Pathways of the reactions of nucleophilic addition of H₂O and HF molecules to formaldehyde in the gas phase and in the complex with formic acid: *ab initio* calculations

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The gradient pathways of the reactions of nucleophilic addition of H₂O and HF molecules to formaldehyde in the gas phase and in the XH...H₂CO...HC(O)OH complex (X = OH, F) were calculated by the *ab initio* RHF/6-31G**, MP2(fc)/6-31G**, and MP2(full)/6-311++G** methods. Both reactions proceed concertedly. The formation of H-bonded bimolecular pre-reaction complexes is the initial stage of the gas-phase reactions; at the same time, no indications of the formation of stable π-complexes were found on the potential energy surfaces of systems under study. The calculated energy barriers to the gas-phase reactions exceed 40 kcal mol⁻¹, while those to reactions in the complex XH...H₂CO...HC(O)OH (X = OH, F) become more than halved.

Key words: *ab initio* calculations, nucleophilic addition, reaction pathway, water, hydrogen fluoride, formaldehyde, formic acid, catalytic power.

Nucleophilic substitution (addition) reactions at the carbon atom of the carbonyl group belong to basic processes in chemistry and biochemistry.[1-3] Investigation of the interaction between formaldehyde and various nucleophilic agents is important for understanding the mechanisms of such reactions.[3-12] Formaldehyde is present in the environment and widely used in industry. Numerous experimental data obtained in the last decade indicate that formaldehyde is a strong mutagen and carcinogen (in the cell, it reacts strongly with cellular nucleophiles, producing damages).[13] Formaldehyde and its halo-substituted derivatives form weakly bonded bimolecular pre-reaction complexes XYCO...HZ (X, Y = H, F, Cl, Br; Z = F, Cl, Br)[14-17] that can play an important role in the chain of stratospheric chemical reactions affecting the formation and dynamics of the "ozone holes."[17]

Many theoretical studies dedicated to the reactions of nucleophilic addition of water,[3,8,11,14] ammonia,[3,5,6,10,11] hydrogen,[18] hydrogen fluoride,[19] and other compounds[5,7,11,20] to formaldehyde have been reported; however, the structure of the potential energy surface (PES) of the formaldehyde+nucleophile system remains to a great extent unclear. It is necessary to know the complete topological structure of the PES not only for establishing the true reaction pathway and, hence, the reaction mechanism, but also for performing dynamic calculations using the PES obtained.

In this work, we calculated the continuous gradient pathways[9] of nucleophilic addition of XH (X = OH, F) to formaldehyde (reaction (1)) in the gas phase by the RHF/6-31G**, MP2(fc)/6-31G**, and MP2(full)/6-311++G** *ab initio* methods[21-23] and established the topological structure of the PES of the systems in question in the configurational region of reaction.
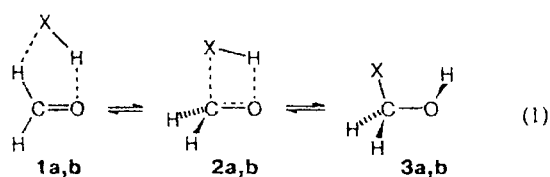
X = OH (a), F (b)

To study the effect of acid-base catalysis on the energetics and mechanism of nucleophilic addition of H₂O and HF to formaldehyde, the reaction (2) in the complex 4 with formic acid was also investigated.
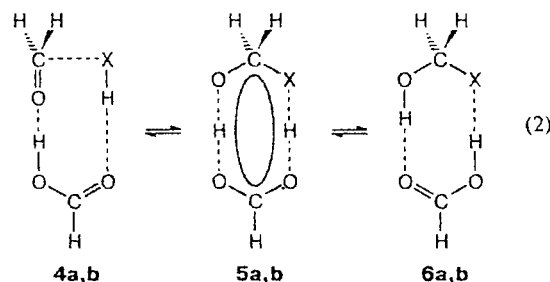
X = OH (a), F (b)

Table 1. Total energies (E_{tot}/au),[a] dipole moments (μ/D), zero-point harmonic vibrational energies (ZPE/au) and harmonic vibrational frequencies (ω_i/cm^{-1}) calculated by the RHF/6-31G**, MP2(fc)/6-31G** (figures in brackets), and MP2(full)/6-311++G** (figures in parentheses) methods for the H_2O, HF, H_2CO, and HC(O)OH molecules (experimental values are given in braces[b])

Structure (symmetry)	E_{tot}	ZPE	μ	ω_1	ω_2	ω_3	ω_4	ω_5	ω_6
H_2O	−76.02361	0.02319	2.15	1770	4146	462			
(C_{2v})	[−76.21979]	[0.02189]	[2.11]	[1682]	[3893]	[4032]			
	(−76.29395)	(0.02171)	(2.19)	(1628)	(3891)	(4010)			
			{1.85}	{1594}	{3657}	{3756}			
HF	−100.01169	0.01023	1.94	4492					
($C_{\infty v}$)	[−100.19464]	[0.00955]	[1.88]	[4191]					
	(−100.29794)	(0.00957)	(1.97)	(4138)					
			{1.80}	{4138}					
H_2CO	−113.86974	0.02898	2.66	1336	1377	1668	2026	3120	3195
(C_{2v})	[−114.18350]	[0.02739]	[2.23]	[1218]	[1296]	[1586]	[1791]	[3025]	[3103]
	(−114.27923)	(0.02698)	(2.39)	(1208)	(1279)	(1560)	(1774)	(2980)	(3051)
			{2.34}	{1180}	{1257}	{1507}	{1748}	{2780}	{2847}
HC(O)OH	−188.77056	0.03708	1.63	692	712	1193	1272	1433	1545
(C_s)	[−189.26050]	[0.03453]	[1.31]	[625]	[710]	[1072]	[1152]	[1333]	[1443]
	(−189.41893)	(0.03419)	(1.34)	(634)	(670)	(1063)	(1146)	(1314)	(1430)
			{1.41}	{508}	{552}	{990}	{1000}	{1178}	{1772}

[a] 1 au = 627.5095 kcal mol^{-1}.
[b] Data taken from Refs. 24—29.

Using the *ab initio* RHF/6-31G** and MP2(fc)/6-31G** calculations, it was established that the reaction mechanism in the complex changes and that the energy barriers to nucleophilic addition of H_2O and HF to formaldehyde become more than halved as compared to those of reaction (1).

The procedure for calculations was described earlier.[6]

Results and Discussion

The structure of H_2O, FH, H_2CO, and HC(O)OH molecules in the gas phase. To test the adequacy of the *ab initio* methods used for predicting the properties of the molecules under study, physical characteristics of the H_2O, FH, H_2CO, and HC(O)OH molecules were calculated using three different methods (RHF/6-31G**, MP2(fc)/6-31G** and MP2(full)/6-311++G**). The energy characteristics of these molecules, the electric dipole moments, and vibrational frequencies calculated by the *ab initio* methods at different levels of theory, and the experimental data are listed in Table 1.

The geometric parameters of the molecules calculated by the MP2(fc)/6-31G** and MP2(full)/6-311++G** methods are in best agreement with each other and with experimental gas-phase data. The dipole moments of the formaldehyde and formic acid molecules calculated by the same methods are also in good agreement with each other and with the experimental data. The dipole moments of water and HF molecules predicted by any of the *ab initio* methods used are somewhat overestimated (by ~0.1—0.3 D) as compared with the experimental values. The vibrational frequencies calculated in the

harmonic approximation are overestimated, on the average, by 10% in the SCF/6-31G** and by 5% in the MP2(fc)/6-31G** and MP2(full)/6-311++G** calculations as compared to the gas-phase experimental data.[21] At the same time it is significant to note that as can be seen from the data in Table 1, the experimental harmonic vibrational frequencies for formaldehyde[28] are in good agreement with the calculated values. Thus, it can be concluded that the Hartree—Fock calculations give a reasonably good semiquantitative account of the systems under study, whereas the calculations with inclusion of electron correlation energy give a quantitative description and that the values predicted by the MP2(fc)/6-31G** and MP2(full)/6-311++G** methods differ insignificantly.
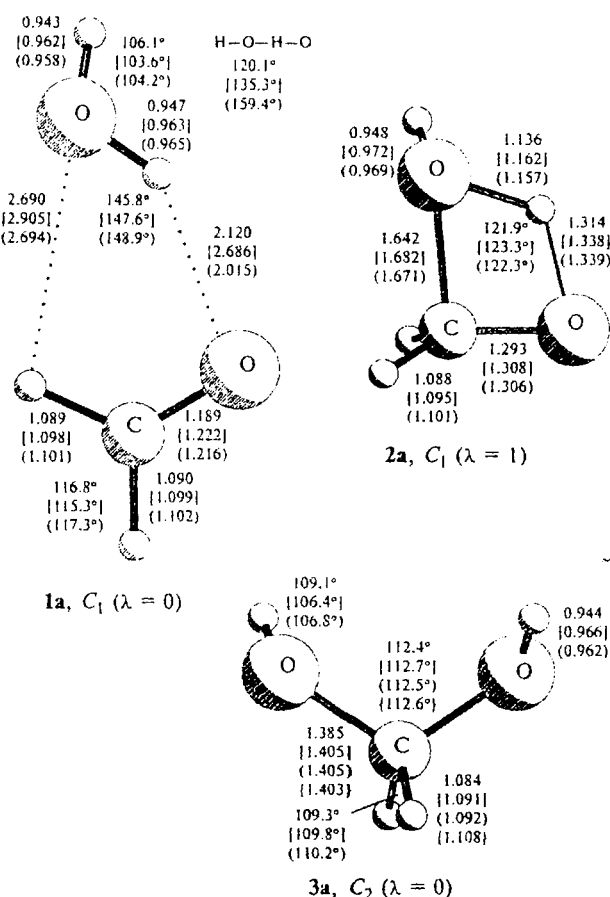
Gradient pathway of the reaction of nucleophilic addition of the water molecule to formaldehyde in the gas phase. According to the calculations, the structures **1a** and **3a** correspond to the minima ($\lambda = 0$; hereinafter λ is the number of negative eigenvalues of the Hesse matrix at a given critical point)[6] while structure **2a** corresponds to the saddle point ($\lambda = 1$) on the PES of the $H_2O...H_2CO$ system. The geometric and energy characteristics of structures **1a**—**3a** predicted by the *ab initio* methods are shown in Fig. 1 and listed in Table 2.

The geometric parameters of the pre-reaction complex **1a**, the transition structure **2a**, and the product, methanediol **3a**, calculated in this work are in fairly good agreement with the previously obtained theoretical results[8,20,30,31] and experimental data.[32,33] According to the calculations, the bimolecular complex **1a** is more

Table 2. Total energies (E_{tot}/au), relative energies $(\Delta E/kcal\ mol^{-1})$, the number of negative eigenvalues of the Hessian (λ), zero-point harmonic vibrational energies (ZPE/au), and the imaginary or the lowest harmonic frequencies $((i\omega/\omega_1)/cm^{-1})$ calculated by the RHF/6-31G**, MP2(fc)/6-31G** (figures in brackets), and MP2(full)/6-311++G** (figures in parentheses) methods for structures 1—3, 7, and 8 in the HX...H$_2$CO system (X = OH (**a**), F (**b**))

Structure (symmetry)	E_{tot}	ΔE	λ	ZPE	$i\omega/\omega_1$
1a (C_1)	−189.90172	0	0	0.05554	121
	[−190.40985]	[0]	[0]	[0.05168]	[60]
	(−190.58161)	(0)	(0)	(0.05178)	(95)
2a (C_1)	−189.81662	53.4	1	0.05513	i1976
	[−190.34774]	[39.0]	[1]	[0.05189]	[i1709]
	(−190.51251)	(43.4)	(1)	(0.05116)	(i1709)
3a (C_2)	−189.91659	−9.3	0	0.06229	401
	[−190.42663]	[−10.5]	[0]	[0.05895]	[410]
	(−190.59293)	(−7.1)	(0)	(0.05863)	(406)
1b (C_s)	−213.89432	0	0	0.04324	120
	[−214.39383]	[0]	[0]	[0.04134]	[169]
	(−214.58982)	(0)	(0)	(0.04026)	(66)
2b (C_s)	−213.81328	50.8	1	0.04076	i2057
	[−214.32573]	[42.7]	[1]	[0.03872]	[i1802]
	(−214.51373)	(47.7)	(1)	(0.03797)	(i1875)
3b (C_1)	−213.90908	−9.3	0	0.04893	389
	[−214.40392]	[−6.3]	[0]	[0.04644]	[400]
	(−214.59308)	(−2.0)	(0)	(0.04602)	(396)
7 (C_{2v})	−213.89145	1.8	1	0.04161	i83
	[−214.38833]	[3.4]	[1]	[0.03925]	[i105]
	(−214.58727)	(1.6)	(1)	(0.03898)	(i89)
8 (C_s)	−213.90522	−6.8	1	0.04786	i415
	[−214.39900]	[−3.2]	[1]	[0.04532]	[i441]
	(−214.58742)	(−1.5)	(1)	(0.04491)	(i481)

Fig. 1. Geometric characteristics of the structures **1a** and **3a** corresponding to the minima and those of the transition structure **2a** corresponding to the saddle point on the PES of the H$_2$O...H$_2$CO system calculated by the *ab initio* RHF/6-31G**, MP2(fc)/6-31G** (figures in brackets), and MP2(full)/6-311++G** (figures in parentheses) methods. The X-ray data for dimethoxymethane[33] are given in braces (see structure **3**). Bond lengths (Å) and bond angles are shown.

stable than other previously found intermolecular complexes belonging to this type[20] and has a non-planar structure in which the O—H bond deviates from the molecular plane by an angle lying within the limits 20° to 60° (the value depends on the method of calculation). The experimental frequencies (68, 256, and 437 cm^{-1}) in the far IR spectra of complex H$_2$O...H$_2$CO in an argon matrix corresponding to intermolecular torsional vibrations[32] are in fairly good agreement with corresponding harmonic frequencies calculated by the RHF/6-31G**, MP2(fc)/6-31G** (figures in brackets) and MP2(full)/6-311++G** (figures in parentheses) methods: 121 [60] (95), 303 [237] (334), and 521 [325] (482) cm^{-1}. The bond lengths and bond angles in the water and formaldehyde molecules in complex **1a** vary slightly as compared to those in the free state, which is in agreement with the conventional concept used when calculating rotational spectra of such complexes, according to which they consist of rigid monomeric units.[14,32,34] The stabilization energy of bimolecular complex **1a** relative to the individual fragments (without

inclusion of the basis set superposition error *(BSSE)* and zero-point harmonic vibrational energy *(ZPE)* predicted by the RHF/6-31G**, MP2(fc)/6-31G**, and MP2(full)/6-311++G** methods is equal to 5.3, 4.1, and 5.3 kcal mol^{-1}, respectively. The inclusion of *ZPE* correction reduces these values to 3.1, 2.6, and 3.3 kcal mol^{-1}, respectively (see Table 2). In this case the expansion of the basis set and taking into account the electron correlation energy slightly affect the stabilization energy of complex **1a**; at the same time, they substantially change the intermolecular geometric parameters (see Fig. 1). The rather high stabilization energy of complex **1a** is due to the formation of two weak nonlinear intermolecular hydrogen bonds C—H...O and O...H—O, the former being formed between the carbon and oxygen centers. Currently, intensive studies of similar C—H...O bonds are carried out (see Ref. 35), since

they are widely present in biological systems.[36] It is important to note that no pre-reaction π-complexes similar to that formed in the ammonia—formaldehyde system[6] was found on the PES of the $H_2O...H_2CO$ system. The reaction **1a ⇌ 2a ⇌ 3a** occurs concertedly (in one stage) via a four-center transition state **2a** with the overcoming of an energy barrier of 53.4 kcal mol⁻¹ (RHF/6-31G**), 39.0 kcal mol⁻¹ (MP2(fc)/6-31G**), and 43.4 kcal mol⁻¹ (MP2(full)/6-311++G**). The inclusion of electron correlation reduces the energy barrier by more than 10 kcal mol⁻¹. The conformation of methanediol **3a** (the end product of reaction (1)) with C_2 symmetry obtained in this work is in agreement with that calculated previously[8,31] and with the experimental X-ray data for dimethoxymethane.[33] The calculated continuous gradient reaction pathway issuing out of the saddle point **2a** along both directions of the transition vector and arriving at both minima **1a** and **3a** indicates that the trajectory of the approach of water molecule to formaldehyde differs from the Burgi pathway, which is the optimum trajectory of the approach of nucleophile to the carbon atom of carbonyl group.[4]

Gradient pathway of the reaction of nucleophilic addition of the hydrogen fluoride molecule to formaldehyde in the gas phase. According to the *ab initio* calculations, both HF and H_2O molecules form the pre-reaction complex **1b** corresponding to a minimum (λ = 0) on the PES of the $H_2CO...HF$ system. Stationary points **2b** (λ = 1), **3b** (λ = 0), **7** (λ = 1), and **8** (λ = 1) corresponding to three saddle points and a minimum were also found on the same PES in the configurational region of reaction (1). The geometric and energy parameters of structures **1b—3b**, **7**, and **8** calculated by the *ab initio* methods are shown in Fig. 2 and listed in Table 2.

7, C_{2v} **8**, C_s
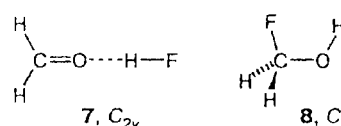
It is noteworthy that the existence of the stable bimolecular complex **1** (X = F) with the structure similar to structure **1b** shown in Fig. 2 in the gas phase was first predicted theoretically (see literature cited in

1b, C_s (λ = 0)   **2b**, C_s (λ = 1)   **3b**, C_1 (λ = 0)   **8**, C_s (λ = 1)   **7**, C_{2v} (λ = 1)
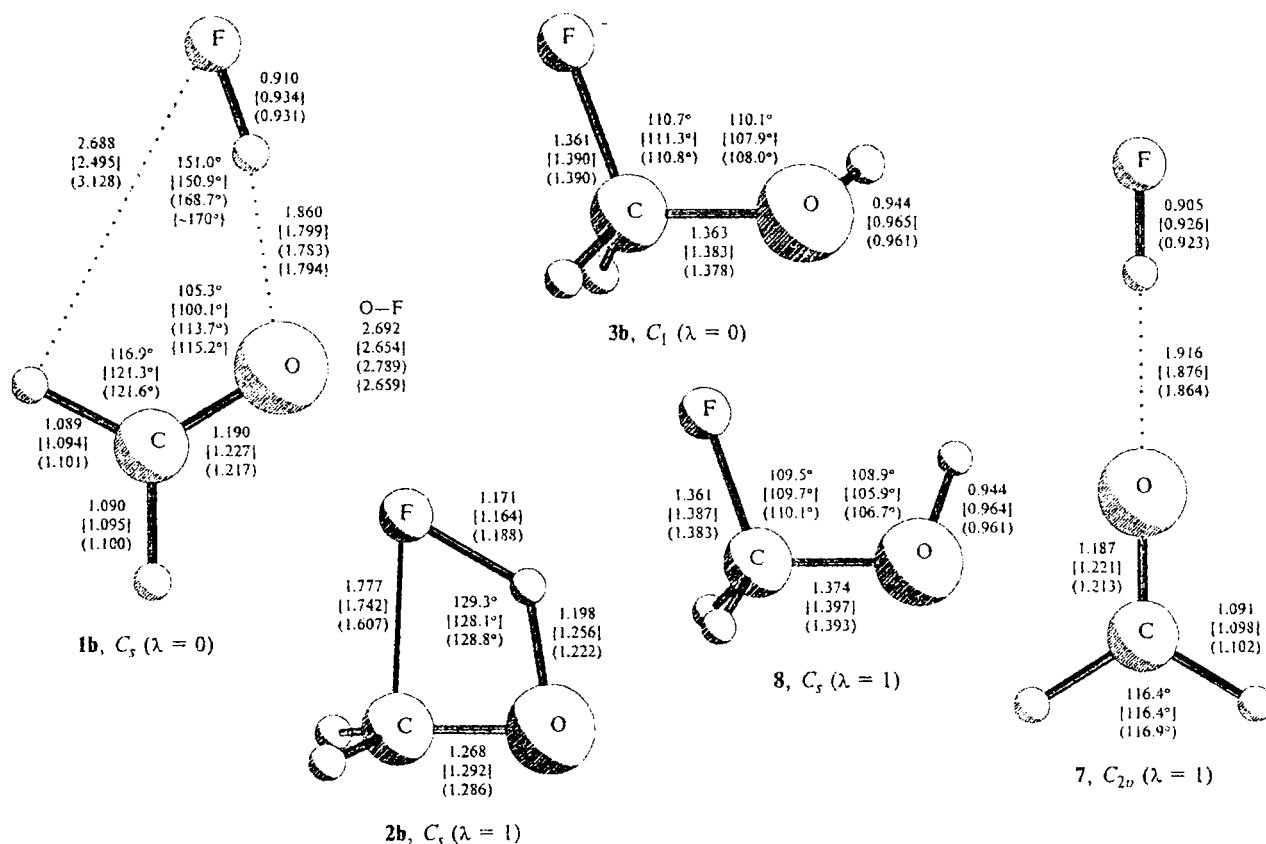
Fig. 2. Geometric characteristics of the structures **1b** and **3b** corresponding to the minima and those of the transition structure **2b**, and structures **7** and **8** corresponding to the saddle points on the PES of the $H_2CO...HF$ system calculated by the *ab initio* RHF/6-31G**, MP2(fc)/6-31G** (figures in brackets), and MP2(full)/6-311++G** (figures in parentheses) methods. The experimental data[14] are given in braces (see structure **1b**). Bond lengths (Å) and bond angles are shown.

Refs. 14 and 34). Only after more than a decade of theoretical investigations[34] was such a complex detected by molecular beam electron resonance spectroscopy[14] and its rotational spectrum recorded. The intermolecular geometric parameters of complex **1b** found from the rotational spectrum assuming the rigid monomeric unit structure[14] are shown in Fig. 2 (see figures in braces). As can be seen in this figure, there is a fairly good agreement between the experimental and calculated values. The bond lengths and bond angles in the HF and H_2CO molecules vary slightly on complexation, which confirms the assumption[14] of rigidity of monomeric units in complex **1b**. The stabilization energy of bimolecular complex **1b** relative to the individual fragments (without inclusion of *BSSE* and *ZPE* corrections) predicted by the RHF/6-31G**, MP2(fc)/6-31G**, and MP2(full)/6-311++G** methods is equal to 8.1, 9.8, and 7.9 kcal mol^{-1}, respectively. The inclusion of *ZPE* corrections reduces the stabilization energy to 5.6, 7.1, and 5.6 kcal mol $^{-1}$, respectively. Unlike the formaldehyde—water complex, in this case the expansion of the basis set and taking into account the electron correlation energy affect strongly the stabilization energy of complex **1b**. The predicted intermolecular distances in structure **1b** change appreciably as the level of calculations changes (see Fig. 2), though the stationary point indices (λ) remain unchanged. As in the case of complex **1a**, the high stabilization energy of complex **1b** is due to the formation of two nonlinear intermolecular hydrogen C—H...F and F—H...O bonds. The experimental electric dipole moment of complex **1b** (4.01 D)[14] is fairly close to the values 3.56, 3.69, and 3.11 D calculated by the RHF/6-31G**, MP2(fc)/6-31G**, and' MP2(full)/6-311++G** methods, respectively. It is also significant to note that no indications of the formation of pre-reaction π-complexes were found on the PES of the HF...H_2CO system.

The structure **7** is a transition structure of the reaction of planar HF reorientation from one lone electron pair of the oxygen atom of the formaldehyde molecule to the other one. The energy barrier to this reaction calculated by the RHF/6-31G**, MP2(fc)/6-31G**, and MP2(full)/6-311++G** methods is 1.8, 3.4, and 1.6 kcal mol^{-1}, respectively (see Table 2).

1bA, C_s **7,** C_{2v} **1bB,** C_s (3)
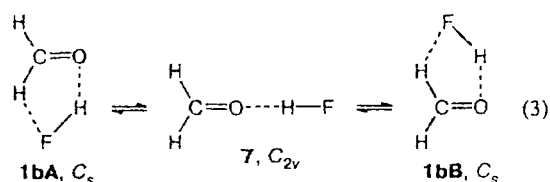
The first and the last values obtained for the energy barrier to reaction (3) are in surprisingly good agreement with the value 1.6 kcal mol^{-1} obtained for this barrier using the Buckingham—Fowler electrostatic model.[34] It is most likely that in this case the MP2(fc)/6-31G** method overestimates the energy barrier to reaction (3)

due to overestimating the C—H...F interaction, since the H...F distance predicted by this method is the shortest distance in complex **1b** (see Fig. 2).

The structure **8** is a transition state of internal rotation about the C=O bond in fluoromethanol (reaction (4)). The energy barrier calculated by the RHF/6-31G**, MP2(fc)/6-31G**, and MP2(full)/6-311++G** methods is equal to 2.5, 3.1, and 0.5 kcal mol^{-1}, respectively.

**3bA,** C_1 **8,** C_s **3bB,** C_1 (4)
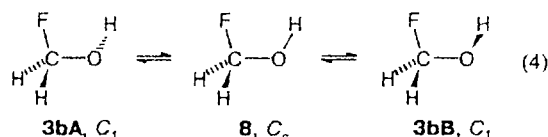
Unfortunately, experimental data on the structure and energy barrier to internal rotation in fluoromethanol are unknown; therefore the calculated barrier to rotation can be compared with analogous values for methanol (1.07 kcal mol^{-1})[37] and ethyl fluoride (3.31 kcal mol^{-1})[38] obtained using microwave spectroscopy. It should be noted that it is just the MP2(full)/6-311++G** method that is best to describe the F...H interaction that becomes stronger in the eclipsed conformation of **8** and that this fact is likely the reason for obtaining the lowest barrier. Because of this, the adequacy of the method used for predicting the barrier can hardly be judged unambiguously from comparing theoretical and experimental data. At the same time, it is surprising that the barrier (0.5 kcal mol^{-1}) calculated by this method is so low.

The addition reaction (1) occurs concertedly through the four-center transition state **2b** with the overcoming of an energy barrier of 50.8 kcal mol^{-1} (RHF/6-31G**), 42.7 kcal mol^{-1} (MP2(fc)/6-31G**), and 47.7 kcal mol^{-1} (MP2(full)/6-311++G**). As in the preceding case, the inclusion of electron correlation energy reduces the energy barrier by about 10 kcal mol^{-1}. On the qualitative level, the structural and energy characteristics of the transition state obtained in this work are fairly close to those calculated previously by the RHF/4-31G method.[19]

Based on the calculations of gradient lines (the steepest descent lines) issuing out of the saddle points **2b, 7,** and **8** along both directions of transition vectors at these saddle points, the correlation between the eigenvalues and the eigenvectors of the Hessian along these lines, the retaining of the mirror plane (C_s) along the pathways **1bA** ⇌ **7** ⇌ **1bB** and **7** ⇌ **2** ⇌ **8**, and the absence of conserved symmetry elements along the pathway **3bA** ⇌ **8** ⇌ **3bB**, it is possible to conclude that the topology of the PES of the H_2CO...HF system in the reaction region can be described by a model surface whose two-dimensional map is shown in Fig. 3.

The model surface was chosen as an analytical function (see Ref. 39), the topology of which (the relative arrangement of stationary points and their λ indices) qualitatively coincides with that of the PES of the FH...H_2CO system in the reaction region. All gradient lines in the reaction region were calculated for the
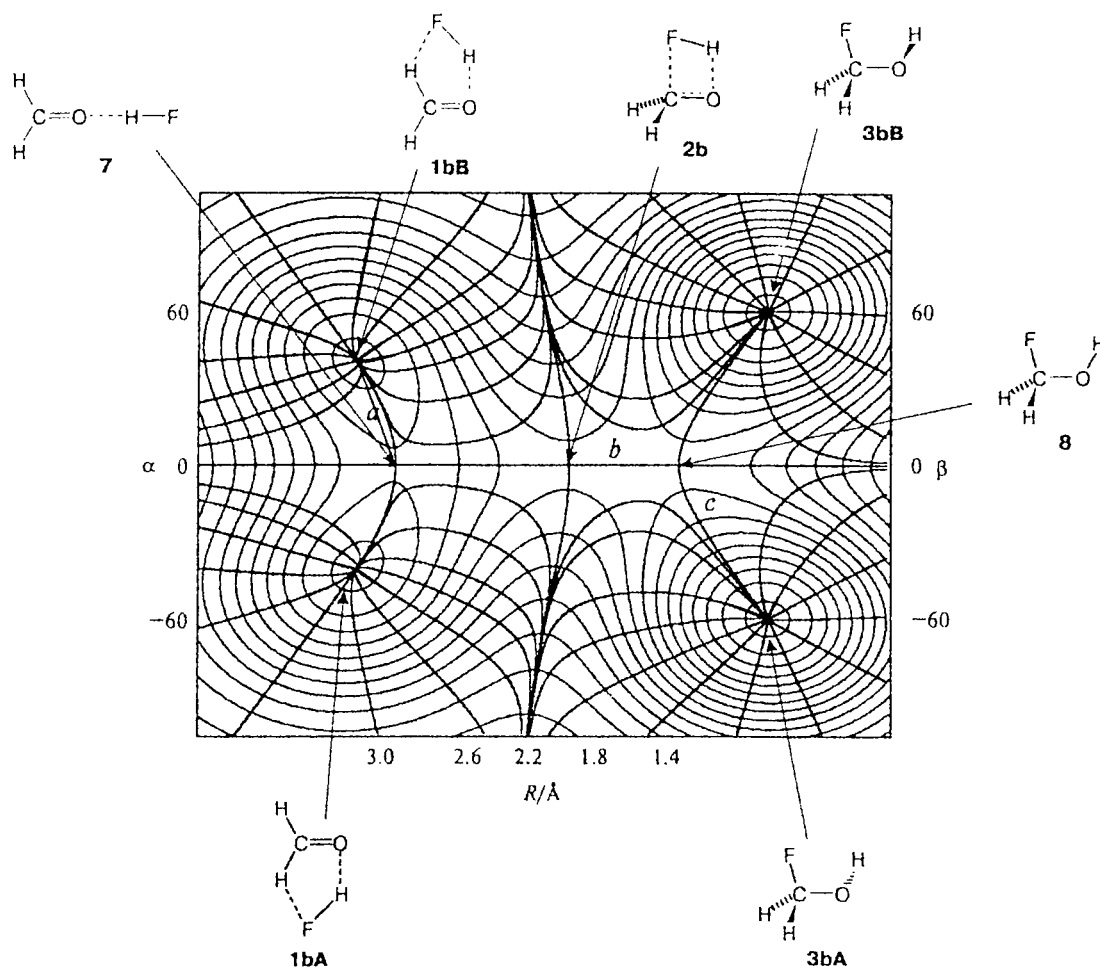
Fig. 3. Two-dimensional map of the analytical function used to approximate the PES of the FH...H_2CO system in the region of the reaction of nucleophilic addition of FH to H_2CO and its orthogonal trajectories (gradient lines). Thin closed lines are the level lines; thin lines orthogonal to the level lines are the gradient lines. The gradient reaction pathway consists of three different gradient lines, **1bA** $\rightleftharpoons$ **7** $\rightleftharpoons$ **1bB** (*a*), **7** $\rightleftharpoons$ **2b** $\rightleftharpoons$ **8** (*b*), and **3bA** $\rightleftharpoons$ **8** $\rightleftharpoons$ **3bB** (*c*). Line *a* corresponds to the reorientation reaction (3), line *b* corresponds to the nucleophilic addition reaction (1), and line *c* corresponds to internal rotation of the OH group about the C—O bond; *R* is the distance between the X and C atoms; φ is the angle of rotation of the OH group about the C=O bond; $\varphi = 0°$ corresponds to the eslipsed conformation of **8**.

model analytical function; they are also shown in Fig. 3. As can be seen, all gradient lines issue out of or terminate at stationary points ($\nabla E = 0$) or go to infinity.[10,21] The gradient lines at regular points ($\nabla E \neq 0$) can neither disappear nor appear. Each pair of the minima **1bA** and **1bB**, and **3bA** and **3bB** is connected by the only gradient line passing only through the saddle point **7** and **8**, respectively. The saddle points **7** and **8** are connected by the only gradient line that passes through the third saddle point **2b** and does not arrive at any minimum.

Thus, the gradient pathway of the reaction of nucleophilic addition of HF to H_2CO consists of three different gradient lines. The first of them passes through the saddle point **7** and corresponds to the reorientation reaction (3), the second line passes successively through three saddle points **7, 2b,** and **8,** and the third gradient

line passes through the saddle point **8** and corresponds to internal rotation (4). The direction of the movement of the system over the PES is twice changed by the perpendicular direction.

Gradient pathway of the reaction of nucleophilic addition of XH to formaldehyde in the complex HC(O)OH...XH...H_2CO (X = OH, F). As was shown by *ab initio* calculations of the gas-phase reaction (2), the results obtained by the RHF/6-31G**, MP2(fc)/ 6-31G**, and MP2(full)/6-311++G** methods exhibit qualitative agreement, while the MP2(fc)/6-31G** and MP2(full)/6-311++G** methods give nearly quantitatively coinciding results. Therefore, to save computing time, further calculations of the structures corresponding to the stationary points on the PES of the HC(O)OH...XH...H_2CO system (X = OH, F) were car-

4a, C_1 ($\lambda = 0$)   5a, C_1 ($\lambda = 1$)   6a, C_1 ($\lambda = 0$)
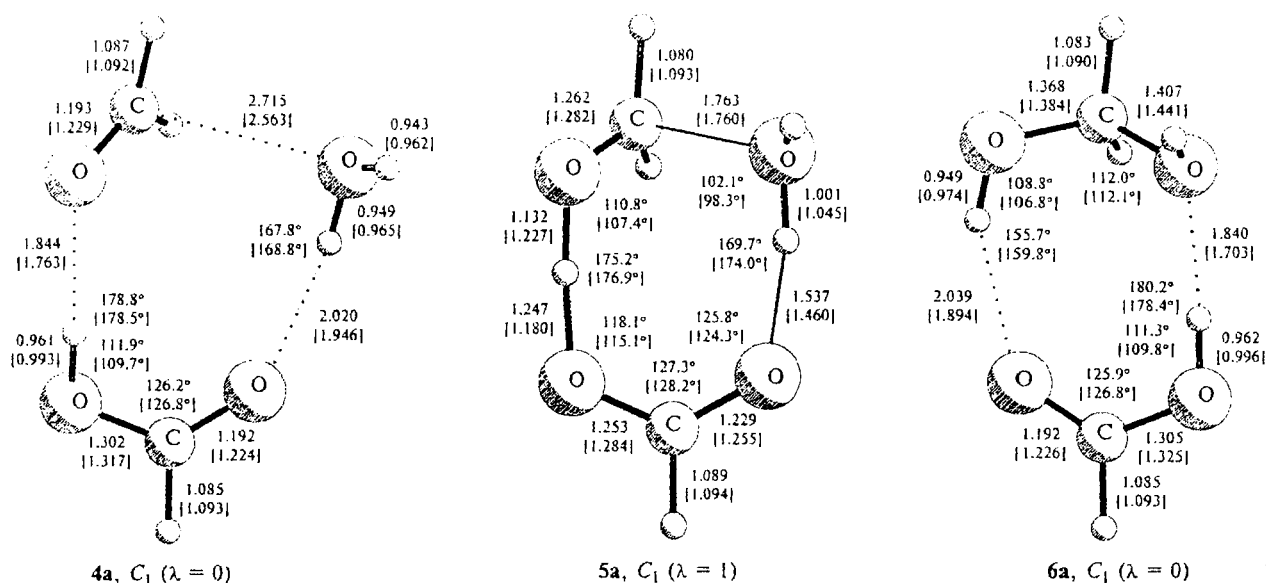
Fig. 4. Geometric parameters of complexes 4a and 6a corresponding to the minima, and 5a corresponding to the saddle point on the PES of the $H_2O...H_2CO...HC(O)OH$ system calculated by the RHF/6-31G** and MP2(fc)/6-31G** (figures in brackets) methods. Bond lengths (Å) and bond angles are shown.

4b, C_1 ($\lambda = 0$)   5b, C_1 ($\lambda = 1$)   6b, C_1 ($\lambda = 0$)
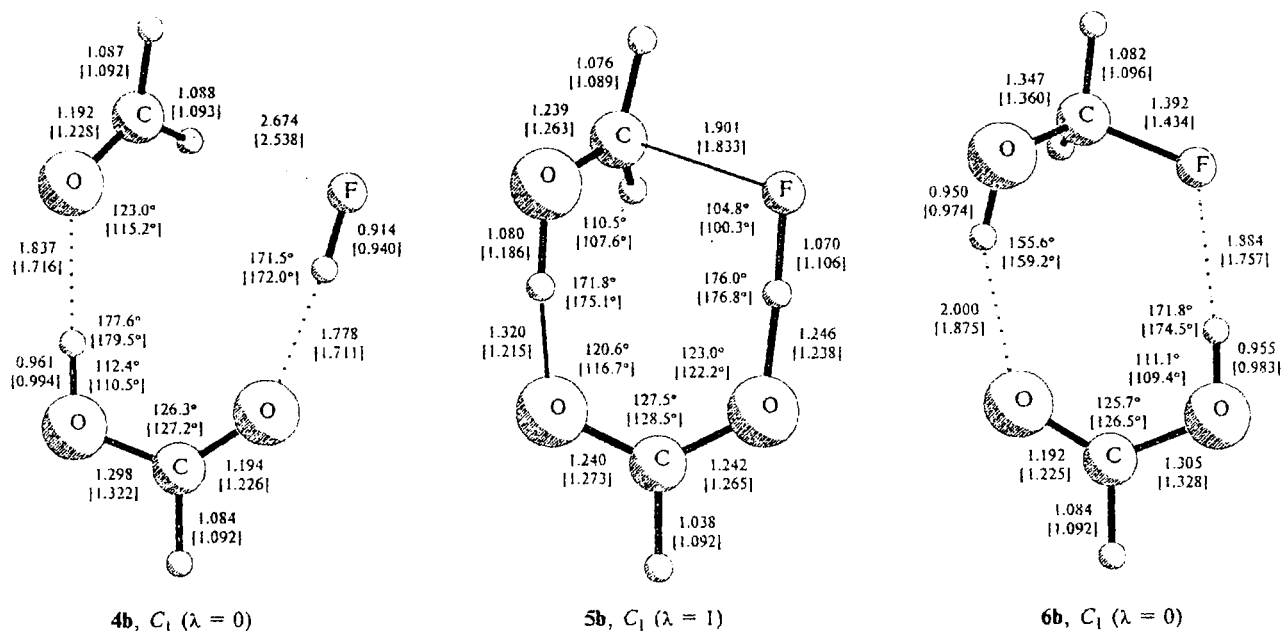
Fig. 5. Geometric parameters of complexes 4b and 6b corresponding to the minima, and 5b corresponding to the saddle point on the PES of the $HF...H_2CO...HC(O)OH$ system calculated by the RHF/6-31G** and MP2(fc)/6-31G** (figures in brackets) methods. Bond lengths (Å) and bond angles are shown.

ried out by the RHF/6-31G** and MP2(fc)/6-31G** methods, while those for the continuous reaction pathways were performed by the RHF/6-31G** method. According to the RHF/6-31G** and MP2(fc)/6-31G** calculations, structures 4a,b and 6a,b correspond to the minima ($\lambda = 0$) while structures 5a,b correspond to

the saddle points ($\lambda = 1$) on the PES. The calculated geometric and energy characteristics of structures 4—6 are shown in Figs. 4 and 5 and listed in Table 3.

The trimolecular complexes 4a,b are stabilized due to the formation of two H-bonds and a rather strong donor-acceptor C...X interaction. According to the

Table 3. Total energies (E_{tot}/au), relative energies $(\Delta E/kcal\ mol^{-1})$, the number of negative eigenvalues of the Hessian (λ), zero-point harmonic vibrational energies (ZPE/au), and the imaginary or the lowest harmonic frequencies $((i\omega/\omega_1)/cm^{-1})$ calculated by the RHF/6-31G** and MP2(fc)/6-31G** (figures in brackets) methods for structures 4—6 in the HC(O)OH...HX...H$_2$CO system (X = OH (a), F (b))

Structure (symmetry)	E_{tot}	ΔE	λ	ZPE	$i\omega/\omega_1$
4a (C_1)	−378.69007	0	0	0.09548	33
	[−379.69589]	[0]	[0]	[0.09092]	[32]
5a (C_1)	−378.65291	23.3	1	0.09510	i1031
	[−379.67918]	[10.5]	[1]	[0.09046]	[i754]
6a (C_1)	−378.70734	−10.8	0	0.10253	59
	[−379.71414]	[−11.4]	[0]	[0.09675]	[53]
4b (C_1)	−402.68280	0	0	0.08256	39
	[−403.67512]	[0]	[0]	[0.07834]	[40]
5b (C_1)	−402.64451	24.0	1	0.07940	i1015
	[−403.65426]	[13.1]	[1]	[0.07591]	[i1078]
6b (C_1)	−402.69804	−9.6	0	0.08876	45
	[−403.68871]	[−8.5]	[0]	[0.08393]	[37]

RHF/6-31G** and MP2(fc)/6-31G** calculations, the stabilization energies of complexes **4** (without inclusion of *BSSE* and *ZPE* corrections) relative to the individual molecules are equal to 16.4 and 20.1 kcal mol^{-1}, respectively, for X = OH (**4a**) and −19.3 and 22.9 kcal mol^{-1}, respectively, for X = F (**4b**). The inclusion of *ZPE* corrections reduces the complexation energy down to 12.5 and 15.7 kcal mol^{-1} for X = OH and to −15.4 and 18.6 kcal mol^{-1} for X = F. In the case of trimolecular complexes **4a,b** it is important to evaluate their enthalpies of formation from free formaldehyde, formic acid, and XH (X = OH, F) molecules. The enthalpies of formation of complexes **4** calculated by the RHF/6-31G** and MP2(fc)/6-31G** methods under standard conditions (at $T = 298.1$ K and $p = 1$ atm) are equal to 13.0 and 14.5 kcal mol^{-1}, respectively, for X = OH (**4a**) and to −16.1 and 19.5 kcal mol^{-1}, respectively, for X = F (**4b**). It should be noted that, first, in this case the inclusion of the electron correlation energy insignificantly increases the stabilization energy of complexes **4** and, second, the enthalpy of complexation for the trimolecular complexes **4a,b** remains nevertheless high. The lengths of the O—H...O and O...H—F bonds predicted by calculations are within the limits of the known experimental values of the lengths of similar bonds in organic[2,40,41] and biological structures.[2,36] It is noteworthy that the O—H bond of formic acid is directed toward the lone electron pair of the O atom of formaldehyde located on the hybrid sp^2-orbital,[42] which results in a tilt of the C=O bond of the formaldehyde molecule and its deviation out of the plane in which the formic acid molecule lies, *i.e.*, in complete asymmetrization of the system. In complexes **4a,b**, the C=O bond of formaldehyde and the X—H bond of the hydride

participating in the formation of the H-bond, and the O—H bond of formic acid are somewhat longer as compared to analogous bonds in the individual molecules, which indicates a slight activation of the molecules in complexes **4a,b**. Reaction (2) proceeds concertedly *via* the corresponding transition state **5a,b**, whose structure is similar to the structure of initial complexes **4a,b**, and results in the formation of bimolecular complex **6a,b**, H-bonded molecules of formic acid, and a substituted methanol. The energy barriers to reaction (2) predicted by the RHF/6-31G** and MP2(fc)/6-31G** methods are equal to 23.3 and 10.5 kcal mol^{-1}, respectively, for X = OH and to 24.0 and 13.1 kcal mol^{-1}, respectively, for X = F (see Table 3). Thus, the introduction of formic acid as catalyst considerably decreases the barrier to reaction (2) as compared to that to reaction (1).

The nature of catalytic action of formic acid can be explained by joint action of the following factors: (1) formic acid makes the reaction centers of the formaldehyde and XH molecules come close together to "organize" a unified reagent—nucleophile π-complex, which is independent of the nucleophile type and cannot be formed in the gas phase; in this complex, the donor-acceptor interaction between the frontier orbitals of the reagent—nucleophile system occurs almost ideally; (2) due to acid-base interaction, formic acid activates the reagents; the C=O bond of formaldehyde and the X—H bond are lengthened as compared to the analogous bonds not only in the free molecules, but also in complex **1** (see Figs. 1 and 2); (3) the OH...O and O...HX hydrogen bonds differing little from the stereochemically most favorable linear H-bonds[40—42] are formed in complex **4**; in this case all the bond angles are close to the corresponding optimum standard bond angles; unlike reaction (1), in the course of which an extremely strained four-membered cycle is formed in transition state **2**, in the course of reaction (2) the protons move along the most favorable pathways (hydrogen bridges), while the electronegative atom X approaches the C atom following the stereochemically most favorable Burgi's pathway;[4] and (4) the final state **6** is stabilized by hydrogen bonds to a slightly greater extent than the initial pre-reaction complex **4**.

References

1. W. P. Jencks, *Catalysis in Chemistry and Biochemistry*, McGraw-Hill, New York, 1969.
2. A. J. Kirby, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 707; *Adv. Phys. Org. Chem.*, 1994, **29**, 87.
3. V. I. Minkin, B. Ya. Simkin, and R. M. Minyaev, *Quantum Chemistry of Organic Compounds. Mechanisms of Reactions*, Springer-Verlag, Berlin, 1990, 270 pp.

4. H. B. Burgi and J. D. Dunitz, *Acc. Chem. Res.*, 1983, **16**, 153.

5. Y.-T. Chang and G. H. Loew, *J. Am. Chem. Soc.*, 1994, **116**, 3548.

6. R. M. Minyaev, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 13 [*Russ. Chem. Bull.*, 1998, **47**, 8 (Engl. Transl.)].

7. A. Fiedler, D. Schroder, H. Schwarz, B. L. Tjelta, and P. B. Armentrout, *J. Am. Chem. Soc.*, 1996, **118**, 5047.

8. O. N. Ventura, E. L. Coitino, A. Lledos, and J. Bertran, *J. Comput. Chem.*, 1992, **13**, 1037.

9. R. M. Minyaev, *Usp. Khim.*, 1994, **63**, 939 [*Russ. Chem. Rev.*, 1994, **63**, 883 (Engl. Transl.)].

10. H. Yamataka, S. Nagase, T. Ando, and T. Nanafusa, *J. Am. Chem. Soc.*, 1986, **108**, 601.

11. I. H. Williams, *Chem. Soc. Rev.*, 1993, **22**, 277.

12. C. Kozmutza, E. M. Evleth, and E. Kapuy, *J. Mol. Struct. (Theochem.)*, 1991, **233**, 139.

13. F. Leng, R. Savkur, I. Fokt, T. Przewloka, W. Priebe, and J. B. Chaires, *J. Am. Chem. Soc.*, 1996, **118**, 4731 (and references cited therein).

14. F. A. Baiocchi and W. Klemperer, *J. Chem. Phys.*, 1983, **78**, 3509.

15. L. Schriver, O. Abdelaoui, and A. Schriver, *J. Chem. Phys.*, 1992, **96**, 8069.

16. O. Abdelaoui, L. Schriver, and A. Schriver, *J. Mol. Struct.*, 1992, **268**, 335.

17. A. Nowek and J. Leszczynski, *J. Chem. Phys.*, 1996, **104**, 1441.

18. T. Yamabe, C.-D. Zhao, M. Koizumi, A. Tachibana, and K. Fukui, *Can. J. Chem.*, 1985, **63**, 1532.

19. K. Yamashita, T. Yamabe, and K. Fukui, *Theor. Chim. Acta*, 1982, **60**, 523.

20. J. D. Madura and W. L. Jorgensen, *J. Am. Chem. Soc.*, 1986, **108**, 2517.

21. J. B. Foresman and E. Frisch, *Exploring Chemistry with Electronic Structure Methods*, 2nd Ed., Gaussian, Inc., Pittsburgh, 1996, 302 pp.

22. M. J. Frish, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. AlLaham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker,

J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, *GAUSSIAN-94, Revision B.3*, Gaussian, Inc., Pittsburgh (PA), 1995.

23. M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, *J. Comput. Chem.*, 1993, **14**, 1347.

24. K. S. Krasnov, N. V. Filippenko, V. A. Bobkova, N. L. Lebedeva, E. V. Morozov, T. I. Ustinova, and G. A. Romanova, *Molekulyarnye postoyannye neorganicheskikh soedinenii* [*Molecular Constants of Inorganic Compounds*], Khimiya, Leningrad, 1979, 446 pp. (in Russian).

25. Y. Yamada, T. Nakagawa, K. Kuchisu, and Y. Morino, *J. Mol. Spectrosc.*, 1971, **38**, 70.

26. J. L. Derissen, *J. Mol. Struct.*, 1971, **7**, 67.

27. A. D. Buckingham, *J. Mol. Struct.*, 1991, **250**, 111.

28. D. E. Reisner, R. W. Field, J. L. Kinsey, and H.-L. Dai, *J. Chem. Phys.*, 1984, **80**, 5968.

29. O. A. Osipov, V. I. Minkin, and A. D. Garnovskii, *Spravochnik po dipol'nym momentam* [*Handbook of Dipole Moments*], Vysshaya Shkola, Moscow, 1971, 414 pp. (in Russian).

30. T. K. Ha, J. Makarewicz, and A. Bauder, *J. Chem. Phys.*, 1993, **97**, 11415.

31. I. H. Williams, *J. Am. Chem. Soc.*, 1987, **109**, 6299.

32. B. J. Nelander, *J. Chem. Phys.*, 1980, **72**, 77; *Chem. Phys.*, 1992, **159**, 281.

33. E. E. Astrup, *Acta Chem. Scand.*, 1971, **25**, 1494.

34. A. C. Legon and D. J. Millen, in *Principles of Molecular Recognition*, Eds. A. D. Buckingham, A. C. Legon, and S. M. Roberts, Blackie Academic and Professional, London, 1993, 16.

35. T. Steiner, J. A. Kanter, and J. Kroon, *J. Chem. Soc., Chem. Commun.*, 1996, 1277.

36. G. A. Jeffrey and W. Saenger, *Hydrogen Bonding in Biological Structures*, Springer-Verlag, New York, 1991, 569 pp.

37. R. M. Lees and J. G. Baker, *J. Chem. Phys.*, 1968, **48**, 5299.

38. D. R. Herschbach, *J. Chem. Phys.*, 1956, **25**, 358.

39. R. M. Minyaev and E. A. Lepin, *Mendeleev Commun.*, 1997, 80, 189; ftp://soul.rnd.runnet.ru/pub/gorguts.zip.

40. F. Hibbert, *Adv. Phys. Org. Chem.*, 1986, **22**, 113.

41. M. C. Etter, *J. Phys. Chem.*, 1991, **95**, 4601.

42. S. Scheiner, *Acc. Chem. Res.*, 1994, **27**, 402.