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Infrared and Raman spectra, conformational stability, barriers to internal rotation, normal-coordinate calculations and vibrational assignments for vinyl silyl bromide

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Abstract

The infrared $(3200-30 \text{ cm}^{-1} \text{ spectra of gaseous and solid, the Raman spectra <math>(3200-30 \text{ cm}^{-1})$ of the liquid and solid vinyl silyl bromide, CH₂CHSiH₂Br, have been recorded. Additionally, quantitative depolarization values have been obtained. Both the *gauche* and *cis* conformers have been identified in the fluid phases but only the *gauche* conformer remains in the solid. Variable temperature studies from 0 to -87° C of the Raman spectrum of the liquid was carried out. From these data, the enthalpy difference has been determined to be $22 \pm 6 \text{ cm}^{-1}$ ($0.26 \pm 0.08 \text{ kJ/mol}$), with the *gauche* conformer being the more stable form. The predictions from the *ab initio* calculations up to MP2/6-311 + + G(2d,2p) basis set favor the *gauche* as the more stable form. A complete vibrational assignment is proposed for both the *gauche* and *cis* conformers based on infrared band contours, relative intensities, depolarization values and group frequencies. The vibrational assignments are supported by normal coordinate calculations utilizing the force constants from ab initio MP2/6-31G(d) calculations. Complete equilibrium geometries have been determined for both rotamers by ab initio calculations employing a variety of basis sets up to 6-311 + + G(2d,2p) at levels of restricted Hartree-Fock (RHF) and/or Moller-Plesset (MP) to second order. The results are discussed and compared to those obtained for some similar molecules. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Conformational stability; FT-IR spectra; ab initio calculations; Vinyl silyl bromide

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1. Introduction

The conformational stability of the allyl halides (3-halopropenes) CH_2CHCH_2X where X = F, Cl, Br and I have been the subject of several studies in the past decade [1–8]. From these studies it has been concluded that these molecules exist as a mixture of *cis* and *gauche* conformers in the fluid

1386-1425/00/\$ - see front matter © 2000 Elsevier Science B.V. All rights reserved. PII: S1386-1425(99)00204-8 phases but only the fluoride molecule has the *cis* conformer the more stable form.

Ab initio calculations have been carried out for both the allyl fluoride and allyl chloride (gauche more stable form). For the chloride, the correct conformer stability is predicted at all level of the calculations up to MP2/6-311 + + G(d,p) but the energy difference of 457 cm⁻¹ (5.47 kJ/mol) is much larger than the experimentally determined enthalpy difference of 96 ± 5 cm⁻¹ (1. 15 ± 0.06 kJ/mol) from a variable temperature of a krypton solution and 147 + 20 cm⁻¹ (1.76 + 24 kJ/mol) for the xenon solution. For the fluoride molecule the MP2/6-311 + + G(d,p) ab initio predict the gauche conformer to be the more stable form by 117 cm⁻¹ (1.40 kJ/mol) whereas the experimental enthalpy value was determined to be 60 + 8 cm⁻¹ (0.72 + 0.10 kJ/mol) from a xenon solution and 81 ± 1 cm⁻¹ (0.97 + 0.001 kJ/mol) from a krypton solution. Therefore the ab initio predictions appear to favor the gauche conformer by at least 200 cm^{-1} (2.39 kJ/mol) for these allyl halides. In order to determine whether a similar problem exists for the corresponding vinyl silyl halides, CH_2CHSiH_2X where X = F, Cl, Br, we have initiated a study of the conformational stabilities of these molecules, both experimental and from ab initio calculations.

The first of these silvl compounds we investigated was vinyl silyl chloride [9,10]. Prior to our recent conformational study [11] of this molecule, the enthalpy difference was determined from a variable temperature study of the Raman spectrum of the liquid [10] where an enthalpy value of $98 \pm 11 \text{ cm}^{-1}$ (1.18 $\pm 0.13 \text{ kJ/mol}$) was reported with the *cis* conformer the more stable form. This result was at variance with the conformational stability prediction from the RHF/6-31G(d) calculations [10] However, it is well known that the conformer that is the most stable form in the liquid may not be the most stable rotamer in the gas. Therefore, we carried [11] out variable temperature infrared studies for both xenon and krypton solutions and determined enthalpy differences of 112 ± 24 cm⁻¹ (1.34 ± 0.29 kJ/mol) and $81 \pm 8 \text{ cm}^{-1}$ (0.97 $\pm 0.10 \text{ kJ/mol}$), respectively with the cis conformer the more stable form. We [11] also carried out ab initio calculations with full

electron correlation by the perturbation method to second order (MP2) with larger basis sets than previously utilized [10]. From the MP2/6-311 + G(d,p) calculation the *gauche* conformer is predicted to be more stable by 123 cm⁻¹ (1.47 kJ/mol) and even at the level of MP2/6-311 + G(2d,2p) the *gauche* conformer is still predicted to be more stable by 21 cm⁻¹ (0.25 kJ/mol). Thus, the ab initio calculations seem to favor the *gauche* conformer for vinyl silyl chloride but maybe not by quite as large amount as for the corresponding carbon compounds.

As a continuation of our studies on silicon analogues of the 3-halopropenes, we have recorded the infrared and Raman spectra of the fluid and solid phases of vinyl silvl bromide along with variable temperature studies of the Raman spectra of the liquid to determine the conformational stability. We have also carried out ab initio calculations employing a variety of basis sets up to 6-311 + + G(2d,2p) at levels of restricted Hartree-Fock (RHF) and with full electron correlation by the Moller-Plesset (MP) perturbation method to second order to obtain complete equilibrium geometries. The force constants, vibrafrequencies, infrared and tional Raman intensities, and conformational stabilities have also been obtained from the ab initio calculations. The results of these vibrational spectroscopic and theoretical studies are reported herein.

2. Experimental

Vinyl silyl bromide was prepared in two steps. First vinyl silyl trichloride was reduced with lithium aluminum hydride in dry dibutyl ether to obtain vinyl silane. The later compound was purified first then reacted with tin(IV) bromide at 50°C for 40 h. Vinyl silyl bromide was purified using a low pressure, low temperature fractionation column and the purity of the sample was checked with infrared spectroscopy and mass spectrometry.

The Raman spectra of vinyl silyl bromide from 3200 to 30 cm⁻¹ (Fig. 1) were recorded on a SPEX model 1403 spectrophotometer equipped with a Spectra-Physics model 164 argon ion laser

operating on the 5145Å line. Laser power at the sample ranged from 0.4 to 1 W depending on the



Fig. 1. Raman spectra of vinyl silyl bromide in the (A) liquid; and (B) annealed solid.



Fig. 2. Mid-infrared spectra of vinyl silyl bromide in the (A) gas; (B) annealed solid.



Fig. 3. Mid-infrared spectra of vinyl silyl bromide (A) gas; (B) calculated spectrum of the mixture of both conformers ($\Delta H = 22 \text{ cm}^{-1}$); (C) calculated spectrum of the *cis* conformer; (D) calculated spectrum of the *gauche* conformer.

physical state of the sample. The spectrum of the liquid was obtained from the sample sealed in a glass capillary. The spectrum of the solid was obtained by condensing the liquid in a Miller–Harney cell [12] cooled by boiling liquid nitrogen. Multiple annealings were carried out to obtain good polycrystalline material, which was indicated when no further changes in the spectrum were noted. The reported frequencies are expected to be accurate to ± 2 cm⁻¹.

The mid-infrared spectra of gaseous and solid vinyl silyl bromide (Figs. 2 and 3A) were recorded on a Perkin-Elmer model 2000 Fourier transform interferometer equipped with a ceramic source, Ge/CsI beamsplitter and a DTGS detector. A 10 cm cell with CsI windows was used to obtain the spectrum of the gas. The spectrum of the solid was obtained by condensing the sample on a CsI substrate held at -196° C by boiling liquid nitro-

gen. The sample was repeatedly annealed until no further changes were observed in the spectra.

The far infrared spectrum of the gas (Fig. 4A) was recorded on a Bomem model DA3.002



Fig. 4. Far infrared spectra of vinyl silyl bromide in (A) gas, (B) unannealed solid, and (C) annealed solid. The bands labeled with an asterisk are due to the rotational transitions of HBr.



Fig. 5. Internal coordinates of vinyl silyl bromide.

Fourier transform interferometer equipped with a vacuum bench, a Globar source, and a liquid He cooled silicon bolometer with a wedged sapphire filter and polyethylene windows. The gaseous sample was contained in a 1 m cell equipped with polyethylene windows and recorded at a spectral resolution of 0.2 cm⁻¹ with a 6.25 μ m Mylar beamsplitter. The far infrared spectrum of the solid (Fig. 4B and C) was recorded on the previously described Perkin-Elmer model 2000 interferometer. A grid beamsplitter and a cryostat cell with polyethylene windows were used and the sample was deposited on a silicon substrate cooled by boiling liquid nitrogen. All observed infrared and Raman bands with significant intensities are listed in Table 1.

3. Ab initio calculations

The LCAO-MO-SCF restricted Hartree-Fock calculations were performed with the Gaussian-94 program [13] using Gaussian-type basis functions. The energy minima with respect to nuclear coordinates were obtained by the simultaneous relaxation of all of the geometric parameters using the gradient method of Pulay [14]. The structural optimizations for both the *gauche* and the *cis* conformers were carried out with initial parameters taken from those of vinyl silyl chloride [11]. The 6-31G(d) and 6-311 + G(d,p) basis sets were employed at the level of restricted Hartree-Fock (RHF) and Moller-Plesset (MP2) to second order and the determined structural parameters are listed in Table 2.

The ab initio NIP2/6-31G(d) calculations were utilized to obtain force constants for both the gauche and the cis conformers of vinyl silyl bromide, and the resulting wavenumbers were used for comparison with the experimental results. To obtain the approximate descriptions of the normal modes the ab initio force fields of Cartesian coordinates were transformed into force fields in internal coordinates. The corresponding transformation matrices, B, were generated using the Cartesian coordinates obtained from the optimized geometries and the complete set of 24 internal coordinates are shown in Fig. 5. This

Infrared				Raman			Assignment		
Gas	Rel. Int.	Solid	Rel. Int.	Liquid	Rel. Int. and Depol.	Solid	Rel. Int.	v _i ^b	Approximate description
3078 R 3072 Q, A 3066 P	W	3058	W	3067	w 0.47	3063	W	v ₁	CH ₂ antisymmetric stretch
3032 max	vw	3021 3014	VW W	3025	sh, vw	3019	vw		
2995 max	VW	2989	vw	2990	m 0.06	2994 2978	W VW	v_2, v'_3	CH ₂ symmetric stretch
2967 max	vw	2949	w	2956	vw 0.11	2953	w	v_3, v_2'	CH stretch
2194 Q, C	vs	2212	m	2197	sh,s 0.07	2220	m	v_4	SiH_2 antisymmetric stretch
2187 Q, A 2181 P	VS	2202	VS	2183	vs. 0.07	2205	VS	<i>v</i> ₅	SiH ₂ symmetric stretch
1940 R 1937 min, A 1931 P	VW								Overtone
1604 R									
1598 QA 1593 P	W	1589 1588	m m	1596	m 0.01	1591	m	v ₆	CC stretch
1421 Q, A		1430	VW						
1409 R 1403 Q, A 1398 P		1405 1382	m vw	1409 1402	w 0.27 w 0.27	1409 1385	W VW	<i>v</i> ₇	CH ₂ deformation
1274 R 1270 Q,A 1264 P	VW	1263 1259	VW VW	1295 1266	m 0.06	1260	m	v ₈	CH in-plane bend
1008 max	w	1014	Vw	1013	bd,w 0.66	1015	W	v ₉	CH ₂ wag
1001 Q 997 Q	W	1012 1003 999	vw s m					v_{10}	CH ₂ twist

Table 1 Observed infrared and Raman wavenumbers (cm^{-1}) for vinyl silyl bromide^a

1069

Infrared				Raman		Assignment			
Gas	Rel. Int.	Solid	Rel. Int.	Liquid	Rel. Int. and Depol.	Solid	Rel. Int.	v _i ^b	Approximate description
971 Q,C 967 QC	m m	972	s	970	sh,vw 0.75	976	vw	v'_{11}	CH ₂ rock
960 R 955 min, B 948 P	m			944	bd,w 0.75			v'_{12}	
948 R 943 min, B 939 P	m	927 912	s vw	944	bd,w 0.75	924	m	v_{12}	SiH ₂ deformation
855 R 850 Q, A 844 Q, A	VS VS	844 837 820	sh,m s s	840	w 0.60	848 830	W VW	v' ₁₃ v ₁₃	SiH ₂ wag
740 R 735 Q,C 727 Q,C	W W	737	W	734	w 0.33	747	m	$v_{18} v_{18}'$	SiH ₂ twist
696 R 693 min, B 685 P	w	691	m	695	m 0.13	703 698	sh,m m	<i>v</i> ₁₅	S-C stretch
669 R 664 min, B 657 P	VW			666	w 0.18			<i>v</i> ′ ₁₅	
609 Q, C	m			610	VW			v'_{16}	
592 Q, C	m	586	m	590	vw 592	602 vw	VW	v_{16}	SiH ₂ rock
500 max	w	512 505	sh,w m	498	w 0.33	522 515	m w	v_{17}	CH bend (out-of-plane)
469 sh 434 max	VW VW	455 393 382	m w m	460 430 404 352	sh,vw m 0.05 s 0.06	459 396 387	vw sh,m s	$v'_{18} v_{18}, v'_{17} v'_{17}$	SiBr stretch
190 max	W	280 190	VW VW	280 168 140	w 0.27 m 0.09 sh,m 0.75 sh,m	281 205 137	m m	$v_{19} v_{19} v_{20} v_{20}' v_{21}' v_{21}$	SiCC bend CSiBr bend Asymmetric torsion
		73 50 42				122 98 80 48 34			Lattice modes

^a Abbreviations used: s, strong; m, moderate; w, weak; v, very; bd, broad; sh, shoulder; A, B, and C refer to infrared band envelopes; P, Q, and R refer to the rotational-vibrational branches.

^b v and v' refer to the assignments made for the *gauche* and *cis* conformers, respectively.

1070

Parameters	RHF/6-31G(d) M		MP2/6-31G(d)		MP2/6-311+G	i(d,p)	MP2/6-311+C	6(2d,2p)	MP2/6-311 + + G(2d,2p)	
	gauche	cis	gauche	cis	gauche	cis	gauche	cis	gauche	cis
SiBr	2.231	2.228	2.229	2.226	2.234	2.230	2.253	2.247	2.253	2.247
C ₃ Si	1.858	1.864	1.850	1.857	1.851	1.857	1.857	1.853	1.847	1.8.3
C_4C_3	1.325	1.324	1.344	1.342	1.347	1.345	1.340	1.338	1.340	1.338
SiH ₅	1.469	1.470	1.480	1.481	1.472	1.472	1.468	1.468	1.468	1.468
SiH ₆	1.469	1.470	1.480	1.481	1.471	1.472	1.467	1.468	1.467	1.468
C_3H_7	1.079	1.081	1.089	1.091	1.089	1.091	1.082	1.084	1.082	1.084
C_4H_8	1.077	1.077	1.087	1.087	1.087	1.087	1.080	1.080	1.080	1.080
C_4H_9	1.077	1.076	1.087	1.086	1.088	1.086	1.081	1.080	1.081	1.080
C ₃ SiBr	110.8	110.6	110.3	109.3	109.8	109.9	109.5	109.4	109.5	109.4
C ₄ C ₃ Si	122.1	125.5	121.1	124.3	121.7	125.2	121.4	124.9	121.4	124.9
H ₅ SiBr	107.3	107.1	107.6	107.4	108.2	107.5	107.8	107.3	107.8	107.3
H ₆ SiBr	106.2	107.1	106.6	107.4	106.4	107.5	105.9	107.3	105.9	107.3
H ₇ C ₃ Si	119.3	116.3	120.2	117.4	120.0	117.1	120.4	117.5	120.4	117.5
$H_8C_4C_3$	122.2	121.9	122.3	122.0	121.9	121.5	121.9	121.6	121.9	121.6
$H_9C_4C_3$	122.2	122.2	121.8	121.6	121.6	121.7	121.5	121.3	121.4	121.3
C ₄ C ₃ SiBr	114.7	0.0	113.0	0.0	117.0	0.0	117.1	0.0	117.0	0.0
H ₅ SiBrC ₃	119.8	121.6	118.8	121.3	118.9	121.0	118.9	121.0	118.9	121.0
H ₆ SiBrC ₃	-121.6	-121.5	-122.0	-121.3	-121.5	-121.0	-121.6	-121.0	-121.6	-121.0
H ₇ C ₃ SiC ₄	179.6	180.0	180.3	180.0	179.3	180.0	179.6	180.0	179.6	180.0
H ₈ C ₄ C ₃ Si	179.3	180.0	179.8	180.0	179.3	180.0	179.5	180.0	179.4	180.0
$H_9C_4C_3H_8$	179.9	180.0	180.0	180.0	179.7	180.0	179.8	180.0	179.8	180.0
А	10 335.4	6859.2	10 086.0	6689.0	10 290.0	6739.0	10 238.6	6710.2	10 231.8	6710.8
В	1474.1	1938.1	1490.2	1994.9	1475.7	1962.6	1471.0	1965.1	1471.4	1965.4
С	1368.4	1537.7	1381.2	1564.6	1369.0	1547.1	1363.3	1547.0	1363.7	1547.2
$ \mu_{\rm a} $	2.504	2.135	2.483	2.102	2.512	2.105	2.467	2.057	2.464	2.055
$ \mu_{\rm b} $	0.225	0.188	0.193	0.145	0.352	0.291	0.258	0.219	0.258	0.220
$ \mu_{\rm c} $	0.040	0.000	0.043	0.000	0.016	0.000	0.021	0.000	0.022	0.000
$ \mu_{\rm t} $	2.515	2.143	2.491	2.107	2.537	2.125	2.480	2.069	2.478	2.067
-(E+2937)	0.487251	0.486491	0.975143	0.974977	4.066079	4.065415	4.126099	4.126056	4.126468	4.126383
$\Delta E \ (\mathrm{cm}^{-1})$		167		36		146		10		19

Table 2 Structural parameters^a, rotational constants, dipole moments and energy for vinyl silyl bromide

^a Bond distances in Å, bond angles in degrees, rotational constants in MHz, and dipole moments in Debye.

Table 3					
Symmetry	coordinates	for	vinyl	silyl	bromide

Species	Description	Symmetry Coordinate ^a
A	CH ₂ antisymmetric stretch	$S_1 = r_1 + r_2$
	CH stretch	$S_2 = r_3$
	CH ₂ symmetric stretch	$S_3 = r_1 + r_2$
	SiH_2 antisymmetric stretch	$S_4 = r_4 - r_5$
	SiH ₂ symmetric stretch	$S_5 = r_4 + r_5$
	CC stretch	$S_6 = R_2$
	CH ₂ deformation	$\mathbf{S}_7 = 2\alpha - \beta_1 - \beta_2$
	CH in-plane bend	$S_8 = \psi_1 - \psi_2$
	CH ₂ wag	$\mathbf{S}_9 = \mathbf{\beta}_1 - \mathbf{\beta}_2$
	CH ₂ twist	$S_{10} = \mu$
	CH ₂ rock	$S_{11} = \xi_1$
	SiH ₂ deformation	$S_{12} = 4\varepsilon - \theta_1 - \theta_2 - \gamma_1$
	SiH ₂ wag	$S_{13} = \gamma_1 + \gamma_2 - \theta_1 - \theta_2$
	SiH_2 twist	$S_{14} = \theta_1 - \theta_2 - \gamma_1 + \gamma_2$
	Si–C stretch	$S_{15} = R_1$
	SiH ₂ rock	$S_{16} = \theta_1 - \theta_2 + \gamma_1 - \gamma_2$
	CH bend (out-of-plane)	$S_{17} = \xi_2$
	SiBr stretch	$S_{18} = T$
	SiCC bend	$S_{19} = 2\pi - \psi_1 - \psi_2$
	CSiBr bend	$S_{20} = 5\omega - \varepsilon - \theta_1 - \theta_2$
		$-\gamma_1 - \gamma_2$
	Asymmetric torsion	$S_{21} = \tau$

 $^{^{\}rm a}$ Symmetry coordinates $S_4,\,S_{11},\,S_{13},\,S_{14},\,S_{16},\,S_{17}$ and S_{21} are A'' modes for the cis conformer.

complete set of internal coordinates used to form the symmetry coordinates are listed in Table 3. The resulting force fields in internal coordinates for the *gauche* and *cis* conformers can be obtained from the authors. These force constants were input along with the unsymmetrized G-matrices and scaling factors, into the perturbation program written by Schachtschneider [15]. Initially, all scaling factors were kept fixed at a value of 1.0 to produce the pure ab initio calculated vibrational frequencies. Scaling factors of 0.88 for carbonhydrogen stretches, 0.90 for silicon-hydrogen and heavy atom stretches, carbon-hydrogen bends and 1.0 for heavy atom bends and asymmetric torsion were used to obtain the 'fixed scaled' force fields and vibrational wavenumbers along with the potential energy distributions (P.E.D.). All of these data are listed in Table 4 for the gauche and cis conformers.

4. Conformational stability

There are several fundamentals, which show conformer doublets in both the infrared and Raman spectra of the fluid phases. The two bands at 693 and 664 cm⁻¹ in the Raman spectrum of liquid are assigned to the Si–C stretching modes, but in the spectrum of the solid only the higher frequency band remains. Similarly, the two Qbranches at 609 and 592 cm⁻¹ in the infrared spectrum of the gas are assigned as SiH₂ rocks, but this time the lower frequency band remains in the spectrum of the solid. Other bands which are observed in the spectra of the fluid phases and amorphous solid but not present in the spectrum of the annealed solid are observed at 971, 727, 434 and 348 cm⁻¹.

These data clearly show that there are two conformers present in the fluid phases at ambient temperatures but only one rotamer remains in the polycrystalline solid. The band at 352 cm^{-1} is the only one predicted by the ab initio calculations in the 300 cm⁻¹ region and is definitely assigned to the Si-C=C bend of the *cis* conformer. Since this band disappears from the spectrum of the solid (Fig. 4), it can be concluded that only the gauche conformer remains in the annealed solid. Further support for this conclusion is found from the assignments for the Si-C stretch and SiH₂ rock which are assigned at 664 and 609 cm⁻¹ for the cis form in the gas phase and at 693 and 592 cm^{-1} , respectively, for the gauche rotamer. Only the latter gauche bands remain in the spectrum of the polycrystalline solid. Similarly, the other listed bands which disappear upon solidification and annealing are all assigned as arising from the cis conformer, and they will be discussed later. Therefore, all the spectral data indicate that the gauche form is the stable conformer in the annealed solid.

In order to gain information about enthalpy difference between the two conformers variable temperature studies in liquified xenon and krypton were attempted. Unfortunately, the compound decomposed to siloxanes when dissolved in both rare gas solutions. The decomposition was believed to be due to a small amount of water in the noble gases. In another attempt to determine

		Description	gauche						cis							
			ab initio ^a	Fixed scale ^b	IR. Int. ^c	Raman act. ^d	dp. Ratio ^d	Obs. ^e	P.E.D.	ab initio ^a	Fixed scale ^b	IR. Int. ^c	Raman act. ^d	dp. Ratio ^d	Obs. ^e	P.E.D.
A	v_1	CH ₂ antisymmetric stretch	3286	3083	9.5	81.6	0.64	3072	99S ₁	3297	3092	6.8	58.9	0.69	3072	99S ₁
	v_2	CH stretch	3216	3017	2.0	148.5	0.20	2995	91S2	3188	2990	3.9	97.0	0.50	2967	87S ₂ , 12S3
	v_3	CH ₂ symmetric stretch	3097	2999	7.9	41.3	0.56	2967	9283	3208	3006	7.2	142.6	0.16	2995	87S ₃ , 12S ₂
	v_4	SiH ₂ antisymmetric stretch	2348	2228	134.8	64.8	0.74	2194	100S4	2340	2219	142.1	83.3	0.75	2194	$100S_{4}$
	v ₅	SiH ₂ symmetric stretch	2333	2213	108.5	157.4	0.05	2187	10085	2332	2212	130.6	196.3	0.06	2187	100S ₅
	v ₆	CC stretch	1675	1589	11.0	30.9	0.16	1598	6186, 3387	1680	1594	3.9	22.0	0.14	1598	$63S_6, 30S_7$
	v_7	CH ₂ deformation	1485	1409	19.1	33.0	0.38	1403	6687, 2686	1483	1404	18.1	24.4	0.46	1403	70S ₇ , 24S ₆
	v ₈	CH (in-plane-bend)	1319	1253	0.6	15.1	0.29	1270	60s8, 26S9	1320	1258	3.4	10.9	0.27	1270	62S ₈ , 26S ₉
	v ₉	CH ₂ wag	1058	1035	11.7	0.7	0.74	1008	61S9, 29S8	1053	1033	41.6	4.6	0.68	1008	61S ₉ , 28S ₈
	v_{10}	CH ₂ twist	1053	1004	17.8	1.1	0.75	1001	63\$10, 29\$17	1052	999	31.6	1.0	0.75	1001	62S ₁₀ , 15S ₉ , 258S ₁₇
	v ₁₁	CH ₂ rock	997	946	72.3	5.4	0.64	967	88S11	1009	957	148.0	24.2	0.71	971	99S ₁₁
	v ₁₂	SiH ₂ deformation	986	935	102.4	15.1	0.75	943	89812	1001	952	17.4	0.2	0.75	955	96S ₁₂
	v ₁₃	SiH ₂ wag	904	857	366.1	12.0	0.71	850	96813	890	844	306.5	13.3	0.70	844	86S ₁₃
	v_{14}	SiH ₂ twist	780	742	6.5	10.7	0.75	735	73814, 12815	762	728	29.9	5.1	0.75	727	78S ₁₄
	v ₁₅	SiC stretch	729	693	22.1	6.0	0.33	693	63815, 17814	690	654	8.1	7.0	0.34	664	81S ₁₅
	v ₁₆	SiH ₂ rock	606	577	43.0	3.0	0.54	592	73816	647	617	46.5	7.9	0.75	609	65S ₁₆ , 18S ₁₅ , 10S ₁₆
	v_{17}	CH bend (out-of-plane)	523	505	20.0	10.5	0.73	500	36S17, 16S18, 10S20, 19S10	420	399	0.2	12.7	0.75	393	$47S_{17}, 28S_{16}, 20S_{10}$
	v ₁₈	SiBr stretch	426	405	24.3	7.6	0.21	393	77S18, 10S17	460	440	36.4	8.0	0.13	434	66S ₁₈ , 17S ₁₉
	V19	SiCC bend	278	271	0.7	3.7	0.32	280*	78S19, 14S21	369	360	8.6	4.2	0.64	352*	56S ₁₉ , 32S ₁₈
	v ₂₀	CSiBr bond	168	166	2.0	5.7	0.73	168*	76S20	148	147	0.7	2.0	0.64	140*	79S ₂₀ , 19S ₁₉
	v ₂₁	Asymmetric torsion	74	74	0.1	9.2	0.74	(137)	77821, 11820	116	116	0.1	5.0	0.75	-	98S ₂₁

Table 4 Observed and calculated frequencies for gauche and cis vinyl silyl bromide

^a Calculated with the MP2/6-31G(d) basis set.

^b Scaling factors of 0.88 for carbon-hydrogen stretches, 0.90 for silicon-hydrogen and heavy atom stretches, carbon-hydrogen bends and 1.0 for heavy atom bends and asymmetric torsion.

^c Calculated infrared intensities in km/mol.

 d Calculated Raman activities in Å^4/amu, and dp ratio using RHF/6-31G(d) basis set.

^e Frequencies are taken from the infrared spectrum of the gas, except the one in parentheses, which is taken from the Raman spectrum of the solid and the ones with asterisks are taken from the Raman spectrum of the liquid.

f For a description of the symmetric coordinates see Table 3.

 ΔH , a variable-temperature study of the Raman spectra of the liquid was performed (Fig. 6). The relative intensities of the Raman lines at 690, 663, 428 and 397 cm⁻¹ were measured. By utilizing the equation $-\ln K = (\Delta H/RT) - (\Delta S/R)$, one can determine ΔH from a plot of $-\ln K$ versus the inverse temperature where $\Delta H/R$ is the slope of the line. In this equation, K is the ratio of I_c/I_g , where I is the intensity of the Raman lines, and it is assumed that ΔH is not a function of temperature.



Fig. 6. Temperature dependent Raman spectra of vinyl silyl bromide.

Table 5

Temperature and intensity ratios for the conformational study of liquid vinyl silyl bromide

T (°C)	1000/T (K)	I_{690}/I_{663}	I_{397}/I_{428}
0	3.66	1.9037	2.5810
-24	4.02	1.8482	2.5819
-42	4.33	1.7610	2.5249
-64	4.78	1.8218	2.5072
-87	5.38	1.7714	2.4737
$\Delta H^{ m a}$		24 ± 13	19 ± 3

^a Average value of 22 ± 6 cm⁻¹ (0.26 \pm 0.08 kJ/mol) with the *gauche* conformer the more stable form.

Five sets of spectral data were obtained at various temperatures ranging from 0 to -87° C (Table 5). A value of 24 ± 13 cm⁻¹ was obtained from the 690/663 cm⁻¹ pair and 19 ± 3 cm⁻¹ from the 397/428 cm⁻¹ pair. The average value from these two determinations is 22 ± 6 cm⁻¹ (0.26 \pm 0.08 kJ/mol) with the *gauche* conformer the more stable rotamer.

5. Vibrational assignments

The conformational analysis of vinyl silyl bromide shows that the molecule exists in two stable conformations in the gas and liquid states. The cis conformer has a plane of symmetry which includes the *a* and *b* axis (C_s) and the 21 normal modes span 14A' and 7A" species. The 14 A' modes should produce polarized Raman bands and A/B-type infrared band contours, whereas the 7 A" modes should be depolarized in the Raman spectrum and give rise to C-type infrared band envelopes. The gauche conformer has only the trivial C_1 symmetry and all 21 vibrations should yield polarized Raman bands and A/B/C-type infrared band contours. Guided by these considerations and also by the calculated spectral intensities predicted wavenumbers from the ab initio calculations, we proposed the vibrational assignments in Table 1.

The assignments of the carbon-hydrogen modes have been previously reported [10,11] for vinyl silyl chloride, and with only minor wavenumber shifts, they remain essentially the same for vinyl silyl bromide. In fact, the spectra of these two compounds look remarkably similar down to about 1000 cm⁻¹. The SiH₂ stretches give rise to a very strong and polarized band in the Raman spectrum of the liquid, which splits into two bands, one at 2194 cm⁻¹ for the antisymmetric stretch and another at 2187 cm^{-1} for the symmetric stretch in the spectrum of the solid. The corresponding SiH₂ wag is well resolved and appears as Q-branches at 850 cm^{-1} for the gauche form and 844 cm⁻¹ for the *cis* conformer in the infrared spectrum of the gas. The C-type Q-branches located at 735 and 727 cm^{-1} in the infrared spectrum are assigned to the SiH₂ twists

with the *gauche* conformer having the higher frequency, whereas the other C-type Q-branches located at 609 and 592 cm⁻¹ are assigned to the SiH₂ rock with the lower frequency band assigned to the *gauche* rotamer.

The Si-C stretching conformer pair is observed in the Raman spectrum of the liquid at 695 and 666 cm⁻¹ for the *gauche* and *cis* conformers, respectively, where only the former band is observed in the spectrum of the crystalline solid. The polarized Raman bands at 430 and 404 cm⁻¹ are assigned to Si-Br stretch for the gauche and the cis conformers, respectively. The SiC=C bend vibration at 348 cm⁻¹ of the *cis* form is evident in the far-infrared spectrum of the amorphous solid but disappears upon annealing (Fig. 4). The ab initio calculations predict very weak infrared intensities for the CSiBr bend and asymmetric torsions for both conformers. They are expected to be about 160 and 140 cm⁻¹ for the former mode and about 74 and 116 cm^{-1} for the latter mode for the cis and gauche conformers, respectively. These modes are not observed in the far infrared spectrum of the gas, but the CSiBr bend of the gauche form is assigned to the band at 190 cm⁻¹ observed the infrared spectrum of the solid. The two Raman lines at 168 and 140 cm^{-1} in the spectrum of the liquid are assigned to the CSiBr bends of the gauche and cis rotamers, respectively. The asymmetric torsion is assigned at 137 cm⁻¹ a Raman band in the spectrum of the annealed solid whereas no band was observed to be assigned for the same mode for the *cis* rotamer.

6. Discussion

The structural parameters listed in Table 2 are fairly consistent among the three ab initio calculations with full electron correlation with the major exceptions occurring for the Si–Br and Si–H distances. The Si–Br distance becomes longer and the Si–H distance shorter with the larger basis sets with polarization functions. The C–Si bond distance is approximately 0.006 Å shorter for the *gauche* conformer compared to the corresponding parameter for the *cis* form with all basis sets. The CCSi bond angle is approximately 3.5° smaller for the *gauche* conformer compared to this parameter in the *cis* rotamer, again for all basis sets. Additionally, a comparison of the structural parameters obtained for vinyl silyl bromide with the corresponding ones previously reported [11] for vinyl silyl chloride reveals many interesting similarities. Comparing structural parameters obtained from the MP2/6-311 + G(d,p) calculations for the bond distances and bond angles between these two molecules shows that the bond distances are within 0.007 Å and the angles are within 2° with the exception of the Si–Cl and Si–Br distances and angles.

The frequencies for the Si-H stretching modes in vinyl silvl bromide are exactly the same as those found for the corresponding modes in vinyl silyl chloride. Since we made the isotopomer CH₂CHSiHDCl, we utilized the isolated CH stretching vibrational frequency to obtain the SiH bond distance. We obtained a value of 1.480 ÅA for this distance for both the cis and gauche conformers. Therefore, we expect the same values for the SiH bond distance in the bromide. As will be seen in Table 2, the predicted SiH distance is 1.472 A from the MP2/6-311 + G(d,p) calculations which is essentially the same values predicted at this level of calculation for the chloride. Therefore, the SiH distance is estimated to be too short by approximately 0.008 Å from this level of calculation; however, the MP2/6-31G(d) calculations predict the correct values for the SiH distances. Many of the other parameters from the MP2/6-31G(d) calculations are similar to those predicted with the larger basis set, MP2/6-311 + G(d,p), which indicates that the predicted parameters from the smaller basis set, i.e. MP2/6-31G(d), are reasonably accurate if one uses full electron correlation. Thus, such calculations can be utilized to predict reasonably well structural parameters for these types of molecules.

We have measured the depolarization values of most of the pronounced Raman lines (Table 1) and the values have been obtained from the RHF/6-31G(d) calculations. For many of them the agreement is satisfactory, particularly for the ones that have depolarization ratios near 0.75. However, there are a significant number of them that have depolarization ratios lower than those pre-

Table 6

Potential energy parameters (cm^{-1}) for the confortnational interchange of vinyl silyl bromide

Parameter	mp2/6-31G(d)				
V1	37				
V2	-153				
V3	671				
V4	90				
V5	3				
V6	-49				
ΔΕ	36				
dihedral angle	113.0				
cis/gauche barrier	634				
gauche/gauche barrier	747				
gauche/cis barrier	670				



Fig. 7. Potential function of the asymmetric torsion of vinyl silyl bromide from MP2/6-31G(d) calculations. A dihedral angle of 0° corresponds to the *cis* conformer.

dicted from the ab initio calculations. Nevertheless, there is some useful information obtained from the predicted depolarization ratios for making the vibrational assignment.

The potential function parameters obtained from the data of the MP2/6-31G(d) calculations are listed in Table 6. The barriers of the *cis* to *gauche*, *gauche* to *gauche* and *gauche* to *cis* wells are 634, 747 and 670 cm⁻¹, respectively with an energy difference of 36 cm⁻¹. Therefore, the potential function is nearly threefold, with the *gauche* and *cis* conformers having almost the same barriers for interconversion (Fig. 7).

Raman and infrared spectra (Figs. 3 and 8) for vinyl silyl bromide were calculated using the fre-

quencies, scattering activities and intensities determined from the MP2/6-31G(d) calculations. The Gaussian-94 program [13] with the option of calculating the polarizability derivatives was used. The evaluation of Raman activity by using the analytical gradient method has been developed [16,17]. The activity S_i can be expressed as:

$$S_i = g_i (45\alpha_i^2 + 7\beta_i^2)$$

where g_j is the degeneracy of the vibrational mode j, α_j is the derivative of the isotropic polarizability, and β_j is that of the anisotropic polarizability. The Raman scattering cross sections, $\partial \sigma_j / \partial \Omega$, which are proportional to the Raman intensities, can be calculated from the scattering activities and the predicted frequencies for each normal mode using the relationship [18,19]:



Fig. 8. Raman spectra of vinyl silyl bromide: (A) experimental spectrum of the liquid; (B) calculated spectrum of the mixture $(\Delta H = 22 \text{ cm}^{-1})$; (C) calculated spectrum of the *cis* conformer; (D) calculated spectrum of the *.gauche* conformer.

$$\frac{\partial \sigma_j}{\partial \Omega} = \left(\frac{2^4 \pi^4}{45}\right) \left(\frac{(v_0 - v_j)^4}{1 - \exp\left[\frac{-hcv_j}{kT}\right]}\right) \left(\frac{h}{8\pi^2 cv_j}\right) S_j$$

where v_0 is the exciting frequency, v_i is the vibrational frequency of the *j*th normal mode, h, c and k are universal constants, and S_i is the corresponding Raman scattering activity. To obtain the polarized Raman scattering cross section, the polarizabilities are incorporated into S_i by $S_i[(1 -$ $(r_i)/(1+r_i)$] where r_i is the depolarization ratio of the *i*th normal mode. The Raman scattering cross sections and calculated frequencies are used together with a Lorentzian line shape function to obtain the calculated spectrum. Since the calculated frequencies are $\approx 10\%$ higher than those observed, the frequency axis of the theoretical spectrum was compressed by a factor of 0.9. The predicted Raman spectra of the cis and gauche pure conformers are shown in Fig. 8C and D, respectively. The predicted Raman spectrum of the mixture of the two conformers with a determined ΔH of 22 cm⁻¹ is shown in Fig. 8B. This spectrum should be compared to the experimental spectrum of the liquid (Fig. 8A). The calculated Raman spectrum is quite similar to the experimental spectrum with the exception of the intensities of the CH₂ deformation and CH (in-and out-of-plane bends) fundamentals which are predicted too weak. The same problem was encountered with the calculated spectrum of vinyl silyl chloride [11] where the same type of modes were also predicted to be weak compared to the experimental intensities. Actually, the calculated dipole moment of the gauche conformer is larger than that of the cis (Table 2), which should stabilize the gauche form in the condensed phases. This factor, coupled with other packing interactions, may be the reason why the gauche conformer is more stable in the solid.

Infrared intensities were also calculated based on the dipole moment derivatives with respect to the Cartesian coordinates. The derivatives were taken from the ab initio calculations and transformed to normal coordinates by:

$$\left(\frac{\partial \mu_{\mu}}{\partial Q_{i}}\right) = \sum_{j} \left(\frac{\partial \mu_{\mu}}{\partial X_{i}}\right) L_{ji}$$

where the Q_i is the *i*th normal coordinates, X_j is the *j*th Cartesian displacement coordinates, L_{ji} is the transformation matrix between the Cartesian displacement coordinates and normal coordinates. The infrared intensities were then calculated by:

$$I_{i} = \frac{N\mu}{3c^{2}} \left[\left(\frac{\partial\mu_{x}}{\partial Q_{i}} \right)^{2} + \left(\frac{\partial\mu_{y}}{\partial Q_{i}} \right)^{2} + \left(\frac{\partial\mu_{z}}{\partial Q_{i}} \right)^{2} \right]$$

In Fig. 3C and D, the predicted infrared spectra of the two conformers are shown. The combination of the spectra of the two conformers with a ΔE of 36 cm⁻¹ predicted from MP2/6-31G(d) calculation is shown in Fig. 3B. The experimental infrared spectrum of the gas is also shown for comparison. Excluding the overtones, and combination bands that are present in the spectrum of the gas, the agreement between the observed and calculated spectra is satisfactory and it provided support for the vibrational assignments.

The vibrational modes of CH_2CHSiH_2Br are relatively pure as can be seen from the P.E.D. given in Table 4. The exception is in the CH bend (out-of-plane) mode, which is extensively mixed with the CH₂ twist, Si-Br stretch and CSiBr bend for the *gauche* conformer and the CH₂ twist and SiH₂ rock for the *cis* form.

Using scaling factors of 0.88 for the carbonhydrogen stretches, 0.90 for all the other vibrations except 1.0 for the heavy atom bends and asymmetric torsion, the wavenumbers for the fundamentals are predicted from the MP2/6-31G(d) calculation to be within 1.2% for the *gauche* conformer and 1.15% for the *cis* conformer. Therefore, the frequency predictions from the MP2/6-31G(d) calculations are quite good and very helpful in the vibrational assignment. These results show that two scaling factors are sufficient to adequately predict the frequency for the observed fundamentals for this type of molecule.

All the basis sets favor the *gauche* conformer as the more stable form. The ΔE varies from 36 cm⁻¹ from the MP2/6-31G(d) calculations to 10 cm⁻¹ from the MP2/6-311 + G(2d,2p) calculations with full electron correlation which is a reasonable trend. However, the ΔE has a value of 146 cm⁻¹ from the MP2/6-311 + G(d,p) calculation. The failure of the variable temperature study in the noble gases to determine the enthalpy difference between the two conformers does not give the opportunity to check the ab initio predictions. Since the ab initio calculation predict higher dipole moment for the *gauche* form rather than the *cis* form, it is expected that *gauche* form will be slightly more stable in condensed phases relative to its stability in the gas phase. Therefore, the ΔH of 22 ± 6 cm⁻¹ with the *gauche* conformer the more stable form is expected to be the higher limit for the ΔH in the gas.

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