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The chirped pulse, Fourier transform microwave spectrum of 1-chloromethyl-1-fluorosilacyclopentane

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ABSTRACT

The microwave spectrum of 1-chloromethyl-1-fluorosilacyclopentane has been recorded for the first time using the chirped pulse, Fourier transform microwave technique. Quantum chemical calculations show the two lowest energy conformers as being a twist-trans and a gauche form with the gauche form previously being shown as having two separate conformations, a gauche+ (lower in energy) and gauche- (higher in energy) form. Analysis of the spectrum provided the observation of the twist-trans conformer only, with 253 and 85 transitions being assigned to the ^{35}Cl and ^{37}Cl isotopologues, respectively. *R*-branch, *a*- and *b*-type transitions were observed. The spectrum was fit to a Watson S-reduced Hamiltonian and consisted of rotational constants, quartic centrifugal distortion constants, and nuclear quadrupole coupling constants, including the determination of the off-diagonal nuclear quadrupole coupling constant, χ_{ab}. Interpretation of the structure was provided using second moments and is found to have a similar ring structure to other known silacyclopentanes. Analysis of the χ_{zz} has been carried out and compared to other similar molecules. An investigation of the known quantum chemical energies of the gauche conformer reveals that the reported B3LYP energies do not align with the observed microwave results.

1. Introduction

The substitution of carbon for a silicon atom has been of much structural interest. The general elongation of the silicon bond compared to that of the typical carbon bond provides interesting differences in the structure and chemistry of silicon compared to that of the carbon analogue. This is particularly true in alkane and ring molecules where structural flexibility can lead to a conformation in the silicon-containing species that is lower in energy to that of a carbon analogue.

In order to better understand and address these structural differences, we have recently started to undertake the rotational spectroscopy of many silicon-containing molecules in order to address the chemical differences exhibited in these species [1–5]. These systems have led to interesting physiochemical results like ring puckering motions, planar vs. nonplanar ring structures, or C_2 symmetry in straight-chain alkane species where one may expect C_{2v}. From a quantum chemical standpoint, the potential energy surfaces of the ring puckering motion containing the silicon atom have been shown to be overall flatter at the base through the puckering coordinate than the carbon analogues. These results are not necessarily intuitive because we often think of silicon as having very similar chemistry to carbon. Because of these differences in structure and chemistry from their carbon counterparts, it is important to study these molecules further in order to build a stronger foundation of expectation for silicon-containing species.

We present the first known report on the microwave spectrum of 1-chloromethyl-1-fluorosilacyclopentane using the chirped pulse, Fourier transform microwave (CP-FTMW) technique. Analysis of the resulting spectrum and structure is aided by quantum chemical calculations and is discussed along with making comparisons amongst known similar molecules of the title species.

2. Quantum chemical calculations

Quantum chemical calculations were carried out on 1-chloromethyl-1-fluorosilapentane at the B3LYP/Def2TZVP level using the Grimme D3BJ dispersion [6] utilizing the Gaussian16 program suite [7]. Structure optimization led to two stable low energy conformers, a twist-trans conformer and a gauche conformer. These structures are presented in the a,b-, a,c-, and b,c-planes in Figs. 1 and 2. Previous quantum chemical structural work on the molecule determined that there are

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Table 1
Quantum chemical calculations for the lowest energy conformers of 1-chloromethyl-1-fluorosilapentane performed for this work compared with the literature.

Value	Twist-trans conformer			Gauche conformer				
	This work	Ref. [8]		This work	Ref. [8] Gauche+		Ref. [8] Gauche-	
Level	B3LYP-D3BJ/ Def2TZVP	MP2/ aug-cc-pVTZ	B3LYP/ aug-cc-pVTZ	B3LYP-D3BJ/ Def2TZVP	MP2/ aug-cc-pVTZ	B3LYP/ aug-cc-pVTZ	MP2/ aug-ccpVTZ	B3LYP/ aug-cc-pVTZ
Relative Energy/ kJ mol^{-1}	0	0	0	6.388	14.94	5.86	17.45	6.36
A/MHz	1751.7	1744.3	1716.2	2504.6	2501.3	2432.3	2298.4	2336.4
B/MHz	1128.3	1297.4	1105.2	852.2	919.6	837.3	971.3	836.3
C/MHz	878.9	964.9	859.0	781.1	829.5	764.9	883.7	783.1
χ_{aa}/MHz	16.074	–	–	−29.507	–	–	–	–
$\chi_{bb} - \chi_{cc}$/MHz	−95.011	–	–	23.953	–	–	–	–
χ_{ab}/MHz	45.352	–	–	30.062	–	–	–	–
χ_{ac}/MHz	0.381	–	–	−49.923	–	–	–	–
χ_{bc}/MHz	−0.652	–	–	22.166	–	–	–	–
$\lvert\mu_a\rvert$/D[a]	0.42	0.27	0.41	2.18	1.71	2.32	2.74	2.27
$\lvert\mu_b\rvert$/D[a]	0.22	0.19	0.48	0.75	1.18	0.94	0.20	0.89
$\lvert\mu_c\rvert$/D[a]	0.09	0.02	0.09	1.81	1.75	1.99	0.78	1.95

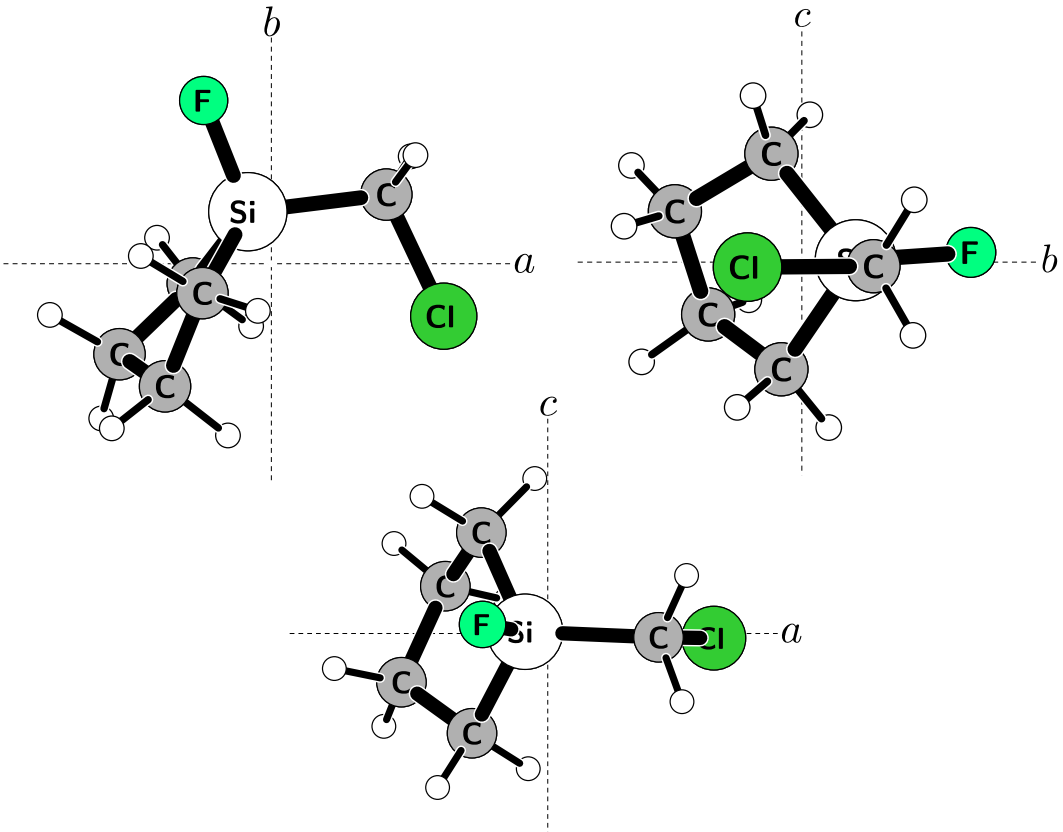

Fig. 1. The 1-chloromethyl-1-fluorosilacyclopentane twist-trans structure in the a,b-, a,c-, and b,c-planes as calculated at the B3LYP-D3BJ/Def2TZVP level.

two, slightly different gauche conformers which are referred to as gauche+ and gauche- in Ref. [8]. This work on the gauche form agrees structurally with the lower energy gauche+ conformer. Important geometric and electronic structural parameters for all calculations are presented in Table 1.

The primary difference between the two conformers is, obviously, the Cl-C-Si-F dihedral angle. In the twist-trans, it is slightly less than 180 degrees (varies with level of theory), while in the gauche form, it lies in the range of 65–75 degrees depending on level of theory and structure (gauche+ or gauche-). In all cases, though, the change of this dihedral angle has two consequences. The first being that the energy rises. As is shown in Table 1, this could be a somewhat marginal (≈6 kJ mol^{-1}) or a very significant (≈15–17.5 kJ mol^{-1}) increase in energy. However, the dipole moment increases considerably (from 0.48 D overall to 2.98 D in our calculations). If the energies are closer, this significant difference in dipole moment may mitigate the effects of the population difference and be visible in the microwave spectrum. In Ref. [8], the DFT energy differences were utilized as the basis of a Boltzmann population analysis, but it was not clear from the results whether the observation of the gauche+ and gauche- conformers supported the MP2 or B3LYP energy calculation. On the other hand,

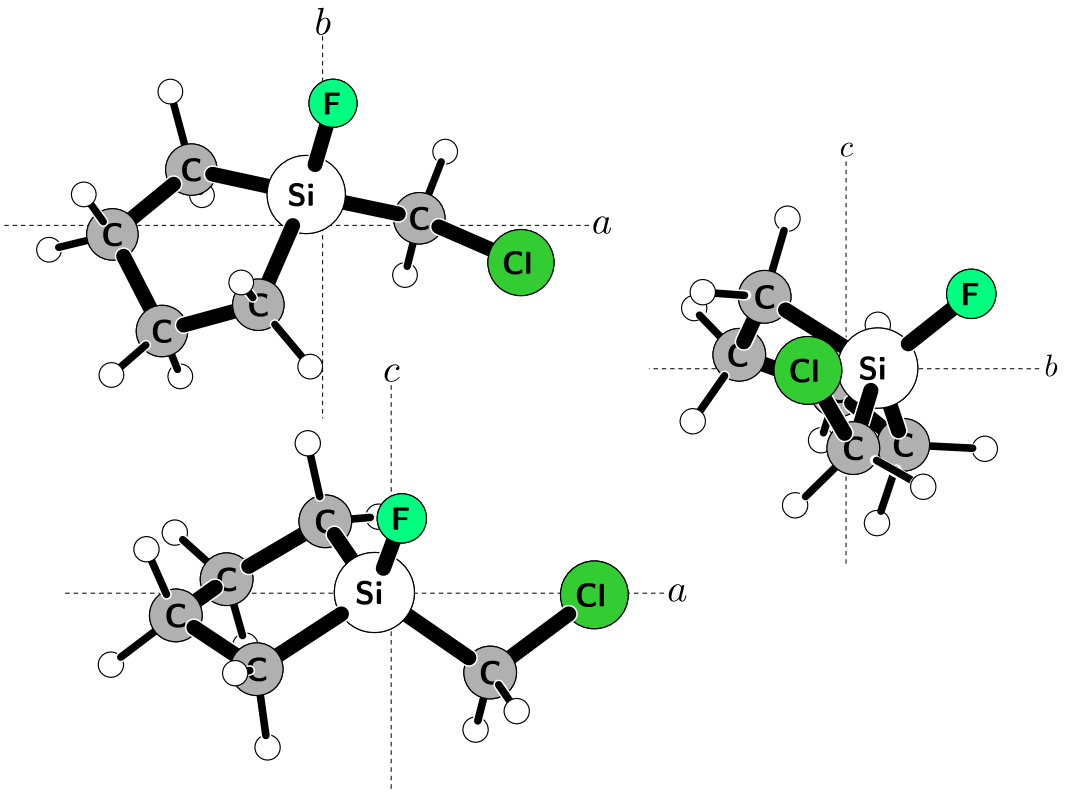

Fig. 2. The 1-chloromethyl-1-fluorosilacyclopentane gauche structure in the a,b-, a,c-, and b,c-planes as calculated at the B3LYP-D3BJ/Def2TZVP level.

Ref. [8] does detail the observation of the twist-trans, gauche+ and gauche- conformations.

Because there were previous quantum chemical calculations performed, it is important to address why more calculations were performed in this work. Previous work using Def2TZVP with D3BJ dispersion basis sets has proven a reliable approach for achieving optimized structures that agree well with rotational spectroscopy measurements for molecules containing elements up to the third row [9]. It was important for this work to continue to investigate the reliability of the accuracy of the optimized structures relative to the experimentally measured structure.

3. Experimental methods

The sample of 1-chloromethyl-1-fluorosilacyclopentane was prepared by coupling the double Grignard of 1,4-dibromobutane to chloromethyltrichlorosilane in dry ether with refluxing overnight under positive argon gas. The product 1-chloromethyl-1-chlorosilacyclopentane was purified by trap-to-trap separation and the sample was fluorinated using freshly sublimed antimony trifluoride without solvent at room temperature for 3 h. The product 1-chloromethyl-1-fluorosilacyclopentane was identified by NMR spectra and IR spectra.

After synthesis, the rotational spectrum of the sample was investigated using a CP-FTMW spectrometer. The details of the spectrometer have been described previously [10–12]. The instrument utilizes supersonic nozzle sample introduction into a vacuum chamber held at 10^{-6} torr. In order to introduce the sample entrained in the supersonic expansion, 25 psig (≈ 2.70 atm absolute pressure) of industrial grade argon was flowed through the sample inserted into the reservoir of our heated nozzle setup previously described [13]. Although not heated, the reservoir setup allows for the sample to be as close to the orifice of the Parker-Hannifin™ Series 9 solenoid valve as possible, minimizing sample condensation issues arising from bubbling a carrier gas through a sample holder or "U" tube. 4 μs chirps were utilized in the 8–16 GHz region of the electromagnetic spectrum, but stronger signals generally still arise outside this excitation range. Spectra were collected at nozzle repetition rate of 3 Hz with 3,20 μs free induction decays (FIDs) being collected per nozzle pulse. Approximately 54,500 FIDs were collected and averaged before sample was consumed. The average of the FIDs was then fast Fourier transformed using a Bartlett windowing type in Kisiel's FFTS program [14].

4. Results and analysis

Fig. 3 shows the resultant spectrum. Analysis of the spectrum was undertaken using Pickett's SPFIT/SPCAT program suite [15] implemented in conjunction with Kisiel's AABS package [16] from the PROSPE website [17,18]. Fits of the assigned quantum numbers were made utilizing a Watson S-reduced Hamiltonian in the I^r representation [19]. The 251 and 85 transitions were assigned to the ^{35}Cl and ^{37}Cl isotopologues of the twist-trans conformer, respectively, consisting of R-branch, a- and b-type transitions. This is consistent with the dipole moment predictions from the quantum chemical calculations. No transitions associated with the gauche conformer were observed. All assigned transitions and fits can be found in the *Supplemental Data* which has been provided in presentation format through a combination of Kisiel's PISLIN and PIFORM programs also available on PROSPE.

As presented in Table 2, rotational constants A, B, and C, quartic centrifugal distortion constants D_J, D_{JK}, D_K, and d_1, and nuclear quadrupole coupling parameters χ_{aa}, $\chi_{bb} - \chi_{cc}$, and $|\chi_{ab}|$ were determined for 1-chloromethyl-1-fluorosilacyclopentane. Fig. 4 shows the excellent agreement between the predicted and observed transitions. In the analysis of ^{37}Cl spectrum, D_K and $|\chi_{ab}|$ were not determinable, but including them improved the fit. For D_K, the value was held to the determined ^{35}Cl value of 1.182 kHz. $|\chi_{ab}|$, however, being dependent on the nucleus in question, was adjusted by the ratio 1.26 in accordance with the ^{35}Cl/^{37}Cl literature ratio for their quadrupolar moments and held [20]. Although this lowered the RMS and, therefore, increased the overall quality of the fit, $|\chi_{ab}|$ was the poorest determined parameter

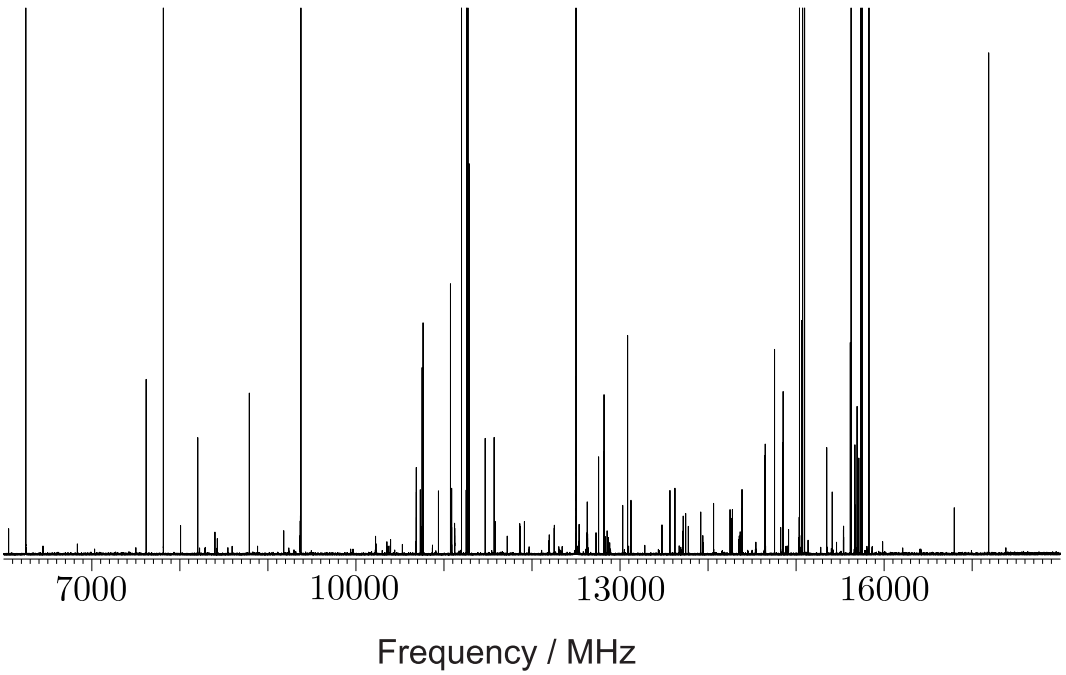

Fig. 3. Full collected microwave spectrum of 1-chloromethyl-1-fluorosilacyclopentane. The saturated lines are typically manmade when at exact frequencies (i.e. 6.25 GHz, 12.5 GHz, etc.). Otherwise, saturated transitions generally belong to the parent isotopologue.

Table 2
Spectroscopic parameters of the twist-trans form of 1-chloromethyl-1-fluorosilacyclopentane.

Parameter	$C_4H_8SiFCH_2{}^{35}Cl$	$C_4H_8SiFCH_2{}^{37}Cl$
A/MHz	1774.6509(13)[a]	1768.7304(24)
B/MHz	1133.51448(45)	1107.3516(13)
C/MHz	885.98321(34)	868.4821(11)
D_J/kHz	0.3506(29)	0.3555(82)
D_{JK}/kHz	−1.018(10)	−1.117(25)
D_K/kHz	1.182(62)	[1.182][b]
d_1/kHz	−0.1191(17)	−0.1465(56)
χ_{aa}/MHz	16.329(21)	11.48(12)
$\chi_{bb} - \chi_{cc}$/MHz	−90.528(48)	−69.58(24)
$\lvert\chi_{ab}\rvert$/MHz	38.7(50)	[30.7][b]
N[c]	251	85
Microwave RMS[d] /kHz	12.8	19.3
P_{aa}/uÅ^2	365.74541(18)	376.28309(50)
P_{bb}/uÅ^2	204.67060(18)	205.62759(50)
P_{cc}/uÅ^2	80.10598(18)	80.10223(50)
Δ_0	−160.21195(35)	−160.20444(99)

[a]Numbers in parentheses give standard errors (1σ, 67% confidence level) in units of the least significant figure.
[b]Value held. For D_K, the value is held to the parent determined parameter and for χ_{ab}, parameter is held to the parent value divided by the quadrupolar moment ratio for$^{35}Cl/^{37}Cl$. See text for details.
[c]Number of observed transitions used in the fit.
[d]Microwave RMS is defined as $\sqrt{\left(\sum\left[(\text{obs}-\text{calc})^2\right]/\text{N}\right)}$.

in the ^{35}Cl fit which may be part of the reason for the overall increase in the ^{37}Cl RMS fit value.

5. Discussion

Given the reference of the prior work on the title molecule, there are two major areas that this microwave rotational spectroscopic study sets out to address. Those are: (i) to validate, experimentally, the geometric structure of the molecule and to assess the accuracy of the B3LYP-D3BJ/Def2TZVP calculations on the observed twist-trans conformer; (ii) to utilize the chlorine nuclear quadrupole coupling constant as a probe for understanding chloromethyl substituents in a variety of environments; and (iii) to try to provide some insight on the energy difference calculations.

The rotational constants and nuclear quadrupole coupling constants of our quantum chemical calculations are in good agreement with the experimentally observed values, providing strong evidence between the consistency between the two structures. Along with this, the observed transition types also agree with the two strongest calculated dipole moment components, providing further evidence toward the reliability of the accuracy of the quantum chemical structure and consistency with the experimental structure. Because there is no isotopologue information other than the ^{37}Cl species, Kraitchman substitution of the experimentally derived heavy-atom positions other than chlorine to provide a r_S structure could not be provided. However, there has been a significant amount of structural spectroscopy work performed previously on silacyclopentane and derivatives where the hydrogens on the silicon atom have been singly or doubly substituted [1,21–24]. These studies provide a framework to give some experimental structural insight using reliable quantum chemical calculations combined with second moment analysis [25] across the family.

A listing of the second moments derived from Kisiel's PLANM program for some of these molecules is provided in Table 3. The second moments listed in Table 3 are quantifications of the out-of-plane mass distribution for a molecule in the principal axis system [25,26]. From inspection of the table, all of the molecules with the exception of 1-chloromethyl-1-fluorosilacyclopentane exhibit a P_{bb} value of approximately 80 uÅ^2. These are all a consequence of the silicon-containing ring having very similar structures and mass distribution off of their respective *ac*-planes. Upon further inspection of Table 3, it is shown that P_{cc} for 1-chloromethyl-1-fluorosilacyclopentane has the value of 80.10598(18) uÅ^2, consistent with the P_{bb} trend. To understand if this is due to the ring or just coincidental, refer to the visual representation of the quantum chemical calculations from this work provided in Fig. 1. P_{cc} is a measure of the mass out of the *ab*-plane. Fig. 1 shows that the carbon, chlorine and fluorine atoms (the largest contributors to any second moment value apart from the ring) mainly lie in the *ab*-plane, contributing very little to the P_{cc} value. From this, we can say that the

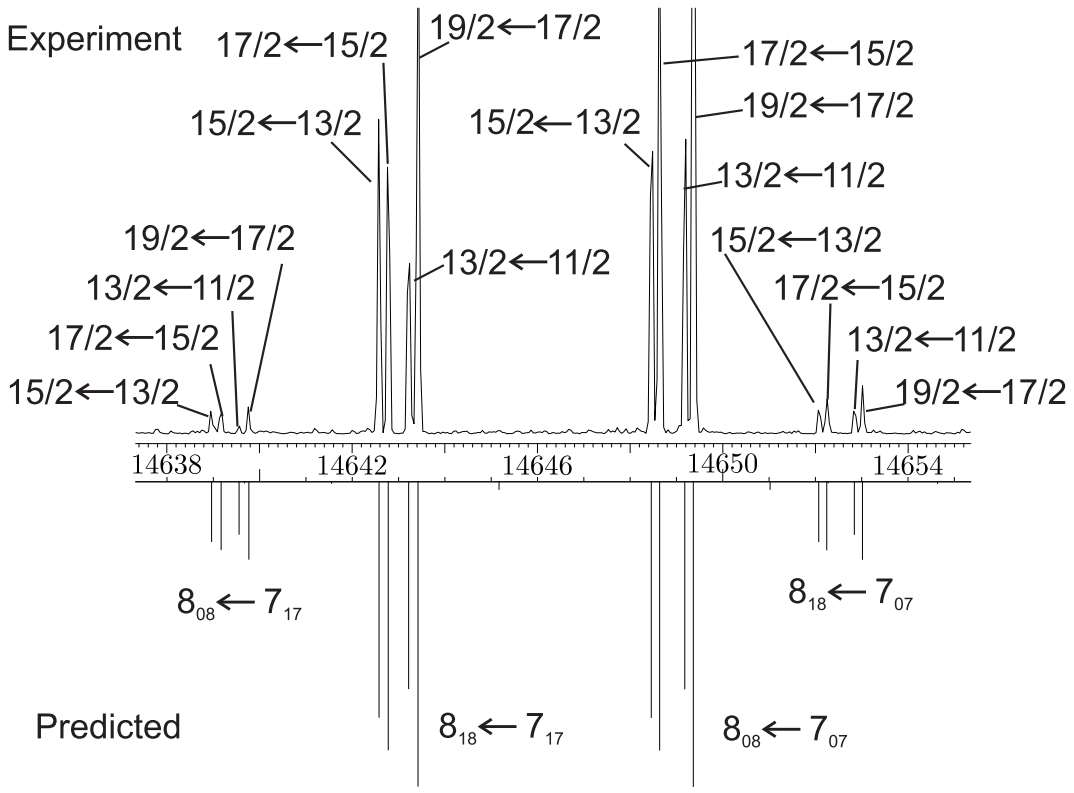

Fig. 4. Agreement of the predicted and observed transition positions for ^{35}Cl isotopologue of 1-chloromethyl-1-fluorosilacyclopentane. $J', K_a', K_c' \leftarrow J\varepsilon, K_a\varepsilon, K_c\varepsilon$ are in the predicted groups while F quantum number assignments are labeled in the experimental groups. Frequencies are in MHz.

Table 3
Comparisons of second moments for multiple parent isotopologues of various silacyclopentanes.

Molecule	P_{aa}/uÅ^2	P_{bb}/uÅ^2	P_{cc}/uÅ^2	Reference
1-chloromethyl-1-fluorosilacyclopentane	365.74541(18)[a]	204.67060(18)	80.10598(18)	This Work
silacyclopentane	109.85405(84)	80.02742(84)	12.30640(84)	[21]
1-fluorosilacyclopentane	185.674479(48)	79.818879(48)	27.703952(48)	[22]
1-chlorosilacyclopentane[b]	286.08	79.50	40.49	[23]
1-bromosilacyclopentane[b]	460.08	79.89	45.22	[24]
1,1-difluorosilacyclopentane	227.27110(12)	83.037692(12)	67.164670(12)	[1]

[a]Numbers in parentheses give standard errors (1σ, 67% confidence level) in units of the least significant figure.
[b]Reported as an experimental/calculated estimated r_0 value.

experimental P_{cc} value of 80.10598(18) uÅ^2 is effectively due to the silacyclopentane ring which implies that, as expected, the structure of the ring is very similar to the other known molecules in the family.

The next thing for which this study can provide context is the differences in electronic environment for molecules containing a chloromethyl substituent. For this, we will use the ^{35}Cl nuclear quadrupole coupling constant as a probe. Although the effect has a $\frac{1}{r^3}$ functionality and is typically utilized to investigate immediate electronic bonding environments, it has been shown that this effect can be used to monitor environmental electronic distribution changes broader than those immediately around the nucleus in question. To make this comparison, we first need to diagonalize the known nuclear quadrupole coupling matrices (made up of components χ_{aa}, χ_{bb}, χ_{cc}, etc.) into the axis system of the chlorine nucleus (χ_{xx}, χ_{yy}, and χ_{zz}) with χ_{zz} representing the direction of the chemical bond (in this case, the C–Cl bond). Comparisons in the electronic environment can then be monitored with changes in χ_{zz}. This has been done for a few different chloromethyl-containing molecules in Table 4.

To provide context for Table 4, it is important to employ a Townes–Dailey approach [31]. That is, if the electronic environment were perfectly spherically symmetric about the nucleus in question and not being distributed amongst the atoms in a bonding motif, the nuclear quadrupole coupling constant would be zero (completely ionic). Any changes in magnitude effectively monitor the electronic distribution/covalency in a system because there is deviation in the electronic

Table 4
Comparisons of χ_{zz} for^{35}Cl of similar chloromethyl-containing molecules.

Molecule	χ_{zz}/MHz	Reference
1-chloromethyl-1-fluorosilacyclopentane	−70.6(37)[a]	This Work
(Chloromethyl)fluorosilane	−73.53(70)	[27]
Chloromethyl Radical	−66.09(22)	[28]
Epichlorohydrin (Chloromethyl)oxirane	−72.513(33)[b]	[29]
Epichlorohydrin (Chloromethyl)oxirane	−70.054(47)[b]	[30]
(Chloromethyl)cyclopropane	−70.58(19)[b]	[30]

[a]Numbers in parentheses give standard errors (1σ, 67% confidence level) in units of the least significant figure.
[b]Value represents lowest energy conformation observed for that species.

distribution from this spherical symmetry. This is shown in Table 4 where the chloromethyl radical has the smallest nuclear quadrupole coupling constant magnitude [28] of the family because the ability of the molecule to distribute electron density is limited. From the table, it is noticed that, although the magnitudes are very similar amongst the systems shown, that the system with an electron withdrawing group connected to the silicon atom (i.e. (Chloromethyl)fluorosilane) has a significantly different χ_{zz} value than those that do not. This is probably because more electron sharing from the chlorine atom due to the electron density is being pulled away from the silicon atom and, by extension, the carbon atom of the chloromethyl group. Although 1-chloromethyl-1-fluorosilacyclopentane does not qualify as being significantly different in this case, the large uncertainty in χ_{zz} is attributed to the larger uncertainty in the determined χ_{ab} value. It is speculated that if this value were determined with more precision, it would result in a similar, significantly different value like the others containing electron withdrawing groups, but there is not enough certainty from the fits to confirm that.

The last item to address is if the energy difference between the twist-trans and gauche conformers aligned more with the B3LYP or MP2 calculations. Depending on the conformer in question, the B3LYP and MP2 calculations differed in energy by 8–11 kJ mol^{-1}. These experiments were performed utilizing a supersonic expansion with an argon carrier which would mean the rotational temperature is approximately 3 K [32] but if the barrier to interconversion between conformers is > 400 cm^{-1} when using argon, the conformer distribution is comparable to that of the equilibrium distribution before entering the expansion. Because the differences in energies amongst the two lowest conformer energies are > 400 cm^{-1} (smallest difference is 489 cm^{-1})[33], it can be safely assumed that we use a Boltzmann distribution at 300 K to approximate the conformation populations in the beam. This would mean the population differences for the calculated conformations would break down as follows: B3LYP-D3BJ/Def2TZVP - Twist-trans 92.8%, Gauche 7.2%; B3LYP/aug-cc-pVTZ - Twist-trans 85.2%, Gauche+ 8.1%, Gauche- 6.7%; MP2/aug-cc-pVTZ - Twist-trans 99.7%, Gauche+ 0.2%, Gauche- 0.1%.

Signal intensity in a CP-FTMW experiment is given by $S \propto \omega \cdot \mu^2 \cdot E_{\text{pulse}} \cdot \Delta N_0 \cdot \left(\frac{\pi}{\alpha}\right)^{\frac{1}{2}}$ where ω is the frequency of the transition, μ is the transition dipole moment, E_{pulse} is the electric field strength imparted on the molecules, ΔN_0 is the population difference at equilibrium (for the transition), and α is the sweep velocity of the pulse [34,35]. Across the conformations, these can be considered to be basically the same with the exception of the population of the conformer and the dipole moment because the differences in the rotational constants are negligible due to their similar values. Because the calculated dipole moments are very similar across the species, we can use the values given for our calculations in Section 2 to illustrate. If the populations were equal (1:1), the signal response in the chirp would be $2.98^2/(0.48)^2 = 38.5$ times stronger for the gauche form. Without including dipole moments, the current population distribution for the B3LYP-D3BJ/Def2TZVP, B3LYP/aug-cc-pVTZ, and MP2/aug-cc-pVTZ calculations are 12.9:1, 12.7:1.2:1, and 997:2:1, respectively. If the B3LYP energy calculations were accurate, there would be an expectation of observing at least one gauche form in the spectrum and this was not observed. This lends credibility to the argument that, although the structure is accurate in the B3LYP calculations, the energy is probably not accurate. It does not, however, mean that the MP2 calculation is accurate as this cannot be confirmed from this study but, rather, that the energy orderings are larger, i.e. ≥9.2 kJ mol^{-1}, than the B3LYP calculations predict.

6. Conclusions

The CP-FTMW spectrum of the synthesized molecule 1-chloromethyl-1-fluorosilacyclopentane has been recorded and is reported. The minimum energy structure is twist-trans as determined by previous spectroscopic work [8] and predicted by quantum chemical calculations. Analysis of the structure of the twist-trans conformer using second moments indicates that the 5-atom ring structure inclusive of the silicon is very similar to previous silacyclopentanes studied. Interpretation of the chlorine nuclear quadrupole coupling constants have been undertaken and compared to other chloromethyl-substituted species. Species with electron-withdrawing groups attached to the atom attached to the chloromethyl group work to increase the covalency of the C–Cl bond of the chloromethyl species. Finally, an analysis of the dipole moments and populations for the calculated conformer relative energies show that the B3LYP energies are too low when accounting for the absence of the conformer in the microwave spectrum.

CRediT authorship contribution statement

Tiara Pulliam: Spectroscopic experiments and fitting. **Frank E. Marshall:** Spectroscopic experiments and fitting. **Theodore Carrigan-Broda:** Synthesis of molecule. **Daniel V. Hickman:** Synthesis. **Gamil Guirgis:** Synthesis, Editing. **G.S. Grubbs II:** Writing, Editing, Financial.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Garry Grubbs II reports financial support was provided by National Science Foundation.

Data availability

Data will be made available on request.

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