FISEVIER

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt



High resolution study of strongly interacting $\nu_1(A_1)/\nu_3(F_2)$ bands of ${}^{\rm M}{\rm GeH_4}$ ($M\!=\!76,74$)



M.A. Koshelev a,b,c, A.P. Velmuzhov a,c, I.A. Velmuzhova a, P.G. Sennikov a, N.I. Raspopova d, E.S. Bekhtereva d, O.V. Gromova d, O.N. Ulenikov d,*

- ^a G.G. Devyatykh Institute of Chemistry of High Purity Substances, Russian Academy of Sciences, 603950 Nizhny Novgorod, Russia
- ^b Institute of Applied Physics, Russian Academy of Sciences, 603950 Nizhny Novgorod, Russia
- ^c N.I. Lobachevsky State University of Nizhni Novgorod, National Research University, 603950 Nizhny Novgorod, Russia
- ^d Institute of Physics and Technology, National Research Tomsk Polytechnic University, Tomsk 634050, Russia

ARTICLE INFO

Article history: Received 29 April 2015 Received in revised form 26 May 2015 Accepted 1 June 2015 Available online 10 June 2015

Keywords: ν_1/ν_3 interacting states of GeH₄ High resolution spectrum of GeH₄ Spectroscopic parameters

ABSTRACT

The infrared spectra of GeH_4 were measured in the $1900-2300~cm^{-1}$ 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. 1550 transitions with $J^{max.}=31$ were assigned to the ν_3 and ν_1 bands of $J^{76}GeH_4$. Rotational, centrifugal distortion, tetrahedral splitting, and resonance interaction parameters for the (0010) and (1000) vibrational states were determined from the fit of experimental line positions. The obtained set of parameters reproduces the initial experimental data with accuracy close to experimental uncertainties. The result of analogous analysis of the $J^{74}GeH_4$ isotopologue (the number of assigned transitions is 750 with $J^{max.}=27$) is presented also.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

The interest in high resolution study of germane infrared spectra is motivated by several reasons. Firstly, high resolution spectra of germane can be interesting for studying the atmospheres of giant gas-planets, such as Jupiter and Saturn, Refs. [1–5], and its presence should be taken into account when studying their atmospheric composition and chemistry. Germane in a natural isotopic composition is used for producing high-purity germanium. Various physical devices (e.g., high-sensitivity detectors of nuclear radiation) are manufactured on its base, Ref. [6]. For that reason, laboratory investigations of high resolution spectra of germane are interesting and important (the

The present paper is the continuation of our earlier study, Refs. [7–9], of germane high-resolution spectra in the region of the ν_2/ν_4 dyad. Here, our attention is focused on the pair of strongly interacting stretching bands ν_3 and ν_1 . The ν_3 band has F_2 -symmetry and the ν_1 bands has A_1 -symmetry. As a consequence, it is forbidden in absorption by the symmetry of the molecule and its transitions can appear in the spectrum only because of resonance interaction with (borrowing intensity from) the ν_3 band. In this case, the resonance interaction is strong enough because the difference between centers of the bands ν_3 and ν_1 is decreased from 1.3 cm $^{-1}$ for the 70 GeH $_4$ isotopologue down to 0.04 cm $^{-1}$ for 76 GeH $_4$.

The region of the ν_3 and ν_1 bands was discussed earlier in Refs. [10–14,16]. The ν_3 band of four different species, M GeH₄ (M=70,72,74,76), was recorded with a medium resolution and analyzed by Wilkinson and Wilson in

E-mail address: Ulenikov@mail.ru (O.N. Ulenikov).

review of earlier spectroscopic studies of germane can be seen in our recent paper, Ref. [7]).

^{*} Corresponding author.

Ref. [10]. Later, the ν_3 band was discussed in 1972 in the papers by Corice et al., Ref. [11], and Kattenberg et al., Ref. [12]. In Ref. [11] the spectra of all five isotopic species were recorded with a moderately high resolution (resolution from 0.18 to 0.45 cm $^{-1}$, depending on the spectral region) in the 600–5000 cm $^{-1}$ range. Raman spectrum of the ν_3 band was recorded in Ref. [12] with low resolution of about 1 cm⁻¹. In all the mentioned references, isotopic and/or tetrahedral splittings in the ν_3 band were observed only partially resolved, or were not observed at all. Results of the first high resolution studies of the region of the ν_3 band were presented in Refs. [13] and [14]. In the study described in Ref. [13], the isotopic and partially the tetrahedral splittings were resolved for the first time. Some tetrahedral splitting parameters were obtained, and lines, belonging to the "forbidden" ν_1 band have been assigned for the first time. The work [14] was devoted to the problem of measuring and analysis of several absolute line strengths in the ν_3 band of isotopically enriched GeH₄. The main dipole moment parameter for the ν_3 band was estimated numerically. Careful ro-vibrational analysis of absorption spectra of all five germane isotopologues with a resolution of 0.06–0.02 cm⁻¹ was made in Ref. [15]. For each of the five isotopic species, about 100 transitions assigned both to the ν_3 and ν_1 bands were fitted with an overall standard deviation of 0.006 cm⁻¹, using 10 adjustable parameters. In Ref. [16] the high resolution (0.005 cm⁻¹)spectrum in the region of the *Q*-branch of ν_1 (2108.4–2110.6 cm⁻¹) was recorded for the first time with the Raman spectrometer. Assignments of Raman transitions were made $(I^{\text{max.}} = 11)$. Raman line positions were used as input data together with the earlier results from Ref. [15] in the fit procedure, the results of which allowed reproducing the Raman line positions with rms = 0.003 cm⁻¹.

In this paper we present results of our analysis of the high resolution Fourier transformed spectra of M GeH₄ (M=74,76) in the 1950–2250 cm $^{-1}$ region where the ν_1 and ν_3 bands are located. The experimental details are given in Section 2. The theoretical background of the study is briefly discussed in Section 3. The results of the analysis and discussion are presented in Section 4.

2. Experimental details

The experimental technique and methods used in the current study are similar to those employed in our previous work Ref. [7]. Briefly, an enriched and purified sample of germane containing ⁷⁶GeH₄ (88.1%), ⁷⁴GeH₄ (11.5%), ⁷³GeH₄ (0.07%), ⁷²GeH₄ (0.17%), ⁷⁰GeH₄ (0.12%) was spectroscopically studied using a Brucker IFS125HR Fourier transform spectrometer (Nizhny Novgorod, Russia). The experimental details

are summarized in Table 1. The high resolution spectra were recorded in the 1900-2300 cm⁻¹ range at different pressures using two different cells: a 20-cm long single-pass cell and a multi-pass cell with 2.25 m optical path length. This allows studying both strong ν_3 band and forbidden weak ν_1 band of the GeH₄ molecule as well as covering a wider range of the rotational quantum number J. The resolution due to the maximum optical path difference was 0.003 cm⁻¹ and the Norton-Beer (weak) apodization function was applied. 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 calibrated using about 200 most intense and isolated water peaks located in the studied wavelength range whose parameters are tabulated in HITRAN database Ref. [17]. After calibration the standard deviation of the difference between the measured and tabulated peak positions was estimated to be 1.6×10^{-4} cm⁻¹.

3. Description of the spectrum and assignment of the transitions

The survey spectra I and III in the region of 1900–2300 cm $^{-1}$, where the ν_3 and ν_1 bands of the germane molecule are located, are shown on the top trace of Fig. 1. All three branches of the ν_3 band of both recorded species are

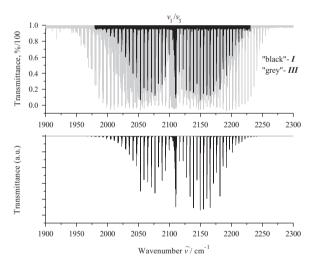


Fig. 1. Survey spectra of $^{76}\text{GeH}_4$ and $^{74}\text{GeH}_4$ in the region of $\nu_3(F_2)$ and $\nu_1(A_1)$ bands: (a) the top trace presents two experimental spectra, I ("black") and III ("grey"). Experimental conditions: absorption path length is 20 cm; room temperature; number of scans is 1050; sample pressure is 0.04 Torr for the black spectrum and 4 Torr for the grey spectrum. (b) The bottom trace presents for illustration simulated spectrum I.

Table 1 Experimental setup for the regions $1950-2250 \text{ cm}^{-1}$ of the infrared spectrum of ${}^{M}\text{GeH}_{4}$ (M=74,76).

Spectr.	Resolution (cm ⁻¹)	Measuring time (h)	No. of scans	Source	Detector	Beam- splitter	Opt. path- length (m)	Aperture (mm)	Temp. (°C)	Pressure /Torr	Calibr. gas
I	0.003	35.2	1050	Globar	MCT	KBr	0.2	1.3	21.4	0.04	H ₂ O
II	0.003	33.5	1000	Globar	MCT	KBr	0.2	1.3	21.9	0.4	H_2O
III	0.003	33.5	1000	Globar	MCT	KBr	0.2	1.3	24.5	4	H_2O
IV	0.003	35.2	1050	Globar	MCT	KBr	2.25	1.3	21.4	3.5	H_2O

clearly pronounced. The ν_1 band, being the forbidden band, is considerably weaker and totally overlapped by the ν_3 band. A small portion of the recorded high resolution 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 Fig. 2 are presented in Fig. 3. One can see a totally resolved tetrahedral

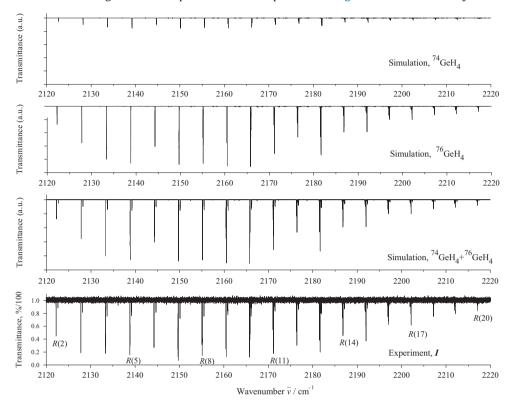


Fig. 2. Small portion of high resolution spectrum of 76 GeH₄ and 74 GeH₄ in the region of R-branch of ν_3 and ν_1 bands. The bottom trace is the experimentally recorded spectrum I (see experimental conditions in the caption to Fig. 1). Two traces on top are simulations of ν_3 and ν_1 bands transitions for the 74 GeH₄ (first trace) and 76 GeH₄ (second trace) molecules. The third trace is the sum of two first separate traces. As the spectrum I is weak, transitions belonging to the ν_1 band of 76 GeH₄ are seen as extremely weak lines on the second trace. Analogous transitions of the 74 GeH₄ species are not seen.

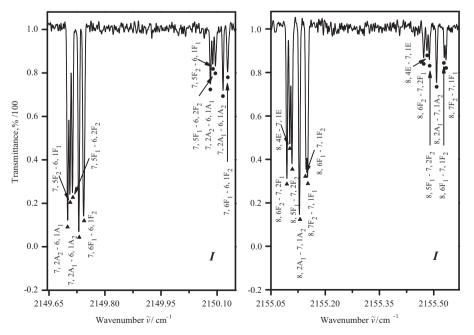


Fig. 3. Small fragments of R-branch of the ν_3 band in the region of R(6) and R(7) transitions. The tetrahedral structure of clusters is totally resolved. Assignments of transitions can be seen: transitions belonging to the $^{76}\text{GeH}_4$ and $^{74}\text{GeH}_4$ species are marked by dark triangles and dark circles, respectively.

structure of clusters (to the best our knowledge, it was done for the first time) both for the $^{76}\text{GeH}_4$ and $^{74}\text{GeH}_4$ molecules. A small portion of the recorded spectrum with the transitions assigned to the ν_1 band of $^{76}\text{GeH}_4$ and $^{74}\text{GeH}_4$ are shown in Fig. 4. In this case, experimental spectrum III is shown in Fig. 4, because the transitions belonging to the ν_1 band are considerably weaker than transitions of the ν_3 band.

GeH₄ is a spherical top molecule with a symmetry group which is isomorphic to the T_d point symmetry group. As a consequence, transitions in absorption are allowed only between vibrational states $(v\Gamma)$ and $(v'\Gamma')$ for which the relation

$$\Gamma \otimes \Gamma' \in F_2$$
 (1)

is fulfilled (the \otimes denotes a tensorial product). So, from the ground vibrational state (symmetry is A_1) transitions are allowed by symmetry only to the F_2 -type vibrational states (in our case, the ν_3 band). Transitions to the vibrational states of any other symmetry can be appeared in the absorption spectra only because of resonance interactions with the F_2 -type vibrational states (in our case, it is the ν_1 band).

At the first step of transitions assignment of the ⁷⁶GeH₄ molecule, the Ground State Combination Differences method was used. In this case, energy values of the ground vibrational state were calculated with the parameters from Ref. [7]. As a result of assignment, about 310 and 280 transitions were assigned to the ν_3 , ν_1 bands of 76 GeH₄. The second step of assignment was made after fit of the transitions assigned at the first step. Finally, more than 1360 and 440 transitions with the maximum value of upper quantum number I^{max} . equal to 31 and 20 were assigned to the above mentioned ro-vibrational bands (see also the statistical information in Table 2). A complete list of assigned transitions is presented in the Supplementary Material. It should be mentioned that the total number of assigned transitions ⁷⁶GeH₄ is about 18 times more than in the last paper [15] devoted to the high resolution study of the ν_3 and ν_1 bands of germane.

The transitions belonging to the $^{74}\text{GeH}_4$ species are considerably weaker than the transitions of $^{76}\text{GeH}_4$ 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 $^{74}\text{GeH}_4 \leftarrow ^{76}\text{GeH}_4$ have been made. In this case, the results of assignment of lines of the $^{76}\text{GeH}_4$ molecule were used as an initial information. In general, about 680 and 80 transitions with the maximum value of the upper quantum number J^{max} equal to 27 and 14 were assigned to the bands ν_3 and ν_1 of the $^{74}\text{GeH}_4$ species. A complete list of the assigned transitions is also presented in the Supplementary Material. As for the $^{76}\text{GeH}_4$ molecule, the total number of the transitions assigned to the $^{74}\text{GeH}_4$ species is about 7 times more than in Ref. [15].

4. Hamiltonian model used for the fit of experimental

Because of the symmetry of the GeH₄ 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 ,

Table 2 Statistical information for the ν_1 and ν_3 bands of the $^{76}\text{GeH}_4$ and $^{74}\text{GeH}_4$ molecules.

Band	Center (cm ⁻¹)	J ^{max}	N_t^{a}	$N_l^{\mathbf{b}}$	rms	m_1^{c}	m₂ ^c	m₃ ^c
1	2	3	4	5	6	7	8	9
$\nu_3(76) \\ \nu_1(74)$	2110.69177 2110.73231 2110.70046 2111.14205	20 31 14 27	79	714 47	1.85 2.39		19.2 26.6	3.3 10.1

^a N_t is the number of transitions.

^c Here $m_i=n_i/N\times 100\% (i=1,2,3); n_1,n_2$, and n_3 are the numbers of levels (transitions) for which the differences $\delta=E^{exp.}-E^{calc.}(\delta=\nu^{exp}-\nu^{calc})$ satisfy the conditions $\delta\leq 2\times 10^{-4}~{\rm cm}^{-1}$, $2\times 10^{-4}~{\rm cm}^{-1}<\delta\leq 4\times 10^{-4}~{\rm cm}^{-1}$, and $\delta>4\times 10^{-4}~{\rm cm}^{-1}$.

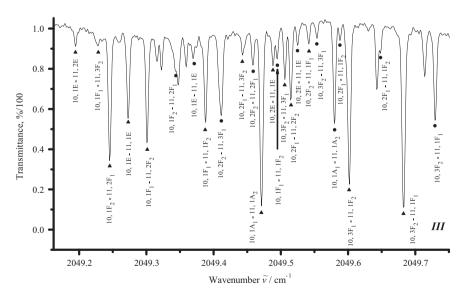


Fig. 4. Small fragments of P-branch of the ν_1 band in the region of P(11) transitions. Assignments of transitions can be seen: transitions belonging to $^{76}\text{GeH}_4$ and $^{74}\text{GeH}_4$ species are marked by dark triangles and dark circles, respectively.

^b N_l is the number of upper levels.

Table 3 Ro-vibrational term values for the (0010, F_2) vibrational state of the ⁷⁶GeH₄ and ⁷⁴GeH₄ molecules (in cm⁻¹)^a.

<i>J</i> 1	n	γ	E ₇₆	δ	E ₇₄ 4	δ 5	J 1	n	γ	E ₇₆	δ	E ₇₄	δ 5	<i>J</i> 1	n	γ	E ₇₆ 2	δ	E ₇₄	δ 5
							· ·													
0	1	F_2	2110.7322	-1	044=0040		6	2	F_2	2221.6843	-1	2222.0966	-2	9	7	F_1	2354.4273	1	2354.8022	0
1	1	A_2	2116.6276	-1	2117.0313	-2	6	3	F_2	2223.7603	1	2224.1361	-2	9	1	F_2	2349.1848	-1	2349.6024	1
1	1	Е	2115.8324	0	2116.2450	-2	6	4	F_2	2225.1260	1	2225.5122	2	9	2	F_2	2349.2567	0	2349.6896	0
1	1	F_1	2115.8215	0	2116.2352	-1	6	5	F_2	2225.1465	-1	2225.5351	0	9	3	F_2	2351.9287	0	2352.3266	1
1	1	F_2	2116.3640	-1	2116.7706	-2	7	1	A_1	2261.1144	0	2261.5197	0	9	4	F_2	2352.2212	0	2352.6080	-2
2	1	A_1	2126.2553	-1	2126.6709	-1	7	2	A_1	2262.8927	-1	2263.2784	-1	9	5	F_2	2352.6199	1		
2	1	Ε	2127.0893	-1	2127.4941	-2	7	1	A_2	2258.9024	-1	2259.3144	0	9	6	F_2	2354.4045	0	2354.7807	-1
2	1	F_1	2126.2758	-1			7	2	A_2	2262.8761	1	2263.2579	0	9	7	F_2	2354.4283	0		
2	2	F_1	2127.0969	0	2127.5035	-1	7	1	Ε	2258.7884	-1	2259.2117	-2	10	1	A_1	2402.3966	1		
2	1	F_2	2126.2891	-1			7	2	Ε			2259.3372	-2	10	2	A_1	2405.5667	1		
2	2	F_2	2127.6161	0	2128.0167	-2	7	3	Ε	2261.3413	1			10	3	A_1			2408.5324	6
3	1	A_1	2143.2148	0	2143.6212	-2	7	1	F_1	2258.7880	-3	2259.2105	1	10	1	A_2	2405.8418	0		
3	1	A_2	2142.1093	0			7	2	F_1	2258.8049	2	2259.2237	0	10	2	A_2	2408.1595	0	2408.5321	0
3	1	E	2142.0973	-1			7	3	F_1	2261.0486	0	2261.4392	-1	10	1	E	2402.3737	-1	2402.7937	1
3	1	F_1	2142.0636	0	2142.4813	-1	7	4	F_1	2261.3130	1			10	2	Ε	2402.4581	0	2402.8914	0
3	2	F_1	2143.1962	-1	2143.5992	0	7	5	F_1	2262.8844	0	2263.2673	-1	10	3	Ε	2405.3886	0		
3	3	F_1			2144.3609	5	7	1	F_2	2258.8171	1	2259.2409	-1	10	4	Ε	2406.3053	0		
3	1	F_2	2142.1023	0			7	2	F_2	2258.9125	0	2259.3315	0	10	1	F_1	2402.3848	-1	2402.8015	2
3	2	F_2			2143.5775	-3	7	3	F_2	2261.0013	0	2261.3970	-5	10	2	F_1			2402.8895	0
3	3	F_2	2143.1754	-1			7	4	F_2	2261.3699	1			10	3	F_1	2402.5688	-2	2402.9884	-1
4	1	A_1	2165.6623	-2	2166.0558	-2	7	5	F_2	2262.8798	-1	2263,2621	-1	10	4	F_1	2405.4248	1	2405.8074	_3
4	1	A_2	2164.5884	0	2164.9943	-2	8	1	A_1	2301.3265	- 1	2301.7567	2	10	5	F_1	2405.7153	0	2406.0907	-3
4	1	E	2163.2276	0	2101.3313	2	8	2	A_1	2305.9938	0	2306.3727	0	10	6	F_1	2406.3206	0	2 100.0307	,
4	2	E	2164.6580	0	2165.0506	-2	8	1	A_2	2301.3807	0	2301.8132	1	10	8	F_1	2408.1789	1	2408.5537	1
4	1	F_1	2104.0300	U	2163.6968	-2 -2	8	2	A_2	2303.7734	0	2304.1776	-3	10	1	F_2	2402.3591	1	2403.3337	-4
4	2	F_1	2164.6901	0	2165.0894	-2 -2	8	1	E E	2301.3430	0	2304.1776	-3 -4	10	2	F_2	2402.3953	0	2402.7743	-4 -1
4	3	F_1	2165.6670	0	2166.0613	-2 -0	8	2	E	2303.8825	_1	2304.2588	-4 -2	10	3	F_2	2402.5701	_3	2402.8239	- 1 1
4	ა 1		2163.2238	0	2100.0013	-0	8	3	E E	2304.3090	- 1 0	2304.2588	-2 -1	10	3 4	F_2	2402.3701	-3 -1	2402.9934	1
4	2	F_2	2103.2236	U	2162 6060	4	8	3 4	E E		-1		- 1 - 1	1	5			- 1		
4		F_2	2104 0211	2	2163,6869	-1		•		2305.9753		2306.3542	- 1 2	10	5 6	F_2	2406.2893	_	2400 5212	2
•	3	F_2	2164.6311	-3	2165.0282	1	8	1	F_1	2301.3291	-2	2301.7568		10		F_2	2408.1587	-1	2408.5313	2
4	4	F_2	2165.6709	-1	2166.0655	-3	8	2	F_1	2301.4754	-2	2301.8962	2	10	7	F_2	2408.1823	1	2408.5568	1
5	1	A_1	0400 =004		2190.2382	-1	8	3	F_1	2303.9867	0	2304.3843	-1	10	8	F_2	2408.1893	0	2408.5607	5
5	1	A_2	2189.7284	0	2190.1525	0	8	5	F_1	2305.9783	-1	2306.3584	-1	11	1	A_1	2460.9664	0	2461.4072	5
5	2	A_2	2192.7355	-1	2193.1273	-1	8	6	F_1	2305.9983	2	2306.3798	0	11	2	A_1	2464.4084	0	2464.8118	2
5	1	E			2190.2162	-2	8	1	F_2	2301.3204	0	2301.7380	0	11	3	A_1			2467.6098	1
5	2	Ε	2191.5220	0	2191.9126	-1	8	2	F_2	2301.3586	0	2301.7820	0	11	1	A_2	2460.9059	1	2461.3334	0
5	3	Ε	2192.7274	3	2193.1187	3	8	3	F_2	2301.4692	1	2301.8881	1	11	2	A_2	2461.0945	2	2461.5208	-2
5	1	F_1	2189.7424	0	2190.1595	0	8	4	F_2	2303.8397	0	2304.2256	-2	11	3	A_2	2467.2770	0	2467.6419	-2
5	2	F_1	2189.8089	0	2190.2244	-1	8	5	F_2	2304.2796	1			11	1	Е	2460.8593	0		
5	3	F_1	2191.4742	0	2191.8534	-3	8	6	F_2	2305.9716	-0	2306.3494	-2	11	2	Ε			2461.5054	1
5	4	F_1	2192.7194	0	2193.1093	-1	8	7	F_2	2306.0004	-3	2306.3828	-2	11	3	Ε	2464.6651	1		
5	1	F_2	2189.7374	0			9	1	A_1			2349.7831	-2	11	5	Ε	2467.2300	0	2467.6011	-2
5	2	F_2	2191.3837	1	2191.7886	0	9	2	A_1	2352.6563	1			11	6	Ε	2467.2572	0	2467.6252	0
5	3	F_2	2191.5446	-1	2191.9327	-3	9	1	A_2			2349.5900	0	11	1	F_1	2460.8559	0	2461.2719	2
5	4	F_2	2192.7304	-2	2193.1221	-1	9	2	A_2	2352.5961	0		-	11	2	F_1	2460.8812	-1	2461.2950	-4
6	2	A_1	2223.6805	0	2224.0381	-2	9	3	A_2	2354.4300	-1	2354.8092	-1	11	3	F_1	2460.9746	1	2461.4123	0
6	1	A_2	2223.7851	0	2224.1618	-3	9	1	E	2349.2063	0	2349.6339	-1	11	4	F_1	2464.2361	0	2 101.1123	v
0		E	2223.7031	0	2222.0296	-3 -1	9	2	E	2349.3595	0	2349.7807	- 1 - 1	11	5	F_1	2464.6024	-1		

E ₇₄		2467.6030 2467.6224	2467.6385	2461.3063	2461.4040	2461.5112	2756 9731	10.00013	2748.1745	2748.1882	2748.3337	2/48.5668					2756.9030	2757.0316 2757.0495	27.78.2018	2748.3234	2748.4450	2748.5680					2756.9768	2757.0295	2033,0300	2842.4019	2842.6170	2833.1908			2842.5599	2833.0864	7833 5773	7033.3723		2833.0898	2833.2644 2833.3295	
∞ m	2	0 -1	-1	2	_	c	- c	7	0	0	0	0 [-	3	0	 		> -	0	0	-1	Ξ,	- 1	1	0	-	، 1	7 -	. [-1	0	0	-2	,	- -	- 	- I O	·	0	0 0	
E ₇₆	2465.3151	2467.2317 2467.2547	2467.2711	2460.8871	2460.9715	2464 1601	2756 6219	2756.6972	2747.7670	2747.7804	2747.9122	2752.2089	2752.7673	2753.5713	2754.7228	2756.3887	2756.5478	2756 7036	27.702,7030	2747.9040	2748.0228	2748.1188	2752.1150	2753.0440 2753.6647	2754.7179	2756.5498	2756.6257	2756.6823	2839.0517	2842.0496	2842.2758	2832.7756	2837.2174	2839.1736	2842.2145	2832.6806	2832.8330	2837.3743	2838.3643	2832.6833	2832.8435 2832.9095	
۸.	F_1	F1	F_1	F ₂	F_2	F ₂	F Z	ш	F_1	F_1	F_1	I i	F_1	F_1	F_1	F_1	F_1	Γ1	r.1	F ₂	$\overline{F_2}$	F_2	F_2	F ₂	F ₂	$\overline{F_2}$	F_2	F ₂	Ā.	. 'Y	A_1	A_2	A_2	A_2	A ₂	ı L	J [пп	ч	F_1	F_1	
и	9	~ «	6	- 0	7 7	n 4	۲ ۲	· ∞	1	7	m ·	4 г	9	7	∞	6	10	11	7 -	7	3	4	2	0 1	· ∞	6	10	Ξ.	7	1 K	4	1	2	ς,	4 -	٦ ،	٦ ٢	o 4	2	_	3 2	
7 -	11 :	= =	11	11	11	= =	15	15	15	15	15	c1 7	15	15	15	15	15	CI 75	. t	15	15	15	15	J 7	15	15	15	15	16	16	16	16	16	16	16	16	16	01	16	16	16 16	
5 5	-3	-1 -2	-	-1	-3	7	٦ ٢	· "	0	-	-3			-1	0	1	_۲ س	ī	0	1		-2	e (7		2	0		- 0	-1					m (7-	† 0	n C	-1			
E ₇₄	2352.5699	2354.8050 2349.6171	2349.6362	2349.7815	2352.4021	2354 7762	2601 7454	2594.1620	2594.2844	2594.3867	2597.9424			2601.6248	2601.6856	2601.7288	2668.5536	2668.841/	2676 7556	2668.8264		2676.6608	2668.5419	2668.6715		2676.6604	2676.7304	2668.5481	2668 7808	2668.8561					2676.6920	26/6./489	2668.5270	2668.3643	2668.8553			
∞ m	0	- -	-1	-2		7	-	1	0	0	0 ,	- 0	7	-1	-4	0	-1	0 0	- c	- 1-	-1	0	_ ,	 4 %		0	0	0 (v C	0	1	0	0	7	0	7 -		- 0	0	0		
E ₇₆	2352.1804	2354.4264 2349.1940	2349.2164	2349.3609	2352.0405	2352.6395	26013896	2593.7507	2593.8637	2593.9420	2597.5671	2598.0603	2599.3876	2601.2570	2601.3237	2601.3725	2668.1444	2668.3941	2676.707	2668.3791	2672.9633	2676.3025	2668.1312	2668.2504	2673.4167	2676.3020	2676.3787	2668.1383	2668 3540	2668.4157	2672.2551	2672.7238	2673.4698	2676.1916	2676.3367	26/6.39/8	2669 1512	2668.1512	2668.4169	2672.8341	2673.3645 2674.3883	
۸.	E	чĘ	F_1	F	F ₁	<u>,</u> 4	_ 4	F ₂	F_2	F_2	F ₂	F ₂	F ₂	F_2	F_2	F_2	A ₁	A ₁	, 4	A ₂	A_2^{-}	A_2	ш	ц	ш	Е	Е	т <u></u> п	7	. H	F_1	F_1	F_1	F_1	г Г	L 4	1.2 E	7 2	F ₂	$\overline{F_2}$	F ₂	
z z	κ ι	ა 1	2	ω,	4 r	ი ყ	10	1	2	33	4 ı	ი ა	7	∞	6	10		7 6) <	1 -	2	33	, с	7 6	, 4	9	7	, ,	7 6	9	5	9	7	6	10	= -	۱ ر	7 6	4	5	9	
~ -	6	ი ი	6	6	o o	n 0	13	13 5	13	13	13	73	13	13	13	13	14	4 7	7 7	14	14	14	4 ;	4 4	14	14	14	4 5	1 4	14	14	14	14	14	4 ;	4 5	7 7	4 4	1 4	14	4 4	$\cdot \mid$
8	-1	ဂ – 0	-2	0	<u>۾</u> ا	0 0	>		3	0	4	0	1			7	1		<u> </u>		1		0				0	ī		0	-1				0 ,	- -	- - -	ī	2	-3		
E ₇₄	2223.9224	2225.5149	2222.1141	2223.9409	2224.1032	2225.5274	1710:7777		2467.6057	2467.6393	2525.0731	2532 0278	2525.1844			2525.0934	2525.2517		2531 9944	2532.0310	2525.0771		2525.3238				2531.9946	2532.0292	2523.0700	2525.2272	2525.3398				2531.9697	2532.0158	7707 7047	7334.474	2601.6944	2594.1514		
ω m	0	-3	0	0	0	o c	1	0		1	0 ,		-	0	_	7	0 7	1 - 0	7 -	3	1	2	-2	ī ī	1	-2	0			-1	0	0	_	7	0 7	- -		- -	•	0	1	
E ₇₆	2223.5212	2221.6037	2221.6932	2223.5412	2223.7294	2225.1390	2464 7438	2465.3395		2467.2734	2524.6568	2529.6/39	2524.7636	2528.1781	2529.7024	2524.6805	2524.8109	2528.3198	2526.35001	2531.6700	2524.6618	2524.7994	2524.9031	2528.5681	2529.6839	2531.6016	2531.6303	2531.6669	2524.0378	2524.7946	2524.9130	2528.2663	2528.8551	2529.6935	2531.5994	2531.6549	2501.0760	2394.0032 2598 5982		2593.7416	2598.4064 2601.2556	
* * *	E	F F	F_1	F_1	F ₁	r, 7,	F. 2	F ₂	F_2	F_2	Α1	A A	Α,	A_2	A_2	E	E	I I	J [1	н	F_1	F_1	F ₁	r,	F_1	F_1	F_1	F ₁	r ₂	F ₂	$\overline{F_2}$	F_2	F_2	F_2	F ₂	F ₂	1 2 A	A 4	¥	A_2	A_2 A_2	
u	2	η -	2	ω,	4 r	ე ←	٠ د	9	7	∞	- (7 6	-	2	n	_	7 7	n <	† ւ	9	-	2	m ×	4 ռ	9	7	00	o -	2	1 m	4	2	9	7	∞ ∘	y 6	5 -	- <	1 CC	_	3 2	
	9	9	9	9	9 (9 9	7	= =	11	11	12	7 2	12	12	12	12	12	12	17	12	12	12	12	21 C1	12	12	12	12	17	12	12	12	12	12	12	77	12	C E	13 5	13	13	

 Table 3 (continued)

0	0 1 7	- 3 0	2 0 0 -2 -2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	0 2	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	-1 0 0
2833.5760	2842.5210 2833.0720 2833.1098	2833.2388 2833.5745 2833.5745	3130.7951 3130.9030 3119.1950 3119.2887 3119.3871	3120.1689 3120.1689 3130.7858	3225.0582 3226.1836 3237.5322 3224.9823 3226.1844	3224.9313 3225.2160 3225.5641
1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1	-2 0 0	1 1 0 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	1 - 1 - 2 - 1 - 1 - 1	0 0 1 1 1 0 0 1 1	1 0 1 1 2 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7	
2833.1233 2837.8680 2838.4374 2839.0998 2840.3535 2841.8370	2842.0525 2842.1734 2842.2752 2832.6666 2832.7028	2832.8214 2833.1217 2833.1217 2837.3182 2838.1270 3125.0949 3125.0781 3126.0321 3127.2703 3127.2703	3129.9550 3130.4633 3130.5745 3130.6215 3118.7889 3118.8755 3118.9734	3119.2158 3119.7094 3124.1265 3125.5807 3126.2829 3127.2456 3130.2613 3130.4528	3224,6617 3225,7235 3232,4111 3236,3326 3237,2104 3224,5708 3225,7331 3228,5703	3232.7713 3236.9736 3224.5259 3224.8097 3225.1448 3230.2606
F1 F1 F1	F ₁ F ₂ F ₂	F ₂ F ₂ F ₂ F ₃ F ₄ F ₁	F ₁ F ₁ F ₁ F ₂	F2 F	4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4	A ₂ E E E
4 5 9 7 8 6	11 11 12 17 17 17 17 17 17 17 17 17 17 17 17 17	3 6 6 7 7 7 7 10 110	13 14 16 16 3	44 6 7 7 8 8 9 112 113	t	0 2 3 3 7 9 9 9
16 16 16 16	16 16 16 16	16 16 16 16 19 19 19 19	19 19 19 19 19	19 19 19 19 19 19	20 20 20 20 20 20 20 20	70 70 70 70 70 70 70
2 0 4 .	7 7 7	2 - 2 - 2 - 1	1 0 0 -2 0	1 1	2 0 0 -1	2 0 0 2 2
2676.7301 2748.3268 2756.7508	2748.4713	2748.4307 2748.5733 3018.6121 3018.7206 3019,3856	3029.4787 3029.5893 3018.5970 3018.7160 3018.7777 3018.9529	3029.4864	3018.5993 3018.6526 3018.8050 3018.9482 3019.3859	3029.3488 3029.5758 3029.5896 3119.3400
0 0 1 - 2 - 0 0	0 0 0 1	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	5 0 0 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	0 1 1 1 0 0 0	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	7 1 0 1 1 0 1 1 1 1 1 1 1 1 1 1 1 1 1 1
2676.1903 2676.3022 2676.3779 2747.9049 2752.5830	2747.8142 2748.0473 2754.7139 2756.6666 2747.7674	2748.0104 2748.1240 2752.8574 2753.6272 2756.381 3018.2079 3018.3086 3023.2865 3024.9497	3028.7711 3029.1416 3029.2581 3018.1931 3018.3030 3018.3597	3018.9299 3023.3378 3024.0827 3025.0907 3025.972 3027.4760 3029.0103 3029.1499	3018.1973 3018.2504 3018.250 3018.5250 3018.9290 3024.2247 3024.8447 3025.9187	3028.7721 3029.0088 3029.2440 3029.2580 3118.9276 3124.9113
$F_2 $ $F_2 $ $A_1 $ $A_1 $	A_2 A_2 E	ппппппппппп	E E E E E E E E E E E E E E E E E E E		7 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	F ₂ F ₂ F ₃ F ₄ A ₁ A ₁
8 10 10 2 2 5 7	7 2 8 4 1	2 6 7 8 9 1 2 8 9 5 9	V 8 6 1 7 8 4	5 6 8 8 10 11 13	t - 2 c 4 5 9 7 8 6	11 12 13 17 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2
4 4 4 5 5 5 5 5	51 51 51 51	15 15 15 15 18 18 18 18 18	8 8 8 8 8 8 8	81 82 83 83 84 84 84	2 8 8 8 8 8 8 8 8 8	18 18 18 19 19
1 2 0 -2	-4 2 3 1	-1 2 2 0	0 7 1 - 1 - 1 - 1	1 0 0	0 0 0 0	0 7 0 0
2601.7228 2594.1845 2594.3593 2594.4532	2601.6253 2601.7415 2594.1706 2594.1917 2594.3754	2594.4476 2601.6867 2601.7261 2842.5286 2842.5968 2842.6388	2923.4450 2923.8534 2933.3174 2923.2132 2923.8510	2933.4804 2923.2539 2923.4145 2923.5229	2923.2280 2923.2572 2923.4249 2923.5174 2923.8511	2933.3199 2933.4390 2923.2216 2923.3329
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	-1 2 0 0	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1 - 1 - 1 - 1 - 0 0 1 - 1	1 0 1 1 1 0 1 1	2 1 1 2 1 0 0 1 0 0 1 0 0 0 0 0 0 0 0 0	2 - 7 - 7 - 7 - 7 - 7 - 7 - 7 - 7 - 7 -
2601.3669 2593.7699 2593.9235 2594.0235 2597.9997 2599.3800	2601.3844 2593.7570 2593.7791 2593.9397	2594.0188 2597.6890 2597.6890 2601.3257 2601.3682 2839.1394 2840.3466 2841.8361 2842.2541 2842.2541	2923.0260 2923.3979 2929.1817 2932.9738 2922.8095 2923.3964 2923.3964	2933.1445 2922.8493 2922.9974 2923.0976 2928.3589 2929.8983 2931.2727	2933,1227 2922,8233 2922,8530 2923,0075 2923,0075 2923,3961 2927,7772 2929,0767	2931.2703 2932.7969 2932.9764 2933.1013 2933.1377 2922.8176
A ₂ E E	E F_1 F_1	7. L.	7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7	A ₂ .	3 3 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4	F1 F1 F1 F2 F2 F2 F3
412645	0 7 1 7 0	4 6 8 8 8 8 10 11 11 13	1 2 8 4 1 2 8	4 5 1 2 6 4 5 9 8	0 0 1 2 8 4 3 5 7 8 8	0 11 12 17 2 7 2 7 2 7 2 7 2 7 2 7 2 7 2
ET E	1	13 13 13 16 16 16 16	17 17 17 17 17 17 17 17 17 17 17 17 17 1	17 17 17 17 17 17 17 17 17 17 17 17 17 1	71 71 71 71 71 71 71 71 71 71 71 71 71 7	17 17 17 17 17 17 17 17 17 17 17 17 17 1

	_	
- 1	٣	

ω ι Ω	Ξ.	0	1-	0	1	-1	-2				-4		-1	-2	-2	-	5	1	-2	-2	-1	>				-2		-1	0	-2	-2	7					-4	ſ	- 7 - 1	•	-4	
E ₇₄	3237.3032	3237.5413	3225.0083	3225.0598	3225.2003	3225.5628	3226.1845				3237.0515		3237.5368	3224.9382	3224.9911	3223.0392	3573.1630	3573.4101	3573.6174	3574.0353	3574.5752	2010:0706				3588.2779		3573.1755	3573.6756	3573.9695	3574.5657	53/3.3109					3588.5105	000000000000000000000000000000000000000	3701.0253		3715.7880	
οn	7	<u> </u>		0	-1	-1	0 +	_ (o -	0	0	0	-1	-1	- 0) -	0	0	0	-	0 7	- -	- 1-	3	0 +	- -	0	-	- 0	0	-1	0 0	o –	· ന	0	0	0	,				
E ₇₆	3233.8113	3236.9752	3224.6004	3224.6484	3224.7917	3225.1419	3225.7239	3231.0983	3232,5776	3233.8319	3236.7190	3237.1254	3237.2142	3224.5330	3224.5860	3224.0200	3572.7541	3573.0096	3573.2227	3573.6370	3574.1594	3578 4887	3580.5752	3581.7855	3587.5996	3588.1747	3588.3873	3572.7657	3573.2806	3573.5668	3574.1482	3582 3306	3583.2283	3584.8110	3587.0986	3587.6334	3588.1998	3588.3381	3699.6351	3708.7683		
7	E	д н	F_1	F_1	F_1	F_1	F ₁	Ξ.	7 4	F ₁	F. 1	F_1	F_1	F_2	F_2	r ₂	а г	F_1	F_1	F_1	F ₁	7 4	F_1	F_1	F ₁	C 4	F_1	F_2	F_2	F ₂	F ₂	r ₂	r ₂	F ₂	F_2	F_2	F_2	F_2	A 4	. F	A_1	
и	9	2 =	: _	2	3	4	2	1 0	<u> </u>	0 6	13	14	15	_	7	ر د	7 -	2	3	4	2	o	6	10	16	<u> </u>	19	2	ω.	4 -	2	0 5	2 =	12	14	16	17	. 18	- 6	1 M	9	
J 1	20	70	20	20	20	20	20	07	70	20	20	20	20	20	70	20	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	24	24	24	
5 5	3	[2	1	- с	7		2	1 %	-4	-2	0	m (7 –	4	0			c	- 1	-2				1	2	4-	_ (0 -	-					,		3	5	-1	
E ₇₄	3130.8800	3119.4230			3119.1961	3119.3210	3119.6447	3120.1689		3130.6003	3130.9127	3119.1634	3119.2154	3119.3502	3119.6444	5120.16/5	3465.8760	3452.5010			0.00	3452.2738	3453.8688				3451.9467	3451.9619	3452.1703	3452.5746	3453.0407	5435,6095						3465.8914	3466.1702	3451.9466	3452.1074	
3 %	0	7 0	-2	_	0	0	0 +	- (7 -	-2	1 (1)	-1	0	-	(O +	-	-2	-2	_	-3	- -	- 1	-1	-1) 		-1	-1	0	[-	- <	t C		2	-1	$-\frac{2}{2}$	0	7 -)	-1	
E ₇₆	3130.5481	3119.0065	3130.2560	3130.6317	3118.7951	3118.9021	3119.2229	3119.7097	3125.1725	3130.2637	3130.5861	3118.7598	3118.8149	3118.9408	3119.2236	3119.7090	3466.1373	3452.0941	3462.6179	3466.0463	3451.5555	3452.6260	3453.4047	3457.7404	3460.0358	3466.0052		3451.5499	3451.7664	3452.1726	3452.6216	3455 8176	3457.7963	3458.8941	3460.3727	3461.2738	3462.5886	3465.5701	3465.8511 3466 1216		3451.7085	
٨	A ₁	A ₂	A ₂	A_2	Е	E	ш	J L	n n	П	ш	F_1	F_1	F_1	<u>1</u> .	r ₁	₹ ₹	A ₂	A_2	A_2	ы	n n	н	E	ш	u 14	F_1	F_1	F_1	F ₁	7 1	1 4	T 4	F_1	F_1	F_1	F ₁	F ₁	I d	F ₂	F_2	
и	2 - 2	7 6	4	2	1	7	m z	4 r	ი	6	01	_	2	3	4 r	0 (0 /	1	3	2	— с	7 6	4	9	<u></u>	12	-	2	ω,	4 -	2	0 1	- 00	6	10	11	12	16	7 2	· -	2	
~ -	19	91	19	19	19	19	19	19 01	<u>5</u>	19	19	19	19	19	19	פו נ	77	22	22	22	22	22	22	22	22	77	22	22	22	22	77	27	22	22	22	22	22	22	77	22	22	
5	2 -1						7	7-	0 6	1		2				-	1						-2	2	-2	n	-2	2			7 -		- 0)		2		-1	4 -	•	-1	
E ₇₄	2923.4749 2923.8503						2933.3983	2933.4/29	3018.5862			3029.5156				טרשר שררר	3253.5359						3237.4661	3237.5631	3335.9246	5556,7003	3335.9533	3336.7113			3335.9072	3336 3013	3337,4231			3349.2188	3349.3854	3335.8640	3335.9162 3336.0912		3336.7024	
ωm	0 -1	0 0	0	1	0	1	0 +	- -	o c	· -	0	-1	0	-2	-2	- -		0	-2	0	0	0 0	-1	-1	+	- 1	-3	1	7	-2	-	-	1	0	-1	-1	,	-1	ا د ر	2 1	0	
E ₇₆	2923.0535	2927.6580	2928.9602	2929.9323	2931.2751	2932.8000	2933.0569	2933.1366	3018.1822	3022.2382	3023.4552	3027.4741	3029.1824	3018.5092	3024.5121	3027.4798	3225.1500	3225.7239	3230.2072	3232.6829	3233.7899	3236.7116	3237.1432	3237.2401	0000	3343.6433	3335.5547	3336.2931	3342.6933	3348.9042	2225 6200	5555.0233	3336.9602	3342.4147	3345.5959	3348.8961		3335.4574	3335.4978 3335.6943	3335.9140	3336.2832	
γ	F ₂	F 2	. 2 F ₂	F_2	F_2	F_2	F ₂	F ₂	A A	¥ 7	Υ - Y	A_1	A_1	A_2	A ₂	A ₂	r ₂	$\overline{F_2}$	F_2	F_2	F ₂	F2	F ₂	F_2	A ₁	₹ ₹	A ₂	A_2	A ₂	A ₂	n n	I I	J 143	E	Е	Е	Е	r ₁ r	T H	F ₁	F_1	
и	ε 4 -	2 9	7	8	6	11	12	I3	1 2	1 M	4	2	9	-	7	n -	4 10	9	7	6	10	J 4	15	16	- с	7 m	-	2	_{در} در	9	٦ ,	7 6	J 4	. 5	7	10	Ξ,	- (7 %	4	2	
	17	17	17	17	17	17	17	10	∞ ∞	2 8	18	18	18	18	18	δ .	20	20	20	20	20	20	20	20	21	21	21	21	21	21	77	17	7 7 7	21	21	21	21	21	7 17	77	21	

1	
3699.5016 3701.2603 3699.4882 3700.6183 3715.8440 3699.8270 3700.5741 3701.2721 3702.3310 3699.4920 3699.4920 3699.4920 3699.4920 3699.7932 3701.2669 3715.9557 3832.3070 3832.4269	
4 2 2 2 2 1 0 2 1 2 1 1 1 2 2 1 1 1 1 1 1	-4 -1 3
3699.0911 3700.8437 3699.7631 3700.2205 3710.5308 3715.8142 3699.4257 3699.4257 3700.8567 3700.8567 3700.8567 3700.8563 3700.8510 3700.8510 3700.8510 3700.8510 3700.8510 3700.8510 3700.8510 3700.8510 3700.8510 3715.4323 3831.9042 3848.3823 3831.9042 3847.5648 4128.2218 4129.1334 4273.2682 4277.2615 4277.2615 4277.2410 4277.2410 4277.2410 4277.2410 4277.2410 4277.2410 4277.2410 4277.2410 4277.2410 4277.2195 4277.2195 4277.2195 4277.2195 4277.2195 4277.2195 4277.2195 4277.2195 4277.2195 4277.2195 4277.2195	4584.5024 4747.0288 4748.3477
$\mathcal{L}_{\mathcal{L}}}}}}}}}}$	A_1 A_1
1	6 19 9
2 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4	30 31 31
	-5
3452.5459 3453.8700 3453.8700 3573.5107 3573.7500 3574.0037 3574.5716 3574.7673 3984.7673 4109.5382 4112.2327 4109.5192	4128.5202
1	1 - 1
3451.9126 3452.1418 3452.418 3453.4054 3453.4054 3453.4053 3455.9013 3465.0140 3466.1016 3573.0626 3573.0460 3583.3876 3582.710 3583.3876 3582.710 3583.3876 3582.710 3582.711 3582.711 3586.7412 3986.7412 3986.7412 3986.7413 34128.6693 4111.8218 4111.8218 4111.8218	4110.1452 4113.2517
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC	F ₂ F ₂
E 4 4 5 9 7 8 8 1 5 1 7 1 7 7 8 8 1 7 8 8 1 7 8 8 1 8 1 8 1	4 7 18
22 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	27 27 27
4	-3
3337,4231 3349,0057 3349,3937 3335,8837 3336,0038 3336,2610 3336,7065 3336,2018 3331,9275 3831,9275 3833,1247 3833,1247 3833,1247 3830,9039 3831,288 3830,9095 3831,3077 3833,1181 3833,1181	3968.4405
2	_2 1 3
3336.9600 3339.5764 3341.4775 3343.4126 3343.0124 3343.0124 3335.6012 3335.6012 3335.6012 3335.6012 3335.6012 3335.6012 3335.6012 3342.2359 3342.2359 3343.0255 3343.0255 3451.2381 3831.7106 3848.7758 3831.7106 3848.7758 3831.7106 3848.7758 3831.7106 3848.7758 3831.7106 3831.7106 3831.7106 3831.7106 3831.7106 3831.7106 3831.7106 3831.7106 3831.7106 3831.7106 3831.7106 3831.7106 3848.2010 3848.2010 3848.2010 3848.2010 3848.400 3848.400	3968.0427 3985.6370 3968.8699
	A_2 E
0	1 6
222222222222222222222222222222222222222	26 26 26

 $^{\rm a}$ In Table 3, δ is the difference $E^{\rm exp.}-E^{\rm colc.}$ in units of $10^{-4}~{\rm cm^{-1}}.$

 F_2). The differences between centers of the bands ν_3 and ν_1 for different $^M\text{GeH}_4$ isotopologues are less than 1.3 cm $^{-1}$ (this difference decreases from 1.3 cm $^{-1}$ for the $^{70}\text{GeH}_4$ isotopologue down to 0.04 cm $^{-1}$ for $^{76}\text{GeH}_4$). For that reason, the spectrum of GeH $_4$ in the discussed region of 1900–2300 cm $^{-1}$ can be analyzed correctly only in the frame of the model which takes into account strong resonance interactions between the (0010, F_2) and (1000, A_1) vibrational states. Moreover, high symmetry of the GeH $_4$ molecule necessitates using a special

mathematical formalism (the theory of Irreducible Tensorial Sets, see, e.g., Refs. [18–20] and the recent review in Ref. [21]) 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. [22], Moret-Bailly, Ref. [23], and Champion, Ref. [24], on the one hand, and to recent review of Boudon, et al., Ref. [25], on the other

Table 4 Ro-vibrational term values for the $(1000, A_1)$ vibrational state of the 76 GeH₄ and 74 GeH₄ molecules (in cm⁻¹)^a.

J	n	γ	E ₇₆	δ	E ₇₄	δ	J	n	γ	E ₇₆	δ	E ₇₄	δ	J	n	γ	E ₇₆	δ	E ₇₄	δ
1			2	3	4	5	1			2	3	4	5		1		2	3	4	5
1	1	F_1	2116.0480	1			11	1	F_1	2463.2042	0			15	3	F_2	2751.0368	-4		
2	1	F_2	2126.7615	0	2126.7877	0	11	2	F_1	2463.4197	0	2463.4908	4	15	4	F_2	2751.3719	-0		
3	1	A_2	2142.8372	2	2142.8634	-2	11	3	F_1	2463.4618	0	2463.5469	2	16	1	A_1	2835.9107	0		
3	1	$\overline{F_1}$	2142.8138	4			11	1	F_2	2463.2160	1			16	2	A_1	2836.3513	0		
3	1	F_2	2142.8198	1			11	2	F_2	2463.3684	1			16	1	A_2	2836.0277	- 1		
4	1	A_1	2164.2285	0			11	3	F_2	2463.5569	1	2463.6201	1	16	1	E	2835.8138	- 1		
4	1	E.	2164.2119	-1	2164.2374	1	12	1	A_1	2527.1572	2			16	2	Ε	2836.0057	1		
4	1	F_1	2164.2208	-1			12	2	A_1	2527.4734	-1			16	3	Ε	2836.3098	0		
4	1	F_2			2164.2715	-3	12	1	A_2	2527.1686	0			16	1	F_1	2835.8260	1		
4	2	F_2	2164.2389	-1			12	1	E	2527.3323	-2			16	2	F_1	2835.9698	- 1		
5	1	E			2191.0293	-2	12	2	E	2527.4653	1	2527.5739	0	16	3	F_1	2836.2000	- 1		
5	1	\overline{F}_1	2190.9650	3			12	1	\overline{F}_1	2527.1740	0			16	4	F_1	2836.4526	– 1		
5	2	F_1	2190.9941	-2	2191.0243	-2	12	2	F ₁	2527.3743	0			16	1	F_2	2835.8449	0		
5	1	F_2	2190.9522	1	2101,0213	_	12	3	F_1	2527.5371	-1	2527.6056	0	16	2	F_2	2836.0872	0		
6	1	A_1	2223.0290	0	2223.0999	-1	12	1	F_2	2527.1797	1	202710000	ŭ	16	4	F_2	2836.5387	0		
6	1	E	2223.0236	0	2223.0945	0	12	2	F_2	2527.4187	-1	2527.5434	2	17	1	A_1	2926.6697	1		
6	1	F_1	2223.0484	0	2225.0545	O	12	3	F_2	2527.4107	1	2527.6848	1	17	1	A_2	2926.7046	0		
6	1	F_2	2223.0364	2			13	1	A_1	2596.7402	-1	2327.00-10	•	17	1	E	2926.1751	-2		
6	2	F_2	2223.0304	-1	2223.1399	-3	13	1	A_2	2596.7082	-1	2596.8385	3	17	2	E	2926.4406	-2		
7	1	A_2	2260.5798	0	2260.6097	-4	13	1	E	2596.4363	0	2550.0505	,	17	3	E	2926.9172	1		
7	1	E	2260.4587	1	2260.5282	-1	13	2	E	2596.9429	-1	2597.0075	2	17	1	F ₁	2926.1484	2		
7	1	F_1		2	2260.5282	- 1 - 5	13	1	F_1	2596.4173	-1 -2	2397.0073	2	17	2	F_1	2926.1975	2		
7	2	F_1	2260.4328	2	2260.5330	-1	13	2	F_1	2596.6267	-2 -2			17	3	F_1	2926.1973	0		
7	1	F_2	2260 4290	0	2200.3330	- 1	13	3			-2 -2	2506 9719	3	17	4	F_1		1		
7	2		2260.4280 2260.5370	1			13	4	F_1 F_1	2596.7682 2596.9056	-2 -1	2596.8718 2596.9810	-2	17	5	F_1	2926.6912 2926.8710	-2		
8	1	F_2	2200.3370	1	2303.2930	2	13	1		2596.9036	0	2590.9610	-2	17	1	•		-2 0		
8	4	A_1	2202 2702	-2	2303.2930	2	13	2	F_2 F_2	2596.4219	-2			17	2	F_2 F_2	2926.1184	0		
8	1	A_1 E	2303.2783 2303.1452	-2 0	2303.2154	0	13	3	F_2	2596.5986	0	2596.8584	2	17	3	F_2	2926.3481 2926.2950	1		
8	2	E	2303.1432	- 1	2303.2134	_3	14	1	_	2671.3480	0	2671.5005	3	18	1	A_1	3021.7030	- 1		
8	1	E F ₁	2303.2347	0	2303.3070	-3 1	14	1	A_1	2671.1615	0	20/1.3003)	18	1		3021.7030	0		
		F_1		1	2303.2287	0	14	1	A ₂ E	2670.9453	0				2	A_2	3021.8624	0		
8	2		2303.2805				14		E					18	2	A_2				
8	1 2	F_2	2303.1615	0	2303.2557	0	ı	2	E E	2671.1230	1			18		E	3021.8967	-1 2		
8		F_2	2303.3320	-1	2303.3786 2351.3157	-4 2	14			2671.3527	3			18	1	F_1	3021.7262	0		
9 9	1	A_1	2251 2060	1			14	1	F_1	2670.9602	1 -1			18		F_1	3022.1293	- 1		
9	1	A_2	2351.2060	-1	2351.3111	2	14	2	F_1	2671.2288	_	2671 5504	2	18	4	F_1	3022.3930	- 1 4		
-	1	E	2351.4290	0	2351.4797	2	14	3	F_1	2671.4493	1	2671.5504	3	18	3	F ₂	3021.7824	_		
9 9	1 2	F_1	2351.1985	1	2251 2025	1	14	1 2	F_2	2670.9608	-2 2			18	5	F ₂	3022.0380	1		
9	3	F_1	2351.3483	-1	2351.3925	-1	14		F_2	2671.1490	2			18 19	1	F_2	3022.5320	-1		
		F_1	2351.4102	-1	2351.4655	-1	14	3	F_2	2671.3294	0	2671 6142	1			A_2	3122.7552	1		
9	1	F_2	2351.1924	-1	2251 2600	2	14	4	F_2	2671.5491	1	2671.6143	1	19	2	A_2	3123.4056	2		
9	2	F_2	2351.3217	1	2351.3690	-2	15	1	A_1	2750.7717	1			19	1	Е	3122.5377	0		
10	1	A_1	2404.7281	-1	2404.8362	0	15	1	A_2	2750.7851	1			19	3	Е	3123.2491	1		
10	1	E	2404.5423	1	2404 7022	0	15	2	A_2	2751.4573	1			19	2	F_1	3122.4906	0		
10	2	E	2404.7578	1	2404.7938	0	15	1	E	2751.0674	0			19	3	F_1	3122.6977	0		
10	1	F_1	2404.5656	-1			15	2	Ε	2751.3183	0			19	2	F_2	3122.5664	1		
10	2	F_1	2404.7793	-1			15	1	F_1	2750.7556	0			19	3	F_2	3122.6642	2		
10	1	F_2	2404.5511	0			15	2	F_1	2750.9111	0			19	5	F_2	3123.3036	0		
10	2	F_2	2404.7180	2	2404.7635	1	15	3	F_1	2751.1942	1			20	3	Е	3228.7138	2		
10	3	F_2	2404.8587	0	2404.9055	-2	15	4	F_1	2751.2111	0			20	5	F_1	3229.3277	0		
11	1	A_2	2463.6249	-1	2463.6689	0	15	1	F_2	2750.7595	-1			20	1	F_2	3228.4752	-3		
11	1	Е	2463.2270	0			15	2	F_2	2750.9487	1			20	2	F_2	3228.6138	0		
11	2	Ε	2463.4916	0	2463.5726	2	I													

^a In Table 4, δ is the difference $E^{exp.} - E^{calc.}$ in units of 10^{-4} cm⁻¹.

hand). For that reason, only a brief theoretical basis of our present study is given in this section.

As the basis for the analysis, the effective Hamiltonian model was taken which is widely used in the high resolution rotation-vibration theory of polyatomic molecules, Refs. [26,27]:

$$H^{vib.-rot.} = \sum_{v,\tilde{v}=1} |v\rangle \langle \tilde{v}| H^{v\tilde{v}}, \tag{2}$$

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

For GeH₄, because of its high symmetry, the effective Hamiltonian (2) should be rewritten in the form which uses the notations of the Irreducible Tensorial Sets theory (see, e.g., Refs. [23,24,28,29]):

$$H^{vib.-rot.} = \sum_{\nu\gamma,\nu'\gamma'} \sum_{n\Gamma} \sum_{\Omega K} [(|\nu\gamma\rangle \otimes \langle \nu'\gamma'|)^{n\Gamma} \otimes R^{\Omega(K,n\Gamma)}]^{A_1} Y_{\nu\gamma,\nu'\gamma'}^{\Omega(K,n\Gamma)}.$$
(3)

Here $|\nu\gamma\rangle$ are the symmetrized vibrational functions which are equivalent to the vibrational functions $|\nu\rangle$ in Eq. (2) (the value γ in the function $|\nu\gamma\rangle$ is its symmetry); Γ is the symmetry of the direct product $(|\nu\gamma\rangle\otimes\langle\nu'\gamma'|)$ of vibrational wave functions; $Y^{\Omega(K,nI)}_{\nu\gamma,\nu'\gamma'}$ are different spectroscopic parameters; and Ω and K ares the power and rank of the irreducible rotational operator, respectively, $R^{\Omega(K,nI)}$ of the of the T $_d$ point symmetry group (for more details see Ref. [23]; we recommend also Ref. [30] where the algorithm of determination of the G-matrix elements in analytical form is presented for the XY $_4$ (T $_d$ symmetry) molecules). For the problem discussed in the present paper, the general formula, Eq. (3), is reduced to the following

expression:

$$\begin{split} H^{\textit{vib.-rot.}} &= \sum_{\Gamma} \sum_{\Omega} |1000, A_1\rangle \langle 1000, A_1| R^{\Omega(K,A_1)} Y_{(1000,A_1),(1000,A_1)}^{\Omega(K,A_1)} \\ &+ \sum_{\Gamma} \sum_{\Omega K} [(|0010,F_2\rangle \otimes \langle 0010,F_2|)^{\Gamma} \\ &\otimes R^{\Omega(K,\Gamma)}]^{A_1} Y_{(0010,F_2),(0010,F_2)}^{\Omega(K,\Gamma)} \\ &+ \sum_{\Omega K} (|1000,A_1\rangle \otimes \langle 0010,F_2|)^{F_2} \otimes R^{\Omega(K,F_2)}]^{A_1} Y_{(1000,A_1),(0010,F_2)}^{\Omega(K,F_2)} \\ &+ \sum_{\Omega K} [(|0010,F_2\rangle \otimes \langle 1000,A_1|)^{F_2} \otimes R^{\Omega(K,F_2)}]^{A_1} Y_{(1000,A_1),(0010,F_2)}^{*\Omega(K,F_2)}. \end{split}$$

The first two terms in Eq. (4) describe the unperturbed rotational structure of the vibrational states $(1000, A_1)$ and $(0010, F_2)$, the last two terms are the operators which describe strong interaction between the states $(1000, A_1)$ and $(0010, F_2)$.

Following the Irreducible Tensorial Sets theory, [18,23], one can easily determine symmetrized vibrational–rotational wave functions (for analogous problem in symmetric top molecules see, et al., Refs. [31–33]) that can then be used for constructing the matrix of the symmetrized Hamiltonian (3), and obtain spectroscopic parameters which should be taken into account in the effective Hamiltonian (4). The Hamiltonian in the form of Eq. (3) was used as the basis for the Fortran code SPHETOM. With this code, the experimental data were analyzed.

5. Ro-vibrational analysis of the $(1000, A_1)$ and $(0010, F_2)$ states

As was discussed in Section 3, more than 1360, 440, 680, and 80 transitions with the maximum values of upper quantum numbers J^{max} equal to 31, 20, 27, and 14 were assigned to the ν_3 and ν_1 bands of the $^{76}\text{GeH}_4$ and $^{74}\text{GeH}_4$ molecules, respectively. On the basis of these data and

Table 5Relations between values of parameters, $Y^{\Omega(K,I)}$, used in the SPHETOM and XTDS calculation schemes.

SPHETOM 1	XTDS 2	SPHETOM 1	XTDS 2
$\frac{1}{Y_{(0000),(0000)}^{2(0,A_1)}}$ $\frac{Y^{4(0,A_1)}_{(0000),(0000)}}{Y^{4(0,A_1)}_{(0000),(0000)}}$ $\frac{Y^{4(4,A_1)}_{(0000),(0000)}}{Y^{6(4,A_1)}_{(0000),(0000)}}$ $\frac{Y^{6(2,A_1)}_{(0000),(0000)}}{Y^{6(0,A_1)}_{(0000),(0000)}}$ $\frac{Y^{6(0,A_1)}_{(0000),(0000)}}{Y^{6(0,A_1)}_{(1000),(1000)}}$ $\frac{Y^{2(0,A_1)}_{(1000),(1000)}}{Y^{4(4,A_1)}_{(1000),(0100)}}$ $\frac{Y^{4(4,A_1)}_{(1000),(0100)}}{Y^{4(4,A_1)}_{(1000),(0100)}}$ $\frac{Y^{3(3,F_2)}_{(1000),(0010)}}{Y^{4(4,F_2)}_{(1000),(0010)}}$	$\begin{array}{c} 2\\ Y_{(0000),(0000)}^{2(0,A_1)}\\ Y_{(0000),(0000)}^{4(0,A_1)}\\ Y_{(0000),(0000)}^{4(4,A_1)}\\ Y_{(0000),(0000)}^{6(4,A_1)} \times 16\\ Y_{(0000),(0000)}^{6(4,A_1)}\\ Y_{(0000),(0000)}^{6(0,A_1)}\\ Y_{(0000),(0000)}^{6(0,A_1)}\\ Y_{(0000),(0000)}^{4(0,A_1)}\\ Y_{(0000),(0000)}^{4(0,A_1)}\\ Y_{(0000),(0000)}^{4(0,A_1)}\\ Y_{(0000),(0000)}^{4(0,A_1)}\\ Y_{(1000),(0000)}^{4(4,A_1)}\\ Y_{(1000),(0010)}^{4(4,A_2)} \times 4/\sqrt{3}\\ Y_{(1000),(0010)}^{4(4,A_2)} \times 8/\sqrt{3}\\ Y_{(1000),(0010)}^{4(4,A_2)} \times 16/\sqrt{3} \end{array}$	$ 1 \\ Y_{(0010),(0010)}^{1(1,F_1)} \\ Y_{(0010),(0010)}^{2(2,A_1)} \\ Y_{(0010),(0010)}^{2(2,F_2)} \\ Y_{(0010),(0010)}^{2(2,F_2)} \\ Y_{(0010),(0010)}^{2(3,F_1)} \\ Y_{(0010),(0010)}^{3(3,F_1)} \\ Y_{(0010),(0010)}^{3(3,F_1)} \\ Y_{(0010),(0010)}^{4(2,F_2)} \\ Y_{(0010),(0010)}^{4(2,F_2)} \\ Y_{(0010),(0010)}^{4(4,A_1)} \\ Y_{(0010),(0010)}^{4(4,F_2)} \\ Y_{(0010),(0010)}^{4(4,F_1)} \\ Y_{(0010),(0010)}^{4(4,F$	$\begin{array}{c} 2\\ Y_{(0010),(0010)}^{(1,1F_1)} \times 2/\sqrt{3}\\ Y_{(0010),(0010)}^{(2(0,A_1)} + Y_{(0010),(0010)}^{(0010)} \times \sqrt{3}\\ Y_{(0000),(0000)}^{(2(2,E))} + Y_{(0010),(0010)}^{(0010)} \times (-2\sqrt{2})\\ Y_{(0010),(0010)}^{(2(2,E))} \times (-4/\sqrt{3})\\ Y_{(0010),(0010)}^{(3(1F_1))} \times (-8/3)\\ Y_{(0010),(0010)}^{(3(3,F_1))} \times 8/\sqrt{3}\\ (Y_{(0000),(0000)}^{(4(0,A_1))} + Y_{(0010),(0010)}^{(4(0,A_1))}) \times \sqrt{3}\\ Y_{(0010),(0010)}^{(4(2,E))} \times 8\sqrt{2}/3\\ Y_{(0010),(0010)}^{(4(2,E))} \times 16/3\\ (\sqrt{3}Y_{(0010),(0010)}^{(4(4,E))} \times 16/3\\ Y_{(0010),(0010)}^{(4(4,E))} \times 8\sqrt{2}\\ Y_{(0010),(0010)}^{(5(1F_1))} \times 8\sqrt{2}\\ Y_{(1000),(0010)}^{(5(1F_1))} \times 32/3\sqrt{3} \end{array}$
$Y_{(1000),(0010)}^{5(3,F_2)}$ $Y_{(1000),(0010)}^{5(0,A_1)}$ $Y_{(0010),(0010)}^{0(0,A_1)}$	$Y_{(1000),(0010)}^{(3(3F_2))} \times (-32/3)$ $Y_{(0000),(0010)}^{(0(3F_2))} \times \sqrt{3}$	Y _{(1000),(0010)} Y _{(1000),(0010)}	$Y_{(1000),(0010)}^{5(3,F_1)} \times (-32/3)$

rotational energies of the ground vibrational states from Ref. [7], the ro-vibrational energies of the (1000, A_1) and (0010, F_2) vibrational states of ⁷⁶GeH₄ and ⁷⁴GeH₄ were determined. They are presented in columns 2 and 4 of Tables 3 and 4.

The obtained values of upper energies of the ⁷⁶GeH₄ molecule were used in the weighted fit procedure with the Hamiltonian (4) on the basis of the SPHETOM Fortran code, Ref. [7]. A set of 24 varied parameters (15 parameters of the $(0010, F_2)$ vibrational state, 4 parameters of the $(1000, A_1)$ state, and 5 resonance interaction parameters were obtained. Taking into account that the most of the readers are more familiar with the XTDS software developed in Dijon, Ref. [34], than with the SPHETOM Fortrancode, values of spectroscopic parameters obtained in our study were recalculated to the values of corresponding parameters used in the XTDS code (Table 5 presents list of coefficients which provide transformation from the "SPHE-TOM" parameters to the "XTDS" ones). Namely these values are presented in column 3 of Table 6 and in column 2 of Table 7 together with their 1σ statistical confidence intervals (the lasts are shown in parentheses). Necessary for calculations parameters of the ground vibrational state (they are taken from Ref. [7], also re-calculated to the XTDS notations, and shown in column 2 of Table 6). One can see more than satisfactory correspondence both between the values of fitted rotational parameters of different vibrational states, and between parameters of the excited and ground vibrational states. Finally, the set of 24 fitted parameters reproduces the 863 initial energy values (more than 1810 transitions) of the $(0010, F_2)$ and $(1000, A_1)$ vibrational states of 76 GeH₄ with d_{rms} = 2.0×10^{-4} cm⁻¹ (d_{rms} = 1.9×10^{-4} cm⁻¹ was obtained for the 714 rovibrational energies of the $(0010, F_2)$ state, and $d_{rms} = 2.1$ $\times 10^{-4} \, \text{cm}^{-1}$ was obtained for the 149 ro-vibrational energies of the $(1000, A_1)$ state: see also the statistical information in Table 2), which is comparable with experimental uncertainties. This can be considered to be a good confirmation of the correctness of the model used. Also for an illustration, column 9 of Supplementary Material and columns 3 and 5 of Tables 3 and 4 present the differences δ (in units 10^{-4} cm⁻¹) between experimental and calculated values of ro-vibration energies.

The fit of ro-vibrational energies of the $^{74}\text{GeH}_4$ molecule was made analogously to $^{76}\text{GeH}_4$. In this case, only 6 parameters were fitted. Values of all other parameters were fixed to the values of the corresponding parameters of the $^{76}\text{GeH}_4$ 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 6 and columns 3 of Tables 7 and 8 together with their 1σ statistical confidence intervals (the lasts are given in parenthesis). One can see that the values of the fitted parameters of $^{74}\text{GeH}_4$ are very close to the values of the corresponding parameters of $^{76}\text{GeH}_4$ (this fact is the consequence of a very small value of the ratio (M(76) - M(74))/M(76)). The obtained set of

Table 7 Spectroscopic parameters $Y_{\nu_{\gamma},\nu_{\gamma'}}^{\Omega(K,n_{\Gamma})}$ of the $(0010,F_2)$ vibrational state of Germane (in cm⁻¹)^{a,b}.

$\Omega(K, n\Gamma)$ 1	⁷⁶ GeH ₄ 2	⁷⁴ GeH₄ 3
$\begin{array}{c} 0(0,0A_1) \\ 1(1,0F_1) \\ 2(0,0A_1) \\ 2(2,0E)10^2 \\ 2(2,0F_2)10^2 \\ 3(1,0F_1)10^5 \\ 3(3,0F_1)10^5 \\ 4(0,0A_1)10^4 \\ 4(2,0E)10^7 \\ 4(4,0E)10^7 \\ 4(4,0E)10^7 \\ 4(4,0E)10^6 \\ 5(1,0F_1)10^9 \\ 5(5,0F_1)10^9 \\ 5(5,1F_1)10^9 \\ 6(0,0A_1)10^8 \\ 6(4,0A_1)10^{10} \\ \end{array}$	2110.7323088(58) -0.5686669(15) -0.014686010(52) 0.2234550(91) -0.447832(10) -0.76349(41) -0.64671(23) 0.0 0.9537(34) -0.6775(34) 0.0010694(64) 0.1407(50) -0.20740(32) -0.558(12) 0.370(11) -0.639(20) 0.0	2111.1420507(44) -0.56236859(65) -0.014695020(20) 0.2254772(52) -0.447832 0.76349 -0.64671 0.0 0.9537 -0.6775 0.0010694 0.1407 -0.20740 -0.558 0.370 -0.639 0.0
$6(6,0A_1)10^{10}$	0.0	0.0

^a The $\gamma = \gamma' = F_2$ in Table 7.

Table 6 Spectroscopic parameters $Y_{\nu_{\nu,\nu',\nu'}}^{O(K,nT)}$ of the ground and $(1000,A_1)$ vibrational states of Germane (in cm⁻¹)^{a,b}.

$\varOmega(K,n\Gamma)$	⁷⁶ GeH₄		74 GeH $_4$	
	Ground	(1000, A ₁)	Ground	(1000, A ₁)
1	2	3	4	5
$0(0, 0A_1)$		2110.691769(11)		110.7004560(79)
$2(0,0A_1)$	2.695870305	-0.01799331(14)	2.695864734	-0.01799331
$4(0,0A_1)10^4$	-0.3341682	-0.0019367(28)	-0.3341682	-0.0019367
$4(4,0A_1)10^5$	-0.1547079	-0.000420(12)	-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 The $\gamma = \gamma' = A_1$ in Table 6.

 $^{^{\}rm b}$ Values in parentheses are 1σ statistical confidence intervals. Parameters of $^{74}{\rm GeH_4}$ presented in column 3 without confidence intervals were constrained to the values of corresponding parameters of the $^{76}{\rm GeH_4}$ isotopologue and were fixed in the fit.

^b Values in parentheses are 1σ statistical confidence intervals. Parameters of ⁷⁴GeH₄ presented in column 5 without confidence intervals were constrained to the values of corresponding parameters of the ⁷⁶GeH₄ isotopologue and were fixed in the fit.

parameters reproduces more than 760 transitions ($J_{max} = 27$) of the ⁷⁴GeH₄ molecule with $d_{rms} = 2.1 \times 10^{-4}$ cm⁻¹.

As an additional illustration of correctness of the obtained results, Fig. 5 shows the fit residuals for line positions as a function of the quantum number J. Fig. 6 presents a diagram of the calculated reduced energy levels for a pair of states $(0010, F_2)$ and $(1000, A_1)$ as defined by the equation:

$$E_{ln\gamma}^{red.}/hc = E_{Jn\gamma}/hc - B_{gr}J(J+1) + D_{gr}J^2(J+1)^2 - \dots$$
 (5)

Also as an illustration, simulation of the spectrum in the region of the ν_3 and ν_1 bands is presented in Figs. 1 and 2. The whole spectrum is shown in Fig. 1. Fig. 2 presents the R-branch more in details. Two traces on top of Fig. 2 are simulations of transitions in the ν_3 and ν_1 bands for the

Table 8 Spectroscopic parameters $Y_{\nu_y,\nu_{\gamma'}}^{\Omega(K,n\Gamma)}$ of the $(1000,A_1)/(0010,F_2)$ Coriolis Interaction (in cm⁻¹)a,b.

$\Omega(K, n\Gamma)$ 1	⁷⁶ GeH₄ 2	⁷⁶ GeH₄ 3
2(2,0F ₂)10 ²	- 0.8076987(80)	- 0.8091897(42)
3(3,0F ₂)10 ⁵	- 0.14853(63)	- 0.14853
4(2,0F ₂)10 ⁶	- 0.10836(66)	- 0.10836
4(4,0F ₂)10 ⁶	- 0.15996(77)	- 0.15996
5(5,0F ₂)10 ⁹	0.2873(90)	0.2873

^a The $(v\gamma) = (1000, A_1)$ and $(v'\gamma') = (0010, F_2)$ in Table 8.

 74 GeH₄ and 76 GeH₄ species. The third trace is the sum of two first separate traces. As the spectrum I is weak, the transitions belonging to the ν_1 band of 76 GeH₄ are seen as extremely weak lines on the second trace. Analogous transitions of the 74 GeH₄ species are not seen, at all. The relative line strengths necessary for the comparison were calculated using only one main dipole moment parameter and then calibrated with the transition [5, 1 A_2 ←6, 1 A_1] at 2076.5522 cm^{−1} and 2076.9765 cm^{−1} for the 76 GeH₄ and 74 GeH₄ species, respectively. A simple Doppler profile was used for the line shapes. Comparison of two bottom traces shows a good correlation between the experimental and simulated spectra.

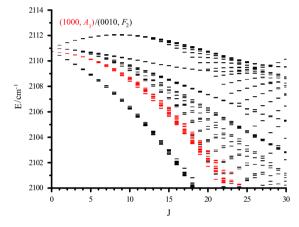


Fig. 6. Calculated reduced ro-vibrational energy levels for the states $(0010, F_2)$ and $(1000, A_1)$ of 76 GeH₄ (see text for details).

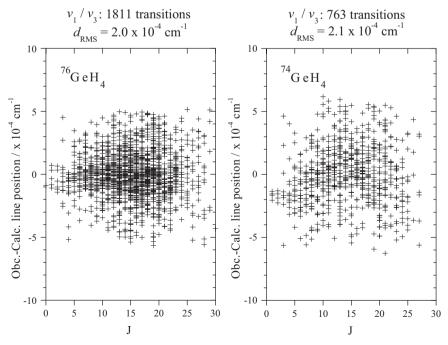


Fig. 5. Observed–calculated line positions and fit statistics for ν_1/ν_3 bands of the $^{76}\text{GeH}_4$ and $^{74}\text{GeH}_4$ molecules.

 $^{^{\}rm b}$ Values in parentheses are 1σ statistical confidence intervals. Parameters of $^{74}{\rm GeH_4}$ presented without confidence intervals were constrained to the values of corresponding parameters of the $^{76}{\rm GeH_4}$ isotopologue and were fixed in the fit.

6. Conclusion

The high resolution Fourier transform spectra of the $^{76}\text{GeH}_4$ and $^{74}\text{GeH}_4$ molecules in the region of the u_3 and ν_1 bands were recorded with a high resolution under different experimental conditions and were analyzed theoretically. As the result of analysis, the number of the assigned experimental transitions was increased by more than 18 times for the ⁷⁶GeH₄ and by more than 7 times for the ⁷⁴GeH₄ species in comparison with the data known in the literature, Ref. [15]: about 1810 transitions with the value of $I^{max.} = 31$ were assigned to $^{76}GeH_4$, and about 760 transitions with the value of $J^{max} = 27$ were assigned to ⁷⁴GeH₄. The weighted fit of the experimental data with the parameters of the Hamiltonian (4) leads to the set of 24 plus 6 fitted parameters which reproduce the initial experimental data for the ⁷⁶GeH₄ and ⁷⁴GeH₄ species with $d_{rms} = 2.0 \times 10^{-4} \text{ cm}^{-1}$.

Acknowledgements

The work was supported by the project "Leading Russian Research Universities" (Grant FTI-120 of the Tomsk Polytechnic University). Part of the work was supported by the Foundation of the President of the Russian Federation (Grant MK-4872.2014.2) and by the RFBR. M.A.K. (Grant No: 15-02-07887A) and A.P.V. also acknowledge partial support through agreement No. 02..49.21.0003 of August 27, 2013 between MON RF and NNSU.

Appendix A. Supplementary data

Supplementary data associated with this paper can be found in the online version at http://dx.doi.org/10.1016/j.jqsrt.2015.06.003.

References

- [1] Chen F, Judge DL, Wu CYR, Caldwell J, White HP, Wagener R. Highresolution, low-temperature photoabsorption cross sections of C₂H₂, PH₃, AsH₃, and GeH₄, with application to Saturn's atmosphere. J Geophys Res 1991;96:17519–27.
- [2] Atreya SK, Mahaffy PR, Niemann HB, Wong MH, Owen TC. Composition and origin of the atmosphere of Jupiter an update, and implications for the extrasolar giant planets. Planet Sp Sci 2003;51: 105–12.
- [3] Lodders K. Jupiter formed with more tar than ice. Astrophys J 2004;611:587–97.
- [4] Lodders K. Atmospheric chemistry of the gas giant planets. Geochemical Society. (http://www.geochemsoc.org/publications/geochemicalnews/gn142jan10/); 2010.
- [5] Fink U, Larson HP, Treffers RR. Germane in the atmosphere of Jupiter. Icarus 1978;34:344–54.
- [6] Haller EE. Germanium: from its discovery to SiGe devices. Mater Sci Semicond Process 2006;9:408–22.
- [7] Ulenikov ON, Gromova OV, Bekhtereva ES, Raspopova NI, Sennikov PG, Koshelev MA, et al. High resolution study of MGeH₄ (M = 76, 74) in the dyad region. | Quant Spectrosc Radiat Transf 2014;144:11–26.
- [8] Cheglokov AE, Kuritsin YuA, Snegirev EP, Ulenikov ON, Vedeneeva GV. High-resolution spectroscopy of the P₂ Q branch of GeH₄, with a computer-assisted, pulsed-diode laser spectrometer. J Mol Spectrosc 1984;105:385–96.

- [9] Cheglokov AE, Kuritsin YuA, Snegirev EP, Ulenikov ON, Vedeneeva GV. Study of the ν_2 infrared band of GeH₄: Q-branch. Mol Phys 1984;53:287–94.
- [10] Wilkinson GR, Wilson MK. Infrared spectra of some MH₄ molecules. I Chem Phys 1966;44:3867–74.
- [11] Corice J, Fox K, Fletcher WH. Studies of absorption spectra of GeH $_4$ in the 2–17 μ region. J Mol Spectrosc 1972;41:95–104.
- [12] Kattenberg HW, Gabes W, Oksam A. Infrared and laser raman gas spectra of GeH₄. | Mol Spectrosc 1972;44:425–45.
- [13] Daunt SJ, Halsey GW, Fox K, Lovell RJ, Gailar NM. High resolution infrared spectra of ν_3 and $2\nu_3$ of germane. J Chem Phys 1978;68: 1319–21.
- [14] Fox K, Halsey GW, Daunt SJ, Kennedy RC. Transition moment for ν_3 of $^{74}\text{GeH}_4$. J Chem Phys 1979;70:7–5326.
- [15] Lepage P, Champion J-P, Robiette AG. Analysis of the ν_3 and ν_1 infrared bands of GeH₄. | Mol Spectrosc 1981;89:8–440.
- [16] Mao SQ, Saint-Loup R, Aboumajd A, Lepage P, Berger H, Robiette AG. Continuous wave stimulated Raman spectroscopy of the ν_1 band of natural GeH₄. | Raman Spectrosc 1982;13:257–61.
- [17] Rothman LS, Gordon IE, Babikov Y, Benner DC, Bernath PF, Birk M, et al. The HITRAN2012 molecular spectroscopic database. J Quant Spectrosc Radiat Transf 2013;130:4–50.
- [18] Fano U, Racah G. Irreducible tensorial sets. New York: Academic Press: 1959.
- [19] Wigner EP. Quantum theory of angular momentum. New York: Academic Press; 1965.
- [20] Varshalovitch DA, Moskalev AN, Khersonsky VK. Quantum theory of angular momentum. Leningrad: Nauka; 1975.
- [21] Ulenikov ON, Bekhtereva ES, Albert S, Bauerecker S, Niederer HM, Quack M. Survey of the high resolution infrared spectrum of methane (¹²CH₄ and ¹³CH₄): partial vibrational assignment extended towards 12000 cm⁻¹. J Chem Phys 2014;141 234302_1-234302_33.
- [22] Hecht T. The vibration–rotation energies of tetrahedral XY₄ molecules. Part I. Theory of spherical top molecules. J Mol Spectrosc 1960;5:355–89.
- [23] Moret-Bailly J. Sur l'interpretation des spectres de vibration-rotation des molecules a symmetrie tetraedrique ou octaedrique. Cah Phys 1961;15:238–314.
- [24] Champion JP. Developpement complet de l'hamiltonien de vibration-rotation adapte a l'etude des interactions dans les molecules toupies spheriques. Application aux bandes ν_2 et ν_4 de 12 CH₄. Can J Phys 1977;55:1802–28.
- [25] Boudon V, Champion JP, Gabard T, Loëte M, Rotger M, Wenger. Spherical top theory and molecular spectra. In: Quack M, Merkt F, editors. Handbook of high-resolution spectroscopy, vol. 3. Chichester, NY, John Wiley & Sons, 2011. p. 1437-60.
- [26] Nielsen HH. The vibration–rotation energies of molecules. Rev Mod Phys 1951;23:90.
- [27] Papousek D, Aliev MR. Molecular vibrational–rotational spectra. Amsterdam, Oxford, New York: Elsevier Scientific Publishing Company: 1982.
- [28] Ulenikov ON, Bekhtereva ES, Albert S, Bauerecker S, Hollenstein H, Quack M. High resolution infrared spectroscopy and global vibrational analysis for the CH₃D and CHD₃ isotopomers of methane. Mol Phys 2010;108:1209–40.
- [29] Ulenikov ON, Bekhtereva ES, Fomchenko AL, Litvinovskaya AG, Leroy C, Quack M. On the "expanded local mode" approach applied to the methane molecule: isotopic substitutions CH₃D←CH₄ and CHD₃←CH₄. Mol Phys 2014;112:2529–56.
- [30] Cheglokov AE, Ulenikov ON. On determination of the analytical formulas for reduction matrices of tetrahedral-symmetry molecules. | Mol Spectrosc 1985;110:53–64.
- [31] Tarrago G, Ulenikov ON, Poussigue G. Dipole moment matrix for vibration rotation transitions in $C_{3\nu}$ molecules. J Phys 1984;45: 1429–47.
- [32] Ulenikov ON, Malikova AB, Alanko S, Koivusaari M, Anttila R. Highresolution study of the 2ν₅ hybrid band of the CHD₃ molecule. J Mol Spectrosc 1996;179:175–94.
- [33] Ulenikov ON, Onopenko GA, Tyabaeva NE, Alanko S, Koivusaari M, Anttila R. Precise study of the lowest vibration–rotational bands ν_5 and ν_3/ν_6 of the CHD $_3$ molecule. J Mol Spectrosc 1997;186:293–313.
- [34] Wenger C, Boudon V, Champion JP, Pierre G. Highly-spherical top data system (HTDS) software for spectrum simulation of octahedral XY6 molecules. J Quant Spectrosc Radiat Transf 2000;66:1–16.