Energies of the $S_0 \rightarrow S_1$ vertical transitions of low electronic states of optically active hydrogen bonding complexes

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Energies of the $S_0 \rightarrow S_1$ vertical transitions were calculated for hydrogen bonding complexes which can be formed in the atmosphere from interactions of water molecules with each other and with other hydrogen-containing molecules (for example, HF). An excitation energy is localized in the OH bond of one water molecule, what leads to preservation of the Rydberg character of the $S_0 \rightarrow S_1$ transition and the photodissociation type of the absorption band. Interaction of molecules in a complex results in broadening of the absorption bands of $(H_2O)_n$, $n = 2 - 6$, and $(H_2O...HF)_n$, $n = 1 - 4$, and their shift to the blue region with respect to the corresponding bands of the water monomer. It was determined that this shift for $(H_2O)_n$, $n = 2 - 6$, complexes is from 5566 cm^{-1} (water dimer) to 7259 cm^{-1} (water cluster), while for $(H_2O...HF)_n$ (olygomer structure $n = 1, 3, 4$) it is from 6211 cm^{-1} ($n = 1$) to 7582 cm^{-1} ($n = 4$) and 8550 cm^{-1} (cyclic structure $n = 2$).

1. Introduction

Hydrogen bonding complexes can be formed in the atmosphere as H_2O molecules interact with each other or other hydrogen-containing molecules, such as, for instance, HF, which are among most ecologically dangerous components emitted by industrial enterprises.

Molecular complexes $(H_2O)_n$ are of interest for analysis of processes of optical radiation extinction in the atmosphere and clouds. In particular, the contribution of such optically active complexes in the experimentally observed anomalous extinction of optical radiation by clouds[1] is yet to be rigorously treated.

Complexes of the $(H_2O)_n(HF)_m$ type can appear and exist in plumes of industrial enterprises, while the HF molecules are formed practically at all stages of interaction of uranium hexafluoride and products of its hydrolysis in emissions of nuclear fuel cycle enterprises. The HF molecules interacting with the atmospheric water vapor can form the stable gas-phase HF...H_2O complex (hydrate), as well as the weakly bound nonrigid $(HF)_n...(H_2O)_n$ complexes of donor−acceptor type with several types of large-amplitude motions.[2−4] The absorption bands of such complexes can be used for remote analysis of the composition and volume of emissions from nuclear fuel cycle or other enterprises emitting chemically active fluoride compounds into the atmosphere.

Complexes of $(H_2O)_n$, $(HF)_m$, and $(H_2O)_n(HF)_m$ types are also interesting from the viewpoint of fundamental spectroscopy. The detailed study of the structural nonrigidity effects (especially, for molecules and molecular complexes with several types of large-amplitude motions) stimulates development of a new field in spectroscopy of molecules and weakly bound complexes and provides for obtaining new data for further development and revision of some concepts of molecular and chemical physics, theory of reactivity, thermodynamics, formation of complexes, and others.[4]

2. Technique and calculated results

The systems under consideration in this work are water clusters $(H_2O)_n$, where $n = 2 - 6$, and $(HF...H_2O)_n$ complexes with $1 \le n \le 4$. The excited electronic states S_1 of such complexes result from exciting an electron from the double occupied molecular orbital t $_n$ to the first empty virtual orbital t $_v$ (at combining with the appropriate spin function). These orbitals define a nature of the excited electronic state and the type of the electronic transition. In this case the complex is considered as a supermolecule. The nature of the resulting electronic term of a transition can be judged from the electronic density redistribution and cross section of the potential energy surface of the excited electronic state. The energy of the $S_0 \rightarrow S_1$ vertical transition was calculated as a difference of the total energies $E(S_0)$ and $E(S_1)$ determined by two methods: the self-consistent field (SCF) method and the restricted Hartree−Fock (RHF) method for open shells.[5−8]

An optimum geometry of each complex was determined by the BFGS (Broyden−Fletcher−Goldfarb−Shano) method[9] using the 6−31G* basis and the MONSTERGAUSS software package.[10]

3. Results and discussion

The obtained values of the excitation energy ε for the $S_0 \rightarrow S_1$ transitions of the $(H_2O)_n$ and $(H_2O...HF)_n$ complexes are given in Table 1. The excitation energy of the complexes under consideration is localized in one of the bonds of the component water molecules. This follows from the analysis of the electron density redistribution. Stretching of the OH-bond of the water molecule, in which the excitation is localized, indicates the dissociative nature of the $E(S_1)$ electronic term.

The photodissociative nature of the $\tilde{A}^1B_1$ state governing the first band of the water monomer ($\lambda \sim 165$ nm):

$$H_2O(\tilde{X}^1A_1) + h\nu \rightarrow H_2O(\tilde{A}^1B_1) \rightarrow$$
$$\rightarrow H(^2S) + OH(X^2\Pi),$$
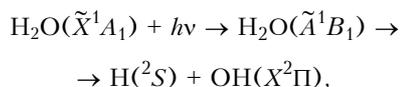
is well known.[14]

Table 1. Energies ε of the $S_0 \rightarrow S_1$ vertical transitions of the $(H_2O)_n$ and $(H_2O...HF)_n$ complexes (RHF, 4-31G)

n	ε, $(H_2O)_n$, eV	n	ε, $(H_2O...HF)_n$, eV
1	7.8 (monomer)		
2	8.35 (dimer)	1	8.57 (dimer)
3	8.4 (cycl.)		
4	8.7 (cycl.)	2	8.86 (cycl.)
5	8.63 (cycl.)	3	8.64 (olygomer)
6	8.51 (cycl.)	4	8.74 (olygomer)

In the complexes considered in this paper the Rydberg nature of the S_1 electronic state is preserved; the type of the $S_0 \rightarrow S_1$ electronic transition can be defined as $\pi \rightarrow \sigma^*$.

Table 2 presents some physical and chemical properties of the $H_2O...HF$ complex and the energies of the $S_0 \rightarrow S_1$ electronic transition of the HF and H_2O monomers (with the zero-point energy correction) in comparison with the results of Refs. 11–14.

Table 2. Physical and chemical properties of the $H_2O...HF$ complex and the energies ε for the HF and H_2O monomers

R_{OF}, Å	D_e, kcal/mol	Bond angle (H...OF), deg.	ε, HF, eV	ε, H_2O, eV
2.71 (Ref. 11)	9.29 (Ref. 11)	–	~10.4 (Ref. 14)	7.4 (Ref. 14)
2.72 (Ref. 12)	9.1 (Ref. 12)	–	–	–
2.65 (Ref. 13)	10.2 (Ref. 13)	4.5 (Ref. 13)	–	–
2.72*	9.55*	3.7*	~10*	7.6*

*Our calculation.

The data of this table are indicative of a close agreement between the results obtained and the experimental and calculated results of other authors.[11–14]

The maximum of the absorption band corresponding to the $S_0 \rightarrow S_1$ electronic transition in the considered complexes shifts toward higher frequencies with respect to the absorption band of the water monomer (Fig. 1). This fact is indicative of weakening of the hydrogen bond.[15]
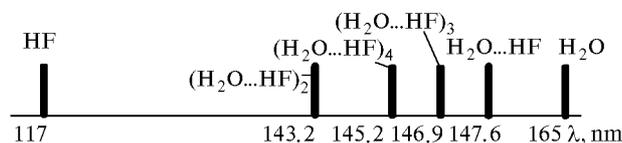
Fig. 1. Relative positions of the maxima of the absorption bands in the $(H_2O...HF)_n$ complexes.

Actually, the calculated binding energies D_e for the water dimer[16] and $H_2O...HF$ dimer in the S_1 electronic state amount to 2 kcal/mol and 1.6 kcal/mol, respectively. The binding energies D_0 of the S_0 ground state of the $(H_2O)_2$ and $H_2O...HF$ dimers are 5.5 kcal/mol and 9.55 kcal/mol. According to Pimentel,[15] the shift of a purely electronic transition depends on the difference between the binding energies of the ground and excited states (D_e^0 and D_e^*): $\Delta\nu = \nu_{complex} - \nu_{monomer} = D_e^0 - D_e^*$. The shift of the maximum of the absorption band depends not only on the difference between D_e^0 and D_e^*, but also on the Frank–Condon energies ω_e, because as the system absorbs a frequency ν, it transits into a certain point at the upper potential surface, which corresponds to the nonequilibrium value ω_e of the potential energy. For the water dimer $\omega_e = 12.5$ kcal/mol, for $H_2O...HF$ $\omega_e = 3.77$ kcal/mol, and correspondingly for the $(H_2O)_2$ dimer $\Delta\nu_e = 0.65$ eV and $\Delta\nu_{max} = D_e^0 - D_e^* + \omega_e = 0.69$ eV, while for the $(H_2O...HF)_2$ dimer we have $\Delta\nu_e = 0.77$ eV and $\Delta\nu_{max} = 0.5$ eV. The frequency shift $\Delta\nu$ falls in the $0.65 - 0.69$ eV interval for the water dimer and in the $0.5 - 0.77$ eV interval for the $H_2O...HF$ dimer. For the $(H_2O...HF)_n$ complexes ($n = 1 - 4$) the largest shift $\Delta\nu_e$ is observed for the cyclic structure $(H_2O...HF)_2$ with $D_e^0 = -14.68$ kcal/mol, namely, $\Delta\nu_e = 1.06$ eV. For the olygomer structures $(H_2O...HF)_3$ and $(H_2O...HF)_4$ with $D_e^0 = -7.59$ kcal/mol and $D_e^0 = -8.39$ kcal/mol the corresponding values $\Delta\nu_e$ are 0.84 eV and 0.94 eV. The optimum geometry of the $(H_2O)_n$ complexes, $n = 2 - 6$, can be found in Refs. 16 and 17, while the optimum geometry of the $(H_2O...HF)_n$ complexes, $n = 1 - 4$, is presented in Figs. 2–4 and Tables 3–6.
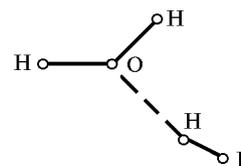
Fig. 2.

Table 3. Geometry of the $H_2O...HF$ complex

Bond length, Å		Bond angles, deg		Torsion angles, deg	
$R(OH)$	0.949	HOH	106.4	FH...OH	88.2
$R(H...O)$	1.805	FH...O	172.9	–	
$R(FH)$	0.921	H...OH	125.0	–	
$R(FO)$	2.720				

Table 4. Geometry of the $(H_2O...HF)_2$ complex

Bond length, Å		Bond angles, deg		Torsion angles, deg	
$R(O_1O_2)$	2.769	$F_3O_2O_1$	84.0	$F_4F_3O_2O1$	0
$R(FO)$	2.827	$H_5O_1O_2$	126.0	$H_5O_1O_2F_3$	180
$R(F_3F_4)$	2.588	$H_6O_2F_3$	92.6	$H_6O_2F_3F_4$	0
$R(H_8O_2)_b$	0.953	$H_7O_2F_3$	119.6	$H_7O_2F_3F_4$	180
$R(H_6O_1)_b$	0.958	$H_8F_3F_4$	96.6	$H_8F_3F_4O_1$	0
$R(H_5O_1)_f$	0.946	$H_9F_3O_2$	98.7	H_9F3O2O_1	0
$R(H_7O_2)_f$	0.947	$H_{10}F_4F_3$	102.5	$H_{10}F_4F_3O_2$	0
$R(H_6...O_2)$	1.874	–		–	
$R(H_8...F_3)$	1.908	–		–	
$R(H_9F_3)$	0.929	–		–	
$R(H_{10}F_4)$	0.940	–		–	
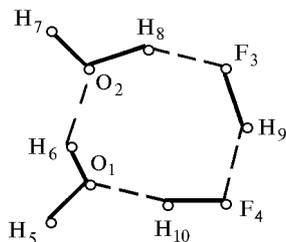
Fig. 3. Geometrical structure of the $(H_2O ... HF)_2$ complex.

Table 5. Geometry of the $(H_2O...HF)_3$ complex

Bond length, Å		Bond angles, deg		Torsion angles, deg	
$R(O_2H_1)_f$	0.949	$H_3O_2H_1$	105.0	$F_4H_3O_2H_1$	180
$R(O_2H_3)_b$	0.953	$H_7O_6O_8$	107.3	$H_5F_4H_3O_2$	0
$R(F_4H_3)$	1.994	$H_{12}O_{11}H_{13}$	107.5	$O_6H_5F_4H_3$	0
$R(F_4H_5)$	0.929	$F_4H_3O_2$	190.8	$H_7O_6F_4H_3$	0
$R(H_6...O_5)$	1.724	$H_5F_4H_3$	120.8	$H_8O_6F_4H_3$	180
$R(O_6H_7)_f$	0.947	$H_7O_6H_5$	127.7	$F_9O_6F_4H_3$	180
$R(O_6H_8)_b$	0.955	$H_{10}F_9H_8$	131.3	$H_{10}F_9O_6F_4$	180
$R(F_9...H_8)$	1.876	$H_{12}O_{11}H_{10}$	129.1	$O_{11}F_9O_6F_4$	180
$R(H_{10}F_9)$	0.929	$H_{15}F_{14}H_{13}$	139.3	$H_{12}O_{11}F_9O_6$	0
$R(O_{11}H_{10})$	1.721	$F_9H_8O_6$	180.0	$H_{13}O_{11}F_9O_6$	180
$R(O_{11}H_{12})_f$	0.948	$O_6H_5F_4$	180.0	$F_{14}O_{11}F_9O_6$	180
$R(O_{11}H_{13})_b$	0.952			$H_{15}O_{11}F_9O_6$	180
$R(F_{14}H_{13})$	1.989	–		–	
$R(F_{14}H_{15})$	0.914	–		–	
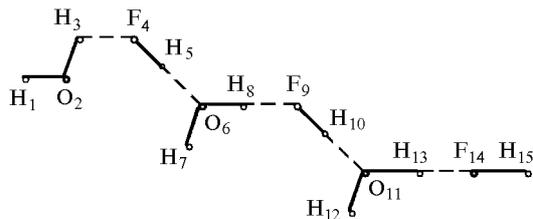
Fig. 4. Geometrical structure of the $(H_2O ... HF)_3$ complex.

Table 6. Geometry of the $(H_2O...HF)_4$ complex

N	Coordinates, Å			
	Atom	X	Y	Z
1	H	0.000	0	0.000
2	O	0.000	0	0.946
3	H	0.919	0	1.192
4	F	2.907	0	1.303
5	H	3.432	0	0.534
6	O	4.421	0	−0.863
7	H	4.140	0	−1.766
8	H	5.376	0	−0.863
9	F	7.234	0	−0.896
10	H	7.790	0	−1.644
11	O	8.821	0	−2.980
12	H	8.600	0	−3.900
13	H	9.773	0	−2.916
14	F	11.650	0	−2.822
15	H	12.274	0	−3.508
16	O	13.446	0	−4.755
17	H	14.381	0	−4.588
18	H	13.324	0	−5.700
19	F	13.030	0	−7.671
20	H	13.670	0	−8.389

Conclusions

In the complexes considered the excitation energy is localized in the O–H bond of one of the component H_2O molecules. This results in preservation of the Rydberg nature of the $S_0 \to S_1$ transition and the photodissociative type of the absorption bands corresponding to this transition, as in the water monomer.

As a result of the interaction of molecules in the complex, the absorption bands of $(H_2O...HF)_n$, $n = 1 - 4$, and $(H_2O)_n$, $n = 2 - 6$, complexes broaden, and their maximum shifts toward shorter waves with respect to the corresponding absorption bands of the water monomer.

The estimates show that this shift for the $(H_2O)_n$, $n = 2 - 6$, complexes is from 5566 cm^{-1} (dimer) to 7259 cm^{-1} (cluster), and for the $(H_2O...HF)_n$ complexes (olygomer structure, $n = 1, 3, 4$) it is from 6211 cm^{-1} ($n = 1$) to 7582 cm^{-1} ($n = 4$) and 8550 cm^{-1} (cyclic structure, $n = 2$).

Acknowledgments

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