Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Spectroscopic Identification of the Ammonia−Mercapto Radical Complex

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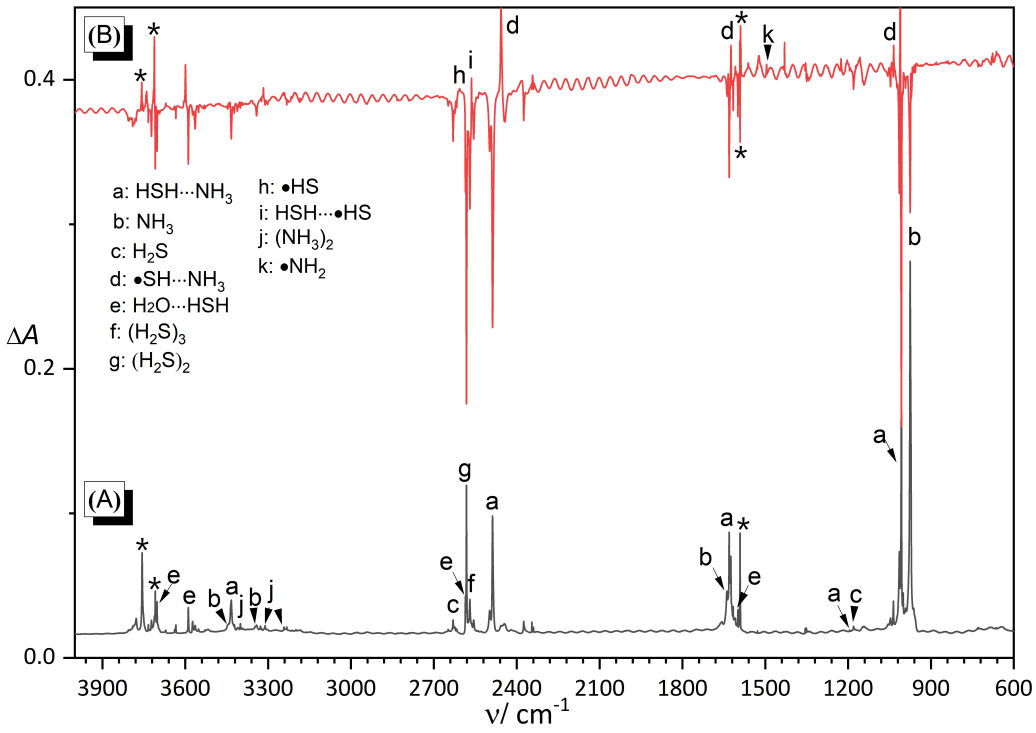

Fig. S1 (A) IR spectrum of a 3:8:1000 mixture of $H_2S/NH_3/Ar$ at 10 K. (B) IR difference spectrum reflecting the photodecomposition of a 3:8:1000 mixture of $H_2S/NH_3/Ar$ upon irradiation at 193 nm (3.2 mJ, 30 min) at 10 K. The IR bands for H_2O are marked with asterisks.

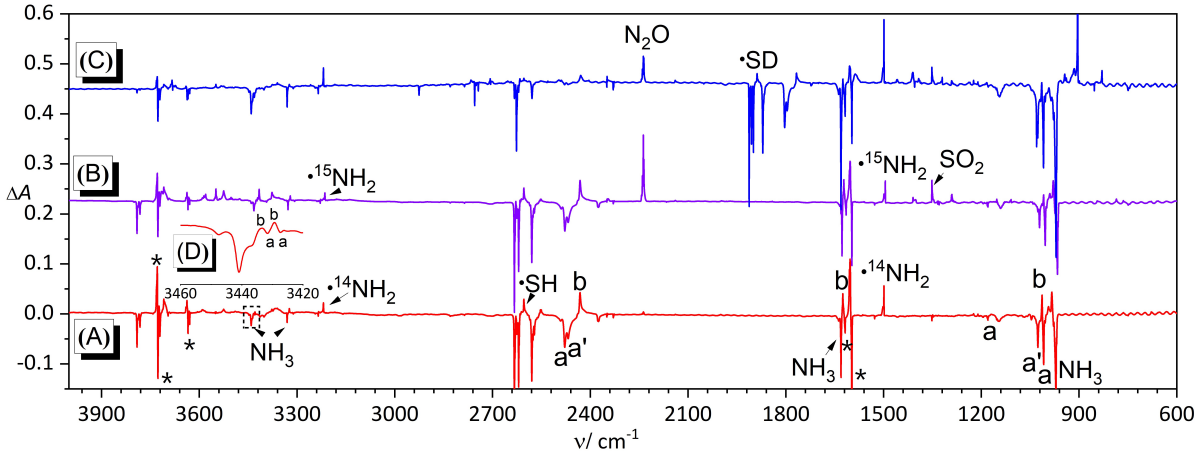

Fig. S2 (A) IR difference spectrum reflecting the photodecomposition of a 3:8:1000 mixture of $H_2S/NH_3/N_2$ upon irradiation at 193 nm (3.2 mJ, 42 min) at 10 K. (B) IR difference spectrum reflecting the photodecomposition of a 3:8:1000 mixture of $H_2S/^{15}NH_3/N_2$ upon irradiation at 193 nm (3.2 mJ, 42 min) at 10 K. (C) IR difference spectrum reflecting the photodecomposition of a 3:8:1000 mixture of $D_2S/NH_3/N_2$ upon irradiation at 193 nm (3.2 mJ, 42 min) at 10 K. (D) Part of IR spectrum A in the range of 3420-3460 cm^{-1}. The main IR bands for the HSH···NH_3 (**a**) and •SH···NH_3 (**b**) complexes are labeled. The IR bands for •SH···NH_3 can be grouped according to the concomitant changes during the photolysis.

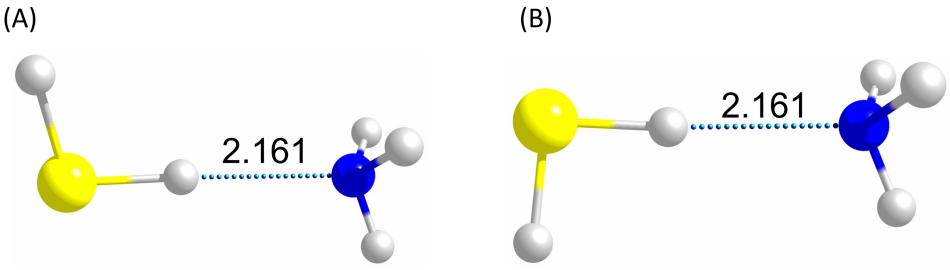

Fig. S3 Calculated two energetically identical structures of HSH···NH_3 complex (bond length in Å) at the B3LYP-D3(BJ)/6-311++G(3df,3pd) level of theory.

Table S1 Calculated and observed IR data for $HSH\cdots NH_3$ complex.

Obs.[a]		Conformer A Cal.[b]		Conformer B Cal.[b]	
N_2-matrix	Ar-matrix	B3LYP(harm)	B3LYP(anharm)	B3LYP(harm)	B3LYP(anharm)
3431.5	3433.2	3591.6 (9)	3418.5 (5)	3591.7 (9)	3424.7 (5)
3427.3	3422.0	3590.4 (9)	3417.5 (5)	3588.6 (9)	3407.3 (4)
3311.8	3310.5	3471.0 (< 1)	3324.5 (2)	3470.3 (< 1)	3322.9 (2)
2491.0	2497.3	2691.9 (1)	2553.6 (< 1)	2697.2 (1)	2529.0 (< 1)
2478.5	2487.0	2513.8 (407)	2441.0 (260)	2514.0 (409)	2441.1 (255)
1629.2	1630.5	1660.0 (20)	1619.4 (12)	1661.0 (20)	1613.8 (12)
1619.5	1615.9	1660.6 (20)	1615.4 (13)	1660.0 (20)	1623.1 (12)
1193.7	1194.5	1238.5 (3)	1187.0 (4)	1238.8 (2)	1187.8 (< 1)
1008.7	1006.7	1052.0 (145)	972.7 (142)	1052.9 (144)	977.0 (142)

[a] Observed band positions in different matrixes; [b] Calculated harmonic and anharmonic IR frequencies and intensities (km mol^{-1}, in parentheses) at the B3LYP-D3(BJ)/6-311++G(3df,3pd) level of theory.

Table S2 Experimental and calculated frequencies, frequency shifts relative to the monomer, the isotopic frequency shifts (in cm^{-1}) and relative intensities for the $HSH\cdots NH_3$ complex.

Obs.[a]			Cal.[b]		Cal.[c]	Obs.[c]	Cal.[c]	Obs.[c]
N_2-matrix	Ar-matrix	$\Delta\nu$	harmonic	anharmonic	$\Delta\nu(^{14}N/^{15}N)$		$\Delta\nu$(H/D)	
3431.5 (2)	3433.2 (1)	-9.3	3591.6 (9)	3418.5 (5)	-8.3	-8.4	1.5	< 0.5
3427.3 (2)	3422.0 (< 1)	-13.5	3590.4 (9)	3417.5 (5)	-8.5	-8.1	1.3	< 0.5
3311.8 (< 1)	3310.5 (1)	-18.9	3471.0 (< 1)	3324.5 (2)	-0.7	-3.8	1.4	< 0.5
2491.0 (< 1)	2497.3 (5)	-141.9	2691.9 (1)	2553.6 (< 1)	4.4	-1.0	-756.2	-768.2
2478.5 (100)	2487.0 (100)	-141.3	2513.8 (407)	2441.0 (260)	0.0	< 0.5	-708.1	-674.7
1629.2 (5)	1630.5 (21)	-1.6	1660.0 (20)	1619.4 (12)	-2.8	-3.0	0.5	< 0.5
1619.5 (5)	1615.9 (4)	-11.3	1660.6 (20)	1615.4 (13)	-4.0	-3.0	0.8	< 0.5
1193.7 (< 1)	1194.5 (< 1)	14.0	1238.5 (3)	1187.0 (4)	-0.2	< 0.5	-349.8	-329.7
1008.7 (51)	1006.7 (70)	45.4	1052.0 (145)	972.7 (142)	-4.1	-5.0	-0.4	< 0.5

[a] Observed band positions and relative intensities (in parentheses) in different matrixes; [b] Calculated harmonic and anharmonic IR frequencies and intensities (km mol^{-1}, in parentheses) at the B3LYP-D3(BJ)/6-311++G(3df,3pd) level of theory; [c] Calculated and observed isotope shifts in N_2-matrix; [d] Not observed in the present spectral range due to low IR intensities.

Table S3. Electron density (ρ) and Laplacian of the electron density ($\nabla^2\rho$) at the bond critical point in all the complexes obtained from the AIM calculations using wavefunction obtained at the B3LYP/6-311++G(3df,3pd) level of theory. All the values are in a.u.

Complex	Band path	ρ	$\nabla^2\rho$
•SH···NH_3	H···NH_3	0.0230	0.0590
HS•···NH_3	S···NH_3	0.0288	0.0702

Table S4 Calculated and observed IR data for H_2O, •NH_2, and the HOH···•NH_2 complex.

	Obs. [a]		Cal. [b]	
	N_2-matrix	Ar-matrix	B3LYP (harm)	B3LYP (anharm)
H_2O	3727.3	3733.5	3913.1 (60)	3728.0 (55)
	3634.8	3638.2	3814.0 (5)	3641.4 (5)
	1597.4	1593.2	1626.5 (72)	1572.7 (74)
•NH_2	n.o.[c]	n.o. [c]	3448.7 (< 1)	3279.5 (< 1)
	3218.8	3216.6	3361.5 (11)	3207.4 (14)
	1499.0	1495.8	1528.7 (26)	1485.1 (26)
HOH···•NH_2	3705.1	n.o.[d]	3881.7 (74)	3705.0 (58)
	3524.8	3530.0	3661.3 (412)	3495.5 (284)
	n.o. [c]	n.o. [c]	3478.7 (2)	3313.4 (1)
	3214.5	n.o. [c]	3387.4 (6)	3216.5 (7)
	n.o. [d]	n.o. [d]	1651.9 (47)	1595.7 (38)
	1495.1	n.o. [c]	1525.8 (20)	1488.6 (17)
	n.o.	n.o.	622.0 (106)	536.0 (75)

[a] Observed band positions in different matrices; [b] calculated harmonic and anharmonic IR frequencies and intensities (km mol^{-1}, in parentheses) at the B3LYP/6-311++G(3df,3pd) level; [c] Not observed in the present spectral range due to low IR intensities; [d] Not resolved due to overlap with other IR bands in the spectrum.

Table S5 Calculated IR data for NH_3, $•NH_2$, $•NH_2\cdots NH_3$ and $NH\cdots NH_3$.

NH_3 [a]		$•NH_2$ [a]		$•NH_2\cdots NH_3$ [a]		$NH\cdots NH_3$ [a]	
harm	anharm	harm	anharm	harm	anharm	harm	anharm
3591.6 (4)	3424.0 (3)	3448.7 (< 1)	3279.5 (< 1)	3590.8 (8)	3471.2 (5)	3587.7 (9)	3412.8 (6)
3472.5 (4)	3330.4 (5)	3361.5 (11)	3207.4 (14)	3588.3 (8)	3359.3 (4)	3587.6(9)	3413.0 (6)
1660.8 (16)	1616.4 (17)	1528.7 (26)	1485.1 (26)	3471.6 (2)	3351.2 (242)	3470.5 (1)	3323.6 (2)
1025.5 (149)	939.1 (151)			3422.2 (24)	3254.7 (188)	3196.2 (85)	3077.1 (34)
				3303.1 (121)	3180.8 (58)	1662.0 (18)	1620.4 (16)
				1662.5 (17)	1623.3 (12)	1661.9 (18)	1621.6 (16)
				1660.8 (18)	1608.7 (13)	1065.9 (150)	992.8 (137)
				1552.5 (16)	1503.3 (9)		
				1057.4 (151)	977.4 (132)		

[a] Calculated harmonic and anharmonic IR frequencies and intensities (km mol^{-1}, in parentheses) at the B3LYP-D3(BJ)/6-311++G(3df,3pd) level.

Table S6 TD-B3LYP/6-311++G(3df,3pd) calculated vertical transitions of •SH, $•SH\cdots NH_3$, $HSH\cdots NH_3$ and $HSH\cdots•NH_2$.

•SH		$•SH\cdots NH_3$		$HSH\cdots NH_3$		$HSH\cdots•NH_2$	
Trans energy (nm)	Oscillator strength (*f*)	Trans energy (nm)	Oscillator strength (*f*)	Trans energy (nm)	Oscillator strength (*f*)	Trans energy (nm)	Oscillator strength (*f*)
313	0.0024	500	0.0009	237	0.0246	549	0.0011
229	0.0017	286	0.0016	216	0.0085	252	0.0005
209	0.036	241	0.0068	201	0.1161	239	0.0001
179	0.0037	227	0.0097	195	0.0237	229	0.0177
176	0.0138	209	0.0002	186	0.0054	226	0.0111
167	0.1045	200	0.017	183	0.0044	214	0.0055
165	0.0098	199	0.1193	170	0.0049	202	0.0001
160	0.0002	190	0.0529	169	0.0237	194	0.0247
		188	0.0001	163	0.0054		
				162	0.0052		

Computed Atomic Coordinates (in Angstroms) and Energies (in Hartrees) for All Optimized Structures at the B3LYP/6-311++G(3df, 3pd) Level of Theory

NH_3

N	-0.000006000000	0.000012000000	-0.112221000000
H	0.737147000000	0.586059000000	0.261853000000
H	0.139048000000	-0.931400000000	0.261825000000
H	-0.876153000000	0.345261000000	0.261866000000

Zero-point correction= 0.034179 (Hartree/Particle)
Thermal correction to Energy= 0.037050
Thermal correction to Enthalpy= 0.037994
Thermal correction to Gibbs Free Energy= 0.015114
Sum of electronic and zero-point Energies= -56.553369
Sum of electronic and thermal Energies= -56.550498
Sum of electronic and thermal Enthalpies= -56.549554
Sum of electronic and thermal Free Energies= -56.572434

H_2S

S	0.000000000000	0.103080000000	0.000000000000
H	0.969572000000	-0.824670000000	0.000000000000
H	-0.969572000000	-0.824603000000	0.000000000000

Zero-point correction= 0.015042 (Hartree/Particle)
Thermal correction to Energy= 0.017891
Thermal correction to Enthalpy= 0.018835
Thermal correction to Gibbs Free Energy= -0.005165
Sum of electronic and zero-point Energies= -399.414727
Sum of electronic and thermal Energies= -399.411878
Sum of electronic and thermal Enthalpies= -399.410934
Sum of electronic and thermal Free Energies= -399.434934

$NH_3\cdots HSH$ (A)

N	-2.176731000000	0.006211000000	-0.000123000000
H	-2.552946000000	0.520483000000	-0.788065000000
H	-2.548266000000	0.425456000000	0.844307000000
H	-2.538047000000	-0.939094000000	-0.054259000000
S	1.338263000000	-0.080842000000	0.000001000000
H	1.480125000000	1.253236000000	0.000000000000
H	-0.015958000000	-0.010089000000	-0.001143000000

Zero-point correction= 0.051622 (Hartree/Particle)
Thermal correction to Energy= 0.058112

Thermal correction to Enthalpy= 0.059056
Thermal correction to Gibbs Free Energy= 0.021481
Sum of electronic and zero-point Energies= -455.974652
Sum of electronic and thermal Energies= -455.968162
Sum of electronic and thermal Enthalpies= -455.967218
Sum of electronic and thermal Free Energies= -456.004794

NH_3···HSH (B)

N	-2.175488000000	0.005541000000	0.000903000000
H	-2.551890000000	-0.691305000000	0.633539000000
H	-2.531413000000	-0.199650000000	-0.925428000000
H	-2.552967000000	0.903594000000	0.281035000000
S	1.339939000000	-0.078975000000	0.000269000000
H	1.441401000000	1.258571000000	-0.000321000000
H	-0.015737000000	-0.046399000000	0.000547000000

Zero-point correction= 0.051640 (Hartree/Particle)
Thermal correction to Energy= 0.058113
Thermal correction to Enthalpy= 0.059057
Thermal correction to Gibbs Free Energy= 0.021492
Sum of electronic and zero-point Energies= -455.974618
Sum of electronic and thermal Energies= -455.968145
Sum of electronic and thermal Enthalpies= -455.967201
Sum of electronic and thermal Free Energies= -456.004766

•SH

S	0.000000000000	0.000000000000	0.079189000000
H	0.000000000000	0.000000000000	-1.267030000000

Zero-point correction= 0.006085 (Hartree/Particle)
Thermal correction to Energy= 0.008446
Thermal correction to Enthalpy= 0.009390
Thermal correction to Gibbs Free Energy= -0.012417
Sum of electronic and zero-point Energies= -398.771595
Sum of electronic and thermal Energies= -398.769235
Sum of electronic and thermal Enthalpies= -398.768291
Sum of electronic and thermal Free Energies= -398.790098

•SH···NH_3

N	2.105895000000	0.000325000000	-0.000445000000
H	2.475176000000	-0.727041000000	-0.601670000000
H	2.471371000000	-0.160992000000	0.930904000000
H	2.479310000000	0.884648000000	-0.325067000000
S	-1.384086000000	0.000030000000	-0.000051000000

H -0.021748000000 0.000627000000 -0.000234000000

Zero-point correction= 0.042791 (Hartree/Particle)
Thermal correction to Energy= 0.048172
Thermal correction to Enthalpy= 0.049116
Thermal correction to Gibbs Free Energy= 0.015117
Sum of electronic and zero-point Energies= -455.331310
Sum of electronic and thermal Energies= -455.325929
Sum of electronic and thermal Enthalpies= -455.324985
Sum of electronic and thermal Free Energies= -455.358984

•HS···NH_3

N 1.646083000000 -0.000602000000 -0.000001000000
H 2.020912000000 0.438920000000 -0.829659000000
H 1.876176000000 -0.984637000000 -0.000072000000
H 2.020840000000 0.438797000000 0.829755000000
S -1.035032000000 -0.071894000000 0.000000000000
H -0.880001000000 1.261442000000 -0.000009000000

Zero-point correction= 0.042760 (Hartree/Particle)
Thermal correction to Energy= 0.048411
Thermal correction to Enthalpy= 0.049355
Thermal correction to Gibbs Free Energy= 0.014225
Sum of electronic and zero-point Energies= -455.330929
Sum of electronic and thermal Energies= -455.328278
Sum of electronic and thermal Enthalpies= -455.327333
Sum of electronic and thermal Free Energies= -455.362464

NH_2•

N 0.000000000000 0.141635000000 0.000000000000
H 0.805456000000 -0.495723000000 0.000000000000
H -0.805456000000 -0.495723000000 0.000000000000

Zero-point correction= 0.018997 (Hartree/Particle)
Thermal correction to Energy= 0.021834
Thermal correction to Enthalpy= 0.022779
Thermal correction to Gibbs Free Energy= 0.000030
Sum of electronic and zero-point Energies= -55.886133
Sum of electronic and thermal Energies= -55.883296
Sum of electronic and thermal Enthalpies= -55.882351
Sum of electronic and thermal Free Energies= -55.905100

NH_2•···HSH

N -2.313903000000 0.011561000000 0.002566000000

H	-2.944544000000	0.190977000000	-0.786567000000
H	-2.943532000000	-0.216435000000	0.779877000000
S	1.293329000000	-0.080240000000	-0.015948000000
H	1.444633000000	1.227303000000	0.243074000000
H	-0.052507000000	0.001077000000	0.000826000000

Zero-point correction= 0.036045 (Hartree/Particle)
Thermal correction to Energy= 0.042852
Thermal correction to Enthalpy= 0.043796
Thermal correction to Gibbs Free Energy= 0.005384
Sum of electronic and zero-point Energies= -455.305695
Sum of electronic and thermal Energies= -455.298888
Sum of electronic and thermal Enthalpies= -455.297944
Sum of electronic and thermal Free Energies= -455.336356

HO•···NH_3

N	-1.258574000000	-0.000069000000	-0.000278000000
H	-1.629636000000	-0.852299000000	-0.404468000000
H	-1.629277000000	0.777779000000	-0.534057000000
H	-1.627747000000	0.075097000000	0.940796000000
O	1.632127000000	-0.000003000000	-0.000016000000
H	0.639664000000	-0.000070000000	-0.000198000000

Zero-point correction= 0.046597 (Hartree/Particle)
Thermal correction to Energy= 0.051305
Thermal correction to Enthalpy= 0.052249
Thermal correction to Gibbs Free Energy= 0.021023
Sum of electronic and zero-point Energies= -132.322393
Sum of electronic and thermal Energies= -132.317685
Sum of electronic and thermal Enthalpies= -132.316741
Sum of electronic and thermal Free Energies= -132.347967

HOH···•NH_2

N	1.466429000000	-0.012602000000	0.031071000000
H	2.100390000000	-0.752776000000	-0.286229000000
H	2.069803000000	0.802747000000	0.178328000000
O	-1.503751000000	0.045629000000	-0.101209000000
H	-1.863419000000	-0.306832000000	0.716277000000
H	-0.540063000000	-0.002753000000	0.002827000000

Zero-point correction= 0.043594 (Hartree/Particle)
Thermal correction to Energy= 0.049615
Thermal correction to Enthalpy= 0.050559
Thermal correction to Gibbs Free Energy= 0.015615

Sum of electronic and zero-point Energies= -132.336064
Sum of electronic and thermal Energies= -132.330044
Sum of electronic and thermal Enthalpies= -132.329100
Sum of electronic and thermal Free Energies= -132.36404

•NH_2···NH_3

N	1.444857000000	-0.026100000000	-0.001411000000
H	1.979223000000	-0.653432000000	-0.591142000000
H	1.820413000000	-0.100600000000	0.936968000000
H	1.626509000000	0.917945000000	-0.322919000000
N	-1.792717000000	0.126765000000	0.001333000000
H	-2.213087000000	-0.809967000000	-0.002207000000
H	-0.778043000000	-0.058600000000	-0.020155000000

Zero-point correction= 0.055749 (Hartree/Particle)
Thermal correction to Energy= 0.062225
Thermal correction to Enthalpy= 0.063169
Thermal correction to Gibbs Free Energy= 0.026142
Sum of electronic and zero-point Energies= -112.445221
Sum of electronic and thermal Energies= -112.438745
Sum of electronic and thermal Enthalpies= -112.437801
Sum of electronic and thermal Free Energies= -112.474828

NH···NH_3

N	-1.324806000000	-0.000044000000	0.000568000000
H	-1.704093000000	-0.792397000000	0.506353000000
H	-1.690563000000	-0.044219000000	-0.943781000000
H	-1.701764000000	0.837619000000	0.429200000000
N	1.926753000000	0.000077000000	-0.000100000000
H	0.882788000000	-0.001239000000	0.004947000000

Zero-point correction= 0.044425 (Hartree/Particle)
Thermal correction to Energy= 0.049824
Thermal correction to Enthalpy= 0.050768
Thermal correction to Gibbs Free Energy= 0.017536
Sum of electronic and zero-point Energies= -111.795357
Sum of electronic and thermal Energies= -111.789958
Sum of electronic and thermal Enthalpies= -111.789013
Sum of electronic and thermal Free Energies= -111.822245