MOLECULAR BEAM STUDIES WITH F^+ IONS

Walter S. Koski

Department of Chemistry, The Johns Hopkins University
Baltimore, Maryland 21218

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Introduction

There have been very few beam studies of reactions involving F^+ ions. In recent years, however, there has been an increasing number of publications of detailed studies of 3 atom-ion-molecule reactions of the type $A^+ + BC \rightarrow AB^+ + C$ involving hydrogen molecules and elements of the second row of the Periodic Table. The F^+ ion has been included in some of these studies. The main objectives of such studies has been to shed light on the details of the collision process and on the distribution of energy in the ionic product. The reactions are frequently classified as direct or proceeding through persistent complex formation. The rotational period of the system ($\sim 10^{-12}$ sec) offers a convenient kinematic clock. The symmetry of the velocity distribution of the ionic product in the center of mass coordinate system can be determined from the measured angular and energy distribution of the product ions. If the projectile ion interacts with the target molecule for a time longer than the rotational period of the system the velocity distribution is symmetrical about a line passing through the center of mass and perpendicular to the projectile ion direction. Such a distribution suggests that the reaction is proceeding through a persistent complex formation. On the other hand if the distribution is forward of the center of mass and consequently asymmetric relative to the $\pm 90^\circ$ direction the projectile and target molecule have an interaction time less than the rotational period of the system then reaction is classified as direct. Obviously, other criteria can be used for direct and complex formation mechanisms. However, the above is a convenient experimental approach.

In beam experiments the amount of available energy that has gone into internal energy of the ionic product is simply determined from the difference of the kinetic energy of the products and reactants. The distribution of internal energy between the rotational and vibrational degrees of freedom of the

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ionic molecular product is not easy to determine due to limitations of instrumental resolution. However, the current state of the art permits a surmounting of this obstacle so that in the near future one can expect to be able to see vibrational structure in the energy spectra of the ionic products. At present one can infer the information from line widths in the energy spectra or from optical emission in those cases where such emission can be observed.

In this presentation we will report on the total reactive cross section measurements of the reaction of F^+ with molecular hydrogen and its isotopic variants, on some charge transfer processes and on the angular and energy variation of the FD^+ products from the reaction $F^+(D_2,D)FD^+$. Some preliminary cross section measurements for some reactions of F^+ with CH_4 will also be mentioned.

Experimental

The cross section measurements were made with an apparatus described previously (1). The instrument consists of a primary mass spectrometer (PMS) in tandem with a secondary mass spectrometer (SMS). The PMS is a 1 cm radius of curvature 2500 G permanent magnet mass analyzer. The SMS is a 60° magnetic sector instrument with an 8 in. radius of curvature. The detection of product ions was made by counting ions with a 17 stage electron multiplier. The gas pressure in the reaction cell was measured with an MKS Baratron differential pressure gauge. For reactions proceeding by direct mechanisms the instrument was calibrated with the reaction $Ar^+(D_2,D)ArD^+$ (2).

The spectrometer used for reactive scattering measurements has also been described elsewhere (3). Briefly, the instrument consists of two quadrupole mass filters and two hemispherical analyzers in tandem. F^+ ions were formed by electron bombardment of CF_4 in a source chamber. The ions were then extracted and focussed into the primary quadrupole mass filter. The ion beam is then decelerated into the first electrostatic analyzer. From the analyzer, the ions are accelerated and focussed into the reaction cell which contains the target gas. The cell consists of two concentric cylinders, with the inner cylinder being capable of rotation through an angle of $\pm 45^\circ$. The reaction cell is the center of the axis for the angular movement of the detecting system. The detection system moves in a planar direction, pivoting the inner cylinder as the system is moved by a mechanical feed through. The ions leaving the reaction cell are energy and mass analyzed in the detecting system by another 180° electrostatic analyzer and by the secondary quadrupole mass filter respectively. After this the ions proceed to the electron multiplier where they are counted. Pulse counting techniques are used to collect and store the data gathered from the angular and energy distributions for both the reactant and

product ions.

Results and Discussion

Electronic State of Projectile Ion.

The F^+ ions were produced by electron bombardment of CF_4 . In general, under such conditions one expects the resulting beam to be composed of ions in more than one electronic state (4).

In order to determine the beam composition the attenuation of the beam was studied in a suitable gas. If a single electronic state is present the beam attenuation can be represented by a simple exponential expression $I = I_0 \exp(-n\sigma l)$, where I is the beam intensity when the number density is n and I_0 is the corresponding intensity when $n = 0$, σ is the total cross section for all processes leading to attenuation, and l is the reaction path length. A semilogarithmic plot of I/I_0 vs. pressure gives a straight line. If two states are present the attenuation is given by the sum of two exponentials $I = I_0 \exp(-n\sigma_1 l) + I_0 (1-f) \exp(-n\sigma_2 l)$, where f is the fractional abundance of the excited state. A semilogarithmic plot now gives a curved line which can be resolved into its two simple exponential components and the abundances of the two states can be determined. Figure 1(a) gives typical results obtained for electron bombardment of CF_4 with electrons of various energies. It is clear that the fractional abundance of the upper state can be varied by varying the electron energy. However, in lowering the electron energy there is a concomitant decrease in the yield of the F^+ ion, a situation which is frequently not tolerable. In some instances (5) one of the states could be eliminated by simply raising the gas pressure in the primary ion source. This approach was not successful here presumably because the ground state of F^+ is a 3P and the first excited state 1D and to deactivate the excited state to the ground state would involve a singlet triplet transition which is forbidden. In such instances (6) the addition of a paramagnetic impurity accomplished the desired result. In Fig. 1(b) one has the attenuation results when 30% NO was added to the CF_4 . To within experimental error the slope is a straight line indicating the presence of only one electronic state.

By studying the variation in abundance of the excited state with electron energy and then plotting the abundance vs. electron energy one can identify the excited state of F^+ as the 1D state from the appearance potential. The electron energy scale was calibrated using neon.

Charge Transfer Reaction $F^+(Ne, F)Ne^+$.

Probably the simplest reaction of a gaseous positive ion is charge transfer. Fig. 2 gives the cross section measurement of

the charge transfer reaction between F^+ and Ne (7). The curve in Figure 2 represented by the circles was obtained by measuring the charge transfer reaction with F^+ produced by electron bombardment of a $CF_4 + NO$ mixture which judging from the attenuation curves gives only the ground state (3P) of F^+ . This charge transfer cross section curve supports the fact that the F^+ ion is in the ground state since the use of the ground state reactant ion would be expected on the basis of thermodynamic data to give a reaction threshold of 8.4 eV which agrees with the experimental observation. The curve in Fig. 2 represented by the triangles was obtained with F^+ obtained from 70 eV electron bombardment of CF_4 . In this case a mixture of 3P and 1D states exists but the beam composition is given by the corresponding attenuation data. By subtracting the contribution of the ground state and normalizing one obtains the cross section behavior of the reaction $F^+(^1D)(Ne,F)Ne^+$. The appearance potential measurements referred to above showed that this state was the 1D state of F^+ and the charge exchange results are consistent with this. Both of the charge exchange reactions are expected to be endothermic. The cross section curves consequently go through a broad maximum as a function of energy; however, the excited state (1D) reaction is the one which has a smaller energy defect and its maximum occurs in a lower energy region as expected.

Reaction of the F^+ With Molecular Hydrogen.

The next simplest reaction of F^+ is the reaction with molecular hydrogen and its stable isotopic variants. A typical result is given in Fig. 3 where the cross sections of the reaction of $F^+(^3P)$ and $F^+(^1D)$ are plotted vs. center of mass kinetic energy assuming that the reaction is proceeding by a direct mechanism involving one atom of the diatomic molecule. The measurements indicate that the cross sections corresponding to the two states are about the same at the higher energies but diverge measurably at the lower energies. The fact that a divergence between the two states is to be expected is borne out by statistical phase space calculations the results of which are illustrated by the dashed lines in the figure. The calculated cross sections are too high but the shapes of the curves are consistent with experimental observations as is the fact that the two cross sections diverge at lower energies. The following considerations illustrate the factors that contribute to this behavior. Use of Shuler's (8) adiabatic correlation rules indicates that the following reactions are permitted in our energy domain:

The dissociation energy (9) of $FH^+(^2\Pi)$ is 3.59 eV and of $FH^+(^2\Sigma)$ 0.45 eV. The heats of reaction are obtained from known thermochemical data (10).

For reactions involving the excited state $F^+(^1D_g)$ statistical phase space theory predicts a higher cross section than for the ground state $F^+(^3P_g)$ reaction because of the lower exothermicity of the latter reaction. From the conservation of energy we can write down (11)

$$E_t = E_f + E(n_f) + [M_f(M_f + 1)\hbar^2]/2I_f + Q_{fi},$$

where E_t is the total energy, E_f the relative energy of the final products, M_f the rotational quantum number of the final diatomic product, I_f the two body moment of inertia of the final product, and Q_{fi} is the exothermicity of the reaction.

Furthermore, the requirement that the strong coupling complex be able to dissociate over the final state orbital angular momentum barrier restricts L_f by

$$L_f(L_f + 1)\hbar^2 \leq 4\mu_f C_f^{1/2} [1/3E_f]^{1/2},$$

where L_f is the orbital angular momentum quantum number.

So for the same diatomic products and the same total energy, if Q_{fi} is increased, the conservation of energy requires that E_f will tend to become smaller; and, hence, L_f will be smaller and the orbital angular momentum barrier will be lower and the cross section correspondingly higher. This is the situation at the low energy.

As the translational energy increases, more energy goes into internal energy and the factor E_f increases so increasing Q_{fi} does not cause as much lowering of E_f as in the lower energy case. Therefore, this factor as well as the probability that the dissociation energy of the $^2\Sigma^+$ product will be exceeded leading to dissociation tends to make the two cross sections converge as the projectile kinetic energy increases.

Finally, as far as cross section measurements are concerned, mention should be made of the isotope effect in the reaction of F^+ with molecular hydrogen (7). Typical results are summarized in Fig. 4 where the cross sections as a function of F^+ kinetic energies are given for FH^+ and FD^+ products for the reaction of F^+ with HD . It is clear that at low energies (below 8 eV) the production of FD^+ is favored and above this energy FH^+ is favored. It will also be noted that the isotope ratio becomes rather large at the higher energies. Yuan

and Micha (12) have used such isotope effects with considerable success to elucidate the collision dynamics of stripping reactions such as $\text{Ar}^+(\text{H}_2, \text{H})\text{ArH}^+$. Corresponding studies of the reaction $\text{F}^+(\text{H}_2, \text{H})\text{FH}^+$ are in progress.

The latter reaction is an interesting ion-molecule reaction from a mechanistic point of view since the H_2F^+ ion has been observed (13) as a stable ion arising from the reaction $\text{HF}^+(\text{HF}, \text{H})\text{H}_2\text{F}^+$. The existence of the ion, H_2F^+ , shows that there is a deep potential well for the $\text{F}^+ - \text{H}_2$ system; hence, the interesting possibility of a persistent complex formation exists. However, without detailed knowledge of the potential energy surfaces it is not clear whether this potential well is available to the reacting system or if the system can exist in such a well for a time longer than the rotational period. In order to get answers to such questions Wendell et al. (14) have studied the reactive scattering of F^+ in D_2 .

Dynamics of the Reaction $\text{F}^+(\text{D}_2, \text{D})\text{FD}^+$.

In this study the energy and angular distributions of the ionic product, FD^+ , were measured as a function of the kinetic energy of F^+ . This laboratory data was then reduced to a center of mass coordinate system and is presented in Fig. 5 as a contour map of the FD^+ ion velocity distribution in Cartesian coordinates in the center of mass system for several barycentric energies. If a persistent complex is formed and lives for a number of rotational periods then the distribution would be expected to be symmetrical about a line passing through the center of mass and perpendicular to the beam direction. It is clear that for all three cases the peak of the velocity distribution is forward of the center of mass. In the case of the lowest energy (0.21 eV) there is a high degree of symmetry to the distribution but the peak is slightly forward of the center of mass. This indicates that there is a strong interaction between all three particles involved in the collision. This interaction does not last much more than $\sim 10^{-12}$ sec. As the F^+ kinetic energy increases the center of the distribution occurs progressively further from the center of mass and the reaction is proceeding by a direct process which is approximated by a stripping mechanism. In this model of the reaction mechanism as the F^+ approaches, the D_2 is strongly polarized and as the distance further decreases there is an electron jump to the F^+ followed by reaction to form FD^+ (12). The process proceeds in such a manner that the neutral D atom experiences very little momentum change and hence acts as a "spectator."

Another type of information that can be obtained from these measurements is Q the translational exoergicity (which is the difference between the translational energy of the products and

reactants). From the definition of Q and the application of the principles of conservation of energy and momentum one can relate Q to the masses and the kinetic energies of the projectile (E_1) and product ions (E_3). For the case where the product ions are proceeding in the projectile ion beam direction the expression for Q for the $F^+(D_2, D)FD^+$ reaction is

$$Q = \frac{m_1 + 2m}{m} E_3 + \frac{m_1(m_1 + m) - 2m^2}{(m_1 + 2m)m} E_1 - 2 \left[\frac{m_1(m_1 + m)}{m} E_1 E_3 \right]^{1/2}$$

where m_1 is the projectile ion mass and m is the mass of the D atom. Conservation of energy also permits the following relation for Q

$$T_R + U_R - \Delta H = T_P + U_P$$

$$Q = U_R - U_P - \Delta H$$

T and U represent the translational and internal energies of the reactants (R) and products (P), respectively and ΔH is the heat of reaction. The last expression indicates that Q reaches a limiting value when the internal energy reaches the bond dissociation energy of FD^+ . The dissociation energies of the $^2\Pi$ and $^2\Sigma^+$ states of FD^+ have been accurately determined by Berkowitz (9) as 3.46 eV and 0.46 eV respectively. Coupling this information with ΔH as determined from known thermodynamic data (10) one obtains a minimum value of Q of -0.68 eV and -0.81 eV for reactions to form FD^+ in $^2\Pi$ and $^2\Sigma^+$ electronic states respectively. Fig. 6 gives the translational exoergicity for the reaction $F^+(D_2, D)FD^+$ as a function of primary ion energy. Q appears to reach a limiting value corresponding to approximately 0.8 eV and one is tempted to conclude that the product FD^+ is being formed in $^2\Sigma^+$ state. However, information such as the width of the FD^+ line in the energy spectrum and careful cross section measurements indicate that the $^2\Sigma^+$ state is not formed to a significant degree. This apparent conflict is currently being investigated in the author's laboratory and the preliminary indications are that the observed lowering of the apparent value stems from the presence of a dynamic rotational barrier to dissociation of FD^+ which results from the rotational excitation of the FD^+ ion product during the course of the reaction.

There is another interesting feature to the plot in Fig. 6. Q has been measured for a number of three atom systems and it

approximately obeys the relation (15)

$$Q = Q_0 - BT$$

where T is the projectile ion kinetic energy and Q_0 is the value of Q at $T = 0$. For an ideal stripping reaction $Q_0 = 0$. For many ion-molecule reactions involving hydrogen molecules Q_0 has been reported to have positive values of about 0.15 eV (16). It is clear from Fig. 6 that Q remains negative down to energies < 0.7 eV in the laboratory system and that its limiting value at $T = 0$ appears to be zero. This suggests that at low primary ion energy, assuming that the reactants are in their ground states, that the bulk of the heat of reaction to produce $FD^+(^2\Pi)$ is converted into internal energy of the product ion and a negligible amount is converted in product ion translational energy. Since $\Delta H = -2.78$ eV and the dissociation energy is 3.46 eV and the product ion line width is only 0.285 eV at a projectile energy of 1.30 eV and width of 0.067 eV (FWHM) it appears that ΔH is deposited into a relatively few high lying vibrational levels of the FD^+ ion and the vibrational population in the product ion is highly inverted.

Reaction of F^+ with CH_4 .

As far as the author is aware there have been no reports of F^+ ion beam studies with complex target molecules with the exception of some preliminary work on the $F^+ + CH_4$ reaction. Using ground state F^+ Jones et al. (17) have made some observations on the production of CH_3^+ and HF^+ from these reactions. The cross section for CH_3^+ formation was 0.39 A at 2.5 eV and fell with increasing F^+ energy and about 20 eV the curve flattened off to about 0.09 A remaining flat to 60 eV which was the highest energy studied. It is of interest to compare this reaction to the corresponding C^+ reaction where (18) at 2.5 eV CH_3^+ is formed with a 7 A cross section and it falls with kinetic energy and then flattens out at cross section of about 3 A. Both of these similar reactions probably proceed by hydride ion abstraction at low energy and dissociative charge transfer at the higher energies. The differences in the cross sections and the position of the plateau are probably due to the greater exothermicity of the F^+ reaction. This results in a greater internal energy deposition in the intermediate with corresponding greater fragmentation into simpler products.

The reaction involving the formation of HF^+ is very similar to the corresponding C^+ reaction. The F^+ reaction cross section is essentially constant from 9 eV to 60 eV at a value of 0.07 A. The C^+ reaction also gave approximately a constant cross section of about 0.3 A up to 200 eV. These reactions very likely arise from dissociative charge transfer processes but other mechanisms

are possible.

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Abstract

F^+ ion beam studies using simple atomic or molecular targets are summarized. The charge transfer between F^+ and Ne, the reaction F^+ with molecular hydrogen and its stable isotopic variants, dynamics of the $F^+(D_2,D)FD^+$ reaction and some reactions of F^+ with methane as a function of projectile ion kinetic energy are covered and examined for the information that they give on reaction mechanism and internal energy of the product ion.

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Figure Captions

1. The upper figure gives the attenuation curves for F^+ produced from CF_4 by electron bombardment. Neon was used as an attenuating gas. The ion source pressure was 20 microns and the F^+ ion energy was 15 eV. The electron energy was 100 eV (θ), 80 eV ($\square$), 60 eV (Δ), and 50 eV (∇). The curve E represents the attenuation of ions in the excited state. In the lower curve the attenuation of F^+ in neon is given when the F^+ ions are produced by electron bombardment of a 70% - 30% CF_4 -Ne mixture. All other parameters were the same as for the upper figure.
2. Charge exchange cross sections for the reaction $F^+(Ne,F)Ne^+$. 3P state (θ), $^3P + ^1D$ states (Δ), and 1D state ($\square$).
3. Cross sections for the reactions of $F^+(^3P) + H_2(\theta)$ and $F^+(^3P) + D_2(\square)$ and $F^+(^1D)$ with $H_2(\theta)$ and $D_2(\Delta)$. The dashed curves give the corresponding results assuming the phase space theory of ion-molecule reactions.
4. Cross sections of F^+ ion kinetic energy for the reaction $F^+(^3P) + HD$. $FH^+(\theta)$ and $FD^+(\Delta)$.
5. FD^+ ion velocity distributions shown in Cartesian coordinates in the center of mass system for barycentric energies (a) 0.21 eV, (b) 0.39 eV, and (c) 0.91 eV. (+) indicates the velocity of the center of mass of the system, and (X) indicates most probable velocity of the ideal spectator stripping product at 0° . Solid circle corresponds to the most probable values of $Q = -0.20, -0.26, -0.55$ for (a), (b), and (c), respectively and the dotted circle corresponds to the spectator stripping values of $Q = -0.12, -0.21, -0.50$ for (a), (b), (c), respectively. The single contour lines to the right of each product distribution correspond to the 50% intensity profile of the primary ion beam.
6. Translational exoergicity for the reaction $F^+(D_2,D)FD^+$ as a function of primary ion energy in the laboratory system. Arrows indicate energies at which contour maps were made.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Scattering
cross section

Fig. 5

Scale: 100 m/sec
100 m/sec

Fig. 6

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