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Generation of 30 fs pulses at 635 nm by frequency doubling of cavity-dumped chromium-doped forsterite laser, and its application to spectroscopy

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Abstract. A cavity-dumped Kerr-lens mode-locked chromium-doped forsterite (Cr:F) laser was developed. The fundamental frequency of 1270 nm was converted into 635 nm by second-harmonic generation in an LBO crystal. A pulse duration of 30 fs was obtained at 635 nm with energy of 3.8 nJ. The developed laser was applied to single-wavelength pump-probe measurements of dyes, malachite green (MG) and phenol blue (PB).

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The development of ultrashort-pulse lasers has greatly contributed to the achievement of time-resolved spectroscopy. In particular, the advent of Kerr-lens mode-locked Ti: sapphire (Ti:S) laser was truly a revolution because of its stability and its easy-to-handle features [1]. It could be said that the application of ultrafast spectroscopy to a wide range of scientific fields was not possible without the Ti:S laser. However, as with other lasers, the limited oscillation wavelength has been found to restrict its range of application in the case of resonant spectroscopy.

The fundamental wavelength of a Ti:S laser is 750–900 nm and its second harmonic (SH) is in the range 370–450 nm. It is said that there is a "dark window" in the visible spectrum between 500 nm and 700 nm. The generation of pulses at these wavelengths is possible by the optical parametric technique; however, it is unstable and costly because amplification is necessary. The simplest solution for such a problem is to use alternative laser material. For example, the fundamental wavelength of a chromium-doped forsterite (Cr:F) laser is close to 1260 nm and its SH around 630 nm can cover the "dark window" of the Ti:S laser.

Here we report the development of a frequency-doubled cavity-dumped self-mode-locked Cr:F laser that generates 30 fs FWHM pulses at 635 nm. This ultrashort pulse can be used to directly excite the electronic transitions of many interesting chemical and biological systems, such as model compounds of the photosynthetic reaction center [2], triphenylmethane dyes [3], bacteriorhodopsin [4], and blue copper proteins [5]. The cavity-dumper was included in the cavity to reduce the repetition rate and increase the peak power. A lower repetition rate is necessary to avoid optical damage, especially for delicate samples such as photosensitive proteins. The application of the laser to an ultrafast pump-probe experiment of some dyes is also presented.

1 Laser performance

The layout of the laser is shown in Fig. 1a. The cavity contains a 19 mm Cr:F crystal, an SF6 Brewster prism pair, and a Bragg cell. The Cr:F crystal and mirrors were purchased from Laser for Photochemistry Ltd. The 4% output coupler was from the CVI Corporation. The Bragg cell, the cavity-dumper driver and its booster were purchased from Camac Systems Inc. An output of 8 W at 1064 mn from a diode-pumped Nd:vanadate (Coherent/Compass) laser was focused into the Cr:F crystal by a 9 cm focusing lens. The Cr:F crystal was cooled to $-6\,^{\circ}$C. The prism distance was 21 cm, which was shorter than the previously reported value of 27 cm [6].

Two different values of group delay dispersion (GDD) and third-order dispersion (TOD) have been reported for a Cr:F crystal [7, 8]. Recently it has been shown [9] that the values reported in [8], namely 42 fs^2/mm for GDD and 116 fs^3/mm (double pass) for TOD, were the more accurate and we decided the prism distance by using these values. The radius of the curved mirrors were all 10 cm. The folding angles, 2θ, of the beam around the Cr:F crystal and Bragg cell were 30° and 13°, respectively. These values were determined from the following equation to compensate for astigmatism [10, 11]:

$$\theta = \cos^{-1}\left[\frac{t}{2Rn^3}\left(1-n^2 \pm \sqrt{1-2n^2+n^4+\frac{4R^2n^6}{t^2}}\right)\right],$$

where θ is the angle of incidence on the curved mirror, t is the length of the dispersive medium, R is the radius of the

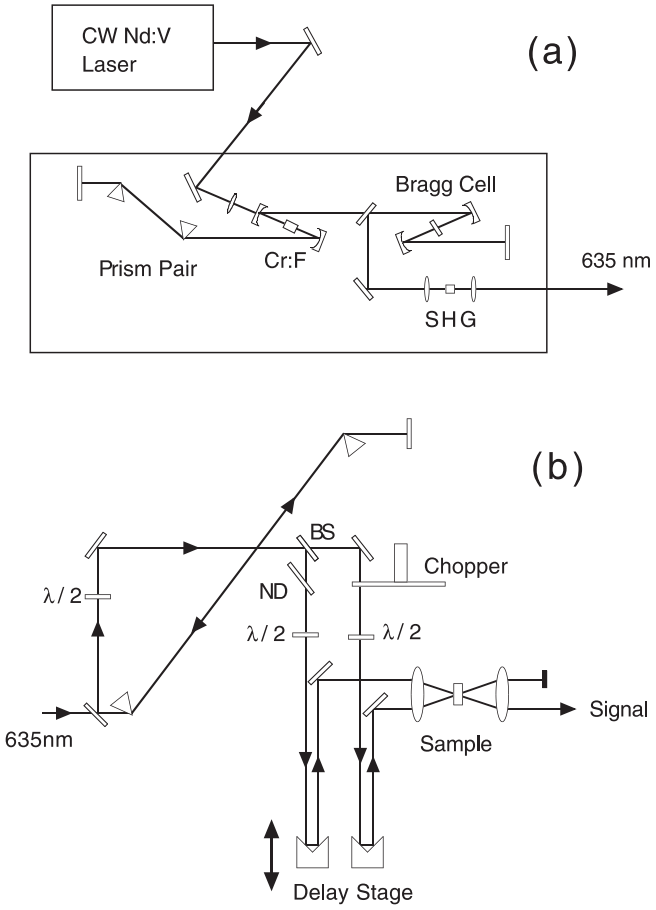

Fig. 1. a Cavity layout of the Cr:F laser. **b** Setup for the autocorrelation measurement and single-wavelength pump-probe measurement: λ/2, halfwave plate; BS, beam splitter; ND, neutral density filter

curved mirror, and *n* is the refractive index of the dispersive medium.

Mode locking was started by vibrating one of the prisms. The output from the 4% output coupler was 200 mW with an 80 MHz repetition rate. The reflection of the output from a glass plate was focused into a photodiode, which was used to synchronize the cavity-dumping with the laser. Another reflection of the output was focused into a photodiode connected to an oscilloscope that monitored the energy of the pulse train. The time dependence of the pulse energy with active cavity-dumping is shown in Fig. 2a. It can be seen from that diagram that about 30% of the intracavity energy is dumped by the Bragg cell. For a Ti:S laser, cavity-dumping efficiency as high as 80% has been previously reported [12]. The low efficiency of the Cr:F laser was due to its operating wavelength in the IR. The intracavity pulse energy is assumed to be about 63 nJ from 200 mW output from the 4% output coupler. Efficiency of 30% gives an estimated dumped energy of 19 nJ; the actual output from the Bragg cell was about 15 nJ.

The dumped fundamental beam was focused into a 4-mm-long LBO crystal (type I) for SH generation. The small value of group velocity mismatch, 6.8 fs/mm, enables the utilization of such a long crystal length [13]. The conversion efficiency was about 25% and the pulse energy generated at 635 nm was about 3.8 nJ. The spectral peak of the SH can be tuned from 615 nm to 640 nm by changing the insertion of one of the intracavity prisms. The shortest pulse duration, of 30 fs, was obtained when the spectral peak was tuned to 635 nm; the pulse duration became as long as 50 fs at shorter wavelengths. The autocorrelation trace and the spectrum of the 30 fs pulse at 635 nm are shown in Fig. 2b and c. Gaussian fits of the data are also shown for comparison.

To our knowledge, this is the shortest SH pulse ever generated from a cavity-dumped Cr:F laser. For Cr:F lasers without cavity-dumping, a fundamental pulse duration of 25 fs was reported using a 19 mm Cr:F crystal with SF6 prisms [14] and a pulse duration of 20 fs was reported for a 7 mm Cr:F crystal with SFS01 prisms [9]. However, the pulse duration of a previously reported cavity-dumped Cr:F laser was 54 fs for the fundamental pulse and 49 fs for the SH pulse [6]. The FWHM of the spectrum shown in Fig. 2c was 27 nm, which gives a time–bandwidth product of 0.60. The system has not yet reached the transform limit. Further improvements, such as shortening the Cr:F crystal or changing the prism material, may result in shorter pulses.

2 Single-wavelength pump-probe measurements

To confirm the applicability of the cavity-dumped Cr:F laser to ultrafast spectroscopy, single-wavelength pump-probe (PP) measurements of dyes, malachite green (MG) and phenol blue (PB) were carried out. Single-wavelength PP measurement is one of the simplest method to observe electronic

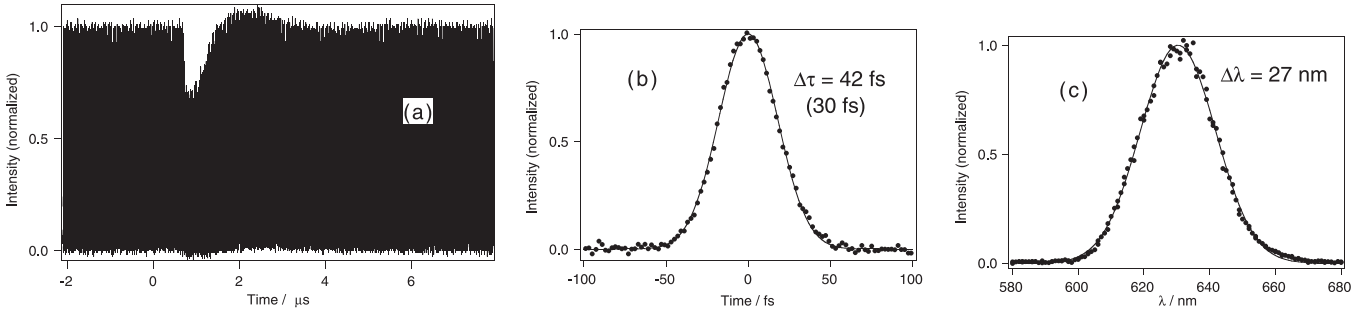

Fig. 2. a Time evolution of the intracavity energy of the Cr:F laser. The dent represents the 30% cavity-dumping. **b** Autocorrelation trace of the second-harmonic pulse of the Cr:F laser. Gaussian fit gives a 30 fs pulse duration. **c** The second-harmonic spectrum with FWHM of 27 nm, again assuming a Gaussian spectral shape

ground-state recovery from an excited state. The signal is a combination of ground-state bleach, stimulated emission, and impulse-stimulated-resonance Raman scattering. MG is a well-studied triphenylmethane dye that is known to have an ultrashort electronic excited state lifetime that depends on its solvent viscosity [15]. PB is also a dye well-known for its solvatochromic nature [16]. To our knowledge, ours was the first femtosecond measurement carried out for PB. The molar extinction coefficients of BG and PB at the absorption maximum are about 80 000 and 22 000 respectively. Normalized absorption spectra of the dyes were compared with the SH spectrum of the Cr:F laser, as shown in Fig. 3. Note that both dyes cannot be resonantly excited by the fundamental or SH of a Ti:S laser.

The experimental setup shown in Fig. 1b was used for the measurements of the autocorrelation and PP signal. After passing through a precompensation prism pair, the SH beam was split into pump and probe beams by a 50% beam splitter. At the sample position, the pump-beam energy was about 0.6 nJ and the probe-beam energy was reduced to 60 pJ by a neutral density filter. A rotating sample cell was used in order to avoid optical damage to the sample. The sample length was 0.5 mm and the optical densities of the dyes were set to about 1.2. The signal was integrated for 5 and 7 seconds/point for MG and PB respectively.

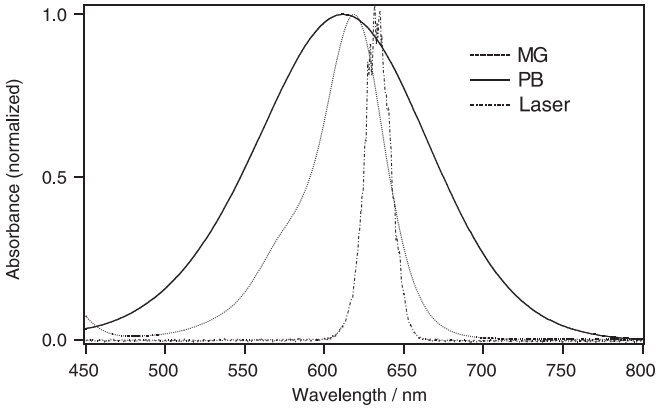

Fig. 3. Normalized absorption spectra of malachite green and phenol blue in methanol, compared with the second-harmonic spectrum of the Cr:F laser

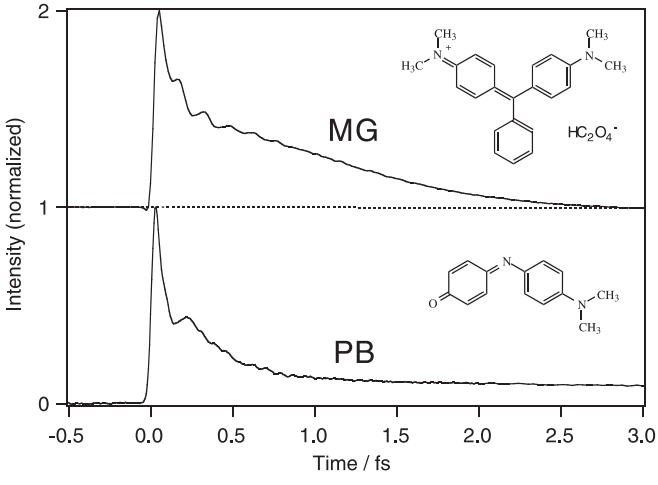

Fig. 4. Single-wavelength pump-probe signals of malachite green and phenol blue in methanol, with 635 nm excitation

The measured pump-probe signals of MG and PB are shown in Fig. 4. The ultrafast dynamics of MG had been extensively studied by femtosecond dye-laser systems, but not with such a high time resolution and signal-to-noise ratio as those observed here. The fluctuation of the normalized signal is less than ± 0.0025. The quantum beat of MG with a 150 fs period can be clearly seen. This quantum beat is assigned to the skeletal breathing mode of MG with a frequency of 225 cm^{-1} [17]. The signal decay was fitted by a multi-exponential function with decay-time constants of 160 fs and 610 fs. A rise component with time constant of 390 fs was also observed, which indicates an intermediate state. Detailed analysis of the signal for MG will be reported elsewhere [18]. In the signal of PB, at least two vibrations, with frequencies of 150 cm^{-1} and 420 cm^{-1}, were detected. Detection of a weak vibration with such a high frequency as 420 cm^{-1} was possible by the high signal-to-noise ratio. The fluctuation of the normalized signal is less than ± 0.007 which is not as small as MG due to a nearly four times smaller extinction coefficient. The PB signal features bi-exponential decay with time constants of 260 fs and 11 ps. Since the time constants are so different in value, each component should represent a different type of dynamics. Detailed analysis of the signal for PB will also be reported elsewhere [19].

3 Conclusion

A cavity-dumped Kerr-lens mode-locked chromium-doped forsterite laser was developed for ultrafast spectroscopy. The fundamental frequency of 1270 nm was converted into 635 nm by second-harmonic generation in a LBO crystal. A pulse duration of 30 fs was obtained at 635 nm, which is the shortest visible pulse ever generated from a cavity-dumped Kerr-lens mode-locked Cr:F laser. The developed laser was applied to single-wavelength pump-probe spectroscopy of dyes, malachite green and phenol blue. Signals were obtained with an extremely high signal-to-noise ratio. Nonexponential decays and quantum beats with frequencies as high as 420 cm^{-1} were observed.

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References

1. C. Spielmann, P.F. Curley, T. Brabec, F. Krausz: IEEE J. Quantum Electron. **QE-30**, 1100 (1994)
2. A. Osuka, N. Malaga, T. Okada: Pure Appl. Chem. **69**, 797 (1997)
3. Y. Maruyama, O. Magnin, H. Satozono, M. Ishikawa: J. Phys. Chem. A **103**, 5629 (1999)
4. R.A. Mathies, C.H. Brito Cruz, W.T. Pollard, C.V. Shank: Science **240**, 777 (1988)
5. L.D. Book, D.C. Arnett, H. Hu, N.F. Scherer: J. Phys. Chem. A **102**, 4350 (1998)
6. E. Slobodchikov, J. Ma, V. Kamalov, K. Tominaga, K. Yoshihara: Opt. Lett. **21**, 354 (1996)
7. A. Sennaroglu, C.R. Pollock, H. Nathel: IEEE J. Quantum Electron. **QE-30**, 1851 (1994)

8. V. Yanovsky, Y. Pang, F. Wise: SPIE **2116**, 293 (1993)
9. Z. Zhang, K. Torizuka, T. Itatani, K. Kobayashi, T. Sugaya, T. Nakagawa: IEEE J. Quantum Electron. **QE-33**, 1075 (1997)
10. H.W. Kogelnik, E.P. Ippen, A. Dienes, C.V. Shank: IEEE J. Quantum Electron. **QE-8**, 373 (1972)
11. A. Penzokofer, M. Wittmann, M. Lorentz, E. Siegert, S. Macnamara: Opt. Quantum Electron. **28**, 423 (1996)
12. M.S. Pshenichnikov, W.P. de Boeij, D.A. Wiersma: Opt. Lett. **19**, 572 (1994)
13. X. Liu, L. Qian, F.W. Wise: Opt. Commun. **144**, 265 (1997)
14. V. Yanovsky, Y. Pang, F. Wise: Opt. Lett. **18**, 1541 (1993)
15. M. Yoshizawa, K. Suzuki, A. Kubo, S. Saikan: Chem. Phys. Lett. **290**, 43 (1998)
16. T. Yamaguchi, Y. Kimura, N. Hirota: J. Phys. Chem. A **101**, 9050 (1997)
17. J. Chesnoy, A. Mokhtari: Phys. Rev. A **38**, 3566 (1988)
18. Y. Nagasawa, Y. Ando, T. Okada: Chem. Phys. Lett. **312**, 161 (1999)
19. Y. Nagasawa, A. Watanabe, Y. Ando, T. Okada: J. Mol. Liq. accepted