

Is There an Entrance Complex for the F+NH<sub>3</sub> Reaction?Hao Feng,<sup>\*,[a]</sup> Weiguo Sun,<sup>[a]</sup> Yaoming Xie,<sup>[b]</sup> and Henry F. Schaefer III<sup>\*,[b]</sup>*Dedicated to Professor Yuan T. Lee on the occasion of his 75th birthday*

**Abstract:** Challenges associated with the theoretical and experimental kinetics of the F+NH<sub>3</sub>→HF+NH<sub>2</sub> reaction suggest the need for a more-precise potential surface. We have investigated the reactants and the products of the reaction, as well as the transition state and two complexes, with rather rigorous ab initio methods. The F·····NH<sub>3</sub> complex existing in the entrance valley

is predicted to lie 13.7 kcal mol<sup>-1</sup> below the reactants. A small classical barrier of 2.0 kcal mol<sup>-1</sup> separates this entrance well from products HF+NH<sub>2</sub>. These results explain the observation by Persky

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of unprecedented inverse temperature dependence for the F+NH<sub>3</sub> rate constants. The strong hydrogen-bonded complex FH·····NH<sub>2</sub> exists in the exit valley, and with a binding energy of 9.9 kcal mol<sup>-1</sup> relative to separated products. The vibrational frequencies of all stationary points are predicted with the CCSD(T)/aug-cc-pVQZ method.

## Introduction

After the H+H<sub>2</sub> reaction,<sup>[1]</sup> the F+H<sub>2</sub> system is probably the best understood of all chemical reactions.<sup>[2–6]</sup> The experiments of Y. T. Lee and co-workers<sup>[4–6]</sup> were singularly important in the characterization of the F+H<sub>2</sub> reaction. For molecular systems larger than A+BC, both the potential energy hypersurfaces and reaction dynamics are necessarily more complicated. This is certainly the case for the F+NH<sub>3</sub> reaction, the subject of this research. Although F+NH<sub>3</sub>→HF+NH<sub>2</sub> shares the substantial exothermicity of F+H<sub>2</sub>, other features (for example, possible entry and exit complexes) add significant challenges compared to what is known about the prototype F+H<sub>2</sub> reaction.

The reaction of a fluorine atom with an ammonia molecule is particularly important in understanding the dynamics of atom-molecule reactions in which a long-lived exit complex may play a special role.<sup>[7]</sup>



However, relatively few experimental and theoretical studies have been devoted to such reactions.<sup>[7–18]</sup> Based on infrared chemiluminescence studies, in the 1980s Sloan and co-workers reported the vibrational energy partitioning in the reaction of F atoms with NH<sub>3</sub> and ND<sub>3</sub>.<sup>[8–10]</sup> They found that the reaction gave a non-inverted product, HF, and that the lower HF vibrational levels were preferentially occupied. In 1987, Wategaonkar and Setser<sup>[14]</sup> determined nascent HF vibrational distributions from the infrared chemiluminescence in a fast-flow reactor and found no HF in high vibrational levels. Based on their infrared and EPR spectroscopic studies, in 2000 Wight, Misochko, and co-workers<sup>[7,16]</sup> observed the intermediate complex FH·····NH<sub>2</sub> for the first time. To account for non-inverted HF state distribution, they assumed that a long-lived exit complex was formed during the reaction. In 2007, Persky<sup>[18]</sup> determined experimental rate constants for the F+NH<sub>3</sub> reaction. The reported kinetic results may indicate an intermediate complex in the entrance valley of the potential energy surface, in addition to the strong hydrogen-bonded intermediate complex between the products in the exit valley.

As suggested above, the most important recent F+NH<sub>3</sub> experimental paper<sup>[18]</sup> is that of Persky (2007). Persky used a discharge-flow mass spectroscopic method to measure rate constants in the temperature range 276–327 K for F+NH<sub>3</sub>→HF+NH<sub>2</sub>. Persky reported an inverse temperature dependence that is “significantly stronger than what has been re-

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ported until now for any other reaction". Persky's result does not agree with the 1983 paper of Walther and Wagner,<sup>[19]</sup> who reported a conventional temperature dependence. Recent observations<sup>[20]</sup> of inverse temperature dependence have been understood<sup>[21]</sup> in terms of entrance channel complexes (intermediates). Thus the existence or nonexistence of a  $F\cdots NH_3$  complex becomes an important issue.

The first ab-initio study of this reaction was performed by Leroy and co-workers in 1985<sup>[11]</sup> at the UHF/6-31G level. Using MP2/6-311G\*\* and CISD/6-311G\*\* methods, two years later J. D. Goddard et al.<sup>[13]</sup> studied both the  $F+NH_3$  and  $F+NH_2$  reactions. They found low vibrational excitation of HF for the  $NH_3$  reaction, compared to the  $NH_2$  reaction. The hydrogen-bonded complex  $FH\cdots NH_2$  exists in the exit channel, and the MP2 binding energy including zero-point vibrational energy corrections was predicted to be 8.1 kcal mol<sup>-1</sup>. In contrast, in 2000, Misochko et al.<sup>[16]</sup> reported a 12.3 kcal mol<sup>-1</sup> binding energy for  $FH\cdots NH_2$  with density functional theory. However, only the reactants, products, and the  $FH\cdots NH_2$  complex were studied in the above theoretical studies, and the search for the transition state was uneventful. In 1997, Espinosa-García and Corchado<sup>[15]</sup> employed a semi-empirical potential-energy surface to study the kinetics of the  $F+NH_3$  reaction by the variational transition state theory method. Their attempt to find the transition state by means of ab-initio methods yielded a similar negative result. Therefore, they adopted the properties of the hydrogen-bonded complex  $FH\cdots NH_2$  and the absence of a transition state as reference data to parameterize their new potential surface. However, their rate constant  $k_{F+NH_3}$  at 298 K is one order of magnitude lower than the latest experimental result.<sup>[18]</sup> Thus, the semi-empirical potential energy surface with no saddle-point supposed by Espinosa-García and Corchado may not be entirely reliable.

The diversity of previous theoretical and experimental results suggests that a more accurate potential energy surface may be needed. Herein, we report a theoretical investigation of all stationary points of the  $F+NH_3$  reaction, using high level coupled cluster CCSD(T) methods.

## Theoretical Methods

The equilibrium geometries of the reactants (F and  $NH_3$ ), products (HF and  $NH_2$ ), intermediate complexes ( $F\cdots NH_3$  and  $FH\cdots NH_2$ ), and the transition state are optimized using single and double excitation coupled cluster theory with perturbative triples [CCSD(T)].<sup>[22–24]</sup> Two core orbitals are frozen (doubly occupied) in all our computations. The CCSD(T) method was used with the Dunning augmented correlation-consistent quadruple zeta (aug-cc-pVQZ) basis sets,<sup>[25]</sup> denoted as (13s7p4d3f2g/6s5p4d3f2g) for nitrogen and fluorine, and (7s4p3d2f/5s4p3d2f) for hydrogen. Restricted Hartree-Fock reference wave functions (RHF or ROHF) were always employed as the zeroth-order description of the electronic structure. For all open-shell systems,

i.e., the F atom,  $NH_2$ , the complexes, and the transition state, the ROHF-UCCSD(T) method<sup>[26–28]</sup> was used, where the coupled cluster energies were computed with no restrictions placed on the amplitudes. Zero-point vibrational energies (ZPVEs) were deduced from the CCSD(T)/aug-cc-pVQZ harmonic frequencies.

All computations were carried out with the CFOUR program package.<sup>[29,30]</sup> The PSI3 program<sup>[31]</sup> was also used as a double checking tool for some jobs. The CCSD(T) energies were converged to 10<sup>-10</sup> E<sub>h</sub> and the geometry optimization convergence criteria were set to 10<sup>-7</sup> for all systems in order to ensure high numerical precision.

## Results and Discussion

### Geometrical Structures

All structures optimized with the CCSD(T)/aug-cc-pVQZ method are displayed in Figure 1. The early experimental geometries for  $NH_3$  and HF are  $r_e(N-H)=1.0116$  Å,  $\Theta_e(H-N-H)=106.7^\circ$ ,<sup>[32]</sup> and  $r_e(H-F)=0.9168$  Å.<sup>[33]</sup> The recent accurate  $r_e$  structural parameters for  $NH_3$  and HF, obtained by correcting experimental rotational constants with the CCSD(T)/cc-pVQZ vibration-rotation interaction constants, are  $r_e(N-H)=1.0116$  Å,  $\Theta_e(H-N-H)=107.25^\circ$ , and  $r_e(H-F)=0.9169$  Å.<sup>[34]</sup> Our CCSD(T)/aug-cc-pVQZ equilibrium parameters in Figure 1 are within 0.001 Å of these experimental values.

The reactant complex  $F\cdots NH_3$  has the same  $C_{3v}$  symmetry as the reactant  $NH_3$ , but the N–H bond length becomes shorter, decreasing from 1.013 Å to 1.005 Å. The H–N–H bond angle widens from 106.5° to 115.3°.

The transition state  $F\cdots H\cdots NH_2$  has  $C_s$  symmetry. The H–N bond being broken is stretched to 1.042 Å, which is 0.037 Å longer than that for the  $F\cdots NH_3$  complex. Simultaneously the F–H bond length is shortened to 1.500 Å compared to the complex (1.944 Å), thus indicating that the H atom is beginning to break away from the  $NH_2$  moiety and form a F–H bond.

The  $C_{2v}$  symmetry  $FH\cdots NH_2$  exit complex has a planar equilibrium structure, similar to the previous theoretical results reported by Goldschleger et al.<sup>[7,16]</sup> at the B3LYP/aug-cc-pVTZ//B3LYP/EP-3 level, and by Goddard et al.<sup>[13]</sup> at the MP2/6-311G\*\* level. However, our CCSD(T)/aug-cc-pVQZ optimum structure has a shorter  $FH\cdots N$  hydrogen bond distance. Our CCSD(T)/aug-cc-pVQZ bond length of  $FH\cdots N$  is 1.757 Å whilst Goldschleger et al.'s B3LYP value is 1.783 Å and Goddard et al.'s CISD value 1.789 Å.

The product  $NH_2$  is very similar to that in the  $FH\cdots NH_2$  complex, with its N–H bond length slightly longer (by only 0.003 Å), and with its H–N–H bond angle smaller by 2.5°. Goddard et al.<sup>[12,13]</sup> reported the N–H bond length of 1.026 Å and the H–N–H angle of 102.1° at the CISD/6-311G\*\* level. The early experimental values for the N–H bond length and the H–N–H angle for the ground state  $NH_2$  are 1.024 Å and 103.3°, respectively.<sup>[35]</sup> The recent reported experimental values by the extension of the low-pres-

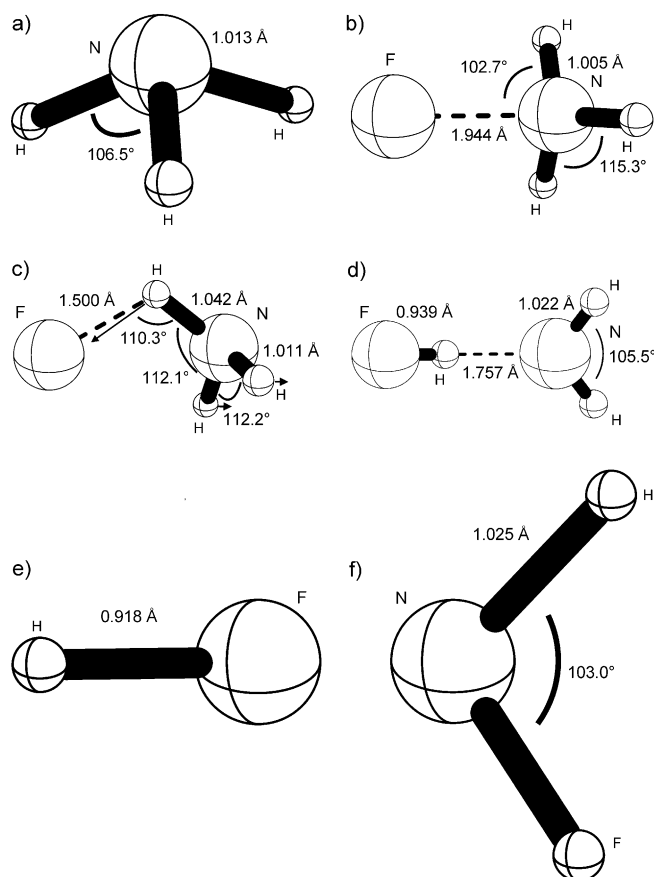


Figure 1. CCSD(T)/aug-cc-pVQZ optimized geometries of a)  $\text{NH}_3$ , b) a  $\text{F}\cdots\text{NH}_3$  complex, c) the transition state, d) the  $\text{FH}\cdots\text{NH}_2$  complex, and e, f) the HF and  $\text{NH}_2$  products (bond lengths are in Å, bond angles in degrees). The arrows shown in the transition state (c) represent the normal mode corresponding to the imaginary vibrational frequency.

sure infrared chemiluminescence technique are almost the same, i.e.,  $\text{NH}_2$  are 1.024 Å and 103.4°, respectively.<sup>[13]</sup>

### Classical Energetics

The classical energies of all stationary point structures of the  $\text{F}+\text{NH}_3$  reaction at the CCSD(T)/aug-cc-pVDZ, CCSD(T)/aug-cc-pVTZ, and CCSD(T)/aug-cc-pVQZ levels of theory are reported in Table 1.

The energy of the  $\text{F}\cdots\text{NH}_3$  complex is lower than that of the reactants ( $\text{F}+\text{NH}_3$ ) by 13.2 kcal mol<sup>-1</sup> with the CCSD(T)/aug-cc-pVTZ method or 13.7 kcal mol<sup>-1</sup> with the

more reliable CCSD(T)/aug-cc-pVQZ. The product complex  $\text{FH}\cdots\text{NH}_2$  has a hydrogen bond between the H and N atoms, and its energy is lower than the HF products plus  $\text{NH}_2$  by about 9.9 kcal mol<sup>-1</sup> with both the CCSD(T)/aug-cc-pVTZ and CCSD(T)/aug-cc-pVQZ methods. The transition state is predicted to have its energy higher than the reactant complex  $\text{F}\cdots\text{NH}_3$  by 2.10 or 2.04 kcal mol<sup>-1</sup> with the CCSD(T)/aug-cc-pVTZ and CCSD(T)/aug-cc-pVQZ methods, respectively. The classical potential energy surface for the  $\text{F}+\text{NH}_3$  reaction is plotted in Figure 2.

### Vibrational Frequencies

The harmonic vibrational frequencies at the CCSD(T)/aug-cc-pVTZ and CCSD(T)/aug-cc-pVQZ levels of theory are reported in Table 2. The transition state has one imaginary vibrational frequency of 554  $i$  cm<sup>-1</sup> with CCSD(T)/aug-cc-pVTZ or 594  $i$  cm<sup>-1</sup> with the CCSD(T)/aug-cc-pVQZ method. The imaginary vibrational mode is predominantly (64 %) of  $r(\text{F}-\text{H})$  character, as well as (25 %) of  $\Theta(\text{F}-\text{H}-\text{N})$  and 3 % of  $r(\text{H}-\text{N})$ , revealing the simultaneous F-H bond formation and H-N bond breaking. The normal mode corresponding to the imaginary frequency is indicated in Figure 1c by the arrows. This mode is clearly connecting the reactants and the products, i.e., moving toward  $\text{HF}+\text{NH}_2$ .

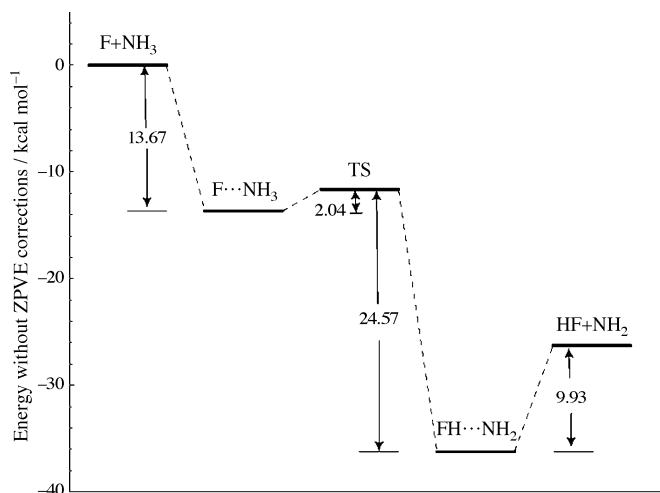


Figure 2. A schematic illustration of the classical energetics of the  $\text{F}+\text{NH}_3$  reaction including the reactants, intermediate complexes, transition state, and products with the CCSD(T)/aug-cc-pVQZ method.

Table 1. Theoretical predictions of the total (in hartrees) and relative energies (in kcal mol<sup>-1</sup>) of the stationary-point structures of the  $\text{F}+\text{NH}_3$  reaction using the CCSD(T) method with the Dunning augmented correlation consistent basis sets. Relative energies ( $\Delta E_e$ ) are reported with respect to the reactants obtained at the same levels of theory.

2*	aug-cc-pVDZ		aug-cc-pVTZ		aug-cc-pVQZ	
	Energy	$\Delta E_e$	Energy	$\Delta E_e$	Energy	$\Delta E_e$
$\text{F}+\text{NH}_3$	-155.975559	0.00	-156.108341	0.00	-156.148585	0.00
$\text{F}\cdots\text{NH}_3$	-155.996630	-13.22	-156.129399	-13.21	-156.170375	-13.67
Transition state	-155.992722	-10.77	-156.126053	-11.11	-156.167125	-11.63
$\text{FH}\cdots\text{NH}_2$	-156.031394	-35.04	-156.165247	-35.71	-156.206272	-36.20
$\text{HF}+\text{NH}_2$	-156.015602	-25.13	-156.149408	-25.77	-156.190447	-26.27

Table 2. Theoretical harmonic vibrational frequencies (cm<sup>-1</sup>) of all stationary points of F+NH<sub>3</sub> at the CCSD(T)/aug-cc-pVTZ and CCSD(T)/aug-cc-pVQZ levels of theory.

HF		NH <sub>2</sub>		NH <sub>3</sub>	
aug-cc-pVTZ	aug-cc-pVQZ	aug-cc-pVTZ	aug-cc-pVQZ	aug-cc-pVTZ	aug-cc-pVQZ
4125	4142	1540	1542	1063	1060
		3360	3374	1673	1674
		3454	3469	1673	1674
				3464	3476
				3593	3607
				3593	3607

F....NH <sub>3</sub>		FH....NH <sub>2</sub>		Transition state	
aug-cc-pVTZ	aug-cc-pVQZ	aug-cc-pVTZ	aug-cc-pVQZ	aug-cc-pVTZ	aug-cc-pVQZ
341	348	213	213	554 <i>i</i>	594 <i>i</i>
341	348	246	248	452	455
450	460	303	305	487	481
684	656	800	802	785	827
1624	1620	832	837	1539	1532
1624	1620	1544	1544	1615	1620
3530	3542	3408	3422	3066	3084
3711	3729	3506	3522	3550	3561
3711	3729	3670	3675	3651	3663

### Zero-Point Vibrational Energies and Gibbs Free Energies

The harmonic ZPVE values obtained from the CCSD(T)/aug-cc-pVQZ method are 21.58 (for NH<sub>3</sub>), 22.90 (for F....NH<sub>3</sub>), 21.76 (for TS), 20.83 (for FH....NH<sub>2</sub>), 5.92 (for HF), and 11.99 (for NH<sub>2</sub>) kcal mol<sup>-1</sup>. After the harmonic ZPVE corrections, the energy of the F....NH<sub>3</sub> complex is below that of the reactants by 12.36 kcal mol<sup>-1</sup>, the energy of the FH....NH<sub>2</sub> complex is below the products by 7.01 kcal mol<sup>-1</sup> with the CCSD(T)/aug-cc-pVQZ method. The energy barrier of the transition state from the F....NH<sub>3</sub> complex is reduced in this way to only 0.86 kcal mol<sup>-1</sup>.

It is well-known that the above procedure, neglecting anharmonicity, overestimates ZPVE corrections. A more reliable approach is to scale the harmonic ZPVEs. For NH<sub>3</sub>, our harmonic ZPVE is 7549 cm<sup>-1</sup>, whilst one half of the sum of the experimental fundamentals<sup>[32]</sup> is 7214 cm<sup>-1</sup>. The ratio of the theoretical harmonic to experimental fundamental frequencies is 1.046. For HF, the theoretical fundamental frequency is 4142 cm<sup>-1</sup>, whilst the experimental fundamental<sup>[33]</sup> is 3959 cm<sup>-1</sup>. It is only accidental that ratio  $\omega/\nu$  is again 1.046.

Thus, for all stationary points on the F+NH<sub>3</sub> potential surface, we divide the harmonic ZPVEs by 1.046. This process gives the F....NH<sub>3</sub> entrance complex an energy 12.4 kcal mol<sup>-1</sup> below separated F+NH<sub>3</sub>. Similarly the exit complex FH....NH<sub>2</sub> lies 7.1 kcal mol<sup>-1</sup> below separated FH+NH<sub>2</sub>.

The theoretical prediction of activation energies, i.e., barriers corrected by a proper treatment of vibrational degrees of freedom, is always a bit murky. Using the procedure described in the previous paragraph, we deduce a ZPVE corrected barrier of 0.91 kcal mol<sup>-1</sup>. Of course, the rigorous way to predict an activation energy is to compute rate constants quantum mechanically with a global potential energy hypersurface, and then fit these rate constants to an Arrhenius expression.

When the Gibbs free energy is considered, temperature is another factor to consider. As the entropy for the F....NH<sub>3</sub> complex increases faster than that for the transition state when the temperature rises, the free energy barrier  $\Delta G^\ddagger$  will become considerable if the temperature is high enough. The  $\Delta G^\ddagger$  value is predicted by the CCSD(T)/aug-cc-pVQZ level of theory to be 0.71, 0.68, 0.80, 1.01, and 1.27 kcal mol<sup>-1</sup> at 100 K, 200 K, 300 K, 400 K, and 500 K, respectively. In Persky's experimental temperature range of 276–327 K,<sup>[18]</sup> our theoretical free-energy barrier is predicted to be 0.76–0.85 kcal mol<sup>-1</sup>.

### Concluding Remarks

The F+NH<sub>3</sub> reaction has been studied using the highly correlated ab-initio electronic structure theory, up to the CCSD(T)/aug-cc-pVQZ level of theory. Two intermediate complexes and a transition state were found for the reaction. The F....NH<sub>3</sub> complex shows that what is energetically comparable to a strong (relative to separated F+NH<sub>3</sub>) hydrogen bond is formed in the reactant complex, whilst the FH....NH<sub>2</sub> product complex indicates that there is a true hydrogen bond between HF and NH<sub>2</sub> prior to the formation of the products. For the first time, a transition state of F....H....NH<sub>2</sub> structure with a single imaginary vibrational frequency at 594 *i* cm<sup>-1</sup> is found for this reaction. The corresponding normal mode displays the beginnings of formation of the F–H bond leading to the product complex FH....NH<sub>2</sub>. The classical barrier with respect to the F....NH<sub>3</sub> complex is predicted to be 2.04 kcal mol<sup>-1</sup>. Including estimated ZPVE corrections, the theoretical energy barrier from the F....NH<sub>3</sub> complex to the transition state is only 0.95 kcal mol<sup>-1</sup> at the CCSD(T)/aug-cc-pVQZ level of theory, though the energy of the transition state is lower than that of the reactants (F and NH<sub>3</sub>) by 11.4 kcal mol<sup>-1</sup>. The deep entrance complex and small energy barrier are

consistent with Persky's observation of exceptionally strong inverse temperature dependence of the  $F+NH_3$  rate constant.

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