PAPER

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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We have theoretically investigated the low energy conformers of neutral glycine (NH_2CH_2COOH) and its isomer methylcarbamic acid ($CH_3NHCOOH$) in the gas phase. A total of 16 different levels of the theory, including CCSD(T), MP2 and B3LYP methods with various Pople and Dunning type basis sets with and without polarization and diffuse functions were used. We found eight low energy glycine conformers, where the heavy atoms in three have a planar backbone, and four low energy methylcarbamic acid conformers all with non-planar backbones. Interestingly at all levels of theory, we found that the most stable methylcarbamic acid conformer is significantly lower in energy than the lowest energy glycine conformer. The MP2 level and single point CCSD(T) calculations show the lowest energy methylcarbamic acid conformer to be between 31 to 37 kJ mol^{-1} lower in energy than the lowest energy glycine conformer. These calculations suggest that methylcarbamic acid might serve as a precursor to glycine formation in the Interstellar Medium (ISM). We also report the theoretical harmonic vibrational frequencies, infrared intensities, moment of inertia, rotational constants and dipole moments for all of the conformers. In order to understand how glycine or methylcarbamic acid might be formed in the ISM, larger calculations which model glycine or its isomer interacting with several surrounding molecules, such as water, are needed. We demonstrate that B3LYP method should provide a reliable and computationally practical approach to modeling these larger systems.

Introduction

Scientists have been fascinated by the Interstellar Medium (ISM) for more than half a century, and they have had a special interest in the origin and the formation of the amino acids in the ISM. Because, the presence of the amino acids in the ISM may provide important information about the delivery of the prebiotic molecules to Earth and the origins of life on Earth.[1–3] Glycine (NH_2CH_2COOH) is the simplest of the amino acids and just one of the many building blocks of polypeptides, and methylcarbamic acid ($CH_3NHCOOH$) is the simplest member of the alkylcarbamic acids (R-NHCOOH). They are both important molecules in astrochemistry, and if either molecule exists in the ISM, they are likely to occur in or on the surface of an icy grain of a dense molecular cloud. Astronomical observations of these icy grains suggest they are mostly composed of water (H_2O)[4] with other species such as carbon monoxide (CO),[5–7] carbon dioxide (CO_2),[8] methanol (CH_3OH)[9] and ammonia (NH_3).[10] Consequently, in order to characterize glycine and methylcarbamic acid in the ISM, details on how these molecules interact with the different molecules in the ISM are needed. For example, while neutral glycine (NH_2CH_2COOH) is the more stable form in the gas phase, it is well known that the glycine zwitterion ($^+NH_3CH_2CO_2^-$) becomes the preferred form in water.[11] In a related study aimed at exploring how glycine could be formed in the ISM, recently we have theoretically investigated the interactions between two possible components of glycine: methylamine (CH_3NH_2) with carbon dioxide (CO_2) in the presence of zero to 20 water (H_2O) molecules.[12] When there are no water molecules present, we found the two molecules form a weakly bound van der Waals complex where the nitrogen to carbon from CO_2 distance is 2.7 Å. However, with just two water molecules present, we find that the methylcarbamic acid zwitterion ($CH_3NH_2^+CO_2^-$) forms in a barrier free reaction. The presence of the two water molecules causes the N–C distance to be dramatically shortened by an Å to 1.7 Å, the presence of additional water molecules around the zwitterion causes further, but smaller, reductions in the N–C distance.[12]

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Experimental and theoretical studies on the structure and conformational potential energy surface of glycine (NH_2CH_2COOH) began in late 1930's. Beside the experimental studies using micro wave[13] and mm wave[14,15] spectrum of the gas phase glycine, X-ray diffraction studies on crystalline glycine have also been performed.[16–18] There are also plenty of more experimental studies available on neutral glycine in the gas phase.[19–21] On the other hand, the first theoretical study, an RHF/4-31G level *ab initio* study investigating the rotational potential energy surface of the glycine, was published by Vishveshwara and Pople.[22] In this study they calculated the torsional parameters and found twenty structures in around the 40 kJ mol^{-1} relative energy range by using these parameters. Dykstra *et al.*[23] performed self-consistent electron pairs calculations on the stability of the two minimum energy interstellar glycine conformers. Jensen and Gordon investigated the conformational potential energy surface of nonionized gas phase glycine using *ab initio* (RHF/6-31G* and RHF/STO-2G), MP2/6-31G*//RHF/6-31G* and semiempirical (AM1 and PM3) methods.[24] Vijay and Sathyanarayana[25] calculated theoretical IR spectra of glycine at HF/4-21G level. The calculated IR band intensity pattern shows good agreement with the experimental spectrum of glycine. From a complete assignment of the vibrational fundamentals observed from the IR spectra of glycine and its several isotopic molecules, a stretched framework planar conformer was concluded to be the more stable form, reconfirming the results of the other studies on nonionized glycine. Hu *et al.*[26] applied *ab initio* quantum mechanical methods, including the self-consistent field (SCF), single and double excitation configuration interaction (CISD), the single and double excitation coupled cluster (CCSD), and the single, double, and perturbative triple excitation coupled cluster [CCSD(T)] to five C_s, conformers and four of their C_1 counterparts on the potential energy hypersurface of glycine. Császár[27] performed correlated level *ab initio* calculations [MP2, MP4, CCSD, CCSD(T) computations] for 13 conformers of nonionized glycine, including all 8 possible conformers with planar heavy atom arrangements using a 6-311++G(d,p) basis set and a much larger basis set consisting of 350 contracted Gaussian functions which included both polarization and diffuse functions on all of the atoms. His results were in agreement with the previous theoretical studies indicating that the backbone of heavy atoms in the lowest energy form of glycine has a planar structure. On the other hand, he found that the second most stable conformer of gas phase glycine has a non-planar heavy atoms backbone structure at all levels of theory. His calculations at MP2/6-311++G(d,p) level suggested that glycine has 8 minima on the potential energy surface and the first, the sixth and the seventh lowest energy conformers have planar structure while the rest has non-planar structure. Recently, Császár and coworkers[28] further characterized the two lowest energy, planar and non-planar, conformers of glycine at CCSD(T)/cc-pVTZ level. They concluded that the lowest energy conformer of the nonionized glycine has a planar equilibrium structure, while the second lowest energy conformer has a non-planar structure whose equilibrium torsion angle (N–C–C–O) characterizing the deviation of its heavy atom framework from planarity, is 11 ± 2°. Even more recently, Balabin[29] has performed even higher level

ab initio calculations which estimate the CCSD(T)/complete basis set (CBS) limit relative glycine conformer energies using CCSD(T)/aug-cc-pVTZ, MP3/aug-cc-pVQZ, and MP2/aug-cc-pV5Z calculations at the B3LYP/aug-cc-pVTZ optimized geometries. Balabin obtained the same eight low energy glycine conformers as found by Császár and coworkers[28] but improve the difference in their relative energies to a 17–70 cm^{-1} uncertainty.

Carbamic acid derivatives, particularly alkylcarbamic acids (R-NHCOOH) and alkylcarbamates (R-NHCOO$^-$) have also received previous attention in astrochemistry. The formation of the carbamic acids and their carbamates in interstellar medium has been investigated by using different approaches. Khanna and Moore[30] investigated the formation of carbamic acid (NH_2COOH) by subjecting water, ammonia and carbon dioxide ices to 1 MeV proton irradiation at low temperature. Holtom *et al.*[31] performed a combined experimental and theoretical study and investigated the formation of glycine (NH_2CH_2COOH) and methylcarbamic acid ($CH_3NHCOOH$) *via* secondary electrons generated in the track of galactic cosmic ray particles in extraterrestrial ices. In their experiments, interstellar ice analogs consisting of a methylamine and carbon dioxide mixture at 10 K were irradiated by 5 keV electrons. Their results indicated the formation of glycine and its methylcarbamic acid isomer. Chen *et al.*[32] carried out irradiations of ice mixtures containing water, carbon dioxide and ammonia with UV/extreme UV photons provided by a synchrotron source in the 4–20 eV range, and investigated the formation of carbamic acid (NH_2COOH). Bossa *et al.*[33–35] studied the formation of glycine (NH_2CH_2COOH), methylcarbamic acid ($CH_3NHCOOH$) and methylammonium methylcarbamate [$CH_3NH_3^+$][CH_3NHCOO^-] using thermal and VUV photolysis processes. They also presented the relative energies of the four conformers of methylcarbamic acid calculated at B3LYP/6-31G(d) level, without a detailed geometrical analysis.[35] Lee *et al.*[36] exposed the methylamine, carbon dioxide and water ice analogs to UV irradiation at 56 K, and their spectral results indicated the photochemical synthesis of methylcarbamic acid and glycine. Lattelais *et al.*,[37] investigated the relative stability of several different glycine isomers using B3LYP/6-311G(d,p) calculations and showed that glycine (NH_2CH_2COOH) is less stable than its amide ester isomer (NH_2COOCH_3) and methylcarbamic acid isomer ($CH_3NHCOOH$) by 19 kJ mol^{-1} and 42 kJ mol^{-1}, respectively. But they did not compare the stability of different possible conformers belonging to each isomer.

Clearly there are already many different published studies available in the literature related to the stability of the glycine conformers. However, since it is still unclear whether glycine (NH_2CH_2COOH) or its isomer, methylcarbamic acid ($CH_3NHCOOH$), exist in the ISM, the main goal of this paper is to compare the relative energies and structural features for the different low energy conformers for the two isomers. As a consistency check we have performed the calculations using many different levels of the theory. We have also performed these different levels of theory to evaluate which of the lower quality methods still give physically realistic results without large computational expense. Reliable cheaper computational methods are needed to investigate larger systems which simulate the possible interactions taking place between either glycine or

methylcarbamic acid and some of the surrounding molecules present in icy grains. In the next section we describe the computational methods used. The results are given in the third section and we present relative energies, geometry information, vibrational frequencies and other useful properties for the different glycine and methylcarbamic acid conformers. We also give a discussion of the quality of the calculated properties obtained by using the different computational methods in the results section. Concluding remarks are given in the final section of the paper.

Computational method

In this study, we determined the different stable conformations of glycine and its methylcarbamic acid isomer at the MP2/aug-cc-pVTZ, MP2/aug-cc-pVDZ and MP2/6-311++G(d,p) levels of theory.[38–41] We also performed B3LYP density functional calculations using the same basis sets we used for the MP2 calculations plus for the 6-311+G(d,p), 6-311G(d,p), 6-31++G(d,p), 6-31+G(d,p), 6-31+G(d), 6-31G(d,p), 6-31G(d) and 6-31G basis sets.[38–49] We searched for different glycine and methylcarbamic acid conformers by performing full geometry optimizations on both initial structures built based on chemical intuition as well several other randomly generated initial geometries. Once the conformations of glycine and methylcarbamic acid structures were optimized, we performed vibrational frequency calculations to verify that the structures were proper local minimum with 3N-6 real vibrational frequencies. The energy results given in the next section include zero point vibrational energy corrections. To check the quality of the MP2 calculations, we also performed single point CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ and CCSD(T)/6-311++G(d,p)//MP2/6-311++G(d,p) energy calculations corrected with the MP2 zero point vibrational energy on each conformer.[38,40,48–51] All of the geometry optimization and vibrational frequency calculations were performed using the GAMESS[52] program suite.

Results

In Table 1 we summarize the relative energies obtained for different methylcarbamic acid and glycine conformers computed at the various levels of theory. We have found four low energy methylcarbamic acid conformers (MCA-1 to MCA-4) and eight low energy glycine conformers (Gly-1 to Gly-8) where the conformers are labeled in order of their increasing energy. Much to our initial surprise, we predict at all of the different levels of theory that the most stable methylcarbamic acid MCA-1 conformer is at least 31 kJ mol^{-1} more stable than the lowest energy glycine Gly-1 conformer. This result might explain why glycine has not been readily observed in the ISM, simply because other isomers of glycine, such as methylcarbamic acid or its related amide ester isomer,[37] are more readily formed because they are lower in energy. Furthermore, our recent calculations investigating the interaction of methylamine with carbon dioxide in the presence of surrounding water molecules found that the methylcarbamic acid zwitterion more readily forms than the glycine zwitterion.[12] Table S1 in the Supplementary Material† lists the total energies and zero point vibrational energy corrections for all the different conformations.

Generally we take the MP2/aug-cc-pVTZ calculations as reference for comparison with the other different levels of theory since the aug-cc-pVTZ basis is the largest basis set we used in this study. With the MP2/aug-cc-pVTZ calculations we computed the methylcarbamic acid MCA-1 conformer to be 37 kJ mol^{-1} more stable than the glycine Gly-1 conformer. Support showing that MP2 is able to provide reliable estimates for the different conformers' relative energies is given by the single point CCSD(T)/aug-cc-pVTZ energies computed at the MP2/aug-cc-pVTZ optimized geometries and with the zero point energy corrections listed in Table 1, and also by the calculations on glycine by Császár and coworkers. Below we describe in more detail the structures and properties for the different low energy glycine and methylcarbamic acid conformers.

Glycine

There have already been several theoretical studies on the low energy glycine conformers. In agreement with the careful study by Császár[27] and the more recent Balabin calculations,[29] we have found eight different stable glycine conformers with relative energies which differ over an approximately 30 kJ mol^{-1} range

Table 1 The relative energies (in kJ mol^{-1}) of the glycine and methylcarbamic acid conformers calculated at the different levels of theory

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
CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ	32.9	27.5	5.6	0.0	34.1	38.3	39.3	41.2	44.9	53.4	58.1	58.3
CCSD(T)/6-311++G(d,p)//MP2/6-311++G(d,p)	35.9	28.7	5.7	0.0	31.0	36.0	36.5	37.7	40.2	52.9	59.0	59.0
MP2/aug-cc-pVTZ	33.7	28.6	5.5	0.0	37.0	40.0	41.8	43.8	47.6	56.8	60.4	61.4
MP2/aug-cc-pVDZ	34.1	28.0	5.5	0.0	32.3	35.9	37.4	39.0	42.5	51.9	56.7	57.1
MP2/6-311++G(d,p)	37.3	30.2	5.7	0.0	34.0	37.9	39.4	40.7	43.3	56.5	61.7	62.5
B3LYP/aug-cc-pVTZ	32.3	28.4	5.9	0.0	42.1	45.2	47.0	49.2	53.1	61.3	63.8	65.9
B3LYP/aug-cc-pVDZ	33.4	28.2	6.2	0.0	38.2	41.2	42.9	45.1	48.0	57.3	60.0	61.9
B3LYP/6-311++G(d,p)	36.0	31.7	5.3	0.0	41.2	44.0	46.7	47.5	52.0	63.2	65.9	69.0
B3LYP/6-311+G(d,p)	35.9	31.2	5.3	0.0	41.2	43.9	46.7	47.6	52.1	63.2	65.9	69.1
B3LYP/6-311G(d,p)	37.8	33.2	7.2	0.0	45.3	47.9	52.8	52.1	58.7	67.6	69.9	74.8
B3LYP/6-31++G(d,p)	36.0	32.5	5.0	0.0	41.7	44.4	47.7	47.9	52.7	64.4	67.2	70.9
B3LYP/6-31+G(d,p)	35.8	32.7	5.0	0.0	41.7	44.5	47.8	47.9	52.9	64.5	67.4	71.1
B3LYP/6-31+G(d)	36.5	33.5	5.2	0.0	47.1	50.0	53.6	53.2	58.3	70.2	74.0	77.3
B3LYP/6-31G(d,p)	36.5	32.8	5.2	0.0	44.6	49.2	53.0	51.5	58.9	67.4	71.7	75.0
B3LYP/6-31G(d)	36.7	33.2	5.2	0.0	49.3	53.8	57.9	56.2	63.6	72.3	77.4	80.9
B3LYP/6-31G	42.2	38.5	6.0	0.0	55.9	56.2	62.2	62.2	68.8	82.5	84.9	82.9

15776 | *Phys. Chem. Chem. Phys.*, 2011, **13**, 15774–15784

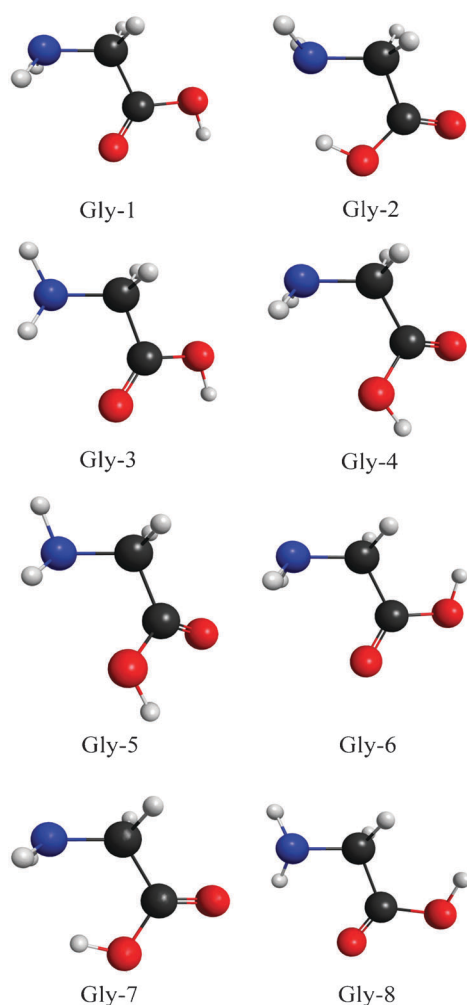This journal is © the Owner Societies 2011

Fig. 1 The minimum energy structures of the glycine conformers optimized at MP2/aug-cc-pVTZ level (atom types: white = H, gray = C, blue = N, red = O, and figure in color is available in the online version).

and where the five lowest energy conformers are within *ca.* 10 kJ mol^{-1} of each other. Fig. 1 shows the optimized structures for glycine conformers obtained with the MP2/aug-cc-pVTZ calculations. The relative conformer energies, with the Gly-1 energy taken as zero, obtained using the different computational methods with zero point vibrational energy corrections are given in Table 2 for the large basis sets only. In the Supplementary Material† we provide the complete set of results for all the methods and basis sets for Tables 2 through 8. Our reference CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ relative conformer energies are in very good agreement with the

Balabin's CBS relative conformer energies of 0.0, 4.0, 4.8, 7.4, 11.3, 19.6, 23.6 and 24.4 kJ mol^{-1} obtained by including the B3LYP zero point energy correction.[29] Structural properties of all glycine conformers calculated at MP2/aug-cc-pVTZ level and a comparison of the Gly-1 geometrical parameters calculated at the different levels of the theory are given in Table 3. Császár and coworkers previously pointed out that glycine can form conformers where the N–C–C–O or N–C–C=O backbone is either planar or non-planar.[27,28] In agreement with the previous results we find Gly-1, Gly-6 and Gly-7 to have planar backbones, while the Gly-2, Gly-3, Gly-4, Gly-5 and Gly-8 structures are found to be non-planar with 10.6, 162.9, 1.9, 33.4, 165.3° N–C–C–O dihedral angle. We find the carboxylic acid group in each conformer to be essentially planar with either a zero or 180° O=C–O–H dihedral angle. The planar Gly-1 conformer presumably has the lowest energy because it can form two equal intramolecular N–H···O=C hydrogen-bonds. Whereas, the non-planar Gly-2 conformer has two local minima related as mirror images, only forms a single O–H···N hydrogen-bond causing the conformer to have slightly higher energy. Császár and coworkers also found a planar Gly-2 structure which forms a very low energy barrier separating the two non-planar Gly-2 local minima.[27,28] Due to the interaction between nitrogen and hydrogen, the N–C (1.464 Å) and O–H (0.984 Å) bond lengths in the Gly-2 structure are found to be longer than in the other seven conformers. Gly-3 has a single intramolecular N–H···O=C H–bond, and Gly-4 and Gly-5 form single N–H···O–H hydrogen bonds. The higher energy Gly-6, 7 and 8 conformers appear to be destabilized by repulsive forces between the hydrogen on the carboxylic acid group and the hydrogen atoms on the methylene group in Gly-6 and Gly-8 structures, and also between the hydrogen atoms on the amine group in Gly-7 structure. Consequently the Gly-6, 7 and 8 conformers have the smallest O=C–O (120.4, 121.5 and 120.5°) bond angles, and the shortest C=O (1.204, 1.205, 1.204 Å) and O–H (0.966, 0.969, 0.966 Å) bond lengths when compared with the other conformers in Table 3.

Table 4 summarizes the results of IR vibrational frequency calculations on the optimized geometries of glycine conformers obtained at the MP2/aug-cc-pVTZ level and compares the Gly-1 fundamentals with those calculated at the other different levels of theory. Table 4 does not use any scaling factors which are often used to compensate for the theoretical frequencies tending to be systematically higher than the experimental values. The CO$_2$H rocking, CO$_2$ bending, CO$_2$ wagging, C–C, C–O and C=O stretching, NH$_2$ symmetric and asymmetric stretching and O–H stretching fundamentals of Gly-1 conformer

Table 2 The relative energies (in kJ mol^{-1}) 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

Table 3 Geometrical parameters (bond lengths in Å, bond angles and dihedrals in °) for the glycine conformers

Level	Conformer	NH_2-CH_2 N–C	CH_2-CO_2H C–C	CO_2H C–O	CO_2H C=O	CO_2H O–H	CO_2H O=C–O	NH_2-CH_2-CO_2H N–C–C	NH_2-CH_2-CO_2H N–C–C–O	NH_2-CH_2-CO_2H N–C–C=O	CO_2H O=C–O–H
MP2/aug-cc-pVTZ	Gly-8	1.450	1.515	1.356	1.204	0.966	120.5	110.0	165.3	16.7	177.8
	Gly-7	1.446	1.529	1.353	1.205	0.969	121.5	119.1	0.0	180.0	180.0
	Gly-6	1.445	1.523	1.361	1.204	0.966	120.4	115.4	180.0	0.0	180.0
	Gly-5	1.458	1.507	1.355	1.209	0.970	123.0	111.7	33.4	144.4	1.0
	Gly-4	1.448	1.518	1.355	1.210	0.970	122.9	118.9	1.9	178.2	0.0
	Gly-3	1.452	1.504	1.352	1.210	0.970	123.4	109.8	162.9	19.0	1.1
	Gly-2	1.464	1.527	1.341	1.207	0.984	123.4	111.1	10.6	170.5	179.2
	Gly-1	1.446	1.514	1.355	1.210	0.970	123.2	115.4	180.0	0.0	0.0
MP2/aug-cc-pVDZ	Gly-1	1.456	1.523	1.367	1.220	0.974	123.2	115.5	180.0	0.0	0.0
MP2/6-311++G(d,p)	Gly-1	1.449	1.520	1.357	1.209	0.969	123.4	115.5	180.0	0.0	0.0
B3LYP/aug-cc-pVTZ	Gly-1	1.447	1.522	1.355	1.203	0.969	122.9	116.0	180.0	0.0	0.0
B3LYP/aug-cc-pVDZ	Gly-1	1.451	1.524	1.359	1.211	0.971	122.8	115.9	180.0	0.0	0.0
B3LYP/6-311++G(d,p)	Gly-1	1.449	1.525	1.356	1.204	0.970	122.9	116.0	180.0	0.0	0.0

are calculated to be 511, 636, 647, 831, 1136, 1809, 3530, 3623, 3781 cm^{-1} at MP2/aug-cc-pVTZ level, respectively, are in good agreement with the experimental values 501, 637, 620, 799, 1101, 1781, 3200, 3414, 3566 cm^{-1}, respectively, obtained from the IR spectroscopy of neutral crystalline glycine in argon matrices at 10 K[53] and 20 K.[54] Additionally, the calculated intensities for these vibrational modes are found to be 0.49×10^{-17}, 0.10×10^{-17}, 1.45×10^{-17}, 1.45×10^{-17}, 4.18×10^{-17}, 4.17×10^{-17}, 0.07×10^{-17}, 0.18×10^{-17} and 1.29×10^{-17} cm molecule^{-1}, respectively, and they are also in good agreement with the experimental intensities listed as weak or strong bands.[53] Nevertheless, because the frequency calculations are for isolated glycine conformers in the gas phase the NH_2 and O–H stretching modes above 3000 cm^{-1} are calculated at around 200 cm^{-1} higher than the experimental values. Shifts in the frequencies of the vibrational modes of the different glycine conformers do occur. For instance, the CO_2H rocking mode at 511 cm^{-1} in Gly-1 is blue shifted to 574 cm^{-1} in the Gly-8 conformer. The CO_2 bending mode is calculated to be between 628 and 656 cm^{-1}, except for Gly-4 and Gly-5 conformers where it is found at 594 cm^{-1}. Likewise, the intensities of the different vibration modes vary with glycine conformer, the CO_2 bending mode of Gly-1 is weakly IR active with an intensity of 0.10×10^{-17} cm molecule^{-1}, whereas Gly-7 produces the most intense CO_2 bending mode with 1.17×10^{-17} cm molecule^{-1}. The intramolecular O–H···N hydrogen bond in Gly-2 structure, discussed above, not only affects geometrical parameters, but it also affects vibrational frequencies enormously. This effect makes the Gly-2 O–H stretching mode quite distinctive in Table 4. This vibrational mode of Gly-2 appears at 3459 cm^{-1} and is red shifted by 322 cm^{-1} from the Gly-1 O–H stretching frequency. The intensity of the Gly-2 O–H stretching mode is computed to be 4.95×10^{-17} cm molecule^{-1} and much higher than the 1.02×10^{-17} to 1.61×10^{-17} cm molecule^{-1} found for the other conformers. This shift of the Gly-2 O–H stretching frequency illustrates the typical expected frequency shifts caused by hydrogen-bonding when glycine is in a condensed phase *versus* the present calculations which treat glycine in the gas phase. Another vibrational mode affected by the intramolecular hydrogen bond formation is the C–O stretching mode of Gly-2 conformer, which appears at 1239 cm^{-1} and blue shifts by around 100 cm^{-1} from the Gly-1 value. The intensity of this mode decreases to 0.40×10^{-17} cm molecule^{-1}. Even though Gly-1 and Gly-4 of the other conformers involve N–H···O hydrogen bonding, the symmetric and asymmetric stretching fundamentals of NH_2 do not vary significantly, ranging between 3514–3573 cm^{-1} and 3613–3695 cm^{-1}, respectively, for the eight different conformers of glycine.

The moments of inertia, rotational constants and dipole moments of glycine conformers are given in Table 5. The theoretical rotational constants, A_e, B_e and C_e, are calculated using the rigid rotor approximation and are computed using the theoretically optimized equilibrium geometry. In contrast the experimental rotational constants, denoted by A_0, B_0 and C_0, are the effective rotational constants which reproduce the experimental rotational spectra and include vibrational corrections and electronic contributions to the equilibrium molecular geometry of the molecule's lowest vibrational state.[55]

15778 | *Phys. Chem. Chem. Phys.*, 2011, **13**, 15774–15784

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Table 4 Vibrational frequencies (in cm^{-1}) for the glycine conformers. The IR intensities ($\times 10^{-17}$ cm molecule^{-1}) are given in parentheses

Level	Conformer	CO_2H rocking	CO_2 bending	CO_2 wagging	C–C stretching	C–O stretching	C=O stretching	NH_2 sym. stretching	NH_2 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)
MP2/ aug-cc-pVDZ	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)	Gly-1	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)
Experimental	Gly-1	501,[a] 498[b]	637[b]	620,[a] 618[b]	787,[a] 799[b]	1101,[a] 1100[b]	1781,[a] 1781[b]	3200[b]	3414,[a] 3410[b]	3566,[a] 3560[b]

[a] Experimental values are taken from ref. 54. [b] Experimental values are taken from ref. 53.

Table 5 Moment of inertia ($\times 10^{-45}$ kg m^2), rotational constants (in MHz) and dipole moments (in Debye) for the glycine conformers

Level	Conformer	Moment of inertia			Rotational constants[a]						Dipole moment
		I_A	I_B	I_C	A_e	B_e	C_e	A_e/A_0	B_e/B_0	C_e/C_0	
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
MP2/aug-cc-pVDZ	Gly-1	0.83	2.18	2.92	10122.9	3838.8	2874.8	0.9788	0.9904	0.9872	1.178
MP2/6-311++G(d,p)	Gly-1	0.82	2.17	2.89	10253.7	3867.1	2900.7	0.9915	0.9977	0.9961	1.198
B3LYP/aug-cc-pVTZ	Gly-1	0.81	2.18	2.90	10350.3	3843.2	2894.1	1.0008	0.9915	0.9939	1.152
B3LYP/aug-cc-pVDZ	Gly-1	0.82	2.19	2.91	10262.0	3826.4	2878.6	0.9923	0.9872	0.9885	1.171
B3LYP/6-311++G(d,p)	Gly-1	0.81	2.19	2.91	10321.8	3830.4	2885.2	0.9980	0.9882	0.9908	1.168
Experimental	Gly-1				10342,[b] 10341.8[c]	3876,[b] 3876.2[c]	2912,[b] 2912.4[c]				1.000 ± 0.150[b]
	Gly-2				10130[b]	4071[b]	3008[b]				4.5[d]

[a] A_e, B_e, C_e indicate calculated rotational constants at the equilibrium geometries while A_0, B_0, C_0 indicate experimental (effective) ones. [b] Experimental values are taken from ref. 15. [c] Experimental values are taken from ref. 19. [d] Experimental values are taken from ref. 13.

Nevertheless, in the comparison of calculated and experimental rotational constants, the vibrational corrections and electronic contributions are mostly ignored because of their small effect. Table 5 shows good agreement between the theoretical and experimental rotational constants with the A_e/A_0, B_e/B_0 and C_e/C_0 ratios being very close to 1 for Gly-1 and Gly-2 conformers using the MP2/aug-cc-pVTZ optimized geometries.

Methylcarbamic acid

We only found four different low energy conformers for methylcarbamic acid and their MP2/aug-cc-pVTZ geometry optimized structures are shown in Fig. 2. We compute the MCA-1 to MCA-4 conformer relative energies to differ by 33.7 kJ mol^{-1} at the zero point vibrational energy corrected MP2/aug-cc-pVTZ level of theory. Methylcarbamic acid has

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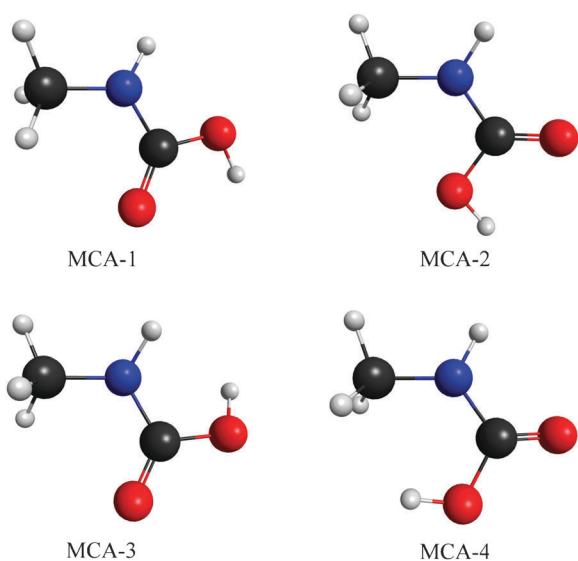*Phys. Chem. Chem. Phys.*, 2011, **13**, 15774–15784 | 15779

Fig. 2 The minimum energy structures of the methylcarbamic acid conformers optimized at MP2/aug-cc-pVTZ level (atom types: white = H, gray = C, blue = N, red = O, and figure in color is available in the online version).

fewer lower energy conformers than its isomer glycine because the N–H group cannot form intramolecular hydrogen-bonds with either of the two oxygen atoms in the neighboring carboxyl acid group. Instead MCA-1 and MCA-2 appears to form intramolecular C–H···O=C and C–H···O–H hydrogen bonds, respectively. While at 28.0 kJ mol^{-1} higher energy than MCA-1, the MCA-3 and MCA-4 conformers involve repulsions between the hydrogen atom on the carboxyl acid and the hydrogen on the NH or CH$_3$, respectively. The relative methylcarbamic acid conformer energies, with zero point vibrational energy corrections, for the different levels of theory are presented in Table 1. The bond lengths, bond angles and dihedrals of methylcarbamic acid conformers calculated at MP2/aug-cc-pVTZ level and a comparison of MCA-1 geometrical parameters at the different levels of theory are given in Table 6. The C–N–C–O backbones for all four MCA-1, MCA-2, MCA-3 and MCA-4 conformers are found to be non-planar: the conformer dihedral angles for C–N–C–O are 174.1, 5.7, 173.7 and 10.5°, and for C–N–C=O are 6.8, 174.9, 7.9, 170.4°, respectively. The non-planarity of C–N–C–O backbone can be traced to the lone pair on the nitrogen resulting in the four conformers having C–N–C bond angles of 120.8°, 124.6°, 117.6° and 125.7°, respectively. It is interesting in the various B3LYP calculations using different basis sets that the C–N–C–O dihedral angle in MCA-1 approaches 180° to give a planar backbone when the C–N–C bond angle is around 122°. This is in agreement with the previously reported B3LYP/6-311G(d,p) calculations by Lattelais et al.[37] which found the lowest energy methylcarbamic acid conformer to be planar with a C–N–C–O angle of 179.98° and a C–N–C=O angle of -0.03°. Apart from the dihedral angle differences, the most prominent bond length and bond angle differences among the four conformers in Table 6 are the increase in the N to carboxylic acid C distance and the reduction in the O=C–O bond angle in MCA-3 and MCA-4. These differences reflect steric repulsions between the H atom on the carboxyl acid and the H on the NH or CH$_3$.

Table 6 Geometrical parameters (bond lengths in Å, bond angles and dihedrals in ° for the methylcarbamic acid conformers

Calculation level	Conformer	CH$_3$–NH C–N	NH–CO$_2$H N–C	CO$_2$H C–O	CO$_2$H C=O	CO$_2$H O–H	CO$_2$H O=C–O	CH$_3$–NH–C C–N–C	CH$_3$–NH–CO$_2$H C–N–C–O	CH$_3$–NH–CO$_2$H C–N–C=O	CO$_2$H O=C–O–H
MP2/aug-cc-pVTZ	MCA-4	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
	MCA-1	1.447	1.352	1.364	1.216	0.967	123.5	120.8	174.1	6.8	0.2
MP2/aug-cc-pVDZ	MCA-1	1.457	1.362	1.376	1.227	0.971	123.6	120.0	171.9	9.3	0.2
MP2/6-311++G(d,p)	MCA-1	1.454	1.361	1.366	1.215	0.966	123.7	119.5	168.6	13.0	1.0
B3LYP/aug-cc-pVTZ	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-pVDZ	MCA-1	1.453	1.357	1.370	1.220	0.968	123.0	122.3	176.7	3.8	0.2
B3LYP/6-311++G(d,p)	MCA-1	1.453	1.355	1.368	1.213	0.966	123.0	122.7	179.6	0.5	0.0

Table 7 Vibrational frequencies (in cm^{-1}) for the methylcarbamic acid conformers. The IR intensities ($\times 10^{-17}$ cm molecule^{-1}) are given in parentheses

Level	Conformer	CO_2 bending	CO_2 wagging	C–O stretching	N–C stretching	C=O stretching	N–H stretching	O–H 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)

Table 8 Moment of inertia ($\times 10^{-45}$ kg m^2), rotational constants (in MHz) and dipole moments (in Debye) for the methylcarbamic acid conformers

Level	Conformer	Moment of inertia			Rotational constants			Dipole moment
		I_A	I_B	I_C	A_e	B_e	C_e	
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

The results from IR vibrational frequency calculations at the MP2/aug-cc-pVTZ level on the four optimized methylcarbamic acid conformers are given in Table 7. The frequencies for each vibrational modes generally show only a small dependence on the specific methylcarbamic acid conformer, with the main effects being determined by whether the carboxylic acid OH is on the same (MCA-1 and MCA-3) or opposite (MCA-2 and MCA-4) side of the molecule to the N–H bond. For instance, the C=O stretching vibration is the mode calculated to have the greatest intensity. The MCA-1 and MCA-3 conformers with O–H and N–H groups on the same side of the molecule give C=O stretching frequency (intensity) are 1815 cm^{-1} (7.58 $\times 10^{-17}$ cm molecule^{-1}) and 1834 cm^{-1} (6.02 $\times 10^{-17}$ cm molecule^{-1}), whereas MCA-2 and MCA-4 give 1823 cm^{-1} (10.86 $\times 10^{-17}$ cm molecule^{-1}) and 1839 cm^{-1} (9.70 $\times 10^{-17}$ cm molecule^{-1}), respectively. Likewise, the MCA-1 and MCA-3 pair (12126, 1120 cm^{-1}) and the MCA-2 and MCA-4 pair (1089, 1088 cm^{-1}) both have very similar C–O stretching vibrational frequencies, but the MCA-1 and MCA-2 vibrational intensities are much larger than the MCA-3 and MCA-4 intensities. Although experimental IR band positions and assignments for pure methylcarbamic acid are available,[33] these data belong to methylcarbamic acid dimer in which the methylcarbamic acid monomers interact with each other through their carboxylic acid groups. Hence this situation is expected to affect the fundamentals for the –CO$_2$H group, drastically. Consequently, the experimental methylcarbamic acid values at 1679 and 3062 cm^{-1} corresponding to C=O and O–H stretching modes in the dimer are quite far from our calculated values, 1815 and 3799 cm^{-1}, for the MCA-1 conformer.

The moments of inertia, rotational constants and dipole moments of methylcarbamic acid conformers are given in Table 8. We are not able to compare our data with experiment because, to the best of our knowledge, there is no published experimental data related to the moment of inertia, rotational constants and dipole moments of methylcarbamic acid available in the literature. At the MP2/aug-cc-pVTZ level, moment of inertia components of MCA-1 are found to be 0.78×10^{-45}, 2.03×10^{-45} and 2.76×10^{-45} kg m^2 while equilibrium rotational constants are found to be 10691.5, 4126.3, 3036.6 MHz for A_e, B_e and C_e respectively. Dipole moment of MCA-1 is calculated to be 2.465 Debye and it has an increasing trend for MCA-2, MCA-3 and MCA-4 conformers with 2.826, 4.824 and 5.556 Debye, respectively. Our rotational constants (10719.1, 4064.6, 3003.1 MHz) and dipole moment (2.383 Debye) for MCA-1 conformer calculated at the B3LYP/6-311G(d,p) level are in good agreement with previously reported correlated theoretical values (10714.5, 4088.3, 3016.2 MHz and 2.4 Debye)[37] obtained at the same level.

Comparison of the different computational methods

To more fully understand whether glycine can be formed in the ISM, or if instead the lower energy isomer methylcarbamic acid is preferentially formed, many larger calculations which incorporate interactions from the other molecules making up the ISM are needed. It is not computationally practical to perform these larger calculations at the MP2/aug-cc-pVTZ quality of theory, and in this section we compare how well more the feasible computations using the B3LYP density functional theory method and lower quality basis sets give conformer

energies, geometries and vibrational frequencies relative to the MP2/aug-cc-pVTZ calculations.

The energy calculations in Tables 1 and 2 show that using CCSD(T)/aug-cc-pVTZ and the MP2 and B3LYP methods with the aug-cc-pVTZ and aug-cc-pVDZ basis set produce very similar relative conformer energies for both glycine and methylcarbamic acid. Likewise the 3 sets of conformer relative energies obtained with CCSD(T), MP2 and B3LYP calculations and the 6-311++G(d,p) basis set are also very consistent with each other. However, we find the 6-311++G(d,p) basis set to systematically give slightly higher energies than the aug-cc-pVDZ and aug-cc-pVTZ for the high energy conformers Gly-6, Gly-7, Gly-8, MCA-3 and MCA-4. We also found that although the B3LYP calculations reproduce the MP2 relative energies for the individual series of either glycine or methyl-carbamic acid conformers, the B3LYP method gives slightly larger energy differences between the MCA-1 to Gly-1 conformers than those obtained with MP2 calculations which use the same basis set. Larger calculations become more computationally tractable with smaller basis sets. Tables 1 and 2 and Table S2 show that the B3LYP/6-311+G(d,p) still give reasonable conformer relative energies, but the elimination of the diffuse basis functions on the heavy atoms in the B3LYP/6-311G(d,p) calculations gives unacceptable conformer energies. Tables 1 and 2 and Table S2 also show that double zeta valence quality basis set augmented with a diffuse on the heavy atoms, that is the B3LYP/6-31++G(d,p), B3LYP/6-31+G(d,p) and even B3LYP/6-31+G(d), all give acceptable relative energies for the glycine and methyl carbamic acid conformers.

Tables 3 and 6 list the optimized geometrical parameters for lowest energy glycine Gly-1 and methylcarbamic acid MCA-1, respectively, obtained with the different computational methods. Our general finding is that the B3LYP results are the same as MP2 optimized geometry when both methods use the same basis set. The only real exception to this finding is that the B3LYP optimized MCA-1 conformer has a more planar C–N–C–O backbone and an approximately 2° wider C–N–C

bond angle than obtained in the MP2 optimized MCA-1 structures. Thus we expect no significant difference in the optimized geometries obtained with MP2/6-311++G(d,p) calculations and B3LYP calculations which use basis sets with a diffuse functions on the heavy atoms such as 6-311++G(d,p), 6-311+G(d,p), 6-31++G(d,p), 6-31+G(d,p). We also expect the B3LYP/6-31+G(d) calculations to give glycine and methyl-carbamic acid geometries very similar to the MP2/6-311++G(d,p) geometry. The MP2 and B3LYP optimized structures obtained by using the Dunning aug-cc-pVTZ and aug-cc-pVDZ basis sets do deviate very slightly from each other, although not significantly, and are consistent with the results from the 6-311++G(d,p) basis set. The same sort of comments can be made about how the different computational methods compute the Gly-1 and MCA-1 vibrational frequencies given in Tables 4 and 7, and Table S4 and S7. Once again we found the B3LYP/6-31+G(d) method to compute glycine and methylcarbamic acid vibrational frequencies which are very similar to those obtained with the MP2/6-311++G(d,p) calculations.

Table 9 provides a statistical analysis comparing how well the different levels of theory compute the relative energies for the different glycine and methylcarbamic acid conformers against the CCSD(T)/aug-cc-pVTZ energies using MP2/aug-cc-pVTZ optimized conformer geometries. The mean signed error (MSE), the mean unsigned error (MUE), the root mean squared deviation (RMSD) values are based on the combined relative energies for all of the glycine and methylcarbamic acid conformers, whereas R_{Gly}^2 and R_{MCA}^2 obtained from the linear fitting of relative energies of glycine and methylcarbamic acid conformers separately. The MSE data in Table 9 indicate that only CCSD(T)/6-311++G(d,p)//MP2/6-311++G(d,p) (-0.87 kJ mol^{-1}) and MP2/aug-cc-pVDZ (-1.11 kJ mol^{-1}) levels tend to reproduce lower relative energies with negative MSEs whereas all the other methods give higher energies varying from 1.30 kJ mol^{-1} [MP2/6-311++G(d,p)] to 17.40 kJ mol^{-1} (B3LYP/631G). The MUEs show that MP2/aug-cc-pVDZ level with an MUE of 1.39 kJ mol^{-1} performs better than

Table 9 Mean signed error (MSE), mean unsigned error (MUE), root mean squared deviation (RMSD) (all in kJ mol^{-1}), and R^2 values obtained at the different levels of theory for the relative energies of the glycine and methylcarbamic acid relative to the CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ results

Level	[a]MSE	[a]MUE	[a]RMSD	[b]R_{Gly}^2	[c]R_{MCA}^2	[d]R_{Av}^2
CCSD(T)/6-311++G(d,p)//MP2/6-311++G(d,p)	−0.87	2.58	3.03	0.9914	0.9989	0.9952
MP2/aug-cc-pVTZ	1.91	1.94	2.23	0.9973	0.9998	0.9986
MP2/aug-cc-pVDZ	−1.11	1.39	1.59	0.9994	0.9998	0.9996
MP2/6-311++G(d,p)	1.30	1.73	2.42	0.9952	0.9992	0.9972
B3LYP/aug-cc-pVTZ	5.05	5.14	6.16	0.9968	0.9985	0.9977
B3LYP/aug-cc-pVDZ	2.40	2.40	2.83	0.9935	0.9998	0.9967
B3LYP/6-311++G(d,p)	5.74	5.79	6.62	0.9965	0.9978	0.9972
B3LYP/6-311+G(d,p)	5.70	5.76	6.61	0.9965	0.9984	0.9975
B3LYP/6-311G(d,p)	9.47	9.47	10.72	0.9899	0.9984	0.9942
B3LYP/6-31++G(d,p)	6.39	6.49	7.45	0.9967	0.9953	0.9960
B3LYP/6-31+G(d,p)	6.47	6.58	7.56	0.9966	0.9941	0.9954
B3LYP/6-31+G(d)	10.43	10.50	12.17	0.9944	0.9938	0.9941
B3LYP/6-31G(d,p)	9.34	9.42	10.87	0.9920	0.9958	0.9939
B3LYP/6-31G(d)	12.74	12.81	14.95	0.9894	0.9952	0.9923
B3LYP/6-31G	17.40	17.40	19.82	0.9850	0.9943	0.9897

[a] MSE, MUE and RMSD values are based on the relative energies of both glycine and methylcarbamic acid. [b] R^2 values are based on the relative energies of the glycine conformers. [c] R^2 values are based on the relative energies of the methylcarbamic acid conformers. [d] The average of R_{Gly}^2 and R_{MCA}^2.

15782 | *Phys. Chem. Chem. Phys.*, 2011, **13**, 15774–15784

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the both MP2/aug-cc-pVTZ (1.94 kJ mol^{-1}) and CCSD(T)/6-311++G(d,p)//MP2/6-311++G(d,p) (2.58 kJ mol^{-1}). The superior performance of MP2/aug-cc-pVDZ level is a bit surprising because it performs better for the reference data which is based on CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ level than the MP2/aug-cc-pVTZ level itself. The RMSD and R^2 values also excellently agree with this situation. The MP2/aug-cc-pVDZ level has an RMSD of only 1.59 kJ mol^{-1} and R_{Av}^2 of 0.9996, whereas MP2/aug-cc-pVTZ has 2.23 kJ mol^{-1} and 0.9986, and CCSD(T)/6-311++G(d,p)//MP2/6-311++G(d,p) has 3.03 kJ mol^{-1} and 0.9952 of RMSD and R_{Av}^2, respectively. These findings make the MP2/aug-cc-pVDZ level "the choice" in the energy calculations of glycine and methylcarbamic acid conformer at a very reasonable computational cost within the all methods used in this study. Another interesting finding is, similar to what was found for the glycine and methylcarbamic acid geometries, adding diffuse functions to the hydrogen atoms do not have any considerable influence on the energies. On the other hand diffuse functions are important for the heavy atoms. The MUE, RMSD and R_{Av}^2 are found to be 5.79 kJ mol^{-1}, 6.62 kJ mol^{-1}, 0.9972 for B3LYP/6-311++G(d,p), 5.76 kJ mol^{-1}, 6.61 kJ mol^{-1} and 0.9975 for B3LYP/6-311+G(d,p) that are very similar to B3LYP/6-311++G(d,p) values, and 9.47 kJ mol^{-1}, 10.72 kJ mol^{-1}, 0.9942 for B3LYP/6-311G(d,p) that differ from other two levels quite much. Similar statistics are found for the double-zeta quality Pople type basis sets and although we even obtain slightly higher MUE, RMSD values of 10.50 kJ mol^{-1}, 12.17 kJ mol^{-1} for the B3LYP/6-31+G(d) calculations, the R_{Av}^2 value is still 0.9941 indicating that this level of theory should be adequate for performing calculations on larger systems. Hence, Table 9 suggests that inclusion of polarization functions at least to the heavy atoms are vital to compute reasonable energies.

Conclusions

We have theoretically investigated the low energy conformers of the glycine and methylcarbamic acid isomers using different levels of theory. Our most significant finding is that the most stable methylcarbamic acid MCA-1 conformer is appreciably lower in energy than the lowest energy glycine Gly-1 conformer. The MP2 level and the single point CCSD(T) calculations at the MP2 geometry indicate that the MCA-1 conformer is between 31 to 37 kJ mol^{-1} lower in energy than the Gly-1 conformer. We have found four low energy methylcarbamic acid conformers which, apart from the calculations using the 6-311++G(d,p) basis, are all lower in energy than the Gly-1 conformer. Because of the many different types of hydrogen bonding between the terminal amino and carboxylic acid groups there are eight low energy glycine conformers, instead of four which are found for methylcarbamic acid.

Although, methylcarbamic acid and glycine have not been detected in the ISM yet, the detection of methylamine, carbon dioxide and water in the ISM has been confirmed. The experimental studies discussed in the introduction, performed by Holtom et al.[31] and Bossa et al.[33–35] using methylamine and carbon dioxide and by Lee et al.[36] using methylamine, carbon dioxide and water as reactants to investigate interstellar glycine, all commonly indicated that methylcarbamic acid is also formed in the intermediate steps of the reactions. The theoretical results obtained in this study supports these experimental findings suggesting that methylcarbamic acid might play a role as a precursor in the formation of glycine. More quantum chemistry calculations are needed to aid in understanding how methylcarbamic acid and glycine might be formed, where the required calculations should model how glycine and methylcarbamic acid interact with neighboring molecules present in the icy grains in the ISM. However, MP2 calculations with large basis sets are not computationally feasible as a routine method for modeling glycine or its isomer in the presence of, for example, several water molecules. The computation requirements for B3LYP calculations scale much more favorably with system size than MP2 calculations. The present calculations demonstrate that B3LYP computes conformer energies, geometries and vibrational frequencies which agree well with the MP2 results and should provide a reliable and more computationally practical approach to modeling these larger systems. An important ingredient for the basis set used in B3LYP calculation is that it should include a diffuse basis function on the heavy atoms. We find that even the small 6-31+G(d) basis gives useful results which should facilitate large exploratory calculations for different geometries of either a glycine or methylcarbamic acid isomer surrounded by several of the neighboring molecules present in an icy grain.

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Phys. Chem. Chem. Phys., 2011, 13, 15774–15784 | 15783

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