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Vibrational relaxation of highly excited diatomics. IV. $HF(v=1-7) + CO_2$, N₂O, and HF

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Vibrational relaxation rate constants are measured for HF(v = 1-4) with $Q = CO_2$, N_2O , and HF by the fast flow infrared chemiluminescence technique using four HF(v) generating reactions whose initial vibrational distributions are found be be unrelaxed. The data are combined with earlier results for v = 5, 6, and 7 to provide information on v dependence and quenching mechanism. The rate constants, $k_{v,v-1}^Q$ range from 1.2×10^{-12} to 4.5×10^{-10} cm³ s⁻¹ and increase with power law exponents n of 2.7 to 3.0 in $k \propto v^n$ for all three quenchers. The relaxation is principally V–V for CO₂ and N₂O, but mainly V-R,T for HF, at least for the higher v levels. The relaxation rate constants are compared with theoretical estimates and form a valuable data base for future theoretical work.

INTRODUCTION

Studies of the vibrational relaxation of HF(v) have been stimulated by high power laser applications and have benefitted from the interplay of experimental measurement with theoretical prediction. The relatively large magnitude of the measured relaxation rate constants compared to other diatomics such as HCl, OH, or NO,¹ presumably due to its large dipole moment and anharmonicity, has facilitated the study of its energy transfer processes including its v dependence,² temperature dependence,³ and relative importance of multiquantum transfer.^{4,5}

The advantages of the fast flow infrared chemiluminescence method in providing vibrational relaxation rate constants for a wide range of v levels and quencher molecules have been demonstrated in previous papers^{2,6,7} of this series. Although the absolute accuracy of these measurements is only about 25% to 30%, they provide data sets of good comparability and consistency. While, in principle, a single generating reaction, say, $H + F_2$ $\rightarrow HF(v) + F$, may be used to derive a whole set of quenching rate constants for v = 1 to v = 7, the highest populated level, in practice, only the top two or three rate constants $k_{v,v-1}^Q$ can be determined with sufficient accuracy because of cascade pile-up effects.⁶ This limitation is circumvented through the use of generating reactions with different initial vibrational state distributions.

In part III of this series, ² rate constants were reported for quenching of HF(v = 5, 6, 7) by eight collision partners. In the present study, k's are measured for v = 1 to 4 for three of these eight, CO₂, N₂O, and HF. Since the generating reactions now involve F atoms, it is not possible to use H containing quenchers. The resultant 21 rate constants for the three quenchers represent the first, major, self-consistent data base, since earlier work⁸ has been shown to have introduced systematic errors for the higher v levels. The experimental data serve to compare with and guide theoretical calculations and to provide insight into the nature of the relaxation process.

EXPERIMENTAL

The apparatus and experimental procedure have been previously described.⁶ The infrared chemiluminescence is viewed through a cooled circularly variable filter (CVF) by an InSb detector directly above the fast mixing, pseudostirred-flow reaction zone. The emission is modulated at 13 Hz by applying a square wave pulse to the microwave power generator that produces the Fatom reactant. The signal enters a phase sensitive detector and is digitally integrated using a voltage-to-frequency converter and a counter whose output is converted into computer compatible RS232 format (SERDEX, Analog Devices). The integration period, typically 7.6 s at each CVF angle, is 25 times longer than previously, resulting in an improvement of nearly a factor of 5 in signal to noise ratio. The digital integration is delayed 1.5 s at each step (1° CVF angle, ~0.013 μ m) to avoid microphonic interference. The digital integration and data acquisition are synchronized with the CVF stepping motor scan for automatic collection of spectra. At each experiment's completion, the data are computer analyzed as previously described.⁶

Fluorine atoms for the generating reactions were produced in modulated microwave discharges of CF_4 -He mixtures at $[CF_4] \sim 4 \times 10^{12}$ cm³ in the sidearm (Ref. 6, Fig. 1) at estimated atom concentrations of 20% to 50% of $[CF_4]$ and diluted tenfold in entering the main flow tube. The molecular reactants, HBr, H₂, CH₄, and H₂O, of the generating reactions were added at concentrations of (1 to 6)×10¹² cm⁻³ in the main flow tube. All reactants and quenchers were high purity or research grade gases and were used without further purification.

Unrelaxed IR chemiluminescence spectra were obtained before and after each quencher addition to check the constancy of the emission intensity. Typical signal drifts were small, the two sets of quencher-free HF(v)concentrations differing by less than 5%. Most of the data were obtained at a flow tube pressure of ~0.7 Torr, average flow velocity of 90 m s⁻¹, and residence time of 0.2 ms in the field of view of the CVF spectrometer.

= 1



FIG. 1. Emission spectrum of F + HBr reaction without added quencher. +... experimental, -... computer fit corresponding to relative populations of v = 1, 0. 281; v = 2, 0. 586; v = 3, 0. 924; v = 4, 1. 00. Initial concentrations: $[F] \simeq 2 \times 10^{11} \text{ cm}^{-3}$; $[HBr] = 2.5 \times 10^{12} \text{ cm}^{-3}$.

Figure 1 shows a typical emission spectrum of the fundamental band of HF(v) from the F + HBr generating reaction without added quencher. The calculated spectrum closely fits the experimental points obtained with $[F]^{-4} \times 10^{11}$ and $[HBr]^{-2}.5 \times 10^{12}$ cm⁻³. The synthetic spectrum was calculated using the Dunham coefficients of Mann *et al.*,⁹ the Herman-Wallis factors of Tamagake and Setser,¹⁰ and the Einstein coefficients of Sileo and Cool.¹¹ The rotational distribution was assumed to be thermally equilibrated at 298 K as earlier described^{2,6,7} and experimentally supported by all of our work. Figure 2 shows the contributions of individual bands to the total emission intensity of this synthetic HF(v) spectrum.

RESULTS AND DISCUSSION

Initial distributions

The four generating reactions used in this study were

TABLE I. Initial relative vibrational populations of HF from $F + H_2 \rightarrow HF(v) + H$.

<i>v</i> =1	2	3	Method	Ref.
0.29	1.00	0.47	Arrested Relaxation	18
0.31	1.00	0.48	Arrested Relaxation	19
0.29	1.00	0.76	Measured Relaxation	20
0.29	1.00	0.50	Measured Relaxation	21
0.31	1.00	0.47	Arrested Relaxation	22
0.31	1.00	0.50	Arrested Relaxation	23
0.35	1,00	0.45	Arrested Relaxation	24
0.28	1.00	0.47	Arrested Relaxation	25
0.28	1.00	0.55	Arrested Relaxation	26
0.28	1.00	0.50	Arrested Relaxation	27
0.29	1.00	0.52	Fast Flow	This work

TABLE II. Initial relative vibrational populations of HF from $F + CH_4 \rightarrow HF(v) + CH_3$.

		the second s		
v = 1	2	3	Method	Ref.
. 33	1.00	0.23	Measured Relaxation	20
). 31	1.00	0.23	Measured Relaxation	21
. 38	1.00	0.26	Fast Flow	28
. 34	1.00	0.20	Arrested Relaxation	23
. 36	1.00	0.14	Arrested Relaxation	24
. 22	1.00	0.17	Arrested Relaxation	25
. 28	1.00	0.14	Arrested Relaxation	27
. 27	1.00	0.26	Fast Flow	29
) . 3 0	1.00	0,15	Arrested Relaxation	30
. 29	1.00	0.30	Fast Flow	31
. 22	1.00	0.27	Fast Flow	31
.32	1.00	0.20	Fast Flow	This work

 $\mathbf{F} + \mathbf{H}_2 \mathbf{O} \rightarrow \mathbf{H} \mathbf{F} (v = 1) + \mathbf{O} \mathbf{H} , \qquad (1)$

$$\mathbf{F} + \mathbf{H}_2 - \mathbf{H}\mathbf{F}(v \le 3) + \mathbf{H} , \qquad (2)$$

$$\mathbf{F} + \mathbf{CH}_4 - \mathbf{HF}(v \le 3) + \mathbf{CH}_3 , \qquad (3)$$

$$F + HBr \rightarrow HF(v \le 4) + Br$$
. (4)

The reaction

$$H + F_2 - HF(v \le 7) + F$$
(5)

had been used earlier² to measure relaxation rates for the high levels. The large rate constants of the H-abstraction reactions (1) to (4), $k \sim (1 \text{ to } 7) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ (Refs. 12 to 17), coupled with the high detection sensitivity, permit the use of low reagent concentrations, and thereby the observation of unrelaxed initial v distributions.

Tables I to III summarize the available results for the unrelaxed initial distributions due to reactions (2) to (4), while the much less extensive information on reaction (1) is discussed below. The agreement among the eleven

96 80 Intensity (arbitrary units) 64 I TOTA 48 32 16 C 2.3 2.7 2.9 3,1 2.5 3.3 Wavelength (μ)

FIG. 2. Synthetic emission spectrum of Fig. 1 showing the contributions of the 1-0, 2-1, 3-2, and 4-3 bands.

TABLE III. Initial relative vibrational populations of HF from $F + HBr \rightarrow HF(v) + Br$.

v = 1	2	3	4	Method	Ref.
0.75	1,30	1.25	1.00	Measured Relaxation	32
0.38	0.75	1.00	1.00	Fast Flow	33
0.46	0.56	0.92	1.00	Arrested Relaxation	34
0.29	0.68	0.97	1.00	Fast Flow	35
5.00	3.05	1.50	1,00	Arrested Relaxation	36
0.26	0.63	0.97	1,00	Fast Flow	29
0.36	0.44	0.77	1.00	Arrested Relaxation	29
0.51	0,65	0.95	1.00	Arrested Relaxation	37
0.25	0.60	0.90	1.00	Fast Flow	This work

studies of $F + H_2$, all but ours either by the arrested or measured relaxation methods, is quite good. Normalized to the v = 2 population, the average of ten v = 3 populations is 0.49 ± 0.03 (omitting only the anomalously high 0.76 of Jonathan *et al.*²⁰) while ours is 0.52, and for all 11 sets, the v = 1 population is 0.29 ± 0.02 , ours also being 0.29.

For the F + CH₄ reaction, Table II, 12 measurements (five by arrested relaxation, two by measured relaxation, and five by fast flow methods) give 0.21 ± 0.05 for v=3 compared to our 0.20, and 0.30 ± 0.05 for v=1, ours being 0.32.

For F + HBr, reaction (4), Table III, there are nine studies of which two^{32,36} describe highly relaxed distributions, one using measured relaxation³² and the other using arrested relaxation.³⁶ The remaining seven include three arrested relaxation and four fast flow experiments. Normalized to the v = 4 population, the average for v = 3 is 0.93 ± 0.08 compared with our 0.90; for v = 2 it is 0.62 ± 0.10 with our 0.60; and for v = 1, 0.36 ± 0.10 with our 0.25.

These comparisons cannot be taken too seriously, because the spectral deconvolution procedures of the different studies are not exactly equivalent. Different potential parameters and transition probabilities have been used by different authors, but these variations are fairly minor and have introduced differences of probably less than 5% into the population ratios, less than the experimental uncertainties of the measurements. The poorer agreement among the F + HBr studies compared with F + H₂ or CH₄ very likely reflects the efficient vibrational relaxation of HF(v) by HBr.

The importance of this very satisfactory agreement of our initial distributions with those of the best work elsewhere lies not so much with its confirmatory value *per se* as with the fact that it rules out interference by unaccounted quenching processes in our relaxation measurements. It was the existence of such processes that led Poole and Smith⁸ to underestimate quenching rate constants for HF(v) relaxation, the discrepancies increasing with increasing v because of the rising contribution of unaccounted removal processes.

The initial distribution of the $F + H_2O$ reaction was shown by Chang *et al.*²⁸ to be complicated by the faster secondary step, $F + OH \rightarrow HF(v) + O$ which is able to populate $v \le 3$ compared to v = 1 for reaction (1). Chemiluminescence from $v \le 3$ has been reported by Sloan *et al.*³⁸ using the arrested relaxation technique and was also seen in our experiments. The populations were found to be a strong function of [F] and [H₂O], i.e., larger [F] produced larger v = 2 and 3 yields. Since H₂O is a very efficient relaxer, it is not feasible to use very large [H₂O]/[F] ratios in order to inhibit the secondary reaction. Quenching experiments were therefore performed under conditions representing a compromise, i.e., the v = 3 concentration was kept very small, v = 2 was < 20% of v = 1, and the small cascade correction due to this v= 2 population was included in the analysis.

Quenching rate measurements

Quenching rate constants $k_{\nu,\nu-1}^{Q}$ were determined using the modified Stern-Volmer analysis described earlier⁶ on the assumption of single quantum energy transfer. From plots of the left-hand side of Eq. (6) vs quencher concentration [Q],

$$\frac{N_{v}^{0}}{N_{v}} + \frac{k_{p}}{k_{l}} \sum_{m=1}^{m_{max}} \left(\frac{N_{v \neq m}^{0} - N_{v \neq m}}{N_{v}} \right) = 1 + \frac{k_{v,v-1}^{Q}}{k_{l}} \left[Q \right]$$
(6)

the desired quenching rate constant is obtained by multiplying the slope of the linear plot by k_i , the total, firstorder loss rate constant. The latter is dominated by the pumping loss term $k_p \sim 5000 \text{ s}^{-1}$. For these measurements of HF(v=1 to 4) relaxation, [Q] was in the range $(0.5 \text{ to } 40) \times 10^{14} \text{ cm}^{-3}$.

A typical plot for Q = HF is shown in Fig. 3. The relatively slow relaxation of v = 1 necessitated larger quencher additions as well as higher total pressures (~1.1 Torr) and lower average flow velocities (~50 m s⁻¹) in some experiments. The dilution effect of these larger quencher concentrations was experimentally minimized by corresponding decreases in the He carrier gas flow rates. In a few cases of large [Q], the data were cor-

FIG. 3. Modified Stern-Volmer plot, Eq. (6), for HF(v) + HF with F+HBr generating reaction.

TABLE IV. Quenching rate constants and probabilities for $HF(1 \le v \le 7)$ by CO₂.

	v = 1	2	3	4	5	6	7	Ref.
kCO2	0.180 ± 0.003	•••	•••	•••	• • •	•••	•••	41
$(10^{-11} \text{ cm}^3 \text{ s}^{-1})$	0.180 ± 0.006	•••	• • •		•••	•••	•••	42
	0.11ª	0.44 ²	0.64 ^ª	1.20ª	$\geq 2.00^{a}$	•••	•••	43
	0.110 ± 0.006	•••	•••	• • •	• • •	•••	• • •	44
	0.150 ± 0.009^{b}	•••	•••	•••	•••	•••	• • •	45
	0.13 ± 0.02	•••	•••	•••	•••	•••	•••	46
	0.13	0.48	0.51	•••	•••	•••	•••	47
	•••	•••	1.1	• • •	•••	•••	•••	48
	0.12 ± 0.01	0.61 ± 0.06	1.15 ± 0.12	• • •	•••	•••		49
	• • •	0.34	0.70	1,25	2,70	3.50	3.2	8
	0.12	•••	•••	• • •	• ••	• • •	•••	50
	0.12 ^c	0.48°	0.60°	1,1°	1.6°	1,9°	•••	51
	•••	• • •	1.01 ± 0.16	2.25 ± 0.43	• • •	•••	•••	52
	•••	•••	1.04 ± 0.13	• • •	• • •	•••		53
	•••	•••	•••	2.16 ± 0.18	• • •	7.1 ± 2.4		54
	•••	•••	1.08 ± 0.12	3.08 ± 0.12	8,25 ± 1,23	•••		55
	0.12	0.52	1.1	2, 3	8,0	16	29	This work
$k_{\rm r,r} (10^{-10} {\rm cm}^3 {\rm s}^{-1})$	3,33	3.38	3, 43	3,48	3,55	3,61	3.68	
P	0,0036	0.015	0.032	0.066	0.23	0.44	0.79	
$\Delta E (cm^{-1})$ based on 2349 cm ⁻¹	1613	1440	1273	1110	950	794	640	

^aCorrected for improved radiative lifetimes by Ref. 8.

^bCorrected for gas dynamic effects by Ref. 46.

"Relative rates only; values are normalized to $k_{2,1}/k_{1,0} = 4.0$ and $k_{1,0} = 1.2 \times 10^{-12}$ cm³ s⁻¹.

 $^{d}k_{5,4}$, $k_{6,5}$, and $k_{1,6}$ previously published, Ref. 2.

rected as previously described [Ref. 7, Eq. (1)].

The results are summarized in Tables IV to VI which also include our previously reported rate constants for v = 5 to 7 and $Q = CO_2$, N_2O , and HF. The tables also list collisional relaxation probabilities, $P_v^Q = k_{v,v-1}^Q/k_{LJ}$, where $k_{LJ} = \pi d_{AB}^2 \overline{c} \Omega^{(2,2)}$ as before.^{2,6,7} The quantities $d_{AB} = (d_A + d_B)/2$ and $\epsilon_{AB} = (\epsilon_A \epsilon_B)^{1/2}$ were obtained from transport properties³⁹ and the collision integrals $\Omega^{(2,2)}$ from Hirschfelder *et al.*⁴⁰ The rotationless energy defect, ΔE , was obtained using HF vibrational quanta of 3962, 3789, 3622, 3459, 3299, 3143, and 2989 cm⁻¹ for the 1-0, 2-1, etc., to 7-6 transitions, respectively. The following sections present and compare these results, examine their consistency, and consider the effect of allowing some contributions of two-quantum energy transfer.

Quenching by CO₂ and N₂O

As Tables IV and V show, the quenching rate constants of HF(v = 1 to 7) by CO_2 and N_2O are very similar and rise rapidly with increasing v. The energy transfer probability per gas kinetic (Lennard-Jones) collision ranges from 4×10^{-3} to 0.8. For CO_2 , with the exception of the IR chemiluminescence study of Poole and Smith,⁸ and the relative rate data of Brown *et al.*⁵¹ that also strongly underestimate $k_{v,v-1}$ for high v's, most investigations have reported results for only one or a few vlevels.

It is reassuring to note the excellent agreement of our rate constants with the multiphoton laser excitation results of Douglas and Moore⁵² for v=3 and 4, of Jursich *et al.*⁵⁵ for v=3, 4, and 5, and with the laser-initiated,

TABLE V.	Quenching rate	constants and	probabilities for	$\mathrm{HF}(1 \leq v \leq$	7) by N_2O .
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	<i>v</i> =	1	2	3	4	5	6	7	Ref.
k ^N 20	0.1	104 ± 0.009	•••	• • •			•••		56
$(10^{-11} \text{ cm}^3 \text{ s}^{-1})$	0.0	038	0.068	•••	•••	•••	•••	• • •	47
		•••	1.0	2.5	3.0	5.2	7.4	• • •	8
		•••	•••	1.41 ± 0.13	•••	•••	• • •	• • •	53
		•••	•••	•••	5.9 ± 0.7	•••	12 ± 4	•••	54
	0.1	13	0,29	1.4	4.9	12	18	30	This work ^a
$k_{\rm LJ} \ (10^{-10} \ {\rm cm}^3 \ {\rm s}^{-1})$	3.3	35	3.41	3.46	3.51	3,58	3,65	3.71	·····
Р	0.0	039	0.0085	0.040	0.14	0.34	0.49	0.81	
$\Delta E \text{ (cm}^{-1}\text{)}$ Based on 2224 cm ⁻¹	173	38	1565	1398	1235	10 75	919	765	

 $k_{5,4}$, $k_{6,5}$, and $k_{7,6}$ previously published, Ref. 2.

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	<i>v</i> = 1	2	3	4	5	6	7	Ref.
k ^{HF} _{v,v-1}	0.226 ± 0.002^{2}		• • •		• • •	•••	•••	42
$(10^{-11} \text{ cm}^3 \text{ s}^{-1})$	0.14 ± 0.01	•••	•••	•••	•••	•••	•••	42
	0.16	2,0	•••	•••	•••	•••	•••	58
	•••	1.6 ^b	1.7 ^b	≥ 4. 4 ^b	≥ 6.5 ^b	•••	• • •	43
	0.25	•••	•••	•••	• • •	•••	• • •	59
	0.31	•••	•••	•••	• • •	•••	•••	60
	0.18	•••	•••	•••	• • •	•••	•••	61
	0.18 ± 0.02^{2}	•••	•••	•••	• • •	• ••	•••	62
	0.22 ± 0.03	0.47 ± 0.12	•••	•••	• • •	•••	• • •	63
	* * *	•••	4.9	•••	• • •	•••	• • •	64
	0.22 ± 0.02^{a}	•••	• • •	•••	• • •	•••	•••	65
	0.18 ± 0.02	2,0	•••	•••	• • •	• • •	• • •	66
	0.17	2.5 ± 0.7	4.9 ± 1.5	4.3 ± 1.9	•••	•••	•••	67
	0.145 ± 0.006	• • •	• • •	• • •	•••	•••	• • •	68
	0.16 ± 0.07	1,6+0.5	2.6 ± 1.0	2.7 ± 1.0	0.86 ± 0.50	•••	• • •	69
	0.18	• • •	•••	•••	• • •	• • •	• • •	70
		• • •	• • •	• • •	5.8	10.1	•••	71
		1,3	1.9	3.2	4.6	5.2	~4.3	8
	•••	• • •	2.8 ± 0.4	7.2 ± 0.5	•••	• • •	•••	4
	•••	•••	•••	7.0 ± 0.9	• • •	• ••	•••	52
	• • •	•••	3.2 ± 0.6	8.8 ± 1.1	•••	• • •	• • •	72
	• • •	•••	3.0 ± 0.3	$7,3\pm0,3$	15.1 ± 0.8	• • •	• • •	5
	• • •	• • •	3.1 ± 0.2	$7,2\pm 0,1$	14.9 ± 1.0	• • •	• • •	3
	$0.146 \pm 0.010^{\circ}$	$1,98 \pm 0.10$	•••	•••	• • •	•••	•••	73
	0.18	1,9	3.1	7,3	14	29	45	This work ^d
$k_{\rm LJ} \ (10^{-10} \ {\rm cm}^3 \ {\rm s}^{-1})$	2.73	2.78	2.84	2, 89	2.96	3.03	3,10	
P	0.0066	0,068	0.11	0,25	0.47	0.96	1,45	
$\Delta E \ (\mathrm{cm}^{-1})$	0	-173	- 340	- 503	- 663	- 819	- 973	

TABLE VI. Quenching rate constants and probabilities for $HF(1 \le v \le 7)$ by HF(v = 0).

^aCorrected for gas dynamic effects by Ref. 66.

 $^{c}k_{1,0}$ determined for $T = 320 \pm 15$ K.

 ${}^{d}k_{5,4}$, $k_{6,5}$, and $k_{7,6}$, previously published, Ref. 2.

time-resolved chemiluminescence study of Smith and Wrigley⁵⁴ for v = 4. Our disagreement with the latter work for v = 6 may be due in part to their estimated correction factor based on modeling of precursor HI photolysis and its subsequent chemistry. Our results agree very well with theirs for v = 4 where there is no correction for precursor HBr photolysis, and also agree very well with Crim's group for v=5. It seems strange that the v = 6 rate constant should be smaller than that for v= 5, and we suggest, therefore, that the correction factor should be removed which would raise Smith and Wrigley's k to 1.1×10^{-10} cm³ s⁻¹, in better agreement with our 1.6×10^{-10} . While the discrepancy with Poole and Smith's⁸ data is very likely due to quenching by Ar and HF in their slowly pumped system, that with Brown et al.⁵¹ may be due to reagent HBr and HI, as is also seen in the initial distribution of Ref. 36 in Table III.

For $Q = N_2O$, there are fewer data available. The agreement with Smith and Wrigley's^{53,54} time-resolved measurement is excellent for v = 3 and moderately good for v = 4 and 6. For v = 6, removal of the above mentioned correction factor would give excellent agreement. The large disagreement with Kwok and Cohen⁴⁷ for v = 1 and 2 is difficult to understand, particularly since there is good agreement for v = 1 with Bott and Cohen.⁵⁶

Our reported k's are normally averages of three separate experiments, each involving five to six different quencher additions and agreeing within $\pm 15\%$. Although in most cases only a single generating reaction is used

for a given level, e.g., $H + F_2$ for v = 5, 6, and 7, there is some overlap here and there. For v = 4, e.g., the F + HBr generating reaction gives $k_{4,3}^{CO2} = 2.3 \times 10^{-11}$ and $k_{4,3}^{N_2O} = 4.9 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. In spite of large cascade contributions, the results from $H + F_2$ are surprisingly close: $k_{4,3}^{CO2} = 2.5 \times 10^{-11}$ and $k_{4,3}^{N_2O} = 4.1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. Similarly, for v = 2, $F + H_2$ gives 0.54 and 0.30×10⁻¹¹ cm³ s⁻¹, respectively, for CO₂ and N₂O, whereas F + HBrgive 0.34 and 0.24×10⁻¹¹ cm³ s⁻¹.

Turning now to the v dependence of our rate data, Fig. 4 shows the power law fit $k \propto v^n$ as a log k vs log v plot. With considerable scatter, the n values are 2.8±0.3 for CO₂ and 3.0±0.3 for N₂O when all seven points are included. Our earlier correlation² for v=5, 6, and 7 had given 3.8 for CO₂ and 2.7 for N₂O. $k_{2,1}^{N_2O}$ is particularly far off that line and all other correlations, yet it shows no other experimental abnormalities. The CO₂ points suggest smooth curvature of increasing n with rising v, while the N₂O points are more randomly scattered with exception of $k_{2,1}^{N_2O}$ which is nearly a factor of two too small. The power law model is useful for modeling, but lacks physical justification.

If a simple V-V energy transfer mechanism is assumed to predominate, a semiempirical energy gap model may be tested in the form of the Lambert-Salter⁵⁷ plot of vP^{-1} vs ΔE , where ΔE is the rotationless V-V energy gap. This is shown for CO₂ and N₂O in Fig. 5, where ΔE is based on V-V transfer to the asymmetric stretch, $v_3 = 2349$ cm⁻¹ for CO₂ and 2224 cm⁻¹ for N₂O.

^bCorrected for improved radiative lifetimes by Ref. 8.

The correlation appears fairly normal, the positive slopes of $(3.6 \pm 0.2) \times 10^{-3}$ cm for CO₂ and (3.9 ± 0.4) $\times 10^{-3}$ for N₂O are somewhat smaller than Lambert's value of $\sim 4.9 \times 10^{-3}$ and our previously published 6.4 $\times 10^{-3}$ for CO₂ and N₂O guenching of HCl(v). Considering the large values of ΔE , the Lambert-Salter lines lie more than an order of magnitude below those of HCl at equal ΔE , reflecting the very large relaxation rates at energy gaps of 600 to 1200 cm⁻¹. If the ordinate did not include the somewhat artificial factor v, the line would extrapolate to totally unreasonable values of P^{-1} as ΔE -0, i.e., corresponding to nearly 100 times gas kinetic for resonant transfer. The Lambert-Salter correlation neglects rotational energy transfer effects which are particularly important when the vibrational energy gap is large. In the present case, it suggests that the V-Vmechanism applies, but it sheds little light on the details of the process.

Quenching by HF(v = 0)

Because of its importance in chemical laser modeling, the self-relaxation of HF(v) has been the subject of many studies as is shown in Table VI. For the lower v levels, there is generally good agreement, e.g., 15 reported values of $k_{1,0}^{HF}$ give an average of $(1.9 \pm 0.5) \times 10^{-12}$ cm³ s⁻¹ compared to our 1.8×10^{-12} . The agreement with direct laser excitation, lifetime measurements is particularly encouraging. For v=3, four such studies^{3,4,5,72} have given 3.1, 2.8, 3.0, and 3.2×10^{-11} cm³ s⁻¹ and we report 3.1×10^{-11} . For v=4, five laser studies^{3,4,5,52,72} have reported 7.2, 7.2, 7.3, 7.0, and 8.8×10^{-11} compared to our 7.3×10^{-11} , and for v=5, two laser studies^{3,5} find 1.49 and 1.51×10^{-10} cm³ s⁻¹ compared to our 1.4×10^{-10} . There is thus no question of the correctness and consistency of the reported data set.



FIG. 4. Power law plot of $\log k_{v,v-1}^{Q}$ vs $\log v$ for $Q = CO_2$, N_2O , and HF. Least squares slopes, n, are 2.8 ± 0.3 for CO_2 , 3.0 ± 0.3 for N_2O , and 2.7 ± 0.2 for HF.



FIG. 5. Lambert-Salter plot for $HF(v) + CO_2$ and N_2O . Slopes are $(3.6 \pm 0.2) \times 10^{-3}$ cm for CO_2 and $(3.9 \pm 0.4) \times 10^{-3}$ cm for N_2O . Slopes are defined as $\ln(vP^{-1})/\Delta E$ (cm⁻¹).

It is also reassuring to find that for relaxation of HF(v=2 and 3), three different generating reactions, $F + H_2$ (two experiments), $F + CH_4$ (two experiments), and F + HBr (three experiments) gave identical average results of 1.9 and $3.1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, respectively.

The power law plot, Fig. 4, shows the v dependence of $k_{v,v-1}^{HF}$ to be surprisingly similar to those of CO₂ and N₂O, $n = 2.7 \pm 0.2$, even though the process must be very different: The V-V contribution to self-relaxation must become negligibly small for large v where the quenching reaction is very fast, yet its V-V channel is highly endothermic. By contrast, V-V relaxation by CO₂ or N₂O comes closer to resonance at higher v suggesting the increasing importance of the V-V channel. In a later paper, we will provide experimental evidence for the decreasing V-V fraction of the self-relaxation with increasing v.

Although a nicely linear Lambert-Salter plot can be constructed for the reverse, exothermic V-V process, it is not shown here, because it makes no physical sense, i.e., implies a 100 times gas kinetic rate constant for HF(v=6)+HF(v=1)-HF(v=7)+HF(v=0), and because it is in conflict with both measurement and theory that show the process to be V-R, T in nature.

Multiquantum energy transfer

One of the major assumptions of the modified Stern– Volmer analysis is the exclusively single quantum transfer in HF(v) relaxation. Although there is both experimental^{4,5} and theoretical^{74,75} support for this assumption, recent work by Sirkin and Pimentel^{76,77} has suggested the possibility of multiquantum V-R transfer with Δv as large as five. These authors observe rotational laser emission by HF in its photoelimination from vinyl fluoride or 1, 1-difluoroethylene in the presence of inert

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	F	H ₂ ex	pt.		F+HBr expt.						$H + F_2$	expt.				
Δ	$\Delta v = 1$ $\Delta v = 1$		$\Delta v = 1, 2$		$\Delta v = 1, 2$			v = 1		$\Delta v = 1, 2$			v = 1		$\Delta v =$	1, 2
v	k _{v,v-1}	v	k _{v,v-1}	k _{v,v-2}	v	k _{v,v-1}	\overline{v}	k _{v,v-1}	k _{v,v-2}	v	k _{v,v-1}	v	k _{v,v-1}	k _{v,v-2}		
1	0.12	1	0.11		2	0.45	2	0.35	0.04	4	2.6	4	2,1	0.21		
2	0.49	2	0.44	0.04	3	0.94	3	0.80	0.08	5	8.3	5	7.0	0.70		
3	1.1	3	1.0	0.10	4	2.1	4	1.9	0.19	6	17	6	15	1.5		
										7	27	7	25	2.5		

TABLE VII. Quenching rate constants of HF($1 \le v \le 7$) by CO₂ calculated with $k_{v,v=2}^{CO_2} = 0$ and $k_{v,v=2}^{CO_2} = 0$. 10 $k_{v,v=1}^{CO_2}$.

^aUnits of 10^{-11} cm³ molecule⁻¹ s⁻¹.

gas⁷⁶ and other collision partners including CO_2 .⁷⁷ The emission corresponds to near-resonant V-R energy redistribution within the HF molecule induced by the HF-Q collision.

While there is no question regarding the reality of this collisional V-R redistribution it is important to estimate its importance as a relaxation channel for HF(v). Here, the evidence is overwhelming that it is a minor channel, probably < 1% of the total measured relaxation for any quencher. The evidence includes the following components: (a) In our own work and in that of others. He and Ar were found to be very poor quenchers of HF(v). We would give a rough upper limit of $k < 10^{-14} \text{ cm}^3 \text{ s}^{-1}$, Smith and Wrigley⁵⁴ report upper limits of 1×10^{-15} for v = 3, 2×10^{-15} for v = 4, and 6×10^{-15} for v = 6 when Q = Ar, Since rotational relaxation is guite fast even for high J, a fast V-R redistribution with $\Delta v \ge 1$ induced by He or Ar collisions would be followed by rotational relaxation and would therefore become a fast overall quenching process. This has not been observed; (b) Direct laser pump and probe experiments^{4,5} have shown the preponderance of $\Delta v = 1$ relaxation; (c) Setser and co-workers^{29,31} have observed partially unrelaxed rotational distributions from certain generating reactions, e.g., $F + GeH_4$, HBr, PH₃, but only for the initial reaction products, not resulting from subsequent relaxation events: (d) Hinchen⁷⁸ has probed the time-resolved rotational distribution of HF(v=0) in laser double resonance experiments following excitation to HF(v=1, J=3)and finds a small fraction of the HF molecules arriving in $J \ge 12$ following collisional relaxation. It seems, therefore, that the observed rotational lasing in the photoelimination experiments is a consequence of the high efficiency of that lasing process, but represents a very small fraction of the total collisional relaxation.

To test the importance of multiquantum relaxation in our modified Stern–Volmer analysis⁶ we included $\Delta v = 2$ collisional relaxation steps and obtained the new equation

$$\frac{N_{\nu}^{0}}{N_{\nu}} + \frac{A_{\nu+1,\nu-1}}{k_{I}} \frac{(N_{\nu+1}^{0} - N_{\nu+1})}{N_{\nu}} + \frac{k_{p}}{k_{I}} \sum_{m=1}^{m_{max}} \frac{(N_{\nu+m}^{0} - N_{\nu+m})}{N_{\nu}} - \frac{k_{\nu+1,\nu-1}^{Q}[Q]}{k_{I}} \frac{N_{\nu+1}}{N_{\nu}} = 1 + \frac{(k_{\nu+\nu-1}^{Q} + k_{\nu,\nu-2})}{k_{I}} [Q] .$$
(7)

With the assumption that the fraction of two-quantum transfers is fixed, i.e., $k_{v,v-2}^Q/k_{v,v-1}^Q = \alpha$, the equations are solved starting with $v = v_{\max}$. The effect of the two-quantum terms becomes larger the farther v is below v_{\max} . Table VII shows the calculated k's for three typi-

cal experiments, one each for $F + H_2$, F + HBr, and H + F_2 in which $\alpha = 0.1$ was assumed, and all k's were calculated iteratively. The first column for each experiment gives $k_{n,n-1}$ assuming $\alpha = 0$, i.e., single quantum transfer only, and the next two columns give the best fit for 10% two-quantum relaxation. In each experiment, for v_{max} , $k_{v,v-1}$ in the first column equals the sum of the two k's in the second and third, by definition. But for levels below v_{\max} , this is no longer true. The new $k_{v,v-1}$ now become somewhat smaller than 90% of column one, because there is a greater network of relaxation steps available. However, the effect is not large, amounting to a ~10% reduction three levels below v_{max} for H + F₂. We assert, therefore, that small contributions of multiquantum processes will have, not surprisingly, small effects in decreasing the derived quenching rate constants. Since there is no evidence, whatsoever, that multiquantum relaxation is a major process, we conclude that the derived $k_{v,v-1}^{Q}$ values are substantially correct.

Comparison with theory and discussion

Dillon and Stephenson⁷⁹ did a quantum mechanical scattering theory calculation for vibrational and rotational energy transfer of HF, DF, and HCl to CO₂. Table VIII shows their calculated quenching rate constants for HF(v = 1 to 5). The agreement is quite good up to v = 4 even though the v dependence is underestimated. For v = 5, the calculated k is too low by a factor of 4. The calculated contribution of two-quantum transfer was very small, rising from less than 0.2% for v = 2 to 0.4% at v = 5.

For Q=HF, three classical or semiclassical trajectory calculations have recently been reported. Their results are shown in Table VIII along with our experimental values. The error limits given by Billing and Poulsen⁷⁴ and by Coltrin and Marcus⁷⁵ only reflect the statistics of the Monte Carlo sampling technique, not the many assumptions and approximations, and should not be taken seriously. Among the differing assumptions are the interaction potential well depth ($6.9^{74,75}$ vs 2. 7^{80} kcal mol⁻¹) which strongly affects the importance of complex formation, the anharmonicity of HF (equivalent harmonic oscillator⁷⁴ vs Morse oscillator⁷⁵), vibration-rotation coupling, and classical path approximation⁷⁴ vs quasiclassical trajectory moment method.⁷⁵

Coltrin and Marcus's⁷⁵ cross-correlation calculation seems to be the most realistic in terms of these assumptions, and its results are within about a factor of two of the experimental values for v=2 to 7. The calculated

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v	<i>v</i> = 1	2	3	4	5	6	7	Ref.
	0.27	0.88	1.4	2.0	2.0		•••	79
CO_2	0.12	0.52	1.1	2.3	8.0	16	29	This work
	0.081 ± 0.028	0.64 ± 0.22	1.0 ± 0.4	1.9 ± 0.7	2.7±1.0	4.3 ± 1.5	8.2±2.9	74
	0.17	2.2	2.9	3.3	4.2	5.1	•••	80
HF(v=0)	-0.08 ± 0.08	1.6 ± 0.3	2.8 ± 0.3	3.8 ± 0.5	6.3 ± 0.6	13.6 ± 1.4	54.2 ± 6.5	75
	0.18	1.9	3. 1	7.3	14	29	45	This work

TABLE VIII. Comparison of experimental and theoretical quenching rate constants for $HF(1 \le v \le 7)$.^a

^aUnits of 10⁻¹¹ cm³ molecule⁻¹ s⁻¹.

v dependence of the total rate constant increasing gradually from v = 2 to 6 corresponding to a power law exponent rising from n = 1.4 to 4, and then sharply to 9 for v = 6 to 7. As our subsequent paper will show, the calculation also seriously overestimates the V-V contribution to the rate constant for v = 2 to 4. It would be very useful if such theoretical treatments could present estimates of probable errors connected with their assumptions rather than only with the mechanics of the calculation. In the absence of a sensitivity analysis, the quantitative comparison between theory and experiment has little significance. This uncertainty is further increased by the recent test comparison⁸¹ of the crosscorrelation moment method⁷⁵ with accurate quantum dynamics close coupling calculations for the breathing sphere HF-HF interaction potential. This comparison shows increasing discrepancies for decreasing V-V transition probabilities and thereby throws doubt on the correctness of the moment method.

Coltrin and Marcus's⁷⁵ finding that multiple collisions, i.e., complex formation, account for about 35% of the trajectories but for 90% of the energy transfer in their calculation raises the question of the role of predissociation of such energy-rich complexes as a relaxation mechanism. In the absence of stabilizing collisions, the predissociation lifetime of the complex, with or without vibrational energy transfer is, of course, very short, and the point is moot. If one assumed that every close collision, single or repeated, had equal probability of energy transfer, 90% transfer from 35% multiple collisions would require 17 close collisions, on average, per multiple collision. This seems excessive and may suggest a contribution of predissociation. An alternative explanation may, of course, be that the 65% nonmultiple collisions are more glancing in nature and therefore have a lower probability of resulting in relaxation. Since the lifetime of multiple collision complexes with multiples of < 10 is of the order of 10^{-12} s, the predissociation rate would have to be very fast, indeed. It would have to be very much faster than Dixon et al.⁸² heuristic estimate of $\sim 10^{-10}$ s, based on V-T transfer probability as applied to HF(v=1) relaxation which Coltrin and Marcus's theory miscalculates. The recent, high-resolution, spectroscopic study of Pine and Lafferty⁸³ has found little broadening of the bonded hydrogen stretching vibration in the clearly identified dimer spectrum, corresponding to a predissociation lifetime in the range 0.5 to 3 ns, much too long to provide an observable path in relaxation processes under conditions described in our experiments. Experimentally, the con-

tribution of predissociation of long-lived complexes should result in a pressure-dependent (third-order) component of the relaxation rate constant due to the spontaneous dissociation of collisionally stabilized complexes. This might only be observable at low temperature where the equilibrium fraction of dimers is sufficiently large. The fact that the vibrational relaxation of HF(v) by CO_2 and N₂O is approximately as fast as the self-relaxation, even though the potential well depth is likely to be considerably smaller due to the absence of strong dipoledipole attraction, suggest that predissociation is not an important contributor in these relaxation processes.

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