Coriolis interaction parameters of the \((2100; F_2)\) bands of SiH\(_4\) and GeH\(_4\). A test of local mode models

F.-G. Sun \(^a\), X.-G. Wang \(^a\), Q.-S. Zhu \(^{a,b,*}\), C. Pierre \(^b\), G. Pierre \(^b\)

\(^a\) Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, People’s Republic of China
\(^b\) Laboratoire de Physique, Unité Associée au CNRS, Université de Bourgogne, 6 boulevard Gabriel, 21000 Dijon, France

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Abstract

The high-resolution spectra of the \((2100; F_2, N)\), \(N = 1\) and \(2\), bands of SiH\(_4\) and GeH\(_4\) have been recorded and preliminarily analyzed. The Coriolis interaction parameter \(2B\ell_3\) is obtained; it provides a test of three widely used models: the harmonically coupled anharmonic oscillators model with two different kinds of variables, and the normal mode model with Darling–Dennison resonance included.

1. Introduction

During the past 60 years, the vibration–rotation spectroscopy of tetrahedral molecules has been one of the challenging topics for spectroscopists (for references, see review [1]). Their overtone spectra have been of particular interest, since the rotational structures of some stretching overtone bands of SiH\(_4\) [2], GeH\(_4\) [3] and SnH\(_4\) [4] were found to have a typical \(C_3v\) symmetry top pattern, indicating that the vibrational energy in their upper states is extremely bond localized, and therefore better described by the local mode model, which uses single bond oscillators as the basis states and a set of new vibrational quantum numbers – the local mode quantum numbers. Some theoretical studies [5–8] have been carried out to explain the observed striking rotational structures of the local mode vibrational states and to try to establish a convenient model for calculating the vibration–rotational spectra for tetrahedral hydrides by using the local mode vibrational states as the zeroth-order basis states. At present, attention has been concentrated on the vibration–rotational spectroscopy of the most local states \((n000)\) of the tetrahedral hydrides. Other stretching states, e.g. \((n100)\) and \((n110)\), etc., have not been studied so far, but they are essential for testing the theoretical models. For example, Child and Zhu [9] have shown that the effective Coriolis coupling parameter \(2B\ell_3\) in the \((n000; F_2)\) states diminishes rapidly to zero as the molecule approaches the local mode limit \((\lambda/\lambda_m \rightarrow 0)\), which is qualitatively consistent with the observation. However, the values of \(2B\ell_3\) in the \((n000; F_2)\) states are so small that they are difficult to be determined experimentally, therefore a quantitative test of the theory requires measurement of the effective Coriolis parameters of the \((n100; F_2)\) and \((n110; F_2)\) states, which have significantly large values, and so can be measured precisely and provide a

\(^*\) Corresponding author.
crucial test of the theoretical models used in calculations.

In the present work the high-resolution Fourier transform spectra of the \( \nu = 3 \) polyad regions of SiH\(_4\) and GeH\(_4\) have been recorded and preliminarily analysed. The lowest (2100; \( \text{F}_2 \)) stretching bands, denoted as (2100; \( \text{F}_2, 1 \)), are assigned for both molecules. The rotational constants and Coriolis interaction parameters \( 2B_3 \) are estimated and compared with the values calculated by means of the three models frequently used for the molecules close to the local mode limit.

2. Spectra and assignments

The absorption spectra of SiH\(_4\) in the region 6240–6570 cm\(^{-1}\) and of GeH\(_4\) in the region 6020–6420 cm\(^{-1}\) with resolution 0.02 cm\(^{-1}\) were recorded using a Bomem DA3.002 Fourier transform spectrometer with an InSb detector and a quartz-halogen light source. A White-type multipath absorption cell with effective path length 56 m, sample pressure 50 Torr and 200 co-added scans were used for the SiH\(_4\) spectrum, while that of 44 m, 35 Torr and 350 co-added scans were used for the GeH\(_4\) spectrum.

Comparing with a previous calculation [10], the weak band with its origin close to 6362 cm\(^{-1}\) in the SiH\(_4\) spectrum and the strong band near 6128 cm\(^{-1}\) in the GeH\(_4\) spectrum were assigned as the (3000) bands, while the strong one near 6497 cm\(^{-1}\) and the weak one near 6499 cm\(^{-1}\) for silane were assigned as the (2100; \( \text{F}_2, N \)), \( N = 1 \) and 2, bands. The spectrum of GeH\(_4\) is more complicated due to its five isotopic species. However, only the transitions of 70GeH\(_4\), 72GeH\(_4\) and 74GeH\(_4\) were assigned since 76Ge and 73Ge are less abundant. In the GeH\(_4\) spectrum, two other well formed bands are also observed and assigned as the \( \nu_1 + 4\nu_2 + \nu_3 \) and \( 2\nu_1 + 2\nu_2 + \nu_3 \) bands of CO\(_2\) [11].

<table>
<thead>
<tr>
<th>( J )</th>
<th>( P(J + 1) )</th>
<th>( Q(J) )</th>
<th>( R(J - 1) )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>exp.</td>
<td>calc.</td>
<td>exp.</td>
</tr>
<tr>
<td>1</td>
<td>6485.950</td>
<td>6485.943</td>
<td>6497.313</td>
</tr>
<tr>
<td>2</td>
<td>6480.053</td>
<td>6480.050</td>
<td>6497.078</td>
</tr>
<tr>
<td>3</td>
<td>6474.092</td>
<td>6474.056</td>
<td>6496.801</td>
</tr>
<tr>
<td>4</td>
<td>6467.873</td>
<td>6467.959</td>
<td>6496.303</td>
</tr>
<tr>
<td>5</td>
<td>6461.669</td>
<td>6461.795</td>
<td>6496.092</td>
</tr>
<tr>
<td>6</td>
<td>6455.351</td>
<td>6455.481</td>
<td>6455.541</td>
</tr>
<tr>
<td>7</td>
<td>6534.190</td>
<td>6534.216</td>
<td>6534.190</td>
</tr>
</tbody>
</table>
In the F\textsubscript{2} triply degenerate vibrational state of a spherical top molecule, the rotational angular momentum \(J\) and vibrational angular momentum \(l\) are coupled by Coriolis interaction to give rise to a resultant angular momentum \(R\). For example in an \(l = 1\) state, every \(J\) level will split into three sub-levels with \(R = J + 1, R = J\) and \(R = J - 1\), which have the first-order corrected rotational energies:

\[
E(J, R = J + 1) \quad (\equiv F^+ (J)) \\
= \nu_0 + BJ (J + 1) + 2B\xi_3 J,
\]

\[
E(J, R = J) \quad (\equiv F^0 (J)) \\
= \nu_0 + BJ (J + 1) - 2B\xi_3,
\]

\[
E(J, R = J - 1) \quad (\equiv F^- (J)) \\
= \nu_0 + BJ (J + 1) - 2B\xi_3 (J + 1).
\]

The infrared selection rules for strong transitions are: \(\Delta R = 0\) and \(\Delta K = 0\), as well as \(A_1 - A_2\), \(E - E\), \(F_1 - F_2\) and \(\Delta N = 0\). When these apply, the \(P(J + 1)\), \(Q(J)\) and \(R(J - 1)\) transitions will reach different upper sub-levels (with the same \(J\) but different \(R\) values).

Therefore, when the Coriolis splitting is significant, no combination difference relation exists, this makes the spectrum difficult to assign. However, as long as we can estimate the value of the effective parameter \(2B\xi_3\) from one set of well-formed \(P(J + 1)\) and \(R(J - 1)\) transitions (for example, the \(P(2)\) and \(R(0)\), or \(P(3)\) and \(R(1)\) transitions, etc.), we can 'compensate' the observed transition frequencies and use the 'pseudo'-combination difference relations. For example, knowing the energy of the \(J = 2\) level of the ground vibrational state, we can assign the transitions of \(P(3)\), \(Q(2)\) and \(R(1)\) by searching for a set of observed spectral lines which fulfill (within experimental uncertainty) the 'pseudo-' combination difference relations:

\[
E''(J = 1) + R(1) + 6B\xi_3 \\
= E''(J = 2) + Q(2) - 2B\xi_3 \\
= E''(J = 3) + P(3) - 4B\xi_3.
\]

This method has enabled us to assign some transitions for both molecules (Tables 1 and 2). In the spectrum of SiH\textsubscript{4}, in addition to the strong band (2100; \(F_2, 1\)) a weak band was also found and assigned to be the (2100; \(F_2, 2\)) band. In the spectrum of GeH\textsubscript{4}, the (2100; \(F_2, 1\)) bands of three isotopic species \(^{74}\text{GeH}_4\), \(^{72}\text{GeH}_4\) and \(^{70}\text{GeH}_4\) were found. Figs. 1 and 2 show the reduced energies of their upper levels plotted against the rotational quantum
number $J$. The reduced energy of an upper level is defined as

$$E_{\text{red}} = E_{\text{obs}} - \nu_0 - B J (J + 1),$$

(3)

where the band origin $\nu_0$ and rotational constant $B$ have been derived from the assigned transitions and are listed in Table 3. Both plots clearly show the Coriolis splittings between the $+l$ and $-l$ sub-levels, although the $-l$ levels of SiH$_4$ are obviously perturbed, so cannot be determined for $J \geq 3$. From the observed Coriolis splittings, we could derive the effective values of $2B\zeta_3$, which are of great importance since they provide a test of the following widely used theoretical models.

3. Effective Coriolis parameter $2B\zeta_3$

The effects of vibrational localization on rotational energy level structures can be conveniently discussed by means of the effective rotational Hamiltonian [12], which can be obtained by averaging the vibration–rotational Hamiltonian over all vibrational coordinates using the wavefunction of the vibrational state concerned. Then we obtain a Hamiltonian involving only rotational angular momentum operators with effective vibration–rotational parameters. The wavefunction of the stretching vibrational states can be obtained by the following different ways.

In the normal mode model with Darling–Dennison resonance included (NMDD) model [13], the zeroth-order basis states of stretching vibrations of SiH$_4$ and GeH$_4$ are the normal mode symmetric stretch $\nu_1$ and antisymmetric stretch $\nu_2$, as well as their overtones and combination states, the states within the same manifold (i.e. having the same total stretch vibrational quantum number $\nu$) are coupled with one another by Darling–Dennison resonance. For the $\nu = 3$ stretching manifold, the $A_1$ symmetry basis states are: $|3; 000\rangle$, $(1/\sqrt{3})(|1; 200\rangle + |1; 020\rangle + |1; 002\rangle)$ and $|0; 111\rangle$; the $F_{2\alpha}$ symmetry basis states are: $|2; 100\rangle$, $|1; 011\rangle$, $|0; 300\rangle$ and $(1/\sqrt{2})(|0; 120\rangle + |0; 102\rangle)$ etc., where the notation $|\nu_1, \nu_3_{\alpha}, \nu_3_{\beta}, \nu_3_{\gamma}\rangle$ is used. Using the matrix elements given by Mills and Robiette [13], we set up a $3 \times 3$ matrix for $A_1$ symmetry and a $4 \times 4$ matrix for each of the $F_{2\alpha}$ ($\alpha = x, y$ and $z$) symmetries, and then diagonalized to give rise to the real vibra-
tional energy levels and wavefunctions. Using the wavefunctions obtained by this method, Child and Zhu [9] have calculated the effective Coriolis interaction parameters $2B\xi_3$ in the $(n000)$, $(n - 1, 100)$ and $(n - 2, 110)$ states, $n = 1 - 5$, of SiH$_4$ and several other tetrahedral molecules. They found that the value of $2B\xi_3$ in the $(n000; F_2)$ states diminishes rapidly to zero as the molecule approaches the local mode limit ($\lambda/x_m \to 0$). This agrees qualitatively with the observed results. However, the values of $2B\xi_3$ in the $(n000; F_2)$ states of SiH$_4$ and GeH$_4$ are too small to be determined precisely from fitting the observed transitions. The Coriolis interaction parameters $2B\xi_3$ in the $(2100; F_2, 1)$ states of SiH$_4$ and GeH$_4$ are quite large (see Table 3), and so provide a quantitative check on the theoretical model. It is found that the difference between the observed values and the calculated ones by means of the NMDD model [9] is nearly 100%, indicating that the wavefunctions obtained by using the NMDD model are not precise enough for calculating the effective vibration-rotational parameters. In fact, in the calculation the inter-manifold couplings (i.e. the couplings between the vibrational states with different total vibrational quantum number $v$) are omitted and only the anharmonic terms up to fourth order are kept in the bond-oscillator potentials. If we add the inter-manifold coupling and higher-order anharmonic terms, the number of unknown parameters may become too large to handle.

However, in order to consider the inter-manifold couplings and higher-order anharmonic terms it is convenient to use the HCAO model, which was first proposed by Watson et al. [14], Child and Lawton [15] and then further developed and turned into a computer program by Halonen and Child [10] to calculate the eigenvalues, eigenvectors and transition dipole moments of the stretching vibrations of tetrahedral molecules. In this model, the bond oscillators are considered as the Morse oscillators and the zeroth-order stretching Hamiltonian is a sum of four Morse oscillators Hamiltonian, which are coupled with one another by a kinetic term

$$ g_{i\lambda j\mu} \sum_{i \neq j}^4 p_i p_j \quad (4) $$

and a potential term

$$ f_{i\lambda j\mu} \sum_{i \neq j}^4 r_i r_j \quad (5) $$

Since the potential function with term (5) has no correct asymptotic limit at large amplitude displacements, another potential function has been proposed [10], in which the coupling term is

$$ \frac{1}{d^2} f_{\lambda \mu} \sum_{i < j}^4 y_i y_j \quad (6) $$

where $y_j = 1 - \exp(-a r_j)$, $a$ is the Morse parameter, which can be calculated from the anharmonicity constant $\omega_x$. The model with potential term (5) is called HCAO model I, while the model with term (6) is HCAO model II. In both models there are only three parameters needed to be determined: the Morse oscillator frequency $\omega_m$, anharmonicity $\omega_x$, and the potential coupling parameter $f_{\lambda \mu}$, and the inter-manifold couplings can be included in the calculation (‘global fit’) without introducing new parameters. The effective Coriolis parameters

$$ \xi_{\text{eff}} = \xi_3 \langle 2100; F_2, N | \hat{f}_{z}, 2100; F_2, N \rangle, \quad (7) $$

where $N = 1$ and 2 denote the lowest and the second

<table>
<thead>
<tr>
<th></th>
<th>$^{28}$SiH$_4$ (2100; F$_2$, 1)</th>
<th>$^{28}$SiH$_4$ (2100; F$_2$, 2)</th>
<th>$^{74}$GeH$_4$ (2100; F$_2$, 1)</th>
<th>$^{74}$GeH$_4$ (2100; F$_2$, 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>observed</td>
<td>0.036</td>
<td>$\approx 0^a$</td>
<td>-0.165</td>
<td>$\approx 0^a$</td>
</tr>
<tr>
<td>calc. by NMDD</td>
<td>0.0206</td>
<td>0.0130</td>
<td>-0.079</td>
<td>-0.051</td>
</tr>
<tr>
<td>calc. by HCAO I</td>
<td>0.0346</td>
<td>0.00366</td>
<td>-0.132</td>
<td>-0.0011</td>
</tr>
<tr>
<td>calc. by HCAO II</td>
<td>0.0201</td>
<td>0.0132</td>
<td>-0.0835</td>
<td>-0.0527</td>
</tr>
</tbody>
</table>

$^a$ Cannot be determined within experimental uncertainty.
lowest \((2100; F_2)\) states, \(\xi_3\) is the Coriolis parameter of the \(r_3\) fundamental and the vibrational angular momentum operator \(\hat{I}_z\) is now expressed by means of the curvilinear internal coordinates \(r_i, i = 1, 2, 3\) and \(4\), and their conjugate momenta \(p_i\),
\[
\hat{I}_z = \frac{1}{2} \left( (r_1 p_4 - r_4 p_1) + (r_4 p_2 - r_2 p_4) \right) + (r_2 p_3 - r_3 p_2) + (r_3 p_1 - r_1 p_3) \right],
\]
which is derived from the regular expression
\[
\hat{I}_z = q_{3x} p_{3y} - q_{3y} p_{3x}
\]
by a linear transformation
\[
q_{3x} = \frac{1}{2} (r_1 - r_2 + r_3 - r_4),
\]
\[
p_{3x} = \frac{1}{2} (p_1 - p_2 + p_3 - p_4),
\]
\[
q_{3y} = \frac{1}{2} (r_1 - r_2 - r_3 + r_4),
\]
\[
p_{3y} = \frac{1}{2} (p_1 - p_2 - p_3 + p_4),
\]
\[
q_{3z} = \frac{1}{2} (r_1 + r_2 - r_3 - r_4),
\]
\[
p_{3z} = \frac{1}{2} (p_1 + p_2 - p_3 - p_4).
\]

The wavefunctions of the SiH\(_4\) \((2100; F_2, N)\), \(N = 1\) and \(2\), states are obtained in the three models. They are
\[
\Phi(2100; F_2, 1) = 0.3598 \ket{2100; 1F_2} + 0.9327 \ket{2100; 2F_2}, \tag{11a}
\]
\[
\Phi(2100; F_2, 2) = 0.9329 \ket{2100; 1F_2} - 0.3598 \ket{2100; 2F_2}, \tag{11b}
\]
for the NMDD model with \(\lambda = -0.58 \text{ cm}^{-1}, x_m = -33.9 \text{ cm}^{-1}\) [9],
\[
\Phi(2100; F_2, 1) = 0.9950 \ket{2100; 1F_2} + 0.0927 \ket{2100; 2F_2}, \tag{12a}
\]
\[
\Phi(2100; F_2, 2) = -0.0932 \ket{2100; 1F_2} + 0.9950 \ket{2100; 2F_2}, \tag{12b}
\]
for the HCAO I model with \(\omega_m = 2253.09 \text{ cm}^{-1}, \omega_s = 33.599 \text{ cm}^{-1}, f_{rr'} = 1591.28 \text{ cm}^{-1}\) [10], and
\[
\Phi(2100; F_2, 1) = -0.3629 \ket{2100; 1F_2} - 0.9307 \ket{2100; 2F_2}, \tag{13a}
\]
\[
\Phi(2100; F_2, 2) = 0.9313 \ket{2100; 1F_2} - 0.3632 \ket{2100; 2F_2}, \tag{13b}
\]
for the HCAO II model with \(\omega_m = 2254.86 \text{ cm}^{-1}, \omega_s = 33.69 \text{ cm}^{-1}, f_{rr'} = 1672.6 \text{ cm}^{-1}\) [16], where the terms with coefficients less than 0.03 are omitted. The wavefunctions of GeH\(_4\) are also calculated and found to be similar to those of SiH\(_4\).

Using these wavefunctions we calculated the \(2B_3\) values of \((2100; F_2, N)\), \(N = 1\) and \(2\) states for these two molecules, which are listed in Table 3. It is seen that the values obtained by using the HCAO I model agree quite well with the observations, while those by the HCAO II and NMDD models are significantly different from observations, because the wavefunctions given by them (Eqs. (11) and (13)) are quite different from that of the HCAO I model (Eq. (12)). This result suggests that only the HCAO I model provides a good tool for studying the vibration–rotational spectroscopy of the \(v = 3\) stretching overtones. In addition, since it only contains three unknown parameters, it is convenient to include the intermanifold couplings and the higher anharmonic terms for high overtone studies. Although the HCAO II model also uses Morse oscillators as the basis and has the correct asymptotic limit at large amplitude displacements, the potential (6) does not describe well the energy region of the \(v = 3\) states. On the other hand, the NMDD model is equivalent to the HCAO I model only at low order of approximation [13]; it may not be suitable when higher-order terms need to be taken into consideration.

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References