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Nascent product vibrational state distributions of ion-molecule reactions: The proton transfer reactions F^+ +HX \rightarrow HF(v)+X⁻, X=CI, Br, and I

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Nascent vibrational state distributions are obtained for the HF products of the proton transfer reactions $F^- + HX \rightarrow HF(v) + X^-$, X = Cl, Br, and I. The reactions are carried out in a flowing afterglow apparatus in which the reagents are fully thermalized (300 K). The product states are measured by low resolution infrared chemiluminescence spectra obtained with a Ge:Cu infrared detector and a circular variable filter. The nascent HF(v) distributions are as follows: for $F^- + HCl$, $N_1:N_2:N_3 = 0.46:0.33:0.21$; for $F^- + HBr$, $N_1:N_2:N_3:N_4 = 0.28:0.27:0.24:0.21$; for $F^- + HI$, $N_1:N_2:N_3:N_4:N_5 = 0.20:0.23:0.22:0.20:0.15$. All three reactions channel the available exothermicity quite efficiently into product vibration. Product rotational state information cannot be obtained due to collisions with the He carrier gas. In spite of the deep attractive wells of the $F^- + HX$ potential energy surfaces, in all three cases the degree of vibrational excitation in the ion-molecule reactions. The results strongly suggest that these ion-molecule reactive collisions are direct encounters and that the kinematic effect of the mass combination (transfer of a light particle between two heavy particles) dominates over the influence of the shape of the potential energy surface in determining the product vibrational state distributions.

I. INTRODUCTION

For neutral A + BC chemical reactions, the relationship between the qualitative shape of the potential energy surface and the propensity of an exothermic reaction to deposit energy into product vibrational, rotational, and translational degrees of freedom is well understood.¹ These concepts have emerged from the mutually beneficial feedback between experimental product distributions, both state and angle resolved, and theoretical calculations. In particular, quasiclassical trajectory calculations on model potential energy surfaces provide important insights into the dynamics of reactions.² The reaction coordinate on neutral A+BC surfaces often proceeds monotonically downhill to products after overcoming a small barrier. Such features as the barrier location and the abruptness of the descent into the product valley may be correlated with the propensity to populate the various product degrees of freedom.³

Ion-molecule reactions provide an experimental and theoretical opportunity to study exothermic reactions that proceed on potential energy surfaces of dramatically different shape. The typical ion-molecule surface has no barrier to reaction and exhibits an ion-induced dipole attractive well that extends far into the entrance and exit valleys. One consequence of the long range ionneutral attraction is the existence of enormous reaction cross sections; $100-200 \text{ Å}^2$ cross sections are not uncommon.⁴

Relatively little is known about energy disposal in thermal ion-molecule reactions. Ion beam experiments have provided considerable information about product translational states for lab frame collision energies greater than about 1 eV.⁵ Internal states of electronically excited products of high collision energy reactions have been studied by visible chemiluminescence.⁶ Very recently, the feasibility of detecting infrared chemiluminescence from thermal energy ion-molecule reactions in a flowing afterglow apparatus has been demonstrated.⁷ Several proton transfer and associative detachment reactions have already been shown to populate high vibrational states very efficiently.⁷⁻¹⁰

The present work is an extension of the ion-molecule IR chemiluminescence studies to a series of proton transfer reactions $F^+HX - HF(v) + X^-$, X = Cl, Br, and I. These reactions are sufficiently exothermic to populate HF vibrational levels up to v=3, 4, and 5 for X = Cl, Br, and I, respectively. A continuously variable wavelength scanning IR detection system allows low resolution spectra of the HF product emission to be obtained. Nascent product vibrational state distributions are extracted from best fits to the chemiluminescence spectra. The F^- + HX reaction series provides an opportunity for detailed comparison to the often studied F + HX series.¹¹⁻¹³

II. EXPERIMENTAL

The flowing afterglow infrared chemiluminescence apparatus has been described earlier.⁸ Details unique to the F^+ HX studies will be given here. The primary modification involves the infrared detection system. In the present work, a background limited, liquid He cooled Ge:Cu detector views IR chemiluminescence spectrally resolved with a circular variable interference filter (CVF). Modulated signals due to the ion-molecule reaction are acquired at different wavelengths by stepping the position of the CVF through the HF spectral region. Use of a 1.5 mm wide slit gives a low resolution (60-80 cm⁻¹ FWHM) HF emission spectrum. A least squares computer fit (Sec. III A) is used to analyze the spectrum in terms of its component vibrational bands to yield raw

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FIG. 1. Schematic of flow tube configuration and detection geometry.

HF vibrational state distributions N_v . Consistency checks on the relative populations are carried out. (Sec. III B). Finally, small corrections for radiative cascading are applied to the raw distributions (Sec. IIIC) to obtain the nascent vibrational state distributions N_v^0 .

A. Flow tube conditions

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Figure 1 shows a schematic of the flow tube and detection geometry. F⁻ ions are produced in the source region by electron impact on F₂. The largest F⁻ currents at the mass spectrometer are obtained by introducing a very small flow of 5% F₂ in He near the electron gun (filament). The partial pressure of F₂ in the flow tube is smaller than 10⁻⁵ Torr as compared to a typical He carrier gas pressure of 0.7 Torr (1 Torr = 133.322 Pa). The emission current from the - 100 V filament (either tungsten or thorizated iridium) is typically regulated at 10 mA. The estimated F⁻ density in the reaction zone of the flow tube is ~ 10⁹ ions cm⁻³.

In order to minimize the effects on the product state distributions of radiative cascading, vibrational relaxation, and diffusion to the walls (Sec. III C), it is desirable to minimize the partial pressure of HX and the distance between the point of HX addition and the viewing region, consistent with a reasonable signal-to-noise ratio. The distance between the HX inlet and the center of the viewing window is typically 5 cm. For all three reactions, this distance fixes the mean time between creation and observation of a product HF molecule at $\langle t_{\rm obs} \rangle = 0.20 \pm 0.04$ ms. Calculation of $\langle t_{\rm obs} \rangle$ involves the mean axial flow tube velocity for F⁻ ions¹⁴ ($\bar{v}_{\rm ion} = 1.4 \times 10^4$ cm s⁻¹), the rate constant of the chemical reactions, the pressure of HX, and the rate of regeneration of F⁻ by a chain reaction mechanism explained below.

The usual HX partial pressure in the flow tube is 0.5 mTorr, sufficient to completely react all of the initial F^- ions in 2-3 cm. HCl (electronic grade, nominal purity 99,99%) and HBr (nominal purity 99.8%) are used

directly from lecture bottles. HI (nominal purity 98%) is purified by freeze-pump-thaw cycles between 77 K and room temperature to remove H₂. HI is introduced into the flow tube through opaque Teflon tubing to prevent photolysis by room lights. H₂, Cl₂, Br₂, or I₂ impurities cause no problems because the reaction $F^{-}+H_{2} \rightarrow HF + H^{-}$ is endothermic and analogous $F^{-}+Cl_{2}$, Br₂, and I₂ reactions, although moderately exothermic, would lead to products that emit weakly at much longer wavelengths than HF. It is estimated that less than 5% of the observed product HF molecules have diffused to the flow tube walls in the ~0.25 ms between formation and observation, so that partial wall deactivation of HF(v) is an unimportant process.

B. Measurement of F⁻⁺HX rate constants

The F^+ +HX (X = Cl, Br, and I) thermal rate constants are measured using the standard flowing afterglow technique.¹⁴ The mass spectrometer is tuned to the F^- peak and the depletion of F^- current vs calibrated flow of HX is measured with an electrometer. When F_2 is used as the source of F^- , the resulting plots of $\ln(F^-/F_0)$ vs HX flow are nonlinear. Further investigation indicates that the chain reaction sequence

$$\mathbf{F}^{-} + \mathbf{H}\mathbf{X} \xrightarrow{k_{1}\mathbf{X}} \mathbf{H}\mathbf{F} + \mathbf{X}^{-}$$
(1)

$$X^{-} + F_2 \xrightarrow{h_{2X}} XF + F^{-}$$
, (2)

causes the F⁻ current to reach a steady state rather than decay to zero as the HX flow is increased. Reaction (2) is exothermic and fast for X = Cl, Br, and I, as demonstrated by the direct reaction of X⁻ with F₂ in the flow tube. To avoid the complications of a chain process, the rate constants k_{1X} are obtained using CHF₃ as the F⁻ precursor. The analogous chain propagation step X⁻+CHF₃-CHF₂X + F⁻ is endothermic. Using CHF₃, the log plots are linear over nearly two decades of F⁻ current. The resulting room temperature (295±3 K)

Reaction	k _{exyt} ² (cm ³ molecule ⁻¹ s ⁻¹)	k_{ADQ}^{b} (cm ³ molecule ⁻¹ s ⁻¹)	$-\Delta H^{c}$ kcal mol ⁻¹	$v_{\max}{}^{d}$ (for HF)
F ⁺ +HCl	$(1.55 \pm 0.31) \times 10^{-9}$	1.57×10^{-9}	38.1	3
F ⁻ +HBr	$(1.24 \pm 0.25) \times 10^{-9}$	1.40×10^{-9}	47.9	4
F ⁻ +HI	$(1.01 \pm 0.20) \times 10^{-9}$	1.39×10^{-9}	57.1	5
F+HC1	$(8.07 \pm 0.50) \times 10^{-12}$	•••	33.1	3
F+HBr	$(4.50\pm0.40)\times10^{-11}$	• • •	48.7	4
F+HI	$(4.09 \pm 0.08) \times 10^{-11}$	•••	64.9	6

TABLE I. Rate constants and thermochemistry for $F^+HX \rightarrow HF + X^-$ and $F + HX \rightarrow HF + X$.

^aThe room temperature (295±3 K) experimental rate constant. Ion-molecule results are from the present work. Each rate constant is an average of four measurements at He pressures between 0.3-0.7 Torr. Error limits are $\pm 1\sigma$. Neutral rate constants are taken from Ref. 16. ^bCalculated "average dipole orientation" (ADO) capture rate constant (300 K) from the prescription of Su and Bowers (Ref. 15).

^eCalculated from the bond dissociation energies of Ref. 17 and the electron affinities of Ref. 18. ^dThe highest HF vibrational state that can be populated with the given exothermicity.

rate constants are collected in Table I along with the average dipole orientation (ADO) capture rate constants calculated according to the prescription of Su and Bowers.¹⁵ For all three reactions, nearly every capture collision results in a reactive event, as is common for simple exothermic proton transfer reactions. For comparison purposes, Table I also displays the rate constants and exothermicities of the corresponding neutral F + HX reactions. The ion-molecule reactions are 20-200 times faster than the corresponding neutral reactions.

The rate constants k_{2x} [Eq. (2)] for the X⁻ + F₂ reactions can be crudely estimated from the variation of the steady state F⁻ current with the pressure of 5% F₂/He added through a downstream inlet (Sec. II D). The estimates are only approximate because the true partial pressure of F₂ in the mixture is not well known. For all three reactions, k_{2x} is ~ 1×10⁻⁹ cm³ molecule⁻¹ s⁻¹, which again agrees well with the calculated ion-molecule capture collision rate constants.

C. Infrared detection system

The infrared detector for these studies is a 3 mm× ×10 mm Ge:Cu crystal mounted on a liquid He cooled Kovar block. The measured detectivity under background limited conditions at 2 μ m is $D^* = 1.2 \times 10^{12}$ cm Hz^{1/2}W⁻¹ with a 10 kHz response frequency. The detector views the emission region through a rotatable circular variable interference filter (CVF) and a 1.5 mm ×12 mm slit (Fig. 1); both are cooled at 77 K. Liquid He cooled MgF₂ and sapphire windows mounted directly on the detector heat sink serve as a long wavelength ($\lambda > 5.5 \mu$ m) blackbody cutoff filter. Infrared emission exits the flow tube through a 2.5 cm diam NaCl window and is collected and imaged onto the detector by a 5.1 cm diam f/1 CaF₂ lens.

The CVF is a 90° segment of a quartz annulus coated with continuously varying thicknesses of multiple dielectrics. Each radial slice through the annulus is a narrow bandpass interference filter whose peak transmission wavelength varies linearly from $2.5-4.5 \ \mu m$ around the circumference of the annulus. The "intrinsic" (zero slit width) FWHM resolution of the filter at any wavelength is given by $\Delta\lambda/\lambda \approx 0.01$. The CVF is mounted on a rotatable wheel which permits manual scanning of the CVF past the slit while the detector, CVF, and slit are cooled. A calibration dial permits reset of a given CVF position relative to the slit.

The peak transmission wavelength vs CVF position is calibrated to $\pm 0.005 \ \mu m$ using a broadband infrared source and a monochromator. The wavelength can be reset to better than 0.01 μm . The combined transmission function of the CVF and 1.5 mm slit is obtained at various wavelengths for well-collimated, narrow-band light from the monochromator. The transmission curves at all wavelengths in the 2.5-3.5 μm range are very well represented by a Gaussian function having $\Delta \lambda =$ 0.060 μm FWHM, indicating that the resolution is slitwidth limited. The corresponding energy resolution varies from 96 cm⁻¹ (at 2.5 μm) to 55 cm⁻¹ (at 3.3 μm).

In order to measure the relative sensitivity (volts/ photon) of the detector and filter combination vs wavelength, the output of a calibrated 424 ± 1 K blackbody is chopped and imaged onto the detector. The relative detector output is measured by a lock-in amplifier and recorded vs CVF wavelength setting. The resulting curve is normalized to a calculated 424 K blackbody emission curve (photons/ μ m vs wavelength) to obtain the desired detector and filter sensitivity curve (volts/photon) under conditions close to the actual operating conditions. The relative sensitivity curve rises smoothly from 1.00 to 1.33 as the wavelength increases from 2.5 to 3.4 μ m.

D. Determination of an HF emission spectrum

The F⁻ current is modulated by applying -12 V, 0.3 ms rectangular pulses to a 95% transmission tungsten mesh at 7.5 ms intervals. The mesh covers the cross sectional area of the flow tube at a position 40 cm down-stream of the ion source (Fig. 1) The modulation is monitored by observing F⁻ counts at the mass spectrometer vs time; a large fraction of the F⁻ ion current is modulated at the peak of the cycle. The modulation makes it possible to distinguish ion-molecule chemi-luminescence signals from large steady-state interfering signals due to neutral reactions such as F + HX - HF(v) + X. The IR detector sees a modulation of the infrared

light intensity due to a decrease in emission from ionmolecule reaction products when F^- reactants are briefly removed from the flow. The area of the dip in the IR signal is proportional to the number of F^- ions removed from the flow and to the intensity of HF emission from the desired ion reaction products at the chosen CVF wavelength. The detector output is digitized and signal averaged by summing many cycles of the modulating voltage pulse. Figure 5 of Ref. 8 shows a typical detector output vs time trace.

An HF chemiluminescence spectrum is obtained by manually stepping the CVF through the 2.5-3.5 µm region. At each wavelength, $\sim 10^4$ periods of the modulated detector output are signal averaged and the area of the IR emission dip is determined. In practice, data points are taken at 0.0154 μ m intervals, corresponding to about four data points per FWHM resolution element of the CVF. During the 2-4 h required to complete a spectrum, it is necessary for all flows and pressures to remain stable. This is checked periodically by returning the CVF to a "reference wavelength" and measuring the integrated IR signal. Stability at the reference point to within $\pm 5\%$ during the entire spectrum is demanded of all spectra used for population analysis. The wavelength is varied in such a way as to distribute any instabilities across the entire spectrum.

Although the chain reaction sequence [Eqs. (1) and (2)] that occurs when F_2 is used as the F⁻ source is an annoyance in the rate constant measurements, it serves to enhance the infrared signals in the actual chemiluminescence experiments. The strongest signals are obtained by using <0.1 mTorr of 5% F_2/He to generate the ions initially and by adding ~4 mTorr of 5% F_2 /He downstream between the modulating mesh and the HX inlet (Fig. 1). The F ions formed upstream are cycled through the F + HX reaction several times by the chain sequence. The downstream addition of F_2 enhances the cycling rate by increasing the rate of $X' + F_2$, leading to a factor of 2-3 improvement in the IR emission signals. The He density in the flow tube is ~ 1400 times larger than the HX density, so that the F⁻ ions regenerated by $X^{-}+F_{2}$ are completely thermalized before reacting again with HX. The chain causes no experimentally observable alteration of the emission spectrum of HF molecules produced by F^{*}+HX.

Spectra for the three F + HX reactions are shown in Figs. 2(a), 2(b), and 2(c). These spectra have been corrected for the relative detector and filter sensitivity at each wavelength. Three, four, and five partially resolved intensity maxima appear in the HF emission spectrum from F' + HC1, F' + HBr, and F' + HI, respectively. The HF rotational constant ($B_e = 20.96 \text{ cm}^{-1}$) and anharmonicity $(\omega_e x_e = 89.9 \text{ cm}^{-1})^{17}$ are such that for a 300 K Boltzmann distribution of emitting rotational states (see Sec. III B) the P branch of the v - v - 1 emission band overlaps the R branch of the v + 1 - v band very closely. Thus the peak at 2.59 μ m is primarily a superposition of the P branch of the v=1-0 band and the R branch of v=2-1; the peak at 2.71 μ m is due to the P branch of 2-1 and the R branch of 3-2, etc. The number of peaks in each spectrum is in accord with the highest energeti-



FIG. 2. HF chemiluminescence spectra from (a) F^+ +HCl, (b) F^- +HBr, and (c) F^- +HI, corrected for relative detection sensitivity. The solid lines are the least-squares fits to the spectra.

cally accessible vibrational level in each reaction, i.e., $v_{\rm max}$ = 3, 4, and 5 for HCl, HBr, and HI (Table I). The R branch of the v = 1-0 transition peaks at 2.4 μ m and is not covered by the range of the CVF. The relative contribution of the 1-0 band is evaluated using only the P branch.

E. Experimental checks on the spectra

A variety of checks are performed to determine that the modulated signal is in fact due to HF molecules produced by the F +HX ion-molecule reaction. First of all, a "two-mesh" experiment shows that greater than 98% of the total modulated signal is due to ion-molecule, as opposed to neutral, reactions. In this experiment, a second tungsten mesh is inserted across the flow tube 6 cm upstream of the usual mesh shown in Fig. 1. A dc potential of -50 V is applied to the upstream mesh to diminish the F^{*} current by at least a factor of 150. The other experimental conditions are as usual (Sec. IIA). including the repetitive -12 V, 0.3 ms ion-off modulation on the downstream mesh. Total infrared emission is viewed through a broadband quartz filter which transmits all of the HF(v=1-5) emission region. For all three F + HX reactions, the modulated total emission signal is more than 60 times smaller with the F current blocked (-50 V on upstream mesh) than with the normal F⁻ current (no voltage on upstream mesh). Thus less than 2% of the modulated signal in the HF region is due to processes not requiring ions in the flow.

In the Cl⁻+HI reaction studied earlier,⁸ it was observed that large modulation voltages caused detachment of Cl⁻ at the tungsten mesh, leading to modulated Cl atoms and a sharp *positive-going* component of signal due to an *increase* in emission from the fast, quite exothermic Cl+HI neutral reaction. No such positive-going signals are observed for the F⁻+HX reactions under any conditions of modulation. This is expected, since the neutral F⁻+HX reactions are 25-200 times slower than the corresponding F⁻+HX reactions (Table I) so that detachment of F⁻ to form F would have little effect on the infrared emission.

There remains the possibility that ion-molecule reactions other than F +HX might result in chemiluminescent products that emit in the 2.5–3.3 μ m region. This is unlikely since very few molecules have vibrational frequencies as high as HF. Other negative ion reactions can be eliminated from consideration because the negative ion mass spectra show that F⁻ is the only negative ion produced from F2. Addition of HX converts the mass spectrum to two peaks, a large X peak from F' + HX - HF + X' and a residual F' peak due to the steady state F current in the chain reaction scheme [Eqs. (1) and (2)]. Since F_2 forms positive ions very poorly, the positive ion mass spectrum with only F₂ flowing exhibits peaks primarily due to minor impurities in the flow tube. Ions such as He⁺, H_2O^+ , H_3O^+ , NO⁺, and O_2^+ are typical. It is conceivable that modulated OH stretch emission from H_2O^+ or H_3O^+ could contaminate the HF spectrum near 3.0 μ m. Small background signals amounting to about 5% of the total signal from F + HXare observed through a broadband quartz filter when F_2 , but no HX, is flowing. Tests with available bandpass filters suggest that the background signal peaks at $\lambda > 3.6 \ \mu m$, outside the HF region. No background signal could be observed at all when dispersed with the CVF in the 2.5-3.5 μ m region.

Addition of 0.3 mTorr of O_2 upstream collapses about half of the positive ion spectrum to O_2^* . There is no

background IR signal through a broadband filter with only F_2 and O_2 flowing, suggesting that the O_2 circumvents some positive ion chemistry that leads to the weak background emission. Final spectra were also taken with 0.3 mTorr of O_2 flowing to serve as an additional check. The O_2 has no effect on the negative ion mass spectra, and HF chemiluminescence spectra taken with and without the O_2 additive are identical within experimental uncertainty for all three reactions. Positive ion reactions thus do not contribute significantly to the spectrum obtained with F_2 , HX, and O_2 flowing.

III. POPULATIONS FROM SPECTRA

Relative HF vibrational state populations are derived from the raw chemiluminescence spectra by a linear least squares fitting procedure in which the products (A_v, N_v) of Einstein spontaneous emission coefficients (A_{v}) and relative populations (N_{v}) of each vibrational state are adjustable parameters. The N_v are then obtained by dividing out the values of A_v , which have been experimentally determined by Sileo and Cool.¹⁹ Small corrections are applied to the N_{v} for the radiative and collisional cascading between the time of formation of HF and the time of observation of HF emission. The resulting nascent vibrational state populations N_{ν}^{0} are proportional to the individual thermal (295 K) rate constants k_v for reaction into the specific HF vibrational states. Finally, vibrational surprisal plots are extrapolated to v=0 to obtain estimates of $N_{v=0}^0$ and $\langle f_v \rangle$, the average fraction of the available energy deposited in product vibration.

A. Curve fitting procedure

First, the raw spectral data (obtained as described in Secs. II A, II C, and II D) are normalized to the relative detector and CVF sensitivity curve (Sec. II C) to yield experimental data such as those displayed in Figs. 2(a), 2(b), and 2(c). A computer model of the relative intensity vs CVF wavelength per unit population of each HF(v) state is constructed as follows. For each v + v - 1band, a stick spectrum consisting of the wavelength and relative emission intensity of the various P and R lines is calculated from the known Dunham coefficients and the expression^{19, 20}

$$I_{\rm em}(vJ - v'J') \propto |R_{vJ - v'J'}|^2 \nu_{vJ - v'J'}^3 (J + J' + 1) \\ \times (Q_v^{\rm rot})^{-1} \exp(-E_{vJ}^{\rm rot}/kT_{\rm rot}) .$$
(3)

Equation (3) gives the emission intensity (photons/s) for a Boltzmann distribution of upper state rotational levels at temperature T_{rot} . $|R_{vJ+v'J'}|^2$ is the square of the transition moment¹⁹; v^3 is the frequency factor for a given line; (J+J'+1) is the rotational line strength factor; Q_v^{rot} is the rotational partition function of vibrational level v at temperature T_{rot} ; and E_{vJ}^{rot} is the rotational energy of the vJ level. Evidence that emission occurs from a Boltzmann distribution of rotational levels within each vibrational state is given in Sec. III B below. At each CVF wavelength λ_i , the stick spectrum for each $v \rightarrow v - 1$ band is convolved with the experimentally determined filter transmission function (a Gaussian of $0.060 \ \mu$ m FWHM at all λ_i) to yield the calculated $v \rightarrow v - 1$ emission intensity per unit population at λ_i ,

TABLE II. Relative HF vibrational state populations from F⁺+HX.

Reaction		$v = 0^{\mathbf{b}}$	<i>v</i> = 1	<i>v</i> = 2	v = 3	v = 4	v = 5
F"+HCl ²	Nascent N_v^0 Raw N_v	(0,60±0.14)	$0.46 \pm 0.04 \\ 0.48 \pm 0.04$	$\begin{array}{c} 0.33 \pm 0.03 \\ 0.33 \pm 0.03 \end{array}$	0.21 ± 0.02 0.19 ± 0.02		
F"+HBr ²	Nascent N_v^0 Raw N_v	(0,31±0,09)	0.28 ± 0.04 0.29 ± 0.04	0.27 ± 0.03 0.29 ± 0.03	0.24 ± 0.02 0.24 ± 0.02	0.21 ± 0.02 0.18 ± 0.02	
F"+HI ²	Nascent N_v^0 Raw N_v	(0.18±0.10)	0.20 ± 0.04 0.22 ± 0.04	$\begin{array}{c} 0.23 \pm 0.03 \\ 0.24 \pm 0.03 \end{array}$	$\begin{array}{c} 0.22 \pm 0.02 \\ 0.22 \pm 0.02 \end{array}$	0.20±0.02 0.19±0.02	0.15 ± 0.02 0.13 ± 0.02
F ⁻ +HCl ^e	z = 10 cm Corrected N_v^0		0.45 ± 0.04	0.35 ± 0.03	0.20 ± 0.02		
F ⁻ +HBr ^c	z = 10 cm Corrected N_v^0		0.24 ± 0.04	0.35 ± 0.03	0.23 ± 0.02	0.18 ± 0.02	
F*+HI¢	z = 10 cm Corrected N_v^0		0.17±0.04	0.28 ± 0.03	0.19 ± 0.02	0.22 ± 0.02	0.13±0.02
F ⁻ +HCl ^d	z = 10 cm $P_{\text{HCl}} = 1.0 \text{ mTorr}$ Corrected N_v^0		0.42 ± 0.04	0.36 ± 0.03	0.22 ± 0.02		
F ⁺ +HCl ^e	HF cell in raw N _v		0.04 ± 0.04	0.33 ± 0.03	0.21 ± 0.03		
F*+HBr*	HF cell in raw N _v		0.05 ± 0.03	$\textbf{0.28} \pm \textbf{0.03}$	0.25 ± 0.03	0.16 ± 0.02	
F"+HI"	HF cell in raw N _v		0.03 ± 0.03	0.24 ± 0.03	$\textbf{0.25} \pm \textbf{0.03}$	0.18±0.02	0.10±0.02

^aRaw N_v distributions are averages of least-squares fits to three separate spectra using $P_{HX}=0.5$ mTorr and an HX inlet-viewing window distance of z=5 cm. Nascent N_v^0 distributions are obtained by applying a small cascading correction using $\langle t_{obo} \rangle = 0.20$ ms (Sec. IIIC) to the raw N_v distributions. The z=5 cm data are *a priori* the most reliable and provide the final "best" values to be used.

^bThe $N_{i=0}^{0}$ populations are obtained by extrapolation of vibrational surprisal plots (Sec. IIID).

^cCorrected N_{ν}^{0} distributions derived from spectra using $P_{\rm HX} = 0.5$ mTorr but an HX inlet-viewing window distance of z = 10 cm. For HBr and HI, the results are an average of two spectra each, whereas the HCl results are from a single spectrum. For z = 10 cm, the cascading correction uses $\langle t_{\rm obs} \rangle = 0.41$ ms.

^dCorrected N_{ν}^{0} distribution from a single F⁻+HCl spectrum using $P_{HCl} = 1.0$ mTorr and z = 10 cm.

^eRaw N_v distributions from single spectra obtained with $P_{HX} = 0.5$ mTorr, z = 5 cm, and HF cold gas filter cell interposed between detector and flow tube. The $v \ge 2$ part of the distributions should be compared to the raw N_v distributions in the upper section of the table.

labeled $I_v(\lambda_i)$. Since the lines in the stick spectrum are much narrower than the experimental resolution, $I_v(\lambda_i)$ simply amounts to a sum of the emission intensities for all v + v - 1 lines, each weighted by the amplitude of 0.060 μ m FWHM Gaussian centered at λ_i .

The relative vibrational state populations N_{ν} are derived by a linear least squares fit²¹ of the calculated spectrum

$$I_{calc}(\lambda_i) = \sum_{\nu} N_{\nu} I_{\nu}(\lambda_i)$$
(4)

to the experimental spectrum with $A_v N_v$ as the adjustable parameters in the fit. There is an A_v factor hidden in I_v of Eq. (4). A statistical estimate of the variance $\sigma_{N_v}^2$ of each N_v is also calculated.²¹ The least squares problem is highly overdetermined in the sense that only three, four, or five parameters are obtained from some 40-60 data points.

Computer calculated best fit spectra using $T_{rot} = 300$ K are displayed as the solid lines in Figs. 2(a), 2(b), and 2(c). The fit is qualitatively very good in each case. The N_{ν} entries in Table II are averages of the results

from at least three spectra obtained under conditions that minimize $v \rightarrow v - 1$ cascading in the time between formation and detection of HF (Sec. IIIC). The reported distributions are normalized so as to sum to unity. For each reaction, the reported error limits encompass the maximum and minimum values for the entire set of bestfit results over all the spectra. The statistical estimates for the standard deviation of each N_v are typically smaller than this. The ratio of any two relative populations N_v/N_v , for a given reaction is typically accurate to $\pm 15\%$.

B. Experimental checks on populations

1. Variation of detection geometry

The transmission function of the CVF/slit combination is measured (Sec. IIC) using well collimated light exiting a monochromator slit. However, depending on the experimental geometry (Fig. 1), an appreciable fraction of the IR emission collected from the flow tube may impinge on the CVF at angles as great as $30^{\circ}-40^{\circ}$ from normal incidence. Multilayer interference filters show a characteristic shift of the transmission curve towards short wavelength as the incidence angle moves away from normal. Early HF spectra taken with the detector and CaF_2 lens as close to the flow tube window as possible showed poorer resolution and more extended tails towards long wavelength than the spectra of Figs. 2(a)-2(c). The computer simulation yields qualitatively poor fits to these early spectra. The difficulty involves offnormal incidence light. The effective transmission function for the close-in detection geometry is a complex linear combination of the Gaussian for normal incidence light and various blue-shifted Gaussians for the off-normal incidence light. The shift towards the blue of the transmission curve at each CVF setting results in a shift towards the red of the spectrum intensity when the CVF wavelength is scanned past fixed-frequency HF emission lines. As the CaF_2 lens and detector are moved away from the flow tube the spectral peaks sharpen up and the tail on the red edge of the spectrum diminishes. The final geometry (Fig. 1) was chosen so that the spectra are indistinguishable from those obtained at half the detector height. A factor of 5 in signal intensity was discarded as compared to the close-in geometry.

2. Emission from highly excited HF rotational states

A 300 K Boltzmann distribution of emitting HF rotational states is used in the calculated spectra. This assumes that rotational relaxation of HF is fast within each vibrational level, while vibrational relaxation is slow, during the time between formation and detection of an HF product molecule. As discussed in Sec. III C, the relevant time is about 0.20 ms, during which an HF molecule suffers ~ 2000 hard sphere collisions with He.

Sung and Setser²² have obtained rotationally resolved HF chemiluminescence spectra from neutral F+HBr, HI, H₂S, H₂CO, SiH₄, and GeH₄ reactions in a flowing afterglow which is similar to the one used here. The results indicate that in 1 Torr of Ar, $HF(J \le 9)$ states relax to a Boltzmann distribution within 0.4 ms. A fraction of the higher rotational state $HF(J \ge 10)$ population tends to "hang up" in a non-Boltzmann distribution for much longer periods in Ar. Substitution of He for Ar gives a much greater degree of rotational relaxation. Quick and Wittig²³ see no evidence of very high HF rotational states on a ~ 5 μ s time scale after multiphoton dissociation of fluorinated ethanes in 12 Torr He.

In order to check whether or not $HF(J \ge 10)$ levels might be populated in the F + HX reactions and survive longer than 0.20 ms in 0.7 Torr He, attempts were made to observe IR emission through a bandpass filter which is ~65% transmitting in the range 2.12-2.38 μ m $(4200-4700 \text{ cm}^{-1})$. This filter transmits the HF lines $R(J \ge 6)$ for v = 1 - 0 and $R(J \ge 16)$ for v = 2 - 1. Only 0.6% of the HF molecules in a 300 K rotational equilibrium would have $J \ge 7$. The IR signals through the bandpass filter are extremely weak. Comparison of the signal through this filter with the total IR emission intensity viewed through quartz yields an estimated upper bound on the fraction of the v=1 molecules emitting from $J \ge 7$. The estimates are < 1% for F⁺+HCl; < 7% for F⁺+HBr; and <8% for F⁺+HI. The v > 1 levels have less exothermicity available for HF rotation, so it is likely that

smaller fractions of the v > 1 molecules are born in high J states.

For the computer calculated spectra, the goodness-offit parameter (sum of squared errors) is insensitive to the rotational temperature T_{rot} over the range 300-450 K. The sum of the squares of the deviations increases rapidly at higher T_{rot} . The relative N_v vary by less than the error estimates in Table II as T_{rot} varies from 300-350 K. The reaction exothermicity raises the temperature of the He buffer by much less than 1 K above room temperature. Thus a great deal of evidence supports the validity of the calculated spectra using $T_{rot} = 300$ K.

3. The ratio (total emission intensity)/(v > 1 emission intensity)

An experimental consistency check on the best-fit populations N_v (Table II) is performed with an HF cold gas filter cell to absorb the v=1-0 emission. For each reaction, the ratio of the total infrared emission intensity to the intensity from all levels with v > 1 is given by

$$R = \left(\sum_{\nu>0} A_{\nu} N_{\nu}\right) / \left(\sum_{\nu>1} A_{\nu} N_{\nu}\right)$$
$$= 1 + \left(A_{1} N_{1}\right) / \left(\sum_{\nu>1} A_{\nu} N_{\nu}\right) , \qquad (5)$$

where A_v and N_v are the v - v - 1 Einstein coefficients and the relative populations for HF(v). The ratio R can be obtained in three ways. First, it can be calculated from the best fit populations N_v using the independently measured A_{v} ; call this result R_{pop} . The other two techniques involve interposing a 2 cm long filter cell with ~30 Torr of HF gas at 300 K between the flow tube and the IR detector. The filter cell selectively absorbs all HF 1-0 emission from the rotational states present in a 300 K Boltzmann distribution and passes all other HF emission. The ratio of the total IR emission intensity viewed through quartz without and with the HF cell in place gives an independent measure of R [Eq. (5)] which is labeled $R_{in/out}$. In practice, $R_{in/out}$ is obtained either by freezing the HF into a 77 K sidearm or by physically removing the HF cell, which requires a "cell factor" correction for window reflections and light piping. The two methods agree very well.

As a third alternative, R is obtained by recording an entire HF emission spectrum with the HF gas cell in place. Figure 3 shows such a spectrum for F^{*}+HCl. The peak at 2.59 μ m, which has a major P(1-0) component, is noticeably diminished as compared to the complete spectrum in Fig. 2(a). By normalizing the spectra with and without the HF cell to match each other at long λ and then comparing the areas under the two spectra, another measure of R, labeled $R_{spectra}$, is obtained.

The results for the three techniques of obtaining R are collected in Table III. The good agreement among R_{pop} , $R_{in/out}$, and $R_{spectra}$ for all three reactions serves as further confirmation of the validity of the relative vibrational state populations N_v derived from the $T_{rot} = 300$ K computed spectrum.



FIG. 3. HF chemiluminescence spectrum from F^+ +HCl taken with a HF cold gas cell interposed between the detector and the flow tube. Compare with Fig. 2 (a) to see that a fraction of the peak at 2.59 μ m due to the P branch of the v = 1-0 band has been absorbed.

4. Spectra taken through HF cold gas filter

The spectra recorded with the HF cold gas filter cell in place are also fit to yield raw distributions N_v . These should agree with the raw N_v distributions obtained without the HF filter in place, except that N_1 should equal zero, since the filter absorbs all 1-0 emission from thermalized J states. The distributions derived from spectra with the HF filter cell in place are included at the bottom of Table II next to the label "HF cell in, raw N_v ." The distributions are in good agreement with those at the top of Table II (no HF cell) except that, indeed, $N_1 \simeq 0$. This provides yet another consistency check on the raw N_v and on the unimportance of non-Boltzmann rotational state populations.

C. Corrections for vibrational cascading

The HF spontaneous emission rates $A_{v \rightarrow v'}$ and the $v \rightarrow v - 1$ collisional relaxation rates are just large enough to warrant small cascading corrections to the best fit populations N_v (Table II). For each HF vibrational state v, a small fraction of the nascent population radiates or deactivates collisionally to v - 1 or v - 2 in the ~ 0.20 ms between formation and detection. The largest correction factor applies to the highest state populated, v_{\max} , since it is only depleted, whereas all lower states are both depleted and repopulated from above. Corrections to $N_{v_{\max}}$ are never larger than a factor of 1.20, while corrections to the lower state populations require factors in the range 1.00-1.10.

The HF cascading kinetic model includes radiative rates (Einstein A coefficients) for both $v \rightarrow v - 1$ and $v \rightarrow v - 2$ from Sileo and Cool¹⁹ and collisional $v \rightarrow v - 1$ rates. The latter rate constants are distilled from the rather extensive HF vibrational relaxation literature.^{24,25} For 0.7 Torr He, 0.5 mTorr HX, 0.3 mTorr O₂, and ~ 0.2 mTorr F₂, the near-resonant transfer rate to HX is the only important v + v - 1 collisional rate. The radiative v + v - 1 rates are always at least five times larger than the collisional deactivation rates. The cascading corrections are evaluated at a time corresponding to the mean time between formation and observation of an HF molecule in the flow tube, $\langle t_{obs} \rangle = 0.20 \pm 0.04$ ms. This $\langle t_{obs} \rangle$ is shorter than the transit time computed from $\overline{v}_{1\,on} = 1.4 \times 10^4$ cm s⁻¹ (the mean axial ion velocity)¹⁴ and z = 5 cm (the distance between the HX inlet and the center of the observation window) because of the cycling of the chain reaction [Eqs. (1) and (2)]. Insertion of an average time into the cascading formulas rather than averaging over a distribution of times is appropriate in the limit of small cascading corrections, which applies here.

The best values for the relative nascent populations N_v^0 for the F⁻+HX reactions are shown at the top of Table II. The error limits are almost entirely due to uncertainties in the computer-derived N_v ; uncertainties in $\langle t_{obs} \rangle$ and in the various cascading rates contribute insignificantly to the uncertainties in the N_v^0 .

Two spectra of each reaction were also taken with z = 10 cm rather than 5 cm between the HX inlet and the center of the viewing window. This increases $\langle t_{obs} \rangle$ by nearly a factor of 2 to 0.41 ms. Application of the same cascading corrections to these results yields nascent populations in reasonable agreement with those obtained at z = 5 cm; the correction factors however are significantly larger so that the N_v^0 in Table II from z = 5 cm data are *a priori* more reliable. Similarly, the corrected populations from a spectrum using z = 10 cm and a two-fold larger HCl flow (1.0 mTorr) are in good agreement with the "standard condition" data taken for z = 5 cm and 0.5 mTorr HCl. All of these results are collected in Table II.

D. Estimates of $N_{\nu=0}^0$ and $\langle f_{\nu} \rangle$ from surprisal plots

Chemiluminescence experiments can give no information about the importance of the HF(v=0) channel. In order to estimate $\langle f_v \rangle$, the average fraction of the available energy deposited in product vibration, vibrational surprisal plots²⁶ are constructed for each F^- + HX reaction. Extrapolations of such plots to v=0 are used to obtain a rough estimate of $N_{u=0}^0$ and thus of $\langle f_v \rangle$.

TABLE III. Ratio of total HF emission intensity to v > 1 HF emission intensity.

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Reaction	R _{pop} ¹	R _{in/out} ^b	R _{spectra} c
F"+HCl	1.45 ± 0.04	1.38 ± 0.03	1.45 ± 0.08
F ⁻ +HBr	1.19 ± 0.03	$\textbf{1.15} \pm \textbf{0.02}$	1.18 ± 0.05
F ⁻ +HI	1.11 ± 0.02	1.07 ± 0.03	1.14 ± 0.03

^aCalculated from Eq. (5) using the raw populations N_v of Table II and the Einstein A-coefficients A_v of Ref. 19. ^bExperimental ratio of total emission intensities without and with the HF cold gas filter cell between detector and flow tube.

Each entry is an average of three determinations. ^cRatio of the integrated area of complete spectral scans without and with the HF cold gas filter cell. See Sec. III B 3 for details.



FIG. 4. Vibrational surprisal plots. The P_v are the best nascent experimental distributions, taken from the top of Table II, while P_v^0 are the prior distributions. The solid lines are smooth curves drawn through the data points. For the sake of clarity, each curve has been displaced vertically by an additive constant.

The average total energy available to products is computed (assuming no barrier in the entrance valley) from $\langle E_{tot} \rangle = -\Delta H + (5/2)kT$, using T = 298 K and the ΔH values from Table I. The prior vibrational state distribution P_v^0 is calculated from the formula $P_v^0 \propto \sum_J (2J+1) [\langle E_{tot} \rangle - E_{v,J}]^{1/2}$, using the exact HF energy levels $E_{v,J}$. There are no severe *a priori* angular momentum constraints on the products since the reduced mass changes very little from reactants to products.

The surprisal plots, displayed in Fig. 4, are distinctly nonlinear, yet similarly shaped for all three reactions. It is noted in passing that with the possible exception of F+HBr, the corresponding neutral reactions yield surprisal plots with better linearity.^{11,12} Each curve is smoothly extrapolated to $f_v = 0$ (Fig. 4) to obtain a crude estimate of $N_{w=0}^0$. These are included in Table II. The $\langle f_v \rangle$ calculated from the experimental N_v^0 for $v \ge 1$ and the extrapolated $N_{w=0}^0$ is 0.31 ± 0.04 , 0.40 ± 0.04 , and 0.45 ± 0.06 for F⁺+HCl, F⁺+HBr, and F⁻+HI, respectively. These can be compared to the values of 0.48, 0.56, and 0.57 from the results of Setser *et al.*¹¹ for the corresponding neutral reactions F+HCl, F+HBr, and F+HI.

The experimental $v \ge 1$ vibrational state distributions and the surprisal plots suggest nothing unusual about the v=0 channel. However, the possibility that the v=0channel completely dominates the product states cannot be fully eliminated. As a consistency check on the notion that N_0 is of comparable magnitude to the other N_v , the relative total infrared emission intensity per product HF molecule is measured for all three F⁻ +HX reactions. For a constant F⁻ current in the flow tube, the total emission intensity through a quartz filter is measured for each F⁻ +HX reaction as a function of added HX pressure. The chain mechanism [Eqs. (1) and (2)] is avoided by omitting the F_2 /He addition downstream. In each case, the HX pressure is increased until the emission intensity levels off, indicating complete reaction of the F⁻ current prior to the viewing region. This requires 1.1, 1.2, and 1.5 mTorr for HCl, HBr, and HI. The required pressure increases from HCl through HI because the reaction rate constants decrease correspondingly (Table I). The resulting relative total emission intensities are in the ratio 1.00:1.22 $\pm 0.03:1.44\pm 0.03$ for F⁻ +HCl, F⁻ +HBr, and F⁻ +HI, respectively. The ratio should tend to increase down the series because the reaction exothermicity increases and, in addition, the Einstein A coefficients increase for the higher HF levels.

It is qualitatively clear from the small variation in relative total emission intensity that the three reactions behave similarly with respect to the v = 0 channel. If v = 0 dominates the products of one reaction, then it must do so for all three, since similar amounts of total fluorescence come from each reaction. In addition, the experimental ratios 1.00: 1.22: 1.44 are entirely consistent with total intensity ratios which are calculated from the $N_v^{0,v}$ s in Table II. The conclusion is that the surprisal plot extrapolations probably give reasonable estimates of the $N_{v=0}^{0}$.

IV. DISCUSSION

A. Energetics of FHX⁻ and FHX

The present ion-molecule F + HX product vibrational state distributions can be compared to the corresponding neutral F+HX reactions, which have been studied by Setser and co-workers¹¹ and by Polanyi and co-workers.¹² Table I summarizes the exothermicities of the F' + HXand F+HX series of reactions. The corresponding ion and neutral reactions have nearly identical exothermicities because the electron affinities of F, Cl, Br, and I are very similar.¹⁸ In addition, the mass combination for pairs of corresponding reactions is essentially identical. However, the shape of the potential energy surface on which corresponding reactions occur is strikingly different. The neutral F+HX reaction presumably^{11,12} occurs on a surface having a small, ~1 kcal/mol barrier in the entrance valley and proceeding essentially monotonically downhill along the "reaction coordinate" from the crest of the barrier to the product valley (Fig. 5). In contrast, the ion-molecule F + HX reaction occurs on a surface having a deep potential well corresponding to the stable ion FHX; it is unlikely that there is any barrier in the entrance valley. The vibrational state distribution in the reaction products is governed both by kinematic effects and surface shape. The comparison of the present results with those from F+HX represent an initial attempt to explore the relative importance and exact nature of these effects in the F + HX systems.

To a very good approximation, the F^- +HX reactions occur adiabatically on a single potential energy surface, unlike many positive ion-molecule reactions. All reactants and products are closed-shell species whose excited states occur at very high energy. The neutral re-



FIG. 5. Schematic of F⁺+HCl and F+HCl reaction energetics.

action $F({}^{2}P_{3/2,1/2})$ + HX involves six surfaces, at least two of which provide low energy paths to HF+X. Some of the possible effects of nonadiabaticity on the product state distributions have been considered.^{11,12} If such effects are important, it may be inappropriate to infer the influence of the shape of potential energy surfaces from comparisons of F⁻+HX and F+HX product states.

In addition to the F+HX reaction exothermicities, information about the series of FH-X bond strengths in the FHX bihalide ions is available from mass spectroscopic and ion cyclotron resonance studies.²⁷ The bond strengths provide a reasonable measure of the depth of the attractive wells on the F⁺+HX potential surfaces, as shown schematically in Fig. 5 for the F+HCl case. The bihalide ion FHCl" sits in a presumably global minimum about 14 kcal/mol below the HF+Cl⁻ product asymptote. Similarly, FHBr and FHI are stable by about 13 and 12 kcal/mol, respectively, relative to HF+Br and HF+I. There are no data on the gas phase geometries and vibrational frequencies of the FHX anions. In this context it is interesting to note that there is evidence for the existence of a stable neutral HIF molecule (note the specific ordering of the atoms) from F_2 + HI crossed beam studies.²⁸ A lower bound of 19 kcal/mol is set on the HI-F bond energy. The stability of the HXF molecule presumably decreases as X becomes more electronegative.

B. Comparison of $HF(\nu)$ distributions from $F^- + HX$ and F + HX

Figure 6 compares the present HF vibrational state distributions for the ion-molecule F + HX reactions (Table II) with those of Setser and co-workers¹¹ for the corresponding neutral F+HX reactions. For F+HCl the arrested relaxation data of Polanyi and co-workers¹² is in good agreement with the flowing afterglow results of Setser and co-workers.¹¹ There is presently a discrepancy in the results from the two groups for the F+HBr reaction. Polanyi *et al.* obtain a nearly statistical vibrational distribution which peaks at v = 1 and decreases monotonically for higher v, in considerable contrast to Setser *et al.* distribution, which is reproduced in Fig. 6.

The ion-molecule product vibrational state distributions are qualitatively very similar to the neutrals in t that both are much hotter than statistical. However there is a noticeably smaller degree of vibrational excitation in the ion reactions. We attribute this to the effect of the deep potential minimum in the ion reactive surfaces. The similarities, however, appear to outweigh the differences. This may be a surprising result in view of the dramatic differences in the shape of the potential surfaces on which the neutral and ion-molecule reactions proceed. A kinematic effect common to both types of reaction may dominate over the major change in the shape of the potential energy surface.

C. Dynamics

The deep potential wells in the F^+ HX surfaces might suggest that the product vibrational state distributions should be statistical, in contrast to the very hot distributions which are actually observed. However, the wells are shallow (~13 kcal/mol relative to HF +X⁻ in all three cases) compared to the 40-60 kcal/mol reaction exothermicities (Fig. 5). The collision partners gain a tremendous amount of kinetic energy as they are drawn together by the attractive well. The "transition state"



FIG. 6. Bar graphs of nascent product vibrational state distributions N_{ν}^{0} for F⁺+HX (Table II) and for the F+HX results of Setser and co-workers (Ref. 11).

thus contains a great deal of internal energy relative to the product asymptote and has only four vibrational degrees of freedom among which to distribute this energy (assuming linear FHX⁻). It is therefore not surprising that a nonstatistical product state distribution is observed, suggesting short-lived, direct reactive encounters. Indeed, a simple RRKM estimate²⁹ of the lifetime of an activated FHX⁻molecule relative to HF + X⁻ dissociation yields $\tau \simeq 0.1$ ps, comparable to a "direct collision" time.

Given that direct reactive encounters are quite plausible on an F + HX potential surface, it remains to explain the strong propensity of these reactions to deposit their exothermicity in product vibration. The most likely explanation involves a kinematic effect associated with the mass combination involved, namely, the exchange of a light particle between two heavy particles $(H + LH' \rightarrow HL + H')$. In properly skewed coordinates that diagonalize the kinetic energy, ¹ the angle between the entrance and exit valleys of a collinear surface is a mer ϵ 15°, i.e., the two valleys are nearly parallel. The effect of such an extreme skew angle is well understood for typical exothermic "neutral-like" surfaces such as London-Eyring-Polanyi-Sato surfaces (small barrier, no deep attractive well).^{1,3,30} Both "attractive" (early barrier) and "repulsive" (late barrier) surfaces efficiently funnel energy into product vibration for the H + LH' mass combination. For other mass combinations, the repulsive surface favors product translation. but for H + LH', many trajectories efficiently "cut the highly skewed corner" leading to "mixed energy release" and extensive vibrational excitation of the products.³

Experience with quasiclassical trajectories on "ionmolecule-like" surfaces having deep potential wells is quite limited.³⁰ However, the recent work of Chapman³¹ on a semiempirical Cl⁺+HBr collinear surface clearly suggests that the same H + LH' kinematic effect dominates any influence of the deep potential well. The Cl⁺ + HBr surface used has a 15.6 kcal/mol exothermicity and the bottom of the well lies 9.1 kcal/mol below theHCl+Br product limit. The well is displaced towards the product valley. Chapman finds about 80% direct trajectories. Interestingly, even the long-lived trajectories tend to preserve motion in the diagonal direction corresponding to the light H atom rapidly vibrating between the heavy Cl and Br nuclei once such motion is excited, Momentum transfer from the oscillating H atom to the heavy Cl is inefficient even after dozens of encounters. The system prefers to oscillate between the nearly parallel outside repulsive walls of the entrance and exit valleys. This motion remains as product vibration when the system finally manages to find the product valley.

This kinematic effect is the most likely explanation for the efficient population of product vibrational states in the F^- +HX reactions and in the previously studied Cl^- +HX reactions.⁸ Some caution is appropriate since the effect is so far documented for only one collinear ion-molecule surface. The enormous F^- +HX reactive cross sections indicate little or no preference for collinear approach of reactants, even though the gas phase FHX⁻ ions are probably linear. Apparently the longrange, spherical ion-induced dipole forces make the approach of F and HX attractive from all directions. This suggests that rather complicated trajectories involving migration of the H atom must be important in three dimensions. Quantum mechanical tunneling effects may also be important.³¹

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 $R_{vj-v,j} = R_v^{v'} (m=0) [1.0 + c_1 m + c_2 m^2 + c_3 m^3],$

where m = -J' for *P*-branch transitions, m = j' + 1 for *R*branch transitions. The values for R_{ν}^{ν} (m = 0) and the expansion coefficients c_i are taken from K. Tamagake and D. W. Setser, J. Phys. Chem. 83, 1000 (1979). The relative Einstein in coefficients $A_{\nu} = |R_{\nu}^{\nu}(m = 0)|^2 \nu_0^3$ are in the ratio $A_1:A_2:A_3:A_4:A_5 = 1.00:1.71:2.17:2.39:2.43$.

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