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DOE/ER/03573--T1MOLECULAR LASER STUDIES IN THE 7-16 μ m RANGE

Final Report

Paul D. Coleman, R. Adams, D. Kim and J. Leap
Electro-Physics Laboratory
Department of Electrical Engineering
Engineering Experiment Station
University of Illinois
Urbana, Illinois 61801

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Molecular Laser Studies in the 7-16 μm Range

Abstract

This final report on ERDA EY-76-S-04-3573, describes exploratory research efforts on obtaining 7.7, 8.6, 12 and 16 μm wavelength radiation by means of multi-photon pumping of molecular gases and by means of metal oxidation chemical lasers.

A strong 822.6534 cm^{-1} lasing signal was obtained from NH_3 by a two photon pumping process to excite the $2\nu_2$ a(53) energy level, with lasing taking place to ν_2 s(63). The pump lines were the $P_9(24)$ line of $^{12}\text{CO}_2$ and the $P_9(8)$ line of $^{13}\text{CO}_2$. An output energy of 0.5 mJ was obtained at 12.16 μm wavelength, with a total input energy of 60 mJ.

Progress toward realizing a metal fluoride chemical and glow discharge laser is described. In the chemical laser system studied, a flow of metal atoms was obtained by heating the metal to elevated temperatures. The critical problem associated with this research effort is diagnostics to probe the flames for gain or loss. Theoretical calculations of matrix elements and relaxation rates for these metal fluorides is presented.

Molecular Laser Studies in the 7-16 μm Range

1. Contract Objective for Period 1 October 1976-30 September 1977

The general contract objective was an exploratory research effort to find a molecular gas laser system that would yield efficient, high pulse power lasing at precise wavelengths around either 7,7, 8.6, 12 or 16 μm .

The specific problems to be studied were:

- 1) Strong single photon pumping of molecular gases to observe nonlinear and Raman processes,
- 2) Strong multi-photon pumping of molecular gases to access a very large number of possible lasing levels,
- 3) Density matrix analysis of various systems,
- 4) Metal-oxidation lasers.

2. Summary of Results

Radiation at 822.6534 cm^{-1} (12.15579 μm) has been obtained from NH_3 using the $2\nu_2$ a(53) to ν_2 s(63) transition with the $2\nu_2$ a(53) level being accessed via the ν_2 s(43) and G a(33) level with two photon pumping, as shown in Figure 1.

The Manley-Rowe efficiency for this system is seen to be 40% from Equation (1).

$$\text{MANLEY ROWE-EFF.} = \frac{822.7}{1011.2 + 1043.2} \times 100\% = 40\% \quad (1)$$

Figure 1. Two Photon Pumping of NH_3 to Obtain 822.6534 cm^{-1} Radiation.

In a hole coupled, unoptimized cavity cell, 0.5 mJ of $12.16 \text{ }\mu\text{m}$ radiation was obtained with 16 mJ of $P_9(8)$ and 45 mJ of $P_9(24)$ pump energy for an experimental efficiency of approximately 1% with NH_3 . The pulse width was $0.4 \text{ }\mu\text{sec}$.

It was experimentally shown that the addition of N_2 increased the output at $12.16 \text{ }\mu\text{m}$ by a factor of 4 while the addition of He gave an increase of more than 2 when operating at a lower NH_3 pressure than optimum.

A density matrix analysis has been made for a three photon-four level system, a computer program written and gain curves calculated. Assumptions made were: 1) the pump frequency spectral width small compared to the absorption widths, 2) $T_1 = T_2$ (not true for NH_3), 3) a Lorentzian linewidth, 4) steady state. These calculations over-estimate the gains, but they do give good qualitative agreement.

The basic problem with our metal oxidation laser studies has been limited diagnostics. It was assumed that the exploding wire experiments were a laser existence proof and that one should try for CW lasing in the first experiments. If the system lased, the lasing signals could be the diagnostics. However, if the system fails to lase, this diagnostic tool is obviously lost and other diagnostics must be found.

While beautiful, long burning metal-fluoride flames were achieved, lasing could not be detected. Hence it was decided to build a smaller flame device and essentially place it in a double beam IR spectrometer to measure any gain or loss. A White cell configuration is used to obtain a long path length through the flame. At the end of this contract year, this new system is about 80% complete.

3. Two Photon Pumping of NH_3 to Yield 822.6534 cm^{-1} Radiation

3.1 Introduction

Single photon pumping of molecular gases has been very

effective in yielding many laser lines in the 10 to 1800 μm wavelength range. However, this technique accesses only a few of the available energy levels of a given molecule and hence limits the laser frequencies that can be produced.

The LIS problem has posed a new requirement on optically pumped molecular lasers in that precise frequencies are required. In the two photon-three level pumping system now used, the chances of finding a laser line (i.e., CO_2) - absorption match to levels 1-3 and a specified laser frequency associated with levels 3-2, in the ground electronic state fundamental vibrational modes of a molecule is rather slim. However, if one considers all the possible transitions in a given molecule in the overtone and combination bands, the possibility of generating a given specified frequency greatly increases. To pump a given level will in general require more than one step, i.e., a multi-photon pump system. This is the strategy adopted and pursued in this grant work.

Multiple photon pumping of a molecule not only accesses many more energy levels of the system but has a greater possibility of frequency matches. The trade-off is a reduction of the efficiency over single photon pumping of a factor of two or three.

3.2 Location of Desirable Frequency Transitions in NH_3 and Strategy of Finding Two Photon Frequency Matches

The first requirement in locating a possible desired frequency transition in a molecule is to have accurate energy level

data. Fortunately, NH_3 has been studied extensively and the spectroscopy well-known.^{1,2} A table of values for the ground state G, the ν_2 and $2\nu_2$ state for JK up to (12,12) is given in Table 1, the selection rules being $\Delta v = 0, \pm 1$, $\Delta K = 0$, $\Delta J = 0, \pm 1$ and $a \leftrightarrow s$.

Given an energy level, in ν_2 or $2\nu_2$, there are in general six possible transitions in NH_3 as illustrated in Figure 2. Three transitions will be pure rotational transitions ($a \leftrightarrow s$) and three vibrational-rotational transitions.

Figure 2. Energy Level Diagram of NH_3 Illustrating Six Possible Transitions from Each Energy Level.

Using data from Table 1, it is seen from Figure 3 that three transitions in the $2\nu_2$ to ν_2 band of NH_3 yield frequencies of

Table 1. Energy Levels of $^{14}\text{NH}_3$.

J	K	GROUND STATE		ν_2 STATE		$2\nu_2$ STATE	
		SYMMETRIC	ANTISYMMETRIC	SYMMETRIC	ANTISYMMETRIC	SYMMETRIC	ANTISYMMETRIC
0	0	-	.7934	-	986.1220	-	1882.1757
1	0	19.8903	-	952.5705	-	1617.7694	-
1	1	16.1408	16.9311	948.5628	984.1411	1613.5736	1898.0092
2	0	-	50.4146	-	1027.4325	-	1940.3131
2	1	55.8075	56.6779	988.8132	1023.5321	1654.2662	1936.7686
2	2	44.8674	45.4587	976.7920	1012.4073	1641.5096	1926.1137
3	0	119.2411	-	1053.1125	-	1719.7406	-
3	1	115.8069	116.2485	1049.1323	1082.9584	1715.4526	1994.8734
3	2	104.2948	105.0564	1037.1516	1071.7029	1702.5410	1984.2257
3	3	85.8750	86.3712	1017.1316	1052.9236	1681.1258	1966.4653
4	0	-	199.2994	-	1165.5486	-	2075.8869
4	1	194.8789	195.5838	1129.4238	1161.9061	1796.9556	2072.3394
4	2	183.7037	184.4276	1117.5027	1150.5330	1784.0221	2061.6882
4	3	165.0458	165.8025	1097.5753	1131.9497	1762.5371	2043.9447
4	4	138.8562	139.6614	1069.5583	1105.5708	1732.8186	2019.1023
5	0	297.8501	-	1233.5460	-	1903.1433	-
5	1	293.8436	294.6053	1229.6008	1260.4757	1898.8206	2169.1052

Table 1. (continued)

J	K	GROUND STATE		v_2 STATE		$2v_2$ STATE	
		SYMMETRIC	ANTISYMMETRIC	SYMMETRIC	ANTISYMMETRIC	SYMMETRIC	ANTISYMMETRIC
5	2	282.8142	283.4937	1217.7429	1249.2832	1885.8273	2158.4591
5	3	264.2332	264.9432	1197.9346	1230.6131	1864.2462	2140.7288
5	4	238.1517	238.9073	1170.0822	1204.4177	1834.2109	2115.8922
5	5	204.5021	205.3204	1134.0747	1170.6540	1796.1793	2083.9892
6	0	-	416.8989	-	1382.2636	-	2288.6995
6	1	412.6024	413.2158	1349.5254	1378.5726	2020.9692	2285.1604
6	2	401.5276	402.1575	1337.7510	1367.4263	2007.9320	2274.5197
6	3	383.0373	383.6963	1318.0754	1348.8252	1986.2347	2256.7979
6	4	357.0849	357.7852	1290.4210	1332.7353	1956.0344	2231.9789
6	5	323.6019	324.3601	1254.6673	1289.1006	1917.5191	2200.0829
6	6	282.5022	283.3379	1210.6598	1247.8558	1817.3648	2161.1286
7	0	554.4063	-	1492.9316	-	2167.7618	-
7	1	550.7389	551.3006	1489.0375	1516.0842	2163.3706	2420.4349
7	2	539.7270	540.3037	1477.3633	1504.9971	2150.2512	2409.8028
7	3	521.3432	521.9441	1457.8517	1486.4900	2128.4353	2392.0904
7	4	495.5377	496.1787	1430.4169	1460.5181	2098.0918	2367.2945
7	5	462.2470	462.9409	1394.9522	1427.0351	2059.3151	2335.4277
7	6	421.3847	422.1493	1351.3114	1385.9789	2012.3703	2296.4908
7	7	372.8463	373.7040	1299.3009	1337.2684	1958.3189	2250.5051

Table 1. (Continued)

J	K	GROUND STATE		v_2 STATE		$2v_2$ STATE	
		SYMMETRIC	ANTISYMMETRIC	SYMMETRIC	ANTISYMMETRIC	SYMMETRIC	ANTISYMMETRIC
8	0	-	712.3665	-	1676.5896	-	2578.4401
8	1	708.2189	708.7270	1647.9841	1672.9072	2325.9941	2574.8996
8	2	697.2780	697.7996	1636.4195	1661.8860	2312.7789	2564.2789
8	3	679.0102	679.5590	1617.0744	1643.4708	2290.8320	2546.5802
8	4	653.3748	653.9544	1589.8913	1617.6421	2260.2713	2521.8070
8	5	620.3010	620.9283	1554.7595	1584.3457	2221.2616	2489.9645
8	6	579.7065	580.3976	1511.5204	1543.5010	2174.0152	2451.0592
8	7	531.4835	532.2634	1460.0019	1495.0411	2118.7910	2405.0990
8	8	475.5250	476.4095	1399.9917	1438.8918	2055.8955	2352.0934
9	0	888.5101	-	1830.0084	-	2513.2106	-
9	1	884.8925	885.3465	1826.1801	1848.9065	2508.7657	2748.4923
9	2	874.0303	874.4964	1814.7208	1837.9452	2495.4547	2337.8818
9	3	855.8998	856.3793	1795.5752	1819.6518	2473.3483	2720.1999
9	4	830.4442	830.9620	1768.6591	1793.9774	2442.5643	2695.4505
9	5	797.6118	798.1711	1733.8833	1760.8846	2403.2676	2663.6384
9	6	757.3131	757.9301	1691.0862	1720.2841	2355.6702	2624.7702
9	7	709.4504	710.1420	1640.1130	1672.1179	2300.0313	2578.8540
9	8	653.9028	654.6919	1580.7400	1616.2903	2236.6572	2525.8991
9	9	590.5318	591.4483	1512.7024	1552.7035	2165.9014	2465.9163

Table 1. (Continued)

J	K	GROUND STATE		v_2 STATE		$2v_2$ STATE	
		SYMMETRIC	ANTISYMMETRIC	SYMMETRIC	ANTISYMMETRIC	SYMMETRIC	ANTISYMMETRIC
10	0	-	1304.5812	-	2047.5499	-	2944.6828
10	1	1080.5944	1080.9952	2023.4185	2043.9233	2711.6312	2941.1495
10	2	1069.8181	1070.2296	2012.0826	2033.0392	2698.2139	2930.5502
10	3	1051.8209	1052.2644	1993.1381	2014.8680	2675.9302	2912.8871
10	4	1026.5785	1027.0355	1966.5186	1989.3754	2644.8981	2888.1639
10	5	994.0078	994.5022	1932.1102	1956.4950	2605.2823	2856.3856
10	6	954.0348	954.5791	1889.8026	1916.1825	2557.2950	2817.5588
10	7	906.5603	907.1702	1839.4061	1868.3368	2501.1953	2771.6914
10	8	851.4672	852.1627	1780.7237	1812.8781	2437.2895	2718.7928
10	9	788.6195	789.4269	1713.4979	1749.7020	2365.9311	2658.8739
10	10	717.8625	718.8166	1637.4329	1678.7120	2287.5206	2591.9470
11	0	1298.7031	-	2243.2070	-		
11	1	1295.1453	1295.4949	2239.4865	2257.7899		
11	2	1284.4618	1284.8207	2228.2782	2246.9874		
11	3	1266.6385	1266.9899	2209.5617	2228.9654		
11	4	1241.5965	1241.9950	2183.2469	2203.6630		
11	5	1209.3095	1209.7405	2149.2388	2171.0282		
11	6	1169.6868	1170.1612	2107.4295	2131.0128		
11	7	1122.6317	1123.1631	2057.6523	2083.5305		

Table 1. (Continued)

J	K	GROUND STATE		v_2 STATE		$2v_2$ STATE	
		SYMMETRIC	ANTISYMMETRIC	SYMMETRIC	ANTISYMMETRIC	SYMMETRIC	ANTISYMMETRIC
11	8	1068.0323	1068.6381	1999.6963	2028.4767		
11	9	1005.7477	1006.4505	1933.3395	1965.7683		
11	10	935.6349	936.4648	1858.2810	1895.2858		
11	11	857.5210	858.5188	1774.1836	1816.9277		
12	0	-	1532.1780	-	2493.8938		
12	1	1528.3535	1528.6548	2474.1616	2490.3242		
12	2	1517.7692	1518.0784	2463.0830	2479.6061		
12	3	1500.0810	1500.4424	2444.5805	2461.7209		
12	4	1475.3039	1475.6472	2418.5853	2436.6261		
12	5	1443.3202	1443.6915	2384.9908	2404.2532		
12	6	1404.0722	1404.4808	2343.7258	2364.5848		
12	7	1357.4654	1357.9230	2294.5968	2317.4996		
12	8	1303.3832	1303.9096	2237.4194	2262.9086		
12	9	1241.7113	1242.3159	2171.9554	2200.6989		
12	10	1172.2873	1173.0008	2097.9451	2130.7738		
12	11	1094.9508	1095.8079	2015.0729	2053.0306		
12	12	1009.5175	1010.8079	1922.9511	1967.3582

Figure 3. Transitions of Interest for LIS in NH_3 .

interest for LIS. Jacobs³ et al. studied the $2\nu_2$ s(54) to ν_2 a(54) at 15.88 μm and the $2\nu_2$ s(44) to ν_2 a(44) at 15.95 μm , but these frequencies are not as close to 15.974 μm as those shown in Figure 3.

The problem with single photon pumping is obvious from Figure 3 in that the upper laser levels of interest lie in the $2\nu_2$ band and cannot be reached. At least a two-step process, i.e., from G to ν_2 to $2\nu_2$ must be used and that requires two photon pumping. As seen from Figure 2, each of the $2\nu_2$ desired laser levels can be accessed from two levels in ν_2 and each ν_2 level can be accessed from three levels in the ground state G. Hence, there are six two photon, vibration-rotation, paths to the laser levels in $2\nu_2$ as illustrated in Figure 4.

Figure 4. Six Two Photon, Vibration-Rotation, Paths to Reach Upper Laser Level in $2\nu_2$ in NH_3 .

The specific case of accessing $2\nu_2$ a(53) is given in Figure 5 along with the transitions associated with the six paths. Notice the total two photon energy required is the same for two pairs of paths.

Figure 5. Two Photon Paths for Accessing $2\nu_2$ a(53) of NH₃.

- 1) Ga(33) - ν_2 s(43) - $2\nu_2$ a(53)
 $1011.2041 + 1043.1535 = 2054.3576 \text{ cm}^{-1}$
- 2) Ga(43) - ν_2 s(43) - $2\nu_2$ a(53)
 $931.7728 + 1043.1535 = 1974.9263 \text{ cm}^{-1}$
- 3) Ga(43) - ν_2 s(53) - $2\nu_2$ a(53)
 $1032.1321 + 942.7942 = 1974.9263 \text{ cm}^{-1}$

- 4) $\text{Ga}(53) - \nu_2\text{s}(43) - 2\nu_2\text{a}(53)$
 $832.6321 + 1043.1535 = 1875.7856 \text{ cm}^{-1}$
- 5) $\text{Ga}(53) - \nu_2\text{s}(53) - 2\nu_2\text{a}(53)$
 $932.9914 + 942.7942 = 1875.7856 \text{ cm}^{-1}$
- 6) $\text{Ga}(63) - \nu_2\text{s}(53) - 2\nu_2\text{a}(53)$
 $814.2385 + 942.7942 = 1757.0327 \text{ cm}^{-1}$

The next step in the strategy is to find two laser lines from CO_2 and/or N_2O that match the desired frequencies, the overall match being more important than the intermediate match. A study of the CO_2 laser lines⁴ yields the data in Table 2. All frequency matches are less than 0.01 cm^{-1} (300 MHz).

TRANSITION	$\text{Ga}(33) - \nu_2\text{s}(43)$	$\nu_2\text{s}(43) - 2\nu_2\text{a}(53)$	$\text{Ga}(33) - 2\nu_2(53)$
FREQUENCY	1011.2041	1043.1535	2054.3576
$P_9(24) \text{ }^{12}\text{CO}_2$	—	1043.1633	
$P_9(8) \text{ }^{13}\text{CO}_2$	1011.2010	—	
DIFF.	-0.0031 cm^{-1}	$+0.0098 \text{ cm}^{-1}$	$+0.0067 \text{ cm}^{-1}$

Table 2. Two Photon Matches for Path 1 in NH_3 Leading to 822.6534 cm^{-1} Lasing.

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3.3 Experimental Arrangement

In designing the optical cavity of a two photon pumped molecular gas laser, care must be taken to suppress unwanted and competing laser lines. The unwanted laser lines that occur in pumping $2\nu_2$ a(53) are shown in Figure 6.

The 12.6 μm line is a desirable laser line since it depopulates the lower laser level ν_2 s(63) of the 12.16 μm transition, but the other laser lines 10.6, 12.0, and in particular 26.4 μm rob desirable populations. The 10.6 and 12.0 lines are

Figure 6. Possible Lasing Lines Competing with 822.6534 cm^{-1} .

weak and hence are not of major consideration but the 26.4 μm line is a very strong laser line and must be suppressed if an efficient 12.16 μm line is to be seen. Suppression of the 26.4 μm radiation is achieved by placing a ZnSe Brewster window in the optical cavity to act as a high pass filter, passing the 12.16 μm radiation but blocking the 26.4 μm radiation.

The experimental arrangement is shown in Figs. 7a-7b. The outputs from two CO_2 TEA lasers (one $^{12}\text{CO}_2$ and one $^{13}\text{CO}_2$) are combined into a collinear beam by two pairs of mirrors and a Ge beamsplitter, and focused into the NH_3 cell through a KCl window, by reflecting the pump beams off of the ZnSe filter. Alignment of these two beams is important.

The NH_3 cell is 80 cm long with a one curved mirror ($R = 4\text{m}$) and a flat mirror containing a 0.5 mm hole for output coupling of the laser radiation. This hole coupling is certainly not an optimum situation, a much better arrangement being a dielectrical coated mirror reflecting at 10 μm and partially transmitting at 12.16 μm . However, the hole coupler is broad band and desirable to use in diagnosing the laser process in an initial experiment.

The laser output is passed through a low pass filter and into a monochrometer and detector, or power meter.

For a two photon pump source to be successful, the two CO_2 TEA lasers must be synchronized in time. Since the pump pulses are the order of 200 nsec, this means controlling the time of

Figure 7a. Experimental Arrangement for Two Photon Pumping of a Molecular Gas.

Figure 7b. Photograph of Optical Layout.

the laser pulses to less than 20 nsec if good time overlap is to be achieved.

It was found that a CO_2 TEA laser, triggered by a spark gap, had too much time jitter. To solve this problem, the spark gaps were replaced by hydrogen thyratrons (7666/KU73). This permitted the two lasers to be precisely triggered at the same time or one laser ahead of or later than the other.

The $^{12}\text{CO}_2$ laser using a flowing gas and had a $^{12}\text{CO}_2$ CW gain cell in its optical cavity to prevent mode locking. The $^{13}\text{CO}_2$ laser was a sealed-off system, which could be refilled from time to time, to conserve the expensive $^{13}\text{CO}_2$ gas.

Both of these CO_2 TEA lasers were laboratory built and driven lightly, the $^{12}\text{CO}_2$ laser typically run from 60-200 mJ per pulse on $P_9(24)$, while the $^{13}\text{CO}_2$ laser run from 20-30 mJ per pulse on $P_9(8)$.

3.4 Experimental Results

Three different pump schemes, shown schematically in Figure 8, were studied in generating the 12.16 μm radiation via the $2\nu_2$ a(53) to ν_2 s(63) transition.

Gullberg et al.⁵ in 1973 has observed lasing from $2\nu_2$ a(53) at 36 and 65 μm but strangely missed the much stronger 26.4 μm lasing transition observed for the first time in our experiments. Even though the lower pump level ν_2 s(43) is at 1097.6 cm^{-1} , it is possible to obtain sufficient population at higher NH_3 pressures to yield strong lasing at 26.4 μm ,

Figure 8. Three Different Pumping Systems Studied for 12.16 μm Radiation Generation.

which suppresses the desired 12.16 μm lasing. This single photon pumping experiment demonstrated that efficient lasing at 12.16 μm would not be achieved unless the 26.4 μm signal was suppressed. This was accomplished by shortening the NH_3 cell and installing an intracavity ZnSe filter-window.

The threshold for 12.16 μm lasing at 8 torr NH_3 pressure was the order of 50 mJ with the CO_2 laser unmode-locked and 100 mJ mode-locked, the 12.16 μm output the order of 50 μJ .

Adding H_2 reduced the 12.16 μm radiation, N_2 increased it some 60%, while Ar had little effect.

Since two CO_2 pumps were available, the experiment shown schematically in Figure 8b was tried. It was expected that if the population of the lower laser level $v_2 s(63)$ was depleted that the 12.16 μm signal would increase. The effect observed was that the addition of the second pump (P(26)) extinguished the 12.16 μm signal. This result was not pursued but it is believed that it is caused by rotational relaxation between $v_2 s(43)$ and $v_2 s(63)$.

The experiment of interest is that of Figure 8c, where the thermal population of $G a(33)$ is 100 times that of $v_2(43)$, see Figure 6 for more details. In this experiment, three lasing lines were seen, one at 12.16, plus lines at 10.6 and 12.6 μm . With the P(24) pump off and P(8) alone, 12.0 μm was also seen. The 12.6 μm laser line is desirable since it depletes the lower laser level of the 12.16 μm radiation. Fortunately, the 10.6 μm radiation was weak and did not compete appreciably with the 12.16 μm radiation.

The waveforms of the various lasing signals are shown in Figure 9. Note there is a small delay of the 12.6 μm signal compared to the 12.16 μm signal because of the cascade process.

The pulse energies of the CO_2 pump used were 25 mJ for P(8) and 70 mJ for P(24). Of this 95 mJ total pump energy, only 60 mJ was injected into the NH_3 gas cell because of beamsplitters,

P(24) PUMP 0.1 μsec
EARLIER THAN P(8)

2 TORR NH_3
HgCdTe DETECTOR

Figure 9. Waveforms of Lasing Signals.

reflection losses, etc. The measured energy of the desired 12.16 μm laser signal was 0.5 mJ.

The theoretical efficiency for this two photon pumping process is given by the Manley-Rowe relationship

$$\eta_T = \frac{\nu_{12.16}}{\nu_{P(8)} + \nu_{P(24)}} \delta \times 100\% = \frac{822.7 \times 100}{1011.2 + 1043.2} \delta = 40\delta\% \quad (1)$$

where δ is the fraction of pump energy absorbed in the NH_3 gas.

The experimental efficiency was measured to be

$$\eta_{\text{exp}} = \frac{0.5}{60} \times 100\% \approx 1\% \quad (2)$$

This measured efficiency is considered to be a good value since the experiment has not been optimized. The mode volumes of the pump lasers in the NH_3 cell and mode volume of the 12.16 μm signals were not matched and a hole coupled mirror was used to extract the 12.16 μm signal. It is believed that the experimental efficiency could be improved by a factor of 10 by an optimum design.

To evaluate the effect of time overlap of the two pump signals, the 12.16 μm signal strength was measured versus the relative time delay of the P(24) and P(8) pump signals. This result is shown in Figure 10. It is seen that the FWHM points on the curve occur around $\pm 0.5 \mu\text{sec}$. The fact that the data is so smooth is an indication of how well the 7666 thyatron switches used in the CO_2 TEA lasers were working.

Figure 10. Effect on Signal of Relative Time Delays of Pumps.

The effect of adding N_2 and He with the NH_3 on the 12.16 μm signal is displayed in Figures 11 and 12. The initial pressure of NH_3 was 1 torr, a value below the optimum pressure of 2-3 torr, hence some improvement in output signal was expected due to pressure broadening of the lines and more pump power absorption.

The N_2 case is more interesting than He since the increase in signal output is greater and there is a rather sharp fall in output beyond 30 torr total pressure. There may be some collisional energy exchange between the $2v_2(53)$ level of NH_3 at 2140.7283 cm^{-1} and the $v=1$ level of N_2 at 2326 cm^{-1} , accounting for some of the effect. This point was not pursued.

A typical 12.16 μm signal output versus NH_3 and/or added N_2 pressure curve is shown in Figure 13. For these conditions, adding N_2 was more effective than adding NH_3 , since one did not start with the optimum NH_3 pressure.

The threshold pump energies for the 12.16 μm signal were 1 mJ P(8) mode-locked, plus 3 mJ P(24) singlemode.

To further explore the 12.16 μm signal, 58 cm long NH_3 absorption cell was placed between the spectrometer and HgCdTe detector, as shown in Figure 14, and the signal pulse shape measured versus NH_3 pressure in the absorption cell. It will be observed that a notch exists in the 12.16 μm pulse which might indicate two signals present. However, all parts of the pulse appears to attenuate evenly with absorption cell pressure.

Figure 11. Effect of N₂ Addition of 12.16μm Signal.

Figure 12. Effect of He Addition on 12.16μm Signal.

Figure 13. A Typical 12.16 μ m Signal Versus Pressure Curve.

Figure 14. Attenuation of 12.16 μ m Radiation in NH₃ Absorption Cell.

The log of the Signal S is plotted versus pressure p in Figure 15. From the expression $S = S_0 e^{-\alpha x}$, it is seen that

$$\ln S = \ln S_0 - \alpha x \quad (3)$$

where S_0 is the signal at $p=0$.

The absorption constant α for the case where the line is pressure broadened can be represented by the expression

$$\alpha_p = \frac{Ap^2}{(\nu_0 - \nu)^2 + (ap)^2} \quad (4)$$

where A and a are constants and ν_0 is the line center frequency, while in the Doppler regime

$$\alpha_D = Bp \quad (5)$$

where B is a constant.

From Figure 8c, $(\nu_0 - \nu) \approx 200$ MHz and the value of a , for NH_3 , is approximately 15 MHz/torr, hence for $p > 50$ torr, the value of α_p , and hence $\ln S$ should be constant. The Doppler width is approximately 37 MHz, hence for $p > 3$ torr the line is predominately pressure broadened.

While the data of Figure 15 is not precise, it does indicate that $(\nu_0 - \nu)$ may be greater than 200 MHz, since the curve does not appear to be flattening out even at 300 torr.

A density matrix calculation of the gain $g(s)$ for a two photon-three level system is given in Figure 16. If $(\nu_p - \nu_{31})$ is taken as 225 MHz and $\Delta\nu = 15$ MHz, then $\phi_p = 15$. Typical

Figure 15. Logarithm of 12.14 Signal Versus NH_3 Absorption Cell Pressure.

values of various parameters for the NH_3 experiment are:

$$E \approx 10^6 \text{ volts/meter} \quad \Delta\nu \approx 15 \text{ MHz}$$

$$\mu_{13} \approx 5.4 \times 10^{-31} \text{ coul-meters}$$

Figure 16. Gain Versus Frequency in Two Photon-Three Level System Showing AC Stark Splitting.

hence $w_p \approx 10^3$. From the curves in Figure 16, maximum gain occurs at an offset of $\phi_s = 40$ or $(\nu_s - \nu_{32}) \approx 600 \text{ MHz}$.

Thus for

$$(ap)^2 \geq 10(\nu_o - \nu)^2 \quad (6)$$

the pressure p must be greater than 150 torr, a value more compatible with the data of Figure 15. The AC Stark shift causes the generated signal to be further off resonance than the pump is off resonance.

4. Metal Oxidation Chemical Laser Studies

4.1 Introduction

At the time when the metal oxidation laser studies were initiated on this ERDA grant, the LASL exploding wire experiments had been done and were taken as an existence proof that metal oxidation lasers were feasible on a CW basis. Hence, the research plan was to design a fast flow, fast mixing system, obtain a flame that had a good visual appearance, and look for lasing. Since the expected spontaneous radiation, in the absence of lasing, was in the 10-20 μm wavelength range, it would have been difficult to measure with the high temperature background. Lasing was to be the diagnostic tool to be used to identify the lasing energy levels of the molecule, the maximum gain regions of the flame, hopefully the chemical rate constants, the effect of different carrier gases, etc. Unfortunately, the designed system with several modifications, did not lase and the experimental configuration of the flame and apparatus did not permit easy diagnosis. Also the stainless steel construction did not permit rapid turn around time in making experimental modifications.

If the problem was to be solved on a shorter time scale, a new research strategy had to be initiated. Diagnostics were absolutely necessary if one were to determine if any gain existed in the flame and evaluate the processes contributing to the excitation and relaxation.

During the last 5-6 months of the grant, the research strategy was adopted to design a fast flow, fast mixing flame that could essentially be placed in a multipass IR spectrometer and do the flame spectroscopy in situ. In this manner, one could generate a gain/absorption curve of the flame and determine which energy levels were being populated. One could then vary the various parameters of the system to find the optimum gain conditions and decide if a laser were possible.

In the meantime, a theoretical effort was mounted to calculate dipole matrix elements of the product molecules and estimate V-T and V-V relaxation rates, to aid in determining if a laser were possible and to support the experimental work.

The apparatus for this new experimental strategy was some 80% complete at the termination of the grant.

4.2 Experimental Work on Initial System

The experimental set-up and configuration was described in detail in last year's annual report. Modifications made were improved clamping of the halogen spray bars and other parts to prevent warpage during the high temperature runs.

Repeated runs were made with Li, Mg, and Zn with an F_2 oxidizer and Ar carrier gas and the flame probed with a pair of Fabry-Perot mirrors over a ± 1.2 cm horizontal and ± 5 vertical scan, with no lasing detected. These excellent visual appearance flames could be readily maintained for the order of 20-30 minutes, ample time to make optical scans.

4.3 Exploration of a Glow Discharge Metal Fluoride Laser

An ideal diagnostic tool for probing a metal fluoride flame laser, would be to have a glow discharge metal fluoride laser, even if the lasing signal were rather weak. This would mean operating the glow discharge laser at elevated temperatures to obtain the needed vapor pressure of the metal salts.

The high temperature cell that was constructed is shown in Figure 1/. It is made with a quartz and alumina cylindrical tube and heated by a Lindberg clamshell type heater. The heated active region of the tube is 60 cm long and has a 2.7 cm ID and can be run up to 1100°C.

Initially, a 5C22 thyatron modulator was used to drive the system, but it was replaced by a low inductive capacitor and gas discharge switch which could supply voltages up to 24 kV.

To check the system, a $\text{CO}_2\text{-N}_2\text{-He}$ mixture was placed in the tube. Lasing could be detected up to 500°C with a 21 kV, 1 pps drive. Next, an $\text{SF}_6\text{-H}_2$ mixture was tried and lasing obtained up to 1050°C, for voltages between 12 and 24 kV, and 1 pps repetition rates, on HF.

These tests verified the thermal stability of the optical system and the negligible effects of temperature gradients. They also set a record for lasing at high temperatures.

Various metal salts (LiF , LiI , LiCl , PbO , PbS , LiBr , KF , etc) were then tried in turn, with and without carrier gases, but no lasing was seen.

Figure 17. High Temperature Laser Cell.

Next, mixtures of SF_6 and the metal salts were studied to explore possibilities^{1,2} such as

but still no lasing could be detected.

The system was then modified to be F_2 compatible to try mixtures of F_2 and the metal salts, i.e.,

Also $\text{Ni}(\text{CO})_4$ ³ and $\text{Fe}(\text{CO})_5$ ⁴ were secured to try metal donor molecules. These experiments were not brought to a conclusion at the end of the grant period.

4.4 An Attempt to Use a Black Body Source Probe

A black body, carbon rod, radiation source,^{5,6} capable of being heated to greater than 2500°K , existed in our laboratory for general use. This source, along with KBr focusing lenses and assorted optics, monochrometer, Golay cell and lock-in amplifier, were assembled around the 1.5 meter length of the metal flame reaction cell. However, the diffraction losses could not be controlled sufficiently and the black body radiation detected beyond $10\text{ }\mu\text{m}$ wavelength. This experiment did show that with a properly designed smaller flame and multipass system, it would be feasible to work in the $10\text{-}20\text{ }\mu\text{m}$ range with a black body source.

4.5 Double Beam Spectrometer Experiment

The new metal flame diagnostic system is a double beam spectrophotometer in which a 30 cm long, CW reaction cell functions as the sample chamber. An optical layout of the system is shown in Figure 18.

The heated carbon rod is used for the black body source. The black body radiation beam is split and recombined by means of synchronous reflection choppers. One beam enters the reaction region which has been made into a White cell.⁷ After leaving the White cell, the two beams are combined and focused into a monochromator. The flame assembly can be moved relative to the mirrors so that it can be spatially probed.

Once the apparatus was assembled, it was planned to check it out by using a known gas in the reaction cell in a typical grating spectroscopy measurement.

4.6 Calculation of Matrix Elements and Relaxation Rates

For laser modelling studies and gain calculations, it is necessary to know matrix elements and relaxation rates for the diatomic molecule.

For polar diatomic molecules, the matrix element μ_{10} associated with vibrational states⁸ $v=1$ and $v=0$ can be expressed as

$$\mu_{10} = \left| \frac{d\mu}{dr} \right| \sqrt{\frac{h}{8\pi^2 m v_{10}}} \quad (7)$$

where m is the reduced mass, v_{10} the energy level spacing, and

Figure 18. Double Beam IR Gain Experiment.

$$\frac{d\mu}{dr} = 3q - \frac{2\mu_o}{r_e} \quad (8)$$

where μ_o is the permanent electric dipole moment of the diatomic molecule and r_e the equilibrium separation of the atoms.

Pauling⁹ gives an expression for determining μ_o as

$$f = \frac{\mu_o}{qr_e} = 1 - \exp \left(\frac{-(\chi_A - \chi_B)^2}{4} \right) \quad (9)$$

where χ_A and χ_B are the electronegativities of atoms A and B.

In Table 3 is listed calculated and experimental data, where available, for some molecules of interest. Comparison of the data shows agreement to within 20% for both μ_o and μ_{o1} for polar gases. For non-polar gases, the values of μ_o compare favorably but the value of μ_{10} is less accurate as expected.

It is seen from Table 3 that μ_{10} for alkali fluorides that $0.3 \leq \mu_{10} \leq 0.4$ debye, while for alkali-earth fluorides that $0.25 \leq \mu_{10} < 0.35$ debye. Laser gain g varies as $|\mu_{10}|^2$.

Collisional relaxation of chemically excited states is extremely important in chemical laser systems; accordingly, an attempt was made to calculate V-T and V-V relaxation rates for the metal oxidation products. Precise calculations were greatly hampered by the lack of experimental measurements concerning many of the metallic salts, but qualitative and still useful results were obtained from the analyses.

First considering V-T relaxation, the well-known SSH theory with modifications can be applied with some reservations. Since

Table 3. Electric Dipole Moments of Diatomic Gases

POLAR GASES												
GAS	⁶ LiCl	⁵ LiF	NaF	HF	RbF	CsF	BeF	MgF	CaF	SrF	BaF	ZnF
$a, b_{1/\lambda} (\text{cm}^{-1})$	662	910.34	536.10	426.04	373.27	352.56	1266.9	721.6	587.4	498.0	468.9	(630)
$a, b_{r_e} (\text{\AA})$	2.018	1.5639	1.9260	2.1715	2.2704	2.3455	1.361	1.7500	1.931	2.0757	2.163	
f_{theo}	0.695	0.895	0.902	0.918	0.918	0.921	0.766	0.832	0.892	0.899	0.908	.692
$f_{\text{theo } e} (\text{D})$	6.74	6.72	8.34	9.58	10.0	10.4	5.01	6.99	8.27	8.96	9.43	
$b, c_{\mu_0} (\text{D})$	7.13	6.33	8.16	8.60	8.55	7.88						
$\mu_{1,0}^{\text{exp}} (\text{D})$	0.517	0.391	0.327	0.361	0.371	0.412	0.329	0.301	0.276	0.269	0.264	
$\mu_{1,0}^{\text{theo}} (\text{D})$	0.553 ^a	0.499 ^e										
NCN-POLAR GASES												
GAS	CO	HF	HCl	HBr	HI							
$a, b_{1/\lambda} (\text{cm}^{-1})$	2169.82	4138.32	2990.95	2643.98	2308.09							
$a, b_{r_e} (\text{\AA})$	1.1283	0.91680	1.2745	1.4145	1.6090							
f_{theo}	0.180	0.547	0.206	0.134	0.0515							
$f_{\text{theo } e} (\text{D})$	0.976	2.41	1.26	0.910	0.398							
$b, c_{\mu_0} (\text{D})$	0.112	1.82	1.084	0.82	0.445							
$\mu_{1,0}^{\text{exp}} (\text{D})$	0.0929	0.0679	0.963	0.105	0.119							
$\mu_{1,0}^{\text{theo}} (\text{D})$	0.104	0.099	0.067	0.037								

^aB. Rosen, Ed., *Constantes Sélectionnées, tables des Constantes et Données Numériques*

^b*Données Spectroscopiques Relative aux Molecule Diatomiques*, vol. 17, 1970.

^cD. Gray, Ed., *AIP Handbook*, 3rd edition, 1972.

^eR.C. Weast, Ed., *Handbook of Chemistry and Physics*, 47th edition, 1957.

^dT. Moran and J.W. Trischka, *J. Chem. Phys.*, 34, no. 3, 923 (1961)

^eReference 8.

^fK.L. Bell, *J. Phys.*, 3: *Atom Molec. Phys.*, 3, p. 1426 (1970)

these metallic salts are highly polar, the simple close approach interaction potential of SSH theory may be inadequate. Further, the Lennard-Jones potential parameters are not experimentally available for these salts and cannot be estimated confidently for polar diatomics. Nevertheless, the SSH treatment can be used as a starting point, especially since temperatures above 300°K are involved. The "redefined impulse approximation" SSH equation for the V-T transfer probability for a collision between diatomics BC and AD is¹⁰

$$P_{V-T} = \left(\frac{A^2 BC}{(B+C)(A+B)^2 \mu} \right) \sqrt{\frac{8\pi}{3}} \frac{\theta'}{\theta} \left(\frac{\theta'}{T} \right)^{1/6} e^{-1.5 \left(\frac{\theta'}{T} \right)^{1/3}} e^{-\frac{\theta}{2T}} e^{-\frac{\epsilon}{kT}} \quad (10)$$

where $\mu = \frac{(A+D)(B+C)}{(A+D)+(B+C)}$, A is mass of atom A, etc., $\theta = \frac{\hbar\omega}{k}$ where $\hbar\omega$ is the energy of the vibrational quantum, $\theta' = \frac{4\pi^2 \mu L^2 a^2}{k}$ where L is the interaction turning point (usually taken as 0.2Å but actually determined by numerical solution of a transcendental equation); and ϵ is the well depth of the Lennard-Jones potential. Since L is a function of temperature and the Lennard-Jones parameters ϵ and σ , for comparison purposes, the calculations, shown in Table 4, were performed using $L = 0.2\text{\AA}$, $\epsilon = 0$ and thus may be in error by perhaps an order of magnitude. The tabulated result for each collision pair is the orientational average of Equation (10). As can be seen by inspecting the table, argon or nitrogen diluents are much less likely to V-T relax MF than is He, mainly to the mass differences. Further,

Table 4. SSH Collision Probabilities for V-T Relaxation.

ASSUMING $L = 0.2\text{\AA}$, $T = 500^\circ\text{K}$, $t = 0$

COLLISION PAIR	LiF-LiF	LiF-Li	LiF-F	LiF-Li ₂	LiF-F ₂	LiF-Ar	LiF-He	LiF-N ₂
P_{averages}	6×10^{-5}	4×10^{-3}	4×10^{-4}	4×10^{-4}	6×10^{-5}	8×10^{-5}	1×10^{-2}	1×10^{-4}
COLLISION PAIR	MgF-MgF	MgF-Mg	MgF-F	MgF-Mg ₂	MgF-F ₂	MgF-Ar	MgF-He	MgF-N ₂
P_{averages}	1×10^{-4}	6×10^{-4}	1×10^{-3}	3×10^{-5}	1×10^{-4}	2×10^{-4}	1×10^{-2}	2×10^{-4}

Table 5. Short-Range and Long-Range Collision Probabilities for LiF-LiF V-V Relaxation.

$\text{LiF}(v) + \text{LiF}(0) \rightarrow \text{LiF}(v-1) + \text{LiF}(1)$ where

$T = 600^\circ\text{K}$ $L = 0.117\text{\AA}$ $\Delta J = 0$ $J = 12$ $\sigma = 2.62\text{\AA}$ $\eta_{1,0} = 0.391D$

v	$ \Delta\omega(\text{cm}^{-1}) $	$p^{\text{S}\cdot\text{R}}$	$p^{\text{L}\cdot\text{R}}$
1	0	5.0×10^{-2}	
2	15.9	1.0×10^{-1}	
3	31.7	1.5×10^{-1}	
4	47.6	1.9×10^{-1}	8.3
5	63.4	2.3×10^{-1}	8.3
10	143	3.6×10^{-1}	5.3
20	301	3.0×10^{-1}	1.3

from this simple treatment it appears that MF-MF self relaxation should not be a major problem, as is the case for HF-HF. From a V-T viewpoint, it would appear more desirable to run the $\text{Li} + \text{F}_2$ system F_2 rich and the $\text{Mg} + \text{F}_2$ system Mg rich, but this is probably not a major effort.

The V-V relaxation situation is also complicated by the fact that the salt molecules are quite polar. The short range contribution to the V-V collision probability is described by either a SSH or a Rapp interaction potential, depending on the energy mismatch between the colliding molecules.¹¹ The analytical expressions are involved and again depend upon the short range turning distance L which cannot be accurately estimated for these salt vapors; therefore, one again can gain only qualitative information from the calculations.

The off resonance long range V-V collision probability is based upon the dipole-dipole interaction potential and has a rather simple form,¹¹ which, of course, involves the infrared electric dipole moments but again, unfortunately, a Lennard-Jones potential parameter which cannot be accurately estimated.

Table 5 lists some typical values for a calculation for excited LiF colliding with ground state LiF (however, the theory is general in that both molecules can be excited in any V, R energy levels). The short range results, although quite large compared to V-T probabilities, seem reasonable since LiF is comprised of one light and one heavy atom and can thus

have considerable steric effects. Indeed, these results are very similar to experimental values for $\text{HF}(v) + \text{HF}(0) \rightarrow \text{HF}(v-1) + \text{HF}(1)$ where $p_{2-1} = 9 \times 10^{-2}$, $p_{3-2} = 1.0 \times 10^{-1}$, $p_{4-3} = 2.5 \times 10^{-1}$, $p_{5-4} = 3.8 \times 10^{-1}$.¹² The long range theory, applicable for off resonance collisions, predict extremely large collisional transfer probabilities, much higher than observed in HF. This result is not too surprising though, since all of the metallic salt vapors under consideration are much more polar than HF and thus should naturally have stronger dipole-dipole forces acting between them.

The net result of these relaxation calculations is that probably V-V transfer in the salt vapors is at least as fast if not faster than for the HF chemical laser system. On the other hand, since the electric dipole matrix elements are longer, the gain should be even higher than that for HF. The reasonable V-T and fast V-V rates support our goals of fast mixing and sonic flows in the CW cell and uniform pre-mixing and microsecond pulsing in the pulsed cell.

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5. Personnel Associated with Grant

	<u>Title</u>	<u>Percent of Time</u>
Paul D. Coleman	Principal Investigator	5%
Richard Adams	Research Assistant	50%
David Kim	Research Assistant	50%
John Leap	Research Assistant	50%
Donald Fulton	Electronics Technician	10%
Jimmie Smith	Secretary	5%