Database of structure-energy and spectral characteristics of $(H_2O)_mM_n$ complexes in gas phase

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The first version of the database of structure, energy and spectral characteristics of H_2O complexes with diatomic HX molecules, where X = F, Cl, and the number of molecules in a complex varies from two to six, is considered.

Introduction

Real-time monitoring of gaseous emissions from industrial enterprises is now carried out by remote sensing methods with IR lasers.[1] The efficient use of these lasers and the development of physical principles for new diagnostics methods requires systematically ordered information about the structure, physical-chemical and optical characteristics of such components of gaseous emissions as molecules and molecular complexes. Chemically active molecules of anthropogenic origin (fluorides, hydrides, and others) interact with water vapor yielding the formation of complexes of $(H_2O)_mM_n$ type, where $m, n \geq 1$.

In addition to the gas-phase reactions, whose probability is rather high at a relatively high concentration of reagent molecules, formation of stable molecular complexes of the donor-acceptor type is possible in the atmosphere. The binding energies in such complexes can amount up to several tens of kilocalories.[2,3] The complexes can show the optical activity high enough for their detection in the atmosphere by remote methods. As a rule, these complexes are characterized by several types of high-amplitude motions,[3–6] leading to the transformation of vibrational spectra of the molecular components and the appearance of new absorption bands, corresponding to intermolecular vibrations.

The characteristics of optical spectra of individual molecules can be found, in a systematized form, in databases, such as, for example, HITRAN.[7] For molecular complexes, no such a systematization is available, despite the urgent practical need.

This paper considers the structures of databases, compiled by analogy with HITRAN,[7] for the complexes of H_2O with diatomic molecules $(H_2O)_mM_n$, where $1 \leq m, n \leq 6$.

Characteristics of $(H_2O)_mM_n$ complexes

Consider a set of characteristics of the complexes and their spectra, which should be included into the database and determine the database structure, with the $(H_2O)_m(HF)_n$ complex taken as an example. For the simplest H_2O ... HF complex, a rather detailed information on the structure, energy, and spectral characteristics is available.[7,8]

Tables 1 and 2 from Ref. 8 illustrate how the amount of information to be included into the database increases as the complex forms (Fig. 1).

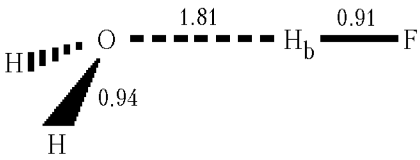

Fig. 1. Geometric structure of $H_2O...HF$ complex (C_s symmetry) calculated by the HFR/6-31G** method; $E_{tot} = -176.0497$ a.u., H–O–H angle of 107°, O–H_b–F angle of 176°; internuclear separations are given in Å; H_b is the bridge atom.

As the number of molecules in the complex increases up to three and more, the complex can exist in several configurations with significantly different structure, energy, and spectral characteristics. Thus, for the $H_2O...(HF)_2$ complex, two of all possible configurations (Fig. 2) are stable. They are characterized by the binding energies of 15 and 21 $kcal \cdot mol^{-1}$, corresponding to the open (Fig. 2*a*) and closed (Fig. 2*b*) structures. The closed configuration of the $H_2O...(HF)_2$ complex is more stable. The frequencies and intensities of intramolecular vibrations for the $H_2O...(HF)_2$ complex with the open and closed structures are given in Table 3 on the basis of the data from Ref. 8, and the frequencies and intensities of intermolecular vibrations are given in Table 4.

As can be seen from Tables 3 and 4, the formation of complexes changes the frequencies of intramolecular vibrations and leads to appearance of the bands corresponding to low-frequency intermolecular vibrations.

Table 1. Geometric and energy characteristics of HF, H_2O monomers, and $H_2O...HF$ complex, calculated by different methods and obtained experimentally[a]

Molecule	Symmetry	Method	ΔE, kcal·mol^{-1}	R_e, Å			Angle, deg		
				H_b–F	O–H	O–F	H–O–H	α	H_b–F–O
HF	$C_{\infty v}$	HFR/6-31G**[b]	–	0.90	–	–	–	–	–
		Experiment, Ref. 9	–	0.92	–	–	–	–	–
H_2O	C_{2v}	HFR/6-31G**[b]	–	–	0.94	–	106	–	–
		Experiment, Ref. 10	–	–	0.96	–	105	–	–
$H_2O...HF$	C_s	HFR/6-31G**[b]	9	0.91	0.94	2.72	107	134	4
		MP2/6-31G**[b]	11	0.93	0.96	2.67	105	131	6
		MP2/6-311G** [Ref. 11]	11	0.92	0.96[c]	2.64	105[c]	129	5
		MP3/6-311G**[Ref. 11]	11	0.92	0.96[c]	2.65	105[c]	133	3
		Experiment, Refs. 11, 12	–	–	–	2.66	–	134	–
		MP4/6-311+G(2d,2p) [Ref. 13]	9[d]	0.92[d]	–	2.72[d]	–	–	5[d]
		Experiment, Ref. 14	10	–	–	–	–	–	–

[a] Atomic designations in the complex are shown in Fig. 1; ΔE is the binding energy between monomers in the complex; α is the angle between the axis O–F and the bisector of H–O–H angle. [b] Calculation from Ref. 6. [c] In the calculation of Ref. 11 by the Möller–Plesset perturbation theory of the second (MP2) and third (MP3) orders, the geometric parameters of the H_2O molecule had experimental values.[10] [d] Calculation by the Möller–Plesset perturbation theory of the fourth order (MP4) with the geometric parameters optimized by the HFR method in the 6-31G* basis.

Table 2. Harmonic frequencies (ω_i/cm^{-1}) of vibrations of HF and H_2O monomers and $H_2O...HF$ complex

$H_2O...HF$			H_2O			HF		
Calc.[a]	Exp. [Ref. 15]	Assignment[b]	Calc.[a]	Exp. [Ref. 10]	Assignment[b]	Calc.	Exp. [Ref. 9]	Assignment[b]
4270	3608 ± 2	$\upsilon(H_bF)$	4265[a]	3939	$\upsilon^{as}(OH)$	4493[a]	4138	$\upsilon(HF)$
4258	3756	$\upsilon^{as}(OH)$	4052[c]	–	–	4212[c]	–	–
4142	3657	$\upsilon^{s}(OH)$	4010[d]	–	~	4119[d]	–	–
1765	1595	$\delta(HOH)$	4148[a]	3835	$\upsilon^{s}(OH)$	–	–	–
760	696 ± 30	$\delta_i(OH_bF)$	3909[c]	–	–	–	–	–
626	666 ± 30	$\delta_0(OH_bF)$	3863[d]	–	–	–	–	–
236	180 ± 30	$\upsilon(H_2O...H_bF)$	1770[a]	1648	$\delta(HOH)$	–	–	–
206	145 ± 50	$\delta_0(HOH_b)$	1674[c]	–	–	–	–	–
194	170 ± 50	$\delta_i\ (HOH_b)$	1620[d]	–	–	–	–	–

[a] Calculation of Ref. 6. [b] For the complex (see Fig. 1) the frequencies (υ) [Ref. 15] of fundamental transitions are presented. Designations: υ^s and υ^{as} are stretching symmetric and antisymmetric vibrations, respectively; δ are bending vibrations in the plane of the H_2O molecule (δ_i) and out of the plane (δ_0). [c] Calculation [Ref. 6] by the MP2 method in the 6-31G** basis. [d] Calculation [Ref. 16] by the MP2 method in the 6-31++G** basis.

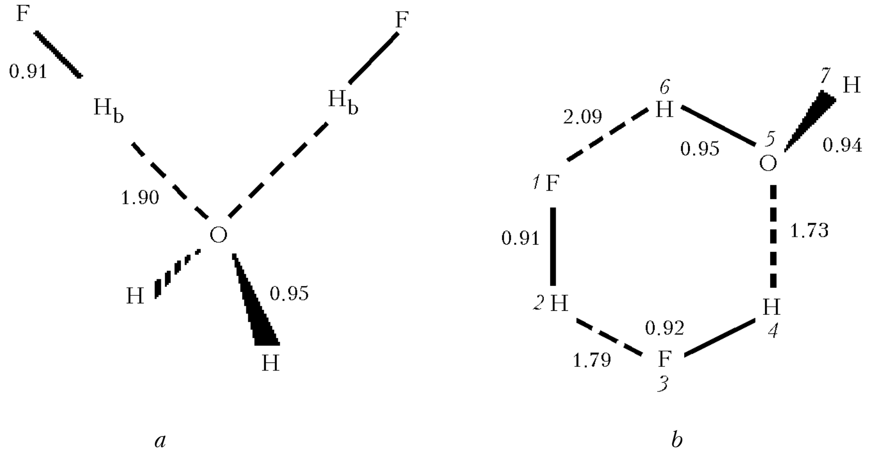

Fig. 2. Geometric structure of the complexes: $H_2O–(HF)_2$ of C_{2v} symmetry (*a*) and $H_2O–(HF)_2$ of C_1 symmetry (*b*), calculated by the HFR/6-31G** method. Internuclear separations are given in Å, the angles between bonds and binding energies are tabulated in Tables 1 and 7.

Table 3. Frequencies (ω_i; cm^{-1}) and intensities of IR vibrational bands (S_i; $km \cdot mol^{-1}$) of $H_2O...(HF)_2$ complexes with open (C_{2v}) and closed (C_1) structure

Complex (symmetry)	$\omega_i(S_i)$	Assignment
$H_2O \cdot (HF)_2$ (C_{2v})	1765(121)	$\delta(HOH)$ (A_1)
	4120(81)	$v(OH)$ (A_1)
	4230(152)	$v(OH)$ (B_1)
	4331 (839)	$v(H_bF)$ (B_2)
	4357(142)	$v(H_bF)$ (A_1)
$H_2O \cdot (HF)_2$ (C_1)	1777(112)	$\delta(H_6O_5H_7)$
	4024(555)	$v(H_4F_3)$
	4103(190)	$v(O_5H_6)$
	4228(154)	$v(O_5H_7)$
	4268 (544)	$v(H_2F_1)$

Table 4. Intermolecular harmonic vibrational frequencies of $H_2O \cdot (HF)_2$ complexes (cm^{-1}) and the corresponding intensities of IR bands

Complex (symmetry)	$\omega_i(S_i)$
$H_2O \cdot (HF)_2$ (C_{2v})	691 (65)
	690 (349)
	647 (238)
	592 (362)
	250 (114)
	199 (23)
	175 (0)
	167 (3)
	100 (0)
	32 (12)
$H_2O \cdot (HF)_2$ (C_1)	1055 (121)
	805 (409)
	669 (378)
	548 (91)
	522 (240)
	334 (60)
	266 (6)
	236 (103)
	223 (7)
	162 (11)

Architecture of the database on structure–energy and spectral characteristics of complexes

The developed version of the database on the characteristics of $(H_2O)_mM_n$ complexes assumes the input and systematization of the information about the following characteristics:

– geometry of a complex in the equilibrium state;

– binding energies of the component molecules;

– frequencies of intra- and intermolecular vibrations;

– intensities of vibrational IR bands;

– electro-optical characteristics (dipole moment, polarizability);

– concentrations of monomer molecules, forming the complex, and complexes in the gas medium (atmosphere);

– sources of information (in each column).

Table 5 summarizes the designations used in the database. A database string format is illustrated in Table 6.

Table 5. Designations of characteristics included in the database for $(H_2O)_m(HX)_n$, X = F, Cl, complexes

Symbol	Characteristic
R_e	Equilibrium bond length
ΔE	Binding energy between monomers
α	Angle between the axis O–F and the bisector of ∠H–O–H
ω_i	Frequencies of vibrational bands
v_s	Stretching symmetric vibrations
v_{as}	Stretching antisymmetric vibration
Δ	Bending vibrations
δ_i	Bending vibrations in the plane of the H_2O molecule
Δ_0	Bending vibrations out of the plane of the H_2O molecule
N	Equilibrium concentration of complexes
A	Intensity of absorption band
a	Calculation by the HFR/6-31G** method
b	Calculation by the MP2/6-31G** method
c	Calculation by the Möller–Plesset perturbation theory MP2/6-311G**
d	Calculation by MP3/6-311G**
e	Calculation by MP4/6-311+G(2d,2p)
f	Calculation by MP2/6-31++G**
g	Calculation by HFR/6-31G**+VP^s
h	Calculation by HFR/6-31G**+VP^s(2d)^s
j	Calculation by MP2/6-31G**+VP^s(2d)^s
μ, α	Dipole moment and polarizability

Table 6. String format

Parameter	Units
Type of the complex	
Equilibrium bond length	Å
Angles between bonds	deg
Binding energy of monomers in complex	$kcal \cdot mol^{-1}$
Frequencies of vibrational bands	cm^{-1}
Intensity of vibrational bands	$km \cdot mol^{-1}$
Equilibrium concentrations of complexes and monomer molecules	m^{-3}
Dipole moment	D

Every string corresponds to one or several columns. The first column gives the chemical formula of the complex. The string section "complex geometry in the equilibrium state" includes six columns, which contain the calculated and experimental values of equilibrium bond lengths and angles between bonds. The next column presents the calculated and experimental values of the energy of interaction between the molecules in the complex. The string section corresponding to the frequencies of intra- and intermolecular vibrations contains the number of columns equal to the number of the main types of vibrations (calculated and experimental values), and their assignment. The next string section, presenting the intensities of vibrational bands, is constructed similarly to the previous one, but the values in it are unfortunately absent because of the lack of reliable information. The string section "equilibrium configuration" includes three columns giving the information about the concentration of the monomer molecules and complexes formed by them in a gas at the standard temperature and pressure. The last column includes the data on the dipole moment and polarizability of the complex.

Table 7. Database string structure for H_2O...HF complexes taken as an example

Complex	Geometric structure											
	R_e, Å						Angles, deg					
	$H_{(2)}$–$F_{(2)}$		$O_{(1)}$–$H_{(1)}$		$O_{(1)}$–$F_{(2)}$		$H_{(1)}$–$O_{(1)}$–$H_{(1)}$		α		$H_{(2)}$–$F_{(2)}$–$O_{(1)}$	
	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
H_2O...HF	0.91^{a}		0.94^{a}		2.72^{a}		107^{a}		134^{a}	134 (Ref. 15)	4^{a}	
	0.93^{b}		0.96^{b}		2.67^{b}		105^{b}		131^{b}		6^{b}	
	0.92^{c}		0.96^{c}		2.64^{c}		105^{c}		129^{c}		5^{c}	
	0.92^{d}		0.96^{d}		2.65^{d}		105^{d}		133^{d}		3^{d}	
	0.92^{e}				2.72^{e}							

ΔE, kcal·mol^{-1}		Frequencies of vibrational bands, cm^{-1}								
		HF			H_2O			H_2O...HF		
Calc.	Exp	Calc.	Exp.	Assignment	Calc.	Exp.	Assignment	Calc.	Exp.	Assignment
9^{a}	10 Ref. 10	4493^{a}	4138 Ref.9	ν(HF)	4265^{a}	3939 Ref. 10	ν_{as}(OH)	4270^{a}	3608±2, Ref. 15	$\nu(H_{(2)}F_{(2)})$
11^{b}		4212^{b}			4052^{b}			4258^{a}	3756, Ref. 15	$\nu_{as}(O_{(1)}H_{(1)})$
11^{c}		4119^{f}			4010^{f}			4142^{a}	3657, Ref. 15	$\nu_{s}(O_{(1)}H_{(1)})$
11^{d}					4148^{a}	3835 Ref. 10	ν_{s}(OH)	1765^{a}	1595, Ref. 15	$\delta(H_{(1)}O_{(1)}H_{(1)})$
9^{e}					3909^{b}			760^{a}	696±30, Ref. 15	$\delta_{i}(O_{(1)}H_{(2)}F_{(2)})$
					3863^{f}			626^{a}	666±30, Ref. 15	$\delta_{0}(O_{(1)}H_{(2)}F_{(2)})$
					1770^{a}	1648 Ref. 10	δ(HOH)	236^{a}	180±30, Ref. 15	$\nu(H_2O...HF)$
					1674^{b}			206^{a}	145±50, Ref. 15	$\Delta_{0}(H_{(1)}O_{(1)}H_{(2)})$
					1620^{f}			194^{a}	170±50, Ref. 15	$\delta_{i}(H_{(1)}O_{(1)}H_{(2)})$

A, km·mol^{-1}		Equilibrium concentration, m^{-3}			μ, D
Calc.	Exp.	$n(H_2O)$	n(HF)	$n(H_2O...HF)$	
		$1.85 \cdot 10^{19}$ Refs. 17, 18	$6.66 \cdot 10^{20}$ Refs. 17, 18	$10.03 \cdot 10^{15}$ Refs. 17, 18	4.03^{a}

Table 7 shows the string with the data for the H_2O...HF complex.

Conclusions

The first version of the database on the energy, structure and spectral characteristics of molecular complexes of H_2O with diatomic molecules has been proposed. Now the database contains the material on the $(H_2O)_m(HX)_n$ complexes, where X = F, Cl with $1 \le m$, $n \le 2$, based on the data of theoretical and experimental investigations.

This database can be used as information support in developing optical remote methods for monitoring of the gas composition of the atmosphere over industrial centers.

In the future it is planned to complement the database with the information about the complexes with m, $n > 2$, as well as on the complexes of water with triatomic molecules of natural and anthropogenic origin.

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