

Absolute Concentrations of Potassium by Picosecond Pump/Probe Absorption in Fluctuating, Atmospheric Flames

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ABSTRACT—We demonstrate a picosecond pump/probe absorption instrument for measuring absolute concentrations in a rapidly fluctuating flame environment at atmospheric pressure. The instrument is based on a regeneratively mode-locked Ti:Sapphire laser. Atomic potassium is seeded into an atmospheric, premixed CH₄/air flame. A detection limit for atomic potassium of $1.1 \times 10^{11} \text{ cm}^{-3}$ is obtained for an integration time of 1 second without the need for calibration. We predict a detection limit for CH of $1.0 \times 10^{13} \text{ cm}^{-3}$ if simple modifications are made to the pump/probe instrument, including a reduction in laser spectral bandwidth by a factor of 50. The spatial resolution for our measurements is 0.137 cm. We have also demonstrated the temporal resolution that the picosecond pump/probe instrument offers. Here, 50-Hz fluctuations were induced in an otherwise laminar flame, and the resulting fluctuations in the potassium concentration were resolved on power spectral density (psd) plots. A detection limit of $1.5 \times 10^{11} \text{ cm}^{-3}$ was obtained for the psd system. We estimate that a corresponding detection limit of $1.5 \times 10^{13} \text{ cm}^{-3}$ for CH is possible. The temporal resolution of our system is presently limited to that of the borrowed detection electronics, and simple modifications will allow resolution beyond 1 MHz.

Key Words: Combustion diagnostics, turbulence, spectroscopy, absorption, laser-induced fluorescence, concentration

INTRODUCTION

In this paper we discuss the development and demonstration of an instrument for making spatially and temporally resolved concentration measurements of radical species in practical combustors. A wide variety of combustion studies would benefit from this instrument. Existing laser diagnostic methods are not appropriate for measurements in many reactors. We demonstrate a new method for concentration measurements based on picosecond pump/probe absorption spectroscopy using regeneratively mode-locked Ti:Sapphire lasers. In this demonstration, atomic potassium is seeded into a premixed methane/air flame and the potassium concentration is then measured on an absolute basis, without the need for calibration. Results are found to agree with concentration measurements obtained from line-of-sight absorption spectroscopy. The flame is acoustically driven to simulate the fluctuating environment that is characteristic of many practical combustors. The pump/probe signal is then manipulated using a fast-Fourier transform (FFT), and rapid fluctuations are thereby identified. The detection limit of the FFT system is measured. Based on these results, we

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recommend future experiments using this laser technology with the pump/probe method.

This paper is organized as follows: The motivation for our experiments is described, and the difficulties with past laser-based flame diagnostics are considered. Next, we discuss the type of instrument we selected for these experiments, followed by a description of the type of laser upon which this instrument is based. We then describe the specific equipment and procedural details that are unique to our present experimental apparatus, followed by a presentation and discussion of our results.

MOTIVATION

The picosecond pump/probe absorption instrument has a number of important features that should prove beneficial to combustion research:

1. Temporal resolution down to $\sim 1 \mu\text{s}$ and spatial resolution below 1 mm.
2. Concentration measurements independent of the collisional environment.
3. Absolute concentrations without the need for calibration.
4. Detection of minor and major species, including species with very low fluorescence yield.

We now consider some specific situations that would benefit from the pump/probe instrument.

Applications

A number of fields of research in combustion would benefit from the above features of the picosecond pump/probe absorption instrument. A partial list includes turbulent combustion, combustion instability, and ignition phenomena.

Characterization of the fundamental properties of turbulent reacting flows is of critical importance. Models and experiments are necessary because both mixing and finite-rate chemical kinetics control the overall rate of reaction and the final product mix. It is therefore necessary to develop the capability to measure chemical species (major and minor) at the characteristic time and length scales in a turbulent flow field. Turbulence frequency spectra, which can often go out to 10 kHz, can be used to identify turbulence regimes and scales (Bradley, 1992). In the past, experimental work has centered on laser doppler anemometry and on corrected, fine-wire thermocouple measurements of velocity and temperature spectra; composition fields are likely to contain length and time scales different than those of the velocity field (Pope, 1990). It would therefore also be beneficial to make spatially- and temporally-resolved concentration measurements of key species in turbulent flames. Turbulence length and time scales cannot be resolved if the measurement scale or time is greater than the smallest (Kolmogorov) scales of interest, which are typically hundreds of microns in length and less than one hundred microseconds in time (Daily, 1975). A measured concentration power spectral density (psd) can be used to infer all the length and time scales of importance. Moreover, a system which is capable of detecting psd's is also capable of acquiring probability density function (pdf's), but at a much faster data collection rate.

A second example is combustor instability. Combustors such as ramjets or rockets can exhibit instabilities on a kilohertz scale (Culick, 1988; Samaniego *et al.*, 1993; Candel, 1992). Spectral measurements can give insight into stability and acoustic behavior. Measurement of species concentration psd's would make it possible to correlate spatially resolved chemical effects with acoustic disturbances.

A third example is ignition, which can require measurements to be completed on a millisecond timescale. The event may take place at a known, periodic rate, such as ignition in an internal combustion engine (Gutheil, 1993), or it may occur at an unpredictable instant in time, as with the study of ignition of bulk metals (Abbud-Madrid *et al.*, 1993; Brzustowski and Glassman, 1964; Nguyen and Branch, 1987). Our instrument may even be able to probe concentrations in detail during ignition, giving information such as psd's and pdf's during the transient event.

Existing Diagnostics

Optical methods of measuring minor species concentrations have provided new insights into the combustion process (Eckbreth, 1988). Although a variety of techniques has been successfully applied to flames, such as absorption and laser-induced fluorescence (LIF), these techniques have major drawbacks for use in fluctuating combustion environments. The most widely used laser-based diagnostic is LIF (Lucht, 1987), because its favorable signal-to-noise ratio (SNR) allows detection of minor species such as the hydroxyl radical. In turbulent flames, fluctuations in the collisional environment can cause uncertainty in the LIF signal (Lucht, 1987; Fiechtner *et al.*, 1992). A number of approaches have been taken to this problem. One of the most successful corrections for collisional quenching is made possible with simultaneous Raman scattering measurements of major species concentrations and temperatures (Barlow and Carter, 1994). However, conventional Q-switched laser technology is necessary to obtain sufficient photons for practical measurements. These lasers exhibit repetition rates of ~ 10 – 100 Hz, requiring single-shot measurements of probability distribution functions. Even with successful single-shot results, information between pulses is lost. In many cases, single-shot data are not possible due to an inadequate SNR, with averaging being necessary. Not all species have significant fluorescence yields, so LIF is appropriate for a limited set of molecules. In addition to these drawbacks, the LIF method requires calibration using a second experimental technique to put results on a quantitative basis. Typically, a calibration can be done using absorption spectroscopy. Although LIF will always be applicable to many combustion studies because of its utility, there remain a number of cases where it is not adequate.

Excellent temporal resolution has been demonstrated for laser absorption measurements (Chang, 1991). When the signal is generated by a cw laser, the speed of the measurement is limited by the electronics used. All species absorb radiation, so this approach can be applied to a very wide range of molecules. Unfortunately, absorption is a line-of-sight technique, and thus has poor spatial resolution.

Coherent Anti-Stokes Raman Spectroscopy (CARS) is a two-photon nonlinear technique, so it has much lower sensitivity than LIF. It is a background-free four-wave mixing process. CARS produces a coherent, collimated and spectrally bright signal beam. This makes it possible to spatially filter spurious scattered light from the signal

beam, and it requires less optical access than LIF. In addition, CARS measurements of OH concentration have been reported at high flame pressures (Attal-Trétout *et al.*, 1990). Because it is a nonlinear process with small cross sections, CARS requires the use of high power pulsed lasers, limiting temporal resolution. Thus previous high-pressure measurements of OH were taken with 30 averages at 10 Hz, and the spatial resolution was approximately 20 mm (Attal-Trétout *et al.*, 1990).

An example of a spatially and temporally resolved species PSD measurement is presented by Wrobel and Pratt (1978), who used a cw dye laser to observe sodium fluorescence in a turbulent flame. The resulting signals were fast-Fourier transformed out to 10 kHz. Their same instrument could be used to acquire PDF's. While PDF's can be measured using pulsed lasers, cw diagnostics increase the data rate significantly. Wrobel and Pratt (1978) encountered systematic problems related to the use of low-power dye lasers, and they quote $\pm 30\%$ uncertainty in the sodium measurement due to collisional quenching of fluorescence. While their work was a significant step, we use both a new laser device and new diagnostics.

PICOSECOND PUMP/PROBE ABSORPTION SPECTROSCOPY

To overcome the difficulties associated with existing laser diagnostics, we have pursued an instrument based on the conventional pump/probe configuration (Fleming, 1986). A typical example is shown in Figure 1. Here, the output of a picosecond laser system is split into two beams, the pump and the probe, so that both beams have the same pulse repetition rate. The pump is modulated with a chopper for low frequencies (< 10 kHz), or an electrooptic modulator for higher frequencies (> 1 MHz). The pump and probe are crossed in the flame using an LDV configuration, and the pump beam is directed to a beam stop after the flame. The probe is detected after the flame using either a photodiode or a photomultiplier. The signal is sent to a lock-in amplifier, which is triggered at the modulator frequency. An optical delay line is placed in the pump-beam path before the flame as a convenient way to temporally overlap the pump and probe pulses in the flame where the two beams cross. Because gasdynamic events occur on > 100 ps time scales, picosecond pulses are used to remove any dependence on the collisional environment.

The pump/probe instrument has been extensively applied in the past. Initial demonstrations of the pump/probe method in a flame environment used a synchronously mode-locked dye laser as the source of picosecond pulses (Beaman, 1985; Langley *et al.*, 1985; Langley *et al.*, 1986; Beaman *et al.*, 1986; Jones, 1987). The pump was modulated at megahertz frequencies, and the $2S_{1/2} - 2P_{1/2,3/2}$ transition (671 nm) of atomic lithium (which had been seeded into the slot burner) was detected. An impressive detection limit $6.5 \times 10^4 \text{ cm}^{-3}$ was obtained for a lock-in time constant of 1 second; this detection limit corresponds approximately to the limit defined by shot noise on the probe laser. Although the scope of these initial demonstrations did not include minor species diagnostics in flames, Fiechtner (1992) and Fiechtner *et al.* (1994) applied a rate equation analysis to estimate that a corresponding detection limit for OH would be $2.3 \times 10^{12} \text{ cm}^{-3}$ for synchronously mode-locked dye lasers. Unfortunately, synchronously mode-locked dye lasers were found by Fiechtner *et al.* (1994) to lack

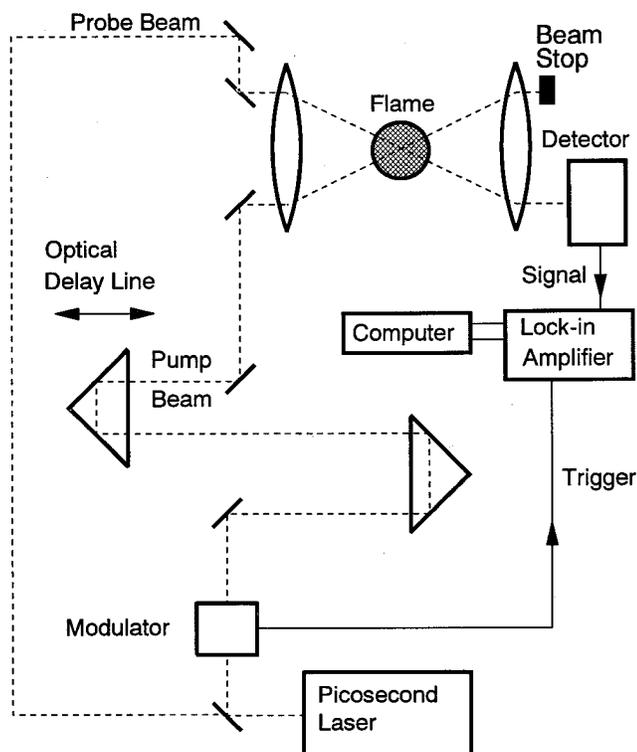


FIGURE 1 Conventional pump/probe instrument.

sufficient power for detection of important minor species such as OH, CH, and NO. In the present study, we seek to retain the potential of the previous tests by replacing the synchronously mode-locked dye lasers with regeneratively mode-locked Ti:Sapphire lasers. Ti:Sapphire lasers have a number of advantages, including an improvement in average power by a factor of up to 1000 over older synchronously mode-locked dye lasers. This should allow an improved detection limit for species such as CH, as discussed below.

In the pump/probe method, the pump modulation is impressed on the resonant molecules. The molecules then modulate the probe where the two beams intersect, changing the irradiance at the chopper rate. This change in irradiance is defined as the modulation depth, expressed as a fraction of the total probe irradiance. Unlike the previous pump/probe experiments of Fiechtner *et al.* (1994), the present scheme is fully quantitative; the probe modulation depth will be proportional to the concentration of molecules, and this modulation depth can be readily measured (Blanchard and Wirth, 1986). The spatial profile of our present laser system is a reliable TEM-00 profile, allowing an excellent estimate of the interaction length between the pump and probe beams. For optically-thin conditions, the modulation depth will be less than 1%. Nevertheless, it is now well known that for mode-locked lasers, the minimum detectable modulation depth is approximately 10^{-8} , allowing excellent detection limits and

a large dynamic range (Heritage, 1983). In our experiments, the pump and probe beams are crossed in the flame with the geometry of Figure 2, and both beams are in resonance with the same transition; in this case, the modulation depth can be expressed (Fiechtner, 1992; Fiechtner *et al.*, 1994)

$$\alpha_{MOD} = \frac{g_2}{g_1} \left(1 + \frac{g_2}{g_1} \right) \left[\ln \left(\frac{1}{\sqrt{2}-1} \right) \right]^2 \frac{c^4 A_{21}^2 P_{AVE}^{PUMP} N_T L}{16\pi^3 D^2 h \nu_{12}^5 f^L (\Delta\nu_{1/2}^L)^2}, \quad (1)$$

where h is Planck's constant, c is the speed of light, and the remaining variables and their present values are given in Table I. Each of the variables in this expression is

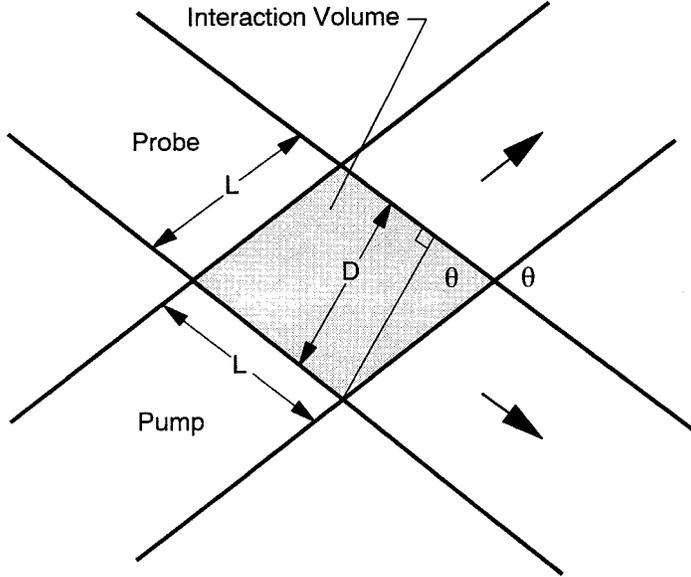


FIGURE 2 Crossed-beam geometry used in our experiments.

TABLE I

Operating parameters and important constants for present experiments. Variables are Used in Equation (1)

Symbol	Description	Value
g_1	degeneracy of the ground state	2
g_2	degeneracy of the excited state	4
D	focal diameter	116 μm
L	interaction length	0.137 cm,
f^L	laser repetition rate	82 MHz
ν_{12}	1 - 2 transition frequency	$3.912 \times 10^{14} \text{ s}^{-1}$
$\Delta\nu_{1/2}^L$	laser bandwidth (FWHM)	$2.3 \times 10^{11} \text{ s}^{-1}$
P_{AVE}^{PUMP}	average laser power of pump beam	$4 \times 10^{-3} \text{ W}$
A_{21}	Einstein coefficient for spontaneous emission	$0.4 \times 10^8 \text{ s}^{-1}$

known or easily measured. Therefore, if the modulation depth is measured, the absolute concentration, N_T , can be obtained, as we demonstrate below.

CHOICE OF A PICOSECOND LASER

Mode-locking is one of several techniques for producing short pulses from lasers. There are numerous, compelling advantages associated with the use of such a laser:

1. Mode-locked lasers have high (70–100 MHz) repetition rates because the laser is cw pumped (vs. pulsed). It is therefore possible to achieve excellent signal-to-noise ratios with wide bandwidth using phase sensitive detection.
2. Mode-locking gives excellent longitudinal mode stability, eliminating the pulse-to-pulse mode hopping experienced with multi-mode pulsed laser systems.
3. With efficient mode-locking, pulses are nearly transform-limited. Thus a measurement of temporal pulsewidth yields a reliable estimate of the spectral bandwidth. This is important for absolute concentration measurements.
4. Mode-locked lasers provide a beam with a well-defined TEM-00 spatial profile characteristic of many cw lasers. This allows a good estimate of the spatial resolution of the instrument (the interaction length of Eq. (1)) (Blanchard and Wirth, 1986).

In contrast, signals generated by pulsed lasers often require averaging because single-shot measurements are accompanied by large variability. The turbulence frequency spectrum that can be resolved is limited to half of the rate at which the laser is pulsed (10 Hz to 500 Hz), divided by the number of averages required; this restricts the type of flowfield that can be studied. Moreover, pulsed, single-shot measurements utilize much larger peak power. They become limited by saturation or breakdown of the medium, and the detector dynamic range must be large.

We now discuss some potential advantages of Ti:Sapphire lasers as a source of high repetition rate, picosecond pulses. A number of excellent, in-depth discussions of mode-locked lasers is available (Siegman, 1986), and so the present discussion is limited accordingly.

Mode-locking techniques introduce some form of modulation into a cw laser at the $c/2l$ frequency spacing of the laser longitudinal modes (c is the speed of light, l is the overall cavity optical path length). Each longitudinal mode is then individually modulated, with side-bands at the frequency of the next-nearest longitudinal mode. These side-bands injection-seed the nearest neighbors (since the modulation frequency is adjusted to do so), and this occurs from mode to mode, over the entire gain bandwidth of the medium. By doing this, all the longitudinal modes have a fixed phase relationship forced upon them, and thus they can coherently add to give short pulses. The temporal pulsewidth is thus governed by the spectral bandwidth of the laser.

Until recently, tunable mode-locked pulses could only be achieved by synchronous pumping of a dye laser. Typically the pump laser is either an actively mode-locked Ar:Ion laser or an actively mode-locked, frequency doubled cw Nd:YAG laser. Active mode locking involves the placement of a modulator into the cavity of a cw laser, commonly done with amplitude modulation of the intra-cavity loss. In Nd:YAG lasers this typically produces 60–80 ps, 1064 nm wavelength pulses at repetition rates from

70–100 MHz, with 7–20 W of average power. This is then frequency doubled to pump a folded-cavity dye laser. The dye laser has an adjustment for overall cavity length which is manually matched to the cavity length of the pump laser. When length match is achieved, the pump pulses arriving at the dye jet produce intra-cavity gain modulation at the $c/2l$ mode frequency spacing of the dye laser, and so the dye laser becomes synchronously mode-locked. This can produce pulses on the order of 2–5 ps, with average power levels around 300 mW, depending on the dye that is used. A birefringent tuner (sometimes called a Lyot filter) with one, two, or three birefringent plates is used to tune the wavelength of the dye laser. This filter rotates the polarization of all the wavelengths except the desired wavelength. These rotated wavelengths then experience loss at every intra-cavity polarization component and hence they do not oscillate within the resonator. Additional plates (practically limited to 3) narrow the bandwidth passed through the tuner. If the pulses are transform limited, then the product of the temporal pulsewidth and the spectral bandwidth is equal to a constant, the value of which depends upon the pulse shape (Siegman, 1986). Thus, at the transform limit, pulsewidth and bandwidth are inversely related. These tuning elements can therefore be used to control both bandwidth and pulsewidth. Where a restricted spectral bandwidth is more advantageous than ultra-short pulses, an étalon is added to the laser cavity together with a three-plate birefringent filter to reduce the spectral bandwidth.

Synchronously-pumped dye lasers have several limitations which have excluded them from wide application to combustion diagnostics. Because dyes have relatively low gain, the average power is limited to approximately 300 mW (3.7 nJ/pulse) with ~ 5 -ps pulse. Dyes can cover the near IR (880 nm) up through yellow (570 nm), producing the greatest output at 600 nm in R6G dye. This output must be frequency doubled to reach important UV transitions. Unfortunately, the UV power produced (less than 15 pJ per pulse) is too small to be useful (Fiechtner, 1992; Fiechtner *et al.*, 1994). Previous studies with synchronously pumped dye lasers were also hampered by sizable baseband noise on the laser output that was amplified by the frequency doubling process (Von der Linde, 1986).

Titanium-doped sapphire is a fairly new, solid state laser gain medium which remains the subject of intensive research. It is a broad-bandwidth material which can mode lock (in a random and noisy manner) even without modulation. Recent advances in regenerative mode-locking (Kafka *et al.*, 1992) have produced as much as 2 W of tunable radiation (at the gain peak) with 2-ps pulses (24.7 nJ/pulse), at ~ 80 -MHz repetition rates. The tuning range is roughly 750 nm to 920 nm at 2 W, but one can cover 720 nm to 1000 nm and stay above 500 mW. These lasers have been frequency doubled, tripled and quadrupled to give as much as 700 mW at 410 nm, 120 mW at 272 nm, and 10 mW at 210 nm (see the references provided by Kafka *et al.*). Ti:Sapphire pulses have also been amplified into the microjoule regime at hundreds of kilohertz repetition rates (Norris, 1992).

The laser we have used is a Spectra-Physics regeneratively mode-locked Ti:Sapphire device pumped by a cw, non-mode-locked argon-ion laser. In regenerative mode-locking (see Figure 3), the acousto-optic mode-locker is operated off-resonance, producing from 1–5% optical modulation (Kafka *et al.*, 1992). The frequency for the RF (~ 40 MHz) drive to the mode-locker is derived from a fast photodiode which samples the laser output. Longitudinal mode beating on the photodiode at

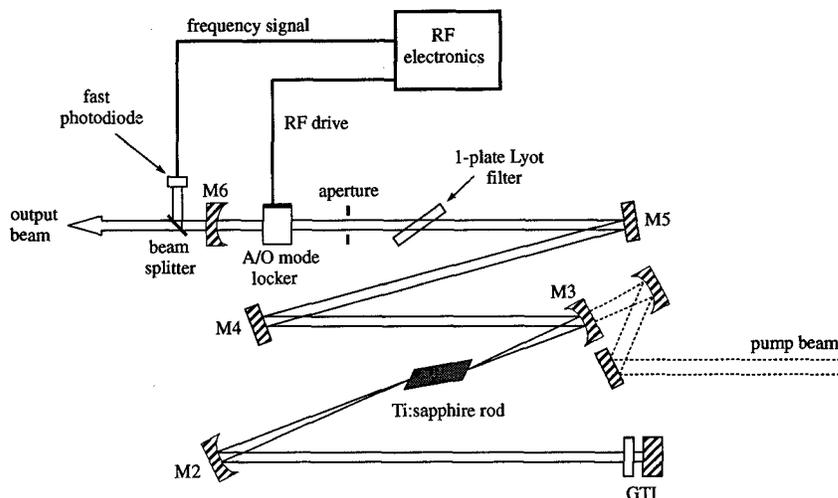


FIGURE 3 Diagram of the regeneratively mode-locked Ti:Sapphire laser cavity.

$c/2l$ frequencies provides the initial input signal for the RF frequency, after which the naturally occurring pulse frequency is used. Since the mode locker frequency is locked to the cavity length, no length mismatch occurs even as the laser cavity length drifts with time. Short pulses passing through the laser rod experience positive group velocity dispersion (GVD) and some self phase modulation (optical Kerr effect), broadening the pulse. In the device we used, a Gires-Tournois interferometer (GTI) provides negative GVD in compensation. It consists of a high reflector and a 4% reflector, spaced about 80- μm apart. The negative GVD is varied by piezoelectric control of the spacing. The operator adjusts the GTI until acceptable mode locking is achieved. Our laser is equipped with a 2-ps GTI and a single-plate birefringent tuner. Two or three birefringent plates would have been optimum, although they are not available in our laboratory. We purge the cavity with dry nitrogen because there are many atmospheric absorption lines within the bandwidth of Ti:Sapphire. Even small intra-cavity absorption can cause tuning discontinuities in the laser.

When pumped with 7 W from an argon-ion laser, our laser produces about 900 mW of output with autocorrelation pulse-widths near 1.4 ps (assuming a sech^2 pulse shape). The transform-limited bandwidth is about 0.5 nm, consistent with our monochromator measurements. For spectroscopists, the 2-ps pulsewidth is too short because the transform-limited bandwidth is typically 100 times the spectral bandwidth of the atom or molecule of interest. It would be straightforward to obtain high power levels at narrow bandwidths by broadening the temporal pulsewidth and narrowing the spectral bandwidth. This can be achieved by switching to a 50- to 60-ps GTI, installing a three-plate birefringent tuner, and perhaps using an étalon.

We are not aware of any noise comparisons between Ti:Sapphire lasers and dye lasers that are synchronously mode-locked by mode-locked Nd:YAG lasers. Kafka *et al.* (1992) found Ti:Sapphire noise properties to be favorable, while Son *et al.* (1992)

found the noise from a mode-locked Ti:Sapphire to be favorable when compared to a colliding-pulse mode-locked dye laser. We are planning to investigate this topic during future experiments.

The level of performance offered by mode-locked Ti:Sapphire is a significant improvement over the older dye laser technologies. It offers the possibility for detection of species that absorb at wavelengths that were previously unreachable. Indeed, the power available is now sufficient to perform nonlinear optical techniques in optically-thin flames (Linne and Fiechtner, 1994).

APPARATUS AND PROCEDURE

Our complete experimental layout is similar to that of Figure 1. In the present studies, the output from the Ti:Sapphire laser is split into two portions: the pump beam is directed through a 1-kHz chopper, and is then focused in the flame with a 7.5 cm focal length lens, where it then crosses the probe beam. An LDV configuration with an inclusive angle of 4.85° is selected. The pump-beam modulation is then impressed on the population being measured, which in turn modulates the probe beam in the interaction volume. For our geometric configuration, the interaction length is 0.137 cm. After the flame, the pump beam reaches a beam stop, and the probe beam is detected using a RCA 1P28 photomultiplier tube. The photomultiplier current is synchronously demodulated using a lock-in amplifier. The probe pulses are delayed by approximately 2 pulsewidths relative to the pump pulses to prevent the influence of a "coherent spike" on the pump/probe absorption signal (Fiechtner, 1992).

Measurement of the modulation depth is trivial given a detector with excellent linear range and low drift (Blanchard and Wirth, 1986). Many photodiodes and photomultipliers satisfy these requirements. In our measurements, the probe beam is first detected in absence of modulation, giving a signal for the case of 0% modulation depth. This value is subtracted from all subsequent lock-in output voltages. Next, the chopper is placed in the probe beam, and the probe is again detected. This signal corresponds to the case of 100% modulation depth. Knowing these limiting modulation depths, we can calculate the modulation depth for any intermediate signal level. The chopper is then placed in the pump beam path, so that any modulation of the probe is a result of the pump/probe interaction in the flame. The resulting lock-in output voltage is divided by the voltage corresponding to a 100% modulation depth.

The burner is a Perkin-Elmer aspirating unit fitted with a Meeker-type burner head, operated with an equivalence ratio of 0.92 for CH_4 and air. Various solutions of KCl in water are aspirated into the flow to provide controlled, reproducible levels of atomic potassium in the flame. Potassium is studied because it has strong lines near the peak of Ti:Sapphire. In the pump/probe experiments described below, the laser is tuned to the $4^2S_{1/2} - 4^2P_{3/2}^o$ transition of atomic potassium at 766.5 nm. To avoid optical saturation of this transition, the pump power is set to 4 mW (49 picojoules per pulse) and the probe power is set to 5 mW (61 picojoules per pulse) (Fiechtner, 1992; Fiechtner *et al.*, 1994). All concentrations of atomic potassium are optically thin.

A line-of-sight absorption measurement is performed for comparison with our pump/probe data. Here, several different solutions, with different concentrations of

KCl, are atomized into the flame. Light from a tungsten lamp is passed through the flame and then detected with an optical multichannel analyzer (OMA); the OMA signal is integrated for 26.7 μ sec and averaged 4095 times. The absorption of the lamp emission by the $4^2S_{1/2} - 4^2P^o_{3/2}$ transition of atomic potassium is measured and used to calculate the potassium concentration in the flame. Confidence intervals (95%) result from the uncertainty in calculating the integrated lamp absorption, due largely to OMA detector noise. The same KCl solutions are then atomized into the flame during picosecond pump/probe measurements, for which a lock-in bandwidth of 1 Hz is used. For each concentration, 6 pump/probe measurements are taken, and the spread of values is used to estimate 95% confidence intervals. It is important to note that the line-of-sight absorption method is not used to calibrate the pump/probe instrument. The pump/probe instrument yields absolute concentrations without calibration. The line-of-sight technique merely provides a second measurement of concentration for comparison.

Finally, to demonstrate that this system can detect rapid concentration fluctuations, a small audio speaker on the fuel/air line is driven with a frequency synthesizer at 50 Hz. The loud speaker induces a known disturbance in an otherwise laminar flame. The visible flat flame front then oscillates vertically above the burner surface through a distance of approximately 1/2 cm. Stronger fluctuations can be produced by increasing the voltage to the speaker, but these disturbance levels often extinguish the flame. Despite the spatial fluctuation of the reaction-zone position, no significant beam steering is observed. Since the pump beam is modulated at 1 kHz, the flame disturbance also results in 50-Hz sidebands about the 1-kHz signal. The lock-in amplifier (an Ithaco model 395) bandwidth is set to its maximum of 200 Hz, so that the 50-Hz frequency remains on the lock-in output (Weingarten, 1988; Weingarten *et al.*, 1988). Our choice to study a 50-Hz flame disturbance in no way implies a bandwidth limitation to the picosecond pump/probe instrument. In fact, using commercially-available equipment, the instrument has the potential to measure fluctuations over 10 MHz (Fiechtner, 1992). The present frequency limit is defined by the existing lock-in-amplifier. The synchronously demodulated lock-in output is directed to a PC based A/D system with an FFT board. The signal is sampled in record lengths of 8192 points at a rate of 500 Hz. This record length is then divided into 8 individual bins of 1024 points, which are FFT'ed and averaged together. This is repeated for all KCl solutions, allowing an estimate of the FFT-system detection limit.

RESULTS AND DISCUSSION

The absolute concentration measurements obtained from the picosecond pump/probe absorption instrument are compared to the line-of-sight lamp absorption measurement for 11 different potassium concentrations in Figure 4. A perfect correlation would have a slope of unity and an intercept at the origin, shown by the solid line. Note that all of the data fall close to this line. In fact, a linear least-squares fit to the data yields a slope of 1.1 ± 0.29 and an intercept of $-1.6 \times 10^{10} \pm 5.4 \times 10^{10} \text{ cm}^{-3}$ (at 95% confidence), as shown by the dotted line. Again, since picosecond laser pulses are used, the concentration measurement is independent of the collisional environment. Clearly, this

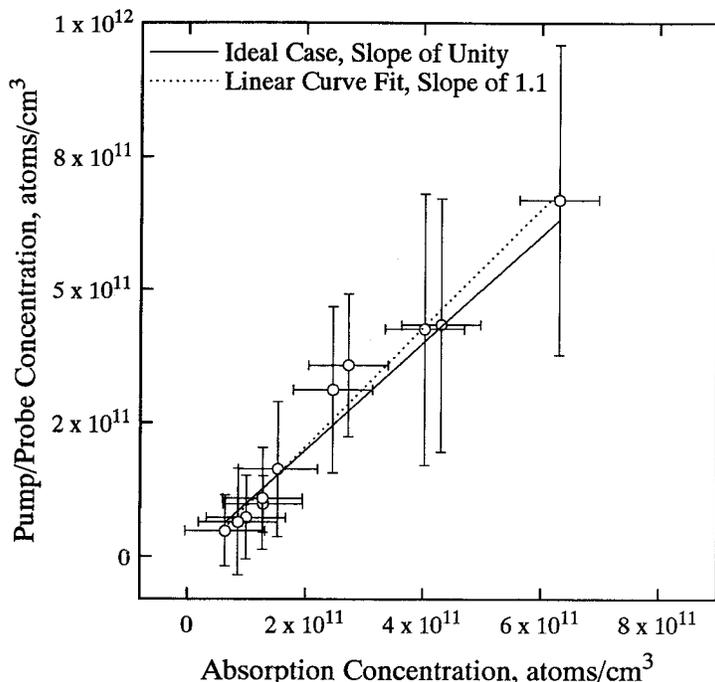


FIGURE 4 Absolute concentration measurements obtained from the picosecond pump/probe absorption instrument, plotted versus line-of-sight lamp absorption measurement for 11 different potassium concentrations. The solid line represents a perfect correlation between the two techniques, with slope of unity and an intercept at the origin. The dotted line represents a linear least squares fit to the data with a slope of 1.1 and an intercept of $-1.6 \times 10^{10} \text{ cm}^{-3}$. The absolute detection limit is approximately $1.1 \times 10^{11} \text{ cm}^{-3}$ of atomic potassium, defined by a SNR of unity.

technique offers a fully quantitative, spatially resolved measurement of concentration. Moreover, these measurements have the potential for detecting minor species (Fiechtner, 1992; Fiechtner *et al.*, 1994), including species with very low fluorescence yields.

The present absolute detection limit is approximately $1.1 \times 10^{11} \text{ cm}^{-3}$ of atomic potassium. This is limited by the present detection electronics, which are not optimized for use with the picosecond pump/probe instrument, and by fluctuations in the laser bandwidth, wavelength, and irradiance. The present laser spectral bandwidth is ~ 50 times too broad for efficient resonant interaction with gas phase species. This results in a large amount of background light that is not modulated but contributes to noise. A reduction in bandwidth (discussed above) by a factor of 50 would improve the SNR by 2,500 as dictated by Equation (1), where the bandwidth appears raised to the second power in the denominator. The resulting detection limit is $4.8 \times 10^8 \text{ cm}^{-3}$. Our minimum detectable modulation depth is $\sim 10^{-4}$. It has been demonstrated that a detection limit that is four orders of magnitude lower than our result can be obtained by applying modulation at higher (1 MHz or greater) frequencies with a more suitable lock-in amplifier (Beaman, 1985; Langley *et al.*, 1985; Langley *et al.*, 1986; Beaman

et al., 1986; Jones, 1987). We should achieve similar detection limits after replacing the electronics and after enhancing the performance of the present laser system.

The temporal resolution of our instrument is demonstrated in Figure 5, where the FFT was obtained for a potassium concentration of $6.3 \times 10^{11} \pm 5 \times 10^{10} \text{ cm}^{-3}$. The 50-Hz modulation is clearly visible. A subharmonic flame fluctuation at 25 Hz is also observed, emanating somewhere in the burner system, although we make no attempt to explain a mechanism for its presence. A peak SNR of unity results for a concentration of $1.5 \times 10^{11} \pm 7 \times 10^{10} \text{ cm}^{-3}$, which we define as the psd-system detection limit. The peak SNR represents the magnitude of the 50-Hz spike divided by the magnitude of the noise, and is plotted against concentration in Figure 6. As expected, a plot of peak SNR versus concentration is linear. The noise we encountered was caused by the lack of an instrumentation amplifier, and as a result, the signals were of a magnitude close to noise in the A/D converter. Amplification of the lock-in output would therefore directly increase the SNR of the FFT system. The modulation rates (mechanical chopper and acoustic loud speaker) were all slow because we were using borrowed equipment, none of which is fast. Lock-in amplifiers with higher bandwidths (10 kHz) are now commercially available. If necessary, a demodulator could be constructed to provide even wider bandwidths (Weingarten, 1988; Weingarten *et al.*, 1988).

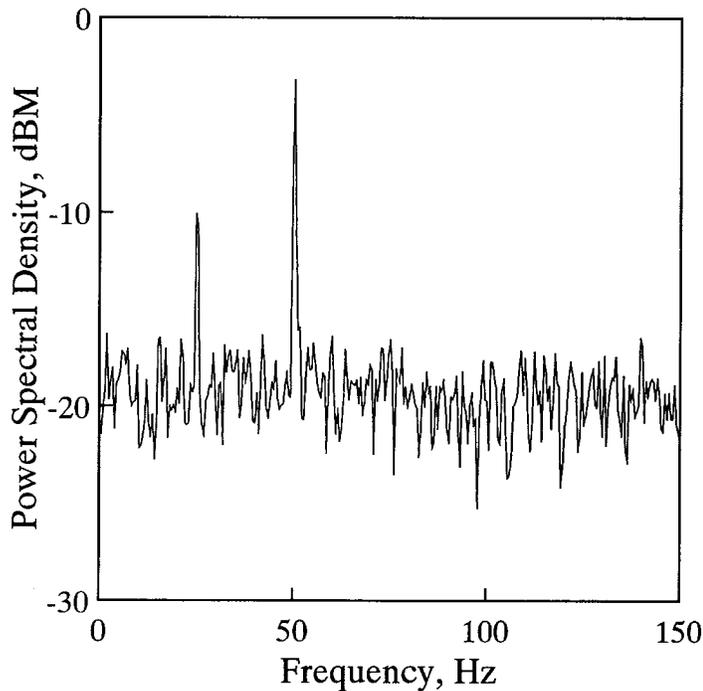


FIGURE 5 Demonstration of the temporal resolution of our instrument. The fast-Fourier transform (FFT) of the lock-in amplifier output is obtained at a sampling rate of 500 Hz, and represent the averages of 8 individual FFT's. The flame is driven with an audio speaker at 50 Hz. The FFT is obtained for a potassium concentration of $6.3 \times 10^{11} \text{ cm}^{-3}$ and clearly shows the 50 Hz modulation. A subharmonic flame fluctuation at 25 Hz is also observed.

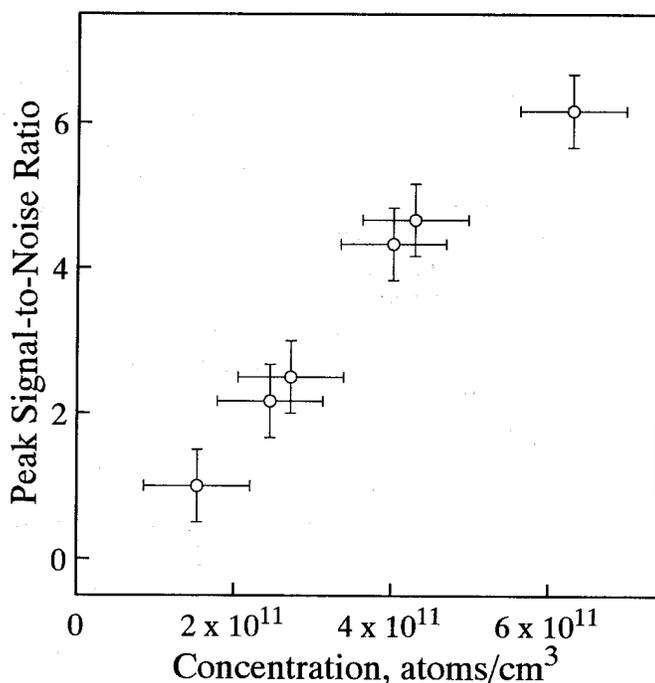


FIGURE 6 The peak signal-to-noise ratio (SNR) of the 50-Hz spike of the pump/probe FFT's plotted vs. concentration. As expected, a plot of SNR versus concentration is linear. The SNR reaches unity for a concentration of $1.5 \times 10^{11} \text{ cm}^{-3}$, which we define as the detection limit for the FFT system.

Future measurements will be done on flame radicals. This will require that the Ti:Sapphire laser radiation be frequency doubled or mixed to produce the desired wavelength. We are presently adding the necessary nonlinear crystals. This new laser technology thus allows at least two orders of magnitude more UV power than for previous laser systems, as discussed above; moreover, this additional laser radiation need not be attenuated, since the predicted saturation irradiance for diatomic species such as OH is $\sim 900 \text{ mW}$ (Fiechtner, 1992; Fiechtner *et al.*, 1993). In addition, we note that several diatomic species fall within the frequency-doubled Ti:Sapphire laser tuning range, including CH ($^2\Delta - ^2\Pi$) at 431.5 nm and CN ($^2\Sigma - ^2\Sigma$) at 400.0 nm. Using the pump/probe model of Fiechtner *et al.* (1994) for CH with a pump power of 700 mW, we obtain a detection limit of $2.6 \times 10^{16} \text{ cm}^{-3}$. While this value may be high, the additional assumption of a reduction in laser bandwidth by a factor of 50 results in a more useful estimate of $1.0 \times 10^{13} \text{ cm}^{-3}$. For the FFT system, the corresponding detection limits for CH are estimated to be $3.6 \times 10^{16} \text{ cm}^{-3}$ and $1.5 \times 10^{13} \text{ cm}^{-3}$, respectively.

SUMMARY AND CONCLUSIONS

We have successfully demonstrated an instrument based on picosecond pump/probe absorption spectroscopy for measuring absolute concentrations in a rapidly-fluctuat-

ing flame environment at atmospheric pressures. In the future, we hope to demonstrate measurements at higher pressures. This will cause additional difficulties, such as beam steering, which may adversely influence the pump/probe signal. We will assess these difficulties during future experiments. We have obtained a detection limit for atomic potassium of $1.1 \times 10^{11} \text{ cm}^{-3}$ without the need for calibration. A simple reduction in the spectral bandwidth of the laser by a factor of 50 would reduce this detection limit to only $4.8 \times 10^8 \text{ cm}^{-3}$. Using a picosecond pump/probe absorption model (Fiechtner, 1992; Fiechtner *et al.*, 1994), we predict corresponding detection limits for CH of $2.6 \times 10^{16} \text{ cm}^{-3}$ and $1.0 \times 10^{13} \text{ cm}^{-3}$, respectively. We feel that this limit would be of value to the combustion community, and are thus adding nonlinear crystals to the laser to obtain the necessary wavelength range for measurements of flame radicals. In all our measurements, the spatial resolution was 0.137 cm. In future, this resolution can be improved, but only at the expense of the signal level (Equation 1). We have also demonstrated the excellent temporal resolution that the picosecond pump/probe instrument offers. Here, 50-Hz fluctuations in the potassium concentration were easily resolved on power spectral density plots. A detection limit of $1.5 \times 10^{11} \text{ cm}^{-3}$ was obtained for the psd system. Using the picosecond pump/probe absorption model, we find a corresponding detection limit of $3.6 \times 10^{16} \text{ cm}^{-3}$ for CH; for an improvement in bandwidth-coupling by a factor of 50, the detection limit improves to $1.5 \times 10^{13} \text{ cm}^{-3}$, again of value to the combustion community. The temporal resolution of our system is presently limited to that of the borrowed detection electronics, and based on the success of these experiments, we are obtaining electronic equipment to extend our resolution beyond 1 MHz.

Finally, we note that this type of measurement is not limited to detection of absorption and stimulated emission. We have recently demonstrated picosecond degenerate four-wave mixing (DFWM) measurements of atomic potassium with the same laser system (Linne and Fiechtner, 1994). DFWM is also a coherent technique, but is advantageous in that the signal is potentially background free. As a result of our success with DFWM measurements, we are planning to perform them simultaneously with pump/probe absorption measurements while in resonance with CH transitions.

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