

The vibrational-rotational high-resolution spectrum in the region of $3\nu_4$, $\nu_2 + 2\nu_4$ and $2\nu_2 + \nu_4$ bands of the $^{72}\text{GeH}_4$ molecule

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The high-resolution spectrum of the $^{72}\text{GeH}_4$ molecule was recorded on a Bruker IFS 125HR Fourier spectrometer with an optical resolution of 0.003 cm^{-1} . The line positions were analyzed for ten interacting vibrational-rotational bands $3\nu_4$ ($1F_2$, F_1 , $2F_2$), $\nu_2 + 2\nu_4$ ($1E$, F_1 , F_2 , $2E$) and $2\nu_2 + \nu_4$ ($1F_2$, F_1 , $2F_2$) in the range $2350\text{--}2750\text{ cm}^{-1}$. As a result of the analysis, 1726 experimental lines were identified with the maximum value of the quantum number $J_{\text{max}} = 17$; then used in the fitting procedure with parameters of the effective Hamiltonian. The resulting set of 35 spectroscopic parameters describes the vibrational-rotational structure of the spectrum with $d_{\text{rms}} = 7.5 \cdot 10^{-4}\text{ cm}^{-1}$.

Keywords: GeH_4 , spectroscopic parameters, vibrational spectrum analysis, high-resolution Fourier spectra.

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Introduction

Before the middle of the seventies our knowledge about the composition of atmospheres in the giant planets of the solar system had not progressed much. Further, thanks to fast development of ground infrared technology, multiple molecular compounds were found with a hydrogen bond in atmospheres of the solar system planets, and among this variety there was a molecule GeH_4 [1]. In particular, study of Saturn atmosphere composition was conducted on the basis of remote probing using ground and low-earth telescopes, as well as interplanetary orbital spaceships. These studies played an important role in study of the chemical composition of stratosphere and upper layers of troposphere of the Saturn and made it possible to establish presence of germane molecule and its isotope-substituted modifications [2–6]. This molecule was also found in the atmosphere of the Jupiter [7–9] and in the Mars atmosphere in a small quantity [10]. However, full-scale research of giant planet atmospheres requires precise simulation of infrared spectra of GeH_4 molecule and its isotopologues. As a result, the research of vibration rotation spectra of germane molecule and production of highly accurate spectroscopic information about the characteristics of spectral lines from experimental data is a problem being solved for many years [11–21].

This paper for the first time completed the study of the high resolution spectrum of molecule $^{72}\text{GeH}_4$ in the octad band range. Namely, seven combination bands were analysed: $\nu_2 + 2\nu_4$ ($1E$, F_1 , F_2 , $2E$), $2\nu_2 + \nu_4$ ($1F_2$, F_1 , $2F_2$), as well as three overtone ones $3\nu_4$ ($1F_2$, F_1 , $2F_2$). Use of isotope-enriched sample made it possible to considerable bring down the difficulties in analysis of the spectrum

related to the need of taking into account the lines of other germane isotopologues. The spectrum analysis identified 1726 transitions for 10 vibration bands of molecule $^{72}\text{GeH}_4$, which were used as input information to solve inverse spectroscopic problem. As a result, the following parameters were produced: band centers, rotational parameters and centrifugal distortion, tetrahedral splitting and parameters of resonance interactions between vibration stages.

Experiment details

To record the spectrum of germane molecule, Fourier spectrometer Bruker IFS125HR was used. The experimental setup was equipped with a Globar source, a light divider from KBr and a detector based on indium antimonide (InSb). Briefly, the sample preparation method consisted in the following. A germane sample (with stated purity of 99.9%) with natural content of isotopes was synthesized in the Institute of Chemistry of High-Purity Substances, Russian Academy of Science, in Nizhny Novgorod by a reaction between GeCl_4 and NaBH_4 with subsequent purification using rectification method. Then the sample was enriched with isotope ^{72}Ge by centrifugal method in a production association „Electrochemical Plant“ town of Zelenogorsk, Russia). The enriched method was again cleaned by rectification method.

The spectrum was recorded with resolution 0.003 cm^{-1} in frequency range $2350\text{--}2750\text{ cm}^{-1}$ at 24.2°C . The experiment used Norton-Bier apodization function (weak). All measurements used a multi-pass White cell with base length 0.75 m, which was always connected to the vacuum system of the gas sample, the turbomolecular pump and capacitance pressure gauges in the range of

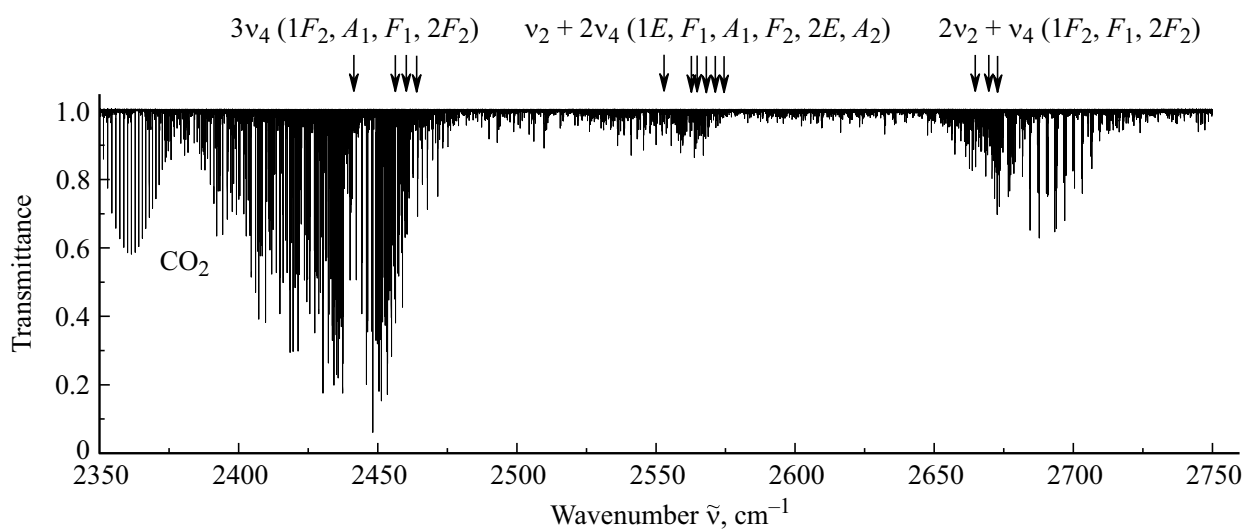


Figure 1. Overview spectrum of molecule $^{72}\text{GeH}_4$ in region $2350\text{--}2730\text{ cm}^{-1}$ (arrows specify centers of bands $3\nu_4$, $\nu_2 + 2\nu_4$ and $2\nu_2 + \nu_4$).

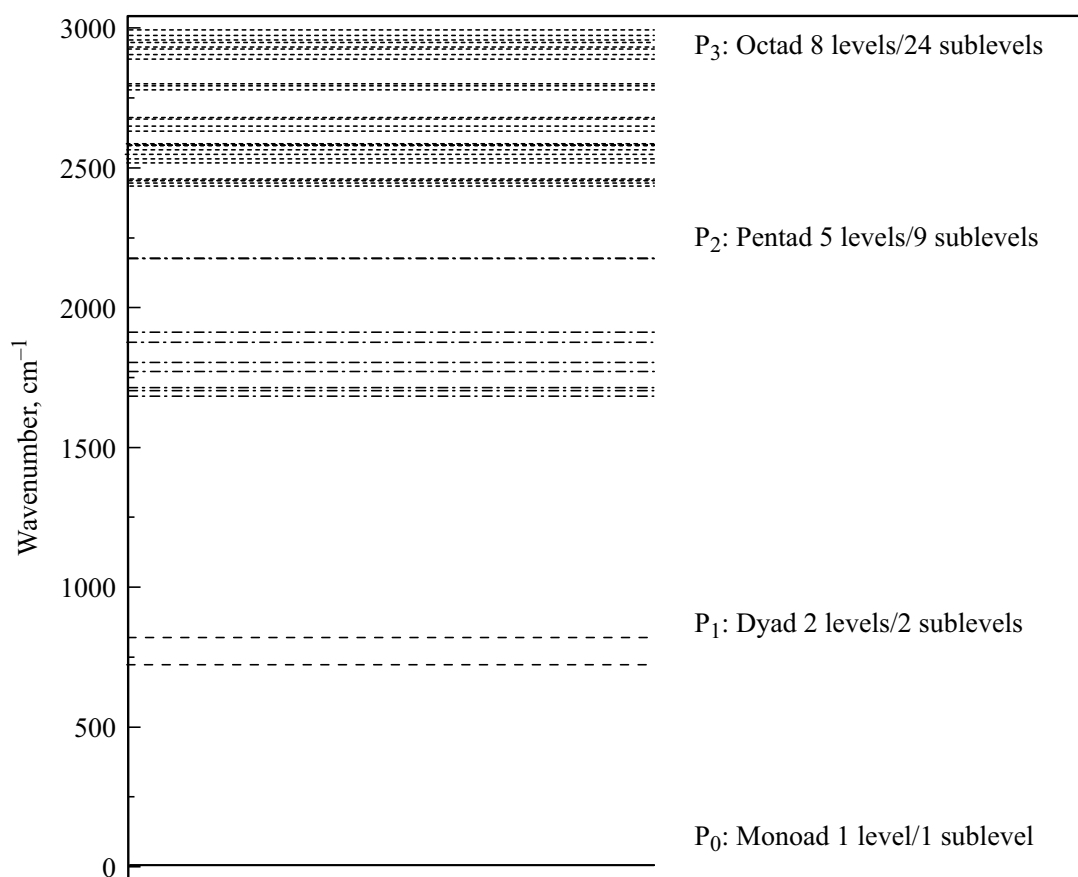


Figure 2. Polyad scheme of molecule GeH_4 , including main state P_0 , dyad P_1 (ν_2, ν_4), pentad P_2 ($\nu_1, \nu_3, 2\nu_2, 2\nu_4, \nu_2 + \nu_4$) and octad P_3 ($\nu_1 + \nu_2, \nu_1 + \nu_4, \nu_3 + \nu_2, \nu_3 + \nu_4, 3\nu_2, 2\nu_2 + \nu_4, \nu_2 + 2\nu_4, 3\nu_4$).

Table 1. Statistical information for bands $3\nu_4$, $\nu_2 + 2\nu_4$ and $2\nu_2 + \nu_4$ of molecule $^{72}\text{GeH}_4$

Band	Center of band ^{a)} , cm^{-1}	J^{max}	$N_{\text{tr}}^b)$	d_{rms} , cm^{-1}
$3\nu_4$ ($1F_2$)	2440.5569	17	475	$7.4 \cdot 10^{-4}$
$3\nu_4$ (A_1) ^{c)}	2458.57			
$3\nu_4$ (F_1)	2461.8360	17	96	
$3\nu_4$ ($2F_2$)	2464.7400	17	117	
			688	
$\nu_2 + 2\nu_4$ ($1E$)	2557.7538	17	119	$7.2 \cdot 10^{-4}$
$\nu_2 + 2\nu_4$ (F_1)	2569.2424	14	100	
$\nu_2 + 2\nu_4$ (A_1) ^{c)}	2570.54			
$\nu_2 + 2\nu_4$ (F_2)	2573.0315	17	173	
$\nu_2 + 2\nu_4$ ($2E$)	2575.0113	14	55	
$\nu_2 + 2\nu_4$ (A_2) ^{c)}	2578.11			$7.9 \cdot 10^{-4}$
			447	
$2\nu_2 + \nu_4$ ($1F_2$)	2676.0054	17	297	
$2\nu_2 + \nu_4$ (F_1)	2682.1692	16	160	
$2\nu_2 + \nu_4$ ($2F_2$)	2684.9711	15	134	
			591	

Note. ^{a)} Band centers here mean energies of vibration states with account of vibration resonances between stages. ^{b)} N_{tr} — number of found transitions. ^{c)} These bands are treated as „dark“.

0.01–100 Torr. The optical compartment of the spectrometer was pumped by a mechanical pump to 0.02 Torr, and this pressure remained constant for the entire experiment. As a result, the spectrum was recorded with length of optical path 3.75 m and pressure 4 Torr. The final spectrum (fig. 1) was obtained by averaging 1250 scans and calibrated by most intense and well-resolved spectral lines of molecule CO_2 , parameters of which were taken from data base HITRAN [22]. After calibration the standard deviation between measured and tabular positions of peaks in the selected lines was assessed as below $3 \cdot 10^{-4} \text{ cm}^{-1}$.

Theoretical background for research of high symmetry molecule spectra

This paper is aimed at research of bands $3\nu_4$ ($1F_2$, F_1 , $2F_2$), $\nu_2 + 2\nu_4$ ($1E$, F_1 , F_2 , $2E$) and $2\nu_2 + \nu_4$ ($1F_2$, F_1 , $2F_2$) of molecule $^{72}\text{GeH}_4$. All listed overtone and combination vibration bands may be grouped in a polyad of interacting bands, which form a so called octad (fig. 2). This polyad is characterized by an integer quantum number

$$P = k_1\nu_1 + k_2\nu_2 + k_3\nu_3 + k_4\nu_4, \quad (1)$$

where ν_1 , ν_2 , ν_3 and ν_4 — vibration quantum numbers for four normal modes of molecule GeH_4 , k_1 , k_2 , k_3 , k_4 — integer numbers selected to break vibration levels into polyads in accordance with their wave numbers.

The most widely used model applicable to research of polyatomic molecules is an effective rotation-vibration Hamiltonian. Since in the current problem we consider

the polyad of interacting stages in the octad region, the Hamiltonian operator will be written as

$$H^{\text{vib-rot}} = H_{P_0} + H_{P_1} + H_{P_2} + H_{P_3}, \quad (2)$$

where H_{P_0} — effective Hamiltonian of the main vibration state of germane molecule or so called monad of interacting states (fig. 2). $(H_{P_0} + H_{P_1})$ — dyad operator (fig. 2), where individual terms of the sum in H_{P_1} may be divided into two groups: the first one includes operators describing corrections to similar parameters of the main vibration state (in particular, corrections to rotary and centrifugal constants); the second group includes additional (absent in H_{P_0}) operators (dyad band centers, parameters of resonance interactions and tetrahedral splits). $(H_{P_0} + H_{P_1} + H_{P_2})$ — pentad operator (fig. 2), where for operator H_{P_2} it is necessary to repeat all the above regarding the operator H_{P_1} . $(H_{P_0} + H_{P_1} + H_{P_2} + H_{P_3})$ — octad operator (fig. 2). It should be noted that such Hamiltonian structure is provided for in the Dijon software complex, which was used in our paper to solve the inverse spectroscopic problem. More detailed description of the Hamiltonian may be found in paper [23]. Various terms of sum H_{P_i} are expressed in the following form:

$$H_{P_i}^{\text{vib-rot}} = \sum_{v, \tilde{v}} |v\rangle \langle \tilde{v}| H^{v, \tilde{v}}, \quad (3)$$

where $|v\rangle$ and $\langle \tilde{v}|$ — vibration functions of interacting vibration states, $H^{v, \tilde{v}}$ — non-diagonal units describing interaction between states $|v\rangle$. Explicit form of operators $H^{v, \tilde{v}}$ for various types of polyatomic molecules may be found in [24–27]. It is commonly known that germane is a tetrahedral molecule of spherical symmetry and is related to point group T_d . Because of its high symmetry the research is based on using tensor formalism [28]. Then the initial Hamiltonian operator (3) may be rewritten in tensor symbols as follows:

$$H^{\text{vib-rot}} = \sum_{v\gamma, v'\gamma'} \sum_{n\Gamma} \left[(|v\gamma\rangle \otimes \langle v'\gamma'|)^{n\Gamma} \otimes R^{\Omega(K, n\Gamma)} \right]^{A_1} Y_{v\gamma, v'\gamma'}^{\Omega(K, n\Gamma)}, \quad (4)$$

where $|v\gamma\rangle$ — symmetrized vibration functions, which are equivalent to vibration functions $|v\rangle$ in equation (3) (value γ in function $|v\gamma\rangle$ is its symmetry), $R^{\Omega(K, n\Gamma)}$ — rotation operators, Ω and K — degree and rating of irreducible operators $R_m^{\Omega(K)}$, transformed under irreducible representation $D^{(K)}$ of rotation group $\text{SO}(3)$ [29], Γ — symmetry of direct product of vibration wave functions $(|v\gamma\rangle \otimes \langle v'\gamma'|)$, which obviously matches symmetry of rotation operators $R^{\Omega(K, n\Gamma)}$, n differentiates potential operators $R^{\Omega(K, n\Gamma)}$, $Y_{v\gamma, v'\gamma'}^{\Omega(K, n\Gamma)}$ — spectroscopic parameters.

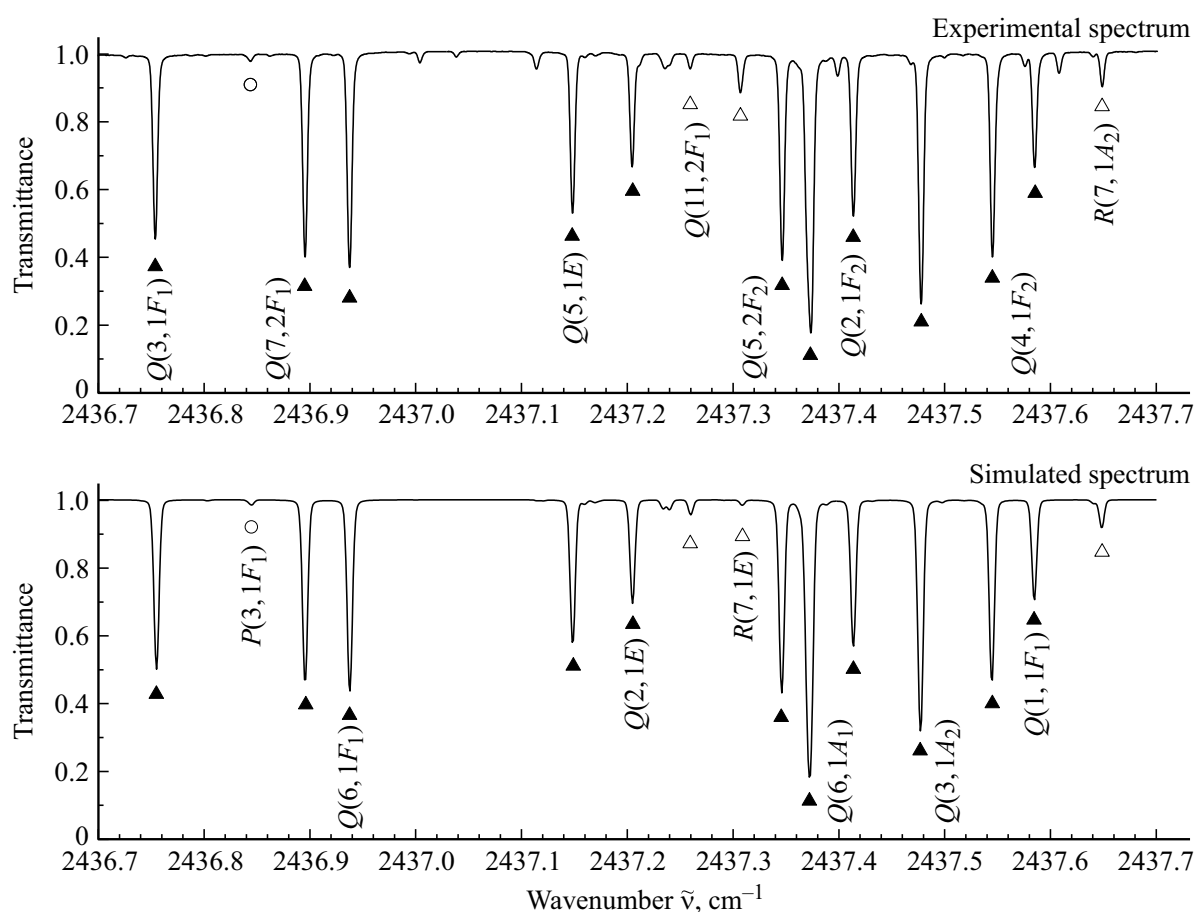


Figure 3. Small part of experimental spectrum of molecule $^{72}\text{GeH}_4$ of band $3\nu_4$ (upper part of the figure). The lower graph shows corresponding simulated spectral lines of band $3\nu_4$.

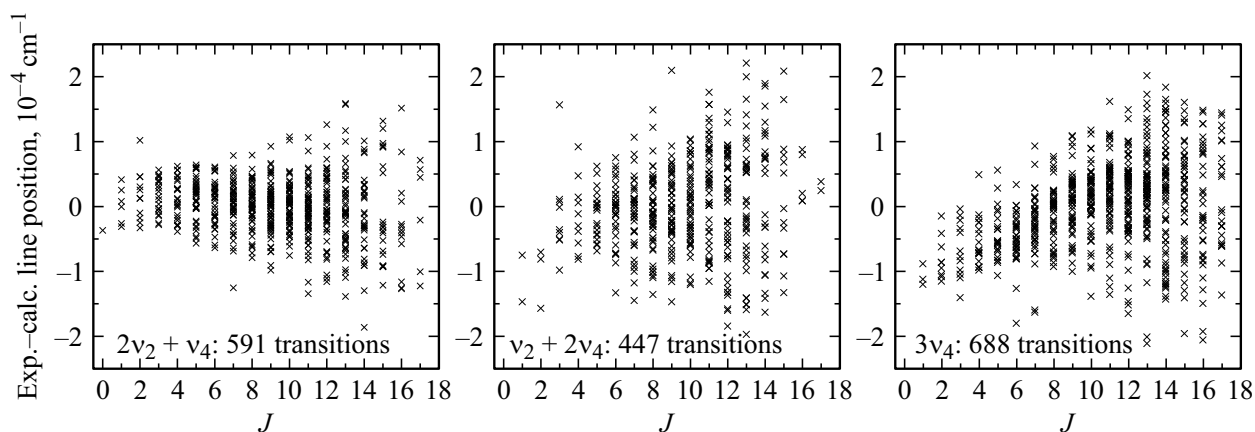


Figure 4. Values of disparities for transition frequencies depending on quantum number J for bands $2\nu_2 + \nu_4$, $\nu_2 + 2\nu_4$ and $3\nu_4$.

Spectrum analysis of molecule $^{72}\text{GeH}_4$ and definition of spectroscopic parameters

Fig. 1 presents high resolution experimental spectrum of molecule $^{72}\text{GeH}_4$ in the range $2350\text{--}2750\text{ cm}^{-1}$ with rather clearly expressed structure of bands $3\nu_4$, $\nu_2 + 2\nu_4$ and $2\nu_2 + \nu_4$. To illustrate high resolution, fig. 3 shows the

spectrum close-up. Dark triangles mark transitions related to band $3\nu_4$ ($1F_2$), light triangles — to $3\nu_4$ (F_1) and light circles — to $3\nu_4$ ($2F_2$).

As it was noted before, GeH_4 relates to molecules of spherical top type with symmetry group that is isomorphic to point group T_d . It follows that transitions are allowed between vibration states $(\nu\gamma)$ and $(\nu'\gamma')$, for which the

Table 2. Small fragment of found transitions in spectrum of molecule $^{72}\text{GeH}_4$ in octad region

$J \gamma_r^{(a)} n$	$J' \gamma_r'^{(a)} n'$	$\nu^{\text{exp}}, \text{cm}^{-1}$	$E^{\text{gr}}, ^{(b)} \text{cm}^{-1}$	Transmission, %	$E, ^{(c)} \text{cm}^{-1}$	$\delta \cdot 10^{-4}, ^{(d)} \text{cm}^{-1}$	Band
1	2	3	4	5	6	7	8
3 F_1 23	4 F_2 1	2653.1245	53.9056	88.2	2707.0302	2.0	$2\nu_2 + \nu_4$ ($1F_2$)
3 F_1 23	3 F_2 1	2674.6845	32.3456	78.0		2.5	$2\nu_2 + \nu_4$ ($1F_2$)
6 A_1 15	7 A_2 1	2635.6900	150.8649	86.0	2786.5559	−9.5	$2\nu_2 + \nu_4$ ($1F_2$)
6 A_1 15	6 A_2 1	2673.3922	113.1628	62.0		−9.8	$2\nu_2 + \nu_4$ ($1F_2$)
8 F_2 53	7 F_1 1	2701.4863	150.8489	88.1	2852.3353	3.3	$2\nu_2 + \nu_4$ (F_1)
8 F_2 53	9 F_1 3	2609.9494	242.3859	88.5		3.8	$2\nu_2 + \nu_4$ (F_1)
9 F_1 59	8 F_2 1	2705.1877	193.9310	88.8	2899.1188	1.8	$2\nu_2 + \nu_4$ (F_1)
9 F_1 59	10 F_2 3	2602.9231	296.1957	87.3		1.9	$2\nu_2 + \nu_4$ (F_1)
6 A_1 14	6 A_2 1	2660.9226	113.1628	86.7	2774.0854	−8.1	$2\nu_2 + \nu_4$ ($2F_2$)
6 A_1 14	7 A_2 1	2623.2205	150.8649	85.4		−8.8	$2\nu_2 + \nu_4$ ($2F_2$)
9 A_2 20	9 A_1 1	2653.1376	242.3736	88.0	2895.5112	−3.8	$2\nu_2 + \nu_4$ ($2F_2$)
9 A_2 20	10 A_1 1	2599.3475	296.1638	88.4		−3.2	$2\nu_2 + \nu_4$ ($2F_2$)
9 A_2 20	8 A_1 1	2701.6086	193.9026	87.5		−3.1	$2\nu_2 + \nu_4$ ($2F_2$)
7 F_2 2	8 F_1 4	2452.4824	150.8702	53.6	2603.3527	5.1	$3\nu_4$ (F_2)
7 F_2 1	8 F_1 4	2452.5019	150.8508	48.6		5.1	$3\nu_4$ (F_2)
8 F_1 1	9 F_2 9	2481.6355	193.9043	89.5	2675.5398	8.8	$3\nu_4$ (F_2)
9 F_1 2	9 F_2 9	2433.1793	242.3605	41.0		9.0	$3\nu_4$ (F_2)
10 A_1 1	9 A_2 4	2379.8759	296.1638	88.2	2676.0397	7.5	$3\nu_4$ (F_2)
8 A_1 1	9 A_2 4	2482.1371	193.9026	88.0		8.0	$3\nu_4$ (F_2)
9 A_1 1	9 A_2 6	2459.8995	242.3736	88.3	2702.2731	0.4	$3\nu_4$ (F_2)
10 A_1 1	9 A_2 6	2406.1093	296.1638	47.0		1.1	$3\nu_4$ (F_2)
8 F_1 2	7 F_2 11	2414.7993	193.9406	88.6	2608.7400	−5.8	$3\nu_4$ (F_2)
8 F_1 1	7 F_2 11	2414.8357	193.9043	48.5		−5.4	$3\nu_4$ (F_2)

Note. ^{a)} Symmetry of corresponding vibration-rotation functions. ^{b)} Energy values of rotation terms of the main vibration stage produced in paper [18]. ^{c)} Energy values of excited vibration-rotation states. ^{d)} Differences between experimental ν^{exp} and design ν^{calc} values of line positions.

condition is met [30,31]

$$\gamma \otimes \gamma' \subset F_2. \quad (5)$$

Therefore, bands $3\nu_4$ ($1F_2$, $2F_2$), $\nu_2 + 2\nu_4$ (F_2) and $2\nu_2 + \nu_4$ ($1F_2$, $2F_2$) are „allowed“ by symmetry, and other bands with symmetry different from F_2 — „forbidden“. At the initial stage the positions of the lines were analyzed using Dijon XTDS software suite. For initial approximation, parameters of the main state, dyad and pentad were used as in paper [21]. As a result, 688 lines were assigned for bands $3\nu_4$ ($1F_2$, F_1 , $2F_2$), 447 lines for $\nu_2 + 2\nu_4$ ($1E$, F_1 , F_2 , $2E$) and 591 lines for $2\nu_2 + \nu_4$ ($1F_2$, A_1 , $2F_2$) with maximum quantum number $J^{\text{max}} = 17$. Detailed statistical information is provided in table 1. This research could not identify transitions related to bands $3\nu_4$ (A_1) and $\nu_2 + 2\nu_4$ (A_1 , A_2). Therefore, such bands are considered as „dark“. However, despite the absence of the found transitions, these bands influence the overall vibration-rotation structure of considered bands due to presence of resonance interactions. Some found transitions are presented in table 2.

All 1726 transitions were used as initial information in the inverse spectroscopic problem to identify effective Hamiltonian parameters (4). Values of spectroscopic parameters produced as a result of variation procedure are given in column 4 of table 3 together with their confidence statistic intervals (1σ). Values of parameters that are presented

without confidence intervals were taken as equal to values of corresponding parameters of isotopologue $^{76}\text{GeH}_4$ and were taken from paper [32]. As a result of analysis, 35 spectroscopic parameters (table 3) were defined, which reproduce 1726 experimental lines of ten vibration stages of molecule $^{72}\text{GeH}_4$ with error of $d_{\text{rms}} = 7.5 \cdot 10^{-4} \text{ cm}^{-1}$. In the lower part of fig. 3 there is a theoretically calculated spectrum produced based on parameters from table 3. To estimate relative intensities, five parameters of effective dipole moment (one main parameter of effective dipole moment for each of five symmetry bands F_2). Relative values of these five main parameters of effective dipole moment were estimated along specially measured 10 lines in the experimental spectrum, and as it was estimated, correlate to each other in proportions $6.0/0.9/(-1.1)/3.0/1.3$ for bands $3\nu_4$ ($1F_2$, $2F_2$), $\nu_2 + 2\nu_4$ (F_2) and $2\nu_2 + \nu_4$ ($1F_2$, $2F_2$).

Conclusion

Research of high resolution vibration-rotation spectrum of molecule $^{72}\text{GeH}_4$ was completed. As a result of analysis, 1726 transitions were identified with the maximum value of quantum number of the upper vibration-rotation state $J^{\text{max}} = 17$ for ten vibration states. Produced transitions were engaged in the variation procedure with the effective Hamiltonian, which made it possible

Table 3. Spectroscopic parameters of vibration states (0300)/(0201)/(0102)/(0003) of molecule $^{72}\text{GeH}_4$ (in cm^{-1})

(v, γ)	(v', γ')	$\Omega (K, n\Gamma)$	$Y_{v\gamma, v'\gamma'}^{\Omega(K, n\Gamma)}$	(v, γ)	(v', γ')	$\Omega (K, n\Gamma)$	$Y_{v\gamma, v'\gamma'}^{\Omega(K, n\Gamma)}$
1	2	3	4	1	2	3	4
(0300, E)	(0300, E)	$0(0, A_1)10^2$	-6.249	(0201, $1F_2$)	(0003, $1F_2$)	$1(1, F_1)10^3$	-9.143
(0300, A_1)	(0300, A_1)	$0(0, A_1)10^1$	-3.1675	(0201, $1F_2$)	(0003, $2F_2$)	$0(0, A_1)10^2$	-9.2794(63)
(0300, A_2)	(0300, A_2)	$0(0, A_1)10^1$	-1.160	(0201, F_1)	(0003, $1F_2$)	$1(1, F_1)10^2$	1.4865(18)
(0300, E)	(0201, F_1)	$1(1, F_1)10^3$	-4.700	(0201, F_1)	(0003, A_1)	$1(1, F_1)10^2$	1.5087(22)
(0300, A_1)	(0201, F_1)	$1(1, F_1)10^2$	1.0707	(0201, F_1)	(0003, F_1)	$0(0, A_1)10^1$	-2.1667(10)
(0300, A_2)	(0201, F_2)	$1(1, F_1)10^3$	-6.040	(0201, F_1)	(0003, $2F_2$)	$1(1, F_1)10^2$	-2.0540
(0201, $1F_2$)	(0201, $1F_2$)	$0(0, A_1)10^2$	-6.80325(66)	(0201, $2F_2$)	(0003, $1F_2$)	$0(0, A_1)10^1$	-2.22916(74)
	(0201, $1F_2$)	$1(1, F_1)10^3$	1.3965	(0201, $2F_2$)	(0003, A_1)	$2(2, F_2)10^4$	-2.424
(0201, $1F_2$)	(0201, F_1)	$1(1, F_1)10^3$	1.4251	(0201, $2F_2$)	(0003, F_1)	$1(1, F_1)10^2$	-1.5157
	(0201, F_1)	$2(2, E)10^5$	3.530	(0102, $1E$)	(0102, $1E$)	$0(0, A_1)10^1$	-2.04389(14)
(0201, $1F_2$)	(0201, $2F_2$)	$0(0, A_1)10^2$	-7.19115(94)		(0102, $1E$)	$2(0, A_1)10^5$	4.918
(0201, F_1)	(0201, F_1)	$0(0, A_1)10^2$	-2.7130(14)	(0102, $1E$)	(0102, A_2)	$2(2, E)10^5$	-9.731
	(0201, F_1)	$1(1, F_1)10^3$	2.3085	(0102, $1E$)	(0102, $2E$)	$0(0, A_1)10^2$	1.8759(25)
(0201, F_1)	(0201, $1F_2$)	$1(1, F_1)10^3$	-5.2568		(0102, $2E$)	$2(0, A_1)10^5$	-2.971
	(0201, $1F_2$)	$2(2, E)10^5$	-3.077	(0102, $1E$)	(0102, F_1)	$1(1, F_1)10^3$	7.011
(0201, $2F_2$)	(0201, $2F_2$)	$0(0, A_1)10^2$	-5.3110(15)	(0102, $1E$)	(0102, F_2)	$1(1, F_1)10^3$	-9.569
	(0201, $2F_2$)	$1(1, F_1)10^3$	-1.4003		(0102, F_2)	$2(2, F_2)10^5$	4.798
(0201, $1F_2$)	(0102, F_1)	$1(1, F_1)10^3$	-5.7282	(0102, A_1)	(0102, A_1)	$0(0, A_1)10^2$	-5.3854
(0201, $1F_2$)	(0102, F_2)	$0(0, A_1)10^2$	2.2661(17)	(0102, A_1)	(0102, F_1)	$1(1, F_1)10^2$	1.0346
	(0102, F_2)	$1(1, F_1)10^3$	-2.5781	(0102, A_2)	(0102, A_2)	$0(0, A_1)10^2$	-4.6393
(0201, F_1)	(0102, $1E$)	$1(1, F_1)10^3$	2.444	(0102, A_2)	(0102, $2E$)	$2(2, E)10^5$	-5.693
(0201, F_1)	(0102, F_1)	$0(0, A_1)10^1$	-1.17198(29)	(0102, A_2)	(0102, F_2)	$1(1, F_1)10^3$	-2.4403(29)
(0201, F_1)	(0102, F_2)	$1(1, F_1)10^3$	4.306	(0102, $2E$)	(0102, $2E$)	$0(0, A_1)10^2$	1.4506(31)
(0201, $2F_2$)	(0102, $2E$)	$1(1, F_1)10^3$	2.144	(0102, $2E$)	(0102, F_1)	$1(1, F_1)10^3$	-1.973
(0201, $2F_2$)	(0102, F_1)	$1(1, F_1)10^3$	5.013		(0102, F_1)	$2(2, F_2)10^5$	7.552
(0102, $2E$)	(0102, F_2)	$1(1, F_1)10^4$	2.355	(0102, F_2)	(0003, F_1)	$1(1, F_1)10^2$	-1.78127(60)
(0102, F_1)	(0102, F_1)	$0(0, A_1)10^1$	-1.31525(24)		(0003, F_1)	$2(2, E)10^4$	-1.1936
	(0102, F_1)	$1(1, F_1)10^3$	7.9247(52)	(0102, F_2)	(0003, $2F_2$)	$0(0, A_1)10^2$	8.2441(42)
	(0102, F_1)	$2(0, A_1)10^5$	2.925		(0003, $2F_2$)	$1(1, F_1)10^3$	3.880
(0102, F_1)	(0102, F_2)	$1(1, F_1)10^2$	-1.41120(47)	(0102, F_2)	(0003, $2F_2$)	$2(0, A_1)10^4$	-1.174
	(0102, F_2)	$2(2, E)10^5$	-6.705	(0003, $1F_2$)	(0003, $1F_2$)	$0(0, A_1)10^1$	-2.367679
(0102, F_2)	(0102, F_2)	$0(0, A_1)10^2$	-3.9715(22)		(0003, $1F_2$)	$1(1, F_1)10^3$	6.8382(26)
	(0102, F_2)	$2(0, A_1)10^5$	-1.597		(0003, $1F_2$)	$2(0, A_1)10^5$	-2.704
(0102, $1E$)	(0003, $1F_2$)	$2(2, F_2)10^5$	4.619		(0003, $1F_2$)	$2(2, E)10^4$	-1.0838
(0102, $1E$)	(0003, $2F_2$)	$1(1, F_1)10^3$	-8.104		(0003, $1F_2$)	$2(2, F_2)10^5$	5.433
(0102, A_1)	(0003, F_1)	$1(1, F_1)10^3$	-6.853	(0003, $1F_2$)	(0003, A_1)	$2(2, F_2)10^4$	-1.8230(13)
(0102, A_1)	(0003, $2F_2$)	$2(2, F_2)10^4$	2.6442	(0003, $1F_2$)	(0003, F_1)	$1(1, F_1)10^3$	9.5073(39)
(0102, A_2)	(0003, $1F_2$)	$1(1, F_1)10^2$	1.4413		(0003, F_1)	$2(2, E)10^4$	-1.9745
(0102, A_2)	(0003, F_1)	$2(2, F_2)10^5$	-5.936	(0003, $1F_2$)	(0003, $2F_2$)	$0(0, A_1)10^2$	-8.8536(15)
(0102, $2E$)	(0003, $1F_2$)	$1(1, F_1)10^3$	8.499		(0003, $2F_2$)	$2(0, A_1)10^4$	-2.2784
(0102, $2E$)	(0003, $2F_2$)	$1(1, F_1)10^3$	-2.315		(0003, $2F_2$)	$2(2, E)10^4$	-3.7255
(0102, F_1)	(0003, A_1)	$1(1, F_1)10^3$	-9.6148(64)	(0003, A_1)	(0003, A_1)	$0(0, A_1)10^2$	-5.1854(43)
(0102, F_1)	(0003, F_1)	$0(0, A_1)10^1$	1.52185(47)	(0003, A_1)	(0003, F_1)	$1(1, F_1)10^3$	-9.4548(42)
	(0003, F_1)	$1(1, F_1)10^3$	1.817	(0003, F_1)	(0003, F_1)	$0(0, A_1)10^2$	3.0626(24)
(0102, F_1)	(0003, $2F_2$)	$1(1, F_1)10^2$	1.8650		(0003, F_1)	$1(1, F_2)10^2$	-1.09980(45)
	(0003, $2F_2$)	$2(2, E)10^5$	6.32		(0003, F_1)	$2(0, A_1)10^5$	-5.435
(0102, F_2)	(0003, $1F_2$)	$0(0, A_1)10^1$	-1.91414(50)	(0003, F_1)	(0003, $2F_2$)	$1(1, F_1)10^3$	-1.4097(42)
	(0003, $1F_2$)	$1(1, F_1)10^3$	7.920	(0003, $2F_2$)	(0003, $2F_2$)	$0(0, A_1)10^2$	-2.7229(20)
	(0003, $1F_2$)	$2(0, A_1)10^5$	-6.979		(0003, $2F_2$)	$2(0, A_1)10^5$	5.216

to determine spectroscopic parameters, namely parameters of spectroscopic distortion, resonance interactions and tetrahedral splits. The produced set of 35 spectroscopic parameters makes it possible to reproduce 1726 initial experimental positions of the lines with error of $d_{\text{rms}} = 7.5 \cdot 10^{-4} \text{ cm}^{-1}$. Produced results will be sent to be added to the spectroscopic data base HITRAN and will help to confirm the surface of potential energy in molecule GeH_4 .

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Conflict of interest

The authors declare that they have no conflict of interest.

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