Reviews

Vibrational spectra of volatile inorganic hydrides in the liquid state

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The results of studies of IR and Raman spectra of volatile inorganic hydrides of Group IV—VI and Periods 3 and 4 elements in the liquid state are surveyed and analyzed. The mechanisms of intermolecular interactions in these liquids are discussed.

Key words: IR and Raman spectra, correlation functions, vibrational and rotational relaxation, intermolecular hydrogen bond.

Volatile inorganic hydrides of elements of Group IV—VI and Periods 3—5 of the periodic system found wide practical use in the late 1960s in the production of high-purity elements, synthesis of optical materials, and growing and doping of semiconducting epitaxial layers. In recent years, this technology known as the "chemical vapor deposition" (CVD) method has been developed especially vigorously. This, in turn, has stimulated the study of previously unknown properties of hydrides and revision of the known data using high-purity samples of these compounds. Exhaustive data on the physicochemical properties of volatile inorganic hydrides and methods for their purification and analysis have been published.[1—3] Some physicochemical characteristics of volatile hydrides are presented in Table 1.

The results of studies of the vibrational spectra of hydrides have been surveyed in a classical monograph.[4] In recent years, interest in the study of the spectral properties of hydrides has substantially increased, which is due, on the one hand, to the appearance of fundamentally new methods and investigation techniques, which made it possible to refine many important characteristics of molecules, and, on the other hand, to the above-mentioned practical application of hydrides, because spectroscopic methods, most of all IR spectroscopy, are widely used to estimate the degree of purity of hydrides and to study the mechanisms of hydride reactions.[5—9]

A large number of studies devoted to the analysis of the IR absorption spectra of volatile hydrides in the gas and solid phases and in low-temperature matrices have been published. The IR spectra of ammonia have been studied in the greatest detail (see, for example, Refs. 10—12). Much less data have been reported for the hydrides of elements of the 4th and 5th periods. Raman spectra of hydrides and vibrational spectra of volatile

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Table 1. Physicochemical properties of volatile inorganic hydrides[1,2]

Hy-dride	M.p.	B.p.	Cr.p.	ΔH_{melt}	ΔH_{boil}	p_{cr}	$p_{300\ K}$	α	n_D[b]
		K		kcal mol^{-1}		atm		/Å^3 [a]	
SiH_4	88.5	161.5	269.4	0.159	2.687	41.7	—	4.61	1.290
GeH_4	107.3	184.7	308.0	0.200	3.608	48.4	31.9	—	1.601
NH_3	195.4	239.7	405.6	1.352	5.581	112	10.6	2.40	1.355
PH_3	139.4	187.2	324.5	0.270	3.362	59.0	32.1	4.75	1.368
AsH_3	156.2	219.7	374.5	0.286	3.798	65.8	15.4	5.66	1.523
H_2S	187.6	213.0	373.6	0.568	4.483	78.6	20.5	3.60	1.460
H_2Se	207.4	231.9	410.6	0.601	4.460	83.9	10.4	4.54	1.773

[a] Polarizability of hydride molecules.[14]

[b] The refractive index of liquid hydrides at the boiling point.[14]

hydrides in the liquid phase are poorly studied. However, such data would provide valuable information on the structural features and dynamics of the interaction of molecules and, hence, on the character of intermolecular interactions.

The purpose of this work is to generalize the main results of studies of the vibrational spectra of thermodynamically stable volatile inorganic hydrides of Group IV—VI elements (SiH_4, GeH_4, NH_3, PH_3, AsH_3, H_2S, and H_2Se) in the liquid phase obtained during the last 15 years. Data for the gas phase and for solutions in liquefied inert gases are presented only for comparison with the results obtained for liquids.

Volatile hydrides have low critical temperatures and boiling points and narrow temperature ranges of the liquid state under atmospheric pressure (see Table 1); however, this range can be extended by working at elevated pressures (Fig. 1). Therefore, quantitative study of the vibrational spectra of liquid hydrides has required the design of special cryostat cells, which withstand pressures of up to 50 atm.[3—15] The measurement of the integral absorption coefficients of intense bands of fundamental modes in the IR spectra of liquid hydrides faces substantial methodological difficulties; it is necessary to use several micron-thick optical layers in combination with pressures of several tens of atmospheres in the cryostat cell. In addition, the bands of deformation vibrations in the IR and Raman spectra of liquid hydrides of Group IV—VI elements are poorly resolved at relatively high temperatures (250—300 K), while the bands of stretching vibrations (except those in the Raman spectra of liquid methane[16,17]) are not resolved at all.[14] In these cases, reliable mathematical methods for approximation of complex vibration bands (especially for the measurement of integral absorption coefficients) taking into account the physicochemical properties need to be used.[15,18,19]

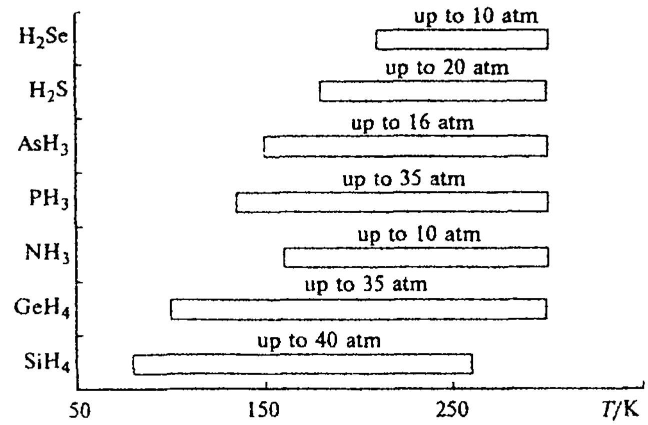

Fig. 1. Region of existence of the liquid phase of cryosolvents, *viz.*, hydrides of Group IVA—VIA elements, at temperatures ranging from the boiling point to 293 K (for silane, from the boiling point to the critical point).

Hydrides of Group IV elements

The molecules MH_4 (M is a Group IV element) belong to the T_d point group of symmetry and possess four normal modes with the symmetry types

$$\Gamma_{vib} = A_1 + E + 2F_2.$$

All four vibrations are active in the Raman spectrum, whereas only two triply degenerate modes, ν_3 and ν_4, are IR active. The vibrational spectra of methane[10,12] and silane[10,12,20—22] have been studied most comprehensively, and the spectra of germane[22] have been somewhat less studied (Table 2). A comparative study of the IR spectra of hydrides MH_4 recorded at a relatively low resolution has been carried out[23]; high-resolution IR spectra of the ν_3 and ν_4 bands of silane and germane have been discussed[22]; the integral intensities of these bands have been determined[24—27]; in the case of silane, the results are contradictory. The values for the intensity of the ν_3 band of germane found in various studies[24—28] are in satisfactory agreement with one another.

The intensities of the ν_3 and ν_4 bands markedly increase on passing from CH_4 to SiH_4 and GeH_4; the values for germane and silane are rather close to each other (see Table 2). The intensity of ν_3 in the spectrum

Table 2. Frequencies (ν/cm^{-1}), integral absorption coefficients ($A \cdot 10^8$/cm^2 molec.$^{-1}$ s^{-1}), and relative intensities ($A_{\rm rel}$) of bands in the IR spectra of CH_4, SiH_4, and GeH_4 in the gas phase[12,23–28]

Type of	CH_4			SiH_4			GeH_4		
vibrations	ν	A	$A_{\rm rel}$	ν	A	$A_{\rm rel}$	ν	A	$A_{\rm rel}$
ν_4	1306	16.8	500	913	199[24] 147[25]	1000 920	820	122[26] 140[27]	810
ν_3	3019	33.6	1000	2191	151[24] 160[25]	760 1000	2114	150[26] 153[27]	1000
$\nu_2+2\nu_4$	4123	0.02	0.6	—	—	—	—	—	—
$\nu_1+\nu_4$	4216	0.54	16	—	—	—	—	—	—
$\nu_3+\nu_4$	4313	0.45	13	3110	—	—	—	—	—
$\nu_2+\nu_3$	4546	0.15	4.5	3150	—	—	—	—	—
$2\nu_1$	—	—	—	4308	—	—	4154	—	—
$2\nu_3$	6006	0.22	6.5	4379	—	—	—	—	—
$\nu_1+\nu_3$	—	—	—	4309	—	—	—	—	—
$3\nu_1$	—	—	—	6362	—	—	—	—	—
$2\nu_1+\nu_3$	—	—	—	—	—	—	—	—	—
$\nu_1+2\nu_3$	—	—	—	6496	—	—	—	—	—
$3\nu_3$	—	—	—	6000	—	—	—	—	—

of germane is somewhat larger than the intensity of ν_4, whereas in the case of silane, contradictory data have been obtained,[24–27] which is due to insufficient accuracy of determination of the absorption coefficients. Only in the case of methane and, to a lesser degree, silane are experimental data on the frequencies and intensities of the overtone and complex bands available. The results of studies of the IR spectra of gaseous silicon and germanium hydrides are substantially supplemented by studies of the IR spectra of their solutions in liquefied noble gases.[22] The use of a multi-pass cell made it possible to identify for the first time the numerous weak bands for complex and overtone vibrations in the 900—6500 cm^{-1} range up to the 3rd order transitions and to revise the intensity ratio for the ν_3 and ν_4 bands in the spectra of silicon and germanium hydrides.[22]

The IR absorption spectrum of liquid silane in the region of main vibrations has been studied at an optical length of ~1 μm;[29] later,[30–32] the IR spectra of SiH_4 and GeH_4 in the liquid phase were studied in a wider region, 800—5000 cm^{-1} (Table 3, Fig. 2), but at a larger optical length; this gave no way of elucidating the temperature dependence of the frequency, form, or intensity of the main vibration bands.

Table 3. Frequencies (ν/cm^{-1}) of bands in the IR spectra of liquid CH_4,[33–35] SiH_4, and GeH_4 [29,34] at various temperatures

Type of vibrations	CH_4 (117 K)	SiH_4 (190 K)	GeH_4 (246 K)
ν_4	1300	910	~820
$2\nu_4$	2600	—	—
$\nu_2+\nu_4$	2820	1860	1730
ν_3	3015	2200	~2100
$3\nu_4$	—	2685	2415
$\nu_1+\nu_4$	—	2837	2660
$\nu_3+\nu_4$	—	3090	2910
$\nu_2+\nu_3$	—	3130	—
$2\nu_2+2\nu_4$	—	—	—
$\nu_3+2\nu_4$	—	—	—
$\nu_2+\nu_3+\nu_4$	—	4040	3713
$\nu_1+\nu_3$	—	—	—
$2\nu_3$	—	4295	4125

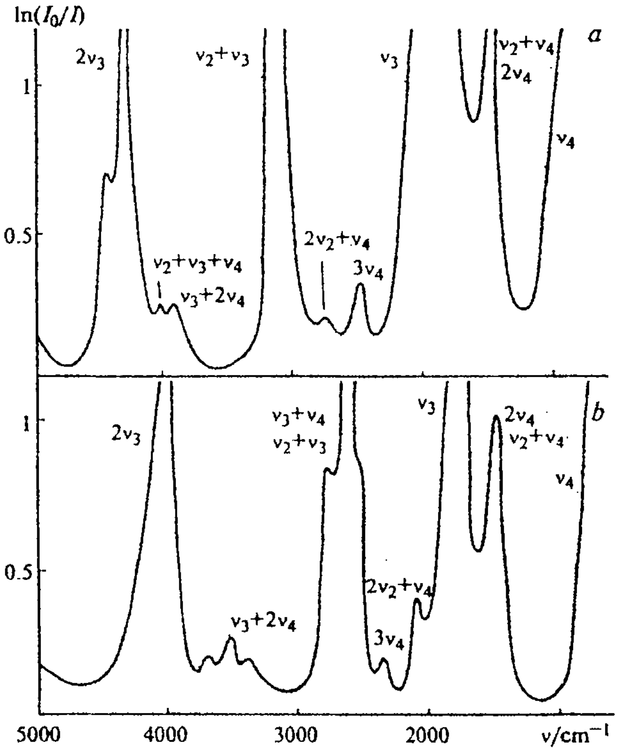

Fig. 2. IR absorption spectra of liquid SiH_4 (*a*) and GeH_4 (*b*) at 190 and 246 K, respectively; the layer thickness was 0.5 mm.

The Raman spectra of SiH_4 and GeH_4, as their IR spectra, have been studied mostly in the gas[36–38] and solid[29,39] phases. Primary attention was devoted to the measurement of the crossection of the Raman process in gaseous silane and germane, spectroscopic manifestations of isotope effects, and the structures of SiH_4 and GeH_4 in the crystalline state. Raman spectra of liquid silane have been considered[29] briefly (Table 4), and those of liquid germane have been studied in detail[40] in the 200—300 K temperature range. Like IR spectral bands, Raman lines of liquid silane and germane including the overall line of stretching vibrations, which is a superposition of lines corresponding to the ν_1 and ν_3 modes, resolved under experimental conditions, undergo a substantial shift to lower wavelengths on going from gas to the liquid phase (see Table 4). The ν_4 line of germane is the only exception; its maximum, on the contrary, slightly shifts to higher frequencies. Study of the temperature dependence of the frequencies of Raman lines of liquid germane has not revealed any substantial changes of their maxima.[40] Comparative analysis[40] of

Table 4. Frequencies (ν/cm^{-1}) of lines of the fundamental vibrations in the Raman spectra of silane and germane in the gas[36—38] and liquid[29,40] phases

Type of vibrations	SiH_4 Gas (293 K)	SiH_4 Liquid (98 K)	GeH_4 Gas (293 K)	GeH_4 Liquid (290 K)
ν_1	2185.7		2110.6	
		2171.0		2091.5
ν_3	2189.1		2111.5	
ν_2	972.1	961.7	930.6	916.0
ν_4	913.3	—	821.0	826.2

the vibrational and rotational correlation functions and the vibration (τ_V = 1.5 ps) and orientation (τ_R = 4.5 ps) relaxation times of the GeH_4 molecules in the liquid phase demonstrated that the τ_V and τ_R values virtually do not change over the whole temperature range and that germane molecules are involved in the rotation movement, normal for nonassociated liquid systems, and reorient themselves as separate kinetic particles. Their movement is described by a Debye type model (small-angle rotaional diffusion),[19,41—44] and the angle of unit rotation of the germane molecule at the first step of diffusion does not exceed 4—5°.

Hydrides of Group V elements

The NH_3, PH_3, and AsH_3 molecules belong to the C_{3v} point group of symmetry; all four vibrations of these molecules having the types of symmetry

$$\Gamma_{vib} = 2A_1 + 2E$$

are active both in the IR and Raman spectra (Table 5).

Table 5. Frequencies (ν/cm^{-1}) and absolute ($A \cdot 10^8$/cm^2 molec.$^{-1}$ s^{-1}) and relative (A_{rel}) intensities of bands in the IR absorption spectra of gaseous ammonia,[12] phosphine,[12] and arsine[15]

Type of vibrations	NH_3 ν	NH_3 A^a	NH_3 A_{rel}	PH_3 ν	PH_3 A^b	PH_3 A_{rel}	AsH_3 ν	AsH_3 A^c	AsH_3 A_{rel}
$2\nu_4$	3219	1.0	1						
ν_1	3337	3.3	4	2321			2112		
					58.2	100		125^d	100
ν_3	3444	2.3	3	2327			2127		
ν_2	968	82	100	992	9.2		905		
						45		21	17
ν_4	1627	14.5	18	1122	11.4		1007		

[a] The total A for the ν_1, ν_3, and $2\nu_4$ bands of ammonia in the gas phase[46] is $6 \cdot 10^{-8}$ cm^2 molec.$^{-1}$ s^{-1}.

[b] According to published data,[47] $A(\nu_1) = 14 \cdot 10^{-8}$ and $A(\nu_3) = 49 \cdot 10^{-8}$ cm^2 molec.$^{-1}$ s^{-1}.

[c] According to published data,[48,49] ν_1 = 2115 cm^{-1}; ν_3 = 2126 cm^{-1}; ν_2 = 907 cm^{-1}; ν_4 = 999 cm^{-1}.

[d] According to published data,[45] $A(\nu_1,\nu_3) = 123 \cdot 10^{-8}$ cm^2 molec.$^{-1}$ s^{-1}.

The IR absorption spectra of these compounds in the gas phase have been studied[45—52] in the region of complex and overtone vibrations; the IR spectra of solutions of PH_3 and AsH_3 in liquid argon have also been studied.[50—53] Figure 3 shows the IR absorption spectra of liquid nitrogen, phosphorus, and arsenic hydrides in the region of fundamental vibrations near room temperature. Table 6 presents the spectral parameters of bands observed[15,50,52] in the IR spectra of liquid hydrides of Group V elements.

In the spectrum of NH_3 in the gas and liquid phases, the band due to the ν_2 deformation mode (ν_{def}) is the most intense, whereas in the spectra of hydride analogs, the most intense bands are those due to the ν_1 and ν_3 stretching modes (ν_{str}). In general, the intensity of the ν_1 and ν_3 bands increases, whereas the intensity of the deformation bands, ν_2 and ν_4, decreases on going from earlier to later Group V elements.

The stretching bands of NH_3 noticeably shift to lower frequencies on the gas—liquid transition, whereas bands

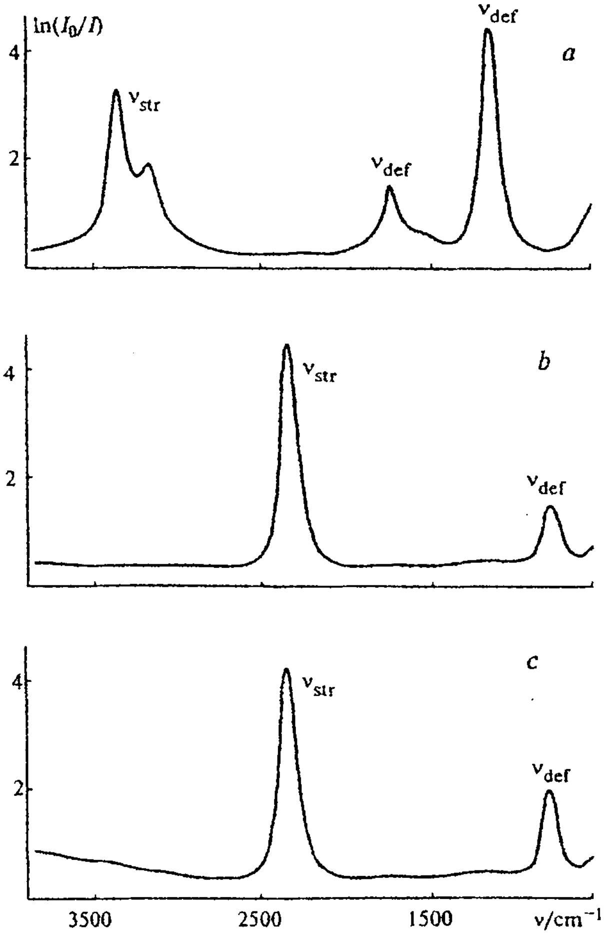

Fig. 3. IR absorption spectra of liquid NH_3 (*a*), PH_3 (*b*), and AsH_3 (*c*) in the region of fundamental vibrations at 293, 292, and 289 K, respectively. The layer thickness was 13 (*a*), 18 (*b*), and 20 (*c*) μm.

Table 6. Frequencies (ν/cm^{-1}) and absolute ($A \cdot 10^8$/cm^2 molec.$^{-1}$ s^{-1}) and relative (A_{rel}) intensities of absorption bands in the IR spectra of liquid ammonia (298 K), phosphine (292 K), and arsine (298 K)[15,50]

Type of	NH_3*			PH_3			AsH_3		
vibrations	ν	A	A_{rel}	ν	A	A_{rel}	ν	A	A_{rel}
$2\nu_4$	3252								
ν_1		48.1	75						
				2314	72.0	1000	2116	128.1	1000
ν_3	3385								
ν_2	1053	59.5	100	~1000			905		
					4.0	350		26.9	210
ν_4	1632	9.9	17	~1100			980		
$\nu_{str}+\nu_{def}$	6055	0.06	0.1	3402	0.9	13	3076	0.8	6
$2\nu_{str}$	6530	0.85	1.4	4532	0.6	8	4132	0.9	7

* For liquid ammonia, according to published data,[54,55] (ν_1, $2\nu_4$) = 3230 cm^{-1}; ν_3 = 3360 cm^{-1}; ν_2 = 1068 cm^{-1}; ν_4 = 1630 cm^{-1}; according to another publication,[56] (ν_1, $2\nu_4$) = 3250 cm^{-1}; ν_3 = 3382 cm^{-1}; ν_4 = 1628 cm^{-1}. According to published data,[55] $A(\nu_1, \nu_3, 2\nu_4) = 55 \cdot 10^8 \cdot$ cm^2 molec.$^{-1}$ s^{-1}; $A(\nu_2) = 50 \cdot 10^8$ cm^2 molec.$^{-1}$ s^{-1}; $A(\nu_4) = 13 \cdot 10^8$ cm^2 molec.$^{-1}$ s^{-1} at T = 218 K.

of deformation vibrations slightly shift to higher frequencies. The integral absorption coefficient of the band of stretching vibrations as a whole (including the weak band of the $2\nu_4$ overtone overlapped with it) substantially increases, while the intensity of the ν_2 and ν_4 bands remains nearly the same. These features virtually cannot be observed in the spectra of liquid PH_3 and AsH_3, in which the frequency and the intensity of bands of fundamental vibrations change only slightly on passing from gas to the liquid phase (especially in the case of arsine).

The IR absorption spectra of ammonia, phosphine, and arsine in the liquid phase have been studied in detail[57] over a broad temperature range (150—300 K). In the spectra of liquid ammonia, the stretching vibration band* (ν_{str}) slightly shifts to lower frequencies (by 4 cm^{-1}) upon a temperature decrease; the integral absorption coefficient increases ~1.3-fold as the temperature changes from 289 to 218 K. In the same temperature range, the maximum of the band of the symmetrical ν_2 deformation mode markedly (by 13 cm^{-1}) shifts to the high-frequency region with a simultaneous increase in the integral absorption coefficient by ~15%. The frequency of the band corresponding to the ν_4 deformation mode barely changes in the temperature range from 289 to 203 K, and the integral absorption coefficient remains constant to within the experimental error.

On going from ammonia to phosphine, the above-noted tendencies markedly smooth out. Thus the frequency of the ν_{str} mode virtually does not change as the temperature varies in the 290—153 K range, and its integral absorption coefficient slightly increases. The band of the ν_2 deformation mode undergoes a substantial (9 cm^{-1}) low-frequency shift, whereas the band intensity ($A(\nu_2)$) remains roughly the same. Conversely, the maximum of the ν_4 deformation mode shifts to higher frequencies by 11 cm^{-1} on decreasing the temperature of the experiment, and the intensity of this band somewhat increases.

On going from phosphine to arsine, the spectral pattern sharply changes. When the temperature of liquid arsine changes in the 295—157 K range, the ν_{str} band undergoes a relatively large (12 cm^{-1}) low-frequency shift, while its integral absorption coefficient decreases. The frequencies of the ν_2 and ν_4 deformation modes in the IR spectrum of arsine remain virtually constant, but their intensity changes. As the temperature decreases from 295 to 157 K, the $A(\nu_2)$ increases almost 1.5-fold, whereas $A(\nu_4)$, conversely, decreases by ~25%.

At higher temperatures (250—290 K), traces of the rotational structure of the P- and R-branches can be detected in the absorption spectra of liquid hydrides.[57] When the temperature decreases, this structure collapses, and at relatively low temperatures (≤200 K), the shape of the bands can be described by a dispersion curve. Assuming the Lorentzian shapes of the band contours[58—62] for the deformation modes of liquid phosphine and arsine, the upper limits of the correlation times of the angular moment τ_{rot} were estimated to be 0.1 ps at T = 150 K for both liquid hydrides; *i.e.*, they do not differ significantly from the corresponding values for solutions of phosphine and arsine in liquid argon at T = 96±2 K (0.19 and 0.21 ps, respectively).

The differences between the spectral characteristics of liquid nitrogen, phosphorus, and arsenic hydrides can be explained[15,50,57] by different strengths of local intermolecular interactions in these compounds. The substantial shift (≥ 40 cm^{-1}) of the ν_{str} band to lower frequencies on going from gas to the liquid phase, observed in the case of NH_3, the increase in the integral intensity of this band following a decrease in the temperature of the liquid phase, and the high-frequency shift of deformation bands with their intensity remaining virtually constant are typical of systems with hydrogen bonds. The above-mentioned facts are consistent with the views[63,64] on the associative processes in gaseous and liquid NH_3; they are not at variance with the data obtained in a study of the IR spectra of $(NH_3)_2$ in low-temperature matrices[65] and can serve as evidence supporting the formation of pair associates of ammonia in the liquid phase. The formation of fairly strong H-bonded complexes in ammonia is also indirectly indicated by the results of study of the IR spectra of hydrides of Group VA elements in solutions in liquefied noble gases.[15,50—52,66] Unlike phosphine and arsine, whose solubility in liquid Ar (T = 96±2 K) amounts to $4.2 \cdot 10^{-2}$ and $2.8 \cdot 10^{-2}$ mol L^{-1}, respectively,[67,68] ammonia is virtually insoluble in liquid argon or krypton.

The enthalpies of intermolecular interactions in liquid ammonia, phosphine, and arsine were estimated[15,50]

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* The bands for the ν_1 and ν_3 stretching modes of the hydrides MH_3 (M = N, P, As) in the liquid phase entirely overlap; therefore, the overall band $\nu_{1,3}$ can be designated by ν_{str}.

assuming that, on the average, one H-bond is formed between two molecules.[63] The $\Delta H_{290} = -1.7$ kcal mol^{-1} value, found from the IR spectra of liquid ammonia, is in good agreement with the value calculated[69] by quantum-chemical methods for the dimer $(NH_3)_2$. For liquid phosphine, $\Delta H_{298} = -0.1$ kcal mol^{-1}; this also does not contradict the results of quantum-chemical calculations of the enthalpy of the $(PH_3)_2$ dimer ($\Delta H_{298} = -0.3$ kcal mol^{-1}).[70] For liquid arsine, the ΔH_{298} value is nearly zero.

Transition from a hydride of a Period 2 element (NH_3) to hydrides of 3rd (PH_3) and 4th (AsH_3) period elements within the same group is apparently accompanied by a decrease in the tendency of molecules to form H-bonds, if for no other reason than the decrease in the electronegativity of the hydride-forming element. At the same time, an increase in the energy of nonspecific (van der Waals) interaction due to the increase in the polarizability should be expected in the same series (see Table 1). All this should be reflected in the spectral properties of the studied hydrides in the liquid state. In particular, the substantial low-frequency shift of the ν_{str} band in the IR spectrum of liquid arsine observed on decreasing the temperature[57] with the integral absorption coefficient remaining virtually constant is apparently due to the enhancement of nonspecific van der Waals interactions between AsH_3 molecules. Additional information concerning this point can be obtained from the Raman spectra of liquid hydrides.

Unlike IR absorption spectra, the Raman spectra of liquid hydrides of Group VA elements are very little studied, which is due most of all to the absence of experimental equipment that would satisfy the safety requirements for handling large quantities of these reactive and toxic liquids. The Raman spectra of liquid NH_3, ND_3, and ND_2H in the region of fundamental vibrations at 298 and 202 K,[71,72] the Raman spectra of gaseous NH_3[73—75] and gaseous PH_3 in the 293—903 K temperature range,[76,77] and the Raman spectrum of solid AsD_3[78] have been studied.

The Raman spectra of liquid phosphine and arsine in the 180—300 K temperature range have been described systematically; the temperature dependences of the line shapes, widths, and shifts were analyzed[57] (Figs. 4, 5, Tables 7, 8).

The region of stretching vibrations of liquid phosphine and arsine exhibit one Raman line (ν_{str} or $\nu_{1,3}$), which is a superposition of lines corresponding to the ν_1 and ν_3 modes. A similar line has been recorded[72] in the Raman spectra of liquid ammonia at two different temperatures.

Analysis of the Raman spectra of liquid PH_3 and AsH_3,[57] and also NH_3,[72] indicates that the ν_{str} frequencies of ammonia (3300 cm^{-1}, $T = 298$ K), phosphine (2307 cm^{-1}, $T = 298$ K), and arsine (2096 cm^{-1}, $T = 298$ K) virtually do not change when the temperature decreases. In the 298—202 K (NH_3),[72] 298—181 K (PH_3), and 298—182 K (AsH_3)[57] temperature ranges, only slight (2, 3, and 3 cm^{-1}, respectively) low-frequency shifts of these Raman lines are observed. The line for the ν_2 symmetrical deformation mode of ammonia (1046 cm^{-1}, $T = 298$ K) shifts to higher frequencies by 24 cm^{-1} as the temperature decreases by 96 °C, whereas the frequency of the ν_4 mode does not change (1638 cm^{-1}) over the same temperature range (298—202 K). The ν_2 deformation mode of phosphine undergoes a slight high-frequency shift (7 cm^{-1}) as the temperature decreases from 298 to 181 K, whereas the frequency of the ν_4 line, conversely, shifts in the same temperature range by 7 cm^{-1} to lower frequencies.

On going to arsine, the high-frequency shift of the ν_2 mode somewhat increases (12 cm^{-1} in the temperature range from 298 to 182 K), while the frequency of the ν_4 mode, similarly to the Raman line in the spectrum of phosphine, undergoes a slight (4 cm^{-1}) shift to lower frequencies over the same temperature range.

The substantial high-frequency shift of the ν_2 line in the Raman spectrum of liquid ammonia following a temperature decrease is correlated with enhancement of self-association of molecules through the formation of

Table 7. Frequencies (ν/cm^{-1}) and half-widths ($\Delta\nu_{1/2}$/cm^{-1}) of lines due to stretching and deformation vibrations in the Raman spectrum of liquid phosphine as a function of temperature[57]

T/K	Stretching vibrations		Deformation vibrations			
	$\nu_{1,3}$	$\Delta\nu_{1/2}{}^{1,3}$	ν_2	$\Delta\nu_{1/2}{}^{2}$	ν_4	$\Delta\nu_{1/2}{}^{4}$
181	2304	10.7	981	15.2	1110	60.0
198	2304	11.0	980	15.7	1112	64.2
222	2305	11.2	978	16.1	1115	70.3
243	2306	11.7	977	16.9	1114	74.9
250	2305	11.9	976	17.0	1114	75.7
265	2306	12.4	975	17.2	1115	80.5
277	2306	13.5	975	18.0	1118	83.4
289	2307	14.7	974	18.5	1117	89.7
298*	2307	14.9	974	18.1	1117	92.1

* According to published data,[76] the frequency of the overall ν_1 and ν_3 stretching line in the Raman spectrum of gaseous phosphine at -20 °C amounts to 2318 cm^{-1}.

Table 8. Frequencies (ν/cm^{-1}) and half-widths ($\Delta\nu_{1/2}$/cm^{-1}) of lines due to stretching and deformation vibrations in the Raman spectrum of liquid arsine as a function of temperature[57]

T/K	Stretching vibrations		Deformation vibrations			
	$\nu_{1,3}$	$\Delta\nu_{1/2}{}^{1,3}$	ν_2	$\Delta\nu_{1/2}{}^{2}$	ν_4	$\Delta\nu_{1/2}{}^{4}$
182	2093	7.6	910	14.6	985	67.1
200	2094	7.7	909	14.9	985	70.7
221	2094	7.9	908	15.1	986	75.2
243	2095	7.9	905	16.2	989	91.8
250	2095	7.9	903	16.5	988	92.4
267	2095	8.0	901	17.4	990	95.6
280	2096	8.1	899	17.9	988	97.1
290	2096	8.1	898	18.3	988	99.7
298	2096	8.2	898	18.6	989	102.8

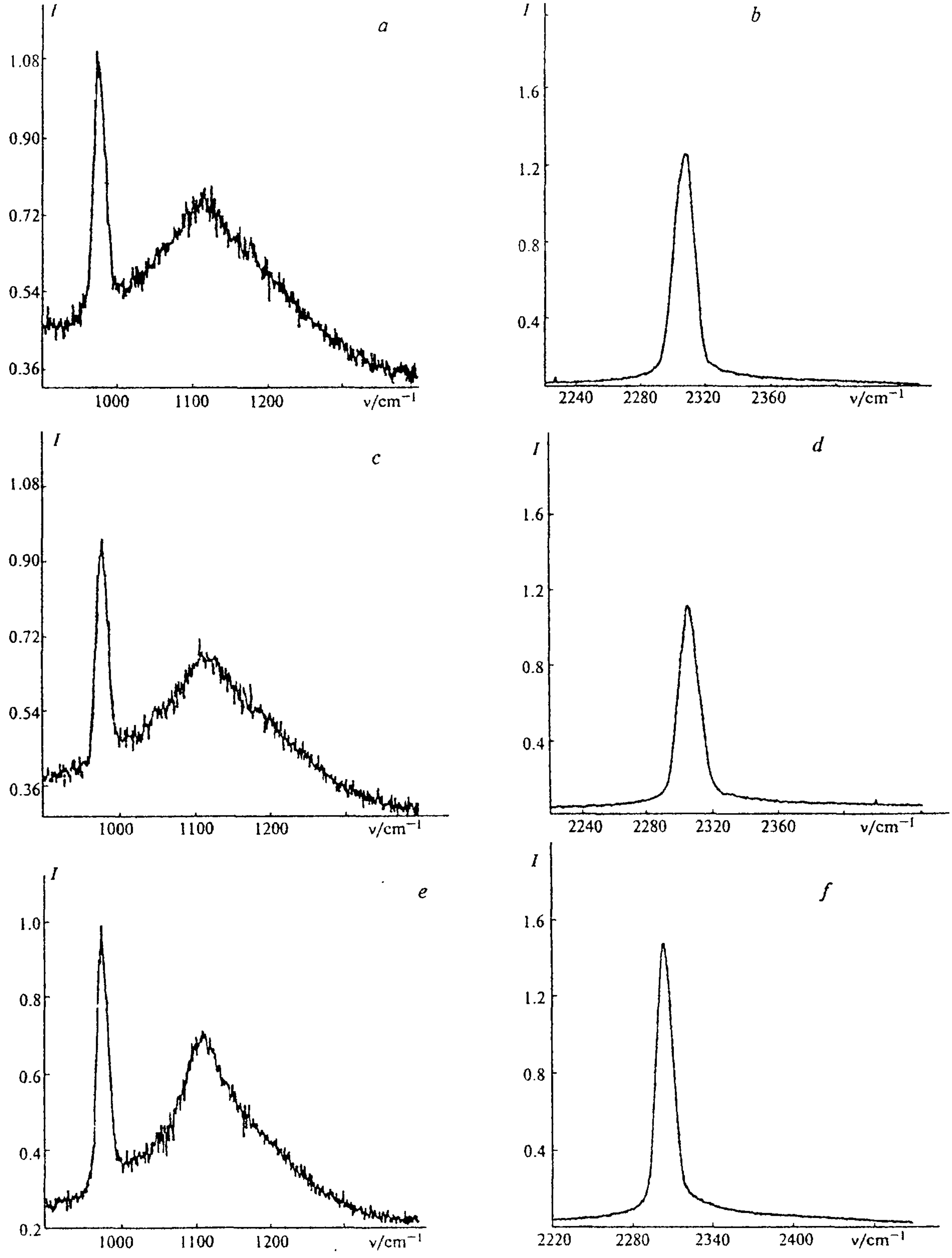

Fig. 4. Raman spectra of liquid PH_3 at 289 (*a*, *b*), 243 (*c*, *d*), and 198 K (*e*, *f*) in the region of deformation (*a*, *c*, *e*) and stretching (*b*, *d*, *f*) vibrations.

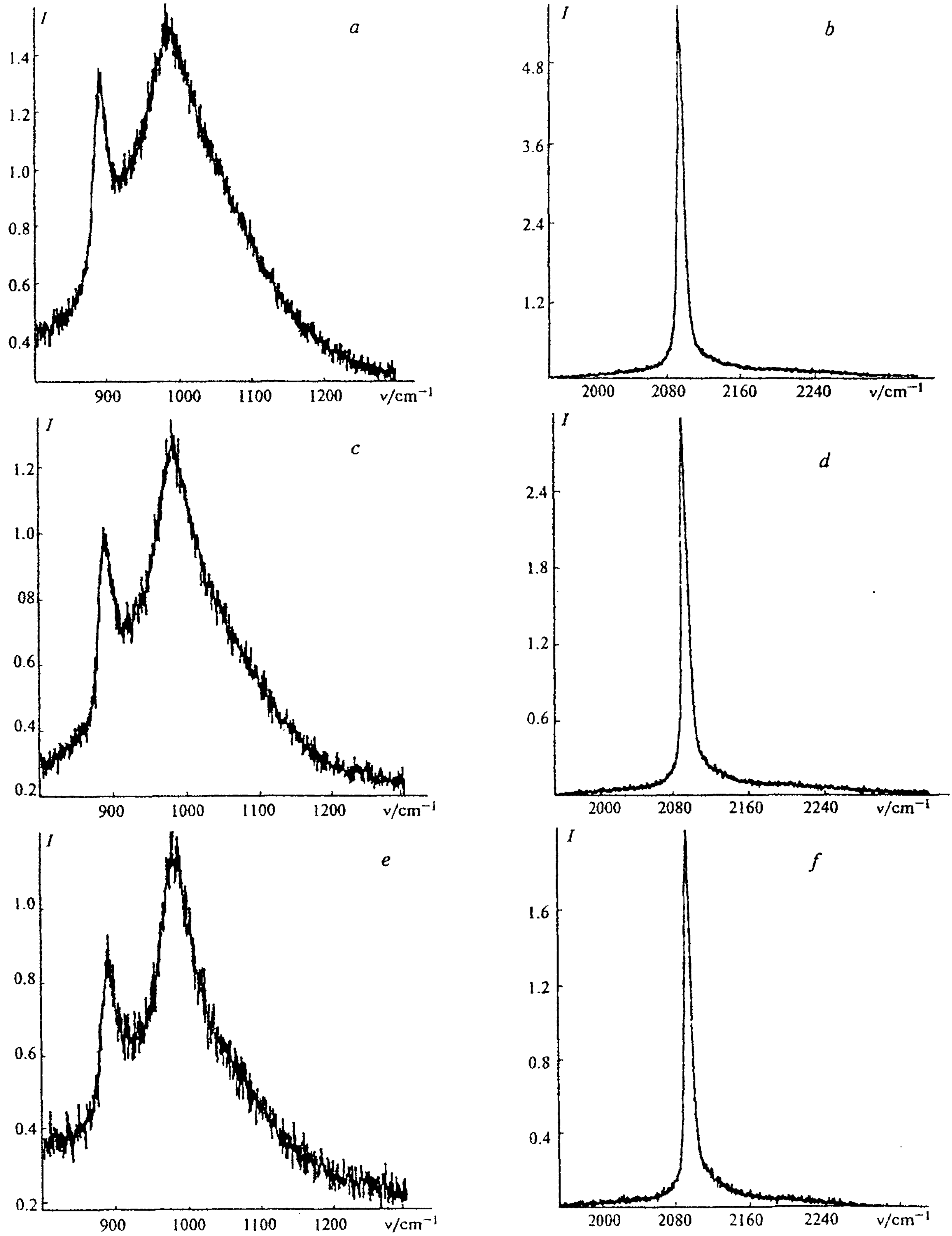

Fig. 5. Raman spectra of liquid AsH_3 at 290 (*a*, *b*), 243 (*c*, *d*), and 200 K (*e*, *f*) in the region of deformation (*a*, *c*, *e*) and stretching (*b*, *d*, *f*) vibrations.

intermolecular H bonds.[72] In the IR spectrum of liquid NH_3, this process is manifested[57] as a low-frequency shift of the overall stretching band. In terms of this assumption, the small high-frequency shift of the ν_2 line in the Raman spectrum of liquid arsine[57] on decreasing the temperature may indicate a sharp decrease in the tendency of AsH_3 molecules to form H-bonded associates in the liquid state. In order to obtain additional data on the character of intermolecular interactions and molecular dynamics in liquid PH_3 and AsH_3, the contour of the line of the ν_2 mode in the Raman spectra of these molecules was studied in detail.[57,79]

Time correlation functions for the vibrational and orientational relaxation of PH_3 and AsH_3 molecules were calculated and the corresponding characteristic times for these processes were determined. Analysis of the behavior of the rotational relaxation time τ_R in the 298—181 K temperature range showed that τ_R increases ~2.5-fold (from 3.3 to 7.4 ps) for PH_3 and by more than an order of magnitude (from 0.4 to 4.8 ps) for AsH_3. As in the case of liquid PH_3,[79] this pattern of variation of τ_R as a function of temperature can be due to the decrease in the number of interparticle collisions per unit time, resulting from a decrease in the angular rate of molecules and their kinetic energy, and to the enhancement of intermolecular interactions on decreasing the temperature. The unusually great change in τ_R observed for arsine was interpreted[57] as being due to the predominance of associative processes in this liquid. According to IR spectroscopy,[50] liquid arsine hardly contains any H-bonded self-associates; therefore, this change in τ_R may be mostly due to the enhancement of the van der Waals interaction between AsH_3 molecules at lower temperatures.

Thus, the comparative analysis of the IR and Raman spectra of liquid ammonia, phosphine, and arsine and the comparison of the estimates of the enthalpy of intermolecular interactions lead to the conclusion that liquid NH_3 possesses the most pronounced tendency for self-association upon the formation of H-bonds. In the case of liquid PH_3, the tendency to form H-bonded self-associates is much less pronounced, and liquid AsH_3 virtually does not form these associates. Thus, in terms of the energy of specific intermolecular interactions, the liquid hydrides of Group VA elements can be arranged in the following series: $NH_3 > PH_3 \geq AsH_3$.

However, the set of dynamic parameters found for the molecules of phosphorus and arsenic hydrides over a broad temperature range provide grounds for the conclusion that arsine molecules are more prone to undergo self-asscociation than phosphine molecules in the liquid phase, due to the enhancement of nonspecific van der Waals interactions at lower temperatures.

Hydrides of Group VI elements

Molecules of the H_2X type (X = S, Se) belong to the C_{2v} point group of symmetry. All three normal modes of these molecules with the types of symmetry

$$\Gamma_{vib} = 2A_1 + B_1$$

are both IR and Raman active.

A lot of experimental studies dealing with IR absorption spectra of H_2S in the gas phase, including high-resolution spectra, have been published.[10,12,80—82] The integral absorption coefficients A were determined only for the bands corresponding to the fundamental vibrations of hydrogen sulfide.[10,12] Quantum-chemical calculations of the A values of all the IR bands of H_2S in the 1190—10000 cm^{-1} range were carried out.[80] The IR absorption spectra of hydrogen selenide are less studied, especially in the region of overtones and complex modes.[10,12,83,84] Only in a few papers[85—88] were the integral absorption coefficients A for the bands of fundamental vibrations determined experimentally. Quantum-chemical calculations of A values were performed for all bands in the 1190—10000 cm^{-1} range in the IR spectrum of H_2Se.[84]

When comparing the experimental values for the integral absorption coefficients of the bands of fundamental vibrations of H_2S and H_2Se in the gas phase with one another and with the corresponding A value for water (Table 9), one can notice the following facts:

— stretching (ν_{str}) and deformation bands (ν_{def}) in the spectrum of H_2S are much less intense than those in the spectrum of H_2O;

— the deformation band in the spectra of both water and hydrogen sulfide is much more intense than the ν_{str} band. The ν_{str} band in the spectrum of gaseous H_2S has an abnormally low intensity;

— the bands for stretching vibrations in the spectrum of gaseous H_2Se are more intense than the bands for deformation vibrations.

The IR absorption spectra of liquid H_2S and H_2Se have been studied[85,89—92] over broad spectral (9000—500 cm^{-1}) and temperature (170—300 K) ranges (Tables 10, 11, Fig. 6). Comparison of the data presented in Tables 9 and 10 shows that the ν_{str} band in the spectrum of H_2S markedly shifts to lower frequencies ($\Delta\nu \approx$ 34 cm^{-1} at T = 292 K) and the ν_{def} band shifts to higher frequencies ($\Delta\nu \approx$ 50 cm^{-1} at T = 292 K) on passing from the gas phase to the liquid phase. The position of

Table 9. Frequencies (ν/cm^{-1}) and absolute ($A \cdot 10^8$/cm^2 molec.$^{-1}$ s^{-1}) and relative (A_{rel}) intensities of absorption bands in the IR spectra of gaseous water,[10,12] hydrogen sulfide,[10,12] and hydrogen selenide[10,12,85] (T = 293 K)

Type of	H_2O			H_2S			H_2Se		
vibrations	ν	A	A_{rel}	ν	A	A_{rel}	ν	A	A_{rel}
ν_1	3657	1.3	3.8	2615	0.06	25	2345	6.5	100
ν_3	3756	21.5	72.1	2625			2358		
ν_2	1596	25.3	100	1183	0.24	—	1034	0.8	12
$2\nu_{str}$	7200	2.0	5.9	—	—	—	—	—	—

the ν_{def} band depends substantially on the temperature; it shifts to lower frequencies when the temperature decreases. The ν_{def} = 1186 cm^{-1} value at 202 K is in good agreement with the 1180 cm^{-1} value observed in the Raman spectra of liquid hydrogen sulfide.[93,94] It was shown[90,92] that on decreasing temperature, the integral absorption coefficient of the ν_{str} band in the spectrum of liquid H_2S increases from 11.2 · 10^{-8} cm^2 molec.$^{-1}$ s^{-1} at 300 K to 18.1 · 10^{-8} cm^2 molec.$^{-1}$ s^{-1} at 180 K, while that of the ν_{def} band somewhat decreases.

Comparison of the data of Tables 9 and 10 for hydrogen selenide shows that on going from gas to liquid, the ν_{str} band shifts to lower frequencies by ~40 cm^{-1}, while the position of the ν_{def} band remains virtually unchanged. The integral absorption coefficients are close to the corresponding values for H_2S. However, unlike hydrogen sulfide, the ν_{str} band of liquid hydrogen selenide has a lower maximum intensity. When the temperature decreases, the integral absorption coefficient of the ν_{str} band in the spectrum of liquid H_2Se somewhat increases (from 14.6 · 10^{-8} cm^2 molec.$^{-1}$ s^{-1} at 295 K to 15.1 · 10^{-8} cm^2 molec.$^{-1}$ s^{-1} at 213 K), while the absorption coefficient of the ν_{def} band does not depend on the temperature to within the experimental error.[90]

The IR spectra of liquid H_2S and H_2Se have been studied[89] in the frequency range of up to 4th order transitions inclusively (see Table 11). Analysis of the band contour of the first overtone of stretching vibrations $2\nu_{str}$ in the spectrum of liquid hydrogen sulfide demonstrates (Fig. 7) that its half-width increases, while the absorption coefficient decreases as the temperature is raised. Decomposition of the $2\nu_{str}$ band with a maximum at 5100 cm^{-1} into elementary components in the Lorentzian approximation yields four components with maxima about 4870, 5025, 5144, and 5320 cm^{-1}. It is noteworthy that the complex shape of the $2\nu_{str}$ band contour found in a recent study[89] differs markedly from that reported in an earlier[95] work in which this band was approximated by only one curve. Apparently, this is due to the fact that in the earlier paper,[89] the spectrum of hydrogen sulfide was recorded at a higher temperature (348 K) and with a thicker absorption layer (2.5 cm).

The relative intensity of the band for the first overtone of stretching vibrations of H_2Se is much higher than those of liquid H_2O and H_2S (see Fig. 7,*b*). As the

Table 10. Frequencies (ν/cm^{-1}) and absolute (A · 10^8/cm^2 molec.$^{-1}$ s^{-1}) and relative (A_{rel}) intensities of absorption bands in the IR spectra of liquid water,[10] hydrogen sulfide,[85,89] and hydrogen selenide[85,89] in the region of fundamental vibrations (T = 293 K)

Type of	H_2O			H_2S			H_2Se		
vibrations	ν	A	A_{rel}	ν	A	A_{rel}	ν	A	A_{rel}
ν_{str}	3400	488	100	2580	12.0	100	2305	14.0	100
ν_{def}	1648	27.1	23.1	1186	2.9	15.4	1030	2.4	17.1
$\nu_{str}+\nu_{def}$		—	—	3757	1.4	10.8	3323	0.8	5.7
$2\nu_{str}$	6920	0.68	0.6	~5100	0.24	19	~4530	1.0	7.2

Table 11. Frequencies (ν/cm^{-1}) and absolute (A · 10^8/cm^2 molec.$^{-1}$ s^{-1}) and relative (A_{rel}) intensities of absorption bands in the IR spectra of liquid hydrogen sulfide and hydrogen selenide in the region of fundamental, complex, and overtone vibrations[90]

Type of	H_2S			H_2Se		
vibrations	ν	A	A_{rel}	ν	A	A_{rel}
ν_{str}	2580	13.0	10000	2305	14.0	10000
ν_{def}	1236	2.0	1540	1030	2.4	1710
$\nu_{str}+\nu_{def}$	3757	1.4	1080	~3323	0.8	570
$2\nu_{str}$	~5100	0.24	185	~4530	1.0	715
$2\nu_{str}+\nu_{def}$	~6200	0.046	35	~5540	0.02	14
$3\nu_{str}$	~7500	0.006	5	~6680	0.04	26
$3\nu_{str}+\nu_{def}$	~8590	0.002	1.5	~7650	0.001	0.7
$4\nu_{str}$				~8740	0.002	1.4

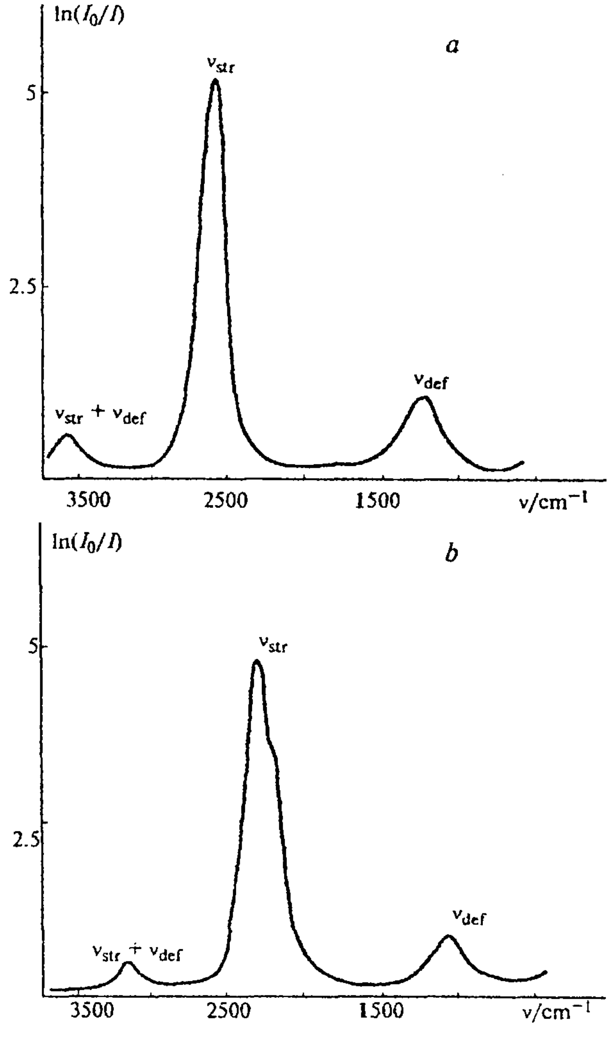

Fig. 6. IR absorption spectra of liquid H_2S (*a*) and H_2Se (*b*) in the region of fundamental vibrations at 294 and 293 K, respectively. The layer thickness was 0.1 mm.

temperature decreases, the integral absorption coefficient of the $2\nu_{str}$ band virtually does not change. Unlike $2\nu_{str}$ (H_2S), the corresponding band for H_2Se has only one inflection on the high-frequency wing. However, in this case too, components of this band at 4530, 4320, and 4630 cm^{-1} can be distinguished.[89]

Analysis of the frequency positions and shapes of absorption bands in the spectra of liquid hydrogen sulfide and hydrogen selenide and their temperature dependences led to several conclusions[89,92,96] concerning the character of intermolecular interactions in these liquids. Before discussing them, let us briefly consider the results obtained by other experimental and theoretical methods used to study intermolecular interactions in hydrides of Group VI elements.

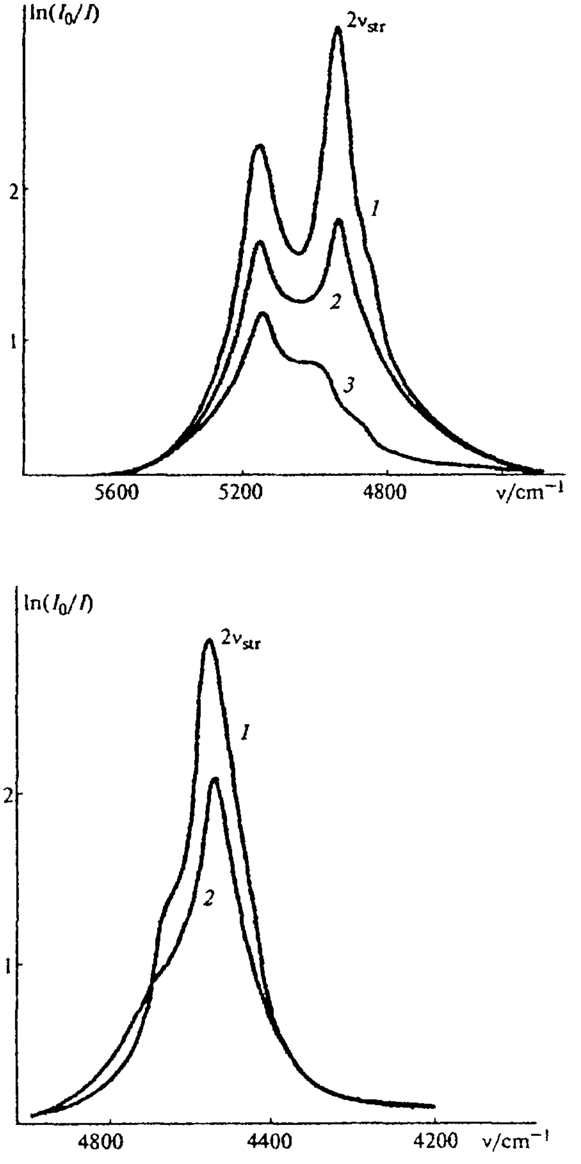

Fig. 7. IR absorption spectra of liquid H_2S (*a*) and H_2Se (*b*) in the $2\nu_{str}$ region at various temperatures (*T*/K): *a*. *1*, 199; *2*, 247; *3*, 292; *b*. *1*, 213; *2*, 293. The layer thickness was 5 (*a*) and 1.5 (*b*) mm.

Unlike water, for which the self-association in liquid phase has been comprehensively studied both experimentally and theoretically,[97] the slow neutron scattering,[98] neutron diffraction,[99] and X-ray diffraction[100] studies of liquid H_2S did not confirm the presence of any substantial self-association of its molecules. Quantum-chemical calculations for the hydrogen sulfide dimer, carried out using the broadest possible basis set including the zero-point vibration energies,[70] give a very low (≤ 1 kcal mol^{-1}) bonding energy for this dimer; hence, the term "hydrogen bond" in the generally accepted meaning seems not to apply[70] to this dimer. However, the data of IR spectroscopy in the gas phase at elevated pressures,[101,102] photoelectron spectroscopy in molecular beams,[103] and IR spectroscopy in inert gas matrices[104—106] can be interpreted from the viewpoint of formation of relatively stable H_2S associates. Two theoretical papers devoted to Monte-Carlo and molecular dynamics studies of liquid H_2S and H_2Se have been published.[107,108] The author of one study[107] considers the occurrence of a hydrogen bond in liquid hydrogen sulfide at the boiling temperature to be unlikely. Liquid hydrogen selenide, as shown by analysis of some of its microscopic properties by molecular dynamics, is an "ordinary liquid largely free of hydrogen bonds."[108]

Thus, the data on self-association of hydrogen chalcogenide molecules in the liquid state are quite contradictory. The low energy of intermolecular interactions in the $(H_2S)_2$ dimer, predicted theoretically, and the slight changes in the electron density of the monomers following dimerization make the description of these interactions in terms of either hydrogen bonding or, say, dipole-dipole interactions a purely terminological problem. The IR-spectroscopy data permit drawing quite definite conclusions on the character of associative processes in liquid H_2S and H_2Se.

It can be seen from Tables 9 and 10 that the character of variation of the bands of fundamental vibrations in the absorption spectra of H_2S and H_2Se upon transition from gas to liquid does not differ qualitatively from that observed for H_2O, in which the occurrence of hydrogen bonds is a well-established fact. Thus, when hydrides pass to the liquid state from a medium in which association hardly occurs and the interactions with the environment are weak (gas or a solution in CCl_4),[14] the bands of the X—H stretching vibrations undergo a substantial low-frequency shift, which decreases from 300—350 cm^{-1} for H_2O to 30—40 cm^{-1} for H_2S and H_2Se.

In the systems with hydrogen bonds, the band of the ν_2 deformation mode tends to undergo a slight high-frequency shift; this is actually observed for H_2O and H_2S (~50 cm^{-1}). The maximum of the ν_2 band in H_2Se virtually does not shift. In the spectra of liquid water, hydrogen sulfide, and hydrogen selenide, the band of the deformation mode ν_{def} becomes much less intense than the band for the stretching mode ν_{str}. It should be noted that the intensity of the ν_{str} band of hydrogen sulfide appreciably increases, more than 200-fold, on passing from gas to liquid (in the case of water, this increase is an order of magnitude smaller). A similar increase in the intensity of the band due to the weak S—H bond in a CCl_4 solution with respect to that in the gas phase has also been noted[109] upon the formation of H-bonds of hydrogen sulfide with proton acceptors. This does not mean, however, that the ability of hydrogen sulfide to form associates increases equally sharply upon the transition from gas to liquid, because the strength of an H-bond is not estimated[110] from simply the ΔA value but rather from the value $\Delta A^{1/2} = A_{bound}{}^{1/2} - A_{free}{}^{1/2}$, where A_{free} and A_{bound} are the integral absorption coefficients of AH groups in an isolated proton-donating molecule and in the AH...B complex, respectively. A correlation between the enthalpy of the hydrogen bond ΔH and the $\Delta A^{1/2}$ value has been found[110]:

$$\Delta H = -2.9(A_{bound}{}^{1/2} - A_{free}{}^{1/2}). \qquad (1)$$

Here ΔH is expressed in kcal mol^{-1} and the A value is given in cm mmol^{-1}. This applies to all the bonds of the A—H...B type (A = O, N, C, S, *etc.*) and covers all classes of hydrogen bonds in the 1 : 1 complexes in the 0.1—15 kcal mol^{-1} range of energies, including those in pure associated liquids.[111]

Although some limitations on the applicability of relation (1) to very weak H-bonds, whose energies are ≤1 kcal mol^{-1}, have been noted,[112] this is apparently the only sufficiently justified method for estimating the enthaplies of H-bonded complexes in systems in which the concentration dependence of the equilubrium constant of complex formation cannot be studied. The slightly associated liquids (hydrogen chalcogenides) and, to a certain extent, hydrides of Group V elements discussed here are examples of this type of system.

The enthalpy of the hydrogen bond in liquid H_2S was estimated using[85—88] relation (1) in a somewhat modified form:

$$-\Delta H = 2.9[(A_{bound}/m)^{1/2} - A_{free}{}^{1/2}], \qquad (2)$$

where m is the number of hydrogen bonds formed by a proton-donating molecule. Judging by the structure of the H_2S molecule, it can be suggested that the m value changes over the $1 \le m \le 2$ limits. The $A_{free} = 0.0014 \cdot 10^4$ cm mmol^{-1} value corresponds to the integral absorption coefficient of the $\nu_{1,3}$(SH) band in the gas phase (see Table 9) to within the $L(n)$ factor (n is the refractive index of H_2S from Table 1), which takes into account the change in the intensity of the light wave field on passing from gas to liquid,[113] while $A_{bound} = 0.335 \cdot 10^4$ cm mmol^{-1} corresponds to the integral absorption coefficient of the ν_{str}(SH) band in liquid (see Table 10). Then the enthalpy of the SH...S hydrogen bond in liquid hydrogen sulfide varies from −1.0 to −1.6 kcal mol^{-1} at 213 K (the boiling point of the hydride), depending on the structure of the hypothetical isolated associate.

Additional information on the associative processes in liquid hydrogen sulfide can be gained from analysis of the $2\nu_{str}$ band at 5100 cm^{-1}, which has, as noted above, a complex shape (see Fig. 7, *a*).[89] As the temperature decreases, the integral intensity of the component of this band at 5025 cm^{-1} increases, whereas the component at 5144 cm^{-1} becomes less intense; the correlation coefficients for these dependences are fairly high.

By analogy with solutions of ethanethiol in CCl_4,[114] it was suggested[89] that the former band (in the case of EtSH, its maximum occurs at 4998 cm^{-1}) is due to hydrogen-bonded SH vibrations (in three- or four-coordinate H_2S molecules), while the latter component (for EtSH, at 5056 cm^{-1}) belongs to "free" SH groups in H_2S molecules in the liquid state. The temperature variations of the components at 4870 and 5320 cm^{-1} of the $2\nu_{str}$ band follow a similar pattern. These components might also reflect the associative processes in H_2S (a similar situation has been observed[115] for liquid water); however, since these bands are weak, it is difficult to evaluate uncontrolled instrumental errors caused by the fallibility of the procedure of resolution of the overall band into unit forms.

Thus, by analogy with liquid water,[116] the equilibrium between the proton-donor and proton-acceptor fragments of the H_2S molecule occurring in liquid hydrogen sulfide can be described by the following simple chart:

$$-\mathrm{H} + :\mathrm{S} \rightleftharpoons -\mathrm{H}...:\mathrm{S}\langle\,. \qquad (3)$$

The equilibrium constant for reaction (3) can be expressed as follows[114]:

$$K = X_{bound}/[X_{free}X(:\mathrm{S}_{free})] = X_{bound}/X_{free}{}^2, \qquad (4)$$

where X_{bound} and X_{free} are the mole fractions of "bound" and "free" SH groups determined from the Lambert—Beer equation.

Combination of these equations gives

$$K = \mathrm{const} \cdot (B_{bound}/B_{free}{}^2) \cdot (A_{free}{}^2/A_{bound}). \qquad (5)$$

Since A_{bound} and A_{free} do not depend on the temperature, we have

$$K = \mathrm{const} \cdot B_{bound}/B_{free}{}^2. \qquad (6)$$

Using the van't-Hoff equation in the form

$$\ln K = \ln(B_{bound}/B_{free}{}^2) \cdot \mathrm{const} = -\Delta H^\circ/(RT) + \mathrm{const}, \quad (7)$$

the average enthalpy of formation of hydrogen bonds (ΔH°) in liquid hydrogen sulfide can be estimated to be −(1.5±0.2) kcal mol^{-1}. This result is in good agreement with the upper estimate for ΔH based on the analysis of the intensity of the ν_{str} band for liquid H_2S.

The subsequent analysis of the intensities of the components of the $2\nu_{str}$ band in the spectrum of liquid H_2S made it possible[89] to find the proportion of "bound" and "free" S—H oscillators in the liquid phase; this was used to calculate the integral absorption coefficients of the corresponding components of the stretching band in the IR spectrum of liquid H_2S. They were found to be the following: $A_{free}(\nu_{str}) = 0.12 \cdot 10^4$ cm mmol^{-1} and $A_{bound}(\nu_{str}) = 0.6 \cdot 10^4$ cm mmol^{-1}. Taking into account relation (2), we find that, according to these estimates, the enthalpy of formation of the hydrogen bond between the hydrogen sulfide molecules in liquid ($-\Delta H^0$) lies in the 0.6—1.2 kcal mol^{-1} range. This result is in satisfactory agreement with the quantum-chemical calculations of the energy of formation of the $(H_2S)_2$ dimer with allowance for the energy of zero-point vibrations.[70] Evidently, $\Delta H = -0.6$ kcal mol^{-1} is the lower estimate of the enthalpy of formation of the hydrogen bond in liquid hydrogen sulfide.

Thus, the data of the IR spectrum in the region of stretching vibrations and their first overtone indicate the formation of hydrogen bonds in liquid hydrogen sulfide; however, these bonds are substantially weaker than those in liquid water. The proportion of "free" H_2S molecules (α) in the liquid phase at 290 K amounts to 75%.[89] Note for comparison that for EtSH, $\alpha = 49\%$ according to computer simulation data,[107] and for liquid water this value is 15% at 290 K, according to various experimental data.[117]

The general character of variation of the IR absorption spectra of liquid hydrogen selenide in the stretching vibration region also points to the possible formation of weak associates. In fact, as was shown previously,[89] the integral absorption coefficient of the ν_{str}(SeH) band generally increases by ~30% as the temperature decreases (for comparison, the integral absorption coefficient of the ν_{str}(SH) band increases by 60%). On cooling, the contour of the ν_{str}(SeH) band also changes: the contribution of the low-frequency component with a maximum at 2330 cm^{-1}, which can be attributed to "bound" H_2Se molecules, to the total intensity increases. Both components mentioned above can be observed even in the spectrum of solid hydrogen selenide. This may indicate that under these conditions, the proportion of "free" H_2Se molecules is still high. As has already been noted, in the case of liquids with stronger intermolecular interactions (hydrogen sulfide and, especially, water), the ν_{str} band is not separated into components. Unfortunately, a relatively correct resolution of the ν_{str}(SeH) band into unit components proved to be impossible, because this band is highly asymmetric. The same is true for the $2\nu_{str}$(SeH) band (see Fig. 7,*b*). Therefore, the degree of association of hydrogen selenide in the liquid state and the A_{bound} and A_{free} values were not estimated.[89]

Thus, the only possible way to estimate the enthalpy of hydrogen bonds in liquid hydrogen selenide is provided by the Iogansen equation in form (1), because a substantial proportion of H_2Se molecules in the liquid remains "free." The assumption that $A_{bound} = A_{liq}$ and $A_{free} = A_{gas} \cdot L(n)$ seems more justified, because, as can be seen from Table 9, the ν_{str}(SeH) band, unlike ν_{str}(SH), does not belong to the type of abnormally weak bands. When $A_{bound} = 0.314 \cdot 10^4$ cm mmol^{-1} and $A_{free} = 0.170 \cdot 10^4$ cm mmol^{-1} ($T = 206$ K), we obtain $\Delta H = -0.4$ kcal mol^{-1}, *i.e.*, according to the IR absorption spectra, the intermolecular hydrogen bonds in liquid hydrogen selenide are weaker than those in hydrogen sulfide and, especially, in water. This statement is apparently supported by the facts that the relative intensity of the $2\nu_{str}$ band of hydrogen selenide is higher than that of H_2S and H_2O (see Tables 9 and 10) and that the solubility of hydrogen selenide in liquid krypton is much higher than that of hydrogen sulfide.[118—121]

As in the case of the above-considered hydrides of Group IV and V elements, the Raman spectra of hydrogen chalcogenides are much less studied than their IR spectra; this is especially true for hydrogen selenide. Studies dealing with the Raman spectra of hydrogen sulfide in the gas phase[122,123] and hydrogen selenide in the solid state[124] have been reported. The spectra of liquid H_2S have been described in several papers,[93,94,123,125] while those of H_2Se have been considered in only one study[94] (Table 12). It follows from Table 12 that similarly to the vibrational spectra of hydrides of Group IV and V elements and to the IR spectra of H_2S and H_2Se, the line of the stretching vibrations, which is a superposition of lines due to the ν_1 and ν_3 modes, not resolved under experimental conditions, undergoes a substantial low-frequency shift upon the gas—liquid transition. At the same time, the frequency positions of lines of the deformation vibrations remain virtually unchanged. Analysis of the shape of the ν_2 line in the Raman spectrum of liquid hydrogen sulfide in the 188—295 K temperature range showed[93,94] that the contour of this band is of rotational origin. Unlike other hydride molecules considered above, whose rotation is described in terms of the small-angle rotational diffusion model, reorientation of H_2S molecules occurs as a single jump.[18,19,42,126] Analysis of the correlation functions of the vibrational and rotational relaxation, the corresponding characteristic times of these processes, and the angles of rotation of hydrogen sulfide molecules made it possible to assume[93,94] that weak associates are formed in this liquid.

Thus, the data of vibrational spectroscopy allow the conclusion that liquid hydrogen chalcogenides are weakly

Table 12. Frequencies (ν/cm^{-1}) of the lines of fundamental vibrations in the Raman spectra of hydrogen chalcogenides in the gas[122] and liquid[93,94] phases at various temperatures

Type of vibration	H_2S Gas (293 K)	H_2S Liquid (207 K)	H_2Se Gas (293 K)	H_2Se Liquid (272 K)
ν_1	2611.2	2580.0	2340.6	2308.5
ν_3	2627.1		2355.5	
ν_2	1183.0	1179.7	1031.6	1030.0

associated due to intermolecular hydrogen bonds; the energy of H-bonds decreases in the series water—hydrogen sulfide—hydrogen selenide.

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Study of the vibrational spectra of molecules in gases provide a lot of information concerning their structure and molecular dynamics. Transition to the liquid phase supplements this information by the data on the structure of the liquid and the character of intermolecular interactions under conditions of high-density molecular assembly. These known statements are clearly illustrated by the numerous results of studies of the IR and Raman spectra of gaseous and liquid water (see, for example, Ref. 97). It can be seen from the data presented here that for liquid volatile inorganic hydrides, these studies have been started only recently and the results obtained are far from being final. However, in relation to liquid hydrides of Group V elements, phosphine and arsine, one can see how the investigation of their IR spectra combined with Raman spectra over a broad temperature range not only provides purely spectroscopic (very important) information on the molecular dynamics but also reveals the differences in the mechanisms of intermolecular interactions in these liquids. Unfortunately, no systematic studies of the Raman spectra of liquid hydrogen sulfide and hydrogen selenide have been published; however, the available data on their IR spectra make it possible to describe the type of intermolecular interactions in liquid H_2S in terms of formation of weak H-bonded associates. Specific, although much weaker, intermolecular interactions occur also in liquid H_2Se. The IR and Raman spectra of liquid silane and germane in the region of fundamental vibrations at various temperatures have been little studied. These investigations would provide deeper insight into the regularities of the van der Waals intermolecular interactions in systems containing an M—H fragment whose M atom does not carry a lone electron pair, *i.e.*, in molecules for which almost no specific interactions are possible.

Study of the vibrational spectra of liquid hydrides of Group IV—VI elements would be of interest for yet another reason. Comparison of the phase transition temperatures of hydrides, presented in Table 1, shows that these substances can be attributed to the class of so-called cryogenic solvents, used in IR spectroscopy. Liquid inert and stable gases that are transparent over a wide spectral range are the most usual representatives of this class of compounds.[127] A drawback of liquid hydrides as solvents of this type is the substantial intrinsic absorption in the medium-IR region. However, these solvents can remain in the liquid state up to temperatures above room temperature (except for silane). The high chemical reactivity of these compounds can be regarded as both an advantage and a drawback. For example, liquid hydride media can be used to study chemical processes involving compounds dissolved in them[6—9] with concentrations of several percent or even less over a broad temperature range. One interesting example of the employment of this approach is the study of the molecular state of ethanol and water admixtures in liquid volatile inorganic hydrides.[128—132] Known data on the vibrational spectra of liquid hydrides allow IR spectroscopy to be used for quantitative analysis of liquid hydrides. For instance, quantification of CO_2 in silane and germane,[22] hydrocarbons, N_2O, CO_2, and water in liquid phosphine,[5,133] carbon disulfide in liquid hydrogen sulfide,[134,135] and water in liquid hydrides of Group V and VI elements[14,129,130,136—140] have been reported.

Thus, study of the vibrational spectra of volatile inorganic hydrides in the liquid state is a significant line of research in molecular spectroscopy associated with the development of its cryogenic version.[127] The information obtained in these works is of interest for investigation of the reactivity of inorganic hydrides, their ultrapurification, and analysis.

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