Analysis of Torsion in a Three–Top Molecule. Torsional Barrier and Moment of Inertia of Trimethyl Ethynyl Germane

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Internal rotation effects for a large number of molecules containing one or two symmetric internal rotors have been investigated using microwave spectroscopy. The high resolution of molecular beam Fourier transform microwave spectroscopy revealed now the internal rotation fine structure in the rotational spectrum of trimethyl ethynyl germane, $(CH_3)_3GeC{\equiv}CH$. After assigning the rotational transition $J = 1 \rightarrow 0$ in the vibrational and torsional ground state to the symmetry species of the molecular symmetry group G_{162}, the torsional barrier V_3 and the rotational constant B_0 could be determined to (4.5±0.2) kJ/mol and (1823.370±0.010) MHz, respectively.

Introduction

The molecular symmetry group G_{162} of trimethyl ethynyl germane (Fig. 1) has been worked out by Lehmann and Pate [1]. Unfortunately the results could not be applied to experimental data. Now this has been possible with its microwave spectrum recorded, using a molecular beam Fourier transform (MB–FTMW) spectrometer. It should be pointed out, that for symmetric three top molecules a torsion fine structure can be observed. This is different for symmetric rotors like CH_3SiH_3. Group theory was used to assign the torsional line pattern of trimethyl ethynyl germane. Thereby we noticed degeneracies reducing the number of components in the torsional line pattern to six.

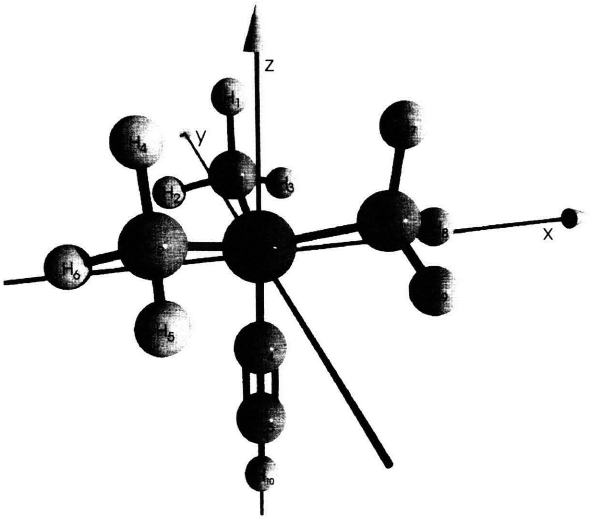

Fig. 1. Trimethyl ethynyl germane.

Experimental Methods

Sample preparation

Trimethyl ethynyl germane has been prepared according to the method given by MacLean and Sacher [2]. From 15 g of a commercially available slurry of 18% sodium acetylide in xylene the liquid phase was distilled off and the solid residual was dried at 80 °C in vacuo. Subsequently 50 ml nitrobenzene, dried over calcium chloride, and 4 g trimethyl chlorogermane have been added in a dry inert gas flow. The mixture has been stirred over night under exclusion of air and subsequently warmed up to 50 °C. The volatile reaction products could easily be separated from the nitrobenzene by a vacuum distillation at room temperature and yielded about 3 ml trimethyl ethynyl germane in a purity of 95% (checked by gas chromatography).

Microwave measurement

The used MB–FTMW spectrometer contains a tunable confocal microwave cavity, which is mounted

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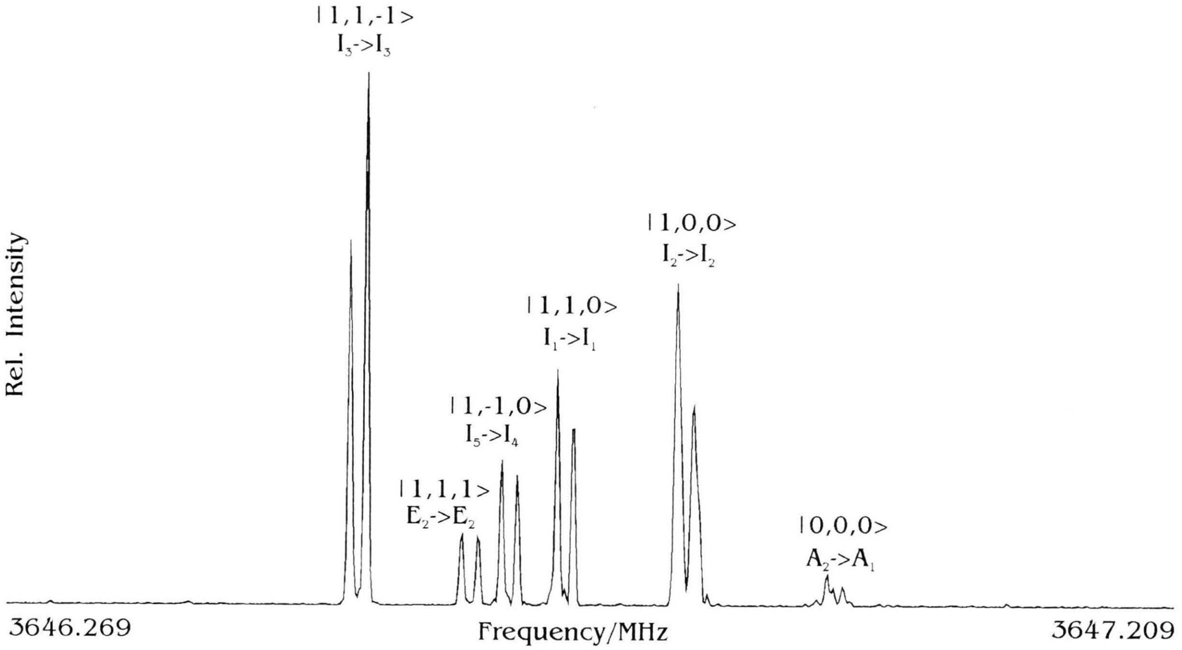

Fig. 2. Power spectrum of the rotational transition $J = 1 \rightarrow 0$ of the trimethyl ethynyl germane principal isotopomer (^{74}Ge): The measurement of the decay was performed with 8 *k* data points, a sample interval of 40 ns and 32 *k* accumulated cycles. After supplementing 8 *k* zeros to the end of the decay, the interval between two points in the spectrum is 1.5 kHz. The power spectrum shown in this figure is convoluted with a Welch window (1 *k* = 1024).

inside a vacuum tank. One microwave mirror contains near its center a nozzle for the generation of a pulsed molecular beam propagating parallel to the cavity axis. After the end of a molecular pulse and a short delay time a microwave pulse polarizes the beam. After a further delay time the decaying molecular emission signal is digitally recorded for some microseconds. Owing to repetition and coherent averaging, the molecular decay can be lifted over the noise. More detailed descriptions can be found in [3], [4], and [5]. The measurement of the rotational transition $J = 1 \rightarrow 0$ was performed with a sample interval of 40 ns with 8 k data points and 32 k accumulated cycles. The microwave power and pulse width were 2.8 mW and 2.0 µs, respectively, at a polarisation frequency of 3646.74 MHz and a recording time of 328 µs for one cycle. The time for the overall measurement was 27 min for 32 k cycles. To cool down the rotational and vibrational degrees of freedom, the sample was diluted to 1 % using argon as a carrier gas. Figure 2 shows the power spectrum convoluted with a Welch window [6] and transformed using 16 k data points for the rotational transition $J = 1 \rightarrow 0$ in the vibrational ground state of the most abundant isotopomer. Because the molecular beam of the used spectrometer propagates parallel to the resonator axis, every rotational transition is split into a Doppler doublet. Figure 2 indicates also the assigned rotational torsional symmetry species of the molecular symmetry group G_{162}, which will be explained below. Table 1 contains the measured frequencies of the isotopomeres with ^{70}Ge (20.5 %), ^{72}Ge (27.4 %) and ^{74}Ge (36.5 %).

Table 1. Frequencies of the measured transition $J = 1 \rightarrow 0$ in the vibrational and torsional ground state of trimethyl ethynyl germane. The uncertainties of the frequencies are estimated to be 1 kHz. The differences between the measured and the calculated frequencies are below 1 kHz.

Rotational–torsional symmetry species	Frequency/MHz ^{70}Ge	^{72}Ge	^{74}Ge
$A_2 \rightarrow A_1$	3650.447	3648.669	3646.939
$I_2 \rightarrow I_2$	3650.326	3648.547	3646.816
$I_1 \rightarrow I_1$	3650.228	3648.449	3646.719
$I_5 \rightarrow I_4$	3650.184	3648.404	3646.674
$E_2 \rightarrow E_2$	3650.151	3648.372	3646.642
$I_3 \rightarrow I_3$	3650.062	3648.282	3646.552

Analysis

Model and Hamiltonian

For the analysis of the measured rotational spectrum in the vibrational and torsional ground state a model of a rigid molecular frame with three rigid symmetric internal tops is assumed. The internal rotation axes are equal to the symmetry axes of the methyl–groups. If α_k labels the rotation angle of the k-th top, then the operator of the k-th internal angular momentum is

$$\hat{p}_k = \frac{\hbar}{i}\frac{\partial}{\partial \alpha_k}. \qquad (1)$$

In the principal axis method system (PAM) one obtains with the definition of the generalized angular momentum $\hat{\boldsymbol{P}}_a$

$$\hat{\boldsymbol{P}}_a := \begin{pmatrix} \hat{P}_x \\ \hat{P}_y \\ \hat{P}_z \\ \hat{p}_1 \\ \vdots \\ \hat{p}_n \end{pmatrix}, \qquad (2)$$

where $\hat{P}_g, g = x, y, z$, are the Cartesian components of the overall angular momentum operator in the molecule fixed coordinate system. The rotational Hamiltonian $\hat{H}$ for a molecule with n symmetric internal tops may be written as [7]

$$\hat{H} = \frac{1}{2}\hat{\boldsymbol{P}}_a^{\top}\,\mathbf{I}_a^{-1}\,\hat{\boldsymbol{P}}_a + V(\alpha_1, \alpha_2, \ldots, \alpha_n) \qquad (3)$$

with

$$\mathbf{I}_a^{-1} := \left(\begin{array}{c|c} \mathbf{I}^{-1} + \boldsymbol{\rho}\,\mathbf{S}^{-1}\,\boldsymbol{\rho}^{\top} & -\boldsymbol{\rho}\,\mathbf{S}^{-1} \\ \hline -\mathbf{S}^{-1}\,\boldsymbol{\rho}^{\top} & \mathbf{S}^{-1} \end{array}\right), \qquad (4)$$

$$\boldsymbol{\rho} := \begin{pmatrix} \rho_{x1} & \rho_{x2} & \cdots & \rho_{xn} \\ \rho_{y1} & \rho_{y2} & \cdots & \rho_{yn} \\ \rho_{z1} & \rho_{z2} & \cdots & \rho_{zn} \end{pmatrix}, \qquad (5)$$

$$\rho_{gk} := \frac{I_{\alpha k}}{I_g}\lambda_{gk}, \ \lambda_{gk} := \boldsymbol{e}_g \cdot \boldsymbol{e}_{\alpha k} \qquad (6)$$

with $g = x, y, z$ and $k = 1, \ldots, n$ and

$$\mathbf{S} := \begin{pmatrix} r_1 I_{\alpha 1} & q_{12} I_{\alpha 1} I_{\alpha 2} & \cdots & q_{1n} I_{\alpha 1} I_{\alpha n} \\ q_{21} I_{\alpha 2} I_{\alpha 1} & r_2 I_{\alpha 2} & \cdots & q_{2n} I_{\alpha 2} I_{\alpha n} \\ \vdots & \vdots & \ddots & \vdots \\ q_{n1} I_{\alpha n} I_{\alpha 1} & q_{n2} I_{\alpha n} I_{\alpha 2} & \cdots & r_n I_{\alpha n} \end{pmatrix} \qquad (7)$$

with

$$r_k := 1 - \sum_{g=x,y,z} \lambda_{gk}^2 \frac{I_{\alpha k}}{I_g}, \ q_{kl} := -\sum_{g=x,y,z} \frac{\lambda_{gk}\lambda_{gl}}{I_g}. \qquad (8)$$

Here $\boldsymbol{e}_g$ and $\boldsymbol{e}_{\alpha k}$ are the unit vectors in the direction of the principal axis g and the internal rotation axis k, respectively. Furthermore, **I** labels the tensor of the moment of inertia in the PAM system and $I_{\alpha k}$ the moment of inertia of the k-th internal top around its symmetry axis. Moreover the definition

$$\mathbf{F} := \frac{1}{2}\mathbf{S}^{-1} \qquad (9)$$

is used in the following.

Now the Hamiltonian $\hat{H}$ has to be spezialized for the molecule trimethyl ethynyl germane. For that purpose a molecule fixed Cartesian right handed coordinate system with axes, labeled x, y, and z, and origin in the center of mass of the molecule is defined as shown in Figure 1. The y–axis of the coordinate system lies in the plane containing also the z–axis and the carbon–nucleus C_1.

The internal rotation angles α_k, $k = 1, 2$ and 3 of the three methyl–groups in Fig. 1 are set to zero, if the H–nuclei No. 1, 4, and 7 are in trans position to the ethynyl–group. Then the methyl–groups are to be found in their equilibrium positions. This has been computed in an ab–initio calculation with Gaussian 92 for the molecule trimethyl ethynyl silane [8] being assumed also for trimethyl ethynyl germane. The internal rotation angles are with a visual direction from the methyl–carbon to the germanium measured anticlockwise. Moreover the angles between the z–axis and the germanium–methyl bonds are labeled with w_1. Because of the C_{3v}–symmetry of the molecule these three angles are equal. The angles between the projections of these bonds in the xy–plane are in consequence of symmetry 120°.

With these definitions one gets for trimethyl ethynyl germane with $\boldsymbol{\lambda} := (\lambda_{gk})$

$$\boldsymbol{\lambda} = \begin{pmatrix} 0 & -\frac{\sqrt{3}}{2}\sin w_1 & \frac{\sqrt{3}}{2}\sin w_1 \\ \sin w_1 & -\frac{1}{2}\sin w_1 & -\frac{1}{2}\sin w_1 \\ \cos w_1 & \cos w_1 & \cos w_1 \end{pmatrix}, \qquad (10)$$

and with the defining equation (6) for $\boldsymbol{\rho}$ and $I_{\alpha 1} = I_{\alpha 2} = I_{\alpha 3} =: I_\alpha$

$$\boldsymbol{\rho} = I_\alpha \begin{pmatrix} 0 & -\frac{\sqrt{3}\sin w_1}{2I_x} & \frac{\sqrt{3}\sin w_1}{2I_x} \\ \frac{\sin w_1}{I_y} & -\frac{\sin w_1}{2I_y} & -\frac{\sin w_1}{2I_y} \\ \frac{\cos w_1}{I_z} & \frac{\cos w_1}{I_z} & \frac{\cos w_1}{I_z} \end{pmatrix}. \qquad (11)$$

After inserting $\boldsymbol{\lambda}$ of (10) in (8) for r_k and q_{kl}, and noting that $I_x = I_y$, one gets for trimethyl ethynyl germane with $r := r_1 = r_2 = r_3$ and $q := q_{12} = q_{13} = q_{23}$:

$$r = 1 - I_\alpha \left(\frac{1}{I_x} \sin^2 w_1 + \frac{1}{I_z} \cos^2 w_1 \right) \qquad (12)$$

and

$$q = \frac{1}{2I_x} \sin^2 w_1 - \frac{1}{I_z} \cos^2 w_1 . \qquad (13)$$

Thereby the diagonal elements S of $\mathbf{S}$ are

$$S = I_\alpha - I_\alpha^2 \left(\frac{1}{I_x} \sin^2 w_1 + \frac{1}{I_z} \cos^2 w_1 \right), \qquad (14)$$

and the off–diagonal elements S'

$$S' = I_\alpha^2 \left(\frac{1}{2I_x} \sin^2 w_1 - \frac{1}{I_z} \cos^2 w_1 \right). \qquad (15)$$

The diagonal and off–diagonal elements F and F', respectively, of $\mathbf{F}$ in dependence of S and S' are

$$F = \frac{1}{2} \frac{S^2 - S'^2}{S^3 + 2S'^3 - 3SS'^2}, \qquad (16)$$

$$F' = \frac{1}{2} \frac{S'^2 - S'S}{S^3 + 2S'^3 - 3SS'^2}. \qquad (17)$$

Because $S' \approx 0$ we may write in a good approximation

$$F \approx \frac{1}{2S}, \qquad (18)$$

$$F' \approx 0. \qquad (19)$$

For the torsional potential $V(\alpha_1, \alpha_2, \alpha_3)$ the definition

$$V(\alpha_1, \alpha_2, \alpha_3) = \frac{1}{2} V_3 \sum_{k=1}^{3} (1 - \cos 3\alpha_k), \qquad (20)$$

which is the first approximation of a Fourier expansion, is used. With this approximation especially torsion–torsion interactions are neglected. For two top molecules their contribution is according to experience below 5 % [9].

Symmetry Considerations

Let us consider the Hamiltonian of the internal rotation

$$\hat{H}_{\text{tor}} = F \sum_{k=1}^{3} \hat{p}_k^2 + \frac{V_3}{2}(1 - \cos 3\alpha_k), \qquad (21)$$

which is a part of $\hat{H}$. The solutions of the eigenvalue equation of $\hat{H}_{\text{tor}}$ are well known and can be labeled with the quantum numbers v_1, v_2, v_3 and $\sigma_1, \sigma_2, \sigma_3$ [10]. In the case of a high torsional barrier like in trimethyl ethynyl germane, the separation between energy levels of different v_k quantum numbers are much larger than the separation between energy levels with equal v_k but different σ_k quantum numbers. In consequence of the low beam temperature, most trimethyl ethynyl germane molecules are in states with $v_1 = v_2 = v_3 = 0$, but states with different σ–values are occupied. Depending on the σ-values of the tops there are $3^3 = 27$ possible different $|\sigma_1, \sigma_2, \sigma_3\rangle$–combinations. To find out which $|\sigma_1, \sigma_2, \sigma_3\rangle$–states are degenerate, symmetry considerations are useful. In the following there are used some basic terms, which are for example explained in [7] or [11].

The molecular symmetry group of trimethyl ethynyl germane has been worked out in [1]. This group, called G_{162}, has 162 elements and 13 symmetry species. The group contains the operations $D := (C_1\, C_3\, C_2)\,(1\,7\,4)\,(2\,8\,5)\,(3\,9\,6)$, $R_1 := (C_1\, C_2)\,(2\,3)\,(4\,7)\,(5\,9)\,(6\,8)^*$, $d_1 := (1\,3\,2)$, $d_2 := (4\,6\,5)$,

Table 2. Character table of the group G_{162}. The first line gives representative elements of a class, the second line the number of elements in a class; $\epsilon = e^{i\frac{2}{3}\pi}$.

	E	$d_1d_2d_3$	$d_1d_2^{-1}$	$d_1^{-1}d_2$	d_1	d_1d_2	$d_1^{-1}d_2d_3$	D	d_1D	$d_1^{-1}D$	R_1	d_2R_1	$d_2^{-1}R_1$
	1	2	3	3	6	6	6	18	18	18	27	27	27
A_1	1	1	1	1	1	1	1	1	1	1	1	1	1
A_2	1	1	1	1	1	1	1	1	1	1	–1	–1	–1
E_1	2	2	2	2	2	2	2	–1	–1	–1	0	0	0
E_2	2	2	2	2	–1	–1	–1	2	–1	–1	0	0	0
E_3	2	2	2	2	–1	–1	–1	–1	2	–1	0	0	0
E_4	2	2	2	2	–1	–1	–1	–1	–1	2	0	0	0
I_1	6	–3	0	0	0	–3	3	0	0	0	0	0	0
I_2	6	–3	0	0	3	0	–3	0	0	0	0	0	0
I_3	6	–3	0	0	–3	3	0	0	0	0	0	0	0
I_{4a}	3	3	$3\epsilon^*$	3ϵ	0	0	0	0	0	0	1	ϵ	ϵ^*
I_{4b}	3	3	3ϵ	$3\epsilon^*$	0	0	0	0	0	0	1	ϵ^*	ϵ
I_{5a}	3	3	$3\epsilon^*$	3ϵ	0	0	0	0	0	0	–1	$-\epsilon$	$-\epsilon^*$
I_{5b}	3	3	3ϵ	$3\epsilon^*$	0	0	0	0	0	0	–1	$-\epsilon^*$	$-\epsilon$

Table 3. Eigenfunctions $|\sigma_1, \sigma_2, \sigma_3\rangle$ of $\hat{H}_{\text{tor}}$ for the torsional ground state $v_1 = v_2 = v_3 = 0$ and assigned symmetry species of G_{162}.

Species	$\lvert\sigma_1, \sigma_2, \sigma_3\rangle$
A_1	$\lvert 0,0,0\rangle$
I_2	$\lvert 1,0,0\rangle, \lvert 0,1,0\rangle, \lvert 0,0,1\rangle,$ $\lvert -1,0,0\rangle, \lvert 0,-1,0\rangle, \lvert 0,0,-1\rangle$
I_1	$\lvert 1,1,0\rangle, \lvert 0,1,1\rangle, \lvert 1,0,1\rangle,$ $\lvert -1,-1,0\rangle, \lvert 0,-1,-1\rangle, \lvert -1,0,-1\rangle$
I_4	$\lvert 1,-1,0\rangle, \lvert 0,1,-1\rangle, \lvert -1,0,1\rangle,$ $\lvert -1,1,0\rangle, \lvert 0,-1,1\rangle, \lvert 1,0,-1\rangle$
I_3	$\lvert 1,1,-1\rangle, \lvert -1,1,1\rangle, \lvert 1,-1,1\rangle,$ $\lvert -1,-1,1\rangle, \lvert 1,-1,-1\rangle, \lvert -1,1,-1\rangle$
E_2	$\lvert 1,1,1\rangle, \lvert -1,-1,-1\rangle$

$d_3 := (7\,9\,8)$, all combinations of these operations and the identity operation E. Here C_1, C_2, C_3 mean the methyl-carbon nuclei and the numbers $1, \ldots, 9$ the numbers of the hydrogen nuclei as shown in Figure 1. The thirteen symmetry species are called A_1, A_2, E_1, E_2, E_3, E_4, I_1, I_2, I_3, I_{4a}, I_{4b}, I_{5a}, and I_{5b}. The characters of I_{4a} / I_{4b} and I_{5a} / I_{5b} respectively are conjugate complex to each other. Therefore the assigned energy levels are degenerate [12]. These representations are collected to the representations with the names I_4 and I_5 respectively. The character table of the group G_{162} is shown in Table 2.

In [1] the zero barrier eigenfunctions of the three tops were assigned to the symmetry species of the group G_{162}. The analogous assignment for the eigenfunctions $|\sigma_1, \sigma_2, \sigma_3\rangle$ of $\hat{H}_{\text{tor}}$ is shown in Table 3 and the assignment of the symmetric top eigenfunctions in Table 4.

Table 4. Symmetric rotor functions $|J, K, M\rangle$ and assigned symmetry species of G_{162}.

Species	Quantumnumbers	Basis
A_1	$K = 0$ and J even	$\lvert J, 0, M\rangle$
	$K = \pm 3, \pm 6, \ldots$	$\lvert J, K, M\rangle + (-1)^J \lvert J, -K, M\rangle$
A_2	$K = 0$ and J odd	$\lvert J, 0, M\rangle$
	$K = \pm 3, \pm 6, \ldots$	$\lvert J, K, M\rangle + (-1)^{J+1} \lvert J, -K, M\rangle$
E_1	$K = \pm 1, \pm 4, \ldots$ $K = \pm 2, \pm 5, \ldots$	$\lvert J, K, M\rangle$

The direct product of the torsional and the rotational representations provides the representations for the eigenfunctions of $\hat{H}_{\text{tor}} + \hat{H}_{\text{rot}}$. The further consideration of the rotation torsion interaction, which is also a part of $\hat{H}$, leaves these representations invariant because the interaction operator is invariant under operations of the group G_{162}. Because other interactions are not considered in the model, the rotational torsional symmetry species are appropriate to assign the spectral lines. Eigenfunctions of the states $v_1 = v_2 = v_3 = 0$, which belong to the same symmetry species, are degenerate. Therefore one gets the maximum number of lines of the rotational torsional pattern. For trimethyl ethynyl germane there are for the rotational transition $J = 1 \rightarrow 0$ six different rotational torsional symmetry species, which are assigned in Figure 2 to the measured spectrum.

Least Squares Fit

The least squares fit has been performed with the program 'i3fit' written by H. Hartwig. The torsional

Table 5. Assumed parameters for the least squares fit of the rotational transition $J = 1 \longrightarrow 0$ in the rotational torsional ground state of trimethyl ethynyl germane. β is the angle between the z–axis and the column–vectors of $\boldsymbol{\varrho}$.

	^{70}Ge	^{72}Ge	^{74}Ge
$(A - B)/MHz$	1231.640	1232.313	1232.970
F/GHz	160.87	160.87	160.87
β/rad	1.002	1.002	1.002

potential is approximated by (20), and F' is assumed to be zero. For the computation of the eigenvalues of the complete Hamiltonian matrix, first a diagonalization of the submatrices of the internal tops in the free rotor basis is computed. This is done in the molecule fixed ρ–systems. After back transformation to the principal axis system, these three matrices are added to the rigid symmetric rotor matrix and the diagonalization of the overall Hamiltonian matrix is computed. The theoretical foundations are described in [13].

The three parameters V_3, B_0 and ρ, which is the magnitude of the column vectors of $\boldsymbol{\rho}$, could be determined in a least squares fit of splittings of the rotational transition $J = 1 \longrightarrow 0$ (Table 6). The remaining parameters have been fixed. They were assumed from an electron diffraction measurement of the molecules trimethyl chloroethynyl germane and trimethyl ethynyl silane ($I_\alpha = 3.18$ amu Å^2, $w_1 = 110.60°$) [14] (Table 5).

The error of V_3 and ρ is estimated to be 5%. Reasons for the errors are, that trimethyl chloroethynyl germane could have a slightly different structure compared with trimethyl ethynyl germane. Moreover the vibration averaging is different for the microwave measurement. A further reason for V_3 is the neglect of higher terms in the Fourier expansion of the torsional potential. The methodological error of the rotational constant B_0 in the rotational and torsional ground state is estimated to be 10 kHz. The fitting errors are far below the methodological errors.

Table 6. Molecular constants of trimethyl ethynyl germane determined with the least squares fit.

Isotopomer	^{70}Ge	^{72}Ge	^{74}Ge
V_3 / kJ/mol	4.5(2)	4.5(2)	4.5(2)
B_0 / MHz	1825.125(10)	1824.235(10)	1823.370(10)
ρ	0.0124(6)	0.0124(6)	0.0124(6)

Higher rotational transitions and look–out

The rotational transitions of trimethyl ethynyl germane have been measured from $J = 1 \longrightarrow 0$ to $J = 4 \longrightarrow 3$. The transitions from $J = 2 \longrightarrow 1$ to $J = 4 \longrightarrow 3$ are with respect to centrifugal distortion (which is very small) described relatively well, but there are some additional splittings in the spectrum. Furthermore some few splittings are larger than computed by i3fit. We intend to improve the used model and publish the results later. For the determination of the constants B_0 and V_3, the analysis of the transition $J = 1 \longrightarrow 0$ is sufficient.

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[1] K. K. Lehmann and B. H. Pate, J. Mol. Spectrosc. **144**, 443 (1990).

[2] D. I. MacLean and R. E. Sacher, J. Organometal. Chem. **74**, 197 (1974).

[3] U. Andresen, H. Dreizler, J.-U. Grabow, and W. Stahl, Rev. Sci. Instrum. **61**, 3694 (1990).

[4] J.–U. Grabow and W. Stahl, Z. Naturforsch. **45a**, 1043 (1990).

[5] J.–U. Grabow, Dissertation, Beiträge zur apparativen Entwicklung der Fourier–Transform Technik und neue Molekularstrahl Experimente im Fabry–Perot Resonator, Christian–Albrechts–Universität Kiel, 1992.

[6] W. H. Press, B. P. Flannery, S. A. Teukolsky, and W. T. Vetterling, Numerical Recipes in C, Cambridge University Press, Cambridge 1988, page 441.

[7] K. Voges, Diplomarbeit, Molekulare Symmetrie und Mikrowellenspektroskopie von Trimethyl–ethinylsilan, Christian–Albrechts–Univeristät zu Kiel, 1994.

[8] M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Steward, and J. A. Pople, Gaussian 92, Rev. A, Gaussian Inc., Pittsburgh PA 1992.

[9] Landolt–Börnstein, Molecular Constants, Group II, Vol. **14a**, Chap. 2.8, Springer Verlag, Berlin 1982.

[10] W. Gordy and R. L. Cook, Microwave Molecular Spectra, John Wiley & Sons, New York 1984, Chapter XII.

[11] P. R. Bunker, Molecular Symmetry and Spectroscopy, Academic Press, New York 1979.

[12] Loc. cit. [11], S. 92.

[13] J. M. Vacherand, B. P. Van Eijck, J. Burie, and J. Demaison, J. Mol. Spectrosc. **118**, 355 (1986).

[14] W. Zeil, J. Haase, and M. Dakkouri, Disc. Farad. Soc. **47**, 149 (1969).