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Thermodynamic functions of germane isotopologues ^{A}GeH$_4$ ($A = 70, 72, 73, 74, 76$) calculated from high-resolution IR spectra

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ARTICLE INFO

ABSTRACT

Standard thermodynamic functions of germane isotopologues ^{70}GeH$_4$, ^{72}GeH$_4$, ^{73}GeH$_4$, ^{74}GeH$_4$, and ^{76}GeH$_4$ are calculated in "harmonic oscillator – rigid rotator" and "anharmonic oscillator – oscillating non-rigid rotator" approximations and by the direct summation of the experimental energy values. To found the values of thermodynamic functions in the 200–700 K temperature range, approximation coefficients are determined by regression analysis. The isotope effect influence on the values of the standard isobaric heat capacity, entropy, enthalpy of heating, and the reduced isobaric-isothermal potential of germane is established. Limiting requirements for the accuracy of determining the spectral parameters for detecting the influence of the isotope effect on the thermodynamic functions and interatomic distances in the germane molecule are formulated.

1. Introduction

Germane in a natural isotopic composition contains five stable isotopes of germanium: ^{70}Ge, ^{72}Ge, ^{73}Ge, ^{74}Ge and ^{76}Ge. A systematic study of properties of the germane isotopic forms is an urgent scientific task. Fundamental interest in the study of the germane spectral characteristics is due to the fact that this substance was discovered in the atmospheres of Jupiter and Saturn [1–3]. The study of the processes taking place on these planets requires more precise information about the intensities and broadening parameters of vibration–rotation lines in the germane spectra.

Applied interest in the study of germane isotopologues is due to the design of a hydride method for high-purity isotopically enriched germanium preparation [4]. This material is promising for making the quantum computing devices and detectors of neutrinoless double beta decay [5,6]. At present, germanium tetrafluoride is principally used to prepare isotopically enriched germanium [7]. However, the chemical transformation of GeF$_4$ into polycrystalline germanium, which consists of several stages, leads to losses and contamination of the resulting product. An alternative method is the isotopic enrichment of germane and its subsequent one-stage thermal decomposition at low temperatures. Germanium hydride, in contrast to fluoride, does not show chemical activity towards the equipment materials used in the

decomposition (silica glass, stainless steel, rubber seals). It significantly simplifies the preparation technique of isotopically enriched germanium, increases the purity and yield of the target product. Isotopically enriched simple substances prepared by hydride technology have properties differed from their analogs with natural isotopic composition [8,9].

The most important fundamental properties of substances are their thermodynamic functions. They determine the stability of compounds under various conditions and make it possible to calculate the equilibrium concentrations of components in chemical systems with these compounds. To calculate the thermodynamic functions of gases, the method of statistical thermodynamics, based on the calculation of partition function of molecules, is most often used [10]. The information for calculations is the data from the vibration–rotation spectra. Statistical calculation has great practical importance, since direct experimental measurement of thermodynamic properties of gases is usually difficult and laborious. The accuracy of the statistical calculation of the gases thermodynamic quantities is usually comparable to the calorimetric measurement results.

The thermodynamic functions of germane with the natural isotopic germanium composition calculated by the methods of statistical thermodynamics are given in [11–13]. There are no data for the isotopic varieties of germane in the literature. The rotational- vibrational

Table 1
Isotopic composition of enriched germane samples. The composition of germane with natural isotopic composition is given according to IUPAC [42].

Sample	Isotopic composition, at. %				
	^{70}Ge	^{72}Ge	^{73}Ge	^{74}Ge	^{76}Ge
^{72}GeH$_4$	0.0050(1)	99.9530(5)	0.0180(3)	0.0230(6)	0.002(1)
^{73}GeH$_4$	< 0.00010	0.0405(3)	99.8960(8)	0.0633(5)	0.0002(1)
^{74}GeH$_4$	<0.00010	0.0010(5)	0.0605(10)	99.9355(11)	0.0029(2)
^{76}GeH$_4$	0.060(8)	0.090(9)	0.051(9)	11.592(19)	88.207(19)
nat. GeH$_4$	20.38 (18)	27.31 (26)	7.76 (8)	36.72 (15)	7.83 (7)

partition functions $Q(T)$ of germane isotopologues tabulated in the HITRAN 2020 database [15] were calculated by Gamache et al. [14] by simple multiplication of the rotational and vibrational partition functions without taking into account the rotation-vibration interaction. Herein, the rotational part was calculated using the spherical-top formula proposed in [16], and the vibrational part was calculated in the harmonic oscillator approximation. For these calculations, the data obtained from the spectra of germane with the natural germanium isotopic composition [17,18] were used.

To calculate the thermodynamic functions of germane isotope varieties and to reliably establish the isotope effect influence, it is necessary to use the high-resolution vibration–rotation spectra of the isotopically enriched samples. Until recently, experimental studies of the infrared (IR) spectra of the germane isotopic varieties contained fragmentary information. In most of them, the spectroscopic information for each isotopologue was obtained from the spectra of germane sample with natural isotopic composition registered at a maximum resolution of 0.02 cm^{-1} [19–28]. Previously, we have studied the high-resolution IR spectra (3×10^{-3} cm^{-1}) of the isotopically enriched germane samples [29–37]. Based on the data obtained, about 41,900 vibration–rotation transitions were identified for the fundamental bands, overtones, and combination absorption bands (including "hot" bands) of ^{A}GeH$_4$

molecules (A = 72, 73, 74, 76) up to the values of the rotational quantum number J_{max} = 27–31. Information on the parameters of the effective Hamiltonian, which takes into account the interactions between different vibrational states, was obtained that made it possible to simulate the spectra of germane isotopic varieties in the range of 700–4500 cm^{-1} with the frequency accuracy of 2×10^{-4} cm^{-1}.

The purpose of this work was to calculate the thermodynamic functions of the germane isotope varieties ^{A}GeH$_4$ (A = 70, 72, 73, 74, 76) using the method of statistical thermodynamics in the "harmonic oscillator – rigid rotator" and "anharmonic oscillator – oscillating non-rigid rotator" approximations based on the data of high-resolution vibration–rotation spectra. Additionally, the equilibrium interatomic distance in the germane molecule and the interatomic distance at the zero vibrational level of its isotopologues were calculated.

2. Experimental

2.1. Samples for research

Germane of a natural isotopic composition was prepared at the Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences (Nizhny Novgorod, Russia) by reacting germanium tetrachloride and sodium borohydride, followed by its purification by low-temperature rectification [38,39]. The isotope enrichment of germane was carried out at Joint Stock Company "Production Association Electrochemical Plant" (Zelenogorsk, Russia) by gas centrifugation [40]. The enriched samples were repeatedly purified by the rectification method. The isotopic composition of the resulting germane samples was determined by inductively coupled plasma mass spectrometry (Table 1) [41].

According to the results of IR spectroscopy, chromatography/mass spectrometry (CMS) and gas chromatography (GC) the content of molecular impurities (CO, CO$_2$, hydrocarbons, silicon and sulfur fluorides) in the prepared isotopically enriched germane samples was less than 10^{-4} vol% [43,44].

Table 2
Spectral parameters of isotopic germane modifications.

Parameter	^{70}GeH$_4$	^{72}GeH$_4$	^{73}GeH$_4$	^{74}GeH$_4$	^{76}GeH$_4$
ν_1, cm^{-1}	2110.7188265(2)	2110.708802(3)	2110.704270(8)	2110.700456(8)	2110.691769(11)
ν_2, cm^{-1}	929.901385(6)	929.905236(4)	929.9070002(5)	929.909306(15)	929.913028(12)
ν_3, cm^{-1}	2112.030716(14)	2111.573940(3)	2111.354585(4)	2111.142051(4)	2110.732309(6)
ν_4, cm^{-1}	821.544336(9)	821.116777(4)	820.911086(6)	820.71185(8)	820.327003(10)
ω_1, cm^{-1}	2194.4(4)	2194.5(4)	2194.6(4)	2194.6(4)	2195.1(3)
ω_2, cm^{-1}	943.9(4)	944.2(4)	944.4(5)	944.6(4)	945.0(4)
ω_3, cm^{-1}	2194.4(4)	2194.4(4)	2194.6(4)	2194.6(4)	2195.1(3)
ω_4, cm^{-1}	836.7(3)	836.6(3)	836.5(4)	836.5(2)	836.4(3)
B_0, cm^{-1}	2.69585545(3)	2.69585944(3)	2.69586298(11)	2.6958647(3)	2.6958703(6)
$D_0 \cdot 10^5$, cm^{-1}	−3.34168(3)	−3.341682	−3.341682	−3.341682	−3.341682
$\alpha_1 \cdot 10^2$ cm^{-1}	1.7988113	1.7988113	1.7988113	1.799331	1.799331
$\alpha_2 \cdot 10^3$, cm^{-1}	0	0	0	0	0
$\alpha_3 \cdot 10^2$, cm^{-1}	1.4713344	1.47050657	1.4700452	1.469502	1.468601
$\alpha_4 \cdot 10^2$, cm^{-1}	−0.1082241	−0.1075775	−0.1070517	−0.10672896	−0.1060455
$\beta_1 \cdot 10^6$, cm^{-1}	0.17727	0.17727	0.17727	0.19367	0.19367
$\beta_2 \cdot 10^6$, cm^{-1}	−0.4052	−0.4052	−0.4052	−0.4052	−0.4052
$\beta_3 \cdot 10^8$, cm^{-1}	0.397	0.397	0.397	0	0
$\beta_4 \cdot 10^6$, cm^{-1}	−0.370472	−0.370472	−0.3653	−0.3653	−0.3653
X_{11}	−8.497(12)	−8.501(14)	−8.52(3)	−8.510(14)	−8.56(3)
X_{12}	−7.0(4)	−6.7(4)	−6.7(5)	−6.7(4)	−6.6(3)
X_{13}	−33.988(11)	−34.004(14)	−34.09(3)	−34.04(13)	−34.23(3)
X_{14}	−5.85(19)	−5.89(9)	−5.9(9)	−6.05(9)	−6.08(10)
X_{22}	−0.43(5)	−0.45(4)	−0.45(6)	−0.44(4)	−0.47(4)
X_{23}	−7.0(9)	−7.10(9)	−7.3(9)	−7.43(9)	−7.68(5)
X_{24}	0.22(2)	0.21(3)	0.20(2)	0.20(3)	0.19(3)
X_{33}	−15.295(15)	−15.302(13)	−15.34(3)	−15.318(14)	−15.40(3)
X_{34}	−5.19(8)	−5.21(8)	−5.26(2)	−5.33(8)	−5.48(6)
X_{44}	−2.28(2)	−2.30(4)	−2.31(3)	−2.31(3)	−2.32(3)

2.2. Spectra recording

Vibration-rotation high-resolution spectra of isotopically enriched germane samples were recorded using a modified IFS 120 HR Fourier transform IR spectrometer (Bruker, USA). Spectrometer calibration was carried out using about 400 OCS lines and above 600 most intense lines of atmospheric H_2O and CO_2 basing on spectroscopic information from the HITRAN database and NIST calibration tables [45,46]. After calibration, the standard deviation of the line positions from the reference values was less than 10^{-4} cm^{-1}. The spectra were measured using a multi-pass White gas cell with an optical path length set in the range of 0.75–3.75 m and a single-pass optical cell with a fixed length of 20 cm. Spectra were recorded in the range of 650–4400 cm^{-1} with a nominal resolution (1/MOPD, maximum optical path difference) of 0.003 cm^{-1}. The germane pressure in the measuring cell was changed from 0.01 up to 600 mm Hg depending on the line intensity in the studied spectral range. To improve the signal to-noise ratio, ensuring reliable identification of lines and determination of their parameters, the spectra were obtained by averaging of about 1000 scans.

A shape of spectral lines was described by the Voigt function. The profile parameters of each line were determined by regression analysis. The values of vibrational and rotational constants for germane isotopic modifications $^AGeH_4$ ($A = 72, 73, 74, 76$) were calculated [29–37] using the method of effective Hamiltonians taking into account the interaction between different vibrational states of molecules. The spectral data for $^{70}GeH_4$ were obtained from analysis of the spectrum of natural isotopic composition germane.

3. Thermodynamic modeling

The thermodynamic functions of isotopic germane modifications were calculated by the method of statistical thermodynamics for the state of an ideal gas in the "harmonic oscillator – rigid rotator" (HORR) and "anharmonic oscillator – oscillating non-rigid rotator" (AOONR) approximations. In the HORR approximation, the initial data for the calculation were the central positions of the main vibrational bands and the ground vibrational state rotational constants of germane molecules found from high-resolution vibration–rotation spectra. In the AOONR approximation, the initial data were: vibrational constants of the main vibrations (ω_λ); a rotational constant of the ground vibrational state (B_0); a quartic centrifugal distortion coefficients (D_0); anharmonicity constants ($X_{\lambda\mu}$); vibration–rotation interaction constants (α_i, β_i) (Table 2). The parameter values and methods of their calculation are given in [29,30,33,34,47]. The standard thermodynamic functions of germane $^{76}GeH_4$ at 298.15 K were additionally calculated using the values of the vibration–rotation level energies found directly from the high-resolution IR spectra.

3.1. HORR approximation

The total partition function Q_{total} was represented as the multiplication of the nuclear Q_n, electronic Q_e, translational Q_{tr}, rotational Q_{rot}, and vibrational Q_{vib} sums, as well as the $e^{-\frac{E_o}{kT}}$ factor, which takes into account zero energy of the molecule:

$$Q_{total} = Q_n \cdot Q_e \cdot Q_{tr} \cdot Q_{rot} \cdot Q_{vib} \cdot e^{-\frac{E_o}{kT}} \tag{1}$$

The expressions for the partition functions in the HORR approximation are given in [10,48]. Practical (virtual) values of the thermodynamic functions usually given in databases do not take into account the nuclear partition function. It is determined that the nuclear spin does not change during chemical reactions. Stable germanium isotopes have zero nuclear spin, except for the ^{73}Ge isotope, for which spin is + 9/2 [48]. Therefore, in calculating the nuclear partition function of germanes with mass numbers 70, 72, 74, and 76, the protium spin was only taken into account. The total electronic spin of the germane molecule in the ground electronic state is zero; therefore, at low temperatures the electronic distribution does not contribute to the partition function, and the Q_e value is taken equal to 1.

The temperature dependences of the standard entropy $S^0(T)$ (virtual), isobaric heat capacity $C_p^o(T)$, reduced heating enthalpy $\frac{H^o(T)-H^o(0)}{RT}$, and reduced isobaric-isothermal potential (reduced Gibbs energy) $\Phi^o(T) = -\frac{G^o(T)-H^o(0)}{T} = S^o(T) - \frac{H^o(T)-H^o(0)}{T}$ were calculated. The expressions used for calculating the thermodynamic functions through partition functions of the molecules are given in [10]. According to the estimate given in [49], for polyatomic molecules, a fairly accurate calculation of thermodynamic functions from spectral data is possible up to a temperature of $T < 0.06 \frac{hc}{k} E_{dis}$, where E_{dis} is the dissociation energy of the molecule. For germane ($E_{dis} = 1138 \pm 5$ kJ/mol [45,55]) this value is about 1000 K. However, it is known from experimental data that germane almost completely decomposes in a flow reactor above 650 K, with formation of crystalline germanium [4,50]. Therefore, in this work, the upper limit of the temperature was set to 700 K.

The absolute expanded uncertainty $U(y)$ (0.95 level of confidence) of a thermodynamic function y calculated in the HORR approximation was estimated by differentiating the corresponding expressions for the thermodynamic functions:

$$U(y) = k \cdot \sqrt{\sum \left[\left(\frac{\partial y}{\partial x} \right)_{B_0, \nu_{i, \dots}} u(x) \right]^2}, \tag{2}$$

where y – a thermodynamic function ($S^0(T)$, $C_p^o(T) \dots$), $x - \nu_i$, B_o and fundamental constants; $u(x)$ – uncertainty of these quantities, k is the coverage factor assumed to be 2 for 0.95 level of confidence [51]. Differentiation was carried out with the respect to the variables ν_i, B_o and fundamental constants. The values of $\Delta\nu_i$ and ΔB_o were (1.6–2.5) $\times 10^{-4}$ cm^{-1} and (3–8) $\times 10^{-7}$ cm^{-1}, respectively, depending on the specific parameter and the germane isotopologue. The fundamental constants are Boltzmann constant $k = 1.3806504(24) \times 10^{-23}$ J/K; molar gas constant $R = 8.314472(15)$ J/(K $\times$ mol); Planck's constant $h = 6.62606896(33) \times 10^{-34}$ J $\times$ s; speed of light in vacuum $c = 299792458$ m/s (exact); atomic mass unit $m_u = 1.660538782(83) \times 10^{-27}$ kg [42]. The errors determined by equation (2) characterize the accuracy of calculations within the considered approximation and are not an assessment of the model adequacy.

3.2. AOONR approximation

In the AOONR approximation, the rotational term was calculated by the equation (3):

$$F_\nu = B_\nu J(J+1) - D_\nu J(J+1)^2; \tag{3}$$

$$B_\nu = B_0 - \sum_{i=1}^{4} \alpha_i \left(\nu_i + \frac{d_i}{2} \right); \tag{4}$$

$$D_\nu = D_0 - \sum_{i=1}^{4} \beta_i \left(\nu_i + \frac{d_i}{2} \right); \tag{5}$$

$$\alpha_i = B_0 - B_i; \tag{6}$$

$$\beta_i = D_0 - D_i \tag{7}$$

where J – rotational quantum number; α_i and β_i – vibration–rotation constants, d_i – degree of degeneracy.

The vibrational term was calculated by the following equation:

$$G(\nu) = \sum_\lambda \omega_\lambda \left(\nu_\lambda + \frac{d_\lambda}{2} \right) - \sum_{\lambda \leq \mu} X_{\lambda\mu} \left(\nu_\lambda + \frac{d_\lambda}{2} \right) \left(\nu_\mu + \frac{d_\mu}{2} \right), \tag{8}$$

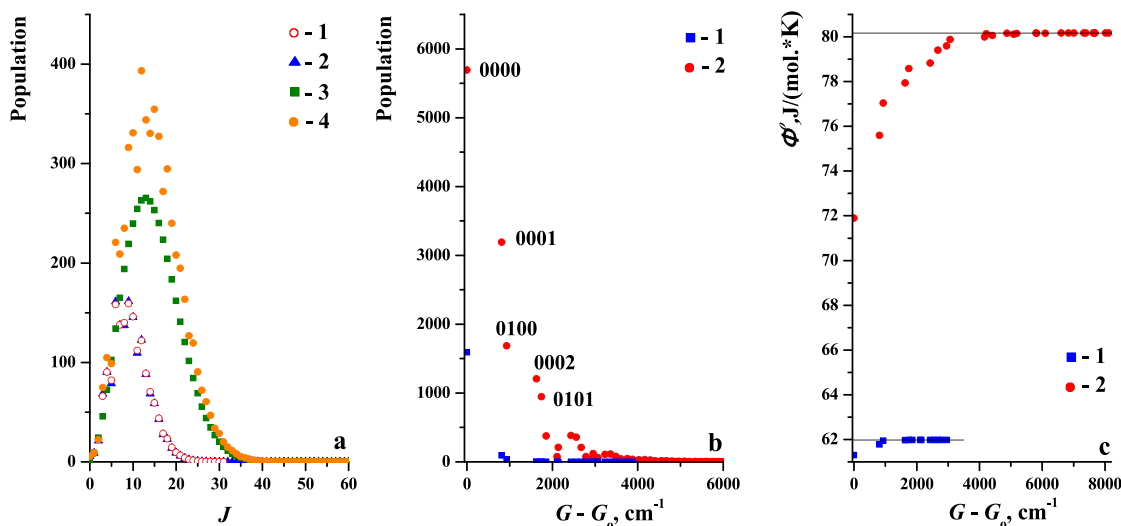where ω_λ – vibrational constant; $\nu_{\lambda,\mu}$ – vibrational quantum number, $d_{\lambda,\mu}$

Fig. 1. Distribution of the ^{76}GeH$_4$ molecules by (a) rotational states in the ground vibrational state, (b) vibration states energies, Reduced Gibbs energy $\Phi^o(T)$ vs vibration states energies is plotted in panel (c). 1a – calculation based on experimental energies (split states with the same j were summed), $T = 298.15$ K; 2a – calculation in the AOONR approximation taking into account the nuclear spin of protium, $T = 298.15$ K; 3a – calculation in the AOONR approximation with a statistical weight of states of $(2J+1)^2$, $T = 700$ K; 4a – calculation in the AOONR approximation taking into account the nuclear spin of protium, $T = 700$ K; 1b – calculation in the AOONR approximation, $T = 298.15$ K; 2b – calculation in the AOONR approximation, $T = 700$ K. (c) Reduced Gibbs energy $\Phi^o(T)$ vs vibration states energies calculated in the AOONR approximation at 298.15 K (1) and 700 K (2).

– degree of degeneracy; $X_{\lambda\mu}$ – anharmonicity coefficient.

The partition function was calculated for each set of (v_1, v_2, v_3, v_4) when changing J from 0 to J_{max}. Array of $Q_{rot}(v_1, v_2, v_3, v_4)$ values was received.

$$Q_{rot}(v) = \sum_{J=0}^{J_{max}} g_J \exp\left(-\frac{hc}{kT}F_v(J)\right) \quad (9)$$

where g_J – rotational level statistical weight.

$$g_J = (2J+1)\dot{g}_J(J) \quad (10)$$

For large values of the quantum number J the parameter $\dot{g}_J$ is approximately equal to $(2J+1)/\sigma$ [52]. The calculation of $\dot{g}_J(J)$ for the lowest rotational levels of a spherical XH$_4$ top with four protium atoms (nuclear spin ½) is given in [53].

The vibration–rotation partition function was calculated as

$$Q_{vib-rot} = \sum_{v_1 v_2 v_3 v_4=0}^{v_{max}} p Q_{rot}(v) \exp\left(-\frac{hc}{kT}G(v)\right) \quad (11)$$

where p – vibrational level statistical weight,

$$p = \prod \frac{(v_i + d_i - 1)!}{v_i!(d_i - 1)!} \quad (12)$$

d_i – degree of degeneracy. To determine the thermodynamic functions, the first and second derivatives of $Q_{vib-rot}$ with respect to temperature were calculated:

$$T\frac{dQ_{vib-rot}}{dT} = \overline{Q}_{vib-rot} \quad (13);$$

$$T^2\frac{d^2 Q_{vib-rot}}{dT^2} = \overline{\overline{Q}}_{vib-rot} \quad (14)$$

Expressions for $\overline{Q}_{vib-rot}$ and $\overline{\overline{Q}}_{vib-rot}$ are given in [49]. The upper limit of summation was estimated based on the fact that the contribution of the term to the value of thermodynamic functions does not exceed 5×10^{-5} J/(mol·K). This corresponds to the absolute error of the HORR approximation calculated by equation (2). Such an estimate is applicable for not very high temperatures, when the main contribution to the partition function is made by low-energy vibration–rotation levels of the

molecule ground electronic state [49].

Based on the obtained set of $Q_{vib-rot}, \overline{Q}_{vib-rot}$ and $\overline{\overline{Q}}_{vib-rot}$ values, thermodynamic functions due to the vibration–rotation motion of the molecule were calculated as

$$\frac{C_p^o(T)}{R} = \frac{\overline{\overline{Q}}_{vib-rot}}{Q_{vib-rot}} - \left(\frac{\overline{Q}_{vib-rot}}{Q_{vib-rot}}\right)^2 \quad (15)$$

$$\frac{S^o(T)}{R} = \ln Q_{vib-rot} + \frac{\overline{Q}_{vib-rot}}{Q_{vib-rot}} \quad (16)$$

$$\frac{H^o(T) - H^o(0)}{RT} = \frac{\overline{Q}_{vib-rot}}{Q_{vib-rot}} \quad (17)$$

$$\frac{\Phi^o(T)}{R} = \ln Q_{vib-rot} \quad (18)$$

To calculate the total thermodynamic functions, the contributions from the translational motion of the molecule were added to the obtained values. The estimation of the limiting absolute error of calculations in the AOONR approximation, due to the accuracy of the spectral parameters and fundamental constants, was carried out according to equation (2). The calculated error was an order of magnitude greater than that for the HORR approximation due to the larger error in the values of the constants ω_i compared to ν_i. It does not imply a lower accuracy of the AOONR approximation, since the estimated error does not take into account the model adequacy.

3.3. Summation of experimental energy values

The most accurate method for calculating the vibration–rotation partition function at low temperatures is a direct summation, taking into account the level energy values obtained from the experimental spectra. For germane molecules $Q_{vib-rot}$ was calculated as

$$Q_{vib-rot} = \sum_{J=0}^{J_{max}} g_J \exp\left(-\frac{hc}{kT}G_{exp}\right) \quad (19)$$

where G_{exp} – experimental vibration–rotation term; g_J – statistical weight:

Table 3
Standard thermodynamic functions of germane isotopologues. Numbers between parentheses are absolute expanded uncertainties in the unit of the last digit quoted.

Function	Approach	$^{70}GeH_4$	$^{72}GeH_4$	$^{73}GeH_4$	$^{74}GeH_4$	$^{76}GeH_4$	$^{nat}GeH_4$ (literature)
$S^o(298.15)$, J/(mol·K)	HORR	216.5827(**8**)	216.9191	217.0845	217.2470	217.5666	217.259 [11], 226.710 [12],
	AOONR	216.71(**4**)	217.05	217.21	217.37	217.69	217.149 [56]
	Exp.	–	–	–	–	217.656 (**2**)	
$C_p(298.15)$, J/(mol·K)	HORR	44.9714(**8**)	44.9800	44.9842	44.9882	44.9960	45.017 [11],
	AOONR	45.03(**4**)	45.04	45.04	45.05	45.06	42.36 [12], 45.019 [56]
	Exp.	–	–	–	–	45.133(**2**)	
$H^o(298.15) - H^o(0) / RT$	HORR	4.33372(**8**)	4.33408	4.33426	4.33443	4.33476	4.3377 [56]
	AOONR	4.331(**4**)	4.332	4.332	4.332	4.332	
	Exp.	–	–	–	–	4.33785 (**2**)	
$\Phi^o(298.15)$, J/(mol·K)	HORR	180.5502(**8**)	180.8836	181.0474	181.2085	181.5254	181.084 [56]
	AOONR	180.6956(**4**)	181.0290	181.1927	181.3539	181.6707	
	Exp.	–	–	–	–	181.5889(**2**)	

$$g_J = (2J+1)n, \tag{20}$$

where n – statistical weights due to nuclear spin, is equal to 5 for A_1 and A_2 symmetry levels; 2 for E level; 3 for F_1 and F_2 levels [52].

The calculation from the experimental data was performed up to the energy values corresponding to the P_3 polyad (octad). Transitions with $J_{max} = 26$–31 were identified directly from the experiment that is sufficient to calculate the partition functions at 298.15 K. For calculating the partition function at higher temperatures, the energies of high-lying levels are required. Information about these levels is not available from the experimental spectra. We used an experiment-based partition function supplemented with that calculated for the high-energy levels in the framework of the AOONR approximation.

3.4. Interatomic distances

The average interatomic distance for the zero vibrational energy level $r_0(\text{Ge} - \text{H})$ was calculated using the equation

$$r_0(\text{Ge} - \text{H}) = \sqrt{\frac{3h}{64\pi^2 cm_H B_0}} \tag{21}$$

where m_H – mass of a hydrogen atom, kg.

To find the equilibrium interatomic distance $r_e(\text{Ge} - \text{H})$, the rotational constant B_e was calculated as [17].

$$B_e = B_0 - \frac{1}{2}\sum_{i=1}^{4} d_i(B_i - B_0) \tag{22}$$

$$r_e(\text{Ge} - \text{H}) = \sqrt{\frac{3h}{64\pi^2 cm_H B_e}} \tag{23}$$

where d_i – degree of level degeneracy. The error of calculating the interatomic distances was estimated from the equation (2).

4. Results and discussion

The thermal distribution of the $^{76}GeH_4$ molecules by the rotational states in the ground vibrational level is shown in Fig. 1a. At 298.15 K the deviations of the population calculated in the AOONR approximation from the experimental values are 1–2 % for the most populated levels. The contribution of rotational levels with quantum number $J > 30$, up to which experimental energy values are available, does not exceed 1×10^{-3} % of the total value of Q_{rot}. At 700 K, such a contribution is achieved for levels with $J > 46$, which were not assigned in the experiment. Neglecting the nuclear spin of protium (curve 3a) in the calculation of virtual functions led to a significant underestimation of the level population.
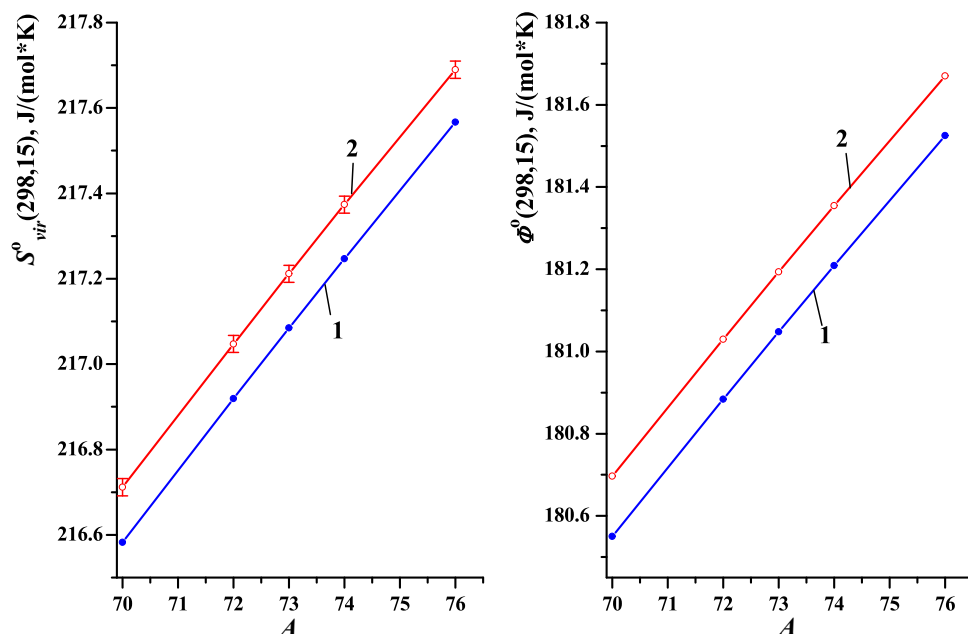

Fig. 2. Dependence of the standard entropy (a) and reduced isobaric-isothermal potential (b) of the $^AGeH_4$ on the germanium isotope mass number at 298.15 K. 1 – HORR approximation; 2 – AOONR approximation.

Table 4

Values of the approximating coefficients for the thermodynamic functions of germane isotopologues in the temperature range of 200–700 K.

Substance	Model	Coefficient							$\chi^2 \cdot 10^{11}$
		$\varphi_1 \cdot 10^{-1}$	φ_2	$\varphi_3 \cdot 10^4$	$\varphi_4 \cdot 10^2$	$\varphi_5 \cdot 10^{-2}$	$\varphi_6 \cdot 10^{-2}$	$\varphi_7 \cdot 10^{-3}$	
^{70}GeH$_4$	HORR	1.8490	−0.5255	1.6505	−6.469	1.2368	−3.9086	0.8583	4.3142
	AOONR	1.8978	−0.3855	1.5304	−6.150	1.2092	−3.7861	0.8379	6.9652
^{72}GeH$_4$	HORR	1.8537	−0.5233	1.6479	−6.463	1.2367	−3.9085	0.8584	4.3307
	AOONR	1.9026	−0.3832	1.5281	−6.144	1.2090	−3.7850	0.8378	6.9783
^{73}GeH$_4$	HORR	1.8559	−0.5221	1.6467	−6.460	1.2366	−3.9085	0.8584	4.3390
	AOONR	1.9047	−0.383	1.5274	−6.142	1.2089	−3.7851	0.8379	6.9848
^{74}GeH$_4$	HORR	1.8582	−0.5211	1.6455	−6.457	1.2366	−3.9084	0.8585	4.3471
	AOONR	1.9069	−0.3815	1.5263	−6.140	1.2088	−3.7850	0.8380	6.9889
^{76}GeH$_4$	HORR	1.8626	−0.5190	1.6431	−6.451	1.2365	−3.9084	0.8585	4.3610
	AOONR	1.9107	−0.3815	1.5263	−6.140	1.2089	−3.7852	0.8382	6.9951
	Exper.	1.9644	−0.2416	1.4794	−5.956	1.1606	−3.3693	0.6743	5.5447

A distribution of the ^{76}GeH$_4$ molecules by vibrational states at temperatures of 298.15 and 700 K is shown in Fig. 1b. The values of the function $\Phi^o(T)$ corresponding to these distributions are shown in Fig. 1c. $\Phi^o(T)$ was calculated up to the energy levels above which the contribution to this function does not exceed 5×10^{-5} J/(mol·K). At 298.15 K the upper limit of the calculation corresponds to the pentad range for which the experimental data are available. Therefore, the values of the energy levels found directly from the high-resolution spectra of germane are sufficient to calculate the standard thermodynamic functions at 298.15 K with an accuracy determined by the fundamental constant values. At 700 K the calculation should be carried out up to energies of ~ 8200 cm^{-1}. Such a calculation is possible by combining the experimental data and a higher energy levels extrapolation, for example, in the AOONR approximation.

The results of calculations of the standard thermodynamic functions of the germane isotopologues ^{A}GeH$_4$ ($A = 70, 72, 73, 74, 76$) at 298.15 K using the partition functions in the framework of the HORR and AOONR approaches and by summing the experimental energies are shown in Table 3. The greater the mass of the germanium atom, the greater the values of thermodynamic functions. This dependence is close to linear (Fig. 2) similar to that for the spectral parameters which is typical for molecules of the spherical top type [54]. The isotope effect shows itself in the entropy and the reduced isobaric-isothermal potential values of germane is 0.164 J/(mol·K) for 1 a.m.u. germanium isotope; for the heat capacity and reduced enthalpy of heating the effect is 0.003 and 0.3 J/(mol·K), respectively. These values exceed the errors in the calculation of thermodynamic functions in the HORR approximation due to the accuracy of determining the spectral parameters and fundamental constants. The calculation error in the AOONR approximation exceeds the contribution of the isotope effect to the values of the heat capacity and the reduced enthalpy of heating. The obtained values of thermodynamic functions are expectedly close to some literature data for natural germanium. The main result of this work is that thermodynamic functions are calculated for each isotope separately.

Previously, the vibration–rotation partition function for the ^{76}GeH$_4$ molecule was given as 1634.1 at 296 K [14]. This value was calculated in the approximation of a harmonic oscillator and the equation proposed in [16]. For comparison, in the present work, the vibration–rotation partition function of ^{76}GeH$_4$ at 296 K, calculated in the HORR approximation, was 1703.6; in approximation AOONR – 1733.7. Such differences in the partition functions lead to a discrepancy in the value of the reduced isobaric-isothermal potential of about 0.5 J/(mol·K), which is comparable to the isotope effect. In [55] the *ab initio* calculated partition function for ^{74}GeH$_4$, was 1737.7 at 298 K; in the present work 1756.8. The higher the temperature, the greater the absolute deviations. The differences between our calculated partition functions and the results of [14] and [55] are likely caused by the use of more complete and accurate parameters obtained from the experimental spectra of the isotopically enriched samples. Moreover, our calculations are based on a model which takes into account anharmonicity, nonrigidity, and vibration-

rotation interaction.

The values of standard thermodynamic functions at 298.15 K, calculated using the experimental data, can be taken as conditionally true values in relation to approximate calculation methods. In this case, the absolute error of the HORR approximation for $\Phi^o(298.15)$ is 0.06 J/(mol·K). Despite this value is rather small, it is larger than the errors by 2 orders of magnitude than the errors due to the accuracy of the spectral parameters and fundamental constants (0.0008 J/(mol·K)). Therefore, the main contribution to the error budget of the calculated thermodynamic functions in the HORR approximation comes from the assumptions about the nature of vibrational and rotational motions in the molecule. Using the AOONR method, the values of the partition function at the 298.15 K are overestimated compared to the calculation from the experiment. The differences between the values of $\Phi^o(298.15)$ calculated in the AOONR approximation and from the experiment exceed those between the HORR and experiment. However, starting from 360 K, the AOONR method gives results closer to the experiment and at 700 K the difference is only 0.007 J/(mol·K).

To represent the temperature dependences of the thermodynamic functions, they were approximated in the temperature range of 200–700 K. The approximating equation of the reduced dimensionless isobaric-isothermal potential adopted in some thermodynamic handbooks and databases [48] was used:

$$\frac{\Phi^o(T)}{R} = \varphi^o(x) = \varphi_1 + \varphi_2 \ln x + \varphi_3 x^{-2} + \varphi_4 x^{-1} + \varphi_5 x + \varphi_6 x^2 + \varphi_7 x^3, \quad (24)$$

where φ_i – approximation coefficients; $x = T/T_x$ – reduced temperature, $T_x = 10^4$ K. The approximating equations for the rest of the thermodynamic functions, taking into account their relationship with $\Phi^o(T)$, have the following forms:

$$\frac{C_p^o(T)}{R} = \varphi_2 + 2\varphi_3 x^{-2} + 2\varphi_5 x + 6\varphi_6 x^2 + 12\varphi_7 x^3; \quad (25)$$

$$\frac{S^o(T)}{R} = \varphi_1 + \varphi_2(1 + \ln x) - \varphi_3 x^{-2} + 2\varphi_5 x + 3\varphi_6 x^2 + 4\varphi_7 x^3; \quad (26)$$

$$\frac{H^0(T) - H^0(0)}{RT_x} = \varphi_2 x - 2\varphi_3 x^{-1} - \varphi_4 x + \varphi_5 x^2 + 2\varphi_6 x^3 + \varphi_7 x^4. \quad (27)$$

Values of the coefficients φ_i for the HORR and AOONR approximations are given in Table 4. The correspondence of the approximation to the calculated values of the thermodynamic functions was characterized by the reduced χ^2-criterion [57]. The relative deviations of the calculated thermodynamic functions values from the approximation equations range from 1.5 % at 200 K to 0.1 % at 700 K. The approximated values are systematically lower than the calculated ones, but the absolute isotope effect is retained with a high accuracy.

Using the obtained values of the function $\frac{\Phi^o(T)}{R}$, the influence of the isotope effect on the equilibrium constants of reactions involving isotope modifications of germane can be estimated. For practice, the thermal

Table 5

Calculation results for the moment of inertia I_0 and r_0(Ge-H) of germane isotopologues. Errors in the parentheses are statistical uncertainties that are the same for all isotopologues.

Parameter	⁷⁰GeH₄	⁷²GeH₄	⁷³GeH₄	⁷⁴GeH₄	⁷⁶GeH₄	ⁿᵃᵗGeH₄,
$I_0 \cdot 10^{46}$, kg·m²	1.037411(**6**)	1.037410	1.037408	1.037408	1.037406	–
r_0(Ge-H), Å	1.525362(**4**)	1.525361	1.525360	1.525360	1.525358	1.48 [18], 1.5251(5) [25], 1.53 [20]

decomposition reaction is important.

$$^{A}\text{GeH}_4(\text{g.}) \rightleftarrows {^{A}}\text{Ge(g.)} + 2\text{H}_2(\text{g.}). \tag{28}$$

The equilibrium constant K_p of this reaction can be calculated from the equation

$$\ln K_p(T,A) = \frac{\Delta_r \Phi^o(T,A)}{R} - \frac{\Delta_r H^o(298.15)}{RT} \tag{29}$$

To calculate $\Delta_r H^o(298.15)$, it is necessary to know the enthalpy of formation of germane, which cannot be determined from spectral data. Assuming an independence of this quantity and all thermodynamic functions of gaseous germanium from the isotope mass one can write

$$\ln K_p(T,A_2) - \ln K_p(T,A_1) \approx \frac{\Delta_r \Phi^o(T,A_2)}{R} - \frac{\Delta_r \Phi^o(T,A_1)}{R}$$
$$= \frac{\Phi^o(T,A_1)}{R} - \frac{\Phi^o(T,A_2)}{R} \tag{30}$$

therefore

$$\frac{K_p(T,A_2)}{K_p(T,A_1)} = \frac{p_{A_2 Ge} p_{A_1 GeH_4}}{p_{A_1 Ge} p_{A_2 GeH_4}} = \alpha \approx \exp\left(\frac{\Delta \Phi^o(T)}{R}\right), \tag{31}$$

where $\Delta \Phi^o(T) = \Phi^o(T,A_1) - \Phi^o(T,A_2)$, p_i – equilibrium vapor pressure of the i-th component, α – separation coefficient. Using the results from Tables 3 and 4 it follows that at 298.15 K the difference K_p of type (28) reactions per 1 a.m.u. is about 2 %. This value is practically independent of temperature over the entire calculation interval. The absolute value of the reaction (28) equilibrium constant increases with a decrease of the germanium isotope atomic mass. Considering the ratio of equilibrium constants is equal to the separation coefficient α of a chemical reaction then α = 1.02 for the $^{A}\text{GeH}_4/^{A+1}\text{GeH}_4$ systems. The result turned out to be substantially higher than that obtained in [58] ($\alpha^{76-70} = 1.013$), where only vibrational partition functions calculated from simplified expressions were used. The obtained value of the parameter α allows us to consider the reaction of thermal decomposition of germane as potentially suitable for isotopic separation in the case of multiple repeated, when separation factor $F = \alpha^n$, where n is the number of germane decomposition/synthesis stages.

The value of the equilibrium interatomic distance r_e(Ge–H), which is independent of the isotope mass in the Born–Oppenheimer approximation, was determined as 1.51710(2) Å for the GeH₄ molecule. This value coincided with the result presented in [17], which was obtained from the spectra of natural germane registered with a resolution of 0.0019 cm⁻¹. Unlike r_e, the distance r_0 depends on the isotopic composition of the molecule. The calculated values of r_0 and the moment of inertia I_0 are given in Table 5. As the mass of the germanium isotope increases, r_0 decreases linearly. The average change in r_0 per 1 a.m.u. is $7 \cdot 10^{-7}$ Å with a calculation error of $2 \cdot 10^{-7}$ Å. There are no published data on the effect of isotopic composition on interatomic distances in tetrahedral molecules. However, the obtained value coincides within the error with that for the diatomic molecules, in particular with H⁷⁹Br and H⁸¹Br [59].

On the basis of the data obtained, a back statistical problem was solved: limiting requirements were formulated for the accuracy of determining the spectral parameters for detecting the isotope effect influence on the thermodynamic functions of germane in the HORR approximation. It was found the uncertainties of the central frequencies and rotational constant should be lower than 2×10^{-3} cm⁻¹ and 2×10^{-2} cm⁻¹, respectively. To detect the influence of the isotope effect on the interatomic distances r_0 in the GeH₄ molecule, the parameter B_0 must be determined with an uncertainty of 2×10^{-6} cm⁻¹ or less. Such accuracy is ensured not only by the spectrometer resolution, but also by a high signal-to-noise ratio, which is achieved by a long-time signal accumulation. The isotopic enrichment and chemical purity of the samples are of great importance for accurate calculation of the spectral parameters since a wider range of rotational states j can be covered and more reliable assignment of the lines can be made.

5. Conclusions

The standard thermodynamic functions of germane isotopologues $^{A}\text{GeH}_4$ ($A = 70, 72, 73, 74, 76$) were calculated by statistical thermodynamics methods, using high-resolution spectral data. For germane $^{76}\text{GeH}_4$, the most accurate values of the heat capacity, entropy, enthalpy of heating, and the reduced isobaric-isothermal potential were obtained by combining the experimental energy values with the anharmonic oscillator – nonrigid oscillating rotator approximation. The influence of the isotope effect on the values of thermodynamic functions at 298.15 K is 0.164 J/(mol·K)/a.m.u. for the entropy and reduced isobaric-isothermal potential; 0.003 J/(mol·K)/a.m.u. for the heat capacity and 0.3 J/(mol·K) for the reduced enthalpy of heating. Approximation coefficients were calculated to find the values of the germane isotopologue thermodynamic functions in the temperature range 200–700 K. Influence of the isotope effect on the value of the thermal decomposition standard equilibrium constant of germane was estimated to be 2 %/a.m.u. The equilibrium interatomic distance r_e(Ge–H) in the germane molecule, independent of the mass of the isotope, was determined as 1.51710(2) Å. The interatomic distance at the zero vibrational level r_0(Ge–H) decreases with an increase in the mass of the germanium isotope by 1×10^{-6} Å/a.m.u. Limiting requirements were formulated for accurate determining the rotational constant and the central position of the bands in order to detect the influence of the isotope effect on the thermodynamic functions and interatomic distances of germane isotopologues.

CRediT authorship contribution statement

I.A. Velmuzhova: Writing – review & editing, Visualization, Methodology, Investigation. **M.A. Koshelev:** Writing – review & editing, Investigation. **A.P. Velmuzhov:** Writing – review & editing, Visualization, Methodology, Investigation. **O.N. Ulenikov:** Writing – review & editing, Investigation. **O.V. Gromova:** Writing – review & editing, Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgement

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