**USE OF RELATIVISTIC ELECTRON BEAMS FOR
THE STUDY OF CHEMICAL AND RARE GAS LASER SYSTEMS**

Barton Krawetz
(Ph. D. Thesis)

March 12, 1974

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Preface

The author wishes to express thanks to the following people:

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USE OF RELATIVISTIC ELECTRON BEAMS FOR THE STUDY OF CHEMICAL AND RARE GAS LASER SYSTEMS

Abstract

Chemical ($\text{NF}_3 + \text{H}_2$) and rare gas molecular (Kr_2 , KrF_2 , Ar_2) laser systems are examined. Intense relativistic electron beams are used as a source of initiation and stimulation respectively. For the high gain chemical system, nonlinear amplification and pulse propagation are examined. The experimental result shows all the qualitative features of the theoretical prediction. In addition certain kinetic excitation and deactivation mechanisms are studied through the short stimulation time available with the electron

beam. Results obtained from the examination of laser action of the test system compare well with more conventional schemes for kinetic rate data extraction.

For rare gas molecular systems, the electron beam provided an excellent tool for studying the energy flow beginning with formation of the diatomic excimer to final decay by spontaneous radiative decay. Laser action in Krypton (Kr_2) is predicted. Symmetry in excitation mechanisms is demonstrated for the rare gases as a class.

Introduction

A. GENERAL

This study represents a synthesis of two separate experiments linked together by their common use of pulsed electron beams.

Taken in chronological order, the first portion of this work treats the gain properties of explosive mixtures of nitrogen trifluoride (NF_3) and hydrogen (H_2) gas. The amplifying medium, initiated by the electron beam, was probed with the coherent light from a sulfur hexafluoride (SF_6)/ H_2 "spiral pin discharge" oscillator. The operating characteristics of the oscillator, except as otherwise noted, were chosen so as to generate the longest possible pulses. The oscillator output was then taken as continuous wave (cw) relative to the physics under study in the amplifier.

Data extracted from the chemical laser study fell into three categories:

- Calculation of chemical pumping rates prevailing during small signal (linear) amplification.
- Calculation of overall population growth time constant. This demonstrated the dominance of binary kinetic processes over a wide range of reactant pressures.
- Examination of nonlinear amplification processes occurring in the amplifier at pressures in excess of 15 Torr. The nonlinear processes referred to here are those resulting from the interaction of material polarization and the stimulating field.¹

The second major area of study was that of the spontaneous emission spectra of several noble gases (Xe, Ar, Kr). Recent work in the Soviet Union on the possibility of noble gas laser action stimulated this phase of the investigation. The experimental apparatus used for the chemical laser work made the change-over to the noble gas very easy. The feature of this experiment that made it unique relative to other efforts² was the excitation rate and intensity made available by the electron beam generator. The pure gases and argon/xenon mixtures were examined at pressures up to 5 atm.

The results of this study are summarized as follows:

- 1) Time resolved spectra showing the formation and decay of the low lying triplet and singlet states of R_2^* were obtained. (R_2^* represents an electronically excited rare gas dimer.) One concludes from a study of these spectra that the excited states are formed in a condition of high vibrational excitation with subsequent rapid decay to the ground vibrational state.
- 2) Certain energy cascades from high lying molecular states (excited core configuration) were observed to occur in a systematic way for all the rare gases.
- 3) Line narrowing was observed in krypton gas over the range of pressure 3-5 atm. Thus, it is expected that laser action in pure krypton may be possible.
- 4) Energy transfer rates and processes were examined in the mixed rare gas system composed of argon and xenon.

B. CHEMICAL SYSTEMS

Chemically produced population inversion leading to laser action was first demonstrated by Pimentel³ in the first half of 1967. The current interest in chemical lasers is best understood by a consideration of the dominant gain producing mechanisms that attend the detonation of $H_2 + F_2$. These processes are:

(where F denotes a free fluorine radical and HF^* denotes a vibrationally excited molecule).

It has been verified^{4,5} that up to 72% (reaction 1) and 44% (reaction 2) of the reaction enthalpy could appear as vibrational excitation of the HF molecule. A simple calculation suggests that a properly prepared detonation of $H_2 + F_2$ could yield 100-200 kJ/mole, all of which is potentially available for stimulated emission. One can be assured of efficient energy extraction if the HF production rate exceeds the fastest of the various deactivation rates. Typical deactivation processes can be represented by the following reactions:

where $X^* = F^*, H^*$

where $M = NF_3, H_2, F_2$

Assuming that favorable rate competition can be realized, one is tempted to consider the construction of large efficient laser systems employing chemical pumping. Chemical systems can operate with an efficiency that greatly exceeds 100%. That is, one can expect to generate laser light output whose total energy exceeds the investment in initiation energy, if the energy to produce the reactants is ignored.

With the foregoing argument in mind, an experimental program was undertaken to assess the gain properties of a particular reactant system ($NF_3 + H_2$) that was known⁶ to produce vibrationally excited HF via chemical detonation. During the formulation phase of this study, it was noticed that the literature^{7,8} contained references to the laser properties of HF^* produced in so called "pin laser" configurations. These devices were all characterized by hot arc discharges between opposed pairs of individually ballasted points. A schematic view of such a device appears in Fig. 1.

Ballasted pin systems produce nonuniform and unrepeatable gain across the active aperture. The non-uniformity becomes pronounced where the total reactant pressure exceeds 150 Torr. In order to produce energetic laser systems (one of the major inter-

*This technique was conceived by R. E. Kidder, B. Krausz, D. W. Gregg, and patented in 1972.

Fig. 1. Schematic representation of a pin discharge laser.

ests of the A.E.C.) one has to postulate the extension of any initiation technique to large apertures (several tens of centimeters) and high reactant pressure (several atmospheres). It is well known⁹ that pin discharges condense to hot arcs well below 760 Torr and are therefore unacceptable. As the reactant pressure is increased, the characteristic time for binary kinetic processes scales as (pressure)⁻¹. One is, therefore, faced with the additional requirement of finding initiation schemes suitable for high pressure operation. In this study a pulsed, relativistic, electron beam* technique is employed for chemical initiation. The electron beam method is potentially useful for arbitrarily large gain apertures. Initiation pulse widths of several nanoseconds are well within the state of the art. Uniformity of initiation is assured if the electron range substantially exceeds the areal density of the reactants traversed by the beam. (Range and area density are normally given in units of g/cm².)

The value of uniform initiation is immediately seen when one realizes the effect of hydrodynamic shock waves on the homogeneity of the optical (gain producing) medium. The appearance of shock waves will

terminate laser action by producing unpredictable density gradients and elevating the gas kinetic temperature of the exploding medium. The electron beam produces about 10¹⁵ initiations per gram of material, consequently no discrete shocks form until long after the end of laser action.

The first step toward proving the feasibility of the electron beam initiation idea was to build a small enclosure run in an oscillator configuration. It was decided that H₂ + F₂ was too hazardous a combination for our initial experiment. A better choice was H₂ + NF₃; it is readily mixed and not given to spontaneous detonation. Several combinations of hydrogen and fluorine-bearing molecules were examined before reaching this conclusion (N₂F₄/H₂, N₂F₄/B₂H₆). Some details of this experiment are given in Ref. 6.

Figure 2 outlines the arrangement of the test volume for this preliminary experiment.

The laser cavity shown in Fig. 2 was formed by one front surface gold coated, 10 m mirror with 97% reflectivity at 3.0μ, and one 50% reflective (gold reflector), NaCl flat. The laser action observed on several

Fig. 2. Proof of principle apparatus.

vibration-rotation transitions of HF encouraged further experimentation. An objection to the initial experimental arrangement was that one could not conclude that electron beam effects alone were responsible for the excitation leading to laser action. One could reasonably expect the leading edge of the electron pulse to charge the far wall of the pyrex cell (because of the small capacitance of the structure, few electrons would be required to bring the potential of the pyrex surface up to that of the beam) thereby stopping the succeeding electrons in the small volume. Subsequent arcing would certainly occur, thereby casting doubt on the spatial uniformity and character of the ignition mechanism. It was because of this doubt that the experiment to be described below was conceived. For the remainder of the study, the electron beam is run axially down a large volume reaction

pipe made of Teflon and constrained by a magnetic field to a diameter small compared to the inside diameter of the reaction vessel (6.35 cm). The aspect ratio of the vessel was chosen such that end effects leading to capacitive charge buildup could be ignored (actual length/diameter $\approx 10.5/1$). Finally, it was decided to study the $\text{NF}_3 + \text{H}_2$ system in an oscillator-amplifier configuration so that one could attempt the understanding of linear* amplification characteristics of the system rather than the necessarily nonlinear behavior characteristic of an oscillator alone.

*Linear amplification was not observed in this system at total pressures above 15 Torr. (See Sec. II-B.)

I. Description of Experimental Apparatus

A. ELECTRON BEAM GENERATOR

Principles of Operation

This device is an 80-stage "Febetron"[†] Marx generator. Each stage (for this experiment) was charged to 35 kV producing 2.5 MV across a field emitting diode consisting of a thin (1.5 mil) titanium anode and a fork-like array of needles serving as the cathode; the effective impedance of the diode being about 400 Ω . The machine contains an internal dc solenoid that serves to guide the electron beam repeatedly through the titanium output window. The solenoid is driven by 700 A dc supply and is energized for about 20 sec at each firing. This extended "on" time heats the solenoid enough to limit the repetition rate for repeatable electron beam outputs to one firing every 7 min. Overheating of the internal solenoid coupled with the necessity for pumping exploded gases out of the amplifier section resulted in a maximum repetition-rate of six firings/hr.

The temporal output of the machine as monitored by a capacitive voltage divider connected across the field emitting diode is represented by Fig. 3.

[†]Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U. S. Atomic Energy Commission to the exclusion of others that may be suitable.

Electron Beam Generator Output Characteristics

The effective electron energy as determined by an average penetrating power measurement, see Fig. 4, is taken as 1.4 MeV. A peak charging voltage of 2.8 MV (35 kV/stage $\times$ 80 stages) results in 2.5 MV actually appearing across the tube.

The peak current = $\frac{2.5 \text{ MV}}{400 \Omega} = 6.25 \text{ kA}$. Taking the pulse width to be 80 nsec (FWHM) and the average current to be 4.5 kA, the energy delivered per pulse is:

$$\bar{I}_p \cdot \bar{I} \cdot \bar{V} = \text{energy/pulse} = 475 \text{ J} \quad (3)$$

where $\bar{I}_p$ = average pulse length = 80 nsec

$\bar{I}$ = average total current = 4.5 kA

$\bar{V}$ = average electron voltage $\approx 1.4 \text{ MeV}$

This figure agrees well with the 450-500 J stored in the capacitor stack. For further calculations, the average current will be taken 4.5 kA emitted in 4.0 cm^2 beam.

Triggering of the machine is accomplished by a low jitter trigger amplifier consisting of a precharged length of coaxial cable switched by a hydrogen filled thyratron. This arrangement delivers a 20 kV pulse to the trigger electrodes of the first Marx stage. The spark gaps of succeeding stages are illuminated by the first stage discharge photons (as well as being over-voltaged) resulting in lowered "staging time" jitter.

Fig. 3. Voltage vs time across field emitting diode.

Fig. 4. Electron energy spectrum.

The machine consistently produced triggering jitter of less than ± 1.5 nsec, as measured on a 519 oscilloscope. Typical electron beam tube life was 1500 shots at 30 kV (1.4 MeV average electron energy). It was found from machine diagnostics data taken on each shot that when the tube failed it did not do so gradually. It was a simple matter to diagnose tube malfunction, replace it, and then repeat suspect experiments.

The machine is characterized by the following operating parameters:

- Jitter ± 1.5 nsec.
- Propagation delay (Marx erection time) 425 nsec.
- Average energy/electron = 1.4 MeV (as measured by a mean range parameter).
- Peak output current 6 ± 0.3 kA (as measured by Faraday cup).
- Current rise time 10 nsec $\begin{smallmatrix} +5 \\ -0 \end{smallmatrix}$
- Current width 80 nsec $\begin{smallmatrix} +10 \\ -5 \end{smallmatrix}$
(as measured by Faraday cup)
- Nominal internal magnet field = 4 ± 0.4 kG

Electromagnetic Noise Environment

The inductance of the electron beam current path is of the order of a few microhenries. With dI/dt calculated from the performance figures given above, one expects radiated field strengths of several kilovolts/meter near the generator. Appropriate

screen room and noise suppression procedures were therefore crucial to the attainment of acceptable signal-to-noise ratios.

Sample Calculation

$$V = L \frac{dI}{dt} = 2 \times 10^{-6} \times 10^9 = 2 \text{ kV}$$

$$V/L = 2 \text{ kV}/1 \text{ m} \Rightarrow |\vec{E}| = 2 \times 10^3/\text{m} \quad (4)$$

(1 m = characteristic size of system)

B. OSCILLATOR

The oscillator/power supply systems examined included all combinations of linear and spiral pin oscillators driven by high impedance reactive and Marx bank devices. For reasons of mode uniformity and energy delivered/pulse it was decided to use the spiral system as shown in Figs. 5 and 6.

Pairs of opposed pins constructed of Kovar were arranged in interwoven helices such that 50 pin pairs, completing 3 revolutions of the helix placed 1 cm apart defined as active length of 70 cm.

Each of the anode pins was ballasted with a 500 Ω , 20 W noninductive wire wound resistor giving an effective total ballast impedance of 10 Ω ; this resistance proved adequate to stabilize the discharge without excessive source energy dissipation.

Fig. 5. Spiral pin array oscillator.

Fig. 6. SF_6/H_2 oscillator cavity.

- A: Grating fixture
- B: "Spiral" pin oscillator tube
- C: Piezoelectric output mirror mount
- D: Electron beam generator, Marx tank

Gases (SF_6 , H_2) were introduced into a flow control manifold, mixed and fed into opposite ends of the tube labeled "input"; spent gas was extracted from the opposed centrally located fixture labeled "output", by a 2 cfm mechanical pump. This arrangement permitted extended operating life (100 hr) without window fogging even when running with inputs of 40 J/pulse.

This particular tube diameter and electrode spacing was chosen as a compromise between excessive heating of the glass walls and mechanical pumping capacity when the system was operated in the mode requiring 40 J/pulse input energy.

Power Supply

For low pressure, long pulse width applications the oscillator was operated with the approximately 2-k Ω output-impedance, capacitor-SCR-transformer arrangement at 10-20 pps. The voltage input to the oscillator peaked at 14 kV with 200 nsec rise time. An adjustable width, series spark gap was used to steepen leading edge. Typical outputs were ~ 1 mJ in 1 μsec .

For high pressure, short pulse width applications the oscillator was operated with the Marx generation source; 40 J/pulse (2 stage, 20 kV/stage transmission-line coupled) with voltage rising to ≈ 60 kV at breakdown depending on pressure and stoichiometry of SF_6/H_2 mixture. This source was used in that portion of the study seeking to assure the maximum likelihood of saturated amplifier performance. Typical outputs were 25-30 mJ/pulse when no dispersion was used in the cavity. Typical repetition rates were 1-2 pps.

Operation with the Marx generator was characterized by 150 nsec pulses (FWHM) with peak power of 250 kW.

Cavity

The discharge tube described above was inserted in a 1.5 m cavity having two distinct configurations, again depending on the mode in which data was being taken; see Figs. 7 and 8.

In both cases the output mirror is held in a piezoelectric mount to permit axial mode selection (Fig. 6). It should be noted that in the high energy mode of operation, no experiments requiring single mode performance were attempted. Care and attention to single mode operation was attempted only in the low energy mode.

This particular oscillator arrangement, after careful alignment and adjustment of the cavity length to an integral multiple of $\lambda/2$, provided stable operation for

Fig. 7. Oscillator cavity, low energy, long pulse, single mode operation.

C = Laser tube illustrated in Fig. 5.

A = 3-m radius miniscus type silicon output mirror, 50% reflecting.

B = Grating blazed at $(61^\circ 10')$ useful range 2-4 μ ; 625 lines/mm. The ruling of the grating was sufficient to resolve adjacent rotational lines under all experimental conditions.

D, D' = Apertures used for alignment; D' provided transverse mode control as well.

E = Piezoelectric positioning device for axial mode control.

Fig. 8. Oscillator cavity, high energy, short pulse mode.

C = Laser tube described in Fig. 5.

DD' = Apertures, (D' used for transverse mode control).

A = 1/4 in. thick sapphire flat output mirror.

B = Front surfaced gold, 3 m mirror 97% reflecting at 3 μ .

periods of 5-10 min. This we defined as operation in which the amplitude of mode beats did not exceed 20% of the unperturbed pulse amplitude. After that time thermal cycling and associated strain of the cavity caused unacceptable intermode mixing, forcing a minor readjustment of the cavity length.

Amplified Spontaneous Emission - Oscillator

The gain of an H-F system is known to be very high.¹⁰ In the experimental situation, high gain caused persistent parasitic oscillations unless rather extreme precautions were taken.

Low Pressure - Long Pulse Mode - This mode was defined by 0.5 J/pulse (input) and typical output pulse length of several μsec , reactant pressure about 30 Torr. Care was taken to match the TEM_{00} mode size to the volume of the active region. This clearly is beneficial from the standpoint of maximizing the

output of the system, but too large a mode diameter carries with it the problem of the inherently non-uniform gain distribution as measured across the active volume. Thus, about half the full gain diameter was used in this study.

Further, all mode controlling apertures had to be fitted with some material that was highly lossy for wavelengths in the emission region of HF^* ($\lambda \approx 3 \mu$). This was done using cardboard sprayed with paint whose infrared absorption was measured at $> 90\%$ for $2\mu < \lambda < 30\mu$. Optics at exterior surfaces were all antireflection coated. The succeeding amplifier stage and apertures necessary for detection had Brewster's angle windows and antireflection paint respectively. Under these conditions it was impossible to observe amplified spontaneous emission. When under grating control, no oscillator emission but that selected by the appropriate grating angle was observed. The detection sensitivity was $20 \mu\text{V}/\text{cm}$. For reference, the same detection arrangement gave 500 mV signals when the grating was tuned to resonance with a transition exhibiting gain.

High Pressure - Short Pulse Mode - This mode was defined by 40 J/pulse (input) and typical output pulse length of 150 nsec, reactant pressures were

about 150 Torr. It was experimentally determined that optimum output coupling was achieved using a NaCl flat as an output mirror. In this configuration, emission peaked in energy by a factor 6 over that in which no output mirror was used. In no case, quite independent of precautions, was it possible to reduce the amplified spontaneous emission to unobservable levels.

With the grating detuned and the output mirror removed it was only possible to achieve attenuation of 10^3 in emission of the strongest line P(4) 2-1. Thus, in this case, complete decoupling of the oscillator-amplifier regions was never achieved. By proper aperture selection it was possible to obtain TEM_{00} performance as verified by observation of burn spots on film and the use of a movable pinhole in conjunction with a calorimeter in the far field of the oscillator.

C. AMPLIFIER

Turning Mirror

A special feature of the amplifier geometry is the turning mirror shown in Fig. 9. This mirror serves two functions. First, it reflects the oscillator beam into the reaction vessel and second, it permits transmission of the electron beam through the mirror and

Fig. 9. Beryllium turning mirror.

Fig. 10. Close-up of amplifier, mirror housing section.

- A: Sapphire entrance window.
- B: Mirror positioning fixture.
- C: Electron beam output fixture.
- D: Solenoid encasing teflon reaction pipe.

down the axis of the amplifier tube. Beryllium was chosen for its obviously favorable density-to-strength ratio. The mirror was fabricated from a 1/8 in. thick blank, 2.25 in. dia, with the back of the mirror being etched with a rib-like pattern. Etching was accomplished by electrolytic erosion.

The front face of the blank was then lapped and polished to ± 1.5 wavelengths flatness (sodium-D). The structure was extremely rigid and calculation showed that no more than $\sim 10\%$ transmission loss would be suffered. The mirror's contribution to scattering losses was considered negligible when compared with the losses associated with the other scattering elements. The mirror and its associated housing were suspended on a 3/8 in. dia stainless steel shaft from a heavy-duty Varian rotation-translation fixture, Figs. 6 and 10, and was exposed to the full impact of the chemical explosive occurring in the reaction pipe. After several hundred firings, neither the flatness nor the infrared reflectivity of the mirror were seriously degraded by the effects of the explosive reaction. A light film produced by reaction products slightly degraded the mirror's reflectivity at 6328Å.

The mechanical stability of the structure was examined using a He-Ne alignment beam directed onto the beryllium mirror, Fig. 11, and then detected by an SDG-100 photodiode, 15 ft away from the mirror. The electron beam was made to penetrate the mirror and then the time for spot traversal of the

sensitive area of the diode was measured. As shown in Fig. 12, no motion occurred during the first 8 μsec after the beam fired. After 8 μsec , a slow drift of the reflected beam occurred with the spot returning to its precise prefiring position within about 50 msec. The observed 8 μsec interval of stability correlates well with the sound transit time across the diameter of the mirror.

Fig. 12. Data on mirror motion.

Amplifier Geometry

The beryllium mirror serves the dual task of turning the oscillator beam down the pipe while at the same time causing minimum perturbation to the electron beam in its path down the tube.

All obstructions to the free electron motion down the tube contribute to beam spread and absorption. The influence of these effects will be assessed in the section on electron beam propagation below. In summary, the energy loss due to ionization is under 10% and the rms scattering angle is under 30° . In Sec. I-H it is shown that the mirror is a minor contributor to the electron loss. The scattering, being predominantly forward, is relatively insignificant because of the effectiveness of the longitudinal magnetic field in confining the divergent electrons.

The amplifier section is taken to include the mirror housing section, the amplifier tube (reaction vessel), and the output housing, Fig. 13.

The mirror section, aside from containing the mirror, allowed for the attachment of the entrance Brewster window and for high speed pump-out of the exploded gases through a 5/8 in. air operated, 2 ksi, Nupro valve. The mirror section is shown schematically in Fig. 14.

Fig. 11. Test geometry for mirror motion studies.

Fig. 13. Four major sections of the amplifier.

Amplifier Reaction Tube

In early experiments the reaction tube was standard industrial glass pipe cleaned with ethyl alcohol and then pumped for several days until a base pressure of $< 5 \times 10^{-7}$ Torr was attained. The glass was sealed with KEL-F (a fully fluorinated hydrocarbon) O-rings and secured with standard industrial glass pipe flanges. Gases were then introduced, exploded, and the amplifier output examined. It was noticed that after each firing, it became increasingly difficult to pump the system down and the output became weaker and more erratic. This was especially true when the mixtures were near stoichiometric for the reaction:

(Note: Reaction (5) is the ultimate result of complete combustion at $\text{NF}_3/\text{H}_2 = 2/3$ and is not representative of what actually occurs during laser action.)

Post explosion mixtures were sampled by flowing explosion products into a previously evacuated ir cell built of Monel with AgCl windows.* Spectrophotometer traces of post explosion mixtures showed a strong SiF_4 band, evidence of a reaction between HF and the glass walls. The gain of the system contaminated with SiF_4 became small and generally unpredictable. Several alternative reaction vessel materials were examined including ceramics and various metals

Fig. 14. Top view of input and mirror section.

*This cell was shown to be inert with respect to catalysis of the NF_3/H_2 reaction over periods of several days.¹¹

(e.g. stainless steel and Monel). Ceramics were rejected on the grounds of difficulty of fabrication and possibility of reaction with the HF formed in this reaction. All the metallics were rejected because of their conductivity. For reasonable tube thicknesses the magnetic field diffusion times are unacceptably long, see Sec. I-H below.

The material finally chosen was Teflon machined to the same shape as the glass tube. Teflon did not react with the HF to any noticeable degree but did suffer the disadvantage of being more porous than glass. The best base pressure at 15 min was higher than that of glass ($\approx 8 \times 10^{-7}$ Torr). Teflon performed acceptably throughout the experiment. The magnetic field alignment relative to the reaction tube axis was important to prevent puncture of the tube, after several shots, by the formation of discharge tracks in the material.

The Teflon amplifier section was wrapped with copper tubing forming a solenoid that, when energized, provided an axial magnetic field centered about the tube axis. The solenoid is effectively infinite (for the purpose of inductance calculations) with fringing of the field occurring at about one coil diameter away from the end of the solenoid. The magnetic field circuit oscillates, essentially undamped, with a quarter period of 50 μ sec. The electron beam is introduced into the amplifier section at about the time ($\pm 0.5 \mu$ sec) that the voltage induced in the pickup coil passes through zero ($E_{\text{pickup}} \propto di/dt$) or equivalently, the current in the main solenoid is a maximum. This externally induced magnetic field was taken to be constant during and immediately after the electron beam was introduced (total duration of beam is 80 nsec). Figure 15 demonstrates the effectiveness of the confining field.

Figure 15a shows the beam propagating in 300 Torr of argon with a containment field of ~ 2.7 kG. The entire surface of the tube is illuminated. The visible emission is due to fluorescence of the glass tube as well as bulk emission from the gas. Figure 15b depicts the same experiment with the containment field increased to ~ 8 kG. The illumination in this case is due solely to the thin pencil beam down the axis of the tube.

Amplifier Exit Region

This region consists of a Varian "tee" (stainless steel) that couples to the glass amplifier section on one end; to the output Brewster angle fixture on the

Fig. 15. Electron beam in air
(a) with insufficient containment field (2.7 kG),
(b) with 8 kG containment field.

other, and to the filling, purge and pressure monitoring hardware on the center of the "tee", Fig. 16.

A pair of braided copper straps, Figs. 10, 16, 17, connect the output housing to the mirror housing forming a low inductance return path for the electron beam primary electrons. The output tee also provides a sink for beam primaries guided by the fringing fields to the tee walls. This protects the sapphire output window from any but a trivial exposure to direct electrons from the beam. Even after about a one thousand firings there was no evidence of radiation damage to the windows.

Guide Field Solenoid

The magnetic field solenoid was constructed of 1/4 in. o. d. copper tubing. Hollow tubing is totally acceptable since even at the design resonant frequency of 5 kHz the skin depth is about 0.9 mm. The tubing is wrapped on a lucite tube of 8.2 cm o. d. forming 42 turns in a length of 60 cm. Another lucite tube, whose inside diameter was such that it could be slipped over the wound coil, was fitted and then clear potting material was flowed between the windings and allowed to "set up". The coil, thus potted, was held in a fixture that supported it independently of the amplifier tube.

This entire assembly is then slipped over the end of the amplifier and shimmed to be concentric with the teflon tube axis. The coil fixture was made fast to the granite optical bench by weighting with about

Fig. 16. Amplifier output section.

100 lb of lead bricks. The amplifier section was supported, to this point, at the mirror housing end only, and was subsequently positioned by adjusting its center to be coincident with a He-Ne alignment laser beam shone into the input window and reflected down the tube axis by the beryllium turning mirror.

The final alignment of the Teflon tube axis with the magnetic axis was checked by experimentally measuring the path of the electron beam using plastic discs put in the beam path, see Sec. II-C. The bleached center of this series of discs, when compared to the geometric center of the tube, allows the final adjustment of the solenoid. No further alignment was required until an equipment malfunction required disassembly and complete realignment.

D. INSTRUMENTATION

The data commonly gathered during this investigation consisted of:

- 1) Oscillator/amplifier pulse shape data - Cu:Ge (liquid helium cooled).
- 2) Monochromatry - Perkin Elmer E-1.
- 3) Calorimetry - Scientech Inc. (Model 1602).
- 4) Electron beam performance data - capacitive voltage divider across field emitting diode.
- 5) Magnetic confinement field monitoring - dB/dt probe.

The pulse shape data acquisition system evolved in three distinct stages. First, in the earliest experimental stage Au doped Germanium (Philco-Ford 201A) was used for monitoring the oscillator input, amplifier output, and monochromator output. These detectors had the advantage of operating over a wide dynamic range (saturation at 10 V output into 50 Ω) and requiring only liquid nitrogen cooling; their major drawback showed up as a rather low bandwidth resulting in poor resolution of pulse shapes, Fig. 18. In addition, the high-Z dopant (gold) rendered the devices quite sensitive to the hard x-ray bremsstrahlung generated by the electron beam machine.

Next we tried InSb photo resistive detectors. These devices, produced by Mullard, had the advantages of greater bandwidth (see Fig. 19), operation at room temperature, use of d.c. power supplies rather than batteries, and remarkable insensitivity to the hard x-ray environment mentioned above. Their only drawback was a limited dynamic range that resulted in saturation at signal levels of 200 mV into 50 Ω .

The final configuration of detectors was liquid helium cooled, Cu doped, germanium (Cu:Ge). These detectors combined high sensitivity with wide dynamic range and the largest bandwidths of all detectors examined.

These crystals were originally intended for use at 10.6 μ and were therefore peaked in sensitivity for this range. Due to an accidental overdoping of copper

Fig. 17. Amplifier section.

- A: Fill/purge/pressure sensing hardware
- B: Guide field solenoid
- C: Copper ground return straps
- D: Nupro 5/8" exhaust valve

Fig. 18. Dual beam recording comparing frequency responses of gold doped germanium with copper doped germanium detectors, using 1A1 preamp, and 555 scope at 100 nsec/cm and 0.02 V/cm. No electron beam.

Upper trace: Cu:Ge

Lower trace: Au:Ge

Note: Display is limited by the bandwidth of the 555 oscilloscope.

Fig. 19. Dual beam recording comparing frequency responses of indium antimonide with copper doped detector, using 1A1 preamp and 555 scope at 200 nsec/cm and 0.01 V/cm. No electron beam.

Upper trace: Cu:Ge

Lower trace: InSb

Note: This display is limited by the bandwidth of the 555 oscilloscope.

however, their sensitivity at 3μ was substantially improved over the original design requirements. These devices, installed in liquid He Dewars, were checked for response time with a 20 psec Nd:glass oscillator and found to have an inverse bandwidth corresponding to about 5.0 nsec. The data to be reported later will, unless otherwise specified, be exclusively that collected with the Cu:Ge devices. Figure 20 shows a typical arrangement of optical components used for detection and monochromatry.

E. FAST FILL SYSTEM

A particular hazard associated with chemical lasers is a tendency for various mixtures of fuel and oxidizer to detonate spontaneously. For this reason rather elaborate precautions were taken to permit complete remote control of all gas handling including filling the amplifier, mixing the gases, pressure monitoring, detonation, pumpout, and gaseous helium purge.

The key apparatus necessary to accomplish this task is a fast fill system. This device allowed precise pressure and stoichiometry control over a range of 20-80 Torr of explosive mixture. To permit the desired firing rate, it was necessary to introduce the fresh charge immediately before firing to minimize prereaction with incompletely removed explosion products from a previous firing. Similarly immediate exhausting of spent gases, followed almost simultaneously with a clean helium gas purge, was necessary to eliminate the residence time of the chief reaction product, HF.

The fast fill system was of a general purpose design that permitted mixing any pair of high vapor pressure fuels and oxidizer by imposing a constant pressure on the upstream side of preset metering valves. Some of these fuels and oxidizers, not including $\text{NF}_3\text{-H}_2$, were unstable with respect to spontaneous exothermic decomposition. It was therefore necessary to minimize any friction that might serve to detonate the gases. Figure 21 shows a simplified schematic of the system for a single gas. The symmetry of the system is such that it may be imagined extended to any number of gases.

The regulators for the pusher gas and fuel/oxidizer gas are set to the same pressure. The operation is quite simple. After remote evacuation of the storage and metering regions, valve 1 is opened to allow fuel/oxidizer gas to fill the storage tube to the preset regulator pressure. Valve 1 is then closed. The laser fill command then simultaneously opens valves 2 and 3 for a preset length of time. The function of the pusher

Fig. 20. Electron beam driven chemical laser system.

Fig. 21. Schematic of smallest functional part of fast fill system.

(argon gas) is to impress a fixed pressure of active gas on the high pressure side of the needle valve (N.V.) so as to keep a steady flow rate essentially independent of the amount of fuel/oxidizer exhausted. After the preset flow period both valves 2 and 3 close simultaneously leaving the storage tube filled (in the optimum case) with only argon gas. The laser fill valve (not shown in this figure) is then closed and the laser is fired. Exhausting through a separate pump-down path prevents explosion products from ever contaminating the fill section of the apparatus, Fig. 22.

Typical operating pressures in the storage tube were 30-50 psia. Consequently for low pressure laser fills this system was necessarily quite wasteful of reactants. At high pressure amplifier fills, however, this was not the case. The storage tubes as shown in Figs. 21-23 are long and slim in order to minimize mixing of the pusher gas with the pushed gas. The fact that argon impurities were quite small was verified by mass spectrometer studies performed for worst case conditions (long flow times). Figure 23 schematically represents the system used in this experiment.

Valves with common numberings are always operated in pairs (a single solenoid controls both valves).

Valves 4 facilitate pumpout of the system by bypassing the needle valves with a high conductance path. The entire system is constructed from high pressure stainless steel tubing, valve bodies were all 200 psig stainless steel, and all components with the exception of the needle valves could stand pressurization to 2000 psig. Needle valves were limited to only 150 psig across the seat to guarantee 1×10^{-10} std cm^3/sec helium leak rate. This was never a problem since pressure differences in excess of 50 psig were never used.

The system was carefully interlocked so that it was virtually impossible to raise the laser pressure to the 50 psig setting of the regulators. The system was fail-safe in the sense that either a power failure or air pressure leak rendered the system harmless with respect to leaking explosive or toxic gas into the experimental area.

The entire gas handling system, the laser amplifier, and the pressure detection systems were enclosed in a chemical hood that was capable of safely withdrawing and exhausting 5 lb of NF_3/H_2 mixture.

Each arm of the gas fill system was individually calibrated for the particular gas under test so that mixture ratios could be preset by rotating the needle valve micrometers to indicated numerical values. A typical calibration run is shown in Fig. 24.

Fig. 22. Fast fill system/gas handling plumbing.

- A: Hydrogen metering section (fast fill system)
- B: NF_3 metering section (fast fill system)
- C: Fast fill output tube (mixed gases to amplifier)
- D: Barocell pressure monitoring device

X = Pneumatically open; spring loaded close; Nupro valves

Fig. 23. Functional schematic of fast fill system.

Fig. 24. Typical fast fill system calibration data.

The curves shown in Fig. 24 were determined by flowing one gas at a time with the pusher section activated. Each point represents the following sequence:

- evacuate fill system,
- close valves 1, 2, 3,
- load storage manifold
- flow gas A or B with particular needle valve settings for a time = t_1 ,
- measure amplifier pressure,
- exhaust and pump out amplifier system,
- return to a.

The nonzero ordinate at $t=0$ arises because it is impossible to construct the system without "dead volume" between the needle valves and the main storage exhaust valves (3). Thus, if valves 3 are opened at all, a small volume of gas leaks through the needle valves. This places a lower limit on the useful operating range of this system.

After the metered gases leave the output "tee" of the fill system, they proceed by a circuitous path through an all metal line and valve arrangement to the laser amplifier proper. It was important, at the outset, to determine whether the total pressure in the amplifier, after an "on time" of the fill system, would correspond to the sum of the two ordinates shown in Fig. 21 and whether the gases, by virtue of their low conductance paths to the amplifier, would mix intimately. Fortunately, both the answers were in the affirmative.

The sum of the individual pressures equalled the final pressure to within $\pm 3\%$ as determined by experiment. The amplifier was filled normally using the

fast fill system. The "fill" valve located at the amplifier was then closed, thereby isolating the amplifier. A sample of the (unexploded) amplifier gas was flowed into an infrared cell and scanned in an infrared spectrophotometer for the dominant NF_3 peaks (1870 and 1800 cm^{-1}). The peak absorption was then compared with previously calibrated samples to determine the quantity of NF_3 in the amplifier gas. By subtraction it was then possible to verify that the ratio of NF_3/H_2 was that determined by the calibrations shown in Fig. 24 above.

As a further check for the presence of the monatomic pusher gas, a sample whose pressure and volume was known was condensed (NF_3 , Ar) over liquid nitrogen and the uncondensed gas pressure (H_2) was then remeasured. This technique checked with spectroscopy to within 1.0% (the experimental error) thus indicating that at most 100 ppm Ar was present in the amplifier sample.

In order to achieve high total pressure fills under strongly nonstoichiometric conditions, (e.g. 8/1 NF_3/H_2) it was necessary to have large needle valve openings for NF_3 and small openings for H_2 because of its molecular size. The valve timers were typically set to operate for 5-8 sec. Under the strongly nonstoichiometric conditions discussed above, it was observed that the argon concentration rose to $\sim 5\%$ of the total pressure as verified by mass spectrometer studies.

F. ELECTRICAL AND MECHANICAL INTERCONNECTIONS

The combination schematic and flow diagram shown in Fig. 25 illustrates the scheme used for coincidence timing of the oscillator pulse, electron beam pulse, and the guide field solenoid. It should be noted that the oscillator is run at a fixed repetition rate of about 2.5 pulses/sec with SF_6/H_2 mixture ratios chosen to optimize the pulse shape for the particular investigation undertaken. The repetitively pulsed oscillator was deemed necessary in order to establish steady state thermal conditions and flow mixtures. The entire firing system was enabled by a mechanical (camera-type) shutter that served the dual functions of permitting only one oscillator pulse to traverse the amplifier and initiating the triggering sequence. The primary reason for admitting but one oscillator pulse was to prevent the calorimetry from integrating a large number of pulses before the amplifier fired.

Substantially all of the timing and triggering electronics were located in a control room area behind

3 ft thick interlocking concrete blocks. Exceptions to this rule were the oscillator firing pulser and the Febetron trigger generator. These were located inside the "blockhouse" directly adjacent to their respective driven units. All the detection equipment, oscilloscopes, monochromatry and calorimetry were located in a double walled copper mesh screen room with "portholes" cut in solid copper plates to allow the light signals to enter. The only nonoptical signals to enter the screen room were those of the capacitive voltage divider (potential across field emitting diode) and scope triggers from a monitor output on the electron beam triggering chassis. Screen room effectiveness is demonstrated by noting that peak-to-peak noise with the screen room closed was < 1.0 mV. With the door open ≥ 20 V peak-to-peak signals were common.

In addition to the electrical equipment directly related to the fast-fill system, a switching array permitted remote operation and monitoring of the entire fill and pumpout procedure. This equipment was designed in a master-slave configuration such that completely identical operations could be performed inside the experimental area and in the control room. A photo of the chassis involved appears in Fig. 26.

Figure 27 illustrates the overall mechanical/physical arrangement of the experimental area. The high magnetic field strength, associated with the pulsed guide field and internal electron beam guide magnet, required that the entire amplifier be constructed of nonmagnetic material. The optical bench for the amplifier hardware was a tool-room-quality granite table isolated from the floor by a stack of alternated wooden blocks and rubber pads. The table supporting structure, of all steel construction, was far enough from the field sources to make the effects of magnetic forces unobservable.

The path length from the oscillator output mirror to the detector is of the order of 30 ft. For this rather sizable propagation distance it was necessary to eliminate air currents insofar as possible. Failure to do so produced noticeable wandering of the oscillator beam caused by index of refraction variations along the optical path. With proper air baffles it was possible to reduce this motion to rms angular deviations of 10^{-4} rad (or 1 mm output spot excursions). The time variations of this effect were slow ($\sim 1/2$ sec) and therefore utterly negligible during the 1 μsec over which the typical experiment was run.

The experimental area, as indicated in Fig. 27, was entirely enclosed by 3-ft thick concrete walls and a 16-in. thick wood ceiling. It therefore exhibited a

Fig. 25. Overall electrical timing and interconnection scheme.

Fig. 26. Experiment control electronics

- A: Master clock
- B: Timing chassis
- C: Fast fill system control panel
- D: Remote valve control panels
- E: Amplifier pressure monitor

Overall Physical Arrangement

Fig. 27. Overall mechanical view of experimental area.

"high Q" with respect to acoustic disturbances generated by passing trucks or loud noises generated in close proximity to the experiment. The oscillator cavity stability was the element most seriously affected by these phenomena. Active cavity stabilization was judged quite difficult for a pulsed laser and therefore not attempted. It was necessary to resort to working with the system during its stable periods. These would last several minutes at a time, after which we restabilized by piezoelectrically adjusting the cavity length.

The usual precautions attendant with operating in high noise environment were taken. For example:

- Line filters. These included both the lumped L-C variety and the inductive common-mode rejection techniques used to discriminate against ground noise carried by ground sheaths.
- Signal isolation by 1:1 isolation transformers.
- Single point grounding.
- Specially designed high level (± 15 V) digital logic.
- Physical shielding (lead) of sensitive electronics and detectors.
- Careful selection of oscilloscopes, trigger generator, etc., for their inherent resistance to electromagnetic effects.

G. VACUUM SYSTEMS

It was originally intended to use liquid-nitrogen-trapped mercury diffusion pumps to evacuate the amplifier and fast fill systems. These pumps were soon rejected because of the appearance of mercury vapor throughout the system and the hazard of occasional contact between unexploded gases and the diffusion pump traps. This error required careful warming of the traps to remove the condensed gases and then restarting the trap cooling and pumping process. This would consume the better part of a working day.

Fortunately a 400 l/sec turbomolecular pump became available. The diffusion pumps were removed from the system and a new vacuum manifold was constructed. The virtues of the turbomolecular pump were that it produced its rated pumping speed independent of pressure from 10^{-3} – 10^{-9} Torr, was insensitive to momentary large gas loads (e.g., exposure to the ambient atmosphere), had negligible back diffusion of lubricating oils, required no down time for maintenance. After about 20 exposures to explosion products (the amplifier tube was never turned on to the turbo pump system until the system was roughed out to $\approx 50 \times 10^{-3}$ Torr) pumping speed did

suffer in the sense that the pump throat pressure levelled off at high pressure (10^{-7} Torr) for about twice as long as after the first exposure of the day. This effect was accentuated the nearer to stoichiometric the explosive mixtures became. This indicated that HF produced some product of rather low volatility in and around the pump manifold. The primary cause of the temporary pressure plateau was a glass-enclosed ionization gauge mounted on the pump inlet manifold, with SiF_4 the reaction product.

H. CALCULATIONS

Low Energy Oscillator Mode

The cavity length was set as near to 1.50 m as possible. A grating (Baush and Lomb #35-63-05-720) functioned as the back ($> 90\%$) mirror and a 3.0 m silicon 50% mirror as the output device. The output mirror was of a meniscus type, the output face of which was antireflection coated 3μ .

The cavity mode structure can be represented by the following equation:^{12, 13}

$$\Delta \nu_{\text{cavity}} = \left[q + (m + n + 1) \frac{\cos^{-1}(g_1 g_2)}{\pi} \right] \frac{c}{2L} \quad (6)$$

where $g_1 = 1 - \frac{L}{R_1}$

$$g_2 = 1 - \frac{L}{R_2}$$

q, m, n = longitudinal, transverse mode numbers respectively

c = velocity of light

R_2, R_1 = mirror radii of curvature

For this case:

$$g_2 = 1; g_1 = 1 - \frac{L}{2L} = \frac{1}{2}; g_1 g_2 \approx \frac{1}{2}, \cos^{-1} \frac{1}{2} = \frac{\pi}{3}$$

$$\begin{aligned} \Delta \nu_{\text{cavity}} &= (q + (m + n + 1) \frac{2}{3}) \frac{c}{2L} \\ &= (q + (m + n + 1) \frac{1}{3}) 10^8 \text{ Hz.} \end{aligned} \quad (7)$$

giving axial mode spacing of 10^8 Hz.

Also of interest are the spot sizes at the grating and output mirrors as well as the diffraction limited beam spread. The general equations for Gaussian beam propagation in a cavity of length L and mirror radii R_1 and R_2 are:

$$w_1^2 = \frac{L\lambda}{\pi} \sqrt{\frac{g_2}{g_1(1-g_1g_2)}} \quad (8)$$

$$w_2^2 = \frac{L\lambda}{\pi} \sqrt{\frac{g_1}{g_2(1-g_1g_2)}} \quad (9)$$

$$g_1 = 1 - \frac{L}{R_1} = 1 - \frac{1.50}{3.0} = \frac{1}{2} \quad (10)$$

$$g_2 = 1 - \frac{L}{R_2} = 1 - \frac{1.50}{\infty} = 1 \quad (11)$$

Substituting these values for g_1, g_2 into Eqs. (8), (9) above gives

$$w_1 = \left(\frac{2L\lambda}{\pi} \right)^{1/2} = 1.70 \text{ mm} \quad (12)$$

$$w_2 = w_0 = \left(\frac{L\lambda}{\pi} \right)^{1/2} = 1.20 \text{ mm} \quad (13)$$

where w_1 = spot size at output mirror, w_2 = spot size at grating, where w_0 = minimum beam diameter; defining

the diffraction angle $\theta_d = \frac{\lambda}{\pi w_0}$ gives $\theta_d = 8.0 \times 10^{-4}$ rad.

Since the oscillator output window is approximately 1.0 in from the entrance to the amplifier section, and the amplifying section is 60 cm long, the average output spot diameter as it traversed the amplifier was taken as ≈ 2.7 mm. At various times during the course of this study, reflecting and refracting telescopes were used to enlarge the beam diameter to fill the entire amplifier aperture. The experimental results with and without beam expansion devices revealed no qualitative differences. The extra optics were difficult to align and were of such suspect quality that their use was discontinued. In cases where large apertures were required (e.g., the high power oscillator mode for saturation of amplifier to extract total energy) it was found that high order oscillator modes did the job adequately.

Cavity Losses

Using the tables given by Fox and Li¹⁴ one can estimate the cavity diffraction losses due to:

The Unapertured Cavity The mirrors are 5.08 cm diameter; cavity length 3.0 meters; wavelength = 3.4×10^{-4} cm.

The Fresnel number (N) of the cavity is $\frac{a^2}{\lambda L} \approx 70$ where $a = d/2$; d = mirror diameter; λ = wavelength; L = cavity length. The losses for this high Fresnel number cavity can be neglected (loss < .01%).

The Apertured Cavity Aperturing is required to constrain the oscillator to the TEM₀₀ mode. Experimentally the aperture diameter required for TEM₀₀ performance was measured to be 4.5 mm. Thus the Fresnel number for this case is:

$$N = \frac{(2.25)^2}{3 \times 10^{-4} \cdot 3 \times 10^2} \approx 0.562$$

$N = 0.562$ implies a loss of about 3%/pass.

Cavity Polarization

The grating was placed in the holder with the rulings vertical; this produced a preferred horizontal polarization. The oscillator and amplifier Brewster angle windows were aligned relative to the horizontal polarization so as to minimize reflection losses throughout.

Brewster Window Losses

These losses for sapphire at 3μ are estimated to be about 1%/window; 2 windows imply 2%/pass.

Grating Losses

The grating is blazed at 2.81μ with a manufacturer's quoted efficiency in excess of 90%. The transitions studied were at approximately $\lambda = 2.76 \mu$. It is reasonable to estimate the grating losses at < 10%.

The total cavity losses (excluding output coupling) are therefore estimated to be $\approx 15\%$ /pass.

The silicon output mirror was coated to allow 50% reflection at 3μ .

Oscillator Linewidths

The oscillator was run in two separate configurations; low pressure, low energy input (0.5 J/pulse); high pressure, high energy input (30 J/pulse). Low pressure mixtures: 20 Torr total with 16 Torr SF₆; 4 Torr H₂. High pressure mixtures: 120 Torr total with 96 Torr SF₆; 24 Torr H₂.

The Doppler width for the oscillator is easily calculated from the expression

$$\Delta\nu_D = \left(\frac{8kT \ln 2 \nu_0^2}{M_0 c^2} \right)^{1/2} \quad (14)$$

where $M_0 c^2$ is the molecular weight of HF in MeV = 18620 MeV.

T = translational temperature,

kT ($T \approx 300^\circ K$) = 0.025 eV = 2.5×10^{-8} MeV,

ν_0 ($\lambda = 2.7604 \mu$) = 1.087×10^{14} Hz.

Substituting, one obtains

$$\Delta\nu_D = 0.297 \times 10^9 \text{ Hz}$$

which, when compared to the axial mode spacing from Eq. (6) above shows that approximately 3 axial modes exist within the Doppler linewidth. The need for axial mode control is clearly demonstrated.

The homogeneous linewidths for oscillator and amplifier are calculated from the equations which follow and the use of Table 1 below.

The collisional linewidth is given by

$$\frac{1}{\tau_i} \equiv n_i \sigma_i \bar{v}_i \quad (15)$$

where n_i = density of i th species with which the HF collides, σ_i = is corrected collision cross section for the hard sphere collision approximation between HF and species (i), $\bar{v}_i$ = relative velocity of encounter.

The ideal gas law, $n = \frac{P}{kT}$, gives $n = \frac{P_{\text{Torr}}}{760} \frac{10^6}{kT} \text{ #/cm}^3$

$$\sigma_i = \frac{\pi}{4} [d_{\text{HF}} + d_i]^2 \cdot [\text{CF}] \text{ cm}^2 \quad (16)$$

where $[\text{CF}]$ = correction factor¹⁵ for deviation from gas kinetic collision diameters

d_i = gas kinetic diameter (cm)

$$\bar{v}^2 = (\bar{v}_1 + \bar{v}_2) = \bar{v}_1^2 + \bar{v}_2^2 + 2\bar{v}_1 \cdot \bar{v}_2$$

$$\approx \bar{v}_1^2 + \bar{v}_2^2$$

where $\bar{v}_i$ = mean speed $\equiv \left(\frac{8}{\pi} \frac{kT}{M_i} \right)^{1/2}$ cm/sec

$$v = \left(\frac{8}{\pi} kT \right)^{1/2} \left[\frac{M_1 + M_2}{M_1 \cdot M_2} \right]^{1/2} \quad (17)$$

M_i = molecular weight of molecule i .

Combining Eqs. (15), (16), and (17) gives

$$\frac{1}{\tau_i} = 11.03 \left(\frac{P_{\text{Torr}}}{\sqrt{T}} \right)_i [d_{\text{HF}} + d_i]^2 \left[\frac{M_{\text{HF}} + M_i}{M_{\text{HF}} \cdot M_i} \right]^{1/2} \times [\text{CF}] \text{ MHz} \quad (18)$$

where T is given in $^\circ K$

d_i is in $\text{\AA}$

M_i is in amu $\left(\frac{P_{\text{Torr}}}{T} \right)_i$ = pressure of i th constituent in Torr

The parameter values for substitution into Eq. (18) above for various collision processes are given in Table 1.

Recalling that

$$\frac{1}{\tau} = \sum \frac{1}{\tau_i} \quad (19)$$

and substituting from Table 1 into Eq. (19) for: $\text{SF}_6/\text{H}_2 = 4/1$ at 20 Torr, gives

$$\frac{1}{\tau_{\text{H}_2-\text{HF}}} = 11.74 \text{ MHz/Torr (H}_2\text{)}$$

$$\frac{1}{\tau_{\text{HF}-\text{SF}_6}} = 13.16 \text{ MHz/Torr (SF}_6\text{)}$$

$$\frac{1}{\tau} = 12.9 \text{ MHz/Torr at } 4/1 \text{ SF}_6/\text{H}_2$$

Similarly for the amplifier $1/\tau$ becomes

$$\frac{1}{\tau} = 10.3 \text{ MHz/Torr at } 4/1 \text{ NF}_3/\text{H}_2$$

Thus the homogeneous linewidth for the oscillator is about 90% of the Doppler width at this pressure.

The HF-HF collision contribution has been neglected because of the very low concentrations of HF formed in the times of interest. This assumption is justified by the calculation which follows.

Table 1. Parameter values for calculation of pertinent collisional linewidths.
F-N-F angle = 102.9°, N-F length = 1.37 Å, F-F length = 2.14 Å.
(F molecular radius taken as radial distance at which 2p shell charge distribution peaks = 0.38 Å,¹⁶)

Collision type	d _{HF} Å	d (collision partner) Å	M (HF) amu	M (partner) amu	Correction factor
HF - SF ₆	4.35	4.96 ^a	20	146	1.0
HF - H ₂	4.35	2.70	20	2	0.5
HF - NF ₃	4.35	3.50 ^b	20	71	1.0
HF - HF	4.35	4.35	20	20	2.5

^aCalculated from viscosity data using $\sigma_0 = \pi d^2 = \frac{.377}{\eta} (\text{mK})^{1/2}$ where η is viscosity in poise.¹⁵

^bEstimated from known bond angles and lengths for NF₃.

Let us assume that in a gain length of 60 cm, a small signal enhancement of 10^{40} is observed (this is consistent with computer results to be presented in a later section).

Thus $e^{g_0 L} = 10^{40} = e^{g_2}$ where g_0 is small signal gain

$$g_0 = \frac{92}{60} = (1.66) (92) 10^{-2} = 1.53 \text{ cm}^{-1} \quad (20)$$

but $g_0 = \frac{8\pi^2}{hc} |\mu|^2 \frac{\nu}{\Delta\nu} \Delta n$

Using $\mu = 0.1$ Debye = 10^{-19} esu-cm

$$\Delta\nu_D = \Delta\nu = 1 \text{ GHz}$$

$$\nu = 1.1 \times 10^5 \text{ GHz}$$

$$h = 1.05 \times 10^{-27} \text{ erg-sec}$$

$$c = 3 \times 10^{10} \text{ cm/sec}$$

$$\Delta n = N_2 - N_1 \frac{g_2}{g_1} = \text{inversion density}$$

which when substituted gives an upper bound on Δn as:

$$\Delta n \approx 1 \times 10^{14} / \text{cm}^3.$$

Thus at 100 Torr total reactant pressure the HF concentration (not all of which is excited) is ≈ 50 ppm. This justifies the assumption of negligible contribution to the homogeneous width by HF-HF collisions.

The natural linewidth (spontaneous width) is given, for completeness, by:

$$\frac{g'}{\tau_{\text{spont}}} = \frac{4e^2 \omega^3 |X_{v'v}|^2}{hc^3} \quad (\text{Ref. 13}) \quad (21)$$

where $\omega \approx 6.28 \times 10^{14}$ ($\lambda = 3 \mu$) and

$$|X_{v'v}|^2 = v' |X_{10}|^2 S_J \cdot F_{v'}^{J'} \quad (\text{Ref. 17}) \quad (22)$$

$$X_{10} = 0.105 \text{ Debye}^{18}$$

g' = degeneracy (multiplicity of upper state)

$$S_J = J \text{ for P transitions}^{18}$$

and

$$\frac{1}{\tau_{\text{spont}}} \approx 128 J v' (\text{sec}^{-1}) \quad (23)$$

which for P (4) 2 → 1

$$= 1.02 \text{ kHz.}$$

Mechanical Stability

As discussed above, the oscillator for the experiment was mounted on a 1.5 m Ealing rail (aluminum). If one assumes the stability criterion that the cavity not change length by more than one wavelength due to thermal expansion of the rail (conservative) one calculates

$$\Delta T (^\circ\text{F}) \leq \frac{\Delta L}{L} \frac{1}{\alpha} \approx 0.15^\circ\text{F} \quad (24)$$

where

$$\Delta L = 3 \mu\text{m}$$

$$L = 1.5 \text{ m}$$

α = coefficient of thermal expansion¹⁹

$$\approx 13 \times 10^{-6} / ^\circ\text{F}$$

A temperature stability of $\pm 0.1^\circ\text{F}$ was quite difficult to achieve and its control was therefore not attempted. One was forced to take stability where it came and retune the cavity after each firing.

Dose-Depth Calculations

Assumptions:

- Range of the electrons is large compared to areal density through which electrons are made to pass.
- Electrons travel unperturbed by pulsed guide field until they enter the containment region as defined by the entrance plane of the reaction pipe.
- Electrons proceed in the gaseous medium in such a way as to suffer predominantly small angle scatters. This is equivalent to saying that they remain relativistic throughout their traversal and that ionizing collisions with valence electrons represent the dominant transfer mode to the chemical medium. This also implies that the integrated path length is of the order of the geometric length of the tube and that deviations from simple dE/dx absorption can be explained by other than straight line trajectories.

Under these assumptions; one can give an expression for the range of these electrons as:²⁰

$$R(\text{gm/cm}^2) \approx 0.542 E - 0.133 E > 0.18 \text{ MeV} \quad (25)$$

for $E = 1.40 \text{ MeV}$

$$R \approx 0.626 \text{ gm/cm}^2 \quad (26)$$

Since reactant pressures never exceeded 200 Torr in the case of NF_3/H_2 , it is a conservative approximation to calculate the areal density of 200 Torr of pure NF_3

$$(\text{At wt})_{\text{NF}_3} = 71 \text{ amu}$$

$$\begin{aligned} \text{Molecules/cm}^3 @ 200 \text{ Torr} &= \frac{200}{760} 2.4 \times 10^{19} \\ &= 6.3 \times 10^{18} \end{aligned}$$

$$\rho_{\text{NF}_3} @ 200 \text{ Torr} = 0.74 \times 10^{-3} \text{ gm/cm}^3. \quad (27)$$

Taking 75 cm as the total length through which the beam must travel in NF_3

$$\rho_{\text{NF}_3}^* = 5.55 \times 10^{-2} \text{ gm/cm}^2 \quad (28)$$

where ρ^* is areal density.

The beryllium mirror is $43.2 \times 10^{-3} \text{ cm}$ thick and is inclined at 45° with respect to the beam axis. The structural ribbing of the mirror completely shadows 10% of the beam.

Calculation of rms Scattering

Various obstructions to free electron beam propagation necessarily exist between the beam source and the entrance to the amplifier section. These are itemized as

- The electron tube output window (1.5 mil titanium).
- The pressure seal separating explosive gases from the electron tube face (4 mil titanium)
- The reactants contained in the "dead region" prior to effective electron containment by the magnetic guide field. A worst case condition for the purposes of calculation is 200 Torr of NF_3 . The "thickness" of the NF_3 layer is 10 cm.
- The beryllium turning mirror ($43.2 \times 10^{-3} \text{ cm}$ beryllium).

The equation for rms scattering angle for relativistic electrons is given by Fermi²⁰ as:

$$\sqrt{\theta^2} = \left[\frac{8\pi NDZ^2 z^2 e^4}{v^2 p^2} \ln \left[\frac{a_0 v p}{2Z^{4/3} z c^2} \right] \right]^{1/2} \quad (29)$$

where D = distance of traversal

N = number of atoms/cm³

z = charge units of projectile (1 for electrons)

Z = charge units of target

e = electronic charge

$vp \approx cp \approx$ kinetic energy of projectile

a_0 = Bohr radius

Calculations show²⁰ that for materials of interest, the logarithmic factor is of order 10.0. Simple manipulation produces

$$\theta_{\text{rms}} = 1.77 \frac{Z}{E} \left(\frac{\rho D}{A} \right)^{1/2} \text{ rad} \quad (30)$$

where the units are:

E in MeV

ρ in gm/cm³

D in cm

Z = atomic number of target

A = atomic weight of target in amu

For 4 mil Ti = 3.8×10^{-3} cm one obtains

$$\Delta\theta_{rms} = 0.907 \text{ rad} = 51.8^\circ.$$

For 43.2×10^{-3} cm Be one obtains

$$\Delta\theta_{rms} = 28.6^\circ.$$

For 10 cm of NF_3 @ 200 Torr one obtains

$$\Delta\theta_{rms} = 0.115 \text{ rad} = 6.2^\circ - (\text{negligible}).$$

Thus for a 4 mil titanium diaphragm placed 3 in. from the onset of the guide field, taken as 1 coil diameter in from the coil start, one can consider that the energy lost in arriving at the reaction tube is simply a beam divergence effect with the energy lost in scattering in 200 Torr NF_3 and in the Be diaphragm being initially neglected. Figure 28 shows the geometry for this calculation.

Magnetic Guide Field Design

It is assumed that, in the event of a 90° scatter by a 1 MeV electron, a sufficiently strong axial B field would be present to constrain the scattered electron to a circular path whose diameter would be ≤ 1.0 cm. In this calculation it is assumed that the scattered electron is free and that during an orbit it is not re-scattered. This assumption is poor and results in a requirement for higher fields than those calculated below. On the other hand, assuming a V_L corresponding to 1 MeV is extremely conservative and the field thus calculated will be, experimentally, entirely adequate. Force balance

$$\frac{q}{c} \left(\frac{v}{B} \right) = \frac{mv^2}{R} \quad (31)$$

or

$$B = \frac{c}{q} \frac{mv}{R} = \frac{c}{q} \frac{p}{R}.$$

Fig. 28. Geometry for scattering loss calculation.

But recalling

$$W^2 = p^2 c^2 + (m_e c^2)^2 \quad (32)$$

with $W \approx 1.0$ MeV

$m_e c^2 \approx 0.511$ MeV

one obtains

$$pc \approx 0.86 \text{ MeV} = 1.37 \times 10^{-6} \text{ ergs.}$$

Thus

$$B = \left(\frac{1}{qR} \right) 1.37 \mu\text{G.} \quad (33)$$

Using

$$\begin{aligned} q &\approx 4.8 \times 10^{-10} \text{ esu} \\ R &\approx 0.5 \text{ cm} \end{aligned}$$

the B resulting is

$$B \approx 6 \text{ kG.}$$

The circuit to give such a field is the simple R-L-C arrangement shown in Fig. 29.

Fig. 29. Lumped circuit used to generate guide field.

where L is an excellent approximation to an infinite solenoid (length to diameter ratio (10/1)) whose inductance is given by:

$L = 19.2 \mu\text{H}$, R-L-C Bridge ELI Model #2500A

$R = 50 \text{ m}\Omega$, R-L-C Bridge ELI Model #2500A

$C' = 5.0 \mu\text{F}$ (Note: There are 4 capacitors of $5.0 \mu\text{F}$ each in parallel, each with an internal inductance of 80 nH . Thus $C = 4C' = 20 \mu\text{F}$).

$$H(\text{gauss}) = \frac{4\pi n i}{10} \quad (\text{Ref. 19}) \quad (34)$$

where $n \approx \text{turns/cm} = 0.688$.

Using 6 kG for H gives

$$I = 7.3 \text{ kA.}$$

The solution for the R-L-C circuit in Fig. 29 above is straightforward and satisfies the well known differential equation

$$\ddot{Q} + \frac{R}{L} \dot{Q} + \frac{1}{LC} Q = 0, \quad (35)$$

subject to the initial conditions

$$Q(0) = Q_0 = CV_0 \text{ and } \dot{Q}(0) = 0.$$

The method of Laplace transforms gives

$$Q(s) = \frac{Q_0 s}{s^2 + \nu s + \omega^2} + \frac{Q_0 V_0}{s^2 + \nu s + \omega^2}$$

where

$$\nu = R/L, \quad \omega = \frac{1}{LC}.$$

The time domain representation for $i(t) = \frac{dQ(t)}{dt}$ is:

$$i(t) = \frac{Q_0}{2\omega'} \left(\omega'^2 + \frac{\nu^2}{2} \right) \exp \left[-\frac{\nu t}{2} \right] \sin \omega' t \quad (36)$$

where $\omega' \equiv (4\omega^2 - \nu^2)^{1/2}$.

Taking the derivative of i with respect to time, setting it to zero, and solving for $t_{\max}$ gives $i_{\max}$ as

$$\begin{aligned} i_{\max} &= \frac{CV_0}{2\omega'} \left(\omega'^2 + \frac{\nu^2}{2} \right) \exp \left[-\frac{\nu}{2\omega'} \tan^{-1} \left(\frac{\omega'}{\nu} \right) \right] \\ &\times \sin \left[\frac{1}{2} \tan^{-1} \left(\frac{\omega'}{\nu} \right) \right]. \end{aligned}$$

Assuming $\nu \ll \omega$ implies $\frac{L\omega}{R} \gg 1$ for $|L| = |C|$, which is very nearly true in this case, results in the requirement:

$$\frac{1}{R} \gg 1.$$

But $\frac{1}{R} \approx 20$, therefore in this approximation $\omega' \rightarrow 2\omega$

$$\begin{aligned} i_{\max} &\approx CV_0 \sin \left(\frac{\pi}{4} \right) = 0.707 \frac{CV_0}{LM} \\ &= 0.707 \frac{C}{L} V_0. \end{aligned} \quad (37)$$

For this system, where 15 kV charging voltage was routinely used, Eqs. (37) and (34) give:

$$i_{\max} \lesssim 10 \text{ kA} \quad (38)$$

$$B_{\max} \lesssim 8.2 \text{ kG.} \quad (39)$$

It is shown in Sec. II-C that the diameter of the electron beam exceeds by 50% that implied by the $B_{\max}$ of result (39) above. This result is to be expected because of the effects of scattering and, to a lesser degree, electrostatic repulsion generated from the net negative charge of the beam interior during plasma formation times. Experimentally it is observed that $r \propto \left(\frac{1}{B}\right)^{1/2}$.

Formation of Fluorine Radicals

The details of the dynamic interaction of intense, magnetically guided, relativistic, electron beams with high pressure (20-200 Torr) complex molecular systems like NF_3 is not understood in minute detail. It is known,²¹ however, that during the formation and propagation of such a beam the secondary electrons produced by direct interaction of NF_3 with 1.2 MeV primaries generate substantial collisional ionization, are accelerated to produce avalanche effects due to nonuniform ionization density, and, in this case, are inhibited from normal diffusion by the existence of an intense ($\approx 10 \text{ kG}$) axial magnetic field. It was not the intent of this study to produce detailed information (e.g., electron density vs. time) on the state of this plasma, but rather to produce an initiation scheme that could reasonably be expected to be uniform throughout the volume of the laser vessel.

In Secs. I and II it is shown, through the use of open shutter photography, calorimetry, and isodensitometry, that a uniform energy deposition ($\pm 20\%$ along the tube axis) was achieved. For future comparisons with calorimetry, however, some calculations of the energy delivered are presented. The average energy per electron is $\sim 1.4 \text{ MeV}$ when it leaves the electron tube exit plane; passing through the burst diaphragm and the beryllium turning mirror degrade that average to 1.2 MeV.

If one assumes that the integrated electron path length in the amplifier is large compared to the electron range and that the total path length is approximately the geometric length, one calculates the energy lost per electron in traversing the amplifier as:

$$\frac{\rho}{R} (1.2 \times 10^6) \text{ MeV/cm electron} \quad (40)$$

where ρ is the gas density (gm/cm^3) and R is the range of the electrons (gm/cm^2). Recalling that the number of electrons generated is

$$\frac{I_{\text{av}}}{4\pi} t_p A = \frac{2.25}{4} \times 10^{15} \text{ electrons} \quad (41)$$

where $I_{\text{av}} = 4.5 \text{ kA}$.

t_p = average electron pulse length = 80 nsec.

A = No. of electrons/Coulomb = 6.25×10^{18} .

The factor of 1/4 in Eq. (41) above is to account for geometric factors and attenuation before the beam arrives at the entrance region. One obtains, for the total energy loss

$$E_{\text{lost/cm}^3} = 2.14 \times 10^{20} \frac{\rho}{R} \text{ eV/cm}^3. \quad (42)$$

Using the range (R) appropriate to 1.2 MeV electrons, and recalling that about 30 eV is spent for each ion-electron pair, the number of secondary electrons of $\sim 15 \text{ eV}$ average energy is given as

$$\text{Ion pairs/cm}^3 = 1.33 \times 10^{19} \rho. \quad (43)$$

Thus for 100 Torr NF_3 (neglect secondaries generated by H_2) in a sample amplifier charge, the secondary electron density becomes:

$$N_e = 5 \times 10^{15} \text{ electrons/cm}^3 (\rho_{100 \text{ Torr}}) \\ = 0.37 \text{ mg/cm}^3.$$

With fractional ionization

$$\frac{N_e}{N_A} = \frac{5 \times 10^{15}}{(2.7 \times 10^{19}) \left(\frac{100}{760}\right)} = 1.4 \times 10^{-3} = 0.14\% \quad (44)$$

where N_A = No. density of atoms at 100 Torr.

Calculation Pertinent to Magnetic Field Diffusion

In Sec. I-C it was mentioned that metallic substances were rejected for the chemical reaction vessel. The calculation given below justifies that rejection. Consider the Maxwell equations

$$\vec{\nabla} \times \vec{E} + \frac{1}{c} \frac{\partial \vec{B}}{\partial t} = 0 \quad (45)$$

$$\vec{\nabla} \times \vec{B} = \frac{4\pi}{c} \vec{J} \quad (46)$$

[where $\vec{\nabla} \cdot \vec{J} = 0$ has been assumed or equivalently, neglect displacement current] and Ohm's Law:

$$\vec{J} = \sigma \left(\vec{E} + \frac{\vec{V} \times \vec{B}}{c} \right). \quad (47)$$

Combining Eqs. (45-47) so as to eliminate $\vec{E}$ gives

$$\frac{\partial \vec{B}}{\partial t} = \vec{\nabla} \times \left(\vec{V} \times \vec{B} \right) + \frac{c^2}{4\pi\sigma} \nabla^2 \vec{B}. \quad (48)$$

Considering the reaction tube at rest, then

$$\frac{\partial \vec{B}}{\partial t} = \frac{c^2}{4\pi\sigma} \nabla^2 \vec{B}. \quad (49)$$

Relation (49) is the diffusion equation, where

$$\frac{4\pi\sigma L^2}{c^2} = \tau = \text{characteristic diffusion time.} \quad (50)$$

L = characteristic length over which the field must diffuse. Take 0.3 cm for wall of reaction vessel.

σ = conductivity (in seconds) for iron¹⁹ $\approx 9.27 \times 10^{16}$ sec

c = velocity of light = 3×10^{10} cm/sec

$$\tau = \frac{4\pi(9.27 \times 10^{16})(0.3)^2}{9 \times 10^{20}} = 116 \mu\text{sec} \quad (51)$$

Recall however that the magnetic field is near its maximum value for only about 20 μsec . Thus field diffusion cannot take place fast enough for electron beam containment.

II. Results of Chemical Studies

A. LINEAR GAIN CALCULATIONS AND P, R BRANCH GAIN RATIOS

Measurements in the linear amplification regime ($I/I_0 = e^{g_0 t}$, $g_0 \equiv$ small signal gain coefficient) were useful in extracting overall rate data for formation of gain in the NF_3/H_2 system and, in comparing corresponding P and R branch populations, to arrive at the relative rate of chemical pumping into the $\nu=1$ and $\nu=2$ vibrational levels. Careful measurements of gain properties normally require oscillators of high stability which, preferably, operate in a continuous wave mode. Stable oscillators were not available for this study so that an approximation to the ideal was necessary. The spiral pin laser described earlier satisfied these constraints when operated in low power, long pulse mode. The long pulse mode (several microseconds of slowly decreasing amplitude) permitted stabilization of the cavity mode structure which enabled extraction of the amplifier gain history. Low power operation restricted operation to the $\Delta\nu=2 \rightarrow 1$ vibrational transition. In this mode $\Delta\nu=3 \rightarrow 2$ was rarely observed. It is noted that $\nu=1 \rightarrow 0$ performance was possible but the oscillator output was always characterized by a series of short pulses as a result of relaxation of the directly pumped $\nu=1$ vibrational level and relaxation of the $\nu=1$ population formed

by spontaneous emission from the $\nu=2$ vibrational state.

In summary, the peculiarities of the oscillator/amplifier and intercavity coupling restricted the systematic evaluation of the gain history to low lying $\nu=2 \rightarrow 1$ transitions and to stoichiometries not too different from $\text{NF}_3/\text{H}_2 = 4/1$. The higher-lying rotational transitions suffered from too high a gain, making suppression of amplified spontaneous emission impossible.

Figure 30 summarizes the small signal behavior of P(4) $2 \rightarrow 1$ transition in the range 4-20 Torr, $\text{NF}_3/\text{H}_2 = 4/1$. The plot is peak gain vs $1/P$. This curve is described by the relation:

$$pr = 8.3 \pm 1.0 \text{ nsec-atm} \quad (52)$$

where p = pressure of reactants ($\text{NF}_3/\text{H}_2 = 4/1$) in atmosphere

τ = time to maximum gain in nanoseconds.

Data for small signal gain ceases at pressures in excess of 15 Torr for the reason that amplified spontaneous emission could no longer be suppressed. Gain data was verified as linear by testing I/I_0 (I = output intensity, I_0 = input intensity) for values of I_0 larger than those used for the data taking; in all cases below 15 Torr I/I_0 was independent of I_0 .

Fig. 30. Small signal gain rise time vs $1/P$.

Chemical Rate Ratios

With some care, it was possible to cause the oscillator to operate on at least one R-branch transition $R(2) 2 \rightarrow 1$ under grating control. It was observed that this line when repeatable was quite weak and required large concentrations of H_2 relative to SF_6 (approximately $H_2/SF_6 = 1/2$). As the data in Fig. 31 demonstrate, it was possible to study the gain history of the R-branch transition only for times shorter than the onset of P-branch superradiance (amplified spontaneous emission) by the amplifier. If superradiance of the P transition corresponding to this R-line ($P(4) 2-1$) occurred, it simply served to diminish the population of the upper lasing level $\nu = 2, j = 3$, (see Fig. 32). For a given ratio of upper state density/lower state density, P-branch gain always exceeds R-branch gain and no R-branch gain appears until

$$\frac{N_2}{N_1} > 22.23$$

This explanation is completely consistent with the experimental observation that the disappearance of R-branch emission was exactly coincident with the appearance of spontaneous emission: (not R-branch).

Measurements of corresponding P-, R-branch small signal gain at the same time after reaction initiation

permitted the direct calculation N_2/N_1 , where N_2 is the population density of the $\nu = 2$ vibrational level and similarly N_1 is the density of the $\nu = 1$ level. The data presented graphically in Fig. 31 gives the normalized P-, R-branch gain as a function of pressure with stoichiometry as a parameter.

Calculation of Vibrational Occupation Numbers

The following calculation exhibits the theoretical relation between N_2 and N_1 as a function of the P and R branch gain. This calculation is performed for a pressure of 15 Torr with $NF_3/H_2 = 4/1$ and at a time of 120 nsec after the onset initiations. Assumptions pertinent to this calculation are

- Rotational equilibrium.
- Temperature of 300°K.

These assumptions are reasonable when the diluent concentration is high. (Diluent here is considered the undissociated NF_3 at early times.)

The rotational term values for the vibrating rotator given by¹⁸

$$F_v(J) = B_v J(J+1) - D_v J^2(J+1)^2 \quad (53)$$

are used, but the approximation $D_v \approx D_e = \frac{4(B_e^3)}{e^2}$ is employed where

Fig. 31. Gain vs pressure for corresponding P and R branch transitions.

Fig. 32. A pair of corresponding P and R branch transitions.

$$B_v = B_e - a_e \left(v + \frac{1}{2} \right) \quad (54)$$

$B_e = 20.939 \text{ cm}^{-1}$, $a_e \approx 0.23 \text{ cm}^{-1}$, $\omega_e \approx 4138.52 \text{ cm}^{-1}$. It can be shown²³ that the optical gain coefficient for a vibration-rotation transition $v = 2$, $J \rightarrow J+1$ in the Doppler broadened approximation is given by:

$$a_{2J+1, J+1} = \frac{8\pi^3 c^4 K_{12}}{3kT} \left(\frac{2\pi kT}{M} \right)^{1/2} \times (J+1) \left\{ N_2 B_2 \exp \left[-F_2(J) \frac{hc}{kT} \right] - N_1 B_1 \exp \left[-F_1(J+1) \frac{hc}{kT} \right] \right\} \quad (55)$$

and

$$a_{2,1}^{1,1} = \frac{8\pi^2 c^4 K_{12}}{3kT} \left(\frac{2\pi kT}{M} \right)^{1/2} \left\{ \begin{aligned} &N_2 B_2 \exp \left[-F_2(J) \frac{hc}{kT} \right] \\ &- N_1 B_1 \exp \left[-F_1(J-1) \frac{hc}{kT} \right] \end{aligned} \right\} \quad (56)$$

where a is the gain coefficient; K_{12} is the vibrational part of the matrix element, squared. Forming the ratio of Eqs. (55) and (56) above gives,

$$\frac{a_p}{a_r} = \frac{(J+1)}{(J)} \times \left\{ \frac{N_2 B_2 \exp \left[-F_2(J) \frac{hc}{kT} \right] - N_1 B_1 \exp \left[-F_1(J+1) \frac{hc}{kT} \right]}{N_2 B_2 \exp \left[-F_2(J) \frac{hc}{kT} \right] - N_1 B_1 \exp \left[-F_1(J-1) \frac{hc}{kT} \right]} \right\} \quad (57)$$

Notice that forming the ratio $\frac{a_p}{a_r}$ removes assumptions about the sources of linewidth.

Let $\frac{a_p}{a_r} = a'$; and using the following definitions

$$e^{-F_2(J)hc/kT} = \xi, \quad e^{-F_1(J+1)hc/kT} = \delta, \quad e^{-F_2(J-1)hc/kT} = \eta,$$

also assume $N_2 = pN_1$.

Solving for p produces

$$p = \frac{1}{(B_2/B_1)\xi} \left\{ \frac{a' J}{J+1} \eta - \delta \right\} \left\{ \frac{a' J}{J+1} - 1 \right\} \quad (58)$$

a' (experimental) = 3.43

$$\frac{J}{J+1} = 0.75$$

$$B_2/B_1 = 0.988$$

$$\xi = 0.31$$

$$\delta = 0.1399$$

$$\eta = 0.557$$

$$p = 2.67 = N_2/N_1 \text{ (15 Torr.)}$$

$NF_3/H_2 = 4/1$, $\tau = 170 \pm 10$ nsec after rise of electron current).

Figures 33 and 34 show typical traces from which R and P branch gains were calculated.

Fig. 33. Typical "R" branch data.

Fig. 34. Typical "P" branch data.

B. NONLINEAR AMPLIFICATION

It was desired to compare the results of the experimentation in the nonlinear regime with the current theory developed by Hopf and Rhodes.²⁴ The current state of this theory places certain restrictions on the oscillator:

- The oscillator emission is to be composed of a single cavity mode.
- The stimulating wave entering the amplifier is to be nearly plane.
- The oscillator is to be tuned to a vibration-rotation transition exhibiting gain in the amplifier medium.

The fundamental reason for these restrictions is that the equations used to describe the process are necessarily nonlinear. One does not, therefore, expect the principle of superposition to apply. If, experimentally, one sets up a condition such that the oscillator light is composed of a linear combination of signals of differing phase and amplitude, it follows that coherent (phase sensitive) processes will tend to be averaged out. It is noted that when the oscillator was tuned to allow simultaneous, high Q oscillations for a number of modes and transitions the effects to be described below were completely absent.

As described in Sec. I-B the oscillator was built and operated in a mode-beat-free, single transition manner. Stability could be achieved in the relatively hostile experimental environment for several minutes at a time. The quality of the plane wave approximation could not be directly measured because the operating characteristics of the oscillator required very low output energy pulses to achieve the required temporal purity. Further, the geometry of the amplifier test volume and the severe mechanical demands placed on the beryllium turning mirror made it experimentally impossible to examine in detail the spatial properties of the stimulating beam.

As was mentioned above in Sec. I-B it was necessary to prepare the same oscillator in a high energy output pulse configuration (≈ 30 mJ/pulse) to attempt, in a different phase of this experiment entirely, to extract the maximum possible energy from the exploding $\text{NF}_3\text{-H}_2$ gas. With the oscillator thus prepared, it was possible to qualitatively examine the spatial behavior of the oscillator beam as it entered the amplifier and

as it emerged. These data suggest that the pulse at the input to the oscillator had a 3 mm diam and roughly gaussian shape. The output pulse emerged with about a 15 mm effective diam; substantially larger than the diffraction limited divergence. The high beam divergence is attributed to the deviation from flatness of the beryllium turning mirror resulting from hundreds of exposures to the shock wave generated by the detonating explosives. Thus the "effective" average beam diameter is taken to be about 8 mm. Figures 35-38 exhibit the oscillator input at the left and the amplifier output at the right. The second "hump" in the oscillator pulse is a result of direct x-ray induced conductivity in the Cu:Ge detector crystal and was unavoidable even with some substantial lead shielding of the detector, (Fig. 39). The oscillator in Figs. 35 and 36 was being operated at quite a low output energy $<10^{-4}$ J/pulse and in Figs. 37 and 38 with 10^{-5} to 10^{-6} J/pulse, requiring maximum vertical sensitivity on the oscilloscopes for signal detection.

The signature of the amplified signal is a short, ~ 10 nsec (FWHM) high intensity pulse followed by a weaker second peak and long 50-100 nsec tail. Typically the fraction of the energy contained in the leading edge spike is from 5% - 30% of the total output energy (depending on the detailed operating conditions). When the noise due to x-ray effects is removed the remaining oscillator output signal is a decaying triangular pulse that changed slowly on the time scale of the amplifier output. The detection and display equipment were a liquid-He-cooled Ar:Ge detector and a Hewlett-Packard 183A oscilloscope with overall bandwidth capable of displaying pulses of

Fig. 35. Oscillator/amplifier traces showing nonlinear behavior at 47 Torr $\text{NF}_3/\text{H}_2 = 4/1$.

P = 95 Torr, NF_3/H_2 4/1

Fig. 36. Oscillator/amplifier traces at 95 Torr $\text{NF}_3/\text{H}_2 = 4/1$.

99 Torr NF_3/H_2 4/1 low level oscillator

Fig. 37. Oscillator/amplifier traces at 99 Torr $\text{NF}_3/\text{H}_2 = 4/1$.

108 Torr NF_3/H_2 4/1 low level oscillator

Fig. 38. Oscillator/amplifier traces at 108 Torr $\text{NF}_3/\text{H}_2 = 4/1$.

about 6-10 nsec duration. The system rise time was limited, not by the bandwidth of the 183A scope, but by the inductive nature of the circuitry associated with the detector Dewar.

The data presented below characterize the oscillator input, amplifier output features and pertinent gain parameters that result from taking ratios of peak heights and areas. All correction factors associated with filters are given for reference only and have been factored into the figures appearing in Tables 2-5.

Data selected from Tables 2 through 5 have been plotted in Figs. 40 and 41 to permit later comparison with the theoretical calculations on a code developed by Hopf and Rhodes.²⁴ Figure 40 shows typical gain versus pressure curves indicating that saturation

has definitely occurred; that is, intensity in the non-linear effect regime grows linearly with the amount of material traversed, (or linearly with pressure at a fixed amplifier length) rather than exponentially as in the range $0 < p \lesssim 20$ Torr. It is noted that the P(5) 2→1 data is suspect because of the inordinately high oscillator and amplifier coupling experienced. The P(4) 2→1 data suffered no detectable coupling and is therefore to be trusted.

Figure 41 shows the characteristic time between the first and second "spikes" as a function of pressure. Again it is seen that the time scale of events depends very nearly on $1/p$ as is to be expected from a situation that is controlled by binary collision processes. The discussion below will explain more fully the significance of these data.

Table 2. Chemical laser operation data extracted from oscilloscope traces (nonlinear amplification); P(4) 2-1 $\lambda_{\text{vac}} = 2.7604 \mu$; stoichiometry $\text{NF}_3/\text{H}_2 = 4/1$.

Pressure (Torr)	47	95	143
Spike area ^a (nsec-V)	105	200	660
Oscillator area ^b (nsec-V)	14	14	14
Amplifier area ^b (nsec-V)	1371	1870	2085
Area gain (dimensionless)	98	134	174
Peak gain (dimensionless)	300	714	2500
Contrast ratio ^b (dimensionless)	≥ 1.65	≥ 1.60	≥ 2.60
Δt (time between two peaks) (nsec)	130	72	50
τ decay (final decay) (nsec)	470	300	100

^aNormalization: An area of 1.0 nsec-V corresponds to 1.2×10^{-4} J of oscillator energy entering the amplifier section.

^bContrast ratio: Defined as ratio of spike amplitude to second pulse amplitude.

Fig. 39. Data collection area (screen room).

- A: Liquid helium cooled, copper-doped germanium detectors
- B: Perkin-Elmer E-1 monochromator
- C: Lead bricks for X-ray shielding
- D: Hewlett-Packard 183A oscilloscopes

Table 3. Chemical laser operation data extracted from oscilloscope traces (nonlinear amplification):
P(5) 2-1 $\lambda_{\text{vac}} = 2.7951 \mu$; stoichiometry $\text{NF}_3/\text{H}_2 = 4/1$.

Pressure (Torr)	19.8	36	96	130
Spike area (nsec-V)	—	—	1420	1400
Oscillator area (nsec-V)	2.2	3.3	2.14	1.74
Amplifier area (nsec-V)	738	1940	4220	4140
Area gain ^a (dimensionless)	39.4	50.6	201	237
Peak gain ^a (dimensionless)	34.3	68.0	506	733
Contrast ratio (dimensionless)	—	—	2.0	1.83
Δt (time between two peaks) (nsec)	—	—	60	35

^aGain on this transition was high enough to permit use of a narrow band transmission filter (OCLI) that passes 2.79 $\rightarrow$ 2.84. Even so, it was impossible to completely decouple the oscillator and amplifier sections.

Table 4. Chemical laser operation data extracted from oscilloscope traces (nonlinear amplification):
P(5) 2-1 $\lambda_{\text{vac}} = 2.7951 \mu$; stoichiometry $\text{NF}_3/\text{H}_2 = 7.5/1$.

Pressure (Torr)	31	70.8	108	150
Spike area (nsec-V)	—	1248	1440	1200
Oscillator area (nsec-V)	25.2	20.25	17.25	21.2
Amplifier area (nsec-V)	2074	6240	7740.0	9890
Area gain ^a (dimensionless)	82.3	375	548	561
Peak gain ^a (dimensionless)	31.1	138.6	240	300
Contrast ratio (dimensionless)	≥ 1.86	≥ 1.5	≥ 2.02	≥ 1.85
Δt (time between two peaks) (nsec)	380	~ 200	100	80

^aSame footnote as with Table 3.

Fig. 40. Area gain vs pressure for large oscillator input.

Table 5. Chemical laser operation data extracted from oscilloscope traces (nonlinear amplification);
 $P(4) 2-1 \lambda_{vac} = 2.7604 \mu$; stoichiometry $NF_3/H_2 = 7.5/1$

Pressure (Torr)	30	72	124	267
Spike area (nsec-V)	192	460	800	300
Oscilloscope area (nsec-V)	1.6	1.4	2.1	1.94
Amplifier area (nsec-V)	524	2020	1600	600
Area gain ^a (dimensionless)	153.5	675.6	378.7	148.0
Peak gain ^a (dimensionless)	130.0	657.1	1000	1111.0
Contrast ratio (dimensionless)	—	2.55	3.13	3.67
Δt (time between two peaks) (nsec)	—	~ 100	40	20

^aIn order to minimize the effects of oscillator-amplifier coupling, two narrow pass filters were placed at the oscillator output. The effective band pass was between 2.74 - 2.77 μ ; the transmission of the two filters was 23% for 2.7604 μ .

Fig. 41. Δt vs $1/p$ for two transitions.

C. ELECTRON BEAM DOSIMETRY

Figure 42 is a scan of a thin, sensitive plastic disc that bleaches proportional to the energy absorbed. The isodensitometer records density variations by a coded sequence of single dots, double dots, dashes, spaces and color changes and represents time integrated energy absorption.²⁵ The figure was obtained with the amplifier charged with 1 atm air at 15 kV charging voltage on the magnetic capacitor bank (about 8 kG).

The limb regions are at reference density and the center corresponds to a region of highest absorbed dose (or minimum density). There is a 50% density change from center to edge.

Figure 43 shows that $\sim 90\%$ of the total dose is absorbed in a circle of diameter ≈ 2 cm. This diameter may also be obtained approximately from a to-scale measurement of the emission diameter in the open shutter photograph Fig. 15b. Compare this result with the calculation on Eq. (33) and the conclusion on beam diameter in the discussion following Eq. (39).

Fig. 42. Time integrated isodose profile of electron beam.

Fig. 43. Dose distribution across amplifier diameter.

To obtain a time-integrated picture of deposition versus length down the amplifier, a sequence of experiments were run with a separate disc at each of five stations down the amplifier tube. The stations correspond to positions in the tube as pictured in Fig. 44. Figure 45 shows the result. The beam center may be seen to drift +3.5 mm (x) in horizontal deflection and -3.0 mm (y) in vertical deflection. This represents a motion along each axis of about (0.1) diameter of beam.

Fig. 44. Experimental placement of bleachable discs.

Fig. 45. Results of exposure of disc to electron beam.

In addition to discovering the spatial distribution of the beam versus distance from the source, the beam size versus magnetic guide field strength at a fixed position was also determined and is shown in Fig. 46.

The linear decrease of beam diameter with magnetic field follows the simplified analysis represented in Eq. (33). There was never any evidence of beam non-uniformity or "anomalous" absorption of the beam as might occur with a rapidly growing (e.g. two-stream) plasma instability.²⁶

D. CALORIMETRY

A carbon block calorimeter with an iron-constantan thermocouple was constructed to get a rough measurement of the energy content of the electron beam as it traversed the amplifier reaction vessel.

Parameters of carbon block: $1/3 \text{ in.}^3 = 2.047 \text{ cm}^3$
 $C_p = 0.170 \text{ cal/gm}^\circ\text{C}$
 @ 25°C ²⁷
 $\rho \approx 2.267 \text{ gm/cm}^3$
 @ 25°C ²⁷

This calorimeter has an energy of sensitivity = $0.75 \pm 15\% \text{ cal}^\circ\text{C}$ @ 25°C . The thermocouple generated $61 \mu\text{V}^\circ\text{C}$. Therefore the overall sensitivity factor is $\approx 53 \text{ J/mV}$.

Based on these data one sees that approximately 65 J are absorbed by the gas in the amplifier chamber (1 atm. air). The effective path length of the average electron can then be simply calculated by assuming that whatever the "real" path length is, it is small compared to the classical range.

The effective length X is given by

$$\frac{\rho}{R} X (E_{\text{in}}) = E_{\text{absorbed}} \quad (59)$$

where E_{in} = input energy = 151 J

$$\begin{aligned} E_{\text{absorbed}} &= E_{\text{in}} - E_{\text{out}} = 65 \text{ J} \\ \rho &= 1.3 \text{ mg/cm}^3 \text{ (air at STP)} \\ R &= \text{range of 1.2 MeV electrons} \\ &= 0.517 \text{ gm/cm}^2 \end{aligned}$$

X is thus

$$X = 171.0 \text{ cm} \quad (60)$$

Taking the geometric path length to be 60 cm we see that the magnetic confinement increased the absorption by $171/60 = 2.85$ fold. The energy deposited/cm³ in 100 Torr NF₃ is then

$$\frac{\text{PNF}_3(171)}{R} X(151) \approx 100 \text{ mJ/cm}^3$$

This agrees with Eqs. (26) and (27) which assumed a gain length of 75 cm.

Figure 47 shows the results obtained with this calorimeter. They agree within 15% with the calculation presented above.

Fig. 46. Amplifier beam diameter vs magnetic field strength.

Fig. 47. Plot of calorimeter reading vs distance down tube.

E. MAXIMUM ENERGY EXTRACTION

The oscillator described above was fitted with a gold coated back mirror and a sapphire flat for an output coupler and operated in the high energy, short pulse mode. In this mode, typical inputs to the amplifier were about 20 mJ/pulse with a pulse width of about 250 nsec (FWHM).

The amplifier was charged to about 275 Torr $\text{NF}_3/\text{H}_2 = 7.5/1$. At high pressure it was impossible to operate at near stoichiometric proportions; mechanical failure of the pressure vessel would have been certain. Measurements indicated that at 2.5 Torr the

chemical reaction resulting in laser action lasted for about 250-300 nsec.

The oscillator and amplifier were timed so that the stimulating light was on when the amplifier chemistry began and was off just after the amplifier gain disappeared. The calorimeter was placed directly at the output of the amplifier so as to receive all of the output light. Under these conditions the maximum energy extracted was ≈ 90 mJ, an energy gain $I/I_0 = 90/20 = 4.5/1$ (saturated operation).

It is noted for completeness that if the amplifier is allowed to radiate spontaneously (i.e., oscillator blocked off) under the conditions described above the calorimeter reading decreased to ≈ 40 mJ.

III. Discussion of Chemical Studies

A. REACTION RATES

The preceding section presented calculations and data that resulted in an experimental value of N_2/N_1 (N_i = population of the i th vibrational level) given by

$$\frac{N_2}{N_1} = 2.67. \quad (61)$$

The relative populations of two levels at any time depend both on activation and deactivation processes; thus one can conclude that

$$\frac{k_2}{k_1} > \frac{N_2}{N_1} = 2.67,$$

where k_i = reaction rate associated with population of the i th vibrational level. This value is to be compared with the work of Jaffe and Anderson⁴ who gave $k_2/k_1 = 1.88$ and Polyani and Tardy⁵ who gave $k_2/k_1 \geq 3.5$ at 300°K. The work of these authors was concerned with the specific reaction:

It is thus reasonable to assert that the dominant gain producing reaction in the NF_3/H_2 system is in fact reaction (62). This result is significant in that it is extracted directly from analysis of the laser output of the NF_3/H_2 system. The experimental procedure used to extract k_2/k_1 will be similarly useful in obtaining information about k_j/k_i in the event that stable cw H-F probe oscillators become available.

B. GAIN ACTIVATION RELATION

The study of various deactivation processes contributing to the loss of stored energy has been undertaken by various authors. Among the reactions studied are radical deactivation described by Eqs. (63) and (64), and molecular deactivation described by Eqs. (65) and (66).

Each of these processes described above are binary in nature and can be described by a relation of the form

$$p\tau = k \text{ (nsec-atm)} \quad (67)$$

where p = pressure of deactivating constituent in atmospheres

τ = collision deactivation time in nanoseconds

k = a constant.

This study permitted the examination of the binary assumption in the small signal gain formation process. It was found that, indeed, activation could be described by the relation:

$$p\tau_a = 8.3 \pm 1.0 \text{ nsec-atm} \quad (68)$$

where τ_a = time constant for gain buildup.

τ_a is an effective time resulting from a complex interaction of various excitation and deactivation processes. A detailed calculation, following the prescription of Curry and Kidder,²⁸ has been performed under the assumptions:

- $F \cdot + H_2 \rightarrow HF^* + H$ is the primary energy producing reaction.
- No linear chaining or chain branching chemistry occurs after the initial production of $F \cdot$ radicals by the electron beam.
- Reactions (63) through (66) are the only significant deactivators.
- The amplifier is operating in the small signal gain regime.
- $k_2/k_1 \geq 2.67$ (see Sec. III-A).

The calculation predicts the time to maximum small signal gain as a function of pressure at the stoichiometry of interest ($NF_3/H_2 = 4/1$) as

$$p\tau = 8.5 \text{ nsec-atm} \quad (69)$$

This is in excellent agreement with the 8.3 nsec figure quoted in Eq. (52). A disappointing consequence of this result is that assumption (2) above is correct. The absence of chain branching severely limits the energy extractable from the reactants. Pearson²⁹ has reported that energy densities achieved experimentally are ~ 10 joules/liter at one atmosphere (300°K). On these grounds, this chemical system is a poor competitor to existing N_2 -CO₂ laser systems.

C. MAXIMUM ENERGY EXTRACTION

The results on energy extraction at high pressure indicate that the gain of the system was so high that stimulation of the amplifier produced only moderate enhancement of the yield from spontaneous emission alone. It can only be concluded that one must resort to some sort of traveling wave device to achieve an orderly removal of stored energy. A difficulty with long wavelength (far infrared) light is that most surfaces are excellent reflectors. Excellent reflectivity, coupled with the severe restrictions placed by the chemistry on any vessel, seriously limit conditions under which high energy HF emission can be obtained.

D. KINETIC PROCESSES

Once the primary beam is off one must consider the secondary electron plasma and how it decays. The primary difficulty in such a consideration is the reaction

(Little is known in this regard about the NF_3 molecule.)

The hot secondary plasma immediately cools by ionization and dissociation producing collisions to a temperature of about ≤ 1 eV.²⁸ If it is assumed that the dissociation energy of NF_3 is about 4 eV (the energy below which an electron cannot form $\text{F}^\bullet$) one concludes that the figure of 10^{15} electrons/cm³ [Eq. (44)], if taken as the number of free fluorine radicals formed, will certainly be an over-estimate. To this author's knowledge no evidence of chaining exists in the NF_3/H_2 system. Several authors have obtained satisfactory agreement with experiment²⁹⁻³¹ assuming that the following reaction scheme is dominant

and that neither the NF_2 nor hydrogen radical contribute to further linear (thermal) chaining or chain branching.^{30, 32} Results of experiments on gain his-

tory suggest that either the equilibrated plasma electrons continue to produce fluorine radicals as in reaction (72) above or that cold HF may be re-excited to produce lingering sources of $\text{HF}^\bullet$ for periods of 200-300 nsec at 100 Torr $\text{NF}_3/\text{H}_2 \sim 4/1$ or equivalently, several μsec at pressures 20-40 Torr.

E. NONLINEAR AMPLIFICATION

Many authors, among them Hoff, et. al.³³ and Hopf and Rhodes,²⁴ have concerned themselves with the investigation of the nonlinear interactions that occur when an inhomogeneously broadened amplifying medium interacts simultaneously with an intense, coherent field and the polarization of an ensemble of radiators (the active medium). Substantial experimental work has been accomplished with negative amplifiers (absorbers). Evidence of "optical-nutation" of the effective material polarization has been observed in CO_2 by Hoff, et. al.³³ The class of effects that can be understood by the theoretical formalism (carried over from the field of nuclear magnetic resonance) applied to this problem include photon spin echo and self-induced transparency.³⁴ The comparison of experiment and theory achieved in this study established the first evidence for the so called quasi-steady state " π "-pulse³⁵ propagation in high gain media.

The calculational model with which the experiment was compared was built by Hopf and Rhodes.²⁴ The reader is commended to Ref. 24 for specific details of the code. Essential features of the code, in the version that existed prior to the results given in this study, are presented below:

1) The code treats the field classically (justified by the high photon flux for this problem) and the molecular system quantum mechanically. The coupled Maxwell and Schrodinger equations are solved numerically using the density matrix formulation under conditions that the phase and amplitude of the stimulating pulse change slowly in space and time. (Slowly is defined relative to $1/\omega$ for the time scale and $1/|k|$ for the space scale; ω = optical frequency; $1/|k|$ = wavelength.)

2) The input specified:

- Initial inversion density (or small signal gain).
- Various characteristic times (e.g. T_2 = homogeneous dephasing time $\approx 1/n\nu$, T_1 $\equiv$ natural lifetime; T_1' = intra-rotational relaxation time; T_1'' = inter-rotational relaxation time = degeneracy $\times T_1'$.)

3) T_1 , specified the maximum rate at which energy could be withdrawn from the upper level rotational reservoir. The ratio T_1''/T_1' specified the total energy stored in the bath that was potentially available for extraction.

A moment's reflection reveals that this initial version of the code could not properly specify the physical mechanisms at work within the chemical amplifier. For the experimental situation it is clear that at $t=0$ the gain was zero, (i.e., the chemistry had not yet been initiated). Further, the stimulating field was established in the amplifier just prior to the turn-on of the chemistry thereby further inhibiting the accumulation of inversion density. (These points will receive more detailed discussion later on in this section.)

The code was modified to account for physically reasonable gain build-up profiles by allowing the specification of a time dependent inversion density. Figure 48 depicts the analytical form of this pumping history, where γ specifies small signal gain growth and decay and β specifies length (in time) of maximum inversion. If $\beta = 0$ one has then specified a triangular gain profile.

For a typical example of experimental results showing amplifier output stimulated by an oscillator

Fig. 48. Gain profile for calculating performance in a chemical laser.

input whose profile is that of a slowly decreasing linear ramp, see Fig. 36.

Figure 49 is a computer calculation corresponding to the 95 Torr case, Fig. 36, without chemical gain effects included.

It is immediately seen that the signature of both figures is a short, highly peaked initial pulse followed by a second pulse of longer duration but smaller amplitude. For both cases substantially all the area (energy) is contained in the second pulse.

The striking difference between Figs. 30 and 49 is the time scale over which the second pulse develops.

Fig. 49. Computer output; amplifier response without chemical effects. Constant oscillator pulse $e^{80l} = 10^4$. $T_2 = 0.8$ nsec, $T_2' = 0.8$ nsec, $T_1' = 1$ nsec, $T_1'' = 2$ nsec, $T_1''' = \infty$, $T_1 = \infty$ (Entire pulse history shown.)

For Fig. 36 the time scale follows almost exactly the relation:

$$p\tau = 8.3 \pm 1 \text{ nsec-Torr}$$

where τ = time to maximum gain. This equation was derived under small signal gain conditions, i.e., $p \leq 15 \text{ Torr @ } 4/1 \text{ NF}_3/\text{H}_2$, where one expects a reasonable description of the unperturbed gain history of the system.

For Fig. 49 one expects the second pulse to develop with a time scale characteristic of the rotational feed-in time ($T_1 = 2.0 \text{ nsec}$ was the input parameter) and indeed this occurs. The experimental detection bandwidth corresponds to about 6-10 nsec because of the inductance associated with the particular Dewar/cable geometry available for the Cu:Ge detector. Amplitude of the initial spike is surely underestimated because of system bandwidth effects.

Figure 50 shows the calculated amplifier output that results when a chemistry risetime $\alpha = 70 \text{ nsec}$ is specified. Three features of this result are particularly noteworthy. First the leading edge spike, indicative of coherent behavior, still appears but no longer dominates, in amplitude, the long second pulse. Second, after the initial transient has subsided, the amplifier output follows the chemically produced inversion exactly. Third, there is a trailing edge perturbation

generated by the rapid decrease in gain. The trailing edge phenomenon is believed to be "real" but recall that detector resolution prevented seeing a perturbation this fast experimentally.

Figures 51-55 represent computer generated amplifier outputs for all parameters fixed as in Fig. 50 except for α (the chemical rise time). The sequence is arranged in order of decreasing α .

Figures 50 and 51 taken together clearly demonstrate the extent to which tracking of the inversion history occurs after the nonlinear perturbation subsides.

The horizontal scales of Figs. 52-55 are expanded to better show the spike development; the trailing edge performance is not shown.

As α is decreased from 70 nsec we see the spike amplitude increasing to the point where, at $7 \text{ nsec} = \alpha$, its amplitude clearly exhibits a qualitative behavior similar to the experimental results (Fig. 36). The requirement for fast rising gain (small α) was at first a source of some concern. It was difficult to imagine the gain growing faster than $1/\tau = (70.0 \text{ nsec})^{-1}$.

This troublesome requirement for an explanation of initially large $d(\text{gain})/dt$ is satisfied as follows:

Recall the assumption that only $(F^\bullet + H_2 \rightarrow HF^\bullet + H)$ contributed to gain production and that the electron beam had deposited substantially all of its initiation energy within one chemical reaction time.

Fig. 50. Computer output, amplifier response with chemical effects. Chemical buildup time = 70 nsec (triangular shape-fall time = 70 nsec). Constant oscillator pulse $e^{801} = 10^{43}$. $T_1 = 5 \text{ nsec}$, $T_2^* = 20 \text{ nsec}$, $T_1' = 10 \text{ nsec}$, $T_1'' = 50 \text{ nsec}$, $T_1''' = 20 \text{ nsec}$. (Entire chemical history shown.)

Fig. 51. Small signal gain profile used as a mockup of chemistry input to code.

Fig. 52. Calculated amplifier output with chemical buildup time = 70 nsec. Constant oscillator pulse $e^{80t} = 10^{108}$ (pulse fully developed at 10^{40}). $T_2 = 5$ nsec; $T_2' = 20$ nsec; $T_1' = 10$ nsec; $T_1'' = 50$ nsec; $T_1''' = 20$ nsec. (Expanded time scale: Only first part of the chemical history is shown.)

Fig. 53. Calculated amplifier output with chemical buildup time = 30 nsec. Constant oscillator pulse $e^{gol} = 10^{108}$ (pulse fully developed at 10^{40}). $T_2 = 5$ nsec, $T_2^* = 20$ nsec, $T_1' = 10$ nsec, $T_1'' = 50$ nsec, $T_1''' = 20$ nsec. (Expanded time scale: Whole chemical history not shown.)

Fig. 54. Calculated amplifier output with chemical buildup time = 7.0 nsec. Constant oscillator pulse $e^{gol} = 10^{108}$ (pulse fully developed at 10^{40}). $T_2 = 5$ nsec, $T_2^* = 20$ nsec, $T_1' = 10$ nsec, $T_1'' = 50$ nsec, $T_1''' = 20$ nsec. (Expanded time scale: Entire chemical history not shown.)

Fig. 55. Calculated amplifier output with chemical buildup time = 1.0 nsec. Constant oscillator pulse $e^{\text{gol}} = 10^{108}$ (pulse fully developed at 10^{cd}). $T_2 = 5$ nsec, $T_3 = 20$ nsec, $T_1' = 10$ nsec, $T_1'' = 50$ nsec, $T_1''' = 20$ nsec. (Expanded time scale: Whole chemical history not shown.)

This implies

$$\left. \frac{dN_{\text{HF}}}{dt} \right|_{t \approx t_p} \approx \left. \frac{N_F(t_p)}{\tau} \right|_{t \approx t_p} > \left. \frac{dN_{\text{HF}}}{dt} \right|_{t > t_p} \quad (74)$$

where N_{HF} = HF concentration (excited)

N_F = fluorine concentration

τ = mean time between chemical reactions

t_p = electron beam pulse duration = 80 nsec.

This argument can be made graphically as well.

Assume that Fig. 56 characterizes the long second pulse.

Taking $\tau = t_m$ is equivalent to taking the average growth rate represented by the line labelled A. Physically the coherent effect "runs away" in times of the order of the dephasing time (taken as 5 nsec for this series). In the first 5 nsec, the slope of the gain curve is more correctly represented by the line labelled B. It is clear that slope B > slope A.

Fig. 56. Chemical gain history input for computer simulation.

The excellent agreement between experiment and calculation (Figs. 36 and 55) confirmed that nonlinear, field-molecule coupling was observed. Earlier in this section the comment was made that the time from initiation to the peak of the second pulse was identical to the value obtained from studies of small signal gain behavior, Eq. (52). One concludes that once saturation of the nonlinear effect occurs, subsequent behavior of the amplifier output becomes adiabatically coupled to the gain chemistry. Reference 32 makes it clear that nonlinear coupling is favored when $d(\text{gain})/dt$ is high. This condition occurs only immediately after initiation; consistent with the assumption that chain branching chemistry is not involved, Eqs. (71 - 73).

The computer generated output, Figs. 49-55, verify the statement that amplifier output rigorously tracks the chemical gain history at late times. One can visualize the adiabatic coupling result in an alternative way. Immediately after initiation, the rate of change of gain and the gain itself are high; nonlinear coupling occurs. Once the rapidly formed inversion reservoir is emptied via the nonlinear effect, the optical field intensity/gain rate are such as to generate a faithful record of the inversion-producing chemistry.

Prior to this study, the theoretical model²⁴ was capable of predicting the existence of, and conditions for, nonlinear pulse formation/propagation. The results presented in this section are the first evidence of "steady state" pulse propagation in a high gain medium. The adiabatic coupling hypothesis/verification is entirely new.

IV. Rare Gas Studies

A. INTRODUCTION

The ultraviolet continua of the excited rare gas systems have been known since the 1930's.³⁶ These continuum emissions have also been examined more recently³⁷ and have found application as convenient light sources covering essentially the entire vacuum ultraviolet for wavelengths longer than approximately 1000Å. These continuous radiations originate from bound-free transitions of the molecular dimers (e.g., Ar₂, Kr₂, or Xe₂). In typical cases of interest the excited state is characterized by a potential function that has a substantial potential minimum at the equilibrium internuclear separation and that supports several vibrational levels. In contrast, the ground state interatomic potential is generally strongly repulsive although it does exhibit a relatively shallow van der Waals minimum at internuclear distances substantially greater than the equilibrium separation of the excited state. It is characteristic that the triplet state lies somewhat below the singlet level due to exchange. In the literature the data on He₂ and Xe₂ are the most complete although large uncertainties nevertheless do exist in the precise location of many of the potential curves even in these cases.^{38, 39} The complex nature of these molecular systems is immediately recognized by the fact that over 60 electronic states are currently known for even the simplest system, He₂⁺.

To a very good approximation, these excited molecular dimers can be regarded as Rydberg states. In this view the molecular configurations are then composed of two parts; the molecular ion core (e.g., He₂⁺) and a single excited electron orbiting largely outside of the region occupied by the core. One then has a relatively simple Rydberg series⁴⁰ characteristic of that core state. This model predicts that the equilibrium internuclear separation, the molecular vibrational frequency, and the molecular moment of inertia are determined largely by the corresponding properties of the molecular ionic core. The potential curves given by Ginter and Battino³⁹ for He₂⁺ quite strikingly indicate the validity of this approximate model. It would appear that this feature introduces a very desirable simplification into an otherwise rather complicated situation, since it should be possible to formulate meaningful estimates of matrix elements on the basis of an essentially one electron picture.

An interesting property of these systems is that continuous bands are observed with very similar characteristics in all three phases, gas, liquid, and solid. For example, the argon continuum centered near 1300Å resulting from excitation by Americium α -particles exhibits essentially identical lineshapes (within $\sim 10\%$) for all three phases.⁴¹ On the basis of this observation, one is strongly motivated to conclude that the excited species in all cases very closely resemble the gaseous dimer which is only negligibly influenced by the weak van der Waals forces of the surrounding neighbors in the liquid and solid. This immediately suggests the possibility that these systems may be successfully operated at liquid or solid density. In this connection it is useful to note that at an active density of $2 \times 10^{19} \text{ cm}^{-3}$ (~ 1 atmosphere) and assuming roughly one Rydberg per system the stored energy density corresponds to nearly 50 J/l.

Recent Soviet experiments with xenon excited by high energy electrons reported by N.G. Basov, et. al.⁴² have demonstrated the feasibility of coherent generation with these systems at liquid density. The Russian workers have also indicated in private communication that they have obtained similar results in high pressure xenon gas. It is anticipated that oscillation may be obtained from the other rare gases in a similar manner.

The basic purpose of this work is to provide a more detailed experimental analysis of the rare gas systems excited by pulsed, high current, relativistic electron beams. In order to achieve this goal we have begun experiments that enable us to measure the time resolved spontaneous emission spectrum of the material excited by the electron beam. In this way we have obtained data concerning the kinetic steps and time scales associated with these systems. Herein we present some preliminary data and analysis relating to our experiments examining Ar, Kr, and Xe at pressures from 0-5 atm.

B. EXPERIMENTAL MODIFICATION FOR RARE GAS WORK

Previous sections detail the physical and electrical arrangement used to study the gain properties of the NF₃/H₂ system, Figs. 5-27. In this section, the changes to the chemical apparatus necessary to study noble gas processes will be examined.

The electrical interconnection scheme as outlined by Fig. 25 was left unchanged. Mechanically, the following modifications proved necessary:

The Reaction Vessel

The Teflon amplifier vessel was replaced with industrial glass pipe carefully cleaned with ethyl alcohol before pump-out. As discussed earlier the teflon, while chemically inert, proved to be porous and therefore made hard vacuums $< 10^{-7}$ Torr unattainable. Glass pipe permitted base pressures of $< 5 \times 10^{-8}$ Torr and allowed safe operating conditions up to pressures of 10 atm. (Pressure capability of the glass pipe was verified by hydrostatic test of a sample unit.)

Prior to installation of the glass section, all components exposed to chemical detonation products were thoroughly cleaned and vacuum baked at temperatures in excess of 200°C for about 48 hr.

Output Optics and Line of Sight Path

The transitions of interest in the rare gas systems all lie in the vacuum ultraviolet region of the spectrum. It was therefore necessary to replace the sapphire output windows (useful at 3 μ for H-F) with LiF to provide useful transmission down to wavelengths $\sim 1075\text{\AA}$. Further, the light path connecting the output window to the vacuum spectrometer (SPEX model 1500 DP with a grating blazed at 1500Å) required evacuation. Both the line-of-sight pipe and the spectrometer were evacuated with a single turbomolecular pump (450 l/sec) to a base pressure $< 10^{-6}$ Torr.

One 90° turn was required to direct the output beam from along the electron beam path to the screen room, see Fig. 57. It was necessary to install a magnesium fluoride overcoated, aluminum mirror housed

in a vacuum chamber in an attempt to minimize absorption and scattering losses. At the time this experiment was performed no facilities existed at LLL to verify reflectivity at wavelengths shorter than 2000Å, hence no absolute intensity calculations were possible. Fortunately, there was always sufficient signal/noise available for adequate data collection and interpretation.

Gas Handling Systems

The various gases studied (Xe, Kr, Ar) were Matheison research grade, (99.995% pure). Introduction of the gases was accomplished via the all metal, prebaked fill line used in the chemical phase of this work. Pressures never exceeded 150 psia because of the pressure limitation of certain small toggle valves appearing in the system. After the initial bake-out of the system, the gas under study was flowed into the system and let stand for about 24 hr at 1 atm (absolute). This procedure forced absorption of the gas into system components that may not have been reached by the cleaning procedures discussed above. This technique helped assure the general contamination-free state of the system. As further insurance, several dozen firings of the electron beam into the "clean" system were performed to scour the surfaces with scattered electrons. Data taking began only after the cleanup procedure was complete.

Instrumentation

The primary detection system was composed of the SPEX (1500 DP) monochromator/spectrometer operated in the monochromator mode. The detection device was an Amperex, 56 TUV photomultiplier (gain $\approx 10^8$) viewing a sodium salicylate uv converter. The converter formed the spectrometer output window and vacuum/atmosphere interface. Data were displayed via oscilloscope pictures (Tektronix 7904, 2 nsec risetime) and subsequently digitized. A computer routine developed by E.P. Sims⁴³ produced the time resolved spectra appearing in Sec. V-B, below.

Because of the extreme sensitivity of the photomultiplier to ionizing radiation, extensive lead shielding of both tube and the spectrometer were required. The tube was housed in a lead "pig" providing 2.5 in. of lead shielding from all directions save for a 3/8 in. dia opening through which the sodium salicylate fluorescence could be monitored. The entire spectrometer was enclosed in 1/4 in. lead sheet.

Substantial x-radiation was to be expected in the case of the heavier rare gases where the fraction of

Fig. 57. Diagram of system interconnections.

primary loss appearing as radiation approaches 10% (Xe).²⁰

Additional lead shielding was provided in any path directly connecting the radiation source with the phototube or oscilloscope. The lead bricks were placed both beside the entrance region and reaction vessel of the amplifier and directly along the screen room walls. The average thickness of this shielding was about 25 cm. Total source-to-phototube shielding thickness including "pig" thickness $\approx$ 31 cm.

Recall that the peak x-ray energy available via the bremsstrahlung process was 2.5 MeV. The total attenuation coefficient for lead at this energy is $\approx 0.4 \text{ cm}^{-1}$.⁴⁴

The attenuation expected is therefore:

$$\frac{I}{I_0} = e^{-(0.4)(31)} = 4 \times 10^{-6} \quad (75)$$

On the other hand, the typical electron gain of this tube for the bias voltage used was 10^8 . Therefore about 400 secondary electrons for each primary are to be expected. The noise signals were never reduced to unobservable levels but in all cases the signal/photon noise $\gtrsim 50/1$.

Alignment Procedure

To assure proper alignment, the entrance region sapphire window and beryllium turning mirror used

in the chemical study were left in place. A He-Ne alignment laser was placed in the position that the spiral pin laser formerly occupied. The beam was made to shine through the entire system including spectrometer. The spot appearing at the output of the spectrometer was easily bright enough to allow precise positioning of the photomultiplier.

Pressure Diaphragm

For the lightweight noble gases (Ar, Kr, He, Ne) operation at 10 atm could be achieved with a 5 mil thick titanium diaphragm separating the pressure vessel from the electron source. With Xe, however, the diaphragm was violently deformed after one firing. The deformation was due to the high absorption coefficient of Xe coupled with its high mass (inhibited heat conduction). The high local deposition adjacent to the diaphragm produced sufficient heating and peak pressure to destroy the 5 mil diaphragm on the second exposure. Ten mils was the minimum thickness that permitted long life ≈ 100 shots at 10 atm absolute. This diaphragm "dished" out after the first firing but no further deformation occurred. When failure did finally result, an examination revealed that work hardening in the region of the most intense electron deposition accounted for the thin cracks that appeared.

V. Results of Rare Gas Experiments

A. Ar/Xe ENERGY TRANSFER

Substantial investigation^{2, 45} has recently been undertaken into rapid noble gas molecule-atom energy exchange as represented by the following reaction:

The referenced work was undertaken under conditions of relatively weak excitation (with high repetition rate) in order to study the time integrated emission spectra of the mixed systems. The signature of reaction (76) is the disappearance of the normal molecular continuum associated with $\text{Ar}_2^* \rightarrow \text{Ar} + \text{Ar} + h\nu$ when

relatively small concentrations of impurity (Xe) are added. The noteworthy feature of the work to be described below is the extremely high excitation rate available with the electron beam source at our disposal. (Again, the constant energy deposition/gram available with high energy electrons permitted homogeneous excitation of substantial gas volumes up to the pressure limits of the apparatus.)

The excitation power available is approximated by

$$E/t_p \approx 375/(80 \times 10^{-9}) \approx 5 \text{ GW}$$

where energy loss due to bremsstrahlung is considered unimportant in the Ar_2^* formation process.

Figure 58 shows the pure argon emission vs time at 1300Å (850 Torr).

Fig. 58. Argon emission @ 1300Å, 850 Torr (12 kG magnetic field). Horizontal scale: 100 nsec/cm. Vertical scale: 400 mV/cm. $S/N \geq 80/1$, where the noise (N) is defined as the residual signal with the detector blinded.

This emission, centered at about 1300Å for Ar_2^* , 1500Å for Kr_2^* , and 1700Å for Xe_2^* , has been explained by Mulliken.⁴⁰ Further discussion appears in the next section.

The addition of Xe (30 Torr) to the system while keeping the total number density fixed (850 Torr total Ar + Xe) produces the result shown in Fig. 59. Vertical, horizontal sensitivities and monochromator settings are identical in Figs. 58 and 59.

Fig. 59. Ar/Xe mixture @ 1300Å, with 820 Torr argon + 30 Torr xenon (12 kG magnetic field). Compare with Fig. 58. Horizontal scale: 100 nsec/cm. Vertical scale: 200 mV/cm. $S/N \geq 40/1$.

The threshold for near total extinguishment of the Ar_2^* continuum occurs at xenon concentration of 2000 ppm, a substantially greater impurity level than previously reported.²

In the next series of experiments, the appearance of Xe_2^* emission via the reaction (77) was examined

With the monochromator tuned to $1700\text{Å} \pm 5\text{Å}$ (still preserving the Xe/Ar concentrations at 30/820) one observes the gradual appearance of the characteristic Xe_2^* continuum emission, see Fig. 60.

Fig. 60. Xe_2^* emission (1700Å) in Ar/Xe mixture, 820 Torr argon + 30 Torr xenon (12 kG magnetic field). Horizontal scale: 100 nsec/cm. Vertical scale: 200 mV/cm.

Figure 61 is a repeat of the exposure leading to Fig. 60 but at a sweep speed of 500 nsec/cm to show the complete time development of the 1700Å emission.

Fig. 61. Xe_2^* emission (1700Å) in Ar/Xe mixture but with compressed horizontal scale, 500 nsec/cm. Cf. Fig. 60.

These results are completely consistent with conclusions of Gedanken, et. al.² except in the matter of the xenon impurity concentration necessary to accomplish complete elimination of Ar_2^* emission.

A comparison of Figs. 58 and 60 suggests strongly that the Xe_2^* emission may be the time integral of the Ar_2^* emission shown in Fig. 58. This is consistent with the proposition of very efficient transfer from

$\text{Ar}_2^* \rightarrow \text{Xe}(^1\text{P}_1)$. The $(^1\text{P}_1)$ is then expected^{46, 47} to relax to $^3\text{P}_2$ via collisional cascade. It is from $^3\text{P}_2$ that Xe_2^* is most readily formed. It was not possible at this writing to conclude how precisely the "integral" assumption was followed. Additional work⁴⁸ involving absolute intensity measurements should shed more light on this point. It is interesting to postulate the possibility of complete inversion of the $\text{Xe}(^1\text{P}_1) \rightarrow \text{Xe}(^1\text{S}_0)$ transition by this process. A conservative approximation would be to find that Ar_2^* concentration for which the rate of formation of $\text{Xe}(^1\text{P}_1)$ by the reaction

exceeds the $\text{Xe}(^3\text{P}_1) \rightarrow \text{Xe}(^1\text{S}_0) + \gamma$ emission rate (untrapped).

The untrapped transition rate for this process² (10^{-4} Torr Xe) is $5 \times 10^6/\text{sec}$.

The cross section for energy transfer from Ar_2^* to $\text{Xe}(^1\text{P}_1)$ is given² as $2.9 \times 10^{-13} \text{ cm}^2$

$$\frac{1}{\tau_{\text{Ar}_2^*-\text{Xe}}} = N_{\text{Ar}_2^*} \sigma \bar{v} = N(2.9 \times 10^{-13}) \frac{1}{8} \times 10^5$$

Thus, for the collisional rate [Eq. (78)] to exceed the $\text{Xe}(^3\text{P}_1)$ radiative rate,

$$3.625 \times 10^{-9} N > 5.0 \times 10^8.$$

This implies

$$N > 1.5 \times 10^{17}/\text{cm}^3, \quad (79)$$

where $N_{\text{Ar}_2^*} = \text{Ar}_2^*$ concentration (cm^{-3}),

σ = energy transfer cross section for $\text{Ar}_2^* \rightarrow \text{Xe}^*$
 10^{-16} cm^2 ,

$\bar{v}$ = relative approach speeds Ar_2^* , Xe cm/sec, or about 4 Torr Ar_2^* . This concentration should be easily achievable with the apparatus operated at about 10 atm of Ar.

The required Ar_2^* concentration as derived above is clearly conservative because $\text{Xe}(^1\text{P}_1 \rightarrow ^1\text{S}_0)$ is strongly allowed and radiation trapping accounts for an increase of effective lifetime of four orders of magnitude to 10 μsec at Xe pressures of 0.1 Torr.²

The existence of complete inversion should be readily apparent experimentally. One should observe

increasingly immediate and more intense emission as the concentration of absorbers approaches zero. This kind of study is presently underway.⁴⁸

B. Xe, Kr, Ar STUDIES

In this series of experiments, samples of pure Ar, Xe, and Kr were studied over a wide range of pressures. The data for this phase consisted of a series of intensity vs time traces taken with 5.0Å resolution in 50Å steps from 1100Å to 2500Å. A set of traces for each pressure of interest was taken. The photographs were then converted to digital data and, with the aid of a computing machine, time resolved spectra were obtained. It was anticipated that with this data time dependent atomic and molecular properties could be appraised. Structural strength considerations limited test gas pressure to ≤ 850 Torr. More recent work has permitted examination of molecular behavior up to 10 atm.⁴⁹

Argon

The time resolved spectra of argon at 850 Torr are illustrated in Figs. 62 and 63. Figure 62 gives the spectra for times of 50, 75, 100, 125, and 150 nsec after $t = 0$ ($t = 0$ is defined as the time at which the voltage across the field emitting diode reached 50% of its peak value). Figure 63 similarly represents argon at 850 Torr but at later times (150, 200, 250 300, and 400 nsec).

The main spectral feature of Fig. 62 centered about 1300Å is attributable to the principle continuum generated by the vibrationally relaxed transition $1^1\Sigma_u^+ \rightarrow 1^1\Sigma_g^+$. Additional prominent features of this spectrum are the wide "continuum" observed in the range $1800\text{Å} < \lambda < 2400\text{Å}$, and the marked time dependence of the emission (compare Figs. 62 and 63). Long wavelength emissions have been observed under other experimental conditions.^{50, 51} It has been suggested by Hurst, et. al.⁵² that such emissions are explained by recombination radiation "involving the formation of argon excimers with binding energies of about 4.0 eV". The information available on He³⁸ and Xe³⁹ and the expected decreased binding energy one expects in the progression $\text{He}_2^* \rightarrow \text{Ne}_2^* \rightarrow \dots \rightarrow \text{Xe}_2^*$ suggests that a value of 4 eV is excessive. These long wavelength emissions will be considered more fully in Sec. VI below.

Fig. 62. Time resolved spectra for pure argon; 850 Torr, $t \leq 150$ nsec, ($t=0$ taken as the 50% point on the rise of the voltage across the field emitting diode). Magnetic field 12 kG.

Krypton

As in the case of argon, emission spectra at 850 Torr for two time sequences are presented (see Figs. 64 and 65).

The spectral prominence at $1500\text{\AA}$ is attributed to $^3\Sigma_u^+, ^1\Sigma_u^+ \rightarrow ^1\Sigma_g^+$ transitions. The resolution of this data is inadequate to clearly distinguish between them. As in the case of argon, krypton exhibits

another spectral prominence in the $2200\text{\AA}$ region. Figure 64 reveals that the $2200\text{\AA}$ feature is broad at early times and subsequently narrows. At the same time, the $\text{Kr}_2^*(^1\Sigma_u^+, ^3\Sigma_u^+)$ emission centered at $1500\text{\AA}$ appears to exhibit a reciprocal behavior. This strongly suggests an energy feed-in from the states responsible for the $2200\text{\AA}$ behavior. This radiative cascade has not been attributed unambiguously to the ground state core of Kr_2^* . This matter is discussed further in Sec. VI.

Fig. 63. Time resolved spectra for pure argon; 850 Torr, $150 \leq t \leq 400$ nsec.

Xenon

Experiments were conducted on pure xenon under conditions identical to the argon and krypton studies. Figure 66 illustrates a typical result for the spectrum observed in xenon at 850 Torr for times of 50, 75, 100, 125, and 150 nsec after the initiation of the electron beam. Under these circumstances the peak emission is located somewhat longward of 1800Å. In the spectral region from 1100Å to 2500Å essentially all of the observed radiation is confined to the

interval between 1600Å and 2000Å. On the basis of Mulliken's approximate curves,³⁹ and to within the 50Å resolution of these measurements, it is possible to associate the peak $\sim 1850\text{Å}$ from the lowest vibrational levels of the $^3\Sigma_u^+$ state undergoing a transition to the repulsive $^1\Sigma_u^+$ state. Of course, since the $^1\Sigma_u^+$ state is believed to be relatively close to the $^3\Sigma_u^+$ level, a component due to this state may also be present. However, the shape of the observed spectrum in xenon has somewhat different properties

Fig. 64. Time resolved spectra for pure krypton; 850 Torr; $t \leq 150$ nsec.

at lower density (e.g., 400 Torr). Under these conditions a second peak is seen at $\sim 1700\text{\AA}$. In this connection it is interesting to note that the laser oscillation recently observed⁵³ in high pressure xenon gas occurred at the wavelength of $1716\text{\AA}$ with an approximate width of $\sim 17\text{\AA}$. This indicates that the transitions involved in the stimulated emission process $\sim 1716\text{\AA}$ differ from those generating the peak of the spontaneous emission spectrum in our experiments at the pressure of 850 Torr. The wavelength difference suggests a differential of $\sim 4000\text{ cm}^{-1}$ in the degree of excitation of these two sets of states. Again, on

the basis of Mulliken's potential curves,³⁹ the $1700\text{\AA}$ component may be due to the high vibrational levels of the $1\Sigma_u^+$ and $3\Sigma_u^+$ states.⁵⁴ This is consistent with the more marked appearance of the $1700\text{\AA}$ peak in spontaneous emission at lower pressure, since rapid vibrational relaxation at the higher pressures will have a tendency to broaden the band and cause the $1700\text{\AA}$ peak to merge with the adjacent continuum at $\sim 1850\text{\AA}$. The shoulder visible at $1700\text{\AA}$ in Fig. 66 is indicative of this type of behavior.

Fig. 65. Time resolved spectra for pure krypton; 850 Torr, $150 \leq t \leq 400$ nsec.

Fig. 66. Time resolved spectra for xenon gas; 850 Torr, $t \leq 150$ nsec.

VI. Discussion of Rare Gas Studies

A. BASIC PROCESSES

The following are the basic formation processes for noble gas molecular species (taking Xe as an example).

Reaction (80) represents the direct excitation by primary electrons and sufficiently energetic secondaries. Primary electrons can also lose energy via bremsstrahlung. For xenon, the worst case, these losses amount to 8% and will be ignored.⁵⁵ The bremsstrahlung spectrum associated with 2.2 meV electrons is expected to contain only a trivial fraction of its energy in precisely the range to directly excite the gas of interest to a state which readily combines to give the noble gas molecule. The result of these radiations is certainly to ionize and therefore to contribute to the production of Xe^+ as in ionizing Coulomb collisions, reaction (81). Reaction (84) is fast enough for the case of Helium.⁵⁶ For Helium, the lack of an appropriate crossing of a dissociative neutral state and the bound ionic molecular state is believed to explain this effect.⁵⁷

The vibrational wave function in the ground state is a gaussian, and the number of vibrational quanta increases as one approaches the correspondence limit of the "wave function" of a classical oscillator. Thus when a radiation from $1, 3\Sigma_u^+ \rightarrow 1\Sigma_g^+$ occurs we know we have a transition from an harmonic oscillator upper state to an unbound (oscillatory wave function) lower state. Reactions (82) and (83) represent the three body collisional combinations to form Xe_2^* and Xe_2^+ respectively. The result of reaction (83) is to prepare the way for the dissociative recombination of $\text{Xe}_2^+ + e^- \rightarrow \text{Xe}^* + \text{Xe}$ [reaction (84)]. Reaction (83) and (84) will not be discussed further since their effect is to produce a slightly delayed Xe^* concentration, although presumably of much larger amount than from reaction (80).

Consider now the states of Xe^* which participate

in the formation of Xe_2^* via reaction (82) and the characteristics of these molecular states. The molecular continua emitted show that rare gas emissions are of two types.^{2, 40} The so-called first structured continuum of the heavier rare gases Ar, Kr, Xe starts at the lowest atomic resonance line and extends toward the red. The first continuum was explained by Mulliken⁴⁰ as resulting from transitions of highly vibrationally excited species of the lowest two molecular bound states ($1\Sigma_u^+$ and $3\Sigma_{uj}^+$ with the triplet state lying lower than the singlet because of exchange). Once vibrational relaxation occurs, one observes what is commonly known as the second continuum, appreciably red shifted from the first. The magnitude of the red shift is comparable to the binding energy of the bound state. These features are summarized by Fig. 67.

Figure 68 illustrates the behavior of the emission from the bound upper state to the dissociative ground state as a function of the extent of vibrational excitation. Thus the 2200Å continua mentioned in connection with Fig. 64 Sec. IV, which early exhibit broad spectral emission and subsequently narrow, can be thought of as representative of the approach to vibrational equilibrium. The extent to which the emission appears double-humped at early times represents the tendency for the system (Xe_2^*) to be "born" at highly excited vibrational levels.

The states contributing to the lowest molecular state formation are of the spectroscopic form $nP^5(n+1)S$. The spin-orbit combination rules dictate that they should be in order of increasing energy $3P_2, 3P_1, 3P_0, 1P_1$. Note that the highest J value lies lowest in a given spin multiplet because of the greater than half-filled (nP^5) shell.¹⁸

All of these states are long lived at high pressure:

- $1P_1, 3P_1 \rightarrow 1S_0$ are dipole allowed resonance transitions, and as such are strongly trapped.⁴⁶
- $3P_0 \rightarrow 1S_0$ is strictly forbidden in any multiple approximation,
- $3P_2 \rightarrow 1S_0$ is allowed via magnetic quadrupole,
- $3P_0 \rightarrow 3P_1, 3P_2$ is allowed via magnetic dipole and electric quadrupole respectively.

Mulliken⁴⁰ has shown that $3P_1, 3P_2$ form the molecular states of interest. ($1\Sigma_u^+, 3\Sigma_u^+$) and that $3P_0, 1P_1$ lead to antibonding states.

Fig. 67. Plot of potential energy vs internuclear separation.

Another feature of the molecular transition matrix elements is that one would expect to see $1\Sigma_u^+$ emission dominate over $3\Sigma_u^+$ at large internuclear separation. The dipole transition amplitude vanishes at large separations because

must proceed via $3p_z \rightarrow 1s_0$, which is forbidden. The same transition at large separation for $1\Sigma_u^+ \rightarrow 1\Sigma_g^+$ is more strongly allowed because $3p_1$ can proceed via dipole radiation emission.

Consider the following reactions

Equation (85) represents the spontaneous emission of Xe_2^* to the repulsive ground state. In the heavier molecules (Kr_2 , Xe_2) this reaction proceeds quite rapidly due to breakdown of the spin selection rule. In the case of Ar_2 one would expect a lower rate for 3Σ decay (spin rule) than for 1Σ decay.

Equation (86) represents vibrational relaxation of the molecules. This reaction is expected to proceed rapidly via resonant atom exchange. Again helium is anomalous, Callear and Hedges⁵⁸ report the $\text{He}_2^*(a^3\Sigma_u^+, v=1)$ relaxation as "abnormally slow" because a long range repulsive potential keeps the collision partners apart, thus inhibiting the atom exchange.

The following equations:

Fig. 68. Influence on emission spectrum of vibrational excitation of upper state.

represent excited atom relaxation via atomic and electronic processes respectively. For atomic collision partners the cross sections are of the order of 10^{-19} cm² whereas Phelps⁵⁹ has suggested that the relaxation of $^3P_1 \rightarrow ^3P_2$ via electron (spin exchange) collision proceeds with cross sections of $\sim 10^{-13}$ cm².

The following equations:

represent photoionization and Penning ionization, respectively. These two processes will operate to place an upper bound on the Xe_2^* concentration and therefore on the gain of the laser system.

Since the lowest excited molecular ground state is more than halfway up from the molecular ground state to the convergence of the Rydberg series at the ground molecular ionic state,⁶⁰ the frequency of $^3\Sigma_u \rightarrow ^1\Sigma_g$ is clearly high enough to ionize the $^3\Sigma_u$ state. This then is counted as a stimulated loss process serving to diminish the gain on the $^3\Sigma_u \rightarrow ^1\Sigma_g$ transition.

The Penning process Eq. (90) is undesirable because it removes two excited xenon molecules from action and therefore limits the achievable Xe_2^* concentration.

Given the pumping time scale 80 nsec, we ask at what Xe_2^* concentration does the Penning rate become comparable to the pump rate? Unfortunately the cross section for Xe_2 is not known but the following reaction cross section has been measured:⁶¹

$$\sigma = 10^{-14}$$

Assuming the σ for reaction (90) is of the same order, we find that

$$N\bar{v}\sigma \approx 1/\tau$$

where $\tau = 80$ nsec,
 $\sigma = 10^{-14} \text{ cm}^2$

$\bar{v}$ = relative velocity $\approx \frac{1}{8} \times 10^5 \text{ cm/sec}$,

N = number of density of Xe_2^* ,
 gives

$$N \approx 6.25 \times 10^{16} / \text{cm}^3. \quad (92)$$

Assuming about 8.0 eV/ Xe_2^* available; the upper bound on the energy storage becomes 110 J/l. This fundamental limitation clearly emphasizes the need for rapid excitation.

B. SOURCE OF 2200Å CONTINUUM

At this writing the source of the long wavelength emission for the rare gases is not precisely known. It is tempting to attribute this emission to a state between the first excited molecular state and the series limit corresponding to the ionization of Xe_2^* to form Xe_2^+ (ground state).

It is immediately seen that in the case of Krypton, the available energy between the $\text{Kr}_2(3\Sigma_u^+)$ state and the lowest corresponding ionic state $\text{Kr}_2^+ + e$ admits a minimum wavelength in excess of 2200Å. The same systematics occur in the case of Ar_2^* and Xe_2^* (in the case of the 3000Å continuum) as pointed out by Mulliken.⁴⁰ If one wishes to assign the origin of these spectral features to the rare gas dimer states, an alternative description is required. One possibility, although

by no means a certainty, is a resort to the states of an excited core configuration⁶² as suggested by Mulliken in the example of xenon.³⁹ It has not been possible to definitely establish the excited core proposition, but the systematic nature of the experimental observations provides a strong suggestion that the origins of these emissions are related in a regular fashion in the three materials under study.

C. EXCITED ATOM DECAY PROCESSES

This section will deal primarily with the atomic/molecular process associated with the transfer of electronic energy between Ar_2^* and $\text{Xe}(1^1S_0)$ and the subsequent decay of Xe^* as represented by the following reactions:

For laser applications it is desirable to achieve the highest inversion densities possible. As noted earlier the lifetime of the heavy rare gas dimers is unacceptably low. This, coupled with the limitations of Penning collision, puts a fundamental upper bound on the inversions achievable.

This limitation can be circumvented if reaction (93) can be employed to store energy in the metastable $\text{Xe}(3P_2)$ state. Radiation can then be extracted via two-photon processes (e.g., stimulated anti-Stokes processes on $\text{Xe}(3P_2)$ with CO_2 light). This procedure permits high density energy storage at zero gain.

Two-photon processes generally obey the following class of differential equation:

$$\frac{dI}{d\xi} = \alpha I^2$$

where I = intensity at amplifier output, α = effective gain for a two-photon process whose solution is of the form:

$$I = \frac{I_0}{1 - \alpha I_0 x}; \quad (95)$$

where x = amplifier gain length.

Thus at low stimulating intensity $I = I_0$. As $\alpha I_0 x \approx 1$, I becomes large. This leads to subsequent complete removal of stored energy.

Figure 61 suggests that the lifetime of the 3P_2 state of xenon is of the order of 2 μsec and is considerably longer than that of the molecular system Xe_2^+ [estimated to be of the order of 10 nsec (dipole allowed)].

Reaction (93) has been observed² to produce Xe^* by two different methods depending on the Xe pressure. At low pressure the Ar_2^+ continuum is known to cover the range 1150Å - 1400Å which overlaps the $\text{Xe}(^1P_1)$ at 1296Å; rapid transfer is therefore expected to occur and is evidenced by strong 1296Å emission.

At higher Xe concentrations, one observes not 1P_1 emission but rather 3P_1 emission located at 1497Å. Gedanken, et. al.² have postulated a rapid $^1P_1 \rightarrow ^3P_1$ collapse via the process:

with subsequent radiative decay to

(As discussed in Sec. VI-A, $^3P_1 \rightarrow ^3P_2$ proceeds very rapidly.)

Thus, one can control the Xe^* population by choosing a ratio of $\text{Ar}/\text{Xe} \gg 1$ thereby inhibiting Xe_2^+ formation via reaction (94). Further, 1P_1 formation should be of no consequence because radiation trapping⁶³ provides a very long effective lifetime (10 μsec @ 0.1 Torr Xe). Both experimentally, Fig. 61, and theoretically, the prospects for storage of energy in the metastable $\text{Xe}(^3P_2)$ appear to be excellent.

D. LASER GAIN ESTIMATE FOR Xe_2^+

The spontaneous lifetime of Xe_2^+ is expected to be

$$\tau \approx 20 \text{ nsec (failure of L-S spin selection rule).}$$

The gain of the transition is given by

$$g = \frac{8\pi^2}{hc} |\mu|^2 \frac{\nu}{\Delta\nu} \Delta N$$

or

$$g_{\text{gain}} = \frac{8\pi^2}{hc} |\mu|^2 \frac{\nu}{\Delta\nu} \quad (98)$$

$$|\mu|^2 = \frac{h\lambda^3}{(\tau_{\text{spont}}) 32\pi^3} \quad (99)$$

Combining Eqs. (98) and (99) gives us

$$g_{\text{gain}} = g/N = \frac{\lambda^2}{\tau_{\text{spont}} 4\pi \Delta\nu} \quad (100)$$

where $\lambda = 1.7 \times 10^{-5} \text{ cm}$

$$\tau_{\text{spont}} = 2 \times 10^{-8}$$

$$\Delta\nu = \frac{1}{2} 10^{15} \text{ (derived from experimental bandwidth measurements)}$$

giving

$$g_{\text{gain}} = 7.2 \times 10^{-18} \text{ cm}^2. \quad (101)$$

A competing process serving to deplete $^3\Sigma_u^+$ in the presence of a stimulating field is photoionization of Xe_2^+ to yield Xe_2^+ .

Bardsley and Biondi⁵⁷ give the cesium photoionization cross section as $0.22 \times 10^{-18} \text{ cm}^2$ at the ionization band head. Cesium is used in approximating the Xe_2^+ Rydberg state because of its single outer 6s electron. Thus the net gain cross section can be written as

$$g_{\text{net}} = (g_{\text{gain}} - \sigma_{\text{photoelectric}}) = 7 \times 10^{-18} \text{ cm}^2 \quad (102)$$

The density of Xe_2^+ that produces 5%/cm net gain (probably 5% is required because of high cavity losses in the vacuum ultraviolet region) is

$$N = \frac{5 \times 10^{-2}}{7 \times 10^{-18}} \approx 7 \times 10^{15} / \text{cm}^3 \approx \frac{1}{3} \text{ Torr.} \quad (103)$$

The current needed to produce $7 \times 10^{15} \text{ Xe}^*/\text{cm}^3$ can be estimated as follows: One requires about 10 eV of excitation to produce a Xe^* atom. Thus the energy dumped by the electron beam must exceed $7 \times 10^{16} \text{ eV/cm}^3$.

Recalling Eq. (42), the energy deposited per cm^3 per A/cm² for a medium of density ρ by 1.2 MeV electrons is:

$$\text{Energy/Ampere-cm} = 3.7 \times 10^{17} \rho. \quad (104)$$

The density of Xe gas at 1 atm is approximately $5.85 \times 10^{-3} \text{ gm/cm}^3$. Thus the energy/A-cm-atm delivered to the medium at 1 atm is:

$$2.1 \times 10^{-5} \text{ eV/A-cm.}$$

The number of A/cm² required at 1 atm is therefore:

$$\frac{7 \times 10^{16} \text{ eV/cm}^3}{2.1 \times 10^{15} \text{ eV/A-cm}} = 33 \text{ A/cm}^2. \quad (105)$$

Assuming 90% of the energy deposited is lost (i.e., does not wind up in Xe⁺) one obtains for 5%/cm gain:

$$330 \text{ A/cm}^2 \text{ @ 1 atm}$$

or

(106)

$$33 \text{ A/cm}^2 \text{ @ 10 atm.}$$

Current densities of this order are readily attainable with the existing apparatus.

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