# Interaction of Water with GeCl<sub>4</sub>, SnCl<sub>4</sub>, and AsCl<sub>3</sub>

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**Abstract**—The interaction of water with  $\text{GeCl}_4$ ,  $\text{SnCl}_4$ , and  $\text{AsCl}_3$  was studied by IR spectroscopy. The results demonstrate that these chlorides contain molecular water in monomeric form. At water concentrations above  $10^{-2}$  mol/l,  $\text{GeCl}_4$  also contains  $\text{H}_3\text{O}^+$  ions. The mechanisms of  $\text{GeCl}_4$  and  $\text{AsCl}_3$  hydrolysis were studied over a wide range of water concentrations.

#### INTRODUCTION

The possibility that the readily hydrolyzable compounds germanium, tin, arsenic, silicon, and titanium chlorides may contain molecular water was first examined in [1–4]. This issue is not only of scientific interest in gaining insight into the state of water in inorganic substances but also of practical importance in the search for ways of improving the purity of the chlorides widely used in micro- and optoelectronics and fiber optics.

The volatile Group IV and V chlorides, except carbon tetrachloride, were initially believed to contain little or no water. IR spectroscopic studies of liquid GeCl<sub>4</sub>, SnCl<sub>4</sub>, AsCl<sub>3</sub>, PCl<sub>3</sub>, SiCl<sub>4</sub>, and TiCl<sub>4</sub> showed, however, the following:

(1) SiCl<sub>4</sub>, TiCl<sub>4</sub>, and PCl<sub>3</sub> contain only hydrolysis products, without molecular water (detection limit at a level of  $10^{-4}$  mol/l).

(2)  $GeCl_4$ ,  $SnCl_4$ , and  $AsCl_3$  contain molecular water in equilibrium with hydrolysis products.

(3) In chlorides containing trace amounts of water, some impurities (e.g., chalcogens) undergo chemical transformations.

The hydrolysis of chlorides and the lability of sulfur-, selenium-, and tellurium-containing species limit the effectiveness of fine-purification processes and require detailed investigation [5–7].

The objective of this work was to systematically study the state of water in GeCl<sub>4</sub>, SnCl<sub>4</sub>, and AsCl<sub>3</sub> and to elucidate the mechanisms of GeCl<sub>4</sub> and AsCl<sub>3</sub> hydrolysis over a wide range of dissolved water concentrations using various approaches to interpreting IR transmission spectra (composition dependences, deuteration, and HCl additions).

# INTERACTION OF WATER WITH GERMANIUM TETRACHLORIDE

The IR spectra of water dissolved in high-purity germanium tetrachloride were recorded from 1100 to 4000 cm<sup>-1</sup> on a UR-20 spectrophotometer using cells with CaF<sub>2</sub> windows. At low water concentrations in  $GeCl_4$  (<10<sup>-2</sup> mol/l), the spectrum shows absorption bands at 1600, 2760, 2845, 2950, 3603, and 3691 cm<sup>-1</sup>, which become progressively stronger with increasing water concentration (Fig. 1). Since germanium tetrachloride hydrolyzes readily, the dissolved molecular water is in equilibrium with the products of partial GeCl<sub>4</sub> hydrolysis. The addition of anhydrous hydrogen chloride increases the strength of the bands at 2760, 2845, and 2950  $\text{cm}^{-1}$ . The 3603- $\text{cm}^{-1}$  band weakens sharply in comparison with the 1600- and 3691-cm<sup>-1</sup> bands as a result of hydrolysis suppression (Fig. 1). These findings lead us to assign the bands at 2760, 2845, and 2950 cm<sup>-1</sup> to hydrogen chloride; the band at 3603 cm<sup>-1</sup> to the product of partial GeCl<sub>4</sub> hydrolysis; and the bands at 1600 and 3691 cm<sup>-1</sup>, which have correlated intensities, to molecular water.

The decrease in the intensity of the bands at 1600 and  $3691 \text{ cm}^{-1}$  upon dissolution of hydrogen chloride in germanium tetrachloride (Fig. 1) is probably due to the reduction in water solubility. Indeed, saturation of GeCl<sub>4</sub> with hydrogen chloride leads to the formation of greenish drops of concentrated hydrochloric acid, which is easy to identify by IR spectroscopy.

The bands at 1600 and 3691 cm<sup>-1</sup> are assigned, respectively, to the bending mode  $\delta(H_2O)$  and stretching mode  $v_{as}$  of the water monomer, in line with earlier results for water vapor [8] and water dissolved in organic compounds [9]. The  $v_s$  mode of water (3600 cm<sup>-1</sup>) is indiscernible in the spectra of the solutions because it is obscured by the strong band at 3603 cm<sup>-1</sup> due to the



**Fig. 1.** IR transmission spectra of water solutions in germanium tetrachloride (1-cm absorbing layer): (1)  $2.2 \times 10^{-3}$ , (2)  $6.9 \times 10^{-3}$ , (3)  $1.23 \times 10^{-2}$ , (4)  $3.45 \times 10^{-2}$ , (5, 5')  $8.48 \times 10^{-2}$  mol/l H<sub>2</sub>O; (5') with the addition of hydrogen chloride.



Fig. 2. IR transmission spectra of (1)  $H_2O$  and (2)  $H_2O + D_2O$  solutions in GeCl<sub>4</sub> (1-cm absorbing layer).

hydrolysis product. The shift of the  $v_{as}$  band relative to that in the spectrum of water vapor is attributable to the dispersion interaction between water and GeCl<sub>4</sub> molecules. The energy of this interaction, evaluated by the Yukhnevich–Karyakin equation [10], is  $\approx 6.15$  kJ/mol.

The assignment of the bands at 1600 and 3691 cm<sup>-1</sup> to the fundamental modes of water is supported by deuteration results. The addition of D<sub>2</sub>O to a solution of H<sub>2</sub>O in GeCl<sub>4</sub> shifts the bands due to water from 1600 to 1178 and from 3691 to 2745 cm<sup>-1</sup> (Fig. 2) as a result of isotope exchange. The respective isotope shift coefficients are  $\delta(\text{HOH})/\delta(\text{DOD}) = 1600/1178 = 1.358$  and  $\nu(\text{OH})/\nu(\text{OD}) = 3691/2745 = 1.344$ . This provides conclusive evidence that the bands at 1600 and 1178 cm<sup>-1</sup> arise from the  $\delta(\text{H}_2\text{O})$  and  $\delta(\text{D}_2\text{O})$  modes, respectively, and the bands at 3691 and 2745 cm<sup>-1</sup> arise from the  $\nu_{as}$  modes of the H<sub>2</sub>O and D<sub>2</sub>O molecules, respectively.

Deuteration also reduces the intensity of the  $3603 \text{-cm}^{-1}$  band as a result of partial isotopic substitution and gives rise to an absorption band at  $2672 \text{ cm}^{-1}$ . The frequency change from 3603 to  $2672 \text{ cm}^{-1}$ , with v(OH)/v(OD) = 1.348, indicates that this absorption is due to stretches of OH groups.

Germanium tetrachloride hydrolysis is known to involve the formation of soluble intermediate products with the general formula  $\text{Ge}(\text{OH})_n \text{Cl}_{4-n}$  [11]. The fact that the OH stretching region contains only one absorption band, that at 3603 cm<sup>-1</sup>, with a full width at half maximum (FWHM) of 36 cm<sup>-1</sup>, suggests that, at water concentrations below 10<sup>-2</sup> mol/l, GeCl<sub>4</sub> hydrolysis proceeds according to the scheme

$$GeCl_4 + H_2O \implies Ge(OH)Cl_3 + HCl.$$

Therefore, the 3603-cm<sup>-1</sup> band can be assigned to the stretching mode of the relatively weakly bonded

ν, cm <sup>-1</sup>	Assignment	A	A <sub>3603</sub> /A <sub>2845</sub>	A	A <sub>3603</sub> /A <sub>2845</sub>
		$2.2 \times 10^{-3} \text{ mol/l H}_2\text{O}$		$6.9 \times 10^{-3} \text{ mol/l H}_2\text{O}$	
3603	Ge(OH)Cl <sub>3</sub>	0.144	3.20	0.385	3.23
2845	HCl	0.045		0.119	

Maximum absorbances (A) on the 3603- and 2845-cm<sup>-1</sup> bands and their ratio in the IR transmission spectra of H<sub>2</sub>O solutions in GeCl<sub>4</sub>

OH group in Ge(OH)Cl<sub>3</sub>, and the 2672-cm<sup>-1</sup> band is due to the v(OD) mode of the Ge(OD)Cl<sub>3</sub> molecule. The  $\delta$ (GeOH) and  $\delta$ (GeOD) bands are indiscernible because they are obscured by GeCl<sub>4</sub> fundamentals. The energy of the interaction of the OH group of Ge(OH)Cl<sub>3</sub> with GeCl<sub>4</sub> molecules, evaluated by the Sokolov equation [12], is 0.22 kJ/mol. The absorption at 2845 cm<sup>-1</sup> is assigned to fundamental HCl stretches, in line with earlier results [13, 14].

The presence of two broad absorption bands at 2760 and 2950 cm<sup>-1</sup> in the spectrum of HCl dissolved in GeCl<sub>4</sub> (Fig. 1) seems to be a manifestation of the rotational–vibrational structure in the spectra of HCl dissolved in "inert" liquids [13, 14]. These bands are envelopes of the rotational fine structure in the spectrum of HCl for the *P*- and *R*-branches, respectively.

The proposed mechanism of germanium tetrachloride hydrolysis at low concentrations of dissolved water  $(<10^{-2} \text{ mol/l})$  is supported by the fact that the intensities of the bands at 2845 and 3603 cm<sup>-1</sup> are correlated with the water concentration in GeCl<sub>4</sub>. Moreover, the ratio of the maximum absorbance *A* on the 3603-cm<sup>-1</sup> band to that on the 2845-cm<sup>-1</sup> band is independent of the total amount of water dissolved in germanium tetrachloride (table).

These data also demonstrate that, in the range of water concentrations in question, hydrogen chloride is present only in molecular form.

Increasing the concentration of water dissolved in germanium tetrachloride to above 10<sup>-2</sup> mol/l increases the intensity of the bands at 1600, 3603, and 3691  $\text{cm}^{-1}$ and reduces that of the 2845-cm<sup>-1</sup> band (Fig. 1). Besides, additional bands appear at 1192, 1310, 1415, 1434, 1833, 3100-3500 (broad, composite band with well-defined maxima at 3330 and 3406 cm<sup>-1</sup>), and 3810 cm<sup>-1</sup>, which respond differently to deuteration. For example, the intensity of the broad absorption band around 3330 cm<sup>-1</sup> sharply decreases, and a new, broad band emerges at 2480 cm<sup>-1</sup> (Fig. 2). The shift from 3330 to 2480 cm<sup>-1</sup>, with v(OH)/v(OD) = 1.342, indicates that this band is due to v(OH) stretching vibrations. The fact that the OH stretching region contains, along with the v(OH) band of Ge(OH)Cl<sub>2</sub> (3603 cm<sup>-1</sup>), a broad band at  $\approx 3330 \text{ cm}^{-1}$  points to further GeCl<sub>4</sub> hydrolysis with the formation of  $Ge(OH)_n Cl_{4-n}$  hydroxychlorides. The latter band can be assigned to the v(OH) stretching mode of  $\text{Ge}(\text{OH})_n \text{Cl}_{4-n}$ . Since the OH groups of the  $\text{Ge}(\text{OH})_n \text{Cl}_{4-n}$  species are close in vibrational frequencies, the corresponding absorption bands overlap to form the broad, unresolved band at 3330 cm<sup>-1</sup>. The rather large shift and broadening of this band compared to the 3603-cm<sup>-1</sup> band, corresponding to the stretching mode of the more weakly bonded OH group of Ge(OH)Cl<sub>3</sub>, are also attributable to the formation of hydrogen bonds. The same refers to the band around 2480 cm<sup>-1</sup>, due to the v(OD) mode of the Ge(OH)\_nCl<sub>4-n</sub> molecules.

The IR spectra of hydrogen-bonded systems are known to be highly sensitive to temperature [15]. This feature, however, cannot be drawn on in our case because the various hydrolysis and polycondensation processes in the system under study depend on temperature in different ways.

The addition of  $D_2O$  has no effect on the absorption bands at 1310, 1415, and 1434 cm<sup>-1</sup> (Fig. 2). The intensity of these bands increases with increasing water concentration but is independent of the isotopic composition of the water dissolved in GeCl<sub>4</sub>. It seems likely, therefore, that these bands arise from germanium oxychlorides. Clearly, at a higher degree of germanium tetrachloride hydrolysis, the process involves condensation (dehydration) reactions resulting in molecular water release:

$$2\text{Ge}(\text{OH})\text{Cl}_3 \Longrightarrow \text{Ge}_2\text{OCl}_6 + \text{H}_2\text{O},$$
$$\text{Ge}(\text{OH})_2\text{Cl}_2 \Longrightarrow \text{Ge}\text{OCl}_2 + \text{H}_2\text{O}.$$

These reactions can be promoted by removing hydrogen chloride, e.g., via HCl extraction with an inert gas or fractional distillation. Indeed, after vacuum distillation of germanium tetrachloride, the spectrum of the condensate shows strong bands at 1310 and 1420 cm<sup>-1</sup> and a band at 3603 cm<sup>-1</sup>, which is notably weaker in comparison with the starting GeCl<sub>4</sub> (Fig. 3). The broad band at 1420 cm<sup>-1</sup> results from the overlap of the bands at 1415 and 1434 cm<sup>-1</sup>. The spectrum contains very weak or no bands due to water, HCl, or Ge(OH)<sub>n</sub>Cl<sub>4-n</sub>.

The formation of  $\text{Ge}_2\text{OCl}$  during partial hydrolysis of  $\text{GeCl}_4$  in solutions of ethyl ether, chloroform, and pentane at 195 K was mentioned in [11]. This oxychloride also forms via oxidation of  $\text{GeCl}_4$  at 1220 K [16].



**Fig. 3.** IR transmission spectra of germanium tetrachloride (1-mm absorbing layer): (1) starting  $\text{GeCl}_4$ , (2) light fraction of  $\text{GeCl}_4$  vacuum distillation, (3) condensate.

Also possible is the formation of other  $\text{Ge}_n\text{O}_{n-1}\text{Cl}_{2n+2}$  homologues.

The band at 1310 cm<sup>-1</sup> is probably due to predominantly stretching vibrations v(GeO) of  $\text{GeOCl}_2$ , and the bands at 1415 and 1434 cm<sup>-1</sup> are attributable to different …GeOGeOGeO… stretches in Ge<sub>2</sub>OCl<sub>6</sub> or Ge<sub>n</sub>O<sub>n-1</sub>Cl<sub>2n+2</sub> molecules.

The decrease in the intensity of the HCl band at 2845 cm<sup>-1</sup> and the appearance of the bands at 1192, 1833, and 3406 cm<sup>-1</sup> at water concentrations above  $10^{-2}$  mol/l (Fig. 1) are likely due to the electrolytic dissociation of HCl and formation of the hydroxonium ion H<sub>3</sub>O<sup>+</sup> as a result of changes in the relative HCl and H<sub>2</sub>O concentrations. The weak band at 1192 cm<sup>-1</sup> is then attributable to the symmetric bending mode  $\delta_s$ (H<sub>3</sub>O<sup>+</sup>), the strong band at 1833 cm<sup>-1</sup> is due to the doubly degenerate bending mode  $\delta_e$ (H<sub>3</sub>O<sup>+</sup>), and the 3406-cm<sup>-1</sup> band corresponds to the v<sub>as</sub>(OH) stretching mode of the hydroxonium ion [17, 18].

The  $\delta_e(H_3O^+)$  band is in most cases broader and weaker than  $\delta_s(H_3O^+)$ , which is commonly used to identify the hydroxonium ion in solution. The intensity of  $H_3O^+$  stretching bands is much higher than that of bending bands, but the former are very broad and heavily overlap. For this reason, they are always difficult to reveal. Moreover, in the spectra of  $H_2O$  solutions in GeCl<sub>4</sub>, the v(OH) bands of the  $H_3O^+$  ion are strongly obscured by the broad v(OH) band of Ge(OH)<sub>n</sub>Cl<sub>4-n</sub>.

The bands due to the  $H_3O^+$  ion in solutions of  $H_2O$ in GeCl<sub>4</sub> were also assigned using deuteration. The addition of D<sub>2</sub>O was found to sharply reduce the intensity of the bands at 1833 and 3406 cm<sup>-1</sup> and to give rise to absorptions at 3354 and 2552 cm<sup>-1</sup> (Fig. 2). Moreover, deuteration improves the resolution of the composite band in the range 3100–3500 cm<sup>-1</sup>, which can be decomposed into components at 3330, 3354, and 3406 cm<sup>-1</sup>. The shift from 3406 to 2552 cm<sup>-1</sup>, with an isotope shift coefficient of 1.335, suggests that these features are due to the  $\text{Ge}(\text{OH})_n \text{Cl}_{4-n}(\text{OH})$  mode of  $\text{H}_3\text{O}^+$  and  $\text{Ge}(\text{OH})_n \text{Cl}_{4-n}(\text{OD})$  mode of  $\text{D}_3\text{O}^+$ , respectively. The 3354-cm<sup>-1</sup> band is probably due to the v(OH) stretching mode of the  $\text{H}_2\text{DO}^+$  or  $\text{HD}_2\text{O}^+$  ion. The other bands corresponding to different isotopic compositions of the hydroxonium ion are indiscernible since they are obscured by strong absorption bands due to germanium hydroxy- and oxychlorides.

The absorption band at  $3810 \text{ cm}^{-1}$ , which responds to changes in water concentration and deuteration in the same manner as the bands related to water (Figs. 1, 2), is attributable to the *R*-branch in the vibration–rotation spectrum of the water monomer in GeCl<sub>4</sub>, similarly to the analogous band in the transmission spectrum of water dissolved in CCl<sub>4</sub> [9].

#### INTERACTION OF WATER WITH TIN TETRACHLORIDE

The IR transmission spectra of water solutions in tin tetrachloride were recorded from 1100 to 4000 cm<sup>-1</sup>. In this range, the spectra contain absorption bands at 1586, 3553, and 3636 cm<sup>-1</sup>. The intensity of the bands increases with water concentration (Fig. 4), indicating that they are due to water. The bands can be assigned, respectively, to the  $\delta(H_2O)$  bending mode and the v<sub>s</sub> and v<sub>as</sub> stretching modes of the water monomer, in agreement with earlier results for water vapor [8] and water dissolved in organic compounds [9]. The bands in the IR spectrum of water dissolved in tin tetrachloride are markedly shifted relative to those in the spectrum of water vapor (1594.59, 3656.56, and 3755.59 cm<sup>-1</sup> [8]), presumably because of the interaction between H<sub>2</sub>O and SnCl<sub>4</sub>. The energy of this interaction, evaluated



**Fig. 4.** IR transmission spectra of water solutions in tin tetrachloride (1-cm absorbing layer): (1)  $8.2 \times 10^{-4}$ , (2, 2')  $2.4 \times 10^{-3}$  mol/l H<sub>2</sub>O; (2') with the addition of D<sub>2</sub>O; (3) IR transmission spectrum of crystalline SnCl<sub>4</sub> · *n*H<sub>2</sub>O (mulled in Nujol).

from the shift in the stretching frequencies of water using the Yukhnevich–Karyakin equation [10], is 10.5 kJ/mol. The shifts in  $v_s$  and  $v_{as}$  are almost identical, indicating that the water molecules dissolved in SnCl<sub>4</sub> experience a symmetrical stress (identical force constants of the bonds). These findings agree well with the calculations reported by Yukhnevich [19], which demonstrate that, under symmetrical stress, the difference  $v_s - v_{as}$  lies in the range 100–110 cm<sup>-1</sup>. The slight decrease in this difference is probably due to the Fermi resonance between the symmetrical stretching mode of water and the second harmonic  $2\delta(H_2O)$  of its bending mode, which are identical in symmetry. For the same reason, the intensity of the  $v_s$  band is higher than that of  $v_{as}$  (Fig. 4).

The  $\delta((H_2O))$  bending frequency of water dissolved in SnCl<sub>4</sub> is markedly lower than that of water vapor. At the same time, it is well known [20] that, upon the formation of hydrogen bonds in water-water and waterorganic solvent molecular complexes, the reduction in the  $v_s$  and  $v_{as}$  stretching frequencies of water is accompanied by an increase in the  $\delta(H_2O)$  bending frequency. This is well illustrated by the IR spectrum of crystalline  $SnCl_4 \cdot nH_2O$ , which shows the  $\delta(H_2O)$  band at 1628 cm<sup>-1</sup> and a broad v(OH) band at 3430 cm<sup>-1</sup> due to associated water. The  $\delta(H_2O)$  band is substantially weaker than the v(OH) band, in contrast to the spectrum of water dissolved in tin tetrachloride, where the  $\delta(H_2O)$  band is markedly stronger than the v<sub>s</sub> and v<sub>as</sub>. This "anomalous" behavior of the  $\delta(H_2O)$  band seems to be related to the particular character of the interaction between water and tin tetrachloride molecules, which involves the lone electron pair of the oxygen atom.

The assignment of the bands at 1586, 3553, and 3636 cm<sup>-1</sup> to the fundamental modes of water is supported by deuteration results. The addition of  $D_2O$  to a solution of  $H_2O$  in SnCl<sub>4</sub> reduces the intensity of these

bands and gives rise to additional bands at 1178, 1402, 2600, 2649, 2704, and 3591 cm<sup>-1</sup> as a result of isotope exchange (Fig. 4). The shift in band positions from 1586, 3553, and 3636 to 1178, 2600, and 2704 cm<sup>-1</sup>, respectively, with isotope shift coefficients of 1.346, 1.366, and 1.344, leads us to assign the bands at 1586 and 1178 cm<sup>-1</sup> to the  $\delta(H_2O)$  and  $\delta(D_2O)$  modes, the bands at 3553 and 2600 cm<sup>-1</sup> to the  $v_s$  modes of H<sub>2</sub>O and D<sub>2</sub>O, and the bands at 3636 and 2704 cm<sup>-1</sup> to the  $v_{as}$  modes of H<sub>2</sub>O and D<sub>2</sub>O, respectively. The 1402-cm<sup>-1</sup> band is then attributable to the  $\delta(HOD)$  mode, and the bands at 2649 and 3591 cm<sup>-1</sup> can be assigned, respectively, to the v(OD) and v(OH) modes of the HOD molecule.

The fact that the spectrum of the H<sub>2</sub>O + D<sub>2</sub>O solution in SnCl<sub>4</sub> contains two bands related to HDO, one in the v(OD) region and the other in the v(OH) region, whose frequencies (2649 and 3591 cm<sup>-1</sup>) are roughly equal to ( $v_s + v_{as}$ )/2, indicates that all of the water molecules in SnCl<sub>4</sub> retain the  $C_{2v}$  symmetry [8].

## INTERACTION OF WATER WITH ARSENIC TRICHLORIDE

The IR spectra of water dissolved in high-purity arsenic trichloride were recorded from 900 to 4000 cm<sup>-1</sup> on a UR-20 spectrophotometer using cells with NaCl and AgCl windows. At low water concentrations in AsCl<sub>3</sub> ( $<4 \times 10^{-2}$  mol/l), the spectrum shows absorption bands at 966, 1600, 2800, 3525, 3574, and 3659 cm<sup>-1</sup>, which become progressively stronger with increasing water concentration (Fig. 5). Since arsenic trichloride hydrolyzes readily, the dissolved molecular water is in equilibrium with the products of partial AsCl<sub>3</sub> hydrolysis. The addition of anhydrous hydrogen chloride sharply increases the intensity of the band at 2800 cm<sup>-1</sup>. In addition, as a result of hydrolysis suppression, the bands at 966 and 3525 cm<sup>-1</sup> disappear, while the bands



Fig. 5. IR transmission spectra of water solutions in arsenic trichloride (1-mm absorbing layer): (1)  $7.2 \times 10^{-3}$ , (2)  $1.43 \times 10^{-2}$ , (3)  $3.06 \times 10^{-2}$ , (4)  $8.74 \times 10^{-2}$  mol/l H<sub>2</sub>O.



Fig. 6. IR transmission spectra of water solutions in arsenic trichloride (1) without and (2) with hydrogen chloride; 1-mm absorbing layer,  $1.73 \times 10^{-2}$  mol/l H<sub>2</sub>O.

at 1600, 3574, and 3659 cm<sup>-1</sup> become stronger (Fig. 6). These findings lead us to assign the band at 2800 cm<sup>-1</sup> to hydrogen chloride, the bands at 966 and 3525 cm<sup>-1</sup> to the product of partial AsCl<sub>3</sub> hydrolysis, and the bands at 1600, 3574, and 3659 cm<sup>-1</sup> to molecular water.

The bands related to water can be assigned, respectively, to the  $\delta(H_2O)$  bending mode and the  $v_s$  and  $v_{as}$ stretching modes of the water monomer, in agreement with earlier results for water vapor [8] and water dissolved in organic compounds [9]. The bands in the IR spectrum of water dissolved in AsCl<sub>3</sub> are markedly shifted relative to those in the spectrum of water vapor [8], presumably because of the interaction between water and arsenic trichloride molecules. The energy of this interaction, evaluated from the shift in the stretching frequencies of water using the Yukhnevich–Karyakin equation [10], is 8.74 kJ/mol. The shifts in the v<sub>s</sub> and  $v_{as}$  frequencies are almost identical, indicating that the water molecules dissolved in AsCl<sub>3</sub> experience a symmetrical stress (identical force constants of the bonds). These findings agree well with the calculations reported by Yukhnevich [19]. The slightly reduced difference between the  $v_{as}$  and  $v_s$  frequencies in the spectrum water dissolved in AsCl<sub>3</sub> is probably due to the Fermi resonance between the symmetrical stretching mode of water and the second harmonic  $2\delta(H_2O)$  of its bending mode.

We also examined the effect of the carbon tetrachloride diluent on the  $v_s$  and  $v_{as}$  bands of H<sub>2</sub>O solutions in AsCl<sub>3</sub>. With decreasing AsCl<sub>3</sub> content, the  $v_s$  and  $v_{as}$ frequencies decrease in a similar way as a result of the weaker H<sub>2</sub>O–AsCl<sub>3</sub> interaction (Fig. 7), but the frequency difference between the stretching bands remains almost unchanged. The water molecules in the



**Fig. 7.** Plots of (a) the (1)  $v_{as}$  and (2)  $v_s$  frequencies in the IR transmission spectrum of the H<sub>2</sub>O–AsCl<sub>3</sub>–CCl<sub>4</sub> system and (b) the energy of water–solvent interaction vs. AsCl<sub>3</sub> content.

 $H_2O-AsCl_3-CCl_4$  system retain the  $C_{2v}$  symmetry. Clearly, the interaction between water and AsCl<sub>3</sub> molecules involves the lone electron pair of the oxygen atom.

The assignment of the bands at 1600, 3574, and 3659 cm<sup>-1</sup> to the fundamental modes of water is supported by deuteration results. The addition of D<sub>2</sub>O to a solution of H<sub>2</sub>O in AsCl<sub>3</sub> reduces the intensity of the bands related to water and gives rise to additional bands at 1179, 1408, 2670, 2726, and 3620 cm<sup>-1</sup> as a result of isotope exchange (Fig. 8). The shift in band positions from 1600, 3574, and 3659 to 1179, 2670, and 2726 cm<sup>-1</sup>, respectively, with isotope shift coefficients of 1.357, 1.339, and 1.342, leads us to assign the bands at 1600 and 1179 cm<sup>-1</sup> to the  $\delta$ (H<sub>2</sub>O) and  $\delta$ (D<sub>2</sub>O) modes, the bands at 3574 and 2670 cm<sup>-1</sup> to the v<sub>s</sub> modes of H<sub>2</sub>O and D<sub>2</sub>O, and the bands at 3659 and 2726 cm<sup>-1</sup> to the v<sub>as</sub> modes of H<sub>2</sub>O and D<sub>2</sub>O, respectively. The 1408-cm<sup>-1</sup> band is attributable to the  $\delta$ (HOD) mode, and

the band at 3620 cm<sup>-1</sup> can be assigned to the v(OH) mode of the HOD molecule. The v(OD) band of HOD (2700 cm<sup>-1</sup>) is indiscernible because it is obscured by the strong  $v_{as}$  band of D<sub>2</sub>O (2726 cm<sup>-1</sup>).

The fact that the spectrum of the H<sub>2</sub>O–D<sub>2</sub>O–AsCl<sub>3</sub> system contains, in the v(OH) stretching region, one band related to HOD, whose frequency (3620 cm<sup>-1</sup>) is roughly equal to  $(v_s + v_{as})/2$  for H<sub>2</sub>O, indicates that all of the water molecules in arsenic trichloride retain the  $C_{2v}$  symmetry [8].

Deuteration also sharply reduces the intensity of the bands at 966 and 3525 cm<sup>-1</sup> and gives rise to a new band at 2618 cm<sup>-1</sup>, with an isotope shift coefficient of 1.346, which suggests that this band is due to the v(OH) stretching mode of arsenic hydroxychloride. The band at 966 cm<sup>-1</sup> shifts to the fundamental absorption range of arsenic trichloride. The intensity of this band correlates with that of the 3525-cm<sup>-1</sup> band, and it can be assigned to the  $\delta$ (AsOH) bending mode.

Arsenic trichloride hydrolysis involves the formation of soluble intermediate products with the general formula As(OH)<sub>n</sub>Cl<sub>3-n</sub>. The fact that the OH stretching region contains only one, narrow absorption band, that at 3525 cm<sup>-1</sup> (FWHM = 60 cm<sup>-1</sup>) suggests that, at water concentrations below  $4 \times 10^{-2}$  mol/l, hydrolysis proceeds according to the scheme

$$AsCl_3 + H_2O \implies As(OH)Cl_2 + HCl.$$

Therefore, the bands at 966 and 3525 cm<sup>-1</sup> can be assigned, respectively, to the  $\delta$ (AsOH) bending mode and the v(OH) stretching mode of the OH groups in As(OH)Cl<sub>2</sub>, the 2800-cm<sup>-1</sup> band is due to stretching vibrations of hydrogen chloride, and the 2618-cm<sup>-1</sup> band corresponds to the v(OD) mode of the As(OD)Cl<sub>2</sub> molecule.

The shift and broadening of the v(OH) band of As(OH)Cl<sub>2</sub> in the spectrum of water dissolved in AsCl<sub>3</sub>



Fig. 8. IR transmission spectra of (1)  $H_2O$  and (2)  $H_2O + D_2O$  solutions in AsCl<sub>3</sub> (1-mm absorbing layer).



Fig. 9. IR transmission spectra of water solutions in arsenic trichloride (1) without and (2) with hydrogen chloride; 1-mm absorbing layer,  $8.74 \times 10^{-2}$  mol/l H<sub>2</sub>O.

(v(OH) = 3525 cm<sup>-1</sup>, FWHM = 60 cm<sup>-1</sup>) in comparison with the v(OH) band of Ge(OH)Cl<sub>3</sub> in the spectrum of water in GeCl<sub>4</sub> (v(OH) = 3603 cm<sup>-1</sup>, FWHM = 36 cm<sup>-1</sup>) seem to be evidence for a stronger interaction of the OH group of As(OH)Cl<sub>2</sub> with AsCl<sub>3</sub> molecules. The energy of this interaction, evaluated by the Sokolov equation [12], is 5.44 kJ/mol. The stronger intermolecular interactions in the H<sub>2</sub>O–AsCl<sub>3</sub> system are also responsible for the shift of the stretching band of HCl and the absence of the envelopes of the rotational fine structure.

At water concentrations in arsenic trichloride above  $4 \times 10^{-2}$  mol/l, the IR transmission spectrum shows a band at 1253 cm<sup>-1</sup> and a broad band around 3150 cm<sup>-1</sup> (Fig. 5). On the addition of anhydrous hydrogen chloride, these bands disappear (Fig. 9), and the intensity of the bands due to water decreases, clearly because, without hydrolysis, the water solubility in arsenic trichloride is lower (according to our results,  $3.59 \times 10^{-2}$  mol/l at 303 K). These findings indicate that the bands at 1253 and 3150 cm<sup>-1</sup> are related to the products of AsCl<sub>3</sub> hydrolysis. These bands could be assigned using deuteration results. The addition of D<sub>2</sub>O to a solution of H<sub>2</sub>O in AsCl<sub>3</sub> sharply reduces the intensity of the 3150-cm<sup>-1</sup> band and gives rise to a broad absorption around 2350 cm<sup>-1</sup> (Fig. 8). The shift in band position from 3150 to 2350 cm<sup>-1</sup>, with v(OH)/v(OD) =3150/2350 = 1.34, suggests that this band is due to OH stretches. The fact that the OH stretching region contains, along with the v(OH) band of As(OH)Cl<sub>2</sub> (3525 cm<sup>-1</sup>), the broad band around 3150 cm<sup>-1</sup> points to further AsCl<sub>3</sub> hydrolysis with the formation of  $As(OH)_n Cl_{3-n}$  hydroxychlorides:

$$AsCl_3 + nH_2O \implies As(OH)_nCl_{3-n} + nHCl.$$

The 3150-cm<sup>-1</sup> band can be assigned to the v(OH) stretching mode of  $As(OH)_nCl_{3-n}$ . Since the OH

groups in As(OH)<sub>n</sub>Cl<sub>3-n</sub> are close in vibrational frequencies, the corresponding absorption bands overlap to form the broad, unresolved band at 3150 cm<sup>-1</sup>. The rather large shift and broadening of this band compared to the 3525-cm<sup>-1</sup> band of As(OH)Cl<sub>2</sub>, are also attributable to the formation of hydrogen bonds. The same refers to the band around 2350 cm<sup>-1</sup>, due to the v(OD) mode of the As(OD)<sub>n</sub>Cl<sub>3-n</sub> molecules.

The addition of  $D_2O$  to a solution of  $H_2O$  in AsCl<sub>3</sub> further reduces the intensity of the 1253-cm<sup>-1</sup> band (Fig. 8). Since the intensity of this band depends on the total concentration of water dissolved in arsenic trichloride but is independent of the isotopic composition of the water, it seems likely that this band arises from arsenic oxychloride. The fact that only one, narrow band (1253 cm<sup>-1</sup>) is present in the spectral range 1000– 1300 cm<sup>-1</sup> suggests that this band can be assigned to predominantly stretching vibrations of the "isolated" multiple bonds AsO in AsOCI [21, 22], which forms by the reactions

$$As(OH)_2Cl \implies AsOCl + H_2O$$
,  
 $As(OH)Cl_2 \implies AsOCl + HCl$ .

The formation of  $As(OH)_nCl_{3-n}$  and AsOCl can be promoted by removing hydrogen chloride. Indeed, after rectification of arsenic trichloride, the still contains viscous, oily liquid, whose spectrum shows strong bands at 1253, 3150, and 3525 cm<sup>-1</sup>, while the absorption band due to HCl is missing. The IR spectra of arsenic trichloride samples prepared by different procedures also indicate that the contents of hydrolysis products and molecular water in AsCl<sub>3</sub> depend on HCl concentration. Figure 10 displays the IR spectra of AsCl<sub>3</sub> samples prepared by arsenic chlorination and liquid-phase As<sub>2</sub>O<sub>3</sub> hydrochlorination. The spectrum of the former sample shows a strong band due to HCl (2800 cm<sup>-1</sup>)



Fig. 10. IR transmission spectra of arsenic trichloride prepared by (1) arsenic chlorination and (2) liquid-phase  $As_2O_3$  hydrochlorination; 1-mm absorbing layer.

and weak bands due to water (1600, 3574, and  $3659 \text{ cm}^{-1}$ ) and  $As(OH)Cl_2$  (1253 cm<sup>-1</sup>). The bands related to  $As(OH)_nCl_{3-n}$  (3150 cm<sup>-1</sup>) and AsOCl (1253 cm<sup>-1</sup>) are missing. At the same time, the AsCl<sub>3</sub> prepared by liquid-phase  $As_2O_3$  hydrochlorination contains substantial amounts of molecular water, hydroxy-chlorides, and oxychlorides (2 × 10<sup>-1</sup> mol/l), whereas the HCl concentration is insignificant. The large amount of hydrogen chloride in arsenic trichloride inhibits hydrolysis and reduces water solubility.

### CONCLUSIONS

The IR spectroscopic study of  $H_2O$  solutions in  $GeCl_4$ ,  $SnCl_4$ , and  $AsCl_3$  leads us to the following conclusions:

(1) High-purity GeCl<sub>4</sub>, SnCl<sub>4</sub>, and AsCl<sub>3</sub> contain, along with trace impurities (a total of  $10^{-4}$  to  $10^{-5}$  mol/l), substantial amounts of molecular water ( $10^{-1}$  to  $10^{-2}$  mol/l). Germanium tetrachloride and arsenic trichloride also contain partial hydrolysis products: HCl, Ge(OH)<sub>n</sub>Cl<sub>4-n</sub>, germanium oxychlorides (GeOCl<sub>2</sub>, Ge<sub>2</sub>OCl<sub>6</sub>, or Ge<sub>n</sub>O<sub>n-1</sub>Cl<sub>2n+2</sub>), As(OH)<sub>n</sub>Cl<sub>3-n</sub>, and AsOCl (a total of  $10^{-1}$  to  $10^{-2}$  mol/l, depending on the HCl concentration).

The water in GeCl<sub>4</sub>, SnCl<sub>4</sub>, and AsCl<sub>3</sub> is in monomeric form. At water concentrations above  $10^{-2}$  mol/l, GeCl<sub>4</sub> also contains H<sub>3</sub>O<sup>+</sup> ions. The interaction between water and SnCl<sub>4</sub> or AsCl<sub>3</sub> molecules involves the lone electron pair of the oxygen atom.

At low water concentrations in GeCl<sub>4</sub> ( $<10^{-2}$  mol/l) and AsCl<sub>3</sub> ( $<4 \times 10^{-2}$  mol/l), the main hydrolysis products are Ge(OH)Cl<sub>3</sub> and As(OH)Cl<sub>2</sub>. At higher water concentrations in GeCl<sub>4</sub> and AsCl<sub>3</sub>, the degree of hydrolysis is higher, and the main products are Ge(OH)<sub>n</sub>Cl<sub>4-n</sub>, As(OH)<sub>n</sub>Cl<sub>3-n</sub>, germanium oxychlorides (GeOCl<sub>2</sub>, Ge<sub>2</sub>OCl<sub>6</sub>, or Ge<sub>n</sub>O<sub>n-1</sub>Cl<sub>2n+2</sub>), and AsOCl.

The results described in this work were used to develop techniques and processes for producing highpurity chlorides suitable for microelectronic and fiber optics applications.

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