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ROTATIONAL RELAXATION STUDIES OF HYDROGEN FLUORIDE(U)
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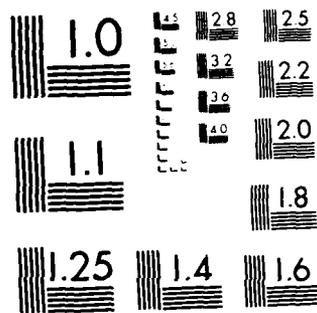
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20. ABSTRACT (CONT'D)

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Rotational Relaxation Studies of Hydrogen Fluoride

Final
Annual Report

by

J. J. Hinchey and R. H. Hobbs

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Rotational Relaxation Studies of Hydrogen Fluoride

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SUMMARY

Laser double resonance experiments in HF were extended to probing levels as high as $J = 13$ to define the processes of population transfer between rotational levels and transfer from vibration to rotation.

In the first part of this report rotational transfer experiments are described and the results are compared with three different kinetic models. Using the criteria of transfer rates and signal shapes for evaluation, the Polanyi-Woodall model was found to best describe the data.

The second part of the report describes observations of direct transfer of vibrational ($v=1$) population to rotational levels $J = 10-13$ of $v=0$. Very fast transfer by this route was measured but only a small fraction of the $v=1$ population was involved. Dilution of the HF sample by rare gases was found to enhance V-R transfer in accordance with observations reported for rotational HF lasers.

ROTATION TO ROTATION POPULATION TRANSFER IN HF

Abstract

Laser double resonance measurements of rotational population transfer in HF previously reported were extended to higher rotational levels to provide experimental criteria for evaluating kinetic models. In $V=1$, rotational levels $J=2$ through $J=7$ were pumped with pulsed laser radiation and a cw laser probed the rate of transfer to levels up to $J=13$. Rotation-translation transfer, rotation-rotation exchange and power law scaling models were compared with the data. Taking model parameter from linewidth fits, the rotation-translation (Polanyi-Woodall) model proved to best describe the double resonance transfer rates and also the individual probe signal shapes.

Introduction

The hydrogen fluoride molecule is attractive for studies of molecular energy transfer because it possesses a simple structure, large vibrational and rotational energy spacings and a strong interacting dipole. Rates for energy transfer in this molecule are of special interest for chemical laser modeling. By using laser pump-probe techniques, one would hope to obtain unique state to state rates for vibrational and rotational population transfer. However, the systems are intimately coupled so that multiple transfers are simultaneously operating. For rotational studies a pulsed laser has been used to pump population into a single rotational level of the empty $V=1$ vibrational level and a cw laser was used to probe population transfer to other rotational levels. Since there are many of these levels and $\Delta J > 1$ transfer occurs, simple state to state kinetics cannot be obtained and the experimental results must be interpreted through a kinetic model.

In a previous paper⁽¹⁾ we reported data for pumping levels $J = 2, 3, 4$ and 5 and probing levels $J' = J+1$ up to $J=8$. The experimental traces of the probe signals were characterized by measuring the time at which the signal reached $1/e$ of its maximum value. Copeland, et al⁽²⁾ made similar measurements pumping $J = 0-4$ in the $v=2$ manifold and probing $J' = 2-6$ and their results compared within a factor of two (slower) to ours.

We analyzed our data in terms of a rotation-rotation exchange model. Other models, such as the Polanyi-Woodall⁽³⁾ or the inverse power law⁽⁴⁾ are found to reproduce these data equally well, but extrapolation to higher probe levels results in very different predictions for the transfer rates.

To evaluate different kinetic models requires data over a wider range of rotational levels. To this end we have extended pump-probe measurements by pumping levels up to $J = 7$ and probing as high as $J = 13$. In comparing the results to the models we used the following criteria for evaluation.

1. Model predictions for rotational relaxation are compared with pressure broadened HF line widths⁽⁵⁾ to determine the constants for each model for best fits with the data.
2. The models with determined constants are compared with $1/e$ times for development of probe laser signals for pumping $J = 3$ and probing $J = 4$ to 13. In this case of pumping near the maximum of the final rotational equilibrium distribution, the signals are near exponential from both the models and experiment.
3. For pumped levels far from the equilibrium maximum, for example $J = 5$ and $J = 7$, the probe signals have distinctive shapes determined by the flow of population towards equilibrium. Comparison of individual signal shapes and absolute intensities for experiment and models forms the final criteria.

Experimental

The double laser resonance experiment previously described⁽¹⁾ was used in the present studies with a few modifications. Both the pulsed and cw HF lasers were grating tuned for single line pumping and probing of individual rotational levels in a static HF gas sample. The cw probe laser⁽⁶⁾ range was extended to the 2P14 transition by incorporation of one internal mirror (100% reflection) and a grating with a zero order outcoupler as the optical cavity and by increasing the discharge current up to 500 ma and the vacuum pumping capacity to 60 l/s. Transient absorption of the cw laser intensity was measured by probing the radiation through a 1/2 meter monochromator to a AuGe (77K) detector. Signals from the detector were led to a fast transient digitizer (Tektronix 7912AD) followed by storage in a PDP-11 computer for signal averaging and processing. A schematic diagram of the experimental arrangement is shown in Figure 1.

Kinetic Models

The first of the three models that are considered in the analysis is the Hinchin-Hobbs (H-H) model. The physical concept for this model is that an excited molecule in $v = 1$, J_1 collides with a ground state molecule in $v = 0$, J_0 and both molecules change rotational states with the nonresonant energy going into translation. With that assumption the rate equations governing the process are:

$$\frac{d}{dt} n_j^{v=1} = \sum_{i \neq j, k, l} \left(n_k^{v=0} n_i^{v=1} \kappa_{ijkl} - n_k^{v=0} n_j^{v=1} \kappa_{jikl} \right) \quad (1)$$

where n_j^v is the population in the vibrational state v and rotational level j ,

$$K_{ijkl} = K_0 \bar{n}_j \bar{n}_l e^{-\alpha \left(E_j^{v=1} - E_i^{v=1} \right) + \left(E_l^{v=0} - E_k^{v=0} \right) / kT} \quad (2)$$

where K_0 is a constant. \bar{n}_j is the normalized Boltzmann population.

This definition of K_{ijkl} satisfies detailed balance explicitly and assumes the rate to be proportional to the exponential of the energy defect in the collision (i.e. to the energy transferred to or from translation). Summing Eq. 1 over the unobserved ground state levels one obtains

$$\frac{d}{dt} n_j^{v=1} = P_i \sum_{j \neq i} \left(n_i^{v=1} \kappa_{ij} - n_j^{v=1} \kappa_{ji} \right). \quad (3)$$

The energy gap model of Polanyi and Woodall⁽³⁾ (PW) for rotational relaxation is based on a complete transfer of energy to translation as a molecule collisionally changes levels by ΔJ . This model was first proposed for the deactivation of HF by argon but it has also been used to describe self deactivation.

The rate K_{ij} is given by

$$K_{ij} = K_0 e^{-\alpha \Delta E / RT} \quad (4)$$

where K_0 and α are constants and ΔE is the energy for ΔJ . This form of the rate K_{ij} applies for positive ΔE while detailed balance is used to supply K_{ij} for negative ΔE . By substituting Eq. 4 into Eq. 3 rates for HF transfer from J to J' are calculated.

Pritchard and co-workers⁽⁴⁾ introduced a power law scaling and successfully modeled rotation to translation energy transfer in a number of atom-molecule systems when ΔE_{ROT} was less than 20% of the kinetic energy. At room temperature this is generally not the case for HF. A simplified statement of the power law scaling is:

$$K_{ij} = K_0 \frac{\bar{n}_i}{|\Delta E_{ROT}|^\alpha} \quad (5)$$

Barnes et al⁽⁷⁾ used the inverse power law to describe rotational relaxations of HF by rare gases in their laser induced rotational fluorescence in an molecular beam experiment. We include this model (IP) also in the analysis of the double resonance data.

The three models were fitted to pressure broadened linewidths⁽⁵⁾ on the assumption that the fastest collisional process in HF is rotational relaxation. The comparison is shown in Figure 2 and the best values of the constants for the models are:

	$K_0(\text{sec}^{-1} \text{ torr}^{-1})$	α
HH	400×10^6	0.96
PW	60×10^6	1.00
IP	20780×10^6	0.93

With these constants the model predictions are compared below with double resonance results.

Experimental Results

The observable in the double resonance experiment is a transient absorption of the cw probe laser intensity as population is collisionally transferred from the pumped to the probe level. If the pumped level is at, or near, the maximum of the final equilibrium distribution then the signals appear pseudo-exponential even though several pathways contribute to the transfer. Examples of such signals are found in series of data for pumping $J = 2$ and $J = 3$; one such example is shown in Figure 3. The development of population in each level after pumping $J = 2$ is demonstrated in Figure 4 where a computer simulation using the P-W model is shown. The traces are separated by 0.1 microseconds. Curves such as the one in Figure 3 can be characterized by measuring the $1/e$ time which can be compared to the model curves which also appear exponential.

The $1/e$ transfer times have been measured for pumping levels $J = 2, 3, 4, 5, 6, 7$ and probing levels up to $J = 13$. Transfer times for pumping lower levels are corrected for the pump pulse width and for diffusion⁽¹⁾ out of the probe beam to give T_{ij} which is used to obtain a rate constant for comparison with models;

$$k_{ij} = \bar{n}_j (1/PT_{ij}),$$

where \bar{n}_j is the normalized Boltzmann factor for the probed state j and P in the HF gas pressure. The transfer times for pumping $J = 3$ extended up to $J = 13$ at various pressure are plotted in Figure 5. These data are shown in Figure 6 as $1/PT_{ij}$ for various probe levels, along with values calculated from the three models, HH, PW, IP, using the parameters derived from the line width. In this comparison, the PW model best describes the experimental data.

As a matter of record, the experimental values for $1/PT_{ij}$ for all of the measurements are listed in Table I. Pumped levels far from the equilibrium maximum produce probe signals that have complex shapes such as one shown in Figure 7 for pumping $J = 7$ and probing $J = 8$. This is a result of a transient overpopulation of $J = 8$ before rotational equilibrium is reached as demonstrated in the computer simulation of Figure 8 using the PW model. Such signals furnish a sensitive test of a model's ability to reproduce the individual shapes. Model predictions and experimental signals are shown in Figures 9, 10, 11. In Figure 9, the signals for pumping $J = 2$ and probing $J = 3$ are pseudo-exponential and all the three models reproduce the signal. Pumping $J = 4$ and probing $J = 5$ (Figure 10) produces a small overpopulation which is best described by the PW model. For pumping $J = 7$ and probing $J = 8$ (Figure 11) a very large overpopulation is found and the PW model by far gives the best agreement with the experimental trace.

Table I

J_i Pump	J_j Probe	Experimental $1/PT_{ij}$ $\mu s^{-1} Torr^{-1}$
2	3	124.7
2	4	50.4
3	4	96.2
3	5	25.1
3	6	16.1
3	7	14.7
3	8	9.72
3	9	7.08
3	10	3.26
3	11	1.91
3	12	1.69
3	13	1.82
4	5	54.3
4	6	18.4
5	6	60.3
5	7	23.7
5	8	8.19
5	9	5.03
5	10	5.40
5	11	1.21
5	12	0.99
5	13	1.51
6	7	71.1
6	8	36.9
7	8	160.2

Conclusions

Employing experimental data as criteria for evaluating kinetic models of rotational population transfer the following statements can be made.

1. The three models, HH, PW and IP all agree satisfactorily with collision rates from pressure broadened linewidths. The HH model fits data for lower J levels somewhat better while the other models do better at high J levels.
2. Using parameters determined by linewidth fitting, the PW model was found to best describe the kinetic data for transfer from J = 3 to levels J = 4 through J = 13.
3. With the model parameters fixed by the linewidth fit, the PW model reproduced the individual probe signal shapes with considerable accuracy as compared to the other models.

At this juncture the PW model appears to best predict rotational population transfer for our experiments with pure HF at room temperature. It should be noted, however, that Barnes et al found the IP model best fit their data for molecular beams of argon and HF at high translational energy. Also we find that application of the PW model to DF disappointing in that it required a reassignment of model parameters.⁽⁸⁾ Based on results reported here, use of the PW model is recommended for chemical laser computer codes that include rotational nonequilibrium.

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VIBRATION TO ROTATION POPULATION TRANSFER IN HF

Abstract

Definite evidence has been obtained for V-R transfer in HF through double resonance experiments which pump population to $V=1$ and probe for the arrival of this population in high rotational levels of $V=0$. It is found that only a small fraction of the $V=1$ population transfers by this path, but the transfer rate is 10 to 100 times faster than transfer to lower rotational levels. Rare gases were found to promote the transfer with argon being the most effective in accordance with reported studies of rotational lasing.

Introduction

A major modification to vibrational relaxation theory is introduction of the concept that vibrational energy can be converted to rotational energy (V-R) in near-resonant collisional exchange. Since only a small amount of energy need go into translation, relaxation rates can be very fast. Cottrell and Matheson⁽¹⁾ suggested V-R exchange may account for their observed slower relaxation times for CD_4 and SiD_4 as compared to CH_4 and SiH_4 . Moore⁽²⁾ developed a two parameter model for V-R energy transfer and Chen and Moore⁽³⁾ used this model to describe the temperature dependence for their measured HCl and DCl relaxation rates. They concluded from these studies that in a collision between a vibrationally excited and a ground state molecule, the vibrator will have most of the rotational energy after the collision while the collision partner will be hardly affected.

Additional evidence for V-R transfer in HF is furnished in a number of studies of lasing from high rotational levels. Observations of lasing between rotational levels of HF formed in photoelimination reactions of CH_2CHF and CH_2CF_2 diluted in argon (1/100) by Sirkin and Pimentel⁽⁴⁾ and by Smith and Robinson⁽⁵⁾ are particularly relevant. Both of these studies showed lasing at high rotational levels grouped around the energy of the next one or two higher vibrational levels. The authors of these papers ascribed a strong role for V-R transfer in populating the lasing levels. High dilution in argon is required for the rotational lasing; it was suggested that the argon may promote rotational relaxation leading to increased population inversions. In a similar study of rotational lasing in OH and NH formed in photoelimination reactions, Smith and Robinson⁽⁶⁾ found dilution by rare gases (1/100) necessary and of the gases employed argon produced the most intense radiation.

In this paper we report ir double resonance studies of V-R transfer in HF by searching for the arrival of population in high rotational levels of $V=0$ on relaxation of $v=1$ population. In this method, population is pumped to $v=1$ in a gas sample by absorption of $1P_4$ radiation from a pulsed HF laser. A single line cw laser is used to probe arrival of population in discrete rotational levels up to $J=14$ of $v=0$. The appearance of population is observed as a temporal absorption of the cw radiation intensity. This kind of experiment furnishes a simple test for purely collisional transfer without the complications of chemical pumping of many levels that are part of laser experiments.

Experimental

The experimental arrangement described in the preceding portion of this report on rotational transfer was used without modification except to operate the probe laser on $1P$ rather than on $2P$ transitions.

Results

An illustration is shown in Figure 12 of absorption signals that were obtained with pure HF and with HF-argon mixtures (1:100). These traces furnish direct evidence for transfer of population to the levels J_{10} - J_{14} from $v=1$. The addition of argon increases the rate of population of the probed level and also subsequent depopulation of this level by apparant rotational relaxation. There is also an increase of about four in the absorption signals where argon is added.

For pure HF the $V=0$ levels $J=4$ through $J=14$ were probed after pumping $V=1$, $J=4$. The intensity of the probe beam, I_0 , and the size of the absorption signal, ΔI_{abs} , were measured to determine the transient populations in each rotational level from

$$-\ln(I_0 - \Delta I_{abs}) / I_0 = \alpha L P, \quad (1)$$

where α , L , P are the absorption coefficient, cell length and pressure of the population arriving in each level respectively. These data for pressures 0.1-0.3 torr are plotted as relative number density for the different levels in Figure 13. Compared to the solid line in this figure for an equilibrium distribution, the levels $J=10$ - 14 are about equally populated and represent a real increase above this distribution. These data cannot be accounted for by the temperature rise of about 5°C expected from absorption of energy from the laser pulse.

By measurements of the pulsed pump energy actually absorbed at 0.3 and 0.4 torr it was determined that about $1-1.5 \times 10^{12}$ molec/cc were pumped to $v=1$. Absorption signals for probing $J=13$ account for $7-9 \times 10^8$ molec/cc or about 0.1% of the pumped molecules. This value is in accord with the data of Figure 13 for levels $J=9-13$ from absolute absorption measurements. For mixtures of HF in argon the amounts in high levels are approximately four times greater. These values may be considerably less than the total amount transferred by V-R because population is passing through the level monitored to lower levels by rotational relaxation and other processes. One other possible mechanism for depleting the levels is rotational lasing; we have searched for such radiation without finding any evidence for lasing or superfluorescence.

A characteristic of all of the signals in Figure 12 is an extremely fast development of absorption. The average time for this is about 4 μ sec in pure HF which can be compared with the accepted vibrational relaxation time of about 110 μ sec at the HF pressure of 0.15 torr. These observations lend firm support to the proposition of very fast V-R and R-V transfers leading to an equilibration between $v=1$ and high levels of $v=0$ with subsequent decay of the combined system. The addition of argon can be seen in Figure 12 to increase the V-R transfer and subsequently to increase the rate of population loss from the high J levels. This observation seems to be in accord with speculations on the role of argon in rotational lasing. In pure HF the absorption signals for levels $J=10$ and lower are observed to develop at about the vibrational relaxation times. The rate, $1/P_t$, of population arrival in levels $J=5-13$ of $v=0$ is shown as a plot in Figure 14 where the abrupt change in rates at $J=10$ is apparent.

A comparison of the effect of neon, argon and krypton as added gases on V-R transfer to $J=13$ can be made by examining the absorption signals shown in Figure 15. Argon can be seen to be the most effective in the fast rate of arrival in $J=13$, the amount transferred to this level and the fast relaxation of the $J=13$ population. Argon is followed by neon and then krypton; this trend follows the observations of Smith and Robinson on the influence of rare gases in rotational lasing in HF, OH and NH.

Conclusions

The double resonance studies have provided definite evidence for V-R transfer of HF population from $v=1$ to high J levels of $v=0$. Although only a small fraction of the $v=1$ population appears to go by this route, the majority of population going directly to a Boltzmann distribution, the V-R transfer is much faster than the general vibrational relaxation. This faster rate to high J levels can lead to a temporal inversion over the more slowly populated lower levels. Addition of rare gases to the HF samples promotes the V-R transfer with Argon being the most effective agent. The results are in accord with the observation reported of rotational lasing pumped by V-R transfer, but indicate that only a small fraction of HF molecules may be involved in the process.

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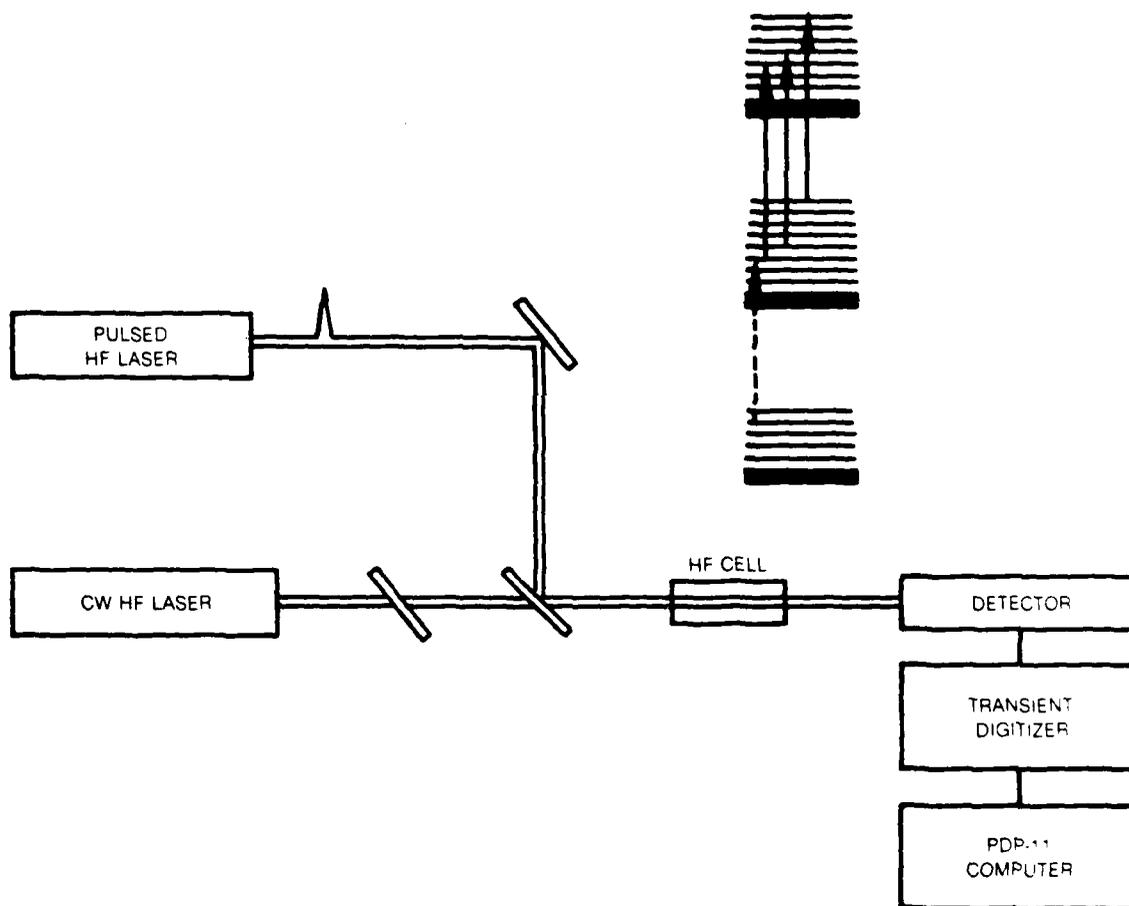
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1. Collision Processes in Chemical Laseres. J. J. Hinchey: Applied Atomic Collision Physics, Vol. 3, Chapter 7, p. 191, Academic Press, 1982.

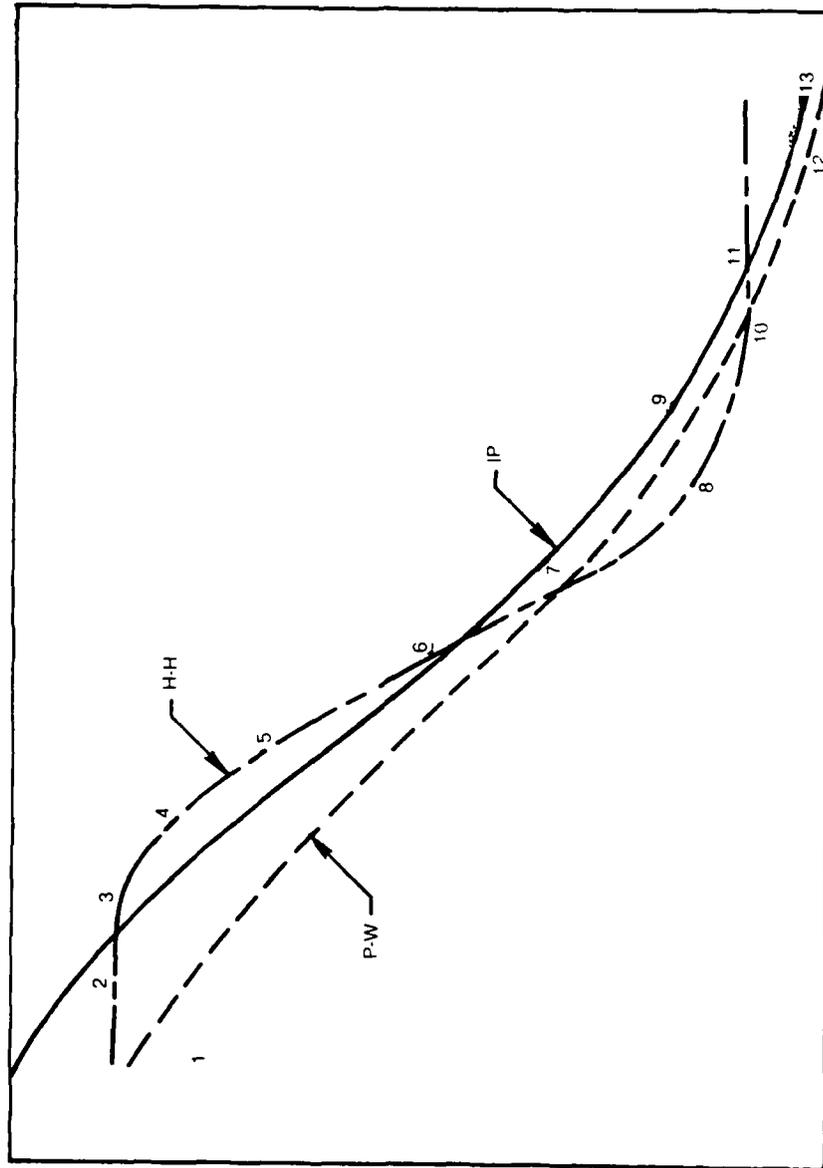
Publications in Preparation

1. Rotational Population Transfer in DF: J. J. Hinchey and R. H. Hobbs.
2. Rotation to Rotation Population Transfer in HF: J. J. Hinchey and R. H. Hobbs.
3. Vibration to Rotation Population Transfer in HF: J. J. Hinchey and R. H. Hobbs.

ROTATIONAL RELAXATION EXPERIMENT



LINEWIDTH RATES FOR HF



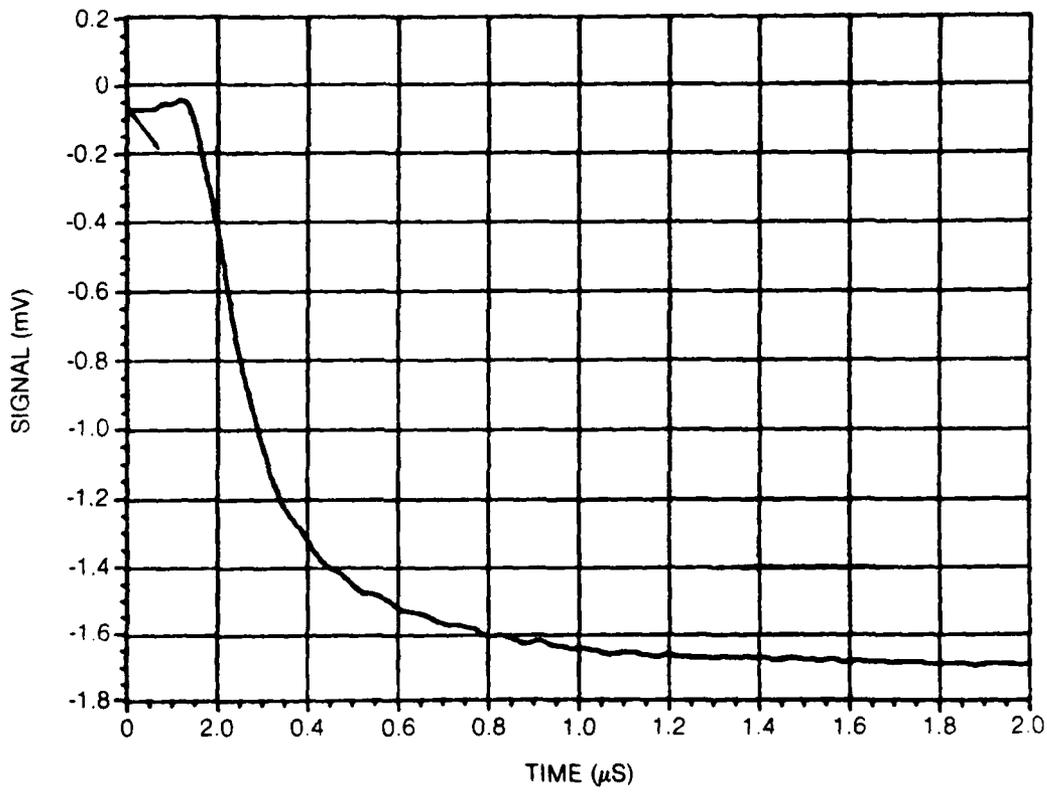
ROTATIONAL LEVEL, J

COLLISION RATE

POPULATION TRANSFER

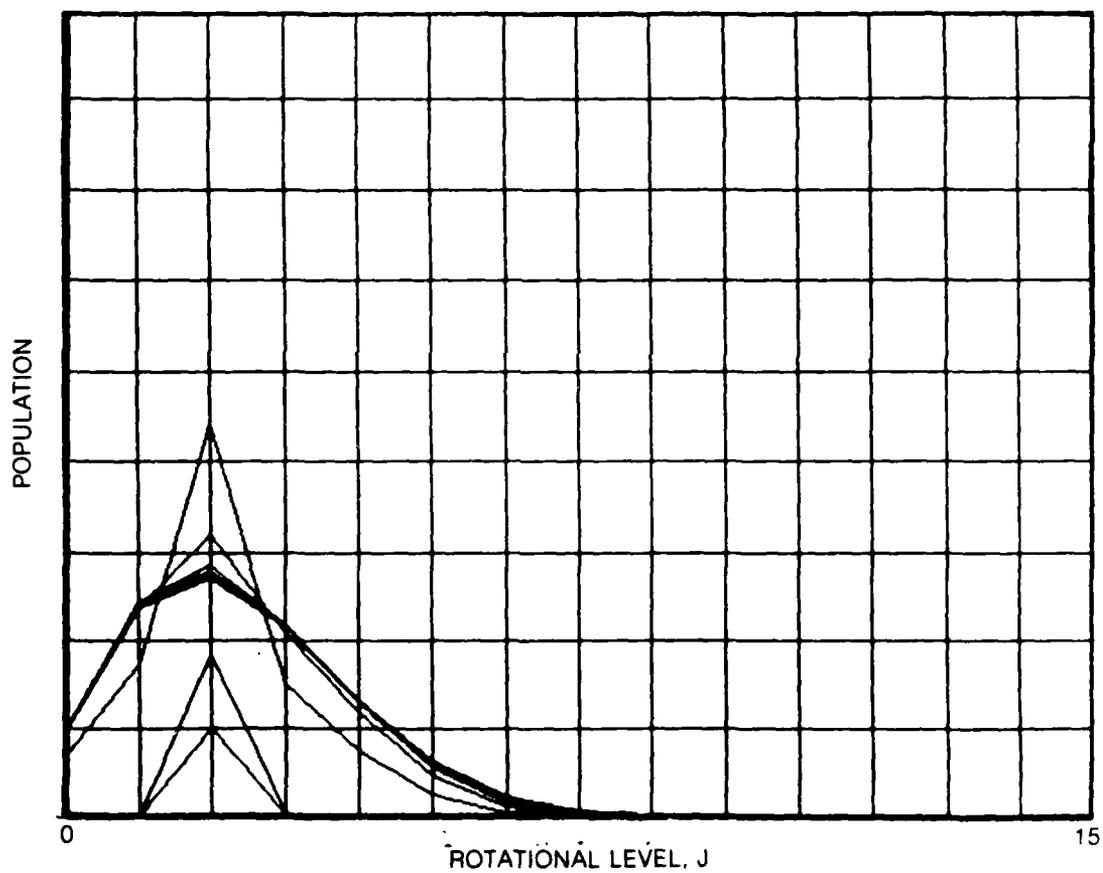
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HF = 0.06 torr

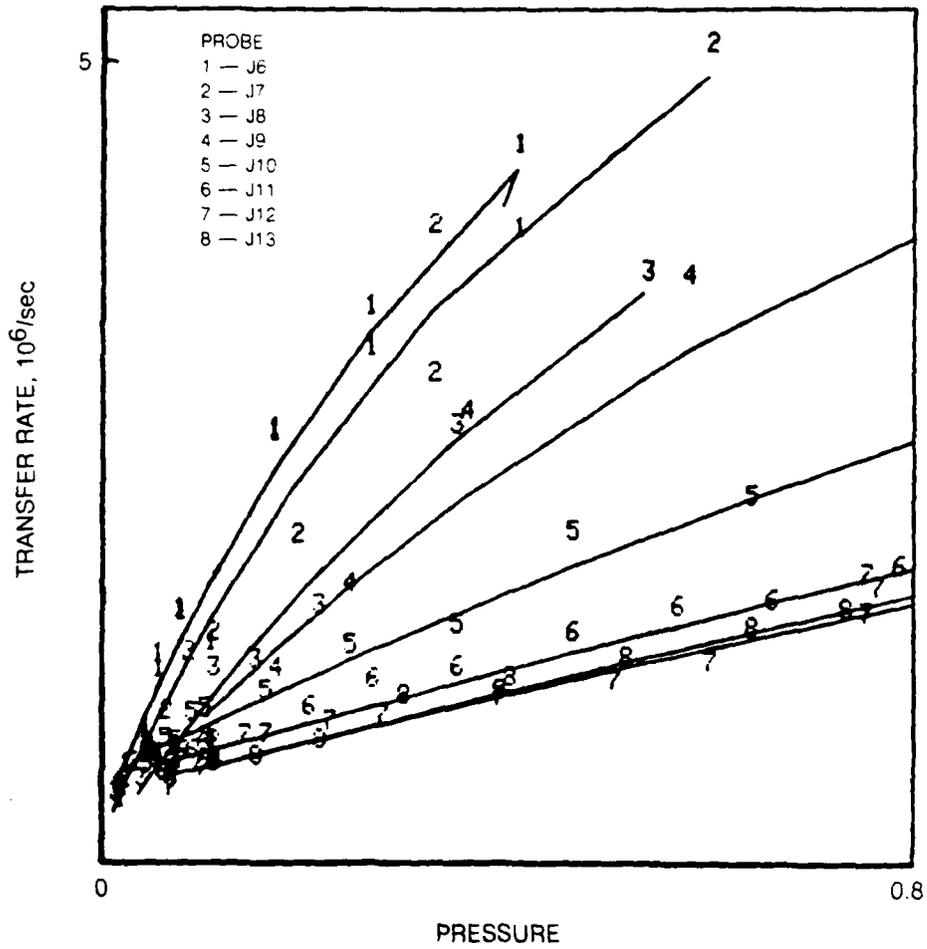


RELAXATION OF J = 2

HF 0.06 torr

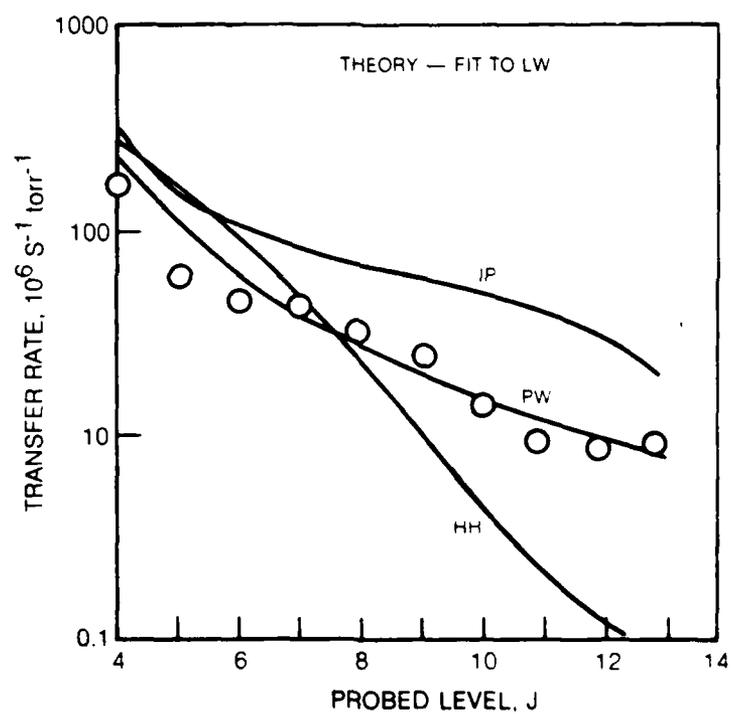


TRANSFER OF POPULATION FROM HF (J = 3)



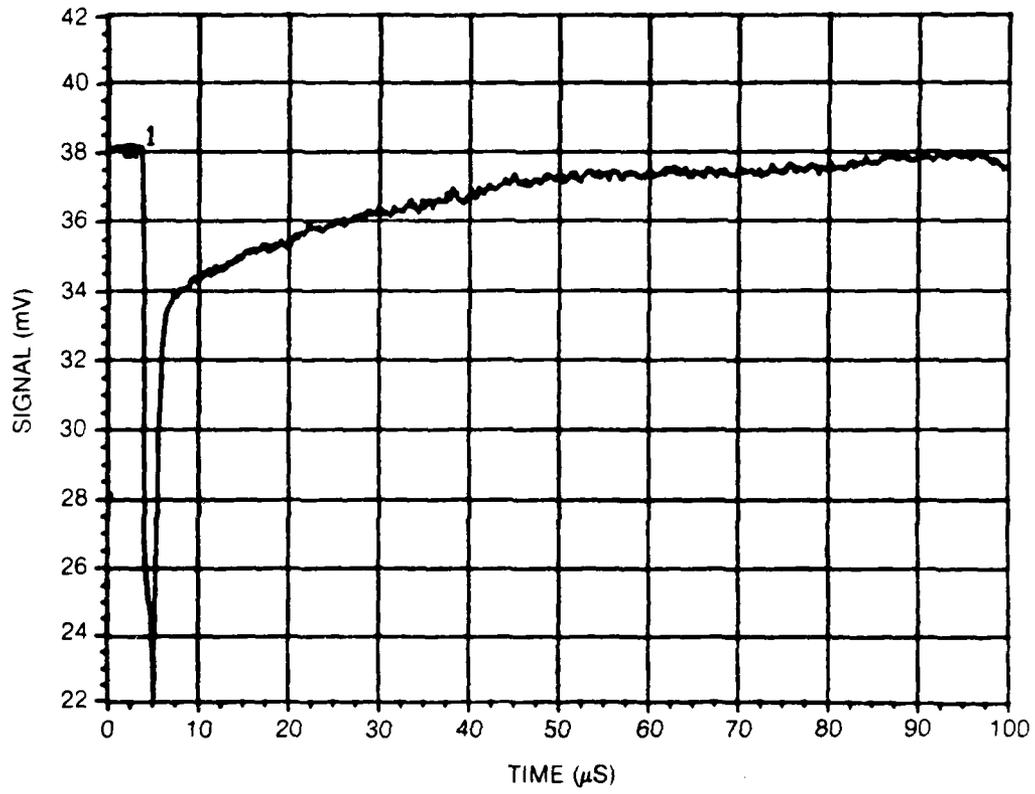
HF DOUBLE RESONANCE TRANSFER RATES

PUMP J = 3, PROBE J



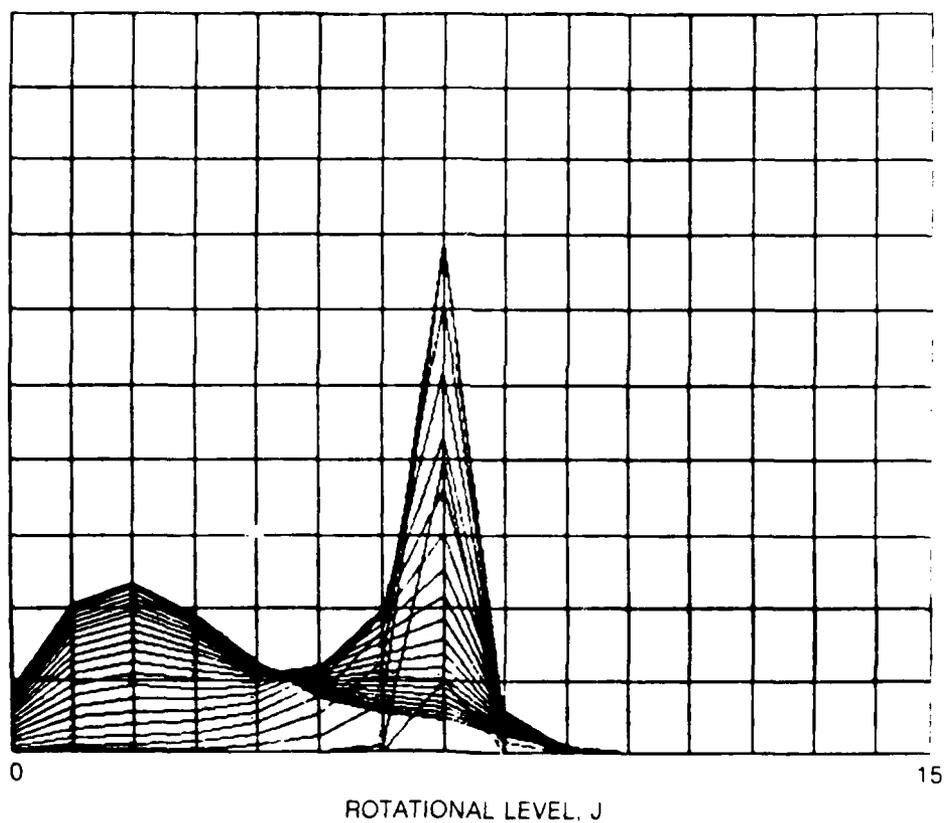
POPULATION TRANSFER

PUMP J = 7, PROBE J = 8
HF 0.66 10¹¹



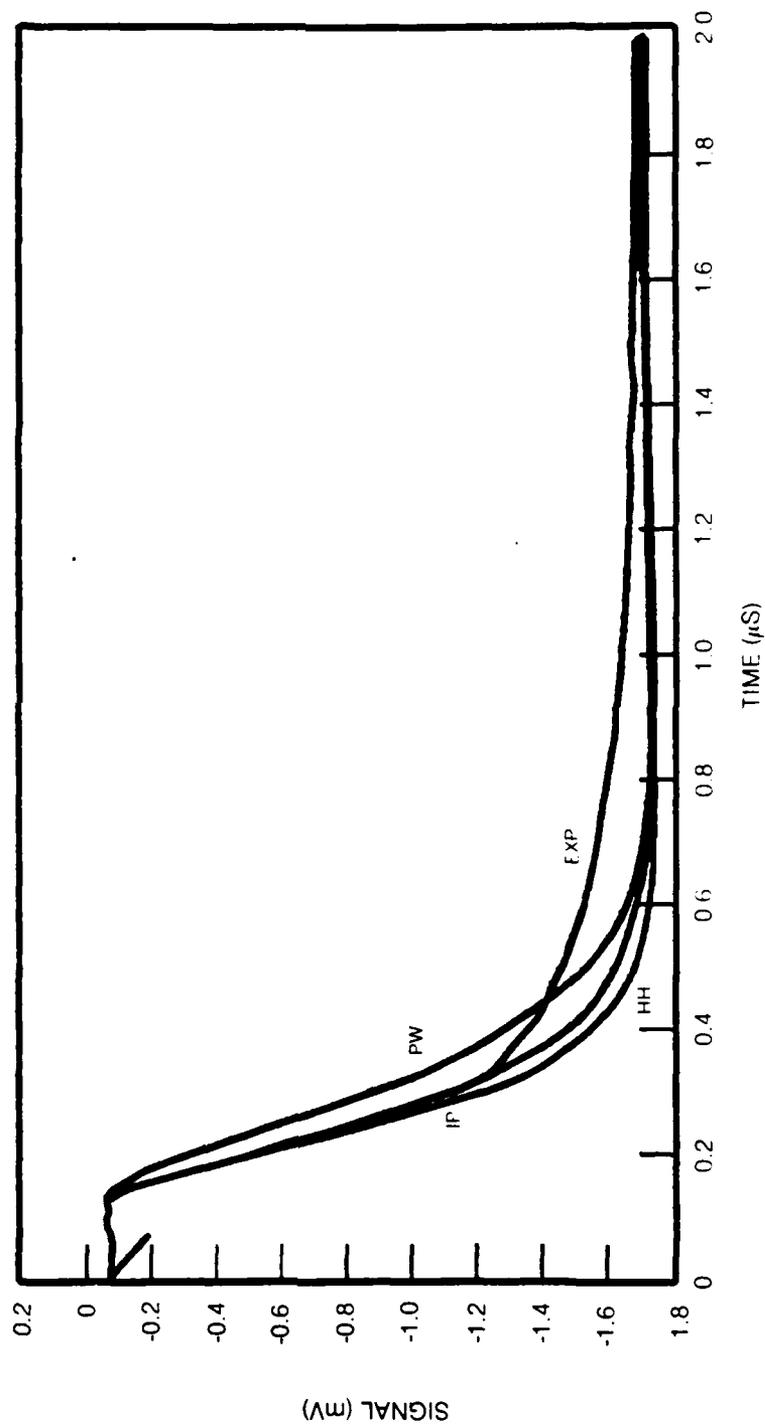
RELAXATION OF J = 7

HF = 0.06 torr



POPULATION TRANSFER

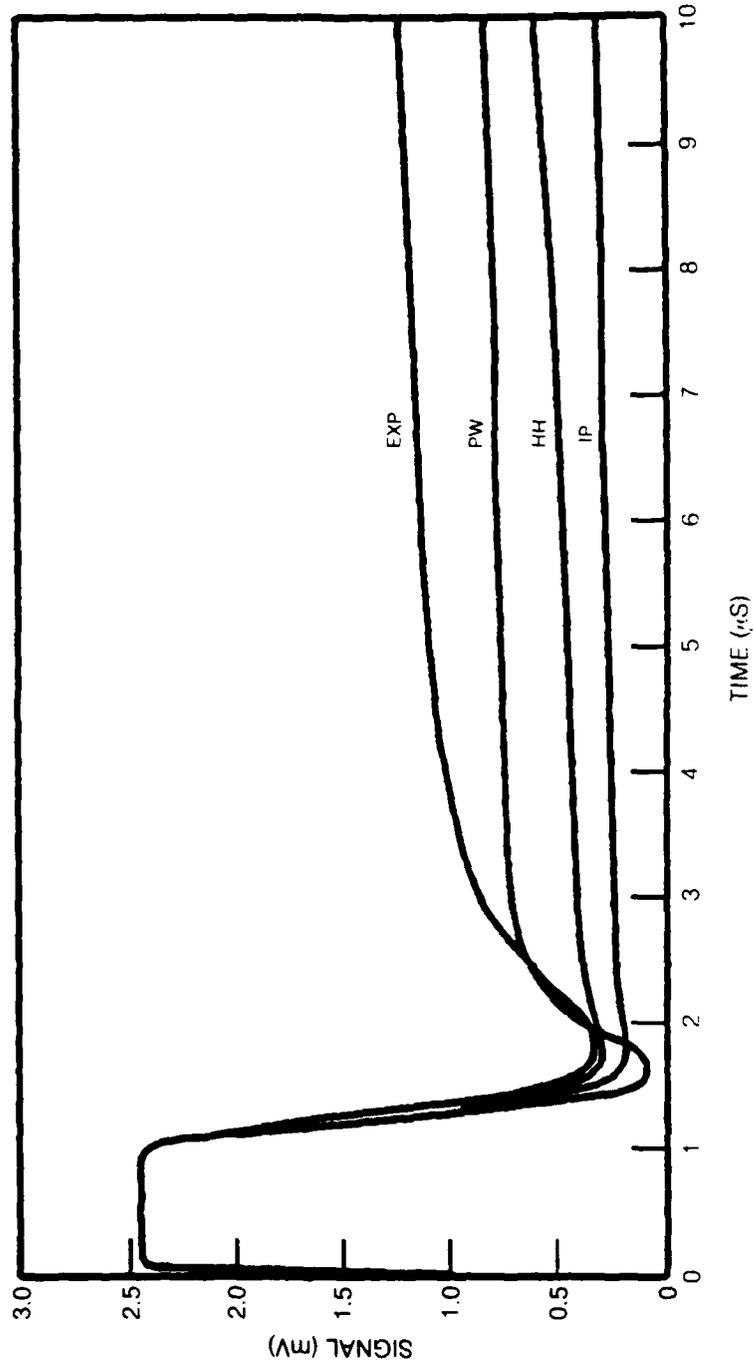
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POPULATION TRANSFER

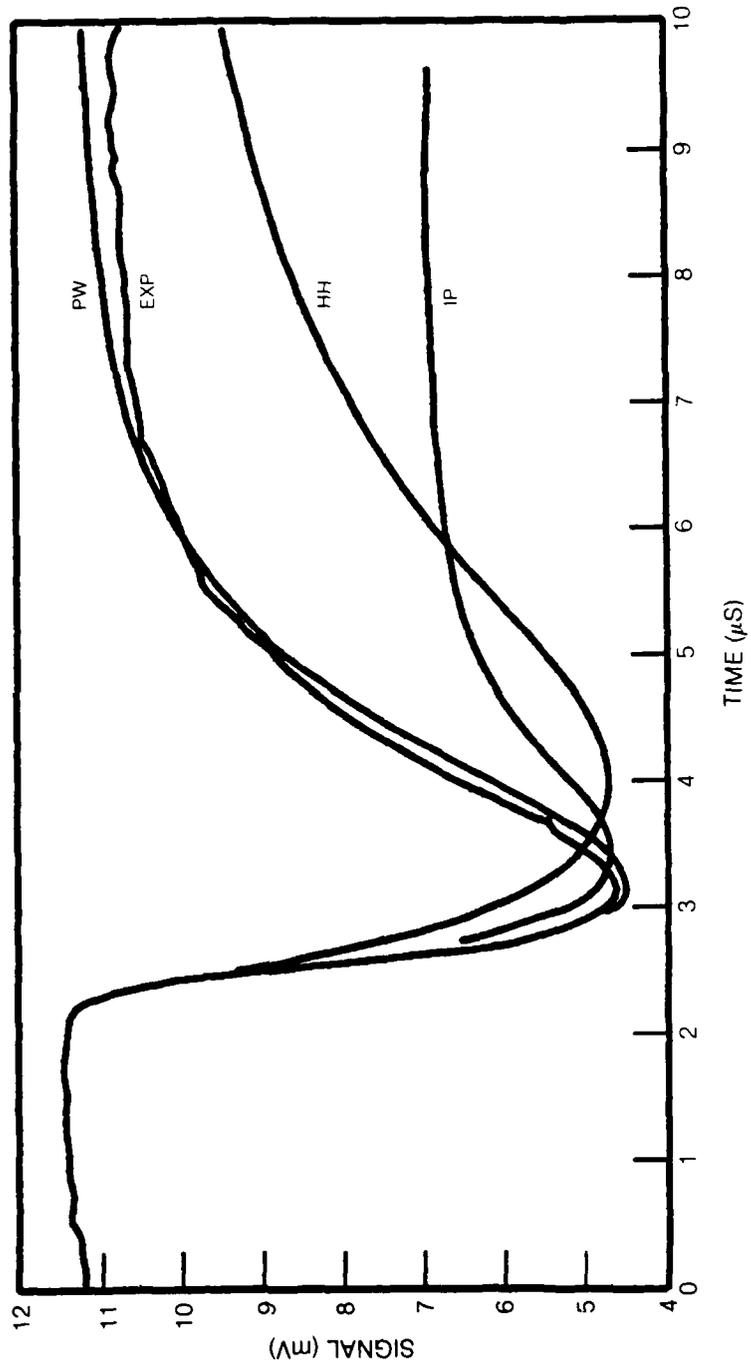
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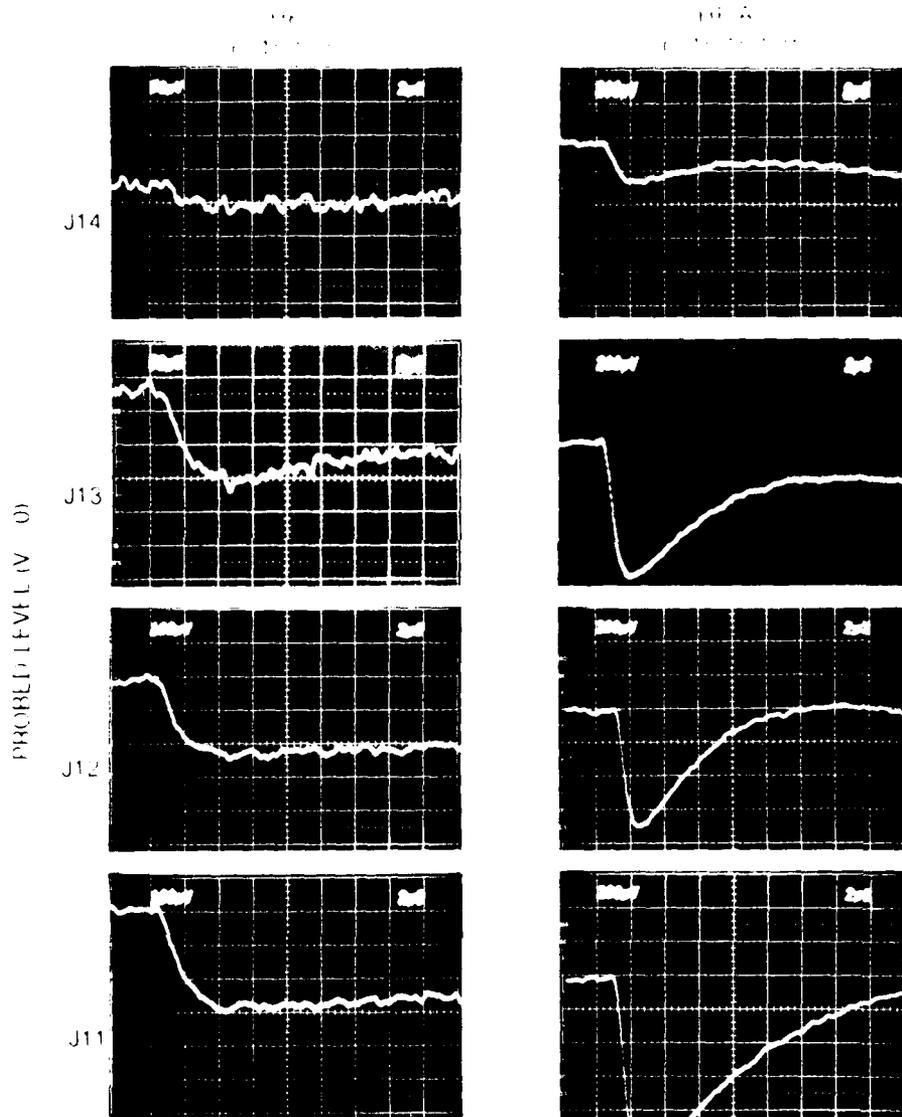


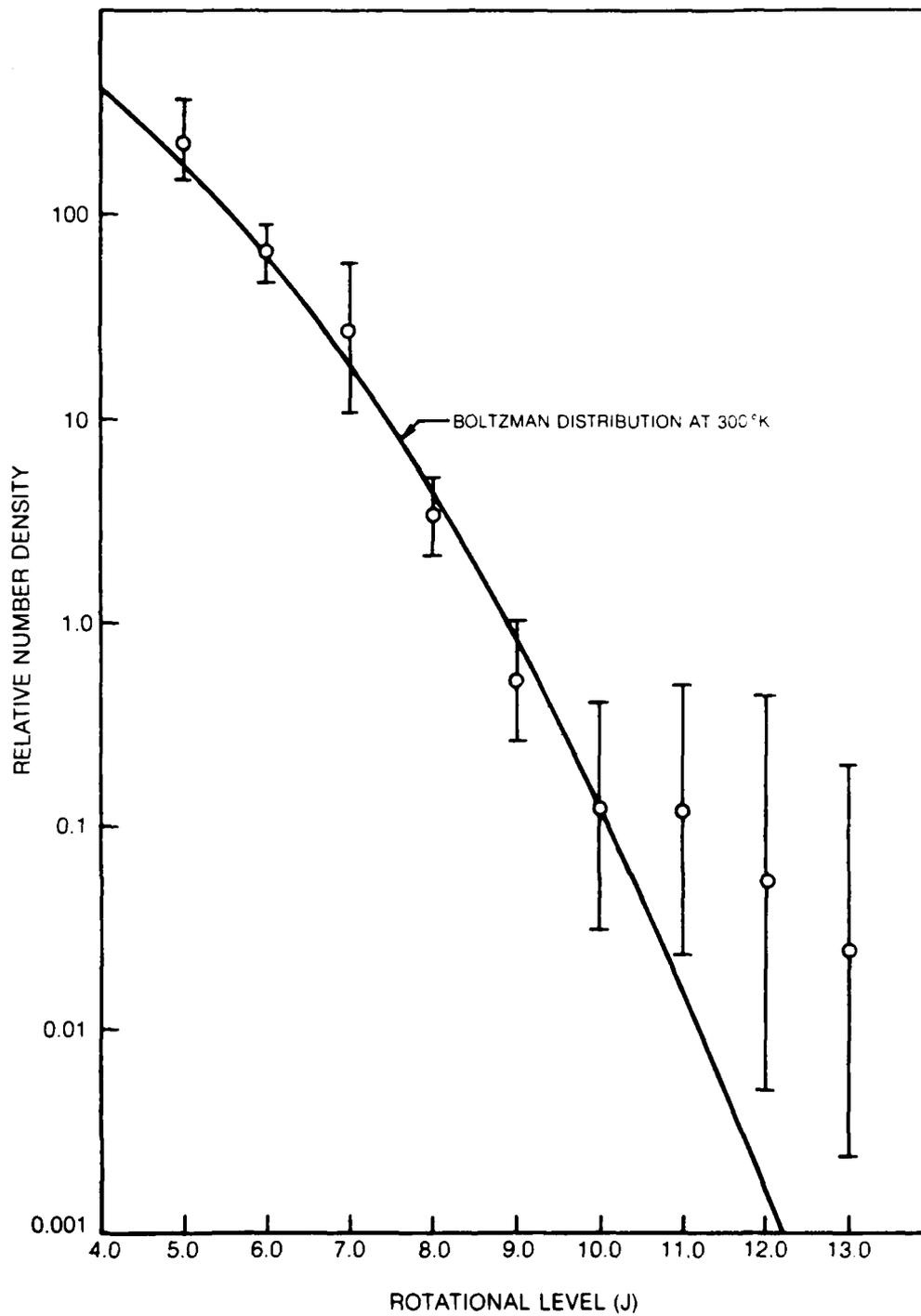
POPULATION TRANSFER

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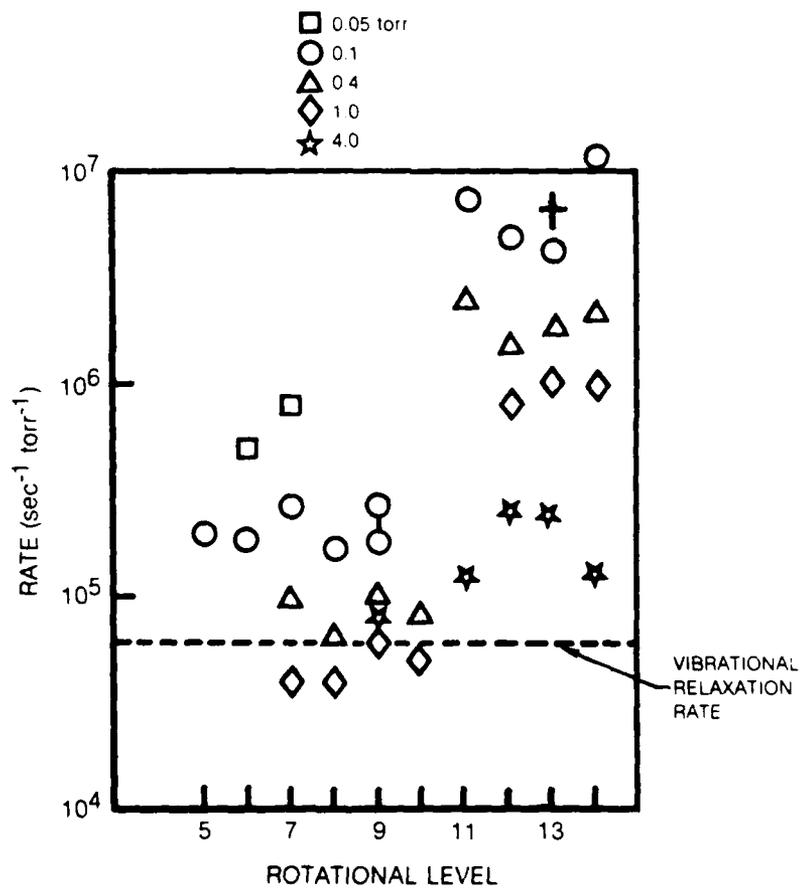


V-R TRANSFER IN HF



HF POPULATION DISTRIBUTION IN $V=0$ AFTER V TO R TRANSFER

RATE OF APPEARANCE OF POPULATION IN LEVEL J



V-R TRANSFER J3 → J13

HF = 0.5 Torr 1/100 RARE GAS

