Energy Levels for Internal and Over-All Rotation of Two-Top Molecules. I. Microwave Spectrum of Dimethyl Silane*

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A method is given for analyzing barrier-dependent "tunnel effect" splittings in rotational spectra of molecules with two equivalent tops. The perturbation treatment is an extension of the "principal axis" method for single-top molecules, and is limited to torsional states in which the two principal torsional quantum numbers are identical. Tables of perturbation coefficients are given from which the effects of top-top coupling on the rotational spectrum may be calculated. The microwave spectra of six isotopic species of dimethyl silane have been investigated in the region 8 to 25 kMc. Changes in moments of inertia with isotopic substitution yield the following structural parameters:

CIT	1.492 + 0.005 A	TICIT	107%50/ + 20/		
SIH	$1.483 \pm 0.005 \text{ A}$	HSIH	107 30 ±20		
СН	$1.095 \pm 0.005 \text{ A}$	HCH	$108^{\circ}0' \pm 20'$,		
$2\theta = 110^{\circ}59' + 1^{\circ}$.					

where 2θ is the angle between the symmetry axes of the methyl groups. From splittings in the rotational spectrum the angle 2θ is found to be $110^{\circ}50' \pm 20'$. Analysis of splittings for $(CH_3)_2SiH_2$, $(CH_3)_2SiD_2$, and $(CH_3)(CD_3)SiH_2$ indicates that coupling between tops is very small. Assuming no coupling, the barrier to internal rotation is 1647 ± 3 cal/mole. From Stark effect measurements the dipole moment is found to be 0.75±0.01D.

THE results of a large number of microwave studies¹ L of single-top asymmetric rotor molecules, such as acetaldehyde (CH₃CHO), have demonstrated that by far the most important mechanism for the production of barrier-dependent "tunnel effect" splittings in the rotational spectrum is that of coupling between angular momenta of internal and over-all rotation. A rather elegant and very practical method for the analysis of rotational spectra of single-top molecules has been developed by Wilson and his co-workers.² This method, sometimes referred to as the "principal axis" method, treats top-frame coupling by perturbation theory, and because the necessary perturbation sums have been extensively tabulated, 2b,3 it has the great advantage that much of the analysis of spectra can be carried out by using standard techniques and tables developed for rigid asymmetric rotor molecules.

The present work is the first of a series of papers which will deal with the problem of analyzing "tunneleffect" splittings in the rotational spectra of two-top molecules such as dimethyl silane $[(CH_3)_2SiH_2]$ and ethyl silane (CH₃CH₂SiH₃). These molecules have a unique feature not present in single-top molecules; the possibility of coupling between tops as well as between tops and frame. In our approach to the twotop problem, we try to make as much use as possible of the theory and tables^{2b,3} developed for single-top molecules. This objective requires in the zeroth order that the tops be independent, so that our treatment is limited to cases where top-top coupling is relatively "weak."

In this paper consideration is limited to rotational spectra arising from torsional states (of molecules with equivalent tops) in which the two principal torsional quantum numbers are identical (vv states). The results given here will be in part applicable to, but not adequate for, torsional states in which the two principal torsional quantum numbers are different (vv' states). Work on the vv' problem is in progress and will be reported in IV of this series. Numbers II and III will deal with the analysis of rotational spectra of the two kinds of molecules with nonequivalent tops; (a) (CH₃) (CD₃)S-type molecules,⁴ and (b) CH₃CH₂SiH₃type molecules.⁵ In so far as vv states of molecules with equivalent tops are concerned, Swalen and Costain have already shown that in the absence of top-top coupling, analysis of rotational spectra requires only single-top perturbation coefficients.⁶ In this work the effects of top-top coupling in both the kinetic and

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¹ For literature references and summaries of microwave barrier ¹ For literature references and summaries of microwave barrier studies, see E. B. Wilson, Jr., Proc. Natl. Acad. Sci. U. S. **43**, 816 (1957), "The Problem of Barriers to Internal Rotation in Molecules," *Advances in Chemical Physics* (Interscience Publishers, Inc., New York, 1959), Vol. II; C. C. Lin and J. D. Swalen, Revs. Modern Phys. **31**, 841 (1959). ² (a) R. W. Kilb, C. C. Lin, and E. B. Wilson, Jr., J. Chem. Phys. **26**, 1695 (1957); (b) D. R. Herschbach, J. Chem. Phys. **31**, 91 (1959). ³ (a). D. R. Herschbach, *Tables for the Internal Rotation Prob-lem* (Department of Chemistry, Harvard University, Cambridge

lem (Department of Chemistry, Harvard University, Cambridge, Massachusetts, 1957); J. Chem. Phys. 27, 975 (1957); (b) R. W. Kilb, Tables of Degenerate Mathieu Functions (Department of Chemistry, Harvard University, Cambridge, Massachusetts, 1956). Copies of these tables are available on request to Professor E. B. Wilson, Jr.

⁴ M. Hayashi and L. Pierce, Symposium on Molecular Structure and Spectroscopy, Ohio State University (1960).

⁶ D. H. Petersen and L. Pierce, Symposium on Molecular Structure and Spectroscopy, Ohio State University (1960). ⁶ J. D. Swalen and C. C. Costain, J. Chem. Phys. **31**, 1562 (1959). See also P. Kasai and R. J. Myers, *ibid*. **30**, 1096 (1959).

potential energy are considered.⁷ The effects of coupling in the kinetic energy are shown to be expressable in terms of products of tabulated^{2b} single-top perturbation sums, and also quite often to be completely negligible. Perturbation sums from which the effects of coupling in the potential energy can be calculated have been evaluated. The theoretical results are applied to the analysis of the rotational spectrum of dimethyl silane.

I. THEORY

1. Notation

g = x, y, z refers to principal axes of the entire molecule.

- I_g = principal moments of inertia of the entire molecule.
- I_{α} = moment of inertia of either internal top about its symmetry axis.
- λ_{gk} = direction cosines between kth top and the principal axes.

$$r = 1 - \sum_{g} \lambda_{gk}^2 I_{\alpha} / I_{g}, \qquad (k = 1 \text{ or } 2).$$
$$q = -\sum_{\alpha} \lambda_{g1} \lambda_{g2} I_{\alpha} / I_{g}.$$

- P_q = components of the total angular momentum along the principal axes.
- p_k = total angular momentum of kth top along its symmetry axis.

$$\mathcal{P}_k = \sum_g P_g \lambda_{gk} I_\alpha / I_g$$

- v_k = principal torsional quantum number of the kth top.
- σ_k = a symmetry index giving the periodicity of the torsional wave function for the kth top.

 α_k = angle of internal rotation for kth top.

2. Model and Hamiltonian

The model adopted for molecules such as (CH₃)₂SiH₂ or (CH₃)₂S consists of two equivalent rigid symmetric tops attached, with symmetry axes not coincident, to a rigid asymmetric framework. There are then, five degrees of freedom; three for over-all rotation and two for internal torsion or rotation. The kinetic energy^{2b,8} for the model may be written as (see Notation above)

$$H_r + F[(p_1 - \mathcal{O}_1)^2 + (p_2 - \mathcal{O}_2)^2] + F'[(p_1 - \mathcal{O}_1)(p_2 - \mathcal{O}_2) + (p_2 - \mathcal{O}_2)(p_1 - \mathcal{O}_1)], \quad (1)$$

where H_r is the rigid rotor Hamiltonian

$$\mathbf{H}_{r} = a P_{z}^{2} + b P_{x}^{2} + c P_{y}^{2}, \qquad (I^{r}). \tag{2}$$

The quantities $p_1 - P_1$ and $p_2 - P_2$ represent, respectively, the angular momenta of tops 1 and 2 relative to the framework. F and F' are inverse reduced moments of inertia for internal rotation and are conveniently defined by the equation

$$F_{\pm} = F \pm F' = \hbar^2 / 2 (\mathbf{r} \pm q) I_{\alpha}. \tag{3}$$

The tops are assumed to have threefold symmetry so that the Fourier expansion of the potential energy gives

$$V(\alpha_1, \alpha_2) = V_0 + \frac{1}{2} V_3 (2 - \cos 3\alpha_1 - \cos 3\alpha_2)$$

+ $V_3' \cos 3\alpha_1 \cos 3\alpha_2 + V_3'' \sin 3\alpha_1 \sin 3\alpha_2$
+ terms in $3n\alpha_1, 3n\alpha_2; \qquad n=2, 3, \cdots$ (4)

Implicit in the perturbation treatment described below are the assumptions that: (a) terms in $V(\alpha_1, \alpha_2)$ having higher than threefold symmetry in α_1 or α_2 are negligibly small,⁹ (b) the barrier to internal rotation is relatively high so that top-frame coupling may be treated as a perturbation, (c) $V_3' \ll V_3^*$, $V_3'' \ll V_3^*$ and, $F' \ll F$, where $V_3^* = V_3 - 2V_3'$, so that top-top coupling terms as well may be treated by perturbation theory. With these assumptions a very appropriate form for the Hamiltonian is

$$H = H_r + 2F_+ (p_+ - \Theta_+)^2 + 2F_- (p_- - \Theta_-)^2 + \frac{1}{2}V_3^* (2 - \cos 3\alpha_1 - \cos 3\alpha_2)$$

$$+V_3'(1-\cos^3\alpha_1)(1-\cos^3\alpha_2)+V_3''\sin^3\alpha_1\sin^3\alpha_2, (5)$$

where

and

$$\mathcal{P}_{\pm}=\frac{1}{2}(\mathcal{P}_{1}\pm\mathcal{P}_{2}),$$

$$p_{\pm} = \frac{1}{2}(p_1 \pm p_2).$$

Except for the occurrence of top-frame coupling terms $-4F_{\pm}p_{\pm}O_{\pm}$ the Hamiltonian is separable into purely rotational and purely torsional parts. Thus in high barrier cases, it would be practical to treat these terms by perturbation theory. However, one of the principal objectives of this paper is to make fullest possible use of existing theoretical methods and tables^{2b,3} for single-top molecules, and to do this it proves necessary to treat both top-top and top-frame coupling terms by perturbation theory. Consequently, we choose the zeroth-order Hamiltonian as

$$H^{(0)} = H_r + F(p_1^2 + p_2^2) + \frac{1}{2}V_3^*(2 - \cos 3\alpha_1 - \cos 3\alpha_2),$$

⁷ In the perturbation treatment of footnote 6 (Swalen and Costain) a portion of the top-top kinetic energy coupling terms are retained and the rest disregarded. One of the results of the present investigation shows that in general, it will be a much better approximation (for *w* states) to disregard *all* rather than just part of these coupling terms. See also, L. Pierce, J. Chem. Phys. **31**, 547 (1959). ⁸ B. L. Crawford, J. Chem. Phys. **8**, 273 (1940).

⁹ This assumption seems justifiable in view of the fact that for single-top molecules, spectra have thus far been satisfactorily interpreted by using only a V_3 term in the Fourier expansion of the potential energy. See for example, D. R. Herschbach and J. D. Swalen, J. Chem. Phys. **29**, 761 (1958).

TABLE I. Symmetry of the torsional basis functions.

	Function ^a		Species	
v = v':	v0v0		A_1A_1	
	v0v1, $v1v0$, $v0v-1$, $v-1v0$		EE	
	v1v1, v-1v-1		A_1E	
	v1v-1, v-1v1		EA_1	
<i>v≠v</i> ′:	$(1/\sqrt{2}) (v0v'0\pm v'0v0)$ or ^b	$+\atop{A_1A_1\\A_1A_2}$		$\begin{array}{c}-\\ A_2A_2\\ A_2A_1\end{array}$
	$\begin{array}{c} (1/\sqrt{2}) (v1v'1\pm v'1v1) \\ (1/\sqrt{2}) (v-1v'-1\pm v'-1v-1) \end{array}$	$\Big\}A_1E$		A_2E
	$ \begin{array}{c} (1/\sqrt{2}) \left(v1v' - 1 \pm v'1v - 1 \right) \\ (1/\sqrt{2}) \left(v - 1v'1 \pm v' - 1v1 \right) \end{array} $	EA_1		EA_2
	v1v'0, v'0v1, v-1v'0, v'0v-1		EE	
	v0v'1, v'1v0, v'-1v0, v0v'-1		EE	

^a $v\sigma_1 v'\sigma_2 = U_{v\sigma_1}(\alpha_1) U_{v'\sigma_2}(\alpha_2)$.

^b The first alternative if v and v' have the same parity, the second alternative if v and v' have opposite parity.

and the perturbation Hamiltonian as

$$H^{(1)} = 2F_{+} \mathcal{O}_{+}^{2} + 2F_{-} \mathcal{O}_{-}^{2} - 4F_{+} p_{+} \mathcal{O}_{+} - 4F_{-} p_{-} \mathcal{O}_{-}$$
$$+ F'(p_{1} p_{2} + p_{2} p_{1}) + V_{3}'(1 - \cos 3\alpha_{1})$$
$$\times (1 - \cos 3\alpha_{2}) + V_{3}'' \sin 3\alpha_{1} \sin 3\alpha_{2}. \quad (6b)$$

Each of the basis functions for the perturbation treatment then, consists of a rotational factor (asymmetric rotor functions) and a torsional factor for each of the tops (periodic Mathieu functions). In standard one-top notation the two torsional factors are

where

$$U_{v_1\sigma_1}(\alpha_1) U_{v_2\sigma_2}(\alpha_2),$$

$$U_{v\sigma}(\alpha) = \exp(i\sigma\alpha) \sum_{k} A_{k^{v}} \exp(3ik\alpha), \quad \sigma = 0, \pm 1, \quad (7)$$

and the $A_{k^{v}}$ depend only on a reduced barrier parameter s, where

 $s = 4V_3 * / 9F.$

3. Symmetry Considerations

The application of symmetry principles to rotationinternal rotation levels of two-top molecules has been discussed in detail by Myers and Wilson.¹⁰ They have shown that for molecules such as $(CH_3)_2SiH_2$ or $(CH_3)_2S$, the group I of the Hamiltonian (5) is the direct product of two simple groups, i.e., $C_{3\nu} \times C_{3\nu}$. The reader is referred to their paper for derivation of the possible species for energy levels, their statistical weights, and selection rules. For our purposes, the only required elaboration of their work is the determination of the transformation properties of the zeroth-order torsional functions

$$U_{\boldsymbol{v}\boldsymbol{\sigma}_1}(\boldsymbol{\alpha}_1)U_{\boldsymbol{v}^{\prime}\boldsymbol{\sigma}_2}(\boldsymbol{\alpha}_2); \qquad U_{\boldsymbol{v}^{\prime}\boldsymbol{\sigma}_1}(\boldsymbol{\alpha}_1)U_{\boldsymbol{v}\boldsymbol{\sigma}_2}(\boldsymbol{\alpha}_2) \qquad (8)$$

under the operations of the group I. For high barriers (high s) the zeroth-order torsional energy levels are ninefold degenerate when v=v' and eighteen fold degenerate when $v\neq v'$. Using the following relations;

$$U_{v0}(-\alpha) = (-1)^{v} U_{v0}(\alpha)$$

$$U_{v1}(-\alpha) = U_{v-1}(\alpha)$$

$$U_{v0}(\alpha + 2\pi n/3) = U_{v0}(\alpha)$$

$$U_{v1}(\alpha + 2\pi n/3) = w^{n} U_{v1}(\alpha)$$

$$U_{v-1}(\alpha + 2\pi n/3) = w^{2n} U_{v-1}(\alpha), \qquad (9)$$

where n=1, 2 and $w = \exp(2\pi i/3)$, it can be shown that when (a) v'=v, the nine functions (8) contain the irreducible representations A_1A_1 , A_1E , EA_1 and EE once each; (b) $v' \neq v$ and vv' = ee or oo, the eighteen functions (8) contain the irreducible representations A_1A_1 , A_2A_2 , A_1E , EA_1 , A_2E , EA_2 once each and EEtwice; (c) $v' \neq v$ and vv' = eo or oe, the eighteen functions (8) contain the irreducible representations A_1A_2 , A_2A_1 , A_1E , EA_1 , A_2E , EA_2 once each and EE twice. The linear combinations of (8) which transform as irreducible representations of I are given in Table I.

It is important to note that while the top-frame coupling operators of $H^{(1)}$ belong to the totally symmetric species of I, their individual factors do not. Thus p_+ and \mathcal{O}_+ belong to the species A_1A_2 , p_- and $\mathcal{O}_$ belong to the species A_2A_1 , while $p_\pm\mathcal{O}_\pm$ is in A_1A_1 . The nonzero matrix elements of p_\pm and \mathcal{O}_\pm are given in Table II. Note that the dipole moment is of species A_1A_2 so that the p_+ connections of Table II are also the selection rules.

Finally we note that there is a class of molecules with two equivalent tops having less symmetry than $(CH_3)_2SiH_2$. Two examples are dimethyl amine and *cis* 2,3-epoxybutane. Sage¹¹ has shown that for such

TABLE II. Nonzero matrix elements of p_{\pm} and \mathcal{O}_{\pm} .^a

<i>p</i> ₊ or <i>P</i> ₊	<i>p</i> _ or <i>(</i> P _	
$A_1A_1 \leftrightarrow A_1A_2$	$A_1A_1 \leftrightarrow A_2A_1$	
$A_2A_2 \leftrightarrow A_2A_1$	$A_2A_2 \leftrightarrow A_1A_2$	
 p_+	<i>p</i> _	
 $A_1 E \leftrightarrow A_1 E$	$A_1 E \leftrightarrow A_2 E$	
$A_2 E \leftrightarrow A_2 E$	$EA_1 \leftrightarrow EA_1$	
$EA_1 \leftrightarrow EA_2$	$EA_2 \leftrightarrow EA_2$	
$EE \leftrightarrow EE$	$EE \leftrightarrow EE$	

^a For p_{\pm} the symmetry species refer to species of the zeroth-order torsional functions, while for \mathcal{P}_{\pm} they refer to species of asymmetric rotor functions. Note that there are only four species of asymmetric rotor functions.

¹¹ M. Sage, thesis, Harvard University (1960).

¹⁰ R. J. Myers and E. B. Wilson, Jr., J. Chem. Phys. 33, 186 (1960).

molecules the group \mathbf{I}' of the Hamiltonian (5) is also the direct product of two simple groups; in this case $\mathbf{C}_{3\nu} \times \mathbf{C}_3$. The effective rotational Hamiltonians given in the next section are equally applicable to $(CH_3)_2SiH_2$ or dimethyl amine type molecules. They are labeled, however, according to the symmetry of the torsional sublevels under I. Their symmetry under I' is easily obtained if we note that the relation between the species of $\mathbf{C}_{3\nu}$ and its subgroup \mathbf{C}_3 is

$$A_1 \rightarrow A, A_2 \rightarrow A, E \rightarrow E_a + E_b.$$

4. Perturbation Treatment

The methods employed here for two-top molecules are a natural extension of the so-called principal axis method for single-top molecules. Therefore, we shall, before proceeding to the problem of two-tops, briefly review the perturbation treatment of top-frame coupling in single-top molecules. In the "semirigid" approximation the Hamiltonian is

$$H = H_r + F(p - \Theta)^2 + V(\alpha). \tag{10}$$

Treating the terms $-2F \not p \Theta$, $F \Theta^2$, and the asymmetric part of H_r as perturbations, the Hamiltonian matrix is off-diagonal in the rotational (symmetric top) quantum number K and the principal torsional quantum number v. The boundary condition of invariance under $\alpha \rightarrow \alpha + 2\pi$ requires that the zeroth-order torsional functions be periodic Mathieu functions, which for tops of threefold symmetry have the form (7) and are either of period $2\pi/3$ in α ($\sigma=0$, A species of C_3), or 2π in α ($\sigma=\pm 1$, E species). For each value of vthere are then two torsional sublevels, $vA(\sigma=0)$ and $vE(\sigma=\pm 1)$, and physically, the separation of these levels may be regarded as a result of "tunneling" through the potential barrier.

Approximate v diagonalization of (10) is effected by applying successive Van Vleck transformations¹² to reduce the off-diagonal matrix elements of $-2Fp\varphi$ to an order high enough so that they may be neglected. If, in applying the Van Vleck transformations, the spacing of rotational levels is considered negligible compared to the spacing of torsional levels, then the Hamiltonian matrix approximately factors into smaller matrices $H_{v\sigma}$, one for each torsional state, where $H_{v\sigma}$ has the form^{2b}

$$H_{v\sigma} = H_r + F \sum_n W_{v\sigma}^{(n)} \mathcal{O}^n.$$
(11)

Formally, the neglect of rotational energy differences allows \mathcal{O} to be regarded as a parameter rather than as an operator for the purpose of approximate v diagonalization, so that the $W_{v\sigma}^{(n)}$ are simply the usual *n*thorder perturbation sums encountered in nondegenerate perturbation theory.¹³ Herschbach^{2b} has shown that, for sufficiently high s, the $W_{v\sigma}^{(n)}$ are simply proportional to the vA, vE torsional energy difference; thus making apparent the fact that "tunneling" affects rotational spectra indirectly via the top-frame coupling term.

The two-top problem differs from the one-top problem in two fundamental ways. First, regardless of whether coupling terms are included or not, there are four species of purely torsional functions for v=v', and eight species for $v \neq v'$. Thus in general the rotational spectrum should consist of quartets for torsional states with v=v' and octets for torsional states with $v\neq v'$, as opposed to doublets for any torsional state of a single-top molecule. Second, and more important, is the fact that with more than one top, terms are introduced into the Hamiltonian which have no analogs in the one-top Hamiltonian. Regarded as perturbations, these top-top coupling terms will affect "tunneling rates" and thus, through the top-frame coupling terms, will have an effect on the rotational spectrum.

The present perturbation treatment of two-top molecules will be restricted to finding effective rotational Hamiltonians for torsional states having v=v'. First let us assume that top-top coupling terms are negligible, i.e., set F', V_3' , and V_3'' equal to zero. In this approximation $H^{(1)}$ reduces to $-4F(p_+ \mathcal{O}_+ + p_- \mathcal{O}_-)$ $+2F(\mathcal{O}_+^2 + \mathcal{O}_-^2)$. Application of the Van Vleck transformation reduces matrix elements of $H^{(1)}$ which are off-diagonal in v to second order so that if rotational energy differences are neglected, the effective rotational Hamiltonian to second order has the form^{14,15}

$$H_{vv} = H_r + F \sum_{n} \left[w_{vv}^{(+n)} \mathcal{O}_{+}^{n} + w_{vv}^{(-n)} \mathcal{O}_{-}^{n} \right], \quad n = 0, 1, 2.$$
(12)

$$W_{v^{(2)}} = 4\Sigma | p_{vv'}|^2 / (W_{v^{(0)}} - W_{v'^{(0)}}) + 1.$$

¹⁴ For simplicity, one term, which ordinarily will be negligibly small for molecules that can be treated by the present theory, has been omitted from Eq. (12). This term has the form $Fw_{vv}^{(x2)}(\Phi_+\Phi_-+\Phi_-\Phi_+)$ where $w_{vv}^{(x2)}=W_{v2}^{(2)}-W_{v2}^{(2)}$ if $\Gamma_{vv}=EE$ and $w_{vv}^{(x2)}=0$ if $\Gamma_{vv}=A_1A_1$, A_1E_1 or EA_1 . By suitably rotating the principal axes, this term can be absorbed into H_r . Usually this rotation will be negligibly small. For example, in the case of dimethyl silane, a rotation of considerably less than one minute of arc in the a-b plane is required to remove the $\Phi_+\Phi_-$ cross terms for the ground torsional state.

¹⁵ In the absence of top-top coupling, the effective rotational Hamiltonian may be written in the alternative form

$$H_{vv} = H_r + F\Sigma_n [W_{v\sigma_1}{}^{(n)}\mathcal{O}_1{}^n + W_{v\sigma_2}{}^{(n)}\mathcal{O}_2{}^n],$$

where $\sigma_1\sigma_2$ is taken as 00, 10, 11, and 1-1 for $\Gamma_{vv}=A_1A_1$, EE, A_1E , and EA_1 , respectively. This form of H_{vv} contains the term in $(\mathcal{P}_+\mathcal{P}_-+\mathcal{P}_-\mathcal{P}_+)$ which is omitted in Eq. (13) (see the preceding footnote), i.e., it is correct to the second order (n=2). In the third and higher orders it is only approximately correct because it neglects certain cross terms between \mathcal{P}_1 and \mathcal{P}_2 . We have not investigated the perturbation coefficients for these cross terms.

¹² E. C. Kemble, Fundamental Principles of Quantum Mechanics (McGraw-Hill Book Company, Inc., New York, 1937), p. 395.

 $^{^{13}} W_{v\sigma}{}^{(2)}$ is not exactly a second-order perturbation coefficient. The term $F \Theta^2$ contributes only in the first order to $H_{\tau\sigma}$ and this contribution is lumped together with the second-order contribution of $-2F p \Theta$ so that

TABLE III. Definition of the $w_{vv}^{(\pm n)}$ in terms of the $W_{v\sigma}^{(n),a}$

Γ_{vv}	$w_{vv}{}^{(1)}$	$w_{vv}^{(-1)}$	$w_{vv}^{(\pm 2)}$
A_1A_1	0	0	2Wv0 ⁽²⁾
A_1E	$2W_{v1}^{(1)}$	0	$2W_{v1}^{(2)}$
EA_1	0	$2W_{v1}^{(1)}$	$2W_{v1}^{(2)}$
EE	${W}_{v1}{}^{(1)}$	$W_{v1}^{(1)}$	$(W_{v0}^{(2)} + W_{v1}^{(2)})$

^a The perturbation sums $W_{1\sigma}^{(n)}$ are defined and tabulated in footnotes 2b and 3a.

For every v there are four such Hamiltonians, H_{vv} ; one for each of the torsional sublevels $vv(A_1A_1)$, $vv(EA_1)$, $vv(A_1E)$, and vv(EE). In each case the $w_{vv}^{(\pm n)}$ are simple linear combinations of the $W_{vo}^{(n)}$ defined and tabulated by Herschbach.^{2b} The appropriate linear combinations are listed in Table III according to the symmetry of the torsional sublevels. While in general the rotational spectra will consist of quartets, it should be noted that the odd n terms will not contribute, except in the second or higher order in the H_r (asymmetric rotor) basis, to the rotational energy levels. Thus, if the matrix elements of the odd nterms in the H_r basis are small compared to the spacing of levels that they connect, the rotational spectrum will consist of symmetrical triplets.

If top-top interaction terms are included in $H^{(1)}$ the effective rotational Hamiltonian becomes

$$H_{vv} = H_r + F \sum_{n} [W_{vv}^{(+n)} \mathcal{O}_{+}^{n} + W_{vv}^{(-n)} \mathcal{O}_{-}^{n}], \quad n = 0, 1, 2,$$
(13)

where the $W_{vv}^{(\pm n)}$ are comprised of the $w_{vv}^{(\pm n)}$ plus a power series in the parameters

$$x = F'/F = -q/r$$

$$y = V_3'/V_3^*$$

$$z = V_3''/V_3^*.$$
 (14)

To the first order in x, y, and z we define the $W_{vv}^{(\pm n)}$ as

$$W_{vv}^{(\pm n)} = w_{vv}^{(\pm n)} + xX_{vv}^{(\pm n)} + yY_{vv}^{(\pm n)} + zZ_{vv}^{(\pm n)}.$$
 (15)

The $X_{vv}^{(\pm n)}$ and $Y_{vv}^{(\pm n)}$ are defined in Tables IV and V. Here $Z_{vv}^{(\pm n)}$ can be shown to be identically zero for n=0, 1, 2. Thus it appears that the coupling term $V_3'' \sin 3\alpha_1 \sin 3\alpha_2$ gives rise to no \mathcal{O}_{\pm}^n dependence in the effective rotational Hamiltonian for torsional states with v=v'. (It is, however, a very important term for states with $v=v'\pm 1$.)

The $W_{vv}^{(\pm n)}$, unlike the $w_{vv}^{(\pm n)}$, cannot be regarded as simple nth-order perturbation coefficients. The $X_{vv}^{(\pm n)}$ and $Y_{vv}^{(\pm n)}$ are actually perturbation sums of the (n+1)st rather than *n*th order. In this regard the $X_{vv}^{(\pm n)}$ are somewhat special. Because top-frame coupling terms are multiplied by $F_{\pm} = F(1 \pm x)$, a rather large $x \mathcal{P}_{\pm}^{n}$ dependence is obtained in the *n*th order. However, a portion of the (n+1)st order contributions arising from cross terms between $F'(p_1p_2+$ p_2p_1) and the top-frame coupling terms cancels this large $x\mathcal{P}_{\pm}^{n}$ dependence, so that the $X_{vv}^{(\pm n)}$ are composed of only (n+1)st-order perturbation sums. Fortunately, the $X_{vv}^{(\pm n)}$ are very easy to evaluate because they can be expressed as linear combinations of products of perturbation sums of lower order than the (n+1)st. They are, in fact, linear combinations of products of the $W_{v\sigma}^{(n)}$ which have been extensively tabulated by Herschbach.^{2b} Inspection of Tables III and IV shows that the order of magnitude of the $X_{vv}^{(\pm n)}$ is $\sim \lceil W_{v\sigma}^{(2)} \rceil \lceil w_{vv}^{(\pm n)} \rceil$. Since $W_{v\sigma}^{(2)} \ll 1$ for high s and low v, it is apparent that it will often be an excellent approximation to set F'=0 for v=v' torsional states. However, for $v = v' \pm 1$ the terms in F' like those in V_3'' become very important.

Unfortunately, we have found no obvious way to simplify the $Y_{vv}^{(\pm n)}$. It is necessary to evaluate them directly from the matrix elements of p and p^2 tabulated by Herschbach^{3a} and Kilb.^{3b} The $Y_{vv}^{(\pm n)}$ are defined in Table V as functions of the expectation value of an operator $\theta = (1 - \cos 3\alpha)$ and the perturbation sums $\gamma_{v\sigma}^{(n)}$, $\delta_{v\sigma}^{(2)}$. The sums, $\gamma^{(1)}$, have been calculated for v=0 and 1 at 14 values of s, $16 \le s \le 100$. The sums, $\gamma^{(2)}$, are much more difficult to evaluate and have thus far been calculated for v=0, and 1 at only four s values, s=20, 28, 40, and 60. For s>20 and v=0, or 1 the $\delta_{v\sigma}^{(2)}$ are negligible. Calculation of γ 's and δ 's is still in progress and a complete report will be given in II of this series. Table VI lists empirical formulas from which the $Y_{vv}^{(\pm n)}$ may be calculated. These formulas reproduce the $Y_{vv}^{(\pm n)}$ thus far computed to about 2%.

TABLE IV. Definition of the $X_{vv}^{(\pm n)}$ in terms of the $W_{v\sigma}^{(n),a}$

Γ_{vv}	$X_{rr}^{(1)}$	$X_{rr}^{(-1)}$	X _{vv} (±2)	
$A_{1}A_{1}$	0	0	$\pm 2[W_{v0}^{(2)}]^2$	
A_1E	$2W_{v1}^{(2)}W_{v1}^{(1)}$	0	$ \pm 2 [W_{v1}^{(2)}]^2 + 3 W_{v1}^{(1)} W_{v1}^{(3)} \mp 2 [W_{v1}^{(1)}]^2 W_{v1}^{(d)} $	
EA_1	0	$-2W_{v1}^{(2)}W_{v1}^{(1)}$	$ \pm 2 [W_{v1}^{(2)}]^2 - 3W_{v1}^{(1)}W_{v1}^{(3)} \mp 2 [W_{v1}^{(1)}]^2 W_{v1}^{(d)} $	
ĒΕ	${W_{v0}}^{(2)}{W_{v1}}^{(1)}$	$-W_{r0}^{(2)}W_{r1}^{(1)}$	$\pm 2W_{v0}^{(2)}W_{v1}^{(2)} \mp [W_{v1}^{(1)}]^2 W_{v0}^{(\mathbf{d})}$	

^a The perturbation sums $W_{v\sigma}^{(n)}$ are defined and tabulated in footnotes 2b and 3a.

Γ_{vv}	$\begin{array}{c} Y_{vv}^{(1)}\\ \text{[apart from a factor}\\ \text{of } -(9/2)s\text{]} \end{array}$	$\begin{array}{c} & & & \\ & & & \\ [apart from a factor \\ & & of - (9/2)s] \end{array}$	Y _{vv} ^(±2) [apart from a factor of 9s]			
A_1A_1	0	0	$2\langle\Theta\rangle_{v0}\gamma_{v0}^{(2)}$			
A_1E	$2\langle\Theta angle_{v1\gamma_{v1}}^{(1)}$	0	$2[\langle \Theta \rangle_{v1}\gamma_{v1}{}^{(2)}\pm \delta_{v1}{}^{(2)}]$			
EA_1	0	$2\langle\Theta angle_{v1}\gamma_{v1}$ ⁽¹⁾	$2\left[\left\langle\Theta\right\rangle_{v1}\gamma_{v1}^{(2)}\mp\delta_{v1}^{(2)}\right]$			
EE	$\langle \Theta \rangle_{v \mathfrak{d} \gamma_{v \mathfrak{l}}}^{(1)}$	$\langle \Theta \rangle_{v0} \gamma_{v1}{}^{(1)}$	$\langle \Theta angle_{v_0 \gamma_{v_1}^{(2)}} + \langle \Theta angle_{v_1 \gamma_{v_0}^{(2)}}$			
	$ \langle \Theta \rangle_{v\sigma} = (v\sigma \mid \Theta \mid v\sigma) $ $ \gamma_{t\sigma}^{(1)} = \begin{cases} \sum_{v'} \frac{\phi \Theta + \Theta \phi}{\Delta'} \\ \gamma_{t\sigma}^{(2)} = \begin{cases} \sum_{v',v''} \frac{\phi \phi + \phi}{\Delta'} \\ \delta_{v\sigma}^{(2)} = \frac{1}{2} [\gamma_{t\sigma}^{(1)}]^2 - \langle \Theta \rangle \end{cases} $	$\begin{cases} \\ \sigma \\ \frac{\Theta p + \Theta p p}{\Delta ' \Delta ''} - \langle \Theta \rangle_{v} \sum_{v'} \frac{p p}{(\Delta')^{2}} \\ \\ \Theta \rangle_{v\sigma} \langle p \rangle_{v\sigma} \sum_{v'} \frac{p \Theta + \Theta p}{(\Delta')^{2}} \end{cases}$	$-\langle p \rangle_{v} \sum_{v'} \frac{p \Theta + \Theta p}{(\Delta')^2} \bigg\}_{\sigma}$			

TABLE V. Definition of $Y_{vv}^{(\pm n)}$.

It is interesting to note that the $Y_{vv}^{(\pm 1)}$ contribution to $W_{vv}^{(\pm 1)}$ is percentagewise virtually identical to the $Y_{vv}^{(\pm 2)}$ contribution to the $W_{vv}^{(\pm 2)}$. Thus the problem of estimating V_3' for a two-top molecule is similar to the problem of estimating V_6 for a single-top molecule; in general, measurements for more than one torsional state are required. The vv = 11 state of a $(CH_3)_2$ -type isotopic species would, together with the vv=00 state, provide an excellent determination of V_3' as well as V_3 . However, rotational transitions from the 11 state would, in general, be weak and difficult to assign. For $(CD_3)_2$ -type molecules the study of the 11 state is more feasible, but it is likely that in molecules for which the present theory is applicable, no splittings would be observed for vv=00. The study of vv'=01 states is probably the best way to get at V_3' . However, the present treatment does not suffice to interpret rotational spectra arising from 01 states.

 $\Delta' = W_{v}{}^{(0)} - W_{v'}{}^{(0)}$

 $p\Theta = (v \mid p \mid v') (v' \mid \Theta \mid v)$, etc.

Unsymmetrical isotopic substitution can be used to get some information about V_3' without the necessity of studying excited torsional states. For the ground torsional state of a $(CH_3)_2$ -molecule species the ratio of $V_{00}^{(\pm n)}$ to $w_{00}^{(\pm n)}$ is roughly -1.7 to -1.8 in the range 30 < s < 100, while for $(CH_3) (CD_3)$ -type molecules the corresponding ratio (for the CH₃ group) is about -1.3. This difference is sufficient to obtain a crude estimate of V_3' from only ground-torsional-state rotational spectra.

II. MICROWAVE SPECTRUM OF DIMETHYL SILANE

1. Experimental

Samples of $(CH_3)_2SiH_2$ and $(CH_3)_2SiD_2$ were prepared by reducing $(CH_3)_2SiCl_2$ with LiAlH₄ and LiAlD₄ in ethyl ether at 0°C. $(CH_3)(CD_3)SiH_2$ was prepared by reacting CD_3MgI with CH_3SiH_2Cl in ethyl ether at 0°C. The CH_3SiH_2Cl was prepared in the manner described by Kilb and Pierce.¹⁶

Spectra were observed with a conventional Starkmodulated (100 kc) spectrometer employing phasesensitive detection. Frequency measurements were made with a crystal-controlled microwave frequency standard which was monitored by the 10 Mc WWV signal. Weak absorptions due to Si^{29,30} and C¹³ isotopic species were measured in natural abundance on a re-

TABLE VI. Formulas for $\langle \Theta \rangle_{v\sigma} \gamma_{v\sigma'}{}^{(n),\mathbf{a}}$ $B_n \langle \Theta \rangle_{v\sigma} \gamma_{v\sigma'}{}^{(n)} / W_{v\sigma'}{}^{(n)} = a + bs + c/s^{\mathbf{b}}$

п	υσ	$v\sigma'$	a	b	с
1	00	01	-1.7613	-0.0013124	2.4382
1	01	01	-1.8003	-0.0010086	3.5604
1	10	11	-6.0296	0.0043701	48.7719
î	ĨĬ	11	-5.6873	0.0019475	37.3250
-		••	010070	0.001/1/0	
2	60	00	-1 8744	-0.0000943	4 6211
2	01	01	-1 8510	-0.0005313	4 6724
2	10	10	-4 7380		15 5627
2	11	11	- 4.7300	0.0114064	6 8513
2	11	11	-4.3/4/	-0.0114004	0.0313
$B_n\{\langle \epsilon \rangle$) γ _{vσ} γ _{vσ} ⁽ⁿ⁾	$+\langle \Theta \rangle_{v\sigma}$	$\gamma_{v\sigma}^{(n)}\}/(W_{v\sigma}^{(n)})$	$(n) + W_{v\sigma'}(n) = 0$	$a+bs+c/s^{b}$
		,		7	_
n	$v\sigma$	むす	a	0	С
2	00	01	-1.9232	0.0004219	6.1163
2	10	11	-2.6808	-0.0285468	-34.4660

* For n=1, these formulas are accurate to 1% in the range $16 \le s \le 100$. For n=2, the formulas are accurate to about 3% in the range $20 \le s \le 60$. b $s=4V_3*/9F$. $B_1=-(9/2)s$, $B_2=9s$.

¹⁶ R. W. Kilb and L. Pierce, J. Chem. Phys. 27, 108 (1957).

cording potentiometer and may be uncertain by as much as ± 0.20 Mc. Spectra of the enriched isotopic species were displayed and measured on an oscilloscope with an estimated uncertainty of less than 0.05 Mc. Special effort was made to get accurate splittings, and for the enriched isotopic species the splittings are estimated to be uncertain by less than 0.02 Mc. Several absorption frequencies for $(CH_3)_2SiH_2$ and $(CH_3)-(CD_3)SiH_2$ were reported in a previous communication.⁷ These frequencies have been remeasured and the new values given here are somewhat more accurate.

2. Spectra and Dipole Moment

Apart from the fact that each rotational transition is a triplet (except in the case of $(CH_3)(CD_3)SiH_2$), the ground-state rotational spectrum of dimethyl silane is typical of an asymmetric rotor with "b"-type transitions. Below J=4 the transitions were positively identified by their character Stark effects. Transition frequencies for $(CH_3)_2SiH_2$, $(CH_3)_2SiD_2$, and $(CH_3) (CD_3)SiH_2$ are listed in Table VII.

The Q-branch series for these species cannot be reproduced very accurately with the rigid rotor approximation. Deviations of measured frequencies from the rigid rotor values are as large as 5 Mc in the case of the $6_{06} \rightarrow 6_{15}$ transition. No centrifugal distortion corrections

TABLE VII. Ground-state rotational transitions (Mc).*

Transition	$(\mathrm{CH}_3)_2\mathrm{SiH}_2\mathrm{b}$	(CH ₃) ₂ SiD ₂ ^b	$(CH_3) (CD_3) SiH_2^{\mathbf{c}}$
$1_{01} \rightarrow 1_{10}$	11 857.06 11 858.19 11 859.33	8 993.41 8 994.12 8 994.82	10 397.79 10 398.58
2 ₀₂ 2 ₁₁	12 978.49 12 979.76 12 981.03	10 112.93 10 113.72 10 114.53	11 309.18 11 310.02
3 ₀₃ 3 ₁₂	14 792.71 14 794.11 14 795.50	11 958.60 11 959.51 11 960.42	12 776.79 12 777.78
404 413	17 441.16 17 442.72 17 444.27	$\begin{array}{r} 14 \ \ 695.69 \\ 14 \ \ 696.75 \\ 14 \ \ 697.84 \end{array}$	14 909.62 14 910.75
5 ₀₅ 5 ₁₄	21 068.32 21 070.13 21 071.97	18 462.82 18 464.11 18 465.35	17 823.41 17 824.74
6 ₀₈ 6 ₁₅	25 771.55 25 773.65 25 775.75		21 604.75 21 606.33
000 111	21 649.82 21 651.08 21 652.35	18 438.12 18 438.86 18 439.63	19 082.67 19 083.52
212 303	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{c} 24 \ 013.39 \\ 24 \ 012.92 \\ 24 \ 012.43 \end{array}$	19 664.24 19 663.69

^a Estimated uncertainty: ±0.05 Mc.

^b The triplet components are listed in the order (A_1E+EA_1) , EE, A_1A_1 (according to the symmetry of the torsional sublevel).

• The doublet components are listed in the order E, A (in single-top notation).

TABLE VIII. Ground-state transitions measured in natural abundance (Mc).^a

Transition	$(CH_3)_2Si^{29}H_2$	(CH ₃) ₂ Si ³⁰ H ₂	(C ¹³ H ₃) (CH ₃) SiH ₂
4 ₀₄ →4 ₁₃	17 394.96 (17 396.51)ь (17 398.06)ь	17 353.41 17 354.68 17 356.26	17 180.01 17 181.68 17 183.30
5 ₀₅ 5 ₁₄	21 086.34 21 088.16 21 089.93	21 106.76 21 108.42 21 110.22	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
606 615			24 142.60 25 144.60 (25 146.60) ^b
0 ₀₀ 1 ₁₁	21 489.88 21 491.07 21 492.33	21 337.99 21 339.18 21 340.20	21 379.40 21 380.70 21 382.00

^a Estimated uncertainty: ±0.20 Mc.

^b Obscured by a nearby strong absorption line. Frequency estimated from splitting for a barrier of 1660 cal/mole.

have been applied. For these three species rotational constants have been calculated from the $O_{00}\rightarrow 1_{11}$, $1_{01}\rightarrow 1_{10}$ and $2_{02}\rightarrow 2_{11}$ transition frequencies (a small correction for internal rotation was applied to these frequencies). Centrifugal distortion effects are small for these low J transitions and in the structure analysis used here these small effects largely tend to cancel.

The measured spectra of $Si^{29,30}$ and C^{13} species are given in Table VIII. Since mostly high J transitions were measured for these species the rotational constants had to be calculated in a different manner. It was assumed that centrifugal distortion effects were for these species identical to those for the parent species, $(CH_3)_2$ -SiH₂. The transition frequencies thus empirically corrected were analyzed in the rigid rotor approximation. Rotational constants and moments of inertia are listed in Table IX.

The assignments of transitions to Si^{29,30} and C¹³ species were not confirmed by temperature dependence studies. However, in the case of the Si²⁹ and Si³⁰ isotopic species each transition can be used to calculate the b coordinate of the silicon atom, and all lines are in excellent $(\pm 0.0010 \text{ A})$ agreement with each other on the value of b_{Si} . Furthermore, the observed change in $I_a + I_b - I_c$ (see Table IX) when Si²⁹ or Si³⁰ replaced Si²⁸ is in the theoretically expected direction for an atom lying on or very near a principal axis.17 In the case of the C13 species the assignment of Table I gives, when Kraitchman's equations are used, a b coordinate for the carbon atom which is in excellent agreement with the value obtained from the first moment equation (see Sec. II. 3). In all three cases comparison of the Stark effect and triplet spacing with that of the parent species clearly indicated that J values were correctly assigned.

The dipole moment of dimethyl silane was determined from Stark effect measurements on the $O_{00} \rightarrow 1_{11}$

¹⁷ V. W. Laurie and D. R. Herschbach, Symposium on Molecular Structure and Spectroscopy, Ohio State University (1960).

Ξ

TABLE IX. Rotational constants (Mc) and moments of inertia (amu A2).

		a	b	с
(CH ₃) ₂ SiH ₂	1675	4.24 5	5945.44	4896.50
$(CH_3)_2Si^{29}H_2$	1660	6.85 5	5945.56	4883.83
$(CH_3)_2S_{130}H_2$	1640	7.26	945.50	4871.52
$(C^{13}H_3)(CH_3)SiH_2$	1660	5.08 5	5785.65	4775.22
$(CH_3)_2SiD_2$	1371	6.25 5	5749.07	4722.39
$(CH_3)(CD_3)SiH_2$	1474	0.79 5	5198.82	4342.47
	Ia	I_b	Ic	$I_a + I_b - I_c$
(CH ₃) ₂ SiH ₂	30.1733	85.0283	103.2433	11.9583
$(CH_3)_2Si^{29}H_2$	30.4411	85.0266	103.5111	11.9566
(CH ₃) ₂ Si ³⁰ H ₂	30,6992	85.0274	103.7727	11.9538
(C ¹³ H ₂) (CH ₂)SiH ₂	30 4444	87 3766	105.8654	11 9555
(CH _a) _a SiD _a	36 8563	87 9326	107 0498	17 3762
(CH.) (CD.) SH.	34 2047	07 2305	116 4155	15 1187
(C113) (CD3) 51112	54.2947	71.2393	110.4155	15.1107

^a Corrected for internal rotation effects. Conversion factor: 505 531 Mc amu A².

and $1_{10} \rightarrow 1_{01}$ transitions of the common isotopic species. The apparatus was calibrated with OCS. Using the dipole moment of OCS as determined by Marshall and Weber,18 the dipole moment of dimethyl silane was calculated to be $0.75 \pm 0.01D$.

3. Structure of Dimethyl Silane

The preferred method of calculating structures from ground-state rotational parameters involves the use of changes in moments of inertia with isotopic substitution rather than moments of inertia as such.^{19,20} The data obtained for dimethyl silane are more than sufficient to employ this technique. The coordinates [in the principal axis system of $(CH_3)_2SiH_2$ of the carbon and silicon atoms] were obtained from Kraitchman's equations.²¹ In the case of the carbon atom, changes in the a and b moments of inertia were used, while for the silicon atom the change in the *a* moment was used.

The various alternative combinations of ΔI 's give only slightly different values for the carbon and silicon coordinates simply because the change in $I_a + I_b - I_c$ is small for C13 or Si29,30 substitution and because the carbon and silicon coordinates are large (>0.5 A).

TABLE X. Atom coordinates $[(CH_3)_2SiH_2 \text{ principal axes}].$ (A)

	a	b	с
Si	0	0.5218	0
С	± 1.5385	-0.5351	0
H(Si)	0	1.3954	± 1.1983
$H_a(CH_3)$	± 1.5711	-1.1785	± 0.8857
H _s (CH ₃)	± 2.4400	0.0858	0

¹⁸ S. A. Marshall and J. Weber, Phys. Rev. 105, 1502 (1957).

¹⁹ C. C. Costain, J. Chem. Phys. **29**, 864 (1958).
 ²⁰ L. Pierce, J. Mol. Spectroscopy **3**, 575 (1959).
 ²¹ J. Kraitchman, Am. J. Phys. **21**, 17 (1953).

However, use of changes in a rather than c moments is preferable because of the fact that the former are more accurately determined.

Substitution of deuterium atoms for the silicon hydrogens produces a large change in $I_b + I_c - I_a$ (0.03 amu A). This change is much larger than the experimental uncertainties in the moments of inertia. Consequently, each of the coordinates adopted for these atoms is the average of coordinates calculated from two combinations of ΔI 's.

In calculating the coordinates of the methyl hydrogen atoms, it was assumed that methyl groups were symmetric with symmetry axes coincident with the SiC bond axes. The CH distance and HCH angles were then varied to give the best possible (least-square) fit of differences in moments of inertia between $(CH_3)_2$ -

TABLE XI. Structure of dimethyl silane.^a

				_
CSi	1.867±0.002 A	CSiC	110° 59′±10′	
SiH	$1.483{\pm}0.005~\mathrm{A}$	HSiH	107° 50′±20′	
CH	$1.095{\pm}0.005~\mathrm{A}$	нсн	108° 0′±20′	
	$2\theta^{\rm b} = 110^{\circ}$	$50'\pm 20'$		

Structural checks [(CH ₃) ₂ SiH ₂]				
	\mathbf{obs}	calc		
I_a (amu A ²)	30.0941	30.1733		
I_b	84.8421	85.0283		
Ic	102.7705	103.2433		
$\Sigma m_i b_i = 0.009$ amu A				

^a Conversion factor: 505 531 Mc amu A². Atomic masses taken from C. H. Townes and A. L. Schawlow, Microwave Spectroscopy (McGraw-Hill Book Company, Inc., New York, 1955).

^b 2θ = angle between the symmetry axes of the two methyl groups.

 SiH_2 and $(CH_3)(CD_3)SiH_2$. The fit obtained was excellent. Deviations were less than 0.01 amu A². Tilting the methyl group symmetry axes by as little as one degree resulted in a significantly poorer fit of the ΔI 's.

Coordinates of atoms in the $(CH_3)_2SiH_2$ principal axis system are given in Table X, and bond distances and angles in Table XI.

4. Internal Rotation Analysis

The operators \mathcal{P}_{\pm} in the case of $(CH_3)_2SiH_2$ and $(CH_3)_2SiD_2$ can be written

where

and

 $\alpha = \lambda_{z1} I_{\alpha} / I_{z} = -\lambda_{z2} I_{\alpha} / I_{z}$

$$\beta = \lambda_{x1} I_{\alpha} / I_x = \lambda_{x2} I_{\alpha} / I_x.$$

TABLE XII. Internal barrier calculations. Multiplet separation (Mc).^a

Transition	(CH ₃) ₂ SiH ₂ obs calc	$(CH_3)_2SiD_2$ obs calc	$(CH_3) (CD_3) SiH_2$ obs calc
$1_{01} \rightarrow 1_{10}$ $2_{02} 2_{11}$ $3_{03} 3_{12}$ $4_{04} 4_{13}$ $5_{05} 5_{14}$ $6_{06} 6_{15}$ $0_{00} 1_{11}$ $2_{12} 3_{03}$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
V_3 (cal/mole) ¹	⊳ 1649±3	1646 ± 3	1647 ± 3
2 <i>θ</i> °	110° 26′	111° 10′	110° 52′
I_{α} (amu A ²)	3.1635	3.1635	$\begin{cases} 3.1635 \ (CH_3) \\ 6.3221 \ (CD_3) \end{cases}$
F (kMc)	174.95	172.25	$\begin{cases} 173.01 \ (CH_3) \\ 94.91 \ (CD_3) \end{cases}$
F' (kMc)	-11.18	-8.69	-10.59
α	0.086113	0.070809	$\begin{cases} 0.073085 \ (CH_3) \\ 0.157128 \ (CD_3) \end{cases}$
β	0.021224	0.020334	$\begin{cases} 0.019850 \ ({\rm CH}_3) \\ 0.034002 \ ({\rm CD}_3) \end{cases}$
S	43.95	44.53	$\begin{cases} 44.37 \ (CH_3) \\ 80.89 \ (CD_3) \end{cases}$

^a Estimated uncertainty: <0.02 Mc.

^b Assuming $V_{3'}=0$.

^c 2θ =angle between symmetry axes of the methyl groups.

Because of the smallness of α and β , for the transitions of Table VII, the separation of internal and over-all rotation need only be carried out to second order, i.e., in Eq. (13) only terms with $n \leq 2$ need be retained.^{14,15} For J>3, Eq. (13) may further be simplified by dropping the n=1 term, in which case the effective rotational Hamiltonian has the pseudo-rigid rotor form

$$H_{vv} \approx H_r + FW_{vv}^{(2)} [\beta^2 P_x^2 + \alpha^2 P_z^2]. \tag{17}$$

(The terms which make $W_{vv}^{(2)} \neq W_{vv}^{(-2)}$ are negligibly small for dimethyl silane.) For J < 3, the rather small effect (0.06 Mc max) of the terms in αP_z may be exactly evaluated from equations given in references 2b or 16. In all cases the βP_x term is negligible.

The $X_{vv}^{(\pm n)}$ are for dimethyl silane completely negligible in comparison with the $w_{vv}^{(\pm n)}$. Assuming $V_3'=0$, the splittings are reproduced to within the small experimental uncertainty of ± 0.02 Mc by taking $V_3 = 1649 \pm 3$ cal/mole for $(CH_3)_2SiH_2$ and $V_3 = 1646 \pm 3$ cal/mole for $(CH_3)_2SiD_2$. The uncertainty of ± 3 cal/mole represents only the effect of errors in measurement of splittings. Uncertaintites in structural parameters, I_{α} in particular, could affect the value of V_3 by as much as 30 cal/mole.

In the case of $(CH_3)(CD_3)SiH_2$, if top-top coupling terms are ignored, the effective rotational Hamiltonian can be taken as the single-top Hamiltonian (11). This is so because tunnel effects due to the CD₃ group in the ground state are negligibly small. Analysis of the $(CH_3)(CD_3)SiH_2$ splittings yield a barrier $V_3 =$ 1647 ± 3 cal/mole, which is in excellent agreement with the values obtained for $(CH_3)_2SiH_2$ and $(CH_3)_2SiD_2$. The calculations for all three species are summarized in Table XII.

It was pointed out in Section I.4 that there is a small but significant difference in the $V_{vv}^{(\pm n)}$ contribution to $W_{vv}^{(\pm n)}$ for $(CH_3)_{2^-}$ and $(CH_3)(CD_3)$ -molecular species. This fact allows us to make a crude estimate of V_3' for dimethyl silane. For all three species the $W_{vv}^{(\pm n)}$ are believed to be experimentally determined with an accuracy of 1%. To within this accuracy the $W_{vv}^{(\pm n)}$ can be fitted by taking

$$V_3^* = 1647 \pm 3 \text{ cal/mole}$$

 $V_3' = 0 \pm 60 \text{ cal/mole}$
 $V_3 = 1647 \mp 120 \text{ cal/mole}.$

Table XII lists a value of 2θ for each of the three isotopic species. In analyzing the splittings, two parameters were used; V_3 and the ratio α/β . The calculated splittings are quite sensitive to α/β and thus to the angle between the symmetry axes of the tops and the principal axes of the molecule. The three values of 2θ are in excellent agreement with each other and give an average 2θ of $110^{\circ}50'\pm20'$ which is also in good agreement with 2θ as determined from changes in moments of inertia. Thus apart from a small experimental error, the methyl group symmetry axes can be said to be coaxial with their SiC bond axes.

ACKNOWLEDGMENTS

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