

A microwave and quantum chemical study of allyltrifluorosilane

H. Møllendal^{a,*}, G.A. Guirgis^b

^aDepartment of Chemistry, The University of Oslo, P.O. Box 1033 Blindern, N-0315 Oslo, Norway

^bDepartment of Chemistry and Biochemistry, College of Charleston, Charleston, SC 29424, USA

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Abstract

The structural and conformational properties of allyltrifluorosilane, $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{SiF}_3$, have been explored by microwave (MW) spectroscopy and high-level ab initio and density functional theory quantum chemical calculations. The microwave spectrum was investigated in the 18–62 GHz spectral regions. The *a*-type *R*-branch transitions of one conformer were assigned for the ground as well as for 10 vibrationally excited states. The $\text{C}=\text{C}-\text{C}-\text{Si}$ chain of atoms in this rotamer takes an *anti*-clinal ('skew') conformation, with a dihedral angle calculated to be 111.6° from the *syn*-periplanar (0°) conformation. The question whether a $\text{C}=\text{C}-\text{C}-\text{Si}$ *syn*-periplanar conformer exists as a high-energy form in the gas phase remains open. In most of the quantum chemical calculations this conformation is predicted to be a transition state. However, in the most advanced calculations (B3LYP/aug-cc-pVTZ level of theory) the *syn*-periplanar conformer is predicted to be a stable rotamer that is calculated to be 6.5 kJ/mol higher in energy than the *anti*-clinal form. Since there is no indication in the MW spectrum for the presence of high-energy form(s), it is concluded that the *anti*-clinal conformer is at least 4 kJ/mol more stable than any other hypothetical rotamer.

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1. Introduction

The influence of the trifluorosilane (SiF_3) group on structural and conformational properties of free molecules has received rather limited attention in the past. In fact, only a few studies exist. The symmetric top methyltrifluorosilane (H_3CSiF_3) is the simplest example. This compound was found by microwave (MW) spectroscopy to have a C–Si

bond length of 181.2(14) pm [1], much shorter than the corresponding bond length in methylsilane (H_3CSiH_3) which is 186.4(1) pm [2]. The barriers to internal rotation in these two compounds are strikingly different being 4951.19(17) J/mol in H_3CSiF_3 , [3] and 7084.31(86) J/mol in H_3CSiH_3 [2].

Another example is cyclopropyltrifluorosilane ($\text{C}_3\text{H}_5\text{SiF}_3$) [4], which was found to have a barrier of internal rotation of 5.02 kJ/mol, as determined by vibrational spectroscopy. This value is again much lower than in the corresponding silyl (SiH_3) derivative ($\text{C}_3\text{H}_5\text{SiH}_3$), where a barrier of 8.28 kJ/mol was obtained using the same method [5].

* Corresponding author. Tel.: +47-22-85-56-74; fax: +47-22-85-54-41.

E-mail address: harald.mollendal@kjemi.uio.no (H. Møllendal).

A study of vinyltrifluorosilane ($\text{H}_2\text{C}=\text{CHSiF}_3$) [6] revealed that the barrier to internal rotation of the trifluorosilyl group is surprisingly high, 7.1(4) kJ/mol, as found by vibrational spectroscopy [6].

Only one conformation is possible for the simple molecules H_3CSiF_3 , $\text{C}_3\text{H}_5\text{SiF}_3$ and $\text{H}_2\text{C}=\text{CHSiF}_3$. Larger compounds may display rotational isomerism. Conformational studies using infrared and Raman spectroscopy assisted by ab initio calculations have previously been made for a few compounds possessing the SiF_3 group and capable of rotational isomerism. One of these investigations was made for cyclopropylmethyltrifluorosilane, $\text{C}_3\text{H}_5\text{CH}_2\text{SiF}_3$, [7] where two conformers were found. The preferred form of this molecule has a *syn-clinal* (**sc**), about 60° from the *syn-periplanar* (**sp**) (0°) conformation, for the Si–C–C–H link of atoms [7]. This rotamer was determined to be 5.9(15) kJ/mol more stable (by enthalpy) than the *anti-periplanar* (**ap**) (180°) conformer [7].

A second study includes 2-chloroethyl trifluorosilane [8]. Two rotameric forms **ac** and **sc**, exist for this compound, the former being favored by 3.8 kJ/mol.

The title compound allyltrifluorosilane ($\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{SiF}_3$) was recently studied by IR and Raman spectroscopy in the gaseous, liquid and solid states, as well as in liquified xenon [9]. This investigation was supplemented by quantum chemical ab initio calculations. One conformer presumed to be the *anti-clinal* (**ac**) form where the C=C–C–Si dihedral angle is roughly 120° from *syn-periplanar*, was seen to be the predominant one in all three states of aggregation as well as in xenon solution. The solid state was found to consist solely of the **ac** conformer. The results for the gaseous state were a bit more uncertain. The **ac** form certainly was the predominant one here as well, but a tiny amount of other form(s) could not be completely ruled out.

Two rotamers, **ac** and **sp** (see Fig. 1) were found to exist in the fluid state [9]. In addition to the predominating **ac** conformer a small amount of what was assumed to be the **sp** form was observed. The enthalpy difference between **sp** and **ac** forms in xenon solution was determined to be as large as 17.7(15) kJ/mol [9].

It was also possible to determine the barrier to internal rotation of the SiF_3 group in the gaseous state. The value derived using the C–Si torsional

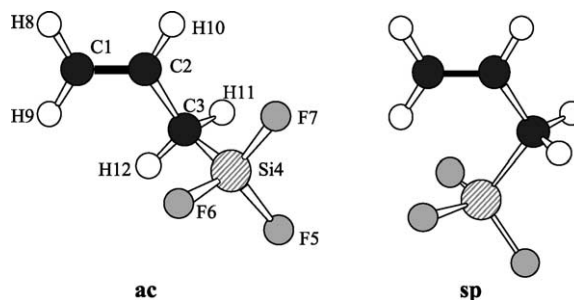


Fig. 1. The *anti-clinal* (**ac**) and *syn-periplanar* (**sp**) rotameric forms of allyltrifluorosilane. Atom numbering is given on **ac**.

fundamental frequency observed in the far IR (48 cm^{-1}) was a barrier of 6.28 kJ/mol, which is actually quite high in comparison with the barriers in methyltrifluorosilane (4951.19(17) J/mol) [1] and in cyclopropyltrifluorosilane (5.02 kJ/mol) [4].

The examples given above show that compounds containing the trifluorosilyl group have unique physical properties that generally differ markedly from their silyl counterparts. The little explored trifluorosilyl series of compounds is thus of interest in its own right.

The present MW study of allyltrifluorosilane was undertaken to supplement the IR and Raman findings and the ab initio predictions [9]. A MW study should serve as a critical test of the previous work [9] because of the inherent specificity and accuracy of this method. In addition, MW spectroscopy is able to provide a series of interesting physical parameters that are not available from the vibrational spectra.

Quantum chemical ab initio calculations at various theoretical levels were reported [9]. These calculations are extended considerably in this work. In particular, high-level density functional theory (DFT) calculations have been made in order to compare them with the traditional ab initio calculations and secondly to augment the present MW investigation.

2. Experimental

The sample of allyltrifluorosilane utilized in this work was synthesized and purified according to the published procedure [9]. The MW spectrum was studied using the Oslo Stark spectrometer, which has been described briefly [10]. The 18–62 GHz

spectral region was investigated. Radio frequency microwave frequency double resonance (RFMWDR) experiments were made as described by Wordarczyk and Wilson [11] using the same equipment as mentioned in Ref. [12]. The microwave absorption cell was cooled to dry ice temperature (-80°C) during most of the experiments. The pressure was 4–10 Pa when the spectra were recorded and stored electronically using the computer programs written by Waal [13]. Overlapping lines often occur, especially in the crowded pile-up regions of the aR -branch transitions. The accuracy of the spectral measurements is therefore no better than ± 0.12 MHz. The resolution was approximately 0.5 MHz.

3. Results and discussion

3.1. Quantum chemical calculations

Ab initio calculations at the RHF/6-31G*, MP2/6-31G* and MP2/6-311++G** levels of theory have already been reported for the **ac** and **sp** conformations [9].

Two different computational schemes have been employed here. In the first of these, electron correlation was included using the second order Møller–Plesset (MP2) perturbation theory [14]. In the second, DFT calculations were made employing the B3LYP computational scheme [15].

The GAUSSIAN 98 program package [16] running on the HP superdome in Oslo was used. This program also provides the basis sets used here. MP2 and B3LYP calculations were made for the **sp**, **ac** and **ap** conformers. The calculations were started using C1=C2–C3–Si4 dihedral angles of about 10, 120 and 170° for the **sp**, **ac**, and **ap** conformations, respectively. The structures were fully optimized. No symmetry restrictions were imposed.

Initially, the 6-31++G** and 6-311++G** basis sets [16] were used both in MP2 and in the B3LYP calculations that were made for all three conformations. The **ac** conformer was found to be ‘stable’, i.e. a minimum on the energy hyper surface, as no imaginary (negative) vibrational frequencies were predicted [17].

The other calculations always refined to the **sp** or to the **ap** conformation, respectively. However, one

imaginary vibrational frequency to be associated with the C2–C3 torsional fundamental vibration was found both for the **sp** and the **ap** forms. The interpretation of this is that the MP2 and B3LYP methods with the 6-31++G** and 6-311++G** basis sets predict the **sp** and **ap** forms to be transition states, and thus not stable conformers [17].

Finally, rather large B3LYP computations were carried out using the correlation-consistent polarized triple- ζ basis set augmented with diffuse functions (aug-cc-pVTZ) [18]. These calculations were restricted to the **sp** and **ac** forms, which are generally found to be preferred by allylic compounds. Selected results of these calculations are shown in Table 1.

Not surprisingly, the **ac** conformer was again predicted to be stable in these B3LYP/aug-cc-pVTZ calculations, just as in the more limited calculations alluded to above. However, the **sp** form is now predicted to be stable, in contrast to the MP2 computations above. It is of course impossible to say for sure whether these large calculations actually *prove* that **sp** indeed exists as a stable form of the molecule. Its energy is, after correcting for zero-point vibrational energy, 6.5 kJ/mol (7.2 kJ/mol without this correction) higher than the energy of the **ac** conformer.

Interestingly, the C1=C2–C3–Si4 dihedral angle of the **ac** conformer is predicted to be as small as 111.6° . The ‘normal’ value is 120° . The same dihedral angle is predicted not to be exactly 0° , but 3.3° in the **sp** conformer (Table 1). This shallow minimum indicates that there is a low barrier to interconversion at the planar conformation, but this barrier height was not calculated. It is also noted that the C2–C3–Si4 angle opens up from 113.4° in **ac** to 118.4° in **sp**. The deviation by 3.3° (from 0°) for the C1=C2–C3–Si4 dihedral angle and the 5° increase of the C2–C3–Si4 angle (from 113.4 in **ac** to 118.5° in the **sp** form) is taken as an indication that steric repulsion is prominent in the latter rotamer. It is conjectured that this effect is the major reason why **ac** is preferred by the title compound.

It is of interest to compare the B3LYP structure in Table 1 to experimental structures found in closely related compounds. When the allyl moieties, H8H9C1=C2H10–C3H11H12, of **ac** and **sp** are compared to the accurate substitution structure of propene [19] it is seen that bond lengths deviate by

Table 1

Structures, rotational constants, dipole moment components of the *anti-clinal* and *syn-periplanar* conformers of allyltrifluorosilane as predicted in the B3LYP/aug-cc-pVTZ calculations

	Conformer	
	ac	sp
Bond lengths/pm		
C1=C2	132.7	132.6
C1–H8	108.1	108.1
C1–H9	108.3	108.3
C2–C3	150.3	150.6
C2–H10	108.5	108.6
C3–Si4	185.3 ^a	185.1
C3–H11	109.4	109.6
C3–H12	109.3	109.6
Si4–F5	159.4 ^b	159.4
Si4–F6	159.2 ^b	159.3
Si4–F7	159.4 ^b	159.2
Bond angles/deg		
C2–C1–H8	121.2	120.9
C2–C1–H9	121.9	123.0
H8–C1–H9	116.9	116.2
C1=C2–C3	125.0	127.2
C1=C2–H10	119.1	118.4
C3–C2–H10	115.9	114.4
C2–C3–Si4	113.4	118.5
C2–C3–H11	110.7	109.7
C2–C3–H12	111.0	109.7
Si4–C3–H11	106.9	106.6
Si4–C3–H12	107.6	106.9
H11–C3–H12	107.0	104.5
C3–Si4–F5	111.1	109.7
C3–Si4–F6	112.3	113.3
C3–Si4–F7	111.7	112.9
F5–Si4–F6	107.0	106.9
F5–Si4–F7	107.1	106.9
F6–Si4–F7	107.1	106.8
Dihedral angles/deg		
H8–C1–C2–C3	179.4	–179.8
H8–C1–C2–H10	0.0	0.0
H9–C1–C2–C3	–0.6	0.0
H9–C1–C2–H10	–179.9	179.8
C1–C2–C3–Si4	–111.6	–3.3
C1–C2–C3–H11	128.3	–125.9
C1–C2–C3–H12	9.6	119.9
H10–C2–C3–Si4	67.8	176.9
H10–C2–C3–H11	–52.3	54.3
H10–C2–C3–H12	–171.0	–59.9
C2–C3–Si4–F5	–173.2	178.9
C2–C3–Si4–F6	67.0	59.7
C2–C3–Si4–F7	–53.5	–61.9
H11–C3–Si4–F5	–50.9	–56.9
H11–C3–Si4–F6	–170.7	–176.2

Table 1 (continued)

	Conformer	
	ac	sp
H11–C3–Si4–F7	68.8	62.2
H12–C3–Si4–F5	63.7	54.4
H12–C3–Si4–F6	–56.1	–64.9
H12–C3–Si4–F7	–176.6	173.5
Rotational constants/MHz		
<i>A</i>	3591.5	3398.8
<i>B</i>	1304.9	1502.6
<i>C</i>	1292.7	1413.1
Dipole moment ^d /10 ^{–30} C m		
μ_a	6.69	6.77
μ_b	1.52	5.31
μ_c	3.95	0.16
Energy difference ^e /kJ mol ^{–1}		
ΔE	0.0	6.5

Atom numbering is given in Fig. 1. Dihedral angle of the *syn-periplanar* conformation of four linked atoms is defined to be 0°.

^a 181.2 pm is preferred in the *plausible* structure; see text.

^b 157.4 pm is preferred in the *plausible* structure; see text.

^c Measured from *syn-periplanar*.

^d Note units. 1 debye = 3.3356 × 10^{–30} C m.

^e Energy difference corrected for zero-point vibrational energy relative to the **ac** conformer. The total B3LYP/aug-cc-pVTZ energy of the **ac** conformer is –1 855 571.42 kJ/mol.

less than 1 pm for corresponding bonds. The bond angles in the most stable **ac** conformer deviate by less than 1.5° from their counterparts in propene. Somewhat larger differences are found for some of the corresponding bond angles in the strained high-energy **sp** conformation.

Two gas-phase studies have been made for H₃CSiF₃ [1,20]. This compound contains a sp³-hybridized carbon atom attached to the trifluorosilyl group, just as in the title compound. The C–Si and the Si–F bond lengths were found to be 181.2(14) and 157.4(7) pm, respectively, by MW spectroscopy [1]. The combined MW-electron diffraction study [20] yielded almost the same result (182.8(4) and 157.0(2) pm). The calculated values (Table 1) are 185.3 (**ac**) and 185.1 pm (**sp**) for the C–Si bond length, whereas the Si–F bond lengths are predicted to be 159.2–159.4 pm in the two forms.

The B3LYP bonds are thus longer than the experimental ones in H_3CSiF_3 by 3–4 pm in the case the C–Si bond length, and longer by about 2 pm in the case of the Si–F bond lengths. It is expected that the C–Si and Si–F bond lengths should be quite similar in H_3CSiF_3 and in $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{SiF}_3$. It is therefore concluded that the present B3LYP/aug-cc-pVTZ calculations are likely to be insufficient in reproducing accurately the bonding properties of the trifluorosilyl group.

3.2. MW spectrum and assignments

Allyltrifluorosilane is rather heavy by MW standards (the molecular weight of the ^{28}Si -isotopomer is 126.01) and has nine normal modes with frequencies below 500 cm^{-1} according to vibrational spectroscopy [9]. The partition function will consequently have a large value even at dry ice temperature. Each MW transition was therefore predicted to be comparatively weak in spite of the fact that the largest component of the dipole moment along a principal inertial axis is predicted by quantum chemical calculations to be sizable ($6-8 \times 10^{-30}\text{ C m}$; note units) regardless of which conformer(s) might be present.

Predictions of the rotational constants for selected values of the C=C–C–Si dihedral angle revealed that any conformer of allyltrifluorosilane should be close to a prolate symmetrical top with the asymmetry parameter κ close to -1 . Moreover, the largest component of the dipole moment was invariably predicted to lie along the a -inertial axis. These considerations indicated that characteristic series of pile-ups of transitions should occur approximately at frequencies given by $(B_v + C_v)(J + 1)$, where B_v and C_v are rotational constants of the vibrational state v , and J is the principal quantum number, regardless of which conformer(s) would be present. Moreover, the ground-state lines should be accompanied by many vibrationally excited states because there are several low-frequency vibrational fundamentals [9]. Very crowded pile-ups were thus foreseen to occur for each $J + 1 \leftarrow J$ transition.

The first survey spectra that were taken at field strengths of about 100, 600 and/or 1000 V/cm, respectively, revealed that very weak lines occur every few MHz throughout the entire spectral

range. In addition, the characteristic series of pile-ups of much stronger lines separated by about 2.67 GHz protruded from the background of weaker ones, just as predicted above. The fact that the theoretical calculations (Table 1) yield $B + C = 2.60\text{ GHz}$ for the **ac** conformer and 2.92 GHz for the **sp** conformer was taken as the first evidence that the pile-ups indeed belong to the former rotamer.

No other pile-up series than the one originating from the **ac** rotamer were seen. This is decisive evidence that **ac** is indeed the predominating rotamer. Intensity considerations lead us to conclude that the **ac** rotamer must be at least 4 kJ/mol more stable than any other hypothetical rotameric form of the molecule. This is in agreement with the theoretical result in Table 1 and elsewhere [9].

The rather complex $J = 8 \leftarrow 7$ pile-up series of the **ac** form taken at Stark voltage of about 100 V/cm is shown in Fig. 2 for illustration. This pile-up region extends over about 250 MHz. Most of the lines in this spectrum have been assigned to different vibrational states. The strongest line marked GS is the ground vibrational state. A total of 10 vibrationally excited states could be assigned, as indicated in this figure. The assigned excited states to lower or higher frequencies than GS are denoted L1–L5 and H1–H5, respectively. It should be pointed out that each

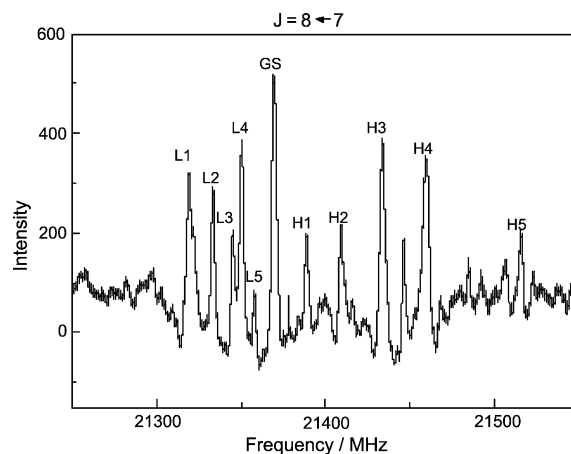


Fig. 2. The $J = 8 \leftarrow 7$ transition of allyltrifluorosilane. The ground vibrational state (GS) is accompanied by many vibrationally excited states denoted L1–L5 and H1–H5, respectively. The assignments of the excited states are discussed in the text.

Table 2

Frequencies/MHz and approximate values of the sum of the $B + C$ rotational constants of the ground and vibrationally excited states of allyltrifluorosilane

	$J = 7 \leftarrow 6$	$J = 8 \leftarrow 7$	$J = 9 \leftarrow 8$	$\approx (B + C)/\text{MHz}$
Vibrational state ^a				
L1	18654.18	21318.97	23983.43	2664.9
L2	18666.33	21332.95	23999.41	2666.6
L3	18676.66	21344.70	24012.61	2668.1
L4	18681.56	21350.06	24018.95	2668.8
L5	18687.94	21357.70	24027.35	2669.7
Ground state	18698.19	21369.48	24040.54	2671.2
H1	18714.59	21388.46	24062.54	2673.6
H2	— ^b	21409.19	24085.18	2676.1
H3	18754.32	21433.54	24112.34	2679.2
H4	18777.88	21459.36	24141.78	2682.5
H5	18826.45	21515.68	24204.46	2689.5

See text.

^a See Fig. 2 and text for labeling of the excited vibrational states.

^b Not measured.

assigned line in Fig. 2 is actually composed of several unresolved aR -transitions where K_{-1} is larger than 2. Moreover, transitions with K_{-1} less than 2 from one vibrational state often overlap with other vibrational states.

There are three stable isotopes of silicon, ^{28}Si (92.2%), ^{29}Si (4.7%) and ^{30}Si (3.1%). Model calculations indicate that the spectra of the ^{29}Si and ^{30}Si isotopomers are buried underneath the stronger vibrationally excited state transitions (L1–L5). Consequently, no assignments could be made for isotopomers containing the ^{29}Si or the ^{30}Si isotope.

Centrifugal distortion is presumably rather small for $J = 8 \leftarrow 7$ (Fig. 2) as well as for the $J = 7 \leftarrow 6$ and $J = 9 \leftarrow 8$ transitions. One consequence of this is that the peak of each line is relatively narrow. This made it possible to determine approximate values of $B + C$ by using the frequencies (ν) of the peaks of these three transitions assuming $B + C \approx \nu/(J + 1)$. The frequencies of the peaks are listed in Table 2 together with the average approximate values of $B + C$ derived from these observations.

Centrifugal distortion becomes more prominent as J and K_{-1} increases. Instead of the sharp peaks seen in Fig. 2, the lines first broaden and then split up into unresolved K_{-1} doublets as J increases. The $J + 1 \leftarrow J$ pile-up regions now gradually become extremely dense and complicated with

lots of overlapping lines often making definite assignments next to impossible. The pile-up regions may now extend over many hundred MHz. Fig. 3 shows the situation for the ground state $J = 23 \leftarrow 22$ transition where the number above each line gives the value of K_{-1} . This spectrum has been taken at a Stark voltage of only about 20 V/cm. The lowest K_{-1} -lines are not modulated at this voltage, which simplifies this spectrum considerably. Each vibrationally excited state has a pattern that is weaker but similar to that shown in Fig. 3.

The resolved K_{-1} -levels of the aR -branch transitions that make up the pile-ups must be assigned in order to obtain accurate rotational and centrifugal distortion constants. The following assignments procedure was employed: Several of the $K_{-1} = 3$ with $J \geq 11$ doublets which are split into two components by the asymmetry of the molecule, were first assigned using the very specific RFMWDR technique [11]. In this manner it was possible to make unambiguous assignments of $K_{-1} = 3$ lines for the ground state (GS) as well as the L2, L4 and H4 excited states. In this manner, the H3 state was actually seen to consist of two overlapping states denoted H3a and H3b.

Unfortunately, the $K_{-1} = 3$ doublets of the L1, L3, L5, H1, H2 and H3 excited states were too weak to be

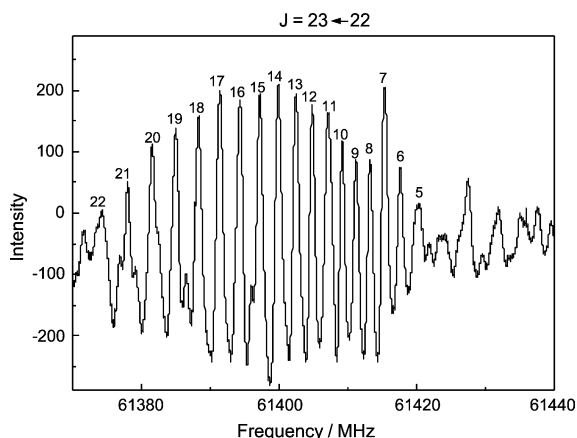


Fig. 3. The ground vibrational (GS) state of the $J = 23 \leftarrow 22$ transition showing the $K_{-1} \geq 5$ doublets that are modulated already at a Stark field strength of about 20 V/cm. The value of K_{-1} is indicated above each assigned line. The $K_{-1} = 7$ is rather strong presumably because it is overlapped. This spectral region becomes increasingly dense as the Stark voltage is increased because many more transitions become modulated.

assigned. Only the approximate values of $B + C$ shown in Table 2 are therefore available for these states. It should be mentioned that L1 is suspected of consisting of several overlapping states since no sufficiently strong double resonance signals could be observed for this line which is apparently relatively strong, as seen in Fig. 2.

The $K_{-1} > 3$ lines occur as unresolved doublets. These doublets have very rapid Stark effects and will consequently be the only ones that are modulated at low Stark fields. The example shown in Fig. 3 is typical. The great simplification of the spectrum at low field strengths made it possible to make unambiguous assignments of the high- K_{-1} lines in the cases of the GS, L2, L4 and H4 states. The spectra of the H3a and the H3b states were too weak to allow definite assignments to be made for their $K_{-1} > 3$ transitions.

The spectra of the GS, L2, L4 and H4 states were now fitted to Watson's Hamiltonian employing the A -reduction I -representation [20]. The **ac** conformer is an asymmetric top with $\kappa \approx -0.98$. Only Δ_J and Δ_{JK} could therefore be determined from the aR -type transitions assigned here. Using the information now at hand the frequencies of the $K_{-1} = 2$ transitions

were predicted and ultimately assigned for the GS, L4 and H4 states. An unambiguous assignment for these lines could not be made for the L2 state owing to the spectral complexity and the relative weakness of the transitions in question.

The assignments of the $K_{-1} = 1$ transitions were even more difficult to make because they depend critically upon the A rotational constants. These lines have slow Stark effects. Transitions having rapid Stark effect were now 'removed' by superimposing an AC Stark field on a DC bias of a few Volts. This 'trick' was helpful for the assignments of the $K_{-1} = 1$ as well as $K_{-1} = 0$ lines of the GS. Unfortunately, no unambiguous assignments of these types of transitions could be made for the L4 and H4 states for reasons mentioned.

Attempts were now made to assign b - and c -type transitions for the ground vibrational state among the many weak lines that occur in this spectrum outside the pile-up regions. However, no definite assignments could be made, presumably because these lines are so weak.

A total of about 700 resolved aR -transitions were assigned for L2, L4, GS, H3a, H3b and H4 states. The full spectra are available from H.M. upon request. The spectroscopic constants are shown in Table 3. An accurate value of the A rotational constant was determined only for the ground state, while accurate B and C rotational constants were found for the other states (Table 3). Accurate values have been found for the Δ_J and Δ_{JK} centrifugal distortion constants (Table 3) in the cases of L2, L4 GS and H4 states. These two centrifugal distortion constants are comparatively large owing to several low-frequency vibrational fundamentals. It is seen that while Δ_J remains almost the same in each state, Δ_{JK} varies quite a lot.

Few transitions were assigned for the H3a and H3b states. The values of B and C reported in Table 3 for these two states were obtained by fixing A , Δ_J and Δ_{JK} to the values obtained for the ground vibrational state. Not surprisingly, the values of $B + C$ reported in Table 2 agree well with the values that can be calculated from the entries in Table 3.

It is not straightforward to assign vibrational fundamentals to the excited states shown in Fig. 2 because there are nine fundamentals below 500 cm^{-1} [9]. Nor is it possible to perform accurate determination of the normal vibrational

Table 3

Spectroscopic constants of the ground and vibrationally excited states of the **ac** conformer of allyltrifluorosilane

Vibrational state ^a	Ground	L2	L4	H3a	H3b	H4
A/MHz	3678.6(24)	4129(63)	3721(36)	3678.6 ^b	3678.6 ^b	3073(106)
B/MHz	1343.4788(27)	1342.74(12)	1341.818(51)	1348.21(33)	1348.88(12)	1349.35(24)
C/MHz	1327.8605(26)	1323.88(12)	1327.083(51)	1330.98(37)	1330.58(13)	1333.24(24)
Δ_J /kHz	0.51025(96)	0.4730(31)	0.4792(14)	0.5102 ^b	0.5102 ^b	0.5332(16)
Δ_{JK} ^c /kHz	1.9060(16)	1.4103(38)	1.3050(19)	1.906 ^b	1.906 ^b	2.5569(23)
No of transitions in fit	256	98	164	6	3	152
Rms deviation/MHz	0.116	0.141	0.109	0.247	0.061	0.116

A-reduction, I^l -representation [21]. Uncertainties represent one standard deviation.^a See text for identifications of excited states.^b Fixed at this value in the least-squares fit.^c Further quartic centrifugal distortion constants preset at zero.

frequencies by relative intensity measurements because each peak consists of the $K_{-1} = 1$ pile-ups rather than individual transitions. Relative intensity determinations have however been performed largely as described by Esbitt and Wilson [22], but have large uncertainties because the $K_{-1} = 1$ -pile-ups had to be used. The intensities of the GS and the excited state in question were compared in each case.

The two lowest vibrational fundamentals are the ν_{30} , the SiF₃ torsion, at 48 cm⁻¹ and ν_{29} , the torsion around the C2–C3 bond (Fig. 1), at 54 cm⁻¹, according to Ref. [9]. The third lowest fundamental, ν_{28} , the lowest SiF₃ rocking mode, has a frequency of 142 cm⁻¹. ν_{27} is second lowest SiF₃ rocking mode at 216 cm⁻¹, whereas ν_{26} is the C2–C3–Si4 bending mode at 257 cm⁻¹ [9]. The present B3LYP/aug-cc-pVTZ calculations (unscaled) yielded 52, 71, 144, 209 and 255 cm⁻¹, respectively, for these normal modes (not reported in Table 1) in fair agreement with the vibrational analysis [9].

The two most intense excited states observed in the MW spectrum are the L4 and H4 vibrations (see Fig. 2). Relative intensity measurements [22], yielded 55(25) cm⁻¹ for L4 and 65(20) cm⁻¹ for H4, respectively. L4 is tentatively assigned as the first excited state of the ν_{29} fundamental (the C2–C3 torsion), while H4 is tentatively assigned as the first excited state of the ν_{30} (SiF₃ torsion). We think that L2 is the second excited state of ν_{29} . Its frequency was determined to be 100(30) cm⁻¹ by relative intensity

measurements [22]. L1 apparently consists of several partly resolved overlapping lines (Fig. 2). One of them is presumably the third excited state of ν_{29} .

The frequency of L3 was determined to be 139(30) cm⁻¹. This is perhaps the first excited state of ν_{28} (142 cm⁻¹) [9]. This fundamental could also be one of the two vibrational states that make up H3. There are several candidates for ν_{27} (216 cm⁻¹) and ν_{26} (257 cm⁻¹) [9], e.g. H1 (173(40) cm⁻¹), H2 (175(45) cm⁻¹), H5 (261(50) cm⁻¹), L5 (280(60) cm⁻¹) and not to forget, the two H3 states, whose intensities could not be determined quantitatively. It is, however, impossible to suggest more definite assignments in these cases. It should be added that none of the vibrational states showed any signs of being split by tunneling of the CF₃ group.

The experimental rotational constants of the ground vibrational state shown in Table 3 are systematically larger than the rotational constants obtained in the B3LYP calculations (Table 1) by 2.4, 3.0 and 2.7%, in the cases of A, B and C, respectively. It was remarked in the previous paragraph that the calculated C–Si and Si–F bond lengths are likely to be too large by a few pm. A new calculation of the rotational constants assuming the C–Si bond length to be 181.2 and the three C–F bond lengths each to be 157.4 pm as in the MW structure of H₃CSiF₃ [1] while retaining the rest of the B3LYP structure in Table 1 yielded A = 3678.1, B = 1335.9 and C = 1321.9 MHz. These rotational constants deviate only by 0.0, 0.5 and 0.5%, respectively,

from the experimental ones shown in Table 3. This is another indication that the B3LYP calculations actually fail to reproduce the geometry of the trifluorosilyl group properly.

4. Conclusions

One conformer denoted **ac** has been assigned for allyltrifluorosilane. This rotamer has an **ac** arrangement for the C=C–C–Si chain of atoms. The ground vibrational state as well as ten vibrationally excited states were assigned for this conformer. There is no evidence in the MW spectrum for further rotameric forms other than **ac**.

Quantum chemical calculations at various levels of theory have been made. The most advanced ones were made at the B3LYP/aug-cc-pVTZ level. The last-mentioned calculations predict a C=C–C–Si dihedral angle to be as small as 111.6° from the **sp** (0°) conformation. They also predict that a less stable **sp** form of the molecule coexists with **ac** at an energy that is 6.5 kJ/mol higher than that of **ac**.

The B3LYP calculations predict a plausible structure for the allyl moiety. However, the calculated C–Si and Si–F bond lengths are believed to be about 4 and 2 pm, respectively, too long and this is assumed to be the main reason why the B3LYP rotational constants are systematically larger than the experimental ones.

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References

- [1] J.R. Durig, Y.S. Li, C.C. Tong, *J. Mol. Struct.* 14 (1972) 255.
- [2] M. Wong, I. Ozier, W.L. Meerts, *J. Mol. Spectrosc.* 102 (1983) 89.
- [3] W.L. Meerts, I. Ozier, *Chem. Phys.* 71 (1982) 401.
- [4] T.S. Little, M. Qtaibat, J.R. Durig, M. Dakkouri, A. Dakkouri, *J. Raman Spectrosc.* 21 (1990) 591.
- [5] J. Laane, E.M. Nour, M. Dakkouri, *J. Mol. Spectrosc.* 102 (1983) 368.
- [6] J.R. Durig, K.L. Hellams, *J. Mol. Struct.* 6 (1970) 315.
- [7] T.S. Little, C.A. Vaughn, X. Zhu, M. Dakkouri, J.R. Durig, *J. Raman Spectrosc.* 25 (1994) 735.
- [8] P. Klæboe, C.J. Nielsen, V. Aleksa, A. Groudís, G.A. Guirgis, Y.E. Nashed, J.R. Durig, *J. Mol. Struct.* 567 and 568 (2001) 167.
- [9] G.A. Guirgis, Y.E. Nashed, P. Klæboe, V. Aleksa, J.R. Durig, *Struct. Chem.* 10 (1999) 1.
- [10] G.A. Guirgis, K.M. Marstokk, H. Møllendal, *Acta Chem. Scand.* 45 (1991) 482.
- [11] F.J. Wodarczyk, E.B. Wilson Jr., *J. Mol. Spectrosc.* 37 (1971) 445.
- [12] K.-M. Marstokk, H. Møllendal, *Acta Chem. Scand., Ser. A* 42 (1988) 374.
- [13] Ø. Waal. Personal communication, 1994.
- [14] C. Møller, M.S. Plesset, *Phys. Rev.* 46 (1934) 618.
- [15] A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648.
- [16] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, P. Salvador, J.J. Dannenberg, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian, Inc., Pittsburgh, PA, 2001.
- [17] W.J. Hehre, L. Radom, P.v.R. Schleyer, *Ab Initio Molecular Orbital Theory*, Wiley, New York, 1986, p. 227.
- [18] T.H. Dunning Jr., *J. Chem. Phys.* 90 (1989) 1007.
- [19] D.R. Lide, D. Christensen, *J. Chem. Phys.* 35 (1961) 1374.
- [20] B. Rempfer, H. Oberhammer, N. Auner, *J. Am. Chem. Soc.* 108 (1986) 3893.
- [21] J.K.G. Watson, in: J.R. Durig (Ed.), *Vibrational Spectra and Structure*, vol. 6, Elsevier, Amsterdam, 1977, p. 1.
- [22] A.S. Ebbitt, E.B. Wilson, *Rev. Sci. Instrum.* 34 (1963) 901.