Force Field for SiF₄

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The force field of SiF₄ has been determined using both Coriolis coupling constants obtained from an investigation of the band contour of ν₃ at 195 °K and isotopic shifts. The force fields are equally well determined using both methods and are in agreement.

Key Words: Band contour, Coriolis constant, force field, infrared, isotopic shift, low temperature, SiF₄

In determining the general valence force field for silicon tetrafluoride from various sources of molecular information, McKean [1] noted a significant discrepancy in the range of values for the stretch-bend interaction force constant characterized separately by the isotopic frequency shift ∆ν₄ and by the Coriolis constant 4. Since the estimate of 4 from the band shape of ν₄ contains a relatively large uncertainty, as a consequence of an inability to locate precisely the P and R branch maxima, we examine in this communication the contour of the ν₃ fundamental at 195 °K in order to obtain a reliable zeta value for constraining the force field. In addition to confirming the potential function for SiF₄ by comparing the force constants calculated from alternate methods, rotation-vibration interaction data from the two F₂ vibrations provide further tests concerning the utility of the band contour method for estimating Coriolis parameters.

The contours for both infrared active fundamentals, ν₃ and ν₄, were recorded at 310 and 195 °K with a double beam grating spectrophotometer equipped with interference filters to separate the orders. Spectral slit widths varied between 0.7 and 0.9 cm⁻¹. For low temperature measurements, a 5-cm path length copper cell, surrounded by an evacuated glass shell, was in contact with a solid CO₂ and acetone mixture.

Figure 1 displays a representative scan of the ν₃ contour at 310 and 195 °K. A hot band at approximately 1029 cm⁻¹ distorts the contour sufficiently at 310 °K to preclude a valid P–R measurement for use in the Coriolis constant determination. The attenuation of the hot band transition at 195 °K, however, reveals definite P, Q, and R branch features. Additional absorptions, attributed to the naturally occurring isotopes of ²⁹Si and ³⁰Si, are also observed. These values, summarized in table 1, agree well with Heicklen and Knight's frequencies obtained from isotopically enriched compounds [2].

For ν₃, an average value of 8.3 cm⁻¹ for ∆ν₃/R was determined from twelve expanded traces, recorded at several spectral slit widths. Repeated determinations of the P and R branch maxima by a second investigator suggests an uncertainty in ∆ν₃/R of less than 0.5 cm⁻¹. For the ν₄ vibration, it is more difficult to determine ∆ν₃/R owing to the relative breadth of the P and R branch features. Measurements in a 10-cm path length cell at 310 °K, with varying sample pressures and instrumental conditions, give 23.4 ± 1.0 cm⁻¹ for

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Figures in brackets indicate the literature references at the end of this paper.

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Figure 1. The vibration-rotation band contour for the ν₃ fundamental of SiF₄.

(a) 310 °K, (b) 195 °K, (c) 195 °K. The frequencies are labeled in cm⁻¹.
Δν_p-R, in agreement with Heicklen and Knight’s single value of 23.1 cm⁻¹.

Table 1. Observed data for SiF₄
Δν_p-R represents the p-R separation in cm⁻¹. The frequencies are in cm⁻¹; the ζ’s are dimensionless.

<table>
<thead>
<tr>
<th>Frequency (cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1030.7</td>
<td>²⁸SiF₄ hot band</td>
</tr>
<tr>
<td>1029.5</td>
<td>²⁸SiF₄</td>
</tr>
<tr>
<td>1022.1</td>
<td>²⁸SiF₄</td>
</tr>
<tr>
<td>1013.5</td>
<td>³⁰SiF₄</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Observed frequency (cm⁻¹)</th>
<th>Δν_p-R (cm⁻¹)</th>
<th>ζ₁</th>
<th>Σζᵢ</th>
<th>Sum rule</th>
</tr>
</thead>
<tbody>
<tr>
<td>ν₂</td>
<td>1030.7</td>
<td>8.3 ± 0.5 ᵃ  ³  c</td>
<td>0.53 ± 0.03</td>
<td>0.46 ± 0.06</td>
</tr>
<tr>
<td>ν₄</td>
<td>389.4</td>
<td>23.4 ± 1.0 ᵇ</td>
<td>-0.07 ± 0.05</td>
<td>0.46 ± 0.06</td>
</tr>
</tbody>
</table>

ᵃ 195 °K.
ᵇ 310 °K.
ᶜ The estimated uncertainty of 0.5 cm⁻¹ represents twice the maximum deviation from the value obtained from averaging twelve traces of the spectrum.

Edgell and Moynihan’s expression (3) in terms of the rotational constant B and absolute temperature T, relates the Coriolis constant ζ to the measured Δν_p-R values. Perturbations to the contour from the ²⁸Si and ³⁰Si isotopes are ignored in this calculation. A summary of the calculated Coriolis constants appears in table 1. The zeta sum of 0.46 ± 0.06 for the two Coriolis values, compared to the theoretical sum of 0.50, supports the consistency of the data determined by the contour method.

The Coriolis coefficients ζ and the isotopic frequency shifts Δν, respectively, provide force field information through analogous expressions; namely

ζ = L⁻¹G(L⁻¹)ᵀ,  

(1)

and

\[ \frac{2\Delta\nu}{\nu} = L^{-1}\Delta G(L^{-1})^T. \]

(2)

L⁻¹ represents the normal coordinate vector matrix; G is a function of the atomic masses and the molecular geometry, and ΔG represents the change in the G matrix as a result of isotopic substitution. Since the L matrix relates the force field to the experimental parameters, figure 2 presents plots of the dependence of ζ and Δν₄ upon the interaction force constant F₃₄ for the F₂₂ symmetry species.

The use of eq (2) with the L⁻¹ matrices for both the ²⁸S and ³⁰Si isotopes demonstrates the uncertainty in the force field fixed by a value for Δν₄. The lower portion of figure 2 displays the relevant plots. The solid circles locate the experimental point for Δν₄ of 3.0 ± 0.1 cm⁻¹ (1, 2), while the shaded areas represent the uncertainty in the experimental measurement. A vertical dotted line gives the average value for F₃₄ from the perturbation calculation. The solid circles and shaded areas in the upper portion of the figure represent the experimental Coriolis constants and their uncertainties, respectively. The vertical line originating from ζ₃ in the plot defines the preferred force field using the more certain Coriolis value. The L⁻¹ matrix for the ²⁸Si species formed the basis for the Coriolis plot in the figure. Definitions for the symmetry coordinates, as well as the details of the vibrational calculation, appear in reference [4].

The force constants, constrained by (a) Δν₄, (b) ζ₃ and ζ₄, and (c) ζ₅ alone appear in table 2. The dispersions in the F’s are assumed to arise from the uncertainties in the experimental data alone; that is, the errors due to anharmonicity and the uncertainty in

<table>
<thead>
<tr>
<th>Force constant</th>
<th>Δν₄</th>
<th>ζ₃ and ζ₄</th>
<th>ζ₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>F₂₁</td>
<td>6.28 ± 0.22</td>
<td>6.21 ± 0.31</td>
<td>6.40 ± 0.16</td>
</tr>
<tr>
<td>F₂₄</td>
<td>-0.23 ± 0.10</td>
<td>-0.20 ± 0.15</td>
<td>-0.28 ± 0.07</td>
</tr>
<tr>
<td>F₃₄</td>
<td>0.44 ± 0.01</td>
<td>0.45 ± 0.02</td>
<td>0.44 ± 0.01</td>
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The units of F are expressed in millidynes per angstrom.
the normal coordinates are neglected. The very good agreement for the force fields between the two types of constraints confirms the potential function for SiF₄. Although the frequency shift method reflects an optimistic estimate of ±0.1 cm⁻¹ uncertainty in the Δν₄ measurement (1, 2), the estimated dispersions in the crucial interaction force constant $F_{34}$ suggest that the Coriolis and the isotopic shift constraints are about equally effective for this molecule.

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References