Molecular complexes of water with atmospheric gases

Sh.Sh. Nabiev and P.G. Sennikov[1]

Russian Scientific Center "Kurchatov Institute," Moscow
[1] *Institute of Chemistry of High-Purity Substances,*
Russian Academy of Sciences, Nizhnii Novgorod

Received December 14, 2000

The data of recent experimental and theoretical studies of weak molecular complexes formed by water with major (N_2, O_2, CO_2) and minor (CH_4, CO, NO, N_2O, O_3) atmospheric constituents, as well as some important pollutants (halogens, halides, halogen-containing inorganic and organic molecules, volatile halogenides and hydrides, hydrocarbons) are analyzed and generalized. It is shown that formation of such complexes should be taken into account when evaluating the capabilities of the methods of optical monitoring as applied to the atmosphere.

Introduction

Real-time monitoring of gaseous and aerosol emissions by industrial enterprises becomes increasingly urgent in connection with the aggravated ecological situation and the growing public concern about injurious impact of these objects on the environment. Of particular concern are possible consequences of emergencies at nuclear and chemical plants whose production cycle involves emission of both radioactive substances and various chemically active and toxic compounds.[1] Similar problems arise at some enterprises of non-ferrous metallurgy and electronic industry that use electrolysis or so-called CVD technology (deposition of chemical compounds from the vapor phase).[2]

The methods of remote laser sensing are now most promising in real time obtaining of reliable information on the concentration and chemical (molecular) composition of emissions.[3] Profitable application of these methods is possible only with detailed information on absorption and emission spectra of molecular components. Generally speaking, the corresponding data can be found almost in all existing spectroscopic databases such as, for example, HITRAN,[4] GEISA,[5] etc. However, when solving the problems of laser monitoring of emission components (especially, from nuclear plants), such data should be used with some care.[6,7] The reason is that chemically active particles can interact with major atmospheric constituents, first of all, with water, whose mass content in the atmosphere at low altitudes is from 0.02 to 4%. In addition to the products of just chemical (first of all, photochemical) reactions, whose probability is high only for the particles of relatively high concentration, formation of molecular complexes with the energy from several tens calories to several kilocalories is possible as well.[8]

Optical activity of such donor-acceptor or H-bonded complexes can be rather high, what may cause additional radiative losses in the atmosphere of industrial regions and variations of solar radiation fluxes. Gas-phase complexes with participation of water molecules are characterized, as a rule, by several types of large-amplitude motions (LAM).[7,8] This, in its turn, leads to transformation of the vibrational spectra of their components (spectral shift can reach tens and even hundreds reciprocal centimeters relatively free molecules) and to appearance of new bands corresponding to intermolecular vibrations.[6,8,9] Effects connected with large-amplitude motions in the gas-phase complexes may cause considerable methodic problems in detection of molecular pollutants in the atmosphere by the remote laser sensing method.[6,7] In addition, the fact that a considerable portion of some pollutants (for example, nitric acid[10]) is present in the form of complexes can affect significantly a number of problems of atmospheric chemistry.

In the last years, the study of the structure and properties of weakly bounded molecular complexes has become an intensely developed field at the junction of physics and chemistry, involving up-to-date experimental (mostly spectroscopic) and theoretical (quantum-chemistry) methods. In the literature the term "Van der Waals complex" or "Van der Waals molecule" is often used instead of the term "weak molecular complex." Hobza and Zahradnik[11] believe that as such a complex (AB supersystem) is formed of two subsystems A and B:

1) a covalent bond does not form and break;

2) the geometry and electron structure of the subsystems A and B change only slightly;

3) the stabilization energy accompanying the process of formation of such a complex is usually lower than 10 $kcal \cdot mol^{-1}$;

4) the spacing between two the closest atoms of the subsystems A and B is usually more than 2 Å;

5) the supersystem AB is formed spontaneously by the scheme $B...A \Leftrightarrow B + A$, and the coordinate of the reaction has a "sloping" character.

Formally, this definition covers a large group of molecular complexes, one subsystem of which includes a fragment X–H, and another contains a fragment Y; the atoms X and Y have rather high electronegativity, and the atom Y, in addition, has an unshared electron pair.

Instead of the atom Y, the molecule B may contain a π-electron system. Such complexes are called complexes with a hydrogen bond or H-complexes. Their characteristic distinction from the typical Van der Waals complexes is a so-called “directivity” of the hydrogen bond implying that the unshared electron pair of the atom Y is oriented directly toward the bridge proton. This is favored by hybridization of valent orbitals of the atom Y, taking place, in particular, in the oxygen atom of a water molecule. The uniqueness of the water molecule is that it can form simultaneously up to four stable H-bonds. Theoretical and experimental methods for studying the water molecule are considered in detail in Ref. 12.

The great interest demonstrated in the recent time by researchers to water complexes is connected, on the one hand, with the study of the nature of intermolecular interactions and, on the other hand, with a wide variety of practical problems in different fields of science and technology, in which these complexes play a significant role. As an example, we can mention a considerable influence of the process of formation of weakly bounded gas-phase complexes with the energy ≤ 2 kcal·mol^{-1} between molecules of water and the basic substance to the depth of distillation purification from water of volatile inorganic hydrides of the elements of VA–VIA groups.[13] The problem of interpreting the mechanisms of extinction of far IR radiation under the conditions of the Earth’s atmosphere is also pertinent to the topic under consideration. One of the traditional approaches connects the so-called excess absorption of IR radiation with water dimers having the energy of -3.6 kcal·mol^{-1} (Ref. 14) and entering into the composition of water vapor.[15,16]

The aim of this paper is to analyze the state of the art in research into structure and spectroscopic parameters of weakly bounded and structurally nonrigid molecular complexes formed by water molecules with the major (N_2, O_2, CO_2) and minor (CH_4, CO, NO, N_2O, O_3) atmospheric constituents, as well as some important pollutants of industrial origin (halogens, halides, halogen-containing inorganic and organic molecules, volatile halogenides and hydrides, hydrocarbons, oxides, etc.).

Formation of the complexes was considered in the ground electronic state. Obviously, in the actual atmosphere exposed to UV radiation, the formation of complexes existing only in excited electronic states (excimers, exciplexes) is possible. Although the role of the above compounds in chemical reactions may be significant, their consideration is beyond the scope of this paper.

1. Experimental and theoretical methods for studying weakly bounded molecular complexes in gas phase

Traditional thermochemical methods, as well as any indirect methods based on analysis of macroscopic (thermodynamic or transport) properties of a gas are unfit, with rare exception, for determination of the dissociation energy of complexes, because they give large errors. Therefore, the preference in practice is usually given to the methods dealing with individual characteristics of particles, first of all, rotational and rotational-vibrational high-resolution spectroscopy. In addition, these methods give information on the structure of weak molecular complexes and their potential surface.

For the overwhelming majority of molecular gases, the depth of the intermolecular potential well D_e has the same order of magnitude as the translational energy of molecules at the critical temperature T_c: $D_e = k\,T_c$. At $T < T_c$ the energy of molecular interaction exceeds the thermal energy, and just this leads to formation of stable gas-phase complexes. For the equilibrium process of complex formation, which can be described by a simple scheme

$$\mathrm{XH} \ldots \mathrm{Y} \Leftrightarrow \mathrm{XH} + \mathrm{Y}, \qquad (1)$$

the equation for the equilibrium constant has the form[17,18]

$$(n_{\mathrm{XH}\ldots\mathrm{Y}}/n_{\mathrm{XH}}\,n_{\mathrm{Y}}) = (h^2/2\pi kT\mu)^{3/2} \exp\,(D_0/RT), \qquad (2)$$

where $n_{\mathrm{XH}\ldots\mathrm{Y}}$ and n_{XH}, n_{Y} is the number of complex compounds and interacting particles in unit volume in the equilibrium rotational-vibrational state; D_0 is the energy of dissociation corresponding to this state, and

$$\mu = (M_{\mathrm{XH}}\,M_{\mathrm{Y}})/(M_{\mathrm{XH}} + M_{\mathrm{Y}}). \qquad (3)$$

Here M_i is the molar mass.

The equilibrium constant can be determined experimentally using the traditional methods of IR spectroscopy by measuring absolute intensities of rotational-vibrational or purely rotational transitions of the components taking part in reaction (1) in some nonequilibrium gas mixture. If the equilibrium constant is determined, then we can estimate rather strictly the energy of dissociation D_0 in the zero rotational-vibrational state. The value of D_0 is connected with the total energy of dissociation D_e as[18,19]:

$$D_e = D_0 + \sum_i \frac{h}{2}\nu_i^{\mathrm{XH}\ldots\mathrm{Y}} + \sum_i \frac{h}{2}\nu_i^{\mathrm{X}} + \sum_i \frac{h}{2}\nu_i^{\mathrm{HY}}\,, \qquad (4)$$

where the summands in the second, third, and fourth terms are the contributions from all vibrational states, except for intermolecular bending vibrations in the gas-phase of the complex XH…Y.

The energy of dissociation in almost all known molecular complexes is usually so low, that high-excited states are populated already at the room temperature, and the depth of the potential well may be only ≈ 100 cm^{-1}. Therefore, to study the nature and mechanisms of intermolecular interaction in weak molecular complexes, it is worth applying methods of long-wave IR and microwave (rotational) spectroscopy, which are highly informative, but, unfortunately, relatively inaccessible, as compared to traditional methods of IR spectroscopy,. These methods allow recording new and, as a rule, very weak lines and bands of intermolecular vibrations in the spectra of complexes. Spectroscopic manifestation of formation of a complex can be also recorded in the region of intramolecular vibrations of its components. For water, this is the region of stretching ($\approx 3600-3800\ \text{cm}^{-1}$) and bending ($\approx 1600\ \text{cm}^{-1}$) vibrations.[12] The characteristic sign of formation of a complex with the H-bond is a shift of the band ν_{str} of the proton donor toward lower frequencies and significant increase in the intensity of this band.

In the experiments with weak molecular complexes, one should keep in mind that their relative content in the gas phase is low, and it can decrease drastically with the distance from the line of phase transition between the gas and condensed phases. Therefore, specialized techniques were developed for obtaining relatively high content of complexes having low translational-rotational temperatures $T \le 10-50$ K.

The first group of these techniques employs the gas-dynamic method of generation of complexes, in which the initial mixture of the complex components in argon or helium (whose concentration is $\ge 90\%$) at the room temperature and pressure of 1–5 atm expands adiabatically into vacuum through a narrow nozzle. As a result, a jet (in the absence of collimation) or molecular beam (if the paraxial part of the jet is separated with a collimator) arises. As this takes place, the effective temperature drops down to 0.1–50 K, and the region of interaction of the formed complexes with microwave or optical radiation in spectrometers usually localizes in the part of a spectrometer, where molecules move almost without collisions. Under these conditions, i.e., in lower energy states, complexes are almost not subject to dissociation and can be studied for rather long time until their destruction due to collisions with the walls of the vacuum chamber. For these purposes, long and narrow waveguides of ordinary microwave spectrometers are unsuitable, because molecules must interact with radiation in large-volume chambers.

Two types of microwave spectrometers with gas-dynamic generation of complexes were proposed. In the pulsed-jet microwave Fourier transform spectrometer,[20,21] the pulsed gas jet having the speed about $5\cdot 10^4\ \text{cm}\cdot\text{s}^{-1}$ in the nozzle direction, is injected into the Fabry–Perrot large-volume resonator with the frequency $\cong 10$ pulse/s. Molecules in the resonator cooled down to $T \cong 5$ K are excited by a short microwave pulse. The signal of induced molecular polarization with duration of about 100 μs at the frequency of rotational transition of the complex leaves the resonator and is recorded in the absence of an intense polarizing pulse, because its decay time is almost 10^3 times shorter. After the corresponding processing of the signal and its Fourier transform, the spectrum is obtained, in which each line is splitted due to the Doppler effect.

In the method of electroresonance spectroscopy of a molecular beam,[22,23] a collimated molecular beam is used. The beam passes through an inhomogeneous electric field and enters a mass-spectrometer, which serves as a detector. The microwave radiation is directed normal to the beam. Falling in resonance with this transition, it changes population of the corresponding states and, consequently, the number of molecules reaching the detector. Advantages of the above technique using high-speed jets and molecular beams are determined by the high concentration of even very weak complexes formed at expansion without collisions in combination with the high Doppler-limited resolution. This allows the study of the fine structure of transitions and the high-accuracy determination of rotational constants and dipole moments of complexes. Processing of purely rotational spectra of complexes can give the value of the centrifugal distortion constant D_J related to the force constant of the translational vibration of the intermolecular bond k_σ as

$$k_\sigma = 16\,\pi^2 B^2 \mu / D_J, \tag{5}$$

where B is the rotational constant; μ is the reduced mass of the complex.

Equation (5) is valid only for diatomic molecules.[24] However, its application to lesser compound bimolecular complexes is justified, because the intermolecular equilibrium distance r_e, as a rule, 3 to 4 times exceeds typical lengths of ordinary chemical bonds. Knowing the values of k_σ and r_e, we can estimate the depth of the intermolecular potential well of the complex by expanding the Lennard–Jones potential into a series at the point of the minimum of the potential curve[25]:

$$\varepsilon = 1/72\ k_\sigma\, r_e^2. \tag{6}$$

Table 1 gives some molecular parameters of the complexes of water with various molecules. These parameters were determined using the spectroscopic methods described above.

The alternative technique for generation of weak complexes at the minimal distorting effect of the ambient medium is the technique of low-temperature matrix isolation. In one of the variants of this method, mixtures of the complex components with a diluent gas (argon, krypton, nitrogen, oxygen, etc.) are supplied independently onto a substrate cooled down to 4–20 K. Such a temperature is sufficient for the diluent gas to form a solid matrix containing the complex under study.[59] In another variant, the components of the complex are preliminary mixed in the diluent gas, and the formed complex is then studied under matrix conditions. Bands of monomers and complexes in the 1:1 mixture can be observed at the same time under such conditions only at large content of the diluent gas (the concentration ratio of the substances under study and the diluent gas exceeds 10^3). Otherwise, as this ratio decreases, the bands of more complex associates appear.

Table 1. Molecular constants of water complexes with various molecules in gas phase (from the data of microwave spectroscopy)

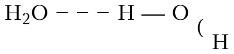
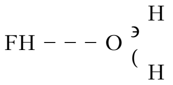
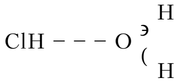
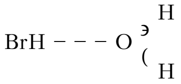
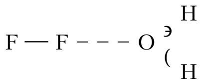
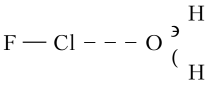
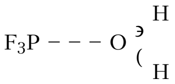
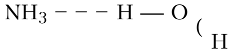
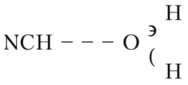
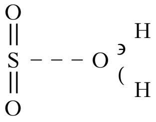
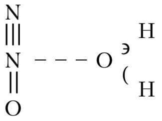
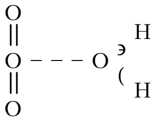
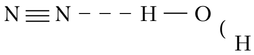
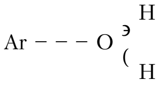
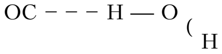
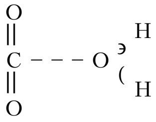
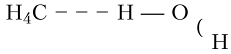
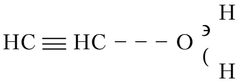
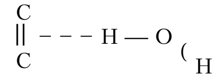
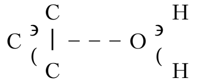
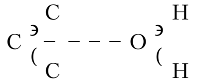
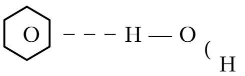
Molecule	Intermolecular distance, Å*	Force constant k_s, N·m^{-1}	Dipole moment μ, D	Scheme of the complex	Reference
1	2	3	4	5	6
H_2O	2.05 (O...H)	11.7	2.64307	 $\mathrm{H_2O}---\mathrm{H}—\mathrm{O}\diagdown\mathrm{H}$	26
HF	2.662 (F...O)	24.9	4.073	 $\mathrm{FH}---\mathrm{O}\begin{smallmatrix}\diagup\mathrm{H}\\ \diagdown\mathrm{H}\end{smallmatrix}$	27–30
HCl	3.215 (Cl...O)	12.5	–	 $\mathrm{ClH}---\mathrm{O}\begin{smallmatrix}\diagup\mathrm{H}\\ \diagdown\mathrm{H}\end{smallmatrix}$	31
HBr	3.411 (Br...O)	10.5	–	 $\mathrm{BrH}---\mathrm{O}\begin{smallmatrix}\diagup\mathrm{H}\\ \diagdown\mathrm{H}\end{smallmatrix}$	32
F_2	2.72 (F...O)	3.63	–	 $\mathrm{F}—\mathrm{F}---\mathrm{O}\begin{smallmatrix}\diagup\mathrm{H}\\ \diagdown\mathrm{H}\end{smallmatrix}$	33
ClF	2.575 (Cl...O)	14.2	–	 $\mathrm{F}—\mathrm{Cl}---\mathrm{O}\begin{smallmatrix}\diagup\mathrm{H}\\ \diagdown\mathrm{H}\end{smallmatrix}$	34
PF_3	3.250 (P...O)	7.3	2.325	 $\mathrm{F_3P}---\mathrm{O}\begin{smallmatrix}\diagup\mathrm{H}\\ \diagdown\mathrm{H}\end{smallmatrix}$	35
NH_3	2.02 (N...H)	14.5	2.972	 $\mathrm{NH_3}---\mathrm{H}—\mathrm{O}\diagdown\mathrm{H}$	36
HCN	3.139 (C...O)	11.1	–	 $\mathrm{NCH}---\mathrm{O}\begin{smallmatrix}\diagup\mathrm{H}\\ \diagdown\mathrm{H}\end{smallmatrix}$	37–40
SO_2	2.824 (S...O)	5.3	1.984	 $\begin{matrix}\mathrm{O}\\ \Vert\\ \mathrm{S}\\ \Vert\\ \mathrm{O}\end{matrix}---\mathrm{O}\begin{smallmatrix}\diagup\mathrm{H}\\ \diagdown\mathrm{H}\end{smallmatrix}$	41
N_2O	2.97 (N...O)	–	1.48	 $\begin{matrix}\mathrm{N}\\ \equiv\\ \mathrm{N}\\ \Vert\\ \mathrm{O}\end{matrix}---\mathrm{O}\begin{smallmatrix}\diagup\mathrm{H}\\ \diagdown\mathrm{H}\end{smallmatrix}$	42
O_3	3.208 (O...O)	3.8	0.830	 $\begin{matrix}\mathrm{O}\\ \Vert\\ \mathrm{O}\\ \Vert\\ \mathrm{O}\end{matrix}---\mathrm{O}\begin{smallmatrix}\diagup\mathrm{H}\\ \diagdown\mathrm{H}\end{smallmatrix}$	43
N_2	2.42 (N...H)	–	0.833	 $\mathrm{N}\equiv\mathrm{N}---\mathrm{H}—\mathrm{O}\diagdown\mathrm{H}$	44
Ar	3.398 (Ar...O)	0.9	0.73	 $\mathrm{Ar}---\mathrm{O}\begin{smallmatrix}\diagup\mathrm{H}\\ \diagdown\mathrm{H}\end{smallmatrix}$	45–47
CO	2.407 (C...H)	2.74	–	 $\mathrm{OC}---\mathrm{H}—\mathrm{O}\diagdown\mathrm{H}$	48–50
CO_2	2.836 (C...O)	6.4	1.8522	 $\begin{matrix}\mathrm{O}\\ \Vert\\ \mathrm{C}\\ \Vert\\ \mathrm{O}\end{matrix}---\mathrm{O}\begin{smallmatrix}\diagup\mathrm{H}\\ \diagdown\mathrm{H}\end{smallmatrix}$	51
CH_4	3.702 (C...H)	1.53	0.728	 $\mathrm{H_4C}---\mathrm{H}—\mathrm{O}\diagdown\mathrm{H}$	52
C_2H_2	2.229 (H...O)	6.5	2.0124	 $\mathrm{HC}\equiv\mathrm{HC}---\mathrm{O}\begin{smallmatrix}\diagup\mathrm{H}\\ \diagdown\mathrm{H}\end{smallmatrix}$	53

Table 1 (continued)

1	2	3	4	5	6
C_2H_4	$2.48\ (\overset{C}{\underset{C}{\|}}\ldots H)$	–	1.0943		54, 55
C_3H_6	$2.34\ (\overset{C}{\underset{C}{\vert}}\ldots H)$	–	1.209		56
C_3H_8	4.35 (C...O)	–	0.73		57
C_6H_6	3,347	–	–		58

* The distance is given for the pair of atoms in parenthesis.

In addition, the significant inhomogeneous broadening in matrices complicates studying the shape and intensity of spectral bands of the complexes and, as a consequence, obtaining quantitative information on their composition and energy. The technique of matrix isolation is commonly used when studying weak complexes by the traditional method of low-resolution IR spectroscopy. In the case of H-bonded complexes, the relative stability of the complex can be judged qualitatively from the low-frequency shift of the stretching band of the proton donor. Application of this method to studying molecular complexes is reviewed in Refs. 60–63.

Table 2 presents the results of studying complexes of water with various molecules by the method of low-temperature matrix isolation.

The overwhelming majority of the treated below complexes of water with molecules interesting for atmospheric physics and chemistry have been studied just by the considered methods of microwave and IR spectroscopy in combination with gas-dynamic and matrix techniques for generation of weak complexes. Although these methods allow obtaining a great deal of information on the structure and molecular properties of the complexes under study, they have a general principal disadvantage: from the viewpoint of the thermodynamic state of complexes, they fall in the category of non-equilibrium methods, and thus the direct data on the enthalpy of a complex formation and its other thermodynamic functions cannot be obtained.

Therefore, the traditional methods of high-resolution IR spectroscopy (with Fourier transform or use of semiconductor lasers) or microwave spectroscopy (with Stark modulation) remain the main source of such data. The latter uses cells (waveguides) having long optical path that allow experiments to be conducted at the temperature no higher than 200 K without significant loss due to condensation of both initial substances and complexes,[93,94] what, as a rule, poses great technical difficulties.

The alternative way to increase the concentration of complexes under these conditions is to increase the pressure. This is accompanied by the sharp broadening of bands, as well as by the increase in the probability of formation of a number of different complexes.

Table 2. Wavenumbers (ν_i, cm^{-1}) of fundamental vibrations of the water molecule in the free state and in a complex with various molecules (from the data of IR spectroscopy in argon matrix)

Molecule	ν_1	$\Delta\nu_1$ ¹⁾	ν_3	$\Delta\nu_3$ ¹⁾	ν_2	$\Delta\nu_2$ ¹⁾	Ref.
Free H_2O (gas)							
	3657		3756		1595		12
H_2O in complexes with various molecules							
Ar	3638		3734		1589		64
H_2O ²⁾	3575	63	3710	24	1621	−22	64
H_2O ³⁾	3634	4	3723	5	1594	3	64
HF	3554	84	–	–	–	–	65
HCl	3630	8	3750	−16	1590	−1	66, 67
HBr	3629	9	3749	−15	1588	1	66, 67
HI	3631	7	3741	−7	1588	1	66, 67
SiF_4	–	–	3730	−4	1591	2	68
BF_3 ⁴⁾	3590	–	3660	–	–	–	69
F_2	3638	0	3745	−10	1590	−1	70
Cl_2	3637	1	3724	10	1587	2	71
Cl_2O	3629	9	3715	19	1588	1	71
ClO_2	3636	2	3729	5	1590	−1	71
HOCl	3634	4	3722	12	1592	−3	71
H_2SO_4	3640	−2	3745	−11	1600	−11	72
NH_3	3435	204	3702	32	1625	−36	73, 74
H_2S	3536	102	–	–	1614	−25	75
SO_2	3631	7	3723	11	1591	−2	76
SO_3 ⁵⁾	3613	–	3804	–	1595	–	77, 78
NO ⁴⁾	3605	–	3722	–	1600	–	79
CO	3628	29	3724	10	1596	2	80–84
CO_2 ⁴⁾	3634	–	3727	–	1597	–	85
H_2O_2							86
H_2CO	3585	53	3709	25	1610	−22	87
C_2H_2	3640	−2	–	–	1593	−4	88
C_2H_4	3613	25	3718	16	1595	−6	89, 90
C_3H_6	3648	−10	–	–	1622	−33	91
C_6H_6	3620	18	–	–	–	–	90, 92

Notes. ¹⁾ $\Delta\nu_i$ (cm^{-1}) are shifts of vibrational bands of water in a complex relative to the corresponding values of ν_i for free H_2O molecules in argon matrix; ²⁾ H_2O serves as a proton donor in water dimer; ³⁾ H_2O serves as a proton acceptor in water dimer; ⁴⁾ nitrogen matrix was used; ⁵⁾ neon matrix was used.

Therefore, in spite of a significant progress achieved now in high-resolution spectroscopy, the list of substances, the spectra of whose complexes can be obtained under equilibrium conditions, is limited. Among the complexes considered here, only the sufficiently strong H-bonded complex of water with anhydrous hydrogen fluoride is in this list.

Methods of quantum chemistry play a significant role in description of the structure and molecular properties of weakly bounded gas-phase complexes. Many original papers and reviews are devoted to this problem.[95–102] As in other fields of quantum mechanics in general and quantum chemistry in particular, when studying weak intermolecular interactions, of great importance are both methods of approximate solution of the Schrödinger equation: the variational method and the perturbation method. In the former, the interaction energy ΔE that is responsible for formation of the supersystem (complex) AB as the result of association of the subsystems A and B, is determined by the difference between the energy of the supersystem E_{AB} and the total energy of subsystems:

$$\Delta E = E_{AB} - (E_A + E_B). \tag{7}$$

The difficulty in calculation by this method is connected with the fact that the interaction energy ΔE is calculated as a difference of two large and very close values. In addition, the basic method of quantum chemistry – the Hartree–Fock method – does not completely take into account the correlation of electron motion. As a result, a part of the total energy, the so-called correlation energy, is neglected within the framework of this method. This energy is especially significant for weak intermolecular interactions. In the perturbation methods, on the contrary, the interaction energy ΔE is directly calculated as a sum of several terms, corresponding to the first and second approximations of the method. These terms include the Coulomb energy, induction energy, dispersion energy, charge transport energy, and the energy of exchange repulsion.

In spite of the seeming convenience of the perturbation method, the interaction energy for various complexes is now calculated in most cases by the variational method. This is explained by the formal simplicity and convenience of variational calculations, as well as by the circumstance that standard quantum-chemistry computational programs can be used in such calculations. The correlation energy E_{cor} (roughly corresponding to the dispersion energy in the perturbation theory) is considered within the framework of the Moller – Plesset perturbation theory. The second approximation of this theory (MP2) takes into account all paired correlations of electrons. Higher approximations describe correlation of pairs, triplets, and so on. Now the calculations are practically performed up to the approximation MP4, and the corrections are often determined at a fixed complex geometry found in the Hartree – Fock approximation.

In calculation of the interaction energy ΔE by Eq. (7), one more problem arises. It lies in the fact that the energy of the supersystem is calculated with the use of a larger basis set than the basis sets used for calculation of the energy of the subsystems. In this case, the application of the variational principle naturally gives the lower energy of the supersystem, thus overestimating the interaction energy. This basis set superposition error (BSSE) can be eliminated by using the so-called counterpoise correction method proposed in Ref. 103. In this method, the energy of the supersystem and the energies of subsystems are calculated in the same basis. As the results of numerous calculations made in the last 10–15 years show, the contribution of BSSE to the total interaction energy ΔE can be rather large.

The decisive condition for obtaining correct results on the structure and energy of weakly bounded complexes by methods of quantum chemistry is the optimal choice of the basis set of wave functions of atomic orbitals. This problem is considered, for example, in the series of papers by Latajka.[104,105] Any used basis must include diffusion and polarization *s*-, *p*-, *d*-, and *f*-functions, the increase of which makes the basis set closer to the Hartree – Fock limit, and its practical usage is finally determined by the cost of computation. It should be noted that, as was shown, e.g., in Ref. 106, the approach of the basis set to saturation in calculation of ΔE is accompanied by the decrease in BSSE down to 0–1 kcal·mol^{-1}.

Quantum-chemical computations determine not only the electronic interaction energy ΔE (with regard for the correlation energy and BSSE), but also standard thermodynamic functions of some complex formation by the well-known equation

$$\Delta G_T^0 = \Delta H_T^0 - T\,\Delta S_T^0, \tag{8}$$

which can be rewritten in the following way:

$$\Delta G_T^0 = \Delta E + \Delta ZPE + \Delta H_T - T\,\Delta S_T^0. \tag{9}$$

Here ΔE is the electronic interaction energy (change in the energy at association); ΔZPE is the change in the energy of zero vibrations at association; ΔH_T is the temperature change of the interaction enthalpy. The values of ΔE and ΔZPE are determined from quantum-chemical calculations; to find other terms of Eq. (9), methods of statistical thermodynamics can be used.

The interaction energy of water complexes calculated by quantum-chemistry methods is given in Table 3.

Table 3. Quantum-chemical calculations of complexes of water with various molecules

Complex	Basis	R, Å 1)	r, Å 2)	Θ, 3) deg	ΔE (MP2), 4) kcal·mol^{-1}	ΔE (MP2+ +BSSE), 5) kcal·mol^{-1}	ΔE+ZPE, 6) (a) ΔH^0, (b) kcal·mol^{-1}	Ref.
1	2	3	4	5	6	7	8	9
H_2O...HF	6–311**	2.639	0.923	4.5	−9.64		−8.9 7) (a)	107
	6–31+*G*(2*d*,2*p*)	2.720	0.922	4.6	−9.0		−7.4 7) (b)	108
	PS–31*G*** and frame pseudopotential	2.702	0.912	3.8		−8.2 8)		109
	EXRHF 3/[7*s*,4*p*,2*d*/4*s*,4*p*]	2.635		1.7			−9.1 (a)	110
	6 − 31*G***	2.72	0.91	3.0	−9.03			111,112
(H_2O)$_2$...HF	6–31++*G*(2*d*,2*p*)				−20.69	−17.58	−14.95	113
	6–31*G***	2.0(O...H) 1.749(O...H)	0.919		−20.24			114–116
H_2O...(HF)$_2$	6–31++*G*(2*d*,2*p*)				−19.65	−17.25	−14.23	113
	6–31*G***	1.895(O...H) 1.734(O...H) 1.786(F...H)	0.907 0.921 0.912		−14.79 −21.26			114–116
(H_2O...HF)$_2$	6–31*G***	1.874(H...O) 1.930(H...F)	0.915 0.928		−32.67			114–116
(H_2O...HF)$_3$	6–31*G***	1.976(F...H) 1.674(H...O) 1.851(H...F) 1.678(H...O) 1.980(H...F)	0.922 0.922 0.903		−35.97			114–116
H_2O...HCl	6–311**+VP^s(2*d*)^s	3.281	1.289	3.4	−5.42	−4.74	−3.96 (b)	94
	6–31+*G*(2*d*,2*p*)	3.343	1.277	2.2	−5.8		−4.43 7) (b)	108
	PS–31*G*** and frame pseudopotential	3.268	1.282	2.4		−4.93 8)		109
	6–311** and [4*s*,3*p*,2*d*/2*s*,1*p*] for H_2O 6–31*G*(2*d*,2*p*) for HCl	3.19	1.290		−6.59			107
	6–31*G*(2*d*,*p*)					−5.23	−3.13 (b)	117
	6–31*G***	3.25	1.277	2.2	−5.2			118, 119
H_2O...(HCl)$_2$	6–31*G***	2.08(O...H) 2.7(H...Cl)	1.27 1.276		−8.5			118, 119
(H_2O)$_2$...HCl	6–311*G*(2*d*,*p*)					−7.64 9)	−4.65 9) (b)	117
	6–31*G***	2.11(O...H) 2.8(Cl...H)	1.279		−11.1			118,119
(H_2O)$_3$...HCl	6–311*G*(2*d*,*p*)					−7.04	−5.67 9) (b)	117
H_2O...HBr	PS–31*G*** and frame pseudopotential	3.496	1.430	2.5		−4.12 8)		109
H_2O...HI	PS–31*G*** and frame pseudopotential	3.830	1.612	2.6		−3.45 8)		109
H_2O...ClF	6–31++*G*(3*df*,2*p*)	2.564 10)	1.685 11)		−6.30 −5.49 12)		−4.86 7) (a) −4.05 12) (a)	120
H_2O...HOCl 13)	6–311++*G*(3*df*,2*p*)	1.709	0.960		−8.20 14)		−5.9 7,14) (a)	121
H_2O...SiF$_4$	6–311++*G*(2*d*,*p*)				−5.4	−2.7	−1.4 (b)	122,123
	6–31++*G*(2*d*,*p*)				−4.6	−2.7		
	CC–pvtz				−4.9	−2.7		
H_2O...HNO$_3$	6–311*G*++ (2*d*,*p*)	1.769	0.963			−8.24	−7.2 (a)	36

Table 3 (continued)

1	2	3	4	5	6	7	8	9
$H_2O...HCN$	6–31G (d,p)	3.082	1.073	0.0	−6.90	−5.48	−4.18 (a)	124
							−4.76 (b)	
	D95++(d,p)	3.127	1.076	0.0	−6.22	−4.95	−3.80 (a)	
							−3.79 (b)	
$H_2O...NH_3$	6–31G++(2d,2p)	3.039	0.955	2.3	−6.6		−4.7 (b)	108
	6–31G*				−8.0			125
	6–31G**+VP^s(2d)	3.096	0.930	4.6	−6.48	−5.74	−4.16 (b)	126
$H_2O...PH_3$	6–31G++(2d,2p)	3.918	0.949	3.0	−2.2		−0.8 (b)	108
$HOH–SH_2$	6–31G++(2d,2p)	3.774	0.949	3.4	−2.7		−1.3 (b)	108
	6–311G++(3df,3pd)	3.480	0.963	2.8		−2.87		127
$H_2O...HSH$	6–31G++(2d,2p)	3.619	1.327	3.0	−3.0		−1.5 (b)	108
	6–311G++(3df,3pd)	3.527	1.337	2.0		−3.60		127
$H_2O...N_2$	6–311G++//6–31G*	3.236	0.950			−1.2	−0.55 (a)	128
	4–31G		0.950		−1.7 $^{8)}$	−1.0 $^{8)}$		129
	6–31G**		0.961		−1.63	−0.93		130
$H_2O...O_2$	$^{17)}$				−0.86			131
$H_2O...O_3$	4–31G(d,p)	3.18			−2.9 $^{16)}$			132
$H_2O...CO$	6–31G**		0.962			−1.34		130
	6–31G++(d,p)	3.379	0.962	10		−1.46		133
$H_2O...CO_2$	6–31G++(2d,2p)				−3.0	−2.3	−2.91 (b)	134, 135
	6–31G*				−3.26	−2.66		136
	TB S(spdf+b) $^{17)}$	4.434			-2.63 $^{14)}$			137,138
$H_2O...SO_3$	6–31G++(d,p)						−8.4 $^{15)}$ (a)	139
$H_2O...SO_2$	6–31G++(d,p)	2.84	1.48		−3.58		−1.72	140
$H_2O...H_2O_2$	6–311G++(3d,2p)				−7.15	−6.4		141
$H_2O...CH_4$	6–31G++(2d,2p)	4.122	1.087	0.0	−0.72	−0.42		142
$H_2O...C_2H_2$	6–31G(d,p)	3.220	1.062	0.0	−4.09	−2.88	−1.92 (a)	124
							−2.33 (b)	
$H_2O...CH_3F$	6–311G++**					−1.35		143
$H_2O...CH_2F_2$	6–311G++**					−2.11		143
$H_2O...CHF_3$	6–311G++**					−3.16		143
$H_2O...OCH_2$	6–31G(d,p)	3.220	1.062	0.0	−4.09	−2.88	−1.92 (a)	144
							−2.33 (b)	

Notes. $^{1)}$ Distance between X and Y atoms bounded by the hydrogen bond (X–H...Y); $^{2)}$ X–H bond length in a complex; $^{3)}$ angle between the X–H bond and the linear X–Y bond; $^{4)}$ interaction energy with regard for correlation energy calculated by the method MP2; $^{5)}$ the same, but with BSSE correction; $^{6)}$ electronic energy of complex from the previous column with regard for the energy of zero vibrations (a), enthalpy of complex formation (b); $^{7)}$ BSSE correction was neglected; $^{8)}$ the correlation energy was neglected; $^{9)}$ the value of ΔE corresponds to the reaction $(H_2O)_n...HCl \rightarrow (H_2O)_n + HCl$; $^{10)}$ intermolecular distance Cl...O; $^{11)}$ length of the Cl–F bond in a complex; $^{12)}$ correlation energy was determined by the QCISD method; $^{13)}$ data for the most stable conformer (atoms H of the water molecule and atom Cl of the molecule HOCl are in the same plane); $^{14)}$ correlation energy was determined by the method MP4; $^{15)}$ the MP4SDQ method was used, the BSSE correction was neglected; $^{16)}$ the method MP4 was used; $^{17)}$ for description of the basis, see the corresponding reference.

2. Complexes of water with atmospheric gases

Now we consider properties of individual complexes. The sequence of their consideration proposed below is connected with the tendency of some or other groups of molecules to form the intermolecular hydrogen or donor-acceptor bonds with water molecules, rather than with the generally accepted classification mentioned above (major and minor atmospheric constituents, gaseous pollutants[145]).

2.1. Complexes with halogen hydrides HX (X = F, Cl, Br, I)

Among the $H_2O...HX$ complexes (X = F, Cl, Br, I), the complex $H_2O...HF$ is most thoroughly studied both experimentally and theoretically. For the first time, the existence of this complex in the gas phase under equilibrium conditions at the temperature of 315 K was found experimentally by Thomas by the traditional IR spectroscopy method.[146] Formation of the complex is indicated by three bands, the first corresponds to stretching vibrations of the HF molecule, the second – to bending vibrations of water molecule, and the third – to two bending vibrations of the hydrogen bond itself. The energy of the complex formation determined from spectroscopic data with allowance made for zero vibrations turned out to be equal to 7 kcal·mol^{-1}.

The first works on studying the rotational spectrum of this complex were made by Bevan and Legon with colleagues in 1975 and 1980.[27,147] More recently the rotational spectrum of the H_2O...HF complex was studied by the Legon group under both nonequilibrium[28,29,148] and equilibrium conditions.[30,149] The structure of this complex is discussed in detail in reviews 93, 150, and 151.

The comprehensive analysis of the rotational spectrum of H_2O...HF has shown that this complex is featured by two conformations of the pyramidal structure of the C_s symmetry having the same energy. They are separated by the energy barrier equal to 0.4 kcal·mol^{-1} and corresponding to the plane structure of the complex with the C_{2v} symmetry. In the both structures, the HF molecule (proton donor) lies along the axis passing through the unshared electron pair of the oxygen atom of the water molecule. The strength of the formed H-bond of O...HF is characterized, as was mentioned above, by the force constant of its stretching vibrations k_s equal to 24.9 N·m^{-1} (see Table 1). The intensities of rotational transitions of the molecules H_2O and HF and the complex H_2O...HF in the ground states under equilibrium conditions in the gas phase were measured in Ref. 149. These data were then used in calculation of the equilibrium constant and energy of the complex formation, accounting for zero vibrations, equal to −10.2 kcal·mol^{-1}. Reference 30 presents the standard thermodynamic functions of formation of the H_2O...HF complex. The obtained data allow estimating the concentration of the complex in the equilibrium gas mixture under typical conditions of a spectroscopic experiment at the equal partial pressures of the initial components $P_{HF} = P_{H_2O} = 100$ mTorr. In this case, the content of the complex in the mixture is 1%. For comparison, in the case of the HCN...HF complex ($k_s = 11.1$ N·m^{-1}), the degree of transformation is only $5 \cdot 10^{-4}$%.

Table 4 gives some most important spectroscopic constants and frequencies of transitions of the H_2O...HF complex; these data were obtained from the analysis of its rotational and rotational-vibrational spectra.

Formation of the complexes H_2O...HCl and H_2O...HBr was found using the method of pulsed-jet microwave Fourier spectroscopy.[31,32] The structure of these complexes is similar to the structure of H_2O...HF, but, as is seen from analysis of Table 1, the strength of complexes decreases drastically when passing from HF to HCl and then decreases a little when passing to HBr.

Table 4. Spectroscopic constants and frequencies of transitions of the H_2O...HF complex

Molecular parameter	Value	Reference
A, GHz	391.1	152
B_0, MHz	7263.36	152
C_0, MHz	7139.69	152
D_J, kHz	36.0	152
D_{JK}, kHz	1.96	152
$\nu_{\beta(0)}$, cm^{-1}, 0 → 1	64	153
$\nu_{\beta(0)}$, cm^{-1}, 0 → 2	267	153
$\nu_{\beta(i)}$, cm^{-1}	157	153
ν_σ, cm^{-1}	176	153
$\nu_{B(0)}$, cm^{-1}	666	25
$\beta_{B(i)}$, cm^{-1}	696	25
ν_s, cm^{-1}	3608	25

Concluding the discussion of microwave spectra of water complexes with halogen hydrides, note that the rotational spectrum of the H_2O...HF complex in the equilibrium gas phase at 250 K was first observed in the submillimeter region from 180 to 350 GHz with the RAD spectrometer.[154] Belov et al.[154] far increased the amount of the experimental data (including the data on the excited states of the complex) as compared to the results of Refs. 27–32 and 147–153, corrected the assignment of some spectral lines, and refined spectroscopic constants. The promise of studying the spectra of molecular complexes in the equilibrium gas phase, using the spectrometer with an acoustic detector, was demonstrated. This spectrometer has far higher sensitivity as compared to a microwave spectrometer with a Stark modulation.

Complexes of water with halogen hydrides have been also intensely studied by the method of matrix-isolation IR spectroscopy starting from Ref. 155, in which the H_2O...HCl complex in the nitrogen matrix was considered. Later on the complexes of water with HCl, HBr, and HI were studied in argon[66,156,157] and nitrogen[67,109] matrices (see Table 2). The H_2O...HF complex in the argon matrix has been studied thoroughly in Ref. 65. It was shown that halogen hydrides were proton donors in all cases. The complexes have a plane structure and rotate around the axis passing through the heavy atom. The strength of the H_2O...HX complexes decreases in the series X = F, Cl, Br, and I as is indicated by the value of the stretching band spectral shift (in cm^{-1}) of the HX molecule changing as follows: −364.5 (X = F), − 207.5 (X = Cl), − 163.5 (X = Br), − 89.0 (X = I).[158] In some cases, complexes with more compound constitution than 1:1 were observed in a matrix. This is especially typical for complexes of anhydrous hydrogen fluoride in the argon matrix.[65] Andrews and Johnson[65] detected complexes of the following formulations: $H_2O...(HF)_2$ of open structure, ordinary complex H_2O...HF, in which water serves as a proton donor (acid), and the so-called inverse complex HF...HOH, in which anhydrous hydrogen fluoride is a proton acceptor (base). The first complex, according to the data of Ref. 65, is more stable. The complex $(H_2O)_2...HF$ was not found because of the masking effect of strong absorption bands of water dimers.

The presence of a large number of reliable experimental data on complexes of water with halogen hydrides, especially on their structure in the gas phase, stimulated numerous quantum-chemical calculations of these parameters. Due to the high level of up-to-date quantum-chemistry methods, the results of such calculations often significantly complement the experimental data. As was already mentioned, Table 3 presents the main results on the structure and energy of water complexes considered in this paper. These results are borrowed from the papers published during the last 10–15 years, in which wide bases including diffusion and polarization functions were used, and the data on the energy of intermolecular interaction were presented with allowance for correlation of electron motion and the BSSE correction. It should be also noted that most cited papers present comprehensive data on vibrational spectra of complexes and other molecular properties that are not discussed here.

The complex $H_2O...HF$ has been most fully considered in the literature (see Table 3). In line with the available experimental data (see Tables 1 and 2), it was found that the equilibrium structure corresponds to the pyramidal C_s configuration of the complex, however the energy difference between this configuration and the plane one with the C_{2v} symmetry is so small that these two configurations can be treated equiprobable. The energy of formation of the complex determined in Refs. 107 and 110–112 occupies the intermediate place between the results obtained by the methods of vibrational[146] and rotational[27] spectroscopy. It should be noted that Szczesniak et al.[107] and Del Bene[108] ignored the BSSE correction in determination of the energy of formation of the complex. In Ref. 110, it is shown that this correction can markedly improve the agreement between the calculation and the experiment. Reference 159 is devoted to construction of *ab initio* dynamic models including several types of large-amplitude motions in weakly bounded complexes with participation of water molecules. With the $H_2O...HF$ complex as an example, the low-frequency shift $\Delta\nu$ of the vibrational band $\nu(HF)_{compl}$ relative to the band of the free molecule $\nu(HF)_{free}$ was studied using three model approaches:

1. 1D model of an independent harmonic oscillator HF ($\Delta\nu = 254$ cm^{-1}).
2. 1D model of an independent anharmonic oscillator HF ($\Delta\nu = 305$ cm^{-1}).
3. 2D model of an anharmonic oscillator HF interacting with the stretching intermolecular mode $H_2O...HF$ ($\Delta\nu = 306$ cm^{-1}).

The comparison with the experimental value $\Delta\nu = 354$ cm^{-1} (Ref. 146) points to the considerable contribution of anharmonic corrections to the value of the low-frequency shift $\Delta\nu$. Upon the analysis, the approaches (2) and (3) were recommended in Ref. 159 for studying spectroscopic characteristics of a wide variety of molecular complexes with water molecules under conditions of the actual atmosphere.

Interesting results for the clusters $(H_2O)_m...(HF)_n$ ($m, n \le 3$) were obtained in Refs. 113–116. The aim of Ref. 113 was to study the nature of the so-called inverse complex HF...HOH found, as was mentioned above, in the low-temperature matrix,[65] as well as the complex $(H_2O)_2...HF$, which Andrews and Johnson[65] failed to detect experimentally. Quantum-chemical calculations have shown that there are two conformations with energy minima separated by a low barrier for the complex of the composition 1:2. The complex of the composition 2:1 has only one stable configuration. It turned out that the experimentally observed vibrational frequency of 3915.5 cm^{-1} corresponding to the vibration of the H–F bond in the inverse complex cannot be assigned to any calculated energy minimum. Thus, the existence of the inverse complex, in which water serves as a proton donor, is an open question by now.

In more recent papers,[114–116] the complexes $(H_2O)_m...(HF)_n$ with $m \ne n = 1, 2$ and $m, n = 2, 3$ were systematically studied. For the complexes with $n, m = 1, 2$ the results were obtained that confirmed the existence of complexes of the composition 1:2 of both open and closed types, being identical in the interaction energies to the configurations obtained in Ref. 113. The complex of the composition 2:1, as in Ref. 113, has only one stable configuration of the closed (cyclic) type. For the complex with $n, m = 2$ the stable structure is the cyclic structure with the interaction energy $\Delta E = -32.67$ kcal·mol^{-1}. For the complexes with $n, m = 3$ the oligomeric structure with $\Delta E = -35.97$ kcal·mol^{-1} is preferable. The complexes with $n, m = 2, 3$ are characterized by the maximum deviation $\Delta\nu$ of the stretching frequency of the H–F bond as compared to the monomer HF: $\Delta\nu$ ($n, m = 2$) ~ 900 cm^{-1} and $\Delta\nu$ ($n, m = 3$) ~ 1000 cm^{-1}. In Refs. 114–116, the energy of vertical transitions $S_0 \to S_1$ in the complexes $(H_2O)_m ... (HF)_n$ with $m \ne n = 1, 2$ and $m, n = 2, 3$ was calculated. In these complexes, the excitation energy localizes on the O–H bond of one of H_2O molecules. This causes preservation of the Rydberg character of the $S_0 \to S_1$ transition and the photodissociation type of the absorption band corresponding to this transition.

Molecular characteristics of the complex $H_2O...HCl$ were calculated in Refs. 107–109, 117–119, and 160. A good agreement between the theory and experiment (rotational spectroscopy and IR spectroscopy in matrices) is observed for structural and spectral parameters. In Ref. 117, the geometry and energy for formation of clusters $(H_2O)_m...HCl$ ($m = 1$–3) were calculated. It has been shown that the cluster has the shape of a ring with hydrogen bonds, and the HCl molecule is a proton donor. It is significant that the length of the H–Cl bond increases and the stretching band of HCl markedly shifts toward longer waves, as the size of the cluster increases. The energy of separation of the HCl molecule from the cluster is markedly higher in the case of trimer and tetramer in accordance with the effect of cooperativity of the hydrogen bond. In Ref. 107, some differences between complexes of the HF and HCl molecules with water were found; these differences are demonstrated in Table 3.

The HF molecule has a larger dipole moment as compared to the HCl molecule, therefore the contribution of electrostatic interaction to the energy of the hydrogen bond based on HF is larger. At the same time, the complex $H_2O...HF$ is almost twice as strong as the complex $H_2O...HCl$. The contribution of the electron correlation to the energy of the former complex is markedly smaller (about 2% of the total energy) because of the less polarizability of the HF molecule (lower energy of dispersion interaction). For the $H_2O...HCl$ complex, the contribution of electron correlation achieves 25%. In Ref. 117, comparison of the structure, energy, and vibrational properties of the complexes of halogen hydrides was extended to the HBr and HI molecules. As is seen from Table 1, the energy of the complexes decreases at passing down in the group, however the C_s symmetry found experimentally and theoretically for the complexes with participation of HF and HCl keeps for their structural analogs as well. The disadvantage of the data obtained in Ref. 117 is that the correlation energy, whose role must increase sharply when passing from elements of the 3rd period to elements of the 4th and 5th periods, was neglected in calculation of the molecular properties of the complexes.

Recently, in Refs. 118 and 119, it was shown that the molecular complexes $(H_2O)_m...(HCl)_n$ of the composition 1:2 had two conformations corresponding to the energy minimum: as an open and closed structure with the interaction energy $\Delta E = -8.5$ kcal · mol^{-1} and -7.64 kcal·mol^{-1}, respectively. The closed structure with the interaction energy $\Delta E = 11.1$ kcal·mol^{-1} corresponds to the complex with two water molecules of the composition 2:1. For the corresponding complexes with the stronger hydrogen bond $(H_2O)_m...(HF)_n$, the interaction energies have the values -14.79, -21.16, and -20.24 kcal·mol^{-1}. For these complexes the closed (or cyclic) structures are more stable. With 1:2 complexes of water with hydrogen chloride used as an example, it was demonstrated that cyclic structures not always were more stable.

The structure of more compound complexes, such as $H_2O...(HCl)_n$ ($n = 1$–5) was studied in Ref. 161. It was shown that the structure with $n = 1$–3 not accompanied by transport of a proton was the most stable. Calculated IR spectra of the complex $H_2O...(HCl)_n$ point to the significant longwave shift of stretching bands of the O–H (more than 600 cm^{-1}) and H–Cl (313 cm^{-1}) groups.

2.2. Complexes with halogens and some halogen-containing molecules

Complexes of water with halogens and halogen-containing molecules were studied experimentally by the methods of microwave spectroscopy and matrix-isolation IR spectroscopy. In Ref. 33, the force constants and the geometry of the $H_2O...F_2$ complex of the donor-acceptor type were determined from analysis of the rotational spectrum of the mixture of fluorine and water vapor. It was found that this complex can exist in two configurations: plane (symmetry C_{2v}) and pyramidal (symmetry C_s), and the latter is preferable from the energy point of view. Judging from the value of the force constant k_s (see Table 1), this complex is far less strong than the complex $H_2O...HF$ considered earlier. In Ref. 34, the complex of water with chlorine monofluoride was studied by the method of rotational spectroscopy. This complex also has the donor-acceptor nature, and the molecule ClF is oriented by the chlorine atom to the oxygen atom of the water molecule. Its geometry is similar to the geometry of the complex $H_2O...F_2$, and the strengths, judging from the value of k_s, is somewhat higher, although being lower than that of the complex $H_2O...HF$.

The photochemical reaction between H_2O and F_2 was studied for the first time by Noble and Pimentel by the method of matrix isolation in Ref. 162. In this work, formation of the HOF acid in the complex with HF was proved. The complex $H_2O...F_2$ and the complexes HF...HOF, HO...HF, and FO...HF produced as a result of photochemical transformations were studied in Ref. 70. The complex $H_2O...F_2$ is formed at joint deposition of components in the Ar matrix. Narrow bands centered at 3745.6 and 3717.6 cm^{-1} and lying within the rotational-vibrational band ν_3 of the isolated water molecule at 3756.4 and 3711.5 cm^{-1}, narrow perturbed band of the F_2 molecule centered at 877.5 cm^{-1}, as well as intense bands of symmetric vibrations at 3638.0 and 1590.0 cm^{-1} lying near the corresponding water fundamental bands (most intense bands are presented in Table 2) were assigned to this complex. The wide bands centered near 3727 and 3567 cm^{-1} were assigned to the complex $(H_2O)_2...F_2$. The discovered complex may have both the H-bonded structure $HOH...F_2$ and the donor-acceptor structure $H_2O...F_2$. Comparing the experimentally observed shifts of the bands with the results of quantum-chemical calculations, McInnnis and Andrews[70] concluded that the second structure of the complex is more probable. The water molecule in the complex rotates at least around one axis. The complexes between the radicals FH...OH that are formed at photolysis of the matrix containing water and fluoride were characterized in detail as well.

In Ref. 71, the method of IR spectroscopy in the Ar matrix was applied to the study of the complexes Cl_2, ClOCl, OClO, and HOCl, as well as their photochemistry. The complexes of molecular chlorine with water were also studied in the nitrogen and argon matrices.[163,164] The interest to this problem appeared in connection with the intense study of chemistry of chlorine compounds on the surface of solid particles of stratospheric clouds in the polar zone and their role in development of ozone holes.[165] During the polar winter, $ClONO_2$, in the form of which chlorine is largely contained in the atmosphere, hydrolyzes fast on the surface of the solid particles mentioned above with formation of HOCl (Ref. 166):

$$ClONO_2\ (gas) + HOH\ (solid) \rightarrow HOCl + HNO_3. \quad (10)$$

In spring, the Antarctica receives enough sunlight for HOCl photolysis[165] resulting in formation of atomic chlorine

$$HOCl\ (gas) + h\nu \rightarrow OH\ (gas) + Cl\ (gas). \quad (11)$$

The latter, in its turn, serves as a catalyst for ozone destruction. Hydrolysis of $ClONO_2$ in the gas phase is very slow; therefore, the heterophase reaction (10) makes the largest contribution to formation of the ozone hole in the Antarctica in spring.

The study of matrix IR spectra has shown that the molecules Cl_2, ClOCl, and OClO form donor-acceptor complexes with the water molecule. In these complexes, water gives an unshared electron pair to the nearest chlorine atom.[71,164] The structure of the complex $H_2O...Cl_2$ was studied by the method of rotational spectroscopy in Ref. 167. Three heavy atoms in this complex lie along a straight line, and the axis of the C_2 symmetry of the water molecule makes a nonzero angle with this line. The inversion barrier is low, therefore the complex $H_2O...Cl_2$ has the effective symmetry C_{2v}. This allows the complex to rotate around the C_2 axis in argon matrix.[164] Once the complex $H_2O...Cl_2$ is exposed to near UV radiation, the complex HOCl...HCl with H-bond is formed,[71] and the molecule of hydrogen chloride becomes now the proton donor. However, in contrast to the system $H_2O...F_2$ (Ref. 70), the quantum yield of the complex HOCl...HCl is many times lower than that of the complex HOF...HF, and it is not formed at all in the nitrogen matrix. The complex $(HCl)_2...O_2$ is a photochemical product of the complex ClOCl with water, and the complex $H_2O...ClO_2$ under the exposure to UV radiation gives the complex H_2O...ClOO. The HOCl molecule also forms a complex with water serving as a proton donor.

Ab initio calculation of the complex of hypochlorous acid with water is considered in Refs. 121 and 168. It has been found that two conformers correspond to this complex, and in the both cases the molecule HOCl serves as a proton donor. The calculated shifts of vibrational bands of the monomer at formation of the complex agree well with experimental data for low-temperature matrix.[71]

In Ref. 169, the complex of water with chlorine monofluoride was studied by the method of rotational spectroscopy. It was proposed that this complex had a plane or effectively plane structure, and the oxygen atom of the water molecule was connected with the chlorine atom of the molecule ClF (H_2O...ClF). The quantum-chemical calculations[120] point to formation of a pyramidal complex with the C_s symmetry in the gas phase. The plane complex H_2O...ClF is a transient structure. The transition from the pyramidal structure to the plane configuration is practically free of the energy barrier. The energy of the complex H_2O...ClF is about 4 $kcal \cdot mol^{-1}$. Another possible complex HOH...FCl with the H-bond is much less stable (the energy of its formation is 0.68 $kcal \cdot mol^{-1}$).

2.3. Complexes with volatile inorganic fluorides (SiF_4, GeF_4, BF_3, PF_3)

Due to extensive use of various fluoride technologies, the atmosphere is polluted with volatile inorganic fluorides. For example, production of superphosphate emits a great amount of fluorides in the gas phase, mostly, in the form of silicon tetrafluoride – one of the main potential industrial sources of fluorine.[170] The complex $SiF_4...H_2O$ of the 1:1 composition was first identified by the method of IR spectroscopy in the Ar matrix.[68]

Based on the linear correlation between the position of the intense stretching vibrational band of the Si–F bond in the region of 960–990 cm^{-1} and closeness of eight oxygen- and nitrogen-containing bases (including water) to proton, it was concluded that this complex falls in the category of donor-acceptor complexes. The complex $GeF_4...H_2O$ has the similar structure.[171] However, judging from the degree of perturbation of the corresponding vibrational bands, this complex is stronger than the complex $SiF_4...H_2O$. In the opinion of Walther and Ault,[171] this is connected with the fact that the germanium atom has more diffuse *d*-orbitals as compared to the silicon atom. As a result, the effect of $d_\pi - p_\pi$ interaction between occupied *p*-orbitals of fluorine atoms and unoccupied *d*-orbitals of silicon atom decreases when passing from Si to Ge. As a consequence, the capability of the *d*-orbitals of the latter to acceptance of electronic density from the oxygen atom of water increases.

The structure, nature of the chemical bond, and energy of the complex $SiF_4...H_2O$ were analyzed in Refs. 122 and 123 by quantum-chemistry methods. It was shown that the complex of the 1:1 composition is stable under standard conditions ($\Delta H = -1.4\ kcal \cdot mol^{-1}$). The complex has the C_s symmetry with the intermolecular bond Si...O. At the same time, the *s*- and *p*-orbitals, rather than *d*-orbitals of silicon play the major role in formation of the complex, although the degree of charge transfer is insignificant. Thus, the complex is formed most likely due to electrostatic, rather than donor-acceptor interaction between molecules. The structure and binding energy of the complex $2SiF_4...H_2O$, having a sole conformation, as well as the complex $SiF_4...2H_2O$, which is stable in two conformations, were calculated. It is interesting to note that the latter complex is characterized by significant transfer of the electronic density from the water molecule to the molecule of silicon tetrafluoride, and the decisive role in formation of the donor-acceptor bond between the components is played by *d*-orbitals of the silicon atom.

The complex $BF_3...H_2O$ was studied by the method of IR spectroscopy in the nitrogen matrix[69] (see Table 2), as well as with quantum-chemical calculations, but in a limited basis. It was shown that the complex of the 1:1 composition has the same C_s symmetry, as the complex $SiF_4...H_2O$, but the typical donor-acceptor nature.

The complex $PF_3...H_2O$ was studied experimentally by the method of rotational spectroscopy in molecular beams and theoretically in a limited $6-31G^*$ basis[35] (see Table 1). The experimental results suggest that, by analogy with the water complexes with fluorides considered above, this complex also has the C_s symmetry, and its configuration with the intermolecular hydrogen bond is unstable.

2.4. Complexes with inorganic acids (H_2SO_4, HNO_3, HCN)

Sulfuric and nitric acids are important trace gases in the atmosphere. The interest to properties of gaseous sulfuric acid is caused mostly by its role in formation of aerosol and acid rains, i.e., precipitation having pH lower than 5.6 (pH = 5.6 is maintained as a result of equilibrium between water and atmospheric CO_2). The mechanism of formation of H_2SO_4 in the atmosphere involves the fast reaction of SO_3 with H_2O in the gas phase or on the surface of aerosol particles, likely, through formation of the complex $SO_3...H_2O$ (Ref. 172). However, quantum-chemical calculations give the high energetic barrier ($\cong 19$ kcal·mol^{-1}) for formation of sulfuric acid from bimolecular adduct. Therefore, it was proposed[173] that H_2SO_4 is formed through the intermediate trimolecular cyclic complex $(H_2O)_2...SO_3$.

The IR spectra of the vapor of concentrated sulfuric acid in the argon matrix were studied in Ref. 72. Free molecules of H_2O, SO_3, and H_2SO_4, as well as complexes containing H_2O and H_2SO_4 were detected. The complexes $(H_2O)_n...(SO_3)_n$ were not found. The temperature dependence of the complex $H_2O...H_2SO_4$ indicates its reversibility, as well as the fact that the most stable configuration of this complex is the configuration with the open chain $H_2O...HO-SO_2-OH$. More compound complexes $(H_2O)_2...(H_2SO_4)$ were also found; sulfuric acid in them plays the role of a proton donor only with respect to one water molecule: $H_2O...H_2O...HO-SO_2-OH$.

The role of nitric acid in the atmosphere is important as well. This acid is in equilibrium with the oxides NO and NO_2, whose concentration affects the degree of catalytic binding of stratospheric ozone.[10,174] The effect of formation of the complex of HNO_3 with water on atmospheric chemistry of nitric acid was studied theoretically in Ref. 175. It has been shown (see Table 1) that the complex $H_2O...HNO_3$, having a ring structure with the strong H-bond between the OH-group of nitric acid and oxygen of the water molecule, is stronger than the water dimer (−9.5 vs. −4.7 kcal·mol^{-1} for the same basis as in Table 3). The equilibrium constant of formation of the complex $H_2O ... HNO_3$ was calculated in this work as well. It turned out that, in spite of relatively high strength, the fraction of the complexes near the ground did not exceed 1% and decreased fast with height because of the sharp decrease of the water concentration. For example, if in the lower stratospheric layers $T \approx 200$ K, $K_p = 240$ atm^{-1}, and $P_{H_2O} \approx 5 \cdot 10^{-7}$ atm, then the fraction of the complexes is only 10^{-4}. This value is roughly 10^2 times higher than the fraction of water dimers in the lower atmospheric layers. A possible consequence of complexes of nitric acid with water presence in the stratosphere may be the red shift of the UV spectrum of HNO_3; this would lead to the increase in the rate of photolysis of the acid. However, in the opinion of Fu-Ming Tao et al.,[175] this is unlikely.

Hydrocyanic acid HCN forms rather strong H-bonds with different proton acceptors.[38] The dimer $H_2O...HCN$, in which the acid is a proton donor, was studied by the methods of rotational spectroscopy in Refs. 37–40, as well as the trimers $(H_2O...HCN)...Ar$. The values of the force constant of the complex (see Table 1) and the energy of intermolecular interaction (see Table 3) are indicative of its considerable strength as compared to other considered complexes.

2.5. Complexes with inorganic hydrides of elements of the V and VI groups (NH_3, PH_3, AsH_3, H_2S, H_2Se)

Among this class of substances, of greatest interest for atmospheric chemistry are ammonia and hydrogen sulfide. Other hydrides can be in trace concentrations in the atmosphere of specialized rooms intended, for example, for production of semiconductor epitaxial structures of the $A^{III}B^{V}$ type and optical materials by chemical deposition from the vapor phase (CVD technology).

The structure of the complex $H_2O...NH_3$ was studied for the first time by the method of rotational spectroscopy in Refs. 37 and 176. It has been found that this complex has a linear hydrogen bond with the O–N distance of 2.98 Å (see Table 1), and water is a proton donor. Numerous further studies of the complexes of ammonia with various molecules have shown that NH_3 exhibits almost exclusively proton-acceptor properties, i.e., it is a base.[177] The microwave and far IR spectra (36–86 and 520–800 GHz, respectively) of the complex water-ammonia were studied in Ref. 178. Almost free rotation of the NH_3 molecule in the complex with the barrier of (10.5 ± 5.0) cm^{-1} was observed, as well as the tunneling effect of H_2O leading to the exchange of two protons in the water molecule with the barrier of 700 cm^{-1}. Fine spectral effects in the region of inversion vibrations of NH_3 centered at 1021 cm^{-1} were studied with a specialized IR spectrometer in Ref. 179. In the opinion of Fraser and Suenram,[179] the observed set of vibrationally averaged rotational constants is best described by the presence of a “bent” hydrogen bond in the complex (deviation of 10 ° from a straight line). It is also found that the binding energy in this complex must be no less than 1021 cm^{-1} (0.35 kcal·mol^{-1}), i.e., the frequency of the CO_2 laser used in the spectrometer.

The complex $H_2O...NH_3$ in low-temperature matrices was studied by the method of IR spectroscopy in the regions of 4000–300 cm^{-1} (Ref. 74) and 4000–10 cm^{-1} (Ref. 73). The results obtained in Refs. 73 and 74 indicate that water is the proton donor in this complex. As is seen from the data of Table 2, the longwave shift $\Delta\nu_{OH}$ of the bands ν_1 and ν_2 of water in the complex $H_2O...NH_3$ relative to the corresponding values for free water is the largest among all complexes and almost twice as large as that of water dimer.[180] Based on the almost linear dependence between the enthalpy of complex formation ΔH_f and the value of $\Delta\nu_{OH}$ for a series of proton acceptors at the same proton donor,[181] we can suppose that ΔH_f for this complex is roughly twice as large as that for the water dimer, i.e., (-5.2 ± 1.5) kcal·mol^{-1} (Ref. 182). In Ref. 73, the emphasis was on the analysis of low-frequency bands of intermolecular vibrations in the complex. For example, the band at 19.5 cm^{-1} was assigned to the torsion vibration of the linearly (N...H–O) hydrogen-bonded water molecule around the symmetry axis of the complex, whereas the ammonia molecule was considered motionless relative to the matrix. Stockman et al.,[178] taking into account the results of microwave and IR spectroscopic studies of this complex in the gas phase, assigned this band to rotational-tunneling transitions of water between 20 and 22 cm^{-1}.

Among the theoretical papers describing the structure, rotational-vibrational spectrum, and energy of the complex $H_2O...NH_3$, Ref. 126 should be noted first. The calculated geometry of the complex agrees well with the experimental data.[126] Its hydrogen bond is almost linear, and the geometry of subsystems is almost unchanged when passing from the free state to the bounded one. The electronic binding energy is roughly equal to 6 kcal·mol^{-1}, and the enthalpy of formation at 298 K is equal to −4.2 kcal·mol^{-1}. These values are far from the values predicted in Ref. 182. The vibrational spectrum of the complex was calculated as well. It has all features of the spectrum of systems with the intermolecular hydrogen bond. The quantum-chemistry study of the potential surface of the complex $H_2O...NH_3$ and its vibrational spectrum was undertaken in Refs. 125 and 183–186 as well.

Complexes of hydrides of the elements of the VA group from lower periods (PH_3, AsH_3) with water in the gas phase are poorly known. In Ref. 100, the comparative calculation of the structure and energy of the complexes $H_2O...NH_3$ and $H_2O...PH_3$ was carried out (see Table 3). As is seen, the strength of the complex with participation of phosphine is several times lower than that of the complex with ammonia.

Before discussing the complexes of water with hydrides of elements of the VIA group, note that water dimers $(H_2O)_2$, whose role in the extinction of far IR radiation was already mentioned in Introduction, formally fall in this group. Because of great significance of these particles for many fields of chemistry, molecular physics, biology, and other sciences, the number of papers devoted to experimental and theoretical study of the properties of dimers is very large (see, for example, Refs. 17, 75, 187, and 188 and references therein). Therefore, here we omit considering the structure and properties of $(H_2O)_2$ in detail. We only note that, according to rather reliable thermochemical, spectroscopic, and quantum-chemistry data,[17,187] water dimer is a strong complex (among the weak complexes under consideration): $K_p = 0.011$ atm^{-1}, $\Delta G^0 = 3.34$ kcal·mol^{-1}, $\Delta H^0 = -3.63$ kcal · mol^{-1}, $\Delta S^0 = -18.61$ e.u. This is also indicated by the value of the force constant of the intermolecular hydrogen bond in the dimer (see Table 1). Therefore, even taking into account the sharp decrease of the concentration of water with height [its content in the stratosphere is estimated as 10^{-3}–10^{-4}% mass (Ref. 145)], water dimers can play a certain role in the total extinction of IR radiation.

The number of experimental and theoretical papers devoted to study of complexes of inorganic hydrides of VIA elements of the 3rd and 4th periods with water is limited. The complex $H_2O...H_2S$ was studied only in low-temperature matrices (see Table 2) in Refs. 189 and 190. It turned out that there are two types of complexes: HOH ... SH_2 and H_2O ... HSH in the argon matrix. In the more polar nitrogen matrix, the complexes of the second type, in which hydrogen sulfide is a proton donor, prevail. Spectral bands that can be assigned to the complexes $2H_2O$ ... H_2S were recorded as well. The question, which of subsystems in the complex H_2O ... H_2S exhibits mostly proton-donor properties, and which one exhibits proton-acceptor properties was considered in a number of theoretical works (see, for example, Refs. 100, 127, 191, and 192). In Refs. 100–192, the structure of $H_2O...HSH$ was found to be a little more stable, but the use of the maximally wide basis, allowance for the correlation energy by the MP4SDQ method, and the BSSE correction gave just the opposite result.[127] Recently, in Ref. 193, equilibrium geometries and harmonic vibrational frequencies of the complexes $H_2S...(H_2O)_n$ ($n = 5, 7$) were calculated. The data obtained show that formation of mixed clusters is accompanied by significant changes in the structure and spectra of the complexes.

We know only one paper, in which the structure and energy characteristics of the complex $H_2O...H_2Se$ along with the complex of hydrogen sulfide were studied theoretically by the method of pseudopotential.[192] No significant differences in the structure and energy of the both complexes (with water as a proton acceptor) were found. Note in conclusion that the relative strength of the intermolecular hydrogen bonds, formed by water with the molecules of hydrides of PH_3, AsH_3, H_2S, and H_2Se, was studied using IR spectra of its solutions in these hydrides at the room temperature and increased pressure (in the liquid phase).[26] According to these data, the strength of the bonds $HOH...XH_3(XH_2)$ changes as:

$$HOH...SH_2 > HOH...SeH_2 >$$

$$> HOH...PH_3 > HOH...AsH_3.$$

2.6. Complexes with some small molecules (O_2, O_3, N_2, CO, CO_2, NO, N_2O, SO_2, SO_3, H_2O_2, Ar, H_2)

Molecules listed in the title of this section fall in the categories of both major (O_2, N_2, CO_2) and minor (CO, O_3, NO, N_2O) gaseous constituents of the atmosphere, as well as pollutants of various (including anthropogenic) origin.

In Ref. 194, nitrogen broadening of lines in the IR spectrum of water vapor was studied experimentally. It was shown that excessive, relative to H_2O monomers, absorption was clearly observed in limited spectral intervals. The absorption has a character of continuum, and the absorption coefficient depends linearly on the pressure of water vapor. In Ref. 15, this absorption was proposed to be associated with formation of the complex $H_2O...N_2$. Using the data on the structure and energy of the complex obtained in the simple $6-31G^*$ basis neglecting the correlation energy,[195] Vigasin and Chlenova[15] calculated the envelope of the spectrum of low-frequency intermolecular vibrations of the complex $H_2O...N_2$. It turned out that the linear (with respect to the pressure of water vapor) part of the excessive absorption of water vapor in the mixture with nitrogen in the far IR spectral region could actually be connected with the complexes mentioned above, whose concentration was $\approx 10^{-5}$ mole fractions with respect to nitrogen. Then the energy, structure, and vibrational spectrum of the complex of water with nitrogen were calculated in wide bases with allowance for all possible corrections in Refs. 128–130 and 196 (see Table 3). Experimentally this complex was studied by the method of rotational spectroscopy in Ref. 44 (see Table 1). According to these data, the complex has the almost linear hydrogen bond with the energy about 1 kcal·mol^{-1}.

Molecular complexes of water with the second, in significance, component of the atmosphere – oxygen (mass content of 23.1%) are poorly known. We fail to find any experimental data on this complex. In one of the first theoretical papers (Ref. 197), the analytical potential of intermolecular interaction in this system was drawn based on calculations in the $6-31G^*$ basis. The stable structure (with the binding energy ≤ 1 kcal·mol^{-1}) corresponds to the hydrogen-bonded complex $HOH...O_2$, and the depth of the potential well almost halves when passing from the complex with nitrogen to the complex with oxygen.

In Ref. 131, it was found that the most stable structure among five possible configurations of the complex is the structure corresponding to the donor-acceptor interaction with the C_{2v} symmetry and the binding energy of -0.86 kcal·mol^{-1} (see Table 3).

The complex with participation of carbon monoxide being an isoelectronic analog of the nitrogen molecule was studied thoroughly both experimentally and theoretically. For the first time, the complex $H_2O...CO$ was experimentally identified by the method of IR spectroscopy in the argon matrix[80] from the band of 2148.8 cm^{-1}. In Ref. 81, formation of the complex $H_2O...CO$ was studied at joint deposition of CO and H_2O in the mixture with oxygen. In this experiment, because of the low ratio of the matrix gas to the studied substance, formation of aggregates with bifurcation rather than a linear structure was observed in the spectrum. In Refs. 82 and 83, the experiment also was conducted in the oxygen matrix, but the complex was produced by photooxidation of the initial substance – formaldehyde. Two types of the complex: HO–H...CO and HO–H...OC were observed. Finally, in Refs. 84 and 198, the complex $H_2O...CO$ was studied in the nitrogen matrix. The complex in the gas phase was studied by the methods of microwave spectroscopy and laser spectroscopy with the use of tunable far IR lasers.[48,49] In Ref. 49, the spectroscopic constants of the complex were determined using the technique of electroresonance spectroscopy of a molecular beam. The hydrogen bond HO–H...CO differed from the linear one by 11.5°, and the equilibrium H...C distance was 2.41 Å (see Table 1). The effect of tunneling between the free and weakly bounded states of the hydrogen atom in the water molecule was studied in Refs. 48 and 49; the barrier of this effect was found to be ≈ 0.6 kcal·mol^{-1}.

Quantum-chemical calculations of the complex by different methods in qualitatively different bases were performed in Refs. 130, 196, and 199–205. We note here only some of these results (Table 3 presents the data from two papers). In Ref. 130, the potential energy surface of the complex was calculated. Seven possible structures of the complex were revealed; among them, only two linear structures – HO–H ... CO and HO–H ... O–C – had no imaginary vibrational frequencies, i.e., were stable. Their energies were found to be equal to 1.34 and 0.63 kcal·mol^{-1}. In Ref. 200, this complex was studied by the method of molecular mechanics for clusters. The electrostatic model pointed to a somewhat higher stability of the structure HO–H...OC. Similar calculations in wide dispersion-optimized bases were carried out in Refs. 196 and 201. The results of these calculations showed that they did not reconstruct the difference of 11.5° from the linear

H-bond in the configuration HO–H...CO that was found experimentally. This fact is explained in Ref. 201 by anisotropy of the complex.

The structure, energy, and vibrational spectrum of the complex $H_2O...CO$ were calculated by perturbation theory method using the supermolecule approach with more than 20 bases of different complexity.[133,204] The contributions to the total energy of intermolecular interaction were determined for the both stable structures HO–H...CO and HO–H...OC (the former is more stable), and the BSSE correction was analyzed for different bases. In Ref. 205, the method of molecular mechanics was involved in the analysis of vibrational band shift of the C–O bond at the complex formation. The clusters $H_2O...2(CO)$ were studied theoretically in Refs. 202 and 203 and experimentally by the microwave spectroscopy method in Ref. 50. The calculated results are indicative of the existence of two stable H-bonded structures of the cluster. At the same time, it follows from the experimental results that the trimer has a cyclic structure.

The complex $H_2O...CO_2$ was studied experimentally by the methods of microwave spectroscopy[51] and matrix-isolation IR spectroscopy.[85] The results obtained by the both spectroscopic methods suggest that the complex does not belong to the type of H-bonded complexes, and its plane structure is due to interaction of the unshared electron pair of the oxygen atom with unoccupied $2\pi_u$-orbitals of the CO_2 molecule. This conclusion is confirmed by quantum-chemical calculations,[135,137,138,206] and the results of studying this complex by the methods of IR spectroscopy with optothermal detection in a supersonic jet.[135] In Ref. 135, it was noted that molecules in this complex experienced inner rotation with the barrier of 0.97 kcal·mol^{-1}. Thermodynamics of the process of the complex $H_2O...CO_2$ formation under standard conditions in the gas phase was calculated in Ref. 136 by the quantum chemistry and statistical physics methods (so-called theory of existence of clusters): $K_p = 0.007$ atm^{-1}, $\Delta G = 2.89$ kcal·mol^{-1}, $\Delta H = -2.91$ kcal·mol^{-1}, $\Delta S = -19.45$ e.u. These results somewhat differ from the experimental results obtained in Ref. 207 at determination of the second virial coefficient of the mixture of water with compressed CO_2 [$K_p = 0.008$ atm^{-1}, $\Delta H^0 = (-4.8 \pm 0.4)$ kcal·mol^{-1}, $\Delta S^0 = (-25.9 \pm 25.9)$ e.u]. The data of Table 3 indicate that the complex of water with CO_2 is somewhat stronger than the complex $H_2O...CO$.

The study of weak complexes $H_2O...SO_2$ and $H_2O...SO_3$ is interesting in connection with the already mentioned problem of acid rains. Sulfur dioxide coming to the atmosphere is mostly of anthropogenic origin.[1] In the process of further chemical transformations, sulfur dioxide transforms into SO_3 that, being dissolved, gives H_2SO_4. The IR absorption spectrum of the complex $H_2O...SO_2$ in a matrix was first studied in Ref. 76 (see Table 2). It has been concluded in this paper that the absorption bands assigned to the water molecule in the complex are close to those in the water molecule playing the role of proton acceptor in the dimer $(H_2O)_2$. This gave the grounds to Schriver et al.[76] to assume that the oxygen atom of the water molecule is an electron donor, and the SO_2 molecule is an electron acceptor, i.e., the complex has a T-shaped configuration similar to the configuration of the complex $H_2O...CO_2$. The analysis of the force field of the complex has shown that the OH and SO groups are equivalent and both subsystems keep the local C_{2v} symmetry. Similar conclusions on the structure of the complex were drawn based on the study of its rotational spectrum.[41] Thermodynamics of the complex $H_2O...SO_2$ of the donor-acceptor type (the oxygen atom of the water molecule is the donor of electronic density) was calculated in Ref. 140: $\Delta H^0 = -1.8$ kcal·mol^{-1}, $K_p = 1.29 \cdot 10^{-4}$ atm^{-1}. The low binding energy is indicative, as is believed in Ref. 140, of the insignificant role of this complex in atmospheric processes. The calculated vibrational and rotational frequencies agree well with the experimental data.[41]

The complex $H_2O...SO_3$ in the neon matrix was studied by the method of IR spectroscopy in Refs. 77 and 78. Unlike Ref. 173 cited above, formation of the associate of 1:1 composition was detected in these papers, and this associate did not regroup into H_2SO_4 at the temperature of 5 K in the neon matrix. At large amount of water, the clusters $H_2SO_4...nH_2O$ were detected. It was assumed that, in contrast to the single water molecule, two H_2O molecules reacted intensely with SO_3 with formation of hydrated sulfuric acid. This assumption is supported, to some degree, by the results of quantum-chemical calculations of the gas-phase reaction $SO_3 + H_2O$ (Ref. 139).

Complexes of water with nitrogen oxides are also of interest in connection with the problem of acid rains. However, they are much more poorly studied as compared to sulfur oxides. We know only two experimental works devoted to these complexes. In Ref. 42, the structure of the complex $H_2O...N_2O$ was studied by the rotational spectroscopy method (this complex has a T-shaped configuration without formation of H-bond similarly to the complexes $H_2O...CO_2$ and $H_2O...SO_2$, see Table 1) and the complex $H_2O...NO$ was studied by the method of IR spectroscopy in the nitrogen matrix. However, in the latter case, the IR absorption spectrum was very complex because of formation of nitrogen oxide dimers, and no conclusions on the structure of the complex were drawn. The quantum-chemical calculation of the complex $H_2O...N_2O$ was carried out in Ref. 134, and its results confirmed the structure described in Ref. 42. The measurements of the second virial coefficient of the mixture of H_2O with compressed N_2O have shown that reversible aquation of the nitrogen oxide takes place here, just as in the case of the H_2O mixture with CO_2 (Ref. 207). The thermodynamic functions of the complex $H_2O...N_2O$ reconstructed from these data under standard conditions are the following: $K_p = 0.006$ atm^{-1}, $\Delta H^0 = (-3.5 \pm 0.5)$ kcal·mol^{-1}, $\Delta S^0 = (-21.6 \pm 1.4)$ e.u.

Ozone and, to a lesser degree, hydrogen peroxide play an important role in complex chemical and photochemical transformations in the atmosphere.

The complex $H_2O...O_3$ was studied by the rotational spectroscopy method in Ref. 43 (see Table 1). It has been found that this complex is characterized by almost free rotation of the H_2O molecule, although, judging from the value of its force constant, its strength is comparable with the strength of the complexes of water with CO, CO_2, and SO_2. This conclusion is supported by the quantum-chemical calculations,[132] whence it follows that the complex $H_2O...O_3$ with the C_s symmetry has a close-to-linear H-bond with the energy about -3 kcal·mol^{-1}.

The detailed calculation of the structure, vibrational spectrum, and energy of the complex of water with hydrogen peroxide was made in Ref. 132. This complex has a cyclic structure with two hydrogen bonds and relatively high binding energy of -6.4 kcal·mol^{-1} (see Table 3).

Argon also can be classified as a major atmospheric constituent (1.286% mass). In spite of *a priori* very weak interaction between the monoatomic molecule of this inert gas and the water molecule, the complex $H_2O...Ar$ as a model of the system with the so-called hydrophobic interaction was studied rather thoroughly both theoretically and experimentally. Table 1 presents the results of the study by the rotational spectroscopy and far IR diode laser spectroscopy methods.[45–47] Some papers were devoted to calculation of the potential surface of the complex $H_2O...Ar$ (Refs. 46 and 208–212). The common conclusion is the following. The complex has a plane geometry with a slightly nonlinear hydrogen bond. The geometry with the Ar atom in the molecular plane is energetically more profitable than the off-plane structure. The rotation barriers in the plane are 26.29 cm^{-1} [$Ar...H_2O$] at $R = 3.702$ Å and 17.18 cm^{-1} at $R = 3.518$ Å [$Ar...OH_2$]. The hydrogen-bonded orientation Ar...HOH is 3.4 cm^{-1} less stable and requires the length of the Van der Waals bond to be increased up to $R = 3.70$ Å. The geometry without the hydrogen bond ($Ar...OH_2$) is 11.1 cm^{-1} higher than the global minimum, and it is characterized by significantly shorter bond length $R = 3.460$ Å. The global minimum corresponds to 142.98 cm^{-1} (0.41 kcal · mol^{-1}) at $R = 3.636$ Å according to the data of Ref. 46, or 130.2 cm^{-1} (0.37 kcal · mol^{-1}) at $R = 3.603$ Å according to Ref. 210.

The mechanisms of intermolecular interaction in the system H_2O/H_2 were studied experimentally by the methods of scattering of a molecular beam,[213] IR spectroscopy in the argon matrix,[214] spectroscopy of vibrational predissociation[215] of the complexes $(H_3O^+)(H_2O)_n(H_2)$, and rotational spectroscopy of hydrogen in liquid water.[216] Quantum-chemical calculations of the complex $H_2O...H_2$ were performed in Refs. 217 and 218. According to the results of these papers, the molecule H_2 in interaction with the molecule H_2O can play the roles of both proton donor and acceptor. In the configuration with the minimum of energy (-0.56 kcal·mol^{-1}), H_2 is oriented to the oxygen atom of water collinearly with the C_2 axis of the molecule H_2O. In the second attraction region with the minimum of -0.53 kcal·mol^{-1}, the molecule H_2 forms a T-shaped structure with the O–H bond of the water molecule (the axis H_2 is normal to the plane of H_2O). The potential energy surface of the complex has high anisotropy because of the large contribution of the electrostatic component to the total interaction energy.

2.7. Complexes with some hydrocarbons (CH_4, C_2H_2, C_2H_4, C_3H_6, C_3H_8, H_2CO, CH_3F, CH_2F_2, CHF_3, C_6H_6)

Among minor tropospheric constituents of hydrocarbon origin, the most important is methane produced at the ground level in anaerobic decay of organic substances. The complex $H_2O...CH_4$ was studied by the method of microwave spectroscopy[52] and far IR diode laser spectroscopy[219] (see Table 1). According to these data, methane is a proton acceptor relative to water. Judging from the value of the force constant of the intermolecular bond, this complex in its strength occupies the intermediate position between $H_2O...CO$ and $H_2O...Ar$. The results of quantum-chemical calculation of the complex $H_2O...CH_4$ are contradictory. Thus, in Ref. 220, it was found that according to the experimental data, its configuration with the intermolecular bond C...H–O is just more stable (by 0.2 kcal·mol^{-1}). To the contrary, in Refs. 142 and 221, as well as in more recent Ref. 222, it was shown that the only stable structure of the complex is realized in the hydrogen bond C–H...O. Our analysis has shown that the question on stability of the both configurations remains open and additional studies are needed to answer it.

One of the products of photochemical oxidation of methane in the atmosphere is formaldehyde (H_2CO). Since formaldehyde is the simplest carbonyl-containing compound, in some papers it is considered as a model of the reaction of hydration of complex biochemical systems. A sufficient number of papers are devoted to quantum-chemical study of the complexes $H_2O...H_2CO$ (see, for example, Refs. 63 and 223 and references therein). According to Ref. 223, the most stable is the ring structure with the C_1 symmetry, in which one of hydrogen atoms in the water molecule is directed toward carbonyl oxygen, and the oxygen atom of H_2O is oriented toward one of C–H groups. In Ref. 144, it was shown that the configuration of the complex O–H...C=O with almost linear H-bond is energetically more stable. For this structure, the vibrational spectrum was calculated; it agrees well with the experimental data obtained from matrix-isolation spectra.[87]

Sequential injection of three fluorine atoms into the methane molecule leads to strengthening of the intermolecular H-bond C–H...O (Ref. 221). Thus, the value of ΔE (kcal · mol^{-1}) determined in the basis MP2//6 − 311 + $G(2d, 2p)$ with regard for the BSSE correction, changes in the following way: CH_4 (− 0.25) < CH_3F (− 0.71) < CH_2F_2 (− 1.48) < < CHF_3 (− 2.45). The absolute values of ΔE in Refs. 142 and 143 (see Table 3) are somewhat different, however its relative change in the mentioned series is almost the same.

Some works are available on experimental determination of the geometry of the complexes of water with acetylene,[53] ethylene,[54,55] propane,[57] and cyclopropane[56] (see Table 1) by the microwave spectroscopy method. These complexes have significantly different structures. Thus, in the complex $H_2O...C_2H_2$, acetylene exhibits proton donor properties. The complex $H_2O...C_2H_4$ has the H-bond OH...π. In the complexes of water molecules with propane and cyclopropane, the hydrogen bond is not formed at all. The results of the study of the complexes of the considered hydrocarbons (except for propane) in the argon matrix are tabulated in Table 2.

The complexes of water with aromatic hydrocarbons were studied experimentally (by different spectroscopic methods[58,90,92,224–226]) and theoretically[58,228] only for benzene. This complex has the hydrogen bond OH...π with participation of the aromatic system of the benzene molecule. The binding energy (MP2///6 − 31G^* basis with BSSE correction[58]) is about −1.8 kcal·mol^{-1}.

Conclusion

As is seen from the data presented in this paper, the water molecule can form complexes with almost all components of the atmosphere, both major and minor. The emphasis in this paper is on discussion of the structure of these complexes and their relative stability. All the complexes can be considered as weak (or weakly bounded), and their energy varies from ≈ 10 kcal·mol^{-1} (for the complex $H_2O...HF$) to 0.4 kcal·mol^{-1} (for the complex $H_2O...Ar$). It should be noted here that the overwhelming majority of the systems were studied under nonequilibrium conditions (molecular beams, low-temperature matrices, etc.). Thus, it is impossible, for example, to calculate the altitude profile of the concentration of these complexes in the atmosphere. A significant progress achieved in development of the current quantum-chemistry methods allows obtaining reliable data on the structure of the complexes and, in some cases, on thermodynamics of complexes formation, as well as on spectroscopic parameters (position and intensity of spectral lines). At the same time, it is obvious that further efforts are needed to improve the sensitivity of the known experimental and theoretical approaches and to develop new approaches to the study of weakly bounded complexes under the conditions of the actual atmosphere.

Taking into account the above-said, the presented data on the relative strength of the complexes of water with atmospheric gases should be considered as tentative when evaluating the feasibilities of using the methods of laser (optical) sensing of the atmosphere. However, as these methods are improved, even a small degree of binding of minor atmospheric constituents and pollutants can lead to marked errors in their quantitative determination because of spectral shifts in analytical bands and change in their integral absorption coefficients.

In practical use of the presented data on the complexes of water with various inorganic and organic substances, one should keep in mind that the atmosphere is a permanent large-scale photochemical process.[145] Therefore, even very small concentrations of neutral complexes, as well as generated excimers and exciplexes, can change significantly the kinetics of atmospheric photochemical processes.

Acknowledgments

The authors are thankful to N.A. Zvereva for useful discussion and the help in preparation of the material for this paper.

The work was partially supported by the Russian Foundation for Basic Research (Project No. 00–05–64919).

References

1. V.C. Marshall, *Major Chemical Hazards* (Ellis Horwood Ltd., Chichester, 1987), 672 pp.
2. A. Sherman, in: *Chemical Vapor Deposition for Microelectronics* (Noyes Data Corp., Park Ridge, 1989), p. 57.
3. E.D. Hinkley, ed., *Laser Monitoring of the Atmosphere* (Springer Verlag, New York, 1976).
4. L.S. Rothman, J. Schroeder, A. McCann, et al., in: *Proc. of the Workshop on Atmospheric Spectroscopy Applications* (Reims, 1996).
5. N. Jacyuinet-Husson, E. Arie, J. Ballard, et al., J. Quant. Spectrosc. Radiat. Transfer **62**, 205 (1999).
6. Sh.Sh. Nabiev and Yu.N. Ponomarev, Atmos. Oceanic Opt. **11**, No. 12, 1093–1098 (1998).
7. N.A. Zvereva, Sh.Sh. Nabiev, and Yu.N. Ponomarev, in: *Abstr. of the NATO Adv. Research Workshop Spectroscopy From Space,* Bratislava (2000), pp. 55.
8. Sh.Sh. Nabiev, P.G. Sennikov, and Yu.N. Ponomarev, in: *Abstr. Vth Colloq. in Atmospheric Spectroscopy Applications* (Reims, 1999), p. CP2.
9. Sh.Sh. Nabiev and L.P. Sukhanov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 8, 1415 (1999).
10. P.O. Wennberg, R.C. Cohen, R.M. Stimpfle, et al., Science **266**, 398 (1994).
11. P. Hobza and R. Zahradnik, Int. J. Quant. Chem. **42**, 581 (1992).
12. A.D. Bykov, L.N. Sinitsa, and V.I. Starikov, *Experimental and Theoretical Methods in Spectroscopy of Water Vapor* (Publishing House of the SB RAS, Novosibirsk, 1999), 376 pp.
13. P.G. Sennikov, "*Molecular state of water in liquid volatile inorganic hydrides*," Author's Abstract of Doct. Chem. Sci. Dissert, Nizhnii Novgorod (1994), 38 pp.

14. L.A. Curtiss, D.J. Frurip, and M. Blander, J. Chem. Phys. **71**, 2703 (1979).
15. A.A. Vigasin and G.V. Chlenova, Izv. Akad. Nauk SSSR, Ser. Fiz. Atmos. Okeana **20**, 657 (1984).
16. R.A. Bohlander, *Atmospheric Water Vapor* (Academic Press, New York, 1980), p. 657.
17. L.A. Curtiss and M. Blander, Chem. Rev. **88**, 827 (1988).
18. G.G. Devyatykh and P.G. Sennikov, Usp. Khimii **64**, No. 9, 872 (1995).
19. A.S. Legon, Chem. Phys. Lett. **135**, 303 (1987).
20. T.J. Balle and W.H. Flygare, Rev. Sci. Instrum. **52**, 33 (1981).
21. A.C. Legon, Ann. Rev. Phys. Chem. **34**, 275 (1983).
22. T.R. Dyke, Top. Curr. Chem. **120**, 85 (1984).
23. W. Klemperer, Farad. Discuss. Chem. Soc. **62**, 179 (1977).
24. H. Herzberg, *Molecular Spectra and Molecular Structure* (Van Nostrand Company inc., Princeton, 1950), Vol. 1.
25. A.A. Vigasin, Zh. Strukt. Khimii **28**, 120 (1987).
26. T.R. Dyke, K.M. Mack, and J.S. Muenter, J. Chem. Phys. **66**, 498 (1977).
27. J.V. Bevan, Z. Kisiel, A.C. Legon, D.J. Millen, and S.C. Rogers, Proc. R. Soc. Lond. Part A **372**, 441 (1980).
28. Z. Kisiel, A.C. Legon, and J. Millen, J. Chem. Phys. **78**, 2910 (1983).
29. Z. Kisiel, A.C. Legon, and J. Millen, J. Mol. Struct. **112**, 1 (1984).
30. A.C. Legon, J. Millen, and H.M. North, Chem. Phys. Lett. **135**, 303 (1987).
31. A.C. Legon and L.C. Willoughby, Chem. Phys. Lett. **95**, 449 (1983).
32. A.C. Legon and A.P. Suckley, Chem. Phys. Lett. **150**, 153 (1988).
33. S.A. Cooke, G. Gina, J.H. Holloway, and A.C. Legon, Angew. Chem. Int. Ed. Engl. **36**, 129 (1997).
34. S.A. Cooke, G. Gotti, C.M. Evans, J.H. Holloway, and A.C. Legon, Chem. Commun., 2327 (1996).
35. M.S. LaBarge, A.M. Andrews, A. Taleb-Bendiab, K.W. Hillig, and R.K. Bohn, J. Phys. Chem. **95**, 3523 (1991).
36. P. Herbine and T.R. Dyke, J. Chem. Phys. **83**, 3768 (1985).
37. A.J. Fillery-Travis, A.C. Legon, and L.C. Willoughby, Proc. R. Soc. London. Ser. A **396**, 405 (1984).
38. S.L. Adebayo, A.C. Legon, and D.J. Millen, J. Chem. Soc. Farad. Trans. **87**, 443 (1991).
39. H.S. Gutowsky, T.C. Germann, J.D. Augspurger, and C.E. Dykstra, J. Chem. Phys. **96**, 5808 (1992).
40. H.S. Gutowsky, C. Aline, S. Hoey, S.L. Tscopp, J.D. Keen, and C.E. Dykstra, J. Chem. Phys. **102**, 3032 (1995).
41. K. Matsumura, F.J. Lovas, and R.D. Suenram, J. Chem. Phys. **91**, 5887 (1989).
42. D. Zolandz, D. Yaron, K.I. Petrson, and W. Klemperer, J. Chem. Phys. **97**, 2861 (1992).
43. J.Z. Gillies, C.W. Gillies, R.D. Suenram, F.J. Lovas, D. Schmidt, and D. Cremer, J. Mol. Spectrosc. **146**, 493 (1991).
44. H.O. Leung, M.D. Marshall, R.D. Suenram, and F.J. Lovas, J. Chem. Phys. **90**, 700 (1989).
45. R.C. Cohen and R.J. Saykally, J. Phys. Chem. **94**, 7991 (1990).
46. R.C. Cohen and R.J. Saykally, J. Chem. Phys. **98**, 6007 (1993).
47. G.T. Fraser, F.J. Lovas, R.D. Suenram, and K. Matsumura, J. Mol. Spectrosc. **144**, 97 (1990).
48. D. Yaron, K.I. Petrson, D. Zolandz, W. Klemperer, F.J. Lovas, and R.D. Suenram, J. Chem. Phys. **92**, 7095 (1990).
49. R.E. Bumgarner, S. Suzuki, P.A. Stockman, P.G. Green, and G.A. Blake, Chem. Phys. Lett. **176**, 123 (1991).
50. K.J. Peterson, R.D. Suenram, and F.J. Lovas, J. Chem. Phys. **102**, 7807 (1995).
51. K.I. Peterson and W. Klemperer, J. Chem. Phys. **80**, 2439 (1984).
52. R.D. Suenram, G.T. Fraser, F.J. Lovas, and Y. Kawashima, J. Chem. Phys. **101**, 7030 (1994).
53. K.I. Peterson and W. Klemperer, J. Chem. Phys. **81**, 3842 (1984).
54. K.I. Peterson and W. Klemperer, J. Chem. Phys. **85**, 725 (1986).
55. A.M. Andrews and R.L. Kuczkowski, J. Chem. Phys. **98**, 791 (1993).
56. A.M. Andrews, K.W. Hillig II, and R.L. Kuczkowski, J. Am. Chem. Soc. **114**, 6765 (1992).
57. D.W. Steyert, M.J. Elrod, R.J. Saykally, F.J. Lovas, and R.D. Suenram, J. Chem. Phys. **99**, 7424 (1993).
58. S. Suzuki, P.G. Green, R.E. Bumgarner, S. Dasgupta, W.A. Goddard, and G.A. Blake, Science **257**, 942 (1992).
59. M. Moskovits and G. Ozin, eds., *Cryochemistry* (Mir, Moscow, 1979), 594 pp.
60. A.J. Barnes, in: *Molecular Interactions*, ed. by H. Ratajczak and W.J. Orwille-Thomas (Willey, London, 1980), p. 273.
61. R.N. Perutz, Ann. Repts. Progr. Chem. **82**, 157 (1971).
62. L. Andrews, Ann. Rev. Phys. Chem. **22**, 109 (1971).
63. T.A. Ford, Can. J. Analyt. Sci. Spectrosc. **43**, 113 (1998).
64. J.P. Ayers and A.D.E. Pullin, Spectrochim Acta. Part A **32**, 1629 (1971).
65. L. Andrews and G.L. Johnson, J. Chem. Phys. **79**, 3670 (1983).
66. Engdahl and B. Nelander, J. Chem. Phys. **84**, 1981 (1986).
67. Schriver, B. Silvi, B. Maillard, and J.P. Perchard, J. Chem. Phys. **65**, 2095 (1977).
68. B.S. Ault, J. Am. Chem. Soc. **105**, 5742 (1983).
69. D.G. Evans, G.A. Yeo, and T.A. Ford, Farad. Discuss. Chem. Soc. **86**, 55 (1988).
70. C. McInnnis and L. Andrews, J. Phys. Chem. **96**, 2051 (1992).
71. K. Johnsson, A. Engdahl, P. Ouis, and B. Nelander, J. Phys. Chem. **96**, 5778 (1992).
72. A. Givan, L.A. Larsen, A. Loewenschuss, and C.J. Nielsen, J. Chem. Soc. Farad. Trans. **94**, 827 (1998).
73. B. Nelander and L. Nord, J. Phys. Chem. **86**, 4375 (1982).
74. A. Engdahl and B. Nelander, J. Chem. Phys. **91**, 6604 (1989).
75. S. Scheiner, Ann. Rev. Phys. Chem. **45**, 23 (1994).
76. A. Schriver, L. Schriver, and J.P. Perchard, J. Mol. Spectrosc. **127**, 125 (1988).
77. L. Schriver, D. Carrere, A. Schriver, and K. Jaeger, Chem. Phys. Lett. **181**, 505 (1991).
78. V.E. Bondybey and J.H. English, J. Mol. Spectrosc. **109**, 221 (1985).
79. L. Fredin, Chem. Scripta **4**, 97 (1973).
80. H. Dubost and L. Abouaf-Marguin, Chem. Phys. Lett. **17**, 269 (1972).
81. W. Hagen and A.G.G.M. Tielens, J. Chem. Phys. **75**, 4198 (1981).
82. T. Tso and E.K.C. Lee, J. Phys. Chem. **88**, 5465 (1984).
83. T. Tso and E.K.C. Lee, J. Phys. Chem. **89**, 1618 (1985).
84. B. Nelander, J. Phys. Chem. **89**, 827 (1985).
85. L. Fredin, B. Nelander, and G. Ribbegard, Chem. Scripta **7**, 11 (1975).
86. T.L. Tso and E.K.C. Lee, J. Phys. Chem. **89**, 1612 (1985).
87. B. Nelander, J. Chem. Phys. **72**, 77 (1980).
88. A. Engdahl and B. Nelander, Chem. Phys. Lett. **100**, 129 (1983).
89. A. Engdahl and B. Nelander, Chem. Phys. Lett. **113**, 49 (1985).

90. A. Engdahl and B. Nelander, J. Phys. Chem. **90**, 4982 (1986).
91. A.J. Barnes and S.L. Paulson, Chem. Phys. Lett. **99**, 326 (1983).
92. A. Engdahl and B. Nelander, J. Phys. Chem. **89**, 2860 (1985).
93. A.C. Legon, Chem. Soc. Rev. **19**, 197 (1990).
94. D.J. Millen, J. Mol. Struct. **113**, 227 (1984).
95. S. Scheiner, J. Mol. Struct. **202**, 177 (1989).
96. S. Scheiner, in: *Reviews in Computational Chemistry*, ed. by K.B. Lipkowitz and D.B. Boyd (VCH, New York, 1991), Vol. 2, p. 165.
97. S. Scheiner, in: *Theoretical Models of Chemical Bonding*, ed. by Z.P. Macsic (Springer, Berlin, 1991), Part 4, p. 171.
98. S. Scheiner, Ann. Rev. Phys. Chem. **45**, 23 (1994).
99. A.A. Hasenein and A. Hinchliffe, *Self Consistent Field: Theory and Application* (Elsevier, Amsterdam, 1990), p. 670.
100. J.E. Del Bene, J. Phys. Chem. **92**, 2874 (1988).
101. J.E. Del Bene, J. Comput. Chem. **10**, 603 (1989).
102. M.J. Frisch, J.A. Pople, and J.E. Del Bene, J. Phys. Chem. **89**, 3664 (1985).
103. S.F. Boys and F. Bernardi, Mol. Phys. **19**, 553 (1970).
104. Z. Latajka, J. Mol. Struct. **205**, 13 (1990).
105. Z. Latajka, J. Mol. Struct. **251**, 245 (1991).
106. E.P.F. Lee and T.G. Wright, J. Chem. Soc. Farad. Trans. **94**, 33 (1998).
107. M.M. Szczesniak, S. Scheiner, and Y. Bouteiller, J. Chem. Phys. **81**, 5024 (1984).
108. J.E. Del Bene, J. Phys. Chem. **92**, 2874 (1988).
109. Y. Hannachi, L. Schriver, A. Schriver, and J.P. Perchard, Chem. Phys. **135**, 285 (1989).
110. I. Roeggen, Mol. Phys. **70**, 353 (1990).
111. N.A. Zvereva, Sh.Sh. Nabiev, and Yu.N. Ponomarev, Atmos. Oceanic Opt. **12**, No. 9, 810–813 (1999).
112. N.A. Zvereva, Sh.Sh. Nabiev, and Yu.N. Ponomarev, in: *Abstracts of Reports at VI Int. Symp. on Atmospheric and Ocean Optics,* Tomsk (1999), p. 30.
113. C. Rovira, P. Constans, M.-H. Whansbo, and J.J. Novoa, Int. J. Quant. Chem. **52**, 177 (1994).
114. Sh.Sh. Nabiev, A.N. Trotsenko, S.K. Ignatov, P.G. Sennikov, N.A. Zvereva, and Yu.N. Ponomarev, in: *Abstracts of Reports at Int. Symp. on Atmospheric Radiation,* St. Petersburg (1999), p. 127.
115. N.A. Zvereva, Sh.Sh. Nabiev, and Yu.N. Ponomarev, in: *Abstr. of the 16th Colloq. on High Resolution Molecular Spectroscopy,* Dijon (1999), p. 289.
116. N.A. Zvereva, Sh.Sh. Nabiev, and Yu.N. Ponomarev, Proc. SPIE **3983**, 9 (1999).
117. M.J. Packer, and D.C. Ceary, J. Phys. Chem. **99**, 14323 (1995).
118. N.A. Zvereva, Sh.Sh. Nabiev, and Yu.N. Ponomarev, in: *Abstr. of Reports at VI Int. Symp. on Atmospheric and Ocean Optics,* Tomsk (2000), p. 41.
119. N.A. Zvereva, Sh.Sh. Nabiev, and Yu.N. Ponomarev, in: *Abstr. of the Intern. Symp. on Current Problems in Atmospheric Radiation,* St. Petersburg (2000), p. 140.
120. A.K. Chandra and Minh Tho Nguyen, Chem. Phys. Lett. **268**, 321 (1997).
121. T.S. Dibble and J.S. Francisco, J. Phys. Chem. **99**, 1919 (1995).
122. P.G. Sennikov, M.A. Ikrin, S.K. Ignatov, A.A. Bagatur'yants, and E.Yu. Klimov, Izv. Akad. Nauk, Ser. Khim., 92 (1999).
123. S.K. Ignatov, P.G. Sennikov, B.S. Ault, A.A. Bagatur'yants, I.V. Simdyanov, A.G. Razuvaev, E.Ju. Klimov, and O. Gropen, J. Phys. Chem. Part A **103**, 8328 (1999).
124. L. Turi and J.J. Dannenberg, J. Phys. Chem. **97**, 7899 (1993).
125. H.S. Rzepa and Min Yan Yi, J. Chem. Soc. Perkin Trans. 2, 943 (1990).
126. Z. Latajka and S. Scheiner, J. Phys. Chem. **94**, 217 (1990).
127. Y.B. Wang, Fu-Ming Tao, and Yuh-Kang Pan, Chem. Phys. Lett. **230**, 480 (1994).
128. D.B. Kitchen, T.P. Ruane, and L.C. Allen, Chem. Phys. Lett. **141**, 525 (1987).
129. M.J. Braesler, V.C.E. Carr, M.G. Gerazounis, N.R. Jugga, G.A. Yeo, and T.A. Ford, J. Mol. Struct. (THEOCHEM) **180**, 241 (1988).
130. T.D. Mokomela, J. Rencken, G.A. Yeo, and T.A. Ford, J. Mol. Struct. **275**, 33 (1992).
131. W. Byers Brown, M.A. Vincent, K. Trollope, and I.H. Hillier, Chem. Phys. Lett. **192**, 213 (1992).
132. I.I. Zakharov, O.I. Kolbasina, T.N. Semenyuk, N.F. Tyupalo, and G.N. Zhidomirov, Zh. Strukt. Khimii **34**, 26 (1993).
133. J. Lundell, J. Phys. Chem. **99**, 1492 (1995).
134. T.M. Tshehla and T.A. Ford, Bull. Pol. Acad. Sci. Chem. **42**, 397 (1994).
135. Nancy Renyou Zhang and D.D. Shillady, J. Chem. Phys. **100**, 5230 (1994).
136. P.A. Block, M.D. Marshall, L.G. Pederson, and R.E. Miller, J. Chem. Phys. **96**, 7321 (1992).
137. J. Sadlej and P. Mazurek, J. Mol. Struct. (TEOCHEM) **390**, 129 (1995).
138. J. Sadlej, J. Makarewicz, and G. Chalasinski, J. Chem. Phys. **109**, 3919 (1998).
139. K. Morokuma and C. Muguruma, J. Am. Chem. Soc. **116**, 1316 (1994).
140. E. Bishenden and D.J. Donaldson, J. Phys. Chem. **102**, 4638 (1998).
141. J.A. Dobado and J.M. Molina, J. Phys. Chem. **98**, 1819 (1994).
142. J.J. Novoa, B. Tarron, Myung-Hwan Whangbo, and J.M. Williams, J. Chem. Phys. **95**, 5179 (1991).
143. J. Alkorta and S. Maluendes, J. Phys. Chem. **99**, 6457 (1995).
144. Tae-Kyu Ha, J. Makarewicz, and A. Bauder, J. Phys. Chem. **97**, 1415 (1993).
145. M.J. McEwan and L.E. Phillips, *Chemistry of the Atmosphere* (Edward Arnold, London, 1975).
146. R.K. Thomas, Proc. R. Soc. Lond. Part A **344**, 579 (1975).
147. J.V. Bevan, A.C. Legon, D.J. Millen, and S.C. Rogers, J. Chem. Soc. Chem. Comm., 341 (1975).
148. A.C. Legon and L.C. Willoughby, Chem. Phys. Lett. **92**, 333 (1982).
149. A.C. Legon, J. Millen, and S.L. Adebayo, J. Chem. Soc. Farad. Trans. **87**, 443 (1991).
150. A.C. Legon and J. Millen, Acc. Chem. Res. **20**, 39 (1987).
151. A.C. Legon and J. Millen, Chem. Soc. Rev., 71 (1992).
152. G. Cazzoli, P.G. Favero, D.G. Lister, A.C. Legon, D.J. Millen, and Z. Kisiel, Chem. Phys. Lett. **117**, 543 (1985).
153. Z. Kisiel, A.C. Legon, and J. Millen, Proc. R. Soc. Lond. Part A **381**, 419 (1982).
154. S.P. Belov, V.M. Demkin, N.F. Zobov, E.N. Karyakin, A.F. Krupnov, I.N. Kozin, O.L. Polyanskii, and M.Yu. Tret'yakov, Preprint No. 192, Institute of Applied Physics of AS USSR, Gor'kii (1988), 17 pp.
155. B.S. Ault and G.C. Pimentel, J. Phys. Chem. **77**, 53 (1973).

156. G.P. Ayers and A.D.E. Pullin, Spectrochim. Acta. Part A **32**, 1641 (1976).
157. C. Amirand and D. Maillard, J. Mol. Struct. **176**, 181 (1986).
158. Y. Hannachi, B. Silvi, and Y. Bouteiller, J. Chem. Phys. **94**, 2915 (1991).
159. L.P. Sukhanov, N.L. Zakamskaya, V.V. Zheleznyakov, and Sh.Sh. Nabiev, in: *Abstr. of the 16th Intern. Conf. on High Resolution Molecular Spectroscopy,* Prague (2000), p. 130.
160. Z. Latajka and S. Scheiner, J. Chem. Phys. **87**, 5928 (1987).
161. S. Re, Y. Osamura, and Y. Suzuki, J. Chem. Phys. **109**, 973 (1998).
162. P.N. Noble and G.C. Pimentel, Spectrochim. Acta. Part A **24**, 797 (1968).
163. L. Fredin and B. Nelander, J. Mol. Struct. **16**, 217 (1973).
164. A. Engdahl and B. Nelander, J. Chem. Phys. **84**, 1981 (1986).
165. F.S. Rowland, Ann. Rev. Phys. Chem. **42**, 731 (1991).
166. W.B. DeMore, S.P. Sander, D.M. Golden, R.F. Hampson, M.J. Kurylo, C.J. Howard, A.R. Ravishankara, C.E. Kolb, and M.J. Molina, *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling* (Jet Propulsion Laboratory, Pasadena, CA, 1992), p. 1.
167. A.C. Legon and L.C. Willoughby, Chem. Phys. Lett. **95**, 449 (1983).
168. T.S. Dibble and J.S. Francisco, J. Phys. Chem. **100**, 817 (1996).
169. S.A. Cooke, G. Cotti, C.M. Evans, J.H. Holloway, and A.C. Legon, Chem. Commun., 2327 (1996).
170. A.A. Ennan and B.M. Kats, Usp. Khimii **43**, 1186 (1974).
171. A.M. Walther and B.S. Ault, Inorg. Chem. **23**, 3892 (1984).
172. A.W. Castleman, R.E. Davis, H.R. Munkelvitz, I.N. Tang, and W.P. Wood, Int. J. Chem. Kinet. Symp. **1**, 629 (1975).
173. K. Morokuma and S. Muguruma, J. Am. Chem. Soc. **116**, 1316 (1994).
174. H.S. Johnston, Ann. Rev. Phys. Rev. **35**, 481 (1984).
175. Fu-Ming Tao, K. Higgins, and W. Klemperer, Geophys. Res. Lett. **23**, No. 14, 1797 (1996).
176. P. Herbine, T.A. Hu, G. Johnson, and T.R. Dyke, J. Chem. Phys. **93**, 5485 (1990).
177. D.D. Nelson, Jr., G.T. Fraser, and W. Klemperer, Science **238**, 5512 (1987).
178. P.A. Stockman, R.E. Bumgarner, S. Suzuki, and G.A. Blake, J. Chem. Phys. **96**, 2496 (1992).
179. G.T. Fraser and R.D. Suenram, J. Chem. Phys. **96**, 7287 (1992).
180. G.A. Yeo and T. Ford, Struct. Chem. **3**, 75 (1992).
181. G.C. Pimentel and A.L. McClellan, Ann. Rev. Phys. Chem. **22**, 349 (1971).
182. H.A. Gebbie, W.J. Burroughs, J. Chamberlain, J.E. Harries, and R.G. Jones, Nature (London) **221**, 143 (1969).
183. C.S. Dykstra and L. Andrews, J. Chem. Phys. **92**, 6043 (1990).
184. E.L. Coitino, O.N. Ventura, and R.M. Sosa, J. Mol. Struct. **254**, 315 (1992).
185. G.A. Yeo and T.A. Ford, J. Mol. Struct. **266**, 183 (1992).
186. E.C. Vauthier, V. Barone, C. Minichino, and S. Fliszar, Can. J. Chem. **68**, 1233 (1990).
187. B. Pulman, ed., *Intermolecular Interactions: From Diatomic Molecules to Biopolymers* [Russian translation] (Mir, Moscow, 1981), 592 pp.
188. I.G. Kaplan, *Introduction to Theory of Intermolecular Interactions* (Nauka, Moscow, 1982), 311 pp.
189. B. Nelander, J. Chem. Phys. **69**, 3870 (1978).
190. A.J. Barnes, R.M. Bentwood, and M.P. Wright, J. Mol. Struct. **118**, 97 (1984).
191. R.D. Amos, Chem. Phys. **104**, 145 (1986).
192. A. Les, Theor. Chim. Acta (Berlin) **66**, 375 (1985).
193. A.V. Shabatina and A.V. Nemukhin, Vestn. Mosk. Univ. Ser.2. Khimiya **40**, 247 (1999).
194. D.E. Burch and D.A. Gryvnak, *Atmospheric Water Vapor* (Academic Press, New York, 1980), p. 47.
195. L.A. Curtiss and C.L. Eisgruber, J. Chem. Phys. **80**, 2022 (1984).
196. J. Sandlej, B. Rowland, J.P. Delvin, and V. Buch, J. Chem. Phys. **102**, 4804 (1995).
197. E.S. Fois, A. Gamba, G. Morosi, P. Demontis, and G.B. Suffritti, J. Chem. Phys. **84**, 751 (1987).
198. L. Fredin, B. Nelander, and G. Ribbegard, Chem. Scripta **7**, 11 (1975).
199. A.E. Reed, F. Weinhold, L.A. Curtiss, and D.J. Pochatko, J. Chem. Phys. **84**, 5687 (1986).
200. C.A. Parish, J.D. Augsburger, and C.E. Dykstra, J. Phys. Chem. **96**, 2069 (1992).
201. J. Sandlej and V. Buch, J. Chem. Phys. **100**, 4272 (1994).
202. J. Lundell and M. Raesaenen, J. Phys. Chem. **97**, 9657 (1993).
203. J. Lundell, M. Raesaenen, and Z. Latajka, Chem. Phys. Lett. **222**, 33 (1994).
204. J. Lundell, J. Phys. Chem. **99**, 1492 (1995).
205. T.D. Mokomela, I. Rencken, G.A. Yeo, and T.A. Ford, J. Mol. Struct. **275**, 33 (1992).
206. J. Langlet, J. Caillet, and M. Allavena, J. Mol. Struct. **450**, 69 (1998).
207. B. Joensson, G. Karlsrom, and H. Wennerstrom, Chem. Phys. Lett. **30**, 58 (1976).
208. C.R. Coan and A.D. King, Jr., J. Am. Chem. Soc. **93**, 1857 (1971).
209. R.C. Cohen, K.L. Busarow, K.B. Laughlin, K.B. Blake, M. Havenith, Y.T. Lee, and R.J. Saykally, J. Chem. Phys. **89**, 4494 (1988).
210. R.C. Cohen, K.L. Busarow, Y.T. Lee, and R.J. Saykally, J. Chem. Phys. **92**, 167 (1990).
211. Fu-Ming Tao and W. Klemperer, J. Chem. Phys. **101**, 1129 (1994).
212. C. Leforestier, J. Chem. Phys. **101**, 7357 (1994).
213. G. Chalasinski, M.M. Szczesniak, and S. Scheiner, J. Chem. Phys. **94**, 2807 (1991).
214. R.W. Bickes, G. Ducuette, C.J.N. van den Meijdenberg, A.M. Rulis, G. Scoles, and K.M. Smith, J. Phys. **B8**, 3034 (1975).
215. A. Moroz, R.L. Sweany, and S.L. Whittenburg, J. Phys. Chem. **94**, 1352 (1990).
216. M. Okumura, L.I. Yeh, J.D. Myers, and Y.T. Lee, J. Phys. Chem. **94**, 3416 (1990).
217. D.G. Taylor and H.L. Strauss, J. Chem. Phys. **90**, 768 (1989).
218. D.W. Schwenke, S.P. Walch, and P.R. Taylor, J. Chem. Phys. **94**, 2986 (1991).
219. Q. Zhang, L. Chenyang, Y. Ma, F. Fish, M.M. Szczesniak, and V. Buch, J. Chem. Phys. **96**, 6039 (1992).
220. L. Dore, R.C. Cohen, C.A. Schmuttenmaer, K.L. Busarow, M.J. Elrod, J.G. Loeser, and R.J. Saykally, J. Chem. Phys. **100**, 863 (1994).

221. M.M. Szczesniak, G. Chalasinski, S.M. Cybulski, and P. Cieplak, J. Chem. Phys. **98**, 3078 (1993).
222. J. Novoa and F. Mota, Chem. Phys. Lett. **266**, 23 (1997).
223. D.E. Woon, P. Zeng, and D.R. Beck, J. Chem. Phys. **93**, 7808 (1990).
224. R.A. Kumpf and J.R. Damewood, Jr., J. Phys. Chem. **93**, 4478 (1989).
225. H.S. Gutowsky, T. Emilsson, and E. Arunan, J. Chem. Phys. **99**, 4883 (1993).
226. A.J. Gotch and T.S. Zwier, J. Chem. Phys. **96**, 3388 (1992).
227. R.N. Pribble, A.W. Garrett, K. Haber, and T.S. Zwier, J. Chem. Phys. **103**, 531 (1995).
228. J.D. Augspurger, C.E. Dykstra, and T.S. Zwier, J. Phys. Chem. **96**, 7257 (1992).