FINAL REPORT

# MILLIMETER AND SUBMILLIMETER WAVE RESEARCH: SPECTROSCOPY, ENERGY TRANSFER, AND TECHNIQUES

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January 16, 1984

U.S. Army Research Office
Contract No. DAAG-29-~~83-K-0078~~ PO C 0026

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# REPORT DOCUMENTATION PAGE

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|---|---|
| 1. REPORT NUMBER: Final Report | 2. GOVT ACCESSION NO.: AD-A137884 |
| 3. RECIPIENT'S CATALOG NUMBER: | |
| 4. TITLE (and Subtitle): Millimeter and Submillimeter Wave Research: Spectroscopy, Energy Transfer, and Techniques | 5. TYPE OF REPORT & PERIOD COVERED: Final Report 5 Nov 79 -5 Nov 83 |
| | 6. PERFORMING ORG. REPORT NUMBER: Duke U. Dept. of Physics |
| 7. AUTHOR(s): Frank C. De Lucia | 8. CONTRACT OR GRANT NUMBER(s): DAAG-29-~~83-K-0078~~ 80-C-0026 |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS: Department of Physics, Duke University, Durham, North Carolina | 10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: |
| 11. CONTROLLING OFFICE NAME AND ADDRESS: U. S. Army Research Office, P. O. Box 12211, Research Triangle Park, NC 27709 | 12. REPORT DATE: January 16, 1984 |
| | 13. NUMBER OF PAGES: approx. 34 |
| 14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office) | 15. SECURITY CLASS. (of this report): Unclassified |
| | 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE: |

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Millimeter Waves
Submillimeter Waves
Spectroscopy
Energy Transfer
Molecular Lasers
Molecular Energy Levels

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The project, "Millimeter and Submillimeter Wave Research: Spectroscopy, Energy Transfer, and Techniques," addresses a broad range of scientific topics and technological developments important to this spectral region. For purposes of discussion, we have divided this report into three categories: (1) the development and evolution of techniques for this spectral region, (2) studies of molecular lasers and processes, and (3) the study of energy levels and transition frequencies in molecules. Also included are lists of publications and of personnel who worked on these projects.

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SUMMARY OF WORK UNDER ARO CONTRACT DAAG-29-83-K-0078

The project, "Millimeter and Submillimeter Wave Research: Spectroscopy, Energy Transfer, and Techniques," addresses a broad range of scientific topics and technological developments important to this spectral region. For purposes of discussion, we have divided this report into three categories: (1) the development and evolution of techniques for this spectral region, (2) studies of molecular lasers and processes, and (3) the study of energy levels and transition frequencies in molecules. Also included are lists of publications and of personnel who worked on these projects.

I. Experimental Techniques and Devices

We have extended our basic source technique to beyond 1 THz so that now the entire NMMW spectral region (100 GHz-1000 GHz) can be covered. This advance came about primarily as a result of a redesign of our non-linear harmonic generators. Figure 1 shows an example of a basic system configured around this source. Simple changes would result in a system appropriate for component studies, detector development, etc.

This technique has a number of favorable attributes:

(1) It is continuously tunable throughout the spectral region, <100 GHz->1000 GHz.

(2) Systems based on the harmonics of phase locked klystrons have resolution limited only by the physical processes being studied. Furthermore, they have absolute frequency calibration by direct reference to WWVB.

(3) Although the amount of power produced by harmonic generation is modest, the systematic increase ($\sim\nu^3$) of the strength of rotational transitions with frequency and our use of cryogenic detection techniques result in a very high sensitivity technique.

(4) The MM/SUBMM lends itself to quasi-optical techniques. These techniques make possible the remote sampling of hostile environments, pressure broadening cells, etc. without affecting the system under study.

(5) It is simple, reliable, and reasonably inexpensive. A number of systems patterned on this design have been built at leading government and university laboratories throughout the world.

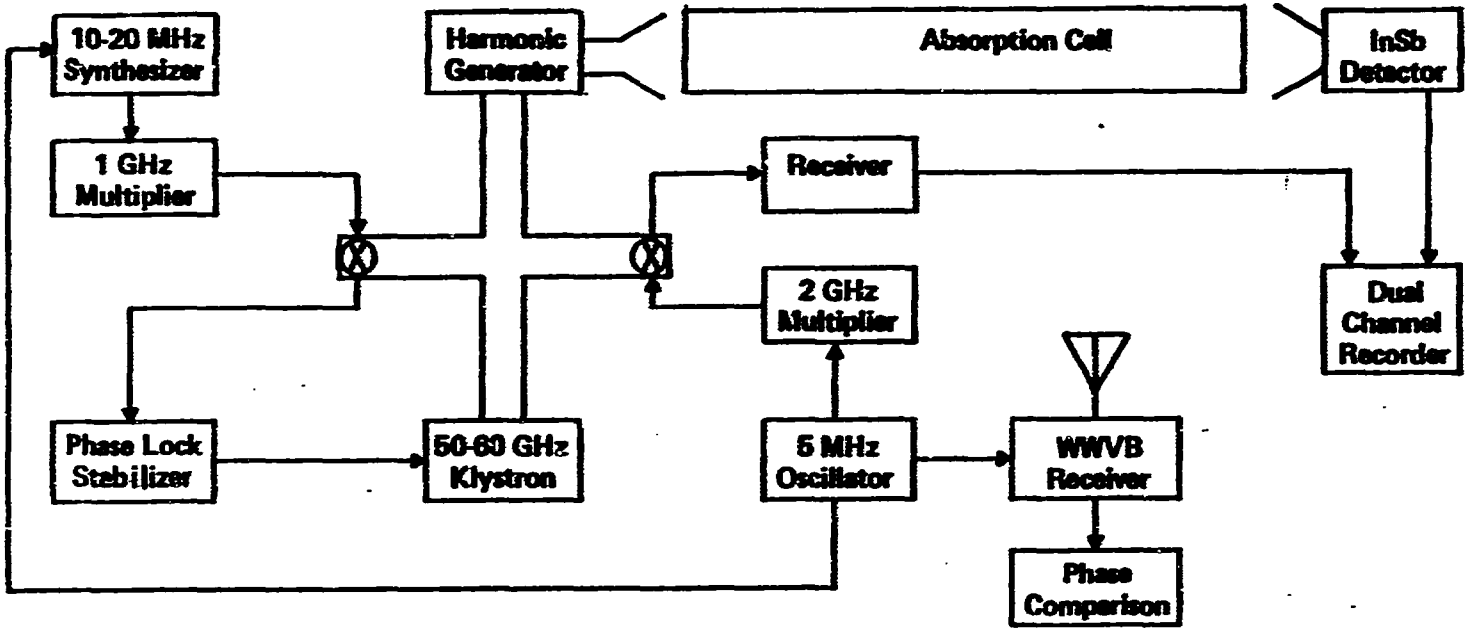



Figure 1. Basic system for work throughout the NMMW spectral region (<100->1000 GHz). Configuration shown is for absorption studies of gases.

For our studies of optically pumped FIR lasers, we have developed the experimental apparatus shown in Figure 2. Briefly, this system consists of a line tunable $CO_2$ laser, tunable MM/SUBMM spectrometer, and a FIR gain cell in which the $CO_2$ laser beam and microwave diagnostic beam copropagate. In order to minimize errors induced by long term drifts and to make possible absolute rather than relative experimental results, the $CO_2$ laser is chopped at ~15 Hz. The data recorded in the absence of the pump, in combination with the well know relations for the absorption coefficients of gases in thermal equilibrium, provide an absolute calibration for our work. This procedure is feasible because the sensitivity of our techniques allows us to observe the absorptions with good signal to noise even in excited vibrational states. This system has made it possible to realistically model for the first time the energy transfer processes in optically pumped FIR lasers. A similar system has been developed for our studies of discharge laser systems.

We have also developed new techniques that have increased the detectability of molecular ions in the NMMW by <u>three orders of magnitude</u>. This is an especially significant fundamental development. Briefly, we use an axial magnetic field to lengthen the ion rich negative glow of an abnormal glow discharge. Figure 3 shows the cell and Figure 4 shows the dramatic effect of this. This technique is being currently adopted by the other workers in this field.

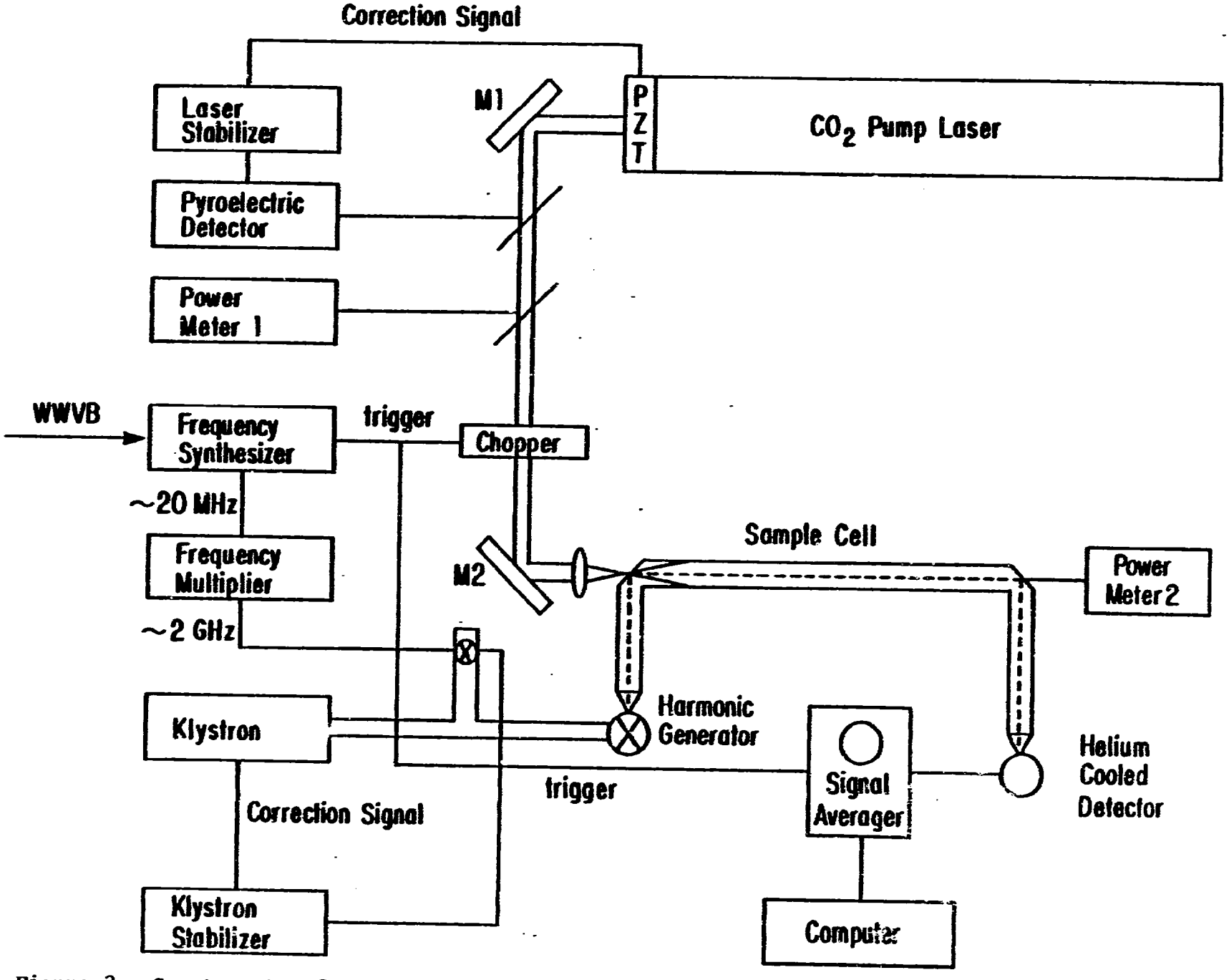



Figure 2. Spectrometer for the study of optically pumped laser systems.

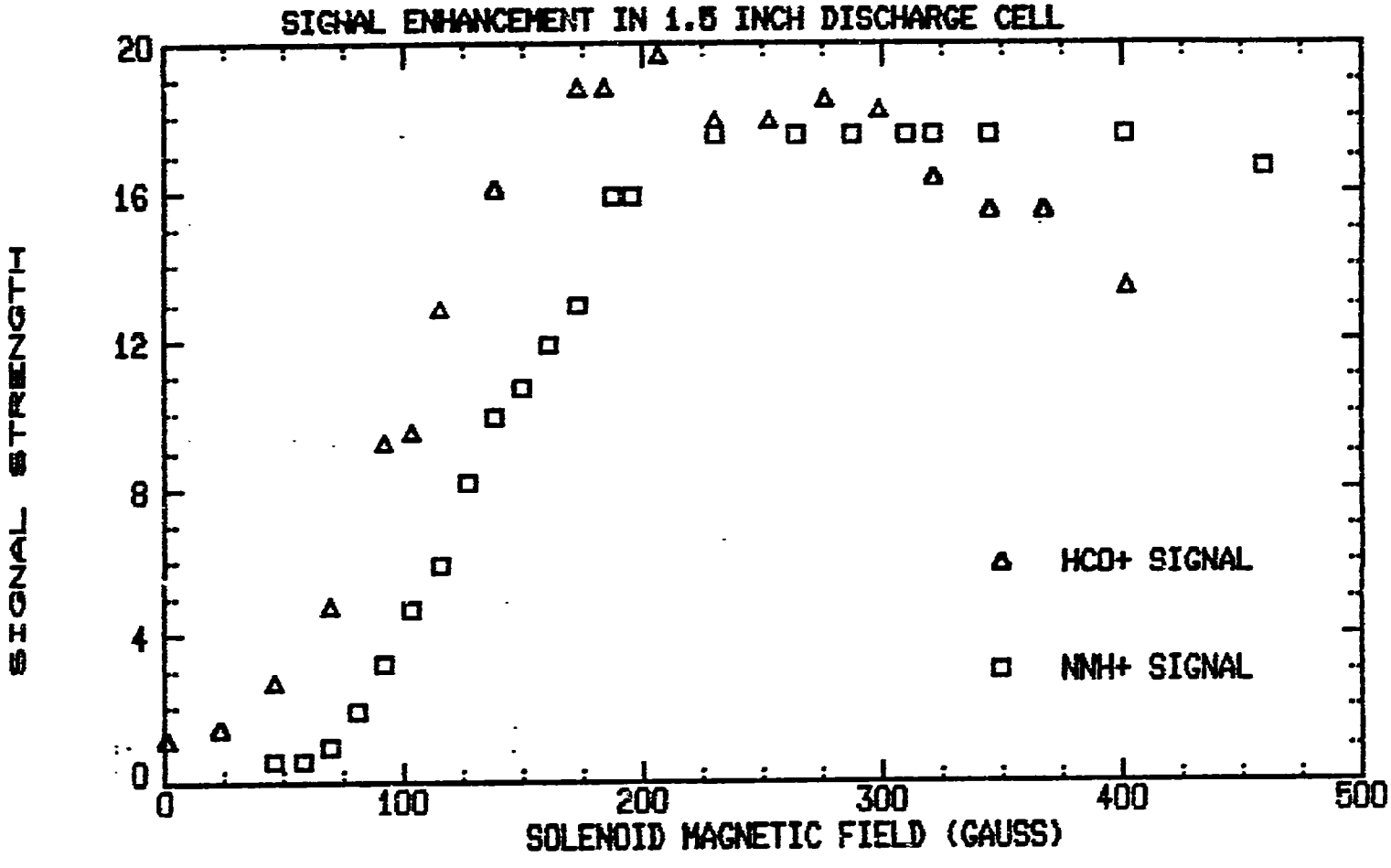



Figure 4a. Signal enhancement with the application of magnetic field.

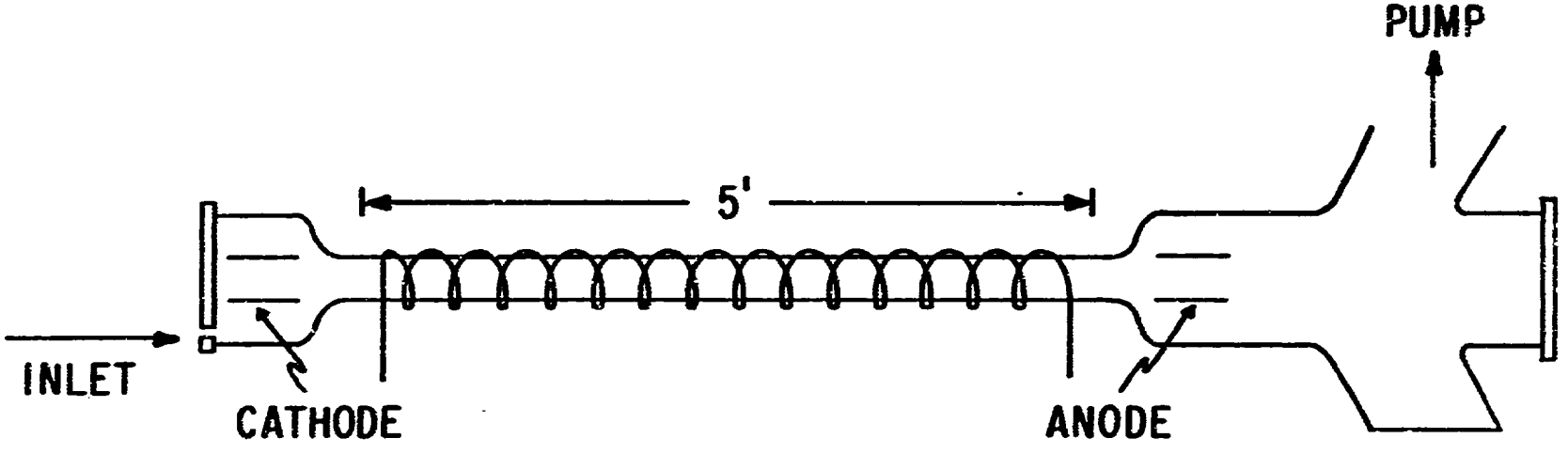



Figure 3. Cell for new magnetic confinement technique for the study of molecular ions.

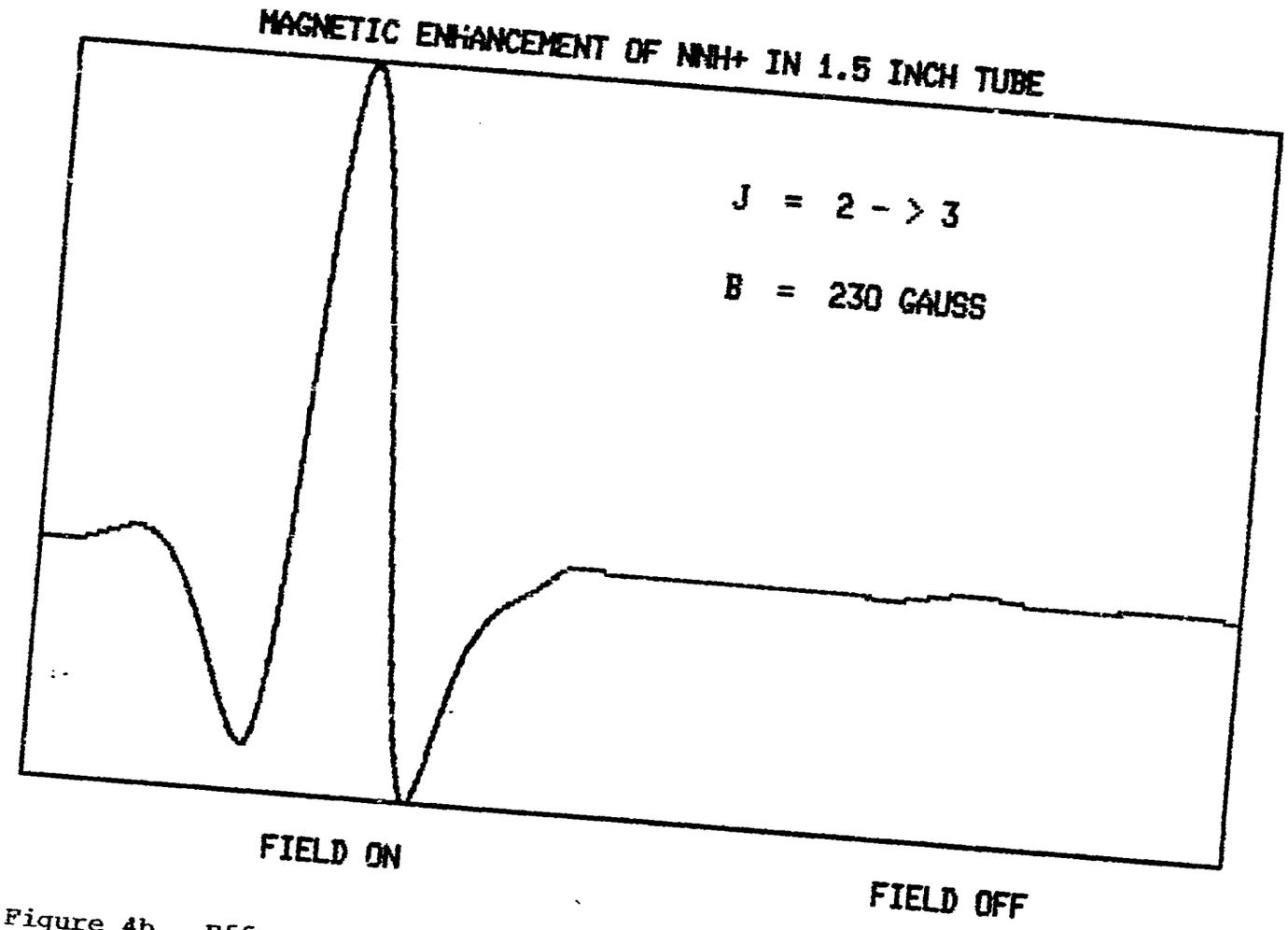



Figure 4b. Effect of magnetic field on signal.

II. Studies of Molecular Lasers and Processes

We have used the system shown in Figure 2 to study the energy transfer processes in optically pumped FIR processes.

Figure 5 shows a pair (pumped/unpumped) of observations for the $\nu_3$, J=4-5, K=3,2,1, and 0 transitions of $^{13}CH_3F$. This figure shows the dramatic effect of the $CO_2$ pump on the $\nu_3$, J=5, K=3 level. Of equal, or perhaps greater importance, is the information given on the K≠3 levels. Careful inspection of these (and all other $\nu_3$, K≠3 levels) show them to have an enhanced absorption and to be in thermal equilibrium with one another. In order to account for these data and data on many other transitions that our continuously tunable technique has allowed us to obtain , we have developed the energy transfer model shown in Figure 6. In this model the experimentally observed rotational thermal equilibrium is implemented via a ground state (K≠3) pool and an excited state (K≠3) pool. We observe substantial deviations from thermal equilibrium within K=3 and the population of each of these states (up to J=42) is allowed to vary independently. The states/pools are allowed to exchange populations via the pump rate (R), the probability of $\Delta J=\pm 1$, $\Delta K=0$ collisional tranfers ($P_{up}/P_{down}$), the probability of collisional exchange between the K=3 states and their respective pools ($P_{in}/P_{out}$), and the probability of collisional exchange between the vibrational pools ($PV_{up}/PV_{down}$). Because these probabilities must obey microscopic reversibility and because one of them must be fixed to define a collision, this system has only three adjustable parameters. In our analysis, we recorded data at 7 pressures and used a non-linear

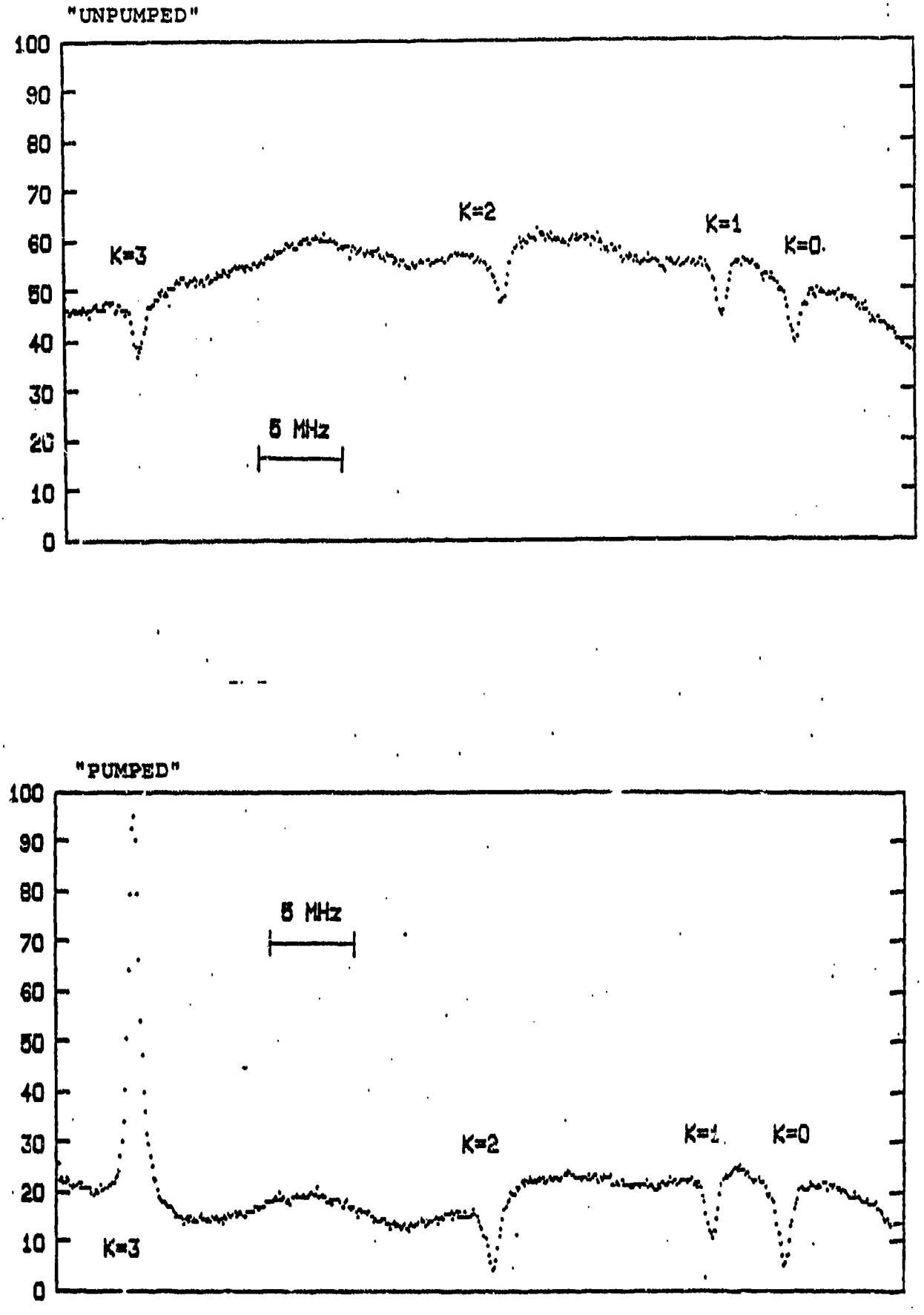



Figure 5. Effect of $CO_2$ laser pumping on the $\nu_3$, J=4-5, K=3,2,1, and 0 transitions of $^{13}CH_3F$.

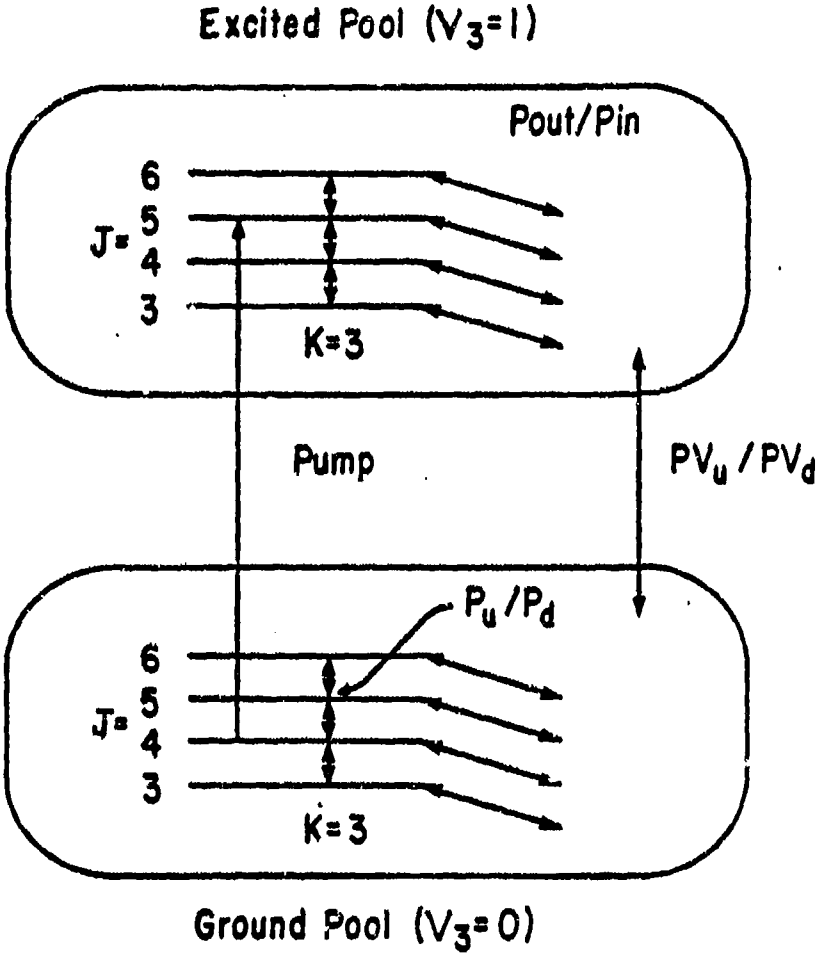



Figure 6. Schematic of energy transfer model for the $^{13}CH_3F$ optically pumped laser.

least squares implementation of a master equation to calculate these probabilities and transition rates. Figure 7 shows the results of these seven fits for the pump rate [photons/(sec-cm$^3$)]. In the absence of saturation, this curve should be a horizontal line. However, an inhomogeneously broadened line should have a saturation factor of $1/\sqrt{1+I_\nu/I_s}$, which is included in our best fit line. Although the pump rates shown in this figure were deduced from our spectroscopic data and theoretical model, we have also made a direct measurement of the laser power absorbed. This measurement gives a number about 20% higher than the spectroscopically deduced value. This is an excellent agreement between two very different (and in one case model dependent) observations. Figure 8 shows a similar result for $1/PV_d$. Our experiments have demonstrated the necessity of distinguishing between "hard" velocity changing collisions and "soft" collisions that induce rotational transitions but which do not appreciably affect the molecular trajectories. This is especially important in energy transfer models of the $^{13}CH_3F$ laser. The collisions that induce $\Delta J=\pm1$, $\Delta K=0$ transitions are ~x20 more likely than the "hard" collisions that lead to random walk processes. Figure 8 also includes a straight line. This line represents a value of $1/PV_d$ calculated for straight line molecular trajectories to the wall (i.e. no random walk) and vibrational equilibriation upon wall collision. This line and our experimental results are again very consistent with our calculation that only ~1-2 hard collisions occur along the trajectory of a molecule to the wall at 10 μ. This small

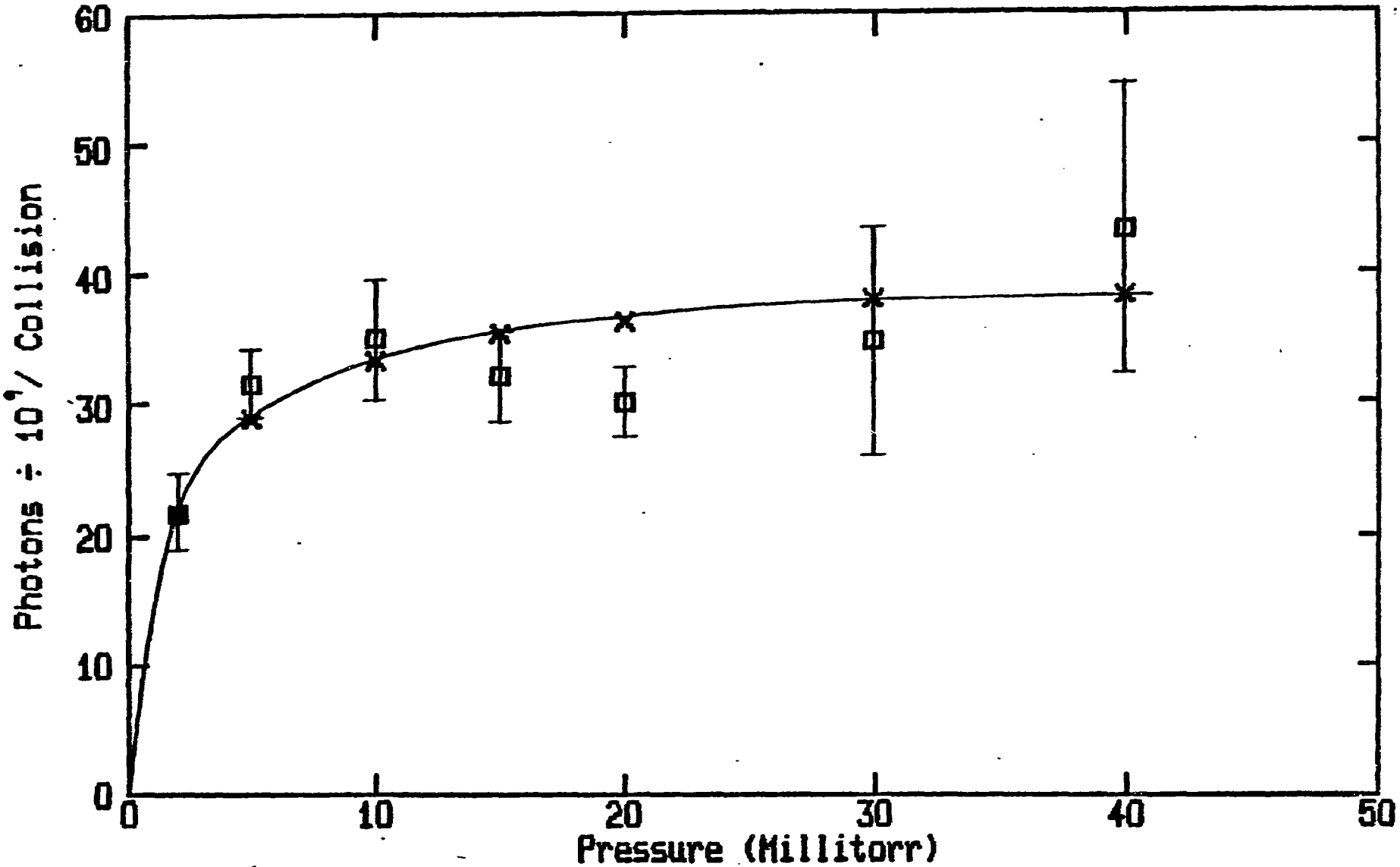



Figure 7. Pump rate of the $^{13}CH_3F$ optically pumped laser. □'s are results from least squares fit to spectroscopic data. X's are points on best fit line.

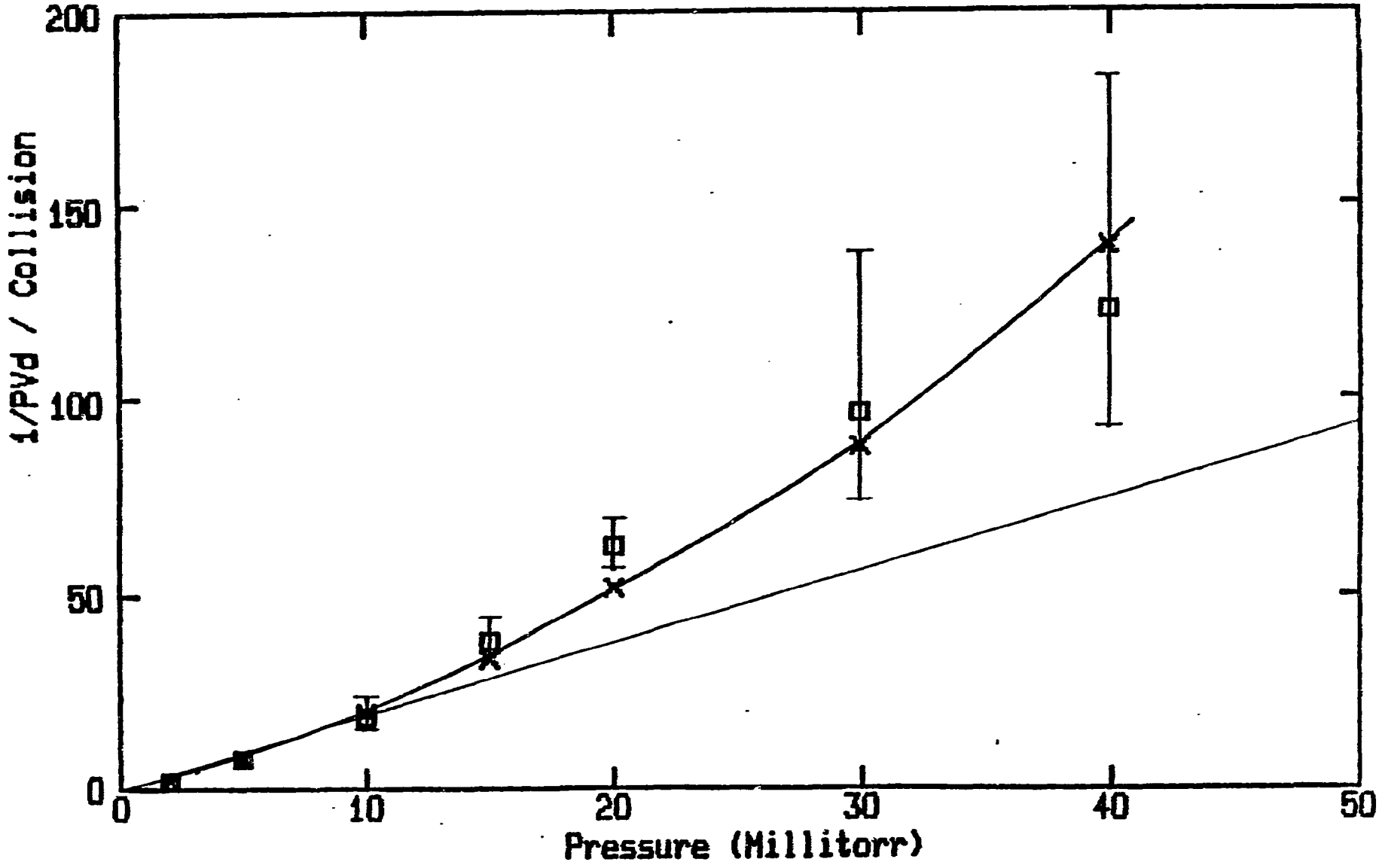



Figure 8. Reciprocal of the vibrational decay probability of the $^{13}CH_3F$ optically pumped laser. □'s are results from least squares fit to spectroscopic data. X's are points on best fit line.

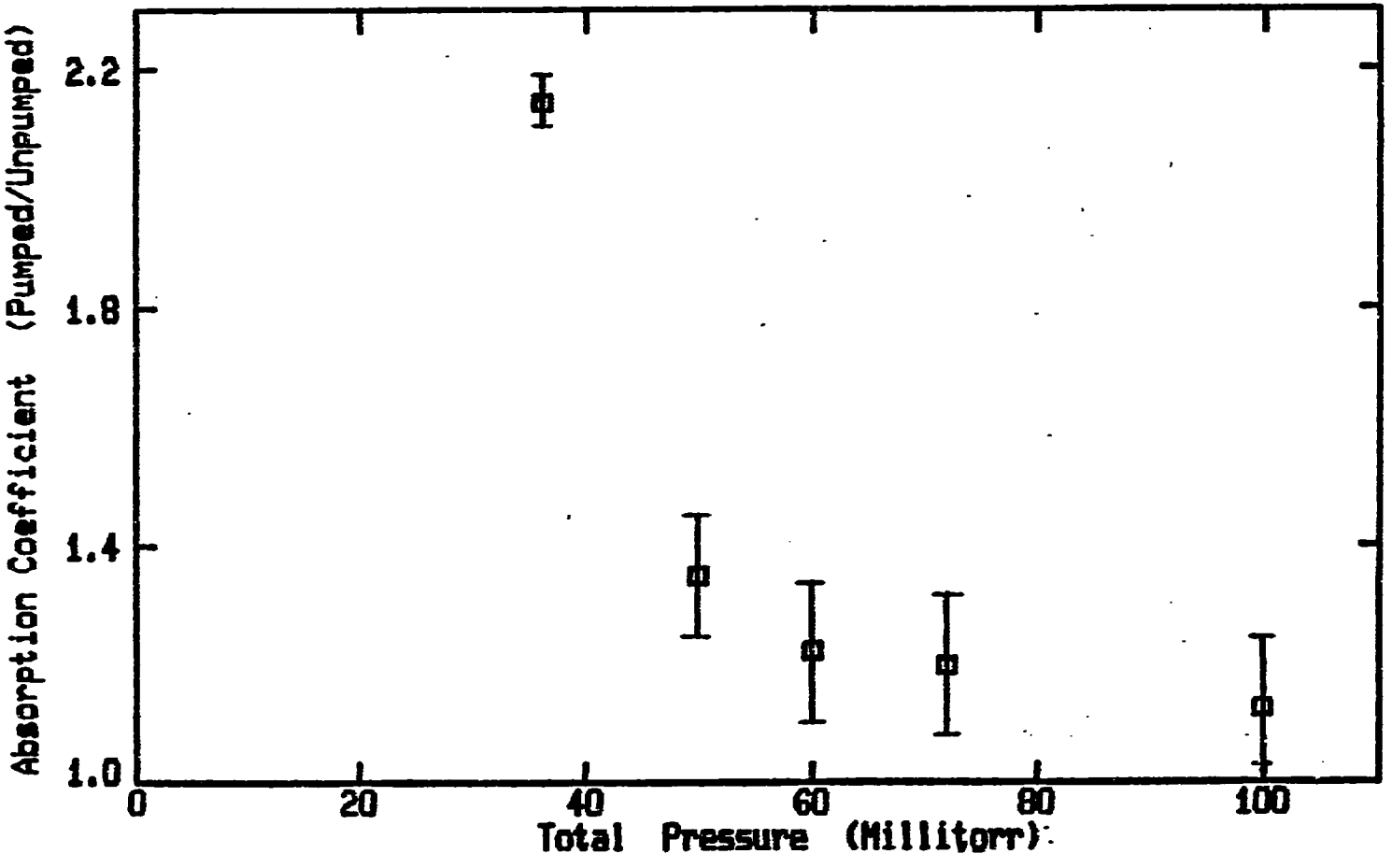



Figure 9. Ratio of pumped/unpumped absorption coefficient for the $\nu_3$= 1, J=4->5, K=2 transition in the 2" cell with hexane

random walk effect is a direct cause of the relatively small K≠3 vibrational enhancement seen in Figure 5. A similar plot can be shown for $P_{in}/P_{out}$, but its interpretation in terms of a vibrationally resonant exchange process is too lengthy to discuss here.

We have also studied the effects of the addition of foreign buffer gases on the operation of optically pumped FIR lasers. An example of the kinds of results obtained in this experiment is shown in Figure 9. The absorption of this transition is a direct measure of vibrational bottlenecking in optically pumped lasers. In pure $^{13}CH_3F$ 10,000 collisions are required to deactivate the $\nu_3$=1 excited vibrational state. From the data shown in this figure, it can be calculated that only 5 collisions with Hexane are required. We have done similar studies with Helium. Figure 10 shows a result calculated from our model. This graph, which is a function of the addition of hexane, shows the change in transtion probability between collisions which force ΔJ=±1 equilibriating transitions and ΔK transitions which empty the lasing stack.

We have used the system shown in Figure 11 to study the HCN FIR discharge laser and vibrational and rotational processes in the OCS system. Figure 12 shows the J=2-3 rotational transitions of the 100, $11^10$, 001, and $01^11$ states of HCN. This is a fortuitious conjunction that allows simultaneous observation of these states under identical discharge conditions. A detailed comparison of the $100/11^10$ and $001/01^11$ pairs show that the bending modes are in thermal equilibrium (at the rotational/translational temperature of the discharge) with their stretching parent mode. However, as shown

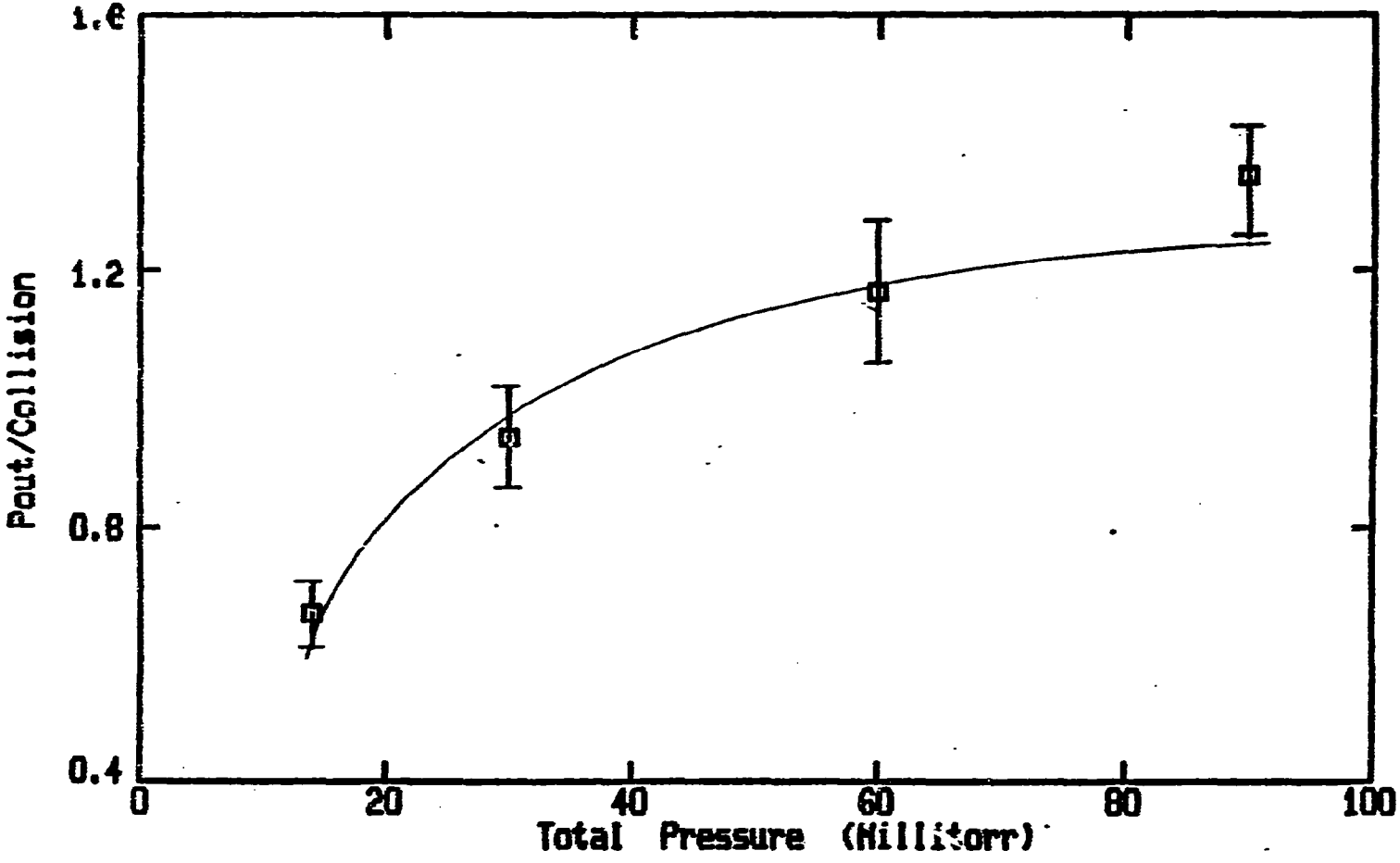



Figure 10. The probability/collision that a molecule in a particular J state of K=3 will decay into the K=3 pool in the 3/4" cell with helium

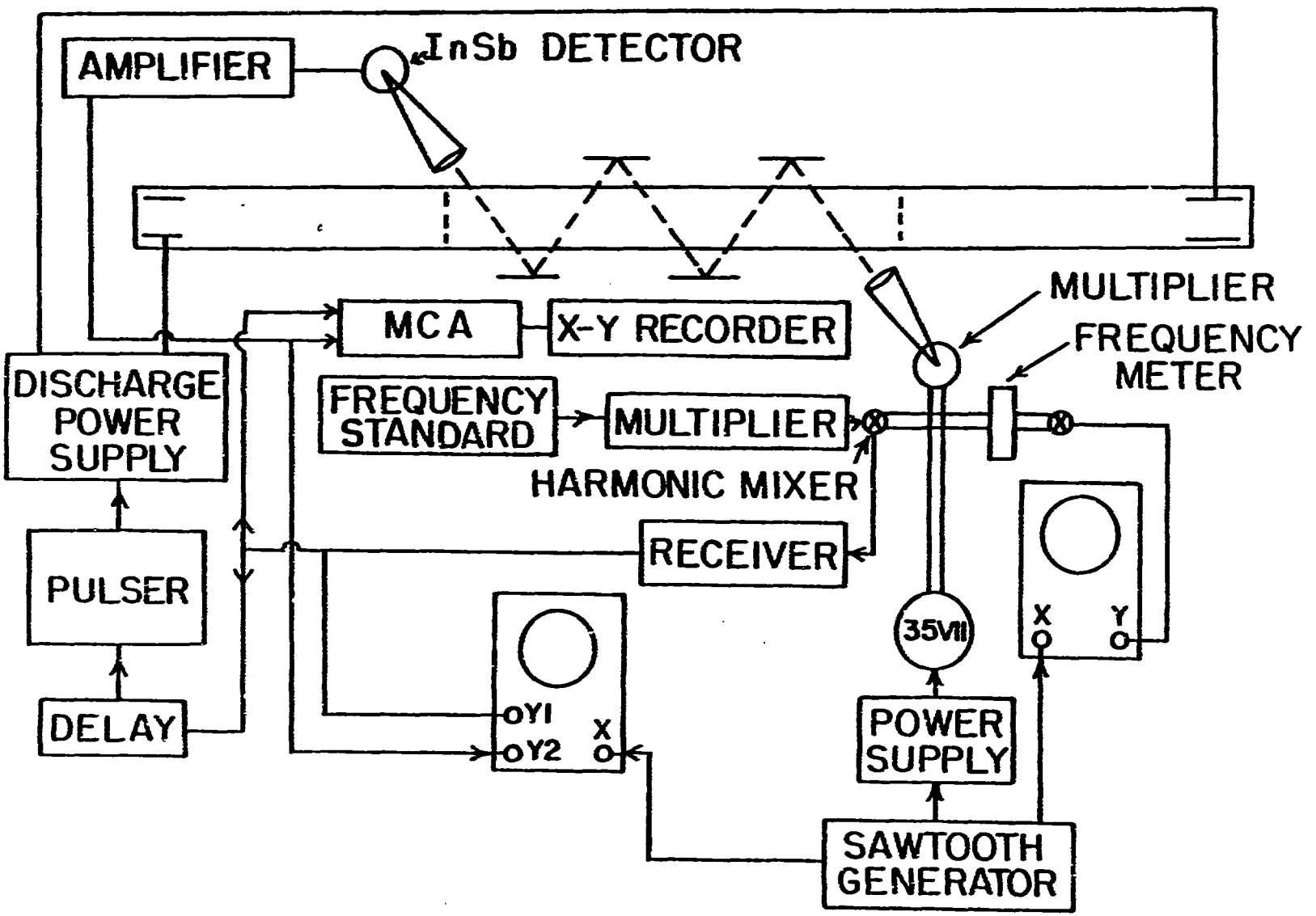
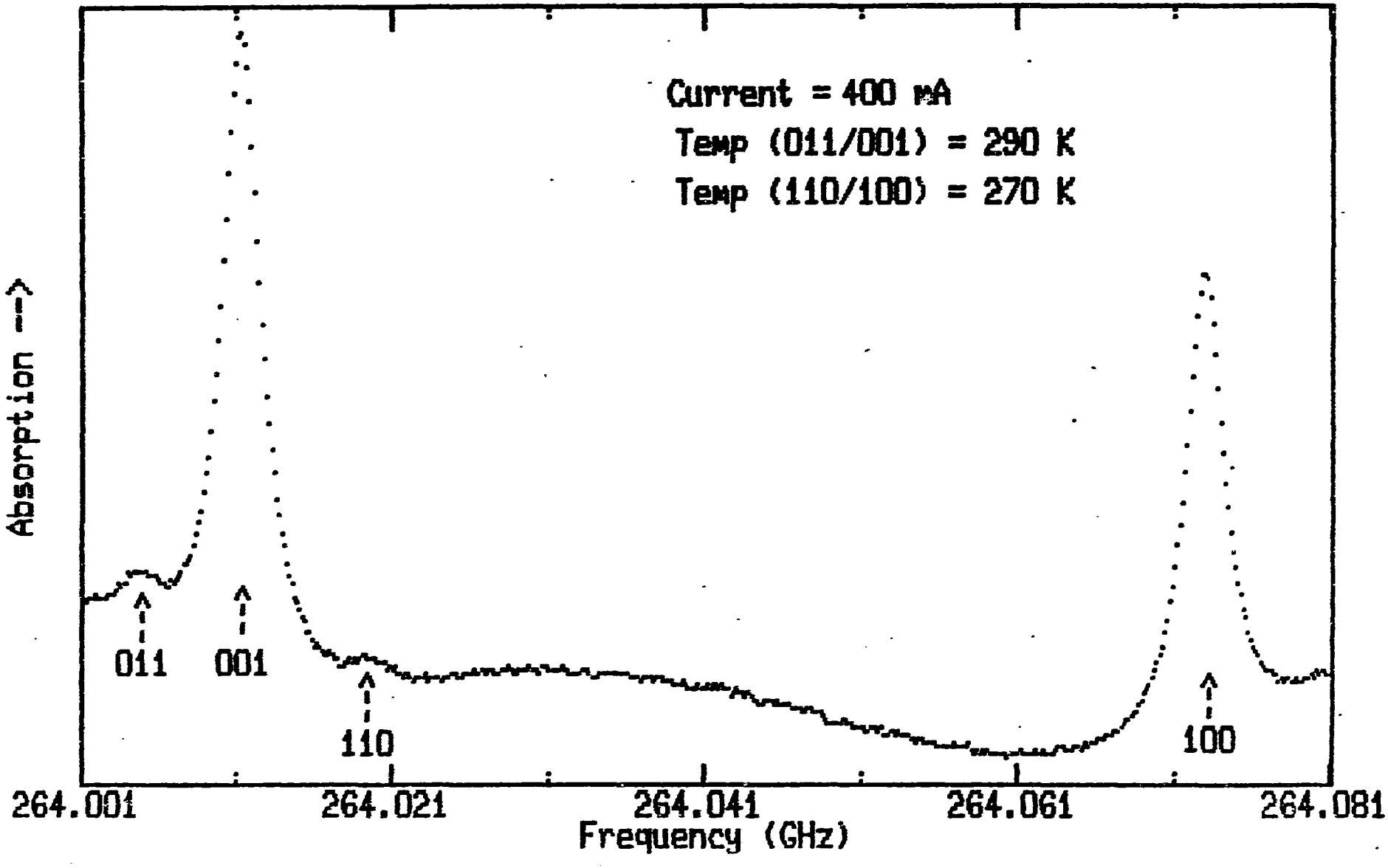



Figure 11. Spectrometer for the study of discharge systems.

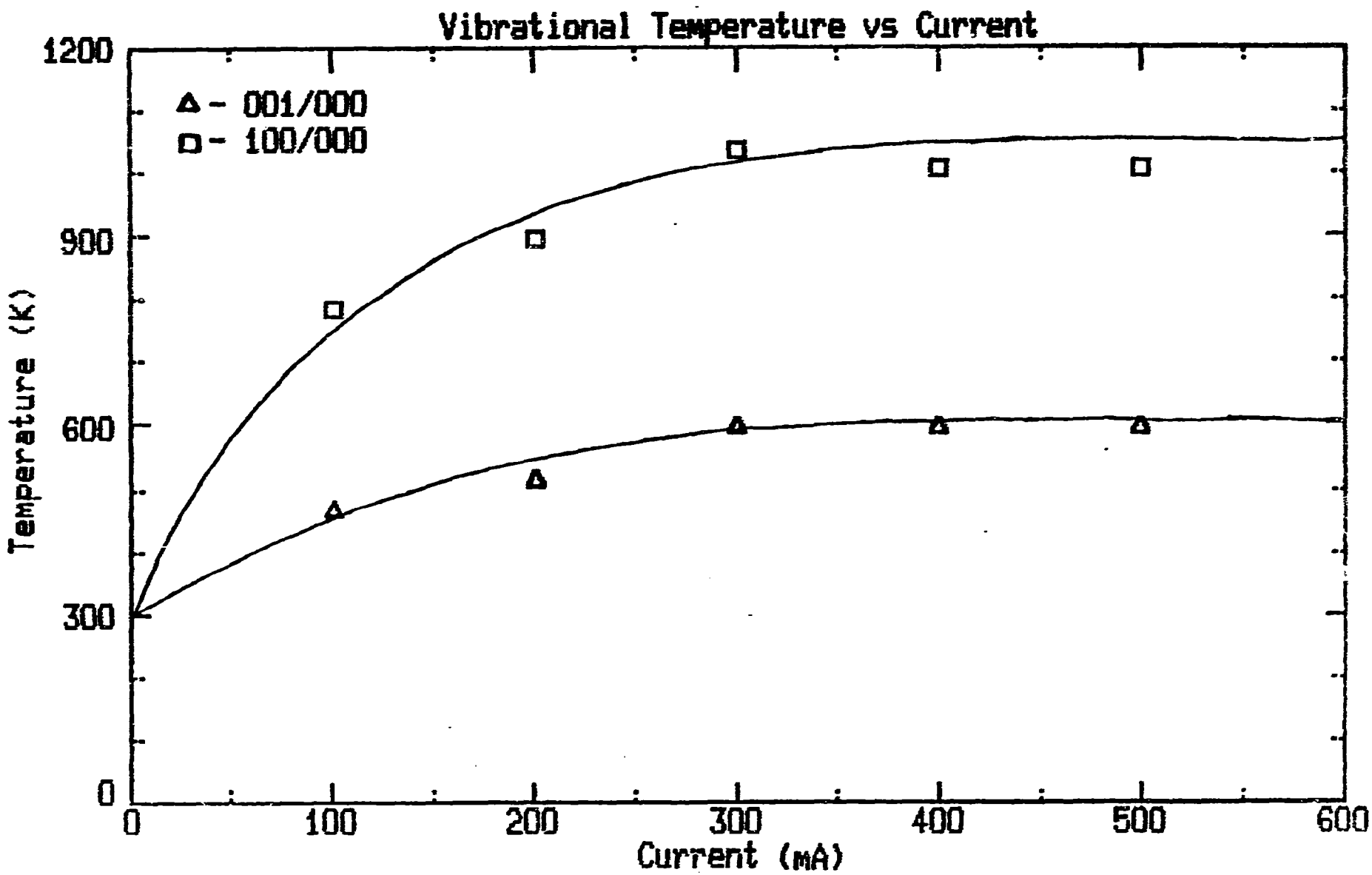
Figure 12. The J=2-3 transitions of the $01^{1}1$, 001, $11^{1}0$, and 100 vibrational states of HCN in the laser plasma.



in Figure 13 both the 100 and 001 are far from thermal equilibrium. Thus, the $11^10$ upper lasing state population vastly exceeds the $04^00$ lower lasing state population. The rapid exchange among bending modes, which is shown by the thermal equilibrium discussed above, allows competition effects to substantially enhance the efficiency of this system.

We have also studied the OCS/CO/CS discharge system. Figure 14 shows that the principal chemical reaction caused by the discharge is the simple decomposition OCS→CO+S, with secondary reactions producing small amounts of CS before the S deposits on the wall. This model is confirmed by chemical analysis of the wall deposits which show them to be >95% sulfur and by the observation that the pressure does not change at the onset of the discharge. In this system we have modeled the time evolution of the rotational/translational temperature and the vibrational temperatures. The time constants associated with the cooling at the end of the discharge pulse can be shown to be in good agreement with those obtained from transport theory. Unlike HCN, we find that the vibrational modes of OCS are not especially "hot". However, CS is substantially out of equilibrium. Figure 15 shows the decay of this excess population after the end of the pulse.

Figure 13. Vibrational temperatures of the 100 and 001 vibrational states.



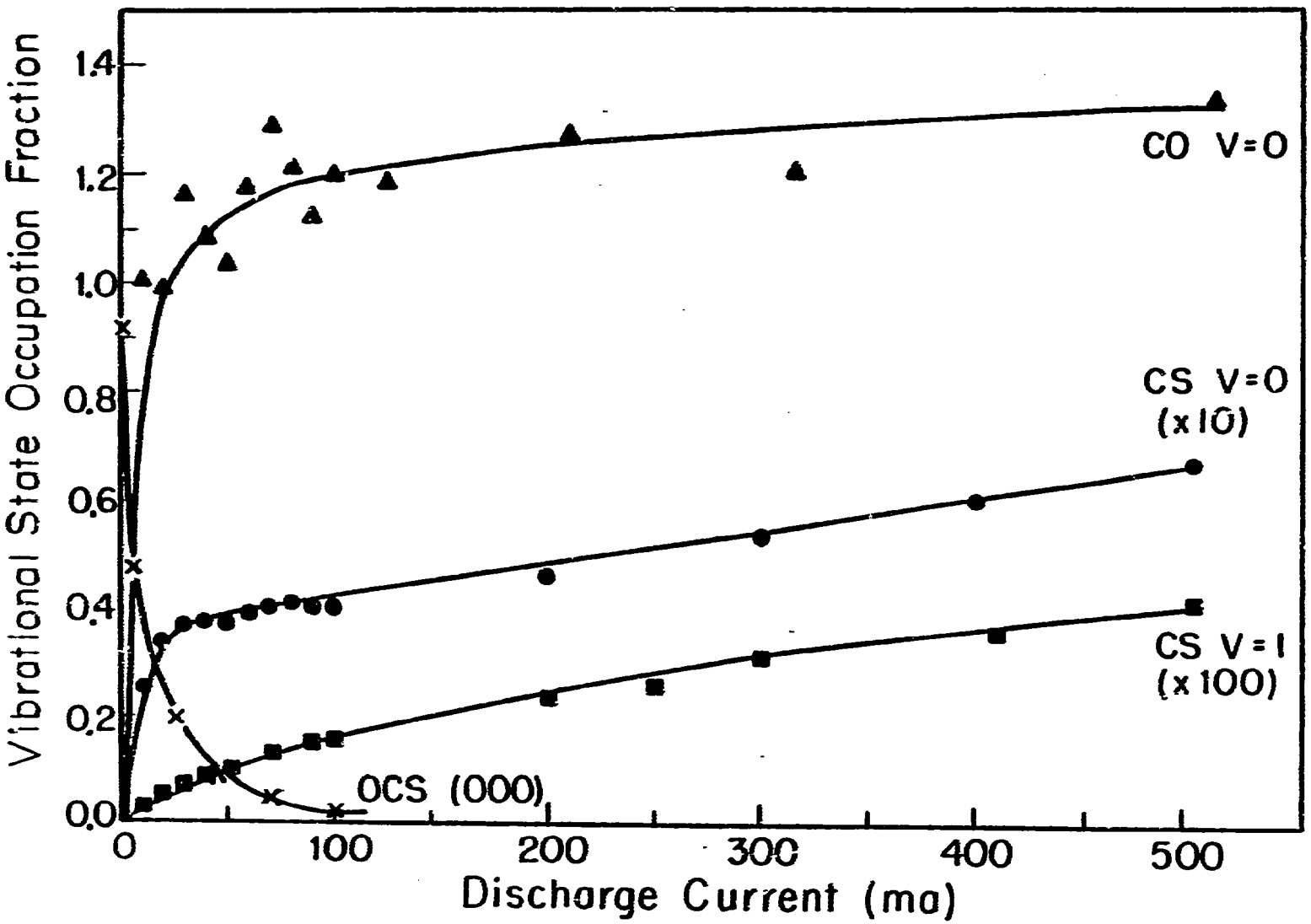



Figure 14. Vibrational state occupation fractions (not normalized) of the major constituents of the OCS/CS/CO discharge system.

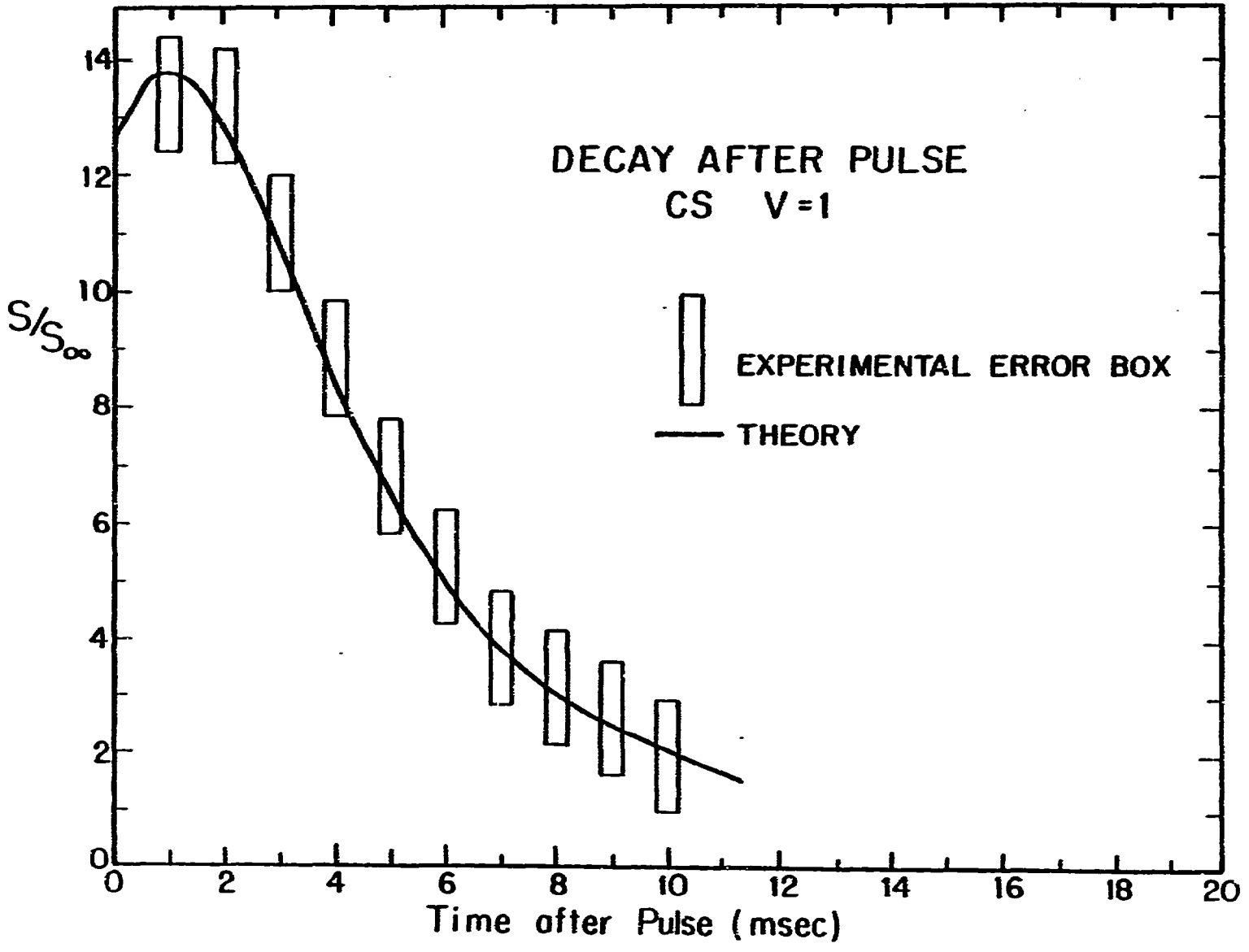



Figure 15, The decay of the vibrational excitation of V=1 CS.

## III. Energy Levels and Transition Frequencies of Molecular Species

This is the traditional domain of the spectroscopist and is the foundation for most of the work discussed in this proposal. Work in the MM/SUBMM has historically been difficult and as a result spectroscopic measurements have been minimal in comparison to those in other spectral regions. This is especially true for studies in excited vibrational states and at higher frequencies. Furthermore, we seek to calculate "complete" sets of energy levels and transition frequencies (including their statistical uncertainties) rather than to simply determine the more important spectral constants. This more stringent goal is necessary if it is desired to use this information as an aid to the understanding of atmospheric transmission, molecular lasers, quantum frequency converters, remote sensing data, energy transfer, etc.

This work has many aspects. One of our papers describes extensive new measurments and analyses in the 400-1100 GHz region on water and its major isotopes. The work in this one paper represents almost 40% of the entire microwave data base for this important species. Most of the remaining data is from our earlier work. With this new work, all of the $H_2O$ transitions that make observable contributions to atmospheric absorption in the NMMW spectral region have now been observed. These are shown in Figure 16. Figure 17 shows another result of this work. Here the very accurate diode laser measurements of Worchesky et al. at Harry Diamond Laboratories are combined with our results to calculate the vibrational frequency of $D_2O$. In conjunction with our studies

Figure 16. Observed Microwave Transitions in the Ground State of $H_2O$ (MHz).

| Transition | Frequency |
|---|---|
| 6(1,6)- 5(2, 3) | 22235.08 |
| 3(1,3)- 2(2, 0) | 183310.12 |
| 10(2,9)- 9(3, 6) | 321225.64 |
| 5(1,5)- 4(2, 2) | 325152.92 |
| 4(1,4)- 3(2, 1) | 380197.37 |
| 10(3,7)-11(2,10) | 390134.51 |
| 7(5,3)- 6(6, 0) | 437346.67 |
| 6(4,3)- 5(5, 0) | 439150.81 |
| 7(5,2)- 6(6, 1) | 443018.30 |
| 4(2,3)- 3(3, 0) | 448001.08 |
| 6(4,2)- 5(5, 1) | 470888.95 |
| 5(3,3)- 4(4, 0) | 474689.13 |
| 6(2,4)- 7(1, 7) | 488491.13 |
| 8(6,3)- 7(7, 0) | 503568.53 |
| 8(6,2)- 7(7, 1) | 504482.69 |
| 1(1,0)- 1(0, 1) | 556936.00 |
| 5(3,2)- 4(4, 1) | 620700.81 |
| 9(7,3)- 8(8, 0) | 645766.01 |
| 9(7,2)- 8(8, 1) | 645905.62 |
| 2(1,1)- 2(0, 2) | 752033.23 |
| 4(2,2)- 3(3, 1) | 916171.58 |
| 5(2,4)- 4(3, 1) | 970315.02 |
| 2(0,2)- 1(1, 1) | 987926.76 |

Figure 17. Vibrational Frequency of $\nu_2$ Calculated from Diode Laser Results and the Rotational Analyses of $D_2O$ ($cm^{-1}$).

| Transition | Observed[a] Frequency | Rotational[b] Contribution | Vibrational[c] Frequency |
|---|---|---|---|
| 6(6, 0) - 5(5, 1)<br>6(6, 1) - 5(5, 0) | 1035.4343 | -142.9397 | 1178.3740 |
| 7(3, 4) - 6(2, 5) | 1035.4921 | -142.8866 | 1178.3787 |
| 11(3, 9) - 10(2, 8) | 1048.7007 | -129.6659 | 1178.3666 |
| 12(2,10) - 11(3, 9) | 1053.9497 | -124.4147 | 1178.3644 |
| 10(1, 9) - 9(2, 8) | 1073.2597 | -105.1165 | 1178.3762 |
| 5(3, 3) - 4(2, 2) | 1079.8632 | -98.5161 | 1178.3793 |
| 10(2, 9) - 10(1,10) | 1084.6568 | -93.7207 | 1178.3775 |
| 9(0, 9) - 8(1, 8) | 1085.7458 | -92.6323 | 1178.3781 |

[a] From Worchesky et al.

[b] Calculated from the analyses of the pure microwave data.

[c] Average calculated vibrational frequency = 1178.3743 $cm^{-1}$.

of the $^{13}CH_3F$ laser, we made extensive measurements in both the ground and excited vibrational states. An interesting feature of this work is that the absorption spectroscopy measurements in the excited vibrational state give a highly precise value of the FIR laser frequency, which is completely uncomtaminated by pump offset and cavity pulling effects. This technique is an important new method for establishing secondary frequency standards throughout the NMMW. A recent measurement of the $^{13}CH_3F$ laser frequency by Mary Tobin of HDL is in good agreement with our value, but our frequencies are dramatically different than the previously accepted value. We have also investigated the energy level structure and transition frequencies of the new lasing species $CHD_2F$. We have combined our measurements with the FIR laser frequencies measured by M. S. Tobin and the known $CO_2$ laser frequencies in a "grand unification" analyses. For this, we used the analysis techniques that we have developed for light asymmetric rotors. The spectral constants that result from this are shown in Figure 18. We have also recently done extensive spectroscopic studies of a number of small fundamental species such as HOOH, $NO_2$, $HNO_3$, etc. Although these are geometrically simple species, many of them have especially difficult spectroscopic problems (internal rotation, unpaired electron spin, light asymmetric rotors, etc.). As a result for most of these very fundamental species, prior to our work, their submillimeter absorption frequencies were unknown. Although this work was done primarily under the sponsorship of other agencies, there has recently been considerable interest in their absorption properties in "disturbed" atmospheres. This is a very good example that new

Figure 18. Spectral Constants of $CHD_2F$(MHz).

| Constant | Ground State[a,b] | $\nu_6$ Excited State[a,b] | |
|---|---|---|---|
| A | 95207.015(7) | 96058. | (10) |
| B | 22405.599(1) | 22133.214 | (45) |
| C | 21284.478(1) | 21255.220 | (45) |
| $\Delta_J$ | 0.0411659(96) | 0.040262 | (84) |
| $\Delta_{JK}$ | 0.276159 (35) | 0.17303 | (118) |
| $\Delta_K$ | 0.744936 (747) | 1.50 | (10) |
| $\delta_J$ | 0.00195258(66) | -0.000588 | (92) |
| $\delta_K$ | 0.150917 (234) | -0.052 | (21) |
| $H_{JK}\cdot10^4$ | ---- | -0.450 | (49) |
| $H_{KJ}\cdot10^2$ | ---- | 0.1592 | (95) |
| $L_{KKJ}\cdot10^4$ | ---- | 0.117 | (25) |
| rms | 0.038 | 0.076 [c] | |

[a]The number of places retained is necessary to insure that the constants reproduce the observed data.

[b]The number in the parenthesis is the standard deviation in terms of the last quoted place.

[c]From an analysis of the microwave data alone.

and fundamental measurements and theory on prevasive and wide spread materials have applications that go far beyond the narrow applications that we all initially visualize.

## Papers That Resulted From This Work

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The Submillimeter Spectrum of Methanol, Eric Herbst, Paul Helminger, J. K. Messer, and Frank C. De Lucia, to be published.

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Vibrational Energy Transfer and Equilibria in the HCN FIR Laser, David D. Skatrud and Frank C. De Lucia, to be published.

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In addition to the above are an approximately equal number of Conference Papers, Abstracts, sections of books, etc. Since these describe essentially the same work, they are not listed here.

## Participating Scientific Personnel

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