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Spectroscopic determination and study of the molecular state of water in ultrapure volatile inorganic substances

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Abstract. The state of the art in methods for the determination and study of the molecular state of the water admixture in high-purity volatile inorganic substances used in processes for the preparation of materials for new technologies is considered. Primary attention is given to spectroscopic methods in the IR and microwave regions with the highest information content. The bibliography includes 182 references.

I. Introduction

Volatile substances have relatively low melting and boiling points, i.e. they are characterised by typical van der Waals intermolecular interaction, sometimes with a small contribution from other types of interaction, e.g., intermolecular hydrogen bonds. A vapour pressure of 1333 Pa at 500 K can be chosen as a criterion defining an arbitrary threshold of volatility.[1] Permanent gases, chlorides and hydrides of a number of elements and some other substances are usually regarded as volatile inorganic compounds. The interest in high-purity volatile inorganic compounds is caused by their wide application for obtaining many materials for new technologies. For example, high-purity volatile chlorides and hydrides are used as starting compounds in manufacturing optical fibres, semiconductors and optical elements by chemical deposition from the vapour phase (the CVD technology). In this case, a high-purity permanent gas usually serves as the carrier.

Among the impurities most frequently encountered in ultrapure volatile inorganic compounds and most difficult to remove, water is foremost.[2-4] This results from the relatively high concentration of moisture in the starting compounds and in the technological atmosphere, as well as from the tendency of water molecules to be adsorbed on the walls of the equipment and even to diffuse through them at an appreciable rate from the environment (see, e.g., Ref. 5). Thorough elimination of water from volatile compounds is frequently complicated by the ability of water molecules to form rather stable complexes, both with one another and with molecules of the main compound in the liquid phase and sometimes in the gaseous phase. Such complexes can initiate avalanche-like nucleation processes followed by the formation of suspended ice or gas hydrate particles.

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Strict requirements are imposed on the purity of the starting compounds and working gases used in the CVD technology for manufacturing optical fibres and semiconducting epitaxial layers. For example, the water concentration in the starting reagents should not exceed 5×10^{-5} mol% in order to attain the lowest optical loss in quartz optical fibres.[6,7] Perfect crystalline epitaxial GaAs layers on silicon can be obtained by the reaction of arsine with trimethylgallium in a hydrogen atmosphere, provided that the admixture of water in the reactor does not exceed the same value of 5×10^{-5} mol%.[8] On the other hand, the samples presented at the Exhibition-Collection of special purity compounds of the Russian Academy of Sciences, which has been permanently open since 1974 at the Institute of Chemistry of High-Purity Substances of the RAS, contain the following mean water concentrations (mol%): 1×10^{-4} in permanent gases, 1×10^{-2} in chlorides and 5×10^{-3} in hydrides.[9] Therefore, the preparation of high-purity compounds with a water admixture below 5×10^{-5} mol% is an urgent problem. At present, a demand is already felt for compounds with an overall content of admixtures within $10^{-6} - 10^{-8}$ mol%.[6,10] Deep dehydration, storage and transportation of compounds with such a low content of water involve considerable difficulties.

The development of methods for the preparation of volatile compounds with a low water content should be paralleled by the development and improvement of the corresponding analytical methods. In our opinion, two interconnected problems should be taken into account when considering the methods for the determination of water in high-purity volatile compounds: highly sensitive determination of the water admixture and study of the state of admixed water, i.e. study of the nature of the chemical bond in complexes involving water and the thermodynamic characteristics of these complexes.

The present review considers both these problems for volatile inorganic hydrides, chlorides and permanent gases. Attention is concentrated on spectroscopic methods in the IR and microwave ranges, because of their high sensitivity and the possibility of their simultaneous application both for analysis and for studying the molecular state of admixed water.

II. Determination of water

Many publications, including several monographs and reviews,[11-14] have dealt with problems of water determination in various media, including high-purity volatile inorganic compounds. Many chemical, physical and physicochemical methods are known; however, their detection limits are not lower than $10^{-4} - 5 \times 10^{-5}$ mol%. The coulometric method and the dew point method are among the most widespread, rather simple methods.

1. The coulometric method and the dew point method

The coulometric method measures the quantity of electricity required for the electrochemical decomposition of water in an analysed volume of a gas.[15,16] The sensitive element of the corresponding device contains a sorbent, usually phosphorus(V) oxide. For this reason, coulometric hygrometers are used only for analysing compounds that do not react with P_2O_5 or in the cases where the contribution from the corresponding reaction to the overall measurement error is insignificant (see Atamanyuk et al., [17] who report a coulometric analysis of gaseous HCl). The detection limit attainable by this method is $(1-5) \times 10^{-5}$ mol%. The coulometric method usually consumes a large amount ($1-3$ dm^3 s^{-1}) of the analysed gas, which is not always acceptable.

A number of other methods for water determination in volatile compounds have appeared in recent years, such as thermal oscillometry,[18] direct potentiometry,[19] cyclic voltammetry [20] and amperometry.[21] However, these methods also suffer to some extent from the above drawbacks.

The measurement of water concentration by the dew point method is based on the visual or optical monitoring of the fogging of a cooled mirror in a stream of the analysed gas.[15,16] The temperature, at which dew appears on the mirror, is measured and the pressure of saturated water vapour corresponding to this temperature is determined. The detection limit can be as low as 10^{-6} mol%. This method is unsuitable for analysing readily condensing gases, such as ammonia, certain other hydrides and hydrocarbons. Various modifications of this method have been described in Refs 22 and 23.

A novel method for the determination of micro admixtures of water based on measuring the temperature of the start of sublimation of a condensate, which is first placed in a definite volume, has been proposed.[24] The authors determined the solubility of water in liquid nitrogen, which was found to be 4×10^{-7} mol%. In their opinion, there is no limit to the detection of water by this method. However, the authors do not report any comparative analyses or methods for preparing the equipment for assaying such a low water content.

Other fairly sensitive methods for water determination include gas chromatography and mass spectrometry.

2. Gas chromatography

Various problems in the application of gas chromatography for the determination of water in volatile compounds have been discussed in a number of communications.[11,25-28] Both direct determination of the water admixture without changing its chemical form and reaction chromatography are used. In order to determine water in gases by reaction chromatography, reactions transforming water into other compounds (most frequently, ethyne) more convenient for gas chromatographic detection were used.[28,29] Ref. 28 reports an estimation of water content in ammonia at a level of $10^{-3}-10^{-4}$ mol% by passing ammonia through a reactor with calcium carbide. The poor reproducibility of the results obtained by a one-step technique, i.e. when the reactor with calcium carbide was directly connected to the chromatograph, was noted. The error probably appeared because not all the water could undergo reaction due to the insufficient reaction rate. In later work the sample was first passed several times through the reactor and only then analysed.

The determination of water in gases based on its reaction with calcium carbide is applicable to a wide range of compounds inert towards calcium carbide, oxide, and hydroxide.

Ref. 30 describes a technique for water determination in volatile hydrides and permanent gases (detection limit: 1×10^{-5} mol%). The technique is based on the oxidation of methane by water and the products of its dissociation in a spark discharge occurring in the reaction vessel. The change of the amount of methane due to its oxidation is detected by a flame ionisation detector. The relative standard deviation was $0.01-0.2$ in the range of water contents of $1 \times 10^{-2}-5 \times 10^{-5}$ mol%.

The improvement of materials for packing chromatographic columns made it possible to determine the water admixture directly in gases without changing its chemical form and to decrease the detection limit. For example, Snopatin et al.[31] determined the water content in hydrogen sulfide, hydrogen selenide, arsine, and germane using the selective adsorption of the hydrides on a Saran charcoal (detection limit: 5×10^{-5} mol%).

Preconcentration is also used in gas-chromatographic determinations of the water admixture. Ref. 32 reports the gas-chromatographic determination of water in high-purity nitrogen (detection limit: 2×10^{-6} mol%). Water was concentrated by adsorption in columns packed with cooled (3 °C) Porapack T, then blown out of the column and detected with a catharometer. A technique for water determination in ammonia (detection limit: 1×10^{-4} mol.%) was reported in Ref. 33. The lowest detection limit of water in nitrogen (2×10^{-6} mol%) was attained when water was concentrated on a sorbent, while gas chromatographic techniques offered limits of water detection within 10^{-3} to 10^{-5} mol%.

3. Mass spectrometry

Similar or even lower limits for water determination can be attained using mass spectrometry. For example, Ref. 34 reports a technique for the mass-spectrometric determination of water and other admixtures in SiH_4, HCl and other compounds (the detection limit was 1×10^{-4} mol%). The authors draw attention to the correctness of the analysis and consider adsorption-desorption processes in the connecting tubes to the quadrupole mass spectrometer, the 'memory' effect of the ion source, and various background ion-molecule reactions. All of these questions are of primary importance for the determination of microamounts of water in gases. Water can be to a considerable extent adsorbed on the walls of the injection system and the ion source of the mass spectrometer, which adversely affects the detection limit. Refs 35 and 36 report results of mass-spectrometric determinations of the water content in the residual atmospheres of evacuated sealed vessels. It was noted that the results obtained in different laboratories are not reproducible. This probably results from the fact that the vapour pressure in the vessels varied within 0.01 – 0.1 atm, so that from three to ten water monolayers were present on the vessel walls. The gas was injected into an ion source, whose volume and surface area were greater than those of the vessel by a factor of several tens. As a result, adsorption and desorption of water in the ion source affected considerably the accuracy of the measurement.

Recent publications deal with the mass spectrometric determination of water in gases.[37,38] Hydrogen and nitrogen were added to a sample, which was then ionised at atmospheric pressure. Water reacted with the N_2H^+ ion in the ion source, which resulted in a decrease in the fraction of these ions

$$N_2H^+ + H_2O \rightarrow H_3O^+ + N_2.$$

The concentration of water was determined from the intensity of the N_2H^+ ion peak using a quadrupole mass spectrometer. The authors succeeded in plotting the dependence of water content on the change in the intensity of the N_2H^+ ion band in the low concentration region down to 5×10^{-7} mol%. However, no data were reported to confirm the validity of the above analytical technique.

Although there are several examples of successful application of gas chromatography and mass spectrometry for water determination in volatile high-purity compounds, these methods have not become widespread. This results from the difficulties in specimen preparation, the considerable probability of uncontrolled substance loss and irreversible transformations of the analysed compounds in chromatographic columns [39-41] and/or in the ionisation chamber.[34]

Spectroscopic methods do not suffer from many of the above drawbacks. These methods have high sensitivity, selectivity and accuracy and provide the possibility of the unambiguous

identification of components in the sample. A water molecule is characterised by intense absorption in many regions of the electromagnetic spectrum. The 'strong' lines in the medium IR and sub-millimeter ranges are the most suitable for performing highly sensitive analyses.

The quantitative absorption spectroscopic analysis is based on the relation between the concentration of absorbing atoms and the change in the intensity of radiation passed through the analysed medium, i.e., the Bouguer – Lambert – Beer law:

$$I(\nu) = I_0(\nu)\exp[-k(\nu)x]. \quad (1)$$

Here $I(\nu)$ and $I_0(\nu)$ are the intensity of the radiation passed through the sample and that of the incident radiation, respectively. The x parameter is related to the concentration of absorbing molecules n, and the length of the optical path l:

$$x = nl; \quad (2)$$

$k(\nu)$ is the absorption coefficient,

$$k(\nu) = Af(\nu - \nu_0), \quad (3)$$

where the $f(\nu - \nu_0)$ function characterises the shape of the spectral line contour (the Lorentz, Doppler or Voigt profile or their combination), and ν_0 is the frequency corresponding to the centre of the absorption line. The A parameter is usually called line intensity, line strength, or integral absorption coefficient.

$$A = \int_{-\infty}^{+\infty} k(\nu)\mathrm{d}\nu, \quad (4)$$

Analysis of Eqns (1) and (4) shows that the dimensionality of A is $\nu[x^{-1}]$, where ν is usually expressed as the wave number (cm^{-1}), and the diversity of measurement units for the concentration and optical path length predetermines the existence of various units for A. The relations between these units have been reported, for example, by Pugh and Rao.[42] Some researchers assume that $x = 1$ in equation (1) (unit concentrations and lengths), and in some cases the absorption coefficient γ is used, which is measured in reciprocal centimetres. The minimum γ determined usually characterises the sensitivity of the spectroscopic method.

Given the known values of A or γ for a spectral line (band) and having measured its integral (peak) intensity, one can determine the desired concentration of the analysed compound. If A or γ are unknown, a calibration plot should be used.

Let us consider the main results in determining micro-amounts of water in volatile high-purity compounds by IR absorption and microwave absorption spectroscopy.

4. Infrared spectroscopy

Table 1 presents the average and relative integral absorption coefficients for the main vibrational bands of water molecules in the gas phase. One can see that the band due to deformation vibrations, ν_2, which is the least affected by intermolecular interactions, has the maximum intensity. Refs 43 and 44 report the calculated and experimental integral absorption coefficients of separate lines in the regions corresponding to the stretching and deformation vibrations. Although the IR region contains the most intense vibrational-rotational transitions of water molecules, standard diffraction instruments, even those equipped with multiple-pass cells, probably do not provide detection limits below 10^{-4} mol%.[11,45]

In recent years, IR spectroscopy with Fourier transformation of the spectrum has found wide use. This method has a much higher sensitivity and selectivity, and its application for determining water in gases shows much promise. Ref. 47 presents a procedure for the Fourier-IR spectroscopic determination of traces of water in gaseous nitrogen and hydrogen chloride (detection limit: 10^{-5} mol%). Andreev et al.[46] proposed a procedure for determination of water in oxygen with a detection limit of 6×10^{-6} mol%. According to this procedure, a stream of the gas to be analysed passes through a multiple-pass cell, whose optical path is 20.75 m. The water concentration was found to be 7×10^{-5} mol%, this limit being imposed by the capacity of the device for the drying of oxygen by cryofiltration.[7]

Table 1. Integral absorption coefficients (A/cm^2 atm^{-1}) of the vibrational–rotational bands in the IR spectrum of water in the gas phase.[42]

Frequency (spectral region)/cm^{-1}	A_{mean} (at 300 K)[a]	A_{rel}[b]
1595 (ν_2)	277.8	100
3152 ($2\nu_2$)	1.73	0.6
3657 (ν_1)	10.2	3.7
3756 (ν_3)	202.3	72.8
2.7 μm	182.8[c]	65.8
1.9 μm	20.3[c]	7.3
1.4 μm	16.7[c]	6.0
1.1 μm	1.78	0.6

[a] The mean value of A given is based on data from different authors. [b] The relative value of A is given (the value of 100 corresponds to A for the most intense band, ν_2). [c] The overall value of A for all the lines in the specified range is given.

It was noted above that the limit of water detection in gases below 10^{-4} mol% cannot be attained by diffraction IR spectrometers, primarily because of the low resolution of these instruments. The resolution of the classical molecular spectroscopic methods in the gas phase is generally restricted by the instrumental resolution of the spectrometers. This value is as low as 0.003 cm^{-1} for interferometric spectrometers.[48] The resolution of dispersion spectrometers is normally 0.1 cm^{-1}. For comparison, the interferometric order of magnitude of the Doppler width of the stretching–rotational absorption lines of molecular gases is 10^{-3} cm^{-1} (in the middle IR region).

It can be shown [42] that the following relation is valid for the intensity of the radiation absorbed by a substance (ΔI) and the incident radiation (I_0)

$$\frac{\Delta I}{I_0} = k(\nu)\frac{\delta\nu}{\Delta\nu}, \quad (5)$$

where $\delta\nu$ is the width of the absorption line and $\Delta\nu$ is the spectral resolution.

It follows from the above that the use of instruments with a higher spectral resolution (low $\Delta\nu$) makes it possible to decrease the instrumental detection limit for molecular admixtures.

The creation of more sensitive analytical IR spectrometers became possible owing to the use of lasers with tuneable wavelength as radiation sources. Lasers have a higher spectral power, and the lines generated by them are narrower than the resolution achieved in dispersion and interference instruments. For example, Kreuzer et al.[49] showed, on an experimental basis, the possibility of determining water vapour in nitrogen and air when its content was ca. 1.4×10^{-6} mol%, using a CO laser and an optical-acoustic detector. The measurements were carried out at a wavelength of 5.94 μm ($\nu = 1683.02\,cm^{-1}$).

The use of a Nd laser makes it possible to record ca. 116 absorption lines of water vapour. The most intense line has an absorption coefficient of 10^{-9} cm^{-2} atm^{-1} (1.7×10^{-8} cm^{-1}),[50] which allowed the authors [51] to attain a ca. 10^{-4} mol% detection limit for the concentration of water in air.

It was proposed [52] to determine the content of water by the optical-thermal method. A CO laser served as the radiation source. From an estimate based on the signal/noise ratio, the practical detection limit for the method is 7.5×10^{-6} mol%.

Record-breaking low limits for the detection of water in various gases were attained using spectrometers based on tuneable diode lasers. The use of such instruments in molecular analysis has been reported in Refs 53 – 56.

The authors [57] managed to determine the minimum width of lines generated by semiconductor $PbS_{1-x}Se_x$-based lasers, which

was as low as 7×10^{-7} cm^{-1} at a wavelength of 5.3 μm. The line width of the radiation of diode lasers is usually $\sim 10^{-5}$ cm^{-1}, but this is much less than the width of the Doppler contour of the absorption line, which is, for example, $\sim 10^{-3}$ cm^{-1} near $\lambda = 10$ μm. On the other hand, the spectral density of the power of diode lasers is $\sim 10^9$ times higher than that of thermal radiation sources, which makes it possible to determine the concentration of molecular admixtures below 10^{-5} mol%.

As noted above, the theoretical maximum sensitivity of high-resolution spectrometers can be characterised by the minimum detectable absorption coefficient, γ_{min}. The following expression for this value was found using the data in Refs 58 – 60:

$$\gamma_{min} = \left[\frac{4}{l\sqrt{2}}\right]\left[\frac{N}{P_0}\right]^{1/2}, \quad (6)$$

where $N = 2h\nu\Delta f$ is the power of the quantum noise ($\Delta f = 0.5\pi\tau$ is the transmission band width of the detection system (Hz); τ is the constant of accumulation time, s; ν is the wavenumber, cm^{-1}; and h is the Planck constant); P_0 is the power of the incident radiation; and l is the optical path length, m.

Assuming that $P_0 = 0.71$ mW, $l = 1$ m, and $\tau = 1$ s, and that a signal/noise ratio of $3\sqrt{2}$ is required for a minimum determination,[58] we obtain $\gamma_{min} = 2 \times 10^{-9}$ cm^{-1}. A relation is known between the absorption coefficient and the concentration x (ppm) of molecules absorbing the radiation, the half-width of the analytical line ($\Delta\nu$), and the pressure in the cell (p).[61]

$$\gamma = \frac{kxp}{\Delta\nu} \quad (7)$$

The proportionality coefficient k is determined from the parameters of the analytical line of the additive in the pure state at the same pressure p. When the concentration of the additive is x, we have:

$$x = \frac{\gamma_{min}}{\gamma_0}\frac{\Delta\nu}{\Delta\nu_0}, \quad (8)$$

where γ_0 and $\Delta\nu_0$ are the above parameters for the pure additive.

Taking into account the data in Refs 44, 46 and 62, the $\gamma_0\Delta\nu_0/\Delta\nu$ value for lines in the region of 1600 cm^{-1} (which is usually chosen as the analytical region for water) can be assumed to be 20 cm^{-1}. Then, the theoretical minimum water concentration that can be determined by this method is as low as 9×10^{-9} mol%.

Relatively few studies dealing with the use of diode laser spectroscopy for water determination in permanent gases are known. In Ref. 63, the study was carried out in a multiple-pass cell with an effective length of 500 m using an analytical line at 1135 cm^{-1}. The detection limit was 5×10^{-6} mol%. In Ref. 64, a differential method was proposed for water determination in helium, nitrogen, oxygen, and argon based on the line at 1653 cm^{-1}. Two laser beams were passed through a reference cell ($l = 7$ cm) containing water vapour at a pressure of 6.7 Pa and then through a working cell ($l = 28$ cm) with a stream of the analysed gas at a pressure of 1.3 kPa. The instrument was calibrated by the standard addition method in the concentration range of $2 \times 10^{-7} - 1 \times 10^{-4}$ mol% for a 2 m absorbing path. Mucha[65] used a simplified version of the instrument described in Ref. 64 for determining ca. 5×10^{-4} mol% water in small volumes (of the order of magnitude of the volume of an integrated microcircuit, 0.01 – 0.1 cm^3). The undesirable effect of gas liberation due to adsorption — desorption was eliminated as a result of the short measurement time ($\leqslant 10$ μs). In Ref. 66, an admixture of water was determined in helium serving as the heat carrier for several types of nuclear reactors. The detection limit was $(1 - 6) \times 10^{-5}$ mol% for the analytical line at 1435 cm^{-1} with an absorption path of 100 m.

The authors of a work cited above [46] report the determination of the water admixture in high-purity oxygen, dehydrated by cryofiltration,[67] using the diode laser spectrometer described in Ref. 68. The analytical line at 1675.17 cm^{-1} was used; the gas pressure in a flow cell ($l = 1.5$ m) was 40 Torr. The minimum measurable absorption coefficient was 2×10^{-7} cm^{-1}, and the water detection limit was 8×10^{-7} mol% (the standard deviation was $s_r = 0.4$ for $c_{H_2O} < 8 \times 10^{-7}$ mol%). These values differ from the above theoretical limiting values of γ_{min} and x_{min}. However, one should take into account that the diode laser used in Ref. 46 operated in a pulse mode with an averaging time $\tau \simeq 10^{-3}$ s. Under these conditions, the corresponding limiting values of the γ and x parameters increase by a factor of ~ 30, according to Eqns (6) and (8). The difference between the values of γ and x predicted and obtained experimentally [46] is not high if one bears in mind that the γ_{min} was estimated assuming an ideal receiving system.

Table 2. Detection limits c_{min} (mol%) and relative standard deviations s_r of the water admixture in high-purity permanent gases and hydrides obtained by absorption diode laser IR spectroscopy together with the half-widths of the analytical line $\Delta\nu$ (cm^{-1}) and its broadening coefficients ξ (cm^{-1} Torr^{-1}).[68,69]

Compound	$c_{min} \times 10^5$	s_r (c_{H_2O})[a]	$\Delta\nu \times 10^2$	$\xi \times 10^3$
O_2	0.08	0.4 ($< 8 \times 10^{-7}$)	0.86	0.24
Ar	0.04	0.17 (1.6×10^{-6})	0.66	0.158
He	0.04	0.11 (1.3×10^{-4})	0.66	0.158
GeH_4	4	0.15 (2.0×10^{-6})	0.66	0.158
H_2Se	1	0.08 (2.0×10^{-3})	3.2	1.06
NH_3	6	0.06 (3.0×10^{-2})	7.2	2.40

[a] The s_r values refer to the water concentrations specified in parentheses.

Ref. 69 reports a technique for determining a micro admixture of water in argon, neon, germane, hydrogen selenide, and ammonia. The analytical part of the instrument was first dried by passing through it dry oxygen with a water content below the detection limit of the method (4×10^{-7} mol%). The above gases were analysed by the pumping in – pumping out technique, rather than in a gas stream. Table 2 presents the water detection limits and some spectral parameters of the analytical line.

One can see that diode laser spectroscopy makes it possible to obtain record-breaking low water detection limits in nonpolar high-purity gases, including those whose molecules are characterised by considerable inherent absorption in the regions of the analytical lines of water (germane, ammonia).

An urgent problem is the determination of water in the condensed phases of low-boiling compounds (permanent gases, halides, hydrides, etc.) and in volatile compounds that are liquid under the usual conditions. IR spectroscopy seems to be the most convenient method for this purpose; however, high- and ultrahigh-resolution spectroscopic methods cannot be used because of the strong broadening of spectral lines due to intermolecular interactions. Increasing the thickness of the absorbing layer used in the traditional IR spectroscopic method is often also impossible because of the overlap of absorption bands (in many cases, even the second- and third-overtones) of the main compound. The above restrictions should be of little importance when analysing liquefied monotonic and diatomic permanent gases that are transparent in the IR region. Low temperatures favour the disappearance of the rotational fine structure of the analytical bands of admixed molecules and their narrowing in comparison with the bands of gases and solutions under the usual conditions. In addition, liquefaction leads to concentration of a number of admixtures, so that relatively thin optical layers can be used. In fact, IR cryospectroscopy has been used successfully for analysing liquid oxygen and certain permanent gases.[70,71] However, the use of this method for water determination in the above objects by measuring the intensities of absorption bands in the regions of stretching or deformation vibrations is hindered by the very small solubility of water at low temperatures. In particular, this follows from the experimental data in Refs 70 and 71. For example, only a broad band of varying intensity (depending on the degree of

Table 3. The positions of the maxima of the analytical bands, detection limits, and standard deviations of the determination of the water admixture and hydroxyl-containing hydrolysis products in liquid volatile inorganic chlorides obtained by IR spectroscopy.[74-76]

Chloride	Substance to be determined	ν/cm^{-1}	$c_{min} \times 10^4$ (mol %)	s_r
$SeCl_4$	H_2O	1600	10	4.32
	$Ge(OH)Cl_3$	3603	80	3.60
$SnCl_4$	H_2O	1586	5	3.23
	H_2O	3553	6	2.69
	H_2O	3636	7	3.05
$AsCl_3$	H_2O	1600	5	3.74
	H_2O	3659	8	4.22
	$As(OH)Cl_2$	3525	3	2.61
$SiCl_4$	$Si(OH)Cl_3$ (see [a])	3670	1-9	–
$POCl_3$	$PO(OH)Cl_2$ (see [a])	3200	5	–

[a]The anticipated hydrolysis products.

drying) in the region of 3000-3600 cm^1, which corresponds to an ice solid phase, is observed in liquid oxygen.

Rebiai et al.[72] reported that they recorded intense narrow lines at 3604 and 3707 cm^{-1} in the IR spectrum of liquid nitrogen exposed to air. These lines were attributed to the stretching vibrations of water, indicating an unusually high ($\sim 10^{-3}$ mol%) solubility of the latter. It has been noted that such interpretation of the observed bands is erroneous;[73] more likely, they correspond to the Fermi-resonance doublet of CO_2 molecules. As noted above, the solubility of water in liquid nitrogen is 4×10^{-7} mol%.[24]

Refs 74-76 describe an IR spectroscopic technique for the determination of the concentrations of water and/or hydrolysis products in liquid high-purity germanium, tin, arsenic, silicon and phosphorus chlorides. Table 3 presents the detection limits found.

Within the scope of an IR spectroscopic study of the molecular state of the water impurity in liquefied high-purity volatile inorganic hydrides of Group V and VI elements (see below), the following estimates of the detection limit of water at 290 K were obtained (mol%):[77] $\sim 3 \times 10^{-4}$ (PH_3), $\sim 7 \times 10^{-5}$ (AsH_3), $\sim 3 \times 10^{-4}$ (H_2S) and $\sim 2 \times 10^{-4}$ (H_2Se).

5. Microwave spectroscopy

Microwave spectroscopy provides high-resolution spectra of the purely rotational transitions of molecules (the relative width of lines in the spectra can be as low as 10^{-6}). The practical application of microwave spectroscopy for the analysis of mixtures is mostly restricted by technical factors: only the millimetre range (4-0.7 cm, 8-40 GHz), in which the line intensities for the majority of light molecules are low, has been developed sufficiently. For water, the most intense rotational transitions (whose intensities are, however, by one or two orders of magnitude lower than those in the IR range) are observed in the submillimetre range (10^{-1} to 10^{-2} cm, 100-1200 GHz).[78,79]

The 'adoption' of the sub-millimetre range started about 30 years ago after sufficiently powerful coherent tuneable radiation sources, the backward wave oscillators (BWO), had been created. However, the construction of 'classical' spectrometers (in which the useful signal is found from changes in the parameters of the radiation passed through a sample) on the basis of these sources did not give the desired result. In fact, expression (6) allows one to estimate the minimum determinable absorption coefficient for any 'classical' spectrometer (CS). For a typical power of a BWO equal to 1 mW (which is an order of magnitude higher than for diode lasers), $\tau = 1$ s, and $l = 1$ m, we obtain $\gamma_{min} \simeq 10^{-10}$ cm^{-1} (for a $3\sqrt{2}$ signal/noise ratio). It should be noted that the actual sensitivity with respect to the absorption coefficient does not exceed 10^{-6} cm^{-1} of separate points of the range [80] due to the considerable interference in the ultrahigh frequency region. The possibilities of the submillimetre spectroscopy were implemented in a radio-frequency spectrometer with acoustic detection (RAD), whose principle of operation is analogous to the above optical-acoustic spectrometer based on a CO-laser.[81] In this case, the expression for the minimum determinable absorption coefficient has the form [81]

$$\gamma_{min} = \frac{3 \times 10^{-9}}{P_0}. \quad (9)$$

For a power of a BWO equal to 1 mW and for a $3\sqrt{2}$ signal/noise ratio, we obtain $\gamma_{min} = 10^{-8}$ cm^{-1}. The actual sensitivity coincides with the predicted value ($\gamma_{min} = 3 \times 10^{-8}$ cm^{-1}, see Ref. 81) and can be as high as 10^{-10} cm^{-1} when a resonator cell is used (see Ref. 82). Using formula (8), one can also estimate the theoretical detection limit for a water admixture on a RAD. For the analytical line at 556.436 GHz, $\gamma_0 = 0.9$ cm^{-1},[79] $\Delta\nu/\Delta\nu_0 = 10^{-1}$ (water in argon [83]), and $x_{min} \approx 1 \times 10^{-7}$ mol%.

The above method was used for assaying water in certain volatile inorganic hydrides.[84] When the analysed gas was passed through a cell, the detection limit was found to be 1×10^{-5} mol%. The considerable difference between the theoretical and actual detection limits results primarily from the design features of the analytical cell of the spectrometer (the presence of a polymer membrane which hindered heating of the cell) and the imperfection of the receiving device, an amplifying microphone. The following results were obtained:

Hydride	NH_3	GeH_4	H_2S	H_2Se	H_2Te
$x_{H_2O} \times 10^3$ (mol %)	0.3	0.8	0.6	1	70

Water determination by submillimetre radio-frequency spectroscopy in volatile inorganic nonpolar silicon and germanium chlorides was studied in Ref. 85. In order to increase the sensitivity, a cylindrical multi-mode nontuneable resonator 20 mm in diameter and 300 mm long with two fixed reflectors was used as the analytical cell. The detection limit in this technique was 9×10^{-7} mol% at a sample pressure of 2.5-13 kPa. It was also reported that, at the optimum pressure in the cell (270-800 Pa), determination of water at a concentration of 3×10^{-7} mol% is possible. However, this requires that the water background be diminished by more thorough degassing or by creating a stream of the analysed compound through the measuring cell. The water contents (in the molecular form) in high-purity samples of $GeCl_4$ and $SiCl_4$ were $(5 \pm 0.3) \times 10^{-5}$ and $(2 \pm 0.2) \times 10^{-5}$ mol%, respectively. According to the data in Ref. 85, hydrolysis of the chlorides in the cell during analysis did not lead to a systematic error in the determination.

The use of resonator cells in the RAD increases the amount of radiation absorbed by the sample. It is also a realistic way of increasing the sensitivity of submillimetre spectroscopy. A gain in signal intensity by a factor of 3-4 can be attained by using the water line at 1097 GHz with $\gamma = 2.8$ cm^{-1} (see Ref. 79). Note that the power of radiation sources in the submillimetre range is 1-2 orders of magnitude higher than that in diode laser spectroscopy, and the averaging times are much longer (by 2-3 orders).

Thus, although the sensitivity with respect to the absorption coefficient of submillimetre radiofrequency spectroscopy is somewhat less than that of diode laser spectroscopy, the sub-millimetre radiofrequency spectroscopy with acoustic detection can be used successfully for high-sensitivity assays of water in volatile compounds, such as inorganic hydrides and chlorides of subgroup IVA elements that are transparent in the microwave region. It would be undoubtedly useful to combine microwave spectroscopy with a 'pure' analytic cell (without foreign internal elements) similar to those used in the 'classical' IR spectrometers (preferably, with retention of the sensitivity of the latter). The first step in this direction is the creation of a microwave spectrometer based on coherent spontaneous radiation (CSR), which currently operates in the 70 GHz region. The expression for the minimum absorption coefficient determinable by this spectrometer is similar

to expression (6)[60]

$$\gamma_{min} = \left(\frac{4}{l}\right)\left(\frac{P_t}{P_0}\right)^{1/2}, \quad (10)$$

where $P_t = 4kT\Delta f$ is the power of the thermal noise (Δf is the pass band of the recording system); l is the length of the measuring cell, whose design is analogous to that of the cell used in diode laser IR spectrometers.

For a BWO power equal to 1 mW, $T = 300$ K, $\tau = 1$ s and a $3\sqrt{2}$ signal/noise ratio, we obtain $\gamma_{min} = 8 \times 10^{-10}$ cm^{-1}, which is somewhat better than for a diode laser IR spectrometer. A sensitivity of 1×10^{-10} cm^{-1} has been obtained experimentally in the region of 37 – 178 GHz.[86] The analytical possibilities of the a CSR spectrometer were also studied in this work for the determination of an admixture of methanol in ethanol. The detection limit was found to be 8×10^{-5} mol%.

Thus, the combination of absorption IR spectroscopic methods with thermal and diode-laser radiation sources as well as microwave spectroscopy in the millimetre and sub-millimetre regions makes possible highly-sensitive determinations of water admixtures in gaseous and liquid inorganic compounds. The preparation of the samples needs particular attention in such cases.

III. Molecular state of water

In order to determine the structural and energetic (thermodynamic) characteristics of complexes formed by water molecules with molecules of the environment, it is necessary to study the properties of such complexes both in the gas and liquid phases. Under real conditions in dilute solutions, the concentration of the complexes is generally low, but they can affect considerably the physicochemical properties of high-purity compounds.[87] Therefore, preliminary investigation of water-based complexes at comparable concentrations of the components or at a small excess of one of them is of great importance. This task is accomplished by theoretical quantum-chemical methods and experimentally, primarily by spectroscopic methods.

1. Water complexes in the gas phase

For most of the gases, the depth of the potential well D_e is of the order of magnitude of the translational energy of molecules at the critical temperature $D_e = kT_k$, where T_k is the critical temperature. At $T < T_k$, the energy of molecular interaction exceeds the thermal energy, and stable complexes are formed. However, the number of complexes is strongly dependent on temperature and pressure. For the equilibrium complex-formation process

$$B..HA \leftrightarrows B + HA \quad (11)$$

the equilibrium constant is expressed as [88]

$$\frac{n_{B...HA}}{n_B n_{HA}} = \left(\frac{h^2}{2\pi kT\mu}\right)^{3/2} \exp\frac{D_0}{RT}, \quad (12)$$

where $n_{B...HA}$, n_B and n_{HA} are the numbers of the corresponding species in a unit volume in the equilibrium vibrational – rotational state; D_0 is the dissociation energy corresponding to this state;

$$\mu = \frac{M_B M_{HA}}{M_B + M_{HA}},$$

where M_i are molecular masses.

The equilibrium constant is determined experimentally by microwave spectroscopy by measuring the absolute intensities of the rotational transitions for two or three participants of reaction (11) in an equilibrium gaseous mixture. This can give the dissociation energy of the complex in the zero-point vibrational – rotational state D_0, which is related to the dissociation energy D_e by the expression [88,89]

$$D_e = D_0 + N_A\sum_i \tfrac{1}{2}h\nu_i(B...HA) - N_A\sum_i \tfrac{1}{2}h\nu_i(B) - N_A\sum_i \tfrac{1}{2}h\nu_i(HA), \quad (13)$$

where the second, third, and fourth terms contain sums of the contributions of zero-point vibrations from all vibrational modes except those of intermolecular deformation vibrations in the complex; N_A is the Avogadro number.

It should be noted that the equilibrium constant of reaction (11) can also be determined purely thermodynamically from the second virial coefficient. In particular, microwave spectroscopy was used to study in detail the dimerisation of water. [88]

In order to calculate theoretically the equilibrium constant of reaction (11), one should know the molecular constants of the complex and its dissociation energy D_e. The latter coincides with the electronic intermolecular interaction energy ΔE, which is found by nonempirical quantum-chemical calculations.

Many studies have been devoted to calculations for complexes of water with light molecules. It is noteworthy that the resulting values of intermolecular interaction energies ΔE depend on the chosen basis set and on the number of corrections introduced additionally, which are related both to physical effects (allowance for the correlation energy ΔE_{cor} in the second- and fourth-order Moeller – Plesset perturbation theory) and the errors in the computational methods (the superposition error due to incompleteness of the basis set ΔE_{BSSE}). These problems are discussed in more detail in Refs 90 and 91 for example.

Table 4 presents the results of a series of studies dealing with the calculation of the energies of the intermolecular interaction of water with certain monotonic and diatomic molecules.

According to the data in Refs 93 and 95, water molecules form linear complexes with molecules of the inert gases, nitrogen, and carbon monoxide. These complexes can be regarded as hydrogen-bonded. Detailed calculations of the potential surface of the HOH...Ar complex showed [94] that other orientations of an argon atom relative to a water molecule are possible, up to a mutually perpendicular orientation of the symmetry axis of the water molecule and the Ar – O axis. In the oxygen complex, the O – O...OH_2 orientation is preferable. On the whole, calculations predict that complexes of water with permanent gases are very weak.

Ref. 100 reports the results of calculations for complexes of water with hydrides. The calculations were performed in terms of the widest possible basis set and took the correlation energy into

Table 4. Results of quantum-chemical calculations of energies of complexes of water and certain permanent gases.

Complex	$-\Delta E$/ kcal mol^{-1}	Method	Ref.
HOH...N_2	0.9	Self-consistent field (SCF), 4-31G and MINI-4 basis sets	92, 93
HOH...Ne	0.1	SCF, 6-31G** basis set with allowance for electron correlation energy in the second-order perturbation theory of Moeller – Plesset	93
HOH...Ar	0.4	ditto	93, 94
HOH...CO	1.3	SCF, 4-31G and MINI-4 basis sets	95, 98
HOH...O_2	0.9	SCF, 6-31G** basis set	96, 97
HOH...H_2	0.6	Moeller – Plesset perturbation theory	99

Table 5. Results of quantum-chemical calculations of the energies and structures of water–hydride complexes [100]

Complex	R/Å	r/Å	θ/deg.	$-\Delta E$/kcal mol^{-1}		$-\Delta H^{298}$/kcal mol^{-1}
				CF	MP4	
HOH...NH_3	3.039	0.955	2.3	4.9	6.6	4.7
HOH...PH_3	3.928	0.949	3.0	1.6	2.2	0.8
HOH...OH_2	2.971	0.952	5.3	4.1	5.3	3.6
HOH...SH_2^a	3.774	0.949	3.4	1.8	2.7	1.3
HSH...OH_2	3.619	1.327	3.0	1.9	2.9	1.5
FH...OH_2	2.720	0.922	4.6	7.6	9.1	7.4
ClH...OH_2	3.243	1.277	2.2	4.1	576	4.4

Note. The following designations are used: R is the distance between the X and Y atoms linked by a hydrogen bond; r is the length of a X–H bond participating in hydrogen bond formation; θ is the angle between the X–H bond and the X–Y line; the structural parameters were calculated by the SCF method in terms of the 6-31G(d) basis set; CF is the electron energy calculated by the SCF method in terms of the 6-31+G(2d,2p) basis set with the geometry optimised in terms of the 6-31G(d) basis set; MP4 is the energy with allowance for electronic correlation calculated by the fourth-order Moeller–Plesset perturbation theory; ΔH is the enthalpy of the complex calculated by the method from Ref 101 using the electronic energy in terms of the MP4/6-31+G(2d,2p) basis and vibrational frequencies in terms of the 6-31G(d) basis set.

account. These results are given in Table 5, together with the complex-formation enthalpies and structural parameters of isolated complexes. The formation of linear H-bonds X–H...Y was found to occur in all the complexes. The HOH...NH_3 complex (C_s symmetry) is the most stable, while the water dimer (C_s symmetry) is markedly less stable. It should be noted that the calculated enthalpy of the latter is in good agreement with the value determined experimentally, [88] which is 3.7± 0.5 kcal mol^{-1}. The structure of the HOH...PH_3 complex is similar to that of the ammonia complex,[100] but the low enthalpy of formation makes it doubtful if the phosphine–water complex exists at room temperature. The same conclusion applies to hydrogen sulfide–water complexes, in which water acts both as a proton donor and a proton acceptor.

An analysis performed for complexes of hydrides with water taking into account ΔE and ΔH_{298} values suggests that their stability changes in the following order:

$$FH...OH_2 > HOH...NH_3 > ClH...OH_2 > HOH...OH_2 >$$
$$> HSH...OH_2 > H_2S...HOH > HOH...PH_3.$$

A comparative calculation of the structures and energies of the complexes of CH_4 and SiH_4 with water [103] in terms of the 6-31G* basis set taking into account the correlation energy showed that the structures of the complexes of CH_4 and SiH_4 with water differ considerably, which is explained by differences in the polarity of the $C^{\delta-}-H^{\delta+}$ and $Si^{\delta+}-H^{\delta-}$ bonds. The water–silane complex ($\Delta E = -2.4$ kcal mol^{-1}) is more stable than the complex with methane ($\Delta E = -1.3$ kcal mol^{-1}).

Despite the considerable progress in the quantum-chemical computational methods achieved in the recent years, experiment remains the main source of information about the structure and energy of weak complexes. High-resolution IR and microwave spectroscopic methods are used primarily for this purpose in the gas phase.

Data on the structure of complexes and their potential surfaces can be obtained by analysing the following spectral features: appearance of new lines corresponding to the complex itself; disappearance or displacement of lines of the starting monomeric components; changes in the intensities of lines corresponding to the monomers and complexes as a function of temperature and pressure.

It is convenient to study the above spectroscopic behaviour in high-resolution spectra, i.e. in the spectra of gases at low pressures and temperatures. This, in turn, means highly sensitive equipment is needed. The known methods for studying weak complexes in the gas phase are usually divided into equilibrium and non-equilibrium ones, depending on the thermodynamic state of the complexes under the experimental conditions.

When equilibrium methods are used, one tries to attain the highest possible concentrations of complexes by performing the measurements near the liquid–vapour phase equilibrium line. This approach makes it possible to measure the equilibrium constant and the enthalpy of formation of the complex. However, it is used only for sufficiently stable complexes, due to the low sensitivity of the equipment available at present.

Thomas [104] used IR spectroscopy to study the spectral characteristics of the $H_2O...HF$ gas-phase complex. Three bands characterising intermolecular hydrogen bonds were found, one band in the region of HF stretching vibrations, another in the region of water deformation vibrations, and the third, around 780 cm^{-1}, which corresponds to vibrations of the complex itself. Estimation of the enthalpy of complex formation gave the value of -6.2 kcal mol^{-1}, which corresponds to $D_0 = -5.5$ and $D_e = -7.1$ kcal mol^{-1}.

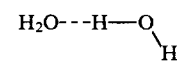
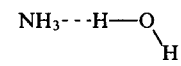
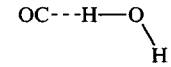
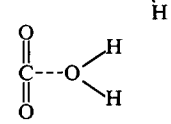
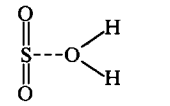
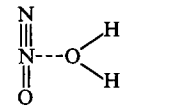
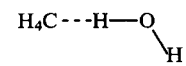
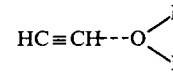
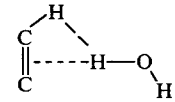
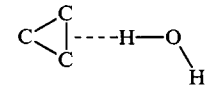
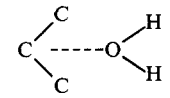
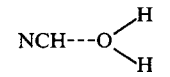
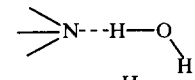
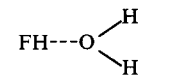
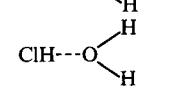
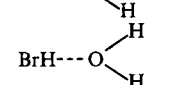
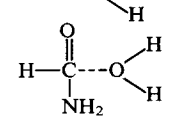
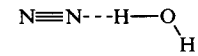
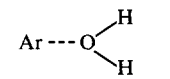
This is the only example, known to us, of a detailed study of a water complex in an equilibrium gas phase by IR spectroscopy in the traditional version using a diffraction spectrometer.

It was noted in a study cited above [47] that, for a resolution of 0.5 cm^{-1}, a broadening of water lines at 3803.8 and 3151.9 cm^{-1} in the region of the stretching vibrations of water was detectable in a gaseous mixture containing 2.6×10^{-3} mol% H_2O. This suggests that a hydrogen-bonded complex is formed in the gas phase between the molecules under consideration even at such a low concentration of water. When the resolution was altered to 2 cm^{-1}, the broadening of lines did not exceed the instrumental function. An indirect confirmation that hydrogen-bonded complexes are formed between water molecules and ammonia and hydrogen selenide in the gas phase at a water concentration of 10^{-2} mol% comes from data on the broadening of the analytical line of water in the region of its deformation vibrations presented in Table 2. Indeed, under the experimental conditions chosen,[47] the width of the absorption bands is mainly determined by the Doppler and collision broadening mechanisms. Taking into account the constancy of the Doppler-type contribution and the gas pressure in the cell, the broadening coefficients, differing by an order of magnitude, may indicate that the type of interaction in mixtures containing water in nonpolar gases (the van der Waals interaction) differs from that in mixtures containing water in polar gases (specific interaction with hydrogen bonds). As predicted by calculation (see Table 5), interaction of water with ammonia is considerably stronger than that with hydrogen selenide.

Thus, new high resolution IR spectroscopic methods, such as diode laser spectroscopy and Fourier-transform spectroscopy, show promise in the studies of weak complexes of water in the gas phase.

Microwave spectroscopy with Stark modulation in the millimetre range up to 75 GHz was used [105,106] to study the above

Table 6. Molecular constants of water complexes in the gas phase according to microwave spectroscopic data.

Molecule	Intermolecular distance[a]/Å	Force constant k_s/N m^{-1}	Dipole moment μ/D	Structure of the complex	Ref.
H_2O	2.05 (O...H)	11.7	2.64307		112
NH_3	2.02 (N...H)	14.5	2.972		113
CO	2.407 (C...H)	2.74	—		114, 115
CO_2	2.836 (C...O)	6.4	1.8522		116
SO_2	2.824 (S...O)	5.3	1.984		117
N_2O	2.97 (N...O)	—	1.480		118
CH_4	3.702 (C...H)	1.53	0.728		119
C_2H_2	2.229 (H...O)	6.5	2.0124		120
C_2H_4	2.481 (C=...H)	—	1.0943		121, 122
C_3H_6	2.34 C...H	—	1.209		123
C_3H_8	4.35 (C...O)	—	0.73		124
HCN	3.139 (C...O)	11.1	—		125, 126
$(CH_3)_3N$	1.82 (N...H)	—	2.37		127
HF	2.662 (F...O)	24.9	4.073		128–131
HCl	3.215 (Cl...O)	12.5	—		132
HBr	3.411 (Br...O)	10.5	—		133
H_2NCHO	—	—	1.05		134
N_2	2.42 (N...H)	—	0.833		135
Ar	3.398 (Ar...O)	0.90	0.73		136–138

[a]The symbols in parentheses indicate which pairs of atoms correspond to the distances specified.

H_2O...HF complex in an equilibrium gas phase. The composition of the following equilibrium mixture has been determined[105] at a pressure of 188 mTorr and a temperature of 238 K: $n_{H_2O} = 1.85 \times 10^{19}$, $n_{HF} = 6.66 \times 10^{20}$, $n_{H_2O...HF} = 10.03 \times 10^{15}$ m^{-3}; using Eqn (12), the dissociation energy of the complex was calculated to be $D_0 = -8.1$ kcal mol^{-1}. The total dissociation energy, $D_e = -10.2$ kcal mol^{-1} is in good agreement with the values in Table 5 obtained by quantum-chemical calculations, but is markedly higher than the spectroscopic value, which is -7.1 kcal mol^{-1}.[104]

The rotational spectrum of the H_2O...HF complex in the equilibrium gas phase at low temperatures was first observed in the submillimetre range of 180–350 GHz on a RAD-type spectrometer.[107] In this study[107] the experimental data (including those on the excited states of complexes) were considerably expanded in comparison with the data of previous studies,[105,106] the assignment of the previously observed spectral lines was corrected, and the spectroscopic constants were revised. The usefulness of studies on the submillimetre spectra of molecular complexes in equilibrium gas phases was demonstrated.

At present, the methods of microwave spectroscopy are used quite widely in studies of weakly bound complexes under non-equilibrium conditions. These methods include primarily molecular-beam electroresonance spectroscopy and the microwave Fourier spectroscopy of a pulsed beam.[108,109] In the former method, the complexes are formed in a gas, which flows into a vacuum from a premix chamber containing a mixture of an inert carrier gas and the gases under study at a pressure of 1–3 atm and $T = 300$ K. In the second method, the complexes are generated by a pulsed flow of a gas injected into a Fabry–Perot resonator at a frequency of $\sim$ 10 pulses per second.

Table 6 presents some molecular parameters of complexes of water with various proton donors and acceptors found by the specified methods. One can see that water exhibits proton-donating properties with respect to the NH_3, CO, CO_2, C_2H_4 and N_2 molecules. Conversely, water acts as a proton acceptor in other cases. One of the important molecular constants determined experimentally is the centrifugal distortion constant D_j. The latter is linked to the force constant of the vibration of the intermolecular hydrogen bond by the relation[110,111]

$$k_s = \frac{16\pi^2 B^3 \mu}{D_j}\eta, \qquad (14)$$

where B is the rotational constant, μ is the reduced molecular mass of the complex, and η is a correction introduced for complexes of a given type.

In turn, k_s is related to the depth of the potential well of the complex D_e by the expression[109]

$$D_e = \tfrac{1}{72} k_s r_e^2,$$

where r_e is the equilibrium intermolecular distance.

It is evident from the data in Table 6 that the complex of water with HF has the highest stability. As noted above, the thermodynamic characteristics of this complex were determined by microwave spectroscopy.[128] At $T = 298$ K and partial pressures of the starting components equal to 1 Torr, ca. 10% of the H_2O and HF molecules are bound in the complex. For comparison, in the case of HCN and HF ($k_s = 11.1$ N m^{-1}), only 5×10^{-4}% of the molecules are involved in complexes.[125] It is impossible to detect such complexes under the usual conditions.

Another method for studying experimentally isolated water-based weak molecular complexes in a nonequilibrium state is IR spectroscopy with low-temperature matrix isolation, in which a mixture of a gas or vapour under study and a diluent gas is rapidly condensed on a support at 4–20 K.[139,140] It is possible to observe simultaneously bands of monomers and 1:1 complexes under such nonequilibrium conditions only at high dilution (when the ratio of the concentrations of the gas under study and the diluting gas exceeds 10^3). Otherwise, bands corresponding to more complex associated species manifest themselves as the above ratio decreases. In addition, the important role of the non-uniform broadening in matrices makes it difficult to measure the shapes and intensities of the spectral bands of the complexes and, hence, to obtain quantitative information about their compositions and energies. The relative stability of the complex can be determined qualitatively from the low-frequency shifts of the bands of the stretching vibrations of water. Table 7 shows the results of studies on certain complexes of water with various inorganic proton acceptors, including two hydrides, viz. ammonia and hydrogen sulfide. It is seen that the band due to the symmetric stretching vibrations of water (ν_1) has the highest sensitivity to the electronic structure of acceptor molecules. Among the compounds studied, the maximum shift of this band is observed for the complex with NH_3, in agreement with the maximum value of the force constant of the NH_3...H_2O complex in the gas phase (see Table 6). The complex with H_2S is less stable than that with ammonia, but is more stable than the water dimer under the matrix conditions. It is noteworthy that, according to the results of studies[148,150] on the H_2S...H_2O complex, hydrogen sulfide displays proton-accepting properties with respect to water (Table 8).

The resulting HOH...SH_2 and HSH...OH_2 complexes have a linear structure. A number of bands were attributed to the $H_2S(H_2O)_2$ complex.

In complexes with hydrogen halides,[141,151–156] water also displays proton-accepting properties. Complexes of water with the halogens[149,157–159] and SO_2 in low-temperature matrices[144] are likely to be of the donor-acceptor type. Analysis of IR spectroscopic data for H_2O in Ar, Kr and N_2 matrices shows that the complexes of water with krypton are the most stable.

Thus, there are few hydrogen-bonded complexes of water with light molecules studied by IR spectroscopy in low-temperature matrices and directly in the gas phase, and complexes of only two hydrides, NH_3 and H_2S, have been studied. It should be noted that this is the only experimental evidence that a weak hydrogen-bonded complex is formed in the case of hydrogen sulfide.

2. Molecular complexes of water in the liquid phase

The interaction of water with the main compound in the liquid phase is more complex, since it can be paralleled by the association of molecules of the main compound as a background. To consider this aspect theoretically, one has to calculate the potential surfaces not only of the simple 1:1 water–main compound complex but also of more complex ones, $H_2O...n$ B, where $n \leqslant 4$ (in accordance with the coordination number of the water molecule). An experimental investigation of association processes in the condensed phase is very difficult because it is impossible to use high-resolution spectroscopy. However, much experience has been accumulated in spectroscopic studies of intermolecular interactions in solutions based on shifts and intensity changes of bands in the spectra of complexes with various compositions (see, for example, Refs 160–162). In particular, the IR spectra of complexes containing a hydrogen bond display bathochromic shifts $\Delta\nu$ of the stretching vibration bands of the proton donor in parallel with an increase in the integral absorption coefficient A relative to the spectral parameters of the isolated proton donor. Many empirical and semiempirical equations relating the $\Delta\nu$ and ΔA values to the stability of complexes characterised by the enthalpy of formation of the hydrogen bond have been proposed. The following relation can be taken as an example:[163]

$$\Delta H = (80 \pm 20)\frac{\nu'_{AH} - \nu''_{AH}}{\nu_{AH}}, \qquad (15)$$

where ν'_{AH} and ν''_{AH} are the frequencies of the stretching vibrations of an AH molecule in the free state and in a complex, respectively.

It seems more correct to use the increment of the integral absorption coefficient, for example in the form of the equation proposed by Iogansen,[164]

$$\Delta H = 2.9\Delta A^{1/2}, \qquad (16)$$

Table 7. Frequencies of the main vibrations of the H_2O molecule (cm^{-1}) in the free state and in complexes with some inorganic molecules according to the data obtained by IR spectroscopy with matrix isolation.

Inorganic molecule	ν_1	$\Delta\nu_1$	ν_3	$\Delta\nu_3$	ν_2	$\Delta\nu_2$	Ref.
Free state of water, H_2O (gas)							
	3657		3756		1595		
Complexes with inorganic molecules							
Ar	3638	19	3734	22	1589	6	141
N_2	3634	23	3728	28	1597	−2	143
Kr	3628	29	3724	32	1586	9	142
H_2O [a]	3575 [c]	63	3710 [c]	24	1611 [c]	−22	141
H_2O [b]	3634 [c]	4	3723 [c]	5	1594 [c]	3	141
SO_2	3631	7	3723	11	1591	−2	144
NH_3	3434	204	3702	32	1625	−36	145–147
H_2S [c]	3536	102	—	—	1614	−25	148
Cl_2	3637	0.5	3724	10	1587	2	149

[a] The water molecule acts as a proton donor.
[b] The water molecule acts as a proton acceptor.
[c] The ν values for complexes in an argon matrix are given.

where $\Delta A^{1/2} = (A'_c/m)^{1/2} - (A')^{1/2}$ is the difference between the integral absorption coefficients (in 10^4 cm mmol^{-1}) of the molecules bound in hydrogen-bond complexes (liquid phase) and of free molecules (gas or an inert solvent), and m is the number of hydrogen bonds.

It is reasonable to estimate the stability of the complexes using relations such as Eqns (15) and (16) for series of isotypical compounds under similar conditions.

The solubility of water is an important factor in experimental studies of the molecular state of water in liquid volatile compounds by IR spectroscopy. It is lower than the method sensitivity in liquefied permanent gases and in some polar compounds. Therefore, it is impossible to detect the changes in the intensity or positions of the stretching vibration bands of water due to its interaction with molecules of environment. However, the molecular state of water in liquid volatile inorganic chlorides of Subgroup IVA and VA elements has been studied by IR spectroscopy in sufficient detail.[165–167]

The IR spectrum of an aqueous solution of germanium tetrachloride ($c_{H_2O} < 10^{-2}$ M) in the region of 4000–1100 cm^{-1} displays bands at 3691, 3603, 2845 and 1600 cm^{-1}.[165] The relation between the intensities of the first two bands was found to be the opposite to that known from the literature for the ν_1 and ν_3 bands of water in CCl_4, an inert solvent structurally related to germanium tetrachloride. It was concluded that the vibrations of free water molecules correspond to the bands at 3691 (ν_3) and 1600 (ν_2) cm^{-1}.

The small low-frequency shift of the ν_3 band relative to the gas phase results from van der Waals interaction HOH...$GeCl_4$, whose energy, estimated from the relation between ΔH and $\Delta\nu$ proposed in Ref. 168, was found to be −1.4 kcal mol^{-1}. The band at 3603 cm^{-1} was attributed to the ν(OH) vibrations of the hydroxyl groups in the hydrolysis products, while the band at 2845 cm^{-1} was attributed to the stretching vibration of the HCl molecule. The hydrolysis of $GeCl_4$ in accordance with the simplest scheme

$$GeCl_4 + HOH \leftrightarrows Ge(OH)Cl_3 + HCl, \quad (17)$$

probably occurs only at low concentrations of water in $GeCl_4$ ($<10^{-2}$ M). When the concentration is increased, the intensities of the bands at 3691, 3603 and 1600 cm^{-1} increase, while that of the band at 2845 cm^{-1} decreases. Simultaneously, a series of new bands appear. Together these facts led the authors[165] to the conclusion that complex germanium hydroxochlorides $Ge(OH)_n.Cl_{4-n}$ and oxochlorides $Ge_nO_{n-1}Cl_{2n+2}$ are formed in solution.

The equilibrium of reaction (17) was studied directly in liquid $GeCl_4$ and in a CCl_4 solution. The hydrolysis constant $K_c = 1.74 \times 10^{-3}$ at 20 °C and concentrations of water in the range 10^{-3}–10^{-2} M, together with its temperature dependence in the range of 10–60 °C, were determined. It has been shown[169] that an admixture of water in $GeCl_4$ influences decisively the chemical forms of microadmixtures of sulfur, selenium, boron, silicon, aluminium, titanium, phosphorus and carbon.

The IR spectra of water solutions in $AsCl_3$ display bands at 3659, 3574 and 1600 cm^{-1} assigned to the ν_3, ν_1 and ν_2 vibrations of a water molecule respectively. The ν(OH) vibrations of hydroxyl groups correspond to a band at 3525 cm^{-1}, while the stretching vibrations of the HCl molecule are observed as a band at 2800 cm^{-1}.[167] The energy of the HOH...$AsCl_3$ interaction is somewhat higher than that for $GeCl_4$ and equals −2 kcal mol^{-1}. When the concentration of water is below 4×10^{-2} M, the hydrolysis follows the scheme

$$AsCl_3 + HOH \leftrightarrows As(OH)Cl_2 + HCl, \quad (18)$$

while at higher concentrations, arsenic hydroxochlorides $As(OH)_nCl_{3-n}$ and the oxochloride AsOCl are formed. The hydrolysis constant remains unchanged up to a water concentration of $\sim 10^{-2}$ M and equals 4.2×10^{-3} at 20 °C.

The IR spectrum of a solution of water in $SnCl_4$ displays bands at 3636, 3563 and 1586 cm^{-1} assigned to the ν_3, ν_1 and ν_2 vibrations of the water molecule.[166] In contrast to the IR spectra of solutions of water in $GeCl_4$ and $AsCl_3$ and the spectrum of the $SnCl_4 \cdot n H_2O$ crystal hydrate, the ν_2 deformation vibration band undergoes a bathochromic shift relative to its position in the gas phase. Taking into account the much higher intensity of the ν_2 band compared with those of the ν_3 and ν_1 bands (as in the gas phase), the authors[166] concluded that the intermolecular bond in the H_2O...$SnCl_4$ complex, involving an unshared electron pair of the oxygen atom in the water molecule and the unoccupied orbitals of the tin atom is of the donor–acceptor type, unlike the hydrogen bonds between the molecules of H_2O and $GeCl_4$ or $AsCl_3$. The energy of this interaction was estimated as −2.4 kcal mol^{-1}. Unlike germanium, arsenic, and tin chlorides, the concentration of free water in liquid silicon tetrachloride is lower than 10^{-4} mol%, which is in agreement with the above radio-frequency spectroscopic determinations of water in $SiCl_4$ in the gas phase.[85]

Table 8. Frequencies of the main vibrations (ν/cm^{-1}) of H_2O and H_2S in the free state and in complexes in a nitrogen matrix.[148,150]

Type of vibration	H_2O...HSH		H_2O			H_2S		
	H_2O	H_2S	monomer	dimer		monomer	dimer	
				D	A		D	A
ν_1	3628.1	2574.2 2570.2	3634.5	3627.2	3550.0	2619.3	2617.7	2579.0
ν_3	3719.0	2625.0 2623.6	3726.9	3715.0	3698.8	2632.4	2630.4	2624.7
ν_2	1597.9		1597.6	1601.0	1618.6	1179.6	1178.0	1181.5

Note. D = proton donor, A = proton acceptor.

Table 9. Spectral parameters of the stretching and deformation vibration bands of water in the gas phase, in CCl_4 solutions, and in liquid hydrides at 298 K.[170-173,180]

Solvent	ν/cm^{-1}								$A \times 10^8$/cm^2 molecule^{-1} s^{-1}	
	ν_1	$\Delta\nu_{1/2}$ [a]	ν_3	$\Delta\nu_{1/2}$	$\Delta\nu_{1/2}^{str}$	$\nu_1-\nu_3$	ν_2	$\Delta\nu_{1/2}^{str}$	$A(\nu^{str})$ [b]	$A(\nu^{def}) \times 10^8$ [b]
Gas	3657	—	3756	—	—	99	1596	—	22.8	25.2
CCl_4	3616	35	3707	45	—	92	—	—	30	—
PH_3	3606	60	3696	160	160	90	1598	~55	84	28
AsH_3	3610	~75	3698	120	170	88	1600	~50	71	35.5
H_2S	3560	~80	3645	110	~150	85	1606	42	203	32
H_2Se	3555	~80	3643	105	~150	88	1600	45	168	33

[a] The half-width of the ν^{str} overall band at half-height. [b] The integral absorption coefficient.

Hence, the equilibrium on the hydrolysis of $SiCl_4$ is almost completely shifted to the right.

$$SiCl_4 + n\,HOH \leftrightarrows SiCl_{4-n}(OH)_n + n\,HCl\,. \quad (19)$$

A similar behaviour of water is observed in phosphoryl chloride, in which the equilibrium of the reaction

$$POCl_3 + HOH \leftrightarrows PO(OH)Cl_2 + HCl\,, \quad (20)$$

is also shifted to the right,[76] and free water is not detected.

Information about the molecular state of water in liquid volatile inorganic hydrides of Group IV–VI elements at concentrations ca. $10^{-2}-10^{-3}$ mol% was obtained by a number of workers.[73,77,170-172] The considerable experimental difficulties encountered in studying the IR spectra of dilute solutions of water in hydrides come from the relatively 'narrow range of existence' of the liquid phase of hydrides and their low boiling points (<273 K). However, IR spectra can be recorded at higher temperatures (~ 300 K for all hydrides except silane, whose b.p. is 269.4 K) at increased pressures, but the cells must then withstand pressures of several tens of atmospheres. The appropriate experimental techniques are reported in Ref. 174. As noted above, the very low solubility of water in liquefied permanent gases at their boiling points precludes the recording of the bands of dissolved water even for considerable thicknesses of the absorbing layer (up to 100 mm). It has been shown [73] that the same problems in recording the bands of dissolved water arise in studies of systems based on nonpolar silane and germane. In addition, the region of stretching and deformation vibrations of water includes the rather intense overtone and combination bands of these hydrides.[77]

A different situation is observed in the case of dilute solutions of water in liquid hydrides of Group V and VI elements:[175,176] the 3400–3700 cm^{-1} region displays bands of the antisymmetric (ν_3) and symmetric (ν_1) vibrations of water molecules (similarly to solutions of water in organic solvents [177] and in liquid volatile chlorides) and a band due to deformation vibrations (ν_2); the integral absorption coefficient of these bands increases approximately by an order of magnitude compared with that in the gas phase (Table 9). This suggests that hydrogen bonds are formed between the molecules of dissolved water and the hydrides. The estimated energies of intermolecular interactions are presented in Table 10. For ΔH, the ranges of values estimated by Eqn (16) are given,[170-172] since the exact number m of hydrogen bonds formed by a water molecule with the hydrides in the liquid phase is unknown. For this reason, the limiting values were adopted — one and two H-bonds per molecule of water, representing the upper and lower limits of the strength of the hydrogen bond.

It follows from these data that, first, the stability of complexes of hydrides of Group VI elements with a proton donor — water — is higher than that of the complexes of Group V elements. Second, the stability of complexes of hydrides of the Fourth Period elements is lower than that of complexes of hydrides of the Third Period elements. It should be emphasised once more that these conclusions refer to two-component liquid solutions with a great excess of the proton acceptor. Nevertheless, the trends noted above are also observed in the calculated enthalpies of the hydrogen bond (see Table 5). The ΔH_{298} values for the complexes of PH_3 and H_2S fall within the range of experimental values. On the whole, the above series of the hydrogen bond strengths follow from the analysis of $\Delta\nu_s$, the low-frequency shift of the band due to the stretching vibrations of the proton donor (the HF molecule) in complexes with hydrides in an argon matrix,[178] although, according to these data, the complex of phosphine is more stable than that of hydrogen sulfide. Also, the data obtained do not contradict the results obtained in studies of the microwave spectra of complexes of certain hydrides in the gas phase [179] and by quantum-chemical calculations for such complexes.[180]

IR spectroscopy has been used[77,170-172] to determine the solubility of water in hydrides of Group V and VI elements, which are correlated with the energy of intermolecular interaction. A similar relationship was also established for the liquid–vapour separation factors α in the systems water–hydrides of Group V and VI elements:[77] although the ideal separation factors are much less than unity, the α value determined experimentally from solubility data is only a little less than unity for the H_2S-H_2O system and is markedly higher than unity for the AsH_3-H_2O system. As follows from Table 10, the intermolecular interaction energies in the systems differ markedly.

According to experimental results,[77] gaseous hydrates stable up to ~ 305 K are formed in saturated solutions of water (water concentrations of $10^{-1}-10^{-2}$ mol%) in hydrides of Group V and VI elements. A thermodynamic analysis of the structures of the hydrates and of the conditions governing their formation in processes involving the extensive purification of hydrides has been carried out.[181]

Table 10. Energy characteristics of hydride–water complexes.

Complex	$\Delta\nu_3$/cm^{-1}	$-\Delta H_{298}$/ kcal mol^{-1}, according to data in Refs		$-\Delta H^{theor}$/ kcal mol^{-1}	$\Delta\nu_s$/cm^{-1}
		77	170–172		
HOH...NH_3	–	–	–	4.7	913
HOH...PH_3	60	1.3	0.4–1.6	0.8	327
HOH...AsH_3	58	1.2	0.2–1.2	–	260
HOH...SH_2	111	1.9	1.2–2.5	1.3	302
HOH...SeH_2	113	2.2	1.0–2.4	–	299

Notes. $\Delta\nu_3$ is the difference between the frequencies of the stretching vibrations (ν_3) in the gas phase and in the complex in the liquid phase; ΔH_{298} is the enthalpy of formation of a hydrogen bond calculated from spectroscopic data for a solution of H_2O in a liquid hydride [from the shift of the ν_3 band according to Eqn (15)][77] or determined by the Iogansen Eqn (16) for $m = 1$ and $m = 2$;[170-172] ΔH^{theor} are the calculated enthalpies of the hydrogen bond (see Table 5); $\Delta\nu_s$ is the difference between the frequencies of the stretching vibrations of an HF molecule in the free state and in a complex with a hydride in an argon matrix.[178]

Table 11. Positions of the bands (cm^{-1}) due to the fundamental vibrations of water dissolved in organic and inorganic bases with different donor numbers (DN) according to Gutmann.[77, 165–167, 182]

Solvent	ν_1	ν_3	ν_2	$\Delta\nu$	DN
Gas	3657	3756	1595	99	–
Trichloro-trifluoroethane	3628	3721	–	93	–
Carbon tetrachloride	3613	3705	–	92	–
Tetrachloro-ethene	3613	3705	–	92	0
Carbon disulfide	3610	3701	–	91	2
Phosphine	3606	3696	1598	90	–
Arsine	3610	3698	1600	88	–
Chloroform	3607	3690	–	83	4
Germanium tetrachloride	–	3691	–	–	–
Toluene	3595	3681		86	4
p-Xylene	3592	3680		88	5
Mesitylene	3590	3677		87	10
Nitromethane	3579	3663	1623	84	6
Anisole	3548	3662		114	9
Arsenic trichloride	–	3659		–	–
Epichloro-hydrin	3542	3653	1621	111	13.9
Benzonitrile	3545	3650		105	11
Hydrogen selenide	3555	3693	1600	88	–
Hydrogen sulfide	3560	3645	1606	85	–
Benzaldehyde	3544	3639		95	16
Tin tetrachloride	–	3636		–	–
Acetonitrile	3543	3636	1632	93	14
Cyclohexanone	3530	3610		80	18
Acetophenone	3535	3612		77	15
Diethyl ether	3518	3590	1628	72	19.2
Dioxane	3517	3584	1639	67	14.8
Dimethyl sulfoxide	3444	3494	1663	50	29
Pyridine	3405	3450		45	33

A review[177] summarises the main spectroscopic parameters of water dissolved in various organic solvents. Some of these data are presented in Table 11. It is seen that an increase in the proton-accepting capacity of solvent molecules (basicity), characterised by the donor number (DN) leads to an increase in the low-frequency shift of the ν_1 and ν_3 bands and a decrease in the difference between them (the bands of symmetric and anti-symmetric vibrations approach each other). Liquid chlorides and hydrides can also be regarded as nonaqueous inorganic solvents. For example, germanium tetrachloride, phosphine and arsine are located in Table 11 between carbon disulfide and toluene, arsenic tetrachloride is located between anisole and epichlorohydrin (DN = 9 – 14), while hydrogen sulfide, hydrogen selenide, and tin tetrachloride occupy a position between benzonitrile and acetonitrile (DN = 13 – 18).

IV. Conclusion

Modern spectroscopic methods make it possible to solve fairly complex problems in the determination and study of the molecular state of water present as an admixture in high-purity volatile inorganic compounds. The theoretical instrumental limit in the detection of water by diode laser spectroscopy and sub-millimetre spectroscopy (10^{-8} mol%) is quite sufficient for analyses in studies on the extensive purification of these compounds. The detection limits actually achieved are generally one or two orders of magnitude higher due to methodologology difficulties resulting from the impossibility of taking full account of all the ways in which background moisture can enter the substance analysed. The use of unique apparatus, the long preparation of spectrometers for analyses, and the use of expensive cooling agents (liquid helium) make the cost of one analysis rather high.

The optimisation of methods for the removal of water from volatile compounds and of the processes for the gas-phase synthesis of materials involving these compounds, as well as investigation of processes associated with the storage of high-purity compounds, especially those tending to react chemically, require data concerning not only the concentration of the water admixture but also the form of its existence in the gas and liquid phases. It was shown above that such information has been obtained for solutions of water in certain liquid high-purity chlorides and hydrides. However, the data on the stability of the resulting complexes, their concentration and the mean number of intermolecular bonds are clearly insufficient. The methods of diode laser spectroscopy and microwave high resolution spectroscopy are promising for investigating the mechanism and thermodynamics of complex formation reactions involving water in the gas phase under equilibrium conditions. However, systematic studies in this field are so far lacking.

It seems very important from the practical viewpoint to study in greater detail the effect of the formation of molecular complexes between the main compound and an admixture in the equilibrium phases on the quantitative characteristics of the processes in the interphase separation of admixtures. It is likely that the weak molecular complexes formed by admixture molecules with those of the main compound due to specific and non-specific interactions can be considered as a new class of admixtures in high-purity substances.

It should be noted that the investigation of the nature of intermolecular interaction in such systems and of the dependences of the characteristics of molecular complexes on the structure of their fairly simple constituent molecules is outside the scope of the chemistry of high-purity compounds but is of definite interest for other branches of chemistry and physics which deal with problems of the theory of intermolecular interactions, as well as for biochemistry.

References

1. G G Devyatykh, in *Poluchenie i Analiz Veshchestv Osoboi Chistoty* (Preparation and Analysis of Specially Pure Compounds) (Gor'kii: Izd. Gor'kovsk. Gos. Univ., 1974) p. 5
2. G G Devyatykh, S G Krasnova, S V Yan'kov, in *Metody Analiza Vysokochistykh Veshchestv* (Ed. Yu A Karpov) (Methods for the Analysis of Ultrapure Compounds) (Moscow: Nauka, 1987) p. 5
3. V A Krylov, V M Nemets, in *Metody Analiza Vysokochistykh Veshchestv* (Ed. Yu A Karpov) (Methods for the Analysis of Ultrapure Compounds) (Moscow: Nauka, 1987) p. 206
4. J W Mitchell *Solid State Technol.* **28** 131 (1985)
5. A Lebovits *Mod. Plast.* **13** 139 (1966)
6. G G Devyatykh, V M Vorotyntsev *Vysokochist. Veshch.* (2) 12 (1987)
7. A N Gur'yanov, D D Gusovskii, S N Miroshnichenko, V F Khopin *Vysokochist. Veshch.* (2) 189 (1988)

8. A Freundlich, A Leycuras, J S Grenet *Appl. Phys. Lett.* **17** 1352 (1987)
9. I D Kovalev, V A Krylov, K K Malyshev, L I Osipova, S V Yan'kov *Vysokochist. Veshch.* (4) 5 (1994)
10. G G Devyatykh, M F Churbanov *Vysokochist. Veshch.* (2) 5 (1987)
11. J Mitchell Jr, D M Smith *Aquametry* Parts I–III (New York: Wiley, 1977–1984)
12. G F Nichugovskii *Opredelenie Vlazhnosti Khimicheskikh Veshchestv* (Determination of the Moisture Content in Chemical Compounds) (Moscow: Khimiya, 1977)
13. K Carr-Brion *Moisture Sensors in Process Control* (New York: Elsevier, 1986)
14. G G Devyatykh, P G Sennikov *Vysokochist. Veshch.* (3) 7 (1990)
15. W S Pappas *Anal. Chem.* **36** 1885 (1964)
16. E A Kochetkova *Zavod. Lab.* **31** 880 (1967)
17. E V Atamanyuk, B I Shatalov, A S Khokhlov, G M Glukh, V G Piskunov, L B Skuratkin, A D Shepelev, Yu Kh Chikulina *Vysokochist. Veshch.* (5) 192 (1990)
18. T Gast, R Talebi *Thermochim. Acta* **119** 37 (1987)
19. M R O Karim *Analyst* **112** 1369 (1987)
20. R T Atanasoski, H H Law, R C McIntosh, C W Tohias *Electrochim. Acta* **32** 877 (1987)
21. H Huang, R K Dasgupta *Anal. Chem.* **62** 1935 (1990)
22. E Flaherty, C Herald, D Murray, S R Thompson *Anal. Chem.* **58** 1903 (1986)
23. K J Clevett, in *Process Analyzer Technology* (New York: Wiley, 1986) p. 1325
24. Yu I Kusaev, N V Smirnov *Vysokochist. Veshch.* (2) 119 (1994)
25. Yu S Drugov *Zh. Anal. Khim.* **35** 559 (1980)
26. Yu S Drugov *Zh. Anal. Khim.* **40** 585 (1985)
27. V A Krylov, Doctoral Thesis in Chemical Sciences, Institute for the Chemistry of High-Purity Substances, Nizhnii, Novgorod, 1986
28. G O Guerrdut *Anal. Chem.* **39** 143 (1967)
29. A Goldup, M T Westaway *Anal. Chem.* **38** 1657 (1966)
30. V G Rezchikov, G S Kuznetsova, E B Badasek, A V Legkov *Zh. Anal. Khim.* **42** 402 (1987)
31. G E Snopatin, A E Ezheleva, L S Malygina, Z A Klemina *Zh. Anal. Khim.* **39** 433 (1984)
32. K Kato, K Sato, H Tomita, T Maeda *Bunseki Kagaku* **36** 267 (1987)
33. G S Beskova, N G Mamakina, L I Butusova, S S Reznikova, in *Tez. Dokl. II Vsesoyuz. Konf. po Analizu Neorganicheskich Gazov* (Abstracts of Reports at the Second All-Union Conference on the Analysis of Inorganic Gases) (Leningrad: Izd. Leningr. Gos. Univ., 1990) p. 185
34. J A Koprio, G Rettinghaus *Abstracts of the 10th International Conference on Advanced Mass Spectrometry* Part 13 (Chichester: University of Chichester, 1986) p. 891
35. R W Thomas, D E Meyer *Solid State Technol.* **17** 58 (1974)
36. K L Perkins, in *Semiconductor Measurement Technology. ARPA/ NBS Workshop V: Moisture Measurement Technology for Hermetic Semiconductor Devices* (Eds H A Schafft, S Ruthberg, E C Cohen) NBS Spec. Publ. No 400-69 (Washington, DC: National Bureau of Standards, 1981) p. 58
37. M Yasukiro, J Takashi, O Hidekazu, S Atsushi *Jpn. J. Appl. Phys.* **32A** 2886 (1993)
38. O Tadahiro, N Masakazu, O Atushi, H Keiji *J. Electrochem. Soc.* **139** 2654 (1992)
39. C P M G A'Campo, S M Lemkowitz, P Verbrugge *J. Chromatogr.* **203** 271 (1981)
40. F Andrawes *J. Chromatogr.* **290** 65 (1984)
41. F Andrawes *Anal. Chem.* **55** 1869 (1983)
42. L A Pugh, K N Rao, in *Molecular Spectroscopy: Modern Research* Vol. 2 (Ed. K N Rao) (New York: Academic Press, 1976) p. 165
43. J M Flaud, C Camy-Peyret *J. Mol. Spectrosc.* **55** 278 (1975)
44. C Camy-Peyret, J M Flaud *Mol. Phys.* **32** 323 (1976)
45. A Lee Smith *Applied Infrared Spectroscopy* (New York: Wiley-Interscience, 1979) (Translated into Russian; Moscow: Mir, 1982)
46. B A Andreev, G G Devyatykh, I I Zasavitskii, O P Lazukina, G A Maksimov, A I Nadezhdinskii, A M Prokhorov, V A Khorshev, S M Shchapin *Vysokochist. Veshch.* (4) 161 (1989)
47. D E Pivonka *Appl. Spectrosc.* **45** 597 (1993)
48. A Bulashov, V Bakrev, I Nesteruk, E Perminov, V Vagin, G Zhizhin *Appl. Opt.* **17** 1716 (1978)
49. L B Kreuzer, N D Kenyon, C K N Patel *Science* **177** 347 (1972)
50. V E Zuev (Ed.) *Spektroskopiya Atmosfernykh Gazov* (Spectroscopy of Atmospheric Gases) (Novosibirsk: Nauka, 1982)
51. A B Antipov, L D Bykov, V E Zuev *Spektr Pogloshcheniya Vodyanogo Para v Raione 0.59 mkm* (Absorbtion Spectrum of Water Vapour in the 0.59 μm Region) (Tomsk: IOA SO AN SSSR, 1979) Preprint No 28
52. A Gerasimchuk, S Kornilov, I Ostrejkovskij, E Protsenko, S Tymper *Appl. Opt.* **B55** 503 (1992)
53. E D Hinkley, K W Nill, F A Blum *Laser Focus* **12** 47 (1976)
54. K W Nill *Laser Focus* **13** 32 (1977)
55. R S Eng, J F Butler, K J Linden *Opt. Eng.* **19** 945 (1980)
56. R S Eng, R T Ku *Spectrosc. Lett.* **15** 803 (1982)
57. C Freed, J W Bielinski, W Lo *Appl. Phys. Lett.* **43** 629 (1983)
58. Yu A Kuritsyn, in *Lazernaya Analiticheskaya Spektroskopiya* (Analytical Laser Spectroscopy) (Ed. V S Letokhov) (Moscow: Nauka, 1986) p.120
59. V I Butkevich, V E Privalov *Zh. Prikl. Spektrosk.* **48** 7 (1984)
60. V L Vaks, L I Gershtein, M L Gershtein *Izv. Vyssh. Uchebn. Zaved., Radiofizika* **27** 1344 (1984)
61. I Tauns, A Shavlov *Radiospektroskopiya* (Radio Spectroscopy) (Moscow: Izd. Inostr. Lit., 1959)
62. J-Y Manden, J-M Fland, C Camy-Peyret *J. Quant. Spectrosc. Radiat. Transfer* **23** 351 (1980)
63. J Reid *Appl. Opt.* **17** 300 (1978)
64. J A Mucha *Appl. Spectrosc.* **36** 393 (1982)
65. J A Mucha *Proc. SPIE* **438** 55 (1983)
66. G T Forrest, D L Wall, A W Mantz *Photonics Spectra* **16** 68 (1982)
67. G G Devyatykh, V A Krylov, O P Lazukina *Vysokochist. Veshch.* (2) 108 (1990)
68. G G Devyatykh, G A Maksimov, A I Nadezhdinskii, V A Khorshev, S M Shapin *Proc. SPIE* **1724** 335 (1992)
69. G A Maksimov, V A Khorshev, S M Shapin, in *Proceedings of the XIth Symposium-School "High-Resolution Molecular Spectroscopy"* (Moscow, N. Novgorod: Institute of General Physics, 1993) p. 153
70. M Yu Bulanin (Ed.) *Molekulyarnaya Kriospektroskopiya* (Molecular Cryospectroscopy) (Sankt-Peterburg: Izd. S.-Peterburg. Univ., 1993)
71. S M Freund, W B Maier II, R F Holland, W H Beattie *Anal. Chem.* **50** 1260 (1976)
72. R Rebiai, R C Scurlock, A J Rest *Adv. Cryog. Eng.* **29** 1005 (1984)
73. G G Devyatykh, P G Sennikov, K G Tokhadze, V E Shkrunin *Vysokochist. Veshch.* (6) 21 (1988)
74. V A Efremov, T A Efremova, A A Efremov, Yu Ya Kharitonov *Vysokochist. Veshch.* (5) 215 (1991)
75. T Y Kometani, D L Wood, J P Luongo *Anal. Chem.* **59** 1089 (1987)
76. K French, P Cukor, C Persiani, J Auborn *J. Electrochem. Soc.* **121** 1045 (1974)
77. P G Sennikov, Doctoral Thesis in Chemical Sciences, Institute for the Chemistry of High-Purity Substances, Nizhnii, Novgorod, 1994
78. M F Kolbe, B Leskovar *J. Quant. Spectrosc. Radiat. Transfer* **30** 463 (1983)
79. A V Burenin, S M Shchapin *Opt. Spektrosk.* **59** 673 (1985)
80. L I Gershtein, V I Vaks, in *Spektroskopiya Vysokogo Razresheniya Malykh Molekul* (High-Resolution Spectroscopy of Small Molecules) (Moscow: Scientific Council on Spectroscopy, 1988) p. 246
81. A F Krupnov, A V Burenin, in *Molecular Spectroscopy: Modern Research* Vol. 2 (Ed. K N Rao) (New York: Academic Press, 1976) p. 93
82. V P Kazakov *Izv. Vyssh. Uchebn. Zaved., Radiofizika* **23** 877 (1980)
83. K Krishnagi *J. Sci. Ind. Res.* **32** 168 (1973)
84. G G Devyatykh, B A Andreev, E A Gushchina, A K Zaburdaev, A F Krupnov, A I Pikhtelev, S M Shchapin *Dokl. Akad. Nauk SSSR* **239** 1132 (1978)
85. G G Devyatykh, B A Andreev, V P Kazakov, A F Krupnov, V A Krylov *Zh. Anal. Khim.* **41** 1812 (1986)
86. V L Vaks, A E Ermoshkin, S I Pripolzin, P G Sennikov, N V Shushunov *Vysokochist. Veshch.* (4) 168 (1992)
87. G G Devyatykh, P G Sennikov, S V Yan'kov *Usp. Khim.* **55** 1233 (1986) [*Russ. Chem. Rev.* **55** 691 (1986)]
88. L A Curtiss, M Blauder *Chem. Rev.* **88** 827 (1988)
89. A C Legon *Chem. Phys. Lett.* **135** 303 (1987)
90. A A Vigasin *Zh. Strukt. Khim.* **28** 120 (1987)
91. B Hobza, R Zahradnik *Chem. Rev.* **88** 871 (1988)

92. B Kitchen, T P Ruane, L C Allen *Chem. Phys. Lett.* **141** 525 (1987)
93. M J Brasler, V C E Carr, M G Gerazonnis, N R Jugga, G A Yeo, T A Ford *J. Mol. Struct. (THEOCHEM)* **180** 241 (1988)
94. G Chalasinski, M M Szczesniak, S Scheiner *J. Chem. Phys.* **94** 2807 (1991)
95. T D Mokomela, J Rencken, G A Yeo, T D Ford *J. Mol. Struct.* **275** 33 (1992)
96. W Byers Brown, M A Vincent, K Trollope, J H Hillier *Chem. Phys. Lett.* **192** 213 (1992)
97. E S Fois, A Gamba, G Morosi, P Demontis, G B Suffritti *J. Chem. Phys.* **84** 751 (1987)
98. J Sadlei, V Buch *J. Chem. Phys.* **100** 4272 (1994)
99. Q Zhang, L Chenyang, Y Ma, F Fish, M M Szczesniak, V Buch *J. Chem. Phys.* **96** 6039 (1992)
100. J E Del Bene *J. Phys. Chem.* **92** 2874 (1988)
101. J E Del Bene, in *Molecular Structure and Energetics* Vol. 1 (Eds J F Liebman, A Greenberg) (Deerfield Beach: Verlag Chemie, 1986) p. 319
102. A Les *Theor. Chim. Acta* **66** 375 (1986)
103. P G Sennikov, R I Sharibdjanov, K Khoudoinazarov *J. Mol. Struct.* **270** 87 (1992)
104. R K Thomas *Proc. R. Soc. London, A Math. Phys. Sci.* **344** 579 (1975)
105. A C Legon *Chem. Phys. Lett.* **135** 303 (1987)
106. G Gazzoli, P G Favers, D G Lister, A C Legon, D J Millen, Z Kisiel *Chem. Phys. Lett.* **117** 543 (1985)
107. S P Belov, V M Demkin, N F Zobov, E N Karyakin, A F Krupnov, I N Kozin, O L Polyanskii, M Yu Tret'yakov Preprint No 192 (N. Novgorod: Institute of Applied Physics, Academy of Sciences, USSR, 1988)
108. T R Dyke, G R Tomashevich, W Klemperer *J. Chem. Phys.* **57** 2277 (1992)
109. A C Legon *Annu. Rev. Phys. Chem.* **34** 275 (1983)
110. T R Dyke *Topics in Current Chemistry* Vol. 120 (Berlin: Springer, 1984) p. 85
111. W Klemperer *Farad. Disc. Chem. Soc.* **62** 179 (1977)
112. T R Dyke, K M Mack, J S Muenter *J. Chem. Phys.* **66** 498 (1977)
113. P Herbine, T R Dyke *J. Chem. Phys.* **83** 3768 (1985)
114. H J Peterson, G T Fraser, D D Nelson, W Klemperer, in *Comparison of ab initio Quantum Chemistry with Experiment for Small Molecules. State of the Art* (Ed. R J Berrlett) (Dordrecht: Reidel, 1985) p. 217
115. D Yaron, K J Peterson, D Zolandt, W Klemperer, F J Lovas, K D Suenram *J. Chem. Phys.* **92** 7095 (1990)
116. K J Peterson, W Klemperer *J. Chem. Phys.* **80** 2439 (1984)
117. K Matsumura, F J Lovas, R D Suenram *J. Chem. Phys.* **91** 5887 (1989)
118. D Zolandt, D Yaron, K J Peterson, W Klemperer *J. Chem. Phys.* **97** 2861 (1992)
119. R D Suenram, G T Fraser, F J Lovas, Y Kawashima *J. Chem. Phys.* **101** 7030 (1994)
120. K J Peterson, W Klemperer *J. Chem. Phys.* **81** 3842 (1984)
121. K J Peterson, W Klemperer *J. Chem. Phys.* **85** 725 (1986)
122. A M Andrews, R L Kuczkowski *J. Chem. Phys.* **98** 791 (1993)
123. A M Andrews, K W Hilliy II, R Kuczkowski *J. Am. Chem. Soc.* **114** 6765 (1992)
124. D W Steyert, M J Elrod, R J Saykally, F J Lovas, R D Suenram *J. Chem. Phys.* **99** 7424 (1993)
125. S L A Adebago, A C Legon, D J Millen *J. Chem. Soc., Faraday Trans.* **87** 443 (1991)
126. A J Fillery-Travis, A C Legon, L C Willoughby *Chem. Phys. Lett.* **98** 369 (1983)
127. M J Tubergen, R L Kuczkowski *J. Am. Chem. Soc.* **115** 9263 (1993)
128. A C Legon, D J Millen, H M North *Chem. Phys. Lett.* **135** 303 (1987)
129. Z Kisiel, A C Legon, D J Millen *J. Chem. Phys.* **78** 7810 (1983)
130. Z Kisiel, A C Legon, D J Millen *J. Mol. Struct.* **112** 1 (1984)
131. J W Beran, Z Kisiel, A C Legon, D J Millen, S C Rogers *Proc. R. Soc. London, A Math. Phys. Sci.* **372** 441 (1980)
132. A C Legon, L C Willoughby *Chem. Phys. Lett.* **95** 449 (1983)
133. A C Legon, A P Suckley *Chem. Phys. Lett.* **170** 173 (1988)
134. G T Fraser, R D Suenram, F J Lovas *J. Mol. Struct.* **189** 165 (1988)
135. H O Leung, M D Marshall, R D Suenram, F J Lovas *J. Chem. Phys.* **90** 700 (1989)
136. R C Cohen, R J Saykally *J. Phys. Chem.* **94** 7991 (1990)
137. G T Fraser, F J Lovas, R D Suenram, K Matsumura *J. Mol. Spectrosc.* **144** 97 (1990)
138. R C Cohen, R J Saykally *J. Chem. Phys.* **98** 6007 (1993)
139. M Moskovits, G A Ozin (Eds) *Cryochemistry* (New York: Wiley-Interscience, 1976) (Translated into Russian; Moscow: Mir, 1978)
140. S Gradock, A J Hinchcliffe *Matrix Isolation* (Cambridge: Cambridge University Press, 1975) (Translated into Russian; Moscow: Mir, 1978)
141. J P Ayers, A D E Pullin *Spectrochim. Acta., Part A* **32** 1629; 1641; 1689; 1695 (1971)
142. A Engdahl, B Nelander *J. Mol. Struct.* **193** 101 (1989)
143. W-J Orville-Thomas, H Ratajczak *Croat. Chem. Acta* **55** 191 (1982)
144. A Schriver, L Schriver, J P Perchard *J. Mol. Spectrosc.* **127** 125 (1988)
145. L Aboauf-Margin, M E Jacox, O E Milligan *J. Mol. Spectrosc.* **76** 34 (1977)
146. A Engdahl, B Nelander *J. Chem. Phys.* **91** 6604 (1989)
147. B Nelander, L Nord *J. Phys. Chem.* **86** 4375 (1982)
148. B Nelander *J. Chem. Phys.* **69** 3870 (1978)
149. K Johnsson, A Engdahl, P Ouis, B Nelander *J. Phys. Chem.* **96** 5778 (1992)
150. A J Barnes, R M Bentwood, M P Wright *J. Mol. Struct.* **118** 97 (1984)
151. B S Ault, G C Pimentel *J. Phys. Chem.* **77** 57 (1973)
152. A J Barnes *J. Mol. Struct.* **60** 343 (1980)
153. A Schriver, B Silvil, D Maillard, J P Perchard *J. Phys. Chem.* **81** 2095 (1977)
154. C Amirand, D Maillard *J. Mol. Struct.* **176** 181 (1988)
155. L Andrews, G L Johnsson *J. Chem. Phys.* **79** 3670 (1983)
156. W B Person, J Del Bene, W Szaida, W Szczepaniak *J. Phys. Chem.* **95** 2770 (1991)
157. L Fredin *Chem. Scr.* **4** 97 (1973)
158. L Fredin, B Nelander *J. Mol. Struct.* **16** 205; 217 (1973)
159. C McInnis, L Andrews *J. Phys. Chem.* **96** 2051 (1992)
160. G C Pimentel, A J McClellan *The Hydrogen Bond* (San Francisco: Freeman, 1960)
161. P Schuster, G Zundel, C Sandorfy (Eds) *The Hydrogen Bond. Recent Advances in Theory and Experiment* Vol. 1–3 (Amsterdam: North Holland, 1976)
162. M D Joesten, L J Schaad *Hydrogen Bonding* (New York: Marcel Dekker, 1974)
163. G V Yukhnevich *Infrakrasnaya Spektroskopiya Vody* (Infrared Spectroscopy of Water) (Moscow: Nauka, 1973)
164. A V Iogansen in *Vodorodnaya Svyaz'* (The Hydrogen Bond) (Ed. N D Sokolov) (Moscow: Nauka, 1981)
165. V A Efremov, A A Efremov *Vysokochist. Veshch.* (3) 143 (1991)
166. V A Efremov, A A Efremov *Vysokochist. Veshch.* (3) 150 (1991)
167. V A Efremov, A A Efremov *Vysokochist. Veshch.* (3) 183 (1991)
168. G V Yukhnevich, A V Karyakin *Dokl. Akad. Nauk SSSR* **156** 681 (1964)
169. A A Efremov, V A Efremov, V A Fedorov, E A Yushina *Vysokochist. Veshch.* (3) 86 (1993)
170. G G Devyatykh, P G Sennikov, K G Tokhadze, V E Shkrunin *Vysokochist. Veshch.* (2) 146 (1990)
171. D A Raldugin, P G Sennikov, K G Tokhadze, V E Shkrunin, S V Yan'kov *Vysokochist. Veshch.* (5–6) 125 (1992)
172. P G Sennikov, D A Raldugin, K G Tokhadze, V E Shkrunin *Vysokochist. Veshch.* (2) 27 (1994)
173. V E Shkrunin, L A Efimychev, P G Sennikov, K G Tokhadze *Vysokochist. Veshch.* (6) 221 (1988)
174. P G Sennikov, V E Shkrunin, S M Melikova, Yu A Lebedeva *Vysokochist. Veshch.* (2) 127 (1992)
175. P G Sennikov, D A Raldugin, V E Shkrunin, K G Tokhadze *Vysokochist. Veshch.* (5–6) 107 (1992)
176. P G Sennikov, D A Raldugin, V E Shkrunin, K G Tokhadze *Vysokochist. Veshch.* (5–6) 118 (1992)
177. J R Scherer *Adv. Infrared Raman Spectrosc.* 5149 (1978)
178. R T Arlinghaus, L Andrews *J. Chem. Phys.* **81** 4341 (1984)
179. A C Legon, D J Millen *J. Am. Chem. Soc.* **109** 356 (1987)
180. P G Sennikov *J. Phys. Chem.* **98** 4974 (1994)
181. V M Vorotyntsev, V M Malyshev *Vysokochist. Veshch.* (6) 50 (1993)
182. Y Markus *J. Solution Chem.* **13** 599 (1984)