Isotope Effects in the Spectra of Hydrogen-Bonded Complexes. Calculation of Vibrational Absorption Spectra of $(D_2CO)_2$ and $D_2CO\cdots DF$ Dimers and $D_2CO\cdots(DF)_2$ and $(D_2CO)_2\cdots DF$ Trimers

© *V.P. Bulychev, M.V. Buturlimova, K.G. Tokhadze*

St. Petersburg State University, St. Petersburg, 199034 Russia

e-mail: v.bulychev@spbu.ru

The frequencies and intensities for the vibrational bands of absorption spectra of hydrogen-bonded $(D_2CO)_2$ and $D_2CO\cdots DF$ dimers, two $D_2CO\cdots(DF)_2$ trimers and four $(D_2CO)_2\cdots DF$ trimers are calculated in the MP2/aug-cc-pVTZ approximation with the basis set superposition error taken into account. Anharmonic values of spectral parameters were obtained using the vibrational second-order perturbation theory. The influence of hydrogen bonds on the spectral parameters was determined from comparison of the values calculated for monomers, dimers, and trimers in the same approximation. The data obtained were compared with the results of previous calculations of $(H_2CO)_2$ and $H_2CO\cdots HF$ dimers and $H_2CO\cdots(HF)_2$ and $(H_2CO)_2\cdots HF$ trimers. It was shown that one $D_2CO\cdots(DF)_2$ trimer and two $(D_2CO)_2\cdots DF$ trimers have significant binding energies and strong absorption bands, which makes them promising candidates for detection by spectroscopic methods.

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

Introduction

Molecular complexes formed by the relatively simple formaldehyde and hydrogen fluoride molecules can be considered as model systems in the studies of hydrogen-bonded complexes containing compounds with the carbonyl group and hydrogen halide molecules. Nonetheless, the structure and spectra of complexes formed by these molecules are still poorly studied, both experimentally and theoretically. The structure of $H_2CO\cdots HF$ dimers in a molecular beam was determined from rotational spectra of these complexes recorded by the method of electric resonance spectroscopy [1]. The infrared spectra of $H_2CO\cdots HF$ complexes in argon matrices were partially studied in the experiments [2,3], where the frequencies of the stretching $H-F$ and $C=O$ vibrations and HF librations in the dimer were determined. The infrared spectrum of $H_2CO\cdots HF$ dimers was studied in more detail in a nitrogen matrix at temperature $T = 8\,K$ [4]. The structure and spectrum of an isolated $H_2CO\cdots HF$ complex was also determined in this study on the basis of an MP2/6-311++G(3df,3pd) electronic structure calculation. Anharmonic values of the frequencies and intensities for absorption bands of the complex were computed with the use of the vibrational second-order perturbation theory [5,6] and the variational method. The theoretical values of spectral parameters were used to interpret the experimental spectra.

To our knowledge, the structure and absorption spectrum of more complicated complexes, formed by the formaldehyde and hydrogen fluoride molecules, were studied so far

only in three papers [7–9]. In [7] the vibrational frequencies of $H_2CO\cdots(HF)_n$ $(n = 1.4)$ complexes were calculated in the harmonic approximation, and the nature of high-frequency shifts of C−H stretching vibrations upon formation of complexes was examined. In [8] the structure and infrared spectrum of a trimer formed by the HF molecule with the planar $(H_2CO)_2$ homodimer were calculated in the MP2/6-311++G(3df, 3pd) approximation. Anharmonic frequency and intensity values for the absorption bands that are most important for experimental observation were determined by the variational method. The MP2/aug-cc-pVTZ method with the basis set superposition error (BSSE) taken into account was adopted in [9] to determine the nuclear configurations of stable $H_2CO\cdots(HF)_2$ and $(H_2CO)_2\cdots HF$ trimers. The geometrical structure, dipole moments, electron charge distribution, and binding energies were computed for two $H_2CO\cdots(HF)_2$ trimers and four $(H_2CO)_2\cdots HF$ trimers. The frequencies and intensities for the vibrational absorption bands of trimers and their constituent monomers and dimers were determined using the second-order peturbation theory [5,6]. It was shown that one $H_2CO\cdots(HF)_2$ trimer and two $(H_2CO)_2\cdots HF$ trimers can be experimentally studied because they possess a significant binding energy from -55 to $-71\,kJ\cdot mol^{-1}$ and the absorption bands of their H−F stretching vibrations are strong with an intensity from 696 to $988\,km\,mol^{-1}$.

The comparative study of different isotopologues of molecules and complexes provides a deeper insight into the internal dynamics of these systems [10]. Isotopic substitution can change the interaction of different degrees

of freedom and forms and amplitudes of nuclear vibrations. This, in turn, changes the influence of anharmonic effects on the frequencies and intensities of spectral transitions. The intensity redistribution between the absorption bands associated with different vibrational coordinates is the striking example of such an influence of isotopic substitution, which was shown, for example, in [11,12] upon H/D and H/T substitution in the $[F(HF)_2]^-$ ionic complex. A drastic intensity decrease was predicted in [13] for overtones of bending vibrations of $[F(HF)_2]^-$ upon H/D substitution. It was shown in [14] that the doublet structure, which was observed in the strongest O$-$H band in the $H_3N\cdots HONO$ complex and was accounted for by the resonance between the first excited state of the H$-$O stretching vibration and the doubly excited state of the HON bending vibration, will not be observed in the spectrum of $H_3N\cdots DONO$ because of the absence of an analogous resonance. The influence of isotopic substitution on structural and spectral parameters of molecular systems has been most vividly demonstrated in the calculations, where a proton was substituted by a K-meson or by a triton, i.e., a six-fold change in the nuclear mass was considered [15,16].

The purpose of this paper is to calculate the frequencies and intensities for vibrational absorption bands of deuterated formaldehyde molecules D_2CO, two $(D_2CO)_2$ homodimers, $D_2CO\cdots DF$ heterodimer, and $D_2CO\cdots (DF)_2$ and $(D_2CO)_2\cdots DF$ trimers using the equilibrium nuclear configurations of complexes obtained in our previous paper [9]. The spectroscopic parameters are determined in the harmonic approximation and with the use of the vibrational second-order perturbation theory [5,6]. Analysis of spectral parameters calculated in the same approximation for the trimers, as well as for the monomers and dimers constituent the trimers, allows us to determine the trends in the changes of these parameters upon formation of complexes. The influence of H/D substitution on spectral parameters of the considered complexes was analyzed by comparing the results obtained in this paper with the data calculated for analogous complexes containing light hydrogen atoms [9].

Calculation method

In this paper, as in [9], the quantum-chemical calculations of the $(D_2CO)_2$ and $D_2CO\cdots DF$ dimers and $D_2CO\cdots (DF)_2$ and $(D_2CO)_2\cdots DF$ trimers were performed by the MP2/aug-cc-pVTZ method with the BSSE taken into account using the Gaussian 16 package of programs [17]. The adopted quantum.chemical method ensures the feasibility of calculations of rather complicated complexes and good accuracy of calculated results. The equilibrium configurations of monomers and complexes, the binding energies of complexes, and dipole moments of these systems, calculated in the framework of the adiabatic approximation, do not depend on the isotopic composition of compounds. Detailed information on the numerical values of geometrical parameters of the compounds studied

is presented in [9]. The equilibrium configurations of the $(D_2CO)_2$ and $D_2CO\cdots DF$ dimers are shown in Fig. 1. The equilibrium configurations of the $D_2CO\cdots (DF)_2$ and $(D_2CO)_2\cdots DF$ trimers are shown in Figs. 2 and 3. The equilibrium configuration of the planar $(D_2CO)_2$ homodimer possesses the C_{2h} point group symmetry, while the symmetry operations of the $FD\cdots D_2CO\cdots DF$ (II) trimer (Fig. 2) are described by the C_{2v} group. In trimer III (Fig. 3) the DF molecule is attached to the planar $(D_2CO)_2$ homodimer, the confiuration of which is only slightly perturbed in this case. In trimer IV the DF molecule enters the planar homodimer and breaks one of its hydrogen bonds. Upon formation of trimer V (Fig. 3) the DF molecule approaches the non-planar homodimer in its symmetry plane. In trimer VI the DF molecule forms the O$\cdots$DF hydrogen bond with the D_2CO monomer that is perpendicular to the symmetry plane of the homodimer. In this case the C_s symmetry of the non-planar homodimer is significantly perturbed. It is known [18] that the non-planar $(D_2CO)_2$ homodimer is more stable than the planar homodimer; therefore, it is this homodimer that is observed in experiments [19]. Of the trimers considered trimers I, II, IV, and VI are most stable. The MP2/aug-cc-pVTZ calculations [9] yield the following binding energy values (in $kJ\,mol^{-1}$) of complexes relative to isolated monomers: -13.97 (planar $(H_2CO)_2$ homodimer), -17.70 (non-planar $(H_2CO)_2$ homodimer), -70.75 (trimer I), -57.11 (trimer II), -48.58 (trimer III), -54.77 (trimer IV), -49.58 (trimer V), and -56.65 (trimer VI). Taking into account that the binding energies of the planar and non-planar homodimers are equal to -13.97 and $-17.70\,kJ\,mol^{-1}$ [9], we obtain the following binding energies for the formation of trimers III$-$VI from the hydrogen fluoride molecule and formaldehyde dimers: -34.61 (III), -40.80 (IV), -31.88 (V), and $-38.95\,kJ\,mol^{-1}$ (VI). From here it follows, in particular, that the O$\cdots$DF hydrogen bond in trimer V is weaker than in trimer III and the bond in trimer VI is weaker than in trimer IV.

The anharmonic calculations of frequencies and intensities for fundamental and overtone spectral transitions in the studied monomers and complexes were performed using the vibrational second-order perturbation theory [5,6].
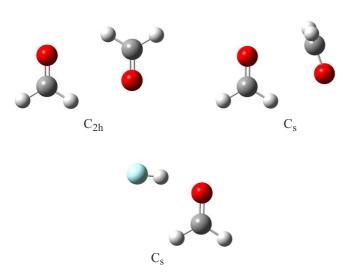
Results of the calculations of spectral parameters

Calculations of frequencies and intensities for the vibrational absorption bands of the DF and D_2CO monomers and $(D_2CO)_2$ and $D_2CO\cdots DF$ dimers

The values of frequency and intensity for the fundamental vibrational band of an isolated DF molecule calculated in the harmonic and anharmonic (in parentheses) approximations are 2988.88 (2899.37) cm^{-1} and 63.4 (62.5) $km\,mol^{-1}$. The theoretical anharmonic frequency value of 2899.37 cm^{-1} is in good agreement with the experimental value of 2906.67 cm^{-1} [20].

Table 1. Harmonic and anharmonic values of frequencies ν (cm^{-1}) and intensities S (km mol^{-1}) for fundamental absorption bands of planar and non-planar $(D_2CO)_2$ homodimers
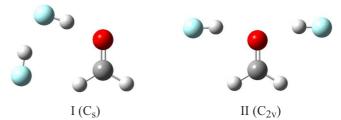
Planar $(D_2CO)_2$					Non-planar $(D_2CO)_2$				
Mode	ν_{harm}	S_{harm}	ν_{ahm}	S_{ahm}	Mode	ν_{harm}	S_{harm}	ν_{ahm}	S_{ahm}
ν_1 (bend, A_u)	53	15	19	1	ν_1 (bend, A'')	77	24	61	17
ν_2 (bend, A_g)	62	0	47	0	ν_2 (O$\cdots$DF str iph)	110	< 1	85	< 1
ν_3 (bend, A_u)	64	15	36	14	ν_3 (D$_2$CO rot ooph)	134	< 1	107	7
ν_4 (bend, B_g)	66	0	56	0	ν_4 (O$\cdots$DF str ooph)	137	42	102	27
ν_5 (O$\cdots$DF str, A_g)	109	0	87	0	ν_5 (bend, A')	180	6	144	13
ν_6 (O$\cdots$DF str, B_u)	120	44	99	38	ν_6 (D$_2$CO rot iph)	202	< 1	142	< 1
ν_7 (CD$_2$ wag, B_g)	969	0	953	0	ν_7 (wag, A')	951	< 1	942	< 1
ν_8 (CD$_2$ wag, A_u)	969	2	950	1	ν_8 (wag, A'')	967	1	953	1
ν_9 (CD$_2$ rock, B_u)	1004	17	986	13	ν_9 (rock, A'')	999	9	986	9
ν_{10} (CD$_2$ rock, A_g)	1003	0	985	0	ν_{10} (rock, A')	1003	10	989	9
ν_{11} (CD$_2$ sci, A_g)	1122	0	1106	0	ν_{11} (CD$_2$ ip sci)	1123	5	1106	4
ν_{12} (CD$_2$ sci, B_u)	1125	9	1108	7	ν_{12} (oop sci)	1127	2	1110	2
ν_{13} (C=O, A_g)	1690	0	1666	0	ν_{13} (C=O)	1697	15	1672	28
ν_{14} (C=O, B_u)	1697	92	1670	88	ν_{14} (C=O)	1701	86	1676	71
ν_{15} (CD$_2$ str, B_u)	2170.3	133	2097	74	ν_{15} (CD$_2$ sym str)	2174	35	2097	26
ν_{16} (CD$_2$ str, A_g)	2170.0	0	2096	0	ν_{16} (CD$_2$ sym str)	2178	70	2099	71
ν_{17} (CD$_2$ str, B_u)	2300	73	2215.9	75	ν_{17} (CD$_2$ asy str)	2295	51	2208	52
ν_{18} (CD$_2$ str, A_g)	2301	0	2215.7	0	ν_{18} (CD$_2$ asy str)	2297	43	2211	45

C_{2h} C_s C_s

Figure 1. Structures of $(D_2CO)_2$ homodimers and $D_2CO\cdots DF$ heterodimer and the corresponding point group symmetries.

I (C_s)   II (C_{2v})

Figure 2. Structures of trimers of composition $(DF)_2\cdots D_2CO$ and the corresponding point group symmetries.

The following notations of the types of vibrations will be used below: wag — out-of-plane wagging of a group of atoms, rock — rocking of a group of atoms in the plane of a molecule, sci — scissoring bending vibration, bend — bending vibration, libr — librational vibration, rot — rotational vibration, sym str and asy str — symmetric and antisymmetric stretching vibrations, oop — out-of-plane bending vibration, in — in-plane bending vibration, ooph — out-of-phase vibration of two groups of atoms, and iph — in-phase vibration of two groups of atoms. Vibrational absorption bands are numbered in tables in the order of increasing
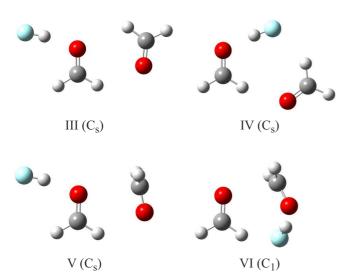
harmonic frequencies. The irreducible representations of the C_{2h} symmetry group are indicated for the vibrational modes of the planar $(D_2CO)_2$ homodimer, the A$'$ and A$''$ irreducible representations of the C_s symmetry group are used to distinguish between some bending vibrations of the non-planar homodimer.

The frequencies ν (in cm^{-1}) and intensities S (in km mol^{-1}) of an isolated D_2CO molecule have the following harmonic and anharmonic values: $\nu_{wag} = 959$ and 947, $S_{wag} = 1.1$ and 1.2, $\nu_{rock} = 998$ and 986, $S_{rock} = 10.04$ and 10.03, $\nu_{sci} = 1126$ and 1107, $S_{sci} = 1.5$ and 1.4, $\nu(C=O) = 1705$ and 1678, $S(C=O) = 55$ and 52, $\nu(CD_2)_{sym\ str} = 2162$ and 2087, $S(CD_2)_{sym\ str} = 66$ and 61, $\nu(CD_2)_{asy\ str} = 2276$ and 2193, $S(CD_2)_{asy\ str} = 62$ and 67. The anharmonic frequency values obtained in this calculation for vibrations of D_2CO are higher than the experimental values [21–23] by 3−31 cm^{-1}. The exception is the stretching vibration of the carbonyl group, the theoretical frequency value of which is 24 cm^{-1} lower than

Table 2. Harmonic and anharmonic values of frequencies ν (cm^{-1}) and intensities S ($km \, mol^{-1}$) for fundamental absorption bands of the $D_2CO \cdots DF$ heterodimer and ratios of $H_2CO \cdots HF$ frequencies to $D_2CO \cdots DF$ frequencies

Mode	ν_{harm}	S_{harm}	ν_{ahm}	S_{ahm}	ν_H/ν_D
ν_1 (C=O$\cdots$F bend)	74	13	64	9	1.141
ν_2 (D_2CO oop rot)	157	1.4	140	1.2	1.348
ν_3 (O$\cdots$DF str)	234	26	204	23	1.022
ν_4 (DF oop libr)	519	59	467	60	1.338
ν_5 (DF ip libr)	548	77	482	70	1.329
ν_6 (CD_2 wag)	968	1	954	1	1.247
ν_7 (CD_2 rock)	1008	13	993	11	1.262
ν_8 (CD_2 sci)	1125	3	1110	5	1.362
ν_9 (C=O)	1692	66	1667	63	1.028
ν_{10} (CD_2 sym str)	2195	53	2119	50	1.351
ν_{11} (CD_2 asy str)	2327	31	2240	35	1.295
ν_{12} (D$-$F str)	2700	459	2630	383	1.362

Figure 3. Structures of trimers of composition $DF \cdots (D_2CO)_2$ and the corresponding point group symmetries.

the experimental value. It was shown in [24] that such lowering of vibrational frequency is caused by an insufficient accuracy of the MP2/aug-cc-pVTZ approximation for describing double bonds.

The values of frequencies ν and intensities S for fundamental bands of two $(D_2CO)_2$ homodimers calculated in the harmonic and anharmonic approximations are listed in Table 1. As in $(H_2CO)_2$, the B_u bands ν_{14}, ν_{15}, and ν_{17} are the strongest absorption bands of the planar $(D_2CO)_2$ dimer. While intensities of the ν_{14} and ν_{15} bands are slightly decreased upon deuteration, the ν_{17} band intensity becomes a factor of 2.2 higher.

In the course of the ν_{13} vibration of non-planar $(D_2CO)_2$ two C=O bonds vibrate in phase. In this case the vibrational amplitude of the C=O group in the monomer lying in the symmetry plane of the dimer is significantly larger than the vibrational amplitude of the other C=O group. In

the course of the ν_{14} vibration two C=O groups vibrate out of phase, and the length of the C=O bond in the monomer perpendicular to the symmetry plane mainly changes. The ν_{15} and ν_{18} stretching vibrations of C$-$D bonds of non-planar $(D_2CO)_2$ belong to the monomer lying in the symmetry plane, while the ν_{16} and ν_{17} modes are localized in the perpendicular monomer. The C$-$D vibrations of different monomers are slightly mixed in the ν_{15} and ν_{16} modes with the symmetric vibration of two C$-$D bonds of a CD_2 group. There is no interaction between the C$-$D vibrations of different monomers in the ν_{17} and ν_{18} modes with the antisymmetric vibration of two C$-$D bonds of the same CD_2 group. The ratios ν_H/ν_D of frequencies of fundamental $(H_2CO)_2$ bands, calculated in [9], to the frequencies of fundamental $(D_2CO)_2$ bands (Table 1) have virtually the same values for the planar and non-planar homodimers and lie in the interval 1.24$-$1.27 for modes $\nu_7-\nu_{10}$ and in the interval 1.31$-$1.37 for modes ν_{11}, ν_{12}, and $\nu_{15} - \nu_{18}$. It is known [25] that the relative changes ν_H/ν_D of fundamental band frequencies upon deuteration of compounds provide information on the contribution of displacements of hydrogen atoms to the normal vibrations and on the degree of anharmonicity of vibrations. These data are often used to identify the details of experimental spectra. For the C=O vibrational bands the frequency ratios between the light and heavy formaldehyde dimers are close to 1.03. The deviation of values of the ν_H/ν_D parameter from unity is accounted for by the change in forms of the ν_{13} and ν_{14} normal vibrations upon deuteration, which contain, apart from the changes in C=O bond lengths, an admixture of changes in the DCD angles. The $\nu_{13}-\nu_{18}$ absorption bands of the non-planar $(D_2CO)_2$ homodimer are rather strong. Upon deuteration of this homodimer, the forms of some vibrations change significantly, intensities of the ν_{13} and ν_{16} bands increase by 65% and 18%, while intensities of the ν_{14} and ν_{15} bands decrease by 25% and 45%.

The theoretical values of vibrational frequencies (in cm^{-1}) of the non-planar $(D_2CO)_2$ homodimer (Table 1) are in good agreement with the data obtained in the experiment [19] with a low-temperature nitrogen matrix at $T = 11$ K: 943.7 (wag), 987.3 (rock), 1095.6 (sci), 1689.9 and 1686.4 (C=O), 2080.0 and 2077.3 (CD_2 sym str). The theoretical value of $4.02 \, cm^{-1}$ of splitting of the C=O vibrational frequency in $(D_2CO)_2$ almost coincides with the experimental value of $3.5 \, cm^{-1}$, and the high-frequency shift of $12 \, cm^{-1}$ predicted by the calculation for the strongest ν_{16} (CD_2 sym str) band of the homodimer relative to the monomeric band is close to the experimental shift value of $8 \, cm^{-1}$.

Table 2 lists the harmonic and anharmonic values of frequencies ν and intensities S for the fundamental absorption bands of the $D_2CO \cdots DF$ heterodimer, as well as the relative changes of frequencies of the heterodimer upon deuteration. The reduced mass and the form of the ν_9 (C=O) vibration significantly change upon H/D substitution, which decreases the frequency of the corresponding spectral transition by 2.7% ($46 \, cm^{-1}$). The values of ν_H/ν_D

presented in Table 2 show that the changes in reduced masses, forms of vibrations, and moments of inertia of fragments of the complex upon deuteration give rise to a more significant frequency lowering for other fundamental transitions of the heterodimer. It is worth noting that the anharmonic frequency values for the ν_4 and ν_5 librational vibrations of DF and the D−F stretching vibration in $D_2CO\cdots DF$ are close to the experimental values of these frequencies (454, 462 and $2630\,cm^{-1}$) obtained for the $H_2CO\cdots DF$ complex in an argon matrix at $12\,K$ [3]. As in the case of $H_2CO\cdots HF$, the ν_4, ν_5, and $\nu_9-\nu_{12}$ bands are the strongest absorption bands of $D_2CO\cdots DF$, which can be recorded in an experiment. Interestingly, the ratios of the intensities of ν_4, ν_5, and ν_{12} absorption bands of $H_2CO\cdots HF$ to the intensities of analogous bands of $D_2CO\cdots DF$ are almost the same, namely, 1.80, 1.93, and 1.83. The ν_9 (C=O) band intensity virtually does not change upon deuteration. In [9] anharmonic values of 26 and $41\,km\,mol^{-1}$ were obtained for intensities of the ν_{10} and ν_{11} bands of $H_2CO\cdots HF$. One can see in Table 2 that in $D_2CO\cdots DF$, unlike $H_2CO\cdots HF$, the ν_{10} band should be the strongest absorption band of CD_2 stretching vibrations. Upon formation of the $D_2CO\cdots DF$ complex the bands of symmetric and asymmetric CD_2 stretching vibrations increase their frequencies relative to the D_2CO monomer values by 32 and $47\,cm^{-1}$, respectively, while the frequency of the D−F stretching vibration is red-shifted by $269\,cm^{-1}$ relative to the frequency of isolated DF. The ν_{12} (D−F str) frequency is sufficiently remote from the frequencies of other strong absorption bands of $D_2CO\cdots DF$ and $H_2CO\cdots HF$, which can facilitate detection of the $D_2CO\cdots DF$ dimer in a spectroscopic experiment.

Calculations of frequencies and intensities of the vibrational absorption bands of trimers $D_2CO\cdots DF\cdots DF$ (I) and $FD\cdots O(CD_2)\cdots DF$ (II)

The frequencies and intensities calculated in the harmonic and anharmonic approximations for the fundamental absorption bands of trimers $D_2CO\cdots DF\cdots DF$ (I) and $FD\cdots O(CD_2)\cdots DF$ (II) are presented in Table 3. In timer I there are two strong hydrogen bands $O\cdots DF$ and $F\cdots DF$ and one weak bond $F\cdots DC$ [7,9]. It follows from [9] that the $O\cdots DF$ hydrogen bridge with the binding energy of $-56.74\,kJ\,mol^{-1}$ and the internuclear distance $R(O\cdots D) = 1.6148\,Å$ is stronger than the $F\cdots DF$ bridge with the binding energy of $-37.57\,kJ\,mol^{-1}$ and $R(F\cdots D) = 1.6939\,Å$. In accordance with these data, the $O\cdots DF$ hydrogen bond stretching vibration of trimer I has a higher frequency ($258\,cm^{-1}$) than the $F\cdots DF$ hydrogen bond stretching vibration ($192\,cm^{-1}$). The ν_{17} (D−F iph str) stretching vibration primarily occurs in the $O\cdots DF$ bridge, but it has an admixture of an in-phase D−F vibration in the $F\cdots DF$ bridge. The ν_{18} (D−F ooph str) vibration is mainly associated with the DF fragment of the $F\cdots DF$ bridge. The ν_{17} vibration is significantly shifted in frequency relative to the frequency of a DF monomer (by $520\,cm^{-1}$)

and the $D_2CO\cdots DF$ heterodimer frequency (by $251\,cm^{-1}$). The ν_{17} (D−F iph str) strong absorption band is removed in frequency from other strong bands of this trimer and bands of the $D_2CO\cdots DF$ heterodimer, which should facilitate an experimental observation of trimer I. The frequency of the ν_{18} (D−F ooph str) absorption band of trimer I is close to the ν_{12}(D−F str) band frequency of a $D_2CO\cdots DF$ dimer. Like the D−F stretching vibrations, librational vibrations of different DF fragments interact with each other. Nevertheless, the ν_7 and ν_8 vibrations occur predominantly in the $F\cdots DF$ bridge, while the ν_9 and ν_{10} vibrations are mainly associated with the $O\cdots DF$ bridge. The $O\cdots DF$ bond becomes stronger on passing from $D_2CO\cdots DF$ to trimer I. The electron density redistribution weakens the C=O bond and strengthens the C−D bonds. The blue frequency shifts of symmetric and asymmetric vibrations of the CD_2 group relative to the D_2CO monomer frequencies become larger by 15 and $26\,cm^{-1}$ than in $D_2CO\cdots DF$. The presence of a weak $F\cdots DC$ bond increases the nonequivalence of two C−D bonds of formaldehyde, which leads to a drastic distinction between intensities of ν_{15} and ν_{16} transitions, though the symmetric and asymmetric forms of two stretching vibrations of the CD_2 group mainly retain. Comparison of the data of Table 3 with the results of calculations of the $H_2CO\cdots HF\cdots HF$ trimer [9] shows that the spectral parameters of transitions $\nu_7 \div \nu_{13}$ and $\nu_{15} \div \nu_{18}$ change most significantly upon deuteration of this trimer. Intensities of the absorption bands $\nu_7 \div \nu_{10}$, ν_{17}, and ν_{18} become about two times lower. The ratios of frequencies of the ν_{11} (CD_2 wag) and ν_{12} (CD_2 rock) bending vibrations of $H_2CO\cdots HF\cdots HF$ to frequencies of the same vibrations of $D_2CO\cdots DF\cdots DF$ are equal to 1.25 and 1.26, while the analogous frequency lowering for vibrations $\nu_7 \div \nu_{10}$, ν_{13}, and $\nu_{15} \div \nu_{18}$ of trimer I upon deuteration is characterized by coefficients ν_H/ν_D lying in the interval 1.35−1.37. For the C=O vibrational band, the frequency ratio of light to heavy trimers I equals 1.028. For trimers II−VI discussed below, the calculations predict virtually the same ν_H/ν_D values: distinctions from the values obtained for trimer I do not exceed 0.01 for $\nu(CD_2$ wag), $\nu(CD_2$ rock), and ν(C=O) and 0.03 for the bands of librational vibrations ν(DF libr), scissoring vibrations $\nu(CD_2$ sci), and stretching vibrations $\nu(CD_2$ str) and ν(D−F str).

In trimer II there are two equivalent hydrogen bands $O\cdots DF$. Judging from the D−F bond lengths ($0.9569\,Å$ and $0.9381\,Å$ in trimer I and $0.9349\,Å$ in trimer II) and the $O\cdots DF$ bond lengths ($1.6148\,Å$ in trimer I and $1.7959\,Å$ in trimer II), the hydrogen bands in trimer II are weaker than in trimer I. In accordance with this fact, the frequencies of intermolecular vibrations $\nu_1 \div \nu_{10}$ of trimer II are essentially lower than the frequencies of the corresponding vibrations of trimer I. It was shown in [9] that the cooperative action of two relatively weak hydrogen bands of trimer II weakens (and elongates) the C=O bond and strengthens (and shortens) C−H bonds to a greater extent than two stronger hydrogen bands of trimer I. This effect retains upon deuteration and manifests itself, in particular, by

Table 3. Harmonic and anharmonic values of frequencies (in cm^{-1}) and intensities (in parentheses, in km mol^{-1}) for fundamental absorption bands of trimers $D_2CO \cdots DF \cdots DF$ (I) and $FD \cdots O(CD_2) \cdots DF$ (II)

$D_2CO \cdots DF \cdots DF$ (I)			$FD \cdots O(CD_2) \cdots DF$ (II)		
Mode	Harm	Anh	Mode	Harm	Anh
ν_1 (oop bend)	53 (8)	42 (8)	ν_1 (FOF bend, A_1)	44 (15)	33 (13)
ν_2 (FFO bend)	82 (4)	72 (7)	ν_2 (bend, B_2)	58 (1)	53 (1)
ν_3 (D_2CO rock)	134 (11)	120 (6)	ν_3 (D_2CO rock, B_1)	86 (18)	66 (12)
ν_4 (D_2CO oop rot)	180 ($<$ 1)	166 ($<$ 1)	ν_4 (O$\cdots$DF str, A_1)	147 ($<$ 1)	130 (1)
ν_5 (F$\cdots$DF str)	218 (19)	192 (17)	ν_5 (bend, A_2)	199 (0)	168 (0)
ν_6 (O$\cdots$DF str)	286 (41)	258 (38)	ν_6 (O$\cdots$DF str, B_1)	244 (51)	198 (35)
ν_7 (DF oop libr)	450 (42)	410 (40)	ν_7 (DF libr, A_2)	445 (0)	389 (0)
ν_8 (DF ip libr)	485 (104)	432 (98)	ν_8 (DF libr, B_2)	464 (121)	408 (118)
ν_9 (DF oop libr)	621 (75)	570 (74)	ν_9 (DF libr, B_1)	479 (9)	415 (3)
ν_{10} (DF ip libr)	720 (75)	656 (59)	ν_{10} (DF libr, A_1)	508 (62)	438 (134)
ν_{11} (CD_2 wag)	980 (1)	964 (1)	ν_{11} (CD_2 wag, B_2)	976 (1)	960 (1)
ν_{12} (CD_2 rock)	1017 (12)	1002 (9)	ν_{12} (CD_2 rock, B_1)	1016 (15)	1000 (17)
ν_{13} (CD_2 sci)	1131 (4)	1109 (3)	ν_{13} (CD_2 sci, A_1)	1124 (6)	1108 (6)
ν_{14} (C=O str)	1680 (75)	1655 (70)	ν_{14} (C=O str, A_1)	1679 (62)	1655 (65)
ν_{15} (CD_2 sym str)	2210 (70)	2134 (58)	ν_{15} (CD_2 str, A_1)	2217 (35)	2138 (33)
ν_{16} (CD_2 asy str)	2352 (9)	2266 (12)	ν_{16} (CD_2 str, B_1)	2360 (14)	2270 (18)
ν_{17} (D$-$F iph str)	2461 (671)	2379 (507)	ν_{17} (D$-$F str, B_1)	2768 (665)	2695 (546)
ν_{18} (D$-$F ooph str)	2751 (313)	2675 (223)	ν_{18} (D$-$F str, A_1)	2788 (51)	2710 (51)

the higher frequency values of C$-$D stretching vibrations in trimer II than in trimer I (Table 3). The difference between the frequencies of ν_{17} and ν_{18} D$-$F stretching vibrations in trimer II is as small as 15 cm^{-1}, and these frequencies are close to the D$-$F vibrational frequency of the F$\cdots$DF bridge in trimer I. The ν_8, ν_{10}, and ν_{17} bands are the strongest absorption bands of trimer II. Interestingly, the total intensity of four absorption bands associated with excitation of librational vibrations of DF has almost the same values in trimers I and II. Upon deuteration of trimer II the frequencies and intensities of fundamental absorption bands change in a regular manner. The intensities of strongest absorption bands ν_8, ν_{10}, ν_{17}, and ν_{18} of the FD$\cdots$O(CD$_2$)$\cdots$DF trimer are approximately twice as low as the intensities of these bands in the FH$\cdots$O(CH$_2$)$\cdots$HF spectrum.

Calculations of frequencies and intensities of the vibrational absorption bands of planar trimers (D$_2$CO)$_2$$\cdots$DF (III) and D$_2CO\cdots$DF$\cdots$D$_2$CO (IV)

The frequencies and intensities calculated in the harmonic and anharmonic approximations for the fundamental absorption bands of trimers (D$_2$CO)$_2$$\cdots$DF (III) and D$_2CO\cdots$DF$\cdots$D$_2$CO (IV) are presented in Table 4. Anharmonic values of parameters for low-frequency bands associated with intermolecular vibrations are not presented because of an insufficient accuracy of their calculation using the second-order perturbation theory. This drawback of calculations with the second-order perturbation theory was discussed, for example, in [26]. The binding energy of trimer III is lowest among all six trimers in question.

In accordance with this fact, the changes in vibrational frequencies upon formation of trimer III from the planar (D$_2$CO)$_2$ homodimer and monomeric DF are, as a rule, insignificant (see Tables 1 and 4). However, the appearance of the O$\cdots$DF bond in trimer III strongly affects the forms of internal vibrations of the homodimer. The intermolecular vibrations of monomers in (D$_2$CO)$_2$ are significantly perturbed both in form and in frequency. The stretching and bending vibrations of D$_2$CO fragments, except for vibrations $\nu_{16} \div \nu_{19}$, become independent and involve atoms of only one fragment. Vibrations ν_{13}, ν_{15}, ν_{21}, and ν_{23} of this group are localized on the fragment involved in the O$\cdots$DF bond and have higher frequencies as compared to vibrations ν_{12}, ν_{14}, ν_{20}, and ν_{22} of the other fragment. The opposite pattern is observed for vibrations $\nu_{16} \div \nu_{19}$. The frequencies of the O$\cdots$DF hydrogen bond stretching vibration, DF librational vibrations of the O$\cdots$DF bridge, and $\nu_{12} \div \nu_{15}$ bending vibrations of trimer III lie appreciably lower than frequencies of analogous vibrations of the stronger trimer I. Interestingly, the frequencies of stretching vibrations of CD$_2$ groups in trimer III are stronger blue-shifted relative to the D$_2$CO monomer frequencies than the vibrational frequencies of the D$_2$CO$\cdots$DF heterodimer. The ν_{24} stretching vibration frequency of trimer III is 295 cm^{-1} lower that the monomeric value. This absorption band of trimer III is close in frequency to the ν_{12}(D$-$F str) band of the D$_2$CO$\cdots$DF dimer. Intensities of the ν_{10}, ν_{11}, and ν_{24} bands of (D$_2$CO)$_2$$\cdots$DF (III) are approximately twice as low as the intensities of these bands in the spectrum of (H$_2$CO)$_2$$\cdots$HF (III). Intensities of other sufficiently strong

Table 4. Harmonic and anharmonic values of frequencies (in cm^{-1}) and intensities (in parentheses, in $km\,mol^{-1}$) for fundamental absorption bands of planar trimers $(D_2CO)_2\cdots DF$ (III) and $D_2CO\cdots DF\cdots D_2CO$ (IV)

$D_2CO_2\cdots DF$ (III)			$D_2CO\cdots DF\cdots D_2CO$ (IV)		
Mode	Harm	Anh	Mode	Harm	Anh
ν_1 (oop bend)	24 (2)	–	ν_1 (oop bend)	37 (< 1)	–
ν_2 (in bend)	33 (4)	–	ν_2 (D_2CO rock)	55 (2)	–
ν_3 (twist)	56 (15)	–	ν_3 (oop bend)	59 (19)	–
ν_4 (D_2CO oop rot)	61 (8)	–	ν_4 (C=O$\cdots$F bend)	69 (3)	–
ν_5 (C=O$\cdots$F bend)	71 (1)	–	ν_5 (CD_2 tors)	83 (4)	–
ν_6 (O$\cdots$DC str)	101(12)	152 (43)	ν_6 (O$\cdots$DC str)	120 (3)	163 (20)
ν_7 (O$\cdots$DC str)	136 (24)	101 (3)	ν_7 (F$\cdots$DC str)	127 (38)	131 (12)
ν_8 (D_2CO oop rot)	172 (1)	156 (1)	ν_8 (D_2CO oop rot)	177 (3)	163 (< 1)
ν_9 (O$\cdots$DF str)	245 (33)	216 (27)	ν_9 (O$\cdots$DF str)	253 (26)	232 (18)
ν_{10} (DF oop libr)	536 (57)	485 (56)	ν_{10} (DF oop libr)	572 (55)	527 (55)
ν_{11} (DF ip libr)	566 (63)	508 (41)	ν_{11} (DF ip libr)	590 (65)	530 (62)
ν_{12} (CD_2 wag)	967 (1)	954 (1)	ν_{12} (CD_2 wag)	974 (1)	1012 (1)
ν_{13} (CD_2 wag)	979 (1)	964 (1)	ν_{13} (CD_2 wag)	983 (1)	967 (1)
ν_{14} (CD_2 rock)	1001 (9)	986 (7)	ν_{14} (CD_2 rock)	1006 (7)	991 (7)
ν_{15} (CD_2 rock)	1012 (10)	999 (9)	ν_{15} (CD_2 rock)	1016 (19)	999 (12)
ν_{16} (CD_2 iph sci)	1119 (3)	1103 (7)	ν_{16} (CD_2 ooph sci)	1129 (4)	1113 (3)
ν_{17} (CD_2 ooph sci)	1124 (10)	1107 (4)	ν_{17} (CD_2 iph sci)	1134 (3)	1108 (< 1)
ν_{18} (C=O iph str)	1683 (43)	1658 (36)	ν_{18} (C=O iph str)	1678 (50)	1656 (50)
ν_{19} (C=O ooph str)	1698 (66)	1675 (65)	ν_{19} (C=O ooph str)	1692 (78)	1669 (72)
ν_{20} (CD_2 sym str)	2174 (58)	2097 (50)	ν_{20} (CD_2 sym str)	2179 (77)	2104 (61)
ν_{21} (CD_2 sym str)	2202 (48)	2122 (35)	ν_{21} (CD_2 sym str)	2198 (64)	2123 (53)
ν_{22} (CD_2 asy str)	2299 (47)	2213 (49)	ν_{22} (CD_2 asy str)	2317 (22)	2232 (21)
ν_{23} (CD_2 asy str)	2346 (14)	2258 (17)	ν_{23} (CD_2 asy str)	2342 (8)	2259 (10)
ν_{24} (D−F str)	2677 (540)	2604 (438)	ν_{24} (D−F str)	2610 (560)	2536 (442)

absorption bands of trimer III virtually do not change upon deuteration.

Upon formation of trimer IV from a planar homodimer and a DF molecule, one O$\cdots$DC hydrogen bond of homodimer is retained and two new bonds, the O$\cdots$DF strong bond and the F$\cdots$DC weak bond with $R(F\cdots D) = 2.3309$ Å (Fig. 3), are formed. It was shown in [9] that the O$\cdots$DC bond in trimer IV is stronger and shorter than in trimer III and in the planar homodimer. The frequencies of all vibrations of trimer IV, except for the stretching vibrations of the C=O and D−F bonds, are higher than the frequencies of the corresponding vibrations of trimer III. The frequency lowering for C=O and D−F stretching vibrations is explained by the weakening and elongation of C=O and D−F bonds as compared to trimer III. The lowering of the D−F vibration frequency relative to the monomeric value, which belongs to the most important parameters of hydrogen bonded complexes, amounts to $363\ cm^{-1}$. The internal vibrations of the same type in different D_2CO monomers of trimer IV virtually do not interact with each other, except for a weak interaction of vibrations of the carbonyl groups. In pairs of vibrations of the same type, for example, ν_{12} and ν_{13}, the atoms of the D_2CO monomer that forms the O$\cdots$DF bond are involved in the vibration with a higher frequency. The strengthening of the O$\cdots$DC bond and appearance of

an additional intermolecular bond F$\cdots$DC give rise to noticeably higher frequency values of ν_{20} and ν_{22} vibrations in trimer IV than in trimer III. The appreciable difference between the absorption band intensities of C=O and CD_2 stretching vibrations in trimers III and IV is worth noting. The intensities of DF stretching and librational vibrations predictably become about a factor of two lower upon deuteration of trimer IV, whereas the intensities of C=O and CD_2 stretching vibrations change irregularly.

Calculations of frequencies and intensities of the vibrational absorption bands of non-planar trimers $(D_2CO)_2\cdots DF$ (V) and $D_2CO\cdots DF\cdots D_2CO$ (VI)

The frequencies and intensities calculated in the harmonic and anharmonic approximations for the fundamental absorption bands of trimers $(D_2CO)_2\cdots DF$ (V) and $D_2CO\cdots DF\cdots D_2CO$ (VI) are presented in Table 5. Because of the low symmetry of the non-planar homodimer the forms of internal vibrations of this homodimer are perturbed to a lesser extent upon formation of trimers V and VI than the forms of vibrations of the planar homodimer upon formation of trimers III and IV. The changes of frequencies of internal vibrations of the non-planar homodimer upon formation of trimers are insignificant, except for the frequencies of C−D stretching vibrations of the fragment

Table 5. Harmonic and anharmonic values of frequencies (in cm^{-1}) and intensities (in parentheses, in km mol^{-1}) for fundamental absorption bands of non-planar trimers $(D_2CO)_2\cdots DF$ (V) and $D_2CO\cdots DF\cdots D_2CO$ (VI)

$(D_2CO)_2\cdots DF$ (V)			$D_2CO\cdots DF\cdots D_2CO$ (VI)		
Mode	Harm	Anh	Mode	Harm	Anh
ν_1 (oop bend)	35 (7)	−	ν_1 (bend)	41 (4)	−
ν_2 (C=O$\cdots$F bend)	40 (7)	−	ν_2 (bend)	51 (9)	−
ν_3 (twist)	73 (14)	−	ν_3 (C=O$\cdots$F bend)	77 (6)	−
ν_4 (O$\cdots$D$_2$C str)	84 (9)	−	ν_4 (O$\cdots$DC str)	111 (6)	−
ν_5 (D$_2$CO rot)	118 (21)	−	ν_5 (D$_2$CO tors)	131 (2)	−
ν_6 (D$_2$CO tors)	137 (< 1)	−	ν_6 (O$\cdots$D$_2$C str)	160 (41)	−
ν_7 (O$\cdots$DC str)	147 (8)	125 (13)	ν_7 (C=O$\cdots$C bend)	180 (3)	102 (11)
ν_8 (D$_2$CO tors)	194 (2)	142 (1)	ν_8 (O$\cdots$DF str)	258 (26)	228 (23)
ν_9 (O$\cdots$DF str)	257 (35)	217 (20)	ν_9 (D$_2$CO tors)	282 (6)	227 (2)
ν_{10} (DF oop libr)	520 (56)	474 (56)	ν_{10} (DF oop libr)	579 (89)	527 (90)
ν_{11} (DF ip libr)	549 (64)	496 (54)	ν_{11} (DF ip libr)	586 (47)	528 (56)
ν_{12} (CD$_2$ ip wag)	957 (< 1)	947 (< 1)	ν_{12} (CD$_2$ wag)	955 (1)	946 (< 1)
ν_{13} (CD$_2$ oop wag)	976 (1)	961 (1)	ν_{13} (CD$_2$ wag)	965 (1)	952 (2)
ν_{14} (CD$_2$ oop rock)	999 (9)	987 (9)	ν_{14} (CD$_2$ rock)	1002 (11)	987 (7)
ν_{15} (CD$_2$ ip rock)	1012 (12)	998 (6)	ν_{15} (CD$_2$ rock)	1008 (12)	995 (10)
ν_{16} (CD$_2$ ip sci)	1123 (7)	1108 (9)	ν_{16} (CD$_2$ ooph sci)	1127 (4)	1108 (1)
ν_{17} (CD$_2$ oop sci)	1128 (3)	1111 (3)	ν_{17} (CD$_2$ iph sci)	1127 (5)	1112 (4)
ν_{18} (C=O iph str)	1686 (51)	1662 (51)	ν_{18} (C=O iph str)	1687 (56)	1662 (13)
ν_{19} (C=O ooph str)	1702 (60)	1675 (56)	ν_{19} (C=O ooph str)	1697 (74)	1676 (106)
ν_{20} (CD$_2$ sym str)	2176 (54)	2098 (48)	ν_{20} (CD$_2$ sym str)	2184 (38)	2105 (39)
ν_{21} (CD$_2$ sym str)	2203 (37)	2126 (38)	ν_{21} (CD$_2$ sym str)	2213 (56)	2132 (49)
ν_{22} (CD$_2$ asy str)	2294 (48)	2207 (46)	ν_{22} (CD$_2$ asy str)	2308 (42)	2220 (36)
ν_{23} (CD$_2$ asy str)	2340 (19)	2253 (23)	ν_{23} (CD$_2$ asy str)	2346 (25)	2259 (15)
ν_{24} (D−F str)	2699 (515)	2619 (395)	ν_{24} (D−F str)	2620 (507)	2541 (398)

involved in the O$\cdots$DF bridge. Because the DF molecule is located outside the homodimer in trimers III and V and inside the homodimer in trimers IV and VI, it is advisable to compare parameters of trimer V with parameters of trimer III and parameters of trimer VI with parameters of trimer IV. Stretching and bending vibrations of one D$_2$CO monomer in trimer V virtually do not interact with analogous vibrations of another D$_2$CO monomer. The ν_{13}, ν_{15}, ν_{16}, ν_{18}, ν_{21}, and ν_{23} vibrations occur in the monomer taking part in the O$\cdots$DF bond. Because the O$\cdots$DF hydrogen bond in trimer V is weaker than in trimer III, the frequencies of librational vibrations of DF (ν_{10} and ν_{11}) of trimer V are lower and the frequencies of C=O and D−F stretching vibrations of trimer V (ν_{18} and ν_{24}) are higher than the frequencies of the corresponding vibrations of trimer III. For trimer V the second-order perturbation theory predicts smaller distinctions between intensities of absorption bands of the same type, for example, ν_{10} and ν_{11}, than for trimer III. In the case of trimer V, as in trimer III, the intensities of absorption bands of librational and D−F stretching vibrations significantly change upon H/D substitution, while the intensities of C−D stretching vibrations remain virtually unchanged.

In trimer VI there exists an additional interaction between the F atom and a DC group, which is confirmed by a rather short distance R(F$\cdots$DC) (2.7510 Å). This interaction is

weaker than in trimers I and IV; nevertheless, it affects the forms and frequencies of intermolecular vibrations. In trimer VI the stretching and bending vibrations of one D$_2$CO monomer, except for stretching vibrations of carbonyl groups, practically do not interact with analogous vibrations of another D$_2$CO monomer. Unlike trimers III−V, in trimer VI the atoms of DF and D$_2$CO monomer, involved in the O$\cdots$DF bond, do not lie, strictly speaking, in the same plane because the dihedral angle DCOF = 166.5°. Nevertheless, the ν_{10} and ν_{11} vibrations can be approximately denoted as librations of DF out of the D$_2$CO plane and in this plane. Vibrations ν_{12}, ν_{15}, ν_{16}, ν_{18}, ν_{21}, and ν_{23} occur in the D$_2$CO$\cdots$DF fragment. The ν_{18} (C=O iph str) vibration has a small admixture of an in-phase C=O vibration of the other D$_2$CO molecule. Comparison of the results of calculations of trimers IV, V, and VI shows that the frequencies of ν_{10} and ν_{11} librational vibrations of trimer VI almost coincide with the frequencies of vibrations of trimer IV, but significantly exceed the frequencies of analogous vibrations of trimer V. This result is quite predictable. The proximity of frequency values of other bending vibrations of D$_2$CO monomers in trimers V and VI and the noticeable differences between the ν(CD$_2$ wag) vibrational frequencies of trimers IV and VI are less obvious. The ν_{24} (D−F str) band that is most important from the view point of a spectroscopic observation has very close

values of frequencies and intensities for trimers IV and VI. Deuteration of trimer VI gives rise to practically the same relative lowering of frequencies of absorption bands as in the case of trimer IV. Upon deuteration the band intensities become lower by a factor of 1.3 and 2.2 for ν_{10} and ν_{11}, a factor of two for ν_{18} and ν_{19}, and a factor of 1.75 for ν_{24}.

The second-order perturbative calculations predict for the complexes of D_2CO and DF considered above a number of overtone absorption bands which lie in the infrared region and possess sufficiently high intensity. These bands are associated with librational vibrations of DF fragments in the $D_2CO\cdots DF$ heterodimer and trimers I and III−VI. The anharmonic values of frequencies ν (in cm^{-1}) and intensities S (in $km\,mol^{-1}$) of these overtones are as follows: $\nu = 876$ and $S = 21$ ($2\nu_4$(DF oop libr) $D_2CO\cdots DF$), $\nu = 1098$ and $S = 21$ ($2\nu_9$ (DF oop libr) trimer I), $\nu = 1270$ and $S = 14$ ($2\nu_{10}$ (DF ip libr) trimer I), $\nu = 917$ and $S = 24$ ($2\nu_{10}$ (DF oop libr) trimer III), $\nu = 992$ and $S = 35$ ($2\nu_{11}$ (DF ip libr) trimer IV), $\nu = 892$ and $S = 23$ ($2\nu_{10}$ (DF oop libr) trimer V), and $\nu = 985$ and $S = 28$ ($2\nu_{11}$ (DF ip libr) trimer VI).

Discussion of the results

The harmonic and anharmonic calculations of spectral parameters for the absorption bands of isolated DF and D_2CO molecules and the dimers and trimers constructed from these molecules performed at the same level of *ab initio* theory allow us to analyze the changes in the spectral parameters upon formation the complexes and the role of anharmonic effects. Comparison of these results with the analogous theoretical results obtained for compounds containing light hydrogen atoms shows the magnitude of isotope effects.

The distinctions between harmonic and anharmonic frequency values of spectral transitions are maximum in the case of H-bond stretching vibrations and librational vibrations of DF (up to 12%) and for stretching vibrations of the C=O, C−D, and D−F bonds (up to 4%). The D−F absorption band intensities of all considered above complexes containing DF become lower on average by 15% upon taking the anharmonic effects into account. The absorption bands of C=O and C−D stretching vibrations are strongest in spectra of $(D_2CO)_2$ homodimers. The close values of frequencies and intensities for the bands of planar and non-planar homodimers can hinder an experimental determination of the type of a homodimer. The D−F stretching vibration bands, which are the strongest bands in spectra of the $D_2CO\cdots DF$ heterodimer and the trimers considered, are shifted by $189-520\,cm^{-1}$ relative to the frequency of an isolated DF molecule. These absorption bands of the heterodimer and of the most stable trimers I, IV, and VI are shifted relative to other strong bands of the complexes, which can facilitate detection of these complexes by spectroscopic methods. The intensities of absorption bands of DF librational vibrations and C=O and C−D stretching vibrations are rather high and, as a rule, exceed

$50\,km\,mol^{-1}$. It is essential that these bands are remote in frequency from one another. The blue shift of C−D stretching vibration bands upon complexation is maximal in trimer II where two relatively weak hydrogen bonds act in cooperation. These shifts are also quite significant in trimers I, IV, and VI, where the frequencies of stretching vibrations of the $O\cdots DF$ bonds are high.

The calculations showed that the values of ratios ν_H/ν_D of vibrational frequencies of complexes with light hydrogen atoms to the frequencies of analogous vibrations of deuterated complexes depend on the types of vibrations. These ratios have virtually the same values for vibrations of a given type in all the considered complexes and, consequently, they can be used to identify the details of experimental spectra. The anharmonic calculation predicts considerable changes in relative intensities for the absorption bands of stretching vibrations of CH_2 groups upon deuteration of $(H_2CO)_2$ homodimers. The absorption band intensities of librational and stretching vibrations of hydrogen fluoride in the $H_2CO\cdots HF$ heterodimer and trimers I−VI significantly, by a factor of 1.3 to 2.2, decrease upon deuteration of these systems.

Conclusions

Parameters of vibrational absorption spectra of the DF and D_2CO isolated molecules, hydrogen-bonded $(D_2CO)_2$ and $D_2CO\cdots DF$ dimers, two $D_2CO\cdots(DF)_2$ trimers, and four $(D_2CO)_2\cdots DF$ trimers were calculated in the MP2/aug-cc-pVTZ approximation with the BSSE taken into account using the Gaussian 2016 package of codes [17]. The anharmonic values of frequencies and intensities of spectral transitions were obtained with the vibrational second-order perturbation theory [5,6]. The changes in spectral parameters upon formation of complexes were determined by comparing the results of calculations of monomers, dimers, and trimers in the same approximation. For each complex, sufficiently strong and characteristic bands were determined, which can be used for spectroscopic detection of these systems. The values of spectral parameters obtained for six trimers with different arrangements of monomers were compared. The changes in frequencies and intensities of absorption bands caused by deuteration of the complexes considered were analyzed.

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by Ego Translating