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Conformational analysis and vibrational assignment of bis-gem-diol of hexafluoroacetylacetone

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HIGHLIGHTS

• Vibrational spectra of 1,1,1,5,5,5-hexafluoropentane-2,2,4,4-tetraol was fully assigned.

• The conformational analysis for the titled compound has been done.

• The titled compound is engaged in two moderate intramolecular hydrogen bonds.

• The hydrogen bond energy was estimated to be about 7.5 kcal/mol per bond.

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1. Introduction

It is well known that carbonyl compounds may be attacked by water molecule to form the hydrated gem-diols. Because of great biological and chemical importance, the hydration–dehydration of the carbonyl compounds in aqueous solutions has been the subject of numerous studies [1–5].

The hydrates organic carbonyl compounds, gem-diols, usually exist in the aqueous solutions and rarely occur as pure substance out of solution. Because their synthesis and stability depend on the existence of very strong electron withdrawing groups, such as trifluoromethyl group, on the carbonyl position [6–9]. For example hexafluoroacetone is completely hydrated in the gas and liquid phases [10]. The equilibrium constant of the hydration, K_h , ranges from 10^{-6} to 10^3 . K_h increases by presence of electron withdrawing substituents and decreases by the presence of bulky substituents [11–14]. K_h for acetone, monofluoroacetone, trifluoroacetone, and

ABSTRACT

A complete conformational analysis of doubly-hydrated hexafluoroacetylacetone, 1,1,1,5,5,5-hexafluoropentane-2,2,4,4-tetraol (HFPTO), was carried out by *ab initio* calculations, at the density functional theory (DFT) level. According to our calculations, 10 stable conformers were obtained. The most stable conformer is stabilized by formation of two intramolecular hydrogen bond (of OHO type) in opposite directions. The calculated geometrical parameters are in agreement with the corresponding values obtained by X-ray diffraction technique. Harmonic and anharmonic vibrational frequencies of the most stable conformer and its deuterated analogue were also calculated and compared with the experimental data. Additionally the Bader theory is applied here showing that characteristics of the bond critical points (BCPs) are useful parameters to estimate the strength of intramolecular hydrogen bonding. Natural bond orbital (NBO) analysis method was performed for the investigation of the relative stability of HFPTO conformers. © 2013 Elsevier B.V. All rights reserved.

hexafluoroacetone is $2\times 10^{-3},$ 0.167, 35, and $1.2\times 10^{6},$ respectively [14].

Many reactions have been found to proceed via gem-diols, as intermediates, such as; the basic hydrolysis of amide [15], the Cannizzaro reaction [16], the enzymatic reactions [17,18], and the alkaline cleavage of chloral hydrate [19], and β -diketones [20].

Hexafluoroacetylacetone (HFAA) has long been known to add water to give the stable doubly-hydrated1,1,1,5,5,5-hexafluoropentane-2,2,4,4-tetraol (HFPTO) [21–24]. This hydrated form, which is a bis-gem-diol, is capable to make complexes with the metals [22,23]. Bouwman et al. [22] and Chekhlov [24] have studied the structure of the tetraol of HFAA by using the X-ray diffraction crystallographic technique.

To the best of our knowledge, unlike HFAA which its vibrational spectra have been extensively studied [25,26], the vibrational spectra of its hydrated species, HFPTO, have not been considered yet.

The aim of the present paper is to predict the structure and vibrational spectra (harmonic wavenumbers, potential energy distribution (PED), and relative intensities for Raman and IR spectra)



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of HFPTO by means of density functional theory (DFT). The calculated geometrical parameters will be compared with X-ray diffraction result [22,24]. The conformational analysis and the nature of the intramolecular hydrogen bond of HFPTO are investigated by means of DFT, natural bond orbital (NBO) theory, and Atom In Molecule (AIM) theory.

The calculated harmonic force constant of HFPTO was also used for predicting the Raman and IR spectra of deuterated specie. The calculated vibrational frequencies of both HFPTO and its deuterated analog are compared with those observed experimentally.

2. Experimental

HFAA, 99.5% pure, was purchased from Aldrich and used as received. HFPTO and its deuterated analogue, HFPTO-d6, are prepared according to the literature [11,22] by adding H_2O or D_2O to the hexane solution of HFAA. The white crystalline precipitate filtered off, washed once with a little ether, and dried in a vacuum over calcium chloride. According to the IR spectrum more than 90% is deuterated. No melting point was observed, sublimed before reaching 115° [11].

The IR spectra were recorded on a Bomem B-154 Fourier transform spectrophotometer in the region 4000–600 cm⁻¹ by averaging 20 scans with a resolution of 2 cm⁻¹. The spectra were measured as KBr pellets. The Far-IR spectra in the region 600–100 cm⁻¹ were obtained using a Thermo Nicolet NEXUS 870 FT-IR spectrometer equipped with a DTGS/polyethylene detector and a solid substrate beam splitter. The spectrum of the polyethylene pellet was collected with a resolution of 2 cm⁻¹ by averaging the results of 64 scans.

The FT-Raman spectra were recorded employing a 180° backscattering geometry and a Bomem MB-154 Fourier transform Raman spectrometer. The instrument was equipped with a ZnSe beam splitter and a TE cooled InGaAs detector. Rayleigh filtration was afforded by two sets of two holographic technology filters. Laser power at the sample was 300 mW. The spectra were collected with a resolution of 2 cm⁻¹ by coadding the results of 700 scans.

3. Method of analysis

The molecular equilibrium geometry and vibrational transitions of HFPTO were computed with the Gaussian 09 [27] software system. All possible conformations of HFPTO were fully optimized at the B3LYP [28,29] level using 6-311++G^{*+} basis set. The second-order Møller–Plesset (MP2) level of theory [30,31] and long rangecorrected version of wPBE, LC-wPBE [32,33], using 6-311++G^{*+} basis set, were also used for optimizing the structure of the most stable conformer of HFPTO, GD1. The LC-wPBE and B3LYP levels, using 6-311++G^{*+} basis set, were used for calculating the vibrational frequencies and IR intensities. The B3LYP/6-311++G^{*+} level was used to obtain the Raman scattering activities. An analysis of the harmonic vibrational frequencies at the B3LYP/6-311++G^{*+} level of the optimized species revealed that all structures are minima (no imaginary frequencies).

In order to assign the observed vibrational transitions, anharmonic frequency calculations [34,35] were also performed for HFPTO and its deuterated analogue, HFPTO-d6, using the LC-wPBE functional and 6-311G^{**} basis set.

The assignments of the experimental frequencies are based on the observed band frequencies and intensity changes in the infrared spectra of the deuterated species and confirmed by establishing one to one correlation between observed and theoretically calculated frequencies.

A normal coordinate analysis was carried out to provide a complete assignment of the fundamental vibrational wavenumbers for the molecules. For this purpose, the full set of 66 standard internal coordinates containing nine redundancies for the titled molecule is defined as given in Table S1 (Supplementary material). From these a non redundant set of local symmetry coordinates was constructed by a suitable linear combination of internal coordinates following the recommendation of Pulay et al. [36]. The contribution of the symmetry coordinates in normal modes was normalized to 100%. We applied the keyword "HPModes" in Gaussian (using LC-wPBE/6-311++G** level) in order to obtain the high precision format (to five figures) for vibrational frequency eigenvectors in the frequency output. The results were used to calculate the internal coordinates for each vibrational mode. By combining the results of the GaussView Program [37], with symmetry considerations, and potential energy distribution (PED), vibration assignments were made with a high degree of accuracy.

Orbital population and Wiberg bond orders [38] were calculated with NBO 3.0 program implemented in Gaussian 03. Natural orbital analysis [39] was performed at the B3LYP/6-311++G^{**} level using NBO 5.0 program [40], which applied the wavefunction information file generated by the earlier version of NBO (3.0).

The Bader theory [41] was applied to have better insight into the nature of the intramolecular hydrogen bonds in HFPTO. Hence the wave functions obtained from B3LYP/6-311++G^{**} level were further applied within the AIM2000 program [42] to find bond critical points (BCPs) and characterize them in terms of electron densities, $\rho(r_c)$, and their Laplacians, $\nabla^2 \rho(r_c)$.

4. Results and discussion

4.1. Conformational analysis

The fully optimized structures, obtained at the B3LYP/6-311++G^{**} level, for HFPTO conformers and their relative energies (in kcal/mol) are shown in Fig. 1. By rotating the O-H groups around C–O bonds and the CF₃–C(OH) group around C2–C3 bond, then fully optimization of the resulting structures. 10 stable conformers were obtained. Some of the structural parameters, obtained at the B3LYP/6-311++G** level, for all stable conformers are compared in Table 1. The atom numbering system for the most stable conformer, GD1 with C2 symmetry, is indicated in Fig. 2. The calculated geometrical parameters of the most stable conformer along with the experimentally reported geometries [22,24] are collected in Table 2. As it is shown in Table 2, the calculated results obtained at the LC-wPBE/6-311++G** level are in best agreement with the Chekhlov experimental data [24]. According to our calculations, the most stable conformer is GD1 (Fig. 2), which is in agreement with the crystallographic results [22,24]. This conformer is engaged in two intramolecular hydrogen bonded (OHO type) systems.

By comparing the relative energies of GD1 and GD2 conformers it may be possible to estimate the strength of the hydrogen bond in the titled molecule. In GD1 there are two hydrogen bonds in opposite directions and in GD2 both hydroxyl groups are rotated and there is no hydrogen bonding in the molecule. Therefore, the energy difference between these two conformers (15.1 kcal/mol) could be considered as the hydrogen bond strength. This energy difference gives an energy of 7.55 kcal/mol per hydrogen bond. Now, how we can interpret the high relative energy of GD3 conformer (8.4 kcal/mol), which is also engaged in two intramolecular hydrogen bonds but in the same direction? By exploring the properties of these conformers, two factors were found to be responsible (at least in part) for this energy difference, weaker hydrogen bond in GD3 relative to GD1 and higher electron delocalization in GD1 relative to GD3. The former will be discussed in Section 4.3 and the latter will be considered in Section 4.2.1. On the other



Fig. 1. The stable conformers of HFPTO. The relative energies obtained at the B3LYP/6-311++G** level (in kcal/mol) are given in parentheses.

 Table 1

 Some of the most important geometrical parameters for stable HFPTO conformers.^a

	GD1	GD2	GD3	GD4	GD5	GD6	GD7	GD8	GD9	GD10
rC-01	1.3875	1.4037	1.4117	1.4198	1.4258	1.4008	1.3997	1.4202	1.3953	1.3960
rC-02	1.4264	1.3981	1.4091	1.3934	1.3973	1.4112	1.3979	1.3851	1.4086	1.4065
rC-03	1.4264	1.3982	1.4009	1.3970	1.4049	1.4112	1.4118	1.4000	1.3987	1.3832
rC-04	1.3875	1.4036	1.3993	1.4021	1.3962	1.4008	1.4039	1.4124	1.4099	1.4184
r0102	2.3264	2.3468	2.3426	2.3435	2.3247	2.3395	2.2680	2.2579	2.2557	2.2524
r0304	2.3264	2.3466	2.3321	2.3244	2.3246	2.3393	2.3387	2.3370	2.3417	2.2569
r0103	2.7259	2.8749	2.7858	2.7158	2.7590	-	2.7105	4.4164	4.3011	4.3098
r0204	2.7260	2.8775	2.7881	2.9103	4.2746	-	4.5252	4.2846	4.4670	4.5761
r01–H	0.9722	-	0.9659	0.9650	0.9664	0.9650	0.9692	0.9654	0.9663	0.9664
r02–H	0.9667	-	0.9658	0.9658	0.9673	0.9650	0.9662	0.9664	0.9651	0.9652
r03–H	0.9667	-	0.9658	0.9691	0.9660	0.9650	0.9652	0.9651	0.9652	0.9653
r04–H	0.9722	-	0.9657	0.9662	0.9703	0.9650	0.9660	0.9651	0.9653	0.9665
<i>r</i> H1···04	1.8944	-	1.9537	-	1.9320	-	-	-		
<i>r</i> H2· · ·O3	-	-	2.0054	-	-	-	-	-		
rH4…01	-	-	-	1.9025	-	-	1.9207	-		
rH3· · ·O2	1.8944		-	-	-	-	-	-		
ϕ 01H04	141.9	-	142.9	139.8	-	-	136.9	-		
ϕ O2HO3	141.9	-	136.7	-	141.5	-	-	-		

^a r, Bond length in Å; φ, bond angle in °; all obtained at the B3LYP/6-311++G^{**} level. The geometrical parameters related to the strongest H-bond are given in italic and bold fonts.



Fig. 2. The most stable conformer and atom numbering system.

 Table 2

 The geometrical parameters of the most stable conformer of HFPTO (GD1).^a

	MP2	B3LYP	LC-wPBE	Expt. [22]	Expt. [24]
Bond length (Å)					
C1-C2	1.539	1.555	1.542	1.530(11)	1.533(4)
C2-C3	1.528	1.538	1.524	1.514(11)	1.523(3)
C3-C4	1.528	1.538	1.524	1.532(11)	1.524(4)
C4-C5	1 539	1 555	1 542	1532(11)	1534(3)
C1-F1	1 341	1 347	1 339	1 334(8)	1 322(3)
C1-F2	1 336	1 342	1 334	1 329(9)	1 324(3)
C1-F3	1 340	1 347	1 339	1.323(3) 1.344(8)	1.321(3) 1.332(3)
C5-F5	1 341	1 347	1 339	1 343(9)	1 326(3)
C5-F6	1 336	1 342	1 334	1.328(10)	1 320(3)
C5-F4	1 341	1 347	1 339	1 345(9)	1 323(3)
C2-01	1 387	1 388	1 379	1 397(9)	1.023(3) 1.408(3)
01_H	0.974	0.972	0.970	1.557(5)	0.82(3)
$(2-0)^{-11}$	1 420	1 426	1 4 1 1	1 408(9)	1 398(3)
02-02 02-H	0.967	0.967	0.964	1.400(3)	0.80(3)
C4-03	1 4 1 9	1 427	1 4 1 1	1410(10)	1405(3)
C4-04	1 387	1 388	1 379	1.410(10) 1.404(10)	1.405(3)
0102	2 3 2 4	2 3 2 6	2 306	1.404(10)	2324(2)
0104	2.524	2,520	2,500	2 600	2.524(2)
0104	2.708	2.720	2.708	2.090	2.093(3)
0203	2.708	2.720	2.708	2.095	2.089(3)
Bond angle (°)					
C1-C2-C3	110.0	110.3	110.0	109.9(6)	110.5(2)
01–H· · ·04	142.1	141.9	141.1		141(3)
01–H· · ·02	74.9	73.6	73.4		80(2)
C2-C3-C3	112.8	113.2	113.0	113.3(6)	113.2(2)
C3-C4-C5	110.0	110.3	110.0	110.7(6)	110.5(2)
F1-C1-F2	107.9	107.6	108.5	107.2(6)	106.3(3)
F1-C1-F3	108.5	108.3	107.7	107.6(6)	108.4(3)
F2-C1-F3	108.0	107.7	107.9	107.6(6)	107.9(3)
F1-C1-C2	110.2	110.4	110.1	111.0(6)	111.1(2)
F2-C1-C2	110.8	111.1	111.6	111.7(6)	111.7(2)
F3-C1-C2	111.3	111.7	111.0	112.0(6)	111.9(3)
F4-C5-F5	108.5	108.3	108.5	108.4(6)	108.4(3)
F4C5-F6	107.9	107.6	107.7	107.2(7)	107.8(3)
F5-C5-F6	108.0	107.7	107.9	107.2(6)	107.6(2)
F1′-C5-C4	110.2	111.1	110.1	110.4(7)	110.6(2)
F5-C5-C4	111.3	111.7	111.6	112.3(7)	111.5(2)
F6-C5-C4	110.7	110.4	111.0	111.1(6)	111.2(2)
01-C2-C1	105.2	105.4	105.4	104.2(6)	108.6(2)
01-C2-C3	114.4	114.5	114.3	114.3(7)	113.8(2)
02-C2-C1	108.0	107.8	107.8	109.5(6)	104.6(2)
02-C2-C3	107.4	107.2	107.7	107.2(7)	107.4(2)
01-C2-02	111.7	111.5	111.5	111.6(6)	111.9(2)
03-C4-C3	107.3	107.3	107.7	107.8(7)	105.4(2)
03-C4-C5	107.5	107.7	107.8	109.2(7)	113.5(2)
04-C4-C3	114.4	114.4	114.3	112.7(7)	110.5(2)
04-C4-C5	105.2	105.2	105.4	104.7(6)	108.4(2)
02-C2-C1-F1	-60.6	-59.1	-59.3		-59.3(3)
01-C2-C1-F1	58.8	60.1	59.9		59.1(3)
H-01-C2-02	-82.0	-85.0	-43.7		40(2)
H-02-C2-C1	72.4	71.6	-84.2		85(2)
C1C2C3C4	173.0	175.1	173.8		178.0(2)

^a All calculated with the 6-311++G^{**} basis set. The standard deviations of the last significant figures are given in parentheses.

hand, as it is shown in Fig. 1, the relative energies for GD4 and GD5, both involved in one intramolecular hydrogen bond, are 8.0 and 7.1 kcal/mol, respectively. This result also supports that the energy of one hydrogen bond is about 7.5 kcal/mol. However, the relative energy for GD7, which also involves in one intramolecular hydrogen bond, is 11.3 kcal/mol. This energy is considerably higher than those for GD4 and GD5 conformers. The high relative energy of GD7 could be explained by considering the repulsion between the fluorine atoms on C1 and C5. The distance between these F atoms in GD4 and GD5 are longer than 4.76 Å, while these distance in GD7 is only 2.76 Å.

The calculated 0...0 distances between the two oxygen atoms on the same carbon atom, obtained at the MP2/6-311++ G^{**} level, is 2.324 Å, which is in excellent agreement with the experimental data (2.324 ± 0.002) [24]. The calculated O···O distance in those systems that the electron lone pairs are not directed towards other neighbor oxygen atom is considerably shorter than 2.32 Å (2.25– 2.27 Å), see Table 1 and Fig. 1. This O...O distance reduction is caused by decreasing of electron lone pair-lone pair repulsion in two vicinal oxygen atoms. However, this system cannot form an intramolecular hydrogen bond since the corresponding OH · · · O angle is highly bent (about 80° [24]). The O···O distance between two oxygen atoms on different carbon atoms, which are engaged in the intramolecular hydrogen bond, as is obtained by X-ray diffraction method, is 2.689-2.695 Å [22,24], which is in good agreement with the theoretical value obtained at the LC-wPBE/6-311++G** level. The H…O distance in GD1 (1.8944 Å, Table 1) is considerably shorter than the sum of the van der Waals radii [43] for oxygen and hydrogen atoms (2.72 Å). According to the Gilli's classification [44], these data suggest formation of two moderate intramolecular hydrogen bonds in GD1, which is also consistent with the $E_{\rm HB}$ obtained at above. The distance between the two oxygen atoms on the same carbon (geminal) is considerably short, about 2.33-2.34 Å, but the corresponding O-H…O angle is too small (less than 75°) to be convenient to form a hydrogen bond with significant strength.

4.2. NBO analysis

4.2.1. Electron delocalization

The natural bond orbital (NBO) [39] analysis of HFPTO molecule is done to estimate the delocalization arrangement of electron density from the principal occupied Lewis-type (bond or lone pair) orbitals to unoccupied non-Lewis (antibonding or Rydberg) orbitals. The interactions result in a loss of occupancy from the localized NBO of the idealized Lewis structure into an empty non-Lewis orbital. For each donor (i) and acceptor (j), the stabilization energy, E(2), associated with the delocalization i \rightarrow j is estimated as:

$$E(2) = \Delta E_{ij} = q_i \frac{F(ij)^2}{\varepsilon_j - \varepsilon_i}$$
(1)

where q_i is the occupancy of the donor orbitals, ε_i and ε_j are the diagonal elements and F(ij) is the off-diagonal NBO Fock matrix elements. The NBO analysis is a powerful tool for studying inter- and intramolecular bonding and provides a convenient basis for investigating charge transferor conjugative interactions in molecular systems [45]

The most important E(2) energies for GD1, GD2, GD3, and DG4 are listed in Table 3. In comparing the GD1, GD2, GD3, and DG4 conformers, the most important delocalization of electron densities are those arise from electron lone pairs of oxygen atoms as donor and σ^* of C–C, C–O, and OH bonds as acceptor. These energies are listed in Table 3. As it is shown in Table 3, the electron donation from the oxygen lone pairs associated with the free hydroxyl

Table 3	Ta	ble	3
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Selected second order perturbation energies E^2 (donor \rightarrow acceptor), kcal/mol, for the most stable conformers.

Donor	Acceptor	GD1	GD2	GD3	GD4
LP (1)03	σ*C4-04	3.67	14.68	16.07	1.26
LP (1)O2	σ*C2-01		2.02	2.00	2.77
LP (2)O2	σ*C2-01	19.11	11.78	12.19	8.57
LP (1)01	σ*C2-02	3.67	1.13	1.36	0.86
LP (2)01	σ*C2-02	5.28	14.71	13.75	16.91
LP (2)O3	σ*C4-04	5.28	1.14		16.67
LP (1)04	σ*C4-03		2.01		2.33
LP (2)04	σ*C4-03	19.11	11.82	16.41	9.5
LP (1)O2	σ*C1-C2		1.18		0.54
LP (2)O2	σ*C1–C2	1.63	7.53	6.48	7.6
LP (1)O2	σ*C2–C3	4.47	0.89	0.86	0.87
LP (2)O2	σ*C2-C3	2.64	0.91		
LP (2)01	σ*C1-C2	8.31	5.73	5.66	2.15
LP (1)O1	σ*C1-C2		1.84		4.85
LP (1)O3	σ*C3–C4	0.58	0.91	4.64	3.96
LP (2)O3	σ*C4–C5	8.31	1.83	3.26	1
LP (1)04	σ*C3-C4	4.47	0.89		3.48
LP (1)04	σ*C3-C4			3.99	0.83
LP (1)04	σ*C4–C5	1.97	1.19		0.89
LP (2)04	σ*C3-C4	2.64		3.22	
LP (2)04	σ*C4–C5	1.63	7.51	2.09	8.89
LP (1)O2	σ*03-H3			3.52	5.16
LP (1)O1	σ*04-H4	4.26		3.16	
LP (2)01	σ*04-H4	3.86			
LP (1)O3	σ*02-H2	4.27			
LP (2)O3	σ*02-H2	3.86			
\sum^{a}		105.35	89.7	98.66	99.09

^a Σ – Sum of all given electron delocalization energies (kcal/mol).

groups to the antibonding σ^* of O–H bonds involved in the intramolecular hydrogen bond (O2-H and O4-H, Fig. 1) seems to be somewhat responsible for lower energy of GD1 than that of GD3. Charge transfer from oxygen atom to the σ^*O-H bond weakens the O-H bond, therefore, increases the strength of the hydrogen bond. As it is shown in Table 3, sum of the second order interacting energies, *E*(2), associated with the electron donation from oxygen lone pairs to σ^* of O-H bonds in GD1 and GD3 is 16.25 and 8.30 kcal/mol, respectively. It is noteworthy that in GD1 both electron lone pairs of each oxygen atoms associated with the free hydroxyl groups are involved in the electron delocalization, while in GD3 only one electron pair is considerably contributes in the delocalization and the contribution of other lone pair in this interaction is small. The sum of all listed electron transfers in Table 3 is also given in this Table. As this summation indicates, among all listed conformers GD1 has the highest electron delocalization, Table 3 also indicates that energy difference between GD1 and GD3 is mainly caused by these interactions.

4.2.2. Charge analysis

The charge distribution on O and H atoms calculated by the NBO method for optimized geometries of GD1, GD2, GD3, GD4, GD5,

Table 4
Natural charge (e) for the most stable conformers. ^a

	GD1	GD2	GD3	GD4	GD5	GD7
01	-0.7721	-0.7105	-0.7481	-0.7044	-0.7239	-0.7190
02	-0.7393	-0.7162	-0.7481	-0.7603	- 0.7588	-0.7461
03	-0.7721	-0.7105	-0.7371	-0.7460	-0.7331	-0.7561
04	-0.7393	-0.7162	-0.7340	-0.7275	-0.7418	-0.7131
H1	0.4927	0.4671	0.4844	0.4704	0.4841	0.4813
H2	0.5035	0.4671	0.4848	0.4840	0.4837	0.5001
H3	0.4927	0.4670	0.4892	0.4986	0.4802	0.4857
H4	0.5035	0.4671	0.4873	0.4767	0.4947	0.4716

^a Acceptor O atoms and H atoms engaged in H-bond are shown in bold.

Table 5 Comparison of selected Wiberg bond orders for the most stable conformers.^a

Bond	GD1	GD2	GD3	GD4	GD5	GD7
01-H1	0.739	0.762	0.745	0.758	0.744	0.715
O2-H2	0.703	0.764	0.745	0.747	0.747	0.749
O3-H3	0.739	0.762	0.728	0.714	0.752	0.744
04-H4	0.703	0.764	0.733	0.754	0.713	0.758
01···H4	0.028	-	0.014	-	-	0.020
03· · ·H2	0.028	-	-	-	-	-
02· · ·H3	-	-	0.019	0.023	-	-
02···H4	-	-	-	-	0.027	-
04· · ·H1	-	-	0.014	-	-	-
0104	0.011	-	0.007	-	-	-
0203	0.011	-	0.008	0.009	-	0.009
0204	-	-	-	-	0.011	-
3 m1 0 111						

^a The O-H bond lengths engaged in the intramolecular H-bonds are given as bold fonts.

and GD7 are tabulated in Table 4. According to this table, the trend in natural charges over O atoms which acts as proton acceptor (shown as bold figures in Table 4) for stable HFPTO conformers is; GD1 > GD4 > GD5 > GD7 > GD3. The trend in positive natural charges over H atoms engaged in the intramolecular hydrogen bonds are also the same as for O atoms except for GD7, shown as follows: GD1 > GD7 > GD4 > GD5 > GD3. This result may be attributed to the inductive effects between F9 and H2 atoms, which in GD7 are in different position compared with other conformers. These results suggest that the trend in the intramolecular hydrogen bond strength could he as follows: GD1 > GD4 > GD5 > GD7 > GD3.

4.2.3. Bond order

The calculated Wiberg bond orders [38] for GD1, GD2, GD3, GD4, GD5, and GD7 are collected in Table 5. This table shows that for the O-H...O systems the O-H bond orders in GD1 are lower and its H...O bond orders are higher than the corresponding bond orders in other conformers. GD2, which is not involved in intramolecular hydrogen bonding, has the highest O-H bond orders. These results also support the existence of the strongest intramolecular hydrogen bond in GD1, compared with other conformers.

The trend in the O–H bond orders are as follows: GD1 < GD5 < GD4 < GD7 < GD3 and the trend in the H \cdots O bond order is in the opposite direction as: GD1 > GD5 > GD4 > GD7 > GD3. These results are also consisted with the electron delocalization data given in Section 4.2.1. As it is shown in Table 5, the bond orders for the free OH and that engaged in the intramolecular hydrogen bond are 0.739 and 0,703, whilst those in GD2, without any hydrogen bond, are 0.764, which are considerably higher than those in GD1. The lowering of Wiberg bond orders of the O–H groups involved in the intramolecular hydrogen bond is mainly caused by charge transfer from electron lone pairs of oxygen atoms to the σ *O–H orbitals, which is discussed in Section 4.2.1.

4.3. Atoms in molecules (AIM) study

The AIM theory proposed by Bader [41] was used to obtain greater insight into the nature of intramolecular hydrogen bonding in HFPTO. AIM calculations were performed using the density functional theory (DFT) wave functions computed at the B3LYP/6-311++G^{**} level for the conformers of HFPTO. Bader's AIM approach provides a very powerful method to analyze electron delocalization. According to the Koch and Popelier [46] studies, for hydrogen bonded systems, $\rho(r)$ lies between 0.002 and 0.04 e/å³. Additionally, $\nabla^2 \rho(r)$ lies between 0.024 and 0.139 e/å⁵ for a hydrogen bonded system. [45].

Table 6

The topological parameters: electron densities $\rho(r)O\cdots$ H, $\rho(r)F\cdots$ H, $\rho(r)O-$ H, their Laplacians $\nabla^2\rho(r)O\ldots$ H, $\nabla^2\rho(r)F\ldots$ H, $\nabla^2\rho(r)O-$ H; local energy densities V(r); hydrogen bond geometrical parameters, and hydrogen bond strength, E_{HB} for HFPTO conformers engaged in the intramolecular hydrogen bonds.^a

		$\rho(r)$ 0····H	$\nabla^2 \rho(r) 0 \cdots \mathbf{H}$	-V(r)	$\rho(r)$ O–H	$\nabla^2 \rho(r)$ O–H	RH···O	RO-H	RO···O	$\delta 0H \cdots 0$	$E_{\rm HB}$
GD1	I	0.0290	0.1074	0.0244	0.3523	-2.495	1.8944	0.9722	2.7260	141.9	7.66
	II	0.0290	0.1074	0.0244	0.3523	-2.495	1.8944	0.9722	2.7260	141.9	7.66
GD3	I	0.0222	0.0876	0.0177	0.3610	-2.534	2.0054	0.9657	2.7881	136.7	5.54
	II	0.0247	0.0962	0.0200	0.3604	-2.533	1.9537	0.9658	2.7858	142.9	6.27
GD4	I	0.0279	0.1084	0.0237	0.3563	-2.519	1.9025	0.9691	2.7158	139.8	7.42
GD5	I	0.02807	0.0985	0.0227	0.3547	-2.497	1.9324	0.9703	2.7590	141.55	7.12
GD7	Ι	0.02677	0.1058	0.0226	0.3558	-2.510	1.9207	0.9692	2.7105	136.9	7.08
		$\rho(r)$ FH	$\nabla^2 \rho(r)$ FH	-V(r)	ho(r)O–H	$ abla^2 ho(r)$ 0–H	<i>R</i> HF	RO-H	<i>R</i> OF	$\delta OH \cdots F$	$E_{\rm HB}$
GD9	I	0.0185	0.0742	0.0157	0.0361	-2.531	2.0341	0.9652	2.8027	135.2	4.9
GD10	Ι	0.0165	0.0647	0.0136	0.3617	-2.526	2.0984	0.9651	2.8328	131.6	4.3

^a R, bond length in Å; δ , bond angle in °; r in e/å³; $\nabla^2 \rho(r)$ in e/å⁵; E_{HB} in kcal/mol and is calculated from $E_{\text{HB}} = -1/2 V(r)$. The geometrical parameters are obtained from Table 1.

The AIM criteria proposed by Popelier that established a classical hydrogen bond were applied to the GD1, GD3, GD4, GD5, GD7, GD9, and GD10 conformers, which all are involved in O-H...O type intramolecular hydrogen bonding, except the last two conformers, which are only involved in O-H...F type intramolecular hydrogen bonding. All of the topological parameters for the O–H and $H \cdots O/P$ H...F bonds of these conformers are listed in Table 6. The charge densities and their Laplacians at the bond critical points (BCPs) for $H \cdots O/H \cdots F$ bonds were in the 0.0165–0.0290 e/å³ and $0.0040-0.0068 \text{ e}/\text{a}^5$ ranges, respectively. The values of the electron density and its Laplacian for the BCPs of $OH \cdots O/OH \cdots F$ systems, in GD1, GD3, GD4, GD5, GD7, GD9, and GD10 conformers, are well within the range specified for the existence of the hydrogen bond in terms of electron density and its Laplacian. No critical point was observed between F and H atoms, except for GD9 and GD10, which indicate existing of one intramolecular hydrogen bond between the O-H and CF_3 groups in these two conformers. Table 6 also presents the local potential energy densities, V(r), for the H...O BCPs in all conformers engaged in the intramolecular hydrogen bond. It was found that V(r) well correlates with the H-bond energy and the relationship $V(r) \approx 1/2E_{\rm HB}$ was found by Espinosa et al. [47]. According to this calculation, the hydrogen bond strength in GD1is 7.66 kcal/mol per bond (see Table 6), which is very close to that obtained by energy difference between GD2 and GD1 energies (7.55 kcal/mol per bond). The sum of the hydrogen bond energies for GD3 is 11.81 kcal/mol. which is 2.51 kcal/mol lower than the corresponding value in GD1, which justifies part of the energy difference between GD3 and GD1 conformers. As it is shown in Table 6, the intramolecular hydrogen bond between OH and CF₃ groups in GD9 and GD10 are 4.9 and 4.3 kcal/mol, respectively.

The trend in the hydrogen bond strength is: GD1 > GD4 > GD5 > GD7 > GD3. This trend is in agreement with trend for natural charge over O atoms (as acceptor) shown in Table 4. The trend in the O–H and H…O bond orders also are in agreement with the trend in the hydrogen bond energy, except for GD5, which indicates abnormally low O–H and high H…O bond orders. This discrepancy could be attributed to the interaction between F9 atom and O3–H3 bond, which are in convenient arrangement for interaction.

It is noteworthy that the hydrogen bond strength in non-hydrated HFAA is estimated to be about 11.8 kcal/mol [25], which is more than 4 kcal/mol stronger than that obtained for HFPTO. This energy difference could be attributed to the π -electron delocalization in the enol ring of the former.

4.4. Vibrational assignment

The fundamental wavenumbers for HFPTO (GD1) obtained with both LC-wPBE and B3LYP levels were compared with the experi-

Table 7					
Regression	parameters	for	vibrational	wavenumbe	rs.

Regression parameters	LC-wPBE	B3LYP
X–H region		
R^2	0.99886	0.99904
SD	124	113
а	0.9096	0.9298
$1470-970 \text{ cm}^{-1}$		
R^2	0.99985	0.99968
SD	16	23
а	0.9738	1.0086
Below 970 cm^{-1}		
R^2	0.99937	0.99954
SD	14	12
а	0.9858	1.0068

mental ones by means of regression analysis separately for 3500–2900, 1500–950, and below 950 cm⁻¹ region. Since OHo are engaged in intermolecular hydrogen bonding the 3394 cm⁻¹ band is excluded from regression analysis. Simple scaling of the theoretical wavenumbers according to the equation $\tilde{v}_{obsd} = a \cdot \tilde{v}_{thoer}$ generally leads to satisfactory agreement with the set of the observed wavenumbers; the least-square scaling factors *a*, regression coefficients R^2 , and standard deviations (*SD*) are listed in Table 7 for all considered frequency regions. The superior quality results are produced from the LC-wPBE level for above 950 cm⁻¹ and from the B3LYP level below 950 cm⁻¹. It has been shown [25] that B3LYP level underestimates the C–F stretching wavenumbers. Therefore, the agreement between the calculated wavenumbers obtained at the B3LYP with the experimental ones for CF₃ stretching modes is not as good as those predicted for non-fluorinated compounds.

GD1 with C2 symmetry has 57 fundamental vibrations, which can be classified as $\Gamma_{vib} = 29A + 28B$. Both A and B vibrational modes are IR and Raman active. Tables 8 and 9 list the calculated scaled harmonic and anharmonic wavenumbers for the most stable conformer of HFPTO, GD1, and its deuterated analogue along with the experimental results, respectively. A comparison of the unscaled calculated and experimental frequencies shows substantial differences. Many factors, such as incomplete basis set, anharmonicity, Fermi resonance, solvent effects, media, intermolecular interactions, may be responsible for the discrepancy between the experimental and computed spectra of HFPTO. For the skeletal modes, the differences between the experimental and calculated frequencies are much smaller than those for C–H, O–H, and O–D stretching frequencies. For this reason, we also calculated the anharmonic vibrational frequencies at the LC-wPBE/6-311G^{*+} level.

4.4.1. OH and CH stretching region

The IR spectra of HFPTO and its deuterated analogue in the OH/ OD stretching and 1600–500 cm⁻¹ regions are compared in Figs. 3

Table 8		
Fundamental b	and assignments	of HFPTO. ^a

Theore	tical						Experimental				Characterization of normal modes with PED (%)
Sym.	F1	$I_{\rm IR}$	F2	$I_{\rm IR}$	R _A	Fan	IR	Ι	R	I	
А	3522	18	3528	16	100	3706	3394	42			vsOHo(58)
В	3521	15	3527	10	47	3705	3394				vaOHo(86)
В	3425	88	3419	100	11	3536	3353	37			vaOHi(83)
Α	3413	9	3404	6	100	3518	3293	37			vsOHi(65)
В	2923	0	2923	0	29	3075	3022	1	3018	1	vaCH ₂ (83)
A	2855	0	2874	0	64	3036	2984	1	2983	3	vsCH ₂ (61), vsC2C3C4(10)
В	1469	17	1488	22	2	1471	1471	21	1470		ω CH ₂ (17), vaC2C3C4(13), vaC-CF ₃ (10), δ aOHi(14), δ aOHo(10)
A	1456	5	1499	4	3	14/2	1459	11	1 4 2 1	2	$VSL-CF_3(11), CH_2SCI.(19), \delta SOHI(14)$
A	1425	0	14/4	2	/	1442			1431	2	$CH_2SCI(31)$, $\delta SOHI(10)$ ScOHo(14) $\nu cCO(11) = cCH(10)$
R	1371	10	1350	1	4	1363	1362	21			$\delta_{2}OH_{0}(11)$, $v_{2}O(11)$, $v_{2}O(2C)$
B	1332	19	1354	27	1	1303	1302	14	1308	3	$\omega CH_{c}(28)$ $\delta_{2} OH_{c}(13)$ $\delta_{2} OH_{c}(12)$
A	1300	0	1307	27	3	1291	1505	14	1308	5	τCH ₂ (17)
A	1281	1	1290	0 0	1	1284	1289	18	1283	3	$\tau CH_2(13)$, $\delta sOHi(13)$, $v s CF_3(10)$, $\delta s CF_3(10)$
В	1260	48	1259	62	2	1291	1274	56	1273	3	$\delta_{a}OHi(12), vaC-CF_{3}(12), vaCO(12)$
В	1217	78	1192	20	3	1236	1223	56	1219	2	vaCF ₃ (37)
А	1212	14	1190	69	1	1236	1223		1219		vaCF ₃ (44)
В	1194	24	1179	26	2	1222	1207	38	1206	4	vaCO(12), vaCF ₃ (14)
Α	1188	14	1178	0	1	1221	1186	63	1187	1	vaCF ₃ (35)
В	1178	100	1159	88	1	1174	1158	33	1149	1	vaCF ₃ (21)
A	1149	100	1135	104	2	1155	1136	100	1136	2	vsCO(12), vaCF ₃ (20), dsOHo(10)
В	1129	1	1112	6	2	1129	1115	42	1117	3	$\delta aOHo(19)$, vaC2C3C4(14), vsCO ₂ (13)
A	1061	4	1017	4	2	1053	007	47	1020	2	$vaCO_2(26)$. $\tau CH_2(16)$, $\rho CO_2(12)$
В	982	10	979	11	3	999	987	47	985	3	$VaC2C3C4(10), VsC0(10), \omega CH_2(11)$
A D	949	2	956	2 7	1	904	970	20	970	5	$v_{SCF_3(15)}, \omega_{CO_2(12)}, v_{SC2C5C4(10)}$
Δ	923 840	0	911 921	1	14	919 840	908	18	800	100	$pcn_2(25), vaco(10)$ $vcC2C3C4(14), vcC0(20), \deltaC2C3C4(11)$
B	796	1	780	1	0	800	785	2	784	4	$v_{SC2C3C4}(14), v_{SC0}(20), v_{C2C3C4}(11)$
A	736	1	734	1	5	742	739	26	739	24	$v_{SCF_2(26)}, v_{ACC} = c_{13}(10), v_{AC2}(26) = (15), v_{SCC}(10)$
В	663	10	664	27	1	598	665	29	662	1	$\delta s CF_3(13), \omega CO_2(11)$
А	646	33	662	11	0	670	665				CO ₂ sci.(13), ysOHi(13), ysOHo(10)
В	629	2	621	1	1	624	617	6	623	1	$\gamma a O Hi(11), \delta a C - C - C F_3(10), \tau C F_3(11)$
В	590	3	599	10	1	582	608	11			δ'aCF ₃ (14), v'aCF ₃ (12), gaOHi(10)
Α	589	2	584	1	0	594	593	8	589	12	δ∋aCF3(23), v′aCF ₃ (18)
А	566	1	575	1	1	554	572	7	575	13	$\delta a CF_3(27)$, va CF ₃ (12)
В	562	11	566	4	2	568	532	4	527	7	γaOHi(29)
В	513	0	521	1	1	511	507	9			$\delta_{a}CF_{3}(25)$
A	512	0	515	0	0	516	45.4	-	450	6	$\delta a CF_3(22), CO_2 sci(19), \gamma sOHi(10)$
В	456	1	459	1	0	462	454	5	458	6	$\delta \ni aCF3(13), \rho CH_2(11), \rho CO_2(13)$
R	448	17	449	10	0	448 /12	/21	6			$\alpha_{3}(31), \pi_{1}(12), \mu_{2}(10)$
A	405	1	422	15	1	409	421	0			ysOHo(16)
B	401	1	406	1	0	410	121				$\tau CO_2(20)$
Ā	348	3	357	2	3	356	374	4	388	16	γ sOHo(16), CO ₂ sci(14), δ aCF ₃ (15), ρ CF ₃ (12)
В	340	18	349	11	0	349	348	2			vaOHo(23)
В	311	0	312	1	1	314	312	4			$\omega CO_2(14), \rho CF_3(14), vaC-CF_3(12)$
А	309	2	311	1	1	316	312				ρCF ₃ (22), γsOHo(13)
А	306	0	307	0	1	302	292	sh			τCO ₂ (31), ρCO ₂ (10)
В	270	1	275	1	0	275	286	5			πCF ₃ (20), γCCCC (11), τCO ₂ (10)
Α	238	0	241	0	0	237	241	2	256	35	πCF ₃ (25), τCO ₂ (19), ρCO ₂ (14)
Α	223	0	225	0	2	225					vsC–CF ₃ (11), δC2C3C4(12)
В	184	0	180	0	0	183	185	4			$δaC-C-CF_3(19)$, $ρCF_3(14)$
В	125	1	129	1	0	129					γ LLLL (23)
A	103	0	96	U	0	93					$\partial SL - LF_3(18), \gamma LLLL(11)$
R	/ C /	0	/ C /	0	0	07 61					$\tau CE_{2}(42), \gamma CCCC(12)$
D A	04 20	0	26	0	0	27					$\gamma CCCC(28)$ $\gamma sOHi(13)$
1	50	U	50	U	U	21					rece(20), /30111(13)

^a F1, calculated at the LC-wPBE/6-311++G^{**} level; F2, calculated at the B3LYP/6-311++G^{**} level; F_{an} , anharmonic wavenumbers calculated at the LC-wPBE/6-311G^{**} level; I_{lR} , relative IR intensity; R_{A} , relative Raman activity; I, relative intensities; sh, shoulder; v, stretching; δ , in-plane bending; γ , out-of-plane bending; ρ , in-plane rocking; π , out-of-plane rocking; α , wagging; sci, scissoring; PED: potential energy distribution (only contribution larger than 10% are given); OHi and OHo stand for inward and outward H atoms, respectively (see the text).

and 4, respectively. The Raman spectra of the light and deuterated HFPTO in the 1600–200 $\rm cm^{-1}$ region are compared in Fig. 5.

The deconvoluted IR spectrum of HFPTO indicates presence of three strong bands at 3394, 3353, and 3293 cm⁻¹, which are assigned to the O–H stretching modes. The first band is due to the A and B symmetry species of O–Ho (outward H atoms) stretching of the free O–H groups. Deviation of more than 200 cm⁻¹ of this frequency from that calculated by considering the anharmonicity may be attributed to the formation of a weak intermolecular

hydrogen bond with other molecules in the solid state, which is consistent with the X-ray crystallographic data reported by Chekhlov [24]. Deviation of the last two bands, which are caused by vOHi (inward H atoms), engaged in the intramolecular hydrogen bond, from the calculated anharmonic wavenumbers is about 100 cm⁻¹. The corresponding bands in the deuterated analogue appear as very strong bands at 2520, 2487, and 2433 cm⁻¹.

Two sharp and weak IR bands at 3023 and 2983 cm⁻¹, which both of them are observed in the Raman spectrum of HFPTO, are

Table 9		
Fundamental band	assignments	of HFPTO-d6. ^a

Theore	retical Experimental								Assignments PED		
Sym.	F1	$I_{\rm IR}$	F2	I_{IR}	R _A	Fan	IR	Ι	R	Ι	
Α	2564	10	2567	8	100	2732	2517	59			vsODo(52)
В	2563	8	2567	5	46	2731			2479	14	vaODo(85)
В	2493	43	2489	45	11	2617	2492	62			vaODi(82)
Α	2484	5	2478	3	100	2604	2445	52	2424	10	vsODi(57)
В	2172	0	2170	0	30	2314	2271		2272	7	vaCD ₂ (78)
А	2078	0	2091	0	59	2227	2176		2178	9	vsCD ₂ (54), δC2C3C4(10)
A	1386	2	1363	2	6	1412	1368	9	1363	6	vsC–CF3(24), vsC2C3C4(20), vsCF ₃ (12)
В	1380	2	1354	2	9	1401	1354	6	1354	5	$vaC-CF_3(15)$, $vaC2C3C4(15)$
В	1305	34	1272	35	0	1310	1285	50	1292	6	$Val = CF_3(10), Val = 2C3C4(13), Val = 0.0000000000000000000000000000000000$
R D	1295	100	1201	100	4	1240	1270	100	1209	6	$v_{3}CU_{2}(12), v_{3}CZC3C4(10)$
A	1218	100	1191	901	4	1240	1177	42	1165	0	$v_{4}CF_{2}(39)$
B	1215	29	1184	21	2	1233	1156	72			va(1)
A	1195	46	1179	39	2	1223	1150	12			$v_{aCC_{2}(20)}$ vaCF ₂ (32), vaCO ₂ (16)
В	1185	35	1176	35	0	1224	1156				$vaC-CF_{3}(25)$
А	1167	26	1143	1	6	1171	1137	40	1144	4	$vaCO_{2}(18), vsCO(15)$
А	1121	4	1106	5	2	1140	1115	60	1118	6	vaCF ₃ (25)
В	1120	13	1119	12	2	1124	1077	37			vsCO ₂ (10), ωCD ₂ (12)
Α	1062	0	1101	0	4	1089			1066	12	CD2 sci(43)
В	1017	36	1039	44	0	1038	1015	75			δaODi(21), ωCD ₂ (14)
А	970	20	987	23	6	975	973	28			vsCO ₂ (16), δsODo(19), δsODi(17)
В	956	1	957	0	0	953	938	4			δaODo(22), δsOHi(18), vsCO(10)
A	856	1	848	1	2	844	856	50	855	11	vaCO ₂ (22). τCD2(38)
В	835	7	842	6	4	838	856	0	855	10	$vaC-CF_3(11), \omega CD2(14), \delta aODi(10), \delta sODo(10)$
A	829	0	835	1	4	828	838	9	838	10	$vsCF_3(14), \delta sODi(12), \delta sODo(10)$
В	809	1	805	2	4	804	809	20	804	27	$VaCO_2(10), \rho CD_2(20)$
A P	792	0	757	0	30	794	762	87	765	100	$VSU_2(13), VSU_2(3)U(12)$
A	705	2	720	1	2 4	703	702	38	705	10	$v_{a} C C_{2} C_{4} (12), w_{C} C_{2} (12), w_{C} C_{3} (10)$
B	638	9	640	7	0	645	650	58	640	1	$v_{3}C_{3}(17), v_{3}C_{3}(13)$
B	593	0	591	0	2	597	583	23	582	sh	$vaCF_{2}(10)$ $\delta aC2C3C4(10)$
Ā	590	2	588	2	0	593	583	25	002	511	$v_{a}CF_{3}(17), \delta_{a}CF_{3}(17), \pi CF_{3}(10)$
В	580	0	577	0	4	587			572	28	vaCF ₃ (14), δaCF3(21)
Α	568	4	565	3	4	570	550	15			δaCF ₃ (21)
А	538	13	537	10	2	535	529	8			δaCF ₃ (26), CO ₂ sci(16)
В	500	3	496	2	0	496	506	16			δaCF ₃ (21), CO ₂ sci(13), δaODi(10)
Α	442	0	445	0	0	444	451	17			δaCF ₃ (32), ρCO ₂ (16), πCF ₃ (14)
В	429	1	431	3	0	431	434	37			δaCF ₃ (24), πCF ₃ (12), πCF ₃ (12)
A	420	2	431	1	2	423	434	_	439	7,br	γsODi(13), ρCF3(10)
В	411	3	428	4	0	399	424	sh			$\gamma_{a}ODi(31)$
В	383	4	387	1	0	38/	383	sn	270	20	$\rho CF_3(10), \gamma a ODI(11)$
R D	250	2	255	2	2	261	264	22	576	29	$\tau CO_2 SCI(11), \gamma SODI(15)$
Δ	310	2	300	2	4	301	504	23	373	30 hr	$o(E_{2}(20), pcD_{2}(18))$
B	306	3	306	2	0	307	305	17	525	55,61	$\rho CF_{3}(21)$
A	296	0	299	0	2	299	303	17			$\tau(O_2(25), \alpha O_2(12), \pi CF_2(10))$
В	265	8	279	8	0	269	277	18			$\gamma_{a}ODo(18), \pi CF_{2}(10)$
В	255	4	264	1	2	260	269	sh	252	60	γ ODo(15), γ CCCC(11), π CF3(12)
А	255	1	263	1	0	255	251	2			γsODo(20), τCO ₂ (12)
А	230	1	234	1	0	228	238	8			πCF3(22), τCO ₂ (16), ρCO ₂ (14)
Α	216	0	218	0	2	220					γsODo(13), δC2C3C4(12)
В	177	0	175	0	0	176					δaC-CF3(19), γaODo(13), ρCF3(12)
В	117	0	120	0	0	121					γCCCC(25)
Α	102	0	95	0	0	92					dsC-CF3(16), γCCCC(11), ρCF3(10)
Α	74	0	73	0	0	61					τCF3(32), γCCCC(15)
В	64	0	60	0	0	61					τCF3(35), γCCCC(16)
A	39	0	35	0	0	22					γCCCC(31), γsODi(13)

^a See footnotes of Table 8.

assigned to the C–H stretching modes. These bands are in fairly good agreement with those predicted by the anharmonic frequency calculation. The corresponding bands in the Raman spectrum of deuterated HFPTO appear at 2272 and 2178 cm⁻¹. The corresponding IR bands, as predicted by calculation, are very weak and observed at 2271 and 2176 cm⁻¹.

4.4.2. 1500–1000 cm⁻¹ region

In this region the O–H in-plane bending, CH₂ scissoring and waging, and C–F, C–C, and C–O stretching modes are expected to be observed. According to the theoretical calculations, the 1471,

1362, and 1305 cm⁻¹ bands, which all of the belong to the B species, are caused by coupling between the CH_2 wagging, OH bending, and asymmetric C2C3C6 and C–CF₃ stretching vibrations. Upon deuteration this coupling somewhat removes and the bands appear at 1354, 1285, and 1044 cm⁻¹. Overtone or combination bands could cause the weak and broad band at about 1450 cm⁻¹. The 1459 cm⁻¹ band is mainly CH₂ scissoring coupled with the symmetric C–CF₃ stretching and OHi bending vibrational modes. Upon deuteration this band moves to 1368 cm⁻¹. The weak Raman band at 1431 cm⁻¹ is assigned to the CH₂ scissoring. The corresponding band in the deuterated species appears at 1066 cm⁻¹.



Fig. 3. The FT-IR spectra of HFPTO (----) and HFPTO-d6 (···) in the OH/OD region.



Fig. 4. The solid state FT-IR spectra of HFPTO (----) and HFPTO-d6 (\cdots) in the 500–1600 cm^{-1} region.



Fig. 5. The Raman spectra of HFPTO (\longrightarrow) and HFPTO-d6 (\cdots).

The strong IR band at 1274 cm^{-1} is caused by asymmetric C–CF₃ and CO₂ stretching and OHi in-plane bending vibrations. Upon deuteration this band shows a blue shift and appears at 1285 cm^{-1} . The relatively strong IR bands at 1223, 1207, 1186, 1158, and 1136 cm^{-1} are engaged in the CF₃ stretching vibrations. These bands are somewhat coupled to the O–H in-plane bending

movements. The corresponding bands in the deuterated analogue observed at 1186, 1177, 1137, and 1115 cm⁻¹. The CF₃ stretching modes in HFAA have been observed at 1270, 1225, and 1187 cm⁻¹ [28].

The 1115 cm^{-1} IR band is mainly asymmetric OH in-plane bending coupled with the asymmetric C2C3C4 and symmetric CO₂ stretching vibrations. Upon deuteration this band moves to 1077 cm^{-1} and couples with the CD₂ wagging vibration.

The strong 1015 cm⁻¹ band in the deuterated IR spectrum is mainly OHi in-plane bending mode.

4.4.3. Below 1000 cm⁻¹

In this region the O–H out-of-plane bending, CO_2 and CH_2 wagging, rocking, and twisting, CF_3 bending, and skeletal vibrations are expected to be observed. The strong IR band at 987 is mainly asymmetric CO_2 stretching, which is coupled with the CH_2 wagging and CO_2 rocking. The corresponding band in the IR spectrum of deuterated analogue observed at 855 cm⁻¹.

The weak IR band at 960 cm^{-1} and medium band at 739 cm^{-1} result from coupling between CF₃ symmetric stretching and CO₂ wagging vibrations. The symmetric CF₃ deformation contributes mainly in the 739 and 665 cm⁻¹ bands. These wavenumber are very close to the corresponding bands observed in the hexafluoroacetone vibrational spectra [44], which have been observed at 738 and 696 cm⁻¹. The very strong Raman band at 822 cm⁻¹is mainly caused by symmetric CO₂ stretching, which is strongly coupled with the symmetric C2C3C4 stretching and C2C3C4 bending vibrations. Upon deuteration, this band shows a red shift and appears at 784 cm⁻¹. Almost all of the asymmetric CF₃ deformations interact with the skeletal vibrations and OH/OD in-plane bending modes. The 617, 593, 532, 527 cm^{-1} bands are mainly engaged in the asymmetric CF₃ deformation vibration. According to the theoretical calculations, the corresponding bands in the deuterated analogue are 583, 572, and 550 cm⁻¹.

Two IR bands at 608 and 572 cm^{-1} are attributed to the OHi out-of-plane bending modes, which upon deuteration move to 434 and 424 cm⁻¹, respectively.

5. Conclusion

The molecular structure, conformations analysis, and vibrational spectra of hydrated hexafluoroacetylacetone have been studied by means of density functional theory calculations.

The calculated vibrational frequencies and geometrical parameters are shown to be in fairly good agreement with the experimental results.

In the most stable conformer, two intramolecular hydrogen bond with a strength of about 7.5 kcal/mol per bond was estimated. The IR spectra also indicate the presence of an intermolecular hydrogen bond in the solid state.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2013. 03.026.

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