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Microwave spectrum of (trifluoromethyl)germane, CF_3GeH_3 *

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Microwave spectra of five isotopic species of CF_3GeH_3 have been investigated in the region 15 000 to 31 000 MHz. The height of the potential barrier hindering the internal rotation was determined to be 1280 ± 150 cal/mole, using the frequency method for rotational satellite transitions. The *sym–sym* case of hindered internal rotor molecules is discussed, and expressions are given for calculating barrier heights using tabulated quantities.

INTRODUCTION

(Trifluoromethyl) germane, CF_3GeH_3, is an example of the ethane-type series of molecules,[1] upon which much attention has been focused with regard to the theory of hindered internal rotation. It, further, is an example of the *sym–sym* case, with two coaxial symmetric internal rotors, comprising an overall symmetric-top molecule. The determination of the internal barrier height in such molecules, from their rotational spectra, has generally proved to be somewhat insensitive to the measured parameters, compared to the *sym-asym* cases, such as CH_3SiH_2F.

Three general approaches have been successfully used, by microwave spectroscopists, for various examples of these *sym-sym* molecules, as follows:

(1) *Intensity method.* Relative intensities for pure rotational transitions of molecules, assigned to the ground and excited torsional vibration states, are used in a Boltzmann factor expression, with an assumed barrier shape (sinusoidal potential, with Mathieu eigenvalues as torsional levels) to calculate the barrier height. Molecules studied by this technique include CH_3CF_3[2] and CF_3SiF_3.[3]

(2) *Frequency method.* This is a semiempirical treatment due to Kivelson[4] in which measured rotational transition frequencies for the ground and excited torsional states are directly fitted to an expression involving only the overall and internal rotation parameters, with other vibrations being treated as a lumped constant. This treatment is also applicable to, and more sensitive for those cases where the torsional satellites appear with observed $A-E$ frequency doublet separations, and has been re-examined by Kirtman.[5,6] The work described below, for CF_3GeH_3, employs this method, and explicit expressions are given for evaluating the parameters which appear in the theory, using quantities described and tabulated by Herschbach.[7] Other molecules for which this method has been used include CH_3SiH_3[4,6] and CH_3SiF_3.[5]

(3) *Asymmetric method.* If the overall molecular symmetry is destroyed by isotopic substitution, so that only a single symmetric internal rotor remains, the resultant molecule fits the (PAM) model,[8] for which, barrier dependent calculations involving $A-E$ frequency differences in both the ground and excited torsional states are described in detail in Ref. 7. This interesting technique has been employed for the molecules CH_3SiH_3 (CH_3SiH_2D)[9,7] and CH_3GeH_3 (CH_2DGeH_3).[10]

Each method brings to light its own inherent difficulties, and some direct comparisons can be found in Refs. 3 and 7. Perhaps the only safe comment is that for the typical high-barrier values of s presented by this series ($s > 20$), the frequency methods, (2) and (3), work best for those molecules which have one "light" internal top, i.e., for which the quantity I_α in the formulas involves three hydrogen atoms or, at most, three deuterons.

EXPERIMENTAL

A twofold excess of $BrCF_3$ was vacuum distilled into a solution of $KGeH_3$[11] in hexamethylphosphoramide. The contents of the vessel were warmed to 0 °C, stirred for 2 minutes, and the volatile products were separated by trap to trap fractionation. A copious yellow precipitate was observed as the solvent melted, indicating extensive decomposition of the reaction mixture. (Trifluoromethyl) germane (yield < 5%) passed through a trap held at − 130 °C and was condensed in one held at − 160 °C. The proton NMR of the product CF_3GeH_3 consists of a 1 : 3 : 3 : 1 quartet at $\tau = 5.87$ with $J_{H-F} = 8.7$ Hz; the ^{19}F NMR shows $J_{H-F} = 8.6$ Hz.

It should be noted that the intense microwave spectrum, characteristic of a symmetric-top molecule, described below, is corroborative of this synthesis.

(Trifluoromethyl) germane appears to be very stable when pure, showing little of the well-known tendency of electropositive metals to eliminate $:CF_2$ with the formation of a metal–fluoride bond.[12] The microwave spectrum of one sample which was left in the copper waveguide for over 2 weeks remained very intense.

The conventional Stark-modulated microwave spectrometer and frequency measuring apparatus described in Ref. 1 were employed. All measurements on CF_3GeH_3 were made with the waveguide absorption cell at room temperature.

OBSERVED SPECTRA

Pure rotational spectra were assigned to the five species of CF_3GeH_3, containing the naturally occurring isotopes $^{70,72,73,74,76}Ge$, as shown in Table I. After assignment of B_0 values, and the identification of the characteristic pattern of vibrational satellites described be-

TABLE I. Observed rotational transitions, in MHz[a], of CF_3GeH_3 isotopic species, showing the correspondence of vibrational satellite patterns. Schematic intensities for a pattern are shown in Fig. 1.

$J \leftarrow J'$	$J=5\leftarrow 4$		$6\leftarrow 5$		$7\leftarrow 6$		$8\leftarrow 7$	
Species	$CF_3{}^{72}GeH_3$	^{74}Ge	^{72}Ge	^{74}Ge	^{72}Ge	^{74}Ge	^{72}Ge	^{74}Ge
v = 0	19 242.70	19 056.00	23 091.95	22 866.44	26 939.74	26 677.27	30 788.30	30 487.25
γ_1			23 086.11	22 860.25	26 933.30	26 670.30		30 480.90
γ_2		19 046.00	23 080.50	22 854.80	26 926.54	26 663.34		
γ_3		19 039.98	23 073.60	22 848.27	26 919.05	26 655.87		
γ_4		19 034.95	23 065.49	22 841.10				
v = 1	19 217.98	19 030.80	23 061.62	22 836.19	26 904.46	26 642.15	30 748.61	30 448.09
•••				22 832.18				
$\beta_1+\gamma_1$		19 025.00		22 829.70		26 634.0[b]		
•••				22 826.16				
•••		19 017.88		22 822.00		26 625.5[b]		
•••				22 813.76				
v = 2	19 193.57	19 006.21	23 032.52	22 807.24	26 870.38	26 607.95	30 709.14	30 409.94
•••				22 802.48				
$\beta_2+\gamma_1$			23 023.56	22 799.39		26 598.75		
•••				22 791.4[b]				
•••				22 789.3[b]				
v = 3	19 170.60	18 983.32	23 005.45	22 779.80	26 838.41	26 576.35	30 672.30	30 372.99
•••		18 978.58				26 571.0[b]		
•••		18 972.61		22 770.39				
δ[c]		19 063.60	23 099.42	22 874.42		26 686.7[b]		

$J \leftarrow J'$	$4\leftarrow 3$			$5\leftarrow 4$	$6\leftarrow 5$	$7\leftarrow 6$
Species	^{70}Ge	^{72}Ge	^{74}Ge	^{70}Ge	^{70}Ge	^{70}Ge
v = 0	15 551.90	15 394.80	15 243.87	19 439.94	23 328.04	27 214.96
γ_1	15 547.94	15 390.93	15 240.32			27 209.52
γ_2			15 236.27	19 430.00	23 315.0[b]	
γ_3			15 232.11		23 310.0[b]	27 194.00
v = 1		15 373.83	15 223.89		23 297.25	27 181.51
v = 2		15 354.91	15 204.17	19 389.32	23 267.04	27 146.00
$\beta_2+\gamma_1$					23 260.33	27 137[d]
δ	15 557.0[b]	15 399.33				

$J \leftarrow J'$	$5\leftarrow 4$	$7\leftarrow 6$	$7\leftarrow 6$
Species	^{76}Ge	^{76}Ge	^{73}Ge
v = 0	18 875.95	26 426.20	26 806.5[b]

[a] Estimated uncertainty ± 0.15 MHz unless indicated.

[b] ± 0.5 MHz.

[c] Higher in frequency than the v = 0 line.

[d] ± 1 MHz.

low, attention was turned primarily to the intense ^{72,74}Ge species with regard to a detailed analysis of the internal barrier.

For each isotopic molecular species, a given rotational transition, $(J+1)\leftarrow J$, presents a complex pattern of vibrational satellites, i.e., pure rotational transitions of molecules which are in excited vibrational states, due to thermal population of those levels. These satellites fortunately cluster near the "main transition" which arises from molecules which are in the ground state for all vibrational modes. The complex pattern of frequencies, however, was regularly repeated, times the integer scale factor $2J$, for all observed transitions. Thus we have assigned to each isotopic species a set of effective rotational constants, B_{eff}, as shown for $CF_3{}^{74}GeH_3$ in Fig. 1, which, when multiplied by $2J$, reproduce the observed transition frequencies, with characteristic relative intensities. The subscript "eff" thus pertains to the *set* of $3N-6$ molecular vibrational quantum numbers, from which we have been able to extract two series, one of which is the torsional mode involving the barrier to internal rotation.

In Fig. 1 we have adopted the Greek letter notation used by Kirtman for his Fig. 1 of Ref. 5, in which β refers to the torsional mode. We also use the notation "v" to refer specifically to this torsional quantum number, following Herschbach[7]; thus $\beta_2 \equiv (v=2)$. For the parameters described by Kivelson[4] we use the modified[5] notation $\mathcal{B}_{\mathcal{V}}$, $\mathcal{F}_{\mathcal{V}}$, $\mathcal{G}_{\mathcal{V}}$, etc., where the subscript "$\mathcal{V}$" refers to all vibrational modes *except* the torsional mode.

The intense series, labelled β, was assigned to the torsion and is discussed in the following section. The closely-spaced series labelled γ also admit of straightforward assignment to another low frequency vibration, which also seems to appear in combination with the excited torsional states $(\beta_1+\gamma_1)$, etc., although the observed signal/noise ratio causes the latter "assignment"

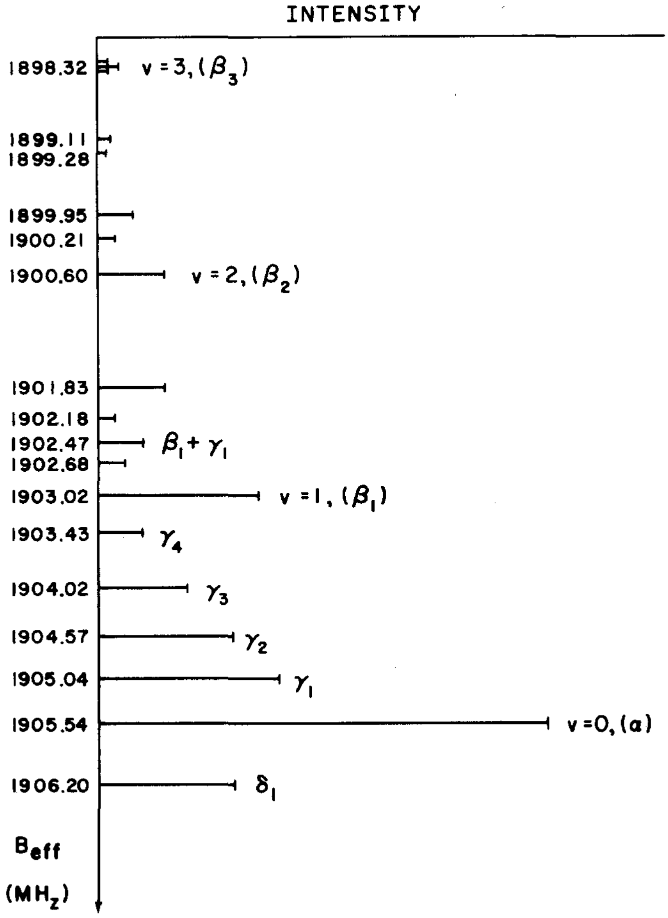

FIG. 1. Schematic intensities and values of B_{eff} for the vibrational satellite pattern of the most abundant species, $CF_3{}^{74}GeH_3$. Values of B_{eff} times the appropriate integer $2J$ reproduce the observed transitions to ±1 MHz.

to be rather speculative. The satellite γ_1 is observed to be slightly more intense than β_1, indicating that the corresponding molecular vibrational frequency is very low, perhaps ~90 cm^{-1}. Only one transition, labelled δ was consistently observed above the main transition.

In Table I the $J = 6 \leftarrow 5$ transition of $CF_3{}^{74}GeH_3$ is taken to be "the pattern," and other observed frequencies are listed in correspondence to this, rather than to use a further arbitrary labelling.

BARRIER TO INTERNAL ROTATION

The barrier to internal rotation, V_3, is expressed in terms of a parameter in the Mathieu equation, s, and the inverse reduced moment of inertia of the internal rotor[7] for the specific molecular species, F, as:

$$s = (\tfrac{4}{9})(V_3/F) \ . \tag{1}$$

The value of s is calculated from an expression given by Kivelson in Ref. 4 as Eq. (27) and by Kirtman in Ref. 5 as Eq. (106),[13] in which the matrix elements have been replaced by appropriate quantities described by Herschbach.[7] Frequencies of the rotational transitions for the ground state and for the pure torsional "v" states (labelled β in Fig. 1), become, in this hybrid notation,

$$\nu_{Jv\sigma} = 2J(B_{eff}) \tag{2}$$

where the appropriate

$$B_{eff} = B_{v\sigma} = \mathcal{B}_{\mathrm{v}} + \mathcal{F}_{\mathrm{v}}\left(\frac{8}{9}\right)\left(\frac{dW_{v\sigma}^{(0)}}{ds}\right) + \mathcal{G}_{\mathrm{v}}\left[W_{v\sigma}^{(0)} - s\left(\frac{dW_{v\sigma}^{(0)}}{ds}\right)\right] \tag{3}$$

and the new subscript σ refers to the possibility of allowed $A-E$ symmetry doublets, for the excited torsional states. Note that, as for CF_3GeH_3, when $A-E$ doubling is not observed (resolved), and the A and E expressions for (3) are effectively equal, the internal barrier may still be derived from the s dependence.

For cases where a given torsional satellite appears with a resolved $A-E$ splitting, it simply affords two separate equations (3) for the algebraic system described below, or alternately, a doublet splitting may be expressed explicitly as

$$\Delta\nu_{J,v,A-E} = 2J\Delta B_{v,A-E} \tag{4}$$

where

$$\Delta B_{v,A-E} = \left[\left(\frac{dW_{vA}^{(0)}}{ds}\right) - \left(\frac{dW_{vE}^{(0)}}{ds}\right)\right]\left[\left(\frac{8}{9}\right)\mathcal{F}_{\mathrm{v}} - s\mathcal{G}_{\mathrm{v}}\right] + \mathcal{G}_{\mathrm{v}}(W_{vA}^{(0)} - W_{vE}^{(0)}) \ . \tag{5}$$

Expressions (4) and (5) are also useful for predicting splittings for higher torsional states.

It should be noted that these expressions, due to approximations employed in the diagonalization of the vibration–rotation coupling Hamiltonian, apply only to states with the rotational quantum number K = 0, or for which the K degeneracy is unbroken, and only to molecular cases for which possible low frequency vibrational modes other than the torsion do not significantly perturb the torsional satellites.[5,6]

For CF_3GeH_3 both K and σ splittings were unobserved, so that, in the following, we refer to the basic Expression (3). In this expression the $W_{v\sigma}^{(0)}$ are tabulated by Herschbach[7] only for v = 0, 1, 2 (in Appendix C). In general, they arise from a Fourier cosine series expansion of the rotation–vibrational levels, first done by Koehler and Dennison[14]:

$$W_{v\sigma}^{(0)} = \frac{9}{4}\sum_{l=0}^{\infty} w_l \cos l(\theta - \theta_0) \ . \tag{6}$$

For the case of the projection quantum number K = 0, one sets $\theta = 0$, and the value of θ_0 determines the A or E type solutions as:

$$\theta_0 = -(2\pi\sigma/3), \begin{cases} \sigma = 0, & \text{for } A \text{ type,} \\ \sigma = \pm 1, & \text{for } E \text{ type.} \end{cases}$$

We calculated only for A-type transitions where

$$W_{vA}^{(0)} = (\tfrac{9}{4})(w_0 + w_1 + w_2 + \cdots) \tag{7}$$

and the w's are sums of Mathieu eigenvalues, given in Ref. 7, Eq. (21). For the high barrier case, to a good approximation

$$W_{vA}^{(0)} = (9/4)b_1 \ ,$$

where b_1 is simply the Mathieu eigenvalue corresponding to a solution of period π, $(\theta = 0, \ \theta_0 = 0)$.

TABLE II. Rotational constants and parameters used in the internal rotation calculations.

Species	B_0
$CF_3{}^{70}GeH_3$	1943.97 MHz
$CF_3{}^{72}GeH_3$	1924.269 MHz
$CF_3{}^{73}GeH_3$	1914.75 MHz
$CF_3{}^{74}GeH_3$	1905.530 MHz
$CF_3{}^{76}GeH_3$	1887.59 MHz

	$CF_3{}^{72}GeH_3$	$CF_3{}^{74}GeH_3$
B_1[a]	1921.767 MHz	1903.015 MHz
B_2	1919.317	1900.587
B_3	1917.024	1898.315
I_α (GeH_3)	6.292 amu Å^2[b]	
F	85,500 MHz[b]	
$\mathcal{B}_v$	1925.537 MHz	1906.811 MHz
$\mathcal{F}_v$	−8.0654 MHz	−7.6565 MHz
$\mathcal{G}_v$	−0.03277 MHz	−0.04138 MHz
s	67 ± 10	70 ± 10
V_3	1280 ± 150 cal/mole	

[a] B_v values for torsional states.

[b] Same for both species; from assumed molecular structure.

For CF_3GeH_3, with $s \simeq 70$, Eq. (5) indicates no resolvable $A-E$ doublets, even for $v = 3$ states. Thus, to solve for s, $\mathcal{B}_v$, $\mathcal{F}_v$, $\mathcal{G}_v$ in Eq. (3) one must use four torsional states for a given J transition, to yield the effective rotational constants $B_v = B_0, B_1, B_2, B_3$. The first three B_v values and an assumed value for s were used in a system of equations (3) to solve for $\mathcal{B}_v$, $\mathcal{F}_v$, $\mathcal{G}_v$, and then to predict a value for B_3. The observed B_3 was fitted by repeating this procedure after allowing the implicit variable s to change by iterative amounts. Note that each time s is allowed to change, a different set of $\mathcal{B}_v$, $\mathcal{F}_v$, $\mathcal{G}_v$ values, which are treated as empirical parameters, is obtained. In solving the algebraic system of equations of type (3), much of the experimental accuracy is subtractively lost, and this results in the large quoted uncertainty in the final value for s.

The derivative $dW^{(0)}/ds$ was evaluated by differencing the logarithms of values of $W^{(0)}$ obtained from tables[15] of the Mathieu eigenvalue b_1, to ten significant figures and for $\Delta s = 2$. In particular, for $s' < s < s''$,

$$\frac{dW^{(0)}(s)}{ds} = W^{(0)}(s)\left(\frac{\ln[W^{(0)}(s'')/W^{(0)}(s')]}{s''-s'}\right). \tag{8}$$

Values of b_1 for $v = 0$ (b_{e0}) and $v = 1$ (b_{o2}) may be found in other sources.[16]

Molecular parameters for $CF_3{}^{72}GeH_3$ and $CF_3{}^{74}GeH_3$ shown in Table II afford a calculated $V_3 = 1280 \pm 150$ cal/mole, with this rather large uncertainty. As mentioned above, no $A-E$ splittings were observed for any transition, so that Expressions (4) and (5) could not be employed. The reported uncertainty is derived from the rotational measurements, where we make the assumption of Ref. 4, that there is no significant perturbation of the torsional states from other vibrations, such as γ.

It is interesting to compare the two alternative approaches for this specific *sym–sym* molecule. The asymmetric method is impractical for CF_3GeH_3, apart from the synthetic difficulties. Only the GeH_3 group can be substituted, and the resultant species, such as CF_3GeH_2D, would have a "heavy" symmetric internal rotor giving rise to negligible $A-E$ differences in the spectrum for the overall asymmetric molecule.

The relative intensity method is less sensitive than the frequency method, for this particular range of the parameter s. If we define an intensity ratio, R, for the torsional satellite lines compared to the ground state (e.g., $v = 1$ to the $v = 0$) or for any pair of satellites (e.g., $v = 2$ to $v = 1$), then

$$\ln R = 9F\Delta b/4kT\ ,$$

where Δb refers to the appropriate Mathieu eigenvalues. For CF_3GeH_3 at $T = 300\,^\circ K$, this ratio for the $v = 1$ to $v = 0$ is calculated to be $R = 0.613$ for $s = 72$, and $R = 0.608$ for $s = 74$. Thus to obtain even the rather limited accuracy for V_3 reported above (±15%), relative intensity measurements accurate to about 5% would be necessary, and this appears to be a rather stringent requirement.[17] The relative merits of these two methods depend strongly, however, on the specific value of s presented by a molecule, i.e., for each of the two methods, the uncertainty in s depends in a complicated way on the values of Δb.

DISCUSSION

Data for relatively few ethane-type molecules with partially fluorinated *carbon* atoms are available, presumably partly due to the difficulty of their chemical synthesis. Schwendeman and Jacobs[18] have observed that such halogen substitution for methyl silanes (CH_2ClSiH_3) leads to an increase in the potential barrier from that of the "parent" molecule. This was also found[1] for the methyl germane species CH_2FGeH_3. The present work, however, indicates that this trend cannot be extrapolated to the fully fluorinated case CF_3GeH_3, for which the barrier, although unfortunately relatively inaccurately determined, appears to be nearly identical to that for the parent molecule, CH_3GeH_3.[10]

It would be very interesting to be able to derive an internal barrier height for those molecules in the excited vibrational state γ_1, from a Kivelson type treatment of the satellites ($\gamma_1, \beta_1+\gamma_1, \beta_2+\gamma_1, \beta_3+\gamma_1$), as discussed in Ref. 6. Experimental conditions and the available sample, unfortunately, do not afford such a study at present.

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