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The Status of Rotational Nonequilibrium in HF Chemical Lasers

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Because of the complexity of accounting simultaneously for gas dynamics, optics, and chemical kinetics in HF chemical lasers all computer modeling codes have simplified drastically at least one of these factors. One way to simplify the details of state-to-state chemistry is to ignore the possibility of rotational nonequilibrium. Rotational nonequilibrium can affect laser power and energy output, time to onset and duration of lasing, and power spectral distribution.

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In this report, we will review, in turn, evidence for rotational nonequilibrium in HF chemical lasers; processes that can lead to rotational nonequilibrium in HF lasers; rotational relaxation of HF; and modeling studies of rotational nonequilibrium effects in HF chemical lasers.

PREFACE

We are grateful to Profs. L. H. Sentman and R. L. Kerber for reading and commenting on an earlier draft of this report.

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I. INTRODUCTION

The successful scale-up of large HF and DF chemical lasers has depended
on the predictions of several computer model/codes developed by different
Department of Defense (DOD) contractors. With varying degrees of success,
these different codes take into account gas dynamics, optics, and chemical
kinetics to model the chemistry and physics of the lasing medium. Because of
the enormous complexity of accounting in great detail for all three of these
factors, all codes have drastically simplified at least one and sometimes two
or even three of them. Physical and chemical effects that were anticipated to
be of minor importance were brushed aside, even when the justification for so
doing was highly arbitrary. An obvious way to simplify the details of state-
to-state chemistry was to ignore the possible effects of rotational nonequi-
librium by assuming at the outset that the molecules in the lasing medium
never deviated significantly from a Boltzmann distribution over rotational
levels.

Although there have been available for many years a few experimental
results that sharply challenged this assumption, the justification of the
approach was not loudly questioned until a few years ago when two kinds of
results came out of some theoretical calculations: (1) that rotation-to-
rotation (R-R) energy transfer processes might not be significantly faster
than vibration-to-vibration (V-V) processes; and (2) that what had been long
interpreted as simple vibration-to-translation (V-T) energy transfer processes
were now looking like vibration-to-translation-and-rotation (V-T,R) processes,
with the implication that large quantities of internal energy could become
tied up in rotational degrees of freedom.

These tentative conclusions have significant consequences in the under-
standing of the fundamental kinetics of HF/DF laser systems. In addition,
there are important practical implications. Rotational nonequilibrium can
affect laser power and energy output, time to onset and duration of lasing,
and power spectral distribution. Knowledge of the power spectral distribution
is essential in order to predict, and therefore anticipate and correct for,

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mirror distortion, possible mirror damage, and aperture loading. If the rotational disequilibrium is sufficiently pronounced, it can lead to pure rotational lasing, which may cause mirror damage, may degrade the vibrational lasing performance, and may provoke far field medium blooming and/or break-down. Because of these consequences, it is necessary that we acquire the information needed to establish or refute the existence of the nonequilibrium phenomena with certainty.

In this report, we will review, in turn, evidence for rotational non-equilibrium in HF chemical lasers; processes that can lead to rotational nonequilibrium in HF lasers; rotational relaxation of HF; and modeling studies of rotational nonequilibrium effects in HF chemical lasers. The summary discussion will include suggestions for further work.

II. EVIDENCE FOR ROTATIONAL NONEQUILIBRIUM IN HF LASERS

Since 1967 there has been a mounting body of evidence that the rotational
populations within a vibrational manifold in HF produced in a chemical laser
are far from an equilibrium distribution. There are several kinds of experi-
mental data that suggest this conclusion. The most obvious is pure rotational
lasing within a particular vibrational manifold. A second is simultaneous
vibrational lasing on more than one rotational level within the same vibra-
tional band. It has been amply demonstrated in computer simulations that if
there is rotational equilibrium, only one j-state, that with the maximum gain
on the band, will lase at one time. Comparison of lasing intensities from
different vibrational lines can also indicate populations far from equi-
librium, though this argument is somewhat more complex and subject to
qualifications.

The earliest report of pure rotational transitions in HF appeared in
1967, when Deutsch[1] found laser action in HF produced in an electrical
discharge through mixtures of various freons--e.g., CF_4, $CBrF_3$, $CClF_3$, and
CCl_2F_2--with H_2 at total pressures of 0.75 to 5.0 Torr. In the CF_4-H_2 mixture
he observed rotational lasing from $v = 0$, $j = 16$, 18-28; $v = 1$, $j = 12$-14, 18,
21-23; $v = 2$, $j = 13$, 20, 22, 29, 30; $v = 3$, $j = 13$-15, 28; and $v = 4$,
$j = 30$. The source of the rotational nonequilibrium was not discussed, except
for the observation that, in similar studies on HCl lasing, "the fact that two
of the transitions were obtained using only CH_3Cl [without H_2 added] suggests
that dissociation reactions can also be used to produce nonequilibrium rota-
tional distributions."

Three years later, Akitt and Yardley[2] reported pure rotational lasing in
HF, HCl, and HBr produced in pulsed electrical discharges through BF_3, BCl_3,
or BBr_3. No hydrogen-containing compounds had been deliberately added to the
flowing gases. The results of Akitt and Yardley were similar to those of
Deutsch.

In 1972, in a similar experiment, Pummer and Kompa[3] reported vibrational lasing from high j levels in a discharge-initiated HF laser produced in mixtures of SF_6-H_2. Transitions up to $P_1(17)$, $P_2(16)$, and $P_3(9)$ were observed. The dependence of pulse duration and lasing line on total pressure was also studied. These authors concluded that high rotational levels (j > 10) are populated in the initial HF-forming reactions. Subsequent rotational relaxation occurs to a varying extent depending on the total pressure, thus shortening pulses and shifting lasing to higher j states as pressures are increased from 0.8 to 8.5 Torr.

Rotational lasing in a completely different experiment was reported by Skribanowitz et al.,[4] who obtained gain and laser oscillations on rotational transitions of HF(v = 1) when the HF was resonantly pumped with another pulse HF laser. Among other things this study demonstrated that there were other ways besides purely chemical processes to produce rotational lasing.

In 1973 Suchard[5] reported time-resolved spectral distributions in a flash-initiated H_2-F_2-He laser operating at a total pressure of 50 Torr. The time sequencing of the emissions in the $5 \to 4$, $4 \to 3$, and $3 \to 2$ bands was inconsistent with rotational equilibrium. Lasing on the $6 \to 5$, $2 \to 1$, and $1 \to 0$ bands followed the proper j-shifting pattern for rotational equilibrium, but the lines frequently overlapped temporally.

Suchard's results were in sharp contrast with those reported just a few months earlier by Parker and Stephens.[6] Their laser was discharge-initiated, at a total pressure of 120 Torr, with a higher proportion of reactive gases (8.3% each of F_2 and H_2) than in Suchard's experiments (1.2% H_2, 2.4% F_2). The time-resolved emission spectra from their pulse indicate in almost all cases an orderly progression of lasing from increasing j levels, but there is still considerable temporal overlap of the lines. These two experiments illustrate the extent to which the spectral output of the laser can depend on either the mode of initiation or nonchemical properties of the system, such as optics details.

Padrick and Gusinow[7,8] published two papers on the HF laser behavior in flash-initiated $CH_3I-N_2F_4$-Ar mixtures. Like Suchard, they found occasional deviations from the j-shifting patterns expected if rotational states are equilibrated. In their earlier paper,[7] they argued that rotational nonequilibrium was questionable, in view of the fast rate of rotational relaxation, 20 nsec at 50 Torr, based on thermal conductivity measurements of Baker.[9] In the second paper,[8] after more detailed analysis, they concluded that the assumption of a Boltzmann rotational distribution gave calculated results in marked disagreement with the experimental data.

In a series of papers on HF rotational lasers produced in flash-photolytically initiated elimination reactions, Pimentel and coworkers addressed the question of the source of the rotational nonequilibrium. Cueller et al.[10] studied two systems: chemically activated CH_3CF_3 (obtained by flash photolyzing a CH_3I-CF_3I-Ar mixture) and photoexcited CH_2CF_2. They claimed that these were "the first examples of rotational laser emission from elimination reactions and probably the first rotational lasers in which chemical pumping is clearly operative." Rotational lasing from $v = 0$, $j = 12-14$; $v = 1$, $j = 13, 14$; $v = 2$, $j = 14$, and $v = 4$, $j = 15$ was reported in the CH_2CF_2 system. The authors concluded that direct pumping of high j levels was an important process, with vibration-to-rotation (V-R) energy transfer unlikely because of the inefficiency of Ar, the principal constituent of the mixture, at relaxing vibrationally excited HF. (Recent trajectory calculations by Thompson[11] suggest that Ar is not inefficient.)

Three years later, Krogh and Pimentel[12] reported studies on flash photolyzed mixtures of ClF_x-H_2-Ar in which vibrational lasing was observed in very high rotational states, up to $v = 1$, $j = 20$, and $v = 2$, $j = 15$. The emission patterns indicated to them that direct population of the high j states could not explain the data, and that the late threshold times and extended durations indicated an energy transfer mechanism involving V-V and V-R processes. Two years later Cuellar and Pimentel[13] concluded that combined V-V and V-R transfer could not explain the rotational laser emission observed from high J states ($v = 0$, $j = 22-33$; $v = 1$, $j = 23-29$; and $v = 2$, $j = 24-25$) in flash-photolyzed mixtures of $ClF-H_2$-Ar. However, multiquantum V-R transfer was not ruled out by the evidence. Very recently, Sirkin and Pimentel[14,15] studied the effects of added CO, CO_2, H_2, D_2, and HCl on rotational laser

emission in HF produced by flash photolysis of CH_2CHF or CH_2CF_2. They found that CO and CO_2 enhanced the number of transitions and also their gain. The results were interpreted as evidence for V-R multiquantum energy transfer by the added chaperone gases.

In 1975, Greiner[16] reported on an HF laser produced by a discharge through SF_6-HI mixtures. The simultaneous onset of lasing on several j transitions was taken as evidence for rotational nonequilibrium.

Chen et al.[17] reported experiments on a pulsed laser in H_2-F_2-He mixtures at 1.1 atm total pressure. By comparing emissions with and without a poly-ethylene filter inserted in front of their calorimeter detector, they found that approximately 10% of the energy was emitted at wavelengths longer than 15 μm, i.e., on pure rotational transitions. However, no experimental details of this simple observation were given. The efficacy of polyethylene at cut-ting off wavelengths shorter than 15 μm depends on its thickness, which was not reported. In the following year, Rice and Oldenborg[18] reported pure rota-tional HF laser transitions in an exploding-wire system: up to 500 Torr of F_2 in the presence of various metal wires. Although no hydrogen-containing com-pounds were deliberately added to the system, HF emissions from high j states were strong: from v = 1, j = 23, 20-14; v = 2, j = 23, 21, 18-16; v = 3, j = 23, 22; and v = 0, j = 19, 18, 16-13 (the j value is that of the upper state). The combined energy in the rotational transitions was reported to be well over half the total energy in the laser output. Added Ar or Xe reduced the laser energy from the v = 0, j = 16 line but increased that from the v = 1, j = 23 line and caused lasing on the v = 0, j = 22 line.

Similar effects of diluent were observed by Vasil'ev et al.,[19] who added C_5F_{12} to a pulsed, photolytically-initiated H_2-F_2 laser. The diluent increased the delay of the onset of lasing but lengthened the laser pulse, increased its amplitude, and caused some additional lines to appear. The results were interpreted in a very general way in terms of the efficiency of the C_5F_{12} in accelerating rotational but not vibrational relaxation of HF.

Another interesting result was obtained recently by Smith and Robinson,[20] who observed pure rotational laser oscillation in HF following flash photol-ysis of various mixtures of a trifluoromethyl halide, acetylenic species, and

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Ar diluent. A comparison of the spectral distribution with that from photo-
lyzed CH_2CF_2 suggested different mechanisms operating to produce the high j
states of HF in the two different types of experiments: in the CF_2X experi-
ments the laser emission intensities typically peaked around j = 10-12 (i.e.,
a few quantum numbers below the rotational states isoenergetic with the low
rotational states of the next higher vibrational manifold); in the CF_2CH_2
experiments, the peak laser intensities occurred around j = 13-17 (i.e., above
the band heads of the next higher vibrational manifold). Smith and Robinson
concluded that in the trifluoromethyl halide experiments, HF molecules were
pumped up by electronically excited I* or Br* atoms. These conclusions, as
well as the implications of the other experiments summarized in this section,
will be discussed further in Section VI. The results are also summarized in
Table 1.

All of the preceding studies dealt with pulsed HF lasers of various
types. There is also evidence for rotational nonequilibrium in continuous HF
lasers. However, what would be the unequivocal evidence of rotational non-
equilibrium, namely rotational lasing, has never been observed. In 1970, Kwok
at el.,[21] in a study of the spectroscopy of both HF and DF continuous chemical
lasers, noted the simultaneous appearance of laser emission from several
lines. They interpreted this appearance as evidence that rotational popu-
lations within vibrational manifolds were not equilibrated. This observation
was made for HF lines $P_1(4)$ through $P_1(7)$ and $P_2(4)$ through $P_2(7)$.

Three years later, Chodzko et al.[22] examined the zero-power gain in a
similar HF supersonic continuous laser and concluded that "The variation of
zero-power gain with rotational quantum number j fits a simple rotational
equilibrium model..." This conclusion was based on observations of j up to 10
for the 2 → 1 and 1 → 0 vibrational bands. Similarly, Rosen et al,[23] in a
study of subsonic HF chemical lasers produced from several chemical reactions
including F + HI, F + HBr, F + CH_4, F + H_2, and F + HCl, found rotational
equilibrium for j values below 8 for vibrational levels up to 6. And the
following year, 1974, Kwok and colleagues[24] studied the chemiluminescence from
a supersonic HF jet produced by the reaction between H_2 and F atoms (resulting
from arc-heated SF_6). Emissions were observed for the 1 → 0 and 3 → 2 bands
up to j = 9, for the 2 → 1 band up to j = 10, and for the 4 → 3 band up to

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Table 1. Evidence for Rotational Nonequilibrium in HF Lasers

A. PULSED LASERS		
REFERENCES	EXPERIMENT	OBSERVATIONS
DEUTSCH[1]	PULSED ELECTRICAL DISCHARGE THROUGH H_2 WITH CF_4, $CBrF_3$, $CCIF_3$, OR CCl_2F_2 AT 0.75-5.0 Torr	ROTATIONAL LASING FROM $V = 0$ $J = 16$, 18-28 $V = 1$ $J = 12-14$, 18, 21-23 $V = 2$ $J = 13$, 20, 22, 29, 30 $V = 3$ $J = 13-15$ $V = 4$ $J = 30$
AKITT & YARDLEY[2]	PULSED ELECTRICAL DISCHARGE THROUGH 0.05-0.2 Torr OF BF_3, BCl_3, OR BBr_3: NO HYDROGENOUS COMPOUNDS DELIBERATELY ADDED: N_2, He, H_2O ADDED IN SOME EXPTS	ROTATIONAL LASING IN HF FROM $V = 0$ $J = 14$, 15, 20-25 $V = 1$ $J = 15$, 16, 22-24 $V = 2$ $J = 16$, 17 $V = 3$ $J = 17$: He INCREASED OUTPUT
PUMMER & KOMPA[3]	PULSED ELECTRICAL DISCHARGE THROUGH 0.7-60 Torr SF_6 + 0.1 - 2.5 Torr H_2: He ADDED IN SOME EXPTS: H_2 REPLACED WITH RH	VIBRATIONAL LASING OBSERVED ON $V = 1$ $J = 3-17$ $V = 2$ $J = 3-16$ $V = 3$ $J = 2-9$
PARKER & STEPHENS[6]	FLASH-INITIATED H_2-F_2- He at 120 Torr	TEMPORAL OVERLAP OF VIBRATIONAL LASING FROM SEVERAL J LEVELS

Table 1. Evidence for Rotational Nonequilibrium in HF Lasers (continued)

	A. PULSED LASERS (Cont'd)	
SUCHARD[5]	FLASH-INITIATED $H_2 - F_2 -$ He AT 50 Torr	VIBRATIONAL LASING ON 6 VIBRATIONAL BANDS; TIME SEQUENCING ON 3 OF THEM IMPLIES ROTATIONAL NONEQUILIBRIUM
PADRICK & GUSINOW[7, 8]	FLASH-INITIATED $CH_3I - N_2F_4 -$ Ar AT 50 Torr	VIBRATIONAL LASING; TIME SEQUENCING SUGGESTS ROTATIONAL NONEQUILIBRIUM
CUELLAR, PARKER, AND PIMENTEL[10]	FLASH PHOTOLYSIS OF $CH_3I - CF_3I -$ Ar AT 50 Torr; AND $CH_2CF_2 -$ Ar AT 62 Torr	ROTATIONAL LASING ON HF FROM CH_2CF_2 ON $V = 0$, $J = 12-14$ $V = 1$, $J = 13, 14$ $V = 2$, $J = 14$ $V = 4$, $J = 15$
KROGH & PIMENTEL[12]	FLASH PHOTOLYSIS OF $CIF_x - H_2 -$ Ar AT 20-80 Torr	VIBRATIONAL LASING ON HF ON $V = 1$ UP TO $J = 20$ $V = 2$ UP TO $J = 15$
CUELLAR & PIMENTEL[13]	FLASH PHOTOLYSIS OF $CIF - H_2 -$ Ar AT ~60 Torr	ROTATIONAL LASING ON $V = 0$, $J = 22-33$ $V = 1$, $J = 23-29$ $V = 2$, $J = 24, 25$
SIRKIN & PIMENTEL[14, 15]	FLASH PHOTOLYSIS OF CH_2CHF OR CHFCHF, ADDED CO, CO_2, H_2, D_2, OR HCl	CO, CO_2 ENHANCED ROTATIONAL LASING

Table 1. Evidence for Rotational Nonequilibrium in HF Lasers (continued)

A. PULSED LASERS (Cont'd)		
GREINER[16]	ELECTRICAL DISCHARGE THROUGH SF_6-H_2 AT 60-100 Torr	VIBRATIONAL LASING ON 6 VIBRATIONAL BANDS; TIME SEQUENCING IMPLIES ROTATIONAL NONEQUILIBRIUM
CHEN, TAYLOR, WILSON, LEWIS, AND FYFE[17]	FLASH PHOTOLYSIS OF F_2-H_2-He AT 1.1 ATM	10% OF ENERGY OUTPUT AT $\lambda \cdot 15\mu$
RICE & OLDENBORG[18]	EXPLODING WIRE IN 500 Torr F_2 (no H compounds added); Ar OR Xe ADDED IN SOME EXPERIMENTS	PURE ROTATIONAL LASING (50% total emission) ON HF ON $V = 0$, $J = 12$-15, 17, 18 $V = 1$, $J = 13$-19, 22 $V = 2$, $J = 15$-17, 20, 22 $V = 3$, $J = 21$, 22
VASIL'EV, GUR'EV, AND TALROZE[19]	FLASH PHOTOLYSIS OF H_2-F_2-C_5H_{12}	C_2F_5 DELAYED ONSET OF LASING LENGTHENED PULSE, INCREASED OUTPUT

Table 1. Evidence for Rotational Nonequilibrium in HF Lasers (continued)

B. CONTINUOUS LASERS		
KWOK, GIEDT, AND GROSS[21]	SUPERSONIC, ARC-DRIVEN LASER ON F (from SF_6) + H_2	SIMULTANEOUS EMISSIONS ON SEVERAL LINES IN $1 \rightarrow 0$ AND $2 \rightarrow 1$ BANDS
CHODZKO, SPENCER, AND MIRELS[22]	SUPERSONIC DIFFUSION LASER ON F (from SF_6) + H_2	VARIATION OF ZERO-POWER GAIN WITH J, FOR $2 \rightarrow 1$ AND $1 \rightarrow 0$ BANDS, $J \leq 10$ IMPLIES ROTATIONAL EQUILIBRIUM
ROSEN, SILEO, AND COOL[23]	SUBSONIC TRANSVERSE-FLOW LASER ON F + HX, F + H_2, F + CH_4 (F from F_2).	V, J STATE POPULATIONS FOR 6 VIBRATIONAL BANDS, $J \leq 10$, IMPLY ROT EQUILIBRIUM FOR $J \leq 7$
KWOK, SPENCER, AND GROSS[24]	SUPERSONIC, ARC-DRIVEN LASER ON F (from SF_6) + H_2	SPONTANEOUS EMISSION OF $1 \rightarrow 0$ (J 9), $2 \rightarrow 1$ (J 10), $3 \rightarrow 2$ (J 9), AND $4 \rightarrow 3$ (J 5) CONSISTENT WITH ROT EQUILIBRIUM
KWOK, GIEDT, AND VARWIG[25]	SUPERSONIC, ARC-DRIVEN LASER ON F (from SF_6) + H_2	EMISSIONS FROM $3 \rightarrow 0$ BAND (J 5) OBSERVED WITH AND WITHOUT LASING OCCURRING

Table 1. Evidence for Rotational Nonequilibrium in HF Lasers (continued)

B. CONTINUOUS LASERS (Cont'd)

| KEPLER, EDWARD, SADOWSKI, ROBACK, MEINZER, AND BRONFIN[27] | SUPERSONIC, ARC-DRIVEN LASER ON F_2 + H_2 | EMISSIONS FROM 2 → 1 BAND (J ≤ 10) IMPLY 2 DISTINCT TEMPERATURE REGIONS |
| CUMMINGS, BROADWELL, SHACKLEFORD, WITTE, TROST, EMANUEL[28] | SUPERSONIC, ARC-DRIVEN LASER ON F_2 + H_2 | EMISSIONS FROM 6 VIBRATIONAL BANDS IMPLY ROT EQUILIBRIUM FOR J ≤ 8 AT 320K; J > 12 EMISSIONS IMPLY T ≈ 2000 K |

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j = 5. The intensities were all consistent with a single rotational temperature, thus indicating rotational equilibrium. (The data presented for the 4 → 3 band could perhaps be interpreted also as indicating a slightly higher rotational temperature, but still reasonably complete equilibration within the vibrational manifold.)

In a later paper, Kwok and coworkers[25] reported further studies on the emissions from an arc-driven supersonic HF jet, both with and without lasing taking place. Emissions from the lowest five rotational lines of the 3 → 0 vibrational transition were monitored. Rotational temperatures were reported for both the power-on and power-off runs; temperatures for the latter were consistently approximately 100 K higher than those for the former. Although not explicitly stated in the paper, there was some noticeable deviation from rotational population equilibrium. More important, however, was an approximate analysis that revealed that spatial variations in translational temperature across the jets could look like variations in rotation temperature and could even be interpreted as deviations from rotational equilibrium. This type of analysis was carried out in greater detail by Emanuel,[26] who concluded that "Non-uniformities [in temperature and concentration] are analytically shown to generate data with the appearance of excess, non-Boltzmann rotational populations in high j rotational states."

All the preceding results on continuous HF lasers come from experiments in which only the "cold" pumping reaction, that between F and H_2, is operating. Emission intensity measurements in HF chain reaction lasers, in which both the "cold" and the "hot" (H + F_2) pumping reactions are occurring, have yielded stronger evidence for rotational nonequilibrium within a vibrational manifold. Kepler et al.,[27] at United Aircraft Research Laboratories, demonstrated that emission data on the 2 → 1 vibrational band indicated unmistakable nonlinearity on a log I versus j (j + 1) plot. The data could be fitted by a double exponential curve, suggesting a temperature of 200 K for the low j levels (0 through 3) and a temperature of 1360 K for higher levels (5 through 10). The authors concluded that these results indicated that "two distinct temperature regions are present in the flow field rather than a smooth distribution of temperatures" (page 162 in their report). Cummings et

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al.[28] at TRW obtained similar results on a HF chain laser for emissions from $v = 1$ through $v = 6$: low rotational levels ($j < 8$) appeared to be equilibrated at 320 K, but high level emissions ($12 < j < 16$) were indicative of a "temperature" of approximately 2000 K. Because "this non-Boltzmann rotational distribution is not observed in $F + H_2$ cold reaction tests," they concluded that "[i]t can be attributed to redistribution of vibrational energy from the upper levels into high rotational states, via V-R processes, and the relatively slow rate of rotational relaxation of high-j states" (page 108 in their report).

The discussion of experimental results in this section does not include an exhaustive study of the literature; however, it does provide a good idea of the data that have been presented in the literature and the arguments and conclusions that have followed from the data. In summary, in both pulsed and continuous HF lasers, there is evidence suggesting that rotational states are not equilibrated in the strictest sense of the term. At least in the case of continuous lasers in which gasdynamic effects come into play, there are other possible factors that can account, in part, for the observations. It is instructive to turn to the various computer modeling studies that have been or can be undertaken. Before reviewing these studies, it is necessary to review two other important issues. The first is the question of what processes, if any, can be responsible for producing rotational nonequilibrium in an HF chemical laser medium; the second is under what conditions relaxation processes will fail to restore rotational equilibrium sufficiently rapidly in a laser medium to prevent undesired side effects.

III.   PROCESSES THAT CAN PRODUCE ROTATIONAL NONEQUILIBRIUM IN HF LAS

In principle, every exothermic molecular process that occurs in HF chemical lasers can lead to rotational nonequilibrium. These processes can be grouped as follows.

    a.   <u>Chemical production of HF(v,j)</u>. This includes not only the simple atom abstraction reactions, such as $F + H_2$, $H + F_2$, $H + ClF$, etc.; it also includes the photoinduced elimination reactions from, for example, CH_2CHF or CH_2CF_2, and atom recombination of $H + F + M$.

    b.   <u>Collisional energy transfer processes involving HF(v,j)</u>. This includes V-V, V-R, R-R, rotational-to-translational (R-T), electronic-to-rotational (E-R) vibrational transfer, and all their inverse processes.

    c.   <u>Radiative processes</u>. This includes processes such as spontaneous and stimulated emission and absorption.

Some of these processes have been studied specifically, and the evidence is reviewed subsequently.

A.   CHEMICAL PROCESSES

It may seem straightforward to determine the nascent rotational populations of HF produced in a chemical reaction. However, in practice it is very difficult to ensure that an experiment is not affected by secondary processes that occur before the HF populations can be observed. Polanyi and his coworkers[29-35] have published several experimental studies of energy distribution among reaction products of both the $F + H_2$ and $H + F_2$ reactions (and their deuterated analogs, not discussed here). The results demonstrate convincingly that the nascent HF product distribution is far from equilibrated (Fig. 1). For $F + H_2$, Polanyi and Woodall[31] observed all rotational states up to $j = 13$, 14, and 6 for $v = 1$, 2, and 3, respectively. The maximum j levels possible based on average available energy of the reaction [activation energy + exothermicity + average (translational + rotational) energy of reagents] were 20, 14, and 6, respectively. Actually, slightly higher levels are energetically possible if one takes into account the greater (translational + rotational) energies of the molecules in the tail of the Boltzmann distribution: e.g., 1% of the reagents have energies more than 2.7 kcal/mole above the average, and 0.1% have energies more than 3.9 kcal/mole above the average.

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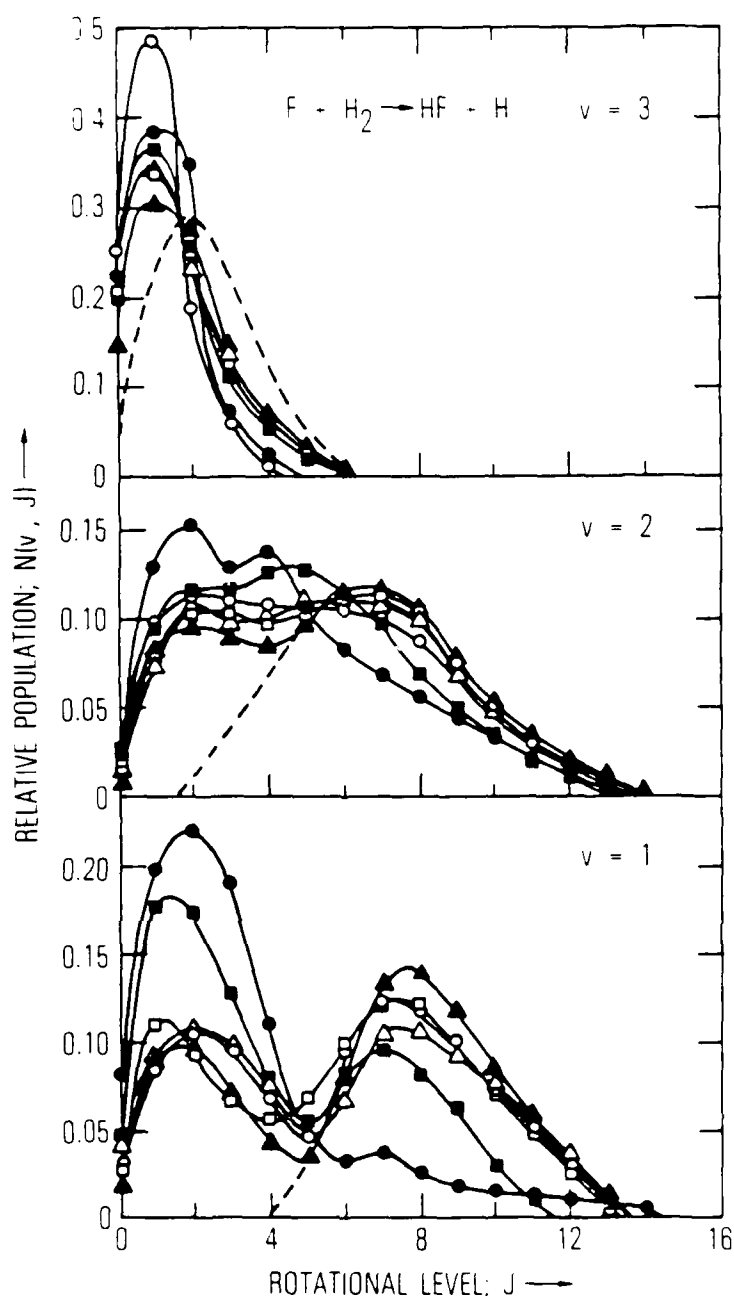
Fig. 1. Experimental Rotational Distributions for HF at 300 K for
F + H$_2$ → HF(v,j) + H obtained by Polanyi and Woodall.[31]
Solid lines connect symbols designating six different experimental conditions. Dashed lines indicate the truncation made to obtain shape of the initial rotational distributions for
v = 1 and 2, and an approximate initial distribution computed for v = 3. The distributions are normalized so that the sum of rotational populations for each vibrational level equals unity. The plots illustrate the sensitivity of the results to experimental conditions, the extent of rotational relaxation that has evidently taken place before the observations were made, and consequently the extent of extrapolation backwards in time required to infer nascent product distributions.

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Similarly, Polanyi, Sloan, and coworkers[32-35] found nonequilibrium product states for the H + F_2 reaction: the initial population distribution produces significant quantities of HF up to j = 8, 10, 12, 14, 13, 9, and possibly 7 for v = 1 through 8, respectively. However, in both cases, the observed emissions were not from the nascent product molecules; they had to be corrected for some rotational relaxation, the exact extent of which is subject to some argument. Theoretical three-dimensional trajectory calculations by Wilkins[36] for the F + H_2 reaction also indicate a rotational product distribution far from equilibrated, though the detailed rate coefficients differ considerably from those inferred by Polanyi and Woodall and reveal much more rotational structure (Fig. 2). Such results are not confined to the simple triatomic reactions of F + H_2 and H + F_2.

Sung and Setser[37] measured product HF formation in the reactions of F atoms with HI, HBr, H_2S, H_2CO, SiH_4, and GeH_4 and invariably observed rotational nonequilibrium. Furthermore, they reported emission measurements for two sets of experimental conditions: one for the "arrested relaxation" method, which presumably sees HF emissions before any relaxation has taken place; the other for a flowing afterglow at 1 Torr Ar pressure, in which 4000 HF-Ar collisions occurred on the average before the excited HF was observed. In the arrested relaxation experiments HF was formed in rotational levels up to 23-26 for v = 1,2,3 in a rather flat distribution. In the second experimental arrangement, the low j levels (j < 5 or 6) had attained approximate Boltzmann equilibrium, intermediate j levels were practically absent, and high j levels were still far from equilibrated. These results were interpreted to mean that rotational relaxation is fast enough among the low j levels to restore equilibrium but is not fast enough among the high j levels.

We have found no information on the rotational product distribution of HF formed in a photoelimination reaction, such as from CH_3CF_3. However, recently there has been published a study of a closely related experiment, namely the laser-induced dissociation of CH_3CF_2Cl to produce HCl. Sondag and Wegdam[38] have studied the rotational distribution of the HCl and found the product molecules to be highly rotationally excited, in states j = 13-18, peaking sharply between j = 14 and 16. One could reasonably expect similar results

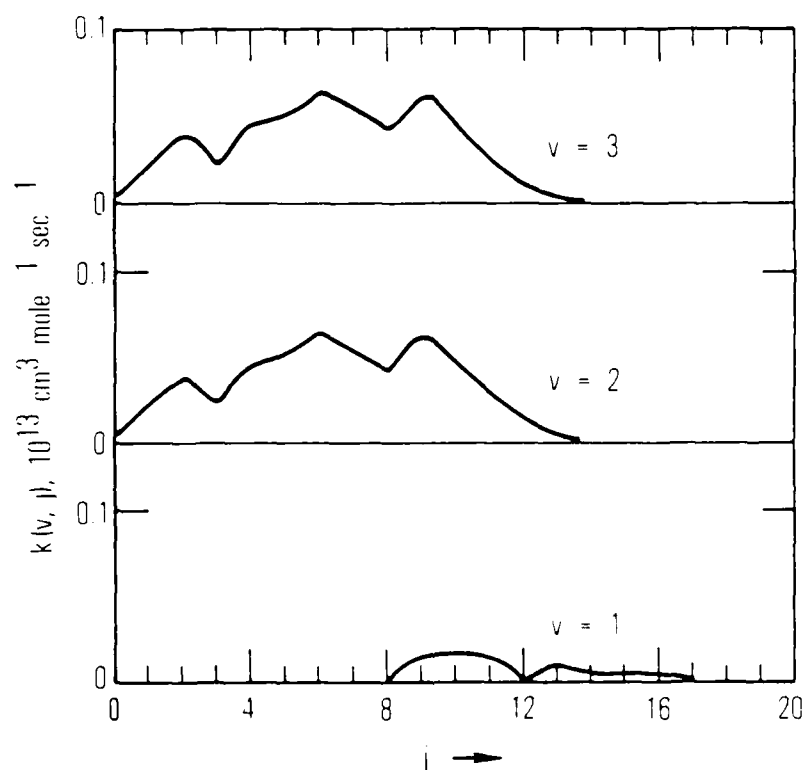Fig. 2. Rotational Distributions for HF at 300 K
for the F + H_2 Reaction Calculated from
Monte Carlo Trajectories by Wilkins.[36]

for any photoelimination process in which the diatomic species eliminated consisted of a heavy and a light atom, because the light atom would probably leave the parent molecule with a proportionately higher escape velocity than the heavy atom, thus resulting in considerable rotation. The laser used by Sondag and Wegdam was a continuous CO_2 laser, which has been shown to produce results similar to those of thermal dissociation. On the other hand, dissociation initiated by flash photolysis is quite a different process, and one could expect even more severe rotational disequilibrium. Thus, the photoelimination initiation step in the experiments of Sirkin and Pimentel could well be a contributory factor to any subsequent rotational nonequilibrium and hence to rotational lasing.

There is no experimental information on the rotational distribution of diatomic molecules formed by three-body atom combination. However, it is easy to show that under the conditions of real laser systems for the time durations of interest, there is negligible three-body combination into any states. This will be true unless pressures exceed 1-10 atm.

B. COLLISIONAL ENERGY TRANSFER PROCESSES

Among the energy transfer processes that can lead to rotational nonequilibrium, V-R is currently believed to be the most important. This is a situation where theoreticians predicted a phenomenon before there was clear experimental evidence for it. In the early 1960s, Cottrell and Matheson,[39] in trying to correlate vibrational relaxation probabilities with molecular properties, observed that some deuterated species have lower relaxation probabilities than their hydrogenated isotopic counterparts. The authors suggested that because the rotational velocity of the H atom is larger than the translational velocity and closer to the average vibrational velocity, the transfer of vibrational to rotational energy should proceed with greater probability than transfer to translational energy. This behavior would account for the slower relaxation of the deuterated species even though they have smaller vibrational energy spacings. In 1965, Moore[40] used this argument as the basis for developing a theory of V-R energy transfer.

In 1971, Chen and Moore[41] concluded that their experimental data on vibrational relaxation in HCl and DCl could best be explained by assuming that the vibrational energy was transferred to rotational energy of the initially vibrationally excited molecule, with little or no energy transferred to the collision partner. At the same time, Shin[42] developed his own theory of V-R energy transfer, which he applied to HCl, DCl, HI, and HBr--the only hydrogen halides for which experimental data were then available--with good results. Bott and Cohen[43] applied Shin's theory to their shock tube measurements of HF vibrational relaxation and found they could not get agreement unless they added a strongly attractive term to the intermolecular potential. They found that 3.5 kcal/mole, approximately half the strength of the hydrogen bond in HF-HF interactions, caused the low temperature rate coefficients to increase inversely with temperature, resulting in good agreement with the room-temperature measurements of Airey and Fried.[44] It later appeared that the agreement may have been fortuitous. None of these studies grasped the implications of V-R energy transfer for the production of high rotational states in HF lasers.

The connection was realized by Wilkins[45] in his extensive series of three-dimensional classical trajectory calculations for HF-HF energy transfer processes. Wilkins found that the most probable states produced in the process $HF(v_1) + HF(v_2 = 0) \rightarrow HF(v_1', j_1') + HF(v_2)$ are $v_1' = v_1-1$, $j_1' = 14$; $v_1' = v_1-2$, $j_1' = 20$, $v_1' = v_1-3$, $j_1' = 24$, etc. A recent surprisal analysis by Wilkins also predicts a similar product state behavior (Fig. 3). An examination of an HF energy level diagram (Fig. 4) indicates that these most probable product states are those in closest resonance with the reacting state. What will happen to these high rotational states once they are formed by this V-R energy transfer process? Although the product rotational states are nearly isoergic with the reactant vibrational states, the reverse rotation-to-vibration (R-V) transfer rate coefficients will be 5 to 10 times slower than the forward rate coefficients because the statistical weights vary as $(2j + 1)$. The much faster R-R/translation energy transfer will cascade the HF molecules down the rotational energy ladder until rotational equilibrium is established.

Wilkins also found that the rate of R-T transfer at high j levels, e.g., j = 15, is about one fifth as probable as R-T transfer at very low j levels. His initial trajectory calculations indicated energy transfer probabilities of
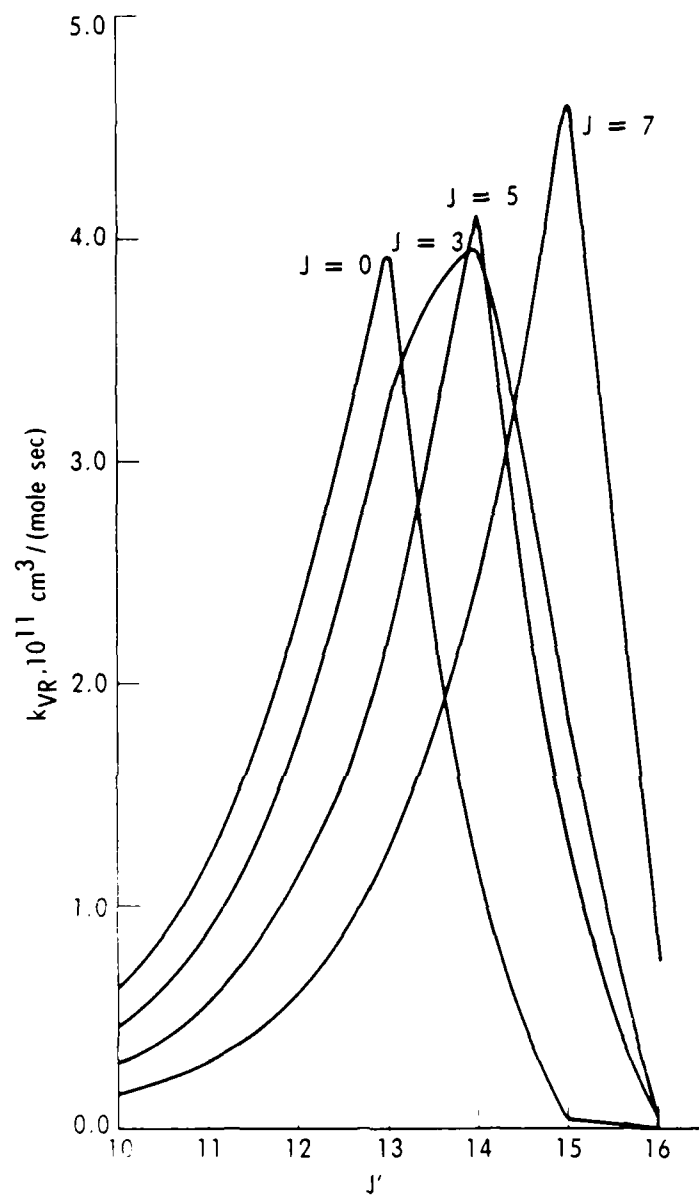
28

Fig. 3. Theoretical State-to-State V-R Energy Transfer
Rate Coefficients for $HF(v = 1, j_1) + HF(v = 0, j_2) \rightarrow HF(v = 0, j_{1'}) + HF(v = 0, j_2)$ at 300 K.
Calculated by Wilkins by Surprisal Analysis (to
be published; private communication).

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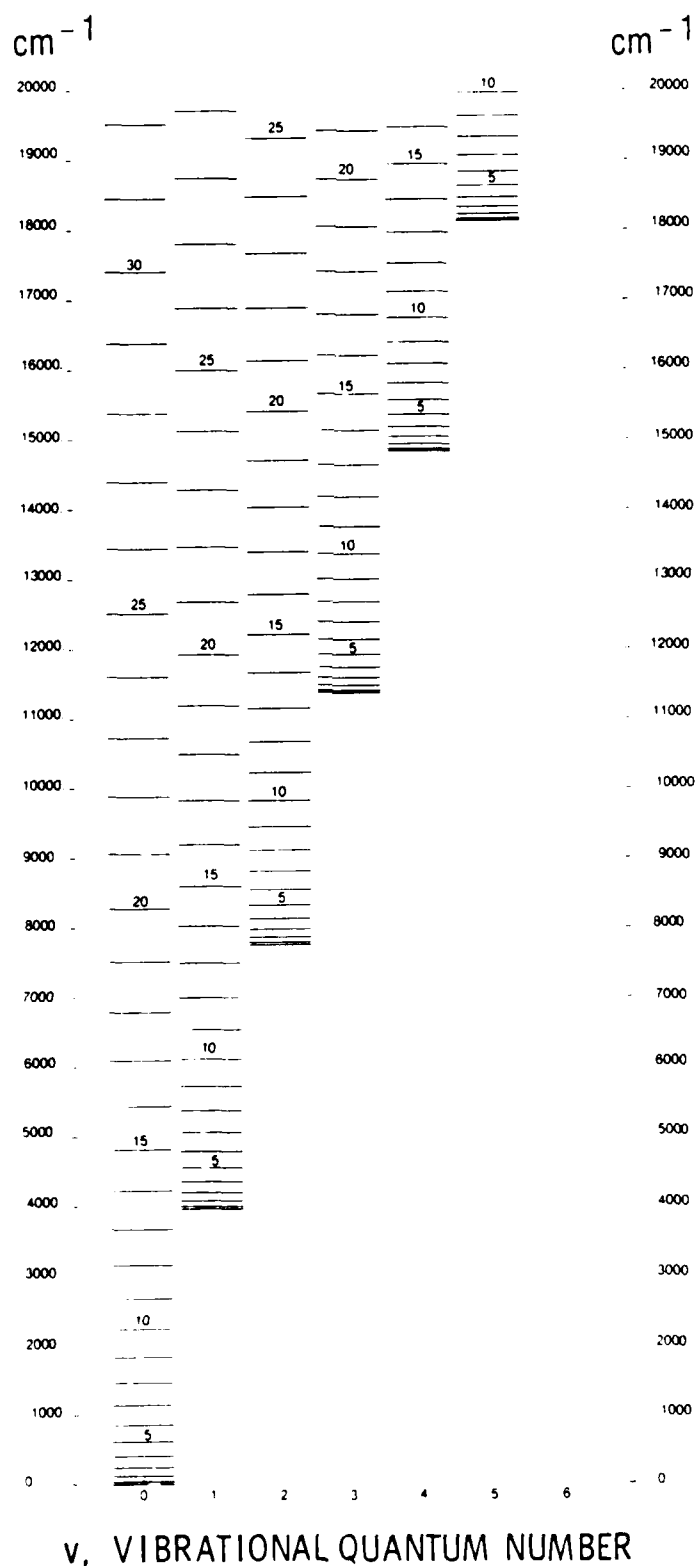
Fig. 4.   HF Energy Level Diagram.

approximately 0.025 for low j, decreasing to 0.005 for j = 15, but he later computed values that were much faster. According to the more recent results, the energy transfer probabilities are on the order of unity for $\Delta j = 1$ transitions in the exothermic direction, decreasing slightly with increasing j, and decrease on the order of a factor of 2 for each increase of 1 in Δj. In any case, the calculations indicate that the process down the rotational ladder will accelerate slightly with each successive step, so that the higher rotational states will be out of equilibrium the longest.

In a follow-on study that was perhaps even more significant, Wilkins and Kwok[46] assembled a detailed state-to-state model for the vibrational relaxation of HF(v = 1) in an HF bath. They did this in an attempt to duplicate the experimental results, which indicate conclusively that the HF-HF vibrational relaxation rate coefficient passes through a minimum at about T = 1000 K (Pτ goes through a maximum at about 1300 K) and increases monotonically as T either increases or decreases from the minimum point. Wilkins and Kwok were able to match this temperature behavior although none of the individual state-to-state rate coefficients exhibited a turnover at any temperature (Fig. 5). The temperature dependence of the vibrational relaxation measurements can be explained as a result of the mathematical formalisms assumed and the manner in which the rate coefficients varied with the j level of the collision partner. It does not necessarily imply a strong attractive HF-HF intermolecular potential that increases the probability of collision (and hence, energy transfer) at low temperatures. When these conclusions became apparent there was some concern that previous experimental measurements of vibrational energy transfer, all of which had been interpreted under the assumption of rotational equilibrium, would have to be reanalyzed with a detailed state-to-state reaction model. Since then, qualitative calculations suggest that the results of vibrational relaxation studies are valid as originally interpreted; however, it must be recalled that caution must be exercised if these rate coefficients are applied to lasing systems, in which the HF is far from rotationally equilibrated. (In a more recent model, the temperature dependence of the experimental vibrational relaxation results primarily from a similar dependence in each of the state-to-state rate coefficients, all of which are nearly identical.[*]

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[*]R. L. Wilkins, private communication.
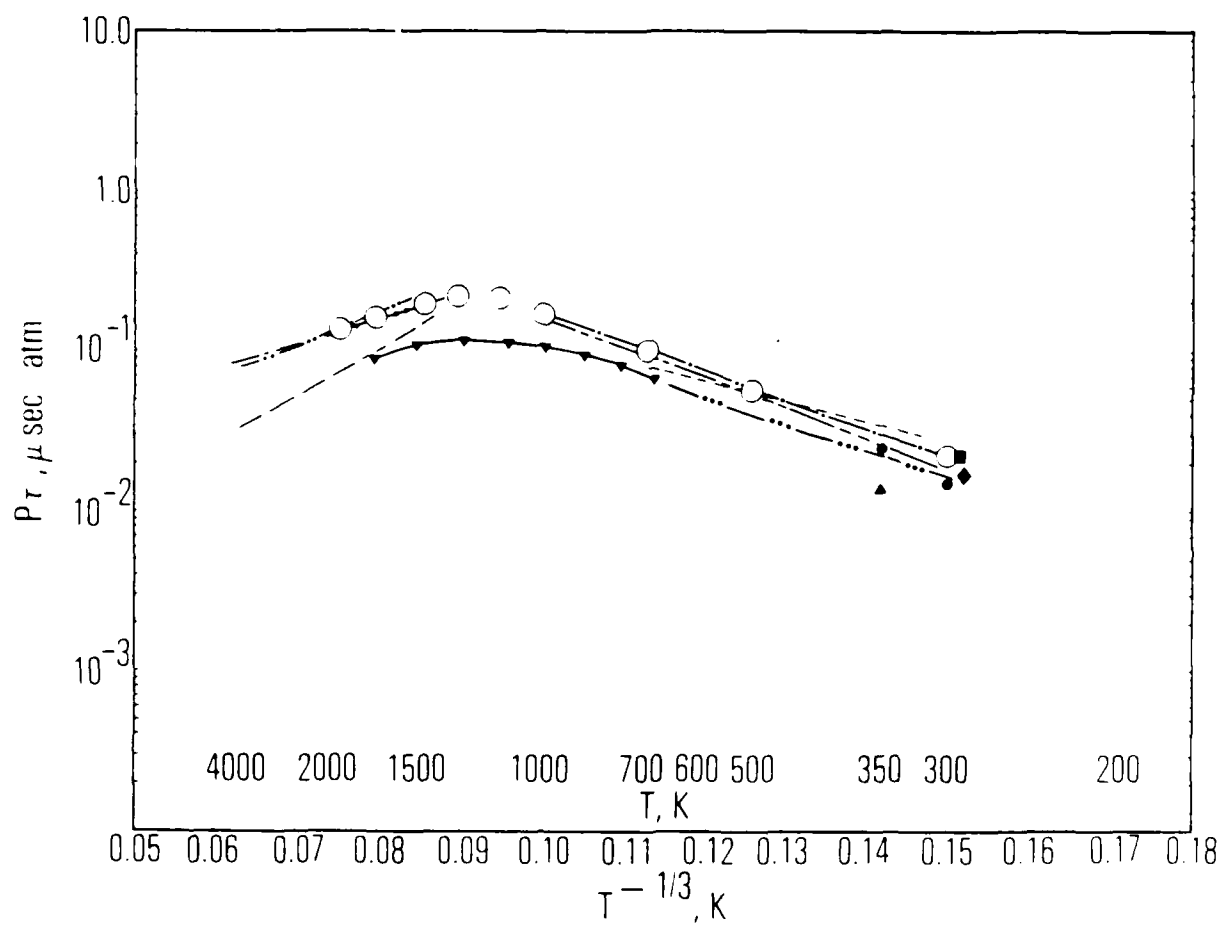
Fig. 5. Pτ Versus $T^{-1/3}$ for HF(v = 1) Vibrational Relaxation. Open circles are calculations of Wilkins and Kwok.[46] Other symbols represent various experimental determinations.

In terms of the subject of this section of this report, however, the implications of Wilkins' and Kwok's study are clear: V-R relaxation may provide an important process resulting in rotational population distribution far out of equilibrium in an HF laser.

The study by Wilkins also provides a tentative answer to the question of whether V-V energy transfer produces rotational disequilibrium. His results indicate that in a V-V process there is also a change in j levels appropriate for minimizing the energy that must go into translation. However, for typical cases studied involving HF in the first six vibrational levels, the energy available to convert to rotational modes would be less than 800 cm^{-1}, which indicates a change of, at most, $\Delta j = 6$ in one molecule if the other were held at fixed j. These processes start typically from rotational equilibrium, which means only low j levels populated at ordinary temperatures. Thus the product j states will not be very high and will therefore relax rapidly back to rotational equilibrium. On the other hand, if such processes occur in a system already far from equilibrium, then that disequilibrium will be preserved in spite of any V-V processes.

There has not yet been any direct experimental confirmation of Wilkins' V-R mechanism, but the theory has been successful in explaining many experimental results in lasers as well as in nonlasing systems. Some of these successes are discussed in Section V. Note that Sirkin and Pimentel,[15] in work discussed in the preceding section on photoelimination HF lasers, concluded that their results provided strong confirmation of the proposal that high rotational states are produced by multiquantum V-R transfer such as was predicted by Wilkins.

On the other hand, Douglas and Moore[47] interpreted their experimental data as indicating that fast transfer from vibrational to high rotational states is not an important process in the deactivation of HF($v = 3,4$). In their experiment HF is pumped directly from $v = 0$ to $v = 4$. Populations of $v = 3$ and $v = 4$ are monitored by observing $\Delta v = 3$ overtone fluorescence. They

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found that $95 \pm 15\%$ of the HF that leaves $v = 4$ appears in $v = 3$ with $j < 5$; therefore, "there cannot be a large population in the high rotational states of $v = 3$" (page 488 in the paper). Douglas and Moore were comparing their observations with the earlier calculations of Wilkins,[45] which as has already been noted, predicted much slower R-T rates than he subsequently calculated. The observations are not incompatible with assuming formation of high j states in the $v = 3$ level that cascade rapidly into the range observed by the photomultiplier. Wilkins and Kwok have in fact found that they can explain the data with their V-R model, provided that they reduce somewhat their previous estimates of the multiquantum rate of V-R transfer.*

In most of the other categories of energy transfer there is little information on processes that can result in rotational nonequilibrium in HF. However, there was one study by Smith and Robinson,[20] referred to earlier, in which it was concluded that electronically excited I* or Br* atoms could transfer energy to HF and produce rotational disequilibrium. It has been independently established that these atomic species can participate in electronic-to-vibrational (E-V) energy transfer with HF;[48,49] whether rotational disequilibrium is also produced has not been verified conclusively.

One recent study[50] on the production of rotationally hot CO by collisions of CO with hot H atoms produced by photodissociation of HBr does suggest that similar processes could occur in HF laser systems resulting in rotationally hot HF via hot H atoms.

C. RADIATIVE PROCESSES

Unless lasing is taking place, radiative processes, i.e., absorption and spontaneous emission, are not generally fast enough to compete with collisional processes in HF systems to produce rotational disequilibrium. However, when there is lasing, the rotational populations are driven down rapidly, as demonstrated by the comparison of the lasing and nonlasing experiments by Kwok et al.[25]

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*R. L. Wilkins, private communication, 1982.

The possibility of producing rotational inversion by optical pumping was demonstrated separately by Skribanowitz et al.[4] and also by Hinchen and Hobbs.[51] In both cases a cell with HF was pumped with an external HF vibrational laser, and rotational lasing which was evidence for rotational population inversions was produced from the states being pumped [e.g., pumping with the $P_1(3)$ line produced lasing or superradiance on the $j = 2 \rightarrow j = 1$ transition of $v = 1$.]

There are, then, at least two collisional mechanisms that can result in rotational disequilibrium in HF systems whether or not lasing is occurring: the initial chemical production step, which demonstrably produces high rotational j states; and the V-R energy transfer processes, which arguably do so as well. The former occurs in all current large-scale HF laser devices; the latter, if it takes place at all, will occur in any HF-containing system. Is there more convincing proof of the contribution of V-R processes to rotational nonequilibrium? Perhaps the most compelling evidence is the CH_2CF_2 photolysis experiments of Sirkin and Pimentel[14,15] and of Smith and Robinson,[20] in which the strongest emissions in the HF rotational laser produced by photoelimination are those originating from $j = 13$, 14, and 15 for $v = 1$ through $v = 4$. These are just the rotational levels that Wilkins predicts will be produced with highest probability in a V-R transfer process.

On the other hand, vibrational relaxation studies of Douglas and Moore,[47] as well as similar experiments of Crim and his colleagues[52-56] (discussed in Section IV), have been satisfactorily interpreted without requiring any involvement of high j states (though emissions from such states were never sought specifically). Evidence that is suggested by laser modeling will be discussed in Section V. First, we will review the experimental and theoretical information concerning the rotational relaxation of HF.

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IV. ROTATIONAL RELAXATION IN HF

As indicated in the preceding section, the evidence for the production of rotational disequilibrium in the HF laser systems is compelling, although the exact contributions of different mechanisms to that disequilibrium are still not known. The next question of concern is, what happens to the rotationally excited HF after it is formed? How rapidly does equilibration take place?

In the early days of chemical laser modeling for HF systems, the possibility of rotational disequilibrium was ignored. There were two reasons for this. First, there was no experimental information on the rate of rotational relaxation in HF. Data on other molecules invariably indicated that rotational relaxation occurred in a few collisions, except in the case of H_2 and its isotopes. Second, it was inconceivable at the time that one could model a laser and keep track of individual rotational levels, because of the enormous computational bookkeeping required.

· If we discount an early derivation of a rotational relaxation rate based on thermal conductivity measurements (relaxation probability per collision was inferred to be approximately 0.1 at 374 K),[9] the first direct determination was reported in 1974. Peterson et al.[57] used a pulsed HF laser operating on a single $P_1(j)$ transition (j = 5 or 6) to deplete the (v = 0, j = 5, 6) levels of HF at 373 K and monitored the filling of the level with the tail of the same laser pulse, attenuated with a Pockels cell. They obtained self-relaxation rates for the $P_1(5)$ and $P_1(6)$ transitions of 78 and 49 μsec^{-1} $Torr^{-1}$, respectively, which was about an order of magnitude faster than gas-kinetic rates calculated from a hard sphere collision model using viscosity diameter measurements. The authors interpreted their results as measuring the repopulation of the bleached state by rotational energy transfer within the v = 0 manifold. However, this repopulation process can involve several neighboring j states; the reported relaxation rate is at best the sum of these many rotational processes, and possibly also the inverse of the pumping process.

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Hinchen and Hobbs[51,58-60] performed similar experiments but used two separate lasers (the double resonance technique): a pulsed laser for pumping and a continuous laser for resonance absorption detection. This technique permitted them to probe several different lines for each pumped line. In most experiments, they pumped with a single $P_1(j)$ line where j varied between 2 and 5, and probed on a $P_2(j')$ line, where j' was one or more levels removed from j (within the same v = 1 manifold). The time-dependent absorption of the probe laser line was interpreted as measuring the rate of population transfer from the pumped j line to the probed j' line. Their results were similar to those of Peterson et al. Phenomenological rate constants for transfer from j to j + 1 were on the order of 5 to 10 times faster than gas kinetic at the lowest j's. For transfer from j to j + Δj, the rate constants decreased with increasing Δj, down to approximately gas kinetic for Δj = 5.

Recognizing that several processes can contribute to populating the (v = 1, j') line, the authors developed a model in which each level population was determined by a sum of processes involving several rate coefficients. A computer simulation was carried out to determine the best values of the state-to-state coefficients that would predict the observed phenomenological rates. The experimental study by Hinchen and Hobbs cannot be regarded as yielding state-to-state rate coefficients because the interpretation of the data is highly model dependent. The model assumed that relevant collision processes were those of the form $HF(v = 1, j_1) + HF(v = 0, j_2) = HF(v = 1, j_1') + HF(v = 0, j_2')$. This formalism includes both R $\rightarrow$ R ($j_2 \neq j_2'$) and R $\rightarrow$ T ($j_2 = j_2'$) processes.

Sentman[61] succeeded in deducing, from Hinchen's first set of data, a general expression for state-to-state rate coefficients using a relationship proposed by Polanyi and Woodall.[62] In this relationship, the probability of energy transfer $P_{jj'} = C_1 exp(-C_2 \Delta E/kT)$, where C_1 and C_2 are constants independent of vibrational level v and $\Delta E = E_j - E_{j'}$, where j and j' are, respectively, the initial and final j quantum numbers. Sentman found C_1 = 2.45 and C_2 = 0.359, consistent with Polanyi and Woodall's values found for relaxation of rotationally excited HCl.

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Sentman's approach seemed reasonable at the time that his study was published. However, in the intervening years, ideas about this energy transfer have changed somewhat. In particular, it has been shown that energy transfer probabilities that scale as an inverse power of ΔE rather than as an exponential function (see subsequent discussion) represent experimental data more accurately, particularly at high values of j'. It has also been shown that in HF-HF collisions the azimuthal quantum number m_j is conserved in a collision. Furthermore, the "constant" C_2 is actually a (weak) function of the translational energy, which means that it will vary if the temperature is varied over a wide range. Some of these difficulties are manifested in the fact that the Polanyi-Woodall expression for $P_{jj'}$, with Sentman's deduced values for C_1 and C_2, exceeds unity for $\Delta E/kT < 2.5$, an inequality that holds for many processes in the HF-HF system.

More recently, Wilkins and Kwok[63] have reinterpreted the experimental data by taking these notions into account and by using a detailed model that permits all the state-to-state processes with $\Delta j < 5$; they found good agreement between experimental data and modeling if sufficient number of coupled levels and sufficient arrays of Δj are considered. The results of some of their calculations are shown in Fig. 6. The figure demonstrates that the calculated buildup curve for HF(v = 1, j = 4), is very dependent on the details of the model used and on the number of levels in the model. Conversely, it indicates that the experimental results cannot be used to extract detailed state-to-state information unless most of the state-to-state rates are already very well known. The block of values for $(P\tau)^{-1}$ shows in detail how the synthesized phenomenological $(P\tau)^{-1}$ (the last column) increases with model complexity, and also how it exceeds any of the individual $(P\tau)^{-1}$ values, because in essence it represents several parallel pathways for relaxation to occur.

Vasil'ev et al.[64] published studies of chemiluminescence from excited HF produced in an F + H_2 + M flowtube, where M was He or Xe. Pressures and flow rates were regulated so that emissions could be observed after a specified number of collisions, ranging from a few to approximately 50. It was found that (1) equilibrium had not been attained within the maximum number of

HF ROTATIONAL RELAXATION
3, 5, 7 LEVEL MODELS

7-LEVEL MODEL
5-LEVEL MODEL
3-LEVEL MODEL

1.0
0.8
0.6
0.4
0.2
0

$\Delta I/I_0$

0   1   2   3   4   5

t, μ sec

3-LEVELS
5-LEVELS
7 LEVELS
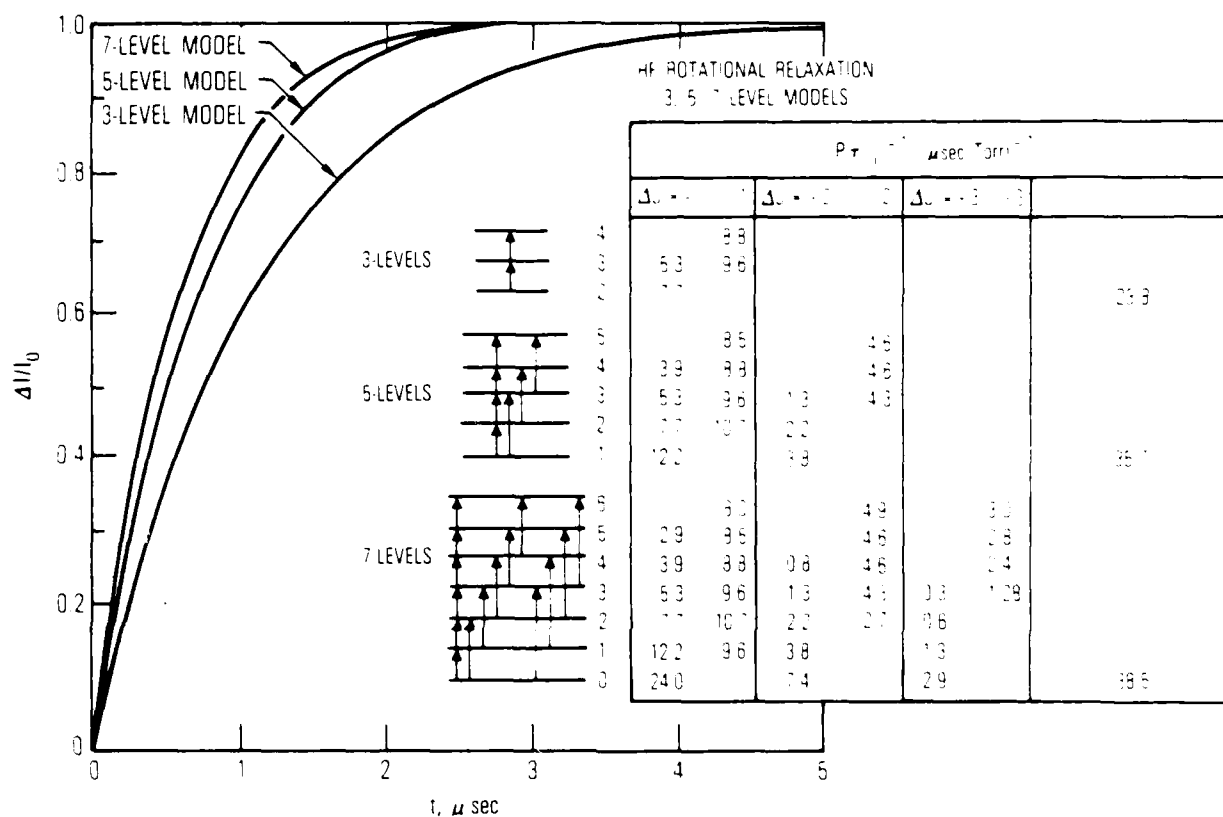
Fig. 6.   Comparison of R-T Relaxation Rate Calculated with Models of
Varying Complexity. The experiment being modeled is that of
Ref. 59, in which HF is pumped by an external HF laser oper-
ating on the $P_1(3)$ line, and the $P_2(4)$ line is probed. The
exponential growth of emission measures the rate of population
of HF($v = 1$, $j = 4$) when HF($v = 1$, $j = 3$) is the only rota-
tional level in the $v = 1$ manifold that initially is
populated. The three curves represent calculations with three
rotational levels ($j = 2,3,4$), five rotational levels
($j = 1...5$), and seven levels ($j = 0...6$) (courtesy Wilkins and
Kwok; to be published).

collisions; (2) more than 100 collisions were necessary to deactivate HF in high (j > 7) rotational states; and (3) H_2 or D_2 rotationally relax HF about an order of magnitude faster than He or Xe. In a later study from the same laboratory, Vasil'ev et al.[65] produced HF emission in shock-heated mixtures of F_2 and H_2. In the temperature regime of 1500 to 2000 K, they found rotational and vibrational relaxation times to be roughly comparable, and deduced that rotational disequilibrium for j = 12 persists for approximately 300 HF-HF collisions and 10^4 HF-Ar collisions. Again, both of these experimental observations reflect the results of concurrent complicated chemistry and energy transfer processes and cannot be used directly to make assertions about the state-to-state processes.

Perhaps the experiments that come closest to measuring state-to-state processes are those of Polanyi and coworkers,[66-68] who used a continuous HF laser to pump selected states of HF that constituted about 1 to 5% of an HF-Ar flow at a total pressure of approximately 0.6 mTorr. Unfortunately for the purposes of this review, only relative HF-Ar rates were reported. Nevertheless, the results are a useful guide to R-T energy transfer in HF with, hopefully, any chaperone. In the first of their reports,[66] it was found that the data could be fitted (but not without some anomalies) to a simple exponential model, $k_{jj'} \propto \exp(-C|\Delta E_{jj'}|)$, where $\Delta E_{jj'}$ is the energy gap between the initial j level and the final j' level (Fig. 7). The constant C was found to be almost invariant with a change in T of 300 to 500 K. The generality of this equation implies that (1) R-T transfer rates decrease with increasing j level, (2) they decrease with the magnitude of energy transferred to translation, and (3) from a given j level, downward transitions are favored over upward ones.

In later work, Barnes et al.[67,68] extended these studies to Ne and Kr chaperones and found the relative rates of energy transfer to be independent of the identity of the collision partner. However, they found that, with sufficient data at hand, the previously proposed exponential gap rule tended to underestimate cross sections for large transfers of energy. The authors correlated their new results more successfully with an expression proposed by Brunner et al.[69] for other systems: $k_{jj'} \propto f(j) (T_f/T_i)^{0.5} |\Delta E_{jj'}|^{-\gamma}$, where T_i

Fig. 7. Experimental R-T Rotational Relaxation Data for HF + Ar with
Initial Relative Translational Energy of 9 kcal/mole, Assuming
Angular Momentum Statistics Appropriate for m_j Randomization. A
linear plot would confirm exponential-gap behavior. Filled
symbols represent downward transitions (j > j'); open symbols,
upward transitions; triangles: j = 1; squares: j = 2;
circles: j = 3; inverted triangles: j = 4; diamonds: j = 5
(from Ref. 68).

and T_f are initial and final relative translational energies (Figs. 8 and 9). The single parameter γ was found to be independent of initial j, T_i, and collision partner, but was dependent on the direction of energy transfer (1.1 for R $\rightarrow$ T, 1.3 for T $\rightarrow$ R). This suggests failure of microscopic reversibility unless there is some peculiar nonrandom distribution over initial m_j (azimuthal quantum number) states. In the above equation, $f(j) = 2j' + 1$ for m_j randomization (Fig. 8); for m_j conserved, $f(j) = (2j + 1)/(2j_< + 1)$ where $j_<$ is the smaller of j and j' (Fig. 9).

The significant conclusion to be drawn from these figures is that we do not know with certainty what the correct empirical correlation of rotational relaxation rate coefficients is although some sort of power law dependence seems useful; hence, extrapolations to conditions that represent unmeasured processes must be done with considerable uncertainty.

Lambert et al.[52] obtained an approximate measure of rotational relaxation by using a flashlamp-pumped dye laser to pump HF into the v = 4, j = 0...5 level and then by watching the buildup of Δv = 3 overtone fluorescence from the v = 4, j = 1,2 levels. They interpreted the delay in reaching fluorescence intensity maxima as representing the time required for the HF to relax from the pumped level into the emitting state, which is a measure of the time for rotational relaxation within the v = 4 manifold. When j = 5 is pumped, the peak comes 1.4 μsec later than it does when j = 2 is pumped. Because τ_{coll} is approximately 3.3 μsec at 0.06 Torr, the authors concluded that relaxation takes approximately one half the collision time. However, the result should be verified by detailed modeling of the experiment, taking into account all the pathways available to the HF. (In a later paper, Jursich and Crim[55] quote the result as implying relaxation in about a third of the gas kinetic collision time.)

In a later study from the same laboratory, Copeland et al.[53] used a NdYAG dye laser to pump HF into v = 2, j, and an HF pulsed laser to probe various $P_2(j')$ lines, where j' > j. They used the rise times of the absorption on the probed lines as measures of the phenomenological relaxation rates rather than trying to deduce state-to-state rate coefficients by assuming some model.

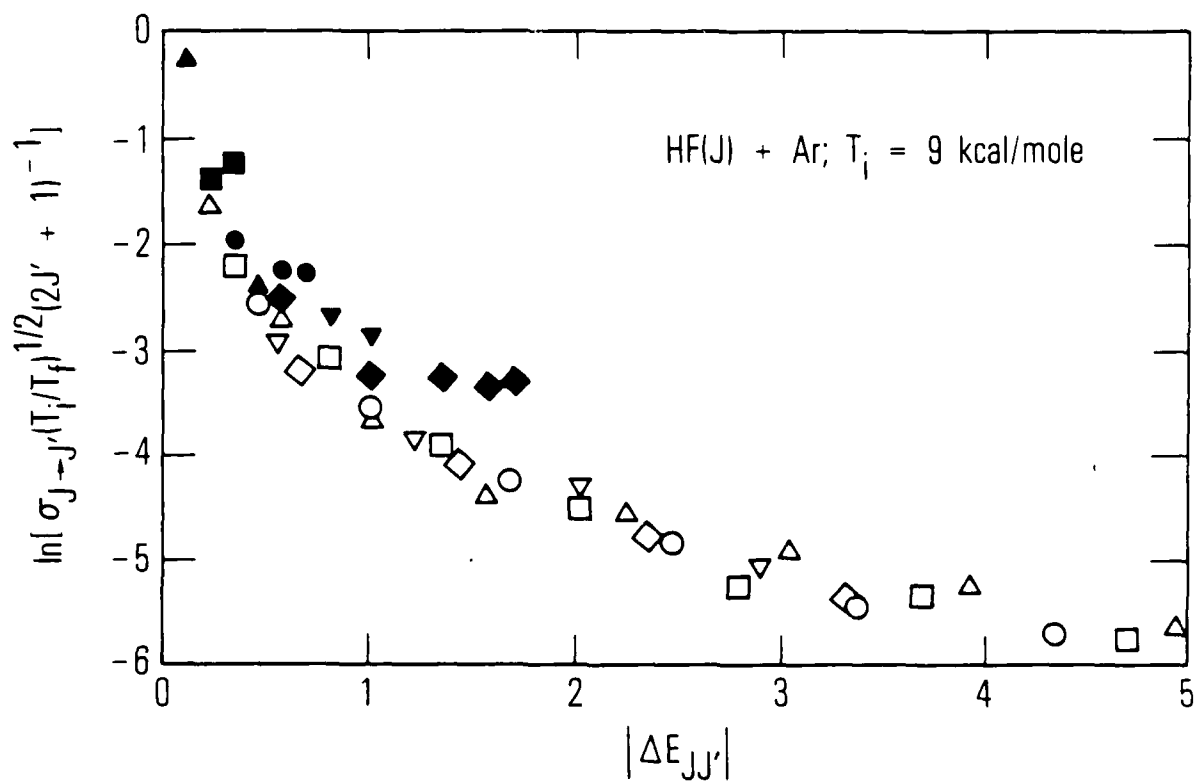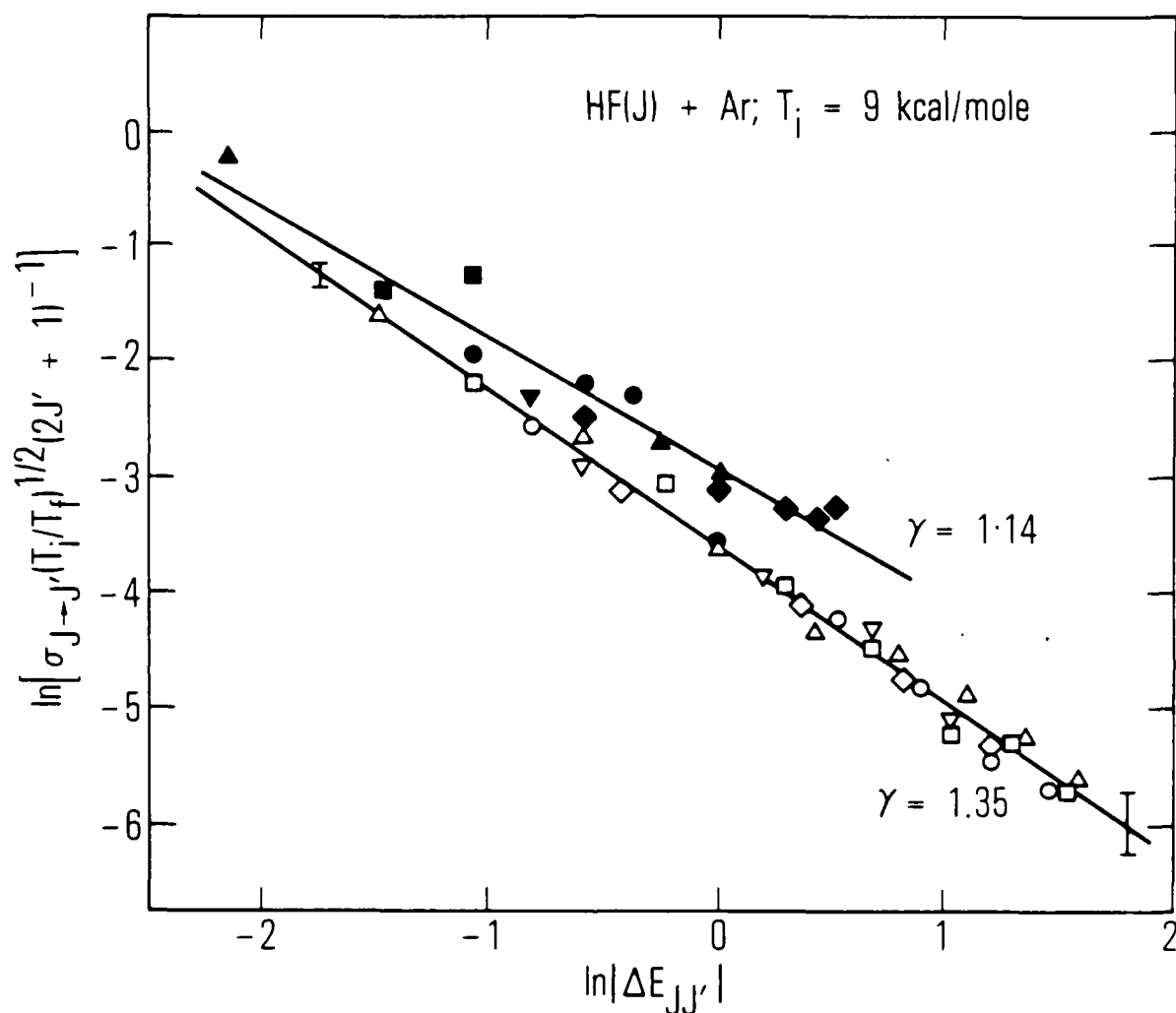Fig. 8.   Log-Log Plot of Experimental R-T Relaxation Data for HF + Ar for
          Initial Relative Energy of 9 kcal/mole, Assuming Angular Momentum
          Statistics Appropriate for m_j Randomization. The linear plot
          confirms power gap behavior. The best-fit lines were obtained by
          treating upward and downward transitions as separate sets of
          data, resulting in the separately labeled values of the
          parameter γ. Other symbols as in Fig. 7 (from Ref. 68).
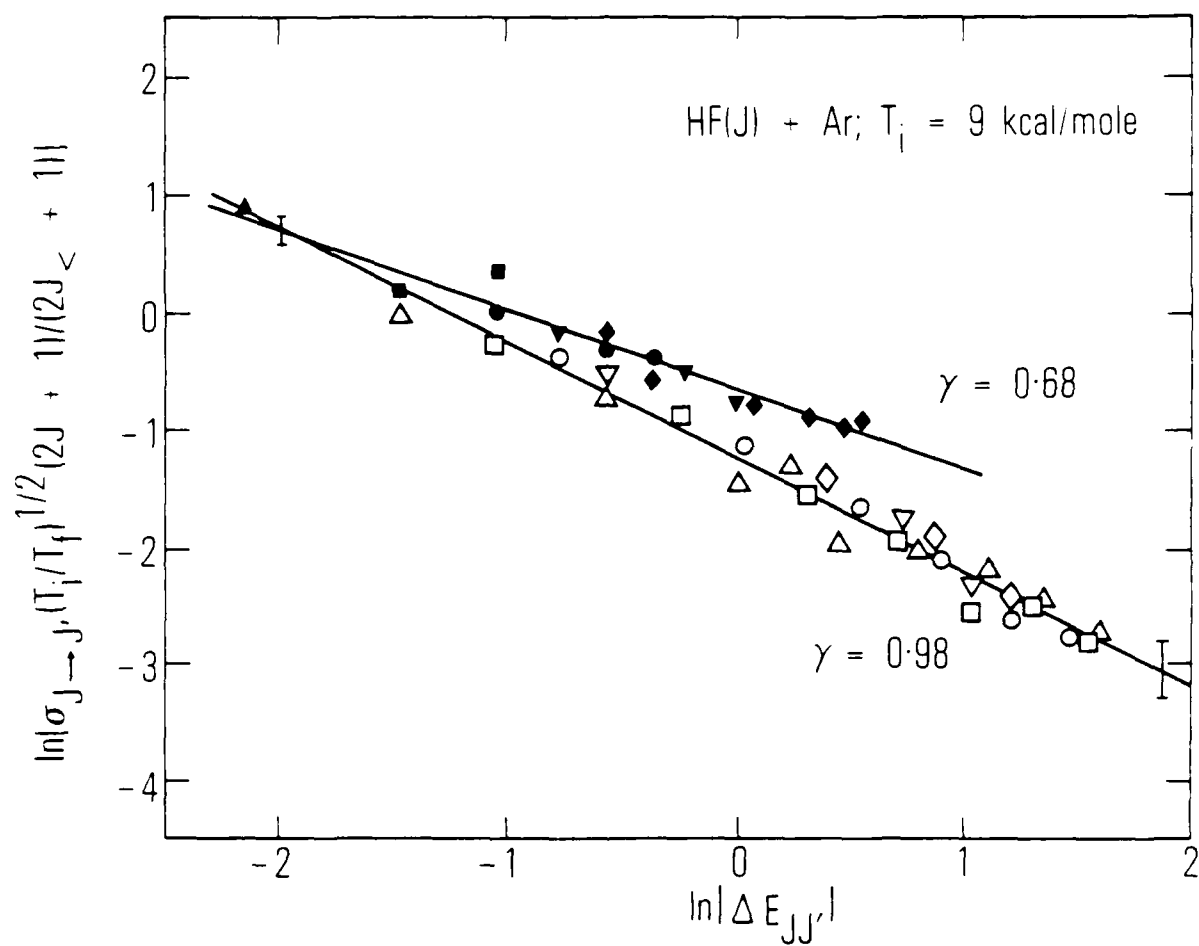
Fig. 9. Same Plot as Fig. 8, but Assuming Angular Momentum Statistics
Appropriate for m_j Conservation (from Ref. 68).

Their results, when plotted as rate constant versus energy defect for the j - j' transition, all fell (within experimental scatter) on the same curve. The results of Hinchen and Hobbs,[59] similarly plotted, fell on a curve lying slightly above the date of Reference 53 (Fig. 10). The only difference between the two sets of data should be that those of Reference 53 are for v = 2 although those from Reference 59 are for v = 1. Recent work by Barnes et al.[67] for the rotational relaxation of HF in Ar under conditions where only single collisions can occur indicate that the vibrational level of the HF does not measurably affect the relaxation rate. It would be surprising if the HF-HF rotational relaxation rates are V-dependent while those for HF-Ar are not; it would be useful to repeat the studies of References 53 and 59 in the same facility to see if the different results are indeed genuine.

There have been numerous theoretical approaches to rotational relaxation and energy transfer; only two, which have been recently applied specifically to the case of HF, will be mentioned here.

BelBruno et al.[70] have applied the energy-corrected sudden scaling (ECS) theory, assuming an exponential gap model for the state-specific rate coefficients. The ECS scaling theory provides an approximate method for calculating the scattering matrix and state-to-state cross sections for inelastic, non-reactive collision processes under conditions when the collision time is sufficiently short. The theory provides a method for inverting HF-HF and HF-Ar pressure broadened spectral linewidths to obtain R-R and R-T rate coefficients. In their paper, they report both detailed state-to-state cross sections and also "total relaxation rates," i.e.,

$$k_{j \to j'} = \sum_{j_2, j_2', j'} k(jj_2j'j_2')P_{j_2}$$

where P_{j_2} is the Boltzmann probability of the collision partner being in state j_2 (Fig. 11). Their total relaxation rates for different rotational states in the v = 1 manifold calculated at 373 K yield rate coefficients in the range of $6 - 12 \times 10^{14}$ cm^3 mol^{-1}s^{-1}, or three to six times gas kinetic. However, it needs to be demonstrated that (1) the rotational cross sections deduced from
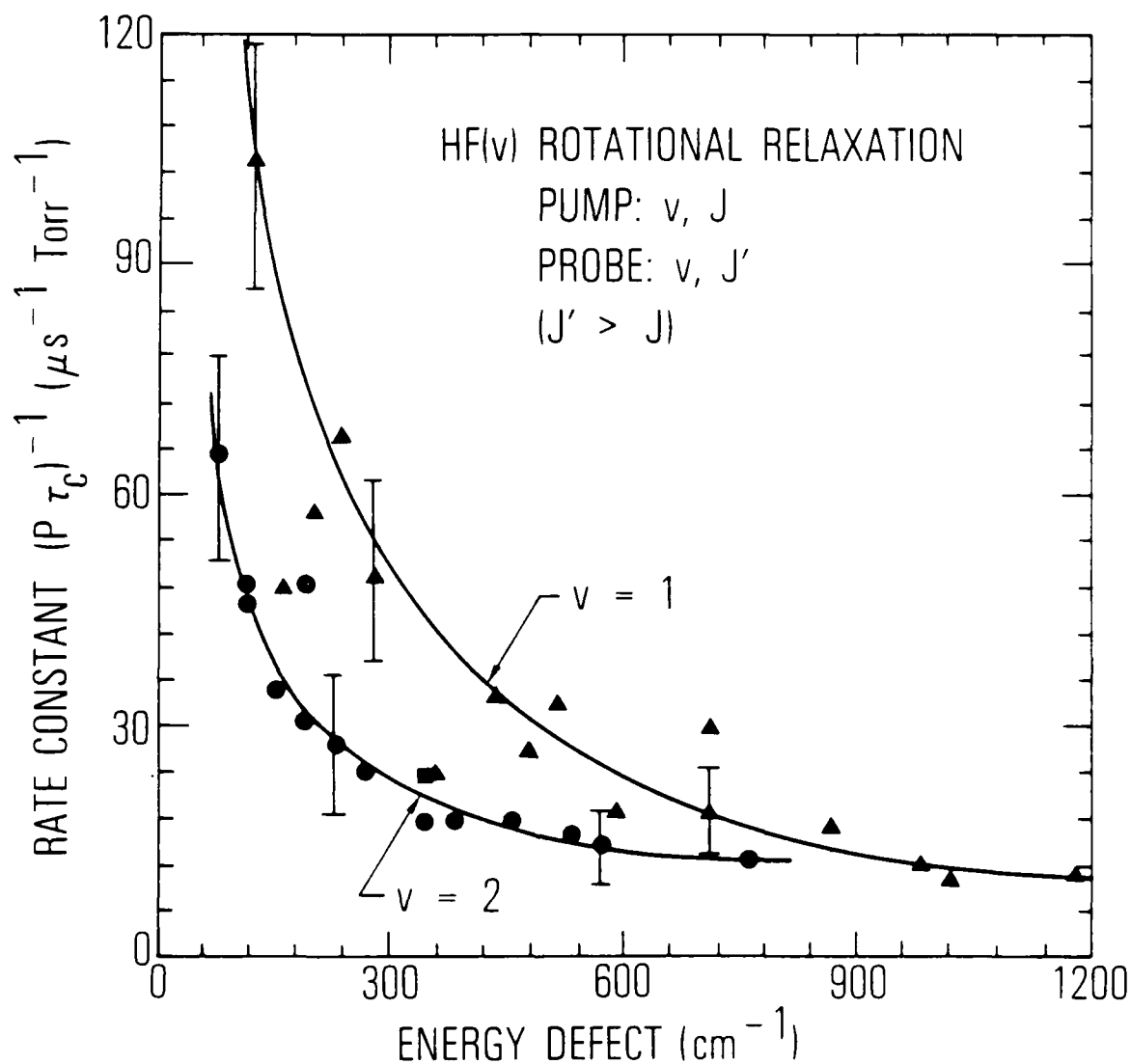
Fig. 10. Experimental Rotational Relaxation Rate Coefficients for HF(v = 1 and 2). Triangles are data from Ref. 59 for v = 1, with error limits as quoted in that paper. Circles are from Ref. 53 for v = 2. The probed rotational level is always at higher energy than the pumped level (from Ref. 53).

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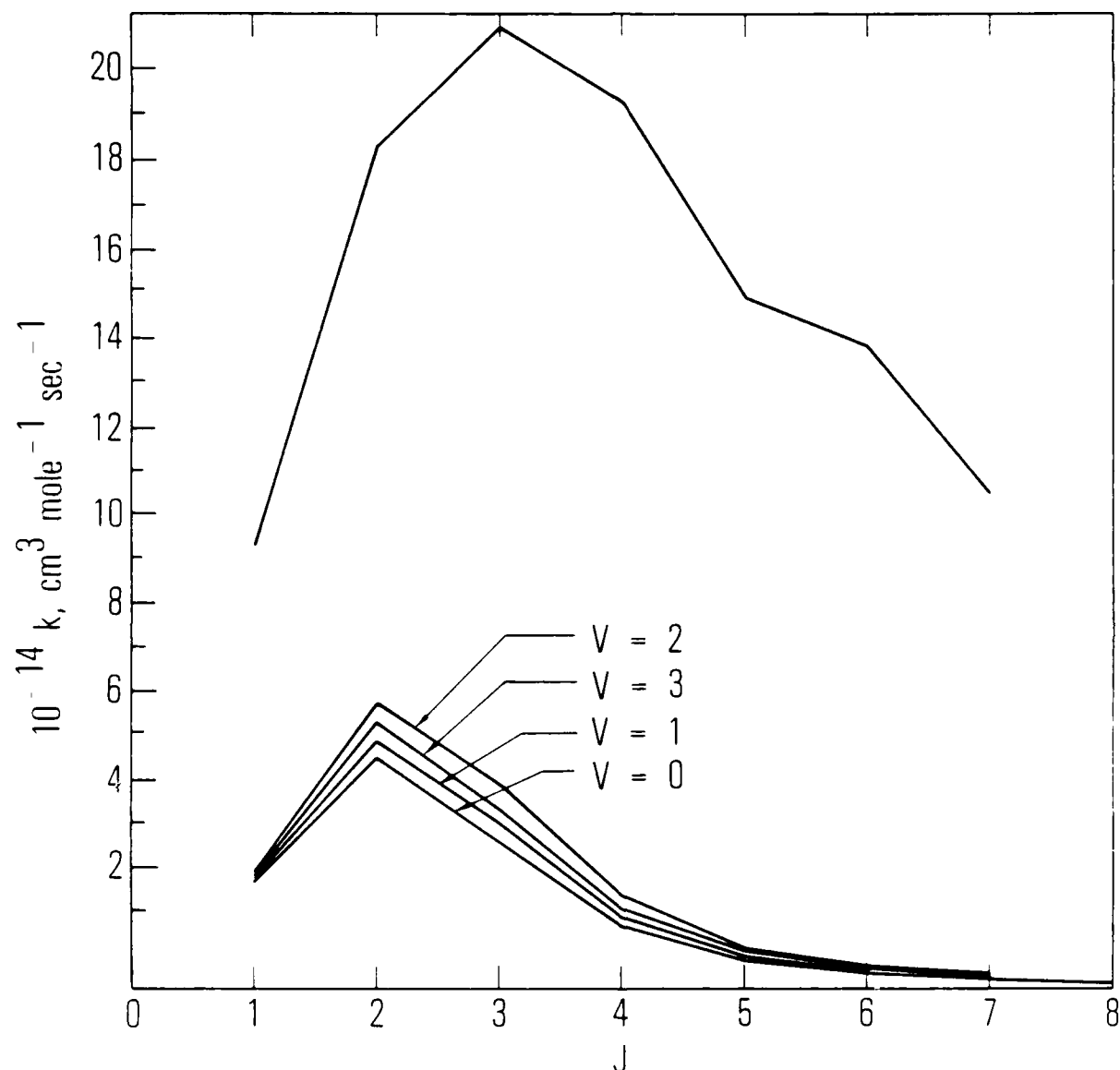
Fig. 11. Rotational Relaxation Rate Coefficients for Pure HF at 373 K,
Calculated from Line Broadening Data. Lower four curves are
R-T transfer coefficients for $\Delta j = -1$ transitions, i.e.,
$HF(v,j) \rightarrow HF(v,j-1)$, for $v = 0$, $v = 1$, $v = 2$, and $v = 3$.
Upper curve is total relaxation rate for sum of all R-R and
R-T processes for $v = 1$ (from Ref. 70).

the pressure-broadening data using an exponential gap model are uniquely determined and (2) the total relaxation rates can be expressed as such a simple function of the state-to-state rate coefficients without a detailed modeling calculation being carried out. Furthermore, it is unlikely that the basic requirement for the sudden approximation theory to be valid is fulfilled for the case of HF, i.e., it is not the case that $\tau_{coll} < h/2\pi \ \Delta E_{Rot}$ for changes in rotational energy on the order of 100 cm^{-1} or more.

Recently there have been two studies of rotational energy transfer using quasi-classical, three-dimensional, molecular trajectory calculations. Thompson[11] investigated the transfer in HF-Ar systems and found that rotational energy transfer is insensitive to the vibrational quantum number; that cross sections decrease as Δj increases (cross sections for $\Delta j = 2$ are approximately one half of those for $\Delta j = 1$); and that cross sections depend only weakly on initial j (at least, when comparing results for $j_1 = 6$ with $j_1 = 10$).

In work cited earlier, Wilkins[45] performed trajectory calculations for HF-HF encounters, which are generally of greater importance than HF-Ar in HF laser systems. As already noted, these calculations indicated that the mechanism of vibrational energy transfer involves large changes in rotational quantum numbers. Wilkins also found that both R-R and R-T processes can be important in deactivating excited HF molecules; that the probability of rotational deexcitation decreases with increasing j; and that single-rotational-quantum transitions are more probable than multiple ones (typically, $\Delta j = 2$ transitions are approximately an order of magnitude less probable than $\Delta j = 1$ transitions). However, the absolute transition probabilities obtained were rather small. They yielded, for example, total rate coefficients on the order of 10^{12} $cm^3 mol^{-1} s^{-1}$ for $HF(v_1 = 1, j_1)$ + $HF(v_2 = 0, j_2) \rightarrow HF(v_1' = 1, j_1' = j_1 + \Delta j) + HF(v_2' = 0, j_2')$, where j_2 is averaged over all states in a Boltzmann distribution at the translational temperature. In subsequent calculations, Wilkins* has increased the magnitude of these transitional probabilities.

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*R. L. Wilkins, private communication.

Several conclusions can be drawn from these facts and theories.

a. State-to-state rotational energy transfer rates depend only weakly on the nature of the collision partner M for inert gas chaperones. In general, absolute rates depend on M, but the j-scaling may not depend on M.

b. Multiquantum state-to-state transitions are less probable than single ones but are not negligible.

c. State-to-state transition probabilities decrease as the amount of energy that must go into translation increases, so that, for R-T transfer, probabilities decrease as initial rotational quantum number increases.

d. Under most experimental conditions, a phenomenological observation of a R-R translational process is a complex convolution of many detailed state-to-state processes.

e. Like the detailed state-to-state probabilities, the phenomenological rotational rates decrease as the energy converted to translational energy increases.

f. Phenomenological rates may be faster than the individual state-to-state processes because they can represent several parallel pathways.

Quantitative statements are somewhat more speculative at this time. For example, the scaling of probability of energy transfer with increasing energy gap depends on the model assumed. The more recent relationship proposed by Pritchard and coworkers[69] predicts that probability varies as an inverse power function of ΔE rather than as the exponential of ΔE. As ΔE gets large compared to about 600 to 1000 cm^{-1}, the new relationship will predict significantly faster energy transfer rates at the intermediate to higher j's. For HF, this means $j_1 \gtrsim 15$ for $\Delta j = 1$.

The sensitivity of scaling to the energy gap model used can be illustrated by calculating the ratio of $k(j = 15 \rightarrow j = 14)$ to $k(j = 4 \rightarrow j = 3)$ for different models at 300 K. Sentman's exponential gap model expression, derived from data of Hinchen, is $k_{jj'} \propto 0.08 \exp(-0.72\Delta E_{jj'}/kT)$, whence $k_{15,14}/k_{4,3} = 0.2$. For the more recently proposed power gap models, $k_{jj'} \propto N |\Delta E_{jj'}|^{-\gamma}$, where $N = 2j' + 1$ if m_j is randomized and $(2j' + 1)/(2j + 1)$ for downhill transitions if m_j is conserved. For the former case, Polanyi et al. found $\gamma = 1.14$ for M = Ar, whence $k_{15,14}/k_{4,3} = 0.9$. For the latter case, they

found $\gamma = 0.68$, yielding $k_{15,14}/k_{4,3} = 0.5$. (These calculations assume γ is the same for HF-HF as it is for HF-Ar collisions.)

The quantitative implications for understanding HF lasers are that we still do not know a great deal about details of *rotational relaxation*. Experiments suggest that relaxation of low j levels is rapid, but of higher j levels is slower; how much slower, we don't know. We can construct and exercise computer models (discussed in the next section) that can explain observations in actual laser experiments, but whether the assumptions regarding rotational relaxation are correct cannot be determined from present direct experimental evidence.

V. MODELING STUDIES OF ROTATIONAL DISEQUILIBRIUM EFFECTS IN HF CHEMICAL LASERS

As noted previously, the earliest models of the behavior of HF and DF chemical lasers were constrained by several radically simplifying assumptions. At the Fourth Conference on Chemical and Molecular Lasers in 1974 two reports were presented on investigations of the effects of rotational nonequilibrium in "cold reaction" pulsed/HF lasers. One report was given by Creighton[71] from Livermore, the other by Hough and Kerber[72] from Michigan State University.

Hough and Kerber[73] published a more detailed account of their findings the following year. Rotational nonequilibrium was taken into account in their model by adding to each HF(v,j) rate equation a term of the form $(N_{eq} - N)/\tau$, where the numerator expressed the deviation of the instantaneous v,j level population from the Boltzmann population, and the denominator represented some global vibrational relaxation time constant, assumed to be of the form $A_{\tau} \exp(B\Delta E/kT)$. In this study, A_{τ} was taken to be some fraction of the collision frequency, varied in different cases, and B was taken to be a constant value of 0.001. A_{τ} was varied from infinitely large to gas kinetic to 0.1 and 1.0 times gas kinetic. The effects were reported on total power in each vibrational band, on power distribution within each band, and on onset and duration of lasing. It was observed that, unlike the earlier, rotational equilibrium calculations, multiline lasing in a given vibrational band was predicted, lasing does not begin immediately after gain reaches threshold, and total power output declines. These are all effects that tended to improve agreement with experimental data.

Kerber and Hough[74] later extended this study to a pulsed chain reaction $H_2 + F_2$ laser in which two rotational relaxation models were considered: the one described previously, called model τ, and a new model that incorporated individual state-to-state rotational relaxation processes, called model Δj. In the new model, each v,j state was collisionally relaxed by chaperones M to the v,j - 1 state. The results of the two models were crudely similar, though

the Δj model did predict somewhat lower pulse energies and powers, more energy out in hot bands, and power distributed over a broader range of V-R lines. Note that in both models, it was assumed that the pumping reactions produced HF(v,j) rotationally equilibrated within the vibrational manifold, which is contrary to current experimental and theoretical evidence.

In a follow-on study, Kerber et al.[75] elaborated upon the previous model by incorporating the V-R transfer mechanism producing very high j states, as calculated by Wilkins; and also by incorporating the non-Boltzmann distributions over j states produced in the pumping reactions, as measured by Polanyi and coworkers. The authors found that the V-R mechanism was necessary to produce pure R-R lasing; the Polanyi distribution mechanism was neither sufficient nor necessary (Figs. 12 and 13). The occurrence of strong rotational lasing did not appear to reduce P-branch lasing energy; however, it did decrease peak power and increase pulse length. The extent of rotational lasing was found to be very sensitive to both V-R energy exchange rates and rotational relaxation rates. The small relaxation rate coefficients initially reported by Wilkins led to unrealistically high gains and long durations for rotational lasing. On the other hand, faster-than-gas-kinetic relaxation rate coefficients, employed because Hinchen and Hobbs obtained such large phenomenological relaxation rates, produced negligible rotational lasing. These studies have continued and are described in several papers and reports.[76-84] A comparison of experimental data for the pulsed HF laser of Reference 6 with model predictions of Kerber et al.[80] is shown in Figs. 14 and 15. The model sensitivity of laser energy and laser spectral distribution to rate magnitudes and patterns can be seen.

There have been other modeling efforts of pulsed HF lasers, particularly in the years before the complications of rotational disequilibrium were appreciated.[85-91] These studies are not discussed further here, because they add nothing new to the results of Kerber and his coworkers. Instead, we turn to a brief examination of modeling efforts of continuous HF chemical lasers. The earliest models, as already noted, assumed rotational equilibrium.[92-94] Sentman[95] and Skifstad and Chao[96] were the first to attempt to account for nonequilibrium rotational effects in continuous HF lasers. Since then, the principal continuing efforts have been by Sentman and coworkers.[97-105]
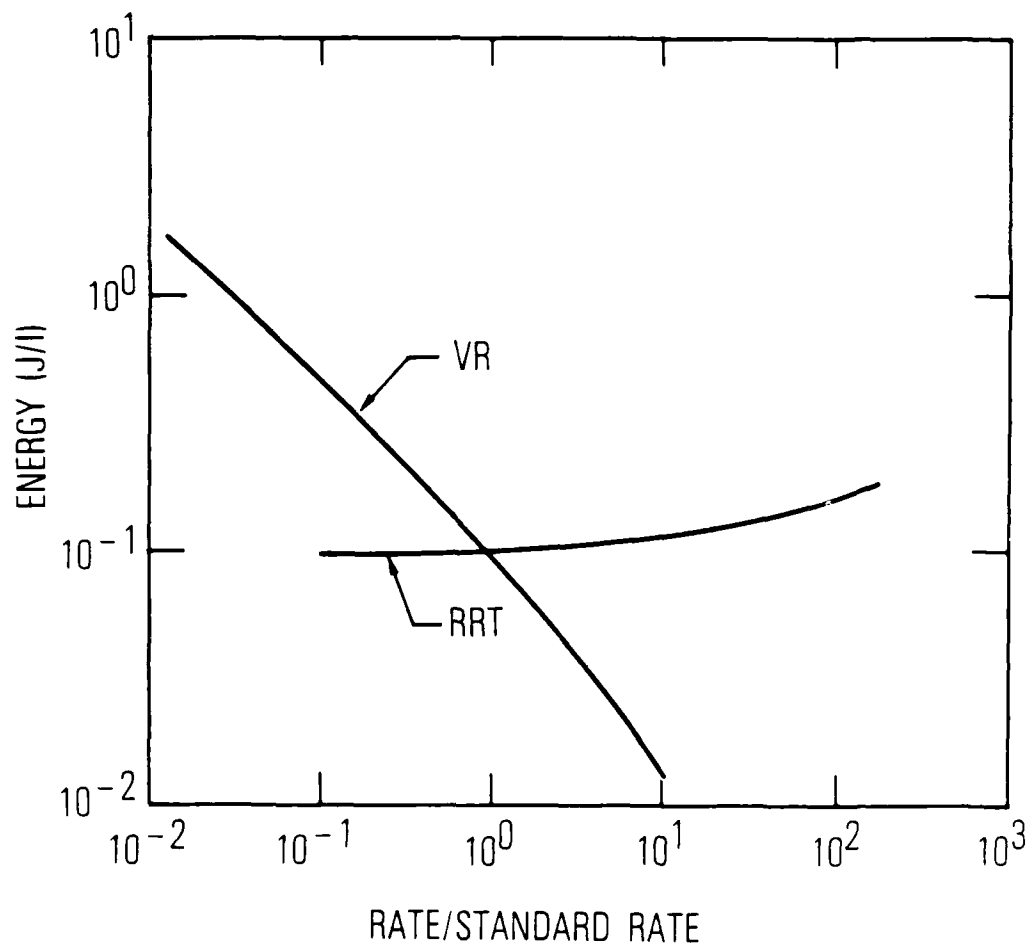
Fig. 12. Effect of Changing V-R and R-R,T Rate Coefficients on Calculated P-Branch Energy in a Pulsed HF Laser in a Mixture of $0.02F : 0.99 F_2 : 1.0 H_2 : 20$ He at 300 K, 20 Torr. Cavity conditions: $R_o = 1.0$, $R_L = 0.7$, mirror separations, 10 cm. Boltzmann distribution over rotational states in pumping reactions is assumed (from Ref. 75).
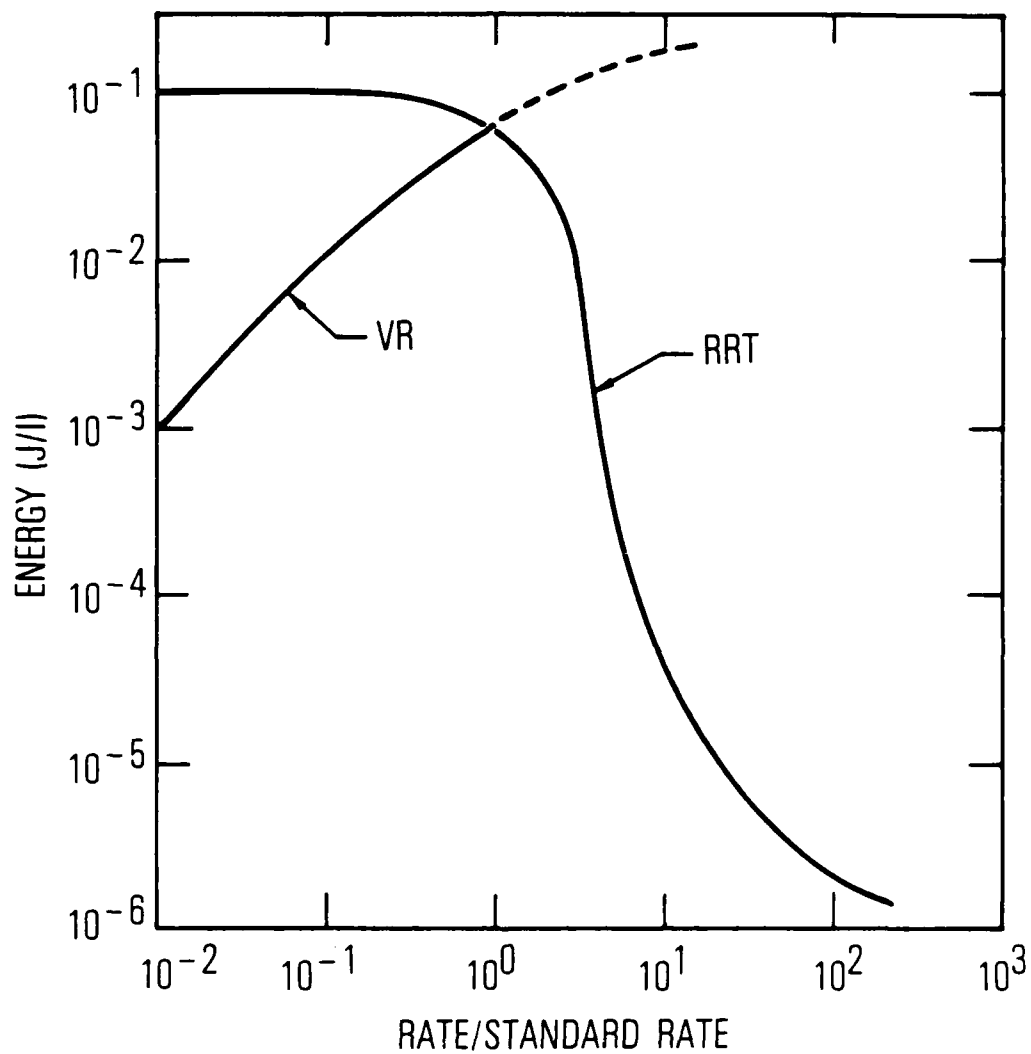
Fig. 13. Effect of Changing V-R and R-R,T Rate Coefficients on
Calculated Rotational Lasing Energy in a Pulsed HF
Laser. Conditions as in Fig. 12 (from Ref. 75).

Fig. 14. Comparison of Experimental Distribution of Band Energy from Pulsed HF Laser of Ref. 6 with Model Calculations of Ref. 82. The laser is operating at 300 K and 36 Torr in a gas mixture of $0.05F : 0.95 F_2 : 1H_2 : 10 He : 0.25 O_2$. Mirror reflectivities are $R_O = 0.8$ and $R_L = 1.0$, separated by 60 cm. The line indicates the onset, duration, and shut-off of each V-R lasing line. The dot indicates peak emission intensity. Fig. 14a is experimental data as replotted in Ref. 82; 14b shows calculations of Ref. 82.

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Fig. 14. Comparison of Experimental Distribution of Band Energy from Pulsed
HF Laser of Ref. 6 with Model Calculations of Ref. 82. The laser is
operating at 300 K and 36 Torr in a gas mixture of $0.05F : 0.95 F_2 :$
$1H_2 : 10$ He $: 0.25 O_2$. Mirror reflectivities are $R_o = 0.8$ and $R_L =$
1.0, separated by 60 cm. The line indicates the onset, duration,
and shut-off of each V-R lasing line. The dot indicates peak emis-
sion intensity. Fig. 14a is experimental data as replotted in Ref.
82; 14b shows calculations of Ref. 82.

Fig. 15. Comparison of Experimental Power Spectral Distribution from Pulsed HF Laser of Ref. 6 with Model Calculations of Ref. 82. Conditions are as in Fig. 16. The top plot reveals experimental results as replotted in Ref. 82. The middle plot reveals model calculations with "standard" rate package (details are given in Ref. 82). The bottom plot reveals results of increasing the fraction of energy that goes into translation in V-R,T energy transfer processes. (In the "standard" case, the product J states are those ranging from $J_{min} - 4$ to $J_{min} + 2$, where J_{min} is that rotational state that gives the minimum energy defect for the process. In the other calculation, J_{min} is that state for which 20% of the energy goes into translation, and the rest goes into rotation.)

Sentman's first study[95] was based closely on the model of Emanuel[92] except for the relaxation of the constant gain formulation and the possibility of rotational nonequilibrium. Density, temperature, and flow velocity were assumed constant; three vibrational levels were considered, with lasing between only two of them. The mechanisms producing rotational disequilibrium, then, were lasing and the initial pumping process. Relaxation occurred by single-quantum V-T,R (i.e., $\Delta v = 1$, all Δj allowed) and multiquantum rotation-to-rotation-and-translation (R-R,T) energy transfer. The rotational relaxation rate coefficients were fitted to an exponential energy gap relation of the sort proposed by Polanyi and Woodall: $k = Z_{coll} C_1 \exp[-C_2 \Delta E/kT]$, where it was further assumed that C_1 and C_2 were the same values as derived for HCl-HCl relaxation. The V-R detailed relaxation rate coefficients were fitted to a similar exponential energy gap relation. The two parameters were selected so that when summed over a Boltzmann distribution of all rotational states, the resultant global rate coefficient agreed with the phenomenological measurements. Sentman's calculations indicated that ". . . as the rate of rotational relaxation increases, the total power produced increases, the percent in the R branch decreases, the peak of the power distribution gradually shifts to higher j, and more power is produced in the higher j transitions . . .Rotational nonequilibrium results in a decrease of 20 to 30% in the total power from the equilibrium case" (page 3531 in the study). As in the case of the pulsed laser, Sentman found that when rotational nonequilibrium is allowed, several j transitions lased simultaneously. In general, allowing rotational nonequilibrium improved agreement with experimental data.

In his next study,[97] Sentman replaced the Fabry-Perot optics of his model with a confocal unstable resonator with 50% geometric outcoupling. His principal results were that when rotational equilibrium is maintained, both resonators predicted about 25 to 30% more power than the nonequilibrium model. For a given kinetic model, both resonators gave practically the same total power output. The spectral distributions for the two resonators were nearly identical for the rotational equilibrium case. For the nonequilibrium case, the Fabry-Perot resonator gave power distributed over many lines, whereas the unstable resonator gave 84% of the power out on one line.

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More recently, there have been modifications made in Sentman's code, principally to permit lasing on two vibrational transitions (2 → 1 and 1 → 0) and to include more detailed kinetics. An example of the calculated power spectral distribution obtained[105] for a particular experimental continuous HF laser is shown in Fig. 16. Furthermore, Sentman has worked with the group at Bell Aerospace to develop a code, NORO-II,[104] which includes all the CNCDE/BLAZE code together with rotational disequilibrium effects (see below). So far, nothing has been published using these newer codes that alters or significantly adds to what was already determined in the earlier modeling studies of disequilibrium effects in continuous lasers. However, one statement did appear in one of Sentman's recent papers that deserves notice in the context of the present discussion: "During this modeling exercise, it was found that the rotational nonequilibrium effects, in particular the PSD (power spectral distribution), were significantly affected by the mixing rate. This implies that for situations in which the fluid dynamics of the mixing process are so complicated that they are represented by a very approximate model, the determination of the mixing parameters using a rotational equilibrium kinetics model could lead to serious errors. The mixing parameters cannot be considered fixed until they have been used in a rotational nonequilibrium model and the correct PSD obtained."[103]

Another code for a continuous HF (or DF) chemical laser has been developed at TRW by Bullock and associates.[106] This code contains fairly detailed kinetics for five vibrational levels with rotational disequilibrium and also non-Maxwellian velocity distributions allowed; it includes variations in flow velocity, density, and temperature, and mixing, and also an unstable resonator cavity. Rotational relaxation is described by a family of equations that includes both R-R and R-T processes. The rate coefficient for any given process,

$$HF(v, j_1) + HF(v', j_2) \rightarrow HF(v, j_1') + HF(v', j_2')$$

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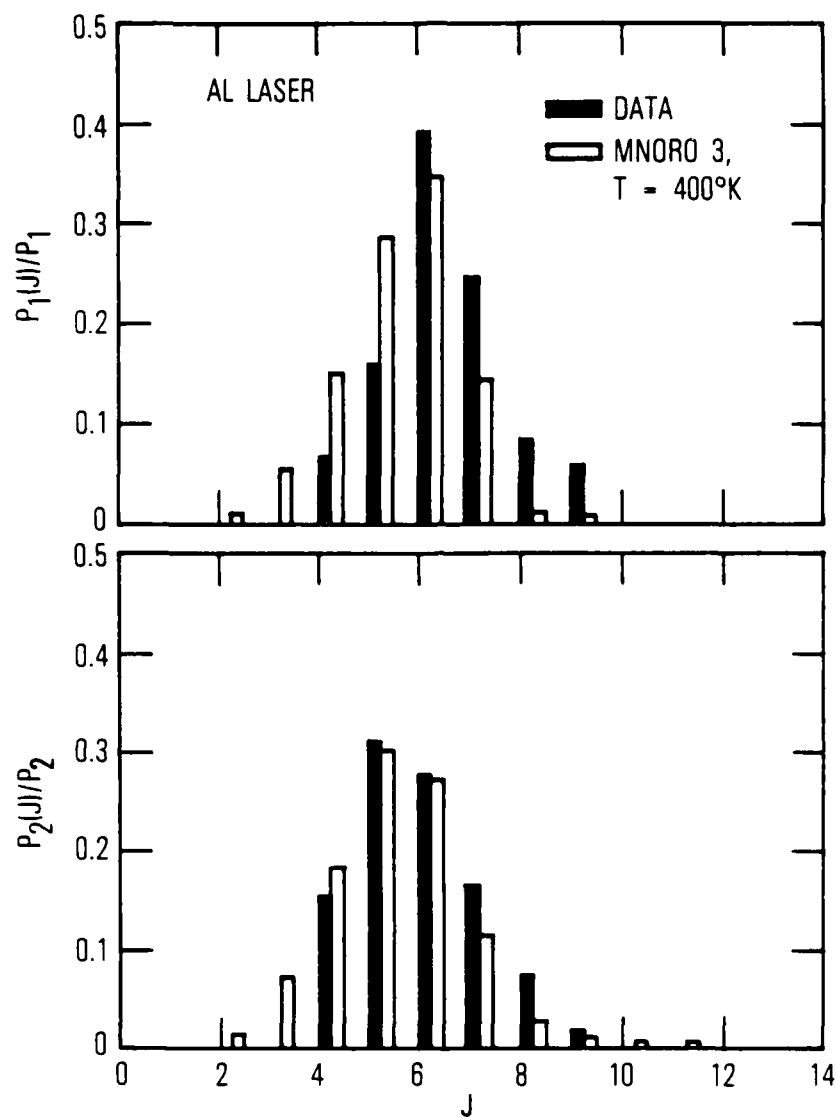
Fig. 16. Comparison of Experimental Power Spectral
Distribution from Continuous HF Laser with
Model Calculations of Sentman and Schmidt
(Ref. 105). The code, MNORO-3, includes
rotational nonequilibrium effects on three
vibrational levels. Experimental data are
from D. J. Spencer, H. Mirels, and
D. A. Durran, "Performance of CW HF
Chemical Laser with N_2 or He Diluent," TR-
0172(2777)-1, The Aerospace Corp., March
15, 1972, as reported in Ref. 105.

is given by an expression that approximates a formalism developed by Hinchen:

$$k_{j_1 j_1' j_2 j_2'} = k_o \ (Q_v)^{-2} \ (2j_1'+1) \ (2j_2'+1) \ \exp[-(2E_{j_1'}+2E_{j_2'}-E_{j_1}-E_{j_2})/kT]$$

where Q_v is the rotational partition function. This expression is somewhat more complicated than the simple Polanyi-Woodall formulation that Sentman uses in his model. Furthermore, the expression behaves quite strangely when $j_2 = j_2'$, i.e., when the transition is R-T transfer. Bullock et al. examined the effect of increasing and decreasing k_o from Hinchen's value by factors of 10; and also of increasing k_o by a factor of 10^{20}, which was equivalent to assuming instantaneous rotational equilibrium. They found that "...for the value of k_o given [by Hinchen], the relaxation rate is so large for even the lowest pressure regime of interest that rotational equilibrium effects are significant. Increasing the rate by a factor of 10 produced results that were hardly distinguishable from those obtained using essentially an infinite rate. Decreasing the rate by a factor of 10 produced sharply enhanced nonequilibrium effects, such as a large number of almost independently lasing transitions" (page 223 in that report).

Other modeling studies, generally with less detailed models, have yielded results consistent with those just described.

We can summarize the principal conclusions of these modeling studies as follows.

a. Rotational disequilibrium is required to account for multiline lasing.

b. Rotational disequilibrium lowers total power, spreads lasing over more lines, and, in pulsed lasers, delays onset of lasing and increases its duration.

c. Pumping of high j states in V-R transfer is required to simulate pure rotational lasing in pulsed HF lasers.

d. Pure rotational lasing does not appear to reduce total P-branch vibrational lasing (at least, in pulsed lasers).

e. Mixing parameters for continuous lasers have to be evaluated with a model that permits rotational nonequilibrium.

f. All the current models give improved agreement with experiment when rotational disequilibrium is allowed.

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VI. DISCUSSION AND CONCLUSIONS

The principal questions to be addressed, if not answered, in this review are: Is there rotational nonequilibrium in chemical hydrogen halide lasers? If so, how serious is it? What causes it? And what can be done about it if it is undesirable for laser performance?

We can start with the well-documented fact that simultaneous multiline lasing (within one vibrational band) occurs in both pulsed and continuous chemical HF lasers. Several factors could account for this: the optical modes do not fill the gain volume; the lasing species are not in rotational equilibrium; or, the medium is not homogeneous. In a fast-flowing system, inhomogeneity could be caused by poor mixing or gas dynamics. Inhomogeneity in a static system is less likely but could be caused by slow prereaction or by parasitic lasing. Multiline lasing in cw systems then need not necessarily imply rotational disequilibrium; however, modeling studies that compare the behavior of systems with and without equilibrium all obtain much better agreement with experiment when disequilibrium is allowed. L. H. Sentman, based on his own extensive experience with modeling continuous HF lasers, feels that the first and third of these possibilities are extremely unlikely. Therefore, multiline lasing is very strong evidence for rotational nonequilibrium.[*] However, the experimental data shown in Fig. 17 could imply inhomogeneity (because the spectral outputs of the upstream and downstream locations differ so much from each other) as well as rotational nonequilibrium (because of simultaneous lasing on several rotational lines of the same vibrational band at a localized spot of the near field pattern).

Pure rotational lasing has been observed, but only in pulsed lasers. This condition necessarily implies that rotational nonequilibrium is present. Of current HF laser models, only those that incorporate energy transfer from vibrational to high rotational states (i.e., multiquantum V-R transfer)

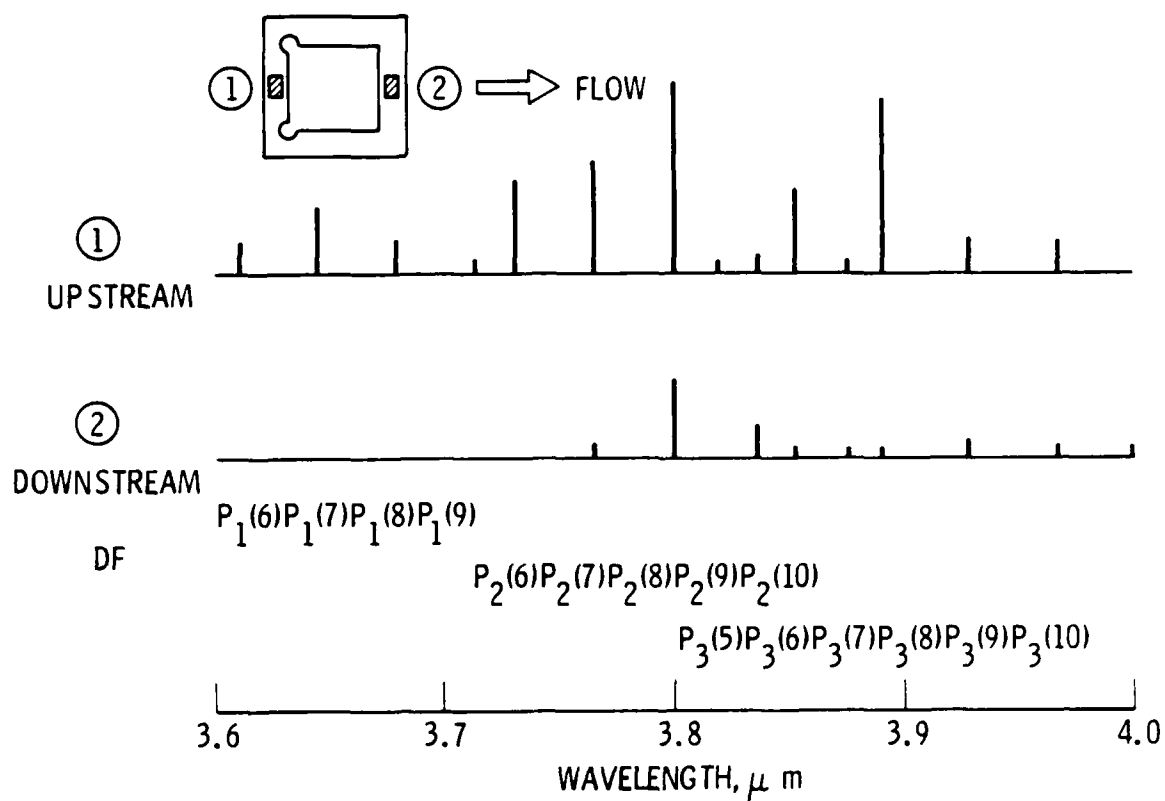[*] L. H. Sentman, private communication, 25 May 1983.

Fig. 17. A 16 kW Supersonic Diffusion Laser Near-Field Pattern Exhibiting the Pronounced Nonuniformity of Laser Spectral Distribution in the Flow Direction. Such nonuniformity may be evidence of rotational non-equilibrium among DF states of lasing transitions. Flow velocity is approximately 1×10^5 cm/sec; mirror width is approximately 10 cm (Ref. 107).

can account for it. This conclusion, however (for the $F + H_2$ reactions), requires some careful examination. For example, the only pumping distributions that have been considered in modeling are an equilibrium distribution over rotational levels and the nonequilibrium distributions deduced by Polanyi and coworkers from their experiments.

These results are taken to indicate that the highest j states observed j = 6, 14, and 14 in v = 3, 2, and 1, respectively, which are close to the maximum permitted on energetic grounds, namely, 6, 14, and 20. The observed distributions are not the true nascent ones because some relaxation had already taken place. There is the possibility that higher j states are formed but were not seen. There is also some question whether the detection scheme used was sensitive enough to observe only a few percent of higher j states. It has already been noted that the usual calculated total available energy may not be quite correct, that a small fraction of reagent molecules could have several kcal/mol internal energy more than the average. What might be the effect of permitting this energy to contribute to rotational excitation of the product HF? In other words, one could probably account for small fractions of lasing energy coming out in pure rotational modes without involving V-R transfer.

There is one other possibility, which is suggested by the fact that pure rotational lasing has been observed only in discharge- or photolytically-initiated systems (i.e., pulsed systems). In these cases the excitation source may be contributing additional excitation energy to the products. Flash photolysis frequently produces fragments with excesses of translational or internal energy because of the difference between the absorption band energy and the dissociation energy. (For example: if F_2 is the fluorine-containing species, as in the experiments of Chen et al.,[17] the maximum in the absorption spectrum is at 280 nm, which is equivalent to approximately 100 kcal/mole. But the F_2 bond strength is only 38 kcal/mole, which leaves an average of 62 kcal/mole to contribute to excess translational energy of the F atoms formed.) A convincing refutation or confirmation of this argument might be a careful search for pure rotational lasing in a thermally initiated laser (such as almost all the continuous devices).

If the V-R mechanism is the correct explanation of pure rotational lasing in pulsed lasers, then high j states must similarly be produced in continuous lasers as well. There is no mechanism in a continuous device that could remove high rotational states that is not also operating in a pulsed device. However, cw rotational lasing might be suppressed because the laser cavity will "see" rotational relaxed gas as well as disequilibrated gas. This is because typical current supersonic diffusion lasers have flow times of about 2 to 10 μsec across the optical cavity, which at the ambient pressures is long enough even for the high j states to relax substantially toward equilibrium.

If the V-R mechanism is correct, why are there not also high j states reported in nonlaser systems? Why haven't these states been observed? There are a few scattered observations, but not consistent results. Kwok and colleagues have looked for high j states in a flow tube and have seen populations of high rotational states five or six orders of magnitude larger than equilibrium populations, but still small compared to the total HF populations within the vibrational band. Such densities would not account for rotational lasing on the order of 10% of vibrational lasing energies, such as reported by Chen; they would certainly not account for the still higher fraction of the total power reported by Rice and Oldenborg. An informative experiment would be to pump an HF-filled cell with an external HF laser and watch for rotational lasing in the cell. If Wilkins' mechanism is correct, an HF sample pumped up to v = 1 should relax to produce v = 0, j = 13, 14, 15, and smaller concentrations of lower j states; and hence to produce rotational lasing on those high j states in an optical cavity. Such an observation would be positive confirmation of the V-R multiquantum mechanism.

The V-R mechanism has basically two parts: (a) the production of high j states and (b) their persisting nonequilibrium populations because rotational relaxation is slow compared to their production rates. Is it possible that (a) is true but not (b)? Modeling of the pulsed lasers suggests a negative answer: when high j states are produced by V-R transfer, the strength of pure rotational lasing on these states depends sensitively on the rate of rotational relaxation. If production of high j states is the cause of rotational nonequilibrium, then, relaxation must be slow (compared to laser mode build-up

times or gas kinetic collision times), or else there would be no visible effects of the nonequilibrium. However, it is not possible to quantify this qualitative argument at present. Every reported experiment to date that has purported to measure rotational relaxation rate coefficients is ambiguous because the conclusions are model dependent.

If the V-R mechanism is correct, and high j states are highly populated compared to equilibrium population, then can a model with rotational equilibrium be of any use at all? Earlier modeling studies suggested that one could make fairly accurate predictions (within a factor of 2) of the grosser features of a chemical laser—pulse length, power output, etc.—without taking detailed state-to-state chemistry into account. But if one is concerned about power spectral distribution, then a good rotational nonequilibrium code is essential. Furthermore, no one has done a careful comparison of two codes— one with rotational equilibrium, the other without, but otherwise comparable-- to see what the detailed effects of the differences are. There have been comparisons of rotational equilibrium codes with rotational nonequilibrium codes. However, by "good" codes we mean models that treat the detailed state-to-state energy transfer processes, with multiquantum transitions permitted. In treating rotational relaxation, we prefer usage of the "power gap" rotational energy transfer probability scaling with the assumption of azimuthal quantum number conservation. Application of information theory surprisal analysis has been found extremely useful to obtain state-specific rates for $V \rightarrow V$ and $V \rightarrow R$ energy transfer processes.

A crucial assumption that has been made but never verified is the justification of building a nonequilibrium code by superimposing finite rotational relaxation rates on what is essentially a rotational equilibrium rate package. Recall that all the energy transfer rate coefficients used in the standard rate package were derived from experiments that were analyzed assuming rotational equilibrium. If the experiments were subject to nonequilibrium effects, then the deduced rate coefficients are incorrect as far as understanding state-to-state processes; however, they may be useful for phenomenological modeling under conditions not far from equilibrium. The question becomes even more complex for models describing behavior under

nonequilibrium high radiative flux conditions, i.e., lasing. But there is no a priori reason why the hybrid models exploring new operating regimes should be expected to be reliable without some carefully controlled evaluations.

If there is rotational nonequilibrium, and its effects are undesirable, is there anything that can be done about it? The implications of experimental evidence are that something can be done. There are polyatomic species that seem to accelerate rotational relaxation without affecting vibrational relaxation. Perhaps a judicious selection of gas composition can do much to minimize rotational nonequilibrium effects without having other deleterious side effects. This question could bear further experimental scrutiny.

We have already implied what work needs to be done to resolve these questions. First, the mechanisms that have been suggested to produce high rotational states need to be investigated in simple, nonlasing systems at low pressures and short resolution times so that their existence can be proved or disproved unambiguously. Second, clean experiments must be devised for the measurement of rotational relaxation rates of HF under conditions where the interpretation of the data is unambiguous. Relaxation rates are particularly important at high j levels in order to determine which of the two proposed scaling laws, $\sigma \propto e^{-\Delta E}$ or $\sigma \propto |\Delta E|^{\gamma}$, is the more accurate. Third, a search should be made in continuous lasers for the existence of rotational lasing or other unambiguous evidence for significant populations of high j states. A parallel effort should be undertaken to put a detailed nonequilibrium code to the test of modeling both pulsed and continuous lasers to see under what conditions rotational lasing might occur in the pulsed but not the continuous lasers. Fourth, the validity of the hybrid kinetics code (one that super-imposes rotational relaxation and state specific production of rotational states on global rate coefficients deduced from equilibrated experimental systems) needs to be tested under various conditions of interest.

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