The Microwave Q-branch Spectrum of Germane in the Vibrational Ground State

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We present an analysis of the rotational spectra of $^{70}GeH_4$, $^{72}GeH_4$ and $^{74}GeH_4$ in the vibrational ground state measured by microwave Fourier transform (MWFT) spectroscopy. All quartic, sextic and octic tensor centrifugal distortion constants have been determined. A discussion of spin-rotation and spin-spin interactions will be given in a subsequent paper.

Introduction

The microwave spectrum of germane, GeH_4, has been a subject of investigations since many years. One reason for the great interest may be due to the tetrahedral and therefore nonpolar equilibrium structure of the molecule. Nevertheless it is possible to observe Q-branch microwave transitions because a nonzero dipole moment exists as a consequence of centrifugal distortion [1]. P- and R-branch transitions have been measured in the IR-region [2]. A great deal of theoretical work has been published in the field of tetrahedral molecules. The major part of these papers investigate the centrifugal distortion effect [3–8]. The Hamiltonian stated there allows very accurate prediction of the line frequencies if the tensor centrifugal distortion constants are known. Only one theoretical treatment of the line shift caused by the isotopic substitution of the central atom is known to the authors [9]. The order of magnitude of this effect is about 100 kHz. A further group of publications [10–16] deals with the spin-rotation and spin-spin interaction caused by the four hydrogen atoms of the tetrahedral molecule in equivalent positions. The resulting hyperfine splittings of the F-type Q-branch transitions reach values up to 100 kHz and have also been observed by MWFT-spectroscopy.

The first microwave spectrum of germane was obtained by Kagann et al. [1] with a Stark-modulation spectrometer using averaging of the spectra. A period in the order of several hours was required to obtain one averaged spectrum. The line width was about 1 MHz (estimated from [1], Figure 1). Only those transitions (E-species) showing a linear Stark effect could be measured. Even at highest voltages the quadratic Stark effect of most of the A- and F-type transitions is too small to give a sufficient modulation. We tried to overcome this restriction by utilizing the MWFT-technique as it has been done already by Bauder's group in Zürich for the investigation of the homologes methane and silane [17, 18]. As a result we observed lines of all symmetry species (A, E, F) quite often with very high signal-to-noise ratio and a line width of 20 kHz within a measuring period of a few minutes. In addition the combination of a Stark cell and a MWFT-spectrometer allowed us to obtain an estimate of the magnitude of the electric dipole moment.

In this paper we intend to report on the centrifugal distortion effect for the species $^{70}GeH_4$, $^{72}GeH_4$ and $^{74}GeH_4$ only.

Experimental

The isotopically enriched (> 90% of the enriched species) samples of $^{70}GeH_4$, $^{72}GeH_4$ and $^{74}GeH_4$ were prepared by R. Opferkuch, Ulm, from the respective dioxides [19]. The percentage of impurities is unknown but probably small. All spectra were recorded by MWFT-spectrometers in the J-,

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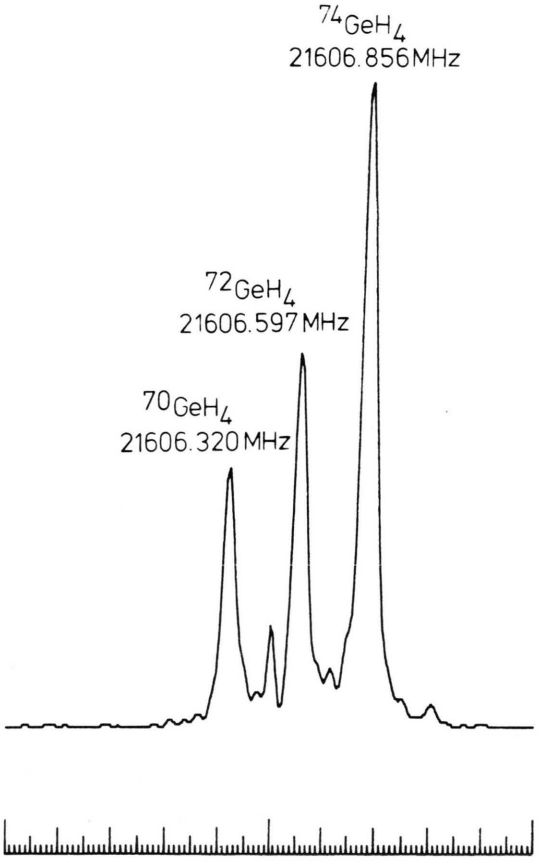

Fig. 1a. A 2-MHz-range of the rotational spectrum of a germane sample containing the isotopic species in natural abundance. The $19A_1(1)-19A_2(1)$ transition was measured at a pressure of 4.6 mTorr and room temperature (about 20 °C). Measuring time 10 minutes, 10 million averaging cycles. Pulse power about 3 Watts at TWTA output, pulse length 700 ns. The transient emission signal was recorded with a sample interval of 20 ns and 1024 data points (extended with zeros to 4096 data points prior to Fourier transformation). Spectral point distance 12.5 kHz.

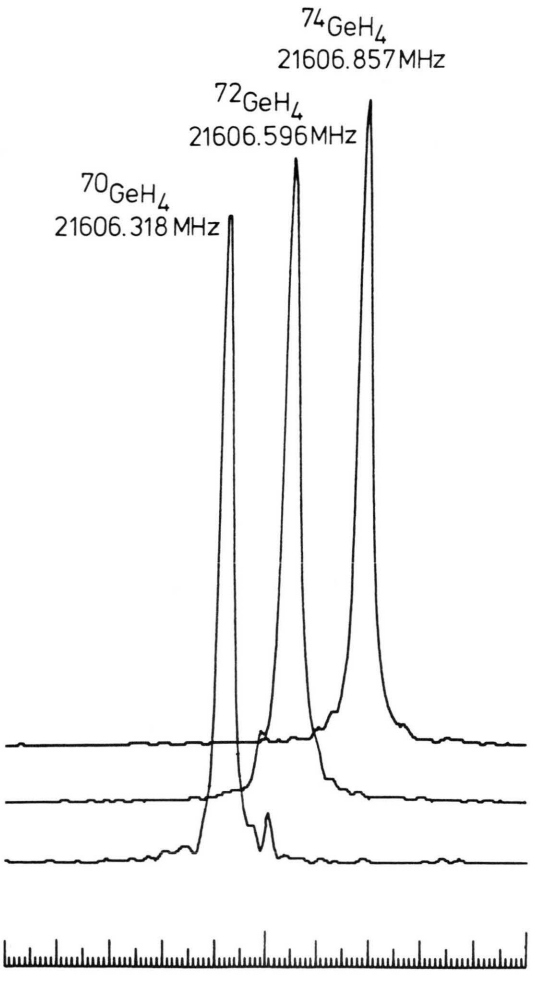

Fig. 1b. The $19A_1(1)-19A_2(1)$ transition recorded under roughly the same conditions as above. Isotopically enriched $^{70}GeH_4$-, $^{72}GeH_4$- and $^{74}GeH_4$-samples were used.

X-, Ku- and K-band, 5–26.4 GHz. The experimental setup has been described already earlier [20–22]. The sample pressure varied from 1 mTorr to 20 mTorr. In the case of lines showing hyperfine structure a pressure lower than 5 mTorr had to be used for higher resolution. All measurements have been carried out at room temperature (about 20 °C). For MWFT-spectroscopy the intensity of the observable signal depends in a "sinusoidal" manner from the power of the polarizing pulse, from the pulse length and the dipole matrix element [23]. In our case the extreme small dipole moment of germane and the experimentally limited pulse power prevented us from reaching the optimum $\pi/2$-condition. A pulse length longer than 700 ns turned out to be not useful. So we always measured at the maximum available pulse power (specifications of the TWTAs: J-band 25 W, X-band and Ku-band 10 W, K-band 3 W) and at a constant pulse length of 700 ns.

Measurements and Analysis

We already pointed out that a lot of theoretical contributions in the field of tetrahedral molecules

exist. Therefore we do not intend do repeat any theoretical treatment. Nevertheless we will give all formulas used for analyzing the data.

The nomenclature used in this article for the classification of energy levels is the same as it has been used by Hougen [14, 24, 25] and other scientists [26]. Some authors use a different classfication method [5, 15, 16].

The probably most important aspect of the analysis concerns the evaluation of the tensorial centrifugal distortion parameters. The frequencies of the measured lines used for this purpose are given in Table 1. The data were weighted as the inverse squares of the estimated experimental errors. In general the F-species transitions have a higher uncertainty than the other lines because the hyperfine splittings prevented an accurate determination of the center frequency. All data were obtained from measurements on the isotopically enriched samples. When we used a sample of natural isotopic composition ($^{70}GeH_4$: 20.52%, $^{72}GeH_4$: 27.43%, $^{73}GeH_4$: 7.76%, $^{74}GeH_4$: 36.54%, $^{76}GeH_4$: 7.76%) in earlier stages of our experiment we often observed weak and superimposed lines. In order to illustrate the shift caused by isotopic substitution of the central atom a spectrum of the natural isotopic mixture and, for comparison, the spectra of the isotopically enriched samples are shown in Figure 1.

For the evaluation of the tensor centrifugal distortion constants the following Hamiltonian [26] was used

$$\begin{aligned} H &= H_S + H_T, \\ H_S &= B_0 J^2 - D_S J^4 + H_S J^6 + L_S J^8, \\ H_T &= [D_T + H_{4T} J^2 + L_{4T} J^4] \Omega_4 \\ &\quad + [H_{6T} + L_{6T} J^2] \Omega_6 + L_{8T} \Omega_8 \end{aligned} \tag{1}$$

with H_S being the scalar and H_T being the tensorial part. J is the operator of the angular momentum, B_0 the rotational constant, D_S, H_S and L_S the scalar centrifugal distortion constants, and Ω_k, $k = 4, 6, 8$, are the k-th rank tensor operators for the tetrahedral molecule. The respective tensor centrifugal distortion parameters D_T, H_{4T}, L_{4T}, H_{6T}, L_{6T} and L_{8T} were determined by fitting the exprimental line frequencies by the fitting procedure XY4FIT [27] in interaction with the program XY4TOP [27] which calculates the energy levels of tetrahedral molecules by direct diagonalization of (1). The results are summarized in Table 2. All errors are standard errors and are given in units of the least significant digit. The correlation matrices are shown in Table 3.

Table 1. Measured lines of $^{70}GeH_4$, $^{72}GeH_4$ and $^{74}GeH_4$. In the case of lines showing hyperfine splittings a center frequency was estimated. Del (in kHz) = Observed frequency (in MHz) − Calculated frequency (in MHz). The columns designated by "*E*" indicate the estimated error: A = 10 kHz, B = 50 kHz, C = 100 kHz. Both, experimental errors and uncertainties in the determination of the center frequency of weak or split lines are included.

			$^{70}GeH_4$		$^{72}GeH_4$		$^{74}GeH_4$	
			Obs.	Del *E*	Obs.	Del *E*	Obs.	Del *E*
19	A2(2)	A1	5043.181	- 4 A	5043.167	- 1 A	5043.155	+ 5 A
14	F2(3)	F1(1)	5405.398	-13 C	5405.465	- 2 C	5405.505	-16 C
13	E(2)	E(1)	5774.185	- 3 B	5774.279	+ 2 A	5774.369	+ 5 A
15	F1(4)	F2(3)	5854.347	+21 C			5854.559	+12 C
17	E(3)	E(2)	6722.723	- 8 A	6722.896	- 4 A	6723.056	-13 B
17	F1(4)	F2(2)	7208.776	- 3 C	7208.848	- 4 C	7208.921	- 7 C
15	E(2)	E(1)	7314.852	- 6 A	7314.925	- 3 A	7314.995	- 6 A
15	F1(3)	F2(2)	7822.174	- 5 C	7822.258	- 4 C	7822.338	- 9 B
14	A1	A2	8920.171	- 6 A	8920.249	- 3 A	8920.323	- 5 A
20	F2(4)	F1(3)			9488.933	+ 2 C	9489.065	+11 C
16	E3	E2			9510.517	- 3 A	9510.709	- 8 B
14	F1(2)	F2(1)			9553.143	0 A	9553.232	- 5 B
18	E(3)	E(2)	9615.170	- 1 A	9615.271	+ 4 A	9615.363	+ 1 A
16	F2(3)	F1(2)	9678.941	-15 C	9679.042	- 6 B	9679.124	-20 B
14	E(2)	E(1)	9950.363	0 B	9950.472	+ 3 C	9950.575	+ 2 A
18	F2(4)	F1(2)	10575.173	- 1 C	10575.304	+ 3 C	10575.427	0 C
16	F1(3)	F2(1)	10654.795	0 C	10654.913	+ 3 C	10655.027	- 2 C
15	A1	A2(1)	10939.187	+ 3 A	10939.374	+ 4 A	10939.551	- 3 A
15	F1(4)	F2(2)			11184.648	-18 C		
17	A2	A1	11358.388	- 2 A	11358.457	+ 1 A	11358.524	- 2 A
15	F1(2)	F2(1)	11692.413	+ 1 B	11692.510	+ 5 B	11692.606	+ 2 B
15	F2(3)	F1(1)	12554.018	+ 4 A			12554.270	- 1 B
17	F2(4)	F1(3)	12630.416	-41 C	12630.731	+ 2 C	12630.990	-12 C
19	F1(4)	F2(3)	12690.721	+13 C	12690.854	+ 2 C	12690.982	- 1 C
17	F2(3)	F1(2)	12892.492	0 B	12892.667	+46 C	12892.757	+ 4 B
20	A1(2)	A2	13576.386	- 2 A	13576.408	-20 B	13576.427	- 2 A
17	E(2)	E(1)	13709.253	0 A	13709.412	+ 7 B	13709.560	- 1 A
19	F2(4)	F1(2)	14380.518	+11 C	14380.678	-23 C	14380.894	+12 C
16	E(2)	E(1)	14691.156	0 A	14691.274	+ 9 C	14691.386	+ 4 A
18	F2(3)	F1(1)	14895.916	+18 C	14895.989	- 3 C	14896.101	+18 B
16	F2(2)	F1(1)	15002.545	+ 1 B	15002.674	+ 9 C	15002.793	0 B
16	A2	A1(1)	15905.511	+ 6 A	15905.677	+ 9 B	15905.843	+ 5 A
20	F1(4)	F2(2)	17027.095	+11 B	17027.316	- 2 C	17027.534	+16 B
18	F1(3)	F2(2)	17058.566	+12 C	17058.760	+ 9 C		
19	F1(3)	F2(2)			17073.711	- 8 C	19212.775	+10 C
19	A1	A2(1)	21606.318	+ 3 A	21606.597	+ 1 A	21606.859	0 A
18	A1(1)	A2(1)	21741.058	- 2 A	21741.188	- 1 A	21741.313	- 2 A
18	E(2)	E(1)	22555.522	- 2 A				

Comparing the centrifugal distortion parameters of the three isotopic species one observes that the standard errors are too large to show an exact isotopic dependence. According to Watson's theory [9] the constants B_0, D_S and D_T should be independent of the central mass m_x, whereas the quartic and sextic centrifugal distortion constants should be affected as indicated in the following formula [9]:

$$\Delta H_{4T} = (7/88)\, \Delta H,$$

$$\Delta H_{6T} = -(15/22)\, \Delta H, \tag{2a}$$

$$\Delta H = -\left(\frac{256}{35}\right)\left[\frac{m_y \Delta m_x}{m_x (M + \Delta m_x)}\right] B_0^5 \tag{2b}$$

$$\cdot\, \zeta_{23}^2\, \zeta_{24}^2 \left(\frac{1}{\omega_3^2} - \frac{1}{\omega_4^2}\right)^2. \tag{2c}$$

Table 2. Tensor centrifugal distortion constants. Standard errors in parentheses (in units of the least significant digit). All data are to be multiplied by a factor given in the last column. The last two lines show the number of fitted lines and the standard deviation of the fit.

	$^{70}GeH_4$	$^{72}GeH_4$	$^{74}GeH_4$	
D_T	6.777466(14)	6.7775865(99)	6.777647(10)	10^{-2} MHz
H_{4T}	− 5.38483(89)	− 5.38735(68)	− 5.38545(69)	10^{-6} MHz
H_{6T}	2.96868(27)	2.97188(20)	2.97435(24)	10^{-6} MHz
L_{4T}	4.033(14)	4.071(11)	4.031(11)	10^{-10} MHz
L_{6T}	− 4.2363(79)	− 4.2518(63)	− 4.2451(71)	10^{-10} MHz
L_{8T}	− 7.908(13)	− 7.912(10)	− 7.922(13)	10^{-10} MHz
Lines	33	35	35	
Standard deviation	10.7	10.9	8.4	kHz

Table 3. Correlation matrices. All correlation coefficients are multiplied by 1000.

$^{70}GeH_4$	D_T	H_{4T}	H_{6T}	L_{4T}	L_{6T}	L_{8T}
D_T	1000					
H_{4T}	−994	1000				
H_{6T}	−27	77	1000			
L_{4T}	979	−995	−119	1000		
L_{6T}	29	−79	−989	125	1000	
L_{8T}	−464	472	−413	−472	425	1000
$^{72}GeH_4$	D_T	H_{4T}	H_{6T}	L_{4T}	L_{6T}	L_{8T}
D_T	1000					
H_{4T}	−994	1000				
H_{6T}	276	−272	1000			
L_{4T}	982	−996	262	1000		
L_{6T}	−292	288	−990	−276	1000	
L_{8T}	−171	172	−298	−173	284	1000
$^{74}GeH_4$	D_T	H_{4T}	H_{6T}	L_{4T}	L_{6T}	L_{8T}
D_T	1000					
H_{4T}	−992	1000				
H_{6T}	−218	264	1000			
L_{4T}	976	−995	−295	1000		
L_{6T}	200	−245	−986	279	1000	
L_{8T}	−328	344	−374	−355	420	1000

m_x and m_y are the masses of the central atom (Ge) and the ligands (H). Δm_x indicates the change of the central mass when the central atom is substituted, ΔH_{4T} and ΔH_{6T} are the respective changes of the quartic and sextic centrifugal distortion constants. The quantities ζ_{23} and ζ_{24} are associated with the diagonal Coriolis constants ζ_3 and ζ_4 by

$$\zeta_{23}^2 = (2/3)(1-\zeta_3), \quad \zeta_{24}^2 = (2/3)(1-\zeta_4) \qquad (3)$$

and ω_3 and ω_4 are the normal frequencies expressed in cm^{-1}. Evaluation of the expressions (2a–c) shows that the predicted changes in H_{4T} and H_{6T} are smaller than the experimental error limits. An explanation of the significantly observed shift of D_T is neither given by Watson's theory nor has it been described elsewhere.

Watson's theory applies to the equilibrium configuration of the molecule while observation deals with the vibrational ground state. This may account for discrepancies between calculated and observed isotope effects. For example, the B_e constant must be the same for all isotopic species under consideration, but the B_0 values as well as the vibrational frequencies are likely to be slightly different, similar to methane ($^{12}CD_4$–$^{13}CD_4$ or $^{12}CH_4$–$^{13}CH_4$) [28, 29]; taking Hecht's expression [3] for D_T,

$$D_T = \frac{1}{5}\left(\frac{1}{\omega_2^2} - \frac{\zeta_{23}^2}{\omega_3^2} - \frac{\zeta_{24}^2}{\omega_4^2}\right) B^5 \qquad (4)$$

one expects a small effect even for the D_T constant.

The accurate data obtained from the measurements on the isotopic species of germane show that the MWFT spectroscopy is a very useful tool for the investigation of molecules with small dipole moments. An improvement of the centrifugal distortion constants will be possible when more lines in higher microwave bands can be measured. We believe that an extension of our MWFT spectrometer to the V band (26 to 40 GHz) is possible.

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