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MOLECULAR SPECTROSCOPY

Calculation of Vibrations of the H-bonds and Electrooptical Parameters of the $[F(HF)_2]^-$ Complex

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Abstract—The problem of calculating the vibrations of the $[F(HF)_2]^-$ complex with hydrogen bonds is considered with allowance for the anharmonicity and interaction of motions in different degrees of freedom. A systematic solution of this problem is proposed which consists in separating the total vibrational system into subsystems, obtaining sufficiently exact vibrational wave functions of subsystems, and expanding the vibrational wave functions of the total system in basis functions constructed from the wave functions of subsystems. At the first stage of our study, the stretching and bending modes of two F…HF hydrogen bonds are considered with the use of an exact kinetic energy operator and a nonempirical three-dimensional potential energy surface. It is shown that these vibrational modes of the complex are characterized by significant mechanical and electric anharmonicities. The calculated values of frequencies of the symmetric and antisymmetric vibrations of hydrogen bonds are in good agreement with the experimental findings. *© 2001 MAIK "Nauka/Interperiodica".*

INTRODUCTION

The $[F(HF)_2]^-$ complex belongs to the most stable compounds with hydrogen bonds. Investigation of this complex can provide much information on the nature of hydrogen bonding and the mechanisms of various manifestations of this type of intermolecular interactions, which are less pronounced in weaker complexes. In spite of this fact, the electronic-shell structure and vibrations of this complex remain insufficiently studied both theoretically and experimentally, as compared, for example, to dimers of hydrogen halides and water molecules. The reason for this lies in the fact that this complex is observed in complicated aggregate states: in crystalline mixtures of compounds, multicomponent solutions, or low-temperature matrices.

The geometric structure of this complex was studied by the methods of X-ray and neutron scattering (see, for example, [1, 2]). In this complex, the central F atom forms hydrogen bonds F…HF with two hydrogen fluoride molecules. The F…F separation and the angle between two H-bonds depend on the surroundings of the complex and are close to 2.33 Å and 134°, respectively. In [3], this system was prepared in neon and argon matrices by bombardment of an initial mixture containing HF molecules by electron beams with energies of 100–400 eV. In this work, the IR spectra of bands associated with the intramolecular vibrations of HF molecules and antisymmetric changes in F…F separations were recorded. The IR spectra of the $[F(HF)_2]^-$ complex in crystals and solutions containing cations of potassium [4] and a number of complicated amines [5, 6] were recorded at temperatures of 12 and 300 K. The IR spectra were studied for the regions of bands of the F…F stretches, the librations of HF subunits, the high-frequency vibrations of molecular partners, and, in some cases, the bending vibration (the H…F…H angle). It was found that different partners have a different perturbing effect on the frequencies and intensities of vibrational bands of the anion and on its geometry, for example, on the position of the H atom in a H-bridge.

In [7], the $[F(HF)_2]^-$ complex was studied by the methods of NMR spectroscopy. The $[F(HF)_2]^-$ anion was prepared in solutions of a mixture of tetrabutylammoniumfluoride and hydrogen fluoride in freons at temperatures of 110–150 K. Based on the experimental data, the magnitudes of chemical shifts were obtained for hydrogen and fluorine atoms, as well as values of the spin–spin interaction constants for different pairs of nuclei. The theoretical study of NMR signals and the electron density distribution in the complex was performed by using the density functional theory and the method of molecular orbitals (GAUSSIAN 94). The results of this work allowed the authors to better understand the geometry of the complex in different surroundings and to study the electron density distribution in it and a possible degree of covalence of hydrogen bonds.

The structure and properties of this complex were the object of a number of quantum-mechanical calculations (see, for example, [8, 9]). As a rule, it was studied among other related complexes, and the calculations were limited to determining its equilibrium geometry, total electronic energy, and vibrational frequencies in the harmonic approximation.

To study the internal dynamics of H-bonded and van der Waals complexes, it is necessary to solve a quantum-mechanical Schrödinger equation. By now, significant experience in solving such problems for systems consisting of atoms and diatomic and triatomic molecules has been gained. In these calculations, effective Hamiltonians are employed, which are obtained by integration over the coordinates of rotation of the complex as a whole, and sometimes over the coordinates of high-frequency intramolecular vibrations [10, 11]. As the potential energy, the results of *ab initio* calculations or various model and semiempirical potentials are used.

At present, many researchers understand that the molecular complexes should be the object of a concerted solution of both the problem of calculation of their electronic structure and electronic energy and the vibrational problem. For example, in [12], a corresponding package of programs is discussed and an attempt is made to calculate the potential energy surface (PES) for a water dimer and the anharmonic vibrational frequencies of this system by the vibrational self-consistent field method.

It is known that hydrogen bonded complexes are characterized by the presence of large-amplitude motions (associated with changes in separations between some atoms and with changes in angles between some bonds), significant anharmonicity of some sections of the PES, coupling between different degrees of freedom, and pronounced isotopic effects. These specific features of hydrogen bonded complexes make their theoretical consideration difficult. Unfortunately, most modern packages of programs for quantum-mechanical calculations of molecular systems, such as GAUSSIAN and GAMESS, can provide the solution of the vibrational problem only in the harmonic approximation. In obtaining a more rigorous solution of a vibrational problem, these programs can be used only to find values of the electronic energy and multipole moments for particular configurations of the system. These configurations are chosen on account of specific properties of each system and objectives of the calculation. In a sufficiently correct calculation, the number of such points may be large (more than 10^4). Because the electronic energy of a complex—which, in the adiabatic approximation, plays the role of the potrential energy for nuclear vibrations—must be computed with very high accuracy, the quantum-mechanical calculations should be carried out with large sets of optimized atomic orbitals, and it is necessary to explicitly account for the electron correlation.

The purpose of this work is primarily to calculate the vibrational frequencies and electrooptical parameters of the $[F(HF)_2]^-$ complex. This problem should be treated with allowance for the complicated behavior of the PES, the presence of large-amplitude vibrations, and the kinematic and dynamic coupling between different degrees of freedom. To our knowledge, calculations of vibrations in this complex in the anharmonic approximation are not available in the literature. To solve this vibrational problem, a nonempirical quantum-mechanical calculation will be preliminarily performed to determine the equilibrium geometry of the complex, sections of its PES, and the dipole moment components.

The complex in question has nine vibrational degrees of freedom. Solution of a nine-dimensional problem presents significant difficulties. In view of this, it is reasonable to consider the internal dynamics of the complex in several steps, first solving problems of smaller dimensionality and using the results obtained for finding a more complete solution.

NONEMPIRICAL CALCULATION OF THE ELECTRONIC STRUCTURE AND ENERGY OF THE $[F(HF)_2]^-$ COMPLEX

The purpose of the *ab initio* electronic structure calculation of the $[F(HF)_2]^-$ complex performed at the first stage of our study was to determine its equilibrium geometry, some characteristics of electron density distribution for this configuration, and values of the electronic energy and dipole moment components necessary for solving the subsequent vibrational problem. We used the MO LCAO SCF method implemented in the GAMESS package [13]. Preliminary calculations showed that results necessary for our purposes can be obtained by using a set of Gaussian atomic orbitals 6–31 G^{**++} without taking into account the effect of superposition of the basis sets of separate partners but with calculation of the correlation corrections by the second-order Möller–Plesset perturbation theory (MP2).

Calculating the complex $[F(HF)_2]^-$ in the regime of searching for an optimized geometry showed that the equilibrium nuclear configuration of this system is characterized by the following values of parameters: the F…H separations are equal to 1.3495 Å, the H–F bond lengths are 1.012 Å, and the H…F…H angle is 130.2°. These results are in good agreement with the experimental data [1, 2] and nearly coincide with the results of calculating the equilibrium configuration carried out by a somewhat different method in [7]. It follows from our calculation of an isolated HF molecule, performed in the same approximation as the calculation of the entire complex, that the molecular bond length is elongated by 0.086 Å upon complexation. Unlike the case of the more stable $FHF]^-$ complex, the H atom is located asymmetrically relative to two fluorine atoms. The total energy of the complex is equal to –299.578206 and –300.175020 au in the SCF and MP2 approximations, respectively. Thus, the correlation correction to the total energy amounts to 0.596827 au. Calculations of the fluorine anion and the hydrogen flouride molecule in the MP2 approximation yield a value of 0.11934 au for the binding energy of the complex. In the equilibrium nuclear configuration, the complex has a nonzero value of the *z*-projection of dipole moment (–0.1275 D) determined with respect to the center of gravity.

The atomic charges *q* and the bond orders *p* between atoms are important characteristics of the electronic structure of molecular systems. In the complex under study, the charges *q*(F) determined according to Mulliken are negative and equal to –0.8746 (the central F atom) and –0.6863 (terminal F atoms), while *q*(H) are positive and equal to 0.6236. It is evident that the negative charge of the anion is not located only at the central F nucleus, but is partially transferred to the other F atoms. As expected for a hydrogen bonded system, the protons of H-bridges are significantly naked (to a larger extent than in the HF molecule, where *q*(H) = 0.4058). Our calculation of the isolated HF molecule shows that *p*(H–F) = 0.793. The deviation of this value from unity is indicative of an appreciable ionicity of the H–F bond. In the complex, $[F(HF)_2]^-$ *p*(H–F) = 0.491. Comparison with the above value indicates a weakening of the H–F bond on complexation. For the H…F pair in the complex, *p* = 0.128, which suggests that the hydrogen bonding in the complex considered partially has a covalent nature and does not reduce to the effects of polarization, charge transfer, and dispersion interactions. To appreciate this fact, assume that the extra electron of the complex is entirely localized at the central fluorine atom. The F^- anion can have a closed neonlike shell, but, in this system, unlike the Ne atom, one of electrons can easily shift to an outer, say, 3*s* or 3*p* orbital. As a result, the F^- anion becomes bivalent and, consequently, can form covalent chemical bonds with two hydrogen atoms. The large weight of the corresponding ionic–covalent structure explains the significant value of bond order *p* (H…F).

FORMULATION OF THE VIBRATIONAL PROBLEM AND METHOD OF ITS SOLUTION

It is difficult to obtain a sufficiently exact solution of a nine-dimensional vibrational problem. Such a solution would require the prior determination of the energy of a complex for a very large number of nuclear configurations. Solution of the vibrational problem itself for such a number of interacting degrees of freedom by using any sufficiently correct approach requires a large amount of computer time. To our knowledge, the maximum dimensionality of such a problem successfully solved to date is six (the calculation of $(HF)_2$ in [14]).

The techniques of real and, at the same time, exact calculations of multidimensional problems rely, as a rule, on separation of the entire system into weakly interacting subsystems, correct consideration of each subsystem, and subsequent allowance for their interaction. The use of eigenfunctions of the effective Hamiltonians of subsystems as the basis functions, in which the wave functions of the full system are expanded, decreases the dimension of the matrix of the total Hamiltonian and allows one to obtain a sufficiently exact solution with reasonable computational efforts.

In our case, at the first stage, it is advisable to consider the intermolecular (stretching and bending) and high-frequency intramolecular modes separately. The calculation of the $[F(HF)_2]^-$ complex by using the GAMESS program yields the following values of harmonic vibrational frequencies (in cm^{-1}): 59.8, 364.8, and 460.1 (bending and symmetric and antisymmetric stretching vibrations of H-bonds); 1158.8, 1184.9, 1193.4, and 1246.6 (librational modes of HF molecules); and 2363.9 and 2710.8 (combinations of the intramolecular modes of HF). From these data one can see that it can be justified to separate the high-frequency librations with frequencies higher than 1000 cm^{-1} from vibrations associated with changes in distances between the central F atom and the HF molecules and with changes in the angle formed by the hydrogen bonds. In analyzing the latter low-frequency modes, this is equivalent to replacing the HF molecules by effective atoms placed at the centers of gravity of molecules and having the masses of molecules. Such an approach was used, for example, in [15], where a portion of the spectrum of a HCN…HF complex was calculated. The results obtained in this paper for the IR bands associated with the stretching vibration of monomers in the complex are in good agreement with experimental data. Therefore, in this work we restrict our consideration to a three-dimensional vibrational problem of calculating the intermolecular stretching and bending vibrations of H-bonds. The calculation is performed for the $[F(HF)_2]^-$ complex and its five isotopomers obtained by a partial or complete substitution of the H atoms by D and T atoms. The results of this calculation are not only useful for solving a fuller problem, but are interesting by themselves because they can be compared to some experimental findings and provide information on the effects of anharmonicity and coupling between separate degrees of freedom.

Positions of the effective atoms with respect to the central fluorine atom were described by using the symmetry coordinates of the C_{2v} group:

$$r_s = \frac{1}{\sqrt{2}}(R_1 + R_2 - 2R_e), \quad r_{as} = \frac{1}{\sqrt{2}}(R_1 - R_2),$$

where R_1 and R_2 are the separations between the fluorine atom and the centers of gravity of the HF molecules, R_e is their equilibrium value, and r_s and r_{as} are the symmetric and antisymmetric vibrational coordinates. The third vibrational coordinate (α) is a change in the angle θ formed by two H-bonds. The potential energy of a vibrating system is computed as a function of the adopted vibrational coordinates.

As mentioned above, the vibrations of the complex can have large amplitudes; hence, it is necessary to use the kinetic energy operator in a form that correctly describes such motions. A kinetic energy operator suitable to any triatomic system ABC was proposed in [16]:

$$\begin{aligned} T \equiv & -\frac{\hbar^2}{4}\left(\frac{1}{\mu_1 R_1^2}+\frac{1}{\mu_2 R_2^2}-\frac{2\cos\theta}{m_{\mathrm{B}} R_1 R_2}\right)\left(\frac{\partial^2}{\partial\theta^2}+\cot\theta\frac{\partial}{\partial\theta}\right) \\ & -\frac{\hbar^2}{4}\left(\frac{\partial^2}{\partial\theta^2}+\cot\theta\frac{\partial}{\partial\theta}\right)\left(\frac{1}{\mu_1 R_1^2}+\frac{1}{\mu_2 R_2^2}-\frac{2\cos\theta}{m_{\mathrm{B}} R_1 R_2}\right) \\ & +\frac{\hbar^2}{m_{\mathrm{B}}}\left(\frac{1}{R_1}\frac{\partial}{\partial R_2}+\frac{1}{R_2}\frac{\partial}{\partial R_1}\right)\left(\sin\theta\frac{\partial}{\partial\theta}+\cos\theta\right) \\ & +\frac{\hbar^2}{2\mu_1}\frac{\partial^2}{\partial R_1^2}-\frac{\hbar^2}{2\mu_2}\frac{\partial^2}{\partial R_2^2}-\frac{\hbar^2\cos\theta}{m_{\mathrm{B}}}\frac{\partial^2}{\partial R_1 \partial R_2}, \end{aligned} \quad (1)$$

where $\frac{1}{\mu_1} = \frac{1}{m_{\mathrm{A}}} + \frac{1}{m_{\mathrm{B}}}$, $\frac{1}{\mu_2} = \frac{1}{m_{\mathrm{B}}} + \frac{1}{m_{\mathrm{C}}}$.

In our case, atoms A and C are the effective atoms located at the centers of gravity of the HF molecules; B is the central fluorine atom; m_{A}, m_{B}, and m_{C} are the masses of the corresponding atoms; and R_1 and R_2 are the separations indicated above. The T operator of this type was used, for example, in [17] to describe nuclear motions in the HCN molecule. Its use allowed the authors to compute all vibrational states with energies up to 1800 cm^{-1} with an accuracy to within 1 cm^{-1}.

We used the operator (1) rewritten in the symmetry coordinates. The desired three-dimensional vibrational wave function was expanded in a finite series of orthonormalized basis functions φ_v:

$$\Psi_n = \sum_v C_{nv}\varphi_v, \quad (2)$$

where C_{nv} are the expansion coefficients for the nth eigenfunction. An approximate value of the total vibrational energy $E_n = \langle\Psi_n|H|\Psi_n\rangle$, where the Hamiltonian $H = T + V$ is a function of the expansion coefficients. The set of coefficients C_{nv} and energies E_n are found from the system of secular equations

$$\sum_v [\langle v'|H|v\rangle - E_n\delta_{v'v}]C_{nv} = 0, \quad (3)$$

where $\langle v'|H|v\rangle$ is the matrix element of the Hamiltonian evaluated with basis functions φ.

To obtain sufficiently correct wave functions with a set of basis functions of a reasonable size, it is necessary to choose these functions taking into account specific features of the problem. In solving the three-dimensional vibrational problem, we chose the basis functions in the form of products of functions describing noninteracting one-dimensional stretching and bending vibrations:

$$\varphi_v = \chi_i^b(\alpha)\chi_j^s(r_s)\chi_k^{as}(r_{as}). \quad (4)$$

The subscipt v of a three-dimensional basis function refers to three indices (i, j, k). As functions χ^b, χ^s, and χ^{as}, the eigenfunctions of corresponding Schrödinger equations are chosen, in which the T operator is obtained from (1) by fixing two other coordinates, while the potential energy is a section of the three-dimensional function V at zero values of the other coordinates. All wave functions of r_s and α are totally symmetric, while the wave functions of r_{as} belong to the symmetry types A_1 or B_2 of the C_{2v} group depending on the number of a solution. The asymmetry in the Hamiltonian of complexes with different isotopes of hydrogen is insignificant; therefore, the symmetrized basis functions were used in calculations of all complexes containing all possible pairs of hydrogen isotopes.

Thus, the solution of the three-dimensional problem reduces to solutions of three one-dimensional problems and a subsequent intermixing of the products of one-dimensional eigenfunctions. To find the latter functions, we also use the variational principle and represent them in a form similar to (2) as linear combinations of one-dimensional eigenfunctions of harmonic oscillators. An additional nonlinear variational parameter having the meaning of an amplitude of zero-point vibrations is introduced in the functions of harmonic oscillators. It was found that it suffices to take in (4) six χ functions for each coordinate to ensure calculation of the frequencies with an accuracy of 1 cm^{-1} for a given potential V. The matrix elements of the Hamiltonian were evaluated by using Gauss–Legendre quadratures with 16 nodes for each variable. For these purposes, values of the potential energy were calculated at all nodes of three-dimensional grid.

Clearly, the potential energy of an isolated complex, as a function of the angle between H-bonds, has two minima and is symmetric with respect to the linear configuration. Calculation of a multidimensional problem with a two-minimum potential presents significant difficulties. However, to our knowledge, this complex was not observed in the gas phase, and, therefore, the solution of the problem with two minima is not topical. Thus, we restricted our study to the consideration of a bending vibration within a single minimum.

DISCUSSION OF THE RESULTS AND CONCLUSIONS

The solution of system (3) gives the eigenfunctions and eigenvalues of the three-dimensional Hamiltonian. Some low-lying excited states can be interpreted as sets of excitations of one-dimensional oscillators. Such states can be labeled by three numbers (i, j, k), which are equal to the numbers of excitations of oscillators associated with a change in the angle and with a symmetric and antisymmetric change in lengths of H-bonds. Clearly, these notations are less rigorous for asymmetric complexes. To determine (i, j, k), the following approaches were used. First, these are the indices of a product in (4) that appears in (2) with a maximum weight. For example, in $[\mathrm{F(HF)_2}]^-$, the wave function of a particular excited state contains the (0,1,0) basis function with a weight (the square of an expansion coefficient) of 0.8719. Secondly, separate indices in (*i*, *j*, *k*) can be found by a procedure similar to the Mulliken analysis of the electron density in the MO LCAO method. For example, to determine the *i* number, one should, for each possible value of *i*, calculate the sum of squares of the expansion coefficients in (2) (summation runs over all values of *j* and *k*). The desired value of *i* is associated with a maximum value of such a sum. For the state of $[F(HF)_2]^-$ mentioned above, these sums are maximum for $i = 0$ (0.9175), $j = 1$ (0.9458), and $k = 0$ (0.9910). The proximity of these four numbers to unity allows us to denote this excited state as (0,1,0). The third approach consists in constructing cuts of the wave functions in different planes. The nodal structure of these pictures reflects the number of excitations in each degree of freedom. It appeared that the states of the three-dimensional system can be interpreted as combinations of vibrations of one-dimensional oscillators if the latter are, as a rule, only singly or doubly excited. For such states, all the three procedures yield the same notation (*i*, *j*, *k*). In higher lying excited states, the one-dimensional oscillators are no longer independent.

For the six isotopomers of the complex, the calculated values of the ground-state energy *E* (0, 0, 0) are equal to 448.9 (H, H), 446.0 (H, D), 443.4 (H, T), 443.2 (D, D), 440.6 (D, T), and 438.0 cm^{-1} (T, T). The hydrogen isotopes entering the complex are shown in parentheses. The energies of three-dimensional vibrational states can be described by using the standard expression [18]

$$G(v_1, v_2, v_3) = \sum_i \omega_i (v_i + 1/2) + \sum_i \sum_{k \geq i} x_{ik} (v_i + 1/2)(v_k + 1/2). \quad (5)$$

Here, *i* and *k* equal to 1, 2, and 3 correspond to the bending, symmetric, and antisymmetric stretching modes, respectively. The application of (5) to approximate the energies of states of the $[F(HF)_2]^-$ complex, in which the one-dimensional modes are still independent, yields the following values for expansion parameters: $\omega_1 = 51.8 \pm 0.6$, $\omega_2 = 371.9 \pm 0.4$, $\omega_3 = 481.3 \pm 0.4$, $x_{11} = -0.1 \pm 0.1$, $x_{22} = -6.5 \pm 0.9$, $x_{33} = -5.6 \pm 1.0$, $x_{12} = -4.0 \pm 0.7$, $x_{13} = 0.7 \pm 0.5$, and $x_{23} = -3.7 \pm 0.4$ cm^{-1}. One can see that the vibrational system considered reveals a considerable anharmonicity and interaction between separate degrees of freedom. Note that the x_{33} constant is practically zero if the interaction of vibration in r_{as} with other modes is ignored. This suggests that, in low-lying excited states of the three-dimensional system, the antisymmetric mode retains its independence in terms of the form of vibration but is no longer harmonic.

Table 1 lists the calculated values of frequencies for transitions from the ground (0, 0, 0) state to excited (*i*, *j*, *k*) states. Our values of frequencies of the (0, 0, 0)–(0, 1, 0) and (0, 0, 0)–(0, 0, 1) fundamental transitions

Table 1. Frequencies of transitions (in cm^{-1}) from the ground (0, 0, 0) state to excited (*i*, *j*, *k*) states of the complexes studied

(*i*, *j*, *k*)	Hydrogen isotopes entering the complex					
	H, H	D, D	T, T	H, D	H, T	D, T
(1, 0, 0)	49.9	49.2	48.5	49.5	49.2	48.8
(2, 0, 0)	99.6	98.2	96.9	98.9	98.2	97.5
(0, 1, 0)	355.6	349.4	343.5	352.4	349.4	346.4
(1, 1, 0)	401.9	394.9	388.4	398.3	395.0	391.7
(0, 0, 1)	468.9	464.9	461.4	467.0	465.3	463.1
(1, 0, 1)	519.4	514.7	510.6	517.1	515.2	512.6
(0, 2, 0)	696.7	683.4	671.2	690.0	683.7	677.3
(1, 2, 0)	737.7	724.9	712.5	731.3	725.1	718.7
(0, 1, 1)	818.6	808.8	799.7	813.7	809.2	804.2
(1, 1, 1)	865.2	854.6	844.9	859.9	855.2	849.8
(0, 0, 2)	926.5	918.5	911.4	922.6	919.2	915.0
(1, 0, 2)	977.6	969.0	961.2	973.4	969.7	965.1
(0, 2, 1)	1158.8	1141.6	1125.8	1150.2	1142.4	1133.7
(1, 2, 1)	1202.9	1185.1	1168.7	1194.0	1186.0	1176.9
(0, 1, 2)	1273.3	1259.1	1246.2	1266.2	1259.9	1252.7
(1, 1, 2)	1320.4	1305.6	1292.0	1313.1	1306.5	1298.8

Table 2. Expectation values of the dipole moment and the transition dipole moments (in D) for transitions from the ground (0, 0, 0) state to excited (*i*, *j*, *k*) states of the $[F(HF)_2]^-$ complex

State	Expectation value	Upper state	Transition moment
(0, 0, 0)	–0.1237	(1, 0, 0)	–0.0016
(1, 0, 0)	–0.1350	(0, 1, 0)	0.0780
(0, 1, 0)	–0.0571	(1, 1, 0)	0.0336
(1, 1, 0)	–0.0565	(0, 0, 1)	–0.3937
(0, 0, 1)	–0.1507	(1, 0, 1)	–0.0615
(1, 0, 1)	–0.1633	(0, 2, 0)	–0.1128
(0, 2, 0)	–0.1433	(0, 1, 1)	–0.0610
(1, 2, 0)	–0.1352	(1, 1, 1)	–0.0349
(0, 1, 1)	–0.0039	(0, 2, 1)	–0.4353
(0, 0, 2)	–0.2065	(0, 0, 2)	–0.1572
(0, 2, 1)	–0.2079	(0, 0, 3)	–0.3950

(355.6 and 468.9 cm^{-1}, respectively) are in good agreement with the experimental results: the frequency of symmetric stretching of H-bonds of the $[F(HF)_2]^-$ complex in different surroundings is 362–460 cm^{-1} [5], and the experimental values of the frequency of the antisymmetric stretch are 472–497 [5] and 484 cm^{-1} [3].

With the use of wave functions (2) and the values of a dipole moment calculated by the GAMESS program at nodes of the three-dimensional grid, we obtained the vibrationally averaged values of the dipole moment and the transition dipole moments for transitions from the ground state to excited states. Table 2 presents these values for some states of $[F(HF)_2]^-$. The matrix elements evaluated for the other isotopomers have almost the same values. The results obtained show that the ground-state average value of the dipole moment (more precisely, of its *z*-component) virtually coincides with the equilibrium value of –0.1275 D, but the average values of the dipole moment in excited states may be several times smaller or larger. Thus, the vibrations can be accompanied by significant changes in the electronic shell. Some transition matrix elements to states associated with excitation of stretching H-bond modes are sufficiently large, so that the corresponding transitions can have a significant intensity. Analysis of the magnitudes of transition dipole moments for the fundamental, overtone, and combination vibrational bands shows that the complex considered possesses a significant electric anharmonicity.

The results of our calculation of the vibrations of H-bonds in the $[F(HF)_2]^-$ complex suggest that the methods adopted here for calculating the electronic structure and solving the vibrational problem allow us to obtain reliable data. The significant effects of mechanical and electric anharmonicity revealed in calculating this complex once again provide support for the necessity of going beyond the harmonic approximation. Subsequent papers will be devoted to the problem of interaction of the stretching and in-plane bending vibrations of H-bonds and internal vibrations of HF monomers.

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