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LASER-BASED MULTIPHOTON EXCITATION PROCESSES IN COMBUSTION DIAGNOSTICS

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Light atomic species such as oxygen atoms (O) and hydrogen atoms (H) are fundamentally important in a wide variety of combustion related phenomena such as flame ignition, propagation, extinction, and in chemical flame reactions. Furthermore, they are difficult to detect by conventional laser based optical methods (laser induced fluorescence) in combustion environments because the necessary resonance excitation wavelengths fall far into the vacuum ultraviolet (vuv) and the requisite tunable laser sources are not generally available. However, recent developments in nonlinear spectroscopic techniques such as multiphoton induced emission (MPE) and multiphoton ionization (MPI) have made direct detection of these light atoms possible. We have utilized a number of laser multiphoton excitation schemes for their detection using tunable lasers in the 190-400 nm range. Similar diagnostic techniques were attempted for the detection of carbon (C) and nitrogen (N) atoms in flames. The effects of laser induced photochemical perturbations on species detection in flames were also investigated. Keywords.

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I. INTRODUCTION

Light atomic species such as oxygen and hydrogen atoms are fundamentally important in a wide variety of combustion processes such as flame ignition, propagation and extinction and in chemical flame reactions. The hydrogen atom/radical, for example, is necessarily important in nearly every combustion process because of its high reactivity and diffusivity, yet its direct detection therein is very difficult. The oxygen atom is of equal importance in pertinent flame processes, flame structure and relevant chemical and mass transfer processes but its direct detection is equally difficult. The nitrogen atom is a constituent of many gaseous, liquid and solid oxidizers (of particular importance to the chemistry of propellant combustion) since it is chemically bound in nitrate, nitro and nitroso compounds, but has never been detected in a flame environment (to our best knowledge). Conventional optical detection of these these light atoms is difficult for a variety of reasons. In particular, the necessary optical resonance excitation wavelengths fall far into the ultraviolet (uv) and the requisite tunable laser sources are generally not available for such flame atomic spectroscopy. For example, the lowest lying resonance states for oxygen and hydrogen atoms lie in the wavelength region of < 140 nm. Likewise, carbon and nitrogen atom resonance transitions (<130 nm) lie in the vacuum ultraviolet (vuv) spectral region, which makes flame spectroscopy very difficult as these wavelengths are absorbed strongly by atmospheric gases (particularly O_2). Historically, several different laser spectroscopic techniques have been employed for both detection and diagnostics of these light atoms in combustion processes.[1-7] One of the most successful methods thus far for flame diagnostics has been laser-induced fluorescence (LIF) primarily because it can yield spatially resolved measurements with a high degree of sensitivity.[3] Since the energy gap between the ground and excited electronic states of the light atoms is typically on the order of 10 or more electron volts (ev), techniques such as two-photon or multiphoton laser excitation methods must be employed. Under high laser intensity (typically using a focused beam of a pulsed laser) two or more laser photons may be absorbed through virtual states, which are not eigenstates of the absorber. Even though these non-stationary states can not retain energy, the assumption may be made that the atom remains for some finite time in the virtual state, typically on the order of 10^{-15} sec. Thus, for absorption to occur on the order of $<10^{-15}$ sec, the photon flux must indeed be very great. Such high flux levels are achieved with the use of high peak-power lasers. Multiphoton excitation of these species can therefore be conveniently provided with commercially available laser sources that can quite easily generate the "one-step" photons that may be used in the "multi-step" excitation process.

The advent of tunable, narrow-linewidth lasers has also enabled the development of another multiphoton technique for the detection of and quantification of species such as light atoms, namely multiphoton ionization (MPI).[8,9] Similar to multiphoton laser induced fluorescence experiments, ionization of the atom can be achieved if the energy of the total number of photons which are absorbed is sufficient to eject an electron from the target species, i.e., greater than the ionization potential (IP). Consequently, the "free electrons" which are liberated or positive ions which are produced are amenable for detection. Flame atomic species have been detected, as such, with resonant multiphoton optogalvanic spectroscopy.[4-7] In general, the term optogalvanic loosely refers to changes in the electrical properties of the

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environment (the flame) because of photoionization or ionization due to collisions involving highly excited states that have been optically populated.[4] Optogalvanic signals are detected in our laboratory using a platinum tipped probe (described in the experimental section of this paper) which is a point source detector and well suited for spatial measurements in combustion environments. Ultimately the ionization signals are related to relative species densities in flames and if properly calibrated, to absolute concentrations. A particular advantage of optogalvanic detection over LIF is that dark or non-emitting species may be studied. However, both the MPI and MPE approaches suffer from limitations. MPE inherently suffers from quenching considerations and signal collection inefficiencies. A recent paper by Meier, et al.,[10] addresses this issue by measuring the efficiency of fluorescence quenching by the various species present in the detection region. They used a versatile discharge-flow system for the determination of quenching rate constants for the relevant species in flame gases. A method for determining the number densities of H and O atoms in flames was developed using two-photon laser excited fluorescence, which attempted to account for the influence of fluorescence quenching. Aside from quenching considerations, the technique of MPI, in comparison, lacks selectivity in signal detection and thus is quite susceptible to background ionization.[3] There also exists the possibility of introducing pertubations as a result of inserting the probe into the flame medium. Furthermore, multiphoton excitation techniques for flame light atoms may suffer from complications which arise from laser photolysis due to the uv wavelengths, tight beam focusing and high peak laser powers which are required and utilized to drive the highly non-linear processes.[11] We have reported in our laboratory findings which have shown that at sufficiently high laser energies, the flame diagnostic probe can become substantially intrusive by promoting multiphoton dissociation of the parent fuel and oxidizer molecules to produce artificially high concentrations of atomic species (relative to that normally found in a flame environment).[11] This dissociation can lead to potentially erroneous concentration measurements and flame profiles. Two other diagnostic techniques have been used for direct detection of atomic species, namely Raman scattering[12] and coherent anti-Stokes Raman spectroscopy.[13] Both have been employed for flame detection and diagnostics, but suffer from sensitivity limits and other spectral interferences that have prevented further development of these spectroscopies for atomic flame detection.

We are particularly interested in the application of lasers for detailed flame chemistry studies and have been in the process of building up a comprehensive and well-equiped research program in this area. This paper presents an extension on our previous work in light atom diagnostics. We have applied the techniques of MPE and MPI to a variety of flames, in particular H_2/O_2, H_2/air, H_2/N_2O, C_2H_2/O_2 and C_2H_2/air, for the purpose of further development and implementation of diagnostic techniques for small atomic species such as H, O, C, and N in combustion environments. A great deal of information on, and insight into the details of the various excitation processes can be gained by measuring laser power dependencies. These power dependencies were measured for the photoexcitation of O atoms in H_2/O_2 and H_2/N_2O flames as well as for the photolytic production and photoexcitation of O atoms in cold flows of the oxidizer components of these flames. Similar investigations were performed on H atoms. Laser power dependencies were measured for the photoexcitation of hydrogen atoms in atmospheric pressure flames and in a molecular-beam time-of-flight mass spectrometer. In the

course of our experimental work we have also become very sensitive to the potentially intrusive nature of the focused laser as a flame diagnostic probe due to photochemical effects caused by the intense uv pulses. We will discuss the effect of photochemical pertubations introduced by lasers in light of our combustion diagnostic work on oxygen atom; in particular, as related to H_2/O_2 premixed flames and reactive gaseous flows. We have investigated the potential utility of the photolytic nature of the focused uv laser with applications to ignition and combustion enhancement by resonant multiphoton photochemical means.[14,15]

II. EXPERIMENTAL SECTION

A schematic of the experimental set-up for the flame diagnostic work is given in Figure 1. Tunable laser radiation was provided by a 10 Hertz Quanta-Ray Q-switched Nd:YAG-pumped dye laser system (DCR-2A, PDL-1) which is equipped with a wavelength extension system (WEX-1). The WEX-1 is a servo-motor based tracking system which houses two modules which contain non-linear crystals (angle-cut KDP) that are used to frequency double the dye laser output and frequency mix it with the fundamental (1064 nm) of the Nd:YAG to generate tunable wavelengths in the deep ultraviolet (uv). The unwanted beams were seperated from the desired uv beam with a Pellin-Broca prism, broad-band filters and an aperture. Typical outputs from the laser system are: two milliJoules (mJ) of uv energy at 226 nm using a doubled rhodamine 590 dye and mixed (two-photon excitation of O atoms, $2p^3 3p^3P \leftarrow 2p^4 {}^3P$), one mJ at 243 nm, using a doubled DCM dye and mixed (two photon excitation of H atoms, n=1→2), 10 mJ at 292 nm, using a double Kiton Red dye (three-photon excitation of H atoms n=1→4), 15 mJ at 308 nm, using an acid shifed (HCl) Rhodamine 640 dye (three-photon excitation of H atoms n=1→3), 5 mJ at 365 nm, using a base shifted (saturated NaOH) Fluorescene 548 and mixed (three photon excitation of H atoms n=1→2) and 70 μJ at 193.1 nm, doubled Kiton-Red, mixed and second anti-Stokes H_2 Raman-shifted (one photon excitation of carbon atoms $^1D_2 \leftarrow {}^1P^0_1$). The measured laser linewidth in the uv was 2.2 cm^{-1} with a temporal width of about 5 nsec. The pulse energy was measured with a Scientech volume-absorbing disc calorimeter (Model 38-0103) and analog meter.

A simple atmospheric pressure jet burner system was fabricated from a Swagelock 0.635-cm stainless steel terminator fitting through which a 0.5 mm hole was drilled. The burner tip was threaded onto a 10 mm stainless steel tube. The fuel and oxidizer were premixed in the burner and the gas flow was regulated by Matheson (Model 620) flowmeters and metering valves that were calibrated with a GCA Precision Scientific wet test meter. For H_2 and O_2, flows up to 2 liters/min were used which resulted in linear flow velocities in the 10^3-cm/sec range. The burner was equipped with a water cooling jacket and shroud of inert argon gas which encircled the flame and minimized mixing with air and recirculating flow. The burner was mounted on a xyz-translation stage and could be manipulated with micrometer positioners. The laser beam (diameter of 7.5 mm) was focused into the flame or gaseous flow with 50 to 500 mm focal length lenses (25 mm diameter). The estimated focal spot diameter size was 50 to 100 μm. The lenses were also similarly mounted in xyz-translation stages. The laser induced fluorescence was collected at right angles to the exciting light with a pair of fused silica biconvex lenses and imaged onto the adjustable slits of a 0.22 m McPherson monochromator (Model 218) which were shielded with the appropriate broad-bandpass and/or interference filters. Fluorescence excitation scans were recorded by tuning

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the monochromator to a particular emission wavelength of an atomic or molecular species of interest and scanning the tunable laser through the electronic resonance transition(s). Dispersed fluorescence spectra were recorded by tuning the laser to the appropriate excitation wavelength and then scanning the monochromator through the emission wavelength(s). The photomultiplier (Hamamatsu R928 or EMI 9659QA) signal was then fed to either a Princeton Applied Research or Stanford Research Systems (SRS) boxcar integrator then plotted on a strip-chart recorder, or fed to either a (model 7912AD) Tektronix transient digitizer (500 MHz) or Hewlett Packard (Model 54111D) digital oscilloscope (500 MHz) in order to capture the temporal profile of the emission. Adjustable time delays for synchronization of the detection electronics with the laser were accomplished with a digital pulse-delay generator, either a BNC Model 7085 or SRS Model DG535. Excimer laser radiation (at 193 nm) was provided by either a Lumonics Hyper-EX Model 440 or Model TE 860 both of which were operated in the unstable resonator mode which yields much less divergent laser beams and narrower focused beam waists than in the stable resonator mode.
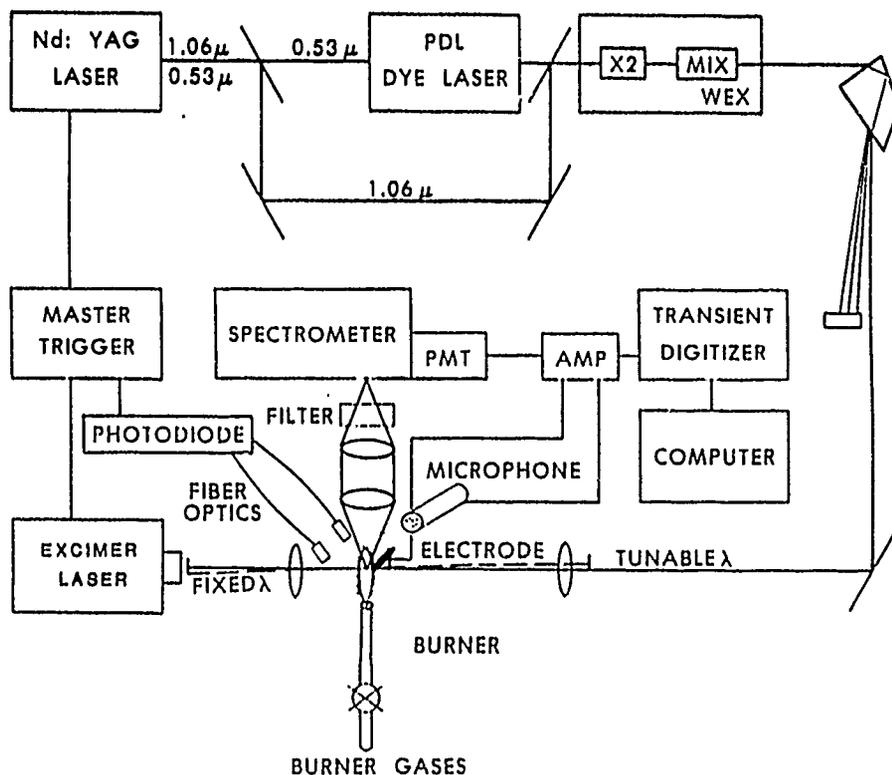
Figure 1. Experimental Schematic for Flame Diagnostic Work

Ions of both atomic and molecular species were detected at atmospheric pressure using an optogalvanic probe which could be forward biased to detect electrons liberated in the laser induced multiphoton photoionization process or reversed biased to detect the resultant positive ionic species. The probe was designed, constructed, characterized and supplied by Professor Terrill A.

Cool of Cornell University.[7] The probe tip is a 1 mm platinium bead (anode) for collecting electrons. The bias voltage between the anode and platinum wire cathode could be adjusted continuously to the point of saturation (about 200 volts) of the electron collection wherein a major fraction of the photo-produced electrons could be detected. Here the saturated probe signal is proportional to the density of the photoionized species over at least four orders of magnitude. At low probe voltages a portion of the signal was lost (due to electron attachment or recombination before reaching the anode) and at higher probe voltages avalanche ionization occured. Signals on the order of 10's of nv were observed when either differentially amplified using a PAR differential amplifier or AC coupled into a Keithly (Model 427) current amplifier. The ionization signal reaches a peak value in about 2 μsec and decays with a single exponential time constant which is established by the RC time constant of the circuit used (about 21 μsec). Signals from positive ions were observed on millisecond time scales and were easily discriminated from electron signals.

Mass spectra were recorded with an R.M. Jordan time-of-flight mass spectrometer. The system is equipped with a pulsed-molecular beam valve and is backed by two rotary direct drive pumps, a 10 inch diffusion pump and a 6 inch turbomolecular pump and could be operated near 10^{-8} torr. Pulsed-beams of 30 μsec temporal duration could be generated while maintaining a chamber operating pressure of 10^{-7} torr. All gases used in these experiments were prepurified and used as is without further purification.

III. RESULTS AND DISCUSSION

A. O-Atoms

MPE. Two-photon absorption from a uv laser beam to excite ground state oxygen atoms to the first excited state of identical spin symmetry was first reported by Bischel, et al.[17] They described a scheme which is illustrated in Figure 2. The photoexcited ^3P state ($2p^33p\ ^3P \rightarrow 2p^4\ ^3P_2$) can radiate in the near infrared (at 844.7 nm) to the ^3S state, which is a useful analytical wavelength for the detection of the emission. The experiments were performed in a low pressure discharge which produced oxygen atoms in their ground electronic state. The radiative lifetime (39 nsec) and quench rate with N_2 ($2.5\times10^{-10}\ cm^{-3}\ sec^{-1}$) were measured. From the results of their experiments they indicated that there was promise for the method as a diagnostic technique for O atoms in flames and plasmas. Subsequently, oxygen atoms were first detected in a realistic combustion environment by Alden, et al., utilizing this scheme.[2] The experiments were performed in fuel lean acetylene/oxygen flame (equivalence ratio of 0.57, temperature = 3000 K). They reported that at this temperature the ground state contains about 60% of the atoms and calculated an oxygen atom mole fraction of around 0.05%. This value was determined to be low in light of the theoretically predicted concentration of 10%: the reason for this discrepancy is not known. They determined the laser power dependence n which is a measure of the number of photons involved in the excitation process and obtained a value of n = 2.6 ± 0.2 from the fitted slope of a log-log plot of signal intensity versus laser energy. The expected power dependence should be near quadratic. A value of 1 to 2 would have been obtained if there were a competing process such as saturation of the two-photon transition or rapid photoionization from the excited ^3P state, although there was no evidence as such reported in their work.

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2p³3p   ³P   88631   ⁵P
                                                        ——— 86633

                        k_3^r k_{35}

                    λ = 844.7 nm k_5^r

2p³3s   ³S ——— 76795   λ = 777.5 nm

                                        ⁵S ——— 73768

                    λ = 130.2 nm

        Laser
        λ = 225.6 nm

                    0 ——— 227
2p⁴ ³P   1 ——— 159
            J=2 ——— 0 cm⁻¹
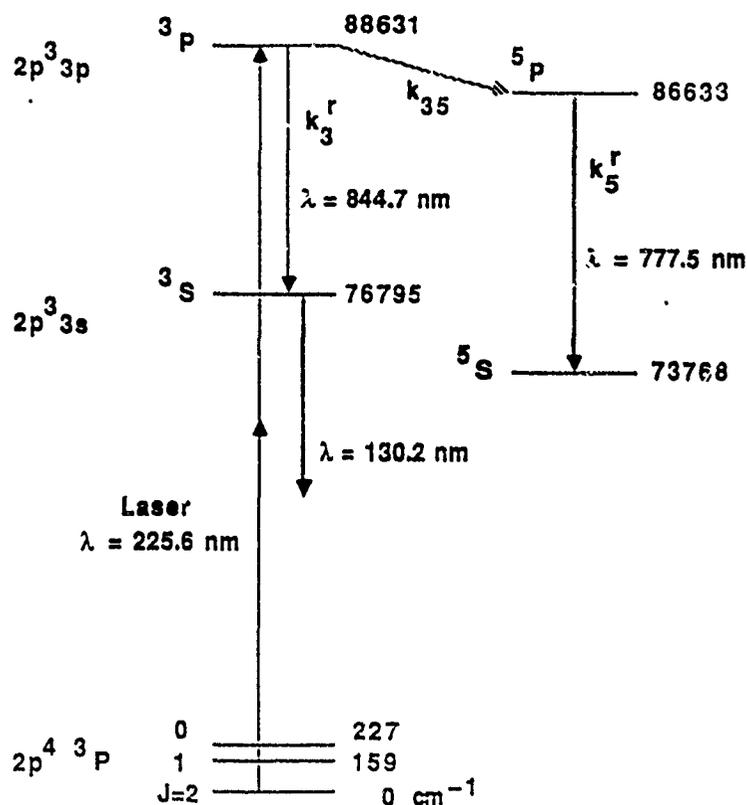
Figure 2. Simple Energy Level Diagram for Oxygen Atoms.
Terms are defined in the text.

We have also utilized this excitation scheme for oxygen detection in our experimental work.[11,14-16] Figure 3 gives the fluorescence excitation scan of ground state O atoms in the primary reaction zone of a premixed stoichiometric (Φ=1.0) H_2/O_2 atmospheric pressure flame (using a 300 mm focal length lens and the laser energy was 0.4 mJ). The ground spin-orbit split states, J=0, 1, 2 are clearly resolved although the excited state splittings were not resolved with the resolution of our laser system. Signals were not normalized to the intensity profile of the doubled and mixed dye laser beam in this experiment due to the nonlinear nature of the transition. The signal to noise ratio was excellent (100:1). The signal strength was found to be highly sensitive to the flame reaction zone that was probed. The signals were strong, although heavily quenched, and followed the temporal profile of the exciting laser beam, Figures 4a and 4b. We measured the laser power dependence for the process (by either varying the gain of the amplifier stage of the Nd:YAG laser or inserting quartz plates into the 226 nm beam to attenuate the energy) and found that there was a quadratic dependence, i.e., n = 1.9 ± 0.2 (the uncertainty was obtained from the standard deviation of the mean from three measurements). We did indeed find that at higher laser energies (> 0.4 mJ) and with a shorter focal length lens we could easily saturate the two-photon transition and also drive higher order nonlinear process such as photoionization of atomic oxygen and photolysis of the parent fuel and oxidizer. Experiments were also performed in a premixed H_2/N_2O and H_2/air

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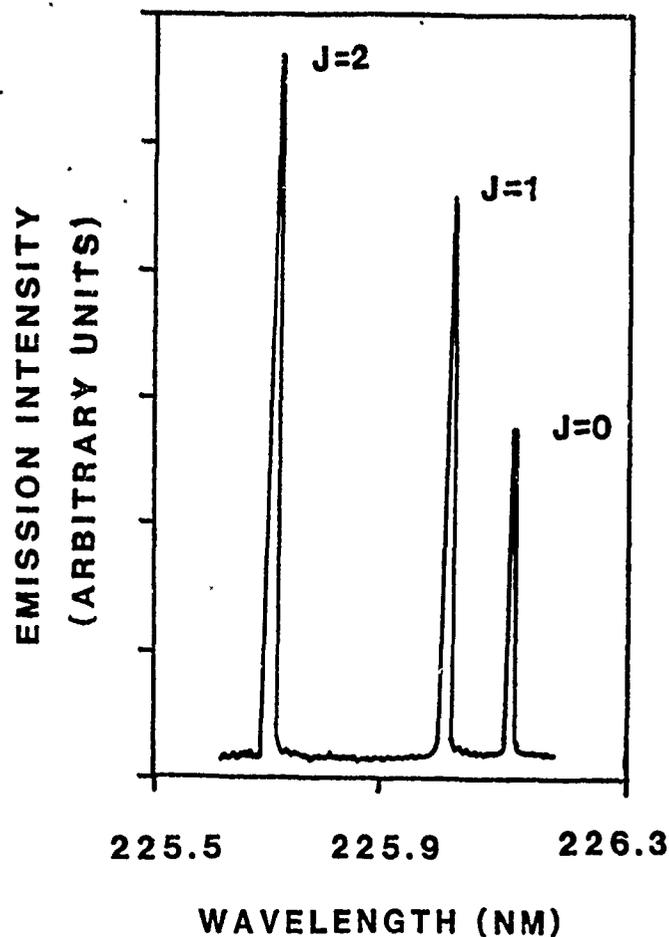
Figure 3. Excitation Spectrum for the Oxygen Atom Emission at 845.7 nm
from Primary Reaction Zone of an H_2/O_2 Atmospheric Pressure Flame.
The spin-orbit split ground states (J=0,1,2) are resolved.

flames and identical experimental results were obtained. Fluorescence spectra
were also obtained using a scanning monochromator with the exciting laser
light tuned to either of the three oxygen atom ground spin-orbit split
states. As previously reported, there was a strong collisional energy
transfer to the ^5P state of oxygen with detectable fluorescence emission at
777.5 nm which was also utilized to perform similar diagnostic
measurements.[11] Stronger signals were obtained at this emission wavelength in
the aforementioned flames, but when the spectral sensitivity of the detection
system (monochromator and photomultiplier) were corrected using a calibrated
standards lamp, it was found that the signal strength from the 844.7 nm
emission was larger.

MPI. Atomic oxygen was also detected in these flame environments using
an optogalvanic probe. Here the probe was inserted into the flame itself and
the laser was focused within <0.5 mm of the platinum anode of the detector
(the burner head itself was grounded). An excitation scan was recorded by
scanning the laser through the three ground spin-orbit split states while
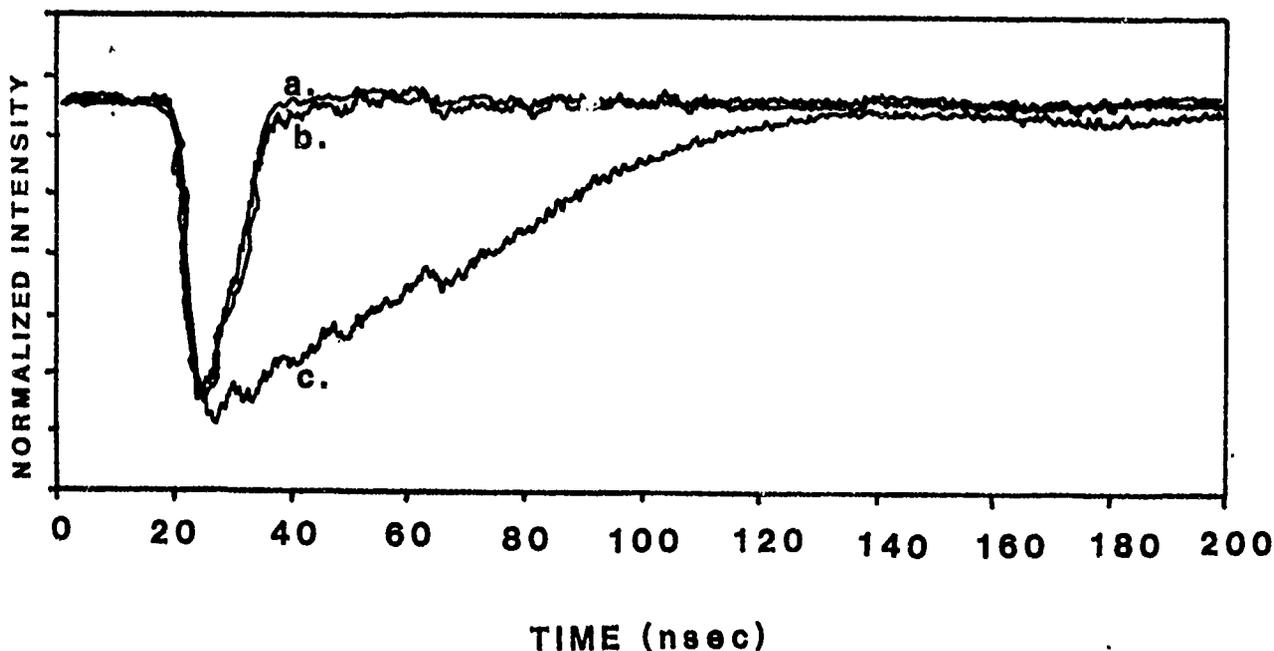
Figure 4. (a) Temporal Profile of the Exciting UV Laser Light at 225.6 nm (Scattered Pulse), (b) The Oxygen Atom Emission in an Atmospheric Pressure H_2/O_2 Flame ($\lambda=777.5$ nm), and (c) The Temporal Profile of the Microplasma Emission ($\lambda=777.5$ nm)

using the probe in the forward biased mode where free electrons which were liberated in the photoionization process could be collected (the spectrum was identical to the emission scan in Figure 3). It was found that the signal strength strongly depended on the distance r of the probe anode to the laser focal spot and that the intensity varied roughly with a $1/r^2$ dependence (r was varied from 0.5 to 2 mm while the probe voltage was held constant at 200 V). The laser power dependence for the process was measured as described earlier. At low laser energy (0.1 to 0.5 mJ) we observed a slope of 2.8 ± 0.3 for n which is indicative of an overall three-photon photoionization process. At higher laser energy (0.6 to 1.2 mJ) a value for n = 2.1 ± 0.2 was obtained which probably indicates saturation of the two-photon step in the 2+1 resonance ionization process. A similar saturation effect was observed by us in our hydrogen atom work as well as recently by Downey and Hozack[18] who observed n change from 3.2 to 2 in a 2+1 photoionization process at power densities of near 10^7 W/cm^2. They reasoned that in most 2+1 resonance ionization pr   ses where the real intermediate states enhance the two-photon cross secti , saturation of the two-photon excitation step usually occurs at lower intensities than does the ionization step. Similar experiments in our laboratory were performed with the probe bias reversed to detect ions that were formed in the photoionization process and comparable results were obtained. In either case it was found that background signals were negligible, but some RF interference was picked up from the laser power supply through the probe. This noise was largely eliminated when the current amplifier which was used with the the probe was shielded from RF pick-up. Principal reasons for utilizing the optogalvanic probe as a diagnostic tool

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for flame detection of atomic species such as O at μs is the high degree of spatial resolution and sensitivity that it provides[7] as well as the capability for looking at dark or non-emitting species. Normalized intensity profiles of atomic oxygen could be made quite easily by fixing the spatial position and relative geometric location of the probe tip and the laser focus, and then translating the flame through this area with a precision micrometer drive stage. Resolution on a submillimeter scale could thus be obtained. A chief disadvantage of the probe used in these experiments (aside from the potential intrusive nature of the insertion of any physical element into a flame) is that the platinum anode is subject to deterioration at temperatures > 1500 K. A similar probe is being designed which will be constructed of tungsten and can withstand much higher temperature flame environments.

Photolytic Effects. Earlier experimental results from our laboratory first indicated that in diagnostic work on oxygen atom detection in a flame environment there was evidence that the focused uv laser and high peak powers that were used led to laser induced multiphoton photolysis of the parent oxidizer molecule N_2O, yielding unusually high concentrations of oxygen atoms (higher than that which would normally be found in a combustion environment).[11] The manifestation of this phenomenon, which also occurs in O_2-containing systems, is clearly illustrated in Figure 5 which gives a normalized intensity profile of atomic oxygen atoms in a premixed H_2/O_2 flame ($\Phi=0.8$). In Figure 5a, the laser was tuned to and fixed at the J=2 ground spin-orbit split state; the observation wavelength was 777.5 nm, a 300 mm focal length lens was used and the laser energy was 0.35 mJ. Each data point represents the running average of 64 laser shots acquired with a digital oscilloscope. It was found that the signal intensity was very sensitive to the positioning of the laser focal spot within the flame environment and reached a maximum at a distance of 3.5 mm above the burner head (the starred point in Figure 5), which was the location of the primary reaction zone, then rapidly fell away as the probe region was translated into the post-flame gases. In Figure 5b, the same experiment was then repeated, however this time a shorter focal length lens was used (100 mm) and the laser energy was increased to 0.8 mJ. Very large signals were observed throughout the flame structure. However, as the the sampled flame region was translated into the post-flame gases it was found that the O atom signal intensity did not drop off rapidly as it had in the previous experiment, Figure 5a. Apparently, the focused uv laser beam was inducing the photodissociation of molecular oxygen to produce excess quantities of atomic oxygen. Furthermore, in a darkened laboratory when a tighter focusing lens was used (50 mm) it was quite evident that the formation of a tiny microplasma was being induced, and in addition a faint acoustic report was audible. (We have utilized photoacoustic techniques as diagnostic but will not discuss them here). Even when the laser energy was attenuated to the point wherein microplasma formation was not evident, it was found that relatively high O atom signal intensities could be found. It is known that molecular oxygen does not absorb substantially at wavelengths > 200 nm at room temperature.[19] However, at these flame temperatures (post-flame gas temperature of ca. 1500 K) O_2 ground state vibrational levels are thermally populated such that single photon excitation at 226 nm through these states (Schumann-Runge bands) which are highly predissociative can lead to the production of excess quantities of O atoms which subsequently may be two-photon excited and emit. As stated before, the laser power dependence for the photolytic process gave a value of n=2. A power dependence was not measured in the post-flame gases but we suspect that at low laser energies when the
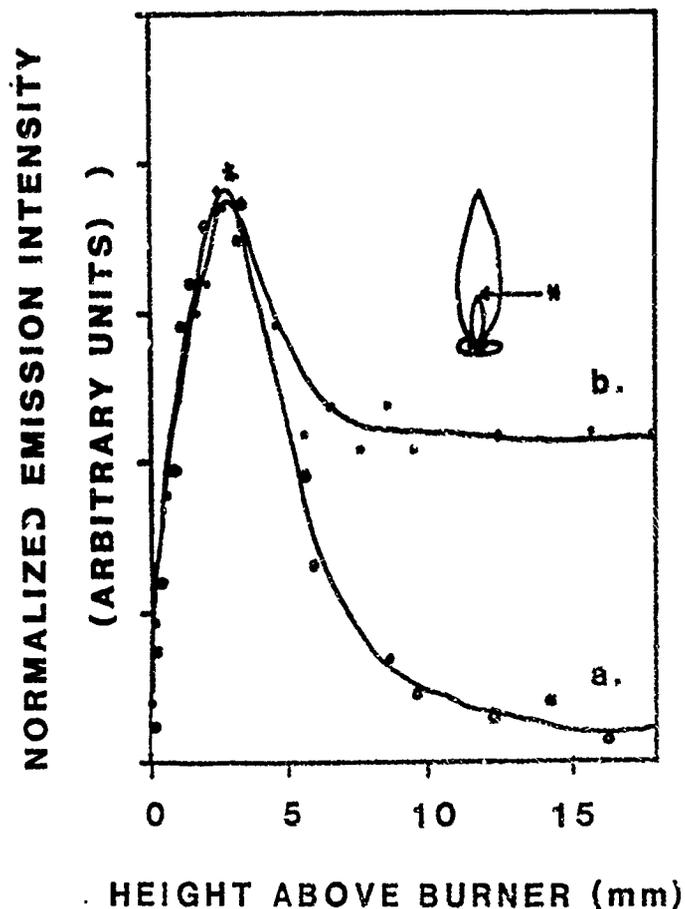
Figure 5. (a) Oxygen Profile Atom in an H_2/O_2 Atmospheric Pressure
Flame and (b) Same Profile Taken at Higher Laser Energy and Shorter Focal
Length Lens as Described in the Text. The starred point (*) indicates
the location of the primary reaction zone.

two-photon excitation process was not saturated a value of n=3 would be
obtained: one photon for a single step photolysis and two-photons for
excitation. Subsequent to our single laser experiments, Goldsmith recently
described a two-laser experiment where he scanned across molecular-oxygen
Schumann-Runge bands at 221 nm in a flame environment and monitored O atom
production with a second laser tuned to the J=2 state at 225.6 nm and found a
similar photolytic production of excess quantities of atomic oxygen.[20]

We have noted in our flame diagnostic work, not only the photolytic
production of O atoms in flames, but also in cold gas flows of O_2, N_2O or air
when no flame was present at all. Apparently, the focused laser was inducing
the photolysis of these gases to produce ground state oxygen atoms which could
then be easily two-photon excited and emission could be detected at 777.5 or
844.7 nm. Figure 6a gives an excitation spectrum of O atoms from the
photolysis of O_2 in a cold flow of O_2 (a similar result was obtained with air
or N_2O). We decided to determine the laser power dependence n for the process
by measuring the signal intensity as a function of laser energy in the cold

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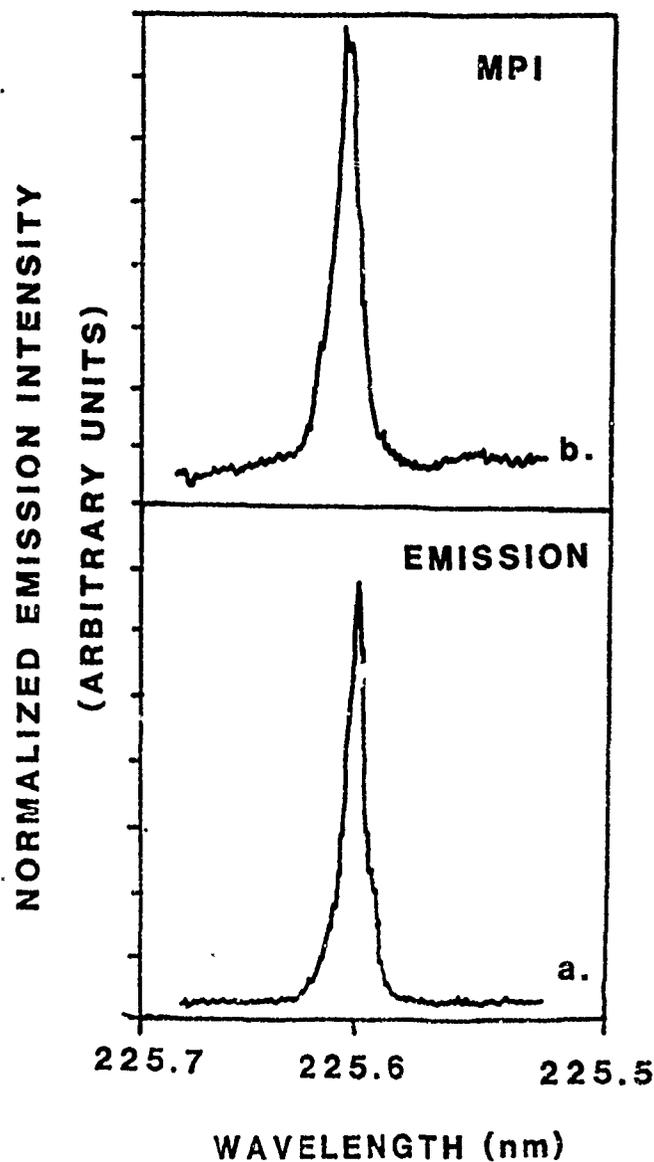
Figure 6. (a) Excitation Spectrum (Emission) of O Atoms from the Photolysis of O_2 in a Cold Flow, and (b) The Excitation Spectrum (MPI) Taken With the Optogalvanic Probe Under the Same Experimental Conditions

flows. We obtained a value of n =3.4 ± 0.3 for an O_2 flow and a similar value for an N_2O flow. Since we have already measured a power dependence of n=2 for the two-photon excitation of atomic oxygen, this result suggests that a two-photon process is responsible for the photolytic production of atomic oxygen from either O_2 or N_2O in a room temperature flow. The actual value obtained is n = 3.4 - 2.0 = 1.4 (the non-integer value is most likely due to some saturation of the two-photon excitation photolysis processes and/or losses due to rapid photoionization which competes with the fluorescence). Losses due to rapid photoionization have been substantiated by performing the same

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measurements utilizing the optogalvanic probe in the flow environment. Under these experimental conditions there were free electrons or positive ions that could be detected with the properly biased probe. Figure 6b gives the excitation spectrum of O atoms taken with the optogalvanic probe (free electrons or positive ions were collected in each scan respectively). At low laser energies we measured a value of n = 4.3 ± 0.3 for the overall process: photolysis of O_2 to produce O atoms (two photons), photoexcitation of O atoms (two photons) and the photoionization of O atoms (1.0 photons) to yield detectable electrons. The overall process probably requires 5 photons (not 4.3) because the photoexcitation or ionization step may have been partially saturated.

Microplasma Formation. The experimental results in the above section clearly indicate that laser photolysis effects can potentially lead to erroneous measurements of species profiles in combustion environments. We can, however, utilize the photolytic behavior of focused uv lasers to enhance combustion related phenomenon such as ignition augmentation of reactive gaseous flows. We have demonstrated that there are indeed wavelength specific interactions with parent fuel and oxidizer photofragments that lead to resonant ionization, the liberation of free electrons within the laser focal volume and ultimately the formation of a laser produced microplasma.[14,15] We have investigated the feasibility of the utilization of these laser produced microplasmas as a technique for the initiation of combustion events and have studied in some detail the chemistry and mechanism involved in this process. Specifically, we have used the uv laser as an ignition source for premixed H_2/O_2 and H_2/N_2O flows at atmospheric pressure. This was the first report of such a strong and sensitive wavelength dependence for the initiation of combustion in a reactive gaseous flow. A sharp wavelength dependence on the amount of incident laser energy required to ignite these mixtures was reported. The wavelength dependence, Figure 7, exhibits a spectral profile similar to the two-photon excitation curve for flame oxygen atoms, Figure 3. Figure 7 gives the amount of incident laser energy (ILE, the energy measured before the focusing lens) required to initiate the combustion event as a function of laser wavelength. Ignition occurred within the shaded areas. The respective peaks correspond exactly to the same spectral positions as the oxygen atom two-photon wavelengths near 225.6 nm. Clearly, oxygen atom production and subsequent excitation is an important step in the efficient (~0.5 mJ ILE required) laser ignition of H_2/O_2 flows in this wavelength region. Time resolved measurements were performed on O_2 and N_2O flows alone and it was found that the resonant formation of a microplasma (with a lifetime on the order of 100 nsec, see Figure 4c.) was responsible. A new combustion initiation phenomenon was discovered which involves atomic resonances in the uv which we have named "multiphoton photochemical microplasma ignition." The mechanism for microplasma formation consists of three major components: (1) the multiphoton photochemical formation of oxygen atoms; (2) multiphoton ionization of these atoms to efficiently form free electrons in the laser focal volume and; (3) the formation of a laser microplasma using the electrons formed in the previous process. The liberated free electrons become the principal absorbers of laser radiation and serve as a heat sink. The laser focal volume (ignition kernel) is heated to a very high temperature such that the reactive gas mixture ultimately transitions into a flame front. The major difference between this and previous work on laser spark formation and gas ignition is that the multiphoton photochemical resonance ionization process provides a more efficient and controllable means of liberating free electrons

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in the laser focal volume which leads to the laser spark formation. Lasers inherently possess certain attractive characteristics such as beam propagation through great distances, as well as excellent time-resolution.
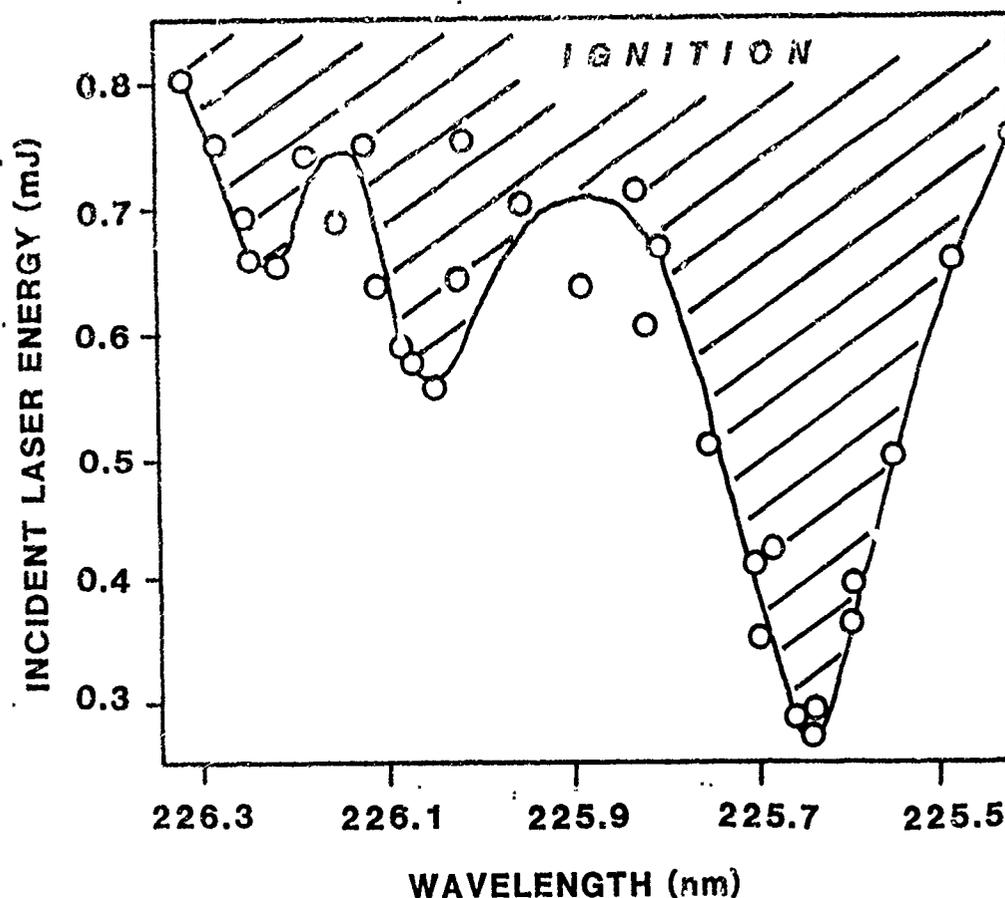

Figure 7. Plot of the Incident Laser Energy Required to Ignite a Premixed Flow of H_2/O_2 as a Function of Laser Wavelength in the Region of 226 nm

B. H-Atoms

MPE. We have also been interested in the detection of hydrogen atoms (the smallest of atoms) because of its extreme importance in nearly every combustion environment and relevant chemical reactions. Many multiphoton excitation schemes have been implemented by various investigators to detect H atoms in a wide variety of flames,[1,3,5,7,10,21] see Figure 8. The first reported measurement of H atom concentrations in a flame by two-photon excited fluorescence was reported by Lucht, et al.,[1] in a premixed $H_2/O_2/Ar$ low pressure flame (20 Torr), scheme 2, Figure 8. They used two-photon excitation of H atoms at 205 nm from the ground state level (n=1) to the excited state level (n=3). Laser induced fluorescence was then observed at 656.3 nm, which is the Balmer-α line because of n=3 to n=2 radiative decay. A decay rate of $(3.7 \pm 0.4) \times 10^8$ s^{-1} was calculated from the tailing edge of the fluorescence

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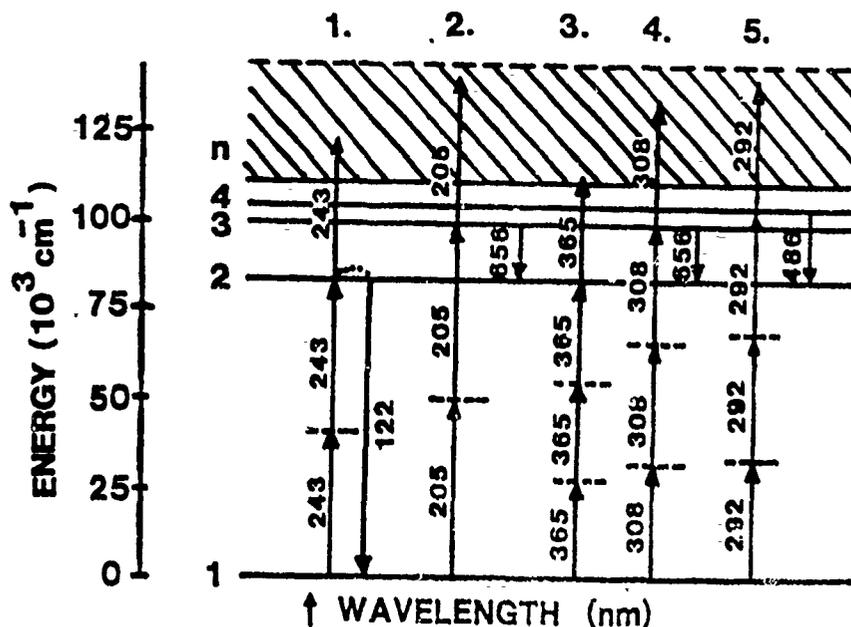
Figure 8. Simple Energy Level Diagram and Multiphoton Excitation Schemes for H Atoms. Energy on the vertical scale is given in wavenumbers. The arrows correspond to photon wavelengths.

pulse and a collisional quenching rate of about $(2.7) \times 10^8$ s^{-1} was calculated at this pressure. Extrapolation of this low pressure result to atmospheric pressure gave a collisional quenching rate of 10^{10} sec^{-1}. We attempted to detect H atoms at this excitation wavelength in an atmospheric pressure flame. The dye laser second harmonic (Rhodamine 59C) was mixed with the Nd:YAG fundamental and focused in a Raman cell. The first Anti-Stokes of the 224 nm beam in a H_2 cell yielded ~50 µJ of tunable laser radiation at 205 nm. No fluorescence signal was detected despite numerous attempts at this elevated pressure (a low pressure burner was not available in our laboratory at that time). This was attributed to the low laser energy which was available and strong quenching of the signal at atmospheric pressure which may dominate over radiative processes.

We attempted to use the three-photon excitation, scheme 4, Figure 8. Absorption of three photons at 308 nm from the n=1 to the n=3 state is followed by observation of emission at 656.3 nm. This particular wavelength is particularly attractive as a diagnostic technique since it coincidentally falls within the spectral gain of a XeCl excimer laser, wherein hundreds of mJ of laser energy are potentially available. However, we were not able to detect H atom emission since there was strong molecular interference from the hydroxyl radical (OH) which has single photon absorption at this wavelength region and also emits second order at 656.3 nm. A large ionization background from photoionization of OH precluded the use of the optogalvanic technique as a diagnostic tool.

H atoms were successfully detected in an atmospheric pressure H_2/O_2 flame using scheme 5, Figure 8. Ground state H atoms were excited from the n=1 to the n=4 level through a three-photon absorption at 292 nm. Fluorescence

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emission at 486 nm due to the n=4 to the n=2 radiative process (Balmer-β emission) was detected. Figure 9a gives an excitation scan recorded as the uv laser was scanned through this three-photon resonance in a stoichiometric H_2/O_2 atmospheric pressure flame while monitoring the emission with a monochromator/filter combination. The fluorescence emission spectrum was recorded by tuning the excitation wavelength exactly to the maximum of the three-photon absorption and scanning the monochromator, Figure 9b. Alden, et al.,[3] have also utilized this excitation scheme and record the excitation scan point by point (so no estimate of the signal to noise ratio could be made). Furthermore, they noted a large background, both on and off resonance of the three-photon transition in the emission spectrum. Our signal to noise ratio was very good and we did not observe any appreciable laser induced background since we used a H_2/O_2 flame and not an C_2H_2/O_2 flame where there was laser-induced fluorescence from large hydrocarbons. We measured the laser power dependence for the three-photon excitation process. Five independent measurements were made and we obtained a value of n = 2.77 ± 0.4 for H atoms in the primary reaction zone. This measurement is consistent with the expected value of n=3. We found that the signal intensity was also highly sensitive to positioning within the flame front. Highly nonlinear power dependencies (n>5) were obtained from very weak signals when the laser focal spot was translated slightly out of the primary reaction zone. This phenomenon is most likely attributable to photolysis of other flame species such as H_2O or OH to produce H atoms which were then three-photon excited. This process would probably require more than three photons. This excitation scheme may prove to be an excellent choice for diagnostic measurements of H atom profiles in combustion environments since strong fluorescence signals could be obtained quite easily (even at atmospheric pressure) and because of the convenient diagnostic wavelength available for the detection of the emission.

MPI. H atoms could also be detected using excitation scheme 3, Figure 8, in cold gaseous flows of H_2 or D_2 and in an atmospheric pressure H_2/O_2 fuel rich flame. H atoms in the flame environment were excited through two-photon excitation from the ground state n=1 to the lowest excited state n=2. For the two-photon excitation of H atoms at 243 nm there is no suitable analytical wavelength which is convenient for the detection of emission other than radiative decay back to the ground state with emission at 122 nm. However this radiation is largely absorbed by the flame gases as well as laboratory air in our experimental set up. An ideal diagnostic technique for H atoms using this excitation scheme would involve the optogalvanic probe since absorption of a third photon from the n=2 level is sufficient to photoionize the atoms. However, the platinum electrode was damaged beyond repair due to the high temperature of the H_2/O_2 flame and precluded its use in this particular experiment. We could induce multiphoton photolysis of the parent fuel in the preheat or post-flame gases in a combustion environment or cold flow of H_2, ionize the atoms and form a laser produced microplasma as had been demonstrated earlier in the discussion of O atom results. Within the high temperature plasma environment there exist collisional excitation and de-excitation processes which produce atomic hydrogen in the n-3 excited state such that the radiative decay at 656.3 nm can be detected. This experiment was repeated with a flow of D_2 and an isotopic blue shift of 22 cm^{-1} was observed in the excitation spectrum which is in excellent agreement with the well known value of 22.4 cm^{-1}. The temporal profile of the emission was indicative of a laser microplasma being produced (the full width at half

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FLAME

FLAME

INTENSITY

292.5   **291.68**   **291.0**

WAVELENGTH (nm)

INTENSITY

**480.0**   **486.2**   **494.5**

WAVELENGTH (nm)
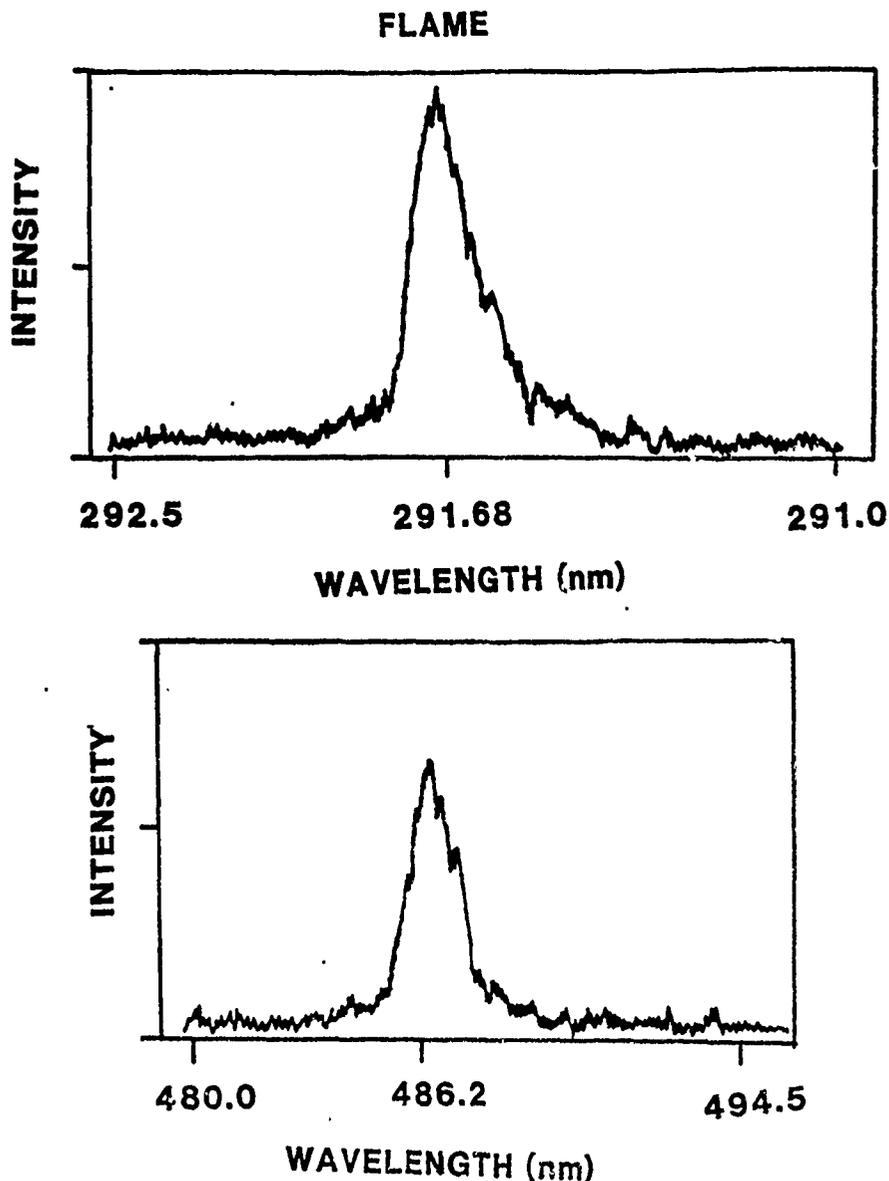
Figure 9. (a) Excitation Spectrum for H Atoms Using the Three-Photon
Excitation (λ=272 nm) Scheme 5 as Depicted in (b). The emission spectrum
taken at 486 nm from the three-photon excitation process (λ=292 nm) for
H atoms.

maximum, FWHM, was ~70 nsec). In order to gain information on the laser power
dependence for the MPI process and without having a suitable ion detector
available for atmospheric pressure measurements, we generated an H or D
molecular beam with a hot wire filament in a time-of-flight mass
spectrometer. Excitation spectia were recorded (Figure 10) by mass gating
either the H^+ or D^+ signal with a boxcar integrator and then scanning the uv
laser beam through the two-photon transition. Very strong ionization signals
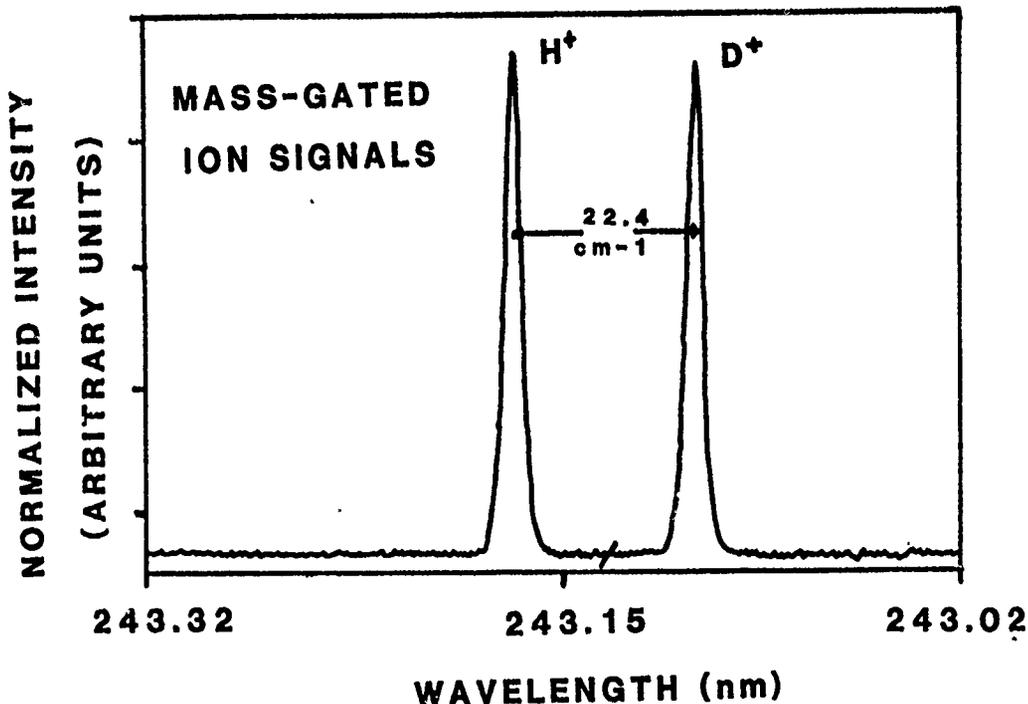
Figure 10. Mass-Gated Ion Signals (Excitation Spectrum) of H^+ and D^+ Taken in a Time-of-Flight Mass Spectrometer. An isotope of 22.4 cm^{-1} is evident. The slash (/) indicates the wavelength position where the mass gate was shifted from H^+ to D^+.

(several volts) were seen using the dual microchannel plate detector (mcp) which was located at the top of a 1.5 m drift tube. A value of n = 2.75 ± 0.2 and 2.63 ± 0.3 was obtained for H and D, respectively, corresponding to two-photon excitation and single photon ionization at low laser energies (<0.5 mJ). These results clearly indicate that the overall excitation and ionization process was a three-photon process. As mentioned earlier, we could easily saturate the two-photon excitation step and record laser power dependencies of ~2.0 for both H and D. We hope to be able to extend these measurements to a flame environment in the near future. Although the promise of the utilization of this two-photon scheme for fluorescence detection is limited, optogalvanic detection should yield excellent results. This is indicated in the results obtained by Tjossem and Cool[7] who excited the same H atom level, n=2, through a three-photon excitation and four-photon ionization at 365 nm using scheme 3, Figure 8. They report a sensitivity of < 1 ppm for low pressure flames. They utilized an excimer-pumped dye laser system and generated the requisite 365 nm uv beam directly from the dye laser; thus eliminating the need to use frequency doubling and mixing techniques. They made no special attempt to maximize the spatial resolution capabilities of the method since the results appeared to be superior to the best efforts achievable by less direct methods. Alden was able to repeat Cool's work in a low pressure flame, but the corresponding experiment failed in an atmospheric pressure flame because of molecular interference from OH, as we had seen in our attempt at implementing the three-photon excitation scheme at 308 nm. We

will continue these experiments on H atom detection when the low pressure burner we are constructing is completed and a new tungsten optogalvanic probe is built.

C. N- and C-Atoms

Here we will briefly discuss our first attempt at the detection of atomic nitrogen and carbon atoms in a combustion environment using tunable uv light. To the best of our knowledge, neither nitrogen atoms nor carbon atoms have ever been detected in a combustion environment using any optical diagnostic technique, although the nascent concentrations are expected to be much lower than that for H or O atoms. Nitrogen atoms were first detected utilizing a two-photon excitation scheme by Bischel, et al.[17] They produced ground-state N atoms in a low pressure microwave discharge then excited the atoms through a two-photon transition at 211 nm ($2p^3 4s^0 \to 2p^2 3p \, ^4D^0$). Fluorescence emission in the near infrared (869 nm) from the radiative process ($2p^2 3p \, ^4D^0 \to 2p^2 3s \, ^4P$) was detected. We tried to utilize this excitation technique to detect ground-state nitrogen atoms in atmospheric pressure fuel lean H_2/N_2O and CH_4/N_2O flames but the signal was swamped by background interference which remains unidentified. Furthermore, only ~40 μJ of laser energy was obtained at 211 nm and the signal, if present at all, was probably heavily quenched. We also attempted to detect carbon atoms in an atmospheric pressure stoichiometric flame by generating tunable radiation in the wavelength region of 193 nm to excite carbon atoms from the metastable $^1D_2$ state to the $^1P^0_1$ at 193.1 nm. This metastable state may be formed through some elementary reaction rate process or by laser photolysis.[22] The production of tunable laser radiation in this wavelength region is described in the experimental section of this work. A suitable wavelength for the detection of the emission is the $^1P^0_1 \to \, ^1S_0$ radiative process at 247.9 nm. We obtained ~70 μJ of tunable laser radiation but found that there were "holes" in the output of the uv beam as it was scanned throughout this wavelength region. It appears that absorption of molecular oxygen through the Schumann-Runge $B^3\Sigma^-_u \gets X^3\Sigma^-_g$ band system bleached holes in the output profile of the laser beam. These are the dominant absorption bands for O_2 and, unfortunately, the R(17) and P(15) absorption bands overlap exactly with the wavelength which corresponds to the carbon atom resonance at 193.1 nm.[19] Clearly if this wavelength is to be used as a diagnostic for C atoms, then the laser beam propagation pathway through the laboratory must be purged of O_2. An enclosed beam tube which is purged with an inert, non-absorbing gas at these wavelengths has recently been constructed in our laboratory.

IV. CONCLUSION

We have investigated the potential utility of the application of multiphoton excitation processes for the detection of light atomic species such as O, H, N, and C atoms in combustion environments. Techniques which were utilized include multiphoton laser-induced fluorescence and ionization, the latter using an optogalvanic probe. Laser power dependencies were determined for most of the excitation schemes which were implemented. These measurements gave detailed information on the mechanism in the photoexcitation process such as the number of photons involved, potential photolytic effects which occured therein and information on saturation effects. It was determined which of these schemes were most successful for the detection of each specific atom in a combustion environment. Clearly multiphoton

excitation is a viable approach for the detection of these light atomic species in combustion environments.

We discussed how the requisite high peak-powers that were utilized in the multiphoton excitation schemes could photochemically produce excess concentrations of atomic species (higher than that normally found in a combustion environment) and lead to erroneous concentration profile measurements. It was described how these photochemical pertubations could be used to augment combustion events such as ignition. This led to the discovery of a new ignition phenomenon which has been named "multiphoton photochemical microplasma ignition." The detailed steps involved in laser produced microplasmas have been determined and further laser ignition studies are currently under investigation.

A large amount of experimental data has been acquired using a very simple home-built atmospheric pressure burner. New sophisticated burner systems (low-pressure burner and strand burner) are under construction which will have mass-spectrometric analytical capabilities and a fourier transform infrared spectrometer, in addition to laser spectroscopic probes. The detection of these light atomic species in combustion environments by these various techniques will be used with flame models to unravel the detailed flame chemistry of the type of flame system of interest to our laboratory.

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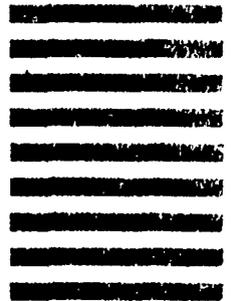
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