved the multi-exponential recovery profile with a very weak oscillation of 160 cm^{-1}.

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Appendix A. Estimation of the absorption difference

In the present system, ΔAbs is given by

$$\Delta\mathrm{Abs} = \frac{4\varepsilon}{\pi r^2}\frac{p\lambda}{hcN_\mathrm{A}}(1 - 10^{-\mathrm{Abs}}). \qquad (A.1)$$

Here, ε is the molar extinction coefficient of the ground state of the sample, r the diameter of laser spot, λ the wavelength of laser, p the power of pump pulse, N_A the Avogadro number, and Abs is the steady-state absorbance of the sample in the laser wavelength. In our experimental conditions ($\varepsilon = 300\,M^{-1}\,cm^{-1}$, $r = 120\,\mu m$, $\lambda = 635\,nm$, $p = 760\,pJ$, $Abs = 1.0$), ΔAbs was estimated to be in the order of 10^{-6} or less. The S/N ratio was considered to be in the order of 10^2 from the experimental data (Fig. 6). Consequently, the expected limit of ΔAbs measurable by the laser system was concluded to be in the order of 10^{-8} to 10^{-7}. Generally, the limit of ΔAbs detectable with a conventional spectrophotometer is in the order of 10^{-3}. The limit of ΔAbs detectable by the photodiode we used was also about 10^{-3}. The sensitivity magnification of the lock-in amplifier was about 10^3. The accumulation time of 1 s per point with 100 kHz repetition rate will raise the sensitivity more than 2 orders of magnitude. Consequently, theoretical limit of measurable ΔAbs was estimated to be 10^{-8}, which agrees with the experimental value. The stabilized laser system, which can detect such a weak ΔAbs as 10^{-8} with 25 fs time resolution, is expected to be applicable to various experiments such as higher order nonlinear spectroscopy.

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