https://doi.org/10.15407/ujpe65.4.304

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A STUDY OF $H_2CO\cdots HF$ COMPLEX BY ADVANCED QUANTUM MECHANICAL METHODS[1]

Our research is focused on the ab initio calculations of the equilibrium structures, binding energies, harmonic and anharmonic vibrational frequencies of a hydrogen-bonded complex, which is formed between formaldehyde H_2CO *and hydrogen fluoride HF, using the Gaussian 09 package of programs with full 6311++G(3df, 3pd) basis sets in the MP2 second-order perturbation theory and CCSD(T) methods. Harmonic and anharmonic vibrational frequencies and intensities of the* $H_2CO\cdots HF$ *complex were calculated by the Gaussian 16 package programs within the same approximation. Geometric changes and frequency shifts at the complex formation were evaluated. The* $H_2CO\cdots HF$ *complex formation energy and the dipole moment were calculated in the CCSD(T)6311++G(3df, 3pd) approximation to be equal, respectively, to 7.78 kcal/mol and 4.2 D. Changes of the geometric, spectral, and energetic parameters of the complex proved the existence of a stable hydrogen bond* $F–H\cdots O=CH_2$ *between the components.*

Keywords: stabilization geometry, hydrogen bond, harmonic and anharmonic frequencies, blue shift, complex formation energy.

1. Introduction

The phenomenon of hydrogen bonding is important in many physical, chemical, and biological systems. Therefore, much efforts have been made in experimental and theoretical investigations to offer reliable models for clarifying the nature of the hydrogen-bonded molecular complexes [1–4]. Formaldehyde H_2CO is the simplest among the aldehyde molecules and belongs to the C_{2v} symmetry group. In [2], the planar homodimer $(H_2CO)_2$ and $(H_2CO)_2\cdots HF$ complexes were investigated. The results are in excellent agreement with the results of the most accurate quantum mechanical calculations available in the literature. The optimized geometry of the $H_2CO\cdots HF$ complex and the values of the frequencies and intensities of fundamental transitions between vibrational states of this heterodimer were determined in [5–7]. In [8], the rotational and hyperfine spectra of the mentioned complex have been obtained using molecular beam electric resonance spectroscopy. Gas-cell microwave spectra of the $H_2CO\cdots X$ (X = HF, DF) and $D_2CO\cdots DF$ complexes were studied experimentally using a conventional microwave absorption cell. The ab initio study of the in-plane intermolecular stretching, bending, and libration vibrations of the complex were made, and the results are compared with the available experimental values [9]. Here, we will study the equilibrium structures, binding energies, harmonic and anharmonic vibrational frequencies of the formaldehyde molecule, H_2CO and its hydrogen-bonded complex $H_2CO\cdots HF$ formed with a hydrogen fluoride molecule. The quantum mechanical calculations of the complex are performed for the first time with the latest version of Gaussian 16 package of programs. We will make the comparative analysis of the binding energies of the $H_2CO\cdots HF$ complex in the isolated stabilized state at various levels of the theory. We will also prove that the anharmonic vibrational frequencies of the complex slightly differ from harmonic vibrational frequencies due to the account for anharmonic coupling constants. The basic

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[1] The paper was presented at XXIVth Galyna Puchkovska International School-Seminar “Spectroscopy of Molecules and Crystals” (August 25–30, 2019, Odesa, Ukraine).

purpose is to update electro-optical parameters of the $H_2CO\cdots HF$ complex in order to describe the recorded high-resolution IR spectra of the complex.

2. Computational Details

Calculations of the optimized geometry and harmonic vibrational frequencies of an $H_2CO\cdots HF$ heterodimer are performed with the help of the Gaussian 09 package of programs [10] at the MP2 level with the 6311++G(3df, 3pd) basis set. Anharmonic vibrational frequencies of the studied complex are calculated by means of the Gaussian 16 package of programs determined by the special “freq = anharmonic” key word [11]. The complex formation energies of the $H_2CO\cdots HF$ heterodimer are calculated in MP2/6311++G(3df, 3pd), and CCSD(T)6311++G(3df, 3pd) coupling cluster approximations, which are the “gold standard” in quantum chemistry.

3. Results and Discussion

3.1. Equilibrium configuration of the complex

The equilibrium geometry of the $H_2CO\cdots HF$ heterodimer calculated in the full MP2/6311++G(3df, 3pd) basis set is displayed in Fig. 1. Calculated geometric parameters of the studied complex are shown in Table 1. Therein, we can compare the selected geometric parameters of the titled complex obtained from the experiment and those calculated in the full and MP2/6311++G(2df, 2pd) basis sets.

One should note that the geometric parameters calculated using the full MP2/6311++G(3df, 3pd) basis set are in good agreement with those derived from the experiment [5]. The changes of the geometric parameters of the $H_2CO\cdots HF$ complex at the complex formation are displayed in Table 2. We have found that the length of the O$\cdots$HF hydrogen bond is equal to 1.7085 Å. The formation of a hydrogen bond between two species of the $H_2CO\cdots HF$ complex can be proved by the following factors: at the complex formation, the distances between the atoms in r(C=O) and r(HF) groups are slightly elongated, as compared to monomers, by 0.006 Å and 0.02 Å, respectively. The harmonic and anharmonic vibrational frequencies of the C=O stretching were shown to decrease by about 13 cm^{-1} and 12 cm^{-1}, respectively. These values exhibits a red shift in accordance with [7, 17]. On the contrary, r(C=H) bond length of a formaldehyde molecule appeared slightly shortened at the complex formation (by about 0.004–0.005 Å), and the calculated values of harmonic and anharmonic C–H stretching vibrational frequencies are increased by about 46 and 52 cm^{-1}, respectively, relative to those of the monomers. Therefore, it should be emphasized that, for the C–H symmetric and asymmetric stretching vibrations, the blue shift is observed at the complex formation. These results indicate the formation of the intermolecular hydrogen bond between O atom of formaldehyde and H atom of the hydrogen fluoride. In addition, a fluoride atom has the largest electronegativity, and formaldehyde has high proton affinity. The proton affinity of formaldehyde is equal to 167.8 $kcal\cdot mol^{-1}$ calculated on the MP2/aug-cc-pVTZ(2df, 2pd) level of the theory in [12], and the experimental value is 170.4 $kcal\cdot mol^{-1}$ [18–21]. The hydrogen bond length is equal to 1.7085 Å and is called the σ-type of a hydrogen bond. The Milliken atomic charges are distributed as O_4(–0.57470) and H_6 (0.54611) in the atoms of the “hydrogen bridge”. The calculated geometric parameters in the higher basis sets are in a better agreement with those derived from the experiment than the values calculated in the lower basis sets of the titled complex. Herein, the used computational theory levels are higher and more advanced as compared with the most of previously available calculations. In this work, the obtained optimized geometric and energetic parameters of the titled complex are in a good agreement with those calculated in the

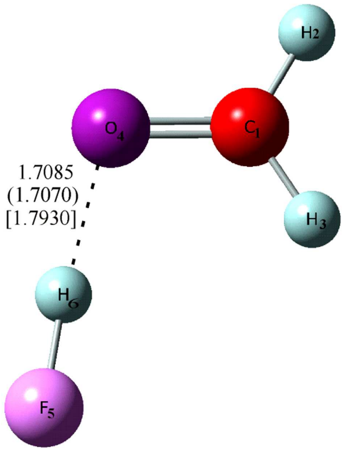

Fig. 1. Equilibrium configuration of the $H_2CO\cdots HF$ complex calculated at MP2/6311++G(3df, 3pd) level. The calculated values are in parentheses, and experimental values from [5] in square brackets

Table 1. **Optimum selected values of geometric parameters of an $H_2CO\cdots HF$ heterodimer calculated in the MP2/6311++G(3df, 3pd) basis set. The bond lengths are in Å, angles are in degrees**

$H_2CO\cdots HF$					
Interatomic distances (Å)					
$r(C_1O_4)$	$r(C_1H_2)$	$r(C_1H_3)$	$r(H_6F_5)$	$r(H_6O_4)$	$r(O_4F_5)$
1.2146	1.0955	1.0966	0.9352	1.7085 1.7070^b 1.7930^c	2.6316 2.6272^b $[2.659]^c$
Angles (deg)					
$\angle C_1O_4F_5$	$\angle C_1O_4H_6$	$\angle C_1H_6F_5$	$\angle O_4C_1H_2$	$\angle O_4C_1H_3$	$\angle H_2C_1H_3$
107.4 104.9^b $[109.5]^c$	111.2 109.5^b $[115]^c$	169.5 166.9^b $[164.5–170]^c$	120.9 120.8^b	121.3 121.4^b	117.8

Table 2. **The changes Δr of the selected geometric parameters of an $H_2CO\cdots HF$ heterodimer at the complex formation**

$H_2CO\cdots HF$			
Interatomic distances (Å)			
$\Delta r(C_1O_4)$	$\Delta r(C_1H_2)$	$\Delta r(C_1H_3)$	$\Delta r(HF)$
0.0058	–0.0048	–0.0037	0.0185

same approximations of the earlier reported scientific papers [5–7]. The blue shift of the C–H stretching frequency of a formaldehyde molecule at the complex formation was demonstrated. It is well known the blue shift of the ν(C–H) stretching vibrational mode is a non-conventional characteristic of the weak H-bonded molecular complexes. In [12], a significant blue shift of the ν(C–H) stretching vibrational mode of fluoroform of about 50–60 cm^{-1} is predicted with a decrease of its infrared intensity, contrary to the well-established red shift in conventional weak hydrogen bonded complexes.

The blue shift phenomenon of ν(C–H) stretching vibrations was first discovered by P. Hobza and his group, and the term "anti H bond" was proposed for the blue-shifted H-bond. In [13], the existence of this unusual H-bonding in a benzene dimer, as well as in C_6H_6–CH_4 and C_6H_6–$CHCl_3$ complexes, was confirmed using correlated *ab initio* computations. In [15], the blue shifting phenomenon has been explained by means of the infrared study of fluoroform + methyl fluoride mixtures in argon and nitrogen matrices. Recently, the main cause for the blue shift of the ν(C–H) stretching was properly explained by R. Gopi *et al.* [14, 16] through the investigation of CHF_3–HCl and CHF_3–H_2O complexes. The authors emphasized that those cumulative effects such as the remote delocalization, rehybridization, and intramolecular hyperconjugation at the formation of complexes are contributing factors for a decrease in the r(C–H) bond length and the observed blue shift of the ν(C–H) stretching frequency of the complexes. In [18], the nature of the weak hydrogen bond and its formation are explained. The book contains about 900 references to the literature on the hydrogen bond.

Notes to the table: *b*-values are calculated in the MP2/6311++G(2df, 2pd) basis set values, and *c*-experimental values taken from Ref. [5] are in square brackets.

In the titled complex, the ν(C–H) stretching frequency of a formaldehyde molecule calculated in the harmonic and anharmonic approaches are blue shifted at the complex formation by 46 and 51 cm^{-1}, respectively, as listed in Table 3. The line intensities at the infrared frequencies are slightly decreased and match the values available in the literature [12].

3.2. Calculated harmonic and anharmonic frequencies of the $H_2CO\cdots HF$ heterodimer

The harmonic and anharmonic vibrational frequencies of the $H_2CO\cdots HF$ complex are calculated in the

Table 3. **Harmonic and anharmonic frequencies ν (cm^{-1}) and intensities S (km·mol^{-1}), of the $H_2CO\cdots HF$ complex and the selected frequency and intensity changes (I^c/I^m) of monomers at the complex formation calculated on the MP2/6311++G(3df, 3pd) level of theory**

Assigment	Harmonic frequencies and intensities $\nu(S)$	$\Delta^{c-m}(I^c/I^m)$	Anharmonic frequencies and intensities $\nu(S)$	$\Delta^{c-m}(I^c/I^m)$
HF stretch	3751.5966 (956.4174)	–424.8123 (8.2)	3751.9948 (955.6995)	–424.3042 (8.2)
CH stretch sym	3017.1877 (47.8098)	45.5454 (0.7)	3118.9762 (41.0028)	50.758 (0.6)
CO stretch	1756.3979 (74.9563)	–13.1037	1756.2840 (74.9510)	–12.0858
CH_2 scissors	1544.8582 (17.0183)	–1.1350 (1.7)	1544.8361 (17.0268)	–1.3812 (1.6)
CH stretch asym	3119.0052 (40.9882)	68.2313 (0.5)	3118.9762 (41.0028)	74.1672 (0.5)
CH_2 rock	1282.8513 (9.6460)	9.5090	1282.8263 (9.6448)	9.0680
CH_2 wag	1212.6410 (7.7352)	11.0165 (1.2)	1212.6228 (7.7361)	9.4062 (1.2)
O···HF bend	803.1237 (149.6547)		802.8124 (149.5946)	
HF* oop wag	794.8007 (112.6166)		794.6014 (112.6522)	
O···H stretch	246.9593 (28.5155)		246.6790 (28.5043)	
HF* oop translation	221.2468 (2.2001)		221.1933 (2.1959)	
CO···H bend	79.2591 (13.8788)		79.2977 (13.8415)	

*oop-out of plane

MP2/6311++G(3df, 3pd) level of the theory. The anharmonic frequencies and intensities were determined by the special “freq = anharmonic” keyword. The calculated and selected vibrational frequency and intensity shifts are showed in Table 3.

The HF stretching frequency decreases down to 424 cm^{-1}, and its infrared intensity increases by about eight times at the complex formation relative to monomers. Therefore, the HF stretching vibration and its libration motions play a crucial role in the formation of the infrared absorption bands of the titled complex.

3.3. Stabilization energy of the $H_2CO\cdots HF$ complex

The stabilization energies of the $H_2CO\cdots HF$ complex are calculated through the difference between the energy of the complex and the sum of energies of the monomers. Then the binding energies were corrected for the basis set superposition error (BSSE), which was evaluated by the counterpoise method by Boys and Bernard [19–22]. The stabilization energy of the titled $H_2CO\cdots HF$ complex was predicted with and without inclusion of BSSE and ZPE corrections in the MP2/(full) 6311++G** approximation and was determined to be equal to 5.6 and 7.9 kcal · mol^{-1}, respectively. The complex formation energy was equal to 7.81 kcal · mol^{-1} calculated in the CCSD(T)6311++G(3df, 3pd) approximation. The dipole moment equals 4.2 D. The almost similar result evaluated as 3.1 D was given in [6]. We evaluated the complex formation energy of the $H_2CO\cdots HF$ complex in excellent agreement with the value obtained in the extended Dynning-type basis set aug-cc-pVTZ and equal to 7.9 kcal · mol^{-1} [12].

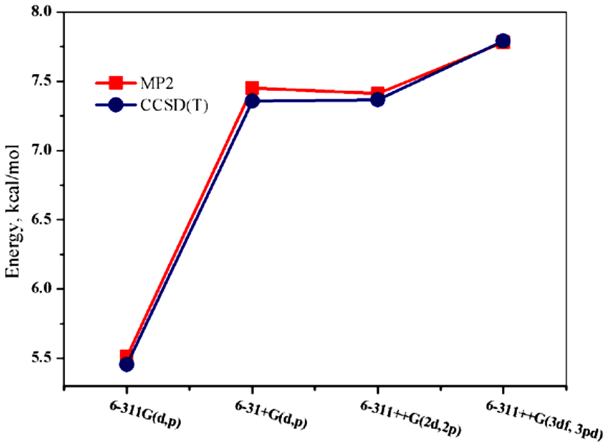

Fig. 2. Graphical presentation of the stabilization energies of the $H_2CO\cdots HF$ complex calculated in the CCSD(T) and MP2 methods as a function of the various basis sets

The graphical relationship between the complex formation energies and basis sets is shown in Fig. 2. In the figure, we can be see clearly that the stabilization energies are gradually increased with increasing the basis sets. When the basis sets approach the limit,

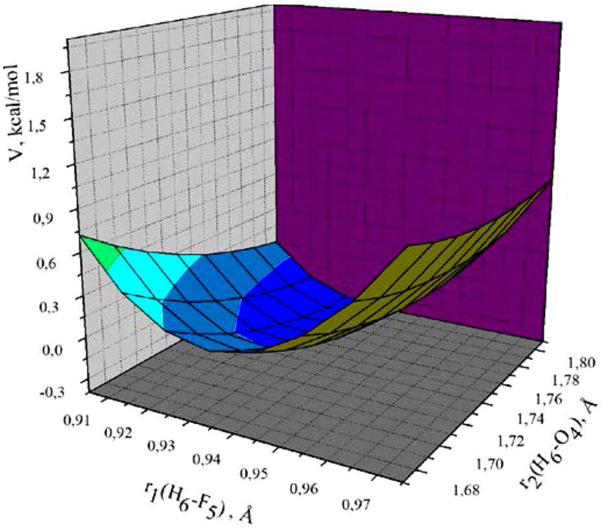

Fig. 3. 3D potential energy curves of the titled complex calculated in the MP2/6311++G(3df, 3pd) approximation. The potential energy is a function of the r(H_6–F_5) and r(H_6–O_4) atomic distances according to the optimaized structure of the titled complex (Fig. 1), respectively

the stabilization energies of the $H_2CO\cdots HF$ complex are the same in both methods.

Additionally, we have found three-dimensional potential energy curves as a function of the interspecies and intermolecular distances in the titled complex (see Fig. 3).

4. Conclusions

1. In the present work, the equilibrium configuration and binding energies, as well as the harmonic and anharmonic fundamental vibrational frequencies, of the $H_2CO\cdots HF$ heterodimer are calculated on the MP2/6311++G(3df, 3pd), and CCSD(T)6311++G(3df, 3pd) levels of theory. The changes in geometric parameters, shifts of the vibrational frequencies and intensities at the the complex formation are investigated and compared with reliable scientific predictions.

2. Fundamental transition intensities of the ν(H–F) stretching vibration are shown to increase by about eight times at the the complex formation. In addition, the ν(C–H) stretching frequency of a formaldehyde molecule is shown to be blue shifted by about 51 cm^{-1}, and its infrared intensity is decreased contrary to the most investigated conventional weak hydrogen-bonded complexes.

3. The obtained results can be used in order to explain the formation of the IR absorption bands of the $H_2CO\cdots HF$ heterodimer. On the other hand, based on this work, a reliable model presenting a better understanding of the nature of hydrogen-bonded molecular complexes can be offered.

The authors would like to thank for the kindly given posibility to use facilities of the Chair of Molecular Spectroscopy of the Physical Faculty at the Saint Petersburg State University of the Russian Federation. This work was supported by the Foundation of Republic of Uzbekistan for Basic Research, grant No. OT-F2-40.

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Received 03.11.19

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ВИВЧЕННЯ $H_2CO\cdots HF$ КОМПЛЕКСУ СУЧАСНИМИ МЕТОДАМИ КВАНТОВОЇ МЕХАНІКИ

Резюме

Виходячи з перших принципів, виконано розрахунки рівноважних структур, енергії зв’язку і частоти гармонійних і ангармонічних коливань комплексу з водневими зв’язками, утвореного формальдегідом H_2CO і фтористим воднем HF. Використано пакет програм Gaussian 09 з повним базисом 6311++G(3df, 3pd) у другому порядку теорії збурень і методи CCSD(T). Частоти та інтенсивності коливань розраховано з пакетом програм Gaussian 16 в тому самому наближенні. Знайдено зміни геометрії і зсуви частот при утворенні комплексу. Енергія утворення комплексу і дипольний момент знайдені в CCSD(T)6311++G(3df, 3pd) наближенні та є рівними, відповідно, 7,78 ккал/моль і 4,2 Д. Зміни геометричних, спектральних і енергетичних параметрів свідчать про наявність стабільного водневого зв’язку $F{-}H\cdots O{=}CH_2$ між компонентами.