Torsion–Rotation–Vibration Effects in the Degenerate Vibrational Fundamental \( (v_{12} = 1 \leftrightarrow 0) \) of \( \text{CH}_3\text{SiH}_3 \)

N. MOAZZEN-AHMADI 1 AND I. OZIER 2

Department of Physics, The University of British Columbia, 6224 Agriculture Road, Vancouver, British Columbia, Canada V6T 2A6

AND

W. L. MEERTS

Fysisch Laboratorium, Katholieke Universiteit, Toernooiveld, 6525 ED Nijmegen, The Netherlands

The lowest-lying degenerate fundamental of a polar symmetric rotor undergoing hindered internal rotation has been studied. The spectrum arising from the excitation \( (v_{12} = 1 \leftrightarrow 0) \) of the silyl rock in \( \text{CH}_3\text{SiH}_3 \) has been measured between 485 and 565 cm\(^{-1}\) with Fourier transform spectroscopy at an effective resolution of 0.0045 cm\(^{-1}\). Almost 1500 lines originating in the ground torsional state have been identified. Two interesting torsional effects are observed in the spectra. First, resonant or near-resonant perturbations are seen between \( (v_{12} = 1, v_6 = 0) \) and \( (v_{12} = 0, v_6 = 3) \) for many different \( \{K, \sigma\} \) series, where \( v_6 \) is the principal torsional quantum number and \( \sigma \) labels the torsional sublevels. The perturbation is shown to result from the \( xy \)-Coriolis interaction and a higher-order Coriolis-like term that arises from the off-diagonal part of the operator responsible for the \( I \)-doubling. Second, for given lower state \( J \) and \( K \), the unperturbed \( \sigma \)-splittings in \( (v_{12} = 1, l = -1) \) and in \( (v_{12} = 1, l = +1) \) are almost identical and, except for a scale factor, approximate the \( \sigma \)-splittings for the lower state. This effect is shown to result from a \( z \)-Coriolis operator linear in the torsional and vibrational angular momenta. The form of the effective Hamiltonian is severely constrained by the large number of precision data obtained earlier on different torsional levels in the ground vibrational state. The global data set of 2011 frequencies is fitted to within experimental error by a model which includes 12 molecular parameters in addition to the 21 constants introduced earlier for \( (v_{12} = 0) \). The effective Hamiltonian for a doubly degenerate vibrational fundamental of \( E_1 \) symmetry and the leading interactions between this state and the ground vibrational state are discussed in detail. © 1989 Academic Press, Inc.

I. INTRODUCTION

The problem of internal rotation in symmetric rotors \( (I) \) offers an excellent opportunity to study the Hamiltonian for an internal degree of freedom over the range from small amplitude oscillation to large amplitude internal rotation. Of the many interesting aspects of this subject, two will form the principal foci of the current work. The first is the torsion–rotation–vibration interactions that couple the torsional stack

1 Present address: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, K1A 0R6, Canada.
2 On leave (1982–83) at the Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, K1A 0R6, Canada.
of levels in the ground vibrational state to the torsional stack in a perpendicular fundamental. The second is the effective Hamiltonian for the stack in the degenerate fundamental in the limit that this torsional stack is isolated from all other such stacks. The current program using CH$_3$SiH$_3$ as a prototype has previously (2–7) been concerned with the torsional stack within the ground vibrational state. In the present paper, the lowest-lying vibrational fundamental ($v_{12} = 1 \leftrightarrow 0$) corresponding to the excitation of the silyl rock is studied.

The pivotal point in the analysis of the spectrum is the resonant or near-resonant perturbation of the vibrational level by a nearby excited torsional level within the ground vibrational state. The problem is illustrated in Fig. 1. Except for the $I$-doubling

![Energy-level diagram and Q-branch transitions showing near-resonant Coriolis shifts for $K^* = 8$. The total energy obtained by diagonalizing the corresponding matrix in Fig. 2 is plotted vertically with a break in the axis. The quantum numbers specified on each level are $J$, $v_6$, $K$, and $\sigma$. For $v_6 = 0$, the $\sigma$-splittings are too small to be seen on the cm$^{-1}$ scale and so are shown on an expanded scale in MHz. In these cases, the quantum number $\sigma$ is shown on the split sublevel. The levels with ($v_{12} = 0$, $v_6 = 3$) are included to illustrate the source of the near-resonant Coriolis shifts. If the Coriolis-type interactions are turned off, then for ($\sigma = 0$) the levels ($v_{12} = 0$, $I = 0$; $J = 11$, $v_6 = 3$, $K = 8$) and (1, $-1$; 11, 0, 0, 7) are separated by only 1.693 cm$^{-1}$. The latter would then take the dashed position shown in the left hand column. When the Coriolis interaction is turned on, the shifts cannot be seen here on the cm$^{-1}$ scale. The only change in the splittings that can be seen on the MHz scale is the increase by 712 MHz in the energy gap between ($\sigma = -1$) and ($\sigma = 0$) in the left hand column. Note that if the Coriolis-type interactions are turned off, the splittings in the left and and right hand columns are identical.](image-url)
levels, the quantum numbers used to label each state are \((v_{12}, \ell; J, v_6, K, \sigma)\). The vibrational angular momentum \(\ell = \pm 1\) in the perpendicular fundamental \((v_{12} = 1)\) and vanishes in the vibrational ground state \((v_{12} = 0)\). The torsional level is specified by \(v_6 = 0, 1, 2, \ldots\), while the torsional sublevel is specified by \(\sigma = 0, +1, -1\). The selection rules for electric dipole transitions in this degenerate fundamental are \(\Delta \ell = \pm 1, \Delta K = \pm 1, \) and \(\Delta J = 0, \pm 1\), while \(\Delta v_6 = \Delta \sigma = 0\). The lower level is the vibrational and torsional ground state \((v_{12} = 0, v_6 = 0)\). The example selected for Fig. 1 is the energy-level diagram relevant for \(pQ\) transitions with \(J = 11\) and \(K = 8\). There are three different such transitions, one for each value of \(\sigma\); these will be denoted \(pQ_{\sigma}(11)\). Both lower and upper states are far below the tops of their respective torsional potentials. Thus in the absence of resonant or near-resonant perturbations, the energy separation between \(\sigma\) sublevels is expected to be small (\(<1 \text{ GHz}\)) for both \((v_{12} = 0)\) and \((v_{12} = 1)\). The \(\sigma\) fine structure in the \(pQ_{\sigma}(11)\) triplet is then expected to be small as well.

However, resonant perturbations do occur and these are strongly dependent on \(\sigma\). The torsional splittings for \((v_{12} = 0, v_6 = 3)\) are known \((6)\) to be large \((\sim 60 \text{ cm}^{-1})\). Thus if the magnitude of energy separation between the levels \((v_{12} = 1, v_6 = 0)\) and \((v_{12} = 0, v_6 = 3)\) is small for one value of \(\sigma\), it will be large for others. This will cause the \(pQ_{\sigma}(11)\) triplet to take the form of a closely spaced doublet (for the two weakly perturbed \(\sigma\) sublevels) and a widely separated third member (for the strongly perturbed \(\sigma\)-level).

The molecule CH$_3$SiH$_3$ is very well suited for this study. For \(v_{12} = 0\), there is an extensive data set including molecular beam \((3)\), microwave \((4, 8)\), Fourier transform \((5, 6)\), and diode laser \((7)\) data. This determines \((7)\) the energies for \(v_6 \leq 2, J \leq 25, K \leq 12\) typically to better than 0.001 cm$^{-1}$. These torsional levels are well below the top of the \((v_{12} = 0)\) torsional barrier and so do not show the full transition to “free” internal rotation. These levels are also well below the vibrational level \((v_{12} = 1)\) so that all perturbation is non-resonant and easily absorbed into effective molecular parameters. For \(v_6 = 3\) and \(4\), the energies predicted by the model of Ref. \((7)\) have a statistical uncertainty \(<0.05 \text{ cm}^{-1}\) typically, but model errors could easily be substantially larger. These two levels are at or above the top of the barrier and bracket or nearly bracket the energy of the \(v_{12}\) fundamental. The next lowest vibrational state \((v_5)\) is high enough in energy that its effect can be treated implicitly. Both pure rotational microwave spectra \((4)\) and low-resolution \((0.15 \text{ cm}^{-1})\) interferometer measurements \((5, 6)\) of the torsional band \((v_6 = 3 \leftarrow 1)\) show that the \(\sigma\) sublevel with the highest energy for given \(v_6 = 3, J,\) and \(K\) is perturbed. Thus CH$_3$SiH$_3$ has a well studied ground vibrational state with evidence of resonant perturbations. Further, an early study of the pure rotational microwave transitions \(J = 1 \leftrightarrow 0\) and \(2 \leftrightarrow 1\) within \((v_{12} = 1)\) is available \((8)\) to provide valuable constraints on the Hamiltonian.

The effective Hamiltonian for \((v_{12} = 1)\) has been discussed by Hirota \((8)\) in the limit that matrix elements off-diagonal in \(v_{12}\) can be neglected. The treatment of Laurie \((9)\) was extended by introducing a term linear in \(l\) and in the torsional angular momentum \(p\). The diagonal matrix elements of this operator were found to be important, but the elements off-diagonal in \(v_6\) were not introduced at the time. It is here shown that these \((\Delta v_6 \neq 0)\) elements play a very important role in two respects. First, they are necessary to obtain the correct energy separation between the \((v_{12} = 1)\) and
(\(v_{12} = 1 \leftrightarrow 0\)) band of CH\textsubscript{3}SiH\textsubscript{3}

(\(v_{12} = 0\)) stacks of torsional levels. Without this effect, there are cases where the resonant perturbations off-diagonal in \(v_{12}\) have the wrong sign. Second, the (\(\Delta v_6 \neq 0\)) matrix elements of \(p_l\) are required to obtain the correct ordering of the different \(\sigma\) sublevels in the multiplet (\(v_{12} = 1, \ell = \pm 1; J, v_6 = 0, K, \sigma\)). For multiplets where the resonant perturbations are absent (or small), it is found that the energy splitting within this multiplet depends only on one quantum number, namely \(G = (K - l)\). Further, the pattern with given \(G\) in (\(v_{12} = 1, v_6 = 0\)) is the same, except for a scale factor, as that in (\(v_{12} = 0, v_6 = 0\)) with the same \(G\).

The coupling between torsional stacks in different torsional states has not been previously discussed for polar symmetric rotors. For ethane, the Coriolis coupling between the lowest degenerate fundamental and the closest torsional level in the ground state stack has been considered (10, 11). However, because of the higher symmetry, the amount of data available is much less than in CH\textsubscript{3}SiH\textsubscript{3} and the test of the model was at the level of \(\sim 1 \text{ cm}^{-1}\) (12). For CD\textsubscript{3}OH (13), the Fermi interaction between the C–O stretch and the level with four quanta of torsion excited has been treated. For CH\textsubscript{3}OH (14), the Fermi interaction has been considered between the O–H bend and the level with one quantum of torsion plus one C–O stretch. However, the stringency of the test made of the model is limited by the asymmetry and by the presence of other nearby vibrational modes.

In the current work, the matrix elements are derived in detail for the (\(v_{12} = 1 \leftrightarrow 0\)) inter-stack coupling for arbitrary values of \(\Delta v_6\). The Coriolis interaction is developed along with a higher-order Coriolis-like term that arises from the off-diagonal part of the operator that leads to the \(l\)-doubling interaction. Each of these is first developed in the limit of small torsional oscillations and converted to large-amplitude internal rotation by requiring that the resulting operator have the correct small-amplitude limit (15, 16). It would be of considerable interest to be able to test this correspondence-type principle to high accuracy.

The experimental basis for the test of the present CH\textsubscript{3}SiH\textsubscript{3} model is the present Fourier transform study of the (\(v_{12} = 1 \leftrightarrow 0\)) band with an effective resolution (after deconvolution) of \(\sim 0.0022 \text{ cm}^{-1}\), along with the earlier data listed above for the ground vibrational stack. The (\(v_{12} = 1\)) portion of the final data set includes 1479 transitions with \(J \leq 25\) and \(K \leq 11\). These can be fitted typically to better than 0.0005 cm\(^{-1}\). The five (\(v_{12} = 1\)) microwave frequencies (8) fit to better than 100 kHz. The model includes 12 molecular parameters in addition to the 21 constants previously introduced to describe the energies for (\(v_{12} = 0\)). The results are summarized in Table I.

The remainder of this paper is divided into six parts. In Section II, the theoretical framework for the model is laid down. Particular attention is paid to the \(l\)-doubling levels since these play such an important role in microwave studies (8). The derivations are presented in detail, but can be largely omitted by the reader interested primarily in a more qualitative understanding of the internal rotor aspects of the spectra. In Section III, the experimental procedure is outlined and a description is given of the features in the spectrum that form the basis of the initial assignments. Section IV discusses the identification procedure and the development of the "minimal model" used to avoid unnecessary correlations among the parameters. In Section V, the \(\sigma\)-splitting is described and explained in terms of the model adopted for both the resonant
TABLE I
Molecular Constants for CH$_3$SiH$_3$

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Present Work</th>
<th>Previous Study$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tilde{A}_0$</td>
<td>MHz</td>
<td>56 176.95 (16)</td>
</tr>
<tr>
<td>$B_0$</td>
<td>MHz</td>
<td>10 904.4705 (105)</td>
</tr>
<tr>
<td>$D_J$</td>
<td>kHz</td>
<td>10.7029 (89)</td>
</tr>
<tr>
<td>$D_{JK}$</td>
<td>kHz</td>
<td>42.778 (83)</td>
</tr>
<tr>
<td>$D_K$</td>
<td>kHz</td>
<td>189.65$^b$</td>
</tr>
<tr>
<td>$D_{P}$</td>
<td>MHz</td>
<td>0.351 9225 (51)</td>
</tr>
<tr>
<td>$F$</td>
<td>MHz</td>
<td>383.2 (2.2)</td>
</tr>
<tr>
<td>$\tilde{v}_5$</td>
<td>cm$^{-1}$</td>
<td>591.3600 (57)</td>
</tr>
<tr>
<td>$\tilde{v}_6$</td>
<td>cm$^{-1}$</td>
<td>3.0167 (48)</td>
</tr>
<tr>
<td>$D_{ja}$</td>
<td>MHz</td>
<td>0.6354 (78)</td>
</tr>
<tr>
<td>$D_{ka}$</td>
<td>MHz</td>
<td>4.245 (69)</td>
</tr>
<tr>
<td>$D_{m}$</td>
<td>MHz</td>
<td>5.550 (53)</td>
</tr>
<tr>
<td>$d_J$</td>
<td>MHz</td>
<td>-0.1406 (12)</td>
</tr>
<tr>
<td>$d_K$</td>
<td>MHz</td>
<td>-0.349 (89)</td>
</tr>
<tr>
<td>$d_m$</td>
<td>MHz</td>
<td>2.218 (91)</td>
</tr>
<tr>
<td>$F_{2J}$</td>
<td>MHz</td>
<td>-133.71 (17)</td>
</tr>
<tr>
<td>$F_{3K}$</td>
<td>MHz</td>
<td>396.2 (2.9)</td>
</tr>
<tr>
<td>$F_{6J}$</td>
<td>MHz</td>
<td>0.62 (15)</td>
</tr>
<tr>
<td>$H_{JK}$</td>
<td>Hz</td>
<td>0.65 (33)</td>
</tr>
<tr>
<td>$H_{Jm}$</td>
<td>Hz</td>
<td>6.93 (59)</td>
</tr>
<tr>
<td>$H_{JKm}$</td>
<td>Hz</td>
<td>-26.9 (9.5)</td>
</tr>
<tr>
<td>$\nu_{ij}$</td>
<td>Hz</td>
<td>298 (163)</td>
</tr>
<tr>
<td>$\nu_{12,6}^c$</td>
<td>cm$^{-1}$</td>
<td>625.5953 (82)</td>
</tr>
<tr>
<td>$\Delta_{12}^c$</td>
<td>MHz</td>
<td>13 674.06 (15)</td>
</tr>
<tr>
<td>$\nu_{12}^c$</td>
<td>kHz</td>
<td>22.88 (116)</td>
</tr>
<tr>
<td>$\nu_{12}^c$</td>
<td>kHz</td>
<td>455.4 (3.8)</td>
</tr>
<tr>
<td>$\Omega$</td>
<td>MHz</td>
<td>86 709 (351)</td>
</tr>
<tr>
<td>$\Delta A_{12}^c$</td>
<td>MHz</td>
<td>195.90 (17)</td>
</tr>
<tr>
<td>$\Delta B_{12}^c$</td>
<td>MHz</td>
<td>-17.660 (23)</td>
</tr>
<tr>
<td>$\Delta D_{12}^c$</td>
<td>kHz</td>
<td>4.89 (11)</td>
</tr>
<tr>
<td>$q$</td>
<td>MHz</td>
<td>21.957 (25)</td>
</tr>
<tr>
<td>$\nu_{12}^d$</td>
<td>cm$^{-1}$</td>
<td>659.02 (43)</td>
</tr>
<tr>
<td>$\nu_{6,1}^d$</td>
<td>MHz</td>
<td>429.8 (1.2)</td>
</tr>
<tr>
<td>$\nu_{5,1}^d$</td>
<td>MHz</td>
<td>14.92 (55)</td>
</tr>
</tbody>
</table>

$^a$ - These values were obtained in Ref. (7) by using a single-band analysis of the component of the current data set which does not involve the excited vibrational state.

$^b$ - This is fixed at the force field value (27).

$^c$ - This is defined in Eq. (33). The vibrational quantum $\tilde{v}_{12}$ is given in Eq. (39).

$^d$ - The relative sign of these two constants was shown to be positive.
and the nonresonant cases. In many respects, this would be of greatest interest for the general reader. In Section VI, various modifications to the current best model are explored, and results are presented for a series of interesting molecular parameters determined from the best fit values in Table I. Section VII provides a brief summary.

II. THEORY

1. Introduction

In analyzing the spectroscopic data on CH₃SiH₃, we must consider both the principal axis method (PAM) and the internal axis method (IAM). In the PAM, the torsional and rotational motions are strongly coupled, but the symmetry properties of the operators and wave functions both for the torsional and for the rotational degrees of freedom are well-defined. On the other hand, in the IAM, the torsion-rotation Hamiltonian is separable in zeroth order, but the symmetry properties cannot be separately defined without methods such as those involving extended groups (17). In large part because of these properties of the PAM and IAM, the torsion-rotation Hamiltonian is first derived in the PAM and then transformed to the IAM.

The vibrational motion is coupled to both torsion and rotation. Because the vibrational mode of interest here is localized in the silyl frame, the terms in the Hamiltonian involving vibrational operators are easily expressed in the PAM, where the axes are fixed relative to the frame. The vibrational operators and wave functions can be transformed to the IAM, but this step is not carried out. This omission has no effect on the results because the PAM-to-IAM transformation involves only the torsion-rotation part of the problem. Operators and wave functions referred to the PAM will be primed, while those referred to the IAM will not.

The effective vibration-torsion-rotation Hamiltonian \( H_{VTR} \) can be expanded as a power series in the angular momenta and vibrational operators and a Fourier series in the torsional angle \( \alpha \). The basic PAM operators in the expansion are the components \( J_i \) \((i = x, y, z)\) of the total angular momentum (exclusive of nuclear spin), the torsional angular momentum \( P' \) about the symmetry axis \( z' \), the normal coordinates \( q_{12a}, q_{12b} \) for silyl rock, the conjugate momenta \( p_{12a}, p_{12b} \), and the trigonometric functions \( \sin 3\alpha' \) and \( \cos 3\alpha' \). Under the permutation-inversion group \( G_{18} \) for CH₃SiH₃ (18), these operators have the irreducible representations

\[
\Gamma(J_z) = \Gamma(p') = \Gamma(\sin 3\alpha') = A_2 \tag{1a}
\]

\[
\Gamma(J_x, J_y) = \Gamma(q_{12a}, q_{12b}) = \Gamma(p_{12a}, p_{12b}) = E_1 \tag{1b}
\]

\[
\Gamma(\cos 3\alpha') = A_1. \tag{1c}
\]

The vibrational angular momentum \( l' \) is defined as in Ref. (19) in terms of the ladder operators \( q_{12±} \) and \( p'_{12±} \).

For matrix elements diagonal in \( v_{12} \) and \( l \), \( H_{VTR} \) will be written directly in its final form with the torsional and rotational operators in the IAM and the vibrational op-

\[3\] It is common to use such terms as torsion-rotation coupling, torsion-rotation Hamiltonian, and rotational transitions. However, it is understood that in this context the term "rotation" refers to the motion associated with the total angular momentum \( J \) (exclusive of nuclear spin) rather than with pure rotation itself.
erators in the PAM. The important operators off-diagonal in \( v_{12} \) and/or \( l \) will then be derived in this form by starting in the PAM. Because of the effect of the PAM → IAM transformation on the Coriolis terms diagonal in \( v_{12} \) and \( l \), the derivation of these particular diagonal terms will be presented as well, thus allowing for the interpretation of the effective Coriolis constant \( A_{fi2} \) in the limit that torsional effects can be neglected. The derivations will be carried out in the context of the contact transformation formalism (19). The \( l \)-doubling levels require special consideration; these are discussed in Section II.6.

2. Effective Hamiltonian for \( (\Delta v_{12} = \Delta l = 0) \)

For matrix elements entirely within the vibrational ground state \( v_{12} = l = 0 \), the effective Hamiltonian has been discussed in detail earlier. This Hamiltonian is here designated \( H_{(8)} \) and was written as \( \left[ H_{TR}^{(0)} + H_{TR}^{(1)} + H_{TR}^{(2)} \right] \) in Ref. (5). For matrix elements diagonal in \( v_{12} \) and \( l \) with \( v_{12} = 1 \), the effective Hamiltonian can be written to first order as

\[
H_{(12)}^{(0)} = H_{12,v}^{(0)} + H_{12,T}^{(0)} + H_{12,R}^{(0)} + H_{12,T}^{(1)} + H_{12,TR}^{(1)}
\]

\[
H_{12,v}^{(0)} = \tilde{v}_{12} - [2(A_f \tilde{v}_{12}) - \eta_{12,J} J^2 - \eta_{12,K} J_z^2] J_z l' + 2(A_f \tilde{v}_{12}) p l' \]

\[
H_{12,T}^{(0)} = F_{12,m} p^2 + V_{12,3} \left( 1 - \cos 3\alpha \right)
\]

\[
H_{12,T}^{(1)} = F_{12,m} p^2 + D_{12,m} p^4 + V_{12,6} \left( 1 - \cos 6\alpha \right).
\]

The division of \( H_{(12)}^{(0)} \) into these six particular terms has been done to simplify the discussion. The zeroth-order "vibrational" Hamiltonian \( H_{12,v}^{(0)} \) contains two leading Coriolis terms in \( (A_f \tilde{v}_{12}) \) and \( (A_f \tilde{v}_{12}) \) that involve the interaction of the angular momentum of vibration with the angular momenta of overall motion and torsion, respectively. \( H_{12,v}^{(0)} \) is defined to include the first-order terms in \( \eta_{12,J} \) and \( \eta_{12,K} \) which characterize the rotational dependence of \( (A_f \tilde{v}_{12}) \). In the zeroth-order torsional Hamiltonian \( H_{12,T}^{(0)} \), \( F_{12} \) is the reduced rotational constant and \( V_{12,3} \) is the height of the torsional potential when one quantum of \( v_{12} \) is excited. The rigid-rotor Hamiltonian \( H_{12,R}^{(0)} \) is parametrized by the rotational constants \( A_{12} \) and \( B_{12} \). The first-order centrifugal distortion Hamiltonian \( H_{12,R}^{(1)} \) is parametrized by the distortion constants \( D_{12,J}, D_{12,K}, \) and \( D_{17,K} \). The first-order Hamiltonian \( H_{12,TR}^{(1)} \) involves the torsional distortion terms which do not involve operators constructed from the components of \( J \). The first-order Hamiltonian \( H_{12,TR}^{(0)} \) consists of the terms in \( \left[ H_{DIST}^{(0)} + H_{TR}^{(1)} \right] \), defined in Ref. (5), which involve products of torsional operators and operators formed from the overall angular momentum; the coupling constants for \( v_{12} = 1 \) are here given a subscript 12.

The transformation from the PAM to the IAM is carried out for \( p' \) and \( J_i' \) using Eq. (10) for Ref. (16). The constant \( \tilde{p} \) is selected so that there is no term of the form \( J \cdot p \) in \( H_{(8)} \). In lowest order, \( \tilde{p} = I_a / I_o \), where \( I_a \) and \( I_o \) are the moments of inertia about the symmetry axis of the top and molecule, respectively. Since this ratio is, in general, a function of \( v_{12} \), a small term in \( J \cdot p \) should be added to \( H_{(12)} \). However, this term is negligible here.
3. The Coriolis Interaction $\hat{H}_{21}$

The Coriolis interaction $H_{21}^{\text{v}}$ is often subjected to a contact transformation \((19)\) to remove the matrix elements off-diagonal in the vibrational quantum numbers. When a resonance occurs between modes $v_u$ and $v_v$, the transformation function $S_{21}^{\text{v}}$ can be selected to remove the nonresonant part of $H_{21}^{\text{v}}$ between these modes and leave the resonant part to be dealt with by diagonalization. Here the coupling is between $v_6$ and $v_{12}$. However, because $v_6$ is very anharmonic, matrix elements with $\Delta v_{12} = \pm 1$ and large changes in the magnitude of $v_6$ must be considered. It is therefore more convenient to treat all the $v_6-v_{12}$ matrix elements explicitly and remove only the other vibrational contributions by contact transformation. $S_{21}^{\text{v}}$ is then given by Eq. (16.1.7) of Ref. (19) but with the terms \((k = 6, l = 12)\) and \((k = 12, l = 6)\) omitted. Here $k$ and $l$ are represented by $u$ and $v$, respectively. The transformed Coriolis Hamiltonian can then be written here for small amplitude motion as

$$
\hat{H}_{21}^{\text{v}} = -\sum_{u,v} \left[ \left[ \begin{array}{c} \omega_u \\ \omega_v \\
 \end{array} \right]^{1/2} q_i^u p_i^u - \left[ \begin{array}{c} \omega_v \\ \omega_u \\
 \end{array} \right]^{1/2} q_i^u p_i^v \right] \sum_i B_i \zeta_i^u J_i^v.
$$

(4)

Each normal mode sum runs over $12a$, $12b$, and $6$; the only diagonal contribution relevant here is within the mode $v_{12}$. The $B_i$ are the rotational constants for direction $i$. The Coriolis constants $\zeta_i^u$ are defined in Ref. (19).

The components $12a$ and $12b$ of the silyl rock can interact only through rotation about the $z$ axis. This contribution to $\hat{H}_{21}^{\text{v}}$ in Eq. (4) can be written

$$
(\hat{H}_{21}^{\text{v}})' = -2(A_{12a} A_{12b}) J_i^v p_i^v.
$$

(5)

Since $I'(l') = A_2$, it is clear from Eq. (1) that $(\hat{H}_{21}^{\text{v}})'$ is totally symmetric. Clearly, a similar operator can be constructed with $J_i^v$ replaced by $p_i^v$:

$$
(\hat{H}_{21}^{m})' = +2(A_{12a} A_{12b}) p_i^v p_i^v.
$$

(6)

This is a Coriolis interaction between $12a$ and $12b$ due to internal rotation. It can be thought of as arising from Eq. (4) by extending the sum on $i$ to include $a$, i.e., $J_i^v = p_i^v$. The sign in Eq. (6) is taken as positive to follow the conventions of Ref. (8).

The total $z$-type Coriolis interaction shown in Eq. (3a) is obtained by transforming $J_i^v$ and $p_i^v$ to the IAM using Eq. (10) of Ref. (16). In Eq. (3a),

$$
(A_{12a} A_{12b}) = (A_{12a} A_{12a}) - \tilde{p} (A_{12a} A_{12a}).
$$

(7)

The tilde indicates an effective value resulting from a transformation (or a redundancy). In the limit that $V_{12,3} \to \infty$, the matrix elements of $p$ diagonal in $v_6$ vanish and it is $(A_{12a})$ that goes into the usual $C_{3p}$ coupling constant. Thus if the PAM is used without including the term in $p_i^v p_i^v$, then the correct limiting behavior is not obtained.

The degenerate mode $v_{12}$ can interact with the torsional mode $v_6$ through rotations about the $x$ and $y$ axes. If it is required that the resulting Coriolis term be totally symmetric, this contribution to $H_{21}^{\text{v}}$ in Eq. (4) can be written
\[
(\hat{H}_{21}^x)_{y'} = B_{\xi,12a}^x \left( \frac{\omega_6}{\omega_{12}} \right)^{1/2} p_6' \left[ q_{12+} J' - q_{12-} J' \right] - \left( \frac{\omega_{12}}{\omega_6} \right)^{1/2} q_{12}' \left[ p_{12+} J' - p_{12-} J' \right].
\]

Equation (8) can be applied to the \( \nu_6 - \nu_{12} \) interaction so long as \( \nu_6 \) is treated as a small-amplitude motion. Since the resonant coupling to \( \nu_{12} = 1, \nu_6 = 0 \) is by a level \( \nu_{12} = 0, \nu_6 = 3 \) which is near the top of the barrier, this condition on the amplitude must be relaxed. To allow for large amplitude motion, the procedure which was introduced by Hougen (15) and discussed with respect to CH\(_3\)SiH\(_3\) in Section III of Ref. (16) has been used. In Eq. (8),

\[
p_6' \rightarrow [s_m]^{-1/4} \left( \frac{2}{3} \right) p';
\]

\[
q_6' \rightarrow [s_m]^{1/4} \left( \frac{1}{2} \right) \sin 3\alpha'.
\]

For matrix elements diagonal in \( \nu_{12} \), the constant \( s_m \) in Eq. (9) is set equal the reduced barrier height \( (4V_3/9F) \) for the value of \( \nu_{12} \) in question. For this particular vibrational state, the proportionality constants in Eq. (9) then ensure that the zeroth-order torsional Hamiltonian goes over to the correct form for a harmonic oscillator in the limit of infinite barrier height. However, the operators in Eq. (9) are to be applied in matrix elements off-diagonal in \( \nu_{12} \), so that an ambiguity arises in the definition of \( s_m \). Since the reduced barrier heights \( s_6 \) and \( s_{12} \) for \( \nu_{12} = 0 \) and 1, respectively, differ by \( \sim 10\% \), this ambiguity may be important. Here \( s_m \) in Eq. (9) is taken as the geometric mean of \( s_6 \) and \( s_{12} \). This point is discussed further in Section VI.

Once the torsional operators \( p' \) and \( \sin 3\alpha' \) are introduced, the IAM form of this Coriolis interaction is obtained by transforming the torsional and overall angular momenta from the PAM to the IAM using Eq. (10) of Ref. (16). When the expression is symmetrized, it is found that

\[
\hat{H}_{21}^x = B_{\xi,6,a} \left[ \frac{1}{2} [p + \tilde{p} J_2] [e^{i\alpha J_2} Q_{12+} J - e^{-i\alpha J_2} Q_{12-} J] + \frac{1}{2} [e^{i\alpha J_2} Q_{12+} J - e^{-i\alpha J_2} Q_{12-} J] \right.
\]

\[
\times \left[ [p + \tilde{p} J_2] - 2\lambda t \sin 3\alpha' [e^{i\alpha J_2} P_{12+} J - e^{-i\alpha J_2} P_{12-} J] \right],
\]

where

\[
\tilde{\xi}_{6,a} = \left( \frac{2}{3} \right) \left( \frac{\omega_6}{\omega_{12}} \right)^{1/2} (s_m)^{-1/4} \xi_{\nu_{12}a}
\]

\[
\lambda t = \left( \frac{3}{8} \right) \left( \frac{\omega_{12}}{\omega_6} \right) (s_m)^{1/2}.
\]

\( \tilde{\xi}_{6,a} \) is an effective Coriolis constant and \( \lambda t \) is a weight factor which determines the magnitude of the term in \( \sin 3\alpha \) relative to that in \( [p + \tilde{p} J_2] \).
4. The Quartic Operator $\tilde{H}_{22}$

In the limit of small-amplitude motion, the quartic term $\tilde{H}_{22}$ can be written in the form (19):

$$\tilde{H}_{22} = \sum \sum \frac{1}{2} [J_i J_j + J_j J_i] [Q_{uw} q_u q_v + P_{uw} p_u p_v].$$

The sums on $u$ and $v$ run over the normal modes. The $P_{uw}$ and $Q_{uw}$ are real coefficients which are invariant under the interchange $u \leftrightarrow v$ and under the interchange $i \leftrightarrow j$.

The matrix elements of $\tilde{H}_{22}$ diagonal in the vibrational quantum numbers account for the dependence of the rotational constants on vibrational state and the $l$-type doubling. The off-diagonal elements of $\tilde{H}_{22}$ contribute various resonance terms, including one which provides an important correction to the Coriolis effect (see below).

In general, the Hamiltonian $\tilde{H}_{22}$ receives contributions from its untransformed counterpart $H_{22}$ as well as from five different commutators as listed in Eq. (16.1.9b) of Ref. (19). These five arise from contact transformations involving three different transformation functions, $S_{03}$, $S_{21}'$, and $S_{12}'$. Two of these, the vibrational commutator $[S_{21}'', H_{21}]$ and the rotational commutator $[S_{21}', H_{02}]_R$, are completely off-diagonal in the vibrational quantum numbers.

When Eq. (11) is specialized to the current problem, $u$ and $v$ are restricted to the diagonal terms for $\nu_{12}$ and the off-diagonal terms for $\nu_{v2}$ and $\nu_{12}$. Because $S_{21}'$ has been formed specifically omitting the terms coupling $\nu_0$ and $\nu_{12}$, neither $[S_{21}', \tilde{H}_{21}]$ nor $[S_{21}', H_{02}]_R$ contributes to $\tilde{H}_{22}$. Expressions for $Q_{uw}$ and $P_{uw}$ can then be read from Eq. (16.1.11a) of Ref. (19) with $i, j, u, v$ here corresponding, respectively, to $\alpha, \beta, k, l$ in Ref. (19). The only modification required is the omission of the terms involving $(\omega_0^2 - \omega_{12}^2)^{-1}$ in accordance with the current form of $S_{21}'$.

For matrix elements diagonal in $\nu_{12}$, $P_{uw} = Q_{uw}$. The $\nu_{12}-\nu_{12}$ contribution from Eq. (11) is denoted $(H_{22}^{\text{Dia}})$. By requiring that this Hamiltonian be Hermitian and be symmetric under $G_{18}$ and time reversal, it can be shown that

$$(H_{22}^{\text{Dia}})' = Q_{ab}(J'+)^2(q_{12-})^2 + (J'-)^2(q_{12+})^2 - Q_{aa}(J_2 J_2 + J_2 J_2)[(q_{12-})^2 + (J_2 J_2 + J_2 J_2)[(q_{12+})^2].$$

Equation (12) has been simplified by using the fact that the diagonal matrix elements of $(q_{12+})^2$ equal those of $(p_{12+})^2$. Further, the notation has been compressed by indicating only the components of mode $\nu_{12}$ in the $Q_{uw}$. These coefficients obey the symmetry relations

$$Q_{aa} = Q_{bb} = -Q_{ba} = -Q_{ab} = Q_{aa}$$

$$Q_{aa} - Q_{ab} = -Q_{ba} = Q_{aa}. \quad (13a)$$

The remaining $Q_{uw}$ either vanish or can be trivially related to those listed in Eq. (13). The IAM form of $H_{22}^{\text{Dia}}$ is given by

$$H_{22}^{\text{Dia}} = H_{22}^{2,2} + H_{22}^{2,-1}. \quad (14a)$$
where
\[
\hat{H}^{2,2}_{22} = Q_{ab}^{xy} \left( e^{2i\bar{\phi}_a} J_+^2(q_{12}^-)^2 + e^{-2i\bar{\phi}_a} J_-^2(q_{12}^+)^2 \right); \tag{14b}
\]
\[
\hat{H}_{22}^{2,-1} = -Q_{ab}^{xy} \left\{ e^{-i\bar{\phi}_a} [J_2 J_- + J_- J_2](q_{12}^-)^2 + e^{+i\bar{\phi}_a} [J_2 J_+ + J_+ J_2](q_{12}^+)^2 \right\}. \tag{14c}
\]
\(\hat{H}_{22}^{2,2}\) and \(\hat{H}_{22}^{2,-1}\) give rise, respectively, to the (2, 2) and (2, -1) terms (19). In the
limit of infinite barrier height, \(4Q_{ab}^{xy}\) becomes the \(l\)-doubling constant denoted \(q_l\) in
Eq. (27b) of Ref. (8) and \(q_{J}^l\) in Ref. (20). To conform more closely to this notation,
the symbol \(q\) will here be used for \(4Q_{ab}^{xy}\).

For matrix elements coupling \(v_6\) and \(v_{12}\), the off-diagonal part of \(\hat{H}_{22}\) can be written
\[
(\hat{H}_{22}^{OFF})' = iQ_{6,a}^{xy} \{(J_-')^2 q_{12}^- - (J_+')^2 p_{12}^+\} q_6 + iP_{6,a}^{xy} \{(J_-')^2 p_{12}^- - (J_+')^2 p_{12}^+\} p_6
\]
\[
- iQ_{6,a}^{yz} \{(J_z J_+ + J_+ J_z) q_{12}^- - (J_z J_- + J_- J_z) q_{12}^+\} q_6
\]
\[
- iP_{6,a}^{yz} \{(J_z J_+ + J_+ J_z) p_{12}^- - (J_z J_- + J_- J_z) p_{12}^+\} p_6. \tag{15}
\]
As was the case for the diagonal \(Q_{ab}^{xy}\), only the component of the mode \(v_{12}\) is specified
in the subscripts \((6, a)\). The \(Q\)-coefficients obey the symmetry relations
\[
Q_{6,b}^{xy} = -Q_{6,b}^{xy} = Q_{6,a}^{xy}; \tag{16a}
\]
\[Q_{6,b}^{xy} = -Q_{6,a}^{xy}. \tag{16b}\]
The remaining \(Q_{ab}^{xy}\) either vanish or can be trivially related to those listed in Eq. (16).
The \(P\)-coefficients obey the same symmetry relations as their \(Q\) counterparts. Because
of the relationships among the terms in Eq. (15), the sum of the terms in \(Q_{6,a}^{xy}\)
and \(P_{6,a}^{xy}\) is denoted \((\hat{H}_{22}^{xy})'\), while the sum of the terms in \(Q_{6,a}^{yz}\) and \(P_{6,a}^{yz}\) is
denoted \((\hat{H}_{22}^{yz})'\).

Since \((\hat{H}_{22}^{OFF})'\) depends on \(q_6\) and \(p_6\), Eq. (15) is valid only for small-amplitude
torsional motion. To allow for large-amplitude internal rotation, \(\sin 3\alpha'\) and \(p'\) are
introduced using Eq. (9). Then the IAM form of \(\hat{H}_{22}^{OFF}\) is
\[
\hat{H}_{22}^{xy} = iQ_{6,a}^{xy} \left\{ \frac{1}{2} [p + \bar{\rho} J_2] [e^{-2i\bar{\phi}_a} J_-^2 p_{12}^- - e^{+2i\bar{\phi}_a} J_+^2 p_{12}^+] + \frac{1}{2} [e^{-2i\bar{\phi}_a} J_-^2 p_{12}^- - e^{+2i\bar{\phi}_a} J_+^2 p_{12}^+] (p + \bar{\rho} J_2) \right\}
+ 2iQ_{6,a}^{xy} \sin 3\alpha [e^{-2i\bar{\phi}_a} J_- q_{12}^- - e^{+2i\bar{\phi}_a} J_+ q_{12}^+]. \tag{17a}
\]
\[
\hat{H}_{22}^{yz} = -iQ_{6,a}^{yz} \left\{ \frac{1}{2} [p + \bar{\rho} J_2] [e^{i\bar{\phi}_a} (J_2 J_+ + J_+ J_2) p_{12}^- - e^{-i\bar{\phi}_a} (J_2 J_- + J_- J_2) p_{12}^+] + \frac{1}{2} [e^{i\bar{\phi}_a} (J_2 J_+ + J_+ J_2) p_{12}^- - e^{-i\bar{\phi}_a} (J_2 J_- + J_- J_2) p_{12}^+] (p + \bar{\rho} J_2) \right\}
- 2iQ_{6,a}^{yz} \sin 3\alpha [e^{i\bar{\phi}_a} (J_2 J_+ + J_+ J_2) q_{12}^- - e^{-i\bar{\phi}_a} (J_2 J_- + J_- J_2) q_{12}^+], \tag{17b}
\]
where
\[
Q_{6,a}^{xy} = (1/4) (s_m)^{1/4} Q_{6,a}^{ij}; \tag{18a}
\]
\[P_{6,a}^{yz} = (2/3) (s_m)^{-1/4} P_{6,a}^{ij}. \tag{18b}\]
A comparison of Eqs. (17b) and (10a) shows that $\tilde{H}_{22}^{yz}$ is very similar to $\tilde{H}_{22}^{xy}$. In fact, if in Eq. (10a) $J_x$ is replaced by $i[J_xJ_y + J_yJ_z]$ and further $p'$ and $q'$ are interchanged, then except for the coupling constants, $\tilde{H}_{22}^{xy}$ is converted to $\tilde{H}_{22}^{yz}$. Thus $\tilde{H}_{22}^{yz}$ will behave in many respects like a higher-order Coriolis interaction. Note, however, that $\tilde{H}_{22}^{yz}$ is only one degree higher in the components of $J$ (not two).

5. Basis Functions, Matrix Elements, and Energies

The form of the effective Hamiltonian matrix $H_{VT'}$ is illustrated in Fig. 2. With $G = (K - l)$, each matrix can be labelled by $(J, G, \sigma)$, since all interactions off-diagonal in these quantum numbers can be neglected. Each Hamiltonian matrix contains three diagonal blocks, labelled by the three possible pairs $(v_{12}, l)$, namely $(0, 0), (1, -1)$, and $(1, 1)$. The entire matrix is evaluated in a basis which diagonalizes the leading torsional Hamiltonian $H_{vt'}^{(0)}$ within each diagonal block:

$$\Psi = |v_{12}\rangle |JKm_{J}\rangle M_{v_{12}K}\sigma(\sigma).$$

(19)

When it is convenient to distinguish a quantum number (such as $v_6$ and $K$) for $(v_{12} = 1)$ from its counterpart for $(v_{12} = 0)$, the former will be indicated with a bar.

In the procedure discussed here, the torsional functions $M_{v_{12}K}\sigma$ in Eq. (19) do not

<table>
<thead>
<tr>
<th>$v_{12} = 0$, $l = 0$;</th>
<th>$v_{12} = 1$, $l = 0$;</th>
<th>$v_{12} = 1$, $l = 1$;</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J$, $K$, $\sigma$</td>
<td>$J$, $(K-1)$, $\sigma$</td>
<td>$J$, $(K+1)$, $\sigma$</td>
</tr>
<tr>
<td>$v_6$</td>
<td>0 1 2 3 4</td>
<td>0 1 2 3 4 5</td>
</tr>
<tr>
<td>0</td>
<td>D</td>
<td>D</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$v_{12} = 0$, $l = 0$;</th>
<th>$v_{12} = 1$, $l = 0$;</th>
<th>$v_{12} = 1$, $l = 1$;</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J$, $K$, $\sigma$</td>
<td>$J$, $(K-1)$, $\sigma$</td>
<td>$J$, $(K+1)$, $\sigma$</td>
</tr>
<tr>
<td>$v_6$</td>
<td>0 1 2 3 4</td>
<td>0 1 2 3 4 5</td>
</tr>
<tr>
<td>0</td>
<td>C C C C C</td>
<td>D</td>
</tr>
<tr>
<td>1</td>
<td>C C C C C</td>
<td>t t D</td>
</tr>
<tr>
<td>2</td>
<td>C C C C C</td>
<td>t t t D</td>
</tr>
<tr>
<td>3</td>
<td>C C C C C</td>
<td>t t t t D</td>
</tr>
<tr>
<td>4</td>
<td>C C C C C</td>
<td>t t t t t D</td>
</tr>
<tr>
<td>5</td>
<td>C C C C C</td>
<td>t t t t t t D</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$v_{12} = 0$, $l = 0$;</th>
<th>$v_{12} = 1$, $l = 0$;</th>
<th>$v_{12} = 1$, $l = 1$;</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J$, $K$, $\sigma$</td>
<td>$J$, $(K-1)$, $\sigma$</td>
<td>$J$, $(K+1)$, $\sigma$</td>
</tr>
<tr>
<td>$v_6$</td>
<td>0 1 2 3 4</td>
<td>0 1 2 3 4 5</td>
</tr>
<tr>
<td>0</td>
<td>C C C C C</td>
<td>L a a a a a</td>
</tr>
<tr>
<td>1</td>
<td>C C C C C</td>
<td>a L a a a</td>
</tr>
<tr>
<td>2</td>
<td>C C C C C</td>
<td>a a L a a</td>
</tr>
<tr>
<td>3</td>
<td>C C C C C</td>
<td>a a a L a</td>
</tr>
<tr>
<td>4</td>
<td>C C C C C</td>
<td>a a a a L</td>
</tr>
<tr>
<td>5</td>
<td>C C C C C</td>
<td>a a a a a L</td>
</tr>
</tbody>
</table>

FIG. 2. The form of the effective Hamiltonian matrix $H_{VT'}$. The matrix is symmetric. The letters within the matrix indicate only the mechanism involved; the same letter at different positions in the matrix can have very different numerical values. $D$ represents the diagonal elements discussed in Section II.2. The letter $t$ represents the matrix elements of the torsional term in $p'l$ in Eq. (3a) off-diagonal in $v_6$. $C$ stands for the Coriolis-like matrix elements given in Eq. (23). $L$ and $a$ stand for the $l$-doubling matrix elements given in Eq. (24). $L$ is diagonal in $v_6$ and has a much larger effect than $a$, which is off-diagonal in $v_6$. For certain special cases, some of these matrix elements vanish by symmetry.
depend on $l$. However, they do depend on $v_{12}$, primarily because the effective barrier height is a function of $v_{12}$. In addition, $H_{x,T}^{(l)}$ is defined differently for $v_{12} = 0$ and 1. For the excited state, this Hamiltonian is taken as the minimal form given in Eq. (3b). However, for the ground state where a large body of microwave, molecular beam and far-infrared data already exists, $H_{x,T}^{(l)}$ is taken to include various distortion effects; $H_{x,T}^{(0)} = [H_{x}^{(0)} + H_{DIST}^{(0)}]$ as defined in Section II of Ref. (5). In Eq. (19), the harmonic oscillator function $|v_{12}angle$ is in the PAM, while the $M_{lK}^{v_{12}}$ and the rotational functions $|J\kappa m\rangle$ are in the IAM.

The torsional functions can be expanded in terms of free rotor functions. For $v_{12} = 0$,

$$M_{lK\kappa}^{v_{12}=0} = \sum_{k=-\infty}^{\infty} A_{3k+\sigma}^{v_{12}=0} (1/\sqrt{2\pi}) \exp[i\alpha(3k+\sigma \hat{\rho} K)] .$$

For $v_{12} = 1$, the same equation applies, but with different expansion coefficients which are denoted $\tilde{A}_{3k+\sigma}^{v_{12}=1}$. The value of $\hat{\rho}$ also depends on $v_{12}$, but the ground state value is used throughout. (See discussion at the end of Section II.2.) It can be shown that

$$A_{3k+\sigma}^{v_{12}=1} = A_{3k+\sigma}^{v_{12}=0}$$

if $K \neq 0$ or $\sigma \neq 0$; (21a)

$$A_{3k}^{v_{12}=0} = (-1)^{\mu} A_{3k}^{v_{12}=0}$$

if $K = 0$ and $\sigma = 0$. (21b)

Equation (21) applies for $\tilde{A}_{3k+\sigma}^{v_{12}=1}$ as well, of course. For each $K$, $\sigma$, and $v_{12}$, the set of $A$-coefficients is calculated (3) for a sufficiently large range in $k$, here taken to be $-10$ to $+10$. This set is determined only to within a phase factor common to all members of the set. This factor is denoted $\epsilon_{K}^{v_{12}}$. Since the $A$'s are real, each $\epsilon$ is (independently) $+1$ or $-1$. Equation (21a) requires that $\epsilon_{K}^{v_{12}=1} = -\epsilon_{-K}^{v_{12}=1}$, but applies no other constraints to the phases. The $\epsilon_{K}^{v_{12}}$ do not affect the energies, but their relative values must be taken into account in assigning transitions that involve the $I$-doubling levels. See Section II.6.

The symmetry properties of the wave functions are summarized in Table II. Although the representations of the rotational and torsional functions are not well-defined individually in the IAM, the representation $\Gamma_{TR}$ of their product is the same as that in the PAM and can be taken from the work of Bunker (21). For $v_{12} = 0$, the representation $\Gamma_{V}$ of the vibrational wave function is $A_{1}$, so that the representation $\Gamma_{VTR}$ of $\Psi$ is simply $\Gamma_{TR}$. For $v_{12} = 1$, $\Gamma_{V} = E_{1}$. For given $l$, $K$, and $\sigma$, the sum of the $\Gamma_{VTR}$ for the different possible combinations of $\pm|\mu|$ and $\pm|\kappa|$ equals $E_{1} \otimes \Gamma_{TR}$. The $\Gamma_{VTR}$ for specific $G$, $l$, $K$, and $\sigma$ can then be deduced from the fact that $\Gamma_{VTR}$ for given $G$, $\sigma$, and ($v_{12} = 1$) equals $\Gamma_{TR}$ for $K = G$, the same $\sigma$, and ($v_{12} = 0$). For $G = 3n (n = 1, 2, \cdots)$ and $\sigma = 0$, there are two different representations present, namely $A_{1}$ and $A_{2}$. These can, in principle, be split, but the splitting is expected to be small and is neglected here. In this limit, all of the levels with $G \neq 0$ are doubly degenerate, with the two sublevels having opposite parity. The symmetry properties of the $l$-doubling states with $K = l = \pm 1$ and $G = 0$ are more complicated; see Section II.6.

The eigenvalues of the total Hamiltonian do not change if the signs of $l$, $K$, and $\sigma$ are simultaneously reversed. Thus the entire spectrum of eigenvalues can be spanned by requiring that $K$ be positive. In order to simplify the notation, this convention is
TABLE II
Symmetry Properties and Selection Rules\textsuperscript{a,b,c,d}

<table>
<thead>
<tr>
<th>$v_{12}^\prime=0$</th>
<th>$v_{6}^\prime=0$</th>
<th>$v_{12}^\prime=1$</th>
<th>$v_{6}^\prime=0$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$v_{12}^\prime=0$</td>
<td>$v_{6}^\prime=0$</td>
<td>$v_{12}^\prime=1$</td>
</tr>
<tr>
<td>$G$</td>
<td>$K''$</td>
<td>$\sigma''$</td>
<td>$\Gamma''_{\text{RT}}$</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$\lambda_1^e$</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0</td>
<td>$\lambda_2^o$</td>
</tr>
<tr>
<td></td>
<td>+1</td>
<td>$\epsilon_4$</td>
<td>+1</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0</td>
<td>$\lambda_4$</td>
</tr>
<tr>
<td></td>
<td>+1</td>
<td>0</td>
<td>$\lambda_5$</td>
</tr>
<tr>
<td></td>
<td>+1</td>
<td>0</td>
<td>$\lambda_6$</td>
</tr>
<tr>
<td></td>
<td>+2</td>
<td>0</td>
<td>$\lambda_7$</td>
</tr>
<tr>
<td></td>
<td>+3</td>
<td>0</td>
<td>$\lambda_8$</td>
</tr>
<tr>
<td></td>
<td>+3</td>
<td>0</td>
<td>$\lambda_9$</td>
</tr>
<tr>
<td></td>
<td>+4</td>
<td>0</td>
<td>$\lambda_{10}$</td>
</tr>
<tr>
<td></td>
<td>+4</td>
<td>0</td>
<td>$\lambda_{11}$</td>
</tr>
<tr>
<td></td>
<td>+5</td>
<td>0</td>
<td>$\lambda_{12}$</td>
</tr>
<tr>
<td></td>
<td>+5</td>
<td>0</td>
<td>$\lambda_{13}$</td>
</tr>
<tr>
<td></td>
<td>+6</td>
<td>0</td>
<td>$\lambda_{14}$</td>
</tr>
<tr>
<td></td>
<td>+6</td>
<td>0</td>
<td>$\lambda_{15}$</td>
</tr>
</tbody>
</table>

a - For $K > 3$, the Table applies modulo 3. Transitions matched as shown are allowed except where $\Gamma_{\text{RTV}}$ is $A_s$ or $A_p$, in which case only the pairing with $\Gamma_{\text{RT}}' = \Gamma_{\text{RTV}}' = A_d$ is allowed. The labels "e" and "o" refer to even and odd $J$, respectively.

b - If the signs of $K$, $\sigma$, and $\lambda$ are reversed, the symmetry is not affected. Only the cases with $K > 0$ and $K = 0$ are given. The cases with $G=O$ (i.e. the $\lambda$-doubling levels) require special consideration.

c - For $G=O$, $\sigma=O$, and $v_{12}=1$, $K$ and $\lambda$ are artificial: $(K,\lambda)=(\pm 1,\pm 1)$ means $v_{12}^\prime=1$, and $(K,\lambda')=(\pm 1,\pm 1)$ means $v_{12}^\prime=-1$. For $G=O$, $\sigma=1$, and $v_{12}^\prime=1$, $(K=\pm 1,\lambda=\pm 1)$ and $(K=-1,\lambda=-1)$ can also be thoroughly mixed. See Sec. 11.6.

d - The table applies for $v_{6}^\prime$ even and any $v_{6}^\prime$. If $v_{6}^\prime$ is odd, the $A_1$ and $A_2$ symmetries are interchanged.

adopted here. It is only for the $\lambda$-doubling states that negative values of $K$ must be considered.

Within the diagonal block ($v_{12} = 0, l = 0$) of the matrix for $H_{\text{VTR}}$ in Fig. 2, no off-diagonal elements are entered. The torsional distortion operators in Eq. (4) of Ref. (5) have selection rules $\Delta v_{12} - \Delta l = \Delta J = \Delta K = 0=0$ with $\Delta v_0$ arbitrary; the off-
diagonal elements are negligible. Within each diagonal block \((v_{12} = 1, l = \pm 1)\), there are corresponding torsional distortion operators with the same selection rules and these are similarly neglected. While the operator involving \(p'l'\) in Eq. (3a) obeys these same selection rules, the coupling constant \(2A'_{12}^{2}\) is \(\sim 200\) GHz and these off-diagonal elements must be taken into account. Because of the large-amplitude motion, the matrix elements between two different torsional levels \(\tilde{v}_6\) and \(\tilde{v}_6'\) can be significant even for \(|\tilde{v}_6 - \tilde{v}_6'| = 3\). These off-diagonal elements change the eigenvalues by over one \(\text{cm}^{-1}\) and play a critical role in different ways for both the resonant and nonresonant cases.

In each of the off-diagonal blocks coupling \((v_{12} = 1, l = \pm 1)\) to \((v_{12} = 0, l = 0)\), there are matrix elements due to the Coriolis interaction \(\mathbf{H}_{21}^{xy}\) and the quartic interaction \(\mathbf{H}_{22}^{xy}\), with both sets of matrix elements obeying the same selection rules. In both Eqs. (10a) and (17b), the terms arising from \(p,\) from \(\tilde{p}_J,\) and from \(\sin 3\alpha\) can be nonzero provided \(\Delta v_{12} = \pm 1, \Delta l = \Delta K = \pm 1,\) and \(\Delta J = \Delta \sigma = 0,\) with \(\Delta v_6 = (\tilde{v}_6 - \tilde{v}_6')\) being arbitrary. For each term, the representation \(\Gamma_{RT}^O\) of the rotation torsion part of the operator is \(E_1\) and the representation \(\Gamma_V^O\) of the vibrational part of the operator is also \(E_1.\) A check of Table II shows that if the above selection rules are satisfied then, as is required,

\[
\Gamma_{RT} (v_{12} = 0) \otimes \Gamma_{RT} (v_{12} = 1) \supset \Gamma_{RT}^O
\]

\[
\Gamma_V (v_{12} = 0) \otimes \Gamma_V (v_{12} = 1) \supset \Gamma_V^O
\]

\[
\Gamma_{VRT} (v_{12} = 0) \otimes \Gamma_{VRT} (v_{12} = 1) \supset A_1.
\]

The \(I\)-doubling levels are discussed in Section II.6.

In the basis of Eq. (19),

\[
\langle \tilde{v}_{12} = 1, \tilde{I} = \pm 1; J, \tilde{v}_6, \tilde{K} = K \pm 1, \sigma [[\mathbf{H}_{21}^{xy} + \mathbf{H}_{22}^{xy}]|v_{12} = 0, l = 0; J, v_6, K, \sigma\rangle
= [J(J + 1) - K(K \pm 1)]^{1/2} \sum_k A_{3k+\sigma}^{v_6,K} A_{3k+\sigma}^{v_6,K+1} (3k + \sigma)
- [B_{3\delta}^{v_6}\tilde{Q}_{6\delta}^{xy}(2K \pm 1)] \sum_k A_{2k+\sigma}^{v_6,K} A_{2k+\sigma+1}^{v_6,K+1} (2k + 1),
\]

The matrix element contains an arbitrary phase factor \(\epsilon_{K\sigma}^{(0)}\) from that for a typical \(A-E\) Coriolis interaction in a \(C_3\) molecule. Consider the matrix elements which couple directly to the upper levels in the spectrum under study, i.e., those with \(\tilde{v}_6 = 0.\) For \((v_6 = +1),\) \(|\langle 0 | \mathbf{H}_{21}^{xy} | v_6 \rangle|\) has its largest magnitude, as expected. However, for \(v_6 = 3\) with \(\Delta \sigma = 3\) rather than 1, the magnitude has fallen only by a factor \(\sim 5.\) Thus while the coupling between \((v_{12} = 1, \tilde{v}_6 = 0)\) and \((v_{12} = 0, \tilde{v}_6 = 3)\) must be considered to be “higher order”, this increase in order does not imply the usual decrease by several powers of 10. Further, as expected from \(C_3\) behavior, the two \(|\langle 0 | \mathbf{H}_{21}^{xy} | v_6 \rangle|\) for \(l = \pm 1\) have a ratio for \((v_6 = 1)\) of approximately the factor calculated from \([J(J + 1) - K(K \pm 1)]^{1/2}\) in Eq. (23). However, for \(v_6 = 3,\) this ratio is off by typically 10\%, while for \(v_6 = 2\) or 4, it is off by a factor of \(\sim 2.\) This behavior of the \(|\langle \tilde{v}_6 | \mathbf{H}_{22}^{xy} | v_6 \rangle|\) can play an important role in the resonant interactions in particular. The quartic matrix element \(|\langle \tilde{v}_6 | \mathbf{H}_{22}^{xy} | v_6 \rangle|\) has the same \((\tilde{v}_6, v_6)\) dependence as
\[ \langle \tilde{v}_6 | \hat{H}_{22}^{v} | v_6 \rangle \], but can be distinguished by the additional factor \((2K \pm 1)\) in its \(K\)-dependence.

The off-diagonal quartic operator \(\hat{H}_{22}^{v}\) in Eq. (17a) has matrix elements with selection rules \(\Delta v_{12} = \pm 1, \Delta l = \mp 1, \Delta K = \Delta J = \Delta \sigma = 0, \) and \(\Delta \tilde{v}_6\) arbitrary. By acting through the blocks off-diagonal in \(v_{12}\), these matrix elements couple pairs of different matrices of the form shown in Fig. 2; in each case the coupled matrices have \(\Delta G - \Delta 3\). However, these resonance terms are not required to fit the current spectrum and are not discussed further.

In the matrix of Fig. 2, the off-diagonal block coupling \((v_{12} = 1, l = \pm 1)\) to \((v_{12} = 1, l = \mp 1)\) contains entries due to the \((2, 2)\) Hamiltonian \(\hat{H}_{22}^{2,2}\) in Eq. (14b). These matrix elements obey the selection rules \(\Delta v_{12} = 0, \Delta l = \Delta K = \pm 2, \Delta J = \Delta \sigma = 0, \) and \(\Delta \tilde{v}_6 = (\tilde{v}_6' - \tilde{v}_6)\) arbitrary. A check of Table II shows that if these selection rules are satisfied, then the conditions here that parallel Eq. (22) are also met. In the basis of Eq. (19),

\[ \begin{align*}
\langle v_{12} = 1, l' = \pm 1; J, \tilde{v}_6', K' = K \pm 2, \sigma | \hat{H}_{22}^{2,2} | v_{12} = 1, l = \mp 1; J, \tilde{v}_6, K, \sigma \rangle \\
= (q/2)(J(J + 1) - K(K + 1))^{1/2}(J(J + 1) \\
- (K \pm 1)(K \pm 2))^{1/2} \sum_k A_{3k+\sigma}^\tilde{v}_6 K A_{3k+\sigma}^\tilde{v}_6'.
\end{align*} \] (24)

Although the matrix elements of \(\hat{H}_{22}^{2,2}\) off-diagonal in \(\tilde{v}_6\) are much less important than the ones diagonal in \(\tilde{v}_6\), both types were included. The most important matrix elements of \(\hat{H}_{22}^{2,2}\) are those which produce the \(l\)-doubling for \((K\quad l) = 0\). These are discussed in Section II.6.

The sum over products of \(A\)-coefficients in Eq. (24) forms an “overlap” integral

\[ I(\tilde{v}_6, K \pm 2, \sigma; \tilde{v}_6, K, \sigma) \]. These integrals contain an arbitrary phase factor \(\epsilon_{K \pm 2, \sigma} \in K, \sigma\) which is implicit in the products of \(A\)-coefficients. For all cases, \(|I(\tilde{v}_6, K \pm 2, \sigma; \tilde{v}_6, K, \sigma)| \leq 1\). In the limit of infinite barrier, the magnitude of these diagonal integrals \(\to 1\). Here, for \(\tilde{v}_6 = \tilde{v}_6 = 0\), the levels are far below the top of the barrier and \(|I|\) is very close to unity for all \((K, \sigma)\). The arbitrary phase factor \(\epsilon_{K \pm 2, \sigma} \in K, \sigma\) is selected so that \(I(0, K \pm 2, \sigma; 0, K, \sigma)\) is positive. This selection defines a convention such that, for \(V_3 \to \infty\) and \(\tilde{v}_6 = \tilde{v}_6 = 0\), the matrix elements of \(\hat{H}_{22}^{2,2}\) in Eq. (24) have the sign of \(q\). The selection is consistent with Eq. (21a). For \(\tilde{v}_6 > 0\), the diagonal integrals \(I(\tilde{v}_6, K \pm 2, \sigma; \tilde{v}_6, K, \sigma)\) can be much smaller in magnitude than unity, can have either sign, and can be very sensitive to \((K, \sigma)\).

The quartic operator \(\hat{H}_{22}^{-1}\) in Eq. (14c) arising from \(\hat{H}_{22}^{\text{DIA}}\) has matrix elements with selection rules \(\Delta v_{12} = 0, \Delta l = \pm 2, \Delta K = \mp 1, \Delta J = \Delta \sigma = 0, \) and \(\Delta \tilde{v}_6\) arbitrary. By acting through the blocks diagonal in \(v_{12}\), these matrix elements couple pairs of different matrices of the form shown in Fig. 2; the coupled matrices satisfy \(\Delta G = \pm 3\). As with \(\hat{H}_{22}^{2,2}\), these terms are dropped because they enter only through resonance interactions that are not detected in the current work.

The energy level scheme for the three interacting stacks of torsional levels is shown in Fig. 3 for \(J = 11, G = 8, \sigma = 0\) as an example. For the resonant states with \((v_{12} = 1, \tilde{v}_6 = 0)\) and \((v_{12} = 0, \tilde{v}_6 = 3)\), not only must the matrix elements between the
closely spaced levels be treated properly, but also the nonresonant interactions with any possible third level must be carefully considered. If the magnitude of the ratio of the off-diagonal element $\langle \tilde{v}_6 | \tilde{H}^{xy}_{\pm 1} | v_6 \rangle$ to the difference $\Delta E$ in the diagonal elements is significant, then the corresponding level must be included in the matrix of Fig. 2. For $(v_{12} = 1, v_6 = 0)$, the coupling to $(v_{12} = 0, v_6 < 3)$ must be taken into account in spite of the large $|\Delta E|$ because $|\langle \tilde{v}_6 | \tilde{H}^{xy}_{\pm 1} | v_6 \rangle|$ is large for small $|\tilde{v}_6 - v_6|$. The shift of $(v_{12} = 1, \tilde{v}_6 = 0)$ by $(v_{12} = 0, v_6 = 4)$ is also taken into account, but the shift by $(v_{12} = 0, v_6 = 5)$ is left out because the matrix elements with $|\tilde{v}_6 - v_6| = 5$ are small. For $(v_{12} = 0, v_6 = 3)$, however, shifts due to levels up to $(v_{12} = 1, \tilde{v}_6 = 5)$ are included. In this case, $|\tilde{v}_6 - v_6|$ is only two, so that the matrix elements are still sizeable. For higher $\tilde{v}_6$, the $\Delta E$ are large enough that the levels can be dropped. Thus the matrix shown in Fig. 2 has dimensions $17 \times 17$. The final energies $E_{VTR}$ are calculated by diagonalizing this matrix.
At first glance, Figs. 1 and 3 appear to be inconsistent with regard to parity. In Fig. 1, levels \( (v_{12} = 1, l = -1; J = 11, \bar{v}_6 = 0, K = 7, \sigma = 0) \) and \((0, 0; 11, 0, 8, 0)\) are shown to have an electric dipole transition moment, while in Fig. 3 they are shown to be coupled by the Hamiltonian. The resolution of this paradox lies in the fact that both levels actually consist of two sublevels of opposite parity. See the discussion of Table II following Eq. (21).

6. The I-Doubling Levels

The levels with \( (v_{12} = 1, l = K = \pm 1) \) are discussed in some detail here because their properties in CH$_3$SiH$_3$ differ in important ways from those of corresponding levels in a C$_{3v}$ molecule. The case where \( \sigma = 0 \) will be treated first; the arguments will be presented in such a way that they can be applied later to the \( (\sigma = \pm 1) \) case. In the absence of all off-diagonal matrix elements in Fig. 2, the state \( (v_{12} = 1, l = +1; J, \bar{v}_6, K = +1, \sigma = 0) \) is degenerate with the state \( (v_{12} = 1, l = -1; J, \bar{v}_6, K = -1, \sigma = 0) \). The I-doubling Hamiltonian \( \hat{H}^{L2}_{22} \) in Eq. (14b) mixes these completely; the representation that diagonalizes the \( 2 \times 2 \) matrix involving these states is

\[
|\tau, J, \bar{v}_6, \sigma\rangle = \frac{1}{\sqrt{2}} \left\{ |l = +1; J, \bar{v}_6, K = +1, \sigma\rangle + \tau |l = -1; J, \bar{v}_6, K = -1, \sigma\rangle \right\},
\]

where \( \tau = \pm 1 \). In Eq. (25), the quantum number \( v_{12} \) has been suppressed. From Eq. (21a), it follows that for \( \tau = +1 \) and \(-1 \), respectively, the symmetry \( \Gamma_{VTR} = A_2 \) and \( A_1 \) if \( J \) is even. If \( J \) is odd, the correspondence is reversed. \( \Gamma_{VTR} \) is independent of \( \bar{v}_6 \) (see Table II). If all other off-diagonal elements are turned off, the energies are denoted \( \tilde{E}(\tau, J, \bar{v}_6, \sigma) \) and the I-doublet splittings are denoted

\[
\Delta \tilde{E}_{LD}(J, \bar{v}_6, \sigma = 0) = \tilde{E}(\tau = +1; J, \bar{v}_6, \sigma = 0) - \tilde{E}(\tau = -1; J, \bar{v}_6, \sigma = 0).
\]

In this limit,

\[
|\Delta \tilde{E}_{LD}(J, \bar{v}_6, \sigma = 0)| = |qJ(J + 1)I(\bar{v}_6, +1, 0; \bar{v}_6, -1, 0)|.
\]

In the current context, there are three important properties whose dependence on \( \tau \) should be discussed. The first deals with the sign of \( \Delta \tilde{E}_{LD} \). For positive \( q \), \( \Delta \tilde{E}_{LD} \) has the sign of \( I(\bar{v}_6, +1, 0; \bar{v}_6, -1, 0) \) which is seen from the computer output to have the sign \( (-1)^{3k} \) once the convention is adopted (see Section II.5) that \( I(0, +1, 0; 0, -1, 0) > 0 \). Thus for \( q > 0 \) and all other off-diagonal terms set to zero, the \( (\tau = +1) \) level is above/below the \( (\tau = -1) \) level as \( \bar{v}_6 \) is even/odd. This result is independent of \( J \) and \( \Gamma_{VTR} \).

The second property deals with the selection rules for the Coriolis interaction. As an example, the first sum in Eq. (23) is considered. In the Wang basis of Eq. (25), this sum is denoted \( T_{r,\sigma}^{\bar{v}_6, v_6} \). From Eq. (21), it follows that

\[
T_{r,\sigma}^{\bar{v}_6, v_6} = \frac{1}{\sqrt{2}} \left\{ \sum_k A_{3k + \sigma}^{\bar{v}_6 + 1} A_{3k + \sigma}^{v_6 0} (3k + \sigma) - \tau \chi \sum_k A_{3k - \sigma}^{\bar{v}_6 + 1} A_{3k - \sigma}^{v_6 0} (3k - \sigma) \right\},
\]
where \( x \) is +1 or -1. If Eq. (27) is specialized to the case \( (\sigma = 0) \) being considered, then \( x = (-1)^{\nu_6} \) and

\[
T_{\tau,0}^{\tilde{v}_6,\nu_6} = \frac{1}{\sqrt{2}} [1 - \tau(-1)^{\nu_6}] \sum_k \bar{A}_{3k}^{\tilde{v}_6+1} A_{3k}^{\nu_60}(3k).
\]

(28)

Similar results arise for the other sum in Eq. (23). For interaction with a specific \( \nu_6 \) (in \( v_{12} = 0 \)), the \( \tau \) levels with \( \tau(-1)^{\nu_6} = +1/-1 \) have zero/nonzero Coriolis matrix elements. This same conclusion can be drawn more simply from the symmetry arguments leading to Table II, but these cannot be applied to the \( (\sigma = \pm 1) \) case. The value of \( \tilde{v}_6 \) does not affect the conclusions. For the case \( \tau(-1)^{\nu_6} = -1 \), the Coriolis matrix element is \( \sqrt{2} \) times the matrix element before the Wang transformation is made. Thus for the resonant interaction between \( (v_{12} = 1, \tilde{v}_6 = 0) \) and \( (v_{12} = 0, \nu_6 = 3) \), the level with \( \tau = -1 \) receives no Coriolis shift, but the level with \( \tau = +1 \) receives twice the normal shift.

The third property deals with the selection rules for electric dipole transitions. The selection rules of interest here are effectively the same as those for a \( C_{3v} \) molecule in general, but the specific case of the \( l \)-doublets requires special treatment. Consider the infrared transition moment for a \( C_{3v} \) molecule as calculated for \( K = 0 \) before the Wang transformation. The transition moment here after the Wang transformation will be the same except for an additional factor

\[
F_{\tilde{v}_6,\nu_6}^{\tau,\sigma} = \frac{1}{\sqrt{2}} \left\{ (-1)^{j+J} \sum_k \bar{A}_{3k}^{\nu_6+1} A_{3k}^{\nu_60} + \tau x \sum_k \bar{A}_{3k}^{\nu_6+1} A_{3k}^{\nu_60} \right\}.
\]

(29)

If this is specialized to the case \( (\sigma = 0) \), then

\[
F_{\tau,0}^{\tilde{v}_6,\nu_6} = \frac{1}{\sqrt{2}} \left\{ (-1)^{j+J} + \tau(-1)^{\nu_6} \right\} \sum_k \bar{A}_{3k}^{\nu_6+1} A_{3k}^{\nu_60}.
\]

(30)

For transitions originating in a specific \( \nu_6 \) with \( v_{12} = 0 \), the \( \tau \) levels with \( \tau(-1)^{\nu_6} = +1 \) will be involved in \( Q \)-branch transitions, but not in \( P \)- or \( R \)-branch transitions. If \( \tau(-1)^{\nu_6} = -1 \), \( P \)- and \( R \)-branch transitions will be allowed, and \( Q \)-branch transitions will not. This conclusion can be drawn directly from the symmetry arguments leading to Table II and the fact that the space-fixed dipole operator transforms by representation \( A_2 \). For the allowed transitions, the electric dipole matrix element is \( \sqrt{2} \) times the matrix element before the Wang transformation. Thus for \( \nu_6 = 0 \), the levels with \( \tau = +1/-1 \) are involved only in \( Q/P, R \) transitions.

Since \( K \) is not a good quantum number for the \( l \)-doubling levels, subbranch labels such as \( 'Q \) for \( K = 0 \) become ambiguous. Here the convention will be adopted that \( \tau = +1 \) and \( -1 \) correspond to \( r \) and \( p \), respectively. Within this convention, it is clear from the selection rules just discussed that the three subbranches with \( K = 0 \) in the lower level are \( ^p_P, 'Q, \) and \( ^p_R \).

For the microwave spectrum, the selection rules are \( (\tau = \pm 1, J + 1, \tilde{v}_6, \sigma = 0) \leftrightarrow (\tau = \pm 1, J, \tilde{v}_6, \sigma = 0) \). The initial and final states are both upper members of their \( l \)-doublet pairs or both lower members.

The case for \( (\sigma = \pm 1) \) is more complicated. As can be seen from Table II, \( \Gamma_{VTR} = E_4 \). In the absence of all off-diagonal matrix elements in Fig. 2, the state
\( (v_{12} = 1 \leftarrow 0) \) BAND OF CH\(_3\)SiH\(_3\)

\( (v_{12} = 1, l = +1; J, \tilde{v}_6, K = +1, \sigma = \pm 1) \) is not degenerate with its "\( l\)-doublet" partner \( (v_{12} = 1, l = -1; J, \tilde{v}_6, K = -1, \sigma = \pm 1) \). With all off-diagonal terms turned off, the energy difference \( \Delta(\tilde{v}_6, \sigma) \) between these two states is given to excellent approximation by

\[
\Delta(\tilde{v}_6, \sigma) = \langle H_{(12)} \rangle^{v_{12} = +1, l = +1}_{\tilde{v}_6, K = +1, \sigma} - \langle H_{(12)} \rangle^{1, -1}_{\tilde{v}_6, -1, \sigma} \quad (31a)
\]

\[
= \left\{ \langle H_{12,T}^{(0)} \rangle^{\tilde{v}_6, K = +1, \sigma} - \langle H_{12,T}^{(0)} \rangle^{\tilde{v}_6, +1, -1, \sigma} \right\} \quad (31b)
\]

\[+ 2(A_f^\tau)^{\tilde{v}_6} \{ \langle p \rangle^{\tilde{v}_6, +1, \sigma} + \langle p \rangle^{\tilde{v}_6, +1, -1, \sigma} \}.\]

This expression has been rearranged using the symmetry properties of the matrix elements so that the first term is seen to arise from the \( \sigma \)-splitting between torsional levels, while the second term is seen to arise from the average \( (K = +1) \) diagonal matrix element for \( \sigma = +1 \) and \( \sigma = -1 \) of the Coriolis-type operator \( \tilde{H}_{\tilde{v}_6}^{(0)} \) as defined by the form of Eq. (6) with \( p' \) replaced by \( p \); see Eq. (3a). This operator also has large matrix elements off-diagonal in \( \tilde{v}_6 \). When these are turned on, the \( \Delta(\tilde{v}_6, \sigma) \) change substantially. The total modified energy difference is denoted \( \Delta_T(\tilde{v}_6, \sigma) \). The Wang transformation can be made for \( \sigma = \pm 1 \), but in Representation (25), the \( 2 \times 2 \) matrix formed by the \( \tilde{l}\)-doublets will not be diagonal. The energy level pattern and selection rules for these levels will depend on the values of the various molecular constants.

For the set of parameters in Table I, however, the behavior of the \( (\sigma = \pm 1) \) levels for \( \tilde{v}_6 = 0 \) will be very similar to that of the \( (\sigma = 0) \) level. Here \( (1/2)\Delta_T(0, \sigma) \) is small compared to the \( l\)-doubling matrix element \( (q/2)J(J + 1)I(0, +1, \sigma = \pm 1; 0, -1, \sigma = \pm 1) \) even for \( J = 1 \). The Wang representation forms a good approximation to the eigenvectors of the \( 2 \times 2 \) matrix. Further, the reduced barrier height is sufficiently high that for the lowest torsional level, the representation \( \Gamma_{\text{VTR}} = E_4 \) acts very much like its \( C_{2v} \) limit (8) of \( A_1 + A_2 \).

As a result, the \( (\sigma = \pm 1) \) \( l\)-doublet states involved in the current study behave the same as the \( (\sigma = 0) \) states with regard to the three properties discussed above. First, the \( (\tau = +1) \) level is above the \( (\tau = -1) \) level. Second, the \( (\sigma = 0) \) Coriolis selection rules are approximately correct. For \( \sigma = \pm 1 \), in Eq. (27), \( X = +1 \) and the \( \sigma \) dependence of the sums is small. The \( (\tau = +1) \) level receives almost twice the normal Coriolis shift from \( (v_{12} = 0, \tilde{v}_6 = 3) \), while the \( (\tau = -1) \) level receives only a small corresponding shift. The approximation can be assessed by calculating the sums in Eq. (27). Third, the \( (\sigma = 0) \) dipole selection rules can be applied to \( (\sigma = \pm 1) \) since in Eq. (29) the \( \sigma \)-dependence of the sums is again small. The intensities of \( (\sigma = \pm 1) \) lines which are counterparts of forbidden \( (\sigma = 0) \) transitions will be small; these intensities can be calculated by evaluating the sums in Eq. (29).

No detailed study has been carried out of the \( (\sigma = \pm 1) \) \( l\)-doublets for \( \tilde{v}_6 > 1 \). It is clear, however, that the \( (\sigma = 0) \) type of behavior cannot be expected. First, \( \Delta_T(\tilde{v}_6, \sigma) \) increases substantially and is much larger than the \( l\)-doubling matrix element, at least for low \( J \). Second, the \( \sigma \)-dependence of the sums in Eq. (27) and (29) becomes important. A study of the hot band \( (v_{13} = 1, \tilde{v}_k = 1) \leftarrow (v_{12} = 0, \tilde{v}_k = 1) \) is underway to investigate this matter further.
III. THE MEASUREMENTS

1. Experimental Details

Fourier transform spectroscopy was used to study the vibrational fundamental ($v_{12} = 1 \rightarrow 0$) from 475 to 575 cm$^{-1}$ at a resolution of 0.0045 cm$^{-1}$. The spectra were recorded with a BOMEM DA3.002 interferometer at the Herzberg Institute of Astrophysics. The source was a globar with an aperture of 2.4 mm. A KBr beamsplitter was used. The cell was 15 cm long and had KBr windows 0.5 cm thick. The detector was a CuxGe photoconductor operating at 4.2 K. The optical band pass extended from 330 cm$^{-1}$, set by the detector sensitivity, to 745 cm$^{-1}$, set by a cold filter in front of the detector.

The maximum optical path difference $L_{\text{MAX}}$ employed was the largest possible in the instrument, namely 250 cm. The apodization was done with a Hamming function $[0.53856 + 0.46144 \cos(\pi L/L_{\text{MAX}})]$, where $L$ is the optical path difference. The resulting full width at half height of the theoretical instrument function was 0.0036 cm$^{-1}$. The actual line width was limited to 0.0045 cm$^{-1}$ by the aperture size. The spectra were deconvolved numerically to reduce the line width by about a factor of two.

The spectra were taken at a temperature of about 170 K obtained by passing nitrogen gas through the cooling coil soldered to the cell. The methyl silane pressure was about $\frac{1}{4}$ Torr. The sample was made by reducing CH$_3$SiCl$_3$ with LiAlH$_4$. A water spectrum taken at room temperature was used to calibrate the interferometer against the reference frequencies of Kauppinen et al. (22).

The final sample interferogram was obtained by coadding 24 separate runs, each of which required 250 sec of data-taking. The final background interferogram was obtained in the same way. The signal-to-noise ratio was better than 10 to 1 for the weakest lines included in the analysis.

2. General Features of the Spectrum

In many respects, the spectrum looks like a perpendicular fundamental of a $C_3v$ molecule with a fine structure arising from the $\sigma$-splitting. Aside from a few exceptions including $'Q_0$, the $Q$ branches formed strong narrow features with no resolvable rotational structure. These envelopes were used only to confirm the assignments.

The most striking feature of the $P$ and $R$ branches is the torsional splitting of the multiplets ($v_{12} = 1, l = \pm 1; J \pm 1, v_6 = 0, K \pm 1, \sigma$) $\leftarrow$ ($v_{12} = 0, l = 0; J, v_6 = 0, K, \sigma$) into their $\sigma$-components with characteristic spin statistical weights. This is illustrated in Fig. 4 for all the possible cases. The original spectrum in Fig. 4a is a better guide for the present purpose since the deconvolution can distort the relative intensities somewhat. For each nonzero value of $K$, there are three possible values of $\sigma$. If $K \neq 3n (n = 1, 2, 3 \cdots)$, the spin statistics ($8$) lead to relative intensities in the ratio 2:2:1, with the weak component being $\sigma = -1$ for $K = (3n + 1)$ and $\sigma = +1$ for $K = (3n - 1)$. If $K = 3n$, the relative intensities are 4:1:1 with the strong component being $\sigma = 0$. In Fig. 4, $'R_{3^+}^0(13)$ and $'R_{3^-}^1(13)$ are not resolved; their combined intensity should be five times the intensity of $'R_{3^+}^0(13)$. If $K = 0$, $\sigma$ takes the values 0
and +1 with corresponding spin statistical weights of 2 and 1. The intensities of the different $\sigma$-components are observed to follow these spin statistical weights.

As can be seen from Eq. (29) and the discussion in Section II.6, a further $\sigma$-dependence enters the intensities through sums such as the overlap integrals $\sum K x_{1}^{K} A_{1}^{Kx} A_{2}^{Kx}$. Computation of these sums using the eigenvectors of $H_{a12}^{(0)}$ shows that this $\sigma$-dependence is very weak. The intensity observations confirm this result and provides strong corroborating evidence that the $(\sigma = \pm 1)$ $l$-doubling states can be treated in the same manner as their $(\sigma = 0)$ counterparts. For example, the line

Fig. 4. Portion of the $'R$ branch: (a) original spectrum at a resolution of 0.0045 cm$^{-1}$; (b) deconvolved spectrum with a resolution about a factor of two better. The values of $K''$ and $\sigma''$ are indicated in (a) and (b), respectively. From left to right, the values of $J''$ for the six multiplets are 22, 7, 10, 13, 16, and 19. For the lowest-frequency multiplet, the upper states are the $(\tau = -1)$ $l$-doubling levels and are $'R$ transitions in the conventions adopted here. Note the characteristic spin statistical weights and the building toward a bandhead as $K$ increases from 1 to 5.
in Fig. 4 is strengthened by a factor of 2 as a result of the full mixing caused by the \( l \)-doubling. The line \( pR_0^{21}(22) \) receives a similar factor, indicating that the \( l \)-doubling produces a comparable amount of mixing. For transitions of the type \( (v_{12} = 1, v_6) \leftrightarrow (v_{12} = 0, v_6) \), with \( v_6 \neq 0 \), the extra \( \sigma \)-dependence in the intensity may be important; certainly for levels near or above the barrier top, one cannot expect the intensities to follow the unmodified spin statistical weights.

The frequency pattern for the \( \sigma \)-splittings in the \( K \)-multiplets of the different branches will be discussed in Section IV.

In the \( pP \) branch, a sequence is formed by the transitions \( (J - 3m, K + m) \), \( m = 0, 1, 2 \cdots \), with lines of higher \( m \) coming at higher frequencies. This pattern arises at low \( K \) and \( m \) because \( 3B_0 \) is less than 5\% larger than \( [A_0 - B_0 - (A^2_{42} + \frac{1}{2})] \); for \( \Delta m = \pm 1 \), a typical frequency difference is 0.1 cm\(^{-1}\). For higher \( K \) and \( m \), this difference is increased in magnitude primarily by the frequency contribution from the change in the effective \( A \)-constant between upper and lower levels. In the \( 'R \) branch, a similar sequence \( (J - 3m, K + m) \) is formed, but lines with higher \( m \) come at lower frequencies for low \( K \) and \( m \). In this case, the frequency spacing with \( m \) is decreased in magnitude by the changes in the effective values of both rotational constants. As can be seen from Fig. 4, these lines come to a head; for \( K \geq 6 \), the sequence reverses and lines with higher \( m \) come at higher frequency. The formation of these "sequence heads" makes it impossible to resolve some of the intermediate \( K \) lines and so these are not included in the data set. Furthermore, at low resolution, these heads have some of the characteristics of \( Q \) branches and make the spectrum appear as though it were a composite of two different fundamentals. The \( pR \) and \( 'P \) branches form sequences \( (J + 3m, K + m) \) which behave in a similar manner, but the intensities are much lower.

IV. ANALYSIS

1. Identification of the Transitions

In the first phase of the analysis, we assigned the quantum number \( \tau \) for the \( (J = 2 \leftrightarrow 1) \) \( l \)-doubling transitions reported by Hirota (8). It was assumed that the \( (\sigma = \pm 1) \) levels would behave qualitatively the same as their \( (\sigma = 0) \) counterparts, an assumption that was later justified (see Section II.6). It follows then that the \( (\tau = -1) \) frequencies will be virtually independent of \( \sigma \) because the levels involved have either no Coriolis shift \( (\sigma = 0) \) or a very small one \( (\sigma = \pm 1) \). The low frequency line shown by Stark shifts to be an unresolved doublet (8) must therefore have \( \tau = -1 \); the high frequency doublet must then have \( \tau = +1 \). This pair is resolved; the \( \sigma \)-identification of its members was easily made (8) on the basis of the spin statistics.

In the second phase, we considered the \( pR \) and \( 'R \) branches of the infrared band (including \( pP_0 \) and \( pR_0 \)). The assignment of all the quantum numbers except \( \sigma \) was done using standard methods applicable to \( C_3v \) molecules (23). A selection was made of individual lines that seemed to be free of serious blending, had good signal-to-noise ratios, and could be assigned \( \sigma \)-values on the basis of relative intensities. This selection included the weak \( \sigma \) components for \( K = (3n + 1) \) and \( (3n - 1) \) and the strong component for \( K = 3n (n = 1, 2, 3 \cdots) \). Both components of \( pP_0(J) \) were assigned to \( \tau = -1 \); the same was done for both components of \( pR_0(J) \). In these cases, the
absorption is to an $l$-doubling level with zero Coriolis shift from \((v_{12} = 0; v_6 = 3)\); see Section II.6. The set of lines selected was restricted so that \(J \leq 15\) and \(K \leq 9\), and further so that no transitions with a large resonant shift were included.

Preliminary fits were then made to the microwave data and this selection of infrared lines using an isolated band model. The ground state parameters were fixed \((7)\). The excited state could be characterized at this level by Eqs. \((32)\) and \((33)\) with only seven parameters being varied: \(\tilde{\nu}_{12}\), \((A^{\tilde{\nu}_{12}}_2)\), \((A^{\tilde{\nu}_{12}}_0)\), \(V_{12,3,}\ \Delta A_{12}, \ \Delta B_{12},\) and \(q\). By testing tentative assignments with this simplified model, all the \(\sigma\)-components for \(J \leq 15\) and \(K \leq 9\) in the \(^pP\) and \(^'R\) bands (including \(^pP_0\) and \(^pR_0\)) were identified with the exception of the lines with \(J \geq 13\) in the resonantly perturbed subbranch \(^pP_{6}^{-1}\). The data set was then expanded to include the stronger lines in the \(^pR\) and \(^'P\) branches.

In the final phase of the identification process, we incorporated the entire \((v_{12} = 0)\) data set as described in Ref. \((7)\) and went to the full diagonalization model described in Section IV.2. This ultimately led to the assignment of the \((\Delta v_{12} = 1)\) data set given in Table III. The limits on \(J\) and \(K\) were raised to 25 and 11, respectively. In these later stages of the process, the four transitions with \(J \geq 13\) in the \(^pP_{6}^{-1}\) subbranch were identified; the lines with \(J > 17\) in this subbranch were too weak to be assigned with confidence. In addition, four \(Q\) subbranches were assigned: \(^Q_{0}\), \(^Q_{6}^{-1}\), \(^Q_{6}^{0}\), and \(^pQ_{6}^{0}\). The last three of these show near resonant or resonant Coriolis shifts. The \(^pQ_{6}^{0}\) subbranch is illustrated in Fig. 5.

2. The Minimal Model and Best Fit

In order to fit the data, a model had to be adopted for the diagonal Hamiltonian \(H_{12}\) in Eq. \((32)\) that represented the information content in the data without introducing unnecessary correlations among the parameters. The approach used follows the arguments given in Section IV of Ref. \((4)\). The first problem involves the separation of \(V_{12,3}\) from the effective vibrational quantum \(\tilde{\nu}_{12}\). To excellent approximation, the torsional energy for the excited state can be expanded in a Fourier series and only the first two terms retained:

\[
\langle H^{(0)}_{12,T}\rangle_{\nu_0=0,K,\sigma} = a^{(E)}_{12,0} + a^{(E)}_{12,1} \cos((2\pi/3)(\tilde{\nu}K - \sigma)).
\]

The coefficient \(a^{(E)}_{12,0}\) is the torsional energy for given \(K\) averaged (unweighted) over \(\sigma\). It is independent of \(K\) except for small corrections that reflect the truncation of the Fourier series. Consequently, \(a^{(E)}_{12,0}\) for \((K = 0)\) provides an excellent measure of the overall mean eigenvalue of \(H^{(0)}_{12,T}\) measured from the minimum in the \((v_{12} = 1)\) torsional potential. Clearly, \(a^{(E)}_{12,0}\) is 100% correlated with \(\tilde{\nu}_{12}\), which measures the energy difference between the bottom of the \((v_{12} = 1)\) potential and the bottom of the \((v_{12} = 0)\) potential. This introduces a very strong correlation between \(\tilde{\nu}_{12}\) and \(s_{12}\). To overcome this difficulty, the origin for the torsional energy was raised by \(a^{(E)}_{12,0}\) and \(\tilde{\nu}_{12}\) was replaced as a fitting parameter by:

\[
\nu_{12,0} = \tilde{\nu}_{12} + a^{(E)}_{12,0}.
\]

Then \(s_{12}\) is free to be determined by \(a^{(E)}_{12,1}\), i.e., by the contribution to the torsional splittings in the excited state arising from the pure torsional Hamiltonian. As discussed
TABLE III
Frequencies in the Infrared ($\nu_{12} - 1 \sim 0$) and Microwave ($\nu_{12} = 1 \sim 1$)

<table>
<thead>
<tr>
<th>$J^1$</th>
<th>$\nu_{obs1}$</th>
<th>$\nu_{obs2}$</th>
<th>$\nu_{calc}$</th>
<th>$J^1$</th>
<th>$\nu_{obs1}$</th>
<th>$\nu_{obs2}$</th>
<th>$\nu_{calc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>524,7593</td>
<td>524,7593</td>
<td>524,7593</td>
<td>2</td>
<td>524,7593</td>
<td>524,7593</td>
<td>524,7593</td>
</tr>
<tr>
<td>0</td>
<td>524,7593</td>
<td>524,7593</td>
<td>524,7593</td>
<td>3</td>
<td>524,7593</td>
<td>524,7593</td>
<td>524,7593</td>
</tr>
<tr>
<td>1</td>
<td>524,7593</td>
<td>524,7593</td>
<td>524,7593</td>
<td>4</td>
<td>524,7593</td>
<td>524,7593</td>
<td>524,7593</td>
</tr>
<tr>
<td>2</td>
<td>524,7593</td>
<td>524,7593</td>
<td>524,7593</td>
<td>5</td>
<td>524,7593</td>
<td>524,7593</td>
<td>524,7593</td>
</tr>
<tr>
<td>3</td>
<td>524,7593</td>
<td>524,7593</td>
<td>524,7593</td>
<td>6</td>
<td>524,7593</td>
<td>524,7593</td>
<td>524,7593</td>
</tr>
<tr>
<td>4</td>
<td>524,7593</td>
<td>524,7593</td>
<td>524,7593</td>
<td>7</td>
<td>524,7593</td>
<td>524,7593</td>
<td>524,7593</td>
</tr>
<tr>
<td>5</td>
<td>524,7593</td>
<td>524,7593</td>
<td>524,7593</td>
<td>8</td>
<td>524,7593</td>
<td>524,7593</td>
<td>524,7593</td>
</tr>
<tr>
<td>6</td>
<td>524,7593</td>
<td>524,7593</td>
<td>524,7593</td>
<td>9</td>
<td>524,7593</td>
<td>524,7593</td>
<td>524,7593</td>
</tr>
<tr>
<td>7</td>
<td>524,7593</td>
<td>524,7593</td>
<td>524,7593</td>
<td>10</td>
<td>524,7593</td>
<td>524,7593</td>
<td>524,7593</td>
</tr>
<tr>
<td>8</td>
<td>524,7593</td>
<td>524,7593</td>
<td>524,7593</td>
<td>11</td>
<td>524,7593</td>
<td>524,7593</td>
<td>524,7593</td>
</tr>
<tr>
<td>9</td>
<td>524,7593</td>
<td>524,7593</td>
<td>524,7593</td>
<td>12</td>
<td>524,7593</td>
<td>524,7593</td>
<td>524,7593</td>
</tr>
</tbody>
</table>

*a* If the signs of $K$, $\sigma$, and $l$ are reversed, the energy is not affected. Only the identifications with $K > 0$ and $K = 0$ are listed.

*b* For the infrared transitions, the lower state is specified by $(\nu_{12} = 0, \ell = -1)$ and $(\nu_{12} = 0, \ell = 0, K^0, \sigma^0)$. The upper state has $(\nu_{12} = 1, \nu_{6} = 0, \sigma' = \sigma)$. The values of $J^0$, $K^0$, and $\ell$ can be deduced from the branch label. Transitions involving the $l$-doubling levels are exceptions. In the $F$ and $R$ branches, $(\Delta K = 1)$ means the lower level has $\tau = 1$; in the $Q$ branch, $(\Delta K = +1)$ implies $\tau = +1$. See Section II.6.

*c* For the microwave transitions, $A_{\nu} = -1$, $A_{\ell} = 0$, and $A_{\sigma} = 0$. For the $l$-doubling levels, $K$ should be interpreted as $\tau$. See Section II.6. When $\sigma = \ast$, an intensity-weighted average has been taken over the unresolved $\sigma$ components.

*d* This is the measured frequency in MHz for the microwave and cm$^{-1}$ for the infrared.

*e* Estimated experimental error in kHz for the microwave and 10$^{-5}$ cm$^{-1}$ for the infrared.

$f$ $\delta$ is observed value minus that calculated from the constants of Table I. The units are kHz for the microwave and 10$^{-5}$ cm$^{-1}$ for the infrared.

*From Ref. (8).*

* $l$-doubling levels are involved.
in Section V there are other nonresonant contributions to this splitting from the term in \(pl'\) in Eq. (3a).

In order to use \(V_{123}\) as a fitting parameter instead of \(s_{12}\), the reduced rotational constant was calculated from

\[
F_{12} = A'/\epsilon (1 - \epsilon)
\]


- TABLE III—Continued

<table>
<thead>
<tr>
<th>(J^*)</th>
<th>(\sigma^* )</th>
<th>(\epsilon )</th>
<th>(J^*)</th>
<th>(\sigma^* )</th>
<th>(\epsilon )</th>
<th>(J^*)</th>
<th>(\sigma^* )</th>
<th>(\epsilon )</th>
<th>(J^*)</th>
<th>(\sigma^* )</th>
<th>(\epsilon )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>515.19778</td>
<td>150</td>
<td>-26</td>
<td>8</td>
<td>-1</td>
<td>514.5374</td>
<td>60</td>
<td>-43</td>
<td>22</td>
<td>1</td>
<td>500.18012</td>
</tr>
<tr>
<td>1</td>
<td>515.92527</td>
<td>60</td>
<td>6</td>
<td>8</td>
<td>0</td>
<td>514.5615</td>
<td>60</td>
<td>19</td>
<td>22</td>
<td>1</td>
<td>500.18549</td>
</tr>
<tr>
<td>2</td>
<td>515.29370</td>
<td>150</td>
<td>41</td>
<td>8</td>
<td>1</td>
<td>514.5663</td>
<td>100</td>
<td>7</td>
<td>21</td>
<td>0</td>
<td>500.09162</td>
</tr>
<tr>
<td>3</td>
<td>515.92685</td>
<td>150</td>
<td>41</td>
<td>8</td>
<td>1</td>
<td>514.5678</td>
<td>100</td>
<td>-7</td>
<td>21</td>
<td>0</td>
<td>500.09102</td>
</tr>
<tr>
<td>4</td>
<td>515.29370</td>
<td>150</td>
<td>41</td>
<td>8</td>
<td>1</td>
<td>514.5663</td>
<td>100</td>
<td>-32</td>
<td>21</td>
<td>1</td>
<td>500.18549</td>
</tr>
<tr>
<td>5</td>
<td>515.92527</td>
<td>60</td>
<td>6</td>
<td>8</td>
<td>0</td>
<td>514.5615</td>
<td>60</td>
<td>19</td>
<td>22</td>
<td>1</td>
<td>500.18012</td>
</tr>
<tr>
<td>6</td>
<td>515.29370</td>
<td>150</td>
<td>41</td>
<td>8</td>
<td>1</td>
<td>514.5663</td>
<td>100</td>
<td>-32</td>
<td>21</td>
<td>1</td>
<td>500.18549</td>
</tr>
<tr>
<td>7</td>
<td>515.92527</td>
<td>60</td>
<td>6</td>
<td>8</td>
<td>0</td>
<td>514.5615</td>
<td>60</td>
<td>19</td>
<td>22</td>
<td>1</td>
<td>500.18012</td>
</tr>
<tr>
<td>8</td>
<td>515.29370</td>
<td>150</td>
<td>41</td>
<td>8</td>
<td>1</td>
<td>514.5663</td>
<td>100</td>
<td>-32</td>
<td>21</td>
<td>1</td>
<td>500.18549</td>
</tr>
<tr>
<td>9</td>
<td>515.92527</td>
<td>60</td>
<td>6</td>
<td>8</td>
<td>0</td>
<td>514.5615</td>
<td>60</td>
<td>19</td>
<td>22</td>
<td>1</td>
<td>500.18012</td>
</tr>
<tr>
<td>10</td>
<td>515.29370</td>
<td>150</td>
<td>41</td>
<td>8</td>
<td>1</td>
<td>514.5663</td>
<td>100</td>
<td>-32</td>
<td>21</td>
<td>1</td>
<td>500.18549</td>
</tr>
<tr>
<td>11</td>
<td>515.92527</td>
<td>60</td>
<td>6</td>
<td>8</td>
<td>0</td>
<td>514.5615</td>
<td>60</td>
<td>19</td>
<td>22</td>
<td>1</td>
<td>500.18012</td>
</tr>
<tr>
<td>12</td>
<td>515.29370</td>
<td>150</td>
<td>41</td>
<td>8</td>
<td>1</td>
<td>514.5663</td>
<td>100</td>
<td>-32</td>
<td>21</td>
<td>1</td>
<td>500.18549</td>
</tr>
<tr>
<td>13</td>
<td>515.92527</td>
<td>60</td>
<td>6</td>
<td>8</td>
<td>0</td>
<td>514.5615</td>
<td>60</td>
<td>19</td>
<td>22</td>
<td>1</td>
<td>500.18012</td>
</tr>
<tr>
<td>14</td>
<td>515.29370</td>
<td>150</td>
<td>41</td>
<td>8</td>
<td>1</td>
<td>514.5663</td>
<td>100</td>
<td>-32</td>
<td>21</td>
<td>1</td>
<td>500.18549</td>
</tr>
<tr>
<td>15</td>
<td>515.92527</td>
<td>60</td>
<td>6</td>
<td>8</td>
<td>0</td>
<td>514.5615</td>
<td>60</td>
<td>19</td>
<td>22</td>
<td>1</td>
<td>500.18012</td>
</tr>
<tr>
<td>16</td>
<td>515.29370</td>
<td>150</td>
<td>41</td>
<td>8</td>
<td>1</td>
<td>514.5663</td>
<td>100</td>
<td>-32</td>
<td>21</td>
<td>1</td>
<td>500.18549</td>
</tr>
<tr>
<td>17</td>
<td>515.92527</td>
<td>60</td>
<td>6</td>
<td>8</td>
<td>0</td>
<td>514.5615</td>
<td>60</td>
<td>19</td>
<td>22</td>
<td>1</td>
<td>500.18012</td>
</tr>
<tr>
<td>18</td>
<td>515.29370</td>
<td>150</td>
<td>41</td>
<td>8</td>
<td>1</td>
<td>514.5663</td>
<td>100</td>
<td>-32</td>
<td>21</td>
<td>1</td>
<td>500.18549</td>
</tr>
<tr>
<td>19</td>
<td>515.92527</td>
<td>60</td>
<td>6</td>
<td>8</td>
<td>0</td>
<td>514.5615</td>
<td>60</td>
<td>19</td>
<td>22</td>
<td>1</td>
<td>500.18012</td>
</tr>
<tr>
<td>20</td>
<td>515.29370</td>
<td>150</td>
<td>41</td>
<td>8</td>
<td>1</td>
<td>514.5663</td>
<td>100</td>
<td>-32</td>
<td>21</td>
<td>1</td>
<td>500.18549</td>
</tr>
</tbody>
</table>

\[ F_{12} = A'_{\text{eff}} / \rho (1 - \rho) \]

\[ (34) \]
using the effective value $A^2_{\text{eff}}$ defined below. In keeping with the use of the superscript $\beta$ defined in Section IV of Ref. (4), the height of the potential obtained in this way is denoted $V_{\beta}$. The value of $\beta$ in Eq. (34) and throughout the analysis is that for the ground state.

The expectation value of $H_{\beta}$, as defined in Eq. (32) and calculated in Representation (20) can also be expanded in a series of form (32). Although the coefficients

<table>
<thead>
<tr>
<th>$\nu$</th>
<th>$\sigma^2$</th>
<th>$v_{\text{obs}}$</th>
<th>$\epsilon$</th>
<th>$\delta$</th>
<th>$\nu$</th>
<th>$\sigma^2$</th>
<th>$v_{\text{obs}}$</th>
<th>$\epsilon$</th>
<th>$\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>1</td>
<td>501.797636</td>
<td>80</td>
<td>68</td>
<td>1</td>
<td>494.79159</td>
<td>80</td>
<td>63</td>
<td>12</td>
</tr>
<tr>
<td>17</td>
<td>1</td>
<td>500.707888</td>
<td>80</td>
<td>68</td>
<td>1</td>
<td>494.79164</td>
<td>80</td>
<td>63</td>
<td>12</td>
</tr>
<tr>
<td>17</td>
<td>1</td>
<td>500.707888</td>
<td>80</td>
<td>68</td>
<td>1</td>
<td>494.79164</td>
<td>80</td>
<td>63</td>
<td>12</td>
</tr>
<tr>
<td>17</td>
<td>1</td>
<td>500.707888</td>
<td>80</td>
<td>68</td>
<td>1</td>
<td>494.79164</td>
<td>80</td>
<td>63</td>
<td>12</td>
</tr>
<tr>
<td>17</td>
<td>1</td>
<td>500.707888</td>
<td>80</td>
<td>68</td>
<td>1</td>
<td>494.79164</td>
<td>80</td>
<td>63</td>
<td>12</td>
</tr>
<tr>
<td>17</td>
<td>1</td>
<td>500.707888</td>
<td>80</td>
<td>68</td>
<td>1</td>
<td>494.79164</td>
<td>80</td>
<td>63</td>
<td>12</td>
</tr>
<tr>
<td>17</td>
<td>1</td>
<td>500.707888</td>
<td>80</td>
<td>68</td>
<td>1</td>
<td>494.79164</td>
<td>80</td>
<td>63</td>
<td>12</td>
</tr>
<tr>
<td>17</td>
<td>1</td>
<td>500.707888</td>
<td>80</td>
<td>68</td>
<td>1</td>
<td>494.79164</td>
<td>80</td>
<td>63</td>
<td>12</td>
</tr>
<tr>
<td>17</td>
<td>1</td>
<td>500.707888</td>
<td>80</td>
<td>68</td>
<td>1</td>
<td>494.79164</td>
<td>80</td>
<td>63</td>
<td>12</td>
</tr>
<tr>
<td>17</td>
<td>1</td>
<td>500.707888</td>
<td>80</td>
<td>68</td>
<td>1</td>
<td>494.79164</td>
<td>80</td>
<td>63</td>
<td>12</td>
</tr>
<tr>
<td>17</td>
<td>1</td>
<td>500.707888</td>
<td>80</td>
<td>68</td>
<td>1</td>
<td>494.79164</td>
<td>80</td>
<td>63</td>
<td>12</td>
</tr>
<tr>
<td>17</td>
<td>1</td>
<td>500.707888</td>
<td>80</td>
<td>68</td>
<td>1</td>
<td>494.79164</td>
<td>80</td>
<td>63</td>
<td>12</td>
</tr>
<tr>
<td>17</td>
<td>1</td>
<td>500.707888</td>
<td>80</td>
<td>68</td>
<td>1</td>
<td>494.79164</td>
<td>80</td>
<td>63</td>
<td>12</td>
</tr>
</tbody>
</table>
now depend on the three coupling constants in Eq. (3c), these coefficients cannot be separated from the $\delta_0$ of Eq. (32) with data involving only $G_6 = 0$. Thus $F_{12,m}$, $D_{12,m}$, and $V_{12,6}$ were all fixed at zero and their effect absorbed into the eigenvalues of $H_{12}$, i.e. into $\tilde{V}$. In general, the rotational constants $A_{12}$ and $B_{12}$ will appear to depend on $\delta_0$ and through expressions parallel to Eq. (15) of Ref. (4). However, with the current data

<table>
<thead>
<tr>
<th>$\iota (\delta_0 = 0)$ BAND OF CH$_3$SiH$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TABLE III—Continued</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$\iota^*$</th>
<th>$\iota^*$</th>
<th>$\iota^*$</th>
<th>$\iota^*$</th>
<th>$\iota^*$</th>
<th>$\iota^*$</th>
<th>$\iota^*$</th>
<th>$\iota^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>12</td>
<td>13</td>
<td>14</td>
<td>15</td>
<td>16</td>
<td>17</td>
<td>18</td>
</tr>
<tr>
<td>$\iota_1$</td>
<td>$\iota_2$</td>
<td>$\iota_3$</td>
<td>$\iota_4$</td>
<td>$\iota_5$</td>
<td>$\iota_6$</td>
<td>$\iota_7$</td>
<td>$\iota_8$</td>
</tr>
<tr>
<td>$\tilde{V}$</td>
<td>$\tilde{V}$</td>
<td>$\tilde{V}$</td>
<td>$\tilde{V}$</td>
<td>$\tilde{V}$</td>
<td>$\tilde{V}$</td>
<td>$\tilde{V}$</td>
<td>$\tilde{V}$</td>
</tr>
</tbody>
</table>

Thus $F_{12,m}$, $D_{12,m}$, and $V_{12,6}$ were all fixed at zero and their effect absorbed into the eigenvalues of $H_{12}$. I.e. into $\tilde{V}$. In general, the rotational constants $A_{12}$ and $B_{12}$ will appear to depend on $\delta_0$ and through expressions parallel to Eq. (15) of Ref. (4). However, with the current data

Now depend on the three coupling constants in Eq. (3c), these coefficients cannot be separated from the $\delta_0$ of Eq. (32) with data involving only $\delta_0 = 0$. Thus $F_{12,m}$, $D_{12,m}$, and $V_{12,6}$ were all fixed at zero and their effect absorbed into the eigenvalues of $H_{12}$, i.e. into $\tilde{V}$. In general, the rotational constants $A_{12}$ and $B_{12}$ will appear to depend on $\delta_0$ and through expressions parallel to Eq. (15) of Ref. (4). However, with the current data
set, this dependence cannot be detected. All the constants in $H_{12,RT}^{(1)}$ in Eq. (2) were fixed at zero. The resulting effective rotational constants for ($v_2 = 1$) then become to first order

$$A_{ij}^{\text{eff}} = A_{ij} - D_{j,i} \langle p \rangle_{0} + F_{i,j} \frac{1}{2} (1 - \cos 3\alpha) \left(\begin{array}{c}
\end{array}\right)_0,$$

(35a)
Each barred matrix element is the unweighted average over $\sigma$ for $\bar{\nu}_k = 0 = K = 0$ of the associated operator. See Eqs. (18) and (28) of Ref. (4). The fitting parameters used were $\Delta A_E = [A_{\text{eff}}^E - A_0]$ and $\Delta B_{\text{eff}} = [B_{\text{eff}}^E - B_0]$. The values obtained for $\Delta A_{\text{eff}}^E$ and $\Delta B_{\text{eff}}^E$ are:

$$
B_{\text{eff}}^E = B_{12} - D_{12,m} \langle p^2 \rangle + F_{12,3,3} \left( \frac{1}{2} (1 - \cos 3\alpha) \right).
$$

(35b)
ABPT included contributions both from the true changes in the rotational constants and from the distortion constants in Eq. (35). AD is defined in a similar manner. Both $D_{12,J}$ and $D_{12,K}$ were set equal to their ground state counterparts. With this "minimal model," it was possible to fit the global data set to within experimental error. The best fit parameters and their uncertainties are listed in Table I. The final $\chi^2$ was 562 for 2011 data points and 33 parameters. The observed and calculated frequencies for the five microwave lines with \( v_{12} = 1 \) and 1479 vibrational transitions \( v_{12} = 1 \) are compared in Table III. The other components of the data set as described in Ref. (7) and outlined here in Section I contain 527 frequencies within the ground vibrational state. These components fit just as well with the current two-band analysis as they did with the earlier one-band treatment. The parameters characterizing this one-band analysis are listed in Table I for comparison.

V. THE (r-SPLITTINGS

With the current best fit model, it is now possible to explain two interesting properties of the \( r \)-splittings within the various multiplets \( (r_{12} = 1, r_{12} = 1^+, r_{12} = 0, r_{12} = 1, r_{12} = 1) \). Here these two properties will be termed (a)
the anomalous variation with J and (b) the anomalous variation with $G = (K - I)$. The former is illustrated in Fig. 6. In Fig. 6a, the multiplet $^pP_8(8)$ is shown. As is well known (19), the upper level in a $^pP$ branch with $J' = K''$ cannot be Coriolis perturbed because the perturbing level would have $J < K$. Thus this multiplet is unperturbed; the $(\sigma = 0)$ component is the high frequency number. In Fig. 6b, the multiplet $^pP_8(11)$ is shown. The $(\sigma = +1)$ and $(\sigma = -1)$ components again form an unresolved doublet; however, the $(\sigma = 0)$ component is now on the low frequency side.

The explanation for their behavior can be seen in Fig. 1, even though this figure illustrates $Q$-branch transitions. For $\sigma = +1$, the vibrational level $(v_{12} = 1, l = -1; J, \bar{v}_6 = 0, K = 7, \nu)$ is $\sim 45 \text{ cm}^{-1}$ above its closest partner $(0, 0, J, 3, 8, \sigma)$ for Coriolis perturbation. The $(\sigma = +1)$ vibrational level is pushed up, but the effect is small. A similar statement can be made for the $(\sigma = -1)$ component. However, for $(\sigma = 0)$, the vibrational level $(1, -1; J, 0, 7, \sigma)$ is less than $2 \text{ cm}^{-1}$ below its closest partner $(0, 0; J, 3, 8, \sigma)$. The resulting Coriolis shift moves the vibrational level from the dashed position in Fig. 1 downward by $\sim 700 \text{ MHz}$, thereby shifting $^pP_8(11)$ from the high-frequency side of the multiplet to the low.

The effect of this Coriolis perturbation is also seen very clearly in Fig. 5, which shows the subbranches $^pQ_5$ for all three $\sigma$. The subbranches $^pQ_4$ and $^pQ_5$ form an unresolved envelope. However, for $(J' \geq 10)$, the Coriolis effect shifts the lines...
FIG. 6. Two sections of the \( ^pP \) branch deconvoluted to a resolution \( \sim 0.0022 \) cm\(^{-1} \) showing the effect of the Coriolis perturbation on the \( \sigma \)-splittings. Each line is labeled with the lower state values of \( J' ', K' ', \) and \( \sigma ' \). The features labeled \( A \) are high \( J \)-lines in the \( ^pP_0 \) subbranch. The horizontal scales for (a) and (b) have the same magnification. The blended lines assigned to \((K' ' = 3, \sigma ' = 0 \text{ and } -1)\) can be used as a reference in comparing the two sections. The triplet \( ^pP_3(8) \) shown in (a) has no Coriolis perturbation; in this case, the \((\sigma ' = 0)\) component is the high-frequency member. The same triplet in (b) shows a significant Coriolis perturbation on the \((\sigma ' = 0)\) component, which is now the low-frequency member. By contrast, the splitting between the \((K' ' = 3, \sigma ' = 0 \text{ and } -1)\) reference and the line for \((K' ' = 8, \sigma ' = -1)\) is almost the same in (b) as in (a).

\( ^pQ_8^G(J' ') \) out of this envelope. The variation of the shift with \( J'' \) as seen in Fig. 5 follows that expected from a Coriolis-like interaction; the model fits these lines to better than 0.0008 cm\(^{-1} \) (see Table III).

It was observed earlier by both microwave measurements (4) and torsional studies (6) that within the \( \sigma \) multiplet \((0, 0; J, 3, K, \sigma)\) the \( \sigma \)-component of highest energy is strongly perturbed while the other components are not. These levels were labelled H for high, as distinct from M for medium and L for low. A family structure was shown to exist (6), with all members of the same family having the same L, M, H label. These earlier observations were confirmed here. In the \( \sigma \)-multiplet \( ^pP_K(J + 1) \), it is always the Coriolis partner of the H member of \((0, 0; J, 3, K, \sigma)\) that shows the largest Coriolis shift. This follows directly from the fact that, for this particular \( \sigma \), the energy separation between interacting levels is smallest. The magnitudes of the corresponding Coriolis matrix elements are not strongly dependent on \( \sigma \). Among the levels \((1, -1; J, 0, K = K - 1, \sigma)\) with large Coriolis shifts, eight different \((K, \sigma)\) cases are near-resonant or resonant. These fall into only two of the nine possible families: \((K, \sigma) = (0, 0), (3, +1), (6 - 1), (9, 0)\) are in one and \((2, 1), (5 - 1), (8, 0)\) and \((11, 1)\) are in the other. See Table V of Ref. (6). Note that the \( K \) used in labelling the families is that for \( v_{12} = 0 \).

In the "normal" ordering of the levels, \((1, -1; J, 0, K = K - 1, \sigma)\) falls above its Coriolis partner \((0, 0; J, 3, K, \sigma)\). However, for low \( J \), the order is inverted for four \((K, \sigma)\) cases: \((6, -1), (9, 0), (8, 0)\) and \((11, 1)\). This inversion is important because it changes the sign of the Coriolis shift. The \((6, -1)\) case is unusual in two respects.
First, the two interacting levels change order above \( J = 16 \), so that for \( J \geq 17 \), the order is no longer inverted. For values of \( J \) near the crossover, the Coriolis matrix element is larger than the difference in the unperturbed energies. Second, for low \( J \), the \((6, -1)\) case is inverted only when the off-diagonal elements of the operator \( pl' \) in Eq. (3a) are taken into account. Thus without the elements labelled \( t \) in Fig. 2, it is impossible to account for the very important subbranch \( ^tQ_6 \).

As the first step in discussing the anomalous variation of the \( \sigma \)-splittings with \( G \), it is convenient to introduce a simple model for the \( \sigma \)-dependent terms in the frequencies. If all the off-diagonal matrix elements in Fig. 2 are set to zero, then for \( (\Delta K = \pm 1) \) these terms can be approximated by

\[
\nu_{\pm 1} (l = \pm 1; K, \sigma) = \{ \langle H^{(0)}_{12, T} \rangle_{\omega_k=0, \pm 1, \sigma} - \langle H^{(0)}_{g, T} \rangle_{\omega_k=0, \sigma} \} \pm 2 (A_{l, T}^{m}) \langle p \rangle_{\omega_k=0, \pm 1, \sigma}. \tag{36}
\]

The subscript on \( \nu \) indicates the value of \( \Delta K \). The \( J \)-dependence has been omitted because it is small for the low \( J \) region of interest here. Now consider the ordering in frequency of the \( \sigma \)-components of a given \((K, K)\) multiplet. Because \( K \neq K \), the \( \sigma \)-ordering in energy of the \( \langle H^{(0)}_{12, T} \rangle_{0, K, \sigma} \) will in general be different from the \( \sigma \)-ordering of the \( \langle H^{(0)}_{g, T} \rangle_{0, K, \sigma} \). The \( \sigma \)-ordering of the upper levels in the multiplet will be further modified by the term in \( p \) in Eq. (36). Thus the \( \sigma \)-pattern for the upper state energies will be different from that in the ground state in a manner which depends on the molecular parameters and on \((K, K)\). It is expected that, even for cases where the Coriolis effect is negligible, the multiplets for \( {}^pP_K(J) \) and \( {}^tR_K(J) \) should look rather different.

The anomaly lies in the fact that, for the cases where the Coriolis shifts are small, the multiplets \( {}^pP_K(J) \) and \( {}^tR_K(J) \) are almost identical. The ordering of the \( \sigma \)-components is always the same and the spacings are very similar. This is illustrated in Fig. 4 which shows \( {}^tR_2(16) \) and Fig. 5 which shows \( {}^pP_2(17) \); the order of the components is the same and the splittings differ by less than 25%. At low \( J \) where the Coriolis effect on the \( (\sigma = 1) \) component in \( {}^pP_2 \) is smaller, the splittings agree to a few percent. This anomaly is further illustrated in Fig. 1. If the Coriolis effect is turned off, the level \((1, -1; 11, 0, 7, 0)\) moves to the dashed position and the other splittings do not change appreciably. On the MHz scale of Fig. 1, the upper state \( \sigma \)-pattern for \((l = -1) \) and \((l = +1) \) are then identical. Furthermore, to the accuracy of the figure, both patterns differ from that in the ground state by only a scale factor. The data make it clear that, in spite of Eq. (36), the torsional splittings depend only on \( G = (K - l) \).

The apparent contradiction is resolved by recognizing the importance of the matrix elements of \( pl' \) off-diagonal in \( \tilde{\nu}_5 \). Equation (36) does not take these into account. When they are added numerically, the predicted patterns agree with those observed.

To understand the reason for this unexpected result, the following Hamiltonian is considered in the PAM,

\[
(H^{(0)}_{12, TRV})' = F_{12}(p')^2 + V_{12,3} \frac{1}{2} (1 - \cos 3\alpha') + B_{12}(J')^2 + (A_{12,F} - B_{12})(J'_z)^2 - 2A_{12,F}J'_z p' + 2(A_{l, T}^{m}) p' l', \tag{37}
\]

where \( A_{12,F} \) is the \((\nu_{12} = 1) \) rotational constant of the silyl frame about the symmetry axis. This is the PAM counterpart of \( H^{(0)}_{12, T} \) plus \( H^{(0)}_{12, R} \) from Eq. (2) together with
From Eq. (6). For \( v_{12} = 0 \), the last term in Eq. (37) is absent; see Table I of Ref. (16). The usual PAM-to-IAM transformation for \( v_{12} = 0 \) replaces \( p' \) by \( [p + \tilde{p} J_z] \), eliminates the term in \( J_z p' \), and introduces the \( K \)-dependence into the eigenvalues of \( H_{x,1}^{(0)} \). For \( v_{12} = 1 \), if \( (A_{12}^{(1)}) = A_{12,F} \), then the last two terms in Eq. (37) can be combined to form

\[
H'_{plz} = -2A_{12,F} (J_z - l') p'.
\]  

A new PAM-to-IAM transformation can then be made which replaces \( p' \) by \( [p + \tilde{p} (J_z - l)] \), eliminates the term in \( (J_z - l') p' \), and introduces into the eigenvalues of the torsional part of \( H_{12,TRV}^{(0)} \) a dependence on \( G = (K - l) \) which is of the same form as the dependence on \( K \) in the ground state. The form of the \( \sigma \)-multiplets then leads to the conclusion that \( (A_{12}^{(1)}) \) must be very close to \( A_{12,F} \). From Table I, \( A_{12,F}^{(1)} = A_{12,F}^{(1)}[1 - \rho] = 86,985(1) \text{ MHz} \), while \( (A_{12}^{(1)}) = 86,709(351) \text{ MHz} \). The two results are in excellent agreement, thus providing strong supporting evidence for the explanation presented. The surprising result that \( (A_{12}^{(1)} = A_{12,F} \) within experimental error will be discussed briefly in Section VI.

VI. DISCUSSION

The model of the Coriolis interaction characterized in Table I reproduces the data very well. Nonetheless, a search was made for alternatives. In the derivation of Eq. (10) for the Coriolis Hamiltonian \( H_{22}^{(0)} \), a specific physical mechanism formed the starting point. However, symmetry arguments alone would lead to an interaction operator of the same form, but with \( (B_{5,6,0}^{(m)}) \) replaced by two independent constants, one for the terms in \( [p + \tilde{p} J_z] \) and one for the terms in \( \sin 3\alpha \). The two constants here will be denoted, respectively, \( (B_{5,6,0}^{(m)}) \) and \( (B_{5,6,0}^{(3)}) \). The fit with the modified model was equivalent in quality to the original. It yielded \( (B_{5,6,0}^{(m)}) = (403 \pm 31) \text{ MHz} \) and \( (B_{5,6,0}^{(3)}) = (435 \pm 6) \text{ MHz} \). Within the errors, these two equal each other and equal the value of \( (B_{5,6,0}^{(1)}) \) as given in Table I. This agreement provides an upper limit \( \sim 30 \text{ MHz} \) to the contributions of other mechanisms to the effective Coriolis coupling constant \( (B_{5,6,0}^{(1)}) \).

The fit with the two independent Coriolis constants was carried out for a second reason. As was mentioned in Section II.3, there is an ambiguity in the definition of \( \lambda_1 \) in Eq. (10c) that follows from the ambiguity in the definition of the reduced barrier height to be used in matrix elements off-diagonal in \( v_{12} \). The uncertainty in \( \lambda_1 \) from this source is \( \sim 5\% \). Unfortunately, the error in the ratio \( (B_{5,6,0}^{(m)}) / (B_{5,6,0}^{(3)}) \) is too large to cast any light on this problem. A microwave study of both \( (v_{12} = 0, \nu_6 = 3) \) and \( (v_{12} = 1; \nu_6 = 0) \) is underway. With the additional data, it may be possible to clarify this issue.

The quartic operator \( H_{22}^{(0)} \) in Eq. (17b) is characterized by two independent parameters: \( \tilde{P}_{5,6}^{(m)} \) for the terms in \( [p + \tilde{p} J_z] \) and \( \tilde{Q}_{6,0}^{(m)} \) for the terms in \( \sin 3\alpha \). This operator acts here as a higher-order Coriolis effect. If both \( \tilde{P}_{5,6}^{(m)} \) and \( \tilde{Q}_{6,0}^{(m)} \) are fixed at zero, then the inverted levels with \( K' \geq 8 \) show systematic differences \( \delta \) between observed and calculated frequencies that indicate the coupling between \( (v_{12} = 1, \nu_6 = 0) \) and \( (v_{12} = 0, \nu_6 = 3) \) is not being treated properly. The introduction of \( \tilde{Q}_{6,0}^{(m)} \) into the fit removes these systematic differences. The constant \( \tilde{P}_{5,6}^{(m)} \) is not capable of fulfilling this same function. A second higher-order Coriolis operator was constructed by symmetrizing...
\( \nu_{12} = 1 \leftarrow 0 \) BAND OF CH\textsubscript{3}SiH\textsubscript{3},

the product of \( \hat{H}_{2}^{\nu_{12}} \) and \( J_{2}^{\nu_{12}} \). The associated constant could not act as a replacement for \( \hat{Q}_{6a}^{\nu_{12}} \). In spite of these tests, it must be recognized that the term in \( \hat{Q}_{6a}^{\nu_{12}} \) absorbs many higher-order perturbations coupling the two stacks of torsional levels.

The absolute signs of \( (B_{12}^{\nu_{12}}) \) and \( \hat{Q}_{6a}^{\nu_{12}} \) could not be determined because the eigenvalues of the matrix illustrated in Fig. 2 were sensitive only to the square of the off-diagonal element \( C \). However, it was possible to establish that the two constants have the same sign.

A comparison is provided in Table I between the current best fit parameters and those determined earlier (7) in a one-band analysis of the part of the current data set with \( \nu_{12} = 0 \) in both upper and lower states. For each parameter that entered the earlier work, the change noted in Table I arises primarily from the different treatment of the nonresonant Coriolis perturbation. In the analysis of the ground state data in Ref. (7), this perturbation was absorbed into the \( \nu_{12} = 0 \) parameters, whereas here this perturbation is treated explicitly. For each operator with a \( J^{2} \) dependence, the change is many times the statistical error. The most striking change is in \( F_{n}G \) which goes from \(-5.32 \text{ MHz}\) in Ref. (7) to \(+0.64 \text{ MHz}\) here. In this particular case, the original value was almost entirely due to the Coriolis interaction between \( \nu_{12} = 0 \) and \( \nu_{12} = 1 \).

By using the best fit characterized in Table I, several interesting additional parameters can be evaluated. First, from Eq. (33), it is found that the band origin

\[ \tilde{v}_{12} = 519.890(36) \text{ cm}^{-1}. \]  

This is in marked disagreement with two values reported earlier on the basis of low-resolution spectra, namely 545 cm\textsuperscript{-1} in Ref. (24) and 540 cm\textsuperscript{-1} in Ref. (25). No explanation can be offered for the apparent difficulty in the interpretation of the older spectra.

Second, from Eq. (35), it is possible to calculate \( \tilde{A}_{12} \) and \( \tilde{B}_{12} \), provided it is assumed that \( D_{12,Km} \) and \( F_{12,K3} \) equal their \( \nu_{12} = 0 \) counterparts. It is then possible to obtain \( \Delta A_{12} \equiv (\tilde{A}_{12} - \tilde{A}_{0}) \) and \( \Delta B_{12} \equiv (\tilde{B}_{12} - \tilde{B}_{0}) \), i.e., to find the changes in the rotational constants that fit the usual definitions (19). It was determined that

\[ \Delta A_{12} = 188.53 \text{ MHz}; \]  
\[ \Delta B_{12} = -2.54 \text{ MHz}. \]

Clearly \( D_{12,Km} \) and \( F_{12,K3} \) contribute a large fraction of \( \Delta B_{12}^{\text{eff}} \), but only a small fraction of \( \Delta A_{12}^{\text{eff}} \).

Third, several Coriolis constants can be determined. Since equilibrium values are not available to separate properly (26) each rotational constant from its \( \xi \), the ground state rotational constant will be used. It then follows from Table I that

\[ \tilde{\xi}_{12} = 0.2434105(20). \]

This is to be compared with the result of 0.24 from a low-resolution study (25) and the force-field value of 0.32 (27). Further it can be shown from the work of Hirota (8) that

\[ \xi_{F} + \xi_{T} = \tilde{\xi}_{12}; \]  
\[ A_{F}\xi_{F} - A_{T}\xi_{T} = (A_{F}^{\nu_{12}}). \]
The subscripts T and F are represented by 1 and 2, respectively, in Ref. (8). $\xi_T$ is the Coriolis constant for the top and $A_T$ is the rotational constant of the top about the symmetry axis. $\xi_F$ and $A_F$ are the corresponding quantities for the frame. Since $(A_{\xi}^T)_{12}$ is equal to $A_F$ to within the experimental error of 0.4%, Eq. (42b) can be approximated by

$$\xi_F = [(1 - \rho)/\rho] \xi_T = 1.$$  \hspace{1cm} (42c)

Eq. (42) can then be solved for $\xi_F$ and $\xi_T$:

$$\xi_F = 0.5098(15) \hspace{1cm} (43a)$$

$$\xi_T = -0.2664(15). \hspace{1cm} (43b)$$

The errors quoted include only the contribution from the 0.4% referred to above. It is plausible (8) that $|\xi_F| > |\xi_T|$ because the silyl rock is localized primarily in the frame. In fact, Eq. (42c) alone has the appealing solution $\xi_F = 1$, $\xi_T = 0$. However, if this were correct, then Eq. (42a) would have to be modified substantially.

The Coriolis constant $\xi_{\xi,12}$ in Eq. (8) for the off-diagonal operator $(B_{\xi,\xi}^T)_{12}$ conforms to the standard definitions of Ref. (19). From Eq. (10b), it has been found that

$$|B_{\xi,\xi}^T| = 2569 \pm 67 \text{ MHz}; \hspace{1cm} (44a)$$

$$|\xi_{\xi,12}| = 0.234 \pm 0.006. \hspace{1cm} (44b)$$

In this determination, the quantum $\nu_{12}$ was taken from Eq. (39). The quantum $\nu_6$ for the highly anharmonic torsion was approximated by the value (190 cm$^{-1}$) calculated here for the origin of the torsional fundamental. The mean reduced barrier height $s_m = 33.711$. The errors quoted in Eq. (44) reflect only the ambiguity in $s_m$ discussed above. In Eq. (18a), the quartic distortion constant $Q_{6,a}$ conforms to the definitions of Ref. (19). It was determined that

$$|Q_{6,a}| = (24.8 \pm 1.1) \text{ MHz}. \hspace{1cm} (45)$$

The ratio of $Q_{6,a}$ to $(B_{\xi,\xi}^T)_{12}$ is $\sim 1/100$, which is a little large, but not unreasonably so, since the operators differ by only one degree in the components of $J$.

Finally, the barrier height is higher in ($\nu_{12} = 1$) than in ($\nu_{12} = 0$) by $(67.64 \pm 0.43)$ cm$^{-1}$. This increase, of course, includes contributions from the fact that several pure torsional parameters were fixed at zero in ($\nu_{12} = 1$). This relatively large change of $\sim 10\%$ calls into question the assumption that vibration and torsion can be decoupled.

**VII. CONCLUSION**

The effective torsion–vibration–rotation Hamiltonian has been developed for a polar symmetric rotor with internal rotation in a degenerate fundamental vibrational state. The leading terms have been taken into account for matrix elements with selection rules $\Delta \nu_{12} = 0, \pm 1$ and $\Delta \nu_6$ arbitrary. The most important off-diagonal operators arise from the Coriolis interaction between the silyl rocking and the torsion. These include both a $z$-type interaction proportional to $p \cdot l$ and an $xy$-type interaction involving $(J_x, J_y)$ and $p$ or $\sin 3\alpha$. The model has been tested with an extensive data set involving almost 1500 lines in the fundamental $\nu_{12} = 1 \leftrightarrow 0$ measured to an accuracy $\sim 0.0005$ cm$^{-1}$ with Fourier transform spectroscopy; the data set also includes over 500 earlier frequencies measured with molecular beam, microwave, and infrared techniques. Fur-
ther work is underway to study the pure torsional band $v_6 = 3 \leftrightarrow 1$, the microwave spectrum in excited torsional and vibrational states, and the vibrational hot band $v_6 + v_{12} - v_6$.

ACKNOWLEDGMENTS

The authors thank Dr. J. W. C. Johns for his generous hospitality in making the BOMEM interferometer available and Dr. J. K. G. Watson for many fruitful discussions on vibration–rotation interactions. The authors are particularly indebted to Dr. H. Jagannath for his assistance with the earlier phases of the identification process. The authors express their appreciation to the Natural Sciences and Engineering Research Council of Canada for its support.

Note added in proof: More accurate values of the calibration frequencies can be found in G. Guelachvili and K. N. Rao, "Handbook of Infrared Standards", Academic Press, New York, 1986. However, the differences from the original work are not significant at the level of accuracy of the present experiment.

RECEIVED: March 27, 1989

REFERENCES

17. J. T. Hougouen, W. L. Meerts, and I. Ozier, manuscript in preparation.