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Interference between femtosecond pulses observed via time-resolved spontaneous fluorescence

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Abstract

We study spontaneous fluorescence excited by a series of phase-controlled femtosecond pulses in an inhomogeneously broadened medium containing a frequency comb of sharp spectral holes. We show that evolution of the spontaneous fluorescence on picosecond time scale is sensitive to interference between the excitation pulses and that varying the relative phase between the excitation pulses changes the time evolution of the fluorescence. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Femtosecond laser pulses have become an indispensable tool to study ultrafast processes in coherently excited molecular ensembles, such as optical dephasing, dynamics of vibrational wave packets, photochemical hole burning, etc. Traditional methods of nonlinear spectroscopy [1], such as photon echo, rely on detecting the coherent scattering from transient grating created by illumination with series of laser pulses. Since the amplitude of the scattered light is proportional to the coherent polarization of the molecules, one can measure the decay of molecular superposition state by varying the delay between the excitation pulses. In 1977, Zewail introduced an alternative approach [2] where the information about the optical coherence is first transferred to non-equilibrium excited state population by interfering two-pulse photon echo with a coherent laser pulse. In this case, the decay of coherence is measured by monitoring the intensity of spontaneous fluorescence of the molecules as a function of delay between the excitation pulses.

In the following years, nonlinear spectroscopic techniques based on spontaneous fluorescence have gained in popularity, in part, because of the fact that in gas phase (and other highly diluted samples) the fluorescence signal can give higher sensitivity of detection than scattering [3,4] and, in part, because fluorescence can be detected also in optically opaque media [5]. Recently, spontaneous fluorescence excited with series of phase-controlled ultrashort pulses has been applied to measure the absorption spectrum of inhomogeneous medium containing sharp spectral holes [6] and to detect motion of vibrational wave packets [7]. Most recently, spontaneous fluorescence

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excited with in an interferometric setup was used to study coherent femtosecond response of an organic crystal [8].

According to the principal idea of experiments [2–8], the first pulse excites the system into a coherent superposition state with a certain amount of excited state population. When the next pulse (or following pulses) is applied with a delay τ_p, shorter than the optical dephasing time, T_2, then final amount of population depends on interference between the excitation amplitudes produced by the first and the second pulse [9]. In case of constructive interference, the second pulse promotes more molecules into the excited state, whereas in the case of destructive interference, the second pulse decreases the number of the excited molecules. Because the spontaneous fluorescence rate is proportional to the total number of the excited molecules, by measuring the overall time-integrated fluorescence as a function of interferometrically controlled delay between the pulses, one obtains information about coherent dynamic properties of the system.

Provided that only one pulse is applied, then in time domain the fluorescence decays monotonously, starting from an initial maximum value immediately after the first pulse. It is clear then that any phase-dependent variation of the fluorescence signal cannot occur before the moment when the second pulse is applied. Immediately after the second pulse, however, the fluorescence signal can either increase or decrease, depending on the delay and the phase of the second pulse.

In the previous experiments such time–domain effects in spontaneous emission were overlooked, primarily because the desired information was obtained directly from *time-integrated* spontaneous emission. In addition, experimentally it is more straightforward to detect time-integrated fluorescence signal, rather than time-resolved emission. On microsecond time scale, abrupt change of time-resolved spontaneous fluorescence at the time of photon echo has been observed in rare earth-doped crystal [10]. On ultrafast time scale, special detector with a response time shorter than the delay between the pulses is required. Therefore, it is perhaps not so surprising that no direct measurement of the time evolution of interference between femtosecond pulses has been performed so far.

In this Letter, we study, for the first time to our knowledge, time-resolved spontaneous fluorescence, excited by a series of phase-controlled femtosecond pulses in inhomogeneously broadened medium. We use a picosecond streak camera to investigate how the phase affects the time evolution of the spontaneous fluorescence in the medium containing a frequency comb of sharp spectral holes. In particular, we verify that the fluorescence after the first pulse is nearly constant, whereas the fluorescence following the second, third, etc. pulses increases or decreases depending on the relative phase between the pulses.

2. Experimental

The experimental arrangement (Fig. 1) comprised a mode-locked Ti:sapphire laser (Coherent Mira 900), pumped by 5 W cw frequency-doubled Nd:YAG laser (Coherent Verdi). The Ti:sapphire laser produced at 75 MHz repetition rate bandwidth-limited pulses with duration of 200 fs. The average power was 400 mW. The laser beam was passed through a Fabry–Perot etalon (Burleigh), with two flat mirrors, positioned 1 cm apart, and having about 90% reflectivity at the laser wavelength. One of the mirrors was mounted on piezo transducers. By applying a bias

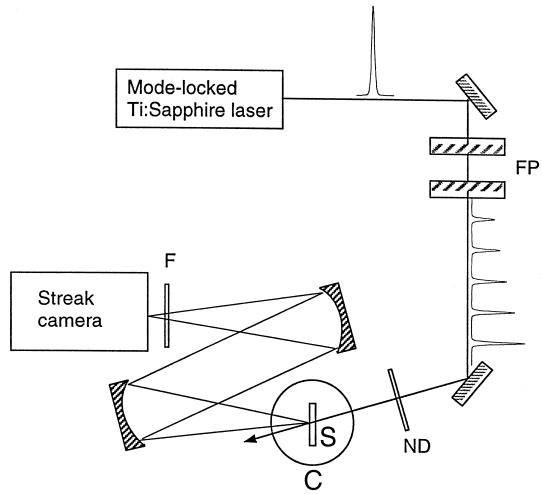

Fig. 1. Experimental arrangement. F, long pass cut-off filter; FP, Fabry–Perot etalon; ND, neutral density filter; C, cryostat; S, sample.

voltage, the distance between the mirrors could be changed by quarter of the wavelength.

The transmitted laser beam was attenuated by a variable neutral density filter and then directed to the sample, which was positioned inside an optical cryostat.

Our sample consisted of a 0.2 mm thick polyvinylbutyral film (PVB) doped with anthraceno-triphthalocyanine (AnPc) molecules at a concentration of about 10^{-3} mol/liter. During the experiment the polymer film was immersed in super-fluid helium at temperature $T = 2$ K. At low temperature, the lowest singlet–singlet electronic transition of AnPc molecules has narrow homogeneous zero-phonon lines, $\Gamma_{\mathrm{hom}} \sim 0.03$ cm^{-1}, and a broad inhomogeneous bandwidth, $\Gamma_{\mathrm{inh}} \sim 200$ cm^{-1}. Estimated optical dephasing time at $T = 2$ K is $T_2 = 400$ ps. Upon illumination, the molecules undergo photochemical tautomerization with a quantum efficiency of about 10^{-3}, which leads to burning of persistent spectral holes (for details about hole burning in AnPc see [11]).

Spontaneous fluorescence was collected at the output side of the cryostat by a spherical mirror with 10 cm diameter and 50 cm focal length. Second spherical mirror was used to focus the light on the entrance slit of a synchroscan streak camera (Hamamatsu 5680). A color filter was placed in front of the streak camera entrance slit to block laser light scattered from the sample and from the cryostat windows.

3. Results and discussion

Fig. 2 shows the absorption spectrum of the sample at low temperature before it is illuminated with femtosecond pulses. The wavelength of the laser was tuned into resonance with the inhomogeneously broadened band of the AnPc $S_0 \leftarrow S_1$ electronic transition at 780 nm.

Our experiment consisted of two steps. In the first step, a periodic frequency–domain pattern of deep and narrow spectral holes was burnt into the inhomogeneous absorption spectrum of the sample. This was accomplished by illuminating the polymer film with the laser beam, transmitted through the etalon. In the frequency domain, the transmission spectrum of the

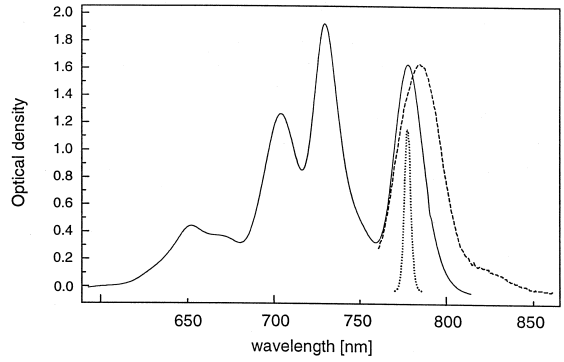

Fig. 2. Absorption (solid) and emission (dashed) spectrum of the sample at low temperature ($T = 4$ K); Dotted curve shows the intensity spectrum of the femtosecond laser.

etalon consists of a comb of frequencies, with a period 0.5 cm^{-1} (15 GHz). The width of the transmitted peaks depended on the alignment and the finesse of the etalon, and was estimated to be less than 0.03 cm^{-1} (1.0 GHz). In time domain, the multiple reflections between the etalon mirrors produced a periodic sequence of pulses, separated by a constant 66.7 ps time interval, and with energy of the pulses decreasing in a geometric progression. Note that the sequence decayed much faster than the repetition rate of the femtosecond laser. The average illumination intensity was 10 mW/cm^2. Optimum contrast of the spectral holes was achieved with 60 s burning exposure time. As a result of this exposure, the transmission of the sample, measured at the frequencies corresponding to the maximum of the etalon transmission spectrum, increased by a factor of ten, while at other frequencies, especially in the intervals between the maximums, the transmission remained nearly unchanged.

In the second step, the sample was illuminated with the same pulse train, but attenuated by a factor of 20. Using a much weaker excitation was necessary in order to minimize further hole burning. During read-out, voltage was applied to the piezo transducers such that the frequency comb shifted by about half the period. In time domain, applying the voltage, corresponds to changing the phase between each consecutive pulse in the sequence by half a wavelength.

Fig. 3a shows time-resolved spontaneous fluorescence obtained without voltage (solid) and with volt-

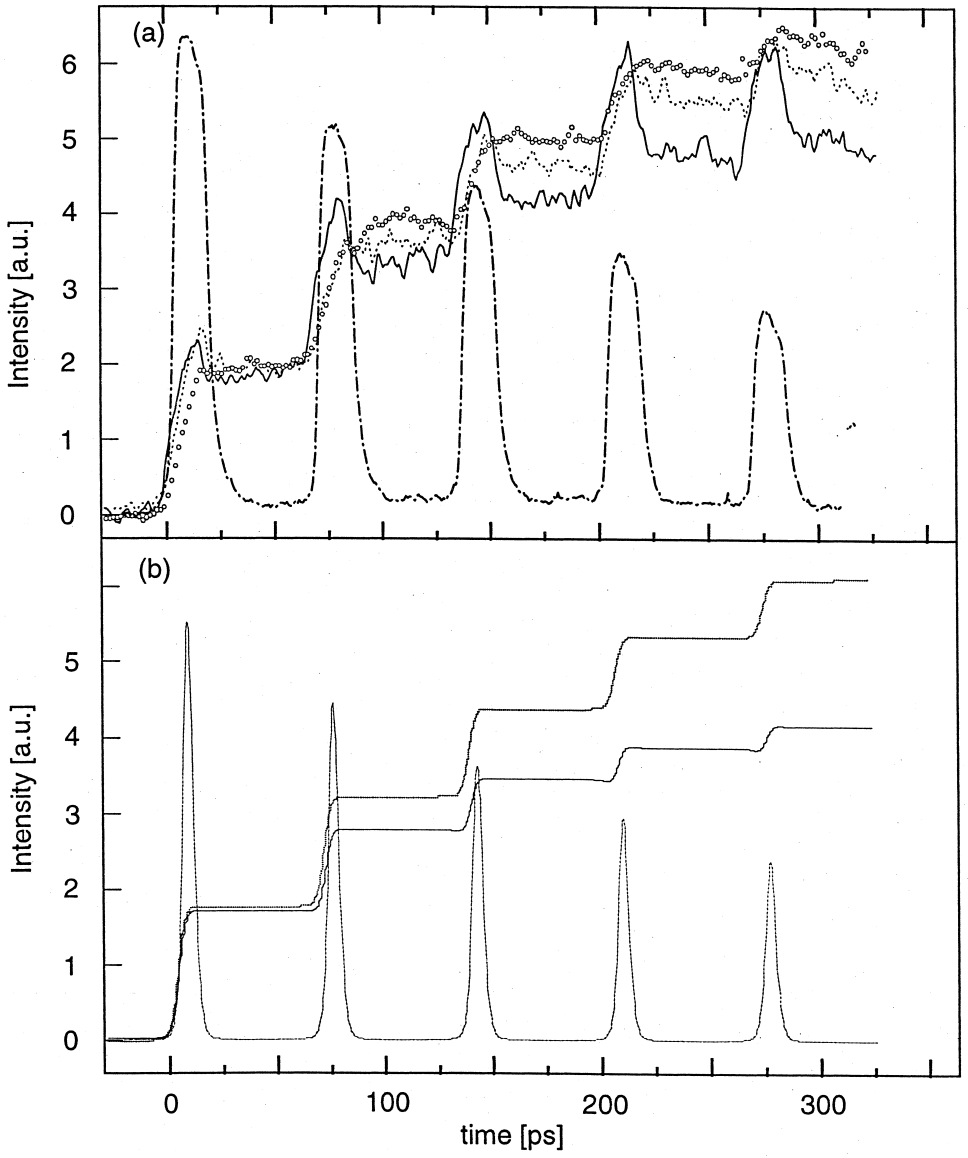

Fig. 3. (a) Time dependence of the spontaneous fluorescence intensity before (open circles) and after (continuous lines) hole burning with a train of femtosecond pulses. Solid line, the phase of the probe pulse train is the same as that of the original pulse rain used for burning train; dashed line, the phase is shifted by half period. Dashed-dotted line shows the intensity profile of the excitation pulse train. (b) Simulation of the time dependence of excited state population based on optical Bloch equations. Lower step-like curve: the phase of the pulse train is the same as during the burning of the spectral holes. Upper step-like curve: the phase is shifted by half period.

age applied (dashed) to the etalon. Each of the traces was measured by accumulating signal over 150 s. As mentioned above, we had to keep the excitation laser intensity at the sample as low as possible to avoid continuous burning of the holes. Our cut-off filter blocked most of the scattered laser light, but still allowed a small fraction leak through to the streak camera. This residual laser light is seen as the rapidly decaying peaks superimposed on top of the more slowly decaying fluorescence. Note that phase-shifted

trace has less residual laser light because of stronger absorption by the sample, as is explained below. Further, in order to collect largest possible amount of fluorescence signal, we opened the entrance slit of the streak camera to 2 mm. This explains why the actual resolution of the measurements presented in Fig. 3 is ten times (20 ps) the nominal resolution of the streak camera (2 ps). The intensity profile of the excitation pulse train detected with open slit is depicted in the lower (dash-dotted) trace.

We notice that the fluorescence signal intensity increases in distinct steps, with each step coinciding with arrival of excitation pulse. We also notice that the height of the step produced by the first pulse does not change upon phase shift, while the steps corresponding to the second and all subsequent pulses does change. Indeed, if the sample is illuminated with the original pulse train used for hole burning, then the fluorescence intensity increases in smaller steps, as compared to illumination with a phase-shifted pulse train. Fig. 3 shows also the fluorescence signal detected when no spectral holes were burnt in the sample (open circles). In that case, the height of the steps is strictly proportional to the energy of the consecutive pulses and does not depend on the phase. Note that the sample without spectral holes contains more absorbing molecules than with spectral holes and it is expected that the unburned sample should give slightly more fluorescence that the burned sample. However, because the integrated area of the frequency comb is less than 1% of the overall absorption, this difference cannot be detected in our experiment.

If we try to explain these results in terms of time-integrated fluorescence, then it is obvious that the emission intensity is proportional to overlap between the power spectrum of the illuminating light and the absorption spectrum of the medium. It is also clear that by shifting the phase the illuminating pulse train with respect to the burning pulse train results in a stronger absorption, and, correspondingly gives a larger integrated fluorescence signal. On the other hand, such purely frequency–domain picture does not explain the observed time evolution of the fluorescence signal. An exhaustive explanation can be given only by solving Maxwell–Bloch equations, which adequately describe interaction of laser pulses with inhomogeneously broadened medium. Fig. 3b

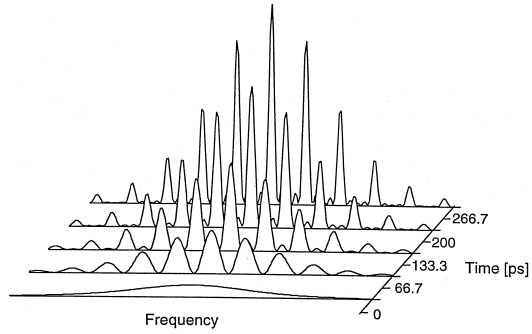

Fig. 4. Simulation of frequency comb formation in the excited state population after the first, second, third, etc. pulses. For simplicity, the period of the frequency comb in the simulation is a factor of 100 larger than that in the experiment.

shows the calculated fluorescence intensity, integrated over frequency, with and without phase shift. Here we present only a model simulation, showing a qualitative agreement with the experiment. A quantitative comparison will be published elsewhere. Fig. 4 shows the temporal changes of the probe spectrum, after arrival of each subsequent excitation pulse. Immediately after the first pulse, the population responds to momentary intensity spectrum, which consists of a broad envelope, with a width much broader than the width of the burnt holes. After the second pulse has arrived, the spectrum acquires a sinusoidal modulation due to interference between the two pulses. The period of this modulation is inversely proportional to the delay, $\delta\nu = 1/\tau_p$, whereas the position of maximums and minimums in this modulation depends on their relative phase. This explains why the amount of fluorescence produced by the second pulse depends on the phase shift of the second pulse. The third, fourth etc. pulses interfere with all previous pulses. As a result of such multi-pulse interference, the peaks in the population become progressively narrower. This means that overlap with the burnt holes becomes more sensitive to the phase change, and, therefore, the difference between fluorescence signal with- and without phase shift increases with the number of pulses.

4. Conclusions

In conclusion, we have shown that by detecting time-resolved spontaneous fluorescence, we can get

direct information about coherent time evolution of population excited by a sequence of femtosecond pulses in an inhomogeneously broadened medium. In particular, if the absorption spectrum of the medium contains a frequency comb of narrow spectral holes, then changing the phase between the pulses can be used to control the time evolution of excited state population and, consequently, the time dependence of spontaneous fluorescence. Our results improve the understanding of physical background of various interferometric techniques using spontaneous fluorescence in femtosecond spectroscopy.

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