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Heterocomplexes in liquid mixtures MeOH—HF

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The IR spectra and densities of MeOH—HF liquid mixtures were measured for component molar ratios ranging from 12 : 1 to 1 : 3. The IR spectra of all of the solutions exhibit bands with maxima at 3500, 2600, and 1800 cm^{-1} and continuous absorption (CA) in the region of 3500—1300 cm^{-1}. The intensities of these bands and the CA increase with an increase in the HF concentration. A similar behavior was found for the difference between the experimental solution density and the additive sum of the solution component densities. *Ab initio* SCF calculations of the $(MeOH)_{5-n}(HF)_n$ cyclic complexes (n = 0—5) were performed using the 6-31G basis set. The observed properties of MeOH—HF liquid mixtures may be due to the formation of heterocomplexes with a stable cyclic fragment consisting of more than four MeOH and HF molecules.

Key words: solutions, hydrogen bond, hydrogen fluoride, methanol, complexes, vibrational spectra, quantum-chemical calculations.

On dissolution in water, alcohols, or other solvents, most hydrogen halides dissociate to form stable charged complexes with a strong quasi-symmetrical H-bond.[1—3] This bond is manifested in the IR spectra as tens or sometimes hundreds of intense second-order vibration bands whose superposition forms continuous absorption (CA) over a broad frequency range.[3] Charged complexes determine the reactivity and the physicochemical properties of solutions of HCl, HBr, and HI. Conversely, HF virtually does not dissociate in water or alcohols.[4] Nevertheless, judging by the IR spectra,[5—9] solutions of HF in organic solvents also contain new molecular structures that are not found in the initial components. In the first comprehensive study[7] of a broad series of organic solvent—HF systems, it was proposed that these structures may be represented by the protonated solvent molecules and $[FHF]^-$ ions. Conversely, in another publication,[8] new molecular species were described as being electrically neutral and possessing very strong hydrogen bonds.

A more detailed structural study of the stable molecular species formed in these solutions[9] was carried out for liquid Pr^{n}OH—HF mixtures; the IR spectra and densities of these mixtures were measured for molar ratios ranging from 12 : 1 to 1 : 3. The spectra of all the solutions studied exhibited absorption bands at 3500, 2600, and 1800 cm^{-1} and the CA in the region of 3500—1300 cm^{-1}, the intensity of these bands increasing in proportion to the fraction of dissolved HF. The difference between the measured solution density (up to the composition Pr^{n}OH—3HF) and the density calculated in terms of the additive approach varies in a similar way. These experimental data imply that the complexes formed comprise at least four inequivalent molecules and contain a quasi-symmetrical hydrogen bond. The molecular beam vibrational pre-dissociation spectra[10—14] of the $(HF)_n$ complexes and theoretical[15—23] investigations of the structures of these complexes and the ν(HF) frequencies attest to a higher stability of cyclic structures, which are mainly represented by pentamers. Analysis of the whole set of presented data led to the hypothesis[9] that heterocomplexes containing a stable five-membered ring as a common structural fragment are formed in a Pr^{n}OH—HF solution. The semiempirical estimates of the stability of various pentamers, $(Pr^nOH)_{5-n}(HF)_n$ (n = 0—5), and their vibration frequencies carried out in terms of this hypothesis showed that 2 : 3 and 3 : 2 complexes, whose vibrational spectra are in satisfactory agreement with experimental data, are the most stable.

This publication represents the next phase in the series of experimental and theoretical studies aimed at elucidation of the molecular structure of HF solutions in organic solvents. The purpose of this work is to study experimentally the MeOH—HF liquid mixture, by analogy with the Pr^{n}OH—HF system and to reveal common features of these systems. Using *ab initio* calculations, we analyzed the influence of the composition and struc-

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ture of a complex on its stability and on the strength of the H-bonds formed taking cyclic pentamers $(MeOH)_{5-n}(HF)_n$ (n = 0—5) as an example.

Experimental

For convenience of comparing the results of experiments with the data obtained earlier for the Pr^{n}OH—HF system, the component molar ratios in the prepared liquid MeOH—HF mixtures were the same as those used in the previous study,[9] namely, 12 : 1, 6 : 1, 3 : 1, 2 : 1, 1.5 : 1, 1 : 1, 1 : 1.5, 1 : 2, and 1 : 3, and the densities and the IR absorption spectra of the solutions were measured. Commercial hydrogen fluoride (99.95%, GOST 12022-88) was additionally purified by recondensation; reagent grade MeOH was used.

The solutions to be studied were prepared by mixing liquid HF with MeOH in vessels made of transparent 4MB fluoroplastic. To this end, MeOH was added to frozen HF using a syringe at a temperature of about −100 °C. The alcohol was added in small portions in order to prevent HF from boiling. After the addition of each portion, the mixture was unfrozen for homogenization and immediately cooled again until a solid phase formed. The composition of the solution was checked by weighing. This procedure was used to prepare solutions with MeOH : HF molar ratios of 1 : 1, 1 : 1.5, 1 : 2, and 1 : 3. Solutions with lower HF concentrations were prepared, as previously,[9] by diluting the 1 : 1 solution.

The solution densities (ρ) were measured at ~20 °C by the weighing method using a 25-cm^3 fluoroplastic pycnometer. The error of measurements was ±0.001 g cm^{-3}.

The IR absorption spectra of liquid MeOH—HF mixtures were recorded on a JASCO-810 spectrometer. The spectra were recorded stepwise (every 1 cm^{-1}), which ensured a high accuracy of subsequent processing of the primary spectral data. The spectra of 7-micron layers (6.8±0.2 μm) of all solutions were recorded in a demountable fluorite cell with a constant thickness in a frequency range of 4000—1300 cm^{-1}. A CaF_2 plate with a thickness equal to the sum of thicknesses of cell windows was used in the reference channel.

Results and Discussion

Study by IR spectroscopy. The absorption spectra of liquid MeOH—HF mixtures recorded as described above (Fig. 1) show that even for solutions with a mole fraction of HF of < 0.08 (see Fig. 1, *b*), the spectra exhibit new bands with maxima at about 3500, 2600, and 1800 cm^{-1} apart from the MeOH absorption bands. In parallel, the continuous absorption appears in a frequency range of 3500—1300 cm^{-1}. The concentration variations of the spectrum of the mixture under study and the positions of the new bands prove to be the same as those observed for the Pr^{n}OH—HF mixture.[9] The similarity of these systems is also manifested in the linear pattern of dependence of the optical density (D) of the absorption bands at 3500, 2600, 2200, and 1800 cm^{-1} on the HF/MeOH molar ratio. The data presented in Fig. 2 show that the peak intensities of the new bands and the CA (which is described according to the generally accepted procedure[24,25] by the optical density in the 2200—2000 cm^{-1} frequency range) increase virtually in proportion to the [HF]/[MeOH] ratio over the whole concentration range studied. Thus, the IR spectra of the series of mixtures considered differ only in the regions of stretching (3000—2800 cm^{-1}) and bending (1500—1350 cm^{-1}) vibrations of the C—H bonds. This is a natural consequence of the difference between the structures of MeOH and Pr^{n}OH molecules.

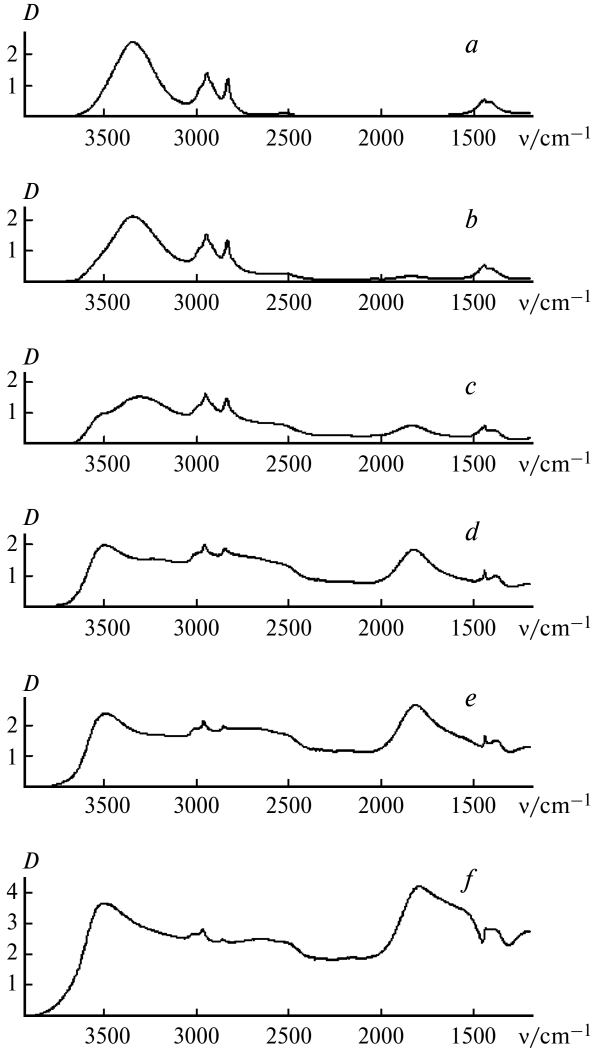

Fig. 1. Absorption spectra of 7-micron layers of liquid MeOH—HF mixtures with component molar ratios of 1 : 0 (*a*), 12 : 1 (*b*), 3 : 1 (*c*), 1 : 1 (*d*), 1 : 2 (*e*), and 1 : 3 (*f*).

The experimental dependence of the density of the liquid MeOH—HF mixture on the content of HF (vol. %) constructed by the procedure described above is shown in Fig. 3 by a continuous line, and the ρ([HF]) dependence calculated for the mixture of the same components by an additive procedure is shown by a dotted line. This plot is

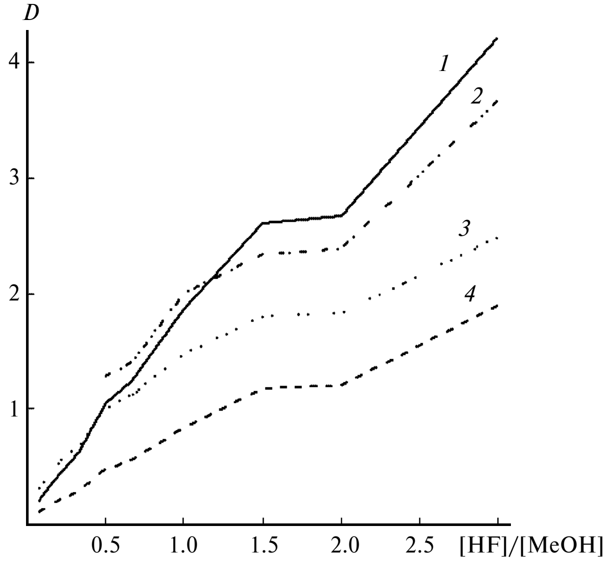

Fig. 2. Optical density of 7-micron layers of the mixtures *vs.* the [HF]/[MeOH] molar ratio for the bands at 1800 (*1*), 3500 (*2*), and 2600 cm^{-1} (*3*) and for the CA around 2200 cm^{-1} (*4*).

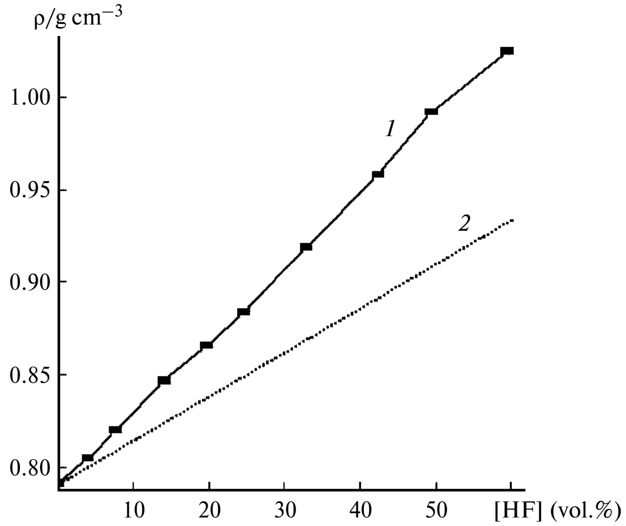

Fig. 3. Density of the liquid MeOH—HF mixtures (ρ) *vs.* the volume fraction of HF: experimental data (*1*) and calculation by the additive procedure (*2*).

linear in the chosen coordinates. The experimental values for the density also fit well on a straight line in the concentration range considered. This indicates that an increase in the content of HF in the mixture entails an increase in the number of the $(MeOH)_m(HF)_n$ heterocomplexes, their composition (or the composition of the main structural fragment) remaining virtually invariable. The linear increase in the density of the MeOH—HF mixture with concentration up to the composition 1 : 3 also means that a complex with a molar ratio of ≤1 : 5 is most stable in this system. This conclusion is fully consistent with the data[9] obtained for the Pr^{n}OH—HF system.

Table 1. Difference (Δρ) between the real density of the MeOH—HF and Pr^{n}OH—HF liquid mixtures with different molar ratios and the density calculated by the additive approach

System	Δρ/g cm^{-3}					
	6 : 1	3 : 1	2 : 1	1 : 1	1 : 2	1 : 3
MeOH—HF	0.019	0.024	0.033	0.057	0.089	0.106
Pr^{n}OH—HF	0.004	0.008	0.010	0.019	0.032	0.042

The observed excess of the real density over the calculated one is much higher for the MeOH—HF mixture than for the Pr^{n}OH—HF mixture with the same molar ratio (Table 1). This difference can be understood on general lines by taking into account the fact that the heterocomplex is formed only due to interaction between the HF molecules and the OH groups of the alcohol molecules. This gives rise to H-bonds, which increase the density of the ROH—HF system. This effect should be most pronounced when HF is dissolved in MeOH, because this alcohol has the smallest alkyl group. As the relative bulk of the alcohol functional groups not involved in complexation increases, the excess of the real density of the mixture over the calculated density would become less pronounced.

In order to calculate the density of the MeOH—HF mixture in the additive approximation, it is necessary to know the densities of both components as exactly as possible. Due to the volatility and corrosiveness of liquid HF, the values for its density determined by different researchers[26,27] do not always coincide. Here we used the value $\rho_{HF} = 0.957$ g cm^{-3} given in a handbook.[27]

It follows from the experimental results that the variations of the IR spectra and the density change of the liquid MeOH—HF mixture following the change in the concentration are in full agreement with the corresponding changes observed for the Pr^{n}OH—HF mixture. This suggests that both systems contain the same stable structural fragment.

Thus, the following conclusions can be drawn:

(1) independence of the spectral manifestation of the $(ROH)_m(HF)_n$ complexes on the molar ratio of the solution components indicates that the structure and the composition of the key fragment remain constant over the whole concentration range studied;

(2) continuous absorption in the IR spectrum of heterocomplexes gives ecvidence for a strong quasi-symmetrical hydrogen bond within these complexes;

(3) differences between the intensities of the stretching and bending bands for the Me groups and between the rates of increase in the density of the mixture observed upon dissolution of HF in MeOH or in Pr^{n}OH are due to the difference between those fragments of the MeOH and Pr^{n}OH molecules that are not incorporated in the central cyclic moiety of the heterocomplexes.

***Ab initio* calculations for the $(MeOH)_{5-n}(HF)_n$ complexes (n = 0—5).** The effect of the composition and structure of the $(MeOH)_m(HF)_n$ complex on its stability and on the strength of the H-bonds existing within the complex was analyzed by *ab initio* calculations in relation to the following cyclic pentamers: $(MeOH)_5$, $(MeOH)_4HF$, $(MeOH)_3(HF)_2$, $(MeOH)_3(HF)_2$*, $(MeOH)_2(HF)_3$, $(MeOH)_2(HF)_3$*, $MeOH(HF)_4$, and $(HF)_5$ (from here on, the structural isomers in which HF molecules are not located next to one another are asterisked). In addition, the required characteristics for the MeOH and HF molecules and the $(MeOH)_2$ and $(HF)_2$ dimers were also calculated. The geometry of these species was optimized and the total energy, harmonic vibration frequencies, and atom charges were calculated using the self-consistent field method (SCF) with the 6-31G basis set by means of the GAUSSIAN-94 program package.[28] The system energies at the stationary points were additionally calculated in terms of the second-order Møller—Plesset perturbation theory (MP2). This approximation cannot provide rigorous quantitative conclusions; however, the calculation still allowed us to elucidate the general features in the structure and charge distribution for the $(MeOH)_{5-n}(HF)_n$ heteropentamers (n = 1—4) and to estimate the relative stability of the species and the strengths of hydrogen bonds.

The values for the total energy and the overall strength of the H-bonds in the molecular systems under study are summarized in Table 2. Comparison of these results with the estimates of the relative stability of the $(Pr^nOH)_{5-n}(HF)_n$ pentamers (n = 0—5) performed previously[9] by a semiempirical method shows that the formation of heterocomplexes from the HF and ROH molecules is highly favorable from the energy standpoint. Indeed, any of the $(MeOH)_{5-n}(HF)_n$ pentamers (n = 1—4) is 1.5—2 times more stable than the cyclic structures $(MeOH)_5$ or $(HF)_5$. The most stable heterocomplexes are those containing two or three HF molecules. The total energies of the structural isomers of these complexes show that the most stable complexes are those where the HF molecules do not adjoin each other (see Table 2).

Table 2. Total energies (E_{tot}/au) of the MeOH and HF molecules, the $(MeOH)_2$ and $(HF)_2$ dimers, and the $(MeOH)_n(HF)_{5-n}$ cyclic pentamers (n = 0—5) and overall strength of the H-bonds (ΣE_b/kcal mol^{-1}) in the system calculated in the SCF and MP2 approximations

Molecular system	SCF		MP2	
	$-E_{tot}$	ΣE_b	$-E_{tot}$	ΣE_b
MeOH	114.9881656	—	115.2018341	—
HF	99.9834255	—	100.1113062	—
$(MeOH)_2$	229.9887733	7.95	230.4179522	8.98
$(HF)_2$	199.9787945	7.51	200.2351419	7.66
$(MeOH)_5$	575.0251872	54.73	576.1062867	62.50
$(MeOH)_4HF$	560.0307107	89.10	561.0243240	94.38
$(MeOH)_3(HF)_2$	545.0301857	99.93	545.9371805	103.14
$(MeOH)_3(HF)_2$*	545.0342910	99.61	545.9403300	102.70
$(MeOH)_2(HF)_3$	530.0271276	105.36	530.8474877	107.14
$(MeOH)_2(HF)_3$*	530.0322743	106.24	530.8517185	107.86
$MeOH(HF)_4$	515.0217365	102.21	515.7553580	102.62
$(HF)_5$	500.0070505	58.57	500.6544934	59.33

* Structural isomers in which HF molecules do not adjoin one another.

The calculation showed that cyclic structures with a nearly planar central fragment are preferred in all cases. The bending of the central fragment (described by dihedral angles of ≤15°) is due to the mutual repulsion of the Me groups of the alcohol molecules, especially if they are located next to each other. Following the Me groups, the corresponding O atoms also deviate from the plane of the ring in opposite directions. It is noteworthy that the geometric parameters of the central ring barely depend on the composition of the complex (Table 3). The greatest difference between the lengths of H-bonds within one ring is ~0.15 Å. The average H-bond lengths in different rings vary in a similar way. Generally, the hydrogen bridges in the pentamers are much shorter than in the $(HF)_2$ or $(MeOH)_2$ dimers. The lengths of the covalent bonds (especially those not included in the central fragment) are even less dependent on the composition of the complex than the hydrogen bond lengths. The O(F)...H—F(O) and H—F(O)...O(F) angles in different pentamers are equal to 163—173° and 112—124°, respectively, while the O—C—H and C—O—H angles are nearly the same as those in the free MeOH molecule (±1—3°).

Data on the charges on the atoms in these molecular systems are listed in Table 4. It can be seen that the charge distribution between the OH and Me groups is virtually the same in the free methanol molecule and in this molecule incorporated in the $(MeOH)_5$ complex. The OH groups in MeOH bear a great (about –0.3 au) negative charge; therefore, the cyclic fragments in all complexes containing these molecules are also negatively charged. The inclusion of the HF molecules in the ring entails a pronounced polarization, first of all, of the alcohol molecules situated next to them, and, as a consequence, the charge on their OH groups increases. When analyzing the calculation results, we found no correlation between the charge of the ring and the average strength of the H-bonds forming this ring or between the charge of the OH groups and the strength of the hydrogen bridges incorporating these groups.

The properties of the intermolecular bonds that ensure high stability of the heterocomplexes in ROH—HF solutions with different concentrations were of particular interest. Therefore, data on the relative strengths of the H-bonds in the cyclic complexes of different compositions were obtained by two independent methods. In one method, the strength of the H-bond in the XH...Y bridge

Table 3. Calculated bond lengths (Å) in the MeOH and HF molecules, $(MeOH)_2$ and $(HF)_2$ dimers, and $(MeOH)_n(HF)_{5-n}$ cyclic pentamers (n = 0—5)[a]

Bond	MeOH	$(MeOH)_2$	$(MeOH)_5$	$(MeOH)_4HF$	$(MeOH)_3(HF)_2$	$(MeOH)_3(HF)_2$*	$(MeOH)_2(HF)_3$	$(MeOH)_2(HF)_3$*	$MeOH(HF)_4$	$(HF)_5$	$(HF)_2$	HF
C—H [b]	1.077	1.078,[c] 1.076 [d]	1.079	1.079	1.078	1.078	1.078	1.077	1.077	—	—	—
C—H [e]	1.084	1.085,[c] 1.082 [d]	1.083	1.082	1.082	1.081	1.081	1.080	1.080	—	—	—
C—O	1.431	1.423, [c] 1.438 [d]	1.426	1.427	1.430	1.430	1.432	1.434	1.438	—	—	—
O—H	0.950	0.957,[c] 0.950 [d]	0.971	0.977, 0.973, 0.970, 0.962	0.979, 0.971, 0.959	0.975, 0.964, 0.962	0.977, 0.959	0.965, 0.961	0.960	—	—	—
H^O...O(F)	—	1.864	1.696, 1.696, 1.698, 1.704, 1.708	1.646, 1.686, 1.708, 1.731	1.627, 1.701, 1.774	1.658, 1.684, 1.728	1.645, 1.782	1.678, 1.730	1.743	—	—	—
F—H	—	—	—	0.979	1.002, 0.952	0.983, 0.975	1.009, 0.960, 0.945	0.994, 0.978, 0.952	0.997, 0.959, 0.950, 0.943	0.947	0.925,[c] 0.923 [d]	0.921
H^F...O(F)	—	—	—	1.461	1.391, 1.524	1.448, 1.728	1.371, 1.482, 1.578	1.411, 1.467, 1.526	1.404, 1.490, 1.549, 1.596	1.574	1.795	—

[a] Structural isomers in which HF molecules do not adjoin each other *; the H atoms connected by covalent bonds to the O or F atoms are designated by H^O and H^F, respectively.

[b] The C—H bond of the MeOH molecule lying in one plane with the OH group.

[c] Parameter for the proton-donor molecule.

[d] Parameter for the proton-acceptor molecule.

[e] The C—H bond of the MeOH molecule that does not lie in one plane with the OH group.

Table 4. Calculated charges on the atoms (au) in the MeOH and HF molecules, the $(MeOH)_2$ and $(HF)_2$ dimers, and $(MeOH)_n(HF)_{5-n}$ cyclic pentamers (n = 0—5)[a]

Atom	MeOH	$(MeOH)_2$	$(MeOH)_5$[b]	$(MeOH)_4HF$	$(MeOH)_3(HF)_2$	$(MeOH)_3(HF)_2$*	$(MeOH)_2(HF)_3$	$(MeOH)_2(HF)_3$*	$MeOH(HF)_4$	$(HF)_5$	$(HF)_2$	HF
H [c]	0.182	0.162,[d] 0.203 [e]	0.157(3)	0.165(5)	0.170(7)	0.171(5)	0.175(8)	0.181(1)	0.188	—	—	—
H [f]	0.143	0.128,[d] 0.155 [e]	0.146	0.152(7)	0.158(2)	0.162(3)	0.166(3)	0.171(1)	0.178	—	—	—
C	−0.119	−0.106,[d] −0.125 [e]	−0.095(3)	−0.095(2)	−0.096(3)	−0.096(1)	−0.098(2)	−0.097(1)	−0.100	—	—	—
Me	0.349	0.312,[d] 0.388 [e]	0.354(2)	0.393, 0.373 0.366, 0.360	0.411, 0.382 0.373	0.412, 0.401 0.384	0.424, 0.395	0.430, 0.422	0.444	—	—	—
O	−0.749	−0.808,[d] −0.790 [e]	−0.879(4)	−0.921, −0.888 −0.879, −0.870	−0.934, −0.889 −0.868	−0.922, −0.910 −0.878	−0.935, −0.876	−0.921, −0.908	−0.916	—	—	—
H^O	0.400	0.478,[d] 0.418 [e]	0.525(1)	0.546, 0.528 0.524, 0.485	0.554, 0.528 0.482	0.546, 0.504 0.489	0.554, 0.485	0.511, 0.501	0.506	—	—	—
HF	—	—	—	−0.016	−0.020(1)	−0.013(1)	−0.016(3)	−0.012(4)	−0.009(3)	0.000	−0.027,[d] 0.027 [e]	0.000
H^F	—	—	—	0.592	0.608, 0.552	0.595, 0.591	0.613, 0.566 0.549	0.607, 0.594 0.555	0.610, 0.568 0.561, 0.550	0.562	0.509,[d] 0.509 [e]	0.483
Cycle	—	—	−1.770	−1.491	−1.168	−1.195	−0.819	−0.854	−0.445	0.000		

[a] See note[a] in Table 3.

[b] The charge dispersions on equivalent atoms of the complex expressed in 0.001 au are given in parentheses.

[c] The C—H bond of the MeOH molecule lying in one plane with the OH group.

[d] Parameter for the proton-donor molecule.

[e] Parameter for the proton-acceptor molecule.

[f] The C—H bond of the MeOH molecule that does not lie in one plane with the OH group.

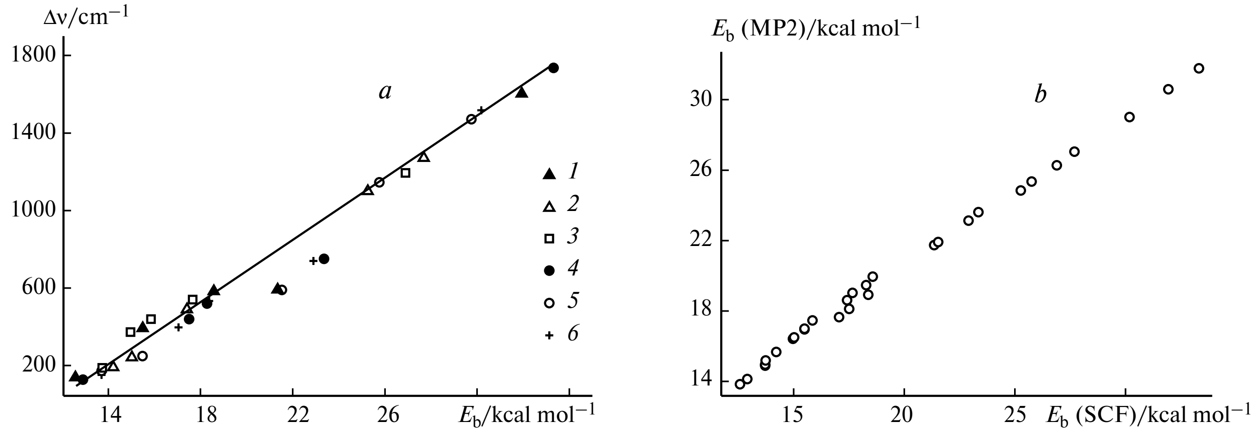

Fig. 4. Shift of the stretching vibration frequency ν(XH) (*a*) and the E_b value calculated by the MP2 method (*b*) *vs.* the E_b value found by SCF calculations; *a*: $(MeOH)_3(HF)_2$ (*1*), $(MeOH)_3(HF)_2$* (*2*), $(MeOH)_4HF$ (*3*), $(MeOH)_2(HF)_3$ (*4*), $(MeOH)_2(HF)_3$* (*5*), and $MeOH(HF)_4$ (*6*).

(X = O, F; Y = O, F) was described in terms of the shift of the ν(XH) stretching frequency with respect to this frequency in the free MeOH (HF) molecule. The Δν(XH) values for all the H-bonds involved were calculated in the harmonic approximation using the data of these calculations. The second method for estimating the H-bond strength was based on the assumption that the total energy of the complex can be represented as the sum of the energies of individual fragments and the bonds between them. The strengths of H-bonds (E_b) determined in this way (by subtracting the energies of "frozen" fragments from the total system energy) are well correlated with the Δν(XH) values for any of the systems considered (Fig. 4, *a*). The E_b values found using the total energies of the complexes determined by the SCF and MP2 calculations (Fig. 4, *b*) are not strictly proportional but show the same pattern of variation.

It follows from the obtained results that the $(MeOH)_{5-n}(HF)_n$ heterocomplexes (n = 1—4) have a number of general features. The enthalpies of their formation are 10—20% higher than the enthalpies of formation of the $(HF)_5$ or $(MeOH)_5$ complexes. The overall strengths of the H-bonds determining the stability of heterocomplexes (89—106 kcal mol^{-1}) depend only

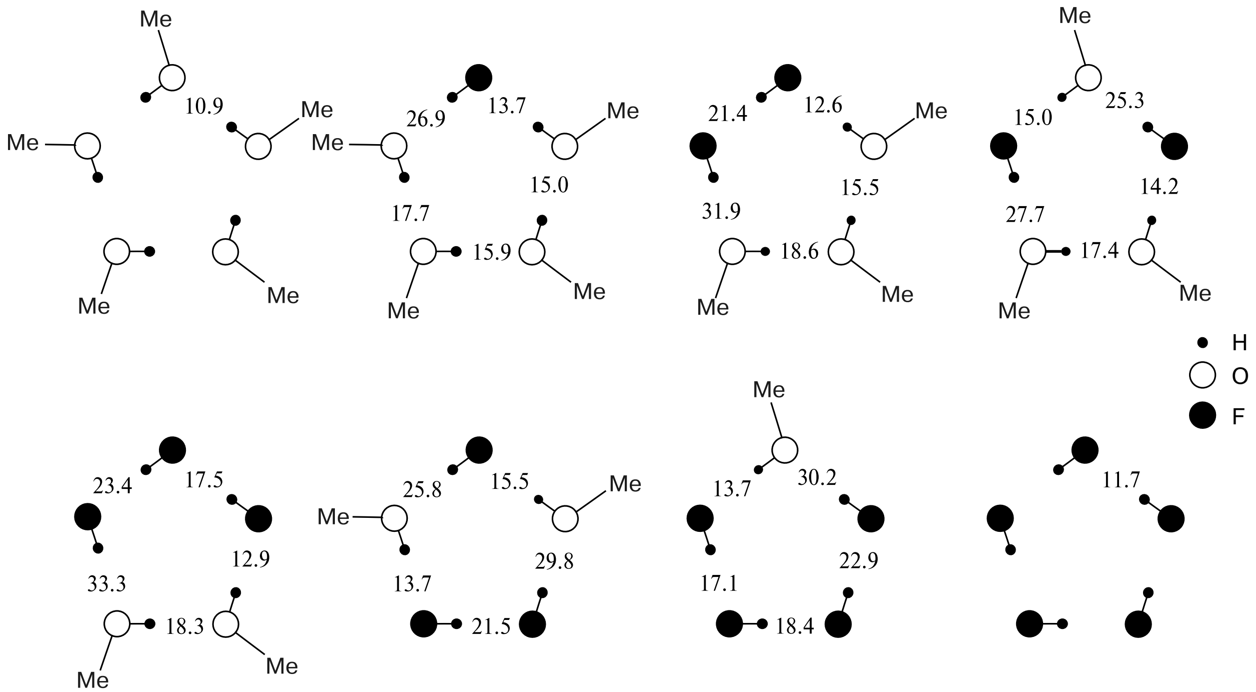

Fig. 5. Calculated strengths of hydrogen bonds (kcal mol^{-1}) in the $MeOH_{5-n}HF_n$ pentamers (n = 0—5).

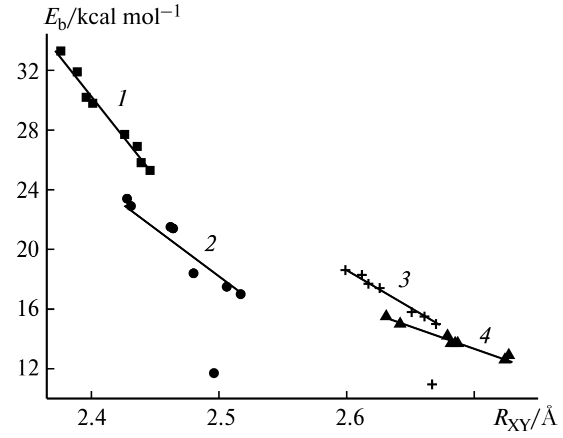

Fig. 6. Strength of the H...Y bonds (E_b) *vs.* the R_{XY} distance in the XH...Y bridges (X = O, F; Y = O, F): FH...O (*1*), FH...F (*2*), OH...O (*3*), and OH...F (*4*).

slightly on their composition. In all cases, the hydrogen bonds of the F—H...O bridges (Fig. 5) in which the H atom is shifted most appreciably to the electron-donating atom are the strongest (the bond energy is ~4 times as high as E_b in the dimer) (see Table 3). These results, which are consistent with the data of the pervious publication,[9] strongly suggest that the F—H...O bridges are responsible for the continuous absorption observed in the IR spectra of the ROH—HF mixtures. The strengths of the individual H-bonds within each pentamer are determined by the order of arrangement of the MeOH and HF molecules (see Fig. 5). A spectral consequence of the substantial difference between these values (which may differ by a factor of 2—2.6) may be the presence of ν(XH) stretching bands located ~1000 cm^{-1} away from each other. The H-bonds in the O—H...F bridges are the weakest bonds in the complexes in question; however, even these bonds are markedly stronger than the H-bonds in not only dimers but also the $(MeOH)_5$ or $(HF)_5$ pentamers. Note that there exists a strict correlation between the strength of an H-bond and the length of the bridge containing this bond. These correlations plotted for the bonds of different compositions (F—H...O, O—H...O, F—H...F, and O—H...F) are close to linear (Fig. 6). Two points with sharply different parameters in these plots correspond to the F—H...F and O—H...O fragments in the $(HF)_5$ and $(MeOH)_5$ pentamers.

The experimental measurements and calculations carried out in this work and in the earlier publication[9] show that the liquid mixtures MeOH—HF and Pr^{n}OH—HF contain heterocomplexes with a stable cyclic fragment consisting of HF molecules and OH groups of the alcohol. The formation of such complexes increases the density of the mixture and gives rise to the CA and the bands with maxima at 3500, 2600, and 1800 cm^{-1} in the IR spectra. The stable fragment incorporates at least four molecules, and the enthalpy of its formation is much higher than the enthalpy of formation of complexes containing only HF or MeOH molecules. The available data do not suffice to elucidate precisely the composition and the mutual arrangement of the molecules in the structure-forming rings of the ROH—HF system. Determination of the size of the stable fragment and, all the more, the structure of heterocomplexes containing this fragment requires further investigations.

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