

Vibrational relaxation of highly excited diatomics. II. HCl (v7)+20 quenchers

B. M. Berquist, L. S. Dzelzkalns, and F. Kaufman

Citation: *The Journal of Chemical Physics* **76**, 2984 (1982); doi: 10.1063/1.443338

View online: <http://dx.doi.org/10.1063/1.443338>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/76/6?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

Vibrational relaxation of highly excited diatomics. VII. DF(v=9–12) and HF(v=5–7)+HF(v=0), DF(v=0) in all combinations

J. Chem. Phys. **81**, 4975 (1984); 10.1063/1.447482

Vibrational relaxation of highly excited diatomics. VI. DF(9≤v≤12)+N₂, CO, CO₂, and N₂O and HF(v=5–7)+CO

J. Chem. Phys. **80**, 6114 (1984); 10.1063/1.446712

Vibrational relaxation of highly excited diatomics. IV. HF(v=1–7) + CO₂, N₂O, and HF

J. Chem. Phys. **79**, 3836 (1983); 10.1063/1.446248

Vibrational relaxation of highly excited diatomics. V. The V–V channel in HF(v)+HF(0) collisions

J. Chem. Phys. **79**, 3363 (1983); 10.1063/1.446237

Vibrational relaxation of highly excited diatomics. I. Method, analysis, and application to HCl(v≤7)+CO₂ and N₂O

J. Chem. Phys. **76**, 2972 (1982); 10.1063/1.443391



Vibrational relaxation of highly excited diatomics. II. HCl ($v \leq 7$) + 20 quenchers

B. M. Berquist,^{a)} L. S. Dzelzkalns, and F. Kaufman

Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

(Received 19 August 1981; accepted 9 December 1981)

120 vibrational relaxation rate constants $k_{v,v-1}^Q$ are measured at 298 K for HCl ($v \leq 7$) collisions with six diatomics: N₂, CO, NO, HCl, DCl, and HF; three triatomics: CO₂, N₂O, NO₂; and eleven polyatomics: CH₄, C₂H₆, C₃H₈, iso-C₄H₁₀, CH₃Cl, CH₃F, CF₄, SF₆, CF₃Cl, CF₂Cl₂, and CFCl₃. For most quenchers, k^Q increases with increasing v independent of whether the vibrational energy gap is reduced or increased. Large collisional relaxation probabilities for high v , of order 0.1 to 1 gas kinetic, are encountered for 11 of 20 quenchers. For $Q = \text{HCl}$ ($v = 0$), the relaxation is shown experimentally to be mainly $V-R, T$ for high v . The rates reflect a mix of effects due to dipole and dispersion interactions, energy gap, rotation, and complex formation, and present interesting problems of interpretation.

INTRODUCTION

Although substantial progress has been achieved in experimental measurement and theoretical understanding of collisional $V-V$ energy transfer processes, large gaps remain. Laser methods have provided accurate data for selected relaxation steps, but they are neither well adapted to reach many upper v levels of a donor molecule nor have they been applied to cover a wide range of acceptor molecules. Thus, there may have been a tendency to oversimplify the $V-V$ process in terms of the energy gap model without sufficient attention to the importance of other physical mechanisms such as dipole-dipole, dispersion, rotation effects, and complex formation.

The preceding paper has shown how the infrared chemiluminescence method of Smith and co-workers¹⁻³ was modified to measure $V-V$ relaxation rates of HCl ($v=1$ to 7) by CO₂ or N₂O under fast flow conditions, and the present paper extends these measurements to 18 additional quencher molecules ranging from diatomics to polyatomics. The limitations of the present method should be kept in mind: it is applicable only to relatively fast processes, i.e., $P \gtrsim 3 \times 10^{-4}$, where P is the probability of relaxation per collision; it is not highly accurate, $\pm 25\%$ – 30% single standard deviation; it assumes stepwise, $\Delta v=1$, relaxation; and it is not well adapted to temperature variation, although this last point is not a rigorous restriction. Its advantages are that it generates rate data for several v levels, including the high ones, of a given donor in one experiment and is easily repeated for a large variety of acceptor molecules provided that they do not react with the precursor species of the generating reactions and that the relaxation occur by $\Delta v=1$ steps. The last condition is well obeyed for donors with large vibrational quanta and has been proven experimentally for HF in two recent studies.⁴

The principal goals of this work are thus (a) to clarify the v dependence of HCl ($v=1$ to 7) relaxation rates and (b) to examine their dependence on the nature of the

acceptor molecules for series of related compounds. These series include: nonpolar diatomics N₂, CO, and NO; polar (HX) diatomics HCl, DCl, and HF; triatomics CO₂, N₂O, and NO₂; hydrocarbons CH₄, C₂H₆, C₃H₈, and iso-C₄H₁₀; halomethanes CH₃Cl and CH₃F; and fully halogen substituted nonpolar and polar compounds CF₄, SF₆, CF₃Cl, CF₂Cl₂, and CFCl₃.

EXPERIMENTAL

The apparatus, infrared chemiluminescence measurements, and data analysis were described in the preceding paper. Cylinder gases of high purity were used without further purification in most cases. NO was purified by slow passage through ascarite at atmospheric pressure to remove higher oxides of nitrogen. Since most measured quenching rate constants were of order 10^{-12} cm³ s⁻¹ or larger, small impurities ($\ll 1\%$) as indicated in source analyses could not affect the results.

Two complicating effects need to be discussed briefly: For some quenchers such as CO, NO, and NO₂, slow recombination reactions of atomic reactant with quencher upstream of the chemiluminescence cell were minimized and taken into account by calculation. For CO or NO, for example, the low pressure, three-body reactions $\text{H} + \text{CO} + \text{M} \rightarrow \text{HCO} + \text{M}$ or $\text{H} + \text{NO} + \text{M} \rightarrow \text{HNO} + \text{M}$ followed by reaction of HCO or HNO with another H would lower the rate of formation of HCl[†] and thus mimic a quenching process by its dependence on $[Q]$. This effect was controlled by moving the quencher injector tube closer to the chemiluminescence cell and noting any dependence of the quenching effect on injector distance at constant $[Q]$. Furthermore, since the relevant recombination rate constants are well known, a simple calculation showed that the removal rate of H was negligible in the short residence time. For $Q = \text{NO}_2$, H atom precursor could, of course, not be used because of the very fast $\text{H} + \text{NO}_2$ reaction. The $\text{Cl} + \text{HI}$ and $\text{Cl} + \text{HBr}$ generating reactions had to be used which restricted the attainable HCl v levels to ≤ 4 . The reduction of $[\text{Cl}]$ and thereby of $[\text{HCl}^\dagger]$ by the fast $\text{Cl} + \text{NO}_2 + \text{M}$ reaction ($k_r = 7.2 \times 10^{-31}$ cm⁶ s⁻¹) was calculated by $N_0(\text{corr}) = N_0 \exp[-k_r[\text{NO}_2][\text{M}]/(a/\bar{u})]$, where a is the quencher

^{a)}Present address: Westinghouse Bettis Atomic Power Laboratory, West Mifflin, PA 15122.

TABLE I. Quenching rate constants for $\text{HCl}_{v,v-1}$ by N_2 , CO , and NO .

		$v = 1$	2	3	4	5	6	7
N_2 2330 cm^{-1}	k^Q ($10^{-12} \text{ cm}^3 \text{ s}^{-1}$) ^a	(0.14) ^b	0.45	0.81	1.2	0.70
	k_{LJ} ($10^{-10} \text{ cm}^3 \text{ s}^{-1}$)	3.02	3.06	3.10	3.14	3.19	3.24	3.29
	$P(10^{-2})$	8.9×10^{-3}	...	(0.045)	0.14	0.24	0.37	0.21
	νZ	1.12×10^4	...	(6600)	2900	2000	1600	3300
	ΔE (cm^{-1})	556	452	349	246	143	41	-61
	k^Q ($10^{-12} \text{ cm}^3 \text{ s}^{-1}$)	0.027 ^c						
CO 2143 cm^{-1}	k^Q ($10^{-12} \text{ cm}^3 \text{ s}^{-1}$)	...	(1.2)	1.7	4	17	35	38
	k_{LJ} ($10^{-10} \text{ cm}^3 \text{ s}^{-1}$)	3.07	3.11	3.15	3.20	3.25	3.30	3.35
	$P(10^{-2})$	0.026	(0.4)	0.54	1.3	5.2	10.6	11.3
	νZ	3800	(500)	560	310	96	57	62
	ΔE (cm^{-1})	743	639	536	433	330	228	126
	k^Q ($10^{-12} \text{ cm}^3 \text{ s}^{-1}$)	0.08 ^d						
NO 1876 cm^{-1}	k^Q ($10^{-12} \text{ cm}^3 \text{ s}^{-1}$)	0.29	0.68	2.5	10	27	51	37
	k_{LJ} ($10^{-10} \text{ cm}^3 \text{ s}^{-1}$)	2.99	3.03	3.07	3.11	3.16	3.20	3.25
	$P(10^{-2})$	0.10	0.22	0.81	3.2	8.5	16	11.4
	νZ	(1000)	910	370	125	59	38	61
	ΔE (cm^{-1})	1010	906	803	700	597	495	393

^aFor each Q , top line k^Q from this work, bottom line k^Q from given references.

^bBracketed values are less accurate.

^cReferences 7-9.

^dReferences 7 and 8.

injector to cell distance. This further reduces the accuracy of the quenching rate constants.

A second complication arose for inefficient quenchers, in experiments where $[Q]$ was no longer negligibly small, i.e., of order $\geq 10\%$ of total flow. Since with added Q , the total pressure rose fractionally less than the total flow, all concentrations decreased, and k_p increased slightly with increasing $[Q]$ giving the appearance of quenching when the effect was only one of dilution. Simple analysis shows that in terms of the correction factor $D \equiv (p' \phi_T) / (p \phi_T') \lesssim 1$, where primes denote the presence of added quencher, the simple Stern-Volmer equation (for the highest populated v level) becomes

$$D^3 \frac{N_v^0}{N_v} = 1 + \frac{k^Q D^2 [Q]}{k_p} \quad (1)$$

Since all N_v 's as well as the precursor concentrations, say, $[\text{H}]$ and $[\text{ICl}]$, are equally affected by the dilution effect, the D^3 and D^2 adjustments can be applied also in the more general cascade expression to provide a first-order correction for k^Q . When $[Q]$ is small, i.e., for $k^Q \geq 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, the correction is negligible, but it was included where $\phi_Q \geq 10\%$ of total flow.

RESULTS AND DISCUSSION

In this section, our experimental results are presented, grouped together for related quenchers, in a series of tables and, in some cases, also in the form

of Lambert-Salter plots. Each table shows the quenching rate constants for the particular v states, a Lennard-Jones collision frequency $k_{\text{LJ}} \equiv \pi d_{\text{AB}}^2 \Omega^{(2,2)} [8RT / \pi \mu]^{1/2}$, where $d_{\text{AB}} = (d_A + d_B)/2$ and $\epsilon_{\text{AB}} = (\epsilon_A \epsilon_B)^{1/2}$ were obtained from transport properties,⁵ and $\Omega^{(2,2)}$ as function of ϵ_{AB} from Hirschfelder, Curtiss, and Bird,⁶ the relaxation probability $P \equiv k^Q / k_{\text{LJ}}$, $\nu Z \equiv \nu P^{-1}$ for the Lambert-Salter plots, and ΔE (cm^{-1}), the vibrational energy gap, where simply defined. Inclusion of the $\Omega^{(2,2)}$ integral makes k_{LJ} larger than its corresponding hard sphere collision frequency by factors ranging from 1.2 (N_2) to 1.72 (CH_3Cl). As indicated in the preceding paper, d_{AB} was corrected for the increasing size of HCl^\dagger which increased k_{LJ} ($v=7$) about 20% over k_{LJ} ($v=0$). The vibration frequencies of polyatomic quenchers are also given in the tables. Unless otherwise stated, the accuracy of the k^Q 's is about $\pm 30\%$ (single standard deviation). In the few cases where other measurements are available, their results are also included.

N_2 , CO , and NO

For $Q = \text{N}_2$, the only published data pertain to $k_{1,0}^{\text{N}_2}$, where three measurements⁷⁻⁹ have given $(2.7-2.9) \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$, too slow for us to measure. Three experiments, two with $\text{H} + \text{ICl}$ and one with $\text{H} + \text{Cl}_2$, gave the k^Q values for $v=3$ to 7 shown in Table I. These include fairly large corrections for the dilution effect, and some of them, especially that for $v=3$, have larger uncertainties. The k^Q 's show the expected increase with de-

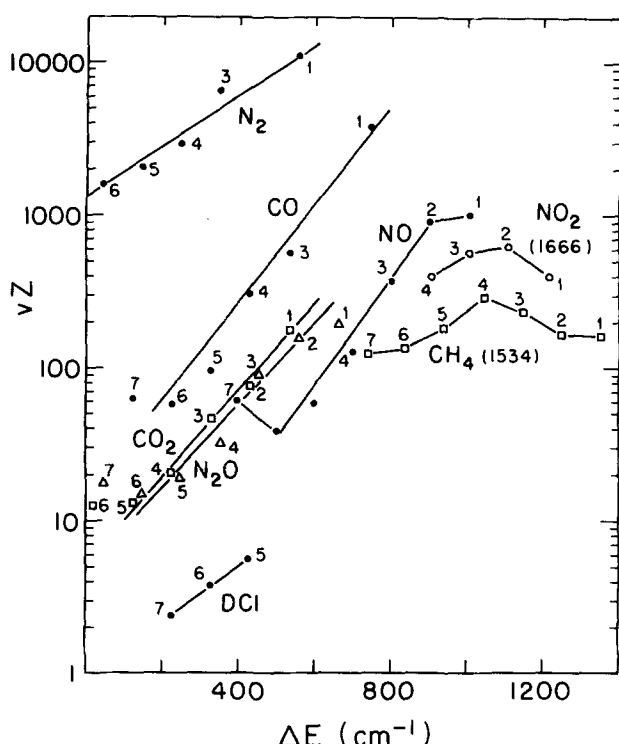


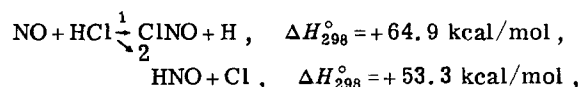
FIG. 1. Lambert-Salter plot.

creasing energy gap and give a fairly normal Lambert-Salter plot in Fig. 1 with a slope $C=3.8 \times 10^{-3}$ cm and intercept of about 1000, in rough agreement with the plot for $HX + N_2, O_2, D_2$ in Lambert's book.¹⁰ It is reassuring to find that k^Q goes through a maximum at $v=6$ where $\Delta E=41$ cm⁻¹, in agreement with the energy gap model and is about 40% smaller at $v=7$ where $V-V$ transfer is 61 cm⁻¹ endothermic.

The only published data for CO, as for N₂, are those for $v=1$, 8.3×10^{-14} and 7.3×10^{-14} cm³ s⁻¹.⁸ One experiment each with $H + ICl$ and $H + Cl_2$, gave the rate constants listed in Table I. They are much larger than the corresponding ones for N₂ even though ΔE is nearly 200 cm⁻¹ larger, presumably due to the strong dipole transition moment of CO. Although a tolerably good Lambert-Salter plot is obtained (Fig. 1), its slope is almost twice as large as that of N₂, and its intercept is a factor of 100 smaller. This is in poorer agreement with Lambert's¹⁰ empirical correlation where it appears that the $HX + AB$ plots fall onto two parallel lines when $X=Cl$ or Br , one for AB infrared inactive and the other for AB infrared active.

No published data seems to be available for HCl^+ relaxation by NO where the energy gap is considerably larger, from 1010 cm⁻¹ for $v=1$ to 393 cm⁻¹ for $v=7$. Four experiments were run, two with $H + ICl$ and one each with $H + Cl_2$ and $Cl + HI$. The results are shown in Table I and Fig. 1. Because k^{NO} does not decrease rapidly as v goes from seven to four, the error accumulation in the cascade is small as is shown by the good agreement of the $k_{4,3}^{NO}$ value of 1.06×10^{-11} from $H + Cl_2$, where $v=4$ is the highest level populated, with 1.00 and 0.82×10^{-11} cm³ s⁻¹ from $H + ICl$ experiments. Considering the large energy defects, the relaxation is very

fast, levels five to seven being relaxed at 8.5%, 16%, and 11% of gas kinetic (Lennard-Jones) collision frequency or 11%, 21%, and 14% of hard sphere collision frequency. k^{NO} , $v=2$ to 6, lie well on a line in Fig. 1 with a slope $C=8.0 \times 10^{-3}$ cm similar to that of CO, but strongly displaced towards smaller νZ and extrapolating to an intercept of less than one. Furthermore, the $v=1$ and 7 points deviate, the former slightly [a plot of $\log Z$ rather than $\log(\nu Z)$ would show much less of a break] but the latter very strongly, since k^{NO} goes through a maximum at $v=6$. It is tempting to consider the two reactive channels:



which become exothermic for HCl , $v=6$ and 5, respectively, but it is unlikely that they are very important for the following reasons: (a) the reverse of (1) has a total rate constant of about 1.6×10^{-11} cm³ s⁻¹¹¹ which, when combined with the fractional yields of HCl^+ given in Table III of the preceding paper, gives 6.4×10^{-13} and 2.4×10^{-12} cm³ s⁻¹ for the rate constant of formation of HCl , $v=6$ and 5, not large enough to suggest that the forward reaction represent a major fraction of HCl^+ removal; (b) the trend in k^{NO} with increasing v does not seem to indicate the opening up of a new channel for $v=6$. On the contrary, there is a decrease from $v=6$ to $v=7$ where the reactive channel should become more important; (c) the removal of HCl $v \geq 5$ by these steps would have complicated the Stern-Volmer analysis which assumes a stepwise cascade, yet the species conservation in the cascade seemed normal. Still, the very efficient quenching process for high v is puzzling. Since rotational effects or strong dipole-dipole forces can be ruled out, and since ΔE is large, one may look to the formation of weakly bound complexes due to the free radical character of NO. Yet, ϵ_{AB} is estimated to be only 400 cal/mol by the simple combination rules, and if such complexes were important, one would expect them to be more prevalent for lower rather than for higher v . The spin-orbit splitting of the $^2\pi_{1/2}$ and $^2\pi_{3/2}$ states of NO (121 cm⁻¹) may be involved in reducing the energy gap as shown by the strikingly parallel Lambert-Salter lines of NO and CO in Fig. 1, but their energy difference of 350 to 400 cm⁻¹ is much larger than the spin-orbit splitting.

HCl, DCl, and HF

The relaxation of HCl^+ by ground-state HCl was the most thoroughly studied quenching process in our laboratory and probably the most successful one. As Table II shows, it has the remarkable property of becoming faster for high v where the endothermic energy defect rises. If the large collisional quenching probability for $v=7$ (15% per Lennard-Jones, 25% per hard-sphere collision) is ascribed to $V-V$ transfer, it would require a three to five times gas kinetic rate in the exothermic ($HCl^6 + HCl^1 \rightarrow HCl^7 + HCl^0$) direction. Combined with the similar findings for $Q=DCI$ where the vibrational energy defect does become small for HCl^+ and for $Q=HF$ where the $V-V$ process is highly endothermic, these results suggest strongly that the process for high

TABLE II. Quenching rate constants for $\text{HCl}_{v,v-1}$ by HCl , DCl , and HF .

		$v = 1$	2	3	4	5	6	7
HCl 2886 cm^{-1}	k^Q ($10^{-12} \text{ cm}^3 \text{ s}^{-1}$) ^a	...	3.4	3.1	(3.6) ^b	18	39	58
	k_{LJ} ($10^{-10} \text{ cm}^3 \text{ s}^{-1}$)	3.52	3.56	3.60	3.65	3.69	3.75	3.79
	P (10^{-2})	...	0.96	0.86	(1.0)	4.9	10.4	15.3
	vZ	...	209	350	400	103	57	46
	ΔE (cm^{-1})	0	-104	-207	-310	-413	-515	-617
	k^Q ($10^{-12} \text{ cm}^3 \text{ s}^{-1}$)		2.6-3.1 ^c 1.4 ²	1.8 ²				
DCl 2041 cm^{-1}	k^Q ($10^{-12} \text{ cm}^3 \text{ s}^{-1}$)	33	59	112
	k_{LJ} ($10^{-10} \text{ cm}^3 \text{ s}^{-1}$)	3.51	3.55	3.59	3.64	3.68	3.73	3.78
	P (10^{-2})	9.0	16	30
	vZ	56	38	24
	ΔE (cm^{-1})	845	741	638	535	432	330	228
	k^Q ($10^{-12} \text{ cm}^3 \text{ s}^{-1}$)		(0.5)	2.5	8	25	45	52
HF 3958 cm^{-1}	k_{LJ} ($10^{-10} \text{ cm}^3 \text{ s}^{-1}$)	3.90	3.95	4.00	4.05	4.10	4.15	4.20
	P (10^{-2})		(0.1)	0.6	2	6.1	10.8	12.3
	vZ		(1600)	480	200	82	55	56
	ΔE (cm^{-1})	-1072	-1176	-1279	-1382	-1485	-1587	-1689

^aFor each Q , top line k^Q from this work, bottom line k^Q from given references.^bBracketed values are less accurate.^cReferences 12-14.

v is mainly $V-R$, T , aided by the strong dipole-dipole interaction in the collision.

Seven experiments were performed for $Q=\text{HCl}$, five with $\text{H}+\text{ICl}$, and one each with $\text{H}+\text{Cl}_2$ and $\text{Cl}+\text{HI}$ as generating reactions. Since the $\text{H}+\text{HCl} \rightarrow \text{H}_2+\text{Cl}$ reaction is moderately fast $k_{298}^{298} \approx 4 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ the quencher injector-to-cell distance was reduced to 10 cm, and the small loss of H due to that reaction was calculated and taken into account. The results for $k_{2,1}^{\text{HCl}}$ may be compared with published data by both laser¹²⁻¹⁴ and infrared chemiluminescence methods²; for $k_{3,2}^{\text{HCl}}$ only with chemiluminescence data,² and for $v \geq 4$, ours are the first available data. As discussed in the preceding paper (Table I), the agreement with the laser data is good, while that with Smith's group² is fair, their k 's being too small for reasons discussed in the preceding paper.

On the assumption that there is $V-V$ relaxation for low v 's but $V-R$, T relaxation for high v 's, the trend in the k_v^{HCl} values is qualitatively explained as the sum of a decreasing or flat k ($V-V$) and increasing k ($V-R$, T) bringing about a flat v dependence for $v=2$ to 4 followed by a sharp rise to $v=7$. Since the $V-R$, T quenching of $v=1$ to $v=0$ is known to be very slow, $k_{1,0}^{\text{HCl}} = 2.6 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$,¹⁵ a direct, experimental confirmation of the above assumption was obtained. If $V-V$ relaxation predominates throughout, the concentration of $\text{HCl } v=1$ must rise sharply as relatively small amounts of HCl quencher are added. Figure 2 shows that this is not so, i.e., that while the $v=7$, 6, and 5 concentrations drop, there is no equivalent increase of $v=1$. This is

made more quantitative by calculating the average fraction of $V-V$ relaxation $F_V \approx -\Delta N_1 / \Delta N_T$, where ΔN_1 is the increase in $[\text{HCl}, v=1]$ and ΔN_T is the sum of the concentration changes in all $v \geq 2$, i.e., $\Delta N_T = 2\Delta N_2 + \sum_{n=3}^{v_{\text{max}}} \Delta N_n$, where ΔN_2 is doubled because for each N_2 , two N_1 are formed by relaxation with N_0 . In three

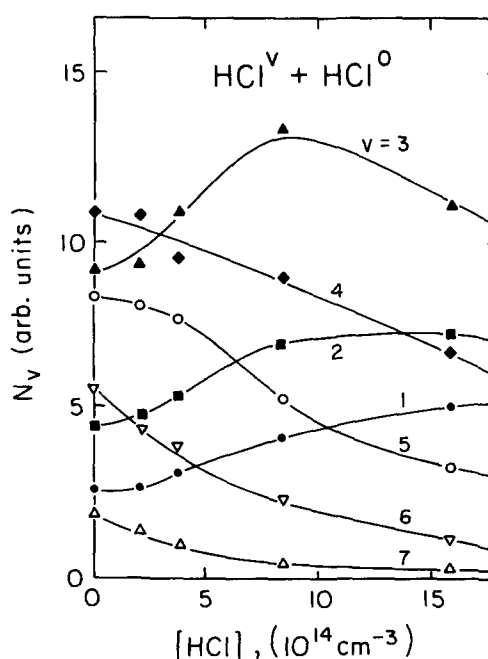
FIG. 2. Relaxation of $\text{HCl } (v=1 \text{ to } 7)$ by $\text{HCl } (v=0)$.

TABLE III. Quenching rate constants for $\text{HCl}_{v,v-1}$ by CO_2 , N_2O , and NO_2 .

		$v = 1$	2	3	4	5	6	7
CO_2 1343 cm^{-1} 667 2349	k^Q ($10^{-12} \text{ cm}^3 \text{ s}^{-1}$) ^a	1.9	9.0	23	70	139	173	102
	k_{LJ} ($10^{-10} \text{ cm}^3 \text{ s}^{-1}$)	3.47	3.51	3.55	3.60	3.64	3.69	3.74
	$P(10^{-2})$	0.55	2.6	6.5	19.4	38	47	27
	νZ	180	78	46	20.6	13.1	12.8	26
	ΔE (cm^{-1})	537	433	330	227	124	22	-80
	k^Q ($10^{-12} \text{ cm}^3 \text{ s}^{-1}$)	2.9 ^b						
N_2O 1277 cm^{-1} 589 2224		2.05 ²	6.8 ²	15.5 ²				
	k^Q ($10^{-12} \text{ cm}^3 \text{ s}^{-1}$)	1.8	4.5	12	45	96	149	152
	k_{LJ} ($10^{-10} \text{ cm}^3 \text{ s}^{-1}$)	3.51	3.55	3.59	3.64	3.68	3.73	3.78
	$P(10^{-2})$	0.51	1.27	3.34	12.4	26.1	40	40
	νZ	195	158	90	32	19	15	17.4
	ΔE (cm^{-1})	662	558	455	352	249	147	45
NO_2 1358 cm^{-1} 757 1665.5	k^Q ($10^{-12} \text{ cm}^3 \text{ s}^{-1}$)	1.4 ^c						
		0.95	(1.2) ^d	2.0	4.0			
	k_{LJ} ($10^{-10} \text{ cm}^3 \text{ s}^{-1}$)	3.85	3.89	3.94	3.99	4.04	4.09	4.14
	$P(10^{-2})$	0.25	(0.31)	0.51	1.0			
	νZ	400	(650)	590	400			
	ΔE (cm^{-1})	1220	1116	1013	910			

^aFor each Q , top line k^Q from this work, bottom line k^Q from given references.

^bReferences 16 and 17.

^cReference 16.

^dBracketed values are less accurate.

experiments, with the $\text{H} + \text{ICl}$ generating reaction and with relatively small added HCl quencher concentrations, F_V was found to be 0.05 to 0.07, whereas with the $\text{Cl} + \text{HI}$ generating reaction, F_V increased from 0.13 to 0.63 with increasing quencher concentration or decreasing k_p . These experiments provide semiquantitative support for the proposed relaxation mechanism but are not sufficiently precise to allow a calculation of the $V-R, T$ branching ratio for intermediate v levels. For $v=6$ and 7, $V-R, T$ predominates.

With a small, available supply of DCl , it was possible to conduct only a single experiment whose results (Table II) for $v=5-7$ show very large relaxation rate constants. Although these three points lie on a good Lambert-Salter line of slope $C=4.3 \times 10^{-3} \text{ cm}$, the magnitude of the k 's is out of line with other HX data.¹⁰ It seems reasonable, therefore, to ascribe the relaxation to the $V-R, T$ process analogous to $Q=\text{HCl}$.

In view of the fast relaxation by HF for which there is a large, endothermic energy defect, the observed process can only be one of $V-R, T$, since the calculated $V-V$ process in the exothermic direction for $v=6$ or 7 would have to be about 500 times faster than gas kinetic. Of the seven experiments with various generating reactions, two had to be discarded for experimental reasons, and the others showed somewhat greater scatter than usual. The results shown in Table II are very similar to those for the equivalent $Q=\text{HCl}$ processes

for $v=5$ to 7, in agreement with the proposed $V-R, T$ mechanism. For $v=2$, k^{HF} is much smaller than k^{HCl} which is also reasonable, since there is no near-resonant $V-V$ channel available in HF . There are no published data available from other sources for comparison.

CO_2 , N_2O , and NO_2

For the sake of completeness and comparison, the data on CO_2 and N_2O from the preceding paper are included here in Table III and Fig. 1.

NO_2 reacts very rapidly with H and could therefore be studied only with HCl ($v \leq 4$) using the $\text{Cl} + \text{HI}$ (two experiments) and $\text{Cl} + \text{HBr}$ (one experiment) generating reactions. The quenching rate constants are listed in Table III, and the Lambert-Salter plot is shown in Fig. 1. Considering the large vibrational energy defect, based on ν_3 of NO_2 , the relaxation is very fast. Furthermore, it does not obey the Lambert-Salter correlation. NO_2 has low-lying, highly perturbed excited electronic states, but their energies are too high to be accessible. Yet the quenching rate constants are quite large even for $v=2$ and 3.

Overtone or combination frequencies such as $2\nu_1$ ($2601, 2667 \text{ cm}^{-1}$)¹⁸ and $\nu_2 + \nu_3$ (2220 cm^{-1}) may be excited. The free radical nature of NO_2 may aid the formation of weakly bound complexes that would favor in-

TABLE IV. Quenching rate constants for $\text{HCl}_{v,v-1}$ by CH_4 , C_2H_6 , C_3H_8 , and iso- C_4H_{10} .

		$v = 1$	2	3	4	5	6	7
CH_4	k^Q ($10^{-12} \text{ cm}^3 \text{ s}^{-1}$) ^a	(3.8) ^b	3.8	4.2	6.0	12	20	25
3019(3) cm^{-1}	k_{LJ} ($10^{-10} \text{ cm}^3 \text{ s}^{-1}$)	4.14	4.19	4.26	4.32	4.37	4.43	4.48
2916	$P(10^{-2})$	0.63 ^c	0.9	1.0	1.4	2.7	4.5	5.6
1534(2)	νZ	160 ^c	168	237	290	185	133	125
1306(3)	ΔE (cm^{-1})	-133 ^d	-237	-340	-443	-546	-648	-750
		+1352 ^e	1248	1145	1042	939	837	735
	k^Q ($10^{-12} \text{ cm}^3 \text{ s}^{-1}$)	2.6 ^f						
C_2H_6	k^Q ($10^{-12} \text{ cm}^3 \text{ s}^{-1}$)	20	21	20	23	27	43	53
2954-85	k_{LJ} ($10^{-10} \text{ cm}^3 \text{ s}^{-1}$)	4.44	4.59	4.65	4.70	4.76	4.81	4.87
2896	$P(10^{-2})$	4.5	4.6	4.3	4.9	5.7	8.9	10.9
1468/9	νZ	22	44	70	82	88	67	64
etc. to 289								
C_3H_8	k^Q ($10^{-12} \text{ cm}^3 \text{ s}^{-1}$)	47	41	38	38	53	86	96
2900-2980	k_{LJ} ($10^{-10} \text{ cm}^3 \text{ s}^{-1}$)	4.88	4.93	4.99	5.04	5.10	5.16	5.22
etc. to 217	$P(10^{-2})$	9.6	8.3	7.5	7.5	10.4	16.7	18.4
	νZ	10	24	40	53	48	36	38
iso- C_4H_{10}	k^Q ($10^{-12} \text{ cm}^3 \text{ s}^{-1}$)	65	55	56	62	75	104	121
2850-2970	k_{LJ} ($10^{-10} \text{ cm}^3 \text{ s}^{-1}$)	5.24	5.32	5.40	5.48	5.56	5.64	5.73
etc. to 225	$P(10^{-2})$	12.4	10.3	10.4	11.3	13.5	18.4	21.1
	νZ	8.1	19	29	35	37	33	33

^aFor each Q , top line k^Q from this work, bottom line k^Q from given references.

^bBracketed values are less accurate.

^cBased on laser value, Ref. 7.

^d ΔE for transfer to 1534 cm^{-1} .

^e ΔE for transfer to 3019 cm^{-1} .

tramolecular $V-V$ redistribution and $V-R$ transfer upon dissociation. A reactive channel $\text{HCl}^v + \text{NO}_2 \rightarrow \text{HONO} + \text{Cl}$ is thermodynamically open for $v \geq 3$, but, in view of the gradual increase of k^{NO_2} with v , it is unlikely to be of major importance. None of these rationalizations seem entirely satisfactory.

CH_4 , C_2H_6 , C_3H_8 , and iso- C_4H_{10}

Relaxation rate constants by the paraffin hydrocarbons, shown in Table IV, present another puzzling problem of interpretation. The data for CH_4 are based on eight experiments, three with $\text{H} + \text{ClI}$, four with $\text{H} + \text{Cl}_2$, and one with $\text{Cl} + \text{HBr}$. The only point of comparison is a laser experiment⁷ for $v=1$ whose $k_{1,0}^{\text{CH}_4} = 2.6 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ is probably to be preferred over our 3.8×10^{-12} that includes a downward correction for the $\text{Cl} + \text{CH}_4$ reaction. k^{CH_4} is fairly constant for $v=2$ to 4 and then rises to 2.5×10^{-11} for $v=7$, where the energy defect with respect to the $\text{C}-\text{H}$ stretching vibrations of CH_4 has become about -750 cm^{-1} so that the process would have to proceed at more than twice the gas kinetic collision rate in its exothermic direction, which is most unlikely. If the infrared-inactive $\text{H}-\text{C}-\text{H}$ bending vibration (1534 cm^{-1}) is taken to be the acceptor, the energy defect is extremely large and positive, and the Lambert-Salter correlation is wrong both in shape and general position. Several alternate explanations may be ad-

vanced, none of them entirely satisfactory: (a) CH_4 has a large rotational constant ($B = 5.2 \text{ cm}^{-1}$) and can carry off a substantial part of the energy defect as rotational energy. For the nearly spherical CH_4 molecule, however, the required collision dynamics would seem unusual. Furthermore, the comparison with the higher paraffins leads to difficulties discussed below. (b) Overtone or combination frequencies may be excited. Although there are such frequencies, e.g., 2600 cm^{-1} ($2\nu_4$) and 2823 cm^{-1} ($\nu_2 + \nu_4$), the transition moments are too weak to explain the high efficiency of the relaxation process. (c) A weakly bound complex may be formed as suggested for NO and NO_2 above. This seems even less probable for CH_4 whose Lennard-Jones well depth, $\epsilon \approx 300 \text{ cal/mol}$. Studies of the temperature dependence may be helpful, although results for $\text{HCl} (v=1) + \text{N}_2$, CO , and D_2^8 all indicate a very slight drop of k^Q with increasing T followed by a slow rise, not very dependent on the nature of Q .

Six experiments were performed for C_2H_6 , four with $\text{H} + \text{ClI}$ and two with $\text{H} + \text{Cl}_2$, (The $\text{Cl} + \text{HBr}$ generating reaction cannot be used with the higher paraffins because the $\text{Cl} + \text{RH}$ reaction is too fast); two for C_3H_8 (one each for $\text{H} + \text{ClI}$ and Cl_2); and three for iso- C_4H_{10} (one $\text{H} + \text{ClI}$ and two $\text{H} + \text{Cl}_2$). No published data are available for comparison.

The trends of k^Q for C_2H_6 , C_3H_8 , and iso- C_4H_{10} are

TABLE V. Quenching rate constants for $\text{HCl}_{v,v-1}$ by CH_3Cl , CH_3F , CF_4 , and SF_6 .

		$v = 1$	2	3	4	5	6	7
CH_3Cl	k^Q ($10^{-12} \text{ cm}^3 \text{ s}^{-1}$)	...	9.5	30	110	170	285	330
3042(2) cm^{-1}	k_{LJ} ($10^{-10} \text{ cm}^3 \text{ s}^{-1}$)	4.17	4.23	4.29	4.36	4.42	4.49	4.56
2928	P (10^{-2})	...	2.2	7.0	25	38	63	72
1460(2)	vZ	...	89	43	16	13	9.4	9.6
1355								
1020(2)								
732								
CH_3F	k^Q ($10^{-12} \text{ cm}^3 \text{ s}^{-1}$)	< 9	11	26	35	72	98	80
3006(2) cm^{-1}	k_{LJ} ($10^{-10} \text{ cm}^3 \text{ s}^{-1}$)	3.48	3.53	3.59	3.65	3.70	3.76	3.82
2965	P (10^{-2})	< 2.6	3.1	7.2	9.6	19.4	26	21
1467(2)	vZ	> 39	64	41	42	26	23	33
1464								
1182(2)								
1049 cm^{-1}								
CF_4	k^Q ($10^{-12} \text{ cm}^3 \text{ s}^{-1}$)	0.18	0.36	0.27	0.39	0.47
1283(3) cm^{-1}	k_{LJ} ($10^{-10} \text{ cm}^3 \text{ s}^{-1}$)	3.38	3.43	3.49	3.55	3.60	3.65	3.70
909	P (10^{-2})	0.05	0.1	0.075	0.1	0.13
631(3)	vZ	5800	3900	6700	5600	5500
435(2)								
SF_6	k^Q ($10^{-12} \text{ cm}^3 \text{ s}^{-1}$)	0.55	(0.1) ^a	≤ 0.1	≤ 0.1	≤ 0.1	~ 0.1	~ 0.16
947(3) cm^{-1}	k_{LJ} ($10^{-10} \text{ cm}^3 \text{ s}^{-1}$)	4.00	4.06	4.12	4.18	4.24	4.30	4.37
770	P (10^{-2})	0.14	(0.02)	(≤ 0.02)	≤ 0.02	≤ 0.02	~ 0.02	~ 0.037
640(2)	vZ	730	(8000)	$\geq 12\,000$	$\geq 16\,000$	$\geq 20\,000$	25 000	19 000
615(3)								
522(3)								
345(3)								

^aBracketed numbers are less accurate.

simple: there is an increase of k^Q for the high v levels roughly proportional to the number of C atoms or to the dispersion energy, polarizability, etc. There is a somewhat larger increase for the low v 's from CH_4 to C_2H_6 followed by a moderate rise for C_3H_8 and C_4H_{10} . Thus, the total range of k^Q for iso- C_4H_{10} is less than a factor of 2 from $v=1$ to 7. Although the characteristic stretching and bending frequencies shift very little, decreasing about 100 cm^{-1} from CH_4 to C_4H_{10} , the larger carbon skeleton gives rise to low frequency torsion and C-C-C bending modes, and there are many more frequencies available altogether, albeit of similar magnitude. The low frequency modes may be collisionally excited along with the $1300\text{--}1400 \text{ cm}^{-1}$ CH_3 bending and deformation modes to take up the large HCl quantum. However, it is not only the low frequency motions that seem to be required, but the presence of hydrogen atoms whose large vibrational amplitudes couple with those of the HCl donor. This is shown below in the comparison with $Q=\text{CF}_4$ and SF_6 . The excitation of external rotation, explanation (a) for CH_4 , does not carry over to C_2H_6 , C_3H_8 , and C_4H_{10} , since their B values are small. If (a) is important for CH_4 , we must assume that the torsional motions more than make up for the loss of rotational excitation for the higher paraffins. It is also tempting to invoke density of states arguments for the higher paraffins even though only $\sim 2300\text{--}2600 \text{ cm}^{-1}$ is being transferred, but this explanation runs into difficulties with SF_6 below.

CH_3Cl , CH_3F , CF_4 , and SF_6

This group of quenchers probes the effects of dipole moment, dispersion forces, and density of vibrational states. The data for CH_3Cl and CH_3F in Table V should be compared with those of CH_4 in Table IV. Six experiments were run for CH_3Cl , two each with $\text{H}+\text{ClI}$, $\text{H}+\text{Cl}_2$, and $\text{Cl}+\text{HI}$; and three for CH_3F , one each for the above three generating reactions. Interference by the $\text{Cl}+\text{CH}_3\text{Cl}$ or CH_3F reactions makes the results of the $\text{Cl}+\text{HBr}$ experiments unreliable. For the upper v 's there is a dramatic increase of k^Q from CH_4 to CH_3F to CH_3Cl . Since the vibration frequencies are unaffected except for the addition of C-X stretching modes at 1048 (CH_3F) and 732 cm^{-1} (CH_3Cl), this effect must be ascribed to dipole moment (1.85 and 1.87 D) and dispersion forces ($\epsilon_{\text{LJ}} = 290 \text{ cal mol}^{-1}$ for CH_3F , 700 for CH_3Cl). The dipole-dipole interaction should be cleanly applicable in CH_3F , where the dispersion forces are small and whose k^Q should be comparable to the $Q=\text{HX}$ cases discussed above. It is reassuring to note that the k^Q 's are indeed comparable for $v=5\text{--}7$, and we suggest $V\text{--}R$, T relaxation for CH_3F . For the lower levels, $V\text{--}V$ relaxation should be faster in CH_3F than in HF and probably also in HCl . The further increase of k^Q from CH_3F to CH_3Cl for high v levels is probably due to the additional dispersion forces, since the dipole moments are equal. The efficiency of CH_3Cl for relaxing HCl , $v=6$ and 7, is surprisingly large, 60%–70% of the Lennard-Jones collision rate or 100%–120% of the hard

TABLE VI. Quenching rate constants for $\text{HCl}_{v,v-1}$ by CF_3Cl , CF_2Cl_2 , and CFCl_3 .

		$v = 1$	2	3	4	5	6	7
CF_3Cl	k^Q ($10^{-12} \text{ cm}^3 \text{ s}^{-1}$)	0.14	0.34	0.65	0.95	1.2
1212(2) cm^{-1}	k_{LJ} ($10^{-10} \text{ cm}^3 \text{ s}^{-1}$)	3.86	3.92	3.98	4.04	4.10	4.16	4.23
1105	$P(10^{-2})$	0.035	0.084	0.16	0.23	0.28
560(2)	νZ	(8500)	(4800)	3200	2600	2500
476								
350(2)								
CF_2Cl_2	k^Q ($10^{-12} \text{ cm}^3 \text{ s}^{-1}$)	< 0.1	0.3	1.6	3.2	4.9
1162 cm^{-1}	k_{LJ} ($10^{-10} \text{ cm}^3 \text{ s}^{-1}$)	4.23	4.29	4.36	4.43	4.49	4.56	4.63
1099	$P(10^{-2})$	< 0.02	0.07	0.36	0.70	1.06
922	νZ	> 13000	5700	1400	860	660
667								
457								
446								
435								
322								
262								
CFCl_3	$k(10^{-12} \text{ cm}^3 \text{ s}^{-1})$		(0.02) ^a	0.28	0.75	2.4	6.7	15
1085 cm^{-1}	k_{LJ} ($10^{-10} \text{ cm}^3 \text{ s}^{-1}$)	4.82	4.89	4.96	5.04	5.11	5.19	5.27
847	$P(10^{-2})$		(0.03)	0.056	0.15	0.47	1.29	2.8
535	νZ		(6500)	5300	2700	1060	460	246
398(2)								
350(2)								
241(2)								

^aBracketed numbers are less accurate.

sphere collision rate.

In sharp contrast, both CF_4 and SF_6 are very inefficient quenchers, so much so that their rate constants are less accurate, because so much quencher gas had to be added that there were substantial dilution corrections. For CF_4 , three $\text{H} + \text{ICl}$ and two $\text{H} + \text{Cl}_2$ experiments were run, and for SF_6 two $\text{H} + \text{ICl}$, two $\text{H} + \text{Cl}_2$, and one $\text{Cl} + \text{HBr}$. There seems to be a small increase of k^Q with increasing v for CF_4 , but even for $v=7$, k is less than 5×10^{-13} , and the relaxation probability is about 10^{-3} per collision. The comparison with CH_4 is instructive. Since it was concluded that $V-V$ transfer to the high C-H stretching frequencies could not be involved for high v 's of HCl (see above), the large difference (factor of ~ 50) between CH_4 and CF_4 cannot be explained simply on the basis of vibration frequencies, because, except for the C-H stretches, these are not very different. The explanation must then rest on rotational effects ($B=0.18 \text{ cm}^{-1}$ for CF_4 vs 5.2 cm^{-1} for CH_4) or on a hydrogen amplitude effect since other interactions (dipole, polarizability) would predict opposite trends.

SF_6 , which is often used as an efficient vibrational relaxer, is still more inefficient and appears to have a barely observable k^Q for $v=6$ and 7. Quite unexpectedly, both $\text{H} + \text{Cl}_2$ experiments and the $\text{Cl} + \text{HBr}$ experiment showed that the lowest $v=1$ state of HCl was the most rapidly quenched of all v levels. We are unable to explain this fact which is unique among our 20 quenchers. The high density of vibrational levels at 2300 to 2800 cm^{-1} excitation energy does not result in a fast quenching process.

CF_3Cl , CF_2Cl_2 , and CFCl_3

Lastly, we report the results of a few experiments with three chlorofluoromethane quenchers that, together with CF_4 , are intended to shed light on dipole moment and dispersion effects in the absence of high H-stretching frequencies. Two $\text{H} + \text{ClI}$ and one $\text{H} + \text{Cl}_2$ for CF_3Cl and CF_2Cl_2 and one $\text{H} + \text{ClI}$ and two $\text{H} + \text{Cl}_2$ for CFCl_3 experiments were run. Table VI shows the expected increase of k^Q with increasing Cl-substitution for the highest v levels, especially for $v=7$. This effect has a surprisingly strong dependence on v , i.e., the ratio $k^{\text{CFCl}_3}/k^{\text{CF}_3\text{Cl}}$ goes from about 12 for $v=7$ to 7 for $v=6$ to less than 4 for $v=5$ and to about 2 for $v=4$. If CF_4 is also included in the series, the overall ratio $k^{\text{CFCl}_3}/k^{\text{CF}_4}$ is larger still, as would be expected (~ 30 to ~ 20 to ~ 9 for $v=7, 6, 5$) and seems to wash out towards the lower v 's. The dipole moments of the three chlorofluoromethanes are roughly equal, 0.50, 0.51, and 0.45D with increasing Cl , so that the rise of k^Q with Cl-substitution must be ascribed to dispersion force effects. Cl-substitution also adds more low frequency vibrations and lowers the higher frequency ones. It seems surprising, then, that the k^Q ratio increases so sharply towards the highest v levels if it is due to dispersion forces, since these should not be very dependent on v .

CONCLUDING REMARKS

Approximately 120 vibrational relaxation rate constants are reported in these two papers. They need to be compared with theoretical prediction, particularly regarding the relative effects of donor excitation and

quencher structure. There is an abundance of theoretical work on vibrational relaxation, but it deals mainly with isolated cases where the success of calculating a given k^Q more or less accurately does not assure the correctness of the basic physical model. Furthermore, the theoretical models cannot, in general, be extended to take account of the complexities of polyatomic quencher molecules.

Most of the theories calculate the probability of collisional energy transfer on the basis of an interaction potential by perturbation or detailed trajectory methods, while others use a phenomenological, e.g., information-theoretic¹⁹ approach. The former cover interactions of simple repulsion,^{20,21} long range multipole attraction,²² detailed semiclassical,²³ or *ab initio* quantum mechanical^{24,25} potential energy surfaces, and they use various approximate treatments of the collision trajectories. Recent results have been particularly encouraging in the HF(v)+HF(0) case^{24,25} where the calculations have predicted the preponderance of V - R , T relaxation for high v levels and have given reasonable numerical results²⁵ for the absolute magnitude of the total relaxation rate constant and of its v dependence. These findings are directly applicable to and supported by the HCl(v)+HCl(0) data presented here.

It seems obvious that calculations which include such detailed description are not feasible for most polyatomic quenchers for lack of information on potential energy surfaces and on trajectories. Even if that information were available, the requirements of computer time to carry out the trajectory calculations would be excessive. On the other hand, the appealing phenomenological approach based on the controlling importance of the energy gap seems not to be supported by our data. It is tempting to appeal to complex formation²⁶ as the *deus ex machina* to rationalize fast relaxation rates, but neither the v nor Q dependence appear to fit. The observed rates are thus probably the reflection of a complicated superposition of V - V , V - R , T , dipole-dipole, dispersion forces, and weakly bound complex formation effects. If so, it is important to try to isolate the different effects experimentally as we have tried to do here and are continuing to do in a series of HF(v) quenching experiments; and it is particularly important that theoretical work be initiated to calculate the contributions of the different mechanisms to overall relaxation processes using the best *ab initio* and semiempirical models.

ACKNOWLEDGMENTS

This work was supported by the Advanced Research

Projects Agency and by the Air Force Office of Scientific Research under Grant No. AFOSR 80-0207A.

- ¹G. Hancock and I. W. M. Smith, Appl. Opt. **10**, 1827 (1971); G. Hancock, C. Morley, and I. W. M. Smith, Chem. Phys. Lett. **12**, 193 (1971); G. Hancock, B. A. Ridley, and I. W. M. Smith, J. Chem. Soc. Faraday Trans. 2 **68**, 2117 (1972).
- ²B. A. Ridley and I. W. M. Smith, J. Chem. Soc. Faraday Trans. 2 **68**, 1231 (1972).
- ³J. R. Airey and I. W. M. Smith, J. Chem. Phys. **57**, 1669 (1972).
- ⁴D. J. Douglas and C. B. Moore, Chem. Phys. Lett. **57**, 485, (1978); G. M. Jursich and F. F. Crim, J. Chem. Phys. **74**, 4455 (1981).
- ⁵R. C. Reid and T. K. Sherwood, *The Properties of Gases and Liquids* (McGraw-Hill, New York, 1966) p. 632.
- ⁶J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1964).
- ⁷H.-L. Chen and C. B. Moore, J. Chem. Phys. **54**, 4080 (1971).
- ⁸J. M. Allée, M. Margottin-Maclou, J. Ménard, and L. Doyenette, C.R. Acad. Sci. Paris B **279**, 305 (1974).
- ⁹J. F. Bott and N. Cohen, J. Chem. Phys. **63**, 1518, 1975.
- ¹⁰J. D. Lambert, *Vibrational and Rotational Relaxation in Gases* (Clarendon, Oxford, 1977), p. 109.
- ¹¹H. Gg. Wagner, U. Welzbacher, and R. Zellner, Ber. Bunsenges. Phys. Chem. **80**, 1028 (1976).
- ¹²B. M. Hopkins and H.-L. Chen, J. Chem. Phys. **57**, 3816 (1972).
- ¹³I. Burak, Y. Noter, A. M. Ronn, and A. Szöke, Chem. Phys. Lett. **17**, 345 (1972).
- ¹⁴S. R. Leone and C. B. Moore, Chem. Phys. Lett. **19**, 340 (1973).
- ¹⁵H.-L. Chen and C. B. Moore, J. Chem. Phys. **54**, 4072 (1971).
- ¹⁶L. Doyenette, F. A. Adel, A. Chacroun, M. Margottin-Maclou, and L. Henry, J. Chem. Phys. **63**, 1479 (1975).
- ¹⁷H. L. Chen, J. C. Stephenson, and C. B. Moore, Chem. Phys. Lett. **2**, 593 (1968).
- ¹⁸G. Herzberg, *Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand, New York, 1945), p. 284.
- ¹⁹I. Procaccia and R. D. Levine, J. Chem. Phys. **63**, 4261 (1975).
- ²⁰R. N. Schwartz, Z. I. Slawsky, and K. F. Herzfeld, J. Chem. Phys. **20**, 1591 (1952).
- ²¹F. I. Tanczos, J. Chem. Phys. **25**, 439 (1956).
- ²²R. D. Sharma and C. A. Brau, J. Chem. Phys. **50**, 424 (1969); R. D. Sharma, Phys. Rev. A **2**, 173 (1970).
- ²³H. K. Shin, J. Chem. Phys. **63**, 2901 (1975); H. K. Shin and Y. H. Kim, *ibid.* **73**, 3186 (1980).
- ²⁴G. D. Billing and L. L. Poulsen, J. Chem. Phys. **68**, 5128 (1978).
- ²⁵M. E. Coltrin and R. A. Marcus, J. Chem. Phys. **73**, 4390 (1980).
- ²⁶R. J. Gordon, J. Chem. Phys. **74**, 1676 (1981).