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

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Z. Naturforsch. 51 a, 299–305 (1996); received February 13, 1995

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, \((\text{CH}_3)_3\text{GeC}≡\text{CH}\). 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 \((4.5±0.2) \text{ kJ/mol}\) and \((1823.370±0.010) \text{ MHz}\), 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 \(\text{CH}_3\text{SiH}_3\). 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.

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. 1. Trimethyl ethynyl germane.

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Microwave measurement

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

<table>
<thead>
<tr>
<th>Rotational–torsional symmetry species</th>
<th>$^{70}$Ge Frequency/MHz</th>
<th>$^{72}$Ge Frequency/MHz</th>
<th>$^{74}$Ge Frequency/MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_2 \rightarrow A_1$</td>
<td>3650.447</td>
<td>3648.669</td>
<td>3646.939</td>
</tr>
<tr>
<td>$I_2 \rightarrow I_2$</td>
<td>3650.326</td>
<td>3648.547</td>
<td>3646.816</td>
</tr>
<tr>
<td>$I_1 \rightarrow I_1$</td>
<td>3650.228</td>
<td>3648.449</td>
<td>3646.719</td>
</tr>
<tr>
<td>$I_3 \rightarrow I_4$</td>
<td>3650.184</td>
<td>3648.404</td>
<td>3646.674</td>
</tr>
<tr>
<td>$E_2 \rightarrow E_2$</td>
<td>3650.151</td>
<td>3648.372</td>
<td>3646.642</td>
</tr>
<tr>
<td>$I_3 \rightarrow I_3$</td>
<td>3650.062</td>
<td>3648.282</td>
<td>3646.552</td>
</tr>
</tbody>
</table>
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 \( \alpha_k \) labels the rotation angle of the \( k \)-th top, then the operator of the \( k \)-th internal angular momentum is

\[
\hat{p}_k = \frac{\hbar}{i} \frac{\partial}{\partial \alpha_k}.
\]

(1)

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

\[
\hat{P}_a := \begin{pmatrix} \hat{p}_x \\ \hat{p}_y \\ \hat{p}_z \\ \vdots \\ \hat{p}_n \end{pmatrix},
\]

(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]

\[
\hat{H} = \frac{1}{2} \hat{P}_a \Gamma_a^{-1} \hat{P}_a + V(\alpha_1, \alpha_2, \ldots, \alpha_n)
\]

(3)

with

\[
\Gamma_a^{-1} := \begin{pmatrix} I^{-1} + \rho S^{-1} \rho^T \\ -\rho S^{-1} \\ -S^{-1} \rho^T \\ S^{-1} \end{pmatrix},
\]

(4)

\[
\rho := \begin{pmatrix} \rho_{x1} & \rho_{x2} & \cdots & \rho_{xn} \\ \rho_{y1} & \rho_{y2} & \cdots & \rho_{yn} \\ \rho_{z1} & \rho_{z2} & \cdots & \rho_{zn} \end{pmatrix},
\]

(5)

\[
\rho_{gk} := \frac{I_{gk}}{I_g} \lambda_{gk}, \quad \lambda_{gk} := e_g \cdot e_{ak}
\]

(6)

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

\[
S := \begin{pmatrix} r_{11}I_{a1} & q_{12}I_{a1}I_{a2} & \cdots & q_{1n}I_{a1}I_{an} \\ q_{21}I_{a2}I_{a1} & r_{22}I_{a2} & \cdots & q_{2n}I_{a2}I_{an} \\ \vdots & \vdots & \ddots & \vdots \\ q_{n1}I_{an}I_{a1} & q_{n2}I_{an}I_{a2} & \cdots & r_{nn}I_{an} \end{pmatrix}
\]

(7)

with

\[
r_k := 1 - \sum_{g=x,y,z} \lambda_{gk}^2 \frac{I_{ak}}{I_g}, \quad q_{kl} := -\sum_{g=x,y,z} \lambda_{gk} \lambda_{gl} I_g.
\]

(8)

Here \( e_g \) and \( e_{ak} \) 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 \( I_{ak} \) the moment of inertia of the \( k \)-th internal top around its symmetry axis. Moreover the definition

\[
F := \frac{1}{2} S^{-1}
\]

(9)

is used in the following.

Now the Hamiltonian \( \hat{H} \) has to be specialized 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 \( c \)-axis and the carbon–nucleus \( C_1 \).

The internal rotation angles \( \alpha_k, k = 1, 2 \) 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 \( 120^\circ \).
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, ..., 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_4, I_5, I_6, and I_7. The characters of I_4, I_5, and I_6, 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_1 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 |σ_1, σ_2, σ_3⟩ of \(\hat{H}_{\text{tor}}\) is shown in Table 3 and the assignment of the symmetric top eigenfunctions in Table 4.

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
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 $p$-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 $\rho$, which is the magnitude of the column vectors of $\rho$, could be determined in a least squares fit of splittings of the rotational transition $J = 1 \rightarrow 0$ (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 ($I_o = 3.18$ amu Å$^2$, $\omega_1 = 110.60°$) [14] (Table 5).

The error of $V_3$ and $\rho$ 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.

**Higher rotational transitions and look-out**

The rotational transitions of trimethyl ethynyl germane have been measured from $J = 1 \rightarrow 0$ to $J = 4 \rightarrow 3$. The transitions from $J = 2 \rightarrow 1$ to $J = 4 \rightarrow 3$ 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 $J = 1 \rightarrow 0$ is sufficient.

**Acknowledgements**

We thank the members of our group especially Prof. Dr. W. Stahl and Dipl. Phys. et Chem. J. Rottstegge for stimulating discussions. Funding by the Deutsche Forschungsgemeinschaft, the Fond der Chemie and the Land Schleswig-Holstein is gratefully acknowledged.

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**Table 5. Assumed parameters for the least squares fit of the rotational transition $J = 1 \rightarrow 0$ in the rotational torsional ground state of trimethyl ethynyl germane. $\beta$ is the angle between the $z$-axis and the column-vectors of $\rho$.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$^70\text{Ge}$</th>
<th>$^72\text{Ge}$</th>
<th>$^74\text{Ge}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(A - B)/\text{MHz}$</td>
<td>1231.640</td>
<td>1232.313</td>
<td>1232.970</td>
</tr>
<tr>
<td>$F/\text{GHz}$</td>
<td>160.87</td>
<td>160.87</td>
<td>160.87</td>
</tr>
<tr>
<td>$\beta/\text{rad}$</td>
<td>1.002</td>
<td>1.002</td>
<td>1.002</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Isotopomer</th>
<th>$^70\text{Ge}$</th>
<th>$^72\text{Ge}$</th>
<th>$^74\text{Ge}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_3$ / kJ/mol</td>
<td>4.5(2)</td>
<td>4.5(2)</td>
<td>4.5(2)</td>
</tr>
<tr>
<td>$B_0$ / MHz</td>
<td>1825.125(10)</td>
<td>1824.235(10)</td>
<td>1823.370(10)</td>
</tr>
<tr>
<td>$\rho$</td>
<td>0.0124(6)</td>
<td>0.0124(6)</td>
<td>0.0124(6)</td>
</tr>
</tbody>
</table>