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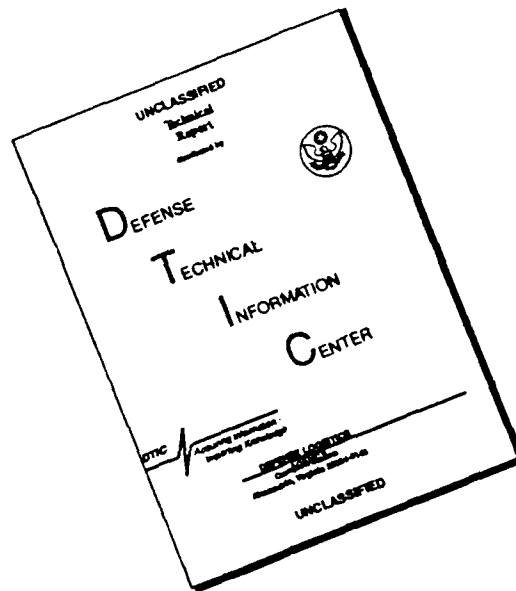
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13. ABSTRACT (Maximum 200 words) Two successful approaches to the formation of electronically inverted atomic and diatomic configurations based on (1) highly efficient near resonant intermolecular energy transfer and (2) highly efficient and selective fast direct chemical reaction are outlined. Near resonant energy transfer pumping from selectively formed metastable states of SiO and GeO is used to form thallium, gallium, sodium, and potassium atom laser amplifiers at $\lambda = 535, 417, 569, 616, 819, \text{ and } 581 \text{ nm}$. The gain condition in the Tl, Ga, Na, and K systems forms the basis for full cavity oscillation on the Tl $7^2S_{1/2} - 6^2P_{3/2}$ transition at 535 nm and the Na $4d^2D - 3p^2P$ transition at 569 nm. The extremely high cross section $\text{Na}_n (n=2,3) - \text{X}(\text{Cl}, \text{Br}, \text{I})$ reactions are employed to create a continuous electronic population inversion based on the chemical pumping of sodium dimer (Na_2). Optical gain through stimulated emission has been demonstrated in select regions close to 527, 492, and 460 nm. The considered amplifiers are being optimized and modeled with a focus to increasing amplifier gain length and amplifying medium concentration so as to facilitate their conversion to visible chemical laser oscillators. The study of additional analog systems suggests that the two concepts considered will be generic.					
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Final Report

to

Army Research Office, Durham

Selective Reactivity, Ultrafast Energy Transfer and the
Development of Chemically Pumped Visible Lasers

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Foreword

This project has been concerned with the development of the first visible chemical laser amplifiers and oscillators. Two novel approaches to form electronically inverted atomic and molecular diatomic configurations, making use of (1) highly efficient near-resonant intermolecular electronic energy transfer and (2) highly efficient and selective fast "electron jump" reactive encounters, have been employed to produce amplification and oscillation.

This report details studies in which we have used a very near resonant energy transfer from selectively formed metastable states of SiO and GeO ($a^3\Sigma^+, b^3\Pi$) to select metal atoms in order to form thallium, gallium, sodium, and potassium atom laser amplifiers at $\lambda = 535, 417, 569, 616, 819,$ and 581 nm. The metastable triplet states are generated in high yield from a select group (Ge-O₃, Si-N₂O, Si-NO₂) of oxidation reactions. The energy stored in these generated triplet states is transferred in a highly efficient electronic energy transfer process to pump ground state Tl, Ga, Na, and K atoms to excited states such that an inversion is created with respect to an intermediate lower electronic level (three level system). Adopting a pumping sequence in which a premixed Group IV A metalloid-receptor atom combination is oxidized, we observe a system temporal behavior which suggests the creation of a population inversion producing a gain condition in the Tl, Ga, Na, and K systems and forming the basis for full cavity oscillation on the Tl $7^2S_{1/2} - 6^2P_{3/2}$ transition at 535 nm and the Na $4d^2D - 3p^2P$ transition at 569 nm. Concepts employed to create amplification and oscillation in these systems also appear applicable to the efficient energy transfer pumping of potential amplifying transitions in the lead (Pb), copper (Cu - analog of Cu vapor laser), and tin (Sn) receptor atoms.

A second approach to visible chemical laser development is signaled by the successful production of visible chemical laser amplifiers using the highly efficient and selective formation of alkali dimer, $M_2 = Na_2, (Li_2)$, excited states from the alkali trimer-halogen atom ($M_3 - X(Cl, Br, I)$) reactions. These chemical laser amplifiers have already employed the extremely high cross section $Na_n (n=2,3) - X(Cl, Br, I)$ reactions to create a continuous electronic population inversion based on the chemical pumping of sodium dimer (Na_2). Optical gain through stimulated emission has been demonstrated in select regions close to $527, 492,$ and 460 nm. A model which invokes the vibrational and rotational selectivity inherent to a dissociative ionic recombination

process ($\text{Na}_3^+ + \text{X}^- \rightarrow \text{Na}_2 + \text{NaX}$), in correlation with the coupling between select sodium dimer excited states, appears to provide a semiquantitative explanation of the observed behavior. An assessment of the manner in which gain is generated in these fast reactive encounters suggests that a considerable enhancement can be obtained with a versatile source configuration. The considered amplifiers are therefore being optimized with a focus to increasing amplifier gain length and amplifying medium concentration using a device designed to allow the ready movement of extended length alkali trimer and halogen atom slit sources relative to each other so as to create interacting alkali and halogen atom reacting sheaths. The controlled intersection of these sheaths can form an extended reaction - amplification zone. This extended gain zone facilitates the conversion of the created amplifiers to visible chemical laser oscillators. Finally, this report suggests extrapolation on the sodium trimer - halogen atom systems including the potential excimer forming M_3 ($\text{M}=\text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$)- $\text{F}(\text{Cl})$ reactions.

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INTRODUCTION

Chemically driven visible lasers offer clear, attractive alternatives to their infrared counterparts. However, their development, which has represented an elusive and challenging problem for the past quarter century,¹ has met with little success until several recent breakthroughs²⁻⁶ in our laboratory supported in large part by the Army Research Office. In addressing this problem, we have been concerned with the implementation of two generic approaches to produce chemically pumped lasing throughout the visible region. Both approaches depend strongly on the development of new insights with regard to near resonant electronic energy transfer processes and the manner in which long range highly efficient and selective interactions are influenced by electronic excitation.⁷

The primary goal of the research program has been the demonstration and quantification of laser amplification and oscillation across the visible region employing highly efficient chemical pumping techniques. The basis for generic development requires not only innovative approaches to the generation of electromagnetic radiation but also a detailed understanding of the underlying factors which influence the creation of these electronic inversions.⁸ The research program, has taken advantage of the unique features associated with certain high cross section, highly selective, exothermic reactions and several recent observations made in the study of ultrafast energy transfer processes in high temperature molecules.⁹ We have relied on (1) the creation of electronically inverted atomic configurations through highly efficient near-resonant electronic energy transfer from electronically excited metastable storage states and (2) the unique dynamics inherent to the oxidation of small (few atom) metal clusters involving the alkali and alkaline earth metals.

We employ certain unique aspects of a very select group of highly exothermic metal oxidations in order to create electronically inverted atomic and diatomic configurations based on (1) highly efficient intermolecular electronic energy transfer³⁻⁶ and (2) highly efficient and selective fast direct chemical reaction.^{2,4,6} One class of these systems operates in either a pulsed (Tl, Ga - pulse width ~ 5 ns FWHM) or continuous (Na,K) configuration and relies on fast, near resonant, intermolecular energy transfer from metastable storage states³⁻⁶ formed in chemical reaction to produce subsequently lasing thallium (535nm), gallium (417nm), sodium (569,616,819nm),

or potassium (581nm) atoms. The second is believed to operate on the creation of a continuous population inversion based on the direct chemical pumping of vibronically selective electronically excited states of sodium dimer.^{2,4,6} The sodium trimer-halogen atom reactions produce Na₂ amplifiers in the wavelength regions close to 527, 492 and 460nm.

Curve Crossings, Electronic Energy Transfer Collisions, and Efficient Chemical Pumping

"A Highly Efficient and Selective Electron-Jump-Harpoon Process"

The collision dynamics of processes proceeding on electronically excited surfaces is fundamental to the attainment of population inversions based on electronic transitions in the visible spectral region.^{7,8} A particular subgroup of these electronic energy transfer processes involves metal atoms or molecules of low ionization potential. These species react very efficiently with atoms or molecules of significant electron affinity via what is termed the electron jump-harpoon process. **It is this process, specifically involving the reaction of metal trimers and forming the product metal dimer and metal halide, that may represent one of the few direct chemical routes to produce electronically inverted products.** The alkali trimer molecule, Na₃, readily provides an electron to harpoon a hungry halogen atom, X, producing a switch from the interaction of two neutral species to that of two ions (Na₃⁺ + X⁻). The convergence, crossing, and interaction of the two potentials describing the neutral (covalent) and ionic (coulombic) constituencies allows an effective switch of the reactants (curve crossing). For Na₃, with its low ionization potential, the curve crossing occurs at very long range (> 10Å) leading to a high cross section for product Na₂ formation. Based upon the experimental results obtained thusfar in our laboratory, the sodium trimer reactions show not only vibrational but also rotational selectivity as they create electronic population inversions in the product Na₂. Theoretical considerations (see also following sections) would suggest that these trimer reactions and their analogs represent key processes to yield electronically inverted products in direct chemical reaction.^{7,8}

"Efficient, Fast, Intra- and Intermolecular Energy Transfer Pumping"

A major aspect of our approach to the development of the first visible chemical laser amplifiers has relied on our belief that the majority of successful electronic transition chemical lasers will require a two-step approach.^{10,11} Chemical energy is produced and stored in a first step and then transferred in a collision induced process to an appropriate lasing medium in a second step. Following this scheme, we can attempt to produce inversions using (1) "ultrafast" intramolecular energy transfer among the excited electronic states of small diatomic molecules¹²⁻¹⁵ or (2) intermolecular transfer from electronically excited metastable storage states to readily lasing atomic receptors. Both processes inherently involve the curve crossing of electronic states.

Electronically and highly vibrationally excited molecules, with their inherently diffuse electron density and large amplitude vibrational motions simply interact more effectively than do ground state molecules in their lowest vibrational-rotational levels. We have determined that several diatomic metal monoxides display collision induced electronic-to-electronic (E-E)¹²⁻¹⁶ and vibrational-to-electronic intramolecular energy (V-E)¹⁷ transfers which proceed at rates comparable to or far in excess of gas kinetic. Transfers from metastable to shorter lived excited states may proceed at rates which approach 500 times gas kinetic (cross sections in excess of $4000 \text{ \AA}^2$). It appears that even the low-lying electronic states of several simple high temperature molecules (the products of metal oxidation) interact with a collision partner which induces energy transfer with a much larger impact parameter than previously anticipated. In a sense we are dealing with "pseudo-macromolecules" which display many of the characteristics inherent to Rydberg states¹⁸ with their large transfer and relaxation cross sections. In several cases the rates for the observed transfers may be comparable to the radiative lifetimes associated with the usually shorter lived and potentially useful upper levels in which the intramolecular transfer terminates.⁹ Rates of this magnitude, properly employed, can be competitive with optical pumping!

At some point, the distinction between fast intramolecular energy transfer processes, correlating with electronic state couplings and the periods of molecular vibrations (rotations), and intermolecular energy

transfer governed by the duration of collisions with electronically excited states may be mute.^{7,8} It may be reasonable to expect certain near resonant intermolecular energy transfers to proceed with extremely high cross sections.¹⁹ One might consider that an electronically excited molecule, with its diffuse electron density, has the ability to send out more feelers or interaction lines as it influences reaction and collision partners. The increased interaction rates which several experiments now suggest are certainly encouraging for the development of visible chemical lasers from energy transfer processes. It is precisely these very exciting results which we have already made use of in the initial formulation and development of the systems of interest.

SUMMARY OF SPECIFIC SYSTEMS

Energy Transfer Pumping and Lasing Atomic Receptors

The concept of near resonant intermolecular energy transfer³⁻⁶ from metastable states of SiO or GeO has now been used to produce super-fluorescence from Tl and Ga atoms at 535 and 417nm (see also details in Appendix A) and amplified spontaneous emission (ASE) from Na at 569, 616 and 819nm (see also details in Appendices B-E). ASE has also been monitored in preliminary experiments on K at 581nm. The energy stored in the SiO and GeO is transferred to pump (Fig. 1) $X^2P_{1/2}$ Tl or Ga atoms to their lowest lying $^2S_{1/2}$ state and (Fig. 2) $X^2S_{1/2}$ Na(K) atoms to their excited $3d^2D$, $4d^2D$ ($5d^2D$ in potassium), and $5s^2S$ ($6s^2S$) states. Adopting a pumping sequence in which a premixed Group IV A metalloid-receptor atom combination is oxidized, we observe a system temporal behavior which suggests the creation of a population inversion and gain condition in the Tl, Ga, Na, and K systems and forms the basis for full cavity oscillation on the Tl $7^2S_{1/2} - 6^2P_{3/2}$ transition at 535 nm and the Na $4d^2D - 3p^2P$ transition at 569 nm. We have now completed a group of definitive gain measurements and have demonstrated significant proof of continuous laser action based on the Na $4d^2D - 3p^2P$ transition (569nm) pumped by SiO metastables. Preliminary experiments to extend the concept to the pumping of Pb (lead), Cu (copper), and Sn (tin) atomic transitions suggest that the concept will be generic. In fact, the extension of the three level excitation scheme within itself offers a considerable range of radiative

configurations (lifetimes) commensurate with a variety of potential three and four level laser systems. They provide a range of conditions under which amplification can be created in a laser cavity. Experiments carried out on the SiO-Na system are summarized below and in detail in Appendix E.

Formation of Amplifiers (Oscillators) Through Direct Chemical Reaction

Na₂ chemical laser amplifiers have been produced^{2,4,6} in our laboratory employing the high cross section Na_n (n = 2,3) - X(Cl,Br,I) electron jump reactions to create a continuous electronic population inversion based on the chemical pumping of sodium dimer (Na₂). Sodium trimer molecules produced in supersonic expansion (see following and Appendix B) are reacted with halogen atoms to create the inversions on electronic transitions in Na₂. Optical gain through stimulated emission has been demonstrated in select regions close to 527, 492, and 460 nm with potential extension to the (412.5), ~395, ~365, and 350 nm regions. Results obtained are in close analogy to optically pumped alkali dimer lasers. A model which invokes the vibrational and rotational selectivity inherent to a dissociative ionic recombination process (Na₃⁺ + X⁻ → Na₂ + NaX), in correlation with the coupling between select sodium dimer excited states, may provide a semiquantitative explanation of the observed behavior. The observed gain (max. of 4% at ~527 nm corres. to 8 x 10⁻³/cm for individual rotational levels (see following)) can be enhanced considerably with a more versatile source configuration.

We are well into the testing of an up-scaled supersonic expansion system (see following and Appendix D) to study the chemically pumped Na₂ amplifiers produced from the Na₃-X(Cl,Br,I) reaction systems. This device has been constructed to provide an increased amplifier gain length and amplifying medium concentration to facilitate the conversion of the Na₂ amplifiers to continuous visible chemical laser oscillators. We have also completed modifications of a Phase I Na₃ system (Appendix B) to study the Na₃ - F, F₂ reactions and have begun to extrapolate on the Na₃-halogen atom amplifier concept. We suggest that lithium trimers may undergo similar metatheses with halogen atoms and therefore have constructed a molybdenum based supersonic expansion source to be operated in our Phase I (Appendix B) system.

The Na₂ amplifiers which we have characterized and potential lithium dimer amplifiers operate on bound bound transitions. It is not difficult

Figure 1(a): Tl atom energy levels.

Figure 1(b): Tl $7^2S_{1/2} - 6^2P_{3/2}$ (535.1nm) superfluorescence observed at a signal trigger level of 0.2V (fluorescent level $\sim 0.045V$). The trigger of the superfluorescence is by signal level and not by reactant mixing which occurs on a much longer time scale. The measured FWHM is 6.5 nsec compared to $T \sim 7.5$ n-sec, the radiative lifetime of the $7^2S_{1/2}$ level. A return to the fluorescence level is seen subsequent to the superfluorescent pulse. No such superfluorescent pulse is associated with the Tl $7^2S_{1/2} - 6^2P_{3/2}$ (377.7nm) transition.

Figure 1(c): Tl $7^2S_{1/2} - 6^2P_{3/2}$ (535.1nm) superfluorescent oscillation observed with full laser cavity configuration. The superfluorescence/fluorescence ratio (fluorescence following self-termination of lasing action) is now in excess of 100.

Figure 2(a): Na atom energy level scheme and pumping cycles to produce $4d^2D$ and $5s^2S$ excited states.

Figure 2(b): Typical energy transfer pumping spectrum for Na $4d^2D - 3p^2P$ and $5s^2S - 3p^2P$ transitions and $3p^2P - 3s^2S$ sodium D-line emission. The D-line emission results both from direct energy transfer pumping from ground state N_2O and from fluorescence to the $3p^2P$ level.

Figure 2(c): Energy transfer pumping spectrum corresponding to Na $3d^2D - 3p^2P$ transition.

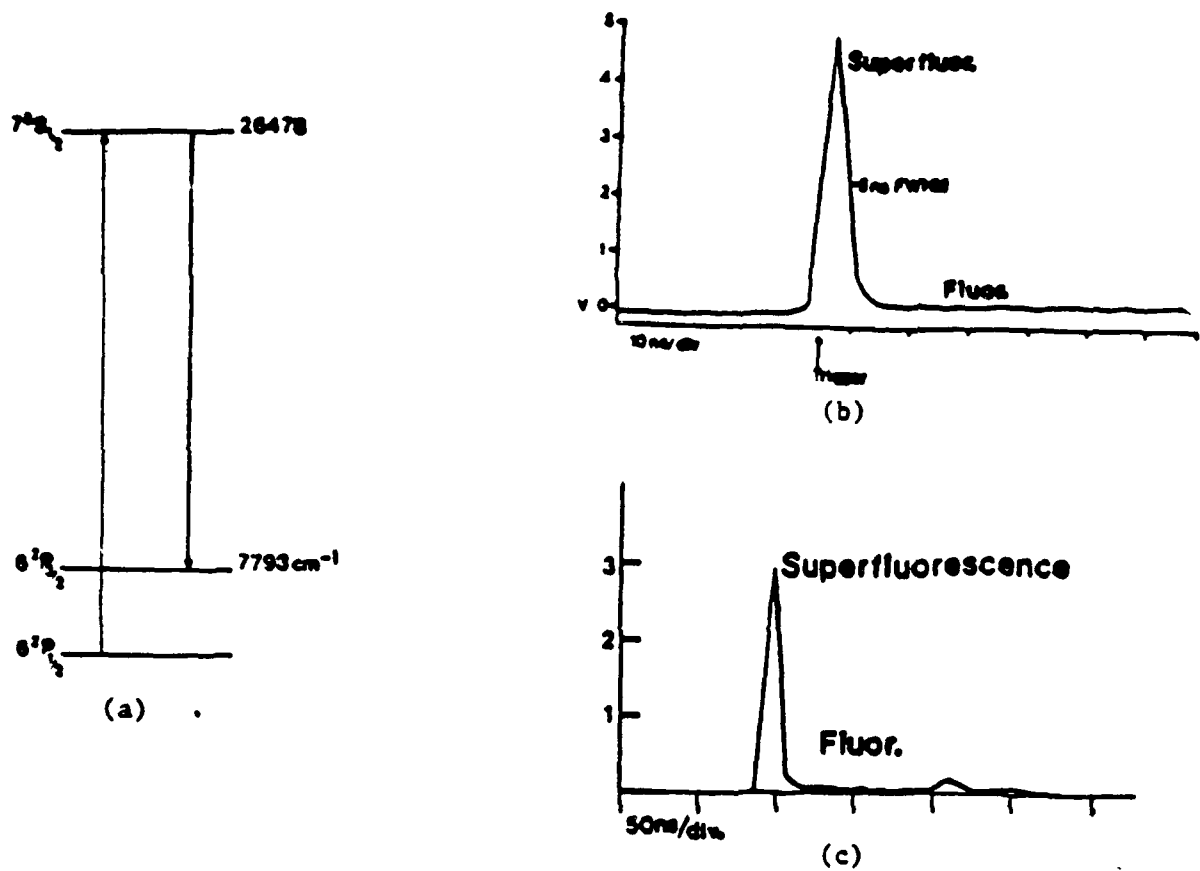


Figure 1

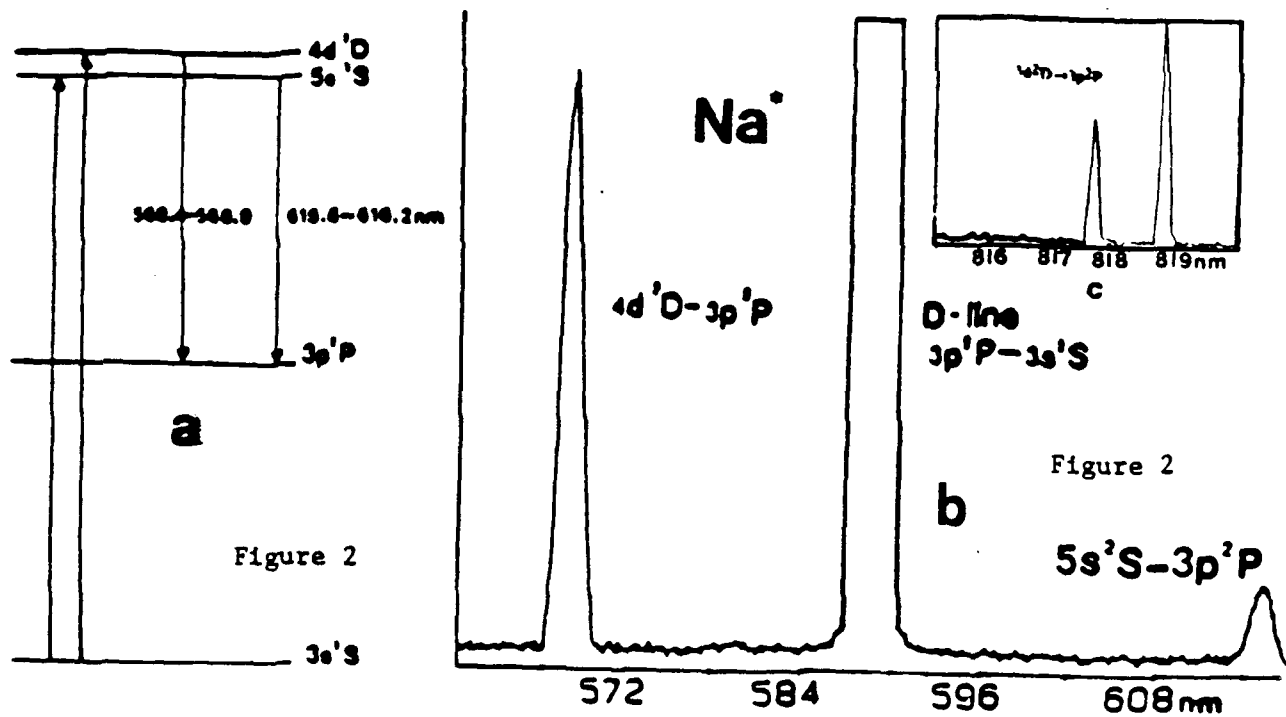


Figure 2

to envision an extrapolation on the $\text{Na}_3\text{-X}$ reactive encounters which involves the formation of excited state excimers undergoing bound-free transition. We are therefore drawn to the alkaline earth trimers, Mg_3 , Ca_3 , Sr_3 , and Ba_3 which, once formed, might react with a halogen atom to create dimer excited states which undergo bound-free transition²⁰ to the very weakly bound dimer ground state. We have begun a study of the reactions of magnesium trimer with fluorine and chlorine atoms (Appendix G) in the hope of producing an excimer based amplifier. Finally, we are formulating a theoretical model to explain the selective nature of the $\text{Na}_3\text{-X}$ reactive encounters.

Low-Lying Electronic States and Thermodynamic Stability in the Bismuth-Fluorine System

The suggestion of an energy pooling - energy transfer pumping of BiF excited states, employing metastable NF , to develop a visible chemical laser system has lead to considerable interest in this molecule. Recent results, which suggested a much larger bond energy for the BiF molecule than had previously been believed, sparked our interest in this alternate visible chemical laser candidate. We have carried out an extensive study of the bismuth-fluorine system focusing primarily on the spectroscopy of excited states which might contribute to the creation of a population inversion on the A-X transition. The correlation of this work with the recent observations of Dr. Wally Warren and coworkers at Pacific Research is quite encouraging.

Impetus and Implications

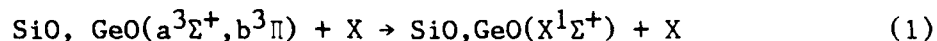
We believe (1) that the apparent initial successes and lessons learned in developing the current amplifiers signal the establishment of generic concepts to formulate new amplifiers, (2) that we have been successful in the first stages of converting these amplifiers to chemical laser oscillators, (3) that these amplifier-oscillator conversions will be considerably improved and further characterized in the short term, and (4) that the success of this conversion, in conjunction with the generalization of those concepts entailed in the development of the current amplifiers, will lead to a new class of visible laser oscillators. Our primary goal has been to develop and

characterize those sodium based amplifiers and oscillators which we have already demonstrated. We have pursued this effort using newly developed apparatus configurations (outlined in detail in Appendices C-E) which have undergone continual modification to improve both the definition of the amplifying medium and its interaction with cavity optics. These experiments have been paralleled by preliminary studies on additional promising systems. The techniques which we establish in our initial measurements can thus be applied to expand the range of potential amplifiers and oscillators.

NEAR RESONANT ENERGY TRANSFER FROM METASTABLE ENERGY STORAGE STATES OF SiO AND GeO TO FORM ATOM BASED LASER AMPLIFIERS

Pulsed thallium and gallium and continuous sodium and potassium laser amplifiers have resulted from studies in our laboratory whose focus has been to characterize the constraints of spin conservation, internal excited electronic state relaxation, and fast energy transfer, associated with the formation of copious quantities of the metastable SiO and GeO $a^3\Sigma^+$ and $b^3\Pi$ states as the products of the primarily spin conserving Si-N₂O,²¹ Si-NO₂,²² and Ge-O₃²³ reactions. We have used these long-lived triplet states as an energy reservoir for fast intermolecular energy transfer to excite potentially lasing atomic transitions. Using this approach we have obtained amplification from thallium at 535 nm (gain coeff. $\alpha > 2.5/\text{cm}$), gallium at 417 nm ($\alpha \sim 1.5$), sodium at 569 nm ($\alpha \sim 0.15/\text{cm}$), 616 nm ($\alpha \sim 0.05/\text{cm}$), and 819 nm ($\alpha \sim 0.03/\text{cm}$), and potassium at 581 nm. We have also obtained evidence for full cavity oscillation in the Tl and Na systems.

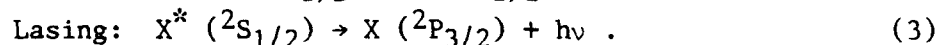
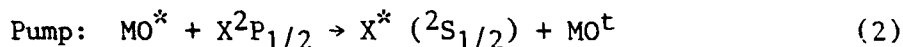
One might envision the SiO and GeO " $a^3\Sigma^+$ " and " $b^3\Pi$ " states forming a combined metastable triplet state reservoir which is, at best, weakly coupled to the ground electronic $X^1\Sigma^+$ state (minimal nonradiative transfer). This reservoir can be maintained and can transfer its energy to pump the atom of interest if a near resonant energy transfer is feasible. We make use of an efficient intermolecular energy transfer process



where X might represent the $X^2P_{1/2}$ ground state of thallium or gallium or the $X^2S_{1/2}$ ground state of sodium or potassium, X^* represents the electronically

excited atomic species from which we wish to obtain lasing action, and the energy transfer involves the formation of SiO or GeO ground state molecules. The success of the above scheme depends on the rate constants for the reactions of interest,²⁴ the branching ratio for formation of the SiO or GeO $a^3\Sigma^+$ and $b^3\Pi$ states, and the rate of the MO^* ($M=Si,Ge$) - X intermolecular energy transfer (strongly influenced by near resonances between the MO^* and X^* energy levels).

For thallium (see Appendix A for detailed discussion) we consider the sequence (Fig. 1(a))



The metal oxide excitation is transferred to the Tl atom, pumping the $X^2P_{1/2}$ state to the energetically accessible electronically excited $^2S_{1/2}$ level. The atom subsequently emits a photon (potential laser), corresponding to the $^2S_{1/2} - X^2P_{3/2}$ transition to an initially unpopulated $^2P_{3/2}$ spin orbit component ($N_{3/2} \leq e^{-10} (N_{1/2})$ at $T \leq 1100K$).

The efficiency of the outlined process for $X = Tl (^2P_{1/2})$, which does not react to form the metal monoxide, is such that a "superfluorescent" laser spike (Fig. 1(b)) some 25 times the normal $^2S_{1/2} - ^2P_{3/2}$ fluorescent intensity (after correction for instrumental response) is generated on an 5ns time scale. As the population of the $P_{3/2}$ metastable level builds in these systems, the $^2S_{1/2} - ^2P_{3/2}$ population inversion is lost and lasing ceases. The light level in the remainder of the temporal scan corresponds to $^2S_{1/2} - ^2P_{3/2}$ fluorescence.

We have extended the Tl atom laser amplifier concept to develop the corresponding laser oscillator. In a stable resonant cavity intermediate to a near planar - near confocal configuration ($g_1=g_2=17/20$) with 3% output coupling, we obtain a substantial increase in output power ($\sim 10X$) accompanied by a substantial increase in the ratio of superfluorescence to fluorescence (≥ 100 (Fig. 1(c)) versus the single pass amplifier. This output is obtained with up to three passes through the amplifying medium on the time scale over which the population inversion is maintained³⁻⁶ ($\sim 3-5$ ns). Amplification and oscillation are obtained with high reactant concentrations ($Si(Ge) > 2 \times 10^{14}/cm^3$, $Tl \geq 1 \times 10^{16}/cm^3$, oxidant $\geq 5 \times 10^{14}/cm^3$) and only in those systems in which the Si or Ge and Tl are premixed before the oxidation -

energy transfer - amplification cycle is initiated.³ The results obtained are in excellent agreement with the study of "superradiance" in Tl discharges by Isaev and Petrash.²⁵

The nature of the thallium laser amplifier and oscillator is discussed in detail elsewhere (see also Appendices A-C), however, the attributes, characteristics, and disadvantages of this system should be considered for a comparative assessment of additional candidates. The Ge-GeO-Tl system must be triggered by the oxidation of premixed Ge(Si)/Tl at concentrations exceeding $10^{15}/\text{cc}$.³⁻⁶ The threshold for lasing⁸ on the Tl $7\text{ }S_{1/2} - 6\text{ }P_{3/2}$ transition is low, the potential for a highly efficient near resonant ($\Delta E \leq 250\text{ cm}^{-1}$) pump of ground state Tl $6^2P_{1/2}$ atoms to the $7^2S_{1/2}$ excited state is manifest, and the formation of TlO is precluded so as to considerably minimize interference with the formation of SiO and GeO metastables. These advantages are, however, balanced by the short radiative lifetime associated with the $2^2S_{1/2}$ level and the metastability of the $2^2P_{3/2}$ terminal laser level. The self-terminating, $\lambda = 535\text{ nm}$, Tl laser amplifier is superfluorescent. Thus, the conversion of the Tl system to a laser oscillator, strongly influenced by the cooperation length²⁶ of the stable cavity configurations employed in this effort, produces an output obtained with up to three passes through the amplifying medium on the time scale over which the population inversion is maintained³⁻⁶ ($\sim 3\text{-}5\text{ ns}$). The Tl system is difficult to oscillate because of its short pulse mode. Further, because it is superfluorescent,²⁶ the output power obtained on full cavity oscillation does not greatly exceed ($\times 10$) the output for single pass amplification.

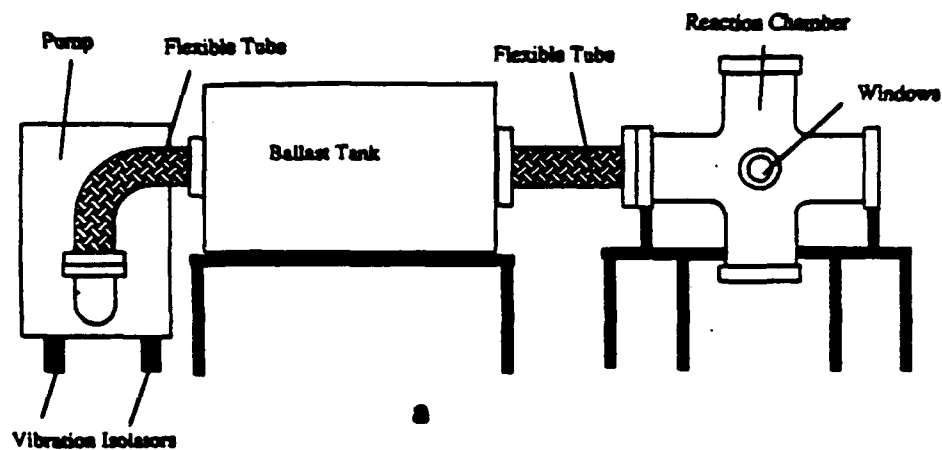
In response to the shortcomings inherent to the Tl atom system, we have extended the energy transfer concept to the more nearly resonant atomic sodium and potassium atoms (see also Appendices A-D) as a means of forming higher duty cycle laser amplifiers and oscillators. By choosing the Na and K based systems, we also focus on longer-lived emitters²⁷⁻²⁹ as a means of enhancing energy storage in the laser cavity. Both metastable SiO and GeO can be used to energy transfer pump from the $3s^2S$ (Figure 2(a)) Na ground state ($4s^2S$ in K) to the $4d^2D$ and $5s^2S$ levels ($5d^2D$ and $6s^2S$...in K). In the Tl system laser action is terminated through the filling of the $P_{3/2}$ level. However, in the sodium system (Fig. 2(a)) the terminal laser level is the short-lived upper level of the Na D-line. The $3p^2P - 3s^2S$ transition,²⁷ with its high oscillator strength, facilitates rapid loss of the terminal laser level to

create ground state sodium atoms which are again amenable to near resonant energy transfer pumping (Figs. 2(a) and 2(b)). While the $5s^2S$ and $4d^2D$ levels are not readily accessed in an optically pumped transition, SiO metastables formed in the Si-N₂O reaction, have successfully energy transfer pumped Na atoms to the ^2S and ^2D levels where they subsequently emit radiation at $\lambda \approx 616$ nm as they undergo transition to the $3p^2P$ levels. The accessed Na cycle with its 50^{28} ($4d^2D - 3p^2P$) to $\sim 100^{29}$ nanosecond upper state radiative lifetimes (vs. Tl $^2S_{1/2}$ at $\sim 7_{\text{nsec}}$.³⁰) and short-lived terminal laser level would appear ideally suited to obtain higher duty cycle laser amplifiers and oscillators. As indicated in Figure 2(c), we also obtain evidence for the energy transfer pump of the Na $3d^2D$ level with which is associated an atomic emission at $\lambda \approx 819$ nm ascribed to the Na $3d^2D - 3p^2P$ transition.

In order to study amplification in the sodium and potassium systems, we have constructed a relatively versatile device (Fig. 3) which allows us to obtain a moderately long amplification path length.⁶ This construction can take advantage of three entrainment flow configurations for silicon or germanium in the cycle producing SiO and GeO metastables, one of which is depicted in Fig. 3. These flow configurations produce the longest path length SiO metastable flame ($\sim 5 + \text{cm}$) yet obtained. The entrainment flow configuration must be designed to create large concentrations of SiO (GeO) metastables which are intersected at $\sim 90^\circ$, in subsonic flow, by a high concentration of sodium or potassium atoms. The entrained silicon and sodium flows can also be moved in-situ relative to each other and hence with respect to the reaction - energy transfer - amplification zone to optimize conditions for formation of the gain medium.

The entrainment flow device depicted in Figure 3 can be surrounded by a variety of optical trains to measure gain and lasing in the Si-SiO-Na system. The three sodium atom transitions at $\lambda \approx 569$ nm ($\alpha \sim 0.1-0.15/\text{cm}$), $\lambda \approx 616$ nm ($\alpha \sim 0.03-0.05/\text{cm}$), and $\lambda \approx 819$ nm ($\alpha \sim 0.02-0.03$) demonstrate continuous gain, although optimal gain on each line is monitored under slightly different mixing in the amplification zone (App. B). The gain has been measured (Appendices B,E) at all three wavelengths using the ingenious design of Roll and Mentel.³¹ We compare the (paraxial) single vs. double pass amplified spontaneous emission emanating from the 5 cm amplification zone of Fig. 3. Further, at 569 nm, two additional gain measurements have been performed

Figure 3: (a) Schematic of reaction chamber and windows defining optical train, ballast tank to moderate pumping fluctuations, and pumping configuration, for extended path length Si-SiO (Si-N₂O)-Na reaction amplification zone. (b),(c) Side and overhead views of reaction chamber showing positioning of Si oven source, relative locations of Si and Na oven sources, oxidant injection system, and relative positions of these devices with respect to the optical train. (d),(e) Closeup view of silicon and sodium oven assemblies. (f) Schematic overview of reaction chamber-amplification zone, ballast, and pump for extended path length Si-SiO(Si-N₂O)-Na gain medium. The figure indicates the course alignment path (~ 15 ft) for the HeNe laser and its correlation with the optical train surrounding the reaction zone and terminating at the monochromator.



Overall Apparatus Configuration

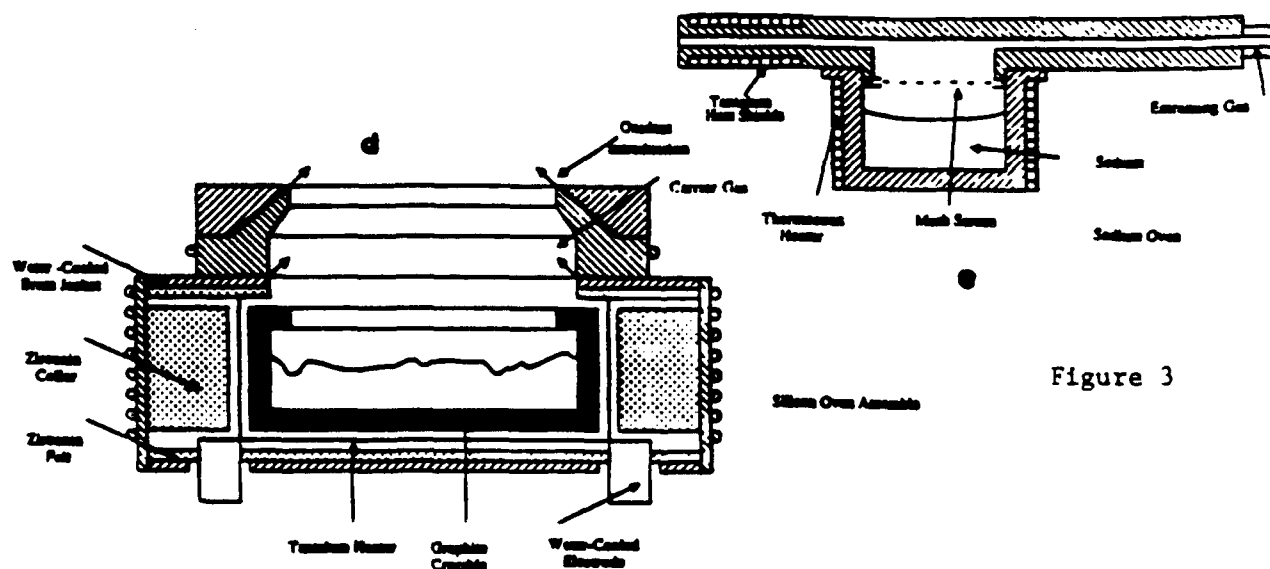
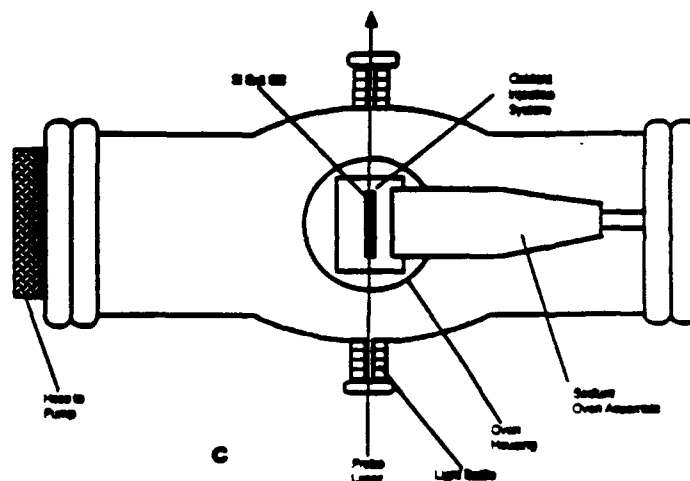
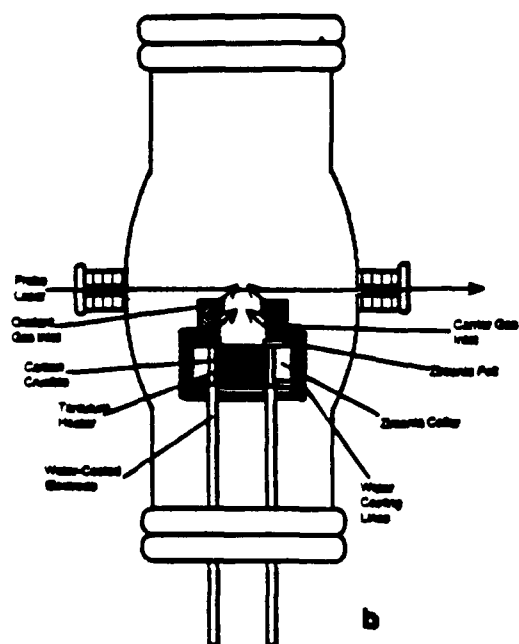
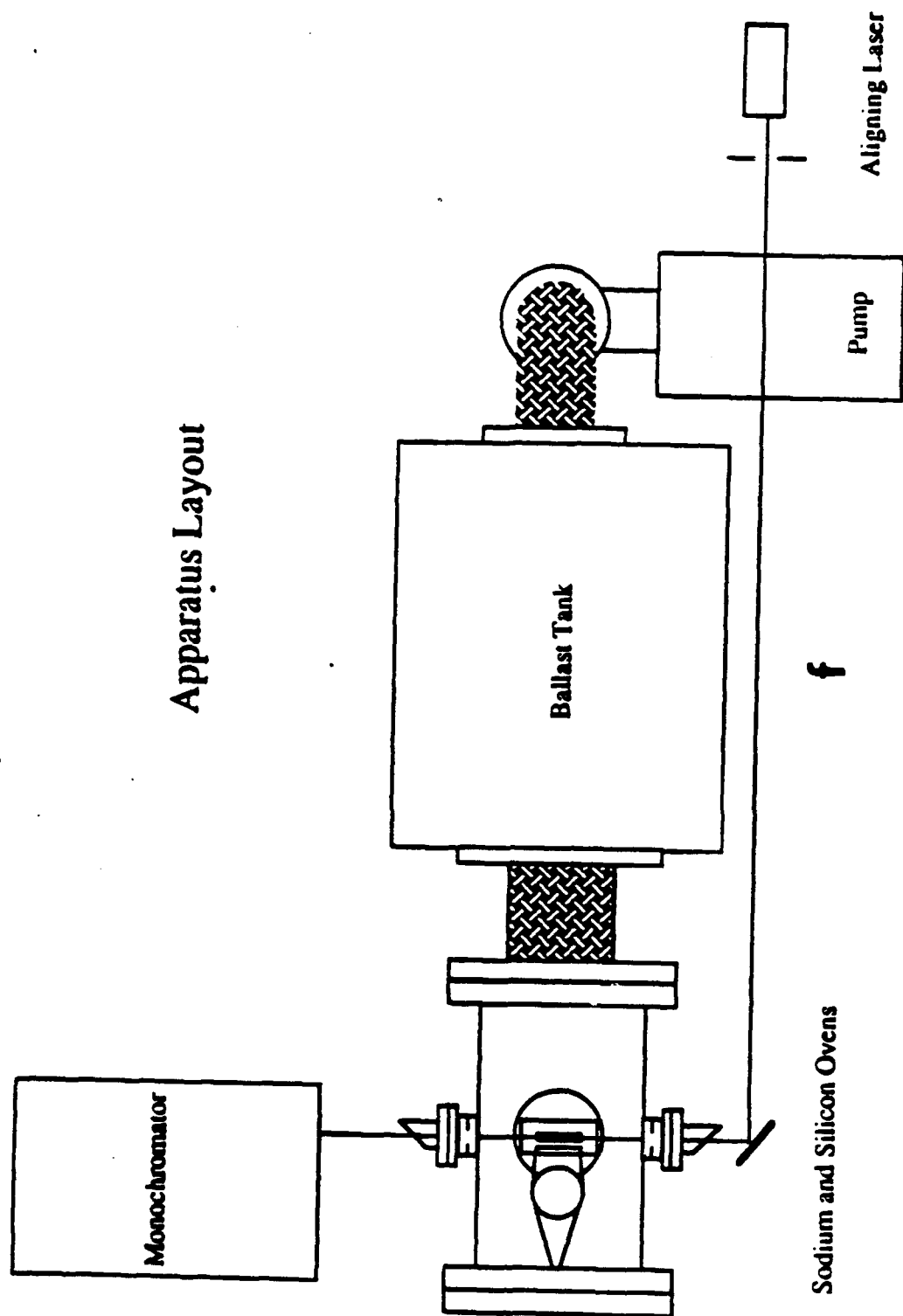


Figure 3



Apparatus Layout

Figure 3

(Detailed - Appendix E), one deducing the amplification of the $4d^2D - 3p^2P$ transition from a sodium discharge lamp and a second employing a scanning single-mode ring dye laser. Preliminary measurements at 616 nm using the sodium discharge lamp also demonstrate a continuous gain condition.

"Full Cavity Measurements"

Full cavity measurements have also been made on the sodium system. The results of these measurements at 569 nm for a 0.2% output coupled stable cavity configuration are shown in Figure 4. We find that the ratio of the output for full cavity operation to that obtained with a blocked high reflector easily exceeds 10^3 . Compare also the signal level observed with the blocked high reflector and that monitored with a completely blocked detector. The corresponding ratio obtained for pure fluorescence (cavity below threshold) using the 0.2% output coupled cavity was slightly greater than 1.8 for the Na D-line. These results clearly indicate continuous laser oscillation in the sodium system.

"Improvement of the Cavity Configuration"

Our focus in continually improving the system must be, in large part, on the optimization of reactant mixing, considering the rate limiting effect of the silicon concentration, the importance of virtually complete sodium atomization, and the confinement of the reactants and receptors to the cavity axis region. Further, we must insure that the reactant and entrainment flows (reaction zones) are controlled so as to protect the cavity windows from the condensation of silicon or germanium oxide and/or sodium or potassium. This latter requirement is met, in part, using "self cleaning" optical windows³² with a protective helium flow. The "rate limiting" silicon concentration signals a focus on the modification of the oven source configuration depicted in Figure 3 to continually improve the silicon atom flux and the flow conditions whereby this reactant is transferred to the reaction-energy transfer-amplification zone. As such, we must be concerned with the evaluation and improvement of reactant flow patterns in the cavity as well as with the simultaneous improvement of the optical train surrounding the reaction zone.

Figure 4: Full cavity output created with $\sim 0.2\%$ output coupling for the continuous Si-SiO(Si-N₂O)-Na amplifier at $\lambda=569$ nm. These measurements were taken in continuous flow with the cavity configuration depicted in Fig. 3(b). The full cavity output is compared to that obtained with both a blocked high reflector and with the entire cavity isolated from the signal detection system. The ratio of the output obtained for the full cavity to that obtained with a blocked high reflector exceeds $10^3/1$.

Resonant Cavity

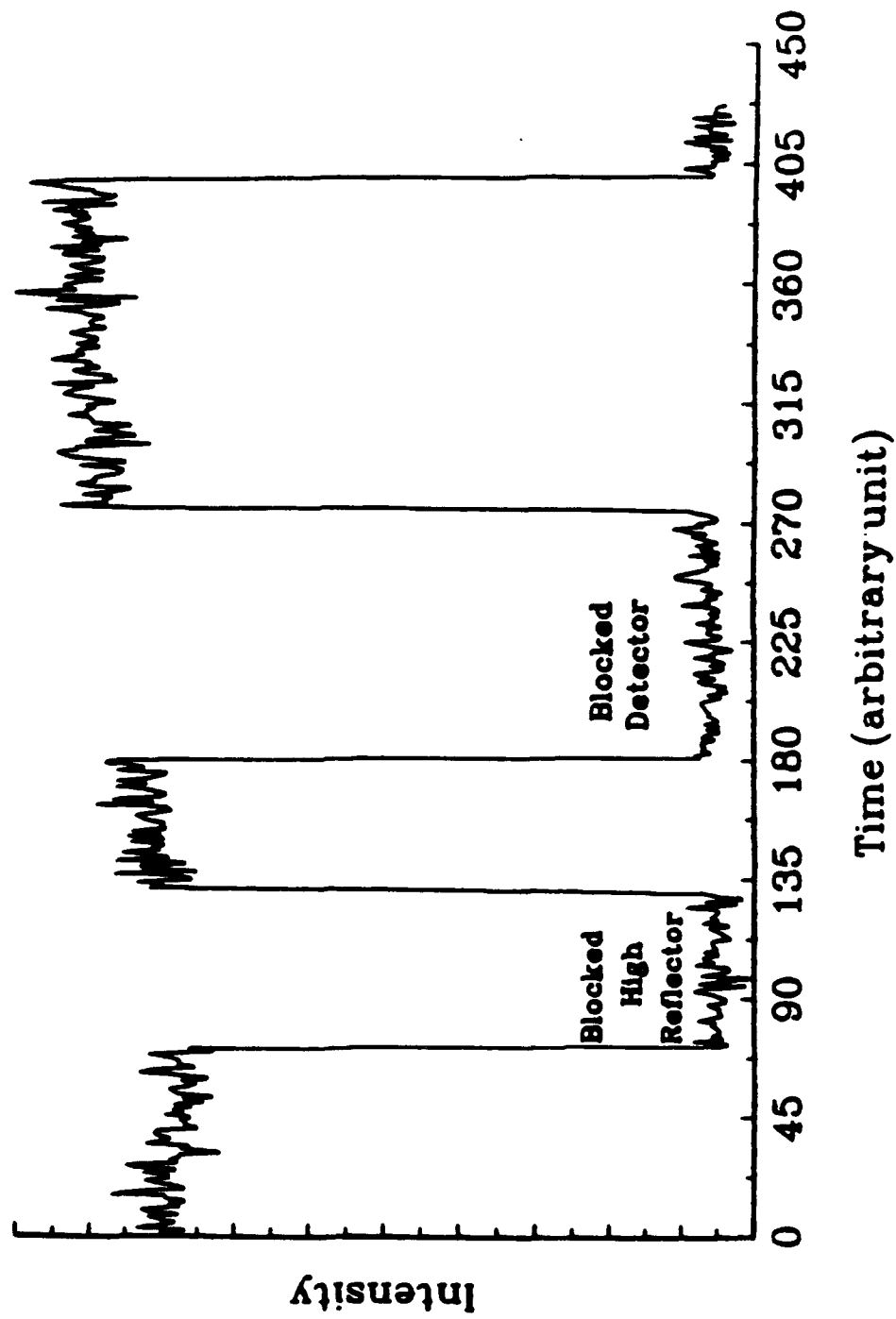


Figure 4

The mixing zone depicted in Figure 3 is greatly stabilized by the moderate sized (~15 cubic feet) ballast separating the 150 cfm pump and reaction chamber. While this insures that the 90° intersection of the SiO and sodium atom flows can be used to establish a continuous lasing action, the reactant intersection is by no means optimal. We have been in the process of constructing an appropriate concentric as opposed to 90° SiO-Na intersection region. Once in place, this configuration should further improve the results outlined in Fig. 4. The experiments conducted thusfar have made use of only two distinct output coupling configurations. As well as improving reactant concentrations, the optimum output coupling for the current cavity remains to be evaluated. Finally, we are constructing a modification which will allow removal of the cavity windows whose presence represents a significant loss in the optical train. With these improvements, the output from our full cavity configuration should be substantially enhanced.

Extension of Near Resonant Intermolecular Energy Transfer Concept to Additional Energy Transfer Pumped Atomic Receptors

While we have emphasized the results obtained thusfar for the sodium system based on an SiO metastable pump, it is also feasible to use GeO metastables. In fact, we have obtained evidence that the energy transfer pumping of the sodium analog potassium based amplifiers associated with the $5d^2D - 4p^2P$ ($\lambda = 581, 583$ nm), $4d^2D - 4p^2P$ ($\lambda = 694, 697$ nm), and $6s^2S - 4p^2P$ ($\lambda = 691, 694$ nm) potassium atom transitions might best be accomplished with pumping by GeO metastables.

We have also successfully energy transfer pumped potential amplifying transitions in lead (Pb), copper (Cu), and tin (Sn) receptor atoms. Two of these systems are particularly intriguing. Figure 5 demonstrates the results we have obtained when interacting SiO metastables (Si-N₂O) with lead receptor atoms. Observed Pb transitions are indicated to the right of the figure. First, we notice that self absorption involving ground state Pb atoms is so dominant that no emission to the X $^3P_0$ ground state is observed. Second, we find significant pumping of both the $^1S_0$ and $^1D_2$ levels. The corresponding transitions from the $^1S_0$ level terminate in the lowest X $^3P_2$ (531.2 nm) and X $^3P_1$ (462 nm) levels. It is thought that collisional quenching and relaxation of the $^1S_0$ level will be minimal relative to that of the X ^3P

manifold.³² This may lead to potential inversions and amplification at $\lambda = 462, 531 \text{ nm}$.³³ The well known lead laser transition at $\lambda = 723 \text{ nm}$ ³⁴ with an A value $\sim 10^6 \text{ sec}^{-1}$ terminates on the $^1D_2$ level. Surprisingly, we find no evidence for this transition which emanates from the upper $^3P_1^o$ level (Fig. 5). We do find evidence for the $^3P_1^o - X \ ^3P_1$ and $^3P_1^o - X \ ^3P_2$ transitions and for the $^1D_2 - ^3P_1$ transition at 733 nm .³⁵ This suggests that the $^3P_1 - ^1D_2$ transition may be self-absorbed due to a significant $^1D_2$ population. If we have observed the manifestation of a substantial $^1D_2$ population, does this result from direct energy transfer pumping or is the $^1D_2$ state populated by the 723 nm transition at times considerably shorter than the time scale for the present observations? This must be assessed in future experiments. The results obtained for the energy transfer pumping of lead atoms certainly suggest the possibility of additional amplifier systems. It is particularly encouraging that some of these may represent four level systems which obviate the self absorption bottleneck that may plague the Si-SiO-Na system at high Na concentration.

The near resonant energy transfer pumping of copper vapor is of interest not only because of the close analogy which it bears to the sodium and potassium systems but also, as Figure 6 indicates, because it is possible to energy transfer pump the copper vapor laser transitions³⁶ using metastable SiO (Si-SiO-Cu system). However, it is also of interest that the results demonstrated in Figure 6 were obtained using an approach which represents a significant extrapolation from the configuration in which a "premixed" Tl/Ge mixture has been used to obtain pulsed amplification on the Tl $^2S_{1/2} - ^2P_{3/2}$ transition. Here, Si and Cu were premixed and co-vaporized from a single crucible. The resulting mixture was then oxidized to yield the observed energy transfer pumping spectrum depicted in Figure 6. (It is worth noting that N_2O , used as the oxidant, produces a dark reaction with copper vapor.)

The results presented in Figures 5 and 6 clearly demonstrate that there are intriguing variations on the thallium, gallium, and sodium based systems. In fact the level structures which are depicted also in Figure 1 and 2 suggest that the three level excitation scheme may offer a considerable range of radiative configurations (lifetimes) which can be accessed in near resonant pumping.

Figure 5: Comparison of lead - SiO ($a^3\Sigma^+, b^3\Pi$) near resonant energy transfer spectra. Metastable SiO molecules were created in the reaction $\text{Si} + \text{N}_2\text{O} \rightarrow \text{SiO}^* + \text{N}_2$. (a) The spectrum corresponds to a portion of the SiO metastable emission spectrum before lead atoms are brought into the reaction zone. (b) Spectrum recorded with high Pb flux (~ 1 torr vapor pressure) showing the manifestation of energy transfer pumping to produce electronically excited $3p^0$, $1S_0$, and $1D_2$ levels of the lead atom. (c) Energy levels for the lead atom with observed transitions as indicated in (b).

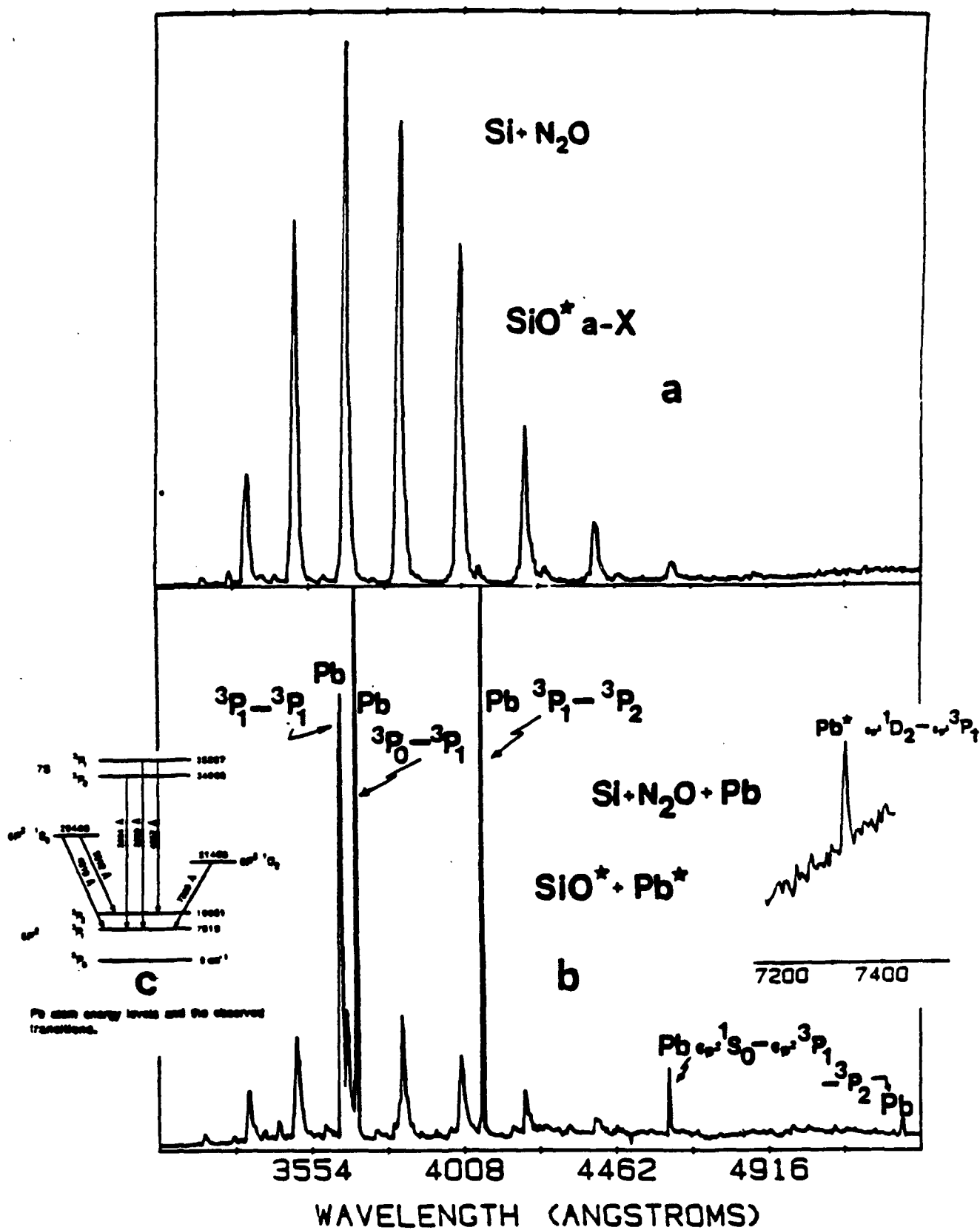


Figure 5

Figure 6: Copper - SiO ($a^3\Sigma^+, b^3\Pi$) near resonant energy transfer spectra generated from a "premixed" Si-Cu mixture subsequently oxidized with N₂O. (a) Spectrum showing a portion of the SiO metastable emission, the Cu $2P_{3/2} - {}^2D_{5/2}$ blue green emission line (copper vapor laser) and the Cu $2P_{3/2,1/2} - {}^2D_{3/2}$ yellow-orange emission features. (b) Energy levels for the copper atom.

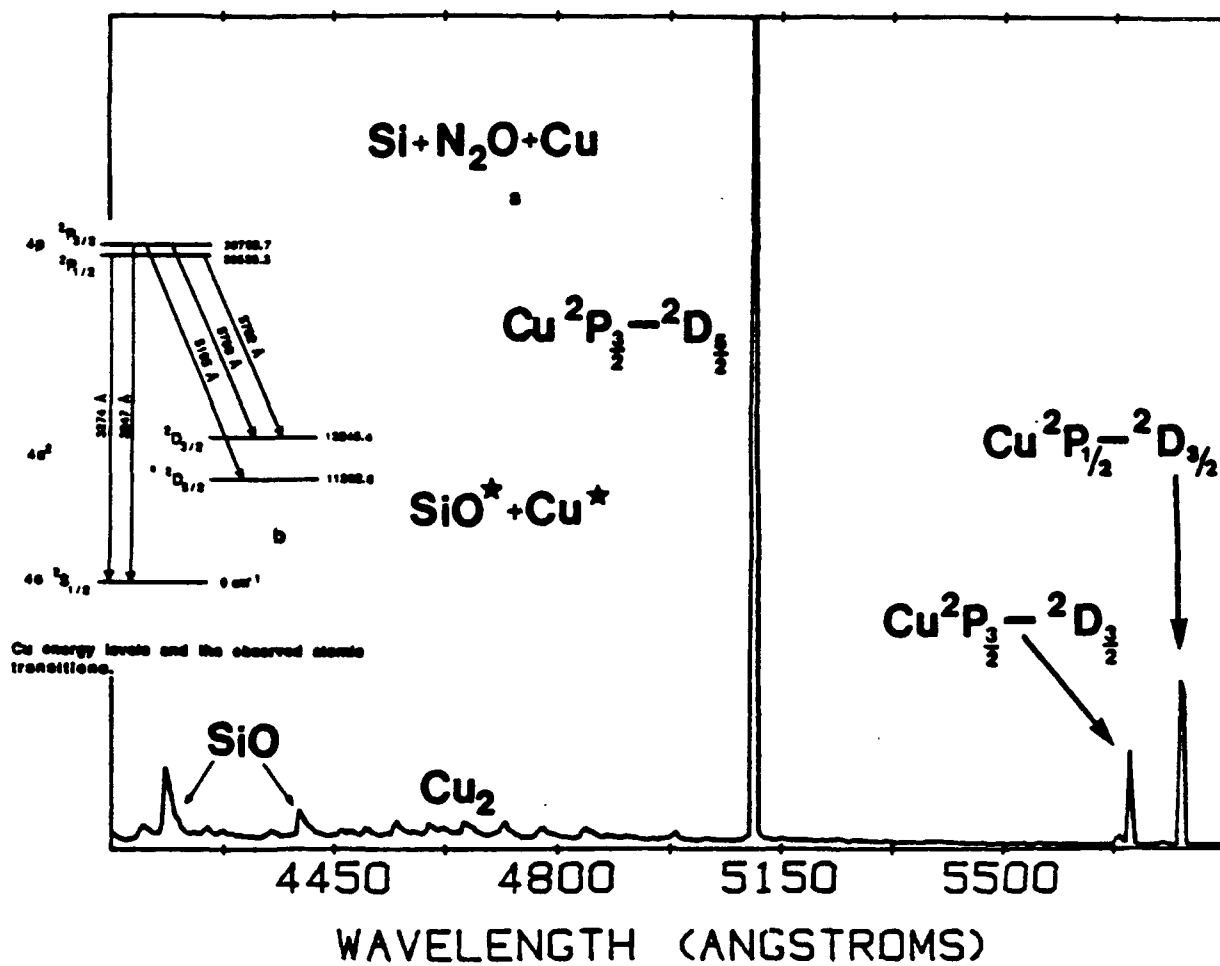
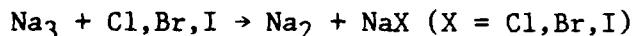


Figure 6

CONTINUOUS CHEMICAL LASER AMPLIFIERS IN THE VISIBLE REGION BASED ON HIGHLY EFFICIENT AND SELECTIVE CHEMICAL REACTION

Efficient chemical laser oscillators should be developed from the high cross section, highly exothermic $\text{Na}_3 - \text{X}$ (Cl, Br, I) reactions which selectively form Na_2^* in a limited number of its excited electronic states (Fig. 7(a)). The optical signatures for the processes



encompass emission from a limited number of Na_2 band systems. Surprisingly, the observed emission is characterized by sharp well defined emission regions (Figs. 7(b), 7(c)) superimposed on a much weaker but perceptible and analyzable Na_2 background fluorescence. As Fig. 7(c) demonstrates, these sharp emission features are not readily explained by invoking a purely fluorescent process.

The sharp nature of several of the B-X, C-X, and C'-X Na_2 fluorescence features (Figs. 7(b), 7(c)) their correlation in certain regions to the emission characteristic of optically pumped Na_2 laser systems³⁷ (ex: ~ 528.2 nm (v', v'') = (6,14) B-X), and the near exponential growth of these features relative to the background Na_2 fluorescence spectrum with increasing Na_3 concentration, suggests the possibility that stimulated emission might be associated with certain of the emitting Na_2 reaction products. Laser gain measurements were carried out to assess this possibility.

In order to do these gain studies, we further developed (Fig. 8(a)) a unique source configuration which allows the supersonic expansion of pure sodium vapor to create a Na_3 concentration not previously attained in a reaction-amplification zone. Using argon ion pumped dye lasers to study the $\text{Na}_3 + \text{Br}$ reaction we have scanned (Fig. 8(b)) the entire wavelength region from 420 to 600 nm (Figure 7(b)) in ~ 3 nm intervals at 0.5 cm^{-1} resolution (FWHM) and the regions around 527 nm and 460 nm (Fig. 7(c)) at 0.007 cm^{-1} resolution.^{2,4,6} We find that laser gain and hence amplification is associated with very limited regions of the spectrum. The observations suggest that several of the sharp emission features apparent in Figure 7 correspond to a stimulated emission process and the establishment of a population inversion. Optical gain through stimulated emission (0.5 cm^{-1}

Figure 7(a) Approximate potential curves for select states of Na_2 .

Figure 7(b) Chemiluminescent emission resulting from the reaction $\text{Na}_3 + \text{X} \rightarrow \text{Na}_2 + \text{NaX}$ with $\text{X} = \text{Br}, \text{I}$. The spectra display sharp fluorescence features in the visible at 527, 492, and 460.5 nm superimposed on a broader Na_2 background emission.

Figure 7(c) Comparison of (a) observed and (b) calculated emission spectra for the Na_2 B-X emission system. The experimental spectrum corresponds to the chemiluminescence from the Na_2 -Br reaction. The calculated spectrum, which was obtained for a rotational temperature, $T_{\text{rot}} \approx 1000\text{K}$, represents an estimate of effective rotational temperatures in a system operated under single collision conditions and therefore not at equilibrium. Relative vibrational populations input for Na_2 B-X, $v' = 0-6$ were in the ratio 1.00:1.17:1.33:1.50:1.67:1.54.

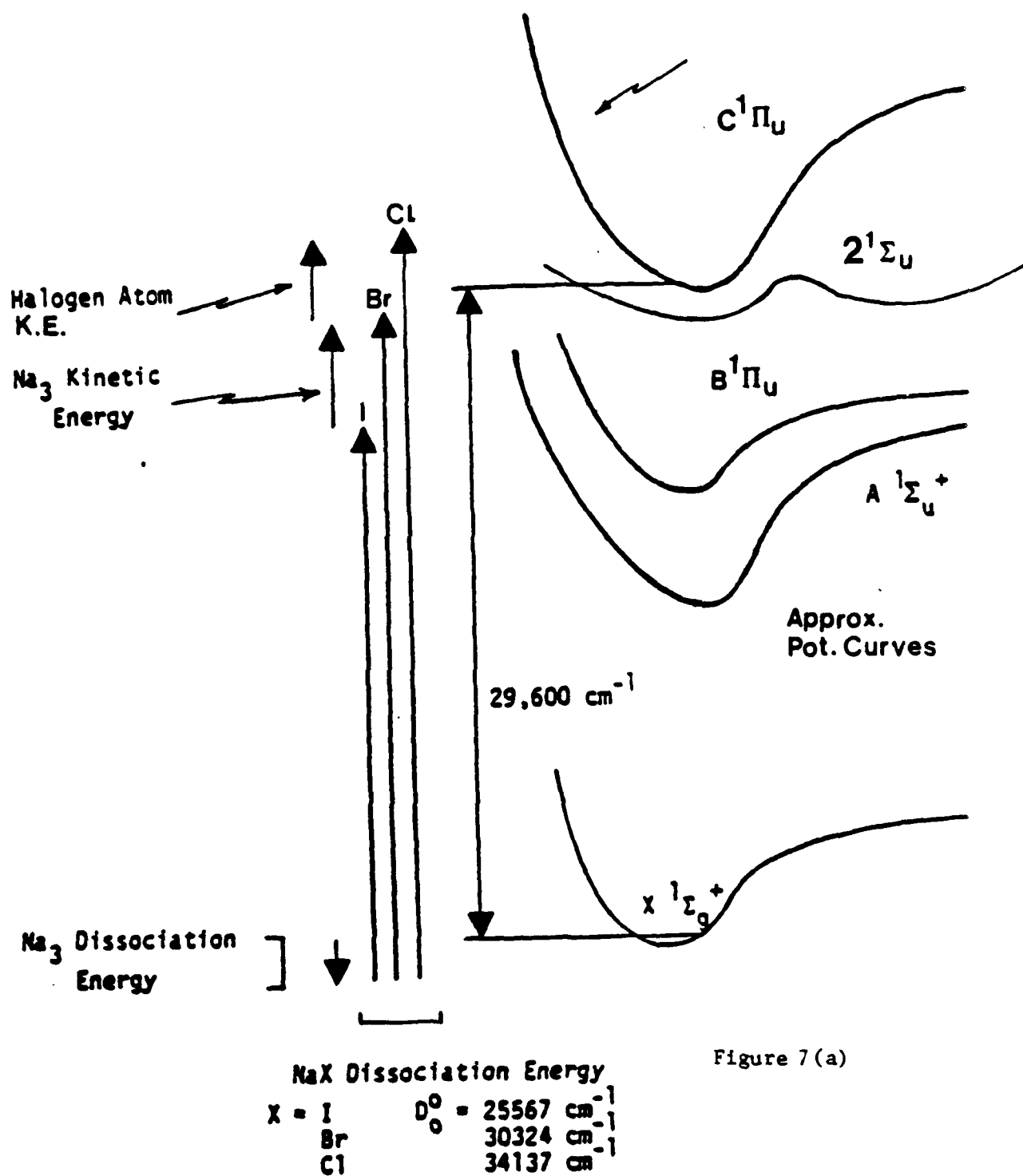


Figure 7(a)

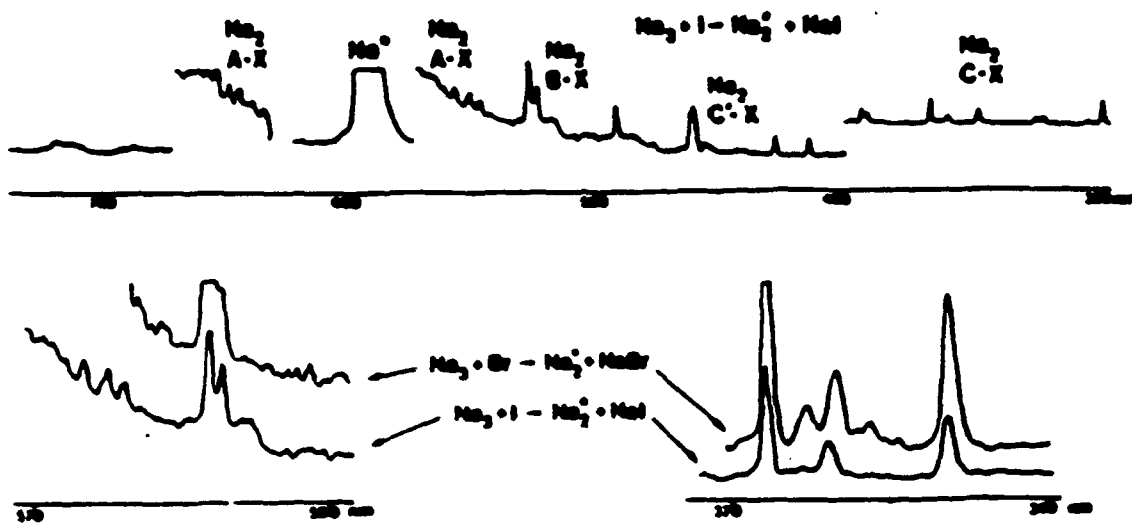


Figure 7(b)

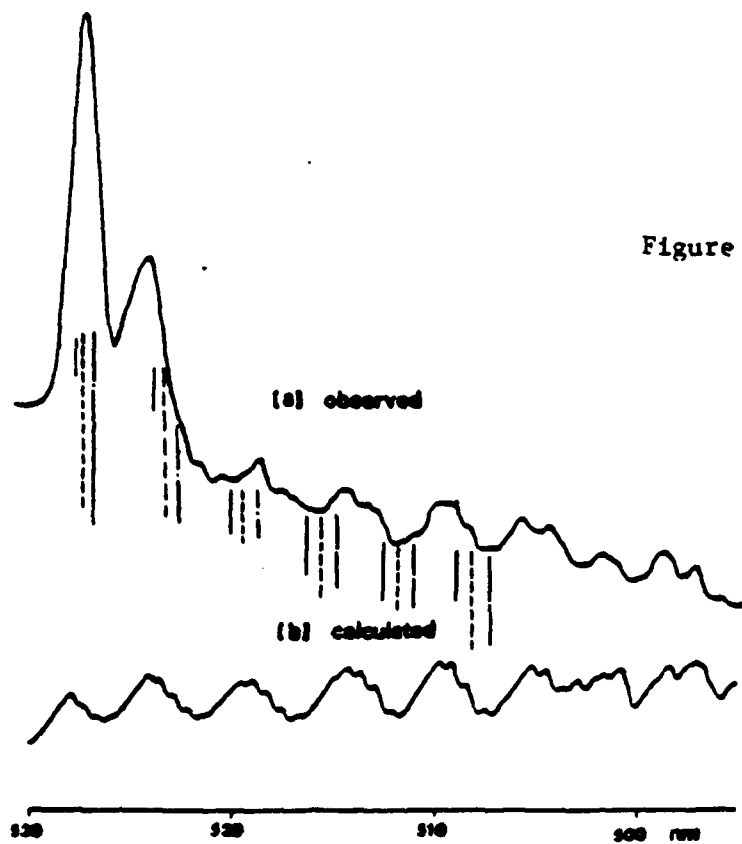


Figure 7(c)

Figure 8: Schematic of (a) apparatus for the study of the chemiluminescent Na_3 - X reactions and (b) the arrangement of the experimental configuration for measuring gain from the Na_3 - X metathesis.

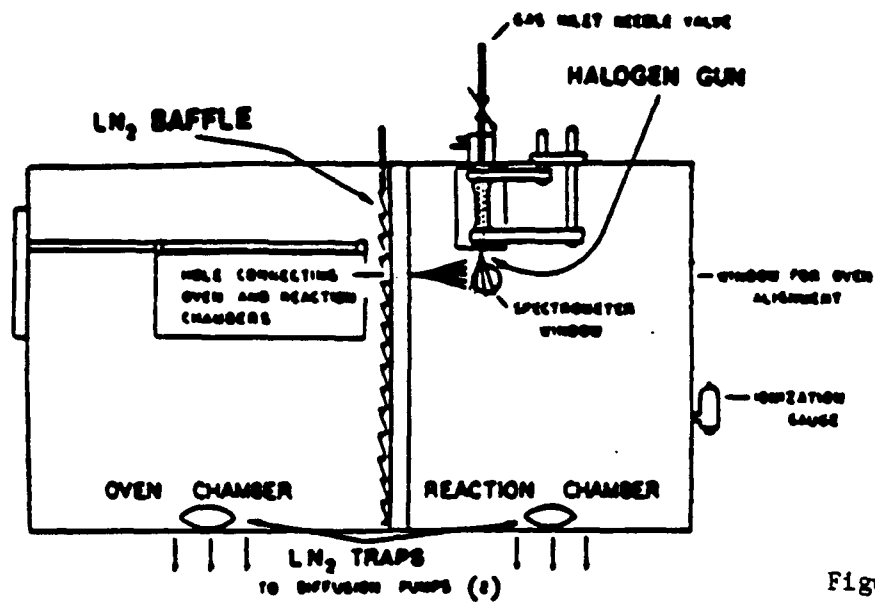
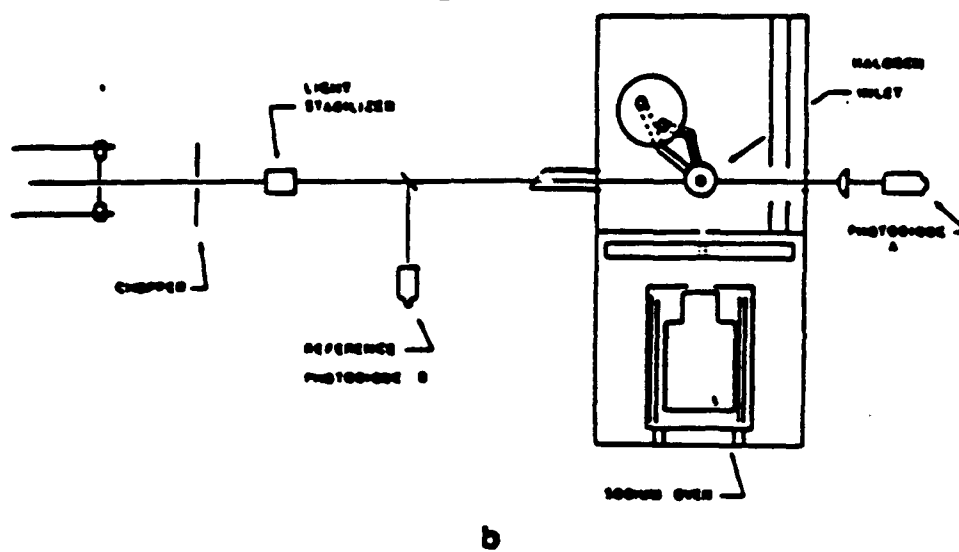


Figure 8



resolution) in the regions close to 527 nm (1%), 492 nm (0.3%), and 460.5 nm (0.8% gain) correlates precisely with the reactive process and the relative intensities of those features observed while monitoring the light emitted from the $\text{Na}_3\text{-Br}$ and $\text{Na}_3\text{-I}$ reactions. High resolution ring dye laser scans in the 527 nm region indicate that the gain for the system is a minimum of 3.8% for an individual rovibronic transition with approximately four to seven individual rotational transitions showing gain. At 459.8 nm, we have measured an $\sim 2.3\%$ gain for an individual rotational transition. The results demonstrate the continuous amplifying medium for a visible chemical laser in at least three wavelength regions.^{2,4,6} At no other scanned wavelengths have we observed gain. In fact, in scanning the 420-600 nm region, we generally observe losses of the laser photon flux due primarily to scattering (to only a negligible extent, absorption) on transit through the $\text{Na}_3\text{-Br}$ reaction zone. In the region of the sodium D-line, a substantial absorption and hence loss is monitored as a function of the trimer-halogen atom reaction.^{2,4,6}

Because of the low Na_2 ionization potential and the high halogen electron affinities,³⁸ the Na_3 -halogen atom reactions are expected to proceed via an electron jump mechanism with extremely high cross sections,³⁹ producing substantial Na_2 excited state populations. The question of why the $\text{Na}_3\text{-X}$ reactions appear to demonstrate vibrational and rotational selectivity associated with certain wavelength regions may be dealt with by invoking a model for the dissociative ionic recombination, $\text{Na}_3^+ + \text{X}^- \rightarrow \text{Na}_2^* + \text{NaX}$, and the curve crossings which influence the distribution of product molecules for this process.⁴⁰ This model, coupled with an analysis of the electronic coupling between select sodium dimer excited states, may provide a semi-quantitative explanation for the created population inversions.

The population inversions monitored thusfar are thought to be sustained (1) by the large number of free halogen atoms reacting with Na_2 molecules in those ground state levels on which the transitions emanating from the Na_2 excited states terminate and (2) collisional relaxation of the ground state sodium dimer molecules. The cross section for reaction of vibrationally excited ground state Na_2 is expected to be at least comparable to the cross section for collision induced vibrational deactivation of the Na_2 manifold. Extremely efficient reactions greatly assist the depletion of the lower state levels in this system allowing one to sustain a continuous population inversion.

We are continuing our modeling of Na_2 excited state formation from the $\text{Na}_3 - \text{X}(\text{Cl}, \text{Br}, \text{I})$ system attempting to correlate our observations with the coupling of certain dimer excited states. In this effort, we have been in contact with Professors W. C. Stwalley (University of Iowa) and Klass Bergmann (Univ. of Kaiserslautern, F.R.G.). Further, in collaboration with Dr. Edmund Mansky,⁴⁰ we are attempting to assess the origin of the selective vibrational-rotational excitation inherent to the Na_2 reaction products. A model which invokes the vibrational and rotational selectivity inherent to a dissociative ionic recombination process ($\text{Na}_3^+ + \text{X}^- \rightarrow \text{Na}_2 + \text{NaX}$), in correlation with the coupling between select sodium dimer excited states, may provide a semi-quantitative explanation of the observed behavior.

Development of an Extended Path Length $\text{Na}_3 - \text{X}(\text{Cl}, \text{Br}, \text{I})$ Reaction - Amplification Zone

We desire to considerably improve the magnitude of the amplification demonstrated for the sodium dimer amplifiers at ~ 527 , ~ 492 , and ~ 460 nm. The apparatus depicted in Figure 8 now produces a substantial Na_3 concentration ($\geq 10^{13}/\text{cc}$) albeit in a limited reaction-amplification zone. In order to demonstrate continuous chemical laser oscillation, however, it is desirable to create an enhanced sodium trimer - halogen atom reaction zone not only in terms of reactant concentration but also with respect to the amplification zone path length. The overall apparatus design depicted schematically in Figure 9 and pictured in Figure 10 is meant to accommodate high intersecting reactant flows from both sodium trimer and (dual rotatable) halogen atom sources in order to produce an enhanced concentration of Na_2 amplifiers over a significantly extended path length.

The apparatus in Figs. 9 and 10 attempts to increase the Na_3 reaction - amplification zone concentration by repositioning the trimer and halogen atom sources relative to each other and facilitating the halogenation process much closer to the alkali nozzle itself, in a gas dynamic configuration. We also have incorporated the facility for the in-situ adjustment of the alkali and halogen source positions. This includes the ability to rotate the dual alkali-trimer-flow-encompassing halogen atom slit sources (Figs. 9(b), 9(d)) so as to optimize flow mixing. Further, as a means of increasing the reaction zone and gain length, we have developed and are testing continuous flow slit

Figure 9: Schematics of upscaled Na₃-halogen atom reactive flow configurations. (a) Schematic of sodium slit source configuration with argon entrainment flow device for seeded expansion, (b),(c) Front and side views of upscaled reaction-vacuum chamber configuration showing positions of halogen and sodium sources, (d) Schematic of upscaled vacuum chamber and pumping configurations.

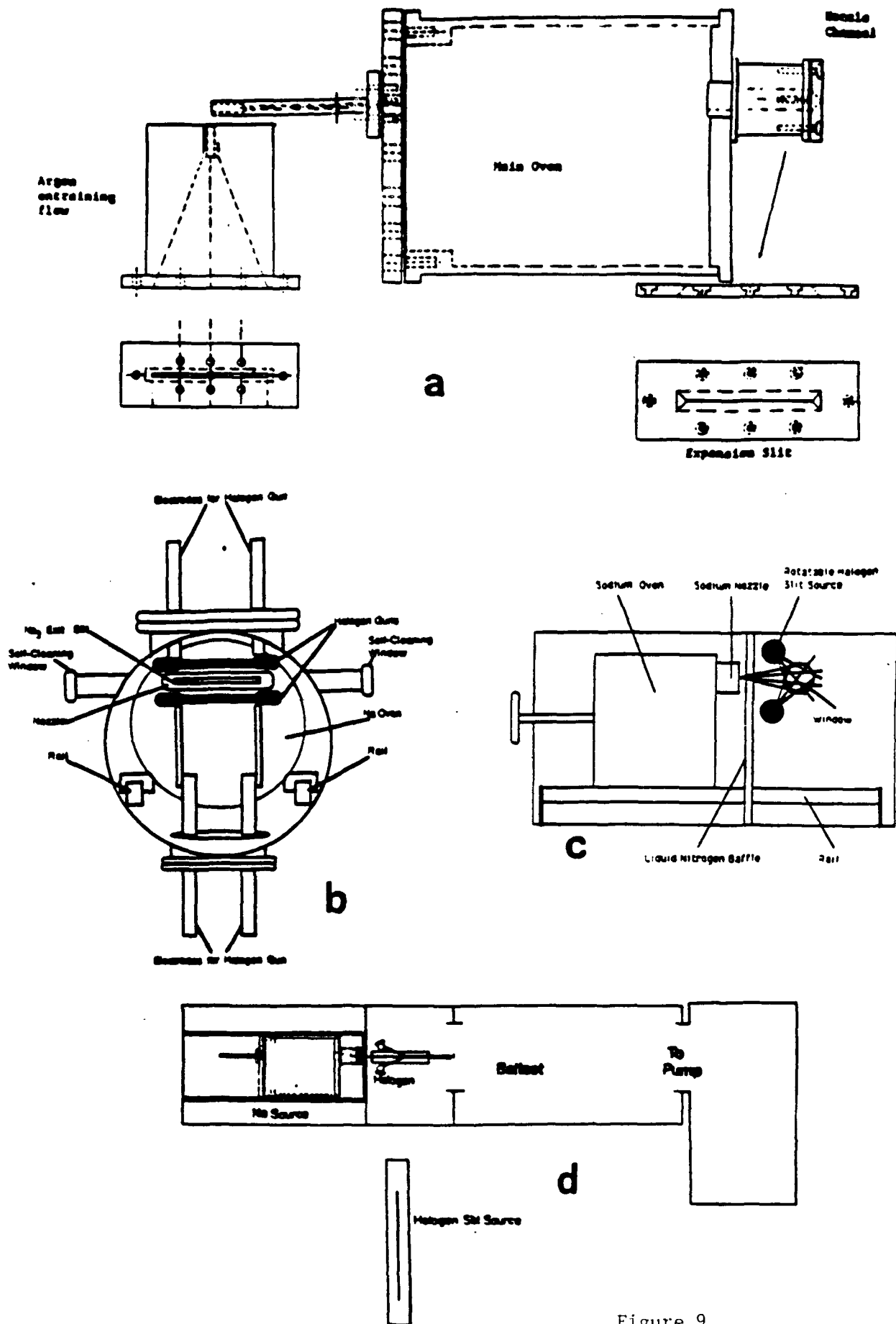
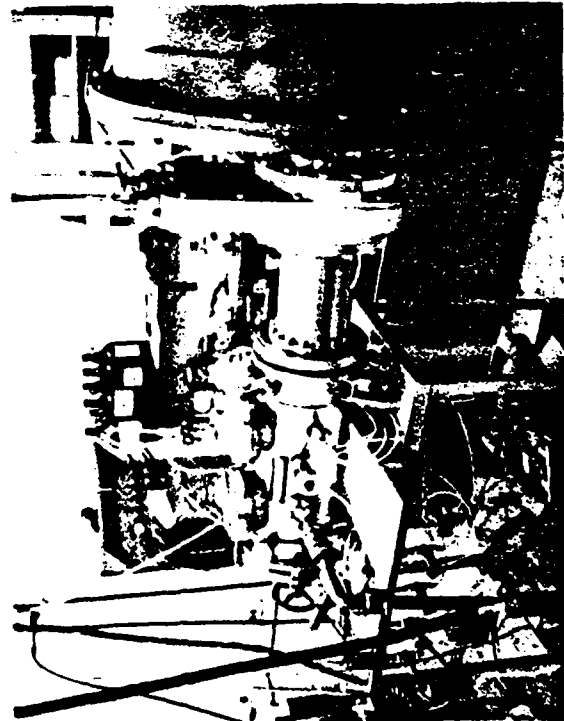
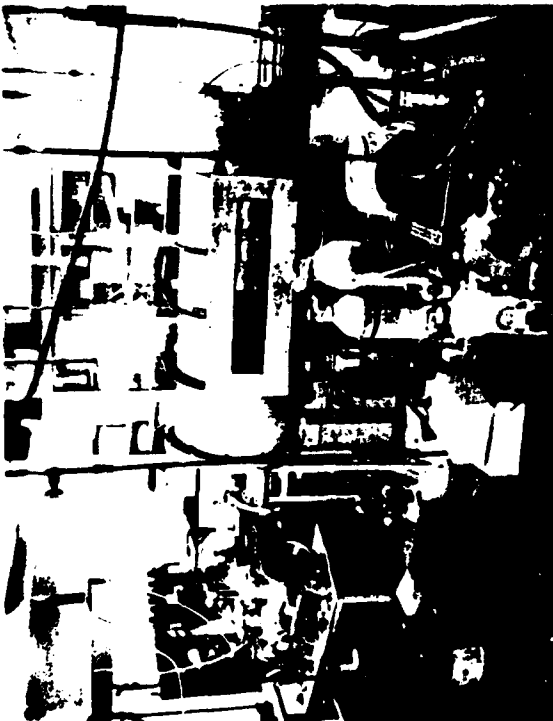
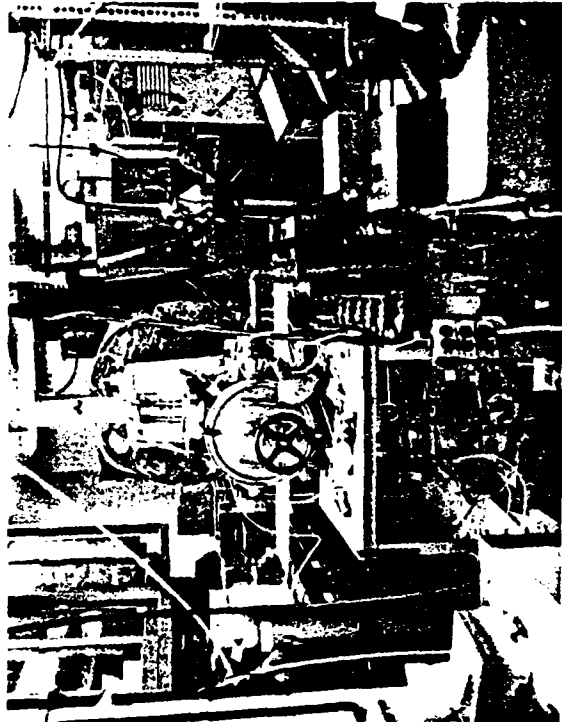
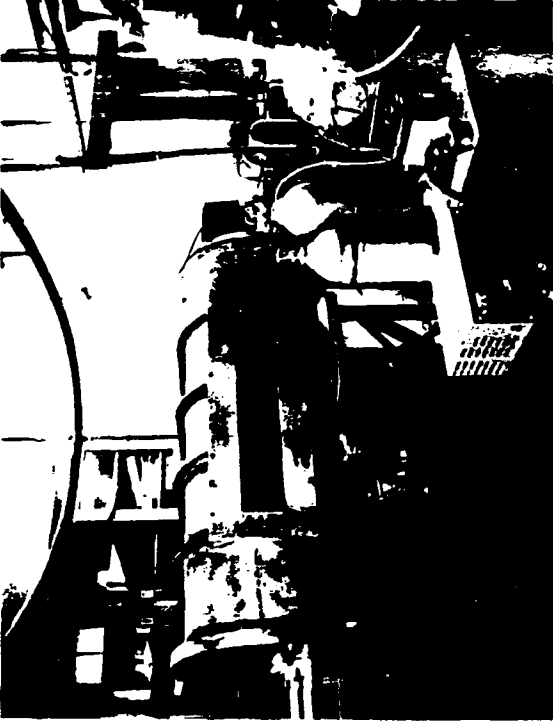


Figure 9

Figure 10



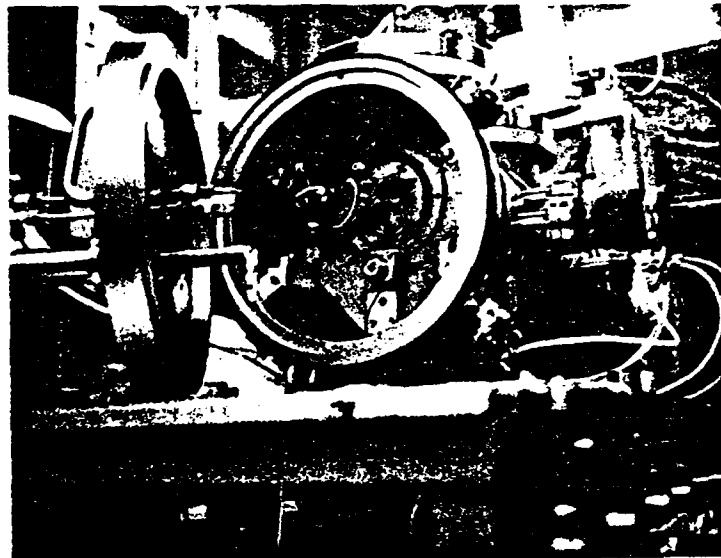
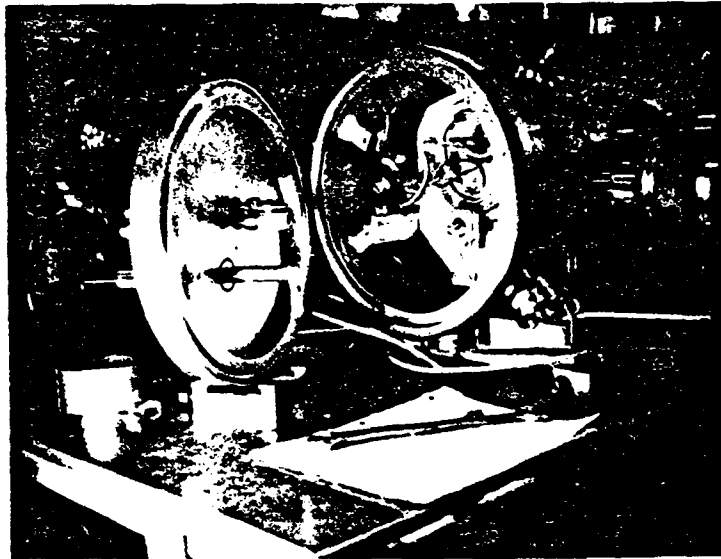
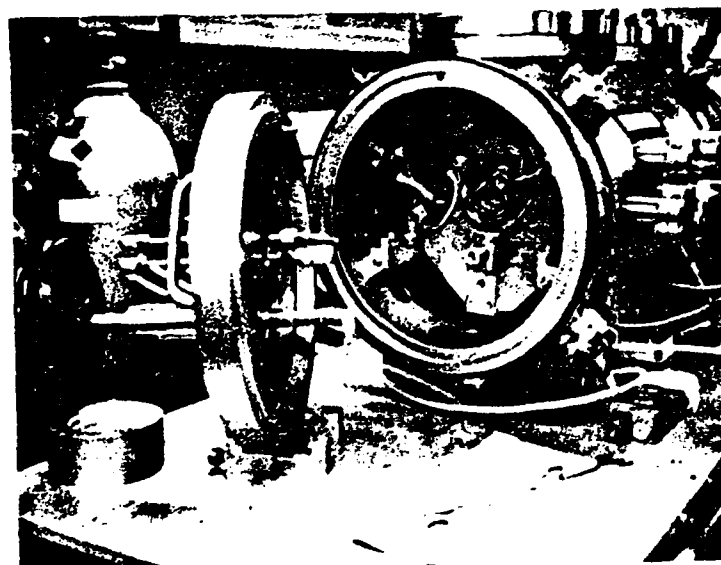


Figure 10



source technology (Appendix D for more detailed discussion).

In a pure sodium supersonic expansion, the Na_3 constituency is dominated by a much larger atom and cold dimer concentration.⁴¹ These constituencies do not absorb at the Na_2 amplifier wavelengths characteristic of the Na_3 -halogen atom reaction systems. However, it is desirable to minimize the atom and dimer while increasing the trimer concentration. The trimer concentration can be altered and improved through an appropriate adjustment of the supersonic expansion conditions shifting the distribution to higher sodium polymers. By seeding the expansion with helium, argon, or other noble gas atoms, several researchers⁴² have demonstrated that the atom and dimer concentrations can be made quite small relative to the much larger sodium polymers.⁴² We do not wish to operate at these extreme expansion conditions but, rather, seek a middle ground which will allow us to produce primarily the trimer and a few larger clusters.⁴³ This condition can be achieved through the appropriate adjustment of parameters which can be manipulated in the expansion including (1) the rear oven stagnation pressure (argon + sodium), (2) the frontal nozzle temperature, and (3) the ratio of the supersonic expansion source pressure to the overall expansion chamber pressure.

The sodium slit source, connected to a liquid nitrogen cooled bulkhead apparent in the figure, is positioned relative to the dual halogen slit sources located above and below what we envision as the position of an alkali sheath created upon expansion from the alkali slit source. The reaction zone cavity configuration is designed to allow for 1) short transit of the reactants Na_3 and $\text{X} = \text{Cl}, \text{Br}, \text{I}$ to the reaction - amplification zone, 2) flexible movement of these sources with respect to each other and with respect to the flow patterns created in the system and 3) minimal interaction of these reactants with laser cavity windows. To insure this minimal interaction, the self-cleaning optical windows noted previously³² are used.

We are in the final stages of testing our extended amplification zone device. We anticipate that the improvements which we have outlined will produce at least a 20 fold improvement in the overall gain. Under these circumstances, the Na_3 -Br reaction should be capable of producing a visible chemical laser oscillator at 527 nm.

Extension of the $\text{Na}_3 - \text{X}(\text{Cl}, \text{Br}, \text{I})$ Amplifier Concept

Although the experimental configuration which we have used to demonstrate amplification from the $\text{Na}_3\text{-Br}$ reaction is not optimal for producing a chemical laser oscillator, it can readily be used to assess the possibility of forming chemical laser amplifiers from the reactions of lithium trimer with halogen atoms and to evaluate the extension of the oxidation process to fluorine atoms. The later experiments, specifically studies of the $\text{Na}_3\text{-F}$ reactive encounters are now underway. We have also constructed a molybdenum based double oven lithium supersonic expansion source which can be used to test the viability of lithium trimer-halogen atom reactions as a means of producing lithium dimer chemical laser amplifiers.

The Na_2 amplifiers which we have characterized in the visible region operate on bound-bound transitions. It is not difficult to envision an extrapolation on the $\text{Na}_3\text{-X}$ reaction concept which involves the alkaline earth metal trimers and the formation of excited state dimers which can undergo bound-free excimer transitions. With this focus, we are attempting to generate the M_2 excimer analogs of the Na_2 laser amplifiers discussed previously. The ground electronic state of Mg_2 is very weakly bound.²⁰ However, detailed calculations suggest the $\text{Mg}_2 - \text{Mg}$ bond strength may be on the order of 0.6 eV,⁴⁴ quite comparable to that of Na_3 . We are now forming magnesium molecules, specifically Mg_2 and Mg_3 , and observing the excited state products of their oxidation with F and Cl atoms. A halogen atom discharge source which we have developed to study the $\text{Bi}_2 + \text{F}$ reaction⁴⁵ is being used to investigate the $\text{Mg}_2\text{-F}$, $\text{Mg}_3\text{-F}$, $\text{Mg}_2\text{-Cl}$, and $\text{Mg}_3\text{-Cl}$ reactions. These studies will soon be extrapolated to the heavier alkaline earths, $\text{Ca}_x - \text{Ba}_x$. To date, we have not observed strong Mg_2 emission from the $\text{Mg}_3 - \text{F}$, Cl reactions, however, surprisingly, preliminary results on this system signal the formation of excited state Mg_xF and Mg_xCl charge transfer complexes where x is most likely two (Appendix G). Although we have not yet demonstrated the potential for forming an Mg_2^* based excimer amplifier laser system, the creation of a long-lived Mg_xF complex suggests that, with some modification, this may be feasible.

LOW-LYING STATES OF BISMUTH FLUORIDE - LASING ON THE BiF A-X TRANSITIONS

In studying the chemiluminescent reaction of helium entrained bismuth vapor and molecular and atomic fluorine over a substantial pressure range (60-333 Pa), we have obtained results, which cast new light on the low-lying states of the BiF molecule. This study of the $\text{Bi}_x + \text{F}_2$ and $\text{Bi}_2 + \text{F}$ reactions has provided evidence for two distinct electronic transitions of BiF in the region 565-740 nm, at least one of which is thought to terminate in the BiF "1" (X_21) state arising from the $3\Sigma^-(\sigma^2 \pi^4 \pi^{*2})$ configuration of BiF. The observed transitions with $\nu_{00} \sim 17631 \text{ cm}^{-1}$ and $\nu_{00} \sim 15244$ or 15784 cm^{-1} exhibit pronounced upper state vibrational relaxation and are characterized, especially at the highest pressures, by a dominance of progressions emanating in $v' = 0$ and terminating in several v'' lower state levels. The higher energy transition with $\nu_{00} \sim 17631 \text{ cm}^{-1}$ is believed to terminate in the recently observed BiF "1" state with $\nu_{00} \sim 6768 \text{ cm}^{-1}$ ($X_21-X_10^+$). The upper state, denoted A', with $T_0 \sim 24400 \text{ cm}^{-1}$ is believed also to be a "1" state based on limited high resolution data for at least two bands of the system. The correlation made here is in close accord with recent quantum chemical calculations which suggest that the "1" state lies $\sim 7200 \text{ cm}^{-1}$ above $v'' = 0$, XO^+ .⁴⁶ The levels of the A' upper state appear to correlate precisely with several BO^+ perturber state levels. This perturber state, thought to lie less than 2000 cm^{-1} above the $AO^+(\text{II})$ state appears to play an important role with respect to energy disposal among the excited states of the BiF molecule. The second transition with $\nu_{00} \sim 15244$ or 15784 cm^{-1} also appears to terminate in the "1" state suggesting a second upper state, denoted A'', lying at $22552 \pm 545 \text{ cm}^{-1}$ virtually isoergic with $AO^+(\text{II})$. Alternatively, the second transition might emanate from the $v' = 0$ upper state level at $T_0 \sim 24400 \text{ cm}^{-1}$ terminating in a lower state with $T_0 \sim 8615 \text{ cm}^{-1}$. In order to establish the dissociation energy of the BiF molecule and to determine whether this controversial bond is closer to 3^{47} or 5 eV ,⁴⁸ both the $(\text{Bi}, \text{Bi}_2) + \text{F}_2$ and $(\text{Bi}, \text{Bi}_2) + \text{F}$ reactive systems have been studied. Combined results based on the observation of the chemiluminescent $\text{Bi}_x + \text{F}_2$ and $\text{Bi}_2 + \text{F}$ reactive encounters producing BiF $AO^+(\text{II}) - XO^+$ and $BO^+ - XO^+$ emission features suggest that the BiF bond energy is close to 4 eV . These revised assignments and the discovery of two longer-lived (A' and A'') excited electronic states ($\tau = 60 \mu\text{second}$) very close in energy to the BiF A state ($\tau \sim 5 \mu\text{seconds}$), have now

been confirmed by E. H. Fink et al. (Wuppertal, Germany) using high resolution Fourier Transform spectroscopy.

The two newly discovered states would appear to play a key role in the recent observations by Wally Warren and coworkers (Pacific Applied Research) of potential lasing action in BiF. In collaboration with the Pacific Applied Research staff and with the help of data generated by E. H. Fink and coworkers, we are attempting to analyze the cavity output vs. chemiluminescent emission depicted in Figure 11. The features labeled in the full cavity configuration, which are not readily explained in terms of the lowest vibrational levels of the BiF A state, may result from the population of the longer-lived low-lying A' state, the collision induced vibronic relaxation of this state and the subsequent or simultaneous collision induced near energy resonant intramolecular energy transfer from the $v = 0,1,2$ levels of this state to the $v' = 4,5,6$ levels of the A state. The analysis of this possible mechanism and of the role which the newly assessed electronic states play in the chemistry of excited state BiF formation continues in our laboratory.

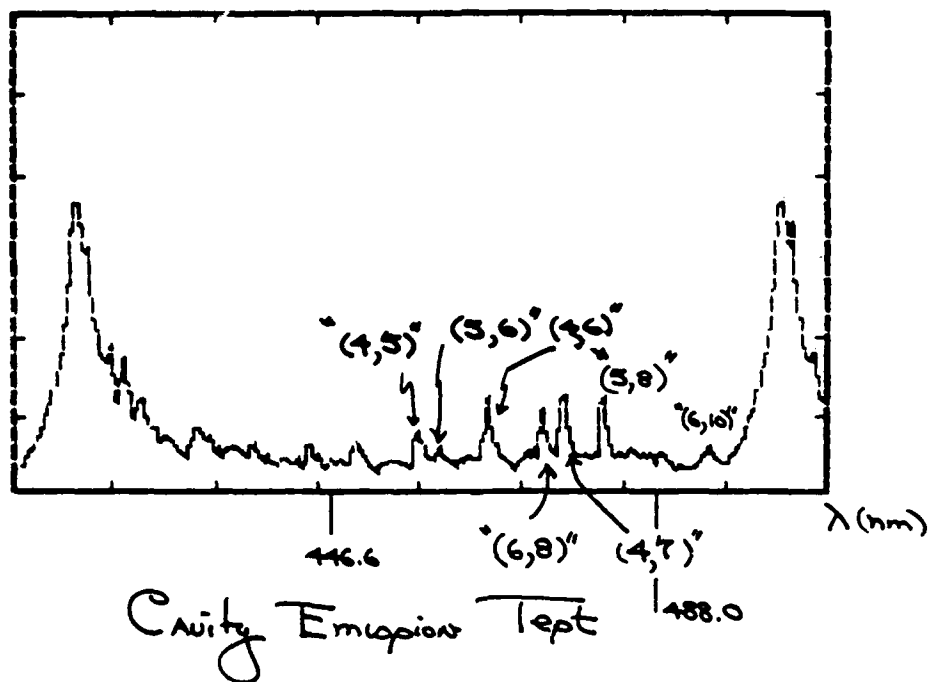
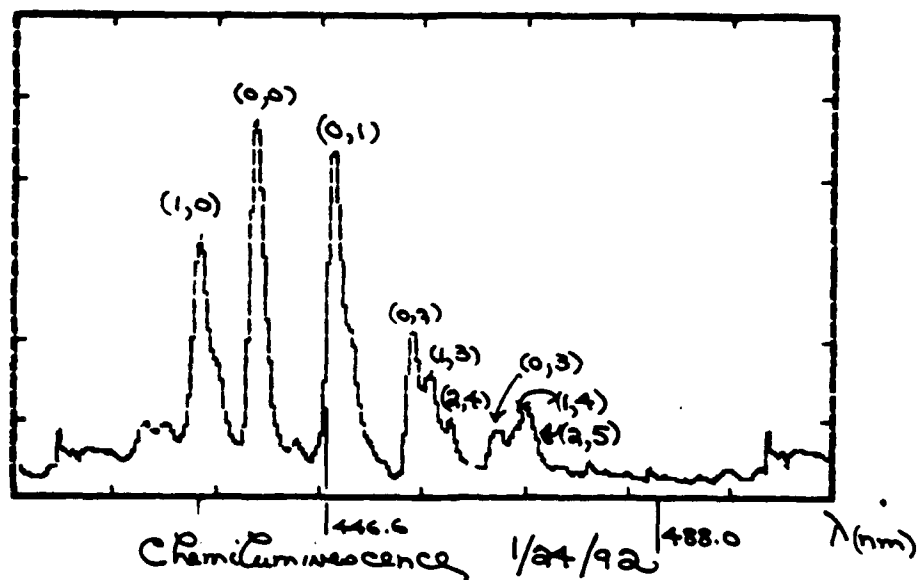


Figure 8 11

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"A Chemically Driven Visible Laser Transition Using Fast Near-Resonant Energy Transfer to Group IIIA Metals", with J. R. Woodward, S. H. Cobb, and K. K. Shen, invited paper in Special Issue of the IEEE Journal of Quantum Electronics on Electronic Transition Gas Lasers, JQE 26, 1574 (1990).

"Chemically Driven Pulsed and Continuous Visible Laser Amplifiers and Oscillators", with K. K. Shen, J. R. Woodward, S. H. Cobb, and J. R. Doughty, Proceedings of the Eighth International Symposium on Gas Flow and Chemical Lasers, SPIE, Volume 1397 (1991) pg. 125.

"On the BiF Bond Dissociation Energy and the Evaluation of the BiF Red Emission Band Systems", with T. C. Devore, L. Brock, R. Kahlscheuer and K. Dulaney, Chemical Physics 155, 423 (1991).

"The Unique Dynamics of Metal Cluster Oxidation and Complexation", to appear in Advances in Metal and Semiconductor Clusters, Vol. I, Spectroscopy and Dynamics, ed. M. A. Duncan, JAI Press.

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"The Unique Nature of Metal Cluster Oxidation", J. L. Gole, in Physics and Chemistry of Finite Systems: From Clusters to Crystals, Volume II, Edited by P. Jena, S. N. Khanna, and B. K. Rao, NATO ASI Series, Vol. II, pg. 1025 (1992).

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"Evidence for Continuous Visible Chemical Lasing from the Fast Near Resonant Energy Transfer Pumping of Atomic Sodium", with K. K. Shen and H. Wang, JQE, in press.

"Electronically Excited Charge Transfer Complex Formation in Magnesium Molecule - Halogen Atom Reactions", with T. C. Devore, R. Kahlscheuer, and D. A. Dixon.

"The Chemistry of Group IIA Halide Formation From Alkaline Earth Atom - Halogen Molecule Interactions", with H. Wang and J. Towson, in preparation.

"A Chemiluminescent and Laser Induced Fluorescent Probe of New Low-Lying Electronic States in the Silver Halides", with H. Wang.

Invited Talks (International Meetings) Given on ARO Sponsored Research

Fifth International Laser Science Conference, Stanford University (1989) - Invited Talk - "Chemically Driven Pulsed and Continuous Laser Amplifiers and Oscillators".

Eighth International Symposium on Gas Flow and Chemical Lasers, Madrid, Spain (1990) - Invited Talk - "Chemically Driven Pulsed and Continuous Visible Laser Amplifiers and Oscillators".

Southeastern Section APS Meeting - Atlanta, Georgia (1990) "Chemically Driven Laser Amplifiers Using Fast Near Resonant Energy Transfer".

Laser M2P, Second International Conference, Grenoble, France (1991) - Invited Talk - "Chemically Driven Pulsed and Continuous Visible Laser Amplifiers and Oscillators".

202nd A.C.S. Meeting and American Chemical Congress, New York, N.Y. (1991), Symposium on Gas Phase Metal Reactions - Invited Talk - "The Unique Complexation and Oxidation of Metal Based Clusters".

Seventh Interdisciplinary Laser Science Conference, Monterey, California (1991) - Invited Plenary Lecture - "Chemically Driven Pulsed and Continuous Visible Laser Amplifiers and Oscillators".

International Symposium on the Physics and Chemistry of Finite Systems: From Clusters to Crystals, Richmond, Virginia (1991) - Invited Talk - "The Unique Complexation and Oxidation of Metal Based Clusters".

Lasers and Electro-Optics Society, Annual Meeting, San Jose, California (1991) - Invited Talk - "Chemically Driven Pulsed and Continuous Visible Laser Amplifiers and Oscillators".

XXth Informal Conference on Photochemistry, Atlanta, Georgia, "Chemically Driven Pulsed and Continuous Visible Laser Amplifiers and Oscillators".

23rd AIAA Plasma Dynamics and Lasers Conference, Nashville, Tennessee, "Chemically Driven Pulsed and Continuous Visible Laser Amplifiers and Oscillators", invited keynote talk in session on Short Wavelength Chemical Lasers.

Additional Invited Talks

East Coast Symposium on the Chemistry and Physics of Clusters and Cluster Ions, Johns Hopkins University - Invited Talk - "Formation and Unusual Oxidation of Small Clusters".

Department of Chemistry, University of Georgia - Invited Talk - Department Colloquium, "Chemically Driven Visible Laser Systems".

Department of Chemistry, Penn State University - Invited Talk - "Development of Chemically Driven Visible Laser Systems".

Phillips Laboratory, Kirkland Air Force Base - Invited Talk - "Development of Chemically Driven Visible Laser Systems".

Department of Physics, Virginia Commonwealth University, Workshop on Metal Clusters and Their Reactions - Invited Talk - "The Unique Aspects of Metal Cluster Oxidation".

Scientific Personnel Supported by this Project (Degrees Awarded)

James L. Gole (Principal Investigator).

K. K. Shen (Pulsed and continuous energy transfer systems, cavity construction, laser amplifier and oscillator based on energy transfer from SiO to Na). Ph.D. anticipated, March-June, 1993.

D. Grantier (Cavity construction for Na₃-X amplifier system, development of Na₃-F chemiluminescent probe studies).

He Wang, Postdoctoral (partial-assistance in cavity construction and modification, development of high resolution laser gain experiments and laser probes of chemical laser reaction products, extrapolation of Na₃-X reaction schemes, extrapolation of SiO-Na energy transfer scheme to SiO-Pb, SiO-Cu, and SiO-Sn systems).

C. B. Winstead (partial assistance in experiments and cavity construction).

R. Kahlscheuer - Master of Science in Physics awarded (formulated expts. to study alkaline earth trimer - halogen atoms rxns (Mg₃-F...), assisted in cavity construction and source development).

T. C. Devore (analysis of Mg_x-F, Bi_x-F, F₂, reactive systems).

D. A. Dixon (quantum chemistry on Mg_x-F reactive system).

E. J. Mansky (formulation of theories to explain selectivity in Na₃-X reactions).

John Bray (assistance in cavity construction, study of copper molecule - halogen atom extrapolations on alkali (Na) metal system - NSF REU program).

Jason Pugh (assistance in cavity construction - NSF REU program).

Alan Kauppi and Douglas Dawson (undergraduate assistants to K. K. Shen and He Wang).