Computational Studies Onmolecular Structure Of Ch3cho•••Hx(X=F, Cl) Complexes

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Abstract: *In this work, the optimal geometries, charge distribution, bond energies, harmonic and anharmonic spectral parameters of hydrogen-bonded CH3CHO•••HX (X= F, Cl) complexes were calculated using non-empirical (ab initio) calculations based on the MP2/6-311++G(3df,3pd) set of functions. In the formation of heterodimers, changes in the frequency and intensity of monomeric vibrations were investigated.*

Keywords: *acetaldehyde, hydrogen haloid, hydrogen bond, harmonic and anharmonic frequencies.*

INTRODUCTION

Among the non-covalent bonds, hydrogen bonding is important and plays a crucial role in the formation of the vibration-rotation spectra of molecular complexes in the gas phase [1, 2]. Therefore, the experimental and theoretical study of the absorption-vibration spectra of hydrogen-bonded systems is one of the current problems of modern spectroscopy. A variety of kinetic and dynamic interactions influence the spectroscopic manifestation of hydrogen bonds in hydrogen-bonded complexes. The absorption bands of hydrogen-bonded complexes may differ in general shape, integral intensity, width, structure. These properties are governed by the fact that the potential energy of a molecular complex depends on its degrees of vibrationfreedom, the wave functions of the vibration depend on the mass of the nucleus, and the dipole moment function corresponds to each other.Therefore, it is impossible to interpret the structure of the absorption spectral ranges without a sufficiently accurate solution to the problem of the internal dynamics of the complex and a reliable calculation of its electronic shell.Only by well-coordinating the theoretical spectrum of the complex with the experimental spectrum can it confirm the correctness of the

theoretical method.These show that it is necessary to conduct experiments and theoretical calculations with an optimal approach in determining the mechanisms of formation of complex absorption regiones of hydrogen bonded complexes.Experimental research should be adapted to obtain large amounts of data on electro-optical parameters. The calculation method should take into account all degrees of vibrationfreedom, which significantly affect the parameters obtained from the interaction of the complex [3].

Non-empirical calculations of harmonic and anharmonic approximations lead to a high level of quality in spectroscopic studies as well as high-level advantages in analysis.The study of isolated complexes also allows obtaining information about the structure of complexes in the gas phase, rotational constants, vibration frequencies and other spectral parameters [4].

The study of complexes of aldehydes with hydrogen halides is important in the study of hydrogen-bonded complexes. Recently, we studied the mechanism of formation and electro-optical parameters of the formaldehyde (H_2CO) and hydrogen fluoride (HF) complexes formed by hydrogen bonding [5].

K.G. Tokhadze and his scientific team have conducted many experimental and theoretical studies on aldehyde and hydrogen halides [2,6-9].

Acetaldehyde (CH_3CHO) is one of the most important aldehydes, formed and destroyed by photolysis in the Earth's atmosphere.It is an important spectroscopic intermediate between formaldehyde (H_2CO) and acetone (($CH_3)_2CO$).It is formed from formaldehyde as a result of the replacement of the CH_3 radical with hydrogen.P.Limao-Vieira et al studied the high-precision photo-absorption cross section of acetaldehyde using synchrotron radiation in the range of 3.0–11 eV [10]. Raman spectra of liquid CH_3CHO and CH_3CDO were obtained and the photoelectric and depolarization ratios were determined by J.C. Evanse et al. [11].

Weak hydrogen bonding systems $H_2CO\cdots HX$ (X = F, CI, Br and I) were studied by Y.B. Ding et al. [12].Luis Rinco´n et al studied the energy, structural, and thermodynamic properties of hydrogen fluoride clusters using quantum-chemical calculations (DFT, ab-initio).He also found that cyclic structural clusters are the most stable clusters [13].The bond topology of various hydrogen-bonded complexes of hydrogen fluoride was theoretically studied by Boaz G. Oliveira [1].Hydrogen fluoride forms strong hydrogen bonds with suitable bases and is a useful model for more complex and widespread systems. Molecules containing two or three carbon-carbon bonds have been shown to be good bases for complex formation with HF [14].

Anharmonicity and matrix effects play an important role in determining proton stretching frequencies in hydrogen-bonded complexes of hydrogen holoids (HCl and HBr) with NH_3 and $N(CH_3)_3$. These effects were investigated by non-empirical calculations by Meredith J. T. Jordan and Janet E. Del Bene for HCl and HBr complexes [15].

The purpose of this work is to determine the role of various effects in the formation of hydrogen-bonded complexes $CH_3CHO\cdots HX$ (X = F, Cl), as well as changes in geometric parameters, charge distribution, vibration frequencies, their characteristics and intensities.

COMPUTATIONAL DETAILS

All calculations were performed using the Gaussian 09 package program [18] at the MP2 level with the 6-311++G(3df,3pd) basis set. Anharmonic calculations were performed using second-order vibration theory.Potential energy distribution (PED) analysis was performed to more accurately and quantitatively describe the contribution of a group of atoms in a molecule to normal vibration modes. PED analysis was performed using VEDA 4.0 software[19].

RESULTS AND DISCUSSION

The optimal geometries of heterodimers $CH_3CHO\cdots HX$ (X = F, Cl) calculated using theMP2/6-311++G(3df,3pd)set of bases are shown in Figure 1.These heterodimers are formed by hydrogen bonding between the oxygen atoms of acetaldehyde (CH_3CHO) and hydrogen halides (HF, HCl). In these complexes, the C=O functional group of acetaldehyde acts as a proton acceptor, while hydrogen halides act as a proton donor.
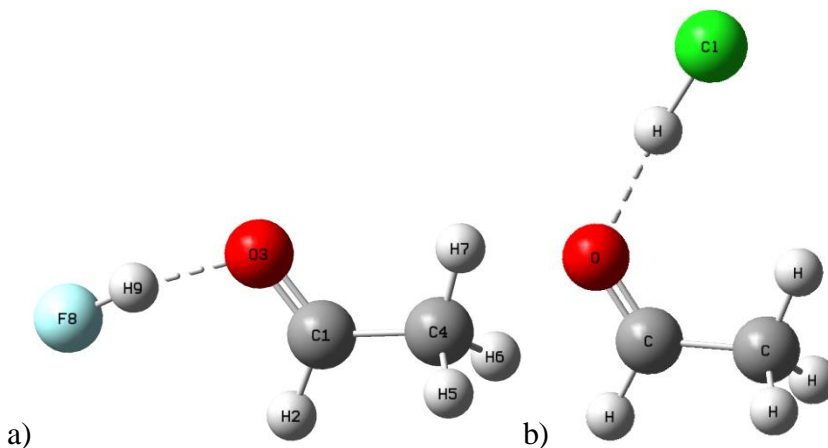

Figure 1: Optimal geometric structure of $CH_3CHO…HX$ (X=F, Cl) complex

The lengths of the hydrogen bonds in the formation of the $CH_3CHO\cdots HX$ (X= F, Cl) complexes were obtained to be 1.677 and 1.827 Å, respectively, and the binding energies were 10.98 and 7.10 kcal/mol, respectively.It appears that the $CH_3CHO\cdots HF$ complex forms a stronger bond than the $CH_3CHO\cdots HCl$ complex.

Table 1 Geometric parameters of $CH_3CHO…HX$ (X=F, Cl) complexes

Bond length (Å)				Angle (Degree)			
Atoms	CH_3CHO	$CH_3CHO + HF$	$CH_3CHO + HCl$	Atoms	CH_3CHO	$CH_3CHO + HF$	$CH_3CHO + HCl$
C_1-H_2	1.104	1.101	1.102	$H_2-C_1-O_3$	120.004	119.511	119.080
C_1-O_3	1.211	1.218	1.217	$H_2-C_1-C_4$	116.825	116.723	116.059
C_1-C_4	1.505	1.489	1.493	$O_3-C_1-C_4$	123.171	123.765	124.861
C_4-H_5	1.088	1.090	1.090	$H_5-C_4-H_6$	107.536	106.851	106.832
C_4-H_6	1.088	1.090	1.090	$H_5-C_4-H_7$	109.623	110.444	110.296
C_4-H_7	1.086	1.085	1.085	$H_6-C_4-H_7$	109.626	110.443	110.297
X_8-H_9	0.916, 1.271, 0.000	0.938	1.295	$C_1-C_4-H_5$	109.021	109.028	108.863
$O_3…H_9$		1.677	1.827	$C_1-C_4-H_6$	109.019	109.031	108.867
				$C_1-C_4-H_7$	111.910	110.938	111.551
				$C_1-O_3-H_9$		110.960	120.232
				$X_8-H_9-O_3$		170.763	174.187

As a result of the influence of molecular hydrogen bonding, the geometric, electro-optical and spectroscopic parameters of the molecules change. The geometric parameters corresponding to the optimal structures of CH_3CHO, HF and HCl monomers and $CH_3CHO\cdots HX$ (X = F, Cl) complexes are given in Table 1. It can be seen from the table that the bond lengths between the atoms of hydrogen halides (HF, HCl) increased by 0.220 and 0.024 Å, respectively, when the complex was formed relative to the monomer state. It was also obtained that the distance between the C_1 and O_3 atoms of acetaldehyde increased by 0.07 and 0.06 Å, respectively, due to hydrogen bonding. The angles at which molecules form complexes are almost unchanged ($\approx 1^0$) (Table 1).

It is known that the nature of intermolecular forces depends on the electromagnetic properties of molecules. Calculating the electron density distribution of atoms in a molecule helps to understand the chemical and ionization potentials. Atomic charge affects the dipole moment, polarizability, electronic structure, and other molecular properties of the system. Table 2 shows the Mulliken charge distribution of the CH_3CHO, HF, HCl monomers and the $CH_3CHO\cdots HX$ (X = F, Cl) complex. Calculations have shown that the electron density of the hydrogen atom of hydrogen halides (HF, HCl) decreases significantly during complex formation. The electron density of the oxygen atom of the acetaldehyde molecule changes to the same value as that of the HF and HCl molecules. The electron density distribution of the positively charged hydrogen H (2) atom of the acetaldehyde molecule decreases with complex formation with HF molecule, but increases sharply with complex formation with HCl molecule and remains negatively charged. One of the main reasons for this is the orientation of the molecules in the formation of the complex (Figure 1).

Table 2 Mulliken charge distribution of $CH_3CHO\ldots HX$ (X=F, Cl) complexes

Atoms	Mulliken charge distribution		
	CH_3CHO	CH_3CHO+HF	CH_3CHO+HCl
C_1	0.688	0.883	0.906
H_2	0.007	0.019	-0.017
O_3	-0.660	-0.836	-0.836
C_4	-0.090	-0.162	-0.158
H_5	0.028	0.032	0.027
H_6	0.028	0.032	0.027
H_7	-0.001	-0.014	-0.005
X_8	(F) -0.510, (Cl) -0.192,	-0.671	-0.390
H_9	0.510, 0.192,	0.717	0.438

Figure 2a shows the whole IR spectrum of acetaldehyde calculated at a harmonic approximation. As can be seen from the figure, the spectral band with the highest intensity (136.195 km/mol) in the finger-print region is located at a frequency of 1778.44 cm^{-1}, and this spectral band belongs to the stretching of C=O. In the high-frequency region, the corresponding spectral bands of stretching of CH, symmetric and asymmetric stretching of CH_3 are located. Among these, the highest intensity (102.43 km/mol) belongs to the C-H stretching vibration, with a frequency of 2963 cm^{-1}. The intensities of the spectral bands (asymmetric stretching) corresponding to the asymmetric vibrations of the CH_3 modes (3.75 and 4.85 km/mol) are stronger than the intensities of the symmetric stretching corresponding to their symmetrical vibrations (1.91 km/mol) (Table 3).
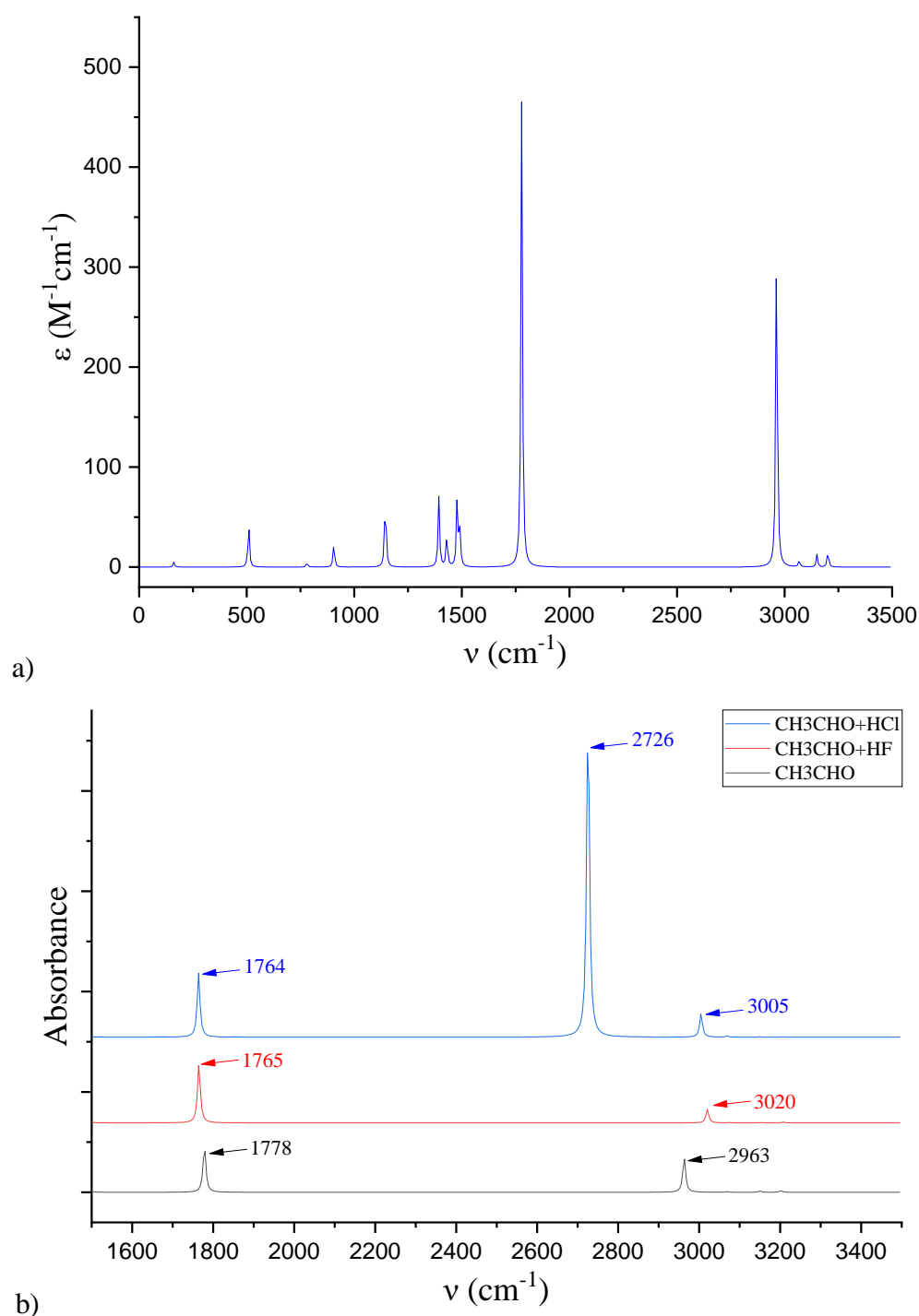
Figure 2: Calculated IR spectra of acetaldehyde: (*a*) the whole spectrum, (*b*) the bands in an interval of 1500-3500 cm^{-1} and (c) 1600-1800 cm^{-1} of $CH_3CHO \cdots HX$ (X=F, Cl) complexes

Table 3 Calculated and experimental IR frequencies and assignment of the vibrational modes for acetaldehyde*

Mode	Harmonic		Anharmonic		Experimental (solid) [20]	Experimental (vapor) [21]	Assignment PED (%)
	Frequency (cm⁻¹)	Intensity (km/mol)	Frequency (cm⁻¹)	Intensity (km/mol)	Frequency (cm⁻¹)	Frequency (cm⁻¹)	
1	161.29	1.404	146.36	6.823		150	τ(HCCO) 98
2	509.25	12.758	508.57	4.420	517	509	δ(OCC) 78 + τ(HCCO) 11
3	780.15	1.402	765.65	1.325	772	880	τ(HCCO) 14 - γ(CCOH) 79
4	904.99	7.070	865.16	42.215	888	919	ν(CC) 65 - τ(HCCO) 23
5	1138.22	0.006	1110.82	106.903	1103	1104	ν(CC) 19 + δ(HCH) 13 - δ(OCC) 17 + τ(HCCO) 42
6	1144.26	21.930	1116.33	9.936	1120	1122	δ(HCH) 17 - γ(CCOH) 16 - τ(HCCO) 65
7	1392.95	20.301	1353.52	16.516	1349	1352	δ(HCH) 44 + δ(HCH) 38 - δ(HCO) 14
8	1430.29	9.839	1407.61	7.868	1390	1410	δ(HCO) 79
9	1478.62	21.591	1435.85	21.188	1429	1441	δ(HCH) 47 - τ(HCCO) 21 - δ(HCH) 31
10	1491.10	9.826	1443.01	24.015	1422	1441	δ(HCO) 79
11	1778.44	136.195	1738.43	0.022	1740	1743	ν(CO) 89
12	2962.91	102.432	2743.07	4.425	2733	2804	ν(CH) 99
13	3068.17	1.907	2964.41	1.516	2967	2917	ν_s(CH₃) 97
14	3150.48	3.750	3015.71	12.280	3001	2967	ν_{as}(CH₃) 100
15	3201.74	4.847	3063.93	1.349	3432	3024	ν_{as}(CH₃) 97

*τ – torsion, ν – stretching, δ – bending, γ – out-of-plane vibration

Table 3 shows the calculated frequencies of the acetaldehyde molecule in harmonic and anharmonic approximations and with the frequencies determined experimentally [21, 22].

The normal vibration frequencies of the complexes formed by the acetaldehyde molecule with hydrogen haloide (HF, HCl) molecules are given in Table 4.The frequencyof the C=O stretching of the acetaldehyde molecule (1778.44 cm⁻¹)shifts to a lower frequency of 13.5 and 14.4 cm⁻¹, respectively, in the formation of CH₃CHO···HX (X = F, Cl) complexes. The frequency of the C-H stretching (2962.91 cm⁻¹) shifts to higher frequencies of 57.42 and 41.72 cm⁻¹(Figure 2b). Intensities also increased 1.27 and 1.36 times, respectively. The vibration frequencies of hydrogen halides (HF, HCl) shift to a lower frequency of 496.64 and 332.35 cm⁻¹, respectively. Also, the intensity decreased by 2.62 and 1.74 times, respectively.

Table 4 Calculated IR frequencies and intensities of the vibrational modes for $CH_3CHO\cdots HX$ (X=F, Cl, Br) complexes

Mode	CH_3CHO+HF		CH_3CHO+HCl	
	Frequency (cm^{-1})	Intensity (km/mol)	Frequency (cm^{-1})	Intensity (km/mol)
1	61.62	5.7677	72.88	2.5865
2	81.15	2.7003	75.34	2.5480
3	163.85	0.7088	158.18	27.1121
4	224.31	11.9863	159.67	0.3972
5	530.43	40.6341	515.00	16.5650
6	777.37	50.1467	551.65	18.6480
7	844.26	150.8052	585.47	40.1696
8	846.71	59.0796	789.87	2.4260
9	922.61	2.9173	910.92	5.8298
10	1147.62	0.1407	1143.46	0.0259
11	1160.35	18.7781	1158.10	21.3003
12	1397.61	20.7024	1398.64	25.1614
13	1439.30	10.3730	1436.34	6.5724
14	1476.32	26.4062	1478.97	21.7009
15	1488.97	10.8390	1489.83	8.1215
16	1764.89	173.3509	1764.04	184.9641
17	3020.17	39.1385	2725.67	962.3338
18	3071.54	0.8610	3004.63	68.0294
19	3152.82	1.0197	3069.33	3.3108
20	3207.70	2.4770	3150.37	1.2623
21	3680.98	1215.9073	3205.31	0.9431

CONCLUSION

Optimal geometries, charge distribution, binding energies, harmonic and anharmonic spectral parameters of $CH_3CHO\cdots HX$ (X=F, Cl) heterodimers were calculated in the set of bases MP2/6-311++G(3df,3pd).The binding energy of $CH_3CHO\cdots HF$ heterodimer was found to be 10.98 kcal/mol and stronger than that of other heterodimers. For acetaldehyde, the vibation frequencies calculated at the anharmonic approximation corresponded to the experimental frequencies. In the formation of$CH_3CHO\cdots HX$ (X=F, Cl) heterodimers the frequencyof the C=O stretching of acetaldehyde shifts to lower frequencies 13.5 and 14.4 cm^{-1}, and the frequencyof the CH stretching shifts to higher frequencies of 257.23 and 241.72 cm^{-1}. The results of this work will help to better understand the molecular structure and vibration properties of acetaldehyde and its hydrogen halide complexes, as well as the nature of hydrogen bonding.

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