Infrared Chemiluminescence Studies of CI + HI, HBr, DBr, PH₃, PD₃, and GeH₄: Vibrational Energy Disposal and Rate Constants

M. A. Wickramaaratchi and D. W. Setser'

Department of Chemistry, Kansas State University, Manhattan, Kansas 66506 (Received: June 3, 1982; In Final Form: September 9, 1982)

The Cl + HI, HBr, DBr, GeH_4 , PH_3 , and PD_3 reactions were studied at room temperature with infrared chemiluminescence from a flowing afterglow apparatus. The HCl and DCl vibrational energy distributions and the relative rate constants for $Cl + PH_3$, GeH_4 and HI were measured. Since the rate constant for the Cl + HI reaction is available in the literature, the relative measurements can be converted to absolute rate constants. The HCl distribution from Cl + HI was $v_1:v_2:v_3:v_4 = 0.07:0.24:0.49:0.20$, which is in good agreement with cold-wall, arrested-relaxation results. The vibrational energy distributions are $v_1:v_2:v_3 = 0.79:0.19:0.02$ for GeH₄, $v_1:v_2:v_3 = 0.54:0.43:0.03$ for PH₃, $v_1:v_2:v_3:v_4 = 0.20:0.48:0.22:0.10$ for PD₃, $v_1:v_2 = 0.75:0.25$ for HBr, and $v_1:v_2:v_3 = 0.33:0.55:0.12$ for DBr. The Cl + GeH₄ and PH₃ reactions are approximately two times faster than Cl + HI. Einstein coefficients for a range of vibrational-rotational levels of HCl, HF, DCl, and DF are presented in the Appendix.

Introduction

The HCl vibrational-rotational distributions from the Cl + HI reaction was one of the first studied by Polanyi's group¹⁻³ using the infrared chemiluminescence arrestedrelaxation technique, and it has served as the prototype for discussion of the dynamics of the X + HX' class of reactions.⁴ In the present work we have studied the reactions between Cl atoms and some hydrides and deuterides (GeH₄, PH₃, PD₃, and DBr) and reinvestigated the Cl + HI, HBr reactions using a room temperature, flowing-afterglow technique. We previously have used the flowing-afterglow technique to study H, F, and O atom reactions yielding HCl, HBr, HF, and OH.^{4a,5-8} The Cl + HI reaction was used as a reference reaction for determining the relative rate constants for Cl + GeH₄ and PH₃ and to test the flowing afterglow technique as a means of obtaining initial HCl vibrational distributions. The absolute rate constant for Cl + HI reaction is (1.55 ± 0.8) \times 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ at 295 K, as reported by Mei and Moore⁹ in their study of the temperature dependence of the Cl + HI and HBr reactions.

The bond dissociation energies, the enthalpies of the reactions, and the total energy available for the products are listed in Table I. The ΔH_0° values given in Table I

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TABLE I: Bond Dissociation Energies, Enthalpies of **Reaction**, and Available Energies

$\begin{array}{c} \text{Cl} + \text{H-R} \rightarrow \\ \text{HCl} + \text{I} \end{array}$	$D_0^{\circ}(H-R), c$ kcal mol ⁻¹	$\Delta H_0^{0,a}$ kcal mol ⁻¹	$\langle E \rangle_{avail}^{b}$ kcal mol ⁻¹	ref for $D_0^0(H-R)$
$\frac{\text{Cl} + \text{HI} \rightarrow}{\text{HCl} + \text{I}}$	70.4	-31.9	34.4	10
$\begin{array}{r} Cl + HBr \rightarrow \\ HCl + Br \end{array}$	86.6	-15.7	18.2	10
$Cl + DBr \rightarrow DCl + Br$	87.7 ^c	~15.8	18.3	С
$Cl + PH_3 \rightarrow HCl + PH_3$	79.0	-23.3	26.1	12b
$Cl + PD_3 \rightarrow DCl + PD_1$	81.7 ^c	-21.8	24.6	С
$Cl + GeH_4 \rightarrow HCl + GeH_2$	78.0	-24.3	27.1	13

 $^{a} - \Delta H_{0}^{0} = D_{0}^{0}(\text{H-Cl}) - D_{0}^{0}(\text{H-R}); D_{0}^{0}(\text{H-Cl}) = 102.3 \text{ kcal}$ mol⁻¹ from ref 10; $D_{0}^{0}(\text{D-Cl}) = 103.5 \text{ kcal mol}^{-1}$ obtained by making zero point energy correction to D_0^0 (H-Cl). The vibrational constants for HCl and DCl were taken from ref 14. $^{b}\langle E \rangle_{avail} = -\Delta H_{0}^{\circ} + E_{a} + nRT/2$ (*n* = 5 for linear molecules and 6 for nonlinear molecules); E_{a} was assumed as 1 kcal mol⁻¹ for all the reactions. ^c Obtained by making zero point energy corrections to $D_0^{\circ}(H-R)$. The vibrational frequencies of PH, and PD, were taken from ref 15 and those of PH, and PD, were taken from ref 16. The vibrational constants for HBr and DBr were taken from ref 14.

apply to ground state $Cl(^{2}P_{3/2})$, $Br(^{2}P_{3/2})$, and $I(^{2}P_{3/2})$ atoms. The energy differences between the two spin-orbit states of Cl is 2.5 kcal mol⁻¹ and the reactions will be

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dominated by the $Cl(^{2}P_{3/2})$ reactant state at room temperature. The available energies are sufficient to yield $HCl(v \le 4)$ from HI, $HCl(v \le 3)$ from PH₃ and GeH_4 , HCl- $(v \le 2)$ from HBr, DCl $(v \le 4)$ from PD₃, and DCl $(v \le 3)$ from DBr. The limited range of available vibrational levels gives much more weight to the population in v = 0, relative to F atom reactions with these hydrides. The use of deuterium substituted compounds adds one more observable vibrational level and aids in the extropolation to find the DCl(v=0) population.

Experimental Section

The experimental apparatus in this work is similar to that described in previous work.⁵⁻⁸ The reactions were carried out in a 5.5-cm o.d. Pyrex flow reactor. Chlorine atoms were produced by passing Cl₂ through a microwave discharge in an alumina tube which was interfaced to the flow reactor along the flow axis. The reactions were carried out in Ar carrier with a flow velocity of about 120 ms⁻¹ and a total pressure of 0.7 torr. The total Ar flow was about 9 mmol s^{-1} ; 10% of this was added to the Cl₂ flow. Infrared emission was observed perpendicular to the flow axis through a NaCl window situated about 3.5 cm downstream from the reagent inlet. Thus, the reaction time was ≈ 0.3 ms.

The DBr was synthesized^{17a} from the reaction of PBr₃ with D_2O . The other product, D_3PO_3 , was pyrolyzed^{17b} to synthesize PD_3 . Both DBr and PD_3 were purified and the purity was checked by spectroscopic methods. The Cl₂, GeH_4 , PH_3 , HBr, and HI (Matheson Co.) were treated by freeze-pump-thaw cycles before the dilute reagent/Ar mixtures were prepared. The mixtures were stored in glass reservoirs. The reagent flow rates were measured by calibrated capillary flow meters. Both PH_3 (or PD_3) and GeH_4 are pyrophoric and must be handled with great care.

The HCl and DCl emission spectra were recorded with a Fourier transform spectrometer equipped with an InSb detector. The height of each rotational line was divided by the corresponding Einstein coefficient and also by a factor proportional to the detector response, to obtain the relative rotational population, N_J , of each J level. The detector response was obtained by calibration with a blackbody standard. The relative vibrational populations, P_{v} , were then obtained from plots of $\ln \left[N_{J} / (2J + 1) \right]$ vs. J(J + 1). The sum of the vibrational populations is proportional to the total HCl product formed at the observation window. This sum was used in the relative rate constant plots, which are first-order plots of this sum vs. reagent concentration.

The Einstein coefficients for HF, HCl, and HBr were reported^{7,18} in previous work from this laboratory. The same computation method was used to calculate the Einstein coefficients of DCl and the results are given in the Appendix of this paper. The Einstein coefficients of HCl reported in ref 18 were calculated by use of the dipole moment expansion coefficients given in ref 22. There is a typographical error in ref 22; hence, the HCl Einstein coefficients were recalculated with the correct dipole constants²³ and these new HCl Einstein coefficients, which



Figure 1. The HCI vibrational energy distributions from CI + HI as a function of Cl₂ flow (in μ mol s⁻¹). A Cl₂ flow of 1 μ mol s⁻¹ corresponds to a Cl atom concentration of 2 × 10¹² atoms cm⁻³, assuming 50 % dissociation of Cl₂. [HI] = 1.2×10^{12} molecules cm⁻³.

were used in the present work, are also tabulated in the Appendix. Even though the DF Einstein coefficients are not used in this paper, for convenience, they also are included in the Appendix.

In recording HCl spectra, a quartz filter was placed in front of the detector to reduce the unwanted low-frequency background. Unfortunately, the fundamental IR spectrum of DCl lies beyond the cutoff region of this filter. Therefore, a band-pass filter which covered only the DCl(v < 4) spectral region (2200–1800 Å) was used to record the DCl spectra. The spectral response for the system with the band-pass filter was measured and corrections were made to the DCl line intensities before they were converted to relative vibrational populations. Due to the weak nature of DCl emission (Einstein coefficients of DCl are about 4 times smaller than those of HCl), we experienced considerable difficulty in recording the DCl spectra. In order to achieve a good signal-to-noise ratio, we collected 1000 scans for DCl spectra, whereas extremely good HCl spectra normally could be obtained with 100 scans. Due to the limited quantities of deuterated reagents and since collecting 1000 scans at 1-cm⁻¹ resolution requires \sim 3 h, some of the DCl spectra (especially Cl + DBr) were obtained with a resolution of 4 cm^{-1} . Since many of the DCl lines are overlapped, only a few rotational lines could be used in the calculation of relative populations. Thus, the uncertainty in the DCl(v) population is approximately two times larger than for HCl(v).

Results

Our first goal was to demonstrate that the flowing-afterglow technique gave initial HCl vibrational distributions from a well-characterized reaction vielding HCl(v). Therefore, the Cl + HI reaction was first studied. The emission intensities were shown to be first order in both HI and $Cl_2(Cl)$ flow rates. The rotational distributions were found to be Boltzmann (300 K) for all v levels; emission from rotational levels above J = 10 was not observed. Acceptable HI and $Cl + Cl_2$ concentration ranges were found for which the HCl(v) populations were independent of reagent concentrations. Below $\sim 0.6 \ \mu mol \ s^{-1}$ $(\sim 1 \times 10^{12} \text{ molecule cm}^{-3})$ of Cl₂, see Figure 1, and 2 μ mol s^{-1} of HI (not shown) there was no significant variation of

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		P _v (HC	$(D)^d$ or $P_v(D)$	$(Cl)^d$				
reaction	v = 0	<i>v</i> = 1	<i>v</i> = 2	v = 3	v = 4	λV^{e}	$\langle f_V \rangle$	ref
Cl + HI		0.07	0.24	0.49	0.20			this work
	0.03^{a}	0.07	0.23	0.48	0.19	-6.2 ± 0.6	0.64	
		0.10	0.15	0.43	0.32			1
	0.02^{a}	0.10	0.15	0.42	0.31		0.68	
	0.03	0.10	0.21	0.40	0.26		0.65	19
		0.10	0.23	0.48	0.19			20
	0.03	0.10	0.22	0.47	0.18		0.64	
Cl + HBr		0.75	0.25					this work
01 112	0.33^{b}	0.50	0.17			-3.0	0.38	01110 // 0111
		0.71	0.29			••••		1
		0.89	0.11					20
		0.90	0.10					21
$C \cup DBr$		0.33	0.55	0.12				this work
$OI \neq DDI$	0.11^{a}	0.00	0.49	0.12		-48 ± 01	0.52	this work
	0.11	0.20	0,40	0.11			0.02	
$Cl + PH_3$		0.54	0.43	0.03				this work
	0.09^{a}	0.49	0.39	0.03		-7.8 ± 1.5	0.44	
Cl + PD.		0.20	0.48	0.22	0.10			this work
	0.04^{a}	0.19	0.46	0.21	0.10	-9.0 ± 0.51	0.51	
		0.50	0.10	0.00				
$CI + GeH_4$	0 450	0.79	0.19	0.02		0 5 1 0	0.01	this work
	0.45	0.43	01.0	0.02		-2.7 ± 1.2	0.21	
	0.29°	0.55	0.14	0.02			0.27	

^a The value of $P_{v=0}$ was obtained from the linear surprisal extrapolation. ^b The value of $P_{v=0}$ was obtained by using $P_1/P_0 = 1.5 \pm 0.3$ from ref 19. The linear surprisal extrapolation gives $v_0:v_1:v_2 = 0.31:0.51:0.17$. ^c This entry corresponds to $P_{v=0} \approx 1/2P_{v=1}$. ^d Experimental uncertainties are approximately $\pm 10\%$ and $\pm 20\%$ for the $P_v(\text{HCl})$ and $P_v(\text{DCl})$ values, respectively; the uncertainties are larger for Cl + HCl and DCl (see text). ^e A three-body prior was used for the Cl + HX reactions, but the rotational degree of freedom of PH₂ or GeH₃ was added to the three-body prior for the germane and phosphine reactions. This affects the λ_V values but not the $\langle f_V \rangle$ values.

 P_{ν} (HCl) with reduction of flow rate of either reagent. The HCl distribution $(v_1:v_2:v_3:v_4 = 0.07 \pm 0.01:0.24 \pm 0.01:0.49 \pm 0.01:0.20 \pm 0.02)$ obtained from the average of several experiments at low [HI] and [Cl₂] is given in Table II. This distribution compared favorably with the coldwall-arrested relaxation results from Polanyi's laboratory $(v_1:v_2:v_3:v_4 = 0.10:0.15:0.43:0.32)$. The apparent difference mainly is a consequence of the use of different Einstein coefficients to convert intensities to relative populations, as will be considered in the Discussion section. Our results also agree with the distribution from chemical laser experiments. The Cl + HI reaction, thus, establishes that the infrared chemiluminescence flowing-afterglow technique is applicable to Cl atom reactions yielding HCl.

The dependence of the relative HCl vibrational populations on GeH₄ and PH₃ concentration are shown in Figure 2. These experiments were done with a Cl₂ flow of 0.3 µmol s⁻¹ (i.e., [Cl] = 8.2×10^{11} molecule cm⁻³ assuming 50% dissociation). Below GeH₄ or PH₃ flows of ~2 µmol s⁻¹ there was no apparent change in relative HCl(v) population. Even with the lowest possible flows, the population of v = 1 was always larger than that of v= 2 for both GeH₄ and PH₃; the mean distributions from the low flow rate experiments are tabulated in Table II. The two distributions differ appreciably with the v_1/v_2 ratio from PH₃ being nearly unity and that for GeH₁ larger than unity. Evidence for secondary reactions was observed for high Cl₂ flow or longer reaction times; these results are mentioned at the end of this section.

The difficulties associated with recording DCl spectra were mentioned in the Experimental Section. Even after collecting 1000 scans, it was impossible to obtain an analyzable spectrum from the slow Cl + DBr reaction by using the reagent concentrations quoted in the previous paragraph. Therefore, Cl + DBr spectra were recorded at low resolution (4 cm⁻¹) with a Cl_2 flow of 0.6 μ mol s⁻¹. Even though this Cl_2 flow is two times greater than that used



Figure 2. Dependence of HCl vibrational distribution for Cl + GeH₄, PH₃ on reagent concentration (molecules cm⁻³). If we assume a 50% dissociation of Cl₂, [Cl] = 0.8×10^{12} atoms cm⁻³, which according to Figure 1 gives little or no relaxation.

for other reactions, only a very little relaxation of DCl(v), if any, can be expected because the HCl spectra taken under the same conditions for Cl + HI did not show any significant relaxation. Since Cl + PD₃ is a faster reaction, recording of DCl spectra from this reaction with a Cl₂ flow of 0.3 μ mol s⁻¹ was possible by improving the signal-tonoise ratio by collecting 500-1000 scans.

The Cl + HBr reaction was not extensively studied because only HCl(v=1) and HCl(v=2) can be observed. However, experiments were done so that comparison with

TABLE III: Comparison of Relative Rate Constants

reaction	rel rate constant	ref
 $Cl + HI^a$	1.0	9 ^d
Cl + HBr	0.05	9 ^a
Cl + DBr	0.033	32^d
$Cl + PH_3$	1.6 ± 0.3	this work; P _o not included
	1.7 ± 0.6	this work; P_{o} included
$Cl + GeH_4$	1.9 ± 0.3	this work; P_0 not included
	2.8 ± 0.6	this work; P_0 from entry 2. Table II
	2.4 ± 0.6	this work; P_0 from entry 3. Table II
	16 + 11	33d
$F + HI^{b}$	1.0 - 1.1	00
F + HBr	1 1	34^d
F + DBr	0.78	34d
F + PH	17	120
F + GeH	8 1	31
$O + HI^{c}$	1.0	
O + HBr	0.02	35 ^d
O + GeH	2.2	8
4		

^a The absolute rate constant is $k(Cl+HI) = (1.55 \pm 0.08) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ at 294.5 K from ref 9, which also reports k at other temperatures. ^b The absolute rate constant is $k(F+HI) = (4.09 \pm 0.08) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ at 293 K from ref 34 which also reports k at other temperatures. ^c The absolute rate constant is $k(O+HI) = 1.6 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ at 300 K from ref 35 which also reports k as a function of temperature. ^d The absolute values given in these references were converted to the relative values given in this table.

Cl + DBr could be made. The results tabulated in Table II are the mean value from two experiments, which were done with a Cl₂ flow of 0.6 μ mol s⁻¹ of Cl₂ and less than 1.0 μ mol s⁻¹ of HBr. (See Note Added in Proof for additional results.)

So that the relative rate constants for the $Cl + PH_3$ and GeH₄ reactions could be determined, it is necessary to obtain values for $P_{\nu=0}$. Approximate values of P_0 were obtained from linear surprisal extrapolations. The three-body prior was used for Cl + HI, HBr, and DBr and the model II prior,^{13c} which includes the rotational degrees of freedom of the polyatomic product fragment, was used for Cl + GeH₄, PH₃, and PD₃. These results are summarized in Table II and the plots of P_v vs. f_V are shown in Figure 3 together with surprisal plots. The P_0 from the surprisal plot closely agress with the v = 0 population measured¹⁹ for Cl + HI by the chemical laser technique. The PH₃ and PD₃ linear surprisals have approximately the same λ_{V} . Thus, we consider that P_0 is uncertain only for $Cl + GeH_4$; see the Discussion section. The DBr surprisal also is linear and the λ_V and $\langle f_V \rangle$ values parallel the HI results. On the basis of the line through the two data points, the slope of the HBr surprisal is lower than that for DBr; but, the experimental uncertainty of the HBr and DBr results preclude a final decision on the point.

The relative rate constants, given in Table III, were obtained from the slopes of plots (Figure 4) of the total relative $HCl(v \ge 1)$ concentration against the reagent concentration for the same [Cl]. The plots are linear, and for reagent concentrations up to about 2.5×10^{12} molecules cm⁻³ the HCl(v) intensity (concentration) was first order. Most effort was spent on the Cl + HI reaction, which was shown to serve well as a reference reaction for future work using relative HCl infrared emission intensities to measure HCl product formation rate constants. Due to the limited quantites of the reagents, the rate constants were not



Figure 3. Vibrational surprisal and vibrational distribution plots. The surprisal plots for (a) and (b) used model II priors; (c) and (d) used model I priors; (a) Cl + PH₃, PD₃, and GeH₄ (the low $P_{v=0}$ choice in Table II was plotted for Cl + GeH₄; hence, the surprisal plot is not shown. (b) O + GeH₄, F + GeH₄ and PH₃; results taken from ref 8, 13d, and 12b, respectively. (c) Cl + HI, HBr, and DBr. The dotted line is for the Cl + HBr points and is shown only to illustrate the apparent difference relative to Cl + DBr. (d) O + HI, F + HI and HBr; results taken from ref 8 and 4a, respectively.



Figure 4. Plot of relative HCI($\nu \ge 1$) product concentration vs. reagent concentration for CI + HI, PH₃, and GeH₄.

determined for the $Cl + PD_3$ and Cl + DBr reactions. No effort was made to determine the rate constant for Cl + HBr, since it is well established.⁹

Recently Zwier et al.²¹ reported the reactions between Cl^{-} ions and HI and HBr. The HI reaction can yield $HCl(v \leq 2)$. The possibility of a contribution from the reaction

$$Cl^- + HI \rightarrow HCl + I^- \qquad \Delta H^\circ = -19 \text{ kcal mol}^{-1}$$
 (4)

in our system was eliminated in the following experiment. A pair of copper grids was placed perpendicular to the flow, just before the reagent inlet. This grid system was operated at a floating potential of about +30 V to collect any negative ions. The relative vibrational populations given by the spectra obtained under these conditions were the same as those obtained without the grid.

If the chemiluminescence from $Cl + PH_3$ or GeH_4 was observed for long reaction times ($\sim 2 \text{ ms}$) or for high Cl₂ flows (<10 μ mol s⁻¹), weak HCl emission from high v levels $(v \le 5 \text{ for GeH}_4 \text{ and } v \le 4 \text{ for PH}_3)$ could be observed. Both reactions also generate a weak blue-green chemiluminescence under these conditions. The HCl(high v) and visible emission undoubtedly is a consequence of fast secondary (and possibly tertiary) reactions between Cl atoms and PH_2 and GeH_3 . The visible emission from Cl + PH₃ was recorded with a McPherson 1-m monomchromator equipped with an RCA C-31034 photomultiplier. The slit widths were between 100 and 300 μ m. The spectrum is extremely weak; however, some bands of the v' = 0 progression of PCl(A³ $\Pi \rightarrow X^{3}\Sigma^{-}$) could be identified. Visible emissions were also observed from the reactions of O and F atoms with PH_3 and GeH_4 . The F + PH_3 spectrum was recorded with the above-mentioned experimental setup; the emission from the F atom system was more intense than from Cl + PH₃. Some bands of the v' = 0 and 1 progressions of PF(A³II \rightarrow X³ Σ^{-}) and the $\Delta v =$ 0 sequence of $PF(b^1\Sigma^+ \rightarrow X^3\Sigma^-)$ could be easily identified in the visible and near-IR regions. A banded feature around 3400 Å cannot be assigned for any known PF systems. This may be the 0–0 band of the PH($A^{3}\Pi \rightarrow X^{3}\Sigma^{-}$) system. However, this assignment cannot be confirmed without further experiments. These observed results for $F + PH_3$ may be explained in terms of the following reaction channels:

$$+ PH_2 \longrightarrow PH_2F \xrightarrow{PF^* + H_2} \Delta H^{\circ}_{0} \sim -97 \text{ kual mol}^{-1}$$

F

TABLE IV: Comparison of HCl Einstein Coefficients

	Eins coef	stein f, s ⁻¹		Ein coef	stein f, s ⁻¹
transition	this work	ref 3	transition	this work	ref 3
A 1-0	34.6	33.9			
A_{2-1}^{1}	59.5	61.7	A_{2-0}	4.2	2.32
A_{3-2}	74.4		A 3-1	13.4	6.44
A_{4-3}	79.7		A_{4-2}	28.3	11.9
A_{3-4}	75.8		A_{a}^{\dagger}	49.6	18.2

Discussion

I. Cl + HI, HBr, and DBr. The present study demonstrates that the flowing-afterglow method can give initial HCl vibrational distributions from Cl atom reactions provided that the Cl and reagent concentration range is $\lesssim 10^{12}$ molecule cm⁻³. The apparent difference between our $P_{v}(\text{HCl})$ from Cl + HI and those from cold-wall-arrested relaxation experiments³ is mainly a consequence of the Einstein coefficients. In Polanyi's pioneering studies, the Heaps and Herzberg²⁴ expression with the dipole moment coefficients of Benedict et al.²⁵ were used to obtain Einstein coefficients. More recently, accurate dipole moment functions have become available.^{22,26} We have used the Herbelin and Emanuel's²² dipole function to obtain accurate A_{vJ} (HCl) for a wide range of v and J (see Appendix). The two sets of vibrational Einstein coefficients are compared in Table IV. Since Polanyi and co-workers³ used both $\Delta v = 1$ and $\Delta v = 2$ transitions from a wide range of J levels to obtain their relative vibrational populations, making adjustments to their vibrational distribution is not straightforward. Nevertheless, it is evident from the variation of $A_{v \rightarrow v-2}$ with v that the two studies would obtain different relative populations for v = 3 and 4 and that the older Einstein coefficients would give somewhat larger v= 3 and 4 populations. In fact, scaling Polanyi's populations by the ratios of the two sets of $\Delta v = 2$ Einstein coefficients changes their P_v values into close agreement with our result.

Using the chemical laser technique, Bittenson¹⁹ reported population ratios for Cl + HI: $P_1/P_0 = 3.8 \pm 1.3$, P_2/P_1 = 2.2 ± 0.5, $P_3/P_2 = 1.9 \pm 0.6$, and $P_4/P_3 = 0.65 \pm 0.12$. After normalization this distribution becomes 0.03:0.10:0.21:0.40:0.26. The experimental results based on the chemical laser technique employed by Bittenson¹⁹ depend upon establishment of the rotational equilibrium within each vibration manifold of the laser species. Since rotational nonequibrium effects, in fact, were observed,¹⁹ exact agreement between the two sets of data cannot be expected. However, the agreement is within experimental uncertainty, and, above all, the chemical laser work gives an experimental measurement for P_0 . The vibrational distribution reported by Berquist eq al.²⁰ for Cl + HI, also in flowing-afterglow experiments, is in close agreement with ours (Table II).

The vibrational (and rotational) energy disposal pattern for Cl + HI, $\langle f_V(\text{HCl}) \rangle = 0.64$, closely parallels that for F + HI,^{4a} F + HBr,^{4a} or O + HI;⁸ $\langle f_V \rangle = 0.59$, 0.59, and 0.67, respectively. The surprisal plots are all approximately linear (see Figure 3). Trajectory calculations on repulsive type potential surfaces reproduce the general features of the energy disposal, although there are unresolved questions pertaining to the magnitude of the rate constants,

⁽²⁴⁾ Heaps, H. S.; Herzberg, G. Z. Phys. 1952, 133, 48.

⁽²⁵⁾ Benedict, W. S.; Herman, R.; Moore, G. E.; Silverman, S. J. Chem. Phys. 1957, 26, 1671.

⁽²⁶⁾ Werner, H. J.; Rosmus, P. J. Chem. Phys. 1980, 73, 2319.

the kinetic isotope effect, and rotational energy disposal.^{4a,b}

The HCl emission from Cl + HBr was weak because of the reduced reaction rate, see Table III. Since this reaction was not extensively studied, the vibrational distribution given in Table II has greater uncertainty, 0.75 ± 0.2 and 0.25 ± 0.1 , than for Cl + HI. In his chemical laser work, Bittenson¹⁹ reports $P_1/P_0 = 1.5 \pm 0.3$ for Cl + HBr. The value of P_0 determined by the linear surprisal extrapolation (footnote of Table II) is in fair agreement with this value. Thus, the HCl(v) distribution from Cl + HBr is bell shaped and resembles that for Cl + HI on an f_V plot; see Figure 3c. A quasi-classical trajectory calculation^{27a} gave a distribution of 0.27:0.53:0.20 in close agreement with our experimental result. There is not quantitative agreement between the various studies of Cl + HBr,^{1,20,21} and use of different Einstein coefficients do not explain these differences in vibrational distributions. The general trend of all the measurements is the same, i.e., P_1 is larger than P_2 ; but the disagreement on the P_1/P_2 ratio is real. Our study was not done in sufficient depth to resolve the difference between the low-resolution flowing-afterglow studies^{20,21} and the early arrested relaxation work. Two points are worth noting. A larger P_1/P_2 ratio makes the surprisal plot less steep, and a linear extrapolation of such a plot does not give Bittenson's P_1/P_0 ratio. Also, the $\langle f_V \rangle$ would be reduced leading to an even larger difference in the energy disposal between Cl + HBr and Cl + HI. On the other hand, MacDonald and Moore²⁹ argue from detailed balance and the rate constant for chemical reaction ov Br with HCl(v=2) that $P_2 \leq 0.07$. Further work is required to definitely assign the energy disposal from Cl + HBr. We would recommend that Cl + DBr be studied simultaneously. (See also Note Added in Proof.)

The observation of DCl emission from Cl + DBr was difficult because of the reduced Einstein coefficients for DCl, compared to those of HCl, and the kinetic isotope effect, which is reported²⁹ to be 1.5 at 300 K. Nevertheless, it was possible to show that the DCl(v) distribution has a maximum at v = 2, even though there is $\pm 20\%$ uncertainty in the relative populations. Thus, the DCl(v) distribution from Cl + DBr confirms the assignment of P_0/P_1 < 1.0 for Cl + HBr, as discussed above, and the general shape of the vibrational energy distribution resembles Cl + HI; but $\langle f_V \rangle$ may be somewhat lower. The linear surprisal plot, Figure 3, for Cl + DBr gives larger λ_V and $\langle f_V \rangle$ values than for the Cl + HBr reaction, although the difference may not be significant given the experimental uncertainties. Nevertheless, the implied difference is intriguing and the Cl + HBr(DBr) pair offer a possible example for study of isotope effects on the energy disposal. This, as well as the detailed balance considerations for the reverse reactions, makes further study worthwhile. If there is an isotope effect on energy disposal, it probably arises from constraints associated with quantization of the HCl vibrational and rotational energy from the low available energy.

II. $Cl + PH_3$, PD_3 , and GeH_4 . These reactions have not been studied by arrested-relaxation technique. The only Cl + HR (R = polyatomic fragment) systems studied³⁰ by use of the arrested-relaxation technique are the $Cl + H_2S$ and CH_3SH reactions yielding $HCl(v \le 1)$ and $HCl(v \le 2)$, respectively. At this stage, no comparison can be made

on the vibrational distribution from the flow reactor vs. that from the arrested-relaxation technique for the Cl atom reactions with polyatomic hydrides. Thus, it is not possible to pursue the analogy between the chemiluminescence from reactions of F and Cl atoms by the arrested-relaxation technique. For some F + HR systems, unexplained trends in the HF vibrational distribution with reduction of reagent flows have been discovered^{4a,12} in the arrestedrelaxation studies in the very low flow regime; these unexplained changes in HF distributions are manifested as high yields of HF in low v levels. It would be of interest to know if Cl + HR reactions show the same phenomena. In the present work, the initial HCl(v) distributions for room temperature Boltzmann reaction conditions were obtained in the flow reactor by proper selection of the reagent and Cl concentrations. Thus, we have established that the fast-flow reactor is well qualified for obtaining initial vibrational distributions from the Cl + diatomic or polyatomic hydride reactions, which have large rate constants.

Previous work^{4a,b,12,13} from our laboratory has shown that the HF vibrational energy disposal from $F + PH_3$ and GeH₄, $\langle f_V(HF) \rangle = 0.59$ and 0.58, respectively, closely parallels the results from F + HI (or Cl + HI). At first glance, the data of Table II suggest a difference in vibrational energy disposal between Cl + HI and $Cl + GeH_4$, PH_3 , or PD_3 which have distributions peaking at HCl(v=1)and DCl(v=2). However, before reaching definite conclusions the v = 0 populations must be carefully evaluated. The Cl + PD₃ and DBr distributions peak at DCl(v=2). So that a similar $\langle f_V \rangle$ can be obtained, the HCl distributions from $Cl + PH_3$ and HBr must peak at an intermediate f_V , and the HCl(v=1) and HCl(v=2) points may lie on either side of the hypothetical maximum. If this is assumed and if model II (the rotational degrees of freedom of $PH_2(PD_2)$ are included in the prior) surprisal plots are used to assign P_0 , the vibrational energy disposal for Cl + PH_3 and PD_3 becomes similar to Cl + HI. The apparent difference in the vibrational energy distributions between $Cl + PH_3$ and PD_3 is a consequence of the difference in vibrational spacings of HCl and DCl. We conclude that the energy disposal to HCl(v) from $Cl + PH_3$ does not show a large difference relative to the diatomic hydrogen halides. The analogy between Cl and F atom reactions with PH₃ also can be examined. The vibrational energy disposal pattern for Cl + PH₃(PD₃) resembles that for $F + PH_3^{12}$ but, $\langle f_V(\text{HCl}) \rangle$ is substantially lower than $\langle f_V(\text{HF}) \rangle$, 0.45 vs. 0.59 (also see Figure 3).

The situation for $Cl + GeH_4$ is less certain than that for $Cl + PH_3$. Since the available energy is sufficient to populate HCl(v=3), the P_1/P_2 ratio from $Cl + GeH_4$ might be expected to resemble that of $Cl + PH_3$. However, this ratio is closer to that of Cl + HBr, for which $\langle E \rangle$ is just enough to populate low J levels of HCl(v=2). A forced fit, model II linear surprisal extrapolation for $Cl + GeH_4$ gives $P_0/P_1 \approx 1$. As noted in Table II, $-\lambda_V$ is much smaller than for $Cl + PH_3$, and the degree of linearity is poor for Cl +GeH₄. Comparison with F + GeH₄¹³ and O + GeH₄,⁸ $\langle f_V(\text{HF}) \rangle = 0.58$ and $\langle f_V(\text{OH}) \rangle = 0.54$ (also see Figure 3), suggests the P_0/P_1 ratio could be less than 0.5 for Cl + GeH₄. The third entry in Table II corresponds to arbitrarily setting $P_0 = 1/2P_1$. A definite conclusion about the vibrational energy disposed for $Cl + GeH_4$ cannot be made without results from $Cl + GeD_4$ or a direct measurement of P_0 (HCl). We tend to favor a direct abstraction process with $P_0 < P_1$ and $\langle f_V(\text{HCl}) \rangle \ge 0.27$, i.e., the third entry of Table II. However, reservation should be maintained since an addition-elimination mechanism may be in competition

^{(27) (}a) Brown, J. C.; Bass, H. E.; Thompson, D. L. J. Phys. Chem.
1977, 81, 479. (b) Parr, C. A.; Polany, J. C.; Wong, W. H. J. Chem. Phys.
1973, 58, 5.

 ⁽²⁸⁾ MacDonald, R. G.; Moore, C. B. J. Chem. Phys. 1980, 73, 1681.
 (29) Mei, C.-C.; Moore, C. B. J. Chem. Phys. 1979, 70, 1759.

⁽³⁰⁾ Dill, B.; Heydtmann, H. Chem. Phys. 1978, 35, 161.

TABLE V: Dipole Moment ExpansionCoefficients^a for HCl

ref	M _o	<i>M</i> ₁	M 2	M 3	$M_{_4}$	
22	1.095	0.905	-0.066^{c}	-0.730	-0.644	
26^{b}	1.102	0.885	-0.039	-0.696	-0.075	
37	1.0935	0.947	0.015	-0.814	0.0	

^{*a*} M_1 values are in the units of D A⁻¹. ^{*b*} These coefficients were obtained by fitting the data in ref 26 into a fourth-order polynomial. ^{*c*} This value has been quoted incorrectly in ref 22. The correct value was obtained from ref 23.

with direct abstraction.

Within the classical limit, an isotope effects on the energy disposal of the isotopic pairs of reactions, Cl + HBr(DBr) and Cl + PH₃(PD₃) is not expected.^{27b} An exception may arise from possible fortuitous quantum effects arising from the energy spacings of product vibrational-rotational levels and low $\langle E \rangle$ values, such as Cl + HBr(DBr). Within the limits of our experimental uncertainty, no isotope effects on $\langle f_V(HCl) \rangle$ vs. $\langle f_V(DCl) \rangle$ were observed for PH₃ vs. PD₃.

III. Rate Constants. The relative rate constants are given in Table III and are compared with corresponding F and O atom reactions; k(Cl + HBr) is about 20 times smaller than k(Cl+HI). Our results indicate that the PH₃ and GeH₄ reactions are approximately two times faster than Cl + HI. Our rate constant for Cl + GeH₄ is in



Figure 5. Dipole moment functions and the Morse potential for HCI: (I) fourth-order polynomial of Herbelin and Emanuel (ref 22); (II) Werner and Rosmus's (ref 26) data fitted to a fourth-order polynominal; and (III) third-order polynomial of Smith (ref 37).

modest agreement with the result of a discharge flow reaction study in which [Cl] was monitored by resonance fluorescence.³³ We did not experience the difficulty with

TABLE VI: Transition Moment Expansion Coefficients^a and the Vibrational Einstein Coefficients^b for HCl

υ΄	υ''	<i>a</i> ₁	a 2	<i>a</i> ₃	a ₄	$A_v^{v_i}$	
			$\Delta v = 1$				
1	0	$0.6193 (-1)^c$	-0.8719(-3)	0.1388(-5)	-0.6608(-7)	34.6	
2	1	0.8578(-1)	-0.1278(-2)	-0.1181(-6)	-0.9960 (-7)	59.5	
3	2	0.1016	-0.1621(-2)	-0.3460(-5)	-0.1279(-6)	74.4	
4	3	0.1116	-0.1939(-2)	-0.9216(-5)	-0.1516(-6)	79.7	
5	4	0.1159	-0.2242(-2)	-0.1794(-4)	-0.1681(-6)	75.8	
6	5	0.1137	-0.2538(-2)	-0.3078 (-4)	-0.1701(-6)	64.1	
			$\Delta v = 2$				
2	0	-0.7814(-2)	0.2633(-4)	-0.1793(-5)	0.1048(-7)	4.2	
3	1	-0.1474(-1)	0.5335(-4)	-0.3500 (-5)	0.2347(-7)	13.4	
4	2	-0.2271(-1)	0.8893(-4)	-0.5598(-5)	0.4264(-7)	28.3	
5	3	-0.3194(-1)	0.1365(-3)	-0.8113 (+5)	0.7039(-7)	49.6	
6	4	-0.4259(-1)	0.1991 (-3)	-0.1112(-4)	0.1108 (-6)	77.9	

^a All terms must be multiplied by 1.095, D, the value of the permanent dipole, to obtain absolute Einstein coefficients. ^b Values in s⁻¹. The following are the $A_{v}^{b'}$ values calculated from Smith's³⁷ dipole function; $A_{1}^{a} = 38.4$, $A_{2}^{1} = 67.1$, $A_{3}^{2} = 86.5$, $A_{4}^{3} = 97.0$, $A_{5}^{4} = 99.2$, $A_{6}^{5} = 94.1$; $A_{2}^{a} = 3.7$, $A_{3}^{1} = 11.7$, $A_{4}^{2} = 24.0$, $A_{5}^{3} = 40.7$, $A_{6}^{4} = 61.2$. The following are the $A_{v}^{b''}$ values calculated with a fourth-order polynomial fit to Werner and Rosmus'²⁶ dipole function: $A_{1}^{a} = 33.4$, $A_{2}^{1} = 58.1$, $A_{3}^{2} = 74.5$, $A_{4}^{3} = 83.0$, $A_{5}^{4} = 84.2$, $A_{5}^{5} = 78.9$; $A_{2}^{a} = 3.6$, $A_{3}^{1} = 11.1$, $A_{4}^{2} = 22.6$, $A_{5}^{3} = 38.0$, $A_{6}^{4} = 56.8$. ^c The number in the parentheses is the power of 10; for example, 0.6193 (-1) = 0.6193 \times 10^{-1}.

TABLE VII:	Transition Mome	ent Expansion	1 Coefficients ^a	' and the	Vibrational	Einstein	Coefficients ^b	' for !	DCl
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 υ΄	υ΄΄	<i>a</i> ₁	a 2	a 3	a ₄	$A_v^{v''}$	
			$\Delta v = 1$				
1	0	$0.5266 (-1)^c$	+0.5246(+3)	0.8372(-6)	-0.1850(-7)	9.5	
2	1	0.7359(-1)	-0.7609(-3)	0.6916(-6)	-0.2745(-7)	17.2	
3	2	0.8858(-1)	-0.9558 (-3)	0.6782(-7)	-0.3499 (+7)	23.0	
4	3	0.9986(-1)	-0.1131(-2)	-0.1003(-5)	-0.4183(-7)	27.0	
5	4	0.1081	-0.1296(-2)	-0.2598 (-5)	-0.4930 (-7)	29.1	
6	5	0.1135	-0.1455(-2)	-0.4817(-5)	-0.5295 (-7)	29.4	
			$\Delta v = 2$				
2	0	-0.5386(-2)	0.1277(-4)	-0.5797(-6)	0.2068(-8)	0.77	
3	1	-0.9917(-2)	0.2469(-4)	-0.1104(-5)	0.4380 (-8)	2.4	
4	2	-0.1491(-1)	0.3925(-4)	-0.1706(-5)	0.7348 (~8)	5.0	
5	3	-0.2047(-1)	0.5691(-4)	-0.2396(-5)	0.1133(-7)	8.7	
6	4	-0.2665(-1)	0.7857(-4)	-0.3188(-5)	0.1715(-7)	13.6	

^a All terms must be multiplied by 1.095 D, the value of the permanent dipole, to obtain absolute Einstein coefficients. ^b Values in s⁻¹. ^c The number in parentheses is the power of 10; for example, 0.5266 (-1) = 0.5266×10^{-1} .

TABLE VIII: Transition Moment Expansion Coefficients^a and the Vibrational Einstein Coefficients^b for DF

υ'	υ''	a ₁	a2	<i>a</i> ₃	a ₄	$A_{v'}^{v''}$
			$\Delta v = 1$	••••••••••••••		
1	0	$0.4672 (-1)^{c}$	-0.9062(-3)	0.8900(-6)	-0.1318(-7)	55.7
2	1	0.6555 (-1)	+0.1308(-2)	0.8111(-6)	-0.2041(-7)	99.5
3	2	0.7936 (-1)	-0.1636 (-2)	0.3188(-6)	-0.2827(-7)	132.4
4	3	0.9025(-1)	-0.1929(-2)	-0.5621(-6)	-0.3399 (-7)	155.1
5	4	0.9890 (–1)	-0.2202(-2)	-0.1893 (-5)	-0.4222(-7)	168.5
6	5	0.1056 `´´	-0.2462 (-2)	-0.3749 (-5)	-0.4876 (-7)	173.5
			$\Delta v = 2$			
2	0	-0.4950(-5)	0.3939(-4)	-0.3278(-6)	0.4461(-8)	4.8
3	1	-0.8915(-2)	0.7202(-4)	-0.6330(-6)	0.8646 (-8)	14.1
4	2	-0.1312(-1)	0.1074(-3)	-0.9840(-6)	0.1509 (-7)	27.6
5	3	-0.1762(-1)	0.1473(-3)	-0.1408(-5)	0.2146(-7)	45.2
6	4	-0.2245 (-1)	0.1915 (-3)	-0.1896 (-5)	0.3147 (-7)	66.4

^a All terms must be multiplied by 1.7982 D, the value of the permanent dipole, to obtain absolute Einstein coefficients. ^b Values in s⁻¹. ^c The number in the parentheses is the power of 10; for example $0.4672(-1) = 0.4672 \times 10^{-1}$.

TABLE IX: Transition Moment Expansion Coefficients^a and the Vibrational Einstein Coefficients^b for HF

υ'	υ''	<i>a</i> ₁	a2	<i>a</i> ₃	<i>a</i> ₄	$A_v^{v''}$
			$\Delta v = 1$	1		
1	0	$0.5496 (-1)^{c}$	-0.1481(-2)	0.1348(-5)	-0.5829(-7)	195.7
2	1	0.7668(-1)	-0.2155(-2)	0.6218(-7)	-0.9162(-7)	332.3
3	2	0.9199(-1)	-0.2717(-2)	-0.2844(-5)	-0.1221(-6)	418.8
4	3	0.1031	-0.3230(-2)	-0.7737 (-5)	-0.1492 (-6)	459.5
5	4	0.1105	-0.3718(-2)	-0.1523(-4)	-0.1708 (-6)	460.4
			$\Delta v = 2$	2		
2	0	-0.6994(-2)	0.7641(-4)	-0.1075(-5)	0.2113(-7)	23.2
3	1	-0.1279 (-1)	0.1427(-3)	-0.2128(-5)	0.4442(-7)	68.0
4	2	-0.1912 (-1)	0.2184(-3)	-0.3422(-5)	0.7726(-7)	132.5
5	3	-0.2609 (-1)	0.3075 (-3)	–0. 4992 (–5)	0.1228(-6)	214.6

^a All terms must be multiplied by 1.7982 D, the value of the permanent dipole moment, to obtain absolute Einstein coefficients. ^b Values in s⁻¹. ^c The number in the parentheses is the power of 10; for example 0.5496 $(-1) = 0.5496 \times 10^{-1}$.

 PH_3 reported by Schlyer et al. The fast reactions of PH_3 and GeH_4 can be expected since their corresponding reactions with F and O atoms also have large rate constants (Table III).

Conclusions

In this work, we have demonstrated that HCl infrared chemiluminescence from a fast flow reactor can be used successfully to obtain the *initial* HCl vibrational distributions for H abstraction reactions by Cl atoms, providing the Cl and reagent concentrations are controlled. In previous work, the same technique was used for the study of H abstraction reactions by F and O atoms.^{4a,8,13b} The recording of HCl emission under conditions which gave initial HCl(v) distributions from Cl + HI, PH_3 , and GeH_4 could be done easily. The rate constants for $Cl + PH_3$ and GeH_4 are approximately two times larger than for Cl + HI. Since Cl + HBr is a slower reaction, observation of emission for sufficiently low [Cl] and [HBr] so that relaxation was avoided was more difficult. Although the Einstein coefficients of DCl are about 4 times smaller than those of HCl, the observation of DCl emission from Cl + PD_3 and DBr was possible under conditions such that relaxation of DCl(v) was avoided.

As an additional check for possible relaxation, the Cl +PH₃ reaction was independently investigated in a 4-cm i.d. flow reactor with a reagent mixing zone of 1.2 cm, which corresponds to a reaction time of less than 0.1 ms.^{12b} The [Cl] was maintained between 2.0×10^{11} and 5.0×10^{11} molecules cm^{-3} . Under these conditions, the HCl(v) distribution was 0.52:0.43:0.05, which is in a good agreement with the results in Table II. These experiments, thus, confirmed that the $Cl + PH_3$ distribution obtained with a reaction time of 0.3 ms in Table II is free of relaxation.

The vibrational energy disposal for Cl + HI closely resembles that for F and O + HI. The results from Cl +HBr(DBr) are less certain because the smaller available energy makes P_0 very important and because the measurements have higher uncertainty. The DCl(v) distribution shows that the general energy disposal pattern from Cl + HBr (DBr) resembles that for Cl + HI; however, $\langle f_V \rangle$ may be somewhat reduced. Further work with the Cl + HBr(DBr) pair is required before the apparent isotope effect on the energy disposal suggested by this work is accepted as established. The HCl(v) distribution from Cl + $PH_3(PD_3)$ appears to be somewhat broader than the distribution from Cl + HI or F + PH₃ with $\langle f_V(HCl) \rangle$ = 0.50 ± 0.05 rather than 0.60 ± 0.05 . The $(f_V(\text{HCl}))$ from GeH₄ is considerably lower than $\langle f_V(HF) \rangle$ for GeH₄. The dynamics associated with the direct transfer of the light H atom from the hydride molecule to an approaching F or Cl atom are very similar and tend to override differences in potential surfaces. The result in a narrow range of $\langle f_V \rangle$ with distributions of the type shown in Figure 3; this is especially evident from inspection of the results from the large number of F + HR reactions.^{4b,12b} With this as a framework, the results from $Cl + GeH_4$ imply (i) a rather drastic difference in potential surface for a direct reaction or (ii) a different interaction mechanism. Since k(Cl+- GeH_4) is actually larger than for Cl + HI, the GeH₄ surface is unlikely to be more repulsive than for Cl + HI. Therefore, the low $\langle f_V(HCl) \rangle$ from GeH₄ may be associated with a combination of direct abstraction plus addition to

⁽³¹⁾ Smith, D. J.; Setser, D. W.; Kim, K. C.; Bogan, D. J. J. Phys. Chem. 1977, 81, 898.

⁽³²⁾ Bergmann, K.; Moore, C. B. J. Chem. Phys. 1975, 63, 643. (33) Schlyer, D. J.; Wolf, A. P.; Gaspar, P. P. J. Phys. Chem. 1978, 82, 2633. This reference gives $k(Cl+GeH_4) = (2.4 \pm 1.8) \times 10^{-10}$ cm³ mole-cule⁻¹ s⁻¹. The entry in Table III was obtained by dividing the above value by k(Cl+HI) from ref 9.

Ge followed by HCl elimination. Since Ge is a fourth row element, the addition channel may be more likely than for PH_3 .

Note Added in Proof. Additional experiments have been done for the Cl + HBr reaction. These observations were made in a 4-cm i.d. flow reactor with a reaction time of 0.1 ms. For a [Cl] of 1.4×10^{12} atom cm⁻³, assuming 50% dissociation of Cl₂, and HBr variable from 2×10^{12} to 9 \times 10¹² molecular cm⁻³ the mean $P_1:P_2$ values was (0.73 ± $(0.03):(0.27 \pm 0.03)$ based upon four experiments. For [Cl] = 4×10^{12} atom cm⁻³, for which there is evidence for some relaxation (see Figure 1), with HBr = 2×10^{12} to 9×10^{12} molecule cm⁻³ the mean $P_1:P_2$ value was (0.77 ± 0.03):(0.23) \pm 0.03) based on four experiments. These more extensive data cooroborate the entry in Table II.

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Appendix

The method employed in calculating the Einstein coefficients of HF, HCl, and HBr were reported in previous work^{7,18} from our laboratory. The same method was used in the present calculations of DCl and DF Einstein coefficients. A summary also is given for HCl and HF for completeness and consistency in notation. For convenience of introducing the notation, some of the equations given in ref 7 will be reproduced here. The Einstein coefficients for spontaneous emission are given by,

$$A_{v'J'}^{v''J''} = A_{v'}^{v''}(m) = \frac{64\pi^4\nu^3|m|}{3h}|R_v^{v'}(m)|^2$$

where ν is the line frequency, $R_{\nu}^{\nu''}(m)$ is the transition moment, and m = J or -(J + 1) for R and P lines, respectively. $R_{v'}^{v''}(m)$ can be expressed as a third order polynormial of $m^{18.7}$

$$R_{v'}^{v''}(m) = a_1 + a_2m + a_3m^2 + a_4m^3$$

Thus, $R_{n'}^{\nu''}(m)$ can be calculated for any value of m by using the parameterized constants a_1 , a_2 , a_3 , and a_4 . Then the

 $A_{vJ'}^{v'J''}$ values can be obtained by substituting the $R_{v'}^{v''}(m)$ values into first equation above.

The critical part of the calculations is to use a correct dipole moment function; $\mu(R)$ is usually given as power series expansion of the type

$$\mu(R) = \sum_{l=0}^{n} M_{l} (R - R_{e})^{l}$$

where R and R_e are the internuclear distance and equilibrium internuclear distance, respectively. Three dipole moment functions have been reported for HCl (and DCl) by Herbelin and Emanuel,²² Werner and Rosmus,²⁶ and Smith;³⁷ the coefficients M_1 are listed in Table V. These dipole functions are plotted in Figure 5. The second entry in Table V was obtained by fitting Werner and Rosmus's data to a fourth-order polynormial. A third-order polynomial fit gives a very similar curve. Based on the arguments used in ref 7, we favor a dipole function which does not diverge over the range of R used in calculations. Thus, the first entry in Table V was chosen for the present calculations of Einstein coefficients for HCl and DCl (see Experimental Section regarding a comment on HCl Einstein coefficients). The expansion coefficients for $R_{v'}^{v''}(m)$ and the rotationless Einstein coefficients for HCl and DCl are given in VI and VII, respectively. Actually the calculated Einstein coefficients are similar for all three dipole functions. This can be verified by comparison of the rotationless values for the $\Delta v = 1$ and $\Delta v = 2$ transitions, which are given in the footnote of Table VI.

The dipole moment expansion of Herbelin and Emanuel²² was used for HF and DF. The results are summarized in Tables VIII and IX. The HF results in Table IX supersede those in ref 5.

Registry No. Cl. 22537-15-1: HI, 10034-85-2: HBr, 10035-10-6: DBr, 13536-59-9; GeH₄, 7782-65-2; PH₃, 7803-51-2; PD₃, 13537-03-6; HCl, 7647-01-0; DCl, 7698-05-7; Br, 10097-32-2; I, 14362-44-8; PH₂, 13765-43-0; PD₂, 15117-85-8; GeH₃, 13765-45-2.

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