

Theoretical Study of the NF₃ Dissociation by Hydrogen Atoms

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The use of NF₃ as fluorine source in lasers, ion-molecule experiments and etching processes has prompted us to investigate the occurrence of thermal decomposition of it with hydrogen by a two steps mechanism:



The work presented in this paper represents a theoretical study of the reactions (R1) and (R2) using the direct transition state theory method [1-4], where the rate coefficients, can be written as:

$$k_{TST}(T) = \frac{k_B T}{h} \frac{Q_X}{Q_{\text{Reactants}}} \exp\left(-\frac{V_a^G}{RT}\right) \quad (1)$$

where $Q_{\text{Reactants}}$ and Q_X are the partition functions of the reactants and transition state (TS), respectively, k_B is the Boltzmann's constant, h is the Planck's constant, T is the temperature, R is the universal gas constant and V_a^G is the potential barrier:

$$V_a^G = V_{MEP} + \varepsilon_{ZEP} \quad (2)$$

where ε_{ZPE} is the harmonic zero-point energies (ZPE) and V_{MEP} is the Eckart classical potential energy [5] of the saddle point measured from the overall zero of reactants' energy.

Introducing the transmission coefficient, $\kappa^{W/E}(T)$, equation (1) becomes:

$$k_{TST}^{W/E}(T) = \kappa^{W/E}(T) k_{TST} \quad (3)$$

where $\kappa^{W/E}(T)$ is the Wigner ($\kappa^W(T)$) or Eckart transmission coefficient ($\kappa^E(T)$) and it is well described in the reference [3,5-8].

The characteristics of the MEP and the rate constants, with the Wigner and Eckart tunneling correction, were determined using our own code [1, 2, 9] and the rate constants were written in the Arrhenius form, as:

$$k(T) = AT^n \exp\left(-\frac{E_a}{RT}\right) \quad (4)$$

The geometries, vibrational modes and energies are calculated using the GAUSSIAN03 program [10] at MP2/6-311++G(d,p) level. The geometric parameters are given in table 1 and the TSs geometries in figure 1, while the frequencies are presented in table 2 for all the stationary points. The geometries and frequencies are compared with experimental reference data, when available, and are in good agreement. The frequencies are scaled by a factor of 96.96% to take into account known deficiencies at this level of calculation. Table 2 gives the unscaled frequencies and the scaled ZPE.

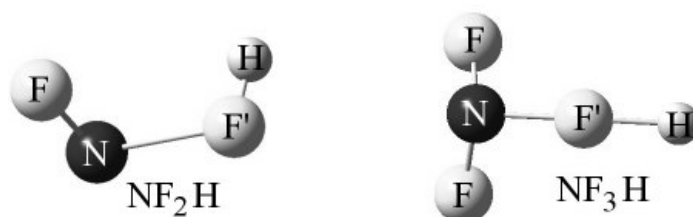


Figure 1: Atomic numbering of the reaction system for reactions $\text{NF}_2 + \text{H} = \text{NF} + \text{HF}$ and $\text{NF}_3 + \text{H} = \text{NF}_2 + \text{HF}$.

Table 1: Geometries of reactant, TSs and products at MP2/6-311++G(d,p) for reactions $\text{NF}_3 + \text{H} = \text{NF}_2 + \text{HF}$ and $\text{NF}_2 + \text{H} = \text{NF} + \text{HF}$ (distances in Å, angles in degrees, data in parentheses are experimental or theoretical values)

Parameters	NF_3	NF_2	NF	HF	NF_3H	NF_2H
R_{NF}	1.3693 (1.371[12]) _e	1.3434 (1.37[12]) _e	1.3162 (1.3173[13])		1.3518 (1.3670[14]) _t	1.3343
A_{FNF}	102.2 (102.9[12]) _e	103.7 (104.2[12]) _e			103.1 (102.6[14]) _t	
R_{HF}				0.9166 (0.9168[12]) _e	1.3429 (1.3448[14]) _t	1.3608
$R_{\text{NF}'}$					1.5117 (1.5368[14]) _t	1.3825
$A_{\text{FNF}'}$					100.9 (100.4[14]) _t	102.4
$A_{\text{NF}'\text{H}}$					176.1 (176.2[14]) _t	125.9

In the transition state, NF_3H and NF_2H , the length of the bond that is broken (NF') increases by 10.4% and 1.3%, respectively, when compared with the bond length in the reactant (NF_3 and NF_2), while the length of the bond that is formed (HF) increases by 46.5% and 50.8%, respectively, when compared with the bond length in the product (HF). It is according to the Hammond's postulate [11], which states that exothermic reactions should be more reactant like than product like (see table 3).

The potential barrier along the MEP as a function of the reaction coordinate are plotted in figure 2(a) and the Arrhenius plot of reaction rate is given in figure 2(b). The Eckart tunneling correction overestimate the reaction rate and we will use the Wigner one. The reaction rate in the Arrhenius form is $k = 7.4588 \times 10^8 T^{1.2432} \exp(-43322/RT)$ for $\text{NF}_2 + \text{H} = \text{NF} + \text{HF}$ and $k = 1.306 \times 10^9 T^{1.3528} \exp(-27568/RT)$ for $\text{NF}_3 + \text{H} = \text{NF}_2 + \text{HF}$.

Table 2: Harmonic vibrational frequencies (in cm^{-1}) and zero-point energies (in kcal mol^{-1}) for reactants and products at the MP2/6-311++G(d,p) level (data in parentheses are experimental or theoretical values).

	NF ₃	NF ₂	NF	HF	NF ₃ H	NF ₂ H
ν_1	505(492[12]) _e	593 (573[12]) _e	1164 (1115.0[12]) _e	4199 (4138[12]) _e	339(309[14]) _t	475
ν_2	670(642[12]) _e	980 (931[12]) _e			392(371[14]) _t	670
ν_3	926(906[12]) _e	1131 (1074[12]) _e			513(472[14]) _t	956
ν_4	1055(1062[12]) _e				529(508[14]) _t	1041
ν_5					647(588[14]) _t	1217
ν_6					977(942[14]) _t	
ν_7					1055(997[14]) _t	
ν_8					1182(1102[14]) _t	
ν_9					2727i(2474i[14]) _t	2282i
ZPE	6.54	3.75	1.61	5.82	7.81	6.04

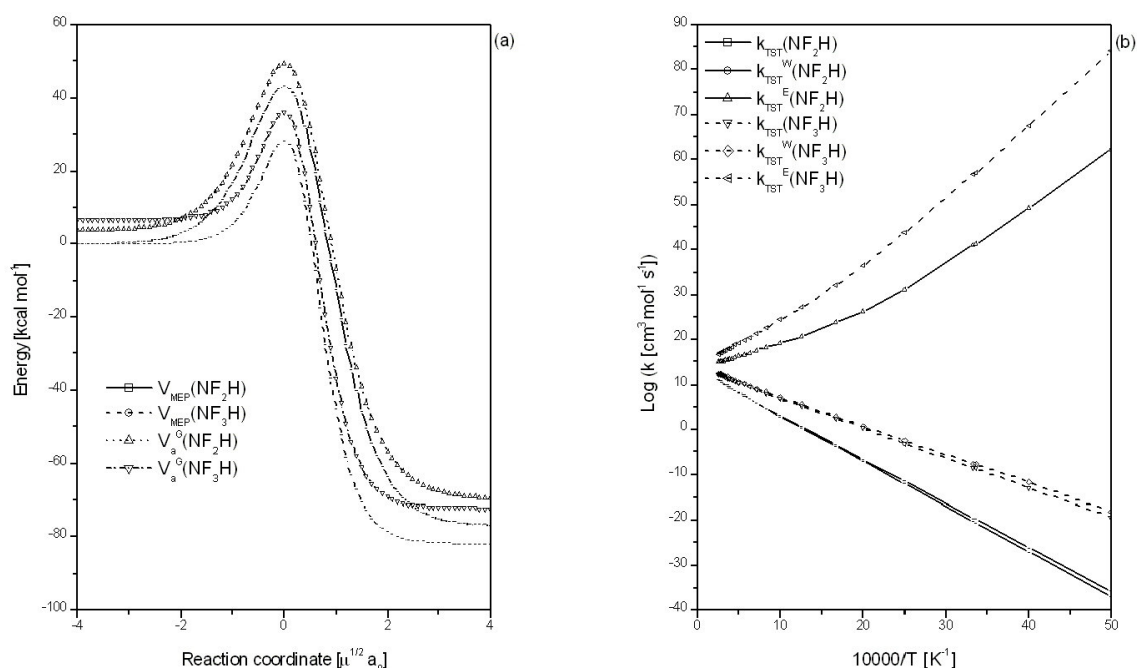


Figure 2: (a) Classical potential energy curves (V_{MEP}) and vibrational adiabatic potential energy curves (V_a^G), as a function of reaction coordinate for reactions $NF_3 + H = NF_2 + HF$ and $NF_2 + H = NF + HF$, (b) Arrhenius plot of the reaction rates against the reciprocal temperature in the range of 200-4000 K for reactions $NF_3 + H = NF_2 + HF$ and $NF_2 + H = NF + HF$.

Table 3 gives the energies for reactant, products and TSs at MP2/6-311++G(d,p), as well as the potential barriers and reaction enthalpies including the ZPE correction. The reaction enthalpies are compared to the reaction enthalpies calculated on the basis of the heat of formation of the reactants and products, and for reaction $NF_3 + H = NF_2 + HF$ with theoretical data obtained at G2(MP2) [14].

Table 3: Total energies (in hartree) for the reactants, products and TS, potential barrier and reaction enthalpy (in kcal mol⁻¹) with ZPE correction

	NF ₃ +H=NF ₂ +HF	NF ₂ +H=NF+HF
reactant	-353.9474284	-254.2985970
product	-354.0776714	-254.4213873
TS	-353.9022974	-254.2296863
Potential barrier	29.59	45.54
Reaction Enthalpy	-78.90	-73.48
Reference	-77.05[12], -76.97[14]	-67.36[12]

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