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FINAL REPORT

RESEARCH AND INVESTIGATION OF GAS DYNAMIC LASERS CASE FILE

L. R. Boedeker and B. R. Bronfin

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EAST HARTFORD, CONNECTICUT 06108

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

November 10, 1971

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ABSTRACT

Chemical mixing laser investigations have been conducted 1) to investigate the properties of a bimolecular exchange laser system pumped by the H + $Cl_2 \rightarrow HCl(v)$ + Cl reaction, initiated by arc dissociated H_2 , with lasing occurring between $\lambda = 3.4$ and $4.0\,\mu$ m, and 2) to establish the feasibility of an atom recombination-transfer laser employing recombination of arc dissociated nitrogen with subsequent transfer of vibrational energy to CO₂ for lasing at 10.6 μ m. Laser power levels with HCl have been low, ~ 0.2 w on v = 1 $\rightarrow 0$, P = 3,4,5, transitions only. One-dimensional analytical results indicate substantially higher results should be obtained with up to $v = 3 \rightarrow 2$ transitions participating. Diagnostic and analytical results have shown that the reaction mechanism during mixing, a back reaction of HCl(v) with H atoms, reaction of Cl with $H_{2}(v)$, moderately fast V-V, V-T processes, and possible HCl(o) initial contaminant level, are among the key features which may explain the present low level of performance. Atom recombination-transfer experiments have employed quenching of arc dissociated $N_{
m P}$ in a plenum wherein transit of recombined ${
m N}_{
m P}$ is fast relative to ${
m N}_{
m P}$ vibrational decay at the quenched temperature. Prior N_2 -CO₂ thermal mixing laser studies have been extended to measure the efficiency of transfer of recombination energy in such a nonequilibrium N₂ source to $10.6\,\mu$ m optical energy. Maximum laser power at $10.6\,\mu$ m of 30 watts was obtained with a 6 kw high enthalpy, highly dissociated N2 arc which corresponds to a recombination energy to laser power conversion efficiency of about 1%. The rather low level of this efficiency, assuming that vibrational energy storage upon recombination is high, suggests that V-T decay processes, very fast at arc temperatures of $\sim 7000^{\circ}$ K, may be preventing vibrational energy freezing until much lower temperatures are achieved and that trapping of energy in long-lived electronic excitation of N_2 may be a factor.

FOREWORD

The work reported herein was performed by the United Aircraft Research Laboratories (UARL) for the National Aeronautics and Space Adminstration under contract NASW-2181 initiated February 10, 1971. This report, which comprises the final report prepared under contract NASW-2181, contains research results obtained during the period from February 10, 1971, to October 10, 1971.

Included among those who cooperated in the performance of the work under Contract NASW-2181 were Dr. Barry R. Bronfin, Project Supervisor; Dr. Laurence R. Boedeker, Principal Investigator; Dr. John A. Shirley and Mr. Robert J. Hall of the UARL Technical Staff and Dr. Wayne G. Burwell, Chief, Kinetics and Thermal Sciences Section of UARL.

This work was conducted under the program management of NASA Headquarters, and the Technical Monitor was Dr. Harry Harrison.

This document is unclassified in its entirety.

Research and Investigation of Gas Dynamic Lasers

SUMMARY AND RECOMMENDATIONS

In order to extend laser power and efficiency levels established with thermal excitation in prior studies, chemical mixing laser investigations have been conducted to investigate the properties of a system pumped by a suitable bimolecular exchange reaction and to investigate the feasibility of an atom recombinationtransfer laser.

After consideration of a range of bimolecular chemical laser systems the $H + Cl_2 \longrightarrow HCl(v) + Cl$ reaction pumped system was selected for investigation. This reaction is highly exothermic and is known to yield efficient vibrational excitation of HCl product molecules. In addition, this HCl system possesses attractive features when compared to others, particularly the well established HF system, e.g., low toxicity, long vibrational lifetime and favorable atmospheric transmission without expensive isotopic substitution to D_2 . Moreover, cw operation of such an HCl laser initiated by thermal dissociation of H_2 in a pure hydrogen arc had just been demonstrated at UARL, a previously unpublished result.

Hydrogen atoms produced in the arc are sustained by fast transit through a plenum at $p_0 \sim 2$ atm in which translational temperature is quenched by Ar dilution. The H atom flow is expanded smoothly through a 2D nozzle. Chlorine and diluents are injected in small amounts into the supersonic flow through a row of perpendicular sonic orifices. The reacted flow proceeds through a transverse laser cavity region at a pressure $p \sim 0.013$ atm.

Laser power levels to date are small; power coupled through apertures or uniformly transmissive optics of ~1 mw and laser power detected as heating of thermally isolated mirrors of ~0.2 w have been measured. Spectral analyses have shown that only $v = 1 \rightarrow v = 0$ transitions have been excited on P = 3,4,5. By varying the transmissivity of the coupling mirror and noting extinction, an average gain coefficient between 0.2 and 0.5 m⁻¹ was indicated. Optimum values of H₂, Ar and Cl₂ flow rates have been observed. Translational pressures have been high due to Cl₂ injection and a relatively slow expansion rate after injection. Various other diagnostic tests including impact pressure, H atom titration with NO, and HCl concentration measurements were investigated. Some qualitative results have been obtained to date. Reduction in Mach No. due to chemical reaction and an increasing H atom concentration with increasing H₂ flow have been observed. In particular formation of HCl was observed with an on-line mass spectrometer due to reaction of Cl₂ with contaminants, probably oil vapor and H₂O on the sample probe

line walls. Further tests, beyond the scope of the present program, are needed to verify that similar reaction of Cl_2 in the injector feed line does not occur which would introduce ground state HCl into the laser cavity.

Predictions of HCl concentration and gain on HCl P branch vibration-rotation transitions have been made with a Corporate-owned computer model which treats reaction, molecular energy transfer, stimulated emission and coupled gas dynamics on a one-dimensional instantaneous mixing basis. The model includes the H + Cl₂ reaction and a fast back reaction of vibrationally excited HCl with H to produce H₂ and Cl. Reaction of Cl with ground state H₂ is slow. The reaction of Cl atoms with vibrationally excited HCl, is moderately fast but has not been included in the analysis as yet. Estimates of the rate of this Cl, H₂(v) reaction have been made which show it likely to be a factor in the experiment and subsequent analysis should take it into account.

Gain calculations for 1% H atom concentration, a likely but uncertain value, indicate maximum gain $g_0 = 1-10 \text{ m}^{-1}$ on v = 3 - 2, 2 - 1, 1 - 0. These gain calculations show gain level to be dependent on reaction stoichiometry and show that v = 3 - 2 and v = 2 - 1 transitions tend to exhibit nonuniform gain profiles across the laser cavity due to V-V, V-T processes while v = 1 - 0 gain is relatively uniform. These factors, plus uncertain H concentration could contribute to observed laser results. Gain calculations showed that ground state HCl in the laser cavity at 0.003 mole fraction would reduce gain below threshold on v = 1 - v = 0 transitions and would not affect v = 3 - 2, and 2 - 1 level gains significantly. Hence such contamination is less than this value or else production of HCl(1) by Cl, H₂(v) reaction diagnostics would be useful. Laser power results show at present that 10 - 100 w of power should be available from the present configuration for $X_H = 0.01$, again if Cl, H₂(v) interaction is not important.

In order to assess the validity of one dimensional theory various characteristic times have been calculated and compared. Consideration of primary $H + Cl_2$ reaction time and mixing time shows that mixing is slow relative to this reaction. However mixing is fast relative to V-V, V-T times. Hence, a two-dimensional model of reaction chemistry would be desirable particularly since a fast reaction of vibrationally excited HCl with H must be considered. However, a one-dimensional instantaneous mixing model of V-V, V-T processes should continue to be valid for long enough optical cavities.

Further investigation of the HCl chemical laser system appears warranted in view of the attractiveness of the system and the potential for improvement of present results indicated by the present experimental and analytical results. Such investigation would include two-dimensional chemical reaction analyses with frozen molecular kinetics to identify favorable mixing geometries for net production of

2 .

vibrationally excited HCl from the H + Cl_2 reaction, and exploration of lasing with more optimum mixing and faster expansion after reaction and somewhat shorter transit times through an optical cavity to reduce Cl, $H_2(V)$ interaction and overcome effects of V-V, V-T processes on gain uniformity for $v = 3 \rightarrow 2$ and $v = 2 \rightarrow 1$ transitions.

In order to perform the first feasibility study of an infrared laser system pumped by the energy release in an atom recombination reaction, experiments have been conducted in which the effluent of a nitrogen arc, containing high concentration of N atoms, is quenched by N2 + Ar dilution in a plenum to a temperature $T \sim 1200^{\circ}$ K where N₂ vibrational energy decay is low during completion of transit through the plenum. Subsequent mixing of CO2 and diluents followed by expansion to supersonic conditions favorable for lasing in a transverse optical cavity has resulted in extraction of $10.6 \,\mu$ m laser power on CO₂ vibration-vibration transitions, $P_{T_1} = 15$ watts when quenching time is about equal to transit time in the plenum. Faster quenching achieved by addition of diluent through an annular slot surrounding the d = 0.003 m arc column exhaust has yielded P_I, up to 30 watts. Corresponding electrical to 10.6 μ optical conversion efficiencies of $\eta_{\rm T} \sim 0.2$ and 0.45% were measured for these cases and upper limits to recombination energy-optical conversion efficiency $\eta_{\rm C}$ would be about 0.4 and 1% respectively. Assuming that population of vibrational levels is significant and the fraction of energy trapped in electronic metastable levels is low, rapid decay of vibrational energy in N_2 which occurs at high arc temperatures may be responsible for these rather low overall efficiencies, quenching being not sufficiently rapid to freeze the vibrational energy at a high level upon attainment of the 1200°K level.

Other experiments have been conducted at high arc flows and low arc enthalpy where N atom concentration is low and the fraction of arc power appearing in dissociated species is lower. Quenching of such flows to low temperature generally resulted in somewhat higher laser power and efficiencies although interpretation in terms of a recombination efficiency is not possible. Maximum laser power of about $P_L = 44$ watts and overall electrical-optical conversion efficiency $\eta_L = 0.8\%$ were obtained. Experiments with a long residence time plenum have been conducted but cannot be interpreted at present since the desired low quenched temperatures at which vibrational energy would decay within the plenum, were not attained.

Modeling studies of the recombination process would appear warranted in order to identify more optimum quenching processes. In addition, consideration should be given to aerodynamic freezing of N atoms followed by recombination and CO_2 transfer in the immediate vicinity of the laser cavity.

INTRODUCTION - CHEMICAL LASERS

Investigations that were conducted by the United Aircraft Research Laboratories (UARL) under Contract NASw-1780 sustained preliminary conclusions that gas dynamic mixing is an efficient approach to the generation of vibrational population inversion in CO2. The results of experimental tests and analytical calculations indicate that thermal excitation, as applied in the gas dynamic mixing laser (GDML), limits overall laser efficiency to a practical range of 1 to 3%, (Refs. 1 and 2). These results further suggest the applicability of the GDML to generate laser power from a purely thermal source at these efficiency levels. However, the consideration of some recent work at UARL and other research laboratories (Refs. 3 to 8), identifies another class of high-efficiency mixing laser -- the chemical mixing laser -- which is particularly adaptable to operation in the GDML configuration. In the chemical mixing laser the selectivity of a chemical reaction in preferentially populating high-lying vibrational energy states in the reaction product molecules can be utilized to achieve order-of-magnitude increases in the power and efficiency levels established with thermal excitation. With this motivation, the development of efficient cw chemical lasers has been accelerating dramatically during the past 12 months. It is in consequence of these developments that the present research program was formulated to extend the previously evolved gas dynamic mixing laser technology to investigate the chemical mixing laser.

BACKGROUND INFORMATION ON CHEMICALLY-PUMPED POPULATION INVERSION

Population Inversion Via Bimolecular Exchange Reactions

The comprehensive basic research background of Polanyi and his students at the University of Toronto (Refs. 9 and 10), have well-established a class of bimolecular exchange reactions in which a major fraction of reaction exothermicity appears as vibrational excitation in the newly-formed molecular species. Suitable reaction systems exhibiting this nonequilibrium effect might be typified by:

$$F + H_2 \longrightarrow HF^* + H \quad \Delta H = 31.5 \text{ Kcal/g-mol} (1.4 \text{ ev})$$
 (1)

in this hydrogen halide formation reaction, and in many of its homologs, more than half of the chemical reaction energy is converted initially into vibrational excitation of the diatomic product, with the balance of the energy distributed among translational and rotational energy of the product species.

Additional experimental measurements of Polanyi and Tardy, at the University of Toronto (Ref. 11), Parker and Pimmentel, at the University of California, Berkeley, (Ref. 12), and theoretical calculations of Anderson, at Yale University (Ref. 13), have established that the distribution of vibrational state populations resulting from Reaction (1) is strongly inverted. A consideration of the energetics of the reaction (see Fig. 1) indicates the likelihood of preferentially populating the HF (v=2) level, which has been verified in the referenced experimental studies.

The development of the population inversion, via the bimolecular exchange reaction, can be exploited to pump a high-power, high-efficiency cw laser. The recent experiments of Spencer, et al., at the Aerospace Corporation (Refs. 7 and 8), and several research groups at UARL (Refs. 3 to 5) have demonstrated cw laser emission from HF formed via Reaction (1) in high-speed flow systems. A characteristic of the laser emission spectra common to these experiments is the observation of a stimulated radiative cascade among vibrational-rotational levels

> v = 2 - v = 1 $\lambda = 2.7 - 3.1 \mu m$ v = 1 - v = 0 $\lambda = 2.6 - 2.9 \mu m$

The rather remarkable appearance of laser transitions to the ground vibrational state validates the initial population distribution measurements of Polanyi (Ref. 11), indicating that negligible populations of HF (v=0) are generated directly by the bimolecular exchange reaction. Since consideration can be given to laser transitions cascading to the ground state, operation approaching 100% quantum efficiency can be envisioned; (cf. 41% quantum efficiency in the well-known CO_2 001 - 100 laser transition).

A first-order estimate of the available laser power via Reaction (1) can be made by coupling population distribution measurements and reaction exothermicity, ~31.5 Kcal/g-mol. This leads to an estimate of laser power at ~1 MJ/lb_m of reactant. This same calculation suggests chemical-to-optical conversion efficiencies >20%. The demonstration of such laser power and efficiency levels recently has been approached with the HF system (Ref. 8), however, the attainment of laser performance near the attractive theoretical limits discussed above for bimolecular systems as a class has not been approached. Such a development would establish the value of chemical lasers for many applications. However, these previous experimental studies (Refs. 3 to 8) generally have not been directed toward an investigation of the complex interactions between the chemical kinetics, laser physics, and fluid dynamics, inherent to the chemical laser. The performance of such a study of the relevant physiochemical mechanisms and their interplay from which the fundamental limits of laser power and efficiency in these devices may be inferred has been initiated with the program reported on here.

Analytical Modeling of the Bimolecular Chemical Laser

Analytical models of cw flowing mixing lasers have been developed previously at UARL to support and guide various United Aircraft Corporation projects in gas dynamic lasers, including that sponsored by NASA under Contract NASw-1780 (Ref. 2). A new one-dimensional analytical model descriptive of cw flowing mixing lasers in which the population inversion is pumped by chemical reactions has been completed (Ref. 1⁴). The insight and understanding afforded by such an analytical model, using which experiments can be performed "on the computer", provides considerable value to parallel systematic experimental studies. As in previous investigations, progress in the present experimental studies has been significantly enhanced through the utilization of this comprehensive computer modeling. Preliminary analyses using the model already have predicted many of the salient characteristics of the laser emission observed in early HF chemical laser experiments. The fully-coupled, internally-consistent modeling of cw chemical lasers which is being pursued at UARL appears to be a significant, unique contribution to the chemical laser field.

Population Inversion Via Atom Recombination

In addition to bimolecular exchange reactions, a separate class of reactions involving recombination of dissociated molecules is known to result in population of electronic and high-vibrational levels of the product-recombined-molecule (Ref. 15). Direct production of electronic or vibrational inversions may be possible since recombination generally proceeds stepwise from initial excited levels near the dissociation energy (Refs. 16 and 17), however, few studies or applications of recombination for initiation of laser activity have been reported. Recombination energies are high enough that the potential may exist for efficient laser activity at new wavelengths in the visible or as short as the uv.

Recombination - Transfer

In a number of tests performed at UARL under prior NASA support (Ref. 2), high thermal-to-optical conversion efficiencies were measured under conditions wherein complete relaxation of the arc-heated nitrogen in a plenum may not have been achieved. Since temperatures existing at the core (centerline) of the nitrogen plasma jet exceed 6000° K (Ref. 18), high concentrations of N-atoms predominate in portions of the plasma effluent, (see Fig. 2) while highly vibrationally and electronically excited N₂ molecules and some atomic nitrogen ions form the balance of the effluent. In these preliminary tests, conditions in the plenum chamber into which the N-atom containing plasma jet issues were adjusted so that a large volume of cold N₂ was intermixed with the plasma jet. The added N₂ gas stream provided both third bodies for the atom recombination

$$N + N + M \longrightarrow N_{2} (v') + M$$

$$\Delta H = 221 \text{ Kcal/g-mol}$$

(2)

and calorimetric reduction in the gas translational temperature (quenching). Normally transit time in the plenum was long enough that an equilibrium distribution of states at the quenched translational temperature would be expected (Ref. 19). The rapid passage of the gas mixture through an aerodynamic nozzle then effected a freezing of the excited vibrational distribution in the N_2 stream. At the low translational temperature (<1200^oK) maintained in the plenum by the added N_2 cooling in the above preliminary tests, however, vibrational relaxation proceeds much more slowly (Ref. 19) than at standard GDML plenum temperatures (>2000^oK). The combination of these nonequilibrium effects resulted in the preferential pumping of the CO_2 upper laser level via

$$N_{2}(v') + CO_{2}(000) \longrightarrow CO_{2}(001) + N_{2}(v'-1)$$
(3)

$$A E \sim 0$$

and the generation of laser power levels in these tests which were significantly greater than would be expected via pumping from a N_2 source in thermal equilibrium, (see Fig. 3). Recombination of N is thought to proceed stepwise from initial excited levels near the dissociation energy (Ref. 16). In the energetic nitrogen recombination reaction electronic and high-lying vibrational levels are populated (Ref. 15). Some electronic levels are short lived; one electronic level is metastable with an apparent long collisional lifetime (Ref. 17) which complicates understanding of the energy decay route in the present investigation. Vibrational quanta survive for a relatively long time except at arc temperatures of ~7000^oK (Ref. 19). A large fraction of the recombination exothermicity likely may appear as vibrational excitation; however, no quantitative measurements of this effect have been reported. This very large heat of reaction, 221 Kcal/g-mol at N₂ formation (to be compared with 32 Kcal/g-mol at HF formation) suggests that a chemical laser pumped by N-atom recombination could provide even higher specific power than available in the attractive hydrogen-halide systems.

This unique concept, identified as the atom recombination laser (ARL), Fig. 4, is essentially a chemical laser pumped by the N-atom recombination energy which appears preferentially in vibration modes of the newly-formed N_2 molecule. Since vibrationally-excited N_2 exhibits no dipole moment, attempts to first establish laser activity directly on single-quantum radiative transitions among vibrational states in pure N_2 would appear fruitless. However, the efficient pumping of CO_2 , and similar triatomic molecules, via near-resonant transfer of vibrational quanta from N_2 is well established (Ref. 20). This suggests that the intermixing of CO_2 with newly formed N_2 molecules readily could establish a population inversion in CO_2 , leading to laser emission, as was accomplished in the early GDML studies (Ref. 2). However, the selectivity of the recombination reaction in populating vibrational quanta in N_2 could yield an order-of-magnitude or more increase in specific laser power beyond that which would be obtainable through production of N_2 vibrational quanta by thermal heating, as was accomplished in early GDML studies.

A variety of sources would exist for the free atom production which establishes the excitation in the atom recombination laser: high-temperature molecular dissociation via electric arc-heating, shock-heating, conventional furnace or other thermal source; chemical reaction; catalytic decomposition; low-pressure, nonequilibrium glow or pulsed discharges; and others. Because of its accessibility and convenience, the arc-heating route available in the GDML apparatus has been employed in preliminary tests reported here.

These ARL studies have been performed using the existing apparatus with only minor modifications to the plenum chamber and expansion nozzle both to allow operation at temperatures well above the dissociation limit and to attempt effective freezing of the vibrational relaxation kinetics. A visualization of the proposed modifications in the GDML geometry is shown in Fig. 4. Since the two stages inherent in the ARL -- molecular dissociation and recombination pumping -- must be separated to avoid destruction of the laser species, this species is mixed into the recombination zone downstream of the arc dissociation region. Hence, a practical embodiment of the flowing gas ARL becomes an extension of the GDML.

These initial studies of the ARL employed the modified apparatus to examine the nitrogen recombination reaction leading to the pumping of the $10.6 \,\mu$ m laser transition in CO_2 . Other recombination reactions (e.g., $0 + 0 + M - O_2 + M$, $N + 0 + M - NO^* + M$) and other laser species (e.g., N_2O , COS, HCl) can be considered; however, the large body of data relative to the CO_2 - N_2 laser system, combined with encouraging initial experimental measurements, suggested that the study of other systems be placed beyond the scope of the current investigation.

DESCRIPTION OF EXPERIMENTAL PROGRAM

Based on the foregoing it is evident that the chemical mixing laser affords a unique mechanism for preferentially populating high lying vibrational energy states in selected molecular species and generating, by means of stimulated emission, power and efficiency levels which are at least one order of magnitude greater than those achievable with thermal excitation. In broad perspective, two classifications of chemical lasers have been identified: those pumped by bimolecular exchange reactions, and those pumped by atom recombination reactions. Whereas the feasibility of the former class of chemical lasers has been demonstrated, that of the latter has not. Therefore, research on chemical lasers pumped by bimolecular exchange reactions appears to offer the greatest return at this time. In consequence of this, primary emphasis within this study has been placed on the bimolecular reaction research. This research is discussed below (Task I). Preliminary research on atom-recombination chemical lasers is also discussed below (Task II).

Bimolecular Exchange

A research program (Task I) has been conducted under the subject NASA contract to investigate the characteristics of a cw flowing chemical laser pumped by a suitable gas-phase bimolecular exchange reaction. This program is an extension of prior experimental investigations under NASA support (Ref. 2), redirected toward an understanding of the following mechanisms and their interactions which are responsible for the development of laser emission in flowing gas chemical mixing lasers:

- (1) chemical reaction kinetics,
- (2) distribution of reaction energy in product species,
- (3) exchange of vibrational energy among the various species present,
- (4) stimulated emission, laser cascade,
- (5) fluid dynamics of
 - (a) mixing,
 - (b) nonequilibrium supersonic flow.

The interaction of these effects will determine the characteristics and limitations of the chemical mixing laser.

Under this program, experiments have been conducted in an existing version of the GDML configuration, as illustrated in Fig. 5. A particularly advantageous feature of this geometry is the isolation of the sequence of phenomena leading to laser emission; viz: arc-induced molecular dissociation, adiabatic nozzle expansion, reactant gas injection, and stimulated emission. The purposeful physical separation of these different regimes in this unique experimental geometry allows considerable freedom in studying many of the relevant physical processes independently. As outlined above, the parallel analytical modeling of the influence of the relevant parameters should validate results of the proposed experiments. The bimolecular system selected is discussed later.

The chemical laser experiments have followed general procedures established as successful in generating HF laser emission during preliminary experimentation (described above). Arc-induced dissociation of conveniently-handled, gaseous compounds has been used as a source of initiating atoms. Gaseous injectants have been used to promote the laser pumping reaction. Some further consideration has been given to improvement of nozzle, injector, and flow channel designs to establish effective freezing of atom recombination kinetics (Ref. 21), effective gas mixing (Refs. 22 and 23), and smooth flow conditions within the active medium.

Variation of reaction stoichiometry, diluent concentration, and flow parameters, have been conducted over reasonable bounds as constrained by apparatus and auxiliary pumping capabilities. The influence of these variations on laser emission has been recorded. An under-coupled, high-Q optical resonator aligned to view the mixing and downstream flow regions of the laser has been employed. The heating of the thermally-isolated mirrors forming this resonator is an effective measure of the available inversion of the medium, as was demonstrated in the early stages of the present contract, (Ref. 2). Hence, the available laser power resident in the medium has been determined conveniently via this under-coupled optical resonator technique and becomes a part of most of the parameter variation tests. In addition, the spectral character of the stimulated emission from the active medium has been analyzed. The emitted light was resolved spectrally in an available scanning/ recording 0.5 m infrared spectrograph.

Atom Recombination-Transfer

Experiments have been directed toward establishing a region of nonequilibrium conditions wherein the atom recombination effect would be manifest. The plasma arc generator power and nitrogen gas feed rates were adjusted for conditions of high specific enthalpy so as to yield high concentrations of N-atoms. Simple modifications in the plenum geometry decreased the residence time, $\tau_{\rm f}$, of nitrogen species between arc-jet exhaust and CO₂ injection from about 10 ms to 1 ms by increase in the plenum gas velocity. The intermix of a secondary stream of cold diluent reduced gas translational temperature calorimetrically. Different thirdbody efficiencies provided by the intermixed quenching gas have been explored briefly as the injectant species could be switched from N₂ to Ar, for example. The choice of injectant species and flow rate were made to achieve long N₂ vibrational relaxation times, $\tau_{\rm V-T}$. Conditions of operation were sought to maximize $\tau_{\rm V-T}/\tau_{\rm f}$, whereas prior GDML studies operated near equilibrium plenum conditions, i.e., $\tau_{\rm V-T}/\tau_{\rm f}$ <1.

Downstream injection of the cold CO_2 into the vibrationally-excited, flow proceeded as in earlier studies which were effective in establishing good mixing. Likewise, extraction of optical energy was accomplished through the utilization of the under-coupled cavity technique, the effectiveness of which was demonstrated at UARL under the previous NASA Contract NASw-1780, (Ref. 2).

Laser power on the expected $10.6 \,\mu$ m $CO_2 \, 001 - 100$ transition as deposited in the thermally-isolated cavity mirrors was measured as a function of arc-power input,

gas feed rates and flow conditions. Attempts were made to find a range of these parameters over which the CO_2 laser emission would be pumped by the N-atom recombination. Extensive determinations of the characteristics of this laser device, however, must be postponed to future investigation.

INVESTIGATIONS OF BIMOLECULAR EXCHANGE SYSTEM

Selection of Bimolecular Reaction

The hydrogen/chlorine bimolecular exchange reaction:

$$H + Cl_{2} \longrightarrow HCl^{*} + Cl \qquad \Lambda H \approx -45 \text{ Kcal/g-mol} (2.0 \text{ ev}) \qquad (4)$$

was selected for investigation in this study. This reaction was first studied as a candidate for laser excitation by Cool, et al., Ref. 6, as discussed below. In selecting this HCl bimolecular reaction for investigation, consideration was given to a wide range of such reaction systems known to result in transfer of a major fraction of reaction exothermicity to highly-excited inverted vibrational states of the product molecule. Among these, the well-known HF system, Eq. (1) discussed above was included. This system has been demonstrated at UARL in the existing arc-excited gas dynamic mixing laser apparatus. In addition, an extensive amount of information is being accumulated on this HF reaction from other programs (Refs. 4,7,8); hence, within the scope of the present study, it was probable that only limited information of significance could be added to the burgeoning HF literature if this reaction had been selected.

These prior studies of the HF laser system have established, however, certain characteristics of the laser medium which might well be disadvantageous for various NASA applications: for example, (1) relatively corrosive and toxic chemical species are present, (2) activity of the medium decays rapidly, Ref. 24, and (3) emission occurs at wavelengths strongly absorbed by the atmosphere, Ref. 25. Note that this latter defect can be circumvented through isotopic substitution, i.e., generation of DF, Ref. 25. Hence, interest in other similar bimolecular exchange systems to generate continuously laser media is evoked. The candidate selected in the present study, as mentioned above, was HCl, formed in vibrationally excited states via reaction (4).

The H + Cl₂ reaction, Fig. 6, is more exothermic than F + H₂ (-45 Kcal/g-mol vs. -32 Kcal/g-mol) and is known to result in an efficient conversion (>50%) of reaction exothermicity to vibrational-state excitation in an inverted distribution (Ref. 26). Vibrational de-excitation by self-collisions is known (Ref. 27) to be significantly slower for HCl than HF; hence, efficient operation over a wider operating range may be feasible. The HCl laser emits at longer wavelengths than HF, (Ref. 6), in a band where atmospheric transmission is more favorable (Ref. 25); hence, expensive isotopic substitution to generate DCl is not necessary. Finally, reaction (4) involves chemicals H₂, Cl₂ and HCl that are relatively easy to handle in the laboratory. The combination of these features would make successful demonstration of an efficient cw HCl laser a significant accomplishment in the chemical laser field.

Thermal Initiation of HCl Laser

Cw lasing has previously been demonstrated with this reaction using a low pressure rf discharge and subsonic flow (Ref. 6). Recently, lasing has been demonstrated at UARL in preliminary experiments involving existing gas-dynamic mixing laser apparatus and initiation by dissociation of H_2 in a pure hydrogen arc. This result, obtained under Corporate-sponsorship and unreported at this early stage of research, is to the best of our knowledge the first successful adaptation of this laser reaction to a thermal initiation scheme.

Other Chemical Laser Systems

In addition to reaction (4) other reaction systems considered as candidates for this study included (Refs. 6,26,28,29), Fig. 5.

Η	+ F ₂ HF*	+ F	Δ H = -98 Kcal/g-mol	(4.3 ev)	(5)
0	+ CS CO*	+ S	Δ H = -75 Kcal/g-mol	(3.2 ev)	(6)
H	+ 0 ₃ OH*	+ 0 ₂	Δ H = -77 Kcal/g-mol	(3.3 ev)	(7)

 $Cl + HI \longrightarrow HCl* + I$ $\Delta H = -32 \text{ Kcal/g-mol} (1.4 \text{ ev})$ (8)

Reactions (5) - (8) are of definite interest for a more extensive study. In particular, Reaction (6) has been demonstrated at UARL in existing gas dynamic mixing apparatus using arc dissociation of O_2 . However, these reactions were not selected for the initial investigation primarily because the reactants or products require special handling procedures or tend to cause special apparatus and optical surface contamination problems in the quantities required for the high (supersonic) convection rates present in the arc-excited experiments. These special procedures or problems were felt to place these systems somewhat beyond the scope of the present bimolecular reaction investigation. Eventual extensive investigations of one or more reactions such as Reactions (5) through (8) in a gas-dynamic mixing experiment are felt to be important for realization of the full potential of infrared chemical lasers.

Experimental Arrangement

The HCl chemical laser experiment that has been conducted under the present contract is shown schematically in Fig. 7, and in more detail in Fig. 8. A photograph of the laser apparatus is shown in Fig. 9. Molecular hydrogen is dissociated in the d.c. arc and cooled by large Ar addition in a plenum at $p_0 \sim 0.2$ atm. H-atom concentration levels are sustained by maintaining transit time through the plenum, τ_f , fast relative to recombination kinetics (Ref. 30) and wall deactivation processes; here $\tau_f \sim 1$ ms. Subsequently, the H-atom flow is expanded smoothly

through a 2-D nozzle of area ratio 3.5. Chlorine and diluents are injected in small amounts into the supersonic flow through a row of perpendicular sonic orifices spaced 0.5 cm apart in the opposing walls of the flow channel. The flow, which is being mixed and reacted, proceeds through the optical viewing/laser cavity region in a 2-D channel which expands 50% in height to offset partially the adverse effects of gas heating due to the reaction in the supersonic stream. The optical cavity employed is described in tabular form in Fig. 7.

Experimental Results

Laser Performance

A tabulation of experimental conditions and results obtained during testing is included in Fig. 7. To date, only v=1 — v=0 transitions have been observed in the low power laser output coupled from the cavity. Spectral analysis of the laser output was accomplished utilizing an 0.5 m Jarrell-Ash grating monochrometer and a Au:Ge detector. Laser tests have been conducted using both hole-coupled and uniformly transmissive cavities, the optical axes of which were oriented transverse to the flow. The position of the laser cavity was successfully varied from the injector plane to locations about 5 cm downstream of the injector. The laser output signal as recorded by the detector often was observed to be unsteady over a 1 sec time scale. In addition the output would often consist of a single strong transition depending primarily on Cl_2 injection rate. Spot size of the output beam from a 0.001 m diameter aperture would be about 0.01 m at a distance of 0.5 m consistent with expected growth of such a multimode laser cavity output beam.

Measurements of mirror heating with a near-confocal, undercoupled cavity have been made. Laser power coupled into the mirrors was monitored through application of flowing water calorimetry. The maximum mirror heating laser power level of 0.2 w (Fig. 7) corresponds to a specific power of ~ 40 w/(kg/sec) based on total flow rate in the experiment, mostly Argon. Corresponding chemical to optical conversion efficiency, assuming X_H = 0.01, is $\eta_{\rm C} \sim 0.1$ per cent.

Variations in gas flow rates have shown that the laser power output from the cavity is sensitive to H_2 flow in the arc. An optimum at $\dot{V}_{H_2} = 80 \times 10^{-6}$ std m³/sec was observed and corresponding plenum pressure was $p_0 = 0.24$ atm. In addition, it has been observed that an optimum injection rate of chlorine exists which varies if Argon is mixed with the Cl₂ injectant flow. The observed variation in optimum Cl₂ flow rate with Argon injection rate is shown in Fig. 10. It is seen that Cl₂ flow rate can be reduced substantially without affecting laser power drastically by mixing with up to 120 x 10⁻⁶ std m³/sec of Argon prior to injection. This tradeoff is believed to be a gas penetration effect indicative of the fact that the lasing occurs as a result of reaction in the bulk gas flow rather than as a result of spurious reaction in slow flow regions near solid confining surfaces. Information about the chemical reaction process likely is contained in this data since the Cl₂

injection rate variation may cover the range from fuel rich to fuel lean relative to H atom concentration. Values of quenched translational temperature in the plenum, T_o , have been calculated (Ref. 31) from knowledge of plenum pressure, flow rate, and the area of the sonic two-dimensional throat which forms the exit for the plenum flow.

Gain

Uniformly transmissive coupling tests were conducted with the center of the optical cavity approximately 3 cm downstream from the chlorine injectors. Dielectric coated mirrors peaked for the $3.5 - 5 \,\mu$ m wavelength region with transmissivities of 2 and 5 percent were employed in a semiconfocal cavity. Stimulated emission was observed in the case of the 2% mirror, but was not observed for the 5% mirror. Neglecting scattering losses and mirror absorption, an average gain coefficient between 0.2 and 0.5 per m would be indicated.

Other Diagnostic Tests

Diagnostic tests have included preliminary tests to measure HCl spontaneous emission, H-atom concentration, flow Mach No. reduction due to chemical reaction and HCl concentrations in the laser cavity. HCl spontaneous emission signal strengths have been below the detectable limits of the sensitive measuring system presently available; hence substantial increases in signal strength appear to be needed to obtain any direct information on the vibrational distribution of HCl.

H-atom Concentration

In order to learn more about the conditions obtained in the laser cavity, a set of experiments was undertaken to determine the hydrogen atom concentration and its dependence on arc power, diluent flow rate, and hydrogen flow rate. Hydrogen atom concentration is most directly measured by means of an isothermal calorimeter (Ref. 30); however, such an instrument would have questionable results in a supersonic flow of reactive gas. It was decided instead to use the established method of NO titration. Nitric oxide reacts with hydrogen atoms in the presence of a third body, M, to form nitroxyl (Ref. 32)

$$H + NO + M \longrightarrow HNO + M$$
 (9)

The HNO formed is in an electronically excited state, from which it decays rapidly, giving rise to strong spontaneous emission in the 6,000-10,000 Å band. In these experiments, nitric oxide was rapidly mixed with the hydrogen containing stream by the addition of NO through the sonic injectors. Optics located approximately 3 cm downstream from the injector focused the HNO emission on the entrance slit of the grating monochromator. This light was detected at a grating setting of 7625 Å by a type 9558QB photomultiplier.

In the first of the series of tests, NO was added in sufficient quantity such that it far exceeded the hydrogen atom concentrations. Under such conditions it is easy to show, at a fixed time from reaction initiation, that

HNO* Intensity
$$\sim$$
[H], (10)

The results of the NO titration experiments conducted to date indicate that the degree of hydrogen dissociation is constant for all hydrogen flow rates used in the lasing tests. However, the large quantity of nitric oxide required caused shorting of the arc, precluding further tests at high NO flow.

Gas Heating Due to Chemical Reaction

The ratio of pressure measured after a normal shock wave generated locally in a supersonic flow, to translational pressure in the undisturbed flow is a function of flow Mach No. and specific heat ratio for an ideal gas (Ref. 31). This ratio of impact pressure to static pressure, p_i/p , is a qualitative indication of Mach No. change in the present experiment. These parameters can be measured readily at the end of the flow channel using an open-ended small tube aligned anti-parallel with the flow to indicate the approximate level of p_i and a wall pressure tap to measure p. Using this technique, reduction in Mach No. due to chemical reaction heating has been separated clearly from Mach No. reduction due to mass addition only as shown in Fig. 11. At higher flow rates of H_2 and Cl_2 reduction in Mach No. to~l, a choking condition, has been observed. Such information indicates reaction likely has occurred to a significant extent but further interpretation must await accurate modeling of the nonequilibrium flow process with suitable boundary conditions.

HCl Concentration Measurement

A gas sampling probe was constructed and installed in the existing chemical mixing laser apparatus to serve as a means for extracting a sample of the flow in the vicinity of the laser cavity which could be analyzed for HCl and Cl_2 content. In particular an infrared absorption cell technique was evaluated to measure HCl concentration and direct on-line measurement of HCl concentration in the probe line flow with a Bendix TOF mass spectrometer was attempted. With the absorption cell it was difficult to acquire a sufficiently concentrated sample to detect the presence of HCl in the available standard 10 cm cell with the low concentrations and pressures in the experiment. Cryogenic trapping of HCl and Cl_2 was attempted to acquire a sample for analysis but since poor Cl_2 results were obtained when known flows of Cl_2 were present the trapping and absorption cell technique was not pursued further.

A mass spectrometer proved sufficiently sensitive to detect concentrations of HCl taken from an authenticated sample at a level $X_{HCl} \sim 10^{-3}$ with a total pressure in the probe line of 0.01 atm ($p_{HCl} \sim 10^{-5}$ atm). Passification of the monel-stainless

steel and glass probe line walls with HCl established reasonably steady reference signal levels. However it was observed that the mass spectrometer HCl signal was very sensitive to the presence of Cl_2 in the flow with hydrogen and HCl calibration flows turned off. It is likely that reaction of Cl_2 with hydrocarbon and H_2O contaminants on the probe line walls occurred, producing HCl. Establishment of wall conditions sufficiently clean to provide reliable determinations proved to be beyond the scope of the present program. There is a small possibility that some reaction of Cl_2 in the injection feed line could have occurred to produce ground state HCl in sufficient concentration to have affected the above laser results.

Translational Pressure Distribution

A typical translational pressure distribution, measured with wall pressure tape located along the center of the flow channel, is shown in Fig. 12. The effects of mass injection into the supersonic flow and chemical reaction are seen to cause a large increase in pressure near the injector and some pressure increase further downstream. The need for a more rapid expansion near the injector than is provided by the existing divergent wedge design, accompanied by an increased vacuum pumping capability, is indicated by the data.

Calculations With Computer Model

Analytical Program

This experimental program is being guided by the predictions of a one-deminsional computer model (previously developed under Corporate-sponsorship) of the HCl laser system. This model fully couples analytical descriptions of the HCl reaction kinetics, stimulated emission, vibration-vibration transfer and deactivation processes, and nonequilibrium gas dynamics (Ref. 14).

Reaction Kinetics

Numerical simulation of the HCl laser experiment has been undertaken with this computer code considering the following condensed chemical reaction kinetics:

$$H + Cl_2 \xrightarrow{K_1(v)} HCl(v) + Cl + (45-E_v) Kcal/g-mol$$
 (11)

$$Cl + H_2(o) \xrightarrow{K_2} HCl(o) + H - 1.2 \text{ Kcal/g-mol}$$
 (12)

$$H + HCl(v) \xrightarrow{K_3(v)} H_2 + Cl + (1.2 + E_v) Kcal/g-mol v \ge 1$$
 (13)

where the HCl vibrational level dependent exothermicity is included in the equation.

Rate constants for processes (11) and (12) are available in Refs. 26, 33 and 34. The rate constants for processes (13) are calculated by applying detailed balancing to rate K_2 and then assuming that negligible activation energy is required for these reactions to proceed.

Preliminary calculations suggest that reaction (13) may rapidly consume vibrational states produced by reaction (11) and, therefore, appreciably reduce optical gain and power output. Results for a stoichiometric case, as shown in Fig. 13, indicate a factor of three reduction in HCl concentration due to reaction (13). Since the rate of reaction (11) increases relative to the rate of reaction (13) at higher Cl₂ concentrations the effect of Cl₂ concentration has been studied, Fig. 14. For $X_{\rm Cl_2}/X_{\rm H} \sim 3-10$ the effect of reaction (13) has been reduced substantially. Temperature affects the rate of reaction (11) but is expected to have little effect on (13), since (13) requires essentially no activation energy. Hence, the effect of temperature on the above results was studied and the results show, Fig. 15, that at T=200°K the back reaction is predicted to reduce potential HCl concentration by a factor of 10 for the stoichiometric case. The back reaction effect causes only about a factor of two decrease in HCl concentration at T=400°K for the stoichiometric case.

The increase in HCl concentration above initial H atom concentration shown in Fig. 15 when $X_{Cl_2}/X_H = 10$ is due to the influence of the slightly endothermic reaction (12), whose rate of reaction is relatively slow with ground state H₂. When H₂ is vibrationally excited as may exist in the arc effluent the rate of (12) is known to increase by about 2 orders of magnitude and vibrationally excited HCl may result (Ref. 35). The effect of this speed-up is considered in later discussion but has not been included in the analysis as yet.

Gain Predictions

Gain calculations have been made with the above HCl computer model in a parameter range relevant to the experiments. A laser cavity pressure p = 0.013 atm has been selected, about the average of the distribution measured, and a constant pressure process has been specified. An initial velocity has been selected which yields a realistic transit time across the cavity and a reasonable supersonic Mach No. $(M \sim 2)$ for all values of temperature. Values of H atom and H₂ molecular concentration $X_{H} = 0.01$, $X_{H_2} = 0.025$ correspond to observed optimum H_2 flow conditions, and the preliminary, but uncertain, value for H concentration obtained from HNO intensity tests. A value for Cl_2 concentration $X_{Cl_2} = 0.03$ corresponds to the highest Cl_2 injection rate used and to the more nearly optimum production of HCl predicted for this value by one-dimensional reaction kinetics. A cavity temperature level T=300°K has been selected which is perhaps a little high considering the high dilution in the plenum, but should account for any gain reduction effects that might be caused by high temperature. Results obtained with the computer model for these conditions are shown in Fig. 16. Significant gains on v = 3 - 2, v = 2 - 1, v = 1 - 0P branch transitions are indicated, all well above threshold of the experimental

cavity employed (Fig. 7). Temperature increase due to reaction was about 50°K. Laser power level predictions, although not included in this report, would be between 10 and 100 watts of extracted power with all 3 vibrational level transitions participating. The possible reasons for the large discrepancy between these predicted results and the observed results, Fig. 7, forms the balance of the presentation on bimolecular systems in this report.

Gain Uniformity

One observation from the results of Fig. 16 is that upper level transitions particularly v = 3 - 2, exhibit nonuniform profiles in the flow direction on a particular P branch. In fact, regions of absorption, not investigated in the analysis as yet, might exist within the optical cavity retarding the development of the spatially distributed mode patterns that exist in the multimode optical configuration employed. Gain on v = 1 - 0 is calculated to be very uniform, enhancing mode buildup on this transition.

Effect of Reduced Cl₂ Concentration on Gain

The effect of reduced Cl_2 concentration, simulating the effect of reduced HCl concentration due to the back reaction (13) has been calculated, Fig. 17. Results for v = 2 - 1 and v = 1 - 0 transitions are shown, adequate to describe the effect. Reduced gain on all transitions is observed except a tendency for improved uniformity of v = 2 - 1 transitions is noted.

Effect of Reduced H-atom Concentration on Gain

Effect of Increased V-V Transfer Rate

In the computer model V-V transfer rates, based on approximate models of such molecular energy transfer, may be somewhat low. The extreme uncertainty in this direction would be about a factor of 10 and gain results show, Fig. 19, that the higher vibrational levels would decay faster with increased gain nonuniformity while v = 1 - 0 gain is sustained temporarily followed by faster decay and some increased gain nonuniformity.

V-T Transfer Rates

Some variations in V-T transfer rates in the model have been made but results are not shown here since sufficiently fast rates have been included in the results of Fig. 16, e.g., a deactivation rate of HCl (1) by H atoms of $(\tau_p)_H = 10^{-8}$ sec atm is used. Of course faster V-T rates do show reduced gains and increased gain nonuniformity on all transitions.

Effect of Initial Ground State HCl Concentrations

Since gas sampling results discussed above suggest Cl_2 reaction with contaminants may have occurred in the feed line as well as the sampling probe line to produce ground state HCl the effect of initial HCl(o) concentration has been studied. Results, Fig. 20, show that v = 1 - 0 gain would be substantially reduced with only small concentrations of such a contaminant. The fact that v = 1 - 0 transitions are observed indicates that such spurious reaction may not be occurring to any great extent in the feed line. This conclusion could be affected by production of HCl(1) levels by reaction of Cl with $H_2(v)$, discussed later.

Discussion of Bimolecular Results

Understanding of the present results depends partly on an understanding of the interaction of mixing in the present experiments with chemical reaction and molecular energy transfer process. The detailed mixing processes occur simultaneously with all physical processes, complicating model analysis and interpretation of experimental data. One is therefore interested in exploring the role of mixing by investigating the system behavior as mixing time is varied relative to chemical reaction, molecular energy transfer and convection times. In general it is helpful to include investigation of some regime where it is possible to check and guide experiments with analysis. At present, analysis is quite well developed when mixing occurs instantaneously and the subsequent reacting flow is one dimensional (Ref. 14). Therefore, a rapid-mixing experimental configuration has been employed which achieves substantial mixing as fast as possible for the scale of the experiment. Operation of the experiment at pressures and temperatures and a flow length scale where this mixing rate is fast relative to chemical reaction, vibrational deactivation and flow convection times appeared feasible, corresponding to a near instantaneous mixing situation.

A set of characteristic times for present experimental conditions is given in Table I, extracted from analytical results and system geometries. It can be seen that mixing is much slower than the $H + Cl_2$ reaction but much faster than molecular transfer processes and flow transit. Hence accurate prediction of reaction products, considering the probable importance of a back reaction such as (13) might not be expected based on an instantaneous mixing calculation. However V-V, V-T processes should be more adequately treated with the one-dimensional model if resultant mixed concentration profiles are reasonably flat. A two dimensional chemically reacting but vibrationally frozen mixing calculation would be helpful to determine the efficiency with which vibrationally excited HCl could be produced. The failure of laser results to be improved at high Cl_2 injection rates, (Fig. 10), could be a result of nonoptimum mixing relative to reaction chemistry.

It is known that vibrationally excited H_2 reacts about a factor of 100 more rapidly with Cl atoms (Ref. 35) than with ground state H_2 and is about 9.8 Kcal/ g-mol exothermic rather than -1.2 Kcal/g-mol endothermic as is reaction (12). Vibrationally excited HCl can be produced up to the v = 1 level and this would tend to inhibit gain on the v = 2 - 1 transition. The rate for this reaction has been estimated for present conditions, Table I and a value equal to the transit time was calculated. Since vibrationally excited H_2 likely is present in the arc effluent and vibrational decay is very slow $(\tau_P)_{H_2-H_2} \sim 10^{-3}$ sec atm Ref. 35, this reaction is expected to be contributing to the observed results. Although analytical results are not available as yet, operation of the experiment at lower pressures and with shorter transit times from the injector across the optical cavity should substantially reduce the effect of Cl, $H_2(v)$ reaction. Quenching of $H_2(v)$ vibrational energy in the plenum, through additives, may be helpful, provided H atom recombination is not enhanced.

The presence of ground state HCl contaminant, as a result of Cl_2 reaction with contaminants in the feed line or recirculation of spent HCl between the active medium and mirrors, could be a contributing factor to low v = 1 - 0 output in general.

It has been shown that V-V and V-T molecular energy transfer processes while not excessively fast result in nonuniform gain profiles across the laser cavity which may contribute to the absence of v = 2 - 1, and v = 3 - 2 transitions particularly if further analyses indicate the presence of absorption regions. Contributions to this gain nonuniformity effect would be, 1) nonuniform slower flow near the walls, which increases transit time and 2) higher pressure near the injectors, which speeds up V-V, V-T processes. Measurements of gain with a probe laser would be useful in exploring this effect, however at present, since work on the HCl system is at such an early stage, a suitable HCl probe laser has yet to be developed. Operation at lower pressures with shorter laser cavity transit time would be helpful.

INVESTIGATION OF ATOM RECOMBINATION - TRANSFER SYSTEM

Experimental Arrangement

The atom recombination experiments as discussed earlier have been conducted utilizing a modification of existing apparatus, Fig. 7, employed to study the HCl bimolecular exchange chemical laser system reported on in a separate section of this study. The modified apparatus is shown detailed in Fig. 21. In particular a slot injector section between plenum and laser sections has been added to provide for addition of CO2 and diluents to achieve near optimum conditions for subsequent laser emission at $10.6\,\mu$ m in the existing laser cavity, described in Fig. 21, as determined by results of the prior investigation of the thermally excited GDML (Ref. 2). A plenum extension unit has been provided to allow investigation of two transit time conditions in the plenum 1) $au_{ au}$ ~ 1 ms with the existing short plenum and 2) $au_{\rm f} \sim$ 10 ms with the extended plenum. These times are nominal values and have been determined in an approximate way based on a Mach number determined by the area ratio between plenum cross sections and the area of the sonic section at the throat of the 2-D contoured expansion which forms the exit to the plenum, Ref. 31. In.jection of CO2 which raises the pressure in the plenum would be expected to increase these times somewhat.

Experimental Conditions

The arc used for these investigations is identical to the one used for dissociating H₂ in the HCl experiments discussed earlier. In order to assist in identification of a recombination effect two N₂ arc operating conditions have been investigated, 1) high N atom concentration obtained by operation with low N₂ arc flow, $\dot{V}_A = 120 \text{ x}$ 10⁻⁶ std m³/sec and average arc enthalpy $\overline{H}_0 \sim 26 \text{ KJ/Kg}$ for which, Fig. 22, temperature based on equilibrium calculations would be $T_0 \sim 7000^{\circ}\text{K}$ and N atom mole fraction X_N ~ 0.65 is indicated; 2) low N atom concentration, with $\dot{V}_A = 400 \times 10^{-6} \text{ std m}^3/\text{sec}$, $\overline{H}_0 \sim 10 \text{ KJ/Kg}$, T-5500°K and X_N ~0.1. The results presented for case 2 suggest a factor of two reduction of N atom flow rate but accurate two-dimensional calculations have not been performed as yet. Values of \overline{H}_0 were determined experimentally through measurements of N₂ flow rate through the arc, electrical power input to the arc and heat loss to the water cooled electrodes.

The arc exhausts into the plenum and is quenched by dilution with large flows of N_2 + Ar where Ar is a convenient representative atomic inert diluent. The objective of the quenching is to achieve a translational temperature in the plenum around $T_0 = 1200^{\circ}$ K while varying the N_2 /Ar diluent ratio. After injection of CO_2 and further diluents a mixing and relaxation process occurs as described in Ref. 2, followed by expansion to supersonic conditions and transit through a transverse optical cavity region where stimulated emission occurs, also as described in Ref. 2. A typical translational pressure distribution as measured with wall taps along the center of the divergent wedge flow in the laser cavity is shown in Fig. 23. Lateral

expansion of the flow occurs and provision is made for ingestion of this side flow by the vacuum system. A 2500 CFM vacuum system provided for these tests exhausted the flow at a pressure a factor of 2 less than the channel exit pressure, insuring fully-developed flow in the channel.

Heat balance measurements of the mirror coolant flow as developed in Ref. 2, provided the primary diagnostic for laser power. Power coupled from a small aperture was monitored with a calibrated thermopile. An inert gas curtain flow in front of the mirrors was provided to purge the region between mirrors and active medium of ground state CO_2 that might be present as a result of residual recirculation and diffusion at the open sides of the supersonic flow.

Experimental Results

High Enthalpy and Fast Transit .

Typical results obtained for short transit time through the plenum au_{r} ~1 ms with high arc enthalpy and high N atom concentration are shown in Fig. 24. Diluent $N_{
m p}$ is seen to improve the laser performance. Laser power, $P_{I_{
m r}}$, up to 15 watts was observed as mirror heating of the very undercoupled cavity and gross electrical to optical conversion efficiency of $\eta_{T} = 0.21\%$ was obtained. Specific power was P_T/m ~2 kw/(Kg/sec) based on total flow of all gases. Laser power results were verified by observing a low tare mirror coolant heating signal when CO2 was turned off. Spurious radiative heating effects have been demonstrated in previous Corporatesponsored studies to be only of the order of microwatts. During lasing for the above conditions up to 0.14 watt was coupled out of the single aperture used to monitor the onset of lasing. Typical gas composition was $X_{N_2} = 0.30$, $X_{CO_2} = 0.12$, $X_{\text{He}} = 0.45$, $X_{\text{Ar}} = 0.13$. Neither a laser emission spectrum, nor 10.6 μ m gain were measured due to limitations in contract scope. However, single aperture output was observed to decrease about 95% when a sapphire flat was inserted in the beam path. Since the absorbtivity of sapphire is known to increase rapidly to this level above $\lambda = 6 \,\mu$ m this result supports lasing as occurring at 10.6 μ m since CO₂ was involved and prior measurements of gain at $10.6\,\mu$ m with a similar arrangement had been made, Ref. 2. The laser output was optimized by adjustment of the micrometer mirror alignment screws provided. The average plenum temperature values, \overline{T}_{0} , shown in the inset table of Fig. 24 are equilibrium values obtained from net measured gas enthalpy level in the plenum. Since freezing of vibrational and electronic energy is known to occur, these values represent upper limits. At low $N_{
m o}$ diluent flow \overline{T}_{O} is higher than desired and further additional Ar dilution would be needed in future testing.

Low Enthalpy and Fast Plenum Transit

The experimental conditions discussed above were repeated except arc N_2 flow was increased to reduce arc enthalpy and dissociation fraction. Results, Fig. 25, show that laser power increased about 50%, at high N_2 diluent flow rates and 100% at low N_2 diluent flow.

Again in these preliminary tests plenum temperatures at low N_2 diluent flow may have been higher than desired.

Slow Plenum Transit

Experimental results obtained to date with the plenum extension in place, producing $\tau_{\rm f} \sim 10$ ms, are shown in Fig. 26. Arc efficiency at high arc N₂ flow was very high for these tests and the low enthalpy condition (2) was not quite achieved. At low diluent N₂ flows these results are lower than achieved with short plenum transit, Figs. 24, 25, but at high N₂ diluent flow these results exceed the short transit values somewhat. In this case the dilution values chosen yielded plenum enthalpy levels that definitely imply that plenum temperature levels were significantly above 1200°K, and vibrational energy levels were probably sustained thermally as the flow proceeded through the plenum.

Maximum Laser Power and Efficiency

By continuing to increase N₂ arc flow rate while reducing electrical power input to near minimum arc operation levels and by increasing N₂ dilution, laser power P_L = 44 watts was obtained corresponding to electrical to optical conversion efficiency, $\eta_L = 0.8\%$. Power coupled out through the single aperture was P_T = 0.5 w. Conditions were $\dot{V}_A = 650 \times 10^{-6}$ std m³/sec through the arc, and $\dot{V}_{N_2} = 3800 \times 10^{-6}$ std m³/sec dilution with a gross arc input power of 5.5 kw.

Discussion

The energy of recombination for N_2 , Eq. (2) corresponds for the estimated dissociation conditions present in the high enthalpy low arc flow tests described above, to a recombination power reservoir of about 3 kw. Hence the results in Fig. 24 correspond at best to a chemical efficiency of $\eta_{\rm C} = 0.5\%$. Assuming that initial population of vibrational levels is substantial and electronic levels decay fast enough, the reason for this low value may be rapid V-T decay of high lying vibrational states of recombined N_2 in the quenching process. This interpretation was arrived at after a comparison, Fig. 27, of approximate values for N recombination time $au_{\rm R}$ by collisions with N₂ or N, V-T relaxation time by self-collision $au_{\rm V_{-}T}$, flow time in the plenum $au_{
m f}$, and translational temperature quenching time, $au_{
m Q}$ for the high enthalpy, short plenum conditions. Values of recombination time were calculated from results of shock tube dissociation studies (Ref. 36) with the assumption that as N atom translational temperature is quenched at relatively constant total pressure by dilution, N density, the ratio of N partial pressure to N translational temperature, remains constant. Vibrational relaxation times were obtained from Refs. 19, 37. For the present plenum quenching is expected to occur on about the same time scale as transit time, $au_{
m Q} \sim au_{
m f}$ and a value 1.5 ms is shown on Fig. 27. As translational temperature is reduced recombination of N by self-collisions (M=N) likely occurs since $\tau_{\rm Q} > \tau_{\rm R}$ (M=N). Since $\tau_{\rm V-T} << \tau_{\rm Q}$ for T > 2500°K decay of recombination energy stored in N₂ vibration would be likely up to that point yielding

a relatively inefficient process. The complex influence of electronic level lifetimes has not been ascertained as yet. Faster mixing and quenching could be achieved by diluting the cylindrical arc flow by injection through an annular gap surrounding the small, d = 0.003 m, arc column as it leaves the anode. The fastest quenching that could be achieved is $au_{
m Q}$ ~ 10⁻⁵ sec in this manner. Recombination would then occur subsequent to quenching on the slower $au_{
m f}$ time scale although it is likely that a more exact analysis of the quenching recombination process would be essential. It has been possible to perform a preliminary check of the feasibility of quenching the arc with large diluent No flow through such an annular injector. Volumetric dilution of the high enthalpy arc column by a factor of four has been achieved maintaining stable arc operation with only a small increase in plenum pressure level. Laser power results corresponding to the high enthalpy case shown in Fig. 24 have been improved at high N_2 dilution by a factor of two to between 25 and 30 watts with an efficiency $\eta_{T_c} \sim 0.45\%$. The upper limit to recombination chemical efficiency would be $\eta_{\rm C} = 1\%$. Corresponding operation at high N₂ arc flow, and low enthalpy, produced P_I between 30 and 35 watts at $\eta_{I} \sim 0.45\%$ about a 50% increase over the results of Fig. 25. Further improvement may be possible through preliminary analytical modeling and identification of a near-optimum quenching process. Verification of features of the analytical model, particularly related to electronic level populations, would probably have to be sought in separate experiments. Aerodynamic freezing of N followed by recombination and mixing of CO2 in the vicinity of the laser cavity should be explored as an alternative to volumetric quenching.

A recombination chemical efficiency $\eta_{\rm C} \sim 10\%$ would represent clear demonstration of the present ARL concept. Such an efficiency level may be possible through improvement in understanding of the relevant physical processes that would result from pursuit of the extensive program suggested above.

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LIST OF SYMBOLS

d	Arc column diameter, mirror coupling aperature diameter, m
D	Mirror diameter, m
E_{v}	Energy of vibrational, level v, ev, Kcal
g _o	Small-signal gain coefficient, m ⁻¹
h _t	Height of 2-D nozzle at minimum area, m
Н	Specific enthalpy of gas, Joules/Kg
Ho	Specific enthalpy of gas in plenum, Joules/Kg
I	Arc current, amps
К	Reaction rate constant of two body encounter, m^3 sec ⁻¹
K ^{lO}	Vibration-vibration rate constant for $v = 0-1$, $v = 1-0$ exchange, m^3 sec ⁻¹
L	Length of active medium within optical cavity, m
Μ	Flow Mach No.
M M _i	Flow Mach No. Molecular weight of Species i
M M _i p	Flow Mach No. Molecular weight of Species i Absolute pressure, atm
M M _i p P _i	Flow Mach No. Molecular weight of Species i Absolute pressure, atm Impact pressure at wall behind normal shock, atm
M M _i p p _i p _o	Flow Mach No. Molecular weight of Species i Absolute pressure, atm Impact pressure at wall behind normal shock, atm Absolute pressure in plenum, atm
M M _i p P _i P P	<pre>Flow Mach No. Molecular weight of Species i Absolute pressure, atm Impact pressure at wall behind normal shock, atm Absolute pressure in plenum, atm Branch designation for vibration-rotation transitions</pre>
M Mi p Pi Po Pc	<pre>Flow Mach No. Molecular weight of Species i Absolute pressure, atm Impact pressure at wall behind normal shock, atm Absolute pressure in plenum, atm Branch designation for vibration-rotation transitions Laser power coupled out of cavity, w</pre>
M Mi p Pi Po P Pc P _L	<pre>Flow Mach No. Molecular weight of Species i Absolute pressure, atm Impact pressure at wall behind normal shock, atm Absolute pressure in plenum, atm Branch designation for vibration-rotation transitions Laser power coupled out of cavity, w Laser power monitored as heating of thermally isolated mirrors, w</pre>
M M _i p P _o P P _c P L R	<pre>Flow Mach No. Molecular weight of Species i Absolute pressure, atm Impact pressure at wall behind normal shock, atm Absolute pressure in plenum, atm Branch designation for vibration-rotation transitions Laser power coupled out of cavity, w Laser power monitored as heating of thermally isolated mirrors, w Mirror spherical radius, m</pre>
M Mi p P _i P _c P L R	<pre>Flow Mach No. Molecular weight of Species i Absolute pressure, atm Impact pressure at wall behind normal shock, atm Absolute pressure in plenum, atm Branch designation for vibration-rotation transitions Laser power coupled out of cavity, w Laser power monitored as heating of thermally isolated mirrors, w Mirror spherical radius, m Temperature, ^OK, translational process</pre>

	v	Velocity, m/sec, vibrational level
•	v	Vibrational process
	v_{arc}	Arc voltage, volts
	vi	Volume flow of gas species i at std conditions, m^3/sec
	x	Distance in flow direction, m
	Xi	Molar concentration of species i
	У	Distance normal to flow and parallel to optical axis, m
	$\Delta_{\rm H}$	Reaction exothermicity, ev/molecules Kcal/g-mol
	η_{L}	Efficiency of conversion of electrical or thermal energy to laser power
	η_{C}	Efficiency of conversion of chemical energy to laser power
	λ	Wavelength, µ m
	т	Characteristic time, sec
	۳ _f	Transit time across plenum or optical cavity, sec
	τ _m	Mixing time, sec
	τ_{Q}	Quenching time of translational temperature by dilution, sec
	$\tau_{\rm R}$	Recombination time, sec/particle
	.π _{R,l}	Characteristic time for H + Cl ₂ reaction, sec
	^τ R,2	Characteristic time for Cl + $H_2(v)$ reaction, $v \ge 1$, sec
	τ V-T	Relaxation time of vibrational energy to translation, sec/particle
	τ V-V	Relaxation time of vibrational energy to vibration, sec/particle
(τ _p) _i	Characteristic time constant for transfer of vibrational energy by collision with species i at pressure p. sec-atm

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TABLE I

Characteristic Times for HCl Experimental Conditions

Mixing Time, $\tau_{\rm m} \sim 10^{-5}$ sec Time for H + Cl₂ Reaction, $\tau_{\rm R,l} \sim 2 \ge 10^{-6}$ sec (Refs. 26,33,34) Flow Transit Time Across Laser Cavity, $\tau_{\rm f} \sim 10^{-4}$ sec Characteristic V-V Time, $\tau_{\rm V-V} = \frac{1}{\kappa_{\rm Ol}^{10} \ge \text{HCl}(\text{v})} \sim 2 \ge 10^{-4}$ sec (Ref. 14)

Characteristic V-T Times (Ref. 27):

Species	Concentration	Time (seconds)	
H, Cl	10-2	10 ⁻⁴	
Cl ₂ , H ₂ HCl	3 x 10-2	3 x 10 ⁻³	
Argon	l	.10-2	

Time for Cl + ${\rm H_2(v)}$ Reaction: ${m au_{\rm R,2}}$

V	$\frac{\tau_{\rm R,2}}{2}$ sec	(Refs 26 33 34)
0	10-2	(IGIB: 20, 50, 54)
1, 2,	10-4	(Ref. 35)





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THERMAL EFFICIENCY OF N_2-CO_2 GAS DYNAMIC MIXING LASER



EXPERIMENTAL DATA

PREDICTIONS OF MODEL





 $N + N + M - N_2^* (V) + M$ $\Delta H = 225.1 \text{ K cal/mole}$ $N_2 (V) + CO_2 (000) - N_2 (V - 1) + CO_2 (001)$ $CO_2 (001) - CO_2 (100) + 10.6 \mu \text{ LASER}$





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STATUS	REPORTED	DEMONASTRATED	POTENTIAL ARC SYSTEM	POTENTIAL ARC SYSTEM	UNDER INVESTIGATION
L ASER	$3.4 - 4.0\mu$	4.6 - 5.9μ	$3.0 - 3.7 \mu$	$3.4 - 4.0 \mu$	$3.4 - 4.0 \mu$
REACTION	$F + D_2 \rightarrow DF^* + D$	$0 + CS_2 \rightarrow \rightarrow C0^* + SO$	$H + O_3 \rightarrow OH^* + O_2$	CI + HI → HCI* + I	$H + CI_2 \rightarrow HCI^* + CI$
INJECTANT	D_2	CS2	03	IH	cı ₂
SPECIES FROZEN	ш	0	н	CI	н
POST ARC FEED	SF 6	02	Η ₂	cl ₂	Ar
CARRIER GAS	N2	År	Ar	Ar	H ₂
SYSTEM		2	3	4	2

REACTION COORDINATE DIAGRAM



REACTION COORDINATE



REACTION COORDINATE





DETAIL OF ARC/MIXING APPARATUS FOR HCI CHEMICAL LASER









ARGON INJECTION RATE, $\dot{V}_i~$ – std $~\rm m^3$ /sec



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FIG. 12

PREDICTED EFFECT OF BACK REACTION ON HCI CONCENTRATION



PREDICTED EFFECT OF Cl2 CONCENTRATION ON HCI CONCENTRATION

T = 300 K

 $X_{H} = 0.01$ $X_{H_{2}} = 0.025$

BALANCE ARGON

BACK REACTION INCLUDED

 $v = 0.85 \times 10^3 \text{ m/sec}$



PREDICTED EFFECT OF TEMPERATURE ON HCI CONCENTRATION

x = 0.05 m

 $X_{H} = 0.01$ $X_{H_{2}} = 0.025$

BALANCE ARGON





:

CALCULATED GAIN DISTRIBUTION IN HCI CHEMICAL LASER





DISTANCE FROM INJECTION x - m

FIG. 16

CALCULATED EFFECT OF CI₂ CONCENTRATION ON GAIN DISTRIBUTION IN HCI CHEMICAL LASER





DISTANCE FROM INJECTION x - m

CALCULATED EFFECT OF H ATOM CONCENTRATION ON GAIN DISTRIBUTION IN HCI CHEMICAL LASER





FIG. 19

CALCULATED EFFECT OF V-V TRANSFER RATE ON GAIN DISTRIBUTION IN HCI CHEMICAL LASER





DISTANCE FROM INJECTION x - m

CALCULATED EFFECT OF INITIAL GROUND STATE HCI CONCENTRATION ON GAIN DISTRIBUTION IN HCI CHEMICAL LASER







DETAIL OF ARC/MIXING APPARATUS FOR ATOM RECOMBINATION INVESTIGATION WITH $N_2 - CO_2$ TRANSFER

K911106-4

FIG. 21



N ATOM MOLE FRACTION, XN

аус. **р**сеилм еитнагрү, <mark>Н</mark> _о − Кј∕К₉

TYPICAL PRESSURE DISTRIBUTION ALONG FLOW IN ATOM RECOMBINATION EXPERIMENTS



TRANSLATIONAL. PRESS URE, P - atm

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EFFECT OF N₂ DILUTION ON 10.6µm LASER POWER FOR HIGH ENTHALPY N₂ ARC CONDITION WITH FAST PLENUM TRANSIT

CONSTANT PLENUM MASS FLOW $\dot{m}_{o} = 3X10^{-3}$ Kg/sec (N₂ + Ar) $\dot{V}_{ARC} = 120X10^{-6}$ std m³/sec (0.15X10⁻³ Kg/sec) $\overline{T}_{ARC} = 7100$ °K PLENUM TRANSIT TIME $\tau_{f} \sim 1$ ms

INJECTED FLOWS $\begin{cases} \dot{\mathbf{v}}_{CO_2} = 1000 \times 10^{-6} \text{ std m } 3/\text{sec} \\ \dot{\mathbf{v}}_{Ar} = 800 \times 10^{-6} \text{ std m } 3/\text{sec} \\ \dot{\mathbf{v}}_{He} = 4000 \times 10^{-6} \text{ std m } 3/\text{sec} \end{cases}$

UNDERCOUPLED CAVITY AXIS AT x = 0.032 m CAVITY PRESSURE $p \sim 0.02$ atm CAVITY TEMPERATURE T $\sim 300 \pm 100$ °K



FIG. 25 EFFECT OF N₂ DILUTION ON 10.6 μ m LASER POWER FOR LOW ENTHALPY N₂ ARC WITH FAST PLENUM TRANSIT CONDITION

CONSTANT PLENUM MASS FLOW $\dot{m}_0 = 3X10^{-3} \text{ Kg/sec} (N_2 + \text{Ar})$ V_{ARC} = 400X10⁻⁶ std m³/sec (0.5X10⁻³ Kg/sec) T_{ARC} = 5600°K PLENUM TRANSIT TIME $\tau_{\rm f} \sim 1 \, {\rm ms}$

 $\dot{V}_{CO_2} = 1000 \times 10^{-6} \text{ std m}^{3/\text{sec}}$ $\dot{V}_{Ar} = 800 \times 10^{-6} \text{ std m}^{3/\text{sec}}$ $\dot{V}_{He} = 4000 \times 10^{-6} \text{ std m}^{3/\text{sec}}$ INJECTED FLOWS

UNDERCOUPLED CAVITY AXIS AT x = 0.032 m

CAVITY p~0.02 atm

CAVITY T ~ 300 ± 100 °K



FIG. 26

EFFECT OF N₂ DILUTION AND ARC ENTHALPY ON 10.6µm LASER POWER WITH SLOW PLENUM TRANSIT

PLENUM EXTENSION EMPLOYED

$$r_{f} \sim 10 \text{ ms}$$

CONSTANT PLENUM MASS FLOW $\dot{m}_{2} = 3X10^{-3} \text{ Kg/sec} (N_{2} + \text{Ar})$

INJECTED FLOW $\begin{cases} \dot{V}_{CO_2} = 1000 \times 10^{-6} \text{ std m}^{3}/\text{sec} \\ \dot{V}_{Ar} = 800 \times 10^{-6} \text{ std m}^{3}/\text{sec} \\ \dot{V}_{He} = 4000 \times 10^{-6} \text{ std m}^{3}/\text{sec} \end{cases}$

UNDERCOUPLED CAVITY AXIS AT x = 0.032 m

CAVITY $_{p}$ ~ 0.02 ofm CAVITY T ~ 300 \pm 100 K



APPROXIMATE NITROGEN RECOMBINATION AND VIBRATIONAL RELAXATION TIMES IN SHORT TRANSIT TIME PLENUM

ARC $N_2: \dot{V}_{ARC} = 120 \times 10^{-6} \text{ std m}^3/\text{sec}$

$$\overline{T}_{ARC} = 7100^{\circ}K$$

DILUENT: $\dot{v}_{N_2} = 2350 \times 10^{-6}$ std m 3/sec



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