Femtosecond transient fluorescence spectrometer based on parametric amplification

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We report an experimental proof-of-principle of a method for recording femtosecond, time-resolved fluorescence spectra in the visible range. The method is based on a noncollinear parametric amplification in a beta barium borate crystal and provides time resolution of the order of 100 fs. We demonstrate that with this method, transient fluorescence spectra as wide as 6000 cm^{-1} can be recorded in a single time-delay scan. Fluorescence decay dynamics and transient spectra of Coumarin 6 dye dissolved in aniline were measured to test the usefulness of the method. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1850591]

Time-resolved ultrafast gating techniques, e.g., up-conversion[1] and Kerr gating,[2] have been extensively utilized[3,4] as powerful tools for investigating fast dynamics of photophysical or photochemical processes proceeding on a femtosecond time scale.

The main disadvantage of the up-conversion technique is a limited bandwidth determined by the phase matching conditions in the nonlinear crystal. Because of that, the nonlinear crystal angle has to be optimized for different wavelengths, and thus the time evolution of a broad fluorescence spectrum is constructed from several separate time scans. Only recently, it has been demonstrated that in a properly designed setup,[5] the bandwidth of the up-converted signal can be as large as 10 000 cm^{-1}.

The useful bandwidth in the Kerr gating method is very large, but its time resolution is limited by the response of the Kerr medium—typically a few picoseconds for molecular liquids that are the most popular. It has been shown recently that application of glasses instead of liquids leads to subpicosecond time resolution with a reasonable efficiency of a few percent.[6,7]

In this letter, we report a method for recording femtosecond time-resolved fluorescence spectra. It is based on a noncollinear parametric amplification: a process that has been widely used for amplification of the white light continuum and which forms the basis of the noncollinear optical parametric amplifier (NOPA) technology.[8–11] The main advantage of using a noncollinear geometry is that it allows for a broadband amplification—a relatively flat gain profile in 550–800 nm range can be achieved.[12] It has been also demonstrated that a NOPA can be applied to light pulses of extremely low energy (femtojoules),[13,14] and it has been suggested that the same scheme can be applied to detect very weak fluorescence.[13] In this letter, we describe construction and performance of a NOPA-type transient fluorescence spectrometer.

The experimental setup of the NOPA-type transient fluorescence spectrometer is shown in Fig. 1. A train of 60 fs, 0.6 mJ pulses from a 1 kHz Ti:sapphire chirped pulse amplifier was split with a 4:1 ratio. The two resulting beams were frequency doubled in 0.5 mm beta barium borate (BBO) crystals to obtain 60 fs, 400 nm pulses. The stronger of the beams served as a gate, while the weaker was used to excite the fluorescence in the sample. The half-wave plates HW1 and HW2 were used to independently control the beam power in both arms from 0 up to ~100 mW (gate beam) and from 0 up to ~12 mW (excitation beam). Yet another half-wave plate HW3 rotated the polarization of the gate beam by 90° in order to achieve appropriate interaction in the parametric amplification process (the crystal was cut for type I phase matching, which requires mutually perpendicular linear polarizations of the fluorescence and the gate beams). The gate beam was focused with a spherical mirror (R = 1 m) onto a parametric amplifier crystal (0.5 mm-thick BBO). The excitation beam was focused with a 300 mm focal length fused silica lens into the sample flow-through cell with net thickness of 0.5 mm and windows 2.5 mm thick. A solution of Coumarin 6 dye in aniline was flowed through the cell.

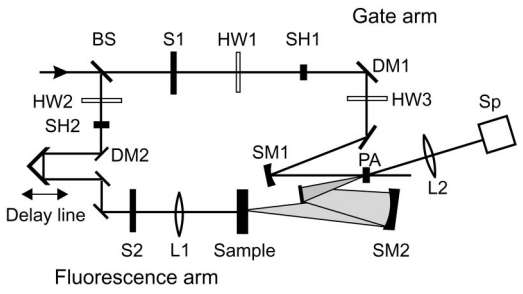

FIG. 1. Scheme of the time-resolved fluorescence spectrometer based on noncollinear parametric amplification. BS:4:1 beam splitter; S1, S2: mechanical shutters; HW1-HW3: half-wave plates; SH1, SH2: 0.5-mm-thick frequency-doubling BBO crystals; DM1, DM2: dichroic mirrors; L1, L2: fused silica lenses; SM1, SM2: spherical mirrors; PA: 0.5-mm-thick parametric amplification BBO crystal; and Sp: spectrograph.

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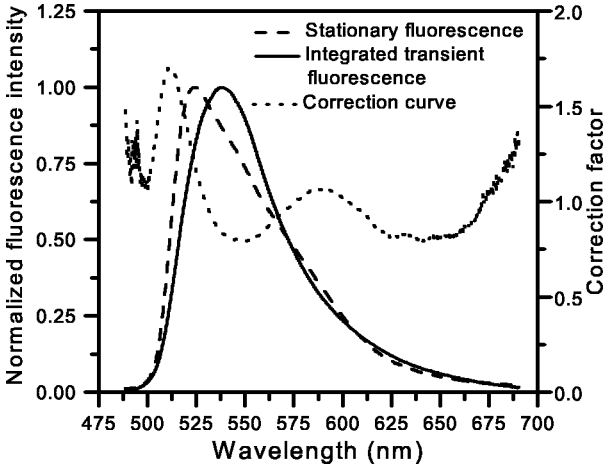

FIG. 2. Comparison of the steady-state fluorescence spectrum and integrated transient fluorescence spectrum of Coumarin 6 in aniline. The latter was obtained by integrating transient spectra over the range of available delay times (0–100 ps). The correction curve used to correct transient spectra is the ratio of the two spectra.

The fluorescence originating in the sample was collected with a 5-cm-diameter spherical ($R=600$ mm) mirror and imaged onto the parametric amplifier crystal. We adjusted the direction of the fluorescence beam to match the apex angle of the parametric superfluorescence cone emitted by the BBO crystal when illuminated by a strong gate pulse. The BBO crystal was rotated to achieve the widest possible spectrum of the parametric superfluorescence ring. Amplified fluorescence was collected with an achromatic lens L2 and focused onto the slit of a grating spectrograph equipped with a CCD array. We found that the amplified fluorescence was so intense that neutral density (ND) filters had to be placed in front of the slit to avoid detector saturation. Depending on the pump beam intensity, the total optical density of the filter set was between 2 and 5. We also recorded the stationary fluorescence spectrum in the same setup, but with the gating pulse blocked and ND filters removed.

To estimate the time resolution of the parametric amplifier, a cross-correlation between 800 nm pulses leaked through the dichroic mirror DM2 and the gate pulses was measured, yielding ~110 fs full width at half-maximum. This measurement has been done with the sample cell removed from the signal arm.

Two mechanical shutters S1 and S2 blocking the gate and the pump beams, respectively, were used to record sequentially the following spectra: (1) the spectrum of the parametric superfluorescence from the BBO crystal in the absence of the sample fluorescence (S1 open, S2 closed), (2) the spectrum of the stationary unamplified fluorescence from the sample transmitted through the BBO crystal (S1 closed, S2 open) and (3) the summary spectrum of the amplified, gated fluorescence and both of the spectra just listed (both shutters open). The raw spectrum of the amplified, gated fluorescence was obtained by subtracting (1) and (2) from (3). This procedure is well justified, because the BBO crystal is totally transparent for visible light. We found that the shape of the raw spectrum was significantly distorted due to nonflat amplifier gain curve. In order to correct this, we assumed that, in the lowest approximation, the shape of the parametric superfluorescence spectrum reflects the profile of the gain curve. The transient fluorescence spectrum was calculated as a ratio of the raw spectrum to the parametric superfluorescence spectrum.

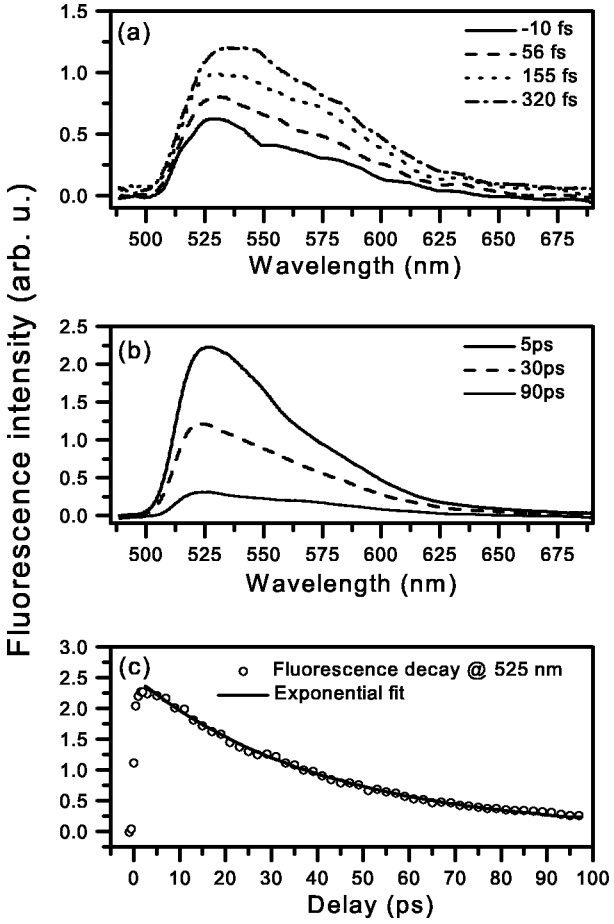

FIG. 3. Time-resolved fluorescence spectra of Coumarin 6 in aniline for short (a) and long (b) delays between excitation and gate pulses. The raise of the signal for short delays is accompanied by a shift of the maximum towards longer wavelengths, presumably caused by a vibrational cooling, whereas the quenching of the fluorescence for longer delays is a result of electron transfer from the solvent to the dye molecules. The kinetic trace of the signal at the maximum of the spectrum together with a monoexponential fit of the decay is shown (c).

The dispersion of the sample cell output window as well as the solvent itself introduces a wavelength-dependent mismatch of the zero delay. In order to correct for this effect, we need to know the group delays for different spectral components of the fluorescence. We obtained values of these delays by utilizing the fact that the fluorescence rise time (defined as a time interval in which the signal rises from 0.05 to 0.95 of the maximum value) was very similar for different wavelengths and was equal to approximately 500 fs. This allowed us to identify the group delay at a specific wavelength with the delay at which the signal at this wavelength reaches one-half of its maximum value. The error of the group delay obtained this way is less than the time resolution of the setup. With the group delays determined as described, we shifted kinetic traces for each wavelength by a proper value.

Figure 2 shows the stationary fluorescence spectrum and the spectrum obtained by integrating the time-resolved fluorescence spectra in the entire delay-time range covered in our experiment (0–100 ps). One would expect that the integrated spectrum should well reproduce the stationary spectrum because the time range is sufficient for the fluorescence to decay down to less than 10% of its maximum value. Nev-

ertheless, a spectral shift of the maxima and a slight difference in the shapes of the two curves are observed. We attribute this effect to the difference between the spectrum of the parametric superfluorescence and the gain curve of the amplification process. All the registered transient spectra were corrected for this distortion by using the ratio of the stationary spectrum to the integrated transient spectrum as a correction function (shown as a dotted line in Fig. 2).

Figures 3(a) and 3(b) show transient spectra of Coumarin 6 dissolved in aniline. It is well known that intermolecular electron transfer from electron-donating solvents like aniline to a Coumarin molecule in the excited state results in efficient fluorescence quenching.[15] Figure 3(c) shows the fluorescence decay measured at 525 nm. A single exponential fit for this decay is also shown in the figure. The fluorescence decay time is 40 ± 1 ps and lies within the range of fluorescence lifetimes measured for different Coumarin dyes dissolved in aniline (10–1000 ps).[15]

Our proof-of-principle setup has not been optimized for either time resolution or sensitivity. For a given laser pulse duration, the time resolution is limited by the dispersion in the sample/cell and group velocity mismatch (GVM) in the amplifier BBO crystal. Our calculations show that in the spectral region of interest (500–700 nm) the GVM varies between ~20 and 150 fs/mm, which results in the time resolution due to the crystal between ~60 and 100 fs in our experiment. The same calculation gives 112 fs for the cross-correlation between the gate pulse and the laser pulse at 800 nm, which is very close to the value we measured.

We did not determine experimentally the sensitivity of our gating method. Since the gain in our parametric amplifier is of the order of 10^5, the sensitivity is not limited by the detector noise. However, the amplification process introduces its own noise,[16] which gives rise to the parametric superfluorescence. In the limit of a very weak fluorescence, the superfluorescence intensity is comparable to the amplified fluorescence—in our setup the ratio of the two was ~1:3. As a result, we had to resort to differential measurements to subtract the superfluorescence signal. In this case, the sensitivity of the method is not limited by the intensity of the amplified fluorescence, but rather by fluctuations of the gate pulse energy.

In conclusion, we have demonstrated experimentally a method for ultrafast fluorescence gating. The method, based on noncollinear optical parametric amplification, provides subpicosecond time resolution, wide spectral bandwidth covering most of the visible range, and sensitivity that is not limited by the detector noise.

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