

Rapid wavelength scans over one octave and application to laser-induced fluorescence

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Rapid excitation scans of laser-induced fluorescence (LIF) have been demonstrated. Broadband light was generated in a photonic crystal fiber and transmitted through a long fiber. Due to group-velocity dispersion in the long fiber, a wavelength scan emerged from the fiber in time. The wavelength was swept over approximately one octave in ~ 150 ns. The generated light was used to excite LD 700 Perchlorate diluted in methanol. The LIF excitation scan had a spectral resolution of ~ 15 nm, and the integrated fluorescence spectrum was found to be within 7% of the integrated absorption spectrum of the dye molecule. The method presented makes possible spatially and spectrally resolved LIF excitation scans with scanning speeds up to the limits set by the excited-state lifetime of the dye molecule. © 2005 Optical Society of America

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Wavelength-tunable light can be employed for the interrogation of spectral features of targets such as gases, liquids, and solid compounds. Such wavelength scans often encompass an appreciable percentage of the center excitation wavelength. For example, reliable inference of water vapor temperatures by tunable absorption spectroscopy in the near infrared benefits from a wide wavelength scan, e.g., over 7% of the center wavelength at $\sim 1.42 \mu\text{m}$.¹ When tunable absorption spectroscopy is applied in dynamic environments, e.g., in combustion, rapid wavelength scans are desirable. In engine measurements a useful wavelength scan duration is generally $50 \mu\text{s}$.¹ In biological applications the time scales are commonly longer, but wavelength-agile scans enable multiple quasi-instantaneous measurements within the biological time scale. Other advantages of rapid scanning are virtual insensitivity to long-term changes in the measurement setup, e.g., window fouling, and insensitivity of the measurement to acoustic noise, vibrations, etc.

Sensing by rapid wavelength scans over a broad wavelength range, also referred to as wavelength-agile spectroscopy, has so far been restricted almost entirely to absorption spectroscopy.¹⁻⁴ In this technique the signal is integrated over the line of sight and provides no axial resolution. Absorption-based laser tomography would circumnavigate this limitation,⁵ but one can also refer to spectroscopic techniques that are intrinsically three-dimensionally resolved. To the latter techniques belong all incoherent resonant and nonresonant scattering techniques, e.g., laser-induced fluorescence (LIF) and Rayleigh scattering, respectively. Since spatially resolved measurements are widely applied to various diagnostic and sensing purposes in inhomogeneous and turbulent media, spatially resolved wavelength-agile techniques would be a valuable supplement to already existing spectroscopic techniques.

In this work we demonstrate wavelength-agile LIF excitation scans; in such scans one measures the dependence of a LIF signal on the excitation wave-

length. In our demonstration we excited dye molecules in a liquid solution by a wavelength-agile laser source. The scan speed was ~ 3 nm/ns, and the scan extended over almost one octave (approximately 500–1000 nm). The average scanning speed within the absorption band of the dye, 550–700 nm, was ~ 2.5 nm/ns, and due to the finite time response of the detection system and the lifetime of the excited state (~ 7 ns combined) the spectral resolution of the excitation scan was limited to ~ 15 nm in this region. Each scan took ~ 100 ns. The recorded LIF excitation spectrum was found to be in 7% agreement with the absorption spectrum of the dye molecule when we compared the integrated area of both spectra, which implies that reliable spectral measurements are possible even at such high speeds.

A sketch of the setup is shown in Fig. 1. We chose a light source based on supercontinua because of its exceptionally broad spectrum. A light source similar to the one used here has been described elsewhere in detail,⁶ and only salient features of the present system are reproduced here. A Nd:LSB microchip laser (Standa 10STA-01) generates 700 ps long light pulses at $1.062 \mu\text{m}$, at a repetition rate of 25 kHz, and with an average power of 120 mW. The pulses are coupled into a 20 m long photonic crystal fiber (Crystal Fibre NL-4.7-1030) by means of two positive lenses. The average optical power of the generated supercontinuum (SC) is 40 mW and stretches from ~ 500 to 2000 nm.

To turn the spectrally broad SC pulses into a wavelength scan they are directed into a dispersion fiber of 1.687 km length and $100 \mu\text{m}$ core diameter (OFS 100/140 μm graded-index multimode fiber). Due to group-velocity dispersion the red portion of the SC spectrum travels faster through the fiber than does the blue portion, and the emerging, stretched pulses represent a wavelength scan in time (red to blue). Multimode step-index or single-mode fibers could also be used for dispersing the SC; single-mode fibers are preferable when agile light of small optical extent is desired, but it was not needed here. The chirped

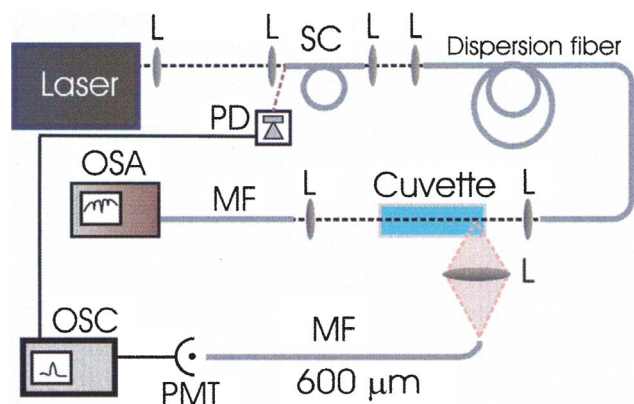


Fig. 1. Experimental setup: L, lens; PD, photodiode; SC, supercontinuum; MF, multimode fiber; OSA, optical spectrum analyzer; PMT, photomultiplier; OSC, oscilloscope.

SC was collimated with an aspheric lens (Thorlabs F230FC-B) and directed through a dye-filled cuvette. Fluorescence from the solution was collected at a right angle at a magnification of 1.6, using a plano-convex lens (Thorlabs LB1761). The dye used (Exciton LD 700 Perchlorate) was diluted in methanol to $\sim 10^{-6}$ molar solution. For spatial filtering purposes, that is, to suppress diffuse reflections and other background light, the fluorescence was imaged onto the front end of a metal-jacketed $600\ \mu\text{m}$ core fiber featuring a numerical aperture of 0.22 (Oxford Electronics, Ltd., HP SIR600P). The collected light was directed onto a photomultiplier (PMT, Hamamatsu R928) operated at $-1\ \text{kV}$, and the PMT was read out by a real-time oscilloscope (Tektronix TDS 7404, 4 GHz analog bandwidth) at a sample rate of 50 ps/point. The oscilloscope was triggered with the output of a fast photodiode (Newport 818-BB-30) that was irradiated with a surface reflection of the laser pulse off the input face of the photonic crystal fiber. To measure the absorption spectrum of the dye solution the light transmitted through the cuvette was coupled into a $62.5\ \mu\text{m}$ graded-index fiber (Optical Cable Corporation AX01-030N-W). The output of the fiber was in turn coupled into an optical spectrum analyzer (Ando AQ-6315-A).

Figure 2 shows the absorption spectrum of the dye solution. This spectrum was measured by detecting the transmitted radiation into an optical spectrum analyzer with and without the cuvette. Also shown is the power spectrum of the dispersed SC, which is preferentially attenuated at shorter wavelengths. This attenuation is due almost entirely to Rayleigh scattering in the dispersion fiber. Despite this drawback, the wavelength-agile light source offered sufficient optical power for conducting LIF excitation scans, as can be seen in Fig. 3. Here, both a time trace of the light emitted from the dispersion fiber (1000 averages) and a LIF trace (single shot) are depicted. Both signal traces were corrected for dark current and a spurious background caused by diffuse reflections. Also shown is the dependence of the laser wavelength on time. Notice the wide scanning range of almost one octave. The time trace of the excitation laser was recorded by replacing the cuvette in Fig. 1 with an aluminum mirror and directing the laser into

the LIF collection arm. The strong laser beam was attenuated with neutral-density filters ($\times 10^{-7.4}$). The sudden rise of the laser power close to the point of origin in the diagram is due to the sensitivity of the PMT cathode.

The PMT signal exhibits a strong rise between 50 and 70 ns (approximately 750–700 nm) due to LIF from the dye molecules. As already discussed, the dye solution absorbs in a wavelength region subject to a strong wavelength-dependent attenuation of the excitation laser (see Fig. 2). Therefore, the decrease in signal for $\sim 80\ \text{ns}$ and later is due to a combined decrease in excitation power and a decrease in the absorption of the dye (see Fig. 2). The signal for earlier times ($< 40\ \text{ns}$) is caused by elastic scattering in the solvent and the amplitude of the scattering is, in comparison to the LIF signal, out of proportion due to the very high excitation power at those wavelengths.

There are several limiting factors to the time resolution of the LIF trace, and hence to the spectral resolution of the excitation scan. First, there is a fundamental limit due to the finite lifetime of the fluorrescer of $\sim 4\ \text{ns}$.⁷ Second, the response time of the PMT used is $\sim 4\ \text{ns}$. Due to the combined effect of

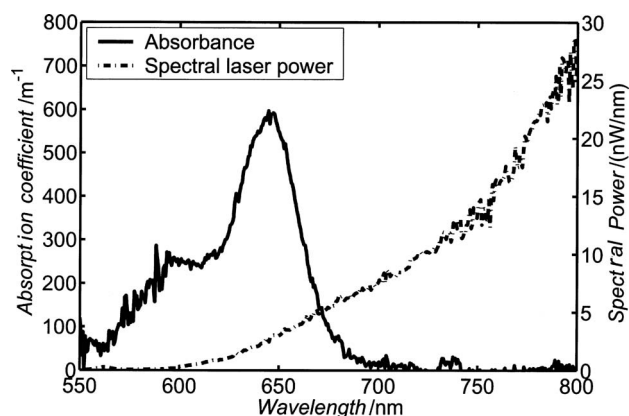


Fig. 2. Absorption coefficient of the dye solution (LD 700 Perchlorate in methanol) and the spectral power of the laser field directed into the dye solution. Spectral resolution, 5 nm.

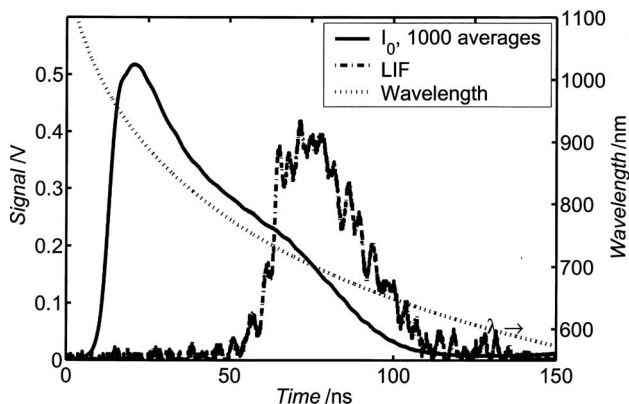


Fig. 3. Time traces of the output from the dispersion fiber (I_0 , 1000 averages) and of the excitation scan of LIF from the dye (single shot). Also shown is the dependence of the excitation wavelength on the scan time. Notice that the wavelength is swept over almost one octave.

both the finite excited lifetime and the response time of the PMT resolution of the excitation scan is ~ 6.6 ns, which was measured by exciting the dye solution with an undispersed SC pulse and by recording the time-dependent LIF signal.

The scan rate of the chirped SC was ~ 2.5 nm/ns within the absorption band of the dye, and the above time response of ~ 6.6 ns hence implies a spectral resolution of ~ 15 nm, which is suitable for resolving the broadband absorption spectrum of large molecules such as the dye molecule excited in this work.

After having successfully demonstrated wavelength-agile LIF excitation scans, the question remains whether the recorded fluorescence maps the absorption spectrum of the target molecule, i.e., whether this method can be used to identify specific absorbers and whether quantities such as concentration and temperature can be derived from the LIF trace. To tentatively answer this question we show a comparison of the excitation scan and the absorption spectrum of the dye solution in Fig. 4. The LIF trace was corrected for variations in laser power, as shown in Fig. 3, by assuming excitation in the linear regime. Figure 4 reveals almost no agreement at all; only the onset of the LIF signal coincides with the absorption curve. The reason for this discrepancy is the strong absorption of the dye. When correcting the optical power of the laser with the transmission of the excitation light through the dye to the measurement location within the cuvette, the agreement is substantially enhanced. To put the agreement on a quantitative footing the scaled spectra in Fig. 4 were both integrated, and the areas were found to agree to within 11%. Another supporting measurement was to lower the mole fraction of the dye by 2 orders of magnitude and repeat the above measurement. Due to the low signal levels the signal-to-noise ratio was substantially larger, but in this case the absorption

curve and LIF/I_0 showed an even better agreement (7% deviation in the scaled areas of both curves). The agreement affirms the potential of deriving measurements such as number densities and temperature from wavelength-agile excitation scans.

To summarize, we emphasize that wavelength-agile spectroscopy offers new venues for sensing in dynamic processes. We have extended the family of wavelength-agile techniques by demonstrating spatially resolved wavelength-agile spectroscopy at a point with rapid LIF excitation scans. The spectral resolution of the rapid wavelength scans for a given dispersion is corrected by the time response of the detection system and the finite lifetime of the excited fluorescent state. The integrated LIF excitation scan was found to be within 7% of the integrated absorption spectrum of the dye.

Potential applications of this technique are various. For example, the temperature dependence of the dye absorption spectrum could be exploited for spatially resolved measurement of temperatures or the pH value in a liquid.⁸ Another example is the spatially resolved sensing of temperature and species concentration of, e.g., hot CO_2 , in engines. However, most combustion constituents of interest absorb in the UV portion of the electromagnetic spectrum and for this task UV wavelength-agile lasers would be needed. Although it is not trivial, a SC based approach might be extended to the UV. Alternatively, an UV version of a wavelength-agile external-cavity laser could be pursued.

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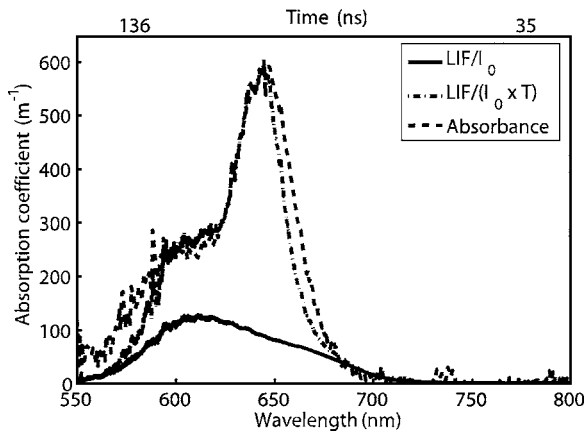


Fig. 4. Combined LIF excitation scan (1000 averages) and the absorption coefficient of the dye solution (taken from Fig. 2). The amplitude of the LIF signal was corrected for the optical power of the excitation laser (solid curve) and for the optical power together with the transmission of the laser beam to the measurement volume (dashed-dotted curve). Signals were scaled to that of the absorption coefficient. The approximate time axis for the LIF excitation scan is shown at the top.

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