Nitrogen Trifluoride as a Bifunctional Lewis Base: Implications for the Adsorption of NF_3 on Solid Surfaces

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The structure, stability, and thermochemistry of isomeric adducts between NF_3 and the Lewis acids $BH_{3-n}F_n$ (n = 0–3) have been investigated at the coupled-cluster and at the Gaussian-3 (G3) level of theory. At the CCD/cc-pVDZ level both the nitrogen- and the fluorine-coordinated structures of all $BH_{3-n}F_n$–(NF_3) (n = 0–3) adducts were characterized as true minima on the potential energy surface, thus providing the first theoretical evidence for the behavior of NF_3 as a bifunctional Lewis base when interacting with neutral Lewis acids. At the G3 level, and 298.15 K, including the contribution of the entropy term, the H_3B–NF_3 adduct is predicted to be more stable than H_3B–F–NF_2 by 4.3 kcal mol^{-1}; this free energy difference is 3.7 kcal mol^{-1} at the CCSD(T)/cc-pVTZ//CCD/cc-pVDZ level of theory. Conversely, at the latter computational level, the fluorine-coordinated isomers of the BH_2F–(NF_3), BHF_2–(NF_3), and BF_3–(NF_3) adducts are practically degenerate with the nitrogen-coordinated ones. $BH_{3-n}F_n$–(NF_3) (n = 0–3) complexes feature typical bond dissociation energies of ca. 1–2 kcal mol^{-1}, and are predicted to be thermodynamically stable only at low temperatures. However, the appreciable influence of the basis set superposition error (BSSE) prevents a quantitative assessment of these small computed dissociation energies. Finally, we briefly discuss the implications of our calculations for the adsorption of NF_3 on solid surfaces.

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Introduction

Nitrogen trifluoride, NF_3 (gas), is extensively used by the electronic industry in etching and cleaning processes,[1,2] e.g. to remove contaminant residues from chemical vapor deposition chambers and in plasma etching and reactive-ion etching of various materials.[3–8] Compared with more traditional fluorinated gases such as CF_4 and C_2F_6, NF_3 offers advantages of a shorter atmospheric lifetime and avoids carbon contamination residues, thereby boosting productivity by > 30% and decreasing effluent emissions by ca. 90%.[1,2] Thus, the recent industrial use of NF_3 has increased remarkably, stimulating considerable experimental and theoretical interest in the interaction of NF_3 and NF_3-based plasmas with material surfaces.[9–22] In particular, a complete understanding of the etching process requires details of the geometric and electronic structure of NF_3 adsorbed on a solid surface. When interacting with Si(001), NF_3 undergoes slow dissociative chemisorption, with spontaneous and competitive formation of Si–N and Si–F bonds.[11,20a,21] Similarly, the interaction of NF_3 with Ru(0001) leads, at least partially, to molecular decomposition on the surface, leaving F, NF or NF_2 fragments, and it has been suggested that all the NF_x moieties (x = 1–3) are oriented exclusively with their nitrogen end toward the metal.[3] Conversely, an investigation[17] on the thermal, electron, and photon-stimulated chemistries of NF_3 adsorbed on Pt(111) at low temperature revealed that adsorption and thermal desorption of NF_3 is molecular, with no evidence for dissociation. This suggests that NF_3 is very weakly held and behaves like a physisorbed species. Interestingly, the available experimental evidence points to different positions of NF_3 and orientations of its dipole moment with respect to the surface and the neighboring molecules. Thus, details of the possible orientation of NF_3 with respect to a metal surface still pose stimulating experimental and theoretical questions. From the fundamental point of view, a first step is to investigate the still unexplored behavior of NF_3 as a bifunctional Lewis base when interacting with a *neutral* Lewis acid. Experimental and theoretical investigations on the ligation of NF_3 to ionic Lewis acids such as H^+,[23,24] Li^+,[25,26] CH_3^+,[27,28] and NF_2^+ [29,30] clearly indicate that both the M–NF_3^+ and MF–NF_2^+ isomeric structures (M = H, Li, CH_3, and NF_2) can, in principle, exist as distinguishable species in the gas phase, and that the nature of the M^+ electrophile has a substantial effect on both the relative stability of the two isomers and on the their energy difference. Conversely, experimental and theor-

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etical studies performed on complexes between NF_3 and neutral Lewis acids, such as BH_3,[31−34] BH_2F,[34] BHF_2,[34] BF_3,[31,33−36] BCl_3,[36] AlH_3,[37] $Ga(CH_3)_3$,[38] HF,[39] and ClF,[40] have invariably assumed that nitrogen trifluoride behaves exclusively as a nitrogen donor that can form adducts such as H_3B-NF_3, F_3B-NF_3, and H_3Al-NF_3. However, in keeping with the behavior of bifunctional base toward ionic Lewis acids, NF_3 could also interact with neutral Lewis acids as a fluorine base, forming adducts such as $H_3B-F-NF_2$, $F_3B-F-NF_2$, and $H_3Al-F-NF_2$. The structure and stability of such complexes appears to be unexplored. Therefore, stimulated by our continuing experimental and theoretical interest in the chemistry of nitrogen trifluoride and closely related neutral and ionic species,[24,26,28,30,41−51] we undertook a detailed theoretical investigation on the structure and stability of the isomeric adducts arising from the ligation of NF_3 to BH_3, BH_2F, BHF_2 and BF_3. The results discussed here confirm the expectation that, even with neutral Lewis acids, NF_3 can behave not only as a nitrogen but also as a fluorine base, forming isomeric structures of comparable stability. Concerning the interaction with solid surfaces, these findings support the suggestion that the molecular physisorption of NF_3 may occur by different orientations, and that this adsorption could be critically affected by the nature of the surface and the strength of the interaction.

Computational Details

Quantum chemical calculations have been performed using the Unix versions of the GAUSSIAN 98[52] and MOLPRO 2000.1[53] sets of programs installed on an Alphaserver 1200 and a DS20E Compaq machine.

Geometries of the investigated species have been optimised by analytical-gradient techniques at the coupled-cluster level of theory,[54,55] including the contribution from double substitutions (CCD), using the Dunning's correlation consistent double-zeta basis set (cc-pVDZ).[56] The located structures were unambiguously characterized as true minima 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 of the $BH_3-(NF_3)$ and the $BF_3-(NF_3)$ adducts were subsequently used to refine their geometries at the CCSD/cc-pVDZ level. For all investigated species, CCD/cc-pVDZ optimised geometries were 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), using the cc-pVTZ basis set. The CCD/cc-pVDZ unscaled frequencies were used to calculate the zero-point vibrational energies (ZPE) of the investigated species and the vibrational contribution to their thermal correction (TC), obtained at 298.15 K by standard statistical mechanics formulas.[57] The overall TC term was finally obtained by adding the translational (1.5 *RT*) and rotational (*RT* or 1.5 *RT* for linear and non-linear species, respectively) contributions at this temperature. Total entropies at 298.15 K of the investigated species were obtained using the CCD/cc-pVDZ unscaled frequencies and moments of inertia. The influence of the basis set superposition error (BSSE) on the dissociation energies calculated at the CCSD(T)/cc-pVTZ//CCD/cc-pVDZ level was estimated using the full counterpoise method by Boys and Bernardi.[58]

Total energies of the $BH_3-(NF_3)$ complexes were also obtained using the G3 procedure of Pople and co-workers.[59] This composite method consists of a sequence of well-defined single-point calculations, at the MP2(fc), MP4(fc), and QCISD(T) levels of theory, used to calculate, according to an additivity scheme, the total energy of a species at its MP2(full)/6-31G(d) optimised geometry ("full" and "fc" denote the inclusion or not of the valence electrons for the calculation of the correlation energies). A small higher-level empirical term is also included, which depends on the number of valence electron pairs. The ZPE is calculated at the HF/6-31G(d) level and scaled by 0.8929, and the G3 energies at 0 K, G3(0 K), corrected at 298.15 K by adding the thermal contribution calculated using the scaled HF/6-31G(d) frequencies for the vibrations in the harmonic approximation and the classical approximation

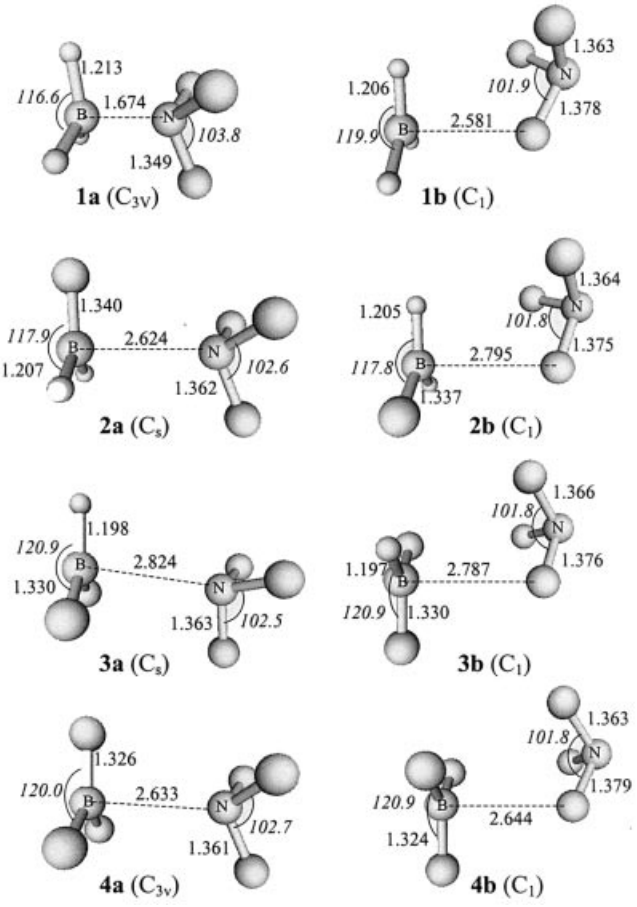

Figure 1. CCD/cc-pVDZ optimised geometries [Å and °] of the $BH_{3-n}F_n-(NF_3)$ ($n = 0-3$) isomeric structures (largest and smallest unlabeled circles are fluorine and hydrogen atoms, respectively)

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for translation (1.5 *RT*) and rotation (*RT* or 1.5 *RT* for linear and non-linear species, respectively). A further *RT* term is added to convert the G3(298.15 K) total energies into G3 enthalpies. The 6-31G(d), 6-31+G(d), and 6-31G(2df,p) basis sets standard in Gaussian 98 were used with six Cartesian d-functions, while the G3large basis set, downloaded from the website suggested in ref.[59], uses five "pure" d-functions. Both the 6-31G(2df,p) and the G3large basis sets use a set of "pure" seven f-functions.

Results and Discussion

Structure, Stability, and Thermochemistry of the $BH_{3-n}F_n-(NF_3)$ ($n = 0-3$) Isomeric Structures

To investigate the conceivable behavior of nitrogen trifluoride as a bifunctional Lewis base when interacting with neutral Lewis acids we searched for distinct isomeric structures arising from the ligation of $BH_{3-n}F_n$ ($n = 0-3$) to the N and the F atom(s) of NF_3. Starting from different initial geometries, we located the $BH_{3-n}F_n-NF_3$ and $BH_{3-n}F_n-F-NF_2$ complexes **1a** and **1b** ($n = 0$), **2a** and **2b** ($n = 1$), **3a** and **3b** ($n = 2$), and **4a** and **4b** ($n = 3$) as true energy minima on the CCD/cc-pVDZ potential energy surface. Their optimised structures (Figure 1) and absolute and relative energies, at the CCSD(T)/cc-pVTZ//CCD/cc-pVDZ level of theory, (Table 1) are given here. The energy, enthalpy and free energy changes of the reaction in Equation (1) for the various isomeric structures are reported in Table 2.

$$BH_{3-n}F_n-(NF_3) \rightarrow BH_{3-n}F_n + NF_3\ (n = 0\text{-}3) \quad (1)$$

For comparative purposes, the geometries of the complexes **1a**, **1b**, **4a**, and **4b** were refined at the CCSD/cc-pVDZ level, but we found only negligible differences with respect to the CCD/cc-pVDZ optimised structures. The geometries of **1a** and **1b** were also optimised at the CCD/aug-cc-pVDZ level of theory, but, with respect to the CCD/cc-pVDZ parameters, the largest variations were only about 0.5° in the bond angles and about 0.05 Å in the bond lengths.

Table 2. CCSD(T)/cc-pVTZ//CCD/cc-pVDZ dissociation energies (ΔE), enthalpies (ΔH), and free energies (ΔG) of $BH_{3-n}F_n-(NF_3)$ isomeric structures into $BH_{3-n}F_n$ and NF_3 ($n = 0-3$) [kcal mol^{-1}] (for connectivities of the species, see Figure 1)

Species	ΔE (0 K)[a][b]	ΔH (298.15 K)[a][b]	ΔG (298.15 K)[a][b]	BSSE
1a	8.7 (9.4)	9.9 (10.6)	−2.4 (−0.7)	3.5
1b	1.2 (1.2)	1.1 (0.9)	−6.0 (−5.0)	2.0
2a	1.0	0.6	−6.1	1.2
2b	1.2	0.7	−5.7	1.9
3a	1.2	0.5	−5.9	1.1
3b	1.5	0.8	−6.5	2.0
4a	1.8	1.1	−6.3	1.4
4b	2.0	1.3	−6.8	2.3

[a] Not including the BSSE. [b] G3 values given in parentheses.

As with all previous theoretical investigations on the geometric and electronic structure of the H_3B-NF_3 complex **1a**,[31−34] the CCD/cc-pVDZ optimised geometry points to an n-donor−p-acceptor complex, with partial electron transfer from the N atom of NF_3 to the B atom of BH_3. The N−F bond length of free NF_3, computed as 1.368 Å at the CCD/cc-pVDZ level of theory (experimental value is 1.365 Å[60]), reduces by 0.019 Å, whereas the B−H distance of free BH_3, computed as 1.207 Å at the CCD/cc-pVDZ level of theory, increases by 0.006 Å. In addition, the $-BH_3$ moiety of **1a** deviates slightly from planarity, and the F−*N*−F angle is larger than that of free NF_3 by 1.7°. At the CCSD(T)/cc-pVTZ//CCD/cc-pVDZ level, the energy changes obtained at 0 K and the enthalpy change at 298.15 K of the reaction according to Equation (1) are, for isomer **1a**, 8.7 and 9.9 kcal mol^{-1}, respectively. The inclusion of the appreciable contribution of the entropy term leads to a free-energy change at 298.15 K of −2.4 kcal mol^{-1}, and the still experimentally unobserved complex **1a**

Table 1. CCSD(T)/cc-pVTZ total energies [atomic units], thermal corrections [atomic units], and total entropies [cal mol^{-1} K^{-1}] of the $BH_{3-n}F_n-(NF_3)$ ($n = 0-3$) isomeric structures (for connectivities of the species, see Figure 1)

Species	CCSD(T)/cc-pVTZ[a]	ZPE[b]	*TC* (298.15 K)[b]	*S* (298.15 K)[c]	ΔE (0 K)[d]	ΔG (298.15 K)[d]
1a	−380.23837	0.04425	0.00527	70.2	0.0	0.0
1b	−380.22159	0.03934	0.00750	87.6	+7.5 (+8.2)	+3.7 (+4.3)
2a	−479.43833	0.03533	0.00795	94.9	0.0	0.0
2b	−479.43835	0.03495	0.00811	95.7	−0.3	−0.4
3a	−578.66098	0.02991	0.00865	101.1	0.0	0.0
3b	−578.66151	0.02994	0.00855	97.9	−0.3	+0.6
4a	−677.87454	0.02436	0.00899	102.3	0.0	0.0
4b	−677.87472	0.02426	0.00898	100.1	−0.2	+0.5
BH_3	−26.53739	0.02644	0.00288	47.3		
BH_2F	−125.75496	0.02286	0.00292	53.2		
BHF_2	−224.97804	0.01819	0.00312	58.5		
BF_3	−324.19061	0.01265	0.00347	63.0		
NF_3	−353.68018	0.01080	0.00349	64.2		

[a] At CCD/cc-pVDZ optimised geometries. [b] Based on CCD/cc-pVDZ harmonic frequencies. [c] Based on CCD/cc-pVDZ harmonic frequencies and moments of inertia. [d] G3 values given in parentheses.

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is predicted to dominate the mixture at equilibrium below ca. −33°C. The energy, enthalpy, and free-energy change of the reaction according to Equation (1) for isomer **1a** were also calculated using the G3 procedure. This method usually furnishes thermochemical data that are as accurate as ca. 2 kcal mol^{-1}.[59] However, the absence of compounds similar to those studied here in the G3 data-base suggests caution in assuming that this "standard" level of accuracy will be obtained here. However, the G3 data agree well with those obtained at the CCSD(T)/cc-pVTZ//CCD/cc-pVDZ level of theory (Table 2), and so we used only the latter approach to calculate the thermochemistry of the more complex $BH_{3-n}F_n-(NF_3)$ ($n = 1-3$) isomeric structures. We note also that, for isomer **1a**, both the CCSD(T)/cc-pVTZ//CCD/cc-pVDZ and the G3 values of ΔE at 0 K of the reaction according to Equation (1) are in good agreement with those previously obtained[33] at the MP2/6-31G(d) and at the B3LYP/6-31G(d) computational levels (8.9 and 9.9 kcal mol^{-1}, respectively).

The C_1-symmetry structure **1b** arises from the ligation of the boron atom of BH_3 with one of the fluorine atoms of NF_3 and its characterization as a true energy minimum on the CCD/cc-pVDZ potential energy surface provides the first theoretical evidence for the behavior of NF_3 as a bifunctional Lewis base when interacting with a *neutral* Lewis acid. Compared with the nitrogen-coordinated isomer **1a**, the optimised geometry of **1b** suggests a much weaker interaction between the two BH_3 and NF_3 building moieties. Thus, the B−F bond length results as large as 2.581 Å, and the other optimised parameters, are quite similar to those predicted for free BH_3 and NF_3. Consistently, from Table 2, the CCSD(T)/cc-pVTZ//CCD/cc-pVDZ energy change at 0 K and the enthalpy change at 298.15 K of the reaction according to Equation (1) are obtained for isomer **1b** as 1.2 and 1.1 kcal mol^{-1}, respectively, and the corresponding free energy change at 298.15 K results as −6.0 kcal mol^{-1}. Therefore, this complex is predicted to be dominant in the equilibrium mixture at temperatures lower than ca. −227 °C. At 0 K, isomer **1a** is predicted to be more stable than **1b** by 7.5 kcal mol^{-1} at the CCSD(T)/cc-pVTZ//CCD/cc-pVDZ level of theory and by 8.2 kcal mol^{-1} at the G3 level. However, consistent with the character of loosely bound species of **1b**, at 298.15 K the free energy difference with **1a** reduces to 3.7 kcal mol^{-1} at the CCSD(T)/cc-pVTZ//CCD/cc-pVDZ level of theory, and to 4.3 kcal mol^{-1} at the G3 level.

The nitrogen-coordinated isomers **2a**, **3a**, and **4a** and the fluorine-coordinated isomers **2b**, **3b**, and **4b** of the adducts between NF_3 and the fluorinated Lewis acids BH_2F, BHF_2, and BF_3 reveal minima on the CCD/cc-pVDZ potential energy surface, which is consistent with the results for $BH_3-(NF_3)$ complexes. This provides additional positive evidence for NF_3 having the character of a bifunctional Lewis base when interacting with neutral Lewis acids. In addition, Figure 1 and Tables 1 and 2 clearly indicate that, on passing from BH_3 to BH_2F, BHF_2, and BF_3, the structure and stability of the $BH_{3-n}F_n-(NF_3)$ ($n = 1-3$) complexes are appreciably affected. Thus, the nitrogen-coordinated structures **2a**, **3a**, and **4a** feature B−N distances that are remarkably longer than for **1a**, and the parameters of the BH_2F, BHF_2, BF_3, and NF_3 moieties are practically coincident with the geometries computed for the free molecules.[61] This is consistent with the weak interaction energies computed between the BH_2F, BHF_2, BF_3, and NF_3 building blocks. At the CCSD(T)/cc-pVTZ//CCD/cc-pVDZ level, ΔE at 0 K for the reaction according to Equation (1) is 1.0, 1.2 and 1.8 kcal mol^{-1} for complexes **2a**, **3a** and **4a**, respectively. The value for **4a** has been computed as 3.0 kcal mol^{-1} at the MP2/6-31G(d) level of theory[33,35] and 1.3 kcal mol^{-1} at the B3LYP/6-31G(d) level.[33] Therefore, passing from BH_3 to BH_2F, BHF_2, and BF_3, the stability of the nitrogen-coordinated isomers of $BH_{3-n}F_n-(NF_3)$ ($n = 0-3$) complexes is drastically reduced. Figure 1 and Table 2 indicate, however, that, on passing from $H_3B-F-NF_2$ isomer **1b** to the analogous fluorine-coordinated structures **2b**, **3b**, and **4b**, the B−F bond lengths are only slightly elongated, and the geometry of the $-NF_3$ moiety remains essentially unaltered. The stability of the four complexes is consistently quite similar and, in particular, at the CCSD(T)/cc-pVTZ//CCD/cc-pVDZ level of theory, ΔE at 0 K for the reaction according to Equation (1), computes as 1.2 kcal mol^{-1} for complexes **1b** and **2b**, 1.5 kcal mol^{-1} for **3b**, and 2.0 kcal mol^{-1} for **4b**. Therefore, whereas the nitrogen-coordinated isomer **1a** of the $BH_3-(NF_3)$ complex is appreciably more stable than the fluorine-coordinated isomer **1b**, the energy difference between the nitrogen- and the fluorine-coordinated isomers of the $BH_2F-(NF_3)$, $BHF_2-(NF_3)$, and $BF_3-(NF_3)$ adducts is considerably smaller. In particular (Table 1), the fluorine-coordinated structures **2b**, **3b**, and **4b** are predicted to be practically degenerate with the nitrogen-coordinated structures **2a**, **3a**, and **4a**. This conclusion is not essentially affected by inclusion of the thermal and entropy contributions at room temperature. Therefore, the present calculations indicate not only that NF_3 could behave as a bifunctional Lewis base when interacting with a neutral Lewis acid, but also that the fluorine-coordinated isomer could be degenerate or even thermodynamically more stable than the nitrogen-coordinated one.

Generally speaking, the interaction between NF_3 and the boranes is very weak and the computed energy changes of the reaction according to Equation (1) could be, in principle, significantly affected by the BSSE. Although the use of the counterpoise method is not undisputed,[62] we employed it to appreciate the influence of the BSSE on our CCSD(T)/cc-pVTZ//CCD/cc-pVDZ interaction energies. The obtained values (Table 2) amount to 3.5 kcal mol^{-1} for isomer **1a** and range around 1.5 kcal mol^{-1} for the other $BH_{3-n}F_n-(NF_3)$ adducts ($n = 0-3$). This confirms that, at least in percentage terms, the BSSE should significantly affect the computed interaction energies of our complexes. Nevertheless, it does not alter the essential conclusions from our calculations, although it suggests caution in the quantitative assessment of our computed interaction energies.

None of the presently investigated $BH_{3-n}F_n-(NF_3)$ adducts ($n = 1-3$) has been experimentally observed. From

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Table 2, the free energy change of the reaction according to Equation (1) for complexes **2a**−**4a** and **2b**−**4b** is invariably predicted to be around −6 kcal mol^{-1}, and all these species should dominate the equilibrium mixtures at well below −200 °C. Interestingly, it has been reported[36] that NF_3 and BF_3 undergo weak association below −125 °C, but the heat of dissociation was so small that a true equilibrium expression was unobtainable.

Nitrogen trifluoride is firmly established as a much weaker Lewis base than ammonia.[63] Comparison of our results on $BH_{3-n}F_n$−(NF_3) adducts (n = 0−3) with the previously investigated $BH_{3-n}F_n$−NH_3 complexes (n = 0−3)[32−34,64] fully confirms this expectation. We note in particular that, at the MP2/TZ2P level of theory,[64] the B−N distance of the F_3B−NH_3 complex is 1.678 Å, which is much shorter than the F_3B−NF_3 of complex **4a**, and the bond energy of F_3B−NH_3 amounts to more than 20 kcal mol^{-1}.

Implications for the Adsorption of NF_3 on Solid Surfaces

As noted in the Introduction, the present theoretical investigation on the conceivable behavior of NF_3 as a bifunctional Lewis base was stimulated by a study on the thermal, electron, and photon-stimulated chemistry of nitrogen trifluoride adsorbed on solid Pt(111).[17] All the peaks observed in the temperature-programmed desorption spectra of adsorbed NF_3 lie below 70 K − suggesting that this molecule is very weakly held and behaves like a physisorbed species. In addition, the available experimental evidence points to different positions of NF_3 and orientations of its dipole moment with respect to the surface and the neighboring molecules. Our calculations provide supporting, although indirect, evidence for conceivably different orientations of NF_3 ligated to a solid surface. Thus, when interacting with the neutral Lewis acids $BH_{3-n}F_n$ (n = 0−3), NF_3 may undergo not only ligation by nitrogen but also by fluorine, leading to isomeric structures that are practically degenerate, especially for the weakest Lewis acids, BH_2F, BHF_2, and BF_3. Although our investigated $BH_{3-n}F_n$−(NF_3) complexes (n = 0−3) are much too simple to be effective models to mimic the interaction of NF_3 with a solid surface, if one perceives the fixation of NF_3 to Pt(111) as an interaction as weak as that occurring in our investigated adducts, it is reasonable to assume that it occurs not only by the nitrogen but also by the fluorine atom(s). Of course, for solids other than platinum, the possible molecular adsorption of NF_3 by different orientations should be critically affected not only by the nature of the surface but also by the strength of the interaction. Due to the widespread industrial use of nitrogen trifluoride in the treatment of solid surfaces, a more detailed investigation of these aspects could be of experimental and theoretical interest.

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