INPE Ministério da Ciência e Tecnologia
Instituto Nacional de Pesquisas Espaciais

Universidade de Brasília

Thermochemistry of $N_xH_yF_z$ Molecule

Patrícia R.P. Barreto
Laboratório Associado de Plasma LAP
Instituto Nacional de Pesquisas Espaciais INPE
patricia@plasma.inpebr
Alessandra F.A. Vilela and Ricardo Gargano
Instituto de Física
Universidade de Brasília-UnB

Abstract

A self-consistent set of thermochemical data for 88 chemical species in the B/F/H/N system are obtained from ab initio electronic structure calculation. Calculations were performed for both stable and radical species. The quantities calculated include the atomization energy (ΣD_0), heat of formation (ΔH_f) at 0K and 298.15K and bond dissociation energies (BDE) for all species. In this work we will present the $N_xH_yF_z$ species, in a total of 16 species, where only 4 species have experimental or theoretical reference data to be compared. First of all the well know species in the N_xF_y and N_xH_y system are analyzed, in a total of 12 species, for which the calculation methodology is tested by comparing the calculated properties with the experimental results. Then we determined the properties for the 16 desired species in the $N_xH_yF_z$ system. Good agreement is found between the calculated data and experimental or theoretical reference data for the quantities analyzed in this work. The error between the calculated thermodynamic properties and the experimental or theoretical reference data for the species analyzed here are compared with the error bar. Polynomial fits of the predicted thermodynamic data (heat capacity, entropy and enthalpy) over the 200-6000K temperature range are also included. The species analyzed here are important in a kinetic mechanism in the growth of boron nitride films in a CVD reactor. It is generally difficult to optimize conditions in a CVD reactor because films properties depend on complex interactions involving heat and mass transport, chemical kinetics, and thermochemistry. Developing a reliable set of thermodynamic data is a necessary first step for system optimization, since it provides important constraints on the possible reaction mechanism.

Introduction

- *There has been considerable interest in recent years, in the growth of boron nitride thin films*
- *Like carbon, boron nitride has different allotropes, the hexagonal (hBN) and cubic (cBN) phases*
- *The hexagonal phase, although electrically insulating, has properties that are very similar to graphite while the cubic phase has properties comparable to diamond*
- *There is little understanding of the chemical process which are involved in and which control the synthesis of either hBN or cBN from the vapor phase.*
- *Theoretical research found in the literature includes thermodynamic equilibrium calculations for mixtures involving B/F/N/H and B/Cl/N/H, as well as limited kinetics studies of the reactions between BCl_3 and NH_3*
- *The species analyzed here are important in a kinetic mechanism for growth boron nitride in a CVD reactor. It is generally difficult to optimize conditions in a CVD reactor because film properties depend on complex interactions involving heat and mass transport, chemical kinetics, and thermochemistry.*
- *Developing a reliable set of thermodynamic data is a necessary first step for system optimization, since it provides important constraints on the possible reaction mechanism.*

Thermodynamic Properties

- Internal energy

$$E = k_B T \left(\frac{\partial \ln Q}{\partial \ln T} \right)_v$$

- Entropy

$$S = k_B \ln Q + k_B \left(\frac{\partial \ln Q}{\partial \ln T} \right)_v$$

- Heat capacity

$$c_v = k_B \left(\frac{\partial \ln Q}{\partial \ln T} \right)_v + k_B \left(\frac{\partial^2 \ln Q}{\partial (\ln T)^2} \right)_v$$

- Enthalpy

$$H \equiv E + pV$$

- Gibbs free energy

$$G = H - ST$$

- Heat capacity

$$c_p = c_v + R$$

Partition Function

$$Q = Q_{trans} Q_{rot} Q_{vib} Q_{elet}$$

	Degrees of freedom	Partition Function	Magnetude order
Translation	3	$Q_{trans} = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2}$	$10^{33}\ m^3$
Rotation – 2D	2	$Q_{rot-2D} = \left(\frac{8\pi^2 I k_B T}{\sigma_e h^2} \right)$	$10 - 10^2$
Rotation – 3D	3	$Q_{rot-3D} = \left[\frac{\sqrt{\pi}}{\sigma_e} \left(\frac{8\pi^2 I_m k_B T}{h^2} \right)^{3/2} \right]$	$10^2 - 10^3$
Vibration	$n = 3N - 5$ $n = 3N - 6$	$Q_{vib} = \prod_{i=1}^{n} \left[1 - \exp\left(-\frac{hc\nu_i}{k_B T} \right) \right]^{-g_i}$	$1 - 10^n$
Electronic	–	$Q_{elet} = \sum_{i=0}^{n} g_i \exp\left(-\frac{\varepsilon_i}{k_B T} \right)$	1

Atomization Energies Heats of formation at 0 and 298.15K, Bound Dissociation Energies

- *Atomization Energy*

$$\Sigma D_0(A_xB_yC_z) = [x\varepsilon_0(A) + y\varepsilon_0(B) + z\varepsilon_0(C)]\ ] - \varepsilon_0(A_xB_yC_z)$$

- *Heats of formation*

$$\Delta_f H^0(A_xB_yC_z,0K) = x\ \Sigma\Delta_f H^0(A,0K) + y\ \Sigma\Delta_f H^0(B,0K) + z\ \Sigma\Delta_f H^0(C,0K) - \Sigma D_0(A_xB_yC_z)$$

$$\Delta_f H^0(A_xB_yC,298K) = \Delta H_f(A_xB_yC,0K) + [H^0(A_xB_yC,298K) - H^0(A_xB_yC,0K)]_{st} - x\Sigma\,[H^0(A,298K) - H^0(A,0)]_{st} - y\Sigma\,[H^0(B,298K) - H^0(B,0)]_{st} - z\Sigma\,[H^0(C,298K) - H^0(C,0)]_{st}$$

- *Bond Dissociation Energies*

$$BDE(AB–C) \equiv \Delta H_{298}{}^0 = \Delta_f H_{298}(AB,g) + \Delta_f H_{298}(C,g) - \Delta_f H_{298}(ABC)$$

Results, Discussion and Conclusion

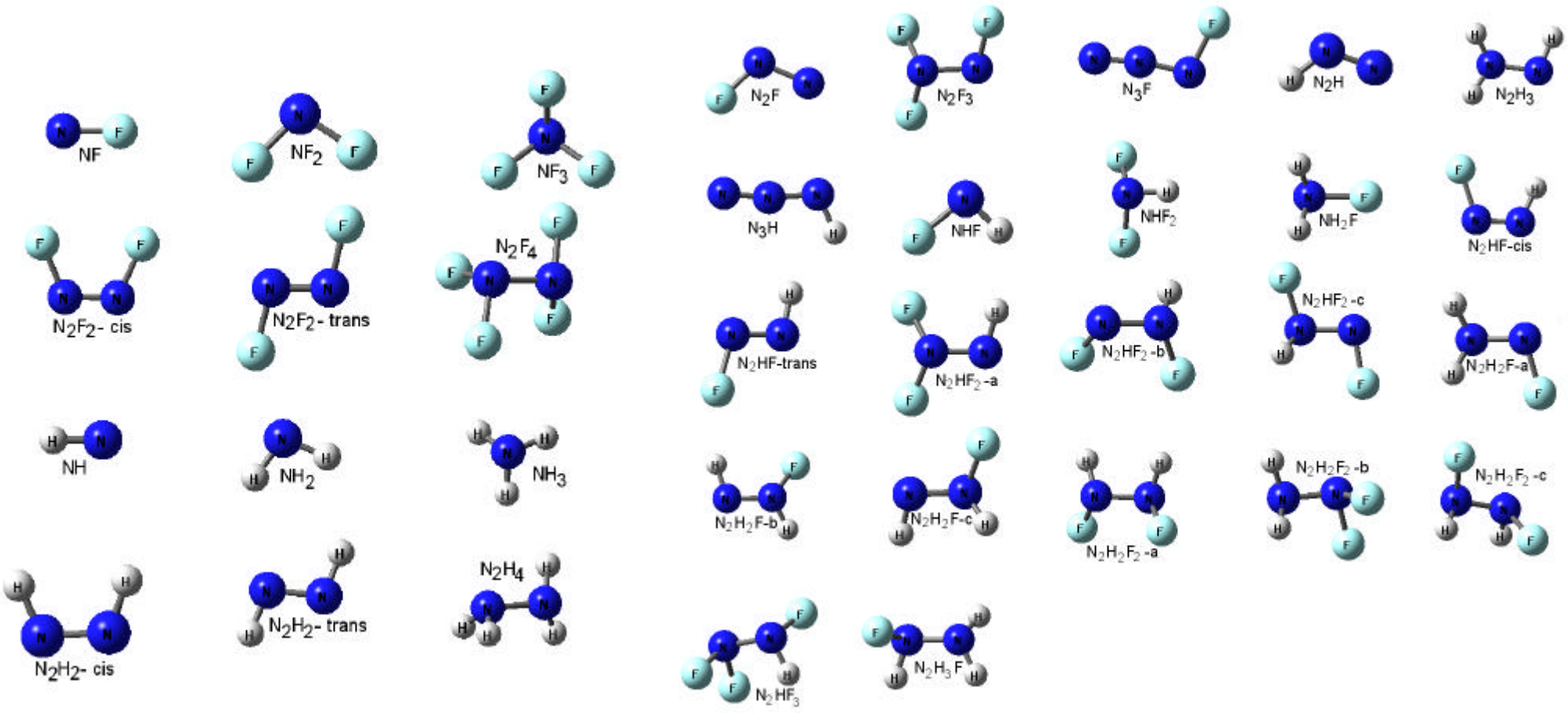
- *Geometries, frequencies and energies were obtained using GAUSSIAN98 program at G3 level.*
- *Geometries, frequencies, atomization energies, heats of formation and bond dissociation energies compared with experimental and theoretical data when avaliable.*
- *Good agreement is found between the calculation and reference heats of formation and atomization energy for the reference molecules.*
- *The maximum error, 3.9kcal mol^{-1}, in a atomization energy is found for BH_2 while for the heat of formation, error of 5.5kcal mol^{-1}, is for the BF_2.*
- *The polynomial fits for the thermodynamic properties is also presented.*

Acknowledgment

Centro Nacional de Processamento de ALTO DESEMPENHO EM SÃO PAULO

CNPq

Sub-system	*molecules*
N_xF_y	**NF, NF_2, NF_3**, N_2F, **N_2F_2-*cis*, N_2F_2-*trans***, N_2F_3, **N_2F_4**, N_3F
N_xH_y	**NH, NH_2, NH_3**, N_2H, **N_2H_2-*cis*, N_2H_2-*trans***, N_2H_3, **N_2H_4**, N_3H
$N_xH_yF_z$	NHF, NHF_2, NH_2F, N_2HF-*cis*, N_2HF-*trans*, N_2HF_2-*a*, N_2HF_2-*b*, N_2HF2-*c*, N_2H_2F-*a*, N_2H_2F-*b*, N_2H_2F-*c*, $N_2H_2F_2$-*a*, $N_2H_2F_2$-*b*, $N_2H_2F_2$-*c*, N_2HF_3, N_2H_3F,


NF
NF2
NF3
N2F2- cis
N2F2- trans
N2F4
NH
NH2
NH3
N2H2- cis
N2H2- trans
N2H4
N2F
N2F3
N3F
N2H
N2H3
N3H
NHF
NHF2
NH2F
N2HF-cis
N2HF-trans
N2HF2-a
N2HF2-b
N2HF2-c
N2H2F-a
N2H2F-b
N2H2F-c
N2H2F2-a
N2H2F2-b
N2H2F2-c
N2HF3
N2H3F

Fully optimized geometry at the MP2/6-31G(d) level

species	Geometry (Å and degrees)
NF	R_{NF} = 1.330 (1.51[1], 1.3173[2], 1.317[3])
NF_2	R_{NF} = 1.359 (1.37[1,4,5]), A_{FNF} = 103.3 (104.2[1], 104.2 [4,5])
NF_3	R_{NF} = 1.380 (1.371[1], 1.3849[6]), A_{FNF} = 101.7 (102.9 [1], 101.661 [6])
N_2F_2-cis	R_{NF} = 1.395 (1.384[1]), R_{NN} = 1.230 (1.214[1]), A_{NNF} = 113.6 (114.5[1])
N_2F_2-trans	R_{NF} = 1.390 (1.44[1]), R_{NN} = 1.250 (1.25[1]), A_{NNF} = 104.0 (115[1])
N_2F_4	R_{NF} = 1.393 (1.37[1]), R_{NN} = 1.460 (1.47[1]), A_{FNF} = 102.7 (108[1]), A_{NNF} = 105.9 (104[1])
NH	R_{NH} = 1.039 (1.038 [1,8], 1.036[3], 1.0377 [9], 1.0238 [10])
NH_2	R_{NH} = 1.020 (1.024[1], 1.02 [3], 1.0255[9], 1.0126[10]), A_{HNH} = 103.3 (103.4 [1], 103 [3], 102.99[9], 104.37[10])
NH_3	R_{NH} = 1.017 (1.0124[1], 1.017 [11], 1.0216 [9], 1.013[12], 1.0025 [10], 1.0125 [13]), A_{HNH} = 106.4 (106.67 [1], 106.6 [9], 106.1 [12], 107.21 [10], 106.4 [13])
N_2H_2-cis	R_{NH} = 1.042 (1.014[1], 1.13[14], 1.0250[15]), R_{NN} = 1.260 (1.23[1], 1.27[14], 1.2383[15]), A_{NNH} = 112.3 (100[1], 112 [14], 116 [15])
N_2H_2-trans	R_{NH} = 1.030 (1.13[14], 1.041[16], 1.029[16], 1.0165[15]), R_{NN} = 1.260(1.28[14], 1.252[16], 1.247[16], 1.2388[15]), A_{NNH} = 105.4 (104[14], 106.3[16], 110[15])
N_2H_4	R_{NH} = 1.020 (1.022[1]), R_{NN} = 1.430 (1.449 [1]), A_{HNH} = 106.9 (109.47 [1]), A_{NNH} = 111.4 (112[1])
N_2F	R_{NF} = 1.345, R_{NN} = 1.370, A_{NNF} = 114.3
N_2F_3	R_{NF} = 1.390, R_{NN} = 1.426, A_{FNF} = 103.2, A_{NNF} = 101.6
N_3F	R_{N1F} = 1.432 (1.444[7]), R_{N1N2} = 1.282 (1.253[7]), R_{N2N3} = 1.150 (1.132[7]), A_{NNF} = 103.8 (103.8[7]), A_{NNN} = 171.7 (170.9[7])
N_2H	R_{NH} = 1.050, R_{NN} = 1.150, A_{NNH} = 121.2

N_2H_3	R_{NH} = 1.012, R_{BF} = 1.350, A_{HNH} = 118.6, A_{NNH} = 112.3
N_3H	R_{N1H} = 1.023 (1.015 [17], 1.0190 [18]), R_{N1N2} = 1.250 (1.243 [17], 1.2438 [18]), R_{N2N3} = 1.159 (1.134 [17], 1.1470 [18]), A_{NNH} = 110.3 (108.8 [17], 109.8 [18]), A_{NNN} = 171.0 (171.3 [17], 169.7 [18])
NHF	R_{NF} = 1.378 (1.373 [19], 1.364 [20]), R_{NH} = 1.030 (1.035 [19], 1.06 [20]), A_{FNH} = 99.9 (102 [19], 109 [20])
NHF_2	R_{NF} = 1.400 (1.400 [21]), R_{NH} = 1.020 (1.026 [21]), A_{FNF} = 103.2 (102.9 [21]), A_{FNH} = 99.6 (99.8 [21])
NH_2F	R_{NF} = 1.434 (1.4329 [21]), R_{NH} = 1.020 (1.0225 [21]), A_{HNH} = 105.0 (106.27 [21]), A_{FNH} = 100.9 (101.08 [21])
N_2HF-cis	R_{NF} = 1.474, R_{NH} = 1.030, R_{NN} = 1.210, A_{NNF} = 110.6, A_{NNH} = 111.7
N_2HF-trans	R_{NF} = 1.422, R_{NH} = 1.030, R_{NN} = 1.230, A_{NNF} = 107.3, A_{NNH} = 103.5
N_2HF_2-a	R_{NF} = 1.391, R_{NH} = 1.020, R_{NN} = 1.300, A_{FNF} = 102.7, A_{NNF} = 113.3, A_{NNH} = 104.5
N_2HF_2-b	R_{NF} = 1.390, R_{NH} = 1.030, R_{NN} = 1.360, A_{FNH} = 102.4, A_{NNF} = 108.6, A_{NNH} = 108.0
N_2HF_2-c	R_{NF} =1.390 , R_{NH} = 1.029, R_{NN} = 1.370, A_{FNH} = 104.6, A_{NNH} = 109.6, A_{NNF} = 100.9
N_2H_2F-a	R_{NF} = 1.400, R_{NH} = 1.016, R_{NN} = 1.350, A_{HNH} = 113.6, A_{NNH} = 109.1, A_{NNF} = 103.1
N_2H_2F-b	R_{NF} = 1.445, R_{NH} = 1.020, R_{NN} = 1.290, A_{HNH} = 103.4, A_{NNH} = 106.6, A_{NNF} = 116.2
N_2H_2F-c	R_{NF} = 1.410, R_{NH} = 1.027, R_{NN} = 1.320, A_{FNH} = 102.8, A_{NNH} = 117.5, A_{NNF} = 109.1
$N_2H_2F_2$-a	R_{NF} = 1.432, R_{NH} = 1.020, R_{NN} = 1.390, A_{FNH} = 100.0, A_{NNH} = 105.2, A_{NNF} = 104.8
$N_2H_2F_2$-b	R_{NF} = 1.453, R_{NH} = 1.020, R_{NN} = 1.370, A_{FNF} = 99.3, A_{HNH} = 110.7, A_{NNH} = 106.3, A_{NNF} = 103.3
$N_2H_2F_2$-c	R_{NF} = 1.452, R_{NH} = 1.020, R_{NN} = 1.360, A_{NNH} = 104.8, A_{NNF} = 105.9, A_{FNH} = 100.6
N_2HF_3	R_{NF} = 1.410, R_{NH} = 1.031, R_{NN} = 1.419, A_{FNF} = 101.1, A_{FNH} = 102.1, A_{NNF} = 102.3, A_{NNH} = 105.6
N_2H_3F	R_{NF} = 1.465, R_{NH} = 1.022, R_{NN} = 1.376, A_{HNH} = 113.6, A_{FNH} = 97.0, A_{NNH} = 109.4, A_{NNF} = 106.3

Scaled harmonic vibrational frequencies at the HF/6-31G(d) level (in cm^{-1})

species	HF/6-31G(d)
NF	1272.5, 1115.0[1], 1141.4 [3, 2] , 1138.5 [2],
NF_2	652.8, 1189.8, 1267.6, 573, 931, 1074,[1], 935, 1074.3 [4], 942.38 [23], 573.4, 930.7, 1069.5 [5], 573.4, 930.7, 1069.6 [5], 1074.987 [22], 1075.0[22]
NF_3	580.2, 756.2, 1221.6, 1236.6, 492.0, 642.0, 906.0, 1032.0[1], 497, 648, 898, 1027 [24], 489.3, 653.7, 959.3, 1061.6[6]
N_2F_2-cis	416.2, 633.9, 909.0 1153.7, 1177.8, 1965.0, 552, 573, 737, 896, 952, 1524[1]
N_2F_2-trans	430.7, 486.2, 709.7, 1219.6, 1282.8, 1968.5, 360, 421, 592, 989, 1010, 1636[1], 364, 423, 603, 991, 1018, 1523[25]
N_2F_4	150.2, 336.0, 356.3, 520.6, 601.9, 693.2, 891.5, 1035.2, 1216.5, 1242.7, 1267.2, 1324.9, 122, 390, 467, 519, 549, 591, 737, 933, 946, 959, 998, 1010[1],
NH	3531.1, 3282.09[1], 3300.0 [8], 3282 [3], 3528.0[10]
NH_2	1710.2, 3606.9, 3708.2 1497.2, 3173, 3220[1], 1499, 3173, 3220 [3], 1480, 3219, 3301[26], 1498.0, 3220.0[28], 1524, 3374, 3481 [29], 1711.0, 3608.0, 3708.0[10], 3219.37, 3301.10 [27],
NH_3	1209.7, 1849.9, 3689.7, 3821.4, 1022, 1691, 3506, 3577[1, 30, 13], 1123, 1725, 3560, 3716[12], 975.0 1637.8, 3346.4, 3436.4[12], 1030, 1690, 3503, 3592, [29], 1141, 1733 , 3546, 3687, [29], 1213.0, 1851.0, 3684.0, 3816.0[30], 1076.0, 1679.0 3471.0, 3600.0[13], 3690.0, 3823.0, [10]
N_2H_2-cis	1415.1, 1515.4, 1719.1, 1907.0, 3472.8, 3545.4, 910, 1360, 1406, 1495, 3095, 3205 [1]
N_2H_2-trans	1473.5, 1477.3, 1761.2, 1906.3, 3571.6, 3606.7, 1288.7, 1316.4, 3120.3[31], 1289.0, 1316.0, 1529.0, 1583.0, 3120.0, 3128.0[16], 1339.0, 1345.0, 1492.0, 1617.0, 3308.0, 3341.0[16],
N_2H_4	474.3, 978.9, 1111.9, 1226.3, 1435.9, 1468.0, 1854.0, 1871.4, 3706.7, 3717.7, 3819.5, 3825.9, 377, 780, 875, 933, 966, 1098, 1275, 1312, 3261, 3280, 3330, 3350[1], 388, 804, 812, 953, 1086, 1261, 1300, 1591, 1608, 3310, 3325, 3350[32]
N_2F	488.1, 1064.4, 1344.4

N_2F_3	160.1, 359.5, 521.6, 623.9, 665.8, 1065.8, 1162.8, 1259.4, 1284.6
N_3F	282.0, 605.8, 757.8, 1045.7, 1225.7, 2384.7, 241.0, 504.0, 658.0, 873.5, 1090.0, 2037.0[7],
N_2H	1263.8, 1662.9, 3280.4
N_2H_3	675.8, 831.7, 1265.1, 1299.1, 1624.1, 1848.2, 3673.8, 3737.6, 3868.1
N_3H	572.1, 677.2, 1253.9, 1451.8, 2509.3, 3722.4, 534, 607, 1151, 1264, 2140, 3336[25], 522.0, 672.0, 1150.0, 1274.0, 2140.0, 3336.0 [33], 533, 1146, 1263, 2135, 3317 [18],
NHF	1185.7, 1612.0, 3632.7, 1000.0, 1430.0, 3200.0[20],
NHF_2	581.0, 1163.4, 1196.0, 1468.4, 1665.5, 3747.6, 503, 879, 968, 1304, 1419, 3192 [24], 500, 888, 972, 1307, 1424, 3193 [25],
NH_2F	1128.5, 1398.5, 1499.4, 1819.5, 3702.6, 3807.8, 920, 1160, 1565, 3270 [34], 900, 1224, 1607, 3101 [34], 891.0, 1233.0[35],
N_2H_3F	357.8, 593.9,751.3, 1047.9, 1245.5, 1262.2, 1492.4, 1666.3, 1852.8, 3753.4, 3770.5, 3888.6, 1013.0, 1091.0, 1282.0, 1311.0[32]
N_2HF-cis	711.8, 943.7, 1142.7, 1509.0, 1987.8, 3635.1
N_2HF-trans	746.0, 1038.9, 1109.7, 1541.9, 1972.2, 3695.7
N_2HF_2-a	503.3, 533.7, 563.5, 623.3, 1011.5, 1091.3, 1240.4, 1513.0, 3703.7
N_2HF_2-b	118.2, 371.9, 748.3, 1026.2, 1144.6, 1198.4, 1266.7, 1591.1, 3700.3
N_2HF_2 - c	150.5, 420.3, 597.9 1031.3, 1192.3, 1249.7, 1329.3, 1600.7, 3715.7
N_2H_2F-a	321.9, 602.3, 902.7, 1093.2, 1281.6, 1475.5, 1802.6, 3733.5, 3860.9
N_2H_2F-b	522.1, 592.9, 957.2, 1091.6, 1272.7, 1494.7, 1644.8, 3711.0, 3786.4
N_2H_2F - c	573.1, 596.7, 946.3 1133.9, 1299.9, 1482.1, 1631.4, 3666.7, 3704.5
$N_2H_2F_2$-a	110.0, 558.3, 598.9, 1043.0, 1043.8, 1114.6, 1253.0, 1344.0, 1661.4, 1679.5, 3750.2, 3780.5
$N_2H_2F_2$-b	353.3, 539.4, 592.3, 680.2, 994.6, 1087.4, 1110.7, 1337.9, 1524.5, 1836.0, 3721.7, 3851.7
$N_2H_2F_2$ - c	194.6, 512.0, 659.0, 1009.4, 1048.4, 1163.0, 1320.5, 1356.3, 1624.6, 1671.2, 3741.6, 3791.5
N_2HF_3	131.8, 351.2, 532.0, 636.3, 671.6, 1066.3, 1165.0, 1225.2, 1268.1, 1399.5, 1651.8, 3719.9

Atomization Energies

species	B3LYP	G2	G3	Ref. Expt.	Ref. Theory.
NF	84.302	76.365	79.097	71.4 ± 8 [1], 82[37], 80.7 [3]	75.7, 76.1[36]
NH	88.207	78.240	82.081	74.02[1], 75.4 [3], 79[38]	77.2, 77.9[36], 77.2[38], 78.36 ± 0.08 [9], 77.3[10], 77.4, 83.4 [39], 77.6, 78.0 [40], 78.1 [41]
NH_2	188.184	170.980	172.721	170.0[38]	168.4, 170.1[36],168.4[38], 169.3[10], 170.52 ± 0.12[9], 169.3, 176.2[39], 169.9, 170.2 [40], 170.2[41],
NH_3	301.206	278.289	278.037	276.72[1], 276.7[38]	276.5[10], 274.2[38], 276.52 ± 0.17 [9], 275.5, 279.8 [39], 274.2, 276.5 [36], 276.6 [40], 276.6 [41], 276.5 [42],
N_2H_4	444.525	407.716	407.496	405.4[38]	401.4, 404.4[36], 401.4[38], 404.3 [41], 403.3, 411.2 [39], 404.2, 404.8 [40]

Deviation of Atomization Energies

	Deviation (Expt. Theory)			Deviation (Theory Theory)			Error bar
species	B3LYP	G2	G3	B3LYP	G2	G3	Ref. Exp.
NF	-12.902	-4.965	-7.697	-8.202	-0.265	-2.997	8 [1]
NH	-14.187	-4.22	-8.061	-10.307	-0.34	-4.181	
NH_2	-18.184	-0.98	-2.721	-18.084	-0.88	-2.621	
NH_3	-24.486	-1.569	-1.317	-24.706	-1.789	-1.537	
N_2H_4	-39.125	-2.316	-2.096	-40.125	-3.316	-3.096	
N_2H_3F	-20.904	-2.958	0.003				

Heat of formation at 0K

species	B3LYP	G2	G3	Ref. Expt.	Ref. Theory.
NF	46.698	54.635	51.903	59.56 ± 7.89 [1]	54 ± 0.9 [43]
NF_2	-3.411	5.845	5.852	10.72 ± 1.91 [1]	8 ± 0.9 [43]
NF_3	-41.310	-35.271	-32.321	-30.23 ± 0.27 [1]	-33.8[44], -30.2 ± 0.9 [43]
N_2F_2-cis	4.556	14.606	15.134	17.87 ± 1.20 [1]	
N_2F_2-trans	6.564	15.901	16.477	20.68 ± 1.20 [1]	
N_2F_4	-20.567	-10.652	-6.695	0.58 ± 2.51 [1]	
NH	75.953	85.920	82.079	90.07 ± 4.0 [1], 85.2 ± 0.4 [45]	86.9[10], 86.2[44], 86.7[47], 85.92 ± 0.08 [9],
NH_2	27.606	44.810	43.069	46.23 ± 1.51 [1], 45.8 ± 0.3 [45]	46.5[10], 45.7[44, 46], 45.2[47], 45.27 ± 0.12 [9],
NH_3	-33.786	-10.869	-10.617	-9.31 ± 0.1 [1]	-9.1[44, 46, 10], -9.1 ± 0.17 [9]
N_2H_2-cis	32.416	52.882	52.003	52.63 ± 5.0 [1]	
N_2H_2-trans	27.220	47.827	46.713	52.4 ± 2 [48]	
N_2H_4	-12.945	23.864	24.084	26.18 ± 0.19 [1]	27.2[44]

Deviation of Heat of formation at 0K

	Deviation (Expt. Theory)			Deviation (Theory Theory)			Error bar	
species	B3LYP	G2	G3	B3LYP	G2	G3	Ref. Expt.	Ref. Theo.
NF	12.86	4.923	7.655	7.302	-0.635	2.097	7.89 [1]	0.9 [43]
NF_2	14.129	4.873	4.866	11.411	2.155	2.148	1.91 [1]	0.9 [43]
NF_3	11.079	5.04	2.09	7.51	1.471	-1.479	0.27 [1]	0.9 [43]
N_2F_2-cis	13.317	3.267	2.739				1.2 [1]	
N_2F_2-trans	14.115	4.778	4.202				1.2 [1]	
N_2F_4	21.148	11.233	7.276				2.51 [1]	
NH	14.121	4.154	7.995	10.247	0.28	4.121	4 [1]	0.08 [9]
NH_2	18.625	1.421	3.162	18.094	0.89	2.631	1.51 [1]	0.12 [9]
NH_3	24.478	1.561	1.309	24.686	1.769	1.517	0.1 [1]	0.17 [9]
N_2H_2-cis	20.216	-0.25	0.629				5 [1]	
N_2H_2-trans	25.18	4.573	5.687				2 [48]	
N_2H_4	39.124	2.315	2.095	40.145	3.336	3.116	0.19 [1]	

Heat of formation at 298K

species	B3LYP	G2	G3	Ref. Expt.	Ref. Theory.
NF	48.277	54.632	51.900	59.5 ± 7.89 [1]	60 ± 8 [49]
NF_2	-0.366	5.213	5.220	10.10 ± 1.91 [1], 8 ± 1 [37]	8.5 ± 2 [49]
NF_3	-36.403	-36.701	-33.752	-31.57 ± 0.27 [1], -29.7 ± 1.8 [50]	-35.3[44], -31.6[51], -30.7 [52], -32.96 ± 1.8 [53], -31.4 ± 1 [49]
N_2F_2-cis	10.347	13.208	13.736	16.40 ± 1.2 [1]	17.9 [49]
N_2F_2-trans	12.201	14.589	15.165	19.40 ± 1.2 [1]	
N_2F_4	-12.071	-13.114	-9.157	-2.00 ± 2.51 [1]	-5 ± 1 [49]
NH	80.664	85.944	82.103	90.000 ± 4.0 [1], 84[35], 84.2 ± 2.3 [37]	86.9[10], 86.3[44], 80 ± 3[49], 87.0[47], 84.3[51], 87.03[54], 84.0[52]
NH_2	38.802	44.123	42.381	45.5 ± 1.51 [1], 47.2 ± 1 [37]	46.05[54], 44.5[51,47,52], 45.08[10], 45.0 [44, 46], 42 ± 3 [49]
NH_3	-14.103	-12.549	-12.297	-10.97 ± 0.1 [1]	-10.98[54], -11.5[10], -11.0 [49], -10.8[44,46,10], -10.0[52], -10.2[51]
N_2H_2-cis	47.757	51.169	50.291	50.901 ± 2.61 [1]	50 ± 5 [49] 50.7[[54]]
N_2H_2-trans	42.980	46.114	45.000	50.7 ± 2 [48]	
N_2H_4	16.902	20.389	20.609	22.79[1], 22.25 [55]	23.7[44], 24.9[51], 22.8 [49,54], 25.3 [52], 70.3 [49]
N_3H	59.931	68.334	64.731	71.7 [56], 71.66 [33]	
NHF	25.208	30.820	30.011	25.5 ± 4 [35]	
NHF_2	-19.629	-18.502	-16.499	-15.6 ± 1.5 [35]	-7.8 [57]
NH_2F	-10.672	-9.107	-7.945	-5[35]	-6.98 [54], -6.6 [57]
N_2H_3F	5.251	9.932	10.803		14.4 [57]

Deviation of Heat of formation at 298K

	Deviation (Expt. Theory)			Deviation (Theory Theory)			Error bar	
species	B3LYP	G2	G3	B3LYP	G2	G3	Ref. Expt.	Ref. Theo.
NF	11.223	4.868	7.6	11.723	5.368	8.1	7.89 [1]	8 [49]
NF_2	10.466	4.887	4.88	8.866	3.287	3.28	1.91 [1]	2 [49]
NF_3	4.833	5.131	2.182	1.103	1.401	-1.548	0.27 [1]	
N_2F_2-cis	6.053	3.192	2.664	7.553	4.692	4.164	1.2 [1]	
N_2F_2-trans	7.199	4.811	4.235				1.2 [1]	
N_2F_4	10.071	11.114	7.157	7.071	8.114	4.157	2.51 [1]	3 [49]
NH	9.336	4.056	7.897	5.636	0.356	4.197	4 [1]	
NH_2	6.698	1.377	3.119	6.198	0.877	2.619	1.51 [1]	
NH_3	3.133	1.579	1.327	3.303	1.749	1.497	0.1 [1]	
N_2H_2-cis	3.144	-0.268	0.61	2.243	-1.169	-0.291	2.61 [1]	5 [49]
N_2H_2-trans	7.72	4.586	5.7				2 [48]	
N_2H_4	5.888	2.401	2.181	6.798	3.311	3.091		
N_3H	11.769	3.366	6.969	10.369	1.966	5.569		
NHF	0.292	-5.32	-4.511				4 [35]	
NHF_2	4.029	2.902	0.899	11.829	10.702	8.699	1.5 [35]	
NH_2F	5.672	4.107	2.945	3.692	2.127	0.965		

	Atomization Energies			Heat of formation at 0K			Heat of formation at 298K		
species	B3LYP	G2	G3	B3LYP	G2	G3	B3LYP	G2	G3
NF	84.302	76.365	79.097	46.698	54.635	51.903	48.277	54.632	51.900
NF_2	152.881	143.625	143.618	-3.411	5.845	5.852	-0.366	5.213	5.220
NF_3	209.250	203.211	200.261	-41.310	-35.271	-32.321	-36.403	-36.701	-33.752
N_2F	91.590	70.964	75.858	151.940	172.566	167.672	154.998	172.018	167.124
N_2F_2-cis	257.444	247.394	246.866	4.556	14.606	15.134	10.347	13.208	13.736
N_2F_2-trans	255.436	246.099	245.523	6.564	15.901	16.477	12.201	14.589	15.165
N_2F_3	262.230	247.793	246.804	18.240	32.677	33.666	24.679	30.927	31.916
N_2F_4	319.507	309.592	305.635	-20.567	-10.652	-6.695	-12.071	-13.114	-9.157
N_3F	295.523	280.387	282.996	60.537	75.673	73.064	66.997	74.422	71.813
NH	88.207	78.240	82.081	75.953	85.920	82.079	80.664	85.944	82.103
NH_2	188.184	170.980	172.721	27.606	44.810	43.069	38.802	44.123	42.381
NH_3	301.206	278.289	278.037	-33.786	-10.869	-10.617	-14.103	-12.549	-12.297
N_2H	232.696	215.462	218.976	43.994	61.228	57.714	51.626	60.525	57.011
N_2H_2-cis	295.904	275.438	276.317	32.416	52.882	52.003	47.757	51.169	50.291
N_2H_2-trans	301.100	280.493	281.607	27.220	47.827	46.713	42.980	46.114	45.000
N_2H_3	357.655	324.842	325.609	22.295	55.108	54.341	44.629	52.559	51.793
N_2H_4	444.525	407.716	407.496	-12.945	23.864	24.084	16.902	20.389	20.609
N_3H	340.762	319.382	322.985	48.458	69.838	66.235	59.931	68.334	64.731
NHF	164.972	151.102	151.911	17.658	31.528	30.719	25.208	30.820	30.011
NHF_2	231.275	218.002	215.999	-30.175	-16.902	-14.899	-19.629	-18.502	-16.499
NH_2F	260.391	241.665	240.504	-26.131	-7.405	-6.244	-10.672	-9.107	-7.945
N_2HF-cis	292.250	276.203	276.623	2.910	18.957	18.537	13.439	17.346	16.926
N_2HF-trans	290.112	274.126	274.410	5.048	21.034	20.750	15.800	19.404	19.120
N_2HF_2-a	297.455	274.406	275.384	16.175	39.224	38.246	27.527	37.057	36.079

N_2HF_2-b	293.742	270.767	271.124	19.888	42.863	42.506	31.505	40.905	40.548
N_2HF_2-c	296.059	273.356	273.631	17.571	40.274	39.999	29.595	38.290	38.015
N_2H_2F-a	338.294	309.712	313.471	8.496	37.078	33.319	25.635	34.791	31.032
N_2H_2F-b	331.608	301.588	302.715	15.182	45.202	44.075	32.199	42.796	41.668
N_2H_2F-c	325.643	296.343	297.179	21.147	50.447	49.611	37.890	48.014	47.178
$N_2H_2F_2$-a	381.411	355.196	353.234	-16.151	10.064	12.026	3.296	7.079	9.040
$N_2H_2F_2$-b	396.072	371.081	369.204	-30.812	-5.821	-3.944	-11.698	-8.921	-7.044
$N_2H_2F_2$-c	387.485	360.487	358.587	-22.225	4.773	6.673	-2.704	1.699	3.599
N_2HF_3	352.424	334.478	331.517	-20.324	-2.378	0.583	-6.258	-5.100	-2.140
N_2H_3F	417.799	385.222	384.351	-19.379	13.198	14.069	5.251	9.932	10.803

Bond Dissociation Energies

species	N-F	N-H	N-N
NF	81.19 (82[37], 62.6[50])		
NF_2	66.20 (65.7[3], 62.2[50])		
NF_3	58.49 (56.9[3], 74.0[50], 70.4[58], 61[35])		
N_2F	-149.75		-1.65
N_2F_2-cis	172.91		90.06
N_2F_2-trans	171.48		88.63
N_2F_3	2.77		25.20
N_2F_4	60.59		19.60 (20.8 ± 1 [58], 20.97 [3], 21 ± 1 [37])
N_3F	48.93		208.88
NH		84.11(79.0 ± 0.4[45], 77.3[10])	
NH_2		92.36 (91.0 ± 0.4[45], 92.0[10])	
NH_3		107.32 (106.7 ± 0.3[45], 106.05 ± 0.05[29,59], 107.2[10], 103.2[3], 106.7[46], 110 ± 2[37], 109 [35])	
N_2H		-6.52 (-9[48])	138.66 (132.1 ± 5[48])
N_2H_2-cis		59.36	113.91
N_2H_2-trans		64.65 (59.8 ± 2 [48])	119.21 (128 ± 9 [48])

N_2H_3		51.14 (53.5 ± 3 [48])	72.69
N_3H		89.13 (85 [37], 92.18 [3], 92 ± 5 [56])	105.85
NHF	71.61	74.53	
NHF_2	66.03 (60 [35])	74.36 (78 [35], 75 ± 2.5 [37])	
NH_2F	69.85 (69 [35])	90.60 (83 [35])	
N_2HF-cis	59.61	202.84	147.28
N_2HF-trans	57.41	200.64	145.09
N_2HF_2-a	2.56	21.78	51.24
N_2HF_2-b	-1.91	25.83	41.36
N_2HF_2-c	-1.57	29.79	187.94
N_2H_2F-a		38.53	63.25
N_2H_2F-b	28.14	27.90	70.45
N_2H_2F-c	17.34	24.58	64.94
$N_2H_2F_2$-a	41.51	79.68	38.56
$N_2H_2F_2$-b	68.23	100.23	67.07
$N_2H_2F_2$-c	53.94	89.59	56.42
N_2H_3F	60.51	72.87	61.59
N_2HF_3	62.21	86.70	37.37

[1] Jr. M. W. Chase., Journal of Physical and Chemical Reference Data, monograph 9, 1998.
[2] M. Bettendorff and S. D. Peyerimhoff., Chemical Physics, 99:55--72, 1985.
[3] A. A. Radzig and B.M. Smirnov., *Reference Data on Atoms, Molecules and Ions*., Springer-Verlag, Berlin, 1985.
[4] M. D. Harmony, R.J. Myers, L.J. Schoen, D.R. Lide, and D.E. Mann., J. Chem. Phys., 35(3):1129--1130, 1961.
[5] M.D. Harmony and R.J. Myers., Journal of Chemical Physics, 37(3):636--641, 1962.
[6] T.A. Ford and D. Steele., J. Phys. Chem., 100:19336--19343, 1996.
[7] D. Christen, H.G. Mack, G. Schatte, and H. Willner., Journal of the American Chemical Society, 110:707--712, 1988.
[8] G. Herzberg., *Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules*, volume 1., Van Nostrand Reinhold Company, New York, second edition, 1950.
[9] D. A. Dixon, D. Feller, and K. A. Peterson., J. Chem. Phys., 115(6):2576--2581, 2001.
[10] J. A. Pople, B. T. Luke, M. J. Frisch, and J. S. Binkley., Journal fo Physical and Chemistry, 89:2198--2203, 1985.
[11] H. Anane, A. Jarid, A. Boutalib, I.N.-Gil, and F. Tom\'as., Journal of Molecular Strucuture (Theochem), 455:51--57, 1998.
[12] L. M. Nxumalo, M. Andrzejak, and T. A. Ford., Vibrational Spectroscopy, 12:221--235, 1996.
[13] J.R. Thomas, B.J. Deleeuw, G. Vacek, T.D. Crawford, Y. Yamaguchi, and H.F. Schaefer III., J. Chem. Phys., 99(1):403--416, 1993.
[14] L.J. Schaad and H.B. Kinser., Journal of Physical Chemistry, 73(6):1901--1911, 1969.
[15] N. W. Winter and R.M. Pitzer., Journal of Chemical Physics, 62(4):1269--1275, 1975.
[16] J. Demaison, F. Hegelind, and H. B\H{u}rger., Journal of Molecular Structure, 413-414:447--456, 1997.
[17] B. P. Winnewisser., Journal of Molecular Spectroscopy, 82:220--223, 1980.
[18] H.-J. Himmel, M. Junker, and H. Schn\H{o}ckel., J. Chem. Phys., 117(7):3321--3326, 2002.
[19] J. Chen and P. L. Dagdigian., Jornal of Molecular Spectroscopy, 162:152--167, 1993.
[20] J. Chen and P. J. Dagdigian., Journal of Chemical Physics, 96(10):7333--7343, 1992.
[21] D. Christen, R. Minkwitz, and R. Nass., Journal of the American Chemical Society, 109:7020--7024, 1987.
[22] K. Hakura and H. Uehara., Journal of Chemical Physics, 74(11):5995--5999, 1981.
[23] H. Uehara and K. Horiai., Journal of Chemical Physics, 84(10):5568--5574, 1986.
[24] R. Lascola, R. Withnall, and L. Andrews., Journal of Physical Chemistry, 92:2145--2149, 1988.
[25] T. Shimamouchi., Journal of Physical and Chemistry - Reference Data, 6(3):993--1102, 1977.
[26] A.R.W.McKellar and M. Vervloet., Journal of Molecular Spectroscopy, 142:319--335, 1990.
[27] T. Amano, P.F. Bernath, and A.R.W.McKellar., Journal of Molecular Spectroscopy, 94:100--113, 1982.
[28] M. Kroll., Journal of Chemical Physics, 63(1):319--325, 1975.
[29] D. H. Mordaunt, R. N. Dixon, and M. N. R. Ashfold., Journal of Chemical Physics, 104(17):6472--6481, 1996.
[30] A. J\H{u}rgensen and R. G. Cavell., Chemical Physics, 273:77--89, 2001.
[31] F. Hegelund, H. B\H{u}rger, and O. Polanz., Journal of Molecular Spectroscopy, 167:1--10, 1994.
[32] R. Lascola, R. Withnall, and L. Andrews., Inorg. Chem., 27:642--648, 1988.
[33] B.L. Evans, A.D. Yoffe, and P. Gray., Chemical Reviews, 59:515--568, 1959.

[34] L. Andrews and R. Lascola., Journal of the American Chemical Society, 109:6243--6247, 1987.
[35] H. Baumg\H{a}rtel, H.-W. Jochims, E. R\H{u}hl, R. Dammel, J. Minkwitz, and R. Nass., Inorganic Chemistry, 28:943--949, 1989.
[36] L. A. Curtiss, K. Raghavachari, G. W. Trucks, and J. A. Pople., J. Chem. Phys., 94(11):7221--7230, 1991.
[37] R. C. West, M. J. Astle, and W. H. Beyer, editors., {\em CRC Handbook of Chemistry and Physics}., CRC Press, Inc., Boca Raton, 65 edition, 1985.
[38] J. A. Pople, H. Gordon, D. J. Fox, K. Raghavachari, and L. A. Curtiss., J. Chem. Phys., 90(10):5622--5629, 1989.
[39] Jr. C.W. Bauschlicher and H. Partridge., Journal of Chemical Physics, 103(5):1788--1791, 1995.
[40] L. A. Curtiss, K. Raghavachari, and J. A. Pople., J. Chem. Phys., 98(2):1293--1298, 1993.
[41] L.A. Curtiss, J. E. Carpenter, K. Raghavachari, and J.A. Pople., J. Chem. Phys., 96(12):9030--9034, 1992.
[42] J. M. L. Martin and T. J. Lee., Chemical Physics Letters, 258:136--143, 1996.
[43] M. Aschi and F. Grandinetti., Journal of Molecular Structure (Theochem), 497:205--209, 2000.
[44] L. A. Curtiss, K. Raghavachari, P. C. Redfern, and J. A. Pople., J. Chem. Phys., 106(3):1063--1079, 1997.
[45] S. T. Gibson, J. P. Greene, and J. Berkowitz., Journal of Chemical Physics, 83(9):4319--4328, 1985.
[46] J. W. Ochterski, G. A. Petersson, and K. B. Wiberg., J. Am. Chem. Soc., 117:11299--11308, 1995.
[47] C. Poon and P. M. Mayer., Canadian Journal of Chemistry, 80:25--30, 2002.
[48] S. N. Foner and R. L. Hudson., J. Chem. Phys., 68(7):3162--3168, 1978.
[49] S. W. Benson., *Thermochemical Kinetics - Methods for the Estimation of Thermochemcial Data and Rate Parameters*., John Wiley & Sons, New York, 1960.
[50] G.T.Armstrong, S. Marantz, and C. F. Coyle., Journal of the Americal Chemical Society, 81:3798, 1959.
[51] L.A. Curtiss, K. Raghavachari, P. C. Redfern, V. Rassolov, and J. A. Pople., Journal of Chemical Physics, 109(18):7764--7776, 1998.
[52] L.A. Curtiss, P.C. Redfern, K. Raghavachari, V. Rassolov, and J. A. Pople., J. Chem. Phys., 110(10):4703--4709, 1999.
[53] L.A. Curtiss, P.C. Redfern, K. Raghavachari, and J.A. Pople., Chemical Physics Letters, 313:600--607, 1999.
[54] M. D. Allendorf and C. F. Melius., J. Phys. Chem. A, 101(14):2670--2680, 1997.
[54] G. Leroy, M. Sana, C. Wilante, and M.-J. van Zieleghem., Journal of Molecular Strucuture, 247:199--215, 1991.
[55] A.M. Hughes, R.J. Corruccini, and E. C. Gilbert., Journal of the Americal Chemical Society, 61(10):2639--2642, 1939.
[56] M.J. Pellerite, R. L. Jackson, and J.I. Brauman., J. Phys. Chem., 85:1624--1626, 1981.
[57] L. Radom, W.J. Hehre, and J.A. Pople., Journal of the American Chemical Society, 93(2):289--300, 1971.
[58] F. A. Johnson and C. B. Colburn., Journal of the American Chemical Society, 83:3043--3047, 1961.
[59] D. H. Mordaunt, M. N. R. Ashfold, and R. N. Dixon., Journal of Chemical Physics, 104(17):6460--6471, 1996.