



# A computational investigation on the mechanism of the reaction between O(<sup>1</sup>D) and NF<sub>3</sub>

Paola Antoniotti <sup>a,\*</sup>, Felice Grandinetti <sup>b,1</sup>

<sup>a</sup> Dipartimento di Chimica Generale ed Organica Applicata, Università di Torino, C.so M. D'Azeglio, 48, 10125 Torino, Italy

<sup>b</sup> Dipartimento di Scienze Ambientali and Istituto Nazionale di Fisica della Materia (INFN), Unità di Viterbo, Università della Tuscia, Largo dell'Università, s.n.c., 01100 Viterbo, Italy

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## Abstract

The mechanism of the reaction between O(<sup>1</sup>D) and NF<sub>3</sub>, experimentally studied by spectroscopic techniques [V.I. Sorokin, N.P. Gritsan, A.I. Chichinin, *J. Chem. Phys.* 108 (1998) 8995], has been investigated at the Coupled Cluster level of theory in conjunction with double-zeta and triple-zeta quality basis sets. The process commences by the exoergic (105.4 kcal mol<sup>-1</sup>) formation, on the singlet surface, of the O–NF<sub>3</sub> intermediate, whose eventual dissociation into NF<sub>2</sub> and OF passes through the isomerization to F<sub>2</sub>N–OF. The energy barrier of this process, 58.8 kcal mol<sup>-1</sup>, is significantly lower than the intersystem crossing from the singlet O–NF<sub>3</sub> to the triplet O(<sup>3</sup>P) and NF<sub>3</sub> dissociation products. This is consistent with the experimental observation that, in the reaction between O(<sup>1</sup>D) and NF<sub>3</sub>, the unreactive quenching to O(<sup>3</sup>P) represents only a minor reaction channel.

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## 1. Introduction

Nitrogen trifluoride, NF<sub>3</sub>, is one of the gaseous compounds most extensively used in the electronic industry to perform etching and cleaning processes by plasma techniques [1,2]. With respect to more traditional fluorinated gases, such as CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub>, NF<sub>3</sub> offers advantages of avoiding carbon contamination residues, boosting productivity by greater than 30%, and decreasing effluent

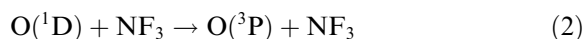
emissions by 90% [3,4]. As a matter of fact, in the last few years, the industrial demand of NF<sub>3</sub> has increased to such an extent that several leading companies have planned or already completed significant capacity expansions in the production and distribution of this substance [5,6]. This widespread industrial use of NF<sub>3</sub> stimulates questions on its conceivable environmental impact, and the atmospheric chemistry of nitrogen trifluoride has been so far investigated by Molina et al. [7]. They have found that NF<sub>3</sub> is a potent greenhouse gas, inert toward the most important tropospheric oxidants and with a global warming potential of ca. 8000 with respect to CO<sub>2</sub> (100 year time horizon). In addition, they suggested that, in the stratosphere, the photodecomposition

\* Corresponding author. Fax: +39-011-6707591.

E-mail addresses: [paola.antoniotti@unito.it](mailto:paola.antoniotti@unito.it) (P. Antoniotti), [fgrandi@unitus.it](mailto:fgrandi@unitus.it) (F. Grandinetti).

<sup>1</sup> Also corresponding author. Fax: +39-0761-357179.

of  $\text{NF}_3$  could compete with the reaction with the atomic oxygen atoms  $\text{O}(^1\text{D})$ . However, they did not investigate the latter process in further detail. More recently, Sorokin et al. [8] have used spectroscopic techniques to investigate, both for fundamental reasons and also as potential laboratory sources of FO radicals, the reactions between excited oxygen atoms  $\text{O}(^1\text{D})$  and the simple fluorides  $\text{HF}$ ,  $\text{F}_2$ ,  $\text{XeF}_2$ ,  $\text{NF}_3$ , and  $\text{CF}_4$ . They have found in particular that, at room temperature,  $\text{O}(^1\text{D})$  reacts with  $\text{NF}_3$  by two competitive processes



although the exothermic [9] fluorine atom abstraction (1) ( $\Delta H_{298} = -30 \text{ kcal mol}^{-1}$ ) resulted by far dominating (>90%) with respect to the unreactive deactivation of  $\text{O}(^1\text{D})$  to ground state oxygen atoms  $\text{O}(^3\text{P})$  ( $\Delta E[\text{O}(^1\text{D}) - \text{O}(^3\text{P})] = 45.4 \text{ kcal mol}^{-1}$ ). It has been suggested [8] that reaction (1) proceeds via formation of the intermediate collisional complex  $\text{O-NF}_3$ . The structures of  $\text{NF}_3$  and of the  $\text{NF}_3$  moiety of  $\text{O-NF}_3$  are in fact quite similar, and the ‘sticking’ of  $\text{O}(^1\text{D})$  to  $\text{NF}_3$ , which does not require significant rearrangement of atoms, is expected to be easy. Although this mechanistic proposal appears quite reasonable, neither experiments nor theoretical calculations have been performed to confirm the active role of  $\text{O-NF}_3$  in reaction (1). Therefore, stimulated by our continuing experimental and theoretical interest in the gas phase chemistry of  $\text{NF}_3$ ,  $\text{O-NF}_3$ , and other related species [10–17], we decided to undertake a computational investigation on the mechanism of the reaction between  $\text{O}(^1\text{D})$  and  $\text{NF}_3$ . The results of this study will be discussed in the present article.

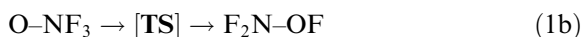
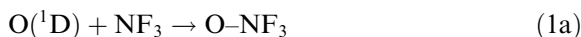
## 2. Computational details

The quantum chemical calculations have been performed using the Unix versions of the GAUSSIAN 98 [18] and the MOLPRO 2000.1 [19] sets of programs installed on a Alphaserver 1200 and a DS20E Compaq machine.

The geometries of  $\text{O-NF}_3$ ,  $\text{F}_2\text{N-OF}$ , and of the various fragments involved in reaction (1) have been first optimized by analytical-gradient techniques at the Coupled Cluster level of theory [20,21], including the contribution from double substitutions (CCD), in conjunction with the Dunning’s correlation consistent double-zeta basis set (cc-pVDZ) [22]. The transition structure connecting  $\text{O-NF}_3$  and  $\text{F}_2\text{N-OF}$  has been located, at the same computational level, using the synchronous transit-guided quasi-Newton (STQN) method [23]. The located structures were unambiguously characterized as true minima or first order saddle points on the surface by computing the corresponding CCD/cc-pVDZ harmonic frequencies, obtained by numerical differentiation of the analytical first derivatives of the CCD/cc-pVDZ total energies. The CCD/cc-pVDZ numerical force constants have been subsequently used to refine the geometries of all the investigated species at the Coupled Cluster level of theory, including the contribution from single and double substitutions. These CCSD/cc-pVDZ optimized geometries have been finally used to perform single-point calculations at the Coupled Cluster level of theory, including the contribution from single and double substitutions and an estimate of connected triples (CCSD(T)), in conjunction with the Dunning’s correlation consistent triple-zeta basis set, enlarged so to include the effect of diffuse functions (aug-cc-pVTZ). The CCD/cc-pVDZ unscaled frequencies of the investigated species were used to calculate their zero-point vibrational energies (ZPE) and the vibrational contribution to their thermal correction (TC), obtained at 298.15 K by standard statistical mechanics formulas [24]. The overall TC term has been finally obtained by adding the translational ( $3/2RT$ ) and rotational ( $RT$  or  $3/2RT$  for linear and non-linear species, respectively) contributions at this temperature. The total entropies at 298.15 K of the investigated species were obtained using the CCD/cc-pVDZ unscaled frequencies and moments of inertia. The crossing point between singlet  $\text{O-NF}_3$  and triplet  $\text{O}(^3\text{P})$  and  $\text{NF}_3$  has been located under the constraint of  $C_s$  symmetry ( $^1A'$  and  $^3A''$ , respectively), using, for the triplet species, the spin-restricted Coupled Cluster theory as implemented in MOLPRO.

### 3. Results and discussion

The results of our calculations confirm the proposal [8] that the O–NF<sub>3</sub> intermediate plays an active role in the reaction between O(<sup>1</sup>D) and NF<sub>3</sub>, and support the following sequence of reactions as the detailed mechanism of the formal fluorine-atom abstraction Eq. (1)



The connectivities of the two intermediates O–NF<sub>3</sub> and F<sub>2</sub>N–OF, and of their interconnecting transition structure TS are shown in Fig. 1, and the CCSD/cc-pVDZ optimized parameters of all the presently investigated species are listed in Table 1.

Fig. 2 shows a diagrammatic free energy profile at 298.15 K of the overall reaction (1), obtained using the theoretical total energies, thermal corrections, and total entropies reported in Table 2.

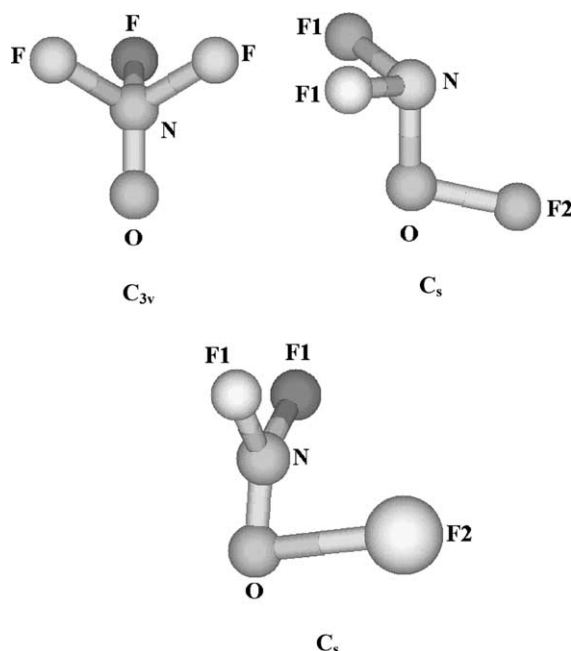


Fig. 1. Connectivities of O–NF<sub>3</sub>, F<sub>2</sub>N–OF, and their interconnecting transition structure TS.

Nitrogen trifluoride is a bifunctional base, and, under the isolated conditions of the gas phase, the ligation of charged monoatomic electrophiles such as H<sup>+</sup> and Li<sup>+</sup> occurs preferentially at the fluorine atom(s) [10,25]. On the other hand, polyatomic electrophiles such as CH<sub>3</sub><sup>+</sup> [13] and NF<sub>2</sub><sup>+</sup> [17,26] coordinate preferentially at the nitrogen atom. The interaction between NF<sub>3</sub> and neutral Lewis acids has been investigated in considerably less detail, although it is generally assumed that the ligation occurs preferentially at the nitrogen atom [27,28]. The results of our calculations on the interaction between O(<sup>1</sup>D) and NF<sub>3</sub> are in line with this expectation. In fact, despite careful searching, we did not locate any adduct arising from the coordination of the singlet oxygen atom to the fluorine atom(s) of NF<sub>3</sub>. Rather, we found that the interaction between these two moieties occurs by the barrier-free association (1a) and leads to the formation of the trifluoroamine oxide O–NF<sub>3</sub>. This compound is of great interest in the inorganic chemistry of nitrogen, and, over the years, its structure, bonding, and properties have been investigated in considerable experimental and theoretical detail [29–31]. We simply note here that our CCSD/cc-pVDZ optimized parameters are in satisfying agreement with the experimental data so far obtained by electron diffraction and microwave spectroscopy [30]. Thus, our N–O distance and F–N–O angle, calculated as 1.165 Å and 117.2°, respectively, are practically coincident with the experimental values of 1.159 ± 0.002 Å and 117.4 ± 0.6°, respectively, and the calculated N–F distance of 1.419 Å favourably compares with the experimental value of 1.432 ± 0.002 Å. In addition, at 298.15 K, the free energy change of reaction (1a), calculated as 105.4 kcal mol<sup>-1</sup> at the CCSD(T)/aug-cc-pVTZ level of theory, is in very good agreement with the experimental value of 103.5 kcal mol<sup>-1</sup>.

The second elementary step of the overall reaction (1) is the isomerization (1b) of O–NF<sub>3</sub> into the perfluorohydroxylamine F<sub>2</sub>N–OF. The structure, stability, and thermochemistry of this compound have not yet been investigated experimentally, and the only information we have comes from relatively old investigations performed at the semiempirical [32] and HF [33] level of theory. At the CCSD/cc-

Table 1

CCSD/cc-pVDZ optimized parameters (Angstroms and degrees) of the molecules and radicals involved in the reaction between O(<sup>1</sup>D) and NF<sub>3</sub> (for the labelling of the atoms, see Fig. 1)

Species	Parameter <sup>a</sup>	Species	Parameter	
O–NF <sub>3</sub> (C <sub>3v</sub> ; <sup>1</sup> A <sub>1</sub> )	N–O: 1.165 (1.159) <sup>b</sup>	F <sub>2</sub> N–OF (C <sub>s</sub> ; <sup>1</sup> A′)	N–O: 1.397	
	N–F: 1.419 (1.432) <sup>b</sup>		N–F1: 1.382	
	F–N–O: 117.2 (117.4) <sup>b</sup>		O–F2: 1.435	
	F1–N–O: 102.5			
	F1–N–F1: 101.4			
	N–O–F2: 102.3			
TS (C <sub>s</sub> ; <sup>1</sup> A′)	N–O: 1.153	NF <sub>3</sub> (C <sub>3v</sub> ; <sup>1</sup> A <sub>1</sub> )	N–F: 1.373 (1.37) <sup>c</sup>	
	N–F1: 1.336		F–N–F: 102.0 (102.4) <sup>c</sup>	
	N–F2: 2.092		N–F: 1.351 (1.353) <sup>d</sup>	
	O–F2: 1.974	NF <sub>2</sub> (C <sub>2v</sub> ; <sup>2</sup> B <sub>1</sub> )	F–N–F: 103.3 (103.2) <sup>d</sup>	
	F1–N–O: 125.8		OF (C <sub>∞v</sub> ; <sup>2</sup> Π)	O–F: 1.366 (1.354) <sup>e</sup>
	F1–N–F1: 108.3			
	N–O–F2: 79.2			
	F2–N–O: 68.0			
N–F2–O: 32.8				

<sup>a</sup> Experimental values in parenthesis.

<sup>b</sup> Taken from [30].

<sup>c</sup> Taken from M. Otake, C. Matsumura, Y. Morino, J. Mol. Spectrosc. 28 (1968) 316.

<sup>d</sup> Taken from R.D. Brown, F.R. Burden, P.D. Godfrey, I.R. Gillard, J. Mol. Spectrosc. 52 (1974) 301.

<sup>e</sup> Taken from F. Tamassia, J.M. Brown, S. Saito, J. Chem. Phys. 112 (2000) 5523.

pVDZ level of theory, the *trans* conformation of F<sub>2</sub>N–OF is characterized as a true energy minimum, with a first positive frequency of 28.5 cm<sup>-1</sup> corresponding to the rotation of the –OF moiety around the N–O bond. The length of this bond is computed as 1.397 Å and is shorter than the N–O distance of the parent H<sub>2</sub>N–OH, computed as 1.443 Å at the CCSD/cc-pVDZ level of theory (the experimental value is 1.47 Å [34]). However, overall,

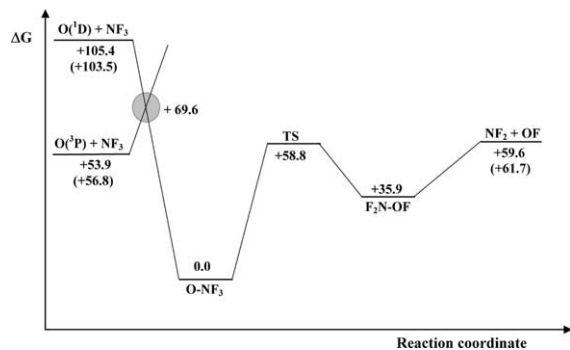


Fig. 2. Relative free energies ( $\Delta G$ , kcal mol<sup>-1</sup>), calculated at the CCSD(T)/aug-cc-pVTZ//CCSD/cc-pVDZ level of theory and 298.15 K, of the species involved in the reaction between O(<sup>1</sup>D) and NF<sub>3</sub>. Experimental values in parenthesis.

replacing hydrogen with fluorine results in an appreciable destabilization of the X<sub>2</sub>N–OX molecule (X = H or F) with respect to the interaction between the NX<sub>2</sub> and OX moieties. Thus, the experimental enthalpy change of the dissociation of H<sub>2</sub>N–OH into NH<sub>2</sub> and OH, 64.8 kcal mol<sup>-1</sup>, must be compared with the endothermicity of the dissociation reaction (1c) of F<sub>2</sub>N–OF into NF<sub>2</sub> and OF, presently computed as 34.4 kcal mol<sup>-1</sup> at the CCSD(T)/aug-cc-pVTZ//CCSD/cc-pVDZ level of theory. Combining this theoretical enthalpy change with the experimental enthalpies of formation of NF<sub>2</sub>, 10.1 kcal mol<sup>-1</sup>, and OF, 26.0 kcal mol<sup>-1</sup>, we estimate as 1.7 kcal mol<sup>-1</sup> the still experimentally unknown enthalpy of formation at 298.15 K of the F<sub>2</sub>N–OF molecule. The relatively weak interaction between the NF<sub>2</sub> and OF moieties of F<sub>2</sub>N–OF reflects also in the optimized geometry of F<sub>2</sub>N–OF, whose NF<sub>2</sub> and OF moieties show only minor differences with respect to the free NF<sub>2</sub> and OF radicals. Thus, the N–F bond distance and the F–N–F bond angle of free NF<sub>2</sub>, computed as 1.351 Å and 103.3°, respectively, are obtained as 1.382 Å and 101.4° in F<sub>2</sub>N–OF, and the O–F bond distance, 1.435 Å, is only slightly elongated with respect to

Table 2

Calculated total energies (atomic units), thermal corrections (atomic units), and total entropies ( $\text{cal mol}^{-1} \text{K}^{-1}$ ), and experimental enthalpies of formation ( $\text{kcal mol}^{-1}$ ) of the molecules and radicals involved in the reaction between  $\text{O}(^1\text{D})$  and  $\text{NF}_3$

Species	CCSD(T)/ aug-cc-pVTZ <sup>a</sup>	ZPE	TC (298.15 K)	S (298.15 K) <sup>b</sup>	H <sub>f</sub> <sup>‡</sup> (298.15 K)
O–NF <sub>3</sub>	–428.79831	0.01614	0.02026	65.8 (66.6)	–39.0
F <sub>2</sub> N–OF	–428.73539	0.01361	0.01839	73.8	
<b>TS</b>	–428.70009	0.01372	0.01829	70.7	
NF <sub>3</sub>	–353.71435	0.01080	0.01429	62.1 (62.3)	–31.6
NF <sub>2</sub>	–253.99295	0.00624	0.00929	59.5 (59.7)	10.1
OF	–174.68494	0.00313	0.00550	50.4 (51.8)	26.0
O( <sup>3</sup> P)	–74.97895		0.00142	36.4 (38.5)	59.6
O( <sup>1</sup> D)	–74.89795		0.00142	34.3	105.0

<sup>a</sup> At the CCSD/cc-pVDZ optimized geometries.

<sup>b</sup> The experimental values in parenthesis are taken from [9].

free OF, 1.366 Å. The results of our calculations indicate that replacing hydrogens with fluorines has also a significant effect on the relative stability of the X<sub>2</sub>N–OX and X<sub>3</sub>N–O isomeric structures (X = H or F). Thus, at the CCSD(T)/aug-cc-pVTZ//CCSD/cc-pVDZ level of theory and 298.15 K, F<sub>2</sub>N–OF is predicted to be less stable than O–NF<sub>3</sub>, and their free energy difference is calculated as 35.9 kcal mol<sup>–1</sup>. On the other hand, the elusive ammonia oxide O–NH<sub>3</sub> [35] is significantly less stable than the hydroxylamine H<sub>2</sub>N–OH, the energy difference between these two species being calculated as 24.8 kcal mol<sup>–1</sup> at the G2 level of theory [35].

The interconversion (1b) between the O–NF<sub>3</sub> and F<sub>2</sub>N–OF isomeric structures occurs through the transition structure **TS**, whose single imaginary frequency of 1024.4i cm<sup>–1</sup> refers to the in-plane motion of the fluorine atom, which shifts from the nitrogen of O–NF<sub>3</sub> to the oxygen of F<sub>2</sub>N–OF. From Fig. 1 and Table 1, at the CCSD/cc-pVDZ level of theory, the N–F2 and O–F2 distances of **TS**, 2.092 and 1.974 Å, respectively, are significantly elongated with respect to the N–F distance of O–NF<sub>3</sub>, 1.419 Å, and the O–F distance of F<sub>2</sub>N–OF, 1.435 Å, and the F2–N–O and N–O–F2 bond angles of **TS**, 68.0° and 79.2°, respectively, differ also appreciably from the corresponding parameters of O–NF<sub>3</sub>, 117.2°, and F<sub>2</sub>N–OF, 102.3°. This significant structural reorganization required to pass from O–NF<sub>3</sub> to **TS** reflects also in the eight of the activation barrier. Thus, at the CCSD(T)/aug-cc-pVTZ//CCSD/cc-pVDZ level of theory and 298.15 K, the free energy difference between **TS** and

O–NF<sub>3</sub> is predicted as large as 58.8 kcal mol<sup>–1</sup>. However, we note from Fig. 2 that the eight of the activation barrier of the reaction (1b) is significantly lower than the exoergicity of the association reaction (1a) between O(<sup>1</sup>D) and NF<sub>3</sub>, 105.4 kcal mol<sup>–1</sup>. Thus, the probably most important finding from our calculations is that, in the reaction between excited singlet oxygen atoms and nitrogen trifluoride, the energy gained in the initial formation of the O–NF<sub>3</sub> intermediate is by far exceedingly larger than the barrier for its isomerization to F<sub>2</sub>N–OF. In addition, from Fig. 2, since the free energy of the NF<sub>2</sub> and OF fragments is practically coincident with **TS** (we note here that our computed free energy difference between NF<sub>2</sub> and OF and O–NF<sub>3</sub>, 59.0 kcal mol<sup>–1</sup>, compares quite favourably with the experimental value of 61.7 kcal mol<sup>–1</sup>), it is reasonable to assume that a significant fraction of the excited O–NF<sub>3</sub> complexes which undergo the isomerization to F<sub>2</sub>N–OF are also in principle able to eventually dissociate according to reaction (1c). Therefore, our calculations provide supporting evidence for the previous proposal by Sorokin et al. [8] on the active role of the O–NF<sub>3</sub> intermediate in the experimentally observed formation of NF<sub>2</sub> and OF from the reaction between O(<sup>1</sup>D) and NF<sub>3</sub>.

As already pointed out in Section 1, it has been experimentally observed [8] that only a minor fraction (less than 10%) of the collisions between O(<sup>1</sup>D) and NF<sub>3</sub> eventually result in the unreactive deactivation to O(<sup>3</sup>P). If one assumes that the O–NF<sub>3</sub> intermediate plays an active role also in

reaction (2), a simple conceivable explanation for the low efficiency of this process is to assume that the barrier for the crossing of the singlet O–NF<sub>3</sub> to the triplet O(<sup>3</sup>P) and NF<sub>3</sub> is appreciably higher in energy than the transition structure **TS** on the singlet potential energy surface. In order to characterize the seam of the crossing, we scanned, under the constraint of the C<sub>s</sub> symmetry (<sup>1</sup>A' and <sup>3</sup>A'', respectively), the CCSD/cc-pVDZ potential energy surface for the interaction between O(<sup>1</sup>D, <sup>3</sup>P) and NF<sub>3</sub>. On the singlet surface, we varied the N–O distance of O–NF<sub>3</sub> from the minimum value of 1.165 Å to a maximum value of 2.4 Å, and, for any N–O distance, we fully optimized the geometry of the –NF<sub>3</sub> part. The total energy of the O–NF<sub>3</sub> complex was found to increase regularly, and no energy barriers emerged for the dissociation into O(<sup>1</sup>D) and NF<sub>3</sub>. On the triplet surface, we approached the O(<sup>3</sup>P) to the nitrogen atom of NF<sub>3</sub>, and varied the N–O distance of the O–NF<sub>3</sub> complex from an initial value of 2.4 Å to a final value of 1.4 Å. For any N–O distance, the geometry of the –NF<sub>3</sub> part was fully optimized, and the energy of the complex was found to increase regularly, with no evidence for any collisional complex between O(<sup>3</sup>P) and NF<sub>3</sub>. The two potential energy curves were found to cross at a N–O distance of 1.8 Å, and the crossing structure resulted of pseudo-C<sub>3v</sub> symmetry, with a N–F distance and a F–N–O angle of 1.373 Å and 115.8°, respectively. In addition, at the CCSD/cc-pVDZ level of theory, this crossing point resulted to be 80.2 kcal mol<sup>-1</sup> higher in energy than the singlet O–NF<sub>3</sub>, and, most importantly, less stable than the transition structure **TS** by 10.8 kcal mol<sup>-1</sup>. Therefore, in line with the experimental observation, it is reasonable to assume that, if the barrier-free association between O(<sup>1</sup>D) and NF<sub>3</sub> leads initially to the formation of the O–NF<sub>3</sub> intermediate, the subsequent isomerization to F<sub>2</sub>N–OF on the singlet surface is by far dominating with respect to the intersystem crossing to the triplet surface. We note here that the expensive character of the involved calculations prevented the location of the crossing point between the singlet O–NF<sub>3</sub> and the triplet O(<sup>3</sup>P) and NF<sub>3</sub> at the CCSD(T)/aug-cc-pVTZ level of theory. However, if one assumes that the energy difference be-

tween this structure and the transition structure **TS** parallels the value obtained at the CCSD/cc-pVDZ level of theory, 10.8 kcal mol<sup>-1</sup>, the energy required to overcome the crossing point from the singlet O–NF<sub>3</sub> to the triplet O(<sup>3</sup>P) and NF<sub>3</sub> is estimated, at the CCSD(T)/aug-cc-pVTZ level of theory, as 69.6 kcal mol<sup>-1</sup>. It is of interest to note that, at the CCSD(T)/6-311G(d,p) level of theory, the energy for the crossing from the singlet O–NH<sub>3</sub> to the triplet O(<sup>3</sup>P) and NH<sub>3</sub> has been estimated as 66.1 kcal mol<sup>-1</sup> [35].

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