**Electronic Supplementary Information**

**Computational Prediction for the Formation of Amides and Thioamides in the Gas Phase Interstellar Medium (ISM)**

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The Cartesian coordinates of formamide, urea, thioformamide, and thiourea are provided for the pre-reactant, transition state (TS), and product complex. Additionally, the magnitude of the imaginary frequencies (only for transition states), charge, and multiplicity are included.

The sequence of the coordinates presented here corresponds to the order provided in the main text.

The same level of theory as given in the main text is used. If an imaginary frequency is not specified, then the structure corresponds to an optimized minimum energy structure.

**Table S1**. The XYZ coordinates and Normal modes of frequencies of formamide, urea, thioformamide, and thiourea are provided for the pre-reactant, transition state (TS), and product complex.

**CO**

XYZ coordinates

C 0.00000000 0.00000000 -0.64611154

O 0.00000000 0.00000000 0.48527854

Vibrational frequency (cm-1)

*2153.72 cm-1*

**NH2**

XYZ coordinates

N 0.000000 0.141135 0.000000

H 0.804043 -0.493971 0.000000

H -0.804043 -0.493971 0.000000

Vibrational frequency (cm-1)

*1540.87*

*3388.48*

*3483.85*

**H2**

XYZ coordinates

H 0.000000 0.000000 0.370069

H 0.000000 0.000000 -0.370069

Vibrational frequency (cm-1)

*4461.05*

**NH3**

XYZ coordinates

N 0.000000 0.000000 0.114051

H -0.000000 0.939797 -0.261140

H 0.813888 -0.469898 -0.261140

H -0.813888 -0.469899 -0.261140

Vibrational frequency (cm-1)

*1037.05*

*1673.38*

*1673.38*

*3488.66*

*3616.94*

*3616.95*

**CO…NH2\_Pre-Reactant**

XYZ coordinates

C 0.902766 0.530918 -0.000905

N -1.983228 -0.213563 0.000534

H -2.164963 0.398841 0.801145

H -2.165928 0.393791 -0.803698

O 1.656727 -0.312287 0.000512

Vibrational frequency (cm-1)

*36.59*

*55.43*

*94.70*

*121.12*

*219.13*

*1543.28*

*2155.39*

*3394.38*

*3488.04*

**CO…NH2\_TS-1**

XYZ coordinates

C -0.480022 0.478956 0.000506

N 1.463911 -0.228645 -0.000085

H 1.786136 0.320978 -0.801385

H 1.786110 0.319589 0.802175

O -1.361898 -0.240574 -0.000413

Vibrational frequency (cm-1)

***301.63i***

*48.29*

*301.68*

*652.15*

*747.29*

*1544.37*

*2080.38*

*3399.04*

*3492.68*

**CO…NH2\_Int-1**

**XYZ coordinates**

C -0.161935 -0.408813 0.000012

N 1.080645 0.093898 -0.000027

H 1.237877 1.092568 0.000116

H 1.869027 -0.523041 0.000143

O -1.217188 0.152904 -0.000003

Vibrational frequency (cm-1)

*230.90*

*532.31*

*622.16*

*1096.28*

*1228.72*

*1616.48*

*1841.25*

*3522.02*

*3731.69*

**CONH2\_H2\_Int-2**

XYZ coordinates

C 0.272293 0.268010 -0.000045

O 1.466711 0.209037 -0.000087

H -2.460366 1.729444 -0.000083

N -0.640043 -0.712425 0.000106

H -0.359478 -1.683351 0.000207

H -1.615085 -0.483813 0.000120

H -3.163315 1.493576 -0.000025

Vibrational frequency (cm-1)

*48.34*

*79.30*

*149.20*

*155.01*

*251.53*

*322.81*

*532.34*

*630.27*

*1100.29*

*1230.58*

*1615.33*

*1840.46*

*3525.06*

*3727.25*

*4433.35*

**CONH2\_H2\_TS-2**

XYZ coordinates

C 0.160108 0.247780 -0.000028

O 1.229812 -0.299982 -0.000127

H 0.021929 1.523560 -0.000065

N -1.064853 -0.306722 0.000133

H -1.175205 -1.307577 0.000187

H -1.877427 0.282153 0.000201

H -0.249754 2.513774 -0.000074

Vibrational frequency (cm-1)

***1380.05i***

*265.36*

*288.07*

*351.29*

*549.45*

*639.77*

*1080.14*

*1136.00*

*1160.64*

*1306.38*

*1452.13*

*1624.24*

*1834.28*

*3576.80*

*3722.34*

**HCONH2 + H\_Product\_1 (Formamide)**

XYZ coordinates

C -0.152938 0.332723 0.004112

O -1.339907 0.076953 -0.000007

H 0.233783 1.363338 0.012090

N 0.838697 -0.593262 -0.000543

H 0.602181 -1.570320 -0.007563

H 1.803114 -0.318377 0.003808

H 3.015464 1.988192 -0.015912

Vibrational frequency (cm-1)

*36.66*

*37.44*

*130.40*

*210.16*

*566.41*

*641.13*

*1047.13*

*1055.05*

*1272.65*

*1419.81*

*1622.97*

*1774.45*

*2984.51*

*3596.62*

*3738.84*

**HCONH\_TS-3**

XYZ coordinates

C -0.107960 0.235945 -0.035759

O -1.237432 -0.126935 0.011746

N 1.180090 -0.082603 -0.095865

H 1.443957 -0.925470 0.436789

H 0.789412 1.112143 0.369617

Vibrational frequency (cm-1)

1720.52*i*

464.18

533.71

744.25

1097.19

1170.74

1864.71

1994.11

3274.28

**HCONH\_Int-3**

XYZ coordinates

C 0.0017553 0.0062994 -0.2949155

N -1.2267896 -0.5661081 0.1118937

H -1.9182231 -0.6112726 -0.6205979

H -1.1061200 -1.4688865 0.5494165

O 0.1109917 1.3584373 -0.0306118

N 1.1483780 -0.6988141 0.1314630

H 1.9509842 -0.0879250 0.1751236

H 1.3539505 -1.4977972 -0.4502975

H -0.6626829 1.6078647 0.4914300

Vibrational frequency (cm-1)

*9.35*

*45.95*

*125.94*

*203.27*

*248.56*

*334.94*

*515.91*

*937.65*

*1067.19*

*1226.85*

*1401.30*

*1675.38*

*3047.85*

*3450.91*

*4437.02*

**HCONH\_H2\_Pre\_Int-4**

XYZ coordinates

C 0.163577 -0.333990 -0.025784

O 1.371658 -0.200970 0.043300

H -0.321514 -1.308726 -0.150970

N -0.684431 0.752892 -0.107909

H -0.313592 1.515092 0.465023

H -3.452367 -1.216714 0.270318

H -3.076244 -0.648199 -0.020704

Vibrational frequency (cm-1)

*18.76*

*35.14*

*136.47*

*208.82*

*566.52*

*641.51*

*1047.05*

*1055.64*

*1272.82*

*1420.16*

*1622.60*

*1774.46*

*2984.99*

*3595.80*

*3738.19*

**HCONH\_H2\_TS\_4**

XYZ coordinates

C 0.233407 0.371739 -0.095203

O 1.315707 -0.132867 0.131228

H 0.106545 1.438630 -0.317644

N -0.917560 -0.375608 -0.226118

H -0.883700 -1.223029 0.340600

H -2.538275 0.810016 0.731976

H -2.006915 0.368365 0.250370

Vibrational frequency (cm-1)

*1167.25i*

*205.74*

*285.95*

*576.17*

*691.03*

*843.62*

*961.45*

*1041.78*

*1161.86*

*1233.72*

*1410.28*

*1707.06*

*2333.48*

*3031.57*

*3484.95*

**HCONH2 + H\_Product-2 (Formamide)**

XYZ coordinates

C 0.159949 0.343826 0.003784

O 1.344715 0.078460 -0.013345

H -0.218015 1.377653 0.013095

N -0.839266 -0.573899 0.013740

H -0.610593 -1.552807 0.005863

H -3.231299 1.775903 -0.009830

H -1.801078 -0.290190 0.027038

**CONH2\_NH3\_Int-5**

XYZ coordinates

C -1.334033 -0.017932 -0.000045

N 2.058788 -0.059478 0.000075

H 2.657801 -0.102310 0.814792

H 1.486859 -0.898332 0.000082

O -0.951780 -1.158307 -0.000106

N -0.629176 1.115412 0.000043

H 0.394435 1.063152 0.000068

H -1.109735 1.993631 0.000067

H 2.657833 -0.102335 -0.814617

Vibrational frequency (cm-1)

95.38

104.62

154.08

203.84

220.50

373.59

483.21

575.26

794.54

1108.44

1129.17

1281.09

1607.53

1671.17

1681.70

1810.65

3289.27

3469.78

3589.55

3613.86

3715.64

**CONH2\_NH3\_TS-5**

XYZ coordinates

C 0.113925 0.172050 -0.111080

N -1.224707 -0.385306 -0.019488

H -1.358089 -1.266947 -0.503068

H -1.644290 -0.643663 1.166355

O 0.272884 1.373919 0.022869

N 1.093726 -0.779427 0.082328

H 2.028827 -0.407679 0.059681

H 0.989042 -1.688587 -0.332908

H -1.889077 0.301784 -0.362907

Vibrational frequency (cm-1)

1319.40*i*

203.95

376.94

433.48

489.91

505.89

590.38

774.86

907.33

955.07

1085.74

1172.95

1220.83

1328.63

1606.08

1640.09

1740.13

3474.02

3579.33

3588.73

**NH2CONH2 + H\_Product\_3 (Urea)**

XYZ coordinates

C 0.095020 -0.000019 0.007632

N -0.631613 1.158673 0.174042

H -1.631348 1.154880 0.084926

H -3.889878 0.015198 -0.121362

O 1.296484 0.004066 -0.199115

N -0.623528 -1.163656 0.175101

H -0.142167 -1.999261 -0.103849

H -1.623167 -1.167144 0.084922

H -0.156361 1.997467 -0.105774

Vibrational frequency (cm-1)

*19.19*

*52.48*

*147.28*

*167.24*

*376.43*

*399.84*

*480.19*

*548.98*

*571.05*

*772.88*

*961.59*

*1019.92*

*1175.00*

*1417.46*

*1632.51*

*1644.39*

*1770.96*

*3602.31*

*3610.95*

*3731.07*

**CONH2\_NH3\_ Protonated\_TS-6**

XYZ coordinates

C 0.122263 0.080891 -0.349517

N -1.132011 -0.697925 0.068574

H -1.629825 -1.154963 -0.683807

H -0.982386 -1.331227 0.851115

O -0.257711 1.281269 0.048214

N 1.343364 -0.443405 0.130445

H 1.938833 0.312089 0.442751

H 1.830079 -1.017364 -0.541874

H -1.317272 0.506000 0.306799

Vibrational frequency (cm-1)

*1722.80i*

*276.49*

*328.97*

*411.55*

*508.95*

*677.21*

*731.10*

*805.50*

*987.73*

*1037.91*

*1078.54*

*1226.43*

*1394.54*

*1409.32*

*1571.15*

*1636.67*

*2063.74*

*3449.32*

*3533.92*

*3595.46*

*3627.75*

**NH2(C=O+)NH2\_NH3\_ Product-4 (Protonated Urea)**

XYZ coordinates

C 0.001755 0.006299 -0.294916

N -1.226790 -0.566108 0.111894

H -1.918223 -0.611273 -0.620598

H -1.106120 -1.468887 0.549417

O 0.110992 1.358437 -0.030612

N 1.148378 -0.698814 0.131463

H 1.950984 -0.087925 0.175124

H 1.353950 -1.497797 -0.450298

H -0.662683 1.607865 0.491430

Vibrational frequency (cm-1)

*130.30*

*263.04*

*417.44*

*453.48*

*476.63*

*560.16*

*703.31*

*789.54*

*901.29*

*1074.12*

*1112.53*

*1224.62*

*1347.97*

*1393.90*

*1637.80*

*1642.82*

*3538.19*

*3546.22*

*3633.60*

*3640.84*

*3748.55*

**CS**

XYZ coordinates

C 0.000000 0.000000 -1.118596

S 0.000000 0.000000 0.423494

Vibrational frequency (cm-1)

1276.01

**CS…NH2\_Pre-Reactant**

XYZ coordinates

C 2.228398 0.000006 -0.000011

N -2.731635 0.000001 0.000029

H -3.366068 -0.803880 0.000039

H -3.366058 0.803889 0.000039

S 0.687575 -0.000004 -0.000012

Vibrational frequency (cm-1)

9.54

11.22

76.72

99.30

142.86

1279.64

1543.79

3396.01

3489.68

**CS…NH2\_TS-1**

XYZ coordinates

C -0.294895 0.922048 0.056456

N 2.602198 -0.275164 -0.080917

H 2.337621 0.658212 -0.409065

H 2.950760 -0.097321 0.865817

S -1.212997 -0.312980 0.006216

Vibrational frequency (cm-1)

**58.30*i***

28.12

89.04

117.87

207.11

1283.87

1547.34

3394.15

3486.00

**CS…NH2\_Int-1**

XYZ coordinates

C 0.403799 -0.438489 0.000008

N 1.595561 0.122452 0.000057

H 1.718204 1.127715 0.000078

H 2.424498 -0.445366 0.000079

S -1.111856 0.069599 -0.000037

Vibrational frequency (cm-1)

*378.64*

*450.80*

*581.90*

*879.70*

*1158.90*

*1510.45*

*1641.84*

*3484.78*

*3663.49*

**CSNH2\_H2\_Int-2**

XYZ coordinates

C -0.289250 0.169161 -0.000004

H -2.526486 1.974347 -0.000045

N -1.302362 -0.670521 0.000148

H -1.170955 -1.674370 0.000251

H -2.245828 -0.322533 0.000166

H -3.266710 1.917767 0.000008

S 1.305980 0.062193 -0.000086

Vibrational frequency (cm-1)

70.00

89.25

177.04

215.81

365.61

386.33

467.94

590.70

880.33

1162.33

1513.60

1640.15

3487.49

3653.28

4414.68

**CSNH2\_H2\_TS-2**

XYZ coordinates

C -0.389486 0.315319 0.000020

H -0.789571 1.505879 -0.000016

N -1.481667 -0.441525 0.000179

H -1.418517 -1.446805 0.000237

H -2.390211 -0.007083 0.000244

H -1.380990 2.366992 -0.000012

S 1.180208 -0.077528 -0.000115

Vibrational frequency (cm-1)

**1405.83*i***

310.78

341.58

419.06

428.35

615.72

858.90

1097.55

1102.94

1320.32

1447.11

1516.09

1640.69

3550.98

3679.93

**HCSNH2 + H\_Product\_1 (Thioformamide)**

XYZ coordinates

C -0.407205 0.348383 0.000045

H -0.804459 1.361182 -0.000773

N -1.369263 -0.585262 -0.000281

H -1.113837 -1.558962 0.000317

H -2.341592 -0.332261 -0.001307

H -3.456623 1.920936 0.000201

S 1.209440 0.064720 0.001462

Vibrational frequency (cm-1)

41.02

49.62

151.43

357.57

434.22

628.49

886.58

966.86

1143.78

1314.52

1462.30

1641.22

3112.18

3569.21

3707.75

**HCSNH\_TS-3**

XYZ coordinates

C 0.441261 0.267440 -0.052322

N 1.703057 -0.104674 -0.071254

H 1.949408 -1.012305 0.353004

H 1.356214 1.067445 0.368214

S -1.126392 -0.054866 0.006580

Vibrational frequency (cm-1)

**1745.77i**

382.08

488.37

678.54

843.30

1090.28

1546.61

2154.09

3231.49

**HCSNH\_Int-3**

C -0.5795063021 0.4187862208 0.0010340339

N -1.5560619265 -0.3921549767 0.0002006841

H -2.4383686711 0.1141041013 -0.0002641869

H -0.6560707302 1.5109737009 0.0000273615

S 1.0938286299 -0.0893730463 -0.0005238926

**HCSNH\_H2\_Pre\_Int-4**

XYZ coordinates

C -0.4494787955 -0.2278868449 -0.0001107304

H -0.8137654823 -1.2533822697 -0.0007754945

N -1.2823630004 0.7336262222 -0.0021915287

H -0.8339751687 1.6499376287 -0.0013223179

H -3.6058551298 -1.5943289084 -0.0011140255

H -3.3119635538 -0.9123537106 -0.0006616388

S 1.2969851305 -0.0832631173 0.0039277359

Vibrational frequency (cm-1)

56.25

84.29

172.98

298.51

311.14

366.78

541.26

715.53

1063.12

1163.40

1373.81

1568.17

3110.35

3449.73

4410.43

**HCSNH\_H2\_TS\_4**

XYZ coordinates

C -0.3345757099 0.4738009021 -0.0851827155

H -0.5729337646 1.5301634097 -0.1826302844

N -1.3692381831 -0.3493210431 -0.1533922175

H -1.1889297869 -1.3068638437 0.1447443321

H -3.1998229964 0.4534158772 0.7648213475

H -2.4949847412 0.120394168 0.2955213005

S 1.2212911821 -0.0886714703 -0.0133027626

Vibrational frequency (cm-1)

***1686.19i***

*170.31*

*275.78*

*447.76*

*683.39*

*925.87*

*944.10*

*997.96*

*1117.49*

*1276.79*

*1347.92*

*1412.67*

*1842.37*

*3128.78*

**HCSNH2 + H\_Product-2 (Thioformamide)**

XYZ coordinates

C 0.3599473297 0.3777247183 0.0009353351

H 0.7015371837 1.4105166828 0.0010406432

N 1.3700483528 -0.5033275278 -0.0001530266

H 1.166589849 -1.4892732525 -0.001518717

H 4.0946397903 1.3550955494 -0.0027661936

H 2.3279096739 -0.1993204245 -0.0013987751

S -1.2396021794 0.0083222544 0.0005587341

**CSNH2\_NH3\_Int-5**

XYZ coordinates

C -0.8789960697 0.7929436246 -0.0000215236

N 2.3182423032 -0.5631530323 0.0000980483

H 2.8822670679 -0.7672202863 0.8155456143

H 1.5396424313 -1.2150398347 -0.0000126333

N 0.2402841912 1.4757253561 0.0000392114

H 1.1498578211 0.9920463236 0.0000756335

H 0.2089489617 2.4806953699 0.0000531918

H 2.8824282435 -0.7671397169 -0.8152575333

S -1.2871289503 -0.7639148039 -0.000058009

Vibrational frequency (cm-1)

83.11

90.28

173.79

210.04

291.10

340.42

441.93

540.10

838.00

871.40

1112.21

1221.55

1517.61

1641.74

1674.12

1677.31

3190.01

3464.53

3583.97

3612.07

3638.84

**CSNH2\_NH3\_TS-5**

XYZ coordinates

C 0.262597 0.08324 -0.096192

N 1.080096 -1.058418 -0.040876

H 1.970624 -0.991921 -0.519944

H 1.535297 -1.447913 1.22607

N 0.958714 1.25123 0.077362

H 0.405176 2.088775 0.032366

H 1.902585 1.334551 -0.262558

H 0.562461 -1.879627 -0.330054

S -1.388962 -0.059562 0.010992

Vibrational frequency (cm-1)

**1258.22i**

213.47

353.15

386.71

427.75

464.21

497.50

732.83

810.48

933.44

1033.31

1113.53

1138.95

1338.69

1428.52

1611.18

1657.61

3495.97

3575.10

3600.04

**NH2CSNH2 + H\_Product\_3 (Thiourea)**

**XYZ coordinates**

C 0.2017981863 -0.0002351996 0.0001180534

N 0.9357604095 1.1446027417 -0.0488556947

H 1.8923585867 1.1430149816 0.2633432507

H 4.2111752708 0.0009866499 0.0076870621

N 0.9360306902 -1.145224883 0.0529936952

H 0.4210277007 -1.9995863197 -0.0610992106

H 1.8924746855 -1.1433662524 -0.2599642274

H 0.4208938 1.9996069323 0.0602477137

S -1.4635023298 -0.0004856507 -0.0036146423

Vibrational frequency (cm-1)

47.29

142.69

318.28

367.69

399.51

458.47

481.27

585.46

639.77

772.19

1070.51

1071.35

1416.45

1429.05

1634.70

1658.86

3574.88

3582.55

3711.36

**CSNH2\_NH3\_ Protonated\_TS-6**

**XYZ coordinates**

C -0.393338 -0.072396 -0.306735

N -0.642689 1.350903 0.061556

H -1.046083 1.913473 -0.679782

H -1.198654 1.440300 0.912367

N -1.357408 -0.996332 0.130975

H -0.956478 -1.905397 0.308098

H -2.154226 -1.083698 -0.485596

H 0.675757 1.278144 0.229678

S 1.315024 -0.230653 0.012996

Vibrational frequency (cm-1)

**1571.65i**

228.33

266.49

344.28

440.25

543.24

690.92

727.56

908.13

1011.94

1065.35

1177.94

1232.11

1263.69

1584.72

1645.56

1727.94

3411.75

3520.92

3541.06

**NH2(C=S+)NH2\_NH3\_ Product-4 (Protonated Thiourea)**

XYZ coordinates

C -0.402446 -0.000010 0.225881

N -1.077623 -1.182183 -0.127246

H -0.596842 -2.004382 0.203796

H -2.047546 -1.200460 0.159642

N -1.077332 1.182313 -0.127189

H -0.597923 2.004365 0.206199

H -2.048097 1.199589 0.156835

H 1.457440 0.001213 -1.293259

S 1.342777 -0.000097 0.063817

Vibrational frequency (cm-1)

73.28

280.94

309.54

358.37

369.52

467.11

641.53

682.17

768.65

928.34

1055.86

1087.38

1343.02

1363.18

1626.87

1659.42

2488.00

3521.81

3522.34

3638.41

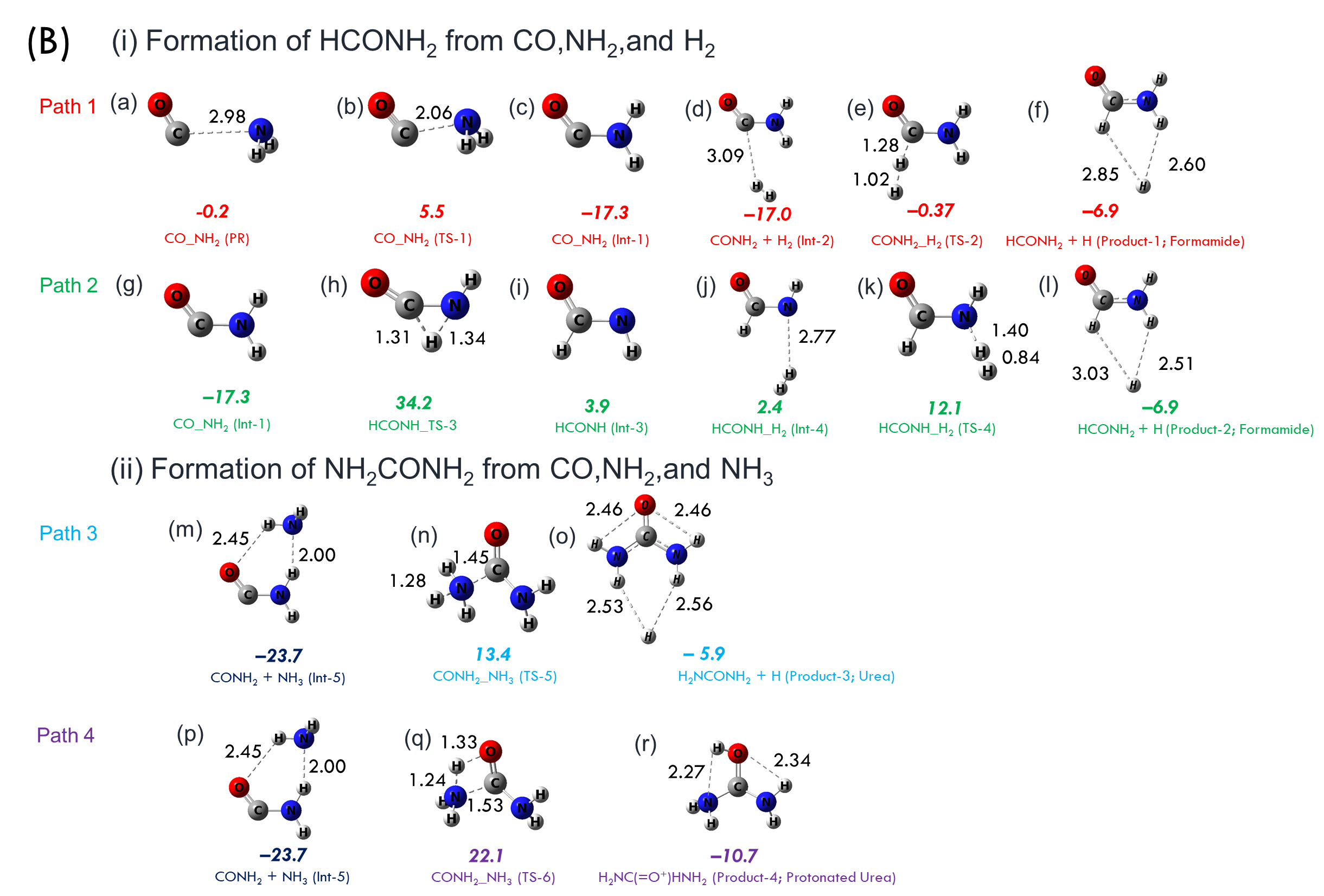
****

Figure SI\_1 (i) Formation of HCONH2 from CO, NH2,and H2 (ii) Formation of NH2CONH2 from CO, NH2, and NH3. The zero-point corrected energy (kcal/mol) was calculated at CC-a/B2PD-a are relative to CO+NH2. All the bond distances are given in Å.

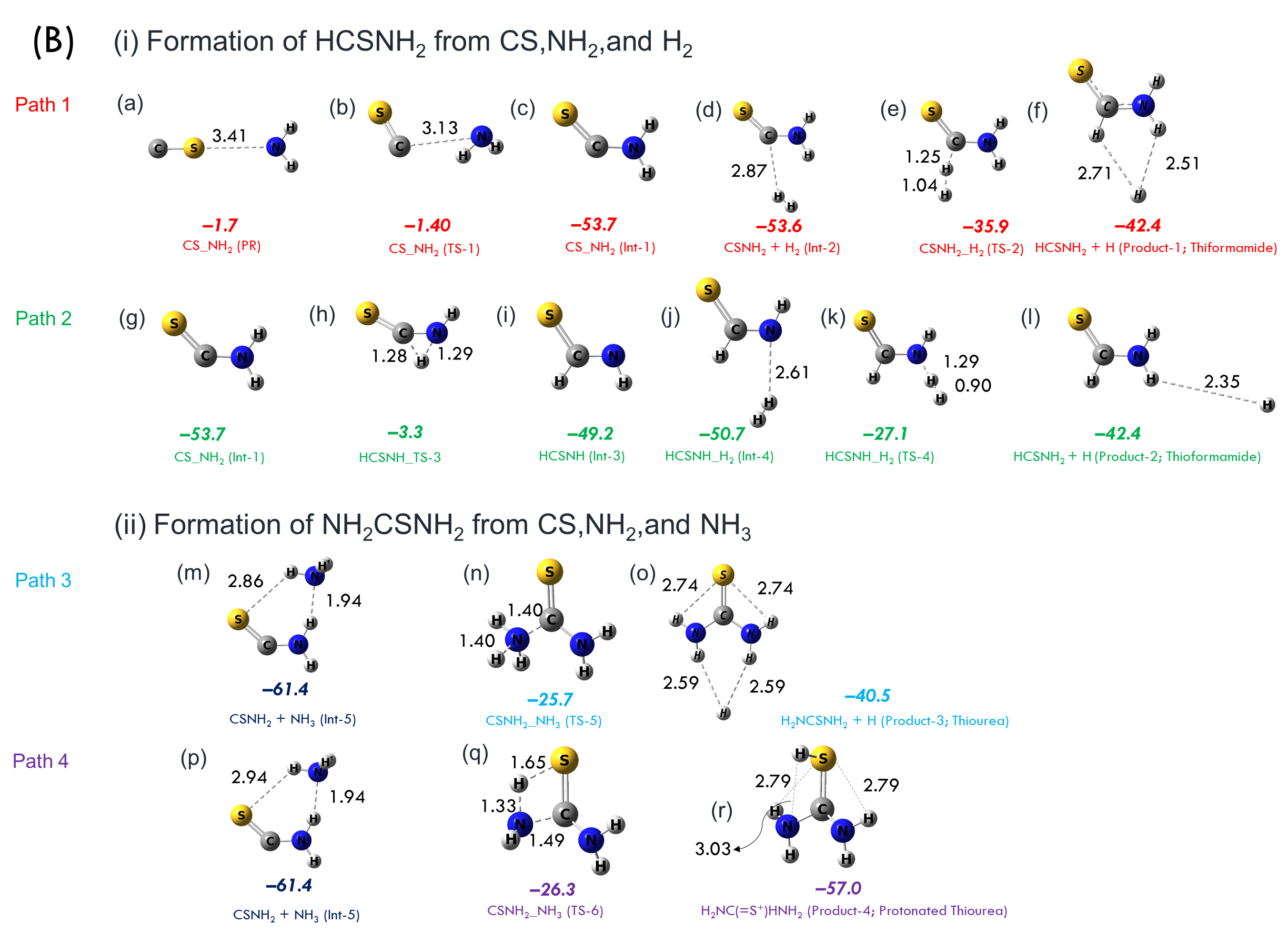


Figure SI\_2. (i) Formation of HCSNH2 from CS, NH2, and H2 (ii) Formation of NH2CSNH2 from CS, NH2, and NH3. The zero-point corrected energy (kcal/mol) was calculated at CC-a/B2PD-a are relative to CS+NH2. All the bond distances are given in Å.

**Comparing the optimized geometries with their energy barriers with different DFT methods on representative TSs.**

Note: The same data presented in the form of energy values (Figure SI\_1 to Figure SI\_12) has been summarized in a Table 1 main text.

**A black background with a black screen

Description automatically generated with medium confidence**

Figure SI\_1: Optimized TSs of CO\_NH2\_TS-1 (ωB97X-D). The geometry being calibrated with two different DFT (B3LYP, M06-2x) methods. Throughout, the aug-cc-pVTZ basis set was used for the optimization. All the resulting optimized geometries are similar. The UCCSD(T)(FC)/aug-cc-pVTZ level of theory is used for the single-point energy calculation. The electronic energy barriers (including zero-point corrections) are given below the structure and the values given in kcal/mol.

**A screenshot of a computer

Description automatically generated**

Figure SI\_2: Optimized TSs of CONH2\_H2\_TS-2 (ωB97X-D). The geometry being calibrated with two different DFT (B3LYP, M06-2x) methods. Throughout, the aug-cc-pVTZ basis set was used for the optimization. All the resulting optimized geometries are similar. The UCCSD(T)(FC)/aug-cc-pVTZ level of theory is used for the single-point energy calculation. The electronic energy barriers (including zero-point corrections) are given below the structure and the values given in kcal/mol.

**A screenshot of a computer

Description automatically generated**

Figure SI\_3: Optimized TSs of HCONH\_TS-3 (ωB97X-D). The geometry being calibrated with two different DFT (B3LYP, M06-2x) methods. Throughout, the aug-cc-pVTZ basis set was used for the optimization. All the resulting optimized geometries are similar. The UCCSD(T)(FC)/aug-cc-pVTZ level of theory is used for the single-point energy calculation. The electronic energy barriers (including zero-point corrections) are given below the structure and the values given in kcal/mol.

**A molecule structure with black background

Description automatically generated with medium confidence**

Figure SI\_4: Optimized TSs of HCONH\_H2\_TS-4 (ωB97X-D). The geometry being calibrated with two different DFT (B3LYP, M06-2x) methods. Throughout, the aug-cc-pVTZ basis set was used for the optimization. All the resulting optimized geometries are similar. The UCCSD(T)(FC)/aug-cc-pVTZ level of theory is used for the single-point energy calculation. The electronic energy barriers (including zero-point corrections) are given below the structure and the values given in kcal/mol.

**A molecule structure with red blue and white balls

Description automatically generated**

Figure SI\_5: Optimized TSs of CONH2\_NH3\_TS-5 (ωB97X-D). The geometry being calibrated with two different DFT (B3LYP, M06-2x) methods. Throughout, the aug-cc-pVTZ basis set was used for the optimization. All the resulting optimized geometries are similar. The UCCSD(T)(FC)/aug-cc-pVTZ level of theory is used for the single-point energy calculation. The electronic energy barriers (including zero-point corrections) are given below the structure and the values given in kcal/mol.

A screenshot of a cell phone

Description automatically generated

Figure SI\_6: Optimized TSs of CONH2\_NH3\_TS-6 (ωB97X-D). The geometry being calibrated with two different DFT (B3LYP, M06-2x) methods. Throughout, the aug-cc-pVTZ basis set was used for the optimization. All the resulting optimized geometries are similar. The UCCSD(T)(FC)/aug-cc-pVTZ level of theory is used for the single-point energy calculation. The electronic energy barriers (including zero-point corrections) are given below the structure and the values given in kcal/mol.

**A black background with a black text and balls

Description automatically generated with medium confidence**

Figure SI\_7: Optimized TSs of CS\_NH2\_TS-1 (ωB97X-D). The geometry being calibrated with two different DFT (B3LYP, M06-2x) methods. Throughout, the aug-cc-pVTZ basis set was used for the optimization. All the resulting optimized geometries are similar. The UCCSD(T)(FC)/aug-cc-pVTZ level of theory is used for the single-point energy calculation. The electronic energy barriers (including zero-point corrections) are given below the structure and the values given in kcal/mol.

**A close-up of a molecule

Description automatically generated**

Figure SI\_8: Optimized TSs of CSNH2\_H2\_TS-2 (ωB97X-D). The geometry being calibrated with two different DFT (B3LYP, M06-2x) methods. Throughout, the aug-cc-pVTZ basis set was used for the optimization. All the resulting optimized geometries are similar. The UCCSD(T)(FC)/aug-cc-pVTZ level of theory is used for the single-point energy calculation. The electronic energy barriers (including zero-point corrections) are given below the structure and the values given in kcal/mol.

A black background with a black and white background with a black and white background with a black and white background with a black and white background with a black and white background with a black and white background

Description automatically generatedFigure SI\_9: Optimized TSs of HCSNH\_TS-3 (ωB97X-D). The geometry being calibrated with two different DFT (B3LYP, M06-2x) methods. Throughout, the aug-cc-pVTZ basis set was used for the optimization. All the resulting optimized geometries are similar. The UCCSD(T)(FC)/aug-cc-pVTZ level of theory is used for the single-point energy calculation. The electronic energy barriers (including zero-point corrections) are given below the structure and the values given in kcal/mol.

**A molecule structure with blue and yellow balls

Description automatically generated with medium confidence**

Figure SI\_10: Optimized TSs of HCSNH\_H2\_TS-4 (ωB97X-D). The geometry being calibrated with two different DFT (B3LYP, M06-2x) methods. Throughout, the aug-cc-pVTZ basis set was used for the optimization. All the resulting optimized geometries are similar. The UCCSD(T)(FC)/aug-cc-pVTZ level of theory is used for the single-point energy calculation. The electronic energy barriers (including zero-point corrections) are given below the structure and the values given in kcal/mol.

**A molecule structure with blue and yellow balls

Description automatically generated**

Figure SI\_11: Optimized TSs of CSNH2\_NH3\_TS-5 (ωB97X-D). The geometry being calibrated with two different DFT (B3LYP, M06-2x) methods. Throughout, the aug-cc-pVTZ basis set was used for the optimization. All the resulting optimized geometries are similar. The UCCSD(T)(FC)/aug-cc-pVTZ level of theory is used for the single-point energy calculation. The electronic energy barriers (including zero-point corrections) are given below the structure and the values given in kcal/mol.

**A computer screen shot of a molecule

Description automatically generated**

Figure SI\_12: Optimized TSs of CSNH2\_NH3\_TS-6 (ωB97X-D). The geometry being calibrated with two different DFT (B3LYP, M06-2x) methods. Throughout, the aug-cc-pVTZ basis set was used for the optimization. All the resulting optimized geometries are similar. The UCCSD(T)(FC)/aug-cc-pVTZ level of theory is used for the single-point energy calculation. The electronic energy barriers (including zero-point corrections) are given below the structure and the values given in kcal/mol.

**Explaining how different sequences of two body reactions lead to the same highly stabilized pre-reaction complex.**

As part of this effort, we handle three entities: CS, NH2, and H2. However, it is evident that the occurrence of three-body collisions in low density gas-phase interstellar chemistry is quite improbable. Within this particular context, we assert unequivocally that we are not suggesting that *the pre-reactant complexes are forming through a three-body collision. Instead, they are generated through a sequential process that involves two bodies colliding.* The exact sequence is inconsequential because all of them lead to the same pre-reactant complex, and no barrier is encountered in the process. After the formation of the pre-reactant complex, the only process taking place is the molecular restructuring of this individual entity, leading to the transition state (TS), which subsequently produces the product complexes. Furthermore, irrespective of the specific sequence of two-body interactions that occur, the pre-reactant complex produced is consistently and considerably stabilized. The same level of theory used in the main-text is used here too. All energies reported are in kcal/mol.

1. The possible sequential two-body collisions for the formation of ***formamide***

*Possible collisions 1*

CO + NH2 → CO•••NH2 ∆E = 0

CO•••NH2 + H2 → HCONH2 + H ∆E = –14.8

CO + NH2 + H2 → HCONH2 + H ∆E = –14.8

*Possible Collision 2*

CO + H2 → CO•••H2 ∆E = 0

CO•••H2 + NH2 → HCONH2 + H ∆E = –14.9

CO + H2 + NH2 → HCONH2 + H ∆E = –14.8

The possible sequential two-body collisions for the formation of ***urea***

*Possible collisions 1*

CO + NH2 → CO•••NH2 ∆E = 0

CO•••NH2 + NH3 → NH2CONH2 + H ∆E = –15.1

CO + NH2 + NH3 → NH2CONH2 + H ∆E = –15.1

*Possible collisions 2*

CO + NH3 → CO•••NH3 ∆E = –0.1

CO•••NH3 + NH2 → NH2CONH2 + H ∆E = –14.9

CO + NH3 + NH2 → NH2CONH2 + H ∆E = –15.1

1. The possible sequential two-body collisions for the formation of ***thioformamide***

*Possible collisions 1*

CS + NH2 → CS•••NH2 ∆E = –0.9

CS•••NH2 + H2 → HCSNH2 + H ∆E = –50.5

CS + NH2 + H2 → HCSNH2 + H ∆E = –51.4

*Possible collisions 2*

CS + H2 → CS•••H2 ∆E = 0.2

CS•••H2 + NH2 → HCSNH2 + H ∆E = –51.6

CS + H2 + NH2 → HCSNH2 + H ∆E = –51.4

The possible sequential two-body collisions for the formation of ***thiourea***

*Possible collisions 1*

CS + NH2 → CS•••NH2 ∆E = –0.9

CS•••NH2 + NH3 → NH2CSNH2 + H ∆E = –49.9

CS + NH2 + NH3 → NH2CSNH2 + H ∆E = –50.8

*Possible collisions 2*

CS + NH3 → CS•••NH3 ∆E = –1.2

CS•••NH3 + NH2 → NH2CSNH2 + H ∆E = –49.6

CS + NH3 + NH2 → NH2CSNH2 + H ∆E = –50.8

All energies reported are in kcal/mol.

**The energy difference between products and reactants of** **Formamide, Urea, Thioformamide, and Thiourea.**

The B2PLYP-D/aug-cc-pVTZ level of theory used, the reactions are exothermic as stated in the main-text.

Table SI\_1: The Reaction of CO + NH2 + H2 → HCONH2 + H.

|  |  |  |
| --- | --- | --- |
| **Reactants** | **Products** | **Energy(ΔE)** |
| CO + NH2 + H2 | HCONH2 + H. | –14.9 |

Table SI\_2: The Reaction of CO + NH2 + NH3 → H2NCONH2 + H.

|  |  |  |
| --- | --- | --- |
| **Reactants** | **Products** | **Energy(ΔE)** |
| CO + NH2 + NH3 | H2NCONH2 + H. | –15.2 |

Table SI\_3: The Reaction of CS + NH2 + H2 → HCSNH2 + H.

|  |  |  |
| --- | --- | --- |
| **Reactants** | **Products** | **Energy(ΔE)** |
| CS + NH2 + H2 | HCSNH2 + H. | –42.4 |

Table SI\_4: The Reaction of CS + NH2 + H2 → H2NCSNH2 + H.

|  |  |  |
| --- | --- | --- |
| **Reactants** | **Products** | **Energy(ΔE)** |
| CS + NH2 + NH3 | H2NCSNH2 + H. | –40.4 |

All energies reported are in kcal/mol.

**Table SI\_5. Imaginary frequencies the Formamide, Urea, Thioformamide, and Thiourea TSs**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Formamide and Urea TSs** | **ωB97X-D** | **B3LYP** | **M06-2x** | **B2LYP-D** |
| CO\_NH2\_TS-1 | 294.52i | 207.75i | 368.34i | 301.62i |
| CONH2\_H2\_TS-2 | 1163.84i | 1039.28i | 1795.40i | 1380.04i |
| HCONH\_TS-3 | 1776.67i | 1752.37i | 1684.37i | 1720.51i |
| HCONH\_H2\_TS-4 | 1242.49i | 1046.23i | 1258.05i | 1167.25i |
| CONH2\_NH3\_TS-5 | 1250.38i | 1159.16i | 1211.14i | 1319.39i |
| CONH2\_NH3\_TS-6 | 1722.36i | 1726.91i | 1564.39i | 1722.80i |
|  |  |  |  |  |
| **Thioformamide and Thiourea TSs** | **ωB97X-D** | **B3LYP** | **M06-2x** | **B2LYP-D** |
| CS\_NH2\_TS-1 | 79.36i | 82.17i | 87.93i | 58.30i |
| CSNH2\_H2\_TS-2 | 1255.31i | 1042.27i | 1815.66i | 1405.82i |
| HCSNH\_TS-3 | 1821.28i | 1815.55i | 1727.08i | 1745.77i |
| HCSNH\_H2\_TS-4 | 1812.23i | 1622.71i | 2035.84i | 1686.18i |
| CSNH2\_NH3\_TS-5 | 1355.51i | 1116.89i | 1325.50i | 1258.21i |
| CSNH2\_NH3\_TS-6 | 1526.38i | 1549.61i | 1535.54i | 1571.65i |

All energies reported are in kcal/mol.

**Table\_SI\_6. The electronic energies for all investigated compounds (in Hartrees)**

|  |  |  |  |
| --- | --- | --- | --- |
|  | Zero-point correction  **B2PLYP-D** | UCCSD(T) | UCCSD(T)+ Zero-point correction |
| CO\_NH2(Pre-Reactant) | 0.02531 | -168.963494 | -168.9381883 |
| CO\_NH2\_TS-1 | 0.02794 | -168.957003 | -168.9290589 |
| CO\_NH2\_Int-1 | 0.03286 | -168.998398 | -168.9655434 |
| CONH2+H2\_Int-2 | 0.04475 | -170.172362 | -170.1276157 |
| CONH2\_H2\_TS-2 | 0.04326 | -170.144232 | -170.1009771 |
| HCONH2+H\_Product-1 (Formamide) | 0.04587 | -170.157253 | -170.1113844 |
| HCONH\_TS-3 | 0.02539 | -168.908775 | -168.8833887 |
| HCONH\_Int-3 | 0.03025 | -168.961907 | -168.9316601 |
| HCONH\_H2\_Int-4 | 0.04267 | -170.139161 | -170.0964952 |
| HCONH\_H2\_TS-4 | 0.04321 | -170.124247 | -170.0810331 |
| HCONH2+H\_Product-2 (Formamide) | 0.04583 | -170.157232 | -170.1113981 |
| CONH2+NH3\_Int-5 | 0.06693 | -225.429497 | -225.3625648 |
| CONH2\_NH3\_TS-5 | 0.06341 | -225.456933 | -225.3935188 |
| H2NCONH2+H\_Product-3 (Urea) | 0.06915 | -225.417928 | -225.348781 |
| CONH2\_NH3\_TS-6 | 0.07344 | -225.474607 | -225.4011672 |
| H2NCONH2+H\_Product-4(Protonated Urea) | 0.02531 | -168.963494 | -168.9381883 |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  | Zero-point correction  **B2PLYP-D** | UCCSD(T) | UCCSD(T)+ Zero-point correction |
| CS\_NH2(Pre-Reactant) | 0.022893 | -491.5025222 | -491.4796292 |
| CS\_NH2\_TS-1 | 0.023131 | -491.5023692 | -491.4792382 |
| CS\_NH2\_Int-1 | 0.031326 | -491.5939881 | -491.5626621 |
| CSNH2+H2\_Int-2 | 0.043546 | -492.7684493 | -492.7249033 |
| CSNH2\_H2\_TS-2 | 0.041759 | -492.7384292 | -492.6966702 |
| HCSNH2+H\_Product-1 (Thioformamide) | 0.044349 | -492.7513523 | -492.7070033 |
| HCSNH\_TS-3 | 0.023727 | -491.5060492 | -491.4823222 |
| HCSNH\_Int-3 | 0.030489 | -491.5859644 | -491.5554754 |
| HCSNH\_H2\_Int-4 | 0.042569 | -492.7628073 | -492.7202383 |
| HCSNH\_H2\_TS-4 | 0.041129 | -492.7235988 | -492.6824698 |
| HCSNH2+H\_Product-2 (Thioformamide) | 0.044239 | -492.7512874 | -492.7070484 |
| CSNH2+NH3\_Int-5 | 0.064958 | -548.0290529 | -547.9640949 |
| CSNH2\_NH3\_TS-5 | 0.061682 | -548.0493163 | -547.9876343 |
| H2NCSNH2+H\_Product-3 (Thiourea) | 0.065965 | -548.0310226 | -547.9650576 |
| CSNH2\_NH3\_TS-6 | 0.067946 | -548.0819001 | -548.0139541 |
| H2NCSNH2+H\_Product-4(Protonated Thiourea) | 0.022893 | -491.5025222 | -491.4796292 |

**Table\_SI\_7**: The Equilibrium constant and rate constants (in cm3 molecule-1 s-1) for CS+NH2→ CS…NH2

|  |  |  |
| --- | --- | --- |
| Temp | **Ke** | **micro-k1** |
| 10 | 2.21E+14 | 7.59E-09 |
| 15 | 1.09E+02 | 3.84E-09 |
| 20 | 7.14E-05 | 2.24E-09 |
| 25 | 1.35E-08 | 1.42E-09 |
| 30 | 4.39E-11 | 9.55E-10 |
| 35 | 7.35E-13 | 6.66E-10 |
| 40 | 3.44E-14 | 4.79E-10 |
| 45 | 3.20E-15 | 3.53E-10 |
| 50 | 4.84E-16 | 2.65E-10 |
| 55 | 1.04E-16 | 2.02E-10 |
| 60 | 2.91E-17 | 1.57E-10 |
| 65 | 9.99E-18 | 1.23E-10 |
| 70 | 4.03E-18 | 9.76E-11 |
| 75 | 1.85E-18 | 7.84E-11 |
| 80 | 9.40E-19 | 6.35E-11 |
| 85 | 5.21E-19 | 5.20E-11 |
| 90 | 3.10E-19 | 4.29E-11 |
| 100 | 1.96E-19 | 2.98E-11 |

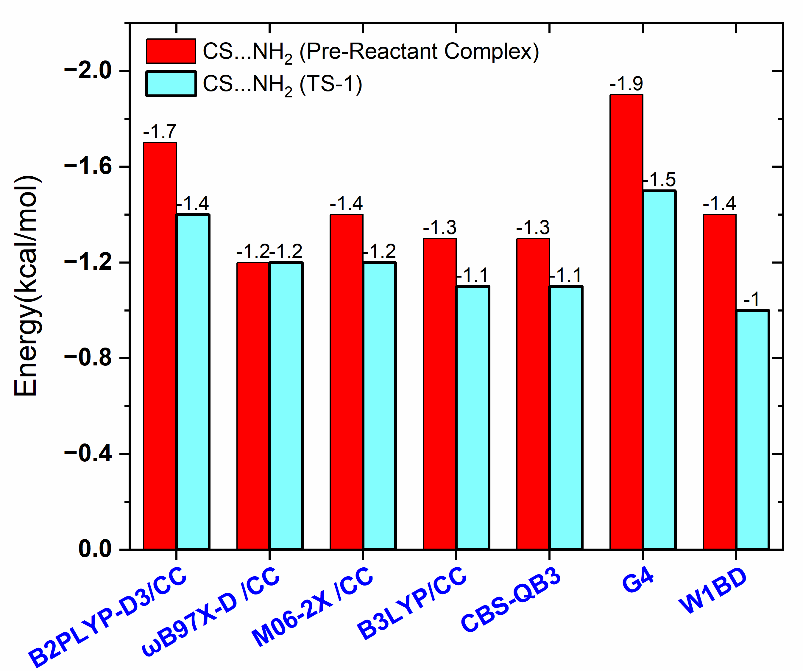


Figure SI\_13: Zero-point corrected energies of pre-reactive complex and TS-1 in the case of CS+NH2 reaction at different levels of theories.