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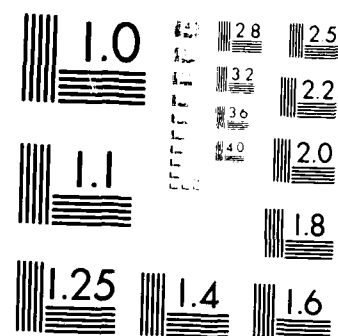
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Rotational Relaxation Studies of Hydrogen Fluoride

Final Summary Report

by

J. J. Hinchey

February 1985

Prepared under Contract F49620-83-C-0098

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ABSTRACT

Two double resonance experiments of collisional hole filling and vibration to rotation transfer have been used to determine rotational relaxation rates for hydrogen fluoride. The rates for rotational levels J2 through J14 range from $55 \times 10^6 \text{ sec}^{-1} \text{ torr}^{-1}$ to $2 \times 10^6 \text{ sec}^{-1} \text{ torr}^{-1}$ and these results are described by kinetic rate models. The rates increase with temperature by about 20% between 300°K and 1000°K. The effect of several added gases on the rates has been measured. Vibration to rotation transfer proceeds by the accepted vibrational relaxation rate. A significant fraction of V=1 population is transferred with about 35% passing through the levels J10-J14 of V=0.

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Rotational Relaxation of Hydrogen Fluoride

Final Summary Report

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Rotational Relaxation of Hydrogen Fluoride

Final Summary Report

INTRODUCTION

This report summarizes the results of research under Contract No. F49620-83-C-0098 to determine experimental rotational relaxation rates for hydrogen fluoride over a range of temperature and for hydrogen fluoride in mixtures of other gases. A further detailed description of the experiments and the data will be provided in planned publications now under preparation.

A long standing need for rotational relaxation rates for HF chemical laser technology has only partially been met by previous experimental and theoretical efforts. Double laser resonance measurements have provided state-to-state transfer rates that can be summed through kinetic models to give rotational relaxation rates, but these results are highly model dependent (Ref. 1). Extrapolation of these models to high rotational levels ($J \sim 13$) gave results differing by orders of magnitude. There is almost no information about the influence of other gases or of temperature on these rates.

The magnitude of relaxation rates for high levels can have a direct effect on chemical laser operation; extremely slow rates would provide a mechanism for storage of population in these high levels, especially if a significant amount of population was transferred to these levels by a V-R mechanism. Relaxation of high levels is also an important ingredient in assessing the role of V-R transfer in the operation of the rotational lasing among high J levels observed by Pimentel and coworkers and by Smith and Robinson (Reference 2).

To address these issues, two double resonance experiments were carried out that are designed to give direct measurements of rotational relaxation rates and the influence of added gases and temperature changes on these rates. The first of these experiments measures the rate of collisional hole filling after one rotational level in the ground state vibrational manifold is depleted of population. The second measures vibration to rotation transfer rates for transfer from $V=1$ to $V=0$ at high rotational levels and rates for the subsequent rotational relaxation of these levels. These experiments along with the results and comparison with kinetic models are separately described below.

COLLISIONAL HOLE FILLING

Discussion

The basic concept for pumping HF molecules out of one rotational level of the ground state vibrational manifold using a single line pulsed laser and monitoring with a CW probe laser the rate of collisional filling of the depleted level is illustrated in Fig. 1. The hole filling process is kinetically a mirror image of pumping molecules to a specific rotational level of an empty vibrational manifold, such as $V=1$, and watching the decay of this pumped population as it is collisionally distributed to the other rotational levels. The original plan was to pump the molecules to $V=3$, far enough away so they would not influence transmission of the probe laser (running on $V(0-1)$) used to monitor the hole filling, which should be 10 to 100 times faster than vibrational relaxation bringing molecules into $V=1$. For this purpose, a pulsed dye laser was used as the source to pump molecules from $J=4$, $V=0$ to $V=3$. Pumping other levels than $J=4$, however, was unsuccessful because of limitations in laser tuning and resort was made to pumping other J levels to $V=1$ with a pulsed HF laser. The limitations of this latter scheme will be discussed below.

Experimental

The experimental arrangement used was essentially the same as that used in our previous double resonance kinetic experiments (Ref. 3). A schematic diagram is shown in Fig. 2. Here, absorption of the single line pulsed laser radiation in a cell containing HF gas creates an "instantaneous" hole in the ground state rotational distribution. Collisional filling of this depleted level is monitored with a cw HF probe laser beam passed collinearly with the pulsed beam through the HF cell. Temporal changes in the increased cw HF laser transmission (gain) due to relaxation of the disturbed distribution is measured using a AuGe (77°K) detector in combination with a fast transient digitizer and a PDP-11 computer. The overall rise time of this complete system is about 2 ns and the computer provides for signal averaging of weak signals. Photoacoustic detection in high pressure HF gas was used to assure that the dye laser was tuned to an HF transition. Pressure in the double resonance cell was measured with a capacitance manometer and the actual HF content was determined by line center absorption of the cw HF laser.

Results for HF

An excimer pumped dye laser which produces pulsed radiation at about 900 nm was first used to pump molecules from an individual J level of $V=0$ to $V=3$. Using the dye H1TC the 0-3 R(4) line was achieved and with the 1P4 cw probe the gain trace of Fig. 3 was obtained. Similar traces were obtained at other HF pressures. No other lines could be made to lase with enough energy within a sufficiently narrow linewidth to an experiment. Likewise, the experiments were not successful with the dyes IR 140 and IR 125 which might pump 0-3P lines.

Further experiments were done using a pulsed HF pump laser running on the same 1P lines as the CW HF probe laser. In this case, population changes are occurring at both the upper and lower levels of the probe laser; a hole is created as population is pumped out of level J, $V=0$ while a spike of population is formed in J-1 of $V=1$. If both levels relax by the same collisional processes, the rate obtained by observing changes in the probe laser transmission should be identical to monitoring only the effect of hole filling. We have previously shown (Ref. 4) that in laser pumped experiments, rotational lasing from the pump level J of $V=1$ to J-1 occurs at ~ 200 ns after the pump pulse. This rotational lasing has the effect of distorting the population decay curve for the pumped level for about 400 ns after which the decay curves are well behaved at HF pressures below about 0.1 Torr. By electronically delaying probe laser signals for 400 ns or more, most of this distortion should be avoidable. The rotational lasing also has the effect of decreasing the population in the pumped level by at least 50 percent. This decrease in the $V=1$, J population allows hole filling in $V=0$ to dominate the temporal changes in the probe laser signal. However, there is some unavoidable mixing between J and J-1 relaxation.

In experiments using both 1P pump and probe lines, the probe signals were delayed 400 ns or more to avoid the complications of rotational lasing. Figure 4 shows a trace for pumping with 1P4 and probing with 1P4. At long time there is a very slow decay of signal as a result of vibrational relaxation of $V=1$ feeding $V=0$.

The data were treated as simple exponential decays and produced straight lines on log plots. The time τ for 1/e decay was determined for the lines 1P2, 1P4, 1P6 and 1P8 at various pressures and the rate $1/\tau$ versus P is shown in Fig. 5. For the 1P4 data, the solid circles are for dye laser pumping with 3R4. That these data fit well with the data for 1P4 pumping (open circles) is some justification for the argument that hole filling dominates the observed decay curves. The slopes of the lines in Fig. 5 give the following rates for HF self relaxation.

<u>Line</u>	<u>Rate 1/Pτ</u>
1P2	51 x 10 ⁶ sec ⁻¹ torr ⁻¹
1P4	31 x 10 ⁶
1P6	22 x 10 ⁶
1P8	17 x 10 ⁶

Effect of Added Gases

Rotational relaxation of HF by other gases was studied in mixtures with DF, H₂, CF₄, N₂, Ar and He. In all cases the data gave a single exponential decay indicating a lack of intermolecular rotational exchange, except in the case of DF. Data for 1/ τ versus pressure for a mixture 1/2 HF in DF are shown in Fig. 6 for 1P6. The solid line is the HF self relaxation rate showing that DF is as an efficient relaxing agent as HF. The following HF relaxation rates for the added gases (M) were obtained from:

$$\left(\frac{1}{P\tau}\right)_{\text{Total}} = \left(\frac{1}{P\tau}\right)_M + \left(\frac{1}{P\tau}\right)_{\text{HF}}$$

using pump-probe lines 1P6-1P6.

<u>Collision Partner</u>	<u>Rate $\left(\frac{1}{P\tau}\right)_M$</u>
HF	22 x 10 ⁶ sec ⁻¹ torr ⁻¹
DF	22 x 10 ⁶
H ₂	1.4 x 10 ⁶
CF ₄	1.6 x 10 ⁶
N ₂	vs
Ar	vs
He	vs

Rates for HF in N₂, Ar and He in mixtures of 1/100 could not be distinguished from pure HF within experimental uncertainty.

Comparison with Models

A summary of relaxation rates for pure HF obtained from the hole burning experiments along with data from V-R transfer (described below) are shown in Fig. 7. These data span the range from $J=2$ to $J=13$ and provide a good test of kinetic models. The lines on Fig. 7 are from calculations for three models. Our previously proposed rotation-rotation exchange model (R-R) is far off at both ends of the scale. Both the Polanyi-Woodall rotation-translation exchange model and the inverse power formulation provide very good fits to the data.

These models have the form

$$\text{PW} \quad \text{Rate } K = K_0 e^{-\alpha(\Delta E/kT)}$$

$$\text{IP} \quad \text{Rate } K = K_0 \frac{1}{|\Delta E|^\gamma}$$

and were fit with the parameters

$$\text{PW} \quad K_0 = 27 \times 10^6 \text{ sec}^{-1} \text{ torr}^{-1}, \quad \alpha = 1$$

$$\text{IP} \quad K_0 = 1.5 \times 10^{10} \text{ sec}^{-1} \text{ torr}^{-1}, \quad \gamma = 1.1$$

By comparison, our double resonance transfer rates for pumping $J=3$ and transfer to $J=4, 5, 6, 7, 8, 9, 10, 11, 12, 13$ fit to the values

$$\text{PW} \quad K_0 = 40 \times 10^6 \text{ sec}^{-1} \text{ torr}^{-1}, \quad \alpha = 0.9$$

$$\text{IP} \quad K_0 = 6.0 \times 10^{10} \text{ sec}^{-1} \text{ torr}^{-1}, \quad \gamma = 1.3$$

Temperature Dependence of Rotational Relaxation

The influence of temperature on rotational relaxation rates was determined using 1P6 pump and probe lines in a hole filling experiment. Figure 8 shows a diagram, approximately to scale, of a high temperature cell used. HF was contained in a closed end sapphire cylinder that was machined from a single piece. With the surrounding furnace the end of the tube could be heated to 1200°K with constant temperature over about 3 cm of length. The pump-probe measurement is made with only the pump laser excited molecules where the laser beams cross. Gas pressure was measured with a capacitance manometer attached to the cell at the room temperature end and calibrated with laser absorption measurements with the cell at 22°C. Corrections were made for density changes that occur as the cell temperature was varied.

Relaxation times at the 1/e decay point were determined using 1P6 lines for a series of gas pressures at each of the temperatures 298°K, 473°K, 733°K, 900°K and 1000°K. From plots similar to Fig. 5, relaxation rates were obtained and these data are presented in Fig. 9 with rate constants in units of cc/molec-sec which conveniently account for gas density rather than pressure at the various temperatures.

The data show that the rate constant is not very sensitive to temperature unlike the very strong function shown for HF vibration rates. We had previously observed a similar weak dependence on temperature of the cross sections for pressure broadening for HF over a much smaller range of temperature (Ref. 5). From the slope in Fig. 9, the activation energy was found as 91 cm⁻¹. Since the rotational energy spacings in the range J=4, 5, 6 is about 40 cm⁻¹, very little translational is required to promote rotational relaxation.

VIBRATION TO ROTATION POPULATION TRANSFER

Discussion

In this section we report results from double laser resonance studies of V-R transfer rates and rates for subsequent rotational relaxation of high rotational levels for pure HF and HF in mixtures with argon, nitrogen, carbon monoxide, hydrogen and helium. This technique studies V-R transfer by searching for the arrival of population in high rotational levels of $V=0$ on relaxation of a $V=1$ population. In this method, which is illustrated in Fig. 10, population is pumped to $V=1$ in a gas sample by absorption of 1P radiation from a pulsed HF laser. A single line cw laser is used to probe arrival of population in discrete rotational levels of $V=0$. The appearance of population is observed as a temporal absorption of the cw radiation intensity.

In earlier work (Ref. 1) we described experimental evidence for the V-R mechanism in observations of population arrival in rotational levels J11-14 of $V=0$ during relaxation of $V=1$. In this work we found anomalously fast rates for V-R which were not in accord with well accepted vibrational relaxation rates from fluorescence or double resonance studies. These fast rates should drive a major fraction of the $V=1$ population to high J levels whereas only small fractions were found there. Our recent work shows that the latter part of these absorption signals were shortened by thermal lensing from heat released during the relaxation processes with the result of apparent fast transfer. Thermal lensing is especially effective in these experiments because the probe signals are weak and strongly affected by small variations in the probe beam intensity. To enhance probe signals pump pulses of much higher energy than usual (5 mJ versus 0.1 mJ) were used which added to the lensing problem. The problem was worse when foreign gases such as argon were added in large quantities due to pressure broadening leading to increased pulse absorption. In sorting out these effects we searched for lasing between the high rotational levels of $V=0$ as a possible cause of the signal shortening. No long wavelength radiation from these levels was found. Since the gain on these transitions is extremely high, the lack of lasing indicates that the V-R transfer process does not form inversions among these rotational levels.

Recently, Haugen, et al. (Ref. 6) described double resonance studies of V-R and rotational relaxation of high J levels in HF. The technique used is similar to the one in the present work, the most notable difference being that they used a tunable F-center as the probe laser. Their results for pure HF are in good agreement with the data from the present study.

Experimental

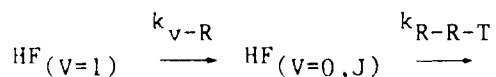
The experiment has been described in previous reports (Ref. 3) and only a few salient features will be treated here. Molecules were pumped from $V=0$ to $V=1$ by a single 1P line pump laser with a pulse duration of 100 ns. To avoid thermal lensing, 1P6 was used in preference to our previously used 1P4 because there is much less absorption by HF of the 1P6 line. Also, for the same purpose HF pressure was restricted to the range of 0.1 to 1.0 torr. The cw chemical laser probe beam operated on single lines that were tuned over 1P10 to 1P14. Both pump and probe beams were made exactly colinear to avoid any possible steering and made to have the same diameter by the use of irises so that they both illuminated the same volume. The HF content in the experimental cell was determined line center absorption using the CW probe laser.

Absolute measurements were made of the amount of HF pumped to $V=1$ and the amount found in the rotational levels of $V=0$. For pumping, measurements of pulse energy entering (using a beamsplitter monitor) and leaving the cell provided for calculations of the pumped population. The intensity of the probe laser was determined by chopping the beam and this data was used with values from the absorption signal due to the V - R transfer in an I/I_0 calculation, including diffusion, of the rotational population. The fraction of pumped population represented by the absorption signal was compared with signals generated using the rate values determined experimentally and assuming all of the pumped population transferred to the level being considered.

Results

A typical trace for pumping with the 1P6 line ($J=5$) and probing at 1P13 are shown in Fig. 11 and on an expanded scale to show the signal rise time in Fig. 12. These traces are an average of 10 signals. A simple analysis of these signals using the kinetic equations for sequential chemical reactions yield rate constants for feeding and loss from $V=0$, J which can be interpreted as rates for V - R transfer and rotational relaxation of level J .

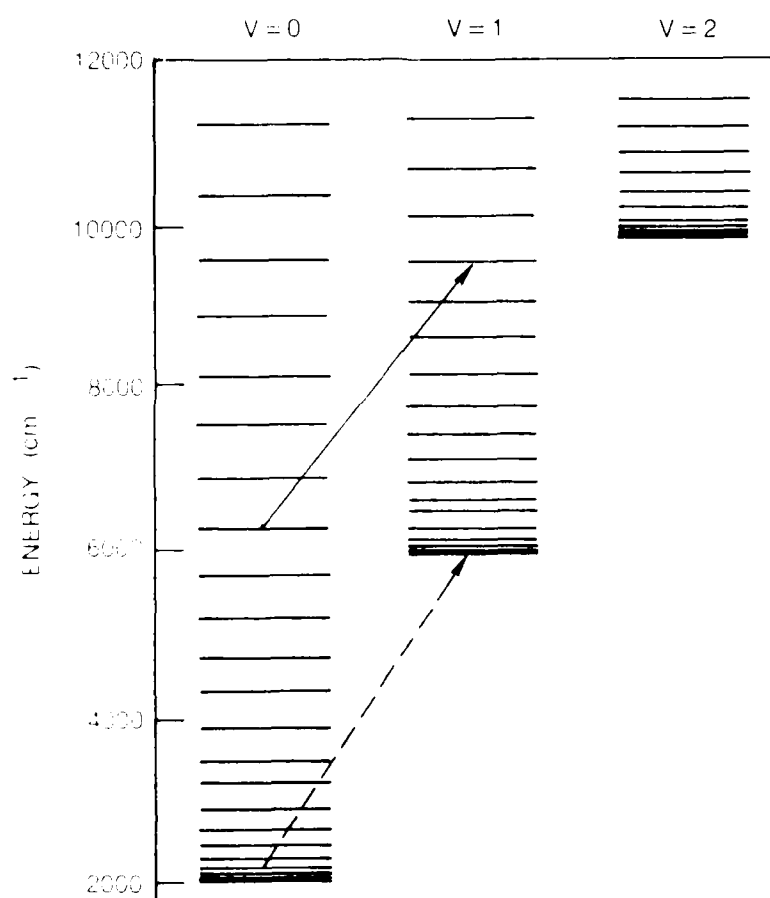
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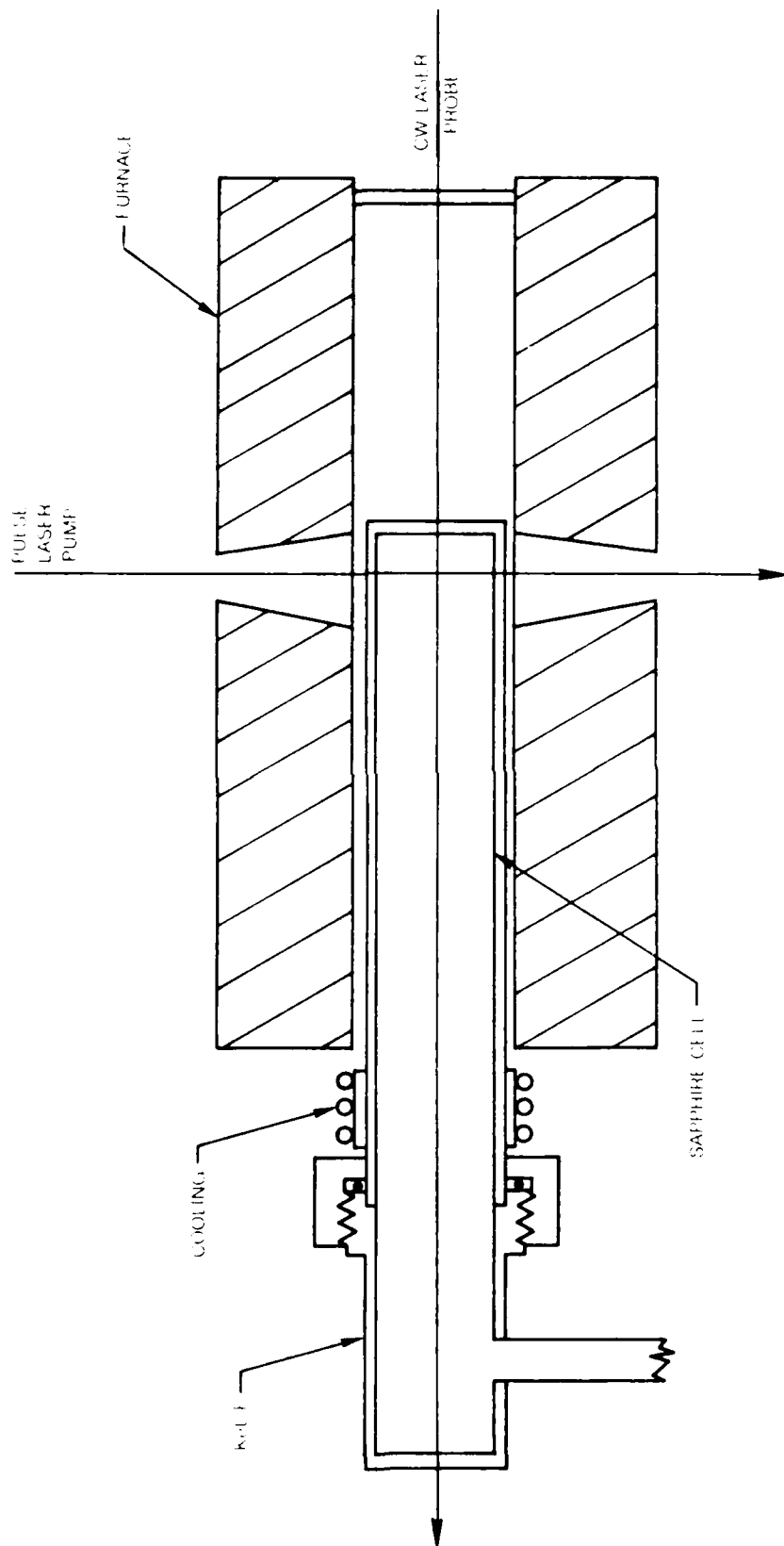
the time dependent population in the probed level J is given by

$$\left[\text{HF}(0, J) \right] = A e^{\frac{k_1}{k_2 - k_1}} \left[e^{-k_1 t} - e^{-k_2 t} \right]$$

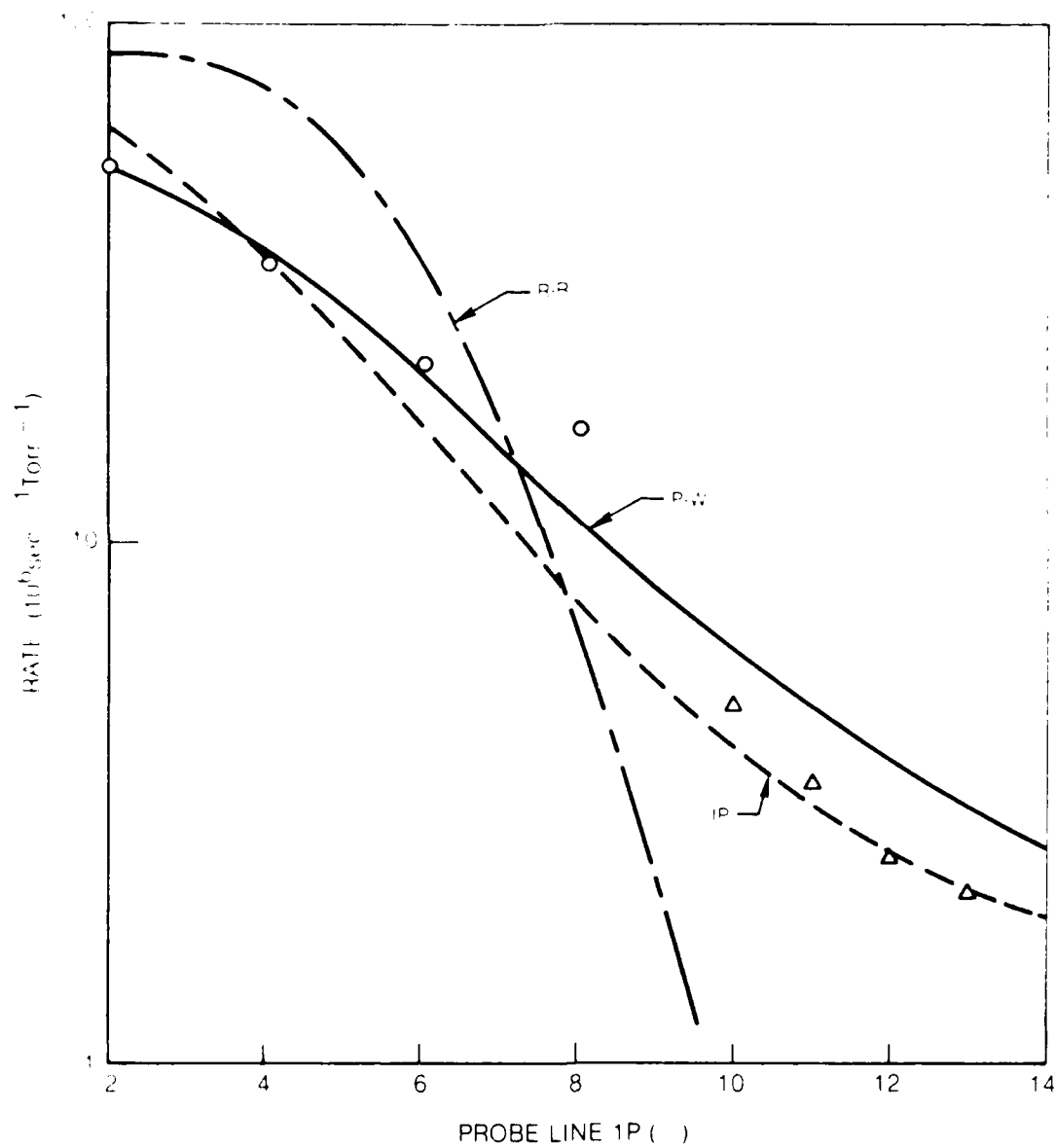
VIBRATION-ROTATION TRANSFER EXPERIMENT



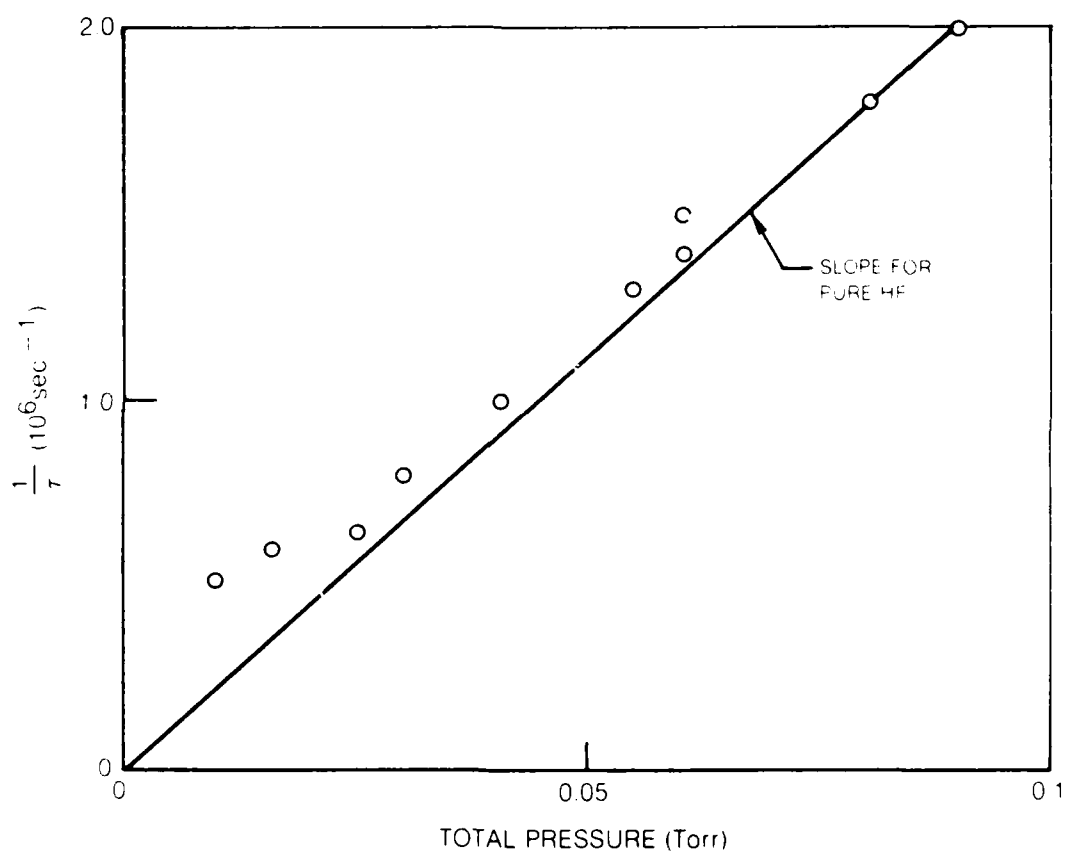
HIGH TEMPERATURE CELL



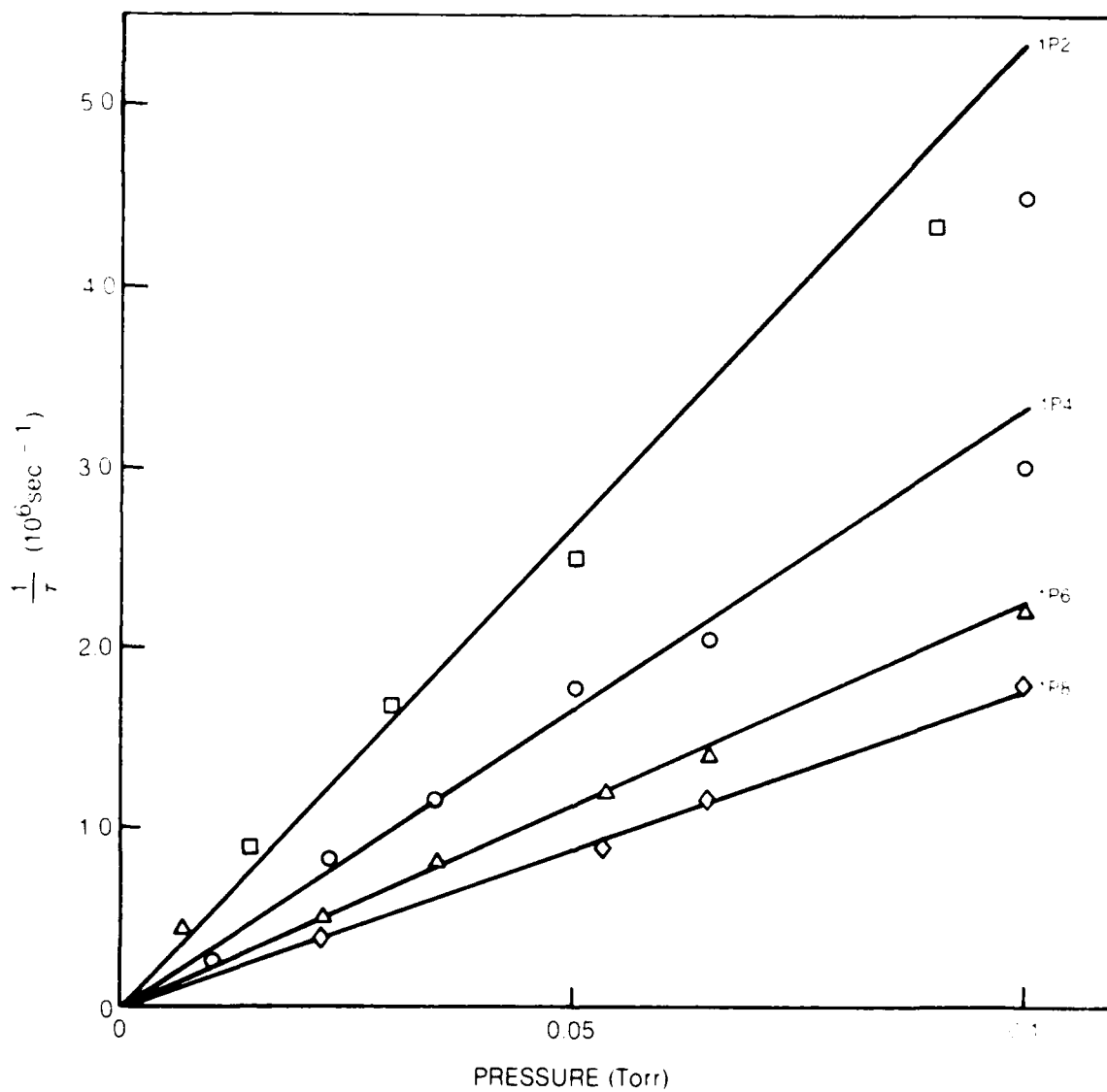
ROTATIONAL RELAXATION RATES FOR HYDROGEN FLUORIDE



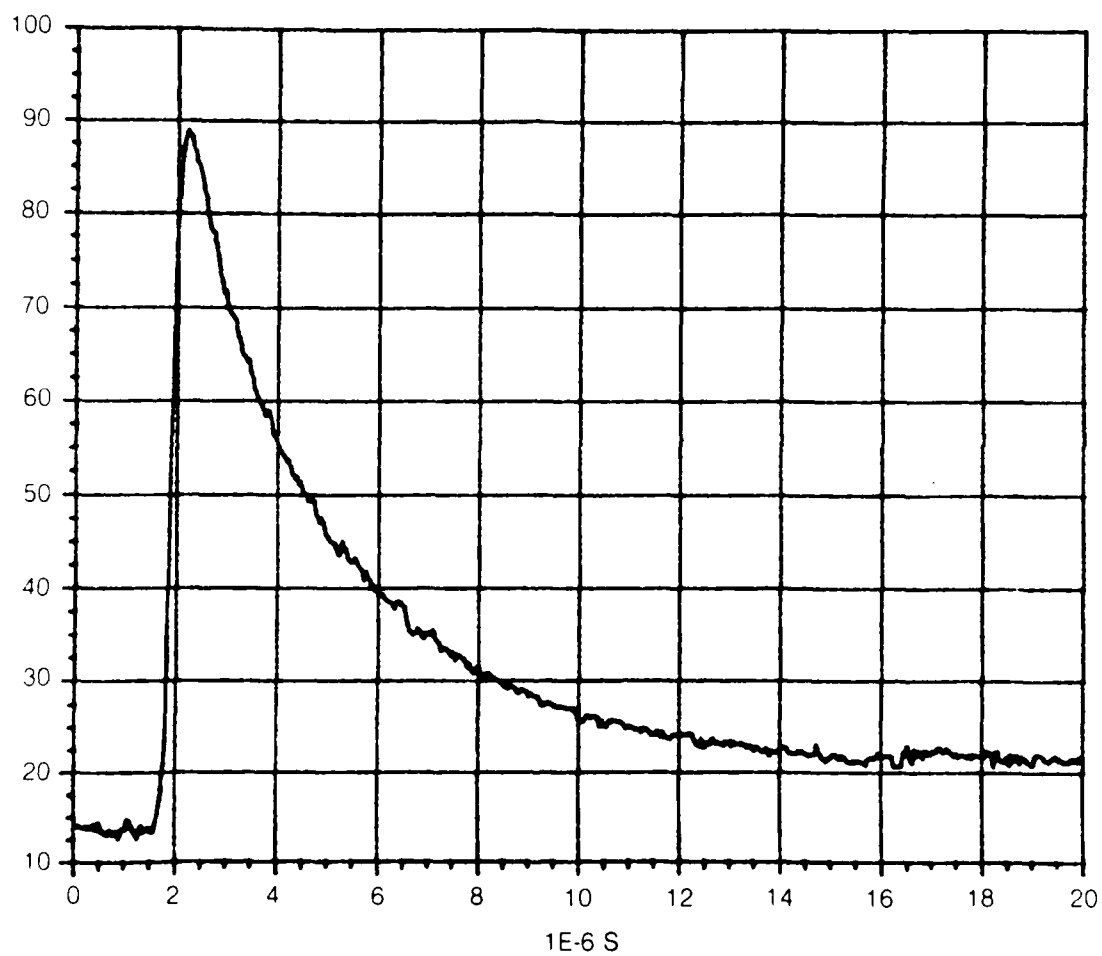
HF ROTATIONAL RELAXATION 1/2 HF/DF MIXTURE
(1P6)



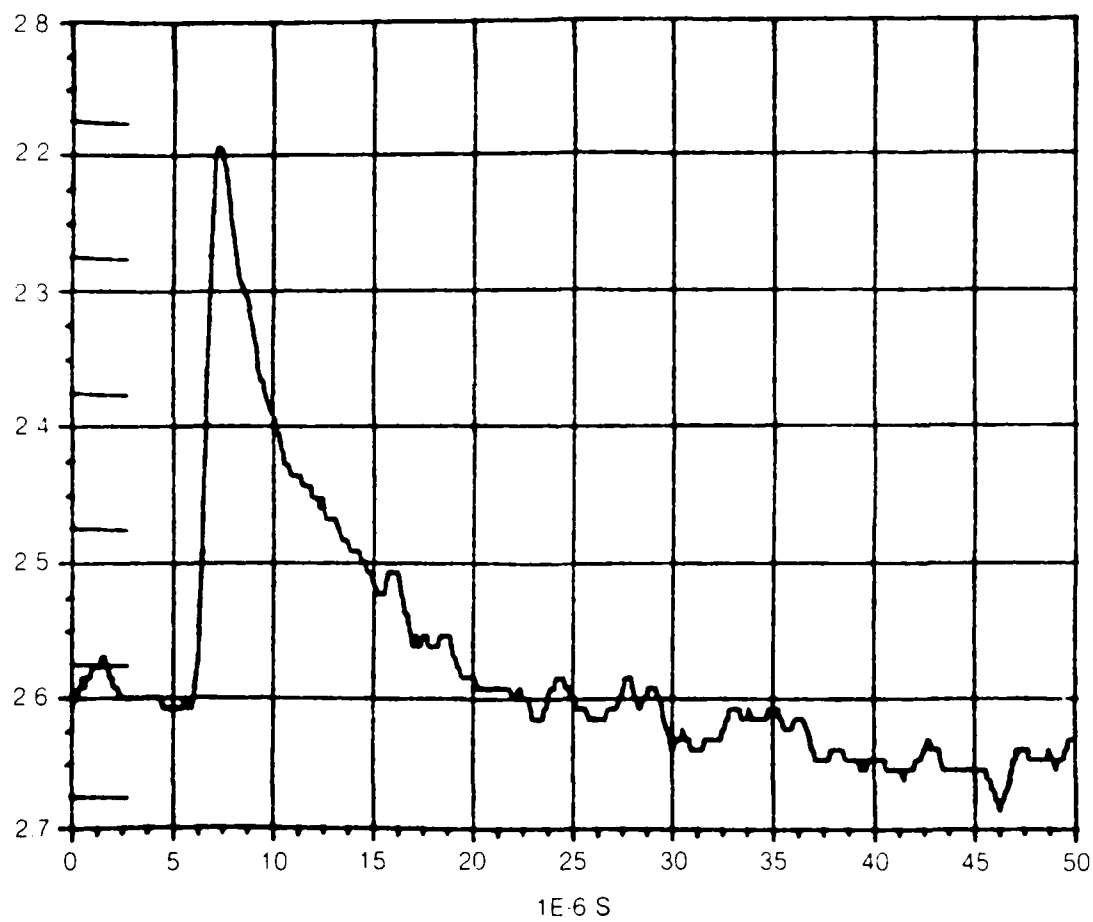
HF ROTATIONAL RELAXATION — PURE HF



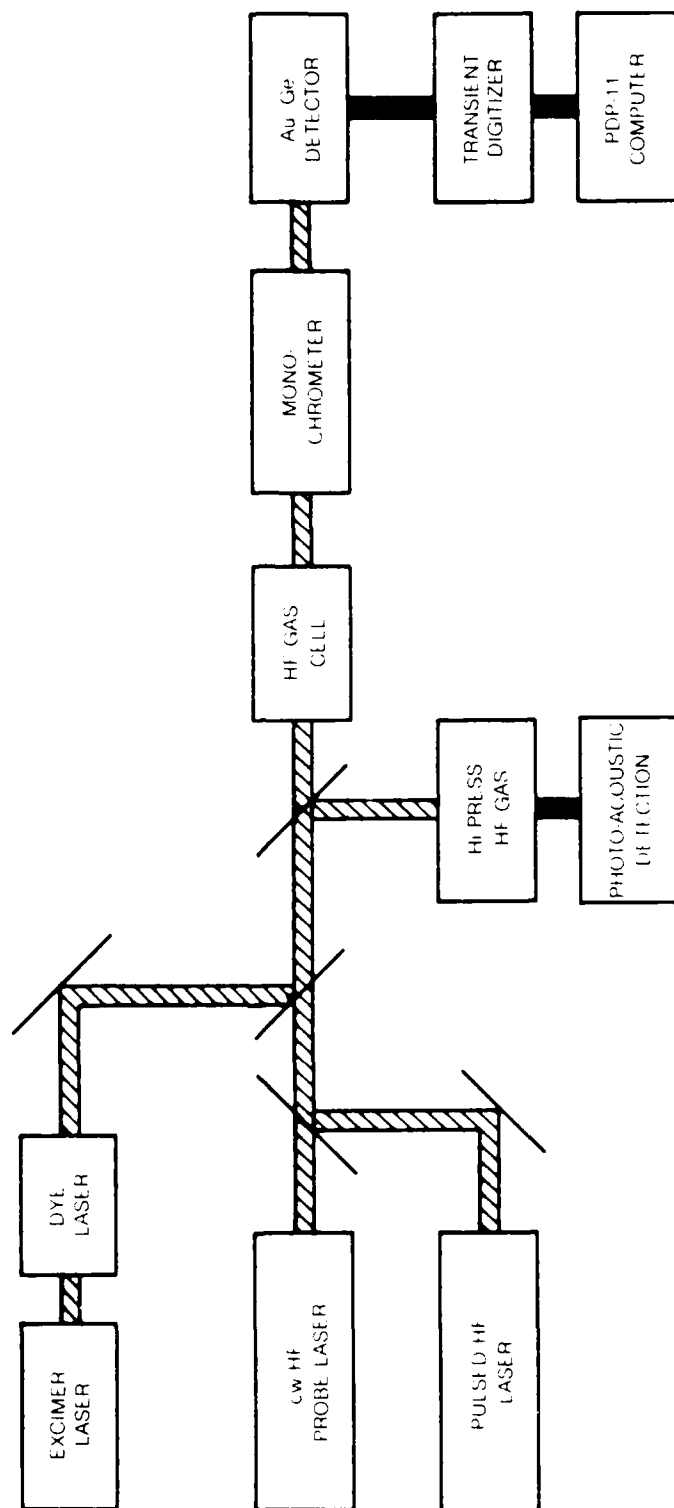
GAIN SIGNAL FOR PUMP 1P4, PROBE 1P4 HF PRESSURE 0.007 TORR



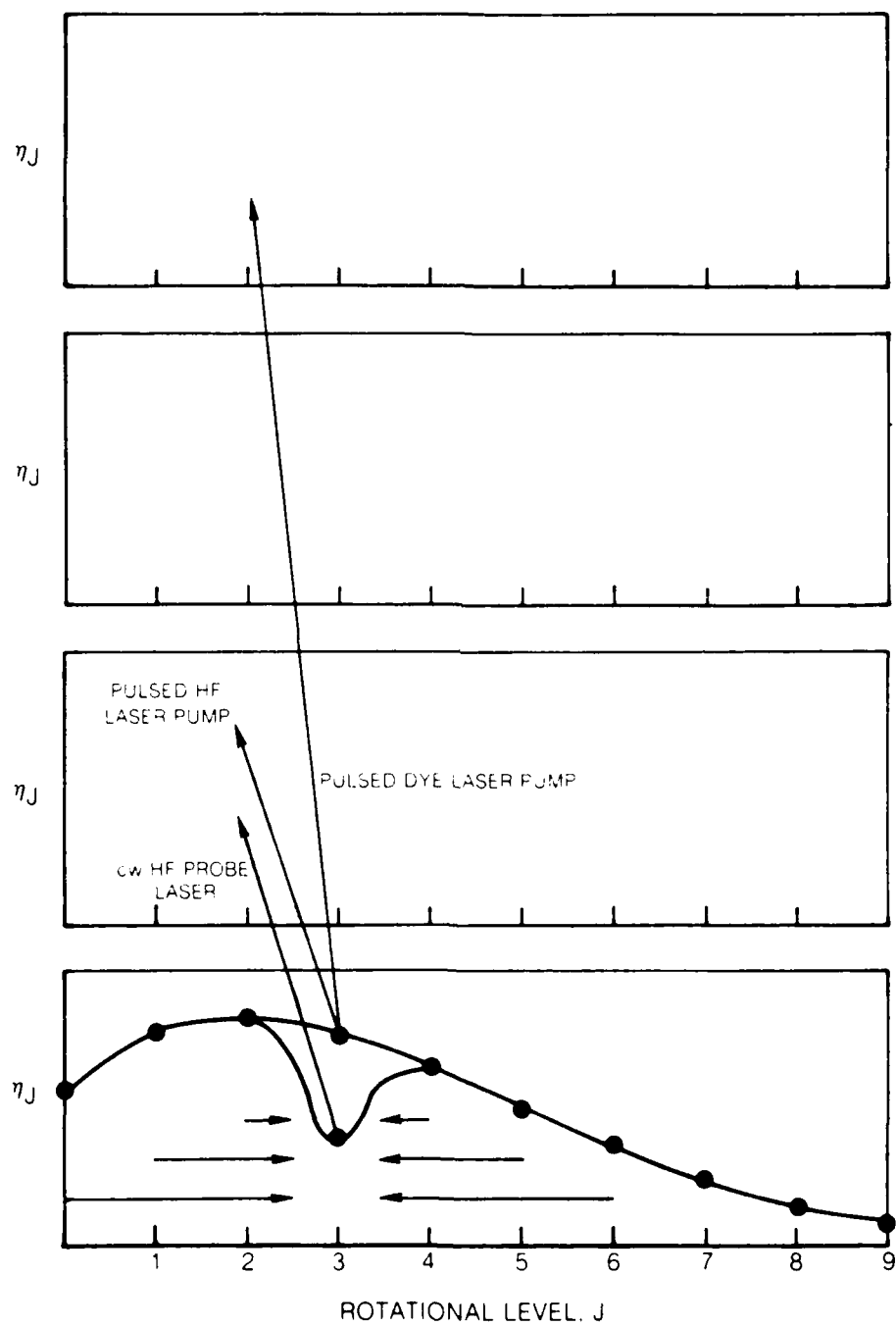
GAIN SIGNAL FOR PUMP 3R(4) DYE LASER, PROBE 1P4 HF PRESSURE 0.01 TORR



EXPERIMENTAL ARRANGEMENT FOR PUMP-PROBE RELAXATION MEASUREMENTS



PUMP-PROBE EXPERIMENT FOR HF ROTATIONAL RELAXATION RATES



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SUMMARY

Double laser resonance experiments in collisional hole filling and vibration to rotation transfer in hydrogen fluoride have been used to determine kinetic rate data for rotational relaxation and V-R transfer. The major results of the work are the following.

- Rotational relaxation rates for HF for the rotational levels J2+J14 range from $55 \times 10^6 \text{ sec}^{-1}\text{torr}^{-1}$ to $2 \times 10^6 \text{ sec}^{-1}\text{torr}^{-1}$.
- The rate variation with J is reasonably described by the Polanyi-Woodall or the inverse power kinetic model.
- Rotational relaxation of HF by DF is as effective as HF self relaxation. The gases H_2 and CF_4 , which have rotational structure are less than 10% as fast. Rare gases and nitrogen are ineffective relaxers.
- Temperature dependence of rotational relaxation is slight; the rate increases by about 20% between 300°K and 1000°K.
- Vibration to rotation transfer proceeds by the accepted vibrational relaxation rate. A significant fraction of V=1 population is transferred with about 35% passing through the levels J10-14.
- Added gases He, Ar, N_2 and CO have only a small effect on the V-R transfer process.

The results for HF in mixtures with Ar, He, Ne, Co and H₂ are listed in Table II.

TABLE II

(rate constant units are sec⁻¹ torr⁻¹)

Level Probed	1/100 Ar			1/100 N ₂		
	K _{V-R}	K _{RRT}	%N _J	K _{V-R}	K _{RRT}	%N _J
J(14)	15x10 ⁴	6x10 ⁶	0.8	30x10 ⁴	6x10 ⁶	0.5
J(13)	20x10 ⁴	8x10 ⁶	4.0	20x10 ⁴	8x10 ⁶	3.0
J(12)	30x10 ⁴	10x10 ⁶		35x10 ⁴	7x10 ⁶	
J(11)	30x10 ⁴	8x10 ⁶				

	1/100 CO		1/100 He		1/1 H ₂	
	K _{V-R}	K _{RRT}	K _{V-R}	K _{RRT}	K _{V-R}	K _{RRT}
J(13)	25x10 ⁴	8x10 ⁶				
J(12)			25x10 ⁴	8x10 ⁶	6x10 ⁴	6x10 ⁶

In general the gases Ar, N₂, CO, and He have little affect on the rates. These gases in concentrations 100 timer the HF content increased the V-R rates by factors of 3-5. There is no discerible effect on the rotational relaxation rates. Both N₂ and CO diminish the probe absorption signals by lowering the population in V=0 by V-V intermolecular transfer. For hydrogen V-V transfer is very efficient; this restricted the addition of H₂ to HF to a ratio of 1/1 in order to have measurable signals. At the concentration no influence of H₂ on the ratess was apparent.

Using this equation, computer simulated absorption curves were fit to the experimental curves by varying values for k_1 and k_2 . Calculated curves included in Figs. 11 and 12 show a reasonably good fit to the experimental curves. A similar analysis of their data was done by Haugen, et al. and as they point out, the front part of the signal is dominated by the R-R-T rate while the decay of the tail is controlled by the V-R transfer.

Absorption signals were recorded and analyzed by this method to obtain k_{V-R} and k_{R-R-T} for the levels $J=10, 11, 12, 13$ and 14 . For each level probed, measurements were made for 10 or more values of pressure in the range of 0.1 to 1.0 torr. For any series, a reasonable fit to the experimental curves could be obtained using single values for k_{V-R} and k_{R-R-T} .

The results for pure HF are shown in Table I where rate constants are averages for the best fits.

TABLE I

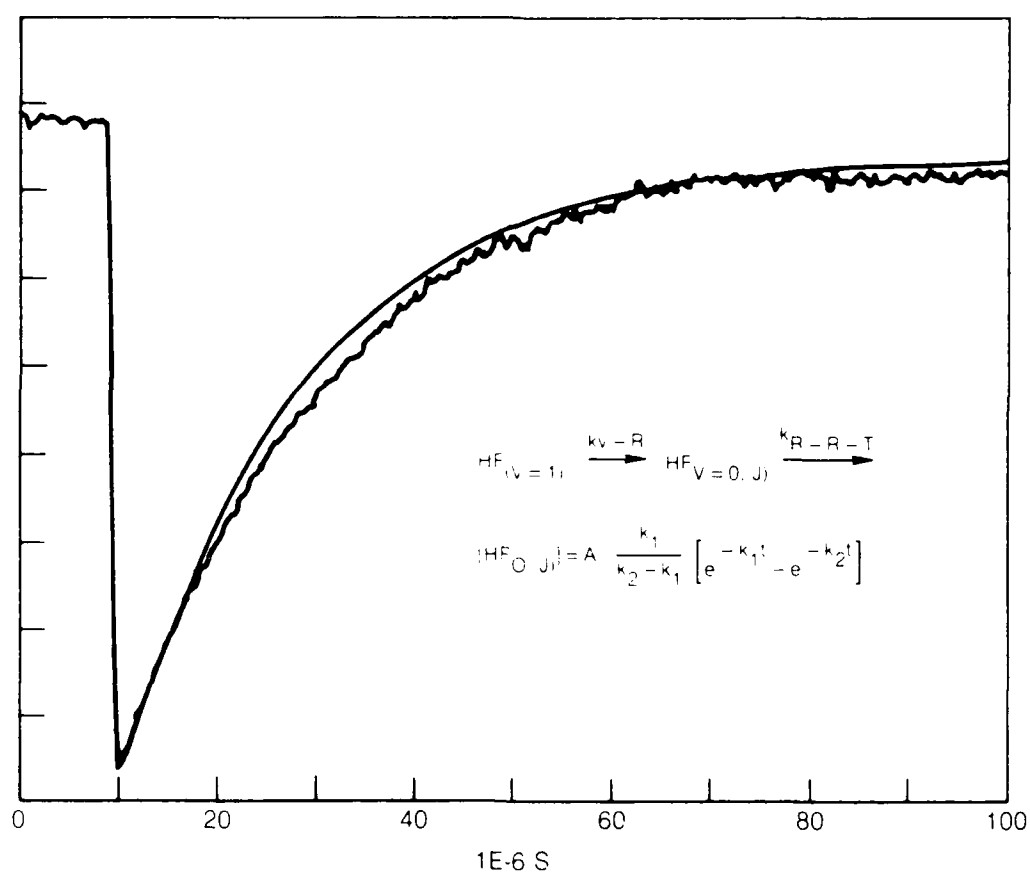
Level Probed	K_{V-R}	K_{R-R-T}	% $N_J/N_{v=1}$
	$10^4 \text{ sec}^{-1} \text{ torr}^{-1}$	$10^6 \text{ sec}^{-1} \text{ torr}^{-1}$	
J(14)	3	2	0.6
J(13)	6	2	3.7
J(12)	6	2.5	6.0
J(11)	6	3	10.5
J(10)	6	4	14.3

These data are in good agreement with the results of Haugen et. al. It is noteworthy to find agreement with % $N_J/N_{v=1}$ because they used very different techniques to determine that percentage.

The value for K_{V-R} (J10-13) is within the range of accepted data for vibrational relaxation (6). For J14, the smaller rate observed might be expected because transfer from $v=1$, low J to J14 is exothermic. Values for rotational relaxation of J10-14 are plotted in Fig. 7. They are found to fit well with data for lower J levels from hole filling experiments and both sets are reasonably described by the PW or IP models.

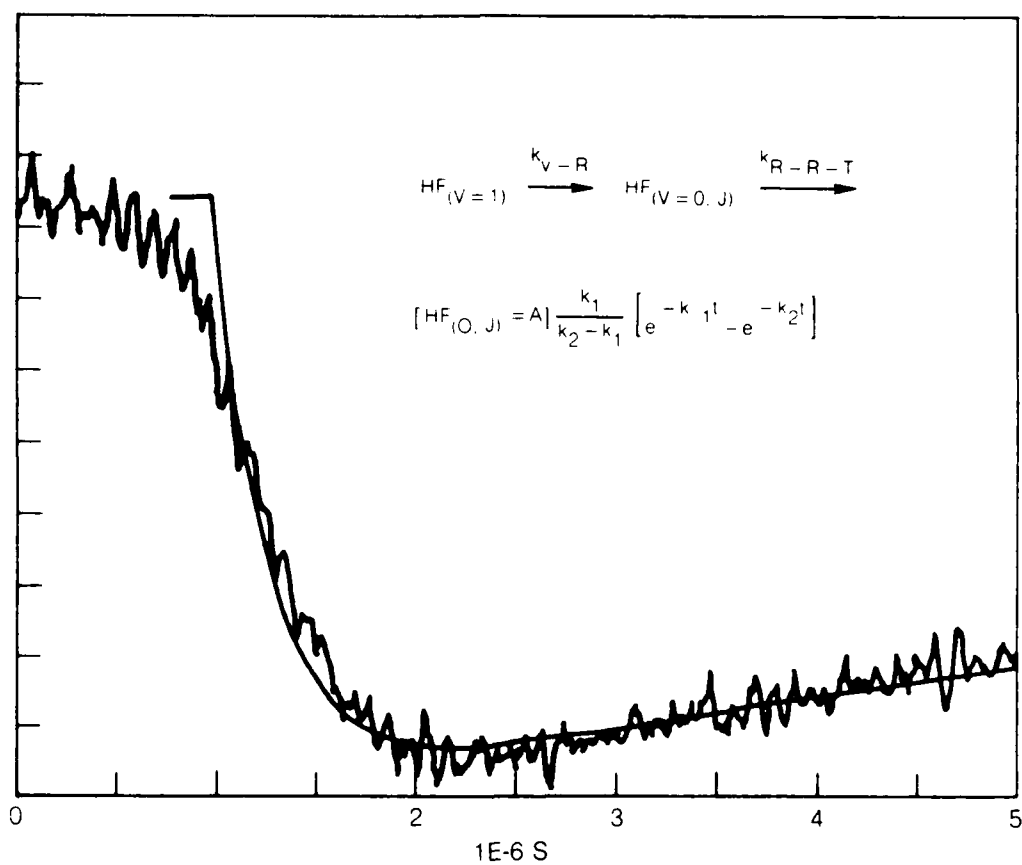
PUMP ($V = 1$), PROBE ($V = 0, J = 13$) HF

HF PRESSURE — 0.50 TORR



PUMP (V = 1), PROBE (V = 0, J = 13) HF

HF PRESSURE — 0.50 TORR



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