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Double-modulation electro-optic sampling for pump-and-probe ultrafast correlation measurements

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We describe a novel electro-optic double-modulation (DM) sampling technique for ultrafast transient spectroscopy, which is characterized by a superior signal-to-noise ratio compared to that of a regular single-modulation technique. DM is achieved by a combined effect of a radio-frequency modulation, which eliminates most of the low-frequency noise, and an audio-frequency modulation, which makes use of a high-performance, low-frequency lock-in amplifier. The DM sensitivity is comparable to that of the more sophisticated schemes involving electrical mixing and the $A-B$ noise reduction method. We show that the DM technique offers superior performance in two-beam transient pump-and-probe correlation measurements compared to the regular single frequency modulation technique and is an ideal scheme for three-beam picosecond correlation measurements. © *1998 American Institute of Physics.* [S0034-6748(98)01103-4]

I. INTRODUCTION

Electro-optical sampling very often requires detection of small signals, of the order of 1 μV, in the presence of a much larger background signal, of the order of 1 V. The latter is, typically, accompanied by background noise of the order of 10 mV. For example, in the standard ultrafast transient pump-and-probe correlation technique,[1] small changes, ΔT, in the sample transmission, T, induced by the pump beam are monitored using a probe beam. The modulated portion of the probe beam intensity, which is proportional to ΔT, can be six orders of magnitude smaller than the total transmitted probe beam intensity, which is proportional to T.[2] The detection of such a small signal in the presence of a large, noisy background is usually achieved by modulating the pump beam intensity at a fixed frequency, Ω, and using a phase-sensitive lock-in detection scheme.[3,4] A narrow-band lock-in amplifier (LIA) referenced at Ω amplifies only the modulated portion of the signal measured by a slow photodetector and filters out most of the background voltage noise.

It is important to choose Ω in a frequency range where the background noise is at minimum. In most cases, this noise is determined by pulsed laser sources, which produce the pump and probe beams. For most commonly used mode-locked lasers, the noise level is high in the audio-frequency (af) range ($f<100$ kHz), and it rolls off as $\sim 1/f$ in the radio-frequency (rf) range ($f>100$ kHz).[5,6] Therefore, it is convenient to use Ω of a few MHz, in the rf range. This scheme, however, is not ideal because of the poor performance of rf LIAs at present, which is due to their relatively high internal noise. The internal noise of a state of the art af LIA, on the other hand, is about two orders of magnitude smaller than that of a rf LIA. In cases where rf modulation is required and it is necessary to achieve sub-μV resolution, various multiple frequency modulation techniques were developed for measuring rf modulated signals with an af LIA.[7–10]

In this article, we present a plain double-frequency modulation (DM) detection technique, which combines the advantages of both rf modulation and af LIA. This straightforward technique can be readily employed in ultrafast transient pump-and-probe measurements without significant changes in the single frequency modulation experimental setup. In addition, unlike previously reported techniques,[7–10] it does not require any auxiliary complex apparatus. This method can also be used in other transient[11] and cw spectroscopic measurements.[12] In particular, we demonstrate its applications and superior sensitivity for two-beam and three-beam ultrafast transient correlation measurements.[4]

II. PUMP-AND-PROBE CORRELATION TECHNIQUE

As the name suggests, this experimental technique usually employs two laser beams, one of which (pump) is used for photoexcitation and the other (probe) monitors the changes in the sample transmission (or reflection) induced by the pump.[1] The laser beams can be either cw or pulsed.[4] In this article, we concentrate on the time-resolved pump–probe measurements using ultrafast fs- and ps-pulsed laser beams. The pump beam intensity is modulated by an acousto-optic modulator (AOM) at frequency Ω, while the probe beam intensity is monitored with a slow photodetector.[2] The small changes in the probe transmission induced by the pump are modulated at the same frequency Ω and can be measured directly with a LIA. The time delay between the probe and pump pulses is controlled by a translation stage.

Typically, the internal noise of a LIA is small compared to the noise associated with an incoming signal. In fact, this external noise is the main reason for using a LIA.[13] By choosing a reference frequency in the frequency region of the noise power spectrum where the noise density is low, and setting a narrow frequency window, we can eliminate most of the rf and af noise. Two kinds of LIAs have been used in this study: (i) low-frequency (af) modulated signals were detected using the SR510 (Stanford Research System, Inc.)

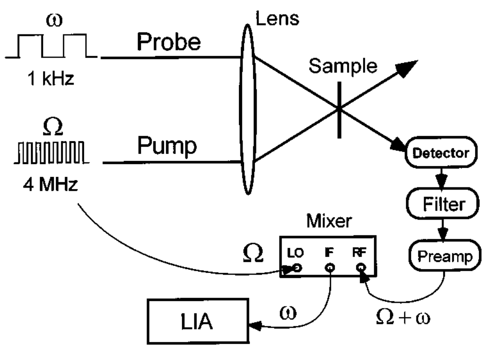

FIG. 1. The double frequency modulation technique; the pump and probe are two ps laser beams.

LIA, and (ii) high-frequency (rf) modulated signals were detected using the PAR 5202 (EG&G Princeton Applied Research) LIA. The af LIA works at frequencies up to 100 kHz and is an ideal device for steady-state photomodulation measurements requiring $\Omega < 10$ kHz. However, for time-resolved measurements in the pico- and femtosecond time domains with typical laser pulse repetition rates in the 50–100 MHz range, modulation frequencies of 1–10 MHz are usually needed; in this case, the rf LIA is required. The performance and the internal noise of the rf LIA are inferior to that of the af LIA and, in fact, quite unacceptable if signal levels are of order $\Delta T/T < 10^{-6}$.

III. DOUBLE MODULATION TECHNIQUE

The internal noise of a rf LIA can be as much as 100 times larger than the af LIA noise. A mixing technique was, therefore, designed which combines the advantages of the high-frequency modulation and the af LIA.[9] Reportedly, this approach improves the signal-to-noise (S/N) ratio up to two orders of magnitude compared with other noise reduction methods.[9] A somewhat simpler approach can be used that also exploits the advantages of the above method.[7] It has been dubbed the double-modulation technique[4,6–8] (Fig. 1). In addition to the pump beam being modulated at a rf Ω, in this technique the probe beam is also modulated at an af ω. The signal is then detected by the same photodetector used in a usual pump–probe setup. However, now it is modulated simultaneously at $\Omega + \omega$ and $\Omega - \omega$ frequencies. After passing through a high-pass electrical filter, eliminating the low-frequency noise, the signal is subsequently mixed with the rf Ω down to the af ω, using a rf double-balanced electrical mixer (''Mini Circuits'').[4,9] The downconverted signal, which is now modulated at ω, can be measured at this stage using the af LIA with a superior S/N ratio.

In the experimental realization of the DM technique a frequency generator (Wavetek 145) supplied both the pump modulation frequency (4 MHz) to the AOM and the driving frequency to the local oscillator input of the electrical mixer.[4] It also allowed a tunable phase shift between the LO and rf inputs of the mixer. The probe beam was modulated at the af of 1–2 kHz with a mechanical chopper. After electrical filtering, preamplification and mixing, the downconverted signal was monitored with the SR510 (Stanford Research Systems) LIA.

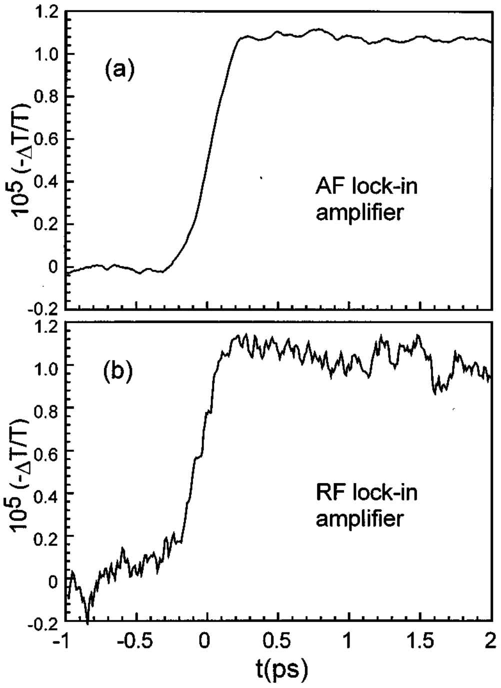

FIG. 2. Single scan $\Delta T/T$ measurements of a thin a-Si film using two methods: double modulation (a) and single modulation (b).

Figure 2 compares the two measuring methods of $\Delta T/T$ photoresponse of an amorphous-silicon thin (~ 1000 Å) film. Both the pump and the probe beams were obtained from a single 100 fs pulsed colliding pulse mode locked (CPM) laser operating at 625 nm.[4,14] Figure 2(a) shows the onset in $\Delta T/T$ at $t = 0$ and its subsequent decay, measured with the slow (af) LIA using the DM technique; whereas Fig. 2(b) shows the same signal measured with the fast (rf) LIA using the more regular single-modulation technique. A significant improvement in the S/N by an order of magnitude is evident. Figure 3 schematically shows a noise reduction diagram; only the main noise sources are shown. The LIA response (solid line) is high at the reference frequency (Ω or ω) and it is negligibly small at other frequencies. The integrated part of the noise spectrum (filled areas of the plots), which falls under the LIA response curve, is the noise observed at the output of the amplifier. It can be seen in Fig. 3 that the detected noise level (DN area) can be significantly

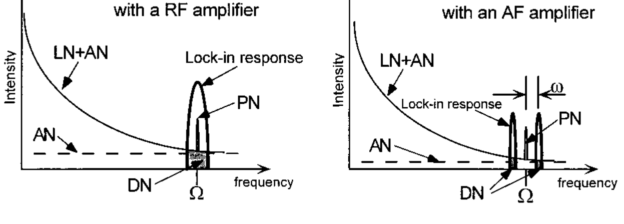

FIG. 3. Noise spectrum diagrams for the two detection methods. AN, amplifier noise; LN, laser noise; PN, noise from scattered pump light; and DN, detected noise.

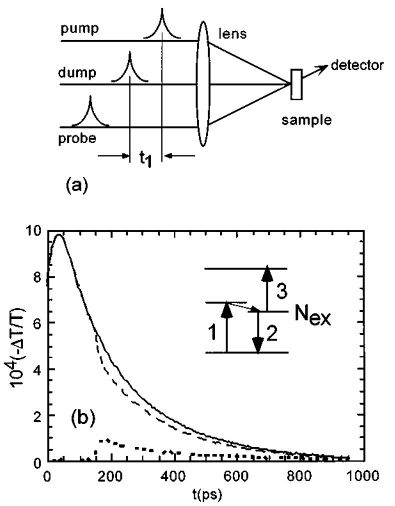

FIG. 4. TBT measurements applied to a DOO-PPV film: (a) the experimental schematic of the TBT; (b) PA decay dynamics in the absolute mode without the dump pulse (solid line), and with the dump pulse at $t_1 = 150$ ps (broken line), and the PA switching effect obtained in the relative mode (dotted line); the inset shows the energy-level diagram of excitonic transitions involved in the TBT measurements.

lower for the DM scheme (right panel) compared to that for the single-modulation scheme (left panel); this results in a higher S/N for the DM technique.

We note that the DM technique is particularly advantageous for measurements with the CPM laser, where both the pump and probe beams are split off the same laser beam.[4] In this case, the major noise contributor is the scattered pump light, which can be somewhat minimized using a configuration with perpendicular polarizations of the pump and probe beams. Then, an analyzer in front of the photodetector optically blocks off most of the transmitted pump light. On the other hand, the scattered pump light can be very effectively eliminated by electrical filtering using DM, as illustrated in Fig. 3. This allows easy measurements even using the configuration with the parallel polarizations of the pump and probe beams. In addition, certain coherent artifacts typically seen in this type of measurement at short time delays around $t=0$, such as the pump light diffracted by a cumulative dynamic grating due to interference fringes between the pump and probe beams,[4] are eliminated as well.

IV. THREE-BEAM DM TECHNIQUE

The DM technique has been found to be especially useful for our three-beam technique (TBT).[4,15] The TBT is a modification of the regular two-beam pump-and-probe technique and has recently been used to characterize various materials, including semiconductors[11] and π-conjugated-polymers.[15] As shown in Fig. 4(a), two different laser beams are used to excite (or deexcite) the sample, whereas the third beam serves as the probe. In the original implementation of the TBT to luminescent conducting polymers,[4,15] one of the pulsed beams (pump), with photon energy larger than the polymer optical gap, photogenerates excitons [transition 1 in Fig. 4(b), inset]. Following fast exciton thermalization, the second laser (dump) beam, with slightly smaller photon energy, induces optical transitions of these excitons back to the ground state through stimulated emission (transition 2). Finally, the third (probe) beam is used to monitor the instantaneous exciton population N_{ex} at various time delays, t, by monitoring photoinduced absorption (PA), i.e., the exciton transition to a higher-energy level [transition 3 in Fig. 4(b), inset].

In general, N_{ex} can be monitored using two different modes: absolute and relative. In the absolute mode the total signal $\Delta T/T$ is detected, which is proportional to the changes in N_{ex} induced by both the pump and the dump beams. It requires a regular single-modulation scheme. However, when it is necessary to observe *relative* changes in the exciton population due to the dump beam alone, then the DM technique should be employed. In this mode the pump beam is modulated at the rf Ω, whereas the dump beam is chopped at the af ω. The measured signal is thus modulated at $\Omega \pm \omega$.

Figure 4(b) shows the measured $\Delta T/T$ photoresponse of 2,5-dioctyloxy poly(p-phenylene–vinylene) (DOO-PPV) conducting polymer film, which reflects the dynamics of photogenerated excitons.[15] We used the TBT in both absolute and relative modes, where the pump, dump, and probe photon energies were 2.2, 2.0, and 0.85 eV, respectively. The pump and dump beams are produced by two ps pulsed synchronously pumped dye lasers, whereas the probe beam is obtained from an infrared color center laser.[4] The pump pulse ''turns on'' the excitonic PA at $t=0$ ps, which decays exponentially with a time constant of 240 ps. The latter process reflects the natural exciton recombination dynamics, as measured with the probe pulse at various delay times without the dump pulse [Fig. 4(b), solid line]. The dump pulse, however, may accelerate the exciton recombination process by stimulated emission, and in part ''switch off'' the excitonic PA[15] at $t=t_1$ [Fig. 4(a)] by partially depleting N_{ex}. This can also be measured using the probe pulse [Fig. 4(b), broken line].

In the relative mode, however, only the changes in the excitonic PA induced by the dump beam may be detected [Fig. 4(b), dotted line]. This relative mode photoresponse is actually the difference between $\Delta T/T$ signals measured with and without the dump pulse, respectively. Although it can be obtained by a simple subtraction of two signals measured using single modulation in the absolute mode, the DM technique offers immediate results with two orders of magnitude higher sensitivity.[4] Such a detection mode is very helpful if the switching efficiency of the dump beam is less than 1%. In this case, it is difficult to observe any dump-induced changes in the PA using the absolute mode alone; thus, the relative mode detection with the DM scheme provides the only alternative.

V. DISCUSSION

We have demonstrated a simple, inexpensive double-modulation electro-optical sampling technique for applications with the transient ultrafast pump-and-probe spectroscopy. We have shown that it can improve the signal-to-noise ratio in transient measurements by an order of magnitude, compared to a more regular single-modulation technique. This technique is very useful in the high-resolution pump-and-probe measurements and is a natural addition to the three-beam probing technique.

ACKNOWLEDGMENTS

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