

## Positive Ion Chemistry of Elemental Fluorine

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**Abstract:**  $F_2^{+}$  ions have been generated in the external ion source of a FT-ICR mass spectrometer, and their reactivity with a choice of neutrals, ranging from noble gases to polyatomic molecules, has been investigated. With the exception of He and Ne, all neutrals react with  $F_2^{+}$  at the collision controlled limit, yielding predominantly electron transfer and fragmentation products. Noteworthy, a formal  $F^+$  transfer process takes place from the reaction of  $F_2^{+}$  with Ar, among the noble gases, and with CO and  $N_2$ , among diatomic molecules. The unimolecular and bimolecular reactivity of  $F_2H^+$ , obtained from the  $F_2^{+}$  reaction with  $H_2$ , allowed the proton affinity of elemental fluorine ( $PA = 79 \pm 5 \text{ kcal mol}^{-1}$ ) to be experimentally derived.

In recent years elemental fluorine has become an extremely useful tool for performing a wide range of reactions. Several of these reactions are characterized by a remarkable selectivity, unexpected from a highly reactive species, which may react explosively unless tamed by a careful choice of reaction conditions. For example, a general, regioselective method has been described recently that uses elemental fluorine to produce biradical negative ions in the gas phase.<sup>1</sup> In the field of organofluorine chemistry, Barton, Rozen, and others have led the way to the use of  $F_2$  diluted with an inert gas as a versatile reagent for introducing fluorine at centers of high electron density.<sup>2</sup> The term "electrophilic fluorination" was introduced to account for reaction processes that could be best described as involving a formal  $F^+$  transfer event. This concept, however, has been the cause of some controversy.<sup>3,4</sup> Elemental fluorine, in particular, is a potential source of fluorine atoms ( $F^{\bullet}$ ) rather than of cationic fluorine ( $F^+$ ), on the basis of the homolytic dissociation energy of  $38 \text{ kcal mol}^{-1}$  compared to the heterolytic dissociation energy of  $361 \text{ kcal mol}^{-1}$ .<sup>5</sup> The delivery of a positive fluorine would be much less energy demanding from  $F_2^{+}$ , whose bond dissociation energy amounts to  $78 \text{ kcal mol}^{-1}$ . This value places  $F_2^{+}$  among the strongest oxidative fluorinators in a quantitative scale developed recently.<sup>6</sup> This scale is based on the relative  $F^+$  detachment energies from neutral Z in  $ZF^+$  ions, derived from local density functional calculations. In view of the scant information available on the gas-phase chemistry of  $F_2^{+}$ ,<sup>7</sup> the reactivity of this powerful oxidant and potential  $F^+$  donor toward simple molecules has been explored by FT-ICR mass spectrometry.<sup>8</sup> In addition, experimental efforts have

been directed toward the determination of the yet unknown proton affinity (PA) of elemental fluorine.

## Experimental Section

A Bruker Spectrospin Apex TM 47e spectrometer equipped with an external ion source and a cylindrical (60-mm diameter) "infinity" cell situated between the poles of a 4.7 T superconducting magnet was used for this study. Typically,  $F_2^{+}$  ions were generated by chemical ionization (CI) of a dilute solution of fluorine (5 mol % in He) in the ion source at  $2 \times 10^{-5}$  mbar, and were transferred into the ICR cell, where experiments were conducted at a room temperature of 298 K. Thermal equilibration of the ion population was ensured by multiple collisions with Ne admitted by a pulsed valve up to the pressure of ca.  $1 \times 10^{-5}$  mbar. After 0.5 s of pumping time the ions of interest were isolated by ejecting all other species by using "single shots".<sup>9</sup> The reaction with the neutral present in the cell was monitored by recording mass spectra at increasing reaction time, yielding a temporal profile of the relative abundances of the reactant and the product ion. Pseudo-first-order rate constants of the ion–molecule reactions were derived from the exponential decrease of the reactant ion abundance vs time and converted to absolute rate constants from the known pressure of the neutral. The concentration of the neutrals was determined from the pressure reading of the ionization gauge, calibrated with the reference reaction  $CH_4^{+} + CH_4 \rightarrow CH_5^{+} + CH_3^{\bullet}$  by using the rate constant value of  $11.7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .<sup>10</sup> This reading was corrected by the relative ionization cross-sections due to different polarizabilities.<sup>11</sup> The reported efficiency (Eff) is given by the  $k_{\text{obs}}/k_{\text{coll}}$  ratio, where  $k_{\text{obs}}$  is the observed second-order rate constant and  $k_{\text{coll}}$  is the collisional rate constant.<sup>12</sup> Bracketing experiments<sup>5,13</sup> were carried out on the reaction of  $F_2H^+$  ions, formed by chemical ionization of  $F_2/He$  and  $H_2$  in the ion source, with reference bases (B) introduced in the cell, by noting whether  $BH^+$  ions were formed. These experiments were hampered by the serious problem that the instrument is blind to ions of low  $m/z$  values, such as  $H_2^{+}$  and  $H_3^{+}$ . Such ions may be formed by CI of  $H_2$  in the ion source, and once transferred into the cell, they may react with B by proton (and electron) transfer,

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\* Abstract published in *Advance ACS Abstracts*, August 15, 1997.

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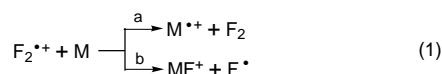
obscuring the reactivity of  $F_2H^+$ . To minimize the possible incursion of pathways and products from  $H_2^+$  and  $H_3^+$  ions, the ion source parameters were carefully selected. For example, the  $H_2$  partial pressure was kept low and the ion residence time long. In any event, each experiment was checked against a blank one, run under otherwise identical conditions except for the exclusion of  $H_2$ . Unfortunately, out of many attempts, only a few systems survived this control. The exact composition of all major ions was checked by the high-resolution measurement of their  $m/z$  value in the narrow band mode.

Collision induced dissociation (CID) experiments<sup>14</sup> were performed on  $F_2H^+$  ions, formed in the ion source and transferred into the ICR cell, to obtain thermochemical information from the threshold translational energy value for dissociation. Controlled conditions with regard to the vibrational and translational energy of the ions were sought by collisional stabilization and thermalization of the  $F_2H^+$  ions by the addition of neon through the pulsed valve up to the pressure of  $10^{-5}$  mbar. The  $F_2H^+$  ions were isolated from other ions in the cell by "single shots" and allowed to cool further by an additional delay time of 1 s. Eventually, the ions were translationally excited by a resonant single-frequency radio frequency pulse of variable duration, at constant peak-to-peak voltage. The total amount of ion kinetic energy ( $E_{lab}$ ) was calculated as described by Sievers et al.<sup>14b</sup> During the following delay time the translationally excited ions underwent collision with the target gas (He) present at the constant pressure of  $3-4 \times 10^{-8}$  mbar in the ICR cell. The delay time allowed for CID was properly chosen so as to maintain single-collision conditions, which is a requisite to obtain reliable threshold energies.<sup>14a</sup> During collision, the ion can gain internal energy from conversion of the center of mass translational energy,  $E_{cm} = \gamma E_{lab}$  ( $\gamma = m_t/(m_t + m_i)$ , where  $m_t$  is the mass of the target gas (He) and  $m_i$  the mass of the ion). The shape of the appearance curve of the products of endothermic reactions has been analyzed.<sup>15</sup> In the linear cross-section approximation, the linear portion of the curve at energies above threshold extrapolates to  $E_{cm}(th) - 3\gamma k_B T$  ( $k_B$  is the Boltzmann constant and  $T$  is the absolute temperature), which then allowed the threshold dissociation energy,  $E_{cm}(th)$ , to be determined.

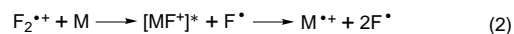
**Materials.** All gases used, including  $F_2$  (5 mol % in He), were purchased from Matheson Gas Products or Union Carbide with stated purity in excess of 99.99%. Aldrich Chemical Co. supplied all other products.

## Results and Discussion

**$F_2^{*+}$  and Noble Gases.**  $F_2^{*+}$ , a ground  $^2\Pi_g$  state,<sup>16</sup> is endowed with a large recombination energy, amounting to 15.70 eV.<sup>5</sup> This feature governs the reactivity of  $F_2^{*+}$  ions, which react exclusively by electron transfer (ET) with the great majority of the investigated neutrals. The reaction with the noble gas series provides a benchmark system. The products listed in Table 1 owe their origin either to electron transfer or to formal  $F^+$  transfer (FT), as shown in eq 1 ( $M$  = noble gas).



As previously reported,<sup>17</sup>  $F_2^{*+}$  is unreactive toward He and Ne on account of their high ionization energies (IE of 24.59 and 21.56 eV, respectively). Furthermore, the alternative reaction channel 1b is calculated to be strongly endothermic, leading to



**Table 1.** Products from Ion-Molecule Reactions of  $F_2^{*+}$  Ions, Studied by FT-ICR

| reactant gas (IE, eV) <sup>5</sup> | products <sup>a</sup>                      |
|------------------------------------|--|
| Ne (21.56)                         |  |
| Ar (15.76)                         | $Ar^{*+}$ (0.56), $ArF^+$ (0.44)           |
| Kr (14.00)                         | $Kr^{*+}$ ( $KrF^+$ , traces)              |
| Xe (12.13)                         | $Xe^{*+}$                                  |
| $H_2$ (15.43)                      | $F_2H^+$                                   |
| $N_2$ (15.58)                      | $N_2^{*+}$ (0.40), $N_2F^+$ (0.60)         |
| $O_2$ (12.07)                      | $O_2^{*+}$                                 |
| $Cl_2$ (11.48)                     | $Cl_2^{*+}$ ( $Cl^+$ , traces)             |
| CO (14.01)                         | $CO^{*+}$ (0.50), $FCO^+$ (0.50)           |
| NO (9.26)                          | $NO^+$                                     |
| $CO_2$ (13.77)                     | $CO_2^{*+}$                                |
| $N_2O$ (12.89)                     | $N_2O^{*+}$ , $NO^+$                       |
| $SO_2$ (12.32)                     | $SO_2^{*+}$ , $SO^{*+}$                    |
| $H_2O$ (12.61)                     | $H_2O^{*+}$                                |
| $BF_3$ (15.56)                     | $BF_2^+$                                   |
| $SiF_4$ (15.7)                     | $SiF_4^{*+}$ , $SiF_3^+$                   |
| $C_2H_2$ (11.40)                   | $C_2H_2^{*+}$ (0.96), $C_2HF^{*+}$ (0.04)  |
| $CH_3OH$ (10.85)                   | $CH_3O^+$ , $CH_3O^+$                      |
| $C_3F_6$ (10.60)                   | $C_3F_6^{*+}$ , $C_3F_5^+$ , $C_2F_4^{*+}$ |
| $C_6F_6$ (9.91)                    | $C_6F_6^{*+}$ , $C_3F_3^+$                 |

<sup>a</sup> Reaction efficiencies are in the range 0.7–1.0.

$HeF^+$  and  $NeF^+$  species that are either weakly bound or unstable with respect to dissociation.<sup>6,18,19</sup> Inter alia, the observed unreactivity of  $F_2^{*+}$  with He and Ne has made it possible to use dilute solutions of  $F_2$  in He in the CI plasma and to effect the collisional quenching of  $F_2^{*+}$  with Ne admitted in the ICR cell at relatively high pressure by the pulsed valve. The onset of the chemical reactivity of  $F_2^{*+}$  with noble gases is reached with Ar.<sup>17</sup> Both ET and FT products are formed in comparable amounts with a rate constant of  $1.0 \pm 0.4 \times 10^{-9}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, corresponding to a reaction efficiency of ca. 1.0. The IE value of 15.76 eV for Ar makes the ET process nearly resonant, in agreement with the fast kinetics observed. The comparably efficient FT reaction is conceivably associated with an exothermic process, which places an upper limit of 343 kcal mol<sup>-1</sup> for the enthalpy of formation ( $\Delta H_f^\circ$ ) of  $ArF^+$ . This value may be compared with the  $\Delta H_f^\circ(ArF^+)$  value of 338 kcal mol<sup>-1</sup>, that resulted from local density functional calculations.<sup>6</sup> At variance with  $ArF^+$ ,<sup>6,18</sup>  $KrF^+$  and  $XeF^+$  are known to exist in condensed phases.<sup>20</sup> However, the expectation of finding these ions as abundant products from the reaction of  $F_2^{*+}$  with Kr and Xe is not fulfilled. These reactions seem to occur almost exclusively by pathway 1a, although an alternative stepwise pathway may be conceived where  $M^{*+}$  is the dissociation product of  $MF^+$  ions, formed primarily by a highly exothermic process (eq 2). The overall exothermicity of reaction 2 is 1 kcal mol<sup>-1</sup> for  $M = Kr$  and 44 kcal mol<sup>-1</sup> for  $M = Xe$ , whereas reaction 2 would be endothermic for  $M = Ar$ .

**$F_2^{*+}$  and Diatomic Molecules.** The reaction of  $F_2^{*+}$  with exemplary homo- and heteronuclear diatomic molecules occurs by an ET process, as shown by the results listed in Table 1. This ET process, which is thermochemically favorable, is likely to occur, at least in part, also in the reaction with  $H_2$ , although the mass of the product ion is below the mass range accessible to the FT-ICR instrument used. Anyhow, the reaction with  $H_2$

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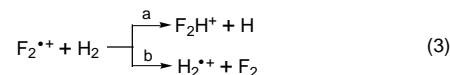
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will be reported in the following paragraph. It can be observed from the data in Table 1 that ion products different from simple ET products are formed only when the IE value of the neutral reactant is  $\geq 14$  eV. Thus, both  $N_2$  and CO yield formal FT products. The  $F_2^{*+}$  reaction with  $N_2$  is characterized by a rate constant of  $8.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , which corresponds to a unit efficiency, as expected from the high exothermicity of both the ET (reaction 1a,  $M = N_2$ ) and FT (reaction 1b) reaction channels. The fluorodiazonium ion,  $N_2F^+$ , is a well-known species which can be prepared in acid media and can be isolated as a salt.<sup>21</sup> By contrast, the formation of  $N_2F^+$  in the gas phase has been reported to be a minor channel in the CI of  $NF_3/HN_3$  gaseous mixtures, where it derived from the dissociation of HF from intermediate  $F_2N-NH^+$  ions.<sup>21e</sup> At present, only the  $F_2^{*+}$  reaction with  $N_2$  provides an efficient route yielding abundant  $N_2F^+$  ions by an ion-molecule reaction occurring in the ICR cell. The enthalpy change of this reaction (reaction 1b,  $M = N_2$ ) is estimated to be  $-53 \text{ kcal mol}^{-1}$ , using the  $\Delta H_f^\circ(N_2F^+)$  value of  $291 \text{ kcal mol}^{-1}$ , recently evaluated by ab initio MO calculations.<sup>21e</sup>

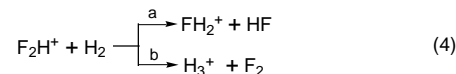
The  $F_2^{*+}$  reaction with CO occurs at the rate of  $5.8 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , with 0.7 efficiency, by competitive ET and FT routes. The formation of  $FCO^+$  is another rare example of a fairly efficient formal  $F^+$  transfer. Conventional routes to  $FCO^+$  ions involved electron impact ionization and fragmentation of suitable precursors. The search for novel reaction pathways to  $FCO^+$  involving ion-molecule reactions of selected fluorinated reactant ions met with poor ion yields and low reaction efficiencies.<sup>22</sup> The heat of formation of  $FCO^+$ , reported to be  $160 \text{ kcal mol}^{-1}$  from a photoelectron spectroscopy study of the  $FCO^+$  radical,<sup>23a</sup> has been recently redetermined as  $178 \text{ kcal mol}^{-1}$  by using photoionization mass spectrometry.<sup>23b</sup> This value implies an exothermicity of  $139 \text{ kcal mol}^{-1}$  for reaction 1b,  $M = CO$ .

Regardless of several ionic products that may be potentially formed in an exothermic fashion from the reaction of  $F_2^{*+}$  with  $O_2$ ,  $Cl_2$ , and NO (for example, the formation of  $FO_2^+$ ,  $FCl^+$ ,  $F_2Cl^+$ , and  $FNO^+$  would be thermochemically allowed), only the ET product is observed. However, the ET product ion may still result from an intimate reaction complex, for example, as a fragmentation product of a highly excited adduct or as the product of pathway 2. Pathway 2 may also account in principle for the formation of  $N_2^{*+}$  and  $CO^{*+}$ . Finally, a last piece of evidence concerns the absence of  $F_3^+$  as a possible product formed by CI of  $F_2/He$  in the ion source. This result is in line with the high fluorinator strength of  $F_3^+$ ,<sup>6</sup> an ion that can be formed exothermically from the  $F_2$  reaction with  $F^+$  rather than  $F_2^{*+}$ .<sup>24</sup>

**The Reaction of  $F_2^{*+}$  with  $H_2$ .** The  $F_2^{*+}$  reaction with  $H_2$  does not occur by ET or FT processes, involving instead formal H-H bond breaking to form  $F_2H^+$  (eq 3a). This reaction might be accompanied by an undetectable ET channel leading to  $H_2^{*+}$  ions (eq 3b). The bimolecular rate constant of  $6.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the reactant ion decay characterizes

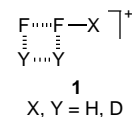
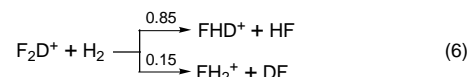
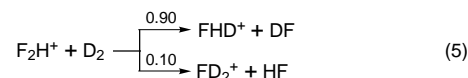


channel 3a as a highly efficient process (Eff = 0.85). A small kinetic isotope effect of ca. 1.1 was found to affect the competing reaction of  $F_2^{*+}$  with a  $H_2/D_2$  mixture. The formation of  $F_2H^+$  is followed by a formal FT process yielding  $FH_2^+$  (eq 4a). This reaction has been independently verified by selecting



$F_2H^+$  ions and evaluating the rate constant of  $5.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Eff = 0.5) for their bimolecular decay in  $H_2$ . Once again, a parallel reaction may occur (eq 4b), which may not be revealed by the instrument.

The reaction of  $F_2H^+$  with hydrogen is exemplary, because it shows that a formal FT processes should not be regarded as actually involving the simple transfer of  $F^+$ . This fact emerges clearly from the branching ratios of the  $F_2H^+$  reaction with  $D_2$  (eq 5) and the  $F_2D^+$  reaction with  $H_2$  (eq 6), which largely favor the formation of  $FHD^+$ , as expected from a reaction involving a four center transition state (**1**). The alternative possibility may



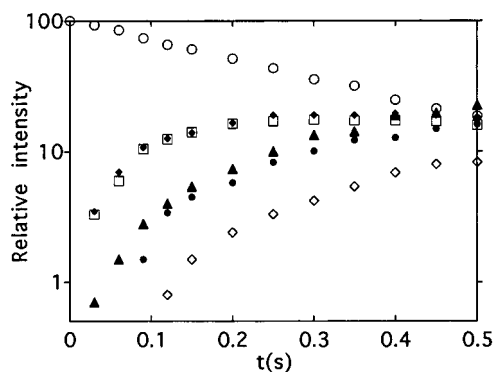
exist that H/D exchange occurs within the  $[F_2X^+ \cdot Y_2]$  or the  $[FX \cdot FY_2^+]$  ion-neutral complexes, possibly involving kinetic isotope effects and accounting for the predominance of the  $FHD^+$  product ion. However, it is difficult to account for the very close branching ratios of eqs 5 and 6 by this hypothesis. Theoretical calculations are planned to shed light on the reaction profile.

The overall bimolecular reactions are characterized by sizable kinetic isotope effects ( $k(F_2H^+ + H_2)/k(F_2D^+ + D_2) \approx 3$ ). The overall kinetic progress of the reaction of  $F_2^{*+}$  with a  $H_2/D_2$  mixture is illustrated in Figure 1.

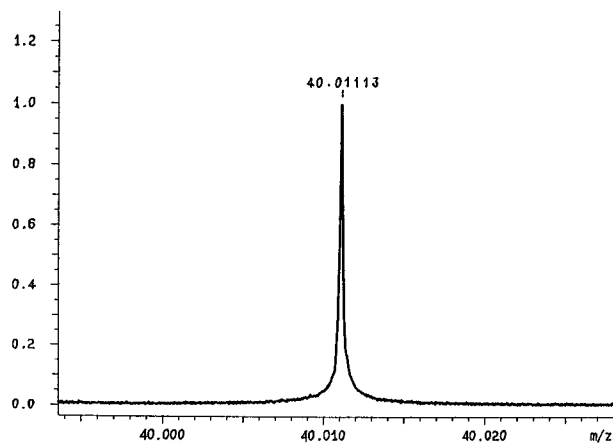
**The Proton Affinity of  $F_2$ .** The reaction of  $F_2^{*+}$  with  $H_2$  provides a unique way to form  $F_2H^+$ , the conjugate acid of one of the least basic elements. To the authors' knowledge, this ion has never been observed experimentally. Figure 2 reports as an example the high-resolution FT-ICR spectrum of  $F_2D^+$  that confirmed the assigned elemental composition. Several studies have addressed the determination of the PA of  $F_2$  by computational methods.<sup>24a,25</sup> Recent calculations predict that  $F_2H^+$  has a triplet ground state.<sup>24a</sup> The calculated PA value of  $88.6 \text{ kcal mol}^{-1}$  places the PA of fluorine below that of such poorly basic substances as  $H_2$ ,  $O_2$ , and  $N_2$ .<sup>24</sup> The dearth of suitable reference bases (B) in this PA range sets a serious limit to the kinetic approach, based on the occurrence or non-occurrence of proton transfer from  $F_2H^+$  to B, the so-called bracketing method.<sup>5,13</sup> As shown by the scant amount of data collected in Table 2, a wide range of uncertainty is left for the

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**Figure 1.** Relative ion intensities following selection of  $F_2^{*+}$ , formed by  $H_2/CI$  of a  $F_2/He$  mixture in the external ion source, in a  $H_2/D_2$  (1:1.2) mixture at  $3.3 \times 10^{-8}$  mbar in the ICR cell ( $\circ$ ,  $F_2^{*+}$ ,  $\square$ ,  $F_2H^+$ ,  $\blacklozenge$ ,  $F_2D^+$ ,  $\bullet$ ,  $FH_2^+$ ,  $\blacktriangle$ ,  $FHD^+$ ,  $\diamond$ ,  $FD_2^+$ ).



**Figure 2.** High-resolution FT-ICR mass spectrum showing the  $F_2D^+$  ion at  $m/z$  40.01113, recorded at the  $D_2$  pressure of  $3 \times 10^{-8}$  mbar.

**Table 2.** Occurrence of Proton Transfer Reaction  $F_2H^+ + B \rightarrow F_2 + BH^+$

| ref base (PA, kcal mol <sup>-1</sup> ) <sup>5</sup> | H <sup>+</sup> transfer <sup>a</sup> |
|---|--------------------------------------|
| CO <sub>2</sub> (131)                               | yes                                  |
| N <sub>2</sub> (118)                                | yes                                  |
| O <sub>2</sub> (102)                                | yes                                  |
| Kr (102)  | yes                                  |
| Ar (89)   | yes                                  |
| Ne (48)   | no                                   |

<sup>a</sup> Whenever observed, the proton transfer reactions are all highly efficient (Eff  $\approx$  1).

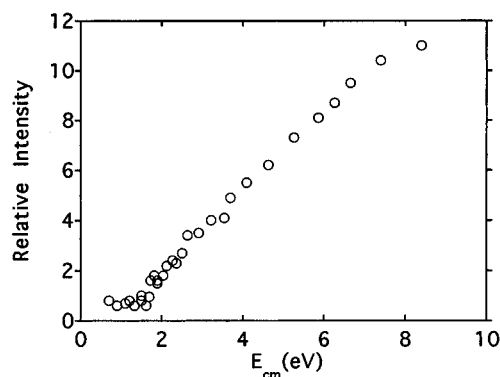
PA of  $F_2$ , which may lie anywhere between 48 and 89 kcal mol<sup>-1</sup>. This window may be narrowed if one considers that the high efficiency of reaction 3a should be bound to  $\Delta H^\circ(3a) \leq 0$ . Within this boundary, a  $\Delta H^\circ_f(F_2H^+)$  value  $\leq 310$  kcal mol<sup>-1</sup> is obtained, which sets a lower limit of 56 kcal mol<sup>-1</sup> to PA( $F_2$ ).

In view of the large uncertainty attached to the direct evaluation of the PA of fluorine, an alternative approach was sought, based on the evaluation of  $\Delta H^\circ_f(F_2H^+)$  from the translation energy dependence of the endothermic dissociation process of eq 7. This technique, based on energy resolved CID experiments, has already been exploited to gain information on the PA of a neutral, by estimating the heat of formation of the protonated species.<sup>26</sup>



From the CID results shown in Figure 3, a threshold dissociation

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**Figure 3.** Threshold curve for low energy collision induced  $F^+$  loss from  $F_2H^+$  with He as the target gas ( $3-4 \times 10^{-8}$  mbar) and a CID delay time of 50 ms. The y-axis represents the ratio of the intensities of the fragment and parent ions.

energy of  $1.6 \pm 0.2$  eV was derived and combined with the known values<sup>5</sup> of  $\Delta H^\circ_f$  for  $HF^+$  and F to obtain  $\Delta H^\circ_f(F_2H^+) = 287 \pm 5$  kcal mol<sup>-1</sup> and hence PA( $F_2$ ) =  $79 \pm 5$  kcal mol<sup>-1</sup>. This result, which represents the first experimental determination of the PA of elemental fluorine, is in fair agreement with the reported theoretical values of 88.6,<sup>24a</sup> 85.0,<sup>25b</sup> and 73 kcal mol<sup>-1</sup>.<sup>25a</sup> At the same time, the threshold dissociation energy obtained for  $F_2H^+$  agrees well with the value of 1.4 eV calculated for the bond dissociation energy of  $F-FH^+$ .<sup>27</sup>

**$F_2^{*+}$  and Polyatomic Molecules.** The reactivity of  $F_2^{*+}$  with selected polyatomic molecules is largely dominated by charge exchange processes (Table 1). Molecular radical cations are formed in all cases except  $BF_3$ , often accompanied by fragment ions whose formation is compatible with the recombination energy of  $F_2$  or is only slightly endothermic. For example, the appearance energy of  $SO^+$  from  $SO_2$  is reported to be equal to 16 eV.<sup>28</sup> As previously discussed for the reaction of diatomic molecules, it may not be excluded that the observed formal ET (and fragmentation) products may derive from intimate ion-molecule complexes of high internal energy, resulting from a favorable dissociation channel. The only evidence for the formation of a covalent complex among the exemplary reactions of Table 1 comes from the formation of  $C_2HF^{*+}$  as a minor product of the reaction with acetylene, which may be suggested to arise from  $F_2^{*+}$  addition to the triple bond followed by HF elimination.

## Conclusions

The reactivity of  $F_2^{*+}$  with selected neutral molecules has been studied in the gas phase at ca.  $10^{-8}$  mbar by the ICR technique, aiming to point out the potential  $F^+$  donor ability. Formal  $F^+$  transfer reactions have indeed been observed, though only in a few of the investigated systems. Whenever they occur, namely from the  $F_2^{*+}$  reaction with Ar, N<sub>2</sub>, and CO, they provide an efficient route to cationic species that may display in turn specific  $F^+$  transfer reactivity. However, the overwhelming reaction channel with most of the investigated neutrals resulted in an electron transfer process leading to radical cations and fragmentation products. The  $F_2^{*+}$  reaction with  $H_2$  was found to yield  $F_2H^+$  ions, providing access to an otherwise elusive ionic species. In fact, since the PA value of  $F_2$  is among the lowest in the PA scale presently available, only a few  $MH^+$  species ( $M = He, Ne, H$ ) can be conceivably used to form  $F_2H^+$  by a proton transfer reaction. The PA value of  $F_2$  has been

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confined within the range 48–89 kcal mol<sup>-1</sup> by bracketing experiments and determined to be  $79 \pm 5$  kcal mol<sup>-1</sup> according to energy resolved CID experiments. The reaction of F<sub>2</sub>H<sup>+</sup> with H<sub>2</sub>, the simplest stable diatomic molecule, provides a neat example that formal F<sup>+</sup> transfer processes occurring between elementary neutral species may in fact involve a complex transition state with a large degree of bond reorganization. This is evident, for example, in the predominant formation of FHD<sup>+</sup> from the reaction of F<sub>2</sub>H<sup>+</sup> with D<sub>2</sub>.

**Acknowledgment.** Financial support by the Italian Ministero dell'Università e della Ricerca Scientifica e Tecnologica is gratefully acknowledged. The authors thank Prof. F. Cacace for many stimulating discussions and Mr. F. Angelelli and Mr. A. Di Marzio for their skilful help.

JA971290V