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Femtosecond pump/supercontinuum-probe setup with 20 kHz repetition rate

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We developed a fast multichannel detection system for pump-probe spectroscopy, capable of detecting single shot super-continuum spectra at the repetition rate (10–50 kHz) of an amplified femtosecond laser system. By tandem pumping the amplifier with three pump lasers we obtain very low noise operation, with less than 0.1% rms intensity fluctuations at the output of the amplifier. We also propose an alternative way of chopping the pump beam. With a synchronized scanning mirror two spots in the sample are illuminated by the train of pump pulses in an alternating fashion, such that when both spots are interrogated by the probe pulse, the duty cycle of the experiment is doubled.

I. INTRODUCTION

Femtosecond pump-probe spectroscopy utilizing supercontinuum probe pulses is a very powerful technique since it can report the full spectral changes/dynamics of the subject under study with femtosecond time resolution.1,2 Broadband probe sources have been available for more than 2 decades, and especially the laser technology has become “off the shelf.” Most pump-probe experiments aim at getting the best possible time resolution, but probably most efforts go for the best signal to noise ratio (S/N) within a reasonable data accumulation time.

When using very high repetition rates, e.g., the output of an oscillator running at 80 MHz, noise can be very much decreased by multiple (RF) modulation schemes,3–5 but these schemes cannot be used with amplified laser sources6 since their repetition rate is typically 5 orders of magnitude less than the oscillators. To make things worse, typically amplification adds noise, so the noise of the probe pulses is higher than that of the oscillator. Obviously, the optical signals generated by the mJ pulses from an amplified laser can be orders of magnitude higher than those from the nJ oscillator pulses. With enough energy in a single pulse, one can in some cases measure a full pump-probe dataset in a single shot using multiplexing techniques,7,8 which can be important when dealing with unstable compounds.

However, in most cases the sample itself limits the pulse energy that can be used for excitation. This is especially true for biological samples and even more so in combination with UV pulses, which are interesting as this is where the amino-acid residues absorb.9,10 Moreover, especially when studying systems with multiple chromophores, coupled by energy transfer, one wants to be well below the one-photon per complex excitation density level to avoid annihilation processes.11–13 Therefore, the goal is not to increase the signal, but to reduce the noise as much as possible, and measure with minimal exposure of the sample. When doing multichannel detection with a supercontinuum probe, one needs sufficient photon numbers over a wide spectral range and the integrated intensity of the probe can in some cases exceed that of the pump, which is not always desirable. The combination of strong pump and probe pulses has its merits,14 however, in what follows we strive to go to the low intensity regime for both the pump and probe pulses, i.e., to be close to the shot noise limit of the detection.

Averaging of signals obviously improves the S/N and for a well-behaved system, the S/N scales with the square root of the number of measurements, which speaks in favour of high repetition rates.

Statistical analysis of a set of individual single shot measurements of the probe light, and elimination of outliers can help improve the quality of signals,15 therefore it is desirable to measure each probe spectrum separately, so as to be able to be selective.

Ideally, the repetition rate of the experiment should be as high as possible in order to get fast data-collection, but it should be low enough to be able to refresh sensitive samples in a moving cell, a flow cell, or a jet, so as to hit them with a low number of shots in order to prevent sample degradation. Here we present a setup running at 20 kHz with full multichannel detection of each shot of the super continuum probe spectrum. We also present an alternative for chopping the pump beam, which allows measurements with a 100% duty cycle.

II. THE LASER SOURCE AND THE UV PROBE GENERATION

Our experience with older 1 kHz amplified Ti:sapphire systems is that one typically obtains a pulse to pulse energy fluctuation of about 0.3%–0.5% rms.16 More recent developments with diode-pumped solid state lasers have improved these figures slightly, and about 0.15% rms pulse to pulse fluctuations can be obtained from commercial systems.

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When increasing the repetition rate one wants to maintain or improve the pulse to pulse stability, since this is crucial for the performances of the techniques described below. Actually, from a signal averaging point of view an increase in repetition rate by a factor $N$ is completely wasted if it comes with an increase in noise by a factor of $\sqrt{N}$.

Our high repetition rate laser source was designed/optimized for low noise operation. Figure 1 shows an overview of the laser and pump-probe setup. The amplifier is a cryogenically cooled regenerative amplifier (Wyvern500, KMLabs), which amplifies a Ti:sapphire oscillator (Halcyon, KMLabs). The amplifier is tandem-pumped by three pump lasers (DS20HE532, Photonics Industries). These Q-switched Nd:YVO$_4$ pump lasers are relatively low noise: we typically measure $<0.5\%$ rms fluctuation in the pulse energy of each of the individual pump lasers (measured over 10,000 shots). Moreover, since we pump with three lasers with uncorrelated noise, the relative noise on the total energy arriving in the laser crystal is reduced by a factor $\sqrt{3}$ compared to pumping with a single laser. Since the accumulation time required to obtain a certain S/N scales with the square of the noise, we get an improvement by a factor 3. Similar pulse energies and repetition rates could have been obtained using a single Nd:YAG pump laser, however, at the cost of noise figures that are significantly worse. Since the amplifier runs in saturation, the output actually has less noise than the pump source. From our experience with different systems we find that the noise of an amplifier is typically half of the noise of the pump light when operated in saturation. For the setup described here we typically measure $<0.1\%$ rms shot-to-shot energy fluctuations at the output of the amplifier. This is the noise (short term stability) that counts when doing pump-probe without a reference to compensate for the fluctuations in the probe beam intensity, i.e., when the correlation between alternate pulses is of importance. As we will show below, we are typically working in a regime where a reference beam is superfluous. The amplifier and pump lasers can work over a wide range of repetition rates (10 kHz–100 kHz), without changing the optics.

### III. THE DETECTION SYSTEM

We set out to increase the repetition rate of the experiment without losing the possibility to measure single shot spectra for each probe pulse. For this we developed a fast multichannel detector with $2^5*12$ pixels (2 * Hamamatsu S11105) that can be read out with pixel rates up to 50 MHz (up to 100 kHz frame rates). The output of the detector arrays is digitized using a fast 14 bits ADC (Spectrum M2i.4022) with 4 channels operating in parallel.

Diode arrays have been the typical choice for multichannel detection. The saturation charge of a typical diode array pixel corresponds to the detection of $5 \times 10^8$ photons, whereas a single pixel (or in the case of binning, the shift register) of a CCD device typically has a full well capacity of $3 \times 10^5$–$5 \times 10^5$ electrons, i.e., three orders of magnitude less. However, compared to CCD detectors the low light performance of a diode array is very poor, with a typical readout noise that is three orders of magnitude larger. Another limitation of a diode array is the maximal pixel readout rate,
which is limited to about 2 MHz, which for an array of 512 pixels means that the maximal frame rate (and repetition rate of the experiment) is a few kHz.

The S11105 detector that we use is bridging the gap between diode arrays and CCD detectors, it has a saturation charge of $7.5 \times 10^5$ electrons, unfortunately the noise is closer to that of the diode arrays (2000 electrons rms), but it can be read out with a pixel rate of up to 50 MHz.

Our detection system can operate with or without a reference channel that records the probe light unaffected by the pump beam. This can be very beneficial when the fluctuations in the probe light are the leading term in the measurement noise. Adding a reference channel and optimizing the signal to noise was recently discussed in this journal. However, our probe light is typically less intense than what was used in that paper, and a simple calculation, presented in Sec. III A, shows that in our case measuring a reference spectrum for each probe pulse would not improve the quality of the signals.

A. Noise considerations

The noise in a pump-probe experiment has been discussed in the past. Here we prefer to present some numerical examples that shed light on the choice of detectors and detection strategies.

Referencing typically improves the S/N of pump-probe measurements when common mode noise, in this case energy fluctuations in the train of probe pulses, is the dominant noise source. However, noise contributed by the detector of the probe and reference pulses are not correlated and thus adding the measurement of the reference pulses can introduce additional noise.

In general, the noise of the probe consists of two sources:

A) Pulse to pulse energy fluctuations of the source of probe light.

B) Detector noise, which consists of readout noise (electronic noise independent of the intensity of the signal) and shot noise, the (quantum) statistical noise associated with measuring $N$ photons, which amounts to $\sqrt{N}$.

Detection schemes that include a reference beam serve to compensate for the pulse to pulse fluctuations (A), here we want to explore under which conditions this is feasible.

Since the sources of noise in the detector are independent, they add up as the square root of the sum of the squares:

\[ \text{Detector noise} = \sqrt{\text{readout}^2 + \text{shot}^2}. \]

Therefore, if we express the readout noise in terms of number of photons, the S/N of a measurement of $N$ photons becomes:

\[ S/N = N/\sqrt{(\text{readout}^2 + N)}. \]

Let us first consider the shot noise limited case, where the readout noise is much less than $\sqrt{N}$, then with 50% splitting the signal of the probe will be halved, while the noise goes down by $\sqrt{2}$, resulting in a decrease of the S/N by a factor $\sqrt{2}$. However, the same detector noise is present in the reference, and the S/N of the ratio of probe and reference total detector noise will be half the value of the original un-split probe measurement.

If the readout noise is dominating, things get worse: in this case the S/N per detector is simply halved, since the noise is independent of the intensity, and combining them leads to a decrease of the S/N ratio by a factor $2\sqrt{2}$.

Therefore, adding a reference is only useful if the noise of the source (energy fluctuation of the probe light) is $\gg 2$ times the detector noise.

Figure 3 shows the S/N as a function of the number of photons for a range of values for the electronic noise of the detector. In this plot the CCD detector has shot noise limited values for all practical light intensities. In our experience, diode arrays have a behavior that is closest to the right-most curve.

For low light intensities, the detector noise of a diode array will be dominated by the electronic noise. In our experiment the noise of “fast” diode arrays is $>1000$ detected photons. Therefore, to have a diode array that measures with less than 1% noise one needs $\gg 10^5$ photons per pixel (an amount of light that already saturates a CCD detector), corresponding to a few percent of the saturation charge of a typical photodiode array. Dobryakov et al. show that indeed, by using very intense probe light, one can reach a regime where measuring a reference beam helps reduce the overall noise, especially if the noise of the laser source is high.

When using less probe light or a detector with less dynamic range the picture is different. The maximal S/N one can obtain with a CCD is $\sqrt{100 000} \approx 300$ (here we use about half the saturation value, since the spectrum of the probe is typically not flat, and most of the spectral range will be far from saturating the detector), or a relative noise level of 0.3%. Therefore, with a CCD detector, referencing is only useful if the noise in the source is $>0.6\%$, and when one takes into account the added complications of the referencing, the turnover point would be for more than 1% source fluctuations.

The noise in our laser source is low, the noise of the Topas is typically 0.5% when operating at large (200 nm) bandwidth, and $<0.3\%$ when operating at 50 nm bandwidth. After achromatic doubling of the TOPAS output (200 nm bandwidth), the noise level of the probe is $<1\%$. We can therefore work without referencing.

FIG. 3. Signal to noise ratio for an ideal source, as a function of the number of detected photons, for a readout noise of 1, 10, 100, 1000, 2000, 10 000 electrons. The curves corresponding to the typical readout noise of a CCD and the detector we are using (Hamamatsu S11105) are plotted as dotted lines.
B. The chopping issue

The pump-probe signals are finally obtained by measuring the probe pulses alternating with and without the pump pulse on the sample. For this one needs a well-synchronized chopper or deflection system. Mechanical choppers are commercially available that can be phase-locked to high frequencies, but a 10 kHz chopper (with reasonable blade window) running in air could easily be mistaken for an evacuation alarm. Here we employ a different scheme: deflecting the pump beam using a resonant scanning mirror (EOPC SC-30), which is running at 10 kHz, phase-locked to the repetition rate of the laser (20 kHz). The scanning mirror is oscillating with a small amplitude (<1°), which results in alternate pulses hitting two well-separated spots in the sample. We explore two ways of synchronizing the mirror to the laser. First, it is possible to use the repetition rate of the laser, electronically divided by 2 to drive the mirror. However, the resonance frequency of this type of mirror is very temperature dependent, and even changing the intensity of the pump beam on the mirror causes small temperature variations, which bring it off the peak of the resonance. Therefore, using the laser as master clock works best when detuning its repetition rate well off the resonance of the mirror, so that the frequency drift of the mirror results in a minor phase drift. The alternative scheme is to use the mirror as the master clock, and phase-lock the laser to it. We implemented the latter scheme by controlling the cavity length of the oscillator using the pico-motor driven translation stage in the Halcyon oscillator. The relative phase deformation mirror pulse compressor, but this is not required for most measurements.

In summary, the multi-pump-laser configuration of our laser system results in an increase of the repetition rate by more than an order of magnitude while maintaining noise characteristics that are at least as good as those of (commercial) 1–5 kHz systems. The high-speed detectors can be read out single shot at 20 kHz frame rates with a signal quality comparable to corresponding 1 kHz detection systems.

IV. APPLICATIONS

Figure 4 shows a typical dataset obtained by pumping aqueous [Fe(bpy)3]2+ at 400 nm, and probing it in the UV. We previously presented similar data, which were obtained using a 1 kHz laser system operating with two NOPA’s; one NOPA was used to generate a pump-pulse at 530 nm, and the other was frequency-doubled to give a broadband UV probe pulse. In that case the probe light was useful over a slightly more limited spectral window.

The data we present here is the result of a single time scan (350 points) where we measured 5000 shots for each delay. The overall data acquisition time was about 3 min. It was not corrected for the temporal chirp of the probe light. The prism compressor inherent to the achromatic doubling setup results in a significant amount of third order dispersion, which manifests itself in the curvature of the early time signal. This dispersion could in principle be eliminated using a deformable mirror pulse compressor, but this is not required for most measurements.

Figure 5 shows a single wavelength trace (310 nm probe wavelength) of the data. Around the temporal overlap region of pump and probe there is a significant amount of cross-phase modulation signal, which is mostly produced in the window of the sample flow cell. In the first picoseconds, we observe the previously reported wave-packet dynamics (oscillation period of 254 fs), A quantitative comparison of the noise in the time traces between the one kHz data and the data presented here shows that the 1 kHz system would require a factor of 15–20 times longer data accumulation times to reach the same spectral range and signal quality we obtain now with the 20 kHz system even though it was obtained with a pump at 530 nm, which corresponds to a three times higher absorption coefficient than at 400 nm. Moreover, the quality of the spectral data is strongly enhanced due to the fact that the probe-light has no significant spatial chirp, and its spectrum is much flatter than that of the probe light used in Ref. 20.

In principle our set up would allow us to further increase the repetition rate of the experiment up to a maximum of 50 kHz. Especially for biomolecules, however, these high repetition rates raise the question of appropriate sample renewal schemes. Whether renewal of the sample with every shot is required has to be carefully checked on a case-to-case basis dependent on sensitivity for photo damage and the production
of long-lived photo products for the molecule. For example, on myoglobins our group recently performed x-ray transient absorption experiments with a repetition rate of 500 kHz still observing the correct dynamics.22

With our chosen repetition rate of 20 kHz and tight focusing (50 μm) sample renewal with every shot requires a flow speed of about 1 m/s which is in principle still feasible with a high speed free jet or flow in a capillary.

The combination of this laser source, achromatic doubling, and the single shot detection system allows us to obtain high quality pump-probe data over a wide spectral range in the UV, with a very high rate of data accumulation. The usefulness of the scheme proposed here is most appreciated in applications such as ultrafast two-dimensional electronic transient absorption spectroscopy, which we describe in Ref. 23

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