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Citation: [Review of Scientific Instruments](#) **84**, 086106 (2013); doi: 10.1063/1.4818977

View online: <http://dx.doi.org/10.1063/1.4818977>

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Note: A transient absorption spectrometer using an ultra bright laser-driven light source

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(Received 16 May 2013; accepted 7 August 2013; published online 20 August 2013)

An apparatus to measure transient absorption spectra for short-lived species in the gas phase was built. This was achieved by coupling a laser-driven plasma light source to a time-gated intensified-CCD spectrometer. Although the laser-driven light source features high brightness, ultra broad bandwidth and long lifetime, we found it possesses a plasma oscillation at a frequency of ~ 200 kHz with a peak-to-peak amplitude of $\sim 7\%$. This oscillation caused significant variation of the baseline of the transient absorption spectra even after averaging. To reduce this problem, we synchronized the detector gate time with the phase of the plasma oscillation. This arrangement results in much greater stability of the spectral baseline. We have tested the performance of the whole system with the time-resolved absorption spectra of excited NO_3 radicals produced by pulsed laser photolysis of N_2O_5 . © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4818977>]

For broadband transient absorption spectroscopy, the requirements of the light source are stringent. One obvious requirement is high brightness, as the total number of photons reaching the detector is limited by the short integration time. A xenon arc lamp or a deuterium (D_2) discharge lamp is often utilized in a broadband absorption experiment. But these two commonly used lamps have rather large discharge volumes and thus, rather limited brightness. Recently, a new type of ultra-bright light source¹ has become available. This light source still utilizes gas discharge to generate light, but the energy source of the plasma is from the electric field of a focused near-infrared laser, not from any metal electrodes. The driving laser beam can be focused into a very small spot such that the resulting plasma has very high energy density and high brightness. The spectral width of this type of light source is very broad (170–2100 nm)¹ because the temperature of the plasma is very high. In addition, because the plasma energy is from the driving laser, there is no electrode lifetime problem as in conventional xenon and deuterium lamps. For a standard model (Energetiq, EQ-99), the manufacturer has demonstrated a small spot size (~ 100 μm) and very high brightness (≥ 10 $\text{mW mm}^{-2} \text{nm}^{-1} \text{sr}^{-1}$),¹ which is higher than conventional xenon lamps and deuterium lamps by about one and two orders of magnitude, respectively. The small source spot would greatly improve the coupling efficiency from the light source to a grating spectrometer with a narrow entrance slit. Furthermore, the light emitted from a small volume can be readily collimated, which is very useful for a long light path experiment.

Here, we consider an integration time of 100 ns and a detected light intensity of 1 μW . Then the detected light energy is 0.1 pJ which is equivalent to 2.5×10^5 photons at 500 nm. The shot noise of 2.5×10^5 photons is about

$\sqrt{2.5 \times 10^5} = 500$, which is equivalent to 0.2% fluctuation in the light intensity. Although 1 μW might seem a small value, it already corresponds to a brightness of $30 \text{ mW mm}^{-2} \text{sr}^{-1}$ if it is focused on a pixel area of $(26 \mu\text{m})^2$ with a $f/4$ spectrometer (solid angle = 0.05 sr). If the spectrometer dispersion is 1 nm per pixel, this brightness is, in fact, higher than that of the EQ-99 light source. In this regard, we can imagine that even using the EQ-99 light source, the shot noise limit of 0.2% is not trivial to achieve for an integration time of 100 ns.

The data points of a transient absorption measurement are often dispersed in two dimensions (2D), time and wavelength. Typically, a pump pulse is used to initiate the dynamics of the system, which is followed by a continuous or pulsed probe. Although it is possible to record these 2D data simultaneously,^{2,3} it is still very often to measure several 1D data sequentially and a 2D map is reconstructed after the measurements. Two approaches are common: (i) Measure a time-dispersed absorption trace with a photomultiplier tube (PMT) at a selected wavelength.^{4,5} (ii) Measure a broadband spectrum at a given delay time with an array or CCD detector.^{6–9} In either of the approaches, due to the sequential nature of the data acquisition or that the reference spectrum of the absorption measurement has to be taken separately, the stability of the light source would affect the quality of the measurements very significantly.

In this work, we coupled the output of an EQ-99 light source to an absorption cell and an iCCD spectrometer (Figure 1). A glass tube (750 mm long, 20 mm inner diameter) with two fused silica windows at both ends was used as the flow sample cell. The output of the EQ-99 light source was collimated by a parabolic mirror (PM1, Newport, 50329AL, $f = 50.8$ mm) before entering the sample tube. Another parabolic mirror (PM2, Newport, 50338AL, $f = 101.6$ mm) was used to focus the light into the slit of the iCCD spectrometer (Spectrometer: Andor SR303i with grating SR3-GRT-0150-0500; iCCD: Andor iStar 334T-18F-73 with

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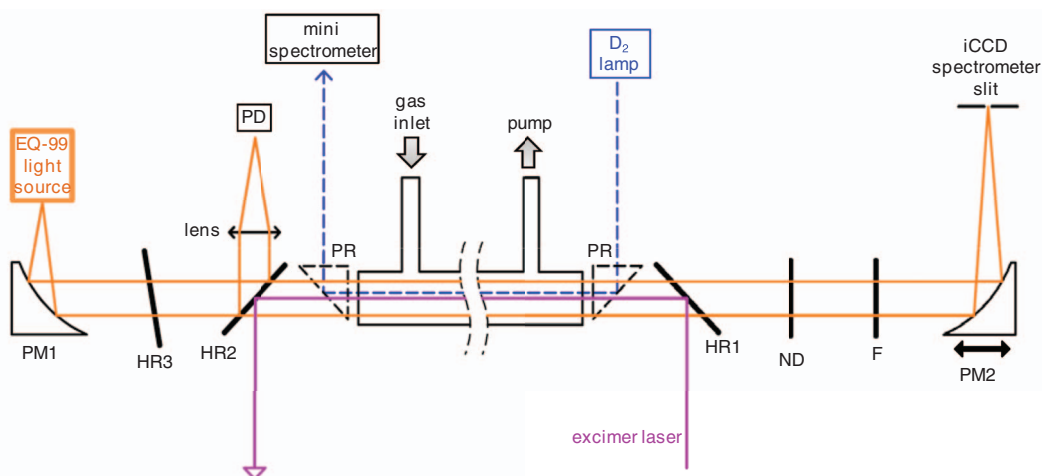


FIG. 1. Experimental schematic (not to scale). The laser-driven light source (EQ-99) was collimated by a parabolic mirror (PM1), and after passing the sample tube, it was focused into the slit of the iCCD spectrometer by another parabolic mirror (PM2). Excimer laser beam was introduced into the flow sample tube by a high reflective mirror (HR1), and to protect the EQ-99 light source from laser exposure, we used two more high reflective mirrors (HR2 and HR3) to reflect the remaining laser beam away. A photodiode (PD, Thorlabs PDA10A) collected a small portion of the EQ-99 light reflected by HR2 for synchronization. Dashed line refers to the light path (D₂ lamp and two SiO₂ prisms, PR) we used only when detecting the long-time chemical compositions in the sample tube, which was moved away during the transient absorption measurement. The length of the sample tube is 750 mm and the overall distance from the light source to the spectrometer slit is about 1950 mm. ND: neutral density filter; F: band pass filter.

VIH photocathode). The photolysis excimer laser beam (Coherent, CompExPro 205F) was introduced into the flow cell by a high reflectance mirror (HR1) for a specific wavelength (193, 248, or 351 nm). In such a collinear design, it is important to avoid the photolysis laser beam from entering the EQ-99 light source. Therefore, after the laser beam pass through the flow cell, we used two additional high reflectance mirrors (HR2 and HR3) to reflect away the remaining laser beam. The ultimate time resolution is mainly limited by the pulse width of the excimer laser (~ 20 ns).

In order to detect the long-time (\sim min) chemical compositions in the flow cell, a D₂ lamp (Ocean Optics, D-2000) coupled with a mini spectrometer (Ocean Optics, USB2000+) was used.

The spectrum of the EQ-99 light source recorded by the iCCD spectrometer and the brightness measurement can be found in the supplementary material.¹⁰ In this setup, the reference and signal spectra have to be taken separately. When testing, we observed significant variations of the baseline of our transient absorption spectra. Later we found the EQ-99 light source possesses a plasma oscillation at a frequency of ~ 200 kHz with a peak-to-peak amplitude of $\sim 7\%$.¹⁰ To solve this problem, we synchronized the gating time of the iCCD spectrometer with the oscillation of the light source, such that every spectrum was recorded at the peak of the oscillation (Figure 2). The photodiode output was AC-coupled to an inverting fast operational amplifier (op-amp, Analog Devices, AD847). The gain of the op-amp was set to a large value such that the theoretical amplified signal exceeds the power supply voltages of the op-amp (± 5 V), resulting in square wave output. This output signal triggered a delay generator (Stanford Research Systems, DG535) which further triggered the rest of the apparatuses (iCCD, excimer laser, etc.). In this scheme, the iCCD gate delay time has to be longer than the maximum photolysis delay time. The system repetition rate was set to 1 Hz to allow refreshing of the sample gas.

The effect of our synchronization control is shown in Figure 3, which shows two transient absorption spectra of NO₃ radicals recorded with and without synchronization to the EQ-99 light source in similar experimental conditions. In the free-running spectrum, not only the baseline is negative after 630 nm, but the noise is also significantly higher. The synchronization control reduces the noise by a factor of ~ 3 . That is, if there is no synchronization, we would need ~ 9 times more data averaging to achieve a similar signal-to-noise ratio. More importantly, the synchronization control gives a stable baseline, not a baseline depending on “luck.” We can also see that some small peaks (e.g., those at 614 and 638 nm) which are clearly observable in the synchronized spectrum are buried under the noise in the free-running spectrum. The peak at 614 nm also indicates our detection limit is down to 0.002 in absorbance (equivalent to about 0.9 mOD). See the supplementary material¹⁰ for further statistical analysis.

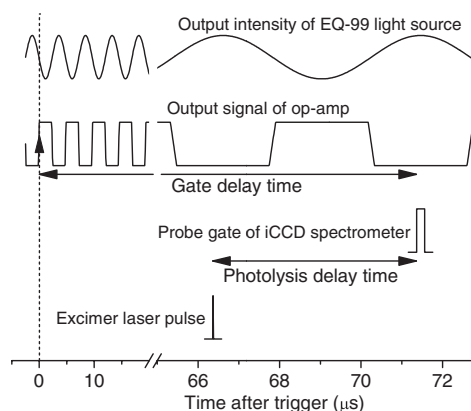


FIG. 2. Schematic of the time sequences used in our synchronization control. Note different scales of the x-axis before and after the break.

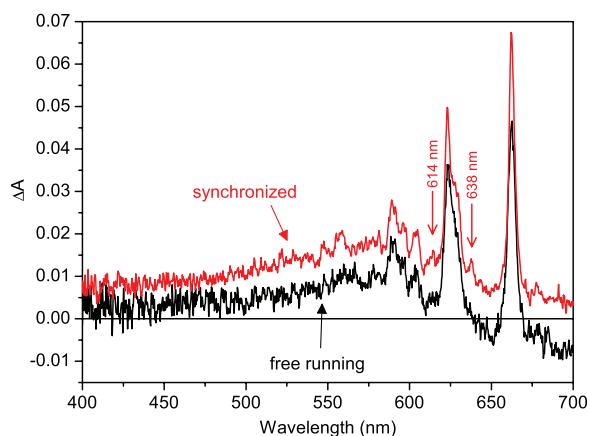


FIG. 3. Example of severe baseline drift (baseline after 630 nm is negative) when detecting NO_3 radicals (produced by photolysis of N_2O_5 at 193 nm) without synchronization to the EQ-99 light source (black line) in comparison with a similar experimental result but with synchronization (red line). Two small peaks at 614 and 638 nm are marked to indicate the improvement in the detection limit in the synchronized detection (Gate delay time: 69.5 μs).

To our best knowledge, the laser-driven plasma light source is unique in its high brightness. See the supplementary material¹⁰ for a direct comparison of using the EQ-99 light source versus a D_2 lamp in transient absorption spectroscopy. The EQ-99 light source outperforms the D_2 lamp very much.

Light emitting diode (LED) can also be a useful light source in absorption spectrometry as demonstrated in Ref. 6. However, current technology only offers bright LED in the visible, near-infrared, and near-UV wavelengths. Although UV LED of wavelengths down to 250 nm is now available, its emitting power is very weak, too weak for a transient measurement.

Contreras-Carballada *et al.*⁹ have reported transient absorption spectra in the solution phase. In their setup of nanosecond transient absorption, a high power Xe lamp (EG&G FX-504) was used as the light source and the sample was contained in a 1 cm quartz cuvette. In their experiments, the signal and reference spectra (I and I_0) were measured simultaneously by using a double-kernel optical fiber and a special data acquisition mode of the detector.⁹ The fluctuation of the light source could be compensated in such a setup. The noise level of their nanosecond transient absorption spectra⁹ is still a bit worse than that of this work, probably due to the lower brightness of their light source (after considering other parameters like gate width and spectral resolution). Although it is desired to measure I and I_0 values simultaneously, it is not trivial to employ the method of double-kernel optical fiber or any other similar method in an experiment of a long optical path length.

For testing, we measured the time-resolved absorption spectra of NO_3 radicals produced by pulsed laser photolysis of N_2O_5 (Figure 4).¹⁰ At 1.0 μs photolysis delay time, the spectrum is similar to the room-temperature NO_3 spectrum in the literature.¹¹ At shorter delay times (0.2 μs), we observed a broad featureless absorption band which was tentatively assigned to vibronically excited (hot) NO_3 .

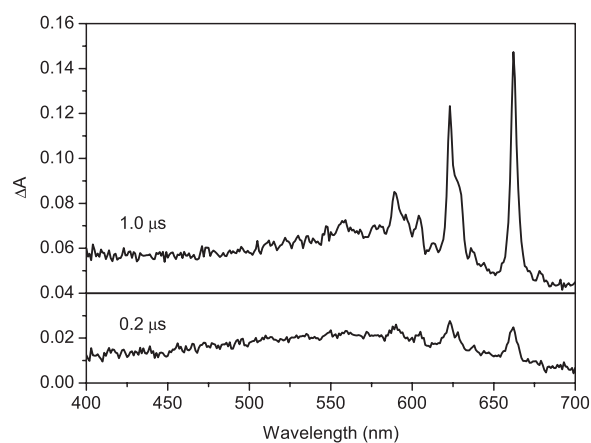


FIG. 4. Transient absorption spectra of NO_3 radicals produced by the photolysis of N_2O_5 at 193 nm at two photolysis delay times. The spectrum at 1.0 μs is shifted upward by 0.04 for visualization (SF_6 buffer gas 30 Torr; N_2O_5 0.0043 Torr; Gate delay time: 69.5 μs).

The high brightness of the laser-driven plasma light source makes it suitable for a transient measurement, especially when the entrance slit of the spectrometer is narrow. Even at a short integration time, the shot noise due to the limited number of detected photons is not significant after moderate averaging. Instead, the short-time stability or oscillation of the light source has the largest effect. Although most of the present test is in the visible region due to the wavelength range of the iCCD photocathode, the design and used optics are all good for ultraviolet (UV) wavelengths down to 200 nm. It is expected that the synchronization method demonstrated here is still helpful for UV transient absorption experiments. At shorter wavelengths, the advantages of the laser-driven light source would be more significant because other light sources, like xenon lamps and LEDs, are relatively much weaker at shorter wavelengths.

This work is supported by Academia Sinica and the National Science Council of Taiwan (NSC 100-2113-M-001-008-MY3). The authors thank Professor Y. T. Lee for discussions.

¹See <http://www.energetiq.com/html/eq99.html> for the spectral radiance, detailed features and datasheet of the laser-driven light source.

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¹⁰See supplementary material at <http://dx.doi.org/10.1063/1.4818977> for the oscillation, spectra and brightness of the EQ-99 light source, analysis on the effect of synchronization, comparison with D_2 lamp as light source, and experimental details of the transient absorption spectra of excited NO_3 .

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