Determination of the rotational constants A and C for a slightly perturbed SiH$_2$CCH molecule

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The rotational constant, $A_0$, for the ground state of SiH$_2$CCH molecule was calculated using a technique which was used earlier for CH$_3$CCH [Tam H S & Roberts J A, Street Chem. 1 (1990) 211] and CH$_3$CN [Al-Share M, Hajalesh J, Qian S W & Roberts J A, Street Chem. 5 (1994) 109]. This technique is based on calculating the moment of inertia tensors in the bent configuration due to the $v_{1'}$ vibrational state, which is associated with the SiCC bending motion. These values of the moment of inertia were fitted with the values calculated from the rotational constant $B$, which is found by measuring the rotational frequencies in the microwave and infrared regions experimentally. From the fitting, the bending angle $\angle$SiCC and the asymmetry parameters were determined for $v_0=1, 2, 3$, and 4 bending vibrational states.

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1 Introduction

Silyl acetylene (SiH$_2$CCH) is a prolate symmetric top molecule with $C_{\infty v}$ symmetry. The rotational constant of the ground state $A_0$ about the axis of highest symmetry cannot be easily obtained to a very high accuracy by direct measurements in symmetric top molecules due to the fact that this constant vanishes from the frequency equation. The disappearance of $A_0$ is a result of the application of the selection rule $\Delta K=0$ in calculating the frequency of a rotational component in the ground vibrational state$^{3,4}$. If the symmetric top molecule is excited to the first few excited vibrational states, the rotational constant $A_0$ does appear in the frequency equation and a set of experimental rotational constants can be determined from the fitting between the experimental and the theoretical values of the frequency for the SiH$_2$CCH molecule$^{5,6}$. These results can be used to obtain the trend of the rotational constant $A_0$ over the $v_{1'}=1, 2, 3$, and 4 vibrational states, and through extrapolation these values to get $A_0$. Carlier and Bauer$^1$ have studied the microwave spectra of SiH$_2$CCH in the $v_{1'}=2$ vibrational state. Carlier and Bauer$^4$ have studied the millimeter wave spectra of SiH$_2$CCH in the ground vibrational state. Bauer and Carlier$^2$ have studied the microwave spectra of SiH$_2$CCH in the $v_{1'}=3$ vibrational state. Carlier et al.$^6$ have studied the microwave spectra of SiH$_2$CCH in the $v_{1'}=4$ vibrational state.

Reeves and Robinson$^b$ have studied the infrared spectra for SiH$_2$CCH and SiD$_2$CCH and determined the frequencies of the ten vibrational modes for both isotopes. Ebsworth et al.$^{10}$ have studied the infrared spectra of silyl acetylene in the region 280-500 cm$^{-1}$. Gerry and Sugden$^1$ have studied the microwave spectra of the ground and the $v_{1'}=1$ vibrational states for six isotopic species of SiH$_2$CCH and determined the molecular structure for it by determining the bond lengths and the bond angles. Tam and Roberts$^{11}$ have outlined a method of using the rotational constant $B$ in the ground and the $v_{1'}=1, 2, 3$, and 4 excited vibrational states of CH$_3$CCH to determine the ground rotational constant $A_0$. The method consists of determining the trend in each rotational constant over the range of vibrations available and using this trend to determine the value of $A_0$ in the limiting case for the ($v_{1'}=0$) ground state. Al-Share et al.$^{12}$ have used this method...
to determine the rotational constant \( A_i \) for the CH\(_3\)CN molecule and its \(^{13}\)C and \(^{15}\)N tagged isotopes.

The aim of this work is to extend this method to determine the rotational constants \( A_i \), the rotational constant \( C \), and the bending angle \( \angle \)SiCC of the \( \nu_{\beta} \) vibration and its overtones, which is associated with the Si-C=C bending motion for SiH\(_3\)CCH molecule\(^9\).

2. Theory

The rotational constant \( B_\gamma \) for each isotope was determined experimentally using data from microwave and infrared spectra for these isotopes\(^{10,11}\). The moment of inertia in the bent configuration of SiH\(_3\)CCH molecule as shown in Fig. 1, can be obtained with respect to the two coordinates systems (x, y, z) and (x', y', z') which are the center of mass coordinates before and after the C\(_3\)v symmetry is broken by the \( \nu_{\alpha} \) vibration and its overtones respectively. The origin is located at the center of mass of the molecule. From basic considerations, the equations used to calculate the moments of inertia about the X-axis and the Z-axis for C\(_3\)v symmetric top molecule were developed by Kesler et al\(^12\). before the symmetry is broken by the \( \nu_{\alpha} \) vibrational state, where the Si-C=C bending angle (\( \delta = \gamma = 0^\circ \)) (Fig. 1). These equations must be modified for the configuration of broken symmetry due to the \( \nu_{\alpha} = 1 \), \( \nu_{\beta} = 2 \), \( \nu_{\gamma} = 3 \) and \( \nu_{\delta} = 4 \) bending vibrational states, and to take into consideration the non-point mass distribution of the three hydrogen atoms in the methyl group. The formulas for the components of the inertia tensor for an arbitrary axis of rotation\(^13,14\) are:

\[
I_x = \sum_{i=1}^{n} m_i (x_i^2 + z_i^2) - \frac{1}{M} \left( \sum_{i=1}^{n} m_i y_i \right)^2 \tag{3}
\]

\[
I_y = \sum_{i=1}^{n} m_i (y_i^2 + z_i^2) - \frac{1}{M} \left( \sum_{i=1}^{n} m_i x_i \right)^2 \tag{4}
\]

\[
I_z = \sum_{i=1}^{n} m_i (x_i^2 + y_i^2) - \frac{1}{M} \left( \sum_{i=1}^{n} m_i y_i \right)^2 \tag{5}
\]

The total mass \( M \) is:

\[
M = \sum_{i=1}^{n} m_i \tag{7}
\]

Although these Eqs (1-7) lack accuracy when the coordinates are not taken with respect to the center of mass of the molecule. It is possible to use them if the products of inertia Eqs (4-6) vanish\(^11,12\). It is convenient as well to utilize symmetry in the molecule to simplify the calculations of these inertia tensors for the broken symmetry configuration. The planes described by one hydrogen, the silicon and the acetylene group (C=C-H) were chosen for the projection plane, and the x'y' plane, for one set of the calculations. The inertia tensors can, now, be expressed in an explicit form for the coordinate set ( \( x', y', z' \)). In the bent configuration (Fig. 1) where the angle of bending for the \( \nu_{\alpha} \) vibrational state is characterized by the angle \( \angle SiCC \). The orientation of the bending of each section of the molecule with respect to the fixed Z-axis is determined by two angles \( \delta \) and \( \gamma \). The C=C-H group is assumed to deviate by the angle \( \delta \) and the SiH\(_3\) group to deviate from the original symmetry axis by the angle \( \gamma \) (Fig. 1). Although this procedure is equivalent to consider only the bending of the C=C-H group by an angle of \( (\delta + \gamma) \), it seems easier to visualize the projection of each component of the inertia tensor by two separate angles \( \delta \) and \( \gamma \). The inertia tensor is then given by:
The effect of the polar orientation of the \( \text{CH}_2 \) group with respect to the \((x', y', z')\) coordinates was studied by Al-share et al.\(^{12}\) for the \( \text{CH}_2\text{CN} \) molecule and by Tam and Roberts\(^{11}\) for \( \text{CH}_3\text{CCH} \) molecule. They showed that when the molecule is bent, the rotating \( \text{CH}_2 \) group has a negligible effect on the bend angle. Also, no effect is found due to the rotation of \( \text{CH}_2 \) group on the rotational constants \( A, B \) and \( C \) of the \( \text{CH}_2\text{CN} \) molecule\(^{16}\).

A function \( M \) is defined such that

\[
M = |1 - \lambda_1| \quad \text{... (11)}
\]

Once the elements of the inertia tensor have been obtained, the secular equation is solved:

\[
|1 - \lambda_1| = 0 \quad \text{... (12)}
\]

and from the solutions of Eq. (12), the values of the rotational constants \( A, B, \) and \( C \) of the molecule can be obtained. The moment of inertia \( I_{xx} \) is related to the rotational constant\(^{11}\) \( B \) through the following relation:

\[
B = \frac{h}{8\pi^2 I_{xx}} \quad \text{... (13)}
\]

The experimental value of the rotational constant \( B \) was inserted in a computer program based on Eq. (12), and the angles \( \delta \) and \( \gamma \) were iterated over a pre-expected intervals to obtain their values which minimize \( M \) to a pre-determined value of 0.0001 or less between the value of \( I_{xx} \) calculated from Eq. (8) and the value calculated from the rotational constant \( B \) from Eq. (13), keeping in mind that \( B \) was obtained experimentally in the microwave and infrared spectra for each vibrational states\(^{13}\). The inertia tensors (Eqs 8-10) showed a small dependency on the angle \( \alpha \), the angle between the figure axis of \( \text{SiH}_3 \) group and the \( \text{Si}-\text{H} \) bonds, over the vibrations (Fig. 1). The value of \( \chi \) was assumed to be constant for all the vibrations. This value is the one, which minimize the function \( M \) for the principal moment of inertia \( I_{xx} \) for the ground vibrational state \((L = 0, \gamma = 0)\). For \( \text{SiH}_3\text{CCH} \) molecule \( \alpha \) was found to be \((66.446^\circ)\). The \( \angle \text{SiCC} \) bending angle for the \( v_{\text{in}} \) vibrational state is constrained by the experimental value of each vibration and is given in terms of the angle \( \delta \) and \( \gamma \) by:

\[
\angle \text{SiCC} = \Pi - (\delta + \gamma) \quad \text{... (14)}
\]

In order to calculate the rotational constants \( A, \)
Table 1—Summary of the average values of the moments of inertia, the rotational constants, the asymmetry parameter $\kappa$, and the bending angle $\angle SICCC$ for SiH$_2$CCH molecule.

<table>
<thead>
<tr>
<th>Constant</th>
<th>$v_{\mu}=1$</th>
<th>$v_{\mu}=2$</th>
<th>$v_{\mu}=3$</th>
<th>$v_{\mu}=4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_{1}$ (amu $\cdot$ Å$^2$)</td>
<td>104.2177</td>
<td>103.8008</td>
<td>103.3880</td>
<td>102.9787</td>
</tr>
<tr>
<td>$I_{2}$ (amu $\cdot$ Å$^2$)</td>
<td>104.2483</td>
<td>104.0485</td>
<td>103.8843</td>
<td>103.7152</td>
</tr>
<tr>
<td>$I_{3}$ (amu $\cdot$ Å$^2$)</td>
<td>5.601527</td>
<td>5.818929</td>
<td>6.071198</td>
<td>6.313009</td>
</tr>
<tr>
<td>$B$ (MHz)</td>
<td>4848.623</td>
<td>4868.095</td>
<td>4887.531</td>
<td>4906.956</td>
</tr>
<tr>
<td>$C$ (MHz)</td>
<td>4847.199</td>
<td>4856.507</td>
<td>4864.183</td>
<td>4872.114</td>
</tr>
<tr>
<td>$A$ (MHz)</td>
<td>90209.7</td>
<td>8683.36</td>
<td>83231.03</td>
<td>80042.98</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>-0.99997</td>
<td>-0.99972</td>
<td>-0.99940</td>
<td>-0.99907</td>
</tr>
<tr>
<td>$\angle SICCC$ $(^\circ)$</td>
<td>170.314</td>
<td>167.0276</td>
<td>165.3068</td>
<td>165.294</td>
</tr>
</tbody>
</table>

Fig. 2—Rotational constant $A$ (MHz) versus the vibrational quantum number $v$.

and $C$, for each vibration, the values of the angles $\delta$ and $\gamma$ for each vibrational state (Table 1), were inserted into a computer program based on Eqs (9) and (10) respectively. Finally the rotational constant $A_0$ is plotted versus the excited vibrational quantum number $v$ (Fig. 2), and the curve is extrapolated to find the value $A_0$ for the ground vibrational state. The values used in these calculations for the atomic masses of the $^{12}$C, $^{28}$Si and $^1$H atoms were 12.00000, 28.0855 and 1.007825 amu respectively, the values of the bond lengths of the C-C" $d_{CC''}$, H-Si-H and the Si-C bonds $d_{SiC}$ and $d_{SiH}$ were 1.208, 1.058, 1.483 and 1.826 Å respectively, the bond angles C-C-H and H-Si-H were 109.85° and 110°12'.

### 3 Results and Discussion

The values of the rotational constants $A$ and $C$, the bending angle $\angle SICCC$ and the values of the asymmetry parameter $\kappa$ were obtained using a computer program based in Eqs (8-10). These values were presented in Table 1. Although, this iteration technique gives more than one set of the angles $\delta$ and $\gamma$ which give the best fit between the value of $B_{exp}$ and $B_{cal}$, the sum of these two angles ($\delta + \gamma$) exhibits very small fluctuations during the fit, which means a small fluctuations in the $\angle SICCC$ bending angle. It is known that a statistical average can be obtained to give a reasonable good estimate for a particular constant, if the fluctuations associated with that constant are small. The nature of the asymmetry parameter $\kappa$ with respect to the excited vibrational levels can be observed so that the degree of the departure from that of a true symmetric top to asymmetric top molecule can be predicted. From Table 1, it can be seen that the angle of bending decreases with increase of the vibrational level, suggesting that the highly excited states are extremely sensitive to the degree of bending in the molecular system. The average values of the rotational constants $A_0$ were calculated for each excited state, which were given in Table 1, these values were reported for the first time for $v_{\mu}=1$, $v_{\mu}=2$, $v_{\mu}=3$ and $v_{\mu}=4$ bending
vibrational states in this work. They show good agreement with the values assumed in microwave and infrared spectra, and also agree with the trend found for CH:CCH molecule. Fig. 2 represents a plot of the rotational constant $A_\nu$ versus the vibrational quantum number $v$, which is a linear relation, then, $A_\nu$ its value for the ground state can be obtained by extrapolating the linear line to intercept with the Y-axis, which was found to be 93607.89 MHz. Fig. 3 represents a plot of the rotational constants $B_\nu$ versus the vibrational quantum number $v$, which shows a linear relation. This line can be used to estimate the value of $B_\nu$ for higher overtones (i.e., $v_{10}=5$, $v_{10}=6$, $v_{10}=7$ and $v_{10}=8$ vibrational states). This constant can be used to start the search for the rotational components for each vibrational state, after measuring these components experimentally in the microwave or infrared regions, this constant can be refined to give the best fit between the experimental and theoretical values of the frequency of these components. Fig. 4 represents a plot of the rotational constants $C_\nu$ versus the vibrational quantum number $v$, which shows a linear relation. Although, the departure of the asymmetry parameter $\kappa$ from its value for the symmetric top molecule seems to be very small (Table I), but it shows an increase with increase of the vibrational quantum number $v$. This departure was less than what was found for the CH:CCH molecule, which can be attributed to the fact that the silyl group is more massive than the methyl group, then the degree of asymmetry is expected to be less for heavy molecule (SiH:CCH) than for lighter molecule (CH:CCH).

4 Conclusion

In this work the value $A_\nu$ of the rotational constant $A$ for the ground state for SiH:CCH molecule was determined to be 93607.89 MHz. Also, the values of the rotational constants $A_\nu$ and $C_\nu$ for the fundamental and the first three overtones of the $v_{10}$ bending vibrational state were determined. A trend was established for determining the rotational constants $A$, $B$ and $C$ for higher overtones of the $v_{10}$ vibrational state (i.e. $v_{10}=5$, $v_{10}=6$, $v_{10}=7$ and $v_{10}=8$ vibrational states). These constants can be used to start the search for the rotational components for these vibrational states. The values of the bending angle $\angle \text{SiCC}$ and the asymmetry parameter $\kappa$ were determined for the first time which leads to more establishment of the geometry of the bending configuration of SiH:CCH molecule.

References

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