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13. ABSTRACT (Maximum 200 words) Significant milestones for quantitative laser-based diagnostics of reacting flows were reached on two separate tasks: (1) the extension of laser-based diagnostics to shorter vacuum ultraviolet (vuv) wavelengths and (2) the development of amplified spontaneous emission (ASE) diagnostics for light atoms. For the first task, phase-matching was applied to produce significant increases in vuv laser intensities, producing over 5 μJ at Lyman alpha (121.6 nm) in a mixture of krypton and argon. Factors affecting the long-term stability of vuv powers were studied. The diagnostic potential of two-photon excited ASE of atomic hydrogen and oxygen was explored in a variety of low-pressure flames. Direct ASE gain measurements gave oxygen concentrations. A model of the ASE signal was developed, and a new understanding of both ASE and laser-induced fluorescence of two-photon excited atoms emerged from this model. DTIC QUALITY INSPECTED 4

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CONTENTS

OBJECTIVES AND SUMMARY.....	1
RESEARCH ACCOMPLISHMENTS	1
Task 1: UV and VUV Generation and Detection Techniques	1
Background and Summary.....	1
VUV Power Improvement	4
Windowless Cells	5
Optics Studies.....	6
Phase Matching.....	8
Lyman Alpha Generation in Hydrogen	9
Phase Matching in Krypton	10
Task 2: Laser-Excited ASE Measurements	13
Background and Summary.....	13
LIF Measurements of H in Flames.....	16
ASE Measurements	19
Atomic Oxygen Measurements	19
dc-Arcjet Measurements of Atomic Hydrogen.....	21
REFERENCES.....	26
PERSONNEL SUPPORTED.....	27
PUBLICATIONS	28
INTERACTIONS/TRANSITIONS	29
Presentations.....	29
Interactions.....	31
Transitions	34
DISCOVERIES.....	34
HONORS/AWARDS	34

ILLUSTRATIONS

1	Schematic of two-photon-resonant difference-frequency mixing approach	3
2	Experimental arrangement for two-photon-resonant difference frequency mixing	3
3	Spectrometer scan of vuv radiation at 125 nm	7
4	Pressure dependence of 125-nm vuv radiation.....	7
5	VUV generation in hydrogen near Lyman alpha	10
6	VUV generation in krypton as a functio of pressure	11
7	Tunable vuv generation in the Lyman- α region in krypton with and without phase matching.....	11
8	VUV generation in krypton at multiple pressures	12
9	LIF corrected for quenching versus reaction time for rich, stoichiometric, and lean 7.2-Torr H ₂ /O ₂ flames	17
10	H atom LIF corrected for quenching versus reaction time for 30-Torr, slightly rich, CH ₄ /air flame	18
11	The time evolution of the atomic state densities for 7.2-Torr H ₂ /O ₂ -rich flame.....	20
12	Measured ASE and predicted ASE for 7.2 Torr rich and lean H ₂ /O ₂ flame.....	20
13	Inverse fluorescence lifetime versus pressure in the center and at the edge of the arcjet plume.....	24
14	H-atom concentration corrected for quenching at r = 0 mm and z = 20 mm.....	25

OBJECTIVES AND SUMMARY

The objective of this project was to develop nonlinear laser diagnostics for combustion and plasma processes. The research was conducted in two tasks as described below.

The research for Task 1 centered on extending laser-based diagnostics to shorter wavelengths. The objectives of this task were to develop new vacuum ultraviolet (vuv) laser sources and techniques, with emphasis on widely tunable radiation with high powers, and to apply this vuv radiation to diagnostics of species not accessible with current visible and near uv laser sources.

The focus of Task 2 was amplified spontaneous emission (ASE) research designed to develop quantitative laser-based diagnostics of atom concentration and flow velocity in highly reactive flow fields that have limited optical access.

For the first task, phase-matching was applied to produce significant increases in vuv laser intensities, producing over 5 μJ at Lyman alpha (121.6 nm) in a mixture of krypton and argon. Factors affecting the long-term stability of vuv powers were studied. The diagnostic potential of two-photon excited ASE of atomic hydrogen and oxygen was explored in a variety of low-pressure flames. Direct ASE gain measurements gave oxygen concentrations. A model of the ASE signal was developed, and a new understanding of both ASE and laser-induced fluorescence of two-photon excited atoms emerged from this model.

RESEARCH ACCOMPLISHMENTS

TASK 1: UV AND VUV GENERATION AND DETECTION TECHNIQUES (G. W. FARIS)

Background and Summary

Although great progress has been made on laser-based detection techniques, some significant challenges remain. Among these are the detection of atomic ions and the single-photon detection of light atoms. These detection problems are similar in that they both require high-power vuv radiation.

The ability to perform quantitative detection of atomic ions is important for studying plasma propulsion, highly ionized flows, plasma etch lithography, magnetically confined fusion, astronomy, and astrophysics. Detection of light atomic ions is difficult because the single-photon transitions from the ground state lie in the extreme ultraviolet (xuv) and no window materials are available in this region. Our approach was to use two-photon-excited fluorescence in the vuv, a strategy that allows the use of windows of materials such as MgF_2 and LiF .

Light atoms can be detected through two-photon techniques in the near ultraviolet region. An alternative technique to two-photon detection is single-photon detection using vuv. Although it requires more complicated laser sources than the two-photon approaches, single-photon vuv detection of light atoms allows more sensitive detection, can avoid photo-induced changes due to high optical intensities, and provides the possibility for planar imaging. Areas where single-photon detection techniques may prove useful include arc jets and hot rarefied flows. Other applications of vuv diagnostics include single- or multiple-photon ionization for very high sensitivity detection techniques and single-photon calibration of multiple-photon diagnostic techniques.

A key part of this research was the production of high power vuv radiation suitable for diagnostics measurements. Because of the lack of suitable nonlinear crystals for vuv generation, frequency conversion must be performed in gases. Because gases are centrosymmetric, four-wave-mixing is the lowest order frequency conversion process that may be used. To obtain high powers, techniques using resonances are required, such as multiorder anti-Stokes Raman shifting¹ and two-photon-resonant sum- and difference-frequency mixing.²

To produce high-power, widely tunable, vuv radiation, we developed a source based on two-photon-resonant difference-frequency generation, using an ArF laser as the pump laser.² A schematic of this frequency mixing approach is shown in Figure 1, an experimental diagram is shown in Figure 2. The output of a tunable ArF excimer laser at frequency ν_{ArF} was mixed with the fundamental or frequency-doubled output from a Nd:YAG-pumped dye laser at frequency ν_{dye} to produce radiation at frequency $\nu_{\text{vuv}} = 2 \times \nu_{\text{ArF}} - \nu_{\text{dye}}$. Enhanced efficiency was achieved by tuning the ArF laser onto resonance with two-photon transitions in the mixing gas (krypton or hydrogen). The vuv wavelength could be varied from 110 to 180 nm by tuning the dye laser frequency.

The mode quality of the lasers is very important to the achievable output power. This work took advantage of our previous work on Raman shifting,¹ for which several modifications were made to a Lambda Physik model 150 dual discharge excimer laser to obtain better spatial mode quality. We obtained over 65 μJ at a wavelength of 133 nm by using this mixing technique.³

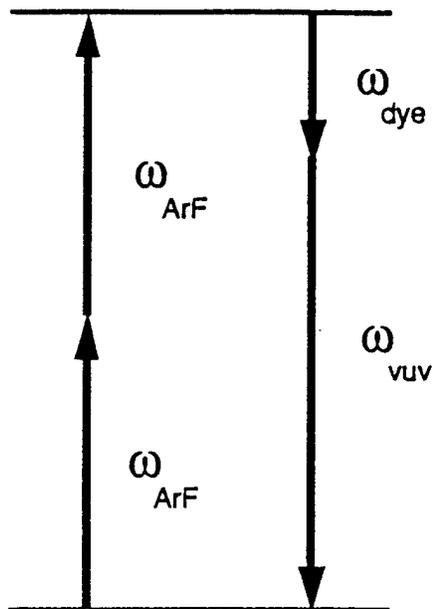


Figure 1. Schematic of two-photon-resonant difference-frequency mixing approach.

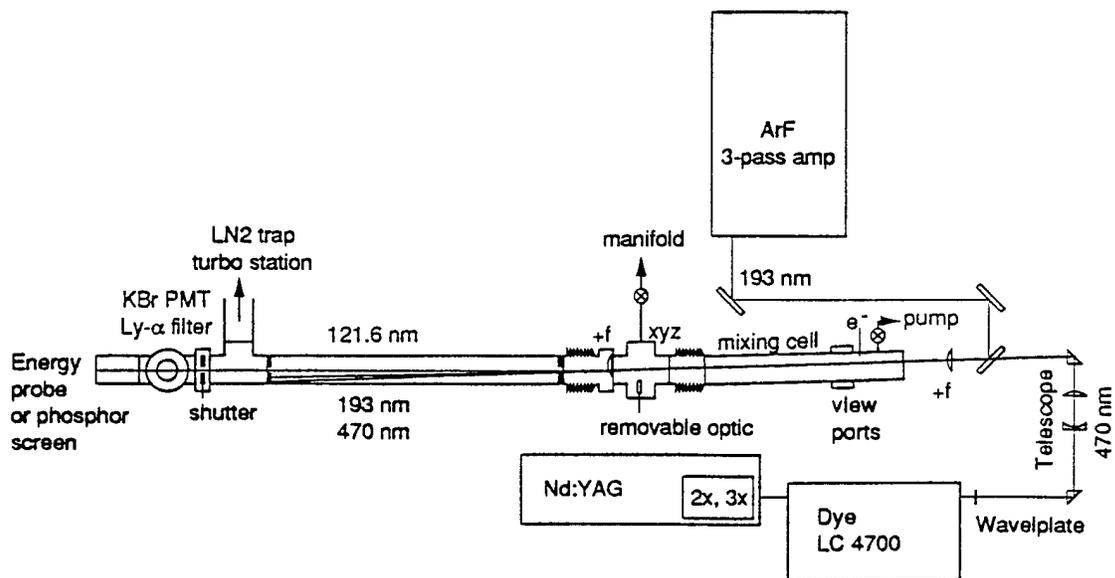


Figure 2. Experimental arrangement for two-photon-resonant difference frequency mixing.

We evaluated the performance of the vuv-based multiphoton spectroscopy through 1+1 resonantly enhanced multiphoton ionization (REMPI) on xenon³ at 147 nm and two-photon-excited fluorescence in neon using 133-nm light.⁴ The latter constitutes a demonstration of the two-photon-excited fluorescence technique in an appropriate wavelength region for atomic ion detection. The excited state lies over 150,000 cm⁻¹ above the ground state. However, the neon measurements were performed at a pressure of about 100 Torr, which is too high for most useful applications for atomic ion detection. Further improvement in laser power was required to achieve useful detection of atomic ions. To this end, we minimized the path length for the vuv through the optics by using an off-axis lens instead of a prism to separate the beams. This change resulted in more than a factor of 3 improvement in vuv energy over what was available for the neon measurements. Further improvement in energy is still required, however.

VUV Power Improvement

Two avenues can be pursued to further improve our laser power. Both concern materials problems. The first involves loss mechanisms that build up as a result of the length of exposure to the high-power vuv. The second deals with mechanisms to improve the efficiency of the mixing gas through phasematching.

Our vuv energies drop during continuous vuv generation over periods of minutes to tens of minutes, apparently due to color center formation,⁴⁻⁶ at least for generation at wavelengths in the region of 133 and 149 nm. Color center losses may be mitigated by reducing the vuv fluence on the optics (by using larger diameter beams and optics), by heating the optics to speed recombination of the color centers, or by separating the vuv beam from the input beams by using a concave grating instead of transmissive optics.

A technique that can help in evaluating the deterioration of optics during vuv irradiation is the generation of vuv ASE in hydrogen.⁷ This process uses the same $E, F(v' = 6) \ ^1\Sigma_g^+ \leftarrow X \ ^1\Sigma_g^+(v'' = 0) \ Q(1)$ two-photon transition in hydrogen that we use for the two-photon-resonant difference-frequency mixing. This ASE can produce unwanted extra vuv lines when the difference-frequency mixing is attempted. However, it also provides a simple, single-laser-based source of vuv of power and wavelength comparable to that from the difference-frequency mixing.

While examining the ASE-based vuv source, we had some false excitement involving unexpected resonances. When varying the excitation wavelength, we found additional excitational resonances that did not coincide with known two-photon resonances of hydrogen. This finding is significant because movement of populations associated with using a resonance to enhance frequency conversion also leads to loss processes such as multiphoton ionization or index of

refraction changes. Unfortunately, these resonances turned out to be due to fractional order transmissions through the spectrometer. Fractional order transmission is not strictly possible in a spectrometer. In our case, fractional order transmission was due to extra reflections in the spectrometer. After the first diffraction from the grating, the ArF beam struck an edge of one of the mirrors, struck the grating again, struck the second mirror, and passed out of the spectrometer. This type of spurious reflection is more likely to be a problem for small-diameter collimated light sources such as our vuv source because of the small size and divergence of the beam.

Windowless Cells

To permit better characterization of aspects of the mixing process in the absence of time-varying, irradiation-dependent window absorptions, we modified the apparatus to allow windowless generation of vuv. Three windowless cell designs were evaluated. Two of the cells were filled with a pulsed valve. To measure the transient pressure in the pulsed cell, we used small electrode ions produced by 2+1 REMPI (resonant enhanced multiphoton ionization) in hydrogen produced by the ArF laser. The ion signal depends on pressure and can be used to monitor the transient pressure during filling with the pulsed valve. Ion signals at well-defined static pressures were found when the main chamber was filled with hydrogen at a known pressure. Through comparison of signals in the static and transient configurations, we can determine the cell pressure during pulsed operation.

The first cell was a short pulsed cell. A Lasertechnik pulsed valve was used to fill a small-volume mixing cell with open ends. This approach was used instead of performing the mixing directly in the supersonic expansion from the pulsed valve because the density and path length in the expansion were too low. The open-ended cell consisted of a glass tube with an inside diameter of 4 mm and a length 10 cm. The tube was inside an evacuated cell that had a Brewster angle window for introduction of the ArF laser at one end and was coupled to a Spex 1500SP 0.5-m vacuum spectrometer at the other.

The ion signal indicated that we could reach pressures of about 50 Torr in the short cell, which is adequate for producing vuv ASE. However, we were not able to observe vuv ASE from the glass cell during transient filling, although static cell measurements showed that we could detect vuv ASE from as little as 5 Torr of hydrogen. We attribute this difference to the longer gain length through the hydrogen for the static cell. We did not expect the longer path length to be necessary for ASE generation, because the confocal parameter for the focusing geometry of the ArF laser is only about 1 cm, while the glass cell is 10 cm long. The ASE arises from a two-photon excitation, so contributions from a distance longer than one confocal parameter should not

be important. The longer path lengths may be required owing to the laser beam not being diffraction-limited, or to saturation of the two-photon transition.

To produce a longer differentially pumped hydrogen path, we converted to a continuously flowing arrangement. A 300- μm pinhole was inserted in place of the glass cell. By flowing approximately 1 standard liter per minute of hydrogen into the outer cell, we could maintain a pressure of about 50 Torr in the outer cell and a pressure of about 500 m in the spectrometer (into which the hydrogen flow is restricted by both the pinhole and the spectrometer slits). Because of the small pinhole diameter, this second cell proved to be too difficult to align through the spectrometer used to separate the generated vuv from the input laser.

The final cell was a longer pulsed cell, consisting of a glass tube about 30 cm long with 4 mm inside diameter. The end closer to the vacuum spectrometer was open. The end facing the laser was sealed with a window. Gas was introduced into the cell near the sealed end using the pulsed valve. Ion signal measurements indicated that the cell reached maximum pressure after about 1 ms. This cell performed quite well.

Optics Studies

We purchased a new MgF_2 window from Acton Research Corporation for studying color center formation. The window was mounted on a rod passing through a vacuum feed-through (Ultratorr type), allowing it to be inserted and removed from the vuv beam. This insertable window allowed comparison of the incident and transmitted vuv powers.

The window was irradiated with vuv from both ASE in hydrogen and difference frequency mixing in hydrogen. The latter light, at 125 nm, was produced using ArF light and 425 nm light from the dye laser. A scan of this radiation taken with a vacuum spectrometer is shown in Figure 3. A pressure dependence for the generation of 125 nm light is shown in Figure 4. The optimal hydrogen pressure for production of 125 nm light is about 20 Torr, or more than a factor of 3 lower than for 133 nm.⁴ The lower optimum pressure demonstrates the increased importance of dispersion at shorter wavelengths. The vuv intensity increases quadratically with density at lower densities, but the dispersion dominates at higher densities, leading to a decline in vuv intensity.

With vuv from both ASE and 125 nm from difference frequency mixing, we found only little degradation of the MgF_2 window transmission. This result is quite different from what we found previously using difference frequency mixing at 133 nm, where dramatic declines in transmission occurred.⁴ This difference may be due in part to improvement in the quality of vuv grade optics since the previous measurements. Another possible explanation is that absorption of

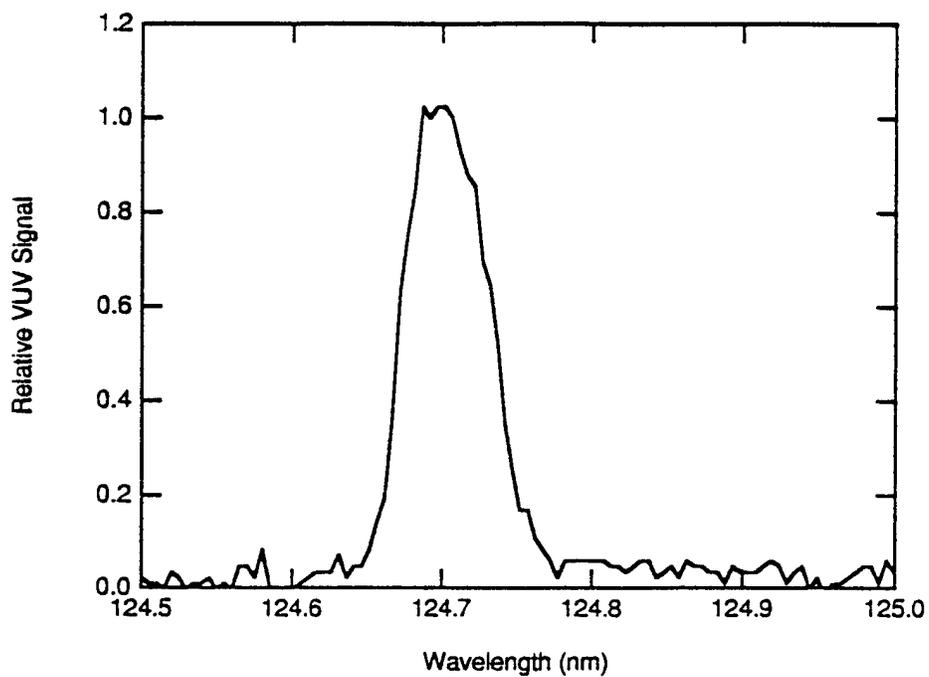


Figure 3. Spectrometer scan of vuv radiation at 125 nm.

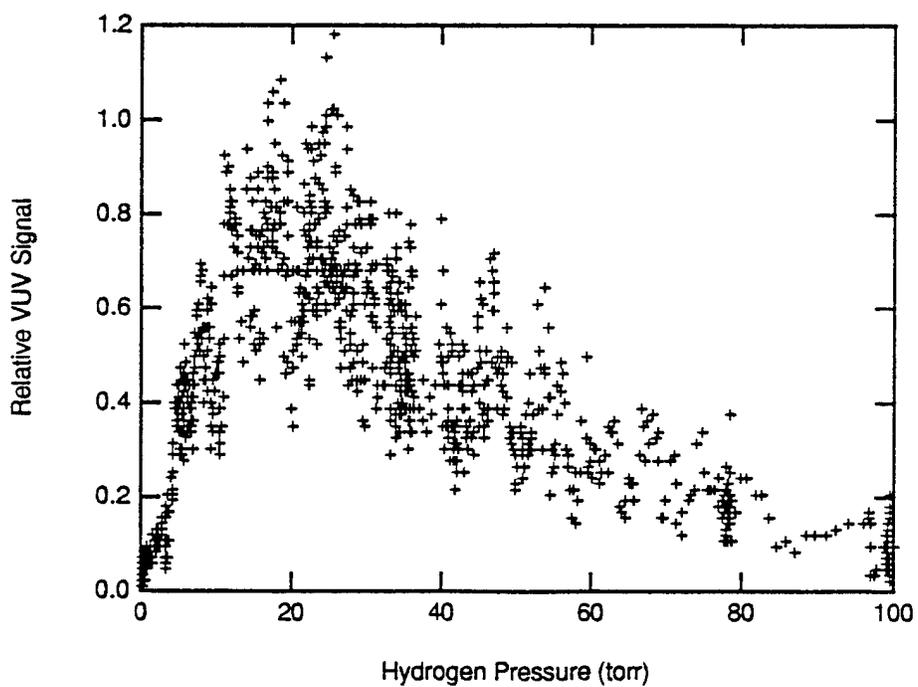


Figure 4. Pressure dependence of 125-nm vuv radiation.

xuv (extreme ultraviolet) radiation produced from a 2+1 (two argon fluoride plus one dye photon) process plays a role in optics degradation. The 2+1 wavelength is shorter for 133-nm generation than for 125-nm generation.

In preparation for studying phase matching, we modified our system to allow total energy detection using a pyroelectric energy probe. During this work, we found a new degradation process—in this case, degradation of the detector. The pyroelectric energy probe showed a decay in its sensitivity within a period of minutes when exposed to high power vuv. This degradation did not occur with exposure to ArF or dye beams, although the detection of the ArF and dye beams also diminished on exposure to the vuv. The pyroelectric probe response recovered over ten minutes to several hours. The process that leads to decaying response for detection of high power photons in vacuum is still not entirely understood. New, robust detectors will be required for future vuv work.

Phase Matching

The efficiency of the vuv generation is related to the nonlinear optical polarizability, which is proportional to the square of the mixing gas density. Improvements in vuv power cannot be realized by increasing the gas density alone, because of index of refraction dispersion for the gas between the input and output beam wavelengths. For nonlinear frequency conversion processes, such as that in our vuv source, the dispersion for different wavelengths led to different phase propagation velocities for the driving (input) and generated waves. When phases did not propagate in conjunction (i.e., there was phase mismatch), the nonlinear conversion process was not optimally efficient. Reducing the effects of material dispersion (phase-matching) significantly improved the vuv power from the source. Some phase-matching was required to achieve significant powers near 120 nm.

Phase-matching in gases can be achieved by using gas mixtures,⁸ noncollinear mixing,⁹ and "quasi-phase-matching."^{10,11} Of the various techniques for phase-matching, the most useful in the vuv region is the use of gas mixtures. This technique uses the anomalous dispersion (decreasing refractive index with increasing photon energy) that gases can exhibit above allowed, ground state, transition frequencies.

We examined phase-matching in the region of Lyman α (121.6 nm), the shortest wavelength we have generated to date. This wavelength may be used for planar imaging or other diagnostics of ground state hydrogen atoms. Krypton gas exhibits negative dispersion in this region, allowing phase matching in gas mixtures containing krypton. We investigated both hydrogen and krypton as vuv generation gases at Lyman alpha.

We purchased new vuv-grade MgF₂ lenses from Optovac and Harshaw-Bicron for these measurements. Both lenses initially yielded >50% transmission at Lyman- α as measured using a vuv spectrometer. To date we have only used the Optovac lens and did not encounter optics degradation problems, perhaps due to improvements in MgF₂ growth techniques.

Lyman Alpha Generation in Hydrogen

Several two-photon absorptions of H₂ lie within the tuning range of the ArF laser, corresponding to Q-branch transitions to $v = 6$ and 7 in the E-F state.¹ We generally use the Q(1) (6,0) because of the large Boltzmann fraction in $J = 1$, but this requires purging the ArF beam path to minimize the effects of absorption from the oxygen Schumann-Runge bands. Conversion efficiency in pure H₂ increases with pressure to a maximum at approximately 50 Torr with our 50-cm focusing lens, then decreases due to increasing phase mismatch. As discussed below, this conversion efficiency is higher than that obtained in pure Kr, and H₂ initially looked promising. Unfortunately, H₂ suffers from several disadvantages: a series of amplified spontaneous emission lines in the vuv, many energy levels, which complicate the χ^3 as a function of wavelength, and most important for this work, production of H atoms in the focal volume.

The effects of H atoms on the conversion efficiency are shown in Figure 5. Structure, which we believe is caused by H₂, appears at 121.0, 121.4, 122.5, and 123 nm, but the most striking feature is the dip at 121.6 nm corresponding to the Lyman- α transition. The asymmetric shape of this feature is due to phase-matching effects. The index of refraction varies rapidly near the strongly allowed Lyman- α transition, which produces a profound effect on the phase matching. On the long wavelength side of Lyman- α , the phase-mismatch increases and conversion efficiency drops. On the short wavelength side, H atoms make a negative contribution to Δk and actually improve the conversion efficiency through improved phase matching. This interpretation is supported by measurements in negatively dispersive gases: when vuv is generated in Kr with H₂ added, the asymmetry is reversed because Δk for Kr is negative in this spectral region.

Manipulation of experimental parameters had some effect on the H atom production, but we could not eliminate the H atoms. Reduction in H₂ pressure and ArF laser power and slight detunings of the ArF laser from resonance met with limited success, but none eliminated the drop at Lyman- α . Adjusting synchronization of the ArF and dye laser to encourage mixing before significant H atom production had no apparent effect. We produce 5-15 μJ near Lyman- α , with a 1-2 order of magnitude dip on resonance where peak energies of about 0.2 μJ are produced.

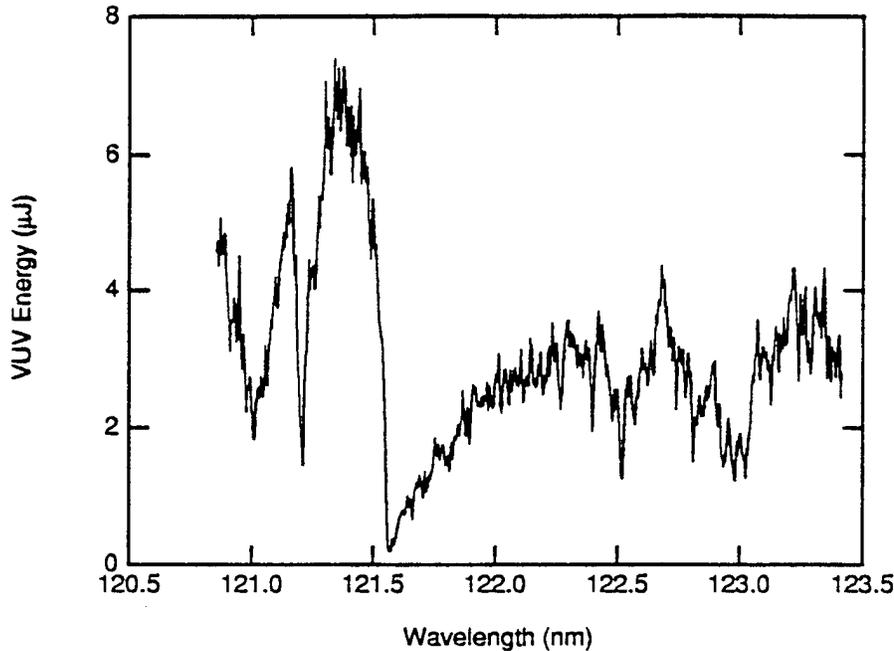


Figure 5. VUV generation in hydrogen near Lyman alpha.

Phase Matching in Krypton

Difference-frequency mixing can be enhanced in Kr by tuning the ArF laser to two-photon transitions to the $6p[5/2,2]$, $6p[3/2,2]$, and $6p[1/2,0]$ states. Transitions to $6p[5/2,2]$ and $6p[1/2,0]$ lie in the wings of the ArF tuning curve, so we chose the $6p[3/2,2]$ transition, although this requires purging of the ArF beam path due to a Schumann-Runge O_2 absorption.¹

VUV generation in pure Kr is less efficient than in pure H_2 because of the large phase mismatch in Kr.¹² Figure 6 shows the pressure dependence of vuv intensity in pure Kr. Peak energies of about $0.2 \mu J$ are produced at an optimum pressure of about 7 ± 3 mbar. This pressure is roughly an order of magnitude lower than the optimum pressure in H_2 . This lower vuv generation is consistent with a calculated phase-mismatch for krypton, which is seven times larger than in H_2 at Lyman- α . Phase mismatch can be eliminated by adding a positively dispersive gas, such as Ar. (Note that we cannot use H_2 because H atoms are produced even when the ArF laser is tuned to the Kr resonance.) With phase-matched mixtures, higher partial pressures of Kr can be used. Figures 6 and 7 show that a 3.9:1 Ar/Kr mixture with 260 mbar of Kr yields about two orders of magnitude improvement over pure Kr. As with H_2 , visible emission is produced along the ArF beam in the gas, especially in the focal region. At the higher pressures used here, dielectric breakdown occurs frequently.

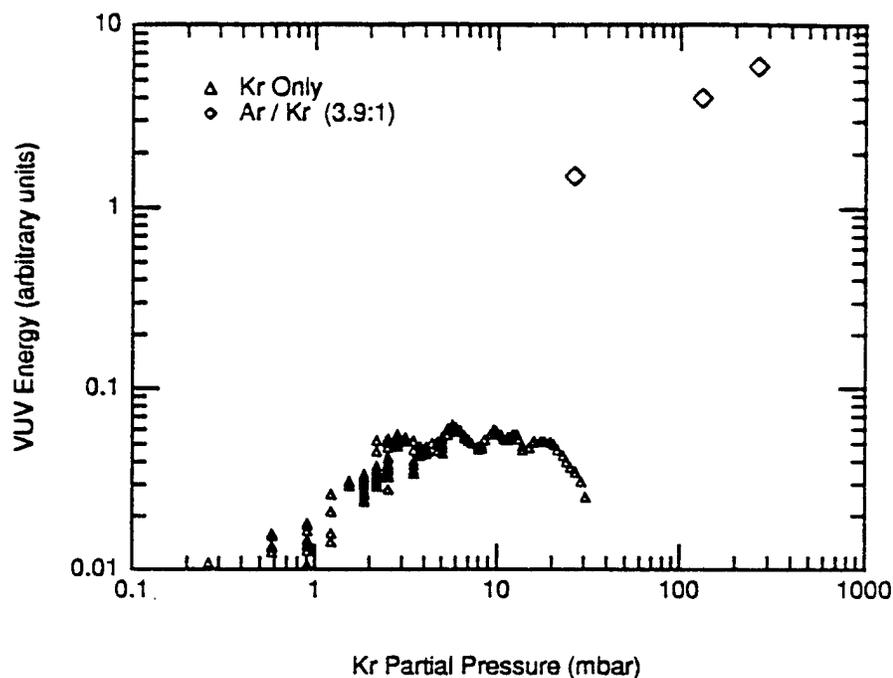


Figure 6. VUV generation in krypton as a function of pressure.

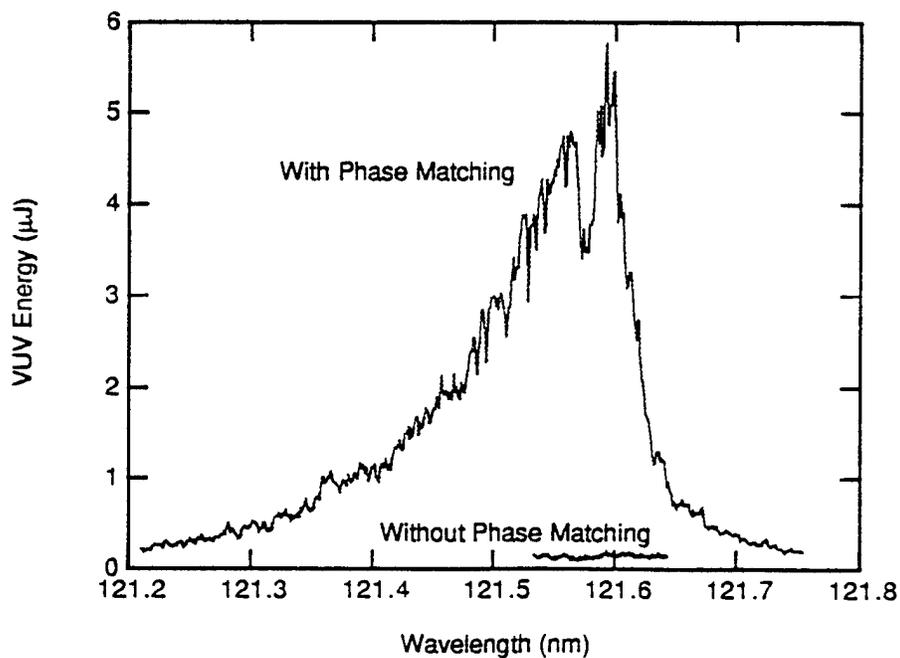


Figure 7. Tunable vuv generation in the Lyman- α region in krypton with and without phase matching.

The spectral tuning ranges for three Kr pressures are compared in Figure 8. Phase mismatch $\Delta k(\lambda)$ does not deviate from linearity enough to account for the asymmetry in the tuning profiles, especially at 260 mbar. We believe the source of the asymmetry lies in the mixing efficiency as a function of Δk . As the ArF and dye beams pass through the focus, each beam acquires a phase shift of at least π over a distance related to its confocal parameter (Guoy effect). Only in the special case where the ArF and dye beams have Gaussian spatial profiles with the same confocal parameter will these shifts cancel (for difference frequency mixing) and produce a symmetric profile.¹³ If the confocal parameters of the input beams differ, the phasematching function, $F(b\Delta k)$, is asymmetric and is higher for the Δk values that best compensate for the different phase shift through the focus.¹⁴ The dashed curves shown in Figure 8 are fits of the theory of Hilber et al.¹⁴ to the tuning curves. The magnitude and direction of the asymmetry should differ in other cases due to different confocal parameters.

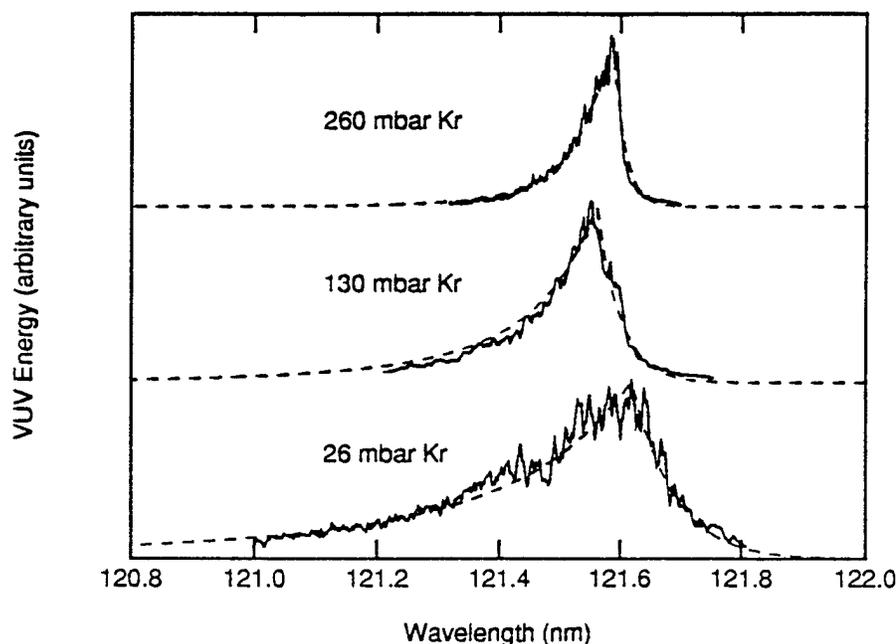


Figure 8. VUV generation in krypton at multiple pressures.

The VUV powers achieved here were limited by the design pressure of the cell and, more fundamentally, by dielectric breakdown in the gas. Figure 6 shows VUV still increasing with

pressure, but dielectric breakdown is already a problem. A longer focal length lens will reduce breakdown by reducing the focal spot intensity. This finding suggests that further improvements are possible with moderate increases in focal length. Additional reductions in breakdown may be possible by changing the buffer gas, since the mixture used here is only 20% Kr. If breakdown is induced by photoionization of the two-photon state, though, this may not be effective. Finally, absorption and/or dispersion by Kr dimers becomes important at very high pressures.

TASK 2: LASER-EXCITED AMPLIFIED SPONTANEOUS EMISSION (ASE) (J. B. JEFFRIES)

The goal of our project on laser-excited amplified spontaneous emission (ASE) was to understand the influence of the competition between ASE, laser ionization, and laser-induced fluorescence (LIF) on quantitative measurements of atom concentration. Optical measurements of the free atoms that reside in the first two rows of the periodic table provide an analytic challenge in practical combustion systems. These atoms have resonance lines in the vacuum ultraviolet region of the spectrum. Because the flame gases strongly absorb in this region, any excitation light or resonance fluorescence is severely attenuated in the flame. Two-photon excitation followed by the detection of the fluorescence to an intermediate state avoids these problems. Two-photon excitation selects an excited state that does not have an allowed one-photon transition back to the ground state. LIF is observed from the excited state to an intermediate state of an atom; in most reactive flows, this intermediate state has no thermal population. However, if a significant population is excited into the two-photon excited state, a population inversion with the intermediate state can be created and the fluorescence can experience gain.

The resulting amplification of the spontaneous emission is called amplified spontaneous emission (ASE) or stimulated emission. The ASE is directed forward and backward along the excitation laser beam instead of isotropic fluorescence from the two-photon LIF. Therefore, any quantitative measurement must understand what fraction of the excited atoms experience ASE and what fraction simply fluoresce. This situation is complicated by laser ionization (REMPI); the two-photon excited state can absorb one more photon from the laser beam and be ionized. Quantitative two-photon LIF must understand the competition between ASE, LIF, and REMPI.

We developed a quantitative model of optical detection of two-photon, excited atomic hydrogen and oxygen using ASE, LIF, and ionization. Two-photon LIF is the established *in-situ* detection method for atomic hydrogen and oxygen for research on reactive flows. For example, Pobst et al. at Philips Laboratory routinely use two-photon LIF of atomic hydrogen to study the performance of dc-arcjet thrusters.¹⁵ At low-excitation pulse energy, their experiments are complicated by optical emission from the arcjet plume. As they increase the excitation laser, they

observe competition between LIF and ASE. During this AFOSR contract, we developed and validated a model to quantitatively predict the amount the LIF signal is depleted by ASE. In addition, quantitative measurements of atom concentration by ASE are attractive in complicated high speed reactive flow combustors. Using our model, we discovered that quantitative ASE gain measurements can be used to determine atom concentration with an experimental arrangement that requires significantly less optical access.

The dynamics of the atomic population and coupled ASE photon field can be described by considering a volume defined by the confocal range of the incident pump beam and the diameter of the beam at its waist. This volume then acts as a mirrorless cavity for the production of ASE photons. We write rate equations for the density of the atoms in the cavity for each of the three atomic levels, the density of the ions generated via a 2+1 REMPI process, the density of the ASE photons, and the density of the photons that leave the cavity and are detected. Assuming that the gain in the cavity is independent of the radial and longitudinal spatial directions, the coupled equations take the following form

$$\frac{dN_e}{dt} = W(t) \left(\frac{g_e}{g_g} N_g - N_e \right) - \sigma_e c N_{ASE} \left(N_e - \frac{g_e}{g_i} N_i \right) G - (A_{ei} + \sigma_{pi} I_p + Q) N_e \quad (1)$$

$$\frac{dN_i}{dt} = \sigma_e c N_{ASE} \left(N_e - \frac{g_e}{g_i} N_i \right) G + A_{ei} N_e - (A_{ig} + Q) N_i \quad (2)$$

$$\frac{dN_g}{dt} = -W(t) \left(\frac{g_e}{g_i} N_g - N_e \right) + Q N_e + (A_{ig} + Q) N_i \quad (3)$$

$$\frac{dN_{ASE}}{dt} = \sigma_e c N_{ASE} \left(N_e - \frac{g_e}{g_i} N_i \right) G + \frac{d\Omega}{4\pi} A_{ei} N_e - \frac{N_{ASE}}{\tau_c} \quad (4)$$

$$\frac{dN_{ions}}{dt} = \sigma_{pi} I_p N_e, \quad \frac{dN_{det}}{dt} = \frac{1}{2} \frac{N_{ASE}}{\tau_c} \quad (5)$$

In the above, N_e , N_i , N_g , and N_{ions} denote the population densities (in units of cm^{-3}) for the excited, intermediate, ground, and ionic atomic states, respectively. N_{ASE} and N_{det} denote the density of ASE photons in the cavity and the density of ASE photons that leave the cavity and are collected by the detector, respectively. The time-dependent, two-photon pumping rate is indicated by $W(t)$, the Einstein A coefficients by A_{XY} , and the quenching rate by Q . The cross sections for stimulated emission and photoionization are denoted by s_e and s_{pi} , respectively.

The expression for the ASE photon density contains a factor that includes any photons spontaneously emitted into the solid angle, dW , defined by the pump beam. It also contains the loss term $-N_{ASE}/t_c$, where t_c denotes the lifetime of the cavity, which we took to be equal to one-half the cavity length divided by the speed of light, c . G denotes the gain experienced by the ASE photon field in the cavity and is calculated from $\exp[sez(N_e - g_e N_i/g_i)]$. The factors g_x denote the degeneracy of the particular states. The time-dependent intensity of the pump laser is denoted by I_p . We tested this model with ASE and LIF measurements of atomic hydrogen in low-pressure flames.¹⁶ The model does a good job of predicting the ASE signal for a variety of collisional quenching rates and as a function of atom number density.

We observed atomic hydrogen and oxygen in discharge flows, low-pressure flames, a dc-arcjet plasma. H atoms were observed with two-photon LIF and simultaneously acquired ASE from Balmer α in a 7.2 Torr H_2/O_2 flame and a 30 Torr CH_4 /air flame. Measurements were made in fuel-rich, stoichiometric, and lean hydrogen/oxygen flames. Model calculations provided concentrations of the major species as a function of reaction time (height above the burner). LIF measurements were corrected for collisional quenching, using the model results, and agreed quite well with the model predictions for the atomic hydrogen concentration. The model predicted both the variation with reaction time and the variation between the flames with different stoichiometry. The ASE measurements in the three hydrogen/oxygen flames were compared with the predictions of a coupled rate model. The absolute ASE signal intensity was in remarkable agreement with the prediction. The variation with stoichiometry and reaction time also agreed well with the model.

The flames were supported on a 6-cm-diameter, water cooled, porous plug burner in an evacuated housing. Atomic hydrogen ASE and LIF signals were monitored in H_2/O_2 and CH_4 /air flames, using conditions identical to previous studies of flame chemistry. A more detailed description of the burner, associated optics, and data acquisition can be found in previous publications.¹⁷ Tunable laser light near 205 nm was produced by tripling a YAG pumped dye laser near 615 nm; the dye laser was doubled in KD*P, and the resultant 307.5 nm light was combined with the residual fundamental 615 nm light in BBO. The excitation light was focused into the burner with a 10-cm lens and hydrogen atoms were excited to $n = 3$; sequential application of two, single-photon, selection rules allowed excitation to only the 3S or 3D states. Balmer α fluorescence to the 2P state was observed as the LIF signal.

If the pumping rate is fast enough, the laser excitation will produce a population inversion on the Balmer α transition; spontaneously emitted photons can experience gain from this population inversion. There is only upper state population along the path of the laser; thus, spontaneous emission can experience gain only along the path of the 205-nm light. This ASE forms a collimated beam near 656 nm, which travels forward and backward along the optical axis

of the excitation laser. We collected the ASE in the forward direction with a lens of the same focal length used to focus the excitation beam; the 205-nm light was separated from the 656-nm light using a dichroic mirror and a colored glass filter (Schott, RG-645). The ASE signal was visible on a white card and was attenuated with neutral density filters and detected with a 1P28 photomultiplier.

The gas temperature was determined from LIF measurements of the OH rotational distribution. The OH LIF signal was kept unsaturated by reducing the laser power. Typical fitting errors of the Boltzmann plots of rotational populations were ± 50 K, which corresponds well with the ± 40 K derived by averaging replicate measurements at the same point in the flame.

The variation of gas temperature with height above the burner is combined with a detailed model of the combustion chemistry. The calculation is performed with the Sandia flame code, which is based on one-dimensional fluid flow including thermal diffusion. The chemical mechanism is GRI-Mech 2.11 which is an optimized mechanism for methane combustion that includes kinetics for hydrogen combustion. The gas pressure, temperature, and flow rate at the burner surface are initial conditions, and the solution is constrained by the measured variation of the gas temperature with reaction time. The use of an empirical temperature profile avoids the difficult assessment of heat loss to the burner surface. We previously determined that flames at pressures less than 20 Torr have significant radial transport. Thus, as a first-order correction for radial diffusion at these low pressures, the cross sectional area of the 7.2 Torr hydrogen/oxygen flame was allowed to increase with height above the burner.

LIF Measurements of H in Flames

We used two-photon LIF to measure the atomic hydrogen concentration and compared it with a model calculation for rich, stoichiometric, and lean 7.2-Torr H₂/O₂ flames. The LIF signal was corrected for collisional quenching by using a fluorescence quantum yield, F, given by

$$\Phi = \frac{A}{A + Q} = \frac{64.5 \mu\text{s}^{-1}}{64.5 \mu\text{s}^{-1} + \sum k_Q^i n_i} \quad (6)$$

where A is the radiative decay rate, Q the first-order quenching rate, k_Q^i the quenching rate constant for the *i*th species, and n_i the concentration of the species *i*. We used our model of the chemistry to predict the concentrations of these colliders and the quenching rate constants of Bitner et al.¹⁸ to calculate F as a function of height above the burner. The LIF signal divided by F is proportional to the atomic hydrogen concentration.

Figure 9 shows the measured atomic hydrogen for the stoichiometric flame, normalized by the model calculation at the peak value to set the absolute scale for the LIF measurements for all three flames. The quenching corrected LIF signals agree quite well with the model predictions for the rise in the flame front. Above a height of 2 cm, the measured atomic hydrogen decreases with height above the burner. This deviation is similar to measurements of other reactive species in this burner and is evidence that radial transport for atomic hydrogen is underpredicted. The agreement between measurements and predictions for the lean flame (fuel equivalence ratio $\phi = 0.67$) and the rich flame ($\phi = 1.42$) is amazingly good. The model predicts the atomic hydrogen concentration to increase by a factor of 2 as the fuel equivalence ratio increases from 0.67 to 1.42, and the measurements agree to within 5%.

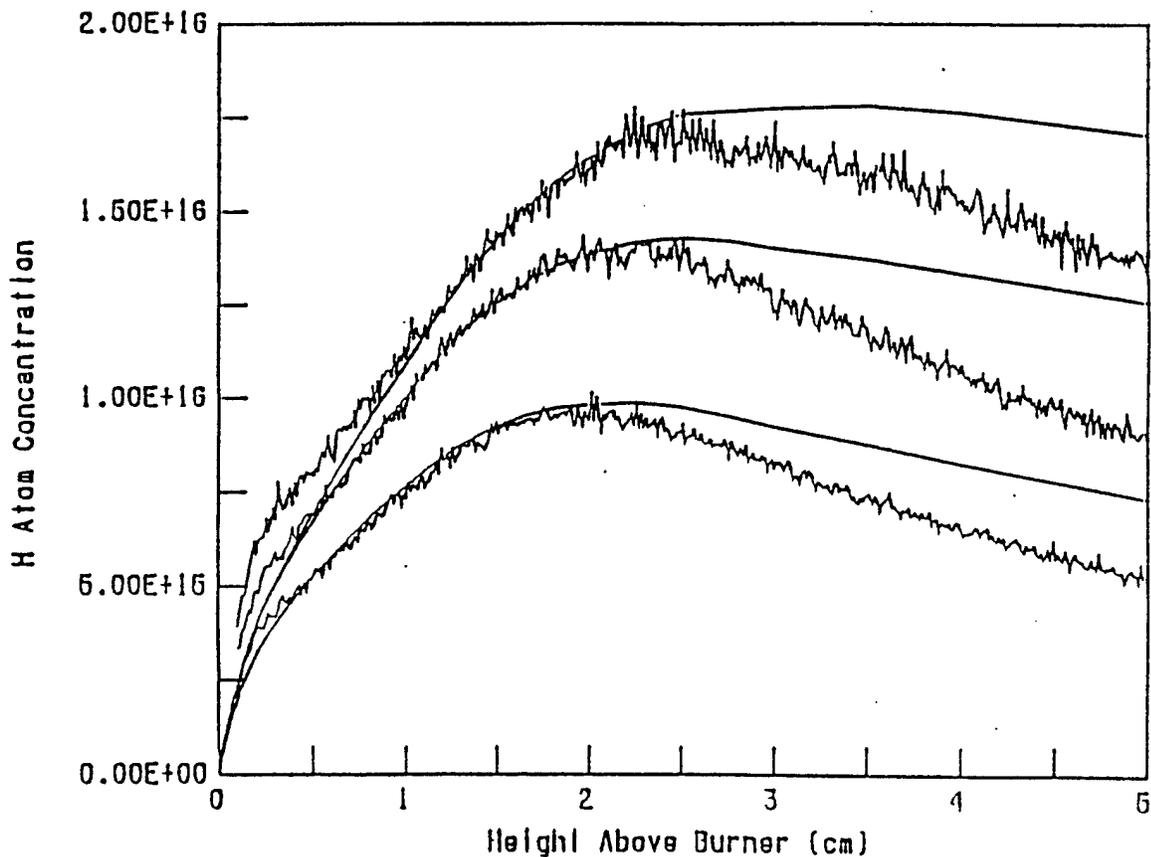


Figure 9. LIF corrected for quenching versus reaction time for rich, stoichiometric, and lean 7.2-Torr, H_2/O_2 flames. Smooth line is model prediction; experiment is normalized only for stoichiometric flame.

Figure 10 compares the measured and predicted atomic hydrogen for a 30-Torr, $f = 1.1$, CH_4/air flame identical to the one extensively studied by Meyer et al.³ Again, the LIF signal is corrected for collisional quenching. The measurement is normalized to the absolute scale of the model prediction at a height 2 cm above the burner. Again, the rise of the atomic hydrogen is well predicted by the model; however, in the burnt gases above the flame front, the model predicts more atomic hydrogen than is observed. We again believe this deviation is the result of radial transport.

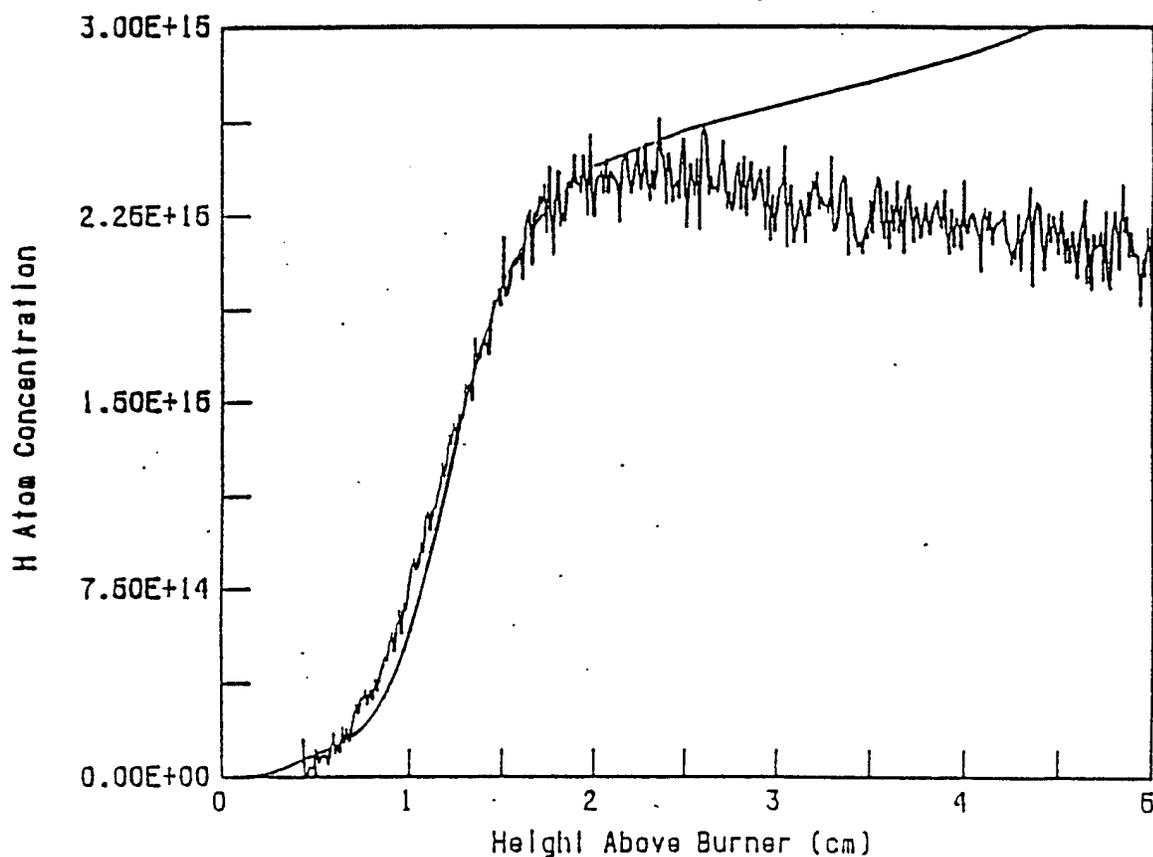


Figure 10. H atom LIF corrected for quenching versus reaction time for 30-Torr, slightly rich, CH_4/air flame. Smooth line is model prediction.

The rate constants for the quenching of excited hydrogen atoms by OH and other H atoms are unknown, and these colliders can be important quenchers in these flames. We chose to set the rate constant of OH quenching to be the same as for H_2O and the rate constant for H the same as

for H_2 . The absolute value of the corrected LIF signal varied significantly with the choice of these quenching rate constants; however, the shape of the profile (the variation with height above the burner) did not appreciably change with the value of these quenching rate constants. Thus, these rate constants are important for absolute H atom LIF calibrations, but they are not important for the relative measurements presented here in Figures 9 and 10.

ASE Measurements

Balmer α ASE was observed in all the flames studied. The ASE signal formed a collimated beam propagating forward and backward along the excitation laser beam. The largest ASE signals were observed in the rich H_2/O_2 flame. We found the ASE signal slightly polarized with a ratio of 3:2, which agrees well with the polarization predicted from the combination of 3S and 3D states initially excited.

In the work reported here, Equations (1) through (6) were solved numerically by using a fourth-order Runge-Kutta scheme and commercial MathCad software. A time step of no more than 4.5 ps was used, and values for the physical constants were taken from the available literature. Figure 11 shows the time evolution of the hydrogen atom state densities predicted by the model for the conditions of the 7.2-Torr H_2/O_2 flame at 2.0 cm above the burner surface. Time zero on the x-axis denotes the arrival of the leading edge of the pump pulse. Due to the high pumping rate of a focused 200-mJ laser pulse, most of the ground state atoms eventually become ionized through a 2+1 REMPI process.

Figure 12 compares the measured and predicted ASE signals in the lean and rich H_2/O_2 flames. The open symbols are the ASE measurements and the closed symbols the model predictions. The ASE measurements are normalized to the absolute value of the model predictions in the burnt gases of the rich flame. The variation between the rich and lean flame for the measured peak ASE agrees well with the prediction. However, the observed ASE rises much faster than predicted in the rich flame and falls much faster than predicted in the lean flame. This deviation is consistent with lower gain in the experiment than in the model. The absolute ASE signal observed is approximately four times smaller than the ASE signal predicted.

Atomic Oxygen Measurements

We also measured simultaneous ASE and LIF of atomic oxygen in a discharge flow. The collimation of the ASE signal was measured as a function of excitation laser pulse energy and confocal parameters. The measurements were compared with our model predictions for ASE

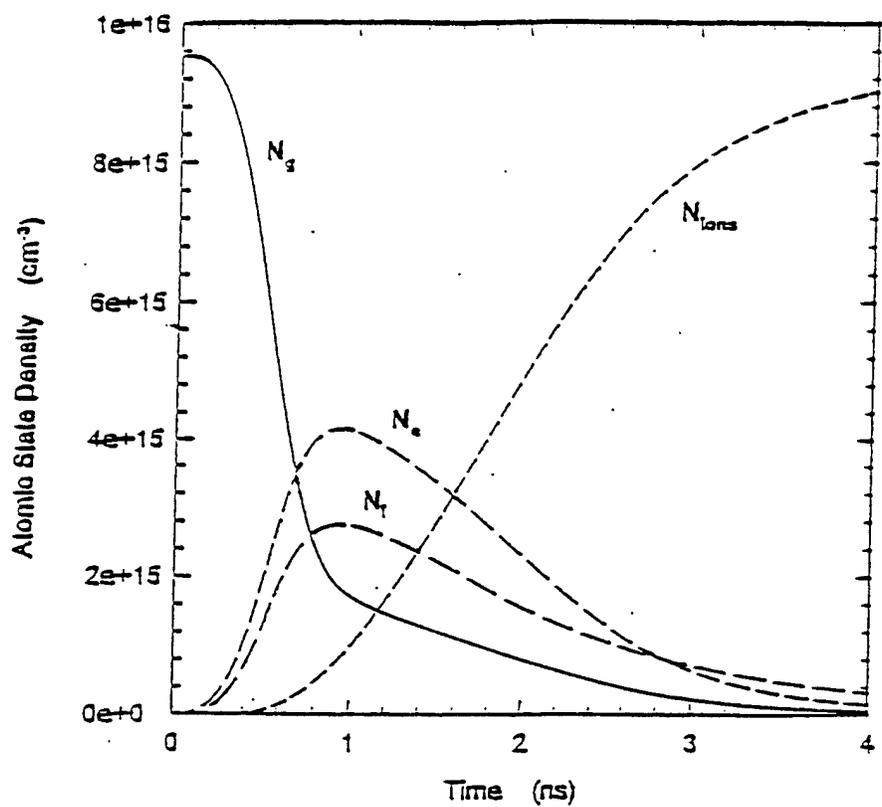


Figure 11. The time evolution of the atomic state densities for a 7.2-Torr H_2/O_2 -rich flame.

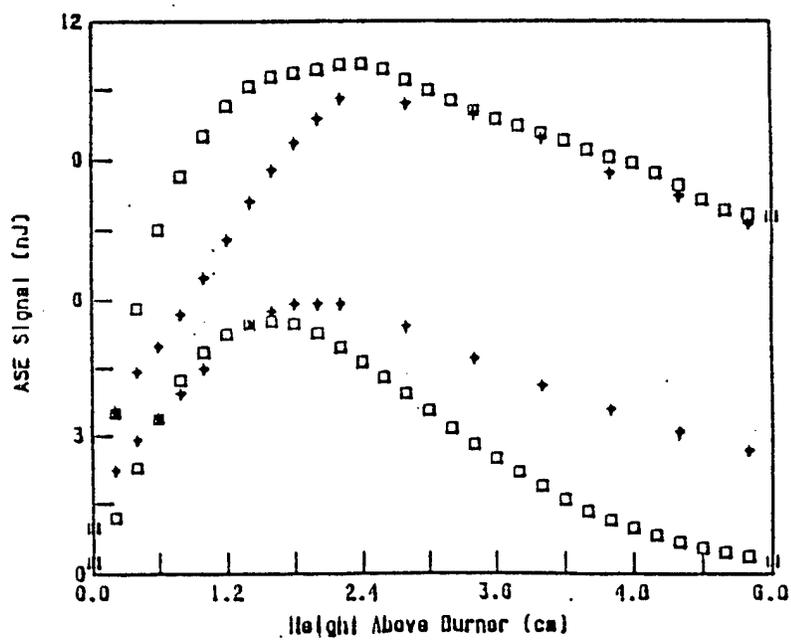


Figure 12. Measured ASE (open symbols) and predicted ASE (closed) for 7.2-Torr rich and lean H_2/O_2 flame.

collimation. Here, we found that spatial variations of the focal volume of the excitation are important and must be included in the ASE model.

Oxygen atoms were excited from the $2p^3P$ ground state to the $3p^3P$ excited with two photons near 226 nm from the doubled output of an excimer pumped dye laser, which is focused through the afterglow of a microwave discharge. The excitation laser pulse energy was varied between 25 mJ and 1 mJ/pulse, and the focusing lens from 10 cm to 1 m focal length. ASE and LIF from the excited $3p^3P$ to the $3s^3S^0$ were observed near 845 nm. The forward ASE was imaged on a CCD camera, and simultaneous LIF was collected normal to both the excitation laser and the gas flow by a filtered red-sensitive photomultiplier tube. Titration of the gas flow was used for absolute calibration LIF signal as a function of atomic oxygen concentration.

We found that the ASE signal from atomic oxygen was dramatically more collimated as the excitation laser pulse energy was increased and/or the focal length of the excitation pulse was increased. The ASE signal near 845 nm was recorded on a CCD camera 52 cm downstream of the focal volume. As the pulse energy increased from 10 to 50 $\mu\text{J}/\text{pulse}$, the solid angle of the ASE signal decreased by approximately a factor of two. If we switched to a 57-cm focal length lens for the 226-nm pump pulse, the ASE was significantly more collimated. The image at 10 $\mu\text{J}/\text{pulse}$ was approximately a 15% larger spot than using 50 $\mu\text{J}/\text{pulse}$, which was nearly the same spot size as the pump pulse. The change in collimation was due to competing processes. For example, near threshold for ASE, the signal beam had a solid angle a factor of two larger than observed with a fivefold increase of pump laser intensity. As the focal length of focusing lens for the excitation laser was increased, larger laser pulse energies were required to reach threshold for ASE. However, non-zero ASE gain over a longer path length promoted a more collimated ASE signal.

We also demonstrated that atom concentrations can be determined from measurements of ASE gain.¹⁹ A cw diode laser was tuned into resonance with the intermediate transition in atomic oxygen. The diode laser was spatially overlapped with the excitation laser pulse, and either gain on the diode laser or depletion of the spontaneous ASE was observed as a function of diode laser intensity. This measurement was conducted in the post-flame gases of a low-pressure premixed flame. The inferred oxygen number density agreed well with predictions of a detailed chemical model of this well characterized flame.

dc-Arcjet Measurements of Atomic Hydrogen

We used a dc-arcjet plasma to produce a flow of argon and hydrogen having a significant dissociation of the molecular hydrogen feedstock with an H atom concentration greater than

$3 \times 10^{16} \text{ cm}^{-3}$. A dc-arc was struck in the apex of a converging/diverging nozzle in a mixture of hydrogen and argon at approximately 6 atmospheres pressure. The effluent from this arc expanded through the nozzle into a reactor maintained at much lower pressure; the reactor pressure was 25 Torr for nearly all the atomic hydrogen measurements. Methane, less than 1% of the feedstock hydrogen, was added into the reactive flow in the diverging nozzle. A luminous plume of reactive gas approximately 1 cm in diameter exited the diverging nozzle and impinged on a water-cooled molybdenum substrate; diamond grew at approximately $50 \mu\text{m/hr}$ beneath the boundary layer from this reactive plume of gas. The optical emission from the plume was collected f6, dispersed with a monochromator, and detected with a photomultiplier.

Langmuir probe measurements²⁰ showed the electron density in the plume to be less than 10 ppm and the electron temperature between 1 and 2 eV. The gas phase precursor to diamond growth must be present at concentrations at least 100 times larger than this ion density to account for the observed diamond growth rate. However, much of the optical emission²¹ from the luminous plume can be attributed to electron impact of atomic hydrogen and CH radicals. The emission from the Swan bands of C_2 is primarily produced by chemiluminescent reaction.

LIF of reactive species in the arcjet plume was excited with light from a pulsed tunable dye laser, and the subsequent fluorescence signal was collected, dispersed, and detected. The spatial resolution was determined by the intersection of the 1-mm-diameter laser beam with the spatially filtered optical collection, producing a LIF spatial resolution of 1 mm^3 . The pulsed LIF signal was distinguished from the bright plume emission with synchronous detection and temporal integration by using a boxcar averager.

On the centerline of the arcjet plume, the CH radical is detected with LIF in either the A-X transition or the B-X transition.²² From the relative intensity of the LIF signal from $N = 4$ and $N = 10$, we can determine the Boltzmann rotational temperature in the electronic ground state of the CH radical. LIF temperature measurements require the detector bandpass to a uniform collection efficiency for all the different transitions excited.

We dispersed the LIF with a monochromator with a wide exit slit to produce a trapezoidal bandpass with uniform collection efficiency for the entire CH B-X (0,0) band. Using a monochromator with a narrow front slit and a wide exit slit, we constructed an optical filter with a trapezoidal bandpass with uniform spectral response for 30 nm. On the centerline of the arcjet plume between the nozzle exit and the substrate, a distance of 38.2 mm, we determined the Boltzmann temperature every 2 mm. Near the nozzle, the rotational temperature increased slightly, remained nearly constant in the freestream of the plume, and then rose rapidly in the boundary layer above the substrate.

The directed velocity of the arcjet plume was determined from the Doppler shift of LIF from NO seeded into the plume. The excitation laser pulse was directed through a small hole in the substrate directly into the oncoming flow of the arcjet plume. The Doppler shift of the excitation wavelength between NO in a cell and NO seeded in the gas flow indicated that the centerline gas velocity was 2.5 km/s.

The electrical power input to the arcjet (1.6 kW) was balanced with power losses due to cooling of the nozzle, enthalpy change in the gas, ionization of the gas, dissociation of H₂, and the directed velocity of the plume. From this calorimetry,²³ we found that 33% of the hydrogen feedstock was dissociated in the arcjet plume. The measured gas velocity was Mach 2.2 for the 46:54 mixture of argon and hydrogen feedstock with 33% hydrogen dissociation. Thus, when the supersonic flow of the arcjet plume impinged on the boundary layer above the substrate, we expected a shock structure to develop. We also expected a pressure rise of 4.5 from a normal isentropic shock structure.

Atomic hydrogen in the arcjet plume was monitored with two-photon excited LIF during diamond film deposition. The LIF signal was calibrated using the calorimetry measurement of hydrogen dissociation. Correlation of the variations of the H atom LIF signal with position in the plume to spatially resolved H atom concentrations required correction for the spatial variation of the collisional quenching. Due to the rapid collisional quenching of atomic hydrogen and a laser pulse length of a few nanoseconds, it was not possible to time resolve the H atom LIF signal at the standard reactor pressure of 25 Torr.

For reactor pressures between 4 and 10 Torr, the H atom LIF quantum yield was directly measured by time resolved LIF as shown in Figure 13. The quenching rates determined from these measurements agreed remarkably well with the calculated quenching from Ar, H₂, and H atoms in the plume and with the room temperature quenching rate coefficients measured by Bitner et al.,¹⁸ which is given in Figure 13 by the dashed lines, with the assumption that the quenching cross section for $n = 3$ H atoms by H atom collisions has the same cross section as quenching by H₂. Therefore, we correct the H atom LIF for quenching using the literature quenching rate coefficients.

The quenching correction for the H atom LIF measurements are very important for reactor pressures above 10 Torr as shown in Figure 14. Here, the solid points are the quenching corrections for the open circles. Above 10 Torr, the quantum yield is dominated by collisional quenching and at our standard condition at 25 Torr, the quenching correction increases the raw relative measurement by a factor of 2.5. The calorimetry measurements are used to put the LIF measurements onto an absolute scale.

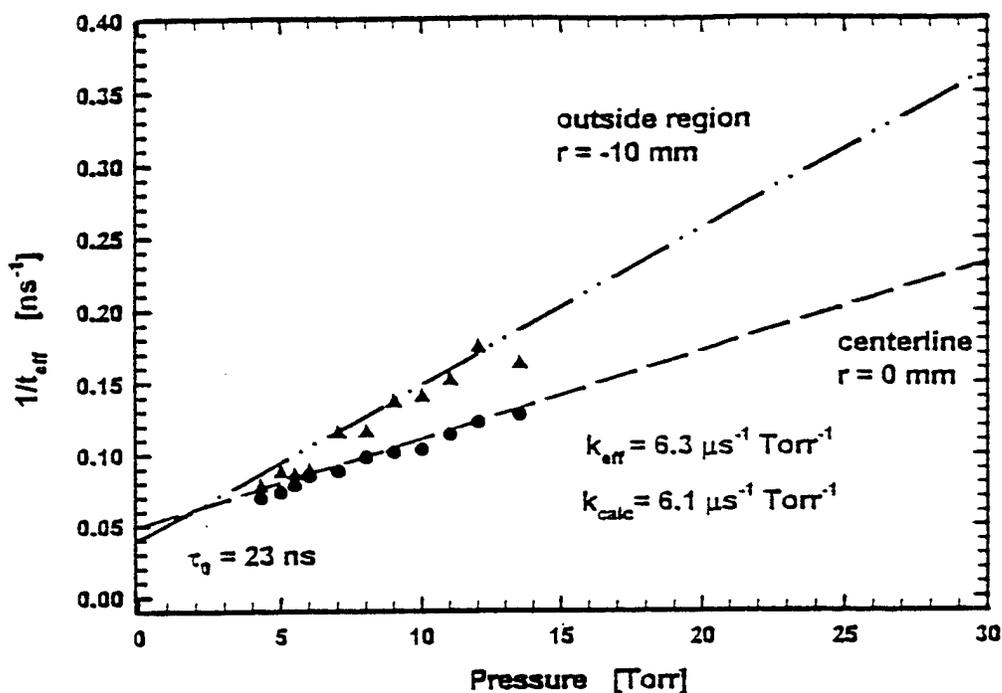


Figure 13. Inverse fluorescence lifetime versus pressure in the center ($x = 0 \text{ mm}$, circles) and at the edge ($r = -10 \text{ mm}$, triangles) of the arcjet plume ($z = 20 \text{ mm}$). Dotted line: calculated effective quenching rate coefficient at $r = 0 \text{ mm}$; dashdot line: calculated effective quenching rate coefficient at $x = -10 \text{ mm}$ with varying temperatures and fractions of dissociation.

We found that nearly one-third of the feedstock hydrogen was dissociated in a 1.6-kW dc-arcjet with a feedstock mixture of 46% hydrogen and 54% argon. The gas temperature of the arcjet plume was measured by laser-induced fluorescence to be 2500 K. Therefore, we found this flow to be kinetically controlled with an atom density far from equilibrium. The plume had an atomic hydrogen concentration of $3 \times 10^{16} \text{ atoms/cm}^3$ more than 10 times the hydrogen atom concentration in the low-pressure flame. The arcjet plume also had a very well-defined gain length. Langmuir probe measurements of electron temperature and ion density showed significantly less than 10 ppm charged particles in the arcjet plume. Therefore, dc-Stark effects are negligible.

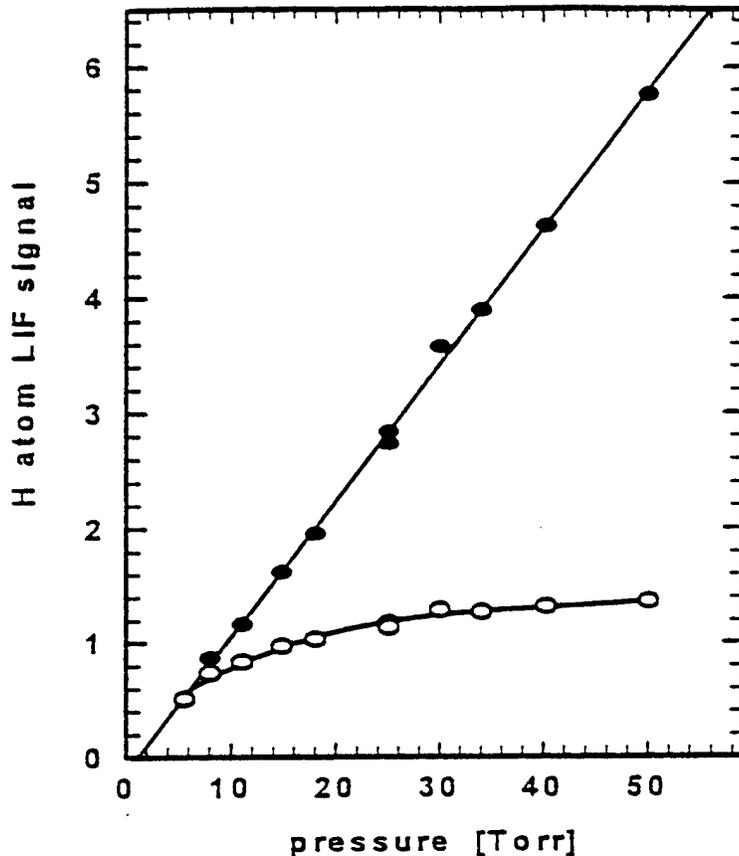


Figure 14. H-atom concentration (open circles) corrected for quenching (filled circles) at $r = 0$ mm and $z = 20$ mm.

In the arcjet plume, we can test the competition between LIF and ASE at very high gain with low enough laser pulse energy that ac-Stark effects can be neglected. In these high gain conditions, we found good agreement between the simple coupled rate model²⁴ and the measurement. We found that it is not necessary to account for the radial distribution of the gain about the centerline of the laser beam or to account for the temporal distribution of the laser pulse energy.²⁴ In the high density of the arcjet plume, we found significant competition between LIF and ASE for narrowband (0.1 cm^{-1}) excitation. However, with a dye laser bandwidth of 1 cm^{-1} we found that the ASE becomes insignificant for excitation energies below 1 mJ/pulse . For 0.25 mJ/pulse , we measured an ASE signal less than 10^{-4} of the LIF signal.

REFERENCES

1. G. W. Faris and M. J. Dyer, "VUV Multiphoton Spectroscopy Using a Raman-Shifted Excimer Laser," *J. Opt. Soc. Am. B*, **10**, 2273-2286 (1993).
2. G. W. Faris and M. J. Dyer, "Multiphoton Spectroscopy Using Tunable VUV Radiation from a Raman-Shifted Excimer Laser," in *Short Wavelength Coherent Radiation: Generation and Applications*, Philip H. Bucksbaum and Natale M. Ceglio, Eds. Optical Society of America, Washington, DC, 1991, pp. 58-61.
3. S. A. Meyer, M. J. Dyer, M. J. Banks, and G. W. Faris, "Experimental Studies using Two-Photon-Resonant Difference-Frequency Mixing with an ArF Excimer Laser," in preparation for submission to *J. Opt. Soc. Am. B* (1997).
4. G. W. Faris and M. J. Dyer, "Two-Photon Excitation of Neon at 133 nm," *Opt. Lett.* **18**, 382-384 (1993).
5. A. Apinov, N. E. Budina, V. M. Reïterov, and L. P. Shishatskaya, "Change in the Spectral Transmission of Magnesium Fluoride Windows Caused by Prolonged Ultraviolet Irradiation," *Sov. J. Opt. Technol.* **50**, 483-485 (1983).
6. L. P. Shishatskaya, P. A. Tsiryul'nik, V. M. Reyterov, and L. N. Safonova, "The Effect of Vacuum Ultraviolet Radiation on the Transmittance of Lithium Fluoride and Magnesium Fluoride Crystals," *Sov. J. Opt. Technol.* **69**, 651-652 (1972).
7. H. Pummer, H. Egger, T. S. Luk, T. Srinivasan, and C. K. Rhodes, "Vacuum-Ultraviolet Stimulated Emission from Two-Photon-Excited Molecular Hydrogen," *Phys. Rev. A* **28**, 795-801 (1983).
8. S. E. Harris and R. B. Miles, "Proposed Third Harmonic Generation in Phase-Matched Metal Vapors," *Appl. Phys. Lett.* **19**, 385-387 (1971).
9. John F. Reintjes, *Nonlinear Optical Parametric Processes in Liquids and Gases*, Academic Press, New York, 1984, pp. 56-57.
10. J. D. McMullen, "Optical Parametric Interactions in Isotropic Materials Using a Phase-Corrected Stack of Nonlinear Dielectric Plates," *J. Appl. Phys.* **46**, 3076-3081 (1975).
11. A. Szilagy, A. Hordvik, and H. Schlossberg, "A Quasi-Phase-Matching Technique for Efficient Mixing and Frequency Doubling," *J. Appl. Phys.* **47**, 2025-2032 (1976).
12. S. A. Meyer and G. W. Faris, "High Power Lyman Alpha Source," in preparation for submission to *Opt. Lett.* (1997).
13. G. C. Bjorklund, "Effects of Focusing on Third-Order Nonlinear Processes in Isotropic Media," *IEEE J. Quantum Electron.* **11**, 287 (1975).
14. G. Hilber, D. J. Brink, A. Lago, and R. Wallenstein, *Phys. Rev. A* **38**, 6231 (1988).

15. J. A. Pobst, I. J. Wysong, and R. A. Spores, "Laser-Induced Fluorescence of Ground State Hydrogen Atoms at Nozzle Exit of an Arcjet Thruster," AIAA 95-1973, 26th AIAA Plasmadynamics and Lasers Conference, June 1995, San Diego, CA.
16. C. A. Mahon, D. E. Heard, M. S. Brown, G. P. Smith, and J. B. Jeffries, "Laser-Induced Fluorescence and Amplified Spontaneous Emission Detection of Hydrogen Atoms in Flames," AIAA 96-0465, 34th Aerospace Sciences Meeting and Exhibit, January, 1996, Reno, NV.
17. K. Kohse-Höinghaus, J. B. Jeffries, R. A. Copeland, G. P. Smith, and D. R. Crosley, Twenty-second Symposium (International) on Combustion, Combustion Institute, Pittsburgh, PA, 1988, 1857; J. B. Jeffries, D. R. Crosley, I. J. Wysong, G. P. Smith Twenty-third Symposium (International) on Combustion, Combustion Institute, Pittsburgh, PA, 1990, p. 1847; D. E. Heard, J. B. Jeffries, G. P. Smith, and D. R. Crosley, Combustion and Flame 88, 137 (1992).
18. U. Bittner, K. Kohse-Hoeninghaus, U. Meier, and Th. Just, Chem. Phys. Lett. **143**, 571 (1988).
19. M. S. Brown and J. B. Jeffries, Applied Optics 34, 1127 (1995).
20. E. A. Brinkman, K. R. Stalder, and J. B. Jeffries, J. Appl. Phys. **81**, 1093 (1997).
21. E. A. Brinkman, G. A. Raiche, M. S. Brown, and J. B. Jeffries, Appl. Phys. B 1997 in press.
22. J. Luque, W. Juchmann, and J. B. Jeffries, J. Appl. Phys. 1997 in press; J. Luque, W. Juchmann, and J. B. Jeffries, Appl. Phys. B. 1997 in press.
23. W. Juchmann, J. Luque, and J. B. Jeffries, J. Appl. Phys. 1997 in press.
24. "Amplified Spontaneous Emission Measurements of Atomic Oxygen and Hydrogen," J. B. Jeffries, D. E. Heard, and M. S. Brown, 33rd Aerospace Sciences Proceedings, AIAA 95-0309, 1995.

PERSONNEL SUPPORTED

The following professional scientists participated in the research supported by this contract in the past year:

TASK 1

- Gregory W. Faris, Research Physicist, Task Leader and Co-Principal Investigator
- Scott A. Meyer, Postdoctoral Associate, experimentalist

- Mark J. Dyer, Research Physicist, specialist in lasers and nonlinear optics
- Michael J. Banks, summer research associate
- David A. Huestis, Associate Director of the Molecular Physics Laboratory, Project Supervisor and Co-Principal Investigator

TASK 2

- Jay Jeffries, Senior Chemical Physicist, Task Leader and Co-Principal Investigator
- Jorge Luque, Postdoctoral Associate, dc-arcjet measurements
- Wolfgang Juchmann, Graduate Student, University of Heidelberg, dc-arcjet measurements
- Christopher R. Mahon, Postdoctoral Associate, ASE model and collimation measurements
- Anna Stampanoni, International Visiting Fellow, Paul Scherrer Institut, Villigen, Switzerland
- Gregory Smith, Senior Chemical Physicist, chemical models of flames and plasma plumes

PUBLICATIONS

1. "Amplified Spontaneous Emission Measurements of Atomic Oxygen and Hydrogen," J. B. Jeffries, D. E. Heard, and M. S. Brown, 31st AIAA Aerospace Sciences Proceedings, AIAA 93-0047, 1993.
2. "Amplified Spontaneous Emission Measurements of Atomic Oxygen and Hydrogen," J. B. Jeffries, D. E. Heard, and M. S. Brown, 33rd Aerospace Sciences Proceedings, AIAA 95-0309, 1995.
3. "Measurement of Atomic Concentrations in Reacting Flows Using Stimulated Gain or Loss," M. S. Brown and J. B. Jeffries, *Appl. Optics* **34**, 1127 (1995).
4. "Laser-Induced Fluorescence and Amplified Spontaneous Emission Detection of Hydrogen and Oxygen Atoms," C. R. Mahon, D. E. Heard, M. S. Brown, G. P. Smith, and J. B. Jeffries, 34th AIAA Aerospace Sciences Proceedings, AIAA-96-0465, 1996.
5. "Atomic Hydrogen Concentration in a Diamond Depositing dc-Arcjet Determined by Calorimetry," W. Juchmann, J. Luque, and J. B. Jeffries, *J. Appl. Phys.*, in press, 1997.
6. "High Power Lyman Alpha Source," S. A. Meyer and G. W. Faris, in preparation for submission to *Opt. Lett.* (1997).

7. "Experimental Studies Using Two-Photon-Resonant Difference-Frequency Mixing with an ArF Excimer Laser," S. A. Meyer, M. J. Dyer, M. J. Banks, and G. W. Faris, in preparation for submission to *J. Opt. Soc. Am. B* (1997).
8. "Laser-Induced Fluorescence and Amplified Spontaneous Emission Detection of Hydrogen Atoms in Low-Pressure Flames," C. R. Mahon, D. E. Heard, M. S. Brown, and J. B. Jeffries, in preparation for submission to *Combustion and Flame* (1997).
9. "Model and Experiment of Two-Photon Excited Laser-Induced Fluorescence and Amplified Spontaneous Emission for Atomic Hydrogen," C. R. Mahon, M. S. Brown, and J. B. Jeffries, in preparation for submission to *Applied Optics* (1997).
10. "Absolute Concentration, Temperature, and Velocity Measurements in a Diamond Depositing dc-Arcjet Reactor," W. Juchmann, J. Luque, J. Wolfrum, and J. B. Jeffries, *Diamond and Diamond Related Mat.*, submitted June 1997.
11. "Two-Photon Laser-Induced Fluorescence of Atomic Hydrogen in a Diamond Depositing dc-Arcjet," W. Juchmann, J. Luque, and J. B. Jeffries, *J. Appl. Phys.*, submitted June 1997.
12. "Measurements of Velocity and Transport in the Plume of a dc-Arcjet During Diamond Deposition," W. Juchmann, J. Luque, and J. B. Jeffries, in preparation for submission to *J. Appl. Phys.* (1997).

INTERACTIONS / TRANSITIONS

PRESENTATIONS

1. "Amplified Spontaneous Emission Measurements of Atomic Oxygen and Hydrogen," J. B. Jeffries, D. E. Heard, and M. S. Brown, 31st AIAA Aerospace Sciences Meeting, Reno, Nevada, January 1993.
2. "Observation of Stimulated Gain from Oxygen Atoms in Low-Pressure Flames," M. S. Brown and J. B. Jeffries, Western States Section of the Combustion Institute, Menlo Park, October 1993.
3. (invited), "Optical Diagnostics of Diamond CVD Plasmas," by J. B. Jeffries in *State-Selected and State-to-State Chemistry II*, John Hepburn, Ed., SPIE, Symposium 2124, Los Angeles, January 1994.
4. "Nonlinear Laser Diagnostic Techniques for Combustion and Plasma Processes," D. L. Huestis, G. W. Faris, and J. B. Jeffries, AFOSR Contractors Meeting for Propulsion, Lake Tahoe, CA, June 8-10, 1994.
5. "Amplified Spontaneous Emission Measurements of Atomic Oxygen and Hydrogen," J. B. Jeffries, D. E. Heard, and M. S. Brown, 33rd Aerospace Sciences Meeting, Reno, Nevada, January 1995.

6. "Laser-Induced Fluorescence and Amplified Spontaneous Emission Detection of Hydrogen Atoms in Low-Pressure Flames," D. E. Heard, M. S. Brown, G. P. Smith, J. B. Jeffries, and D. R. Crosley, Western States Section of the Combustion Institute, San Antonio, TX, April 1995.
7. "Nonlinear Diagnostics for Combustion and Plasma Processes," D. L. Huestis, G. W. Faris, and J. B. Jeffries, AFOSR Contractors Meeting for Propulsion, Ann Arbor, MI, June 1995.
8. "Amplified Spontaneous Emission Measurements of Atomic Oxygen in Flames," J. B. Jeffries and M. S. Brown, Gordon Research Conference on Laser Diagnostics, Plymouth, NH, July 1995.
9. "Progress in High Power Broadly Tunable VUV Generation," G. W. Faris, M. J. Dyer, and M. Banks, Paper WW6, Joint Optical Society of America Annual Meeting - Eleventh Interdisciplinary Laser Science Conference, Portland, Oregon, September 10-15, 1995.
10. "Amplified Spontaneous Emission for O and H Atom Concentration Measurements," R. Mahon, A. Stampanoni, and J. B. Jeffries, Optical Society of America Annual Meeting, Portland, OR, September 1995.
11. "Laser-Induced Fluorescence and Amplified Spontaneous Emission Detection of Hydrogen and Oxygen Atoms," C. R. Mahon, D. E. Heard, M. S. Brown, G. P. Smith, and J. B. Jeffries, 34th AIAA Aerospace Sciences Meeting, Reno, NV, January 1996.
12. "Nonlinear Laser Diagnostic Techniques for Combustion and Plasma Processes," D. L. Huestis, G. W. Faris, and J. B. Jeffries, ARO/AFOSR Contractors Meeting for Chemical Propulsion, Virginia Beach, VA, June 1996.
13. "Resonantly Enhanced Difference Frequency Mixing in the Lyman- α Region," S. A. Meyer, M. J. Dyer, M. J. Banks, and G. W. Faris, Paper CThL6, Conference on Lasers and Electro-Optics (CLEO), Anaheim, CA, June 2-7, 1996.
14. (invited), "Optical Measurements to Characterize a dc-Arcjet Plume During Diamond CVD," J. B. Jeffries, Gordon Research Conference on Diamond Thin Films, Plymouth, NH, August 1996.
15. "Atomic Hydrogen in a dc-Arcjet Plasma Determined by Calorimetry," W. Juchmann, J. Luque, and J. B. Jeffries, Western States Section of the Combustion Institute, Paper 96F-064, USC, October 1996.
16. "VUV Generation near Lyman Alpha Using Resonantly Enhanced Difference Frequency Generation," S. A. Meyer, M. J. Dyer, M. J. Banks, and G. W. Faris, Paper C-00203, Optical Society of America Annual Meeting - 12th Interdisciplinary Laser Science Conference, Rochester, NY, October 20-25, 1996.
17. "Two-Photon Laser-Induced Fluorescence of Atomic Hydrogen in a Diamond Depositing dc-Arcjet," W. Juchmann, J. Luque, and J. B. Jeffries, Western States Section of the Combustion Institute, Paper 97S-014, Livermore, CA, April 1997.

18. (invited), "Optical Measurements to Characterize a Diamond Deposition in a dc-Arcjet," J. B. Jeffries, Gordon Research Conference on Laser Diagnostics for Combustion, Plymouth, NH, July 1997.
19. (invited), "Optical Measurements to Characterize a dc-Arcjet Plasma," J. B. Jeffries, Annual Meeting of the Optical Society of America, Long Beach, CA, October 1997.

INTERACTIONS

We have served as informal advisors on aspects of the work supported by this contract in the following technical interactions.

- Tim Edwards, Wright-Patterson AFB - supercritical diagnostics and diagnostics needs 1994.
- Bish Ganguly, Wright-Patterson AFB - vuv diagnostics and soot formation, atom diagnostic measurements, dc-arc thrusters 1994.
- Galen King, Purdue University - vuv diagnostics and picosecond diagnostics 1994.
- Bill Larson, Edwards AFB - vuv diagnostics 1994.
- Richard Chang, Yale University - vuv diagnostics, droplet diagnostics, and Brillouin scattering 1994.
- Scott Meyer, NASA - continuing informal conversations on vuv generation and diagnostics 1994.
- Ingrid Wysong, Edwards AFB - extensive discussions about atom diagnostics in dc-arc jet thrusters 1994.
- David Weaver, Edwards AFB, discussions on quantitative LIF 1994.
- Ron Hanson, Stanford University, extensive discussions with Hanson and co-workers on diode laser measurements, also the loan of a diode laser 1994.
- Ingrid Wysong, Phillips Laboratory, Edwards AFB, extensive discussions about hydrogen atom measurements in dc-arcjet plumes; we will model ASE and LIF for the conditions used in her experiments. Significant interaction at 1994 Optical Society and 1995 Plasma Diagnostics AIAA Meeting on atom diagnostics in dc-arc jet thrusters.
- Douglas Bamford, Deacon Research, Palo Alto, California, extensive discussions about oxygen atom measurements in NASA's large scale dc-arcjet, which is used to study shuttle tile re-entry. Bamford has made LIF measurements in this arc, and we will model the ASE to determine if the ASE has depleted the measured LIF signal. Significant interaction at 1995 Plasma Diagnostics AIAA meeting.

- Ron Hanson, Stanford University, extensive discussions with Hanson and co-workers on diode laser measurements including the loan of a diode laser; continuing conversations on diode laser diagnostics; frequent visits to Stanford University in 1995.
- Michael Winter, UTRC, ongoing informal discussions on nonlinear gas and liquid phase diagnostic measurements. Significant interactions at the AFOSR Contractors' Meeting, and at the 1995 Gordon Conference on Laser Diagnostics.
- Michael Frenklach, University of California, Berkeley; informal discussions on soot and diamond nucleation in gas phase flows.
- Michael Brown, MetroLaser, Irvine, California, extensive collaboration on the modeling of ASE. (Note: Dr. Brown worked at SRI as a postdoctoral associate in the Laser-Based Diagnostics Group of the Molecular Physics Laboratory.) Dr. Brown visited SRI in 1995.
- Tim Edwards, Wright-Patterson AFB - supercritical diagnostics and diagnostics needs 1995.
- Bish Ganguly, Wright-Patterson AFB - vuv diagnostics and soot formation, atom diagnostic measurements, and dc-arc thrusters 1995.
- Galen King, Purdue University - vuv diagnostics and picosecond diagnostics 1995.
- Bill Larson, Edwards AFB - vuv diagnostics 1995.
- Richard Chang, Yale University - vuv diagnostics, droplet diagnostics and Brillouin scattering 1995.
- Scott Meyer, NASA (now at SRI) - informal conversations on vuv generation and diagnostics 1995.
- Art Fontijn, Rensselaer, discussions on laser diagnostics 1995.
- Jim Reilly and Sheldon Toepke of McDonnell Douglas Aerospace and Mike Gehron of Pratt & Whitney, discussions of Air Force pollution prevention needs, including propulsion and combustion 1995.
- Brief interactions with Alan Garscadden of Wright Lab 1995.
- Contractors' Meeting June 1996, Virginia Beach:
 - Ingrid Wysong, Philips Laboratory, Edwards AFB discussions on two-photon LIF and ASE from atomic hydrogen.
 - Discussions with Tim Edwards and Mel Roquemore (Wright Labs) and Pablo Debenedetti (Princeton University) on supercritical fluids.
 - Discussions with Mitat Birkan (AFOSR), and Bill Rich and Vish Subramaniam (Ohio State) on plume signatures.

Discussions with Richard Chang (Yale) on stimulated scattering measurements.

Discussions with Doug Talley and Roger Woodward (Phillips Lab, Edwards AFB) on supercritical diagnostics.

- Conference on Lasers and Electro-Optics, June 1996, Anaheim, California:

Discussions with Charles Strauss (Los Alamos) on vuv generation and applications.

- May 1996, visit AFOSR with Tishkoff and Birkan:

Discussions on super critical flow diagnostics, arcjet thrusters, and fuel/air mixing issues.

- January 1996, AIAA Aerospace Sciences Meeting, Reno, NV:

Discussions with Dave Weaver, Phillips Lab, Edwards AFB, on LIF diagnostics in arcjet plumes.

Discussions with Mel Roquemore, Wright Labs, on fuel coking at high temperature and pressure.

- Ingrid Wysong, Philips Laboratory, Edwards AFB, telephone conversations on diagnostics of ion thrusters, March 1997.
- Tim Edwards, Wright Patterson AFB, (1993-1997) telephone conversations on diagnostics of high temperature fuels (1996,1997).
- Charles Strauss, Los Alamos, telephone conversation (1996) and conversation at 1997 Conference on Lasers and Electro-Optics on vuv generation and other diagnostics.
- Professor C. K. Law, Department of Mechanical and Aerospace Engineering, Princeton, University, discussions at the 1997 AIAA Aerospace Sciences Meeting in Reno NV and at the 1997 Microgravity Combustion Workshop on the influence of stretch on flame chemistry.
- Dr. Dave Weaver, Philips Laboratory, Edwards AFB, discussions at the 1997 AIAA Aerospace Sciences Meeting in Reno NV on quantitative atom diagnostics in dc-arcjet thrusters.
- Professor Marshall Long and Professor Mitchell Smooke, Department of Mechanical Engineering, Yale University, e-mail correspondence and discussions at the 1997 Microgravity Combustion Workshop on chemiluminescent chemical mechanisms and the origins of CH emission in flames.
- Dr. Ingrid Wysong, Philips Laboratory, Edwards AFB, extended email correspondence on quantitative measurements of H atoms, H atom quenching, and diagnostic measurements in dc-arcjet thrusters.

- Xx, Wright Laboratory, Wright-Patterson AFB, discussions on quantitative laser-based measurements of atoms in plasmas at the 1996 Optical Society Annual Meeting in Rochester, NY.
- Dr. Mark Crofton, Aerospace Corporation, continued discussions at the 1996 Optical Society Annual Meeting in Rochester, NY, and e-mail correspondence on optical diagnostics in dc-arcjet thrusters.
- Dr. Douglas Talley, Fundamental Technologies Division, Phillips Laboratory, Edwards AFB, discussions on arcjet diagnostics and fluid flow at the 1997 AIAA Aerospace Sciences Meeting in Reno, NV.
- Professor Ian Kennedy, University of California Irvine, May 1997 visited UC Irvine and presented Departmental Seminar on research results from AFOSR contract.

TRANSITIONS

None

DISCOVERIES

The following technical concept brief was filed based on an invention conceived under this project: *A Simple and Efficient High-Power VUV Source*, Gregory W. Faris, inventor.

A new, high power, Lyman α light source was discovered.

HONORS / AWARDS

Gregory W. Faris: ARCS Fellow, 1985-1986.

David L. Huestis: Fellow of the American Physical Society (since 1990).

Jay B. Jeffries: Executive Committee of the Western States Section of the Combustion Institute, Chairman, 1995-1997; Applied Spectroscopy Topical Group of the Optical Society of America, Vice Chairman, 1994-1996; Chairman, 1997-1998; OSA Topical Meeting in Laser Applications for Chemical and Environmental Analysis, Orlando, FL, Chairman, March 1996, elected fellow of the Optical Society of America, topical editor for Applied Optics, 1996.