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Intermolecular interactions in the chloroform solution of methyl-ethyl-ketone: Raman spectroscopy and ab initio calculations

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В данной работе межмолекулярные взаимодействия в жидком метил-этил-кетоне (МЭК) и его растворе в хлороформе изучали методами рамановской спектроскопии и расчетов согласно теории функционала плотности (DFT). В агрегатах энергия, соответствующая каждой водородной связи, равна 4.8 ккал/моль, и за счет межмолекулярных взаимодействий полоса валентных колебаний C=O смещена в красную сторону, а полоса валентных колебаний C–H – в синюю сторону. Анализ AIM (атомы в молекулах) показал, что метил-этил-кетон образует агрегаты с молекулами хлороформа за счет межмолекулярных водородных связей.

Ключевые слова: МЭК, спектры комбинационного рассеяния света, водородная связь, метод DFT, раствор, хлороформ.

In this study, intermolecular interactions in liquid methyl-ethyl-ketone and its chloroform solution were studied by Raman spectroscopy and density functional theory (DFT) calculations. In aggregates, the energy corresponding to each hydrogen bond is 4.8 kcal/mol, and due to intermolecular interactions, the band of C=O stretching vibrations is red-shifted, while the band of C–H stretching vibrations is blue-shifted. AIM (atoms in molecules) analysis showed that methyl-ethyl-ketone forms aggregates with chloroform molecules through intermolecular hydrogen bonding.

Keywords: MEK, Raman spectra, hydrogen bond, DFT method, solution, chloroform.

I. Introduction

Hydrogen bonding as a special type of interaction plays an important role in the existence of biomolecules. However, its manifestation in vibrational spectra has not been fully explained to date. Determining the mechanisms of the formation of hydrogen-bonded molecular clusters and general rules of intermolecular interactions, as well as the manifestation of molecular aggregation in vibrational spectra remains one of the important factors determining the progress of the field.

Molecular liquids with intermolecular and intramolecular hydrogen bonding are common in nature. The formation of hydrogen bonds plays an important role in physical and chemical processes, from the unique properties of ordinary water to the special structure of macromolecules. A large amount of information on hydrogen bonding has been obtained by studying vibrational spectra in the gas phase, and existing theories do not provide sufficient information for the liquid state. Therefore, the possibility of obtaining a larger amount of data in the study of intermolecular interactions in liquids through Raman spectroscopy creates the need for scientific research in this area.

Due to the existence of many types of liquid and liquid crystalline systems, the lack of information on structure and the arrangement of molecules in these systems requires a modern theory describing the liquid state [1]. Only the theory describing the equilibrium properties of simple liquids gives good results [2].

Studying the laws that determine physical and chemical properties of particles ranging from a few angstroms to 100 nm is the main problem of physics, because the interaction of forces and degrees of freedom of different natures at these distances leads to the emergence of new effects in molecular systems [3].

Association processes in liquids significantly affect many of their physical and chemical properties. This opinion is confirmed by the data obtained during spectroscopic studies of dimethylformamide, acetonitrile, alcohols, water and other H-bonded liquids [4-8]. The degree of this effect depends on intermolecular interactions as well as the type and amount of association. Therefore, the mechanism of the formation of molecular complexes in solutions has been of interest for a long time. Such effects are clearly manifested in the vibrational spectra of molecules. Currently, vibrational spectroscopy and non-empirical (ab initio) calculations are widely used methods of experimental investigation of H-bonded structures in physics, chemistry, and medicine.

In this study, using Raman spectroscopy and density functional theory (DFT) calculation methods, interactions between methyl-ethyl-ketone (2-butanone) and chloroform ($CHCl_3$) molecules, the mechanism of aggregate formation, and their manifestation in Raman spectra were studied.

Methyl-ethyl-ketone (MEK, chemical formula C_4H_8O is an organic compound with a number of physical and chemical properties useful in various industrial processes and laboratory conditions. It is a clear liquid with a slight odor, soluble in water and many organic solvents. MEK is widely used as a solvent in various industries, including the production of varnishes, adhesives, plastics, rubber products, pharmaceuticals and perfumes. MEK can also be used as an ingredient in the food industry to create flavor additives.

The structure of MEK molecules and their aggregates has been analyzed by vibrational spectroscopy and DFT calculations in several works [9, 10]. Also, in a number of studies [11-13], infrared and Raman spectra of MEK were registered and described.

S. Datta and K. Kumar [14] studied the effect of polar and nonpolar solvents on the C=O stretching vibration of MEK. It is shown that the shift of the parallel and perpendicular components of the C=O vibration in solutions of different concentrations is a concentration-dependent function and that this shift occurs due to the intermolecular dipole-dipole interaction.

Similarly, in our previous work [15], it was shown that the maxima of the polarized (parallel and perpendicular) components of the Raman band of the C=O vibration of MEK do not coincide with each other. Also, when MEK is dissolved in nonpolar (heptane) and polar (pyridine, dimethylsulfoxide, and chloroform) solvents, the changes in the constituents of the C=O vibration band were analyzed. This change was fundamentally different compared to other solvents due to the fact that intermolecular hydrogen bonds can be formed in a solution of MEK in chloroform. It was mentioned that this process occurs as a result of intermolecular dipole-dipole interactions in solutions.

A. Marigliano et al. [16] studied the spectroscopic and thermodynamic parameters of hydrogen-bonded complexes in a mixture of MEK and chloroform. As a result, it was confirmed that MEK and chloroform molecules form dimer (1:1) and trimer (1:2) heteroassociates through intermolecular hydrogen bonding. Although several studies have been performed on the mixture of MEK and chloroform, they do not fully explain the interactions between MEK and chloroform molecules.

In addition, using several DFT methods [17, 18] it was determined that in the aggregation processes of MEK molecules not only electrostatic interactions take place, but also weak hydrogen bonds of donor-acceptor character.

Therefore, the aim of this work is to study the mechanism of molecular aggregates formation in MEK and its chloroform solutions with different concentrations, taking into account dipole-dipole and weak hydrogen bond intermolecular interaction by means of Raman spectroscopy and non-empirical (DFT) calculations.

II. Experimental and computational details

Raman spectroscopy, which is used in the work, is one of the main methods for intermolecular interaction studies. The formation of H-bond, which can be presented as A-H...B, is accompanied by characteristic changes in the vibrational spectrum: new low-frequency vibrational bands appear, and a significant number of vibrational bands of interacting molecules are perturbed.

Raman spectra of pure MEK and its solutions in chloroform at different concentrations (0.3, 0.5, and 0.7 m.f.) were recorded using Renishaw inVia Raman spectrometer at room temperature. An argon laser with a wavelength of 532 nm and a power equal to 50 mW was used as a source of excitation light, along with a diffraction grating with a period of 1200

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lines/mm. A standard Reneshaw CCD camera detector was used to record the scattered light.

All DFT calculations and optimization procedures were performed in the Gaussian 09W program [19]. Geometry of MEK, chloroform, and complexes of MEK with chloroform was optimized using B3LYP and RB97D basis functions. In calculations the 6-311++G(d,p) basis set, which includes diffuse and polarization functions, was used to account for hydrogen bonding as accurately as possible [20-23].

In addition, for a deeper understanding of intermolecular interactions, topological features of the electron density distribution in the most stable structure were obtained using the MULTIWFN [24] program based on the AIM theory.

III. Results and discussions

III.1. Vibrational analysis

The Raman spectrum of a MEK can provide information about its molecular structure and interactions with other molecules. The spectrum can also be used to identify MEK and determine its concentration in solutions. The specific MEK Raman spectrum depends on many factors, such as measurement conditions and solution concentration. In general, the Raman spectrum of MEK can be a useful tool for analyzing its structure and properties under various conditions. The recorded Raman spectrum of MEK is presented in Fig. 1.

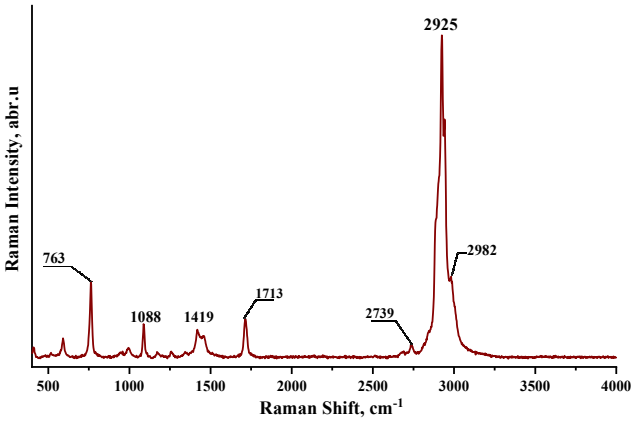


Figure 1. Experimental Raman spectrum of pure MEK.

As can be seen from Fig. 1, the Raman spectra of pure MEK contain several characteristic peaks corresponding to different types of vibrations of the MEK molecule. The most intense bands in the MEK Raman spectrum are in the regions of 2800–3200 cm^{-1} and 1700–1800 cm^{-1}. Bands in the region of 2800–3200 cm^{-1} correspond to asymmetric and symmetric vibrations of C-H bonds in the methyl and ethyl groups. The bands in the region of 1700–1800 cm^{-1} correspond to C=O stretching vibrations. Other bands in the MEK Raman spectrum may be associated with vibrations of other functional groups, such as C-C and C=C bonds. However, these bands are often less intense and wider, which can make them difficult to identify. In solutions with chloroform, the Raman spectra of methyl-ethyl-ketone will differ from the spectra in the gas phase due to the interaction of MEK molecules with solvent molecules. One can observe peak shifts and changes in their intensity (Fig. 2).

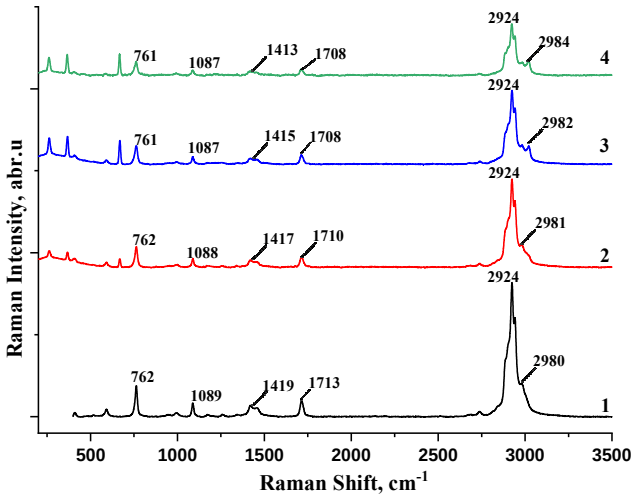


Figure 2. Raman spectra of MEK and its chloroform solutions: 1) pure MEK, 2) MEK+0.9 mol fraction, 3) MEK+0.7 mol fraction, 4) MEK+0.5 mol fraction.

When the fraction of MEK in the solution decreases, it is observed that the intensity of the bands corresponding to asymmetric and symmetric C-H bonds decreases too. The results of the experiments indicate the presence of high-frequency asymmetry in the C-H band, which can be associated with the presence of H-bonded associates in liquid chloroform, to which the high-frequency component of the band is assigned. In addition, the Raman spectra of MEK in solutions may contain additional peaks associated with vibrations of the solvent molecules. Therefore, to identify peaks corresponding only to MEK molecules, it is necessary to analyze the spectra in various solvents and compare them with the spectra in the gas phase. Figure 3 shows the Raman spectra of MEK and its chloroform solutions at different concentrations in the spectral region of the C=O stretching vibrations.

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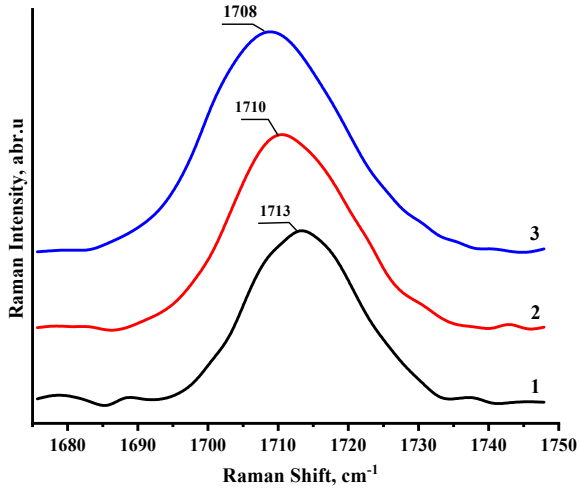


Figure 3. Experimental Raman spectra in the region of C=O vibrations of MEK and its chloroform solutions: 1) pure MEK, 2) MEK+0.9 mol fraction, 3) MEK+0.7 mol fraction.

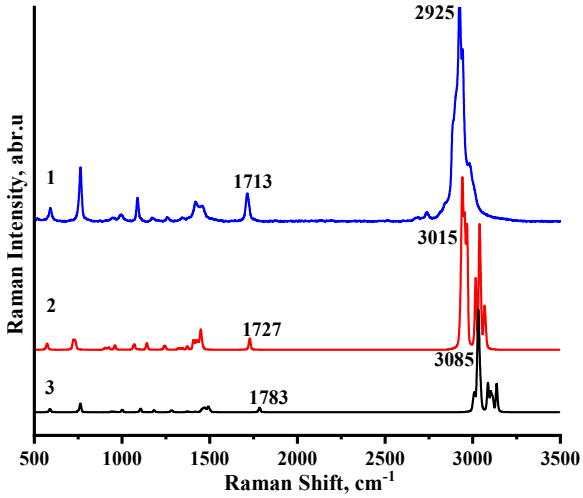


Figure 4. Experimental (1) and calculated (with B97D/6-311++G(d,p) (2), and B3LYP/6-311++G(d,p) (3) basis sets Raman spectra of MEK.

The results of the experiment showed that with a decrease in the amount of MEK in the solution, the changes in Raman spectra in the region of the C=O stretching vibration are observed. When the amount of MEK in the solution is 0.7 m.f., it can be seen that the band is shifted to the low-frequency side up to 5 cm^{-1} compared to pure MEK. In addition, one can observe a change in the half-width of this band, and, accordingly, we found that the asymmetry in the low-frequency side compared to the pure state has also disappeared. The conclusion is that in the mixture of MEK and chloroform, the number of H-bonded aggregates of one type decreases, that is, we know that the above signs belong to the same bond [25, 26], and the other type of heteroassociates of MEK and chloroform molecules can be formed.

The C=O band of MEK is very sensitive to various changes, which makes it possible to use it for experimantal investigations. In order to explain the large half-width of this band (300 cm^{-1}), the relative shift between the componentes corresponding to symmetric and asymmetric vibrations, the depolarization coefficient of the bands belonging to different molecular clusters, and the intermolecular hydrogen bond energies were determined using nonempirical calculations performed for different molecular aggregates of MEK. The interaction between the solute and solvent molecules in the solution has a significant effect on their vibrational spectra. To analyze the spectral manifestation of the interactions between MEK and chloroform molecules, their Raman spectra were calculated (Fig. 4).

When the calculated and experimental Raman spectra of MEK are compared (Fig. 4), the changes in the spectrum due to the formation of aggregates compared to the isolated (gas) state are clearly visible. We used the scaling factor (f = 0.9590) to account for anharmonicity in real systems.

Figure 5 presents the calculated Raman spectra of MEK monomer and its heteroassociates with chloroform. Calculations showed that when the MEK molecule interacts with one chloroform molecule, its C=O stretching frequency ($\nu_{C=O}$=1710 cm^{-1}) is shifted towards lower frequency by 13 cm^{-1}, and when it interacts with two chloroform molecules the red-shift is 28 cm^{-1}.

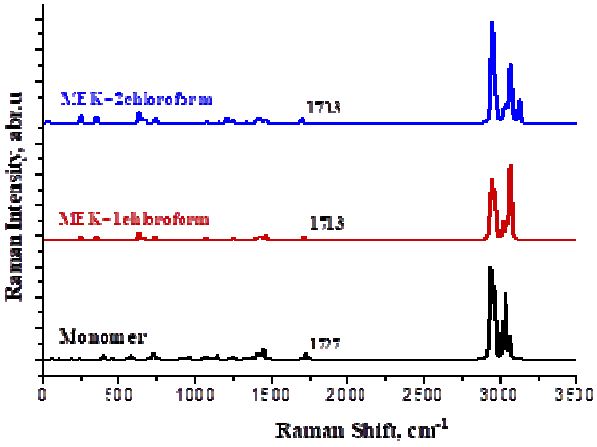


Figure 5. Raman spectrum of MEK monomer and aggregates formed with chloroform molecules (B97D/6-311++G(d,p) basis set).

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It can be seen from Fig. 5 that when MEK interacts with chloroform molecules, the spectral lines corresponding to the C-H vibration of MEK demonstrate a blue shift (are shifted to a higher frequency). The spectral line corresponding to the C-H vibration of chloroform has a red-shift, which is equal to 14 cm^{-1} for the MEK+1chloroform complex and 7 cm^{-1} and 11 cm^{-1} for the MEK+2chloroform complex, respectively.

Similarly, changes are observed in the C=O vibrational band of MEK (Fig. 6). As can be seen, the band of the C=O vibrations is shifted to a lower frequency by 27 cm^{-1}, and this fact agree with our experimental results. Particularly noticeable changes are observed in the asymmetric and symmetric vibrational bands of C-H bonds belonging to methyl and ethyl groups in the region of 2800–3200 cm^{-1} (Fig. 7).

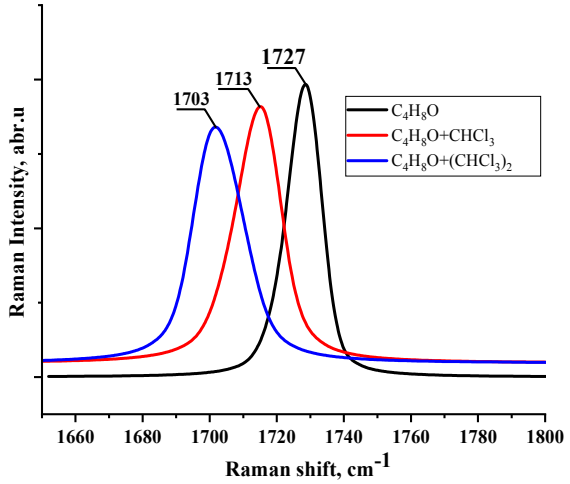


Figure 6. Raman band of C=O stretching vibrations of MEK monomer and aggregates formed with chloroform calculated with the B97D/6-311++G(d,p) basis set.

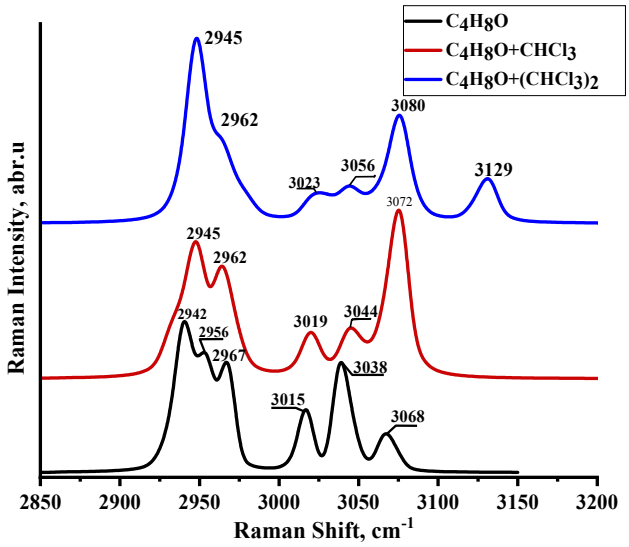


Figure 7. Raman spectrum of MEK monomer and aggregates formed with chloroform calculated in the B97D/6-311++G(d,p) basis set in the 2850–3200 cm^{-1} region.

It was observed that the frequency changes in the bands corresponding to the symmetric and asymmetric vibrations of the C-H are different. Table 1 shows the frequencies of symmetric and asymmetric vibrational bands belonging to the CH group in the mixture of MEK with chloroform.

It can be seen from Table 1 that the frequency values obtained in DFT calculations agree with the experimental results. We observed that this compatibility also depends on the calculation methods. It is seen that the closest result to the experiment in such cases is in the calculations performed in the B97D basis set of functions.

Table 1. The some calculated frequencies of MEK.

Vibrational mode	Experiment	MEK monomer (B3LYP)	MEK monomer (B97D)	MEK+ 1chloroform (B3LYP)	MEK+ 1chloroform (B97D)	MEK+ 2chloroform (B3LYP)	MEK+ 2chloroform (B97D)
CH_3 (asymmetric)	2982	3137	3068	3140	3072	3143	3080
CH_2 (asymmetric)	2939	3031	2967	3033	2969	3036	2975
CH_3 (symmetric)	2925	3040	2956	3042	2962	3043	2961
CH_2 (symmetric)	2739	3007	2930	3008	2933	3007	2938
C=O (stretching)	1715	1783	1727	1769	1713	1753	1703
CH_3 (bending)	1419	1499	1458	1501	1466	1506	1468
C–C–C–C (bending)	763	762	731	768	735	771	741

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III.2. Geometry analysis

MEK can form intermolecular hydrogen bonds with chloroform molecules through an oxygen atom that has two lone electron pairs. In addition, since the chloroform molecule is polar, it enhances the intermolecular interaction [16].

The optimal geometric structures of C_4H_8O+$CHCl_3$ and C_4H_8O+$(CHCl_3)_2$ complexes are shown in Fig. 8. In the C_4H_8O+$CHCl_3$ complex, there is an intermolecular hydrogen bond between the oxygen atom (O5) of MEK and the hydrogen atom (H15) of chloroform, and the length of this bond is 2.1 Å.

In the C_4H_8O+$(CHCl_3)_2$ complex, there are intermolecular hydrogen bonds between the oxygen atom (O5) of MEK and the hydrogen atoms (H15 and H20) of chloroform molecules, and these bonds lengths are 2.15 Å and 2.22 Å, respectively. The intermolecular interaction energies in the two complexes were found to be 4.81 kcal/mol and 8.02 kcal/mol, respectively..

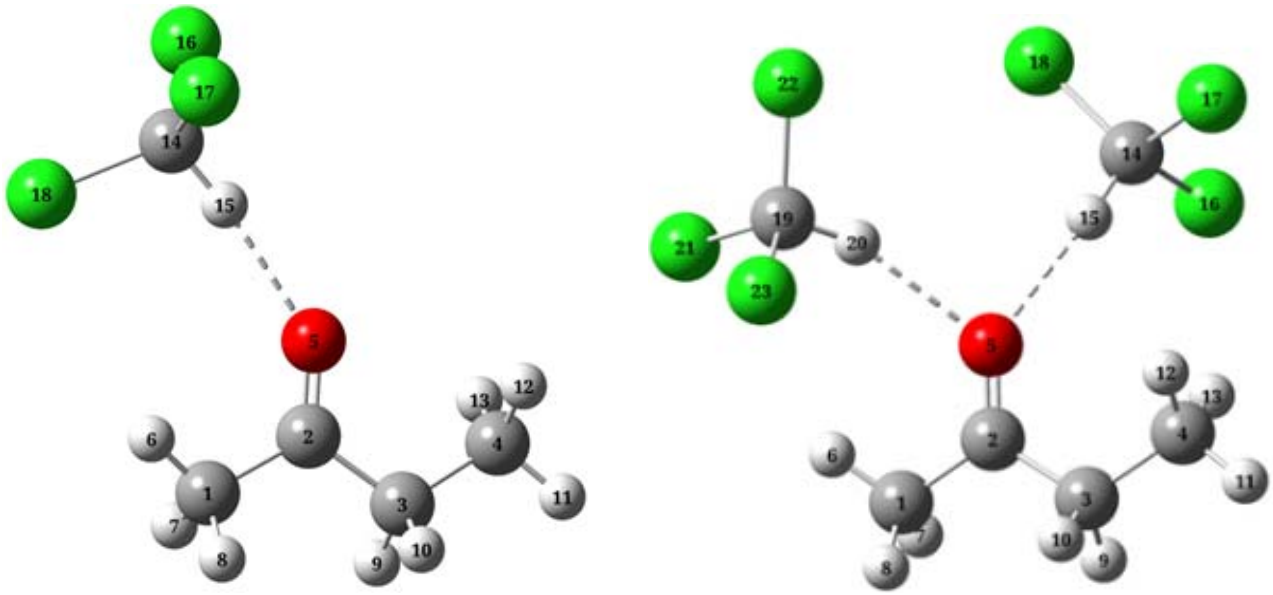


Figure 8. Optimal geometric structures of MEK+1chloroform (a) and MEK+2chloroform (b) complexes calculated at level B3LYP/6-311++G(d,p). Red, grey, white and green balls represent oxygen, carbon, hydrogen and chlorine atoms, respectively.

In the formation of heteroassociates, geometrical parameters of molecules change as a result of intermolecular interactions. The bond length of the C=O functional group of MEK increases by 0.004 Å in the formation of the C_4H_8O+$CHCl_3$ complex, and by 0.008 Å in the formation of the C_4H_8O+$(CHCl_3)_2$ complex, compared to the monomer state (1.2118 Å).

The C3-C2 and C2-C1 bond lengths of MEK, if compared to the monomer (1.5230 Å and 1.5179 Å), decrease by 0.0038 Å and 0.0062 Å in the formation of the C_4H_8O+$CHCl_3$ complex, and by 0.0036 Å and 0.0061 Å in the formation of the C_4H_8O+$(CHCl_3)_2$ complex, respectively (Table 2). The other bonds lengths are almost unchanged. These changes and intermolecular interaction energy show that the C_4H_8O+$(CHCl_3)_2$ complex is more stable than the C_4H_8O+$CHCl_3$ complex.

III.3. Mulliken atomic charge and Molecular electrostatic potential (MEP) surface analysis

Mulliken atomic charge distribution characterizes many parameters such as electronic structure, polarizability, dipole moment, and reactivity of a molecular system. The Mulliken atomic charge distribution in MEK and the change of charge distribution during the formation of the complex are depicted in the form of a histogram in Fig. 9.

Calculation results showed that O5, C1, C3 and C4 atoms of MEK molecule are negatively charged, while C2 and all hydrogen atoms are positively charged.

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Table 2. Geometric parameters of MEK and its complexes with chloroform calculated at B3LYP/6-311++G(d,p) level theory.

Chemical bonds	Bond lengths (Å)			Angles (Degree)			
	MEK	MEK+1chloroform	MEK+2chloroform				
H^{13}-C^4	1.0921	1.0920	1.0921	C^3-C^4-H^{11}	110.5794	110.4598	110.3147
H^{12}-C^4	1.0914	1.0913	1.0914	C^3-C^4-H^{12}	110.9917	111.0531	111.2154
H^{11}-C^4	1.0927	1.0924	1.0922	C^3-C^4-H^{13}	111.0657	111.0980	111.3137
H^{10}-C^3	1.0984	1.0985	1.0987	H^{11}-C^4-H^{12}	108.4762	108.4399	108.1797
H^9-C^3	1.0975	1.0973	1.0971	H^{11}-C^4-H^{13}	108.3206	108.3011	107.8847
H^8-C^1	1.0936	1.0933	1.0928	H^{12}-C^4-H^{13}	107.2870	107.3711	107.8003
H^7-C^1	1.0956	1.0956	1.0959	C^2-C^3-C^4	114.2808	114.4643	115.1290
H^6-C^1	1.0894	1.0894	1.0890	C^2-C^3-H^9	107.9455	107.8330	107.8427
O^5-C^2	1.2118	1.2158	1.2195	C^2-C^3-H^{10}	106.8963	106.7062	106.1083
C^4-C^3	1.5258	1.5259	1.5255	C^4-C^3-H^9	111.3792	111.4752	111.5184
C^3-C^2	1.5230	1.5192	1.5168	C^4-C^3-H^{10}	110.9024	110.9636	110.8431
C^2-C^1	1.5179	1.5143	1.5118	H^9-C^3-H^{10}	104.9092	104.8353	104.7472
				C^1-C^2-C^3	116.3512	116.7295	116.6370
				C^1-C^2-O^5	121.5698	121.6445	121.3471
				C^3-C^2-O^5	122.0774	121.6244	122.0153
				C^2-C^1-H^6	110.0225	110.4534	110.7940
				C^2-C^1-H^7	109.1783	108.9959	108.5543
				C^2-C^1-H^8	111.4093	111.2416	111.3716
				H^6-C^1-H^7	108.8931	108.7740	108.6667
				H^6-C^1-H^8	110.1895	110.2456	110.2500
				H^7-C^1-H^8	107.0667	107.0298	107.0791

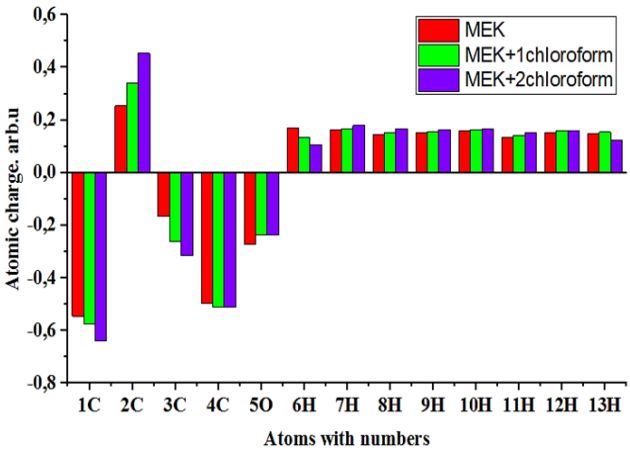
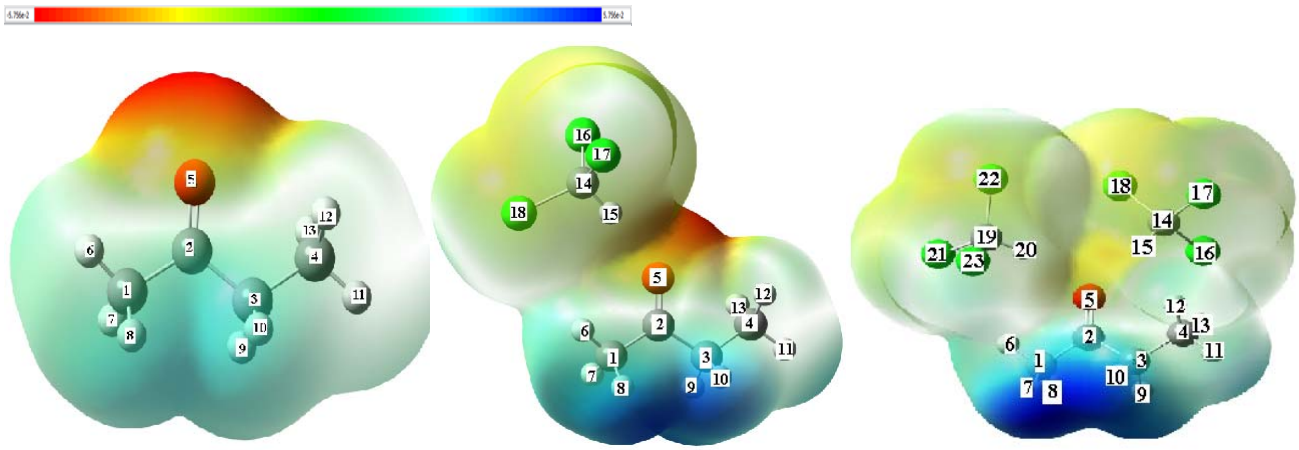


Figure 9. Mulliken charge distribution chart of MEK and its complexes with chloroform.

It can be seen from the histogram that when MEK interacts with chloroform molecules, the amount of charge on atoms is redistributed. As a result, the charge of the oxygen atom (O5) changes from –0.273e to –0.266e (C_4H_8O+$CHCl_3$) and –0.237e (C_4H_8O+$(CHCl_3)_2$.

Molecular electrostatic potential (MEP) surface analysis is one of the important research methods used to determine the electrophilic and nucleophilic regions of hydrogen-bonding molecular systems. The MEP surface represents the electrostatic potential generated on the surface due to the overall charge distribution in the molecular system. Figure 10 illustrates the electrostatic potential with different values marked by different colors. Red color represents electrophilic regiones, blue one – nucleophilic sites.

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a) b) c)

Figure 10. MEP surfaces of C_4H_8O (a), C_4H_8O+$CHCl_3$ (b) and C_4H_8O+$(CHCl_3)_2$ (c) complexes.

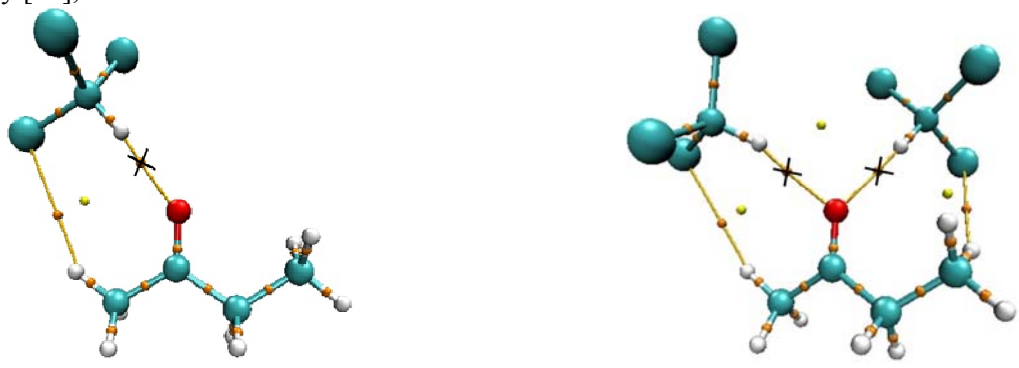
Electroneutral field is represented by green color. It can be seen from the MEP surface of the MEK molecule (Fig. 10a) that the electrophilic region is located around the oxygen atom. Around the hydrogen atoms there is an electroneutral field.

As a result of interaction of MEK with chloroform molecules, internal charge exchange and redistribution of charge occurs. As a result, the MEP surface of the molecular system changes, that is, as can be seen from Figs 10b and 10c, when the complex is formed, a nucleophilic sphere is formed on the hydrogen atoms of MEK (H7, H8, H9 and H10).

III.4. Atoms in molecules (AIM) topological analysis

Atoms in molecules (AIM) analysis is widely used to demonstrate the presence of intermolecular and intramolecular hydrogen bonds. According to Bader's theory [27], when there is interaction between atoms, bond critical points (BCP) are formed between them. The electron density $\rho(r)$ and the electron density Laplacian $\nabla^2\rho(r)$ characterize the nature of such bonds.

The Laplacian of electron density provides information about the tendency of the nuclei to increase or decrease. The electron density Laplacian is related to energetic topological parameters. The negative Laplacian characterizes general interactions such as lone pairs and covalent bonds, the positive Laplacian characterizes ionic, hydrogen bonding, and van der Waals interactions. It is known [28] that the electron density and Laplacian electron density of hydrogen-bonded atoms in BCP are in the range of values 0.002–0.035 and 0.024–0.139 a.u., respectively. Figure 11 shows the critical points between the bonded atoms of C_4H_8O+$CHCl_3$ and C_4H_8O+$(CHCl_3)_2$ complexes.



a) b)

Figure 11. AIM molecular diagrams showing the bond critical points (orange dots) in MEK+1chloroform (a) and MEK+2chlorofom (b) complexes. complexes. BCPs in hydrogen bonds are marked with a cross.

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Table 3. Topological parameters at the bond critical points (BCP) of the $C_4H_8O+CHCl_3$ and $C_4H_8O+(CHCl_3)_2$ complexes. All calculations are performed in the B3LYP/6-311++G(d,p) approximation.

Complex	BCP	Electron density, ρ(r)	Laplacian of electron density, $\nabla^2\rho(r)$	Energy density, $H(r)$	Potential energy density, $V(r)$	H-bond energy, E_{int}
$C_4H_8O+CHCl_3$	$C^2=O^{5\cdots}H^{15}-C^{14}$	0.0179	0.0655	0.0024	-0.0115	3.61
	$C^{14}-Cl^{18\cdots}H^6-C^1$	0.0024	0.0070	0.0004	-0.0001	0.03
$C_4H_8O+(CHCl_3)_2$	$C^2=O^{5\cdots}H^{15}-C^{14}$	0.0157	0.0576	0.0022	-0.0099	3.11
	$C^2=O^{5\cdots}H^{20}-C^{19}$	0.0145	0.0494	0.0018	-0.0088	2.76
	$C^{14}-Cl^{16\cdots}H^{13}-C^4$	0.0028	0.0084	0.0004	-0.0012	0.37
	$C^{14}-Cl^{21\cdots}H^6-C^1$	0.0030	0.0088	0.0005	-0.0013	0.41

Table 3 shows topological parameters of non-covalent BCPs in $C_4H_8O+CHCl_3$ and $C_4H_8O+(CHCl_3)_2$ complexes. Hydrogen bond energy was determined using the formula $E_{int}=-V(r)/2$ [29].

Based on the work of Rozas et al. [30], the hydrogen bond strength is classified as follows: (1) strong hydrogen bond $\nabla^2\rho<0$ and H>0; (2) medium hydrogen bond: $\nabla^2\rho>0$ and H<0; (3) weak hydrogen bonding $\nabla^2\rho>0$ and H>0. The results of AIM topological analysis confirm the presence of weak hydrogen bonds (C2=O5…H15-C14, C2=O5…H15-C14, C2=O5…H20-C19) in $C_4H_8O+CHCl_3$ and $C_4H_8O+(CHCl_3)_2$ complexes (Tab. 3).

IV. Conclusions

The formation of aggregates due to intermolecular interactions of methyl-ethyl-ketone and its chloroform solutions at different concentrations was studied using Raman spectroscopy and non-empirical calculations. It has been determined that the Raman spectra of methyl-ethyl-ketone in solutions with chloroform will differ from the spectra in the gas phase due to the interaction of MEK molecules with solvent molecules. This can lead to peak shifts and changes in their intensity. As the amount of MEK in the solution decreases, it was observed that the intensity of the spectral bands of asymmetric and symmetric vibrations of C-H bonds decreases. The results of the experiments indicate the presence of high-frequency asymmetry of the C-H stretching band due to the presence of H-bonded associates in liquid chloroform, which give to the high-frequency component in the band. In addition, the Raman spectra of MEK in solutions may contain additional peaks associated with vibrations of the solvent molecules. Pure MEK and its chloroform solutions contain aggregates formed via hydrogen bonding and electrostatic interactions. This idea was also confirmed by DFT calculations performed for an isolated molecule of MEK, as well its dimer and trimer with chloroform molecules. Calculations showed that when the MEK molecule interacts with one chloroform molecule, the frequency of C=O vibration shifts toward lower frequencies by 13 cm^{-1}, and when it interacts with two chloroform molecules, the shift is 28 cm^{-1}. In this case, the spectral bands corresponding to the C-H stretching vibrations will have a blue shift. The band of the C-H vibration of chloroform was found to be shifted by 14 cm^{-1} for the $C_4H_8O+CHCl_3$ complex and 7 cm^{-1} and 11 cm^{-1} for the $C_4H_8O+(CHCl_3)_2$m complex. It was shown that MEK can form intermolecular hydrogen bonds with chloroform molecules through an oxygen atom with two lone electron pairs. The intermolecular interaction energies in the complexes were found to be 4.81 kcal/mol and 8.02 kcal/mol, respectively. As a result of charge redistribution, electrophilic and nucleophilic regions of the hydrogen bond system were determined depending on the change in molecular electrostatic potential. During the formation of heteroassociates, it was observed that the C=O stretching vibration frequency of MEK decreases and the C-H vibration frequency increases due to intermolecular interactions. The presence of weak intermolecular hydrogen bonds in the complexes formed by MEK with chloroform was confirmed.

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Суюқ метил-этил-кетон ва унинг хлороформли эритмасидаги молекулалараро таъсирларни Раман спектроскопия ва назарий ҳисоблашлар ёрдамида ўрганиш

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Суюқ метил-этил-кетон ва унинг хлороформли эритмасидаги молекулалараро ўзаро таъсирлар Раман спектроскопияси ва зичлик функционал назарияси (DFT) ёрдамида ўрганилди. Метил-этил-кетон молекулалараро водород боғланиш орқали хлороформ молекулалари билан агрегатлар ҳосил қилиб, агрегатлардаги ҳар бир водород боғланишга ўртача 4.8 ккал/мол энергия тўғри келиши аниқланди. Молекулалараро ўзаро тасирлар туфайли C=O валент тебраниш полосасининг қизил силжиши ва C–H валент тебраниш полосасининг эса кўк силжиши кузатилди. AIM таҳлили метил-этил-кетон молекулалари водород боғланиш орқали хлороформ молекулалари билан агрегатлар ҳосил қилишини тасдиқлади.

Калит сўзлар: МЕК, Раман спектр, водород боғланиш, DFT, AIM, эритма, хлороформ.

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