Molecular Structure and Conformational Composition of 1,3-Dihydroxyacetone Studied by Combined Analysis of Gas-Phase Electron Diffraction Data, Rotational Constants, and Results of Theoretical Calculations. Ideal Gas Thermodynamic Properties of 1,3-Dihydroxyacetone

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The molecular structure of 1,3-dihydroxyacetone (DHA) has been studied by gas-phase electron diffraction (GED), combined analysis of GED and microwave (MW) data, ab initio, and density functional theory calculations. The equilibrium r_e structure of DHA was determined by a joint analysis of the GED data and rotational constants taken from the literature. The anharmonic vibrational corrections to the internuclear distances ($r_e - r_a$) and to the rotational constants ($B_e^{(i)} - B_0^{(i)}$) needed for the estimation of the r_e structure were calculated from the B3LYP/cc-pVTZ cubic force field. It was found that the experimental data are well reproduced by assuming that DHA consists of a mixture of three conformers. The most stable conformer of C_{2v} symmetry has two hydrogen bonds, whereas the next two lowest energy conformers (C_s and C_1 symmetry) have one hydrogen bond and their abundance is about 30% in total. A combined analysis of GED and MW data led to the following equilibrium structural parameters (r_e) of the most abundant conformer of DHA (the uncertainties in parentheses are 3 times the standard deviations): r(C═O) = 1.215(2) Å, r(C−C) = 1.516(2) Å, r(C−O) = 1.393(2) Å, r(C−H) = 1.096(4) Å, r(O−H) = 0.967(4) Å, ∠C−C═O = 119.9(2)°, ∠C−C−O = 111.0(2)°, ∠C−C−H = 108.2(7)°, ∠C−O−H = 106.5(7)°. These structural parameters reproduce the experimental $B_0^{(i)}$ values within 0.05 MHz. The experimental structural parameters are in good agreement with those obtained from theoretical calculations. Ideal gas thermodynamic functions ($S°(T)$, $C_p°(T)$, and $H°(T) - H°(0)$) of DHA were calculated on the basis of experimental and theoretical molecular parameters obtained in this work. The enthalpy of formation of DHA, −523 ± 4 kJ/mol, was calculated by the atomization procedure using the G3X method.

1. Introduction

1,3-Dihydroxyacetone (DHA), or 1,3-dihydroxy-2-propanone (HO−CH$_2$−CO−CH$_2$−OH), is the simplest ketone form of sugars, the most abundant biomolecules on the Earth. This prebiotic molecule provides a direct route to other monosaccharides, including important biochemicals such as glucose and fructose.[1] Recent detection of DHA in the interstellar medium[2,3] has conceived the idea that large biologically relevant organic compounds can be easily generated in space and be delivered to Earth by comets, meteorites, and asteroids.

Despite interest in DHA, there is not enough reliable information about the structure and conformations of this molecule in the gas-phase. The microwave (MW) spectrum of DHA has been recently investigated by Lovas et al.[4] with a Fourier transform microwave spectrometer. The experimental evidence for a C_{2v} structure with two hydrogen bonds to the carbonyl oxygen was obtained from the analysis of the rotational spectrum; however, this result did not agree with the C_2 theoretical structure calculated by the MP2 and B3LYP methods with the 6-311++G(d,p) basis set, and the authors suggested that a higher level of theory appeared necessary in this case. Widicus et al.[5] have also studied the MW spectrum of DHA. The values of rotational constants determined in two MW studies[4,5] are in excellent agreement. From B3LYP/6-31++G-(d,p) calculations,[5] the doubly hydrogen bonded conformer of C_{2v} symmetry was found to be the lowest energy conformer of DHA, while the singly C═O···H−O hydrogen bonded conformer was calculated to be 8 kJ/mol less stable.

The structures and relative energies of the DHA conformers were calculated at the HF, MP2, and DFT levels of theory with the 6-31G(d,p) basis set.[6] Four stable conformers of DHA were determined from these calculations. The conformer of C_2 symmetry with two C═O···H−O hydrogen bonds was found to be the energetically most favorable arrangement, whereas three conformers with O−H···O−H hydrogen bonding were predicted to be less stable by 10.5−19.3 kJ/mol at the MP2/6-31G(d,p) level and by 17.0−23.1 kJ/mol at the B3LYP/6-31G-(d,p) level. One of these conformers has two hydrogen bonds between the hydroxyl hydrogen and the hydroxyl oxygen.

The gas-phase vibrational spectrum of DHA between 800 and 4000 cm^{-1} was investigated by Fourier transform infrared spectroscopy (FTIR) combined with theoretical predictions.[7] A total of six stable conformers were found for DHA at the B3LYP/6-31G(d,p) and MP2/6-31G(d,p) levels of theory. Both methods predicted the doubly hydrogen bonded

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(C═O···H−O) conformer to be the most stable form. The energy difference between this conformer and other stable conformers with one hydrogen bond ranges from 7 to 24 kJ/mol. In contradiction to earlier calculations,[6] C═O···H−O hydrogen bonding was also determined in the next three lowest energy conformers of DHA. From FTIR spectra analysis,[7] it was shown that the spectrum of the isolated molecule is seemingly well reproduced by harmonic fundamental wavenumbers calculated at the different levels of theory. From the temperature-dependent gas-phase spectra of DHA, the weak band near 3680 cm^{-1} was assigned to the second most stable conformer with one C═O···H−O hydrogen bond and one free OH group in the syn position with respect to the C−C bond.

To determine the structural parameters of DHA and investigate the conformational composition of this molecule in the gas-phase, the GED study was undertaken in this work. Due to employment of the MW rotational constants[4] and results of theoretical calculations, it was possible to perform the combined analysis of GED and MW data. Since the structural parameters were previously determined only at the B3LYP/6-31G(d,p) and MP2/6-31G(d,p) levels,[6] the structural analysis was aided by high level quantum chemical calculations. These calculations could also resolve the contradiction in symmetry of the most stable conformer and in structures and energies of the next low-energy conformers predicted earlier.[5−7] The obtained experimental and theoretical results were also used to estimate the ideal gas thermodynamic properties of DHA, which were not published up to now.

The structural parameters of DHA are of obvious interest in comparison with related compounds. MW and GED studies[8−11] were performed for some molecules which are structurally very similar to DHA. The C−O bond length in glycolic acid ($HO-CH_2-COOH$) was determined to be $r_s = 1.406(4)$ Å from MW spectra[8] and $r_\alpha^\circ = 1.407(4)$ Å from analysis of gas-phase electron diffraction data.[9] This value was substantially smaller than the C−O bond in glycolaldehyde ($HO-CH_2-COH$), $r_s = 1.437(1)$ Å, obtained from a MW study.[10] The last value was assumed for the C−O bond length in the interpretation of the MW spectra of hydroxyacetone ($HO-CH_2-CO-CH_3$).[11] It is difficult to explain this large difference in the C−O bond lengths among structurally similar molecules. That is why the structural study of DHA is of interest.

2. Experimental Section

A sample of crystalline powder of DHA with a purity of 98% and melting point about 350 K was purchased from the Merck KGaA company and used without further purification. In order to have a sufficient vapor pressure for the GED experiment, the sample of DHA was heated. Most experiments were carried out with the nozzle temperature between 357 and 378 K. Since the required heating may result in sample decomposition, the vapor composition at the experimental temperature was analyzed by a gas chromatography−mass spectrometric system. The analysis showed that DHA was the main component of the fraction and the amount of volatile impurities did not exceed 1%. Such a level of impurities is not significant for the GED analysis, and qualitative analysis of the substance impurities was not carried out.

Electron diffraction intensities were recorded using the electron diffraction apparatus at Moscow State University. Information about the experimental conditions is listed in Table 1. The electron wavelength was calibrated against diffraction patterns of CCl_4. The optical densities were measured using a commercial Epson Perfection 4870 photo scanner. The data were processed (with a program UNEX[12]) using standard routines. The experimental intensity curves are presented in Figure 1, where the final backgrounds are shown for the average curves for the long and short camera distances. The data are available in Table 1S of Supporting Information.

TABLE 1: Experimental Conditions of Gas-Phase Electron Diffraction Experiment

	long camera	short camera
camera distance (mm)	362.28	193.94
nozzle temperature (K)	360	378
accelerating voltage (kV)	60	60
electron wavelength (Å)	0.049519	0.049860
number of plates used	3	3
range of *s* value ($Å^{-1}$)[a]	3.2−18.6	8.2−30.2
scale factor	0.733(9)[b]	0.642(21)[b]

[a] $s = 4\pi\lambda^{-1}\sin\theta/2$, where θ is the scattering angle and λ is the electron wavelength. [b] Value in parentheses is the estimated standard deviation.

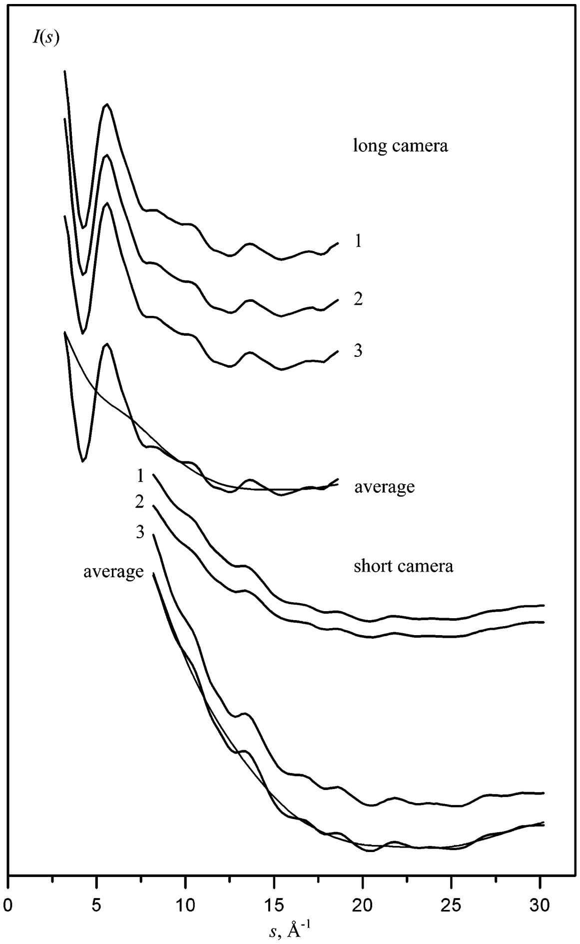

Figure 1. Experimental intensity curves with the background for the model of the conformer mixture.

3. Theoretical Calculations

With four torsional degrees of freedom, DHA can exist in a large variety of conformations. Since the low-energy conformers should be taken into account in the GED structural analysis, the possible conformers of DHA were determined in the present work using the ab initio and DFT calculations with different basis sets. Additionally, the Gaussian-3X (G3X) method[13] was used for energy estimations. The G3X method is one of the composite methods developed to achieve high accuracy in

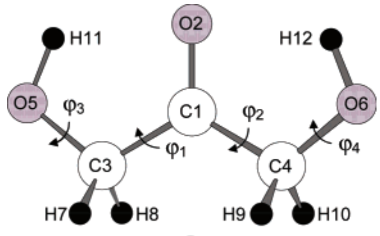

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Figure 2. Structure of the most stable doubly hydrogen bonded conformer of DHA with atom numbering. The torsional angles φ_1, φ_2, φ_3, and φ_4 are the dihedral angles O2−C1−C3−O5, O2−C1−C4−O6, H11−O5−C3−C1, and H12−O6−C4−C1, respectively.

energy calculations. All these calculations were carried out using the Gaussian 03 program package.[14]

Other results provided by the theoretical calculations were the quadratic and cubic force fields which are necessary to estimate the vibrational amplitudes, harmonic, and anharmonic vibrational corrections to the internuclear distances and to the rotational constants. The SHRINK program[15,16] was used to calculate these values.

3.1. Geometry of DHA Conformers. To determine the stable conformers of DHA, first the geometries of 10 possible structures were optimized at the B3LYP/6-31G(d,p) level. The initial values of torsional angles φ_1, φ_2, φ_3, and φ_4 around the C1−C3, C1−C4, C3−O5, and C4−O6 bonds, respectively, (see Figure 2 for atom numbering) were assumed to be 0° or 180° in different combinations. Calculated vibrational frequencies for nine optimized structures were real, confirming that these structures were the true minima on the potential energy surface. The relative energies of nine stable conformers of DHA are listed in Table 2. Assuming IUPAC nomenclature,[17] the conformers can be described by synperiplanar (sp), antiperiplanar (ap), synclinal (sc), and anticlinal (ac) stereochemical arrangements. In the next stage, we searched for the possible low-energy conformers by a series of constrained optimizations at the B3LYP/6-31G(d,p) level. The optimized I−VI structures were used as starting points for the one-dimensional potential energy scans. The energy profiles as a function of torsional angle were determined by alternately scanning four dihedral angles from 0° to 360° at 10° intervals, while the remaining molecular structural parameters were optimized. From calculated torsional profiles, the new low-energy conformers have not been detected.

In accordance with theoretical calculations at different levels of theory, the most stable conformer of DHA has a doubly hydrogen bonded sp,sp,sp,sp configuration (conformer I, Figure 2). For the high level theoretical calculations, the geometry optimization led to the structure of C_{2v} symmetry with $\varphi_1 = \varphi_2 = \varphi_3 = \varphi_4 = 0°$ (Table 2). However, the structures of C_2 symmetry with nonzero torsional angles were obtained at the B3LYP and MP2 levels of theory with 6-31G(d,p) and 6-311++G(d,p) basis sets, whereas a planar heavy atom configuration did not correspond to a true minimum, since one calculated frequency was imaginary. The synperiplanar conformation is defined by the range of torsional angle from 0° to ±30°[17] and so the C_2 forms are also specified as the sp,sp,sp,sp conformer.

The symmetry of the conformer I was verified by frequency calculations at all levels of theory except for the MP2 theory with basis sets cc-pVTZ, aug-cc-pVTZ, and cc-pVQZ. However, the optimization of the C_2 structure by three just listed methods converged to the structure with $\varphi_1 = \varphi_2 \approx \varphi_3 = \varphi_4 \approx 0°$, i.e., the structure of C_2 symmetry was not revealed by these methods. The structural parameters of the most stable conformer I calculated at different levels of theory are presented in Table 3. As is seen from this table, the calculated values of bond lengths and angles are in rather good agreement.

The next lowest energy conformers can be divided into two groups: with a single hydrogen bond (II−VI, Figure 3) or without hydrogen bonding (VII−IX). The values of torsional angles for all stable conformers of DHA obtained from B3LYP/cc-pVTZ calculations are given in Table 4. In conformers II, III, and V, the intramolecular hydrogen bond is formed between the hydroxyl hydrogen atom and the carbonyl oxygen atom (O2···H11 bond). In conformers IV and VI, the hydroxyl hydrogen atom is connected by a hydrogen bond with the hydroxyl oxygen atom (O5···H12 bond). The structural parameters of hydrogen bonds in the conformers I−VI are given in Table 2S of Supporting Information.

The relative energies of singly hydrogen bonded conformers are substantially less than those for conformers with free OH groups (Table 2). The sole exception is the conformer VI, whose energy is close to that of conformer VII. It should be noted that the geometry optimization of conformer VI is the difficult optimization case. This conformer was not found at the B3LYP/6-31G++(d,p) and MP2/6-31G++(d,p) levels because the optimization led to the structurally close conformer IV. Besides, to succeed in the optimization procedure, in a few instances a geometry optimization of conformer VI was preceded by a vibrational frequency calculation.

3.2. Conformational Composition of DHA. The conformational composition can be estimated from the computed values of relative Gibbs free energies of the conformers. The G3X electronic energies were used in these calculations. The values needed for Gibbs free energy calculations are listed in Table 3S (Supporting Information) together with predicted conformer composition. Only conformers II and III have significant abundance at the temperature of the experiment (20% and 10%, respectively), and these conformers were taken into account in the GED analysis of DHA.

3.3. Force Field Calculation. In this study, a structural analysis, including a joint analysis of GED and MW data, was carried out to obtain the experimental−theoretical approach to equilibrium r_e geometry by calculating anharmonic vibrational corrections based on the cubic force field. The equilibrium structure, quadratic, and cubic force constants, and vibrational frequencies for three lowest energy conformers of DHA were calculated at the B3LYP/cc-pVTZ level. The harmonic force constants were calculated from analytical expressions for the second energy derivatives, and the cubic force constants were obtained by numerical differentiation of the second derivatives. From the quadratic and cubic force constants, the amplitudes of vibration (u), harmonic ($r_{h1} - r_a$), and anharmonic ($r_e - r_a$) vibrational corrections to the internuclear distances and to the rotational constants ($B_e^{(i)} - B_0^{(i)}$) were calculated using the SHRINK program.[15,16] The calculated values of amplitudes of vibration and vibrational corrections are given in Table 4S (Supporting Information).

4. Structural Analysis

4.1. Analysis of the GED Data. The theoretical calculations gave evidence for some conformers of DHA, one of which was at substantially lower energy than others. The abundance of the next two low-energy conformers was predicted to be about 30% in total. Such an amount of conformers can be detected by the GED method. At first, we performed a data analysis assuming that the DHA molecule has a single conformation in the vapor phase. Since a C_2 structure was predicted

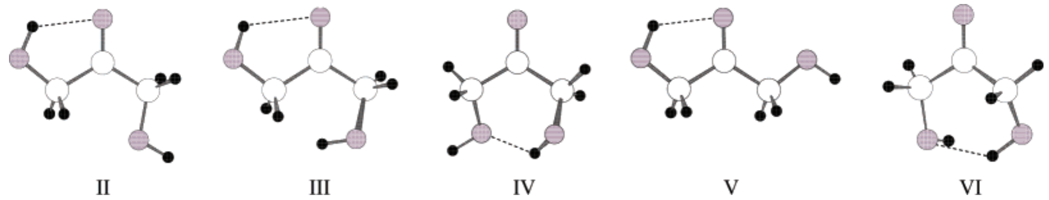

Figure 3. Structures of five singly hydrogen bonded conformers. Hydrogen bonds are shown by dashed lines.

TABLE 2: Relative Energies of DHA Conformers Calculated at Different Levels of Theory (kJ/mol)[a]

				B3LYP			MP2		
	conformer	symmetry	G3X[b]	/6-31G(d,p)	/6-311++G(d,p)	/cc-pVTZ /aug-cc-pVTZ[c]	/6-31G(d,p)	/6-311++G(d,p)	/cc-pVTZ aug-cc-pVTZ[c] /cc-pVQZ[c]
I	sp,sp,sp,sp	C_{2v} or C_2	0 (C_{2v})	0 (C_2)	0 (C_2)	0 (C_{2v})	0 (C_2)	0 (C_2)	0 (C_{2v})
II	sp,ap,sp,ap	C_s	7.9	9.9	7.5	9.1	7.2	7.5	8.9
III	sp,−ap,sp,sc	C_1	10.0	9.3	9.9	10.2	7.2	10.3	10.3
IV	ac,ac,ap,sc	C_1	19.4	20.3	17.3	22.6	13.2	12.6	19.8
V	−sp,−sp,sp,ap	C_1 or C_s	21.1 (C_s)	23.4 (C_1)	21.7 (C_1)	21.8 (C_s)	21.5 (C_1)	18.9 (C_1)	21.3 (C_s)
VI	−ap,ac,sc,sc	C_1	30.3	24.6	d	29.7	19.7	d	28.7
VII	ap,sp,ap,ap	C_s	30.8	36.2	31.1	33.2	31.1	27.8	32.6
VIII	−ap,sp,sc,ap	C_1	33.6	36.2	33.9	35.0	31.5	30.6	34.5
IX	sp,sp,−ap,−ap	C_2	46.1	51.9	47.3	48.1	48.1	41.5	47.4

[a] Relative energies are calculated from total energies $E_{\mathrm{tot},298} = E_e + \mathrm{ZPE} + [H_{298} - H_0]$, where E_e is the electronic energy, ZPE is the zero point energy correction, and $[H_{298} - H_0]$ is the thermal correction. ZPE and thermal corrections are calculated at the B3LYP/6-31G(2df,p) level for G3X energies and at the B3LYP/6-31G(d,p) and MP2/6-31G(d,p) levels for B3LYP and MP2 energies, respectively. [b] The geometry was optimized at the B3LYP/6-31G(2df,p) level. [c] Only the most stable conformer I was investigated with aug-cc-pVTZ and cc-pVQZ basis sets. [d] The conformer was not revealed at this level of theory (see text).

TABLE 3: Structural Parameters of Doubly Hydrogen Bonded Conformer I of DHA Calculated at Different Levels of Theory[a]

	B3LYP					MP2				
parameter	/6-31G(d,p)	/6-311++G(d,p)	/6-31(2df,p)	/cc-pVTZ	/aug-cc-pVTZ	/6-31G(d,p)	/6-311++G(d,p)	/cc-pVTZ	/aug-cc-pVTZ	/cc-pVQZ
symmetry	C_2	C_2	C_{2v}	C_{2v}	C_{2v}	C_2	C_2	C_{2v}	C_{2v}	C_{2v}
r(C═O)	1.222	1.216	1.216	1.214	1.214	1.231	1.221	1.222	1.222	1.219
r(C−C)	1.518	1.516	1.517	1.512	1.513	1.513	1.515	1.508	1.508	1.506
r(C−O)	1.399	1.403	1.397	1.400	1.401	1.405	1.404	1.400	1.402	1.397
r(C3−H7)	1.104	1.100	1.103	1.098	1.097	1.099	1.102	1.094	1.095	1.093
r(C3−H8)	1.102	1.098	1.103	1.098	1.097	1.094	1.095	1.094	1.095	1.093
r(O−H)	0.973	0.969	0.969	0.969	0.969	0.970	0.966	0.968	0.970	0.967
∠C−C═O	119.8	120.3	120.0	120.3	120.4	120.1	120.8	120.4	120.5	120.4
∠C−C−O	111.8	112.2	111.7	112.1	112.1	111.5	112.1	111.6	111.7	111.6
∠C1−C3−H7	107.5	107.8	108.1	108.2	108.5	107.1	106.4	108.0	108.3	108.2
∠C1−C3−H8	108.7	109.0	108.1	108.2	108.5	109.4	109.8	108.0	108.3	108.2
∠C−O−H	105.7	107.0	105.7	106.4	106.9	105.3	105.8	105.0	105.7	105.6
φ(O═C−C3−H7)	118.1	117.3	122.8	122.5	122.3	112.0	106.0	122.3	122.0	122.1
φ(O═C−C3−H8)	−127.3	−127.1	−122.8	−122.5	−122.3	−132.6	−137.9	−122.3	−122.0	−122.1
$\varphi_1 = \varphi_2 = \varphi$(C−C)	−4.7	−4.9	0	0	0	−10.8	−16.5	0	0	0
$\varphi_3 = \varphi_4 = \varphi$(C−O)	6.2	6.2	0	0	0	15.5	25.0	0	0	0
ΔA, %	0.5	0.6	0.9	1.0	0.9	0.7	1.5	0.5	0.3	0.9
ΔB, %	0.1	0.6	0.2	0.1	0.1	0.2	0.6	1.1	0.8	1.3
ΔC, %	0.1	0.5	0.2	0.1	0.1	0.2	0.2	0.9	0.6	1.1

[a] Bond lengths in Å, angles in degrees; ΔA, ΔB, and ΔC are the percentage differences between the observed (reference 4) and calculated rotational constants.

TABLE 4: Torsion Angles of DHA Conformers Calculated at the B3LYP/cc-pVTZ Level[a]

conformer	symmetry	φ_1	φ_2	φ_3	φ_4
I	C_{2v}	0.0	0.0	0.0	0.0
II	C_s	0.0	180.0	0.0	180.0
III	C_1	−0.3	−174.6	−0.2	84.7
IV	C_1	148.3	147.5	176.4	62.2
V	C_s	0.0	0.0	0.0	180.0
VI	C_1	−168.1	138.1	87.6	64.0
VII	C_s	180.0	0.0	180.0	180.0
VIII	C_1	−169.8	−1.8	86.2	−178.8
IX	C_2	14.4	14.4	−173.5	−173.5

[a] Torsional angles φ_1, φ_2, φ_3, and φ_4 are in degrees; their definition is shown in Figure 2.

for the conformer I by several theoretical calculations (see Table 2), a set of preliminary refinements with different starting values for torsional angle $\varphi_1 = \varphi_2$ was carried out ignoring (r_a structure) or including (r_{h1} and r_e structures) vibrational corrections. Assuming a C_2 symmetry for the molecule, the structure of DHA can be described by 15 parameters listed in Table 3. Refinements of this structure were done by the method of least-squares,[12] adjusting simultaneously the eight geometrical parameters, r(C═O), r(C−C), r(C−O), r(C3−H7), ∠C−C═O, ∠C−C−O, ∠C1−C3−H7, and $\varphi_1 = \varphi_2 = \varphi$(C−C), to the experimental molecular intensities. The C−H and O−H bonds were described by only one variable. The differences between their values were constrained at the values from MP2/6-311++G(d,p) calculations. The C−C−H and O−C−H bond angles were refined by the same way. Two geometrical parameters, namely, dihedral angles O═C−C3−H7 and O═C−C3−H8, and vibrational amplitudes were assumed at their theoretical values and were not refined.

TABLE 5: Molecular r_e Structure of DHA Obtained from GED Study[a]

		GED		GED + MW	
parameter	MW[b]	single conformer	mixture of conformers[c]	single conformer	mixture of conformers[c]
r(C═O)		1.211(3)	1.213(2)	1.211(2)	1.215(2)
r(C−C)		1.514(3)	1.512(2)	1.514(2)	1.516(2)
r(C−O)		1.392(2)	1.391(2)	1.392(2)	1.393(2)
r(C−H)		1.103(6)	1.108(5)	1.102(4)	1.096(4)
r(O−H)		$0.975(6)^d$	$0.979(5)^d$	$0.974(4)^d$	$0.976(4)^d$
∠C−C═O		119.8(4)	119.8(3)	120.0(2)	119.9(2)
∠C−C−O		110.9(4)	111.3(3)	110.9(2)	111.0(2)
∠C−C−H		109.8(16)	109.1(18)	110.6(7)	108.2(7)
∠C−O−H		$108.1(16)^e$	$107.3(18)^e$	$108.9(7)^e$	$106.5(7)^e$
O═C−C3−H		120.9(14)	120.2(14)	121.7(5)	122.5(6)
φ(C−C)		0	0	0	0
φ(C−O)		0	0	0	0
A_0	9801.2914(12)	9844.0 [0.4%]	9850.9 [0.5%]	9801.2822 [0.0001%]	9801.2398 [0.0005%]
B_0	2051.5257(7)	2050.3 [0.1%]	2048.6 [0.1%]	2051.5121 [0.0007%]	2051.5046 [0.0010%]
C_0	1735.1645(8)	1736.8 [0.1%]	1737.1 [0.1%]	1735.1816 [0.0010%]	1735.2020 [0.0022%]
mole fraction					
conformer I		1.00	0.70(3)	1.00	0.69(4)
conformer II			0.06		0.11
conformer III			0.24(9)		0.20(10)
R_L		5.4	3.1	5.5	3.3
R_S		7.4	5.1	7.6	6.6
R_{tot}		5.9	3.6	6.0	4.3

[a] Bond lengths in Å, angles in degrees, rotational constants (A_0, B_0, C_0) in MHz; values in parentheses are 3 times the standard deviations; the percentage differences between the MW and GED rotational constants are given in square brackets; together with total value of agreement factor (R_{tot}), the R-factors are given for long (R_L) and short (R_S) camera distance. [b] Reference 4. [c] Parameters for the most stable conformer I are given. [d] O−H bond was refined in the group together with the C−H bond. [e] C−O−H angle was refined in the group together with the C−C−H angle.

The torsional angle $\varphi_3 = \varphi_4 = \varphi$(C−O) describing the rotation of OH groups cannot be refined freely together with other geometrical parameters. Because of this, we attempted to estimate its value by the comparison of R-factors for the models with different assumed values of φ_1 and φ_3. The models with all compositions of φ_1 and φ_3 values from −40° to 40° at 1° steps were calculated using the utility of the two-dimensional scan.[12] The lowest R-factor was obtained for the model with $\varphi_1 = -17°$ and $\varphi_3 = 1°$ (in the terms of the r_a structure). Therefore, the equilibrium value of φ_3 was assumed to be 0° in the following analysis.

The refinement of C_2 structures led to the conformer with near-zero values of torsional angle φ(C−C) for the r_{h1} and r_e structures. Since these structures were corrected for harmonic (r_{h1} structure) or anharmonic (r_e structure) vibrational effects, the determined values of φ(C−C) correspond to the equilibrium position or close to it. The nonzero values of this torsional angle (−12° to −17°) were obtained for the r_a structure when vibrational corrections were not included. Thus, the thermal-average molecular structure (r_a) of DHA derived directly from an analysis of GED data has a nonplanar heavy atom configuration. This suggests a large-amplitude motion about the C−C bonds and is in agreement with rather low values of corresponding torsional vibrations (60 and 99 cm^{-1}). Strictly speaking, the torsional motion about the C−C bonds should be treated as a large-amplitude motion. However, the treatment of the GED dynamic model with a two-dimensional potential presents a considerable challenge for structural analysis.

Since the near-zero values of the torsional angles were obtained for r_{h1} and r_e structures, the structure of C_{2v} symmetry with φ(C−C) = 0° and φ(C−O) = 0° was accepted for DHA in further analyses. The C_{2v} structure of DHA can be described by 10 independent parameters listed in Table 5. Eight of these parameters were chosen as adjustable: r(C═O), r(C−C), r(C−O), r(C−H), ∠C−C═O, ∠C−C−O, ∠C−C−H, and the dihedral angle O═C−C3−H. The C−H and O−H bonds were described by only one parameter. The difference between their values was constrained at the value determined from B3LYP/cc-pVTZ calculation. The C−C−H and C−O−H bond angles were refined in a similar way. There are also vibrational amplitudes constructed by grouping individual amplitudes together; these groups are presented in Table 6. The initial values of geometrical parameters and vibrational amplitudes were taken from the B3LYP/cc-pVTZ calculations. The anharmonic vibrational corrections, ($r_e - r_a$), calculated from the B3LYP/cc-pVTZ cubic force field were used in structural analysis. Table

TABLE 6: Interatomic Distances (r_a) and Experimental and Calculated Vibrational Amplitudes (u) at 369 K[a]

	GED				
	single conformer		mixture of conformers[b]		
bond distance	r, Å	u_{exp}, Å	r, Å	u_{exp}, Å	B3LYP/cc-pVTZ u_{calcd}, Å
O5−H11	0.987	$0.061(6)^1$	0.991	0.069	0.069
C3−H7	1.120	0.070^1	1.125	0.078	0.078
C1−O2	1.214	$0.042(6)^2$	1.215	$0.041(2)^1$	0.038
C3−O5	1.400	$0.046(5)^3$	1.399	$0.047(3)^2$	0.048
C1−C3	1.523	0.051^3	1.521	0.052^2	0.053
C3···H11	1.951	$0.085(9)^4$	1.944	0.100	0.100
O5···H7	2.053	0.090^4	2.052	0.105	0.105
C1···H7	2.167	0.102^4	2.160	0.118	0.118
O2···H11	2.231	$0.219(27)^5$	2.226	0.221	0.221
O2···C3	2.377	$0.065(2)^6$	2.376	$0.065(2)^3$	0.060
C1···H11	2.403	0.169^5	2.396	0.171	0.171
C1···O5	2.420	0.072^6	2.422	0.072^3	0.067
C3···C4	2.626	$0.077(5)^7$	2.620	$0.071(4)^4$	0.077
O2···O5	2.702	0.113^7	2.708	0.106^4	0.112
C3···H9	2.910	$0.159(28)^8$	2.900	0.189	0.189
O2···H7	3.072	0.162^8	3.064	0.192	0.192
C3···O6	3.793	$0.098(6)^9$	3.791	$0.084(4)^5$	0.080
C3···H12	3.902	$0.173(31)^{10}$	3.892	0.176	0.176
O5···H9	4.111	0.177^{10}	4.100	0.180	0.180
O5···H12	4.708	0.203^{10}	4.706	0.206	0.206
O5···O6	4.823	$0.111(14)^{11}$	4.828	$0.088(10)^6$	0.089

[a] Values in parentheses are 3 times the standard deviations. Equal superscripts indicate that these amplitudes were refined in one group; values without superscripts were constrained at theoretical values. Amplitudes calculated at the B3LYP/cc-pVTZ level were used as the initial values in the GED model and in joint analysis of GED and MW data. [b] Values for the most stable conformer I are given.

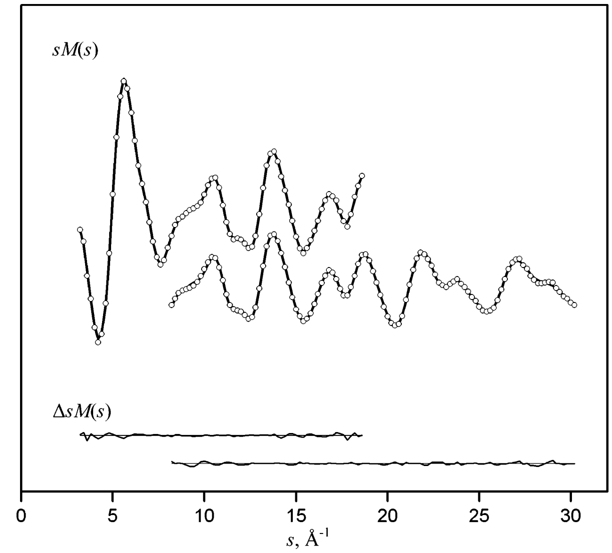

Figure 4. Experimental (○) and theoretical (solid line) molecular intensities $sM(s)$ and the difference curves $\Delta sM(s)$ for the model of the conformational mixture of DHA.

5 shows the final result of least-squares refinement of the GED single conformer model, where all eight geometrical parameters and six vibrational amplitude groups of nonhydrogen interatomic distances were refined simultaneously. The amplitudes of hydrogen distances were obtained from preliminary constrained refinements.

In the following refinements, the model of the mixture of three conformers was tested. The mole fractions of the conformers I and III were determined as additional adjustable parameters. The differences in the bond lengths, bond angles, and vibrational amplitudes of conformers were set to the B3LYP/cc-pVTZ values. The molecular parameters of the major conformer I were refined in the analysis whereas the values of the conformers II and III were deduced by adding the differences to the refined values of the conformer I. The anharmonic vibrational corrections were taken into account for all conformers. Tables 5 and 6 list the results of the final refinement for the conformational mixture, where eight geometrical parameters, the abundances of conformers I and III, and six vibrational amplitudes of nonhydrogen distances were varied simultaneously. The amplitudes of hydrogen distances were constrained at their theoretical values. The refined geometrical parameters of three DHA conformers are listed in the Supporting Information (Table 5S). Table 6S in Supporting Information gives the correlation matrix for the parameters of conformer I. The resulting molecular intensity and radial distribution curves are shown in Figures 4 and 5, respectively.

4.2. Combined Analysis of GED Data and Rotational Constants. With $(B_e^{(i)} - B_0^{(i)})$ corrections calculated from the B3LYP/cc-pVTZ cubic force constants, the rotational constants A_0, B_0, and C_0 determined by MW spectroscopy[4] were converted to A_e, B_e, and C_e values, needed in the joint analysis of GED and MW data (Table 7). By this means, the MW data were transformed to an r_e basis. To bring the GED r_a distances to the same basis by eliminating vibrational effects, the $(r_e - r_a)$ corrections (Table 4S in Supporting Information) were used. The refinements were done by the method of least-squares, adjusting the theoretical intensity data and rotational constants to experimental ones by varying simultaneously most of the molecular parameters.

The weights of the rotational constants relative to the GED intensities were empirically adjusted[18] to obey a balance between a sufficiently accurate reproduction of both rotational constants and GED intensities. This means that the relative weights of the rotational constants are increased until the calculated rotational constants reproduce the experimental values within tenths of a MHz, while the agreement between experimental and calculated GED data still remains reasonable. As is seen from Table 7, the rotational constants calculated from the joint analysis of GED and MW data are very close to the experimental ones. The decrease of relative weights of the rotational constants had practically no effect on the values of GED structural parameters and the *R*-factor. The geometrical parameters resulting from the joint refinement of the GED and MW data are given in Table 5.

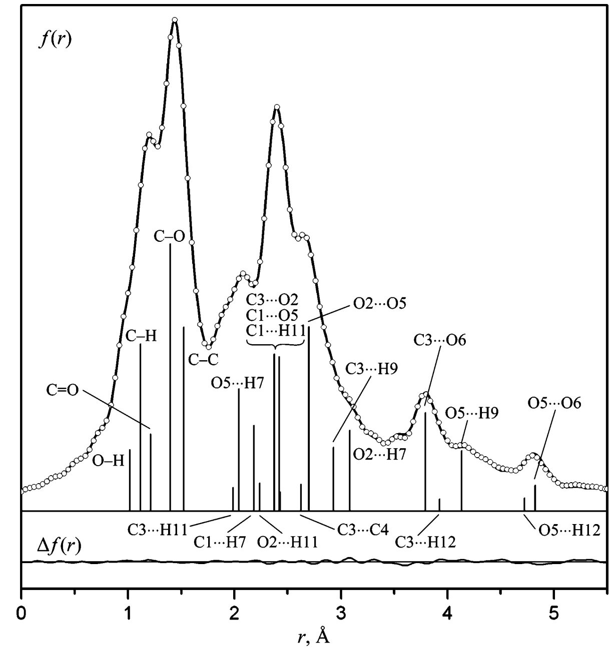

Figure 5. Experimental (○) and theoretical (solid line) radial distribution curves $f(r)$ with the difference curve $\Delta f(r)$ for the model of the conformational mixture of DHA. A damping factor of $\exp(-0.0015s^2)$ is used. Distances distribution for the most stable conformer is indicated by vertical bars.

5. Ideal Gas Thermodynamic Properties

Experimental and theoretical data on molecular parameters of DHA obtained in this work allow one to calculate the thermodynamic properties of this molecule. To our knowledge, no experimental or theoretical data on entropy, heat capacity, and enthalpy of formation of DHA is available in the literature.

5.1. Entropy, Heat Capacity, and Enthalpy. Standard entropies, $S°(T)$, heat capacities, $C_p^{\circ}(T)$, and enthalpies, $H°(T) - H°(0)$, were calculated by standard statistical thermodynamic formulas using the rigid-rotor harmonic-oscillator approximation. Moments of inertia were calculated using the structural parameters of DHA conformers determined from the combined analysis of GED and MW data. The B3LYP/cc-pVTZ vibrational frequencies and G3X relative energies of conformers were used in thermodynamic functions calculation. Calculated vibrational frequencies were scaled using recommended scale factors.[19] Molecular parameters for three DHA conformers and calculated thermodynamic functions are given in Supporting Information (Tables 7S and 8S, respectively). The main errors in the calculated values arise from the approximate treatment of internal rotation and may amount to 3−5 J/(K mol) for $S°(298)$ and $C_p^{\circ}(298)$.

TABLE 7: Comparison between Experimental Rotational Constants (MW) and Those Calculated from Joint Analysis of GED and MW Data for the Model of the Conformer Mixture

	MW			GED + MW		
	$B_0^{(i)}$ (exptl)[a]	$(B_e^{(i)} - B_0^{(i)})$[b]	$B_e^{(i)}$ (exptl)	$B_e^{(i)}$ (calcd)	$B_0^{(i)}$ (calcd)	differences[c]
A, MHz	9801.2914 ± 0.0012	101.5004	9902.7918	9902.7402	9801.2398	0.0516
B, MHz	2051.5257 ± 0.0007	24.3248	2075.8505	2075.8294	2051.5046	0.0211
C, MHz	1735.1645 ± 0.0008	17.8435	1753.0080	1753.0455	1735.2020	−0.0375

[a] Reference 4. [b] Anharmonic corrections calculated from the B3LYP/cc-pVTZ cubic force field. [c] Refer to the difference between $B^{(i)}$(exptl) and $B^{(i)}$(calcd).

5.2. Enthalpy of Formation. The enthalpy of formation of DHA, $\Delta_f H^\circ_{298} = -523 \pm 4$ kJ/mol, is calculated by the atomization procedure using a G3X method.[13] The uncertainty of the computed value is estimated on the basis of our assessment of the G3X method for different organic compounds.[20,21] The values used in the calculation of the enthalpy of formation are given in Tables 9S and 10S in Supporting Information. The $\Delta_f H^\circ_{298}$ value for DHA can be also calculated by the empirical method of group equations[22] from known experimental enthalpies of formation of related compounds:

$$\Delta_f H^\circ_{298}(\mathrm{HO{-}CH_2{-}CO{-}CH_2{-}OH}) - \Delta_f H^\circ_{298}(\mathrm{CH_3{-}CO{-}CH_3}) = \Delta_f H^\circ_{298}(\mathrm{HO{-}CH_2{-}CH_2{-}CH_2{-}OH}) - \Delta_f H^\circ_{298}(\mathrm{CH_3{-}CH_2{-}CH_3})$$

With the use of the experimental $\Delta_f H^\circ_{298}$ values[23] for CH_3COCH_3 (−217.1 ± 0.7 kJ/mol), $CH_2(CH_2OH)_2$ (−408.0 ± 6.0 kJ/mol), and C_3H_8 (−104.7 ± 0.5 kJ/mol), the enthalpy of formation of DHA may be estimated as −520.4 ± 7 kJ/mol. As is seen, both methods give close values of the enthalpy of formation of DHA. Thus, the calculated G3X value gets additional support from the result of the method of group equations, which is a rather accurate estimating scheme if the enthalpies of formation of the reference compounds are determined with high accuracy and if it is possible to choose the reaction with good group balance.

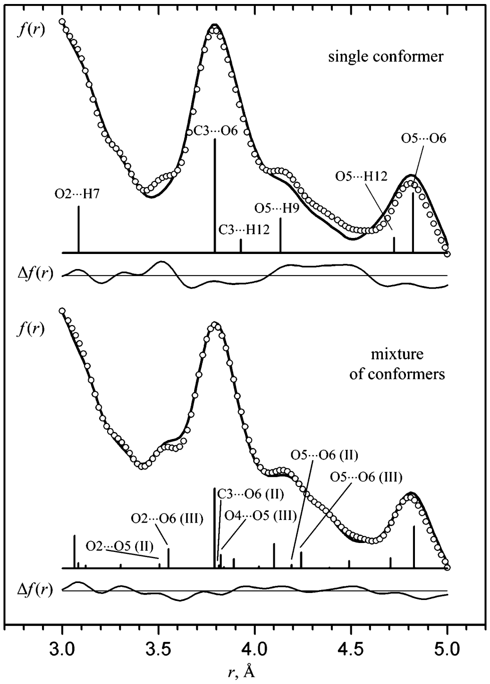

Figure 6. Comparison between experimental (○) and theoretical (solid line) radial distribution curves *f*(*r*) of DHA for the model of the single conformer and the mixture of three conformers. The difference curves, Δ*f*(*r*), are experimental minus theoretical. The distances distribution is indicated by vertical bars. For the model of conformer mixture, only the O···O and C···O distances of conformers II and III are shown. The *R*-factors of 6.0 and 4.3% correspond to two above models.

6. Results and Discussion

The C_{2v} structure with two hydrogen bonds to the carbonyl oxygen was found to be the lowest energy conformer of DHA in agreement with results of MW studies[4,5] and high level theoretical calculations performed in this work. The C_2 symmetry was previously reported for DHA from calculations with 6-31G(d,p)[6] and 6-311G++(d,p)[4] basis sets. In this work, to examine the basis set effects, the geometry optimizations were carried out for planar (C_{2v}) and nonplanar (C_2) geometry using the B3LYP and MP2 method with larger basis sets (cc-pVTZ, aug-cc-pVTZ, and cc-pVQZ). It was found that in all cases the C_2 geometries converged to the planar structures with near-zero values of torsional angles. Vibrational frequency calculations were carried out at the B3LYP/cc-pVTZ and B3LYP/aug-cc-pVTZ levels, verifying that the C_{2v} model represents a true minimum on the potential energy surface.

On the basis of theoretical calculations, the next five lowest energy conformers (II−VI, see Figure 3) have one hydrogen bond, which shows the important role of hydrogen bonding in structure stabilization. The same conformers were determined earlier from B3LYP and MP2 calculations with the 6-31G(d,p) basis set,[7] whereas the conformers with one C═O···H−O hydrogen bond (II and III) were not found in ref 6 using the same methods. The conformers with one O−H···O−H hydrogen bond (IV and VI) were determined in the previous calculations.[6,7] As to the conformer with two O−H···O−H hydrogen bonds,[6] it has one imaginary frequency and therefore is not the true minimum. Compared to previous theoretical calculations,[6,7] three stable conformers without hydrogen bonding, VII−IX (Table 2), were also determined in this work. As would be expected, the relative energies of these conformers are substantially larger than those for the hydrogen bonded conformers. The conformer V with energy Δ*E* = 8.0 kJ/mol was predicted to be the second most stable conformer from B3LYP/6-31++G(d,p) calculations.[5] This result is inconsistent with that obtained in this work and in ref 7, where the conformer V with energy ∼23 kJ/mol was found to be the fifth stable conformer of DHA. This discrepancy may be the result from constrained geometry optimization used in ref 5.

Although a rather low *R*-factor was obtained for a single conformer model (6.0%), there is a distinctive difference between the experimental and theoretical radial distribution curves in the region of the distances from 3 to 5 Å (Figure 6), where the additional peaks from conformers II and III can be detected. As is seen from Figure 6, the model of the conformer mixture shows a better agreement between experimental and theoretical radial distribution curves resulting in a decrease in the *R*-factor to 4.3%. The abundance of the most stable conformer I (69 ± 4%) was determined with a good precision.

TABLE 8: Comparison of Structural Parameters of DHA, Glycolaldehyde, Glycolic Acid, and Hydroxyacetone

	$HO-CH_2-CO-CH_2-OH$		$HO-CH_2-CO-H$		$HO-CH_2-CO-OH$			$HO-CH_2-CO-CH_3$	
	GED + MW[b]	MP2/cc-pVQZ[b]	MW[c]	MP2/cc-pVQZ[b]	MW[d]	GED[e]	MP2/cc-pVQZ[b]	MW[f]	MP2/cc-pVQZ[b]
parameter[a]	r_e	r_e	r_s	r_e	r_s	r_α°	r_e	r_s	r_e
r(C═O)	1.215(2)	1.219	1.2094(3)	1.212	1.210(6)	1.208(1)	1.208	1.216[g]	1.217
r(C−C)	1.516(2)	1.506	1.4987(4)	1.500	1.495(6)	1.517(2)	1.504	1.499[g]	1.512
r(C−O)	1.393(2)	1.397	1.4366(7)	1.396	1.406(4)	1.407(4)	1.399	1.437[g]	1.397
r(C−H)	1.096(4)	1.093	1.0930(3)	1.095	1.097(3)	1.112(5)	1.091	1.093[g]	1.094
r(O−H)	0.967(4)	0.967	1.0510(5)	0.967	0.956(3)	0.967(3)	0.966	1.051[g]	0.969
∠C−C═O	119.2(2)	120.4	122.73(3)	121.6	124.2(4)	123.8(2)	123.4		119.3
∠C−C−O	111.0(2)	111.6	111.47(3)	111.8	111.3(4)	112.5(2)	110.9	110.5[g]	111.5
∠C−C−H	108.2(7)	108.2	109.22(2)	107.7	108.8(3)		108.1		107.9
∠C−O−H	106.5(7)	105.6	101.57(3)	105.4	105.2(1)	104.6(10)	105.9	103.6[g]	104.7

[a] Bond lengths in Å, angles in degrees; values in parentheses are 3 times the standard deviations. [b] This work. [c] Reference 10. [d] Reference 8. [e] Reference 9. [f] Reference 11. [g] Assumed at the values for acetone and glycolaldehyde.

The next stable conformer of DHA is the form III, whose abundance (20 ± 10%) is somewhat larger than that of conformer II. It seems to not be possible to determine with high accuracy how the abundance is shared by the minor conformers. The refined conformational composition of DHA is in agreement with results of theoretical calculations (Table 2 and Table 3S in Supporting Information), which predict about equal amounts of conformers II and III with total abundance of 30%. The gas-phase IR spectrum of DHA[7] was assigned to the predominant conformer I and to the second less-stable conformer III with weak but distinct absorption. From Figure 4 in ref 7, the abundance of conformer III at $T = 320$ K can be approximately estimated at 10−15%, which is somewhat less than the value determined in this work.

The equilibrium structural parameters of DHA determined in this work for both models (single conformer and a mixture of conformers) and by both methods (analysis of GED data alone and joint analysis of GED and MW data, see Table 5) are in good agreement with those obtained from theoretical calculations (Table 3). All parameters are within the range of theoretical values with the exception of the C−O bond length whose value of 1.393(2) Å is slightly less than theoretical ones (1.397−1.405 Å). The combined analysis of GED and MW data, where least-squares refinements were made by simultaneously fitting a theoretical intensity curve to two experimental curves and three rotational constants, had very good agreement to the experimental data: the *R*-factor for the electron diffraction data was 4.3%, and the calculated rotational constants were within 0.05 MHz of the experimental values. Inclusion of the rotational constants in the analysis is important in order to get as good a structure determination as possible. It is believed that the resulting values represent the best structure obtainable for DHA using current methods.

The cubic force field calculation provides a way of getting the approach to equilibrium geometry. The equilibrium structural parameters r_e, as distinct from GED parameters r_a, r_g, r_α°, r_{h1}, are directly comparable to geometries calculated with reliable quantum chemical methods. The determined r_e structure of DHA is in the best agreement with that from the MP2/cc-pVQZ calculation on the highest level of theory applied in the present work (see Table 3).

It is also interesting to compare the structural parameters of DHA with those determined experimentally for molecules with similar structures. The results obtained for glycolaldehyde[10] ($HO-CH_2-COH$), glycolic acid[8,9] ($HO-CH_2-CO-OH$), and hydroxyacetone[11] ($HO-CH_2-CO-CH_3$) are given in Table 8 together with results from MP2/cc-pVQZ calculations carried out in this work. As can be seen, the calculations at a rather high level of theory, MP2/cc-pVQZ, lead to similar values of structural parameters for these molecules. The experiment and theory are in good agreement for glycolic acid and DHA. However, there is a considerable difference in the experimental and calculated C−O bond lengths for glycolaldehyde, where the experimental value is 0.04 Å longer than the calculated one and those for glycolic acid and DHA. This finding puts the accuracy of the experimental value of the C−O bond for glycolaldehyde[10] in doubt.

7. Conclusion

The r_e structure of DHA was determined from the mixed experimental−theoretical approach to equilibrium geometry. The GED + MW structure represents the best combination of the available experimental and theoretical data on this molecule. The derived structural parameters are in good agreement with those obtained from high level theoretical calculations (B3LYP and MP2 with cc-pVTZ, aug-cc-pVTZ, and cc-pVQZ basis sets). It was revealed that the experimental data are well reproduced by assuming that DHA consists of a mixture of three conformers. The most stable conformer has two hydrogen bonds, whereas the next two lowest energy conformers have one hydrogen bond and their abundance is about 30% in total.

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Supporting Information Available: Experimental intensity curves with final backgrounds, hydrogen-bonding structural parameters of DHA conformers, calculation of conformational composition, B3LYP/cc-pVTZ vibrational amplitudes, harmonic, and anharmonic vibrational corrections, geometrical parameters of three DHA conformers determined from GED analysis, correlation matrix for refined parameters, molecular parameters of DHA conformers used in thermodynamic functions calculation, ideal gas thermodynamic functions of DHA, and values used in enthalpy of formation calculation. This material is available free of charge via the Internet at http://pubs.acs.org.

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