Microwave Spectroscopy

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High-Resolution Rotational Spectroscopy Study of the Smallest Sugar Dimer: Interplay of Hydrogen Bonds in the Glycolaldehyde Dimer

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Abstract: *Molecular recognition of carbohydrates plays an important role in nature. The aggregation of the smallest sugar, glycolaldehyde, was studied in a conformer-selective manner using high-resolution rotational spectroscopy. Two different dimer structures were observed. The most stable conformer reveals C_2-symmetry by forming two intermolecular hydrogen bonds, giving up the strong intramolecular hydrogen bonds of the monomers and thus showing high hydrogen bond selectivity. By analyzing the spectra of the ^{13}C and ^{18}O isotopologues of the dimer in natural abundance, we could precisely determine the heavy backbone structure of the dimer. Comparison to the monomer structure and the complex with water provides insight into intermolecular interactions. Despite hydrogen bonding being the dominant interaction, precise predictions from quantum-chemical calculations highly rely on the consideration of dispersion.*

Many processes relevant in biological systems, such as molecular recognition and protein folding, are controlled by a subtle equilibrium of intermolecular interactions. Among them, hydrogen bonding is exceptional. Hydrogen bonds are rather strong (on the order of 20 kJ mol^{-1}) and directional and they profit from cooperativity.[1–4] They are also responsible for the broad variety of carbohydrate recognition, which are widespread in nature,[5–7] forming intramolecular, intermolecular and solvent hydrogen bonds.[8,9]

A molecular-level understanding of the interplay between intra- and intermolecular hydrogen bonding in molecular recognition processes is therefore of great interest. Particularly, it is intriguing to investigate dimer formation of molecules exhibiting relatively strong intramolecular hydrogen bonds,[10,11] for which different scenarios are possible upon dimer formation: The molecules form a complex while maintaining the intramolecular hydrogen bonds, for example via stacking, or the intramolecular bonds are broken for the sake of intermolecular hydrogen bonding, or some intermediate form. Furthermore, other interaction types such as the less directed dispersion can tip the subtle balance towards one or the other form.[12]

Glycolaldehyde is a perfect model system to study molecular recognition in detail when different interaction types are possible, such as to investigate the role of intra- vs. intermolecular hydrogen bonding as well as dispersion. It is the smallest sugar (Figure 1a) and so far the only one detected in interstellar space.[13,14] Its gas-phase structure was determined more than 40 years ago.[15] It provides two characteristic functional groups, a hydroxy group directly neighboring a carbonyl group, so that it can form a relatively strong intramolecular hydrogen bond.[16] Because of its moderate size, high-level quantum-chemical calculations can be performed and used to validate these methods for larger systems of biological relevance. In the solid state, two glycolaldehyde monomers form a chemically bonded six-membered ring (Figure 1b),[17,18] which decomposes into the monomer units upon heating. In the conditions of a supersonic expansion, non-covalently bound dimers are formed from isolated monomers (Figure 1c,d).[19]

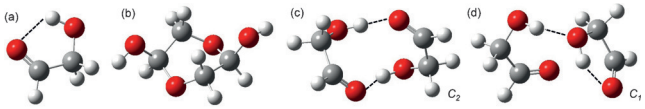

Figure 1. The glycolaldehyde monomer (a) and different structures of the dimer: covalently bound dimer existing in the solid state (b), and the non-covalently bound conformers 1 (c) and 2 (d).

Recently, Altnöder et al. studied the glycolaldehyde dimer using FTIR- and Raman-spectroscopy under isolated conditions in a molecular jet.[19] They identified two conformers, which they assigned to a C_2 symmetric species consisting of two intermolecular hydrogen bonds and a dimer consisting of one inter- and one intramolecular hydrogen bond, which is energetically less favored by about 5 kJ mol^{-1}.[19] However, the calculated potential energy surface[19] exhibits several minima with predicted OH stretching frequencies in comparable frequency ranges. To allow for an unambiguous assignment of the lowest energy conformers of the glycolaldehyde dimer, a rotational spectroscopy study to conclusively determine their structures was encouraged.

Here, we use high-resolution broadband chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy.[20] Structural information, also for molecular clusters, can be obtained because the rotational constants obtained from rotational spectra are directly related to the moments of inertia of the molecules. Molecules as heavy as 325 g mol^{-1} in the case of CpRe(CH$_3$)(CO)(NO) have been addressed with

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CP-FTMW spectroscopy.[21] Quantitative molecular structures can be experimentally determined from an analysis of the rotational spectra of molecular isotopologues. The changes in the moments of inertia of the isotopically substituted species allow for the building up of the substitution structure atom-by-atom using Kraitchman's equations[22] and/or least-squares fits[23,24] of internal coordinates, for example, as it has been recently exemplified for molecular complexes, such as the sevoflurane-benzene[25] and the camphor-$(H_2O)_{1-3}$ complexes.[26] In the present study, the high sensitivity of the technique allowed us to record the ^{13}C and ^{18}O isotopologues of the glycolaldehyde dimer in natural abundance. The additional rotational constants were then used to determine its heavy-atom backbone structure. Quantum-chemical calculations were used to support the spectroscopic assignment.

The rotational spectrum of the glycolaldehyde dimer was recorded in the 2–8 GHz frequency range. A detailed description of the setup can be found in Ref. [27,28]. A sample of glycolaldehyde was purchased from Sigma–Aldrich and used without further purification. The sample is a solid at room temperature and has a melting point between 80 and 90 °C. The sample was heated to 80 °C. Neon was used as a carrier gas with an absolute backing pressure of 3.0 bar, and the gas mixture was supersonically expanded into the vacuum chamber via a pulse nozzle. After this, the molecules were excited by a 1 μs long microwave pulse, which was linearly chirped in frequency. Forty-five microseconds of the molecular response in form of a free induction decay (FID) were recorded, giving a spectral resolution of 25 kHz. In total 2 million FIDs were recorded and averaged. The rotational spectrum was obtained by a Fourier transformation of the experimental data. The spectra were fit to an asymmetric rotor Hamiltonian (Watson S-Reduction in I_r representation)[29] as implemented in the PGOPHER program suite.[30] The additional rotational constants due to isotopic substitution in natural abundance were used to determine the substitution structure of the lowest energy conformer 1 using Kraitchman's equations[22] as implemented in the KRA program package.[31]

As displayed in Figure 1c and discussed in Ref. [19], the predicted lowest energy conformer (conformer 1) consists of two intermolecular hydrogen bonds connecting the hydroxy- and carbonyl-groups forming a ten-membered ring. Thus, dimer formation is accompanied by a rearrangement of the hydrogen bonds. Because of the C_2-symmetry, the dimer has only one non-zero dipole moment component, in the *c*-direction, which is calculated to be $\mu_c = 3.5$ D (Table 1). The experimental broadband spectrum (top trace) and the corresponding fits to asymmetric rotor Hamiltonians for the two dimer conformers (bottom traces) are shown in Figure 2. For conformer 1 (blue) we only observe c-type transitions, revealing a congested Q-branch (following the selection rule $\Delta J = 0$) around 7.8 GHz. We used the computer-assisted auto-assignment program AUTOFIT[32] to get an initial fit of the spectrum of conformer 1 followed by further refinement. Finally, 52 c-type transitions were assigned to this conformer, and the experimentally determined molecular parameters from experiment and quantum-chemical calculations (B3LYP-D3 and MP2) are compared in Table 1. Centrifugal distortion constants obtained from harmonic frequency calculations are also included. There is generally good agreement, with the B3LYP-D3 level of theory giving somewhat better results than the MP2 approach. It is also interesting to compare Ray's asymmetry parameter $\kappa = (2B-A-C)/(A-C)$. This relative value often provides an

Table 1: Experimentally determined and calculated spectroscopic constants for conformer 1 of the glycolaldehyde dimer.[a]

	Experiment	B3LYP-D3/ def2-TZVP	B3LYP-D3/ aVTZ	MP2/ def2-TZVP	MP2/ aVTZ
A [MHz]	2792.67325(87)	2780.962	2783.225	2789.533	2801.957
B [MHz]	1282.99783(41)	1286.011	1283.496	1304.335	1322.20
C [MHz]	1198.16509(39)	1176.691	1166.748	1221.345	1242.145
κ	−0.89	−0.86	−0.86	−0.90	−0.90
D_K [kHz]	1.102(24)	1.140	1.336	1.679	1.336
D_{JK} [kHz]	−0.368(10)	1.951	2.061	0.975	2.061
D_J [kHz]	0.9202(63)	0.747	0.809	0.780	0.804
d_1 [kHz]	0.09567(89)	0.163	0.181	0.128	0.181
d_2 [kHz]	−0.0364(53)	−0.052	−0.055	−0.042	−0.055
$\lvert\mu_a\rvert$ [D]		0	0	0	0
$\lvert\mu_b\rvert$ [D]		0	0	0	0
$\lvert\mu_c\rvert$ [D]		3.4	3.4	3.6	3.6
J_{max}	9				
no. lines (a | b | c)	52 (0 | 0 | 52)				
error [kHz]	4.9				

[a] Numbers in parentheses represent error of one standard deviation in units of the last significant figure. aVTZ corresponds to the aug-cc-pVTZ basis set. The number of assigned lines and the error of the fit are also given.

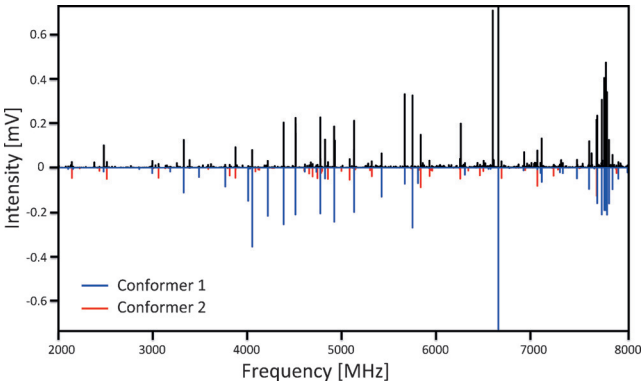

Figure 2. Broadband rotational spectrum of the glycolaldehyde dimer, exhibiting two conformers. The upper trace shows the experimental data. The lower trace displays the simulated spectra based on fits employing an asymmetric rotor Hamiltonian for the most stable conformer 1 (in blue) and for conformer 2 (in red), which is calculated to be 4.9 kJ mol^{-1} higher in energy. Known background lines were removed. Additional spectral lines might be due to impurities or higher order complexes. The noise level of this measurement is 0.2 μV.

additional information for the assignment of conformers based on comparison between experimental and theoretical rotational constants, i.e., when further structural information cannot be extracted such as via isotopic subsition (see below).

We also recorded and assigned transitions arising from all singly substituted ^{13}C- and ^{18}O-isotopologues of conformer 1. Due to its C_2 symmetry, only four different singly substituted ^{13}C- and ^{18}O- isotopologues exist, with an intensity of about 2.2% for ^{13}C and 0.4% for ^{18}O with respect to the parent transitions (i.e., corresponding to twice their natural abundance because of their symmetry). The signal-to-noise (S/N) ratio for the transitions of the ^{18}O isotopologues is about 20:1. An example for the rotational transitions arising from ^{13}C- and ^{18}O-isotopologues is depicted in Figure 3. For each rare isotopologue, between 19 and 29 rotational transitions could be assigned and fit (see also the Supporting Information). For these fits the distortion constants were fixed to the values of the parent species. The data set was then used to determine the precise positions of the carbon and oxygen atoms of conformer 1 using Kraitchman's equations (r_s-structure),[22] as implemented in the KRA program.[31]

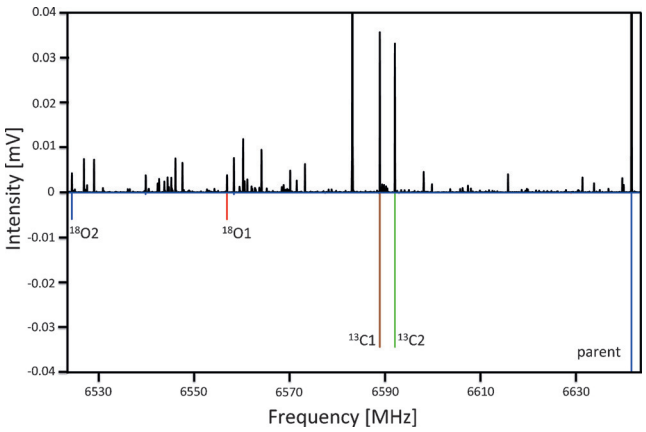

Figure 3. $J'_{K'_a,K'_c} \leftarrow J_{K_a,K_c} = 2_{1,1} \leftarrow 1_{0,1}$ rotational transitions for all singly substituted ^{13}C and ^{18}O rare isotopologues of conformer 1 in natural abundance and the main isotopologue (see Figure 4 for atom labeling). The signal-to-noise ratio for the ^{18}O isotopologues is about 20:1. The large number of unassigned lines may arise from higher order glycolaldehyde clusters or from complexes with water.

A comparison of the experimental structural parameters, for example bond lengths and bond angles, to the parameters obtained from quantum-chemical calculations is given in Figure 4 and in Table 2. Note that the quantum-chemical structure represents the equilibrium structure of the complex, while the r_s structure contains zero-point motions in the ground state, which can cause deviations between the experimental and theoretical structures.[22,33] Although four low-frequency vibrational modes below 100 cm^{-1} were predicted, we do not find a spectroscopic indication of them. The quality of the fits is satisfying for both conformers. Because of the high density of low-intensity transitions, we cannot exclude that spectral features from these low-frequency vibrations might be present.

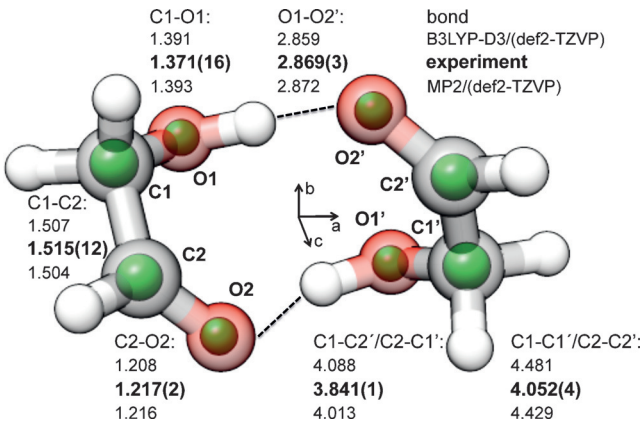

Figure 4. Overlay of the experimentally determined structure (green dots) and the calculated structures using the MP2/def2-TZVP method. A comparison of the experimental and calculated bond lengths is also given. Numbers in parentheses represent the error propagated from the errors in the rotational constants in Tables 1 and S1.

Within the experimental and theoretical uncertainties, the intramolecular geometry parameters are predicted well. Larger deviations are found for the intermolecular parameters and thus for the description of the molecular interactions. This is apparent for the intermolecular carbon-carbon distances C1–C1′ and C1–C2′ (Figure 4). For both parameters the experimental bond lengths are clearly shorter than the ones predicted by theory (significantly more than three standard deviations). For α_1, which is the angle between the atoms C1-O1-O2′ (see Figure 4 for labeling), a deviation of about 3° (more than three standard deviations) from the experimental values is obtained (Table 2). This might come along with an overestimation of the dihedral angle τ_1, which is defined between the O1-C1-C2-O2 atoms of one monomer unit. Calculations using the B3LYP functional, i.e., without the dispersion correction, give a two to three times larger deviation of the rotational constants from the experimentally

Table 2: Experimentally determined bond angles and dihedral angles of conformer 1 (r_s-structure following Kraitchman's approach) compared to values from quantum-chemical calculations.[a]

Bond angles [°]	Exp. r_s	B3LYP-D3/		MP2/	
		def2-TZVP	aVTZ	def2-TZVP	aVTZ
α_1(C1-O1-O2′)	89.79(50)	86.94	91.40	87.85	87.00
α_2(C2-C1-O1)	115.42(31)	114.60	115.44	114.80	114.58
α_3(C1-C2-O2)	123.94(46)	124.72	125.35	124.93	124.71
α_4(C2-O2-O1′)	125.51(15)	125.09	125.71	124.87	125.08
τ_1(O1-C1-C2-O2)	4(1)	5.52	5.29	5.58	5.43
τ_2(C2-O2-O1′-C1′)	107.30(24)	107.14	106.16	107.14	107.10
τ_3(O1-O2′-C2′-C1′)	13.72(61)	14.21	11.03	13.78	14.30
τ_4(C1-C2-C2′-C1′)	−111.9(9)	−116.1	–	−113.7	–
τ_5(C1-C2-C1′-C2′)	68.4(9)	64.1	–	66.8	–

[a] aVTZ corresponds to the aug-cc-pVTZ basis set. Numbers in parentheses represent the error propagated from the errors in the rotational constants in Table 1 and Table S1.

determined values than the calculations using the B3LYP-D3 functional (see the Supporting Information). Without the dispersion correction, the strength of the hydrogen bond seems to be slightly overestimated, which is expressed by a shorter hydrogen bond (1.903 Å compared to 1.933 Å) and an O1-H-O2′ angle closer to linearity (168° vs. 156°) compared to the structure when including dispersion (B3LYP-D3) and compared to experimental values. Therefore, the precise prediction of the intermolecular interaction and with this of the respective changes for the two interacting moieties highly relies on the correct consideration of dispersion.

It is also intriguing to discuss the structural changes of glycolaldehyde itself upon dimer formation. For this, we also included the structural parameters of the monomer in Table S3 and Table S4 in the Supporting Information, as determined in a recent CP-FTMW spectroscopy study.[34] In conformer 1, the C1−C2 and the C1−O1 bonds are affected the most by the dimer formation. In the complex, the C1−C2 bond is clearly elongated by 0.01 Å, while the C1−O1 bond neighboring the hydroxy group is shortened by almost 0.03 Å.

The dimer conformer 2 (Figure 1 d) is less energetically favored by about 5 kJ mol^{-1} (MP2/aug-cc-pVTZ including zero-point correction) and less populated under the cold conditions of our molecular jet. The broadband rotational spectrum and the corresponding fit (in red) are included in Figure 2. In total, 42 transitions (29 b-type and 13 c-type) were assigned to this conformer and fitted to an asymmetric rotor Hamiltonian. The experimentally determined constants and calculated values are given in Table 4. For this conformer, the rotational constants obtained at different levels of theory deviate from each other and from the experimental values. Interestingly, density functional theory employing the B3LYP-D3 level of theory seems to provide slightly worse predictions than the MP2 level of theory, while both approaches worked equally well for conformer 1. Furthermore, the different theoretical approaches give varying results for the dipole moment components. In all calculations, μ_b is predicted to be the strongest dipole moment component (in agreement with our experimental findings of recording strong b-type transitions), but they differ in the prediction of μ_a and μ_c. We assigned b- and c-type transitions with an experimentally determined ratio of the dipole moment components of about 5:1. No a-type transitions could be identified in the spectrum. This ratio of the dipole moment components is only properly predicted by the MP2/aug-cc-pVTZ level of theory. Thus, even though the rotational constants are rather similar, small changes in the arrangement of the two monomers and especially of the polar groups (hydroxy and carbonyl) with respect to each other can lead to a nearly complete cancellation of the dipole moments along certain directions. By comparing the structures resulting from the different calculations, only minor changes of the angles between the two monomer units are visible. However, the calculated potential energy surface (Figure 1 in Ref. [19]) of the glycolaldehyde dimer shows a broad minimum for conformer 2, which might explain the slightly different structures obtained using different quantum-chemical methods and basis sets.

Calculations employing the B3LYP functional without dispersion corrections (see the Supporting Information) show large deviations, up to 160 MHz, from the experimentally determined rotational constants. Without the dispersion correction the structure of the complex opens up. For example, the dihedral angle between all four carbon atoms (C2-C1-C2′-C1′) is increased by 20° when omitting dispersion. This might be caused by an underestimation of attraction.

To obtain further insight into the differences between conformer 1 and conformer 2, a zeroth-order symmetry adapted perturbation theory (SAPT) calculation[35] was performed to decompose the energy contributions to the intermolecular binding forces. Starting from the optimized structures (B3LYP-D3/def2-TZVP), we performed SAPT(0)/jun-cc-pVDZ[36] calculations, which correspond to a reduced aug-cc-pVDZ basis set (without diffuse functions on hydrogen and without diffuse *d* functions on heavy atoms). This is part of the Psi4 electronic structure package,[37] and the results are presented in Table 3.

Table 3: Energy decompositions (kJ mol^{-1}) from a SAPT(0)/jun-cc-pVDZ analysis of the two observed conformers of glycolaldehyde dimer.[a]

	ΔE_{elst}[b]	ΔE_{ind}[c]	ΔE_{disp}[d]	ΔE_{exch}[e]	ΔE_{tot}
conformer 1	−89.6	−26.5	−22.9	75.2	−63.8
conformer 2	−64.8	−18.7	−19.0	58.8	−43.8
$\Delta(\Delta E)$[f]	−24.8	−7.8	−3.9	16.4	−20.0

[a] The calculations are based on the B3LYP-D3/def2-TZVP optimized structure. [b] ΔE_{elst} is the electrostatic or Coulombic exchange. [c] ΔE_{ind} corresponds to the induction and charge-transfer interactions. [d] ΔE_{disp} accounts for the dispersive interactions. [e] ΔE_{exch} represents the repulsion due to quantum-mechanical exchange. [f] $\Delta(\Delta E)$ is the energy difference $\Delta E_{conformer\,1} - \Delta E_{conformer\,2}$.

The total interaction energy is vastly different for both conformers. The largest differences are calculated for the electrostatic interaction, ΔE_{elst}, as well as the repulsion due to quantum-mechanical exchange, ΔE_{exch}. The difference in dispersion energy arises to about 4 kJ mol^{-1}. This relatively small number is somewhat surprising when considering the large changes to the molecular structure of conformer 2 when omitting dispersion.

Due to the lower intensity of the spectrum compared to conformer 1 and a high number of unassigned lines of similar intensity, which might be arising from higher order clusters and clusters with water, for example, it was not possible to make any confident assignment of ^{13}C or ^{18}O isotopologues for conformer 2. Therefore, structural information is limited to a comparison of the determined molecular parameters with calculated values as given in Table 4.

A comparison with the glycolaldehyde–water complex[38] is also of interest here. Under similar experimental conditions as in this study, i.e., employing a supersonic expansion using neon as carrier gas resulting in similar conformational cooling, only one conformer could be identified. The water complex is formed by giving up the intramolecular hydrogen bond of the glycolaldehyde monomer and by forming two intermolecular hydrogen bonds, as in the glycolaldehyde conformer 1. Both the glycolaldehyde dimer 1 and the water

Table 4: Experimentally determined and calculated spectroscopic constants of the higher energy glycolaldehyde dimer conformer 2.[a]

	Experiment	B3LYP-D3/ def2-TZVP	aVTZ	MP2/ def2-TZVP	aVTZ
A [MHz]	2938.82326(40)	2780.678	2780.709	2868.851	2909.259
B [MHz]	1170.31969(17)	1243.932	1233.166	1251.113	1248.777
C [MHz]	964.30907(18)	1015.574	1012.799	1010.304	1009.973
κ	−0.79	−0.74	−0.75	−0.74	−0.75
D_K [kHz]	19.777(41)	12.975	12.618	11.192	11.271
D_{JK} [kHz]	−9.4496(81)	−6.403	−6.608	−5.046	−4.784
D_J [kHz]	2.1772(32)	1.933	2.047	1.529	1.418
d_1 [kHz]	−0.021866(22)	−0.027	−0.026	−0.022	−0.021
d_2 [kHz]	−0.391601(56)	−0.273	−0.331	−0.310	−0.295
$\lvert\mu_a\rvert$ [D]		0.1	0.4	0.2	0.03
$\lvert\mu_b\rvert$ [D]		1.6	1.0	0.9	1.0
$\lvert\mu_c\rvert$ [D]		0.2	0.04	0.01	0.2
J_{max}	8				
no. lines (a | b | c)	42 (0 | 29 | 13)				
error [kHz]	1.9				

[a] Numbers in parentheses represent error of one standard deviation in units of the last significant figure. aVTZ corresponds to the aug-cc-pVTZ basis set. The number of assigned lines and the error of the fit are also given.

complex seem to gain stability by giving up the intramolecular hydrogen bond of the monomer and by generating two newly formed intermolecular hydrogen bonds. However, the water complex is supported by cooperativity. Such a cooperativity effect is also present for the glycolaldehyde conformer 2.

In summary, two conformers of the glycolaldehyde dimer were investigated using broadband microwave spectroscopy in the frequency range between 2–8 GHz. While the glycolaldehyde monomer is characterized by a moderately strong intramolecular hydrogen bond, this is given up upon formation of the lowest energy dimer, conformer 1. It consists of two intermolecular hydrogen bonds, forming a ring of eight heavy atoms, i.e., non-hydrogen atoms, in agreement with a previous molecular jet FTIR spectroscopy study.[19] The initial assignment of the broadband spectrum was achieved using the computer-assisted assignment program AUTOFIT. The high sensitivity of our spectrometer allowed us to also record the rotational signatures of all singly substituted ^{13}C- and ^{18}O-isotopologues in natural abundance for the lowest energy conformer 1 and with this to determine its heavy-atom backbone structure, confirming the structural assignment.

Conformer 2 maintains one intramolecular hydrogen bond and forms one new intermolecular hydrogen bond. It is less energetically favored compared to conformer 1 by about 5 kJ mol^{-1}. The quantum-chemical calculations employed, which either explicitly treat dispersion (MP2) or include corrections for dispersion (B3LYP-D3), show clear deviations of the predicted molecular parameters from the experimental ones. The largest differences were found for the predicted dipole moment components, which demonstrate one of the challenges in quantum-chemical calculations of molecular complexes. Small changes in intermolecular interactions and thus the intermolecular arrangement can result in clearly different molecular parameters that are easily identified by microwave spectroscopy.

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