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Investigation of the $H_2CO\cdots HF$ complex in gas phase by the help of FTIR spectroscopy and computational methods

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Инфракрасные спектры поглощения высокого разрешения комплекса $H_2CO\cdots HF$ и его мономеров записаны в газовой фазе в областях C=O и C-H с помощью спектрометра Bruker HR 125 с разрешением 0.05 $см^{-1}$. При комплексообразовании в полосе растяжения HF комплекса асимметричная форма не наблюдалась из-за слабого взаимодействия связей между C=O и C-H растяжениями комплекса H_2CO HF. Квантово химические расчеты выполнены в приближении mp2//6-311++g(3df, 3pd), рассчитаны геометрические, энергетические и спектральные параметры комплекса.

Ключевые слова: спектры поглощения, водородная связь, фтористый водород, формальдегид.

High-resolution infrared absorption spectra of the $H_2CO\cdots HF$ complex and its monomers are recorded in gas phase in C=O and C−H regions by means of Bruker HR 125 spectrometer recorded with a resolution of 0.05 cm^{-1}. Upon the complexation in the HF stretching band of complex the asymmetrical shape was not observed due to weak interaction between C=O and C−H stretching of the $H_2CO\cdots HF$ complex. Quantum-chemical calculations are performed in mp2//6-311++g(3df, 3pd) approximation and calculated geometrical, energetic, and spectral parameters of the complex.

Keywords: absorption spectra, hydrogen bond, hydrogen fluoride, formaldehyde.

I. Introduction

Hydrogen bond (HB) is important in many physical, chemical, and biological systems in the life, and the hydrogen fluoride (HF) is one of strong proton donor molecule which can be used to investigate the nature of (HB). In [1] ν(HF) stretching band formation mechanisms of B···HF complexes were investigated both experimentally and theoretically in detail. Recently, anharmonic calculations were carried out on the relevant complexes [2]. In [3] for $(H_2CO)_2\cdots HF$ and $H_2CO\cdots(HF)_2$ trimers the accurate spectral parameters were presented through very high level of quantum chemical calculations. The optimal geometry and harmonic spectral parameters and energetic evaluations of the $H_2CO\cdots HF$ complexes were presented in [4]. Formaldehyde dimer $(CH_2O)_2$ has been investigated both experimentally and theoretically by THz spectroscopic and CCSD(T)-F12/aug-cc-pV5Z and MP2/aug-cc-pVQZ quantum-chemical calculations in [5]. In this work dissociation energy of the dimer estimated as D_0=13.8 $kJ\cdot mol^{-1}$ for the global potential energy minimum. Anharmonic calculations using in mp2/6311++G(3df, 3pd) approximation and low temperature matrix-isolation experimental studies were carried in [6]. For the $CH_3CN\cdots HF$ complex both experimental and computational results are shown in our paper [7]. In [8] spectral and geometrical parameters of the $[F(HF)_2]$ and $[F(DF)_2]$ complexes were calculated by using the mp2 theory and multi-dimensional variation methods. Anharmonic calculations play an important role in investigation hydrogen bonded molecular complexes due to well agreement with the experimental results. Therefore, recently numerous works were devoted to solving anharmonic multi-dimensional problems by

the help Schrödinger equations with the variational methods [9-11]. In [12] authors performed fully automated code for the establishment of interatomic force constants and for the identification of rotation-vibrational parameters of some HB molecular complexes. The results are significantly important to analyze internal dynamics, to recognize spectral manifestation of molecular complexes, and to distinguish overlapping spectral lines of noncovalent bonded molecular complexes.

In this work, $H_2CO\cdots HF$ complex and monomers are studied by the help FTIR spectroscopy in gas phase and quantum-chemical calculations. The results obtained were coincidence with the reliable literatures.

II. Experimental and computational methods

The high-resolution absorption spectra of the $H_2CO\cdots HF$ complex and H_2CO monomer recorded by the help Bruker 125 HR spectrometer at resolution of 0.05 cm^{-1} in gas phase. The formaldehyde was transferred from the powder to the gas phase by the phase changer vacuum equipment. The vacuum atmosphere was created inside of cavity cell, and the samples were placed into stainless steel cavity according to the law of real gases. The stainless-steel cavity was 20 cm in length with sapphire and ZnSe windows. Total pressure of the mixture was about 20–100 Torr.

Quantum-chemical calculations are carried out by the help of the latest version of GAUSSIAN 16 software [14] with mp2/6-311++G(3df, 3pd) approximation.The equilibrium geometries, interaction energies and harmonic spectral parameters of the complexes are determined.

III. Results and discussion

Gas phase vibrational spectra of molecular complexes give the extremely more information about the rotational dynamics and complicated intermolecular interactions. Recently, in [6] the $H_2CO\cdots HF$ complex and its monomers have been studied in matrix by the help of FTIR spectroscopy. Absorption spectra in matrix in the C=O and C−H regions were analyzed in detail. The new picks were observed near 2 ν_4 and ν_3 regions upon the complexation.

In Fig. 1 ν(C=O) stretching region of the $H_2CO\cdots HF$ complex and H_2CO molecule are shown. In this region the respective branches of the spectra are appeared. The yellow spectrum belongs to the pure H_2CO molecule at pressure p=0.006 kgf/cm^2 (c), and the green spectrum belongs to the complex recorded at p=90 Torr (b), and blue belongs to the complex at 65 Torr (a); the all three spectra recorded at resolution of 0.05 $см^{-1}$. There are no observations of spectral changes upon the complex formation in the band, the line intensities were increased depending on the sample pressures. The line parameters of the band were in good agreement with HITRAN [13] database.

Intensities of the transitions can be determined through the following formula:

$$S = 2.50643\nu\left[\left\langle i\left|\mu_x\right|f\right\rangle^2 + \left\langle i\left|\mu_y\right|f\right\rangle^2 \left\langle i\left|\mu_z\right|f\right\rangle^2\right], \qquad (1)$$

where S is the absorption intensity of the lines (km/mol), I is initial state, f is final state, ν is the frequency (cm^{-1}), $\left\langle i\left|\mu_x\right|f\right\rangle^2$, $\left\langle i\left|\mu_y\right|f\right\rangle^2$, $\left\langle i\left|\mu_z\right|f\right\rangle^2$ are the dipole moment components (in D). Also, herein the line intensities of the band are increase when increases the pressure from 65 to 95 Torr, respectively.

All the spectral features are related to the H–F, C=O, and C–H stretches and the HF librational vibrations in the $H_2CO\cdots HF$ complex. In contrast with studied complexes in [1], in this work the ν(HF) region of complicated spectral features are not observed upon the complex formation. Due to following reasons the complicated spectral patterns were not observed. Firstly, C=O and HF stretching vibrations are weakly interacting mutually in the complex. Secondly, mechanical anharmonic constant of the HF molecule is sufficiently large and equals to 85 cm^{-1}. Thirdly, H_2CO molecule keeps the inclination to the condition and by the help unique spectroscopic techniques.

In Fig. 2 ν(C−H) stretching region of the $H_2CO\cdots HF$ complex and polymerization in the case of extremely low concentrations are shown. Therefore, we are not considering the focus on ν(HF) region of the complex. It requires further experimental investigations at a convenient H_2CO molecule. The yellow spectrum (c) belongs to the pure H_2CO molecule at pressure p=0.006 kgf/cm^2, and green (b) belongs to the complex which are recorded at p = 90 Torr, and at blue (a) belongs to the complex p = 65 Torr, respectively.The all spectra were recorded at 0.05 $см^{-1}$ spectral resolution.

Quantum-chemical calculations of the $H_2CO\cdots HF$ complex were performed by using the GAUSSIAN 16 software [14] in the mp2/6-311++G(3df, 3pd) approximation with the basis set superposition, error is taken into account. This approximation provides with very accurate information

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for the calculation of spectral parameters of molecular complexes coincidence with experimental data. The band changes (blue or red) for the frequency, and intensity changes were explained in [4] in detail.

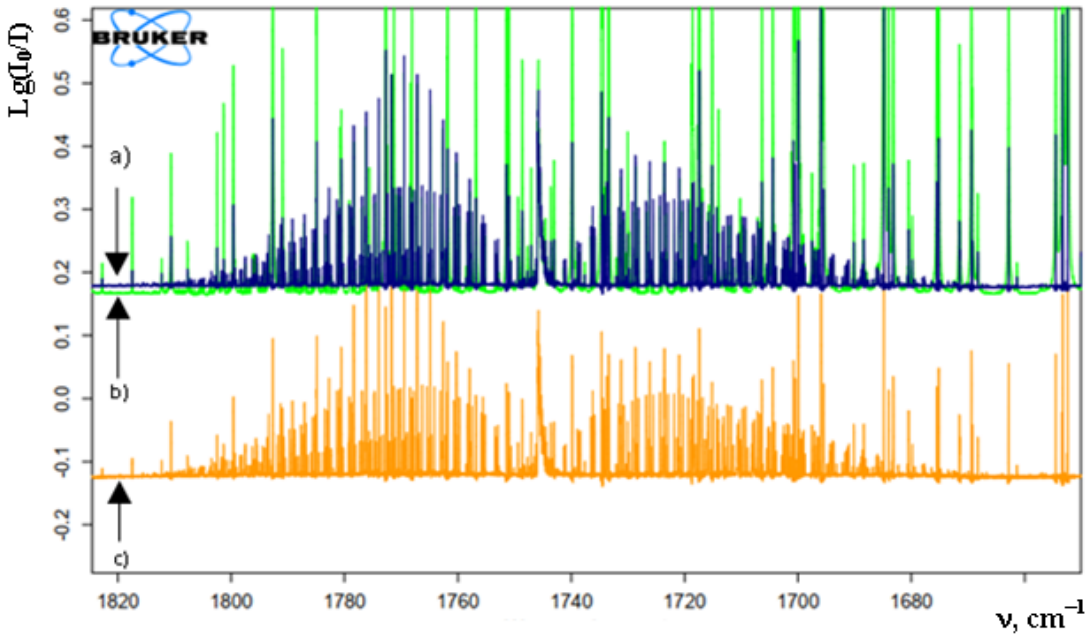


Figure 1. Absorption spectra of pure H_2CO and $HF+H_2CO$ complex in gas phase in the ν(C=O) stretching region. Yellow – pure H_2CO, p=0.006 kgf/cm^2; green – $HF+H_2CO$ complex, p=90 Torr and blue – $HF+H_2CO$ complex, p=65 Torr, resolution 0.05 см$^{-1}$.

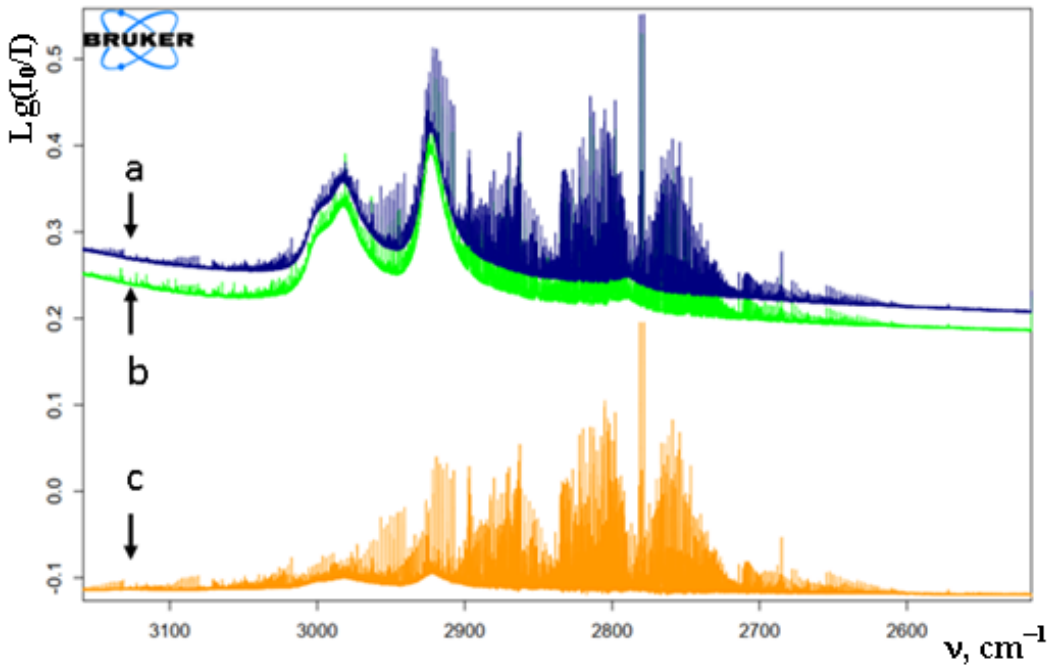


Figure 2. Absorption spectra of pure H_2CO and $HF+H_2CO$ complex in gas phase in the ν(CH) stretching region. Yellow (c) – pure H_2CO, p=0.006 kgf/cm^2; green (b) – $HF+H_2CO$ complex, p=90 Torr and blue (a) – $HF+H_2CO$ complex 65 Torr.

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The equilibrium geometry of the $H_2CO\cdots HF$ complex is presented in Fig. 3.

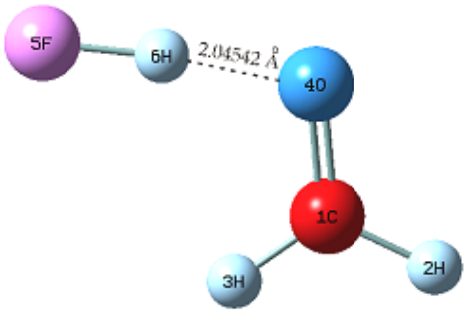


Figure 3. The equilibrium geometry of $H_2CO\cdots HF$ complex calculated at mp2/6-311++g(3df, 3pd) approximation.

Selected geometrical parameters of the complex according to optimal geometry are demonstrated in Table 1. Upon formation of the complex, H–F stretching frequency shortened by 9.89 cm^{-1} and the C=O stretching band of formaldehyde also shortened about 9.7 cm^{-1}. Also, C–H stretch frequencies (blue) shifted of about 39 cm^{-1}, and atomic distance between C and O atoms increased. As a result of computational determination the H–F frequency to be ν_{12} 3546 cm^{-1}, and this value equals to 3573 cm^{-1} in experiment [13]. The frequency of HF molecule according to experimental investigation equals to 3961.40 cm^{-1}. This value shifts toward to the low energy side upon the complex formation by about 345.6 cm^{-1} according to quantum chemical calculation. The all determined geometrical and spectral parameters of the complex are compared with the reported results in [6], and are in good agreement with determined in [6].

Table 1. Calculated stabilization structural parameters of the $H_2CO\cdots HF$ complex.

Distans (Å)	Monomer	Complex	Angles (°)	Monomer	Complex
$r(H_3–F)$	0.915	0.936	$\angle OCH_1$	121.5	121.3
$r(C=O)$	1.207	1.215	$\angle OCH_2$	121.5	121.1
$r(C–H_1)$	1.101	1.096	$\angle OH_3F$	-	166.4
$r(C–H_2)$	1.102	1.097	$\angle COH_3$	-	111.2
$r(O\cdots H_3)$	-	1.753	$\angle COF$	-	141.4
$r(O\cdots F)$	-	2.649	-	-	-

Dipole moment of the complex calculated in CCSD(T)6311++G(3df,3pd) approximation equals to 3.81 D. Change of geometrical parameters upon complex formation are shown in Table 2.

Table 2. The changes of the selected geometrical parameters of the complex.

Interatomic distances (Å) of $H_2CO\cdots HF$			
$\Delta r(C=O)$	0.0057	$\Delta r(CH_3)$	-0.0039
$\Delta r(CH_2)$	-0.0047	$\Delta r(HF)$	0.0186

Table 3 has shown C=O and C–H stretching frequencies and intensities of the $H_2CO\cdots HF$ complex obtained both experimental and theory. The bending energy of the complex equals to –32.3 $kJ\cdot mol^{-1}$, r(H–F) atomic distance in the complex equals to 0.921 Å. Rotational constants (A, B, C) of the complex around the equilibrium position are calculated and equal to A=47.58, B=4.87, and C=4.46 GHz, respectively.

Table 3. Selected harmonic fundamental transition frequencies ν (cm^{-1}) and intensities S ($km\cdot mol^{-1}$) and experimental results of the $H_2CO\cdots HF$ complex and monomers.

Assignments	Harmonic		Experiment	
	ν	S	ν	S
C=O stretch	1758	75	1744	61
C–H in phase stretch	3017	47	2763	42
C–H out of phase	3120	44	2882	39

I. Conclusion

In this work, $H_2CO\cdots HF$ complex is studied by the help FTIR spectroscopy and quantum-chemical calculations. High resolution absorption spectra of the complex in C=O and in C-H regions are analyzed. In the C=O and in C-H stretching regions are analyzed in detail. Quantum chemical calculations are carried out in Gaussian 16 softwere with mp2/6-311++g(3df,3pd) approximation. Dipole moment calculated with CCSD(T)6311++G(3df,3pd) level of theory and it is equal to 3.81 D. The bending energy equals to –32.3 $kJ\cdot mol^{-1}$. Spectral parameters of the complex are determined and found a good agreement between experimental and computational results. The results of this work are coinciding with the results of the rielable relevant literatures. We believe that the results of this work can be used to better realize internal dynamics of the hydrogen bonded B···HF complexes in gas phase.

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Газ фазасида $H_2CO\cdots HF$ комплексни Фуръе инфрақизил спектроскопияси ва ҳисоблаш усуллари ёрдамида тадқиқ қилиш

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Газ фазасида $H_2CO\cdots HF$ комплекс ва унинг мономерларига тегишли бўлган C=O ва C−H соҳаларида юқори ажрата олиш 0.05 cm^{-1} да Bruker HR 125 спектрометри ёрдамида ютилиш спектрлари олинди. Ушбу комплекс ҳосил бўлиши натижасида HF валент тебраниш соҳасида C=O ва C−H валент тебранишларнинг ўзаро кучсиз таъсирлашиши натижасида мураккаб спектрал полоса намоён бўлмади. Ушбу mp2//6311++g(3df, 3pd) назариялар босқичида квант-химик ҳисоблашлар амалга оширилди ва комплекснинг геометрик, энергетик ва спектрал параметрлари ҳисобланди.

Калит сўзлар: ютилиш спектри, водород боғланиш, фторли водород, формальдегид.

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