

Microwave and sub-mmwave study of CH_3SiH_3 including the perturbation-allowed torsion–vibration difference band $(\nu_{12} = 0, \nu_6 = 3) \leftrightarrow (\nu_{12} = 1, \nu_6 = 0)^{\star}$

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Abstract

The vibration–torsion–rotation Hamiltonian in CH_3SiH_3 has been investigated using Fourier transform microwave methods and tunable sideband far-infrared spectroscopy. Four different studies have been carried out. First, the Q -branch of the torsion–vibration difference band $(\nu_{12} = 0, \nu_6 = 3) \leftrightarrow (\nu_{12} = 1, \nu_6 = 0)$ has been measured between 17.8 and 26.6 GHz. When three quanta of the torsional mode ν_6 are excited in the ground vibrational state (gs) for $(\sigma = -1)$ torsional sublevels with $K = 6$, these transitions become allowed through resonant Coriolis-like coupling to the lowest lying degenerate mode ν_{12} with no quanta of ν_6 excited. Second, direct l -doubling transitions in the state $(\nu_{12} = 1, \nu_6 = 0)$ have been observed between 8.3 and 17.5 GHz for both torsional sublevels $\sigma = 0$ and $\sigma = \pm 1$. In the limit that the intervibrational interactions vanish, the σ -splitting between lines of the same J would be difficult to resolve, but frequency differences of more than 1 GHz due to these interactions have been determined. Third, the $(J = 1 \leftarrow 0)$ spectrum just below 22 GHz has been re-measured with higher resolution for $0 \leq \nu_6 \leq 4$ in the gs and for $(\nu_6 = 0)$ in ν_{12} . Finally, the $(J = 45 \leftarrow 44)$ spectrum near 1 THz has been obtained for $0 \leq \nu_6 \leq 2$ in the gs. A global data set of 3423 frequencies has been formed by merging the present 123 measurements with the data set used recently in the simultaneous analysis of the ν_{12} and ν_5 bands by Schroderus et al. [J. Chem Phys. 115 (2001) 1392]. By refining the $(\text{gs}/\nu_{12}/\nu_5)$ Hamiltonian developed in this earlier work in which the torsional motion is grouped with the vibrational degrees of freedom, a good fit to within experimental error has been obtained by varying 45 parameters. A fit of comparable quality has also been obtained using a similar analysis in which the torsional motion is grouped with the rotational degrees of freedom. The values of the molecular constants determined in the two models are compared. © 2004 Elsevier Inc. All rights reserved.

Keywords: Internal rotation; Torsion; Vibration; Methyl silane; Fourier transform microwave; Sub-mmwave; Difference band

1. Introduction

A symmetric top with a single torsional rotor offers an excellent opportunity to study large amplitude motion. One major challenge is to develop a Hamiltonian which

represents the internal motion from the harmonic limit to the free rotor limit. A second major challenge is to determine how the large amplitude torsional motion interacts with the harmonic vibrations. These two questions provide a good deal of the motivation for the current work.

The molecule CH_3SiH_3 has become the prototype for investigating internal rotation in polar symmetric rotors. A large body of experimental data has been accumulated over the years, and has been analyzed recently by Schroderus et al. [1]. Except for minor modifications, this data set is summarized here in Table 1; see

^{*} Supplementary data for this article are available on ScienceDirect (www.sciencedirect.com) and as part of the Ohio State University Molecular Spectroscopy Archives (http://msa.lib.ohio-state.edu/jmsa_hp.htm).

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Table 1
Global data set and its characteristics

| | Selection rules ^a | $(J_{\max}, K_{\max})^b$ | $\epsilon^{c,d}$ | $S^{c,d}$ | N^f | χ^2g | Reference |
|---|--|--------------------------|------------------|-----------|-------|-----------|----------------------|
| 1 | Difference band | (19,5) | 0.010 | 0.0022 | 14 | 1.1 | Table 2 ^h |
| 2 | Direct <i>l</i> -doubling | (26,1) | 0.008 | 0.0039 | 18 | 6.7 | Table 3 ^h |
| 3 | $J = 1 \leftarrow 0$ | (0,0) | 0.010 | 0.0060 | 14 | 5.2 | Table 4 |
| 4 | $J = 45 \leftarrow 44$ | (44,13) | 1.0 | 0.72 | 58 | 22.9 | Table 5 |
| 5 | $v_6 = 2 \leftarrow 0$ | (25,9) | 0.008 | 0.0011 | 313 | 38.8 | [5,6] |
| 6 | $v_6 = 3 \leftarrow 1$ | (25,9) | 0.008 | 0.0029 | 528 | 75.1 | [4] |
| 7 | $v_6 = 5 \leftarrow 0; K = 1, \sigma = -1$ | (25,1) | 0.0006 | 0.00043 | 29 | 14.8 | [1] |
| 8 ⁱ | $v_{12} = 1 \leftarrow 0; \Delta K = l_{12} = \pm 1$ | (25,9) | 0.0005 | 0.00030 | 1279 | 315.8 | [3,4] |
| 9 | $v_5 = 1 \leftarrow 0$ | (25,9) | 0.0006 | 0.00032 | 780 | 168.7 | [1] |
| 10 ^j | $\Delta K = \pm 1, \pm 2; \Delta \sigma = 0, \pm 1$ | (6,1) | 0.015 | 0.0067 | 15 | 4.0 | [2] |
| 11 | $v_6 = 0$ | (15,12) | 0.10 | 0.016 | 82 | 18.6 | [2,7,8] |
| 12 | $v_6 = 1$ | (15,10) | 0.10 | 0.037 | 102 | 13.2 | [7,8] |
| 13 | $v_6 = 2$ | (12,7) | 0.10 | 0.035 | 78 | 9.8 | [7,8] |
| 14 | $v_6 = 3$ | (8,7) | 0.10 | 0.038 | 62 | 21.1 | [7–9] |
| 15 | $v_6 = 4$ | (4,4) | 0.20 | 0.094 | 19 | 10.1 | [7,9] |
| 16 | $v_{12} = 1; l_{12} = \pm 1$ | (8,7) | 0.070 | 0.049 | 32 | 21.1 | [9] |
| Totals for current 45 parameter HB model. See Table 6. | | | | 3423 | 746.9 | | |
| Totals for current 45 parameter FR model. See Table 6. | | | | 3423 | 742.3 | | |
| Totals for 41 parameter HB model of Schroderus et al. [1]. See Table 6. | | | | 3316 | 719.0 | | |

^a Unless otherwise specified, $v_5, v_{12}, l_{12}, v_6, K$, and σ are conserved. In components 1 and 2, $\Delta J = 0$; in components 3, 4, and 11–16, $\Delta J = \pm 1$; in components 5–10, $\Delta J = 0, \pm 1$.

^b Maximum values included in the data set for the quantum numbers of the lower state.

^c A typical experimental uncertainty in a transition frequency.

^d The units are MHz for components 1–4 and 10–16; and cm^{-1} for components 5–9.

^e For each component, this is the standard deviation of the current HB best fit of Table 6.

^f The number of data in each component.

^g For each component, this is the contribution to χ^2 in the current HB best fit of Table 6.

^h See the footnotes in the table cited for further details on the selection rules.

ⁱ Two gs transitions with $v_6 = 3 \leftarrow 0$ are included in this component.

^j For a complete description of the selection rules, see [2,10].

components 5 through 14 and 16. The avoided crossing molecular beam method has been applied to the lowest torsional state ($v_6 = 0$) in the ground vibrational state (gs), and used to determine energy differences between torsional sub-levels with different values of σ and different values of K [2]. Fourier transform infrared spectroscopy has been used to study the lowest-lying perpendicular band v_{12} [3] and the lowest-lying parallel band v_5 [1]. In the process, perturbation-allowed torsional transitions have been measured with ($v_6 = 3 \leftarrow 0$) [3,4] and with ($v_6 = 5 \leftarrow 0$) [1]. Infrared studies have also been made of the first torsional overtone ($v_6 = 2 \leftarrow 0$) [5,6] and its first hot-band ($v_6 = 3 \leftarrow 1$) [4]. Microwave and mm-wave spectroscopy have been used to measure various rotational transitions in the lowest five torsional states of the gs [7–9], and in the ($v_6 = 0$) state of the silyl rock ($v_{12} = 1$) [9].

Considerable progress has been made on the theoretical side. Schroderus et al. [1] were able to get a good fit to within experimental error using a model involving four interacting stacks of torsional levels, one for each of the gs, ($v_5 = 1$), ($v_{12} = 1, l_{12} = +1$), and ($v_{12} = 1, l_{12} = -1$). Here l_{12} is the quantum number for the vibrational angular momentum operator ℓ_{12} . The (gs, v_{12}) interaction arises primarily from the torsion-

mediated Coriolis-like Hamiltonian, and leads to resonant mixing between the gs level ($v_6 = 3$) and the v_{12} level ($v_6 = 0$) for certain values of (l_{12}, J, K, σ) [3]. The (gs, v_5) coupling is dominated by torsion-mediated Fermi-like Hamiltonian, and leads to resonant mixing between the gs level ($v_6 = 5$) and the v_5 level ($v_6 = 0$) for certain values of (K, σ) [1].

However, the depth of the analysis has been limited significantly by the precision of the data, particularly for the higher torsional levels of the gs and the excited vibrational states. It is, of course, for these higher energies that the gs approaches free internal rotation and that the interactions of the torsional motion with the harmonic vibrations become much more important. High resolution infrared data provide a great deal of valuable information, but the experimental error ϵ is typically $\gtrsim 10$ MHz, while microwave/mm-wave methods can achieve values of $\epsilon \sim 10$ kHz or better. The purpose of the present work is to apply Fourier transform microwave (FTMW) spectroscopy to probe the torsion-rotation-vibration energy levels to higher accuracy than has been previously achieved, and to apply tunable sideband far-infrared spectroscopy to extend earlier pure rotational studies up to a much higher values of the rotational quantum number J .

The current work consists of four different studies: see components 1–4 in Table 1. The first measures the energy difference between the resonantly coupled states ($v_5 = 0; v_{12} = 0, l_{12} = 0; J, v_6 = 3, K = 6, \sigma = -1$) and ($v_5 = 0; v_{12} = 1, l_{12} = -1; J, v_6 = 0, K = 5, \sigma = -1$) for a range in J values. The frequency determinations are listed in Table 2. While a FTMW waveguide spectrometer cannot probe vibrational energies directly, it can, in favorable circumstances, measure the difference between vibrational (or torsional–vibrational) energies when these fall at low enough frequency, as is the case here. This provides a very strong constraint on the Hamiltonian, since the two calculated energies, each the order of 500 cm^{-1} above the zero-point state, are required to match the experimental frequency in the 20 GHz range to an accuracy $\sim 10\text{ kHz}$. The second study measures the energy difference in v_{12} between the two l -doublets for $17 \leq J \leq 26$; the frequencies obtained are listed in Table 3. A detailed discussion of the l -doubling states is given in Section II.6 of [3], where the upper/lower members of the l -doublet in the ($v_6 = 0$) level of v_{12} in CH_3SiH_3 are indicated with the quantum number $\tau = +1/-1$. If the interstack coupling is turned off, then the direct l -doubling frequency is independent of σ to excellent approximation. The σ -splitting thus provides an excellent measure of the (gs, v_{12}) coupling in particular. This splitting is over 1 GHz for $J = 22$, and can be measured to $\sim 10\text{ kHz}$ with a FTMW waveguide spectrometer, and so a second severe test of the Hamiltonian is obtained.

In the third study presented here, measurements were made of the ($J = 1 \leftarrow 0$) spectrum; the frequency determinations are listed in Table 4. In the parent isotopomer $\text{CH}_3^{28}\text{SiH}_3$, a FTMW waveguide spectrometer

Table 2
Difference band frequencies^a in $\text{CH}_3^{28}\text{SiH}_3$

| J | ν_{obs} (MHz) | ϵ (kHz) ^b | δ (kHz) ^c |
|-----|--------------------------|-------------------------------|-----------------------------|
| 6 | 19407.052 | 10 | 4.9 |
| 7 | 18988.533 | 10 | -5.5 |
| 8 | 18583.975 | 10 | -2.8 |
| 9 | 18228.958 | 10 | -1.2 |
| 10 | 17965.968 | 5 | -1.0 |
| 11 | 17843.262 | 5 | 1.3 |
| 12 | 17912.067 | 5 | 0.9 |
| 13 | 18221.968 | 10 | 0.0 |
| 14 | 18815.231 | 10 | 0.3 |
| 15 | 19721.810 | 10 | -3.7 |
| 16 | 20956.911 | 10 | -3.2 |
| 17 | 22521.804 | 10 | 3.5 |
| 18 | 24407.148 | 10 | -0.2 |
| 19 | 26597.258 | 20 | 0.8 |

^a Each transition is between the states ($v_5 = 0; v_{12} = 0, l_{12} = 0; J, v_6 = 3, K = 6, \sigma = -1$) and ($v_5 = 0; v_{12} = 1, l_{12} = -1; J, v_6 = 0, K = 5, \sigma = -1$).

^b ϵ is the estimated experimental uncertainty.

^c δ is the observed value minus that calculated from the best HB fit in Table 6.

Table 3
Direct l -doubling frequencies^a in $\text{CH}_3^{28}\text{SiH}_3$

| J | σ | ν_{obs} (MHz) | ϵ (kHz) ^b | δ (kHz) ^b |
|-----|----------|--------------------------|-------------------------------|-----------------------------|
| 17 | 0 | 8314.164 | 5 | 7.3 |
| 18 | 0 | 9281.063 | 10 | 1.3 |
| 18 | ± 1 | 8534.237 | 8 | 2.7 |
| 19 | 0 | 10299.370 | 5 | -1.2 |
| 19 | ± 1 | 9480.276 | 10 | -8.5 |
| 20 | 0 | 11368.782 | 5 | -1.8 |
| 20 | ± 1 | 10475.654 | 12 | -1.0 |
| 21 | 0 | 12488.994 | 5 | -3.7 |
| 21 | ± 1 | 11520.278 | 12 | 4.0 |
| 22 | 0 | 13659.710 | 5 | -1.5 |
| 22 | ± 1 | 12614.065 | 10 | -1.7 |
| 23 | 0 | 14880.625 | 5 | -1.2 |
| 23 | ± 1 | 13756.951 | 10 | -3.6 |
| 24 | 0 | 16151.444 | 5 | -1.4 |
| 24 | ± 1 | 14948.860 | 6 | 3.8 |
| 25 | 0 | 17471.881 | 5 | 4.4 |
| 25 | ± 1 | 16189.692 | 8 | 5.5 |
| 26 | ± 1 | 17479.350 | 8 | -7.4 |

^a Each transition is between the states ($v_5 = 0; v_{12} = 1, \tau = -1; J, v_6 = 0, \sigma$) and ($v_5 = 0; v_{12} = 1, \tau = 1; J, v_6 = 0, \sigma$), where $\tau = +1$ and -1 label the upper and lower l -doubling states, respectively; see Section II.6 of [3].

^b For the definitions of ϵ and δ , see the footnotes of Table 2.

was used to obtain the spectrum for $0 \leq v_6 \leq 4$ in the gs, and for ($v_6 = 0$) in v_{12} . In addition, tentative assignments have been made for ($v_6 = 5$) in the gs, and for ($v_6 = 0$) in v_5 . For ($v_6 = 0$) in the gs, the σ -doublet was partially resolved earlier with a molecular beam electric resonance spectrometer [2]. In the current work, since the σ -splitting was too small to be detected in the waveguide spectrum, this state was re-investigated with the superior resolving power of FTMW cavity spectrometer. Certain anomalies in the cavity spectrum are discussed in the light of what is known about the nuclear hyperfine structure of methyl silane [10]. In almost all cases, these measurements are considerably more accurate than the corresponding earlier determinations [2,7,8,11], and serve to anchor more effectively the low J -end of the constraints on the rotational energy. In the waveguide spectrum, it was possible to identify the gs transitions for $\text{CH}_3^{29}\text{SiH}_3$ in the first four torsional states; these are presented without analysis.

In the final experimental study of the current work, measurements were made of the ($J = 45 \leftarrow 44$) spectrum in the gs of the parent isotopomer for the three lowest torsional states; the frequencies obtained are listed in Table 5. To detect these lines in the 1 THz region, tunable sideband spectroscopic methods were used. The experimental uncertainty ϵ was 1 MHz in this case. However, in spite of this, valuable constraints on the Hamiltonian were obtained, since the highest J for which pure rotational spectra had been previously measured was 15; see Table 1.

A good fit to within experimental error was obtained to the present global data set of 3423 frequencies using

Table 4
Rotational frequencies ($J = 1 \leftarrow 0$) in methyl silane^a

| | v_6 | σ | ν_{obs} (MHz) | ϵ^b | δ^b |
|---|-------|----------|--------------------------|--------------|------------|
| CH₃²⁸SiH₃ | | | | | |
| gs ^c | 0 | 0 | 21937.8811 | 10 | -9.4 |
| gs ^d | 0 | 0 | 21937.885 | 10 | -5.5 |
| gs ^c | 0 | ±1 | 21937.9164 | 5 | 1.0 |
| gs ^d | 0 | ±1 | 21937.913 | 10 | -2.4 |
| gs ^c | 0 | * | 21937.9000 | 10 | 1.2 |
| gs | 1 | 0 | 21873.0507 | 10 | -1.1 |
| gs | 1 | ±1 | 21872.3480 | 10 | -3.5 |
| gs | 2 | 0 | 21808.9469 | 10 | -2.1 |
| gs | 2 | ±1 | 21814.4367 | 10 | 0.1 |
| gs | 3 | 0 | 21768.7299 | 10 | -8.0 |
| gs | 3 | ±1 | 21758.4680 | 10 | -1.2 |
| gs | 4 | 0 | 21737.7842 | 15 | 23.2 |
| gs | 4 | ±1 | 21743.2091 | 15 | 2.7 |
| gs ^{f,g} | 5 | 0 | 21706.7649 | 15 | -219.2 |
| gs ^{f,h} | 5 | 0 | 21703.5770 | 15 | -3407.1 |
| gs ^{f,i} | 5 | ±1 | 21733.0141 | 20 | -262.9 |
| ν_{12} | 0 | 0 | 21937.488 | 20 | 18.3 |
| ν_{12} | 0 | +1 | 21936.973 | 20 | -1.4 |
| ν_{12} | 0 | -1 | 21936.748 | 200 | -56.2 |
| $\nu_5^{\text{e,f}}$ | 0 | * | 21790.0525 | 20 | -65.2 |
| CH₃²⁹SiH₃ | | | | | |
| gs ^c | 0 | * | 21770.9693 | 10 | |
| gs | 1 | 0 | 21706.7649 | 15 | |
| gs | 1 | ±1 | 21706.0753 | 15 | |
| gs | 2 | 0 | 21643.2221 | 15 | |
| gs | 2 | ±1 | 21648.6998 | 15 | |
| gs | 3 | 0 | 21603.3279 | 20 | |
| gs | 3 | ±1 | 21593.1456 | 20 | |

^a In each transition, ν_5 , ν_{12} , l_{12} , v_6 , $K = 0$, and σ are conserved. Unless otherwise noted, the measurements are Fourier transform waveguide values determined here.

^b For the definitions of ϵ and δ , see the footnotes of Table 2. The units here for both are kHz.

^c Fourier transform cavity measurement made here.

^d Molecular beam electric resonance measurement from [2].

^e As indicated by the *, the measurement is for the unresolved σ -doublet; see Section 3.

^f The assignment is only tentative; the measurement is not in the fit.

^g This is preferred by the HB model, but is firmly assigned to the gs line for CH₃²⁹SiH₃ in the ($v_6 = 1$, $\sigma = 0$) state; see Section 3. In the FR model, $\delta = 2.14$ MHz.

^h This is preferred by the FR model, in which $\delta = -1.05$ MHz.

ⁱ In the FR model, $\delta = -295$ kHz.

two different views of the torsional motion. In the High Barrier (HB) Model, the torsional mode is grouped with the vibrational degrees of freedom. This approach was introduced in [3] following a limiting procedure adopted from the work of Hougen [12] and discussed with respect to CH₃SiH₃ in Section III of [13]. In the Free Rotor (FR) Model, the torsional motion is grouped with the rotational degrees of freedom [14]. This approach was introduced recently in the analysis of the (gs, ν_{12}) interactions in CH₃SiD₃ [15]. In the current work, the HB Hamiltonian is characterized by 45 parameters that can be freely varied in the least-squares fit to the data. In the FR Hamiltonian, the same number of free parameters are used, but an additional parameter is needed that

Table 5
Rotational frequencies^a ($J = 45 \leftarrow 44$) in GS of CH₃²⁸SiH₃

| K | σ^b | ν_{obs} (MHz) | ϵ^c | δ^c |
|-----------|------------|--------------------------|--------------|------------|
| $v_6 = 0$ | | | | |
| 2 | * | 983302.1 | 1 | 0.72 |
| 3 | * | 983281.8 | 1 | 0.62 |
| 4 | * | 983252.2 | 1 | -0.41 |
| 5 | * | 983215.4 | 1 | -0.67 |
| 6 | * | 983171.2 | 1 | -0.40 |
| 7 | * | 983119.2 | 1 | 0.41 |
| 8 | * | 983058.2 | 1 | 0.52 |
| 9 | * | 982989.4 | 1 | 0.96 |
| 10 | * | 982912.1 | 1 | 0.52 |
| 11 | * | 982826.8 | 1 | 0.14 |
| 12 | * | 982733.4 | 1 | -0.03 |
| 13 | * | 982631.5 | 1 | -0.27 |
| $v_6 = 1$ | | | | |
| 0 | 0 | 980439.8 | 1 | 0.23 |
| 0 | ±1 | 980403.8 ^d | 3 | -2.63 |
| 1 | 0 | 980429.4 | 1 | -0.66 |
| 1 | +1 | 980417.0 ^d | 2 | -0.18 |
| 1 | -1 | 980392.1 | 1 | -0.78 |
| 2 | 0 | 980403.8 ^d | 3 | -0.55 |
| 2 | +1 | 980417.0 ^d | 2 | -1.18 |
| 2 | -1 | 980380.1 | 1 | -0.65 |
| 3 | 0 | 980368.5 ^d | 1 | -0.58 |
| 3 | +1 | 980403.8 ^d | 2 | 1.04 |
| 3 | -1 | 980368.5 ^d | 2 | -1.50 |
| 4 | 0 | 980331.5 | 2 | 0.31 |
| 4 | +1 | 980368.5 ^d | 2 | 0.19 |
| 4 | -1 | 980355.7 | 1 | -0.63 |
| 5 | 0 | 980294.0 ^d | 3 | -0.80 |
| 5 | +1 | 980317.4 | 1 | -0.38 |
| 5 | -1 | 980331.5 | 2 | -1.16 |
| 6 | 0 | 980259.3 ^d | 2 | -0.53 |
| 6 | +1 | 980259.3 ^d | 2 | 1.36 |
| 6 | -1 | 980294.0 ^d | 3 | 1.67 |
| 7 | 0 | 980220.9 | 1 | -0.93 |
| 7 | +1 | 980194.7 | 1 | -0.95 |
| 7 | -1 | 980231.9 | 1 | -0.96 |
| 8 | 0 | 980174.4 | 1 | 0.88 |
| 8 | +1 | 980135.4 | 1 | 0.34 |
| 8 | -1 | 980156.9 | 1 | -0.55 |
| 9 | 0 | 980107.7 | 1 | -0.54 |
| 9 | +1 | 980073.9 ^d | 3 | -2.05 |
| 9 | -1 | 980073.9 ^d | 3 | 0.95 |
| 10 | 0 | 980023.4 | 1 | -0.29 |
| 10 | +1 | 980013.3 | 1 | -0.38 |
| $v_6 = 2$ | | | | |
| 0 | 0 | 977570.4 | 1 | -0.26 |
| 0 | ±1 | 977827.3 | 1 | 1.24 |
| 1 | 0 | 977596.2 | 1 | -0.78 |
| 1 | +1 | 977691.2 | 1 | -0.08 |
| 1 | -1 | 977934.7 | 1 | 1.49 |
| 2 | 0 | 977674.5 | 1 | -0.37 |
| 2 | -1 | 977921.4 | 1 | 1.10 |
| 3 | 0 | 977790.2 | 1 | 0.95 |
| 4 | 0 | 977875.8 | 1 | 0.94 |
| 4 | +1 | 977530.6 | 1 | 0.58 |
| 4 | -1 | 977633.1 | 1 | 0.08 |
| 5 | 0 | 977836.5 | 1 | 0.65 |
| 6 | 0 | 977681.5 | 1 | -0.51 |
| 7 | +1 | 977745.0 | 1 | -0.33 |
| 13 | +1 | 976877.9 | 1 | 0.23 |

^a In each transition, $\nu_5 = 0$; $\nu_{12} = 0$; $l_{12} = 0$; v_6 , K , and σ are conserved.

^b For transitions labelled with *, the measurement is for the unresolved σ -multiplet; see Section 3.

^c For the definitions of ϵ and δ , see the footnotes of Table 2. The units here for both are MHz.

^d For these cases, two (or three) different calculated frequencies lie very close to the measured value. The different identifications were accepted and the errors increased (with the spin weights in mind) to allow for the calculated separation(s).

can only be varied stepwise. The two best fits obtained are the same in quality. The differences between the models are discussed briefly, along with future prospects for showing one is better than the other. The parameters characterizing the best HB and FR fits are given in Table 6.

2. Theoretical background

The theoretical treatment used in analyzing the current global data set in Table 1 is the same as that developed for the (gs/ v_{12}/v_5) analysis of CH₃SiH₃ [1] and the (gs/ v_{12}) analysis of CH₃SiD₃ [15]. For the notation, basis functions, matrix elements, and calculational procedures, the reader is referred to these earlier works [1,15]. Here the High Barrier and Free Rotor Hamiltonians will be presented, along with a discussion of the transition moment for the difference band observed here.

The analysis was set up in the *hybrid* model introduced by Wang et al. [17]. The torsional angular momentum is written $\tilde{\mathbf{J}}_\alpha = (\mathbf{J}_\alpha - \rho\mathbf{J}_z)$, where \mathbf{J}_α is the usual PAM torsional angular momentum [18]. In lowest order, ρ is the ratio of two moments of inertia about the symmetry axis: one of the methyl top and the other of the entire molecule. In the hybrid model [17], all the calculations are done with the principal axis method (PAM) [18], but the operators are re-grouped so as to retain the major advantages of the internal axis method (IAM) [18].

The effective vibration–torsion–rotation Hamiltonian $\mathbf{H}_{\text{VTR}}^{\text{eff}}$ is summarized in Table 6, where the index i has been introduced to label the molecular parameters X_i (or ΔX_i) which were varied in the fitting process and the corresponding operators \mathcal{O}_i . The different terms are divided into five groups. Three of these characterize diagonal matrix elements: one for the gs ($i = 1$ to 23), one for v_{12} ($i = 24$ to 36), and one for v_5 ($i = 37$ to 42). The last two groups characterize off-diagonal matrix elements: one for (gs, v_{12}) coupling ($i = 43$ to 50) and one for (gs, v_5) coupling ($i = 51$ to 55). The (gs, v_{12}) rows can be further categorized according to whether they apply to the HB and/or the FR models.

To construct $\mathbf{H}_{\text{VTR}}^{\text{eff}}$ using Table 6, all the terms $X_i\mathcal{O}_i$ are added, taking account of the fact that different rows pertain to different elements in the Hamiltonian matrix as described above. In this summation process, three further modifications are required. First, the parameter ρ does not multiply any individual operator, but rather appears implicitly in many operators \mathcal{O}_i through $\tilde{\mathbf{J}}_\alpha$. Second, for some of the excited state parameters, ΔX_i is listed as being varied rather than X_i itself. In these cases, the parameter multiplying \mathcal{O}_i in the Hamiltonian is the corresponding gs parameter plus ΔX_i . Finally, the quartic and sextic distortion terms require special

treatment. Consider as an example one of the possible v_{12} operators of degree 4 in $\tilde{\mathbf{J}}_\alpha$ and the components of \mathbf{J} . If this operator does not appear in Table 6, then it is entered into the Hamiltonian after being multiplied by the corresponding gs parameter. The same is true for all v_5 quartic operators and all v_{12} sextic operators. The v_5 sextic operators are not taken into account here. This default option for the parameters characterizing operators of degree 6 will here be referred to as the ($h_{12} = h_{\text{gs}}, h_5 = 0$) sextic option. This is different from the ($h_{12} = 0, h_5 = 0$) sextic default option used in [1]. In this regard, $X_{16} = F_{0,6J}$ is treated as being associated with a quartic operator, even though \mathcal{O}_{16} is, strictly speaking, sextic.

For the Q -branch difference band transitions observed here, the line strength is much higher than one might expect from the fact that $\Delta v_{12} = \pm 1$ and $\Delta v_6 = \mp 3$. To simplify the explanation, it will be assumed that a two-level analysis [19,20] can be used. In this approximation, the two relevant eigenfunctions of the Hamiltonian can be written:

$$\Psi(l_{12} = 0, K = 6) = a(0, 0)\Phi(l'_{12} = 0, K = 6) + a(0, -1)\Phi(l'_{12} = -1, K = 5); \quad (1)$$

$$\Psi(l_{12} = -1, K = 5) = a(-1, 0)\Phi(l'_{12} = 0, K = 6) + a(-1, -1)\Phi(l'_{12} = -1, K = 5). \quad (2)$$

The full set of quantum numbers are given in Table 2, but here the quantum numbers v_5 , v_{12} , J , v_6 , and σ have been suppressed to simplify the notation. In Eqs. (1) and (2), the $\Phi(l'_{12}, K)$ represent the basis functions that apply in the limit that the (gs, v_{12}) coupling goes to zero, and the $a(l_{12}, l'_{12})$ are the mixing coefficients, taken here to be real. The magnitudes of these coefficients are such that $\Psi(0, 6)$ is always predominantly $\Phi(0, 6)$ in character, and $\Psi(-1, 5)$ is always predominantly $\Phi(-1, 5)$ in character. Following the work of Gordy and Cook [21] leading to their Eq. (2.125), the intensity of a difference band transition between $\Psi(l_{12} = 0, K)$ and $\Psi(l_{12} = -1, K - 1)$ can be shown to be proportional to:

$$|\langle l_{12} = 0, K | \mu | l_{12} = -1, K - 1 \rangle|^2 = \frac{[a(0, 0)a(0, -1)]^2 \mu_0^2}{J(J + 1)}, \quad (3)$$

where $\mu_0 = 0.7345600(33)$ D [22] is the equilibrium dipole moment (except for a small correction). For a direct l -doubling transition, the corresponding expression is the same, except that the factor involving the product of two mixing coefficients is replaced by unity. Thus in the limit of complete mixing, the difference band transition is weaker than its l -doubling counterpart by a factor of only 4, and so can be expected to be very strong. If the corresponding calculation is done for a parallel band where the two resonantly interacting states have the same value of K , then it is found that the square of the

Table 6
Operators^a and spectroscopic parameters in the (gs/ v_{12}/v_5) analysis of CH₃²⁸SiH₃

| i | X_i or ΔX_i | Units | Operator \mathcal{O}_i | High Barrier Model | Free Rotor Model | Ref. [1] (HB) |
|---|---------------------------------|------------------|--|---------------------------|---------------------------|---------------------------|
| <i>Terms for diagonal matrix elements with ($v_5 = 0, v_{12} = 0$)</i> | | | | | | |
| 1 | ρ | Unitless | Implicit | 0.3519209(34) | 0.3519193(34) | 0.3519223(34) |
| 2 | $V_{0,3}$ | cm ⁻¹ | $\frac{1}{2}(1 - \cos 3\alpha)$ | 603.3878(37) | 603.3877(37) | 603.3911(37) |
| 3 | A_0 | MHz | \mathbf{J}^2 | 56176.811(56) | 56177.244(56) | 56177.040(55) |
| 4 | B_0 | MHz | $\mathbf{J}^2 - \mathbf{J}_z^2$ | 10984.4451(34) | 10985.1375(28) | 10984.4416(40) |
| 5 | $D_{0,J}$ | kHz | $-\mathbf{J}^4$ | 10.7087(13) | 10.7054(10) | 10.6894(33) |
| 6 | $D_{0,JK}$ | kHz | $-\mathbf{J}^2 \mathbf{J}_z^2$ | 45.732(15) | 45.826(14) | 45.822(36) |
| 7 | $D_{0,K}$ | kHz | $-\mathbf{J}^4$ | 189.65 ^b | 189.65 ^b | 189.65 ^b |
| 8 | $D_{0,m}$ | MHz | $-\mathbf{J}^4$ | 3.3368(96) | 3.3458(96) | 3.3384(96) |
| 9 | $D_{0,Jm}$ | MHz | $-\mathbf{J}^2 \mathbf{J}_z^2$ | 0.61649(65) | 0.47056(99) | 0.61886(72) |
| 10 | $D_{0,Km}$ | MHz | $-\mathbf{J}^2 \mathbf{J}_z^2$ | 4.198(24) | 4.364(24) | 4.263(27) |
| 11 | $D_{0,sJ}$ | MHz | $-\mathbf{J}^2 \mathbf{J}_z \mathbf{J}_x$ | -0.125460(59) | -0.130897(166) | -0.125463(62) |
| 12 | $D_{0,sK}$ | MHz | $-\mathbf{J}^2 \mathbf{J}_z$ | -0.268(28) | -0.256(28) | -0.326(25) |
| 13 | $D_{0,sm}$ | MHz | $-\mathbf{J}^2 \mathbf{J}_z^3$ | 2.262(43) | 2.271(43) | 2.284(42) |
| 14 | $F_{0,3J}$ | MHz | $\mathbf{J}^2 \frac{1}{2}(1 - \cos 3\alpha)$ | -132.275(37) | -138.581(171) | -132.0449(69) |
| 15 | $F_{0,3K}$ | MHz | $\mathbf{J}^2 \frac{1}{2}(1 - \cos 3\alpha)$ | 395.3(1.4) | 397.9(1.4) | 396.9(1.5) |
| 16 | $F_{0,6J}$ | MHz | $\mathbf{J}^2 \frac{1}{2}(1 - \cos 6\alpha)$ | 0.0 ^c | -0.404(41) | 0.0 ^c |
| 17 | $F_{0,3JJ}$ | kHz | $\mathbf{J}^4 \frac{1}{2}(1 - \cos 3\alpha)$ | 0.3107(95) | 0.2732(30) | 0.340(24) |
| 18 | $F_{0,3JK}$ | kHz | $\mathbf{J}^2 \mathbf{J}_z^2 \frac{1}{2}(1 - \cos 3\alpha)$ | -2.96(18) | -2.36(18) | -3.02(19) |
| 19 | $H_{0,JK}$ | Hz | $\mathbf{J}^4 \mathbf{J}_z^2$ | 0.184(11) | 0.178(10) | 0.0 ^c |
| 20 | $H_{0,KJ}$ | Hz | $\mathbf{J}^2 \mathbf{J}^4$ | 0.0 ^c | 0.0 ^c | 0.98(21) |
| 21 | $H_{0,Jm}$ | Hz | $\mathbf{J}^4 \mathbf{J}_z^2$ | 2.80(20) | 0.0 ^c | 0.0 ^c |
| 22 | $H_{0,JKm}$ | Hz | $\mathbf{J}^2 \mathbf{J}_z^2 \mathbf{J}_x^2$ | 29.2(4.0) | 29.9(3.8) | 34.3(4.2) |
| 23 | $H_{0,Jmm}$ | Hz | $\mathbf{J}^2 \mathbf{J}_x^4$ | 0.0 ^c | 77.2(9.7) | 27.0(7.6) |
| <i>Terms for diagonal matrix elements with ($v_5 = 0, v_{12} = 1$)</i> | | | | | | |
| 24 | \tilde{v}_{12} | cm ⁻¹ | Unity | 624.55258(28) | 624.55303(28) | 624.55291(28) |
| 25 | $V_{12,3}$ | cm ⁻¹ | $\frac{1}{2}(1 - \cos 3\alpha)$ | 659.04(36) | 658.78(37) | 658.49(35) |
| 26 | ΔA_{12} | MHz | \mathbf{J}^2 | 206.341(35) | 203.837(36) | 203.735(37) |
| 27 | ΔB_{12} | MHz | $\mathbf{J}^2 - \mathbf{J}_z^2$ | 0.0 ^c | -3.5773(74) | -2.6011(29) |
| 28 | $\Delta D_{12,J}$ | kHz | $-\mathbf{J}^4$ | 0.0278(23) | 0.0 ^c | 0.0 ^c |
| 29 | $\Delta D_{12,JK}$ | kHz | $-\mathbf{J}^2 \mathbf{J}_z^2$ | 0.770(56) | 0.750(53) | 0.659(66) |
| 30 | $\Delta F_{12,3J}$ | MHz | $\mathbf{J}^2 \frac{1}{2}(1 - \cos 3\alpha)$ | -30.842(16) | 0.0 ^c | 0.0 ^c |
| 31 | $A_{\zeta_{12}}^{\prime}$ | MHz | $-2\mathbf{J}_z \ell_{12}$ | 13681.26(19) | 13681.25(19) | 13681.41(19) |
| 32 | $\eta_{12,J}$ | MHz | $\mathbf{J}^2 \mathbf{J}_z \ell_{12}$ | 0.01688(21) | 0.02044(21) | 0.01616(27) |
| 33 | $\eta_{12,K}$ | MHz | $\mathbf{J}^2 \ell_{12}$ | 0.5507(109) | 0.5455(109) | 0.5753(99) |
| 34 | $A_{\zeta_{12}}^{\prime\prime}$ | MHz | $2\mathbf{J}_x \ell_{12}$ | 87000 ^d | 86997 ^d | 86997 ^d |
| 35 | q_{12} | MHz | $\frac{1}{4}[\mathbf{J}_+^2 \mathbf{q}_{12+}^2 + \mathbf{J}_-^2 \mathbf{q}_{12-}^2]$ | 22.0035(40) | 21.9992(84) | 21.9759(61) |
| 36 | $q_{12,J}$ | Hz | $\mathbf{J}^2 \mathcal{O}_{35}$ | -72.29(14) | -50.64(21) | 0.0 ^c |
| <i>Terms for diagonal matrix elements with ($v_5 = 1, v_{12} = 0$)</i> | | | | | | |
| 37 | \tilde{v}_5 | cm ⁻¹ | Unity | 993.428(85) | 993.526(85) | 993.366(84) |
| 38 | $V_{5,3}$ | cm ⁻¹ | $\frac{1}{2}(1 - \cos 3\alpha)$ | 577.79(21) | 578.04(21) | 577.64(20) |
| 39 | ΔA_5 | MHz | \mathbf{J}^2 | -32.69(20) | -27.70(21) | -32.97(20) |
| 40 | ΔB_5 | MHz | $\mathbf{J}^2 - \mathbf{J}_z^2$ | -76.27(19) | -72.39(20) | -76.56(19) |
| 41 | $\Delta D_{5,JK}$ | kHz | $-\mathbf{J}^2 \mathbf{J}_z^2$ | 0.0 ^c | 0.97(19) | 0.0 ^c |
| 42 | $\Delta D_{5,Jm}$ | MHz | $-\mathbf{J}^2 \mathbf{J}_z^2$ | -0.412(33) | 0.392(34) | -0.459(33) |
| <i>Terms for (gs,v_{12}) coupling</i> | | | | | | |
| 43 | $(B_{5,12a}^{\prime\prime})^x$ | MHz | $\frac{1}{2}[\tilde{\mathbf{J}}_x, \mathbf{J}_+ \mathbf{q}_{12-} + \mathbf{J}_- \mathbf{q}_{12+}]_+$ $-2\lambda_{\zeta} \sin 3\alpha [\mathbf{J}_+ \mathbf{p}_{12-} + \mathbf{J}_- \mathbf{p}_{12+}]$ | 428.56(33) ^e | 0.0 ^f | 429.72(37) ^e |
| 44 | $(B_{5,12a}^{\prime\prime})^y$ | kHz | $\mathbf{J}^2 \mathcal{O}_{43}$ | -3.0836(69) ^e | 0.0 ^f | -4.46(33) ^e |
| 45 | $Q_{6,12a}^{\prime\prime}$ | MHz | $-2i[\mathbf{J}_z, \mathbf{J}_+ \mathbf{q}_{12-} - \mathbf{J}_- \mathbf{q}_{12+}]_+ \sin 3\alpha$ | 13.392(27) ^e | 14.768(27) ^e | 12.82(12) ^e |
| 46 | $M_{6,12a}^{\prime\prime}$ | MHz | $\frac{1}{2}[\mathbf{J}_z, \mathbf{J}_+ \mathbf{q}_{12-} + \mathbf{J}_- \mathbf{q}_{12+}]_+ \frac{1}{2}(1 - \cos 3\alpha)$ | 30.8(1.6) ^e | 52.3(1.6) ^e | 33.7(1.9) ^e |
| 47 | $M_{6,12a}^{\prime\prime}$ | kHz | $\mathbf{J}^2 \mathcal{O}_{46}$ | 7.3(1.7) ^e | 11.3(1.1) ^e | 0.0 ^c |
| 48 | $M_{6,12a}^{\prime\prime}$ | MHz | $\frac{1}{2}[\tilde{\mathbf{J}}_x, \mathbf{J}_+ \mathbf{q}_{12-} + \mathbf{J}_- \mathbf{q}_{12+}]_+$ | 0.0 ^f | 1541.5(2.5) ^e | 0.0 ^f |
| 49 | $M_{6,12a}^{\prime\prime}$ | kHz | $\mathbf{J}^2 \mathcal{O}_{48}$ | 0.0 ^f | -13.951(67) ^e | 0.0 ^f |
| 50 | $M_{6,12a}^{\prime\prime}$ | MHz | $[\frac{1}{2}(1 - \cos 3\alpha) - \frac{3}{4}i \sin 3\alpha]$ $\{\mathbf{J}_+ \mathbf{q}_{12-} [\tilde{\mathbf{J}}_x + \frac{1}{2}\rho] + \mathbf{J}_- \mathbf{q}_{12+} [\tilde{\mathbf{J}}_x - \frac{1}{2}\rho]\}$ | 0.0 ^f | -670 ^{e,g} | 0.0 ^f |
| <i>Terms for (gs,v_5) coupling</i> | | | | | | |
| 51 | $M_{5,0}^{\prime\prime}$ | cm ⁻¹ | $\mathbf{q}_5 \tilde{\mathbf{J}}_z^2$ | -0.22530(41) ^h | -0.22433(41) ^h | -0.22518(41) ^h |
| 52 | $M_{5,0}^{\prime\prime}$ | MHz | $\mathbf{J}^2 \mathcal{O}_{51}$ | 0.1569(93) ^h | 0.0 ^c | 0.1382(76) ^h |
| 53 | $C_{5,0}^3$ | cm ⁻¹ | $\mathbf{q}_5 \frac{1}{2}(1 - \cos 3\alpha)$ | 128.246(13) ^h | 128.271(13) ^h | 128.247(13) ^h |

Table 6 (continued)

| <i>i</i> | X_i or ΔX_i | Units | Operator \mathcal{O}_i | High Barrier Model | Free Rotor Model | Ref. [1] (HB) |
|----------|-----------------------|------------------|---|--------------------|------------------|---------------|
| 54 | $C_{5,0}^{3,J}$ | MHz | $\mathbf{J}^2 \mathcal{O}_{53}$ | $-1.25(19)^h$ | $-30.65(92)^h$ | 0.0^c |
| 55 | $C_{5,0}^6$ | cm^{-1} | $\mathbf{q}_5 \frac{1}{2} (1 - \cos 6\alpha)$ | $1.066(17)^h$ | $1.058(17)^h$ | $1.077(17)^h$ |

^a For terms which are diagonal in both v_{12} and v_5 , the vibrational operators can be taken to be unity. The treatment of the distortion constants in the excited vibrational states is discussed in Section 2. In particular, the ($h_{12} = h_{gs}$, $h_5 = 0$) sextic option was used in the current HB and FR models, while the ($h_{12} = 0$, $h_5 = 0$) sextic option was used in the HB model of Schroderus et al. [1].

^b This is fixed to the force field value given in [16].

^c This is fixed at zero because the parameter (although defined in the model used) could not be determined.

^d This was held fixed at $[A_{12}/(1 - \rho)]$; see [3].

^e The relative signs of the (gs, v_{12}) coupling constants are determined, but not the absolute signs.

^f This is fixed at zero because the parameter is not defined in the model used.

^g This was determined from a stepwise scan; see Section 4.

^h The relative signs of the (gs, v_5) coupling constants are determined, but not the absolute signs.

transition moment matrix element vanishes in lowest order, and the transition relies on higher order terms in the dipole moment expansion.

It should be noted that the discussion above applies only to the Q -branch. For ($\Delta J = \pm 1$), the analysis is straightforward, but expression for the square of the transition dipole matrix element does not simplify easily in large part because $[a(0, 0)a(-1, 0) + a(0, -1)a(-1, -1)]$ need not vanish in this case.

3. Experimental methods and measurements

In Tables 2–4, all the new measurements but two were made with the FTMW waveguide spectrometer at the Eidgenössische Technische Hochschule in Zürich, Switzerland. The instrument design is similar to that of Bestmann et al. [23], and a detailed description can be found in [24]. The experimental procedures are similar to those applied earlier in observing, for example, the ($J = 1 \leftarrow 0$) spectrum of OPF₃ [25]. Here the relevant details will be summarized.

Consider first the spectrometer setup used below 18 GHz with the l -doubling spectrum as an initial example. A waveguide cell of length 6.0 m was used in X -band and a 6.5 m cell was used in P -band; each cell operated in the fundamental mode. The cells were cooled to a stable temperature that, depending on the specific spectrum, was between -50 and -63 °C. The sample pressure was typically 5 mTorr (0.67 Pa). The molecular sample was polarized with a microwave pulse which was 100–200 ns long, and had its peak power in the range from 30 to 40 W. The longer pulses were used at higher values of J where the transition moment was lower. After amplification, the decaying macroscopic molecular polarization produced by the input pulse was down-converted in two steps with a superheterodyne detection scheme to the range 0–5 MHz. The signal was then digitized with a 3-bit A/D convertor at a rate of 10 MHz for 512 channels. By performing a Fourier transform to the frequency do-

main, the power spectrum was recovered with a channel separation of 19.5 kHz. The full-width at half-maximum (FWHM) of the lines was $\Delta\nu \sim 180$ kHz. Due to the spin statistical weights [11], the ($\sigma = 0$) lines are twice as strong as their ($\sigma = \pm 1$) counterparts. Typically, 6×10^6 pulse responses were accumulated for ($\sigma = 0$), and 14×10^6 for ($\sigma = \pm 1$). The corresponding accumulation times were 6.6 and 15.4 min; the signal-to-noise ratio obtained was 10 or higher. For the three difference band lines below 18 GHz, the same conditions were used, except that the pulse length was increased to 400 ns to compensate for the lower transition moment.

For the measurements above 18 GHz in Tables 2 and 4, different spectrometer conditions were employed. A K -band cell with a length of 2.1 m was used at room temperature in the fundamental mode. For the ($J = 1 \leftarrow 0$) study, the microwave pulses were typically 20 ns long with a peak power of from 0.5 to 1 W. The sample pressure was ~ 6 mTorr (~ 0.8 Pa). For the difference band, the pulse length was increased to 200 ns with a peak power of from 2 to 4 W. In this case, the sample pressure was ~ 12 mTorr (~ 1.6 Pa). In most of the scans, the detected microwave emission was down-converted to the range 0–50 MHz and then digitized at a rate of 100 MHz for 512 channels, leading to a power spectrum with a channel separation of 195.3 kHz. The FWHM of the lines was $\Delta\nu \sim 400$ kHz. Between 1×10^6 and 5×10^6 pulse responses were accumulated for ($J = 1 \leftarrow 0$) study, and typically 10×10^6 for the difference band. As at lower frequencies, the signal-to-noise ratio obtained was ~ 10 or higher.

For the difference band and l -doubling study, the frequencies were determined from the power spectrum. Typically, three or four different scans were taken with different microwave polarization frequencies. These were chosen to be between three and five linewidths from the line center, first to one side and then to the other. The values listed in Tables 2 and 3 were obtained by averaging the individual results.

For the ($J = 1 \leftarrow 0$) study, the region from 21 590 to 21 950 MHz was completely covered by overlapping

50 MHz scans. The frequencies were determined by analyzing the time domain signal directly using the method outlined in [26]. In this analysis, one starts with the strongest line in the region, assigns it a Lorentzian lineshape, and subtracts its contribution to the time domain signal. Then one removes the contribution from the remaining lines one at a time in order of decreasing intensity. At each step, one can transform the residual time domain signal and examine the corresponding power spectrum. Ideally, the final residual power spectrum will be indistinguishable from that produced by noise alone. As with the other FTMW waveguide studies, each frequency listed in Table 4 was determined by averaging the results from at least two scans.

As can be seen from Table 4, the frequency region from 21936.5 to 21938.0 MHz contains both the *gs* and the ν_{12} transitions. There was some difficulty in making a reliable frequency determination from this region for the weakest member of the ν_{12} multiplet. In the *gs*, as with any non-degenerate state, the two ($K = 0$) levels with ($\sigma = +1$) and ($\sigma = -1$) are degenerate. Thus, the *gs* ($J = 1 \leftarrow 0$) spectrum consists of a doublet. The ($\sigma = 0$) and ($\sigma = \pm 1$) components have spin statistical weights in the ratio 2:1 [11]. From what was known previously about $\mathbf{H}_{\text{VTR}}^{\text{eff}}$ [1], the σ -splitting is 25 kHz, which cannot be detected with the waveguide spectrometer, and so the doublet appears as a single line. The frequency of this line is the weighted average of the frequencies of the two components with the weights being in the ratio 2:1; see Footnote e in Table 4. On the other hand, in the doubly degenerate state ν_{12} where $l_{12} = \pm 1$, the two levels ($\sigma = +1$) and ($\sigma = -1$) are degenerate for $G = (K - l_{12}) = 0$, *not* for $K = 0$. Thus, the ν_{12} ($J = 1 \leftarrow 0$) spectrum consists of a ($\sigma = 0, +1, -1$) triplet. As can be seen from Table 4, the ($\sigma = 0$) component is closest to the *gs* line, coming only ~ 400 kHz lower in frequency. The ($\sigma = +1$) line is ~ 500 kHz lower again in frequency, and the ($\sigma = -1$) line still lower in frequency by ~ 200 Hz. The fact that the ν_{12} σ -splitting is much larger than that in the *gs* is due primarily to the (*gs*, ν_{12}) interactions [3]. From the statistical weights and the room temperature Boltzmann factor, it is seen that the ($\sigma = 0$) component should be weaker than the *gs* line by a factor ~ 10 . Furthermore, from the spin statistics [11], three σ -components should have intensities in the ratio 2:2:1, with the ($\sigma = -1$) line being weakest. In the spectrum deduced from the analysis of the time domain signal, the *gs* singlet and the two stronger σ -components of the ν_{12} triplet were well above the noise level and were stable in frequency against reasonable changes in the lineshape parameter used. However, the ($\sigma = -1$) component of the ν_{12} triplet was comparable in intensity to the noise in the final residual power spectrum. A comparison of the fits with and without this line in the analysis indicates that the ($\sigma = -1$) component is present, but the level of confi-

dence is not as high as one would like. The experimental uncertainty ϵ for this line was set at 200 kHz, which is $\sim \Delta\nu/2$. In spite of this difficulty, the resolution of the ν_{12} σ -triplet with the much stronger *gs* line being only approximately one linewidth away illustrates the power of the FTMW method.

The ν_5 transition for $\nu_6 = 0$ was tentatively identified by Hirota based primarily on the relative intensity [11]. The frequency was not reported, but from the published stick spectrum, it can be estimated that the unresolved σ -doublet falls at about 21 790 MHz. In the current work, this transition is assigned to the line at 21 790.053(20) MHz; see Table 4. In this case, the primary evidence is that the observed frequency differs from the value predicted by the final HB model in Table 6 by only $\delta = -65$ kHz, and there are no other lines of reasonable intensity within 15 MHz. As can be seen from Table 1, the parallel band ($\nu_5 = 1 \leftarrow 0$) is in the data set (component 9), but there are no pure rotational data. With only the single microwave line available in ν_5 , it was decided, in spite of the strength of the evidence, to categorize the identification as tentative, and leave the frequency out of the fit. The measurement in Table 4 should prove to be useful when a full microwave/mm-wave study of ν_5 is done.

The experimental uncertainty ϵ for the frequencies measured with the FTMW waveguide spectrometer were chosen to reflect the linewidth, the signal-to-noise ratio, and the reproducibility of the measurements. A lower limit of 5 kHz was applied in this process to allow for possible contributions from small effects which were not taken into account in the analysis, such as the hyperfine interactions.

The *gs* ($J = 1 \leftarrow 0$) spectrum for ($\nu_6 = 0$) had been observed earlier using a molecular beam electric resonance spectrometer with a FWHM ($\Delta\nu$) of 13 kHz [2]. The spectrum was reported as a partially resolved σ -doublet. No comment was made on the relative intensities of the two lines or of any further structure. To allow for possible shifts due to the hyperfine interactions, the experimental uncertainty ϵ was set at 10 kHz for each line. The frequencies obtained are listed here in Table 4.

To investigate this ($J = 1 \leftarrow 0$) σ -doublet further, the FTMW cavity spectrometer at the Eidgenössische Technische Hochschule was used. The instrument design is similar to that of Balle and Flygare [27], and a detailed description can be found in [28]. Here, the experimental conditions will be outlined. The gas sample was a mixture of 1% CH_3SiH_3 in argon. At a backing pressure of 1 bar, gas pulses ≤ 1 ms long were injected into the cavity along the axis through a nozzle of 0.5 mm diameter at a repetition rate of 5 Hz. The molecules were polarized using microwave pulses 1 μs long with a peak power of 1 mW. After amplification, the subsequent molecular emission was down-converted to the range

0–5 MHz, and sampled into 2048 channels at a rate of 10 MHz with a 12-bit A/D convertor. From 2048 to 4096 gas pulses were accumulated to achieve a signal-to-noise ratio of at least 10. Five spectra were taken with slightly different microwave polarization frequencies. In each case, the time domain signal was analyzed using the methods discussed above. The frequencies listed in Table 4 were obtained by averaging the individual determinations.

In the initial analysis, it was assumed that the hyperfine effects were negligible. The cavity ($J = 1 \leftarrow 0$) spectrum should then consist of a quartet of lines, made up of two σ -doublets, with the high frequency doublet separated from its low frequency counterpart by the Doppler splitting produced by the motion of the molecules along the cavity axis. The Doppler splitting here is ~ 240 kHz. The two σ -doublets should be identical with the ($\sigma = 0$) partner being at lower frequency and being twice as strong as its ($\sigma = \pm 1$) partner. The predicted σ -splitting is 25 kHz. The time domain signal was therefore analyzed assuming that four lines were present. In the five spectra obtained, the ratio of peak heights of the ($\sigma = 0$) and ($\sigma = \pm 1$) partners was between 0.83 and 0.94, rather than 2. Each ($\sigma = 0$) line was clearly broader than the ($\sigma = \pm 1$) partner. Furthermore, the σ -splitting in the high frequency Doppler component of the spectrum was clearly larger than in the low frequency component, ~ 40 kHz versus ~ 30 kHz, with both of these values being significantly larger than the prediction of 25 kHz.

The explanation for these anomalies appears to lie in the hyperfine Hamiltonian \mathbf{H}_{HYP} . This Hamiltonian [2,10] includes three contributions arising from classical dipolar interactions: $\mathbf{H}_{\text{ss}}^{\text{tt}}$ between two protons in the methyl top; $\mathbf{H}_{\text{ss}}^{\text{ff}}$ between two protons in the silyl frame; and $\mathbf{H}_{\text{ss}}^{\text{tf}}$ between a proton in the top and one in the frame. The last major term in \mathbf{H}_{HYP} arises from the spin–rotation interaction \mathbf{H}_{sr} [2,10]. From arguments similar to those in Section 4 of [10] and the Appendix of [29], the coupling constants that characterize $\mathbf{H}_{\text{ss}}^{\text{tt}}$ and $\mathbf{H}_{\text{ss}}^{\text{ff}}$ are known to be much larger in magnitude than those for $\mathbf{H}_{\text{ss}}^{\text{tf}}$, and are expected to be much larger than those for \mathbf{H}_{sr} . However, it can be shown from simple angular momentum considerations that the diagonal matrix elements of $\mathbf{H}_{\text{ss}}^{\text{tt}}$ and $\mathbf{H}_{\text{ss}}^{\text{ff}}$ vanish for $\sigma = \pm 1$, but not for $\sigma = 0$. The form of the complete torsion–rotation–nuclear spin wavefunctions for gs levels with $K = 0$ are given in the last two lines in Table XIII of Hougen et al. [10]. Consider the total nuclear spin quantum number I_t of the protons in the methyl top and its counterpart I_f for the protons in the silyl frame. For $\sigma = \pm 1$, $I_t = I_f = 1/2$, while for $\sigma = 0$, $I_t = I_f = 3/2$. The top–top interaction $\mathbf{H}_{\text{ss}}^{\text{tt}}$ is a tensor of second rank in the total top nuclear spin operator \vec{I}_t . It follows then that the matrix elements of $\mathbf{H}_{\text{ss}}^{\text{tt}}$ diagonal in I_t must vanish when $I_t = 1/2$, i.e., when $\sigma = \pm 1$. Similarly, the matrix ele-

ments of the frame–frame interaction $\mathbf{H}_{\text{ss}}^{\text{ff}}$ diagonal in I_f vanish when $\sigma = \pm 1$. The same angular momentum arguments show that these diagonal matrix elements of $\mathbf{H}_{\text{ss}}^{\text{tt}}$ and $\mathbf{H}_{\text{ss}}^{\text{ff}}$ will in general be non-zero when $\sigma = 0$. It follows then that the hyperfine contributions to the cavity ($J = 1 \leftarrow 0$) spectrum will be larger for the ($\sigma = 0$) component.

An attempt was made to analyze the time domain signal on the assumption that three lines were present in each Doppler component, rather than two. The stronger pair lines then yielded average frequencies which differed by 25.7(3.6) kHz, in excellent agreement with the calculated value of 24.9 kHz for the splitting between $\sigma = 0$ and $\sigma = \pm 1$. Unfortunately, there were inconsistencies in the numerical results in this case that call the existence of the third line into question. For the ($\sigma = 0$) component, the uncertainty ϵ in the final frequency was taken as 10 kHz to allow for the possible hyperfine contributions. For $\sigma = \pm 1$, ϵ was taken conservatively as 5 kHz, the lower limit adopted for the waveguide measurements.

The frequencies listed in Table 4 were based on the four line analysis. For each value of σ , the FTMW cavity measurements differ from the earlier molecular beam values by less than 4 kHz. It is hoped that the present study of the cavity spectrum will help to stimulate further investigations of the hyperfine interactions in molecules such as CH_3SiH_3 .

To obtain the rotational spectrum ($J = 45 \leftarrow 44$) near 1 THz, the tunable sideband far-infrared spectrometer at the University of Nijmegen in The Netherlands was used. The instrument is that developed originally by Bicanic et al. [30] The experimental setup employed in the current study is illustrated in Fig. 1 of [31]. Further experimental details and a preliminary report of the present study were presented in [32]. Tunable sidebands are generated in a Schottky barrier GaAs crystal-whisker assembly mounted in a modified crossed waveguide harmonic mixer. Under typical conditions, the diode receives 50 mW of power from an HCN laser operating on the 891 GHz line through one mixer input arm, and 150 mW of power from a sweepable, phase-locked klystron through the other input arm. Sum and difference frequency sidebands are re-radiated and leave the mixer through the output arm. Typically, from 0.1 to 1 μW of sideband power enters the input arm of a monochromator which uses a reflection grating to isolate the sideband of interest from the laser carrier and the second sideband. The transmitted sideband is then passed through an absorption cell 1 m in length, and detected with a helium-cooled bolometer. Frequency modulation is applied to the klystron and the second harmonic in the bolometer signal is measured with a lock-in amplifier. Although the sideband radiation is highly monochromatic, the laser is free-running and oscillates at a stable, but unknown frequency, within its

gain curve. In standard operation, this curve has a FWHM ~ 3.5 MHz. Since the calibration procedure described in [31] was not applied, the absolute frequency of the sideband radiation has an uncertainty of 1 MHz.

For the frequency determinations in Table 5, the methyl silane sample was at room temperature and the pressure was ~ 50 mTorr (~ 6.7 Pa). Each absorption line had a FWHM of about 3 MHz. With a time constant ~ 1 s, a signal-to-noise ratio of 20 was obtained for the weakest lines measured. Two scans were taken, one sweeping up and one sweeping down in frequency, and the measurements were averaged. For an isolated line, the experimental uncertainty ϵ was 1 MHz, dominated by the uncertainty in the carrier frequency of the HCN laser. For $v_6 = 0$, the σ -splitting was much smaller than $\Delta\nu$, and the σ -multiplet appeared as a single line. In the fitting process, the calculated frequency in such cases was taken as the weighted average over σ , with the weights determined from the spin statistics. For $v_6 = 1$, the σ -splitting was typically larger than $\Delta\nu$, but there were cases where more than one (K, σ) assignment could be reasonably made for a single line. Where this occurred, each different possible assignment was put into the fit, with the value of ϵ for each increased to allow for the predicted splitting. In these cases, the statistical weights for the individual transitions was used in estimating the value of ϵ .

In the course of studying the ($J = 1 \leftarrow 0$) spectral region for transition frequencies $\text{CH}_3^{28}\text{SiH}_3$, the frequencies of the ($J = 1 \leftarrow 0$) gs transitions for the first four torsional states were measured for the isotopomer $\text{CH}_3^{29}\text{SiH}_3$ in natural abundance; see Table 4. For $v_6 = 0$, the σ -splitting could not be resolved and only the average frequency $\nu(J = 0, v_6 = 0, K = 0, \sigma = *)$ could be determined. The value obtained here agrees with the earlier, less accurate determinations made in [7,33]. The identification of this line has been clearly established by previous work [7,11,33]. The assignment of the lines for the higher torsional states has been firmly established here by calculating the frequency difference $[\nu(0, v_6, 0, \sigma) - \nu(0, 0, 0, \sigma = *)]$ for both isotopomers and dividing the ^{28}Si value by its ^{29}Si counterpart. The ratio was found to be close to unity and constant (1.0095) to 0.1% for all values of (v_6, σ). In addition, the intensities of the ^{28}Si lines were consistent with the known isotopic abundances of the two isotopomers. It is hoped that these frequencies will be useful in later isotopic studies of methyl silane.

4. Analysis and results

In the analysis of the present data summarized in Table 1, the starting point was the 41 parameter HB model and global data set of Schroderus et al. [1]. The FR model was investigated later on. In Phase (1) of the analysis, the

direct l -doubling transitions were considered. For ($\sigma = 0$), the difference δ between the observed value and that predicted by the model of Schroderus et al. [1] was -5 MHz at $J = 18$ and -19 MHz at $J = 25$. The corresponding values for ($\sigma = \pm 1$) were -3 and -16 MHz. The transitions were strong enough and the observed spectrum was sparse enough that the search for the lines and their identification were straightforward. When these lines were added to the starting data set, they could be fit to within experimental error without degrading the overall χ^2 value. The original model of Schroderus et al. [1] was refined by adding $q_{12,J}$, which characterizes the J -dependence of the l -doubling constant q_{12} . The ($h_{12} = 0, h_5 = 0$) sextic option of [1] was still in effect.

In Phase (2) of the analysis, the difference band was taken into account. As can be seen from Table 2, the three lines with $J = 10, 11$, and 12 define the minimum in the plot of frequency against J . These three lines fall in P -band and were measured first. The values of δ from the 41 parameter model of Schroderus et al. [1] were again small enough ($\sim +15.5$ MHz) that the search and identification presented no difficulty, particularly with the unusual J -dependence of the frequencies. It was then straightforward to locate the 11 difference band transitions in K -band. When the 14 difference band frequencies were included along with the l -doubling transitions, a good fit to within experimental error was found with a 45 parameter model which employed the ($h_{12} = h_{\text{gs}}, h_5 = 0$) sextic option.

In Phase (3) of the analysis, the ($J = 45 \leftarrow 44$) spectrum was considered. The search region had been defined earlier, but the 45 parameter model of Phase (2) was used to confirm the identifications. When the frequencies for $v_6 = 0$ and 1 were added to the data set, a good fit could be obtained without changing the selection of parameters used. When the frequencies for $v_6 = 2$ were included as well, a good fit was obtained using the same the number, but a different selection, of parameters.

In Phase (4) of the analysis, the ($J = 1 \leftarrow 0$) data were taken into account. In addition, component 15 of Table 1 was added to the data set. This consisted of the pure rotational frequencies measured by Wong et al. [7] in 1983 for $v_6 = 4$ in the gs. These lines could not be fit [7] with the gs one-stack model that was in use at the time because the intervibrational interactions produce large shifts. The transitions were re-considered in 1996 using the (gs/ v_{12}) three-stack model [9]. However, these lines were only compared to the corresponding predicted values at that time, and have not been included in the fits previously reported. The frequencies (with some corrections from the original) are given in Table 3 of [9]. When components 3 and 15 of Table 1 were added to the data set, the 45 parameter model of Phase (3) yielded a good fit with only minor changes in the values of the molecular constants.

A total of 123 new transitions were added to the global data set; see components 1 through 4 and 15 of Table 1. In addition, 16 lines in the data set of Schroderus et al. [1] were dropped from the present analysis. Of these, four were torsional transitions in component 5 with high values of both J and K ; in this case, there were concerns about the identification. The remaining 12 lines were microwave measurements which had been superseded by later, more accurate determinations.

Overall, the quality of the fit is very good; the total χ^2 was 746.9 for 3423 frequencies. The best fit values of the parameters characterizing the final HB 45 parameter model are given in Table 6. For each component in the fit, Table 1 lists the maximum values of J and K for the lower state, a typical experimental uncertainty ϵ , the standard deviation of the fit S , the number N of transitions, and the contribution to the χ^2 value. For each of the lines measured here, the difference δ between the observed and calculated values for the HB model are listed in Tables 2–5. A summary table with the detailed output from this best HB fit has been placed on file with the Supplementary material Archives of the Journal of Molecular Spectroscopy. For each line included in the analysis, the summary table gives the identification, the measured frequency, the assigned experimental uncertainty ϵ , and the difference δ between the observed and calculated frequencies. The full correlation matrix is also included.

The modifications made in the model because of the addition of the new measurements can be seen from Table 6, where the best fit values of the molecular constants for the 41 parameter HB model of Schroderus et al. [1] are given for comparison. The present model has added seven parameters and removed three. In particular, the changes in parametrization are: $+ [H_{0,KJ} - H_{0,KJ}] + [H_{0,JJm} - H_{0,Jmm}] + [\Delta F_{12,3J} - \Delta B_{12}] + \Delta D_{12,J} + q_{12,J} + M_{6,12a}^{yz,3,J} + C_{5,0}^{3,J}$, where a + sign/– sign indicates that the parameter involved is to be added/removed from the model. The parametrization also changes in that the $(h_{12} = h_{gs}, h_5 = 0)$ sextic option now replaces the $(h_{12} = 0, h_5 = 0)$ sextic option adopted earlier.

Each modification in the model can be understood in the light of the information content of the new measurements. With the addition of the high precision difference band lines up to $J = 19$ and the $(J = 45 \leftarrow 44)$ gs lines for $v_6 \leq 2$, there is more information on the high J -behavior of the gs energy levels, and so $H_{0,KJ}$ is replaced by $H_{0,JK}$ and $H_{0,Jmm}$ is replaced by $H_{0,JJm}$. The constraints applied to the v_{12} energies by the difference band and the l -doubling transitions require a more elaborate treatment of the $(v_{12} = 1)$ diagonal elements of the Hamiltonian. This leads to the introduction of $\Delta D_{12,J}$ and $q_{12,J}$. The parameter $\Delta F_{12,3J}$ introduces a σ -dependence at the quartic level. However, the diagonal matrix elements of $\frac{1}{2}(1 - \cos 3\alpha)\mathbf{J}^2$ have a very weak dependence on K and σ for $v_6 = 0$, and so there is not

enough information available to separate them from the matrix elements of \mathbf{J}^2 itself. Consequently, the value of $\Delta F_{12,3J}$ obtained here absorbs the contribution from ΔB_{12} , which is then dropped from the model. In addition, the sensitivity in the difference band to the high values of J requires a better approximation for the sextic constants in v_{12} , leading to the adoption of the $(h_{12} = h_{gs}, h_5 = 0)$ sextic option. The parameter $M_{6,12a}^{yz,3,J}$ introduces a further J -dependence in the (gs, v_{12}) matrix elements coupling the interacting levels involved in the difference band. The need for $C_{5,0}^{3,J}$ was somewhat surprising at first, since this affects the J -dependence in the (gs, v_5) interactions, and it is at $v_6 = 5$ that the gs is resonantly coupled to v_5 . However, the Fermi-like terms produce sizable shifts in all the torsional levels of the gs; see, for example, the discussion of Table II of [1].

The magnitudes of all of the new parameters seem to be reasonable. As can be seen from Table 6, $H_{0,JK}$ and $H_{0,JJm}$ are smaller than the constants they replace. The difference $\Delta F_{12,3J} = [F_{12,3J} - F_{0,3J}]$ is $\sim 25\%$ of the gs value $F_{0,3J}$ itself. At first glance, this ratio may seem unusually large. However, $\Delta F_{12,3J}$ absorbs ΔB_{12} and $\Delta D_{12,Jm}$, whereas $F_{0,3J}$ has been separated from both B_0 and $D_{0,Jm}$. Each of the relevant ratios for the remaining four new parameters is a sensible order of magnitude: $|\Delta D_{12,J}/D_{0,J}| \sim 3 \times 10^{-3}$; $|q_{12,J}/q_{12}| \sim 3 \times 10^{-6}$; $|M_{6,12a}^{yz,3,J}/M_{6,12a}^{yz,3}| \sim 2 \times 10^{-4}$; $|C_{5,0}^{3,J}/C_{5,0}^3| \sim 3 \times 10^{-7}$. Some small systematic effects remain in the values of δ and so it is clear that some higher order effects are being absorbed into the current effective constants.

The HB values obtained here agree very well with those obtained in the earlier HB analysis of Schroderus et al. [1] Aside from the 10 parameters that are present in one case but not the other, the magnitude of the difference between the [1] value and the present determination is typically smaller than the associated error, being a few times the associated error in the worst case. The one exception is ΔA_{12} , for which the change is ~ 50 times the statistical error. This behavior arises because the spectra are sensitive primarily to $[\Delta A_{12} - \Delta B_{12}]$ and ΔB_{12} is not included explicitly in the current HB model.

Using the FR model, a fit of comparable quality was obtained with 45 parameters; the best fit values are given in Table 6. The most important difference between the FR and HB Hamiltonians concerns their respective leading (gs, v_{12}) interaction operators \mathcal{O}_{48} and \mathcal{O}_{43} . These two operators are identical, except that \mathcal{O}_{48} is missing the term in $\sin 3\alpha$. The absence of this term in the FR model is compensated for primarily by the introduction of \mathcal{O}_{50} , which does not occur in the HB case to the order being considered. Unfortunately, the associated parameter $X_{50} = M_{6,12a}^{zy,3}$ cannot be varied freely because it was too highly correlated with the other (gs, v_{12}) coupling parameters. Since it could not be fixed at zero, $M_{6,12a}^{zy,3}$ was stepped through the range where acceptable fits could be obtained. At each step, the data set was fit

by varying the remaining 45 parameters. The value of -670 MHz given in Table 6 lies in the middle of a broad minimum in the χ^2 surface where $\chi^2 = 742.3$. Of course, in the FR model, the operator $\mathcal{O}_{49} = \mathbf{J}^2 \mathcal{O}_{48}$ replaces the HB operator $\mathcal{O}_{44} = \mathbf{J}^2 \mathcal{O}_{43}$.

Aside from the (gs, v_{12}) interaction operators mentioned above (i.e., those in lines $i = 43, 44$, and 48–50 of Table 6), the set of allowed operators is identical in the FR and HB Hamiltonians, and the same number of operators (namely 43) was selected for each model. However, a different selection of higher order terms was used in the two cases, primarily because of correlations with the (gs, v_{12}) coupling constants. The FR model uses $H_{0,Jmm}$, $F_{0,6J}$, ΔB_{12} , and $\Delta D_{5,JK}$, whereas the HB model used $H_{0,Jm}$, $\Delta D_{12,J}$, $\Delta F_{12,3J}$, and $M_{5,0}^{xx,J}$. Each of these eight parameters is associated with an operator \mathcal{O}_i in the Hamiltonian that explicitly involve \mathbf{J}^2 .

As can be seen from Table 6, the two models yield different numerical values for the parameters varied in the fits. The importance of the (FR – HB) difference in a parameter can be characterized by the ratio A obtained when this difference is divided by the associated error. Aside from the (gs, v_{12}) coupling constants themselves, $|A|$ tends to be largest for the parameters that characterize primarily the J -dependence of the energy. On the other hand, for each parameter that is associated with an operator \mathcal{O}_i that does not explicitly involve \mathbf{J}^2 or \mathbf{J}_z^2 , $|A| \lesssim 1$. For example, $|A|$ is ~ 160 for B_0 and ~ 17 for ΔA_5 , but ~ 0.5 for $V_{12,3}$ and ~ 1.4 for $C_{5,0}^3$. This is not surprising when one considers the change in the parametrization involved and the correlations such as that between ΔA_{12} and ΔB_{12} discussed above. One result of this pattern is that the parameters such as the barrier height and the vibrational quanta that characterize the pure torsional and vibrational degrees of freedom are relatively insensitive to the choice of model. Similar behavior was noted for CH_3SiD_3 [15].

5. Discussion

The measurement of difference band transitions with a Fourier transform microwave waveguide spectrometer

has been demonstrated in the current work. Although an in-depth understanding of the Hamiltonian was used to define the search region and identify the lines, a good deal can be done using only the previous measurements and identifications. From the study of the ($v_{12} = 1 \leftarrow 0$) vibrational band and the observation of perturbation-allowed ($v_6 = 3 \leftarrow 0$) torsional transitions [3,4], combination differences can be used to show that the ($J = 15$) difference band line should fall at $(19\,747 \pm 54)$ MHz. As can be seen from Table 2, the FTMW value is lower than this by only 25 MHz, well within the error. Even with an uncertainty of ~ 50 MHz, the search region does not present a serious problem when a spectrometer with the sensitivity of the FTMW instrument is being used. As regards the identification, this can also be done by applying combination differences. As an example, consider the ($J = 6$) column in Table 7. Frequency $\nu_{\text{gs}}(J = 6)$ is for the gs pure rotational transition for ($v_6 = 3$) [9]. This connects the upper states of difference band transition frequencies $\nu_{\text{db}}(J = 6)$ and $\nu_{\text{db}}(J = 7)$, respectively. Frequency $\nu_{\text{sr}}(J = 6)$ is for the pure rotational transition for the v_{12} (silyl rock) state with $l_{12} = -1$ and $v_6 = 0$ [9]. This connects the lower states of difference band transition frequencies $\nu_{\text{db}}(J = 6)$ and $\nu_{\text{db}}(J = 7)$, respectively. It is easily seen that $\Upsilon(6) \equiv [\nu_{\text{db}}(6) + \nu_{\text{gs}}(6)] - [\nu_{\text{sr}}(6) + \nu_{\text{db}}(7)]$ must vanish. The data are available from [9] to do a similar closed loop calculation of $\Upsilon(J)$ for $J = 7$ and $J = 8$. As can be seen from Table 7, the value of $|\Upsilon(J)| = 0$ to within $\sim (1/3)$ of the loop frequency error calculated in quadrature. This confirms the identification in a model independent manner.

For a difference band obeying the selection rules ($\Delta J = 0$, $\Delta K \neq 0$), the transitions are driven by the permanent dipole moment. The high sensitivity of the FTMW method is very helpful in measuring the lines. However, when the interacting levels are strongly mixed, the sensitivity of a standard Stark spectrometer is sufficient. In fact, in the period right after the three difference band lines in P -band were measured and before the lines in K -band were investigated with the FTMW spectrometer, the ($J = 19$) difference band line at 26.6 GHz was measured with a conventional R -band Stark

Table 7
Closed loop calculations using combination differences^a

| Frequency | Definition ^b | $J = 6$ | $J = 7$ | $J = 8$ |
|----------------------------|--|----------------|----------------|-----------------|
| $\nu_{\text{db}}(J)^c$ | $[E(0; 0, 0; J, 3, 6, -1) - E(0; 1, -1; J, 0, 5, -1)]$ | 19407.052(10) | 18988.533(10) | 18583.975(10) |
| $\nu_{\text{gs}}(J)^d$ | $[E(0; 0, 0; J + 1, 3, 6, -1) - E(0; 0, 0; J, 3, 6, -1)]$ | 152747.528(50) | 174600.320(50) | 196468.928(50) |
| $\nu_{\text{db}}(J + 1)^c$ | $[E(0; 0, 0; J + 1, 3, 6, -1) - E(0; 1, -1; J + 1, 0, 5, -1)]$ | 18988.533(10) | 18583.975(10) | 18228.958(10) |
| $\nu_{\text{sr}}(J)^d$ | $[E(0; 1, -1; J + 1, 0, 5, -1) - E(0; 1, -1; J, 0, 5, -1)]$ | 153166.024(50) | 175004.900(50) | 196823.902(100) |
| Υ^c | 0 | 0.023(72) | -0.022(72) | 0.043(113) |

^a Each measurement is entered in MHz with the error in the last figure shown in parentheses.

^b In E , the quantum numbers are: ($v_5; v_{12}, l_{12}; J, v_6, K, \sigma$).

^c Current measurements taken from Table 3.

^d From [9].

^e $\Upsilon \equiv \nu_{\text{db}}(J) + \nu_{\text{gs}}(J) - \nu_{\text{db}}(J + 1) - \nu_{\text{sr}}(J)$. This must vanish by definition.

spectrometer. The value obtained agreed with the FTMW result in Table 2 to within 3 kHz. This was somewhat fortuitous, of course, as the experimental uncertainty ϵ in the Stark measurement was 50 kHz. For a Q -branch difference band obeying the selection rule $\Delta K = 0$, higher order terms in the dipole expansion will drive the transition. In such cases, the high sensitivity of the FTMW method may well be essential.

The competition between the High Barrier and Free Rotor models has not been resolved. The characteristics of the two fits are such that, even with the present data set, one cannot say which is better. One possible way of distinguishing the models is suggested by the FTMW measurements in the region 21 690–21 750 MHz. The gs pure rotational spectrum for $v_6 = 5$ have not been previously identified. However, the ($J = 1 \leftarrow 0$) lines have been predicted with both the HB and FR models (but not included in the fits); see Table 4. For $\sigma = \pm 1$, the difference [$v_{\text{FR}}^p(\pm 1) - v_{\text{HB}}^p(\pm 1)$] in the two frequency predictions is -32 kHz. For the observed line at 21733.014(20) MHz, the difference δ between the observed and predicted values is ~ -0.3 MHz for both models. Since the intensity of the line is reasonable, this identification, though tentative, seems plausible. On the other hand, for $\sigma = 0$, the difference [$v_{\text{FR}}^p(0) - v_{\text{HB}}^p(0)$] = -2.36 MHz. The HB value of δ is only -0.22 MHz for the observed line at 21706.765(20) MHz. This identification also seems plausible at first glance, but there is overwhelming evidence that this is the gs $\text{CH}_3^{29}\text{SiH}_3$ transition for ($v_6 = 1, \sigma = 0$); see Section 3. Although there is no indication that the $\text{CH}_3^{28}\text{SiH}_3$ ($v_6 = 5, \sigma = 0$) line is blended with either the $\text{CH}_3^{29}\text{SiH}_3$ ($v_6 = 1, \sigma = 0$) transition or its nearby ($v_6 = 1, \sigma = \pm 1$) partner, neither possibility can be ruled out. The FR model prefers the line at 21703.577(20) MHz, for which the value of $\delta = -1.05$ MHz. Unfortunately, the only transitions in the data set involving the gs levels with $v_6 = 5$ are in the perturbation-allowed infrared series ($v_6 = 5 \leftarrow 0$) for ($K = 1, \sigma = -1$), and so it is not possible to draw any conclusions at this point.

Further work is necessary to obtain a full understanding of the vibration–torsion–rotation Hamiltonian in CH_3SiH_3 . Two investigations are clearly necessary. First, a thorough microwave/mm-wave study with the accuracy available today is needed for a wide range of J values in the excited torsional levels of the gs as well as in the lowest torsional levels in v_{12} and v_5 . Second, with an infrared interferometer such as that used recently for CH_3SiD_3 [15], considerable improvement could be made, in particular, for the bands ($v_{12} = 1 \leftarrow 0$) and ($v_6 = 3 \leftarrow 1$). Once our understanding of the (gs/ v_{12}/v_5) system is sufficiently advanced, it might be possible to analyze in detail levels at higher energy.

The question of how the torsional motion should best be treated is also being investigated for other symmetric tops with a single torsional degree of freedom. The HB

model has been used in a (gs/ v_{12}) analysis of CH_3SiD_3 [15], in a (gs/ v_{12}/v_5) analysis of CH_3CD_3 [34], and in a (gs/ v_9/v_3) analysis of CH_3CH_3 [35]. The FR model has also been used in the CH_3SiD_3 work [15]. The parameter $M_{6,12a}^{xy,3}$ is central to the difference between the HB and FR models. In the current work, $M_{6,12a}^{xy,3}$ could only be varied stepwise. However, for CH_3SiD_3 , $M_{6,12a}^{xy,3}$ could be floated, perhaps because crossings were observed between v_{12} levels with $v_6 = 0$ and gs levels with $v_6 = 3$ for three different (G, σ) combinations, in contrast to the current work on CH_3SiH_3 where only one such crossing has been measured. In spite of the fact that $M_{6,12a}^{xy,3}$ could be floated for CH_3SiD_3 , the HB and FR gave comparable fits, and further work is underway. The FR model is currently being applied to the CH_3CH_3 [36]. However, to this point, the HB and FR models again give fits of similar quality. It may be that it is impossible to separate the two models at any practical level of accuracy and range of quantum numbers investigated.

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