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Thermochemistry of BNH_xF_y Molecule

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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 BNH_xF_y species, in a total of 39 species, in which only 8 species have theoretical reference data to be compared. Good agreement is found between the calculation data and theoretical reference data for the quantities analyzed here. 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 for growth 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. This work is complementary to the "Thermochemistry of $N_xH_yF_z$ Molecule", also to be present in this conference.

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**

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

Results, Discussion and Conclusion

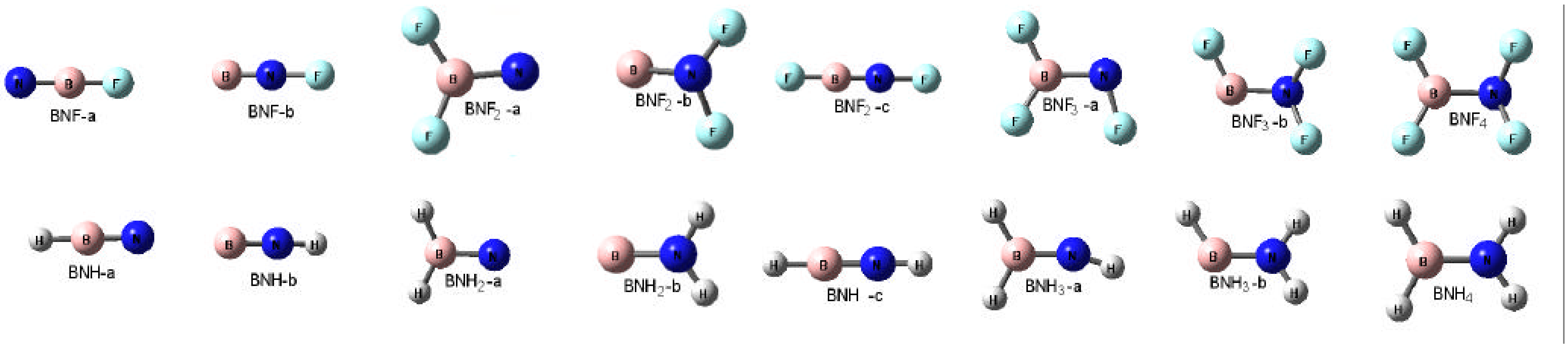
- *Geometries, frequencies and energies were obtained using GAUSSIAN98 program at G3 level.*
- *Geometries, frequencies, atomization energies, heats of formation and bond dissociation energies compared with experimental and theoretical data when avaliable.*
- *Good agreement is found between the calculation 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.*

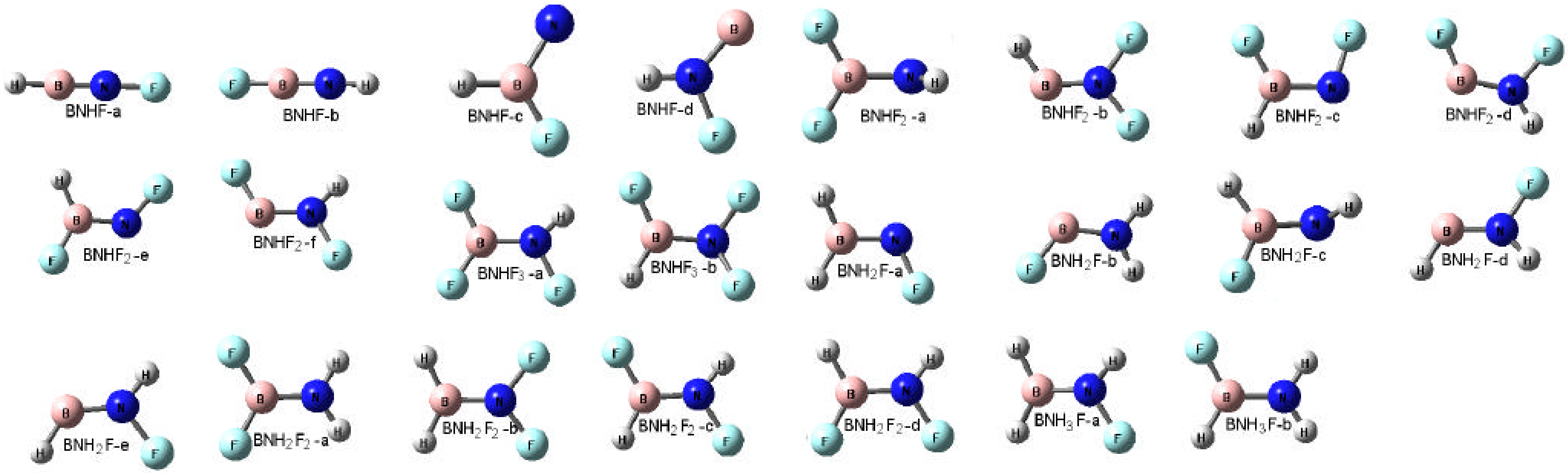
Acknowledgment

CENAPAD SP Centro Nacional de Processamento de ALTO DESEMPENHO EM SÃO PAULO

CNPq

Sub-system	*molecules*
B/N/F	*BNF-a, BNF-b,* *BNF_2-a, BNF_2-b, BNF_2-c,* *BNF_3-a, BNF_3-b,* *BNF_4*
B/N/H	***BNH-a, BNH-b,*** ***BNH_2-a, BNH_2-b, BNH_2-c,*** ***BNH_3-a, BNH_3-b,*** ***BNH_4***
B/N/H/F	*BNHF-a, BNHF-b, BNHF-c, BNHF-d,* *$BNHF_2$-a, $BNHF_2$-b, $BNHF_2$-c, $BNHF_2$-d, $BNHF_2$-e, $BNHF_2$-f,* *$BNHF_3$-a, $BNHF_3$-b,* *BNH_2F-a, BNH_2F-b, BNH_2F-c, BNH_2F-d, BNH_2F-e,* *BNH_2F_2-a, BNH_2F_2-b, BNH_2F_2-c, BNH_2F_2-d,* *BNH_3F-a, BNH_3F-b*


BNF-a
BNF-b
BNF_2 -a
BNF_2 -b
BNF_2 -c
BNF_3 -a
BNF_3 -b
BNF_4
BNH-a
BNH-b
BNH_2-a
BNH_2-b
BNH -c
BNH_3-a
BNH_3-b
BNH_4


BNHF-a
BNHF-b
BNHF-c
BNHF-d
$BNHF_2$ -a
$BNHF_2$ -b
$BNHF_2$ -c
$BNHF_2$ -d
$BNHF_2$ -e
$BNHF_2$-f
$BNHF_3$ -a
$BNHF_3$ -b
BNH_2F-a
BNH_2F-b
BNH_2F-c
BNH_2F-d
BNH_2F-e
BNH_2F_2 -a
BNH_2F_2 -b
BNH_2F_2 -c
BNH_2F_2-d
BNH_3F-a
BNH_3F-b

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

species	Geometry (Å and degrees)
BNH-a	R_{BN} = 1.240 (1.325[2], 1.290[1]) R_{BH} = 1.170 (1.174[2], 1.150[1]), A_{HBN} = 180.0 (180.0[1])
BNH-b	R_{BN} = 1.230 (1.253[2], 1.220[1]), R_{NH} = 0.990 (1.007[2], 0.982[1]), A_{HNB} = 180.0 (180.0[1])
BNH_2-a	R_{BN} = 1.393 (1.470[1]), R_{BH} = 1.190 (1.189[1]), A_{HBH} = 129.8 (121.7[1]), A_{HBN} = 115.1 (119.15[1])
BNH_2-b	R_{BN} = 1.391 (1.401[2], 1.380[1]), R_{NH} = 1.010 (1.024[2], 0.990[1]), A_{HNH} = 114.5 (115[2], 114.15[1]), A_{HNB} = 122.8 (122.92[1])
BNH_2-c	R_{BH} = 1.171 (1.193[2], 1.196[1], 1.141[3]), R_{BN} = 1.240 (1.252[2], 1.220[1], 1.196[3]), R_{NH} = 0.990 (1.005[2], 0.980[1], 1.009[3]), A_{HBN} = 180.0 (179.91[1]), A_{HNB} = 180.0 (179.88[1])
BNH_3-a	R_{BN} = 1.348 (1.398[2], 1.390[1], 1.352[4]), R_{NH} = 1.000 (1.024[2], 0.990[1]), R_{BH} = 1.200 (1.223[2], 1.193[1]), A_{HBH} = 122.1 (132.2[2], 121.08[1]), A_{HBN} = 117.9 (113.7[2], 119.35[1]), A_{HNB} = 162.4 (123.5[2], 132.0[1])
BNH_3-b	R_{BH} = 1.190 (1.191[1]), R_{BN} = 1.380 (1.380[1]), R_{NH} = 1.010 (0.990[1]), A_{HNH} = 113.5 (113.36[1]), A_{HNB} = 123.5 (123.21[1]), A_{HBN} = 123.6 (123.39[1])
BNH_4	R_{BH} = 1.195 (1.193[1], 1.160[3]), R_{BN} = 1.390 (1.380[1], 1.372[3], 1.4000[4]), R_{NH} = 1.010 (0.990[1], 1.019[3]), A_{HBH} = 122.0 (121.22[1], 121.1[3]), A_{HNH} = 113.7 (113.55[1], 112.3[3]), A_{HBN} = 119.0 (119.35[1]), A_{HNB} = 123.1 (123.22[1])
BNF-a	R_{BF} = 1.290, R_{BN} = 1.324, A_{FBN} = 180.0
BNF-b	R_{BN} = 1.228, R_{NF} = 1.320, A_{BNF} = 180.0
BNF_2-a	R_{BF} = 1.332, R_{BN} = 1.420, A_{FBF} = 122.95, R_{FBN} = 118.5
BNF_2-b	R_{BN} = 1.522, R_{NF} = 1.420, A_{FNF} = 104.2, R_{BNF} = 96.8
BNF_2-c	R_{BF} = 1.310, R_{BN} = 1.230, R_{NF} = 1.329, A_{FBN} = 180.0, A_{BNF} = 180.0

BNF_3-a	R_{BF} = 1.320, R_{BN} = 1.490, R_{NF} = 1.376, A_{FBF} = 120.9, A_{FBN} = 123.3, A_{BNF} = 105.4
BNF_3-b	R_{BF} = 1.310, R_{BN} = 1.460, R_{NF} = 1.390, A_{FNF} = 104.9, A_{FBN} = 119.5, A_{BNF} = 112.2
BNF_4	R_{BF} = 1.316, R_{BN} = 1.480, R_{NF} = 1.400, A_{FBF} = 122.3, A_{FNF} = 104.4, A_{FBN} = 118.7, A_{BNF} = 107.7
BNHF-a	R_{BH} = 1.150, R_{BN} = 1.240, R_{NF} = 1.320, A_{HBN} = 180.0, A_{BNF} = 180.0
BNHF-b	R_{BF} = 1.311, R_{BN} = 1.240, R_{NH} = 0.990, A_{HNB} = 180.0, A_{FBN} = 180.0
BNHF-c	R_{BF} = 1.330, R_{BN} = 1.480, R_{BH} = 1.190, A_{FBN} = 118.8, A_{HBN} = 121.6
BNHF-d	R_{NF} = 1.401, R_{BN} = 1.410, R_{NH} = 1.010, A_{BNF} = 118.0, A_{HNB} = 132.7
$BNHF_2$-a	R_{BF} = 1.333, R_{BN} = 1.440, R_{NH} = 1.010, A_{FBF} = 118.3, A_{FBN} = 120.7, A_{HNB} = 118.7
$BNHF_2$-b	R_{BH} = 1.180, R_{BN} = 1.360, R_{NF} = 1.370, A_{FNF} = 105.6, A_{BNF} = 128.0, A_{HBN} = 123.9
$BNHF_2$-c	R_{BF} = 1.320, R_{BN} = 1.480, R_{BH} = 1.180, R_{NF} = 1.380, A_{FBH} = 121.2, A_{HBN} = 117.3, A_{FBN} = 121.5, A_{BNF} = 106.6
$BNHF_2$-d	R_{BF} = 1.320, R_{BN} = 1.380, R_{NF} = 1.400, R_{NH} = 1.000, A_{FNH} = 108.2, A_{HNB} = 130.7, A_{BNF} = 121.3, A_{FBN} = 124.6
$BNHF_2$-e	R_{BF} = 1.320, R_{BH} = 1.187, R_{BN} = 1.480, R_{NF} = 1.370, A_{FNH} = 121.2, A_{HBN} = 117.3, A_{FBN} = 121.4, A_{BNF} = 106.7
$BNHF_2$-f	R_{BF} = 1.335, R_{BN} = 1.390, R_{NF} = 1.390, R_{NH} = 1.010, A_{FBN} = 119.5, A_{HNB} = 132.6, A_{BNF} = 119.0, A_{FNH} = 108.3
$BNHF_3$-a	R_{BF} = 1.328, R_{BN} = 1.400, R_{NH} = 1.000, R_{NF} = 1.400, A_{FBF} = 120.6, A_{FBN} = 121.7, A_{FNH} = 108.6, A_{BNF} = 117.5, A_{HNB} = 129.8
$BNHF_3$-b	R_{BF} = 1.320, R_{BN} = 1.450, R_{BH} = 1.180, R_{NF} = 1.390, A_{FBH} = 123.1, A_{FBN} = 117.4, A_{HBN} = 119.0, A_{FNF} = 105.4, A_{BNF} = 113.5
BNH_2F-a	R_{BH} = 1.189, R_{BN} = 1.460, R_{NF} = 1.380, A_{HBH} = 124.2, A_{HBN} = 120.3, A_{BNF} = 105.6
BNH_2F-b	R_{BF} = 1.340, R_{BN} = 1.390, R_{NH} = 1.010, A_{HNH} = 114.8, A_{HNB} = 122.6, A_{FBN} = 121.8
BNH_2F-c	R_{BF} = 1.341, R_{BN} = 1.420, R_{BH} = 1.190, R_{NH} = 1.010,

	A_{FBH} = 119.0, A_{FBN} = 120.8, A_{HBN} = 120.0, A_{HNB} = 124.6
BNH_2F-d	R_{BH} = 1.180, R_{BN} = 1.360, R_{NF} = 1.410, R_{NH} = 1.010, A_{FNH} = 106.0, A_{HNB} = 133.2, A_{BNF} = 120.8, A_{HBN} = 121.5
BNH_2F-e	R_{BH} = 1.183, R_{BN} = 1.360, R_{NF} = 1.410, R_{NH} = 1.010, A_{HBN} = 128.2, A_{HNB} =131.9 , A_{BNF} =122.2 , A_{FNH} = 105.9
BNH_2F_2-a	R_{BF} = 1.342, R_{BN} = 1.370, R_{NH} = 1.000, A_{FBF} = 117.9, A_{HNH} = 115.3, A_{FBN} = 121.1, A_{HNB} = 122.3
BNH_2F_2-b	R_{BH} = 1.180, R_{BN} = 1.370, R_{NF} = 1.360, A_{HBH} = 127.8, A_{FNF} = 106.4, A_{HBN} = 116.1, A_{BNF} = 126.8
BNH_2F_2-c	R_{BF} = 1.348, R_{BH} = 1.180, R_{BN} = 1.390, R_{NF} = 1.390, R_{NH} = 1.010, A_{FBH} = 121.9, A_{FNH} = 108.4, A_{FBN} = 116.6, A_{HBN} = 121.6, A_{BNF} = 119.4, A_{HNB} = 132.3
BNH_2F_2-d	R_{BF} = 1.336, R_{BH} = 1.190, A_{BN} = 1.390, R_{NF} = 1.390, R_{NH} = 1.000, A_{FBH} = 122.0, A_{HBN} = 116.1, A_{FNH} = 108.6, A_{BNF} = 120.4
BNH_3F-a	R_{BH} = 1.190, R_{BN} = 1.380, R_{NF} = 1.390, R_{NH} = 1.010, A_{HBH} = 125.5, A_{FNH} = 106.8, A_{HBN} = 119.8, A_{BNF} = 121.4, A_{HNB} = 131.8
BNH_3F-b	R_{BF} = 1.352, R_{BN} = 1.390, R_{BH} = 1.190, R_{NH} = 1.010, A_{HNH} = 114.8, A_{FBH} = 119.0, A_{FBN} = 119.4, A_{HNB} = 122.7, A_{HBN} = 121.6

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

species	HF/6-31G(d)
BNH-a	947.2, 947.2, 1892.6, 3033.3 (690.1, 693.9, 1513.9, 2690.8[1], 716.3, 1563.5, 2951.8[4])
BNH-b	586.9, 586.9, 1992.6, 4113.0, (432.5, 1829.6, 3693.7[2], 2035.0, 3675.0[5], 520.0, 520.0, 1778.7, 3676.2[1], 482.3, 1862.3, 3783.1[2])
BNH_2-a	898.7, 1102.2, 1183.3, 1292.6, 2728.4, 2841.4 (766.4, 915.1, 963.6, 1206.9, 2434.4, 2506.6 [1])
BNH_2-b	452.6, 693.8, 1313.3, 1741.3, 3776.9, 3879.9 (404.4, 619.4, 1173.1, 1554.8, 3372.2, 3464.2 [1])
BNH_2-c	593.3, 593.3, 838.6, 838.6, 1976.1, 3027.1, 4134.5 (460.0, 1785.0, 2800.0, 3700.0[5], 461.0, 671.6, 1782.8, 2775.3, 3700.5 [2], 531.2, 695.6, 749.2, 1765.2, 2702.0, 3690.5[1], 492.9, 719.0, 1799.2, 2777.6, 3796.7, [2])
BNH_3-a	146.4, 464.1, 892.6, 1080.4, 1194.6, 1384.0, 2691.6, 2757.8, 3852.6 (129.4, 414.1, 796.8, 964.7, 1066.6, 1235.8, 2403.4, 2462.5, 3440.2 [1])
BNH_3-b	617.1, 818.5, 896.0, 1168.7, 1375.1, 1796.6, 2746.9, 3798.7, 3899.0 (550.8, 730.8, 800.0, 1043.5, 1227.3, 1604.1, 2452.3, 3391.5 3481.4 [1])
BNH_4	628.5, 792.6, 880.1, 1105.5, 1224.6, 1226.1, 1442.3, 1812.0, 2703.4, 2770.8, 3830.6, 3925.5 (561.1, 707.7, 786.0, 987.4, 1093.3, 1095.0, 1288.3, 1617.7, 2413.2, 2472.8, 3419.7, 3504.6[1])
BNF-a	462.5, 481.5, 1050.0, 2024.1
BNF-b	222.8, 222.8, 1115.0, 2191.6,
BNF_2-a	322.0, 476.9, 680.0, 918.0, 1521.0, 1524.7
BNF_2-b	238.7, 306.9, 539.5, 894.8, 1190.0, 1368.5
BNF_2-c	129.7, 129.7, 452.1, 452.1, 809.6, 1429.0, 2483.3
BNF_3-a	62.8, 255.0, 454.0, 587.6, 636.3, 878.9, 1201.4, 1469.3, 1602.1
BNF_3-b	186.9, 235.3, 315.1, 498.4, 597.5, 923.21226.7, 1347.8, 1520.3
BNF_4	94.1, 222.5, 262.7, 443.4, 503.7, 573.5, 727.4, 808.0, 1216.3, 1231.5, 1531.1, 1619.6

BNHF-a	250.3, 250.3, 781.8, 781.8, 1109.9, 2235.8, 3054.2,
BNHF-b	476.6, 476.6, 526.7, 526.7, 1077.4, 2276.4, 4157.3,
BNHF-c	475.6, 906.9, 1029.3, 1193.9, 1458.5, 2818.4,
BNHF-d	251.4, 361.5, 1057.6, 1349.7, 1595.1, 3872.6
$BNHF_2$-a	213.2, 442.0, 507.5, 576.1, 891.6,, 909.6, 1479.7, 1500.4, 3762.3
$BNHF_2$-b	204.6, 420.5, 567.5, 756.2, 901.4, 988.2, 1292.2, 1613.5, 2874.8
$BNHF_2$-c	78.8, 265.1, 702.2, 922.4, 958.7, 1195.2, 1239.3, 1516.0, 2856.2
$BNHF_2$-d	215.6, 223.7, 481.4, 707.9, 1030.3, 1236.0, 1520.5, 1623.3, 3942.1
$BNHF_2$-e	78.9, 265.0, 702.2, 922.5, 958.6, 1195.2, 1239.4, 1516.0, 2855.9
$BNHF_2$-f	186.6, 305.4, 433.4, 524.3, 1140.6, 1317.0, 1440.3, 1632.5, 3888.0
$BNHF_3$-a	68.2, 221.9, 350.9, 451.1, 593.6, 681.6, 909.4, 1233.2, 1446.3, 1579.3, 1680.1, 3930.0
$BNHF_3$-b	177.1, 236.7, 286.2, 502.1, 600.6, 900.9, 976.9, 1167.5, 1254.4, 1357.6, 1555.7, 2886.2
BNH_2F-a	226.3, 418.0, 923.4, 963.9, 1101.0, 1226.1, 1369.3, 2767.9, 2866.3
BNH_2F-b	447.7, 504.7, 614.5, 956.2, 1246.5, 1472.1, 1783.1, 3809.7, 3935.1
BNH_2F-c	246.3, 512.9, 629.2, 1007.8, 1092.8, 1189.8, 1475.1, 2786.3, 3779.9
BNH_2F-d	419.1, 479.9, 804.3, 901.0, 1152.4, 1433.0, 1598.1, 2812.2, 3886.7
BNH_2F-e	431.6, 448.5, 821.9, 969.9, 1053.3, 1400.6, 1586.7, 2846.4, 3921.9
BNH_2F_2-a	398.8, 458.4, 503.3, 579.4, 710.7, 920.0, 985.9, 1523.3, 1526.4, 1797.2, 3851.9, 3954.9
BNH_2F_2-b	183.2, 403.5, 565.2, 621.4, 907.7, 969.9, 1059.8, 1292.5, 1339.3, 1658.6, 2791.8, 2898.9
BNH_2F_2-c	178.0, 310.5, 454.6, 525.7, 983.8, 1133.0, 1160.8, 1317.3, 1443.8, 1664.6, 2855.9, 3911.7,
BNH_2F_2-d	229.6, 230.8, 472.5, 717.0, 982.1, 988.0, 1182.2, 1293.7, 1536.9, 1657.4, 2816.4, 3930.9
BNH_3F-a	395.3, 447.2 , 736.2, 939.8, 1080.9, 1130.7, 1277.9, 1463.5, 1637.9, 2750.5, 2847.3, 3916.1
BNH_3F-b	462.0, 524.9, 648.2, 945.5, 1009.7, 1172.7, 1255.7, 1509.3, 1796.5, 2786.0, 3834.4, 3939.6

Atomization Energies

species	Atomization Energies			Ref. Theory.	Deviation (Theory Theory)		
	B3LYP	G2	G3		B3LYP	G2	G3
BNH-a	204.135	189.355	191.287	203.4[1]	-0.735	14.045	12.113
BNH-b	241.723	226.786	228.801	227.9[1]	-13.823	1.114	-0.901
BNH_2-a	250.364	228.167	230.340	245.7[1]	-4.664	17.533	15.36
BNH_2-b	318.103	300.303	300.728	300[1]	-18.103	-0.303	-0.728
BNH_2-c	359.393	339.491	339.941	337.8[1]	-21.593	-1.691	-2.141
BNH_3-a	389.368	360.383	361.466	355.1[1]	-34.268	-5.283	-6.366
BNH_3-b	396.593	367.500	367.987	368.2[1]	-28.393	0.7	0.213
BNH_4	507.290	474.686	473.074	473.2[1]	-34.09	-1.486	0.126

Heat of formation at 0K

species	Calculated heat of formation at 0K			Ref. Theory.	Deviation (Theory Theory)		
	B3LYP	G2	G3		B3LYP	G2	G3
BNH-a	96.225	111.005	109.073	94.5[1]	-1.725	-16.505	-14.573
BNH-b	58.637	73.574	71.559	70.1[1]	11.463	-3.474	-1.459
BNH_2-a	101.626	123.823	121.650	103.9[1]	2.274	-19.923	-17.75
BNH_2-b	33.887	51.687	51.262	49.6[1]	15.713	-2.087	-1.662
BNH_2-c	-7.403	12.499	12.049	11.8[1]	19.203	-0.699	-0.249
BNH_3-a	14.252	43.237	42.154	46.1[1], 44.5[4]	31.848	2.863	3.946
BNH_3-b	7.027	36.120	35.633	33.1[1]	26.073	-3.02	-2.533
BNH_4	-52.040	-19.436	-17.824	-20.3[1], -15.5[4]	31.74	-0.864	-2.476

Heat of formation at 298K

species	Calculated heat of formation at 298K			Ref. Theory.	Deviation (Theory Theory			Ref. Theo. (Error bar)
	B3LYP	G2	G3		B3LYP	G2	G3	
BNH-a	104.924	110.823	108.891	94.32 ± 1.03 [1]	-10.604	-16.503	-14.571	1.03 [1]
BNH-b	68.197	73.569	71.553	70.03 ± 1.59 [1]	1.833	-3.539	-1.523	1.59 [1]
BNH_2-a	113.720	122.947	120.775	102.93 ± 1.05 [1]	-10.79	-20.017	-17.845	1.05 [1]
BNH_2-b	48.820	51.007	50.581	48.85 ± 1.18 [1]	0.03	-2.157	-1.731	1.18 [1]
BNH_2-c	7.404	11.597	11.148	10.95 ± 1.00 [1] 31[3] 7.05 [5]	3.546	-0.647	-0.198	1.00 [1]
BNH_3-a	32.145	41.961	40.878	44.58 ± 1.18 [1] 43.3[4]	12.435	2.619	3.702	1.18 [1]
BNH_3-b	27.963	34.392	33.906	31.18 ± 1.20 [1]	3.217	-3.212	-2.726	1.20 [1]
BNH_4	-24.845	-22.135	-20.523	-23.19 ± 1.02 [1] -18.4[4] -14[3] -23.02 [5]	1.655	-1.055	-2.667	1.02 [1]

	Atomization Energies			Heat of formation at 0K			Heat of formation at 298K		
species	B3LYP	G2	G3	B3LYP	G2	G3	B3LYP	G2	G3
BNF-a	274.551	261.626	264.017	-7.351	5.574	3.183	-2.054	5.661	3.270
BNF-b	184.047	173.554	174.884	83.153	93.646	92.316	88.502	94.070	92.740
BNF_2-a	359.720	353.135	353.146	-74.050	-67.465	-67.476	-67.597	-67.918	-67.928
BNF_2-b	214.708	210.251	208.818	70.962	75.419	76.852	75.887	75.210	76.643
BNF_2-c	341.744	329.747	330.615	-56.074	-44.077	-44.945	-48.671	-44.093	-44.959
BNF_3-a	463.989	451.388	468.378	-159.849	-147.248	-164.238	-151.439	-148.004	-164.994
BNF_3-b	360.701	346.260	345.518	-56.561	-42.120	-41.378	-48.954	-42.854	-42.111
BNF_4	528.227	518.120	516.035	-205.617	-195.510	-193.425	-195.431	-196.828	-194.743
BNHF-a	301.634	286.521	286.489	17.196	32.309	32.341	27.595	31.818	31.851
BNHF-b	403.557	387.297	388.402	-84.727	-68.467	-69.572	-73.042	-69.088	-70.193
BNHF-c	330.857	313.433	315.544	-12.027	5.397	3.286	-2.506	4.660	2.550
BNHF-d	263.922	251.009	250.662	54.908	67.821	68.168	65.403	67.419	67.766
$BNHF_2$-a	496.217	479.363	480.234	-158.917	-142.063	-142.934	-146.507	-143.167	-144.038
$BNHF_2$-b	315.241	294.659	294.084	22.059	42.641	43.216	32.971	41.466	42.041
$BNHF_2$-c	406.166	387.203	387.017	-68.866	-49.903	-49.717	-57.176	-50.944	-50.757
$BNHF_2$-d	407.209	386.221	386.455	-69.909	-48.921	-49.155	-56.787	-49.957	-50.191
$BNHF_2$-e	406.166	387.203	387.017	-68.866	-49.903	-49.717	-57.177	-50.945	-50.758
$BNHF_2$-f	404.130	383.681	383.953	-66.830	-46.381	-46.653	-53.815	-47.377	-47.649
$BNHF_3$-a	571.451	554.737	553.676	-215.681	-198.967	-197.906	-200.093	-200.475	-199.415
$BNHF_3$-b	473.519	456.331	453.804	-117.749	-100.561	-98.034	-104.212	-102.218	-99.692
BNH_2F-a	348.691	324.207	323.726	21.769	46.253	46.734	35.963	44.919	45.400
BNH_2F-b	452.318	427.818	428.419	-81.858	-57.358	-57.959	-63.878	-58.846	-59.446

BNH_2F-c	440.099	416.609	417.254	-69.639	-46.149	-46.794	-54.217	-47.486	-48.131
BNH_2F-d	355.307	329.684	329.573	15.153	40.776	40.887	31.057	39.281	39.393
BNH_2f-e	357.800	331.842	331.796	12.660	38.618	38.664	28.660	37.128	37.173
BNH_2F_2-a	621.239	600.044	599.176	-232.309	-211.114	-210.246	-211.739	-213.301	-212.432
BNH_2F_2-b	425.427	402.096	399.561	-36.497	-13.166	-10.631	-19.494	-15.241	-12.706
BNH_2F_2-c	516.963	493.806	492.204	-128.033	-104.876	-103.274	-109.107	-106.833	-105.231
BNH_2F_2-d	517.866	494.564	492.954	-128.936	-105.634	-104.024	-109.917	-107.640	-106.030
BNH_3F-a	465.739	437.144	435.036	-43.649	-15.054	-12.946	-21.516	-17.478	-15.369
BNH_3F-b	564.317	536.792	535.473	-142.227	-114.702	-113.383	-118.286	-117.175	-115.856

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Bond Dissociation Energies

species	B-F	B-H	B-N	N-F	N-H
BNH-a		88.80 (98.1 [1])	110.62 (121.0 [1])		
BNH-b			147.04 (152.0 [1])		126.13 (122.3 [1])
BNH_2-a		40.76 (61.6 [1])	71.40 (85.6 [1])		
BNH_2-b			128.29 (132.2 [1])		73.61 (73.3 [1])
BNH_2-c		113.05 (111.2 [1])	176.90 (178.5 [1], 137 [3])		150.38 (135.4 [1])
BNH_3-a		22.91 (18.4 [1])	119.83 (118.0 [1], 122.4 [4])		132.54 (110.4 [1])
BNH_3-b		69.32	114.42		111.47
BNH_4		107.07 (106.4 [1])	141.51 (144.8[1], 141.5 [4], 104 [3])		114.04 (119.8 [1])
BNF-a	161.30		85.26		
BNF-b			95.65	71.83	
BNF_2-a	90.72		63.94		
BNF_2-b			65.07	35.62	
BNF_2-c	157.22		71.82	67.75	
BNF_3-a	139.55		99.34	116.59	
BNF_3-b	138.27		22.29	138.27	
BNF_4	172.15		82.41	49.27	
BNHF-a		113.53	125.99	96.56	
BNHF-b	285.82		127.26		126.10
BNHF-c	125.86	53.36	91.38		
BNHF-d			7.25	23.31	77.61
$BNHF_2$-a	93.36		206.50		128.75

BNHF_2-b		87.24	115.80	9.33	
BNHF_2-c	102.13	58.44	83.02	72.83	
BNHF_2-d	137.48		55.16	-0.48	57.87
BNHF_2-e	102.13	58.44	83.02	72.83	
BNHF_2-f	134.93		52.62	-3.02	55.33
BNHF_3-a	168.74		111.87	74.90	87.06
BNHF_3-b	161.25	110.22	85.27	68.45	
BNH_2F-a		39.09	85.11	94.90	
BNH_2F-b	129.55		76.79		41.89
BNH_2F-c	78.80	30.58	110.59		7.06
BNH_2F-d		81.01	96.56	-8.72	45.10
BNH_2F-e		83.23	98.78	-6.51	47.32
BNH_2F_2-a	172.51		137.26		121.03
BNH_2F_2-b		107.39	96.53	77.63	
BNH_2F_2-c	76.62	107.68	115.60	164.14	107.68
BNH_2F_2-d	164.94	108.48	116.40	77.42	107.91
BNH_3F-a		107.40	123.99	75.77	113.41
BNH_3F-b	169.28	109.05	138.60		120.36