Optics and Spectroscopy, 2023, Vol. 131, No. 6

20

The effect of recrystallization on the IR spectrum of modified glycine

© I.L. Plastun[1], P.A. Zhulidin[1], P.D. Filin[1], R.Yu. Yakovlev[2]

[1] Gagarin Saratov State Technical University, Saratov, Russia
[2] Nauchny Tsentr RTA LLC
121205 Moscow, Russia

e-mail: inna_pls@mail.ru

Received December 28, 2022
Revised February 16, 2023
Accepted February 21, 2023

An explanation is given for the change in the physicochemical and spectral characteristics of glycine resulted from its modification. The experimentally measured infrared (IR) spectra of glycine were compared with the spectra calculated by the methods of the density functional theory. The effect of single water molecules associated with glycine after the recrystallization procedure was analyzed. The effect of hydrogen bonding on the change in the spectral characteristics and physicochemical properties of modified glycine is evaluated.

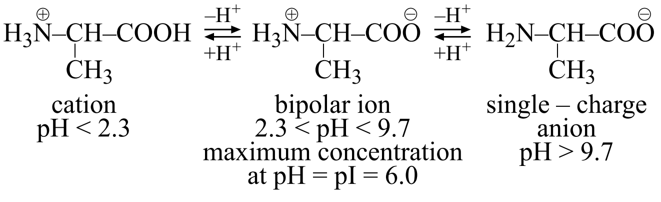
Keywords: glycine, molecular modeling, IR spectrum, density functional theory, hydrogen bonds, cryochemical recrystallization, experimental measurements.

DOI: 10.61011/EOS.2023.06.56667.118-23

Introduction

Glycine (Gly) is a proteinogenic amino acid with the lowest molecular weight, which is composed of two hydrophilic ($-NH^+$, $-COO^-$) and one hydrophobic ($-CH_2$) groups and contains a single hydrogen atom as a side chain. Studies of the physicochemical properties of glycine began quite a long time ago and continue up to the present [1–4]. In particular, it was found that neutral glycine is in the gaseous phase, however, in an aqueous solution and in a solid state in a neutral medium (pH 7), the zwitterionic (ZW) form of glycine shows greater stability than the neutral one. The zwitterionic form, which has a large local charge and a large dipole moment, has strong interactions with water [5]. The process of transformation from neutral to zwitterionic form is described as a direct transition of a proton between two functional groups: from the carboxyl group ($-COO^-$) to the amino group ($-NH^+$) [6] (Fig. 1).

Glycine is one of components of many animal and plant proteins used in living cells for the synthesis of porphyrins which form an integral part of hemoglobin in combination with iron ions. Glycine as a drug is used in neurological practice to remove increased muscle tone, improve metabolism and prevent brain cell death after a stroke [7]. Also, the study reported in [8] proved that glycine, when taken orally in sufficiently high doses (3–9 g), improves the quality of sleep and does not cause serious side effects.



$$\overset{\oplus}{H_3N}-\underset{CH_3}{CH}-COOH \underset{+H^+}{\overset{-H^+}{\rightleftarrows}} \overset{\oplus}{H_3N}-\underset{CH_3}{CH}-CO\overset{\ominus}{O} \underset{+H^+}{\overset{-H^+}{\rightleftarrows}} H_2N-\underset{CH_3}{CH}-CO\overset{\ominus}{O}$$

Figure 1. Ionic forms of glycine.

In recent years, in order to achieve a greater therapeutic effect, much attention has been paid to the search for ways to increase the bioavailability and solubility of poorly soluble drugs. The problem of solubility has forced pharmaceutical companies to look for different approaches to increase the solubility of drugs using chemical and physical manipulations with the active substance, as well as the selection of new carriers of active substances. The chemical method includes the molecular modification of a drug resulting in the formation of new chemical bonds or a change in the structure of substances. Physical methods for increasing solubility work on the principle of reducing the size and increasing the area of the contact surface [9].

Nauchny Tsentr RTA LLC, a developer of new polymorphic modifications of medicinal substances and their co-crystals, which are unattainable under normal synthesis conditions, has recently proposed a new scheme for the modification of glycine. It is based on the technology of cryochemical recrystallization of organic substances, based on the theory of the relative stability of crystalline modifications of the same compound, the Ostwald's step rule [10]. As a result, researchers of the company have succeeded in obtain changes in the morphology of glycine. In the course of the conducted experiments with volunteers, it was found that when glycine is modified, the therapeutic effect increases: the sedative effect occurs faster and at a lower dosage. For comparison, the standard dose for modified glycine is 0.25 g of the substance, while before modification a dose of 1 g is required. The process proposed by Nauchny Tsentr RTA LLC does not involve chemical synthesis but is based on the technology of recrystallization

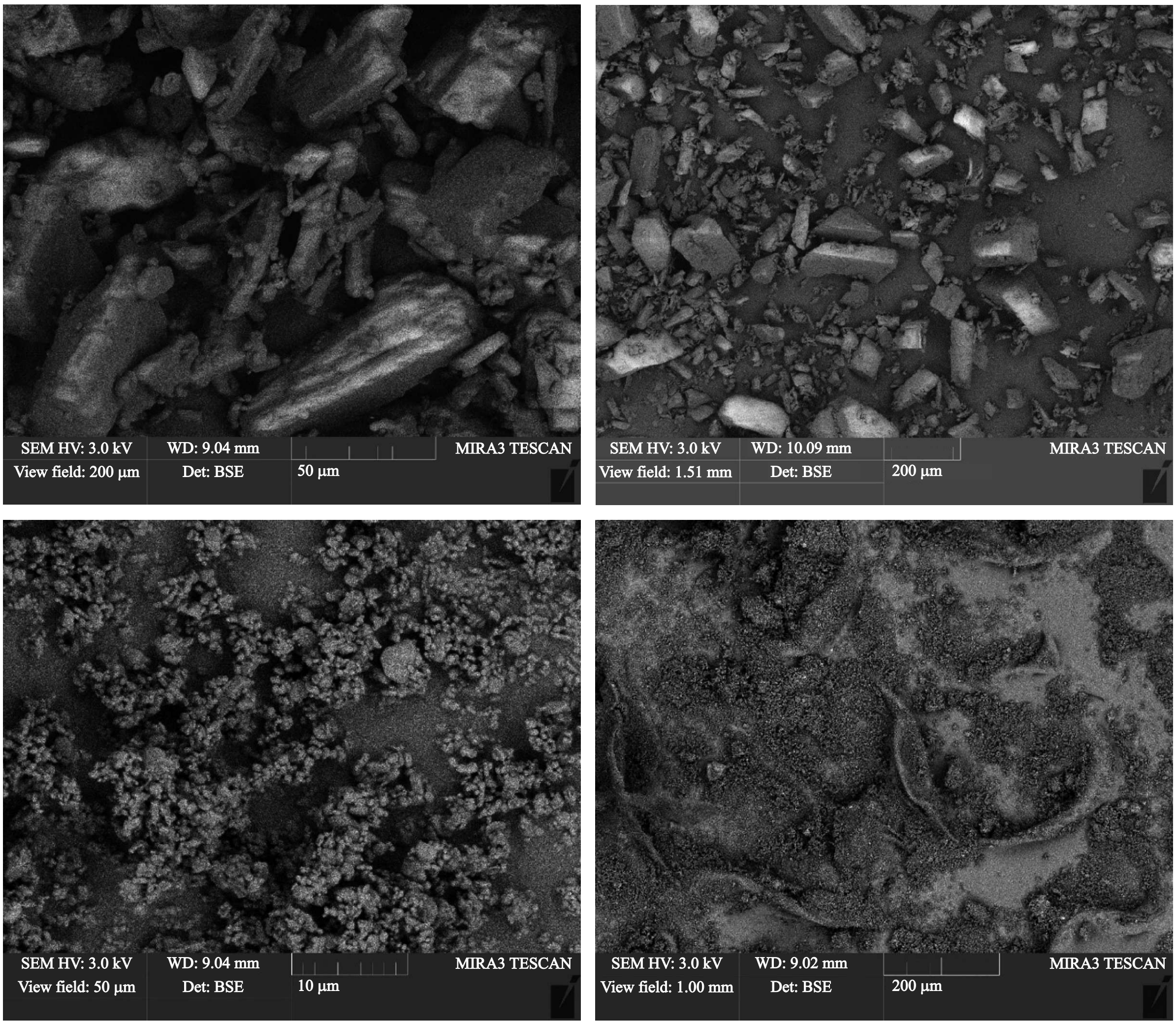


Figure 2. Scanning electron microscopy images of glycine crystals before (top) and after (bottom) modification.

of a ready-made pharmaceutical substance in order to give it new useful properties that affect the efficiency of use.

The purpose of this study is to determine the factors affecting the change in the physicochemical properties and morphology of glycine after modification, and to find out the role of single water molecules by analyzing the calculated structure and comparing the experimentally measured and calculated IR spectra of glycine.

Experimental results

The technology for obtaining a modified form of glycine, developed by Nauchny Tsentr RTA LLC, is based on the technology of cryochemical recrystallization of organic substances and consists of several defining stages: 1) dissolution of glycine until a true solution is formed; 2) obtaining molecules in high-energy conformations, which is achieved by exposing the solution to laser or ultraviolet radiation; 3) cooling/freezing of the solution; 4) lyophilisation. The procedure for obtaining a modified form of glycine is as follows: a weighed portion of glycine (Fluka, USA) weighing 1 g was introduced into a glass beaker containing 50 ml of distilled water, stirred for 10 min at 50 ° C and frozen in liquid nitrogen, lyophilisation was carried out on a Heto 2.5 freeze dryer at a pressure of 0.15 mbar and a temperature of 20 °C for 36 h.

As shown by experimental studies conducted at Nauchny Tsentr RTA LLC, a significant change in the morphology of glycine crystals takes place after the modification (Fig. 2). The study of morphological characteristics was carried out using a TESCANMIRA3 scanning electron microscope (Czech Republic) with a resolution of up to 5 μm (3.0 kV) with a BSE detector. The minimum field of view was 5 μm, the maximum field of view was 200 μm. A significant increase in the specific surface area of glycine was found: from 0.08 m^2/g before the modification to 6.3 m^2/g after the modification. Based on the photos obtained by scanning electron microscopy (Fig. 2), it is clearly seen that the glycine nanoparticles have undergone a restructuring during cryochemical recrystallization.

IR radiation spectra (Fig. 3) were recorded on a SpectrumTwo IR Fourier spectrometer (PerkinElmer, USA) with a diffuse reflectance attachment (without KBr tableting) in the range of 4000–600 cm^{-1} with a resolution of 2 cm^{-1} at a temperature of 20 °C. It can be seen that after modification in the IR spectrum of glycine, a slight decrease in intensity is observed in the range from 800 to 3100 cm^{-1} and there is a sharp increase in intensity in the range from 3200 to 3800 cm^{-1} (Fig. 3). At the same time, the behavior of the spectrum in the high-frequency region changes. This may be indicative of the presence of single water molecules in the modified glycine because the region of the sharp increase in intensity coincides with the fundamental frequencies of the water spectrum. For a deeper analysis of the obtained experimental data, it is necessary to calculate the structure of the IR spectra of glycine and its complexes with water.

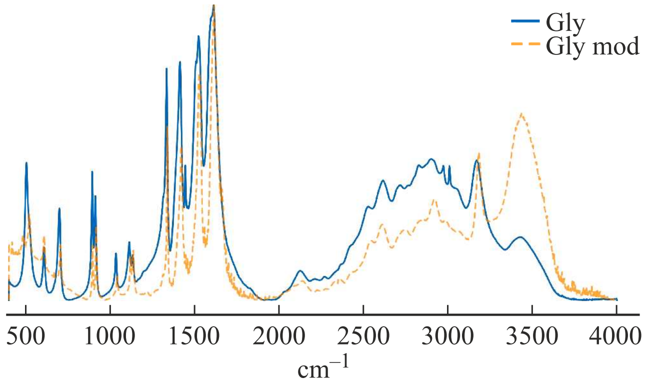


Figure 3. Experimental IR spectra of glycine (blue — before modification, yellow — after modification).

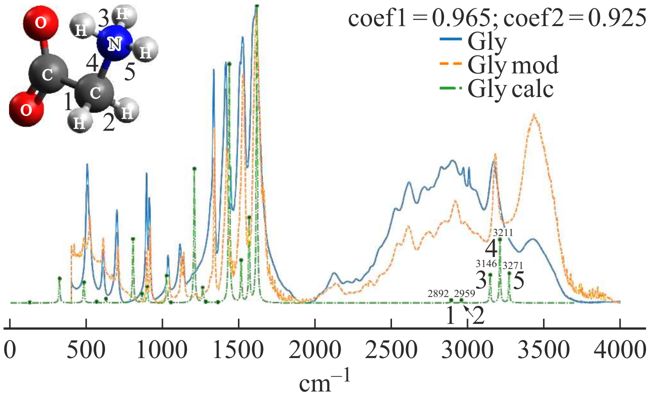


Figure 4. Calculated structure (top) and IR spectra (bottom) of glycine (blue — experimental, orange — experimental modified, green — calculated). Numbers 1–5 show peaks corresponding to vibrations of –CH (1, 2) and –NH (3–5) groups.

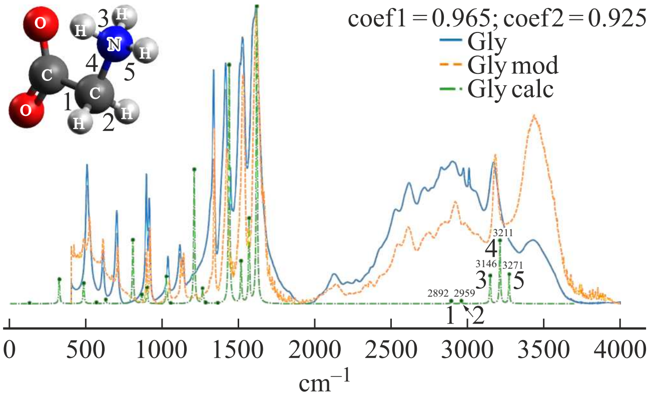


Figure 5. Calculated structure (top) and IR spectra (bottom) of glycine with two water molecules (blue — experimental, orange — experimental modified, green — calculated). Numbers 1–5 show bonds and spectral lines corresponding to vibrations of –CH (1, 2) and –NH (3–5) groups.

Computer modeling of IR spectra of glycine

Modeling of the structure and calculation of the spectra of molecules and their complexes was carried out on the basis of the density functional theory (DFT) [11] using the B3LYP functional and the 6–31++G (3D2F,3P2D) basis set [12]. All molecular modeling procedures, including optimization of molecular structures and calculation of IR spectra, were carried out on the basis of the Gaussian software package [13], which is widely used to solve molecular modeling problems in various fields of computational physics and chemistry, using the Avogadro editor and visualizer of molecular structures [14] and the author IR spectra visualization program that builds the IR spectrum from the numerical values obtained in the Gaussian software.

To improve the matching between the measured and calculated spectra, frequency scaling, which is widely used in world practice, was carried out [15,16]. The scaling factors used were as follows: 0.965 for the frequency range of 0–2000 cm^{-1} and 0.925 for the frequency range of 2000–4000 cm^{-1}.

Energies are minimized, various structures of glycine are optimized using molecular modeling methods: Gly, Gly+$n \cdot H_2O$ (where $n = 2, 3$), 2Gly, 2Gly+$4H_2O$ and 4Gly+$8H_2O$.

To identify the causes of the change in the physicochemical properties of glycine during its modification, it should be noted that at the first stage of modification of glycine crystals, a true solution is created, during which the crystals of the substance are dissolved in water and then frozen at a low temperature. Therefore, it can be assumed that the influence of residual water even after lyophilization can be quite significant. In this regard, it is necessary to analyze and evaluate the degree of influence of water molecules, as well as hydrogen bonding [17] on glycine monomer and polymer

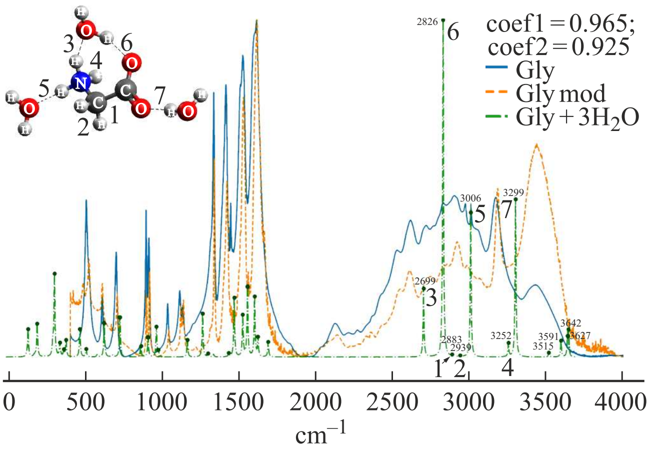


Figure 6. Calculated structure (top) and IR spectra (bottom) of glycine with three water molecules (blue — experimental, orange — experimental modified, green — calculated). Numbers 1–7 show bonds and spectral peaks corresponding to these bonds.

molecules in order to find out the causes and mechanisms of changes in physicochemical properties.

The structure and IR spectrum of the molecular complex of glycine with water was modeled with the successive addition of water molecules to the monomer, dimer and tetramer of glycine. All calculations were carried out for a temperature of 20 °C that corresponds to the experimental conditions. The strength of the formed hydrogen bonds was evaluated by the following characteristics: by the length of the hydrogen bridge, the frequency shift of bond vibrations in the IR spectra of the molecular complex relative to the IR spectrum of individual molecules, and also by the bond energy.

The calculated structure and IR spectrum of the $C_2H_5NO_2$ glycine monomer are shown in Fig. 4. Dots indicate the calculated peaks of the frequencies of vibrations of glycine bonds, superscripts above the dots indicate frequencies of the vibration peaks. Oxygen atoms (O) are marked in red, carbon atoms (C) are marked in dark gray, nitrogen atoms (N) are marked in blue, hydrogen atoms (H) are marked in light gray. The graph in Fig. 4 shows good matching between the calculated and measured IR spectra. Numbers 1–5 show peaks corresponding to vibrations of –CH (1, 2) and –NH (3–5) groups. Vibrations of the –NH amino group correspond to peaks with frequencies of 3146, 3211, 3271 cm^{-1}.

To identify the effect of water, the intermolecular interaction of glycine with two water molecules $(C_2H_5NO_2)-(H_2O)_2$ (Fig. 5) and with three water molecules $(C_2H_5NO_2)-(H_2O)_3$ (Fig. 6) was numerically modeled.

The calculated structure and IR spectrum of the $(C_2H_5NO_2)_2$ glycine dimer are shown in Fig. 7. In this case, the complex of two glycine molecules forms pair bonding between the amino group and carboxyl group, and the bonds are indicated as 4A, 4B. The 4A bond responsible for the formation of the dimer is stronger than the others. It can be seen that the peak corresponding to this bond and appearing at a frequency of 2117 cm^{-1} is also present in the experimental spectrum, which is indicative of the presence of dimers in the composition of the modified glycine.

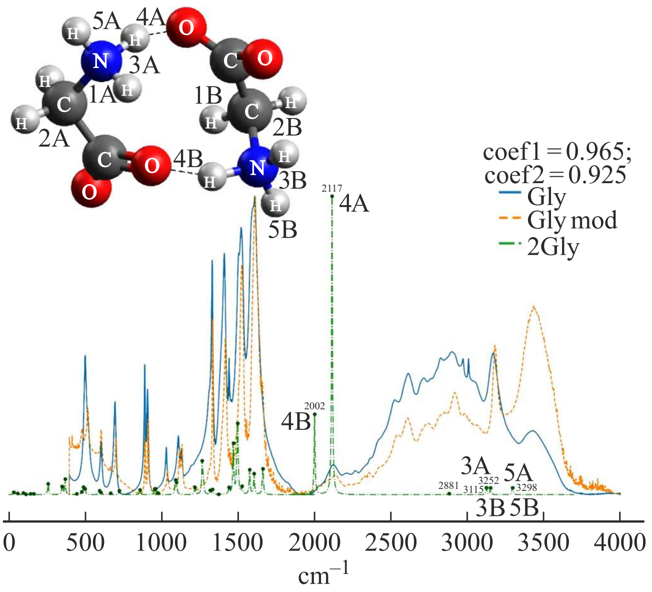


Figure 7. Calculated structure (top) and IR spectra (bottom) of glycine dimer (blue — experimental, orange — experimental modified, green — calculated). Symbols 1A–5A and 1B–5B show bonds and spectral peaks corresponding to these bonds.

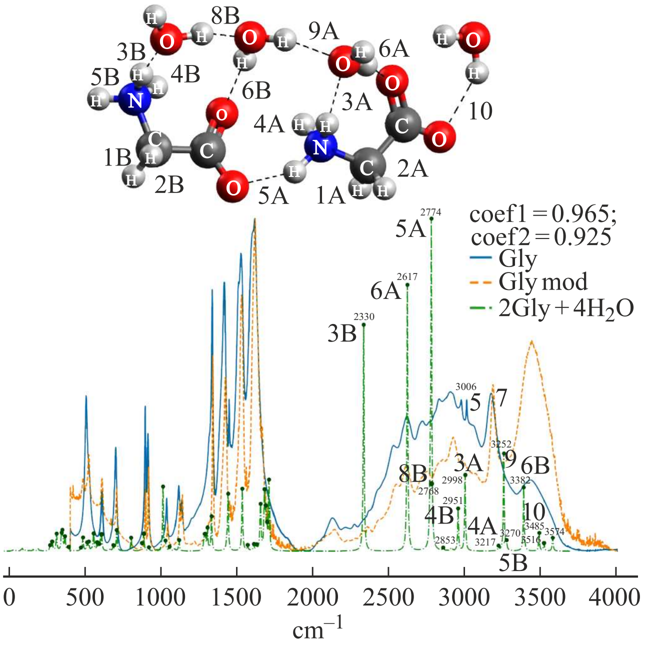


Figure 8. Calculated structure (top) and IR spectra (bottom) of the molecular complex of glycine dimer with water (blue — experimental, orange — experimental modified, green — calculated). Symbols 1A–8A and 1B–9B, 10 show bonds and spectral peaks corresponding to these bonds.

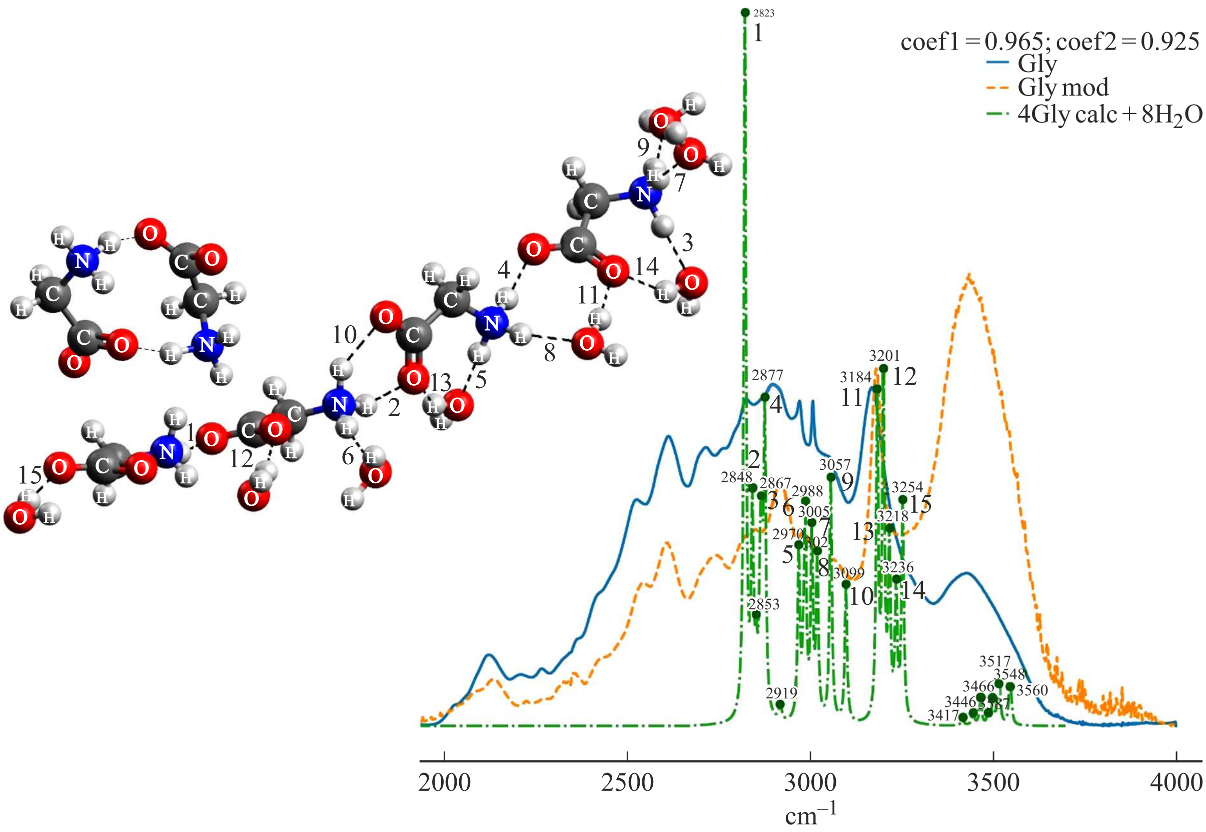


Figure 9. Calculated structure (upper left) and IR spectra (lower right) of four glycine molecules with eight water molecules (blue — experimental, orange — experimental modified, green — calculated).

Calculated structure and IR spectrum of a glycine dimer with four water molecules $(C_2H_5NO_2)_2-(H_2O)_2$ are shown in Fig. 8. The vibrational frequencies of the hydrogen bonds in the calculated spectrum coincide with the peaks of the measured IR spectrum of the modified glycine. This is clearly seen in the high-frequency range of $3200-3610\,\text{cm}^{-1}$. Peaks of free water bonds are located in the region higher than $3650\,\text{cm}^{-1}$.

Calculated structure and IR spectrum of four glycine molecules with eight water molecules $(C_2H_5NO_2)_4-(H_2O)_8$ are shown in Fig. 9. The calculation of this structure demonstrates even greater agreement with the experiment. In comparison with the previous Fig. 5, 6 and 8, Fig. 9 shows that with a multiple increase in the number of glycine molecules and water molecules, an increase is observed in the number of hydrogen bonds formed in the characteristic frequency range corresponding to the stretching vibration of the OH bond of water $(3300-3650\,\text{cm}^{-1})$.

Hydrogen bonding evaluation

Now let us consider separately various complexation combinations of glycine with water and analyze the dynamics of changes in the parameters of the most significant hydrogen bonds. The strength of the formed hydrogen bonds was evaluated by the following characteristics: the length of the hydrogen bridge, the frequency shift of stretching vibrations of H-bonds in molecular complex IR spectra relative to the IR spectrum of individual molecules.

Tables 1 and 2 summarize the following bond parameters: type, R — initial H-bond length, R_b — $N-H\cdots O$ or $O\cdots H-O$ hydrogen bridge length (depending on the bond type), I_{IR} — spectral line peak intensity, $\Delta\nu$ — frequency shift of stretching vibrations of bonds in IR spectra of the molecular complex relative to the IR spectrum of individual molecules, necessary to calculate the bond energy using the empirical Iogansen's formula [18]:

$$-\Delta H = 0.3 \cdot \sqrt{\Delta\nu - 40}. \tag{1}$$

The calculated parameters of hydrogen bonds for molecular complexes of glycine with water molecules are given in Tables 1, 2, where E is the energy of the molecular complex. The strength of the formed hydrogen bonds was evaluated in accordance with the classification given in [19], where hydrogen bonds are considered strong when their energy is 14.34−28.65 kkal/mol and the hydrogen bridge length is 2.2−2.5 Å the medium bond energy is in the range of 3.82−14.43 kkal/mol, and the hydrogen bridge length is 2.5−3.2 Å the energy of weak bonds is less than 2.87 kkal/mol, and the length of their hydrogen bridge is 3.2−4.0 Å.

Table 1. Calculated parameters of hydrogen bonds of the glycine-water H-complex

Bond number	Bond type	R, Å	R_b, Å	ν, cm^{-1}	$\Delta\nu$, cm^{-1}	ΔH, kkal/mol	I_{IR}, *km/mol*
Glycine $E = -284.334404$ a. u.							
1	C–H	1.09		2882			7.00
2	C–H	1.09		2947			9.00
3	N–H	1.02		3147			35.45
4	N–H	1.03		3212			81.50
5	N–H	1.02		3271			37.64
Glycine with two water molecules, $E = -437.237263$ a. u.							
1		1.09		2885			5.80
2		1.09		2941			3.67
3		1.02		3142			82.55
4	N–H$\cdots$O	1.6	2.55	2720	491.71	6.38	341.85
5	N–H$\cdots$O	1.81	2.84	3050	221.30	4.04	581.25
6	O$\cdots$H–O	1.7	2.64	2828			1545.57
Glycine with three water molecules, $E = -513.677916$ a. u.							
1		1.09		2883			3.05
2		1.09		2939			2.69
3	N–H$\cdots$O	1.65	2.64	2700	447.10	6.05	335.94
4		1.022		3253			64.54
5	N–H$\cdots$O	1.78	2.81	3007	264.66	4.50	710.48
6	O$\cdots$H–O	1.59	2.54	2827			1662.87
7	O$\cdots$H–O	1.8	2.78	3299			785.46

Let us consider variants of complexation of glycine monomer with water. Numbers of bonds correspond to each other in different variants. As can be seen from Table 1, when two water molecules are added to the amino group of glycine, two N–H$\cdots$O hydrogen bonds are formed with frequency shifts of 531 and 239 cm^{-1}. They have corresponding spectral peaks with intensities of 342 and 581 kkal/mol. An O$\cdots$H–O bond was also formed with an intensity of 1546 kkal/mol. All three bonds are classified as medium strength hydrogen bonds.

When one more water molecule is added to the monomer, bond 5 from Table 1 is strengthened, which is confirmed by an increase in the frequency shift to 286.12 cm^{-1}, a decrease in the length of the hydrogen bridge, and an increase in the intensity of the spectral peak to 710 kkal/mol. According to the classification of [19], this is a medium-strength bond. The resulting N–H$\cdots$O bond (indicated as bond 3) has a spectral peak intensity of 336 kkal/mol, a frequency shift of 483 cm^{-1}, and also is classified as a medium-strength bond. Due to this bond, the complex has become more stable. The addition of water molecules gives additional peaks in the IR spectrum of the resulting molecular complex (Fig. 5, 6), coinciding with the spectral peaks of the measured IR spectrum of the modified glycine.

Calculation of the IR spectrum both for the glycine dimer and for the monomer showed that the intensity of peaks in the high-frequency range of the spectrum is insignificant. In case of the $(C_2H_5NO_2)_2$ complex, the hydrogen bonds formed when two molecules of glycine are joined together are characterized by high intensity. Frequencies of these bonds are 2003 (bond 4A) and 2117 cm^{-1} (bond 4B). The strength of these bonds is confirmed by high bond energies (10.15 and 10.68 kkal/mol, respectively) and high intensities: 698.73 and 2593.67 km/mol. Thus, these bonds can be classified as medium-strength bonds approaching strong bonds.

Table 2. Calculated parameters of hydrogen bonds of the H-complex of glycine dimer-water

No. bond	Bond type	R, Å	R_b, Å	ν, cm^{-1}	$\Delta\nu$, cm^{-1}	ΔH, kkal/mol	I_{IR}, km/mol
Glycine dimer $E = -568.756390$ a. u.							
1A		1.09		2878			5.50
2A		1.09		2950			1.15
3A		1.03		3126			58.69
4A	N–H···O	1.5	2.56	2117	1094.86	9.74	2593.67
5A		1.02		3295			43.52
1B		1.09		2882			6.54
2B		1.09		2960			1.79
3B		1.03		3152			57.42
4B	N–H···O	1.47	2.54	2003	1208.96	10.26	698.73
5B		1.02		3300			42.65
Glycine dimer with four water molecules, $E = -874.532981$ a. u.							
1A		1.09		2854			13.00
2A		1.09		2902			10.00
3A	N–H···O	1.86	2.80	2999	113	2.56	452.00
4A		1.02		3217			27.00
5A	N–H···O	1.73	2.71	2775	604	7.12	1920.00
6A	O···H–O	1.55	2.55	2618			1581.00
9	O···H–O	1.79	2.74	3252			588.00
1B		1.09		2857			8.00
2B		1.09		2913			10.00
3B	N–H···O	1.57	2.63	2331	781	8.16	1345.00
4B		1.04		2952			251.00
5B		1.02		3271			43.00
6B	O···H–O	1.89	2.83	3383			383.00
8B	O···H–O	1.6	2.59	2768			34200
10	O···H–O	2.12	2.94	3485			108.00

The structure and IR spectrum of the complex of glycine dimer with four water molecules were calculated in a way similar to that for the variants of the complex of glycine monomer with water; the parameters are listed in Table 2. A high intensity of hydrogen bond formation was noted in the high-frequency range from 3200 to 4000 cm^{-1} of the calculated IR spectrum. It is also worth noting that the N–H···O bond (indicated as bond 5A), which forms a dimer, has a bond energy lower than that of a dimer without water. When comparing the parameters of the hydrogen bonds of the complexes, it can be concluded that the energy was redistributed towards water molecules.

Based on the calculation of glycine tetramer, a qualitative assessment of its IR spectrum was carried out. The analysis has shown that with an increase in the number of water and glycine molecules, a large number of hydrogen bond peaks are formed, which are in the range of the valence band of water and coincide with the experimental IR spectrum of the modified glycine.

Conclusions

As a result of studying the physicochemical properties of glycine modified by recrystallization, based on the results of scanning electron microscopy, a change in the crystal morphology, a significant increase in the specific surface area of glycine, and a change in the IR spectrum in the high-frequency region were found.

It was assumed that the spectral characteristics of glycine are affected by single water molecules remaining in the structure of the modified glycine after the recrystallization, leading to a looser crystal structure, and as a result — to a higher degree of solubility due to a significant increase in the specific surface area of glycine .

The effect of single water molecules was found by comparing the measured IR spectra of the original and modified glycine, which clearly shows that after the modification of glycine, the intensity of the band corresponding to the spectrum of water increases significantly.

To confirm this assumption, calculations of the molecular structure and IR spectra of glycine with water were performed and parameters of the resulting hydrogen bonds were analyzed. It was found that when water molecules are added to the monomer, dimer, and tetramer of glycine, an increase in the intensity of the peaks in the high-frequency region of the IR spectrum corresponding to the spectrum of water is observed, as well as the appearance of peaks corresponding to the bonds of water with the amino group and carboxyl group of glycine. The same spectral peaks are also observed in the measured IR spectrum, which is indicative of the presence of intermolecular interaction between water and glycine and the effect of single water molecules on the IR spectrum of the modified glycine.

The analysis of the results of the intermolecular interaction of glycine with water molecules shows that after the recrystallization procedure, single water molecules remain in the modified glycine, interaction with which leads to a change in the physicochemical properties of the modified glycine, which is manifested in a significant increase in the dissolution rate and bioavailability of glycine. This effect can be detected by changes in the IR spectrum of glycine after the modification.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] M. Pita, R. Mosquera. Compounds, **2**(4), 252–266 (2022). DOI: 10.3390/compounds2040021

[2] G. Albrecht, R. Corey. J. Am. Chem. Soc., **61**, 1087–1103 (1939). DOI: 10.1021/ja01874a028

[3] Y. Ding, K.J. Krogh-Jespersen. J. Comput. Chem., **17**, 338–349 (1996). DOI: 10.1002/(SICI)1096-987X(199602)17:3%3C338::AID-JCC8%3E3.0.CO;2-W

[4] W. Wang. J. Mol. Struct., **618**(3), 235–244 (2002). DOI:10.1016/s0166-1280(02)00543-2

[5] S.E. Kruchinin, M.V. Fedotova, Zhurnal fiz. khim., **86** (12), 1968–1973 (2012) (in Russian).

[6] K. Leung, S. Rempe. J. Chem. Phys., **122**(18), 184506(2005). DOI: 10.1063/1.1885445

[7] O.A. Gromova, I.Yu. Torshin, E.I. Gusev, A.A. Nikonov, O.A. Limanova, Trudny patsient, **8** (4), 25–31 (2010) (in Russian).

[8] M. Bannai, N. Kawai. J. Pharm. Sci., **118**(2),145–148 (2012). DOI:10.1254/jphs.11r04fm

[9] *Advanced Topics in Crystallization*, ed.by Yitzhak Mastai (IntechOpen, London, United Kingdom, 2015), P. 191–211. DOI: 10.5772/59627

[10] M. Volmer. *Kinetics of Phase Formation* (Steinkopf Verl, Leipzig, 1939), 220 p.

[11] W. Kohn. Rev. Mod. Phys, **71** (5), 1253–1265 (1999). DOI: 10.1103/RevModPhys.71.1253 .

[12] A.D. Becke. J. Chem. Phys., **98** (7), 5648–5652 (1993). DOI: 10.1063/1.464913

[13] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr.T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, W. Wong, C. Gonzalez, J.A. Pople. *Gaussian03, Revision B.03* (Gaussian, Inc., PittsburghPA, 2003), 302 p.

[14] Avogadro - Free cross-platform molecular editor. [Electronic source]. URLhttps://avogadro.cc/

[15] H. Yoshida, A. Ehara, H. Matsuura. Chem. Phys. Lett., **325**(4), 477–483 (2000). DOI: 10.1016/S0009-2614(00)00680-1

[16] H. Yoshida, K. Takeda, J. Okamura, A. Ehara, H. Matsuura. J. Phys. Chem. A., **106**(14), 3580–3586 (2002). DOI: 10.1021/jp013084m

[17] I.V. Krakulis, A.V. Tulub, A.V. Golovin, V.P. Chelibanov. Opt. Spectrosc., **128** (10), 1488 (2020). DOI: 10.1134/S0030400X20100161.

[18] A.V. Iogansen, *Vodorodnaya svyaz* (Nauka, M.,1981),p. 112–155 (in Russian).

[19] J.V. Steed, J.L. Atwood, *Supramolekulyarnaya khimiya* (Akademkniga, M., 2007), v. 479.

Translated by Y.Alekseev