Some features of the geometrical structure of the $NbOI_3$ molecule may be examined in the framework of the valence electron pair repulsion (VEPR) theory [6]. In accordance with this theory, the O—M—X bond angle in MOX_3 molecules should be greater than tetrahedral, while the X—M—X angle should be less than 109.5° due to lack of equivalence of the electron densities concentrated in the M=O and M—X bonds. This effect should be pronounced in Group V element oxyfluorides. On the other hand, in accord with the VEPR theory, the X—M—X bond angle should increase upon replacing the halogen atom in the series F—Cl—Br—I. Thus, the close-to-tetrahedral values of all the bond angles in $NbOI_3$ should not appear remarkable.

The slightly greater r_α(Nb—I) internuclear distance in the $NbOI_3$ molecule relative to NbI_4 may be attributed to the large effect of the electron cloud of the Nb=O double bond on the adjacent Nb—I bonds in $NbOI_3$.

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GALLIUM DICHLORIDE. COMPOSITION OF SATURATED VAPOR. GEOMETRIC STRUCTURE AND VIBRATIONAL FREQUENCIES OF THE $GaGaCl_4$ MOLECULE

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The saturated vapor above gallium dichloride at 445 K was studied by electron-diffraction and mass-spectrometric methods. It was established that four molecular forms $GaCl_3$, GaCl, $GaGaCl_4$, and Ga_2Cl_6 are present in the vapor. The structural parameters of the $GaCl_3(D_{3h})$ and $GaGaCl_4(C_{2D})$ molecules were determined. The vibrational frequencies of the $GaGaCl_4$ molecule, having different-valence gallium atoms, were determined. The thermodynamic characteristics of the gas-phase reactions $Ga_2Cl_6 \rightleftarrows 2GaCl_3$ and $GaGaCl_4 \rightleftarrows GaCl + GaCl_3$ were obtained from the electron-diffraction data.

In the present work we give the results from a joint electron-diffraction and mass-spectrometric investigation of the saturated vapor of gallium dichloride. Published data on the molecular forms in the gas phase above $GaCl_2$ and $InCl_2$ are contradictory. Values for the molecular constants of $GaCl_2$ and $InCl_2$ and the thermodynamic functions of the gaseous chlorides are given in [1]. However, as shown by the results in [2, 3], the existence of the molecular form MCl_2 in the vapor of gallium and indium chlorides is debatable. Some authors suppose that the gaseous chlorides of these metals exist in the form of MCl_2 molecules [4-7], while others [2, 3, 8, 9] consider that the dichlorides are dimerized.

In almost all the papers it has been demonstrated that the saturated vapor of gallium and indium dichlorides contains several molecular forms with M/Cl stoichiometry of 1/1,

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1/2, and 1/3. Thus, it was established by mass spectrometry that the MCl, MCl_3, M_2Cl_4, M_2Cl_6, and M_2Cl_2 molecules are present in the saturated vapor above solid $GaCl_2$ [2] and $InCl_2$ [10]. According to data in [2], the main components of the saturated vapor above $GaCl_2$ at 436 K are the $GaCl_3$, GaCl, and Ga_2Cl_4 molecules. The content of the dimers Ga_2Cl_2 and Ga_2Cl_6 is approximately an order of magnitude lower than that of Ga_2Cl_4.

In [11] it was concluded from measurements of the mean molecular mass that the molecular form $GaCl_2$ predominates in the gas phase at $T > 400°C$.

According to data from Bernard and Chatillon [12], who also investigated the vapor pressure above the {Ga + $GaCl_3$} system in the range of 600-1000 K, the gas phase of gallium dichloride can contain GaCl, Ga_2Cl_2, $GaCl_2$, Ga_2Cl_4, and $GaCl_3$ molecules, the ratios between which depend on the temperature. They examined several possible alternatives for the composition of the vapor. However, they did not come to a final conclusion, noting that the results were very sensitive to experimental errors in the measurements and to errors in the thermodynamic characteristics of the condensed phase.

We note that the authors of the investigations [4-7, 11, 12] assume that the MCl_2 molecules are present in the gas phase. In [3], however, during investigation of the absorption spectra and the temperature dependence of the vapor pressure it was shown convincingly that gaseous gallium and indium dichlorides exist in the form of M_2Cl_4 dimers and not MCl_2 molecules, and at 400-500°C the partial pressure of the M_2Cl_4 form is of the same order of magnitude as the partial pressures of the MCl and MCl_3 forms. With increase in temperature the MCl form begins to predominate, and the concentration of the other molecular modifications decreases.

A special investigation on determination of the thermodynamic characteristics of Ga_2Cl_4 and In_2Cl_4 was undertaken in [2]. In this paper data are given on the composition of the unsaturated vapor in the MCl–MCl_3, system, according to which the M_2Cl_4 molecules are the main component of the vapor in the region up to 1000 K and their content remains at a fairly high level even at ~1500 K, demonstrating the high stability of the M_2Cl_4 molecules.

Finally, in [13] we established by electron diffraction that the saturated vapor over indium diiodide at 557 K contains the molecular forms InI_3, InI, and In_2I_4 in molar ratios of 59:28:13. Thus, analysis of published data [3-13] makes it possible to predict the qualitative composition of the gas phase corresponding to gallium dichloride.

Several investigations have been devoted to the structure and vibrational spectra of indium and gallium dihalides [14-18]. Thus, in [17] it was established that solid $GaCl_2$ is diamagnetic. This enabled the authors to suggest a dimeric composition for the structural units of the crystal with a covalent bond between the Ga atoms, i.e., $Cl_2Ga{-}GaCl_2$. However, it was shown more recently [18] that the Ga_2Cl_4 dimer contains different-valence Ga atoms and has the structure $[Ga^+][GaCl_4^-]$. The vibrational spectrum of the $GaCl_2$ melt [18] closely reproduced the spectrum of the tetrahedral $GaCl_4^-$ ion. In addition, of the two bands for the stretching vibrations only one could be assigned to the fully symmetric vibrations of the bonds. The authors [18] therefore ruled out the $Cl_2Ga{-}GaCl_2$ structure, which (like the ions formed from it as a result of electrolytic dissociation) should have two fully symmetric Ga–Cl and Ga–Ga vibrations.

It should be noted that there are no data on the vibrations of the free MMX_4 molecules. In [19] we determined the vibrational characteristics of the $InInI_4$ molecules from the spectra of the crystalline indium monoiodide. Here we used the idea of similarity between the vibrational frequencies of the structural unit in the crystal $(InI_2)_2$ and the frequencies of the free $InInI_4$ molecule. The foundation for such an assumption is the almost complete agreement between the vibrational spectra of gaseous M_2Hal_6 (M = Ga, In) and the spectra of the melts and crystals of the respective trihalides [20-23], in which the geometry of the structural units [24] is close to the geometry of the free M_2Hal_6 molecules [19].

EXPERIMENTAL

According to published data [12], five different molecular forms may be present in the saturated vapor above gallium chloride (GaCl, $GaCl_2$, Ga_2Cl_4, Ga_2Cl_2, and Ga_2Cl_6), and the ratio between them depends on the temperature and on the total pressure in the system. Of the listed molecules Ga_2Cl_4 is of particular interest, since there are no data at all on its geometric parameters. To determine the latter reliably by electron diffraction it was

TABLE 1. Mass Spectra of the Vapor Above Gallium Trichloride and Dichloride (intensities of ion currents normalized to $I^+_{GaCl_2}$)

Ions	Ga^+	$GaCl^+$	$GaCl_2^+$	$GaCl_3^+$	Ga_2Cl^+	$Ga_2Cl_2^+$	$Ga_2Cl_3^+$	$Ga_2Cl_4^+$	$Ga_2Cl_5^+$
Gallium trichloride sat. vapor (T = 279 K, U_1 = 50 V) our expt.	72	25	100	5	6	0,5	1,1	8,5	163,7
Unsaturated vapor (T = 270 K, U_1 = 40 V) [3]	16	11	100	34	0,5	0,28	0,45	2,3	68
Gallium trichloride (T = 700 K, U_1 = 50 V) our expt.	29	19	100	15	—	—	—	—	—
superheated vapor (T = 733, K, U_1 = 40 V) [3]	8,8	8	100	34	—	—	—	—	—
Gallium dichloride									
sat. vapor)T = 445 K, U_1 = 50 V) our expt.	96	52	100	23	—	—	6,1	1,7	1,8
(T = 436 K, U_1 = 40 V) [3]	40	39	100	38	—	0,55	17	7,1	3,3

necessary to have a substantial concentration of Ga_2Cl_4 molecules in the vapor. In order to select conditions for the electron-diffraction investigation we therefore first recorded the mass spectra of the vapor above solid $GaCl_2$ at various temperatures (434-484 K).

The following ions were detected in the mass spectrum: Cl^+, Ga^+, $GaCl^+$, $GaCl_2^+$, $GaCl_3^+$, $Ga_2Cl_3^+$, $Ga_2Cl_4^+$, and $Ga_2Cl_5^+$. The range of temperatures in which the relative intensity of the ion currents of $Ga_2Cl_3^+$ and $Ga_2Cl_4^+$ (in our opinion these are the forms produced preferentially during ionization of the Ga_2Cl_4 molecules) was highest was 440-450 K, and it was this that determined the temperature of the electron-diffraction experiment (T = 445 K).

In order to control the conditions under which the electron diffraction patterns were recorded the experiment was conducted on a set of apparatus representing an electron-diffraction camera with an adapted mass spectrometer [25].

The mass spectrum, obtained while the electron-diffraction patterns were being recorded, is given in Table 1. In order to interpret the mass spectrum we carried out additional experiments in which the mass spectra of the saturated (T = 279 K) and superheated (T = 773 K) vapor of gallium trichloride, given in Table 1, were obtained at the same ionizing potential (50 V). The results from [3], in which a detailed mass-spectral investigation of the gas phase in the Ga—Cl system was undertaken, are given for comparison. The difference in the intensities of the ion currents may be due to the different ionization potentials and also to the fact that the concentration of the monomeric $GaCl_3$ moecules at similar temperatures may be higher in the unsaturated vapor of gallium trichloride than in the saturated vapor.

The mass spectrum that we recorded at 279 K can be attributed fully to the Ga_2Cl_6 molecules, since as shown by the results from [26] the partial pressure $P_{Ga_2Cl_6}$ in the saturated vapor above solid $GaCl_3$ under these conditions is approximately 150 times higher than P_{CaCl_3}.

The conditions under which the mass spectra of the superheated vapor of $GaCl_3$ were obtained correspond to the presence of one type of molecule $GaCl_3$ in the gas phase [3]. Thus, the mass spectra of two of the five possible molecular forms in the vapor above $GaCl_2$ at an ionization potential U_i of 50 V become known.

In addition, according to our data the concentration of Ga_2Cl_2 molecules in the vapor above Ga_2Cl_4 must be very small, since the intensities of the molecular ion $Ga_2Cl_2^+$ and the Ga_2Cl^+ ion are comparable with the noise level. A similar conclusion was reached in [3, 27]. Thus, in [3] a conclusion about the presence of an insignificant amount of Ga_2Cl_2 molecules in the vapor of gallium dichloride was reached only on the basis of such indirect data as the low appearance potential of the $Ga_2Cl_2^+$ ion (16.7 eV) and the existence of the Ga_2Cl^+ and Ga_2^+ ions. In [27] it was noted that the content of Ga_2Cl_2 molecules in the vapor is probably very small and thousands of times smaller than the concentration of Ga_2Cl_4. Subsequently, therefore, the molecular form Ga_2Cl_2 was not taken into account during examination of the saturated vapor above $GaCl_2$.

TABLE 2. Least-Squares Analysis of the sM(s) Function for the Saturated Vapor of Gallium Dichloride (445 K)

$s_{min}-s_{max}$, Å	2,4—13,4	5,0—22,0	2,4—22,0	2,4—22,0	2,4—22,0
$GaCl_3$	1	2	3	4	5
r_a(Ga—Cl)	2,0925(14)*	2,0969(7)	2,0928(8)	2,0958(7)	2,0958(6)
l(Ga—Cl)	0,054 **	0,054	0,0500(12)	0,0534(11)	0,0534(10)
r_a(Cl—Cl)	3,5709(74)	3,6142(63)	3,5817(73)	3,5796(63)	3,5806(61)
l(Cl—Cl)	0,1207(75)	0,1214(49)	0,1367(63)	0,1425(55)	0,1417(53)
$GaGaCl_4$					
r(Ga^I—Cl)	2,849(17)	2,893(21)	2,879(26)	2,881(17)	2,883(23)
l(Ga^I—Cl)	0,106(18)	0,142(24)	0,167(20)	0,1362	0,173(18)
f_1, mdyn/Å					
α Expt.	0,48	0,48	0,48	0,53	0,53
β	0,21	0,21	0,21	0,17	0,17
γ	0,23	0,23	0,23	0,24	0,24
R_f, %	5,85	6,51	6,11	5,59	5,39

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*The σ_{LSM} value is given in parentheses.

**The parameters which were not refined in the least-squares method are given.

One interpretation of the mass spectrum of $GaCl_2$ was put forward in [3], where the assumption was made that the molecular precursors of the $Ga_2Cl_4^+$ and $Ga_2Cl_3^+$ ions are only the Ga_2Cl_4 molecules, those of the $GaCl_2^+$ ions are the $GaCl_3$ molecules, those of the $GaCl^+$ ions or Ga^+ ions are the GaCl molecules, while those of the $Ga_2Cl_5^+$ ions are the Ga_2Cl_6 molecules.

Application of these ideas to the data presented in Table 1 leads to the following composition for the vapor above $GaCl_2$: More than 50 mole % of $GaCl_3$, about 40% GaCl, <10% of Ga_2Cl_4, and up to 1% of Ga_2Cl_6

In addition, we tried to interpret the mass spectrum of $GaCl_2$ by means of data for the saturated and superheated vapor of gallium trichloride (Table 1). Here it was assumed that: 1) the mass spectrum of the saturated vapor of $GaCl_3$ (279 K) belongs to the molecular form Ga_2Cl_6; 2) the mass spectrum of the superheated vapor of $GaCl_3$ (771 K) belongs to the molecular form $GaCl_3$; 3) the $GaCl_2^+$ ion mostly has only two molecular precursors, i.e., $GaCl_3$ and Ga_2Cl_6; 4) during dissociative ionization of the Ga_2Cl_4 molecule large amounts of Ga^+ and $GaCl_3^+$ ions are formed in addition to the $Ga_2Cl_4^+$ and $Ga_2Cl_3^+$ ions, since the following dissociation scheme is possible:

$$Ga_2Cl_4 + \bar{e} \Rightarrow Ga^+ + GaCl_4 + 2\bar{e} \Rightarrow Ga^+ + GaCl_3^+ + Cl + 3\bar{e};$$

5) the amount of Ga_2Cl_2 molecules in the vapor above $GaCl_2$ is negligibly small; 6) the intensities of the ion currents of $GaCl^+$ and Ga^+, formed during dissociative ionization of the GaCl molecule, are approximately the same, and the probability of the production of the $GaCl^+$ ion from the Ga_2Cl_4 molecule is small.

The proposed scheme for the interpretation of the mass spectrum of the saturated vapor of $GaCl_2$ leads to the following concentrations (mole %) of the molecular forms:

$$x_{GaCl_3} = 52, \quad x_{GaCl} = 37, \quad x_{Ga_2Cl_4} = 10, \quad x_{Ga_2Cl_6} = 1,$$

and the x_{GaCl} value may be high while the $x_{Ga_2Cl_4}$ value may be low compared with the actual concentrations.

We note that the two methods for interpretation of the mass spectrum of $GaCl_2$ lead to coinciding results.

We used the data obtained during the mass-spectral investigation for the interpretation of the electron-diffraction patterns of the saturated vapor of gallium dichloride.

The electron diffraction experiment was conducted with an accelerating potential of 75 kV (λ = 0.0432 Å) with two distances between the sample tube and the photo plate L_1 = 598 mm and L_2 = 337 mm. The wavelength of the electrons was determined by the diffraction pattern from crystalline standard ZnO, the patterns of which were taken before and after the

TABLE 3. Force Constants and Vibrational Frequencies of the $GaGaCl_4$ and Ga_2Cl_6 Molecules

$GaGaCl_4$				Ga_2Cl_6				
f_i, mdyn/A	ν, cm^{-1}			f_i, mdyn/Å	ν, cm^{-1}		Calculation	expt.
f_t 2,0	$\nu_1 t$		379	f_t 2,51	$\nu_1 +$	A_g	392	413
f_b 1,6	$\nu_2 tb$	A_1	342	f_b 1,0	$\nu_2 b$		300	318
f_r 0,266	$\nu_3 r$		199	f_α 0,125	$\nu_3 \alpha, \beta$		165	167
f_α 0,220	$\nu_4 \alpha, \gamma$		186	f_β 0,190	$\nu_4 \alpha, \beta, \gamma$		87	100
f_β 0,125	$\nu_5 \alpha, \gamma$		109	f_γ 0,084	$\nu_5 \gamma$ —	A_u	54	—
f_γ 0,135	$\nu_6 \gamma$	A_2	138	f_ζ 0,011	$\nu_6 b, \gamma$	B_{1g}	243	243
f_{tb} 0,2	$\nu_7 t$	B_1	387	f_{tb} 0,083	$\nu_7 \gamma$		115	125
f_{tt} 0,4	$\nu_8 \gamma, \alpha$		176	f_{bb} 0,20	$\nu_8 t$	B_{1u}	472	464
f_{bb} 0,054	$\nu_9 \xi$		62	$f_{\gamma\gamma}$ 0,017	$\nu_9 \gamma$		180	—
f_θ 0,078	$\nu_{10} b$	B_2	356		$\nu_{10} \zeta$		29	—
f_δ 0,036	$\nu_{11} r$		166		$\nu_{11} t$	B_{2g}	470	462
f_ζ 0,078	$\nu_{12} \gamma, \alpha$		120		$\nu_{12} \gamma$		104	117
					$\nu_{13} b$	B_{2u}	306	318
					$\nu_{14} \gamma$		103	114
					$\nu_{15} \gamma$ —	B_{3g}	101	109
					$\nu_{16} t$	B_{3u}	390	390
					$\nu_{17} b, \beta$		284	282
					$\nu_{18} \alpha, \gamma$		161	156

electron-diffraction patterns of the investigated vapor. While the electron-diffraction patterns were being recorded a vacuum of $(1.1–1.5)\cdot 10^{-6}$ torr was maintained in the diffraction chamber. The diffraction pattern was recorded on 9 × 12-cm high-contrast photographic plates. Liquid nitrogen was used to cool the evaorator trap.

The experimental temperature was 445 ± 10 K. The temperature of the sample tube was measured by means of a VR 5/20 thermocouple.

Each electron-diffraction pattern was accompanied by the full mass spectrum of the corresponding vapor.

The best electron-diffraction patterns were measured photometrically, and the averaged scattering intensity functions were calculated by means of the program in [28] for the following ranges of scattering angles: $s = 2.4\text{-}13.4$ $Å^{-1}$ (L_1) and $s = 5.0\text{-}22.0$ $Å^{-1}$ (L_2). The graph of the background line $I_{back}(s)$ was plotted in order to derive the molecular component $sM(s)$ from the total scattering intensity $I(s)$.

STRUCTURE ANALYSIS

The experimental $sM(s)$ function was compared with the theoretical analog:

$$sM(s) = \alpha sM(s)_{GaCl_3} + \beta sM(s)_{GaCl} + \gamma sM(s)_{Ga_2Cl_4} + \\ + (1-\alpha-\beta-\gamma) sM(s)_{Ga_2Cl_6}, \qquad (1)$$

where α, β, and γ are parameters related to the concentration of the molecular forms in the vapor.

This model of the vapor contains 22 terms, belonging to the four molecular modifications.

During solution of the problem the following conditions and assumptions were introduced: 1) The r_α(Ga–Cl) and ℓ(Ga–Cl) parameters of the GaCl molecule were calculated from spectroscopic data [29] for the experimental temperature and did not vary in the least-squares treatment; 2) The geometric configuration of the Ga_2Cl_6 molecule has D_{2h} symmetry [30, 31], and since the amount of Ga_2Cl_6 molecules in the vapor is small (as shown by the mass-spectral investigation), independent refinement of the structural characteristics of Ga_2Cl_6 was not undertaken. It was assumed that $r_\alpha(Ga–Cl_t)$ in Ga_2Cl_6 was equal to r_α(Ga–Cl) in $GaCl_3$, that the bridging $Ga–Cl_b$ bond was 0.2 Å longer than the terminal bond, and that the $Cl_t–Ga–Cl_t$ and $Cl_b–Ga–Cl_b$ angles were 124.5 and 90° respectively [30].

TABLE 4. Amplitudes and Correlations on the Perpendicular Vibrations of the $GaGaCl_4$ Molecules, Calculated for T = 445 K

Term		l, Å	$D=\frac{l^2}{r}-\frac{\langle\Delta x^2\rangle+\langle\Delta y^2\rangle}{2r}$, Å
		$GaGaCl_4$	
$Ga—Cl_t$	1—2	0,0602	—0,0083
$Ga—Cl_b$	1—4	0,0645	—0,0033
$Ga^I—Cl_b$	4—6	0,1362	—0,0048
$Cl_t—Cl_t$	2—3	0,0973	—0,0074
$Ga^I...Ga$	1—6	0,1332	—0,0002
$Cl_b...Cl_b$	5—4	0,1148	—0,0009
$Cl_t...Cl_b$	3—4	0,1322	—0,0023
$Ga^I...Cl_t$	2—6	0,2051	0,0065
		Ga_2Cl_6	
$Ga—Cl_t$	1—3	0,0532	—0,0322
$Ga—Cl_b$	3—4	0,0785	—0,0101
$Cl_t...Cl_t$	1—2	0,1068	—0,0458
$Cl_b...Cl_t$	1—4	0,1733	—0,0202
$Cl_b...Cl_b$	4—5	0,1040	—0,0058
Ga...Ga	3—4	0,1028	0,0000
$Cl_t...Cl_t$	1—8	0,1689	0,0018
$Cl_t...Cl_t$	1—7	0,5060	0,0380
$Ga...Cl_t$	1—6	0,2215	0,0001

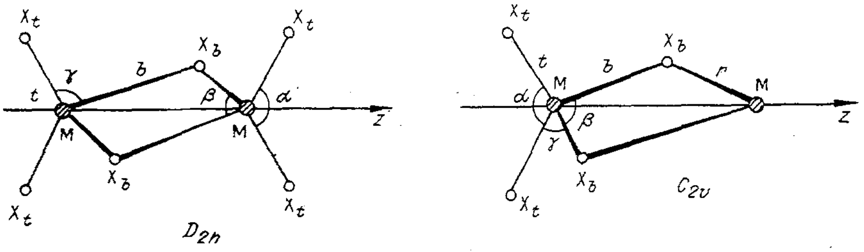

Fig. 1. Geometric structure and internal vibrational coordinates of the $Ga_2Cl_6(D_{2h})$ and $GaGaCl_4(C_{2D})$ molecules.

The amplitudes of the vibrations and the D corrections to the internuclear separations (Table 4) were calculated from the force field (Table 3) for the experimental temperature, used during interpretation of the data on the saturated vapor of gallium trichloride [30]. 3) It was assumed that the Ga_2Cl_4 molecule has a configuration with C_{2v} symmetry with different-valence gallium atoms. As independent geometric parameters we used $r(Ga^{III}—Cl_t)$, $r(Ga^{III}—Cl_b)$, $r(Ga^I—Cl_b)$, $\angle Cl_t—Ga—Cl_t$, and $\angle Cl_b—Ga—Cl_b$ (Fig. 1). The initial approximations to the parallel mean-square amplitudes of the vibrations and the k corrections (Table 4) were calculated from the force constants proposed during evaluation of the vibrational frequencies of this molecule (Table 3).

All the remaining internuclear separations of these molecules were determined from the independent geometric parameters of the Ga_2Cl_6 and Ga_2Cl_4 molecules in terms of the r_α structure at each cycle in the minimization of the divergence factor R_f.

As a result of the introduced assumption the refined parameters of the problem were as follows: r(Ga—Cl), ℓ(Ga—Cl), r(Cl—Cl), ℓ(Cl—Cl) of the $GaCl_3$ molecule, five independent geometric characteristics and amplitudes $\ell(Ga^{III}—Cl_t)$, $\ell(Ga^{III}—Cl_b)$ and $\ell(Ga^I—Cl_b)$ of the Ga_2Cl_4 molecule, and also the α, β, and γ values in Eq. (1).

Of the listed parameters of the problem the following were varied simultaneously: r(Ga—Cl), r(Cl—Cl), ℓ(Ga—Cl), and ℓ(Cl—Cl) of the $GaCl_3$ molecule, $r(Ga^I—Cl_b)$, $\ell(Ga^{III}—Cl_t)$ and $\ell(Ga^{III}—Cl_b)$ of the $GaGaCl_4$ molecule. The other parameters, i.e., the bond angles $Cl_t—Ga—Cl_t$, $Cl_b—Ga—Cl_b$ of the $GaGaCl_4$ molecule and the coefficients α, β, and γ associated with the ratio of the molecular forms in the vapor, were obtained by the network method. On account of the large correlation between the group of distances r(Ga—Cl), r(Ga^{III}—Cl_t) and r(Ga^{III}—Cl_b) the differences Δr_1 = r(Ga^{III}—Cl_t) − r(Ga—Cl) and Δr_2 = r(Ga^{III}—Cl_b) − r(Ga^{III}—Cl_t) were determined by the network method. Identical increments were assigned to the respective amplitudes of the vibrations at each step of the least-squares treatment.

Table 2 gives the results from least-squares treatment of the sM(s) function for the saturated vapor of gallium chloride, the parameters of which were listed above. For the sections obtained in the range of scattering angles of 2.4-13.4 and 5.0-22.0 $Å^{-1}$ the structural parameters of the molecules were determined with the ratios of the molecular forms close to the values obtained on the basis of the mass spectrum.

As seen, the parameters relating to the various sections of the sM(s) functions agree with each other within the limits of $3\sigma_{LSM}$, and the subsequent refinement of the composition of the vapor and the structural characteristics of the molecule was therefore made from the overall sM(s) section (scattering angles s = 2.4-22.0 $Å^{-1}$).

The third form of the calculation was conducted at the same concentrations of the molecular forms as those used in the first two cases. Further refinement of the parameters of the sM(s) function led to small variation of the ratio between the molecular forms and their structural characteristics (the fourth and fifth forms). In the fifth version the possibility of determining the amplitude of the vibrations of the Ga^I—Cl term of the $GaGaCl_4$ molecule was demonstrated.

DETERMINATION OF THE VIBRATIONAL FREQUENCIES OF THE $GaGaCl_4$ MOLECULE

There are no data on the vibrational frequencies of the $GaGaCl_4$ molecule. We determined these characteristics from the vibrational spectrum of the $GaCl_2$ melt [18], which essentially represents the spectrum of the tetrahedral $GaCl_4^-$ ion, and also our interpretation of the spectrum of the $InInI_4$ molecules [13].

The vibrational representation of the $GaGaCl_4$ molecule of C_{2v} symmetry has the following form: $\Gamma = 5\ A_1 + A_2 + 3\ B_1 + 3\ B_2$. The internal coordinates used for solution of the vibrational problem are given in Fig. 1.

We determined the corresponding force constants from the force constants of the tetrahedral $GaCl_4^-$ ion and the $InInI_4$ molecule [13]. The values $f_r = 2.0$, $f_{rr} = 0.16$, $f_\alpha = 0.14$, $f_{\alpha\alpha} = 0.02$ mdyn/Å of the $GaCl_4^-$ ion were calculated from the vibrational frequencies [18] in the approximation of the generalized valence-force field. During determination of the force constants of the $GaGaCl_4$ molecule the decrease in the symmetry of the $GaCl_4$ fragment compared with the $GaCl_4^-$ ion was taken into account. A diagram of the splittings of the frequencies belonging to the $GaCl_4$ fragment in the transition from T_d to C_{2v} symmetry is given in Table 5.

Our recommended force constants and vibrational frequencies of the $GaGaCl_4$ molecule, which we used for calculation of the generalized amplitudes of the vibrations of this molecule, are given in Table 3.

DISCUSSION OF RESULTS

Table 6 gives the independent geometric parameters r_α^- of the molecular structures of the gallium chlorides, determined in two independent experiments (the vapor above $GaCl_2$, T = 445 K, and the vapor above $GaCl_3$, T = 322 K). It is seen that the internuclear separations in the molecular forms $GaCl_3$ and Ga_2Cl_6 present in the two investigations coincide.

It should be noted that the parameters of Ga_2Cl_6 were determined more reliably in [30],

TABLE 5. Vibrational Frequencies of the Tetrahedral $GaCl_4^-$ Ion and the $GaCl_4(C_{2v})$ Fragment in the $GaGaCl_4$ Molecule

$GaCl_4^-$ (T_d)	$\nu_1(A_1)$ 344	$\nu_2(E)$ 121	$\nu_3(F_2)$ 375	$\nu_4(F_2)$ 154
	↓	↙ ↘	↙ ↓ ↘	↙ ↓ ↘
$GaGaCl_4$ (C_{2v}) Our calculation	$\nu_2(A_1)$ 343	$\nu_5(A_1)$ $\nu_6(A_2)$ 109 138	$\nu_7(B_1)$ $\nu_1(A_1)$ $\nu_{10}(B_2)$ 387 379 356	$\nu_{12}(B_2)$ $\nu_3(B_1)$ $\nu_4(A_1)$ 120 176 186

TABLE 6. Structural Parameters of the Ga_2Cl_6, $GaGaCl_4$, and $GaCl_3$ Molecules (internuclear separations and amplitude of vibrations in Å)

Parameter	T=322 K		T=445 K		
	r_α-structure				
	Ga_2Cl_6 [30]		Ga_2Cl_6	$GaGaCl_4$	
$r_\alpha(Ga—Cl_t)$	2,093(5)		2,090	2,130(5)	
$r_\alpha(Ga—Cl_b)$	2,298(6)		2,290	2,210(5)	
$r_\alpha(Ga^I—Cl_b)$	—		—	2,876(43)	
$\angle Cl_t—Ga—Cl_t$	124,5°(1)		124,5°	120°(2)	
$\angle Cl_b—Ga—Cl_b$	90°(1)		90°	100°(2)	
	Expt.	Calc.	Calc.	Expt.	Calc.
$l(Ga—Cl_t)$	0,049(4)	0,047	0,053	0,059(3)	0,060
$l(Ga—Cl_b)$	0,070(4)	0,068	0,078	0,064(3)	0,065
$l(Cl_t—Cl_b)$	0,125(8)	0,145	0,173	—	—
$l(Ga^I—Cl_b)$	—	—	—	0,173(55)	0,136

$GaCl_3$

	r_α-parameter		r_g-parameter
$r_\alpha(Ga—Cl)$	2,09(1)	2,090(5)	2,097(5)
$r_\alpha(Cl—Cl)$			3,586(17)
$\angle Cl—Ga—Cl$	120°		117,5°(1,5)
	Calculation	Expt.	Calculation
$l(Ga—Cl)$	0,047	0,053(3)	0,053
$l(Cl—Cl)$	0,108	0,142(16)	0,128
$\delta(Cl—Cl)$	0,008	0,040(28)	0,012

TABLE 7. Thermodynamic Characteristics of the Reactions with the Participation of Gaseous Gallium Chlorides

Reaction	$\Delta_r H_0^0$, kJ/mole	$\Delta_r S_{298}^0$, J/mole·deg
$Ga_2Cl_6 \rightleftharpoons 2GaCl_3$	93,8(5,0)	160(5)
$GaGaCl_4 \rightleftharpoons GaCl + GaCl_3$	97,6(3,0)	145(8)

since the saturated vapor above gallium trichloride at 322 K consisted predominantly of dimeric molecules Ga_2Cl_6 (79 mole %). In the present work the structural characteristics of the $GaCl_3$ molecules, which are the predominant molecular form of the saturated vapor above gallium dichloride (445 K), were measured reliably for the first time. The ratio of the internuclear separations Ga—Cl and Cl—Cl in $GaCl_3$ indicates that the molecule has planar geometry with D_{3h} symmetry. The effective shortening $\delta(Cl...Cl) = 0.012$ Å, calculated from the vibrational frequencies [29], coincides within the error limits with the experimental value of $\delta(Cl...Cl) = \sqrt{3}r_g(Ga—Cl) - r_g(Cl—Cl) = 0.040(27)$. The experimental and calculated amplitudes of the vibrations of this molecule are also in good agreement.

As far as the molecular form of $GaGaCl_4$ is concerned, its structure has special features which were noticed in [19] for a similar molecule with different-valence metal atoms $InInI_4$. Thus, the $GaCl_4$ fragment has the geometry of a distorted tetrahedron with the terminal bonds shorter than the bridging bonds; the difference amounts to ~0.10 Å. The bond angle Cl_tGaCl_t is larger, while the angle Cl_bGaCl_b is smaller than tetrahedral.

The length of the $Ga^I—Cl_b$ bond substantially exceeds $r(Ga—Cl_t)$ and $r(Ga—Cl_b)$ in the tetrahedral $GaCl_4$ fragment. This fact demonstrates the different nature of the Ga—Cl bonds in the $GaGaCl_4$ molecule, indicating the substantial ionicity of the $Ga^I—Cl_b$ bond, which is characterized by a small force constant (Table 3) and a large internuclear separation (Table 6).

During comparison of the averaged characteristics of the fragments with the tetracoordinated gallium atom in the Ga_2Cl_6 and $GaGaCl_4$ molecules it is seen that the average parameters of the Ga–Cl bonds practically coincide and amount to $\bar{r}$(Ga–Cl) = 2.170(6) and 2.190(6), and $\bar{f}$(Ga–Cl) = 1.75 and .80 mdyn/Å respectively.

By analysis of the data presented in Tables 3 and 6 it is possible to detect a distinct correlation between the internuclear separations, the bond force constants, and the bond frequencies of the vibrations in the molecules of the gallium chlorides.

The obtained values of the coefficients α, β, and γ of Eq. (1) made it possible by using the relation between the molar concentrations and parameters of sM(s) function [32] to establish the concentrations of the molecular forms in the saturated vapor of $GaCl_2$. The obtained values $x_{GaCl} = 0.262$, $x_{GaCl_3} = 0.538$, $x_{GaGaCl_4} = 0.170$ and $x_{Ga_2Cl_6} = 0.03$ were used to calculate the equilibrium constant (445 K) of the gas-phase reactions $Ga_2Cl_6 \rightleftarrows 2GaCl_3$, $GaGaCl_4 \rightleftarrows GaCl_3$. With due regard to the total pressure $P_{tot} = 0.2 \pm 0.1$ mm Hg and the structural and vibrational characteristics of the molecular forms obtained in the present work by means of the third law of thermodynamics we calculated the thermal effects, the changes of entropy in the above-mentioned reactions (Table 7), and the enthalpy of formation of gaseous $GaGaCl_4$.

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