Calculation of spectroscopic parameters of hydrogen and halogen bounded $CH_3CHO\cdots HF$ and $CH_3COH\cdots FH$ complexes

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В данной работе с использованием набора оснований MP2/6-311++G(3df, 3pd) рассчитана равновесная геометрия, энергия связи, гармонические и ангармонические спектральные параметры мономеров молекул CH_3CHO, HF и комплексов $CH_3CHO\cdots HF$, $CH_3COH\cdots FH$. Ангармонические расчеты проводили с использованием теории колебаний второго порядка. Энергии связи комплексов $CH_3CHO\cdots HF$ и $CH_3COH\cdots FH$ составляют 10.1 ккал/моль и 1.7 ккал/моль соответственно.

Ключевые слова: водородная связь, галогенная связь, энергия, гармонические и ангармонические расчетные параметры, интенсивность, неэмпирические расчеты

In this work, equilibrium geometry, bond energy, harmonic and anharmonic spectral parameters of the monomers of CH_3CHO, HF molecules and $CH_3CHO\cdots HF$, $CH_3COH\cdots FH$ complexes were calculated using the set of bases MP2/6-311++G(3df, 3pd). Anharmonic calculations were performed using second-order vibration theory. The binding energies of $CH_3CHO \cdots HF$ and $CH_3COH \cdots FH$ complexes are 10.1 kcal/mol and 1.7 kcal/mol, respectively.

Keywords: hydrogen bonding, halogen bonding, energy, harmonic and anharmonic calculation.

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I. Introduction

Hydrogen bonds are a common type of interaction between molecules that are common in nature. The hydrogen bond is usually denoted by A-H ··· R, and the halogen bond is denoted by A-X ··· R. H is the hydrogen atom involved in the hydrogen bonding and X is the halogen atom involved in the halogen bonding. In hydrogen bonding, groups A-H are called proton donors, and group R is called proton receptors. There is a parallel bond between a halogen bond and a hydrogen bond, and there is an electron-receiver relationship in both interactions (electron donor) [1]. In a hydrogen bond, the hydrogen atom plays the role of an electron acceptor and receives a non-covalent interaction by accepting an electron density from an electron-rich site. In a halogen bond, the halogen atom is the electron acceptor. Simultaneously, the normal covalent bond between H or X and R is weakened, so the electron density at H or X appears to be reduced [2].

II. Method of calculation

In this work, equilibrium geometry, bond energy, harmonic and anharmonic spectral parameters of the monomers molecules and $CH_3CHO\cdots HF$, $CH_3COH\cdots FH$ complexes were calculated. The calculations were performed using a set of bases MP2/6-311++G(3df, 3pd). The anharmonic vibration frequencies of the complex were determined using the Gaussian 09 program with the keyword "freq=anharmonic".

III. Results

III.1. The monomers. Acetaldehyde CH_3COH

Table 1 shows the geometric parameters, harmonic and anharmonic frequencies, and intensities

of fundamental transitions of the acetaldehyde molecule calculated in the set of bases MP2/6-311++G(3df, 3pd).

Table 1. Selected MP2. Calculated parameters of the CH_3COH molecule.

Property (Parameter)	Basis set MP2/6-311++G(3df,3pd)
Total energy (hartree)	-153.545397
r (C_1-H_1) (Å)	1.0903
r (C_1-H_2) (Å)	1.0903
r (C_1-H_3) (Å)	1.0854
r (C_1-C_5) (Å)	1.4981
r (C_5=O_6) (Å)	1.2114
r (C_5-H_7) (Å)	1.1055
$<H_2C_1H_3$ (^{0})	110
$<H_3C_1C_3$ (^{0})	111
$<H_7C_5O_6$ (^{0})	120
ν $(C=O)^h$ stretching (sm^{-1})	1778
ν $(C=O)^{anh}$ stretching (sm^{-1})	1738
ν $(C_5$-$H_6)^h$ stretching (sm^{-1})	2963
ν $(C_5$-$H_6)^{anh}$ stretching (sm^{-1})	2743
ν $(C_1$-$H_3)^h$ stretching (sm^{-1})	3202
ν $(C_1$-$H_3)^{anh}$ stretching (sm^{-1})	3064
A $^a(C=O)^h$ ($km{\cdot}mol^{-1}$)	305
A $^a(C=O)^{anh}$ ($km{\cdot}mol^{-1}$)	245
A $^a(C_5$-$H_6)^h$ ($km{\cdot}mol^{-1}$)	138
A $^a(C_5$-$H_6)^{anh}$ ($km{\cdot}mol^{-1}$)	61
A $^a(C_1$-$H_3)^h$ ($km{\cdot}mol^{-1)}$	6
A $^a(C_1$-$H_3)^{anh}$($km{\cdot}mol^{-1}$)	9

[a]Infrared intensity, [h]Harmonic frequency, [anh]Anharmonic frequency.

Table 2. Selected MP2. Calculated properties of the HF molecule.

Property	Basis set MP2/6-311++G(3df,3pd)
Total energy (hartree)	-100.33282
r (H-F) (Å)	0.9167
ν $(H-F)^h$ valent (sm^{-1})	4176
ν $(H-F)^{anh}$ valent (sm^{-1})	3995
A $^a(H-F)^h$ ($km{\cdot}mol^{-1}$)	112
A $^a(H-F)^{anh}$ ($km{\cdot}mol^{-1}$)	115

[a]Infrared intensity, [h]harmonic frequency, [anh]anharmonic frequency.

III.2. Hydrogen fluoride

The spectroscopic and structural properties of hydrogen fluoride have widely discussed in the literature. The required geometric parameters and harmonic and anharmonic frequencies of hydrogen fluoride calculated in this study are given in Table 2 [6-10].

III.3. The complexes: CH_3CHO···HF and CH_3COH···FH

It was found that the hydrogen and halogen bonding complexes formed between the molecules due to the intermolecular interactions are formed in the structure shown in Figs 1-2.

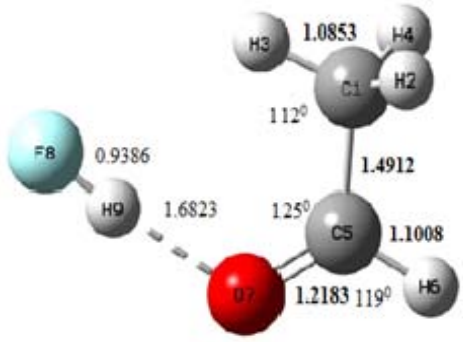


Figure 1. Optimal geometries of CH_3CHO···HF complex.

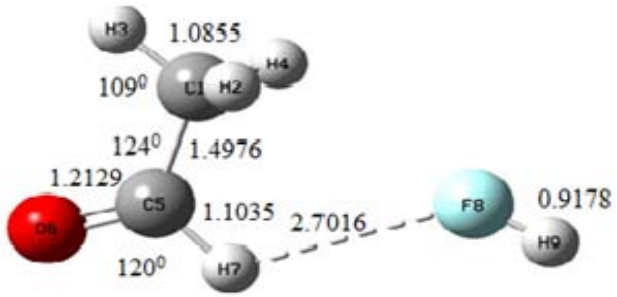


Figure 2. Optimal geometries of CH_3COH···FH complex.

CH_3CHO···HF and CH_3COH··· FH complexes are used to analyze the IR absorption spectra and draw clear scientific conclusions from the experimental results. In addition, the equilibrium geometry, the bond energy, harmonic and anharmonic spectral parameters were calculated using Gaussian 09 program at bases set mp2/6-311++G(3df, 3pd) taking into account error of the approximation for the complexes CH_3CHO···HF and CH_3COH···FH.

As a result of the formation of CH_3CHO·· HF and CH_3COH·· FH complexes, the length of the hydrogen bond is 1.6823 Å and the length of the halogen bond is 2.7016 Å, the difference between the

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hydrogen and halogen bonds vary by 1.0193 Å. An increase in the C=O bond length of hydrogen and halogen bonds is observed [11-12]. That is, in $CH_3CHO\cdots HF$ it is 1.2183, and in $CH_3COH\cdots HF$ it is 1.2129 Å.

III.4. Calculated harmonic and anharmonic frequencies of the $CH_3CHO\cdots HF$ and $CH_3COH\cdots FH$

The frequencies and intensities of harmonic and angarmonic vibrations of hydrogen and halogen bonds were determined. The calculated vibration frequency and intensity shifts are shown in Table 3.

For acetaldehyde and $CH_3CHO\cdot\cdot$ HF and $CH_3COH\cdot\cdot$ FH hydrogen and halogen bonded complexes obtained in Fig. 3, the stretching vibration frequencies C=O band in the range 1700–1900 cm^{-1}, C-H stretching vibration frequencies range from 2800 to 3300 cm^{-1}. These vibrations are called characteristic vibrations. Also, if the frequency of the band C=O corresponding to the halogen bond $CH_3COH\cdots FH$ is

Table 3. Harmonic and anharmonic fundamental transition frequencies ν(cm^{-1}) and intensities S (km mol^{-1}) of the $CH_3CHO\cdots HF$ and $CH_3COH\cdots FH$ complexes.

	Harmonic		Anharmonic		Harmonic		Anharmonic	
	$CH_3CHO\cdots HF$				$CH_3COH\cdots FH$			
	ν	S	ν	S	ν	S	ν	S
ν intermolecular stretchng	170	0.3	153	0.1	172	21	133	4
ν(HF) libration in the yx plane	531	15	526	14	511	12	509	13
ν(HF) libration in the zx plane	776	12	822	18	781	2	767	2
CH_3 rocking	915	4	921	5	908	5	863	9
ν(OCH) bending	1440	9	1404	4	1426	11	1409	12
ν(HCH) bending	1480	27	1446	14	1476	21	1435	28
ν(HCH) bending	1492	11	1442	11	1489	9	1440	10
ν(CO) stretching	1765	163	1737	100	1772	115	1735	142
ν(CH) stretching	3022	80	2894	64	2989	57	2864	86
ν(CH)stretching symmetry	3070	4	2965	2	3073	1	2966	1
ν (C5H6) stretching	3151	1	3014	1	3156	4	3020	3
ν (CH) stretching	3206	1	3070	1	3202	4	3063	7
ν (HF) stretching	3680	1036	3495	791	4157	100	3982	143

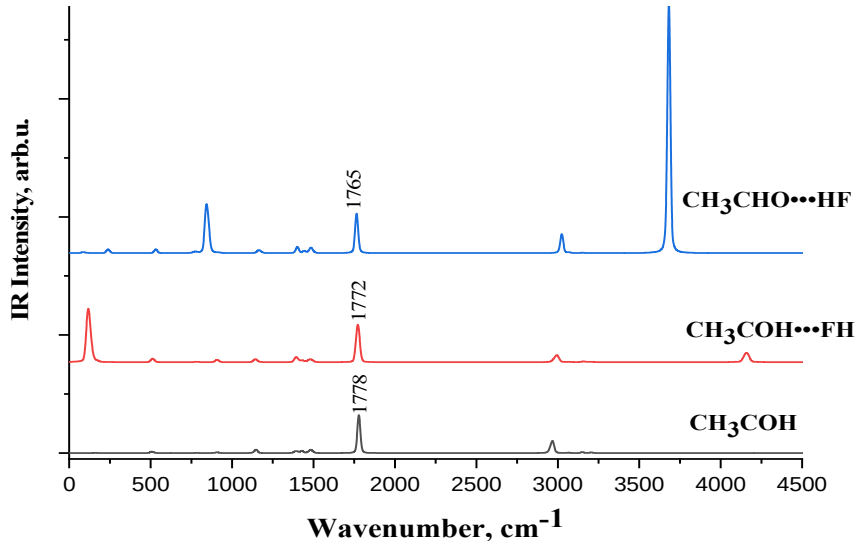


Figure 3. The monomer of the CH_3COH molecule and the complexes $CH_3CHO\cdots HF$ and $CH_3COH\cdots FH$ MP2/6-311++G (3df, 3pd) gaseous vibration spectrum calculated in a set of bases.

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ν_0=1772 cm^{-1}, when $CH_3CHO\cdots HF$ forms a hydrogen bond, we see that the stretching vibrations frequency of the band C=O shifts to the lower frequency side $\Delta\nu$=10÷15 cm^{-1}, that is, ν_0=1765 cm^{-1} [13-18].

III. Conclusions

Intermolecular interactions, including hydrogen bonding, change the spectral parameters of the interacting molecules. This change is due to the energy of the interaction. When the energy of intermolecular hydrogen bonding is close to the Van der Waals interaction energy, the ν(AH) vibration band shifts only in the low frequency side, and the shape of the band almost does not change. The halogen bond energy is much smaller than the hydrogen bond energy. That is, the formation of a halogen-bonded complex of hydrogen fluoride with acetaldehyde results in a binding energy of 1.7 kcal/mol. In the formation of hydrogen fluoride hydrogen bonding complex with acetaldehyde, the binding energy is 10.1 kcal/mol.

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Водород ва галоген боғланган $H_3CHO\cdots HF$ ва $CH_3COH\cdots FH$ комплексларининг спектроскопик параметрларини ҳисоблаш

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Ушбу мақолада CH_3CHO ва HF молекулалар мономерлари ҳамда $CH_3CHO\cdots HF$ ва $CH_3COH\cdots FH$ комплексларининг мувозанат геометрияси, боғланиш энергияси, гармоник ва ангармоник спектрал параметрлари MP2/6-311++G(3df,3pd) базислар тўпламидан фойдаланган ҳолда ҳисобланди. Ангармоник ҳисоблашлар иккинчи тартибли тебраниш назарияси ёрдамида амалга оширилди. $CH_3CHO\cdots HF$ ва $CH_3COH\cdots FH$ комплексларининг боғланиш энергиялари 10.1 ва 1.7 ккал/молларни ташқил қилади

Калит сўзлар: водород боғланиш, галоген боғланиш, энергия, гармоник ва ангармоник ҳисоблаш параметрлари, интенсивлик, ноэмпирик ҳисоблашлар.

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