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Spin-forbidden F^+ transfer between ${}^2NF^+$ and CO: a computational study on the detailed mechanistic aspects

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Abstract

The detailed mechanistic aspects of the ion–molecule reaction between ${}^{2}NF^{+}$ and CO with formation of ${}^{1}FCO^{+}$ and ${}^{4}N$ have been investigated by using density functional theory and ab initio calculations. We have first located on the ground doublet and quartet B3LYP/6-311+G(*d*) (N,F,C,O)⁺ potential energy surfaces the various energy minima and transition structures involved in this process, and subsequently located the minimum energy points lying on the B3LYP/6-311+G(*d*) line of intersection between the two surfaces by using a recently described steepest descent-based method [Theor. Chem. Acc. 99 (1998) 95]. The obtained results indicate that this "spin-forbidden" reaction is a viable process in the gas phase, and could occur by two alternative mechanisms. The first one consists of the formation of the (${}^{2}NF^{+}/CO$) adduct **1** on the doublet (N,F,C,O)⁺ surface, which subsequently undergoes the spin-forbidden isomerization into the loosely bound adduct (${}^{4}N/FCO^{+}$) adduct **5** on the quartet surface via a 1,2 fluorine shift from nitrogen to carbon. Isomer **5** undergoes in turn the barrier-free dissociation into the ${}^{4}N$ and FCO⁺ reaction products. The second conceivable mechanistic route consists of the formation of the adduct **1** and its isomerization into the (${}^{2}N/FCO^{+}$) adduct **7** via an adiabatic process. The eventual spin-forbidden formation of isomer **5** from isomer **7** occurs by a nonadiabatic 1,2 fluorine shift from nitrogen to carbon. (Int J Mass Spectrom 201 (2000) 151–160) © 2000 Elsevier Science B.V.

Keywords: Fluorine; F⁺ transfer; Spin-forbidden; DFT; Ab initio

1. Introduction

The formal transfers of F^+ between elementary neutral species Z_i

$$Z_1F^+ + Z_2 \rightarrow Z_2F^+ + Z_1 \tag{1}$$

are prototype reactions of general interest. Process (1) which occurs in solution and involves monoatomic and simple polyatomic molecules has been intensively

investigated over the last three decades [1–16], and the results of these studies have significantly contributed to the progress in the inorganic chemistry of main-group elements. In the more recent years, the interest has been extended to reaction (1) which occurs in the gas phase and involves monoatomic and biatomic species such as F [17], N₂ [17], NF [18], and CO [17,18]. Of particular interest is the simplest process (1) which involves a change in total spin multiplicity. In fact, besides providing more detailed insight into the still little explored mechanistic aspects of F⁺ transfer reactions, their investigation contrib-

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utes to learn more on "spin-forbidden" reactions, a class of chemical processes which are currently focusing considerably on experimental [19–23] and theoretical [24–29] attention. As part of our continuing interest in the gas-phase ion chemistry of simple fluorinated species [30–36], we have recently performed [37] a joint experimental and theoretical study on the spin-forbidden F^+ transfer reaction

$${}^{1}\mathrm{NF}_{2}^{+} + \mathrm{CO} \rightarrow {}^{1}\mathrm{FCO}^{+} + {}^{3}\mathrm{NF}$$

$$(2)$$

so far observed in the gas phase under low-pressure mass spectrometric conditions. The obtained results provided the first detailed description of the mechanism of a formal F^+ transfer reaction and revealed that both the singlet and triplet potential energy surfaces, and the corresponding crossing hyperline, play a key role in the overall process. Stimulated by the findings concerning reaction (2), we turned attention on the strictly related process

$${}^{2}\mathrm{NF}^{+} + \mathrm{CO} \rightarrow {}^{1}\mathrm{FCO}^{+} + {}^{4}\mathrm{N}$$
(3)

and decided to perform a computational study on its detailed mechanistic aspects. The obtained results, discussed in the present article, indicate that reaction (3) is indeed a viable process in the gas phase. This could stimulate future experimental work aimed at its actual observation and detailed investigation.

2. Computational details

The density functional theory (DFT) and ab initio calculations reported in the present article have been performed using the GAUSSIAN 94 [38] and GAMESS USA [39] sets of programs installed on an Alphaserver 1200 Compaq machine. The geometries of all the minima and transition structures located on the doublet and quartet $(N,F,C,O)^+$ ground potential energy surfaces were optimized, within the specified symmetry constraints, at the DFT level of theory by using the Becke's three-parameter hyrid description of exchange together with the correlation functional of Lee et al. [40] B3LYP [41,42] as implemented in GAUSSIAN 94 [43]. We used both the 6-31G(*d*) [44]

and 6-311+G(d) [45] basis sets, but no appreciable differences were found between the B3LYP/6-31G(d) and B3LYP/6-311+G(d) optimized parameters. The various located critical points were subsequently characterized by computing their B3LYP/6-311+G(d) analytical second derivatives, used also to calculate the vibrational harmonic frequencies and zero-point energy corrections. For selected transition structures, standard intrinsic reaction coordinate (IRC) calculations [46] were performed to make sure that they actually connected the desired pairs of energy minima on the doublet and quartet $(N,F,C,O)^+$ potential energy surfaces. Our attempts to refine the total energies of the various $(N,F,C,O)^+$ structures by performing single-point calculations at the coupledcluster level of theory [47] by using the standard cc-pVTZ basis set by Dunning [48] were frustrated by the fact that the $\langle S^2 \rangle$ expectation values of the UHF wave functions used for the CCSD(T)/cc-pVTZ calculations resulted markedly different from 0.75 for doublets and 3.75 for quartets, thus revealing strong spin contamination. By contrast, the B3LYP/6-311+G(d) wave functions were found to suffer much less spin contamination [49]. Therefore, taking into account the satisfactory description of the singlet and triplet $(N,F_2,C,O)^+$ potential energy surfaces obtained in our recent study [37] by using the B3LYP functional in conjunction with split-valence basis sets, we decided to adopt the B3LYP/6-311+G(d) level of theory as adequate to predict the relative stability of the doublet and quartet $(N,F,C,O)^+$ structures.

The critical points lying on the hyperline of intersection between the doublet and quartet $(N,F,C,O)^+$ potential energy surfaces were located at the B3LYP/ 6-311+G(d) level of theory by using a recently described steepest-descent based method [50]. These crossing points were approximately ascertained to be minima along the 3N - 7 dimensional crossing hyperline (MECPs) by verifying the absence of negative eigenvalues in the corresponding effective projected Hessian matrix [51]. An approximate estimation of the harmonic frequencies and zero-point energy corrections at the crossing points were also obtained in this way. We have also used the IRC-like procedure described in [23] to ascertain whether the various located MECPs were actually connecting the desired pairs of energy minima on the doublet and quartet $(N,F,C,O)^+$ adiabatic surfaces. For all of the located MECPs, we have evaluated the spin-orbit coupling matrix elements, known to drive the intersystem crossing in the vicinity of the crossing point [24,25], by an approximate monoelectronic operator \mathbf{H}^{SO} with first-order configuration interaction/cc-pVTZ wave functions, by using values of the effective nuclear charges so to take into account the neglected contribution of the bielectronic term [52]. The results of these calculations will be reported as the root mean square of the \mathbf{H}^{SO} elements. The results of the configuration interaction calculations revealed also that the wave functions of the various MECPs were by far dominated by a single electronic configuration.

3. Results and discussion

3.1. Structure and stability of the $(N,F,C,O)^+$ isomers

The formal transfer of F^+ between ${}^2NF^+$ and CO is an exothermic process, whose enthalpy change at 0 K amounts to -20.3 kcal/mol [53]. At the B3LYP/6-311+G(*d*) level of theory, we obtain a value of -25.0 kcal/mol, which reinforces the expectation that this computational level is indeed adequate to predict the relative stability of the presently investigated (N,F,C,O)⁺ isomers and interconnecting structures within a few kilocalories per mole.

We have first located on the doublet and quartet $(N,F,C,O)^+$ potential energy surfaces the energy minima corresponding to the various intermediates conceivably involved in the formal F⁺ transfer reaction (3). The B3LYP/6-311+G(*d*) optimized structures of these isomers are shown in Fig. 1, and their absolute and relative energies, at the same level of theory, are collected in Table 1.

Reaction (3) conceivably commences by formation of an encounter complex between ${}^{2}NF^{+}$ and CO on the doublet (N,F,C,O)⁺ potential energy surface. Consistent with the character of CO as a bidentate nucleophile toward simple gaseous cations [54,55],



Fig. 1. B3LYP/6-311+G(d) optimized geometries of the doublet and quartet (N,F,C,O)⁺ isomers. The data of ion **8** are B3LYP/6-31G(d).

we have located two distinct isomers of the $({}^{2}NF^{+}/CO)$ adduct, namely, the C-coordinated isomer 1 and the O-coordinated isomer 2. Both of these two structures revealed to be true minima on the surface. However, in line with the usually larger stability of the C-coordinated isomer of the adducts formed by gaseous cations with CO [54], isomer 1 resulted to be more stable than 2 by 42.6 kcal/mol. The optimized structures of the two isomers indicate in fact that the interaction between ${}^{2}NF^{+}$ and CO with formation of 1, 60.4 kcal/mol, is larger than isomer 2. We note in particular that the C–N bond distance of 1, 1.348 Å, is significantly shorter than the N–O distance of 2, 2.118 Å.

At the B3LYP/6-311+G(*d*) level of theory, the quartet state of NF⁺ (${}^{4}\Sigma^{+}$) is computed to be less stable than the doublet state (${}^{2}\Pi$) by more than 90 kcal/mol. It is therefore not surprising that the two isomers **3** and **4** located as true minima on the quartet (N,F,C,O)⁺ potential energy surface and formally

Table 1

Absolute energies, $\langle S^2 \rangle$ expectation values, zero-point energies (a.u.), and relative energies (kcal/mol) of the (N,F,C,O)⁺ isomers and their fragments

Species	B3LYP/6-311+G(<i>d</i>)	$\langle S^2 \rangle$	ZPE	$\Delta E (0 \text{ K})$
1 (² <i>A</i> ")	-267.476 14	0.757	0.012 78	0.0
	-267.39775^{a}	0.757 ^a	$0.012~72^{\rm a}$	
2 $(^{2}A'')$	-267.40506	0.791	0.009 57	+42.6
3 $({}^{4}A'')$	-267.377 66	3.777	0.009 06	+59.5
4 $({}^{4}A'')$	-267.329 55	3.764	0.008 60	+89.4
5 $({}^{4}A'')$	-267.419 99	3.769	0.010 97	+34.1
6 $({}^{4}A)$	-267.419 32	3.754	0.011 32	+34.7
$7(^{2}A'')$	-267.456 46	0.766	0.013 28	+12.7
8 $(^{2}A')$	$-267.237\ 50^{\rm a}$	0.757^{a}	$0.010~68^{\rm a}$	$+99.3^{a}$
TS12 (^{2}A)	-267.314 72 ^a	0.940^{a}	$0.008 82^{a}$	$+49.7^{a}$
TS17 $(^{2}A'')$	-267.395 05	0.775	0.010 60	+49.5
TS35 $({}^{4}A)$	-267.345 42	3.771	0.007 81	+78.9
MECP1	-267.39570		0.009 06	+48.1
MECP2	-267.419 99		0.009 34	+33.1
MECP3	-267.36840		0.008 01	+64.6
\mathbf{NF}^+ (² Π)	-154.02672	0.753	0.003 63	
NF^+ ($^4\Sigma^+$)	-153.88042	3.755	0.001 19	
FCO ⁺ $(^{1}\Sigma^{+})$	-212.817 63		0.011 19	
$CO(\Sigma^+)$	-113.349 05		0.005 04	
$N(^{4}S)$	-54.60072	3.753		
$\mathbf{N}(^{2}D)$	-54.499 26	0.752		

^a B3LYP/6-31G(d).

arising from the C coordination and the O coordination of ${}^{4}NF^{+}$ to CO, respectively, are significantly higher in energy than the corresponding isomers **1** and **2** on the doublet (N,F,C,O)⁺ surface. In particular, isomers **3** and **4** are less stable than **1** by 59.5 and 89.4 kcal/mol, respectively. Therefore, their order of stability parallels the energy difference between **1** and **2** and likely reflects the more favourable interaction of the ${}^{4}NF^{+}$ ion with the C atom of CO. We note in particular the large N–O distance of **4**, 2.573 Å, and the short C–N distance of **3**, 1.312 Å.

The products of the formal F^+ transfer reaction (3), ⁴N and ¹FCO⁺, conceivably arise from the etherolytic dissociation of a (⁴N/FCO⁺) complex eventually formed on the quartet (N,F,C,O)⁺ potential energy surface. We have in fact located the two isomeric ions **5** and **6**, which must be viewed as complexes between N(⁴S) and ¹FCO⁺. They formally arise from the ligation of N(⁴S) to the C atom and F atom of FCO⁺, respectively, and, overall, their optimized geometries are significantly different. Nevertheless, isomer **5** resulted to be more stable than **6** by only 0.6 kcal/mol. In addition, both of these ions must be perceived as very loosely bound species, since their dissociation energies into $N(^4S)$ and FCO⁺ are obtained as ~1 kcal/mol. Therefore, taking into account the unfavourable contribution of the entropy term, even at low temperatures, isomers **5** and **6** are predicted to be unstable with respect to their dissociation products $N(^4S)$ and FCO⁺. The flat character of the quartet $(N,F,C,O)^+$ potential energy surface in the region of isomers **5** and **6** was confirmed by the location of an additional critical point (not included in Fig. 1 and Table 1) practically degenerate with **6** and of quite similar geometry, which revealed to be the transition structure connecting **5** and **6**.

The two isomeric structures **7** and **8** located on the doublet $(N,F,C,O)^+$ potential energy surface and characterized as true minima are the corresponding analogues of ions **5** and **6** on the quartet surface. We first note that, despite the ground doublet electronic state of the nitrogen atom (^2D) is less stable than the ground quartet state (^4S) by 55.0 kcal/mol [56], the doublet isomer **7** resulted to be more stable than the

quartet isomer 5 by \sim 21 kcal/mol. This likely reflects the favourable interaction that occurs in ion 7 between the formally empty p orbital of the C atom of FCO^+ with the lone pair of the N atom in its excited ^{2}D electronic state. This is suggested by the shorter C-N distance of isomer 7, 1.325 Å, with respect to 5, 1.519 Å. At the B3LYP/6-31G(d) level of theory, the doublet isomer 8 was found to be less stable than 1 by \sim 99 kcal/mol. This species is in fact a high-energy minimum on the ${}^{2}A'$ (N,F,C,O)⁺ potential energy surface and it should not play any appreciable role in the overall mechanism of reaction (3). Therefore, we refrained from a detailed investigation of this species at the B3LYP/6-311+G(d) level of theory, and the data reported in Fig. 1 and Table 1 refer to B3LYP/ 6-31G(d) calculations. We note that structure 7 is less stable than the $(^{2}NF^{+}/CO)$ adduct **1** by 12.7 kcal/mol. Therefore, the latter species results as the most stable among the presently investigated doublet and quartet $(N,F,C,O)^+$ isomers.

3.2. Interconversion of the doublet and quartet $(N,F,C,O)^+$ isomers

We have subsequently located the transition structures (TSs) which connect the various energy minima located on the ground doublet and quartet (N,F,C,O)⁺ potential energy surfaces, as well as the MECPs between the energy minima of different spin multiplicity. Since the aim of the present study was essentially to obtain a detailed description of the conceivable mechanistic path(s) of reaction (3) (vide infra), we have focused particular attention on the location of those structures which allow the evolution of the initially formed complexes 1 and 2 on the doublet $(N,F,C,O)^+$ surface into the eventually formed complex **5** on the quartet $(N,F,C,O)^+$ surface. The B3LYP/6-311+G(d) optimized geometries of the various TSs and MECPs are shown in Fig. 2 and their absolute and relative energies are collected in Table 1.

On the doublet surface, the interconversion between the $(^{2}NF^{+}/CO)$ isomeric adducts 1 and 2 occurs through the transition structure **TS12**. We note that this species was unambiguously characterized as a



Fig. 2. B3LYP/6-311+G(d) optimized geometries of the $(N,F,C,O)^+$ transition structures and minimum energy crossing points. The data of ion **TS12** are B3LYP/6-31G(d).

first-order saddle point on the B3LYP/6-31G(d) potential energy surface. However, using the larger 6-311+G(d) basis set, it resulted to be not fully optimized with respect to the maximum displacement parameter of the algorithm employed for the geometry optimization. Therefore, the optimized parameters of TS12 shown in Fig. 2 and its energy data quoted in Table 1 refer to the B3LYP/6-31G(d) calculations. Inspection of the eigenvector corresponding to the imaginary frequency of **TS12**, 227.7i cm⁻¹, reveals that the interconversion between 1 and 2 occurs essentially by the out-of-plane rotation of the NF moiety. The high energy barrier of this process, 49.7 kcal/mol with respect to ion 1, likely reflects the significant elongation of the N-O bond, which increases up to 2.788 Å in TS12. The interconversion of the doublet $(N,F,C,O)^+$ structures 1 and 7 occurs through the transition structure TS17 and requires 49.5 kcal/mol with respect to 1. The optimized geometry of this species and the analysis of the eigenvector corresponding to its single imaginary frequency of 419.6*i* cm⁻¹ revealed that this process occurs by the in-plane migration of the fluorine atom, which undergoes a 1,2 shift from the nitrogen to the adjacent carbon atom. We have completed our search for the adiabatic transition structures by locating TS35, which connects isomers 3 and 5 on the quartet $(N,F,C,O)^+$ potential energy surface. As already noted for TS17, the imaginary frequency of TS35, 565.8*i* cm⁻¹, refers to the in-plane 1,2 shift of the fluorine atom which migrates from nitrogen to carbon. The energy barrier for this process is computed as 18.4 kcal/mol with respect to ion 3.

Searching for the MECPs between the relevant energy minima on the doublet and quartet $(N,F,C,O)^+$ potential energy surfaces lead to the location of the three distinct structures MECP1, MECP2, and MECP3. The first one allows the interconversion of isomer 1 on the doublet surface and the loosely bound adduct 5 on the quartet surface. This process occurs by an in-plane 1,2 shift of the fluorine atom which migrates from the nitrogen to the adjacent carbon. The relatively low magnitude of the root mean square value of the SOC matrix elements of MECP1, 14 cm^{-1} , is typical for radicals containing exclusively first- and second-row atoms. We note that MECP1 is practically degenerate with the adiabatic transition structure TS17 and is less stable than isomer 1 by 48.1 kcal/mol. The structure MECP2 allows the interconversion between the isomer 7 on the doublet surface and the isomer 5 on the quartet surface. It is less stable than 1 by 33.1 kcal/mol, and the root mean square of its SOC matrix elements is computed as low as 8 cm^{-1} . We have finally located the structure **MECP3**, which allows the interconversion between isomer 1 on the doublet surface and the analogous isomer 3 on the quartet surface. This process requires 64.6 kcal/mol with respect to 1, and the root mean square of the SOC matrix elements of MECP3 is computed as low as 10 cm^{-1} . We have to mention here that, at variance with MECP1 and MECP2, the characterization of **MECP3** as a minimum energy point on the hyperline of intersection between the doublet and quartet $(N,F,C,O)^+$ potential energy surfaces suffered of the fact that the first eigenvalue of the corresponding generalized Hessian matrix was found to be practically zero. This suggests a rather flat crossing hyperline in the vicinity of **MECP3**.

3.3. The formal F^+ transfer between ${}^2NF^+$ and CO: outline of conceivable mechanistic paths

We are now in the position to make more detailed considerations on the mechanism of the formal F^+ transfer reaction (3) between thermalized ${}^2NF^+$ and CO in the gas phase. In particular, the information gained from the detailed investigation of the relative stability of the various doublet and quartet (N,F,C,O)⁺ isomers and their interconnecting structures can be used to outline the mechanistic routes corresponding to the various potential energy profiles diagramatically shown in Figs. 3–5.

We first note that all the proposed reaction paths share the quite reasonable assumption that, under the isolated conditions typical of gas-phase experiments, the formal F^+ transfer reaction (3) conceivably commences by formation of an encounter complex between ${}^{2}NF^{+}$ and CO on the doublet $(N,F,C,O)^{+}$ potential energy surface. Although we have found that the C-coordinated isomer 1 is more stable than the O-coordinated isomer 2 by more than 42 kcal/mol, we can not safely rule out that the interaction between ²NF⁺ and CO initially leads to the formation of both these isomers of the $(^{2}NF^{+}/CO)$ adduct. In fact, it has been repeatedly demonstrated using several alternative techniques [57,58] that the formation of the less stable O-coordinated isomer of the adduct of a gaseous cation with CO can be kinetically favoured with respect to the more stable C-coordinated isomer. Therefore, the various potential energy profiles shown in Figs. 3-5 have been built so to include as the first step the formation of the less stable adduct 2 and its subsequent isomerization to 1 via the transition structure TS12. Assuming the direct initial formation of the more stable isomer 1 from the ligation of ${}^{2}NF^{+}$ with CO just simplifies the reported diagrams but does



Fig. 3. B3LYP/6-311+G(d) relative energies (0 K) of the (N,F,C,O)⁺ ions and their fragments corresponding to the mechanistic sequence (4) (see text).

not alter the essential aspects of the various conceivable mechanistic routes.

The simplest way to visualize the evolution of the isomer 1 (formed directly or arising from the isomerization of 2 via TS12) on the doublet $(N,F,C,O)^+$ surface into the loosely bound adduct 5 (which eventually undergoes the barrier-free dissociation into the FCO⁺ and ⁴N reaction products) on the quartet surface is schematized in Fig. 3 and corresponds to the following reaction sequence:

$${}^{2}\mathrm{NF}^{+} + \mathrm{CO} \rightarrow \mathbf{2} \tag{4a}$$

$$\mathbf{2} \to [\mathbf{TS12}] \to \mathbf{1} \tag{4b}$$

$$1 \to [\text{MECP1}] \to 5 \tag{4c}$$

$$\mathbf{5} \to \mathrm{FCO}^+ + {}^4\mathrm{N} \tag{4d}$$

The key step of this mechanism is the crossing of the doublet and quartet surfaces in correspondence of the minimum energy crossing point **MECP1**, which directly connects isomers **1** and **5**. The energy required for this process, 48.1 kcal/mol, is significantly high but still lower than the energy gained from the association of ${}^{2}NF^{+}$ and CO with formation of **1**, 60.4 kcal/mol. Nevertheless, the actual possibility of overcoming the activation barrier corresponding to **MECP1** could be severely affected by the relatively low spin–orbit coupling expected to occur in the vicinity of this crossing point.

An alternative route to the evolution of the isomer **1** on the doublet $(N,F,C,O)^+$ surface into the loosely bound adduct **5** on the quartet surface is schematized in Fig. 4 and corresponds to the following reaction sequence:



Fig. 4. B3LYP/6-311+G(d) relative energies (0 K) of the (N,F,C,O)⁺ ions and their fragments corresponding to the mechanistic sequence (5) (see text).



Fig. 5. B3LYP/6-311+G(d) relative energies (0 K) of the (N,F,C,O)⁺ ions and their fragments corresponding to the mechanistic sequence (6) (see text).

- $^{2}\mathrm{NF}^{+} + \mathrm{CO} \rightarrow \mathbf{2}$ (5a)
- $2 \rightarrow [TS12] \rightarrow 1 \tag{5b}$
- $1 \to [TS17] \to 7 \tag{5c}$
- $7 \to [\text{MECP2}] \to 5 \tag{5d}$
- $\mathbf{5} \to \mathrm{FCO}^+ + {}^4\mathrm{N} \tag{5e}$

In this case, the first elementary step following the formation of the $(^{2}NF^{+}/CO)$ adduct 1 consists of its isomerization into the $(^{2}N/FCO^{+})$ adduct 7 via the adiabatic transition structure TS17. The eventual spin-forbidden formation of isomer 5 from isomer 7 occurs by the minimum energy crossing point MECP2. The barrier for the adiabatic step, 49.5 kcal/mol, is lower than the energy gained in the formation of **1** from the association of ²NF⁺ and CO but significantly higher than the energy required to isomer 7 to overcome the barrier corresponding to MECP2. However, as already noted for MECP1, the efficiency of the nonadiabatic process will suffer of the relatively low spin-orbit coupling expected to occur in the vicinity of the crossing point. Therefore, simply by using qualitative arguments, it is difficult to identify the adiabatic or the nonadiabatic processes corresponding to TS17 and MECP2, respectively, as the rate-determining step of the overall mechanistic sequence depicted in Fig. 4.

A third conceivable mechanistic route for the formal F^+ transfer reaction (3) is schematized in Fig. 5 and corresponds to the following sequence of reactions:

$${}^{2}\mathrm{NF}^{+} + \mathrm{CO} \rightarrow \mathbf{2} \tag{6a}$$

$$2 \to [TS12] \to 1 \tag{6b}$$

$$1 \to [\text{MECP3}] \to 3 \tag{6c}$$

$$\mathbf{3} \to [\mathbf{TS35}] \to \mathbf{5} \tag{6d}$$

 $\mathbf{5} \to \mathrm{FCO}^+ + {}^{4}\mathrm{N} \tag{6e}$

In this case, the first step (or the second one, if one assumes the initial formation of ion 2 and its subsequent isomerization into 1 via TS12) is the nonadiabatic conversion via **MECP3** of the isomer 1 on the doublet $(N,F,C,O)^+$ surface into the corresponding analogue isomer 3 on the quartet surface. The latter species undergoes in turn isomerization into the more stable isomer 5 passing through the adiabatic transition structure TS35. The reaction sequence (6) appears indeed as the less plausible among the various proposed one. We first note that the energy required to isomer 1 to overcome the barrier corresponding to **MECP3**, 64.6 kcal/mol, is even higher than the energy gained in the formation of 1 from the association of ${}^{2}NF^{+}$ and CO. Combined with the relatively

low spin–orbit coupling expected to occur in the vicinity of **MECP3**, this makes the barrier for the interconversion of **1** into **3** as likely prohibitively large. In addition, even assuming that a non-negligible fraction of ions **1** is able to interconvert into **3**, the eventual formation of isomer **5** via **TS35** would require to overcome an activation barrier which is \sim 19 kcal/mol higher in energy than the (²NF⁺ + CO) entrance channel. This makes the formation of ⁴N and FCO⁺ from thermalized ²NF⁺ and CO according to sequence (6) a likely unviable process.

To summarize, we can reasonably discard the reaction sequence (6) corresponding to the potential energy profile schematized in Fig. 5 as the detailed mechanism of the formal F^+ transfer reaction (3). However, in the absence of further evidence, we must regard the two sequences (4) and (5) corresponding to the potential energy profiles schematized in Figs. 3 and 4, respectively, as equally plausible mechanistic routes. We feel of interest to mention here that the mechanism of the formal F⁺ transfer reaction (2) between ¹NF₂⁺ and CO, unambiguously ascertained by a joint experimental and theoretical study, was found to be strictly analogue to that schematized in Fig. 4 and corresponding to the reaction sequence (5) for the reaction between ²NF⁺ and CO. Thus, the Ccoordinated adduct initially formed from the addition of ${}^{1}NF_{2}^{+}$ to CO was found to undergo an adiabatic 1.2 shift of the fluorine atom from nitrogen to carbon, with formation of a complex between ¹NF and FCO⁺. The latter species was found to undergo the "spin-forbidden" interconversion into a complex between ³NF and FCO⁺, which eventually dissociates (with no energy barrier) into the observed reaction products ³NF and FCO⁺.

4. Concluding remarks

The transfers of F^+ between monoatomic and simple polyatomic molecules have been repeatedly employed over the last three decades as effective routes to the preparation of novel inorganic ions and several processes like reaction (1) must be legitimately regarded as benchmark reactions in the chemistry of main-group elements. However, probably due

to the complicating interference from the solvent, the counterions, the added catalysts, etc., the detailed mechanistic aspects of reaction (1) are still essentially unexplored. Our recent study on the gas-phase reaction between ${}^{1}NF_{2}^{+}$ and CO provided the first detailed appraisal of the mechanism of a formal F^+ transfer reaction, suggesting that, at least for electron-deficient species, the process conceivably occurs by formation of a complex between the reactants and subsequent 1,2 fluorine migration from an atom to the adjacent one. In addition, the study of reaction (2) allowed us to appreciate the detailed aspects of a spin-forbidden ion-molecule reaction. The present computational results concerning the spin-forbidden reaction between ²NF⁺ and CO confirm a mechanistic path based on the formation of a complex between CO and the electron deficient ²NF⁺, followed by a 1,2 fluorine shift from nitrogen to carbon. The latter elementary step could occur by an adiabatic or a nonadiabatic route, but we can not presently discriminate between these two alternatives. The close similarity with the actually observed reaction (2) and the potential energy profiles depicted in Figs. 3 and 4 suggest that reaction (3) is indeed a viable process in the gas phase, although we can not presently estimate its actual efficiency. Therefore, our present theoretical results could stimulate future mass spectrometric experiments aimed at the observation and detailed investigation of this process as a novel additional example of gas phase spin-forbidden ion-molecule reaction.

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