SiH$_2$Cl$_2$: Ab initio anharmonic force field, dipole moments, and infrared vibrational transitions

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The vibrational spectra of SiH$_2$Cl$_2$ have been recorded in the 1000–13 000 cm$^{-1}$ region, utilizing the Fourier-transform spectroscopy and Fourier-transform intracavity laser absorption spectroscopy. Totally 61 band centers and intensities are derived from the infrared spectra. An ab initio quartic force field is obtained by applying the second-order Möller-Plesset perturbation theory and correlation-consistent polarized valence triplet-zeta basis sets [J. Chem. Phys. 90, 1007 (1989); 98, 1358 (1993)]. Most observed bands are assigned by the vibration analysis based on the second-order perturbation theory. Reduced-dimensional ab initio dipole moment functions (two dimensional and three dimensional) have also been calculated to investigate the absolute band intensities of the SiH$_2$ chromophore. The calculated values agree reasonably with the observed ones. © 2005 American Institute of Physics. [DOI: 10.1063/1.2090267]

I. INTRODUCTION

The chlorinated silanes, particularly dichlorosilane and trichlorosilane, attract interests in many applications because they are used as precursors for the chemical-vapor deposition of epitaxial silicon. They also attract fundamental interests in the study of the local-mode nature of the Si–H chromophore. The vibrational transitions of SiHCl$_3$ were studied earlier and recently. He et al. carried out ab initio calculations on reduced-dimensional potential-energy and dipole moment surfaces. Zheng et al. gave an ab initio anharmonic force field, which can reproduce most of the observed vibrational transitions. Dichlorosilane SiH$_2$Cl$_2$ were studied earlier in the fundamentals and from the fifth through eighth Si–H stretching overtones. Due to the lack of high-resolution spectroscopic data, the anharmonic constants and harmonic frequencies have not been obtained yet.

In recent years, much progress has been achieved in the predictions of molecular properties based on accurate ab initio potential-energy surface. Meanwhile, a high-quality anharmonic force field can be very instructive in the studies of rovibrational spectroscopy and thermodynamic and dynamic properties of small molecules. The method of using the second-order Möller-Plesset (MP2) perturbation theory to get a full-dimensional ab initio potential-energy surface up to the fourth-order force constants has been successfully applied to derive the anharmonic force fields of some halide silanes: SiHF$_3$, SiHCl$_3$, and SiH$_2$F$_2$. Here we will present vibrational analysis of the dichlorosilane molecule from infrared-absorption spectroscopy and ab initio calculations. Experimental details to get the band centers and absolute band intensities of SiH$_2$Cl$_2$ are given in Sec. II. The anharmonic force field study and band assignments will be presented in Sec. III. Reduced-dimensional [two-dimensional (2D) and three-dimensional (3D)] ab initio dipole moment functions and the comparison between calculated and observed band intensities will be given in Sec. IV. The results will be summarized in Sec. V.

II. EXPERIMENTAL DETAILS

The dichlorosilane sample was purchased from Nanjing Special Gas Company (China) and the stated purity is 98%. The absorption spectra in the 1000–9000 cm$^{-1}$ region were recorded with a Bruker IFS 120HR Fourier-transform spectrometer with a resolution of 0.2 cm$^{-1}$ at room temperature (293±1 K). Because of the wide spectral range and the large variation of the absorption line intensities, the Fourier-transform (FT) spectra were recorded under several different experimental conditions which are listed in Table I. Some bands recorded by Fourier-transform spectroscopy (FTS) are illustrated in Fig. 1.

Fourier-transform intracavity laser absorption spectroscopy (FT-ICLAS) integrates the high-sensitivity advantage of ICLAS and the high-resolution and the high-precision advantage of FTS. It is very suitable to the quantitative mea-
measurements of weak absorption bands. We have successfully applied it in the study of the high overtones of HDO,\textsuperscript{13} D\textsubscript{2}O,\textsuperscript{14} and C\textsubscript{2}H\textsubscript{2},\textsuperscript{15} Some experimental details can also be found in Ref. 16. In the present study, it was applied to record the $\nu_{\text{Si-H}}$=6 overtone bands located around 12345 cm\textsuperscript{-1} with a resolution of 0.25 cm\textsuperscript{-1} at the temperature about 296 K. An 81.9-cm-long sample cell was placed inside a 162-cm-long Ti:sapphire laser cavity. The sample cell was filled with 203 hPa of dichlorosilane. The interleaved rapid-scan method was applied, and the spectra were recorded at generation times ($t_g$) of 36, 56, and 76 $\mu$s. Same measurements but with empty sample cell were also carried out to get the base line. Figure 2 shows the spectra recorded at $t_g$=56 $\mu$s with (panel a) and without (panel b) sample gas. The transmittance spectrum of SiH\textsubscript{2}Cl\textsubscript{2} (panel c) was obtained by $a/b$. We shall point out that it is essential to stabilize the laser emission in the measurements, otherwise it would be impossible to determine the integrated absorbance of this widely spread vibrational band.

Altogether 61 bands have been observed in the measurements, some of them can be readily assigned, others can also be assigned based on the \textit{ab initio} calculation (see next section).

The vibrational band intensities can be derived from the integrated absorbance

$$I(v_0) = \int_{v_0-H}^{v_0+H} \ln(S(v)/S_0(v))dv/NL,$$

where $v_0$ is the band center and $v_H$ and $v_L$ are the upper and lower limits which define the integral region of each band. The absorbance beside such region is believed to be negligible. $S(v)/S_0(v)$ defines the transmittance, $L$ is the absorption path length, and $N$ is the molecular density which can be deduced from the experimental conditions. The H\textsubscript{2}O and HCl absorption lines were subtracted from the integration. To retrieve the intensity of the $\nu_{\text{Si-H}}$=6 band measured by FT-ICLAS, first the integrated absorbance at each generation time was obtained from direct integration, then a linear fit on the generation time (proportional to the equivalent absorption path length) was applied to get the band intensity. All the retrieved band intensities together with $v_L$ and $v_H$ are presented in Table II. Note that for those closely located bands, it is impossible to experimentally separate the band intensities from each other. In this case, the $v_L$ and $v_H$ were chosen to include all these overlapping bands and only the overall intensity value is given.

The uncertainties in the obtained experimental band intensity values may rise from (1) the uncertainty in base line determination which may introduce about 10\% uncertainty and can be worse when the band is overlapped, (2) the un-

![Figure 1](https://example.com/figure1.png)
III. FORCE FIELD CALCULATIONS AND VIBRATIONAL BANDS ASSIGNMENTS

SiH₂Cl₂ has nine vibration modes (see Table III). Upper states with symmetries of A₁, B₁, and B₂ can be accessed with b-, c-, and a-type transitions, respectively. While upper states with A₂ symmetry are infrared inactive. Because many uncertainties in molecule density, which comes from the difficulty in the determination of the sample pressure (note that the SiH₂Cl₂ molecule can react with water vapor), the temperature fluctuation, and the absorption path length uncertainties, altogether about 5% for FTS measurements and about 10% for FT-ICLAS measurements, and (3) the limited signal-to-noise ratio (SNR) and nonlinear response of the instruments (for example, the detector). We estimate that the absolute intensity uncertainty is around 20% for moderate bands and may be worse for weak or overlapped ones.

TABLE II. Observed band centers (in cm⁻¹) and intensities (in 10⁻²² cm) of SiH₂Cl₂. The symbol “↑” refers to band overlapped with adjacent ones. Band intensity is included in the value of the previous band.

<table>
<thead>
<tr>
<th>Band</th>
<th>ν₁/Obs.</th>
<th>ν₁/ν₁⁻/ν₁⁻</th>
<th>I/Obs.</th>
<th>Band</th>
<th>ν₁/Obs.</th>
<th>ν₁/ν₁⁻/ν₁⁻</th>
<th>I/Obs.</th>
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<tr>
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<td>↑</td>
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</table>

¹From Ref. 31.
²From Ref. 2.
vibrational bands are closely orientated, it is difficult to assign them correctly without any theoretical predictions. In this case, we carry out calculations based on the second-order perturbation theory with the calculated force constants of this molecule.

A. Force field calculation

We adopt the correlation consistent polarized valence basis sets (cc-pVnZ) of Dunning\(^\text{17}\) and Woon and Dunning.\(^\text{18}\) The cc-pVTZ basis set is used for H atom. Whereas for Si and Cl atoms it is replaced with cc-pVTZ+1 basis, which was derived from cc-pVTZ by adding a single set of \(d\) function whose exponent equals to the highest \(d\) exponent in the corresponding cc-pVnZ basis.\(^\text{19}\) It is important to take into account core-polarization effects in the hard \(d\) function in the case of second-row atoms.\(^\text{20}\) This mixed basis set was denoted as VTZ+1. This basis set was successfully applied in the anharmonic force field calculation on the SiHCl\(_3\) molecule.\(^\text{5}\) The geometry optimization and single point energies are calculated at the correlated level of MP2 method by using the GAUSSIAN03 program.\(^\text{21}\) The obtained equilibrium structures are \(R_{\text{SiH}}=1.4641\ \text{Å}, \ R_{\text{SiCl}}=2.0414\ \text{Å}, \ \theta_{\text{HSH}}=112.523^\circ, \) and \(\phi_{\text{SiSCl}}=108.560^\circ.\) It agrees well with the experimental data.\(^\text{22}\)

All force constants are determined based on the central difference formulas. Displacements have been set up in symmetrized internal coordinates and a step size of 0.01 Å or \(0.5^\circ\) was applied for stretching or bending motions, respectively. The symmetrized internal coordinates are defined as

\[
\begin{align*}
S_1(A_1) &= (r_1 + r_2)/\sqrt{2}, \\
S_2(A_1) &= (r_1 + r_2)/\sqrt{2}, \\
S_3(A_1) &= a\alpha - b(\theta_{11} + \theta_{12} + \theta_{21} + \theta_{22}), \\
S_4(A_1) &= c\beta - d(\theta_{11} + \theta_{12} + \theta_{21} + \theta_{22}), \\
S_5(A_1) &= e\alpha + f\beta + g(\theta_{11} + \theta_{12} + \theta_{21} + \theta_{22}), \\
S_6(B_1) &= (r_1 - r_2)/\sqrt{2}, \\
S_7(B_1) &= (-\theta_{11} - \theta_{12} + \theta_{21} + \theta_{22})/2, \\
S_8(B_2) &= (R_1 - R_2)/\sqrt{2}, \\
S_9(B_2) &= (-\theta_{11} + \theta_{12} - \theta_{21} + \theta_{22})/2, \\
S_{10}(B_2) &= (\alpha - \beta)/2, \\
S_{11}(B_2) &= (\gamma - \delta)/2, \\
S_{12}(B_2) &= (\epsilon - \zeta)/2.
\end{align*}
\]

where \(r_i\) and \(R_j\) are the displacement of the SiH\(_i\) and SiCl\(_j\) bond lengths, respectively. \(\alpha, \beta, \) and \(\theta_j\) are the displacements of H–Si–H, Cl–Si–Cl, and H–Si–Cl\(_j\) angles, respectively. \(a, b, c, \) and \(d\) are determined from the orthonormality conditions. The potential-energy expansion in the symmetrized internal coordinates is given as

\[
V = V_{0} + \frac{1}{2} \sum_{i,j} F_{ij} S_i S_j + \sum_{i,j,k} \frac{1}{6} F_{ijk} S_i S_j S_k + \frac{1}{24} \sum_{i,j,k,l} F_{ijkl} S_i S_j S_k S_l.
\]

There are, altogether, 18 quadratic, 52 cubic, and 147 quartic force constants, which are listed in Table IV. All the force constants in symmetrized internal coordinates are transformed to those in normal coordinates through the \(L\) tensor.\(^\text{23}\) Spectroscopic constants are obtained based on the second-order perturbation theory by using the SPECTRO program.\(^\text{24}\)

B. Vibrational bands assignments

All the harmonic and fundamental frequencies of SiH\(_2\)Cl\(_3\) are given in Table III. No vibrational interaction has been included at current stage. The anharmonic correction \(\omega_i - \nu_i\) values are derived from the anharmonic constants \(x_{ij}\) which have been calculated under standard formulas from perturbation theory.\(^\text{25}\) We have iteratively adjusted the nine diagonal quadratic force constants so that the nine calculated fundamental frequencies of SiH\(_2\)Cl\(_3\) can exactly reproduce the experimental values. The final adjusted quadratic force constants are given in the caption of Table IV. Based on the second-order perturbation formulas for asymmetric top molecules, the anharmonic constants \(x_{\text{sym}}, \ k_{\text{asy}}\) are also obtained, which are presented in Table V together with other spectroscopic constants.

The anharmonic constants \(x_{111}, x_{666}\) and \(k_{1166}\) exactly fulfill the empirical \(x, K\) relations\(^\text{26}\) between the symmetric and asymmetric stretching vibrations of SiH\(_2\), which are

<table>
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<th>Symmetry</th>
<th>Mode</th>
<th>(\omega)</th>
<th>(\omega) (adjusted)</th>
<th>(\nu)</th>
<th>(\nu) (adjusted)</th>
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<td>2314.2</td>
<td>2237.0</td>
<td></td>
</tr>
<tr>
<td>(v_7(B_1))</td>
<td>SiH(_2) rock</td>
<td>612.4</td>
<td>611.2</td>
<td>602.0</td>
<td></td>
</tr>
<tr>
<td>(v_8(B_2))</td>
<td>SiCl(_2) wag</td>
<td>903.5</td>
<td>871.7</td>
<td>876.0</td>
<td></td>
</tr>
<tr>
<td>(v_9(B_2))</td>
<td>SiCl(_2) asymmetric stretch</td>
<td>605.0</td>
<td>595.2</td>
<td>590.0</td>
<td></td>
</tr>
</tbody>
</table>

TABLE III. Computed harmonic \((\omega)\) and fundamental \((\nu)\) frequencies (in cm\(^{-1}\)).
TABLE IV. Quadratic, cubic, and quartic force constants. Energy in units of kJ and coordinates in units of Å or rad. The adjusted force constants are \( F_{11} = 3.089 \text{ kJ} \), \( F_{22} = 3.351 \text{ kJ} \), \( F_{33} = 0.516 \text{ kJ} \), \( F_{44} = 0.725 \text{ kJ} \), \( F_{55} = 0.416 \text{ kJ} \), \( F_{66} = 0.741 \text{ kJ} \), \( F_{12} = 2.918 \text{ kJ} \), and \( F_{16} = 0.608 \text{ kJ} \).

Here \( \omega_m \), \( x_m \), and \( \lambda \) are, respectively, the harmonic, anharmonic, and coupling constants in the local-mode interpretation of the SiH\(_3\) stretching vibrations. According to the relations, \( x_m \) is about \(-34 \text{ cm}^{-1}\), which agrees well with the corresponding value of silane.\(^{27}\) Here we adopt a simplified effective Hamiltonian by neglecting all the resonance interactions except the Darling-Dennison resonance between the \( \nu_1 \) and \( \nu_6 \) modes. The diagonal elements of the Hamiltonian matrix are in the form

\[
\tilde{H}_{VV} = \left( \sum_{i=1}^{9} \tilde{R}_i \left( \nu_i + \frac{1}{2} \right) + \sum_{i>j}^{9} F_{ij} \left( \nu_i + \frac{1}{2} \right) \left( \nu_j + \frac{1}{2} \right) \right) \times | \nu_1, \ldots, \nu_6 \rangle \langle \nu_1, \ldots, \nu_6 | ,
\]

and the nonvanishing off-diagonal elements are like

\[
\tilde{H}_{VV} = \frac{k_{1166}}{4} \left( (\nu_6 + 1)(\nu_6 + 2) \nu_1 \nu_1 - 1/2 \right) | \nu_1, \ldots, \nu_6 \rangle \langle \nu_1, \ldots, \nu_6 | .
\]

The energy values of the upper states can be obtained by explicit diagonalization of the effective Hamiltonian matrix. Based on these calculated results, observed band intensities, and symmetry, 61 bands are assigned. The assignments, observed band centers, and the differences between calculated and observed values are given in Table II. It seems to be reasonable to use the simplified Hamiltonian model since the
TABLE V. Calculated anharmonic and spectroscopic constants (in cm\(^{-1}\)) of SiH\(_2\)Cl\(_2\) and some available experimental values.

<table>
<thead>
<tr>
<th>(r)</th>
<th>(s)</th>
<th>(x_{\nu})</th>
<th>(k_{\nu s})</th>
<th>(r)</th>
<th>(s)</th>
<th>(x_{\nu})</th>
<th>(k_{\nu s})</th>
<th>(P)</th>
<th>Calc.</th>
<th>Obs.(^a)</th>
<th>(P)</th>
<th>Calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>−17.110</td>
<td>2</td>
<td>9</td>
<td>1.124</td>
<td>−91.122</td>
<td>(A_0)</td>
<td>0.472 094</td>
<td>0.471 5(27)</td>
<td>(a_0^2 \times 10^3)</td>
<td>3.716 58</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>0.964</td>
<td>3</td>
<td>4</td>
<td>−8.289</td>
<td>−8.202</td>
<td>(B_0)</td>
<td>0.084 833</td>
<td>0.085 8(7)</td>
<td>(a_0^2 \times 10^3)</td>
<td>0.015 30</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>−1.638</td>
<td>3</td>
<td>5</td>
<td>1.106</td>
<td>1.160</td>
<td>(C_0)</td>
<td>0.073 792</td>
<td>0.074 5(7)</td>
<td>(a_0^2 \times 10^3)</td>
<td>0.334 23</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>0.869</td>
<td>3</td>
<td>6</td>
<td>0.153</td>
<td>0.102</td>
<td>(D_{ij} \times 10^7)</td>
<td>0.339 35</td>
<td> </td>
<td>(a_0^2 \times 10^3)</td>
<td>0.473 99</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>2.029</td>
<td>3</td>
<td>7</td>
<td>−2.404</td>
<td>−0.513</td>
<td>(D_{ik} \times 10^6)</td>
<td>0.495 60</td>
<td> </td>
<td>(a_0^2 \times 10^3)</td>
<td>0.399 54</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>−16.700</td>
<td>3</td>
<td>8</td>
<td>−2.508</td>
<td>0.280</td>
<td>(d_{ij} \times 10^6)</td>
<td>−0.540 33</td>
<td> </td>
<td>(a_0^2 \times 10^3)</td>
<td>0.036 04</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>7</td>
<td>−2.984</td>
<td>3</td>
<td>9</td>
<td>−2.912</td>
<td>4.672</td>
<td>(d_i' \times 10^6)</td>
<td>0.808 04</td>
<td> </td>
<td>(a_0^2 \times 10^3)</td>
<td>−0.646 21</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>8</td>
<td>4.974</td>
<td>4</td>
<td>5</td>
<td>2.029</td>
<td>−66.238</td>
<td>(d_i' \times 10^6)</td>
<td>0.963 52</td>
<td> </td>
<td>(a_0^2 \times 10^3)</td>
<td>−0.013 58</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>9</td>
<td>−1.657</td>
<td>4</td>
<td>6</td>
<td>−0.44</td>
<td>−6.612</td>
<td>(H_{ik} \times 10^{13})</td>
<td>0.297 53</td>
<td> </td>
<td>(a_0^2 \times 10^3)</td>
<td>0.407 12</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)From Ref. 22.

largest deviation is 27.9 cm\(^{-1}\) which comes from the eighth overtone.

IV. REDUCED-DIMENSIONAL DIPOLE MOMENT SURFACE AND BAND INTENSITIES

Because most of the observed overtones are due to the SiH\(_2\) vibrations (Si–H stretching and H–Si–H bending) and these vibration modes are well separated from other modes in this molecule, here we just concentrate on the SiH\(_2\) vibrational bands and the related dipole moments. In order to get this \textit{ab initio} reduced-dimensional dipole moment surface, the SiCl\(_2\) part is kept on its equilibrium configurations, and an oriented bisector frame (see Fig. 3) is used. The origin of the coordinates system coincides with the silicon atom, \(z\) axis bisects the H–Si–H and Cl–Si–Cl angles, \(x\) axis is in the SiH\(_2\) plane, and \(y\) axis is in the SiCl\(_2\) plane. The dipole moment is obtained from the energy derivatives with respect to an external electric field. A finite field of ±0.005\(E_0\)/ea\(_0\) along the bisector axis is adopted. All single point energies are calculated at the MP2 level with cc-PVTZ+1 basis sets.

The dipole moment vectors are projected to the bisector frame as

\[
\mathbf{M}(r_1, r_2, r_3) = u_x(r_1, r_2, \theta)\mathbf{e}_x + u_z(r_1, r_2, \theta)\mathbf{e}_z.
\]

The dipole moment \(x\) and \(z\) components can be expanded with a polynomial function of the displacements on the internal coordinates \(\Delta r_1\), \(\Delta r_2\), and \(\Delta \theta\).

![FIG. 3. (Color online) Bisector frame and definition of the \(x\), \(y\), and \(z\) coordinate systems used in \textit{ab initio} calculations. The \(z\) axis bisects the H–Si–H and Cl–Si–Cl bond angles.](image1)

![FIG. 4. (Color online) Dipole moments \(u_x\) and \(u_z\) at different displacements of the Si–H bond lengths.](image2)
moments along the from $-20^\circ$ to $20^\circ$ with a step of $5^\circ$. In Fig. 4, the dipole set I but also with the H–Si–H angle displacements ranging geometries not only with the bond length displacements like two sets of geometrical configurations. At the first step (set I, 2D), 120 geometries are calculated with the bond length displacements ranging from $-0.3$ to $0.4$ Å with a step of $0.05$ Å. At the second step (set II, 3D), we calculate 1020 geometries not only with the bond length displacements like set I but also with the H–Si–H angle displacements ranging from $-20^\circ$ to $20^\circ$ with a step of $5^\circ$. In Fig. 4, the dipole moments along the $x$ and $z$ axes are presented at different displacements of the Si–H bond lengths. The analytical dipole moment functions are then derived by fitting these calculated values according to Eq. (4.2). The resulted dipole moment coefficients are listed in Table VI.

The absolute band intensities can be calculated as

\[ I = K |\langle N | M | 0 \rangle|^2, \]

where $K$ is a constant coefficient, $\nu$ is the band center, and $|N\rangle$ and $|0\rangle$ denote the eigenvectors of the excited and ground states, respectively. $M$ is the reduced-dimensional dipole moment surface discussed above. The vibrational wave functions are calculated variationally based on the simple curvilinear internal coordinate Hamiltonian which has been proposed by Halonen. More details about the Hamiltonian

<table>
<thead>
<tr>
<th>$\varepsilon$ component</th>
<th>3D</th>
<th>2D</th>
<th>$x$ component</th>
<th>3D</th>
<th>2D</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{00}$</td>
<td>0.581 438(12)</td>
<td>0.581 416(02)</td>
<td>$D_{00}$</td>
<td>$-0.932 612(38)$</td>
<td>$-0.932 209(46)$</td>
</tr>
<tr>
<td>$D_{10}$</td>
<td>$-0.805 528(76)$</td>
<td>$-0.805 880(17)$</td>
<td>$D_{20}$</td>
<td>$-0.511 97(21)$</td>
<td>$-0.513 06(25)$</td>
</tr>
<tr>
<td>$D_{20}$</td>
<td>$-0.485 29(45)$</td>
<td>$-0.473 737(97)$</td>
<td>$D_{30}$</td>
<td>0.254 27(46)</td>
<td>0.253 06(62)</td>
</tr>
<tr>
<td>$D_{30}$</td>
<td>0.252 60(91)</td>
<td>0.255 95(22)</td>
<td>$D_{210}$</td>
<td>$-0.078 99(35)$</td>
<td>$-0.075 66(45)$</td>
</tr>
<tr>
<td>$D_{40}$</td>
<td>0.070 9(36)</td>
<td>0.063 50(80)</td>
<td>$D_{40}$</td>
<td>0.074 1(18)</td>
<td>0.080 9(22)</td>
</tr>
<tr>
<td>$D_{110}$</td>
<td>$-0.139 1(30)$</td>
<td>$-0.124 42(66)$</td>
<td>$D_{110}$</td>
<td>0.022 0(16)</td>
<td>0.040 1(19)</td>
</tr>
<tr>
<td>$D_{220}$</td>
<td>0.037 3(21)</td>
<td>0.026 39(47)</td>
<td>$D_{210}$</td>
<td>0.541 24(19)</td>
<td>0.541 24(19)</td>
</tr>
<tr>
<td>$D_{121}$</td>
<td>0.184 15(26)</td>
<td>0.182 738(56)</td>
<td>$D_{221}$</td>
<td>0.109 57(33)</td>
<td>0.109 57(33)</td>
</tr>
<tr>
<td>$D_{021}$</td>
<td>0.065 68(75)</td>
<td>0.067 26(18)</td>
<td>$D_{321}$</td>
<td>$-0.157 9(15)$</td>
<td>0.147 9(15)</td>
</tr>
<tr>
<td>$D_{101}$</td>
<td>0.766 900(49)</td>
<td>0.766 900(49)</td>
<td>$D_{201}$</td>
<td>0.269 8(13)</td>
<td>0.269 8(13)</td>
</tr>
<tr>
<td>$D_{011}$</td>
<td>0.015 7(17)</td>
<td>0.015 7(17)</td>
<td>$D_{102}$</td>
<td>0.062 72(28)</td>
<td>0.062 72(28)</td>
</tr>
<tr>
<td>$D_{022}$</td>
<td>0.278 29(65)</td>
<td>0.278 29(65)</td>
<td>$D_{202}$</td>
<td>0.104 4(14)</td>
<td>0.104 4(14)</td>
</tr>
<tr>
<td>$D_{112}$</td>
<td>0.036 3(30)</td>
<td>0.036 3(30)</td>
<td>$D_{212}$</td>
<td>$-0.037 7(14)$</td>
<td>$-0.037 7(14)$</td>
</tr>
<tr>
<td>$D_{111}$</td>
<td>$-0.291 24(40)$</td>
<td>$-0.291 24(40)$</td>
<td>$D_{111}$</td>
<td>0.269 8(13)</td>
<td>0.269 8(13)</td>
</tr>
<tr>
<td>$D_{002}$</td>
<td>0.056 33(33)</td>
<td>0.056 33(33)</td>
<td>$D_{002}$</td>
<td>0.062 72(28)</td>
<td>0.062 72(28)</td>
</tr>
<tr>
<td>$D_{012}$</td>
<td>$-0.079 39(57)$</td>
<td>$-0.079 39(57)$</td>
<td>$D_{012}$</td>
<td>0.104 4(14)</td>
<td>0.104 4(14)</td>
</tr>
<tr>
<td>$D_{020}$</td>
<td>$-0.107 2(28)$</td>
<td>$-0.107 2(28)$</td>
<td>$D_{020}$</td>
<td>0.104 4(14)</td>
<td>0.104 4(14)</td>
</tr>
<tr>
<td>$D_{120}$</td>
<td>0.187 0(18)</td>
<td>0.187 0(18)</td>
<td>$D_{120}$</td>
<td>0.104 4(14)</td>
<td>0.104 4(14)</td>
</tr>
<tr>
<td>$D_{003}$</td>
<td>$-0.119 50(43)$</td>
<td>$-0.119 50(43)$</td>
<td>$D_{003}$</td>
<td>$-0.037 7(14)$</td>
<td>$-0.037 7(14)$</td>
</tr>
<tr>
<td>$D_{113}$</td>
<td>$-0.048 5(28)$</td>
<td>$-0.048 5(28)$</td>
<td>$D_{113}$</td>
<td>0.269 8(13)</td>
<td>0.269 8(13)</td>
</tr>
<tr>
<td>$D_{004}$</td>
<td>0.018 1(23)</td>
<td>0.018 1(23)</td>
<td>$D_{004}$</td>
<td>0.269 8(13)</td>
<td>0.269 8(13)</td>
</tr>
</tbody>
</table>

rms$(\times 10^{-4})$ | 2.21 | 0.18 | 1.05 | 0.47

FIG. 5. (Color online) Total band intensities of different polyad $Y = \nu_x + \nu_y + (1/2)\nu_z$: observed and calculated (with 3D or 2D dipole moment functions) values.

\[
\mu^a(\Delta r_1, \Delta r_2, \Delta \theta) = \sum_{i,j,k} D_{ijk}^a \Delta r_i^a \Delta r_j^a \Delta \theta^a. \tag{4.2}
\]
TABLE VII. Kinetic- and potential-energy parameters of dichlorosilane. Uncertainties in parentheses are one standard deviations in the last digit.

<table>
<thead>
<tr>
<th>Term</th>
<th>Value</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g_i^e(u^{-1})$</td>
<td>1.027 979</td>
<td>0.760 978(4)</td>
</tr>
<tr>
<td>$g_{i0}^e u^{-1} , \AA^2$</td>
<td>0.967 885</td>
<td>1.414 806(6)</td>
</tr>
<tr>
<td>$g_i^p(u^{-1})$</td>
<td>-0.013 650</td>
<td>0.576 558(4)</td>
</tr>
<tr>
<td>$g_i^p(u^{-1})$</td>
<td>-0.022 517</td>
<td>0.021 880(4)</td>
</tr>
<tr>
<td>$\left(\frac{\partial g_{i0}^e}{\partial r}\right)(u^{-1} , \AA^-1)$</td>
<td>-0.659 727</td>
<td>f_{o0}(A J , \AA^-1)</td>
</tr>
<tr>
<td>$\left(\frac{\partial g_{i0}^p}{\partial r}\right)(u^{-1} , \AA^-1)$</td>
<td>0.009 304</td>
<td>f_{o0}(A J , \AA^-1)</td>
</tr>
</tbody>
</table>

*Constrained values.*

can be found in Ref. 29 and here we just give a brief description. The Hamiltonian only includes the Si–H stretching and H–Si–H bending modes. It takes the form

$$H = H_0 + H_1,$$

where

$$H_0 = \frac{1}{2}g_{rr}(p_1^2 + p_2^2) + \frac{1}{2}g_{rr0}^2 + g_{rr}(p_1 p_2 + g_{rr0}^2) + D_e(y^2 + y_1^2) + \frac{1}{2}f_{o0} d^2 + \alpha^{-2} f_{r0}(y^1 y_2 + \alpha^{-1} f_{e0}(y_1 + y_2) \theta),$$

$$H_1 = \frac{1}{2} \alpha^{-1} \left(\frac{\partial g_{o0}}{\partial r}\right)(y_1 + y_2) p_0^2 + \frac{1}{2} \left(\frac{\partial g_{o0}}{\partial \theta}\right)(p_1 + p_2)(p_0 \theta) + \theta p_0 + \frac{1}{2} \alpha^{-1} f_{e0}(y_1 + y_2) \theta^2,$$

$p_1, p_2,$ and $p_\theta$ are momentum operators conjugate to the curvilinear internal coordinates $r_1, r_2,$ and $\theta.$ The $G$ matrix elements and their derivatives evaluated at the equilibrium configurations are obtained from the book of Wilson et al.\textsuperscript{30} The explicit expression of the coefficients can be found in Ref. 29 and $\theta = 112.45^\circ$ is used here. $D_e$ and $\alpha$ are the Morse parameters. The six potential-energy parameters are optimized by the nonlinear least-squares method using 29 vibrational band centers related to SiH$_2$. The basis-set size is restricted by $m+n \leq 9$ and $\nu \leq 4,$ where $m$ and $n$ are quantum numbers for the Si–H stretching motions and $\nu$ for the scissoring SiH$_2$ bending motion. The Morse basis functions for the stretching states are chosen to be consistent with the Morse parameters $D_e$ and $\alpha.$ The harmonic oscillator basis functions for the scissoring vibration are chosen to be consistent with the harmonic force constant $f_{o0}.$ The $G$ matrix elements and the fitted potential-energy parameters are given in Table VII. The standard deviation of the fit is 1.2 cm$^{-1}.$ Put in the wave functions and the dipole moment function (2D or 3D) into Eq. (4.3), we can get the vibrational band intensities. The calculated values are presented in Table VIII. It can be found that most of the calculated band intensities are within 0.6–3.0 times of the experimental values. As an illustration, the observed and calculated (2D and 3D, respectively) total band intensities of different polyads $[V=\nu_1 + \nu_2 + (1/2)\nu_3]$ are presented in Fig. 5.

From Fig. 5, as well as Table VIII, we can find that for most vibrational polyads, the calculated intensities (both 2D and 3D results) agree reasonably with the observed values. The largest discrepancy takes place at the fundamental bands $V=1.$ The calculated value is about three times of the observed one. First question may be raised that if this discrepancy comes from improper neglect of the SiCl$_2$ motion in the dimethyl sulfitde (DMS) model. Since the SiCl$_2$ group has been fixed at the equilibrium structure to simplify our DMS model, the effects from the SiH$_2$ wag, rock, and twist modes have been neglected. As a comparison, we perform full-dimensional $ab\,\text{initio}$ anharmonic frequency calculation at MP2 level with cc-PVTZ basis sets. The differences in the optimized structure compared with the equilibrium structure obtained from the cc-PVTZ+1 basis sets are within 0.007 Å for bond lengths and within 1.4° for angles. In this case, the calculated band intensities are $9.04 \times 10^4$ and $3.60 \times 10^4$ (in 10$^{-22}$ cm$^{-1}$/molecule) for $\nu_1$ and $\nu_4,$ respectively. The total value is still more than two times of the observed one. It

TABLE VIII. Observed and calculated band intensities (in 10$^{-22}$ cm$^{-1}$/molecule). This symbol “•” refers to band overlapped with adjacent ones. Band intensity is included in the value of the previous band.

<table>
<thead>
<tr>
<th>Band</th>
<th>$I_{Calc}$ (cm$^{-1}$)</th>
<th>$I_{Obs}$</th>
<th>$I_{Calc}$</th>
<th>$I_{Calc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_2$</td>
<td>1907.38</td>
<td>1.64E+2</td>
<td>2.79E+2</td>
<td>$\cdots$</td>
</tr>
<tr>
<td>$\nu_6$</td>
<td>2236.26</td>
<td>7.14E+4</td>
<td>1.31E+5</td>
<td>1.31E+5</td>
</tr>
<tr>
<td>$\nu_1$</td>
<td>2224.65</td>
<td>1.04E+5</td>
<td>9.40E+4</td>
<td>$\cdots$</td>
</tr>
<tr>
<td>$\nu_1 + \nu_6$</td>
<td>3179.34</td>
<td>1.33E+3</td>
<td>9.67E+2</td>
<td>$\cdots$</td>
</tr>
<tr>
<td>$\nu_1 + \nu_1$</td>
<td>3169.67</td>
<td>4.61E+2</td>
<td>$\cdots$</td>
<td>2$\nu_1 + \nu_1 + \nu_6$</td>
</tr>
<tr>
<td>$\nu_1 + 2\nu_2$</td>
<td>4110.16</td>
<td>5.06E+0</td>
<td>7.18E+0</td>
<td>$\cdots$</td>
</tr>
<tr>
<td>$\nu_1 + \nu_6$</td>
<td>4389.62</td>
<td>4.00E+2</td>
<td>1.66E+2</td>
<td>1.95E+2</td>
</tr>
<tr>
<td>$\nu_1$</td>
<td>4463.28</td>
<td>7.92E+1</td>
<td>1.85E+1</td>
<td>1.17E+2</td>
</tr>
<tr>
<td>$\nu_1 + \nu_6$</td>
<td>5322.81</td>
<td>5.32E+1</td>
<td>5.31E+1</td>
<td>$\cdots$</td>
</tr>
<tr>
<td>$\nu_1 + \nu_1 + \nu_6$</td>
<td>5324.00</td>
<td>4.23E+1</td>
<td>$\cdots$</td>
<td>6$\nu_1$</td>
</tr>
<tr>
<td>$\nu_1 + 2\nu_2$</td>
<td>5394.90</td>
<td>7.14E+0</td>
<td>7.91E+0</td>
<td>$\cdots$</td>
</tr>
</tbody>
</table>

$^a$Calculated with 2D DMS.

$^b$Calculated with 3D DMS.
indicates that the dimension reduction is acceptable under present precision of the \textit{ab initio} calculation.

We also carry out the analysis on the contributions from different terms to the transition dipole moments. We can find that for all the bands calculated with 2D DMS and most bands calculated with 3D DMS, the band intensity mainly comes from the direct transition from the zeroth-order local-mode ground-state wave function to the corresponding zeroth-order upper-state wave function. It means that the mixing of the wave functions due to resonance interactions does not give any significant contribution to the band intensities. For $2 \nu_6$ and $\nu_1 + 3 \nu_6$ bands, the 3D model underestimates the band intensities by 4 and 25 times, respectively. The reason is that the contribution from the bending part in the dipole moment function cancels the one from other parts, thus higher-order terms which cannot be well calculated in the dipole moment model plays a much more important role in the transition moment. It also implies that the band intensity is very sensitive to the DMS model.

It is also worthy to note those bands with one or several $\nu_8$ (SiH$_2$ wag mode) quanta excited. The intensities of these bands are quite close to corresponding bands if $\nu_2$ is replaced by $\nu_6$. Note that the frequency of $\nu_8$ mode is close to $\nu_2$. So possibly the $\nu_2 - \nu_8$ interaction plays a role in the molecule.

\section{V. CONCLUSION}

In this work, the vibrational overtones of SiH$_2$Cl$_2$ have been studied with Fourier-transform spectroscopy and sensitive Fourier-transform intracavity laser absorption spectroscopy. Experimental band intensities are also derived from the spectra. An anharmonic quartic force field is obtained by using the MP2 theory and cc-pVTZ+1 basis set under the frozen-core approximation. From the \textit{ab initio} calculated and a minor empirical adjusted force field, fundamental frequencies are derived based on second-order perturbation theory. Based on the predictions given by the vibrational study with an effective Hamiltonian, 59 new bands are assigned and the predictions agree well with the observed values. The rovibrational spectroscopic constants were also presented which give satisfied agreements with available experimental results. Reduced-dimensional \textit{ab initio} dipole moment surfaces of the isolated SiH$_2$ chromophore (including Si–H stretching and H–Si–H bending) are calculated and applied to derive an analytical presentation in terms of the internal coordinate. A simple curvilinear coordinate Hamiltonian is employed to calculate the absolute band intensity. The calculated intensities agree well with most of the experimental data. The discrepancies between the calculated and observed values are also discussed.

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