WJSA R85T-03

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SHORT WAVELENGTH CHEMICAL LASER (SWCL) WORKSHOP

Interim Report under contract F49620-84-C-0104

5 December 1984

Submitted to:
Air Force Office of Scientific Research
Bolling AFB
Washington, DC 20332

and

Strategic Defense Initiative Organization
Office of the Secretary of Defense
Washington, DC 20301

Prepared by:
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The workshop was held for the purpose of identifying the government's interest in SWCL technology, reviewing past and present efforts in this area and presenting the government's plans for a new thrust in SWCL source development. In addition, the workshop was to provide a forum for interaction between members of the Strategic Defense Initiation Organization (SDIO) and the 6.1 agencies with the technical community in order to create an enthusiastic response to the SWCL thrust and to generate new concepts as well as to involve new participants in this technically challenging area.

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A-1

Prepared by:
W. J. Schafer Associates, Inc.
1901 N. Fort Myer Drive, Suite 800
Arlington, Va 22209

W. J. Schafer Associates, Inc. (WJSA) is pleased to submit this summary report on the Short Wavelength Chemical Laser (SWCL) workshop held 14, 15 November 1984 in Charleston, S.C. Attached to this report are the workshop program, the attendance list and abstracts of the technical papers presented.

The workshop was held for the purpose of identifying the government's interest in SWCL technology, reviewing past and present efforts in this area and presenting the government's plans for a new thrust in SWCL source development. In addition, the workshop was to provide a forum for interaction between members of the Strategic Defense Initiative Organization (SDIO) and the 6.1 agencies with the technical community in order to create an enthusiastic response to the SWCL thrust and to generate new concepts as well as to involve new participants in this technically challenging area.

By any of these standards the SWCL workshop was a success. Furthermore, WJSA believes, as a result of extremely favorable comments and letters from a large number of attendees, that the workshop was exceptionally well organized and thereby provided the appropriate environment for achieving the desired objectives.

The interest of the technical community in the SWCL thrust was demonstrated by the 142 attendees from academic, government laboratory, industry and national laboratory research groups. The attendance, which was larger than anticipated, included experts in all the scientific disciplines required for the development of high-power laser sources. Further, as a result of the enthusiastic response of the technical community, the workshop sessions were extended to include papers which were submitted voluntarily. While this restricted somewhat the opportunities for open session discussions it generated a significant level of interaction behind the scenes as well as an exceptional attendance level at all of the technical sessions.

Dr. L. Marquet of SDIO opened the workshop by reviewing the philosophy behind the strategic defense initiative research effort and outlining the goals for the SWCL thrust. He introduced the key SDIO personnel and the 6.1 Agencies through which the research efforts would be contracted and identified the format and schedule for preparing responses. These remarks set the stage well for the review talks which followed immediately and for the more detailed technical sessions.

Since one purpose of the workshop was to inject new blood and concepts into the area, the technical program was designed to provide both a comprehensive review as well as information to guide future efforts. Both objectives were more than satisfied. All current efforts were described from which a consensus was reached, that energy transfer processes are to be preferred over direct excitation for the development of chemically pumped short wavelength lasers. In this regard the organization of the workshop to include sessions on the generation of metastable excited species and on the energy transfer of these and other species was well conceived and extremely valuable.

The overview session was highlighted by Dr. Huestis' talk which laid out the electronic excitation pathways that are required for SWCL development. Other talks described what has been learned from the HF and COIL laser efforts.

In addition to the Energy Transfer session which was mentioned above, the technical presentations were grouped as follows: Metal/Oxidizer Systems; Pyrotechnic Systems; Metastable Species Production and Metastable Transfer Systems. The program which gives the titles and authors of each paper and the names of the session chairs is attached.

Each session opened with a review paper in which the general status of the technology was described by a well known authority in that field. These were followed by more detailed discussions of particular chemi-excitation mechanisms and approaches to short wavelength chemical lasers.

In the metal/oxydizer session interesting papers were given by Professors Djeu and Parsons. Djeu described how the BaO*/Ba transfer had led to a no-loss/no-gain situation on the 1.3 micron transition in Ba while Parsons showed that oxidation reactions of metastable atoms provided higher excited state species densities than could be achieved with ground state atoms.

The use of chemi-excitation light sources for pumping Nd:YAG and other solid-state lasers was described by three authors. Although the results were as yet inconclusive for tactical military applications this approach was found to be more costly than flashlamp excitation for laser fusion.

The session on metastable state production was highlighted by an excellent introduction by Dr. Heidner of Aerospace. He proposed NF(b) transfer to IF and NF(a) transfer to BiF as potential SWCL candidates. Professor Coombe's examination of the potential of azide decomposition for the production of $N_2(A)$ species and Dr. Rossi's discussion of dioxetane decomposition to produce long lived excited ketones were two examples of novel excitation routes to SWCLs.

The IF system and other interhalogens were introduced by Dr. Davis of AFWL. IF appears to be a promising SWCL candidate and has been lased under both optical and electrical excitation of mixtures of iodine with fluorinated hydrocarbons. Davis projected that 10^{-3} - 10^{2} torr of IF would almost certainly lase since vibrational relaxation would concentrate the upper level species in the lowest vibrational state and deactivate the lower level (V" = 4-7) which exhibited a significant Frank-Condon shift. Subsequent speakers discussed the rates of energy transfer into IF(B) from $N_2(A)$, and those for intra- and intermolecular energy transfer processes.

The final session was concerned with the details of energy transfer processes and provided an interpretation of the atomic and molecular physics processes involved. The paper by Prof. George addressed atomic excitation in collisions between gas-phase species and surfaces which was very different than any other reactions that had been described.

In summary the workshop was well organized, well attended and provided a program which has provoked an enthusiastic response from the technical community. WJSA intends to keep current in ongoing and new activities in this area and suggest that the government plan a further workshop to review the status of technology in May 1986. WJSA believes that it has well demonstrated its capabilities to effectively plan and organize such a meeting and would be pleased to be selected again to perform these activities.

SHORT WAVELENGTH CHEMICAL LASER WORKSHOP

MILLS HOUSE HOTEL
Charleston, S.C.

13-15 November 1984

Final Program

November 14 - Hibernian Hall

8:15 - 8:45 Late Registration

8:45 - 8:55 Welcome & Administrative Remarks
Dr. W. Watt, WJSA

8:55 - 12:00 Plenary Session - Chair: Dr. L. Marquet, SDIO

    8:55 - 9:10 Plan for SWCL Thrust
    Dr. L. Marquet, SDIO

    9:10 - 9:50 HF - What Have We Learned?
    Dr. W. Warren, PAR

    9:50 - 10:30 Chemical Oxygen - Iodine Laser Review
    Dr. P. Avizonis, AFWL

10:30 - 10:45 COFFEE BREAK

    10:45 - 11:25 Why So Few Chemical Lasers?
    Dr. D. Huestis, SRI

    11:25 - 12:00 Approach to Efficient Short-Wavelength Chemical Lasers
    Dr. P. Avizonis, AFWL

12:00 - 1:15 LUNCH

1:15 - 3:15 Metal/Oxidizer Systems
Chair: Dr. C. R. Jones, LANL

    1:15 - 1:55 Potential of Metal/Oxidizer Systems
    Prof. J. Gole, Georgia Tech

    1:55 - 2:15 Review of BaO/Ba Transfer Laser Studies
    Prof. N. Djeu, Univ. of South Florida

    2:15 - 2:35 SnO and SmF Studies
    Dr. J. Raymonda, Bell Aerospace

    2:35 - 2:55 Reactions of Transition and Main Group III and IV Metals with Halogens
    Prof. J. Parsons, Ohio State Univ.

    2:55 - 3:15 Mg/N_2O/CO Flame Studies of Mg(3p) Production
    Dr. R. Meinzer, UTRC

3:15 - 3:30 AFTERNOON BREAK

3:30 - 5:10 Pyrotechnic Systems - Chair: Dr. B. Feldman, NRL

3:30 - 4:10 Recent Developments in Chemiluminescence
Prof. A. Fontijn, RPI

4:10 - 4:30 Combustion - Pumped Solid State Lasers
Mr. E. Chicklis, Sanders

4:30 - 4:50 Chemical Flashlamps Employing F_2 Oxydizers
Dr. J. Waymouth, GTE

4:50 - 5:10 Luminous Metal Dust Oxide Reactions as
Potential Laser Pump Sources
Dr. M. Duignan, NRL

November 15 - Hibernian Hall

8:30 - 10:20 Metastable State Production
Chair: Dr. H. Powell, LLNL

8:30 - 9:00 Production and Uses of NF and N_2 Metastables
Dr. R. Hiedner, Aerospace

9:00 - 9:20 Excited-State Chemistry of Molecular Azides
Prof. R. Coombe, Univ. of Denver

9:20 - 9:40 Possible High Density Visible Chemical
Laser Based on Dioxetanes
Dr. M. Rossi, SRI

9:40 - 10:00 Chemiluminescence and Oxidation of Phosphorus
Prof. D. Stedman, Univ. of Denver

10:00 - 10:20 Excited Products from Extremely Exothermic
Reactions
Prof. C. Wittig, USC

10:20 - 10:30 COFFEE BREAK

10:30 - 12:30 Metastable Transfer Systems
Chair: Dr. S. Davis, AFWL

10:30 - 11:00 Overview of Interhalogen Lasers
Dr. S. Davis, AFWL

11:00 - 11:30 Electronic State Energy Transfer and Laser
Possibilities
Prof. D. Setser, Kansas State Univ.

11:30 - 11:50 $N_2(A) \rightarrow IF$ Transfer
Dr. L. Piper, PSI

11:50 - 12:10 $NF(b) \rightarrow IF$ Transfer
Dr. D. Benard, Rockwell Science Center

12:10 - 12:30 The NO (A → X) Laser
Dr. M. Burrows, Los Alamos

12:30 - 1:45 LUNCH

1:45 - 3:40 Energy Exchange Mechanisms
Chair: Dr. M. Lavan, BMDATC

1:45 - 2:20 Vibration to Electronic Energy Transfer in V-V Pumped Molecules
Dr. J. W. Rich, CALSPAN

2:20 - 2:40 Electronic Energy Transfer in Metal Atoms
Dr. S. Leone, JILA

2:40 - 3:00 Energy Transfer Processes Involving Atoms and Molecules
Prof. J. Wiesenfeld, Cornell

3:00 - 3:20 Production of Excited Atomic States by Ion-Surface Charge Exchange
Prof. T. George, Univ. of Rochester

3:20 - 3:40 Reactive and Inelastic Collisions of Electronically Excited Species
Prof. M. Alexander, Univ. of Maryland

3:40 - 3:45 Review of Procedure and Schedule for Submitting Proposals

3:45 ADJOURN

ABSTRACTS

Curt Wittig

Short Wavelength Chemical Laser Workshop

ABSTRACT

There are many chemical reactions involving atoms and small molecules, which are highly exoergic and do not involve particularly exotic substances. With some of these reactions, there is reason to believe that the products will be formed in excited states, and several such systems will be discussed in which the main products are N_2 and/or CO, the two strongest bonds formed in nature. We will use spin conservation and tight 4-center transition states in order to channel the enthalpy release into product internal states. Reactions are identified which are ~ 1000 kJ mol^{-1} exoergic and can produce metastable electronic states, and experiments will be described which measure nascent product distributions from these reactions.

CHEMILUMINESCENCE AND THE OXIDATION OF PHOSPHORUS. D.H. Stedman.

Chemistry Department, University of Denver, Denver, CO 80208

The oxidation of phosphorus and phosphine by various oxidants leads to a bright continuum emission extending from 600 to 800 nm. A quantum yield as high as 0.82 photons per PH_3 has been measured. These and other theoretical, mass spectroscopic and microwave studies combine to yield a suggested mechanism for the emission as

$$O + PO \longrightarrow OPO^*$$

$$OPO^* \longrightarrow h\nu$$

Evidence in favor of this mechanism and an effect of oxygen caused by the unique reaction $PO + O_2 \longrightarrow O + OPO$ is presented, together with some spectroscopic speculation.

POSSIBLE HIGH DENSITY VISIBLE CHEMICAL LASER BASED ON DIOXETANE

Michel J. Rossi
Chemical Physics Laboratory
SRI International, Menlo Park, CA 94025

Thermal decomposition of substituted dioxetanes has been considered by many investigators as a possible approach to a visible chemical laser due to the high energy release and high yields of electronically excited products. However, the prospects for a gas-phase dioxetane chemical laser were judged slim because (1) the temperatures for rapid unimolecular decomposition could not be achieved fast enough and (2) the radiative properties of the excited state (triplet-excited carbonyl compounds) were not suitable for the upper laser level.

We report results of a modeling study where neat crystalline tetramethyldioxetane (TMDX) undergoes decomposition into acetone (A) triggered by irradiation in the near-UV. The salient features of our reaction mechanism are:

- The operation of a quantum chain reaction (A = acetone)

  $$\mathrm{TMDX} + {}^3A^* \rightarrow {}^3A^* + 2A + \mathrm{heat}$$

  which heats up the sample with no loss in triplets. This reaction goes on until the temperature is high enough for the unimolecular decomposition to take over.

- Triplet-triplet energy pooling that results in production of singlet-acetone, which is proposed as the upper laser level:

  $${}^3A^* + {}^3A^* \rightarrow {}^1A^* + \mathrm{heat}$$

We will present detailed results on the kinetic modeling in terms of initiation conditions, incubation times, and profiles of concentrations, temperatures, and pressures versus time. We will use these modeling studies to discuss the potential of this explosive reaction system as a chemical laser.

EXCITED STATE CHEMISTRY OF MOLECULAR AZIDES

Robert D. Coombe
Department of Chemistry, University of Denver
Denver, Colorado 80208

Molecular azides have been shown to be uniquely capable of producing electronically excited species upon photodissociation or reaction with atoms or free radicals. For example, the halogen azides (XN_3, X = halogen) are metastable with respect to dissociation to nitrogen halide diatomics and N_2. In the photodissociation of these compounds, the energy available to the fragments is the sum of the photon energy and the energy borne by the azide, such that very highly excited states are accessible. In this regard, pulsed laser photodissociation of ClN_3 and BrN_3 has been shown to provide a unique source of $N_2(A^3\Sigma_u^+)$ metastables, which can undergo reaction or energy transfer processes with other species present. Reactions of molecular azides with atoms (e.g., halogens, nitrogen, and oxygen) have been shown to efficiently produce electronically excited nitrogen halides, N_2 and NO. The high specificity observed in these processes is largely a consequence of the chemistry of N_3 radicals, which act as an intermediate. The properties of these systems suggest their potential utility in a number of possible chemical laser systems.

CHEMICAL PRODUCTION OF METASTABLE NF AND N_2

R. F. Heidner III
Aerophysics Laboratory
The Aerospace Corporation

ABSTRACT

Our laboratory has endeavored to produce high densities of electronic metastables in order to exploit the energy storage potential of such systems for the production of chemically pumped electronic transition lasers. Early studies of Herbelin et al, firmly established the efficiency of the H + NF_2 reaction for producing NF($a^1\Delta$) and correctly predicted the reaction pathways leading to the production of N(^2D) and N_2* under H atom rich conditions.

Subsequently, studies were performed to scale the production of NF(a) and NF(b) and to utilize these species both for direct lasing experiments and for transfer laser concepts to suitable atomic and molecular receptors. The presentation will be both a review and a status report on current theory and experiments.

This work has been sponsored by the Air Force Weapons Laboratory under U.S. Air Force Space Division (AFSD) Contract F04701-84-C-0085 and by the Aerospace Corporation (Aerospace Sponsored Research and Mission Oriented Investigation and Experimentation).

Luminous Metal Dust/Oxidation Reactions as Potential Laser Pump Sources

Laser Physics Branch,
Naval Research Laboratory
Washington, DC 20375

Michael T. Duignan,* R.W. Waynant, and B.J. Feldman

Highly luminous metal oxidation reactions are a potentially efficient pump source for IR and near IR lasers. Metal powders or dusts offer unique advantages for repetitively pulsed or quasi-continuous pumping in that they are easily entrained in a gas and flowed.

We have conducted preliminary experiments with aluminum, magnesium, and zirconium powders in oxygen atmospheres. Optical emission as a function of time, time-integrated spectra, and dynamic pressure were monitored.

The potential for pumping solid state lasers with metal dust oxidation reactions will be discussed.

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* Potomac Photonics, Inc., Alexandria, VA 22303

October 1984

RECENT DEVELOPMENTS IN CHEMILUMINESCENCE

Arthur Fontijn

Rensselaer Polytechnic Institute
Department of Chemical Engineering & Environmental Engineering
Troy, NY 12180-3590

In August a Symposium was held at the A.C.S. National Meeting on "Gas-Phase Chemiluminescence and Chemi-Ionization". Most of the invited presentations there plus a few additional papers, will be published in a book by the same title as the symposium (North-Holland, May 1985, A. Fontijn, Ed.). In this talk some of the presentations will be reviewed, with emphasis on points of interest to SWCL development. Subjects covered will include selective reaction by particular spin-orbit states, non-statistical population of excited product states, extraction of initial population information from chemiluminescent spectra, chemiluminescent chemi-ionization, chemiluminescence from ion-molecule reactions and the heterogeneous production of excited states. Earlier observations on the highly efficient (high quantum yield Φ) Sn/N_2O reaction will be reviewed. These observations demonstrate the importance of taking reaction temperature and activation energy into account when selecting reactions for laser pumping. A new approach to a high temperature SWCL will be suggested. It is important to realize that a low Φ reaction can nonetheless have a large branching ration R* for excited state production, which (rather than Φ) is the significant factor in selecting pumping reactions. To determine R*, radiative lifetime and quenching rate coefficients have to be considered. Results from a novel method for obtaining this information for longer-lived electronically excited species will be shown.

$Mg/N_2O/CO$ Flame Studies of Mg [^3P] Production

R. A. Meinzer, H. H. Michels and R. Tripodi
United Technologies Research Center
East Hartford, CT 06108

Metastable magnesium atoms, [Mg^3P], appear to represent an attractive energy storage candidate for powering a chemically pumped electronic transition energy transfer laser. They have a relatively long radiative lifetime, 4.5 ms; deactivation of Mg[^3P] by various reagents is slow; spontaneous emission from the metastable electronic energy level to the ground state is in the blue region, $^3P-^1S$:457.1nm; and the metastable magnesium atoms can be chemically generated. A supersonic stream of Mg[^3P] atoms were formed by reacting Mg[^1S] atoms with a N_2O/CO mixture. Our measurements suggest that a $Mg-N_2O$ complex is formed and that it is subsequently reduced by reaction with CO to form metastable magnesium atoms and CO_2. The observed concentrations can be increased by optimizing the reaction conditions and significant increases (>10) are predicted based on the measured rate constant for the $Mg-N_2O$ reaction.

CHEMILUMINESCENT REACTIONS OF METAL ATOMS WITH HALOGENS

Prof. John M. Parson
Department of Chemistry
The Ohio State University
Columbus, OH 43210

ABSTRACT

Electronic chemiluminescence has been used to probe product energy disposal in a variety of beam reactions of metals with halogen molecules. Reaction of group IIIA and IVA atoms with F_2 show highly inverted vibrational populations in the electronically excited monofluoride products. Cu + F_2, on the other hand, gives near statistical vibronic populations in CuF. Chemiluminescent reactions of Sn with F_2 and C $_2$ are greatly enhanced when Sn is generated in the metastable ^1D state, and electronic state inversions are possible with SnF.

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ABSTRACT

TIN OXIDE AND SAMARIUM FLUORIDE STUDIES

by

J.W. Raymonda, R.J. Driscoll, T.E. Furner, W.L. Rushmore,
H.M. Thompson, and G.W. Tregay, Bell Aerospace Textron, Buffalo, NY

and

M.J. Lavan, U.S. Army Ballistic Missile Defense
Advanced Technology Center, Huntsville, Alabama

We will review the status of tin oxide and samarium fluoride as short wavelength chemical laser candidates. The kinetic and spectroscopic data bases will be summarized and Bell's methods for producing high fluxes of metal atom vapors will be described. Emission spectra, number densities and radiation rates obtained at Bell will be presented and prospects for the future will be outlined.

*Funded by U.S. Army Ballistic Missile Defense, Advanced Technology Center, Contracts DASG60-78-C-0030 and DASG60-83-C-0021.

Review of BaO/Ba Transfer Laser Studies

N. Djeu
University of South Florida

ABSTRACT

In the mid and late 70's, the concept of a BaO/Ba chemically pumped energy transfer laser was explored experimentally at the Naval Research Laboratory. The intended laser line in Ba was the (6 p 'D-5d 'D) transition at 1.5 μ. The upper laser level was to be pumped by energy transfer from excited states of BaO or BaF formed from chemical reactions between Ba and N_2O or NF_3. The studies took the forms of both direct gain/loss measurements at 1.5 μ in a Ba + N_2O flame and relaxation measurements of the lower laser level in a number of potential diluent gases. A review of the results from these investigations will be given.

POTENTIAL OF METAL/OXIDIZER SYSTEMS

Prof. J. L. Gole
School of Physics
Georgia Institute of Technology
Atlanta, GA 30332

ABSTRACT

The potential use of metal oxidizer systems to produce chemically driven visible laser candidates is reviewed. A few basic parameters and criteria on which one would like to focus in producing either a directly driven chemical system or a pre-chemically driven-energy transfer laser system are outlined and exemplified. Direct chemically driven systems should be considered which are characterized by selective excited state formation commensurate with high quantum yields and excited state radiative lifetimes on the order of 10^{-6} to 10^{-4} seconds. Previous quantum yield determinations will be critically reviewed both as they (1) apply to direct excited state formation and (2) influence plausible energy transfers to produce lasing media. The criteria for selectivity and high quantum yield require activation energies for excited state formation less than or equal to those for ground state formation and the temperature dependence for any metathesis producing the excited states of interest must be considered. We also consider the possible use of collision induced ultrafast energy transfer ($\sigma_{Trans.}$ >> gas kinetic) among the excited states of high temperature molecules to produce population inversions. Finally we emphasize the possible use of various analogs of the $O_2('\Delta)$ - I_2 energy transfer laser system.

WHY SO FEW CHEMICAL LASERS?

David L. Huestis
Chemical Physics Laboratory
SRI International
Menlo Park, CA 94025

ABSTRACT

A variety of flames are known for their efficiency in producing visible emission. These formed the impetus if not the basis for the search for a visible chemical laser, which has be thus far unsuccessful. Here we present a qualitative theoretical analysis of the electronic potential energy surfaces accessible to the reaction complex and a semiquantitative determination of the probability of diabatic passage through the avoided crossings. We conclude that except for spin-conserving reactions of light atoms, ground state reactants should preferentially yield ground state products. Thus the search for a visible chemical laser should emphasize [1] identification of classes of reactions with high yields of excited electronic states (rather than high yields of fluorescence) and [2] investigation of the mechanisms of chemical reactions that could be used to convert the stored electronic energy into a suitable upper laser level.

ABSTRACT: Short Wavelength Chemical Laser Workshop
Charleston, SC
14, 15 November 1984

HF LASERS - WHAT HAVE WE LEARNED?

Walter R. Warren, Jr.

Pacific Applied Research
6 Crestwind Drive
Rancho Palos Verdes, CA 90274

Hydrogen fluoride (and deuterium fluoride) vibration/rotation chemical lasers, because of their potentials in several high energy laser applications, have benefited from a considerable amount of R and D activity during the past 15 years, and a large body of knowledge now exists on the phenomena governing their operation and growth potentials. Milestones in the development of HF lasers are summarized by discussing, first, contributions from the disciplines of physical chemistry, fluid dynamics, optics, and systems requirements, and second, several interactions between these disciplines that have resulted in important advances. Attempts are made to identify lessons learned that should aid in the development of short wavelength chemical lasers.

ELECTRONIC STATE ENERGY TRANSFER AND LASER POSSIBILITIES

D. W. Setser
Kansas State University
Manhattan, KS 66506

Some excitation-transfer and dissociative excitation-transfer reactions of $N_2(A)$ will be reviewed. There is considerable evidence that quenching with formation of the Franck-Condon favored vibrational states of $N_2(X,v'')$ is the most favorable pathway. Recent studies by the flowing-afterglow technique of excitation-transfer reactions from $N_2(A)$ to SO and to S_2 fit this general model. The total quenching rate constants are large and the product branching fractions for formation of $SO(A^3\Pi)$ and $S_2(B^3\Sigma_u^-)$ appear to be favorable, especially for the SO reaction. In the second part of the presentation, work in our laboratory to develop a suitable flowing-afterglow source for kinetic and spectroscopic studies of NF(b) will be discussed. A summary of some total deactivation rate constants for NF(b) will be presented and compared to the quenching rate constants for $O_2(b)$ and NH(b).

THE EXCITATION OF THE IF ($B^3\Pi_0{}^+$) STATE BY ELECTRONIC ENERGY TRANSFER FROM $N_2(A^3\Sigma_u{}^+)$*

Lawrence G. Piper, William J. Marinelli, B.David Green
and Wilson T. Rawlins

Physical Sciences Inc., Andover, MA 01810

We have studied the electronic energy transfer reaction between $N_2(A^3\Sigma_u{}^+$, v'=0,1) and $IF(X^1\Sigma^+)$. We find strong excitation of the $IF(B^3\Pi_0{}^+)$ state with a rate coefficient of 1.2 x 10^{-10} cm^3 $molecule^{-1}$ s^{-1}. At low pressures, all vibrational levels of IF(B) up through v'=8 are about equally populated. At pressures of a few torr, the populations of the IF(B) shift to the lower vibrational levels, indicating vibrational relaxation of the B-state by argon atoms. The rate coefficient for the quenching of $N_2(A)$ by IF(X) is 2.0 x 10^{-10} cm^3 $molecule^{-1}$ s^{-1}. Thus about 60% of the quenching interactions between $N_2(A)$ and IF(X) result in IF(B) excitation.

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* Supported by the Air Force Weapons Laboratories under Contract #F29601-83-C-0051

NF($b^1\Sigma^+$) -- IF TRANSFER[1]

A. T. PRITT, JR. and D. J. BENARD
Rockwell International Science Center
Thousand Oaks, CA 91360 USA

Production of IF($B^3\Pi(0^+)$), observed in the F + HN_3 + CF_3I (or I_2) flame, has been attributed to a near-resonant electronic energy transfer from NF($b^1\Sigma^+$) to IF($X^1\Sigma^+$).[2] This mechanism has been confirmed by generating a transient concentration of NF($b^1\Sigma^+$) in the prescence of ground state IF. The E-E energy transfer rate constant and the obvserved vibrational distribution of the $B^3\Pi(0^+)$ state depend on the flame stoichiometry. The results of these experiments are explained in terms of an electronic energy transfer mechanism requiring that the individual state-to-state rates are proportional to the probabilities associated with "vertical" transitions.

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[1] This work suppported under Air Force Contract F29601-83-C-0048

[2] A. T. Pritt, Jr, D. Patel, and D. J. Benard, Chem Phys Lett. 97, 471 (1983).

NO(A→X) Laser

M. D. Burrows
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Abstract

Lasing action on the (0,1) and (0,2) γ-bands on NO at 237 and 248 nm, respectively, has been obtained by longitudinal pumping of 0.5 Torr of NO on the (0,0) γ-band transition at 227 nm. Typical output pulse energies were 13 μJ at an intrinsic energy conversion efficiency of approximately 15Δ. Lasing is observed from single rotational lines with linewidths limited only by the NO room temperature Doppler width of 0.1 cm^{-1}. The potential for lasing on other NO γ-bands will also be discussed. The (2,0) band at 205 nm can be pumped by a Raman shifted (first stokes line from D_2, narrow linewidth ArF laser. The resulting NO laser would then operate on the ($\nu' = 2, 1 \leq \nu'' \leq 8$) bands in the 214 to 220 nm wavelength region. If sufficiently fast relaxation within the vibrational manifold of the $A^2\Sigma$ state can be achieved, lasing on the ($\nu' = 1, 1 \leq \nu'' \leq 7$) bands in the 225 to 290 nm region should also be possible.

Vibration-to-Electronic Energy Transfer in V-V Pumped Molecules

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Extreme nonequilibrium overpopulation of high energy vibrational states can be produced in a variety of molecules by vibration-to-vibration (V-V) energy exchange pumping. Recent work is reviewed which shows substantial population of vibrational states above 4 eV in translationally cold CO, N_2, and NO by this mechanism. The process is operative at high, collision-dominated densities, can occur with a variety of means of vibrational mode excitation (electrical, optical, or chemical reaction), and can occur in either pulsed or steady-state experiments.

Current studies show that energy can be transferred from such V-V pumped vibrational levels to selected electronic state acceptors. The CO a $^3\Pi$ and A $^1\Pi$ states are observed to be populated by transfer from V-V pumped CO X $^1\Sigma^+$; NO A $^2\Sigma^+$ and B $^2\Pi$ levels are similarly populated when NO X $^2\Pi$ is V-V pumped. Intermolecular energy transfer has also been observed, notably transfer from CO X $^1\Sigma^+$ to the NO B $^2\Pi$, NO A $^2\Sigma^+$, and HgBr B $^2\Sigma$ states. The application of such vibration-to-electronic energy transfer processes to short wavelength laser action is discussed.

"Electronic Energy Transfer in Metal Atoms"

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A number of ideas for producing short wavelength gas lasers and excimer lasers involve storage of energy in excited states of atoms, followed by collisional or radiative transfer of this energy to the lasing states. Electronic excitation transfer is thus of fundamental importance to the viability and efficiency of such schemes. Detailed results will be presented on state-to-state energy transfer pathways, cross sections, and transfer efficiencies for both Na systems (work of A. Gallagher, JILA) and Ca systems (Leone). These investigations elucidate some of the major factors involved in near resonant energy transfer, collisional up-pumping, associative ionization, and spin-changing collisions. The results provide insight into necessary propensity rules for these energy transfer processes. Recent experiments demonstrate that orbital "alignment" can have a significant influence on near resonant energy transfer processes. These experiments can be a valuable tool in elucidating mechanisms for the major energy transfer pathways in these systems.

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Abstract of a technical presentation at the
SHORT WAVELENGTH CHEMICAL LASER WORKSHOP
held in Charleston, South Carolina, November 14 & 15, 1984

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PRODUCTION OF EXCITED ATOMIC STATES BY ION-SURFACE CHARGE EXCHANGE

The intensity of radiation emitted from ion-surface charge exchange processes can be enhanced if the surface exposed to impinging ions is electronically excited. Semiclassical calculations are carried out for the probabilities of electron transfer for Li^{3+}, alpha particles (He^{2+}) and He^{+} colliding with a Si(111) surface, where a laser is used to excite electrons in silicon from the valence band to surface states. It is shown that with a moderate-power laser (~ W/cm^2), high inversion densities of Li^{2+}, He^{+} and He can be obtained as necessary for high gain.

Inelastic and Reactive Collisions of Electronically Excited Species

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An overview will be given of some new experimental techniques for the study of inelastic and reactive collisions of atoms and molecules in low-lying excited states, with emphasis on spin-orbit as well as rotational state specificity. The current level of understanding of the dynamics of these processes will also be described.

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