SEMI-ANNUAL TECHNICAL STATUS REPORT
ON
MOLECULAR LASER STUDY
3-5 MICRONS
August 1, 1970 Thru January 1, 1971

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1.0 INTRODUCTION

This first Semi-Annual Technical Report is in partial fulfillment of the contract requirements as specified in the Contract Schedule, Section 6, Paragraph 1(B).

Since this is the first technical report written on this contract, it will also present some pertinent background on molecular lasers. This will be in the form of a brief review of \( N_2 - CO_2 - He \) lasers and the operation of our plasma tubes, to be presented in Section 2.0. Discussion of laser emission from a mixture of \( H_2 - C_2 H_2 - He \) will be presented in Section 4.0.

Section 4.0 will outline the proposed experimental work to be carried out in the second half of the contract period.

The operation of the first acetylene laser and identification of the lasing transition were carried out by Dr. Carl F. Shelton. He initiated the experimental program at IBM and was the Principal Investigator for the first quarter of the performance period for this contract.
BRIEF REVIEW OF N₂-CO₂-He LASERS

The pumping mechanisms and operation of the N₂-CO₂-He laser system have been widely discussed in the open literature and thus will only be summarized briefly here.

Excitation mechanisms for pumping CO₂ to the upper laser level include:

(a) Direct electron impact

(b) Vibrational energy transfer through inelastic collisions with N₂*(v = 1)

(c) Recombinations of the form

CO + O → CO₂*(001)

Helium enhances the CO₂ laser output by at least five mechanisms:

1. Helium depopulates the 01 0 mode through inelastic collisions and thus indirectly increases the rate of depopulation of the lower laser level, i.e., the 10 0 level.

2. Helium increases the rate of rotational thermalization within each vibrational level and thus maintains the population inversion on the strongest vibrational-rotational transitions.

3. Helium cools the kinetic temperature of the gas mixture because of its higher thermal conductivity.

4. Helium shifts the electron temperature and/or the electron density to more favorable values for vibrational excitation by electron impact.

5. Helium reduces the diffusion of the excited species to the walls of the plasma tube where they can be de-excited.

Effect (2) shows up in the fact that fewer rotational P-branch lines are observed in N₂-CO₂-He mixtures than in N₂-CO₂ mixtures. Patel observed emission on the P(12) through P(38) lines of the ν₃ - ν₁ band with pure CO₂. Other researchers have observed emission on the P(18) through P(28) lines using
$N_2\cdot CO_2^{(6)}$, the $P(20)$ through $P(26)$ lines using $CO_2\cdot He^{(7)}$ and the $P(20)$ through $P(24)$ using $N_2\cdot CO_2\cdot He^{(8)}$. Again, since only the even $P$-branch lines are allowed this means a reduction from fourteen lines using pure $CO_2$ to four lines using $CO_2\cdot He$ and to three lines using $N_2\cdot CO_2\cdot He$.

The actual effects of He on electron temperature and electron density in the plasma have not been accurately measured during laser emission, however, these effects can be inferred in various ways. Patel\(^{(9)}\), for example, observed an increase in output from his parallel pumped $N_2\cdot CO_2$ laser\(^{(10)}\) with increasing helium partial pressure when the helium was added through the $CO_2$ port and $CO_2\cdot He$ mixed with the vibrationally excited $N_2$ in the interaction region. An even greater increase in power output, by roughly a factor of two, was observed by Patel when the helium was added through the $N_2$ port and was thus in the parallel discharge with the $N_2$ prior to mixing with $CO_2$ in the interaction region. This same effect has been observed with a parallel-pumped tube built at IBM and shown in Figure 3.

The electron-energy distribution in the positive column of a normal glow discharge is controlled in part by the ionization potentials of the components of the gas mixture. The trend is to a higher electron temperature with higher ionization potentials\(^{(4,11)}\). The ionization potentials of $N_2$, $CO_2$, and He are 15.5, 13.79 and 24.58 ev, respectively. Typical mixtures used for laser emission vary, but a mixture of $2/1/10$, $N_2/CO_2/He$ is not uncommon.

Thus, there is some evidence that one of the significant roles played by helium in $N_2\cdot CO_2\cdot He$ lasers is to shift the electron temperature to a slightly higher value for a given total pressure and thus increase the pumping of the upper laser level by direct electron impact and by vibrational energy transfer from $N_2^* (v=1)$.

The pulsed plasma tube used for most of the $H_2\cdot C_2H_2\cdot He$ work is straightforward and is shown in Figure 1. The mirrors are exposed to the vacuum, and are mounted by means of stainless steel bellows. Operation of the tube with $N_2\cdot CO_2\cdot He$ is indicated in Figure 2. The ratio of $N_2\cdot CO_2\cdot He$ used for the data shown was 2:1:4 at 8 Torr and produced pulse energies of 15 to 20 millijoules.
Figure 1. Pulsed Excitation Plasma Tube with Coaxial Kovar Electrodes.
Figure 2

200 USEC/DIV

57.1% He
28.6% N\textsubscript{2}
14.3% CO\textsubscript{2}
P = 8 Torr
The parallel tube shown in Figure 3 produced CW power outputs in excess of 600mW from CO$_2$ which had been pumped only from a resonant energy transfer from N$_2$ which was excited in the parallel discharge. For these experiments a 95% reflectivity dielectric mirror was used for output coupling, and an input power of 220 watts was used. This compares to an output power of the order of 2mW with an input power of 100 watts obtained by Patel\(^{(5)}\).

This parallel tube was also operated in the pulsed mode by the addition of two electrodes near the center of the discharge region to prevent the plasma from traveling down the interaction region. Figure 4 shows a diagram of the modified tube and the pulse circuitry.

A 0-16Kv, 0-12ma dc power supply was used to charge a 0.02uf capacitor. This charge was then applied to the plasma tube when the electrode shown on the right in Figure 4 was switched to ground by the thyatron tube. The pulse repetition rate could be controlled by a pulse generator which triggered the thyatron. Two Welch Model 1397, 15cfm each, mechanical pumps were operated in parallel in order to continuously flow gas mixtures through the plasma tube. Partial pressures and flow rates of up to three component gases could be controlled through the use of needle valves, flow meters and a manifold arrangement. Partial pressures were measured upstream of the plasma tube using a capacitor manometer.

Figure 5 shows the performance of this tube with CO$_2$ under pulsed conditions. Output pulse energies were typically 3 millijoules, and the peak power was approximately 7 watts. The nitrogen flow rate was approximately 60 liters/min at the tube which produced a flow velocity of 400cm/sec in each half of the interaction region. Morgan and Shiff have measured the lifetime of the metastable N$_2^+(v = 1)$ level at a few Torr to be 114msec, which means that if wall collisions are unimportant, the excited molecules travel 45cm in one decay time. Considering both halves of the tube, this represents almost the entire 1 meter length of the interaction region.
DIAGRAM OF PULSED PARALLEL TUBE

Figure 4
CURRENT

LASER

500 MA/DIV

200 USEC/DIV

PULSED N$_2$-CO$_2$-He IN PARALLEL TUBE

Figure 5
3.0 STIMULATED EMISSION FROM $\text{H}_2\text{-C}_2\text{H}_2\text{-He}$

Laser emission near 8 microns has been obtained from a flowing mixture of $\text{H}_2\text{-C}_2\text{H}_2\text{-He}$ under pulsed excitation conditions in a gas discharge (12, 13). This lasing action may result from vibrational excitation of $\text{C}_2\text{H}_2$ via a near resonant energy transfer from the metastable $v = 1$ vibrational level of $\text{H}_2$ which has been excited in the helium rich discharge as well as possible direct electron impact excitation of $\text{C}_2\text{H}_2$. Laser action has been observed, however, without the presence of hydrogen in the discharge.

A Jarrell-Ash one-meter Czerny-Turner spectrometer with a 98 groove/mm IR grating, blazed at 7$\mu$m was used to measure the wavelength of the laser emission. This grating gave a linear dispersion of approximately 102$\AA$/mm and a theoretical resolving power of 8$\AA$ in the first order. The precision of the wavelength counter is $\pm1A$ with a 1180 groove/mm grating. This corresponds to a precision of $\pm12A$ with the 98 groove/mm grating. A liquid nitrogen cooled Ge:Au detector was used in these experiments. This detector has a specified time response of 20ns.

3.1 $\text{H}_2\text{-C}_2\text{H}_2\text{-He}$ LASER CHARACTERISTICS

Representative results with the pulsed tube in Figure 1 showing the current pulse through the $\text{H}_2\text{-C}_2\text{H}_2\text{-He}$ plasma and the laser pulse obtained are shown in Figures 6 and 7. A flowing mixture of approximately 1 torr $\text{C}_2\text{H}_2$, 2 torr $\text{H}_2$ and 20 torr He was used in each case. The values of peak powers given were measured with no attempt being made to optimize the output coupling.

The first results were obtained using an aperture for broadband output coupling and is shown in Figure 6. The laser emission was usually found to be on a single line at 8.040$\mu$m and no rotational structure was observed. However,
Figure 6. First Laser Output Obtained from $\text{H}_2$-$\text{C}_2\text{H}_2$-$\text{He}$ Mixture.
H$_2$-C$_2$H$_2$-HE

2:1 20 Torr

![Graph at 25°C](image)

- $P_p = 0.5$ W

- 200 MA/DIV

- $25^\circ$ C

![Graph at -80°C](image)

- $P_p = 19.4$ W

- 500 MA/DIV

- -80°C

2:1:23 Torr

Figure 7
on one occasion, two lines were observed at 8.034 µ and at 8.040 µ.

The results obtained using narrow band dielectric mirrors are shown in Figure 7. The laser pulses shown are for two cooling jacket temperatures. Figure 7b shows the result obtained when the gas mixture was pre-cooled and the cooling jacket temperature was -80°C. Five emission lines were observed at different times under these conditions. The wavelengths in air of these five lines were measured as 8.0313, 8.0329, 8.0352, 8.0383 and 8.0416 µ using the 12th order of the 6678Å and 6717Å neon lines as a calibration reference. The accuracy of these wavelength measurements was probably better than ±2Å. A 40:1 increase in peak power was observed in cooling the discharge from 22°C to -80°C as noted in Figure 7.

Laser action in H₂-C₂H₂-He in the 1/2 inch i.D. plasma tube could only be obtained over a very narrow range of discharge conditions, i.e., discharge current, and over a very narrow range of gas mixtures. Laser emission was not observed from a pure C₂H₂ plasma or a C₂H₂-H₂ plasma, but it was observed with a C₂H₂-He plasma. Figure 8 shows the results when the hydrogen was removed from the discharge. In the upper curve, the pressures of H₂-C₂H₂-He were 2, 1, and 32 torr, respectively, and in the lower curve the pressures were 0, 1, 32 torr. In both cases, both the gas and cooling jacket were at -60°C. Without hydrogen, the peak power was reduced by a factor of 2, and the pulse energy was reduced even more because of the slight decrease in pulse width. The same spectral lines were observed in the laser output both with and without hydrogen.
CURRENT

LASER
20 MV/DIV

WITH H₂

200 MA/DIV

CURRENT

LASER
10 MV/DIV

WITHOUT H₂

20 USEC/DIV

OPERATION WITHOUT HYDROGEN

Figure 8
Lasing again with reduced output occurred when \( \text{N}_2 \) was substituted for \( \text{H}_2 \). In this case an increasing delay time ranging from 20 to 65 usec accompanied the decreasing output.

These last results indicate that either some species other than \( \text{C}_2\text{H}_2 \) may be producing the laser emission or that direct electron impact excitation of \( \text{C}_2\text{H}_2 \) can alone lead to laser emission. They do not, however, completely rule out resonant energy transfer from \( \text{H}_2^*(v = 1) \) as a possible pumping mechanism.

These results further support the fact that much work is needed in understanding the complex discharge chemistry and various pumping mechanisms involved as discussed in Section 3.3.

Laser emission was obtained at pulse repetition rates from 1 pps up to 250 pps. Power supply limitations, i.e., current capability, prevented operation at higher repetition rates. The discharge ran quite clean, although light carbon deposits were formed near the electrodes after many hours of operation at pulse repetition rates of the order of 26 pps. The side light emission from the plasma was very weak during laser action and, in fact, could not be observed with the eye when the laboratory lights were turned on.

3.2 POSSIBLE IDENTIFICATION OF LASER TRANSITIONS

Acetylene, \( \text{C}_2\text{H}_2 \), is a linear symmetric molecule with five normal modes of vibration\(^{(14)}\). These normal modes are shown in Figure 9. Some of the vibrational energy levels of the ground electronic state of \( \text{C}_2\text{H}_2 \) are shown in Figure 10. In contrast to the \( \nu_3 - \nu_1 \) band of \( \text{CO}_2 \), the \( \nu_2 - \nu_5^1 \) (01000 - 00001) band of \( \text{C}_2\text{H}_2 \) has an allowed Q-branch\(^{(14)}\). This \( \nu_2 - \nu_5^1 \) band Q-branch has been observed in absorption by Bell and Nielsen\(^{(24, 25)}\), with
C\textsubscript{2}H\textsubscript{2} - ACETYLENE
Linear Symmetric Molecule
H-C\equiv C-H

<table>
<thead>
<tr>
<th>NORMAL MODE</th>
<th>ASSIGNMENT</th>
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<tr>
<td>( v_1 )</td>
<td>( \gamma^+ )</td>
</tr>
<tr>
<td>( v_2 )</td>
<td>( \nu^+ )</td>
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<td>( v_4 )</td>
<td>( \pi_g )</td>
</tr>
<tr>
<td>( v_5 )</td>
<td>( \pi_u )</td>
</tr>
</tbody>
</table>

Figure 9. Normal Vibrational Modes of Acetylene
Figure 10. Vibrational Energy Level Diagram of Acetylene
Thus, equation (3-3) can be written as:

$$Q(J) = \nu_0' + (B_U - B_L)J(J + 1) + \ldots$$  \hspace{1cm} (3-4a)

This equation can be used to calculate the energies of the Q-branch lines of the $\nu_2 - \nu_5$ band of C$_2$H$_2$. The results obtained using Herzberg's values of $B$, and the $\alpha_i$'s,

- $B_e = 1.1838 \text{cm}^{-1}$
- $\nu_0' = 1245.28 \text{cm}^{-1}$
- $\alpha_1 = 0.008 \text{cm}^{-1}$
- $\alpha_2 = 0.0063 \text{cm}^{-1}$
- $\alpha_3 = 0.0056 \text{cm}^{-1}$
- $\alpha_4 = -0.0013 \text{cm}^{-1}$
- $\alpha_5 = -0.0022 \text{cm}^{-1}$

giving,

$$B_U = B \nu_2 = 1.17105 \text{cm}^{-1}$$

$$B_L = B \nu_5 = 1.17955 \text{cm}^{-1}$$

or, $\Delta B = B_U - B_L = -0.00850 \text{cm}^{-1}$

are shown in Table 1 for the first twenty Q-branch transitions of the $\nu_2 - \nu_5$ band of C$_2$H$_2$. Normally, for the C$_2$H$_2$ the lines with odd $J$ should be more intense than the even $J$ due to the 3:1 ratio of the statistical weights.

* Herzberg gives a value for $\nu_0' = 1244.7 \text{cm}^{-1}$. We have adjusted this value by 0.58 cm$^{-1}$ to give a better fit to the experimentally determined wavelengths.
### TABLE 1

Q-Branch Lines of the $\nu_2 - \nu_5$ Band of C$_2$H$_2$ Calculated from Herzberg's Data

<table>
<thead>
<tr>
<th>J</th>
<th>$\Delta E$</th>
<th>$\lambda_{\text{calc.}}$</th>
<th>$\lambda_{\text{obs.}}$</th>
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<td></td>
</tr>
<tr>
<td>5</td>
<td>1245.03</td>
<td>8.0298</td>
<td></td>
</tr>
<tr>
<td>6</td>
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<td>1244.80</td>
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*This line observed only once.
The results obtained Keller's values of $B_e$, and the $\alpha_i's$,

$B_e = 1.1845 \text{cm}^{-1}$

$\nu'_o = 1245.20 \text{cm}^{-1}$

$\alpha_1 = 0.0063 \text{cm}^{-1}$

$\alpha_2 = 0.0092 \text{cm}^{-1}$

$\alpha_3 = 0.0053 \text{cm}^{-1}$

$\alpha_4 = 0.00065 \text{cm}^{-1}$

$\alpha_5 = 0.0021 \text{cm}^{-1}$

giving,

$B_U = 1.1673 \text{cm}^{-1}$

$B_L = 1.1786 \text{cm}^{-1}$

or,

$B = B_U - B_L = -0.0113 \text{cm}^{-1}$

are shown in Table 2 for the first twenty Q-branch transitions of the $\nu_2 - \nu_5$ band of $C_2H_2$. All values of $\Delta \nu$ are given for vacuum and wavelengths are given in air.

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** Keller's value for $\nu'_o = 1244.79 \text{cm}^{-1}$ which is an adjustment of 0.41 cm$^{-1}$.**
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*This line only observed once.
A piezoelectric drive was used to scan one laser mirror in order to average pulling effects and assure mode coincidence with any rotational line having sufficient gain to lase. An indication of these effects are that while operating the drive we have seldom found that a rotational line is missing. This is commonly the case with a fixed cavity length. Thus, scanning the cavity provides the best (unshifted) lasing spectrum available.

Phase sensitive synchronous amplification of a Ge:Au detector output was used; the amplifier gives a dc output proportional to the laser emission which is used as input to the Y-channel of an X-Y recorder. A potentiometer mounted to the wavelength drive of the spectrometer gave a dc voltage proportional to the wavelength which then drives the X-channel of the recorder. An additional moveable mirror and an S-1 PMT is used to enable the 12th order of the Ne calibration lines to be recorded on the X-Y recorder along with the C$_2$H$_2$ laser lines. In all cases, dielectric mirrors were used. The total reflector has a 5 meter radius and a reflectivity of 99.5\% ±0.5\% at 8\mu. The output mirror is flat with a reflectivity of 98\% ±5\% at 8\mu.

Figure 11 shows a typical spectrum, and, in addition, shows the calculated wavelength of the rotational lines in the Q-branch for the rotational constants of Herzberg\(^{(14)}\) and Keller\(^{(15)}\). The best fit is seen using the rotational constants of Keller. Although this fit is quite reasonable, all doubts about the identification of the transition should be removed by additional experiments, an absorption in C$_2$H$_2$ planned for the third quarter.
Figure 11
It is also possible that the laser emission is originating from transitions in some other species which is a dissociative product of the discharge. The carbon formation around the electrodes indicates that some dissociation of the $C_2H_2$ is occurring to form free carbon. The dissociation energies of $C_2H_2$ are given by Lathan, et al. The pertinent reactions are

\[
\begin{align*}
C_2H_2 & \rightarrow C_2H + H \quad (4.97\text{ev}) \\
C_2H & \rightarrow C_2 + H \quad (5.76\text{ev}) \\
C_2 & \rightarrow 2C \quad (6.25\text{ev}) \\
C_2H_2 & \rightarrow 2CH \quad (9.95\text{ev})
\end{align*}
\]

These values are the same order of magnitude as the $CO_2 \rightarrow CO + O$ band strength at 5.6ev. Thus, there are certainly many dissociative products of $C_2H_2$ in the discharge.

An observation of the visible spectrum of the discharge showed fairly weak CH lines, $C_2$ Swan bands, $H_\beta$ and He emission lines. None of these observed bands or lines are very strong, including the $C_2$ bands, indicating that the dissociation was not appreciable.

Ethylene, $C_2H_4$, and ethane, $C_2H_6$, could also be formed in the discharge through hydrogenation of $C_2H_2$:

\[
\begin{align*}
C_2H_2 + H_2 & \rightarrow C_2H_4 \\
C_2H_4 + H_2 & \rightarrow C_2H_6
\end{align*}
\]

It is also possible that formation of diacetylene, $C_4H_2$, can occur.

Thus, possible constituents of the plasma include $C_2H_2$, $C_2H_4$, $C_2H_6$, $C_4H_2$, CH, CH$_2$, CH$_3$ and C$_2$H$_5$ as well as ions of these species and the laser emission may be originating from one of these.
The observation of only five emission lines from the laser, probably due to rapid rotational thermalization caused by the high helium content of the plasma, makes a positive identification of the laser transitions from rotational structure difficult.

3.3 DISCUSSION OF POSSIBLE PUMPING MECHANISMS

Assuming that the laser emission is occurring on Q-branch transitions of the $\text{C}_2\text{H}_2 \nu_2 - \nu_5^1$ band, the laser would then be functioning as a classical four level laser (refer again to Figure 10). Two possible pumping mechanisms for obtaining population inversion in $\text{C}_2\text{H}_2$ are direct electron impact excitation and a near resonant vibrational energy transfer from the $\text{H}_2^*(v = 1)$ which has been excited by electron impact in the helium rich plasma.

$$\text{C}_2\text{H}_2 + e \rightarrow \text{C}_2\text{H}_2^* + e$$  \hspace{0.5cm} (3-5)

$$\text{H}_2(v = 0) + e \rightarrow \text{H}_2^*(v = 1) + e$$  \hspace{0.5cm} (3-6)

$$\text{H}_2^*(v = 1) + \text{C}_2\text{H}_2 \rightarrow \text{H}_2(v = 0) + \text{C}_2\text{H}_2^* (\nu_1 + \nu_5^1) + \Delta E = 68.2 \text{ cm}^{-1}$$  \hspace{0.5cm} (3-7)

The excited state produced by the inelastic collision process shown in Equation (4-5) is not indicated since the details of this process are now known at this time, nor is the relative importance of this mechanism in pumping $\text{C}_2\text{H}_2$ known.

The $\text{C}_2\text{H}_2^*(\nu_1 + \nu_5^1)$ level on the right-hand side of process (3-7) can cascade via collisions or radiative transitions to the $\nu_2$ level, which is the upper laser level. The lower laser level, the $\nu_5^1$ level, can be de-populated through the strongly allowed $\nu_5^1$ to the ground vibration level transition.

Vibrationally excited, ground-electronic-state hydrogen molecules have been observed as a long-lived product of a microwave discharge in pure hydrogen gas by Heidner and Kasper (16). These excited molecules were identified by their vacuum-ultraviolet absorption spectrum. They concluded that,
at a pressure of 3 torr, hydrogen passed through a microwave discharge contains approximately 1-4% of the molecules in the \( v'' = 1 \) state 25msec after leaving the discharge. This compares with 30% of the \( \text{N}_2 \) molecules in the \( v'' = 1 \) state in a low pressure microwave discharge in pure \( \text{N}_2 \) as determined by Kaufman and Kelso\(^{(17)} \).

The relaxation time of the \( \text{H}_2^*(v = 1) \) level should be about 250msec at \( T = 300^\circ \text{K} \) and \( p = 3 \) torr\(^{(16, 18)} \). This compares to the relaxation time of 114msec of \( \text{N}_2^*(v = 1) \) at \( T = 300^\circ \text{K} \) and pressures of the order of a few torr as determined by Morgan and Schiff\(^{(24)} \).

The cross section as a function of electron energy, \( \sigma(E) \) for the process (3-6) has been measured by Schulz\(^{(19)} \). It has a peak value of \( 0.55 \times 10^{-16} \text{ cm}^2 \) at 2.2eV compared to a peak value of \( 1.5 \times 10^{-16} \text{ cm}^2 \) at 2.2eV for the vibrational excitation of \( \text{N}_2 \) by direct electron impact. From \( \sigma(E) \), the rate coefficient for the excitation of \( \text{H}_2 \) by direct electron impact can be calculated\(^{(20)} \).

\[
X(t) = N_e(t) \langle \sigma v \rangle \tag{3-8}
\]

where \( N_e(t) \) is the electron density in the plasma and \( \langle \sigma v \rangle \) is Schulz's cross section averaged over the electron velocity distribution in the plasma. Assuming a Maxwellian energy distribution for the electron in the plasma,

\[
\langle \sigma v \rangle = K_o T_e^{-3/2} \int E \sigma(E)e^{-E/T_e}dE \tag{3-9}
\]

where \( K_o = 6.6971 \times 10^7 \) and \( T_e \) is the average electron temperature in ev. The term \( \langle \sigma v \rangle \) given by Equation (3-9) is plotted versus electron temperature in Figure 12. It is clear from Equations (3-8) and (3-9) and from Figure 12...
Figure 12. $\langle \sigma v \rangle$ vs. Electron Temperature
that the rate coefficient for vibrational excitation of $H_2$ by direct electron impact depends both upon the electron temperature and the electron density in the plasma.

Data is available in the literature on the electron temperature in pure gases under normal glow discharge conditions, but very little data is available for gas mixtures. The electron temperature, $T_e$, as a function of ionization potential, $u_i$, pressure, $p$, and tube radius, $R$, and an empirical constant, $c$, which depends on the gas, is given by Brown\(^{(11)}\) (see also von Engel\(^{(12)}\), pages 63 and 242).

$$\left(\frac{U_i}{T_e}\right)^{-1/2} \exp \left\{ \frac{U_i}{T_e} \right\} = 1.16 \times 10^7 c^2 p^2 R^2$$  \hspace{1cm} (3-10)

The derivation of this equation is also presented in Reference 12. The electron temperature versus pressure in the positive column of a low pressure gas discharge in pure $N_2$, pure $H_2$ and pure He calculated from Equation (3-10) is shown in Figure 13. This equation only considers the ionization potential of the gas in determining the electron energy.

The source of electrons in a glow discharge is from ionization of the component gases and from secondary emission from the cathode. The energy of the electrons is controlled by elastic and inelastic collisions with the component gases. The inelastic processes are ionization and electronic excitations of all the components of the plasma, and vibrational and rotational excitations of the molecular components.
Figure 13. Electron Temperature vs. Pressure in Pure Gases
Again considering only the effect of the ionization potential, it can be shown that the electron temperature in a mixture of $H_2$-He can be somewhat higher than for $H_2$ alone at the same total pressure \cite{12}. This same argument can be applied to $H_2-C_2H_2$-He and $C_2H_2$-He mixtures. This implies that high He partial pressures can be used to stabilize the discharge and still maintain high electron temperatures.

The use of pulsed excitation for $H_2-C_2H_2$-He also increases the excitation rate through the higher current density obtainable, by at least an order of magnitude, compared to dc operation with the gas mixture used.
3.4 PARALLEL PUMPING EXPERIMENTS

We conducted experiments with the parallel tube shown in Figure 4 to test the hypothesis of vibrational energy transfer from excited hydrogen to acetylene. A pulsed discharge in mixtures of hydrogen and helium occurred in the side-arm or discharge region of the tube. The gases then flowed into the interaction region of the tube where they were mixed with acetylene at room temperature. In each experiment, the mirrors were aligned by filling the tube with N₂-CO₂-He and adjusting for maximum average power.

A wide range of gas mixtures, flow rates, and total pressures were tried, and estimates indicate that hydrogen flow velocities up to 20 meters/sec were present. In all cases, the results were negative, and we have not observed laser emission from C₂H₂ in the parallel discharge tube.

Two problems with this experiment immediately come to mind: 1) the lower level population in acetylene, and 2) vibrational deactivation by collisions with the wall. The lower level of the laser transition is only 729 cm⁻¹ above the ground state of acetylene. Thus, at room temperature, the population of the lower laser level is 3% to 4% of the ground state population. Larger inversions are required than for the case of CO₂, and the unpumped parts of the interaction region may be a sufficiently large fraction of the total length so that the gain cannot exceed the losses.
Diffusion coefficients have been used to estimate the lifetime of vibrationally excited $H_2$ if wall collisions are the source of deactivation.

The mutual diffusion coefficient, $D_{12}$, for a binary mixture of hard, elastic spheres is (22)

$$D_{12} = \frac{3}{8} \left[ \frac{\pi kT}{2M_r} \right]^{1/2} \frac{1}{\pi N d_{12}}$$

where $M_r$ is the reduced mass $\frac{M_1 M_2}{M_1 + M_2}$,

$N = N_1 + N_2$ is the total number of molecules, and

$d_{12} = \frac{d_1 + d_2}{2}$ is the average molecular diameter.

If each such collision results in a deactivation, the average lifetime of an excited species in an infinite cylinder of radius, $r_0$, is

$$\tau = \frac{1}{D_{12}} \left\{ \frac{r_0}{2.405} \right\}^2$$

Table 3 shows the results of lifetime calculations using these equations. The first entry is representative of the conditions in the parallel tube which results in lifetime of 0.732 msec. Thus, even at the highest estimated flow velocity for hydrogen (2.0 cm/msec), the excited molecules would only travel several centimeters before a very large fraction were deactivated. In our tube, the molecules have to travel approximately 10 cm to reach the interaction region, so if wall collisions are effective it is unlikely that significant numbers of vibrationally excited hydrogen are available to pump the acetylene.

The second and third entries in the table represent the conditions in the simpler, pulsed tube, and the calculations show lifetimes 3 to 4 times greater than those expected in the parallel tube. The last entry is representative
TABLE 3
LIFETIME BY DIFFUSION TO WALLS

<table>
<thead>
<tr>
<th>Pressures (Torr)</th>
<th>Temp (°K)</th>
<th>$D_{12}$ (cm$^2$/sec)</th>
<th>$\tau$ (msec.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2$</td>
<td>He</td>
<td>$N_2$</td>
<td>300</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>28</td>
<td></td>
<td>300</td>
</tr>
<tr>
<td>2</td>
<td>28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td></td>
<td>300</td>
</tr>
</tbody>
</table>

\[ d_{H_2} = 2.74 \text{ Å} \]
\[ d_{He} = 2.18 \text{ Å} \]
\[ d_{N_2} = 3.75 \text{ Å} \]

\[ M_{H_2} = 2.016 \]
\[ M_{He} = 4.002 \]
\[ M_{N_2} = 28.2 \]

\[ r_o = 0.635 \text{ cm} \]
of the situation of $N_2$-$CO_2$-He in the parallel tube. Based strictly on this
lifetime of 2.2msec one would come to the same conclusions reached above
and predict that CO$_2$ would not work in the parallel tube. This is obviously
an erroneous conclusion as evidenced by the pulsed and CW operation re-
ported in Section 2. Thus, some of the assumptions used in the calculation
may be incorrect, at least for the $N_2$-He case. The Lewis-Rayleigh after-
flow, which is a good indication of excited molecular nitrogen, can be seen
throughout the interaction region and even some distance from the laser in
the glass tubing leading to the vacuum pumps. In addition, the effectiveness
of deactivating collisions with He has not been ascertained, and the small
molecular weight of H$_2$ in contrast to N$_2$ may have important implications to
the pumping process.
4.0 FUTURE PLANS

In an effort to further substantiate our identification of the lasing transition, we are planning an intracavity absorption experiment. We will test the ability of normal acetylene to quench the laser, thereby determining whether or not the lasing species is, in fact, acetylene or a discharge product.

We are considering the substitution of neon for helium to see if a heavier buffer gas affects the laser performance. In addition, we hope to further define the role of hydrogen by monitoring the visible emission from discharge products both with and without the presence of \( \text{H}_2 \).

Considering the calculated lifetimes for wall deactivation, estimated flow rates, and the presence of absorption from the lower level population, the parallel pumping experiments have been discontinued until after the absorption measurements are completed. They may be taken up again later with modified equipment.

A new plasma tube will be designed, built, and tested which will minimize the regions containing unexcited gases. Other gases will be investigated with this new tube during the latter portion of the contract period.
REFERENCES

1) V. P. Tychinskii, Soviet Physics Uspekhi, 10, 131 (1967).
4) N. N. Sobolev and V. V. Sokovikov, Soviet Physics Uspekhi, 10, 153 (1967).