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# The ionization potential of $NF_3$: a G3 computational study on the thermochemical properties of $NF_x$ and $NF_x^+$ ($x = 1$–3)

M. Aschi[a], F. Grandinetti[b,*]

[a]Dipartimento di Chimica, Università di Roma “La Sapienza”, P.le A. Moro, 5, 00185, Rome, Italy
[b]Dipartimento di Scienze Ambientali, Università della Tuscia, Via S.C. De Lellis, 01100, Viterbo, Italy

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## Abstract

The adiabatic ionization potential (IP) of $NF_x$ ($x = 1$–3) and the enthalpies of formation of $NF_x$ and $NF_x^+$ have been computed using the Gaussian-3 (G3) theory. The obtained values are generally found in very good agreement with the experimental ones. However, the G3 enthalpy of formation of $NF_3^+$ at 0 K, 261.7 ± 0.9 kcal/mol, and the adiabatic IP of $NF_3$, 12.63 ± 0.04 eV, differ appreciably from the experimental values of 269.6 kcal/mol and 13.00 ± 0.02 eV, respectively, based on photoionization mass spectrometry [J. Berkowitz, J.P. Greene, J. Foropoulos, Jr., O.M. Neskovic, J. Chem. Phys. 81 (1984) 6166] and 268.2 kcal/mol and 12.94 ± 0.01 eV, respectively, based on photoelectron photoion coincidence spectroscopy [R. Rüede, H. Troxler, Ch. Beglinger, M. Jungen, Chem. Phys. Lett. 203 (1993) 477]. This confirms the discrepancy recently noted by Ricca [A. Ricca, Chem. Phys. Lett. 294 (1998) 454] between the theoretical and the experimental adiabatic IP of $NF_3$. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords*: G3 theory; Ionization potential; $NF_3$

## 1. Introduction

The $NF_x$ and $NF_x^+$ species ($x = 1$–3) are of considerable fundamental interest in the inorganic chemistry of nitrogen [1]. In addition, they play an active role in the $NF_3$-based plasma processing of materials employed for the fabrication of electronic devices [2–8]. It is therefore not surprising that the structure, bonding, and thermochemistry of these simple neutrals and ions are the focus of continuing experimental and theoretical interest [9–14]. In particular, the enthalpies of formation of the $NF_x$ and $NF_x^+$ ($x = 1$–3) have been recently evaluated by Ricca [15,16] using the coupled cluster theory (CCSD(T)) in conjunction with extrapolation to the complete basis set. The maximum error bar of the employed theoretical procedure was estimated as 2 kcal/mol and, in fact, the computed enthalpies of formation at 298 K of $NF_x$ and $NF_x^+$ resulted in good agreement with the experimental values [17,18]. The only exception was the enthalpy of formation of $NF_3^+$, whose computed value of 262.88 kcal/mol resulted lower than the experimental value by 5 kcal/mol. A detailed investigation of the origin of this discrepancy revealed that it likely reflects an experimental adiabatic ionization potential (IP) of $NF_3$, 13.00 ± 0.02 eV [19,20], which is probably too large by 0.2–0.3 eV. In fact, at the CCSD(T) level of theory, using basis sets of triple, quadruple, and quintuple-zeta quality, the adiabatic IP of $NF_3$ was computed as 12.64 eV, whereas,

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* Corresponding author. Tel.: +39-761-357116; fax: +39-761-357179.

*E-mail address:* fgrandi@unitus.it (F. Grandinetti).

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at the same computational level and irrespective of the employed basis set, the IPs of NF and $NF_2$ were found to be in very good agreement with the experimental values of 12.26 ± 0.01 [21] and 11.63 ± 0.01 eV [19], respectively. It has been noted by Ricca that the experimental estimate of the IP of $NF_3$ by Berkowitz et al. [19,20] based on photoionization (PI) mass spectrometry, 13.00 ± 0.02 eV, probably suffers of the difficulty of extrapolating the $NF_3^+$ yield curve to the adiabatic limit. It is, however, to be mentioned that the ionization potential of $NF_3$ has been repeatedly measured by various techniques [22–29] and invariably placed around 13.0 eV. In particular, the two most recent estimates are 12.94 ± 0.01 eV using photoelectron photoion coincidence (PEPICO) spectroscopy [28] and 13.5 ± 0.2 eV using electron impact (EI) mass spectrometry [29]. Therefore, the difference noted by Ricca between the experimental and the theoretical adiabatic IP of $NF_3$ marks a discrepancy, which deserves further investigation. As a part of our continuing experimental and theoretical interest in the gas-phase ion chemistry of $NF_3$ [30–38], we decided to use the Gaussian-3 (G3) theory recently proposed by Pople and coworkers [39] to evaluate the enthalpies of formation of $NF_x$ and $NF_x^+$ and the adiabatic IP of $NF_x$ ($x = 1$–3). The obtained results, discussed in the present article, confirm the discrepancy noted by Ricca [15] between the theoretical and the experimental IP of $NF_3$.

## 2. Computational details

The total energies of $NF_x$ and $NF_x^+$ have been computed using the G3 theory [39], which is the third and the more recent member in the series of the methods proposed by Pople and coworkers and referred to as Gaussian-*n* theories. With respect to the previous G2 theory [40], G3 has been found to make a significant improvement in the calculation of the thermochemical properties of certain classes of chemical compounds, including simple fluorinated species such as $CF_4$, $SiF_4$ and $NF_3$. In particular, we note that the G3 enthalpy of formation of $NF_3$ practically matches the experimental value of −31.6 kcal/mol [17]. This reinforces the expectation that G3 is indeed adequate to predict the thermochemical properties of the presently investigated $NF_x$ neutrals and ions. Like G1 and G2, the G3 theory is a composite method which consists of a sequence of well defined ab initio calculations used to calculate the total energy of a species according to an additivity scheme, the results of which are corrected by appending a small higher-level empirical term (HLC). The full details of the procedure involved in the calculation of the G3 total energies of atoms and molecules are given in Ref. [39]. We simply report here the general expression used to calculate the G3 total energies (in hartrees) at 0 K of a polyatomic species

$$\begin{aligned} E_0(\mathrm{G3}) = {} & E[\mathrm{MP4(fc)/6\text{-}31G(d)}] + \Delta E(+) \\ & + \Delta E(\mathrm{2df,p}) + \Delta E(\mathrm{QCI}) + \Delta E(\mathrm{G3large}) \\ & - 0.006386 n_\beta - 0.002977(n_\alpha - n_\beta) + \mathrm{ZPE} \end{aligned}$$

Here, $n_\alpha$ and $n_\beta$ are the number of α and β valence electrons, respectively, and ZPE is the zero-point energy calculated at the HF/6-31G(d) level and scaled by 0.8929 to take account of known deficiencies at this level. The other terms are calculated as follows by performing single-point calculations at the MP2(full)/6-31G(d) equilibrium geometry (“full” and “fc” denote the inclusion or not of the valence electrons for the calculation of the correlation energies)

$$\begin{aligned} \Delta E(+) = {} & E[\mathrm{MP4(fc)/6\text{-}31G+(d)}] \\ & - E[\mathrm{MP4(fc)/6\text{-}31G(d)}] \end{aligned}$$

$$\begin{aligned} \Delta E(2df,p) = {} & E[\mathrm{MP4(fc)/6\text{-}31G+(2df,p)}] \\ & - E[\mathrm{MP4(fc)/6\text{-}31G(d)}] \end{aligned}$$

$$\begin{aligned} \Delta E(\mathrm{QCI}) = {} & E[\mathrm{QCISD(T)/6\text{-}31G(d)}] \\ & - E[\mathrm{MP4(fc)/6\text{-}31G(d)}] \end{aligned}$$

$$\begin{aligned} \Delta E(\mathrm{G3large}) = {} & E[\mathrm{MP2(full)/G3large}] \\ & - E[\mathrm{MP2(fc)/6\text{-}31G(2df,p)}] \\ & - E[\mathrm{MP2(fc)/6\text{-}31+G(d)}] \\ & + E[\mathrm{MP2(fc)/6\text{-}31+G(d)}] \end{aligned}$$

We have also calculated the G3 total energies of the

Table 1
G3 total energies (hartrees) of $NF_x$ and $NF_x^+$ ($x = 1$–$3$)

| | G3 (0 K) | G3 (298.15 K) |
|---|---|---|
| NF | − 154.37119 | − 154.36881 |
| $NF^+$ | − 153.91991 | − 153.91755 |
| $NF_2$ | − 254.15821 | − 254.15516 |
| $NF_2^+$ | − 253.73010 | − 253.72715 |
| $NF_3$ | − 353.93272 | − 353.92927 |
| $NF_3^+$ | − 353.46862 | − 353.46516 |

Table 2
Thermochemical properties (0 K) of $NF_x$ and $NF_x^+$ ($x = 1$–$3$) (enthalpies of formation are given in kcal/mol and ionization potentials in eV)

| | G3 theory | Experiment |
|---|---|---|
| $\Delta H_f^0(NF)$ | $54.0 \pm 0.9$ | $55.6 \pm 0.5$[a] |
| $\Delta H_f^0(NF^+)$ | $336.8 \pm 0.9$ | $338.3 \pm 0.5$[a] |
| IP(NF) | $12.28 \pm 0.04$ | $12.26 \pm 0.01$[b] |
| $\Delta H_f^0(NF_2)$ | $8.0 \pm 0.9$ | $8.3 \pm 0.5$[a] |
| $\Delta H_f^0(NF_2^+)$ | $277.3 \pm 0.9$ | $276.5 \pm 0.5$[a] |
| $IP(NF_2)$ | $11.65 \pm 0.04$ | $11.62_8 \pm 0.01$[a] |
| $\Delta H_f^0(NF_3)$ | $-30.2 \pm 0.9$ | $-30.2 \pm 0.2$[c] |
| $\Delta H_f^0(NF_3^+)$ | $261.7 \pm 0.9$ | $269.6 \pm 0.7$[d]<br>$268.2 \pm 0.4$[e] |
| $IP(NF_3)$ | $12.63 \pm 0.04$ | $13.00 \pm 0.02$[a]<br>$12.94 \pm 0.01$[f] |

[a] Taken from Ref. [19].
[b] Taken from Ref. [21].
[c] By thermal correction at 0 K of the value at 298.15 K.
[d] Based on the IP of $NF_3$ reported in Ref. [19].
[e] Based on the IP of $NF_3$ reported in Ref. [28].
[f] Taken from Ref. [28].

investigated neutrals and ions at 298.15 K by adding to $E_0$(G3) a thermal correction calculated using the scaled HF/6-31G(d) frequencies for the vibrations in the harmonic approximation and the classical approximation for translation ((3/2)R$T$) and rotation (R$T$ for linear species and (3/2)R$T$ for non-linear species).

The G3 thermochemical data have been calculated following the procedures already described in the literature [41,42] and recommended in Ref. [39]. In particular, the G3 enthalpies of formation at 0 K of the $NF_x$ neutrals and ions, $\Delta H_f^0(NF_x, 0\ K)$ and $\Delta H_f^0(NF_x^+, 0\ K)$, respectively, have been obtained according to the following expressions:

$$\Delta H_f^0(NF_x,\ 0\ K) = x\Delta H_f^0(F,\ 0\ K) + \Delta H_f^0(N,\ 0\ K) - D_0(NF_x) \tag{1}$$

$$\Delta H_f^0(NF_x^+,\ 0\ K) = x\Delta H_f^0(F,\ 0\ K) + \Delta H_f^0(N^+,\ 0\ K) - D_0(NF_x^+) \tag{2}$$

where

$$D_0(NF_x) = xE_0(G3,\ F) + E_0(G3,\ N) - E_0(G3,\ NF_x)$$

$$D_0(NF_x^+) = xE_0(G3,\ F) + E_0(G3,\ N^+) - E_0(G3,\ NF_x^+)$$

The values of $\Delta H_f^0(F, 0\ K)$, $\Delta H_f^0(N, 0\ K)$, and $\Delta H_f^0(N^+, 0\ K)$, 18.47, 112.53 and 447.69 kcal/mol, respectively, have been taken from the Janaf Tables [17], and the $E_0$(G3) of N, −54.56434 hartrees, F, −99.68421 hartrees and $N^+$, − 54.03123 hartrees, respectively, have been taken from Ref. [39]. The ionization potentials at 0 K of the $NF_x$ neutrals have been calculated according to the expression

$$IP(NF_x,\ 0\ K) = E_0(G3,\ NF_x^+) - E_0(G3,\ NF_x) \tag{3}$$

All the calculations have been performed using the Unix version of the GAUSSIAN 94 set of programs [43] installed on a Compaq Alphaserver 1200 workstation. We used the 6-31G(d), 6-31G + (d), and 6-31G(2df,p) basis sets standard in this program and the G3large basis set introduced by Pople and coworkers in conjunction with the G3 theory. The latter has been downloaded from the website suggested in Ref. [39]. The 6-31G(d), 6-31G + (d) and 6-31G(2df,p) basis sets use six Cartesian d-functions (6d) while the G3large basis set uses five “pure” d-functions (5d). Both the 6-31G(2df,p) and G3large basis sets use a set of “pure” 7f.

## 3. Results and discussion

The G3 total energies of $NF_x$ and $NF_x^+$ reported in Table 1 have been used to calculate the thermochemical properties at 0 K reported in Table 2. The G3 enthalpies of formation and ionization potentials have been reported with the uncertainties of 0.9 kcal/mol and 0.04 eV, respectively, quoted by

Pople and coworkers [39] for the calculation of these quantities. The experimental data reported in Table 2 have been selected as follows: the enthalpies of formation at 0 K of NF, 55.6 ± 0.5 kcal/mol; $NF^+$, 338.3 ± 0.5 kcal/mol; $NF_2$, 8.3 ± 0.5 kcal/mol; and $NF_2^+$, 276.5 ± 0.5 kcal/mol, as well as the ionization potential of $NF_2$, $11.62_8 \pm 0.01$ eV, have been taken from Berkowitz et al. [19]. The enthalpy of formation at 0 K of $NF_3$, −30.2 ± 0.2 kcal/mol, has been obtained by correcting the enthalpy of formation at 298 K, −31.6 kcal/mol [17], for the enthalpy difference between 0 K and 298 K of $NF_3$ (taken from Ref. [23]). The enthalpy of formation of $NF_3^+$ at 0 K has been obtained combining the enthalpy of formation of $NF_3$ at 0 K with the corresponding adiabatic IP. We decided to quote both the value of 269.6 ± 0.7 kcal/mol based on the IP of $NF_3$ reported by Berkowitz et al. [19,20], 13.00 ± 0.02 eV, and the value of 268.2 ± 0.4 kcal/mol based on the IP of $NF_3$ reported by Rüede et al. [28], 12.94 ± 0.01 eV. We first note from Table 2 that, within their combined uncertainties, the G3 enthalpies of formation at 0 K of NF, 54.0 ± 0.9 kcal/mol, $NF^+$, 336.8 ± 0.9 kcal/mol, $NF_2$, 8.0 ± 0.9 kcal/mol and $NF_2^+$, 277.3 ± 0.9 kcal/mol, are in very good agreement with the experimental values. However, our calculated enthalpy of formation of $NF_3^+$, 261.7 ± 0.9 kcal/mol, significantly differs from the experimental values of 269.6 and 268.2 kcal/mol. In line with the conclusion by Ricca [15], our G3 calculations indicate that the discrepancy between the experimental and the theoretical enthalpy of formation of $NF_3^+$ arises from an appreciable difference between the experimental and the theoretical adiabatic IP of $NF_3$. In fact, whereas the G3 enthalpy of formation of $NF_3$ at 0 K, −30.2 ± 0.9 kcal/mol, practically matches the experimental value, the G3 adiabatic IP of $NF_3$, 12.63 ± 0.04 eV, is larger than the two reported experimental values by ca. 0.3–0.4 eV. It is important to note that the G3 adiabatic ionization potentials of NF and $NF_2$, 12.28 ± 0.04 and 11.65 ± 0.04 eV, practically match the experimental values of 12.26 ± 0.01 and $11.62_8 \pm$ 0.01 eV, respectively.

In conclusion, the G3 adiabatic IP of $NF_3$, 12.63 ± 0.04 eV, is practically coincident with the accurate theoretical estimate of 12.64 eV recently reported by Ricca [15] but larger than the most accurate available experimental values by ca. 0.3–0.4 eV. This reinforces the expectation that additional experimental work on the thermochemistry of ionized $NF_3$ could result in the appreciable refinement of the IP of this molecule. Conversely, if the currently accepted IP of $NF_3$ should be confirmed by further experiments, the theoretical estimate of this quantity would emerge as a challenging test case even for highly accurate computational procedures.

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