Effect of fluorination on methyl internal rotation barriers: Microwave spectra of cyclopropylfluoromethyl silane (*c*-C₃H₅SiHFCH₃) and cyclopropyldifluoromethyl silane (*c*-C₃H₅SiF₂CH₃)

Rachel E. Dorris,^{a)} Bailey C. Luce,^{a)} Sarah J. Stettner,^{a)} Rebecca A. Peebles,^{a)} Sean A. Peebles,^{a)*}

John L. Bullard,^{b)} James E. Bunn,^{b)} Gamil A. Guirgis^{b)}

^{a)} Department of Chemistry, Eastern Illinois University, 600 Lincoln Avenue,

Charleston, IL 61920, USA

^{b)} Department of Chemistry and Biochemistry, College of Charleston, Charleston, SC 29424,

USA

* Corresponding author Tel: (217) 581-2679 Email: sapeebles@eiu.edu

Abstract

Rotational spectra for two conformers of *c*-C₃H₅SiHFCH₃ (cyclopropylfluoromethyl silane, CFMS) and one conformer of *c*-C₃H₅SiF₂CH₃ (cyclopropyldifluoromethyl silane, CDFMS) have been observed by a combination of chirped-pulse and resonant cavity Fourier-transform microwave spectroscopy in the 7.5–16.5 GHz range. All rotational transitions were doubled by up to several megahertz into *A* and *E* states as a result of methyl group internal rotation, and analysis of measured transitions using a combined axis method yielded internal rotation barriers of *ca.* 6.0 kJ mol⁻¹ for the two conformers of CFMS and *ca.* 5.2 kJ mol⁻¹ for CDFMS, revealing a systematic decrease in the barrier as fluorine atoms are added to the silicon. Dipole moment information is also available for the CDFMS species.

Keywords: combined axis method, chirped-pulse FTMW spectroscopy; resonant cavity FTMW spectroscopy; Stark effect; ab initio optimizations; conformers

Introduction

Previous microwave [1] and IR [2] work explored conformational properties of cyclopropylmethylsilane ($c\text{-C}_3\text{H}_5\text{SiH}_2\text{CH}_3$, CMS) and its germanium analog cyclopropylmethylgermane ($c\text{-C}_3\text{H}_5\text{GeH}_2\text{CH}_3$, CMG) [3,4]. The microwave studies revealed that only a single conformer was observed for both molecules and that the methyl group internal rotation barrier was lower in the Ge species than in the Si species. In this work we present rotational spectroscopic assignments for two fluorinated analogs of CMS: cyclopropylfluoromethyl silane ($c\text{-C}_3\text{H}_5\text{SiHFCH}_3$, CFMS) and cyclopropyldifluoromethyl silane ($c\text{-C}_3\text{H}_5\text{SiF}_2\text{CH}_3$, CDFMS). Rotation about the Si—C(cyclopropyl) bond in both compounds gives rise to three possible staggered arrangements. In CDFMS two of these structures will be equivalent conformers with one F atom located over the cyclopropyl ring, with the third structure having the methyl group in that position, while in CFMS the H, F, or methyl group can be located over the cyclopropyl ring, leading to three unique conformers. In the present paper, relative stabilities of these different conformers will be assessed by ab initio calculations and any species present in a supersonic expansion will be characterized via their rotational spectra.

In addition, characterization of the title compounds provides a series of related molecules with none (CMS) [1], one (CFMS) or two (CDFMS) F atoms on the central Si atom, allowing examination of the effect of this fluorination on the barrier to internal rotation of the methyl group. In previous studies of methyl silane and its fluorinated analogs [5,6,7], fluorination was found to reduce the barrier, whereas monofluorination of the all-carbon analog, ethane, actually increases the barrier (see, for example, Table XI in Ref. [8]). Unfortunately, the all-carbon analog for CMS, ethylcyclopropane, is expected to have a small (<0.1 D) dipole moment,

making it poorly suited for microwave characterization, hence only IR and Raman data [9] is available; no data on fluorine substituted ethylcyclopropanes exists.

The goal of the present study is therefore to identify which conformers are present in the supersonic expansion and to characterize their rotational spectra to furnish values for the barrier to methyl group rotation in each case to see how it varies as the degree of fluorination at the silicon atom is changed.

Experimental

Microwave spectroscopic measurements

Samples of cyclopropylfluoromethyl silane (CFMS) and cyclopropyldifluoromethyl silane (CDFMS, CAS Registry Number 57522-86-8) were synthesized and purified at the College of Charleston, South Carolina, as described below, and then sent to Eastern Illinois University for microwave spectroscopic measurements. Rotational spectra for a single conformer of CDFMS and two conformers of CFMS were measured using both a 480 MHz bandwidth chirped-pulse [10] Fourier-transform microwave (FTMW) spectrometer (a scaled-down version of the original design by Pate [11]), and a Balle-Flygare type [12] resonant cavity FTMW spectrometer [13]. Initial scans over the 8-16 GHz region were carried out using the chirped-pulse spectrometer, with a total of 2,000 free induction decays averaged within each 480 MHz frequency segment. Absolute transition frequencies were obtained from a LabView program which compares overlapping spectral segments that are offset by 240 MHz, and assembles the resulting scans into a full broadband spectrum. Gas samples for both molecules consisted of approximately 1% of the molecule of interest seeded in He/Ne (17.5% / 82.5%,

BOC Gases) and delivered to a General Valve Series 9 valve at a total pressure of 2.5 atm. In both chirped-pulse and resonant cavity instruments, the gas sample was introduced into the vacuum chamber perpendicular to the direction of microwave propagation, resulting in transitions with full-widths at half maximum height of around 130 kHz (chirped-pulse instrument) and 30 kHz (resonant cavity instrument). In both cases, transition frequencies were reproducible to 4 kHz or better. Once initial spectral assignments were made from the broadband scan, transitions were remeasured on the resonant cavity instrument to ensure all fine splittings were identified, and to allow measurement of less intense transitions.

Dipole moment measurements were carried out only for CDFMS (since this had more intense transitions) using a pair of steel mesh plates spaced ~31 cm apart and straddling the gas expansion in the resonant cavity instrument. Electric fields of up to approximately 330 V / cm were applied, and were calibrated using the $J = 1 \leftarrow 0$ transition of OCS, assuming a dipole moment of 0.71519(3)D [14].

Synthesis

The samples of *c*-C₃H₅SiHFCH₃, and *c*-C₃H₅SiF₂CH₃ were prepared in two steps. Firstly, cyclopropylbromide was reacted with magnesium in dry ether using the Grignard method and then coupled with methyldichlorosilane or methyltrichlorosilane in dry ether under dry nitrogen gas. Secondly, the product methyldichlorosilylcyclopropane or methylchlorosilylcyclopropane were obtained, respectively and were separated from the ether under reduced pressure and then fluorinated with freshly sublimed antimony trifluoride without solvent. The samples were purified twice by trap-to-trap distillation. The authenticity of the

samples were verified by comparing the infrared, ^1H , ^{13}C , and ^{29}Si NMR, and microwave spectra.

Ab initio calculations

Initial rotational spectroscopic assignments for both compounds were guided by rotational constants obtained from ab initio optimizations using the Gaussian 09 [15] program suite at the MP2/6-311++G(2d,2p) level. No symmetry constraints were imposed during structure optimizations and default optimization thresholds were used. Harmonic vibrational frequency calculations provided zero-point energy corrected energies for identification of the most stable conformers. Principal axis coordinates for all five conformers considered for the two molecules are available as Supplementary Material.

Results

I. Ab initio optimizations

For the doubly fluorinated CDFMS, rotation around the Si–C(cyclopropyl) bond leads to only two possible staggered conformations, with either a fluorine atom (conformer A1, Figure 1) or methyl group (A2, Figure 1) over the cyclopropyl ring. As can be seen from the relative energies in Table 1, conformer A1 is predicted to be most stable, and dipole moment predictions suggest that transitions arising from all three dipole components should be easily visible in the rotational spectrum. Conformer A2, although having similar rotational constants to conformer A1, should be readily distinguishable from A1 based on its quite different dipole moment components.

Conformer A1

Conformer A2

Figure 1 Ab initio conformers A1 and A2 for cyclopropyldifluoromethyl silane (CDFMS).

For the singly fluorinated CFMS, Figure 2 shows the three possible staggered conformers that result from rotation about the Si–C(cyclopropyl) bond, with an H atom (conformer B1), F atom (conformer B2) or methyl group (conformer B3) situated over the cyclopropyl ring; conformer B1 is predicted to be most stable (Table 1). These three conformers should be readily distinguishable by their rotational constants and dipole moment components.

Conformer B1

Conformer B2

Conformer B3

Figure 2 Ab initio conformers B1, B2, B3 for cyclopropylfluoromethyl silane (CFMS).

Table 1 MP2/6-311++G(2d,2p) predicted values of rotational constants, dipole moment components and zero-point corrected relative energies for the lowest energy conformers of cyclopropyldifluoromethyl silane (CDFMS) and cyclopropylfluoromethyl silane (CFMS).

Parameter	CDFMS		CFMS		
	Conformer	Conformer	Conformer	Conformer	Conformer
	A1	A2	B1	B2	B3
A / MHz	3229	3119	4754	4689	4462
B / MHz	1589	1530	1915	2009	2004
C / MHz	1489	1511	1504	1735	1693
μ_a / D	1.11	2.38	1.15	0.32	1.69
μ_b / D	1.81	0.0	1.66	1.79	1.16
μ_c / D	1.28	1.34	0.21	0.32	0.27
ΔE_{ZPE} / cm^{-1} ^{a)}	0	133	0	61	88

^{a)} ΔE_{ZPE} is the zero-point energy corrected relative energy.

II. Rotational spectra

The spectrum for CDFMS was scanned first since it was expected to be more intense due to larger predicted dipole moment components and the expectation that only a single conformer would likely be observed (Table 1). Patterns consistent with expected transitions for conformer A1 were located in the broadband scan close to predicted frequencies. Many transitions exhibited a small doubling (by up to 5 MHz) due to internal rotation of the methyl group; most of these fine splittings were sufficiently large to observe in the original broadband scan, although some required the higher resolution of the resonant cavity spectrometer to fully resolve (Figure 3). After identification of the lowest energy conformer of CDFMS, a large number of additional transitions remained in the spectrum. These were eventually assigned to the most stable

conformer B1 of CFMS (see Table 1) which was present as an impurity in the original CDFMS sample.

Figure 3 Comparison of a rotational transition belonging to the lowest energy conformer (B1) of CFMS measured on both the chirped-pulse (2,000 averages) and resonant cavity Fourier-transform (50 averages) microwave spectrometers. The higher resolution of the resonant cavity instrument is clearly apparent; the smaller doubling on this instrument's measurements arises from the Doppler effect.

For CDFMS, higher transition intensity allowed spectra for much lower abundance ^{29}Si (4.68%) and ^{30}Si (3.09%) isotopologues to be observed in natural abundance on the resonant cavity instrument, although these transitions were still quite weak and hence only a limited number of transitions were measurable. Unfortunately, given the much lower intensity of transitions for CFMS, only the parent (^{28}Si , 92.23%) isotopologue was observable for the two conformers of that species.

All measured rotational transition frequencies were fitted with the XIAM program [16] using a combined axis method which permits simultaneous fitting of A and E internal rotation states. Due to correlations between fitted parameters, it was necessary to fix some spectroscopic

parameters to values obtained from ab initio calculations, or to previous literature data. To facilitate comparison with the CMS species [1], the F_0 value was fixed in all present fits at a value of 159.0 GHz (derived from a methyl group moment of inertia of $3.178 \text{ u } \text{\AA}^2$).

Determination of the parameters δ (angle between the internal rotation axis, i , and a principal axis) and ϵ (angle between b principal axis and the projection of i into the bc plane) was not always possible with the current data set, so some of these parameters were also fixed at ab initio values (see Tables 2 and 3). Even with the constraints imposed on some internal rotation parameters, it was not possible to obtain satisfactory fits without varying some parameters that were correlated; thus for CDFMS there is a strong correlation between V_3 and δ , and for CFMS there are correlations between the rotational constants and Δ_J (conformer B1) and Δ_K (conformer B2). Fitted spectroscopic parameters are presented in Tables 2 (CDFMS) and 3 (CFMS) and lists of all observed rotational transition frequencies for both species are included as Supplementary Materials.

Table 2 Fitted spectroscopic parameters for isotopic species of conformer A1 of cyclopropyldifluoromethyl silane.

Parameter ^{a)}	²⁸ Si	²⁹ Si	³⁰ Si
A / MHz	3253.8315(10)	3253.8190(5)	3253.8101(8)
B / MHz	1592.54587(21)	1590.75873(25)	1589.00851(21)
C / MHz	1493.41354(28)	1491.85141(28)	1490.31886(25)
V_3 / kJ mol ⁻¹ ^{b)}	5.2327(26)	5.218(7)	5.2750(43)
ε / radians ^{c)}	0.242192(fixed)	0.242019(fixed)	0.24185(fixed)
δ / radians	0.9537(17)	0.964(5)	0.9940(27)
$\angle(i, a)$ / degrees ^{d)}	54.64(10)	55.22(28)	56.95(15)
$\angle(i, b)$ / degrees	37.65(9)	37.12(25)	35.53(14)
$\angle(i, c)$ / degrees	78.72(1)	78.65(4)	78.42(2)
N_A, N_E ^{e)}	32,28	13,10	5,7
σ / kHz ^{f)}	2.5	3.4	1.6 ^{g)}

- a) Centrifugal distortion constants were determined for the parent (²⁸Si) isotopic species and then fixed at the following values during fitting of the ²⁹Si and ³⁰Si isotopologues: $\Delta_J = 0.1907(41)$ kHz, $\Delta_{JK} = 1.398(14)$ kHz, $\Delta_K = -1.22(18)$ kHz, $\delta_J = 0.0266(36)$ kHz.
- b) Reported uncertainties are propagated errors from the least-squares fit. A more realistic uncertainty in V_3 , based on possible variation of ε , is ± 0.01 kJ mol⁻¹.
- c) The angle ε was fixed at ab initio values (see text for details and an explanation of these parameters) and F_0 was fixed to 159.0 GHz (consistent with $I_a = 3.17848$ u Å², as used in previous fits of CMS [1] and CMG [3]).
- d) The angles $\angle(i, a)$, $\angle(i, b)$ and $\angle(i, c)$ are angles between the internal rotation axis (i) and the a , b , and c principal axes (and are determined from ε and δ).
- e) N_A and N_E are the numbers of fitted A and E state transitions, respectively.
- f) Standard deviation of the (observed – calculated) transition frequencies.
- g) The small data set for the ³⁰Si isotopologue leads to unrealistically small errors in fitted parameters and hence these parameters should be interpreted loosely.

Table 3 Fitted spectroscopic parameters for the most abundant ^{28}Si isotopologue of two conformers of cyclopropylfluoromethyl silane.

Parameter ^{a)}	Conformer B1	Conformer B2
A / MHz	4789.4614(11)	4718.3712(22)
B / MHz	1924.8239(7)	2006.0952(14)
C / MHz	1513.3495(5)	1733.0811(7)
Δ_J / kHz	0.272(15)	0.610(30)
Δ_{JK} / kHz	2.254(30)	-
Δ_K / kHz	0.48(7)	4.52(12)
δ_J / kHz	0.080(7)	0.112(8)
δ_K / kHz	1.91(14)	-0.73(17)
V_3 / kJ mol ^{-1 b)}	5.95846(32)	6.01091(32)
ε / radians	0.298272(fixed)	0.623494(fixed)
δ / radians	0.949453(fixed)	0.818788(fixed)
$\angle(i, a)$ / degrees ^{c)}	54.40	46.91
$\angle(i, b)$ / degrees	39.00	53.63
$\angle(i, c)$ / degrees	76.18	64.76
N_A, N_E ^{d)}	28,30	16,18
σ / kHz ^{e)}	4.2	4.2

- a) The internal rotation parameter F_0 was fixed at the ab initio value of 159.0 GHz (consistent with $I_\alpha = 3.17848 \text{ amu } \text{\AA}^2$, as used in previous fits of CMS [1] and CMG [3]). Angles ε and δ were also fixed at ab initio values for conformers B1 and B2 of CFMS.
- b) Reported uncertainties are propagated errors from the least-squares fit. A more realistic uncertainty in V_3 , based on possible variation of ε and δ , is $\pm 0.15 \text{ kJ mol}^{-1}$.
- c) Derived from angles ε and δ , hence these angles are computed directly from ab initio results.
- d) N_A and N_E are the numbers of fitted A and E state transitions, respectively.
- e) Standard deviation of the (observed – calculated) transition frequencies.

III. Dipole moment

Stark effect data from measurements of eight M components belonging to 6 different rotational transitions (for a total of 44 measurements) for CDFMS were fit using the QSTARK program [17,18] and resulted in dipole moment components listed in Table 4. Rotational and centrifugal distortion constants were fixed at values given in Table 2 during this fit and frequency shifts were least-squares fitted to dipole moment components. The dipole moment components are consistent with those predicted for the most stable conformer A1. Due to significantly weaker rotational transitions, dipole moment measurements were not carried out on either conformer of the CFMS species.

Table 4 Experimental dipole moment components for cyclopropyldifluoromethyl silane.

Parameter	Value
μ_a / D	1.026(4)
μ_b / D	1.702(3)
μ_c / D	1.126(4)
$N^{\text{a)}$	44
$\sigma / \text{kHz}^{\text{b)}$	4.9

^{a)} N is the number of individual Stark measurements used in the fit.

^{b)} Standard deviation of the fit.

IV. Kraitchman single isotopic substitution analysis

Measurement of spectra for singly isotopically substituted species of CDFMS allows calculation of principal axis coordinates for the silicon atom via Kraitchman's equations [19] as implemented in the KRA program [18]. Table 5 summarizes these results (using both ^{29}Si and ^{30}Si data), where the coordinates are compared to those obtained directly from ab initio optimized structures. In reality, only the a coordinate is sufficiently large to be completely trustworthy, although agreement between this and the ab initio value is good. The b coordinates from the Kraitchman analysis are imaginary, but c agrees reasonably well, especially in light of the small magnitude of this coordinate. Also, despite the large uncertainty in the c -coordinate from ^{29}Si and ^{30}Si substitution, the two values are in excellent agreement with each other. Again, lack of transition intensity for the parent species of the two conformers of CFMS precluded identification of spectra for ^{29}Si and ^{30}Si isotopologues for this species.

Table 5 Principal axis coordinates for the silicon atom in CDFMS determined from application of Kraitchman's equations.^{a)}

	$a / \text{\AA}$	$b / \text{\AA}$	$c / \text{\AA}$
^{29}Si	-0.5985(25)	0.028(53) i	0.037(40)
^{30}Si	-0.5986(25)	0.026(57) i	0.035(43)
Ab initio	-0.600630	-0.026040	0.054315

^{a)} Each coordinate has three entries: coordinates calculated independently from the ^{29}Si and ^{30}Si isotopic substitutions, and ab initio (MP2/6-311++G(2d,2p)) results. Error estimates for the coordinates are Costain errors, derived in reference [20]. Signs are assumed based on the ab initio structure.

Discussion

The agreement of rotational constants obtained from fitting the CDFMS spectrum (Table 2) with those predicted by ab initio (Table 1) for conformer A1 indicate that this is the species likely present in our supersonic expansion, with fitted values of B and C lying within only a few megahertz of the prediction. This conformer's assignment can be further confirmed by an inspection of predicted (Table 1) and measured (Table 4) dipole moment components, which suggest that conformer A2 can be safely eliminated as an option, given that transitions arising from all three dipole moment components were observed. Ab initio estimates at the MP2/6-311++G(2d,2p) level seem to show the usual slight overestimate of predicted dipole moments that we have seen in much of our recent work with weakly bound dimers.

Although some internal rotation parameters had to be fixed at ab initio values during the fitting process, a limited amount of structural data is available from examination of the δ angle (which was determinable for all three isotopic species of CDFMS and is equal to the angle $\angle ia$ between the internal rotor axis i and a principal inertial axis). In CDFMS, $\angle ia$ values of $54.64(8)^\circ$, $55.22(20)^\circ$ and $56.95(8)^\circ$ for ^{28}Si , ^{29}Si and ^{30}Si , respectively, are obtained. These are close to the ab initio angles of 54.37° , 54.36° and 54.35° (assuming the internal rotation axis i is coincident with the Si-CH₃ bond), although the ab initio results do not reflect the observed steady increase in $\angle ia$ as the mass of Si increases. This difference might suggest a dynamic effect in which the deviation of the internal rotation axis from the Si-CH₃ bond increases as the mass of the Si isotope increases. Indeed, this trend is consistent with very limited literature data for methyl groups connected to ^{12}C and ^{13}C atoms in methyl ketene, where a small increase in the angle between the C-CH₃ and i axes is observed in switching from ^{12}C -CH₃ to ^{13}C -CH₃ [21].

For CFMS, two conformers were observed, and comparison of predicted rotational constants and dipole moment components (Table 1) with experiment (Table 3) allows these spectra to be fairly confidently assigned to conformers B1 and B2. In both cases it was necessary to fix the angles related to internal rotation to *ab initio* values, so structural comparisons are limited.

Table 6 presents internal rotation barriers in CDFMS and CFMS alongside values for similar Si and Ge containing compounds. Barriers to methyl group rotation show the expected decrease as fluorine atoms are added to the silicon atom; the CMS value of $6.671 \text{ kJ mol}^{-1}$ [1] is reduced by nearly 0.7 kJ mol^{-1} (to 5.96 and 6.01 kJ mol^{-1} , for conformers B1 and B2, respectively) in CFMS with the substitution of one hydrogen for a fluorine atom, and then another similar decrease of about 0.8 kJ mol^{-1} occurs on going to CDFMS, for which V_3 is approximately 5.2 kJ mol^{-1} . Interestingly, the internal rotation barrier in CDFMS is effectively the same as the barrier in $(\text{CH}_3)_2\text{SiF}_2$, difluorodimethylsilane, where $V_3 = 5.256(3) \text{ kJ mol}^{-1}$ [22] with a similar decrease of $\sim 1.7 \text{ kJ mol}^{-1}$ between the all-hydrogen analog $(\text{CH}_3)_2\text{SiH}_2$ [23] and $(\text{CH}_3)_2\text{SiF}_2$.

Table 6 shows that, within a given series of molecules, the barrier decreases similarly upon addition of successive fluorine atoms to the Si (or Ge) atom. For silicon containing species, the effect of adding one fluorine atom seems to reduce the barrier by about 8-10%, and a second fluorine atom reduces it by a total of 22-26%. The one germane for which relevant data is available suggests a significantly larger reduction in barrier upon fluorination (Table 6); hence measurement of the barrier to rotation in the as yet unstudied molecule, H_3CGeHF_2 , would be interesting to see if the same magnitude decrease that is observed upon addition of a single fluorine atom is continued.

Table 6 Comparison of methyl group rotation barriers in selected silicon and germanium compounds.

Molecule	V_3 (kJ mol ⁻¹)	Method ^{a)}	% decrease ^{b)}	Ref.
H ₃ CSiH ₃	7.11(42)	PAM	-	[5]
H ₃ CSiH ₂ F	6.523(126)	PAM	-8.3	[6]
H ₃ CSiHF ₂	5.251(126)	PAM	-26.2	[7]
(CH ₃) ₂ SiH ₂	6.910(41)	PAM	-	[23]
(CH ₃) ₂ SiF ₂	5.256(3)	CAM	-23.9	[22]
H ₃ CGeH ₃	5.184(105)	PAM	-	[24]
H ₃ CGeH ₂ F	3.94(8)	PAM	-24.0	[8]
H ₃ CSiH ₂ (<i>c</i> -C ₃ H ₅)	6.671(9)	CAM	-	[1]
H ₃ CSiHF(<i>c</i> -C ₃ H ₅)	5.95846(29); 6.01091(30) ^{c)}	CAM	-10.7; -9.9	This work
H ₃ CSiF ₂ (<i>c</i> -C ₃ H ₅)	5.2327(21)	CAM	-21.6	This work
H ₃ CGeH ₂ (<i>c</i> -C ₃ H ₅)	4.736(6)	CAM	-	[3]

a) Method used for internal rotation fitting: PAM = principal axis method; CAM = combined axis method

b) Percent decrease in internal rotation barrier relative to the unfluorinated (all-hydrogen) analog of each component (e.g. H₃CXH₂Y, where X=Si or Ge and Y=H, F, or *c*-C₃H₅).

c) Values for the two different conformers B1 and B2.

Also apparent from an inspection of the values in Table 6 is the effect of the presence of a cyclopropyl group on V_3 . In methyl silane [5], the barrier is 7.11(42) kJ mol⁻¹ while addition of a cyclopropyl group to form CMS results in a reduction to 6.671(9) kJ mol⁻¹ [1], a decrease of 0.44 kJ mol⁻¹. An almost identical decrease (of 0.448 kJ mol⁻¹) is observed for the Ge analog, with values of 5.184(105) kJ mol⁻¹ in methyl germane [24] and 4.736(6) kJ mol⁻¹ in cyclopropylmethylgermane (CMG) [3]. Data is also available to compare the methyl monofluorosilane (H₃CSiH₂F) barrier (6.523(126) kJ mol⁻¹ [6]) with the barrier from the present work for the cyclopropyl analog CFMS (5.95846(29) kJ mol⁻¹ or 6.01091(30) kJ mol⁻¹, for

conformers B1 and B2, respectively), again showing a decrease of about 0.5 kJ mol^{-1} .

Interestingly the methyl difluorosilane value of $5.251(126) \text{ kJ mol}^{-1}$ [22] is unchanged on going to the cyclopropyl analog CDFMS ($5.2327(21) \text{ kJ mol}^{-1}$).

Conclusions

Rotational spectra for two conformers of cyclopropylfluoromethyl silane and one conformer of cyclopropyldifluoromethyl silane have been observed in a supersonic expansion. Experimental rotational constants are consistent with those predicted for the most stable conformers calculated at the MP2/6-311++G(2d,2p) level. Barriers to rotation of the methyl group in each molecule have been determined from splittings between *A* and *E* state transitions in the rotational spectrum and show that in going from CMS to CFMS to CDFMS the V_3 barrier decreases by about 0.8 kJ mol^{-1} with addition of each fluorine atom to the silicon atom. This decrease of internal rotation barrier with increasing fluorination at the silicon atom is consistent with that observed for other silicon containing molecules.

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