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Determination of vibrational parameters of $^{76}GeH_4$ from precision experimental data

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Harmonic frequencies, anharmonic parameters, and tetrahedral splitting parameters have been determined for the $^{76}GeH_4$ molecule, based on experimental data of band centers. As a result, the set of 3 harmonic frequencies, 8 anharmonic parameters, and 8 tetrahedral splitting parameters reproduces 31 initial experimental band centers with a root mean square deviation $0.054\,cm^{-1}$.

Keywords: GeH_4, vibrational parameters, local mode model.

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Introduction

The theoretical description of the ro-vibrational spectra of molecules is of great interest for molecular spectroscopy, physical chemistry, and related fields. Having information on the vibrational parameters of an arbitrary molecule, it is possible to predict with high accuracy the centers of ro-vibrational bands in different regions of the wavelength scale. Progress in determining the parameters and, as a consequence, describing the ro-vibrational spectra of four-atom molecules [1–3] was followed by progress for five-atom molecules of high symmetry (spherical top molecules) [4,5]. For this type of molecules, this kind of information is important because, due to the specific features of their spectra, the combination difference method [6], which is effectively and widely used when studying the spectra of molecules of lower symmetry [7–11], is almost impossible to use for assignment.

The GeH_4 molecule is a striking representative of the spherical top molecule. Germane plays an important role in astrophysics and astrochemistry, being one of the most important components of the atmospheres of the giant planets Jupiter and Saturn [12–14], where germane is found in quantities orders of magnitude greater than their thermochemical equilibrium values in the upper atmosphere. Parameter information extracted from the absorption spectra of the GeH_4 molecule is crucial for the study of such planetary systems and can be used to understand the physical and chemical properties of their atmospheres. The germane molecule is of considerable interest for fundamental molecular physics as a molecule of high symmetry exhibiting the effects of local modes in stretching vibrations. The local mode model was applied to study the ro-vibrational structure of the spectra of the GeH_4 [15–22] molecule, and it was found that this approach is very effective for understanding and interpreting high-resolution germane spectra.

The infrared spectra of germane in the natural abundance have a complex structure due to the existence of five stable isotopologues, namely ^{70}Ge (20.55%), ^{72}Ge (27.37%), ^{73}Ge (7.67%), ^{74}Ge (36.74%) and ^{76}Ge (7.67%), which greatly complicate the pattern of experimentally recorded spectra. Additional complexity arises, both because of the presence of strong resonant interactions between its ro-vibrational bands and because of degeneracy of vibrational modes.

Thus, an important task of molecular ro-vibrational spectroscopy is to precisely determine the vibrational parameters (harmonic frequencies, anharmonicity parameters, and tetrahedral splitting parameters) of a germane molecule. With knowledge of the above set of parameters, it is possible to theoretically calculate and predict band centers.

The vibrational Hamiltonian of XY_4 type molecule

The vibrational energies of a molecule of XY_4 type and T_d symmetry can be obtained as eigen values of a matrix with an effective vibrational Hamiltonian operator of the following form [23]:

$$H^{\text{vib}} = \sum_{v,\tilde{v}} |v\rangle\langle\tilde{v}| H^{v\tilde{v}} = E^{vv}\delta_{v\tilde{v}} + W^{v\tilde{v}}(v_1, v_2, v_3, v_4 n\Gamma), \quad (1)$$

Table 1. The band centers of the ^{76}GeH$_4$ molecule

Band	E, cm^{-1}	Source	Band	E, cm^{-1}	Source
$\nu_4\,(F_2)$	820.3270	[29]	$\nu_2+2\nu_4\,(2E)$	2573.4424	[33]
$\nu_2\,(E)$	929.9130	[29]	$\nu_2+2\nu_4(A_2)$	2576.5357	[33]
$2\nu_4\,(A_1)$	1627.4950	[31]	$2\nu_2+\nu_4\,(1F_2)$	2675.2299	[33]
$2\nu_4\,(F_2)$	1639.2570	[31]	$2\nu_2+\nu_4\,(F_1)$	2681.3912	[33]
$2\nu_4\,(E)$	1642.1422	[31]	$2\nu_2+\nu_4\,(2F_2)$	2684.1880	[33]
$\nu_2+\nu_4\,(F_2)$	1748.3962	[31]	$3\nu_2(E)$	2785.4117	[33]
$\nu_2+\nu_4\,(F_1)$	1752.5031	[31]	$3\nu_2\,(A_2)$	2792.1467	[33]
$2\nu_2\,(A_1)$	1857.2721	[31]	$\nu_3+\nu_4(F_1)$	2924.2427	[34]
$2\nu_2\,(E)$	1860.6673	[31]	$\nu_3+\nu_4\,(E)$	2924.9923	[34]
$\nu_1\,(A_1)$	2110.6918	[30]	$\nu_1+\nu_4(F_2)$	2925.3489	[34]
$\nu_3\,(F_2)$	2110.7323	[30]	$\nu_3+\nu_4(F_2)$	2927.0038	[34]
$3\nu_4(1F_2)$	2438.2407	[33]	$\nu_2+\nu_3(F_1)$	3032.8780	[34]
$3\nu_4(F_1)$	2459.5121	[33]	$\nu_2+\nu_3\,(F_2)$	3033.1864	[34]
$3\nu_4(2F_2)$	2462.4009	[33]	$2\nu_1\,(A_1)$	4152.9765	[32]
$\nu_2+2\nu_4(F_1)$	2567.6835	[33]	$\nu_1+\nu_3(F_2)$	4153.2348	[32]
$\nu_2+2\nu_4(F_2)$	2571.4759	[33]			

where

$$E^{v,\tilde v} = \sum_{\lambda}\omega_\lambda\left(v_\lambda+\frac{d_\lambda}{2}\right) + \sum_{\lambda\mu\geq\lambda} x_{\lambda\mu}\left(v_\lambda+\frac{d_\lambda}{2}\right)\left(v_\mu+\frac{d_\mu}{2}\right) = \sum_{\lambda}\tilde\omega_\lambda v_\lambda + \sum_{\lambda\mu\geq\lambda}\tilde x_{\lambda\mu} v_\lambda v_\mu. \qquad (2)$$

Here, ω_λ and $x_{\lambda\mu}$ — harmonic frequencies and anharmonic parameters, $d_\lambda = 1$ at $\lambda = 1$, $d_\lambda = 2$ at $\lambda = 2$ and $d_\lambda = 3$ at $\lambda = 3.4$.

$$\tilde\omega_\lambda = \omega_\lambda + x_{\lambda\lambda}d_\lambda + \frac{1}{2}\sum_{\mu\neq\lambda} x_{\lambda\mu}d_\mu, \qquad (3)$$

$$\tilde x_{\lambda\mu} = x_{\lambda\mu}. \qquad (4)$$

Values $W^{v\tilde v}(v_1, v_2, v_3, v_4 n\Gamma)$ are complex functions depending on the vibrational quantum numbers v_λ and symmetry of vibrational states v and $\tilde v$. These quantities describe, on the one hand, vibrational resonance interactions and, on the other hand, various kinds of so-called tetrahedral splittings [24].

Table 2. Spectroscopic parameters of the ^{76}GeH$_4$ molecule

Parameter	Value, cm^{-1}	Parameter	Value, cm^{-1}
ω	2194.64(27)	x_{44}	−2.318(20)
x	−8.526(12)	G_{22}	0.878(28)
ω_2	944.46(52)	G_{34}	0.371(21)
ω_4	836.13(21)	G_{44}	2.154(13)
x_{12}	−7.16(25)	T_{23}	0.019(04)
x_{14}	−5.723(80)	T_{24}	−0.254(05)
x_{22}	−0.417(43)	T_{34}	−0.201(07)
x_{23}	−7.47(12)	T_{44}	0.154(03)
x_{24}	0.307(59)	S_{34}	0.303(08)
x_{34}	−5.487(68)	d_{rms}	0.054

Theoretical determination of the vibrational parameters of GeH$_4$

Speaking about the problem of accurate semi-empirical determination of the vibrational parameters of GeH$_4$ molecule, it should be kept in mind, that until recently, it was impossible due to the absence of a proper number of experimental band centers for any of the five stable isotopologues of this molecule. Recently, however, there have been extensive studies of the high-resolution vibrational spectra of various isotopologues of the germane [25–34] molecule (in these works the GeH$_4$ sample, enriched with the isotope ^{76}Ge), was the most studied). This made it possible, as a first step, to put the question of a high-precision determination of the vibrational Hamiltonian parameters of the ^{76}GeH$_4$ molecule based on accurate experimental data on the centers of its bands. It would also be interesting and important to estimate the vibrational parameters not only for the ^{76}GeH$_4$ molecule, but also for the other four stable isotopologues. Unfortunately, the experimental information currently available in the literature is insufficient for such a direct assessment.

For a preliminary estimation of the vibrational parameters, we used the fact that the GeH$_4$ molecule satisfies the conditions of the local mode model [35]. In this case, the vibrational parameters ω_1/ω_3, $x_{11}/x_{13}/x_{33}$, G_{33}, T_{33}, F_{1133} and F_{1333} satisfy with good accuracy the following relations (definitions of all these parameters can be found, for example, in [1]):

$$\omega_1 \simeq \omega_3 = \omega \qquad (5)$$

Table 3. The band centers of the ^{76}GeH$_4$ molecule

Band	Experiment	Calculation	δ	Band	Experiment	Calculation	δ
$\nu_4\,(F_2)$	820.33	820.38	−0.05	$\nu_2+2\nu_4\,(E)$	2573.44	2573.70	−0.26
$\nu_2\,(E)$	929.91	929.76	0.15	$\nu_2+2\nu_4\,(A_2)$	2576.54	2576.72	−0.18
$2\nu_4\,(A_1)$	1627.50	1627.51	−0.01	$2\nu_2+\nu_4\,(F_2)$	2675.23	2675.26	−0.03
$2\nu_4\,(F_2)$	1639.26	1639.20	0.06	$2\nu_2+\nu_4\,(F_1)$	2681.39	2681.44	−0.05
$2\nu_4\,(E)$	1642.14	1642.28	−0.14	$2\nu_2+\nu_4\,(F_2)$	2684.19	2684.11	0.08
$\nu_2+\nu_4\,(F_2)$	1748.40	1748.42	−0.02	$3\nu_2\,(E)$	2785.41	2785.04	0.37
$\nu_2+\nu_4\,(F_1)$	1752.50	1752.48	0.02	$3\nu_2\,(A_1)$	2791.95	2792.05	−0.10
$2\nu_2\,(A_1)$	1857.27	1856.94	0.33	$3\nu_2\,(A_2)$	2792.15	2792.05	0.10
$2\nu_2\,(E)$	1860.67	1860.45	0.22	$\nu_3+\nu_4\,(F_1)$	2924.24	2924.24	0.00
$\nu_1\,(A_1)$	2110.69	2110.69	0.00	$\nu_3+\nu_4\,(E)$	2924.99	2924.99	0.00
$\nu_3\,(F_2)$	2110.73	2110.73	0.00	$\nu_1+\nu_4\,(F_2)$	2925.35	2925.35	0.00
$3\nu_4\,(F_2)$	2438.24	2438.24	0.00	$\nu_3+\nu_4\,(A_1)$	2926.91	2926.91	0.00
$3\nu_4\,(A_1)$	2456.25	2456.46	−0.21	$\nu_3+\nu_4\,(F_2)$	2927.00	2927.00	0.00
$3\nu_4\,(F_1)$	2459.51	2459.54	−0.03	$\nu_2+\nu_3\,(F_1)$	3032.87	3032.87	0.00
$3\nu_4\,(F_2)$	2462.40	2462.39	0.01	$\nu_2+\nu_3\,(F_2)$	3033.19	3033.18	−0.01
$\nu_2+2\nu_4\,(6E)$	2556.20	2556.84	−0.64	$\nu_1+\nu_2\,(E)$	3034.38	3034.31	0.07
$\nu_2+2\nu_4\,(F_1)$	2567.68	2567.54	0.14	$2\nu_1\,(A_1)$	4152.98	4153.11	−0.13
$\nu_2+2\nu_4\,(A_1)$	2568.97	2568.59	0.38	$\nu_1+\nu_3\,(F_2)$	4153.23	4153.11	0.12
$\nu_2+2\nu_4\,(F_2)$	2571.48	2571.60	−0.12				

and

$$x_{11} \simeq \frac{1}{4}x_{13} \simeq \frac{5}{9}x_{33} \simeq -\frac{5}{3}G_{33} \simeq -5T_{33}$$
$$\simeq \frac{1}{4}F_{1133} \simeq \frac{1}{16}F_{1333} = x. \qquad (6)$$

The use of these relations makes it possible to reduce the number of unknown parameters and makes it possible to determine their complete set on the basis of the available limited number of high-precision experimental data on the band centers of the germane molecule.

Thus, in the present study, the vibrational parameters of the ^{76}GeH$_4$ molecule were determined with high accuracy, which allows us to predict the values of the band centers for the higher excited states of this molecule.

Results of determination of vibrational parameters of GeH$_4$

To determine the vibrational parameters of the molecule ^{76}GeH$_4$, we used high-precision experimental data on the band centers of this molecule, which are shown in Table 1.

As a first step, the parameters associated with the deformation oscillations were determined, namely $\tilde{\omega}_2$, $\tilde{\omega}_4$, $\tilde{x}_{22}, \tilde{x}_{24}, \tilde{x}_{44}$, $\tilde{G}_{22}, \tilde{G}_{44}$, $\tilde{T}_{24}, \tilde{T}_{44}$. This choice is due to the fact, that there is a greater number of reliable experimental data on the centers of the bands (21 values of 31, Table 1). Thus, these parameters were determined with high accuracy based on experimental data extracted from high-resolution ro-vibrational spectra of the ^{76}GeH$_4$ molecule.

As a next step, the results of local mode theory in the form of relations (5) and (6) were used to determine the remaining unknown parameters associated with stretching vibrations, since the available experimental data were insufficient to determine their complete set. This reduced the number of unknown parameters and solved the problem.

Thus, the known experimental values of the band centers were used in the fitting procedure of the vibrational parameters and parameters of the tetrahedral splittings. As a result of solving the inverse problem, the set of parameters of the ^{76}GeH$_4$ molecule, shown in Table 2, was obtained. Confidence intervals in brackets for parameter values correspond to a confidence probability of 0.66. The standard deviation in determining this set of parameters is estimated at $0.054\,\mathrm{cm}^{-1}$.

To illustrate the quality of the results obtained, Table 3 shows the calculated and experimental values of the band centers of the ^{76}GeH$_4$ molecule and the differences between them. The good agreement between the calculation and the experiment suggests that the resulting set of vibrational parameters can be used to predict the higher-excited states of the studied molecule.

Conclusion

The complete set of vibrational parameters and tetrahedral splitting parameters of the ^{76}GeH$_4$ molecule has been determined. The obtained information will make it possible to predict the values of the band centers in the ro-vibrational spectra, which will greatly simplify the analysis of the line positions and energy structure of the molecule in question.

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Conflict of interest

The authors declare that they have no conflict of interest.

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