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Isotope Effects in the Spectra of Hydrogen-Bonded Complexes. Calculation of the Structure and Vibrational Absorption Spectra of the $H_2O...HF$, $H_2O...DF$, $D_2O...HF$, and $D_2O...DF$ Complexes

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The frequencies and intensities of IR absorption bands of the $H_2O...HF$, $H_2O...DF$, $D_2O...HF$, and $D_2O...DF$ hydrogen-bonded complexes are calculated using the second-order vibrational perturbation theory. The MP2/aug-cc-pVTZ method with the basis set superposition error taken into account is used to calculate the electronic wave functions in determining the equilibrium configuration, the potential energy and dipole moment surfaces of these complexes, as well as in calculating spectral parameters. It is shown that upon complexation the frequencies and intensities of the stretching vibration of HF (DF) molecules and the intensities of stretching vibrations of H_2O (D_2O) molecules change most significantly. A variational calculation of librational motion of the water molecule in the two-well potential explained the reason for the higher value of the fundamental transition frequency of the ν_1(H−F) mode as compared to the frequency of this mode upon hot transition from the first excited librational state. The dependence of the intermode anharmonic interaction on isotope substitution was analyzed.

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

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Introduction

This paper is devoted to the memory of Professor M.O. Bulanin whose many fruitful ideas were used in our studies of spectra of atomic-molecular systems [1–3]. The $H_2O...HF$ complex, the spectrum of which is calculated in this paper, is the simplest complex with the O...HF intermolecular hydrogen bond. Therefore it can be considered to be a model system in the studies of such complexes. The spectrum of the $H_2O...HF$ complex has been the object of many experimental and theoretical investigations; however, the studies of its isotopologues containing deuterium nuclei are rather scarce.

Much information on the equilibrium nuclear configuration of the $H_2O...HF$ complex, its rotational constants and low-frequency spectrum was obtained by the rotational spectroscopy methods [4,5]. Analysis of rotational spectra [4,5] showed that the $H_2O...HF$ complex has the symmetry of the C_s point group (fig. 1). In figure 1 the z axis goes through the centers of gravity of the monomers, and the y axis lies in the symmetry plane of the complex. The water molecule can librate in the angle θ_1 relative to the planar configuration, which is sometimes called the inversional vibration. In [5] an empirical potential energy function was derived for the librational motion of the water molecule in the $H_2O...HF$ complex with two equivalent minima rotated relative to each other by $92 \pm 16^\circ$ and separated by a barrier $126 \pm 70\,\mathrm{cm}^{-1}$ in height. The barrier is readily penetrable; consequently, the C_{2v} symmetry group can be used to label the vibrational states of the $H_2O...HF$ complex. Estimates of the frequencies of fundamental transitions associated with the low-frequency vibrations of the complex were obtained in [5] from the rotational spectra: $\nu_3(\mathrm{A}_1) = 176 \pm 15$ — the H-bond stretching vibration, $\nu_6(\mathrm{B}_1) = 157 \pm 10$ — the librational motion of H_2O in the xz plane, $\nu_6(\mathrm{B}_2) = 64 \pm 10\,\mathrm{cm}^{-1}$ — the librational motion of H_2O in the yz plane, and $267 \pm 35\,\mathrm{cm}^{-1}$ — the first overtone of the $\nu_6(\mathrm{B}_2)$ transition.

In [6,7] some vibrational absorption bands of the $H_2O...HF$ complex in the gas phase were recorded and interpreted. The following estimates of frequencies (in cm^1) were obtained: $\nu_1(\mathrm{A}_1) = 3608 \pm 2$ — the H−F stretching vibration, $\nu_6(\mathrm{B}_1) = 170 \pm 50$, $\nu_6(\mathrm{B}_2) = 145 \pm 50$, $\nu_3(\mathrm{A}_1) = 180 \pm 30$ — the H-bond stretching vibration, $\nu_5(\mathrm{B}_1) = 696 \pm 30$ — the librational motion of HF in the xz plane, and $\nu_5(\mathrm{B}_2) = 666 \pm 30$ — the librational motion of HF in the yz plane. An estimate of $30\,\mathrm{kJ\,mol}^{-1}$ was obtained for the depth of the H-bond potential well. In [8] the absorption spectra of the $H_2O...HF$ complex and its deuterated isotopologues were studied in argon matrices at a temperature of 12 K. The values 3554.7 ($H_2O...HF$), 3549.0 ($D_2O...HF$), 2621.1 ($H_2O...DF$), and $2613.4\,\mathrm{cm}^{-1}$ ($D_2O...DF$) were obtained for the stretching vibration frequency of hydrogen fluoride in heterodimers. In addition, multiplets associated with librational vibrations of monomers HF and DF in two planes were recorded.

The absorption band of the $H_2O\ldots HF$ complex in the region of the $\nu_1(A_1)$ fundamental transition was studied in [9,10] in the gas phase at room temperature. Spectra of H_2O/HF gas mixtures were recorded at a temperature of 293 K in the range 4000−3400 cm^{-1} at a resolution 0.2−0.02 cm^{-1} with Bruker IFS-113v and Bruker IFS-120 HR vacuum Fourier spectrometers. The spectra of the $H_2O\ldots HF$ complex in the region of the H−F stretching absorption band were obtained by subtracting calculated spectra of free H_2O and HF molecules from experimental spectra. The equilibrium geometry and potential energy and dipole moment surfaces of the $H_2O\ldots HF$ complex were calculated in the MP2 approximation with the TZV++(2df,2p) set of atomic functions without [9] and with [10] taking into account the error of superposition of monomeric basis sets. The parameters necessary for calculating the absorption band in the region of the $\nu_1(A_1)$ vibration were derived from variational solutions of one-, two-, and three-dimensional vibrational problems in the coordinate space of stretching vibrations of the HF monomer and the hydrogen bond and librational motions of the H_2O and HF molecules. The experimentally observed band was reconstructed as a superposition of vibration–rotation bands of the fundamental transition and hot transitions from excited states of low-frequency intermolecular vibrations. The theoretical absorption band of the complex located in the region 3600−3720 cm^{-1} well reproduced main details of the experimental spectrum and explained their origin. It was shown in particular that the $v_1 = 1 \rightarrow 0$ fundamental transition from the ground vibrational state is associated with the central strongest maximum rather than with the low-frequency maximum. This led to a new value 3633.8 cm^{-1} for the $v_1 = 1 \rightarrow 0$ transition frequency in the $H_2O\ldots HF$ complex, which is higher than the value 3608 cm^{-1} adopted before [7]. The position of the fundamental transition in a wide absorption band of the complex refined for the first time in [9] was confirmed subsequently in the low-temperature molecular beam experiment [11]. The structure and absorption spectrum of the $H_2O\ldots DF$ complex were calculated in [10] using the same methods as characteristics of the $H_2O\ldots HF$ complex. For the $\nu_1(DF)$ band of $H_2O\ldots DF$, a frequency value of 2689 cm^{-1} and less structured absorption band shape at room temperature were predicted.

In the theoretical studies performed prior to 2000 the structure of the $H_2O\ldots HF$ complex was calculated, as a rule, using moderate sets of atomic functions, and vibrational frequencies were determined in the harmonic or one-dimensional anharmonic approximations [12–14]. More recent theoretical studies [15–17] were carried out at a higher *ab initio* level; however, the complete vibrational spectrum of this complex has not been studied. In [15] the CCSD(T) method and very complete sets of atomic functions were employed. The dependence of calculated equilibrium geometrical parameters and the dimerization energy ΔE of the complex on the completeness of sets of atomic functions and the basis set superposition error was investigated. The following values were obtained in the most accurate variant of the calculation: $r(OH) = 0.9594$ Å, $r(HF) = 0.9357$ Å, $r(F\ldots O) = 2.6497$ Å, $r(O\ldots H) = 1.7144$ Å, and $\Delta E = -37.74\,kJ\,mol^{-1}$. In [16] the MP2 method with the aug-cc-pV5Z set of atomic functions and the CCSD(T) method with the aug-cc-pVTZ set of atomic functions were used. The most accurate determination of dissociation energy of the heterodimer was the main objective. Vibrational frequencies were calculated both in the harmonic approximation and with anharmonic corrections taken into account using the second order perturbation theory. A value of 37.53 $kJ\,mol^{-1}$ was obtained for the dissociation energy D_e of the heterodimer. A five-dimensional potential energy surface for low-frequency vibrations of $H_2O\ldots HF$ with frozen internal vibrations of monomers was calculated in [17] by the CCSD(T) method with the aug-cc-pVTZ set of atomic functions. The energies and wave functions of low-frequency intermolecular vibrations were calculated by a variational method. A value of 36.61 $kJ\,mol^{-1}$ was obtained for the dissociation energy D_e of the complex.

The purpose of this paper is to perform ab initio calculations of the complexes $H_2O\ldots HF$, $H_2O\ldots DF$, $D_2O\ldots HF$, and $D_2O\ldots DF$ using the MP2/aug-cc-pVTZ method with the basis set superposition error taken into account. The calculation of spectral parameters of these four complexes is very desirable because experimental information on the spectra of the $H_2O\ldots HF$ complex and its isotopologues in both low-frequency matrices and the gas phase is limited and theoretical data on the absorption spectra of the $H_2O\ldots DF$, $D_2O\ldots HF$, and $D_2O\ldots DF$ complexes are absent. The frequencies and intensities for all fundamental and some overtone and combination transitions of the complexes are calculated using the second-order vibrational perturbation theory (VPT2) [18,19]. Data on the $\nu_6(B_2)$ mode are improved with the help of a variational calculation. The reason for the anomalous relationship between the frequencies of the $(v_1 = 1, v_6(B_2) = 0) \rightarrow (v_1 = 0, v_6(B_2) = 0)$ fundamental transition and the $(v_1 = 1, v_6(B_2) = 1) \rightarrow (v_1 = 0, v_6(B_2) = 1)$ hot transition in the complexes considered is explained.

Method of electronic structure calculation of the $H_2O\ldots HF$, $H_2O\ldots DF$, $D_2O\ldots HF$, and $D_2O\ldots DF$ complexes

In this study the quantum−chemical calculations of equilibrium geometry and electronic energy of the $H_2O\ldots HF$, $H_2O\ldots DF$, $D_2O\ldots HF$, and $D_2O\ldots DF$ complexes were performed by the MP2/aug-cc-pVTZ method with a correction for the basis set superposition error using the Gaussian 16 package of programs [20]. This method is more accurate than the method adopted in [9,10] to calculate the $H_2O\ldots HF$ complex. Values of dipole moments and intensities for transitions between vibrational states were calculated with self-consistent field wave functions. The equilibrium nuclear configuration of complexes possesses the C_s symmetry (Fig. 1) and is characterized by the parameters $r(\mathrm{OH}) = 0.9623$ Å, $r(\mathrm{HF}) = 0.9390$ Å, $r(\mathrm{F} \ldots \mathrm{O}) = 2.6617$ Å, $r(\mathrm{O} \ldots \mathrm{H}) = 1.7232$ Å, and $\Delta E = -34.96\,\mathrm{kJ\,mol^{-1}}$; the contribution of the basis set superposition error to ΔE equals $2.48\,\mathrm{kJ\,mol^{-1}}$. These values are in good agreement with the most accurate data available in the literature [15–17]. The dipole moment of the complex in the equilibrium configuration is equal to 1.9685 D. These variants of *ab initio* quantum–chemical methods with the basis set superposition error taken into account were also adopted in performing harmonic, anharmonic, and variational calculations of spectral parameters.

Calculated values of spectral parameters and their discussion

Harmonic calculations of frequencies and intensities for spectral transitions

The fundamental transition frequencies and intensities for the $H_2O\ldots HF$, $H_2O\ldots DF$, $D_2O\ldots HF$, and $D_2O\ldots DF$ complexes were calculated with the second-order vibrational perturbation theory VPT2 [18,19] with the help of the Gaussian 16 package of programs [20]. The results obtained are listed in Table 1. The irreducible representations of the C_{2v} symmetry group were used in notations of normal vibrations of the complexes: $\nu_1(A_1)$ — the H–F (D–F) stretching vibration, $\nu_2(A_1)$ — bending vibration of angle HOH (DOD) of a water molecule, $\nu_3(A_1)$ — hydrogen bond stretching vibration, $\nu_4(A_1)$ — symmetric stretching vibration of O–H (O–D) bond lengths, $\nu_4(B_2)$ — antisymmetric stretching vibration of O–H (O–D) bond lengths, $\nu_5(B_1)$ — libration of a HF (DF) molecule perpendicular to the C_s symmetry plane of a complex, $\nu_5(B_2)$ — libration of a HF (DF) molecule in the C_s symmetry plane of a complex, $\nu_6(B_1)$ — libration of a H_2O (D_2O) molecule perpendicular to the C_s symmetry plane of a complex, and $\nu_6(B_2)$ — libration of a H_2O (D_2O) molecule in the C_s symmetry plane of a complex. The frequency values obtained here for the $H_2O\ldots HF$ complex are in good agreement with the results of the MP2 calculation [16] with a more complete aug-cc-pV5Z set of atomic functions. The difference between results of the two calculations does not $\mathrm{cm^{-1}}$ for most vibrations and equals $11\,\mathrm{cm^{-1}}$ for $\nu_5(B_2)$, $14\,\mathrm{cm^{-1}}$ for $\ni_5$ (B_1), and $20\,\mathrm{cm^{-1}}$ for $\nu_4(A_1)$ and $\nu_4(B_1)$. It should be stressed that the normal coordinate of the $\nu_6(B_2)$ bending vibration describes vibration only in one of two potential energy minima. However, the barrier separating two minima is readily penetrable; consequently, the water molecule should have equal probabilities of being in each of the minima even in the ground vibrational state. The calculation in that the bending vibration occurs only in one of the minima distorts the energy levels of this vibration and increases its interaction with the hydrogen bond stretching vibration. Analysis of forms of normal coordinates of the $H_2O\ldots HF$ vibrations with frequencies 219 and $261\,\mathrm{cm^{-1}}$ and analogous vibrations of other isotopologues showed that each of these vibrations is a mixture of stretching and bending vibrations, with the bending vibration occurring only in one minimum. Therefore, the harmonic values of frequencies and intensities for fundamental transitions involving these two modes should be considered unreliable. The following values of harmonic frequencies and intensities (shown in parentheses) were obtained for the monomers in the MP2/aug-cc-pVTZ approximation: 4123 (121) for HF and 2989 (85) for DF, 1628 (72), 3823 (6), and 3948 (75) for H_2O and 1192 (38), 2756 (4), and 2893 (45) for D_2O. Thus, the frequencies and intensities for the hydrogen fluoride stretching vibration and the intensities of stretching vibrations of water molecules vary most strongly upon formation of complexes.

Table 1. Harmonic values of frequencies ($\mathrm{cm^{-1}}$) and intensities ($\mathrm{km \cdot mol^{-1}}$) (in brackets) of fundamental IR bands of absorption of complex $H_2O\ldots HF$ and its isotopologues

Transition	$H_2O\ldots HF$	$H_2O\ldots DF$	$D_2O\ldots HF$	$D_2O\ldots DF$
$\nu_6(B_2)$	219 (34)	216 (35)	176 (62)	174 (59)
$\nu_6(B_1)$	242 (0.1)	227 (0.03)	181 (0.02)	175 (0.1)
$\nu_3(A_1)$	261 (162)	255 (143)	241 (52)	238 (49)
$\nu_5(B_2)$	701 (156)	516 (121)	695 (134)	506 (86)
$\nu_5(B_1)$	823 (123)	629 (76)	798 (111)	592 (64)
$\nu_2(A_1)$	1631 (73)	1631 (75)	1195 (39)	1195 (41)
$\nu_1(A_1)$	3741 (918)	2717 (472)	3744 (900)	2714 (467)
$\nu_4(A_1)$	3815 (12)	3813 (22)	2748 (18)	2751 (15)
$\nu_4(B_1)$	3933 (115)	3933 (115)	2882 (65)	2882 (65)

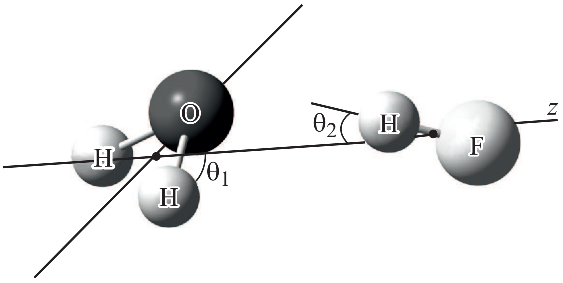

Figure 1. Equilibrium geometry of complex $H_2O\ldots HF$. Axis z passes through centers of mass of fragments H_2O and HF.

Anharmonic calculations of frequencies and intensities for spectral transitions

The values of frequencies and intensities calculated using the second-order perturbation theory VPT2 for fundamental spectral transitions in the studied complexes are presented in Table 2. Some sufficiently strong overtone transitions are also shown there. It was noted earlier [21,22] that using

Table 2. Anharmonic values of frequencies (cm^{-1}) and intensities ($\mathrm{km} \cdot \mathrm{mol}^{-1}$) (in brackets) of IR bands of absorption of complex $\mathrm{H_2O}\ldots\mathrm{HF}$ and its isotopologues

Transition	$\mathrm{H_2O}\ldots\mathrm{HF}$	$\mathrm{H_2O}\ldots\mathrm{DF}$	$\mathrm{D_2O}\ldots\mathrm{HF}$	$\mathrm{D_2O}\ldots\mathrm{DF}$
$\nu_6(\mathrm{B_2})$	74 (98)	83 (106)	98 (80)	102 (80)
$\nu_6(\mathrm{B_1})$	210 (2)	202 (1)	162 (0.4)	159 (0.2)
$\nu_3(\mathrm{A_1})$	280 (23)	278 (22)	232 (6)	232 (6)
$\nu_5(\mathrm{B_2})$	600 (120)	453 (75)	601 (122)	450 (69)
$\nu_5(\mathrm{B_1})$	713 (126)	557 (81)	699 (112)	532 (67)
$\nu_2(\mathrm{A_1})$	1588 (70)	1587 (66)	1172 (32)	1173 (39)
$\nu_1(\mathrm{A_1})$	3598 (666)	2653 (387)	3596 (702)	2634 (345)
$\nu_4(\mathrm{A_1})$	3655 (47)	3648 (17)	2663 (15)	2675 (48)
$\nu_4(\mathrm{B_1})$	3756 (99)	3756 (100)	2786 (58)	2786 (55)
$2\nu_5(\mathrm{B_2})$	1109 (32)	815 (14)	1120 (34)	852 (13)
$2\nu_5(\mathrm{B_1})$	1319 (26)	1054 (9)	1298 (35)	1010 (9)

the VPT2 theory can lead to errors in the case of low-frequency vibrations, in particular, when these vibrations have several potential energy minima separated by low barriers. The perturbation theory VPT2 uses vibrational normal coordinates obtained in the harmonic approximation. It was noted in the preceding section that in the case of the $\mathrm{H_2O}\ldots\mathrm{HF}$ complex and its isotopologues the harmonic calculation describes the $\nu_6(\mathrm{B_2})$ bending vibration only in one of two minima of the potential energy curve. This leads to a distorted description of wave functions and energy levels of the $\nu_6(\mathrm{B_2})$ mode and the hydrogen bond stretching vibration. These drawbacks are partially retained in an anharmonic calculation. Therefore, the anharmonic values of frequencies and intensities calculated with the VPT2 theory [18,19] for low-frequency absorption bands of the complexes in question should also be considered unreliable. The remaining vibrations of the complexes $\mathrm{H_2O}\ldots\mathrm{HF}$, $\mathrm{H_2O}\ldots\mathrm{DF}$, $\mathrm{D_2O}\ldots\mathrm{HF}$, and $\mathrm{D_2O}\ldots\mathrm{DF}$ very weakly interact with the $\nu_6(\mathrm{B_2})$ vibration; therefore, their spectral parameters calculated using the VPT2 perturbation theory are more reliable. The results of Table 2 for the $\mathrm{H_2O}\ldots\mathrm{HF}$ complex are in good agreement with the data obtained in [16] using a combination of results of the CCSD(T)/aug-cc-pV5Z harmonic and MP2/aug-cc-pV5Z anharmonic calculations. The values of the $\nu_1(\mathrm{A_1})$ frequency presented in Table 2 for four isotopologues are $21-47\,\mathrm{cm}^{-1}$ higher than the experimental results in an argon matrix at 12 K [8]. Approximately the same relationship takes place between our frequency values of the $\nu_5(\mathrm{B_1})$ and $\nu_5(\mathrm{B_2})$ librations and the corresponding data of [8]. The discrepancy between the calculated and experimental results may be accounted for by the influence of matrix surroundings on vibrations of complexes. Upon taking the anharmonicity into account, the frequencies of $\nu_1(\mathrm{A_1})$, $\nu_4(\mathrm{A_1})$, and $\nu_4(\mathrm{B_1})$ stretching vibrations are decreased most significantly (by $65-170\,\mathrm{cm}^{-1}$) in all four complexes, the lowering of frequencies of $\nu_5(\mathrm{B_2})$ and $\nu_5(\mathrm{B_1})$ transitions is somewhat smaller ($65-110\,\mathrm{cm}^{-1}$), the $\nu_1(\mathrm{A_1})$ transition intensity lowers by 22%–37%, and the $\nu_5(\mathrm{B_2})$ transition intensity drops significantly (up to 30%). Interestingly, while the transition intensity calculated in the harmonic approximation for the $\nu_4(\mathrm{A_1})$ symmetric stretching vibration of bonds OH (OD) of a water molecule is higher in the complexes containing unlike hydrogen isotopes in the water and hydrogen fluoride molecules, the situation is opposite in anharmonic calculations. At the same time, the $\nu_4(\mathrm{B_1})$ transition frequencies and intensities virtually do not depend on the isotope composition of a hydrogen fluoride molecule in both harmonic and anharmonic calculations. According to the anharmonic calculations, the overtone absorption bands associated with two librations ν_5 can be observed in the region accessible to IR spectroscopic studies.

Analysis of anharmonic interaction constants $\chi_{i,j}$, defined according to [19], provides additional information on intramode and intermode anharmonicity in complexes. The anharmonic constants related to three low-frequency modes, which are calculated less reliably, will not be analyzed here. Of the diagonal constants, the constants of stretching vibrations $\chi_{1,1}$ of monomers HF (DF) are maximum in magnitude, for example, $-129\,\mathrm{cm}^{-1}$ in $\mathrm{H_2O}\ldots\mathrm{HF}$ and $-71\,\mathrm{cm}^{-1}$ in $\mathrm{H_2O}\ldots\mathrm{DF}$. The diagonal constants of librational modes ν_5 and stretching modes ν_4 are a factor of 2–3 smaller than $\chi_{1,1}$. Upon H/D substitution in a monomer involved in a vibration, the magnitude of $\chi_{i,i}$ becomes approximately a factor of two smaller. Of the nondiagonal constants, the constants of interaction of $\nu_4(\mathrm{A_1})$ and $\nu_4(\mathrm{B_1})$ have the largest magnitudes ($-150\,\mathrm{cm}^{-1}$ in $\mathrm{H_2O}\ldots\mathrm{HF}$ and $-159\,\mathrm{cm}^{-1}$ in $\mathrm{H_2O}\ldots\mathrm{DF}$). The constants of interaction of $\nu_1(\mathrm{A_1})$ with librational modes $\nu_5(\mathrm{B_1})$ and $\nu_5(\mathrm{B_2})$ have somewhat smaller values, for example, 105 and $87\,\mathrm{cm}^{-1}$ in $\mathrm{H_2O}\ldots\mathrm{HF}$. These anharmonic constants are also approximately halved upon deuteration of the hydrogen fluoride molecule. The fact that, upon substitution of HF by DF, the anharmonic values of the $\ni_4$ ($\mathrm{A_1}$) frequency and intensity considerably change, while the $\nu_4(\mathrm{B_1})$ spectral parameters virtually do not change (Table 2), correlates with analogous changes in constants of anharmonic interaction of the $\nu_1(\mathrm{A_1})$ mode with the $\nu_4(\mathrm{A_1})$ and $\nu_4(\mathrm{B_1})$ modes. For example, in $\mathrm{D_2O}\ldots\mathrm{HF}$ the constants of interaction of $\nu_1(\mathrm{A_1})$ with $\nu_4(\mathrm{A_1})$ and $\nu_4(\mathrm{B_1})$ are equal to -4.41 and $-4.35\,\mathrm{cm}^{-1}$, in $\mathrm{D_2O}\ldots\mathrm{DF}$ they are equal to -28.31 and $-9.87\,\mathrm{cm}^{-1}$.

Variational calculation of the $\nu_6(\mathrm{B_2})$ librational vibration of a water molecule

In [9,10] the $\nu_6(\mathrm{B_2})$ and $\nu_6(\mathrm{B_1})$ vibrations of the $\mathrm{H_2O}$ molecule in the $\mathrm{H_2O}\ldots\mathrm{HF}$ complex were considered as large-amplitude hindered rotational motions about the molecular center of gravity. The kinetic energy operator of such motions was expressed in terms of the angular momentum operator squared and the corresponding component of the inertia tensor. The H–F and hydrogen bond stretching vibrations were modeled by stretching vibrations of a free HF molecule and a hypothetical diatomic molecule

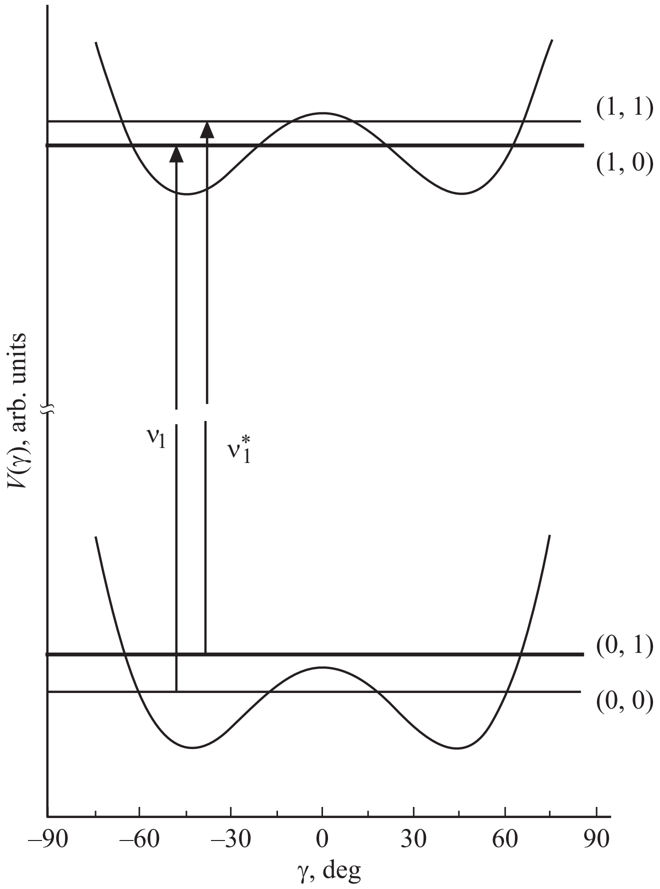

Figure 2. Potential curves for oscillation $\nu_6(\mathrm{B}_2)$, calculated at medium values $r(\mathrm{HF})$ in the main and first excited states of valent oscillation H–F. $\gamma = (180^\circ - \theta_1)$ (fig. 1), $(\nu_1(\mathrm{A}_1),\ \nu_6(\mathrm{B}_2))$ — 2D oscillatory energy levels, arrows ν_1 and ν_1^* demonstrate fundamental and hot transitions.

consisting of the centers of gravity of the monomers. Interactions between these elementary vibrations were taken into account with the help of a superposition of their wave functions in solving multidimensional problems. This approach appeared to be appropriate, in particular, for describing the $\nu_6(\mathrm{B}_2)$ vibration in a two-well potential when the vibrational wave function was sought as an expansion in Legendre polynomials. A value of $89.4\,\mathrm{cm}^{-1}$ was obtained for the $\nu_6(\mathrm{B}_2)$ fundamental frequency in $\mathrm{H_2O}\ldots\mathrm{HF}$ from the solution of a one-dimensional variational equation [10]. Solution of the two-dimensional $(\nu_6(\mathrm{B}_2),\ \nu_3(\mathrm{A}_1))$ anharmonic vibrational problem yielded a value of $88.4\,\mathrm{cm}^{-1}$. The insignificant change of the $\nu_6(\mathrm{B}_2)$ frequency shows that the $\nu_6(\mathrm{B}_2)$ vibration weakly interacts with the hydrogen bond stretching vibration. The $\nu_6(\mathrm{B}_2)$ vibration is stronger coupled to the H–F stretching vibration. Solution of the $(\nu_6(\mathrm{B}_2),\ \nu_3(\mathrm{A}_1),\ \nu_1(\mathrm{A}_1))$ three-dimensional vibrational problem yields a value of $\nu_6(\mathrm{B}_2) = 77.5\,\mathrm{cm}^{-1}$ [10], which is in good agreement with the experimental value $64 \pm 10\,\mathrm{cm}^{-1}$ [5]. One of the important results of [9,10] was the lower frequency value of a $\nu_1(\mathrm{A}_1)$ hot transition from the first excited state of the $\nu_6(\mathrm{B}_2)$ mode than the frequency value of the fundamental transition. This fact allowed the structure of a gas-phase experimental spectrum of $\mathrm{H_2O}\ldots\mathrm{HF}$ to be refined. This anomalous effect was qualitatively explained by the presence of a potential barrier to the $\nu_6(\mathrm{B}_2)$ vibration and the dependence of the height of this barrier on the degree of excitation of the $\nu_1(\mathrm{A}_1)$ vibration.

The influence of the $\nu_1(\mathrm{A}_1)$ vibration on the $\nu_6(\mathrm{B}_2)$ vibration is largely reduced to a change in the vibrational barrier height when the H–F bond length changes. Using the approach proposed in [9,10], the potentials for the $\nu_6(\mathrm{B}_2)$ vibration in the four considered complexes were calculated on the assumption that the length of a HF (DF) molecule takes the equilibrium value r_e, the value $\langle r\rangle_{v=0}$ averaged over the $\nu_1(\mathrm{A}_1)$ vibrational ground state, or the value $\langle r\rangle_{v=1}$ averaged over the $\nu_1(\mathrm{A}_1)$ first excited state. It is apparent that $r_e < \langle r\rangle_{v=0} < \langle r\rangle_{v=1}$ due to anharmonicity of the $\nu_1(\mathrm{A}_1)$ vibration. The wave functions and energy levels of the $\nu_1(\mathrm{A}_1)$ and $\nu_6(\mathrm{B}_2)$ vibrations were calculated by the variational method in the one-dimensional approximation. Table 3 contains the heights of an inversional barrier, the energies of the ground (E_0) and first excited (E_1) levels of the $\nu_6(\mathrm{B}_2)$ mode, and the frequencies $\nu(1 \to 0)$ of a transition between the E_0 and E_1 vibrational levels calculated for the $\mathrm{H_2O}\ldots\mathrm{HF}$, $\mathrm{H_2O}\ldots\mathrm{DF}$, $\mathrm{D_2O}\ldots\mathrm{HF}$, and $\mathrm{D_2O}\ldots\mathrm{DF}$ complexes. One can see in Table 3 that, as the hydrogen fluoride molecule elongates, the inversional barrier height increases and the first excited level of $\nu_6(\mathrm{B}_2)$ becomes lower than the barrier height. In this case the $\nu(1 \to 0)$ frequency drastically decreases. Figure 2 schematically displays the potential curves calculated for $\nu_6(\mathrm{B}_2)$ at $\langle r\rangle_{v=0}$ and $\langle r\rangle_{v=1}$ in $\mathrm{H_2O}\ldots\mathrm{HF}$ or $\mathrm{H_2O}\ldots\mathrm{DF}$. Vertical arrows show the ν_1 fundamental transition involving the hydrogen fluoride stretching vibration and the ν_1^* hot transition. Figure 2 clearly shows that the hot transition frequency should be lower than the fundamental transition frequency. According to the performed model calculation, the difference between these frequencies equals $11.8\,\mathrm{cm}^{-1}$ in $\mathrm{H_2O}\ldots\mathrm{HF}$ and $8.7\,\mathrm{cm}^{-1}$ in $\mathrm{H_2O}\ldots\mathrm{DF}$. Such relative position of frequencies of the fundamental and hot transitions should also take place in $\mathrm{D_2O}\ldots\mathrm{HF}$ and $\mathrm{D_2O}\ldots\mathrm{DF}$. However, in these complexes the frequency difference between the two transitions should be smaller because the level E_1 at $\langle r\rangle_{v=0}$ also lies under the barrier.

Conclusions

In this paper the structure and harmonic and anharmonic values of frequencies and intensities for IR absorption bands of the hydrogen-bonded complexes $\mathrm{H_2O}\ldots\mathrm{HF}$, $\mathrm{H_2O}\ldots\mathrm{DF}$, $\mathrm{D_2O}\ldots\mathrm{HF}$, and $\mathrm{D_2O}\ldots\mathrm{DF}$ were calculated using the Gaussian 16 package of programs [20] and the MP2/aug-cc-pVTZ method with the basis set superposition error taken into account. The anharmonic calculations of spectral parameters were carried out using the second-order vibrational

Table 3. Values of barrier height $V_{\max}$, energies of the main E_0 and first excited E_1 states and transition frequency ν $(1 \leftarrow 0)$ between E_0 and E_1 (in cm^{-1}), calculated for oscillation $\nu_6(B_2)$ of complexes $H_2O\ldots HF$, $H_2O\ldots DF$, $D_2O\ldots HF$ and $D_2O\ldots DF$

r(HF) or r(DF)	Parameter	$H_2O\ldots HF$	$H_2O\ldots DF$	$D_2O\ldots HF$	$D_2O\ldots DF$
r_e	$V_{\max}$	123.2	123.2	127.2	127.2
	E_0	89.5	89.5	78.9	78.9
	E_1	155.9	155.9	112.7	112.7
	ν $(1 \leftarrow 0)$	66.4	66.4	33.9	33.9
$\langle r \rangle_{\nu=0}$	$V_{\max}$	141.2	136.6	145.4	137.7
	E_0	96.8	95.0	85.9	83.0
	E_1	157.8	157.3	115.8	114.6
	ν $(1 \leftarrow 0)$	61.0	62.3	29.9	31.6
$\langle r \rangle_{\nu=1}$	$V_{\max}$	183.6	167.0	188.8	161.0
	E_0	112.1	106.4	100.4	91.5
	E_1	161.3	160.0	122.4	118.4
	ν $(1 \leftarrow 0)$	49.2	53.6	22.0	26.9

perturbation theory VPT2 [18,19]. The calculated results are compared with scarce experimental data and the results of calculations of the $H_2O\ldots HF$ complex available in the literature. The trends in the changes of spectral parameters upon passage from the harmonic to anharmonic calculation and with variation of isotope composition of complexes were analyzed.

The values of structural parameters obtained in this paper for the complexes studied are in good agreement with the most accurate literature data. Comparison with the values of spectral parameters of monomers calculated at the same level of theory showed that the frequencies and intensities of the stretching vibration of HF (DF) molecules and the intensities of stretching vibrations of H_2O (D_2O) molecules experience strongest changes upon formation of the complexes. It was noted that the use of harmonic normal coordinates to calculate vibrations leads to erroneous results for the $\nu_6(B_2)$ librational vibration of a water molecule in both the harmonic and anharmonic calculation because the normal coordinate describes this vibration only in one of two minima of the potential surface. This drawback does not affect the results of calculations of high-frequency vibrations of the complexes. The frequency values obtained in this paper for the fundamental vibrations of the $H_2O\ldots HF$ complex are in good agreement with the results of the calculation [16] with a more complete set of atomic functions aug-cc-pV5Z. The frequency values of the $\nu_1(A_1)$ stretching vibration and the $\nu_5(B_1)$ and $\nu_5(B_2)$ librational vibrations calculated in this paper in the anharmonic approximation are somewhat higher than the corresponding results of the matrix experiment [8], which may be explained by an influence of a matrix surroundings. With the two-well full potential for the $\nu_6(B_2)$ librational vibration, one-dimensional variational calculations of the fundamental frequency of this vibration were performed for all the considered complexes in the ground and first excited states of the $\nu_1(A_1)$ stretching vibration. The figure constructed on the basis of these data clearly explains the reason for the higher frequency value of the $\nu_1(A_1)$ fundamental transition as compared to the hot transition frequency of this mode from the first excited state of the $\nu_6(B_2)$ mode.

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Conflict of interest

The authors declare that they have no conflict of interest.

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