Electronic Supplementary Material (ESI) for Faraday Discussions.


**Electronic Supplementary Information**

# In the search for the bottlenecks of ammonia synthesis over Ru/Vulcan under ambient conditions

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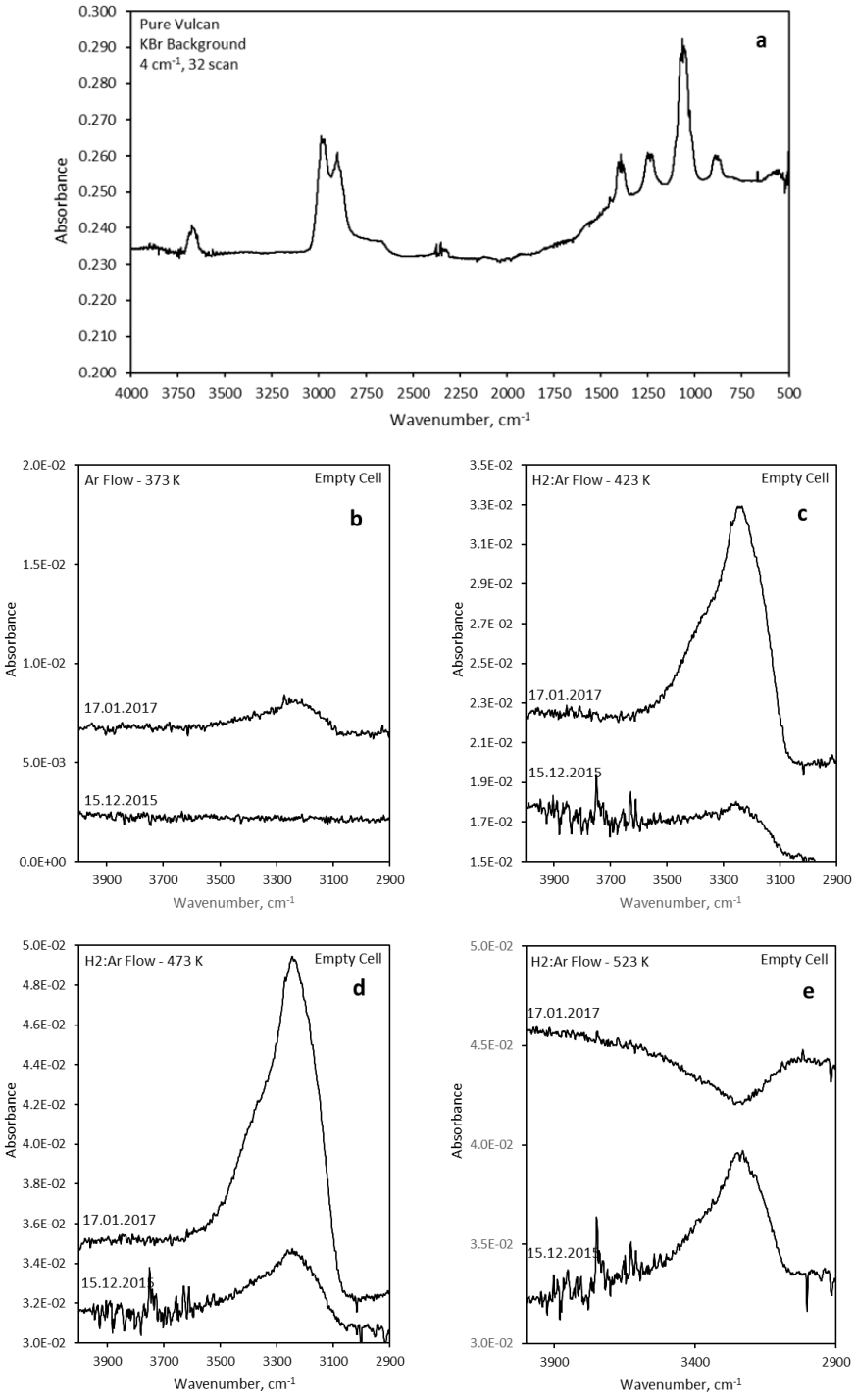
## S.1. IR spectra of bare Vulcan and empty reactor cell



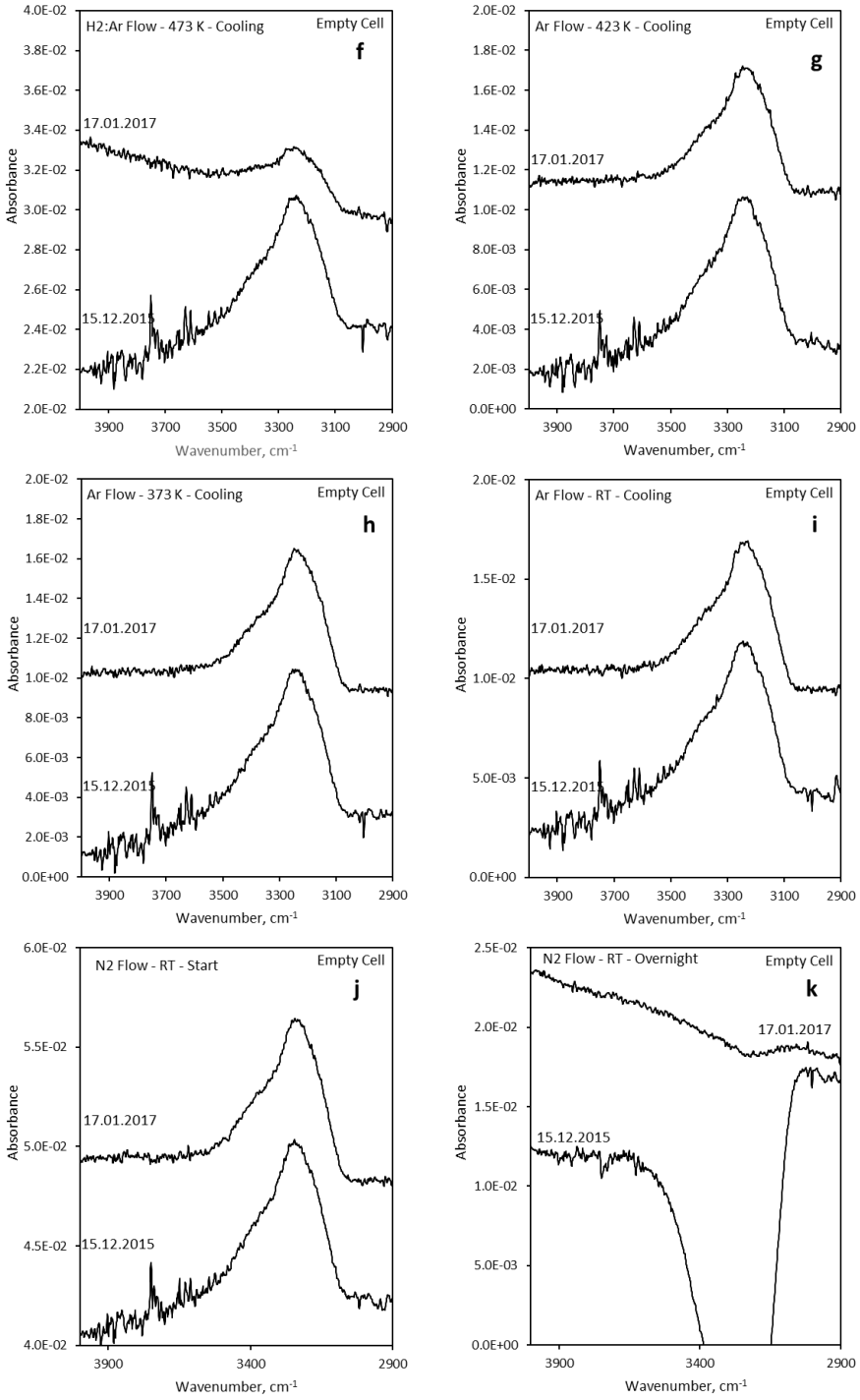



Figure S.1.(a) DRIFT spectra of bare Vulcan; (b-k) DRIFT spectra of empty sample holder between 4000 $cm^{-1}$ and 2900 $cm^{-1}$ wavenumber exposed to experimental steps

## S.2. DRIFTS spectrum of liquid $NH_4OH$

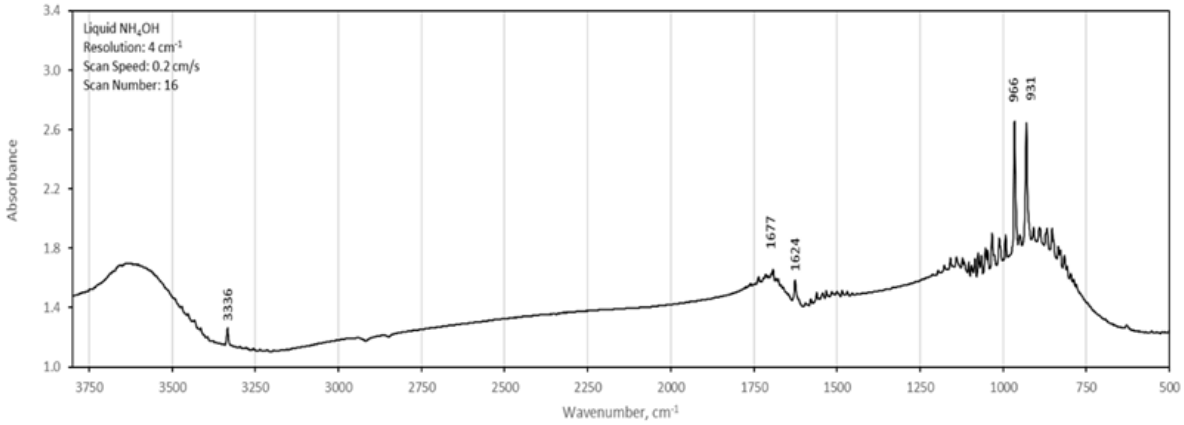



Figure S.2. IR Spectra of Liquid $NH_4OH$ (recorded at room temperature and under atmospheric pressure)

## S.3. $NH_3$ Molecule in Gas Phase

**Table S1.** Calculated vibrational IR frequencies and intensities of $NH_3$.

| Mode | Freq. ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 3526.6 | 0.022 |
| 2 | 3526.1 | 0.022 |
| 3 | 3401.7 | 0.058 |
| 4 | 1620.4 | 0.117 |
| 5 | 1619.2 | 0.117 |
| 6 | 1006.8 | 1.000 |
| 7 | 71.4 | 0.430 |
| 8 | 86.9 | 0.433 |

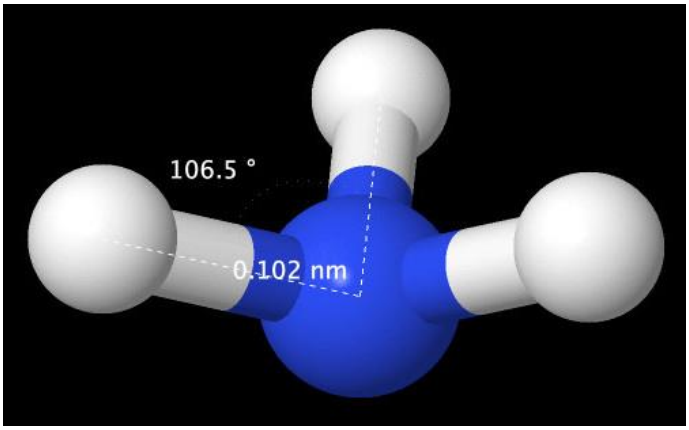



**Figure S3.** DFT-optimized geometry of $NH_3$.

## S.4. N-NH Molecule in Gas Phase

**Table S2.** Calculated vibrational IR frequencies and intensities of N-NH.

| Mode | Freq. ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 2592.9 | 1.000 |
| 2 | 1904.7 | 0.300 |
| 3 | 1093.4 | 0.353 |
| 4 | 80.6 | 0.386 |
| 5 | 19.6 | 0.041 |
| 6 | 15.7 | 0.026 |

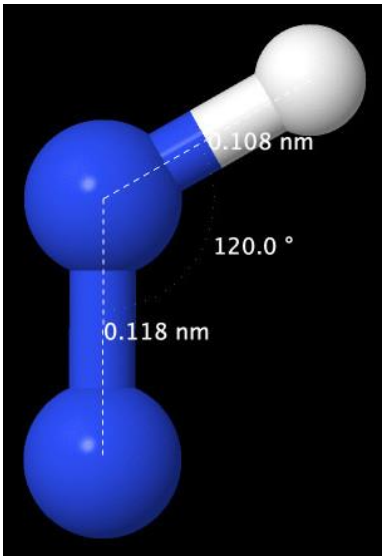



**Figure S4.** DFT-optimized geometry of N-NH.

## S.5. H-atom Addition to N-NH ($N_2H$+H)

**Table S3.** Calculated vibrational IR frequencies and intensities of HN-NH (final structure).

| Mode | Freq. ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 3149.2 | 0.567 |
| 2 | 1314.9 | 0.960 |
| 3 | 1303.3 | 1.000 |

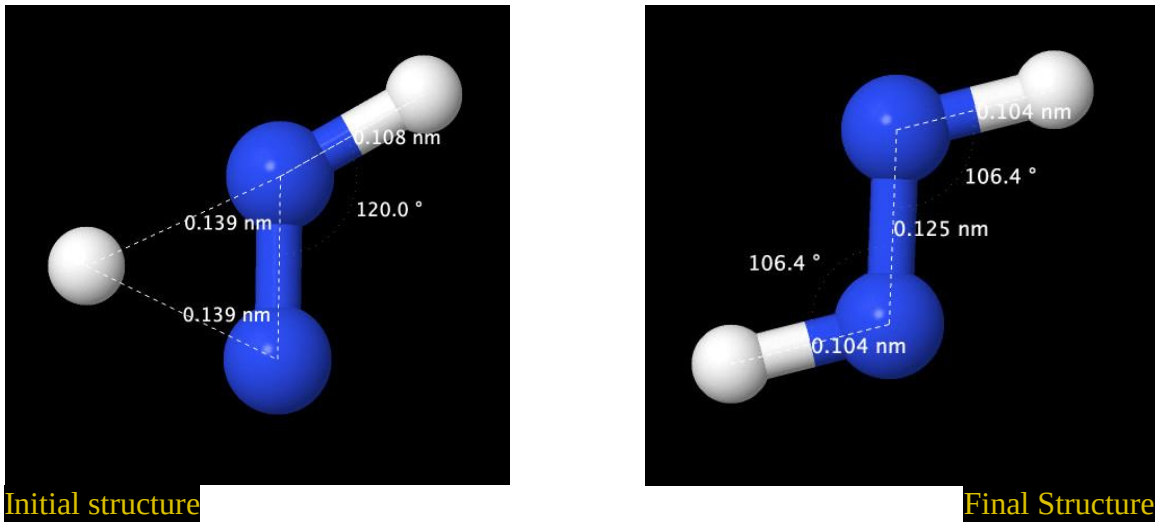



**Figure S5.** Initial (left) and DFT-optimized (right) geometries of N-NH + H .

## S.6. N-$NH_2$ Molecule in Gas Phase

**Table S4.** Calculated vibrational IR frequencies and intensities of N-$NH_2$.

| Mode | Freq. ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 2854.6 | 0.796 |
| 2 | 2730.5 | 1.000 |
| 3 | 1698.7 | 0.079 |
| 4 | 1625.1 | 0.178 |
| 5 | 1284.6 | 0.048 |
| 6 | 996.1 | 0.309 |
| 7 | 66.0 | 0.022 |
| 8 | 38.8 | 0.098 |
| 9 | 13.0 | 0.075 |
| 10 | 10.9 | 0.030 |
| 11 | 7.8 | 0.023 |

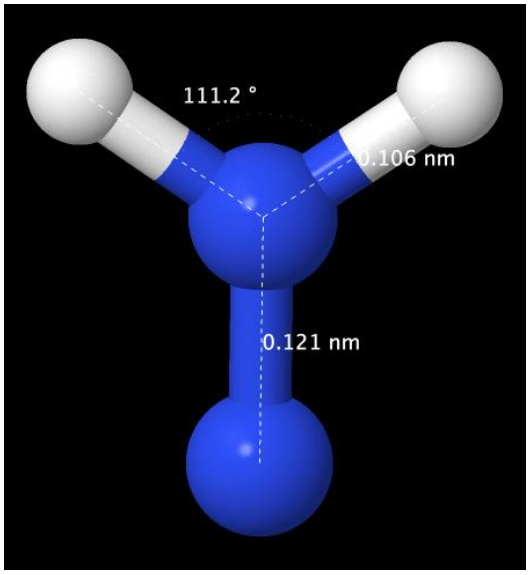



**Figure S6.** DFT-optimized geometry of N-$NH_2$.

## S.7. H-atom Addition to N-$NH_2$ ($N_2H_2$+H)

**Table S5.** Calculated vibrational IR frequencies and intensities of HN-$NH_2$ (final structure).

| Mode | Freq. ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 3548.2 | 0.155 |
| 2 | 3384.7 | 0.053 |
| 3 | 3346.7 | 0.067 |
| 4 | 1605.0 | 0.062 |
| 5 | 1446.4 | 0.126 |
| 6 | 1220.6 | 0.011 |
| 7 | 1099.0 | 0.216 |
| 8 | 659.3 | 0.896 |
| 9 | 489.4 | 1.000 |
| 10 | 36.9 | 0.058 |
| 11 | 33.1 | 0.217 |
| 12 | 30.7 | 0.150 |
| 13 | 28.0 | 0.177 |

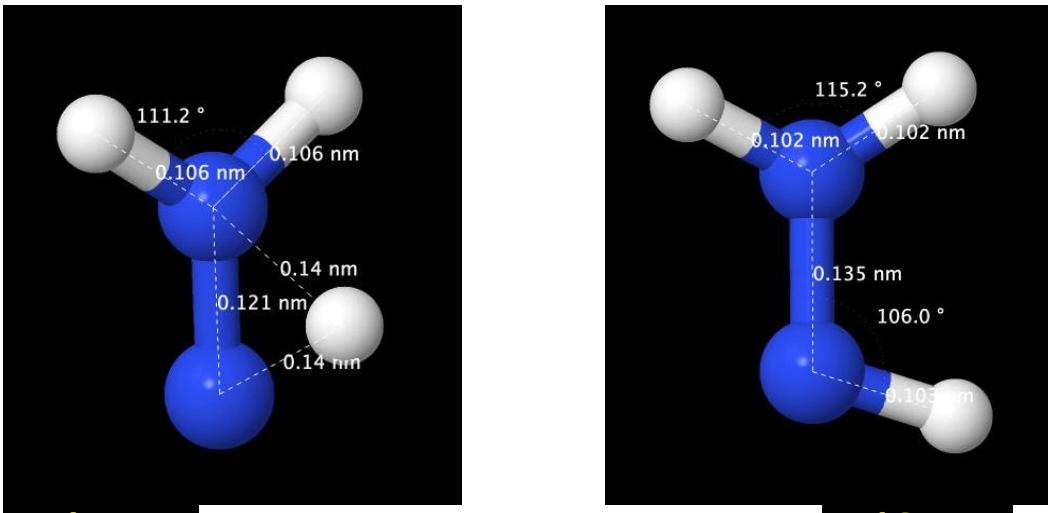



**Figure S7.** Initial (left) and DFT-optimized (right) geometries of N-$NH_2$ + H .

## S.8. N-$NH_3$ Molecule in Gas Phase

**Table S6.** Calculated vibrational IR frequencies and intensities of N-$NH_3$.

| Mode | Freq. ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 3051.9 | 1.000 |
| 2 | 2994.5 | 0.055 |
| 3 | 2994.3 | 0.054 |
| 4 | 1558.0 | 0.038 |
| 5 | 1556.4 | 0.038 |
| 6 | 1415.7 | 0.023 |
| 7 | 939.3 | 0.110 |
| 8 | 936.6 | 0.109 |
| 9 | 771.6 | 0.221 |
| 10 | 40.1 | 0.057 |
| 11 | 19.4 | 0.105 |
| 12 | 22.2 | 0.016 |
| 13 | 24.4 | 0.166 |
| 14 | 43.4 | 0.200 |

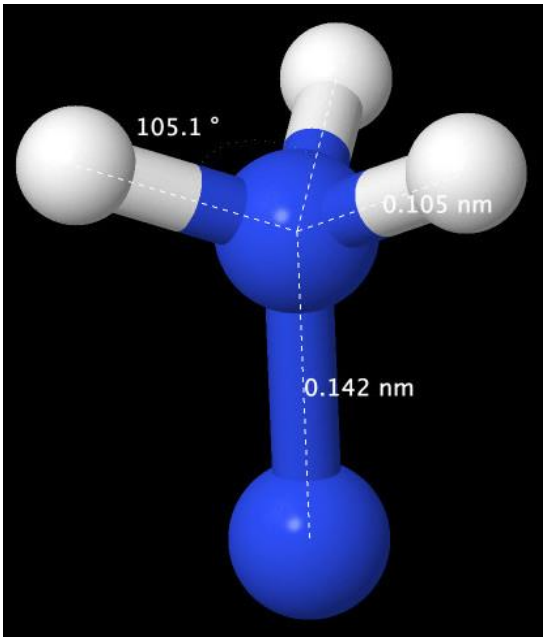



**Figure S8.** DFT-optimized geometry of N-$NH_3$.

## S.9. H-atom Addition to HN-$NH_2$ ($N_2H_3$ + H)

**Table S7.** Calculated vibrational IR frequencies and intensities of $H_2N$-$NH_2$.

| Mode | Freq. ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 3486.6 | 0.013 |
| 2 | 3480.5 | 0.013 |
| 3 | 3383.0 | 0.043 |
| 4 | 3372.2 | 0.171 |
| 5 | 1639.9 | 0.068 |
| 6 | 1625.2 | 0.090 |
| 7 | 1293.5 | 0.021 |
| 8 | 1263.6 | 0.035 |
| 9 | 1099.0 | 0.118 |
| 10 | 955.8 | 1.000 |
| 11 | 761.2 | 0.483 |
| 12 | 444.7 | 0.277 |
| 13 | 103.2 | 0.353 |
| 14 | 64.0 | 0.076 |

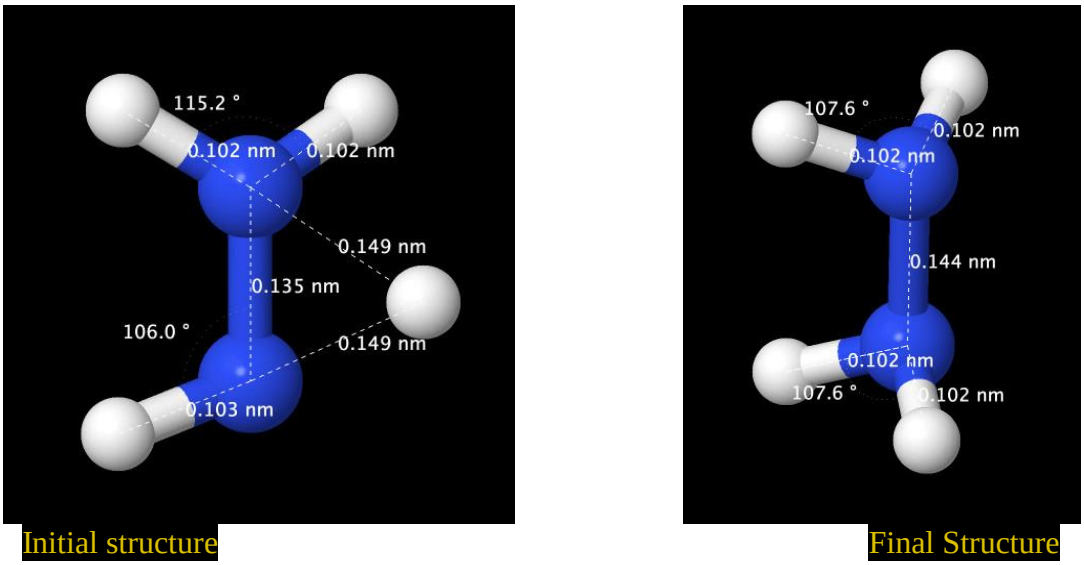



**Figure S9.** Initial (left) and DFT-optimized (right) geometries of HN-$NH_2$ + H .

## S.10. HN-$NH_3$ Molecule in Gas Phase

**Table S8.** Calculated vibrational IR frequencies and intensities of HN-$NH_3$.

| Mode | Freq. ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 3406.2 | 0.059 |
| 2 | 3326.1 | 0.137 |
| 3 | 3041.8 | 1.000 |
| 4 | 2941.0 | 0.120 |
| 5 | 1619.1 | 0.103 |
| 6 | 1577.8 | 0.014 |
| 8 | 1436.7 | 0.023 |
| 9 | 1037.3 | 0.119 |
| 10 | 1013.7 | 0.152 |
| 11 | 814.5 | 0.224 |
| 12 | 372.5 | 0.273 |
| 13 | 58.1 | 0.027 |
| 14 | 37.2 | 0.158 |
| 15 | 25.2 | 0.099 |

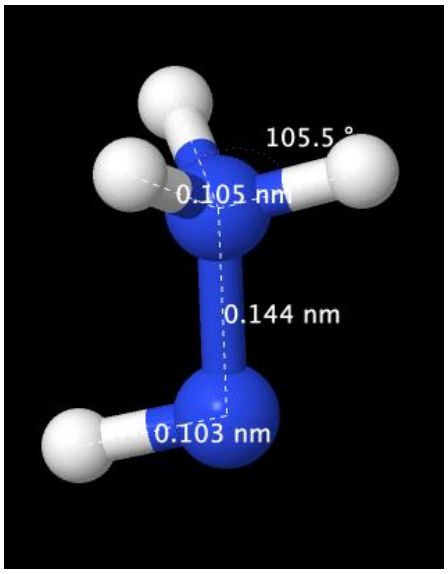



**Figure S10.** DFT-optimized geometry of HN-$NH_3$.

## S.11. Ru-$NH_3$ Molecule in Gas Phase

**Table S9.** Calculated vibrational IR frequencies and intensities of Ru-$NH_3$.

| Mode | Freq. ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 3390.6 | 0.070 |
| 2 | 3390.4 | 0.070 |
| 3 | 3311.3 | 0.388 |
| 4 | 1573.1 | 0.124 |
| 5 | 1570.5 | 0.124 |
| 6 | 1119.1 | 1.000 |
| 7 | 573.2 | 0.032 |
| 8 | 571.7 | 0.032 |
| 9 | 467.7 | 0.024 |
| 10 | 58.0 | 0.015 |
| 11 | 30.9 | 0.055 |
| 12 | 21.1 | 0.072 |

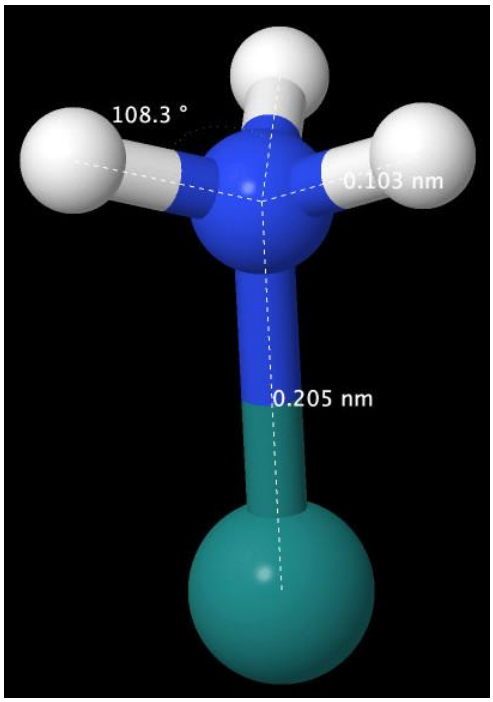



**Figure S11.** DFT-optimized geometry of Ru-$NH_3$.

## S.12. Ru-N-$NH_3$ Structure in Gas Phase

**Table S10.** Calculated vibrational IR frequencies and intensities of Ru-N-$NH_3$ (final structure).

| Mode | Freq. ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 3518.6 | 0.011 |
| 2 | 3516.9 | 0.011 |
| 3 | 3399.3 | 0.060 |
| 4 | 1624.9 | 0.051 |
| 5 | 1621.2 | 0.052 |
| 6 | 1205.5 | 0.288 |
| 7 | 1039.1 | 1.000 |
| 8 | 71.1 | 0.217 |
| 9 | 31.8 | 0.010 |
| 10 | 16.1 | 0.023 |
| 11 | 15.4 | 0.014 |
| 12 | 9.9 | 0.006 |
| 13 | 28.9 | 0.020 |
| 14 | 75.0 | 0.123 |
| 15 | 82.5 | 0.136 |

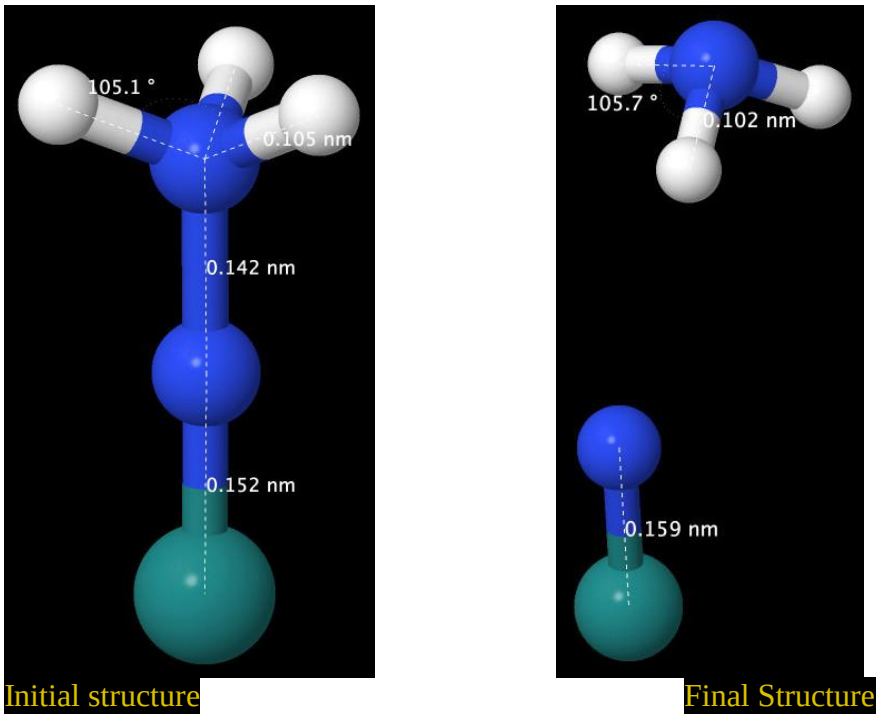



**Figure S12.** Initial (left) and DFT-optimized (right) geometries of Ru-N-$NH_3$.

## S.13. Ru-$N_2H_4$ (Ru+$H_2N$-$NH_2$) Structure

**Table S11.** Calculated vibrational IR frequencies and intensities of Ru-$N_2H_4$ (final structure).

| Mode | Freq. ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 3147.5 | 0.156 |
| 2 | 3130.0 | 1.000 |
| 3 | 3115.0 | 0.132 |
| 4 | 1499.4 | 0.047 |
| 5 | 1488.3 | 0.125 |
| 6 | 1063.1 | 0.022 |
| 7 | 1001.6 | 0.049 |
| 8 | 970.1 | 0.015 |
| 9 | 961.9 | 0.006 |
| 10 | 553.4 | 0.005 |
| 11 | 510.3 | 0.024 |
| 12 | 355.6 | 0.005 |

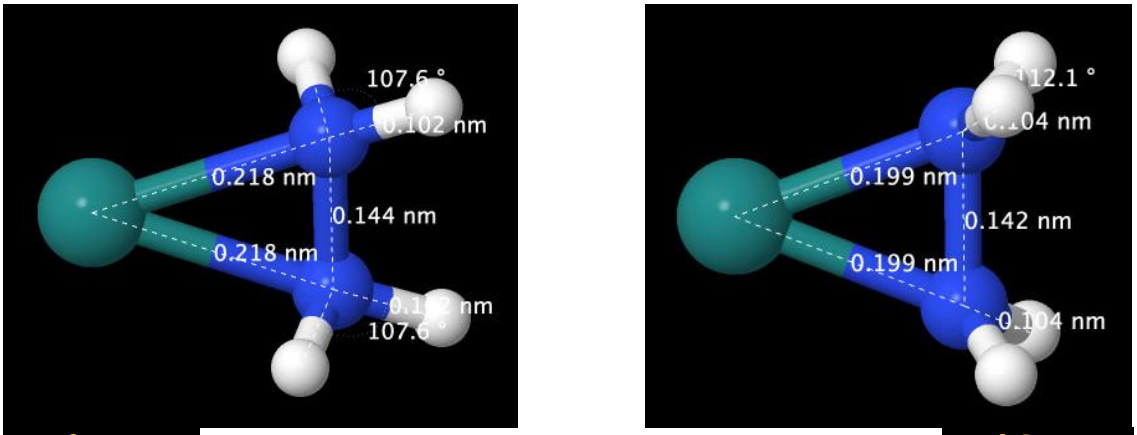



**Figure S13.** Initial (left) and DFT-optimized (right) geometries of Ru-$N_2H_4$ .

## S.14. $H_2O$-$NH_3$ Structure in Gas Phase

**Table S12.** Calculated vibrational IR frequencies and intensities of $H_2O$-$NH_3$ (final structure).

| Mode | Freq. ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 3801.4 | 0.055 |
| 2 | 3529.5 | 0.013 |
| 3 | 3526.8 | 0.014 |
| 4 | 3406.4 | 0.018 |
| 5 | 3352.8 | 1.000 |
| 6 | 1631.0 | 0.004 |
| 7 | 1619.4 | 0.024 |
| 8 | 1608.1 | 0.063 |
| 9 | 1059.9 | 0.164 |
| 10 | 752.5 | 0.095 |
| 11 | 483.4 | 0.100 |
| 12 | 214.5 | 0.055 |
| 13 | 198.1 | 0.044 |
| 14 | 192.3 | 0.016 |
| 15 | 75.2 | 0.105 |
| 16 | 22.9 | 0.011 |
| 17 | 12.3 | 0.009 |

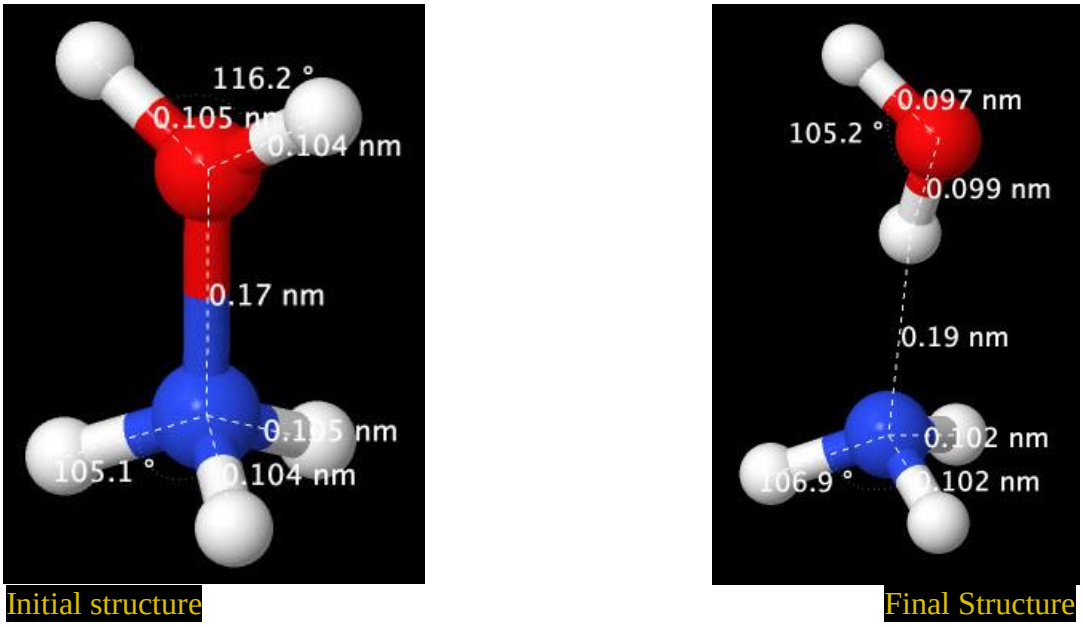



**Figure S14.** Initial (left) and DFT-optimized (right) geometries of $H_2O$-$NH_3$ .