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Nascent product vibrational state distributions of ion-molecule reactions: The $H+F^{-}\rightarrow HF(v)+e^{-}$ associative detachment reaction

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The nascent product vibrational state distribution is obtained for the thermal energy associative detachment reaction $H + F^- \rightarrow HF(v \le 5) + e^-$, $\Delta H = -57.0$ kcal/mol. The relative vibrational populations are as follows: $N_{r=1}^0 = 0.00 \pm 0.06$; $N_{r=2}^0 = 0.23 \pm 0.04$; $N_{r=3}^0 = 0.27 \pm 0.03$; $N_{r=4}^0 = 0.29 \pm 0.03$; and $N_{r=5}^{0} = 0.21 \pm 0.03$. Arguments are presented that suggest that $N_{r=0}^{0} = 0$. The average fraction of the total energy deposited in product vibration is $\langle f_v \rangle = 0.64 \pm 0.03$. The release of the very light electron as one of the reaction products places severe angular momentum constraints on the reaction system. A simple kinematic model predicts a highly non-Boltzmann HF rotational state distribution which increases with increasing J up to some cutoff level. The high degree of vibrational excitation in the HF product has been accounted for by theoretical calculations of Gauyacq using the zero-range potential approximation.

I. INTRODUCTION

In an accompanying article, we report the initial vibrational state distributions in the products of a series of proton abstraction reactions F' + HX - HF(v) + X', X = Cl, Br, and I.¹ The results of this investigation yield a valuable comparison between the dynamics of the ion-molecule reaction and that of their well-studied neutral counterparts $F + HX \rightarrow HF(v) + X$.² The subject of the present study is the thermal energy associative detachment reaction

H + F⁻→ HF(
$$v \le 5$$
) + e^- ,
 $\Delta H = -57.0 \text{ kcal/mol}^{3,4}$ (1 kcal = 4.18 kJ)

As in the preceding paper, we report the nascent product vibrational state distribution for v = 1-5 obtained by detection of infrared chemiluminescence from the HF products formed in a flowing afterglow. In contrast to the proton abstraction reactions, however, at thermal energies there exists no neutral analog with which to compare the associative detachment reaction,

Associative detachment presents an opportunity to study the dynamics of a unique ion-neutral collision process. One of its most important aspects is that an electron is one of the products of the reaction. The release of the extremely light electron has marked consequences for the kinematics which govern the reaction, since the electron is unable to carry away much of the initial orbital angular momentum of the collision partners. This results in a nearly direct mapping of the orbital angular momentum of the reactants into HF product rotation, which in turn affects the observed vibrational distribution.

The transition state of the associative detachment

reaction involves an unstable negative ion, in this case HF". This transient species has been the subject of widespread investigations in many different experimental and theoretical contexts, 5^{-9} since it is the same intermediate that is formed in electron-HF scattering processes. Associative detachment is unique among the methods to probe the negative ion intermediate in that it necessarily samples the HF⁻ intermediate from large initial internuclear separation.

In addition to these aspects common to all associative detachment reactions, the H + F reaction exhibits several features which single it out as an exceptional candidate for detailed study. It involves the association of a two atom system with relatively few electrons to form a diatomic molecule. Furthermore, the reaction at thermal energies is thought to take place without significant interactions with higher lying HF^{*} electronic states.⁹ Both these facts greatly simplify the theoretical treatment of the associative detachment process. The H+F reaction also belongs to an interesting subclass of associative detachment reactions in which the product molecule possesses a large dipole moment ($\mu_{HF} \sim 1.8 \text{ D}$). There is considerable interest¹⁰ in studying the interactions between a large dipole and a slowly departing electron.

Extensive investigations of hydrogen halide negative ions, primarily by means of electron-molecule scattering studies, 6-8, 11-13 have revealed a fundamental deficiency in our understanding of the nature of the negative ion intermediate through which the associative detachment reaction must pass. Electron scattering experiments have shown rather large, sharply peaked threshold cross sections for vibrational excitation⁶ and dissociative attachment^{7,8} processes in hydrogen halides. Such large cross sections can sometimes be attributed to the presence of a shape resonance which traps the electron for a time near the molecule inside an angular momentum barrier. However, it has been suggested¹⁴⁻¹⁶ that the concept of a shape reasonance does not apply here since the hydrogen halide negative ions can decay

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by detachment of an s wave (l=0) electron with no angular momentum barrier to inhibit its escape. One solution which has been proposed involves virtual states, 14-17 which unlike shape resonances may dominate low energy l=0 electron scattering. A great deal more theoretical work is required in order to ascertain the existence and role of virtual states in these systems. As has been pointed out, ¹⁵ any satisfactory explanation of these phenomena must be consistent with all the results from scattering events which proceed through the same negative ion intermediate, namely, vibrational and rotational excitation, dissociative attachment, and associative detachment. It is in this regard that detailed experimental investigations of the associative detachment process are essential as a testing ground for theoretical descriptions of the negative ion intermediate.

To date there exists only one other experimental study of the H + F associative detachment reaction. The rate constant for the reaction was found to be very large, approaching the Langevin theoretical maximum (k=1, 6) $\times 10^{-9}$ cm³ molecule⁻¹ s⁻¹ = 0.8 k_{Langevin}), although this value has a rather large uncertainty of +100%, -50%.¹⁸ This suggests that the HF potential energy curve is attractive into the autodetaching region so that reaction can occur on nearly every collision. However, very little is known about the range of internuclear separations over which electron detachment occurs or about the "lifetime" of the HF intermediate. These details will most certainly affect the energy distribution in the reaction products. The only direct measurement of a vibrational state distribution formed in an associative detachment reaction is for the $H + CI^{-} + HCI(v \le 2) + e^{-}$ system.¹⁹ The present results on the initial (v=1-5)vibrational state distribution in the HF product of the H + F^{*} associative detachment reaction thus represent an important contribution to our understanding of the mechanism which governs this class of reactions.

II. EXPERIMENTAL

The flowing afterglow apparatus used in these studies is identical to that described in the preceding paper.¹ The only significant addition is a hydrogen-atom generator, which has been described in an earlier publication.¹⁹ Hydrogen atoms are generated in a thermal dissociator²⁰ by passing high-purity H_2 over a hot (2000 K) tungsten filament. The filament is contained in a glass watercooled chamber coated with boric acid to inhibit surface recombination. The H atoms and undissociated H₂ enter the flow tube through a Teflon tube at a distance 6 cm before the viewing region. The F ions are modulated by a 0 to -12 V potential on a tungsten mesh positioned 5 cm before the hydrogen atom inlet. The modulated HF product emission is observed by a Ge: Cu detector equipped with a circular variable filter. The detector output is summed in a signal averager and the infrared emission intensity is recorded as a function of wavelength.

As in the preceding paper, care was taken to ensure that the observed emission was due to HF formed in the reaction of F^- with H. A number of checks unique to this particular reaction are reported here. Fairly large



FIG. 1. Infrared chemiluminescence spectrum from the $H+F^- \rightarrow HF(v) + e^-$ associative detachment reaction. The solid line is the least-squares fit to the data.

 H_2 flows, corresponding to densities of 1.5×10^{14} cm⁻³, are necessary in order to generate the 10^{13} cm⁻³ H atom concentrations required to effect significant reaction over the 6 cm between the H atom inlet and product detection. This is a concern since the reaction $F + H_2$, which has a rate constant $k = 2.3 \times 10^{-11}$ cm³ molecule⁻¹ \times s^{-1 21} could potentially mask the F⁺ + H emission. A modulated background emission in the HF spectral region was observed in a flow tube configuration in which the tungsten mesh used to modulate the ions was only 15 cm from the ion source. The background emission occurred even without H atoms present. This spurious emission probably was due to modulated fluorine atoms reacting with H_2 . Modulated F atoms could be produced if filament electrons are perturbed by the close proximity of the mesh. When the ion source-to-mesh distance was increased to 50 cm, the background emission disappeared.

Since both positive and negative ions are modulated in a similar fashion at the mesh, we must also ensure that the observed emission is not from reactions of positive ions with H atoms. This possibility can be eliminated since there were no relative changes in the positive ion mass spectra upon addition of hydrogen atoms. An overall decrease in the size of the mass peaks in the positive ion mass spectrum was observed. This is a consequence of the increased positive ion diffusion coefficient in the presence of the electrons produced in the $H + F^{-}$ reaction.²²

Five spectra were obtained under a variety of experimental conditions. One of these spectra and its leastsquares computer fit are shown in Fig. 1. The results of these spectra and their conditions are summarized in Table I. In particular, three spectra (Nos. 1, 2, and 4) were taken under conditions in which vibrational deactivation of the nascent product state distribution was minimized. Two additional spectra were taken, one at high H_2 flow (No. 3), and the other with the viewing window 15 cm downstream from the H atom inlet (not shown in the table). Considerable deactivation was

Spectrum no.	Conditions ²	Initial relative vibrational populations ^b				
		N ⁰ ₂₌₁	N ⁰ _{v=2}	N ⁰ ₂₂₀₃	N ⁰ _{v=4}	N ⁰ _{v=5}
1	4 mTorr H ₂	-0.04 ± 0.05	0.22±0.03	0.26 ± 0.02	0.30 ± 0.02	0.22 ± 0.01
2	6 mTorr H ₂	-0.04 ± 0.05	0.25 ± 0.03	0.30 ± 0.02	0.26 ± 0.02	0.19 ± 0.01
3	12 mTorr H ₂	0.03 ± 0.04	0.22±0.03	0.25 ± 0.02	0.35 ± 0.02	0,15±0,01
4	6 mTorr H ₂ , HF cell in place	0.01 ± 0.04	0.16±0.03	0.36 ± 0.02	0.26±0.02	0.21 ± 0.01
Best populations ^c		0,00±0.06	0.23 ± 0.04	0.27 ± 0.03	0.29 ± 0.03	0.21±0.03

TABLE I. Nascent product vibrational state populations derived from computer analysis of the infrared emission spectra under the conditions specified.

^aStandard conditions: 0.7 Torr He, 10 mA emission current, 4 mTorr 5% F_2 in He, 10¹³ H/cm³, viewing 6 cm downstream from the H-atom inlet. The H atom density is estimated from an ion-molecule reaction of known rate constant. ^bThe vibrational populations reported here include small corrections for radiative and collisional relaxation. For details, see the text. The negative values under $N_{u=1}^0$ come about from the cascade corrections. The $N_{u=1}^0$ population is zero within experimental uncertainty for all experiments. The v > 1 populations are normalized so as to sum to one. ^cThis is an average of spectra 1 and 2, weighted by the quality of the linear least-squares fits to the spectra, and assuming the $N_{u=1}^0$ population is zero.

apparent in the latter case, giving much less reliable results. Correction of all the results for collisional deactivation and radiative cascading is considered in Sec. III.

III. RESULTS

The relative vibrational populations are derived from the spectra in a fashion described in detail in the accompanying paper.¹ They are reported in Table I, already corrected for radiative cascading and vibrational deactivation. The quoted error bars for an individual spectrum represent one standard deviation in the fitted populations and reflect primarily the scatter in the spectral data. In particular, it is worth noting that spectra 1 and 2, which were taken under similar experimental conditions, exhibit very good reproducibility. A check on the internal consistency of the measurements is available from spectrum 4. It was run under conditions nearly identical to spectrum 2, but with a gas cell containing 30 Torr HF inserted between the flow tube and the Ge:Cu detector. The gas cell quantitatively absorbs rotationally relaxed HF(v=1-0) emission, but should leave the rest of the spectrum virtually unchanged. The contribution to the spectrum from the HF (v=1)emission is calculated by normalizing the data at wavelengths where HF (v = 1) does not emit, and comparing this spectrum to the spectra without the gas cell. The HF (v=1) emission contribution in the spectra taken without the HF gas cell was found to be negligible, which is consistent with the raw population $(N_{\nu=1}=0.01)$ obtained in the direct fits.

The procedure by which we deconvolute the spectrum to obtain relative vibrational populations¹ assumes a 295 K Boltzmann distribution in rotation. Sung and Setser²³ report that high rotational states of HF ($J \ge 10$) are incompletely deactivated in a flow tube with 1 Torr Ar buffer gas (1 Torr = 133.322 Pa) when viewing 0.4 ms after reaction initiation. Under these conditions the rotational distribution at the viewing region is bimodal, with a low J peak well-characterized by a Boltzmann distribution and a high J peak which is a remnant of the high J nascent rotational distribution. They also found helium to be much more efficient at deactivating any high rotational states. In our experiments we need to consider whether high J states formed in the reaction relax to a 295 K Boltzmann distribution by collisions in 0.7 Torr He within 0.20 ms, the average time between formation and detection of HF. If they are not completely relaxed, the rotational distribution in the viewing region might be bimodal, with the high J peak at $J \simeq 14$.

We are unable to use the same experimental test for rotational relaxation in F + H as the one performed in the F⁺+HX studies.¹ There we looked for emission through a bandpass interference filter which transmits wavelengths shorter than 2.38 μ m, corresponding to emission only from R lines with $J \ge 7$ from HF (v = 1) and $J \ge 17$ from HF (v = 2). However, this is not expected to be a valid test here since the best-fit populations show no population in HF(v=1). Also, as discussed below, even the significantly populated (v=2)level is constrained by angular momentum conservation to form J levels less than 18, which are blocked by the filter as well. Indeed, no emission is observed through this filter from the H + F reaction. However, *P*-branch emission wavelengths associated with the high J peak of a bimodal distribution would be observed far out in the red tail of the spectrum. For instance, the P(14) line from v = 3-2 is at 3.36 μ m, while the P(12) line from v = 4-3 is at 3.40 μ m. The negligible emission intensity at these wavelengths (Fig. 1) is a strong indication that the relative populations remaining in these high Jlevels is insignificant. Thus we are confident that the rotational distribution is relaxed.

The vibrational state populations generated from the computer least-squares fit to the spectra must be corrected for radiative cascading and vibrational relaxation in order to obtain the nascent distribution. The only important collisional relaxation term to consider is HF deactivation by H_2 . This could be significant primarily because the H_2 flows required for H atom generation are some ten times greater than the usual reagent flows required to react the ion completely.

Fortunately, studies have been performed on HF (v) deactivation by H₂ for the vibrational levels of interest.²⁴⁻²⁶ From these rates, collisional deactivation appears to be a small correction to our populations. Spectra Nos. 1, 2, and 4 were taken under conditions in which the collisional deactivation corrections to the populations were less than 5%.

The total correction (both radiative and collisional) to our populations never exceed 30% of the population under conditions where the viewing region was 6 cm downstream from the H-atom inlet. A correction of this size is required only for the HF (v = 5) population since its correction contains only removal terms. The corrections to the lower vibrational levels are typically $\leq 10\%$. For instance, the best-fit relative populations for $v \ge 1$ derived from spectrum 1, uncorrected for relaxation are $N_1 = 0.00$, $N_2 = 0.25$, $N_3 = 0.29$, $N_4 = 0.29$, and $N_5 = 0.17$, while the final corrected results are N_1^0 = -0.04, $N_2^0 = 0.22$, $N_3^0 = 0.26$, $N_4^0 = 0.30$, and $N_5^0 = 0.22$. In order to obtain a qualitative measure of the extent of deactivation at "long times," a spectrum was taken viewing 15 cm from the hydrogen atom inlet. Under these conditions the initial distribution showed considerable relaxation, with a corresponding shift in the emission spectrum towards shorter wavelengths. Due to the poor quality of the data and the large factors needed to correct for deactivation and cascading, no attempt was made to obtain nascent distributions from these data. The best-fit populations from this spectrum uncorrected for deactivation showed an HF (v=1) population which was smaller than would have been expected simply from cascading into this level by radiative and collisional mechanisms. There is no obvious explanation for this observation. However, all spectra used to obtain the nascent distributions in both the F + HX reactions¹ and in this work were taken under conditions which minimize the time between reaction and observation, and no unusual effects were observed which might indicate state selective deactivation problems. The spectra taken at 6 cm are a priori much more reliable, both in terms of their signal-to-noise and the magnitude of the deactivation corrections.

The final averaged and corrected result for the best populations is given in Table I. The relative populations are an average of the nascent populations derived from spectra 1 and 2, since these spectra were taken under conditions which minimize deactivation corrections. Error bars are set so as to bracket the scatter in the best-fit populations, and are somewhat larger than the error bars associated with an individual spectrum. The measured HF (v = 1) population of $N_{v=1}^0 = 0.00 \pm 0.06$ suggests very strongly that the HF (v = 0) population will be negligible as well. If we assume $N_{v=0}^0 = 0.00$, the relative populations stated above become absolute branching fractions (since they sum to unity) and the average fraction of the total energy deposited as vibration in the products $\langle f_{v} \rangle$ is 0.64 ± 0.03 .

IV. DISCUSSION

The initial HF product vibrational distribution in the $H + F^*$ associative detachment reaction is strongly





FIG. 2. Relative vibrational state populations in the $H + F^{-}$ associative detachment reaction.

peaked towards high vibrational levels. Such a distribution represents an extremely efficient disposal of available energy into vibration. For comparison, we can juxtapose these results with a fluoride ion reaction¹ of almost identical exothermicity, $F + HI - HF (v \le 5)$ + I⁻, $\Delta H = -57.1$ kcal/mol. The relative populations formed in the associative detachment reaction are presented in Fig. 2, while the F + HI populations can be found in Fig. 6 of the preceding paper. The $\langle f_{u} \rangle$ obtained by extrapolation of the F⁻ + HI surprisal plot is $\langle f_{\nu} \rangle = 0.45$, compared to the value of 0.64 for F⁻+H. The obvious differences between these vibrational distributions reflect the dramatically different reaction dynamics of the two processes. The proton abstraction reaction (F" + HI) occurs on a single potential energy surface. The large exothermicity relative to the well depth and the kinematics of the light-atom exchange provide for efficient disposal of the available energy into product vibration.¹ By comparison, the associative detachment reaction $(H + F^{-})$ deposits even more energy into vibration, with a vibrational distribution which is strongly peaked towards the highest levels accessible. As H and F approach, they eventually reach an internuclear separation R at which HF⁻ is unstable with respect to emission of an electron to form a neutral HF molecule. The distribution of R's at which electron emission occurs determines the vibrational state of the HF product. In addition, the associative detachment product HF(v', J') states are kinematically constrained by the small mass of the product electron.

A. The kinematics of the reaction

During the reaction $H + F \rightarrow HF(v' \le 5) + e^{-}$, the reduced mass changes from that of the hydrogen atom to that of the electron, nearly a factor of 2000. This has marked consequences on the associative detachment reaction dynamics. The light electron is unable to carry away much of the angular momentum associated with the $H + F^{-}$ collision pair, and virtually all of the orbital angular momentum L remains as HF product rotation J', i.e., $J'' \cong L = \mu v_{rel} b$.¹⁹ Here μ is the reduced mass of the reagents approaching with relative velocity v_{rel} at an impact parameter b. Thus, at a given relative velocity, only impact parameters within a particular narrow range will yield HF products in a given rotational state J'. Here, we adopt the primed notation to indicate product states of the associative detachment process.

Such a one-to-one mapping from impact parameter into product rotational state might often be obscured by other dynamical constraints which limit the types of collisions that can react. However, in the present case the near-Langevin cross section¹⁸ associated with the reaction should allow this effect to be seen. The Langevin theory of ion-molecule reactions²⁷ is based on a classical treatment of the reactive collision in which the ion is considered as a point charge and the interaction potential is the ion-induced dipole attraction. In this simple picture, for impact parameters smaller than some maximum value, all trajectories overcome the centrifugal barrier and spiral into the origin to react. This maximum impact parameter defines an upper bound to the rate constant for the reaction which is called the Langevin rate constant. A measured rate constant which is so close to the theoretical maximum suggests that the probability for reaction P(b) is nearly unity for all impact parameters less than some b_{max} , i.e., P(b) $\simeq 1$ for $b \leq b_{max}$ and P(b) = 0 for $b \geq b_{max}$. For the H + F associative detachment reaction, a measurement of the rotational distribution associated with each vibrational level should in this case directly reflect the distribution in impact parameters which formed that vibrational level in the products. 28

Unfortunately, our experiment can provide no information on the nascent rotational distributions due to the fast deactivation of HF rotational states by collisions with helium in the flow tube. However, the above considerations still allow us to predict with some confidence an overall rotational distribution in the HF products. To the extent that P(b) = 1 for $b \le b_{max}$, at a fixed relative velocity the distribution of reactive impact parameters is governed solely by the geometric weighting factor $2\pi b db \propto (2J'+1) dJ'$, which favors large impact parameter collisions. This transformation from impact parameters into HF rotational levels results in an HF rotational distribution proportional to (2J'+1) up to the maximum impact parameter (the maximum L value) which can react. Transforming the experimental cross section into a maximum impact parameter using the mean relative velocity gives $J'_{max} \approx 18$ and an average HF product rotational level $J' \approx 12$. The average rotational energy over this distribution is $\overline{E}_{rot} \simeq 10 \text{ kcal/mol}$. Finally, the average rotational energy can be divided by the total energy available to the products to obtain the average fraction of the total energy channeled into rotation, $\langle f_R \rangle \sim 0.16$. Thus, the experimentally determined $\langle f_{\nu} \rangle$ of 0.64 when combined with the kinematic constraints inherent in the system, suggests that the energy which is not deposited into vibration is distributed approximately equally between HF rotation and electron translation. The electron translational energy is on average equivalent to no more than a single vibrational quantum in HF. Thus the product electron appears to be preferentially ejected with low kinetic energy.

The kinematic constraints imposed by the electron product may also dramatically affect the vibrational distribution observed in these experiments. Since large impact parameter collisions yield large rotational energy in the product, there exists an obvious energy constraint on the range of impact parameters which can form the highest vibrational levels in the products. On average, only ~0.8 of the collisions with impact parameter smaller than the Langevin maximum can form HF (v = 4) while only ~0.3 of them can form HF (v = 5). It is very likely that these energy restrictions are the cause of the abrupt change in the trend towards higher relative vibrational populations in going from HF (v = 4) to HF (v = 5), as was described previously for the Cl⁻ + H associative detachment reaction.¹⁹

The simple model just introduced for the $H + F^{-}$ associative detachment (AD) reaction allows us to predict an HF product rotational distribution summed over the product vibrational levels. Neither our experiment nor this model can give information on how the overall rotational distribution is apportioned among the various vibrational levels. If such rotational information were available, it could be used to predict threshold dissociative attachment (DA) cross sections from a given HF(v',J') level by means of microscopic reversibility arguments. The threshold dissociative attachment process in HF has been studied in some detail recently.^{7,8} Allan and Wong⁷ measured the cross section for dissociative attachment as a function of the initial HF vibrational level for HF (v = 0, 1, 2). They obtain $\sigma_{v=1} : \sigma_{v=0} = 15 \pm 5$ and $\sigma_{\nu=2}$: $\sigma_{\nu=0} = 300 \pm 150$. The experiments in the two different directions can be related by microscopic reversibility since they sample a similar range of H + Ftranslational states.^{29,30} The dissociative attachment results are threshold cross sections for H+F formation, corresponding to slowly departing H + F.

Microscopic reversibility²⁹ in its most fundamental form relates only the forward and reverse processes from completely specified states. For the reaction H + F^- + HF $(v', J') + e^-$, microscopic reversibility states that

$$\frac{\sigma_{AD}(E_T | v'J'E_T')}{\sigma_{DA}(v'J'E_T'|E_T)} = (2J'+1) \left(\frac{\mu'}{\mu}\right) \left(\frac{E_T'}{E_T}\right) \quad . \tag{1}$$

Here 2J' + 1 is the ratio of statistical weights of products to reactants, μ is the reactant reduced mass, E_T is the relative translational energy of the reactants, and μ' and E'_T are the corresponding quantities in the products, all referred to the exothermic (associative detachment) direction.

It is obvious from Eq. (1) that a knowledge of the rotational dependence of $\sigma_{AD}(v')$ is sufficient to obtain rotational information on $\sigma_{DA}(v')$. The ratio of cross sections is given by the ratio of the densities of states for $H + F^{*}$ and $HF + e^{*}$. The (2J' + 1) weighting arises because of the degeneracy associated with the rotational levels in the HF product. There are no corresponding rotational degrees of freedom in $H + F^{*}$. The remaining terms give the ratio of translational densities of states. This ratio contains a rotational dependence indirectly



FIG. 3. Potential energy surfaces for HF⁻ and HF [after Segal and Wolf (Ref. 9)].

through its effect on the amount of translational energy left to the departing electron $E'_T = E_{tot} - E_{v'} - BJ'(J'+1)$. For low J' levels where $E_{tot} - E_{v'} \gg BJ'(J'+1)$ this effect is small.

In order to check the sensitivity of $\sigma_{DA}(v', J')$ to the form of the rotational dependence in the associative detachment reaction, the overall rotational dependence $\sigma_{AD}(J') \propto (2J'+1)$ derived in our kinematic model was assumed to hold within an individual vibrational level as well. In that case the rotational dependence of the dissociative attachment cross section is proportional to $1/E'_T$, which is only weakly dependent on J' for low rotational levels. We can compare the dissociative attachment cross section predicted in this way with that obtained from experiment^{7,8} for HF (v=2), the only vibrational level for which quantitative experimental information is available in both directions. We use the absolute $\sigma_{DA} (v=0)$ of 2×10^{-20} cm², ⁸ the relative measurements for σ_{DA} (v = 2, 1, 0), ⁷ the absolute rate coef-ficient for the AD process, ¹⁸ and the relative k_{AD} 's from this work. Agreement with experiment is very poor, with microscopic reversibility predicting a dissociative attachment cross section nearly 100 times larger than observed by experiment.⁸ A distribution of σ_{AD} (v'=2, J') which weights high J' even more heavily than 2J' + 1is necessary to obtain agreement. This would suggest a correlation between low vibrational levels and high rotational levels in the HF product.

The large mismatch indicates the importance of an accurate knowledge of the rotational dependence of the associative detachment cross section for each vibrational level. Experiments capable of resolving nascent rotational distributions in the associative detachment process would be helpful both in further delineating the dynamics of the process and in providing much more detailed information on the reverse dissociative attachment process. In lieu of such data, models of associative detachment and dissociative attachment must consider the possibility that rotational effects could play an important role in the dynamics of these reactions.

B. Theoretical descriptions of associative detachment

Theoretical descriptions of associative detachment and related processes such as dissociative attachment and vibrational excitation by electron impact are in a state of active development. At the heart of the problem lies the question of the most appropriate description of the transient intermediate species, in this case HF^{*}. As F^{*} and H approach, they eventually reach internuclear separations R at which the HF^{*} species is unstable with respect to emission of an electron to form a neutral HF molecule. Electron emission is a facile process, as indicated by the near-Langevin cross section for F^{*} $+ H \rightarrow HF + e^{-18}$ Theoretical methods for treating the electronic instability at small R include resonance state^{18, 31-33} and virtual state^{14-17, 34} descriptions.

In the resonance state picture of the general $A^{-} + B$ reaction, ³³ the strictly bound state of $A^- - B$ at large R becomes a quasistationary state coupled to the $e^- - AB$ continuum at R less than some crossing point R_c (Fig. 3). At all smaller R's, the quasistationary state is taken to correspond to a resonance of the fixed-R scattering problem, characterized by a local complex potential $V(R) = \frac{1}{2}i\Gamma(R)$. The width $\Gamma(R)$ gives the decay rate into the continuum at each R. Such a description has been applied with a good deal of success to the $H^- + H$ reaction. 32, 35 Two important features of the local complex potential are that it requires Γ to vanish for R greater than R_c and that it neglects nonadiabatic couplings to the continuum (i.e., those due to nuclear motion). Since detachment occurs only for $R < R_c$, the detachment probability must increase with increasing amount of time spent at $R < R_c$; thus the total cross section should increase with decreasing collision velocity. In semiclassical language, the distribution of final AB vibrational states for a resonance model is essentially

governed by the distribution of R's (for $R < R_c$) at which detachment occurs during the collision. The probability of detachment at each R is weighted by the time spent there, the decay rate $\Gamma(R)/\hbar$, and the probability that detachment has not already occurred at a previous position.

As the width Γ becomes very large the notion of a potential energy surface on which an intermediate negative ion exists begins to lose its appeal. In particular, comparing HF with the well-studied case $H_{2}^{\text{-}},\,^{35}$ the former has an open s wave (l=0) detachment channel while the latter does not. This is because the lowest electronic configuration of HF⁻ is $\sigma^2 \pi^4 \sigma^*$, giving rise to the ${}^{2}\Sigma^{+}$ ground state.³⁶ In H₂, a *p*-wave electron is the lowest angular momentum electron that can detach from the σ_{μ}^* orbital. In contrast, the HF⁻ antibonding σ^* orbital has overlap with an s-wave electron. The swave electron which can escape from HF does so without tunneling through an angular momentum barrier. Thus, HF is expected to be very short lived, 14-16 provided that higher angular momentum components of the σ^* orbital are efficiently coupled to the open s-wave channel.

In light of the open s-wave decay channel, an alternative description of the F^{-} + H reaction in terms of virtual states may be more appropriate than a resonance state description.¹⁴⁻¹⁶ A virtual state is an electronic state "almost bound" in a potential well. One very promising model which considers the role of virtual states in associative detachment employs the zero-range potential approximation.^{34,37} The model begins with the physical picture of a low energy (long wavelength) s-wave electron weakly bound at large R in a potential well caused by the HF nuclei. As R decreases, the well depth becomes insufficient to bind the electron, which is ejected into the continuum. Since the wavelength of the electron is much larger than the range of the potential due to the nuclei, the HF molecule is viewed as causing a shortrange distortion of the otherwise field-free electron. The effectively zero-range nuclear potential imposes a boundary condition at the origin of the electronic radial wave function. The variation of this boundary condition with internuclear separation R causes bound-to-free electronic transitions (associative detachment).

Except for this zero-range approximation, the scattering problem in this model can be handled essentially in an exact manner. A very important feature of the model is that "dynamical electronic transitions" induced by the nuclear motion are accounted for explicitly, in contrast to the resonance state model. The nuclear motion can induce detachment at internuclear separations considerably larger than the crossing point R_c (Fig. 3). This formalism has been used to perform detailed calculations on H⁻-rare gas collisions, ³⁴ on vibrational excitation in e^- -HCl collisions, ¹⁴ and most recently by Gauyacq on the F + H and Cl + H associative detachment reactions.¹⁷ The results are very encouraging. In all cases, Gauyacq finds dynamical transitions at large R to be very important. This leads to "undercrossing transitions" in which the electron is emitted at an internuclear separation where the HF⁻ potential is

significantly below the HF potential (Fig. 3). Associative detachment at these large R's leads to a great deal of product vibrational excitation, in qualitative agreement with both the present F' + H and earlier CI' + Hexperimental results.¹⁸ Such large-R contributions to the total detachment cross section increase with increasing collision velocity.

Gauyacq's F' + H calculation¹⁷ uses the *ab initio* $HF'^{2}\Sigma^{*}$ potential energy curve of Segal and Wolf⁹ to fix the boundary condition at the electronic origin for each internuclear separation R. Relative cross sections into each product state HF(v, J) are calculated at various collision energies. These are summed over J and averaged over a Boltzmann distribution of collision energies to obtain an HF(v) distribution.¹⁷ The calculated distribution agrees qualitatively with the experimental one. Both peak at v = 4, but the experimental distribution is somewhat broader. Furthermore, the probable correlation between low vibrations and high rotational levels which was suggested by our microscopic reversibility calculation is also borne out by his results.

Given this qualitative agreement, it seems likely that the zero-range approximation provides an accurate physical picture of the F^{*} + H associative detachment reaction. However, our experiment cannot rule out a theoretical description of the process in terms of a local complex potential. If the HF lifetime were about one vibrational period, it would be just long enough to allow reflection off the inner turning point of an F + H resonance state but short enough so that detachment occurs on essentially every collision. In that case, a mapping of the inner turning point of the HF⁻ curve (where the trajectories slow down) onto the HF neutral curve could again lead to strong product vibrational excitation because the HF and HF curves⁹ mimic each other at short R. Indeed, using very diffuse basis sets, Segal and Wolf⁹ find an apparently stable ${}^{2}\Sigma^{*}$ HF⁻ state in the region of the neutral HF potential minimum and at slightly higher energy (<0.1 eV). The HF⁻ curve crosses the neutral curve at $R_c = 0.97$ Å, very near the bottom of the HF potential well. A partial wave expansion of the $^{2}\Sigma^{*}$ electronic wave function at the energy minimum contains a large non-s-wave component which could exhibit resonance behavior. Segal and Wolf refer to such states as resonance states, but their nature and the magnitude of the coupling of the l > 0 components to the s wave is not yet well understood.

It is possible that experiments measuring the product vibrational state distribution as a function of isotope $(F^+ + D)$ and temperature may provide further important information. In both cases, one would be altering the range of collision energies sampled. As noted above, large R, "nuclear-velocity-induced" transitions would increase in importance at higher collision energy. By contrast, small R, "resonance state-to-continuum" transitions would decrease in importance. Detailed zero-range potential calculations vs collision energy are now available for F⁻ + H and Cl⁻ + H, ¹⁷ and the model is clearly consistent with experimental product vibrational state distributions in each case. Detailed resonance state calculations on the same system are not yet available. These would require a width function $\Gamma(R)$, and it is not clear how to calculate such a function at present.⁹ Further work in both the experimental and theoretical arenas will continue to refine our understanding of associative detachment reactions and their negative ion intermediates.

V. CONCLUSION

We have presented results on the relative rate constants into HF(v=1-5) for the thermal associative detachment reaction $H + F \rightarrow HF(v \le 5) + e^{-}$. The product vibrational state distribution is found to be highly vibrationally excited, peaking at HF (v = 4). However, angular momentum and energy conservation appear to reduce the populations in v = 4 and v = 5, effectively reversing the trend in which v = 5 would be the most populated state. The average fraction of total energy disposed in vibration is $\langle f_{\nu} \rangle = 0.64 \pm 0.03$. The high degree of vibrational excitation in the products is well accounted for by recent theoretical calculations using the zerorange potential approximation. The calculation stresses the importance of dynamical electronic transitions induced by the nuclear motion. The kinematic consequences of an electron as reaction product predict a highly non-Boltzmann distribution in product rotation, sharply peaked toward high J levels. The $\langle f_R \rangle$ and $\langle f_T \rangle$ predicted by this simple model share the remaining energy approximately equally.

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