



# Microwave, infrared, and Raman spectra, structural parameters, vibrational assignments and theoretical calculations of 1,1,3,3-tetrafluoro-1,3-disilacyclopentane



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## ABSTRACT

The FT-microwave spectrum of 1,1,3,3-tetrafluoro-1,3-disilacyclopentane ( $c\text{-C}_3\text{H}_6\text{Si}_2\text{F}_4$ ) has been recorded and 339 transitions for 6 isotopologues have been assigned for the twist conformation. The ground state rotational constants were determined with values for the normal species:  $A = 2102.74026(68)$ ,  $B = 751.34319(32)$ ,  $C = 736.51478(31)$ . Adjusted  $r_0$  parameters are reported with distances (Å):  $r_{\text{C}_\alpha\text{-Si}} = 1.859(2)$ ,  $r_{\text{Si-C}_\beta} = 1.864(2)$ ,  $r_{\text{Si-F}_1} = 1.583(3)$ ,  $r_{\text{Si-F}_2} = 1.578(3)$ , and  $r_{\text{C}_\beta\text{-C}_\beta} = 1.559(3)$ , and angles ( $^\circ$ ):  $\angle\text{SiC}_\alpha\text{Si} = 102.8(3)$ ,  $\angle\text{C}_\alpha\text{SiC}_\beta = 104.3(3)$ ,  $\angle\text{SiC}_\beta\text{C}_\beta = 106.6(3)$ ,  $\tau_{\text{C}_\beta\text{SiC}_\alpha\text{Si}} = 10.7(3)$ , and  $\tau_{\text{SiC}_\beta\text{C}_\beta\text{Si}} = 40.8(3)$ . The conformational stabilities have been predicted from ab initio calculations utilizing several various basis sets. Vibrational assignments have been provided for the observed bands for the twist conformer which are supported by ab initio calculations to predict harmonic force constants, vibrational wavenumbers, infrared intensities, Raman activities and depolarization ratios. The results are discussed and compared to the corresponding properties of some related molecules.

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## 1. Introduction

The saturated five-membered cyclic hydrocarbon ring molecule (cyclopentane) has two “out-of-plane” vibrational modes which are usually described as ring-puckering and ring-twisting modes. When the frequencies of these two modes are nearly equal, the cross terms in the potential function give rise to a vibrational motion which was initially described by Pitzer and colleagues as pseudorotation [1]. This motion was treated by these scientists for the two degenerate out-of-plane ring bending coordinates in terms of an amplitude coordinate  $q$  and a phase angle  $\phi$ . However this concept for cyclopentane was questioned [2] when the low frequency ring mode of this molecule appeared normal but the fundamentals could not be assigned on the basis that cyclopentane had  $D_{5h}$  symmetry. The authors [2] stated that the spectral data

were consistent with a rigid structure with  $C_s$ ,  $C_2$ , or  $C_1$  symmetry. Nevertheless these scientists [2] concluded that a decision among these three rigid models as well as pseudorotation could not be made. There was further reluctance [3,4] to accept the pseudorotation of the puckering motion and the consequent indefiniteness of the cyclopentane conformation persisted. However, a later infrared study [5] of the  $\text{CH}_2$  deformation of cyclopentane clearly showed that the ring was undergoing pseudorotation which was nearly barrier free. Also from this study an estimate of the value of the pseudorotational moment [6] of inertia was obtained from the spectral data.

With the acceptance of the pseudorotation motion there was a number of investigations on the possible conformations of mono substituted cyclopentane molecules and the determination of the most stable structures. Even before the acceptance of pseudorotation motion was reported in the scientific literature [7] Pitzer and his coworkers reported how one could predict the most stable structure of such molecules. Some of the earliest conformational determinations of the mono substituted cyclopentane molecules was for the halides i.e. bromine, chlorine and fluorine. In the initial studies [8,9] of these molecules it was concluded that all three had two conformers present in the fluid phases with the equatorial form the most stable. Later studies [10] of fluorocyclopentane demonstrated that there was only one form in the fluid phases

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and it was the envelope-equatorial form. However several years later [11] it was shown correctly that there was only one form but it was not the envelope conformer but was the twisted form. There has been other reported incorrect conformational structures for five membered rings so it is not easy to predict what the conformational structure will be for many different types of five membered rings.

Recently some investigations of five membered rings [12–14] were initiated where instead of all five ring atoms being carbon one of them has been replaced by a silicon atom. There has been some limited studies of these molecules whether they are in the equatorial, axial or twisted forms or even possibly a planar form. As a continuation of these studies we have expanded the atoms in the ring instead of a single silicon atom to two silicon atoms. For the first molecule we studied [15] with two silicon atoms in the ring, it included an oxygen atom between them instead of the carbon atoms since this molecule was available. For this study we were interested in the determination of the stable conformer which was found to be the twisted form as well as interested in the vibrational assignment of the fundamentals of the ring atoms. As a continuation of this initial study of the five membered rings with two silicon atoms we initiated a study with a carbon atom between the silicon atoms along with fluorine atoms on them i.e. 1,1,3,3-tetrafluoro-1,3-dilacyclopentane ( $c\text{-C}_3\text{H}_6\text{Si}_2\text{F}_4$ ). With the fluorine atoms on the silicon atoms having largest electronegativity it could have a significant effect on the conformational stability of the heavy atom ring and the structural parameters. Additionally a very small fluorine atom should not have any steric effect. From this study we expected to determine the conformational form of the heavy atoms as well as all of the structural parameters of the molecule, and the frequencies of the fundamental vibrations. Additionally we carried out ab initio calculations to evaluate how well relatively small basis sets can predict the conformational stability and structural parameters of the five membered ring. The results of this microwave, infrared and Raman spectroscopic study along with the ab initio predicted values are reported herein.

## 2. Experimental and theoretical methods

The  $c\text{-C}_3\text{H}_6\text{Si}_2\text{F}_4$  compound was prepared by the fluorination of 1,1,3,3-tetrachloro-1,3-dilacyclopentane [16] by freshly sublimed antimony trifluoride without solvent at room temperature for three hours. The sample was first purified by trap-to-trap distillation and finally by low pressure, low temperature sublimation. The purity of the sample was checked by infrared and nuclear magnetic resonance spectroscopy.

The rotational spectrum of  $c\text{-C}_3\text{H}_6\text{Si}_2\text{F}_4$  was studied by using a CP-FTMW spectrometer developed at the University of Virginia, operating in the 6.5–18 GHz range. The chirped pulse methods used in this study have been described in detail previously [17], so only the brief details relevant to this experiment are necessary.

The microwave source was a 24 GS/s arbitrary waveform generator, producing a 12–0.5 GHz linear frequency sweep in 1  $\mu\text{s}$ . The pulse was upconverted to 6.5–18 GHz by a 18.95 GHz phase-locked resonant dielectric oscillator (PDRO), and then amplified by a pulsed 300 W traveling wave tube amplifier. The amplified pulse is then transmitted through free space between two standard-gain microwave horns, where it interacts with a molecular beam generated by five pulsed nozzles (General Valve Series 9) operating perpendicular to the propagation direction of the microwave pulse. On the detection end, the receiver is protected from the high power pulse by a combination of a PIN diode limiter and single-pole microwave switch. The resulting molecular free induction decay (FID) was then amplified and digitized directly on a 100 GS/s oscilloscope with 33 GHz of hardware bandwidth,

with a 20  $\mu\text{s}$  detection time per FID. Due to the speed of this excitation and detection process, a sequence of 10 excitation/detection cycles is possible per gas pulse, and all ten detected FIDs are collected and averaged together before the next valve injection cycle begins. Phase stability of this experiment over the course of many valve injection cycles is enabled by locking all the frequency sources and the oscilloscope to a 10 MHz Rb-disciplined quartz oscillator. For this experiment, approximately 78,000 valve injection cycles of the sample gas were completed at 3.3 Hz to create a time-averaged spectrum of 780,000 molecular FIDs (approximately 6.5 h of averaging). Additionally, the time domain resolution afforded by a 20  $\mu\text{s}$  FID generates an average Doppler broadened linewidth of approximately 130 kHz at FWHM.

The sample for spectral investigation was prepared by balancing  $c\text{-C}_3\text{H}_6\text{Si}_2\text{F}_4$  vapor with approximately 3.4 atm of Ne gas (GTS Welco) for a total sample concentration of approximately 0.1%. This afforded a frequency-domain dynamic range of approximately 4000:1 at 780,000 averages, which enabled assignment of all common heavy atom single isotopologues ( $^{13}\text{C}$ ,  $^{29}\text{Si}$ ,  $^{30}\text{Si}$ ) in natural abundance as well as a double isotopologue ( $^{29}\text{Si}/^{30}\text{Si}$ ). These assignments are listed in Tables 1–3 and the experimental analysis of  $c\text{-C}_3\text{H}_6\text{Si}_2\text{F}_4$  was supplemented with ab initio electronic structure calculations for rotational constant and centrifugal distortion predictions (Table 4). These calculations were performed with the Gaussian 09 suite of programs [18].

The infrared spectrum of the gas (Fig. 1) was obtained from 4000 to 220  $\text{cm}^{-1}$  on a Perkin-Elmer model 2000 Fourier transform spectrometer equipped with a Ge/CSi beamsplitter and a DTGS detector. Atmospheric water vapor was removed from the spectrometer housing by purging with dry nitrogen. The spectrum of the gas was obtained with a theoretical resolution of 0.5  $\text{cm}^{-1}$  with 128 interferograms added and truncated.

Raman spectrum (Fig. 2) of the liquid was collected in back-scattering geometry using the 514.532 nm line of an Argon ion laser as the excitation source, with  $\sim 22$  mW incident on the diamond cell. A Semrock 514 nm edge filter was used to separate the laser line from the Raman scattered light. The scattered light was dispersed in a Spectra-pro 500i spectrograph and detected with a Spec-10 liquid nitrogen cooled CCD detector. Raman spectra were collected using a 2400 g/mm grating with a slit width of 100  $\mu\text{m}$ , which gives spectral resolution of  $\sim 0.2$   $\text{cm}^{-1}$ . The observed bands in the infrared spectrum of the gas and Raman spectrum of the liquid along with their proposed assignments are listed in Table 5.

Additional ab initio calculations were performed with the Gaussian 03 program [19] by using Gaussian-type basis functions. The energy minima with respect to nuclear coordinates were obtained by the simultaneous relaxation of all geometric parameters by the gradient method of Pulay [20]. A variety of basis sets as well as the corresponding ones with diffuse functions were employed with the Møller–Plesset perturbation method [21] to the second order MP2 with full electron correlation as well as with density functional theory by the B3LYP method. The predicted conformational energy differences are listed in Table 6.

In order to obtain descriptions of the molecular motions involved of the fundamental modes of  $c\text{-C}_3\text{H}_6\text{Si}_2\text{F}_4$ , a normal coordinate analysis was carried out. The force field in Cartesian coordinates was obtained with the Gaussian 03 program at the MP2(full) level with the 6-31G(d) basis set. The internal coordinates used to calculate the G and B matrices are given for the twist conformer in Table 7 with the atomic numbering shown in Fig. 3. By using the B matrix [22], the force field in Cartesian coordinates was converted to a force field in internal coordinates. Subsequently, 0.88 was used as the scaling factor for the CH stretches, the SiH stretches, and the  $\text{CH}_2$  deformations and 0.90 was used for all other modes to obtain the fixed scaled force constants and

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