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Calculation of the structure and infrared absorption spectra of hydrogen-bonded complexes of methyl formate with water

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Equilibrium nuclear configurations of four heterodimers formed by the most stable cis conformer of a methyl formate molecule with a water molecule are calculated using the MP2/aug-cc-pVTZ method with the basis set superposition error taken into account. The geometrical parameters of the heterodimers, the binding energies, and the charges on atoms are determined. The frequencies and intensities for the IR absorption bands of heterodimers are calculated in the harmonic approximation and also in the anharmonic approximation with the use of the second-order perturbation theory. The strongest absorption bands of heterodimers that can be used to detect these complexes in an experiment were determined. The correlations were analyzed between the changes of geometrical parameters of monomers, charges on atoms, and shifts of vibrational frequencies arising upon formation of intermolecular hydrogen bonds. The calculated frequency shifts of vibrational absorption bands of monomers upon formation of heterodimers were compared with the data of a low-temperature experiment in solid neon.

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

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Introduction

Methyl ether $HCOOCH_3$ (methyl formate) of formic acid is the simplest carboxylic acid ether. Methyl formate (MF) is widely applied in diverse technological processes, for example, in synthesis of more complex organic compounds, because due to the presence of both the carbonyl and methoxy groups it can take part in different chemical reactions. Consequently, interaction of MF molecules with molecules of other compounds, in particular, formation of intermediate complexes by MF molecules, is of much current interest. Recently, attention of researchers to the study of MF was increased after the detection of its significant presence in interstellar medium [1,2]. For example, the infrared spectra of pure MF and MF in matrices containing H_2O, CO, H_2CO, and CH_3OH at temperature 15 K were studied experimentally in [3] for comparing them with the spectra of ice covering cosmic dust grains. The possibility of using MF as a source of hydrogen atoms for the purposes of hydrogen energetics was considered in [4]. An efficient and economical method was proposed for dehydrogenation of MF in a mixture with water in the presence of KOH and a ruthenium catalyst.

In the ground electronic state the MF molecule has two stable, *cis* and *trans*, conformers of which the *cis* conformer with the zero O=COC dihedral angle is more stable. The theoretical and experimental studies of molecular complexes of MF with the molecules of other compounds are few in number. In [5] 53 hydrogen bonded complexes formed by water molecules with molecules of simple organic compounds, including MF, were considered. The optimal configurations and the binding energies of stable complexes were determined using the method of the density functional theory B3LYP and the perturbative MP2 method with the medium-size 6-31++G(3d,p) set of atomic functions. For the pair H_2O–MF, formation of two complexes involving the oxygen atom of the carbonyl group and one complex with the methoxy oxygen atom of MF was predicted. One stable configuration was found for the *cis*-MF$\cdots H_2O$ complex in the calculation [6] using the B3LYP and MP2 methods with the 6-311G** set of atomic functions. Properties of the heterodimers formed by the water molecule with the molecules of $C_2H_4O_2$ isomers (acetic acid, glycolaldehyde, and MF) were compared in the recent paper [7] devoted to the study of hydrogen bonded complexes in the interstellar medium. The binding energies of heterodimers and changes of the O−H bond lengths in the H_2O monomer upon passing from the monomer to a complex were determined in the MP2/6-311++G(d,p) calculation. Only the configuration of the *cis*-MF$\cdots H_2O$ heterodimer with the H_2O monomer bonded to the carbonyl oxygen atom was considered. The methods of low-temperature matrix isolation in argon at $T = 12$ K were used in [8] to study possible complexes of methyl formate and methyl acetate with H_2O and HCl. Spectral absorption bands of the stretching vibrations C=O, C−O, C−H, and H−Cl were recorded in this work and ascribed to the complexes MF$\cdots H_2O$, MF$\cdots$HCl, MF$\cdots H_2O\cdots$HCl, and MF$\cdots(HCl)_2$ and to the analogous complexes involving the molecules of methyl acetate. Analysis of the spectra obtained showed that such intermolecular complexes can arise on addition of the proton-donor molecules to oxygen atoms of both carbonyl and methoxy groups of ether molecules. The conclusions of this paper on the structure of the considered complexes and the strength of different hydrogen bonds were confirmed by the results of the quantum-chemical calculation [9] of the complexes of formic acid and methyl acetate molecules with HF and HCl molecules carried out using the 4-31G and 6-31G** basis sets. Vibrational absorption spectra of a mixture of MF with water were recorded in solid neon at $T = 3\,\mathrm{K}$ [10]. With the concentration effects taken into account, the spectral bands in the region of $80-6000\,\mathrm{cm}^{-1}$ were assigned to absorption by free MF and H_2O molecules, their homodimers, and complexes $\mathrm{MF}\cdots\mathrm{H_2O}$ and $\mathrm{MF}\cdots(\mathrm{H_2O})_2$. On the basis of the MP2/aug-cc-pVTZ calculation, the possibility of existence of three stable configurations of the $\mathrm{MF}\cdots\mathrm{H_2O}$ complexes, predicted earlier in [5], was confirmed and three stable forms of the $\mathrm{MF}\cdots(\mathrm{H_2O})_2$ trimer were found. Vibrational frequencies of the systems considered in [10] were determined in the harmonic approximation, which allowed the authors to estimate the frequency shifts of spectral bands upon formation of the complexes.

The purpose of this paper is to refine the data on the equilibrium nuclear configurations of the heterodimers formed by the molecules of the most stable *cis* conformer of MF with water molecules and to calculate the frequencies and intensities for the fundamental absorption bands of such heterodimers with the anharmonic interactions taken into account. Information on the anharmonic values of spectral parameters is necessary for more reliable interpretation of experimental spectra of the complexes than on the basis of harmonic calculations. The main objective of this calculation is to find out the possibility of predicting the shifts of vibrational frequencies of the monomers upon formation of the hydrogen-bonded complexes by means of anharmonic calculations of vibrational spectral parameters of monomers and complexes using the second-order perturbation theory [11,12]. The values of frequency shifts of the cis methyl formate and water molecules calculated in this paper will be compared to the experimental results [10]. The changes of spectral and structural parameters of the monomers upon complexation involving different oxygen atoms of MF will also be analyzed in this paper. Apart from purely spectroscopic aspects, comparison of the results calculated for different *cis*-$\mathrm{MF}\cdots\mathrm{H_2O}$ heterodimers will allow us to reveal correlations between the changes in the geometrical parameters and vibrational frequencies of monomers and to discuss the electron density transfer within monomers and between them caused by the formation of complexes.

Adopted methods and the calculated results

Computational procedures

Equilibrium nuclear configurations of stable hydrogen-bonded heterodimers *cis*-$\mathrm{MF}\cdots\mathrm{H_2O}$ were determined by the MP2/aug-cc-pVTZ method with the basis set superposition error taken into account. The calculation was carried out using the package of codes Gaussian 16 [13]. Recently this method was successfully used in calculations of the structure and infrared absorption spectrum of related heterodimers *cis*-$\mathrm{MF}\cdots\mathrm{HF}$ [14] and trimers *cis*-$\mathrm{MF}\cdots(\mathrm{HF})_2$ [15]. Four stable configurations for *cis*-$\mathrm{MF}\cdots\mathrm{H_2O}$ heterodimers obtained by using the tight procedure to optimize structural parameters are shown in Fig. 1. Apart from three configurations found in [5,10] and shown in Fig. 1 with numbers I, II, and III, stable configuration IV was obtained. In this configuration, as in configuration III, the oxygen atom of the methoxy group takes part in the formation of an intermolecular hydrogen bond. The equilibrium nuclear configurations of heterodimers I, II, and IV have a symmetry plane and their properties are described by the C_s point group. In configuration III, the MF monomer virtually retains the C_s symmetry, the dihedral angles made by the nuclei of atoms H_8, C_5, O_3, C_1, H_4, and O_2 differ from 0° or 180° by no more than 0.25°; however, the nuclei of atoms of the monomer H_2O are significantly out of the symmetry plane. The binding energies of heterodimers I–IV in the equilibrium nuclear configurations are equal to -24.30, -21.92, -14.33, and $-14.79\,\mathrm{kJ\,mol^{-1}}$, respectively, and take the values -16.68, -15.19, -9.12, and $-9.42\,\mathrm{kJ\,mol^{-1}}$ with the zero-point energies taken into account. These energies are smaller in magnitude by about $10\,\mathrm{kJ\,mol^{-1}}$ than the binding energies of the analogous configurations of heterodimers *cis*-$\mathrm{MF}\cdots\mathrm{HF}$ [14]. The option „density = current“ was adopted to calculate the dipole moments and charges on atoms in the formalism of natural bond orbitals for monomers and heterodimers. The following values (in D) were obtained for the dipole moments: 1.859 (H_2O), 1.810 (*cis* MF), 1.403 (heterodimer I), 2.181 (heterodimer II), 3.280 (heterodimer III), and 1.670 (heterodimer IV). The calculated value of the dipole moment of an isolated water molecule is in excellent agreement with the experimental value of 1.8473 D [16] and the theoretical value of 1.8549 D [17]. Our dipole moment value 1.810 D obtained for an isolated *cis*-MF molecule differs insignificantly from the experimental value of 1.765 D [18].

Anharmonic values of frequencies and intensities for the fundamental absorption bands of the considered heterodimers were obtained using the vibrational second-order perturbation theory VPT2 [11,12] and the *ab initio* MP2/aug-cc-pVTZ method. Real frequency values were obtained for all fundamental spectral transitions in the calculations of the spectra of monomers and 1 : 1 dimers in the harmonic approximation. The shifts of vibrational frequencies and the changes of intensities of spectral transitions upon complexation were determined from comparison of the spectral parameters of complexes and monomers calculated in the same approximation. To control the stability of the spectral parameters calculated using the VPT2 method, all the calculations were also

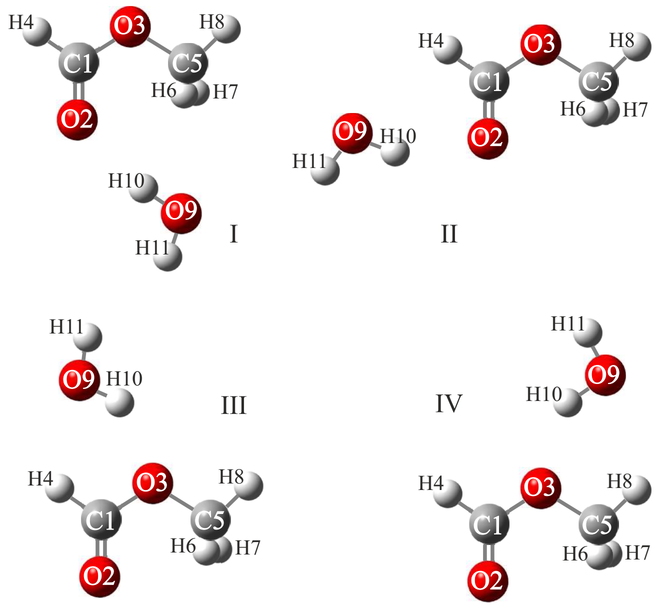

Figure 1. Structures of stable heterodimers I–IV formed by the *cis* methyl formate molecule with the H_2O molecule.

performed with the use of the MP2/6-311++G(3df,3pd) approximation.

Geometrical parameters and charges on atoms

The calculated values of the most important internuclear distances and angles in the *cis*-MF molecule and heterodimers *cis*-MF$\cdots H_2O$ I–IV are presented in Table 1. The values of distance $R(O{-}H) = 0.9614$ Å and angle HOH = 104.1° were obtained for an isolated water molecule. These values are very close to the results 0.95782 Å and 104.48° of the high-accuracy calculation [19]. The values of bond lengths and angles in *cis*-MF listed in Table 1 coincide with the results of [20] derived by the MP2/cc-pVQZ method to within 0.005 Å for the CO bonds, 0.002 Å for the CH bonds, and 0.1° for the angles OCO, COC, and OCH. It is reasonable that the $O_9{-}H_{10}$ bond length in the $O_2\cdots H_{10}{-}O_9$ hydrogen bridge is considerably longer in all the four heterodimers than the O–H bond length in an isolated H_2O monomer. The other O–H bond of the water molecule becomes slightly shorter upon formation of the heterodimers. These changes are more pronounced upon formation of the strongest complexes I and II. As for the internal chemical bonds of *cis*-MF, the bond lengths between the carbon and oxygen atoms undergo the greatest changes upon formation of the heterodimers. The $C_1{=}O_2$ bond becomes considerably longer and, consequently, weaker in heterodimers I and II, whereas its length becomes shorter in heterodimers III and IV. The $C_1{-}O_3$ bond length changes in the opposite way upon formation of complexes involving the carbonyl or methoxy oxygen atom. The $O_3{-}C_5$ bond of methyl formate weakens upon formation of all the four complexes. Its length increases most significantly in heterodimers I and IV, where the oxygen atom of the water molecule is close to the methyl group. The large difference between the distances $R(O_2\cdots H_{10})$ and $R(O_3\cdots H_{10})$ should be noted, which reaches 0.014 Å and is indicative of a significant distinction between the strengths of hydrogen bonds involving different oxygen atoms. The observed changes in the interatomic separations upon formation of *cis*-MF$\cdots H_2O$ complexes are analogous to the changes in the geometrical parameters predicted earlier [14] for the *cis*-MF$\cdots$HF heterodimers, but somewhat smaller in magnitude. In each of the complexes the distances between the oxygen atom of water and the hydrogen atom H_4 or hydrogen atoms of the methyl group of methyl formate are rather small: $R(O_9\cdots H_6) = R(O_9\cdots H_7) = 2.7522$ Å (heterodimer I), $R(O_9\cdots H_4) = 2.6720$ Å (heterodimer II), $R(O_9\cdots H_4) = 2.5874$ Å (heterodimer III), and $R(O_9\cdots H_8) = 2.5861$ Å (heterodimer IV).

Table 2 lists the values of charges (in units of electron charge) on the atoms of isolated *cis*-MF and H_2O molecules and heterodimers I–IV, calculated in the formalism of natural bond orbitals [21]. These data provide information on the electron density distribution between the atoms, the polarity of chemical bonds and the electron density transfer within monomers and between them upon formation of complexes. The bonds $C_1{=}O_2$, $C_1{-}O_3$, $O_9{-}H_{10}$, and $O_9{-}H_{11}$ are most polar in the considered dimers. The $C_1{=}O_2$ bond polarity increases on passing from the isolated *cis*-MF molecule to heterodimers I and II, but becomes smaller in heterodimers III and IV. The $C_1{-}O_3$ bond polarity behaves in the opposite way. In H_2O the polarity increases most significantly in the O–H bond that is a part of the hydrogen bridge.

The electron density is transferred from *cis*-MF to H_2O upon formation of the considered 1 : 1 dimers: 0.0106, 0.0140, 0.0070, and 0.0071 electron charge is transferred in heterodimers I–IV, respectively. The amount of electron charge transferred from *cis*-MF to the proton donor in the *cis*-MF$\cdots H_2O$ complexes is approximately three times as small as upon formation of the stronger *cis*-MF$\cdots$HF heterodimers [14].

The electron population on the oxygen atom of water increases upon formation of heterodimers I–IV by 0.0273 (I), 0.0267 (II), 0.0152 (III), and 0.0177 (IV). The increase of electron charges on the oxygen atoms of *cis*-MF that take part in the H-bond formation is also significant: 0.0396 (I), 0.0331 (II), 0.0299 (III), and 0.0255 (IV). The main part of electron density transferred from MF to H_2O is lost by the C_1 and O_3 atoms in dimer I, the H_4 atom in dimers II and III, and the H_8 atom in dimer IV. The electron charge on the H_{10} atom of the water molecule that is a part of the H-bond bridge decreases relative to the charge in a free H_2O monomer by 0.0173 and 0.0126 upon formation of strong heterodimers I and II and less significantly by 0.0065 and 0.0063 upon formation of heterodimers III and IV. Analysis of natural bond orbitals shows that the changes in the electron charge on atoms C and O upon

Table 1. Equilibrium values of internuclear distances (in Å) and angles (in degrees) in the *cis*-MF monomer and *cis*-MF$\cdots$$H_2O$ heterodimers I–IV, as well as the dipole moments μ (in D) and binding energies D_0 (in kJ mol^{-1}) of heterodimers with the zero-point energies taken into account

Parameter	*cis*-MF	Dimer I	Dimer II	Dimer III	Dimer IV
$R(C_1{=}O_2)$	1.2079	1.2129	1.2139	1.2060	1.2058
$R(C_1\text{-}O_3)$	1.3401	1.3293	1.3324	1.3504	1.3439
$R(C_1\text{-}H_4)$	1.0933	1.0924	1.0922	1.0923	1.0936
$R(O_3\text{-}C_5)$	1.4395	1.4455	1.4409	1.4404	1.4457
$R(C_5\text{-}H_6)$	1.0870	1.0863	1.0868	1.0868	1.0865
$R(C_5\text{-}H_8)$	1.0836	1.0832	1.0834	1.0838	1.0836
$R(O_9\text{-}H_{10})$	–	0.9686	0.9688	0.9650	0.9651
$R(O_9\text{-}H_{11})$	–	0.9606	0.9603	0.9608	0.9608
$R(O_2\cdots H_{10})$	–	1.9680	1.9948	–	–
$R(O_3\cdots H_{10})$	–	–	–	2.1081	2.0863
$\angle O_2C_1O_3$	125.6	126.1	125.1	124.7	125.4
$\angle O_2C_1H_4$	125.1	124.1	124.5	126.1	125.3
$\angle C_1O_3C_5$	114.0	114.8	114.3	114.0	114.4
$\angle O_3C_5H_8$	105.4	105.1	105.3	105.6	105.2
$\angle H_6C_5H_8$	110.9	111.0	111.0	110.9	111.3
$\angle H_6C_5H_7$	109.3	109.3	109.4	109.4	109.6
$\angle H_{10}O_2C_1$	–	135.9	99.7	–	–
$\angle H_{10}O_3C_5$	–	–	–	142.1	102.6
$\angle H_{10}O_9H_{11}$	–	104.6	105.0	105.0	104.9
μ	1.810	1.403	2.181	3.280	1.670
D_0	–	−16.68	−15.19	−9.12	−9.42

formation of 1 : 1 dimers occur primarily on the $2p$ orbitals, while the population of the $2s$ orbitals virtually does not change.

Frequencies and intensities of the vibrational absorption bands of *cis*-MF$\cdots$$H_2O$ dimers I and II

The *ab initio* calculation method adopted in this paper allowed us earlier [14] to determine the vibrational frequencies of *cis*-MF with the accuracy sufficient for reliable interpretation of experimental spectra. The following values of frequencies (in cm^{-1}) and intensities (in parentheses, in km mol^{-1}) were obtained with the anharmonic interactions taken into account by the VPT2 method in the MP2/aug-cc-pVTZ approximation for the fundamental spectral transitions of an isolated water molecule: 1578 (72) (bending vibration), 3654 (4) (symmetric stretching vibration), and 3768 (72) (antisymmetric stretching vibration). These theoretical frequency values are in good agreement with the experimental data 1594.59, 3656.65, and 3755.79 cm^{-1} [22].

The harmonic and anharmonic values of frequencies and intensities for the fundamental IR absorption bands of heterodimers I and II formed by the molecules of *cis* methyl formate and water are shown in Table 3. Table 3 also lists the anharmonic frequency values of the vibrational absorption bands of an isolated *cis*-MF molecule calculated in [14], which are necessary to determine the frequency shifts upon complexation. Anharmonic values of spectral parameters are not presented for three low-frequency transitions of the dimers because they are not calculated accurately enough using the second-order perturbation theory. The possibility of such computational effects is discussed, for example, in [23]. The absorption bands are numbered in the order of increasing harmonic frequency of the absorption bands of dimers. The following notations of the types of vibrations are used in Table 3 and below: wag — out-of-plane wagging

Table 2. Charges on the atoms of free *cis* methyl formate and water molecules and *cis*-MF$\cdots$H$_2$O dimers I–IV in the formalism of natural bond orbitals

Atom	Molecules	Dimer I	Dimer II	Dimer III	Dimer IV
C_1	0.6294	0.6462	0.6360	0.6282	0.6343
O_2	−0.5561	−0.5957	−0.5892	−0.5485	−0.5450
O_3	−0.5132	−0.4998	−0.5010	−0.5431	−0.5387
H_4	0.1136	0.1194	0.1373	0.1371	0.1136
C_5	−0.2201	−0.2263	−0.2202	−0.2166	−0.2232
H_6	0.1821	0.1908	0.1834	0.1844	0.1832
H_8	0.1821	0.1850	0.1844	0.1810	0.1998
O_9	−0.9296	-0.9569	−0.9563	−0.9448	−0.9442
H_{10}	0.4648	0.4821	0.4774	0.4713	0.4711
H_{11}	0.4648	0.4642	0.4649	0.4665	0.4660

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, and dih — dihedral angle vibration of a group of atoms.

One can see in Table 3 that the anharmonic frequency values for the fundamental transitions are always lower than the harmonic values, except for the ν_6(C$_1$O$_3$C$_5$ bend) transition in heterodimer I. In calculations of heterodimers I and II, taking the anharmonic effects into account lowers the transition frequencies most significantly for the ν(H$_2$O ip rock) bending vibrations and the stretching vibrations of the C–H and O–H bonds. The bands of C$_1$–O$_3$, C$_1$=O$_2$, and O–H stretching vibrations are strongest. These transitions become weaker when intramode and intermode anharmonic effects are taken into account, in particular, because of the intensity transfer to other transitions. It should be noted that the intensities of the bands of O–H stretching vibrations in the *cis*-MF$\cdots$H$_2$O dimers are several times lower than the intensity of the analogous H–F vibrational band in the stronger *cis*-MF$\cdots$HF dimers [14]. The ν_{26} vibration in *cis*-MF$\cdots$H$_2$O dimers I and II is a perturbed symmetric stretching vibration of the water molecule in which the R(O$_9$–H$_{10}$) bond length changes with a considerably larger amplitude than the R(O$_9$–H$_{11}$) bond length. The ν_{27} vibration is a perturbed antisymmetric stretching vibration of the water molecule in which the R(O$_9$–H$_{10}$) bond length changes with a smaller amplitude than the R(O$_9$–H$_{11}$) bond length. The symmetric vibrational band in a free water molecule is significantly weaker and has a lower frequency than the antisymmetric stretching vibrational band. In heterodimers I and II the absorption band of the ν_{26} perturbed symmetric vibration also has a lower frequency, because the corresponding vibration retains the symmetricity to some extent; however, its intensity becomes higher than the intensity of the ν_{27} band, because the O$_9$–H$_{10}$ bond is involved in the O$_9$–H$_{10}\cdots$O$_2$ hydrogen bridge. Upon formation of heterodimers I and II the total intensity of two absorption stretching bands of the water molecule increases by factors of 3.71 and 3.82. At the same time, the intensity of the absorption band of the internal bending vibration of water noticeably decreases.

The frequency shifts $\nu_{\mathrm{monomer}}-\nu_{\mathrm{dimer}}$ upon formation of heterodimers calculated using the VPT2 perturbation theory for the bands of the bending, symmetric stretching, and antisymmetric stretching vibrations of H$_2$O are equal to -16, 78, and 31 cm^{-1} for heterodimer I and -14, 97, and 31 cm^{-1} for heterodimer II. These results are in good agreement with the experimental data obtained in solid neon at $T = 3$ K [10]: -17, 85, and 36 cm^{-1} for heterodimer I and -12, 93, and 30 cm^{-1} for heterodimer II. The ratios of band intensities for the symmetric and antisymmetric vibrations of H$_2$O to the band intensity of the bending vibration (3.38 and 1.94 for heterodimer I and 3.25 and 1.51 for heterodimer II) are also in satisfactory agreement with the experimental estimates of these ratios (5.53 and 2.33 for heterodimer I and 3.29 and 1.53 for heterodimer II) [10]. The changes in the frequencies of internal vibrations of *cis*-MF upon formation of heterodimers I and II are less significant than the changes of H$_2$O frequencies. Except for the C$_1$–O$_3$ vibrational frequencies in heterodimers I and II and the C$_1$–H$_4$ vibration in heterodimer II, they do not exceed 12 cm^{-1} in magnitude. The frequency shifts of cis-MF upon formation of heterodimer I were determined experimentally in [10] for nine absorption bands. The theoretical values of frequency shifts in heterodimer I, obtained with the data of Table 3, coincide in sign with the

Table 3. Harmonic and anharmonic values of frequencies ν (in cm^{-1}) and intensities S (in parentheses, in km mol^{-1}) of fundamental absorption bands of *cis*-MF$\cdots$H$_2$O dimers I and II and anharmonic values of frequencies ν (in cm^{-1}) of absorption bands of the isolated *cis*-MF monomer [14]

Dimer I			*cis*-MF	Dimer II		
Band	$\nu(S)_{\text{harm}}$	$\nu(S)_{\text{anh}}$	ν_{anh}	Band	$\nu(S)_{\text{harm}}$	$\nu(S)_{\text{anh}}$
ν_1(H-bond oop bend)	36 (0.02)	–	–	ν_1(H-bond oop bend)	27 (32)	–
ν_2(H-bond ip bend)	92 (9)	–	–	ν_2(O_9H_{11} oop libr)	56 (95)	–
ν_3(O_9H_{11} oop libr)	140 (120)	–	–	ν_3(H-bond ip bend)	60 (14)	–
ν_4(H-bond str)	155 (7)	138 (13)	–	ν_4(H-bond str)	148 (1)	102 (4)
ν_5($C_5H_{6,7,8}$ tors)	191 (2)	173 (5)	–	ν_5($C_5H_{6,7,8}$ tors)	157 (0.02)	126 (0.2)
ν_6($C_1O_3C_5$ bend)	311 (17)	380 (107)	–	ν_6($C_1O_3C_5$ bend)	321 (83)	314 (94)
ν_7(H_2O ip rock)	333 (125)	218 (35)	–	ν_7($C_5O_3O_2H_4$ dih)	356 (18)	341 (7)
ν_8($C_5O_3O_2H_4$ dih)	351 (14)	338 (9)	–	ν_8(H_2O ip rock)	362 (119)	271 (81)
ν_9(O_9H_{10} oop libr)	519 (73)	472 (35)	–	ν_9(O_9H_{10} oop libr)	499 (72)	396 (30)
ν_{10}($O_2C_1O_3$ bend)	775 (5)	766 (5)	762	ν_{10}($O_2C_1O_3$ bend)	778 (7)	768 (7)
ν_{11}(O_3C_5 str)	944 (28)	918 (27)	927	ν_{11}(O_3C_5 str)	955 (27)	927 (25)
ν_{12}(C_1H_4 oop libr)	1052 (0.2)	1031 (0.1)	1025	ν_{12}(C_1H_4 oop libr)	1061 (0.2)	1045 (0.5)
ν_{13}(H_6H_7 tors)	1178 (1.4)	1156 (1.2)	1162	ν_{13}(H_6H_7 tors)	1188 (1.6)	1159 (1.5)
ν_{14}($C_5H_{6,7,8}$ wag)	1202 (41)	1173 (79)	1161	ν_{14}($C_5H_{6,7,8}$ wag)	1199 (51)	1164 (73)
ν_{15}(C_1O_3 str)	1271 (252)	1235 (173)	1208	ν_{15}(C_1O_3 str)	1264 (299)	1223 (218)
ν_{16}(C_1H_4 ip libr)	1406 (2)	1379 (2)	1370	ν_{16}(C_1H_4 ip libr)	1408 (4)	1366 (1)
ν_{17}($C_5H_{6,7,8}$ sym bend)	1481 (9)	1446 (8)	1443	ν_{17}($C_5H_{6,7,8}$ sym bend)	1479 (5)	1440 (5)
ν_{18}($H_6C_5H_7$ sci)	1516 (18)	1468 (10)	1474	ν_{18}($C_5H_{6,7,8}$ asy bend)	1513 (10)	1458 (5)
ν_{19}($C_5H_{6,7,8}$ asy bend)	1518 (12)	1472 (9)	1469	ν_{19}($H_6C_5H_7$ sci)	1519 (11)	1477 (8)
ν_{20}($H_{10}O_9H_{11}$ bend)	1647 (80)	1594 (53)	–	ν_{20}($H_{10}O_9H_{11}$ bend)	1642 (123)	1592 (61)
ν_{21}($C_1{=}O_2$ str)	1758 (329)	1731 (308)	1738	ν_{21}($C_1{=}O_2$ str)	1751 (287)	1715 (285)
ν_{22}($C_5H_{6,7,8}$ sym str)	3104 (14)	3001 (16)	2996	ν_{22}($C_5H_{6,7,8}$ sym str)	3098 (21)	2998 (20)
ν_{23}(C_1H_4 str)	3124 (36)	2970 (31)	2964	ν_{23}(C_1H_4 str)	3134 (12)	2983 (12)
ν_{24}($C_5H_{6,7}$ asy str)	3203 (6)	3063 (8)	3051	ν_{24} ($C_5H_{6,7}$ asy str)	3193 (10)	3056 (12)
ν_{25}($C_5H_{6,7;8}$ asy str)	3231 (6)	3090 (8)	3086	ν_{25}($C_5H_{6,7;8}$ asy str)	3228 (7)	3088 (6)
ν_{26}($H_{10}O_9H_{11}$ sym str)	3728 (245)	3576 (179)	–	ν_{26}($H_{10}O_9H_{11}$ sym str)	3718 (240)	3557 (198)
ν_{27}($H_{10}O_9H_{11}$ asy str)	3914 (130)	3737 (103)	–	ν_{27}($H_{10}O_9H_{11}$ asy str)	3918 (128)	3737 (92)

experimental results and are close to them in magnitude in all cases, excepting the $C_5H_{6,7,8}$ asy bend band, the frequency shifts of which are very small. The frequency shifts upon formation of heterodimer II were obtained experimentally for three bands: $O_2C_1O_3$ bend, $C_1{-}O_3$ str, and $C_1{=}O_2$. In these cases our theoretical values of shifts have the same signs as the experimental results and virtually coincide with them in magnitude.

Frequencies and intensities of the vibrational absorption bands of *cis*-MF$\cdots$H$_2$O dimers III and IV

The harmonic and anharmonic values of frequencies and intensities for the fundamental absorption bands of heterodimers III and IV formed by the molecules of *cis* methyl formate and water are shown in Table 4. The accuracy of the anharmonic values of frequencies and

Table 4. Harmonic and anharmonic values of frequencies ν (in cm^{-1}) and intensities S (in parentheses, in km mol^{-1}) of fundamental absorption bands of *cis*-MF$\cdots H_2O$ dimers III and IV

Dimer III			Dimer IV		
Band	$\nu(S)_{\text{harm}}$	$\nu(S)_{\text{anh}}$	Band	$\nu(S)_{\text{harm}}$	$\nu(S)_{\text{anh}}$
ν_1(H-bond oop bend)	26 (63)	–	ν_1(H-bond oop bend)	21 (26)	–
ν_2(O_9H_{11} oop libr)	47 (42)	–	ν_2(O_9H_{11} oop libr)	62 (114)	–
ν_3(H-bond ip bend)	71 (42)	–	ν_3(H-bond ip bend)	70 (16)	–
ν_4(H-bond str)	123 (1)	–	ν_4(H-bond str)	121 (0.2)	–
ν_5($C_5H_{6,7,8}$ tors)	154 (0.1)	–	ν_5($C_5H_{6,7,8}$ tors)	160 (1.2)	–
ν_6(H_2O ip rock)	280 (121)	–	ν_6(H_2O ip rock)	294 (156)	–
ν_7($C_1O_3C_5$ bend)	312 (12)	–	ν_7($C_1O_3C_5$ bend)	316 (15)	–
ν_8($C_5O_3O_2H_4$ dih)	336 (26)	–	ν_8($C_5O_3O_2H_4$ dih)	334 (4)	325 (0.2)
ν_9(O_9H_{10} oop libr)	383 (91)	–	ν_9(O_9H_{10} oop libr)	371 (76)	368 (26)
ν_{10}($O_2C_1O_3$ bend)	768 (11)	763 (13)	ν_{10}($O_2C_1O_3$ bend)	774 (10)	765 (11)
ν_{11}(O_3C_5 str)	950 (42)	921 (43)	ν_{11}(O_3C_5 str)	941 (38)	910 (33)
ν_{12}(C_1H_4 oop libr)	1053 (0.3)	1025 (0.7)	ν_{12}(C_1H_4 oop libr)	1043 (0.1)	1021 (0.2)
ν_{13}($C_5H_{6,7,8}$ wag)	1182 (173)	1140 (225)	ν_{13}(H_6H_7 tors)	1189 (1.7)	1165 (1.2)
ν_{14}(H_6H_7 tors)	1187 (1.5)	1162 (5)	ν_{14}($C_5H_{6,7,8}$ wag)	1195 (168)	1151 (257)
ν_{15}(C_1O_3 str)	1231 (145)	1204 (2)	ν_{15}(C_1O_3 str)	1241 (171)	1213 (50)
ν_{16}(C_1H_4 ip libr)	1409 (7)	1392 (8)	ν_{16}(C_1H_4 ip libr)	1401 (0.8)	1368 (0.5)
ν_{17}($C_5H_{6,7,8}$ sym bend)	1479 (2)	1441 (2)	ν_{17}($C_5H_{6,7,8}$ sym bend)	1484 (6)	1444 (5)
ν_{18}($C_5H_{6,7,8}$ asy bend)	1510 (10)	1461 (12)	ν_{18}($C_5H_{6,7,8}$ asy bend)	1515 (9)	1471 (8)
ν_{19}($H_6C_5H_7$ sci)	1520 (9)	1477 (6)	ν_{19}($H_6C_5H_7$ sci)	1519 (11)	1482 (6)
ν_{20}($H_{10}O_9H_{11}$ bend)	1631 (92)	1579 (162)	ν_{20}($H_{10}O_9H_{11}$ bend)	1636 (71)	1582 (43)
ν_{21}($C_1{=}O_2$ str)	1772 (263)	1736 (241)	ν_{21}($C_1{=}O_2$ str)	1775 (303)	1742 (266)
ν_{22}($C_5H_{6,7,8}$ sym str)	3098 (23)	2994 (23)	ν_{22}($C_5H_{6,7,8}$ sym str)	3100 (23)	2999 (34)
ν_{23}(C_1H_4 str)	3133 (10)	2993 (11)	ν_{23}(C_1H_4 str)	3109 (31)	2962 (9)
ν_{24}($C_5H_{6,7}$ asy str)	3192 (10)	3048 (16)	ν_{24}($C_5H_{6,7}$ asy str)	3197 (9)	3058 (12)
ν_{25}($C_5H_{6,7;8}$ asy str)	3223 (7)	3082 (10)	ν_{25}($C_5H_{6,7;8}$ asy str)	3231 (0.7)	3094 (1.7)
ν_{26}($H_{10}O_9H_{11}$ sym str)	3781 (79)	3630 (44)	ν_{26}($H_{10}O_9H_{11}$ sym str)	3780 (95)	3618 (72)
ν_{27}($H_{10}O_9H_{11}$ asy str)	3926 (139)	3758 (210)	ν_{27}($H_{10}O_9H_{11}$ asy str)	3925 (147)	3746 (116)

intensities obtained with the VPT2 method for the first nine low-frequency absorption bands of heterodimer III and seven absorption bands of heterodimer IV turned out to be questionable. Estimates of these parameters obtained from one-dimensional and two-dimensional variational calculations showed that the frequencies and intensities for the low-frequency absorption bands of weak heterodimers III and IV are calculated by the VPT2 method with too large inaccuracies. The use of other sets of atomic functions, in particular, the 6-311++G(3df,3pd) and 6-311++G(2df,2pd) sets, in the VPT2 calculation does not improve the situation. Apparently, to correctly calculate the low-frequency absorption bands of heterodimers III and IV, it is necessary to go beyond the second-order perturbation theory. For this reason, anharmonic values of spectral parameters for the above absorption bands of heterodimers III and IV are not presented in Table 4.

The O$-$H stretching vibrations of the H_2O fragment in heterodimers III and IV retain the symmetry properties of vibrations of a free water molecule to a greater extent than in heterodimers I and II. In particular, the amplitude of changes of the O_9-H_{10} bond length in the $\nu_{26}(H_{10}O_9H_{11}$ sym str) vibration is only slightly larger than the amplitude of changes of the O_9-H_{11} bond length. Hence, despite the formation of the $O_3\cdots H_{10}-O_9$ hydrogen bond, the ν_{26} absorption band remains weaker than the ν_{27} band. The increase of the total intensity of two stretching transitions of H_2O upon formation of heterodimers III and IV is approximately the same as upon formation of heterodimers I and II; however, the intensity of the ν_{27} antisymmetric band increases for the most part. The lower frequency value and higher intensity value of the ν_{26} band in heterodimer IV compared to heterodimer III are indicative of a stronger H-bond in heterodimer IV.

The anharmonic calculations with the use of the VPT2 perturbation theory predict the following values of frequency shifts $\upsilon_{\text{monomer}} - \upsilon_{\text{dimer}}$ for the bands of bending, symmetric stretching, and antisymmetric stretching vibrations of H_2O upon formation of heterodimers III and IV: -1, 24, and $10\,\text{cm}^{-1}$ for heterodimer III and -4, 36, and $22\,\text{cm}^{-1}$ for heterodimer IV. The experimentally observed frequency shifts -5, 37, and $20\,\text{cm}^{-1}$ [10] were accounted for by the formation of heterodimer III. Our calculated values of the shifts for heterodimer III have the signs identical to the signs of the experimental results, but they are considerably smaller in magnitude. The shift values predicted in our calculation for heterodimer IV are in excellent agreement with the experimental data in question. It is likely that the absorption bands experimentally observed in [10] should be assigned not to heterodimer III, but to somewhat stronger heterodimer IV, the existence of which had not been predicted in the quantum$-$chemical calculation of the authors of [10].

The most significant changes in the electro-optical parameters of internal vibrations of *cis*-MF upon formation of heterodimers III and IV were predicted for the absorption bands $C_5H_{6,7,8}$ wag (heterodimers III and IV) and C_1H_4 ip libr and C_1H_4 str (heterodimer III). The formation of a hydrogen bond in heterodimers III and IV with the O_3 oxygen atom, rather than with O_2 as in heterodimers I and II, essentially modifies the interaction of the C_1–O_3 and O_3–C_5 stretching vibrations with the $C_5H_{6,7,8}$ wag bending vibration. Unlike the situation in heterodimers I and II, the $C_5H_{6,7,8}$ wag vibration in heterodimers III (the ν_{13} mode) and IV (the ν_{14} mode) contains significant admixtures of the C_1–O_3 and O_3–C_5 vibrations, which gives rise to a sharp increase of intensity of the bending band and lowers its frequency. The strong band of the C=O vibration in *cis*-MF with the frequency shift $\nu_{\text{monomer}} - \nu_{\text{dimer}}$ equal to $-7\,\text{cm}^{-1}$ was observed in the matrix experiment [10]. The authors of [10] assigned this absorption band to the formation of the *cis*-MF$\cdots H_2O$ heterodimer III. It follows from the results of anharmonic calculations presented in Tables 3 and 4 that the frequency shift of the C=O band should be equal to $2\,\text{cm}^{-1}$ upon formation of heterodimer III and $-4\,\text{cm}^{-1}$ upon formation of heterodimer IV. It is possible that the shift of the C=O band observed in [10], as the shifts of H_2O bands discussed above in this section, was connected with the formation of heterodimer IV rather than heterodimer III.

Discussion of the results

The quantum–chemical calculation method adopted in this study turned out to be sufficiently accurate for the calculation of geometrical parameters of stable hydrogen-bonded dimers *cis*-MF$\cdots H_2O$, their binding energy, the electron density distribution, and the dipole moment values. The calculation confirmed the possibility of forming three heterodimers I$-$III, which were discussed earlier by other authors, and predicted the formation of heterodimer IV, the IR absorption bands of which may have been experimentally observed earlier [10] but had not been identified correctly. The calculated signs and magnitudes of changes in the geometrical parameters of monomers upon formation of heterodimers are in agreement with the strength and position of hydrogen bridges. The elongation of the $C_1=O_2$ bond upon formation of heterodimers I and II is accompanied by an increase in its polarity. Opposite effects should occur upon formation of heterodimers III and IV. The characteristics of the C_1–O_3 bond also change differently upon formation of complexes involving the carbonyl or methoxy oxygen atom. However, the characteristics of the O_3–C_5 bond behave in the same way upon formation of all four heterodimers. It is of interest to analyze the electron charges lost or gained by both individual atoms and monomers upon formation of the studied *cis*-MF$\cdots H_2O$ dimers.

It follows from the performed calculations that dimers I and II with the binding energies -24.30 and $-21.92\,\text{kJ mol}^{-1}$ formed by addition of H_2O to the carbonyl oxygen atom of *cis*-MF may exist not only in the low-temperature matrices, but also in the gas phase. The presence of strong absorption bands, associated first of all with the C_1–O_3 and $C_1=O_2$ stretching vibrations and internal stretching vibrations of the H_2O fragment, will allow these complexes to be detected by spectroscopic methods. Upon formation of heterodimers I–IV, both bands of the H_2O stretching vibrations considerably increase their intensity. The interaction of two O–H stretching vibrations of the H_2O fragment becomes significantly weaker in heterodimers I and II. Intensity of the low-frequency absorption band of stretching vibration of the OH group involved in the hydrogen bridge increases to the largest extent. Two stretching O–H vibrations in weak heterodimers III and IV virtually retain the symmetry property of a free water molecule, and the high-frequency antisymmetric band experiences the strongest intensity increase upon formation of a hydrogen bond. It is essential that the frequency shifts $\nu_{\text{monomer}} - \nu_{\text{dimer}}$ predicted by the anharmonic calculations for the IR absorption bands of water and *cis*-MF are in better agreement with the experimental data [10] than the results of harmonic calculations. The frequency shifts calculated in the anharmonic approximation for heterodimers I and II have the same signs as the experimental results [10] and are very close to the latters in magnitude. This is apparent, for example, from comparison of the theoretical values of frequency shifts of three absorption bands of the water molecule upon formation of heterodimer II -14, 97, and $31\,\mathrm{cm}^{-1}$ with the corresponding experimental values -12, 93, and $30\,\mathrm{cm}^{-1}$. Such agreement between the theoretical and experimental results confirms the correct identification of absorption bands of heterodimers I and II in [10]. As for the frequency shifts of absorption bands of monomers H_2O and *cis*-MF upon formation of heterodimers III and IV, our anharmonic results suggest that the absorption bands assigned in [10] to heterodimer III should be assigned to stronger heterodimer IV.

Conclusions

The geometrical parameters of four equilibrium configurations of stable hydrogen-bonded 1:1 heterodimers formed by the cis methyl formate and water molecules, as well as the binding energies of these complexes and the charges on atoms, were determined using Gaussian 2016 package of programs [13] 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 complexes were calculated in the harmonic approximation and with the anharmonicity taken into account using the second-order perturbation theory [11,12]. The reliability of the adopted calculation method was confirmed by good agreement between the calculated frequencies of the IR spectra of the *cis* methyl formate and water molecules and the experimental data. The frequency shifts $\nu_{\mathrm{monomer}} - \nu_{\mathrm{dimer}}$ and the changes in intensities for the absorption bands of monomers upon formation of complexes were determined from comparison of the results of calculations of monomers and dimers using the same method. The values of frequency shifts calculated by the anharmonic method are compared with the frequency shifts obtained in the experiment [10] for three absorption bands of H_2O in heterodimers I–III, nine absorption bands of *cis*-MF in heterodimer I, three absorption bands of *cis*-MF in heterodimer II, and the C=O band of *cis*-MF in heterodimer III. In all the cases, except for one band of *cis*-MF with an insignificant shift, the theoretical and experimental values of frequency shifts of the absorption bands in heterodimers I and II have the same signs and are very close to each other in magnitude. The experimental values of frequency shifts assigned to heterodimer III in [10] differ from the anharmonic results for heterodimer III, but are very close to the anharmonic results obtained for heterodimer IV in the present study. According to the present calculation, heterodimer IV, the existence of which was not assumed in [10], is somewhat stronger than heterodimer III.

The changes in interatomic distances, charges on atoms, and vibrational frequencies caused by the formation of hydrogen bonds were analyzed. Different trends in these changes were observed in the heterodimers formed by addition of H_2O to the oxygen atom of the carbonyl or methoxy group of cis methyl formate. The strong and sufficiently characteristic bands of the *cis* $\mathrm{MF}\cdots\mathrm{H_2O}$ heterodimers were predicted, which may be used for a spectroscopic detection of these systems.

Conflict of interest

The authors declare that they have no conflict of interest.

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