

Intermolecular Hydrogen Bond in Acetic Acid Solutions. Raman Spectra and *ab initio* Calculations

Khakim Khushvaktov¹, Abduvakhid Jumabaev^{1, *}, Valeriy Pogorelov², Ulugbek Tashkenbaev¹, Akhmad Absanov¹, Gayrat Sharifov¹, Barno Amrullaeva¹

¹Department of Physics, Samarkand State University, Samarkand, Uzbekistan

²Department of Physics, Kiev National University, Kiev, Ukraine

Email address:

jumabaev2@rambler.ru (A. Jumabaev)

*Corresponding author

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Abstract: C=O vibrational bands of various aggregated formations of pure acetic acid in the Raman spectra have different values of the depolarization ratio. *Ab initio* calculations using the Gaussian 98 W program in the Hartree-Fock approximation with the basic set of Gaussian functions RHF 6-31G++(d, p) show that this is how it should be. Thus, the formation of aggregates from molecules leads not only to a change in the dipole moment of the molecules, but also to a change in the bond polarizability tensor. Calculations according to this program showed that one of the hydrogen atoms of CH₃ group of acetonitrile can participate in the intermolecular hydrogen bond. This can lead to the formation of closed acetonitrile-acetic acid dimers. However, a comparison of the calculated and experimental data shows that in the case of acid-acetonitrile molecules, the H-bond is formed in the direction of the elongation –O-H...N≡ of acetonitrile molecules. The activity of one of the hydrogen atoms of the CH₃ group of acetonitrile leads to the formation of closed dimeric aggregates in pure acetonitrile with a shift of the C≡N band of acetonitrile towards lower frequencies. The low-frequency asymmetry of C≡N acetonitrile band in the Raman spectra is associated with the presence of such aggregates in liquid acetonitrile.

Keywords: Raman Spectra, *Ab Initio* Calculation, H-Bond, Aggregated Formations, Carboxylic Acids

1. Introduction

Molecules of carboxylic acids in the liquid state can form through a hydrogen bond various aggregated formations [1–18]. The number of possible aggregated formations should increase in solutions with proton-acceptor solvents with comparable content of components. In neutral solvents, the relative content of aggregates of different composition should change. In this paper we present the results of the study of intermolecular interactions between molecules in acetic acid and between molecules of acid and acetonitrile in solutions using Raman scattering spectra (RS) of C=O vibration of the acid and C≡N vibration of acetonitrile. The results of experimental studies are supplemented with *ab initio* calculations.

2. Experimental Part

The Raman spectra of liquid acetonitrile, acid, and acid – acetonitrile mixtures were studied with the help of DFS – 52 spectrometer, argon laser. All measurements were carried out with a 90-degree scattering geometry of linearly polarized exciting light. The polarized components of the bands of the scattered light were distinguished using a polarizing prism. To eliminate the distorting effect of the device, a depolarizing wedge was used. In the experiment we used chemically pure substances that were subjected to additional vacuum distillation before measurements. The error in determining the relative position of the maxima was ± 0.5 , and that for the half-width of the bands was $\pm 0.3 \text{ cm}^{-1}$.

3. Experimental Results

Calculations were carried out on the basis of the Gaussian 98W program in the Hartree-Fock approximation with a basic set of Gaussian functions RHF 6-31G ++ (d, p) [19] of the optimized structure of an isolated monomer and a closed acetic acid dimer (Table 1). Figure 1 (a) shows the calculated optimized isolated acetic acid monomer. Attention should be paid to the following circumstance. Judging by the calculations, the C=O bond and one of the C–H bonds of the CH₃ group lie in the same plane and are directed in the same direction. This corresponds to the minimum energy. In this regard, the positions of the hydrogen atoms of the CH₃ group are not equivalent, which leads to a small difference in the charges of the hydrogen atoms of this group and a small difference in the lengths of C–H bonds. The H(5)–O(3) distance is 2.555 Å. Apparently, for the monomeric molecule, the oxygen atom O(3) interacts with the hydrogen atom of O–H (H (8)) group. The distance H(8) and O(3) is 2.274 Å. The dipole moment of the monomer is 1.97 D. C=O vibration corresponds to the calculated band with $\nu=2009.2\text{ cm}^{-1}$ with the depolarization ratio $\rho=0.38$. N–O vibrational band is characterized by $\nu=4124.7\text{ cm}^{-1}$ and the depolarization ratio $\rho=0.24$. In the book [20], the frequencies of C=O and O–H vibrations of the monomer molecule (gas) correspond to the frequencies 1788 cm^{-1} and 3583 cm^{-1} . This means that $Sf_{\text{C=O}} = \frac{1788}{2009.2}$ and $Sf_{\text{O-H}} = \frac{3583}{4124.7} = 0.86$ (Sf -scaled factor). Note

that the calculated frequencies in the RHF method differ from the experimental ones for valence ones by $\sim 15\%$ and deformation ones by $\sim 30\%$ [21-22]. Both bands are active in RS and IR spectra.

Based on the above method, we calculated the optimized parameters and spatial structure of an isolated closed acetic acid dimer. The results are as follows (Figure 1 (c), Table 1): in the closed dimer C=O bond and one of C–H bonds of the CH₃ group of each molecule are still located in the same plane; the charge of H atom of the bond and the length of this bond of both molecules differ from the corresponding values of the other two hydrogen atoms. It is obvious that the intermolecular hydrogen bond in a dimer most durable is O–H \cdots O=. There are two such bonds, and they are the same in length 1.832 Å. The energy gain during the formation of such two hydrogen bonds is $\sim 12.3\text{ kcal/mole}$, which is close to the experimental value [1]. Compared with the monomeric molecule, there is a change in the bond lengths of each molecule and a change in the charge distribution. Calculations show a decrease in the frequency of C=O vibrations by 82.2 cm^{-1} , which is in good agreement with the experiment. As well as it was supposed, the depolarization ratio also changes: according to calculations for a monomeric molecule, the depolarization coefficient for C=O vibrations $\rho=0.38$, for a dimeric molecule $\rho=0.19$. The dipole moment of the closed dimer is zero.

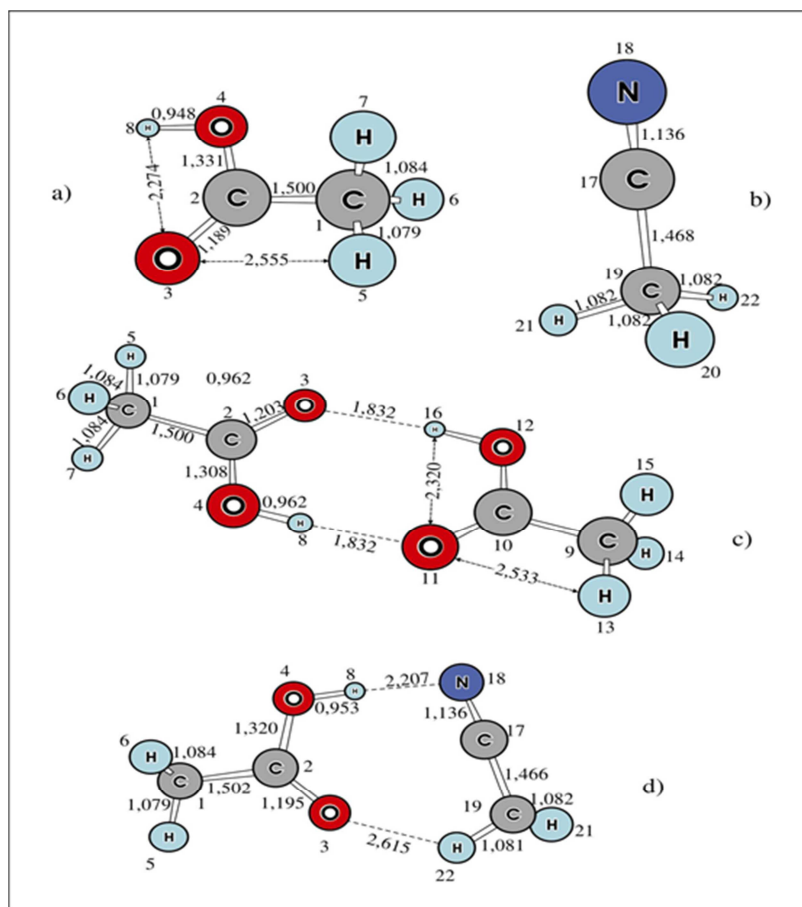


Figure 1. Calculated data and structure of isolated molecules and aggregates of acetic acid and acetonitrile.

Table 1. Charges of atoms in molecules and aggregates.

Acetic acid – monomer (a)	Acetonitrile – monomer (b)	Acetic acid – dimer (c)	Acetic acid + acetonitrile – dimer (d)
1 C -0,371	17 C 0,255	1 C -0,366	1 C -0,360 17 C 0,361
2 C 0,583	18 N -0,464	2 C 0,639	2 C 0,558 18 N -0,527
3 O -0,554	19 C -0,284	3 O -0,653	3 O -0,574 19 C -0,326
4 O -0,520	20 H 0,164	4 O -0,581	4 O -0,534 20 H 0,158
5 H 0,149	21 H 0,164	5 H 0,147	5 H 0,142 21 H 0,158
6 H 0,155	22 H 0,164	6 H 0,158	6 H 0,156 22 H 0,194
7 H 0,155		7 H 0,158	7 H 0,156
8 H 0,403		8 H 0,499	8 H 0,442

Literary data and experiments conducted in our laboratory show that in pure liquid acetic acid, the parallel polarized component ($I_{\parallel}(v)$) of C=O band of vibrations of the Raman spectrum (Figure 2) is complex [11-12]. Three fairly broad lines with frequencies of 1671 cm^{-1} , 1728 cm^{-1} and 1762 cm^{-1} can be distinguished approximately within the band. The most intense line is 1671 cm^{-1} , against the background of which a comparatively low intensity lies a broad line of 1728 cm^{-1} . Little distorted by imposition, but also less intensive and less broad line 1762 cm^{-1} . In the perpendicular component $I_{\perp}(v)$ of the band the intensity distribution pattern of clearly resolving lines is completely different. Within the limits of experimental errors, there are no differences in the

positions of the line maxima in the parallel and perpendicular polarized components of the band: the lines have the same frequency, but their intensities do not differ much from each other. The intensities of the first two low-frequency lines are about the same, and the 1762 cm^{-1} line is somewhat less. This result means that, despite the fact that all these lines belong to the same C=O vibration, the depolarization ratios are different. The complexity of the band, as follows from the literature [1-10, 16-18], as well as from our data [11-15], is due to the presence in the liquid of various aggregated formations - closed dimeric formations (low frequency band), chain aggregates and aggregates with H-bond free C=O group (high-frequency band).

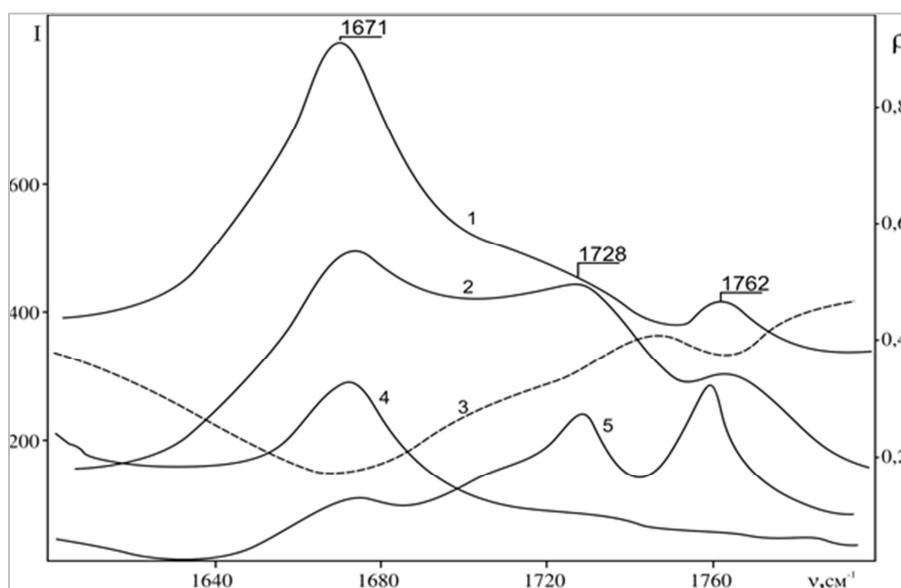


Figure 2. The shape of C=O vibrational band of acetic acid in a pure liquid (1 - I_{\parallel} ; 2 - I_{\perp} ; 3 - depolarization ratio, ρ), in solution with CCl_4 (4 - 0.2 - 0.8 m.f.) and in solution with acetonitrile (5 - 0.2 - 0.8 m.f.). Hereinafter, the intensities are not reduced to a single scale.

These entities correspond within the band of the line not only to different frequencies, but also, as follows from the above, to different values of the depolarization ratio. Thus, the formation of aggregates can change not only the dipole moment of the coupling, which affects the intensity of the band in the IR spectra [1, 4], but also the coupling anisotropy tensor, which leads to a change in the depolarization ratio of the band. Unfortunately, we were unable to calculate other possible aggregated formations of acetic acid molecules. But what was obtained for the closed dimer and described above (the band at 1671 cm^{-1}) is generally consistent with the experimental data, both in terms of the frequency change and

in terms of the change in the depolarization ratio. Different aggregated formations should correspond to different values of the C=O bond polarizability tensor, therefore the calculated result obtained relative to the depolarization coefficient C=O of the monomer oscillations and the closed dimer should also be in accordance with experiment.

What are the results of the study of C=O vibrations of acetic acid in solutions? Let us begin with the results of studies of solutions of CH_3COOH in CCl_4 (Figure 2). The experiment shows that the dilution of CH_3COOH in CCl_4 leads to a strong decrease in the intensity of two high-frequency lines of C=O vibrations, so that with a content of

0.2 m. f. of acetic acid (0.8 m. f. of CCl_4), two high-frequency lines are not observed at all (Figure 2), only one low-frequency line remains, whose position remains practically unchanged as the mixture concentration changes. Taking into account the results of the experiments and the literature data, we conclude that when CH_3COOH is diluted in CCl_4 , only closed dimers remain in the mixture. Polymer chains and CH_3COOH molecules with a free $\text{C}=\text{O}$ bond

already at a content of 0.2 m. f. the mixture is practically absent and the corresponding bands in the spectrum of $\text{C}=\text{O}$ vibrations disappear (or decrease strongly in intensity).

A completely different picture is observed for a solution of CH_3COOH in the proton-acceptor solvent of acetonitrile (Figure 2, Table 2). In this solution, with a strong dilution of the acid, the number of proton-donor groups is in the minority, compared to the number of proton-acceptor groups.

Table 2. Calculation data by Gaussian-98W(RHF-6-31G++(d,p)) for isolated monomeric molecules and aggregates of acetic acid and acetonitrile (Figure 1. (a), (b), (c), (d)).

Formation parameters	Acetic acid monomer (a)	Acetic acid closed dimer (c)	Acetonitrile monomer (b)	Acetonitrile dimer	Acetic acid + acetonitrile dimer (d)
Energy gain in activation (kcal/mole)	-	12,3	-	3,4	5,3
Dipole moment (D)	1,97	0	4,21	0	2,59
Frequency of $\text{C}=\text{O}$ vibration (cm^{-1})	2009,2	1927,0	-	-	1979,0
Depolarization ratio of $\text{C}=\text{O}$ band	0,38	0,19	-	-	0,30
Frequency of $\text{C}\equiv\text{N}$ vibration	-	-	2605,3	2597,9	2596,2
Depolarization ratio of $\text{C}\equiv\text{N}$ band	-	-	0,18	0,13	0,12

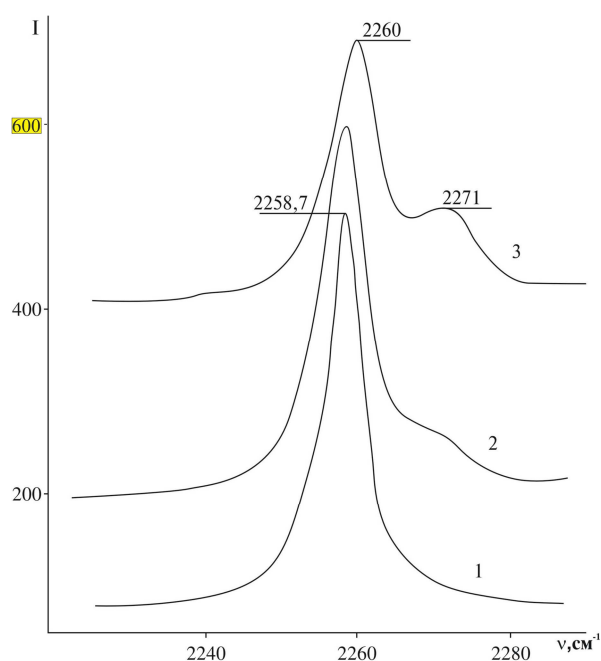


Figure 3. Raman spectra of $\text{C}\equiv\text{N}$ vibrations of acetonitrile in a solution with acetic acid: 1 - 0.95-0.05 m. f.; 2 - 0.3-0.7 m. f.; 3 - 0.1-0.9 m. f.

Changes in the spectrum of $\text{C}=\text{O}$ vibrations should be associated with an increasing number of molecules with free $\text{C}=\text{O}$ bonds. Unlike solutions of CF_3COOH - acetonitrile [13], in solutions of CH_3COOH in this solvent up to a strong dilution of the acid (0.05 m. f., acetonitrile - 0.95 m. f.) all three lines of the band remain, although the ratio changes line intensities: the low-frequency line is greatly reduced in intensity, but its presence is clearly observed; the other two high-frequency lines become equal in intensity (Figure 2). In other words, the relative intensity of the high-frequency line has grown. Thus, these studies of the $\text{C}=\text{O}$ band of an acid in a solution with acetonitrile show that even with a strong dilution of acetic acid, three types of molecular formations are present in the mixture: closed dimeric formations whose relative content is significantly reduced compared to pure

liquid, the polymer chains, the content which is quite large (in a solution with CCl_4 , they are completely destroyed by strong dilution of the acid) and molecules with free $\text{C}=\text{O}$ groups [13] (finite groups of polymer chains, open dimers formations, the content of which is comparable with the content in a mixture of molecules in chains with bound oxygen atoms of the $\text{C}=\text{O}$ group. Judging by the data obtained for solutions of acetonitrile and referring to the data for CF_3COOH [13], the $\text{C}=\text{O}$ group of acetic acid has greater proton-acceptor properties than the CF_3COOH molecule.

The existence of acetic acid - acetonitrile aggregates can be judged by the $\text{C}\equiv\text{N}$ vibration of acetonitrile. In a mixture with CH_3COOH , a line of acetonitrile-acetic acid aggregates of 2271 cm^{-1} appears, but even with strong dilution (Figure 3), the line of monomeric acetonitrile molecules remains.

The calculation based on the above-mentioned program of isolated dimer acetonitrile - acetic acid shows that the lowest energy corresponds to such an aggregate structure, when molecules form a closed dimer with two intermolecular hydrogen bonds (Figure 1 (d)). The length of the hydrogen bond $\text{N}(18)\cdots\text{H}(8)$ is 2.207 Å, and the length of $\text{H}_2\text{CH}(22)\cdots\text{O}(3)$ is 2.615 Å. This formation corresponds to a dipole moment of 2.59 D. The energy gain during dimerization is 5.3 kcal/mole. There is a substantial redistribution of the charges of the atoms of each molecule and a change in the lengths of interatomic bonds (see figure 1). Thus, one of the hydrogen atoms of the CH_3 group of acetonitrile is active and forms a hydrogen bond with the oxygen atom $\text{O}=\text{O}$ of acid (see also [23]). The charge of this hydrogen atom is different from the charges of the other two atoms.

Calculations show that the $\text{C}=\text{O}$ frequency of the acetonitrile - acid dimer is 1979 cm^{-1} (with the depolarization ratio of 0.30), which is 30 cm^{-1} lower than the $\text{C}=\text{O}$ frequency of the monomeric molecule, i.e. lower frequencies, which is observed in the experiment. Calculations also show that the frequency of $\text{C}\equiv\text{N}$ with this molecular orientation also decreases, which contradicts the experimental data. From the experimental data it follows that the formation of

the H-bond leads to an increase in the frequency of $C\equiv N$ frequency by 10 cm^{-1} . However, this discrepancy can be explained on the basis of the following considerations: the $H_2C-H\cdots O$ bond should be weak compared to the $\cdots N\cdots H-O$ bond. The thermal motion of molecules can easily destroy the $H_2C-H\cdots O$ bond. Under these conditions, the acetic acid molecule approaches acetonitrile in the direction of the elongation of the acetonitrile molecule [24]. As the calculations show, in this variant of the convergence of molecules, the frequency of $C\equiv N$ should increase by $\sim 5\text{ cm}^{-1}$. Thus, in a mixture of acetonitrile - acetic acid, the aggregates have the form of a chain with the direction of convergence of molecules towards the elongation of acetonitrile molecules.

4. Conclusions

The calculation based on the Gaussian-98W program in the Hartree-Fock approximation of the spectral parameters and quantities characterizing the monomers of acetic acid, acetonitrile and acetic acid dimers and acetic acid - acetonitrile were performed. The calculations generally correspond to the experimentally observed spectral manifestations of the aggregation of molecules: a different low-frequency shift in the RS of $C=O$ band of different acid aggregates and a different change in the depolarization ratio of the band of different aggregates compared to the monomer band.

For monomers and dimers of acetic acid, as well as acid-acetonitrile dimers, as shown by calculations, there is a weak intramolecular interaction of the oxygen atom $=O$ with the hydrogen atom of the $O-H$ group of the acid.

Acid molecules can form a closed dimer with acetonitrile molecules (calculation) with formation of a strong hydrogen bond between the nitrogen atom of acetonitrile and hydrogen of the $O-H$ group and a weaker hydrogen bond between the oxygen atom $=O$ and one of the hydrogen atoms of the CH_3 group of acetonitrile. At the same time, according to calculations, a low-frequency shift of the $C\equiv N$ band should be observed. When a hydrogen bond is formed between the hydrogen atom of the $O-H$ group and the nitrogen atom in the direction of elongation of the acetonitrile molecule, a high-frequency shift of this band should be observed, which is observed in experiment.

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