Experimental

Commercial Aerosil, with a specific surface of 100 m^2 g^{-1} after repeated activation, was used in the study. The method of thermochemical activation of Aerosil was described in detail previously.[8] The reaction of methylenecyclopropane occurring in the gas phase with $\equiv$Si$^\cdot$ radicals on the Aerosil surface (the concentration of $\equiv$Si$^\cdot$ was $\sim 3 \cdot 10^{15}$ m^{-2}) was carried out at 190 K. Since it was found that under the experimental conditions, the second methylenecyclopropane molecule reacts with the radicals formed faster than with $\equiv$Si$^\cdot$, small quantities of methylenecyclopropane (smaller than the concentration of $\equiv$Si$^\cdot$ on the Aerosil surface) were used, and complete conversion of $\equiv$Si$^\cdot$ into radical products was not attained. The ESR spectrum was recorded on a Varian E-3 radiospectrometer operating in the three-centimeter range.

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Dynamic and electrooptical properties of FH...F and FH...N hydrogen bridges

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The dynamic and electrooptical parameters of the hydrogen bridges in $(HF)_2$, FH...FCD_3, FH...NCH, and FH...$NCCH_3$ complexes were calculated by the MINDO/3 method. Relationships between these parameters have been found. These parameters for the F—H...Y bridges mainly coincide with the relationships previously established for the hydrogen O—H...Y bridges.

Key words: hydrogen fluoride, hydrogen bond; potential energy surface, force constant; dipole moment.

Intermolecular interactions in gases and liquids result in the formation of various complexes and associates. The compositions and structures of these molecular forms affect the different physicochemical properties of a substance and its reactivity. That is why the structures of molecular and ion-molecular complexes have become an object of investigation in various scientific areas. In these investigations, IR spectroscopy is often used, which requires knowledge of the dynamic and electrooptical properties of the intermolecular bonds uniting the molecules into a complex. These properties, characterized by the dynamic and electrooptical parameters of the bonds and angles, are usually determined by solving the inverse spectral problems (ISP) or by quantum-chemical calculations. The dynamic and electrooptical parameters of the different strength hydrogen bonds formed by

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Table 1. Dynamic and electrooptical parameters of the hydrogen bridges F—H...F and F—H...N

Molecule, complex	Conformation	$\Delta\nu_{exp}$	$K_{HF}^{mon} - K_{HF}^{comp}$	K_H	K_H^{HF}	K_β	K_γ	μ_{HF}	μ_H	$\partial\mu_{FH...Y}/\partial q_{FH}$	$\partial\mu_{FH...Y}/\partial q_H$
		/cm^{-1}	10^6 cm^{-2}			10^5 cm^{-2}		D		D Å^{-1}	
HF		0	0	0	0	0	0	1.58	0	0.8±0.05	0
FH...FH	*cis*	94	4.0±0.4	2.30±0.10	0.4±0.1	2.0±0.2	−0.1±0.1	1.70	0.30	1.6±0.05	0.0±0.03
FH...FH	*trans*	94	5.9±0.4	3.47±0.10	0.4±0.1	1.8±0.2	0.1±0.1	1.73	0.32	1.7±0.03	0.0±0.03
FH...FCH$_3$	lin*	178	6.1±0.4	4.00±0.15	0.7±0.2			1.84	0.23	1.9±0.12	−0.2±0.08
FH...FCH$_3$	*cis*	178	5.4±0.4	3.53±0.15	0.7±0.2	2.3±0.2	0.1±0.2	1.83	0.24	1.8±0.14	−0.2±0.08
FH...FCH$_3$	*trans*	178	5.2±0.4	4.81±0.15	0.5±0.2	2.3±0.2	0.2±0.2	1.83	0.25	2.1±0.14	−0.1±0.09
FH...NCH	*cis*	246	8.3±1.0	0.04±0.15	1.0±0.3	5.0±0.4	1.3±0.3	1.94	−0.50	2.4±0.12	−2.6±0.03
FH...NCH	*trans*	246	7.6±1.0	0.04±0.17	0.8±0.3	6.0±0.4	1.7±0.3	2.04	−0.64	2.7±0.11	−2.9±0.03
FH...NCCH$_3$	lin*	337	6.6±1.0	0.45±0.05	0.8±0.1			2.24	−0.87	3.1±0.10	−3.3±0.03
FH...NCCH$_3$	*cis*	337	7.9±1.0	1.90±0.20	0.7±0.3	5.6±0.5	2.3±0.3	2.52	−1.10	3.4±0.13	−3.8±0.06
FH...NCCH$_3$	*trans*	337	7.2±0.8	1.90±0.20	0.6±0.3	6.6±0.6	3.0±0.4	2.51	−1.10	3.7±0.13	−3.8±0.07

* Linear structure.

water molecules have been studied fairly well.[1] The relationships established allow one to determine the structure of almost any aquacomplex from its vibrational spectrum.

Problems requiring knowledge of the structures of complexes formed by hydrogen fluoride molecules, FH...Y, arise in the analysis of a number of questions associated with the environment and chemical engineering. The dynamic and electrooptical parameters of the hydrogen bonds in such complexes have not been studied much. The impossibility of determining these parameters by solving ISP is primarily due to the ambiguity of the interpretation of the observed spectra or often to their absence in the low-frequency region. Therefore, currently one can only give a theoretical estimate of the indicated parameters. It should be admitted that currently available quantum-chemical methods determine these parameters with a low degree of accuracy for any particular system. Nevertheless, these methods adequately reflect the relations between the parameters and the character of their dependence on the strength of the hydrogen bond.[2]

Therefore, it seemed to be possible to clarify two issues. First, the extent to which the relations between the different dynamic parameters of an O—H...Y bridge are retained in a F—H...Y type complex. Secondly, do the electrooptical properties of the FH...Y bridge depend on the strength of the hydrogen bond in a way that is analogous to that found for aquacomplexes.[1] Answering these questions is the goal of this work.

Method of Calculations

The calculations were performed by the semiempirical MINDO/3 method adapted for systems with dependent natural coordinates.[3,4] Complexes FH...FH, FH...FCD$_3$, FH...NCH, and FH...NCCH$_3$ were chosen as objects of the investigation. For these complexes, the bathochromic shifts of the bands of stretching vibrations $\Delta\nu(HF)$[5—8] were reliably measured to be 94 (gas phase), 178 (a Xe matrix), 246 (gas phase), and 337 cm^{-1} (gas phase), respectively. These values were used as a criterion for the strength of the hydrogen bond.

The angles at the hydrogen bond are usually not precisely measured. To estimate their effect on the calculated elasticities of the hydrogen bond and the first derivatives of the dipole moments, some plausible configurations for each complex were analyzed. The parameters found are listed in Table 1 along with their spread, which always exists if the calculated values of the potential energy are approximated by a smooth potential energy surface.[3,4] Table 1 shows for the covalent HF bonds how much the force constants in the complex (K_{HF}^{comp}) are smaller than in the free molecule ($K_{HF}^{mon} = 17.00 \cdot 10^6$ cm^{-2}) calculated by the same method. The 14% overestimation of the value of the force constant of the HF bond (that obtained by solving ISP is equal to $14.848 \cdot 10^6$ cm^{-2}) is typical of all quantum-chemical calculations with an adiabatic approximation.[9] Therefore, using one of these approximate methods we will consider only strong effects whose values appreciably exceed a spread of 15—20%.

Results and Discussion

As can be seen from the data obtained, the differences between the K_{HF} values for structural isomers of all complexes under consideration do not exceed the indicated calculation error. Hence, in analyzing these results the parameters found for isomers of the same complex can be assumed to be approximately equal (of the same order). The electrooptical parameters of the bridge are even more approximate (taking into account that the calculated $\partial\mu_{HF}/\partial q_{HF}$ value is equal to 0.8 D Å^{-1} while that found from the solution to the ISP is equal to 0.32 D Å^{-1}).

Considering the results of the calculations and taking into account the indicated errors one can see the following properties of the potential energy surface of the FH...Y complexes and their electrooptical constants.

1. The force constant of the HF bond decrease substantially as the hydrogen bond in the FH...F and FH...N bridges is strengthened. This decrease (ΔK_{FH}) is approximately an order of magnitude larger than the force constant of the interaction between the covalent and hydrogen bonds ($K^H{}_{FH}$).

2. The force constants of the angles with the F or N atom at the vertex (K_β) are 4—10 times larger than the force constants of the F—H...F(N) angles (K_γ) in all cases considered.

3. The dipole moment of a very weak hydrogen bond ($\Delta\nu \approx 100$ cm^{-1}) directed to the hydrogen atom (a plus sign) reverses its direction (a minus sign) as the H-bond is strengthened ($\Delta\nu \approx 200$—250 cm^{-1}).

4. The derivatives of the dipole moment of the hydrogen bridge with respect to the coordinates of its covalent and hydrogen bonds have opposite signs.

5. The difference between these derivatives, which determines the intensity of the ν(HF) stretching vibration, drastically increases as the hydrogen bond is strengthened. A comparison of the $\partial\mu_{HF}/\partial q_{HF}$ derivatives obtained by the MINDO/3 method and from solving the ISP shows (see Table 1) that by itself the approximation error is 3—5 times less than the total error. Taking this fact into account and setting $\partial\mu_{HF}/\partial q_{HF} = 0.32$ D Å^{-1} for a free HF molecule (from the solution to the ISP), one can assume the dependence ($\partial\mu_{FH...Y}/\partial q_{FH} - \partial\mu_{FH...Y}/\partial q_{H...Y}$) on Δν(HF) (Fig. 1) to be linear.

It follows from the above results that certain relationships are observed in F—H...Y type complexes (as well as in O—H...Y systems[1]).

— The principal manifestation of the hydrogen bond, related to a decrease in the ν(FH) frequency, is due to a decrease in the force constant of the HF bond (ΔK_{FH}), rather than the interaction constant ($K_H{}^{HF}$).

— The ratio of the force constants of the angles K_β and K_γ in the complexes studied is the same as in systems with an O—H...Y bridge.

— The direction of the dipole moment of the hydrogen bond from the H atom to the N atom in the FH...NCH complex coincides with its direction in the water dimer.[10]

— The signs of the derivatives of the dipole moment with respect to the bond coordinates in the compared bridges coincide (a plus sign for a covalent bond and a minus sign for a hydrogen bond).[1]

— The electrooptical parameter of the hydrogen FH...Y bridge increases linearly as the strength of the hydrogen bond increases. There is no reason to discuss the slope of this dependence since, as was mentioned above, the electrooptical parameters are calculated with a very large error.

Thus, the principal relationships characteristic of dynamic and electrooptical properties of hydrogen bridges are the same in the O—H...Y and F—H...Y systems.

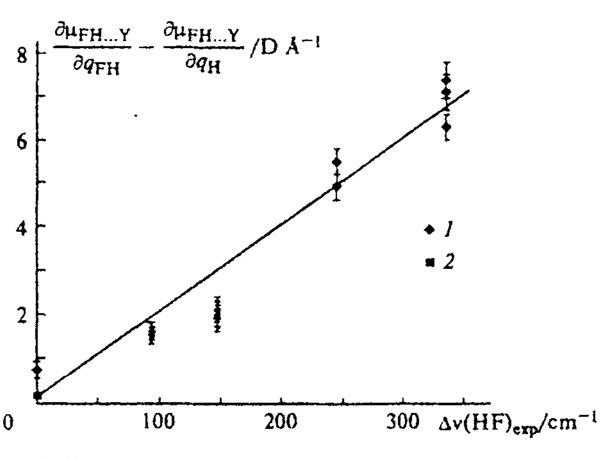

Fig. 1. Dependence of the effective electrooptical parameter of the hydrogen bridge ($\partial\mu_{FH...Y}/\partial q_{FH} - \partial\mu_{FH...Y}/\partial q_H$) on the strength of the hydrogen bond (the total error is assumed to be triple value of the approximation spread).
1, MINDO/3 method; *2*, ISP solution.

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