

DETERMINATION OF RELATIVE NUMBER DENSITY AND DECAY RATE FOR ATOMIC SODIUM IN AN ATMOSPHERIC PREMIXED FLAME BY ASYNCHRONOUS OPTICAL SAMPLING

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Asynchronous Optical Sampling (ASOPS) is a pump/probe method that utilizes a dual timebase scheme to determine number densities and decay rates. In the ASOPS technique, two lasers are mode-locked at slightly different frequencies, causing a relative phase walk-out between the pump and probe lasers. This allows the dynamic measurement of subnanosecond excitation processes in a time scale on the order of milliseconds. The current ASOPS instrument consists of two dye lasers synchronously pumped by two frequency-doubled Nd:YAG lasers at a repetition rate of ~ 82 MHz. The ASOPS signal is obtained by AC amplification of the probe beam voltage, which is measured by a single photodiode at a beat frequency of 10 kHz.

In this paper we report the first use of ASOPS in a flame environment. The relative number density and decay time of atomic sodium are measured by aspirating a sodium chloride solution into an atmospheric premixed $\text{CH}_4/\text{O}_2/\text{N}_2$ flame. The pump and probe beams are each tuned to the D_2 transition (589.0 nm). Both ASOPS and laser-induced fluorescence are used to determine relative concentration profiles and saturation curves. Measurements obtained using these techniques are found to be in close agreement, demonstrating the viability of the ASOPS method as a combustion diagnostic and its potential for use in high-pressure, turbulent flames.

Introduction

Pump/probe methods are commonly employed to measure subnanosecond excited state processes in liquid and gas phase systems.^{1,2} Asynchronous Optical Sampling (ASOPS) is a newly-developed pump/probe method that will potentially allow the determination of number densities and relaxation rates in turbulent, high-pressure flames. In addition, ASOPS should yield a signal-to-noise ratio comparable to that for laser-induced fluorescence in practical combustion environments. The ASOPS method utilizes a coherent, signal-carrying beam and thus requires no more optical access than LDV measurements.

The current ASOPS instrument consists of two dye lasers synchronously pumped by two frequency-doubled, mode-locked Nd:YAG lasers. The two lasers operate at slightly different repetition rates, causing a relative phase walk-out between the pump and probe beams. This strategy allows the

mapping of subnanosecond excitation processes in a time scale on the order of milliseconds.

In previous papers,^{3,4} we reported initial ASOPS studies of Rhodamine B in methanol. We now extend the ASOPS technique to measurement of the relative number density of atomic sodium in an atmospheric $\text{CH}_4/\text{O}_2/\text{N}_2$ flame. The reconstruction of a fluorescence decay from the sodium D_2 transition (589.0 nm) is also used to determine the decay time of atomic sodium under flame conditions. To further demonstrate the viability of ASOPS as a combustion diagnostic, both ASOPS and laser-induced fluorescence (LIF) are used to measure relative concentration profiles and saturation curves. The results obtained using each technique are found to be in close agreement. Moreover, the signal-to-noise ratios of each method are of the same order-of-magnitude. We thus conclude that the ASOPS method has great potential for use in high-pressure, turbulent flames. Although visible pump and probe beams are used in the above experiments, the

ASOPS technique can eventually be extended to ultraviolet wavelengths to monitor molecular species such as the OH radical.

Operating Principles

In conventional pump/probe instruments the pump and probe lasers operate at identical repetition rates, and an optical delay line is used to control the relative timing between pulses from the two lasers. Moreover, some type of mechanical or electro-optical chopping scheme is generally employed to induce an amplitude modulation on the signal which facilitates the use of synchronous detection.^{5,6,7,8} In contrast, the ASOPS instrument employs pump and probe lasers operating at slightly different repetition rates. This induces a repetitive phase walk-out between the pump and probe pulse trains.

The ASOPS process is illustrated in Fig. 1a, which shows the excited state population produced by several pump pulses over which the temporal positions of several probe pulses have been superimposed. Each successive probe pulse is delayed in time relative to the pump pulse train by a constantly increasing duration which is determined by the beat frequency of the system. Thus each probe pulse samples the excited-state population at a slightly later time than the immediately preceding probe pulse. This is equivalent to varying the optical delay in a conventional pump/probe instrument. The entire process of Fig. 1a repeats itself when the cumulative delay equals the period of the pump laser. Hence any modulation of the probe beam, resulting from the creation and subsequent decay of the excited state, repeats at the beat frequency of the system. Therefore, in contrast to a conventional pump/probe instrument, there is no need to amplitude modulate either beam to employ synchronous detection.

Figure 1b illustrates the change in probe intensity which occurs owing to stimulated emission from the excited-state population shown in Fig. 1a. The net effect of the ASOPS technique is that a small amplitude waveform, which is directly related to the fluorescence decay of the species under study, is impressed onto the probe laser intensity. In essence, a temporal transformation of the excited-state decay is performed with the time scales by the factor $[(f_{\text{pump}})/(f_{\text{pump}} - f_{\text{probe}})]$, where f is the repetition rate of the two lasers. The ASOPS technique is thus an optical analog of the sampling oscilloscope.

Since the wavelengths of both the pump and probe lasers can be independently controlled, specific electronic quenching rates and state-to-state relaxation rates for a variety of atomic and molecular species can ultimately be determined. This as-

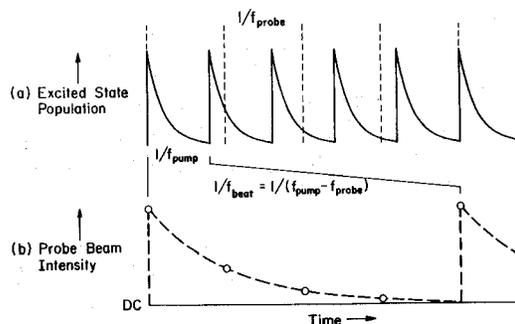


FIG. 1. ASOPS timing diagram showing (a) excited-state population and (b) probe beam intensity. The probe pulses in (a) are indicated by the vertical dashed lines.

sertion is valid because the stimulated emission (absorption) appears as a gain (loss) in the probe laser intensity; therefore, only those states which are directly connected by the probe laser wavelength are sampled. The gain/loss in the probe laser beam provides information on the rate at which the depopulated lower level gains population from neighboring levels within the ground electronic state or the rate at which the populated upper level transfers population to its neighboring levels within the excited electronic state. In other words, the ASOPS technique can yield information about state-to-state relaxation rates within both the upper and lower rovibronic manifolds for molecular species.

The beat frequency of the system is determined by the difference in laser repetition rates, i.e., $f_{\text{beat}} = f_{\text{pump}} - f_{\text{probe}}$. The inverse of the pump frequency, $1/f_{\text{pump}}$, gives the free temporal range of the ASOPS instrument, while the inverse of the beat frequency, $1/f_{\text{beat}}$, represents the collection time for a single decay. The total number of points, N , sampled during the decay is determined by $N = f_{\text{probe}}/f_{\text{beat}}$. The temporal difference between each sampled point within the decay profile is the sampling interval. The sampling interval, and thus the temporal resolution, is determined by the difference in laser periods, or $f_{\text{beat}}/(f_{\text{probe}} f_{\text{pump}})$.

In the present experiments, both the pump and probe beams are tuned to the sodium D_2 transition at 589.0 nm. Thus, the ASOPS signal represents the difference between stimulated absorption from the ground state and stimulated emission from the excited state. Since both beams excite the same transition, the role of the lasers is interchangeable, i.e., both beams modulate the sodium population seen by the other beam at the beat frequency. However, the period of the pump beam is shorter than that of the probe beam. Each successive pump pulse therefore "samples" the atoms at a slightly earlier time than the next probe pulse. Hence, a decay obtained using the "pump" beam would be

reversed temporally from that obtained using the "probe" beam (Fig. 1).⁴

Equipment and Procedure

Since the ASOPS technique requires that the pump and probe lasers operate at slightly different repetition rates, two independent, mode-locked laser systems are needed. Both the pump and probe beams are derived from Spectra-Physics model 375B dye lasers, which are synchronously pumped by frequency-doubled, mode-locked Spectra-Physics series 3000 Nd:YAG lasers. Rhodamine 6G is used as the laser dye. The mode-locking frequencies are generated by two Programmed Test Sources (PTS) model 160 frequency synthesizers operated in a master-slave configuration. Both the pump and probe beams consist of an ~ 82 MHz train of ~ 6 psec pulses, each tuned to 589.0 nm. The spectral bandwidth for both beams is ~ 0.14 nm, which is nearly transform limited. The PTS synthesizers are accurate to 0.1 Hz; hence, the laser repetition rates are very stable. Average powers in excess of 120 mW are obtained at the flame using 800–900 mW of pumping power. The typical operating parameters for the present ASOPS system are summarized in Table I.

A block diagram of the instrument is given in Fig. 2. As shown, each beam is split as it emerges from the laser. The weaker fraction is used to generate a trigger signal at the beat frequency of the system. This is done by separately monitoring each beam with fast photodiodes (EG&G FND-100) and electronically mixing the outputs of the photodiodes with a double-balanced mixer (Anzac MD-141) operating in a high-speed gating mode.⁹ Further de-

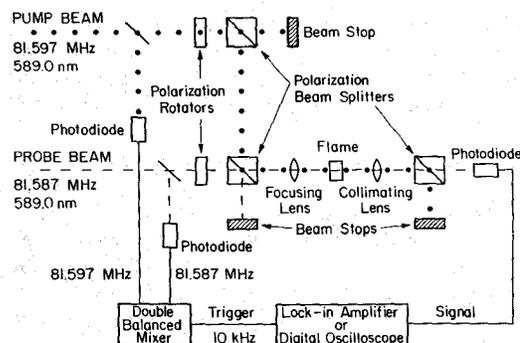


FIG. 2. Block diagram of the ASOPS instrument.

tails are given by Elzinga et al.⁴ and Kneisler et al.¹⁰

The remaining fractions of both the pump and probe beams pass through polarization rotator-beam splitter combinations which provide a convenient means of varying the power in either beam. In addition, the vertical component of the pump beam is combined with the horizontal component of the probe beam at the second polarization beam splitter. The beams pass colinearly through a focusing lens, the flame, and a collimating lens. Finally, the beams are separated by a third polarization beam splitter, after which the probe beam is monitored by a single photodiode (EG&G SGD-100A). Great care is taken to ensure that the pump and probe beams are completely separated at the final beam splitter, so that only the probe beam reaches the photodiode.

The photodiode output is filtered with a 4LE50CD Texscan 50 MHz low pass filter to remove the individual 82 MHz pulses, and is then directed to the appropriate detection system. For the nontemporal studies, which include the concentration profiles and saturation curves, a Stanford Research Systems model 510 lock-in amplifier is used to monitor a single Fourier frequency component of the ASOPS signal at the beat frequency of 10 kHz. For the temporal studies, the output from the filter is amplified using a C-COR 4375-A wideband AC amplifier. The amplified signal is then directed to a Hewlett-Packard 54100A digitizing oscilloscope, which is triggered at the beat frequency of the system. Each point of the oscilloscope signal is the result of 2048 averages.

The colinear configuration described above was chosen to maximize the signal-to-noise ratio in these first flame studies. Because of this configuration, the ASOPS signal is averaged over a pathlength of approximately 1 cm. In future experiments, spatial resolution will be enhanced by crossing the pump and probe beams.

To provide a comparison with the ASOPS results, laser-induced fluorescence (LIF) was used to

TABLE I

Typical Operating Parameters for ASOPS

Pump Repetition Rate (f_{pump})	81.5970000 MHz
Probe Repetition Rate (f_{probe})	81.5870000 MHz
Beat Frequency ($f_{\text{pump}} - f_{\text{probe}}$)	10 kHz
Free Temporal Range ($1/f_{\text{pump}}$)	12.2 nsec
Collection Time ($1/f_{\text{beat}}$)	100 μ sec
Samples per Decay ($f_{\text{probe}}/f_{\text{beat}}$)	8200
Sampling Interval ($f_{\text{beat}}/f_{\text{probe}}f_{\text{pump}}$)	1.5 psec
Pump/Probe Power	0–120 mW
Pulse Width	6 psec
Bandwidth	0.14 nm

obtain additional concentration profiles and saturation curves. The output from one of the previously-described synchronously pumped dye lasers is amplitude modulated at 1 kHz using a PTi model OC 4000 chopper. The beam is then directed through a polarization rotator-beam splitter combination into the flame. Fluorescence is collected by a 15-cm focal-length lens at right angles to the laser beam. To ensure consistency, the fluorescence collection volume includes the same 1-cm pathlength through the flame used for the ASOPS measurements. A specially wired RCA 1P28B photomultiplier¹¹ is used to detect the fluorescence. The photomultiplier signal is monitored using the lock-in amplifier at a reference frequency of 1 kHz.

An atomic absorption slot burner¹² is employed to support an atmospheric premixed $\text{CH}_4/\text{O}_2/\text{N}_2$ flame into which a sodium chloride solution is nebulized. The burner provided fairly constant conditions for about thirty minutes, after which it became less reliable. Atomic sodium was chosen because of the large absorption cross section of its $3S_{1/2} \rightarrow 3P_{3/2}$ electronic transition. Since the 589.0 nm wavelength of the transition lies near the peak of the Rhodamine 6G tuning curve, ample laser power was available to perform the saturation measurements.

Results and Discussion

Figure 3 shows the ASOPS signal for atomic sodium; the signal compares favorably with that expected in Fig. 1. In this study, the pump and probe beam powers were set at 65 mW and 10 mW, respectively. A 400-mm focal length lens was used, giving an approximate beam diameter of 100 μm . The photodiode signal was amplified by a factor of 100. Based on a least square fit, the equivalent decay time is 8.9 μsec . Since the ASOPS technique performs a temporal transformation of the decay, the actual decay will be related to the equivalent decay by

$$t_{eq} = t_{pump} / (f_{pump} - f_{probe}).$$

Thus the actual lifetime of the excited state under flame conditions is 1.1 nsec. This value is consistent with previous decay times (~ 1 nsec) reported in the literature.^{12,13}

Although the ASOPS signal in Fig. 3 appears to be a gain curve, this is clearly not the case. Because the probe beam is directly connected to the ground state, it will be subjected to a combination of ground state absorption and stimulated emission, with the former dominating the latter. To understand the effect of stimulated absorption on the temporal profile of the probe beam intensity, consider the timing diagram in Fig. 4, where I_{pr}^0 de-

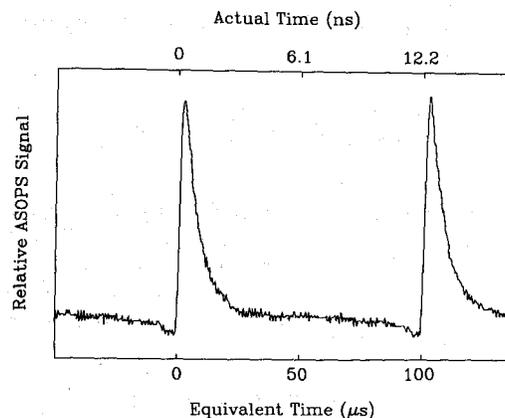


FIG. 3. Temporal decay for atomic sodium obtained with both the pump and probe beams tuned to the D_2 transition (589.0 nm). The lower scale gives the equivalent time displayed on the oscilloscope, while the upper scale gives the actual time. The pump and probe beam powers are 65 mW and 10 mW, respectively.

notes the intensity of the probe beam before the flame. The greater the ground state population when the probe beam arrives, the greater the amount of absorption and the less the intensity of the probe beam after the flame. Hence, when the pump and probe pulses overlap, the ground state population is a minimum and the probe beam intensity is a maximum. This should be compared to the stimulated emission case shown in Fig. 1, where both the excited state population and the probe beam intensity are maximized upon temporal overlap of the pump and probe pulses. However, even though ground state absorption causes a decrease in probe beam intensity and stimulated emission causes an increase in probe beam intensity relative to I_{pr}^0 , the resulting temporal shape is identical because atomic sodium follows the characteristics of a two-level model. Thus, it is clear that any combination of ground state absorption and stimulated emission will simply be an additive process with little or no distortion of the temporal decay.

The decay curve in Fig. 3 was obtained by averaging over 2048 separate single-decay curves. Ideally, the averaging process should take 204.8 msec to complete; however, because of the slow re-arming rate of the oscilloscope, the averaging process took 78 sec. The peak signal-to-noise ratio (SNR) of the average decay curve is 33. We believe that a considerable portion of this noise can be attributed to impedance mismatches at the trigger photodiodes and at the double balanced mixer. Corrections are currently being made in these devices to improve the SNR. Furthermore, suitable upgrades are possible with respect to the performance of both

the Nd:YAG laser systems and the detection electronics.

The ASOPS signal in Fig. 3 contains an additional downward feature at the end of its free temporal range that is not predicted by Fig. 4. We believe that this additional shape is due to competition between the pump and probe lasers. Figure 4 assumes that each probe pulse does not perturb the ground state before the arrival of the next probe pulse. However, this will not always be true in the present experiments because both the pump and probe lasers excite the same transition. For example, the 8199th pump pulse will arrive only 3 psec after the 8198th probe pulse. Thus for this pump pulse to see an unperturbed population, the disturbance caused by the previous probe pulse would have to disappear in 3 psec. This condition is obviously impossible to satisfy.

To further demonstrate the viability of ASOPS as a combustion diagnostic, both ASOPS and LIF were used to obtain relative concentration profiles and saturation curves. The horizontal ASOPS and LIF profiles are plotted in Fig. 5. The pump and probe beam powers are 120 mW and 80 mW, respectively. The 120 mW pump beam is also utilized for the LIF measurements. As shown in Fig. 5, the relative concentration profiles obtained using each method are nearly identical. Furthermore, the SNR for ASOPS was of the same order-of-magnitude as that for LIF. The ASOPS method yielded an inverse relative standard deviation of 34, while the LIF method yielded a value of 44. As was stated above, we expect the ASOPS performance to improve significantly with suitable corrections in the instrument.

The saturation curves obtained using both ASOPS and LIF are plotted in Fig. 6. In this case, a 100-mm focal length lens was used to achieve saturation; hence, the results of Figs. 3 and 5 occurred well within the linear regime of Fig. 6. For the ASOPS method, both the pump and probe beams

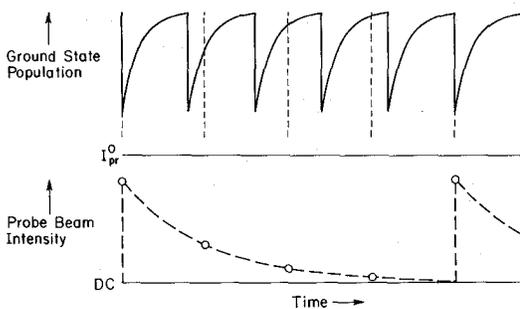


FIG. 4. Timing diagram showing the effect of stimulated absorption on the ASOPS signal. The DC level corresponds to maximum absorption of the probe beam.

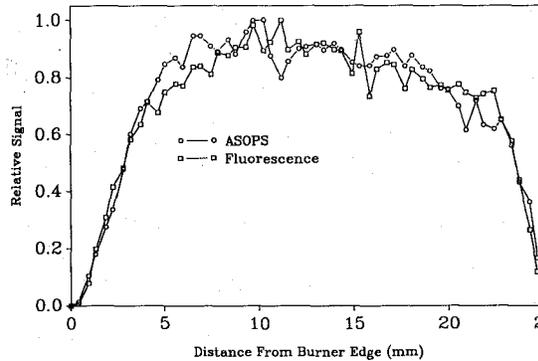


FIG. 5. ASOPS and LIF relative horizontal concentration profiles. Measurements were taken ~ 0.6 cm above the burner. The pump and probe beam powers are 120 mW and 80 mW, respectively.

were again tuned to the sodium D_2 transition. The pump beam power is varied while the probe beam power is held constant at 80 mW. For the LIF method, the probe beam is blocked, while the pump beam power is varied in a similar fashion. Once again, the ASOPS measurements correspond closely with the LIF measurements.

Although the results of Figs. 5 and 6 demonstrate that ASOPS and LIF exhibit similar signal-to-noise characteristics, these data say little about absolute detection limits. If, however, we presume that both the ASOPS and LIF signals are limited by Poisson statistics,⁵ we can provide a plausible scenario for our contention that the ultimate detectivities of these two methods should be similar. Assume that after a single pump pulse, 10^4 atoms are produced in the excited electronic state. If quenching is neglected, spectral and temporal integration of the fluorescence signal for a favorable collection efficiency of one percent gives 10^2 photons/pulse at the detector. At 82×10^6 pulses/sec, integration for one millisecond then gives a total photon count of 8.2×10^6 or a SNR of 2.9×10^3 .

For ASOPS, the minimum probe energy required to sample 10^4 excited atoms for a stimulated quantum efficiency of one percent would contain 10^6 photons/pulse. If we again integrate for one millisecond, the total photon count for the probe laser is 8.2×10^{10} , which gives a background shot noise of 2.9×10^5 photons. Since the ASOPS signal corresponds to 10^4 excited atoms/pulse for the same one-millisecond averaging time, we obtain a total signal count of 8.2×10^3 photons, giving a SNR for ASOPS of 2.9×10^3 which is the same as that for LIF.

Although the above scenario is only approximate, the similarity in SNR confirms that the absolute detection limit for ASOPS should be of the same order-of-magnitude as that for LIF. This conclusion

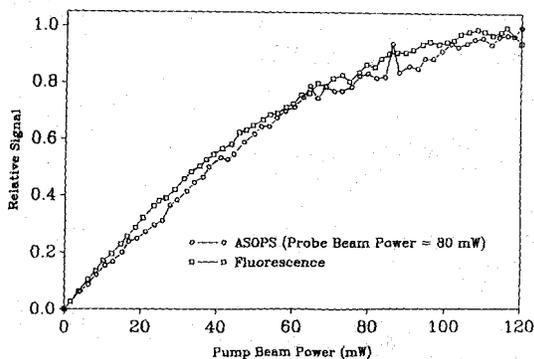


FIG. 6. ASOPS and LIF relative pump-beam saturation curves. The ASOPS curve was obtained by varying the pump power, while the probe power was fixed at 80 mW.

does not depend on quenching, since the temporal ASOPS and LIF signals are equally affected by molecular collisions. In essence, for ASOPS, the coherent signal compensates for a large inherent DC background while, for LIF, the zero-background spontaneous signal compensates for a poor spatial collection efficiency.

Conclusions

In this investigation, we have demonstrated that an ASOPS signal can be obtained in a flame environment. The similarity in results obtained by the ASOPS technique and the LIF method verifies the applicability of ASOPS as a combustion diagnostic. This conclusion is significant since ASOPS has several useful advantages when compared to LIF. For instance, ASOPS does not require the typical collection optics of a fluorescence measurement as the ASOPS signal is contained entirely within the coherent probe beam. LIF studies also require knowledge of quenching rates that are often ambiguous or unavailable; the ASOPS technique inherently supplies such information. Although ASOPS and LIF yielded similar signal-to-noise ratios in the present colinear-beam study, we believe that major improvements in the current ASOPS instrument are possible.

Our ultimate goal is to use the ASOPS method to monitor molecular species such as the OH rad-

ical which occurs naturally in practical combustion environments. Thus future experiments will explore the extension of ASOPS from the visible to the ultraviolet regime. This will require some minor modifications of the present instrument, such as the addition of frequency-doubling crystals.

Acknowledgments

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COMMENTS

K. Rensberger, SRI International, USA. Could you give an estimate of the detection limit for Na in the flame?

Author's Reply. Since the work on sodium presented in this paper does not yet take advantage of several noise-reduction techniques currently under

development in our laboratory, we cannot give a detection limit based on our experiments at this time. However, based on the two orders of magnitude improvement in signal-to-noise ratio for stimulated Raman gain spectroscopy compared to ordinary incoherent Raman scattering,¹ and the detection limit of 10^4 atoms/cm³ for Na fluorescence measurements,² we estimate an ultimate ASOPS detection limit of 10^2 atoms/cm³.

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D. A. Greenhalg, Harwell Laboratory, England.
Do you have an explanation for the negative signal you see in the frequency degenerate experiment? We have also seen such features which are of order of the pulse duration of the laser.

Author's Reply. As indicated in the paper, we believe that the downward feature in the temporal ASOPS signal arises from the influence of the probe pulse on the next pump pulse near the end of the free temporal range. We have recently verified this assertion by employing a probe laser wavelength and a pump laser wavelength of 569 nm and 589 nm, respectively; as expected, the above feature of the ASOPS signal disappears. However, at present, we do not have an explanation for the exact physical mechanism controlling the probe-pump interaction. We plan to look for this effect in upcoming simulation studies.