

HYDRATION OF CBr_3COOH MOLECULES AND $\text{CBr}_3\text{CO}_2^-$ ANIONS IN AQUEOUS SOLUTIONS

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UDC 532.74:541.452:541.571.9:541.65

The optimal structures and the vibrational frequencies of H-bonded complexes formed from one-two CBr_3COOH molecules or the $\text{CBr}_3\text{CO}_2^-$ anion with water molecules are calculated by density functional theory (B3LYP/6-31++G(*d,p*)). The comparison of the obtained results with the known Raman spectra of the $\text{CBr}_3\text{COOH}\cdot\text{H}_2\text{O}$ and $\text{NaCBr}_3\text{CO}_2\cdot\text{H}_2\text{O}$ solutions (with component molar ratios of $\leq 1:16$) shows that they include stable hydrates: $\text{CBr}_3\text{COOH}\cdot\text{H}_2\text{O}$ and $\text{CBr}_3\text{CO}_2^-\cdot(\text{H}_2\text{O})_6$. The first one has a cyclic form, and the second has a cubic globular form. The vibrational band frequencies of the CBr_3COOH molecule and the $\text{CBr}_3\text{CO}_2^-$ anion in the spectra of both solutions are almost completely determined by the mutual arrangement of units in these hydrates.

DOI: 10.1134/S0022476615060128

Keywords: tribromoacetic acid, sodium tribromoacetate, aqueous solutions, vibrational spectrum, DFT calculation, structure of hydrates of CBr_3COOH molecules, structure of hydrates of $\text{CBr}_3\text{CO}_2^-$ anions.

INTRODUCTION

Owing to their high self- and hetero-association ability, carboxylic acids are widely used in studying hydrogen bonding, proton transfer, and molecular self-assembly in the gas phase, matrices, crystals, and solutions [1-15]. One of the important issues is the study of stable hydrated forms of molecules and anions of carboxylic acids. Information on their structure and formation conditions is of interest for the fields of science such as chemistry (homogenous acid catalysis), biochemistry (fermentation catalysis), and atmosphere physics (spray formation, "acid rains").

The structure of hydrates of carboxylic acids, as also of other H-bonded heteroassociates (HAs) of molecules, is conventionally studied in the gas and solid phases. For its determination, the rotational or vibrational spectra of the objects under consideration are compared with the results of quantum chemical calculations (see, for example, [1-6]). It is shown that in the gas phase [1-3] and Ar matrices [4, 5], only the most stable (according to the calculations) hydrates of the molecules of carboxylic acids occur. If the number of water molecules in them does not exceed three, they have a cyclic structure: $\text{HCOOH}\cdot\text{H}_2\text{O}$ and $\text{HCOOH}\cdot(\text{H}_2\text{O})_2$ [1, 4], $(\text{HCOOH})_2\cdot\text{H}_2\text{O}$ [1], $\text{CH}_3\text{CH}_2\text{COOH}\cdot\text{H}_2\text{O}$, and $\text{CH}_3\text{CH}_2\text{COOH}\cdot(\text{H}_2\text{O})_2$ [2], $\text{CF}_3\text{COOH}\cdot\text{H}_2\text{O}$, $\text{CF}_3\text{COOH}\cdot(\text{H}_2\text{O})_2$, $\text{CF}_3\text{COOH}\cdot(\text{H}_2\text{O})_3$ [3, 5]. The $\text{CF}_3\text{COOH}\cdot(\text{H}_2\text{O})_4$ tetrahydrate detected by matrix isolation appears to be a bicyclic compound with an open-book shape [5, 6].

There are few works on the hydration of carboxylic acids in the liquid phase [7-12]. By dielectric relaxation it is shown that in the aqueous NaHCO_2 , NaCH_3CO_2 , and NaCF_3CO_2 solutions at infinite dilution the CHCO_2^- , CH_3CO_2^- , and

CF_3CO_2^- ions are weakly bonded with ~ 20 water molecules [7, 8]. In the entire possible concentration range the anions of acetic and trifluoroacetic acids are strongly hydrated by one-two (mostly two) molecules, and at the limiting saturation of the solution they weakly interact with three–four H_2O molecules. In studying the hydration of acetic [9] and tribromoacetic [10] acids by vibrational spectroscopy methods, the spectra of aqueous solutions of the acid and its sodium salt were compared with the spectra of CH_3COOH , CBr_3COOH molecules and CH_3CO_2^- , $\text{CBr}_3\text{CO}_2^-$ anions calculated (B3LYP/6-311++G(3df,2pd)) under the polarizable continuum model (PCM) approximation. This is a conventional approach to the study of particle solvation in the liquid phase. It facilitates the assignment of vibrational bands in the spectrum of the solution, but generally does not allow one to draw conclusions on the molecular structure of solvates of the units under consideration.

In the study of hydration of tribromoacetic acid by Raman scattering [11], the authors determined the equilibrium composition of the $\text{CF}_3\text{COOH-H}_2\text{O}$ system (100-10% of acid) and showed that, depending on the component ratio, it contained undissociated acid, its hydrates, and hydrated CF_3CO_2^- anions. As a result, they concluded that the hydrate of the CF_3COOH molecule was characterized by the 1:1 stoichiometric ratio and was the $\text{CF}_3\text{COOH}\cdot\text{H}_2\text{O}$ or $\text{CF}_3\text{CO}_2^-\cdot\text{H}_3\text{O}^{+*}$ complex, and the hydrate of the anion was the $\text{CF}_3\text{CO}_2^-\cdot\text{H}_2\text{O}$ complex. In [12], the structures of HAs with different topologies formed from one-two CF_3COOH molecules (or the CF_3CO_2^- ion) with water molecules** were calculated using (B3LYP/6-31++G(d,p)). The comparison of the vibrational spectra of the most stable of these HAs with the spectra of the $\text{CF}_3\text{COOH-H}_2\text{O}$ solutions [11] allowed us to assume that they contained cyclic tetramers $(\text{CF}_3\text{COOH})_2\cdot(\text{H}_2\text{O})_2$ and cyclic dihydrates $\text{CF}_3\text{CO}_2^-\cdot(\text{H}_2\text{O})_2$.

This study was aimed to determine the composition and structure of the hydrates of CBr_3COOH molecules and hydrates of $\text{CBr}_3\text{CO}_2^-$ anions formed in aqueous solutions. To this end, the experimental vibrational frequencies of the hydrated molecule and anion of tribromoacetic acid were compared with the calculated frequencies of the most stable (in a series of conformers) H-bonded HAs with different compositions, including one-two CBr_3COOH molecules (or the $\text{CBr}_3\text{CO}_2^-$ ion) and several water molecules. The experimental values of the frequencies were taken from the Raman spectra [10] of diluted ($\leq 1:16$) $\text{CBr}_3\text{COOH-H}_2\text{O}$ (with the addition of HCl to hinder the dissociation of CBr_3COOH molecules) and $\text{NaCBr}_3\text{CO}_2^-\cdot\text{H}_2\text{O}$ solutions.

RESULTS AND DISCUSSION

The optimal structures and the vibrational spectra for seven neutral $(\text{CBr}_3\text{COOH})_m\cdot(\text{H}_2\text{O})_n$ ($m = 1, 2; n = 1-4$) and ten negatively charged $\text{CBr}_3\text{CO}_2^-\cdot(\text{H}_2\text{O})_n$ ($n = 1-7$) HAs with different topologies were calculated by density functional theory (B3LYP/6-31++G(d,p)) using the GAUSSIAN 98 software [16]. The obtained formation energies of all HAs and the parameters of their shortest hydrogen bridges are given in Table 1. The table also reports the average strengths of H bonds, $\Delta E/n$ (n is the number of H bonds), which allow the estimation of the relative stability of cyclic and branched (rather than “cellular”, for example, bicyclic) complexes with different compositions and structures by their comparison.

For the binary liquid $\text{CF}_3\text{COOH-H}_2\text{O}$ [12] and HF–organic solvent systems (see, for example, [17-19]) it was previously shown that the solutions contain HAs of a strictly specified composition, and out of all possible (according to the

* The authors of [11] were not aware of the existence of the H_3O_2^- ion, whose presence in the $\text{CF}_3\text{COOH-H}_2\text{O}$ system was proved later [15], therefore, they believed that the protons in the solution were in the form of H_3O^+ ions.

** Therein, it is shown that density functional theory (B3LYP) enables the prediction of the vibrational frequencies of stable closed H bonded complexes in the liquid or crystalline phases reasonably well. Thus, the calculations of cyclic $(\text{CBr}_3\text{COOH})_2$ dimers performed with the 6-311++(3df,2pd) basis set [13] reproduce the IR [14] and Raman [13] spectra of 100% tribromoacetic acid (the crystal whose unit cell lattice consists of such dimers) with the average errors of 2.47% and 3.32% respectively, while the calculations with a significantly smaller (6-31++G(d,p)) basis set reproduce them with the errors of 2.84% and 3.57%. A similar calculation predicts the spectra of formic, acetic, and trifluoroacetic acids with an accuracy of 1.18-3.85%.

TABLE 1. Formation Energies (ΔE , kcal/mol) of the Hydrates of the CBr_3COOH Molecule and the $\text{CBr}_3\text{CO}_2^-$ Ion, the Average Strengths of H Bonds of the Cyclic Complexes ($\Delta E/n$, kcal/mol), and the Parameters of Short Hydrogen Bridges (r_{OH} and $r_{\text{H}\cdots\text{O}}$, Å; $\gamma_{\text{HO}\cdots\text{H}}$, deg)

System	Structure	ΔE	$\Delta E/n$	r_{OH}	$r_{\text{H}\cdots\text{O}}$	$\gamma_{\text{HO}\cdots\text{H}}$
CBr_3COOH		–	–	0.972	–	–
CBr_3COO^-		–	–	–	–	–
H_2O		–	–	0.865	–	–
$\text{CBr}_3\text{COOH}\cdot\text{H}_2\text{O}$ ^a	Cycle	12.5	6.3	0.998	1.708	159
$\text{CBr}_3\text{COOH}\cdot 2\text{H}_2\text{O}$ ^a	Cycle	25.6	8.5	1.020	1.574	178
$\text{CBr}_3\text{COOH}\cdot 3\text{H}_2\text{O}$ ^a	Cycle	36.0	9.0	1.025	1.539	172
$\text{CBr}_3\text{COOH}\cdot 3\text{H}_2\text{O}$	2 cycles	32.9	–	1.011	1.614	177
$\text{CBr}_3\text{COOH}\cdot 4\text{H}_2\text{O}$ ^a	2 cycles	47.8	–	1.048	1.469	178
$2\text{CBr}_3\text{COOH}\cdot 2\text{H}_2\text{O}$ ^a	Cycle (C_1)	41.2	10.3	1.023	1.539	176
$2\text{CBr}_3\text{COOH}\cdot 2\text{H}_2\text{O}$	Cycle (C_2)	39.6	9.9	1.036	1.498	179
$\text{CBr}_3\text{CO}_2^-\cdot\text{H}_2\text{O}$ ^a	Cycle	18.9	9.5	0.975	2.064	143
$\text{CBr}_3\text{CO}_2^-\cdot 2\text{H}_2\text{O}$ ^a	Cycle	33.6	11.2	0.993	1.731	174
$\text{CBr}_3\text{CO}_2^-\cdot 3\text{H}_2\text{O}$	2 cycles	44.2	–	0.988	1.788	169
$\text{CBr}_3\text{CO}_2^-\cdot 3\text{H}_2\text{O}$ ^{cis a}	Globule	47.7	–	0.983	1.832	164
$\text{CBr}_3\text{CO}_2^-\cdot 4\text{H}_2\text{O}$ ^{cis a}	Globule 1	62.3	–	0.982	1.852	162
$\text{CBr}_3\text{CO}_2^-\cdot 4\text{H}_2\text{O}$ ^{cis}	Globule 2	59.7	–	0.980	1.892	158
$\text{CBr}_3\text{CO}_2^-\cdot 5\text{H}_2\text{O}$ ^{cis a}	Globule	74.7	–	0.986	1.813	162
$\text{CBr}_3\text{CO}_2^-\cdot 6\text{H}_2\text{O}$ ^a	Globule 1	89.9	–	0.982	1.864	167
$\text{CBr}_3\text{CO}_2^-\cdot 6\text{H}_2\text{O}$ ^{cis a}	Globule 2	88.6	–	0.978	1.913	161
$\text{CBr}_3\text{CO}_2^-\cdot 7\text{H}_2\text{O}$ ^a	Globule	100.0	–	0.982	1.851	168

^{cis} Complex, in which the *cis*-conformer of the $\text{CBr}_3\text{CO}_2^-$ anion occurs.

^a Complex whose vibrational frequencies were compared with the experiment.

calculation) conformers the most stable one occurs. Consequently, in searching for the composition and structure of the hydrates formed in the $\text{CBr}_3\text{COOH}\text{--}\text{H}_2\text{O}\text{--}\text{HCl}$ and $\text{NaCBr}_3\text{CO}_2^-\cdot\text{H}_2\text{O}$ solutions, only the spectra of the most stable calculated structures with the same composition were compared with the Raman spectra [10] (Table 1, complexes with superscript ^a).

As can be seen from Table 1, seven simplest hydrates of tribromoacetic acid molecules have a cyclic or bicyclic structure. The relative stability of cyclic HAs with the composition 1: n ($n \leq 3$) increases (due to cooperative effects) with the number of their constituent water molecules. The most stable ($\Delta E/n \approx 10$ kcal/mol) hydrates of the CBr_3COOH molecules are heterotetramers $(\text{CBr}_3\text{COOH})_2\cdot(\text{H}_2\text{O})_2$. In one of them (with the C_1 symmetry), the acid and water molecules are arranged in pairs, side by side, and in another (with the C_2 symmetry) they are located next by one. Other conformers with the composition 2:2, which have a branched structure rather than a closed one, were not analyzed in this work because they are always less energetically favorable (see, for example, [1, 5, 12, 17-19]).

The above calculation results are fully consistent with the similar data obtained in the study of hydration of CF_3COOH molecules [12]. However, the formation conditions of the hydrates of the molecules of tribromoacetic and trifluoroacetic acids are significantly different. The point is that $\text{CF}_3\text{COOH}\text{--}\text{H}_2\text{O}$ is a binary liquid system. The maximum concentration of the hydrates of the molecules in this system is observed in the equimolar solution (according to the law of mass action [20], the stoichiometric ratio of the molecules in the hydrate is 1:1). Tribromoacetic acid exhibits a much worse water solubility starting to dissolve only from the molar ratio of $\sim 1:8.5$.

In the solutions studied in [10], the component ratio was $\leq 1:16$. The presence of undissociated CBr_3COOH molecules in these solutions was provided artificially, by adding stronger HCl acid (whose presence can also affect the processes of complex formation in a given solution). Based on the law of mass action it is naturally to assume that in the concentration range of $\sim 1:16$ the most stable HAs (with the composition 2:2) do not form, hence the hydrates of CBr_3COOH molecules therein should have another composition.

The calculation of $\text{CBr}_3\text{CO}_2^-(\text{H}_2\text{O})_n$ HAs shows (Table 1) that they are characterized by the following structural features. When $n = 1$ and 2, the hydrate of the $\text{CBr}_3\text{CO}_2^-$ anion has a cyclic structure; when $n = 3$, along with a bicyclic isomer ($\Delta E = 44.2$ kcal/mol), a more stable isomer in a globular form occurs ($\Delta E = 47.7$ kcal/mol). Hereinafter, under the globule we mean a closed H-bonded complex shaped as a polyhedron, at the vertices of which all the constituent oxygen atoms of the complex (and, sometimes, also one-two bromine atoms) are located. When $n = 4-7$, only globules occur.

It is interesting to note that the structure of the hydrated $\text{CBr}_3\text{CO}_2^-$ anion depends on whether its bromine atoms are involved in interactions with water molecules or not. If so (this occurs when $n = 3-6$), under the effect of these interactions, the CBr_3 group turns around the CC bond at 30° , and the *trans*-isomer of the $\text{CBr}_3\text{CO}_2^-$ anion transforms into the less stable *cis*-isomer (which, as follows from the calculation, does not exist as an individual unit). HAs, which underwent these transformations, are denoted by asterisks in Table 1. Our data imply that when $n = 6$, the hydrates of both *trans*- and *cis*-isomer of the $\text{CBr}_3\text{CO}_2^-$ anion can form. The first of these HAs is more stable than the second one by 1.3 kcal/mol (Table 1). The abovementioned feature of the complex formation is likely to be characteristic of the tribromoacetic acid anion (F atoms of the CF_3CO_2^- anion do not interact in such a way with H_2O molecules in the hydrate composition [6, 12]).

The results of the calculation of normal vibrational frequencies for the majority of most stable (in a series of conformers) $(\text{CBr}_3\text{COOH})_m(\text{H}_2\text{O})_n$ and $\text{CBr}_3\text{CO}_2^-(\text{H}_2\text{O})_n$ HAs and the CBr_3COOH molecule and the $\text{CBr}_3\text{CO}_2^-$ anion in PCM (data from [10]) are shown in Tables 2 and 3. Only one of more stable conformers, namely $(\text{CBr}_3\text{COOH})_2(\text{H}_2\text{O})_2$ HA in which the acid and water molecules are arranged in pairs, was not included in Table 2. The reason was a drastic difference between the spectrum of this HA and the measurements [10]. Due to cooperative effects, many vibrations of different acid molecules, which are intense in the Raman spectrum and have the same shape, are manifested in it as two bands with the frequencies differing by 20-130 cm^{-1} , and in the case of νOH , by 650 cm^{-1} . Instead of the spectrum of this HA, we considered the spectrum of a less stable heterotetramer with alternating CBr_3COOH and H_2O molecules. Tables 2 and 3 also report the experimental Raman spectra [10] of the tribromoacetic acid molecules and anions contained in $\text{CBr}_3\text{COOH}-\text{H}_2\text{O}$ (with the addition of HCl) and $\text{NaCBr}_3\text{CO}_2^-\cdot\text{H}_2\text{O}$ solutions respectively.

Note that a detailed analysis of the vibrations of the tribromoacetic acid molecule and anion, along with the assignment of the respective bands in the experimental spectra are reported in [10]. Hence, in this study we focus only on the data needed to solve the task.

It should be emphasized that there is only one, but fundamental difference in the interpretation of the experimental spectrum of the $\text{CBr}_3\text{COOH}-\text{H}_2\text{O}$ solution by the authors of [10] and us. It is caused by different initial models of the interaction of the hydrated CBr_3COOH molecule with its environment. In [10], the effect of water molecules on the acid molecule is averaged, and its OH group remains "free". Consequently, the calculated frequency of rocking vibrations (ρOH)* of this group (503 cm^{-1}) appears to be slightly less than the ρOH frequency of the isolated CBr_3COOH molecule (515 cm^{-1} [10]). Here, the OH group of the acid molecule is always involved in the formation of a hydrogen bond whose strength depends on the number and arrangement of water molecules interacting with the CBr_3COOH molecule. In different HAs this interaction results in an increase in the ρOH frequency to 916-1232 cm^{-1} (Table 1).

The interpretation of the band at 538 cm^{-1} proposed by the authors of [10] does not agree with the Raman spectra of the $\text{CBr}_3\text{COOH}-\text{H}_2\text{O}-\text{HCl}$ and $\text{NaCBr}_3\text{CO}_2^-\cdot\text{H}_2\text{O}$ solutions reported therein. The contradiction is that this band is observed in

* For ease of the analysis of normal vibrations of the hydrated CBr_3COOH molecule and $\text{CBr}_3\text{CO}_2^-$ anion calculated here and in [10], we use the vibrational notations adopted by the authors of [10].

TABLE 2. Vibrational Frequencies (cm^{-1}) of Hydrates of the CBr_3COOH Molecule

Vibration assignment	Raman spectrum [10]	$\text{CBr}_3\text{COOH} \cdot \text{H}_2\text{O}$	$\text{CBr}_3\text{COOH} \cdot (\text{H}_2\text{O})_2$	$\text{CBr}_3\text{COOH} \cdot (\text{H}_2\text{O})_3$	$\text{CBr}_3\text{COOH} \cdot (\text{H}_2\text{O})_4$	$(\text{CBr}_3\text{COOH})_2 \cdot (\text{H}_2\text{O})_2 (\text{C}_2)$	$(\text{CBr}_3\text{COOH})_{\text{aq}}$ [10]
$\rho\text{CBr}_3 / \delta\text{CBr}_3$	139	143	145	147	145	145 _m	135
$\rho\text{CBr}_3 / \delta\text{CBr}_3$	180	176	178	178	183	183 _m	174
$\rho\text{CBr}_3 / \delta\text{CBr}_3$	206	214	218	201	212	177	184
$\delta_s\text{CBr}_3$	271	230	230	216	223	218	204
$\nu_s\text{CBr}_3$	317	320	335	344	359	331	295
$\nu_s\text{CBr}$	400	395	421	424	445	430	367
ρOH^*	538	916	1064	1084	1232	1077 _m	503
$\delta_{\text{as}}\text{CBr}_3 / \rho\text{OH}$	603	578	583	584	582	581 _m	588
$\delta_s\text{CBr}_3 / \delta\text{OCO}$	685	688	702	693	730	697	637
δCCOOH	773	758	760	759	761	759	730
δBrCCOH	799	794	802	800	808	803	799
νCC	922	938	928	940	942	945 _m	905
δCOH	1203	1280	1314	1315	1349	1323	1154
$\delta\text{COH} / \nu_s\text{OCO}$	1401	1471	1502	1491	1543	1517	1338
$\nu\text{C}=\text{O}$	1730	1792	1776	1783	1749	1762	1776
νOH	~2920	3252	2840	2756	2383	2778	3167

ν is the stretching vibration, δ is the bending vibration, ρ is the rocking vibration, ν_s and ν_{as} are the symmetric and asymmetric vibrations.

* Vibration excluded from consideration according to the model of interaction of the hydrated CBr_3COOH molecule with its environment adopted in this study.

_{aq} is the spectrum calculated at the B3LYP/6-311++G(3df,2pd) level under the polarizable continuum model approximation in [10].

_m is the average value of frequencies differing by less than 10 cm^{-1} .

both mentioned spectra, while the solution of sodium tribromoacetate does not contain the CBr_3COOH molecules. The calculation results of this study seem to be more convincing. They imply that the band at 538 cm^{-1} can be due to the intense librational vibrations of water molecules in the hydrate composition. These vibrations are present in the spectra of the hydrates of both acid molecule and anion.

It is no less important to note that the Raman spectrum of the $\text{CBr}_3\text{COOH}-\text{H}_2\text{O}-\text{HCl}$ solution [10] suggests that the ρOH band whose peak frequency is close to 916 cm^{-1} (such a situation occurs in the spectrum of the hydrate with the 1:1 composition) overlaps with the νCC band (922 cm^{-1}). Given the asymmetry of the total profile, in the Raman spectrum the ρOH vibration is less intense than the νCC vibration. This result agrees with the calculation: the frequencies of the bands under consideration are 916 cm^{-1} and 938 cm^{-1} , and their intensities 1.7 times differ. Therewith, in the spectrum of the $\text{NaCBr}_3\text{CO}_2 \cdot \text{H}_2\text{O}$ solution, the νCC band (912 cm^{-1}) has a symmetrical shape. When the hydrates of acid molecules containing at least two water molecules form in the $\text{CBr}_3\text{COOH}-\text{H}_2\text{O}-\text{HCl}$ solution, their ρOH vibrational frequencies appear in a range that does not contain any bands in the Raman spectrum [10]. Then, to agree the calculation data with the experiment, it remains to assume the intensity of the ρOH vibration to be so low that it does not appear in the spectrum. This assumption is not unreasonable since the more intense νCC vibrational band is one of the weakest [10].

Before the comparison of the calculated spectra of different HAs with the experiment, let us point out two things.

1. Based on the above facts, the ρOH vibrational frequencies of the hydrated CBr_3COOH molecules were excluded from the consideration. 2. In the Raman spectra, the νOH vibrational band of the acid molecule completely overlaps with the stretching vibrational bands of water molecules [10]. The estimation of its frequency ($\sim 2929 \text{ cm}^{-1}$) is approximate because of

TABLE 3. Vibrational Frequencies (cm^{-1}) of Hydrates of the $\text{CBr}_3\text{CO}_2^-$ Anion

Vibration assignment*	Raman spectrum [10]	$\text{CBr}_3\text{CO}_2^- \cdot \text{H}_2\text{O}$	$\text{CBr}_3\text{CO}_2^- \cdot (\text{H}_2\text{O})_2$	$\text{CBr}_3\text{CO}_2^- \cdot (\text{H}_2\text{O})_3^{cis}$	$\text{CBr}_3\text{CO}_2^- \cdot (\text{H}_2\text{O})_4^{cis}$	$\text{CBr}_3\text{CO}_2^- \cdot (\text{H}_2\text{O})_5^{cis}$	$\text{CBr}_3\text{CO}_2^- \cdot (\text{H}_2\text{O})_6$	$\text{CBr}_3\text{CO}_2^- \cdot (\text{H}_2\text{O})_6^{cis}$	$\text{CBr}_3\text{CO}_2^- \cdot (\text{H}_2\text{O})_7$	$(\text{CBr}_3\text{CO}_2^-)_{aq}$ [10]
$\rho\text{CBr}_3/\delta\text{CBr}_3$	142	138	136	143	138	129	139	122	140	135
$\rho\text{CBr}_3/\delta\text{CBr}_3$	179	166	168	172	169	182	157	156	158	171
$\rho\text{CBr}_3/\delta\text{CBr}_3$	–	173	172	179	190	202	195 _m	206	198	176
$\delta_s\text{CBr}_3$	218	213	222	221	220	222	217	218	218	199
$\nu_s\text{CBr}_3$	309	289	307	306	306	316	311 _m	294	313	273
$\nu_s\text{CBr}$	398	378	396	391	391	390	393	396	396	362
$\delta_{as}\text{CBr}_3$	608	558	563	553	554	554	576	542	564	544
$\delta_s\text{CBr}_3/\delta\text{OCO}$	718	696	696	698	700	713	700	715	703	689
δCCO_2	767	704	712	722	726	732	730	742	730	691
δCCO_2	821	801	803	804	803	879	824	800	822	812
νCC	912	833	840	859	870	805	893	857	895	833
$\nu_s\text{CO}_2$	1333	1313	1327	1326	1331	1335	1343	1330	1344	1318
$\delta_{as}\text{CO}_2$	1651	1762	1761	1758	1761	1756	1722 _m	1757	1721	1692

* See notes to Table 2.

_m is the average value of similar ($\Delta\nu \leq 10 \text{ cm}^{-1}$) frequencies of two or three vibrations of a given mode, in which different water molecules are involved.

^{cis} is the complex, in which the *cis*-conformer of the $\text{CBr}_3\text{CO}_2^-$ anion occurs.

objective reasons; hence, in the case of the molecule hydrates, two sets of frequencies were considered in parallel: those including and not including the νOH vibration.

We used the average relative deviation of the calculated frequencies from the measured ones (α , %) and the mutual arrangement of bands in the spectrum (σ , %) as the parameters characterizing the error of reproducibility of the experimental spectrum in the calculation. It was estimated by taking the frequency interval Δ containing all vibrational bands analyzed as 100%, expressing as a percentage the $(\nu_j - \nu_i)$ distances between all neighboring band pairs, and calculating the average deviation of the calculated $(\nu_j - \nu_i)/\Delta$ values from the experimental ones. A simultaneous consideration of α and σ parameters (essentially being independent characteristics of the spectrum) significantly increases the reliability of the conclusions on the structure of strong molecular complexes formed in the solution.

The analysis of Table 2 shows that most calculated frequencies of the hydrates of the CBr_3COOH molecule weakly depend on their composition and structure and describe the experiment with an accuracy of 1-6.5%. The frequencies of four vibrations are more responsive to the changes in HA topology and are reproduced with an error of 1-13%, and only in two cases ($\delta_s\text{CBr}_3$ and νOH vibrations) the calculation results differ from the measurements by 8.5-20%. Among the spectra of the hydrates of the CBr_3COOH molecule, there is one spectrum of the 1:4 HAs with much worse agreement ($\alpha = 7.25$, $\sigma = 3.31$) with the experiment (Fig. 1a). In all other cases, the deviation of the calculated frequencies from the measured ones (4.10-5.59%) is less than the respective parameter (6.23%) obtained in the calculation using (B3LYP/6-311++G(3df,2pd)) under the PCM approximation [10]. The mutual arrangement of the bands in the spectra is generally well reproduced: the σ parameter for the hydrates of the molecules (except for the 1:4 HAs) varies in the range of 1.09-1.58%, and for the spectrum of the CBr_3COOH monomer in PCM [10] it is 1.20.

From the data obtained (Fig. 1a) it follows that the vibrational frequencies of the $\text{CBr}_3\text{COOH} \cdot \text{H}_2\text{O}$ heterodimer (its structure is given in Fig. 2a) appear to be closest to the measurements ($\alpha = 4.10$, $\sigma = 1.09$). The addition of subsequent water molecules to the heterodimer leads to an almost symbatic change in both parameters characterizing the error of reproducibility of the experiment by the calculation (Fig. 1a). Therewith, the spectrum of the $(\text{CBr}_3\text{COOH})_2 \cdot (\text{H}_2\text{O})_2$ tetramer

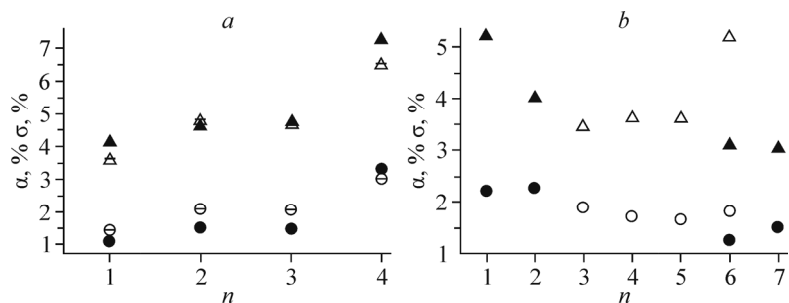


Fig. 1. Dependence of the average relative deviation of the calculated frequencies from the measured ones (α , %, denoted by triangles) and the mutual arrangement of bands in the spectrum (σ , %, denoted by circles) on the number of H_2O molecules hydrating the CBr_3COOH molecule (a) and the CBr_3COO^- anion (b). In Fig. a, the shaded and unshaded crossed signs correspond to the results obtained for the sets of 15 and 14 frequencies; in Fig. b, the shaded and unshaded signs correspond to the hydrates of *trans*- and *cis*-isomers of the CBr_3COO^- anion.

exhibiting a higher relative stability as compared with HAs containing only one CBr_3COOH molecule (Table 1) is in worse agreement with the spectrum of the solution ($\alpha = 5.59$, $\sigma = 1.58$) than the spectra of $\text{CBr}_3\text{COOH} \cdot (\text{H}_2\text{O})_n$ hydrates ($n = 1-3$) ($\alpha = 4.10-4.73$, $\sigma = 1.09-1.54$). This fact confirms the above assumption that the presence of HAs with the composition 2:2 is highly improbable in the studied solutions.

In the series of considered $\text{CBr}_3\text{CO}_2^-(\text{H}_2\text{O})_n$ HAs ($n = 1-7$), the variation range of α and σ parameters is much the same as in the series of the hydrates of the molecules (Fig. 1). The data obtained in [10] under the PCM approximation ($\alpha = 6.39$, $\sigma = 2.26$) describe the spectrum of the $\text{CBr}_3\text{CO}_2^-$ anion in the aqueous solution worse than the calculation results for isolated H-bonded complexes ($\alpha = 3.01-5.22$, $\sigma = 1.25-2.27$). A half of the frequencies of the $\text{CBr}_3\text{CO}_2^-(\text{H}_2\text{O})_n$ hydrates exhibits low sensitivity to the changes in their topology and reproduces the experiment with an accuracy of 0-6.7%. The frequencies of other vibrations are more dependent on the structure of HAs and are reproduced somewhat worse (with an error of 1-13%). The most important fact is that in the case of hydrates of the tribromoacetic acid anion, the results of the comparison of the calculation with the experiment (Table 3, Fig. 1b) are less unambiguous than those in the case of the hydrates of its molecules. This is due to the absence of the systematic change in the α and σ parameters depending on n and the variability of the structure of the $\text{CBr}_3\text{CO}_2^-$ anion in the series of systems under consideration. Recall that when $n = 3-5$, only HAs with the *cis*-isomer of the $\text{CBr}_3\text{CO}_2^-$ anion (Table 1) appear to be stable; and when $n = 6$, two HAs, one of which contains the *trans*-isomer and another contains the *cis*-isomer.

The spectrum of $\text{CBr}_3\text{CO}_2^-(\text{H}_2\text{O})_6$ hexahydrate with the *trans*-structure of the anion is in the best agreement with the experiment: when $n = 6$ and 7, the α values are minimum and differ by 0.06% (the estimation error for this parameter is $\sim 0.1\%$), and the mutual arrangement of the frequencies in the spectrum of 1:6 HAs is significantly closer to the experimental data [10] than in the spectrum of 1:7 HAs. It should be also noted that this hexahydrate has an optimal structure in terms

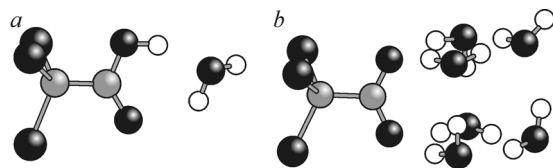


Fig. 2. Structure of the hydrate of the CBr_3COOH molecule (a) and the hydrate of the CBr_3COO^- anion (b) in the $\text{CBr}_3\text{COOH}-\text{H}_2\text{O}-\text{HCl}$ and $\text{NaCBr}_3\text{CO}_2\text{H}_2\text{O}$ solutions.

of molecular “packing density”: the *trans*-isomer of the anion and H₂O molecules involved in three H bonds each (only one of them is involved in two H bonds) form a nearly cubic almost closed unit cell (Fig. 2b).

CONCLUSIONS

In the CBr₃COOH–H₂O–HCl and NaCBr₃CO₂⁻·H₂O solutions, the stable hydrates of the tribromoacetic acid molecule and anion: CBr₃COOH·H₂O and CBr₃CO₂⁻·(H₂O)₆ respectively.

In the spectra of these solutions the frequencies of the vibrational bands of the CBr₃COOH molecule and the CBr₃CO₂⁻ anion are almost completely determined by the mutual arrangement of the units in these hydrates.

The DFT calculation with the 6-31++G(*d,p*) basis set can reproduce with good accuracy the vibrational spectra of stable H-bonded complexes contained in the solution, the molecules of which form closed structures: cycles or globules.

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