

17:34:13

OCA PAD INITIATION - PROJECT HEADER INFORMATION

10/13/87

Active

Project #: G-35-665
Center # : R6402-0A0

Cost share #: G-35-378
Center shr #: F6402-0A0

Rev #: 0
OCA file #:
Work type : RES
Document : GRANT
Contract entity: GTRC

Contract#: NAG-1-818
Prime #:

Mod #: INITIATION

Subprojects ? : N
Main project #:

Project unit: GEO SCI
Project director(s):
BRADSHAW J D GEO SCI

Unit code: 02.010.140

Sponsor/division names: NASA
Sponsor/division codes: 105

/ LANGLEY RESEARCH CTR, VA
/ 001

Award period: 871001 to 880930 (performance) 880930 (reports)

Sponsor amount	New this change	Total to date
Contract value	148,091.00	148,091.00
Funded	148,091.00	148,091.00
Cost sharing amount		14,046.00

Does subcontracting plan apply ? : N

Title: DEVLPMNT OF A TWO-PHOTON/LASER-INDUCED FLUORESCENCE SENSOR..OH RADICALS

PROJECT ADMINISTRATION DATA

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Security class (U,C,S,TS) : U

ONR resident rep. is ACO (Y/N): Y

Defense priority rating : N/A

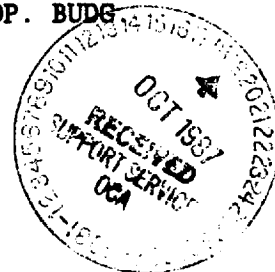
supplemental sheet

Equipment title vests with: Sponsor

GIT X

PRIOR APPROVAL REQUIRED FOR ITEMS OVER \$1,000 IF NOT IN APPROVED PROP. BUDG

Administrative comments -
INITIATION.



GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION

NOTICE OF PROJECT CLOSEOUT

Closeout Notice Date 02/21/91

Project No. G-35-665 _____ Center No. R6402-0A0 _____

Project Director BRADSHAW J D _____ School/Lab E & A SCI _____

Sponsor NASA/LANGLEY RESEARCH CTR, VA _____

Contract/Grant No. NAG-1-818 _____ Contract Entity GTRC

Prime Contract No. _____

Title DEVELOPMENT OF A TWO-PHOTON/LASER-INDUCED FLUORESCENCE SENSOR..OH RADICALS

Effective Completion Date 901031 (Performance) 901031 (Reports)

Closeout Actions Required:	Y/N	Date Submitted
Final Invoice or Copy of Final Invoice	Y	_____
Final Report of Inventions and/or Subcontracts	Y	_____
Government Property Inventory & Related Certificate	Y	_____
Classified Material Certificate	N	_____
Release and Assignment	Y	_____
Other _____	N	_____
CommentsSF-272 WILL SERVE AS THE FINAL VOUCHER. _____		

Subproject Under Main Project No. _____

Continues Project No. _____

Distribution Required:

Project Director	Y
Administrative Network Representative	Y
GTRI Accounting/Grants and Contracts	Y
Procurement/Supply Services	Y
Research Property Management	Y
Research Security Services	N
Reports Coordinator (OCA)	Y
GTRC	Y
Project File	Y
Other _____	N
_____	N

NOTE: Final Patent Questionnaire sent to PDPI.

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

SEMI-ANNUAL REPORT

October 1, 1987 to March 31, 1988

Submitted to:

Project Monitor Dr. Edward Browell

THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

TROPOSPHERIC CHEMISTRY PROGRAM

EARTH SCIENCE AND APPLICATION DIVISION

OFFICE OF SPACE SCIENCE AND APPLICATIONS

WASHINGTON, D.C.

Submitted by:

Dr. John D. Bradshaw, Principal Investigator

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Atlanta, GA 30332-0340

Co-Investigator

Dr. Cornelius VanDijk, Georgia Tech

I. SEMI-ANNUAL PROGRESS REPORT

A. Summary of NASA Workshop on "The Generation of Tunable Infrared Radiation In the 2.8μ Wavelength Region"

A workshop on the generation of tunable IR radiation was held at SRI International with Dr. David Crosley acting as organizer and chairman. Dr. Crosley's summary of this meeting is provided in Appendix I. The workshop has proven to be extremely beneficial to our research effort. The laser experts which Dr. Crosley assembled were able to provide our group with substantial enough recommendations to allow us to focus our research effort. We are especially indebted to Drs. Bischel and Murray for their continued interaction with our research and to Dr. Crosley for organizing the workshop and for his overall scientific commitment in support of atmospheric chemistry programs.

As a result of the IR workshop, our group has focused on three action items, these being: (1) to once again re-evaluate the possible utilization of solid state lasers for either directly pump an OH transition or to be used in a single stage frequency down conversion scheme to indirectly pump an OH transition; (2) to incorporate injection seeding into our Nd:YAG laser in order to provide narrow linewidth and a uniform temporal profile; and (3) to aggressively pursue the double Raman shifting frequency down conversion scheme outlined in our proposal (see also, NSF final report on ATM 85087246).

B. Re-evaluation of Solid-State Lasers

The only possible candidate which has emerged from our re-evaluation is that of Er:YAG pumping the P(4.5) OH line near 2.936μ . However, the frequency mismatch between the Er:YAG laser line and the OH line is approx. 3 cm^{-1} . We have been unable to obtain information as to the temperature tuning coefficient for Er:YAG (dv/dt) for the 2.9μ transition. If we optimistically assume that it has the same coefficient as Nd:YAG at 1.06μ ($0.043\text{ cm}^{-1}/^\circ\text{C}$), then the Er:YAG substrate would

need to be cooled to approximately 220°K in order to provide wavelength overlap with the P(4.5) OH transition. At this point, we have concluded that although feasible, the Er:YAG system is not a practical within the limited scope of our research project.

C. Injection Seeded Nd:YAG Laser System

Modification of our Spectra-Physics DCR-3A Nd:YAG laser to incorporate a Lightwave, Inc. injection seeding system was completed in February. The injection seeded Nd:YAG laser has now successfully undergone a performance evaluation. At this time, the laser system meets all operational specifications applicable to operation under aircraft conditions.

D. Double Raman Shifting of 1.06μ Nd:YAG Laser

We are currently carrying out an extensive series of tests in order to ascertain the optimum Raman cell design and laser beam focusing parameters. The information to be obtained during this research effort will critically effect the final designs of both of the LN₂ cooled deuterium Raman cells and the multi-pass methan Raman Cell. Completion of this phase of research is anticipated by July of 1988. Final construction and testing of the double Raman shifting system is currently scheduled for the Fall of 1988. This latter time schedule reflects the reduced manpower commitment on this project during our groups involvement in the NASA GTE/ABLE-3 expedition. As noted in our original proposal a no cost extension of the original proposal renewal date may be necessary due to our concurrent involvement in the ABLE-III mission.

APPENDIX I



November 11, 1987

Dr. R. J. McNeal
Tropospheric Chemistry Program
National Aeronautics and Space Administration
Washington, DC 20546

Dear Dr. McNeal:

On 29 and 30 October 1987, a workshop was held at SRI International on the generation of tunable infrared radiation in the $2.8 \mu\text{m}$ wavelength region. The objective of the workshop was to review, select, and recommend the most promising techniques for use in a proposed method of laser-induced fluorescence detection of tropospheric hydroxyl radicals. That method, under development at the Georgia Institute of Technology, involves pumping the OH from the ground vibrational level to $v''=1$ using an infrared photon, with ultraviolet pumping from $v''=1$ to the $v'=0$ level of the first excited electronic state, which then fluoresces. This two-photon method avoids two crucial problems, OH generated through laser photolysis of ozone and nonresonant background fluorescence, which have plagued previous measurements of tropospheric OH.

Four experts in the area of infrared generation participated in the workshop. They are: William Bischel, SRI International; Robert Eckardt, Stanford University; Norman Kurnit, Los Alamos National Laboratory; and John Murray, Lawrence Livermore National Laboratory. Also taking part were: David Crosley and Karen Rensberger of SRI, who perform laboratory experiments on OH pertinent to tropospheric measurements; John Bradshaw, Michael Rodgers and Cor Van Dijk of Georgia Tech; and Joe McNeal of NASA. The workshop format was informal; presentations were made by Crosley, describing background on OH measurements; by Bradshaw, on infrared laser requirements and the methods tried at Georgia Tech; by Kurnit, on stimulated Raman shifting (SRS); and by Eckardt, on optical parametric oscillators (OPOs). Most of the time, however, was spent in discussion.

In order to provide adequate sensitivity for detection of tropospheric OH using this method, approximately 10 mJ of tunable laser energy in the wavelength region of $2.8 \mu\text{m}$ and a bandwidth of 0.1 to 0.2 cm^{-1} is needed.

SRI International

333 Ravenswood Ave. • Menlo Park, CA 94025 • (415) 326-6200 • TWX: 910-373-2046 • Telex: 334486 • Facsimile: (415) 326-5512

The availability for use in the monitoring system without laser developmental work, and a capability to be incorporated into a hardened, aircraft-worthy apparatus, were also considered important criteria.

One technique, which was originally proposed by the Georgia Tech group, appears the most promising for implementation of the method within a time frame of one to two years. This is a double SRS of Nd:YAG laser lines at $1.06\text{ }\mu\text{m}$, with improvements suggested at the workshop. It should be capable of delivering the needed laser pulse energy (and perhaps much better), and should be able to be incorporated into a field instrument within two years.

A second method, a single SRS of Nd laser lines at $1.3\text{ }\mu\text{m}$, should be looked into further as another near-term possibility. Other methods, including OPOs, color center lasers, and Ho and Er lasers, have promise for the longer-term future; their development elsewhere should be watched and they should be reconsidered at a later date (perhaps three to five years). In the remainder of this letter, details of these various techniques as discussed at the workshop will be described.

Double Raman shifting of $1.06\text{ }\mu\text{m}$ Nd:YAG lines In this method, a YAG laser is shifted twice, once in liquid-nitrogen-cooled D_2 and once in CH_4 . Tunability of the final $2.8\text{ }\mu\text{m}$ line is provided by temperature tuning of the YAG crystal, and pressure tuning the first shift using mixtures of D_2 and He. Details are provided in the Georgia Tech final report to NSF on grant ATM85-08246.

The low-gain shifter should precede the high gain because of the lower threshold and higher energy available at the shorter wavelengths. It is not clear, a priori, whether the D_2 or CH_4 cell has lower gain. However, thermal considerations (~30% of the initial energy is dumped into the gas) suggest the D_2 cell first. Further, the CH_4 cell will produce a broader linewidth and should be second. Backward scattering (extracting the shifted beam with a dichroic) is preferable to forward, mostly because of the phase conjugation properties of backward scattered SRS, which could be of considerable benefit in a mechanically unstable aircraft environment. A forward scattered call can provide a higher ultimate conversion, but must be made multipass to do so. The more compact nature of a backward SRS cell, to provide higher gain on a single pass, will also have advantages for the D_2 cell on an aircraft-worthy system.

The lower gain obtained in the CH_4 cell requires that it be multipass in any event. However, it is not necessary to have a large number of reflections; two to four passes should be sufficient to provide the necessary gain. This will be considerably easier to construct into a hardened apparatus than the many-pass cell envisioned in the Georgia Tech proposal. Also, a planar multipass configuration can be used to provide rapid gas circulation and avoid heating problems.

Seeding of a single-mode YAG laser, into the $1.06 \mu\text{m}$ laser to be shifted, should be incorporated into the system. This can be done with commercially available components at a cost of some \$20,000. Here, a diode-pumped ring YAG, temperature-tunable over a 2 cm^{-1} range and with a transform-limited (10 ns pulse) bandwidth of 48 MHz, is injected into an unstable self-filtering resonator cavity of the main YAG oscillator. One advantage is a filled-in, nearly diffraction-limited beam, better than the Quanta-Ray doughnut. More important, however, is the smooth temporal pulse shape. Instead of a series of nanosecond and subnanosecond spikes, a smooth and extremely reproducible pulse shape is obtained. The highly nonlinear nature of the subsequent SRS processes means that even 10% temporal fluctuations in the YAG can translate into 100% fluctuations (i.e., below threshold) at $2.8 \mu\text{m}$.

The bandwidth of the seeded laser is a bit narrower than desirable for the ultimate $2.8 \mu\text{m}$ radiation, whose optimum value is $\sim 0.1 \text{ cm}^{-1}$ to match the anticipated pressure broadening of the OH infrared absorption. However, at realistic operating pressures, the CH_4 SRS cell is expected to contribute a linewidth of about this amount. In the D_2 cell, linewidths may be influenced by Stark broadening if the focus is too tight; this is about 25 MHz per GW/cm^2 . It is not yet known how easily a D_2/He mixture can be pressure-tuned, although it is expected that, while the range will be less than for H_2/He investigated experimentally at Georgia Tech, it will be adequate.

Single shift of a $1.3 \mu\text{m}$ Nd line This method, considered earlier at Georgia Tech, should be reevaluated. In it, a $1.3 \mu\text{m}$ Nd laser line is shifted once in H_2 . There are two key questions. First, how readily can the lasing at $1.3 \mu\text{m}$ be obtained while the $1.06 \mu\text{m}$ lines are suppressed? This may require temperature control leading to problems with tuning into resonance, although a variety of crystal hosts for the Nd could be used. Second, can such a system be assembled using

Dr. R. J. McNeal
November 11, 1987
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available components? Norman Barnes of NASA Langley is the expert on this process and these lasers, and his advice should be sought.

Optical parametric oscillators OPOs which can provide the needed laser power are now available on a research basis only. These incorporate new AgGaSe_2 crystals, which are not only efficient but can tolerate extremely high laser energies. For example, it is predicted that in the future 100 mJ of shifted radiation can be obtained from a 1 J pump laser; heating problems would begin to occur at tens of watts input power. A good choice for $2.8 \mu\text{m}$ would be an OPO pumped by a Ho laser at $2.05 \mu\text{m}$. However, neither the OPO nor the Ho laser is available in a mode which could be incorporated now into a field-ready system. Projections of the rate of laser development are very difficult, and the necessary improvements for commercial availability may occur on a time scale of anywhere from one to five years. These developments should be watched for future use but not considered for the system to be built now.

Other methods Ho and Er lasers, for direct use and as input to OPOs, are now under development and should also be reevaluated at a later date. Color center lasers can be made pulsed and in the right wavelength region (perhaps with a $1.6 \mu\text{m}$ Yb pump laser) but are not ready for use now. Infrared dyes, once considered seriously by Georgia Tech, are unlikely to be made to operate stably at the required power levels and should not be reconsidered.

Sincerely,

David R. Crosley
Chemical Physics Laboratory

DRC:djw

cc: Norman Barnes, NASA LaRC
John Bradshaw, Georgia Tech
William Bischel, SRI
Edward Browell, NASA LaRC
Douglas Davis, Georgia Tech
Robert Eckardt, Stanford

James Hoell, NASA LaRC
Norman Kurnit, LANL
Jarvis Moyers, NSF-ATM
John Murray, LLNL
Karen Rensberger, SRI
Michael Rodgers, Georgia Tech
Cor Van Dijk, Georgia Tech

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

(NAG-1-818)

SEMI-ANNUAL REPORT

April 1, 1988 to September 30, 1988

Submitted to:

Project Monitor Dr. Edward Browell

THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
TROPOSPHERIC CHEMISTRY PROGRAM
EARTH SCIENCE AND APPLICATION DIVISION
OFFICE OF SPACE SCIENCE AND APPLICATIONS
WASHINGTON, D.C.

Submitted by:

Dr. John D. Bradshaw, Principal Investigator
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Co-Investigator

Dr. Cornelius van Dijk, Georgia Tech

I. SEMI-ANNUAL PROGRESS REPORT

(Covering Period April 1, to September 30, 1988)

During this reporting period, we have concentrated our research efforts at ascertaining the optimum Raman cell design and laser beam focusing parameters. The information obtained from this research effort will critically effect the final designs of both the LN₂ cooled deuterium Raman cells and the multi-pass methane Raman cell.

Working with room temperature Raman cells we have now defined an optical geometry which can routinely produce in excess of 140mJ of 1.5 micron energy via backward propagating stimulated Raman scattering. This system is currently operating at approximately 42% photon conversion efficiency. The configuration being employed is capable of extended operation without sustaining noticeable optical damage. We are anticipating a further increase in conversion efficiency under LN₂ operating conditions.

Efforts on the second stage methane Raman shifting of this 1.5 micron beam have also been encouraging. To date, we have now generated 4mJ of 2.9 micron forward propagations energy using a single pass methane Raman cell configuration. Our research indicates a significant depletion of the 1.5 micron pump beam and roll-off of 1st stokes 2.9 micron energy with increasing 1.5 micron pump energy. Further optimazation of the forward propagating 2.9 micron 1st stokes beam and characteristics of the backward generated beam is now in progress. At this point we are optimistic that the requisite 2.9 micron energy required for a successful field compatible TP-LIF OH instrument, can be generated via the proposed approach.

Construction and testing of the LN₂ cooled system should be complete in the mid January, 1989 time frame. Final sensitivity test will commence at that time and should be complete by mid June, 1989.

A continuation of funding will be sought upon successful completion of the above stated research objectives. Completion of these objectives should occur within the nine month no-cost extension, which has been granted to this project.

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

(NAG-1-818)

SEMI-ANNUAL REPORT

Performance Period Ending February 28, 1989

Submitted to:

Project Monitor: Dr. Edward V. Browell

THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

LANGLEY RESEARCH CENTER

MAIL STOP 401A

HAMPTON, VIRGINIA 23665

Submitted by:

Dr. John D. Bradshaw

School of Geophysical Sciences

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Atlanta, Georgia 30332-0340

SEMI-ANNUAL REPORT

(Performance Period Ending February 28, 1989)

During this reporting period work has been completed on defining the preferred first stage Raman shifter. This stage will consist of a LN₂ cooled deuterium Raman Cell generating either backwards stimulated first Stokes radiation near 1.5 μ or forward second Stokes near 2.9 μ . Methane was found to give inferior performance as a first state system compared to Deuterium.

As last reported, 4mJ of the 10mJ required from an OH sensor at 2.9 μ had been generated at 2.9 μ from the deuterium/methane tandem Raman shifting configuration. It now appears that a significant fraction of the 1.5 μ deuterium generated beam used to pump the second phase methane cell is being depleted into a backward generated 2.9 μ beam from the methane cell. Work is currently in progress to quantify the energy available in this backward 2.9 μ methane generated beam. Preliminary results suggest that it is much higher energy than the 4mJ forward beam and should contain sufficient energy for an OH sensor.

All tests to date have been carried out at low repetition rates (i.e. 1 H₂). Higher repetition rates are not possible without a stirred or flowing gas cell arrangement. This does not represent any significant technical challenge and has been demonstrated by other investigators to solve thermal diffraction problems in high repetition rate systems. However, current remaining funds are insufficient to construct this style Raman cell. Funds remaining will allow us to construct an LN₂ cooled low repetition (non-flowing) Raman cell and to demonstrate proof of method concept at low

repetition rates (i.e. 1 or 2 H₂).

Completion of this phase of research in which proof of concept is demonstrated, should be achievable by the mid-June 1989 time frame. This proof of concept will leave two scaling factors remaining, these being the number of detection photomultipliers used and the laser repetition rate the former being a well defined scaling factor.

Completion of the final high repetition rate Raman cells will require approximately \$30K from funds which have as of yet, not been well defined.

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

(NAG-1-818)

SEMI-ANNUAL REPORT

Performance Period Ending September 30, 1989

Submitted to:

Project Monitor: Dr. Edward. V. Browell

THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

LANGLEY RESEARCH CENTER

MAIL STOP 401A

Submitted by:

Dr. John D. Bradshaw

**School of Earth and Atmospheric Sciences
Georgia Institute of Technology
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SEMI-ANNUAL REPORT

(Performance Period Ending September 30, 1989)

As reported previously the first stage of the 2.9 micron laser source is comprised of a Nd:YAG laser operating a 1.06 micron which is utilized to pump a backward propagating stimulated Raman source with an output wavelength near 1.5 micron. This 1.5 micron laser source has now demonstrated near diffraction limited beam divergence with pump source conversion efficiencies in excess of 45% and is routinely capable of generalizing 150-200mJ 1.5 micron output energies.

Application of this technology to the production of 1.5 micron "Eyesafe" LIDAR systems has already proven fruitful via our collaboration with existing groups working in the field of LIDAR and LASER RADAR research.

During this reporting period further work was carried out on optimizing the performance characteristics of the second stage methane Raman shifting portion of the 2.9 micron laser source being developed. The 1.5 micron laser source generated via phase conjugate stimulated Raman frequency down conversion in deuterium of a 1.06 micron Nd:YAG pump laser is utilized as a pump source for the second stage production of phase conjugate stimulated Raman frequency down conversion, using methane as the active media. Optimization of this system has now led to the generation of 18mJ of near diffraction limited output energy at 2.9 micron.

Thus we have now successfully generated spectrally narrow-band laser output with low beam divergence that is well in excess of our target goal of 10mJ.

Work is in progress on further improving the efficiency of this 2.9 micron laser system. In addition, work has begun on utilizing a liquid nitrogen cooled deuterium Raman cell in the first stage of this laser source in order to provide the required spectral overlap of the 2.9 micron laser output with that of the desired hydroxyl radical $v''=0 \rightarrow v'=1$ ro-vibronic transition of interest.

"Development of a Two-PHOTON

LIF OH INSTRUMENT"

NAG-1-818

SEMI-ANNUAL REPORT

Performance Period Ending: March 31, 1990

Submitted To:

Project Monitor: Dr. Edward V. Browell

Grant Officer : Mr. John F. Royall

THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

LANGLEY RESEARCH CENTER

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HAMPTON, VA 23665

Submitted by:

Dr. John D. Bradshaw

School of Earth and Atmospheric Sciences

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SEMI-ANNUAL REPORT

PERIOD 9/28/89-2/28/90

As previously reported, a tandem Raman laser has been constructed using a 1.06μ Nd:YAG laser as the fundamental pump source to generate a backward propagating stimulated Raman (D_2 gas) source near 1.5μ (150-200 mJ/pulse), which in turn is used to generate a second backward propagating stimulated Raman (CH_4 gas) source near 2.9μ . This 2.9μ Raman Laser can now produce 18 mJ of near diffraction limited output energy.

The Nd:YAG laser utilized in the above studies has an injection-seeded (linewidth $< 0.01\text{ cm}^{-1}$) laser oscillator using unstable resonator optics. The unstable resonator optics provides a near diffraction limited output beam with approximately 65% of it's energy usable for efficient Raman conversion processes (the remaining 35% contained in higher order modes). In addition, at high average power the output of the laser suffers some depolarization due to increased birefringence caused by high thermal loading, this can affectively reduce energy, which is usable for efficient conversion, by another 10-20% leaving only approximately 55% of the total output energy effectively available for the Raman conversion process. The generation 200mJ of 1.5μ Raman energy corresponds to a 1.06μ total pump energy of 850 mJ in which only 470 mJ are usable. The photon conversion efficiency of the 1st stage D_2 Raman system is 35% of the total Nd:YAG laser output and 64% of the usable 1.06μ energy. In order to improve the overall efficiency of this process we have acquired new resonator optics for the Nd:YAG laser oscillator that are based on gradient reflective mirrors (that produce a gaussian output beam pattern) and depolarization compensation. It is felt this pump laser configuration will provide $> 85\%$ usable energy for stimulated Raman conversion based on similar increases in second harmonic conversion that have been demonstrated. Energy in excess of 400 mJ/pulse at 1.5μ should be attainable using this new configuration. Test are currently underway to verify the attributes of these new resonator optics with anticipation of doubling the energy currently available at both 1.5μ and 2.9μ .

FINAL REPORT

**DEVELOPMENT OF A TWO PHOTON/LASER INDUCED FLUORESCENCE TECHNIQUE
FOR THE DETECTION OF ATMOSPHERIC OH RADICALS**

(NASA Grant NAG 1-818)

Submitted To:

**THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
LANGLEY RESEARCH CENTER
MAIL STOP 401A
Hampton, VA 23665**

Prepared By:

**Dr. John Bradshaw
School of Earth and Atmospheric Sciences
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Atlanta, Ga 30332**

SUMMARY

The successful development of a Two Photon/Laser Induced Fluorescence Sensor for the measurement of tropospheric OH radicals has awaited only the development of a suitable mid-Infrared(IR) laser source in the 2.9μ region. Phase I research efforts, sponsored through the National Science Foundation, evaluated numerous candidate laser systems. Of these, the only candidate system offering promise as a near term solution was the stimulated Raman shifting frequency down conversion of a commercially available Nd:YAG laser. The development of the new mid-IR laser source that was conceived at Georgia Tech was the primary goal of the Phase II NASA sponsored effort reported on here.

During phase II research efforts all of the major uncertainties that were brought out at the NASA sponsored mid-IR workshop (chaired by Dr. Crosely) have now been successfully addressed. The first stage in the frequency down conversion process has now been shown to give optimal performance using the backward stimulated Raman wave generated in Deuterium. This step has now been accomplished with $> 55\%$ photon conversion efficiency yielding > 180 mJ pulse energies in a near diffraction limited beam at an "eye safe" wavelength near 1.56μ . The second stage frequency down conversion scheme has also been demonstrated to yield output energies in excess of it's target goal of 10 mJ. The second stage system, which utilizes the stimulated backward Raman wave generated in methane, has now been shown not to require the complications of a multi-pass Raman gain cell design. A simple rugged system has now been developed that is capable of providing energies of 18 mJ/pulse in a near diffraction limited beam at 2.86μ .

Integration of this laser system into a TP-LIF OH sensor does, however, require one last engineering step, namely the construction of a liquid nitrogen cooled gas cell for the first stage deuterium Raman conversion process. Liquid nitrogen cooling of the D_2 gas is required in order to obtain a laser wavelength that will overlap an OH ro-vibronic transition. This engineering step should not be viewed as a research project, as the wavelengths of all the transitions involved are known and have been verified as part of the Phase I research effort.

The anticipated sensitivity of a TP-LIF OH sensor using this mid-IR source would give signal limited (i.e. background free) limits of detection of 1.4×10^5 OH/cm³ under boundary layer conditions, and 5.5×10^4 OH/cm³ under free troposphere conditions for a five minute signal integration period. This level of performance coupled with the techniques non-perturbing nature (i.e. direct measurement) and freedom from both interferences and background would allow reliable tropospheric OH measurements to be obtained under virtually any ambient condition of current interest.

1. INTRODUCTION

1.a. Overview

The hydroxyl radical (OH) is recognized as one of the pivotal species leading to the oxidation of compounds in the atmosphere. As such OH oxidative pathways lead to the removal of both naturally and anthropogenically produced substances within the troposphere such as CO, NO₂, CH₄, higher carbon number alkanes, and hydro-containing halocarbons (CFC-substitutes). Because of its importance in controlling atmospheric chemical processes, numerous instrumental techniques have been proposed for measuring the levels of atmospheric OH. However, due to its high reactivity (i.e. $OH + CH_4 \rightarrow CH_3 + H_2O$ ($\tau \sim 1.5$ sec)) and relatively slow primary production rate (i.e. $O_3 + h\nu \rightarrow O^1D + O_2$ ($\tau \sim 10^4 - 10^5$ sec) and $O^1D + H_2O \rightarrow 2OH$) the steady state concentration of OH in the atmosphere is low. 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.

Three "field ready" OH measurement systems were brought together in a NASA sponsored ground based and airborne intercomparison study, 1982, 1983. These three systems were: (1) the quasi-remote laser induced fluorescence (LIF) lidar method; (2) the ambient pressure 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, these results have been summarized by Hoell et al., and Beck et al.² The conclusion drawn from this review was that the only two operational systems (both single photon (SP) LIF methods) appeared to lack 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 within a realistically short enough measurement time.

1.b. Status of Current Techniques

More recently, several promising OH measurement techniques, which appear capable of measuring tropospheric OH, have been reported. These techniques are: the Fluorescence Assay with Gas Expansion (FAGE) low pressure LIF method of Hard and co-workers³; the radio-chemical $^{14}\text{CO}/^{14}\text{CO}_2$ oxidation method of Campbell and co-workers⁴; and the Ion-Assisted $^{34}\text{SO}_2/\text{HSO}_4^-$ Oxidation method of Eisele and Tanner^{5,6}. The third generation FAGE instrument, which employs a 308 nm excitation/resonant fluorescence detection, has now apparently overcome the $\text{O}_3/\text{H}_2\text{O}$ interference that was associated with early LIF techniques employing 282 nm excitation and 308 nm non-resonant fluorescence detection (i.e. $\text{O}_3 + \lambda_{282} \Rightarrow \text{O}^1\text{D} + \text{H}_2\text{O} \Rightarrow 2\text{OH}$). This third generation FAGE system has apparently eliminated the need to chemically modulate ambient OH in order to assess background levels^{3,7}. The limit of detection (LOD) of this instrument for a signal to noise ratio (S/N) of 2/1 is, however, still limited to $1 \times 10^6 \text{ OH}/\text{cm}^3$ for a signal integration time of nine minutes³. The radio-chemical $^{14}\text{CO}/^{14}\text{CO}_2$ oxidation method ($\text{OH} + ^{14}\text{CO} \Rightarrow ^{14}\text{CO}_2$ (detected by isotopic decay)) has recently exhibited promise in identifying many of the background problems associated with earlier measurement attempts during the previously discussed OH intercomparison. Present LOD's for this technique⁴ range from 1.5 to 3.0 ($\times 10^5$) OH/cm^3 for an ~ 2 minute sampling time and is apparently limited by background levels of ^{222}Rn . The Ion-Assisted technique also relies on an oxidative conversion step: ($\text{OH} + ^{34}\text{SO}_2 \Rightarrow \text{H}^{34}\text{SO}_3 + \text{O}_2 \Rightarrow ^{34}\text{SO}_3 + \text{H}_2\text{O} \Rightarrow \text{H}_2^{34}\text{SO}_4 + \text{NO}_3^- \Rightarrow \text{H}^{34}\text{SO}_4^-$ (detected via mass spectrometry)). Although the latter approach utilizes much faster reaction (conversion) times, than the radio-chemical method (i.e. ~ 2 seconds vs. 16 seconds), and currently has an instrumental LOD of $1 \times 10^5 \text{ OH}/\text{cm}^3$ for a 5 minute signal integration period, it is apparently limited by a background⁶ equivalent to $7(\pm 5) \times 10^6 \text{ OH}/\text{cm}^3$, which can be "subtracted" leaving a residual component equivalent to $4(\pm 3) \times 10^5 \text{ OH}/\text{cm}^3$.

As a point of reference², the single photon (SP) LIF techniques used in the 1982-1983 OH intercomparisons demonstrated LOD's of .8 to 1.5 ($\times 10^6$) OH/cm^3 for a signal integration time of ~ 50 minutes and background levels of $< 3 \times 10^5 \text{ OH}/\text{cm}^3$.² In addition, representatives from the atmospheric chemistry community evaluated the OH measurement requirements necessary for testing the current understanding of OH photochemistry.⁸ In the lower troposphere (1-3 km) OH can reach maximum levels of $\sim 1 \times 10^7 \text{ OH}/\text{cm}^3$ under mid-day summertime conditions when UV solar flux, H_2O vapor, and O_3 are generally at their yearly maximum values. Even under these favorable conditions OH levels decrease markedly with increasing altitude dropping to $\sim 1 \times 10^6 \text{ OH}/\text{cm}^3$ for mid-day conditions above 6 km. This marked change is primarily a result of the nearly three order of magnitude change in ambient water vapor

concentrations. Many significant tests of our understanding of tropospheric photochemistry, e.g. suspicion that some major reaction sequence has been omitted, can be examined using instruments capable of measuring the ambient OH concentrations of 1×10^6 OH/cm³ with a precision of at least 30% in a reasonable measurement time frame (i.e. < 5 min.).⁸ Instrument sensitivity (LOD) in the 10^5 OH/cm³ range is therefore required, although precise measurements at this level are not always needed.

The third generation FAGE system appears only capable of the measurement precision possible with earlier LIF instruments used in the OH intercomparison but with an ~ 6 fold improvement in temporal resolution (56 min. vs. 9 min.). The FAGE system may be limited in its ability to provide measurements which would be capable of testing photochemical theory under many conditions of interest (e.g. upper free troposphere, low UV solar flux).

Both the radio-chemical technique and the ion-assisted technique currently have similar detection capabilities that would lend themselves to investigating a wider range of atmospheric environments and conditions than afforded by the FAGE instrument. The radio-chemical technique is more limited in its measurement capabilities due to the time associated with preparative separation and analysis of the collected ¹⁴CO₂ samples with data reported to date limited to ~ 1 sample/hour, although this time scale could presumably be shortened. Neither of these techniques, however, provide a direct measurement of OH and may be more prone to a wider array of potential interferences than other more direct measurement approaches. In addition, the applicability of either technique to an airborne platform may pose non-trivial sampling problems, especially with regards to the high variability of ambient conditions found throughout the troposphere. The ion-assisted technique may offer potential advantages as a continuous automated measurement method (for at least ground based applications) once it has proven to give reliable OH measurements.

Even with the emerging techniques discussed above, there is still apparently a great need for the development of new OH measurement techniques - particularly methods that might be capable of directly measuring OH under the wide variety of atmospheric conditions that occur throughout the troposphere and that are capable of being calibrated under field sampling conditions. The two-photon LIF (TP-LIF) OH measurement scheme⁹ remains a viable approach that is potentially capable of fulfilling these goals.

2 DESCRIPTION OF TECHNIQUE

2.a. TP-LIF OH Method

The measurement of ultra-trace levels of atmospheric gases via two-photon LIF and photofragmentation LIF has now proven to be a sensitive and selective method for determining the atmospherically important gases NO¹⁰, NO₂¹¹, and NH₃¹². In addition, all of these systems have now demonstrated their detection capabilities through critical instrument intercomparison ¹³⁻¹⁶. The development of a two-photon/laser induced fluorescence for the detection of tropospheric OH, therefore, builds on what is already an extensive field proven airborne laser detection capability at Georgia Tech.

In the TP-LIF OH approach⁹ depicted in figure 1, 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, λ_1 , near 2.9μ (e.g. 2Π , $v''=0 \rightarrow 2\Pi$, $v''=1$).

[illegible]

- 4 -

Although the TP-LIF OH sensor (Fig. 2) may be considered a new technique, many of the hardware components will be the same as those involved in our field tested SP/LIF airborne OH instrument.¹⁷ In addition, the characteristics required of the λ_2 UV laser (centered at ~ 346 nm), the detection optics (including custom made optical cut-off filters), and the sampling manifold needed for the TP-LIF OH system have already been developed and proven under field sampling conditions^{9,17}. Similarly, most of the technology (electronics, etc.) we have developed for the TP-LIF NO instrument are directly compatible with an OH system. Finally, a calibration methodology capable of routine OH calibrations under actual ambient conditions has also been proven under field sampling conditions¹⁷. The only uncertainty remaining in the successful completion of the TP-LIF OH system has been the development of the suitable mid-infrared laser source that is needed for excitation of specific ro-vibronic transitions in the $2\Pi, v''=0 \rightarrow 2\Pi, v''=1$ manifold near 2.9μ .

Numerous pulsed mid-IR sources have been evaluated. At this time there is no commercially available system capable of generating the energy, linewidth, temporal pulse width, and low beam divergence specifications required for a sensitive TP/LIF OH sensor (i.e. $E_{\lambda 1} = 10 \mu\text{J}$, $\Delta\nu \leq 0.2 \text{ cm}^{-1}$, $\Delta t < 10 \text{ ns}$, $\Delta\theta < 1 \text{ mrad}$, rep. rate $\geq 10 \text{ pps}$).

2.b. Raman Shifted Nd:YAG Laser Source

We have now developed a mid-IR laser source that is capable of meeting the target goals specified above. This source is based on the tandem D_2/CH_4 Raman shifting of a commercially available and field proven 1.06μ Nd:YAG laser.

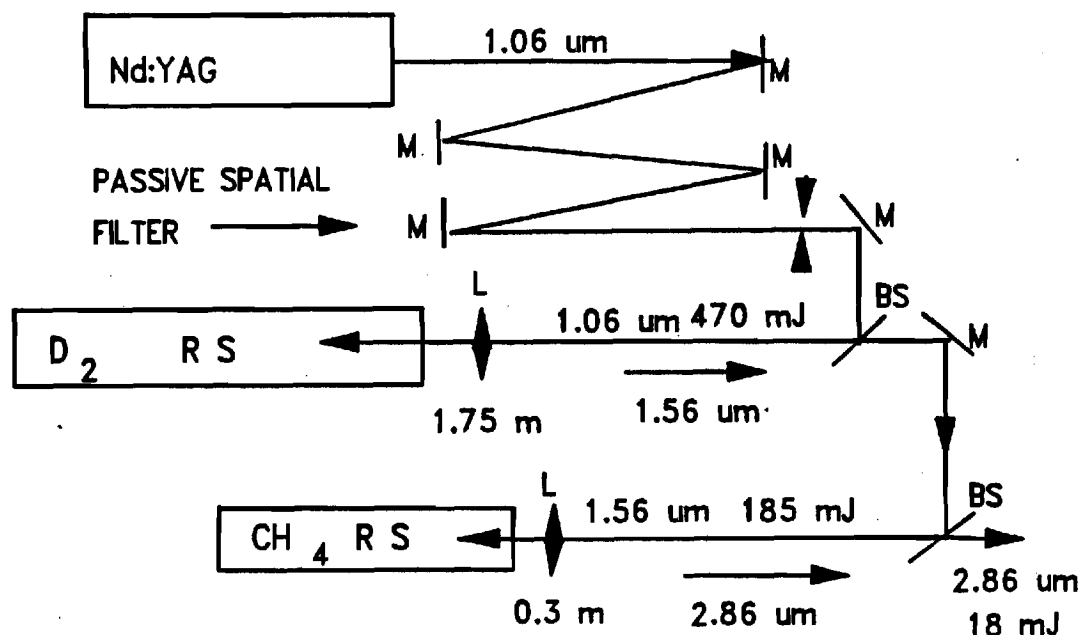


Fig. 3. Schematic representation of tandem D_2/CH_4 Raman shifted Nd:YAG laser system: BS - beam splitter; M - Mirror; L - lens; RS - Raman Shifting gas cell.

This approach, as shown schematically in figure 3, is based on the stimulated Raman frequency conversion of the 1.06μ (9394.7cm^{-1}) Nd:YAG laser. The Q(0) first Stokes Raman transition (2993.5cm^{-1}) provides the first step in this frequency conversion process generating a new laser source near 1.5μ . Tests have now shown the backward generated Raman component to be preferable to the forward generated counterpart, not only in terms of extractable first Stokes energy but more importantly, in terms of the laser beam spatial characteristics, which "echo" the

pump source in the case of the backward propagating wave. The near diffraction limited output from the D₂ Raman source is then used to pump a second Raman source using the ν_1 Raman transition of CH₄ (2916.7cm⁻¹) to yield the final mid-IR laser source at 2.9 μ (3484.5cm⁻¹) that will overlap the P₁(2) ro-vibronic transition of OH (3484.7cm⁻¹). This second Raman laser source was again found to operate optimally using the backward propagating Raman wave. Tunability of this Raman shifted Nd:YAG laser system is obtained through temperature tuning of the Nd:YAG laser (0.9cm⁻¹/20°C).

The Nd:YAG laser used in this system is a Spectra Physics injection seeded - DCR3A having the near transform limited linewidth (< .01cm⁻¹) necessary for efficiently generating the backward propagating Raman wave (i.e. laser linewidth < Raman linewidth). Similarly, the linewidth of the D₂ Raman source (~ 0.1cm⁻¹) is sufficiently less than the CH₄ Raman linewidth (~ 0.2 cm⁻¹) to obtain reasonable energy conversion efficiency from the CH₄ Raman source. Tuning of the Nd:YAG laser (and subsequently the mid-IR frequency) by ± 0.7 cm⁻¹ is easily accomplished via temperature tuning of the all solid state diode pumped Nd:YAG laser used for injection seeding.

The backward stimulated Raman conversion efficiencies were optimized following the guidelines suggested by Murray, et.al.¹⁸. Although CH₄ is often preferred over D₂ for generation of the forward propagating stimulated Raman component, the choice of D₂ rather than CH₄ for the first conversion step was found to be optimal for several reasons, even though CH₄ has a larger Raman cross section (i.e. higher gain). In most higher energy applications gain is of minor importance as the available pump energy density can be made large compared to the energy density required to reach threshold. The "gain difference" between these two gases merely influences the choice of pump beam focal parameters, which through the active volume influences the number density needed in the gain media (i.e. pressure), and does not effect the efficiency of the Raman conversion process (i.e. overall gain for an optimized system is approximately constant). In addition, problems associated with high energy pumping of CH₄ can also be avoided, such as: (1) carbon build up due to multi-photon photodissociation process; and (2) the need for Faraday isolators to protect the pump source from stimulated resonant backward components generated in CH₄ that do not occur in D₂.

The D₂ system was found to give optimal performance using a 1.75m focal length lens coupling the pump beam focal point approximately 1.5m into a 2m gas cell. This combination allowed for sufficiently fast enough build up of the backward component to allow efficient energy extraction while allowing the four wave mixing components in the forward direction to minimize growth of the forward propagating first stokes wave. For laser repetition rates greater than ~ 2 pps a stirred or flowing gas cell design is required. Gas circulation is required to eliminate the laser generated index of refraction gradients that otherwise deteriorate both output energy and beam quality. The CH₄ conversion step was found to give optimal performance using a 0.3m focal length lens with the 1.56 μ focal point occurring ~ 0.2m into the gas cell. It is also recommended that the CH₄ cell should be of a flowing gas design above ~ 2 pps laser repetition rate.

Table I summarizes the tandem Raman laser performance characteristics obtained to date. In addition, recently acquired gradient reflective Nd:YAG resonator optics ("gaussian beam optics") have demonstrated far more usable Nd:YAG laser energy after spatially filtering (725 mJ vs. 470 mJ) than the resonator optics used to obtain the data in Table I. This higher available 1.06 μ pump energy should produce a 1.5 μ D₂ output energy of > 275 mJ and a 2.87 μ CH₄ output energy of > 25 mJ. The Q(2) D₂ transition (2987.2cm⁻¹) was utilized in these experiments due to our current lack of a 2 m liquid nitrogen cooled Raman cell necessary for use of the Q(0) D₂ transition

(2993.5cm⁻¹) required to obtain the final 2.9μ spectral overlap with the P(J"-2.5)1 - transition in OH.

TABLE I - Raman Laser Performance

Laser	output wavelength	linewidth	tuning range	energy/ pulse	photon conv. efficiency
Nd:YAG	1.064μ	< 0.005cm ⁻¹	± 0.7cm ⁻¹	(850mJ)	NA
DCR-OPTICS	(9394.7cm ⁻¹)			470mJ ^a	55%
Backward 1 st Stokes	1.561μ	~ 0.1cm ⁻¹	± 0.7cm ⁻¹	185mJ	58% ^b
D ₂ -Q(2)	(6407.5cm ⁻¹)			0.5mrad beam divergence	58%
(2987.2cm ⁻¹)					
Backward 1 st Stokes	2.865μ	~ 0.25cm ⁻¹	±0.7cm ⁻¹	18mJ	18% ^c
CH ₄ -ν ₁	(3409.8cm ⁻¹)			0.5mrad beam divergence	10% ^b
(2916.7cm ⁻¹)					

a - spatially filtered for lowest order mode

b - conversion efficiency of spatially filtered 1.06μ pump

c - conversion efficiency of 1.5μ D₂ Raman source

3. TP-LIF OH EVALUATION OF SENSITIVITY

As presented in previous publications⁹⁻¹¹ the TP-LIF signal strength, D_{λ3}, can be expressed as the product of five efficiency terms, the LIF probe volume element, and the concentration of OH radicals, namely:

$$D_{\lambda 3} = E_{\lambda 1} \times E_{\lambda 2} \times E_f \times E_d \times E_e \times V \times [\text{OH}], \quad (1)$$

where D_{λ3} is the number of detected signal photons per laser pulse. The efficiency terms in Eq. (1) can be further defined as follows

$$E_{\lambda 1} = \text{optical pumping efficiency at } \lambda_1 \quad (2)$$

$$= (1 - \exp(-P_{\lambda 1} \sigma_{\lambda 1} / a_{\lambda 1})) x f_1,$$

$$E_{\lambda 2} = \text{optical pumping efficiency at } \lambda_2 \quad (3)$$

$$= (1 - \exp(-P_{\lambda 2} \sigma_{\lambda 2} / a_{\lambda 2})) x R,$$

$$E_f = \text{fluorescence} \quad (4)$$

$$= k_f / (k_f + k_q [M]),$$

$$E_d = \text{optical detection efficiency} \quad (5)$$

$$= \gamma_{\lambda 3} \times Y_{\lambda 3} \times Z_{\lambda 3} \times \phi_{\lambda 3},$$

$$E_e = \text{electronic counting efficiency}, \quad (6)$$

$$V = \text{volume of the sampling region} \quad (7)$$

$$= a_{\lambda 2} \times f \text{ for } a_{\lambda 2} < a_{\lambda 1}, \text{ and}$$

$$[\text{OH}] = \text{concentration of OH in molecules/cm}^3. \quad (8)$$

In the above equations P_{λ1} and P_{λ2} represent the number of laser photons per laser that at wavelengths λ₁ and λ₂, respectively; σ_{λ1} and σ_{λ2} are the effective absorption cross sections for OH at λ₁ and λ₂; a_{λ1} and a_{λ2} are the beam areas defined by the λ₁ and λ₂ lasers; f₁ is the fraction of the total OH population in quantum state i that can be pumped a 2.9μm; R is the fraction of OH initially formed in the v"-1 level that survives vibrational, rotational, spin, and parity relaxation; k_f is the reciprocal of the natural lifetime; k_q is the bimolecular electronic rate coefficient and [M] is the concentration of the quenching species.

In Eqs. (5) and (7), γ_{λ3} defines the fraction of the total fluorescence falling within the optical transmission window; Y_{λ3} is the optical collection efficiency of the f/1.4 lens system; Z_{λ3} is the optical filter transmission factor,

$\phi_{\lambda 3}$ is the quantum efficiency of the photomultiplier tube (PMT) at λ_3 ; $a_{\lambda 2}$ is again the effective beam area of the smaller of the two lasers; and f is the effective path length over which fluorescence can be monitored by a single PMT using $f/1.4$ lenses.

Table II. Evaluation of TP-LIF SIGNAL STRENGTH

$E_{\lambda 1}$:	$P_{\lambda 1} = 2.1 \times 10^{17}$ photons/pulse; $a_{\lambda 1} = 0.78 \text{ cm}^2$; $f_1 = 0.12$	$\sigma_{\lambda 1} = 3.6 \times 10^{-18} \text{ cm}^2$;	6.5×10^{-2}
$E_{\lambda 2}$:	$P_{\lambda 2} = 8.7 \times 10^{15}$ photons/pulse; $a_{\lambda 2} = 0.5 \text{ cm}^2$; $R = 0.15$	$\sigma_{\lambda 2} = 1.6 \times 10^{-17} \text{ cm}^2$;	3.6×10^{-2}
E_d :	$\nu_{\lambda 3} = 0.7$; $\Phi_{\lambda 3} = .23$	$Y_{\lambda 3} = 0.012$; $Z = 0.32$;	6.2×10^{-4}
E_f :	$k_f = 1.4 \times 10^6 \text{ s}^{-1}$; $k_q[m]_{FT} = 5.3 \times 10^8$	$k_q[m]_{BL} = 1.3 \times 10^9 \text{ s}^{-1}$	$1.1 \times 10^{-3} \text{ BL}$ $2.6 \times 10^{-3} \text{ FT}$
E_e :			.9
V :	$a_{\lambda 2} = 0.5 \text{ cm}^2$; $f = 1.5 \text{ cm}$.75 cm^3
$D_{\lambda 3}$:	$1.0 \times 10^{-9} \times [\text{OH}]_{BL}$ and $2.5 \times 10^{-9} \times [\text{OH}]_{FT}$		

Based on 15mJ at λ_1 , 5 mJ at λ_2 , $.25 \text{ cm}^{-1}$ convoluted laser/OH overlap at both λ_1 and λ_2 , BL - calculated for boundary layer (1km); FT - calculated for free troposphere (6 km).

Almost all of the terms in Equations (5-7) have been directly measured. In general, values have not changed significantly since our last assessment⁹. The only significant change involves the IR OH absorption cross-section in which recent results of Nelson et.al.^{19,20} have removed most of the uncertainty associated with this term. Table II list the values of each efficiency term. The IR pumping efficiency is now estimated to be less dependent on the 2.86μ laser energy using the revised values of the absorption cross-section (i.e. $(P_{\lambda 1} \sigma_{\lambda 1} / a_{\lambda 1}) \geq 1$). The uncertainty associated with the $D_{\lambda 3}$ evaluation given in Table II is estimated to be less than \pm a factor of 2.

The detection efficiency given in Table II reflects the observed signal counts for the detection photomultiplier tube (PMT). Scaling $D_{\lambda 3}$ to the OH probe configuration used previously having 8 PMT's with opposite sites facing back reflecting mirrors (1.5 fold gain in E_d), and 600 pulses per minute laser repetition rate, the detection efficiency for the OH system shown in Fig. (2) would be:

$$\begin{aligned} D_{\lambda 3} \text{ Boundary Layer} &= 7 \text{ counts/min at } 1 \times 10^6 \text{ OH/cm}^3 \\ D_{\lambda 3} \text{ Free Troposphere} &= 18 \text{ counts/min at } 1 \times 10^6 \text{ OH/cm}^3. \end{aligned}$$

For a five minute signal integration period (the maximum time anticipated using this system) at the $1 \times 10^6 \text{ OH/cm}^3$ concentration range OH measurements could be made with $\pm 17\%$ (1 σ) precision in the boundary layer and $\pm 11\%$ (1 σ) in the free troposphere. The absolute magnitude of the background for this system has been shown to be $< 1 \text{ count/5min}$ under ambient sampling conditions (i.e. $< 2 \times 10^5 \text{ OH/cm}^3$ equivalent). Taking the minimal detectable signal to be 5 photons/integration period the signal limited detection limit of the system would be $1.4 \times 10^5 \text{ OH/cm}^3$ in the boundary layer and $5.5 \times 10^4 \text{ OH/cm}^3$ in the free troposphere (Fig. 4).

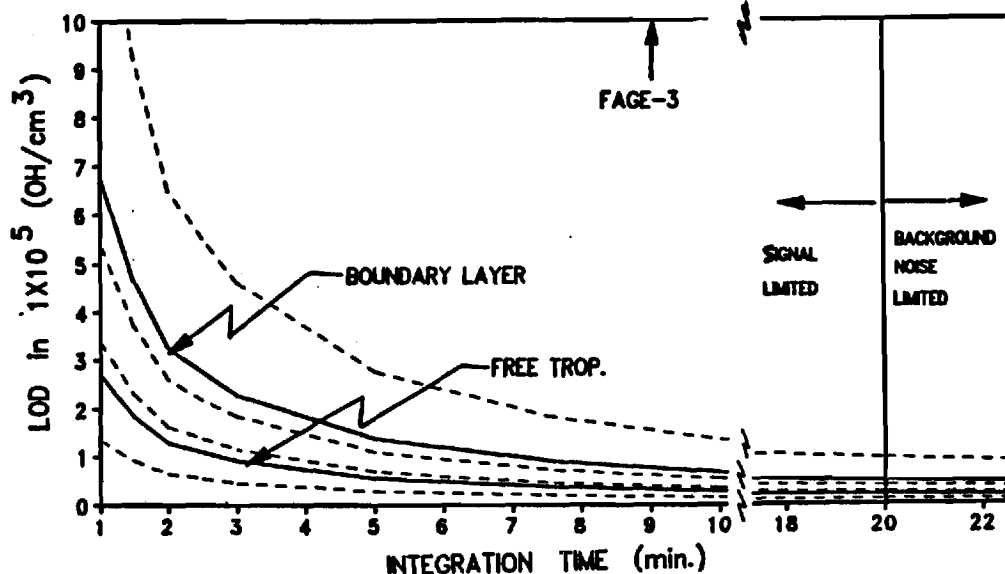


Fig. 4. TP/LIF OH estimated limit of detection (LOD) at $S/N = 2/1$ in units of 1×10^5 OH/cm³ vs. signal integration time from 1 to 20 minutes. Solid line shows values derived from Table II; dashed lines depict \pm factor of two uncertainty limits

4. CONCLUSIONS

Backward propagating stimulated D₂ Raman frequency down conversion of a commercially available 1.06 μ Nd:YAG laser has been shown to generate an efficient source of 1.56 μ radiation with near diffraction limited beam quality. Pulse energies of 180 mJ are routinely obtained. Use of gaussian resonator optics in the Nd:YAG laser should yield 1.56 μ energies in excess of 275mJ/pulse and may provide a useful new source for "eye-safe" LIDAR applications.

The efficient generation of a 2.9 μ laser source has also been achieved using backward propagating CH₄ Raman frequency down conversion of the 1.56 μ pump. A near diffraction limited beam with a pulse energy of 18mJ has now been obtained at 2.86 μ and is far in excess of the system target goal of 10mJ/pulse.

Slightly higher efficiencies have also been obtained for frequency down conversion of the 1.06 μ Nd:YAG using the H₂ Raman shift yielding a near diffraction limited source in the 200mJ range at 1.9 μ . Similar conversion efficiencies could be anticipated as a result of extending the wavelength coverage of recently available Ti:Sapphire pulse lasers to not only cover the 740-860 nm fundamental wavelength range but also the .95 - 1.15 μ and 1.06-1.33 μ range using D₂ and H₂ respectively.

The anticipated sensitivity of a TP-LIF OH sensor using this mid-IR source would give signal limited (i.e. background free) limits of detection of 1.4×10^5 OH/cm³ under boundary layer conditions and 5.5×10^4 OH/cm³ under free troposphere sampling conditions for a five minute signal integration period. This level of performance coupled with the techniques non-perturbing nature (i.e. direct measurement) and freedom from both interferences and background would allow reliable tropospheric OH measurements to be obtained under virtually any ambient condition of current interest, including interstitial cloud sampling. Like most OH sensors, this technique could also be extended to the measurement of the peroxy radical (HO₂) through the chemical conversion process $HO_2 + NO \rightarrow OH + NO_2$.

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