EVALUATION OF LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS) FOR REAL-TIME DETECTION OF HALON ALTERNATIVE AGENTS

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ABSTRACT

We report the results of an initial evaluation of laser-induced breakdown spectroscopy (LIBS) for the detection of candidate halon replacement compounds. A Nd:YAG Q-switched pulsed laser beam was focused into an air flow containing 0,005-5% concentration of the analyte halocarbon compounds. The laser produced plasma emission consisted of a large number of intense fluorine atom lines in the 600-850 nm spectral range. Limit of detection studies indicate that the LIBS technique can detect these compounds in the ppm range. Also, we have recorded single-shot LIBS spectra with good S/N using a photodiode array detector. Our results indicate that LIBS is a promising detector for in-situ and real-time use in full-scale fire suppression testing.

INTRODUCTION

Halons (halogenated hydrocarbons) are principally used in fire extinguishing applications. Halons **1301** (CF_3Br) and **1211** (CF_2ClBr) **are** currently used by the military for fire suppression in combat vehicles. The eventual replacement of these compounds is mandated because of the ozone depleting nature of bromine and chlorine. Virtually all of the halons released on the earth's surface eventually reach the stratosphere (ozone layer) through convection from the troposphere'. At high altitudes the halons are photochemically degraded and the Br and Cl atoms become accessible for reaction with ozone and other free radical chemistry.' The production of new halons has been prohibited in accordance with the Copenhagen Amendment of the Montreal Protocol (Fourth Meeting of the Parties to the Montreal Protocol **1992).** The alternative compounds which are studied in this report are listed in Table I. The detection of the alternative agents is of practical concern in order to monitor their concentrations during full-scale fire suppression tests and ascertain their effect on atmospheric chemistry. A routine method for the detection of these compounds has not been reported. The development of a routine method has potential applications for field detection where identification, quantitation, and distribution are significant parameters. Laser-induced breakdown spectroscopy (LIBS) is investigated here as **a** method for the detection of halon alternative compounds. The emission of fluorine which is liberated in a plasma is used for analysis.

Table I List of Halon Alternative Agents Studied

C_2F_5H
CF_4
CF_3H
CF_2H_2

LIBS is an well-established technique based on the formation of a laser induced plasma of an analyte. **A** laser pulse is focused to a fluence of 10^7 to 10^9 W/cm^2 on or in the sample which produces an avalanche of ionization, or dielectric breakdown, of the analyte. The laser induces multiphoton ionization which generates an initial electron density[2]. Continuum absorption of the laser radiation by the free electrons occurs and electron collisions fbrther ionize and heat the sample. The electron collisions directly generate the plasma by cascade ionization and thus breakdown of the sample. The emission of the atomic and molecular constituents which are excited within the plasma is then collected with lenses or fiber optics.

The instrumentation required for the **LIBS** experiment is simple compared to other atomic techniques such as ICP and spark spectrometry. Complicated sample introduction equipment and electrodes are not necessary for the LIBS experiment as for ICP and spark spectrometry respectively. Also, **LIBS** has the capability of being used in situ while ICP is not readily field deployable. **A** standard sample chamber or probe can be implemented in **LIBS;** a monochromator or acousto-optic tunable filter is used for wavelength selection and a photomultiplier (PMT), photodiode array or CCD for signal detection. Time resolution of the **LIBS** signal is often used because of the presence of an early (<2 µs) strong background emission. The optimum delay for detecting the atomic analytes varies but is typically **1-2 ps.**

The majority of the **LIBS** studies have involved solid samples (e.g., paper, soils, paint, metals, steel); **LIBS** analysis of gaseous samples has been reported for the detection of F, CI, **S,** P, **As** and Hg in air, and column III, IV hydrides (e.g., B_2H_6, PH_3).[3-9] The intent of the studies was the measurement of trace amounts of analytes in hostile environments and gas impurities for the hydride work. Hg was detected at the ppb level in air using a photodiode array detection system which recorded single shot spectra over a range of **20 nm.**[5] Cremers et al. reported limits of detection of 8 and **38** ppm for chlorine and fluorine respectively.' SF_6 and chlorinated fluorocarbons (e.g., $C_2Cl_3F_3$) were the source compounds. The **LIBS** signal was time resolved using a boxcar/PMT for detection. The objective of the present study is the evaluation of **LIBS** for the detection of halon alternative compounds. Spectra are recorded neat and in air since this is a probable environment for samples collected in the field or analyzed in situ. The optimization of parameters unique to our system and an initial description of a practical field device for fire extinguishing applications are described. Some methods for selective detection using **LIBS** are also considered.

EXPERIMENTAL

Schematics of the instrumental setups are shown in Figure 1. The Nd:YAG laser was operated at a repetition rate of 10 Hz and a wavelength of **1064** nm. **A** photodiode illuminated by the laser radiation was the trigger source for the oscilloscope, boxcar (Stanford Research Systems) and pulser/photodiode array intensifier (Princeton Instruments PG-10/Princeton Instruments **IRY1024G)**. The emission from the plasma was detected with a photomultiplier (EMI-Gencom Inc. **9658R)** or gated photodiode array (Princeton Instruments **IRY1024G)**. Optical relay lenses were used to collect the emission for the PMT system and a single strand fiber optic (Thorlabs, FP-600-UHT) was used in the photodiode array system. Data acquisition was computer controlled with an SRS (Stanford Systems **465)** interface for the PMT system and a IBM compatible for the photodiode array system. The sample flow apparatus (Figure **2)** was constructed from stainless steel tubing and swagelock connections and is similar to the configuration reported by Locke et al.[10] Argon was flowed through the outer tube which fbnctioned as a sheath and minimized the mixing of the analyte with room air. The inner tube contains the analyte flow. The sample flow apparatus was mounted on a three dimensional stage in order to adjust the location of the laser beam relative to the analyte stream. The sample was mixed with air for limit of detection calculations. **Gases** flows were controlled by mass flow valves (MKS). Separate flows of air and the diluted analyte (900 ppm) were mixed before the sample probe. The total flow rate was varied between 100 sccm and 2 slm for dilution.

OPTIMIZATION

The optimal experimental conditions for the ***Ar*** sheath used in the sample flow apparatus were determined by varying the ***Ar*** flow rate. Although the primary function of the ***Ar*** sheath is isolation of the plasma from the environment, an improvement of the *S/N* by a factor of **2** in the presence of the sheath was observed for samples mixed with air. Table II **lists** the flow rate and the corresponding S/N for a 1% sample of CF_3H in air with a total sample flow rate of **2** slm. The optimal ***Ar*** flow rate was dependent on the sample flow rate and the position of the plasma. At ***Ar*** flow rates above 1 slm the plasma was physically disrupted (i.e., changes in the shape, ***size*** and position of the plasma within the measurement time). The increase in S/N with the Ar sheath may be due to stabilization of the plasma by isolation or repositioning. The laser beam was positioned approximately 1/8" above the inner tube. The plasma instability increased at lower vertical positions and dilution of the analyte may occur at greater vertical positions.

Table II **Argon** Sheath **Optimization**

Ar Sheath **Flow Rate**	S/N
1.5	*90*
1.0	62
.5	102
.3	68
0	*50*

A plot of S/N vs. laser energy (Figure **3)** indicates that the optimal laser energy is approximately 120 mJ for our system (boxcar/PMT). The data was recorded with an argon sheath flow rate of 500 sccm and a 1% mixture of CF_3H/air. The signal increases 240% at 200 mJ compared to 60 mJ but a substantial increase in the noise degrades the S/N at the higher energy. The laser amplifier was required to obtain energies above **120** mJ. This could increase the shot to shot variation of the laser power. *Also*, the plasma was physically disrupted at high energies (≥ 140 mJ) which could be another source of noise in the measurement.

RESULTS AND DISCUSSION

The energy level diagram for fluorine transitions in the visible which are used for analysis is shown in Figure 4. Neutral atoms of fluorine are detected with the LIBS technique used in this study. Atomic fluorine is released and excited by electron impact in the plasma and relaxes by fluorescence. The relative intensities of the transitions from 683.4 to 690.9 nm are 3.3, 9.4, 3.0, 6.2, 3.0 in order of increasing wavelength for a neat plasma of CF_4. The relative intensities were comparable for the different agents but seemed to vary within and around the plasma. This indicates that the plasma temperature is similar for the agents. Spectra of neat CF_4 collected with the boxcar/PMT system are shown in Figure ***5***. The emission due to F **I is** clearly resolved with the maximum intensity at 685.6nm. Emission from F II was not observed. Emission from the Ar sheath was observed at 810.4nm, 811.4nm and 840.8nm. The LIBS spectra of other agents were similar with the intensity of the peak at 656.3nm substantially increasing due to hydrogen emission as shown in Figure 6A for neat CF_2H_2. This suggests a simple method to distinguish fluorocarbons and hydrofluorocarbons with LIBS. The greater linewidth of the hydrogen emission relative to the fluorine lines is due to stark broadening. The electron density which indicates the degree of ionization can be calculated using the hydrogen linewidth. A spectrum recorded in air (Figure 6B) shows emission from nitrogen and oxygen. The main spectral region for fluorine emission is free from interferences. The peak at 685.6nm was used to determine a limit of detection (LOD) of 40 ppm for fluorine in air using the PMT system. This LOD was determined with a laser energy of 120mJ compared to an LOD of 38 ppm with 190 mJ of laser energy which was reported by Cremer et al.[9] The configuration used in this study does not use windows which is an advantage for sensitivity and cost. It was also observed by Cremer et al. that the slope of the analytical curve is proportional to the number of fluorines in the compounds.[7] *An* agent could be experimentally identified by comparing the slope of a calibration curve to a standard with a known number of halogens. For in field identification, spectral signatures are most useful. In addition to the H line for the hydrofluorocarbons, another means of selectivity is the iodine lines (546.4nm, 516.1nm, 328.8nm, 206.2nm) for CF_3I, which is a possible replacement for CF_3Br. CF_3I is a cardiac sensitizer and thus its detection is significant for safety reasons.

A single shot spectrum of 1% CF_3H recorded with the photodiode array/fiber optic system is shown in Figure 7. The pulse width of the high voltage gating pulse was 20 µs. The optimal delay was not experimentally determined, but 1-2 µs was routinely employed. This delay was reported in the literature for fluorine[g]. The standard deviation for 5 consecutive measurements of shot-to-shot spectra was 8% and the LOD for fluorine in air was 60 ppm. The collection of one shot spectra has significance for field measurements in fire extinguishing applications. After release of the agent in a test facility, its relative distribution can be determined with ns time resolution. The distribution of the agent is an important factor in predicting the efficiency of the agent, safety and for determining how well the distribution system works. Multiple LIBS systems could be used to map the distribution of the agent. This can be accomplished inexpensively and practically with single strand fiber optics and one charge coupled device (CCD). Collection optics are not necessary for the emission fiber. Focusing optics is required to launch the excitation beam into the fiber. Launching the excitation beam into a 1 mm fiber has been considered by other researchers.'' Typical concentrations of the agents for flame extinction are 2-30%, thus one shot spectra can be recorded without employing objectives for the emission fiber. The detector can be remote since the fibers are inexpensive. The emission fiber can transmit to a portion of the CCD. Thus, the response of the LIBS detectors could be monitored simultaneously. It is possible that the plasma could be formed directly in the environment and the LIBS analysis performed without a sampling flow apparatus. For the fire extinguishing application, the primary information needed is an indication the amount of agent present in the area at a specific time.

CONCLUSIONS

LIBS is a selective and sensitive technique for the detection of halon alternative compounds. The field utility of LIBS for fire extinguishing applications is feasible. Single shot spectra can be recorded with ns time resolution. Detection limits are below that required for field detection. It is conceivable that multiple excitation/collection fibers would be used to map the distribution of an agent.

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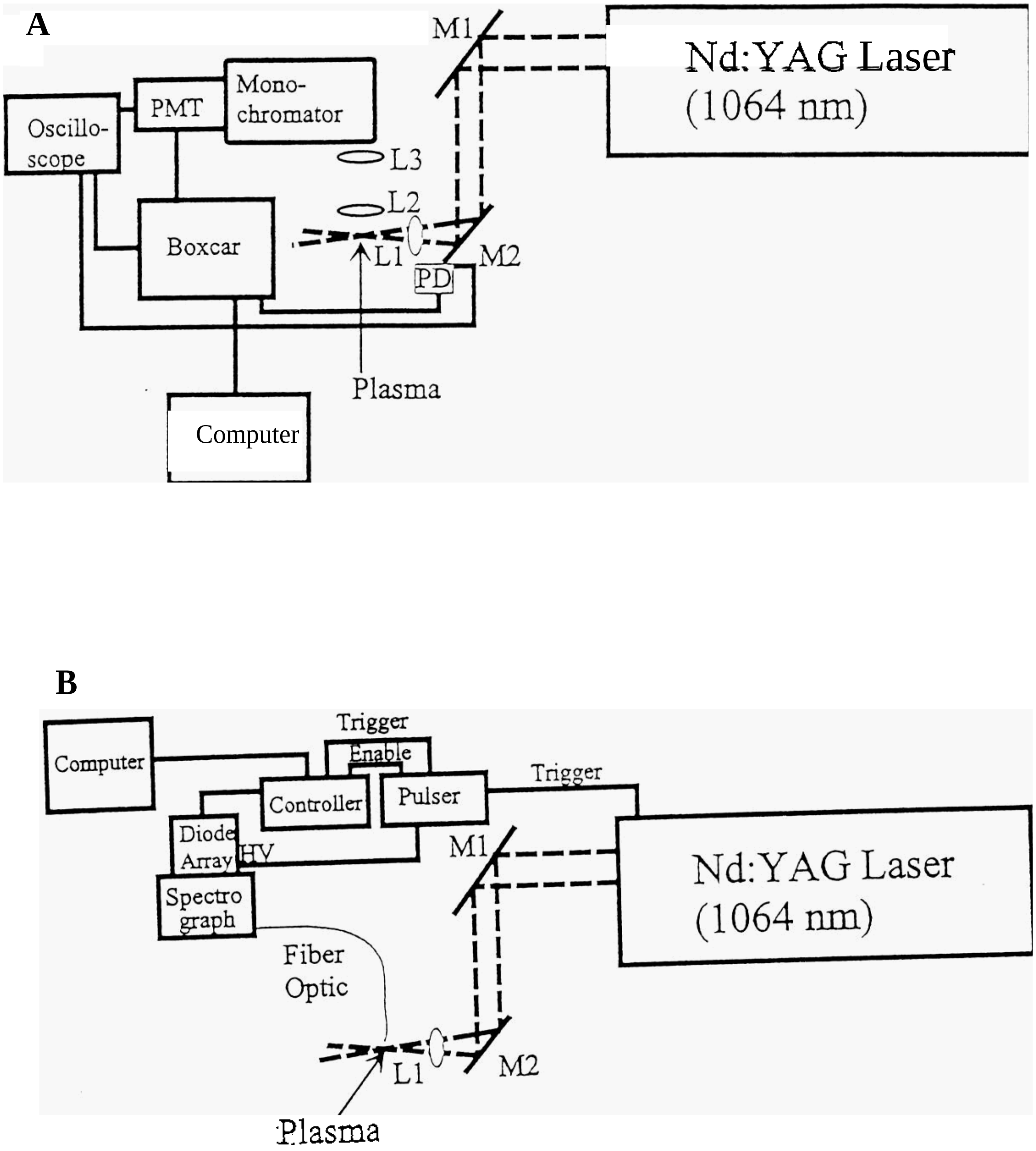

Figure 1. **A)** Schematic of photomultiplier based detection system B) Schematic of photodiode array based detection system.

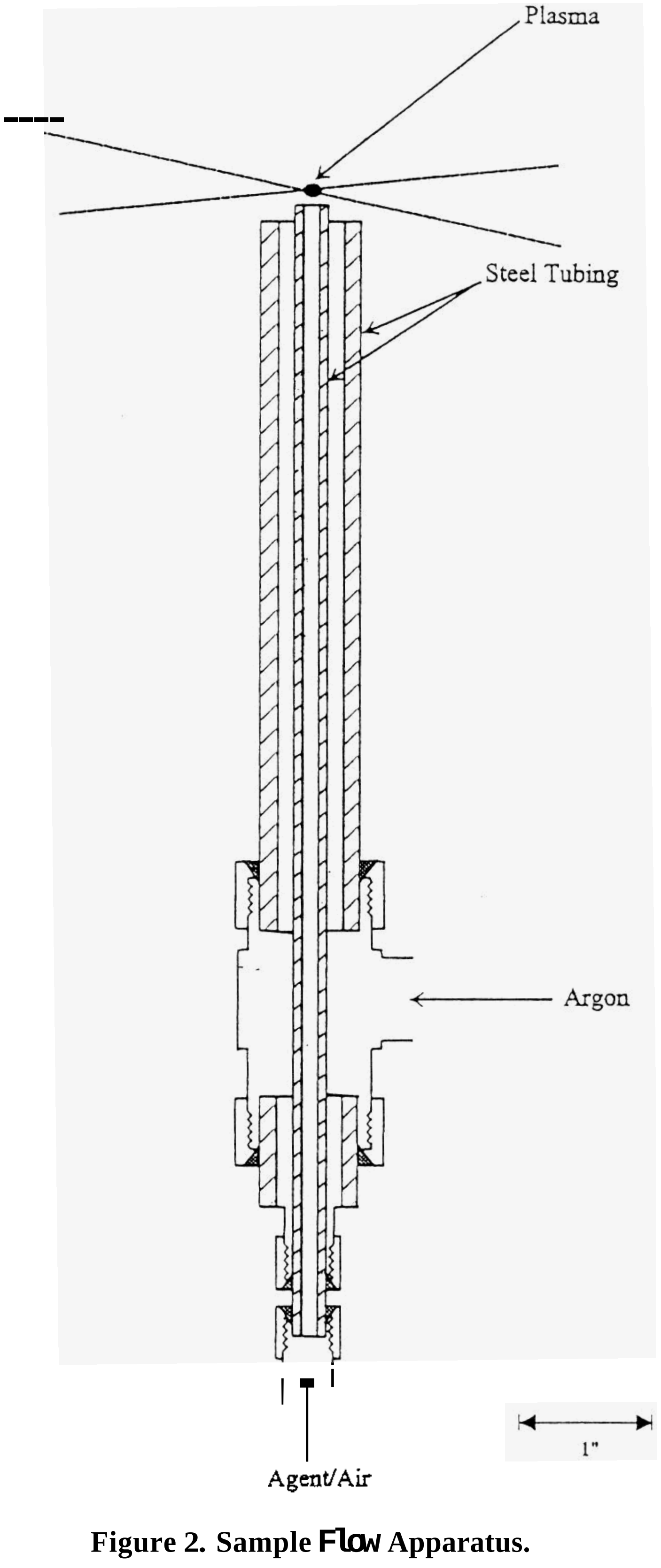

Figure 2. Sample Flow Apparatus.

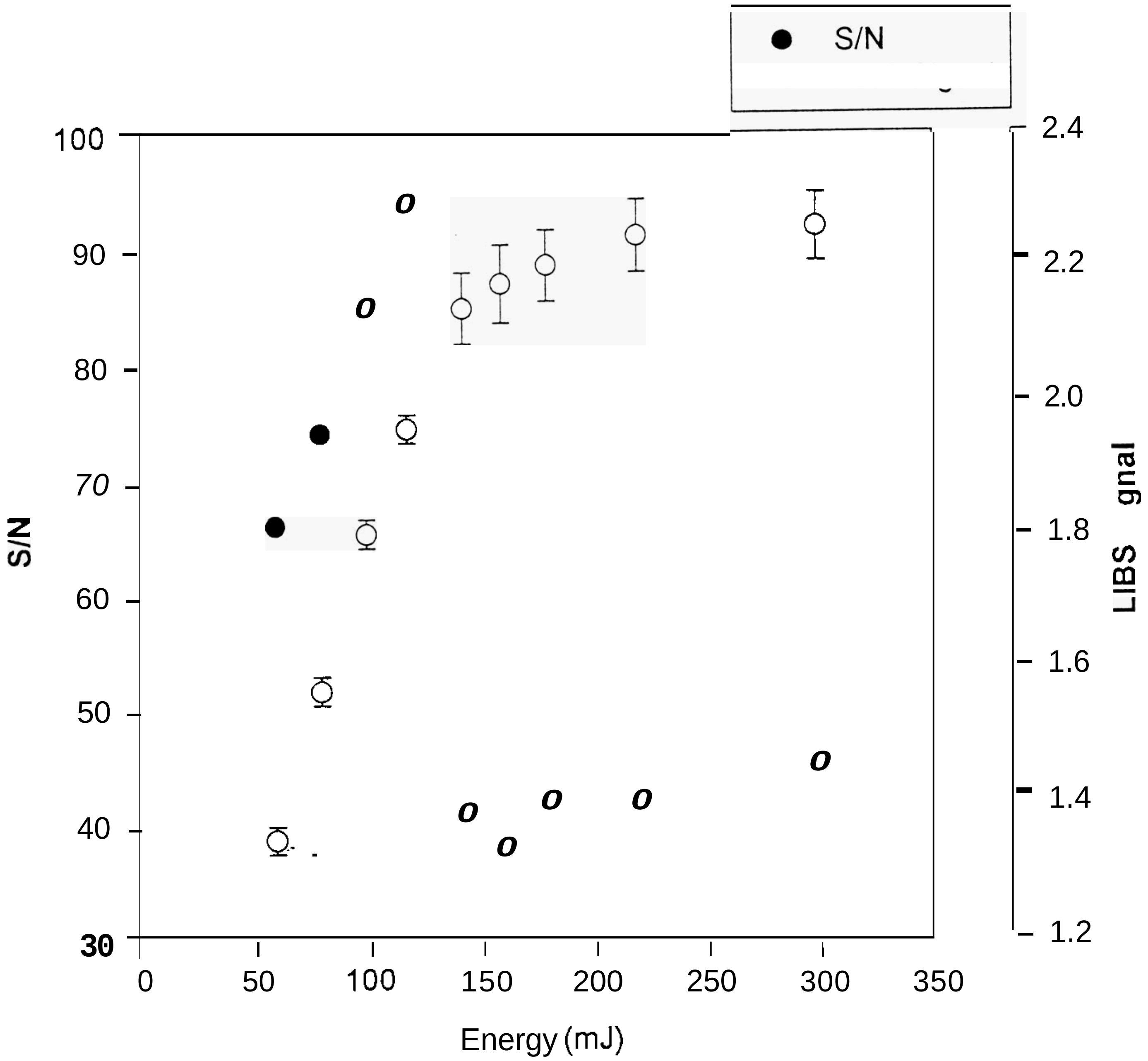

Figure 3. S/N and signal intensity vs. laser energy

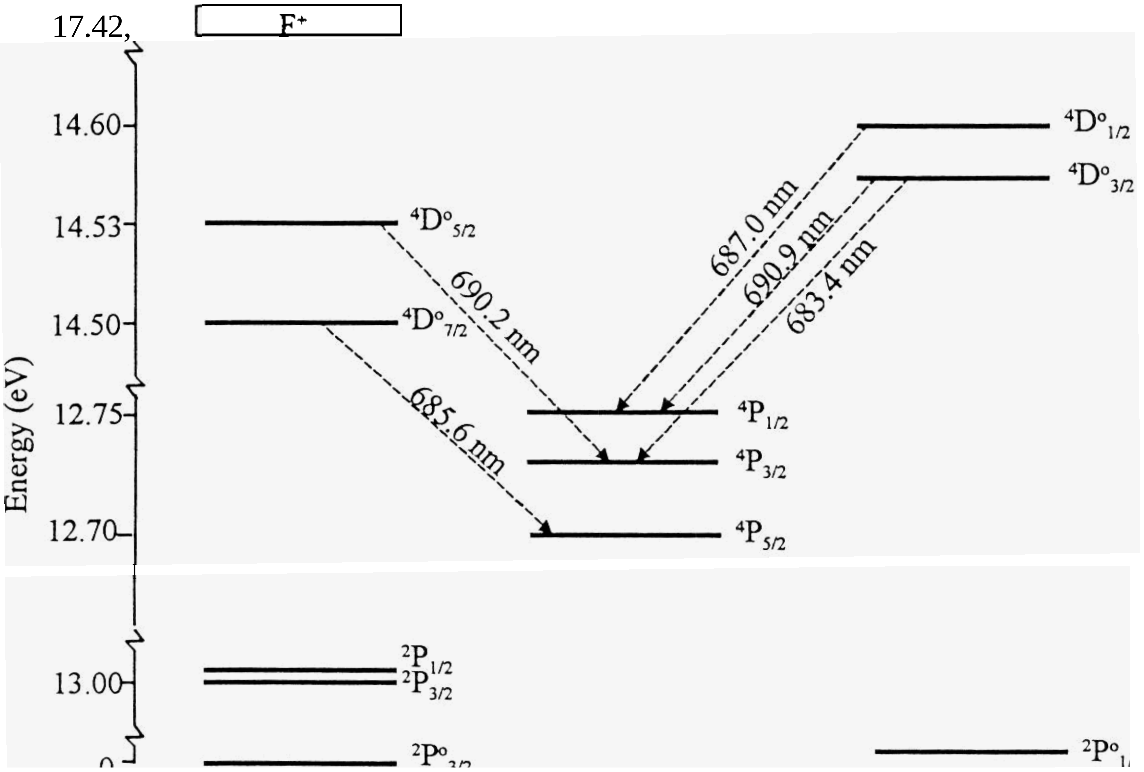

Figure **4.** Partial energy level diagram for fluorine atom and transitions in the visible.

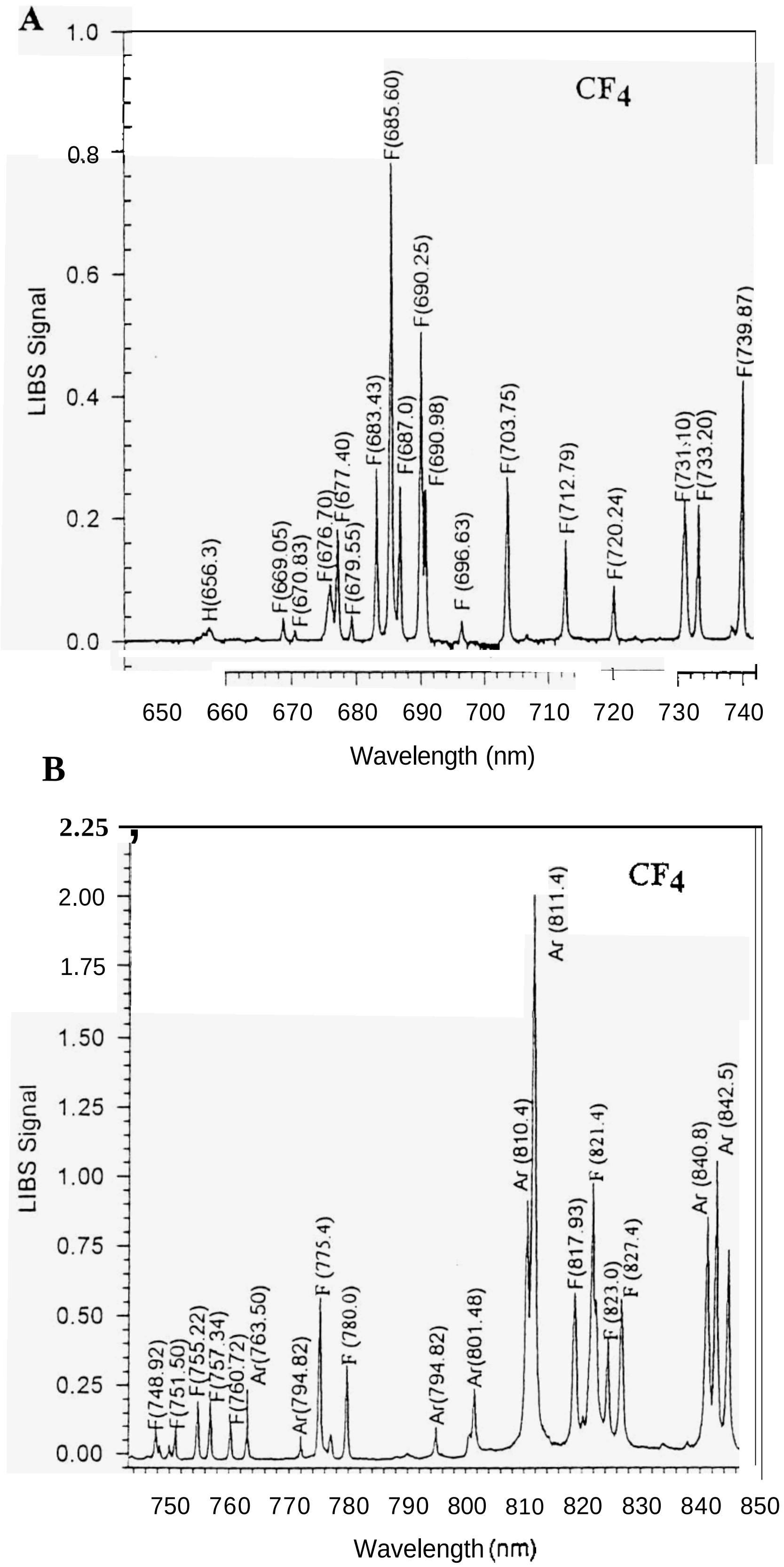

Figure **5**. **A)** LIBS spectrum in the visible for neat CF$_4$ recorded with the PMT detection system B) LIBS spectrum in the near IR for neat CF4 recorded with the PMT detection system.

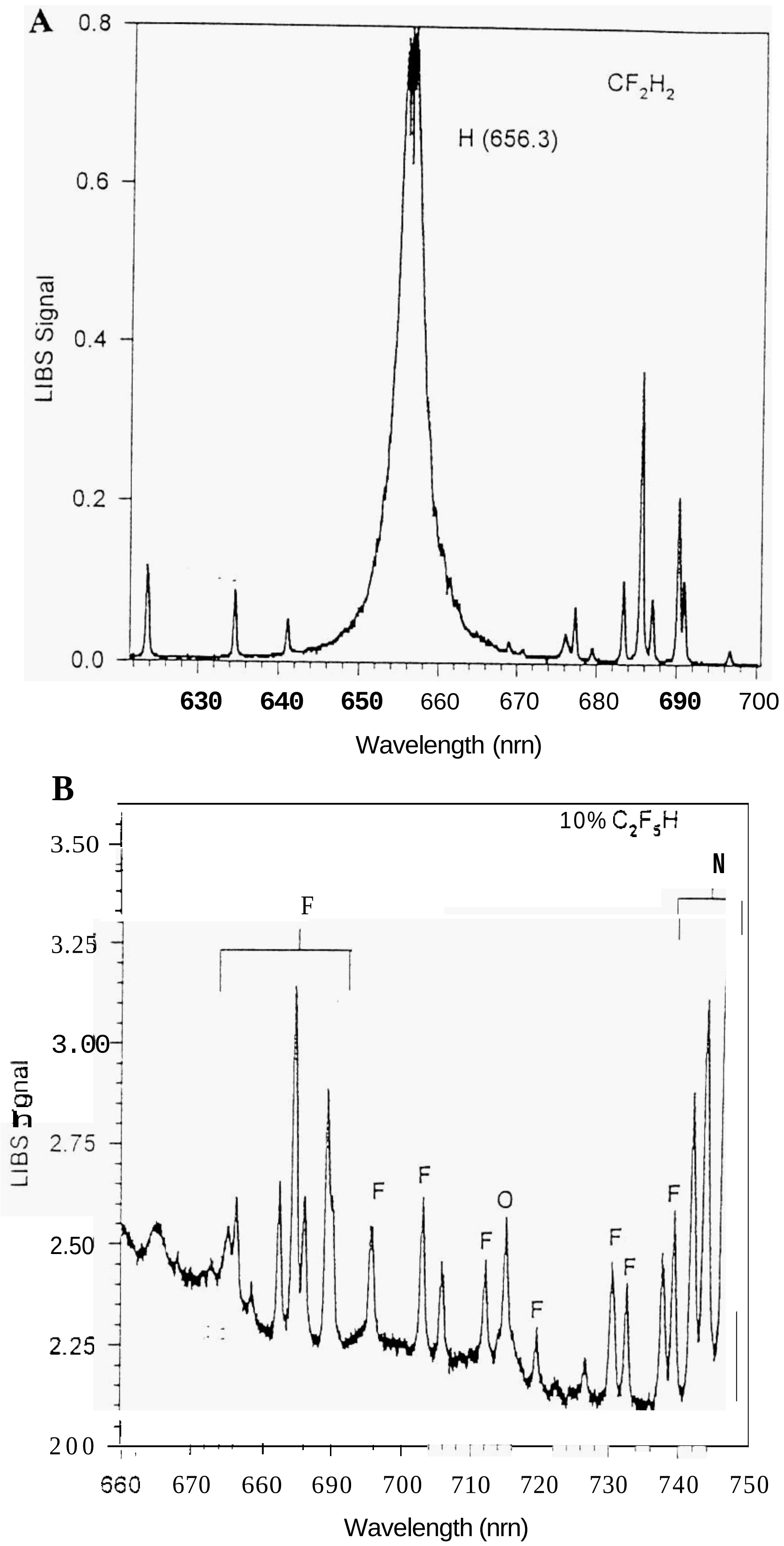

Figure 6. A)LIBS spectrum of neat CF_2H_2 recorded with the PMT detection system B) LIBS spectrum of 10% C_2F_5H in *air* recorded with the PMT detection system.

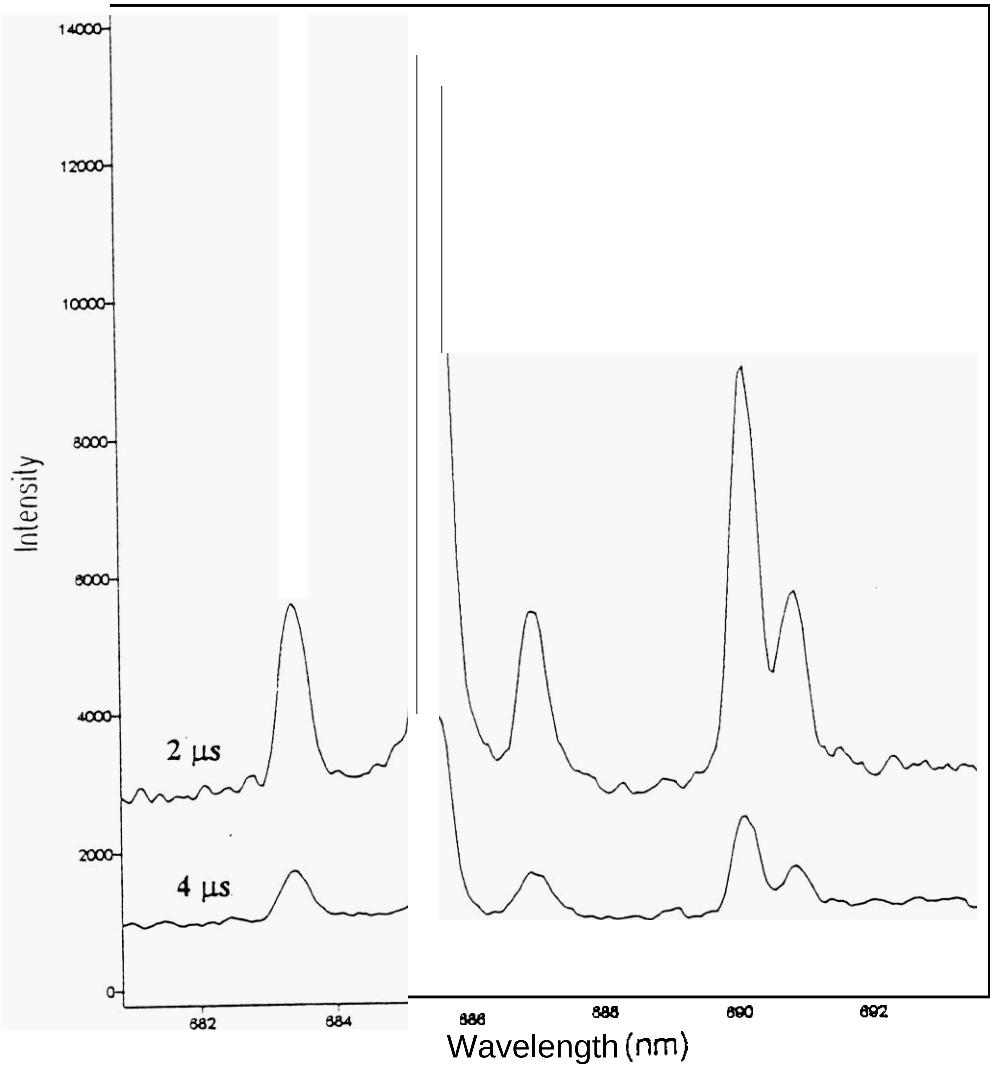

Figure 7. Single shot LIBS spectra of 1% CF_3H in air at 2 µs and 4µs delay times for the HV pulse which gates the photodiode array.