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Supporting Information

Reaction between HN and SN: A possible channel for the interstellar formation of N_2 and SH in the cold interstellar clouds.

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Table S1: Relative energies of various isomers and transition states of the [H,N,N,S] potential energy surface using B3LYP/aug-cc-pvtz, MP2/6-31++G(3df,2pd) and G3B3 methods.

species	B3LYP/ AUG-CC-pVTZ	MP2/ 6-31++G(3df,2pd)	G3B3
^{3}NH+^{2}NS	0.0	0.0	0.0
NH-NS Complex	-0.9	-2.0	-1.5
^{2}1 cis-HNSN	-47.2	-54.0	-48.6
^{2}2 trans-HNSN	-45	-51.2	-44.9
^{2}3 cis-HNNS	-71.7	-68.4	-65.7
^{2}4 trans-HNNS	-74.4	-71.0	-65.8
^{2}5 cNN(H)S	-42.5	-45.2	-38.9
^{2}6 cNS(H)N	-32.4	-38.1	-28.1
^{2}7NN(H)S	-51.6	-46.8	-42.3
^{2}8 NS(H)N	16.2	5.3	11.4
^{2}9 NS(H)N	28	122.3	22.7
T_1 (^{2}TS1/2)	-31.6	-36.5	-31.7
T_2 (^{2}TS1/5)	-13.4	7.7	-11.7
T_3 (^{2}TS2/5)	-13.3	-14.2	-7.9
T_4(^{2}TS3/4)	-68	-64.9	-61.2
T_5 (^{2}TS3/5)	-29.4	-8.5	-24.5
T_6 (^{2}TS4/5)	-52.8	-29	-26.5
T_7(^{2}TS2/8)	24.6	10	16.8
T_8 (^{2}TS4/7)	-20	-20.1	-14.5
T_9 (^{2}TS6/8)	38	54.7	52.1
T_{10} (^{2}TS5/7)	-27.9	-5.6	-2.1
ST_1 (^{2}TSC/4)	1.3	--	3.0
ST_2 (^{2}TSC/3)	4.6	--	8.7
T_{11}(^{2}TSC/1)	-0.3	--	-0.9
T_{12} (^{2}TS3/N2+SH)	-44.3	-35.8	-39.2
T_{13}(^{2}TS5/N2+SH)	-9.8	-11	-4.7

Table S2: Harmonic vibration frequencies (cm^{-1}), IR intensities in KM/mol (in parentheses) and dipole moment of isomers of [H,N,N,S] potential energy surface using the B3LYP/6-31++G(3df,2pd) and MP2/6-31++G(3df,2pd) methods.

Species	Frequencies (Infrared Intensity)	Dipole Moment
C complex	46 (1) 48 (0.1) 89 (1) 279 (98) 293 (99) 1268 (5)	3.9070
	19 (4) 30 (1) 105 (1) 277 (105) 307 (106) 1568 (16)	*3.8138*
^{2}1 cis-HNSN	329 (41) 669 (89) 950 (78) 1023 (36) 1116 (4) 3454 (26)	0.5804
	337 (47) 661 (76) 980 (51) 1067 (40) 1144 (30) 3465 (34)	*0.3218*
^{2}2 trans-HNSN	346 (11) 614 (61) 955 (68) 1051 (81) 1123 (4) 3465 (46)	2.8427
	357 (13) 618 (51) 1025 (39) 1074 (41) 1126 (43) 3478 (59)	*3.1019*
^{2}3 cis-HNNS	382 (10) 658 (37) 785 (24) 1244 (240) 1660 (361) 3182 (3)	1.5476
	402 (28) 403 (1) 870 (51) 1231 (292) 2183 (1243) 3294 (26)	*1.7099*
^{2}4 trans-HNNS	423 (11) 664 (83) 823 (40) 1293 (222) 1613 (250) 3340 (11)	1.3660
	448 (11) 487 (114) 934 (139) 1222 (207) 1992 (1356) 3409 (46)	*1.2037*
^{2}5 cNN(H)S	512 (57) 680 (18) 1006 (42) 1080 (17) 1248 (36) 3340 (5)	1.6612
	614 (60) 777 (9) 1040 (32) 1096 (21) 1258 (33) 3401 (17)	*1.6509*
^{2}6 cNS(H)N	495 (1) 552 (1) 659 (12) 1010 (4) 1350 (5) 2574 (2)	2.9331
	630 (0.1) 636 (0.1) 780 (9) 1046 (5) 1288 (3) 2687 (1)	*2.9287*
^{2}7 NN(H)S	333 (13) 720 (52) 802 (65) 1313 (30) 1403 (142) 3286 (26)	2.5000
	407 (15) 792 (72) 910 (15) 1312 (21) 1458 (8) 3383 (37)	*2.8361*
^{2}8 NS(H)N	318 (51) 462 (5) 895 (29) 967 (5) 1357 (24) 2338 (26)	2.5878
	336 (32) 830 (10) 912 (53) 1111 (13) 1474 (55) 2429 (44)	*2.7749*
^{2}9 NS(H)N	391 (1) 411 (29) 992 (2) 1109 (9) 2300 (3843) 2328 (19)	1.8090
	336 (1) 395 (23) 892 (6) 1251 (27) 2447 (9) 88096 ()	*1.5627*

Table S3: Harmonic vibration frequencies (cm^{-1}), IR intensities (KM/mol) (in parentheses) and dipole moment of transition states of [H ,N,N,S] potential energy surface using B3LYP/6-31++G(3df,2pd) and MP2/6-31++G(3df,2pd) (*Italics*) methods.

Species	Frequencies (Infrared Intensity)	Dipole Moment
T_1	726i (144) 320 (6) 603 (177) 978 (10) 1122 (9) 3552 (115)	2.1416
	907i (195) 394 (60) 785 (462) 1107 (229) 2245 (6357) 3549 (236)	*1.9921*
T_2	988i (131) 683 (19) 736 (21) 859 (25) 1214 (57) 3440 (42)	1.8781
	2218i (3785) 752 (60) 958 (34) 1030 (116) 1314 (49) 3620 (38)	*2.5060*
T_3	1036i (193) 706 (40) 718 (21) 859 (46) 1152 (26) 3345 (3)	2.5101
	2315i (1899) 775 (29) 924 (3) 1207 (71) 1384 (207) 3330 (6)	*2.7206*
T_4	399i (4) 430 (0) 809 (10) 1254 (173) 1739 (243) 3103 (30)	1.4049
	430i (5) 329 (1) 863 (0.1) 1179 (161) 2437 (1091) 3289 (28)	*1.5301*
T_5	1153i (11) 601 (58) 709 (17) 1140 (159) 1306 (31) 3268 (6)	1.7017
	1057i (54) 428 (68) 660 (17) 1198 (87) 1336 (45) 3261 (20)	*1.8038*
T_6	1011i (100) 625 (64) 746 (62) 1214 (74) 1291 (26) 3172 (2)	1.3363
	2002i (123) 653 (35) 958 (89) 1160 (66) 1410 (9) 3216 (1)	*1.1733*
T_7	1431i (14) 285 (3) 360 (13) 967 (8) 1388 (26) 1999 (1)	1.9050
	1326i (12) 361 (11) 581 (0.2) 1111 (16) 1549 (46) 2256 (12)	*2.0514*
T_8	2268i (35) 433 (44) 470 (15) 736 (71) 1525 (327) 2393 (67)	1.5207
	2377i (9) 461 (13) 472 (46) 831 (33) 1603 (108) 2702 (108)	*1.9742*
T_9	344i(23) 491(16) 747(22) 868(2) 892(2) 2125(48)	3.3422
	896i(434) 608(56) 716(351) 1077(93) 1655(312) 2111(82)	*3.4482*
T_{10}	1023i (238) 577 (23) 777 (61) 1217 (40) 1408 (62) 3250 (10)	2.5466
	1040i(13) 597(27) 847(99) 1165(32) 1233(32) 3464(35)	*1.8520*
ST_1	217i(6) 154(9) 249(79) 512(116) 1192(45) 3326(6)	0.9295
ST_2	292i(4) 142(49) 143(5) 559(94) 1136(56) 3276(21)	2.7014
T_{11}	54i(30) 50(2) 53(101) 141(99) 1256(5) 3288(10)	0.4932
T_{12}	1679i(33) 383(27) 661(8) 902(19) 1637(69) 1760(46)	0.8201
	1904i(527) 675(4) 797(8) 1012(29) 1995(149) 2898(404)	*0.7390*
T_{13}	1514i(203) 479(1) 516(3) 902(28) 1319(68) 1711(9)	1.5898
	1473i(347) 559(1) 708(15) 956(37) 1517(97) 1968(20)	*1.6220*

Fragments:

By the thorough analysis of the isomers we have visualized many fragmentation pathways and optimized all the possible fragments. All the optimized fragments are shown in the Figure S1, in the figure along with the fragment names, their electronic states are also presented as superscripts. From the complex (C) and isomers 1-4, the most obvious fragmentation leads to NH and NS. Minimizations of these two fragments show that SN is in doublet state, where as for NH we found that its triplet state is more stable (approximately 50.3 kcal/mol) than the singlet state. Stability of the triplet state is quite obvious as it is isoelectronic with both O and CH_2. Interesting to note that the complex energy is equal to that of the total energies of the two fragments NH and NS, which is a clear indication that the complex formed, is not a hydrogen bonded complex. If it has to be a hydrogen bonded complex, then by VSEPR theory the structure could have been bent than linear. Rather it can be treated as some kind of weak interaction and needs further detailed investigations to ascertain its nature of bonding. Analysis of isomer 1 and 2 also shows that the other fragmentation process will lead to fragments like HNS and N. Optimization of HNS fragment shows that its triplet state is around 1.3 kcal/mol more stable than the corresponding singlet state. Similarly the HNS fragments can also be obtained from the fragmentation of the isomers 5, 6 and 7. Analysis of the isomers 3, 4, 5 and 7 shows that one of the fragmentation channels from this molecule will lead to the formation of HNN and S. Optimized structure of the HNN fragment shows that it is in doublet state and the structure is bent. The other fragmentation channel for the isomers 3, 4, 5, 6 and 7 is the formation of NNS and H. Analysis of the structure of the NNS shows that one is almost in linear form, whereas the other form is the cyclic ring structure, and in both the forms the singlet state is found to be highly stable compared to the triplet state. The linear from of the NNS might be considered as the

fragment from the isomers 3, 4 and 7, whereas the ring from of NNS might be considered as a fragment from the isomer 5 and 6 exclusively. Now fragmentation of isomer 8 and 9 will lead to the formation of NSN and H. Analysis of the optimized structure of the NSN shows that its singlet isomer (linear structure) is around 9.6 kcal/mol more stable than its triplet isomer (bent structure). The other fragmentation process which is important as it will give the N_2 (with SH as the second fragment). Analysis of the isomers shows that isomers capable of this might be isomers 3, 4, 5, 6 and 7.

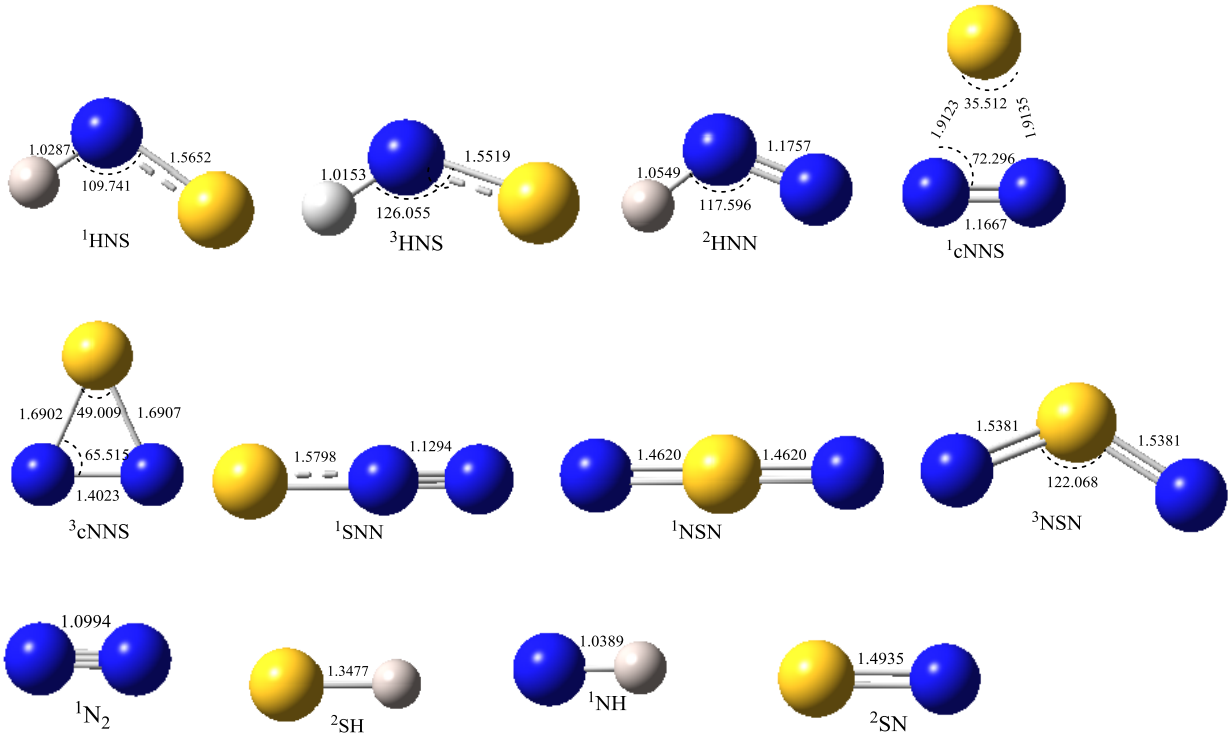


Figure S1: Optimized geometries of various possible fragments of the [H, N, N, S] potential energy surface using B3LYP/6-31++G (3df,2pd) method. Bond lengths are in angstroms and bond angles are in degrees.

MP2/6-31++G(3df,2pd) geometries of isomers and transition states

Isomer 1

H	-1.01202700	-1.50008300	0.00000000
N	-1.27083800	-0.50805300	0.00000000
S	0.00000000	0.41289900	0.00000000
N	1.41541300	-0.22141800	0.00000000

Isomer 2

H	-1.99670200	-0.11475500	0.00000000
N	-1.14900700	-0.69106000	0.00000000
S	0.00000000	0.38760500	0.00000000
N	1.43425000	-0.17850000	0.00000000

Isomer 3

H	1.84429300	0.88566100	0.00000000
N	0.94382100	1.39448700	0.00000000
N	0.00000000	0.54642300	0.00000000
S	-0.52819000	-0.90450200	0.00000000

Isomer 4

H	0.64683600	2.25856100	0.00000000
N	1.00944700	1.29740200	0.00000000
N	0.00000000	0.51924900	0.00000000
S	-0.48206000	-0.93594500	0.00000000

Isomer 5

H	-1.25191400	-0.87749700	0.77009000
N	-0.94308200	-0.53574100	-0.14804200
N	-0.63828300	0.83166100	0.02213600
S	0.77009100	-0.07462100	0.00695300

Isomer 6

H	1.04772800	0.00203200	1.21129300
S	0.71319800	-0.00022100	-0.09150400

N	-0.89010600	-0.66420600	0.01835700
N	-0.88973600	0.66442000	0.01775200

Isomer 7

H	-0.73353100	1.38942300	0.00000000
N	0.00000000	0.66988400	0.00000000
N	1.17915500	1.16968200	0.00000000
S	-0.47003500	-0.89164900	0.00000000

Isomer 8

H	-0.52611200	1.44408900	0.00000000
N	-1.38725400	-0.51725600	0.00000000
S	0.00000000	0.17475800	0.00000000
N	1.46241300	-0.08849000	0.00000000

Isomer 9

H	0.00000000	0.00000000	1.42598900
S	0.00000000	0.00000000	0.06144400
N	0.00000000	1.50805100	-0.17207800
N	0.00000000	-1.50805100	-0.17207800

Complex

N	3.29594400	0.00029600	0.00006700
H	2.26627900	0.00028500	-0.00059600
N	-0.05501800	-0.00105900	0.00000100
S	-1.55954800	0.00031600	0.00000800

T1

H	-1.84750300	0.58578600	-0.63475100
N	-1.38166300	0.13958500	0.15450700
S	0.08240000	-0.21410400	-0.04422000
N	1.45724800	0.26611100	0.03724500

T2

H	1.34602600	0.56050200	0.71317700
N	1.13623200	0.02702900	-0.11954100

S	-0.35287700	-0.50302500	0.02046000
N	-0.52194500	1.04267200	-0.02910800

T3

H	1.74425400	0.53688300	0.64628400
N	1.05843100	0.58587800	-0.11892000
S	-0.03627800	-0.57626300	-0.00095800
N	-1.22468700	0.65459700	0.02878400

T4

H	1.06270500	1.99811800	0.00000000
N	0.06849300	1.71547500	0.00000000
N	0.00000000	0.44854100	0.00000000
S	-0.09638500	-1.07163900	0.00000000

T5

H	-1.07194700	-1.03427400	0.63982300
N	-1.25077900	-0.36766900	-0.12649600
N	-0.58858800	0.73105100	0.06219900
S	0.87172000	-0.09433800	-0.01185900

T6

H	-1.84225900	-0.49331000	0.66391600
N	-1.16613100	-0.42502400	-0.12395800
N	-0.56301600	0.73701000	-0.00334800
S	0.87164300	-0.10566200	0.01420100

T7

H	-0.87437600	1.24251900	0.00048300
N	-1.45134800	-0.28450000	0.00008900
S	0.03509200	0.12510800	-0.00012800
N	1.49604900	-0.17896400	0.00013400

T8

H	-1.36532800	1.01239300	-0.00193200
N	-1.70568000	-0.25252700	-0.00026000

N	-0.51101600	0.22163500	0.00088500
S	1.05513800	-0.04975900	-0.00015300

T9

H	-0.67451600	-1.33239000	0.71837100
S	0.06921300	-0.42289600	-0.08604900
N	-1.16864200	0.58977900	0.00934700
N	1.10680000	0.56718100	0.08471100

T10

H	0.89692200	1.26184400	-0.60200200
N	0.66929300	0.60309300	0.14433100
N	1.28531600	-0.58234100	-0.03305900
S	-0.91119900	-0.08794400	-0.01105600

T11

H	2.20317400	-0.10357900	0.00000000
N	2.26486600	-1.13232400	0.00000000
N	0.00000000	1.04290400	0.00000000
S	-1.12857700	0.04559500	0.00000000

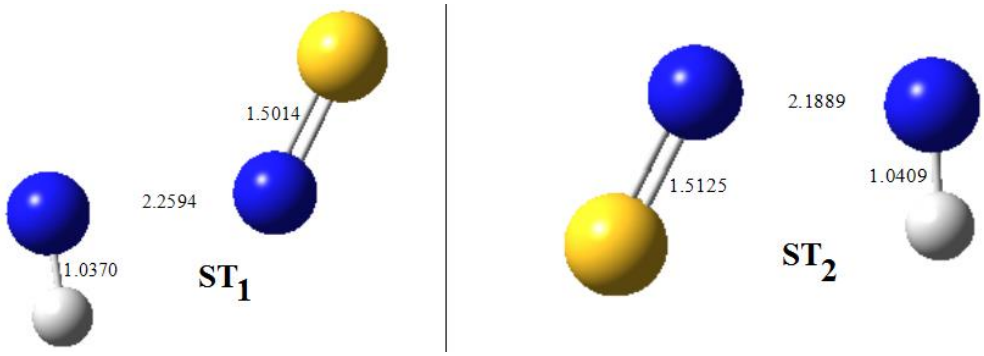
T12

H	0.26934900	1.12169400	0.00015100
N	1.33276500	0.39031600	0.00003300
N	0.80010000	-0.62076000	-0.00009500
S	-0.94996200	0.03071400	0.00001800

T13

H	-0.03555900	1.03797600	0.73813500
N	0.95471400	0.57642600	-0.11364500
N	0.90585300	-0.65983400	0.06922400
S	-0.81177600	-0.02838200	-0.02670000

Two reaction transition states obtained from the B3LYP/6-31++G(3df,2pd) method.

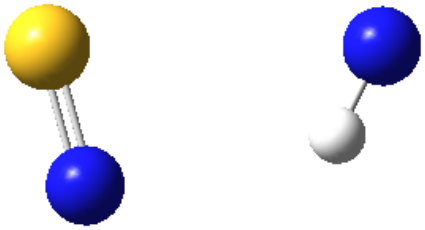


Optimized geometries and the Cartesian coordinates of the complex and the T_{11} obtained using wB97XD/6-31++G(d,p) method.

COMPLEX

N	0.824066	-3.217353	0.000000
H	0.576011	-2.205319	0.000000
N	0.000000	0.071462	0.000000
S	-0.396529	1.514160	0.000000

TRANSITION STATE, T_{11}



H	1.994099	0.721858	0.000331
N	2.532675	-0.170524	-0.000038
N	-0.664533	1.044420	-0.000030
S	-0.941943	-0.427446	0.000009