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Conformational stability, vibrational spectra and ab initio calculations for chloromethyl methyl silane and chloromethyl methyl difluorosilane

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Abstract

The infrared spectra of gaseous and solid chloromethyl methyl silane, $ClCH_2SiH_2CH_3$, and chloromethyl methyl difluorosilane, $ClCH_2SiF_2CH_3$, were recorded. Additionally, the variable temperature infrared spectra of the sample dissolved in liquid krypton and/or xenon were obtained. Both the *trans* and *gauche* conformers are present in the fluid phases but only the *trans* conformer is present in the solid for both molecules. The enthalpy difference between the two conformers for chloromethyl methyl silane was determined to be 180 ± 15 cm^{-1} (2.16 ± 0.18 kJ/mol) and for chloromethyl methyl difluorosilane 236 ± 15 cm^{-1} (2.82 ± 0.17 kJ/mol) in xenon with the *gauche* conformers more stable for both molecules. The enthalpy value for the silane in krypton is 181 ± 18 cm^{-1} (2.16 ± 0.09 kJ/mol). Ab initio calculations were carried out at the RHF/6-31G* and MP2/6-31G* levels for both molecules from which structural parameters and conformational stabilities were determined.

Keywords: Conformational stability; Ab initio calculations; Chloromethyl methyl silane; Difluorosilane

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1. Introduction

Previously we [1] investigated the far infrared and low frequency gas phase Raman spectra of the 1-halopropane molecules, $CH_3CH_2CH_2X$ (X = F, Cl, Br) and from the observed asymmetric torsional transitions of both the *trans* and *gauche* conformers the potential functions governing the conformer interconversions were predicted. However, the experimental determined values had such large uncertainties, that it was not possible to make meaningful comparison with the estimated values. For the corresponding chlorosilane, $ClCH_2SiH_2CH_3$, the stable conformer in the crystalline state was initially found to be the *trans* form but in the liquid state it was estimated that the enthalpy difference was zero between the two conformers [2]. In the vapor state the infrared bands of the conformer pairs are so badly overlapped that measurements of the relative intensities of the bands was not possible [2]. Therefore, to determine the conformer stability in the fluid states we carried out a temperature dependent infrared spectral investigation of chloromethyl methyl silane dissolved in liquid xenon [3]. As a continuation of these studies, we

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Table 1
Temperature and intensity ratios for the conformational study of chloromethyl methyl silane in liquid xenon

T (°C)	T (K)	$1000/T$ (K)	I_{685}/I_{700}	− ln K	I_{738}/I_{700}	− ln K
− 70	203	4.808	0.4587	0.7795	1.159	− 0.1479
− 75	198	5.051	0.4759	0.7426	1.211	− 0.1916
− 80	193	5.181	0.4895	0.7144	1.242	− 0.2168
− 85	188	5.319	0.5058	0.6816	1.281	− 0.2473
− 90	183	5.464	0.5260	0.6424	1.339	− 0.2921
− 95	178	5.618	0.5561	0.5868	1.388	− 0.3278
− 100	173	5.780	0.5701	0.5619	1.454	− 0.3747
ΔH[a]				181 ± 6		180 ± 5

[a] Average ΔH = 180 ± 18 (2.16 ± 0.20 kJ/mol) with the *gauche* conformer more stable.

have investigated the temperature dependent FT-IR spectra of the sample dissolved in liquid krypton. It was hoped that the enthalpy difference between the conformers in krypton along with that in xenon could be used to predict the value in the vapor state [4].

For comparison purposes, we have also carried out vibrational studies of the corresponding silicon–fluoride compound, $ClCH_2SIF_2CH_3$. The infrared spectra of the gas and solid, as well as the sample dissolved in liquid xenon were recorded. Additionally, ab initio calculations at the level of MP2/6-31G* were carried out to predict optimized geometries, conformation stabilities, harmonic force fields, infrared intensities, and vibrational frequencies of $ClCH_2SiF_2CH_3$. The results of these spectroscopic and theoretical studies are reported therein.

2. Experimental

The sample of chloromethyl methyl silane was prepared by the reduction of commercially available chloromethyl methyl dichlorosilane with lithium aluminum hydride in dry n-butyl ether. The sample of chloromethyl methyl difluorosilane was also prepared from chloromethyl methyl dichlorosilane by fluorination with freshly sublimed antimony trifluoride. Purification of both samples was performed with a low-temperature, low-pressure fractionating column, and the purity of the samples was checked by recording the mass and the mid-infrared spectrum of the gases. The samples were stored under vacuum at low temperature.

The mid-infrared spectra of the samples dissolved in liquified krypton and/or xenon as a function of temperature were recorded on a Bruker model IFS 66 Fourier transform interferometer equipped with a globar source, a Ge/KBr beamsplitter and a TGS detector. In all cases 100 interferograms were collected at 1.0 cm^{-1} resolution averaged and transformed with a boxcar truncation function.

3. Conformational stability

The determination of the conformational stability is difficult for both molecules since most of the fundamentals for each conformer are predicted to be near coincident. Nevertheless, it is quite clear from the spectral data for both $ClCH_2SiH_2CH_3$, and $ClCH_2SiF_2CH_3$, that conformers are present in the fluid phases.

For $ClCH_2SiH_2CH_3$, infrared bands with maxima at 685 and 624 cm^{-1} in the spectrum of the amorphous solid, which are also evident in the spectrum of the gas, are absent from the spectrum of the annealed solid. Similarly there are bands at 738 and 580 cm^{-1} which also disappear from the spectrum of the amorphous sample when the sample is annealed to a polycrystalline solid. Similar results are also found for the liquid. Therefore, in both the spectra of the gas and liquid there is clear evidence for the existence of two conformers. The ab initio calculations indicate that the bands, which disappear, are as a result of the *gauche* conformer so the *trans* conformer is the rotamer that is stable in the solid.

The conformer pairs at 685/700 and 738/700 cm^{-1} with the first listed frequency owing to the *gauche*

Table 2
Temperature and intensity ratios for conformational stability determination of chloromethyl methyl silane dissolved in liquid krypton[a]

T (°C)	1000/T (K)	I_{701}/I_{685}	$-\ln K$	I_{701}/I_{740}	$-\ln K$
−105	59.47	0.625	−0.469	4.088	1.408
−110	61.29	0.672	−0.396	4.703	1.548
−115	63.23	0.749	−0.287	4.444	1.491
−120	65.29	0.808	−0.212	4.753	1.558
−125	67.49	0.844	−0.169	5.039	1.617
−130	69.85	0.910	−0.094	5.270	1.662
−135	72.38	0.941	−0.060	5.612	1.724
−140	75.10	1.021	0.020	6.081	1.805
−145	78.03	1.105	0.100	6.560	1.880
−150	81.20	1.199	0.182	6.985	1.943
ΔH[a]			199 ± 10		163 ± 10

[a] Average value: $\Delta H = 181 \pm 8$ cm^{-1} (2.16 ± 0.09 kJ/mol) with the *gauche* conformer more stable.

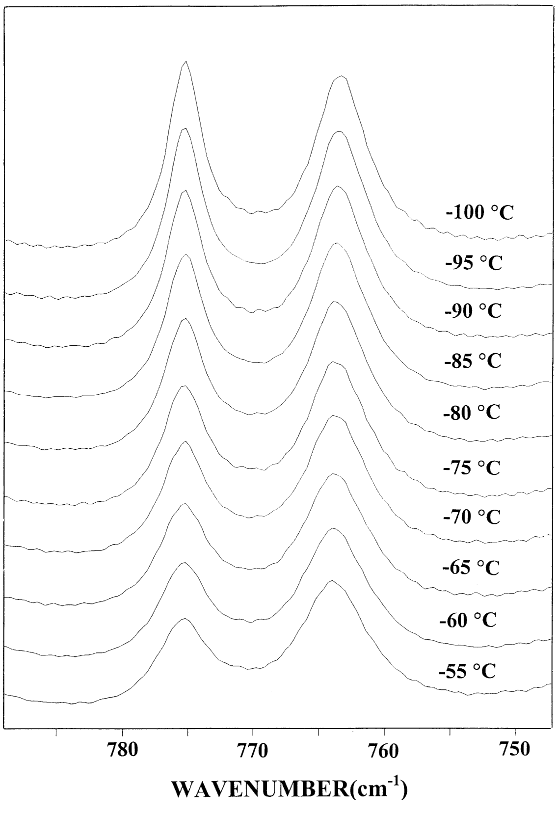

Fig. 1. Temperature dependence of the mid-infrared spectrum of chloromethyl methyl difluorosilane dissolved in liquid xenon.

Table 3
Temperature and intensity ratios for conformational stability determination of chloromethyl methyl difluorosilane dissolved in liquid xenon[a]

T (°C)	1000/T (K)	I_{775}/I_{765}	$-\ln K$
−55	4.58	0.518	0.657
−60	4.65	0.543	0.611
−65	4.80	0.578	0.549
−70	4.92	0.585	0.537
−75	5.05	0.606	0.501
−80	5.18	0.638	0.449
−85	5.31	0.697	0.361
−90	5.46	0.728	0.318
−95	5.61	0.756	0.280
−100	5.78	0.753	0.283

[a] Enthalpy value: $\Delta H = 236 \pm 15$ cm^{-1} (2.82 ± 0.17 kJ/mol) with the *gauche* conformer more stable.

conformer were used to determine the enthalpy difference between the conformers by the temperature dependent infrared spectra of krypton and xenon [3] solutions. These data are listed in Tables 1 and 2 and it should be noted that the values in the krypton and xenon [3] solutions are essentially the same. We believe this indicates that the value in the vapor is 180 ± 10 cm^{-1} with the *gauche* rotamer more stable.

Similar data have also been obtained for $ClCH_2SiF_2CH_3$ in xenon solution. We utilized the conformer pair 775/765 cm^{-1} where the first listed frequency is assigned to the *gauche* conformer. It is clear from the observed spectra (Fig. 1) that the *gauche* conformer is the more stable rotamer. The data are listed in Table 3 and the determined enthalpy value of 236 ± 15 cm^{-1} is significantly higher than that for the corresponding hydrogen analogue. This is consistent with the ab initio calculations, which predict that the value should be nearly twice as large.

4. Ab Initio calculations

Ab initio calculations were carried out at both the RHF/6-31G* and MP2/6-31G* levels from which structural parameters (Table 4) and conformational stabilities were obtained. For both molecules the *gauche* conformers are predicted to be more stable, which is consistent with the experimental data. The predicted energy differences from the MP2/6-31G*

Table 4
Comparison of the structural parameters,[a] rotational constants, dipole moments and energy for chloromethyl methyl silane and difluorosilane

	RHF/6-31G*				MP2/6-31G*			
Parameter[b]	*gauche* SiH_2	*gauche* SiF_2	*trans* SiH_2	*trans* SiF_2	*gauche* SiH_2	*gauche* SiF_2	*trans* SiH_2	*trans* SiF_2
Si_2-C_1	1.882	1.853	1.888	1.858	1.874	1.843	1.880	1.849
C_3-Si_2	1.905	1.881	1.904	1.880	1.897	1.872	1.896	1.872
$Cl-C_3$	1.804	1.799	1.801	1.794	1.794	1.791	1.792	1.787
H_5-C_1	1.086	1.086	1.086	1.086	1.093	1.093	1.093	1.093
H_6-C_1	1.085	1.085	1.087	1.086	1.094	1.092	1.093	1.093
H_7-C_1	1.086	1.086	1.087	1.086	1.093	1.093	1.093	1.093
X_8-Si_2	1.480	1.589	1.475	1.584	1.490	1.613	1.485	1.608
X_9-Si_2	1.475	1.585	1.475	1.584	1.485	1.609	1.485	1.608
$H_{10}-C_3$	1.081	1.081	1.081	1.082	1.092	1.092	1.092	1.093
$H_{11}-C_3$	1.081	1.081	1.081	1.082	1.092	1.092	1.092	1.093
$C_3Si_2C_1$	111.4	115.3	109.3	112.0	110.6	114.4	109.1	109.4
ClC_3Si_2	111.6	111.2	111.3	112.7	111.1	110.6	111.3	109.9
$H_5C_1Si_2$	110.7	110.5	110.7	110.7	111.0	110.8	110.8	110.8
$H_6C_1Si_2$	111.2	111.2	111.5	111.3	110.6	110.9	111.2	111.4
$H_7C_1Si_2$	111.3	111.1	111.5	111.3	111.0	110.7	111.2	111.4
$X_8Si_2C_3$	106.3	105.7	108.5	108.9	106.7	106.0	108.4	108.3
$X_9Si_2C_3$	108.4	108.3	108.5	108.9	108.3	108.5	108.4	108.3
$H_{10}C_3Si_2$	111.8	111.4	112.0	111.0	111.6	111.4	111.5	112.7
$H_{11}C_3Si_2$	112.1	111.8	112.0	111.0	111.5	111.3	111.5	112.7
$ClC_3Si_2C_1$	61.5	52.95	180.0	180.0	59.7	52.10	180.0	180.0
$H_5C_1Si_2C_3$	−179.8	176.9	180.0	180.0	−179.8	175.9	180.0	180.0
$H_6C_1Si_2H_5$	119.9	−120.1	119.7	−119.8	120.0	−120.3	119.8	−119.9
$H_7C_1Si_2H_5$	−120.4	120.1	−119.7	119.8	−120.0	120.3	−119.8	119.9
$X_8Si_2C_3C_1$	120.5	122.0	120.7	−121.7	120.8	121.9	120.8	−121.7
$X_9Si_2C_3C_1$	−122.8	−124.4	−120.7	121.7	−122.2	−124.0	−120.8	121.7
$H_{10}C_3Si_2Cl$	119.2	119.5	119.3	−120.1	119.8	120.0	119.8	−120.6
$H_{11}C_3Si_2Cl$	−119.4	−119.6	−119.3	120.1	−119.6	−119.7	−119.8	120.6
A	7763	3472	15550	3714	7681	3439	15702	3633
B	2237	1349	1705	1329	2289	1353	1741	1332
C	1910	1302	1595	1306	1941	1314	1629	1313
$\lvert\mu_a\rvert$	1.683	0.36/8	2.552	2.112	1.597	1.160	2.517	1.756
$\lvert\mu_b\rvert$	0.793	0.602	1.319	3.318	0.770	0.639	1.333	3.619
$\lvert\mu_c\rvert$	0.924	1.632	0.000	0.000	0.917	1.683	0.000	0.000
$\lvert\mu_t\rvert$	2.077	1.778	2.873	3.933	2.000	1.807	2.849	4.023
$-(E + 1020)$		6.083301		6.081164		6.935774		6.933532
$-(E + 824)$	4.216001		4.215428		4.716628		4.717433	
ΔE (cm^{-1})			126	469			176	492

[a] Bond distances in Å, bond angles in degrees, rotational constants in MHz, dipole moments in Debye and energies in Hartrees.
[b] X is either an H or F atom.

calculations are slightly higher than the experimental enthalpy differences. Also, it should be noted that the predicted dipole moment of the *trans* conformers are larger than those for the *gauche* conformers. This is consistent with the observations of the *trans* conformer of the hydrogen analogue in the crystalline solid state. However, for the corresponding fluoro analogue two types of crystals were observed, one containing the *gauche* conformer and one containing the *trans* conformer [5].

The predicted bond distances between the *trans* and *gauche* conformers for each molecule are very similar with predicted differences of 0.005 Å or less for the Si–C and C–Cl bonds. Also the only significant angle difference with the exception of the ClCSiC dihedral angle is the CSiC angle of the fluoro compound, which is 5° larger for the *gauche* conformer. Also it should be noted that the structural parameters are very similar between the corresponding conformers for both molecules except for the Si–C bond distance and, of course, the silicon–hydrogen and silicon–fluorine parameters.

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