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Theoretical Study of Complexes and Fluoride Cation Transfer between N_2F^+ and Electron Donors

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A theoretical study of the complexes formed by the N_2F cation (fluorodiazonium ion) and a series of small molecules containing nitrogen atoms have been carried out at the MP2 computational level. In addition, fluorine transfer has been studied. The electron density, NMR shielding and indirect coupling constants of the complexes have been evaluated. The covalent or halogen bonding characteristics of the N···F interactions observed in the complexes are defined by the interatomic distance. It has been determined that the limiting value is 1.6 Å.

Introduction

The study of the structural and electronic characteristics of pre-reactive complexes is now possible, considering the last advances in spectroscopic techniques. These complexes, defined by the IUPAC as “weakly bound complexes with a potential minimum that precedes the activation barrier along the reaction path”, present in many cases interaction properties that are absent in other more common complexes. A very illustrative example corresponds to experimental and theoretical studies of complexes formed by halogen fluorides (FF, FCl, and FBr) that show in their complexes characteristics similar to those of the corresponding hydrogen fluoride.[1−7] This kind of interaction has been named “halogen bond” by analogy to the hydrogen bond.

More recent studies have shown the presence of halogen bonds in a number of cases, as in molecular organization in crystal structures,[8−14] gas-phase complex formation,[15,16] as well as molecular folding and ligand binding.[17,18] In most cases, the halogens involved in the interaction are the two largest ones, bromine and iodine.

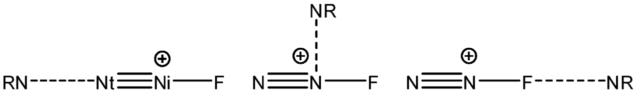
The N_2F^+ is a small system where three electronegative atoms are held together while presenting a net positive charge. It was described for the first time in 1965[19] and spectroscopically characterized.[20,21] The X-ray structure of the $N_2F^+AsF_6^-$ salts shows that N_2F^+ presents the shortest N−F bond known (1.217 Å).[22] It has been used as a precursor of N_5^+ salts[23] and as an electrophilic fluorinating agent.[24] The theoretical studies of this cation have been limited to the characterization of its bonding.[25−27]

In the present article, we will study the complexes formed by the N_2F^+ cation and several systems that present a nitrogen atom that can act as electron donor (Lewis bases). The fluoride transfer process, transition state and final products, have been characterized. The geometry, electron density, harmonic frequencies, NMR shieldings, and indirect coupling constants of the different species obtained in the present work have been analyzed. All these data will provide insight in the intermolecular N−F interactions.

TABLE 1: Comparison of the Interatomic Distances (Å) in the N_2F^+ Cation

	experimental[22]	MP2/6-311++G(2d,2p)	MP2/aug-cc-pVTZ
NN	1.099	1.125	1.125
N−F	1.217	1.243	1.236

SCHEME 1: Configurations of the Complexes Considered[a]



1 **2** **3**

[a] The labels Nt and Ni have been used along the text to differentiate the terminal and inner nitrogen atoms of N_2F^+.

Methods

The geometry of the monomers and complexes have been calculated at the MP2/ 6-311++G(2d,2p)[28,29] computational level within the Gaussian-03 package.[30] The complexes has been confirmed to be energetic minima by frequency calculations at the same computational level. A further optimization has been carried out at the MP2/aug-cc-pVTZ level.[31]

The inherent basis set superposition error (BSSE) in the evaluation of the interaction energy has been corrected with the Boys and Bernardi counterpoise method.[32]

The atomic nuclear shieldings have been obtained with the GIAO methods[33,34] at the MP2/6-311++G(2d,2p) computational level within the Gaussian-03 program.

We have also calculated the four Ramsey[35] contributions to the indirect coupling constant, orbital diamagnetic (DSO), orbital paramagnetic (PSO), spin-dipolar (SD), and Fermi contact (FC). The former two account for the interaction between the nuclear spins and the orbital angular momentum of the electrons, whereas the latter two account respectively for the interaction between the nuclear and electronic spins and the presence of the electronic spins in the nuclear positions.

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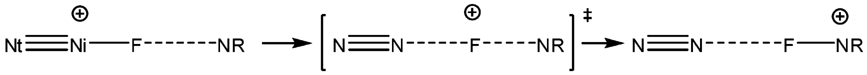
TABLE 2: Intermolecular (Å, deg) Characteristic of the Complexes Studied

	MP2/6-311++G(2d,2p)				MP2/aug-cc-pVTZ			
	1	**2**		**3**	**1**	**2**		**3**
	N···Nt	N···Ni	N,Ni,Nt	F···N	N···Nt	N···Ni	N,Ni,Nt	F···N
N_2	3.075	2.769	98.8	2.667	3.072	2.730	99.0	2.641
NCH	2.838	2.495	102.8	2.449	2.824	2.473	102.9	2.434
NCF	2.827	2.502	102.2	2.452	2.816	2.483	102.1	2.437
NCLi	2.675	1.913	127.2	2.265	2.660	1.915	126.5	2.266
NNO	2.881	2.620	98.7	2.543	2.876	2.588	99.1	2.518
NNS	2.824	2.549	99.5	2.492	2.822	2.524	99.8	2.479
$NNCH_2$	2.801	2.528	101.0	2.483	2.782	2.493	101.4	2.458

SCHEME 2: Fluorine Transfer Reaction



3 **3-TS** **4**

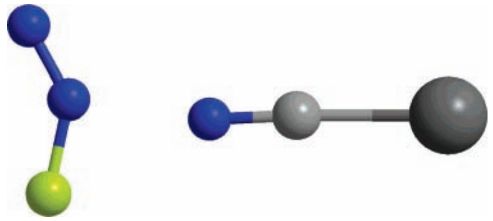


Figure 1. Geometry of the N_2F^+:NCLi complex in configuration **2** obtained at the MP2/aug-cc-pVTZ computational level.

All coupling constants were calculated with the second-order polarization propagator approximation (SOPPA),[36−38] which is based on second-order Møller-Plesset (MP2) perturbation theory. The cc-pVTZ-*J*[39,40] basis set was used. This basis set permits an adequate treatment of the cusp of the wave function at the nucleus and therefore gives a very good description of the FC term. The SOPPA calculations were performed with the Dalton 2 program package.[41]

The electron density of the systems has been characterized with the atoms-in-molecules (AIM) methodology[42] and the AIMPAC[43] programs. The integration within the atomic basins has been carried out trying to obtain a small value of the integrated Laplacian. Previous studies have shown that integrated Laplacian smaller values than 1×10^{-3} in all the atoms of a system lead to small energy and charge errors.[44] In the present article, the largest error in the sum of the atomic energies, when compared to that obtained at the MP2 level, for the whole system is 0.64 kJ/ mol.

Results and Discussion

Geometry and Energy. The isolated N_2F^+ cation presents a linear disposition of its three atoms. The calculated value of the geometrical parameters of the N_2F^+ cation resembles those obtained by X-ray diffraction (Table 1),[22] especially considering the different environment of the theoretical calculations and the experiment.

The present study has been limited to three different dispositions between the N_2F cation and the electron donor systems (Scheme 1). Configurations **1** and **3** present $C_{\infty v}$ symmetry for all the complexes, except for those with diazomethane, N_2CH_2, where they are C_{2v}. The symmetry of **2** is C_s for all the complexes studied. The key of the geometrical features of these complexes are gathered in Table 2.

The results with the two basis sets are very similar, exhibiting the maximum difference in the interatomic distances 0.04 Å, which represents a 1.5% of the value of the corresponding parameter, and less than 1° in the N,Ni,Nt angle of configuration **2**.

TABLE 3: Rotational Constants (MHz) of the Complexes Obtained at the MP2/aug-cc-pVTZ Computational Level

	config. **2**			config. **3**		
complex with	A	B	C	A	B	C
N_2	11246	2554	2082	0	1351	1351
NCH	11305	2851	2277	0	1458	1458
NCF	11277	1307	1171	0	798	798
NCLi	11916	1949	1675	0	1060	1060
NNO	11229	1368	1220	0	828	828
NNS	11254	912	844	0	591	591
$NNCH_2$	10828	1433	1265	272462	856	853

The N_2F^+ geometrical variations are minimal upon complex formation, with the exception of the complex with NCLi in configuration **2**, where an elongation of the Ni−Nt and Ni−F is observed (0.008 and 0.067 Å, respectively) and the Nt−Ni−F angle becomes 140° (Figure 1).

In each series of complexes, the longest interatomic distance corresponds to complexes with N_2, and the shortest is the one with NCLi, an indication that these two systems are the weakest and strongest Lewis basis of the systems chosen in this study. Considering the van der Waals radius proposed by Pauling for N and F (1.55 and 1.35 Å),[45] it should be noted that all the complexes present an intermolecular distance shorter than the sum of the van der Waals radius of the atoms involved.

In microwave spectroscopy, one of the parameters that can easily be compared with the theoretical calculations are the rotational constants. We have reported in Table 3 the rotational constants of the minimum complexes, **2** and **3**.

Energetically, all the complexes in configuration **2** and **3** are minima, while in configuration **1**, only the complex with N_2 is a minimum, and in the rest of the cases, they present two degenerate imaginary frequencies as an indication that they correspond to the TS between the interconversion of **2** with another identical structure. The corrected values of the interaction energy have been gathered in Table 4.

The comparison of the results obtained with the two methods considered here shows that the MP2/aug-cc-pVTZ values are always more negative than the corresponding MP2/6-311++G-(2d,2p) ones, with a relative average difference of about 4.5%. In any case, both methods provide the same qualitative picture of the interactions.

TABLE 4: BSSE Corrected Interaction Energies (kJ/mol) of the Complexes at the MP2/6-311++G(2d,2p) and MP2/aug-cc-pVTZ Computational Levels

	MP2/6-311++G(2d,2p)			MP2/aug-cc-pVTZ		
	1	**2**	**3**	**1**	**2**	**3**
N_2	−7.9	−21.2	−12.6	−8.3	−23.3	−13.6
NCH	−41.8	−83.5	−56.5	−42.7	−87.4	−58.7
NCF	−36.7	−75.3	−50.1	−37.8	−79.6	−52.5
NCLi	−95.2	−203.8	−123.9	−96.6	−208.9	−127.0
NNO	−16.4	−38.5	−23.1	−17.1	−41.4	−24.6
NNS	−22.4	−50.9	−30.4	−22.7	−53.5	−31.6
$NNCH_2$	−28.0	−60.0	−37.6	−29.1	−64.0	−39.8

TABLE 5: Free-Wilson Coefficients (kJ/mol) of the Interaction Energy vs the Configuration and Molecular Parameters

config. **1**	3.9
config. **2**	−39.5
config. **3**	−9.5
N_2	0.0
NCH	−47.9
NCF	−41.6
NCLi	−129.1
NNO	−12.6
NNS	−20.9
$NNCH_2$	−29.2

TABLE 6: Relative Energy (kJ/mol) of 3-TS and 4 with Respect to the Corresponding Structure 3

NR	3-TS	4
N_2	127.63	0.00
NCH	47.34	−180.03
NCF	57.46	−140.66
NCLi	3.72	−356.94
NNO	90.97	−38.17
NNS	42.97	−140.18
$NNCH_2$	a	−342.56

[a] This TS has not been located

TABLE 7: Selected Geometrical Parameters of 3-TS and 4 Calculated at the MP2/6-311++G(2d,2p) Computational Level

	3-TS			**4**	
NR	symm.	Ni⋯F	F⋯N	symm.	Ni⋯F
N_2	D_h	1.656	1.656	C_v	2.667
NCH	C_v	1.480	1.850	C_v	2.767
NCF	C_v	1.504	1.811	C_v	2.757
NCLi	C_v	1.348	2.045	C_v	2.758
NNO	C_s	1.526	1.835	C_s	2.721
NNS	C_s	1.412	2.026	C_s	2.841
$NNCH_2$				C_s	2.894

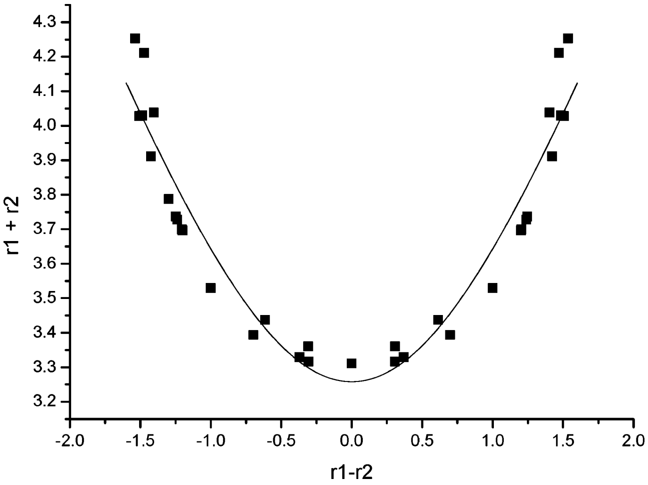


Figure 2. Geometrical relationship of the minima and TS structures involved in the fluorine transfer, **3**, **3-TS**, and **4**. The fitted equation corresponds to eq 3 with an adjusted $r_0 = 1.226$, $b = 0.58$, $R^2 = 0.92$, and the total number of points included 39.

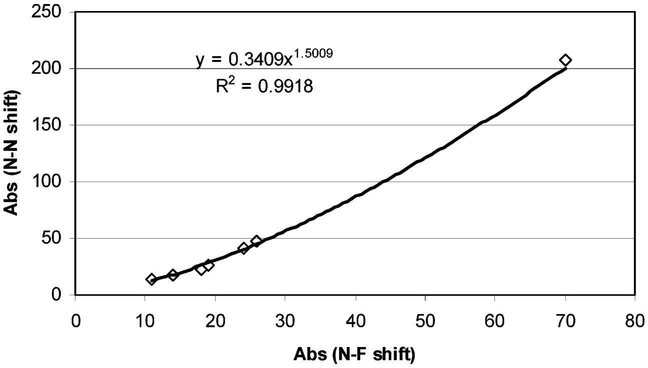


Figure 3. Absolute value of the stretching shift in the N_2F^+ molecule of complexes **3**.

For a given electron donor molecule, the complex in configuration **2** is always stronger than that in configuration **3**, and those in configuration **1**, the weakest ones. Leaving aside the values of configuration **1**, which are not minima for most of the cases, the interaction energy at the MP2/aug-cc-pVTZ computational level ranges between −13.6 to −208.9 kJ/mol. The stronger complex is the N_2F^+:NCLi in configuration **2**, which corresponds to the case where the largest distortion of the N_2F^+ molecule happens (Figure 1). The energetic results obtained for the three configurations considered are highly correlated, which indicates that the interaction energy can be divided as the sum of two contributions, one that corresponds to the configuration itself and the one to the electron donor system. Thus, a Free-Wilson model,[6,46−50] represented by the general eq 1, can be build up using the values obtained at the MP2/aug-cc-pVTZ (Table 4), leading to the coefficients of Table 5, with an R^2 of 0.97. The a_j is the group contribution of the structural feature X in position j in molecule i and μ is the value of a reference or parent compound. The descriptor X_{ij} has a value of 1 if the feature is present in position j in molecule i and 0 in the absence of that feature. The presence and absence of structural elements is indicated by the values 1 and 0, respectively:

$$Y = \Sigma a_j X_{ij} + \mu \tag{1}$$

The coefficients obtained for the configurations are in order of decreasing stability **2** < **3** < **1**, and the basicity of the electron donors decrease in the following order: NCLi≪ NCH < NCF < $NNCH_2$ < NNS < NNO < N_2.

Fluorine Transfer Process. The lability of the N−F bond in the N_2F^+ cation corresponds to its use as fluorinating agent.[24] In the present article, we have studied the barrier of the fluorine transfer between nitrogen atoms starting from the complexes in configuration **3** (Scheme 2).

In all the cases considered, the fluorine transfer is an exothermic process, except for the symmetric N_2F^+:N_2 complex, with TS barriers that range between 127.6 and 3.7 kJ/mol (Table 6). It should be noted that attempts to obtain the complex N_2F^+:NH_3 in configuration **3**, not included in the present work, produce a barrierless F transfer form N_2F^+ to NH_3.

Considering the configurations studied in the present article, **4** is the most stable in all cases, except for the N_2 complex. The difference reaches a maximun value of 321 kJ/mol for the

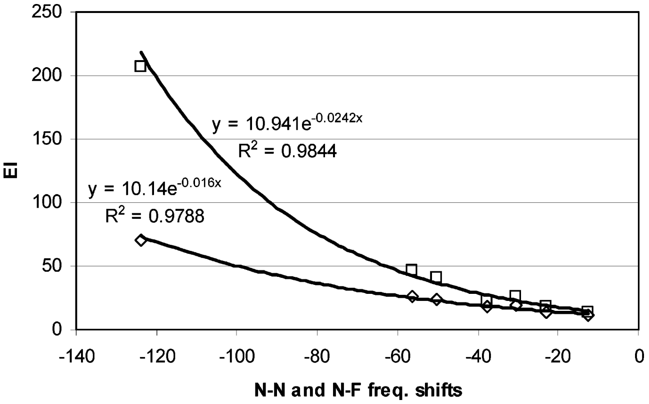


Figure 4. Exponential relationship between the interaction energy (kJ/mol) at the MP2/6-311++G(2d,2p) and the N−N and N−F frequency shifts of the complexes in configuration **3**.

TABLE 8: Calculated Harmonic Frequencies (cm^{-1}) of the Minima Complexes in Configuration 2 and 3

N_2F^+:NR complexes	NN stretching	shift	N−F stretching	shift	NR stretching	shift
			2			
$N_2F\cdots N_2$	2165	5	1081	1	2176	5
$N_2F\cdots NCH$	2169	9	1078	−2	2058	43
$N_2F\cdots NCF$	2169	9	1079	−1	2305	56
$N_2F\cdots NCLi$	2227	67	929	−151	2059	13
$N_2F\cdots NNO$	2169	9	1082	2	2280	101
$N_2F\cdots NNS$	2170	10	1082	2	1820	48
$N_2F\cdots NNCH_2$	2170	10	1081	1	2279	−49
			3			
$N_2F\cdots N_2$	2149	−11	1066	−14	2175	4
$N_2F\cdots NCH$	2134	−26	1033	−47	2046	31
$N_2F\cdots NCF$	2136	−24	1039	−41	2290	41
$N_2F\cdots NCLi$	2090	−70	873	−207	2069	23
$N_2F\cdots NNO$	2146	−14	1062	−18	2249	70
$N_2F\cdots NNS$	2141	−19	1054	−26	1792	20
$N_2F\cdots NNCH_2$	2142	−18	1057	−23	2292	−28

TABLE 9: Variation of the Chemical Shielding (ppm) upon Complex Formation Calculated at the MP2/6-311++G(2d,2p) Level

N_2F^+:NR complexes	ΔNi	ΔNt	ΔF
	2		
$N_2F\cdots N_2$	−0.95	−0.28	−9.65
$N_2F\cdots NCH$	−4.04	−1.99	−29.62
$N_2F\cdots NCF$	−3.81	−1.69	−27.48
$N_2F\cdots NCLi$	−78.74	23.02	−203.43
$N_2F\cdots NNO$	−1.63	−0.35	−13.55
$N_2F\cdots NNS$	−1.85	−0.67	−17.68
$N_2F\cdots NNCH_2$	−2.83	−0.47	−19.82
	3		
$N_2F\cdots N_2$	−1.31	−0.07	−7.90
$N_2F\cdots NCH$	−4.29	−0.16	−14.64
$N_2F\cdots NCF$	−3.92	0.14	−13.44
$N_2F\cdots NCLi$	−9.66	−4.40	−32.82
$N_2F\cdots NNO$	−2.38	0.32	−10.82
$N_2F\cdots NNS$	−3.26	0.31	−14.24
$N_2F\cdots NNCH_2$	−3.45	0.12	−11.86

complex derived from diazomethane, $NNCH_2$, when compared to the energy of configuration **2**.

The geometrical characteristic of the TS structures and complexes in configuration **4** are reported in Table 7. The geometry around the fluorine atom has been analyzed using the bond−valence relationship proposed by Pauling[51,52] that assumes a fix valence for the bonds formed by a given atom along the reaction path. Thus, the total valence of the fluorine atom should be equal to one and can be represented with eq 1, where r_1 and r_2 correspond to the N···F and F···N′ distances in the initial, TS, and final steps of the reaction and r_0 to a reference N−F distance in an isolated case. Equation 2 can be rewritten as eq 3. Thus, in linear systems, $(r_1 + r_2)$ represents the distance between the nitrogen atoms and $(r_1 - r_2)$ the relative position

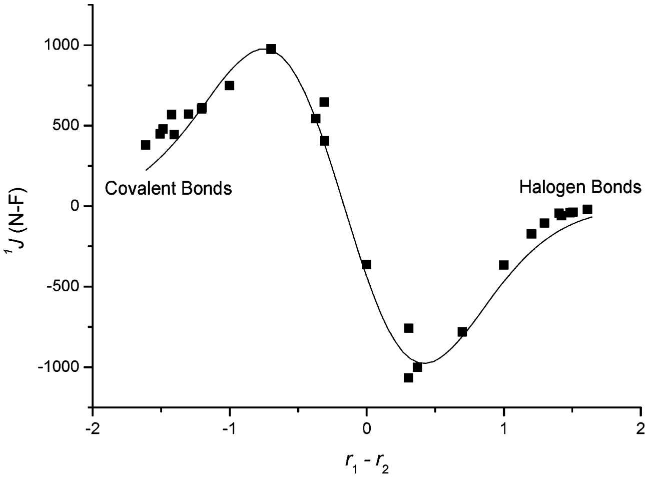


Figure 5. ^1J(N−F) (Hz) vs the $(r_1 - r_2)$ parameter (Å) in the complexes **3**, **3-TS**, and **4**. The fitted curve is the one described in ref 63 and presents a square correlation coefficient of 0.96.

TABLE 10: Experimental and Calculated $J(^{15}N-F)$ Indirect Coupling Constants (Hz) Evaluated with the SOPPA/cc-pVTZ-*J* Computational Level

system	experimental	SOPPA/ cc-pVTZ-J
NF_4^+	323[58]	344.14
NF_3	217[19]	227.97
N_2F^+	$^1J = 459$[19]	$^1J = 553.32$ $^2J = 70.61$
FNNF (trans)	$^1J = +172.8$[59][a] $^2J = -62.8$[59]	$^1J = 196.56$ $^2J = -54.63$
FNNF (cis)	$^1J = +211.0$[59] $^2J = -25.4$[59]	$^1J = 236.37$ $^2J = -13.39$

[a] The "+" in the experimental data indicates that the sign of the coupling constant has been determined.

TABLE 11: Some of the Coupling Constants of the Systems Studied (Hz)

	Ni−Nt	F−Ni	F−Nt	F−N
N_2F^+	−21.64	553.32	70.61	
$N_2F:N_2$ (**2**)	−20.92	548.03	70.04	−12.31
N_2F:NCH (**2**)	−19.48	534.38	68.77	−39.07
N_2F:NCF (**2**)	−19.60	536.29	68.69	−38.49
N_2F:NCLi (**2**)	−14.72	356.57	53.24	−137.36
N_2F:NNO (**2**)	−20.52	545.46	69.34	−21.05
$N_2F:N_2$ (**3**)	−21.34	567.84	69.40	−59.11
N_2F:NCH (**3**)	−20.64	609.87	67.77	−172.34
N_2F:NCF (**3**)	−20.68	602.43	67.57	−174.65
N_2F:NCLi (**3**)	−20.92	748.92	75.89	−365.47
N_2F:NNO (**3**)	−21.23	572.25	68.88	−105.41
$N_2F:N_2$ (**3-TS**)	−13.63	−362.38	41.41	−362.38
N_2F:NCH (**3-TS**)	−20.57	541.99	64.22	−1001.33
N_2F:NCF (**3-TS**)	−19.49	403.70	59.33	−1065.74
N_2F:NCLi (**3-TS**)	−23.91	974.14	93.77	−780.70
N_2F:NNO (**3-TS**)	−18.69	644.86	50.52	−757.70
N_2:FNCH (**4**)	−6.51	−37.32	−1.29	447.96
N_2:FNCF (**4**)	−6.51	−39.80	−1.28	478.24
N_2:FNCLi (**4**)	−6.52	−22.06	−0.95	379.33
N_2:FNNO (**4**)	−6.53	−45.53	−1.16	444.10

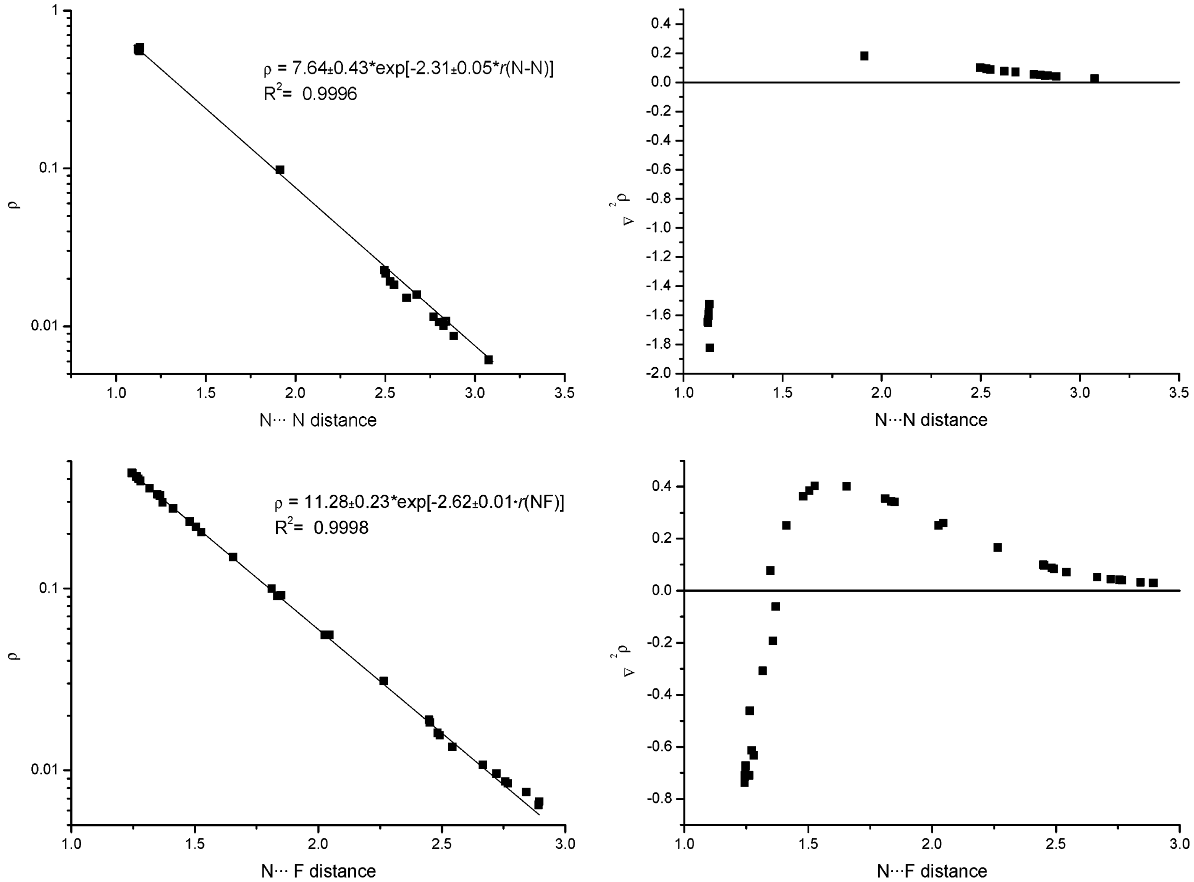


Figure 6. Electron density and Laplacian (au) in the N···N and N···F bond critical point vs the interatomic distance (Å).

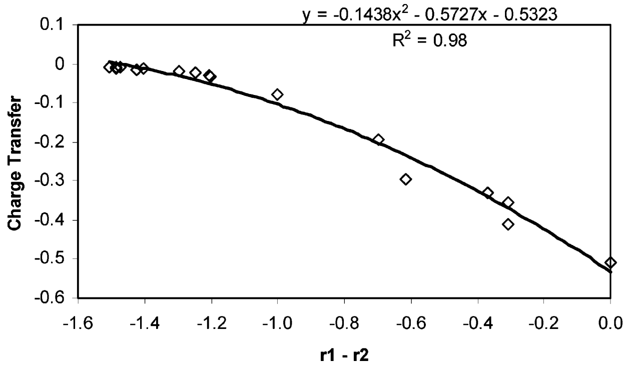


Figure 7. Charge Transfer vs ($r_1 - r_2$) for the complexes **3**, **3-TS**, and **4**. r_1 corresponds to the distance from the electron acceptor molecule to the fluorine atom.

of the fluorine atom between the two nitrogens. Since the values of r_1 and r_2 can be interchanged, the resulting curve is symmetrical about ($r_1 - r_2$) = 0. The results (Figure 2) show that in the present case, this relationship is not able to fit perfectly the geometrical results in contrast with hydrogen-bonded systems where it has been widely applied.[53-57] This could be an indication that in these complexes the fluorine atoms can partially adopt some kind of hypervalent structure which is not possible in the HB complexes due to the electronic nakedness of the hydrogen atom:

$$e^{r_0 - r_1/b} + e^{r_0 - r_2/b} = 1 \qquad (2)$$

$$(r_1 + r_2) = 2r_0 + (r_1 - r_2) + 2b\ln(1 + e^{(-r_1 + r_2)/b}) \qquad (3)$$

Harmonic Frequencies. The harmonic frequencies of the minima complexes **2** and **3** have been collected in Table 8, but in order to simplify the discussion, only the ones corresponding to the N_2F^+ molecule, and the one of the NR bond has been considered.

For complexes **2**, the results show small variations for the stretching frequencies of the N_2F^+, except in the N_2F:NCLi case; as mentioned previously, this system suffered important geometrical changes (Figure 1). In the mentioned complex, the N−N stretching frequency shows a red shift of 67 cm^{-1} and the N−F a blue one of 151 cm^{-1}, even though in both cases a lengthening of the bonds is observed. The NR stretching frequency shift is always positive, except in the diazomethane complex.

In complexes **3**, both the N−N and N−F stretching of N_2F^+ become red-shifted, and the values are correlated for each complex as shown in Figure 3. Both parameters are exponentially related to the interaction energy of the complexes (Figure 4). In addition, linear relationships have been found between the frequency shifts and the distance variation upon complex formation.

NMR. The variations of the calculated chemical shieldings in the N_2F^+ system upon complex formation are collected in Table 9. In the two minima configuration, **2** and **3**, the largest variation for a given complex corresponds to the fluorine atom due to its NMR sensitivity. In contrast to what is expected, the variation of the chemical shielding of F is larger for a given complex in configuration **2** than in **3**, and the opposite happens for Ni. In both configurations, a linear correlation was found between the variation of Ni and F chemical shieldings. Since the slope of these relationships is very different, it can be used to differentiate the formation of one or the other type of complex.

For the study of the indirect coupling constants, *J*, initially, a series of related compounds for which the experimental

TABLE 12: Volume Variation (au) of the Complexes vs the Sum of the Isolated Molecules[a]

	1		**2**		**3**		**3-TS**		4[b]
	complex	N_2F^+	complex	N_2F^+	complex	N_2F^+	complex	N_2F^+	complex
N_2	−0.7	0.5	−10.3	−1.8	−5.6	−0.2	−24.1	24.1	
HCN	−7.8	−1.1	−24.3	−4.1	−13.6	0.3	−28.9	14.2	−3.43
FCN	−6.7	−1.1	−22.9	−4.0	−11.1	0.6	−27.7	16.0	−3.89
LiCN	−14.7	−2.0	−54.2	6.1	−23.4	0.2	−30.7	7.0	−1.27
NNO	−3.8	−0.9	−15.1	−3.0	−7.9	−0.4	−20.3	18.5	−5.27
NNS	−7.9	−0.4	−22.8	−3.6	−13.0	−0.1	−26.7	13.0	−3.37

[a] The variation of the N_2F^+ molecules is included. [b] The volume variation of the complexes in configuration **4** is with respect to the N_2 and FNR+ isolated molecules.

TABLE 13: Energy Variation of the N_2F^+ (kJ/mol) upon Complex Formation[a]

	1		**2**		**3**		**3-TS**	
	N_2F^+	F	N_2F^+	F	N_2F^+	F	N_2F^+	F
N_2	189.81	90.78	168.18	74.66	183.10	103.25	−283.85	460.40
HCN	152.88	77.00	112.41	33.58	138.35	121.28	−80.30	410.12
FCN	130.71	67.27	96.10	27.65	124.53	109.12	−123.26	417.35
LiCN	103.85	55.68	−208.30	−132.75	71.70	168.50	0.11	297.70
NNO	153.81	75.80	126.00	52.12	148.13	96.33	−176.42	336.09
NNS	356.85	173.73	320.95	141.21	351.32	202.25	157.86	365.68

[a] The energy variation of the F atom is included.

TABLE 14: Charge Transfer (e) in the Complexes Studied

	1	**2**	**3**	**3-TS**	4[b]
N2	−0.0043	−0.0182	−0.0157	−0.5078	
HCN	−0.0107	−0.0466	−0.0330	−0.3293	0.010
FCN	−0.0102	−0.0429	−0.0305	−0.3558	0.011
LiCN	−0.0233	−0.4156	−0.0776	−0.1952	0.007
NNO	−0.0070	−0.0247	−0.0186	−0.4098	0.013
NNS	−0.0101	−0.0333	−0.0239	−0.2961	0.009

[a] This value corresponds to the charge of the N_2 molecule.

coupling constants, where available, have been calculated. The results gathered in Table 10 show a good agreement between the calculated and experimental data, except for the N_2F^+ system. It should be noted that the experimental data are obtained for this case in liquid FH solution of the $N_2F^+{\cdot}AsF_6^-$ salt, while the calculations considered only the isolated cation in vacuum.

Some of the coupling constants of the N_2F^+ complexes have been reported in Table 11. All the intra- and intermolecular couplings but the ^2J(F−Nt) ones are dominated by the FC contribution. The ^2J(F−Nt) couplings, however, have a PSO contribution as large as the FC ones in conformations **2** and **3**, and even larger than the FC for conformations **3-TS**.

The fact that some complexes, in their **3-TS** configurations, show a pattern of contributions for the coupling between F and the last nucleus of the coupled molecule with a PSO term larger than or comparable to the FC one (such is the case of N_2F^+:N_2, N_2F^+:NCF and N_2F^+:NNO), would indicate that there already is a conjugation of their π systems, with the possibility of producing, at least, a partial electron electron transfer. Such a pattern (PSO term larger than or comparable to the FC one) is a norm for configurations **4**.

The intramolecular couplings of the N_2F^+ fragment in Table 11 (Ni−Nt, F−Ni, and F−Nt) differ considerably from those of the monomer in the case of the N_2F^+:NCLi complex (conformations **2** and **3**). The ratios with regard to the values of the monomer are in most complexes close to 1; for instance, for N_2F^+:N_2 (**2**) the ratio is $-20.92/-21.64 = 0.967$ (Ni−Nt). The only exception is the N_2F^+:NCLi complex in both conformations, where the ratios are close to 0.7 in the conformation **2** and slightly larger than 1 in conformation **3**. Concerning the transition state **3-TS** the situation is different because not only the N_2F^+:NCLi complex but the N_2F^+:N_2 one is markedly different from the remaining ones.

Another important finding is that the Dirac vector model, which establishes that the sign of the ^1J(X−Y) should be positive, is not fulfilled by ^1J(Ni−Nt) couplings which show negative values. In the case of the N−F coupling constants, both positive and negative values are obtained. The negative values are present in those complexes in which the F−N distances are longer than ∼1.6 Å, whereas for shorter distances the positive sign is present. Thus, all the ^1J(F−Nr) of **2**, **3** and **3-TS**, as well as, ^1J(F−Ni) and ^2J(F−Nt) of **4** are negative. This fact may indicate the transition from covalent (positive sign) to halogen-bond (negative sign). A representation of the ^1J(F−N) of complexes **3**, **3-TS** and **4** versus the $(r_1 - r_2)$ parameter shows a similar curve to the one already described by Limbach et al. between the derivatives of eq 2 and a number of NMR parameters (Figure 5).[60−64]

AIM. The topological analysis of the complexes presents an intermolecular bond critical point (bcp) between the nitrogen atom of the NR molecule and the Nt, Ni and F of N_2F^+ in complexes **1**, **2**, and **3**, respectively. Finally, the structures obtained in the fluorine transfer process show a similar pattern with the fluorine atom involved in two bcps. The analysis of the N−N bcp's, shows two different kind of interactions, a covalent one, with large values of ρ and negative laplacian and those of weak interactions with small values of ρ and positive laplacian. In the case of the N−F bcps, the study of the TS structures has provided a continuous distribution of points from short covalent N−F bonds to weak interactions. The values of ρ in this two bcps have been fitted with a unique exponential equation for the whole range of distances (Figure 6), in agreement with previous reports that have shown similar relationship for other bonds, specially those involved in HB's.[56,65−68] Regarding the evolution of the Laplacian, the N−F profile shows the evolution from the negative values to the positive ones, going through a maximum approximately at 1.6 Å that has been used to differentiate the closed-shell and open-

TABLE 15: Charge (e) in the Atoms of the N_2F^+ Molecule Complex Formation

	1		2		3		3-TS	
	N_2	F	N_2	F	N_2	F	N_2	F
N_2	1.0213	−0.0256	1.0137	−0.0318	1.0054	−0.0211	0.5078	−0.0157
HCN	1.0242	−0.0349	0.9981	−0.0447	0.9756	−0.0086	0.6785	−0.0078
FCN	1.0239	−0.0341	1.0004	−0.0432	0.9792	−0.0097	0.6522	−0.0081
LiCN	1.0252	−0.0485	0.7351	−0.1507	0.9136	0.0088	0.7933	0.0115
NNO	1.0222	−0.0292	1.0107	−0.0355	0.9980	−0.0166	0.6484	−0.0583
NNS	1.0214	−0.0315	1.0065	−0.0398	0.9901	−0.0141	0.7527	−0.0488

shell regions in hydrogen-bonded systems.[68] Significantly, the 1.6 Å distance in the N−F interactions have been shown to define the sign of the coupling constant and consequently the characteristics of the bond.

The atomic integration within the AIM methodology allows analyzing the flow of atomic properties due to the complex formation. In the present article, the volume, energy, and charge variations have been studied.

A volume reduction upon complexation is observed in all the cases (Table 12). The volume variation of both monomers upon complex formation is negative, except for the $N_2F{:}N_2$ in conformation **1**, where the volume of the N_2F^+ molecule is slightly larger than isolated. In addition, the electron donor system loses more volume than the N_2F^+ one in all the cases. In the case of complexes in configuration **4**, the total volume has been compared to the N_2 and FNR^+ molecules. As expected for the small interaction of those complexes, the volume variation is also small.

The molecular contribution to the energetic variation is gathered in Table 13. In all the complexes, the N_2F^+ loses energy when compared to the isolated molecule, except in the $N_2F{:}NCLi$ in configuration **2**. The energy lost in the N_2F+ is redistributed along all the atoms of the molecule, and thus, approximately half of the variation is due to the F atom.

In the TS structures, the N_2F^+ gains energy since part of the positive charge is transferred to the NR molecule, while the fluorine atoms present an important energetic loss.

Regarding the charge variations, as expected, the positively charge molecules retrieve some electron density from the neutral one. The values of the charge transfer are gathered in Table 14. The representation of the charge transfer versus the $(r_1 - r_2)$ parameter around the fluorine atom, in complexes **3**, **3-TS**, and **4** presents a second-order polynomial relationship in the cases studied (Figure 7).

The charges obtained with the AIM method for the atoms of N_2F^+ system have been separated in the N_2 fragment and in the F atom (Table 15). In the isolated N_2F^+ cation, the N_2 fragment possesses a 1.022 positive charge, while the fluorine is negatively charged 0.022 e. In almost all the complexes the F atom is almost neutral with a small negative charge. The positive charge is located in the rest of the molecule bonded to the F atom. Thus, in the TS structure the charge is shared by the two molecules. Based on these results, the fluorine transferred can be considered as in its neutral form.

Conclusion

A theoretical study of the pre-reactive complexes formed by N_2F^+ with a series of molecules with a nitrogen atom that acts as electron donor has been carried out at the MP2/6-311++G(2d,2p) and MP2/aug-cc-pVTZ computational levels. In addition, the fluorine transfer between the interacting molecules has been characterized. Several spectroscopic properties of the systems have been studied, such as rotational constants, harmonic frequencies, NMR chemical shifts and indirect coupling constants as well as electron density.

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