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**RAMAN SCATTERING SPECTRA
AND DFT COMPUTATIONAL ANALYSIS
OF INTERMOLECULAR INTERACTIONS
IN TRIFLUOROACETIC AND ITS SOLUTIONS**

UDC 539

In this work, the mechanisms of molecular clusters formation in liquid trifluoroacetic acid were studied using Raman scattering spectra in different solutions. The polarized components of Raman scattering spectra corresponding of the C=O, O-H stretching bands of pure trifluoroacetic acid consist of three broad bands at 1734, 1754, and 1800 cm⁻¹ with different depolarization ratios. When the acid is strongly dissolved in acetonitrile, the 1800 cm⁻¹ spectral band belonging to the C=O band remains. The intermolecular interactions in the formation of trifluoroacetic acid monomer, dimer, and trimer, as well as clusters with water [CF₃COOH + (H₂O)_n, n = 1–7] and acetonitrile [CF₃COOH + (CH₃CN)_n, n = 1–2] molecules, were analysed using the density functional theory (DFT) method.

Keywords: Raman spectra, trifluoroacetic, structure of hydrogen bond, DFT calculations.

1. Introduction

Noncovalent interactions play an important role in many chemical and biological processes. The most common of these interactions is hydrogen bonding. Although hydrogen bonding is generally weaker in value than covalent bonds, it plays a key role in the formation of molecular clusters important in the

functioning of living organisms, such as DNA or proteins [1]. Carbonic acids, including trifluoroacetic (CF₃COOH), also have a functional group that forms a hydrogen bond because, due to the presence of donor and acceptor groups, they can form a number of supramolecular structures. These systems are mainly used as models for studying the nature of hydrogen bonding [2].

Studying the structure and properties of CF₃COOH, as well as its complexes with water molecules, is important in solving the problems related to atmospheric aerosols and acid rain [3–5]. V.D. Maiorov and others [3, 6] studied CF₃COOH using IR spectra and mentioned that it is in a highly stable state consisting mainly of dimers. In addition, the formation of cyclic complexes of CF₃COOH dimers with one or two water molecules, the shift of

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Цитування: Джумабаєв А., Абсанов А., Хушвактов Х., Булавін Л. Раманівські спектри розсіювання і числові розрахунки в теорії функціоналу густини для міжмолекулярних взаємодій у трифтороцтовій кислоті та її розчинах. *Укр. фіз. журн.* **68**, № 4, 245 (2023).

the maxima of the spectral bands and a decrease in the intensity showed that the CF_3COOH anion is strongly hydrated by two water molecules.

E.G. Tarakanova and others studied the optimal structure of CF_3COOH monomer and dimer through H-bonds with a water molecule using the DFT/(B3LYP 6-31++G(d,p)) method, and the average hydrogen bond energy is said to be ~ 9 – 10 kcal/mol, and DFT calculations obtained on the basis of 6-31++G(d,p) agree with the values in IR and Raman spectra [7]. Hydrogen bond complexes of C–H and O–H stretching vibrational bands of CF_3COOH were studied by the theoretical calculations of IR and Raman spectra [8–20]. In the formation of complexes of CF_3COOH with acetone and diethyl ether, it was mentioned that strong and relatively weak hydrogen bonds with one H-atom of the CH_3 group are formed [8].

John W. Keller investigated the interaction of C=O, COH, and O–H vibrational frequencies of hydrogen bonds in the B3LYP/aug-cc-PVDZ basis set of gas-phase CF_3COOH through FTIR spectra and theoretical calculations. Dipole moments are in the interval 2.3–2.4 D, and the hydrogen bond energy for the dimer is $H_{\text{complex}} = 14.2$ kcal/mol, and it was observed that the vibration frequencies of C=O and O–H decrease due to the hydrogen bonding [10]. The ionic dissociation of CF_3COOH in heavy water (D_2O) was studied by infrared spectroscopy, and it was found that the maximum frequency of C=O stretching vibrations in pure CF_3COOH corresponded to 1800 cm^{-1} , and this maximum shifted to the lower frequency side in the aqueous medium [21].

T. Takamuka *et al.* [22] observed open dimers in addition to cyclic dimers through the hydrogen bonding in CF_3COOH molecules using single crystal X-ray diffraction experiments. In this case, it was noted that a dimer bonded by only one weak hydrogen bond is formed, and the bond length is around 2.9 \AA . Gerosimov and Takhadze studied the C=O and O–H stretching vibrations in CF_3COOH vapor using infrared absorption spectra [23–24]. According to their opinion, it was mentioned that the C=O vibrational frequency of the monomer molecule corresponds to the high-frequency part of the complex bands equal to $\nu = 1827\text{ cm}^{-1}$. It was suggested that the low-frequency part of the band belongs to dimers corresponding to C=O vibrations of CF_3COOH molecules hydrogen-bonded with neigh-

boring molecules. In works [25–29], it was shown that low molecular carbonic acids form various aggregates through hydrogen bonds in the liquid state, and the spectral band has a complex appearance as a result of the overlapping of the bands belonging to these aggregates. In previous works [30, 31], the C=O and O–H stretching vibrational bands of lower molecular carboxylic acids were established. It was mentioned that, in addition to closed dimers, chain aggregations also appear in the liquid, and several bands with different depolarization coefficients and different intensities correspond to these vibrations in the Raman scattering spectra.

It can be seen from the above that the intermolecular interactions of CF_3COOH in different solutions and their manifestation in vibrational spectra have not been fully studied. In particular, the change of the shape of the spectral band in various polarized constituents of pure trifluoroacetic, the formation of molecular clusters as a result of the interaction with proton-acceptor/proton-donor solvents (water, acetonitrile) and their appearance in vibrational spectra were not studied completely.

Therefore, it is necessary to study these complexes further. In this work, the appearance of various polarized constituents of the C=O and O–H vibrational bands of CF_3COOH in the Raman scattering spectra and the monomers, dimers, and trimers of the acid and the simplest form of biologically active substances [$\text{CF}_3\text{COOH}+(\text{H}_2\text{O})_n$, $n = 1$ – 7] interaction with water and [$\text{CF}_3\text{COOH}+(\text{CH}_3\text{CN})_n$, $n = 1$ – 2] acetonitrile molecules are studied using *ab-initio* calculations and compared with experiment.

2. Methods

2.1. Experimental method

Raman spectra of trifluoroacetic acid and its aqueous and acetonitrile solutions were recorded using a DFS-52 spectrometer. The excitation source was an LGN-503 argon laser with a wavelength of 488 nm and a radiation power of 1 W . All measurements were carried out at the 90-degree scattering geometry of linearly polarized excitation light. The polarized components of the scattered light were separated using a polarizing prism. A depolarizing wedge was used to eliminate the distorting effect of the device. Chemically pure substances were used in the experiment, which were additionally subjected to vacuum distilla-

tion before measurements. The spectral width of the slit in all experiments was 1.8 cm^{-1} . The error in determining the relative position of the band maximum was ± 0.5 , and that of the half-width of the band was $\pm 0.3 \text{ cm}^{-1}$. All measurements were obtained at the temperature of $20 \text{ }^\circ\text{C}$. Concentration of solutions was in molar fractions (m.f.) of components.

All calculations were carried out in the Gaussian 09W program [32] using the density functional theory (DFT) approach. The DFT approach has been successfully used for calculating the energy and many physicochemical properties of molecular clusters in solution [33–35]. To account for intermolecular hydrogen bonding, we calculated using the three-parameter B3LYP functional of Becke, Li, Yang, and Parr and the 6-311++G(d,p) basis set, which contains diffusion and polarization functionals. Furthermore, in order to account for the influence of the aqueous and acetonitrile solutions as precisely as possible, all calculations were carried out using the integral equation formalism polarizable continuum model (IEF-PCM).

3. Results and Discussion

Fig. 1 shows the structure of trifluoroacetic (CF_3COOH) molecular clusters. Fig. 1, *a* demonstrates a monomer of the CF_3COOH molecule, and the charge distribution on the atoms gives the molecule's ability to undergo intermolecular interactions. Calculations showed that there is an intermolecular hydrogen bond between the O^6 atom and H^8 atoms of the O–H group in the monomer, with a bond length of 2.356 \AA . According to the harmonic approximation calculations, in monomer to $\text{C}=\text{O}$ stretching vibration corresponds $\nu = 1860.5 \text{ cm}^{-1}$ frequency (depolarization ratio is $\rho = 0.26$ and Raman activity is 11.8) and to O–H stretching vibration corresponds $\nu = 3748.2 \text{ cm}^{-1}$ frequency (depolarization ratio $\rho = 0.24$ and Raman activity 94.3). The dipole moment of the molecule is 2.36 D. In the gas phase, these vibrational frequencies are $\nu_{\text{C}=\text{O}} = 1827 \text{ cm}^{-1}$ and $\nu_{\text{O}-\text{H}} = 3580 \text{ cm}^{-1}$ [23]. In the experiment, the bands $\nu_{\text{C}=\text{O}} = 1800 \text{ cm}^{-1}$ and $\nu_{\text{O}-\text{H}} = 3550 \text{ cm}^{-1}$ correspond to the liquid CF_3COOH monomer molecule in the Raman spectra.

Fig. 1, *b* shows the open structural dimer structure of CF_3COOH . The energy of intermolecular interaction is 3.27 kcal/mol. In the molecule, the double bonds of oxygen and fluorine atoms have a negative charge, and the hydrogen atom has a positive charge.

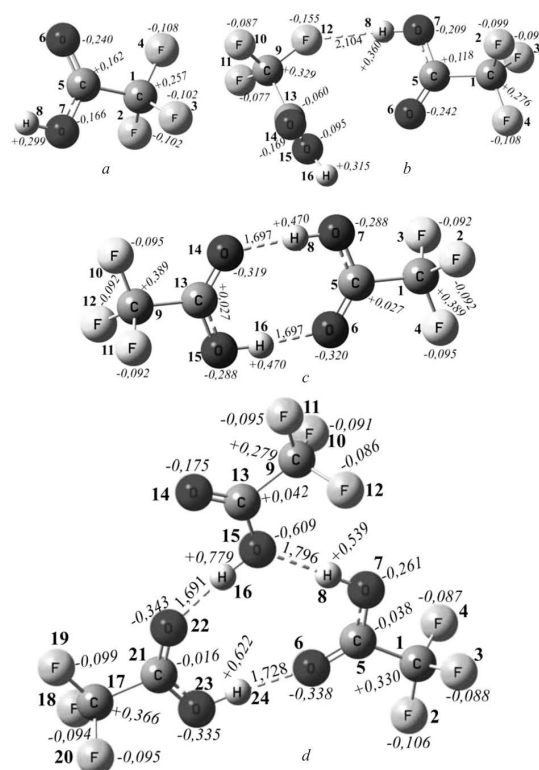


Fig. 1. The optimal geometries and atomic charge distribution of CF_3COOH : monomer (*a*), open dimer (*b*), closed dimer (*c*), trimer (*d*)

itive charge. Therefore, intermolecular interactions take place through these atoms. The bond length of the $\text{O}^7\text{--H}^8$ atoms of the O–H group participating in the bond is 0.973 \AA (0.970 \AA in the monomer) and the bond length between the $\text{C}^5\text{--O}^7$ atoms is changed to 1.329 \AA (1.336 \AA in the monomer). The other bond lengths remain almost unchanged. The charge distribution changes significantly, the charges of O^7 and H^8 atoms increased (in the monomer O^7 (-0.166), H^8 ($+0.299$) and in the dimer O^7 (-0.209), H^8 ($+0.360$)). These atoms participate in the formation of H-bonds. The charges of fluorine and carbon atoms are redistributed (F^2 (-0.102), F^3 (-0.102) and F^4 (-0.108) in the monomer, and F^{10} (-0.087), F^{11} (-0.077), F^{12} (-0.155) in the dimer). The charge of the F^{12} atom is larger than others. There is also a change in the distances between atoms in the CF_3 group (in the monomer $\text{C}^1\text{--F}^2$ -1.345 ; $\text{C}^1\text{--F}^3$ -1.345 ; $\text{C}^1\text{--F}^4$ -1.332 \AA) and in the dimer $\text{C}^9\text{--F}^{10}$ -1.327 ; $\text{C}^9\text{--F}^{11}$ -1.334 ; $\text{C}^9\text{--F}^{12}$ -1.369 \AA , where the distance between $\text{C}^9\text{--F}^{12}$ atoms is larger than the others. This

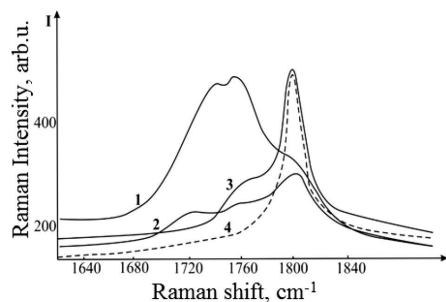


Fig. 2. The shape of the C=O band of vibrations of trifluoroacetic in a pure liquid (I_{\parallel} (1); I_{\perp} (2)), in a solution with acetonitrile (0.5–0.5 m.f. (3)), (0.25–0.75 m.f. (4)). Here and below, the intensities are given in arbitrary units

leads to the conclusion that there is an intermolecular hydrogen bond between H⁸ atom in the O–H group of the acid and one F¹² atom in the CF₃ group of the neighboring molecule, the bond length is 2.104 Å (numbers of atoms and charge changes are shown in Fig. 1, b).

The dipole moment of the open dimer is 1.66 D, which is two times less than that of the monomer. Calculations show that the intermolecular hydrogen bond remains unchanged even in the open dimer. According to calculations, in the harmonic approximation, the frequency corresponding to the O–H stretching vibration is $\nu = 3710.5 \text{ cm}^{-1}$ ($\rho = 0.24$, Raman activity 125.4) and, for the unbonded O–H vibration, it is $\nu = 3749.5 \text{ cm}^{-1}$ ($\rho = 0.22$, Raman activity 65.5) $\nu = 1849.5 \text{ cm}^{-1}$ ($\rho = 0.21$, Raman activity 11.8) and $\nu = 1864.0 \text{ cm}^{-1}$ ($\rho = 0.23$, Raman activity 10.5) for C=O vibrations not involved in H-bonding bands. Both vibrational frequencies are shifted to the lower frequency side compared to the monomer C=O stretching vibration by 11 cm^{-1} and the O–H stretching vibration by 37.7 cm^{-1} (Table 1). In the experiment, the $\nu = 1754 \text{ cm}^{-1}$ band corresponds to the unbound C=O stretching vibrations in the liquid CF₃COOH open dimer in the Raman spectra.

Fig. 1, c shows a cyclic closed dimer. In the cyclic closed dimer, the interaction energy is 14.5 kcal/mol and the average energy of one hydrogen bond corresponds to 7.25 kcal/mol, which is 4 kcal/mol greater than in the open dimer, which gives the conclusion that the cyclic closed dimers are stable. The dipole moment is 0.01 D. The bond lengths of the groups involved in the hydrogen bonding are C⁵–O⁶ – 1.213 Å (1.195 Å in the monomer); C⁵–O⁷ – 1.306 Å (1.336 Å in the monomer); O⁷–H⁸ has a

change of 0.997 (0.970 Å in the monomer). All atoms in both molecules of the acid involved in the intermolecular interaction have the same charge and the same distance between atoms (Fig. 1, c).

A cyclic closed dimer is formed by two identical types of O–H...O= intermolecular hydrogen bonds with the bond lengths of 1.697 Å. According to the calculations, the intermolecular hydrogen bond is retained even in a cyclic closed dimer. In this case, two spectral bands correspond to C=O and O–H stretching vibrations, the vibration frequencies of the monomer ($\nu_{\text{C=O}} = 1860.5 \text{ cm}^{-1}$ and $\nu_{\text{O–H}} = 3748.2 \text{ cm}^{-1}$) C=O stretching vibrations shifted to 100 cm^{-1} , and the O–H stretching vibration shifted to a lower frequency region of to 573.3 cm^{-1} (Table 1). In the experiment, the $\nu = 1734 \text{ cm}^{-1}$ band corresponds to the C=O stretching vibration in the closed dimer in the Raman spectra of liquid CF₃COOH.

Fig. 1, d shows the structure of trimeric molecular clusters of CF₃COOH. The intermolecular interaction energy in the trimer is 19.2 kcal/mol. A bonding energy is an average 6.4 kcal/mol. The dipole moment of the trimer is equal to 1.33 D. The vibrational frequencies of the C=O and O–H vibrations of the trimer is listed in the Table 1. In the trimeric molecular cluster, the C=O and O–H stretching vibration bands are shifted to the lower frequency side compared to the monomer, up to 65 cm^{-1} in the C=O stretching vibration, and up to 477 cm^{-1} in the O–H stretching vibration. A change in the charges of the atoms involved in the intermolecular interaction is observed, the change of charges is presented in Fig. 1. Changes of the bond lengths of atoms participating in the intermolecular interaction: C⁵–O⁶ – 1.209, C⁵–O⁷ – 1.308, O⁷–H⁸ – 0.987 Å (in the monomer; C⁵–O⁶ – 1.995, C⁵–O⁷ – 1.336, O⁷–H⁸ – 0.970 Å), in the second molecule at the intermolecular interaction C¹³–O¹⁴ – 1.191, C¹³–O¹⁵ – 1.344, O¹⁵–H¹⁶ – 0.995 Å, in the third molecule at the intermolecular interaction: C²¹–O²² – 1.210, C²¹–O²³ – 1.307, O²³–H²⁴ – 0.987 Å. These changes indicate that, in the formation of trimer molecular clusters, the atoms of these groups are involved in the intermolecular hydrogen bonding. In the formation of a cyclic dimer, the C⁵–O⁷–H⁸ and O⁶–C⁵–O⁷ angles in the carboxyl group increase from 108.32° and 126.72° to 110.42° and 127.53° , respectively. When a trimer is formed, these angles increase to 111.92° and 128.01° , respectively.

Table 1. Results of *ab-initio* calculations (DFT/B3LYP/6-311++G(d,p)) for CF₃COOH molecular clusters

Type of molecular cluster	Hydrogen bond length (Å)	Frequency C=O, cm ⁻¹ (Raman activity, A ⁴ /AMU)	Depolarization ratio (ρ) C=O	Frequency O-H, cm ⁻¹ (Raman activity, A ⁴ /AMU)	Depolarization ratio (ρ) O-H	Dipole moment, (Debye)	Interaction energy, kcal/mol	Hydrogen bond energy kcal/mol
Monomer CF ₃ COOH	$r(\text{H}_8 \dots \text{O}_6) = 2.355$	1860.5 (11.8)	0.26	3748.2 (94.3)	0.24	2.36	–	–
Dimer CF ₃ COOH (Open)	$r(\text{H}_8 \dots \text{F}_{12}) = 2.104$	1849.5 (11.8) 1864.0 (10.5)	0.21 0.23	3710.5 (125.4) 3749.5 (65.5)	0.24 0.22	1.66	3.27	3.27
Dimer CF ₃ COOH (Closed)	$r(\text{H}_8 \dots \text{O}_{14}) = 1.697$ $r(\text{O}_6 \dots \text{H}_{16}) = 1.697$	1760.1 (21.0) 1813.2 (0)	0.11 0.34	3174.9 (372.1) 3271.3 (0.0014)	0.28 0.29	0.01	14.5	7.25
Trimer CF ₃ COOH	$r(\text{O}_6 \dots \text{H}_{24}) = 1.728$ $r(\text{H}_8 \dots \text{O}_{15}) = 1.796$ $r(\text{H}_{16} \dots \text{O}_{22}) = 1.691$	1795.2 (33.7) 1822.2 (6.8) 1875.9 (14.6)	0.12 0.68 0.19	3271.0 (296.5) 3421.5 (222.7) 3446.9 (90.3)	0.17 0.29 0.73	1.33	19.2	6.4
CF ₃ COOH + CH ₃ CN	$r(\text{H}_8 \dots \text{N}_{14}) = 1.808$	1838.1 (11.3)	0.15	3348.9 (328.3)	0.31	8.05	9.72	9.72
CF ₃ COOH + (CH ₃ CN) ₂	$r(\text{O}_6 \dots \text{H}_{17}) = 2.317$ $r(\text{H}_8 \dots \text{N}_{14}) = 1.745$ $r(\text{N}_{20} \dots \text{H}_{10}) = 2.367$	1822.4 (18.9)	0.16	3201.3 (254.2)	0.32	4.06	16.6	5.55

Fig. 2 shows the various polarized components of the C=O stretching vibrations of pure trifluoroacetic acid. As one can see, both the parallel and perpendicular components of the band are complex and represent at least a combination of three bands. Two low-frequency bands are approximately of the same intensity and have maxima with wave numbers of 1734 cm⁻¹ and 1754 cm⁻¹. The high-frequency band at 1800 cm⁻¹ is significantly lower than the first two in intensity and in the I_{\parallel} and I_{vib} components and appears in the spectrum as a small ledge in the high-frequency part of the total band. However, in the perpendicular component of the total band, the intensity of the last band is the highest. This result means that the components 1734 and 1754 cm⁻¹ and 1800 cm⁻¹ differ in the value of the depolarization ratio. For the last band, the value of the depolarization ratio is the largest.

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According to [24, 36], the band in the high-frequency region of the band should correspond to trifluoroacetic molecules with C=O stretching vibrations free of the hydrogen bond. Our experiments confirm this conclusion. This follows, for example,

from the experimentally obtained high value of the depolarization ratio of this band. Indeed, as we will see below, the bands have a wave number combination of three bands. 1734 and 1754 cm^{-1} refer to different types of associates with hydrogen bonds, in which the oxygen atoms of the C=O group are involved. Such a bond should lead to a redistribution of the electron cloud on this bond compared to the electron cloud of the C=O group in which the oxygen atom does not enter into the hydrogen bond.

Let us discuss the two low-frequency components of the total C=O stretching vibration band. Their depolarization ratios are approximately the same, and it is less than the depolarization ratio of C=O free vibrations. Both bands, in our opinion, correspond to H-bonded C=O stretching vibrations, but, however, to different structures of the complexes. According to [24, 36], closed cyclic dimers and open chains with a structure are possible in trifluoroacetic.

Closed dimer formations in the gas phase correspond to the band at 1790 cm^{-1} [24, 36]. Considering the shift of the band in the liquid state, there is a reason to assume that the low-frequency band (1734 cm^{-1}) corresponds to closed dimers. Its displacement in the liquid phase compared to the gas phase should be associated with a change in the universal interaction in the liquid state [24, 36]. For this kind of C=O associates, the bond should be the most perturbed. Then the band with a wave number of 1754 cm^{-1} should refer to the H-bonded C=O stretching vibrations of open polymers. Note that a similar interpretation of the low-frequency components of the C=O stretching vibrations for liquid acetic acid (CH_3COOH) was proposed in [38, 39].

The most interesting changes in the structure of the C=O band occur in solutions with acetonitrile. It was established that the dilution of trifluoroacetic acid in acetonitrile leads to the fact that, out of the three components of the band, at a sufficiently strong dilution, only one high-frequency vibration is retained, which, in accordance with the above, is C=O free vibrations (although the hydrogen atom of this molecule can participate in the H-bond with another molecule). The other two bands decrease in intensity with dilution and are practically not observed at high dilution (Fig. 2). In addition, the 1800 cm^{-1} band width decreases noticeably with dilution.

The observed phenomena are explained as follows: in the case of a sufficiently strong dilution

of CF_3COOH in an acetonitrile solution, only the high-frequency band is retained. The structure of the dilute solution is explained by the fact that there is an excess of electron-donating groups associated with the nitrogen atom of acetonitrile and that there is active hydrogen in the O-H group of the acid, which is surrounded at its low concentrations by acetonitrile molecules. However, for most trifluoroacetic molecules under such conditions, the C=O group will be free from the H-bond. This means that the high-frequency component of the complex band of C=O stretching vibrations of trifluoroacetic belongs to vibrations of molecules that do not participate in the formation of hydrogen bonds with other molecules using the oxygen of this group. Two low-frequency bands that are observed in pure trifluoroacetic acid but absent in a dilute solution in acetonitrile should be associated with the formation of an intermolecular hydrogen bond involving the oxygen atom of the C=O group of the selected acid molecule.

In [26, 39–43], the low-frequency component of the complex C=O band of vibrations of formic, acetic, and other acids was associated with the formation of cyclic dimers. For trifluoroacetic in the vapor state, C=O vibrations of cyclic dimers are attributed to the line at 1790 cm^{-1} [24]. Accounting for the shift of the band at the transition to the liquid state [39, 44], it should be assumed that, in our case, the line at 1734 cm^{-1} belongs to dimers, i.e., to formations in which the oxygen atom of the C=O group is involved in the intermolecular hydrogen bond. Due to the double hydrogen bond between molecules, such dimers should be stable and have a higher binding energy.

In a saturated CCl_4 solution, the low intensity of the high-frequency band at 1800 cm^{-1} and the almost complete absence of the line with an intermediate frequency indicate that most of the CF_3COOH molecules in this solution exist in the form of dimers [38, 44]. At the same time, the perturbing interaction of H-bonds in this case should differ from the perturbing interaction of H-bonds in the case of dimers. Thus, the combination of literature data and the data obtained by us for CF_3COOH solutions allows us to attribute the line at 1754 cm^{-1} in the complex band of C=O stretching vibrations of liquid acid to the C=O stretching vibrations of the molecule associated in the form of chains. The content of another type of associates (cyclic dimers and chains) in a pure liquid at the studied temperatures is such that

the intensities of the C=O stretching vibration lines of these formations in a complex band are approximately the same.

In full accordance with this interpretation are the data on the depolarization ratios of individual bands of the complex C=O band of liquid acid vibrations. Indeed, the formation of a hydrogen bond should lead to a redistribution of the electron cloud into C=O bonds. The polarizability tensor of the C=O bond does not possess the axial symmetry with respect to the bond line, and, therefore, the shift of the electron cloud during the formation of a hydrogen bond should change the average polarizability and anisotropy of the bond polarizability, and, consequently, the corresponding values of the components of the derivatives of the polarizability tensor with respect to the normal coordinates. Consequently, the C=O stretching vibrations of molecules in which the oxygen atom participates in the H-bond and molecules in which the oxygen atom is free will correspond to different depolarization ratios. As far as possible structures in a pure liquid are concerned, a free stretching vibration of C=O bond is possible only in the case of monomer forms (the number of monomers in a liquid is small) or terminal molecules in open associated formations. In all other cases, the formation of various types of aggregates (dimers, chain polymers) involves the oxygen atom of the C=O group. Hence, from the entire set of C=O bands of vibrations of various formations of trifluoroacetic acid, only the one that differs from the others in value ρ (in our case, the band from 1800 cm^{-1}) will refer to the C=O stretching vibrations free from the H-bond (regardless of the participation of the hydrogen atom of the O-H group of the selected molecule in the formation of the hydrogen bond with other molecules). Note again the low intensity of the 1800 cm^{-1} band in the I_{\parallel} and I_{vib} components. This means that the number of molecules with free C=O bonds in a pure liquid is small.

Let us discuss the results of the study of O-H stretching vibrations. Figure 3 shows the various polarized components of this band, as well as the vibrational component calculated from the relation $I_{\parallel} = I_{\text{vib}}(\nu) + 4/7I_{\text{an}}(\nu)$.

As one can see from the figure, O-H stretching vibrations correspond to a strongly polarized broad band with the maximum at 3200 cm^{-1} and a half-width of 320 cm^{-1} . From the high-frequency

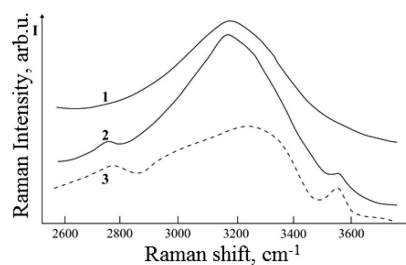


Fig. 3. The O-H vibrations bands of pure trifluoroacetic acid: I_{vib} (1), I_{\parallel} (2), I_{\perp} (3) – polarized components

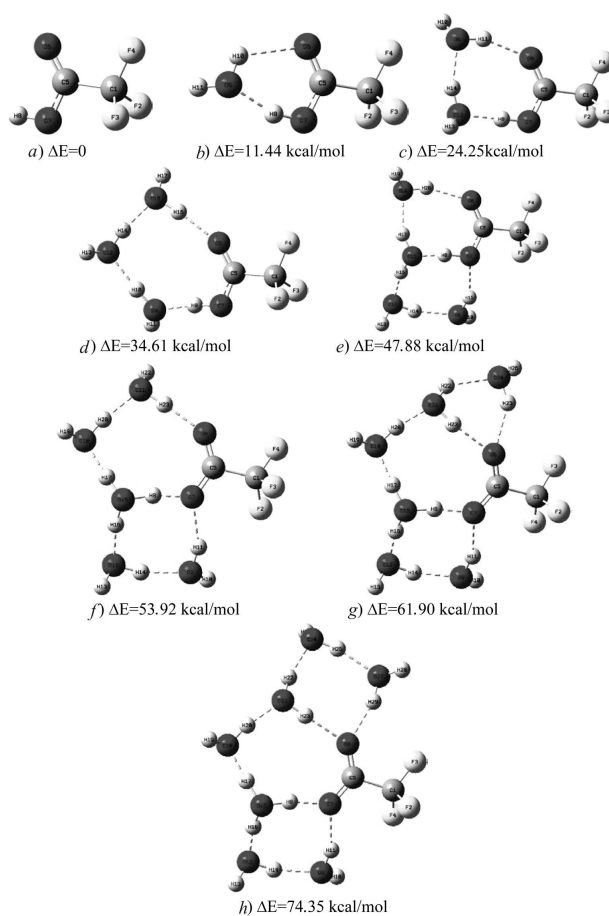


Fig. 4. The optimal geometries of a trifluoroacetic monomer and clusters with water molecules [$\text{CF}_3\text{COOH} + (\text{H}_2\text{O})_n$, $n = 1-7$]

and low-frequency regions of the band, relatively weak maxima are observed with $\sim 2760\text{ cm}^{-1}$ and 3550 cm^{-1} . The latter is close in frequency to the frequency given in [24, 36] for monomer molecules of trifluoroacetic acid in the vapor state. Therefore, there is a reason to believe that the high-frequency

Table 2. Results of calculations of molecular clusters

The types of molecular cluster	The distance of hydrogen bond (Å)	Frequency of C=O vibration, cm^{-1} (Raman activity, $\text{Å}^4/\text{AMU}$)	Frequency of O-H vibration, cm^{-1} (Raman activity, $\text{Å}^4/\text{AMU}$)	Dipole momentum, (Debye)	Energy of intermolecular interaction (kcal/mol)	Average energy of hydrogen bonding (kcal/mol)
CF_3COOH	$r(\text{H}_8\text{...O}_6) = 2.355$	1860.5 (11.8)	3748.2 (94.3)	2.36	–	–
$\text{CF}_3\text{COOH} + \text{H}_2\text{O}$	$r(\text{H}_8\text{...O}_9) = 1.716$ $r(\text{O}_6\text{H}_{10}) = 2.271$	1820.9 (11.8)	3284.9 (152.0)	3.86	11.44	5.72
$\text{CF}_3\text{COOH} + (\text{H}_2\text{O})_2$	$r(\text{O}_6\text{...H}_{11}) = 1.901$ $r(\text{H}_8\text{...O}_{12}) = 1.588$ $r(\text{O}_9\text{...H}_{14}) = 1.745$	1800.8 (14.7)	2907.9 (168.5)	3.51	24.25	8.08
$\text{CF}_3\text{COOH} (\text{H}_2\text{O})_3$	$r(\text{O}_6\text{...H}_{16}) = 1.856$ $r(\text{H}_8\text{...O}_9) = 1.557$ $r(\text{H}_{10}\text{...O}_{12}) = 1.688$ $r(\text{H}_{14}\text{...O}_{15}) = 1.742$	1801.7 (19.0)	2825.2 (187.5)	3.54	34.61	8.65
$\text{CF}_3\text{COOH} + (\text{H}_2\text{O})_4$	$r(\text{O}_6\text{...H}_{20}) = 1.925$ $r(\text{H}_8\text{...O}_{15}) = 1.371$ $r(\text{O}_7\text{H}_{11}) = 2.025$ $r(\text{O}_9\text{...H}_{14}) = 1.819$ $r(\text{O}_{12}\text{...H}_{16}) = 1.754$ $r(\text{H}_{17}\text{...O}_{18}) = 1.787$	1715.8 (22.9)	1912.9 (25.6)	2.08	47.88	7.98
$\text{CF}_3\text{COOH} + (\text{H}_2\text{O})_5$	$r(\text{O}_6\text{...H}_{23}) = 1.744$ $r(\text{H}_8\text{...O}_7) = 1.071$ $r(\text{O}_7\text{...H}_{11}) = 1.859$ $r(\text{O}_9\text{...H}_{14}) = 1.729$ $r(\text{O}_{12}\text{...H}_{16}) = 1.601$ $r(\text{H}_{17}\text{...O}_{18}) = 1.548$ $r(\text{H}_{20}\text{...O}_{21}) = 1.667$	1739.9 (1.1)	2066.3 (28.2)	4.66	53.92	7.7

band with the wave number of 3550 cm^{-1} in the Raman spectrum of liquid trifluoroacetic refers to O–H stretching vibrations of monomers in the liquid, which have a very low intensity.

Figure 4 displays the optimal geometric structures of molecular clusters $[\text{CF}_3\text{COOH} + (\text{H}_2\text{O})_n]$, $n = 1-7$ formed by CF_3COOH acid and water molecules. It is seen from the figure that CF_3COOH and water molecules form different molecular clusters through the intermolecular hydrogen bonding. CF_3COOH can form molecular clusters in different directions with one water molecule, and, among such clusters, cyclic closed structural clusters are the most stable (Fig. 4, Table 2). In the formation of such clusters ($\text{CF}_3\text{COOH} + \text{H}_2\text{O}$), the intermolecular interaction energy is 11.44 kcal/mol, and the average energy corresponding to each hydrogen bond is 5.77 kcal/mol. In the formation of these clusters, acid and water molecules act as both H-donors and H-acceptors. That is, the O–H functional group of

the acid acts as an H-donor, and the C=O group acts as an H-acceptor. Also, in the formation of $\text{CF}_3\text{COOH} + \text{H}_2\text{O}$ clusters, the C=O and O–H vibration frequencies of the acid are shifted towards low frequency side by 39.6 cm^{-1} and 463.3 cm^{-1} respectively, compared to the monomer (Fig. 6, b). Also, the bond lengths of the C=O and O–H groups increase by 0.01 and 0.02 Å during cluster formation compared to the monomer state ($r_{\text{C=O}} = 1.19 \text{ Å}$, $r_{\text{O–H}} = 0.97 \text{ Å}$) (Fig. 5). It can be seen from the change of spectral and geometrical parameters that the $\text{O}^7\text{–H}^8 \dots \text{O}^9$ bond is stronger than the $\text{O}^9\text{–H}^{10} \dots \text{O}^6$ bond.

The geometric structure of the most stable molecular cluster $[\text{CF}_3\text{COOH} + (\text{H}_2\text{O})_2]$ formed by CF_3COOH acid with two water molecules is cyclic (Fig. 4, c), the intermolecular interaction energy is 24.25 kcal/mol. The average energy corresponding to each hydrogen bond increased by 2.3 kcal/mol compared to the $\text{CF}_3\text{COOH} + \text{H}_2\text{O}$ cluster. In the formation of such a cluster, the vibration frequencies of the

C=O and O–H groups of the acid molecule are shifted to the lower frequency side by 60 and 840 cm^{-1} , respectively, compared to the monomer state (Fig. 6, c), and the bond lengths increase by 0.015 and 0.01 Å (Fig. 5).

The molecular cluster $[\text{CF}_3\text{COOH} + (\text{H}_2\text{O})_3]$ formed by the acid with three water molecules is also cyclic, and the energy of intermolecular interaction is 34.61 kcal/mol. The average energy corresponding to each hydrogen bond is 8.65 kcal/mol, which is 0.57 kcal/mol greater than that of $\text{CF}_3\text{COOH} + (\text{H}_2\text{O})_2$. This will make the cluster more stable.

The molecular cluster $[\text{CF}_3\text{COOH} + (\text{H}_2\text{O})_4]$ formed by CF_3COOH acid with four water molecules is bicyclic. The energy of intermolecular interaction in the formation of such a cluster is 47.88 kcal/mol. The average energy corresponding to each H-bond is 7.98 kcal/mol. The vibration frequencies of the C=O and O–H groups of the acid shift to 1715.8 and 1912.9 cm^{-1} , respectively. When the number of water molecules in the molecular cluster reaches five, the proton belonging to the carboxyl group of $[\text{CF}_3\text{COOH} + (\text{H}_2\text{O})_5]$ acid shifts to the water molecule as a result of the strong electrostatic interaction, and $-\text{COO}^-$ anion and H_2O^+ cation are formed. It can also be seen from Fig. 6 that the length of the O–H bond of the acid, that is, the distance between the O^7 and H^8 atoms, increases sharply, when the number of water molecules reaches five. The same process continues in the cases where the number of water molecules is higher than five (Figs. 4, f, g, h). The spectral bands corresponding to the frequencies 2066.3 (f), 2357.4 (g), and 2616.8 cm^{-1} (h) presented in Fig. 6 belong to the O–H vibrations of the H_2O^+ cation.

In Raman scattering spectra, the change in the shape of spectral lines in a solution of CF_3COOH acid in acetonitrile (CH_3CN) is of great interest. Calculations were performed for the molecular clusters of $\text{CF}_3\text{COOH} + \text{CH}_3\text{CN}$ and $\text{CF}_3\text{COOH} + (\text{CH}_3\text{CN})_2$. The mutual orientation of the molecules is presented in the Fig. 7.

According to the calculations, $\text{CF}_3\text{COOH} + \text{CH}_3\text{CN}$ molecules form an open chain dimer based on the $=\text{O}-\text{H}\dots\text{N}$ scheme, the hydrogen bond length $\text{O}^7-\text{H}^8\dots\text{N}^{14} = 1.8$ Å, the energy of dimer formation is 9.72 kcal/mol (Fig. 7, c). The distance between the atoms in the O–H group of the acid is $\text{O}^7-\text{H}^8 = 0.990$ Å (0.970 Å in the monomer), and, in the acetonitrile

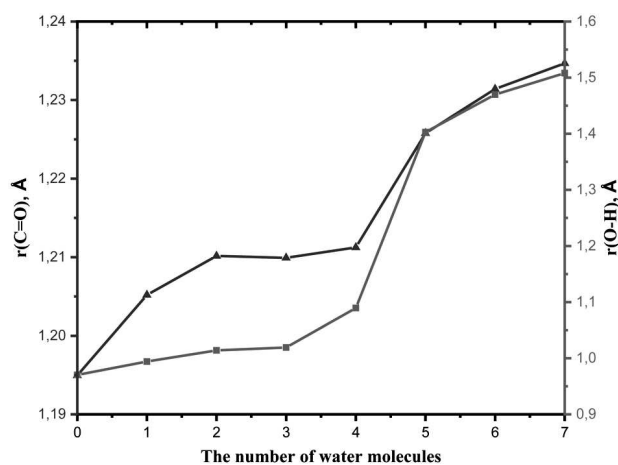


Fig. 5. The dependence of C=O and O–H bonds distances on the number of water molecules in the molecular cluster

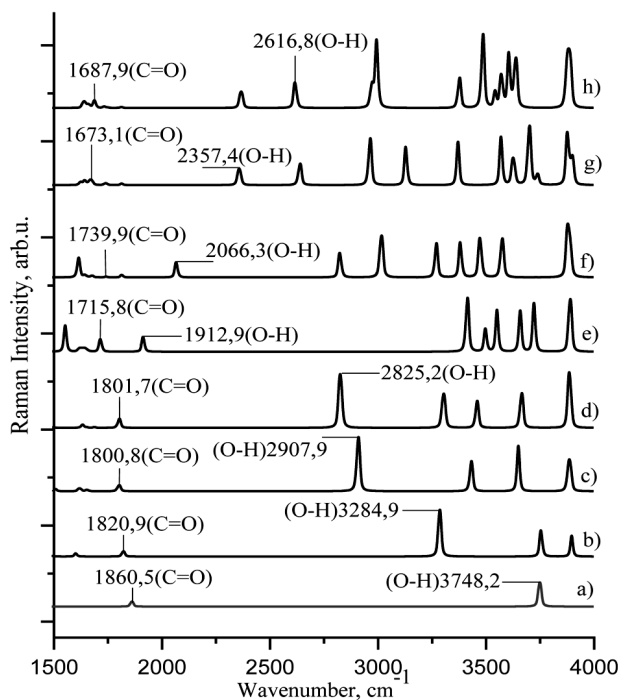


Fig. 6. The bands in an interval of 1500–4000 cm^{-1} of theoretical Raman spectra of molecular clusters: CF_3COOH (a), $\text{CF}_3\text{COOH} + \text{H}_2\text{O}$ (b), $\text{CF}_3\text{COOH} + (\text{H}_2\text{O})_2$ (c), $\text{CF}_3\text{COOH} + (\text{H}_2\text{O})_3$ (d), $\text{CF}_3\text{COOH} + (\text{H}_2\text{O})_4$ (e), $\text{CF}_3\text{COOH} + (\text{H}_2\text{O})_5$ (f), $\text{CF}_3\text{COOH} + (\text{H}_2\text{O})_6$ (g), $\text{CF}_3\text{COOH} + (\text{H}_2\text{O})_7$ (h)

molecule, $\text{C}^9-\text{C}^{13} = 1.453$ Å, $\text{C}^{13}-\text{N}^{14} = 1.150$ Å (in the monomer $\text{C}^9-\text{C}^{13} = 1.456$ Å, $\text{C}^{13}-\text{N}^{14} = 1.153$ Å) change is observed. This confirms the existence of an intermolecular hydrogen bond between the H^8 atom

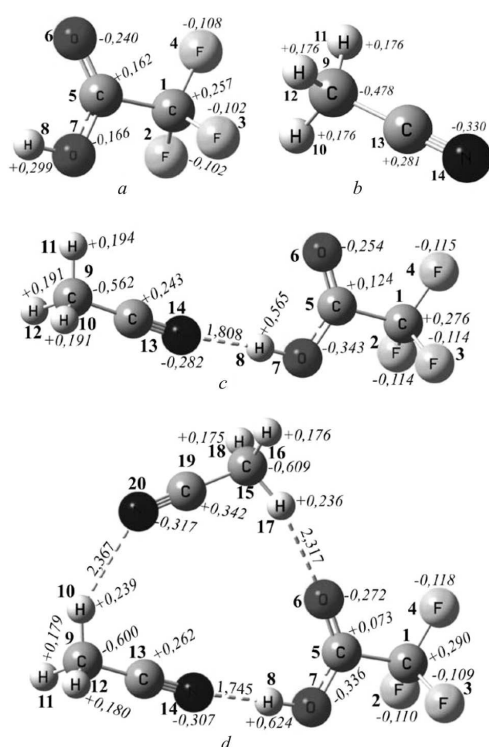


Fig. 7. Isolated $\text{CF}_3\text{COOH} + \text{CH}_3\text{CN}$ complexes: CF_3COOH monomer (a), CH_3CN monomer (b); dimer $\text{CF}_3\text{COOH} + \text{CH}_3\text{CN}$ (c), trimer $\text{CF}_3\text{COOH} + (\text{CH}_3\text{CN})_2$ (d)

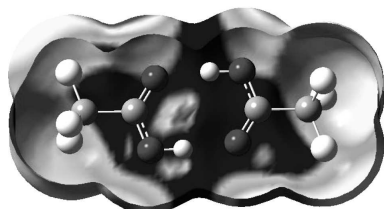


Fig. 8. Calculated electron distribution corresponding to the dimer optimal geometry of CF_3COOH

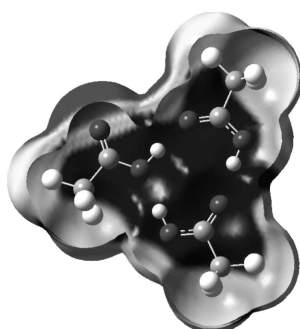


Fig. 9. Calculated electron distribution corresponding to the trimer optimal geometry of CF_3COOH

of the O–H group of the acid and the N^{14} atom of the $\text{C}\equiv\text{N}$ group of acetonitrile. The dipole moment of the dimer is 8.05 D. The unbonded C=O stretching vibration is $\nu = 1838.1 \text{ cm}^{-1}$ ($\rho = 0.15$, Raman activity is 11.3), and the bonded O–H stretching vibration is $\nu = 3348.9 \text{ cm}^{-1}$ ($\rho = 0.31$, Raman activity 328.3) bands match. The vibrational frequency of C=O is 22.4 cm^{-1} lower than that of the monomer, and the vibrational frequency of O–H shifts to $\sim 399.33 \text{ cm}^{-1}$ (Table 1).

Calculations were also carried out for the $\text{CF}_3\text{COOH} + (\text{CH}_3\text{CN})_2$ complex (Fig. 7, d). Trimer formation is interesting because it forms by three H-bonds types of: O–H...N; C–H...O and C–H...N [45–46]. We look at the distances between the atoms involved in bonding in the trimer: $\text{C}^1\text{--C}^5 = 1.555$, $\text{C}^5\text{--O}^7 = 1.313$, $\text{O}^7\text{--H}^8 = 0.998$, $\text{C}^5\text{--O}^6 = 1.204 \text{ \AA}$ of the acid (in the monomer $\text{C}^1\text{--C}^5 = 1.553$, $\text{C}^5\text{--O}^7 = 1.336$, $\text{O}^7\text{--H}^8 = 0.970$, $\text{C}^5\text{--O}^6 = 1.195 \text{ \AA}$) change is observed. In acetonitrile bond of the O–H group of the acid, the distances between the atoms of the (CH_3) -group are $\text{C}^9\text{--C}^{13} = 1.452$, $\text{C}^{13}\text{--N}^{14} = 1.150$, $\text{C}^9\text{--H}^{10} = 0.093$, $\text{C}^9\text{--H}^{11} = 1.092$, $\text{C}^9\text{--H}^{12} = 1.092 \text{ \AA}$ (in the monomer $\text{C}^9\text{--C}^{13} = 1.456$, $\text{C}^{13}\text{--N}^{14} = 1.153$, distances between (CH_3) -group atoms $\text{C}^9\text{--H}^{11} = 1.092$, $\text{C}^9\text{--H}^{12} = 1.092 \text{ \AA}$). From this it can be said that the H8 atom of the O–H group of the acid forms a hydrogen bond with the N14 atom of acetonitrile (Fig. 7, d, Table 1).

In acetonitrile which is bonded by the C=O group of the acid, the bonds between atoms are as follows: $\text{C}^5\text{--O}^6 = 1.204 \text{ \AA}$ of the acid ($\text{C}^5\text{--O}^6 = 1.195$ in the monomer) is slightly increased but the distances between all atoms in the CH_3 group are the same 1.092 \AA . In acetonitrile, it is $\text{C}^{15}\text{--C}^{19} = 1.454 \text{ \AA}$ (1.456 in monomer), $\text{C}^{19}\text{--N}^{20} = 1.153 \text{ \AA}$ (1.153 in monomer). Here, the O^6 atom of the C=O group of the acid forms a hydrogen bond with N^{17} atom of acetonitrile, and the N^{20} atom of the $\text{C}\equiv\text{N}$ group of acetonitrile forms a hydrogen bond with the H^{10} atom of the adjacent acetonitrile molecule (the changes in atomic numbers are shown in the Fig. 7, d). The intermolecular interaction energy of $\text{CF}_3\text{COOH} + (\text{CH}_3\text{CN})_2$ is 16.65 kcal/mol . One hydrogen bond has an average energy of 5.55 kcal/mol . The dipole moment is 4.06 D. Due to the intermolecular hydrogen bonding during the formation of the $\text{CF}_3\text{COOH} + (\text{CH}_3\text{CN})_2$ complex, the C=O stretching vibration frequency of

the acid shifts from 1860.5 to 1822.4 cm, and the O–H stretching vibration frequency from 3748.2 to 3201.3 cm shifts to the low-frequency side (Table 1).

An attempt was also made to study the distribution of electrons in the dimer and trimer states of CF₃COOH. Dimers and trimers of CF₃COOH have strong O–H...O=C hydrogen bonds. These electron distributions were re-simulated according to their previously calculated optimal geometries (Figs. 8 and 9). The dimer and trimer formation energies are 14.5 kcal/mol and 19.2 kcal/mol, respectively. Due to the formation of dimers and trimers around the “hydrogen bond bridge” O–H...O and the oxygen atoms participating in this bond, the relative electron density increases. This is the case highlighted in red. As a result of the complex formation in the yellow, green, and blue regions along the complexes, the distribution of electrons decreases accordingly. It should be noted that the reorientation due to the polarizability is also observed for molecules of CF₃COOH in the cluster, and this electron density scale is kept as a standard.

The results of these *ab-initio* calculations have been scientifically proven to be effective in determining the structure, energetics, orientation, and vibrational spectra of liquid CF₃COOH [47, 48].

4. Conclusions

The polarized Raman scattering spectra of pure liquid CF₃COOH related to C=O and O–H stretching vibration are complex and are associated with the presence of aggregates with different depolarization ratios in the liquid. The formation of various molecular aggregates of different composition in the CF₃COOH + acetonitrile solution leads to a change in the shape of the C=O vibrational band. Mechanisms of formation of CF₃COOH isolated monomer, dimer, trimer and molecular clusters with water and acetonitrile molecules were studied based on DFT method and B3LYP/6-311++G(d,p) set of functions. Calculations show that in the monomers and dimers of CF₃COOH, there may be a weak intramolecular hydrogen bond between the hydrogen atom of the O–H group of the acid and the =O oxygen atom. In the monomer, dimer and trimer of pure CF₃COOH, the spectral bands corresponding to C=O and O–H vibrations are shifted towards low frequency side. This shift is largest in the cyclically closed dimers of CF₃COOH,

suggesting that the cyclic dimers are more stable. CF₃COOH forms various H-bonded clusters with water molecules. As the number of water molecules in the cluster increases, the cluster stabilizes. The most stable cluster is [CF₃COOH + (H₂O)₄], which is formed by CF₃COOH with four water molecules, and is in a bicyclic form. When the number of water molecules reaches five, one proton belonging to the carboxyl group of the acid is transferred to a water molecule and –COO[–] anion H₂O⁺ is formed. CF₃COOH + acetonitrile molecules form various molecular clusters through intermolecular H-bonds. In this case, the H atom of the O–H group of the acid forms a strong hydrogen bond with the nitrogen atom of acetonitrile, resulting in the formation of an open chain dimer. Cyclic closed trimer molecular clusters are observed as a result of a relatively weak hydrogen bond between the O-atom of the C=O group of the acid and one hydrogen atom of the acetonitrile (CH₃) group, and a strong hydrogen bond between the H-atom of the O–H group of the acid and the nitrogen atom of acetonitrile.

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РАМАНІВСЬКІ СПЕКТРИ РОЗСІЮВАННЯ І ЧИСЛОВІ РОЗРАХУНКИ В ТЕОРІЇ ФУНКЦІОНАЛА ГУСТИНИ ДЛЯ МІЖМОЛЕКУЛЯРНИХ ВЗАЄМОДІЙ У ТРИФТОРОЦТОВІЙ КИСЛОТІ ТА ЇЇ РОЗЧИНАХ

Вивчається механізм створення молекулярних кластерів у трифтороцтвовій кислоті на основі використання раманівських спектрів розсіювання в різних розчинах. Ці спектри відповідають поляризованим структурам з вібраційними коливаннями C=O і O-H груп трифтороцтвовой кислоти без домішок і містять три широкі смуги біля 1734, 1754 та 1800 см⁻¹ з різними параметрами деполаризації. Якщо концентрація кислоти в ацетонітрилі дуже мала, то зберігається спектральна смуга біля 1800 см⁻¹, яка відповідає коливанням C=O групи. За допомогою теорії функціонала густини (DFT/V3LYP/6-311++G(d,p)) розглянуто механізм створення кластерів за участю мономера, димера та тримера кислоти з молекулами води [CF₃COOH + (H₂O)_n, n = 1–7] або ацетонітрилу [CF₃COOH + (CH₃CN)_n, n = 1–2].

Ключові слова: раманівські спектри, трифтороцтова кислота, структура водневого зв'язку, розрахунки в теорії функціонала густини.