

GLOBAL ANALYSIS OF 24 ROVIBRATIONAL BANDS OF THE OCTAD OF THE $^{76}\text{GeH}_4$ MOLECULE

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A global fitting method has been developed for spherical top molecules. The octad of the GeH_4 molecule comprising 24 interacting states has been investigated. By solving the inverse spectroscopic problem, positions of the band centers and rotational and resonant parameters are calculated. A total of 70 variable parameters allow 1184 initial experimental rovibrational energies to be reproduced with a standard deviation of $1.2 \cdot 10^{-3} \text{ cm}^{-1}$.

Keywords: Germane molecule, global analysis, spectroscopic parameters.

INTRODUCTION

Germane, along with methane, is a prototype of many more complex molecules, and for this reason, its investigation has been of great interest in chemical physics for understanding of the nature of its chemical bonds, structure, and reactivity over many years up to the present. The interest to the study of the germane spectra stretched from quantum dynamics and chemical reactions, on the one hand, to applications in astrophysics, planetology, and high industrial technologies, on the other hand [1–10]. The high-precision data on the rovibrational spectra and the spectroscopic parameters of the germane molecule are necessary for all its applications. At the same time, until now the volume of such data is very limited for a number of reasons, among which the most important are the high symmetry of the molecule and the presence of a great number of rovibrational bands strongly resonating with each other (the so-called polyads of the interacting vibrational states). To solve this problem, it is necessary to consider on the one hand, the high symmetry of the molecule using the apparatus of irreducible tensor systems, and on the other hand, in the context of the theory of effective rotational operators, to develop a program complex considering simultaneously a great number of interacting rovibrational states of the molecule. The program complex SPHETOM (SPHERical TOP Molecule) [11–15] has already been developed by our research team intended for calculation of a small number of interacting rotational states. In this work, this complex is modified for simultaneous analysis of a great number of rotational states (the *global* analysis of up to several tens of states). As an object of practical application, the previously unexplored system of 24 interacting states of the germane molecule important for practical applications has been chosen. The data obtained by analyzing of more than 2000 lines and band parameters are supposed to be used for high-precision determination of the intramolecular potential function of the germane molecule.

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TABLE 1. Experimental Conditions of Recording the IR Spectra of the GeH₄ Molecule in the Range 2300–3200 cm⁻¹

Spectrum	Recording time, h	Number of scans	Resolution, cm ⁻¹	Detector	Optical path length, m	Temperature, K	Pressure, Torr	Calibration gas	Calibration accuracy ·10 ⁴ , cm ⁻¹
I	33.5	1000	0.003	MCT	0.2	295	0.04	CO ₂	1
II	35.2	1050	0.003	MCT	2.25	295	3.5	CO ₂	1

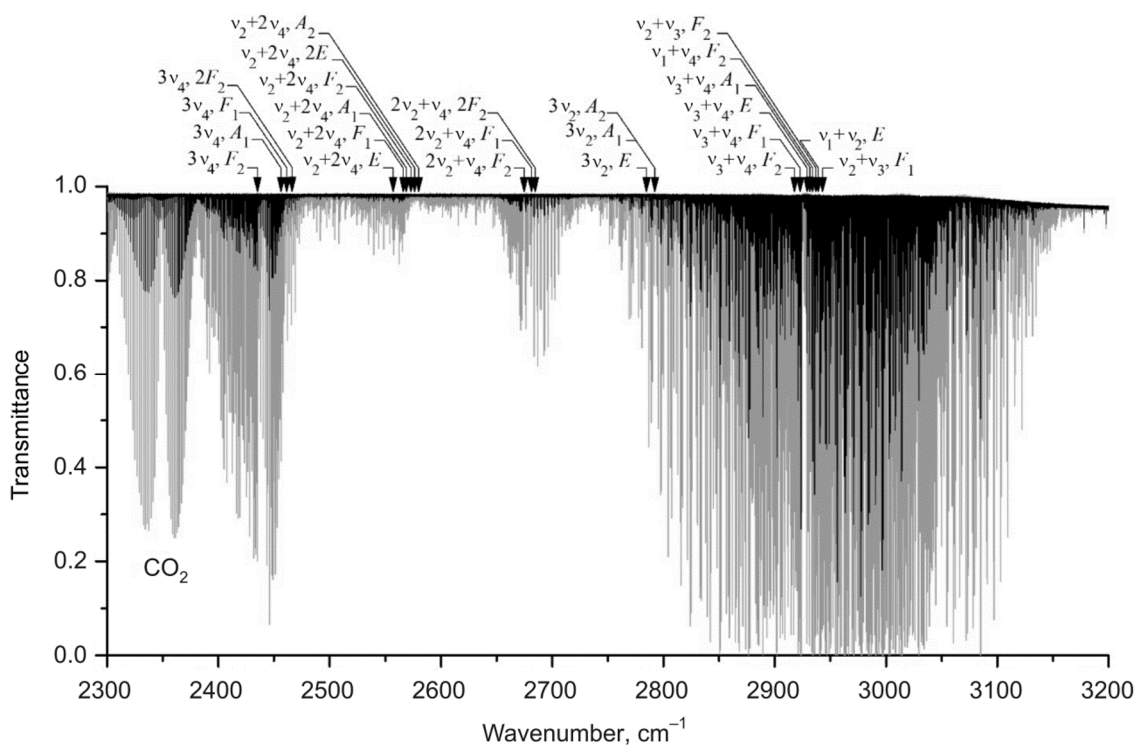


Fig. 1. Absorption spectrum of the ⁷⁶GeH₄ molecule in the range 2300–3200 cm⁻¹.

EXPERIMENTAL CONDITIONS OF RECORDING THE ABSORPTION SPECTRUM OF THE GEH₄ MOLECULE

The high-resolution absorption spectra of the ⁷⁶GeH₄ molecule enriched to 88.1% were recorded using a Bruker IFS 125HR Fourier transform spectrometer at the Institute of Chemistry of High-Purity Substances named after G. G. Devyatikh of the Russian Academy of Sciences (Nizhny Novgorod). The method of sample preparation was described in our work [15]. The optimal instrumental characteristics were reached using a radiation source Globar, a KBr beam splitter, and an IR mercury-cadmium-tellurium (MCT) detector. The conditions of spectrum recording are given in Table 1; the general view of the recorded spectra is shown in Fig. 1 (for vivid presentation, a small part of the spectrum is shown in Fig. 2 in more details).

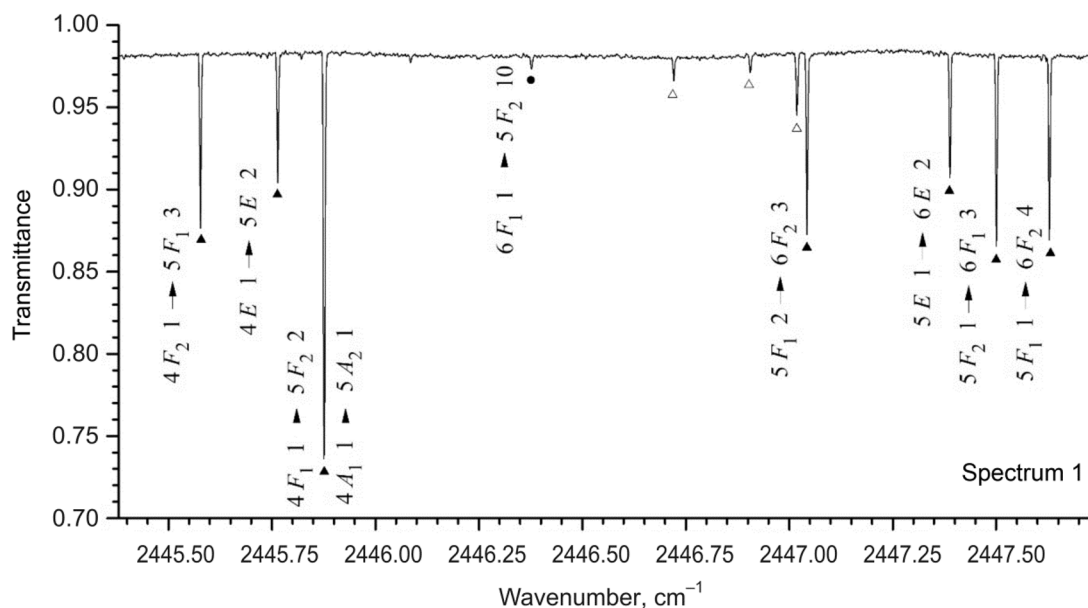


Fig. 2. A fragment of high-resolution spectrum I of the $^{76}\text{GeH}_4$ molecule in the region of the $3\nu_4$ band. Here symbols ▲ and ● indicate transitions of the $3\nu_4$, F_2 and $3\nu_4$, F_1 bands, and symbol Δ indicates transitions of the $3\nu_4$, F_1 band of the $^{74}\text{GeH}_4$ molecule.

ASSIGNMENT OF THE SPECTRUM

As already indicated above, 24 rovibrational bands of the GeH_4 molecule (see also the statistical data in Table 2) lie in the examined range. Due to the symmetry, only eight bands possessing the F_2 symmetry were resolved in the absorption spectra. At the same time, the presence of the Coriolis-type resonant interactions led to partial removal of this forbiddenness, and depending on the force of resonant interactions, weak (or under certain conditions, even strong) lines of the bands forbidden by the symmetry can appear in the experimental spectrum.

Of course, it is impossible to assign the lines belonging to all 24 rovibrational bands, because the intensity of various bands can differ from each other up to 3–5 orders of magnitude. As a consequence, the lines belonging to 17 of 24 aforementioned absorption bands of the experimental spectrum were assigned. The lines were assigned using the traditional method of combinational differences widely used to solve problems of this kind. The specificity of this problem is that the method of combinational differences cannot be used at the initial stage for molecules of this type (spherical top molecules with T_d symmetry), because only one of lines in P -, Q -, or R -branches is strong, whereas the lines-partners in other branches are weaker by orders of magnitude. This problem was solved by a theoretical estimation of the largest spectroscopic parameters of the investigated 24 bands based on the data on the values of the corresponding parameters of the underlying rovibrational states with the subsequent estimation of the positions of lines in the spectrum. Exactly the initial values of the rotational parameters and of the k - l splitting parameters were estimated by interpolation of the corresponding values from the lower lying polyads. This approach allowed us to assign the lines corresponding to small values of the quantum number J , and then to use the procedure of the method of combinational differences of the ground vibrational state (we note that in this case, the parameters of the ground vibrational state were taken from [16]). As already indicated above, more than 2000 lines belonging to 17 of 24 rovibrational bands of the $^{76}\text{GeH}_4$ molecule were identified in the spectrum (see the statistical data in Table 2).

TABLE 2. Statistical Information

Band	E, cm^{-1}	J^{max}	N
$3\nu_4, F_2$	2438.2419	11	238
$3\nu_4, A_1$	2456.3062		
$3\nu_4, F_1$	2459.4522	8	70
$3\nu_4, 2F_2$	2462.4358	9	94
$\nu_2+2\nu_4, E$	2556.2050	10	125
$\nu_2+2\nu_4, F_2$	2567.6821	10	184
$\nu_2+2\nu_4, A_1$	2568.9688		
$\nu_2+2\nu_4, F_1$	2571.4766	9	130
$\nu_2+2\nu_4, 2E$	2573.4396	6	30
$2\nu_2+\nu_4, F_2$	2675.2301	11	178
$\nu_2+2\nu_4, A_2$	2576.5330		
$2\nu_2+\nu_4, F_1$	2681.3866	10	219
$2\nu_2+\nu_4, 2F_2$	2684.1893	10	137
$3\nu_2, E$	2785.4748		
$3\nu_2, A_1$	2792.2628		
$3\nu_2, A_2$	2792.2628		
$\nu_3+\nu_4, F_2$	2918.8195	11	308
$\nu_3+\nu_4, F_1$	2923.6874	8	48
$\nu_3+\nu_4, E$	2929.1458	7	61
$\nu_3+\nu_4, A_1$	2931.0593		
$\nu_1+\nu_4, F_2$	2932.0131	8	48
$\nu_2+\nu_3, F_2$	3033.3474	9	66
$\nu_1+\nu_2, F_1$	3034.6841	6	13
$\nu_2+\nu_3, F_1$	3040.6453	9	20

BRIEF THEORETICAL SUBSTANTIATION OF THE GLOBAL ANALYSIS OF XY_4 TYPE MOLECULES WITH T_d SYMMETRY

The germane molecule is the spherical top with the symmetry group isomorphic to the T_d point group. The vibrational coordinates of this molecule possess the following symmetry: (q_1, A_1) – one-dimensional fully symmetrical vibration, (q_2, E) – doubly degenerate vibration with E symmetry, and (q_3, F_2) and (q_4, F_2) – two triply degenerate vibrations with F_2 symmetry. It is well known (for example, see [17–22]) that the rotational states of such molecules are separated into groups of closely located states called polyads [23]. The octad studied in the present work consists of 24 rotational states (24 rovibrational bands) interacting with each other (the correct account of all interactions taking into account the states with high values of the quantum number J is a very complex problem that requires consideration of tens and hundreds of the parameters, including highly correlated ones). The high symmetry of the molecule engenders one more additional complex problem, namely, the presence of tetrahedral splitting both of the vibrational and rovibrational states. In its turn, this necessitates the use of the sufficiently complex mathematical apparatus of the theory of irreducible tensor systems for a description of the spectrum.

As is well known from the general rovibrational theory [23–26], the Hamiltonian of any polyatomic molecule can be represented in the form

$$H^{\text{vib-rot}} = \sum_{a,b} |a\rangle\langle b| H^{a,b}, \quad (1)$$

where $|a\rangle$ and $\langle b|$ are the basis vibrational functions, the operators $H^{a,b}$ depend only on the rotational operators J_α ($\alpha = x, y, z$), and summation in Eq. (1) is carried out over all interacting states (in our case, over 24 vibrational states). If the molecule possesses the high symmetry (as in the considered situation), expression (1) can be re-written in the symmetrized form [27–29]

$$\begin{aligned} H^{\text{vib-rot}} &= \sum_{\nu\gamma, \nu'\gamma'} \sum_{n\Gamma} \left[(|\nu\gamma\rangle \otimes \langle \nu'\gamma'|)^{n\Gamma} \otimes H_{\nu\gamma, \nu'\gamma'}^{n\Gamma} \right]^{A_1} \\ &\equiv \sum_{\nu\gamma, \nu'\gamma'} \sum_{n\Gamma} \sum_{\Omega K} \left[(|\nu\gamma\rangle \otimes \langle \nu'\gamma'|)^{n\Gamma} \otimes R_{\sigma}^{\Omega(K, n\Gamma)} \right]^{A_1} Y_{\nu\gamma, \nu'\gamma'}^{\Omega(K, n\Gamma)}. \end{aligned} \quad (2)$$

In expression (2), $|\nu\gamma\rangle$ and $\langle \nu'\gamma'|$ are the symmetrized vibrational functions and the symmetries of these functions; $R_{\sigma}^{\Omega(K, n\Gamma)}$ are the symmetrized rotational operators of degree Ω and rank K [29]; Γ is the symmetry of the corresponding operator in the group T_d ; the index n numbers various operators $R_{\sigma}^{\Omega(K, n\Gamma)}$ with the same symmetry; the sign \otimes defines the tensor product; and $Y_{\nu\gamma, \nu'\gamma'}^{\Omega(K, n\Gamma)}$ are the spectroscopic parameters of different types and designations (the band centers, rotational and centrifugal parameters, tetrahedral splitting parameters, and resonant parameters of different types). The rotational operators $R_{\sigma}^{\Omega(K, n\Gamma)}$ symmetrized in the group T_d are defined as follows:

$$R_{\sigma}^{\Omega(K, n\Gamma)} = \sum_m {}^{(K)}G_{n\Gamma\sigma}^m R_m^{\Omega(K)}. \quad (3)$$

Here the operators $R_m^{\Omega(K)}$ are the so-called irreducible rotational operators symmetrized about the complete orthogonal group.

Expression (2) provided the basis for the algorithm and the software package written in MAPLE and FORTRAN languages that allowed us to implement the procedure of the global analysis for molecules with tetrahedral symmetry. Using this program complex, numerical estimations were performed of the initial parameters of the effective Hamiltonian given by Eq. (2) together with all necessary calculations using expressions (2) and (3)

ROVIBRATIONAL ENERGY AND DETERMINATION OF THE SPECTROSCOPIC PARAMETERS OF THE OCTAD

Based on the assignment of the spectrum of rovibrational lines of the $^{76}\text{GeH}_4$ molecule, 1184 rovibrational energies for 17 highly excited rotational states of this molecule were first determined. A small part of the results obtained is given in Table 3 (see the statistical data in Table 2 for more details; the complete list of the transitions and rovibrational lines identified on their basis will be presented in the HITRAN database). It should be noted that the data on the rovibrational energies allow one to describe in detail the spectral range 2300–3200 cm^{-1} of the germane molecule important for practical applications. The results obtained here are very important for their further use in high-precision semiempirical determination of the intramolecular potential function of germane as well as for the subsequent analysis of the line intensities of this molecule.

All 1184 energy levels assigned as a result of analysis were then used as the initial experimental data for solving the inverse spectroscopic problem on the determination of parameters of Hamiltonian (2). A specific feature of problem solution in this case is that it belongs to the class of incorrect inverse problems (tens of parameters of various diagonal blocks strongly correlate with a large number of various resonant parameters), and the so-called regularization is required to solve it. Because of the limited volume of the work, we cannot discuss in details this problem here and note only that when solving these problems in rovibrational spectroscopy, the regularization is reduced to the necessity

TABLE 3. A Part of the Assigned Rovibrational Transitions of the $^{76}\text{GeH}_4$ Molecule

Energy, cm^{-1}	J	n	γ	J'	n'	γ'	Wave number, cm^{-1}	Transmittance, %	$\sigma \cdot 10^3$, cm^{-1}	Band	Spectrum
2508.0998	6	A_1	1	7	A_2	1	2357.2333	96.4	-0.94	$3\nu_4, F_1$	II
2545.1158	6	A_1	2	7	A_2	1	2394.2502	95.5	-0.02	$3\nu_4, F_2$	II
				6	A_2	1	2431.9526	19.7	0.04		II
2671.2409	6	A_1	9	6	A_2	1	2558.0774	93.5	-0.25	$\nu_2+2\nu_4, E$	II
				7	A_2	1	2520.3752	93.8	-0.18		II
2695.6197	6	A_1	11	6	A_2	1	2582.4571	97.5	0.67	$\nu_2+2\nu_4, F_2$	II
				7	A_2	1	2544.7547	92.4	0.55		II
2666.3455	6	A_2	8	6	A_1	1	2553.1679	95.4	-1.34	$\nu_2+2\nu_4, E$	II
2694.6285	6	A_2	10	6	A_1	1	2581.4534	94.9	1.09	$\nu_2+2\nu_4, F_1$	II
2773.1953	6	A_2	13	6	A_1	1	2660.0198	95.4	0.67	$2\nu_2+\nu_4, F_1$	I
2790.4885	6	A_2	14	6	A_1	1	2677.3137	82.8	1.42	$2\nu_2+\nu_4, F_1$	II
2794.0456	6	A_2	15	6	A_1	1	2680.8704	94.3	1.05	$2\nu_2+\nu_4, F_2$	I
2519.8864	6	E	1	5	E	1	2439.0372	94.4	-0.34	$3\nu_4, F_1$	II
				7	E	1	2369.0124	97.5	-0.37		II
2697.6203	6	E	21	7	E	1	2546.7493	97.2	2.60	$\nu_2+2\nu_4, 2E$	II
				6	E	1	2584.4625	97.8	2.19		II
2715.8169	6	E	22	7	E	1	2564.9443	93.6	1.08	$\nu_2+2\nu_4, 2E$	II
2784.9867	6	E	27	6	E	1	2671.8266	94.6	-0.10	$2\nu_2+\nu_4, F_2$	I
				7	E	1	2634.1126	97.6	-0.46		II
2794.7959	6	E	29	7	E	1	2643.9233	96.5	1.09	$2\nu_2+\nu_4, 2F_2$	II
2812.0081	6	E	31	7	E	1	2661.1342	95.7	-0.25	$2\nu_2+\nu_4, F_2$	I
2816.1069	6	E	33	7	E	1	2665.2345	97.4	1.26	$2\nu_2+\nu_4, F_1$	II
				5	E	1	2735.2589	97.9	0.99		II
				6	E	1	2702.9482	97.9	1.33		II
2535.3091	6	F_1	4	6	F_2	1	2422.1508	97.0	2.50	$3\nu_4, 2F_2$	II
				6	F_2	2	2422.1400	95.8	2.81		II
				7	F_2	2	2384.4416	97.1	3.33		II
				5	F_2	1	2454.4679	97.4	2.91		II
2692.4260	6	F_1	28	5	F_2	1	2611.5814	96.3	-0.40	$\nu_2+2\nu_4, F_1$	II
				6	F_2	2	2579.2533	97.5	-0.80		II
2695.5247	6	F_1	29	6	F_2	2	2582.3532	97.7	0.43	$\nu_2+2\nu_4, F_2$	II
				7	F_2	1	2544.6737	95.8	0.35		II
2697.2206	6	F_1	30	5	F_2	1	2616.3761	98.0	-0.35	$\nu_2+2\nu_4, F_2$	II
				7	F_2	2	2546.3488	97.4	-0.99		II
				7	F_2	1	2546.3685	92.0	-0.77		II
2697.6479	6	F_1	31	7	F_2	2	2546.7799	97.4	2.88	$\nu_2+2\nu_4, 2E$	II
2716.0378	6	F_1	32	7	F_2	2	2565.1681	92.6	1.15	$\nu_2+2\nu_4, 2E$	II
3148.5485	6	F_1	80	6	F_2	2	3035.3765	32.9	-0.09	$\nu_1+\nu_2, E$	II
				5	F_2	1	3067.7045	68.3	0.19		I
				7	F_2	2	2997.6777	86.7	0.06		II
2692.4515	6	F_2	29	6	F_1	1	2579.2762	97.8	-1.11	$\nu_2+2\nu_4, F_1$	II
				5	F_1	1	2611.6083	96.2	-0.86		II
2774.7073	6	F_2	41	6	F_1	1	2661.5320	97.9	-1.08	$2\nu_2+\nu_4, F_1$	II
				7	F_1	2	2623.8286	95.4	-0.70		II
2790.1196	6	F_2	42	7	F_1	2	2639.2421	97.7	0.47	$2\nu_2+\nu_4, F_2$	II
				6	F_1	1	2676.9464	85.4	0.92		II
2812.8928	6	F_2	47	7	F_1	1	2662.0433	93.9	0.09	$2\nu_2+\nu_4, F_2$	II
				5	F_1	2	2732.0433	97.5	0.27		II
2813.8207	6	F_2	48	7	F_1	1	2662.9710	93.4	-0.09	$2\nu_2+\nu_4, 2F_2$	II
				5	F_1	2	2732.9706	97.5	-0.23		II
3148.6168	6	F_2	82	7	F_1	2	2997.7385	38.7	-0.26	$\nu_2+\nu_3, F_2$	II
				6	F_1	1	3035.4423	50.2	-0.26		II
				5	F_1	1	3067.7743	68.7	-0.10		I

of numerical estimates of the largest correlating parameters proceeding from those or other physical reasons. In our case, such estimates were made based on the literature data on the spectroscopic parameters of the underlying rovibrational bands of the germane molecule.

The results of solving the inverse spectroscopic problem are presented in Table 4. The whole list of the obtained parameters is quite large and it is difficult to reproduce it considering the limited volume of the work.

TABLE 4. Spectroscopic Parameters of the $Y_{\gamma, \nu' \gamma'}^{\Omega(K, n\Gamma)}$ Vibrational States of the Octad of the $^{76}\text{GeH}_4$ Molecule

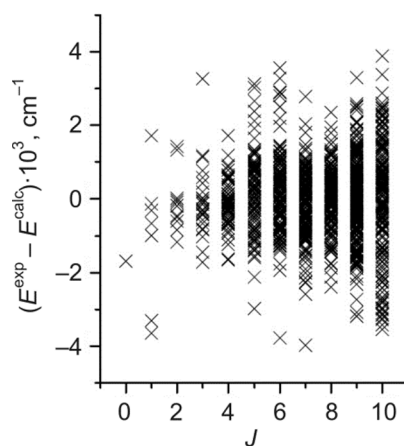
$\Omega(K, n\Gamma)$	$\nu\gamma$	$\nu'\gamma'$	$Y_{\gamma, \nu' \gamma'}^{\Omega(K, n\Gamma)}$
0(0, A_1)	(1100, E)	(1100, E)	-5.92440(32)
1(1, F_1)	(1100, E)	(0110, F_2)	-0.179230(47)
0(0, A_1)	(1001, F_2)	(1001, F_2)	-2.75461(32)
0(0, A_1)	(1001, F_2)	(0011, F_2)	-6.2631(11)
1(1, F_1)	(0110, F_1)	(0110, F_2)	0.6642(58)
0(0, A_1)	(0110, F_2)	(0110, F_2)	-7.296671(64)
1(1, F_1)	(0110, F_2)	(0110, F_2)	-0.358387(67)
2(0, A_1)	(0110, F_2)	(0110, F_2)	0.0094752(43)
2(2, E)	(0110, F_2)	(0110, F_2)	0.0068565(17)
0(0, A_1)	(0011, E)	(0011, E)	-2.42399(92)
1(1, F_1)	(0011, E)	(0011, F_2)	-0.30561(15)
0(0, A_1)	(0011, F_1)	(0011, F_1)	-8.2314(14)
0(0, A_1)	(0011, F_2)	(0011, F_2)	-8.10753(21)
1(1, F_1)	(0300, E)	(0003, F_1)	0.06476(32)
1(1, F_1)	(0300, E)	(0003, F_2)	0.01539(24)
0(0, A_1)	(0201, F_2)	(0201, F_2)	-0.078235(33)
1(1, F_1)	(0201, F_2)	(0201, F_2)	-0.001823(17)
0(0, A_1)	(0201, F_2)	(0201, F_2)	-0.074410(23)
0(0, A_1)	(0201, F_1)	(0201, F_1)	-0.029488(23)
1(1, F_1)	(0201, F_1)	(0201, F_1)	0.0022549(61)
1(1, F_1)	(0201, F_1)	(0201, F_2)	-0.004445(17)
0(0, A_1)	(0201, F_2)	(0201, F_2)	-0.050372(19)
1(1, F_1)	(0201, F_2)	(0201, F_2)	-0.0010587(66)
1(1, F_1)	(0201, F_2)	(0102, E)	-0.002841(25)
1(1, F_1)	(0201, F_2)	(0102, E)	0.007204(21)
1(1, F_1)	(0201, F_2)	(0102, F_1)	-0.001305(17)
0(0, F_1)	(0201, F_2)	(0102, F_2)	0.06044(16)
1(1, F_1)	(0201, F_1)	(0102, E)	0.008014(12)
1(1, F_1)	(0201, F_1)	(0102, A_1)	-0.004988(15)
0(0, A_1)	(0201, F_1)	(0102, F_1)	-0.12450(32)
1(1, F_1)	(0201, F_1)	(0102, F_1)	0.005335(23)
0(0, A_1)	(0201, F_2)	(0003, F_2)	-0.13645(47)
0(0, A_1)	(0201, F_2)	(0003, F_2)	0.03660(42)
0(0, A_1)	(0201, F_1)	(0003, F_1)	0.02279(55)
0(0, A_1)	(0201, F_2)	(0003, F_2)	-0.26189(36)

Therefore, Table 4 presents only the band centers, rotational parameters, and the largest resonant parameters with their 66% confidence intervals given in the parentheses. Values of the parameters of higher order of smallness were estimated theoretically (additional data can be provided by the authors upon request of readers).

The obtained set of 70 variable parameters allows one to reproduce 1184 initial experimental rovibrational energies with a standard deviation of $1.2 \cdot 10^{-3} \text{ cm}^{-1}$ (Fig. 3 shows the diagram of the dependence of $(E^{\text{exp}} - E^{\text{calc}})$ on the quantum number J), which is a quite acceptable result considering the extremely complex rovibrational structure of the octad (Fig. 4). Additional complexity is caused by the circumstance that the intensities of different bands can differ by 2–4 orders of magnitude. As already indicated above, this leads to the fact that the rovibrational lines of ~30% weak bands had not been assigned. Therefore, these bands were considered to be *dark*.

TABLE 4 continued

0(0, A_1)	(0102, E)	(0102, E)	-0.197131(19)
0(0, A_1)	(0102, E)	(0102, E)	0.011551(41)
1(1, F_1)	(0102, E)	(0102, F_1)	0.002505(16)
0(0, A_1)	(0102, A_1)	(0102, A_1)	-0.052591(58)
1(1, F_1)	(0102, A_1)	(0102, F_1)	0.002517(11)
0(0, A_1)	(0102, A_2)	(0102, A_2)	-0.049408(71)
1(1, F_1)	(0102, A_2)	(0102, F_2)	0.009404(25)
0(0, A_1)	(0102, E)	(0102, E)	0.011483(56)
1(1, F_1)	(0102, E)	(0102, F_1)	0.003147(12)
1(1, F_1)	(0102, E)	(0102, F_2)	-0.012627(27)
0(0, A_1)	(0102, F_1)	(0102, F_1)	-0.101789(47)
1(1, F_1)	(0102, F_1)	(0102, F_1)	-0.005296(13)
1(1, F_1)	(0102, F_1)	(0102, F_2)	-0.005564(23)
0(0, A_1)	(0102, F_2)	(0102, F_2)	-0.041639(47)
1(1, F_1)	(0102, F_2)	(0102, F_2)	-0.008038(46)
1(1, F_1)	(0102, E)	(0003, F_1)	-0.007184(34)
1(1, F_1)	(0102, E)	(0003, F_2)	0.004699(30)
1(1, F_1)	(0102, E)	(0003, F_2)	-0.008082(41)
1(1, F_1)	(0102, E)	(0003, F_2)	-0.007630(29)
0(0, A_1)	(0102, F_1)	(0003, F_1)	-0.06279(20)
1(1, F_1)	(0102, F_1)	(0003, F_1)	0.003607(21)
1(1, F_1)	(0102, F_1)	(0003, F_2)	0.011104(36)
0(0, A_1)	(0102, F_2)	(0003, F_2)	-0.052552(56)
1(1, F_1)	(0102, F_2)	(0003, F_2)	-0.001662(15)
1(1, F_1)	(0102, F_2)	(0003, F_1)	-0.004751(55)
0(0, A_1)	(0102, F_2)	(0003, F_2)	-0.14977(56)
1(1, F_1)	(0102, F_2)	(0003, F_2)	0.001923(59)
0(0, A_1)	(0003, F_2)	(0003, F_2)	-0.233910(26)
0(0, A_1)	(0003, F_2)	(0003, F_2)	-0.092072(38)
1(1, F_1)	(0003, F_2)	(0003, F_2)	0.005991(17)
0(0, A_1)	(0003, F_1)	(0003, F_1)	-0.055058(68)
1(1, F_1)	(0003, F_1)	(0003, F_1)	-0.005375(18)
1(1, F_1)	(0003, F_1)	(0003, F_2)	-0.004230(30)
0(0, A_1)	(0003, F_2)	(0003, F_2)	0.020243(68)
1(1, F_1)	(0003, F_2)	(0003, F_2)	0.008011(47)

Fig. 3. Discrepancy values for the energies depending on the quantum number J .

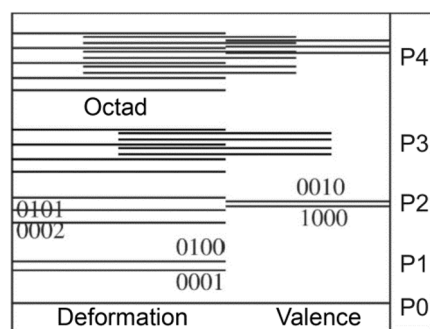


Fig. 4. Scheme of the polyad of the germane molecules comprising dyad P1 consisting of two bands (ν_2 / ν_4), pentad P2 consisting of five bands ($\nu_1/\nu_3 / 2\nu_2/2\nu_4 / \nu_2 + \nu_4$), and octad P3 consisting of eight bands ($\nu_1 + \nu_2/\nu_1 + \nu_4 / \nu_3 + \nu_2/\nu_3 + \nu_4/3\nu_2 / 2\nu_2 + \nu_4/\nu_2 + 2\nu_4 / 3\nu_4$).

CONCLUSIONS

The results obtained in the present work are of interest for solving many problems in astrophysics, planetology, gas analysis, and manufacturing high-purity materials. They are important for solving the problem of high-precision determination of the intramolecular potential function of the germane molecule, where they can be used for calibration of results of *ab initio* calculations, and for independent semiempirical solution of the problem.

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