

This is a self-archived version of an original article. This version may differ from the original in pagination and typographic details.

Author(s): Krupa, Justyna; Kosendiak, Iwona; Wierzejewska, Maria; Lundell, Jan

Title: Experimental and theoretical investigation of hydrogen bonded complexes between glycolic acid and water

Year: 2025

Version: Published version

Copyright: © 2024 The Authors. Published by Elsevier B.V.

Rights: CC BY 4.0

Rights url: <https://creativecommons.org/licenses/by/4.0/>

Please cite the original version:

Krupa, J., Kosendiak, I., Wierzejewska, M., & Lundell, J. (2025). Experimental and theoretical investigation of hydrogen bonded complexes between glycolic acid and water. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 325(15), Article 125081. <https://doi.org/10.1016/j.saa.2024.125081>



Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.journals.elsevier.com/spectrochimica-acta-part-a-molecular-and-biomolecular-spectroscopy



Experimental and theoretical investigation of hydrogen bonded complexes between glycolic acid and water

Justyna Krupa^{a,*}, Iwona Kosendiak^a, Maria Wierzejewska^a, Jan Lundell^{b,*}

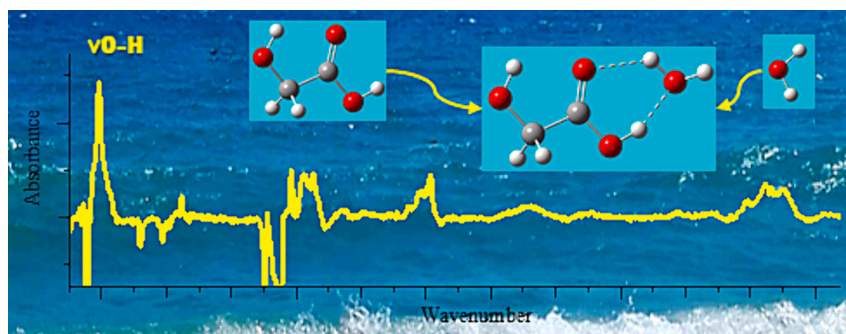
^a Faculty of Chemistry, University of Wrocław, Joliot-Curie 14, 50-383 Wrocław, Poland

^b Department of Chemistry, University of Jyväskylä, FI-40014 Jyväskylä, Finland

HIGHLIGHTS

- Experimental identification of glycolic acid–water 1:1 complexes for the first time.
- Identification of hydrogen bonded GA–H₂O structures present in an argon matrix.
- Computational modelling of structures and spectroscopy of 1:1 complexes between GA and H₂O.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Glycolic acid
Molecular complex
Spectroscopy
Computational chemistry
Matrix isolation
Hydrogen bond

ABSTRACT

Theoretical MP2 and B3LYPD3 calculations, as well as experimental matrix isolation infrared spectroscopy studies, were used to investigate the 1:1 complexes formed between glycolic acid and water. Out of five computationally predicted forms of GA···H₂O complex the most stable one was detected experimentally in solid argon. This structure is characterized by two intermolecular O—H···O hydrogen bonds depicting a six-member ring in which water acts both as a proton acceptor and as a proton donor. Two other structures with the alcoholic OH group acting as a proton donor are also tentatively suggested to be present in solid argon.

1. Introduction

Glycolic acid (GA) is the smallest α -hydroxycarboxylic acid having two functional OH groups in the same molecule, and it is therefore able to form intra- and intermolecular hydrogen bonds. Also, GA is a model species for understanding how competing OH-groups in a molecule affect the ability to form molecular complexes.

The molecular structure and especially probing the conformational space of GA have been the focus of many studies in the gas phase [1–6], solid state [7] and low temperature matrices [8–13]. The most stable SSC conformer of the acid (see Scheme 1) was found to be the predominant species in gas, solid and low-temperature matrix phases. In addition to conformational studies, the OH overtone and UV induced photochemical transformations in low temperature matrices were investigated as

* Corresponding authors.

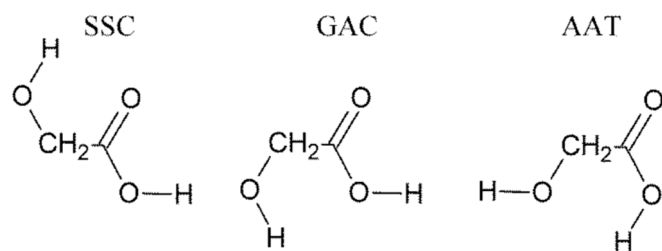
E-mail addresses: justyna.krupa@uwr.edu.pl (J. Krupa), jan.c.lundell@jyu.fi (J. Lundell).

<https://doi.org/10.1016/j.saa.2024.125081>

Received 19 May 2024; Received in revised form 30 July 2024; Accepted 29 August 2024

Available online 30 August 2024

1386-1425/© 2024 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).



Scheme 1. Structure of three most stable conformers of glycolic acid monomer.

well. Near-infrared excitation of the first and second OH stretching overtones of GA were found to initiate conformational photoisomerization reactions [9–11,14], allowing selective formation and identification of less stable conformers. By contrast, excitation using visible green light (532 nm), both forward and backward photoreactions subsequently to IR-photolysis occur between the GA conformers in the argon matrix. This results to a photoinduced equilibrium upon visible photolysis [12]. Recently, UV laser irradiation at 212 and 226 nm has been used to study the photoinduced structural transformations of GA in an argon matrix. It turned out that both photodissociation and photoisomerization occurred upon UV excitation. The main dissociation channel produced molecular complexes of formaldehyde and water with carbon monoxide [13]. The UV-induced processes of GA conformers have been investigated in more detail by Ahokas *et al.* [15] expanding the understanding of the overall photochemistry of the compound employing more extensive kinetic photochemistry measurements. The work employed also theoretical modelling of the kinetic data to reveal and explain the various photoinduced reaction paths taking place upon photolysis.

Much less has been done in the field of glycolic acid molecular complexes. Three recent studies deal with interaction of GA with dinitrogen using infrared and Raman spectroscopies [16–18]. Of the three theoretically predicted GA-N₂ structures involving the SSC conformer, only one hydrogen-bonded complex has been found experimentally. This SSC-N₂ complex exhibit the dinitrogen molecule bound to the carboxyl OH group of the acid. Moreover, this complex structure was found to reside in three different matrix sites, each of these local sites showing a site-selective response upon the ν OH overtone excitation at slightly different wavelengths [17,18].

In turn, the interaction of GA with water has been studied

experimentally in the gas phase in the $4\nu_1$ and $4\nu_2$ OH stretching vibration region using a highly sensitive cavity ring-down spectroscopy [6]. Moreover, several research papers deal with theoretical studies of glycolic acid interacting with various number of water molecules [19–23]. Especially, the study by Gu *et al.* [22] deals with the strength of hydrogen bonding and other properties of the glycolic acid–water complex in comparison with its aromatic analog, 9-hydroxy-9 fluorene carboxylic acid, complexed with water. Such data allowed to predict the binding energy D_0 for the SSC-H₂O global minimum to be 8.51 kcal mol⁻¹. In addition, a valuable discussion on the cooperative and anti-cooperative balance in this complex was presented.

Here, we combine FTIR spectroscopy and a low-temperature matrix isolation technique to study the molecular complexes formed between glycolic acid and water. The main aim of the work is to be able to spectroscopically characterize the 1:1 GA-H₂O complexes prevalent in low-temperature Ar matrices of premixed GA and water gas phase samples. Quantum chemical calculations were performed at the MP2 and B3LYPD3 levels to support the analysis of the experimental data to identify experimentally observed complex species.

2. Experimental

2.1. Matrix isolation FTIR studies

Glycolic acid was purchased from Janssen Chimica (99 %) and argon from Messer (5.0). GA was pumped before use to get rid of volatile impurities. The matrix samples were prepared by passing H₂O/Ar mixtures of the 1/500 or 1/1000 sample ratio through the glass U-tube with GA, situated outside the cryostat chamber. The GA/H₂O/Ar gaseous mixtures were deposited onto a cold CsI window kept at 15 K in a closed cycle cryostat (ARS-2HW, APD-Cryogenics). The matrix deposition conditions were fixed to obtain samples containing mostly monomeric GA and its complexes of the 1:1 stoichiometry. Such experimental conditions do not allow for precise estimation of the GA/H₂O ratio. The pressure of the gas mixtures and the deposition rates were controlled by piezo transducers (model 902B, MKS Instruments) installed in the deposition line. The low temperature was maintained by a Scientific Instruments 9700 temperature controller equipped with a silicon diode. The sample temperature was 10 K during spectral measurements. FTIR spectra between 4000 and 400 cm⁻¹ were collected in a transmission mode with a 0.5 cm⁻¹ resolution averaging over 128 scans on a Bruker IFS 66 Fourier Transform spectrometer equipped with a liquid N₂ cooled

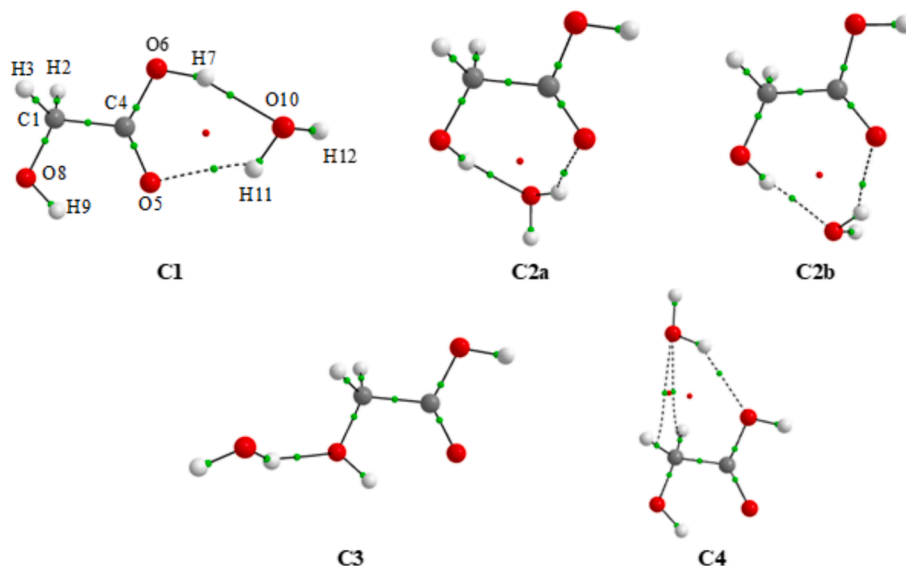


Fig. 1. The MP2 optimized structures of the 1:1 complexes of GA with water. Positions of the bond (3,-1) and ring (3,+1) critical points derived from AIM calculations are shown by small green and red dots, respectively.

Table 1

Computed interaction energies and relative energies compared to the global minimum C1 using MP2, B3LYPD3 and CCSD(T) methods with 6-311++G(2d,2p) basis set (in kJ mol⁻¹).

Structure	Interaction energy E_{int}				Relative Energy ΔE			
	MP2	CCSD(T)/MP2 ^a	B3LYPD3	CCSD(T)/B3LYPD3 ^a	MP2	CCSD(T)/MP2 ^a	B3LYPD3	CCSD(T)/B3LYPD3 ^a
C1	-40.24	-40.19	-48.53	-40.78	0.00	0.00	0.00	0.00
C2a	-35.00	-34.96	-43.33	-35.42	11.08	10.77	10.47	10.88
C2b	-32.78	-32.78	-40.86	-33.20	13.61	13.24	13.13	13.41
C3	-21.98	-21.52	-25.67	-21.31	16.80	16.97	20.86	16.70
C4	-12.43	-12.35	-15.99	-12.43	26.37	26.07	30.54	25.95

^a CCSD(T) calculations are single-point calculations at the MP2 or B3LYPD3 optimized geometries, respectively.

Table 2

Electron density parameters of the intermolecular bond critical points BCP (au) and ring critical points RCP (au) of the GA-H₂O computed at the MP2/6-311++G(2d,2p) level.

Complex	AIM Parameters				
			$\rho(r)$	$\nabla^2\rho(r)$	Elip.
C1	BCP	H7...O10	0.0368	+0.1138	0.030
		H11...O5	0.0212	+0.0757	0.110
	RCP	(6 at.)	0.0135	+0.0590	
C2a	BCP	H9...O10	0.0289	+0.0955	0.061
		H11...O5	0.0233	+0.0856	0.026
	RCP	(7 at.)	0.0089	+0.0378	
C2b	BCP	H9...O10	0.0240	+0.0857	0.010
		H11...O5	0.0201	+0.0737	0.045
	RCP	(7 at.)	0.0081	+0.0341	
C3	BCP	H11...O8	0.0253	+0.0902	0.028
C4	BCP	H11...O6	0.0158	+0.0632	0.108
		H2...O10	0.0059	+0.0261	4.756
		H3...O10	0.0059	+0.0261	4.757
	RCP	(7 at.)	0.0046	+0.0260	
	RCP	(4 at.)	0.0058	+0.0270	

Table 3

Geometric parameters of hydrogen bond bridges in the SSC complexes with water (1:1). The values are computed both at the MP2 and B3LYPD3 levels and denoted as MP2/B3LYPD3 in the Table.

C1	ROH _A	ROH _C	ROH _A ...O	α OH _A ...O	ROH _C ...OH ₂	ROH...O=C	α OH _C ...OH ₂	α OH...O=C
	0.965/0.966	0.982/0.988	2.083/2.132	118.5/116.3	1.818/1.780	2.136/2.074	159.4/158.2	130.6/133.2
C2a	ROH _A	ROH _C	ROH _A ...OH ₂	ROH...O=C	α OH _A ...OH ₂	α OH...O=C		
	0.968/0.973	0.967/0.968	1.940/1.889	2.029/1.945	163.8/162.6	143.6/149.0		
C2b	ROH _A	ROH _C	ROH _A ...OH ₂	ROH...O=C	α OH _A ...OH ₂	α OH...O=C		
	0.967/0.973	0.967/0.968	1.935/1.880	2.028/1.946	161.4/161.2	146.6/150.7		
C3	ROH _A	ROH _C	ROH _A ...O	α OH _A ...O	ROH...OH _A	α OH...OH _A		
	0.967/0.968	0.967/0.968	2.076/2.120	118.7/116.7	1.999/1.958	151.2/152.3		
C4	ROH _A	ROH _C	ROH _A ...O	α OH _A ...O	ROH...OH _C	α OH...OH _C	RCH...OH ₂	α CH...OH ₂
	0.964/0.966	0.967/0.968	2.116/2.167	117.6/115.4	2.198/2.140	142.6/144.4	2.830/2.736	102.5/102.6
SSC monomer	ROH _A	ROH _C	ROH _A ...O	α OH _A ...O				
	0.965/0.966	0.967/0.968	2.108/2.157	118.0/115.8				

The parameters of the GA monomer are marked in gray. OH_A and OH_C denotes alcohol and carboxyl OH group, respectively. Parameters presented relate to distances (R; given in Angstroms) and bond angles (α ; given in degrees).

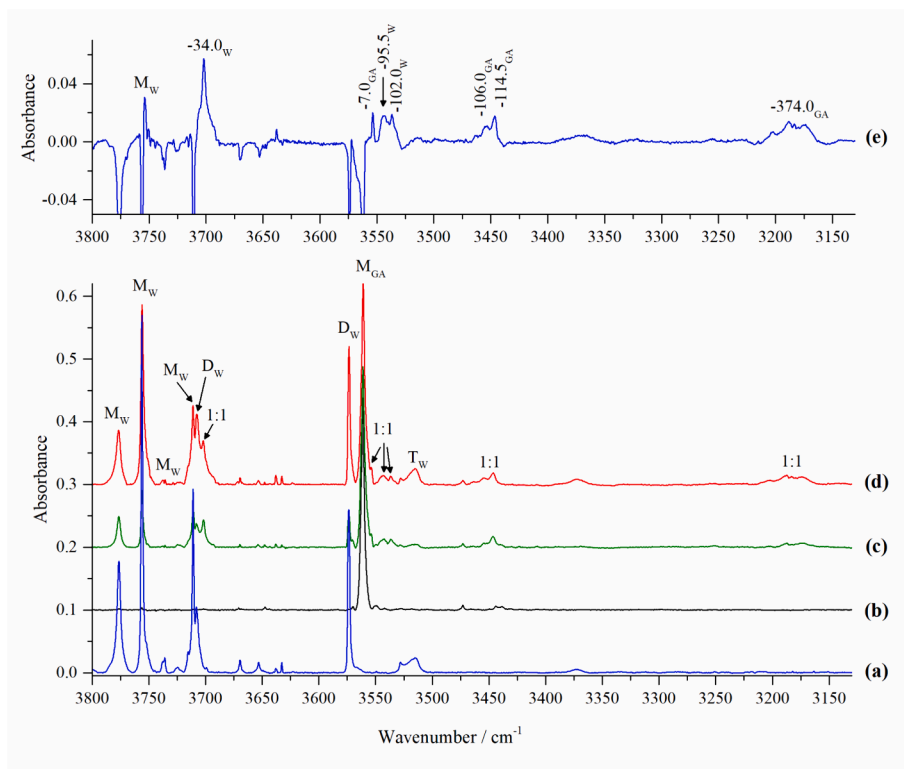


Fig. 2. The νOH region of the infrared spectra of argon matrices of GA co-deposited with $\text{H}_2\text{O}/\text{Ar} = 1/500$ (d) and $1/1000$ (c) compared with $\text{H}_2\text{O}/\text{Ar} = 1/500$ (a) and GA/Ar (b) spectra. The difference spectrum (e) obtained by subtracting spectra (a) and (b) from the spectrum (d) is presented in the upper part of the figure. Letters M, D, and T denote monomer, dimer, and trimer, respectively. W and GA subscripts denote water and glycolic acid.

3. Results and discussion

3.1. Quantum chemical calculations

Among the six stable monomeric structures of GA, the SSC conformer stabilized by the $\text{O}-\text{H}\cdots\text{O}$ intramolecular hydrogen bond was found to be present in low-temperature matrices after deposition with an estimated population of ca. 95 % [10,14]. Thus, our study of the interaction of GA with the water molecule was limited to this most stable form of the acid. According to both B3LYPD3 and MP2 methods applied, there are five stable structures for the SSC- H_2O interaction of the 1:1 stoichiometry. The computed local minima structures for the GA- H_2O complexes are presented in Fig. 1 together with the adopted atom numbering and the relevant energetics shown in Table 1.

Cartesian coordinates of the optimized complexes are provided in Table S1 in the Supplementary material. The values of three topological AIM parameters: the electron density $\rho(\mathbf{r})$, its Laplacian $\nabla^2\rho(\mathbf{r})$ and ellipticity at the critical points obtained for the 1:1 stoichiometry are shown in Table 2.

The most stable structure C1, in accordance with the MP2/aug-cc-pVTZ results [22], is characterized by two intermolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds (see Fig. 1). A six-member ring is formed in which water acts simultaneously as a proton acceptor for the carboxyl OH group, and a proton donor for the carbonyl OH group. For this structure, the intramolecular hydrogen bonding in the GA molecule is preserved and its geometry is slightly deformed by hydrogen bonding to water. In the second and third most stable complexes C2a and C2b (marked in the text generally as C2) water is inserted into the internal hydrogen bond. These structures are also bound by two intermolecular hydrogen bonds. One of them connects the alcoholic OH_A group with the oxygen of the water molecule. For the second hydrogen bond H_2O acts as a proton donor to the carbonyl $\text{C}=\text{O}$ group. The intramolecular hydrogen bond between OH_A and $\text{O}=\text{C}$ is no longer present in these structures for the GA

subunit. This is due to the insertion of the H_2O molecule and changes in geometry under the influence of interaction with water. These forms are similar as to the interaction energy but differ in the orientation of the water molecule relative to the SSC subunit. The alcoholic OH_A group of SSC monomer appears in the same plane as the carbonyl group, but is tilted out of the plane by about 40° in both of the C2a and C2b complexes.

The two other higher energy structures (C3 and C4) contain a water molecule acting as a proton donor for the oxygen atom of the alcoholic OH_A and carboxyl OH_C groups, respectively. For both C3 and C4 forms intramolecular hydrogen bonding is retained in the SSC subunit, showing small deviations from the geometry found for the SSC monomer. Additionally, in the C4 complex, the AIM method predicts low values of electron density and high ellipticity for the bond paths connecting the oxygen atom of the water molecule with the hydrogen atoms of the CH_2 group of the acid (see Fig. 1 and Table 2). This data suggests that $\text{C}-\text{H}\cdots\text{O}$ connections would not exist. However, the presence of two lone electron pairs in the water molecule pointing towards the CH bonds could be related to weak interactions via the CH bonds.

Table 3 contains the calculated bond distances and angles of intermolecular and intramolecular hydrogen bond bridges for the five structures of the SSC- H_2O complex. For comparison purposes, the parameters of the SSC monomer are shown in the lowest part of the table. The shortest intermolecular distance for $\text{H}\cdots\text{O}$ of 1.818/1.780 Å was found in the C1 structure for carboxyl OH_C interacting with the water oxygen. In all other cases, the intermolecular distances are in the range of 1.9 to 2.2 Å. Analysis of the data in Table 3 and Table S2 also suggests that the intramolecular $\text{OH}_A\cdots\text{O}$ hydrogen bond present in the SSC monomer is affected by the $\text{OH}\cdots\text{O}$ intermolecular hydrogen bond formed upon complexation with water. The smaller value of the $\text{ROH}_A\cdots\text{O}$ distance as well as the increase in electron population of the antibonding orbital σ^* of the OH_A bond in both C1 and C3 structures ($\Delta\sigma^* = 0.5$ and 1.1 millielectrons at NBO/MP2, respectively) indicate

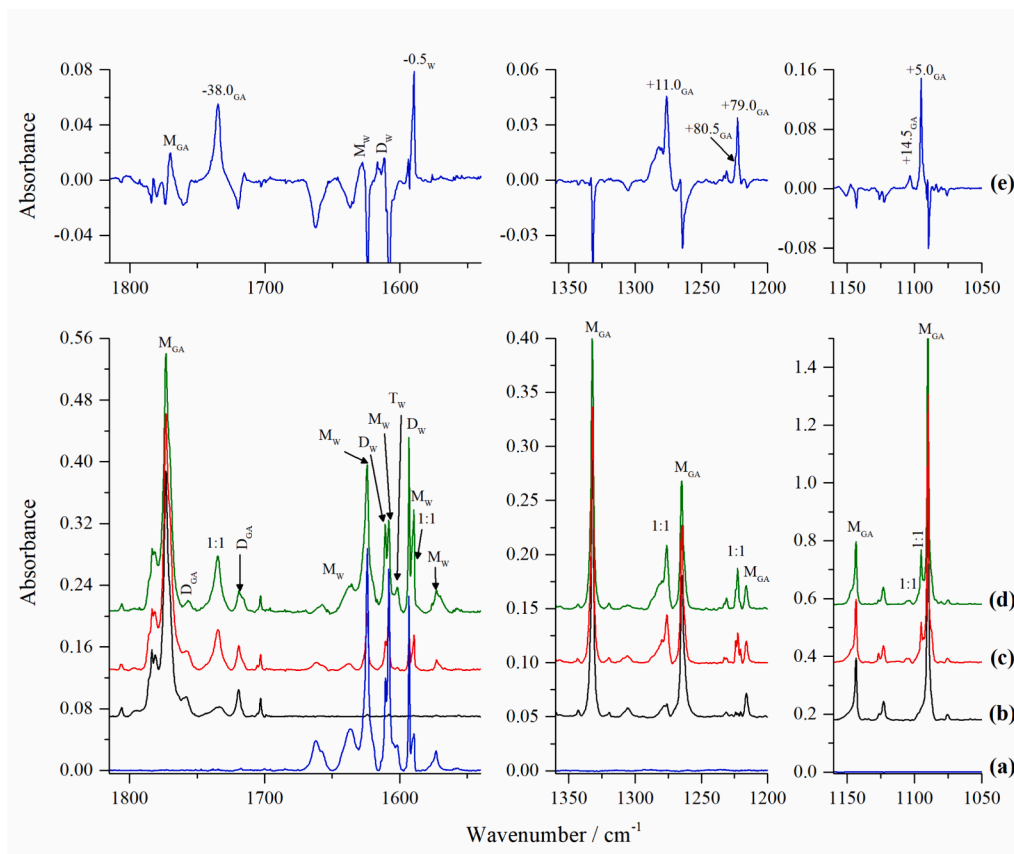


Fig. 3. Selected regions of the infrared spectra of argon matrices of GA co-deposited with H₂O/Ar = 1/500 (d) and 1/1000 (c) compared with H₂O/Ar = 1/500 (a) and GA/Ar (b) spectra. The difference spectrum (e) obtained by subtracting spectra (a) and (b) from the spectrum (d) is presented in the upper part of the figure. Letters M, D, and T denote monomer, dimer, and trimer, respectively. W and GA subscripts denote water and glycolic acid.

Table 4

Selected MP2/6-311++G(2d,2p) calculated wavenumber shifts $\Delta\nu$ (cm⁻¹) and intensities (km mol⁻¹) of the 1:1 GA complexes with water compared to the corresponding experimental shifts.

MP2 ^a					Mode ^b	Ar matrix			Assignment
C1	C2a	C2b	C3	C4		Monomer GA (SSC)/ H ₂ O		GA(SSC)-H ₂ O	
						ν	ν	$\Delta\nu$	
-3	-83	-61	-33	+11	νOH_A	3561.0	3446.5, 3455.0sh	-114.5, -106.0	C2
(75)	(295)	(245)	(206)	(72)			3554.0	-7.0	C1
-305	-2	-2	0	-5	νOH_C	3561.0	3187.0	-374.0	C1
(687)	(58)	(79)	(95)	(104)			3554.0	-7.0	C2
-29	0	-1	-2	+5	$\nu\text{C}=\text{O}$	1773.0	1735.0	-38.0	C1
(224)	(271)	(295)	(255)	(258)			1773.0	0.0	C2
+13	+23	+23	-1	+3	$\omega\text{CH}_2 + \delta\text{OH}_A + \delta\text{OH}_C$	1265.0	1276.0	+11.0	C1
(136)	(37)	(36)	(32)	(22)					
+84	-5	-6	+4	-4	$\delta\text{OH}_C + \nu\text{C}-\text{O}_C + \omega\text{CH}_2$	1143.5	1222.5, 1224.0sh	+79.0, +80.5	C1
(162)	(88)	(79)	(156)	(132)					
+4	+17	+18	-11	-5	$\nu\text{CO}_A + \nu\text{CO}_C$	1090.0	1095.0	+5.0	C1
(166)	(276)	(275)	(222)	(290)			1104.5	+14.5	C2
+22	-2	-2	+5	-3	$\nu\text{CC} + \nu\text{C}-\text{O}_C + \nu\text{CO}_A$	854.0	877.5	+23.5	C1
(27)	(13)	(16)	(31)	(20)					
+222	0	-2	+2	-10	τOH_C	495.5	817.0	+202.5	C1
(123)	(98)	(111)	(122)	(115)					
-39	-38	-31	-30	-14	$\nu_{as}\text{H}_2\text{O}$	3736.0	3702.0	-34.0	C1/C2
(128)	(138)	(128)	(118)	(131)					
-90	-85	-82	-91	-20	$\nu_s\text{H}_2\text{O}$	3638.5	3543.5, 3536.5	-95.5, -102.0	C1/C2
(144)	(289)	(300)	(115)	(37)					
-5	0	+4	+16	+3	$\delta\text{H}_2\text{O}$	1590.0	1589.5	-0.5	C1
(139)	(118)	(65)	(68)	(82)					

^aCorresponding positions of GA(SSC) and H₂O monomers are: 3785, 3786, 1794, 1313, 1175, 1111, 874, 646 cm⁻¹ and 3982, 3862, 1661 cm⁻¹ (MP2/6-311++G(2d,2p)).

^bSubscripts A and C denote alcoholic and carboxyl modes, respectively.

that the strength of the intramolecular hydrogen bond increases compared to the SSC monomer. The opposite effect is observed for the C4 structure where a decrease of the electron population of the σ^* orbital of 0.45 millielectrons was found. These data are consistent with those discussed by Gu *et al.* for different GA hydrogen bonded complexes [22].

3.2. Infrared spectra of matrix isolated 1:1 SSC-H₂O complexes

Under the diluted experimental conditions used, the most likely formation of the GA...H₂O complexes involve mainly the 1:1 stoichiometric ratio. Larger aggregates appearing in the annealing experiment are used here only to exclude other complexes formed than the 1:1 being the focus of this report. A more detailed computational and experimental work on higher GA...H₂O aggregates will be reported separately later.

Figs. 2 and 3 show representative fragments of the infrared spectra measured for argon matrices obtained after co-deposition of GA with two different H₂O/Ar mixtures. The upper parts of the Figures depict the difference spectra, which are obtained by subtracting the spectra (a) and (b) from the spectrum (d). When GA was co-deposited with H₂O/Ar mixtures, notable amounts of new bands appeared, which were not present in the spectra recorded for both monomeric subunits. Selected vibrational band shifts observed after complexation between GA and H₂O are summarized in Table 4. They are compared with the corresponding shifts calculated at the MP2/6-311++G(2d,2p) level. This data obtained at the MP2-level shows generally a better agreement of most vibrational modes compared with the experimental spectra than those computed at the B3LYPD3 level (see Table S3).

As shown in Fig. 2, a set of new bands appeared in the ν OH spectral region due to the complexed water and GA molecules. The most intense band is situated at 3702 cm⁻¹. This is due to the asymmetric stretching mode of the complexed H₂O molecule. It is redshifted by 34 cm⁻¹ from the monomeric ν_{as} of water [43]. Unfortunately, the vibrational band observed for the complex species coincides with theoretical predictions for four different forms of the GA...H₂O complex (see Table 4). The same is true for the symmetric stretching vibration of water. Therefore, it was not equivocally possible to decide on the GA...H₂O structure based on the shifts observed for these vibrational modes of water solemnly. The vibrational mode changes observed for glycolic acid turned out to be more informative for determining the structure of the studied complex. The results suggest the presence of one prevalent structural form (C1), and minor spectral signals due to two less prevalent forms of GA...H₂O, (C2a and C2b) in argon matrices. These assignments are discussed in the following.

The spectral signature of the C1 structure in the ν OH region of GA is characterized by a relatively broad absorption with a large shift of -374 cm⁻¹ (theoretical value -305 cm⁻¹) originating from the perturbed carboxyl OH_C group. In turn, the C2 structures give rise to a doublet situated around 3450 cm⁻¹ due to the alcoholic ν OH_A mode depicting a redshift of ca. 110 cm⁻¹. A weak band situated at 3554.0 cm⁻¹ with a small shift of -7 cm⁻¹ can be assigned either to C1 or C2 forms based on calculations.

As shown in Fig. 3 and Table 4, new features in the vicinity of GA monomer bands were also observed in other spectral regions, and in some cases vibrational bands connected to C1 and C2 forms of the GA...H₂O complex could be distinguished.

The observed perturbation of the carboxyl group of C1 structure manifests itself by a strong band in the region of the carbonyl group stretching mode at 1735.0 cm⁻¹. This vibrational band shows a red shift of -38 cm⁻¹ compared with the theoretical value -29 cm⁻¹. Both in-plane and out-of-plane (torsion) modes of the OH_C group are also strongly shifted to higher wavenumbers by ca. 80 cm⁻¹ and 202 cm⁻¹, respectively. These values are in good agreement with those predicted theoretically by MP2 of 84 cm⁻¹ (δ OH_C) and 222 cm⁻¹ (τ OH_C). In addition to the vibrational bands observed in the ν OH region one additional feature was found due to C2 structures at 1104.5 cm⁻¹. This

band can be assigned as the ν CO_A + ν CO_C vibrational mode. Table 4 shows that wavenumber shifts predicted for the C2a form and the slightly less stable C2b structure are similar. Therefore, one cannot exclude the presence of both complexes in the studied matrices as they are indistinguishable in the obtained spectra due to the structural and spectroscopical similarities.

4. Conclusions

Both MP2 and B3LYPD3 calculations combined with 6-311++G(2d,2p) basis set reveal five local stable structures for glycolic acid complexed with water. Each of the 1:1 complexes contain at least one intermolecular O—H...O hydrogen bond. GA acts as a proton donor for all the complex structures found. Moreover, in the case of cyclic intermolecular H-bonded complexes, water acts as both a proton donor and acceptor depending on the structure in question. Analysis of the experimental infrared spectra of the GA/H₂O/Ar matrices turned out to be quite a difficult task due to the spectral similarity of the theoretically predicted wavenumber shifts for the perturbed water vibrational modes. However, the presence of the most stable C1 complex in argon matrices can be well identified and documented based on its differences from the seven-member ring structures C2a and C2b. The C1 structure is characterized by a six-member ring formed by two intermolecular O—H...O hydrogen bonds formed between the GA carboxyl group and the water molecule. The presence of two other forms of the complex with the GA alcoholic group acting as a proton donor is tentatively suggested based on weak spectral signals separable from the most stable C1 structure. This is also supported by the computational results. The observed C1 form of GA...H₂O complex here clearly corresponds to the structure observed for the glycine-water complex observed in a supersonic jet using microwave spectroscopy [44]. This suggests that for small organic molecules with intramolecular hydrogen bond involving a carboxylic group there is a plausible interaction pattern resolved here. This could be an important piece of knowledge when starting to look for its implications in atmospheric, astrochemical and biological aqua-environments.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

Allocation of computer time from the Wrocław Centre for Networking and Supercomputing (Wrocław, Poland) is gratefully acknowledged. The support of the COST Action CA21101 (COSY) is highly appreciated.

Funding: This research was funded by the Academy of Finland [grant number 332023], for the work performed at the University of Jyväskylä.

Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.saa.2024.125081>.

References

- [1] C.E. Blom, A. Bauder, Structure of glycolic acid determined by microwave spectroscopy, *J. Am. Chem. Soc.* 104 (1982) 2993–2996, <https://doi.org/10.1021/ja00375a009>.

