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RESEARCH ON MOLECULAR LASERS

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Cornell University

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13. ABSTRACT

Research concerning molecular and chemical lasers was conducted in the following areas:

1. Measurement of V→V and V→R, T rates among hydrogen halide molecules and the temperature dependence of the energy transfer rates previously determined for HF, DF, HF/CO_2 DF/CO_2 Systems.
2. Vibrational relaxation studies of $CO_2(00^01)$ in the pressure range 1-100 atm.

3a. Chemical laser studies of the reaction of atomic oxygen and acetylene,
  b. Computer modeling of the CS_2-O_2 chemical laser system.
  c. Chemical laser studies of the reaction of C_3O_2 with oxygen.

4. Experimental study of the relaxation of $CO_2(001)$ and HF(v = 1) by collisions with H and F atoms.
5. Studies of the influence of vibrational excitations on the reaction rate of atom exchange reactions e.g., HF(v) + D_2 → HD + DF.

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14. KEY WORDS	LINK A		LINK B		LINK C	
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Molecular Lasers						
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9.	Telephone Number	(607) 256-3962
10.	Project Scientists	Professor S. H. Bauer (607) 256-4028 Professor T. A. Cool (607) 256-3512 Professor R. A. McFarlane (607)256-4075
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1.0 REPORT SUMMARY

During the period 1 October 1972 - 31 March 1973, the ongoing program concentrated on a number of research areas that were felt to be of significant and practical importance to the successful development of chemical and molecular laser technology. The principal areas of effort were: extension of the V → V and V → R, T studies in the hydrogen halide and HF/CO_2 , DF/CO_2 laser systems; experimental studies of the vibrational relaxation of $CO_2(00^01)$ at high pressure and over a wide temperature range; gain studies in the $C_2H_2 - O_2$ chemical laser system; chemical studies of the production of C_3O_2; experimental study of the $C_3O_2 + O_2$ chemical laser system producing vibrationally excited CO; experimental studies of the vibrational deactivation of HF/DF, $v = 1$, and $CO_2(00^01)$ states by collisions with H, D, F, N, O; study of the effect of vibrational excitation in HF upon the atom exchange reaction $HF(v) + D_2 \rightarrow HD + DF$.

In all cases the primary method was the execution of laboratory experiments designed to provide quantitative results followed by appropriate integration with theory. A detailed statement of results and state of progress will be found in the balance of the report.

2.0 VIBRATIONAL RELAXATION IN HYDROGEN HALIDES, HF-CO_2 AND DF-CO_2 SYSTEMS

Professor T. A. Cool

2.01 HF-HCℓ, HF-HBr, HF-HI, and HF-DF Systems

During the past several months our new high repetition pulsed laser facility has been employed in studies of vibrational relaxation processes with the laser-induced fluorescence method. Of primary concern have been those molecular systems of current interest for the development of chemical lasers. Several promising reaction mechanisms for such devices lead to the formation of vibrationally excited HF in the presence of HCℓ, HBr, HI, and DF molecules. We have determined the rate constants for energy transfer and deactivation in the HF-HCℓ, HF-HBr, HF-HI, and HF-DF systems at 300 and 350°K, typical temperatures for laser operation.

Table I summarizes these measurements.

The present results contribute to the growing study of data concerning vibrational relaxation of HCℓ, HBr, and HF mixtures which has revealed the importance of strong attractive interactions in causing efficient conversion of vibrational energy into rotational motion of the collision pairs. Several rate constants for the present systems exhibit a marked decrease with increasing temperature similar to that found for the self-deactivation rates of HF and DF in recent shock tube and laser-fluorescence studies.

2.02 HF, DF, HF-CO_2 and DF-CO_2 Systems

The temperature dependence of vibrational relaxation processes provides qualitative information concerning the nature of the intermolecular potential between collision pairs. Our new apparatus has enabled a complete study of the temperature dependence from 300 to 700°K for the vibrational relaxation processes of the HF, DF, HF-CO_2 and DF-CO_2 systems. The present results extend our privious measurements made at a single temperature of 350°K.(4)

The results of these measurements are summarized in Figures 1-3.

Figure 1 shows the temperature dependence of the rate constant K_{11} ($sec^{-1} Torr^{-1}$) for the self-deactivation processes

$$HF(v = 1) + HF(v = 0) \rightarrow 2\, HF(v = 0) \qquad (1a)$$

$$DF(v = 1) + DF(v = 0) \rightarrow 2\, DF(v = 0) \quad . \qquad (1b)$$

Figure 2 gives the observed variation with temperature of the rate constant sum, $K_e + K_{12}$, for the processes

$$HF(v = 1) + CO_2(000) \xrightarrow{K_e} HF(v = 0) + CO_2(001) \qquad (2a)$$

$$+ CO_2(000) \xrightarrow{K_{12}} HF(v = 0) + CO_2(000) \qquad (2b)$$

and the analogous processes for DF.

Figure 3 indicates the manner in which the rate constants for deactivation of the upper CO_2 laser level by HF and DF varies with temperature by the process.

$$CO_2(001) + HF(v = 0) \rightarrow CO_2(nm^{\ell}o) + HF(v = 0) \quad (3a)$$

$$CO_2(001) + DF(v = 0) \rightarrow CO_2(nm^{\ell}o) + DF(v = 0) \quad (3b)$$

All of the measured rates exhibit a strong inverse dependence on temperature over the range investigated. This provides further evidence for a strong hydrogen-bonding interaction between HF(DF) and CO_2.

The results of the work summarized above have been submitted to the Journal of Chemical Physics for publication.

1. J. L. Abe and T. A. Cool, "Vibrational Relaxation in the HF-HCℓ, HF-HBr, HF-HI, and HF-DF Systems," to be published, J. Chem. Phys. June 15, 1973.
2. R. A. Lucht and T. A. Cool, "Temperature Dependence of Vibrational Relaxation in the HF, DF, HF-CO_2, and DF-CO_2 Systems," in preparation for J. Chem. Phys.

TABLE I: SUMMARY OF MEASURED RATE CONSTANTS

SYSTEM	SYMBOL	T = 300K RATE CONSTANT ($SEC^{-1} TORR^{-1}$)	T= 350K	$\Delta E_v (cm^{-1})$	COLLISION NUMBERS, Z^c		PRODUCT OF DIPOLE MOMENTS $(DEBYE)^2$	SQUARED VIBRATIONAL MATRIX ELEMENTS ($10^{-40} esu^2 cm^2$)
HF(1) + HF(0)	k_{11}	$7.0 \pm 1.0 \times 10^4$	$4.95 \pm 0.04 \times 10^4$	3962	73	96	$\mu^2_{HF} = 3.31^d$	$\lvert R^1_0 \rvert^2_{HF} = 97^f$
HCl(1) + HCl(0)	k_{22}	1200 ± 300	900 ± 200	2886	5700	7500	$\mu^2_{HCl} = 1.17^d$	$\lvert R^1_0 \rvert^2_{HCl} = 45^g$
HBr(1) + HBr(0)	k_{22}	600 ± 200	600 ± 200	2559	7920	7300	$\mu^2_{HBr} = .67^d$	$\lvert R^1_0 \rvert^2_{HBr} = 14^h$
HI(2) + HI(0)	k_{22}	4800 ± 1000	3200 ± 1000	-81^a	1160	1590	$\mu^2_{HI} = .194^d$	$\lvert R^2_0 \rvert^2_{HI} = .04^i$
DF(1) + DF(0)	k_{22}	$2.6 \pm 0.4 \times 10^4$	$1.8 \pm 0.3 \times 10^4$	2907	192	255	$\mu^2_{DF} = 3.31^e$	$\lvert R^1_0 \rvert^2_{DF} = 70^e$
HF(1) + HCl(0)	$k_e + k_{12}$	$2.9 \pm 0.3 \times 10^4$	$2.2 \pm 0.3 \times 10^4$		213	260	$\mu_{HF}\mu_{HCl} = 1.88$	
	k_e	$1.6 \times 10^4 < k_e < 3.2 \times 10^4$	$1.2 \times 10^4 < k_e < 2.5 \times 10^4$	1076	$193 < Z < 386$	$230 < Z < 480$		
	k_{12}	$< 1.6 \times 10^4$	$< 1.2 \times 10^4$	3962	< 386	< 478		
HCl(1) + HF(0)	k_{21}	$2.0 \pm 0.3 \times 10^4$	$1.6 \pm 0.3 \times 10^4$	2886	309	359		
HF(1) + HBr(0)	$k_e + k_{12}$	7500 ± 2000	3500 ± 2000		810	1500	$\mu_{HF}\mu_{HBr} = 1.49$	
	k_e	$4700 < k_e < 9500$	$2800 < k_e < 5500$	1403	$650 < Z < 1300$	$950 < Z < 1850$		
	k_{12}	< 4700	< 2800	3962	< 1300	< 1850		
HBr(1) + HF(0)	k_{21}	$1.6 \pm 0.3 \times 10^4$	$1.1 \pm 0.1 \times 10^4$	2559	380	475		
HF(1) + HI(0)	$k_e + k_{12}$	3500 ± 2000	2000 ± 1500		1950	3170	$\mu_{HF}\mu_{HI} = 1.03$	
HI(2) + HF(0)	$k_e' + k_{21}$	$1.95 \pm 0.25 \times 10^4$	$1.45 \pm 0.25 \times 10^4$	(b)	350	435		
HF(1) + DF(0)	$k_e + k_{12}$	$13.3 \pm 1.0 \times 10^4$	$9.8 \pm 1.5 \times 10^4$		38	47.5	$\mu_{HF}\mu_{DF} = 3.31$	
	k_e	$7.1 \times 10^4 < k_e < 14.3 \times 10^4$	$4.5 \times 10^4 < k_e < 11.3 \times 10^4$	1055	$35.3 < Z < 71.5$	$41 < Z < 103$		
	k_{12}	$< 4.5 \pm 0.7 \times 10^4$	$< 3.3 \pm 0.5 \times 10^4$	3962	< 115	< 140		
DF(1) + HF(0)	k_{21}	$4.5 \pm 0.7 \times 10^4$	$3.3 \pm 0.5 \times 10^4$	2907	115	140		

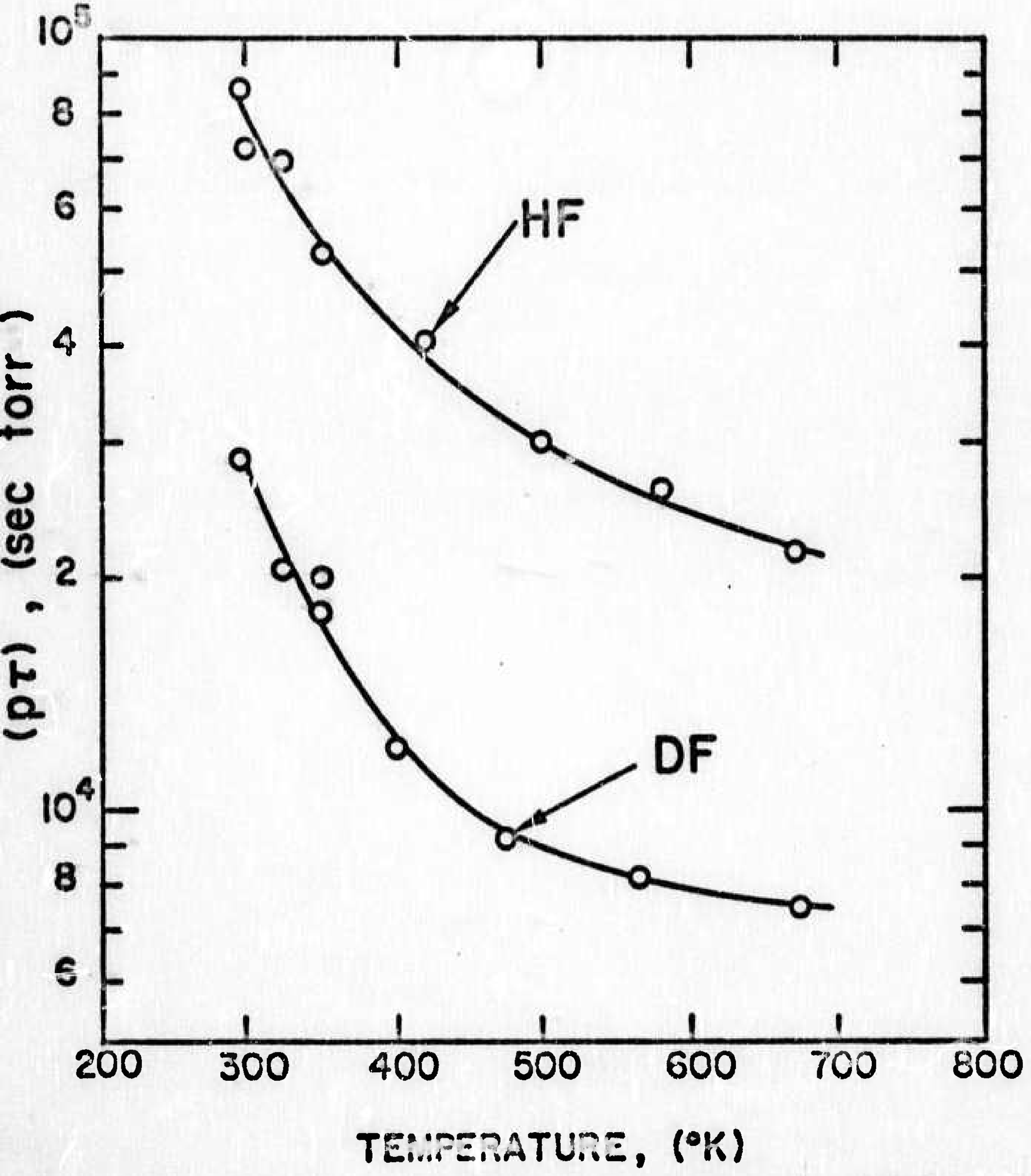

10^5
8
6
4
2
10^4
8
6
200
300
400
500
600
700
800
HF
DF
$(p\tau)^{-1}$, (sec^{-1} torr^{-1})
TEMPERATURE, (°K)

FIGURE 1

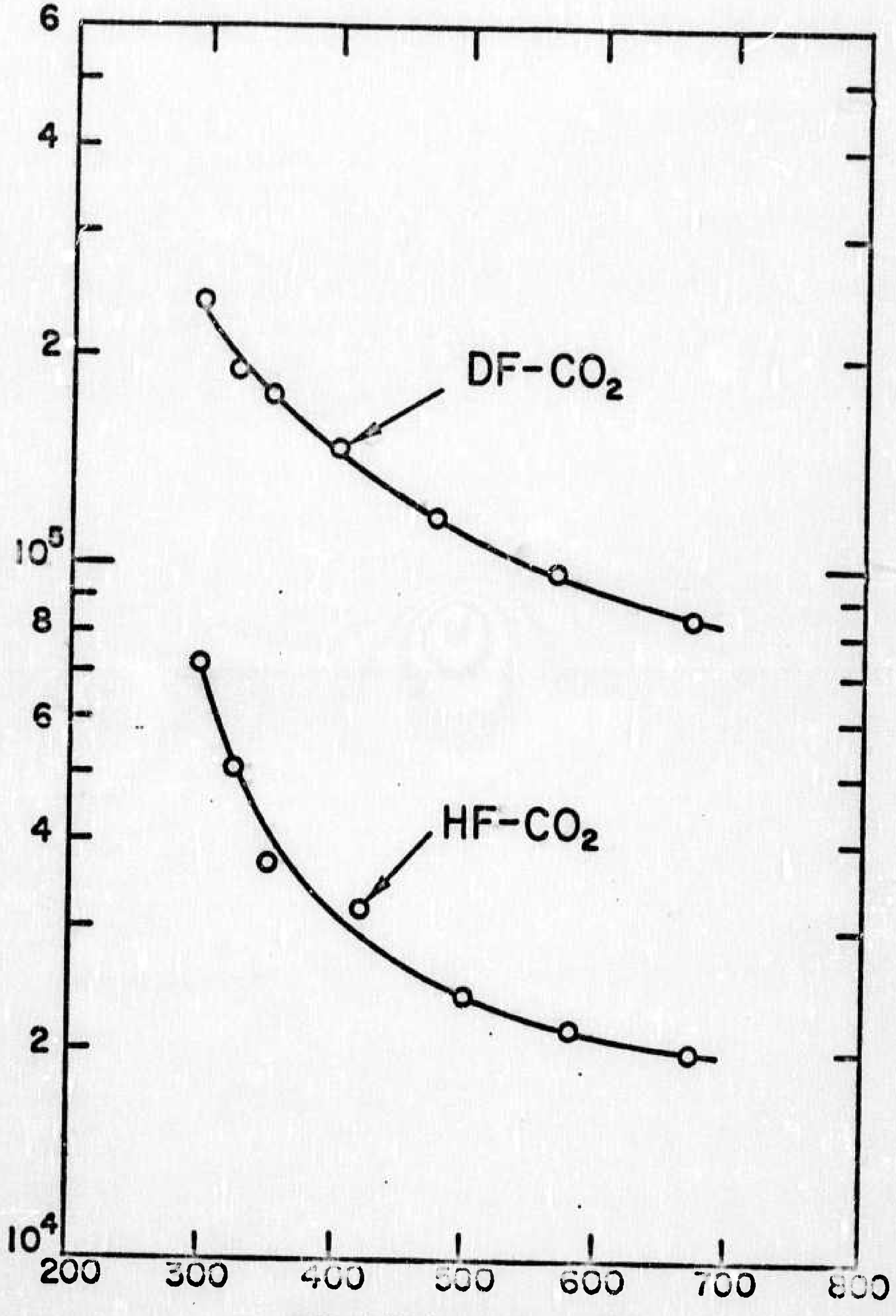

6
4
2
10^5
8
6
4
2
10^4
200
300
400
500
600
700
800
TEMPERATURE, (°K)
$(p\tau)^{-1}$, $(\mathrm{sec}^{-1}\ \mathrm{torr}^{-1})$
$DF-CO_2$
$HF-CO_2$

FIGURE 2

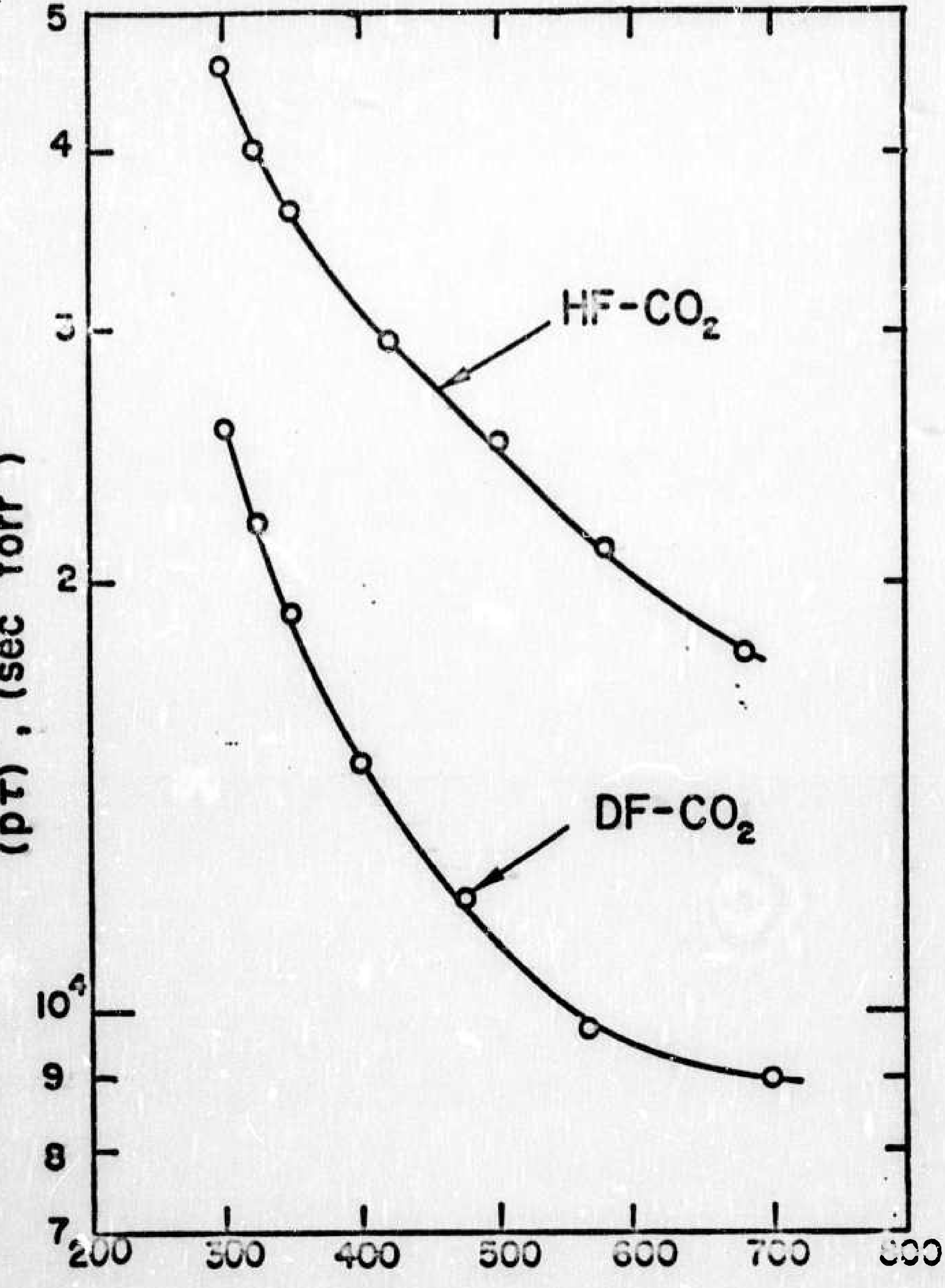

5
4
3
2
10⁴
9
8
7
200
300
400
500
600
700
800
$(p\tau)^{-1}$, ($sec^{-1}\ torr^{-1}$)
TEMPERATURE, (°K)
HF-CO_2
DF-CO_2

FIGURE 3

3.0 VIBRATIONAL RELAXATION AT HIGH PRESSURES

Professors George J. Wolga and Ross A. McFarlane

3.01 A New experimental method has been developed for the high pressure studies of deactivation of $CO_2(00^01)$ by $CO_2(00^00)$ and by other molecules. The experimental apparatus is shown in the accompanying figure. Detectors D_2 and D_3 permit the measurement of the time integrated absorbed energy for the pumping process $CO_2(00^00) + h\nu(4.3\,\mu) \rightarrow CO_2(00^01)$. The detector D_1 permits measurement of the time integrated 10μ fluorescence from $CO_2(00^01)$ described by

$$CO_2(00^01) \rightarrow h\nu(10.6\mu) + CO_2(10^00).$$

The process being studied is

$$CO_2(00^01) + CO_2(00^00) \xrightarrow{k_d(PT)} CO_2(n, m^{\ell}, o) + CO_2(n', m^{\ell'}, o) + \Delta E .$$

We shall show in a later report that so long as the collisional relaxation rate k_d is fast compared to the radiative relaxation of the (00^01) state, then the rate k_d at pressure P is determined relative to k_d at some reference pressure P_o where k_d is known by the relationship

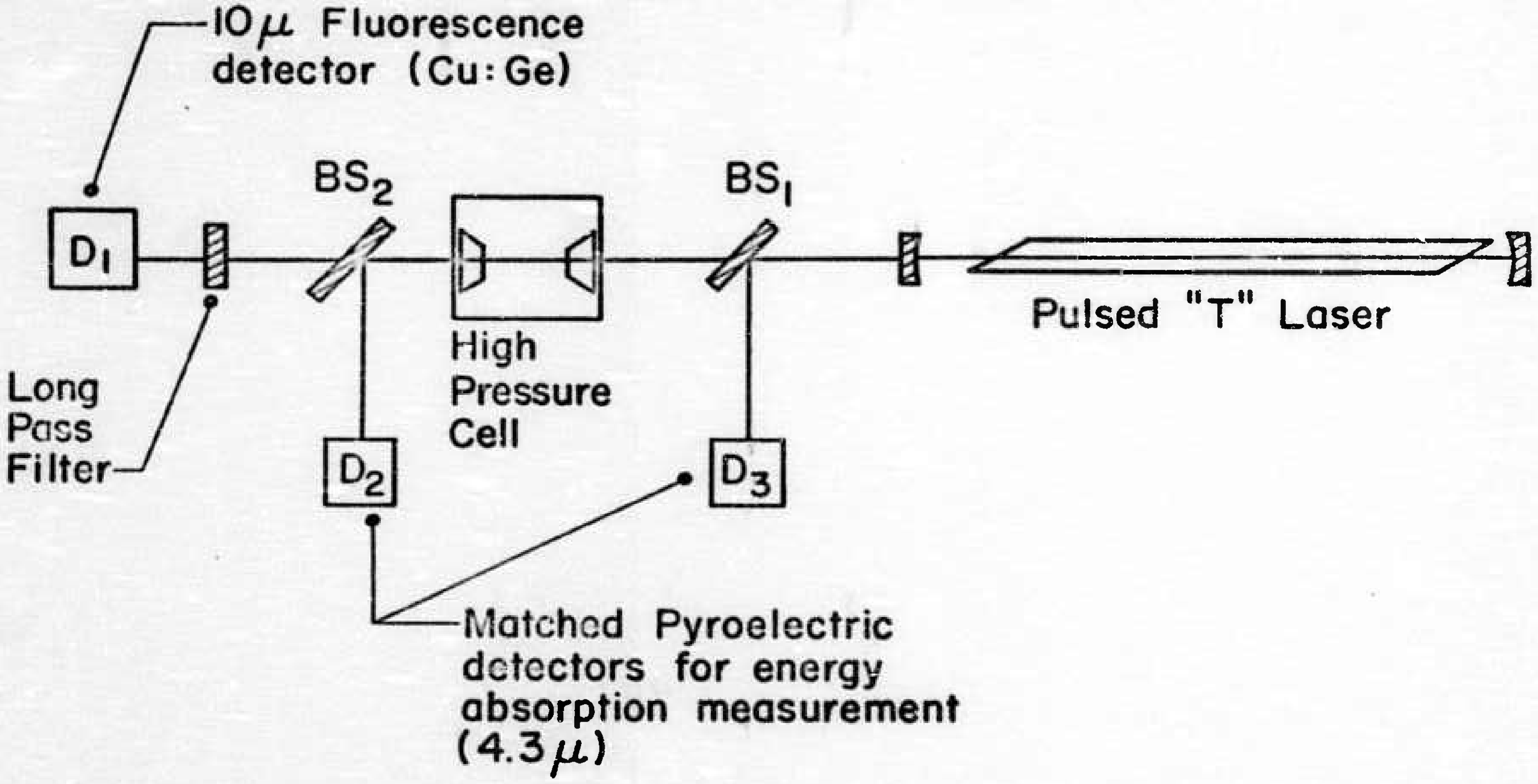
$$\frac{k_d(P)}{k_d(P_o)} = \frac{E_{4.3,\ abs.}(P)}{E_{4.3abs.}(P_o)} \; \frac{E_{10.6\ emitted}(P_o)}{E_{10.6\ emitted}(P)} \; \frac{A_{10.6}(P_o)}{A_{10.6}(P)}$$

where the E's are the time integrated energies discussed above and the A's are the Einstein A coefficients for the 10.6μ transition. The advantage of this method over the usual laser induced fluorescence method is that the 4.3μ pump pulse need not be short compared to the collisional relaxation time, and much better signal to noise is achieved due to use of the entire pump pulse and large detector load resistors permitted because of the relaxation of the requirement for good time resolution. This method is therefore appropriate for very high pressures where k_d becomes very large.

We have tested the method in the range 1-10 atmospheres and excellent signal to noise was achieved. Preliminary results are that k_d increases essentially linearly with pressure up to 75 psia at $T = 300^oK$.

3.02 The Spin Flip Raman Laser instrumentation has been purchased (non ARPA funding) and assembled. It is currently being tested with CO laser pump radiation. A TEA HF laser was constructed and output in the 14μ region from pure rotational transitions was observed. We shall be testing the SFR laser with the 14μ pump in the near future.

HIGH PRESSURE RELAXATION EXP.



4.0 CHEMICAL LASER STUDIES

Professors S. H. Bauer, R. A. McFarlane, and G. J. Wolga

4.01 $C_2H_2 + O_2$

Introduction:

The exothermic reaction of atomic oxygen with acetylene can provide substantial population of excited vibrational levels of carbon monoxide and as reported for the last period it has been possible to produce a total vibrational inversion for levels v = 5 to v = 7 by preferential collisional relaxation using cold CO.

In addition, spontaneous emission studies which yield the detailed relative vibrational populations have shown that Treanor pumping can lead to partial inversions at higher v levels for high fuel flows. It remains however to establish that absolute optical gains, though now known to be positive in regions of the flowing system, are sufficiently large to be of utility for laser purposes. These gains must overcome unavoidable losses in a laser resonator just to reach threshold and must be such as to permit in addition significant output coupling.

The present longitudinal flow system is expected to have a distance dependent gain coefficient as determined by the oxygen/C_2H_2 mixing, time dependent chemistry, vibrational energy transfer and overall relaxation processes. Measurements are being undertaken to determine the net single pass gain of the system at discrete wavelengths under reaction conditions already known to produce total or partial inversion. The period of this report has been devoted to construction of the necessary instrumentation which includes a single frequency CO laser and the detection and signal handling electronics for gain measurements. A schematic of the system is shown in the figure.

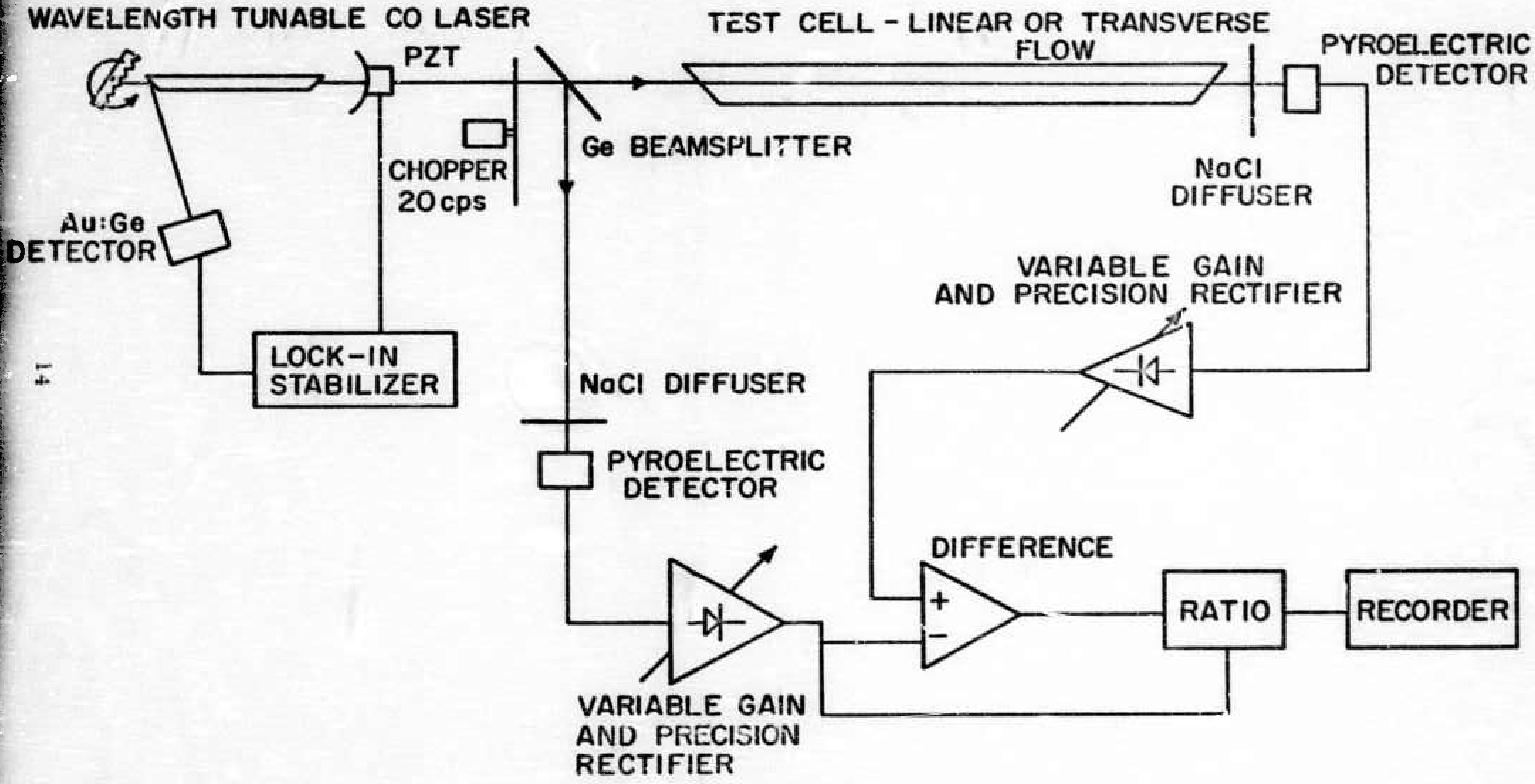
CO Laser

A grating tuned CO laser has been constructed with provision for sealed-off operation. It has been operated with cold water cooling and provision made in the gas handling system for the additions of xenon for closed operation. A current stabilizer has been constructed and placed in use to improve the amplitude stability of the output. During gain measurements the laser will be further stabilized by using a piezoelectric cavity length control to lock onto the center of a particular rotational line.

Signal Processing

Measurement of single pass gain will be carried out using a pair of matched pyroelectric detectors, one to sample input power and the other to measure power transmitted by the test cell. The laser output is chopped at 20 c.p.s. and the a.c. signals from the detectors are at sufficiently high level to obviate the requirement for phase sensitive detectors. Direct rectification of the a.c. signals to provide a d.c. output proportional to input laser power was not adequately accurate over our range of signal levels and the system is being modified to use precision (.05%) R.M.S.

GAIN MEASUREMENT SYSTEM

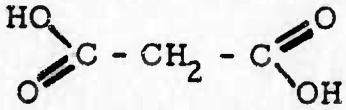


modules to permit detection of gains as low as a few tenths of a percent. The electronic system provides a normalizing function to remove effects due to changes in laser power during a measurement, the final output being

$$V_{out} = K \frac{P_{out} - P_{in}}{P_{in}}$$

and the constant K will be set to provide a full scale response corresponding to 4% gain.

4.02 $C_3O_2 + O_2$

During the past period we continued to search for an improved synthetic procedure to prepare C_3O_2 for use in the C_3O_2/O_2 electric-pulsed laser. The classic method calls for mixing the dry powers of malonic acid  with phosphorous pentoxide (P_2O_5), in 1/10 ratio, and heating the mixture to 150°C in the absence of any solvent. The yield of that procedure is ≃ 10%. In a series of experiments, based on extensive discussions with organic chemists, we tested various solvents, hoping to facilitate direct contact between the malonic acid and P_2O_5 at the molecular scale. Tests were run between temperature 0°C and 60°C. None yielded any substantial amounts of the desired gas. However, all gave evidence of extensive reaction followed by rapid polymerization. The dehydrohalogenation of malonyl dichloride, utilizing basic alumina or triakylamines as HCℓ abstracting agents, was also explored as a possible synthetic route, but with no success. We are now convinced that solvents of any kind should be avoided because these provide the best conditions for C_3O_2 polymerization.

Optimum yields are obtained by: (a) fine grinding of the malonic acid and thorough mixing with the P_2O_5; (b) maintaining the reaction temperature at about 50°C; (c) running a slow stream of helium through the mixture to displace the C_3O_2 from the tacky reaction products as rapidly as possible; (d) stirring continuously to break up the tacky clumps of phosphoric acid coated crystals of malonic acid. Further exploration are in progress for improved reactor design, and possible admixing of acidic dehydrating agents which will reduce the tackiness of the products, and thus permit more complete reaction.

With respect to our laser radiation studies, emissions between 5.1 - 5.4 μ, corresponding to transitions in CO from v' - v" (1--9) to (6-5) have been observed, following pulsed electrical discharge through gaseous mixture of C_3O_2, O_2 and He using two types of laser tubes: the one meter, 2.5 cm I.D. unit, with ring electrodes, and a 1 meter, 6 cm I.D. tube in a TEA configuration. Maximum lasing signal was obtained in the former when a 4.56 nf capacitor was discharged, at 11 Kv, through a mixture of about 0.5 torr C_3O_2, 1.2 torr O_2, and 4.1 torr He. In the TEA configuration lasing intensities were an order of magnitude higher than in the ring electrode tube. Lasing was initiated with a 14.4 nf capacitor, discharged at 20 Kv, through 2 torr of C_3O_2, 13 torr O_2, with no added helium. The need for an efficient preperative method for C_3O_2 is obvious since under our operating conditions, at a partial pressure of 2 torr, C_3O_2 is consumed at the rate of about 2 grams per minute.

Our objectives are to obtain estimates of the vibrational state population of the nascent CO , and to accumulate data on the effect of operating variables to provide a basis for developing a more complete mechanism for the lasing reaction.

4.03 $CS_2 + O$

Parallel with the above development, the formulation of a complete kinetic model for the $CS_2 + O$ reaction is continuing. To date we have carefully reviewed all the models that have been proposed and concluded that these were grossly incomplete with respect to the reactions considered and inadequately documented with respect to the specific rate constants selected for insertion in the kinetics programs. Also they were generally run under the assumption of isothermal conditions, which is far from realistic. Our present computer program permits the solution of the simultaneous equations under totally or partially adiabatic constraints (but, we did not specifically introduce a thermal conductivity term). Also, for practical purposes, we have exhausted the literature on CS_2 and COS pyrolysis, photolysis and oxidation. Now, the numerous proposed mechanisms have to be sifted before we can make a final selection of the steps that are dominant during laser operation, and of the corresponding rate constants. Incidentally, up to now the possible roles of CS_3, O_3, S_2O and in particular $CS^{(v)}$ in controlling the mechanism have not been adequately considered. This we are in the process of doing. It seems that CS_3 is a short lived but very reactive intermediate, and may play an important kinetic role. We hope that within the next two months to have made a series of test runs with our program, in which radiative lifetimes, v - v transfer probabilities, and the exploration of the role of $CS^{(v)}$ have been introduced.

5.0 MOLECULAR RELAXATION VIA ATOMIC COLLISIONS

Professors S. H. Bauer, G. J. Wolga, and R. A. McFarlane

5.01 Testing of the apparatus for the study of the deactivation of HF/DF(v = 1) by H, D, F, O, N has been completed. The HF/DF pump laser has been optimized for v = 1 → 0 transitions and laser induced fluorescence with good signal to noise was observed from HF in the test cell using borrowed R-branch filters. Appropriate blocking filters are scheduled for delivery within two weeks after which data taking will commence. The atom concentration measuring apparatus is in operation. A vacuum blower is being installed in the flow system to increase the atom flow velocities.

5.02 Testing of the apparatus for the study of the deactivation of $CO_2(00^{\circ}1)$ by H, D, F, D, N is in progress. The atom concentration measuring apparatus is in operation. The TEA HBr laser for pumping the laser induced fluorescence experiment is in operation but we are awaiting delivery of a diffraction grating to select a particular HBr pump line in the v = 2 → 1 band. Data taking will commence in the near future.

6.0 VIBRATION ENHANCED CHEMICAL EXCHANGE REACTIONS

Professor G. J. Wolga

6.01 The effect of the vibrational excitation of $HF(v)$ on the rate of the simple atom exchange reaction

$$HF(v) + D_2(v = 0) \rightarrow HD + DF$$

is being studied. A TEA HF laser emitting predominantly on $v = 3 \rightarrow 2$, $2 \rightarrow 1$, and $1 \rightarrow 0$ bands was optimized for maximum overlap in time of the emissions most effective in pumping HF to the $v = 3$ state by successive absorptions on vibrational-rotational transitions. This laser is being used to optically pump HF in a cell also containing D_2. An identical, companion cell is filled with the same gas mixture and is used as a control. After a period of irradiation with the laser both cells are separately analyzed using a mass spectrometer for the HD content. To date reaction enhancement, i.e., conversion of HD by the reaction, of up to 20 percent has been observed. Parametric studies of the enhancement are currently in progress.