Simultaneous time and frequency gating of weak molecular fluorescence in a thick nonlinear crystal

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Time and frequency gating of molecular spontaneous emission at a less than one photon per mode level is achieved using phase matching properties of sum frequency generation in a 3 mm type I BBO crystal. The results of time and frequency resolved fluorescence measurements from a vibrational wavepacket in diatomic potassium molecules are presented. The experimental arrangement is simplified compared to the classical setup which uses a short crystal and monochromator. Both the signal and the signal to noise ratio increase. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2172297]

Sub-picosecond optical measurements are a well established tool for the study of fundamental dynamics of a variety of physical and chemical processes. The early stages of chemical reactions as well as other dynamical phenomena take place on a femtosecond time scale.[1,2] In particular, when combined with frequency selectivity, time-resolved spectroscopy provides insight into dynamics of simple molecules. For instance complete characterization of the quantum state of a molecular vibrational wavepacket is possible using molecular emission tomography (MET).[3–5]

In the classical MET configuration a short laser pulse triggers the process (creates a wavepacket in the molecular potential of the excited electronic state) and a second pulse probes the evolution by sampling the molecular fluorescence. Since the photon statistics of spontaneous emission give much less than one photon per spatio-temporal mode, a noiseless fast gate mechanism is needed to sample the fluorescence with sub-picosecond time resolution. Sum frequency generation of the incoherent fluorescence with a gate pulse in a nonlinear crystal provides a suitable mechanism fulfilling these conditions. Another approach for measuring weak broadband incoherent radiation is based on amplifying the time-gated fluorescence, which necessarily results in a signal to noise ratio of unity at the single photon level.[6–8]

In this letter we present time and spectral gating of molecular spontaneous emission required for tomographic reconstruction of the vibrational state based on the filtering properties of a thick nonlinear crystal replacing the thin crystal and monochromator. Compared to standard time resolved emission detection setups[9,10] this scheme has high sensitivity and is simple while retaining the same excellent time and spectral resolution as the classical MET setup. It has been demonstrated that simultaneous spectral and temporal filtering of the signal from the sum frequency generation with a thick nonlinear crystal can be used for characterization of femtosecond laser pulses containing typically many photons per mode.[11,12] The time gate resolution is determined by the gate pulse duration and the dispersive properties of the nonlinear crystal. Several tens of femtoseconds temporal—and a few nanometers spectral resolution are achievable with relatively high intensity input fields.

To explore the feasibility of the method for very low light levels we performed a measurement of molecular wavepacket emission from potassium dimers. The experimental setup is shown in Fig. 1. An all-sapphire gas cell containing potassium vapor is kept at 400 °C providing a dimer density fraction of around 1%. A train of 90 fs pulses centered at 835 nm from a CPA system with a repetition rate of 2 kHz is split into two arms, forming the pump and gate pulses that can be delayed with respect to each other. The vibrational wavepacket is excited in K_2 by transfering population from the $X\,^1\Sigma_g^+$ ground state to the $A\,^1\Sigma_u^+$ state with resonant laser pulse of around 1 μJ energy and the emitted fluorescence is collected by a pair of 30° off axis parabolic mirrors, with a diameter of 76.2 mm and a focal length of 326 mm, and imaged onto a nonlinear crystal (BBO). The excitation is in the impulsive limit, which means that the pulse length is much shorter than the 500 fs oscillation period of the wavepacket. Mixing the fluorescence with the gate pulse creates sum frequency in the temporal window determined by the duration of the time gate. The generated light is detected with a photomultiplier working in the photon-counting mode. The temporal scanning is done by varying the relative lengths of the two arms.

In our experiment the broad molecular fluorescence spectrum is mixed in a BBO crystal with a gate pulse of 16 nm spectral bandwidth in a type I process obeying energy conservation $\omega_3=\omega_1+\omega_2$ and momentum conservation $\boldsymbol{k}(\omega_3)=\boldsymbol{k}(\omega_2)+\boldsymbol{k}(\omega_1)$ where $\omega_{1,2,3}$ are frequencies of the fluorescence, the gate pulse and the upconverted signal respec-

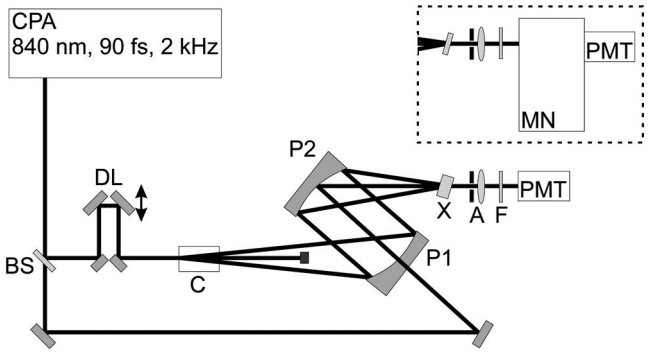

FIG. 1. The experimental setup. BS-beam splitter, DL-variable delay line, C-sapphire K_2 vapor cell at 400 °C, P1, P2-off-axis parabolic mirrors, X-3 mm type I BBO crystal, A-aperture and imaging lens, F-IR blocking passband filter, PMT-photomultiplier. The inset shows the classical setup with a thin crystal and monochromator MN used for comparison.

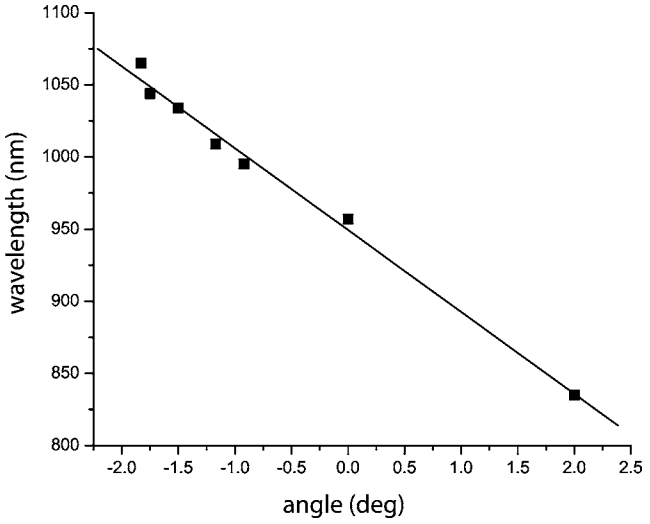

FIG. 2. Measured central wavelength of the upconverted fluorescence as a function of the crystal angle (dots). Also shown is the calculated tuning curve of the BBO.

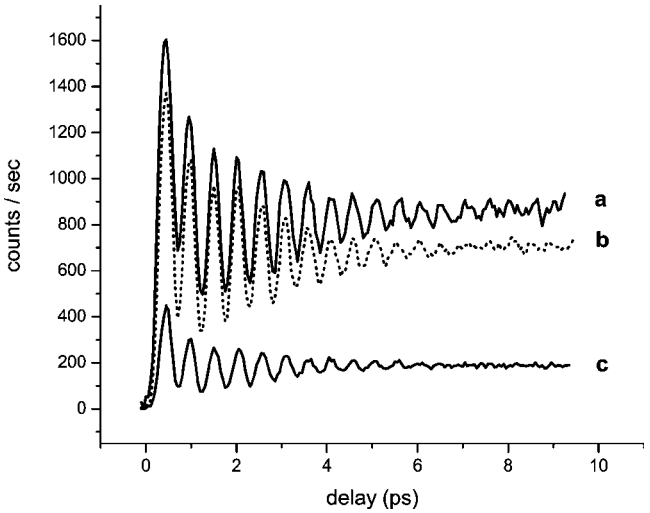

FIG. 3. Time resolved molecular wavepacket fluorescence at 1065 nm measured in the thick-crystal setup 3 mm BBO, without monochromator, an additional ND 0.5 filter used to avoid saturation of the PMT (a). For comparison the same signal measured with the monochromator inserted after the crystal is shown for two crystal lengths: 3 mm (b) and 0.5 mm (c).

tively. The directions of the three wave-vectors are fixed to within the beam divergence and their lengths depend on the frequency via dispersion relations. The efficiency of the sum-frequency generation in the collinear approximation can be expressed as $I_3 \sim \mathrm{sinc}^2(\Delta kL/2)$, with the phase mismatch $\Delta k/2\pi = n_e(\lambda_3)/\lambda_3 - n_o(\lambda_2)/\lambda_2 - n_o(\lambda_1)/\lambda_1$ and the length of the crystal L. The range of wavelengths that are present in the upconverted light can be varied by changing the crystal thickness and the angle between the wave-vectors and the crystal optic axis. A detailed discussion of the spectral filtering properties of a thick crystal can be found in Ref. 13. In principle, a longer crystal has a narrower efficiency window, which in turn gives a smaller spectral bandwidth for the generated sum frequency wave. The calculated bandwidth of the sum frequency generation in a 3 mm BBO crystal is 2 nm, narrow enough to resolve the molecular fluorescence signal spectrally. Temporal pulse broadening due to group velocity dispersion in 3 mm BBO is negligible—a Fourier transform limited 90 fs pulse with center wavelength of 835 nm is stretched to 90.6 fs.

We begin with measurement of the tuning curve of the BBO crystal—the results are presented in Fig. 2. Setting the monochromator at a certain wavelength we recorded the crystal angle that resulted in the highest intensity of the upconverted light.

The time and frequency gated fluorescence was measured in three configurations: first with a 3 mm BBO without monochromator, the PMT placed directly after the crystal with a 40 nm bandpass filter centered at 450 nm, second with a 3 mm BBO and with the monochromator and third in the classical setup with 0.5 mm BBO and the monochromator. The results for the fluorescence emitted at 1044 nm, close to the wavelength corresponding to the outer turning point of the wavepacket oscillatory motion, are plotted in Fig. 3. When the thick crystal was used without monochromator we had to add an ND 0.5 filter to avoid saturation of the photomultiplier photon counting module. A fourfold increase in the signal amplitude is achieved (twelvefold if the filter is taken into account) compared to the classical setup with 0.5 mm BBO and monochromator. The signal to noise ratio does not decrease as expected for a nonamplifying process and the modulation of the quantum beats can be resolved for delays around 8 ps. While using the 3 mm crystal leads to a significant signal increase there is no visible degradation of the 95 fs temporal resolution compared to the short crystal due to the small angle between the gate and the fluorescence beams. Furthermore, the increase in signal level using the long crystal is so dramatic that we are nearly in the regime where without the ND filter photon counting is not the optimal detection method. In fact, the signal should be detectable using gated integration of the photocurrent. The spectral resolution of the setup is ultimately limited by the bandwidth of the gate pulse, as is the case for all such nonlinear schemes. The limitation of the spectral resolution by angular dispersion plays a minor role because the acceptance angle is small. In our setup the resolution is slightly better than for a short crystal with monochromator setup because of the narrow phase matching function that ensues from using a long crystal, which falls within the 3 nm resolution of the monochromator.

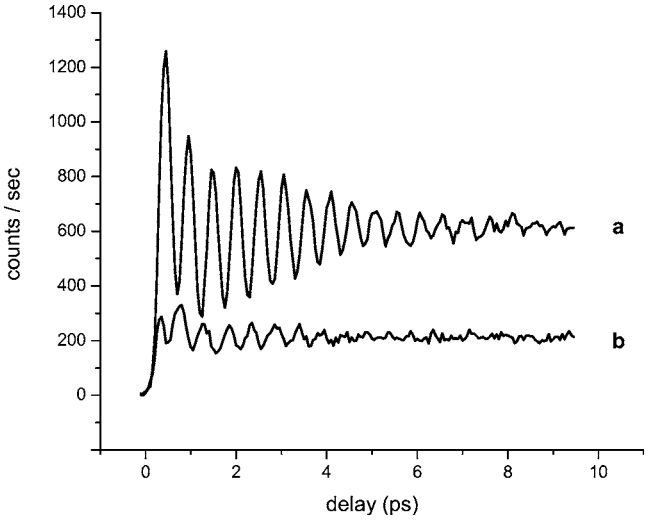

FIG. 4. The fluorescence signal at two wavelengths: 1065 nm corresponding to the outer turning point (a), and 957 nm close to the inner turning point (b).

More challenging measurements required for MET are those at wavelengths approaching the inner turning point of the wavepacket evolution where the intensity of the fluorescence signal drops while the noise from the upconverted gate pulse scattering strongly increases. In Fig. 4 the upconverted fluorescence signal is shown for molecular transitions at 1065 and 957 nm corresponding respectively to the outer- and the vicinity of the inner turning point. The beats, shifted by almost half of the vibrational period, are clearly visible with excellent signal to noise ratio. For these measurements the monochromator was used, acting as a broadband filter to block the upconverted gate pulse scattering, along with the 3 mm BBO crystal.

In conclusion we present a new method for resolving weak fluorescence signals in time and frequency simultaneously using the phase matching properties in a type I thick nonlinear crystal. To demonstrate the feasibility of the method, the molecular wavepacket fluorescence was measured in a simplified setup without monochromator and a significant improvement in the signal level was achieved. The method can be adopted for many situations where measurement of nonstationary weak incoherent fields is required.

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