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Ithaca, New York 14853

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This report summarizes research conducted at Cornell University under ARPA sponsorship during the duration of this contract. The broad objectives of this research were to provide quantitative information concerning molecular and chemical lasers. The parameters dealt with were: new laser transitions and pumping schemes; laser gain and saturation parameters; measurements of relaxation and energy transfer between the translational, rotational, vibrational, and electronic modes of prominent laser molecules.

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8.	Principal Investigator	Professor G. J. Wolga
9.	Telephone Number	(607)-256-3962
10.	Project Scientists	Professor S. H. Bauer (607)-256-4028 Professor T. A. Cool (607)-256-4191 Professor R. A. McFarlane (607)-256-4075
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Topical Report Summary

This report summarizes research conducted at Cornell University under ARPA sponsorship during the duration of this contract. The broad objectives were to provide quantitative information concerning molecular and chemical lasers. The parameters dealt with were: new laser transitions and pumping schemes; laser gain and saturation parameters; measurements of relaxation and energy transfer between the translational, rotational, vibrational, and electronic modes of prominent laser molecules.

The work was conducted over a period of eight years. All of the results obtained have been published. In this report we shall summarize the work done and the results obtained in the following manner. Under the heading of each of the faculty investigators we provide a Program Summary of work done under his direction. In addition, a list of the graduate students trained under sponsorship of this contract is included. Finally, a complete bibliography of research publications sponsored by this contract is included.

Program Summary

(G. J. Wolga)

The work supported by this program was devoted entirely to the study of gas lasers: atomic, molecular, and chemical. The individual areas of study will be briefly reviewed below.

Collisional Effects in Atomic Lasers

Magnetic, double resonance studies on near infrared transitions in He-Ne lasers were used to determine collision dependent decay rates. The theory of magnetic, double resonance was augmented and applied to transitions in the He-Ne laser.

Basic Parameters and Techniques in Molecular Lasers

The gain distribution, population densities, and rotational temperature were accurately measured for the conventional, flowing gas CO_2 - N_2 - He laser in our laboratory. These were the earliest published reliable results and provided insight into the rapid rotational thermalization process. Similar parameters were measured for the N_2O - N_2 - He laser with comparisons to the CO_2 laser. The Lamb dip was studied in CO_2 and N_2O lasers. The technique of sequential Q-switching of a molecular laser was developed. The first direct measurement of the rotational relaxation time in CO_2 was made in our laboratory.

Studies of Optical Saturation in Molecular Systems

The influence of collisions on optical saturation and Lamb dip formation was studied in the CO_2 laser. The use of an intracavity CO_2 absorption cell in a CO_2 laser led to the observation and quantitative study of repetitive passive Q-switching of this laser. Tuned laser spectroscopy of SF_6 permitted the study of optical saturation on a single vibration-rotation transition in this molecule. A theory was developed to describe the complex frequency dependence of optical saturation of molecular vibration-rotation transitions.

Molecular Relaxation

Vibrational deactivation of the (00°1) level of CO_2 by collisions with HF(v=0) and DF(v=0) was first studied in our laboratory. The method of laser induced fluorescence was augmented by electron paramagnetic resonance to permit study of the relaxation of molecules by atoms. The following systems were studied quantitatively with this method to yield room temperature atom-molecule rate constants: HF(v=1), F, O, H, Cl; DF(v=1), O, Cl, F; CO_2(00°1), O, Cl, F. A resonance effect in electronic to vibrational energy transfer was discovered and a rate constant for the V → E process between HF(v=1) and $Br(^2P_{3/2})$ was determined.

Students
(G. J. Wolga)

Student	Degree Granted	Present Affiliation
T. O. Carroll	Ph.D.	State University of New York, Stony Brook
N. Djeu	Ph.D.	Naval Research Laboratory
T. Kan	Ph.D.	Lawrence Livermore Laboratory
Dr. S. Marcus	Post Doc.	MIT Lincoln Laboratory
H. T. Powell	Ph.D.	Lawrence Livermore Laboratory
R. S. Chang	M.S., Ph.D.	Chemistry Department - Kansas State University
G. P. Quigley	Ph.D.	Los Alamos Scientific Laboratory
Dr. M. I. Buchwald	Post Doc.	Los Alamos Scientific Laboratory
C. R. Miller	no degree granted	Raytheon
T. R. Manuccia	no degree granted	Naval Research Laboratory
T. A. Reitter	M.S.	unknown

List of Publications
(G. J. Wolga)

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Program Summary
(S. H. Bauer)

Our research program yielded some successful and some unsuccessful experiments in the sense that the proposed objectives were either achieved or were not. However, in the latter case useful information was developed. We can point to five distinct areas listed below in chronological sequence.

Attempts to develop a chemical CO_2 laser [CO oxidation with N_2O and F_2O under shock tube conditions] failed. The kinetics of N_2O and F_2O decompositions were unraveled.

The vibrational relaxation times of CO_2 with five collision partners were measured over a range of temperatures. These data were useful in modeling and exposition of the CO_2 - GDL operation.

A new chemical lasing system was discovered: $C_3O_2 + O \rightarrow CO + 2CO$ and an atomic boron laser was found. Also very extensive computer modeling of the chemical aspects of the $CS_2 + O$ and $C_3O_2 + O$ lasers was undertaken and completed.

The reaction between H_3B and O atoms were studied in a moderate pressure flow system. A full mechanism was developed for the production of BO^*.

At the termination of the contract we were left with incompleted studies of various fuel plus oxidizer combinations which generated high levels of chemiluminescence in the visible when ignited with a CO_2 laser pulse. The objective was to find appropriate conditions for the production of the electronically excited laser for the visible. The visible laser was not obtained.

Students
(S. H. Bauer)

Student	Degree Granted	Present Affiliation
M. I. Buchwald	Ph.D.	Los Alamos Scientific Laboratory
N. A. Nielsen, Jr.	Ph.D.	Post-Doctorate Fellow at York University
G. K. Anderson	Ph.D.	Los Alamos Scientific Laboratory
P. Walsh	not yet granted	

List of Publications
(S. H. Bauer)

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Program Summary
(T. A. Cool)

Our efforts have been primarily concerned with the study of chemical lasers since the inception of the ARPA supported contract. This support was instrumental in the development of the first purely chemical laser in our laboratory during the summer of 1969. Studies of the performance of this device and of the key kinetic processes involved in its operation were our major concerns for much of the contract period. These chemical laser related studies fell into several categories:

(a) Characterization of the performance of large scale DF-CO_2 transfer chemical lasers.

(b) Spectroscopy and studies of the performance characteristics of a variety of cw hydrogen halide chemical lasers (HF, DF, HCl, etc.).

(c) Measurement of vibrational matrix elements and dipole moment function for HF and DF.

(d) Laser induced fluorescence studies of vibrational energy transfer in several molecular systems over the range 200-700° K.

More recently we have used a CO_2 laser to vibrationally excite the O_3 molecule for studies of vibrational energy transfer in O_3. This work has led to important conclusions concerning the laser enhanced reaction of O_3 and NO. Present studies of this reaction in our laboratory have complemented previous work at NBS and the Naval Research Laboratory.

Students
(T. A. Cool)

Student	Degree Granted	Present Affiliation
J. L. Ahl	M.S.	McDonnell Douglas, St. Louis, MO
E. Devis	Ph.D.	University of the Andes, Bogota, Columbia
R. A. Lucht	Ph.D.	Los Alamos Scientific Laboratory
D. I. Rosen	Ph.D.	McDonnell Douglas, St. Louis, MO
J. A. Shirley	Ph.D.	United Technology, Inc., Hartford, CONN
R. R. Stephens	Ph.D.	Hughes Research Labs, Malibu, CA
W. H. Whitlock	M.S.	Allied Chemical, Morristown, NJ
K. K. Hui	Ph.D.	Hughes Aircraft Co., Culver City, CA

List of Publications
(T. A. Cool)

T. A. Cool and J. A. Shirley, Gain Measurements in a Fluid Mixing CO_2 Laser System, Appl. Phys. Lett. 14, 70 (1969).

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Program Summary
(R. A. McFarlane)

Production and Kinetics of Vibrationally Excited Carbon Monoxide for Chemical Laser Application

This project concerned the utilization of the reaction of atomic oxygen with acetylene to produce vibrationally excited CO

$$O + C_2H_2 \rightarrow CO^* + CH_2 + 51 \text{ kcal/mole}$$

$$O + CH_2 \rightarrow CO^* + 2H + 71 \text{ kcal/mole}$$

of potential use as the active medium of a chemical laser. A high capacity oxygen atom source was developed using a CW microwave magnetron and the above reactions initiated by the injection of C_2H_2 into the flowing atom stream.

By studying the overtone emission from CO at 2.8 microns detailed information on both the nascent and relaxed CO vibrational population distribution was obtained using a computer simulation of the observed spectrum with both N_v, the population density in level v and T, the translation/rotation temperature as controllable parameters. The relaxation rate for the process

$$CO(v) + CO(0) \rightarrow CO(v-1) + CO(1)$$

was obtained for levels v = 2 to v = 13 by using a new analysis appropriate to our very high speed flow conditions and which permitted a

very substantial decoupling of the equations for individual vibrational level populations. It was demonstrated that because of the relatively higher V-V rates for quenching levels v = 5 and v = 6 that a total inversion condition could be established in the chemically formed CO. Further, the modeling of the vibrational distribution as a function of time using the measured V-V rates was entirely consistent with our experimental observations.

The rate at which oxygen atoms lead to the quenching of vibrationally excited CO(v=1) was studied over the temperature range 273° K to 389° K. In this case CO molecules were excited using the second harmonic of a 9.6μ CO_2 laser and by monitoring the change in fluorescence decay rate as a function of O atom concentration the following data were obtained

T°K	k sec^{-1} $torr^{-1}$
389	4.2×10^3
359	2.1×10^3
306	1.3×10^3
273	0.89×10^3

These rates are about a factor of two faster than a simple Landau-Teller extrapolation of similar data taken in a shock tube with temperature near 2000° K.

Milestones

A new technique using high speed flow conditions was developed and applied to measure the rate at which CO(v=0) molecules collisionally relax vibrationally excited CO molecules. A computer model was developed to demonstrate that in the O - C_2H_2 reaction a "total vibrational population inversion" could be obtained using the preferential relaxation by cold CO. Measurements were made in the laboratory of the spontaneous emission from the oxygen-acetylene reaction demonstrating that such an inversion could be realized in practice.

The rate at which oxygen atoms collisionally relax CO(v=1) molecules was measured over the temperature range 273° K to 389° K.

Students
(R. A. McFarlane)

Student	Degree Granted	Present Affiliation
Y. S. Liu	Ph.D	General Electric Research Laboratory
M. S. Lewittes	M.S.	University of Colorado

List of Publications
(R. A. McFarlane)

Y. S. Liu, R. A. McFarlane and G. J. Wolga, Totally Inverted Vibrational Population of CO Formed in the Reaction of Atomic Oxygen with Acetylene, Chem. Phys. Lett. 14, 559 (1972).

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