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Calculation of the structure and IR absorption spectra of hydrogen-bonded complexes of methyl formate with hydrogen fluoride

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Equilibrium nuclear configurations of three dimers formed by the most stable conformer of a methyl formate molecule with a hydrogen fluoride molecule are calculated using the MP2/aug-cc-pVTZ quantum-chemical method and taking the basis set superposition error into account. The frequencies and intensities for the IR absorption bands of dimers are determined both in the harmonic and anharmonic approximations with the use of the second-order perturbation theory. The calculation method was tested in a calculation of the spectrum of an isolated methyl formate molecule and by comparison with experimental data. The changes in the geometrical parameters of monomers and the charges on atoms under the action of hydrogen bonds were analyzed. The shifts of vibrational frequencies of the monomers upon formation of dimers were calculated. The strongest absorption bands of dimers that can be used in detection of these complexes in spectroscopic experiments were determined.

Keywords: hydrogen bond, calculations of spectra of molecular complexes, anharmonic interactions.

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Introduction

Methyl formate $HCOOCH_3$, methyl ether of formic acid, is the simplest carboxylic acid ether. The methyl formate (MF) molecule is an isomer of molecules of acetic acid CH_3COOH and glycolaldehyde $CH_2(OH)CHO$. MF has a wide technological application, first of all, as a precursor in the synthesis of more complex organic compounds. Different processes of synthesis are possible because both the carbonyl and methoxy groups are present in MF. Therefore, interaction of MF molecules with molecules of other substances, in particular, upon formation of intermediate complexes, is of considerable interest. An additional interest in the study of this compound arose after the detection of its significant presence in interstellar medium [1,2].

The structure and spectra of the methyl formate molecule have been sufficiently well studied. In the ground electronic state this molecule has two stable, *cis* and *trans*, configurations separated by a barrier of about $59\,\mathrm{kJ\,mol^{-1}}$ in height [3,4]. The cis conformer with a zero dihedral angle O=COC is more stable. Information on the absorption spectrum of an isolated MF molecule is presented in [5]. Researchers paid less attention to experimental and theoretical studies of complexes formed by MF with other molecules. The possibility of forming complexes by MF molecules with HCl and H_2O molecules was studied in low-temperature matrix isolation experiments in argon at $T = 12\,\mathrm{K}$ [6]. Absorption spectra of mixtures of MF, HCl, and H_2O were recorded in the region of H−Cl, C=O, C−O, and C−H stretching vibrations. On the basis of the spectra obtained it was shown that stable complexes can be formed by the addition of proton donor molecules to oxygen atoms of both carbonyl and methoxy groups of methyl formate. The main conclusions of this work were confirmed by the quantum-chemical calculation [7]. The vibrational spectrum of complexes of HCOOCH3 with H_2O in solid neon at $T = 3\,\mathrm{K}$ was experimentally studied in the region of $80-6000\,\mathrm{cm^{-1}}$ [8]. The calculation in the harmonic approximation was carried out to interpret the spectra obtained. To our knowledge, complexes of MF with hydrogen fluoride have not been studied as yet in experiments. Two MF conformers, mono- and difluoro-substituted MF molecules, protonated systems, and dimers of MF with hydrogen fluoride were calculated in [9]. In the calculations the B3LYP method of the density functional theory and the 6-311++G(3df,3pd) set of atomic functions were used. The main attention was paid to the determination of equilibrium geometries of these systems, the proton affinity energy, intramolecular and intermolecular hyperconjugation, hybridization of atomic functions, and other aspects of the nature of the chemical bond. The quantum-chemical method adopted in the calculation was sufficiently reliable for these purposes. The frequencies of stretching vibrations H−F, C=O, and C−H of the HC=O group were determined in the harmonic approximation.

The purpose of this paper is to determine equilibrium nuclear configurations of MF molecules and the complexes formed by the most stable conformer with the hydrogen fluoride molecule at a higher quantum-chemical level than it was done previously and to calculate the frequencies and intensities for all fundamental absorption bands of the studied systems not only in the harmonic, but also in an anharmonic approximation. Information on anharmonic val-

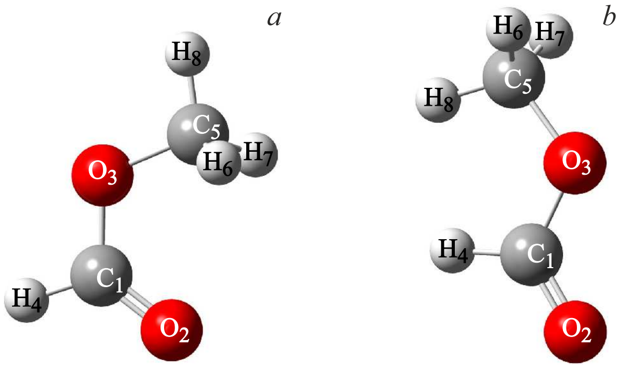

Figure 1. Structures of the *cis*-conformer (*a*) and *trans*-conformer (*b*) of the MF molecule $HCOOCH_3$.

ues of frequencies is necessary for the reliable interpretation of experimental spectra of the complexes, which can be obtained in the future. Analysis is performed of the binding energies of complexes and the changes in structural and spectral parameters upon their formation involving different oxygen atoms of MF. Correlations between the changes in geometrical parameters, electron density transfer, and vibrational frequency shifts upon formation of complexes are considered. Information on properties of complexes of MF with hydrogen fluoride obtained in this study can be useful in consideration of complexes of more complicated ethers of carboxylic acids, quantum-chemical calculations of which require the use of very powerful computers.

Adopted methods and the calculated results

Computational procedures

Quantum-chemical calculations of equilibrium nuclear configurations of two confirmers of methyl formate $HCOOCH_3$ and stable hydrogen-bonded heterodimers formed by the more stable *cis* methyl formate conformer with hydrogen fluoride were performed by the MP2/aug-cc-pVTZ method using the package of codes Gaussian 16 [10]. The equilibrium nuclear configurations were determined using the tight optimization procedure. Figure 1 shows the equilibrium nuclear configurations of *cis* and *trans* conformers of the MF molecule. The electronic energy of the cis conformer is 22.47 kJ mol^{-1} lower than the energy of the trans conformer. The equilibrium configurations of three stable *cis* $HCOOCH_3 \cdots HF$ heterodimers are shown in Fig. 2.

The equilibrium nuclear configurations of all considered systems have a symmetry plane and their properties are described by the C_s point symmetry group. In contrast to the study [9], the correction for the basis set superposition error was taken into account in the present paper by the counterpoise method [11]. The values 35.65, 35.80, and 24.48 kJ mol^{-1} were obtained in this work for the binding energies of heterodimers I, II, and III, respectively. The same relationship between the binding energies of the three dimers was obtained in [9]; however, the values 37.87, 38.99, and 24.85 kJ mol^{-1} obtained there are noticeably higher than our values. The dipole moments and charges on atoms in the formalism of natural bond orbitals were calculated using the „density = current“ option. The following values (in D) were obtained for the dipole moments: 1.8096 (HF), 1.8096 (*cis* MF), 4.2305 (*trans* MF), 3.6635 (heterodimer I), 4.7918 (heterodimer II), and 1.8141 (heterodimer III). Interestingly, the values of dipole moments obtained in this calculation for HF and *cis* $HCOOCH_3$ coincide to five significant figures. The calculated value of 1.8096 D of the HF dipole moment is close to the experimental value of 1.796 D [12]. The dipole moment value obtained for *cis* MF is in satisfactory agreement with a value of 1.99 D calculated with the MP2/cc-pVQZ method in [4] and the experimental value 1.765 D [13].

Anharmonic values of frequencies and intensities for the fundamental and overtone absorption bands of considered monomers and dimers were determined with the use of the vibrational second-order perturbation theory [14,15].

Geometrical parameters and charges on atoms

The calculated values of the most important internuclear separations and angles in the cis and trans conformers of MF molecules and dimers I, II, and III are listed in Table 1. The calculated equilibrium values of the H–F bond length in an isolated HF molecule and in dimers I, II, and III are equal to 0.9218, 0.9387, 0.9409, and 0.9346 Å, respectively. The values of bond lengths and

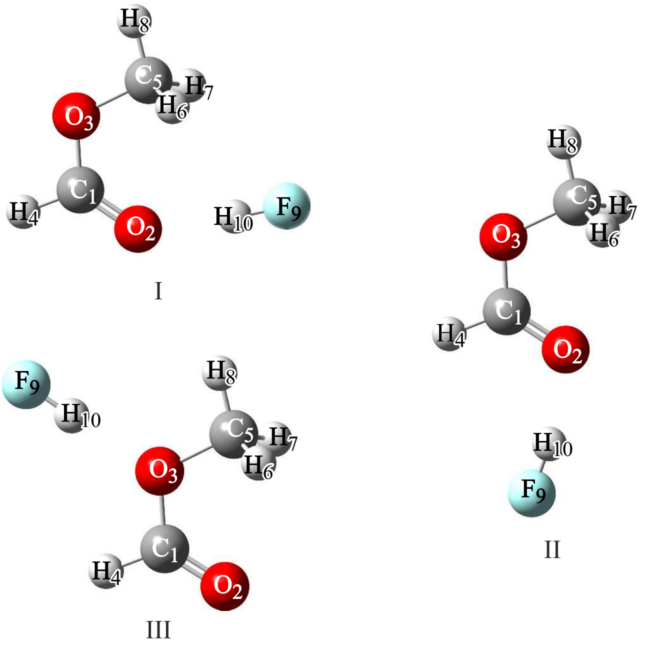

Figure 2. Structures of stable heterodimers I, II and III, formed by the *cis*-MF molecule with the HF molecule.

Table 1. Equilibrium values of internuclear distances (in Å) and angles (in degrees) in *cis*- and *trans*-conformers of MF and dimers I, II and III

Parameter	*cis*-MF	*trans*-MF	Dimer I	Dimer II	Dimer III
$R(C_1 = O_2)$	1.2079	1.2006	1.2153	1.2171	1.2027
$R(C_1 - O_3)$	1.3401	1.3473	1.3246	1.3242	1.3529
$R(C_1 - H_4)$	1.0933	1.1009	1.0912	1.0914	1.0928
$R(O_3 - C_5)$	1.4395	1.4307	1.4459	1.4443	1.4454
$R(C_5 - H_6)$	1.0870	1.0863	1.0863	1.0864	1.0860
$R(C_5 - H_8)$	1.0836	1.0901	1.0829	1.0830	1.0836
$R(O_2 \ldots H_{10})$	–	–	1.7279	1.7133	1.7635
$\angle O_2C_1O_3$	125.6	122.8	126.4	124.9	124.7
$\angle O_2C_1H_4$	125.1	124.2	123.5	124.4	126.0
$\angle C_1O_3C_5$	114.0	116.9	115.3	114.6	114.6
$\angle O_3C_5H_8$	105.4	111.2	105.1	105.2	105.4
$\angle H_6C_5H_8$	110.9	109.5	111.0	111.1	111.1
$\angle H_6C_5H_7$	109.3	110.0	109.6	109.7	109.8
$\angle H_{10}O_2C_1$	–		137.2	112.8	–
$\angle H_{10}O_3C_5$	–		–	–	120.5

angles presented in Table 1 coincide with the results of [9] to within 0.01 Å and 3°. The results of the calculation [4], where a sufficiently accurate *ab initio* method was used, are in better agreement with our results. However, the changes in bond lengths and angles upon transition from *cis* MF to *trans* MF are virtually the same in our calculation and in [4,9]. It is worth noting that the $C_1{=}O_2$ double bond in methyl formate are noticeably shorter than in acetone [16] and formaldehyde [17]. This bond becomes shorter upon transition from *cis* to *trans* methyl formate and also upon formation of dimer III. In contrast, $R(C_1{=}O_2)$ significantly increases upon formation of dimers I and II. The C_1–O_3 bond length experiences opposite changes in this series of systems. The presence of competition between the $C_1{=}O_2$ and C_1–O_3 bonds is evident. The $R(O_3$–$C_5)$ bond length of MF, as well as $R(C_1{=}O_2)$, becomes shorter upon *cis–trans* transition; however, it becomes longer upon formation of all the three dimers. The hydrogen bond in dimer III, which is weaker from the point of view of energy, is characterized by a larger value of $R(O_2 \cdots H_{10})$ and causes, as a rule, smaller changes in geometrical parameters than the hydrogen bonds in dimers I and II. Note that the values of $R(O \cdots H)$ presented in [9] for dimers I, II, and III are smaller than the values of Table 1 by 0.037, 0.036, and 0.025 Å, respectively.

Table 2 lists the values of charges on the atoms of isolated molecules and dimers I–III calculated in the natural bond orbital formalism [18]. This method allows more reliable values of the charges on atoms to be obtained than the widely used Mulliken method. The values of total dipole moments of dimers obtained in this calculation and presented in the preceding section noticeably differ from vector sums of dipole moments of monomers. This fact is indicative of a significant redistribution of electron density within monomers and charge transfer between them upon formation of the complexes. The significant distinction between the values of charges on the atoms C_1 and C_5 is apprehensible because these atoms are involved in fundamentally different chemical bonds. The C_1 atom forms the double bond and one and a half bond with more electronegative oxygen atoms, while the C_5 atom takes part in four bonds, in particular, with three less electronegative hydrogen atoms.

Table 2. Charges on the atoms of *cis*-MF and HF molecules and dimers I, II and III, calculated in the formalism of natural bond orbitals (in units of electron charge)

Atom	Monomers	Dimer I	Dimer II	Dimer III
C_1	0.629	0.657	0.649	0.638
O_2	−0.556	−0.607	−0.597	−0.530
O_3	−0.513	−0.491	−0.489	−0.560
H_4	0.114	0.127	0.135	0.125
C_5	−0.220	−0.226	−0.221	−0.216
H_6	0.182	0.190	0.187	0.188
H_8	0.182	0.189	0.188	0.191
F_9	−0.546	−0.582	−0.584	−0.571
H_{10}	0.546	0.553	0.545	0.546

The H–F bond polarity and electron population of the F atom increase upon formation of dimers I–III. An appreciable amount of electron density is transferred from MF to HF (0.029, 0.039, and 0.025 electron charge in dimers I–III, respectively). These changes are maximal upon formation of the strongest dimer II. It is remarkable that, in all cases, the oxygen atoms of the $O \cdots HF$ hydrogen bridges increase their electron population compared to the MF monomer. The main part of electron density that goes from MF to HF leaves the C_1 atom and the oxygen atom uninvolved in the formation of the hydrogen bond. The $C_1{=}O_2$ bond polarity increases on passing from the MF monomer to dimers I and II, but it decreases in dimer III. The C_1–O_3 bond polarity behaves in the opposite way. The

Table 3. Harmonic and anharmonic values of frequencies ν (in cm^{-1}) and intensities S (in parentheses, in km/mol) of fundamental absorption bands of *cis*-MF molecules and experimental [5] frequency values

Band	$\nu(S)_{\text{harm}}$	$\nu(S)_{\text{anh}}$	Experiment [5]
ν_1 ($C_5H_{6,7,8}$ tors)	155 (0.1)	137 (0.1)	–
ν_2 ($C_1O_3C_5$ bend)	308 (14)	316 (12)	318
ν_3 ($C_5O_3O_2H_4$ dih)	347 (26)	336 (25)	–
ν_4 ($O_2C_1O_3$ bend)	772 (7)	762 (8)	767
ν_5 (O_3C_5 str)	954 (27)	927 (26)	924
ν_6 (C_1H_4 oop libr)	1046 (0.1)	1025 (0.1)	–
ν_7 (H_6H_7 tors)	1187 (2)	1162 (1)	–
ν_8 ($C_5H_{6,7,8}$ wag)	1193 (87)	1161 (125)	1166
ν_9 (C_1O_3 str)	1247 (241)	1208 (165)	1207
ν_{10} (C_1H_4 ip libr)	1399 (1)	1370 (1)	1371
ν_{11} ($C_5H_{6,7,8}$ sym bend)	1479 (4)	1443 (4)	1445
ν_{12} ($C_5H_{6,7,8}$ asy bend)	1512 (10)	1469 (7)	1454
ν_{13} ($H_6C_5H_7$ sci)	1519 (10)	1474 (7)	–
ν_{14} ($C_1{=}O_2$ str)	1769 (289)	1738 (269)	1754
ν_{15} ($C_5H_{6,7,8}$ sym str)	3096 (26)	2996 (29)	2969
ν_{16} (C_1H_4 str)	3112 (35)	2964 (26)	2943
ν_{17} ($C_5H_{6,7}$ asy str)	3189 (12)	3051 (14)	3045
ν_{18} ($C_5H_{6,7;8}$ asy str)	3224 (7)	3086 (9)	–

changes in the polarity of the $C_1{=}O_2$ and $C_1{-}O_3$ bonds upon formation of dimers correlate with the changes in the lengths of these bonds noted above.

The frequencies and intensities of vibrational absorption bands of the HF and *cis* HCOOCH$_3$ monomers

The adopted calculation method yields the fundamental transition frequency and intensity values of an isolated HF molecule equal to 4122.9 cm^{-1} and 121 km mol^{-1} in the harmonic approximation and 3952.4 cm^{-1} and 118 km mol^{-1} in the anharmonic approximation with the use of the second-order perturbation theory [14,15]. The anharmonic frequency value is in good agreement with the experimental value of 3961.43 cm^{-1} [19].

Table 3 lists the harmonic and anharmonic values of frequencies and intensities for fundamental vibrational absorption bands of a *cis* MF molecule. The values of intensity are shown in parentheses. The absorption bands are numbered in the order of increasing harmonic frequency. For comparison, the experimental frequency values for the fundamental absorption bands [5] are also presented in Table 3. The following notations of the types of vibrations are used in Table 3 and below: wag — out-of-plane wagging of a group of atoms, str — stretching vibration, sci — scissoring bending vibration, bend — bending vibration, libr — librational vibration, tors — torsional vibration, sym and asy — symmetric and asymmetric vibrations, ip — in-plane bending vibration of atoms, oop — out-of-plane bending vibration of atoms, dih — dihedral angle vibration of a group of atoms.

One can see in Table 3 that most frequency values calculated for the fundamental transitions are in excellent agreement with the experimental results. The ν_8, ν_9, and ν_{14} vibrational bands are strongest in the MF absorption spectrum. These bands are associated, respectively, with wagging of the methyl group CH_3 as a whole and the changes in the $C_1{-}O_3$ and $C_1{=}O_2$ bond lengths. Note that the $\nu_{14}(C_1{=}O_2$ str) band of cis MF has a high intensity value, like the C=O band in an acetone molecule (243 km mol^{-1}) [20]. Only the C_5H_6 and C_5H_7 bond lengths change in the course of the $\nu_{17}(C_5H_{6,7}$ asy str) vibration. With the $\nu_{18}(C_5H_{6,7;8}$ asy str) vibration, the C_5H_6 and C_5H_7 bond lengths change in-phase with one another, but out-of-phase with the change in the C_5H_8 bond length.

The frequencies and intensities of vibrational absorption bands of dimers I, II, and III

The harmonic and anharmonic values of frequencies and intensities for fundamental absorption bands of dimers I, II, and III formed by molecules of *cis* MF and hydrogen fluoride are presented in Table 4. The absorption bands are numbered in the order of increasing harmonic frequency of absorption bands of dimer I. The assignment of absorption bands to a definite type of vibrations of atoms in complexes is sufficiently correct for all the dimers considered. However, in the case of dimer II, the adopted order of bands according to the frequency values is perturbed in the pairs of bands with close frequencies (ν_1, ν_2) and (ν_{17}, ν_{18}). In the case of dimer III, the structure of which differs more significantly from the structure of dimer I, the adopted order of absorption bands in Table 4 is perturbed in groups of bands $(\nu_{12}, \nu_{13}, \nu_{14})$ and (ν_{17}, ν_{18}).

Table 4. Harmonic and anharmonic values of frequencies ν (in cm^{-1}) and intensities S (in parentheses, in km/mol) of fundamental absorption bands of dimers I, II and III

Band	Dimer I		Dimer II		Dimer III	
	$\nu(S)_{\text{harm}}$	$\nu(S)_{\text{anh}}$	$\nu(S)_{\text{harm}}$	$\nu(S)_{\text{anh}}$	$\nu(S)_{\text{harm}}$	$\nu(S)_{\text{anh}}$
ν_1 (H-bond oop bend)	52 (0.4)	50 (0.4)	49 (< 1)	49 (< 1)	34 (6)	37 (5)
ν_2 (H-bond ip bend)	88 (3)	75 (2)	46 (2)	54 (2)	36 (8)	39 (8)
ν_3($C_5H_{6,7,8}$ tors)	191 (0.3)	169 (0.3)	157 (< 1)	141 (< 1)	151 (< 1)	132 (< 1)
ν_4 (H-bond str)	202 (12)	183 (13)	178 (2)	164 (3)	161 (2)	149 (3)
ν_5 ($C_1O_3C_5$ bend)	316 (11)	289 (5)	342 (45)	344 (33)	310 (15)	318 (12)
ν_6 ($C_5O_3O_2H_4$ dih)	359 (15)	346 (13)	361 (27)	351 (24)	329 (20)	321 (16)
ν_7 (F_9H_{10} oop libr)	691 (101)	612 (100)	717 (99)	638 (97)	583 (102)	516 (103)
ν_8 (F_9H_{10} ip libr)	693 (161)	603 (157)	757 (126)	657 (123)	693 (56)	604 (61)
ν_9 ($O_2C_1O_3$ bend)	779 (7)	771 (3)	796 (46)	788 (11)	774 (12)	761 (12)
ν_{10} (O_3C_5 str)	943 (26)	916 (26)	951 (22)	924 (22)	939 (58)	911 (54)
ν_{11} (C_1H_4 oop libr)	1056 (0.4)	1035 (0.3)	1060 (< 1)	1039 (< 1)	1041 (< 1)	1019 (< 1)
ν_{12} (H_6H_7 tors)	1181 (2)	1157 (2)	1188 (2)	1163 (1)	1189 (1)	1163 (1)
ν_{13} ($C_5H_{6,7,8}$ wag)	1205 (29)	1174 (46)	1204 (24)	1175 (42)	1232 (130)	1204 (41)
ν_{14} (C_1O_3 str)	1283 (275)	1241 (222)	1286 (290)	1243 (208)	1181 (239)	1138 (312)
ν_{15} (C_1H_4 ip libr)	1411 (2)	1388 (17)	1405 (3)	1373 (3)	1402 (< 1)	1372 (3)
ν_{16} ($C_5H_{6,7,8}$ sym bend)	1482 (10)	1447 (8)	1481 (7)	1446 (7)	1483 (2)	1447 (5)
ν_{17} ($H_6C_5H_7$ sci)	1517 (9)	1470 (8)	1518 (11)	1473 (7)	1521 (11)	1473 (4)
ν_{18} ($C_5H_{6,7,8}$ asy bend)	1520 (12)	1475 (10)	1514 (11)	1465 (8)	1511 (11)	1456 (5)
ν_{19} ($C_1{=}O_2$ str)	1754 (379)	1725 (325)	1745 (411)	1717 (326)	1784 (290)	1752 (258)
ν_{20} ($C_5H_{6,7,8}$ sym str)	3104 (12)	3003 (12)	3103 (17)	3002 (17)	3104 (17)	3004 (17)
ν_{21} (C_1H_4 str)	3140 (29)	2987 (29)	3141 (14)	2984 (15)	3122 (20)	2975 (18)
ν_{22} ($C_5H_{6,7}$ asy str)	3204 (5)	3066 (7)	3200 (8)	3062 (9)	3204 (7)	3065 (9)
ν_{23} ($C_5H_{6,7;8}$ asy str)	3234 (5)	3095 (6)	3234 (5)	3096 (6)	3230 (3)	3092 (4)
ν_{24} (F_9H_{10} str)	3757 (867)	3593 (680)	3703 (1171)	3538 (853)	3834 (905)	3671 (705)

The theoretical frequency values of fundamental absorption bands decrease with the anharmonicity taken into account, except for some low-frequency modes, whose spectral parameters are calculated using the second-order perturbation theory less accurately [21]. The largest decrease in frequency was predicted for librational vibrations of an HF fragment (down to 100 cm^{-1}), stretching vibrations of CH bonds (down to 157 cm^{-1}), and stretching vibrations of the HF bond (down to 165 cm^{-1}). The ν_{24} (F_9H_{10} str) bands of stretching vibrations are the strongest absorption bands in the spectra of the dimers considered. When the HF molecule enters dimers I–III, the harmonic H–F vibrational frequency is reduced by 366, 420, and 289 cm^{-1}, while the intensity value increases by a factor of 7.17, 9.68, and 7.48. In the calculation [9] the analogous decrease in the H–F vibrational frequency was equal to 444, 490, and 335 cm^{-1}. The anharmonic frequency of the H–F vibrational band is reduced by 359, 414, and 281 cm^{-1}, and the intensity value is enhanced by a factor of 5.76, 7.23, and 5.97 (Table 4). The decrease in frequency correlates with the binding energies of H-bond formation indicated above and the distances $R(\mathrm{F{-}H})$ and $R(\mathrm{O\cdots H})$ in the dimers. The ν_{24} (F_9H_{10} str) absorption bands of sufficiently strong dimers I and II are remote from strong bands of monomers and possess a high intensity, which can assist the detection of these complexes in a spectroscopic experiment. Two bands of CO bond vibrations (ν_{14} and ν_{19}) and two bands of librational vibrations of HF fragments (ν_7 and ν_8) in the spectra of dimers are also strong. The ν_{14} band of dimers I and II is shifted toward higher frequencies by about 34 cm^{-1} relative to the ν_9 band of MF, while in dimer III, in which the HF fragment is bonded to the oxygen atom of a methoxy group, the ν_{14} band decreases its frequency by 70 cm^{-1} and virtually doubles its intensity. The opposite signs of changes in frequency and intensity on passing from dimers I and II to dimer III are predicted for the ν_{19} band. Such behavior of spectral parameters of the ν_{14} and ν_{19} bands upon formation of dimers correlates with the changes in bond lengths $R(\mathrm{C_1{=}O_2})$ and $R(\mathrm{C_1{-}O_3})$ (Table 1). The stronger dimer II has higher values of librational frequencies, but the relationships between the spectral parameters of the ν_7 and ν_8 bands in dimers I and II are approximately the same. The difference between the frequencies of in-plane and out-of-plane librations of an HF fragment in the spectrum of dimer III is significantly larger than in the spectra of dimers I and II. This may be accounted for by a strong repulsion of the HF fragment from atoms H_4 and H_8, which enhances the in-plane librational frequency.

Of the absorption bands of C–H bond stretching vibrations, the band of a $C_1{-}H_4$ single bond vibration and the band of a symmetric vibration of three C–H bonds of the methyl group are strongest. The bands of C$-$H vibrations, except for the C_1-H_4 band, appreciably lower their intensity upon formation of heterodimers. Of four C$-$H vibrational bands, the C_1-H_4 band experiences a maximum blue shift from 11 to 23 cm^{-1}. It should be noted that along with the absorption bands of isolated *cis* MF, the frequencies and intensities of which significantly change upon formation of dimers, there exist spectral bands, whose parameters remain virtually unchanged. First of all, these are the bands $\nu_4(O_2C_1O_3$ bend), $\nu_6(C_1H_4$ oop libr), $\nu_7(H_6H_7$ tors), $\nu_{10}(C_1H_4$ ip libr), and $\nu_{11}(C_5H_{6,7,8}$ sym bend).

According to the second-order perturbative calculation, several overtone absorption bands can be observed in the spectra of dimers I$-$III, which lie in the infrared region and are sufficiently strong. These bands are associated with librational vibrations of HF. The following values of frequencies ν (in cm^{-1}) and intensities S (in $km\,mol^{-1}$) for these overtones were obtained using the perturbation theory: $\nu = 1110$ and $S = 77$ ($2\nu_8$ dimer I), $\nu = 1189$ and $S = 79$ ($2\nu_7$ dimer II), $\nu = 994$ and $S = 45$ ($2\nu_7$ dimer III), and $\nu = 1132$ and $S = 32$ ($2\nu_8$ dimer III).

Discussion of the results

Good agreement between the frequencies of IR absorption bands of a cis MF molecule calculated in this work with the experimental data [5] is indicative of a sufficiently high accuracy of the method adopted for the calculation of the structure and spectrum of molecular systems. The calculation of the equilibrium geometrical parameters of dimers *cis* MF$\cdots$HF with the basis set superposition error taken into account and the charges on atoms using the natural bond orbital method revealed the correlation between the amount of electron charges transferred between atoms upon formation of complexes and the changes in chemical bond lengths. Distinctions between these correlations were observed for the dimers formed by the addition of an HF fragment to an oxygen atom of the carbonyl or methoxy groups of MF. It is of interest to compare the correlations observed in this work between the changes in two different parameters on passing from one complex to another with the analogous correlations derived in [22]. The correlations obtained in our study between the changes in parameters $q_1 = R(\mathrm{F{-}H}) + R(\mathrm{O\cdots H})$ and $q_2 = (R(\mathrm{F{-}H}) - R(\mathrm{O\cdots H}))/2$ and between the binding energy of a complex ΔE and q_1 on passing between dimers I$-$III coincide with the results of [22]. As for the correlations between the changes in the pair of parameters ΔE and $\Delta A^{1/2}$ and the pair of parameters ΔE and $\Delta(A/\nu)^{1/2}$ (here, A and ν are intensity and frequency of the H$-$F stretching vibration band in a complex), our results for dimers II and III coincide with the correlations obtained in [22]. Dimer I does not conform to the same rule because its binding energy is almost equal to that of dimer II, but the H$-$F band in dimer I has a significantly lower intensity. It is possible that the correlations between the binding energies and the absorption band intensities derived in [22] are not valid for complexes formed by the addition of HF to different electron pairs of the same proton acceptor. It follows from the performed calculations that two dimers formed by the addition of HF to the carboxyl oxygen atom are sufficiently strong and can be observed in an experiment. These dimers can be detected even at low concentration because in their spectra there are several strong absorption bands which are significantly shifted from monomeric strong bands. The calculations showed which structural and spectral parameters of monomers are considerably affected by the addition of the HF molecule to a specific oxygen atom of MF and which parameters remain virtually unchanged. For example, the formation of a dimer with the carbonyl oxygen atom mainly affects the properties of the C_1H_4 bond, but practically does not affect the properties of CH bonds of the methyl group.

Conclusions

Geometrical parameters of equilibrium configurations of methyl formate and hydrogen fluoride molecules and stable 1 : 1 hydrogen-bonded heterodimers formed by these molecules were determined using Gaussian 2016 package of programs [10] in the MP2/aug-cc-pVTZ approximation with the basis set superposition error taken into account. The frequencies and intensities for the IR absorption bands of monomers and dimers were calculated in the harmonic approximation and with the anharmonicity taken into account using the second-order perturbation theory [14,15]. The reliability of the adopted calculation method was confirmed by good agreement of anharmonic frequency values of IR spectra of the MF and HF molecules with the experimental data. The frequency shifts and changes of intensities of absorption bands of monomers upon complexation were derived from comparison of the results of calculations of monomers and dimers using the same method. The correlations between the changes in interatomic separations and charges on atoms and vibrational frequency shifts caused by the hydrogen bonds were analyzed. Strong and sufficiently characteristic bands of heterodimers cis MF$\cdots$HF that can be used to detect these systems by spectroscopic methods were predicted.

Conflict of interest

The authors declare that they have no conflict of interest.

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