

PROJECT ADMINISTRATION DATA SHEET

ORIGINAL  REVISION NO. \_\_\_\_\_

Project No. G-35-627 (R6072-OAO) GTRC/~~COX~~ DATE 01 / 02 / 85

Project Director: J. D. Bradshaw School/~~COX~~ Geo Sci

Sponsor: National Science Foundation

Type Agreement: Grant No. ATM-8508246

Award Period: From 11/15/85 To 4/30/87 (Performance) 7/30/87 (Reports)

Sponsor Amount:	<u>This Change</u>	<u>Total to Date</u>
Estimated: \$	_____	\$ <u>173,700</u>
Funded: \$	_____	\$ <u>173,700</u>

Cost Sharing Amount: \$ 37,500 Cost Sharing No: G-35-362

Title: Development of a Two-Photon/Laser Induced Fluorescence Sensor for the Detection of Atmospheric OH Radicals

ADMINISTRATIVE DATA

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Defense Priority Rating: N/A Military Security Classification: N/A

(or) Company/Industrial Proprietary: N/A

RESTRICTIONS

See Attached NSF Supplemental Information Sheet for Additional Requirements.

Travel: Foreign travel must have prior approval – Contact OCA in each case. Domestic travel requires sponsor approval where total will exceed greater of \$500 or 125% of approved proposal budget category.

Equipment: Title vests with GIT.

COMMENTS:

No funds may be expended after 4/30/87.



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SPONSORED PROJECT TERMINATION/CLOSEOUT SHEET

58553

Date 7/31/87

Project No. G-35-627

School/Dept XXX Geo Sci

Includes Subproject No.(s) N/A

Project Director(s) J.D. Bradshaw GTRC / ~~GI~~

Sponsor National Science Foundation

Title Development of a Two-Photon/Laser Induced <sup>Fluorescence</sup> Sensor for the Detection of Atmospheric OH Radicals

Effective Completion Date: 4/30/87 (Performance) 7/30/87 (Reports)

Grant/Contract Closeout Actions Remaining:

- None
- Final Invoice or Final Fiscal Report
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FINAL PROJECT REPORT  
NSF FORM 98A

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PART I—PROJECT IDENTIFICATION INFORMATION

1. Institution and Address Georgia Institute of Technology School of Geophysical Sciences Atlanta, GA 30332	2. NSF Program Atmospheric Sciences	3. NSF Award Number ATM 8508246
	4. Award Period From 11/15/85 To 4/30/87	5. Cumulative Award Amount \$173,700.00
6. Project Title "Development of a Two-Photon/Laser-Induced Fluorescence Sensor for the Detection of Atmospheric OH Radicals"		

PART II—SUMMARY OF COMPLETED PROJECT (FOR PUBLIC USE)

The stated goal of this instrument development program was to demonstrate that a sequential two-photon/laser-induced fluorescence (TP-LIF) sensor could possess adequate sensitivity to allow the detection of hydroxyl radicals (OH) in the troposphere utilizing current laser technology. In the TP-LIF OH system, the first laser photon,  $\lambda_1$  is used to excite OH from its ground vibrational level at an infrared wavelength near  $2.9\mu$  (eg.  $^2\Pi, v''=0 \rightarrow ^2\Pi, v''=1$ ) followed by a second laser photon,  $\lambda_2$ , near 346nm which further excites the OH radical into a low lying vibrational level in the first electronic excited state of OH (eg.  $^2\Pi, v''=1 \rightarrow ^2\Sigma, v'=0$ ). Fluorescence is then observed at a wavelength near 308nm, which is blue shifted relative to either laser excitation wavelength allowing the system to exhibit virtually complete elimination of laser generated noise. Although the TP-LIF OH sensor may be considered a new technique, many of the hardware components will be the same as those currently utilized in our field tested TP-LIF NO/NO<sub>2</sub> instrument. In addition, the required  $\lambda_2$  laser (centered near 346nm), the required detection optics and electronics, as well as the necessary OH calibration sources and sampling flow lines have been developed and tested. The development of a suitable  $\lambda_1$  infrared (IR) laser system operating near  $2.9\mu$  has been the focus of this current phase of research effort. Several possible IR lasers have now been examined in terms of their potential for satisfying the system needs for a field compatible  $2.9\mu$  laser. The outcome of this phase I research effort has resulted in our defining a  $2.9\mu$  laser system based on the tandem D<sub>2</sub>/CH<sub>4</sub> stimulated Raman shifting of a commercially available and field proven  $1.06\mu$  Nd:YAG laser. Having tested in our laboratory each basic component of this new IR laser system and having extensive research results available from other investigators that indicate the feasibility of carrying out a modest scaling up of the present hardware, we are quite confident that we can achieve the IR laser energies necessary for the final development of an operational OH sensor. At the current projected performance level of this new IR laser system the TP-LIF OH instrument will be capable of measuring  $3.7 \times 10^5$  molecules/cm<sup>3</sup> with a 10 min. integration time at ground level (high water conditions) with a signal to noise (S/N) ratio of 2:1. For an airborne system operating at 6km altitude, an OH concentration of  $3.7 \times 10^5$  molecules/cm<sup>3</sup> would yield a 10:1 S/N ratio for a 10 min. integration time.

PART III—TECHNICAL INFORMATION (FOR PROGRAM MANAGEMENT USES)

1. ITEM (Check appropriate blocks)	NONE	ATTACHED	PREVIOUSLY FURNISHED	TO BE FURNISHED SEPARATELY TO PROGRAM	
				Check (✓)	Approx. Date
a. Abstracts of Theses	X				
b. Publication Citations				X	JAN. 1988
c. Data on Scientific Collaborators			X		
d. Information on Inventions	X				
e. Technical Description of Project and Results		X			
f. Other (specify)					
2. Principal Investigator/Project Director Name (Typed) John D. Bradshaw	3. Principal Investigator/Project Director Signature			4. Date 7/16/87	

**PART IV - SUMMARY DATA ON PROJECT PERSONNEL**

NSF Division \_\_\_\_\_

The data requested below will be used to develop a statistical profile on the personnel supported through NSF grants. The information on this part is solicited under the authority of the National Science Foundation Act of 1950, as amended. All information provided will be treated as confidential and will be safeguarded in accordance with the provisions of the Privacy Act of 1974. NSF requires that a single copy of this part be submitted with each Final Project Report (NSF Form 98A); however, submission of the requested information is not mandatory and is not a precondition of future awards. If you do not wish to submit this information, please check this box

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American Indian or Alaskan Native . . . . .												
Asian or Pacific Islander . . . . .												
Black, Not of Hispanic Origin . . . . .												
Hispanic . . . . .												
White, Not of Hispanic Origin . . . . .	2		1									
Total U.S. Citizens . . . . .												
Non U.S. Citizens . . . . .			1		1							
Total U.S. & Non- U.S. . .	2		2		1							
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FINAL REPORT

DEVELOPMENT OF A TWO-PHOTON/LASER-INDUCED FLUORESCENCE SENSOR  
FOR THE DETECTION OF ATMOSPHERIC OH RADICALS - ATM 8508246

Submitted to:

Atmospheric Sciences Division  
National Science Foundation  
Washington, DC 20550

Submitted by :

Dr. John D. Bradshaw  
School of Geophysical Sciences  
Georgia Institute of Technology  
Atlanta, GA 30332

## FINAL REPORT

### I. OVERVIEW

Because of its importance in controlling atmospheric chemical processes, numerous instrumental techniques have been proposed for measuring the levels of atmospheric OH. However, model estimated levels of OH place the concentration of this species in the part-per-quadrillion to part-per-trillion range ( $10^5/\text{cm}^3$  to  $10^7/\text{cm}^3$ ). Thus, the direct measurement of this species under atmospheric conditions has presented one of the most demanding analytical challenges yet to be undertaken by the atmospheric chemistry community.

To date there have been three general methods used to detect OH in the lower atmosphere. These are single-photon laser-induced fluorescence (SP-LIF) (Wang et al. 1975, 1981, 1984; Bakalyar et al. 1984; Davis et al. 1976, 1979 a,b, 1984; Rodgers et al. 1984, 1985; Hard et al. 1984); long-path UV absorption (Perner et al. 1976, and Hubler et al. 1984); and the radio-chemical  $^{14}\text{CO}/\text{CO}_2$  oxidation technique (Campbell et al. 1979, 1984). From this grouping, the SP-LIF OH method can be further subdivided into three categories: (1) the quasi-remote lidar system (Wang et al. and Bakalyar et al.); (2) the ambient pressure in-situ method (Davis et al. and Rodgers et al.); and (3) the low pressure gas expansion in-situ nozzle system (Hard et al.). These techniques were critically examined in a NASA sponsored workshop "Assessment of Techniques for Measuring Tropospheric  $\text{H}_x\text{O}_y$ " (1982). The results from this 1982 workshop suggested that none of the proposed techniques seem to have a significant advantage over the others in terms of its projected performance.

Subsequently, three "field ready" systems were brought together in a NASA sponsored ground based and airborne intercomparison study, 1982, 1983. These three systems, as labelled above, were: (1) the quasi-remote LIF lidar method;

(2) the ambient pressure SP-LIF in-situ method; and (3) the radio-chemical  $^{14}\text{CO}/\text{CO}_2$  oxidation method. The results of this intercomparison were reviewed by an independent panel, the results of which were summarized by Hoell et al., 1985; and Beck et al., 1987. The conclusion drawn from this review was that none of the systems tested appeared to have the sensitivity needed to routinely measure ambient OH in the clean troposphere at the  $10^6/\text{cm}^3$  level with S/N ratios of 3:1 or greater.

More recently, a NASA-sponsored workshop "Future Directions for  $\text{H}_x\text{O}_y$  Detection" (1985), concluded that with the recent advances made in laser techniques that within 2 to 3 years time reliable OH measurements at the  $10^6/\text{cm}^3$  level should be possible. It was further concluded that reliable measurements at this level should provide the basis for carrying out useful tests of fast photochemical theory. Measurement systems specifically indicated as showing considerable promise were: (1) the long-path absorption method; (2) the low pressure gas expansion LIF system; and (3) the Two-Photon LIF method. It was noted that both of the latter in-situ measurement systems, in principle, appeared to have solved the two major problems that had plagued earlier efforts involving the use of the SP-LIF technique, e.g. the artificial generation of OH via the laser photolysis of atmospheric  $\text{O}_3$  in the presence of  $\text{H}_2\text{O}$ ; and, the problem of extracting a weak OH fluorescence signal from a large fluctuating background fluorescence. This proposal deals with the development of the two-photon LIF (TP-LIF) OH detection system.

The measurement of ultra-trace levels of atmospheric gases via the sequential TP-LIF technique is a scientific accomplishment that has been pioneered by the Atmospheric Chemistry group at Georgia Tech. One of the first applications of this new methodology involved the TP-LIF NO sensor (Bradshaw et al. (1982, 1985)). This new sensor participated in both ground based and

airborne intercomparison tests as part of the NASA sponsored GTE CITE I program (Hoell et al. 1985 and Beck et al 1987). A critical review of the TP-LIF NO results by a NASA review panel found the TP-LIF methodology to be extremely sound. In fact, this new system has unparalleled selectivity as an atmospheric monitoring sensor for the trace gas species NO.

The development of a two photon/laser-induced fluorescence sensor for the detection of atmospheric OH builds on what is already an extensive field proven laser detection capability within our group at Georgia Tech. In the TP-LIF OH system (Bradshaw et al., 1984), the first laser photon is used to excite OH from its ground vibrational level ( $v''=0$ ) into the first vibrational level ( $v''=1$ ) at an infrared wavelength,  $\lambda_1$ , near  $2.9\mu$ . After an appropriate delay time (e.g. 10 to 20 ns), a second laser is fired, generating a UV wavelength,  $\lambda_2$ , near 346 nm. The  $\lambda_2$  wavelength is selected so that it corresponds to an allowed electronic transition from vibrationally excited OH to a low lying vibrational level in the first excited electronic state (e.g.  $^2\Pi, v''=1 \rightarrow ^2\Sigma, v'=0$ ). Fluorescence can then occur at a wavelength  $\lambda_3$ ; near 309 nm. Thus, like the NO TP-LIF detection system, the  $\lambda_3$  fluorescence wavelength is blue shifted relative to both the  $\lambda_1$  and  $\lambda_2$  laser excitation wavelengths. This blue shifted fluorescence presents a unique situation in that it permits virtually complete discrimination against Rayleigh and Raman scatter. Most importantly, the nonresonant broad-band background fluorescence produced by the  $\lambda_1$  and  $\lambda_2$  laser beams can be reduced to near negligible levels via the use of long wavelength optical cut-off filters. Thus, the TP-LIF OH system becomes a signal limited rather than S/N limited system as is the case for the SP-LIF OH sensor.

Although the TP-LIF OH sensor may be considered a new technique, many of the hardware components will be the same as those involved in our field tested  $2\lambda$ -SP/LIF airborne OH instrument. In addition, the required  $\lambda_2$  UV laser (centered at  $\sim 346$  nm) and all detection optics (including custom made optical cut-off filters) needed for the TP-LIF OH system have already been developed and are on hand. Finally, much of the technology (electronics etc.) we have developed for the TP-LIF NO instrument can be transferred to the proposed OH system.

The joint NSF/NASA sponsorship of the development of the TP-LIF OH system has thus far led to the NSF funded Phase I evaluation of several possible IR laser systems. Each of these systems has been examined in terms of its potential for satisfying the need for a field compatible  $2.9\mu$  laser. (The latter wavelength defines  $\lambda_1$  in the proposed TP-LIF OH system.) The outcome of this Phase I research effort has resulted in our defining a  $2.9\mu$  IR laser system based on the tandem  $D_2/CH_4$  Raman shifting of a commercially available and field proven  $1.06\mu$  Nd:YAG laser.

In this new approach, a stimulated Raman laser beam at  $1.5\mu$  is first generated using the first Stokes shift in a  $D_2$  filled cell cooled to  $LN_2$  temperatures. The  $1.5\mu$  beam is then frequency shifted in a second multi-pass Raman cell containing methane. The resulting  $2.9\mu$  radiation can be made to overlap the  $P_{13}$  line of OH, where the necessary tunability is achieved by means of temperature tuning of the Nd:YAG laser rod.

Having tested in our laboratory each of the basic optical elements involved in the proposed new OH system and having extensive research results available from other investigators that indicate the feasibility of carrying out a modest scaling up of the present hardware, we are quite confident that we can achieve our specified goal of generating  $> 10$  mJ of  $2.9\mu$  energy that is spectrally

overlapped with the P<sub>13</sub> OH transition. At this IR energy level, the proposed TP-LIF OH instrument will be capable of measuring  $3.7 \times 10^5$  molec./cm<sup>3</sup> with a 10 min. integration time at ground level (high water conditions) with a S/N ratio of 2:1. At a concentration level reflecting model calculated diurnal averaged values of OH, i.e.  $1.4 \times 10^6$  molec./cm<sup>3</sup>, a 10 min. integration time would yield a S/N ratio approaching 8:1. On the other hand, for an airborne system operating at 6 km, an OH concentration of  $3.7 \times 10^5$  molec./cm<sup>3</sup> would yield a 10:1 S/N ratio for a 10 min. integration time.

In summary, of all the IR laser systems we have evaluated, the proposed tandem D<sub>2</sub>/CH<sub>4</sub> Raman shifted Nd:YAG based 2.9μ laser system is the most promising from four points of view: (1) the basic components of this system have been tested in our lab and the required optical characteristics verified; (2) the attainment of our specified goal of a 10 mJ 2.9μ laser that spectrally overlaps the P<sub>13</sub> OH transition can be achieved with a modest scaling up of the present hardware; (3) the proposed IR laser system will be compatible with both ground-based and airborne field sampling; and (4) the time period required to complete the IR laser development is estimated to be only one year, far shorter than any other competing IR system.

## II. SUMMARY OF NSF SPONSORED IR LASER RESEARCH EFFORT (Dec. 1985 → Dec. 1986)

The initial goal of Phase I of our program was that of developing an IR laser source having the following basic optical characteristics: (1) capable of delivering 10 mJ/pulse ( $\leq 15$  ns pulse-width) to our sampling fluorescence cell at a rep-rate of 5 to 10 Hz; (2) capable of generating an output wavelength that could be made to spectrally overlap one of the strong OH vibrational absorption lines; and (3) a full angle beam divergence of less than 2 mrad.

At the time the project was initiated in December 1985, the most promising of those systems examined involved the use of the first Stokes hydrogen Raman-shifted output from an atomic-iodine laser. The characterization of the atomic-iodine laser was therefore defined as one of the high priorities of our research activity during the first year. However, in addition to this main-line effort, the program was also committed to a critical re-examination of several other possible IR laser systems. In the text below, we discuss the outcome of these investigations, investigations that have been specifically directed toward defining a practical IR laser system that could be field deployed within a two year time frame.

### A. Atomic-Iodine Laser System:

Although atomic-iodine lasers have been in existence since 1964, there is to-date only one commercial laser manufacturer (Vuman, Ltd.). After several negotiations with Vuman Ltd., we determined that certain characteristics of this laser required further investigation in order to obtain the required Q-switched 5 Hz system needed for the TP-LIF OH system. We therefore negotiated a subcontract with Vuman to provide more detailed performance data from an operational single shot Q-switched iodine laser that could be used to predict the potential performance from a 5Hz Q-switched laser.

During the Vuman test period, our efforts were directed towards: (1) defining the exact wavelength mismatch ( $\sim 1\text{cm}^{-1}$ ) between the Raman shifted atomic-iodine laser line and the nearest OH absorption transition ( $P_{14}$ ) at  $2.93\mu$ ; (2) exploring different methods for shifting the atomic iodine line to make it overlap a strong OH transition. Several methods were subsequently explored for tuning the iodine laser output wavelength to achieve an overlap with the OH line ( $P_{14}$ ), these included: etalon tuning the pressure boardened iodine-laser line; Zeeman shifting the atomic-iodine line; and the use of Raman shifting techniques using specially blended high pressure gas mixtures.

In our efforts to obtain an overlap between a specific OH ro-vibronic transition and the output of the atomic iodine laser, early results obtained from Vuman indicated that direct etalon tuning of the atomic iodine laser by  $1\text{cm}^{-1}$  was not feasible. That is, an etalon tuned system could not meet our required specifications of laser output energy and repetition rate and yet be tuned by  $1\text{cm}^{-1}$ . However, the research effort at Georgia Tech, involving Raman shifting in high pressures of blended gases, did provide some encouraging results. This development involved the pressure shifting of the Raman active  $\text{H}_2$  vibrational transition using high pressures of inert buffer gases such as He. The latter finding by our group represents what we now believe is a very significant breakthrough in the context that it has now made possible the tuning of hitherto fixed-frequency laser sources by as much as  $1.3\text{cm}^{-1}$ . Previous to our efforts, the spectral shift of Raman active  $\text{H}_2$  vibrational transitions resulting from the collision of  $\text{H}_2$  with foreign gases had been studied for both the cases of passive and stimulated Raman scattering, May et al (1961), Foltz et al. (1966), Lallemand and Simova (1968), Robert et al. (1985), and Kelly and Bragg (1986). However, only He and Ne had been shown to give the positive valued frequency shifts necessary for tuning the  $\text{H}_2$  Raman shifted output of an

atomic Iodine laser into overlap with the  $P_1(4)$  transition of OH. The spectral shift induced by He and Ne are  $1.1 \text{ cm}^{-1}/100 \text{ atm}$  and  $0.4 \text{ cm}^{-1}/100 \text{ atm}$ , respectively, while the self induced  $\text{H}_2$  pressure shift is  $-0.3 \text{ cm}^{-1}/100 \text{ atm}$ .

In these earlier studies, stimulated Brillouin scattering effects were reported to limit the  $\text{H}_2/\text{He}$  mixing ratio usable for pressure tuning to a value of 60%/40%, Lallemand and Simova (1966). The pressure induced tuning shift of this 60%/40% gas mixture had a predicted value of  $\sim 0.26 \text{ cm}^{-1}/100 \text{ atm}$ . Thus, the Raman cell operating pressure necessary for the  $\sim 1.1 \text{ cm}^{-1}$  shift required by our experiment would be  $\sim 420 \text{ atm}$  ( $\sim 6500 \text{ psig}$ ), yielding a Raman broadened line width of  $\sim 0.9 \text{ cm}^{-1}$ . Subsequent experiments carried out in our lab showed that the partial pressure of He that could be used was dependent on the total pressure of the system. For example, at total gas pressures below  $\sim 70 \text{ atm}$  the onset of stimulated Brillouin occurs for He levels  $> 35\%$ . By contrast, we have found at total gas pressures  $> 100 \text{ atm}$ , the amount of He present can be increased to near 65%. This has resulted in our obtaining tuning coefficients as large as  $\sim 0.6 \text{ cm}^{-1}/100 \text{ atm}$ . In fact, at this time, pressure tuning in excess of  $1.3 \text{ cm}^{-1}$  has been demonstrated using He as an inert buffer gas. Equally important, we have observed very little degradation in either the stimulated Raman-shifting efficiency or linewidth. The observed increase in the stimulated Raman threshold input energy has been shown to follow that predicted by the increase in the  $\text{H}_2$  Raman linewidth due to pressure broadening effects  $\sim 0.2 \text{ cm}^{-1}/100 \text{ atm}$ , Robert et al. (1985), May et al. (1961). In summary, as a result of discovering that a  $\text{H}_2$  Raman shifter could be operated at He levels  $> 60\%$  we have been able to obtain  $\sim 1 \text{ cm}^{-1}$  spectral shifts at  $\sim 2.3\text{x}$  lower total gas pressure yielding a 2.3x narrower linewidth and stimulated energy threshold values lower than those previously reported. The successful completion of this

phase of our program was thus regarded at that time as a major milestone in our efforts to achieve a 2.9 $\mu$  IR laser system.

Unfortunately, the latter development, involving the H<sub>2</sub>/He Raman shifter, was somewhat overshadowed by new information coming from Vuman near the end of the subcontract time period. This new information suggested that several technical questions still remained unsolved as related to the final performance of the iodine laser system. Potentially, the most serious of these involved an unusably large (~ 10 mrad) beam divergence. Thus, to more fully address the seriousness of this problem, we negotiated with Vuman the leasing of their single shot Q-switched iodine-laser system. The results from this effort demonstrated that although modest improvements could be made in beam divergence e.g. by using unstable resonator optical cavity designs, they could only be achieved at a significant cost. This typically involved reduced operating time for the system, due primarily to the build up of pyrolysis products within the laser cavity. For example, the consequences of the pyrolysis product build-up limited the operating time of the iodine-laser system to < 5 hours, yielding a projected cost for operating this system of \$500-\$1000/hour. Furthermore, the pyrolysis problem does not currently appear to have any simple solution. Thus, we have had to conclude that the proposed Q-switched atomic-iodine laser, as characterized in terms of 5Hz operation with >400mJ/pulse with <2mrad beam divergence and with a mean time before failure of  $\geq$ 60 hours, cannot be built with current technology. It is also our belief that the present set of problems will require at least 2 years additional intensive effort to resolve. And, as a corollary to the latter statement, we believe we can say with some conviction that the resolution of these problems is unlikely to be realized by Vuman Ltd., i.e. if they are to be solved more than likely we at Georgia Tech would have to undertake the job.

## B. Evaluation of Other Proposed 2.9 $\mu$ Laser Systems:

As pointed out in our original phase I program, several techniques exist that, in principle, are capable of generating the required 2.9 $\mu$  IR laser radiation for the TP-LIF OH system. Thus, one of our research initiatives during Phase I was to have another serious look at each of these other potential IR sources. As before, these evaluations were based on several criteria; however, a critical bottom-line was that each of these alternative systems had to define a practical field compatible laser system. For example, considerations such as size/weight, power utilization, operating cost, and mean time before failure were paramount in our evaluation. As noted above, the final goal of this effort was to be assured that the generation of 2.9 $\mu$  laser radiation represented more than just a laboratory show piece. The results from these exploratory evaluations have been summarized here in the form of Table I. In short, it can be seen from this table that none of the methods discussed previously in our Phase I proposal leads to a practical field compatible IR laser system in a time frame of < 3 years.

The authors note that the above statement also applies to the Nd:YAG pumped tunable IR dye laser system. As indicated in our original proposal an IR dye laser had been shown to have strong lasing action near 1.3 $\mu$ . Thus, one possible source of 2.9 $\mu$  IR radiation that had been proposed involved the generation of the 1st Stokes H<sub>2</sub> Raman line (near 2.9 $\mu$ ), thereby overlapping the Q<sub>11</sub> ro-vibronic transition in OH. However, new results from a German laboratory (Dr. Werner, private communication) demonstrated that the lasing output from this class of dyes occurs as a train of pico-second pulses. Both the large increase in spectral linewidth and a significant increase in the required stimulated Raman threshold energy associated with operating in the transient response regime therefore resulted in our abandoning this IR generation scheme.

TABLE I. Evaluation of 2.9 $\mu$  Laser Systems

Laser System	Output Energy Req. (Driver Laser)	Status.	Physical Constraints	Capital Equip. Cost	Lab. Develop. Cost	Major Development Task
1. Atomic-Iodine(1.3 $\mu$ ) /1 <sup>st</sup> Stokes High Pressure Hydrogen (2.9 $\mu$ ) (Tunable Raman Shifter)	>150mJ TEM <sub>00</sub> , <2 mrad (1.3 $\mu$ )	Commercial single shot Q-switch 10mrad system available, final system <u>not</u> available (Tunable Raman Shifter complete)	Yes	75K \$	2 yr/min 400K \$	Repetition Rate, Flashlamp Lifetime, laser gas lifetime, <u>beam-divergence</u> , laser pulse width too long
2. I.R. Dye Laser(1.3 $\mu$ ) /1 <sup>st</sup> Stokes Hydrogen (2.9 $\mu$ )	>70mJ TEM <sub>00</sub> , <1 mrad, <0.3 cm <sup>-1</sup> linewidth (1.3 $\mu$ )	Commercial System <u>not</u> available, Requires Dye Development	No	30K \$	2 yr. 200K \$ -300K \$	Existing dyes are unacceptable, output occurs in transform limited picosecond pulses
3. 1.3 $\mu$ Nd:YAG Laser/1 <sup>st</sup> Stokes Hydrogen(2.9 $\mu$ )	>300mJ TEM <sub>00</sub> , <1 mrad, <0.3 cm <sup>-1</sup> linewidth (1.3 $\mu$ )	Commercial System <u>not</u> available	No	80K \$	2-3 yr -300K \$	Lasing transition has 5X higher threshold than 1.06 $\mu$ line, operation at 100°C Amplifier output dumps at 1.06 $\mu$
4. HF Laser 2.9 $\mu$	>50mJ 2P7 line	Commercial HF laser are available, can not generate output on weak 2P7 line	Yes	75K \$ -150K \$	2 yr/min -400K \$	Must set up Osc./Amp. HF laser, Pulse width in current systems is too long
5. Lithium Niobate OPO at 2.9 $\mu$	10mJ <0.3 cm <sup>-1</sup> linewidth	Commercial System not available	Yes	60K \$	2 yr/min -350K \$	Must oscillate idler frequency, operation exceeds damage threshold of components
6. Er <sup>3+</sup> :CaF <sub>2</sub> at 2.85 $\mu$	20mJ <0.3 cm <sup>-1</sup>	Under development at Hughes Aircraft	No	150K \$	2 yr/min -300K \$	Exact output wavelength not known, output pulse width questionable
7. Titanium Sapphire/ (0.85 $\mu$ ) 2 <sup>nd</sup> Stokes Hydrogen (2.9 $\mu$ )	>100mJ <0.2cm <sup>-1</sup> linewidth (0.85 $\mu$ )	Commercial System not available	Yes	150K \$	3 yr/min -300K \$ -500K \$	Narrow linewidth operation, pulse width, Flashlamp/converter lifetime
8. Ho:YLF/(2.0 $\mu$ ) 1 <sup>st</sup> Stokes Co <sub>2</sub> (2.9 $\mu$ )	>150mJ <0.2cm <sup>-1</sup> linewidth TEM <sub>00</sub> <1 mrad (2.0 $\mu$ )	Commercial System not available	No	75K \$	2 yr/min -300K \$ 400K \$	Pulse width, Narrow linewidth operation are questionable
9. Nd:YAG 1.06 $\mu$ /1 <sup>st</sup> * Stokes D <sub>2</sub> (1.5 $\mu$ )/ 1 <sup>st</sup> Stokes CH <sub>4</sub> (2.9 $\mu$ )	>400mJ (1.06 $\mu$ ) <0.2 cm <sup>-1</sup> linewidth, <1mrad, near TEM <sub>00</sub>	Commercial Nd:YAG Laser Available, Raman Shifting Technology demonstrated in laboratory	No	No Additional	1 year -150K \$	Complete Raman Cell Fabrication Complete Nd:YAG Mode Matching Optics

\* New proposed method

### C. New IR Laser Sources

In view of the results outlined in section II, a search for possible new IR sources (e.g. sources not identified in our Phase I proposal) was carried out as part of our Phase I program. From this new exploratory effort only one new method emerged that appeared capable of generating the requisite amount of  $2.9\mu$  energy and also had the potential for becoming a practical field system. This new IR source is based on the tandem Raman-shifting of the  $1.06\mu$  fundamental from a Nd:YAG laser.

In this new approach, a stimulated Raman laser beam at  $1.5\mu$  is generated from the  $1.06\mu$  YAG fundamental using the first Stokes Raman shift in a deuterium filled cell cooled to  $LN_2$  temperatures. The  $1.5\mu$  beam is then frequency shifted in a second multi-pass Raman cell containing methane. Finally, the resulting  $2.9\mu$  radiation is made to overlap the  $P_{13}$  line of OH by means of temperature tuning the Nd:YAG laser rod ( $0.9\text{ cm}^{-1}/20^\circ\text{C}$ ). These new research results together with a discussion of our proposed "new research" are expanded on in the text below.

As discussed previously, our research effort has been focused on evaluating all currently available technologies capable of satisfying the  $2.9\mu$  laser requirements of a TP-LIF OH sensor. Unfortunately, the system that appeared to be the highest probability of success, i.e. the atomic-iodine laser, did not live up to the specifications provided to us by Vuman Ltd. Nevertheless, we are quite optimistic that the Nd:YAG based system involving tandem deuterium/methane Raman shifters will provide  $2.9\mu$  radiation in excess of our 10 mJ requirements. We feel confident, therefore, that the development of a two-photon LIF OH sensor can be put back on schedule. The performance of this new system, with 10 mJ of  $2.9\mu$  radiation, will be the same as stated in our original proposal. For

example, for a 10 min. integration period,  $3.7 \times 10^5$  OH molec./cm<sup>3</sup> could be detected at ground level with a 2:1 S/N ratio. At a concentration level reflecting model calculated diurnal averaged values of OH, i.e.  $1.4 \times 10^6$  molec./cm<sup>3</sup>, a 10 min. integration time would yield a S/N ratio approaching 8:1. On the other hand, for an airborne system operating at 6 km, an OH concentration of  $3.7 \times 10^5$  molec./cm<sup>3</sup> would yield a 10:1 S/N ratio for a 10 min. integration period. (For further details on these signal/noise calculations see Appendix II.)

Also, not to be overlooked in pursuing this new YAG based IR source is the fact that this new laser configuration will be compatible with our future miniaturized/modularized airborne LIF system.\* In principle, therefore, this new airborne system could be switched between NO/NO<sub>2</sub>/NO<sub>y</sub>, NH<sub>3</sub>, SO<sub>2</sub> and OH.

#### (1) Development of a 2.9μ Nd:YAG Based IR Laser System

Spectroscopic Characterization of IR Laser System - We are proposing the development of an IR laser system that will overlap the P<sub>13</sub> line of OH centered at 3484.7 cm<sup>-1</sup> (3484.7cm<sup>-1</sup> defines the center of the Λ double † components of the P<sub>13</sub> line, Amano, 1984). The absorption coefficient/rotational population product of this ro-vibronic transition is comparable to that estimated for the Q<sub>1</sub> transition appearing in our original proposal (See Appendices I and II). Like the originally proposed Q<sub>1</sub> pumping scheme, the P<sub>13</sub> OH line is sufficiently far removed from any strong H<sub>2</sub>O absorption lines that no interference from atmospheric water vapor absorption is expected.

The proposed driver laser for this new 2.9μ IR laser system will be a commercially available Nd:YAG laser. In this context, we have tested the spectral output characteristics of both Quanta Ray DCR-IA and Quanta Ray DCR-IIA Nd:YAG lasers. The "exact" output wavelength of these systems was determined by monitoring the output of a sum-frequency mixed dye laser/1.06μ Nd:YAG laser at

both the direct dye laser wavelength and the sum frequency mixing output wavelength via opto-galvanic signals from Ne, He, or Ar metastable states as generated in a Hollow-cathode discharge lamp. In this case, both laser systems were shown to have frequency outputs at  $9394.7 \pm 0.4 \text{ cm}^{-1}$  when operated with the oscillator cavity box at a temperature between 25 and 35°C. We have also verified that the temperature tuning characteristics of these Nd:YAG lasers is  $\sim 0.9 \text{ cm}^{-1}/20^\circ\text{C}$  over the temperature range of +5°C to +45°C. Finally, we have determined that long term operation of these field compatible laser systems will not be degraded over this temperature range due to decomposition of the polymeric material used in the laser cooling system.

With the Nd:YAG output frequency and tunability defined, the second major element required in the generation of a  $2.9\mu$  laser source is a LN<sub>2</sub> cooled D<sub>2</sub> Raman shifter. The latter element generates a  $1.56\mu$  beam from the first Stokes stimulated-vibrational Raman shifting of the Nd:YAG fundamental at  $1.06\mu$ . The output wavelength at  $1.56\mu$  is produced from the Q(0) transition in deuterium when cooled to liquid nitrogen temperature. Earlier work carried out by Minck et al. (1963 and 1966) suggests that the simulated vibrational Raman gain in a deuterium filled cell should be dominated by the Q(2) transition for temperatures  $\geq 260^\circ\text{K}$ , by the Q(1) transition for temperatures between  $85^\circ\text{K}$  and  $260^\circ\text{K}$ , and finally by the Q(0) transition below  $85^\circ\text{K}$ . These transitions occur at  $2987.2 \text{ cm}^{-1}$ ,  $2991.4 \text{ cm}^{-1}$ , and  $2993.5 \text{ cm}^{-1}$ , respectively.

As noted earlier, verification of the above frequency assignments as well as the production of stimulated Raman scatter at  $2993.5 \text{ cm}^{-1}$ , Q(0) transition, has now been confirmed in our laboratory. These experiments involved the stimulated vibrational Raman shifting of a Nd:YAG pumped dye laser with wavelength verification as described previously in the text. (The liquid nitrogen cooled Raman cell was obtained on loan from a group at Ames Research

Laboratory.) At this point, it must be emphasized that the near  $7 \text{ cm}^{-1}$  shift observed in the spectral line position of the Q(0) transition relative to the normally observed Q(2) transition (at 298K) is essential in obtaining a spectral overlap with the P<sub>13</sub> OH transition at  $2.9\mu$ . This requirement is dictated by the limited wavelength temperature tuning range available from our Nd:YAG laser.

The Raman linewidth for the Q(0) deuterium transition is estimated to fall in the range of  $0.1$  to  $0.2 \text{ cm}^{-1}$ , depending on the gas density employed. These estimates are based upon the broadening coefficients given by Murray and Javan (1972) and Minck, et al. (1966).

The third element required for generating  $2.9\mu$  radiation in our new scheme involves the injection of the  $1.56\mu$  output beam, generated by the LN<sub>2</sub> cooled D<sub>2</sub> Raman cell, into a multi-pass methane Raman cell. The generation of stimulated vibrational Raman scatter in methane using a multi-pass cell geometry has been demonstrated by Owyong et al. (1978). The stimulated Raman spectral features of this polyatomic molecule are more complex than for simple diatomics such as H<sub>2</sub> or D<sub>2</sub>; however, the  $\nu_1$  band has been shown to yield maximum stimulated Raman gain at 298°K in a band centered at  $2916.7 \text{ cm}^{-1}$  (Minck et al. (1961), Owyong et al. (1976) and Henesian et al. (1976)). Independent verification of this frequency assignment was carried out in our lab over the pressure range of 4.5 to 80 atm. The estimated Raman linewidth of this transition is between  $0.15$  and  $0.4 \text{ cm}^{-1}$ , depending on the gas pressure used. (The determination of the optimum pressure to be used in the CH<sub>4</sub> cell will be one of the research tasks in our proposed research program.)

Estimate of Overall  $2.9\mu$  Laser Efficiency - The spatial mode requirements of a pump laser for efficient stimulated Raman conversion are well documented, see for example: Carlsten et al. (1984); Tomov et al. (1983); Armandillo et al. 1985; Natterman et al. (1986); Walmsley et al. (1985); Trunta et al. (1980); and

Manik et al. (1986). The ability of unstable optical cavity resonator designed pump lasers to produce high stimulated Raman conversion efficiencies, due to their nearly TEM<sub>00</sub> diffraction limited beam qualities, has also been well established (see above references). In particular, the diffraction coupled unstable resonator design employed in Quanta-Ray DCR Nd:YAG lasers has been shown to be an extremely efficient pump laser for generating stimulated vibrational Raman scattering (see for example Byer (1980), Trunta and Byer (1980) and, Byer and Trunta (1978)).

In the generation of 2.9 $\mu$  radiation, the LN<sub>2</sub> cooled D<sub>2</sub> Raman cell was chosen to be the first frequency shifting element in the overall system for two reasons: (1) the higher pump energy available from the Nd:YAG laser is required to obtain the highest efficiency for the first Stokes stimulated Raman output in D<sub>2</sub>. (The latter condition reflects the approximate 2x lower gain in D<sub>2</sub> as compared to CH<sub>4</sub>.) And (2), there are some very practical limitations to the physical dimensions of the Raman cell that can be fabricated for a field compatible multi-pass LN<sub>2</sub> cooled D<sub>2</sub> system.

Unfortunately, we were not able to carry out high energy 1.06 $\mu$  conversion efficiency test with the LN<sub>2</sub> cell on loan to us. This was prevented by the relatively short path length of the cell, e.g. 25 cm. We were, however, able to carry out numerous conversion efficiency studies using a D<sub>2</sub> filled Raman cell operated at 298K. In the latter case, it was found that optical waveguide systems that show excellent efficiency at relative low pump energies, i.e. < 50 mJ, (Mannik and Brown (1986), Hartig and Schmidt (1979), Rabinowitz et al. (1976) and Berry et al. (1982)) require excessively large capillary bore diameters when used at high energies, i.e. 400 -700 mJ. These large bore diameters were dictated by material damage problems and optical breakdown within the capillary. We have also found that the output spatial beam qualities of

these large bore systems are typically incompatible with the input beam acceptance criterion of a multi-pass cell. On the other hand, long focal length Raman cell configurations (i.e. > 3 m) have been shown to be efficient at generating first Stokes output by reducing the four wave mixing energy loss into higher order Stokes and anti-Stokes lines, see for example: Trainor et al. (1982); Brueck and Kildal (1982); Duncan et al. (1986); and Walmsey et al. (1985). These systems also are capable of providing high efficiency 1st Stokes output beams of acceptable spatial quality for subsequent use in a multi-pass Raman system. Unfortunately, the physical size of this type system is not compatible with a field sampling platform.

The approach which now appears to eliminate many of the short comings of the systems discussed above utilizes the backward generated 1st Stokes stimulated scatter from the LN<sub>2</sub> cooled D<sub>2</sub> cell. Efficient generation of backward stimulated Raman scatter has been shown by several groups (Tomov et al. (1983); Carlsten et al. (1984) and Brneck and Kidal (1982)). Backward scattered stimulated Raman output differs from its forward scattered counterpart in many respects. The four wave mixing processes that can severely limit forward scattering efficiency are not present in the backward wave. However, the backward generated wave exhibits a significantly stronger dependence on pump laser bandwidth than its forward scatter counterpart. The pump laser bandwidth must be less than the Raman linewidth for generation of backward stimulated Raman scattering (Murray and Javan (1972); Trunta et al. (1979); Djotyan et al. (1986) and Tomov et al. (1983). On the other hand, the Raman linewidth is also larger in the backward direction (Murray and Jarvan (1972). In this system, the YAG linewidth (etalon narrowed) is < .1 cm<sup>-1</sup>; whereas, that estimated for backward scattered stimulated Raman would be in the range of .1 to .2 cm<sup>-1</sup>. A further plus favoring backward scattered Raman output involves the observation

that the optical quality of the backward scattered 1st Stokes Raman beam closely parallels the optical quality of the laser pump beam.

Tests carried out in our lab using a 40 cm long D<sub>2</sub> Raman cell, held at 298K and pumped by the far field image of a Quanta-Ray DCR Nd:YAG laser, produced ~ 90 mJ of backward generated Raman energy at 1.56 $\mu$ . The output beam in this case had a beam divergence of < 1.5 mrad. We estimate that the efficiency of this first step should be further improved with LN<sub>2</sub> cooling due to the higher rotational population density at 77°K and somewhat reduced Raman linewidth (Murray and Javan). Thus, based on a significant amount of testing in our lab as well as considerable work by other investigators, it looks quite encouraging that a high spectral brightness backward propagating 1st Stokes stimulated beam from a LN<sub>2</sub> cooled deuterium cell can be generated.

As discussed earlier in the text, the third major optical element in our proposed 2.9 $\mu$  IR laser system involves the use of a multi-pass methane Raman cell. In our system the input wavelength would correspond to the 1.56 $\mu$  output from a LN<sub>2</sub> D<sub>2</sub> Raman cell. The pump laser beam parameters necessary for efficient Raman conversion in multi-pass cell geometries have been well documented, see for example: Trunta and Byer (1980); Rabinowitz et al. (1978); Rabinowitz et al. (1986); Tashiro et al. (1986); Byer and Trunta (1978); Midorikawa et al. (1985); and Kravstov and Naumkim (1976). The basic principles related to this type of off-axis spherical interferometer (i.e. multi-pass Raman gain cell) and the spatial input laser beam mode matching criterion have also been well formulated, see for example: Fork et al. (1964); Kogelnik and Li (1966); Herriott et al. (1964) and Trunta and Byer (1980). Of key importance to our proposed system is the fact that the 1st Stokes Raman threshold is

inversely proportional to the number of passes within the Raman gain cell for a properly mode matched pump laser beam.

First Stokes stimulated vibrational Raman thresholds in  $H_2$  as low as  $\sim 2$  mJ (200 kw peak power) have been obtained for a 20 pass gain cell using a  $1.06\mu$  Nd:YAG laser pump (Trunta and Byer (1980)). The same pump laser system exhibited a single pass Raman threshold of  $\sim 25$  mJ (3.1 MW peak power). Scaling these  $1.06\mu/H_2$  results to our proposed  $1.56\mu/CH_4$  Raman cell suggests a 4x increase in the expected 1st vibrational Raman threshold, i.e.  $\sim 8$  mJ/for an 8 ns laser pulse. However, to obtain maximum conversion efficiency in  $CH_4$  would require a 4x higher energy than the threshold energy or 32 mJ pulse.

Tests carried out in our lab using a single pass methane Raman cell and a  $1.06\mu$  pump laser have resulted in a measured 1st Stokes threshold energy of 50 mJ/pulse, in good agreement with theoretical estimates of 45 mJ for a pump configuration similar to that used in our experiments. Thus, scaling these single pass  $1.06\mu$   $CH_4$  tests to a single pass  $1.56\mu$  pump laser results in an estimated 4x increase in the observed 1st Stokes Raman threshold for  $CH_4$  (i.e.  $\sim 200$  mJ/pulse). With the use of a multi-pass Raman cell, the projected threshold energy for the  $CH_4$  system would then be 13 mJ/pulse for 16 effective passes. As noted above, however, for maximum conversion efficiency the desired pump energy would be  $\sim 4x$  higher than threshold or 52 mJ/pulse.

Since 1st Stokes simulated vibrational Raman scatter in multi-pass gain cells has been demonstrated to have photon conversion efficiencies of  $\geq 70\%$ , in the absence of 2nd Stokes growth, the anticipated energy conversion efficiency of our proposed  $1.56\mu$  pumped multi-pass methane system is conservatively estimated to be  $\geq 30\%$ . Thus, the generation of  $> 10$  mJ of narrow band IR output at  $2.9\mu$  should be easily achieved based on results on hand.

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