High resolution study of strongly interacting $2\nu_1(A_1)/\nu_1 + \nu_3(F_2)$ bands of $^M\text{GeH}_4$ ($M = 76, 74$)

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A B S T R A C T

The infrared spectra of GeH_4 (88.1 % of $^{76}\text{GeH}_4$, 11.5 % of $^{74}\text{GeH}_4$, and a minor amounts of three other stable isotopic species in the sample) were measured in the 4000–4250 cm^{-1} region with a high resolution of 0.003 cm^{-1} at different pressures with the Bruker IFS 125HR Fourier transform interferometer (Nizhny Novgorod, Russia) and were analyzed theoretically. The 1974 transitions with $J^{max.} = 21$ were assigned to the bands $\nu_1 + \nu_3(F_2)$ and $2\nu_1(A_1)$ of the $^{76}\text{GeH}_4$ isotopologue. Rotational, centrifugal distortion, tetrahedral splitting, and interaction parameters for the (1010, F_2) and (2000, A_1) vibrational states were determined from the fit of experimental line positions. Influence of the (0020, A_1), (0020, E) and (0020, F_2) vibrational states on the structure of the states (1010, F_2) and (2000, A_1) is taken into account. In this case, the main resonance interaction parameters have been estimated on the basis of the local mode model and then fitted. A set of spectroscopic parameters of the effective Hamiltonian obtained from a weighted fit reproduces the initial experimental data with the $\text{d}_{rms} = 4.5 \times 10^{-4}$ cm^{-1}. The results of analogous analysis of the $^{74}\text{GeH}_4$ isotopologue (the number of assigned transitions is 652) are presented also.

1. Introduction

Knowledge of internal properties of the germane molecule is very important for numerous both pure scientific and applied problems of physics, chemistry, astrophysics, industry, etc. Germane is one of the important components of atmospheres of such giant gas-planet, as Jupiter and Saturn, Refs. [1–4], and its presence should be taken into account at studies of the compositions and chemistry of their atmospheres. In particular, in atmospheres of Jupiter and Saturn germane was detected at abundances orders of magnitude greater than their thermochemical equilibrium values in the upper troposphers, Refs. [5]. Germane in a natural isotopic composition is used for producing of high-purity germanium. On that basis various physical devices (e.g., high-sensitivity detectors of nuclear radiation) are manufactured, Refs. [6]. Germane enriched by ^{76}Ge up to 88% can be used as starting substance for production of high purity single-crystal ^{76}Ge which, in its turn, can be used as a source of a double beta decay of its nuclei and, at the

same time, as a detector of this process, Ref. [7]. Because of all of these reasons, laboratory investigations of high resolution spectra of germane are interesting and important.

Germane in a natural isotopic composition produces complex infrared spectra, first of all because of existence of five stable isotopologues with mass numbers 70 (20.55 %), 72 (27.37 %), 73 (7.67 %), 74 (36.74 %), and 76 (7.67 %). Additional complexity of the germane spectra arises from the presence of very strong resonance interactions between its ro-vibrational bands. GeH_4 is a spherical top molecule, hence, it has no permanent dipole moment, and capabilities of the Ground State Combination Differences method which is very efficient for studying the molecules of other type (see, e.g., Refs. [8–11]) are very limited as applied to germane.

Spectra of different $^M\text{GeH}_4$ ($M = 70, 72, 73, 74, 76$) isotopologues of germane were the objects of study during many years (see, e.g., Refs. [12–44]). Up to 1972 the spectra were recorded with low or medium resolution. Starting with 1973, Oka with co-authors extensively studied pure rotational spectra of the XH_4 (T_d symmetry) molecules (X = C, Ge, Si) by the method of infrared-microwave double resonance, Refs. [23–28]. The first high resolution infrared spectrum of germane (ν_3 and $2\nu_3$ bands of all five isotopologues) was studied in Refs. [31]. Spectra of highly excited
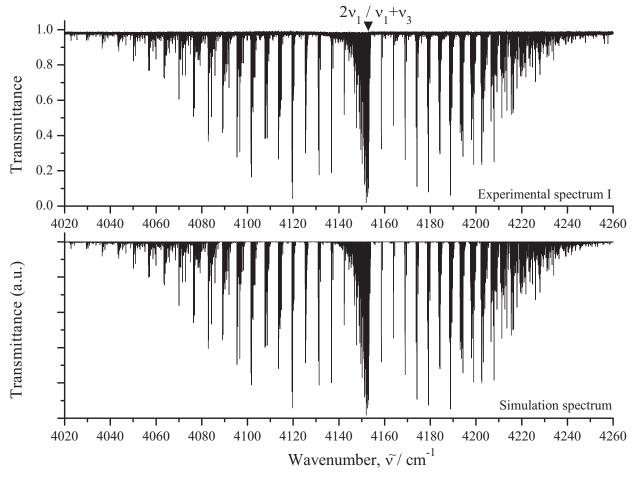
Fig. 1. Survey spectrum I of ^{76}GeH$_4$ and ^{74}GeH$_4$ in the region of 4000–4250 cm^{-1} (the top trace). Experimental conditions: absorption path length is 3.75 m; room temperature; number of scans is 1200; sample pressure is 0.3 Torr. The bottom trace presents, for illustration, simulated spectrum (see text for details).

Table 1
Experimental setup for the regions 4000 – 4250 cm^{-1} of the infrared spectra of ^{M}GeH$_4$ ($M = 74, 76$).

Spectrum	Resolution /cm^{-1}	Measuring time/h	No. of scans	Source	Detector	Beam-splitter	Opt. path-length/m	Aperture /mm	Temp. /^{o}C	Pressure /Torr	Calibr. gas
I	0.003	40.2	1200	Globar	InSb	KBr	3.75	1.0	22.7	0.3	H$_2$O
II	0.003	36.9	1100	Globar	InSb	KBr	0.75	1.0	28.8	1.5	H$_2$O
III	0.003	35.2	1050	Globar	InSb	KBr	3.75	1.0	22.6	3.0	H$_2$O

overtone stretching bands of germane were extensively discussed in a number of papers by Zhu and co-authors, Refs. [38–44], in the frame of the local mode model. As to the stretching bands $\nu_1 + \nu_3$ and $2\nu_1$, they, as to our knowledge, were analyzed earlier with high resolution only in Refs. [31] and [40]. In Ref. [40] the spectrum has been recorded on a Bomem DA3.002 Fourier transform spectrophotometer with a resolution of 0.01 cm^{-1} (that was a higher resolution than in Ref. [31]). Transitions belonging to the $\nu_1 + \nu_3$ and $2\nu_1$ bands have been assigned up to the value $J^{max.} = 8$ and have been used in the fit with the Hamiltonian model from Refs. [38,39], [45–49]. Values of the $\nu_1 + \nu_3(F_2)$ band centers for the ^{76}GeH$_4$ and ^{74}GeH$_4$ species have been estimated as 4153.2261 cm^{-1} and 4153.8246 cm^{-1}, respectively. Reference to the private communication from A. G. Robiette can also be found in Ref. [50]. In this case, the values of the band centers are estimated as 4153.551 cm^{-1} and 4153.833 cm^{-1}.

In this paper we present the results of analysis of the high resolution Fourier transformed spectra of ^{M}GeH$_4$ ($M = 76, 74$) in the region of 4000 – 4250 cm^{-1} where the $\nu_1 + \nu_3(F_2)$ and $2\nu_1(A_1)$ bands are located with a considerably higher resolution and $J^{max.}$

value of assigned transitions. The experimental details are given in Section 2. Description of the spectra and assignment of transitions are discussed in Section 3. Section 4 presents briefly the theoretical background of our study. Results and discussion are presented in Section 5.

2. Experimental details

A sample of germane containing ^{76}GeH$_4$ (88.1%), ^{74}GeH$_4$ (11.5%), ^{73}GeH$_4$ (0.07%), ^{72}GeH$_4$ (0.17%), and ^{70}GeH$_4$ (0.12%) isotopologues was used in the present study. First, the sample of germane in natural abundance was synthesized at the Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences by a reaction between GeCl$_4$ and sodium borohydride with subsequent purification by the rectification method. Then the sample was enriched with the ^{76}Ge isotope using the centrifugal method at the Joint Stock Company "Production Association. Electrochemical Plant", Zelenogorsk, Russia. The enriched sample was repeatedly purified by the rectification method. Finally, the amount of hydrocarbon, carbon dioxide, di-, and tri-germane impurities in the sam-
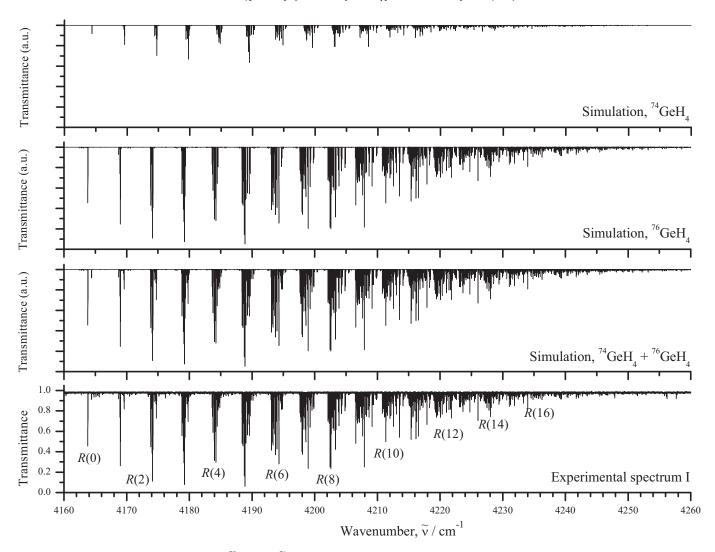
Fig. 2. Small portion of high resolution spectrum of $^{76}GeH_4$ and $^{74}GeH_4$ in the region of $R-$branch of the $\nu_1 + \nu_3$ and $2\nu_1$ bands. The bottom trace is the experimentally recorded spectrum I (see experimental conditions in the caption to Fig. 1 and in Table 1). Two traces on top are simulations of the $\nu_1 + \nu_3$ and $2\nu_1$ bands transitions for the $^{74}GeH_4$ (first trace) and $^{76}GeH_4$ (second trace) molecules. The third trace is the sum of two first separate traces (see text for details).

ple enriched with ^{76}Ge was less than 10^{-5} mole.%, 10^{-4} mole.%, $10^{-1} – 10^{-3}$ mole.%, respectively. The amount of the other impurities was less than 3×10^{-5} mole.%

The enriched and purified gas sample of germane was spectroscopically studied using a Bruker IFS 125HR Fourier transform spectrometer. The experimental details are presented in Table 1. Briefly, the spectrometer was equipped with a Globar source, a KBr beam splitter and a liquid nitrogen cooled indium antimonide (InSb) detector. The sample spectra were recorded with high resolution of 0.003 cm^{-1} (the resolution due to the maximum optical path difference) in the frequency range 4020–4260 cm^{-1}. The aperture size was 1 mm. The Norton–Beer (weak) apodization function was applied. A multi–pass White cell was permanently connected to the vacuum system with a gas sample vacuum system, a turbo–molecular pump, and capacitance pressure gauges covering the $10^{-3} – 100$ Torr range. The optical compartment of the spectrometer was evacuated by a mechanical pump down to 0.02 Torr (or less) and that pressure remained during the experiment.

The final spectra were obtained by averaging more than 1000 scans (see Table 1). In total, three spectra were recorded at two different optical path lengths (0.75 and 3.75 m) and three different pressures, 0.3, 1.5 and 3 Torr (spectrum I, II and III, respectively), to cover a wider range of J numbers and to estimate the value of

possible systematic errors in the line positions caused by pressure shifts. Comparison of the positions of unsaturated unblended lines in these spectra demonstrated a good agreement between the pairs of lines within $\pm 10^{-4}$ cm^{-1}, which demonstrates a negligible effect of the pressure shift. The final spectra were calibrated using most intense and well resolved H_2O lines around 3700 cm^{-1} and HITRAN database line list, Ref. [51]. After calibration the standard deviation of the difference between the measured and tabulated peak positions was estimated to be 2×10^{-4} cm^{-1}.

3. Description of the spectra and assignment of the transitions

The survey spectrum I in the region of 4000–4250 cm^{-1}, where the $\nu_1 + \nu_3$ and $2\nu_1$ bands of the germane molecule are located, are shown on the top trace of Fig. 1. All three branches of the $\nu_1 + \nu_3(F_2)$ band are clearly pronounced. The $2\nu_1(A_1)$ band, being the band forbidden by the symmetry of the molecule, is appears in the experimental spectra only because of strong Coriolis type interaction with the allowed $\nu_1 + \nu_3$ band. A portion of the recorded spectrum I in the region of the $R-$branch is shown at the bottom of Fig. 2 as an illustration. Two more detailed fragments of the high resolution $P-$branch are presented on the top part of Fig. 3. One
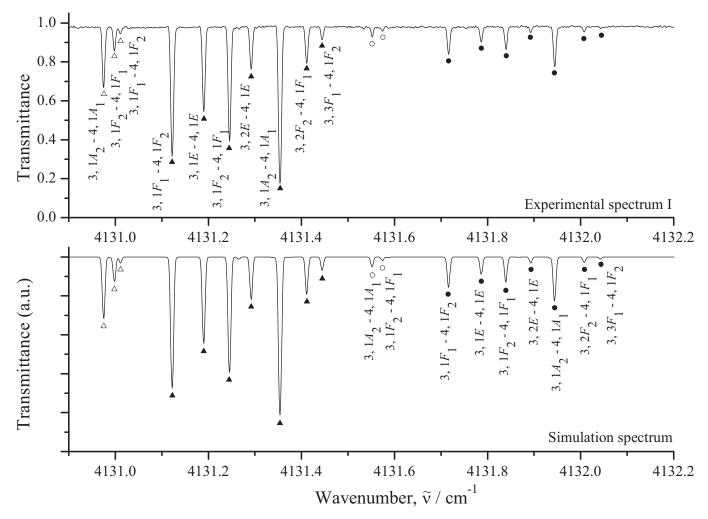
Fig. 3. Small fragment of P−branch of the $\nu_1 + \nu_3$ and $2\nu_1$ bands in the region of the P(4) transitions. The tetrahedral structure of clusters is totally resolved. Assignments of transitions can be seen: transitions belonging to the ^{76}GeH$_4$ species are marked by triangles (dark for the $\nu_1 + \nu_3$ band and open for the $2\nu_1$ band), and transitions belonging to ^{74}GeH$_4$ are marked by circles (also dark for the $\nu_1 + \nu_3$ band and open for the $2\nu_1$ band).

Table 2
Statistical information for the $2\nu_1$ and $\nu_1 + \nu_3$ bands of the ^{76}GeH$_4$ and ^{74}GeH$_4$ molecules.

Band	Center/cm^{-1}		J^{max}	N_t[a]	N_l[b]	m_1[c]	m_2[c]	m_3[c]
	pw[d]	Ref. [50][e]						
1	2	3	4	5	6	7	8	9
			^{76}GeH$_4$					
$2\nu_1(A_1)$	4152.9765	4152.977	19	81	35	60.5	32.1	7.4
$\nu_1 + \nu_3(F_2)$	4153.2348	4153.235	21	1893	565	57.8	21.7	20.5
d_{rms}	4.5×10^{-4} cm^{-1}							
			^{74}GeH$_4$					
$2\nu_1(A_1)$	4153.5505	4153.551	16	31	20	74.2	16.1	9.7
$\nu_1 + \nu_3(F_2)$	4153.8324	4153.833	17	621	341	55.2	22.9	21.9
d_{rms}	4.4×10^{-4} cm^{-1}							

[a] N_t is the number of transitions.
[b] N_l is the number of upper levels.
[c] Here $m_i = n_i/N \times 100\%$ ($i = 1, 2, 3$); n_1, n_2, and n_3 are the numbers of transitions for which the differences $\delta = E^{exp.} - E^{calc.}$ ($\delta = \nu^{exp} - \nu^{calc}$) satisfy the conditions $\delta \leq 2 \times 10^{-4}$ cm^{-1}, 2×10^{-4} cm^{-1} $< \delta \leq 4 \times 10^{-4}$ cm^{-1}, and $\delta > 4 \times 10^{-4}$ cm^{-1}.
[d] Obtained from the fit in the present paper.
[e] Reproduced, for comparison, from Ref. [50].

can see a totally resolved tetrahedral structure of clusters both for the ^{76}GeH$_4$ and ^{74}GeH$_4$ molecules.

The three sub−bands, $2\nu_3(F_2)$, $2\nu_3(E)$ and $2\nu_3(A_1)$, of the $2\nu_3$ band are located around the 4221 cm^{-1} region (see Section 5). However, as is seen from Figs. 1 and 2, they are very weak and are not seen in the spectrum.This is a consequence of the fact which

is explained by the local mode theory (see references to the local mode theory in Section 4.2) as a borrowing of intensity by the $\nu_1 + \nu_3/2\nu_1$ bands from the $2\nu_3$ band because of strong resonance interaction between all of them.

The GeH$_4$ is a spherical top molecule. As a consequence, only transitions from the ground to the F_2-symmetry vibrational states

(the $\nu_1 + \nu_3 (F_2)$ band in our case) are allowed in absorption by the symmetry of the molecule. The $2\nu_1$ is the band of A_1−symmetry, and its ro-vibrational transitions appear in absorption only because of strong Coriolis interaction with the allowed $\nu_1 + \nu_3$ band.

At the first step of analysis of the $^{76}GeH_4$ molecule, the Ground State Combination Differences (GSCD) method was used. In this case, energy values of the ground vibrational state were calculated with the parameters from Ref. [52]. As the result of assignment, 985 and 56 transitions were assigned to the $\nu_1 + \nu_3$ and $2\nu_1$ bands of $^{76}GeH_4$. The second step of analysis was made after fit of the transitions assigned at the first step. Finally, 1893 and 81 transitions with the maximum value of upper quantum number $J^{max.}$ equal to 21 and 19 (that is considerably higher in comparison with the preceding studies) were assigned to the above mentioned ro-vibrational bands, respectively (see also the statistical information in Table 2). The list of assigned transitions is presented in the Supplementary Material I.

The transitions belonging to the $^{74}GeH_4$ species are considerably weaker than the transitions of $^{76}GeH_4$ because of their abundance in the sample. For that reason, at the first step of line assignment, calculation of shifts of the line positions under substitution $^{74}GeH_4 \leftarrow {}^{76}GeH_4$ have been made on the basis of the Isotopic Substitution theory, (see, e.g., Ref. [53]). In this case, the results of assignment of lines of the $^{76}GeH_4$ molecule were used as an initial information. In general, 621 and 31 transitions with the maximum value of the upper quantum number $J^{max.}$ equal to 17 and 16 were assigned to the bands $\nu_1 + \nu_3$ and $2\nu_1$ of the $^{74}GeH_4$ species. A complete list of the assigned transitions is also presented in the Supplementary Material I.

In general, more than 92 % of the experimentally recorded transitions have been assigned to the $\nu_1 + \nu_3$ and $2\nu_1$ bands of $^{76}GeH_4$ and $^{74}GeH_4$. However, about 10 % of assigned transitions belong to the blended lines (most of them are located in the region of the Q-branches, but also there are many blended lines which are located in the regions of the P- and R-branches). Such type lines are not presented in the Supplementary Material I. The remaining (about 8 %) lines recorded in the experimental spectrum and unassigned in the present study are weak and probably belong to the other isotopic species, to the hot transitions of GeH_4, to high J-value transitions of the $2\nu_3$ band, to possible impurities in the cell or look like noise. The list of experimental lines which have not been concluded to the Supplementary Material I, is presented in the Supplementary Material II.

4. Theoretical background

Because of the symmetry of the GeH_4 molecule, its nine vibrational coordinates are distributed between four vibrational modes: one nondegenerate (q_1, A_1), one doubly degenerate (q_2, E), and two triply degenerate (q_3 and q_4, F_2). The difference between the $\nu_1 + \nu_3$ and $2\nu_1$ band centers for the $^{76}GeH_4$ isotopologue is less than 0.3 cm^{-1}. For that reason, the spectrum of $^{76}GeH_4$ in the discussed region of 4000 – 4250 cm^{-1} can be analyzed correctly only in the frame of a model which takes into account strong resonance interactions between the (1010, F_2) and (2000, A_1) vibrational states. Additionally, as the results of the so-called local mode approach show (see, e.g., Refs. [54–59] and a short discussion in Subsection (4.2) of the present paper), interactions with the (0020, A_1), (0020, E) and (0020, F_2) vibrational states should be taken into account. Moreover, high symmetry of the GeH_4 molecule necessitates using a special mathematical formalism (the theory of Irreducible Tensorial Sets, see, e.g., Refs. [60–62] and the recent review in Ref. [63]) for description of its ro-vibrational spectra. Different aspects of application of that formalism to the XY$_4$ (T$_d$−symmetry) molecules were discussed in the spectroscopic literature many times (we do not reproduce here a very long list of the corresponding papers

and refer the reader to the classical papers by Hecht, Ref. [64], Moret-Bailly, Ref. [65], and Champion, Ref. [67], on the one hand, and to recent review of Boudon, et al., Ref. [68], on the other hand). For that reason, only a brief theoretical basis of our present study is given in this section.

4.1. Hamiltonian model used for the fit of experimental data

As the basis for the analysis, we took the effective Hamiltonian model which is widely used in the high resolution rotation-vibration theory of polyatomic molecules, Refs. [69–72]:

$$H^{vib.-rot.} = \sum_{v,\tilde{v}=1} |v\rangle\langle\tilde{v}|H^{v\tilde{v}}. \tag{1}$$

Here $|v\rangle$, $\langle\tilde{v}|$ are vibrational functions of the interacting vibrational states; any of the diagonal blocks, H^{vv} describes the unperturbed rotational structure of the vibrational state $|v\rangle$; and nondiagonal blocks, $H^{v\tilde{v}}$ ($v \neq \tilde{v}$) describe resonance interactions between the vibrational states $|v\rangle$ and $|\tilde{v}\rangle$.

For GeH$_4$, because of its high symmetry, the effective Hamiltonian, Eq. (1), should be rewritten in the form which uses the notations of the Irreducible Tensorial Sets theory (see, e.g., Refs. [65–67]):

$$H^{vib.-rot.} = \sum_{v\gamma,v'\gamma'} \sum_{n\Gamma} \sum_{\Omega K} [(|v\gamma\rangle \otimes \langle v'\gamma'|)^{n\Gamma} \otimes R^{\Omega(K,n\Gamma)}]^{A_1} Y^{\Omega(K,n\Gamma)}_{v\gamma,v'\gamma'}. \tag{2}$$

Here $|v\gamma\rangle$ are the symmetrized vibrational functions which are equivalent to the vibrational functions $|v\rangle$ in Eq. (1) (the value γ in the function $|v\gamma\rangle$ is its symmetry); Γ is the symmetry of the direct product $(|v\gamma\rangle \otimes \langle v'\gamma'|)$ of vibrational wave functions; $Y^{\Omega(K,n\Gamma)}_{v\gamma,v'\gamma'}$ are different spectroscopic parameters; and Ω and K is the power and rank of the irreducible rotational operator $R^{\Omega(K,n\Gamma)}$ in the T$_d$ point symmetry group (for more details see Refs. [65–67]). For the problem discussed in the present paper, summation in the general formula, Eq. (2), is carried out on the vibrational functions $|v\gamma\rangle, |v'\gamma'\rangle = (2000, A_1), (1010, F_2), (0020, A_1), (0020, E)$, and $(0020, F_2)$.

Following the Irreducible Tensorial Sets theory, Refs. [60,65], one can easily determine symmetrized vibrational–rotational wave functions that can then be used for constructing the matrix of the symmetrized Hamiltonian, Eq. (2), and obtain spectroscopic parameters which should be taken into account in the effective Hamiltonian. The Hamiltonian in the form of Eq. (2) has been used as the basis for the Fortran code SPHETOM, Ref. [73], which was used in the present study for analysis of the experimental data.

4.2. Local mode approach and estimation of the main vibrational parameters

The ro-vibrational lines, which have been assigned in the experimental spectra, were used then in the weighted fit of parameters of the effective Hamiltonian, Eq. (2). However, because the three substates, (0020, A_1), (0020, E), and (0020, F_2), are considered in the present study as the "dark" states, it looks reasonable to estimate numerically the values of the main vibrational resonance interaction parameters and of unperturbed vibrational energies before a realization of the fit procedure. It is reasonable because a direct fit of many strongly correlated vibrational parameters may lead to physically unsuitable values of other fitted parameters.

To realize a preliminary estimation of vibrational parameters, we have used the fact that the GeH$_4$ molecule satisfies strongly to the conditions of the local mode model (see, e.g., Ref. [54]). In this case (see, e.g., Refs. [58,63]), the following relations are valid for a set of vibrational parameters ω_1/ω_3, $x_{11}/x_{13}/x_{33}$, G_{33}, T_{33}, F_{1133}, and

Table 3
Spectroscopic parameters $Y_{v\gamma,v'\gamma'}^{\Omega(K,n\Gamma)}$ of the set of interacting vibrational states (0200)/(0101)/(0020) in ^{76}GeH$_4$ (in cm^{-1})[a].

(v, γ)	(v', γ')	$\Omega(K, n\Gamma)$	Theor.[b]	Theor.[c]	Exp.
1	2	3	4	5	6
$(2000, A_1)$	$(2000, A_1)$	$0(0, A_1)$	4204.26	−17.12	−17.12
$(2000, A_1)$	$(0020, A_1)$	$0(0, A_1)$	29.55	29.55	29.586665(25)
$(1010, F_2)$	$(1010, F_2)$	$0(0, A_1)$	4187.20	−34.10	−34.118998(18)
$(1010, F_2)$	$(0020, F_2)$	$0(0, A_1)$	-34.10	−34.10	−34.10
$(0020, A_1)$	$(0020, A_1)$	$0(0, A_1)$	4170.14	−51.42	−51.42
$(0020, F_2)$	$(0020, F_2)$	$0(0, A_1)$	4187.20	−34.10	−34.10
$(0020, E)$	$(0020, E)$	$0(0, A_1)$	4221.40	0.00	0.00

[a] Values in parentheses are 1σ statistical confidence intervals.
[b] In notations of the SPHETOM codes.
[c] In notations of the XTDS codes.

F_{1333} (definition of all the mentioned parameters can be found, e.g., in Refs. [58,63,64]):

$$\omega_1 \simeq \omega_3 = \omega \tag{3}$$

and

$$x_{11} \simeq \frac{1}{4}x_{13} \simeq \frac{5}{9}x_{33} \simeq -\frac{5}{3}G_{33} \simeq -5T_{33} \simeq \frac{1}{4}F_{1133} \simeq \frac{1}{16}F_{1333} = x. \tag{4}$$

For the ^{76}GeH$_4$ studied in the present paper, the pair of independent parameters, ω and x, can be estimated from the values of centers of the bands $\nu_1 = 2110.6918$ cm^{-1} and $\nu_3 = 2110.7323$ cm^{-1}, Ref. [52], and the value of the $\nu_1 + \nu_3$ band center. In this case, following to Refs. [63,64], it is possible to find:

$$\nu_1 = \omega_1 + 2x_{11} + \frac{3}{2}x_{13} \simeq \omega + 8x \tag{5}$$

and

$$\nu_3 = \omega_3 + 4x_{33} + \frac{1}{2}x_{13} + 2G_{33} \simeq \omega + 8x. \tag{6}$$

At the same time, for the pair of the states the results of Refs. [63,64] allow one to obtain the values of the centers of the bands $\nu_1 + \nu_3 (F_2)$ and $2\nu_3(F_2)$ as the solution of equation

$$det\begin{pmatrix} A_{11} - \nu & A_{12} \\ A_{21} & A_{22} - \nu \end{pmatrix} = 0$$

where

$$A_{11} = \omega_1 + \omega_3 + 2x_{11} + 4x_{33} + 3x_{13} + 2G_{33} \simeq 2\omega + 20x, \tag{7}$$

$$A_{22} = 2\omega_3 + 10x_{33} + x_{13} + 6G_{33} - 8T_{33} \simeq 2\omega + 20x, \tag{8}$$

$$A_{12} = A_{21} = \frac{1}{4}F_{1333} \simeq 4x, \tag{9}$$

and ν is the value of the $\nu_1 + \nu_3 (F_2)$ or $2\nu_3(F_2)$ band center. From the solution of Eq. (7), one can easily find that

$$\nu_1 + \nu_3 (F_2) \simeq 2\omega + 24x \tag{10}$$

and

$$2\nu_3 (F_2) \simeq 2\omega + 16x. \tag{11}$$

Now, from Eqs. (5)–(6) and (11) it is possible to obtain[1]): $\omega \approx 2178.9$ cm^{-1} and $x \approx -8.53$ cm^{-1}.

Analogously, the centers of the bands $2\nu_1(A_1)$ and $2\nu_3(A_1)$ can be determined from the solution of the same Eq. (7), however, with the values A_{ij} equal to

$$A_{11} = 2\omega_1 + 6x_{11} + 3x_{13} \simeq 2\omega + 18x, \tag{12}$$

$$A_{22} = 2\omega_3 + 10x_{33} + x_{13} \simeq 2\omega + 22x, \tag{13}$$

Table 4
Spectroscopic parameters $Y_{v\gamma,v'\gamma'}^{\Omega(K,n\Gamma)}$ of the set of interacting vibrational states (2000)/(1010) in Germane (in cm^{-1})[a].

(v, γ)	(v', γ')	$\Omega(K, n\Gamma)$	^{76}GeH$_4$	^{74}GeH$_4$
1	2	3	4	5
$(2000, A_1)$	$(2000, A_1)$	$0(0, A_1)$	−17.12	−17.15
	$(2000, A_1)$	$2(0, A_1)$	0.01008(87)	0.00999042(64)
	$(2000, A_1)$	$4(0, A_1)10^5$	0.1793(58)	0.1793
	$(2000, A_1)$	$4(4, A_1)10^6$	−0.4370(89)	−0.4370
$(2000, A_1)$	$(1010, F_2)$	$2(2, F_2)$	0.01847(18)	0.0185404(18)
	$(1010, F_2)$	$3(3, F_2)10^5$	0.835(74)	0.835
	$(1010, F_2)$	$4(4, F_2)10^5$	0.2389(19)	0.2389
$(2000, A_1)$	$(0020, A_1)$	$0(0, A_1)$	29.586665(25)	29.627518(26)
	$(0020, A_1)$	$2(0, A_1)10^2$	0.334(25)	0.334
$(1010, F_2)$	$(1010, F_2)$	$0(0, A_1)$	−34.118998(18)	−34.159643(13)
	$(1010, F_2)$	$1(1, F_1)$	−0.396(18)	−0.3921452(29)
	$(1010, F_2)$	$2(0, A_1)$	0.02237(35)	0.02225060(23)
	$(1010, F_2)$	$2(2, E)$	−0.04389(41)	−0.04369038(31)
	$(1010, F_2)$	$2(2, F_2)$	−0.01973(32)	−0.01973
	$(1010, F_2)$	$3(1, F_1)10^3$	0.1675(39)	0.1675
	$(1010, F_2)$	$3(3, F_1)10^3$	0.2158(31)	0.2158
	$(1010, F_2)$	$4(0, A_1)10^5$	0.1210(22)	0.1210
	$(1010, F_2)$	$4(2, E)10^6$	0.521(13)	0.521
	$(1010, F_2)$	$4(4, E)10^6$	0.428(18)	0.428
$(1010, F_2)$	$(0020, A_1)$	$2(2, F_2)$	−0.01609(11)	−0.01609
$(1010, F_2)$	$(0020, E)$	$1(1, F_1)$	−3.290(31)	−3.290
	$(0020, E)$	$2(2, F_2)10^2$	0.688(31)	0.688
$(1010, F_2)$	$(0020, F_2)$	$0(0, A_1)$	−34.10	−34.10
	$(0020, F_2)$	$1(1, F_1)$	0.1756(88)	0.1756
	$(0020, F_2)$	$2(0, A_1)10^2$	−0.6665(98)	−0.6665
	$(0020, F_2)$	$2(2, E)$	0.01612(31)	0.01612
$(0020, A_1)$	$(0020, A_1)$	$0(0, A_1)$	−51.42	−51.42
$(0020, E)$	$(0020, E)$	$0(0, A_1)$	0.0	0.0
	$(0020, E)$	$2(0, A_1)10^2$	−0.303(14)	−0.303
	$(0020, E)$	$2(2, E)10^2$	−0.925(16)	−0.925
$(0020, E)$	$(0020, F_2)$	$1(1, F_1)$	1.990(42)	1.991894(19)
$(0020, F_2)$	$(0020, F_2)$	$0(0, A_1)$	−34.10	−34.10
	$(0020, F_2)$	$2(2, F_2)$	−0.01636(30)	−0.01636

[a] Values in parentheses are 1σ statistical confidence intervals. Parameters of ^{74}GeH$_4$ presented in column 5 without confidence intervals were constrained to the values of corresponding parameters of the ^{76}GeH$_4$ isotopologue and were fixed in the fit.

and

$$A_{12} = A_{21} = -\frac{\sqrt{3}}{2}F_{1133} \simeq -2\sqrt{3}x. \tag{14}$$

As to the $2\nu_3(E)$ band center, it is determined by the formula

$$2\nu_3 (E) = 2\omega_3 + 10x_{33} + x_{13} + 6G_{33} + 12T_{33} \simeq 2\omega + 16x. \tag{15}$$

Taking into account the obtained values of parameters $\omega \approx 2178.9$ cm^{-1} and $x \approx -8.53$ cm^{-1} and formulas, Eqs. (7)– (15), one can easily estimate the values of the main vibrational parameters for the $2\nu_1/\nu_1 + \nu_3/2\nu_3$ polyad of ^{76}GeH$_4$. Theoretically estimated values of corresponding parameters are shown in column 4 of Table 3. In the further fit procedure all of them were used as the initial values.

5. Ro-vibrational analysis of the (1010, F_2) and (2000, A_1) states

As was discussed in Section 3, 1893, 81, 621, and 31 transitions with the maximum values of upper quantum numbers $J^{max.}$ equal to 21, 19, 17, and 16

(a) have been assigned to the $\nu_1 + \nu_3$ and $2\nu_1$ bands of the ^{76}GeH$_4$ and ^{74}GeH$_4$ isotopologues, respectively, and
(b) were used then in the weighted fit procedure.

At the first step, the ^{76}GeH$_4$ molecule was considered, and parameters of the Hamiltonian, Eq. (2), were fitted on the basis of the SPHETOM Fortran code, Ref. [52]. In this case, we took into account the results of the preliminary estimation of values of the
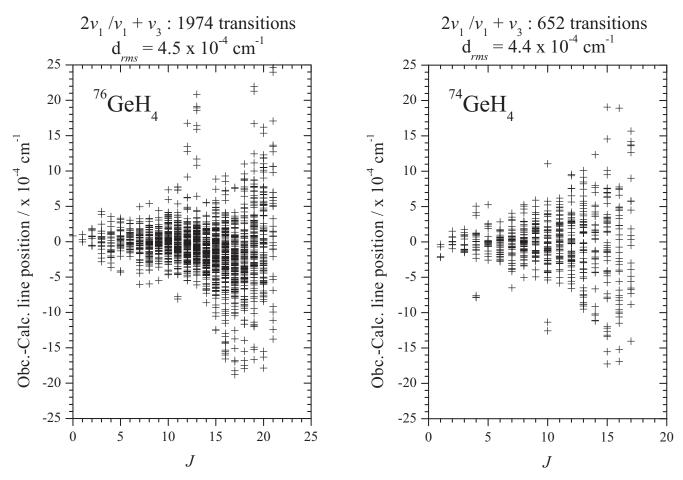
Fig. 4. Observed – calculated line positions and fit statistics for the bands of $^{76}GeH_4$ and $^{74}GeH_4$ studied in the present paper.

largest vibrational parameters which are presented in columns 4–5 of Table 3. As the result of the fit, a set of 28 varied parameters (10 parameters of the $(1010, F_2)$ vibrational state, 3 parameters of the $(2000, A_1)$ state, 12 resonance interaction parameters, and 3 parameters of the "dark" $(0020, F_2)$, $(0020, A_1)$ and $(0020, E)$ states) was obtained. As in our preceding papers, Refs. [52], [73], for the convenience of the reader, the values of obtained parameters were re-calculated to the notations of the XTDS software developed in Dijon, Ref. [74] (relations between effective parameters of the SPHETOM and XTDS codes can be found, e.g., in Ref. [52]). Namely these values are presented in column 4 of Table 4 together with their 1σ statistical confidence intervals (the lasts are shown in parentheses). The parameters presented in column 4 of Table 4 without parentheses were not varied and were constrained to the values theoretically estimated and presented in Table 3. Because (in accordance with the strategy of Ref. [74]) the values of parameters presented in Table 4 are the corrections to the values of corresponding parameters of the lower vibrational states, $(0000, A_1)$, Ref. [73], and $(1000, A_1)/(0010, F_2)$, Ref. [52], Tables 5–7 present values of spectroscopic parameters of these three states and corresponding resonance interaction coefficients. In this respect it should be mentioned, that the unperturbed vibrational energies of the states $(2000, A_1)$, $(1010, F_2)$, $(0020, A_1)$, $(0020, E)$, and $(0020, F_2)$ from column 4 of Table 3, being re–calculated to the values of corresponding parameters in the XTDS notations, have the values presented in column 5 of Table 3. Column 6 of Table 3 shows the values of corresponding parameters obtained from the fit. One can see more than good correspondence between the predicted values and ones obtained from the fit.

Table 5
Spectroscopic parameters $Y_{v\gamma,v'\gamma'}^{\Omega(K,n\Gamma)}$ of the ground[a] and $(1000, A_1)$[b] vibrational states of Germane (in cm^{-1})[c].

$\Omega(K, n\Gamma)$	$^{76}GeH_4$		$^{74}GeH_4$	
	Ground	$(1000, A_1)$	Ground	$(1000, A_1)$
1	2	3	4	5
$0(0, 0A_1)$		2110.691769		2110.7004560
$2(0, 0A_1)$	2.695870305	−0.01799331	2.695864734	−0.01799331
$4(0, 0A_1)10^4$	−0.3341682	−0.0019367	−0.3341682	−0.0019367
$4(4, 0A_1)10^5$	−0.1547079	−0.000420	−0.1547079	−0.000420
$6(0, 0A_1)10^8$	0.114368	0.0	0.114368	0.0
$6(4, 0A_1)10^{10}$	−0.51075	0.0	−0.51075	0.0
$6(6, 0A_1)10^{10}$	−0.15638	0.0	−0.15638	0.0

[a] Reproduced from Ref. [73].
[b] Reproduced from Ref. [52].
[c] The $\gamma = \gamma' = A_1$.

The fit of ro-vibrational energies of the $^{74}GeH_4$ molecule was made analogously to $^{76}GeH_4$. In this case, only 8 parameters were fitted. Values of all other parameters were fixed to the values of the corresponding parameters of the $^{76}GeH_4$ molecule (additional fitting of any of them did not improve the result). The parameters obtained from the fit are shown in column 5 of Table 4 together with their 1σ statistical confidence intervals (the latter are given in parenthesis). One can see that the values of the fitted parameters of $^{74}GeH_4$ are very close to the values of the corresponding parameters of $^{76}GeH_4$ (this fact is the consequence of a very small value of the ratio $(M(76) − M(74))/M(76)$.

Table 6

Spectroscopic parameters $Y_{v\gamma,v'\gamma'}^{\Omega(K,n\Gamma)}$ of the $(0010, F_2)$[a] vibrational state of Germane (in cm^{-1})[b].

$\Omega(K, n\Gamma)$	^{76}GeH$_4$	^{74}GeH$_4$
1	2	3
0(0, 0A_1)	2110.7323088	2111.1420507
1(1, 0F_1)	−0.5686669	−0.56236859
2(0, 0A_1)	−0.014686010	−0.014695020
2(2, 0E)10^2	0.2234550	0.2254772
2(2, 0F_2)10^2	−0.447832	−0.447832
3(1, 0F_1)10^5	−0.76349	−0.76349
3(3, 0F_1)10^5	−0.64671	−0.64671
4(0, 0A_1)10^4	0.0	0.0
4(2, 0E)10^7	0.9537	0.9537
4(2, 0F_2)10^7	−0.6775	−0.6775
4(4, 0A_1)10^5	0.0010694	0.0010694
4(4, 0E)10^7	0.1407	0.1407
4(4, 0F_2)10^6	−0.20740	−0.20740
5(1, 0F_1)10^9	−0.558	−0.558
5(5, 0F_1)10^9	0.370	0.370
5(5, 1F_1)10^9	−0.639	−0.639
6(0, 0A_1)10^8	0.0	0.0
6(4, 0A_1)10^{10}	0.0	0.0
6(6, 0A_1)10^{10}	0.0	0.0

[a] Reproduced from Ref. [52].
[b] The $\gamma = \gamma' = F_2$.

Table 7

Spectroscopic parameters $Y_{v\gamma,v'\gamma'}^{\Omega(K,n\Gamma)}$ of the $(1000, A_1)/(0010, F_2)$ Coriolis interaction (in cm^{-1})[a].

$\Omega(K, n\Gamma)$	^{76}GeH$_4$	^{74}GeH$_4$
1	2	3
2(2, 0F_2)10^2	−0.8076987	−0.8091897
3(3, 0F_2)10^5	−0.14853	−0.14853
4(2, 0F_2)10^6	−0.10836	−0.10836
4(4, 0F_2)10^6	−0.15996	−0.15996
5(5, 0F_2)10^9	0.2873	0.2873

[a] The $(v\gamma) = (1000, A_1)$ and $(v'\gamma') = (0010, F_2)$.

The set of 28 fitted parameters reproduces the 1974 initial experimental transitions of the $\nu_1 + \nu_3$ and $2\nu_1$ bands of ^{76}GeH$_4$ with d$_{rms} = 4.5 \times 10^{-4}$ cm^{-1} (see also the statistical information in Table 2), which is comparable with experimental uncertainties. Analogously, the set of 8 fitted parameters reproduces the 652 initial experimental transitions of the $\nu_1 + \nu_3$ and $2\nu_1$ bands of ^{74}GeH$_4$ with d$_{rms} = 4.4 \times 10^{-4}$ cm^{-1}. All these can be considered as a good confirmation of the correctness of the model used. Also for an illustration, column 9 of Supplementary Material presents the differences δ (in units 10^{-4} cm^{-1}) between experimental and calculated line positions. To give the reader a possibility to judge the quality of the results, Fig. 4 shows the fit residuals for line positions as a function of quantum number J. Bottom parts of Figs. 1 and 3 present the simulated spectra which have been calculated with the parameters from Table 4. Two traces on top of Fig. 2 are simulations of transitions in the $\nu_1 + \nu_3$ and $2\nu_1$ bands for the ^{74}GeH$_4$ and ^{76}GeH$_4$ species. The third trace is the sum of two first separate traces. In all three cases (Figs. 1–3), the relative line strengths have been calculated in accordance with the scheme from Ref. [75]; only one the main dipole moment parameter (equal to 1) and Doppler line shape profile were used in calculations. Comparison of simulated and experimental spectra confirm a good quality of the obtained results.

6. Conclusion

We recorded the high resolution FTIR spectrum of ^{76}GeH$_4$ with a small amount of ^{74}GeH$_4$ (88.1 % of ^{76}GeH$_4$, 11.5 % of ^{74}GeH$_4$, and

a minor amounts of three other stable isotopic species in the sample) in the region of the $\nu_1 + \nu_3$ and $2\nu_1$ bands. As the result of assignment of the experimental transitions, 1974 lines with the value of $J^{max.} = 21$ and 652 lines with the value of $J^{max.} = 17$ were assigned to the ^{76}GeH$_4$ and ^{74}GeH$_4$ isotopologues, respectively. Analysis of the assigned transitions was made on the basis of specially constructed Fortran code, SPHETOM. A set of 28 spectroscopic parameters reproduces the 1974 line positions of ^{76}GeH$_4$ with the d$_{rms.} = 4.5 \times 10^{-4}$ cm^{-1}. Analogously, the additional set of 8 fitted parameters reproduces the 652 line positions of ^{74}GeH$_4$ with the d$_{rms.} = 4.4 \times 10^{-4}$ cm^{-1}.

Footnotes

1). Here we take into account the value of the $\nu_1 + \nu_3 = 4153.2348$ cm^{-1} band center which was derived from the results of assignments of experimental transitions in the present study.

Supplementary material

Supplementary material associated with this article can be found, in the online version, at 10.1016/j.jqsrt.2017.09.025

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