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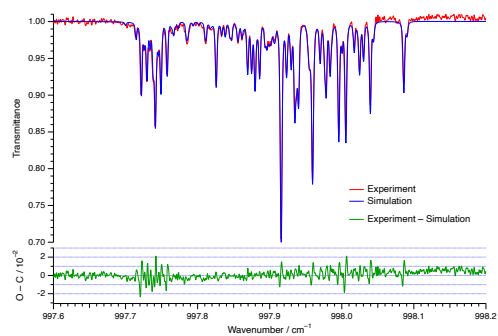
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# Graphical Abstract

## Line positions and intensities for the $\nu_2/\nu_4$ bands of 5 isotopologues of germane near 11.5 $\mu\text{m}$

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## Highlights

**Line positions and intensities for the  $\nu_2/\nu_4$  bands of 5 isotopologues of germane near 11.5  $\mu\text{m}$**

C. Richard, V. Boudon, A. Rizopoulos, J. Vander Auwera, F. Kwabia Tchana

- Complete line position and intensity analysis of the bending region of germane.
- Accurate determination of the Ge–H equilibrium bond length.
- Update of Germane Calculated Spectroscopic Database

# Line positions and intensities for the $\nu_2/\nu_4$ bands of 5 isotopologues of germane near 11.5 $\mu\text{m}$

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## Abstract

Germane is a tetrahedral molecule found in trace abundance in giant gas planets like Jupiter and Saturn. We have recently provided a database of calculated lines of the stretching fundamental bands in the 2100  $\text{cm}^{-1}$  region that is of high interest for planetology (<https://vamdc.icb.cnrs.fr/PHP/GeH4.php>). It is now necessary to study many rovibrational levels, including the lowest ones, in order to access the hot bands and thus to improve the model of the spectral region of interest for Jupiter, especially in the framework of the ongoing Juno mission. We present here a complete analysis and modeling of line positions and intensities in the  $\nu_2/\nu_4$  bending dyad region near 900  $\text{cm}^{-1}$  for all five germane isotopologues in natural abundance. Thanks to the high symmetry of the molecule, we use the tensorial formalism and group theory methods developed in the Dijon group, that allows us to provide a set of effective Hamiltonian and dipole parameters. The present study also leads to a refined value of the Ge–H equilibrium bond length of 1.51714(25) Å. Finally, new calculated germane lines were derived and injected in the GeCaSDa database.

*Keywords:*

Germane, High-Resolution Infrared Spectroscopy, Line positions, Line intensities, Tensorial Formalism

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## 1. Introduction

The presence of germane in the atmosphere of giant planets is known since 1978 and the discovery of the molecule by Fink *et al.* [1] in the atmosphere of Jupiter in trace amount. In 2011, the Juno NASA space probe was launched toward the gas giant carrying the JIRAM

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(Jovian InfraRed Auroral Mapper) spectrometer, covering the large 1.993–5.014  $\mu\text{m}$  range. Since 2016, Juno is orbiting Jupiter, recording data with an accuracy never reached before [2]. Accurate modeling of the  $\text{GeH}_4$  infrared spectrum is now essential, in particular to allow the retrieval of other tropospheric species. In 2018, we have presented the first complete analysis and modeling of line positions and intensities in the strongly absorbing  $\nu_1/\nu_3$  stretching dyad region near  $2100\text{ cm}^{-1}$ , for all five germane isotopologues in natural abundance [3]. This study was recently used by Grassi *et al.* [4] in the analysis of the IR spectro-imager data leading to the creation of latitudinal profiles.

The introduction of our previous paper [3] presented a review of the different spectroscopic analyses conducted by other groups. Since that publication, we can additionally cite the very recent works of Ulenikov *et al.* [5, 6] about the analysis of this same bending dyad and of some hot bands in the  $1100\text{--}1350\text{ cm}^{-1}$  region.

The present work constitutes a complete line position and intensity investigation of the bending region of germane between  $715$  and  $1100\text{ cm}^{-1}$ . Although this region has not the same interest in planetology as the bands analyzed in our previous work, their modeling is an important step in the characterization of hot bands. This study allows us to fit effective Hamiltonian for  $v_2 = 1$  and  $v_4 = 1$  states. The  $\nu_2$  and  $\nu_4$  fundamental bands could be analyzed as an interacting dyad for the five isotopologues that are present in natural abundance:  $^{70}\text{GeH}_4$  (21.23%),  $^{72}\text{GeH}_4$  (27.66%),  $^{73}\text{GeH}_4$  (7.73%),  $^{74}\text{GeH}_4$  (35.94%) and  $^{76}\text{GeH}_4$  (7.44%). We could also perform the fit of the effective dipole moment parameters for these two bands, leading to absolute line intensity predictions. Section 2 details the experimental method, while Section 3 focuses on the theoretical model developed in Dijon. Section 4 presents the line intensity measurements. Then, Section 5 presents and discusses the results of our analyses. The present data also allowed us to determine a new accurate value of the Ge–H equilibrium bond length.

## 2. Experimental details

Ten absorption spectra of germane ( $\text{GeH}_4$ ) have been recorded in the range from  $675$  to  $1210\text{ cm}^{-1}$  using the high-resolution Fourier transform spectrometer (FTS) Bruker IFS125HR located at the LISA facility in Créteil. The instrument was equipped with a silicon carbide Globar source, a KBr/Ge beamsplitter and an optimized home-made MCT detector developed at the AILES beamline [7], used in conjunction with two bandpass optical filters ( $675 - 960$  and  $810 - 1210\text{ cm}^{-1}$ ) to improve the signal-to-noise ratio (S/N). The FTS was continuously evacuated below  $7\text{ Pa}$  by a dry pump to minimize absorption by atmospheric gases. The diameter of the entrance aperture of the spectrometer was set to  $1.5\text{ mm}$ , to maximize the intensity of IR radiation falling onto the detector without saturation or loss of spectral resolution. Interferograms were recorded with a  $40\text{ kHz}$  scanner frequency and a maximum optical path difference (MOPD) of  $473.68\text{ cm}$ . According to the Bruker definition (resolution =  $0.9 / \text{MOPD}$ ), this corresponds to a resolution of  $0.0019\text{ cm}^{-1}$ . The spectra were obtained by Fourier transformation of the interferograms using a Mertz phase correction,  $1\text{ cm}^{-1}$  phase resolution, a zero-filling factor of 2 and no apodization (boxcar option).

Germane 5.0 (99.999 % stated purity) was purchased from Linde Gas and used without further purification. For all the measurements, a small cryogenic cell ( $5.10 \pm 0.01$  cm path length) made of stainless steel to minimize adsorption and corrosion issues, fitted with 9.5 mm diameter, 0.4 mm thick, wedged diamond windows (E6, Netherlands) and housed inside the sample compartment of the Bruker IFS125HR spectrometer, was used. A detailed description of the cell is given in Ref. [8]. The sample pressure in the cell was measured using calibrated MKS Baratron capacitance manometers models 627D (2 and 100 torr full scale) and 628 D (10 torr full scale), characterized by a stated reading accuracy of 0.12 %. Taking into account the uncertainty arising from small variations of the pressure during the recording ( $\sim 0.35$  %), we estimated the measurement uncertainty on the pressure to be equal to 0.5 %. All the spectra were recorded at a stabilized room temperature of  $300 \pm 1$  K.

The following procedure was used to record the spectra. A background spectrum was first collected while the cell was being continuously evacuated. It was recorded at the same resolution as the sample spectra to ensure proper removal of the water vapor absorption lines and of the weak channeling generated by the wedged cell windows. The infrared gas cell was then passivated several times with the  $\text{GeH}_4$  sample. Finally, spectra were recorded for ten different sample pressures of germane. The ten pressures chosen and the number of interferograms recorded and averaged to yield the corresponding spectra are listed in Table 1. All the sample spectra were ratioed against the empty cell background spectrum, and interpolated 4 times. The root mean square (RMS) S/N ratio in the ratioed spectra ranged between 270 and 750. For line position analysis, spectra S2, S4 and S7 were used and were calibrated by matching the measured positions of 32 lines of OCS observed in the 800–1000  $\text{cm}^{-1}$  spectral region to reference wavenumbers available in HITRAN [9] with a RMS deviation of 0.0002  $\text{cm}^{-1}$ . Figs 1 and 2 present an overview of the  $\nu_4$  region for 3 of the spectra recorded and the  $R(4)$  manifold of the  $\nu_4$  band of the five isotopologues studied in the present work, respectively.

### 3. Theoretical model

As already mentioned in our previous work [3], germane is a tetrahedral spherical top molecule with  $T_d$  point group symmetry at equilibrium and possesses four normal modes of vibration. In this study we only focus on the doubly-degenerate mode with  $E$  symmetry,  $\nu_2$ , and the triply-degenerate mode with  $F_2$  symmetry,  $\nu_4$ . They interact and form the  $\nu_2/\nu_4$  bending dyad region and are respectively and approximately centered at 930  $\text{cm}^{-1}$  and 820  $\text{cm}^{-1}$ .

#### 3.1. Effective Hamiltonian operator

Due to the high symmetry of the molecule, we use the tensorial formalism and group theory methods developed in the Dijon group [10, 11]. Let us just recall briefly the principles of this model.

We are here considering an  $\text{XY}_4$  molecule for which the vibrational levels can be grouped into a series of polyads named  $P_k$  with  $k = 0, \dots, n$ ,  $P_{k=0}$  being the ground state (GS). The

Hamiltonian operator is written as follows (assuming that some perturbative treatment such as a contact transformation [12] has been performed to eliminate inter-polyad interactions):

$$\mathcal{H} = \mathcal{H}_{\{P_0 \equiv GS\}} + \mathcal{H}_{\{P_1\}} + \dots + \mathcal{H}_{\{P_k\}} + \dots + \mathcal{H}_{\{P_{n-1}\}} + \mathcal{H}_{\{P_n\}}. \quad (1)$$

where the different  $\mathcal{H}_{\{P_k\}}$  terms are expressed in the following form:

$$\mathcal{H}_{\{P_k\}} = \sum_{\text{all indexes}} t_{\{s\}\{s'\}}^{\Omega(K,n\Gamma)\Gamma_v\Gamma'_v} \beta \left[ \varepsilon V_{\{s\}\{s'\}}^{\Omega_v(\Gamma_v\Gamma'_v)\Gamma} \otimes R^{\Omega(K,n\Gamma)} \right]_{(A_1)}. \quad (2)$$

In this equation, the  $t_{\{s\}\{s'\}}^{\Omega(K,n\Gamma)\Gamma_v\Gamma'_v}$  are the parameters to be determined, while  $\varepsilon V_{\{s\}\{s'\}}^{\Omega_v(\Gamma_v\Gamma'_v)\Gamma}$  and  $R^{\Omega(K,n\Gamma)}$  are vibrational and rotational operators, respectively. For each term,  $\Omega_v$  and  $\Omega$  represent the degree in elementary vibrational operators (creation  $a^+$  and annihilation  $a$  operators), and rotational operators (components  $J_x$ ,  $J_y$  and  $J_z$  of the angular momentum), respectively.  $\varepsilon = (-1)^\Omega$  is the parity under time reversal.  $\beta$  is a factor that allows the scalar terms (terms with  $\Gamma = A_1$ , the totally symmetric irreducible representation of  $T_d$ ) to match the “usual” contributions like  $B_0 J^2$ , *etc.* The order of each individual term is defined as  $\Omega + \Omega_v - 2$ . We deal with the effective Hamiltonians which are obtained, for a given polyad  $P_k$ , by the projection of  $H$  on the  $P_n$  Hilbert subspace:

$$\begin{aligned} \tilde{H}^{<P_n>} &= P^{<P_n>} \mathcal{H} P^{<P_n>} \\ &= H_{\{GS\}}^{<P_n>} + H_{\{P_1\}}^{<P_n>} + \dots + H_{\{P_k\}}^{<P_n>} + \dots + H_{\{P_{n-1}\}}^{<P_n>} + H_{\{P_n\}}^{<P_n>}. \end{aligned} \quad (3)$$

In the case we are interested in,  $\nu_2$  transitions are clearly visible while this band is “forbidden” in absorption. This, and the fact that  $\nu_2$  and  $\nu_4$  are close enough ( $\approx 100 \text{ cm}^{-1}$ ) imply an intensity borrowing by Coriolis coupling. Therefore we shall treat both bands as an interacting dyad, as this is often the case for tetrahedral  $XY_4$  molecules [13, 14, 15].

We thus use the following effective Hamiltonians:

- The ground state effective Hamiltonian,

$$\tilde{H}^{<GS>} = H_{\{GS\}}^{<GS>}. \quad (4)$$

- The  $\nu_2/\nu_4$  bending dyad effective Hamiltonian,

$$\tilde{H}^{<\nu_2/\nu_4>} = H_{\{GS\}}^{<\nu_2/\nu_4>} + H_{\{\nu_2/\nu_4\}}^{<\nu_2/\nu_4>}. \quad (5)$$

### 3.2. Effective dipole moment operator

In order to calculate transition absolute intensities, we also need to expand the effective dipole moment operator in a very similar way to what we did recently in the case of the  $\text{RuO}_4$  [16] and  $\text{SiF}_4$  [17] molecules. This operator, just as the effective Hamiltonian, is expanded as a sum of rovibrational operators, as detailed in Ref. [12]. In the case of the

$\nu_2/\nu_4$  bending dyad, it appears necessary to expand it up to order one plus a single second-order operator (with  $K = 0$  for the rotational part) in the case of  $\nu_4$ . This amounts to a total of four operators and thus to four associated parameters to be fitted using experimental line intensities:

$$\begin{aligned}\tilde{\mu} = & \mu_2^1 \left( R^{1(1,0F_1)} \otimes -V_{\{\text{GS}\}\{\nu_2\}}^{1(A_1E)E} \right)^{(F_2)} \\ & + \mu_4^0 \left( R^{0(0,0A_1)} \otimes +V_{\{\text{GS}\}\{\nu_4\}}^{1(A_1F_2)F_2} \right)^{(F_2)} \\ & + \mu_4^1 \left( R^{1(1,0F_1)} \otimes -V_{\{\text{GS}\}\{\nu_4\}}^{1(A_1F_2)F_2} \right)^{(F_2)} \\ & + \mu_4^2 \left( R^{2(2,0A_1)} \otimes +V_{\{\text{GS}\}\{\nu_4\}}^{1(A_1F_2)F_2} \right)^{(F_2)},\end{aligned}\quad (6)$$

where we used a simplified notation for the effective parameters. Here,  $\mu_4^0$  is the dipole moment derivative relative to the  $q_4$  normal mode coordinates and  $\mu_4^1$  is a rovibrational contribution that corresponds to the usual Herman-Wallis factor, while  $\mu_4^2$  is a second-order rovibrational correction and  $\mu_2^1$  is an induced rovibrational term for the  $\nu_2$  band (this term is induced into the effective dipole moment operator by the contact transformation that isolates the bending dyad; this has been previously explained in the case of methane, CH<sub>4</sub>, see [18]). In Equation 6, the  $R$  and  $V$  symbols represent rotational and vibrational operators, just as in the case of the effective Hamiltonian operator; their construction is detailed in Refs. [12, 19]. In principle, there exist three other rovibrational operators at order two (with  $K = 2$  for the rotational part), but these cannot be determined here (see Section 5.3) and are thus ignored.

### 3.3. Basis sets

The calculation of the effective Hamiltonian and effective dipole moment matrix elements are performed in the coupled rovibrational basis

$$\left| \left[ \Psi_v^{(C_v)} \otimes \Psi_r^{(J,nC_r)} \right]_{\sigma}^{(C)} \right\rangle, \quad (7)$$

where  $\Psi_r^{(J,nC_r)}$  is a rotational wavefunction with angular momentum  $J$ , rotational symmetry species  $C_r$  and multiplicity index  $n$ ;  $\Psi_v^{(C_v)}$  is a coupled vibrational basis set;  $C$  is the overall symmetry species ( $C = C_v \otimes C_r$ ), with component  $\sigma$ . In the present case,  $\Psi_v^{(C_v)}$  contains the relevant functions for the  $\nu_2$  and  $\nu_4$  normal modes of vibration (bending modes),

$$\left| \Psi_{v \sigma_v}^{(C_v)} \right\rangle = \left| (\Psi_{\nu_2}^{(l_2, n_2 C_2)} \otimes \Psi_{\nu_3}^{(l_4, n_4 C_4)})_{\sigma_v}^{(C_v)} \right\rangle, \quad (8)$$

with two contributions:

- For the doubly degenerate mode  $\nu_2$ , we use a symmetrized doubly degenerate harmonic oscillator basis set denoted

$$\left| \psi_{\nu_2 \sigma_2}^{(l_2, C_2)} \right\rangle = \left| \nu_2, l_2, C_2, \sigma_2 \right\rangle, \quad (9)$$

with  $\nu_2 = l_2 = 1$  for the dyad under consideration,  $\nu_2$  and  $l_2$  being the usual vibrational angular momentum quantum numbers and  $C_2 = E$ .



- For the triply degenerate mode  $\nu_4$ , we use a symmetrized triply degenerate harmonic oscillator basis set denoted

$$|\psi_{v_4}^{(l_4, n_4 C_4)}\rangle = |v_4, l_4, n_4, C_4, \sigma_4\rangle, \quad (10)$$

with  $v_4 = l_4 = 1$  for the dyad under consideration,  $v_4$  and  $l_4$  being the usual vibrational angular momentum quantum numbers and  $C_4 = F_2$ , while  $n_4$  is a multiplicity index.

The effective Hamiltonian matrix is diagonalized numerically, and this leads to eigenfunctions obtained from

$$\tilde{H} |\Psi_\sigma^{(J, C, \alpha)}\rangle = E |\Psi_\sigma^{(J, C, \alpha)}\rangle, \quad (11)$$

where  $\alpha = 1, 2, \dots$  numbers functions with the same symmetry  $C$  in a given  $J$  block. This eigenbasis set can be expanded in terms of the initial rovibrational basis set (7) and is used to calculate the matrix elements (in Debye) of the  $Z$  component  $\mu_Z$  of the effective dipole moment operator  $\tilde{\mu}$ , in the laboratory-fixed frame. This  $\mu_Z$  component is related to  $\tilde{\mu}$  from Equation (6) through Stone coefficients [20] and the direction cosines tensor as explained in Section 6.1. of Ref. [10]. The line intensity at temperature  $T$  for a transition at wavenumber  $\tilde{\nu}_{if}$  (in  $\text{cm}^{-1}$ ) between an initial state  $i$  (with energy  $E_i$ , in Joules) and a final state  $f$  is then obtained through:

$$S_{if}(\text{cm}^{-1}/(\text{molecule cm}^{-2})) = \frac{1}{4\pi\epsilon_0} \tilde{\nu}_{if} \frac{8\pi^3}{3hcQ} e^{-\frac{E_i}{k_B T}} \left(1 - e^{-\frac{hc\tilde{\nu}_{if}}{k_B T}}\right) R_{if}, \quad (12)$$

with

$$R_{if} = 3 \sum_{\alpha_i, \alpha_f} \left| \left\langle \Psi_{\sigma_f}^{(J_f, C_f, \alpha_f)} \left| \mu_Z \right| \Psi_{\sigma_i}^{(J_i, C_i, \alpha_i)} \right\rangle \right|^2. \quad (13)$$

$Q$  is the total partition function at temperature  $T$ ,  $c$  the speed of light in vacuum,  $h$  Planck's constant and  $k_B$  Boltzmann's constant. The line strength  $S_{if}$  is expressed here in the so-called "HITRAN unit" [9].

#### 4. Line intensity measurements

As was done in our previous contribution for germane [3], the line intensities were measured using a multi-spectrum fitting program developed in Brussels [21, 22]. This program adjusts a synthetic spectrum to each of any number of observed Fourier transform spectra, using a Levenberg-Marquardt non-linear least-squares fitting procedure. Each synthetic spectrum is the convolution of the molecular transmission spectrum with an instrument line shape function, calculated on a wavenumber scale interpolated 4 times with respect to that of the corresponding observed spectrum. The latter was estimated using the "extended ILS model" of the program *linefit* (version 14.5, [23]) relying on a few isolated strong lines of the  $\nu_4$  band of germane observed in the lowest pressure spectrum, interpolated 16 times and chosen because self broadening could be neglected. Neglecting its wavenumber dependence, the ILS thus determined was used during the multi-spectrum analysis of the spectra. The

profile of the molecular lines was modeled using a Voigt function [24], with Gaussian width always held fixed to the value calculated for the Doppler broadening. The measurements were carried out on small spectral intervals, ranging from 0.015 to 0.60  $\text{cm}^{-1}$  and containing one to several lines. The background in each spectrum was modeled by a polynomial expansion up to the second order.

Of the 10 spectra recorded at pressures in the range 0.13 – 90 torr, 7 were actually used. The measurements performed in the region of the  $\nu_2$  band involved the fitting of the self-broadening coefficients of lines stronger than about  $2.0 \times 10^{-23} \text{ cm}^{-1}/(\text{molecule cm}^{-2})$ . The self broadening coefficients of the other lines were held fixed at  $0.1 \text{ cm}^{-1}\text{atm}^{-1}$ , a rough average of the self broadening coefficients measured in the  $\nu_3$  band [3]. The measurements performed for the  $P$  and  $R$  branches of the weaker  $\nu_2$  band mainly relied on the higher pressure spectra S4 to S7 (Table 1 and Fig. 3). Measurements for high  $J$  lines of the  $P$  branch also involved the lower pressure spectrum S3. Spectrum S7 was excluded from the analysis of the  $Q$  branch of the  $\nu_2$  band because the density of lines combined with pressure broadening led to rather significant overlapping of the lines, as illustrated in Fig. 4. The measurements performed in the region of the  $\nu_2$  band involved the fitting of the self-broadening coefficients of lines stronger than about  $2.0 \times 10^{-23} \text{ cm}^{-1}/(\text{molecule cm}^{-2})$ . It was held fixed at  $0.1 \text{ cm}^{-1}\text{atm}^{-1}$  for the other lines. Spectra corresponding to even higher pressures (30 to 90 torr, S8 to S10 in Table 1) were not used because the blending of lines was obviously more pronounced.

For both bands, the line intensity measurements involved the simultaneous fitting of the selected spectra. The required initial values of the positions and intensities (as well as the assignments) of lines belonging to the  $\nu_4$  and  $\nu_2$  bands of the 5 isotopologues of germane considered in the present work were generated relying on the results of the frequency analysis described in section 5.1. The high quality of the predictions proved to be particularly helpful in the analysis of the  $\nu_2$  band as the lines of the various isotopologues tend to appear close together, as illustrated in Fig. 5. The initial values of the positions and intensities of lines observed in the fitted spectral ranges but not predicted by the frequency analysis (most probably belonging to hot bands) were measured using the program `WSpectra` [25].

Figure 6 presents an example of the results of a fit. It involved 54 lines for a total of 83 fitted parameters. Signatures observed for the stronger lines in the residuals of the lower pressure spectrum may result from an imperfect modeling of the instrument line shape.

Altogether, 447/275, 489/309, 350/183, 512/325 and 355/171 line intensities have been measured for the  $\nu_4/\nu_2$  bands of  $^{70}\text{GeH}_4$ ,  $^{72}\text{GeH}_4$ ,  $^{73}\text{GeH}_4$ ,  $^{74}\text{GeH}_4$  and  $^{76}\text{GeH}_4$ , respectively. They are associated with lines observed in the range from 753 to 1040  $\text{cm}^{-1}$  and range from  $6.1 \times 10^{-24}$  to  $1.2 \times 10^{-19} \text{ cm}^{-1}/(\text{molecule cm}^{-2})$  at 300 K. Although self broadening coefficients have been determined in the present work, we prefer not to report them because of the rather low pressures involved and the fact that most of the lines are rather heavily blended leading to large uncertainties on the measured self broadening coefficients. As a result, no rotational dependence is observed for the 909 measured self broadening coefficients, with average equal to about  $0.075 \text{ cm}^{-1}\text{atm}^{-1}$ .

## 5. Analysis and discussion

### 5.1. Line positions

From Table 1, only experimental spectra S2, S4 and S7 were used in the line position analysis of the  $\nu_2/\nu_4$  bending dyad. Because of the presence of five germane isotopologues in natural abundance, these spectra show a dense structure where many transitions are overlapped. We started the analysis of the most abundant isotopologue,  $^{74}\text{GeH}_4$ , using initial parameters taken from our work on the  $\nu_1/\nu_3$  region and unpublished results that were included in the STDS (Spherical-Top Data System) package [26], part of the XTDS (eXtended spherical-Top Data System) software [27]. The calculation performed using these parameters led to a very good initial spectrum simulation that allowed to assign many transitions in P and R branches.

Assignments were made using the home made software SPVIEW (Spectrum-View) [27] in its new 2.0 beta version. The Q branch shows a higher transition density making assignments not straightforward. However, using a standard iterative Levenberg-Marquardt non-linear least squares fitting procedure, simulations and new assignment sets, we finally reached a total of 1394 assigned transitions, up to  $J = 25$ , with a set of 26 parameters and a root mean squares deviation of  $4.86 \times 10^{-4} \text{ cm}^{-1}$ . Each line position was considered to have the same uncertainty of  $10^{-3} \text{ cm}^{-1}$ , which accounts for both peak position and global calibration uncertainties. GS parameters of the five isotopologues were fixed to their fitted values taken from the results of Ref. [3].

Once transition assignment was completed for the main isotopologue, we have used same parameters to investigate the less abundant isotopologues. For each isotopologue, only the band center was updated, trying to visually match most transitions. The same fit procedure as described above was then repeated. Parameters that could not be correctly fitted were fixed to the value of  $^{74}\text{GeH}_4$ .

The results and fit statistics for all five isotopologues are presented in Table 2. Seven parameters are used to define  $v_2 = 1$  up to order 4, 13 for  $v_4 = 1$  up to order 5 and six interactions parameters between states  $v_2 = 1$  and  $v_4 = 1$ . The last column of the table allows to convert all these constant values to the ‘‘classical’’ notation. We obtained a very good fit whose root mean squares deviation is  $4.58 \times 10^{-4} \text{ cm}^{-1}$ ,  $5.75 \times 10^{-4} \text{ cm}^{-1}$ ,  $3.10 \times 10^{-4} \text{ cm}^{-1}$ ,  $4.86 \times 10^{-4} \text{ cm}^{-1}$  and  $3.03 \times 10^{-4} \text{ cm}^{-1}$  for each isotopologue ( $^{70}\text{GeH}_4$ ,  $^{72}\text{GeH}_4$ ,  $^{73}\text{GeH}_4$ ,  $^{74}\text{GeH}_4$ ,  $^{76}\text{GeH}_4$ ), respectively.

In Ref. [5], Ulenikov *et al.* have presented comparable results, but using a different reduction (fix parameters are not the same). In our case we have significantly high number of assignments up to higher  $J$  values.

Figure 7 presents the fit residuals for line positions. Some polynomial deviation seems to appear in the  $\nu_4$  region (below  $900 \text{ cm}^{-1}$ ). This may correspond to some higher order contributions to the effective Hamiltonian that we could not fit here. But the residuals remain very small, anyway.

Figure 8 shows the reduced energy levels in the case of  $^{74}\text{GeH}_4$ , defined by

$$\tilde{\nu}_{\text{red}} = \tilde{\nu} - \sum_{\Omega} t_{\{\text{GS}\}\{\text{GS}\}}^{\Omega(0,0A_1)A_1A_1} (J(J+1))^{\Omega/2}$$

$$= \tilde{\nu} - B_0J(J+1) + D_0J^2(J+1)^2 - \dots, \quad (14)$$

where  $B_0, D_0, \dots$  are ground state values, *i.e.* we subtract the dominant scalar polynomial terms in order to enhance levels splittings due to molecular symmetry. The colors illustrate the mixings due to the interaction between the two vibrational levels. We give both the calculated and observed reduced energy levels. Observed levels are simply levels reached by assigned transitions which are included in the fit. This gives a good idea of the sampling of the energy spectrum. The four other isotopologues lead to a very similar picture. This figure allows to judge the quality of the simulation performed using the present effective Hamiltonian parameters, when extrapolating to unassigned  $J$  values.

In Ref. [28], we have studied the isotopic dependance of band centers and Coriolis-interaction parameters, using a simple model and the present values. More detail is given in Figure 2 of this reference.

### 5.2. Equilibrium bond length

The determination of the equilibrium bond length  $r_e$  of a spherical-top molecule (which is the unique geometrical parameter that defines its equilibrium structure) is possible if one knows the value of the rotational constant  $B_0$  in the ground state and rotational constant differences in all the vibrational fundamental levels, say  $\Delta B_i = B_i - B_0$  ( $i = 1$  to 4), where  $B_i$  is the rotational constant in an excited state with  $\nu_i = 1$  [29]. The formula giving  $B_e$  (equilibrium value) is [14]:

$$B_e = B_0 - \frac{1}{2} \sum_{i=1}^4 d_i \Delta B_i, \quad (15)$$

where  $d_i$  is the normal mode degeneracy ( $d_1 = 1, d_2 = 2, d_3 = d_4 = 3$ ). The equilibrium bond length is then [14]:

$$r_e = \sqrt{\frac{3h}{64\pi^2 c m_H B_e}}, \quad (16)$$

$h$  being Planck's constant,  $c$  the speed of light in vacuum and  $m_H$  the hydrogen atom mass, whose values are taken from Ref. [30]. The fitted parameters  $B_0 = t_{\{0\}\{0\}}^{2(0,0A_1)A_1A_1}$  and  $\Delta B_i = t_{\{i\}\{i\}}^{2(0,0A_1)\Gamma_v\Gamma_v}$  ( $i = 1$  to 4) result from the line position fits in Table 2 of Ref. [3] and in the present work (see Table 2). Using these fitted values and their standard deviation and averaging over all 5 isotopologues, we get:

$$B_e = 2.72531(95) \text{ cm}^{-1}, \quad (17)$$

and thus:

$$r_e(\text{GeH}_4) = 1.51710(27) \text{ \AA}. \quad (18)$$

It should be recalled that, within the Born-Oppenheimer approximation, structural parameters like  $r_e$  do not depend on the isotopologue.

Somewhat higher values can be found in rather old references. The *CRC Handbook of Chemistry and Physics* [31] reports an experimental value  $r_e = 1.5251 \text{ \AA}$ , while Yu *et al.*

obtain a theoretical *ab initio* value  $r_e = 1.5358 \text{ \AA}$  [32]. However, in our previous work on  $^{70}\text{GeD}_4$  [33], we reported  $r_e = 1.5173(1) \text{ \AA}$ , which is fully consistent with the present determination. Thus, going back to this Ref. [33], we can take again parameter values from its Tables 1 to 3 and include the accurate  $^{70}\text{GeD}_4$  value in our average calculation, leading finally to:

$$r_e(\text{GeH}_4, \text{GeD}_4) = 1.51714(25) \text{ \AA}. \quad (19)$$

Since the present study relies on highly accurate high-resolution spectroscopic data, it should be very reliable. Even considering a  $3\sigma$  uncertainty (that would be  $0.00075 \text{ \AA}$ ), this rules out the previous higher values from the literature that we mentioned above. The value presented here can serve as a benchmark for new quantum chemistry calculations.

### 5.3. Line intensities

As explained in Section 4, the line positions and relative intensities prediction resulting from the effective Hamiltonian fit in Section 5.1 were useful for the measurements of absolute line intensities. By comparison with the theoretical predictions of line positions, this made possible the assignment of these lines for an intensity fit. We could then perform, for each isotopologue, a fit of the four effective dipole moment parameters up to order 2 that we described in Section 3.2 (as already mentioned, other operators at order two cannot be fitted and are ignored here). In this fit we consider only lines for which the relative observed minus calculated difference is below 10 %. This constitutes an extended intensity analysis in the bending dyad of germane, using several hundreds of intensity data for each isotopologue.

The resulting effective dipole moment parameters and fit statistics are displayed in Table 3. We get a very satisfactory result, with a relative standard deviation below 4 %, for all isotopologues.

We can compare these results with the recent work of Ulenikov *et al.* [5]. For each isotopologue we have used around twice more assigned lines and higher  $J$  values by two or three units. We notice that we get different values as well as a much smaller isotopic dependence for the dipole parameters of order 1 and 2.

Figure 9 displays the intensities for assigned lines, as well as the fit residuals for line intensities, for all five isotopologues. Figure 10 shows a simulation of the five germane isotopologues in natural abundance using the parameters derived from the fits in position and intensity discussed above. Figures 11 and 12 show a comparison and the difference between the experimental and simulated spectra (obtained using the effective Hamiltonian and dipole moment parameters fitted in this study) for the  $\nu_4$  region and for a small part of the  $\nu_2$  region, respectively.

## 6. GeCaSDa database update

We have updated the GeCaSDa database [34] by using an polyad scheme adapted to the  $\nu_2/\nu_4$  bending dyad. The first scheme that was defined previously is dedicated to the  $\nu_1/\nu_3$  fundamental bands and the second and new one to the present analysis. The complete database is illustrated in Table 4, where  $P_0$  is the ground state and  $P_1$  contains the fundamental levels ( $v_1 = 1$  and  $v_3 = 1$  for the first scheme and  $v_2 = 1$  and  $v_4 = 1$  for the second

one). An amount of 28 486 new transitions have been included in the database increasing to 60 878 the total number of lines. The calculated data are accessible either through our website at <http://vamdc.icb.cnrs.fr/PHP/gecasda.php> or on the VAMDC portal at [https://portal.vamdc.eu/vamdc\\_portal](https://portal.vamdc.eu/vamdc_portal). Our webpage allows to plot the data and download two sorts of file formats: the line by line list is given following the HITRAN 2004 format [35], while cross section is a simple 2-column flat file. An overview of the GeCaSDa database is displayed Figure 13, as downloadable from our website.

## 7. Conclusion

We have presented here a complete high-resolution study of both line positions and absolute line intensities of the  $\nu_2/\nu_4$  bending dyad of germane, for its five isotopologues in natural abundance. We could determine accurate effective Hamiltonian and dipole moment parameters thanks to a series of high-quality infrared spectra. An accurate value of the Ge–H bond length has been derived. New calculated quantitative line lists have been derived and added to the GeCaSDa database [34], available from the VAMDC portal [36, 37, 38, 39]. These data will also be provided to the other public spectroscopic databases [9, 40].

Lines lists with assignments for line positions and line intensities are provided as supplementary material for this paper.

Although the bending dyad region is not the one used for the planetological detection of germane, the two low-lying vibrational levels which are characterized here are the main source of the hot bands in the  $\nu_1/\nu_3$  stretching region, like  $\nu_3 + \nu_2 - \nu_2$ ,  $\nu_3 + \nu_4 - \nu_4$ , *etc.* The present results are thus an essential first step towards the simulation of such hot bands of planetological interest. The next step will be the study of the upper states of these hot bands, through the analysis of combination bands like  $\nu_3 + \nu_2$ ,  $\nu_3 + \nu_4$ , ...

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# Figures

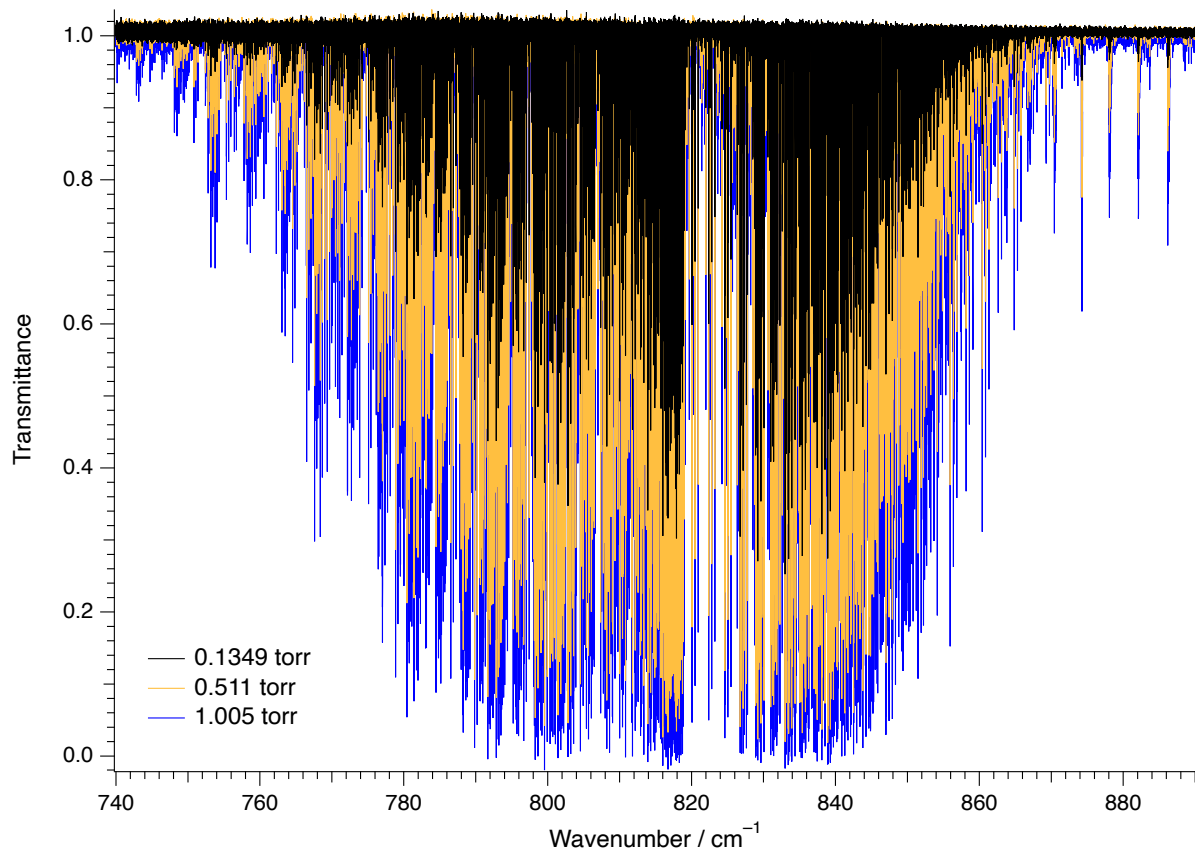


Figure 1: Overview of the high resolution ( $0.0019 \text{ cm}^{-1}$ ) spectrum of the  $\nu_4$  band of a sample of germane in natural isotopic abundance. The temperature and absorption path length were 300 K and 5.1 cm, respectively. The 3 spectra presented (S1 to S3 in Table 1) were used in the present work to retrieve line intensities for that band.

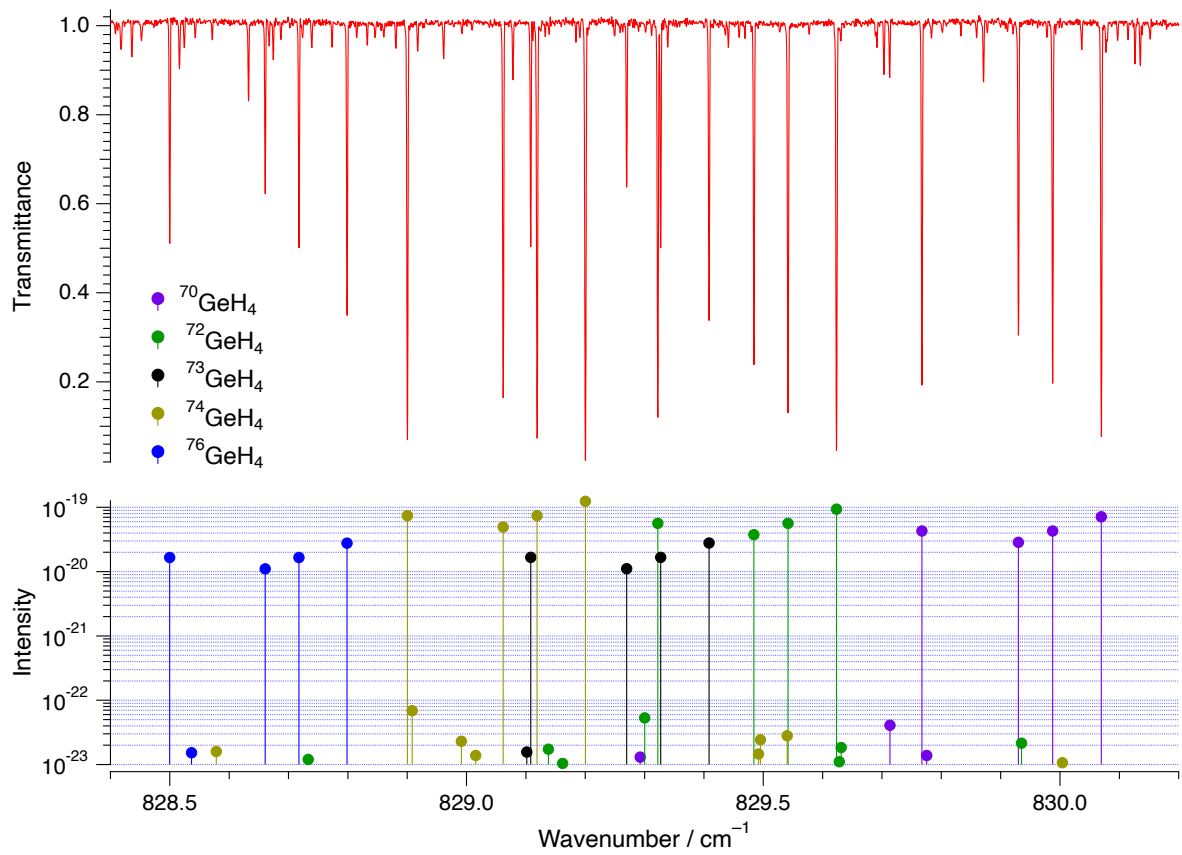


Figure 2: High resolution ( $0.0019 \text{ cm}^{-1}$ ) spectrum of the  $R(4)$  manifold in the  $\nu_4$  band of the 5 isotopologues of germane studied in the present work. The observed spectrum is presented in the upper panel (S2 in Table 1). The lower panel displays the integrated absorption cross sections of the lines of the various isotopologues [in  $\text{cm}^{-1}/(\text{molecule cm}^{-2})$  at 300 K], predicted by the theoretical model.

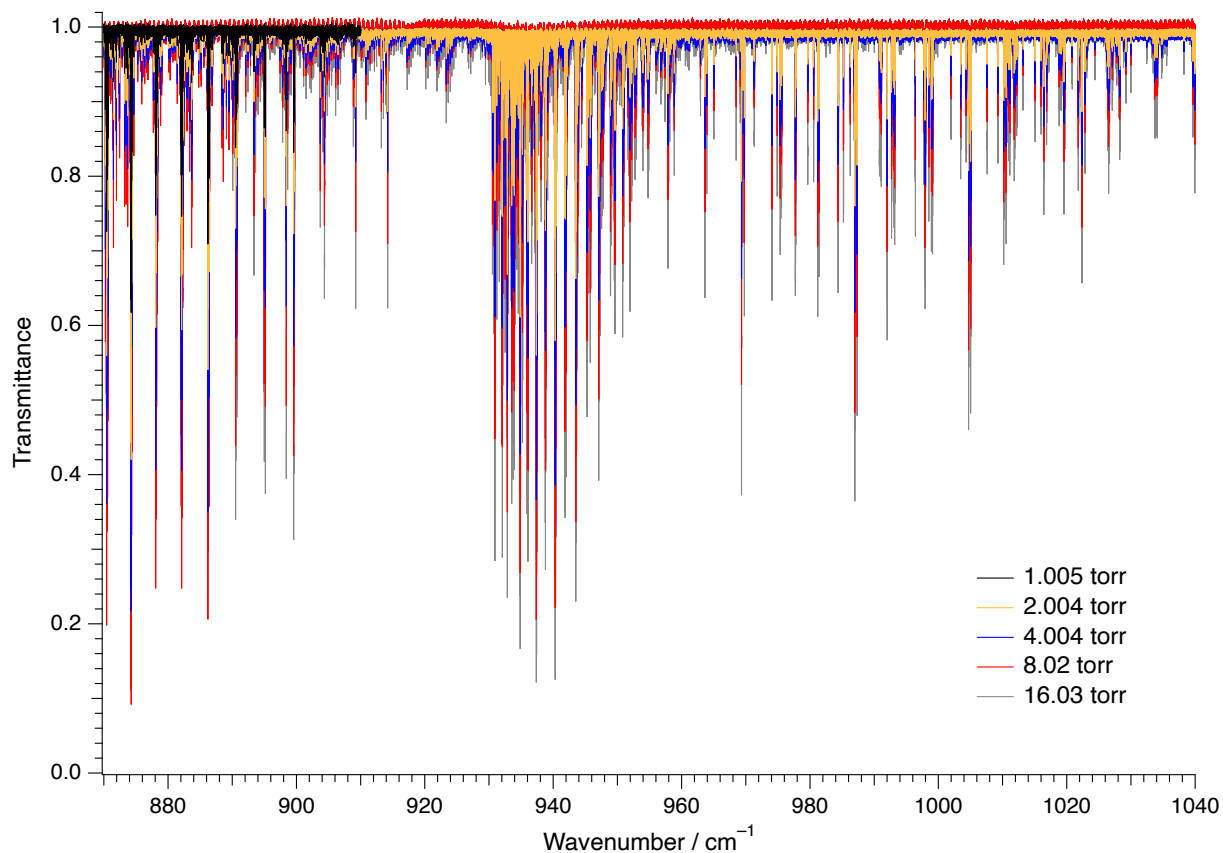


Figure 3: Overview of the high resolution ( $0.0019 \text{ cm}^{-1}$ ) spectrum of the  $\nu_2$  band of a sample of germane in natural isotopic abundance. The temperature and absorption path length were and 300 K and 5.1 cm, respectively. The 5 spectra presented (S3 to S7 in Table 1) were used in the present work to retrieve line intensities for that band.

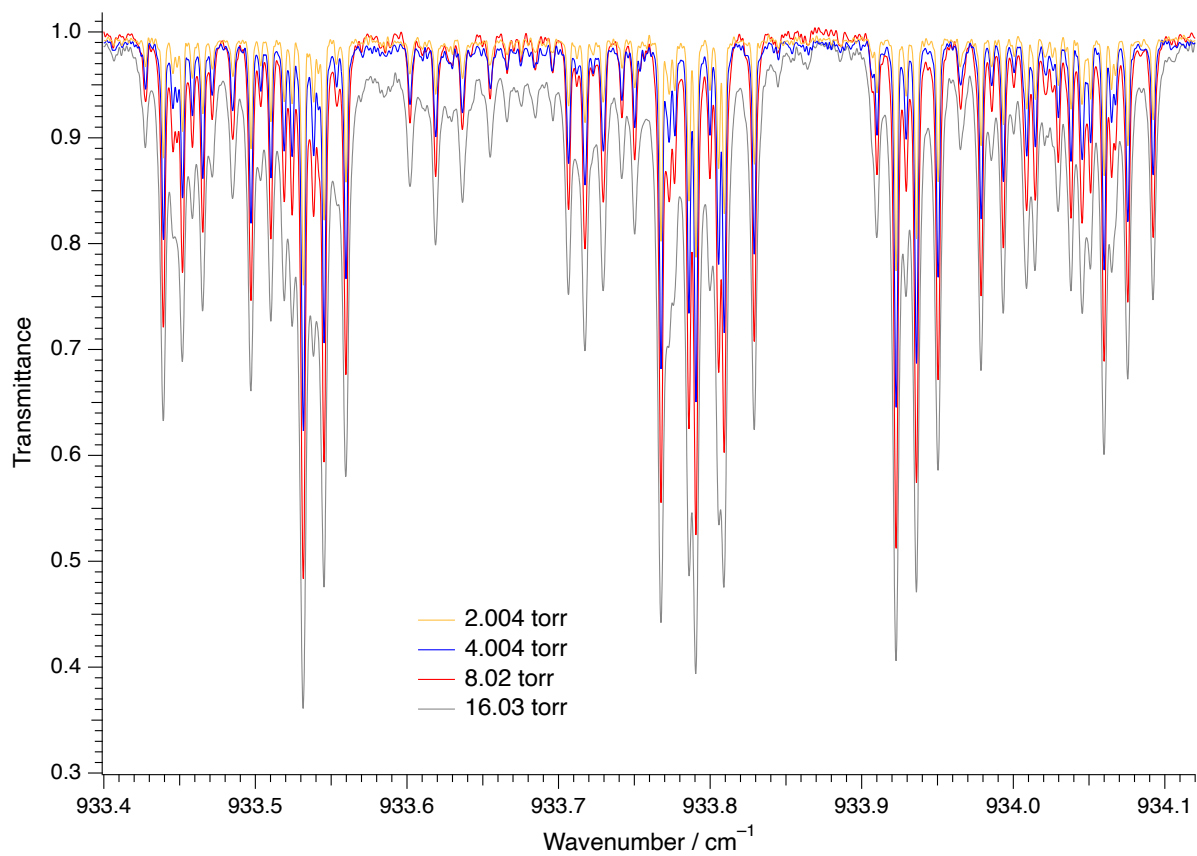


Figure 4: Same as Fig. 3 (upper panel), showing a small part of the  $Q$  branch of the  $\nu_2$  band of the 5 isotopologues of germane studied in the present work.

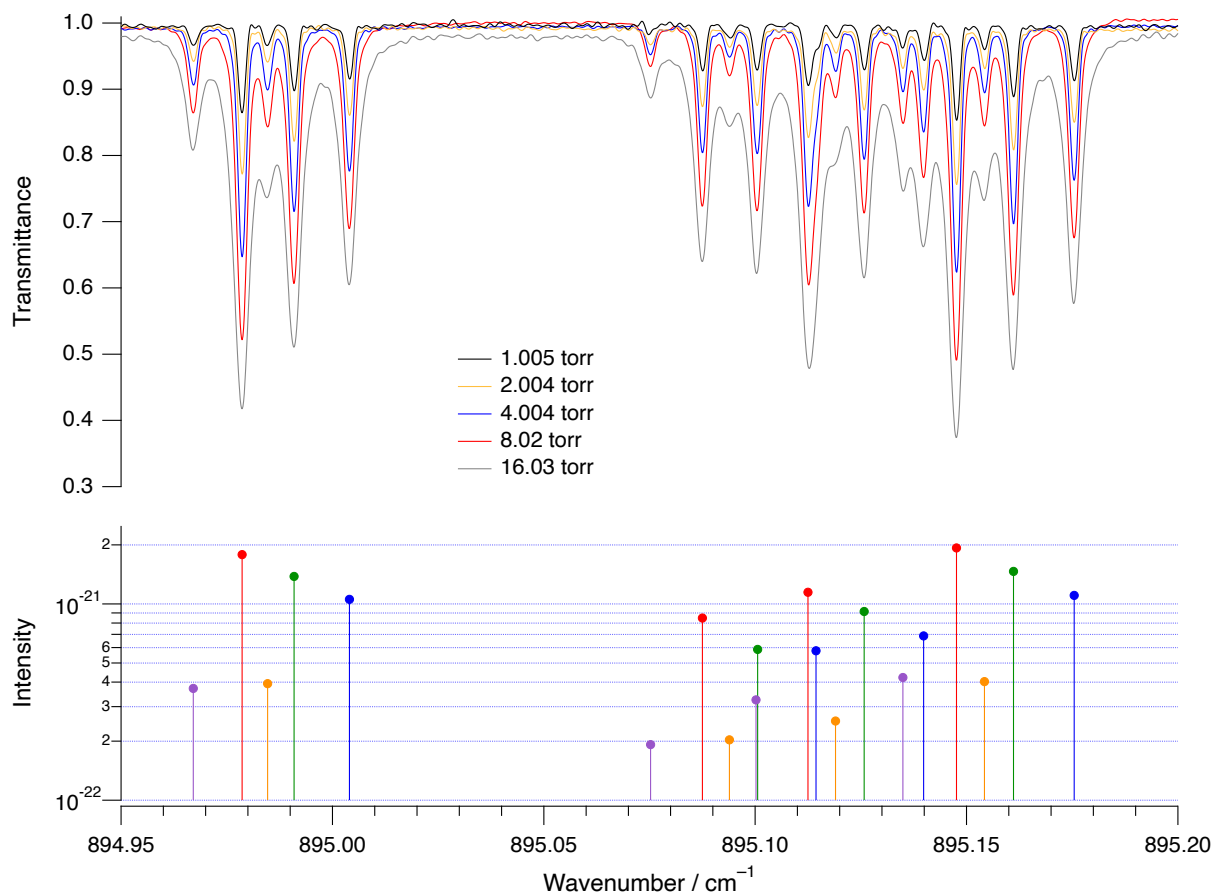


Figure 5: High resolution ( $0.0019 \text{ cm}^{-1}$ ) spectra of a small part of the  $P$  branch of the  $\nu_2$  band of the 5 isotopologues of germane studied in the present work, showing the increase with pressure of the spectral congestion. The lower panel displays the integrated absorption cross sections of the lines of the various isotopologues [in  $\text{cm}^{-1}/(\text{molecule cm}^{-2})$  at 300 K], predicted by the theoretical model (blue:  $^{70}\text{GeH}_4$ ; green:  $^{72}\text{GeH}_4$ ; orange:  $^{73}\text{GeH}_4$ ; red:  $^{74}\text{GeH}_4$ ; violet:  $^{76}\text{GeH}_4$ ).

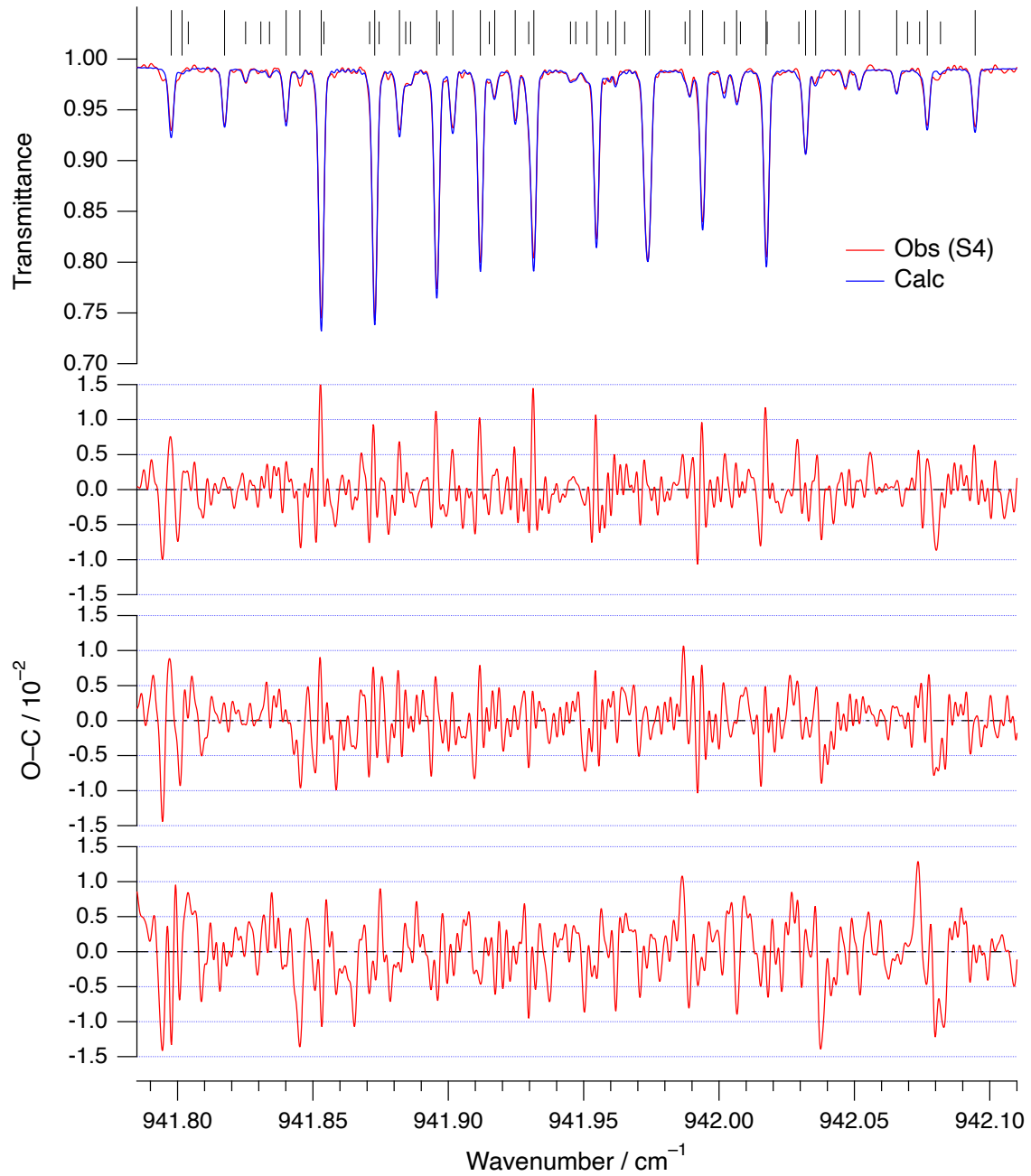


Figure 6: Results of the multi-spectrum analysis applied to 3 spectra (S4 to S6 in Table 1) of a portion of the  $Q$  branch of the  $\nu_2$  band of germane in natural isotopic abundance: observed (spectrum S4; red) and best-fit calculated (blue) spectra (top panel), and best-fit residuals corresponding to spectra S4 to S7 (from top to bottom). The vertical bars at the top indicate the positions of the lines included in the analysis, the taller ones identifying the lines for which at least one parameter (position, intensity or self broadening coefficient) was fitted.



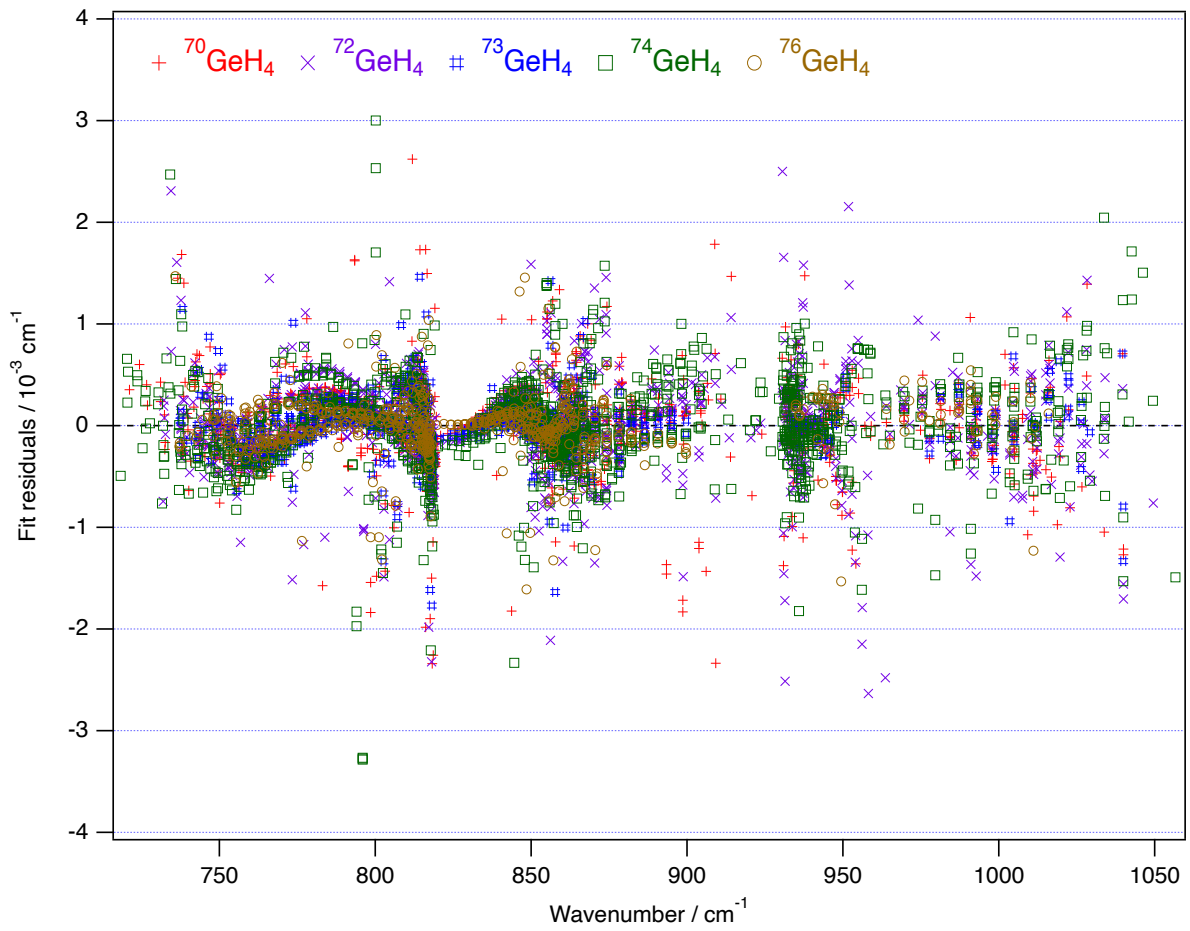


Figure 7: Fit residuals for line positions, for the five isotopologues under consideration, as a function of the wavenumber.

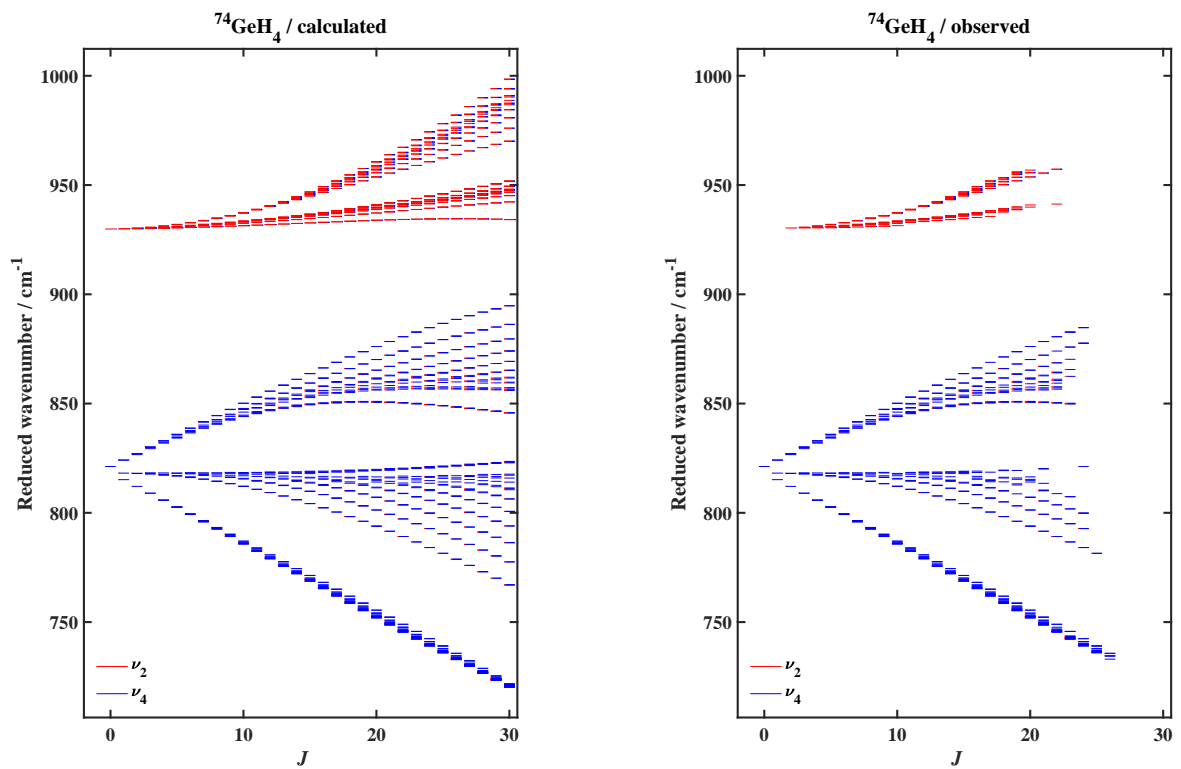


Figure 8: Calculated (left panel) and observed (right panel) reduced energy levels for  $^{74}\text{GeH}_4$ , as a function of the rotational quantum number  $J$ . Observed levels correspond to levels reached by assigned transitions. The colors indicate the mixings between both vibrational levels, *i.e.* the projection of each eigenlevel on the  $\nu_2 = 1$  (red) and  $\nu_4 = 1$  (blue) initial normal mode basis set.

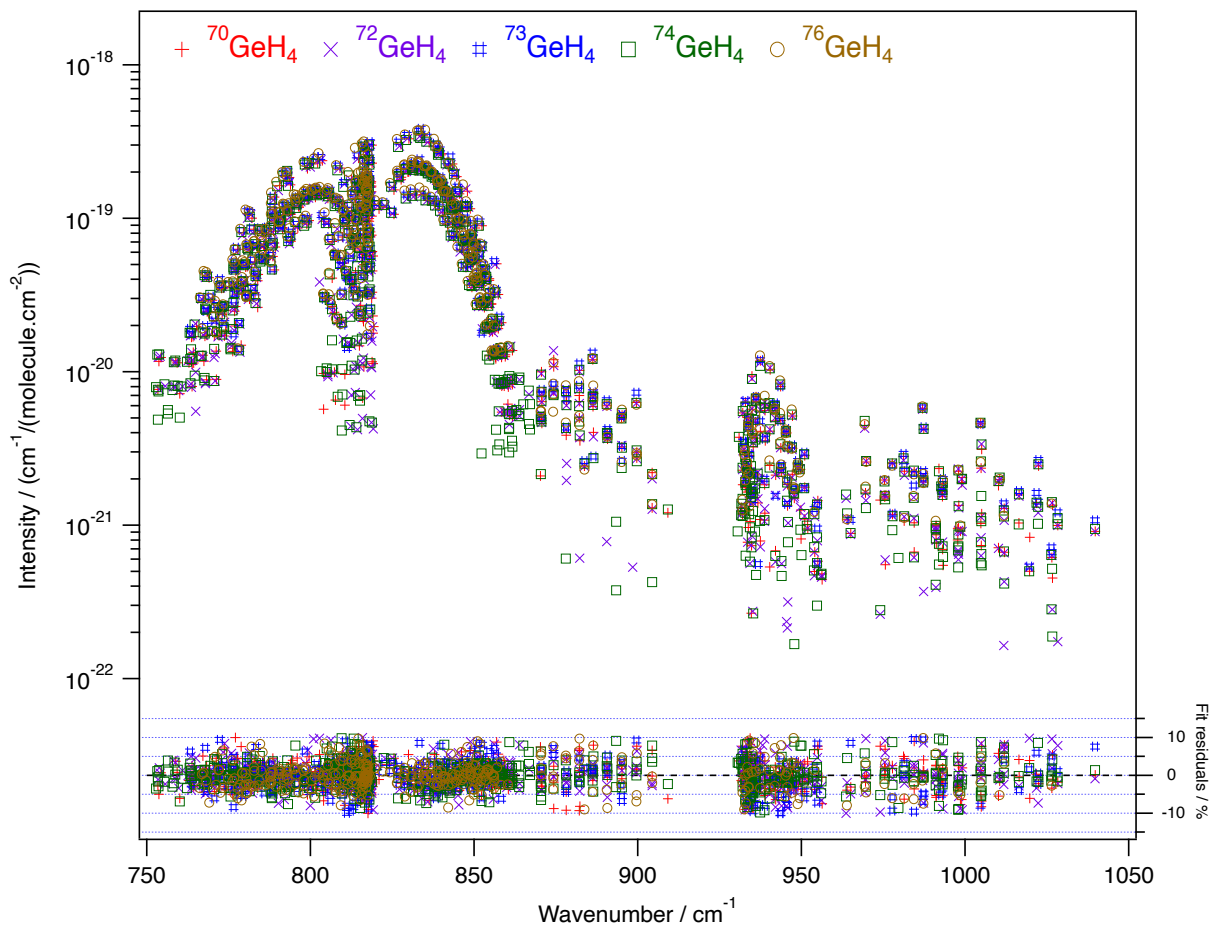


Figure 9: Line intensities for assigned lines (top panel) and relative effective dipole moment fit residuals (bottom panel), for the five isotopologues under consideration, as a function of the wavenumber.

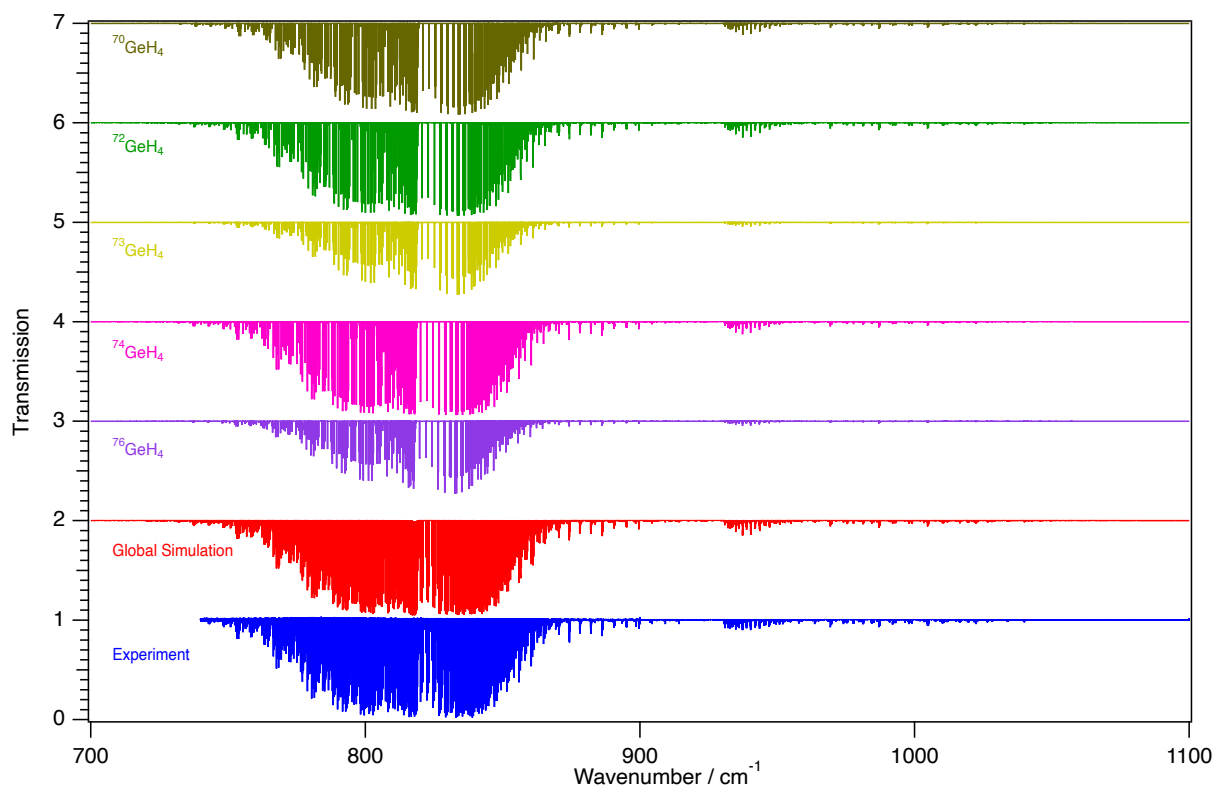


Figure 10: Spectrum simulation overview of all five germane isotopologues in natural abundance. The red curve is the total simulation including all five isotopologues. For the experimental curve (in blue), we used spectra S2 (for the  $\nu_4$  region, below  $900\text{ cm}^{-1}$ ) and S7 (for the  $\nu_2$  region, above  $900\text{ cm}^{-1}$ ) since both bands were recorded under different conditions (see Table 2). On this figure, the intensity of the S7 spectrum was multiplied by a factor 0.12 in intensity, for sake of clarity.

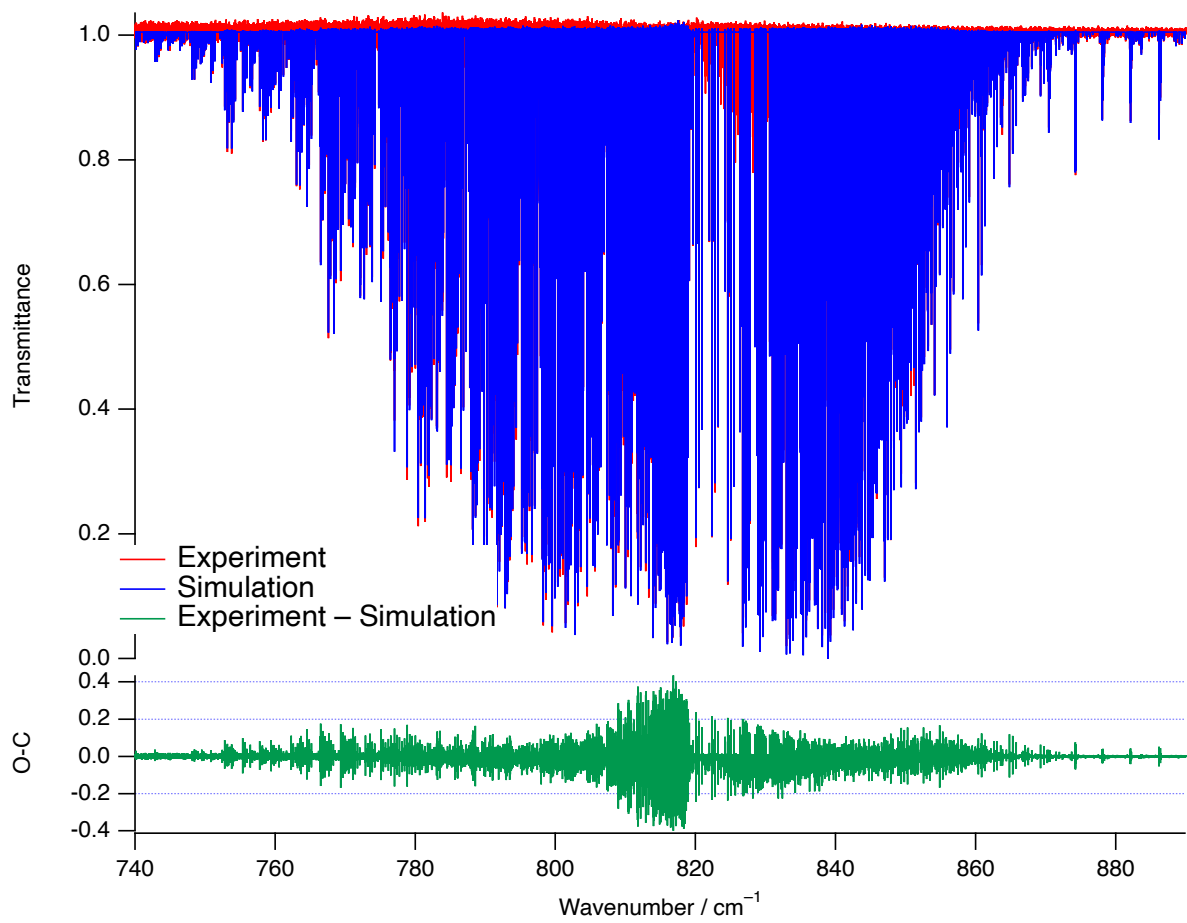


Figure 11: Comparison between experimental spectrum S2 (see Table 1) and the simulation under the same conditions (top panel) in the  $\nu_4$  region for the five isotopologues in natural abundance. The bottom panel displays the difference between these two curves.

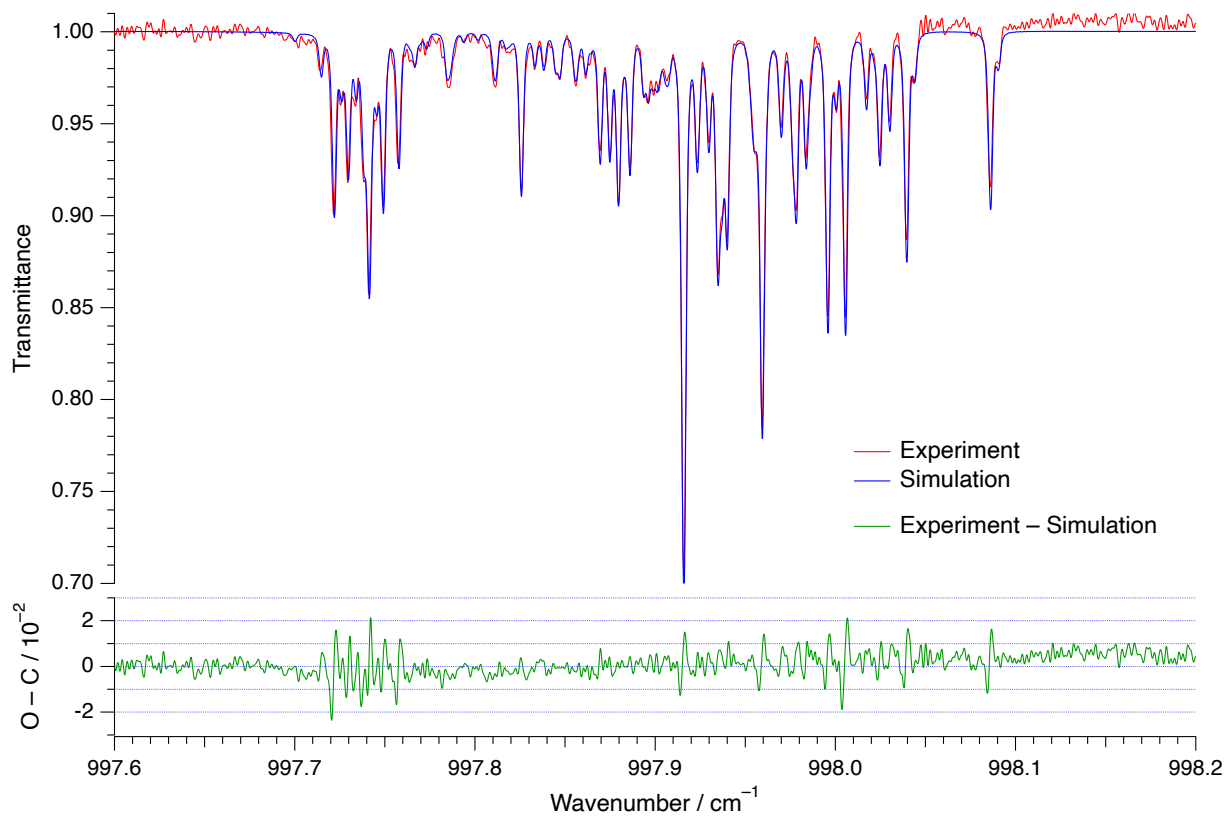


Figure 12: Comparison between experimental spectrum S6 (see Table 1) and the simulation under the same conditions (top panel) in the  $R(10)/R(11)$  manifold region of the  $\nu_2$  band for the five isotopologues in natural abundance. The bottom panel displays the difference between these two curves. The simulated spectrum is calculated using a constant baseline, set to 1.

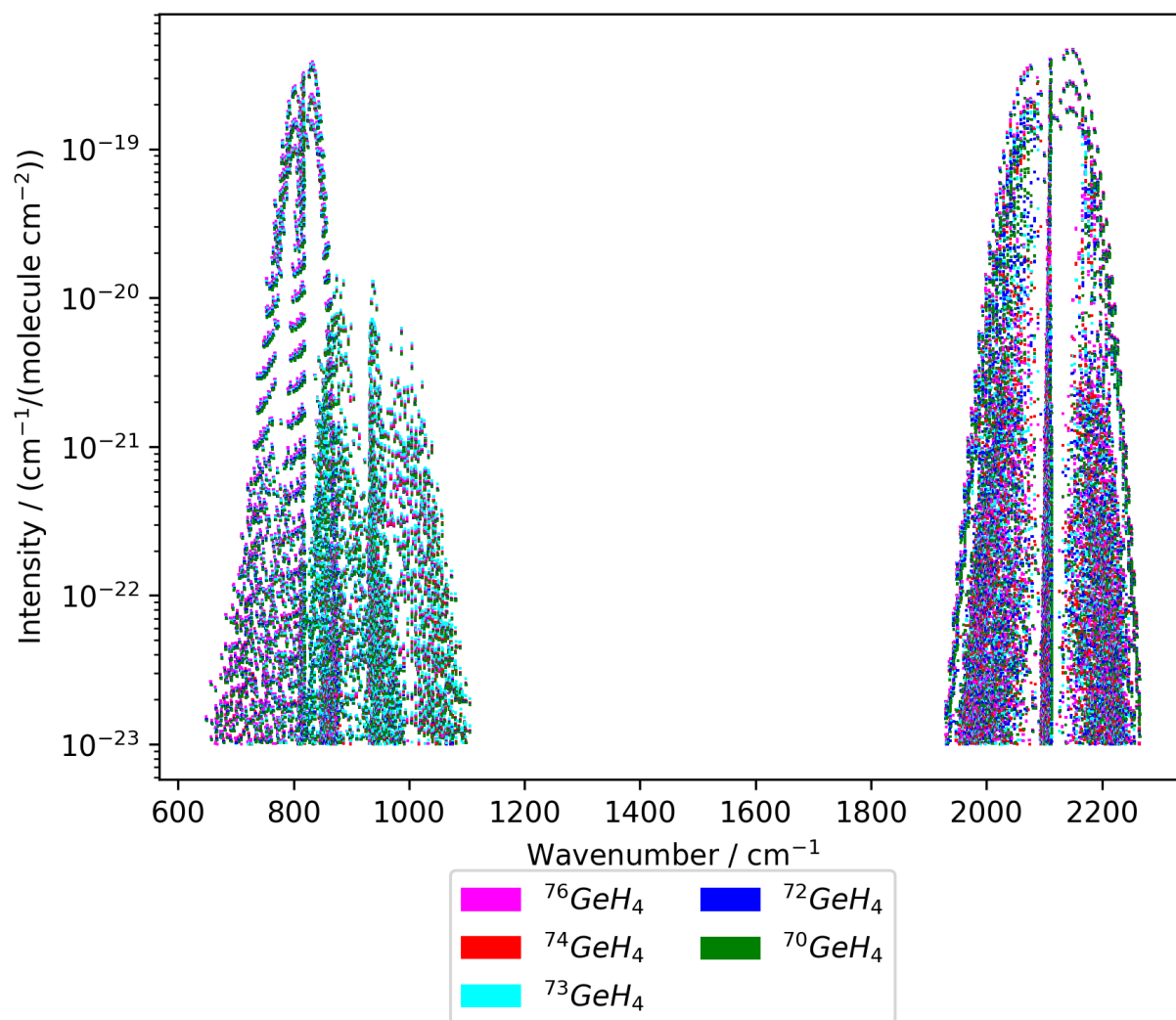


Figure 13: Extracted line by line list plotted on a graph as shown at the GeCaSDa web page (<https://vamdc.icb.cnrs.fr/PHP/GeH4.php>).

# Tables



Table 1: Pressure of GeH<sub>4</sub> (in torr), spectral range recorded and number of interferograms averaged to yield the corresponding spectrum (# scans). All the spectra were recorded with an absorption path length of  $5.10 \pm 0.01$  cm, at a stabilized room temperature of  $300 \pm 1$  K, a resolution (equal to 0.9 divided by the maximum optical path difference) of  $0.0019 \text{ cm}^{-1}$  and an entrance aperture diameter of the interferometer equal to 1.5 mm. The absolute uncertainty on the pressure is equal to 0.5 % of the value given.

#	$P(\text{GeH}_4)$	Range / $\text{cm}^{-1}$	# scans
S1	0.1349 (7)	740 – 900	80
S2	0.511 (3)	740 – 890	80
S3	1.005 (5)	730 – 910	80
S4	2.004 (10)	715 – 1100	240
S5	4.004 (20)	715 – 1100	260
S6	8.02 (4)	715 – 1100	80
S7	16.03 (8)	900 – 1100	80
S8	30.07 (15)	900 – 1100	80
S9	60.05 (30)	900 – 1100	80
S10	89.97 (45)	900 – 1100	240

Table 2: Effective Hamiltonian parameters for the ground vibrational state,  $v_2 = 1$  and  $v_4 = 1$  levels of all five isotopologues of germane. Standard deviation is indicated in parenthesis, in the unit of last two digits.

Vibrational level ( $\tilde{H}$ ) or Transition ( $\tilde{\mu}$ )	Order	$\Omega(K, nC)$	$\{s\}$	$C_1$	$\{s\}$	$C_2$	$^{70}\text{GeH}_4$	$^{72}\text{GeH}_4$	$^{73}\text{GeH}_4$	$^{74}\text{GeH}_4$	$^{76}\text{GeH}_4$	Notation of Robiette <i>et al.</i> (when defined)
GS	0	2(0, 0A <sub>1</sub> )	0000A <sub>1</sub>	0000A <sub>1</sub>	0000A <sub>1</sub>	0000A <sub>1</sub>	2.6958644 †					$B_0$
GS	2	4(0, 0A <sub>1</sub> )	0000A <sub>1</sub>	0000A <sub>1</sub>	0000A <sub>1</sub>	0000A <sub>1</sub>	-3.3418 †					$-D_0$
GS	2	4(4, 0A <sub>1</sub> )	0000A <sub>1</sub>	0000A <sub>1</sub>	0000A <sub>1</sub>	0000A <sub>1</sub>	-1.5464 †					$-(\sqrt{15}/4\sqrt{2}) D_{0t}$
GS	4	6(0, 0A <sub>1</sub> )	0000A <sub>1</sub>	0000A <sub>1</sub>	0000A <sub>1</sub>	0000A <sub>1</sub>	1.142 †					$H_0$
GS	4	6(4, 0A <sub>1</sub> )	0000A <sub>1</sub>	0000A <sub>1</sub>	0000A <sub>1</sub>	0000A <sub>1</sub>	-4.97 †					$(3\sqrt{5}/16\sqrt{2}) H_{4t}$
GS	4	6(6, 0A <sub>1</sub> )	0000A <sub>1</sub>	0000A <sub>1</sub>	0000A <sub>1</sub>	0000A <sub>1</sub>	-1.600 †					$-(\sqrt{231}/64\sqrt{2}) H_{4t}$
$v_2 = 1$	0	0(0, 0A <sub>1</sub> )	0100E	0100E	0100E	0100E	929.90124(19)	929.90513(17)	929.90728(48)	929.90910(15)	929.91308(44)	$\nu_2$
$v_2 = 1$	2	2(0, 0A <sub>1</sub> )	0100E	0100E	0100E	0100E	5.25(30)	5.48(32)	4.80(69)	5.32(22)	4.62(68)	$B_2 - B_0$
$v_2 = 1$	2	2(2, 0E)	0100E	0100E	0100E	0100E	-6.08(26)	-5.88(28)	-6.47(61)	-6.01(19)	-6.64(60)	$\sqrt{3}b_2 + 24(\sqrt{3}/7) C_6$
$v_2 = 1$	3	3(3, 0A <sub>2</sub> )	0100E	0100E	0100E	0100E	-2.542(99)	-2.60(11)	-2.41(18)	-2.527(78)	-2.26(21)	$(1/2) d_2$
$v_2 = 1$	4	4(0, 0A <sub>1</sub> )	0100E	0100E	0100E	0100E	7.92(32)	7.48(28)	7.55(19)	7.64(22)	9.07(76)	$-(D_2 - D_0)$
$v_2 = 1$	4	4(2, 0E)	0100E	0100E	0100E	0100E	-9.06(29)	-8.77(26)	-8.75 †	-8.75(19)	-0.996(70)	$-(3/4) C_5 + (9/7) C_6$
$v_2 = 1$	4	4(4, 0A <sub>1</sub> )	0100E	0100E	0100E	0100E	6.6(1.2)	5.1(1.0)	5.91 †	5.91(85)	1.03(29)	$-(\sqrt{15}/4)(D_{2t} - D_{1t})$
$v_2 = 1$	4	4(4, 0E)	0100E	0100E	0100E	0100E	0.0 †	0.0 †	0.0 †	0.0 †	0.0 †	$-(3\sqrt{3}/7) C_6$
$v_2 = 1/v_4 = 1$ int.	1	1(1, 0F <sub>1</sub> )	0100E	0100E	0001F <sub>2</sub>	0001F <sub>2</sub>	-4.223(17)	-4.205(18)	-4.242(39)	-4.210(13)	-4.246(39)	$-(\sqrt{3}) R_{24} + (\sqrt{3}/10) F_{24b}$
$v_2 = 1/v_4 = 1$ int.	2	2(2, 0F <sub>2</sub> )	0100E	0100E	0001F <sub>2</sub>	0001F <sub>2</sub>	-2.338(30)	-2.365(32)	-2.294(73)	-2.353(22)	-2.288(68)	(undefined)
$v_2 = 1/v_4 = 1$ int.	3	3(1, 0F <sub>1</sub> )	0100E	0100E	0001F <sub>2</sub>	0001F <sub>2</sub>	-1.146(10)	-1.152(13)	-1.115(37)	-1.1502(81)	-1.156(26)	$(3/4) F_{24}^{01} + (3/4) F_{24a} + (9/80) F_{24b}$
$v_2 = 1/v_4 = 1$ int.	3	3(3, 0F <sub>1</sub> )	0100E	0100E	0001F <sub>2</sub>	0001F <sub>2</sub>	3.68(12)	3.51(11)	3.64(12)	3.536(81)	3.98(28)	$-(\sqrt{3}/4\sqrt{10}) F_{24b}$
$v_2 = 1/v_4 = 1$ int.	3	3(3, 0F <sub>2</sub> )	0100E	0100E	0001F <sub>2</sub>	0001F <sub>2</sub>	2.755(72)	2.774(69)	2.89(12)	2.750(64)	2.57(20)	$(\sqrt{3}/2\sqrt{2}) F_{24c}$
$v_2 = 1/v_4 = 1$ int.	4	4(4, 0F <sub>1</sub> )	0100E	0100E	0001F <sub>2</sub>	0001F <sub>2</sub>	2.33(22)	2.13(21)	2.03(23)	2.11(18)	2.96(55)	(undefined)
$v_4 = 1$	0	0(0, 0A <sub>1</sub> )	0001F <sub>2</sub>	0001F <sub>2</sub>	0001F <sub>2</sub>	0001F <sub>2</sub>	821.54462(13)	821.11703(13)	820.91126(15)	820.71165(12)	820.32666(16)	$\nu_4$
$v_4 = 1$	1	1(1, 0F <sub>1</sub> )	0001F <sub>2</sub>	0001F <sub>2</sub>	0001F <sub>2</sub>	0001F <sub>2</sub>	6.36580(32)	6.37276(34)	6.37698(73)	6.37978(23)	6.38703(72)	$3\sqrt{2} B_{\zeta_4} (\nu_4 \text{ Coriolis})$
$v_4 = 1$	2	2(0, 0A <sub>1</sub> )	0001F <sub>2</sub>	0001F <sub>2</sub>	0001F <sub>2</sub>	0001F <sub>2</sub>	-2.42(20)	-2.58(21)	-2.13(46)	-2.49(15)	-2.02(46)	$B_4 - B_0$
$v_4 = 1$	2	2(2, 0E)	0001F <sub>2</sub>	0001F <sub>2</sub>	0001F <sub>2</sub>	0001F <sub>2</sub>	3.72(30)	3.96(32)	3.29(69)	3.82(22)	3.13(69)	$-(1/2)\alpha_{220} - 6\alpha_{224}$
$v_4 = 1$	2	2(2, 0F <sub>2</sub> )	0001F <sub>2</sub>	0001F <sub>2</sub>	0001F <sub>2</sub>	0001F <sub>2</sub>	-1.479(23)	-1.496(24)	-1.444(52)	-1.483(17)	-1.429(52)	$-(3/4)\alpha_{220} + 6\alpha_{224}$
$v_4 = 1$	3	3(1, 0F <sub>1</sub> )	0001F <sub>2</sub>	0001F <sub>2</sub>	0001F <sub>2</sub>	0001F <sub>2</sub>	1.401(15)	1.409(16)	1.383(26)	1.398(12)	1.362(32)	$-(3\sqrt{3}/4)(\sqrt{2}) F_{110}$
$v_4 = 1$	3	3(3, 0F <sub>1</sub> )	0001F <sub>2</sub>	0001F <sub>2</sub>	0001F <sub>2</sub>	0001F <sub>2</sub>	1.75(12)	1.80(13)	1.56(24)	1.707(97)	1.41(27)	$(3\sqrt{5}/2) F_{134}$
$v_4 = 1$	4	4(0, 0A <sub>1</sub> )	0001F <sub>2</sub>	0001F <sub>2</sub>	0001F <sub>2</sub>	0001F <sub>2</sub>	-1.140(23)	-1.113(21)	-1.1113(95)	-1.116(16)	-1.212(53)	$-(D_4 - D_0)$
$v_4 = 1$	4	4(2, 0E)	0001F <sub>2</sub>	0001F <sub>2</sub>	0001F <sub>2</sub>	0001F <sub>2</sub>	-3.91(12)	-3.75(11)	-3.728(47)	-3.797(83)	-4.29(28)	$(\sqrt{3}/8) G_{220} + (3\sqrt{3}/2) G_{224}$
$v_4 = 1$	4	4(4, 0A <sub>1</sub> )	0001F <sub>2</sub>	0001F <sub>2</sub>	0001F <sub>2</sub>	0001F <sub>2</sub>	-1.15(10)	-1.038(89)	-1.055(22)	-1.070(71)	-1.45(24)	$(3\sqrt{3}/16) G_{220} - (3\sqrt{3}/2) G_{224}$
$v_4 = 1$	4	4(4, 0E)	0001F <sub>2</sub>	0001F <sub>2</sub>	0001F <sub>2</sub>	0001F <sub>2</sub>	-3.43(34)	-3.06(30)	-3.15 †	-3.15(23)	-4.36(83)	$-(3\sqrt{5}/4\sqrt{2})(D_{4t} - D_{0t})$
$v_4 = 1$	5	5(1, 0F <sub>1</sub> )	0001F <sub>2</sub>	0001F <sub>2</sub>	0001F <sub>2</sub>	0001F <sub>2</sub>	1.344(83)	1.236(87)	1.43(17)	1.198(73)	0.99(19)	$-(3\sqrt{7}/2) G_{244} + (\sqrt{21}/2\sqrt{22}) G_{246}$
$v_4 = 1$	5	5(3, 0F <sub>1</sub> )	0001F <sub>2</sub>	0001F <sub>2</sub>	0001F <sub>2</sub>	0001F <sub>2</sub>	-1.698(72)	-1.886(69)	-1.79(13)	-1.903(62)	-1.87(12)	$-(9\sqrt{7}/8) G_{244} - (\sqrt{21}/\sqrt{22}) G_{246}$
Abundance / %							21.23	27.66	7.73	35.94	7.44	
Nb. data							1031	1187	603	1394	638	
$J_{\text{max}}$							26	26	23	25	24	
$d_{\text{RMS}}^*$							0.458	0.475	0.310	0.486	0.303	

† Ground state parameters are fixed to  $^{74}\text{GeH}_4$  values from the previous study of the  $\nu_1/\nu_3$  stretching dyad.

‡ Fixed value.

\*  $d_{\text{RMS}}/10^{-3} \text{ cm}^{-1}$ .

Table 3: Effective dipole moment parameter values for the  $\nu_2$  and  $\nu_4$  bands of all five germane isotopologues. Standard deviation is indicated in parenthesis, in the unit of last two digits.

Band	Order	$\Omega(K, nC)$	$\{s\}$	$C_1$	$\{s'\}$	$C_2$	Value / Debye					Description (when available, see Eq. (6))	
							$^{70}\text{GeH}_4$	$^{72}\text{GeH}_4$	$^{73}\text{GeH}_4$	$^{74}\text{GeH}_4$	$^{76}\text{GeH}_4$		
$\nu_2$	1	1(1, 0F <sub>1</sub> )	0000A <sub>1</sub>	0000A <sub>1</sub>	0100E	0100E	-6.0723(16)	-6.1851(17)	-6.5380(17)	-6.2307(19)	-5.5405(16)	$\times 10^{-4}$	$\mu_2^1$
$\nu_4$	0	0(0, 0A <sub>1</sub> )	0000A <sub>1</sub>	0000A <sub>1</sub>	0001F <sub>2</sub>	0001F <sub>2</sub>	3.44763(13)	3.46372(17)	3.567616(64)	3.48751(22)	3.629326(63)	$\times 10^{-1}$	$\mu_4^0 = (\sqrt{3/2}) (\partial\mu_4 / \partial q_4)_0$
$\nu_4$	1	1(1, 0F <sub>1</sub> )	0000A <sub>1</sub>	0000A <sub>1</sub>	0001F <sub>2</sub>	0001F <sub>2</sub>	-2.1005(53)	-2.0749(63)	-2.1678(33)	-1.8940(76)	-2.2371(33)	$\times 10^{-4}$	$\mu_4^1 =$ Herman-Wallis factor
$\nu_4$	2	2(0, 0A <sub>1</sub> )	0000A <sub>1</sub>	0000A <sub>1</sub>	0001F <sub>2</sub>	0001F <sub>2</sub>	-3.4521(34)	-3.6715(40)	-3.1972(23)	-3.7483(48)	-3.12063(23)	$\times 10^{-5}$	$\mu_4^2$
Abundance / %							21.23	27.66	7.73	35.94	7.44		
Nb. data							573	620	389	666	372		
$J_{\text{max}}$							23	21	20	21	19		
$d_{\text{RMS}}/\%$							3.488	3.512	3.925	3.358	3.689		

Table 4: Rovibrational transitions in GeCaSDa. The polyad scheme is described by the  $(i_1, i_2, i_3, i_4)$  multiplet as explained in Section 2 of Ref. [34].

Transitions	Nb. dipolar	Dipolar wavenumber $\text{cm}^{-1}$	Dipolar intensity $\text{cm}^{-1}/(\text{molecule cm}^{-2})$
$^{70}\text{GeH}_4$			
<b>Scheme 1</b> (1,0,1,0)			
$P_1 - P_0$	6426	1930 – 2270	$8 \times 10^{-24} - 4 \times 10^{-19}$
<b>Scheme 2</b> (0,1,0,1)			
$P_1 - P_0$	5666	650 – 1106	$8 \times 10^{-24} - 4 \times 10^{-19}$
$^{72}\text{GeH}_4$			
<b>Scheme 1</b> (1,0,1,0)			
$P_1 - P_0$	6462	1930 – 2270	$8 \times 10^{-24} - 4 \times 10^{-19}$
<b>Scheme 2</b> (0,1,0,1)			
$P_1 - P_0$	5679	649 – 1106	$8 \times 10^{-24} - 4 \times 10^{-19}$
$^{73}\text{GeH}_4$			
<b>Scheme 1</b> (1,0,1,0)			
$P_1 - P_0$	6470	1929 – 2270	$8 \times 10^{-24} - 4 \times 10^{-19}$
<b>Scheme 2</b> (0,1,0,1)			
$P_1 - P_0$	5700	649 – 1105	$8 \times 10^{-24} - 4 \times 10^{-19}$
$^{74}\text{GeH}_4$			
<b>Scheme 1</b> (1,0,1,0)			
$P_1 - P_0$	6509	1929 – 2270	$8 \times 10^{-24} - 4 \times 10^{-19}$
<b>Scheme 2</b> (0,1,0,1)			
$P_1 - P_0$	5700	649 – 1105	$8 \times 10^{-24} - 4 \times 10^{-19}$
$^{76}\text{GeH}_4$			
<b>Scheme 1</b> (1,0,1,0)			
$P_1 - P_0$	6525	1929 – 2269	$8 \times 10^{-24} - 4 \times 10^{-19}$
<b>Scheme 2</b> (0,1,0,1)			
$P_1 - P_0$	5741	648 – 1105	$8 \times 10^{-24} - 4 \times 10^{-19}$
Total	60 878		