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International Journal of Mass Spectrometry 216 (2002) 285–299

International Journal of Mass Spectrometry

www.elsevier.com/locate/ijms

Adducts of NF_2^+ with diatomic and simple polyatomic ligands: a computational investigation on the structure, stability, and thermochemistry

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Received 8 February 2002; accepted 8 March 2002

Abstract

The structure, stability, and thermochemistry of all the gaseous NF_2^+–(L) adducts which have been experimentally investigated to date by mass spectrometric techniques, including L = HF, HCl, H_2O, CO, CO_2, N_2O, and NF_3, have been computationally studied by high-level of theory ab initio and DFT calculations. The investigation has been also extended to the still unexplored adducts of NF_2^+ with H_2S, NH_3, and PH_3. The geometries of all the investigated species have been optimised at the B3LYP/6-31G(d) level of theory, and accurate total energies have been obtained using the G2MS procedure. It has been possible to build up a theoretical scale of difluoronitrenium ion affinity (DFNA) and difluoronitrenium ion basicity (DFNB), defined here as the minus enthalpy and free energy changes, respectively, of the association of NF_2^+ to L with formation of the NF_2^+–(L) adduct. The calculated values (kcal mol^{-1}) of DFNA, 10.1 (L = HF), 10.7 (L = CO_2), 17.0 kcal mol^{-1} (L = NF_3), 17.5 (L = N_2O), 20.7 (L = HCl), 25.0 (L = CO), 33.1 (L = H_2O), 57.6 (L = H_2S), 78.0 (L = NH_3), and 84.7 (L = PH_3), demonstrate the occurrence of periodic trends in the stability of the NF_2^+–(L) adducts. In addition, reasonably good correlations have been found between the DFNA and the proton affinity (PA) and the DFNB and the gas-phase basicity (GB) of the presently investigated ligands. (Int J Mass Spectrom 216 (2002) 285–299) © 2002 Elsevier Science B.V. All rights reserved.

Keywords: DFT; G2MS theory; NF_2^+ cation; Nitrogen trifluoride

1. Introduction

Nitrogen trifluoride, NF_3, is one of the gaseous compounds most extensively used in the electronic industry to perform etching and cleaning processes by plasma techniques [1–5]. With respect to more traditional fluorinated gases, such as CF_4 and C_2F_6, NF_3 offers advantages of shorter atmospheric lifetime and avoidance of carbon contamination residues. In addition, it boosts productivity by >30% while decreases effluent emissions by 90% [6,7]. As a matter of fact, in the last few years, the industrial demand of NF_3 has increased to such an extent that several leading companies have planned or already completed significant capacity expansions in the production and distribution of this substance [8,9].

During the industrial processes, pure or diluted (for example, with helium, argon, or oxygen) NF_3 is dissociated, usually by microwave discharge, to generate the chemically active fluorine atoms. However, a

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1387-3806/02/$ – see front matter
PII S1387-3806(02)00628-0

variety of ionic species, including NF_x^+ ($x = 1$–3), FN_2^+, and NO_x^+ ($x = 1, 2$) are also formed [10], and their conceivable contribution to etching and cleaning is the focus of sustained experimental [11–13] and theoretical [14,15] interest. In particular, the results of these studies point to the difluoronitrenium ion, NF_2^+, as one of the most important ionic fragments able to affect the quality and the yield of the NF_3-based industrial processes. The important role of NF_2^+ in the NF_3-based plasmas is consistent with the current knowledge we have on the gas-phase chemistry of ionised NF_3 and NF_3-based mixtures. Thus, the NF_2^+ cation is the most abundant ionic fragment usually detected from the electron impact [16–18], photon impact [19,20], or charge exchange [21] dissociation of pure NF_3. In addition, the results reported to date by the various research groups which have focused interest on the reactions commenced by the ionisation of NF_3 [22] or mixtures of NF_3 and gaseous compounds such as CH_4 [23], CH_4 and H_2 [23,24], H_2O [25–27], HN_3 [28], H_2N–CN [29], CO [30,31], and N_2O [32], clearly indicate that the reactions involving NF_2^+ play a crucial role in this chemistry. Exemplary processes include the activation of the robust CH_4 [23] and H_2O [26,27], the formal F^+ transfer to CO [30,31], the fixation of inert ligands such as CO_2 [23], and a number of ligand-displacement reactions [22,23]. All these processes involve the intermediacy or the eventual formation of an adduct between NF_2^+ and a diatomic or a simple polyatomic ligand L, and the NF_2^+–(L) complexes must be indeed regarded as key species in the chemistry of ionised mixtures containing NF_3. As part of our continuing interest in this subject [24–32], we decided to undertake a comparative study, at the G2MS level of theory [33], on the structure, stability, and thermochemistry of all the adducts of NF_2^+ which have been experimentally observed to date. The information we have on these species is in fact significantly different. The adducts of NF_2^+ with HCl and CO_2 have been observed in the gas phase under low-pressure conditions [23], but neither experiments nor theoretical calculations have been performed to date to disclose their detailed structure and stability. On the contrary, certain NF_2^+–(L) adducts, including L = HF [22–24], H_2O [27], CO [30,31], N_2O [32], and NF_3 [22] have been experimentally investigated in considerable detail and also studied by ab initio calculations. However, different levels of theory have been employed, which prevents direct comparison. We decided also to extend the investigation to the still unexplored adducts of NF_2^+ with H_2S, NH_3, and PH_3. From the fundamental point of view, these ligands have been selected so to appreciate the conceivable occurrence of periodic trends in the structure, stability, and thermochemistry of the simplest NF_2^+–(L) adducts. As a matter of fact, our computational results are the probably first systematic investigation of the effect of the ligand L on the Lewis acidity of a simple nitrenium ion. The theoretical information reported in the present article could reveal of future interest in the discussion of still unexplored features of the gas-phase ion chemistry of mixtures containing NF_3.

2. Computational details

All the presently reported calculations have been performed using the Unix versions of the GAUSSIAN 98 [34] and the MOLPRO 2000.1[1] sets of programs installed on a Alphaserver 1200 and a DS20E Compaq machine.

The 298.15 K total energies of our investigated molecules and ions have been calculated using the G2MS method [33]. We have already employed this composite procedure to investigate the gas-phase methylation of NF_3 [35] and the gas-phase protonation of NF_3O [36], and we have found that, for the species involved in these processes, the G2MS method is able to achieve the so-called "chemical accuracy" of ca. 1–2 kcal mol^{-1} [37] in the reproduction of known thermochemical quantities. Within

[1] MOLPRO is a package of ab initio programs written by H.-J. Werner and P.J. Knowles, with contributions from R.D. Amos, A. Bernhadsson, A. Berning, P. Celani, D.L. Cooper, M.J.O. Deegan, A.J. Dobbyn, F. Eckert, C. Hampel, G. Hetzer, T. Korona, R. Lindh, A.W. Lloyd, S.J. McNicholas, F.R. Manby, W. Meyer, M.E. Mura, A. Nicklass, P. Palmieri, R. Pitzer, G. Rauhut, M. Schatz, H. Stoll, A.J. Stone, R. Tarroni, T. Thorsteinsson.

the G2MS theory, the equilibrium geometry of a species, obtained at the density functional level of theory [38] using the B3LYP functional [39–41] in conjunction with the 6-31G(d) basis set, is used to perform single-point calculations at the Coupled Cluster level of theory, including the effect of connected triples, CCSD(T) [42,43], and at the second-order Møller–Plesset level of theory [44], in conjunction with the 6-311 + G(2df,2p) basis set. The obtained values furnish a combined energy, E_c (G2MS), according to the expression

$$E_c(\text{G2MS}) = E[\text{CCSD(T)/6-31G(d)}] + E[\text{MP2/6-311 + G(2df, 2p)}] - E[\text{MP2/6-31G(d)}]$$

The CCSD(T)/6-31G(d) calculation forms the basis of the energy expression, and the two MP2 calculations correct for the basis set effects. All the single-point calculations include the valence electrons only (the frozen-core approximation) and the 6-311 + G(2df,2p) basis set is used with six d-type and 10 f-type functions. The value of E_c(G2MS) is subsequently corrected by adding two terms. The first one is a higher-level correction, HLC(G2MS), calculated according to the expression

$$\text{HLC(G2MS)} = -0.19n_\alpha - 5.78n_\beta$$

where n_α and n_β are the number of α and β valence electrons, respectively ($n_\alpha \geq n_\beta$), and the second one is the zero-point energy correction, ZPE, obtained using the unscaled B3LYP/6-31G(d) harmonic frequencies. The G2MS energy at 0 K obtained according to the expression

$$\text{G2MS(0 K)} = E_c(\text{G2MS}) + \text{HLC(G2MS)} + \text{ZPE}$$

is finally corrected at 298.15 K, G2MS (298.15 K), by adding the translational (3/2 RT), rotational (RT or 3/2 RT for linear and non-linear species, respectively), and vibrational contributions at this temperature. The last term is calculated using standard statistical mechanics formulas [45] using the B3LYP/6-31G(d) frequencies. According to the free-rotor approximation, the thermal contribution from vibrational frequencies less than 260 cm^{-1} has been evaluated as 1/2 RT [46]. The total entropies have been calculated using the B3LYP/6-31G(d) harmonic frequencies and moments of inertia.

3. Results and discussion

3.1. Structure, stability, and thermochemistry of gaseous NF_2^+

The structure of NF_2^+ and the relative stability of its various electronic states have not yet been determined experimentally, and the information we have comes from the results of the various ab initio calculations which have been performed over the years on this species [22,23,35,47–53]. The first important conclusion from these studies is that the difluoronitrenium ion has a singlet ground state $^1A_1$ which is more stable than the first excited triplet state $^3B_1$ by ca. 50 kcal mol^{-1}. The most accurate estimate of this singlet–triplet gap, 2.214 eV, has been obtained as part of a MR-SD-CI investigation of seven low-lying electronic states of the NF_2^+ cation [50]. The study of the electronic structure of NF_2^+, based on the topological analysis of the MP2/6-31G(d) electronic wavefunction [23,49], indicates that both the HOMO and the LUMO orbitals have significant contributions from N-centred 2p orbitals. In addition, the nitrogen atom carries a positive partial charge of +1.164. Both of these features point to NF_2^+ as a strong nitrogen-centred gaseous electrophile, prone to undergo addition and insertion reactions rather than, for example, radical abstractions. This suggestion is indeed in line with the experimentally observed and theoretically predicted behaviour of NF_2^+ as a gaseous Lewis acid (vide infra).

The geometric structure of NF_2^+, in its various electronic states, has been as well investigated by theoretical calculations [22,23,35,47–53]. We simply note here that, at the MR-SD-CI computational level, the $^1A_1$ ground state is predicted to be a bent structure of C_{2v} symmetry, with a N–F bond length of 1.242 Å and a F–N–F bond angle of 108.0° [50]. Our B3LYP/6-31G(d) optimised parameters, 1.259 Å and

107.6°, are in good agreement with these previously computed values.

The thermochemistry of NF_2^+ deserves comment. The quoted [54] enthalpy of formation of this species at 298 K, 275 kcal mol^{-1}, is based on the direct measurement of the adiabatic ionisation potential (IP) of the NF_2 radical, so far obtained as 11.62 ± 0.02 eV [55] and subsequently refined as 11.63 ± 0.01 eV [56]. The enthalpy of formation of NF_2^+ at 298 K can be also obtained using its appearance potential (AP) from the ionisation of NF_3. This AP has been so far measured as 14.12 ± 0.01 eV [57], 14.10 eV [20], and 14.04 ± 0.01 eV [56]. Combined with the enthalpies of formation (thermochemical data are taken from [58]) of F, 19.0 kcal mol^{-1}, and NF_3, −31.6 kcal mol^{-1}, theses values furnish enthalpies of formation of NF_2^+ at 298 K of 275, 274.5, and 273.2 kcal mol^{-1}, respectively, which are in good agreement with the value derived from the adiabatic IP of the NF_2 radical. They are also consistent with two recent accurate theoretical estimates of 277.76 [52] and 277.3 ± 0.9 kcal mol^{-1} [53]. Therefore, in the present work, we will use the value of 275 kcal mol^{-1} for the experimental enthalpy of formation of NF_2^+ at 298 K. However, it is to be mentioned here that the AP of NF_2^+ from NF_3 has been also measured as 13.71 ± 0.02 eV [18], which reduces the enthalpy of formation of the ion to 265.6 kcal mol^{-1}. Due to the discrepancy with all the other experimental and theoretical values, we are inclined to take this value with caution. Nevertheless, it suggests that the AP of NF_2^+ from NF_3 should be probably experimentally investigated in greater detail.

3.2. Adducts of gaseous NF_2^+ with diatomic and polyatomic ligands

The B3LYP/6-31G(d) optimised geometries of the adducts between NF_2^+ and HF, HCl, H_2O, H_2S, NH_3, and PH_3, henceforth indicated as **1**, **2**, **3**, **4**, **5**, and **6** are shown in Fig. 1, and those of the adducts between NF_2^+ and CO, CO_2, N_2O, and NF_3, henceforth indicated as **7**, **8**, **9**, and **10** are shown in Fig. 2.

The G2MS total energies at 298.15 K of all the adducts **1**–**10** and their total entropies *S* calculated from B3LYP/6-31G(d) harmonic frequencies and moments of inertia at 298.15 K are collected in Table 1. We have also calculated the G2MS total energies and entropies at 298.15 K of all the presently investigated ligands L and of their protonated forms, and the obtained values are listed in Table 2.

If one defines the difluoronitrenium ion affinity (DFNA) and the difluoronitrenium ion basicity (DFNB) of a ligand L as the minus enthalpy and free energy change, respectively, at 298.15 K, of the reaction

$$NF_2^+ + L \rightarrow NF_2^+\text{–(L)} \quad (1)$$

the energy and entropy data of Tables 1 and 2, corrected for the *pV* contribution, furnish the values of DFNA and DFNB reported in Table 3. We have also reported there the theoretical proton affinities (PAs) and gas-phase basicities (GBs) of the ligands L, calculated at 298.15 K using the G2MS total energies and entropies of Table 2 and assuming the total entropy of H^+ as 26.040 cal mol^{-1} K^{-1}.

Table 1
G2MS (298.15 K) total energies (a.u.) and entropies (*S*, cal mol^{-1} K^{-1}) of the presently investigated adducts of NF_2^+

Species[a]	G2MS (298.15 K)	S^b
1a (0)	−353.95058	70.5
1b (1)	−353.94861	69.0
2a (0)	−713.95055	76.2
2b (0)	−713.94816	74.9
3a (0)	−329.96818	70.6
3b (1)	−329.96306	67.4
4a (0)	−652.60036	73.2
4b (1)	−652.59618	70.3
5a (0)	−310.16473	67.4
5b (1)	−310.16205	65.5
6a (0)	−596.39167	72.1
6b (1)	−596.38781	69.5
7a (0)	−366.80083	70.5
7b (0)	−366.76912	78.9
8 (0)	−441.96095	82.1
9a (0)	−438.05210	81.7
9b (0)	−438.04287	82.0
10a (0)	−607.35039	87.4
10b (0)	−607.33065	90.8

[a] The number of imaginary frequencies is given in parenthesis.
[b] From B3LYP/6-31G(d) harmonic frequencies and moments of inertia and at 298.15 K.

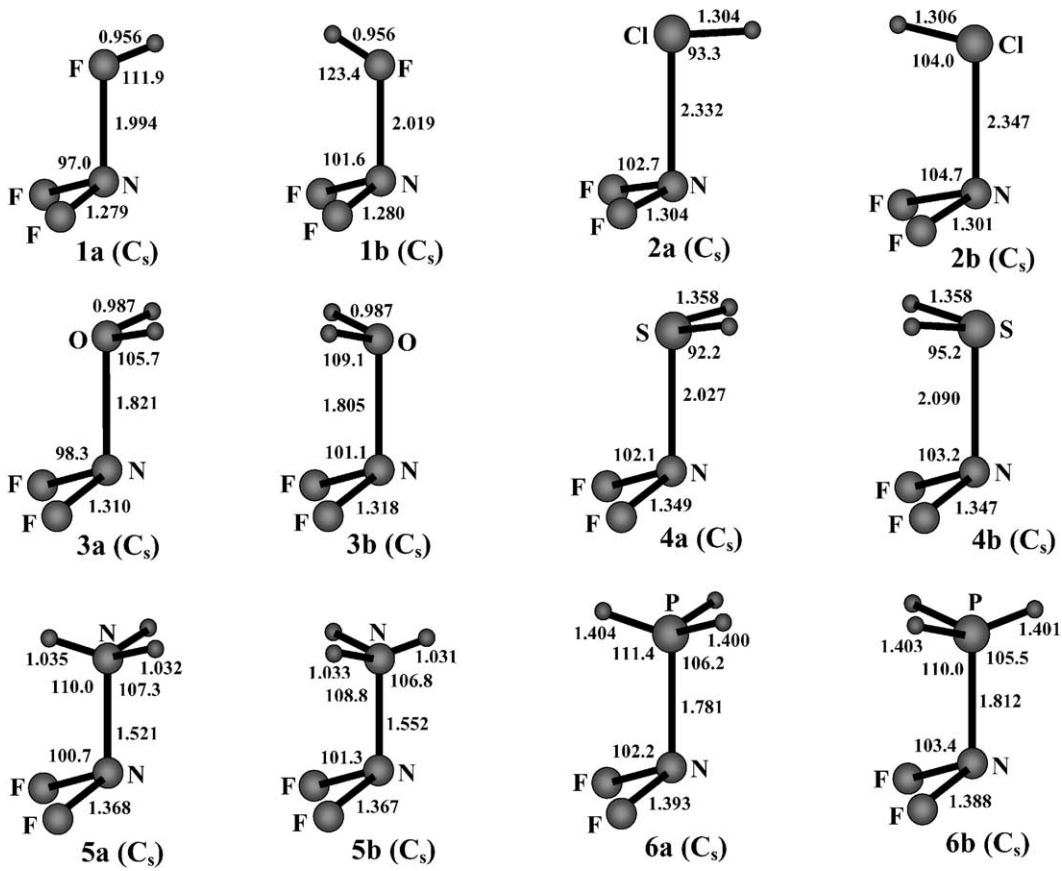

Fig. 1. B3LYP optimised geometries (Å and °) of the adducts of NF_2^+ with HF, HCl, H_2O, H_2S, NH_3, and PH_3 (unlabelled circles are hydrogen atoms).

The corresponding experimental values have been taken from the recent compilation by Hunter and Lias [59].

The adduct of NF_2^+ with HF plays a crucial role in the gas-phase ion chemistry of NF_3. In fact, as firstly suggested by Fisher and McMahon [23], and subsequently confirmed by Schwarz and co-workers [24] the gas-phase protonation of NF_3 occurs preferentially at the fluorine atom and the most stable $(NF_3)H^+$ isomer is indeed a loosely bound complex between NF_2^+ and HF. This conclusion, based on the results of collisionally activated dissociation (CAD) and mass-analysed ion kinetic energy (MIKE) experiments [24], as well as on the study of the reactivity of $(NF_3)H^+$ under ICR conditions [23], has been invariably confirmed by the results of high-level of theory ab initio and DFT calculations [22–24,35]. The NF_2^+–(HF) ion–dipole complex **1a** of C_s symmetry reported in Fig. 1 is in fact invariably predicted to be more stable than the H–NF_3^+ isomer. In particular, at the G2MS level of theory, the energy difference is computed as 2.1 kcal mol^{-1}. The B3LYP/6-31G(d) optimised parameters of **1a** are in very good agreement with previous HF/6-31G(d,p) [23] and MP2/6-31G(d,p) [22] structural data. The novel finding we report here is the location of the conformer **1b**, whose optimised structure is again consistent with an ion–dipole complex between NF_2^+ and HF. However, at variance with **1a**, characterised as a true energy minimum on the B3LYP/6-31G(d) poten-

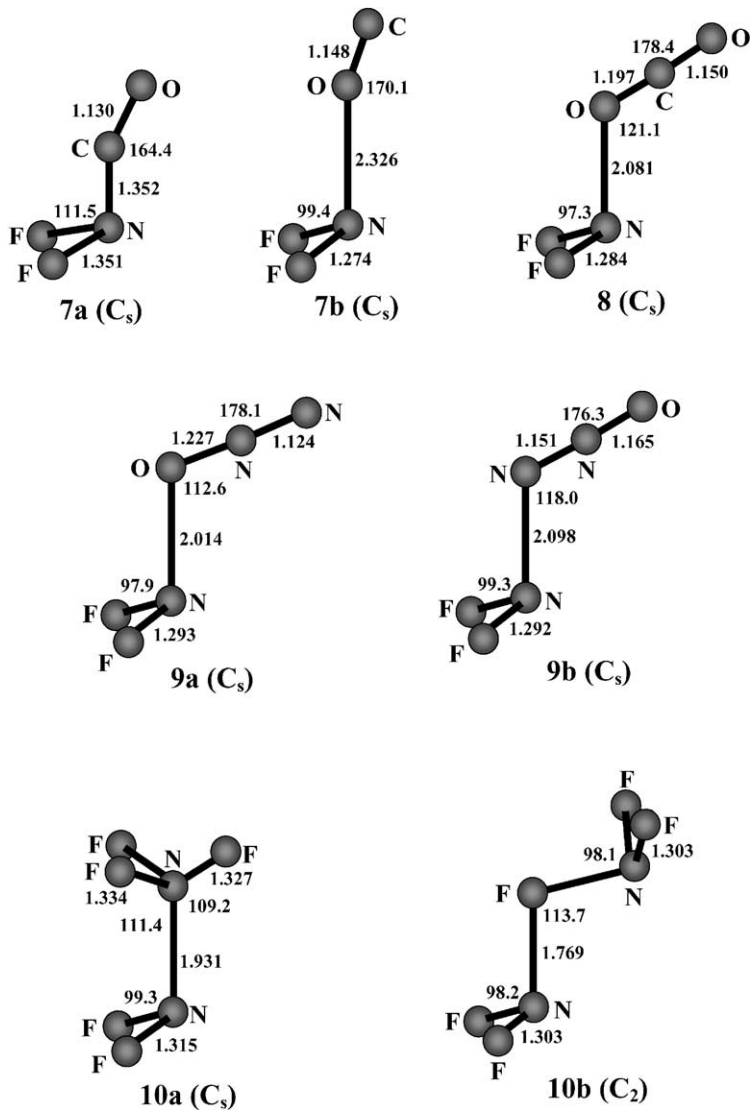

Fig. 2. B3LYP optimised geometries (Å and °) of the adducts of NF_2^+ with CO, CO_2, N_2O, and NF_3.

tial energy surface, ion **1b** resulted to be a first-order saddle point (imaginary frequency: 108.6i cm^{-1}), unstable with respect to the rotation of the H atom around the N–F bond. At the G2MS level of theory, the conformational barrier is evaluated as 1.2 kcal mol^{-1} from the energy difference between **1a** and **1b**, and the DFNA of HF is evaluated as 10.1 kcal mol^{-1}. Within their combined uncertainties, this theoretical estimate compares quite favourably with the experimental value of 11.5 kcal mol^{-1} obtained as the difference between the 298 K enthalpies of formation of NF_2^+, 275 kcal mol^{-1}; HF, −65.3 kcal mol^{-1}; and $(NF_3)H^+$, 198.2 kcal mol^{-1}. The latter value is derived from the experimental PA of NF_3, 135.9 kcal mol^{-1}, and the enthalpy of formation of NF_3, −31.6 kcal mol^{-1}, and H^+, 365.7 kcal mol^{-1}. The G2MS PA of NF_3, with formation of the isomer **1a**, is computed as 134.8 kcal mol^{-1}.

Table 2
G2MS (298.15 K) total energies (a.u.) and entropies (S, cal mol^{-1} K^{-1}) of the presently investigated ligands L, of their protonated forms LH^+, and of NF_2^+

L	G2MS (298.15 K)	S^a	LH^+	G2MS (298.15 K)	S^a
HF	−100.34923	41.6	H_2F^+	−100.53108	45.6
HCl	−460.33225	44.6	H_2Cl^+	−460.54473	49.3
H_2O	−76.33020	45.1	H_3O^+	−76.58985	46.2
H_2S	−398.92329	49.2	H_3S^+	−399.19171	50.0
NH_3	−56.45517	46.0	NH_4^+	−56.77761	44.4
PH_3	−342.67147	50.2	PH_4^+	−342.96734	48.6
CO	−113.17576	47.2	H–CO^+	−113.39898	48.2
			H–OC^+	−113.33892	38.1
CO_2	−188.35858	51.2	HO–CO^+	−188.56234	57.4
N_2O	−184.43902	52.5	HO–NN^+	−184.65679	57.9
			HN–NO^+	−184.64968	56.9
NF_3	−353.73809	62.4	H–NF_3^+	−353.94718	62.3
			F_2N–FH^+	−353.95058	70.5
NF_2^+	−253.58622	57.5			

[a] From B3LYP/6-31G(d) harmonic frequencies and moments of inertia and at 298.15 K.

The adduct **2** between NF_2^+ and HCl has been so far observed by ICR mass spectrometry as the product of the ligand-displacement reaction

$$NF_2^+\text{–(HF)} + HCl \rightarrow NF_2^+\text{–(HCl)} + HF \qquad (2)$$

This finding suggests the occurrence of an exoergic or practically ergoneutral reaction and indicates the NF_2^+–(HCl) adduct as a stable species in the gas phase. We have in fact located the C_s-symmetry isomer **2a** as an energy minimum on the B3LYP/6-31G(d)

Table 3
Calculated and experimental proton affinities (PA) and gas-phase basicities (GB) and calculated NF_2^+ affinities (DFNA) and basicities (DFNB) (kcal mol^{-1}) at 298.15 K of the presently investigated ligands L

L	PA (G2MS)[a]	PA (exp)[b]	GB (G2MS)	GB (exp)[b]	DFNA (G2MS)[a]	DFNB (G2MS)[a]
HF	115.6	115.7	109.0	109.2	10.1, 11.5[c]	1.6
HCl	134.8	133.1	128.4	126.7	20.7	13.0
H_2O	164.4	165.2	157.0	157.7	33.1	23.6
H_2S	169.9	168.5	162.4	161.0	57.6	47.6
NH_3	203.8	204.0	195.6	195.7	78.0	67.2
PH_3	187.1	187.6	178.9	179.5	84.7	74.1
CO (C)	141.6	142.0	134.1	134.5	25.0	14.8
CO (O)	103.9	101.9	93.4	96.1	5.1	−2.6
CO_2	129.3	129.2	123.4	123.3	10.7	2.8
N_2O (O)	138.1	137.5	132.0	131.1	17.5	9.1
N_2O (N)	133.7	131.4	127.3	125.1	11.7	3.4
NF_3 (F)	134.8	135.9	129.5	128.7	4.6	−4.1
NF_3 (N)	132.7		124.9		17.0, 17.7[d]	7.3

[a] Present work.
[b] Taken from [59].
[c] Experimental value based on the PA of NF_3.
[d] Experimental value taken from [22].

potential energy surface and computed the DFNA of HCl as 20.7 kcal mol^{-1}. Therefore, reaction (2) results exothermic by 10.6 kcal mol^{-1} and exoergic, at 298.15 K, by 11.4 kcal mol^{-1}. From Fig. 1, the N–Cl bond distance of **2a** is computed as large as 2.333 Å. The comparison with the B3LYP/6-31G(d) N–Cl distance of NF_2Cl, 1.813 Å (the experimental value is 1.73 Å [60]) indicates **2a** as an ion–dipole complex between NF_2^+ and HCl. We have also located as an additional energy minimum on the potential energy surface the conformational isomer **2b**, which is, however, less stable than **2a** by 1.5 kcal mol^{-1}.

The adduct **3** between NF_2^+ and H_2O has been so far observed [27] from the chemical ionisation (CI) of NF_3/H_2O mixtures. It was characterised by CAD and MIKE spectrometry as the intermediate involved in the following addition–elimination reaction:

$$NF_2^+ + H_2O \rightarrow FN{-}OH^+ + HF \quad (3)$$

the overall occurrence of which was unambiguously ascertained by Fourier-transform ICR (FT-ICR) mass spectrometry. In the same study, the structure and stability of NF_2^+–(H_2O), as well as its unimolecular decomposition processes of lowest energy, have been investigated by G1 ab initio calculations. It is of relevance to note here that the NF_2^+–(H_2O) structure located so far on the MP2/6-31G(d) potential energy surface corresponds to the conformer **3a** presently located on the B3LYP/6-31G(d) potential energy surface. The B3LYP/6-31G(d) N–O distance of **3a**, 1.820 Å, is slightly longer than the MP2/6-31G(d) value of 1.720 Å, and, overall, compared with the MP2 values, the DFT optimised parameters suggest a slightly weaker interaction between NF_2^+ and H_2O. In fact, the G2MS (298.15 K) DFNA of H_2O, computed as 33.1 kcal mol^{-1}, is lower than the G1 value, obtained using MP2 geometries, by 3.2 kcal mol^{-1} [27]. In the present study, we have also located the conformational isomer **3b**, which however revealed a first-order saddle point (imaginary frequency: 204.4i cm^{-1}), unstable with respect to the rotation of the H_2O moiety around the N–O bond. The corresponding conformational barrier is predicted as 3.2 kcal mol^{-1} from the G2MS (298.15 K) energy difference between **3a** and **3b**.

The comparison between the computed DFNAs of HF, 10.1 kcal mol^{-1}, and HCl, 20.7 kcal mol^{-1}, suggests that the interaction of NF_2^+ with second-row atoms should be larger than first-row ones. To better appreciate this periodic trend in the difluoronitrenium ion affinities and basicities, we decided to investigate the still unreported adducts between NF_2^+ and H_2S, NH_3, and PH_3. For all these species we have located two distinct conformes, but the "eclipsed" structures **4b**, **5b**, and **6b** were invariably characterised as first-order saddle points (imaginary frequencies: 142.6i, 212.7i, and 204.3i cm^{-1}, respectively), unstable with respect to the rotation of the H_2S, NH_3, and PH_3 moieties around the N–S, the N–N, and the N–P bonds, respectively. In addition, the G2MS energy differences with the minimum-energy structures **4a**, **5a**, and **6a** were found to be comparable and computed as 2.6, 1.7, and 2.4 kcal mol^{-1}, respectively. The most important finding is that the DFNA of H_2S, 57.6 kcal mol^{-1}, is indeed larger than H_2O by more than 24 kcal mol^{-1}. The DFNA of PH_3, 84.7 kcal mol^{-1}, is also larger than the DFNA of NH_3, 78.0 kcal mol^{-1}, although by a significantly less extent. The appreciable DFNAs of H_2S, NH_3, and PH_3 are consistent with the computed structures of **4a**, **5a**, and **6a**. In particular, we note the relatively short N–S, N–N, and N–P bond distances, 2.027, 1.521, and 1.781 Å, respectively, and the significant elongations of the N–F distances of the NF_2 moieties with respect to free NF_2^+ (N–F: 1.259 Å).

The adducts **7a** and **7b** between NF_2^+ and CO have been so far discussed [31] as the intermediates involved in the following spin-forbidden formal F^+ transfer reaction:

$$^1NF_2^+ + CO \rightarrow {}^1FCO^+ + {}^3NF \quad (4)$$

The detailed mechanistic aspects of this process have been investigated by a combination of mass spectrometric techniques and DFT and ab initio calculations, and we simply mention here that the $F_2N{-}CO^+$ connectivity of **7a** has been ascertained by both CAD and MIKE experiments. Here, we wish to make certain

additional considerations on the detailed structure and stability of **7a** and **7b**, so to place these two species in the more general context of the experimental and theoretical studies on the adducts of CO with simple gaseous cations. The theoretical investigation of the adducts between CO and monoatomic ions M^+ [61,62] clearly indicates that, in the absence of π back donation from M^+ to CO, the σ bonding between the C atom of CO and M^+ results in a tighter C–O bond than in the free molecule, which is reflected in a shorter C–O bond distance and in a blue shift of the C–O stretching frequency. On the opposite, ligation of M^+ to the O atom of CO elongates the C–O bond and red shifts the C–O stretching frequency. In addition, the O-co-ordinated M^+–(CO) isomer is invariably predicted to be less stable than the C-co-ordinated one. Our results on the adducts **7a** and **7b** fully conform to these expectations. The B3LYP/6-31G(d) C–O distance of **7a**, 1.130 Å, is shorter than free CO, 1.138 Å, and the stretching frequency of the CO moiety of **7a**, 2328.6 cm^{-1}, is higher than the vibrational frequency of CO, 2208.2 cm^{-1}. The C–O distance of **7b**, 1.148 Å, is instead longer than CO, and the stretching frequency of the CO moiety amounts to 2117.0 cm^{-1}. In addition, isomer **7a** is more stable than **7b** by 19.9 kcal mol^{-1}. It is of interest to note here that similar evidences have been obtained on the structure and stability of the isomeric SiF_3^+–(CO) ions, so far investigated by selected-ion flow tube (SIFT) spectrometry and DFT theoretical calculations [63]. The G2MS DFNA of CO with formation of **7a** is presently computed as 25.0 kcal mol^{-1}.

The adduct **8** between NF_2^+ and CO_2 has been so far observed by Fisher and McMahon by ICR spectrometry as the product of the ligand-displacement reaction [23]

$$NF_2^+\text{–(HF)} + CO_2 \rightarrow NF_2^+\text{–}(CO_2) + HF \qquad (5)$$

This finding suggests that reaction (5) is an exoergic or practically ergoneutral reaction. Consistently, from Table 3, at the G2MS level of theory, the DFNA of CO_2 is presently computed as 10.7 kcal mol^{-1}, and, at 298.15 K, reaction (5) is predicted to be exothermic by 0.6 kcal mol^{-1} and exoergic by 1.2 kcal mol^{-1}. Generally speaking, the occurrence of gas-phase ionic processes which involve the robust carbon dioxide are of considerable fundamental interest, and the fixation and chemical activation of CO_2 by gaseous cations of main-group [64,65] and transition [66–68] elements have been investigated by numerous research groups. In fact, these studies are expected to throw light on the detailed elementary steps which are conceivably involved in the complex natural and synthetic sequences which result in the fixation of CO_2 and its conversion into useful products under different experimental conditions. Our interest in this topic comes from the experimental observation [69] that the ligation of carbon dioxide to gaseous SiF_3^+ leads to the coupled activation of CO_2 and aromatic C–H bonds. We simply note here that the chemically active SiF_3^+–(CO_2) adduct was obtained from the ligand-displacement reaction

$$SiF_3^+\text{–(HF)} + CO_2 \rightarrow SiF_3^+\text{–}(CO_2) + HF \qquad (6)$$

which is strictly analogous to reaction (5). In addition, it is relevant to mention here the observation reported so far [70] of the ligand-displacement reaction involving protonated AsF_3

$$AsF_3H^+ + CO_2 \rightarrow AsF_2^+\text{–}(CO_2) + HF \qquad (7)$$

The low DFNA of CO_2 is consistent with the computed structure of ion **8**. This species arises from the week interaction between the positive charge of NF_2^+ and the negatively charged oxygen atoms of CO_2, a molecule which has a negative quadrupole moment [71]. As a result, from Fig. 2, one of the C–O bond lengths of **8**, 1.197 Å, is 0.028 Å longer than the other one, 1.150 Å, and the latter is in turn 0.019 shorter than the C–O bond distance of free CO_2.

The adduct **9** between NF_2^+ and N_2O has been so far observed [32] from the CI of NF_3/N_2O mixtures. It was characterised by CAD and MIKE spectrometry as the intermediate involved in the following oxygen-atom abstraction:

$$NF_2^+ + N_2O \rightarrow NF_2O^+ + N_2 \qquad (8)$$

the overall occurrence of which was unambiguously ascertained by FT-ICR spectrometry. At the

MP2(full)/6-31G(d) level of theory, the oxygen-co-ordinated isomer **9a** resulted to be more stable than the nitrogen-co-ordinated isomer **9b** by only 1.4 kcal mol^{-1}. The results of the present more accurate study reveal that this energy difference is probably more pronounced. In fact, at the B3LYP/6-31G(d) level of theory, both ions **9a** and **9b** have been located as true minima on the potential energy surface, and, at the G2MS level of theory, the former species is more stable by 5.8 kcal mol^{-1}. In addition, the DFNA of N_2O with formation of **9a** is obtained as 17.5 kcal mol^{-1}. This value is consistent with typical solvation energies of N_2O with gaseous cations of main-group elements, including, for example, NO^+, $O_2{}^+$, N_2O^+, N_2OH^+, and H_3O^+ [72]. The relatively low energy difference between **9a** and **9b** reflects in the similarity of their computed structure. We note in particular that the overall asymmetries of the N–N and N–O bonds of the two ions with respect to free N_2O are practically coincident and obtained as 0.045 Å for ion **9a** and 0.044 Å for ion **9b** (the B3LYP/6-31G(d) N–N and N–O bond lengths of N_2O are computed as 1.134 and 1.193 Å, respectively).

The ligation of $NF_2{}^+$ to NF_3 has been so far investigated in considerable detail by Hiraoka et al. using pulsed electron-beam mass spectrometry and ab initio theoretical calculations [22]. It is, therefore, of interest to compare our present theoretical results on the $NF_2{}^+$–(NF_3) adducts with these previous experimental and theoretical findings.

Hiraoka et al. have obtained the $NF_2{}^+$–(NF_3) adducts **10** by two different routes. The first one is the direct clustering reaction of $NF_2{}^+$ with NF_3

$$NF_2{}^+ + NF_3 + NF_2{}^+\text{–}(NF_3) \quad (9)$$

whose enthalpy and entropy changes were experimentally measured from a van't Hoff plot as 17.7 kcal mol^{-1} and 32.3 cal mol^{-1} K^{-1}, respectively. Based on the observation that the bond dissociation energy of the $NF_2{}^+$–(HF) adduct is significantly lower than 17.7 kcal mol^{-1} but the dipole moment of NF_3, 0.2 D, is much smaller than HF, 1.9 D, they proposed the formation from reaction (9) of the nitrogen-co-ordinated isomer F_2N–$NF_3{}^+$. This conclusion was supported by the results of ab initio calculations. At the MP4(SDTQ)/6-31G(d)//HF/6-31G(d) level of theory, the F_2N–$NF_3{}^+$ isomer was found to be more stable than the alternative F_2N–F–$NF_2{}^+$ structure by 8.7 kcal mol^{-1}, and the enthalpy change of reaction (9), with formation of the nitrogen-co-ordinated isomer, was computed as 17.0 kcal mol^{-1}, in very good agreement with the experimental value. Our present G2MS theoretical results are fully consistent with this interpretation of the details of reaction (9). At the B3LYP/6-31G(d) level of theory, we have in fact located as true energy minima on the potential energy surface the two distinct isomers **10a** and **10b**, which formally arise from the ligation of $NF_2{}^+$ to the nitrogen and the fluorine atoms of NF_3, respectively. At the G2MS level of theory, **10a** is more stable than **10b** by 12.4 kcal mol^{-1}, and, assuming the formation of **10a**, the enthalpy change of reaction (9), i.e. the DFNA of NF_3, is obtained as 17.0 kcal mol^{-1}, which is in excellent agreement with the experimental and the MP4(SDTQ)/6-31G(d)//HF/6-31G(d) theoretical data. In addition, from Tables 1 and 2, we evaluate the entropy change of reaction (9) as 32.5 cal mol^{-1} K^{-1}, which practically matches the experimental value. The only appreciable differences with the results of Hiraoka et al. are in the optimised geometries of ions **10a** and **10b**. At the HF/6-31G(d) level of theory, they found a staggered conformation as the optimised structure of **10a**, which we have instead characterised as a rotational first-order saddle point on the B3LYP/6-31G(d) potential energy surface. In addition, the HF/6-31G(d) optimised geometry of ion **10b** resulted strongly asymmetric and consisting essentially of a $NF_2{}^+$ ion ligated to the F atom of NF_3 at a distance of 2.122 Å. At the B3LYP/6-31G(d) level of theory, we have instead obtained a fluoronium ion of C_2 symmetry,[2] which consists of two equivalent NF_2 moieties ligated at the central F atom at a bond distance of 1.769 Å. Such differences in the structures computed at the HF and B3LYP level of theory are

[2] Searching under the constraint of C_{2v} symmetry, we have located a first-order saddle point (imaginary frequency: 31.2i cm^{-1}) unstable with respect to the distortion of the two NF_2 moieties. This species is, however, practically degenerate with ion **10b**.

not surprising and likely reflect the partial inclusion of electron correlation effects in the geometry optimisation of **10a** and **10b** performed at the DFT level of theory.

Hiraoka et al. have also obtained the NF_2^+–(NF_3) adduct from the ionisation of a mixture of N_2, H_2, and NF_3. In this case, the formation of the observed NF_2^+–(NF_3) cluster was ascribed to the ligand-displacement reaction

$$NF_2^+–(HF) + NF_3 \rightarrow NF_2^+–(NF_3) + HF \qquad (10)$$

and the ionic product was assigned as the less stable $F_2N–F–NF_2^+$ isomer. This conclusion rested on the observation that the activation energy for the conceivably barrier-free unimolecular dissociation of the NF_2^+–(NF_3) adduct from reaction (10) was experimentally measured from an Arrhenius plot as 8.5 kcal mol^{-1}. This is significantly lower than the dissociation energy of the $F_2N–NF_3^+$ isomer and was found in very good agreement with the MP4(SDTQ)/6-31G(d)//HF/6-31G(d) binding energy of the $F_2N–F–NF_2^+$ isomer of 8.3 kcal mol^{-1}. At the G2MS level of theory, this value is, however, lower and computed as 4.6 kcal mol^{-1}. The kinetically favoured formation of the less stable isomer **10b** from reaction (10) was ascribed to a quite small cross section for the direct formation of the thermodynamically favoured isomer **10a**, and this appears indeed as the most plausible explanation. We have, however, to note that even using the experimental DFNA values of HF, 11.5 kcal mol^{-1}, and NF_3 (with formation of **10b**), reaction (10) results endothermic by 3.0 kcal mol^{-1}. Using the total entropies of the involved species which are listed in Tables 1 and 2, at 298.15 K, the reaction is also endoergic by 3.2 kcal mol^{-1}. Using our G2MS theoretical values, reaction (10) results endothermic by 5.5 kcal mol^{-1} and endoergic by 5.7 kcal mol^{-1}. Since the conditions employed in the high-pressure experiments by Hiraoka et al. should prevent the formation of appreciable amounts of excited F_2N^+–(HF) precursor ions, in principle able to undergo the endothermic and endoergic reaction (10), the kinetically controlled formation of isomer **10b** from reaction (10) should be probably investigated in greater detail.

3.3. Lewis acidity of NF_2^+: the difluoronitrenium ion affinity (DFNA) and basicity (DFNB) scale

The DFNAs of our investigated ligands L, calculated at the G2MS level of theory, are expected to be as accurate as ca. 2 kcal mol^{-1} and span an interval of ca. 80 kcal mol^{-1}, ranging from 5.1 kcal mol^{-1} for L = CO (assuming the formation of the oxygen-co-ordinated isomer **7b**) to 84.7 kcal mol^{-1} for L = PH_3. Taking also into account the variety of the included ligands, this interval is large enough to regard the values listed in Table 3 as a DFNA scale. The theoretical DFNAs of HF, 10.1 kcal mol^{-1}, and NF_3 (with formation of the N-co-ordinated isomer **10a**), 17.0 kcal mol^{-1}, are the only two absolute values of this scale which can be experimentally checked. However, the favourable comparison with the experimental values of 11.5 and 17.7 kcal mol^{-1}, respectively, reinforces the expectation that the DFNAs and DFNBs listed in Table 3 can be used to rationalise or predict the occurrence in the gas phase of exothermic or exoergic NF_2^+ transfer reactions between simple ligands L. As a matter of fact, the two experimentally observed ligand-displacement reactions (2) and (5) are in keeping with the ranking of this theoretical scale.

We have also investigated the conceivable occurrence of a correlation between the DFNA and DFNB of our investigated ligands and their PA and GB. To this end, we have first calculated the PAs of all the ligands at the G2MS level of theory and compared the obtained values with the experimental ones. From Table 3, taking also into account the error bars associated with the two sets of values, the PAs and the GBs calculated at the G2MS level of theory are in very good agreement with the experimental values, thus providing additional evidence for the adequacy of the G2MS theory to reproduce or predict thermochemical quantities of diatomic and simple polyatomic ligands.

A plot of the G2MS DFNAs versus G2MS PAs (both expressed in kcal mol^{-1}) of our investigated ligands is shown in Fig. 3.

Taking into account the variety of the included ligands, the correlation between the two sets of values appears to be reasonably good and expressed by the

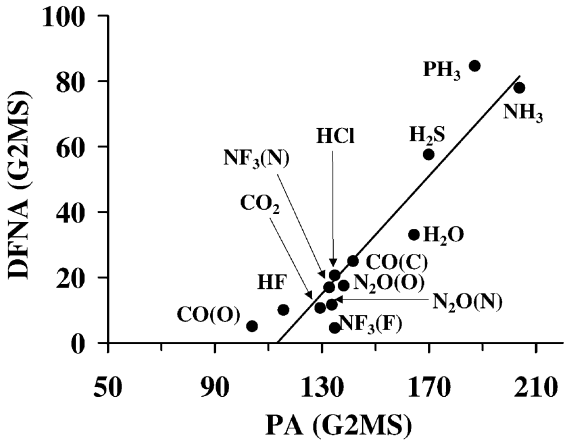

Fig. 3. Plot of theoretical DFNAs (kcal mol^{-1}) vs. theoretical PAs (kcal mol^{-1}) of the presently investigated ligands.

following equation:

$$\mathrm{DFNA(G2MS)} = 0.90\mathrm{PA(G2MS)} - 101.9 \quad (R^2 = 0.875)$$

A quite similar correlation ($R^2 = 0.848$) does exist between the calculated values of DFNB and GB. Although the number of the presently investigated ligands is probably too small to appreciate the general validity of the above correlations between thermochemical quantities, they provide, however, encouraging evidence for the conceivable occurrence of simple relationships between the DFNA and the PA or the DFNB and the GB of a given ligand L. A more detailed discussion of this point, as well as a more critical check of the DFNA and DFNB scales reported in Table 3, would require additional experimental evidence concerning the thermochemistry of the adducts of gaseous NF_2^+. The presently reported theoretical results could stimulate future work along this direction.

As a final point in this section, we wish to place our computational results on the adducts of NF_2^+ with diatomic and simple polyatomic ligands in the more general context of the structure and stability of the complexes of simple nitrenium ions, a topic which is currently attracting considerable experimental [73,74] and theoretical [75] interest. Generally speaking, the type of complexes formed by simple nitrenium ions X–N–Y$^+$ strictly depends on their electronic structure and on the nature of the substituents X and Y. The parent nitrenium ion NH_2^+ has a triplet ground state ($^3B_1$), with two unpaired nonbonding electrons which occupy orbitals of similar energy, centred essentially on the nitrogen atom. In this electronic configuration, NH_2^+ is expected to bind ligands through hydrogen rather than nitrogen, forming loosely bound complexes of general structure L–H–N–H$^+$. This expectation is confirmed, for example, by the recent results reported by Dopfer et al. [73] on the gaseous adducts of triplet ground-state NH_2^+ with the noble gases helium and argon, investigated by photodissociation spectroscopy and ab initio calculations. The experimental and theoretical evidence point to quasi-linear proton-bound species He–H–N–H$^+$ and Ar–H–N–H$^+$, whose bond dissociation energies are evaluated as 273 and 1773 cm^{-1}, respectively. On the contrary, singlet nitrenium ions have two paired nonbonding electrons and a low-energy unoccupied orbital, and should behave more like a carbocation, participating in processes that involve shifts of electron pairs from the ligand to the nitrogen atom. An important confirmation to this qualitative expectation comes, for example, from the experimental results concerning the reactivity of organic nitrenium ions, which usually possess a singlet ground state [76]. Thus, these reactive intermediates behave not only as C electrophiles, which is usually related to the important contribution of imine-like resonance structures, but also N electrophiles. From the experimental point of view, the Lewis acidity of the simplest nitrenium ions in their singlet state is still essentially unexplored. The results of recent ab initio calculations on the adducts of singlet XNH$^+$ ions (X = H, F, Cl, CN, and CH_3) with H_2O [75] clearly indicate that, for a given ligand L, the nature of the substituent X strongly affects the structure and stability of these species. Thus, at the QCISD(T)/6-311 + G(d,p)//QCISD/6-311 + G(d,p) level of theory, the binding energy of the cation to H_2O range from 6.6 kcal mol^{-1} for CH_3NH^+ to 81.2 kcal mol^{-1} for NH_2^+, and the computed structures parallel these trends in the stability. The results of the present computational investigation provide the

probably first evidence concerning the effect of the ligand L on the Lewis acidity of a simple nitrenium ion. We note in particular that, for hydrogen-containing ligands, the DFNAs of second-row molecules are invariably higher than their first-row congeners. However, the extent of the computed difference becomes progressively smaller moving from the right to the left of the periodic system. Thus, the DFNA of HCl, 20.7 kcal mol^{-1}, is more than twice the DFNA of HF, 10.1 kcal mol^{-1}, whereas the DFNA of PH_3, 84.7 kcal mol^{-1}, is only 6.7 kcal mol^{-1} higher than NH_3. For ligands containing exclusively heavy atoms, we note that our computed values of DFNAs are in line with trends expected form previous observations concerning the thermochemistry of their adducts with positive ions. Thus, the oxygen-co-ordinated isomer of the NF_2^+–(N_2O) adduct is predicted to be less stable the nitrogen-co-ordinated structure by ca. 6 kcal mol^{-1}, and this energy difference parallels the order of stability usually computed for the isomeric ions arising from the ligation of a gaseous cation to N_2O, including $(N_2O)H^+$. In addition, the order of stability of the nitrogen- and fluorine-co-ordinated isomers of the NF_2^+–(NF_3) adduct parallels, for example, the thermodynamically favoured ligation of CH_3^+ to the nitrogen atom of NF_3 which is predicted by the results of ab initio calculations on the structure and stability of isomeric CH_3^+–(NF_3) ions [35]. A more detailed theoretical investigation of the effect of the ligand L on the Lewis acidity of simple nitrenium ions is currently in progress in our laboratory.

4. Conclusions

The adducts of NF_2^+ with diatomic and simple polyatomic ligands play a central role in the gas-phase chemistry of ionised mixtures containing NF_3. In the present study, we have performed a comparative investigation, at an uniform and accurate level of theory, of the structure, stability, and thermochemistry of all the gaseous complexes of NF_2^+ which have been experimentally observed to date. We have also extended the scope of the investigation to species which have been not yet experimentally observed, so to appreciate the conceivable occurrence of periodic trends in the Lewis acidity of NF_2^+. It has been so possible to build up a theoretical scale of difluoronitrenium ion affinities and basicities, which should be useful to predict or rationalise NF_2^+ transfer reactions in the gas phase. A more detailed investigation of this scale and its extension to novel ligands could reveal of future experimental interest.

Acknowledgements

The authors wish to thank the Italian Ministero dell' Istruzione, dell' Università e della Ricerca (MIUR) and Consiglio Nazionale delle Ricerche (CNR) for financial support.

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