

**A theoretical investigation of the low energy conformers  
of the isomers glycine and methylcarbamic acid  
and their role in the interstellar medium**

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**Supplementary Material**

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Table S1. Total electronic energies and zero point vibrational energies (in Hartrees) of the minimum energy structures of glycine and methylcarbamic acid conformers.

| Level                         | MCA-4       | MCA-3       | MCA-2       | MCA-1       | Gly-1       | Gly-2       | Gly-3       | Gly-4       | Gly-5       | Gly-6       | Gly-7       | Gly-8       |
|-------------------------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Total Electronic Energy       |             |             |             |             |             |             |             |             |             |             |             |             |
| CCSD(T)/aug-cc-pVTZ //        |             |             |             |             |             |             |             |             |             |             |             |             |
| MP2/aug-cc-pVTZ               | -284.042799 | -284.044877 | -284.053653 | -284.055689 | -284.042921 | -284.041961 | -284.040954 | -284.040218 | -284.038834 | -284.035331 | -284.033505 | -284.033290 |
| CCSD(T)/6-311++G(dp)//        |             |             |             |             |             |             |             |             |             |             |             |             |
| MP2/6-311++G(dp)              | -283.855713 | -283.858224 | -283.867668 | -283.869586 | -283.857861 | -283.856591 | -283.855808 | -283.855578 | -283.854429 | -283.849020 | -283.846575 | -283.846792 |
| MP2/aug-cc-pVTZ               | -283.982173 | -283.984153 | -283.993420 | -283.995385 | -283.981510 | -283.980994 | -283.979689 | -283.978903 | -283.977505 | -283.973745 | -283.972324 | -283.971843 |
| MP2/aug-cc-pVDZ               | -283.735035 | -283.737357 | -283.746536 | -283.748450 | -283.736270 | -283.735417 | -283.734281 | -283.733733 | -283.732398 | -283.728521 | -283.726617 | -283.726307 |
| MP2/6-311++G(dp)              | -283.799663 | -283.802147 | -283.812188 | -283.814095 | -283.801228 | -283.800376 | -283.799226 | -283.798969 | -283.797761 | -283.792123 | -283.790087 | -283.789938 |
| B3LYP/aug-cc-pVTZ             | -284.409717 | -284.411231 | -284.420680 | -284.422739 | -284.406875 | -284.406012 | -284.404872 | -284.404303 | -284.402598 | -284.399143 | -284.398069 | -284.397196 |
| B3LYP/aug-cc-pVDZ             | -284.334871 | -284.336279 | -284.346116 | -284.347987 | -284.333818 | -284.332820 | -284.331767 | -284.331138 | -284.329443 | -284.325885 | -284.324480 | -284.323770 |
| B3LYP/6-311++G(dp)            | -284.385481 | -284.387202 | -284.397947 | -284.399935 | -284.384364 | -284.383665 | -284.382039 | -284.381899 | -284.380104 | -284.375361 | -284.374323 | -284.373036 |
| B3LYP/6-311+G(dp)             | -284.385362 | -284.387085 | -284.397835 | -284.399807 | -284.384228 | -284.383532 | -284.381897 | -284.381789 | -284.379965 | -284.375258 | -284.374206 | -284.372888 |
| B3LYP/6-311G(dp)              | -284.374933 | -284.376377 | -284.387430 | -284.389521 | -284.372986 | -284.372123 | -284.369840 | -284.370376 | -284.367547 | -284.363804 | -284.362461 | -284.360447 |
| B3LYP/6-31++G(dp)             | -284.309636 | -284.311158 | -284.322350 | -284.324206 | -284.308415 | -284.307755 | -284.305907 | -284.306006 | -284.304074 | -284.299211 | -284.298058 | -284.296642 |
| B3LYP/6-31+G(dp)              | -284.309447 | -284.310916 | -284.322203 | -284.324048 | -284.308241 | -284.307533 | -284.305715 | -284.305866 | -284.303838 | -284.299019 | -284.297854 | -284.296399 |
| B3LYP/6-31+G(d)               | -284.296521 | -284.297881 | -284.309379 | -284.311116 | -284.293498 | -284.292786 | -284.290833 | -284.291188 | -284.289080 | -284.284204 | -284.282436 | -284.281337 |
| B3LYP/6-31G(dp)               | -284.291843 | -284.293422 | -284.304323 | -284.306380 | -284.289598 | -284.288415 | -284.286258 | -284.286954 | -284.284020 | -284.280491 | -284.278722 | -284.277045 |
| B3LYP/6-31G(d)                | -284.278928 | -284.280414 | -284.291434 | -284.293434 | -284.274855 | -284.273760 | -284.271455 | -284.272221 | -284.269284 | -284.265670 | -284.263660 | -284.262099 |
| B3LYP/6-31G                   | -284.183931 | -284.185111 | -284.198937 | -284.201278 | -284.179427 | -284.179770 | -284.176168 | -284.176958 | -284.174050 | -284.168445 | -284.167877 | -284.168519 |
| Zero Point Vibrational Energy |             |             |             |             |             |             |             |             |             |             |             |             |
| CCSD(T)/aug-cc-pVTZ //        |             |             |             |             |             |             |             |             |             |             |             |             |
| MP2/aug-cc-pVTZ               | 0.079639    | 0.079656    | 0.080113    | 0.080001    | 0.080210    | 0.080844    | 0.080235    | 0.080220    | 0.080260    | 0.079978    | 0.079955    | 0.079827    |
| CCSD(T)/6-311++G(dp)//        |             |             |             |             |             |             |             |             |             |             |             |             |
| MP2/6-311++G(dp)              | 0.080313    | 0.080083    | 0.080773    | 0.080521    | 0.080592    | 0.081233    | 0.080647    | 0.080887    | 0.080685    | 0.080086    | 0.079998    | 0.080183    |
| MP2/aug-cc-pVTZ               | 0.079639    | 0.079656    | 0.080113    | 0.080001    | 0.080210    | 0.080844    | 0.080235    | 0.080220    | 0.080260    | 0.079978    | 0.079955    | 0.079827    |
| MP2/aug-cc-pVDZ               | 0.079244    | 0.079252    | 0.079854    | 0.079686    | 0.079798    | 0.080345    | 0.079764    | 0.079829    | 0.079837    | 0.079529    | 0.079432    | 0.079280    |
| MP2/6-311++G(dp)              | 0.080313    | 0.080083    | 0.080773    | 0.080521    | 0.080592    | 0.081233    | 0.080647    | 0.080887    | 0.080685    | 0.080086    | 0.079998    | 0.080183    |
| B3LYP/aug-cc-pVTZ             | 0.078578    | 0.078604    | 0.079462    | 0.079281    | 0.079464    | 0.079754    | 0.079332    | 0.079595    | 0.079348    | 0.079018    | 0.078903    | 0.078832    |
| B3LYP/aug-cc-pVDZ             | 0.078858    | 0.078304    | 0.079767    | 0.079265    | 0.079652    | 0.079782    | 0.079388    | 0.079593    | 0.079011    | 0.078992    | 0.078622    | 0.078610    |
| B3LYP/6-311++G(dp)            | 0.078735    | 0.078796    | 0.079511    | 0.079471    | 0.079590    | 0.079946    | 0.079351    | 0.079511    | 0.079462    | 0.078957    | 0.078963    | 0.078863    |
| B3LYP/6-311+G(dp)             | 0.078679    | 0.078633    | 0.079504    | 0.079468    | 0.079579    | 0.079931    | 0.079357    | 0.079576    | 0.079465    | 0.078972    | 0.078971    | 0.078869    |
| B3LYP/6-311G(dp)              | 0.079218    | 0.078923    | 0.080068    | 0.079415    | 0.080153    | 0.080255    | 0.079854    | 0.080096    | 0.079794    | 0.079429    | 0.078961    | 0.078849    |
| B3LYP/6-31++G(dp)             | 0.078828    | 0.079014    | 0.079742    | 0.079694    | 0.079773    | 0.080152    | 0.079555    | 0.079746    | 0.079640    | 0.079215    | 0.079145    | 0.079119    |
| B3LYP/6-31+G(dp)              | 0.078727    | 0.079005    | 0.079743    | 0.079701    | 0.079789    | 0.080137    | 0.079575    | 0.079774    | 0.079641    | 0.079243    | 0.079172    | 0.079131    |
| B3LYP/6-31+G(d)               | 0.078880    | 0.079092    | 0.079819    | 0.079577    | 0.079889    | 0.080289    | 0.079706    | 0.079909    | 0.079736    | 0.079386    | 0.079092    | 0.079247    |
| B3LYP/6-31G(dp)               | 0.079208    | 0.079386    | 0.079777    | 0.079852    | 0.080044    | 0.080623    | 0.079911    | 0.080044    | 0.079933    | 0.079622    | 0.079498    | 0.079097    |
| B3LYP/6-31G(d)                | 0.079376    | 0.079534    | 0.079904    | 0.079915    | 0.080104    | 0.080750    | 0.079987    | 0.080111    | 0.080005    | 0.079706    | 0.079619    | 0.079379    |
| B3LYP/6-31G                   | 0.078775    | 0.078557    | 0.079978    | 0.080048    | 0.079505    | 0.079959    | 0.078635    | 0.079425    | 0.079012    | 0.078654    | 0.078986    | 0.078870    |

Table S2. The relative energies (in kJ mol<sup>-1</sup>) of the glycine conformers at the different levels of theory.

| Level                   | Gly-1 | Gly-2 | Gly-3 | Gly-4 | Gly-5 | Gly-6 | Gly-7 | Gly-8 |
|-------------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| CCSD(T)/aug-cc-pVTZ //  |       |       |       |       |       |       |       |       |
| MP2/aug-cc-pVTZ         | 0.0   | 4.2   | 5.2   | 7.1   | 10.9  | 19.3  | 24.1  | 24.3  |
| CCSD(T)/6-311++G(d,p)// |       |       |       |       |       |       |       |       |
| MP2/6-311++G(d,p)       | 0.0   | 5.0   | 5.5   | 6.8   | 9.3   | 21.9  | 28.0  | 28.0  |
| MP2/aug-cc-pVTZ         | 0.0   | 3.0   | 4.8   | 6.9   | 10.6  | 19.8  | 23.4  | 24.4  |
| MP2/aug-cc-pVDZ         | 0.0   | 3.7   | 5.1   | 6.7   | 10.3  | 19.6  | 24.4  | 24.8  |
| MP2/6-311++G(d,p)       | 0.0   | 3.9   | 5.4   | 6.7   | 9.3   | 22.6  | 27.6  | 28.6  |
| B3LYP/aug-cc-pVTZ       | 0.0   | 3.0   | 4.9   | 7.1   | 10.9  | 19.1  | 21.6  | 23.8  |
| B3LYP/aug-cc-pVDZ       | 0.0   | 3.0   | 4.7   | 6.9   | 9.8   | 19.1  | 21.8  | 23.4  |
| B3LYP/6-311++G(d,p)     | 0.0   | 2.8   | 5.5   | 6.3   | 10.8  | 22.0  | 24.7  | 27.8  |
| B3LYP/6-311+G(d,p)      | 0.0   | 2.8   | 5.5   | 6.4   | 10.9  | 22.0  | 24.7  | 27.9  |
| B3LYP/6-311G(d,p)       | 0.0   | 2.5   | 7.5   | 6.7   | 13.3  | 22.2  | 24.5  | 29.5  |
| B3LYP/6-31++G(d,p)      | 0.0   | 2.7   | 6.0   | 6.3   | 11.0  | 22.7  | 25.5  | 29.2  |
| B3LYP/6-31+G(d,p)       | 0.0   | 2.8   | 6.1   | 6.2   | 11.2  | 22.8  | 25.6  | 29.4  |
| B3LYP/6-31+G(d)         | 0.0   | 2.9   | 6.5   | 6.1   | 11.2  | 23.1  | 26.9  | 30.2  |
| B3LYP/6-31G(d,p)        | 0.0   | 4.6   | 8.4   | 6.9   | 14.4  | 22.8  | 27.1  | 30.5  |
| B3LYP/6-31G(d)          | 0.0   | 4.6   | 8.6   | 6.9   | 14.4  | 23.1  | 28.1  | 31.6  |
| B3LYP/6-31G             | 0.0   | 0.3   | 6.3   | 6.3   | 12.8  | 26.6  | 29.0  | 27.0  |

Table S3. Geometrical parameters (bond lengths in Å, bond angles and dihedrals in °) for the glycine conformers.

| Level               | Conformer | NH <sub>2</sub> -CH <sub>2</sub> |       | CH <sub>2</sub> -CO <sub>2</sub> H |       | CO <sub>2</sub> H |       | CO <sub>2</sub> H |       | CO <sub>2</sub> H |         | NH <sub>2</sub> -CH <sub>2</sub> -CO <sub>2</sub> H |         | NH <sub>2</sub> -CH <sub>2</sub> -CO <sub>2</sub> H |         | CO <sub>2</sub> H |         |
|---------------------|-----------|----------------------------------|-------|------------------------------------|-------|-------------------|-------|-------------------|-------|-------------------|---------|-----------------------------------------------------|---------|-----------------------------------------------------|---------|-------------------|---------|
|                     |           | N-C                              | C-C   | C-O                                | C=O   | O-H               | O=C-O | O=C-O             | O=C-O | N-C-C             | N-C-C-O | N-C-C                                               | N-C-C-O | N-C-C=O                                             | N-C-C=O | O=C-O-H           | O=C-O-H |
| MP2/aug-cc-pVTZ     | Gly-8     | 1.450                            | 1.515 | 1.356                              | 1.204 | 0.966             | 120.5 | 120.5             | 120.5 | 110.0             | 165.3   | 110.0                                               | 165.3   | 16.7                                                | 177.8   | 177.8             | 177.8   |
|                     | Gly-7     | 1.446                            | 1.529 | 1.353                              | 1.205 | 0.969             | 121.5 | 121.5             | 121.5 | 119.1             | 0.0     | 119.1                                               | 0.0     | 180.0                                               | 180.0   | 180.0             | 180.0   |
|                     | Gly-6     | 1.445                            | 1.523 | 1.361                              | 1.204 | 0.966             | 120.4 | 120.4             | 120.4 | 115.4             | 180.0   | 115.4                                               | 180.0   | 0.0                                                 | 180.0   | 180.0             | 180.0   |
|                     | Gly-5     | 1.458                            | 1.507 | 1.355                              | 1.209 | 0.970             | 123.0 | 123.0             | 123.0 | 111.7             | 33.4    | 111.7                                               | 33.4    | 144.4                                               | 144.4   | 1.0               | 1.0     |
|                     | Gly-4     | 1.448                            | 1.518 | 1.355                              | 1.210 | 0.970             | 122.9 | 122.9             | 122.9 | 118.9             | 1.9     | 118.9                                               | 1.9     | 178.2                                               | 178.2   | 0.0               | 0.0     |
|                     | Gly-3     | 1.452                            | 1.504 | 1.352                              | 1.210 | 0.970             | 123.4 | 123.4             | 123.4 | 109.8             | 162.9   | 109.8                                               | 162.9   | 19.0                                                | 19.0    | 1.1               | 1.1     |
|                     | Gly-2     | 1.464                            | 1.527 | 1.341                              | 1.207 | 0.984             | 123.4 | 123.4             | 123.4 | 111.1             | 10.6    | 111.1                                               | 10.6    | 170.5                                               | 170.5   | 179.2             | 179.2   |
|                     | Gly-1     | 1.446                            | 1.514 | 1.355                              | 1.210 | 0.970             | 123.2 | 123.2             | 123.2 | 115.4             | 180.0   | 115.4                                               | 180.0   | 0.0                                                 | 0.0     | 0.0               | 0.0     |
| MP2/aug-cc-pVDZ     | Gly-1     | 1.456                            | 1.523 | 1.367                              | 1.220 | 0.974             | 123.2 | 123.2             | 123.2 | 115.5             | 180.0   | 115.5                                               | 180.0   | 0.0                                                 | 0.0     | 0.0               | 0.0     |
| MP2/6-311++G(d,p)   | Gly-1     | 1.449                            | 1.520 | 1.357                              | 1.209 | 0.969             | 123.4 | 123.4             | 123.4 | 115.5             | 180.0   | 115.5                                               | 180.0   | 0.0                                                 | 0.0     | 0.0               | 0.0     |
| B3LYP/aug-cc-pVTZ   | Gly-1     | 1.447                            | 1.522 | 1.355                              | 1.203 | 0.969             | 122.9 | 122.9             | 122.9 | 116.0             | 180.0   | 116.0                                               | 180.0   | 0.0                                                 | 0.0     | 0.0               | 0.0     |
| B3LYP/ aug-cc-pVDZ  | Gly-1     | 1.451                            | 1.524 | 1.359                              | 1.211 | 0.971             | 122.8 | 122.8             | 122.8 | 115.9             | 180.0   | 115.9                                               | 180.0   | 0.0                                                 | 0.0     | 0.0               | 0.0     |
| B3LYP/6-311++G(d,p) | Gly-1     | 1.449                            | 1.525 | 1.356                              | 1.204 | 0.970             | 122.9 | 122.9             | 122.9 | 116.0             | 180.0   | 116.0                                               | 180.0   | 0.0                                                 | 0.0     | 0.0               | 0.0     |
| B3LYP/6-311+G(d,p)  | Gly-1     | 1.449                            | 1.525 | 1.356                              | 1.204 | 0.970             | 123.0 | 123.0             | 123.0 | 116.0             | 180.0   | 116.0                                               | 180.0   | 0.0                                                 | 0.0     | 0.0               | 0.0     |
| B3LYP/6-311G(d,p)   | Gly-1     | 1.451                            | 1.524 | 1.355                              | 1.204 | 0.969             | 123.1 | 123.1             | 123.1 | 115.5             | 180.0   | 115.5                                               | 180.0   | 0.0                                                 | 0.0     | 0.0               | 0.0     |
| B3LYP/6-31++G(d,p)  | Gly-1     | 1.449                            | 1.526 | 1.357                              | 1.213 | 0.973             | 122.8 | 122.8             | 122.8 | 115.9             | 180.0   | 115.9                                               | 180.0   | 0.0                                                 | 0.0     | 0.0               | 0.0     |
| B3LYP/6-31+G(d,p)   | Gly-1     | 1.449                            | 1.526 | 1.357                              | 1.213 | 0.973             | 122.8 | 122.8             | 122.8 | 115.9             | 180.0   | 115.9                                               | 180.0   | 0.0                                                 | 0.0     | 0.0               | 0.0     |
| B3LYP/6-31+G(d)     | Gly-1     | 1.450                            | 1.527 | 1.358                              | 1.213 | 0.977             | 122.8 | 122.8             | 122.8 | 115.9             | 180.0   | 115.9                                               | 180.0   | 0.0                                                 | 0.0     | 0.0               | 0.0     |
| B3LYP/6-31G(d,p)    | Gly-1     | 1.451                            | 1.525 | 1.355                              | 1.211 | 0.973             | 123.0 | 123.0             | 123.0 | 115.2             | 180.0   | 115.2                                               | 180.0   | 0.0                                                 | 0.0     | 0.0               | 0.0     |
| B3LYP/6-31G(d)      | Gly-1     | 1.452                            | 1.525 | 1.356                              | 1.211 | 0.976             | 123.0 | 123.0             | 123.0 | 115.2             | 180.0   | 115.2                                               | 180.0   | 0.0                                                 | 0.0     | 0.0               | 0.0     |
| B3LYP/6-31G         | Gly-1     | 1.447                            | 1.523 | 1.381                              | 1.233 | 0.983             | 122.5 | 122.5             | 122.5 | 115.1             | 180.0   | 115.1                                               | 180.0   | 0.0                                                 | 0.0     | 0.0               | 0.0     |

Table S4. Vibrational frequencies (in  $\text{cm}^{-1}$ ) for the glycine conformers. The IR intensities ( $\times 10^{-17} \text{ cm molecule}^{-1}$ ) are given in parentheses.

| Level               | Conformer         | CO <sub>2</sub> H rocking           | CO <sub>2</sub> bending | CO <sub>2</sub> wagging             | C-C stretching                      | C-O stretching                        | C=O stretching                        | NH <sub>2</sub> sym. stretching | NH <sub>2</sub> asym. stretching      | O-H stretching                        |
|---------------------|-------------------|-------------------------------------|-------------------------|-------------------------------------|-------------------------------------|---------------------------------------|---------------------------------------|---------------------------------|---------------------------------------|---------------------------------------|
| MP2/aug-cc-pVTZ     | Gly-8             | 574 (0.16)                          | 649 (0.13)              | 574 (0.16)                          | 859 (0.32)                          | 1160 (0.14)                           | 1838 (3.29)                           | 3521 (0.21)                     | 3634 (0.38)                           | 3816 (1.07)                           |
|                     | Gly-7             | 543 (0.08)                          | 656 (1.17)              | 542 (0.08)                          | 847 (0.71)                          | 1130 (0.22)                           | 1829 (4.16)                           | 3573 (0.21)                     | 3695 (0.38)                           | 3718 (1.61)                           |
|                     | Gly-6             | 569 (0.21)                          | 647 (0.22)              | 569 (0.21)                          | 840 (0.53)                          | 1140 (0.63)                           | 1836 (3.45)                           | 3526 (0.10)                     | 3614 (0.21)                           | 3812 (1.02)                           |
|                     | Gly-5             | 545 (0.45)                          | 594 (1.02)              | 698 (1.21)                          | 839 (0.90)                          | 1146 (2.41)                           | 1813 (4.58)                           | 3514 (0.04)                     | 3613 (0.21)                           | 3780 (1.39)                           |
|                     | Gly-4             | 519 (0.37)                          | 594 (0.78)              | 682 (1.63)                          | 809 (1.42)                          | 1172 (3.64)                           | 1802 (4.26)                           | 3542 (0.08)                     | 3640 (0.19)                           | 3770 (1.35)                           |
|                     | Gly-3             | 526 (0.45)                          | 628 (0.63)              | 664 (1.22)                          | 856 (0.19)                          | 1155 (3.52)                           | 1814 (4.01)                           | 3517 (0.09)                     | 3620 (0.32)                           | 3779 (1.39)                           |
|                     | Gly-2             | 508 (0.03)                          | 652 (0.10)              | 555 (0.10)                          | 830 (0.55)                          | 1239 (0.40)                           | 1831 (5.28)                           | 3559 (0.03)                     | 3653 (0.38)                           | 3459 (4.95)                           |
|                     | Gly-1             | 511 (0.49)                          | 636 (0.10)              | 647 (1.45)                          | 831 (1.45)                          | 1136 (4.18)                           | 1809 (4.17)                           | 3530 (0.07)                     | 3623 (0.18)                           | 3781 (1.29)                           |
|                     | Gly-1             | 515 (0.46)                          | 628 (0.10)              | 645 (1.51)                          | 831 (1.13)                          | 1128 (4.34)                           | 1789 (4.07)                           | 3510 (0.05)                     | 3606 (0.12)                           | 3768 (1.20)                           |
|                     | MP2/6-311++G(d,p) | 494 (0.90)                          | 641 (0.10)              | 624 (1.39)                          | 841 (1.17)                          | 1143 (4.17)                           | 1816 (4.35)                           | 3548 (0.05)                     | 3646 (0.14)                           | 3830 (1.23)                           |
| B3LYP/aug-cc-pVTZ   | Gly-1             | 511 (0.54)                          | 635 (0.10)              | 649 (1.40)                          | 813 (1.58)                          | 1117 (3.58)                           | 1810 (4.93)                           | 3501 (0.04)                     | 3580 (0.10)                           | 3761 (0.97)                           |
| B3LYP/ aug-cc-pVDZ  | Gly-1             | 515 (0.47)                          | 630 (0.09)              | 649 (1.48)                          | 815 (1.49)                          | 1123 (3.55)                           | 1805 (4.87)                           | 3492 (0.04)                     | 3574 (0.08)                           | 3766 (0.96)                           |
| B3LYP/6-311++G(d,p) | Gly-1             | 509 (0.69)                          | 637 (0.12)              | 646 (1.56)                          | 813 (1.70)                          | 1119 (3.75)                           | 1812 (5.25)                           | 3508 (0.03)                     | 3589 (0.10)                           | 3781 (0.99)                           |
| B3LYP/6-311+G(d,p)  | Gly-1             | 509 (0.69)                          | 637 (0.12)              | 646 (1.55)                          | 813 (1.71)                          | 1120 (3.73)                           | 1812 (5.26)                           | 3508 (0.04)                     | 3590 (0.11)                           | 3780 (0.99)                           |
| B3LYP/6-311G(d,p)   | Gly-1             | 511 (0.60)                          | 640 (0.13)              | 663 (1.57)                          | 822 (1.38)                          | 1126 (2.72)                           | 1825 (4.59)                           | 3490 (0.01)                     | 3568 (0.03)                           | 3779 (0.81)                           |
| B3LYP/6-31++G(d,p)  | Gly-1             | 510 (0.62)                          | 632 (0.09)              | 653 (1.69)                          | 814 (1.74)                          | 1128 (3.32)                           | 1818 (5.18)                           | 3513 (0.03)                     | 3602 (0.09)                           | 3778 (0.94)                           |
| B3LYP/6-31+G(d,p)   | Gly-1             | 511 (0.63)                          | 633 (0.09)              | 653 (1.68)                          | 814 (1.80)                          | 1128 (3.29)                           | 1819 (5.21)                           | 3515 (0.03)                     | 3606 (0.11)                           | 3778 (0.95)                           |
| B3LYP/6-31+G(d)     | Gly-1             | 515 (0.61)                          | 633 (0.10)              | 661 (1.79)                          | 821 (1.34)                          | 1132 (3.16)                           | 1820 (5.25)                           | 3491 (0.02)                     | 3580 (0.08)                           | 3704 (0.83)                           |
| B3LYP/6-31G(d,p)    | Gly-1             | 511 (0.55)                          | 637 (0.14)              | 671 (1.66)                          | 828 (1.32)                          | 1140 (1.95)                           | 1846 (4.26)                           | 3493 (0.01)                     | 3576 (0.01)                           | 3775 (0.69)                           |
| B3LYP/6-31G(d)      | Gly-1             | 513 (0.55)                          | 637 (0.15)              | 677 (1.73)                          | 831 (1.11)                          | 1144 (1.87)                           | 1848 (4.29)                           | 3468 (0.003)                    | 3554 (0.01)                           | 3706 (0.63)                           |
| B3LYP/6-31G         | Gly-1             | 517 (0.75)                          | 622 (0.22)              | 660 (2.44)                          | 848 (0.31)                          | 1100 (4.62)                           | 1755 (3.54)                           | 3545 (0.03)                     | 3662 (0.06)                           | 3628 (0.31)                           |
| Experimental        | Gly-1             | 501 <sup>a</sup> , 498 <sup>b</sup> | 637 <sup>b</sup>        | 620 <sup>a</sup> , 618 <sup>b</sup> | 787 <sup>a</sup> , 799 <sup>b</sup> | 1101 <sup>a</sup> , 1100 <sup>b</sup> | 1781 <sup>a</sup> , 1781 <sup>b</sup> | 3200 <sup>b</sup>               | 3414 <sup>a</sup> , 3410 <sup>b</sup> | 3566 <sup>a</sup> , 3560 <sup>b</sup> |

<sup>a</sup> Experimental values are taken from Ref [54].

<sup>b</sup> Experimental values are taken from Ref [53].

Table S5. Moment of inertia ( $\times 10^{-45}$  kg m<sup>2</sup>), rotational constants (in MHz) and dipole moments (in Debye) for the glycine conformers.

| Level           | Conformer | Moment of Inertia |                |                | Rotational Constants <sup>a</sup>            |                                            |                                            |                                |                                |                                | Dipole Moment            |
|-----------------|-----------|-------------------|----------------|----------------|----------------------------------------------|--------------------------------------------|--------------------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------|
|                 |           | I <sub>A</sub>    | I <sub>B</sub> | I <sub>C</sub> | A <sub>e</sub>                               | B <sub>e</sub>                             | C <sub>e</sub>                             | A <sub>0</sub> /A <sub>0</sub> | B <sub>0</sub> /B <sub>0</sub> | C <sub>0</sub> /C <sub>0</sub> |                          |
| MP2/aug-cc-pVTZ | Gly-8     | 0.82              | 2.09           | 2.83           | 10221.6                                      | 4008.3                                     | 2959.7                                     |                                |                                |                                | 4.085                    |
|                 | Gly-7     | 0.85              | 2.11           | 2.85           | 9913.0                                       | 3981.4                                     | 2937.6                                     |                                |                                |                                | 4.069                    |
|                 | Gly-6     | 0.83              | 2.15           | 2.88           | 10139.9                                      | 3900.8                                     | 2909.7                                     |                                |                                |                                | 2.928                    |
|                 | Gly-5     | 0.86              | 2.05           | 2.75           | 9766.6                                       | 4083.4                                     | 3049.5                                     |                                |                                |                                | 2.388                    |
|                 | Gly-4     | 0.84              | 2.10           | 2.84           | 9995.1                                       | 3996.3                                     | 2950.0                                     |                                |                                |                                | 1.794                    |
|                 | Gly-3     | 0.81              | 2.10           | 2.83           | 10349.7                                      | 3994.7                                     | 2967.1                                     |                                |                                |                                | 2.025                    |
|                 | Gly-2     | 0.82              | 2.05           | 2.77           | 10163.4                                      | 4088.0                                     | 3026.0                                     | 1.0033                         | 1.0042                         | 1.0060                         | 5.475                    |
|                 | Gly-1     | 0.81              | 2.15           | 2.88           | 10288.9                                      | 3890.6                                     | 2915.7                                     | 0.9949                         | 1.0038                         | 1.0013                         | 1.181                    |
|                 | Gly-1     | 0.83              | 2.18           | 2.92           | 10122.9                                      | 3838.8                                     | 2874.8                                     | 0.9788                         | 0.9904                         | 0.9872                         | 1.178                    |
|                 | Gly-1     | 0.82              | 2.17           | 2.89           | 10253.7                                      | 3867.1                                     | 2900.7                                     | 0.9915                         | 0.9977                         | 0.9961                         | 1.198                    |
| MP2/aug-cc-pVDZ | Gly-1     | 0.81              | 2.18           | 2.90           | 10350.3                                      | 3843.2                                     | 2894.1                                     | 1.0008                         | 0.9915                         | 0.9939                         | 1.152                    |
|                 | Gly-1     | 0.82              | 2.19           | 2.91           | 10262.0                                      | 3826.4                                     | 2878.6                                     | 0.9923                         | 0.9872                         | 0.9885                         | 1.171                    |
|                 | Gly-1     | 0.81              | 2.19           | 2.91           | 10321.8                                      | 3830.4                                     | 2885.2                                     | 0.9980                         | 0.9882                         | 0.9908                         | 1.168                    |
|                 | Gly-1     | 0.81              | 2.19           | 2.90           | 10323.3                                      | 3832.1                                     | 2886.2                                     | 0.9982                         | 0.9887                         | 0.9911                         | 1.175                    |
|                 | Gly-1     | 0.81              | 2.18           | 2.89           | 10342.1                                      | 3851.0                                     | 2897.9                                     | 1.0000                         | 0.9936                         | 0.9952                         | 1.176                    |
|                 | Gly-1     | 0.82              | 2.19           | 2.91           | 10262.8                                      | 3824.7                                     | 2877.6                                     | 0.9923                         | 0.9868                         | 0.9882                         | 1.211                    |
|                 | Gly-1     | 0.82              | 2.19           | 2.91           | 10263.9                                      | 3824.8                                     | 2877.8                                     | 0.9924                         | 0.9868                         | 0.9883                         | 1.209                    |
|                 | Gly-1     | 0.82              | 2.19           | 2.91           | 10255.7                                      | 3822.5                                     | 2875.9                                     | 0.9917                         | 0.9862                         | 0.9876                         | 1.228                    |
|                 | Gly-1     | 0.82              | 2.17           | 2.89           | 10289.4                                      | 3858.3                                     | 2897.9                                     | 0.9949                         | 0.9954                         | 0.9952                         | 1.242                    |
|                 | Gly-1     | 0.82              | 2.18           | 2.90           | 10282.3                                      | 3853.1                                     | 2894.6                                     | 0.9942                         | 0.9941                         | 0.9940                         | 1.258                    |
| Experimental    | Gly-1     |                   |                |                | 10018.8                                      | 3790.9                                     | 2841.5                                     | 0.9687                         | 0.9780                         | 0.9758                         | 0.902                    |
|                 | Gly-2     |                   |                |                | 10342 <sup>b</sup> ,<br>10341.8 <sup>c</sup> | 3876 <sup>b</sup> ,<br>3876.2 <sup>c</sup> | 2912 <sup>b</sup> ,<br>2912.4 <sup>c</sup> |                                |                                |                                | 1.000±0.150 <sup>b</sup> |
|                 | Gly-2     |                   |                |                | 10130 <sup>b</sup>                           | 4071 <sup>b</sup>                          | 3008 <sup>b</sup>                          |                                |                                |                                | 4.5 <sup>d</sup>         |

<sup>a</sup> A<sub>e</sub>, B<sub>e</sub>, C<sub>e</sub> indicate calculated rotational constants at the equilibrium geometries while A<sub>0</sub>, B<sub>0</sub>, C<sub>0</sub> indicate experimental (effective) ones.

<sup>b</sup> Experimental values are taken from Ref [15].

<sup>c</sup> Experimental values are taken from Ref [19].

<sup>d</sup> Experimental values are taken from Ref [13].

Table S6. Geometrical parameters (bond lengths in Å, bond angles and dihedrals in °) for the methylcarbamic acid conformers.

| Calculation Level   | Conformer | CH <sub>3</sub> -NH | NH-CO <sub>2</sub> H | CO <sub>2</sub> H | CO <sub>2</sub> H | CO <sub>2</sub> H | CO <sub>2</sub> H | CH <sub>3</sub> -NH-CO <sub>2</sub> H | CH <sub>3</sub> -NH-CO <sub>2</sub> H | CH <sub>3</sub> -NH-CO <sub>2</sub> H | CO <sub>2</sub> H |
|---------------------|-----------|---------------------|----------------------|-------------------|-------------------|-------------------|-------------------|---------------------------------------|---------------------------------------|---------------------------------------|-------------------|
| MP2/aug-cc-pVTZ     | MCA-4     | C-N                 | N-C                  | C-O               | C=O               | O-H               | O=C-O             | C-N-C                                 | C-N-C-O                               | C-N-C=O                               | O=C-O-H           |
|                     |           | 1.447               | 1.369                | 1.362             | 1.209             | 0.964             | 120.8             | 125.7                                 | 10.5                                  | 170.4                                 | 178.4             |
|                     | MCA-3     | 1.455               | 1.374                | 1.365             | 1.208             | 0.964             | 120.9             | 117.6                                 | 173.7                                 | 7.9                                   | 165.9             |
|                     | MCA-2     | 1.450               | 1.353                | 1.363             | 1.217             | 0.967             | 123.3             | 124.6                                 | 5.7                                   | 174.9                                 | 0.5               |
| MP2/aug-cc-pVDZ     | MCA-1     | 1.447               | 1.352                | 1.364             | 1.216             | 0.967             | 123.5             | 120.8                                 | 174.1                                 | 6.8                                   | 0.2               |
|                     | MCA-1     | 1.457               | 1.362                | 1.376             | 1.227             | 0.971             | 123.6             | 120.0                                 | 171.9                                 | 9.3                                   | 0.2               |
|                     | MCA-1     | 1.454               | 1.361                | 1.366             | 1.215             | 0.966             | 123.7             | 119.5                                 | 168.6                                 | 13.0                                  | 1.0               |
|                     | MCA-1     | 1.450               | 1.352                | 1.366             | 1.212             | 0.966             | 123.0             | 122.4                                 | 177.1                                 | 3.4                                   | 0.0               |
| B3LYP/aug-cc-pVTZ   | MCA-1     | 1.453               | 1.357                | 1.370             | 1.220             | 0.968             | 123.0             | 122.3                                 | 176.7                                 | 3.8                                   | 0.2               |
|                     | MCA-1     | 1.453               | 1.355                | 1.368             | 1.213             | 0.966             | 123.0             | 122.7                                 | 179.6                                 | 0.5                                   | 0.0               |
|                     | MCA-1     | 1.453               | 1.355                | 1.368             | 1.213             | 0.966             | 123.0             | 122.3                                 | 176.9                                 | 3.7                                   | 0.1               |
|                     | MCA-1     | 1.451               | 1.356                | 1.367             | 1.212             | 0.966             | 123.1             | 122.4                                 | 179.9                                 | 0.1                                   | 0.0               |
| B3LYP/6-311++G(d,p) | MCA-1     | 1.453               | 1.356                | 1.369             | 1.222             | 0.969             | 122.9             | 122.7                                 | 179.7                                 | 0.4                                   | 0.0               |
|                     | MCA-1     | 1.454               | 1.356                | 1.369             | 1.221             | 0.969             | 122.9             | 122.3                                 | 176.8                                 | 3.8                                   | 0.2               |
|                     | MCA-1     | 1.455               | 1.356                | 1.370             | 1.221             | 0.973             | 123.1             | 121.8                                 | 174.9                                 | 5.9                                   | 0.2               |
|                     | MCA-1     | 1.450               | 1.358                | 1.369             | 1.219             | 0.969             | 123.2             | 122.2                                 | 180.0                                 | 0.0                                   | 0.1               |
| B3LYP/6-31G(d)      | MCA-1     | 1.450               | 1.359                | 1.368             | 1.219             | 0.972             | 123.2             | 122.1                                 | 176.1                                 | 4.5                                   | 0.2               |
|                     | MCA-1     | 1.459               | 1.357                | 1.393             | 1.243             | 0.978             | 122.8             | 122.2                                 | 180.0                                 | 0.0                                   | 0.1               |

Table S7. Vibrational frequencies (in  $\text{cm}^{-1}$ ) for the methylcarbamic acid conformers. The IR intensities ( $\times 10^{-17}$   $\text{cm molecule}^{-1}$ ) are given in parentheses.

| Level               | Conformer | CO <sub>2</sub><br>bending | CO <sub>2</sub><br>wagging | C-O<br>stretching | N-C<br>stretching | C=O<br>stretching | N-H<br>stretching | O-H<br>stretching |
|---------------------|-----------|----------------------------|----------------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| MP2/aug-cc-pVTZ     | MCA-4     | 563 (0.11)                 | 772 (0.25)                 | 1088 (0.72)       | 1461 (0.47)       | 1839 (9.70)       | 3686 (0.93)       | 3839 (0.85)       |
|                     | MCA-3     | 534 (0.11)                 | 772 (0.20)                 | 1120 (0.13)       | 1548 (1.92)       | 1834 (6.02)       | 3634 (0.47)       | 3833 (0.93)       |
|                     | MCA-2     | 557 (0.38)                 | 779 (0.50)                 | 1089 (2.40)       | 1499 (0.90)       | 1823 (10.86)      | 3672 (1.04)       | 3803 (1.73)       |
|                     | MCA-1     | 512 (0.70)                 | 784 (0.27)                 | 1126 (2.63)       | 1580 (3.62)       | 1815 (7.58)       | 3681 (0.95)       | 3799 (1.75)       |
| MP2/aug-cc-pVDZ     | MCA-1     | 507 (0.68)                 | 770 (0.26)                 | 1117 (2.42)       | 1566 (3.87)       | 1799 (7.39)       | 3668 (0.86)       | 3785 (1.63)       |
| MP2/6-311++G(d,p)   | MCA-1     | 515 (0.73)                 | 775 (0.33)                 | 1132 (2.25)       | 1577 (3.85)       | 1827 (7.72)       | 3686 (0.83)       | 3836 (1.72)       |
| B3LYP/aug-cc-pVTZ   | MCA-1     | 514 (0.68)                 | 778 (0.36)                 | 1106 (2.08)       | 1576 (3.12)       | 1797 (7.89)       | 3660 (0.67)       | 3773 (1.59)       |
| B3LYP/ aug-cc-pVDZ  | MCA-1     | 509 (0.68)                 | 770 (0.34)                 | 1112 (2.08)       | 1569 (3.57)       | 1794 (7.75)       | 3648 (0.67)       | 3772 (1.56)       |
| B3LYP/6-311++G(d,p) | MCA-1     | 515 (0.70)                 | 776 (0.40)                 | 1108 (2.21)       | 1579 (3.45)       | 1801 (8.51)       | 3662 (0.73)       | 3794 (1.66)       |
| B3LYP/6-311+G(d,p)  | MCA-1     | 513 (0.69)                 | 778 (0.42)                 | 1108 (2.29)       | 1570 (3.46)       | 1801 (8.45)       | 3650 (0.73)       | 3791 (1.65)       |
| B3LYP/6-311G(d,p)   | MCA-1     | 514 (0.70)                 | 776 (0.42)                 | 1115 (2.08)       | 1582 (3.39)       | 1819 (7.01)       | 3646 (0.64)       | 3809 (1.46)       |
| B3LYP/6-31++G(d,p)  | MCA-1     | 513 (0.73)                 | 766 (0.40)                 | 1116 (2.02)       | 1585 (3.71)       | 1809 (8.40)       | 3673 (0.72)       | 3791 (1.61)       |
| B3LYP/6-31+G(d,p)   | MCA-1     | 510 (0.71)                 | 768 (0.41)                 | 1116 (2.15)       | 1578 (3.76)       | 1810 (8.34)       | 3661 (0.74)       | 3788 (1.62)       |
| B3LYP/6-31+G(d)     | MCA-1     | 509 (0.77)                 | 770 (0.44)                 | 1120 (2.16)       | 1582 (4.03)       | 1813 (8.20)       | 3652 (0.68)       | 3720 (1.47)       |
| B3LYP/6-31G(d,p)    | MCA-1     | 513 (0.75)                 | 764 (0.51)                 | 1129 (1.77)       | 1590 (3.51)       | 1845 (6.49)       | 3669 (0.60)       | 3786 (1.28)       |
| B3LYP/6-31G(d)      | MCA-1     | 513 (0.73)                 | 766 (0.53)                 | 1132 (1.75)       | 1596 (3.26)       | 1850 (6.47)       | 3646 (0.54)       | 3724 (1.21)       |
| B3LYP/6-31G         | MCA-1     | 503 (0.79)                 | 743 (1.25)                 | 1088 (2.71)       | 1598 (2.59)       | 1768 (6.00)       | 3652 (0.96)       | 3665 (0.60)       |



Table S8. Moment of inertia ( $\times 10^{-45}$  kg m<sup>2</sup>), rotational constants (in MHz) and dipole moments (in Debye) for the methylcarbamic acid conformers.

| Level               | Conformer | Moment of Inertia |                |                | Rotational Constants |                |                | Dipole Moment |
|---------------------|-----------|-------------------|----------------|----------------|----------------------|----------------|----------------|---------------|
|                     |           | I <sub>A</sub>    | I <sub>B</sub> | I <sub>C</sub> | A <sub>e</sub>       | B <sub>e</sub> | C <sub>e</sub> |               |
| MP2/aug-cc-pVTZ     | MCA-4     | 0.81              | 1.99           | 2.74           | 10333.5              | 4211.7         | 3056.5         | 5.556         |
|                     | MCA-3     | 0.79              | 2.01           | 2.74           | 10577.1              | 4167.3         | 3055.4         | 4.824         |
|                     | MCA-2     | 0.79              | 1.98           | 2.72           | 10569.0              | 4237.6         | 3085.1         | 2.826         |
|                     | MCA-1     | 0.78              | 2.03           | 2.76           | 10691.5              | 4126.3         | 3036.6         | 2.465         |
| MP2/aug-cc-pVDZ     | MCA-1     | 0.80              | 2.05           | 2.79           | 10496.9              | 4083.1         | 3001.3         | 2.464         |
| MP2/6-311++G(d,p)   | MCA-1     | 0.79              | 2.03           | 2.76           | 10619.5              | 4126.2         | 3039.0         | 2.301         |
| B3LYP/aug-cc-pVTZ   | MCA-1     | 0.78              | 2.06           | 2.79           | 10747.0              | 4063.1         | 3004.2         | 2.560         |
| B3LYP/ aug-cc-pVDZ  | MCA-1     | 0.79              | 2.07           | 2.80           | 10650.6              | 4046.8         | 2989.3         | 2.580         |
| B3LYP/6-311++G(d,p) | MCA-1     | 0.78              | 2.07           | 2.80           | 10714.0              | 4051.5         | 2995.6         | 2.524         |
| B3LYP/6-311+G(d,p)  | MCA-1     | 0.78              | 2.07           | 2.79           | 10718.1              | 4057.6         | 2999.9         | 2.530         |
| B3LYP/6-311G(d,p)   | MCA-1     | 0.78              | 2.06           | 2.79           | 10719.1              | 4064.6         | 3003.1         | 2.383         |
| B3LYP/6-31++G(d,p)  | MCA-1     | 0.79              | 2.07           | 2.81           | 10646.4              | 4041.9         | 2985.3         | 2.588         |
| B3LYP/6-31+G(d,p)   | MCA-1     | 0.79              | 2.07           | 2.80           | 10651.2              | 4048.3         | 2989.8         | 2.594         |
| B3LYP/6-31+G(d)     | MCA-1     | 0.79              | 2.07           | 2.80           | 10641.5              | 4055.2         | 2993.9         | 2.612         |
| B3LYP/6-31G(d,p)    | MCA-1     | 0.79              | 2.06           | 2.80           | 10655.7              | 4065.0         | 2998.4         | 2.337         |
| B3LYP/6-31G(d)      | MCA-1     | 0.79              | 2.06           | 2.80           | 10644.4              | 4063.3         | 2997.8         | 2.335         |
| B3LYP/6-31G         | MCA-1     | 0.81              | 2.09           | 2.85           | 10335.3              | 4004.3         | 2940.0         | 2.471         |