Supporting Information

# Preparation of Methanediamine ($CH_2(NH_2)_2$) – A Precursor to Nucleobases in the Interstellar Medium

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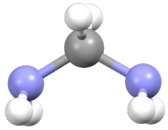
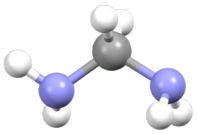
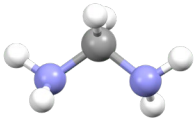
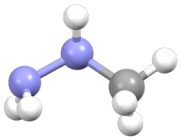
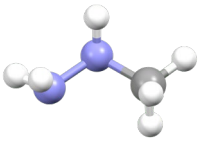
**Table S1.** Calculated Adiabatic Ionization Energies (IE) and Relative Energies ($E_{rel}$) of distinct $CH_6N_2O$ Isomers. Isomers of **1** are labeled with respect to *trans* (*t*) or *gauche* (*g*) configuration of the C-N bond. Absolute energies, geometries, and harmonic frequencies are detailed in full in Table S6.

| | Structure | Name | CCSD(T) IE (eV)[a] | CCSD(T) ΔE (kJ mol$^{-1}$)[b] | CCSD(T) Dipole (D) |
|---|---|---|---|---|---|
| **1a** |  | $C_{2v}$ *tt*-$CH_2(NH_2)_2$ | 8.66 | 0.00 | 1.72 |
| **1b** |  | $C_1$ *tg*-$CH_2(NH_2)_2$ | 8.73 | 2.06 | 1.65 |
| **1c** |  | $C_2$ *gg*-$CH_2(NH_2)_2$ | 8.62 | 3.75 | 1.53 |
| **2a** |  | $CH_3NHNH_2$ | 7.65 | 102.32 | 1.85 |
| **2b** |  | $CH_3NHNH_2$ | 7.52 | 105.46 | 1.92 |

[a] Adiabatic ionization potential by CCSD(T)/CBS from the CCSD(T)/aug-cc-pVTZ geometry and with ZPVE correction in eV.
[b] Relative energy by CCSD(T)/CBS from the CCSD(T)/aug-cc-pVTZ geometry with ZPVE correction in kJ mol$^{-1}$.

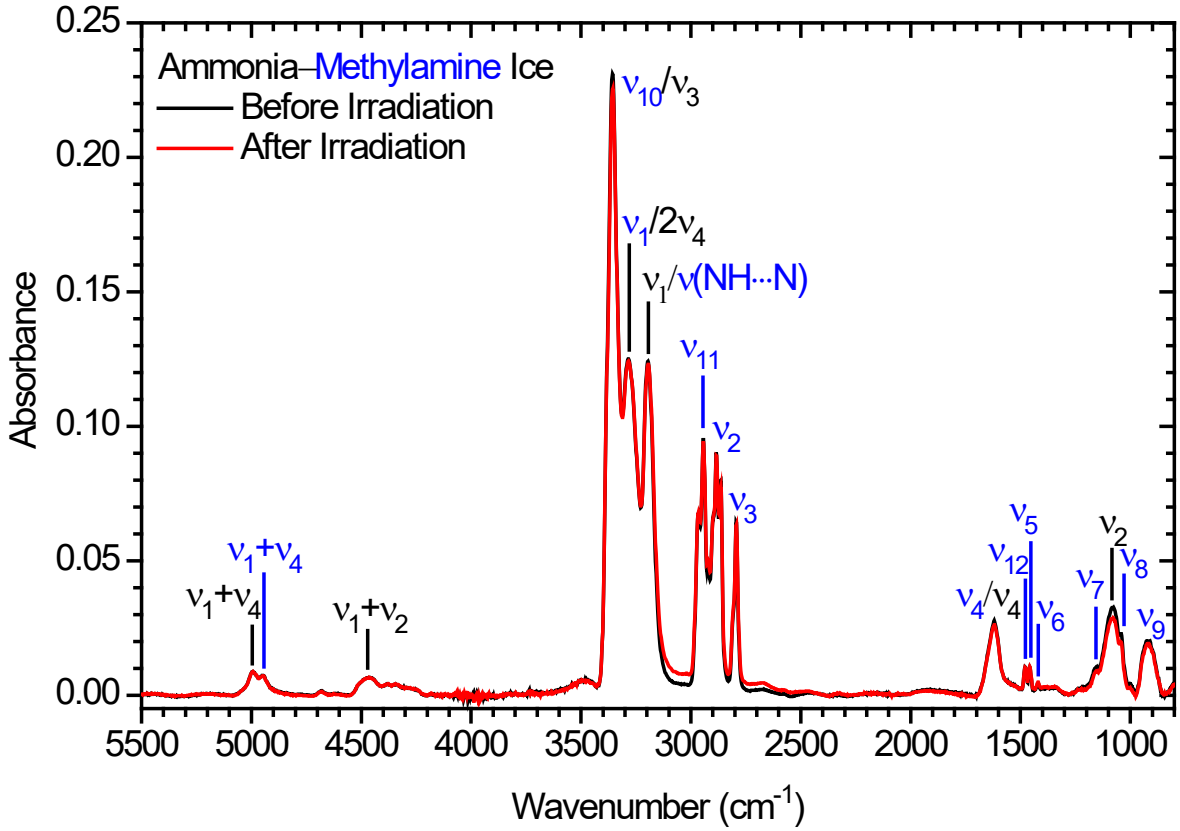



**Figure S1.** Infrared spectra of ammonia–methylamine ice before and after irradiation with assignments also listed in Table S1.

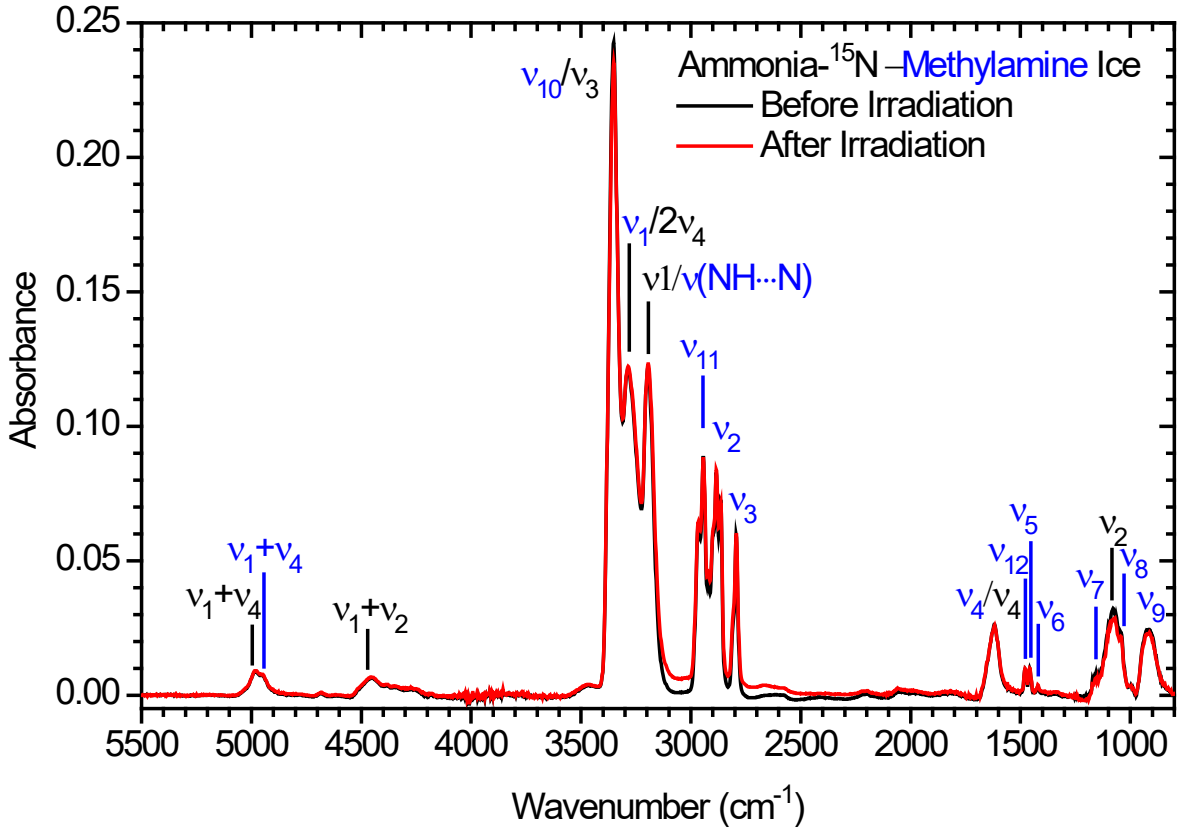



**Figure S2.** Infrared spectra of ammonia-$^{15}$N–methylamine ice before (black) and after (red) irradiation with assignments listed in Table S1.

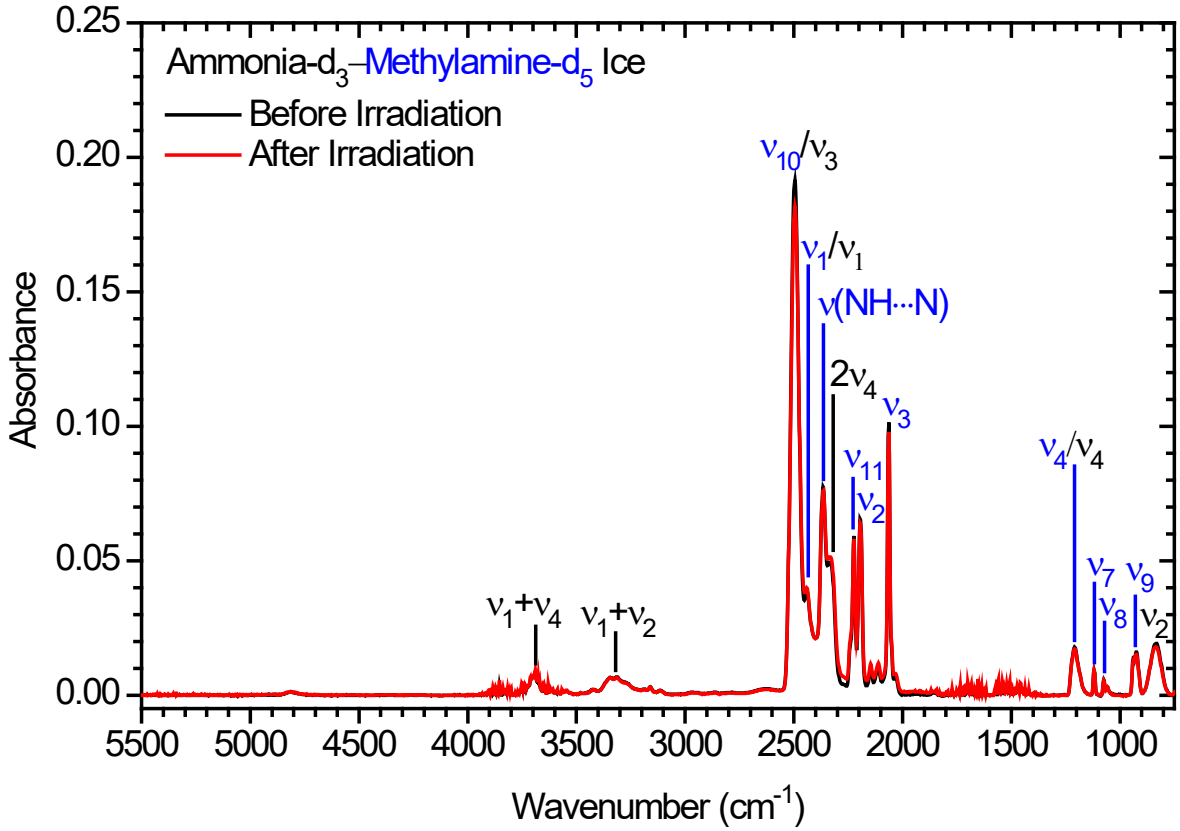



**Figure S3.** Infrared spectra of ammonia-$d_3$–methylamine-$d_5$ ice before (black) and after (red) irradiation with assignments listed in Table S1.

**Table S2**. Infrared Absorption Features Observed in Studied Ices

| Ammonia–Methylamine | Ammonia-$^{15}$N–Methylamine | Ammonia-$d_3$–Methylamine-$d_5$ | Assignment(36, 50) |
|---|---|---|---|
| Wavenumber ($cm^{-1}$) | Wavenumber ($cm^{-1}$) | Wavenumber ($cm^{-1}$) | |
| **Infrared absorptions observed before irradiation** | | | |
| 4992 | 4982 | 3696 | $\nu_1+\nu_4$ (ammonia) |
| 4947 | 4949 | – | $\nu_1+\nu_4$ (methylamine) |
| 4462 | 4454 | 3317 | $\nu_1+\nu_2$ (ammonia) |
| 3356 | 3352 | 2495 | $\nu_3$ (ammonia) |
| 3356 | 3352 | 2495 | $\nu_{10}$ (methylamine) |
| 3284 | 3285 | 2331 | $2\nu_4$ (ammonia) |
| 3284 | 3285 | 2440 | $\nu_1$ (methylamine) |
| 3195 | 3195 | 2440 | $\nu_1$ (ammonia) |
| 3195 | 3195 | 2365 | $\nu$(NH) methylamine H-bonding |
| 2943 | 2942 | 2223 | $\nu_{11}$ (methylamine) |
| 2885 | 2885 | 2194 | $\nu_2$ (methylamine) |
| 2794 | 2793 | 2064 | $\nu_3$ (methylamine) |
| 1619 | 1619 | 1193 | $\nu_4$ (ammonia) |
| 1619 | 1619 | 1208 | $\nu_4$ (methylamine) |
| 1478 | 1479 | - | $\nu_{12}$ (methylamine) |
| 1457 | 1458 | - | $\nu_5$ (methylamine) |
| 1420 | 1420 | - | $\nu_6$ (methylamine) |
| 1155 | 1160 | 1119 | $\nu_7$ (methylamine) |
| 1082 | 1078 | 834 | $\nu_2$ (ammonia) |
| 1042 | 1043 | 1074 | $\nu_8$ (methylamine) |
| 919 | 918 | 924 | $\nu_9$ (methylamine) |
| **Infrared absorptions observed after irradiation** | | | |
| 3200 – 3000 (H) | 3200 – 3000 (H) | 2400 – 2250 (D) | NH/ND stretching(58) |
| 3000 – 2400 (H) | 3000 – 2400 (H) | 2250 – 2000 (D) | CH/CD stretching(58) |

**Table S3**. Experimental Parameters of the Ices: Composition, Thickness, Irradiation Dose, and Photon Energy.

| | Composition | Ratio | Thickness (nm) | Current (nA) | Time (s) | Dose, ammonia (eV molecule$^{-1}$) | Dose, methylamine (eV molecule$^{-1}$) | Photon energy (eV) |
|---|---|---|---|---|---|---|---|---|
| 1 | $NH_3$:$CH_3NH_2$ | 1.1 ± 0.4 : 1 | 720 ± 30 | 0 | 0 | 0 | 0 | 9.20 |
| 2 | $NH_3$:$CH_3NH_2$ | 1.0 ± 0.4 : 1 | 720 ± 30 | 20.3 ± 0.5 | 600 ± 10 | 0.20 ± 0.02 | 0.38 ± 0.04 | 9.20 |
| 3 | $NH_3$:$CH_3NH_2$ | 1.0 ± 0.5 : 1 | 720 ± 30 | 22.3 ± 0.5 | 600 ± 10 | 0.22 ± 0.02 | 0.41 ± 0.04 | 8.00 |
| 4 | $^{15}NH_3$:$CH_3NH_2$ | 1.5 ± 0.5 : 1 | 720 ± 30 | 20.5 ± 0.5 | 600 ± 10 | 0.21 ± 0.02 | 0.38 ± 0.04 | 9.20 |
| 5 | $ND_3$:$CD_3ND_2$ | 1.3 ± 0.4 : 1 | 720 ± 30 | 19.9 ± 0.5 | 600 ± 10 | 0.24 ± 0.02 | 0.45 ± 0.04 | 9.20 |

**Table S4.** Parameters Used in Irradiation Dose Calculation and Resulting Doses

| | | | |
|---|---|---|---|
| Irradiated area | $1.6 \pm 0.1$ cm$^2$ | | |
| Initial kinetic energy of e$^-$ | 5.000 keV | | |
| Irradiation current | 20 nA | | |
| Total number of e$^-$ | $(7.5 \pm 0.04) \times 10^{13}$ | | |
| Total molecules irradiated | $9.93 \times 10^{17}$ | | |
| | ammonia–methylamine | ammonia-$^{15}$N–methylamine | ammonia-$d_3$–methylamine-$d_5$ |
| Approximate density of mixed ice | 0.706 g cm$^{-1}$ | 0.726 g cm$^{-1}$ | 0.850 g cm$^{-1}$ |
| Average Penetration depth | 348 ± 10 nm | 338 ± 10 nm | 298 ± 10 nm |
| Fraction of backscattered e$^-$ | 0.310 | 0.311 | 0.310 |
| Average energy of backscattered e$^-$ | 0.977 keV | 0.981 keV | 0.981 keV |
| Fraction of Transmitted e$^-$ | 0.004 | 0.002 | 0.000 |
| Average energy of transmitted e$^-$ | 0.003 keV | 0.002 keV | 0.000 keV |
| Dose per molecule of ammonia | 0.20 ± 0.02 | 0.21 ± 0.02 | 0.24 ± 0.02 |
| Dose per molecule of methylamine | 0.37 ± 0.04 | 0.37 ± 0.04 | 0.45 ± 0.04 |

**Table S5.** Four-wave mixing schemes employed to generate vacuum ultraviolet (VUV) photons for photoionization in experiments 1 – 6 as labeled in Table S2. All experiments use two dye (Sirah Lasertechnik, Cobra-Stretch) lasers pumped by a neodymium yttrium-aluminum garnet (Nd:YAG, Quanta Ray PRO 270-30 or 250-30) laser harmonic (355 or 532 nm) appropriate for the dye in use.

| Experiment(s) | Medium | $\omega_{VUV} =$ | $\lambda_1$ (nm) | $\omega_1$ Dye | $\lambda_2$ (nm) | $\omega_2$ Dye | Energy (eV) |
|---|---|---|---|---|---|---|---|
| 1, 2, 4 – 6 | Xenon | $2\omega_1 - \omega_2$ | 222.566 | Coumarin 450 | 638.667 | DCM | 9.20 |
| 3 | Xenon | $2\omega_1 - \omega_2$ | 249.628 | Coumarin 503 | 641.228 | DCM | 8.10 |

**Table S6.** CCSD(T)/aug-cc-pVTZ zero-point corrected absolute energies, optimized geometries, and harmonic frequencies for all conformers of both neutral and cationic **1**, **2**.

**1a** $C_{2v}$ *tt*-$CH_2(NH_2)_2$

CCSD(T)/aug-cc-pVTZ Energy = -150.98562899

| | | | |
|---|---|---|---|
| C | 0.0000000000 | -0.0000000000 | 0.5410399634 |
| H | 0.0000000000 | 0.8802805102 | 1.1869990785 |
| H | 0.0000000000 | -0.8802805102 | 1.1869990785 |
| N | 1.2611427532 | 0.0000000000 | -0.2015544911 |
| N | -1.2611427532 | 0.0000000000 | -0.2015544911 |
| H | 1.3149433143 | -0.8148859880 | -0.8048723508 |
| H | 1.3149433143 | 0.8148859880 | -0.8048723508 |
| H | -1.3149433143 | -0.8148859880 | -0.8048723508 |
| H | -1.3149433143 | 0.8148859880 | -0.8048723508 |

| | | | | | |
|---|---|---|---|---|---|
| Wavenumbers [$cm^{-1}$] | 253.07 | 370.19 | 452.04 | 804.59 | 846.84 |
| Wavenumbers [$cm^{-1}$] | 854.94 | 1072.21 | 1087.30 | 1099.65 | 1373.65 |
| Wavenumbers [$cm^{-1}$] | 1388.42 | 1401.34 | 1501.30 | 1653.27 | 1663.92 |
| Wavenumbers [$cm^{-1}$] | 3059.96 | 3106.63 | 3480.94 | 3482.12 | 3566.30 |
| Wavenumbers [$cm^{-1}$] | 3568.59 | | | | |

**1b** $C_1$ *tg*-$CH_2(NH_2)_2$

CCSD(T)/aug-cc-pVTZ Energy = -150.98482771

| | | | |
|---|---|---|---|
| C | -0.5545424891 | 0.0358496387 | 0.0044976614 |
| N | 0.1978825416 | -0.0263594216 | 1.2463891243 |
| H | 0.7673993110 | 0.8075398207 | 1.3502223292 |
| H | 0.8420910645 | -0.8104072378 | 1.1999232281 |
| N | 0.2970508811 | -0.0583011433 | -1.1932383113 |
| H | 0.7971402953 | 0.8147759791 | -1.3349222808 |
| H | -0.2763462302 | -0.1989306341 | -2.0202221572 |
| H | -1.2407112662 | -0.8135819810 | -0.0247177394 |
| H | -1.1592064228 | 0.9498799276 | 0.0375177751 |

| | | | | | |
|---|---|---|---|---|---|
| Wavenumbers [$cm^{-1}$] | 230.90 | 308.42 | 461.48 | 846.55 | 871.93 |
| Wavenumbers [$cm^{-1}$] | 917.53 | 997.50 | 1091.57 | 1183.54 | 1316.11 |
| Wavenumbers [$cm^{-1}$] | 1394.15 | 1426.54 | 1522.73 | 1648.76 | 1666.41 |
| Wavenumbers [$cm^{-1}$] | 3012.85 | 3079.25 | 3471.92 | 3484.73 | 3559.54 |
| Wavenumbers [$cm^{-1}$] | 3566.24 | | | | |

**1c** $C_2$ *gg*-$CH_2(NH_2)_2$

CCSD(T)/aug-cc-pVTZ Energy = -150.98423439

| | | | |
|---|---|---|---|
| C | 0.0000000000 | 0.0000000000 | 0.5749287297 |
| H | -0.0449406520 | 0.8857656171 | 1.2228080814 |
| H | 0.0449406520 | -0.8857656171 | 1.2228080814 |
| N | 1.1734644397 | -0.0454222752 | -0.2930057115 |

| | | | |
|---|---|---|---|
| N | -1.1734644397 | 0.0454222752 | -0.2930057115 |
| H | 2.0217602451 | -0.1022950170 | 0.2603609164 |
| H | 1.2176508780 | 0.8108390026 | -0.8369910373 |
| H | -2.0217602451 | 0.1022950170 | 0.2603609164 |
| H | -1.2176508780 | -0.8108390026 | -0.8369910373 |

| | | | | | |
|---|---|---|---|---|---|
| Wavenumbers [$cm^{-1}$] | 265.16 | 291.47 | 483.27 | 842.62 | 876.86 |
| Wavenumbers [$cm^{-1}$] | 971.35 | 988.82 | 1135.97 | 1219.80 | 1251.70 |
| Wavenumbers [$cm^{-1}$] | 1367.14 | 1454.86 | 1546.94 | 1639.43 | 1641.16 |
| Wavenumbers [$cm^{-1}$] | 2979.51 | 3004.73 | 3487.87 | 3489.66 | 3580.24 |
| Wavenumbers [$cm^{-1}$] | 3580.60 | | | | |

**1a**$^{+}$/**1c**$^{+}$ $C_{2v}$/$C_2$ $CH_2(NH_2)_2^{+}$

CCSD(T)/aug-cc-pVTZ Energy = -150.66881117

| | | | |
|---|---|---|---|
| C | 0.0000000000 | 0.0000000000 | 0.6585439184 |
| H | -0.0000820588 | 0.8980801652 | 1.2694146512 |
| H | 0.0000820588 | -0.8980801652 | 1.2694146512 |
| N | 1.1129825095 | 0.0000079574 | -0.2658893061 |
| N | -1.1129825095 | -0.0000079574 | -0.2658893061 |
| H | 1.3518689827 | -0.8598121679 | -0.7490977806 |
| H | 1.3518102707 | 0.8598129845 | -0.7491536652 |
| H | -1.3518102707 | -0.8598129845 | -0.7491536652 |
| H | -1.3518689827 | 0.8598121679 | -0.7490977806 |

| | | | | | |
|---|---|---|---|---|---|
| Wavenumbers [$cm^{-1}$] | 381.16 | 467.86 | 468.63 | 520.30 | 629.24 |
| Wavenumbers [$cm^{-1}$] | 863.93 | 947.26 | 963.90 | 1125.32 | 1298.45 |
| Wavenumbers [$cm^{-1}$] | 1353.64 | 1363.01 | 1508.31 | 1635.72 | 1647.10 |
| Wavenumbers [$cm^{-1}$] | 3129.60 | 3205.48 | 3493.85 | 3509.06 | 3625.43 |
| Wavenumbers [$cm^{-1}$] | 3628.73 | | | | |

**1b**$^{+}$ $C_1$ $CH_2(NH_2)_2^{+}$

CCSD(T)/aug-cc-pVTZ Energy = -150.6683196

| | | | |
|---|---|---|---|
| C | -0.6612465949 | -0.0000899202 | 0.0007478179 |
| N | 0.2674087435 | 0.0000131671 | 1.1084310225 |
| H | 0.7488580783 | 0.8602556764 | 1.3485385398 |
| H | 0.7495119211 | -0.8598661612 | 1.3485343738 |
| N | 0.2665176152 | -0.0000235704 | -1.1097458944 |
| H | 0.7518321705 | 0.8598768592 | -1.3441865944 |
| H | 0.7531283726 | -0.8592181639 | -1.3440789901 |
| H | -1.2718889920 | -0.8981794368 | 0.0003415317 |
| H | -1.2714076966 | 0.8983473188 | 0.0002117904 |

| | | | | | |
|---|---|---|---|---|---|
| Wavenumbers [$cm^{-1}$] | 367.00 | 473.43 | 492.09 | 522.71 | 631.72 |
| Wavenumbers [$cm^{-1}$] | 861.91 | 938.00 | 961.11 | 1129.09 | 1296.33 |
| Wavenumbers [$cm^{-1}$] | 1348.58 | 1358.97 | 1510.47 | 1626.59 | 1644.69 |
| Wavenumbers [$cm^{-1}$] | 3131.13 | 3207.10 | 3489.28 | 3509.71 | 3626.21 |

Wavenumbers [$cm^{-1}$] 3629.26

**2a** $CH_3NHNH_2$

CCSD(T)/aug-cc-pVTZ Energy = -150.94643872

| | | | |
|---|---|---|---|
| C | -0.0016931433 | 0.2660403359 | -1.2115591609 |
| N | 0.0732305530 | -0.5606219746 | -0.0094465902 |
| N | -0.0389039623 | 0.2035924672 | 1.2012339714 |
| H | -0.6206999772 | 1.0282261749 | 1.0420312863 |
| H | 0.8917220295 | 0.5413140388 | 1.4234662283 |
| H | -0.7046032227 | -1.2099840420 | 0.0031201773 |
| H | -0.0408604333 | -0.3829523657 | -2.0896783548 |
| H | -0.8798670426 | 0.9313170266 | -1.2238860080 |
| H | 0.8974700306 | 0.8832519830 | -1.2791591605 |

| | | | | | |
|---|---|---|---|---|---|
| Wavenumbers [$cm^{-1}$] | 272.07 | 325.25 | 426.60 | 810.61 | 938.98 |
| Wavenumbers [$cm^{-1}$] | 1006.52 | 1140.13 | 1142.77 | 1231.99 | 1322.15 |
| Wavenumbers [$cm^{-1}$] | 1448.11 | 1494.40 | 1497.00 | 1522.18 | 1676.67 |
| Wavenumbers [$cm^{-1}$] | 2957.65 | 3064.05 | 3108.52 | 3399.89 | 3519.87 |
| Wavenumbers [$cm^{-1}$] | 3540.39 | | | | |

**2b** $CH_3NHNH_2$

CCSD(T)/aug-cc-pVTZ Energy = -150.94518069

| | | | |
|---|---|---|---|
| C | 0.0031764690 | 0.2600365250 | -1.2149319206 |
| N | 0.0536900933 | -0.5640192097 | -0.0091153967 |
| N | 0.0343105327 | 0.3005473082 | 1.1435364123 |
| H | 0.4078323275 | -0.2300265721 | 1.9221168098 |
| H | -0.9202909182 | 0.5669768483 | 1.3821768210 |
| H | -0.7606640253 | -1.1736336481 | 0.0020126813 |
| H | -0.0387695532 | -0.3995402574 | -2.0849578733 |
| H | -0.8612784984 | 0.9394269005 | -1.2430500101 |
| H | 0.9124300109 | 0.8594028170 | -1.2650293260 |

| | | | | | |
|---|---|---|---|---|---|
| Wavenumbers [$cm^{-1}$] | 257.57 | 262.66 | 441.18 | 812.21 | 957.13 |
| Wavenumbers [$cm^{-1}$] | 976.01 | 1138.06 | 1164.63 | 1219.26 | 1322.43 |
| Wavenumbers [$cm^{-1}$] | 1447.71 | 1485.36 | 1493.80 | 1523.83 | 1663.69 |
| Wavenumbers [$cm^{-1}$] | 2976.29 | 3077.15 | 3126.52 | 3423.65 | 3455.10 |
| Wavenumbers [$cm^{-1}$] | 3559.95 | | | | |

**2a**$^+$/**2b**$^+$ $CH_3NHNH_2^+$

CCSD(T)/aug-cc-pVTZ Energy = -150.6659698

| | | | |
|---|---|---|---|
| C | 0.0151887453 | 0.2086485714 | -1.2620241608 |
| N | -0.0513085034 | -0.4608143778 | 0.0361288872 |
| N | 0.0408611574 | 0.2385248392 | 1.1516876029 |
| H | -0.0488061694 | -0.2583003476 | 2.0296562820 |
| H | -0.2265006670 | 1.2147506464 | 1.1051551500 |

| | | | |
|---|---|---|---|
| H | 0.1686440024 | -1.4477117867 | 0.1221484094 |
| H | -0.3495628820 | -0.4891942641 | -2.0124075970 |
| H | -0.6269560709 | 1.0895209312 | -1.2340056455 |
| H | 1.0473669781 | 0.4936144353 | -1.4781111728 |

| | | | | | |
|---|---|---|---|---|---|
| Wavenumbers [cm-1] | 142.71 | 356.26 | 434.52 | 513.90 | 615.71 |
| Wavenumbers [cm-1] | 938.68 | 1098.51 | 1126.27 | 1291.96 | 1412.89 |
| Wavenumbers [cm-1] | 1465.42 | 1487.00 | 1499.80 | 1566.03 | 1669.54 |
| Wavenumbers [cm-1] | 3049.15 | 3138.75 | 3176.29 | 3514.44 | 3560.17 |
| Wavenumbers [cm-1] | 3652.44 | | | | |

**Supporting References**


1. M. Bouilloud *et al.*, Bibliographic review and new measurements of the infrared band strengths of pure molecules at 25 K: $H_2O$, $CO_2$, CO, $CH_4$, $NH_3$, $CH_3OH$, HCOOH and $H_2CO$. *Mon. Not. R. Astron. Soc.* **451**, 2145-2160 (2015).
2. C. Zhu *et al.*, A vacuum ultraviolet photoionization study on the formation of methanimine ($CH_2NH$) and ethylenediamine ($NH_2CH_2CH_2NH_2$) in low temperature interstellar model ices exposed to ionizing radiation. *Phys. Chem. Chem. Phys.* **21**, 1952-1962 (2019).
3. G. Socrates, *Infrared and raman characteristic group frequencies: Tables and charts* (Wiley, Chichester, 2004).