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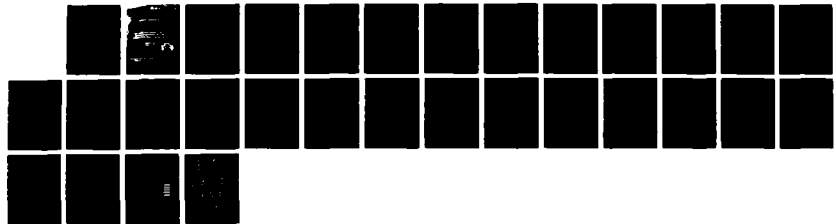
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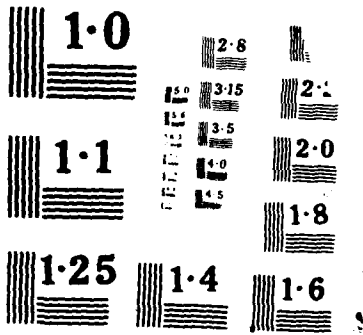
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INTERNAL REPORT BRL-TR-2798

# LASER PHOTOPRODUCTION AND SENSITIVE DETECTION OF CARBON IONS FROM SIMPLE FUEL MOLECULES

ROSARIO C. SAUSA  
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19. ABSTRACT (Continue on reverse if necessary and identify by block number) Excimer lasers are currently being used as a means of photofragmentation and fragment excitation for chemical detection purposes, as well as for activation of reactive mixtures. In the case of small fuel molecules, this phenomenon is generally poorly understood and needs to be studied further. This report, therefore, describes experiments aimed at a better understanding of the interaction of simple carbon-containing fuel molecules with the ArF excimer laser, particularly with respect to potential analytical applications. Such an application, for instance, would be for a gas chromatographic detector of propellant pyrolysis products. Specifically, in this report we describe experiments where carbon atoms were generated by multiphoton photolysis of CO, CH <sub>4</sub> , C <sub>2</sub> H <sub>2</sub> , C <sub>3</sub> H <sub>8</sub> , CH <sub>3</sub> OH and CH <sub>3</sub> COCH <sub>3</sub> using the ArF (193 nm) laser. Their presence was detected by two sensitive methods, laser induced fluorescence (LIF) and resonance ionization emission spectroscopy (RIES), both of which take advantage of the coincident overlap between the ArF laser and the <sup>1</sup> D <sub>2</sub> + <sup>1</sup> P <sub>1</sub> <sup>o</sup> transition at 193.1 nm with emission detection at 247.9 nm. The			
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RIES method detects single photons resulting from the photolytically produced carbon ion recombination and relaxation processes. An enhancement in the RIES signal was observed when a second, tunable laser pulse operating at 247.9 nm followed the ArF laser pulse. Both methods can thus be used for the sensitive detection of the photolytic precursor molecules using the relatively simple experimental apparatus described in this report. Detection levels considerably lower than  $10^{11}/\text{cc}$  for LIF and  $10^{12}/\text{cc}$  for RIES can be estimated based on the observed rates of signal production.

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## I. INTRODUCTION

Laser induced fluorescence of atomic species is a particularly effective method for their detection with demonstrated sensitivities down to the 100 atoms/cm<sup>3</sup> detection level.<sup>1</sup> Traditional LIF has been of limited utility, however, for the detection of light atoms since, typically, their one-photon resonances appear in the far uv or vuv region. Due to the current short wavelength limitation of commercial tunable laser systems of ~200 nm, it is still not possible to detect many of these atoms by single-photon LIF. Two or more photon LIF, however, has recently been utilized to detect the H,<sup>2</sup> O,<sup>3</sup> N,<sup>3</sup> and C<sup>4</sup> atoms in a low pressure environment and the detection of the H and O atoms has even been successfully accomplished in a hostile environment such as flames.<sup>5,6,7</sup> Unfortunately, multiphoton processes cannot usually be driven as effectively as single-photon processes, and this inefficiency can cause a substantial loss of analytical sensitivity.

For the C atom case, there exists an unusual spectroscopic situation which was first reported by Bokor, et al.,<sup>8</sup> involving a coincident overlap between the ArF laser output and the fully allowed  $^1D_2 + ^1P_1^0$  transition at 193.1 nm (see Figure 1). The analytical utility of this situation is further enhanced by the fact that emission at 247.9 nm, due to the strong  $^1P_1^0 + ^1S_0$  transitions can be detected with little or no background noise due to the scatter of the pump laser radiation. This detection scheme was used to detect C atoms in a carbon arc,<sup>9</sup> and from uv laser photolysis of CO,<sup>8</sup> and C<sub>3</sub>O<sub>2</sub>.<sup>10,11</sup> The rate limiting step for full exploitation of this scheme for the sensitive analysis of C atoms and/or their precursor molecules is the efficient production of the C atoms into the metastable  $^1D_2$  state.

The purpose of this report is to explore the analytical utility of the spectroscopic schemes given in Figure 1 for the detection of C atoms and particularly for the detection of their precursor molecules. In our experiments C ( $^1D_2$ ) atoms were generated by the photolysis of CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>3</sub>H<sub>8</sub>, CH<sub>3</sub>OH and CH<sub>3</sub>COCH<sub>3</sub> using the ArF laser. Since the output linewidth of the ArF laser is ~100 cm<sup>-1</sup>, only a small fraction of the available energy pumps the transition at 193.1 nm. Figure 1 also shows that the absorption of a second ArF photon will cause the C atoms to ionize. This ionization, which always occurs to some extent whenever C ( $^1D_2$ ) atoms are exposed to ArF radiation, gives rise to our second method of detection called resonance ionization emission spectroscopy (RIES). This method, which was first demonstrated on Hg atoms,<sup>12</sup> is based on the fact that once C ions are formed, and in the absence of any further energy input, they will eventually neutralize and come to thermal equilibrium. One of the pathways for an excited neutral recombination product to lose energy is through the emission of radiation. Thus, single photons at the wavelengths of strong atomic transitions are generated and detected with great sensitivity, following the initial ionization process. We have observed RIES signals at 247.9 nm due to the formation of C ions as shown in Figure 1 and have explored some of the characteristics of this process which we present in this report. An added impetus for exploring the potential of the ArF laser LIF and RIES methods for the sensitive detection of carbon-containing photochemical precursors, is the fact that the detection methods are instrumentally rather simple, requiring only a fixed frequency laser and standard photodetector and photon counting electronics. The results of our limited survey of parent molecules are encouraging in this respect and are also presented in this report.

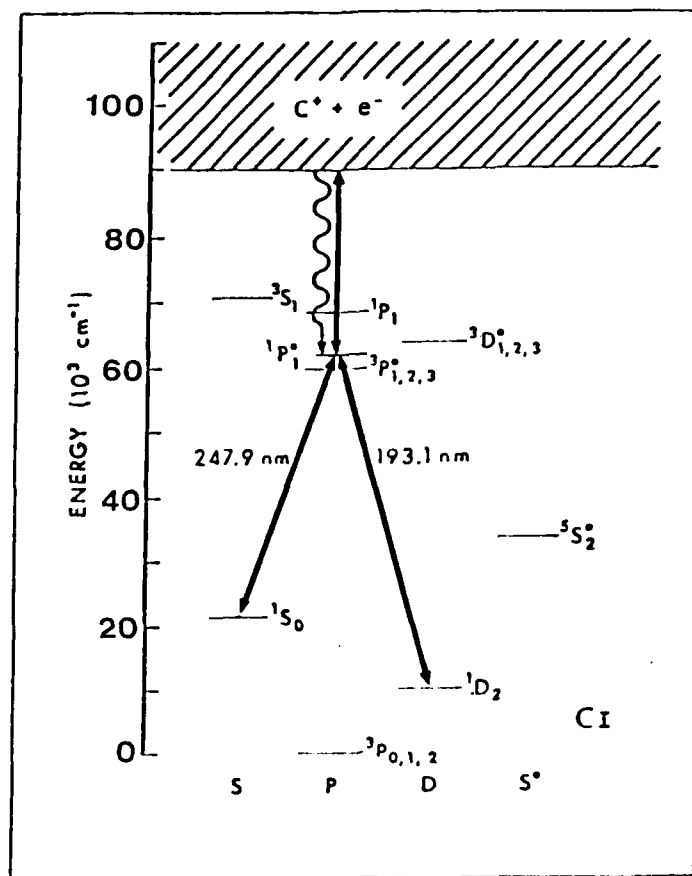


Figure 1. Partial Energy Level Diagram for Carbon Atoms Showing the LIF Transitions (Solid Lines) and the Source of RIES Single Photons (Wavy Line)

## II. EXPERIMENTAL

A schematic diagram of the experimental system is shown in Figure 2. A Lumonics excimer laser model 861M operating with ArF (193 nm) was employed as the photolysis source. Typical energies up to 15 mJ were used at a repetition rate of 10 pps with a pulse duration of 10-15 nsec at FWHM. The laser beam was focused by a 200 mm focal length lens into the cell. Carbon atom fluorescence was also induced by a 247.9 nm beam generated by mixing the frequency doubled Quanta-Ray Nd:YAG pumped dye laser radiation (PDL with DCM dye) with the 1.06 $\mu$  Nd:YAG fundamental in a Quanta-Ray WEX system. This probe beam had an energy of  $\sim 0.35$  mJ/pulse with a pulse width of  $\sim 6$  nsec at FWHM. It was unfocused and counter-propagated along the same axis as the photolysis beam. Typical time delays between the two laser pulses were in the 100-200 nsec range. A representation of the timing arrangement is shown in Figure 3.

Experiments were conducted under flow conditions (linear velocity  $\sim 10^3$  cm/sec) in order to avoid the build-up of reaction products and/or depletion of reactants as well as the outgassing of carbon-containing species from cell walls. The cell utilized was a six-way stainless steel cross fitted

with suprasil windows. The fluorescence, whether prompt (ArF) or delayed (Nd:YAG/dye), was viewed perpendicularly to the pump/probe laser axis and collected by a pair of lenses onto the slit of a 0.35 meter McPherson monochromator fitted with a 1200 L/mm grating blazed for 250 nm. The slits of the monochromator were varied from 35-2000 microns. For LIF measurements, photodetection was achieved with an EMI 9558QA photomultiplier tube. The signal was amplified and digitized by a 7912AD Tektronix digitizer (7A24 amplifier with 0.9 nsec rise time, 7B90P timebase) which was interfaced with a PDP 11/04 computer. For spectral recordings, the output of the PMT was fed into a PAR162 boxcar averager and recorded on a chart recorder. For RIES, the output of the PMT was fed into an Ortec amplifier/discriminator Model 9302 and then into a photon counter Model 9315. The signal was typically accumulated up to 30 seconds and the average of a minimum of two runs was taken. In these experiments, the dark count level was mostly due to the electrical noise pick-up from the excimer laser by the single photon counting electronics.

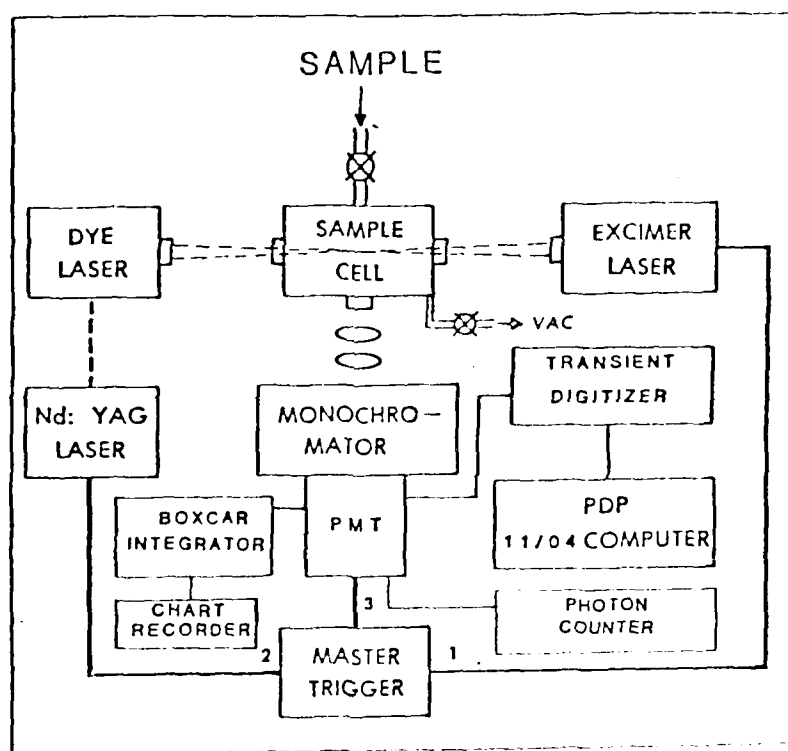


Figure 2. Experimental Schematic for the Detection of LIF and RIES Signals

The pump and the probe laser energy was varied by introducing various transmitting filters (Acton Research) into the beam path and measured by a volume absorbing calorimeter (Sciencetech). Total cell pressure ranged from  $10^{-3}$ -100 torr and was measured with a Datametric 1012 Barocel manometer and a Wallace and Tiernan pressure guage.

Nitrogen, methane, carbon monoxide, acetylene, and propane were taken from standard grade cylinders without purification. Methanol (High purity HPLC grade) was obtained from Burdick and Jackson Laboratories and acetone

(Baker organic residue analyzed) from the Baker Chemical Co. Both methanol and acetone underwent freeze-thaw clean out before each set of experiments. The purity of  $C_2H_2$  is >99% with air as the principal contaminant. An infrared analysis of the acetylene revealed an acetone impurity of <0.5%.

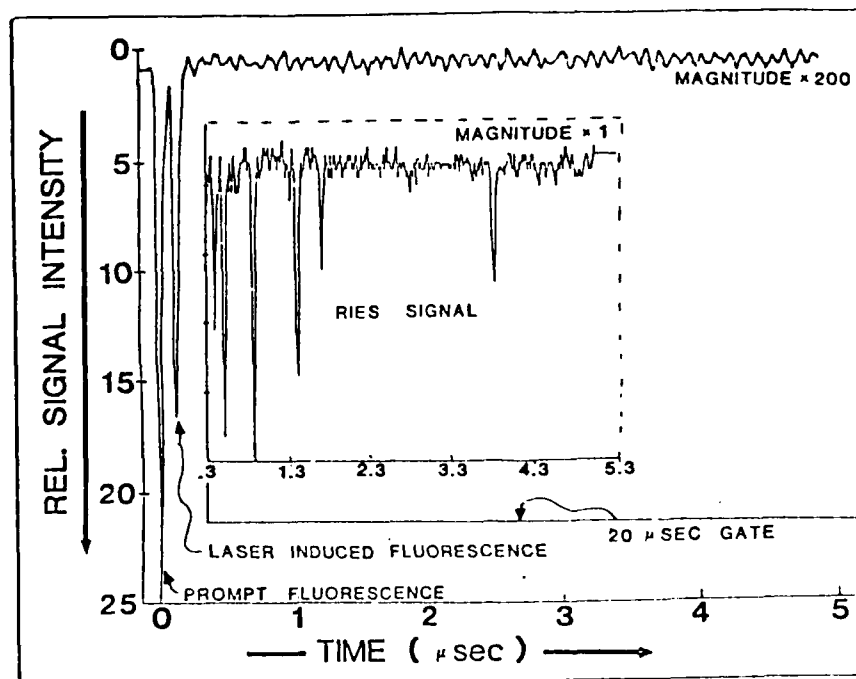


Figure 3. Timing Sequence for the Detection at 247.9 nm of the Prompt ArF LIF, Delayed Nd:YAG/Dye Laser LIF and RIES Single Photons with all of the Carbon Atom Emission Intensities Corrected for Scattered Light. The Photon Counter Gate Width was Set at 20  $\mu$ sec to Capture all RIES Single Photons

### III. RESULTS AND DISCUSSION

The ArF laser is attractive for detecting C atoms and their precursors by the methods described in this report due to the relative simplicity of the necessary equipment. Unfortunately, the only laser parameter that can be explored to better characterize these methods is the variation of laser energy. It is certainly possible to tune the ArF radiation within a limited wavelength range, but this has the disadvantage of possibly affecting the photochemical pathways for the creation of C ( $^1D_2$ ) atoms as well as the fluorescence signals arising from pumping the transition at 193.1 nm.<sup>2</sup> It can be seen from Figure 1 that if the ArF laser photolysis leads to the formation of C ( $^1D_2$ ) atoms, then, at the end of the ArF laser excitation pulse, there should be a distribution of C atoms in the  $^1D_2$  and  $^1S_0$  energy levels as well as some C ions formed. We take advantage of the presence of the metastable C ( $^1S_0$ ) atoms, produced either through the 247.9 nm fluorescence pathway or by nascent photolysis, by pumping the reverse transition with emission detection at 193.1 nm. This is accomplished by a second, tunable Nd:YAG pumped dye laser which is time delayed by one to two hundred nanoseconds from the ArF

laser. Thus, an LIF excitation spectrum is generated and shown in Figure 4 with the expected advantage that the scattered light problem is completely avoided by monitoring emission at 193.1 nm.

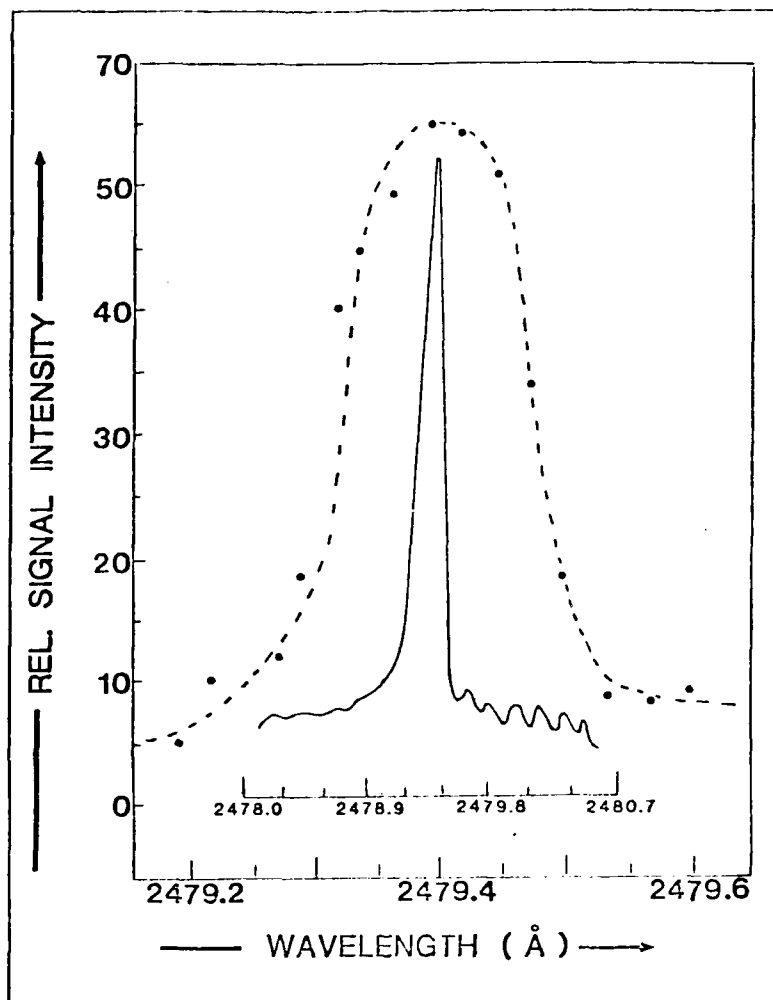


Figure 4. Carbon Atom Excitation Spectra Using the Tunable Nd:YAG/Dye Laser Time Delayed After the ArF Pulse. Prompt LIF (Solid Line) and Delayed RIES (Dashed Line) Signals were Monitored at 193.1 nm

The second laser also made it possible to establish an unambiguous saturation curve for the LIF process. Such a curve is given in Figure 5 and it shows that, as expected, the LIF signal is easily saturated with modest laser energies due to the nature of the strong transition involved. An additional advantage of using a second laser is that it gave us an opportunity to confirm our interpretation of the single photon signals we were observing at 247.9 nm following the ArF laser pulse. As illustrated in Figure 1, the absorption of a second photon at 247.9 nm by  $C(1S_0)$  atoms, should lead to the formation of more C ions and, therefore, a larger RIES signal. This is in fact what was observed, and the RIES excitation spectrum is shown in Figure 4. As can be clearly seen, the RIES excitation spectrum tracks the LIF one very closely.

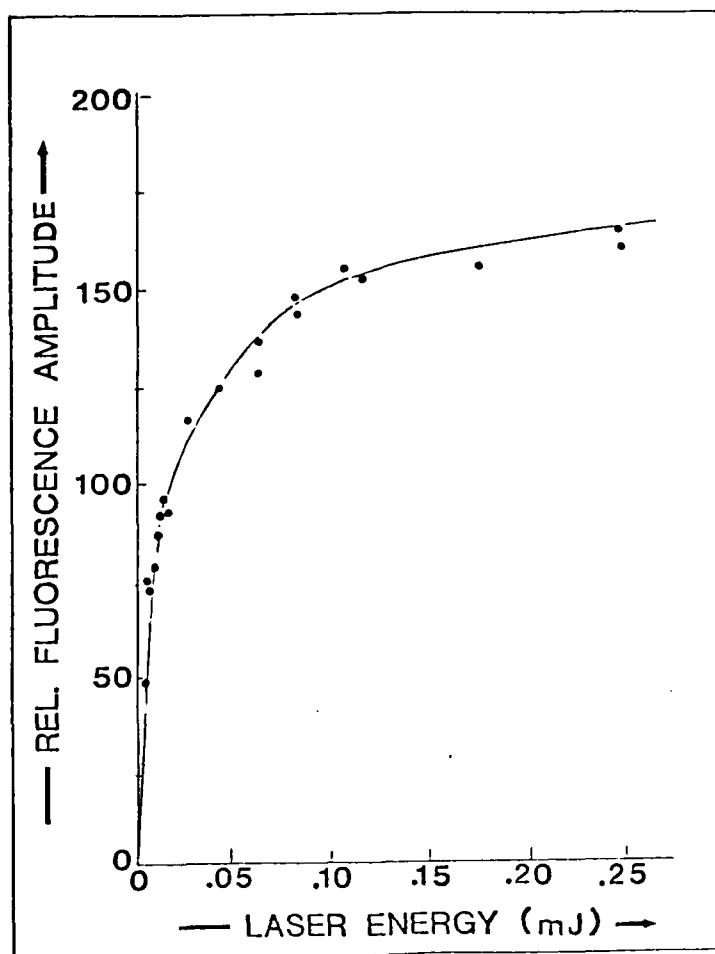


Figure 5. Saturation Curve for the C Atom Transition at 247.9 nm Using the Nd:YAG/Dye Laser

As mentioned before, a major goal of this study was to explore the analytical utility of these two methods for the sensitive detection of carbon-containing precursors. We, therefore, proceeded to measure the relative LIF signal production efficiency for CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>3</sub>H<sub>8</sub>, CH<sub>3</sub>OH and CH<sub>3</sub>COCH<sub>3</sub> under an identical set of experimental conditions. The results are presented in Table 1. It is clear that C<sub>2</sub>H<sub>2</sub> and CH<sub>3</sub>COCH<sub>3</sub> are particularly efficient in generating LIF signals. In the case of C<sub>2</sub>H<sub>2</sub>, this was not too surprising since a previous study by McDonald, et al. indicated a strong interaction between C<sub>2</sub>H<sub>2</sub> and the ArF laser.<sup>13</sup> In their paper, emission bands from various excited photochemical products such as CH and C<sub>2</sub> were presented and their dependencies on laser pulse energy determined. They did not, however, report any C-atom emissions. We chose C<sub>2</sub>H<sub>2</sub> as our C-atom precursor for further characterization of both detection methods. Figure 6 shows the dependence of the LIF and RIES signals on the C<sub>2</sub>H<sub>2</sub> pressure. For LIF detection, most of the data reflect signals generated under "collision-free" conditions. This is certainly not the case for the RIES signals since the detection gate width is in the microsecond region.

TABLE 1. Relative ArF LIF Signal Intensity for C-atom Emissions at 247.9 nm From Different Photolytic Precursor Molecules<sup>a</sup>

Photolytic Precursor	Relative LIF Emission
CO	$1.8 \times 10^{-2}$
CH <sub>4</sub>	$1.5 \times 10^{-3}$ b
C <sub>2</sub> H <sub>2</sub>	0.38
C <sub>3</sub> H <sub>8</sub>	$3.0 \times 10^{-3}$ b
CH <sub>3</sub> OH	0.21
CH <sub>3</sub> COCH <sub>3</sub>	1

- a. Average Laser Energy = 10 mJ, Gas Pressures = 100 mtorr  
 b. Measured at 1 torr pressure due to low signal strength

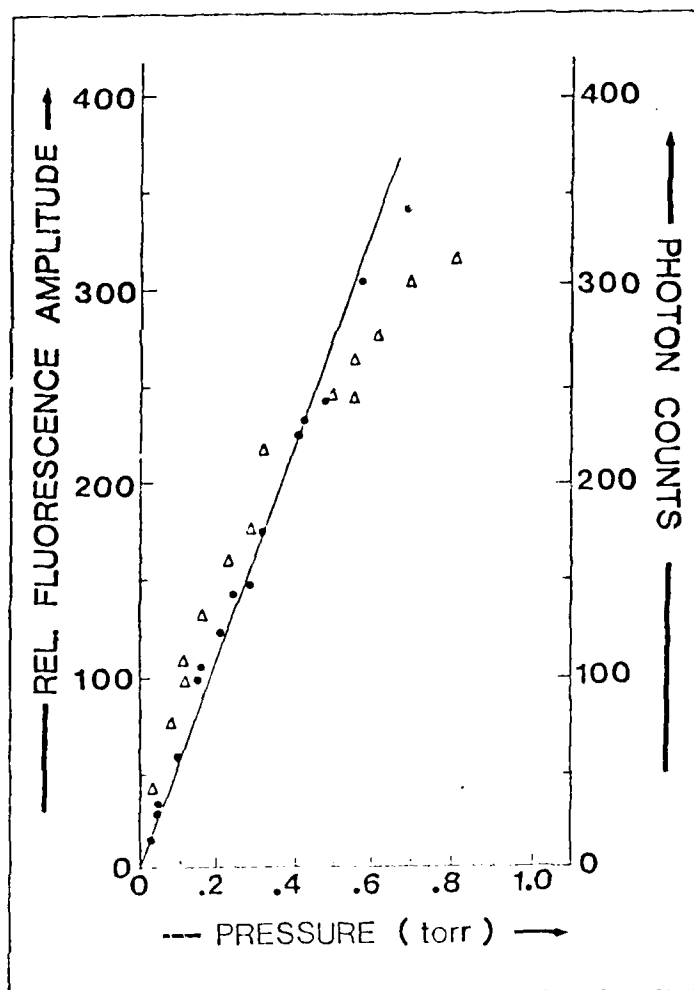


Figure 6. LIF (●) and RIES (Δ) Signal Dependence on C<sub>2</sub>H<sub>2</sub> Pressure

The estimates of the absolute detection limit for carbon-containing precursors by LIF or RIES depends on a number of factors including the collection optics, slit widths, ArF laser energy, etc., all of which affect the rate of signal production. Calculations were made for a particular set of experimental conditions using our present experimental set-up which is far from being optimized. For the LIF signals, the calculations were based on the fluorescence amplitude PMT response of 1 volt due to 1 mtorr of  $C_2H_2$  with the ArF laser energy of 6 mJ/pulse and the spectrometer slits wide open (2 mm). Under these conditions the noise level was measured as 10 mvolts off resonance due to the leakage of stray 193 nm radiation. Thus, a  $S/N=2$  calculation results in a detection limit  $\sim 10^{11}/cc$  for  $C_2H_2$  at low pressures. For the RIES signals, calculations are based on the single photon signal level of  $\sim 3000$  counts from a 300 mtorr flow of  $C_2H_2$  per 30 second integration time. The slits were wide open, a 20  $\mu$ second gate width was used and the ArF laser energy was 6 mJ/pulse. Thus, with an assumed noise level of 1 count per 30 sec, which should certainly be possible with a cooled PMT and adequately shielded electronics, a  $S/N=2$  calculation results in a detection limit of  $\sim 10^{12}/cc$ . The actual sensitivity of the two methods for C-atom precursor detection should be much higher than that indicated by our calculations and the reasons will be discussed in the following paragraphs.

Figure 7 shows the dependence of the LIF and RIES signals as a function of  $N_2$  collision gas pressure with  $C_2H_2$  as the C-atom photolytic precursor. For the LIF signals, collisions are expected not only to cause quenching of the monitored fluorescence intensity, but may also change significantly the photochemical processes that lead to the production of the  $C(^1D_2)$  atoms. In the case of RIES, the situation should be even more complicated since collisions will also affect the dynamics of ion neutralization and the relaxation of excited recombination products. Figure 7 suggests, however, that collisions with  $N_2$  are probably not affecting many of the intermediate steps in a major way and that the primary effect of such collisions is to quench the final step, i.e., the emission at 247.9 nm. Also, the data presented in Figure 7 indicate that both types of signals are still present in a collisional environment, at least for the  $C_2H_2$  C-atom photolytic precursor, and, thus, these methods may possess analytical utility at atmospheric pressure as well. Clearly, in the case of an actual application of either of these two methods for chemical analysis, a more detailed study of signal behavior over a variety of conditions would have to be undertaken.

In order to obtain some insight into the possible photochemical mechanism for the formation of  $C(^1D_2)$  atoms, a study of LIF intensity as a function of the ArF laser energy was performed. Results for  $C_2H_2$  and CO are given in Figure 8. For CO, the near quadratic fluorescence dependence is in agreement with previous results.<sup>2</sup> For  $C_2H_2$ , an order of nonlinearity of 3.6 is found at low laser energies and then starts to level off indicating the onset of saturation of intermediate photochemical steps. In addition, saturation of the strong 193.1 nm absorption process is also expected to occur. The actual photochemical steps that gives rise to  $C(^1D_2)$  atoms are not known, but one possible process may involve the single photon photolysis of the CH radical for which the energetics are favorable for the formation of the metastable state. Clearly, more effort is required to better understand the details of the photochemical process. Figure 9 gives the laser energy dependence for the RIES signal. The near linear dependence of the emission cannot be readily explained and suggests that the processes leading to the single photons

detected are indeed quite complex and poorly understood at this time. Interestingly, a near linear behavior of the RIES signal was also observed in the Hg atom experiments.<sup>12</sup>

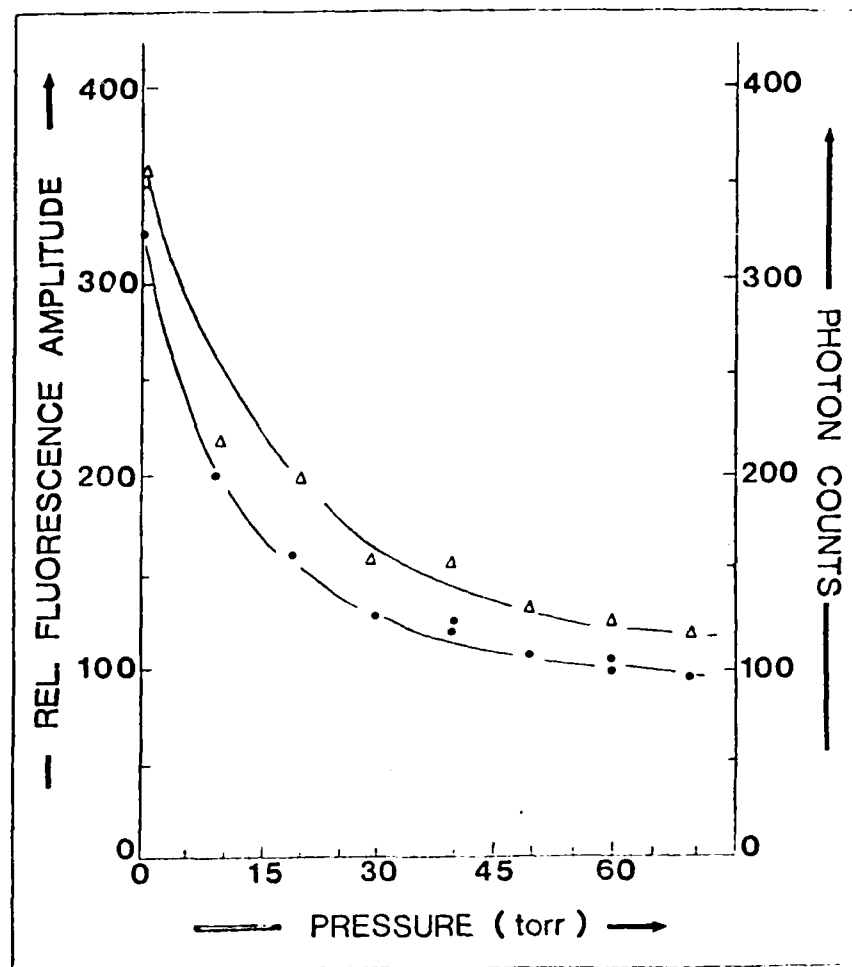


Figure 7. Dependence of LIF (·) and RIES (Δ) Signals on  $N_2$  Pressure.  
 $P_{C_2H_2} = 327$  mtorr and ArF Energy = 4.5 mJ

The data presented in Figures 8 and 9 allow us to estimate better the sensitivity inherent in both methods, especially in light of the fact that commercial excimer lasers are capable of producing ArF pulses in excess of 1 mJ. For LIF, the onset of saturation implies that a substantial increase in sensitivity should result by focussing the ArF laser beam less tightly with increasing laser energy and then observing the correspondingly larger field of view with the spectrometer. Clearly, the introduction of a filter to effectively absorb the scattered ArF laser radiation should result in a negligible background emission level at 247.9 nm. For RIES, it is difficult to assess the validity of extrapolating the curve shown in Figure 9. In any event, it appears that both methods are considerably more sensitive than our detection limit calculations indicate. In fact, the previous RIES experiments on Hg atoms indicated a detection limit of  $\sim 10^8$ /cc at low

pressures, but this is not surprising since in those experiments the atoms themselves were the ones that were the object of analysis rather than their photochemical precursors. An alternative method of analysis might involve the direct detection of the ions formed by the primary photochemical process, particularly by using a mass spectrometer for "noise" ion reduction. Such an approach should afford an even greater improvement in sensitivity, but at the cost of a substantial increase in experimental complexity.

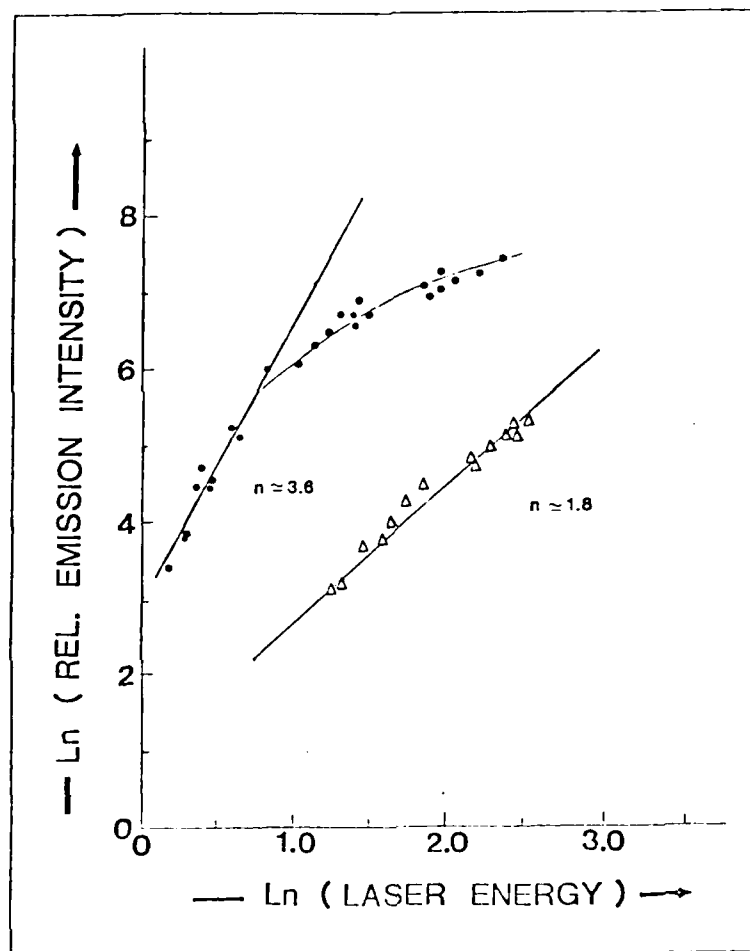


Figure 8. ArF Laser Energy Dependence of LIF Signals for CO ( $\Delta$ ) and  $C_2H_2$  ( $\bullet$ ) Where  $P_{CO} = 450$  mtorr with 400 Micron Slits and  $P_{C_2H_2} = 100$  mtorr with 125 Micron Slits

Efficient production of C atoms by ultraviolet lasers appear not to be limited to just some of the small molecules listed in Table 1. In a recent paper, Whetten, et al., describe the efficient production of neutral carbon atoms in the  $^3P_{0,1,2}$  and  $^1D_2$  state during multiphoton fragmentation of several aromatic molecules under moderate ultraviolet laser fluxes.<sup>14</sup> Thus, the application for sensitive analysis of the two methods described in this paper may extend to larger, aromatic molecules. It should also be pointed out that besides sensitivity, there is also an element of specificity inherent in ArF laser photofragmentation. In particular, each parent molecule has a unique

set of photochemical pathways which result in the formation of a variety of ground and excited state products besides C atoms, such as CH and C<sub>2</sub>.<sup>13</sup> By mapping out characteristic excited state emission patterns for each individual molecule, it should be possible to add the important element of specificity. In addition, such detailed studies of the excited products, as well as similar studies of ground state products using, e.g., laser induced fluorescence from a probe laser, should elucidate the details of the photophysical mechanisms involved. Finally, the question of specificity can be addressed by a different method, i.e., by using a standard pre-separation technique such as gas chromatography. In this case the ArF laser might be used as the ionization means for a GC/MS type of analysis or for standard flame ionization detection.

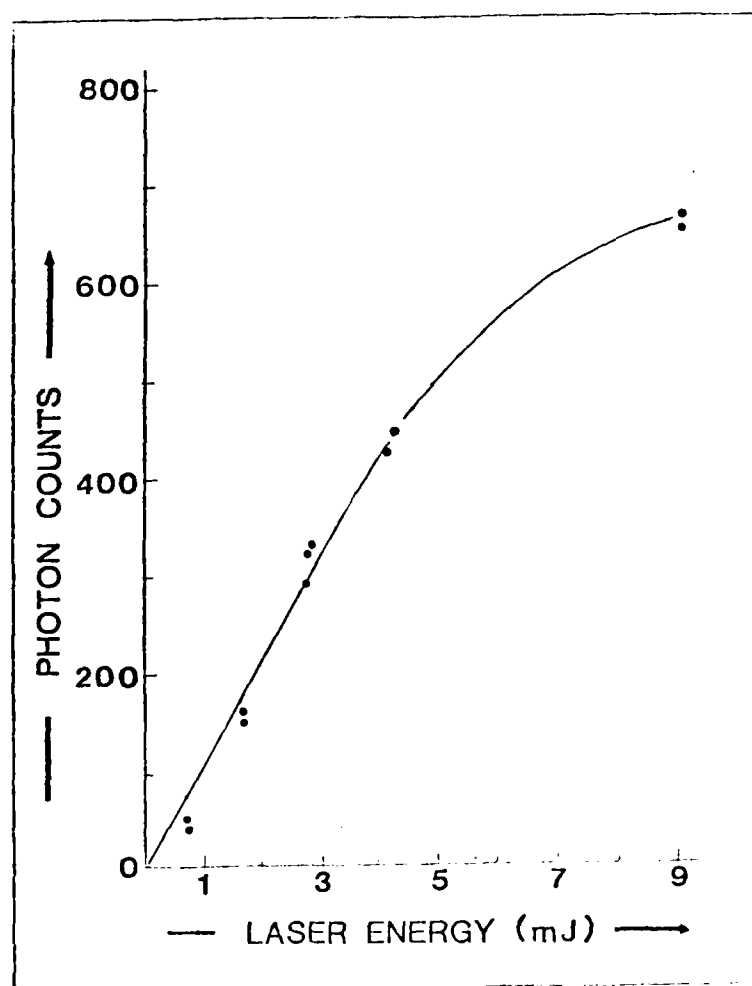


Figure 9. ArF Laser Energy Dependence of RIES Signals for C<sub>2</sub>H<sub>2</sub> where  
P<sub>C<sub>2</sub>H<sub>2</sub></sub> = 300 mtorr With 450 Micron Slits

#### IV. CONCLUSION

We have presented in this report a survey of data indicating the potential of the LIF and RIES methods for very sensitive chemical analysis of certain carbon-containing molecules. The ultimate detection limits for these techniques are hard to project, but could very well be considerably lower than our current estimates indicate. The ArF laser, therefore, offers an experimentally quite simple means for the detection of these molecules. For practical applications, however, a more complete characterization of the detection method and range of application will have to be performed.

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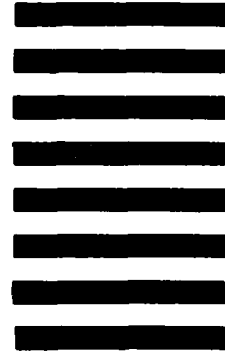
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