

The utilization of rare gas solution for making vibrational assignments and conformation stability determinations of three membered rings

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The use of rare gas solutions in the field of vibrational spectroscopy has been rather slow to develop for several reasons. Firstly, rare gases are liquids only at relatively low temperatures which requires infrared and Raman cells be maintained at relative low temperatures during the experiment. Therefore, the use of rare gas solutions to obtain spectroscopic data is not routine. Another disadvantage is the solubility in rare gas solutions is relatively low and rather poor for very polar molecules. Nevertheless there are a number of advantages for many samples which makes rare gas solutions good. For example, there is very little interaction of the solvent with solute molecules so the frequencies observed for the bands in solution are hardly shifted from the values observed in the gas. Also the rare gases do not absorb infrared radiation so it is possible to use infrared liquid cells with path lengths of several centimeters such as 10 cm. Thus the solutions can be very dilute i.e. 10^{-4} molar, which drastically reduces the association of the solute molecules. Therefore variable temperature studies can be carried out on alcohols, amines, and acids where it is nearly impossible with conventional solvents. In fact it is nearly impossible to obtain enthalpy differences for these molecules with conventional solvents. Therefore some examples will be provided which will demonstrate the ability to determine conformational stabilities and vibrational assignments. © Anita Publications. All rights reserved.

1 Introduction

There were a large number of conformational stability studies carried out in the 1960's and 70's which were determined from variable temperature solutions with non-polar solvents or in some cases the pure liquids. Many different techniques were used but infrared and Raman spectroscopy were the most popular. At that time period there were many reasons for obtaining the most stable conformer such as the structure, steric effect, chemical association, to name a few. However the reasons for determining conformational stabilities have drastically increased from the field of biochemistry and nano-chemistry. These areas have caused a great deal of interest in conformational stability due to its effects on binding sites of proteins in biochemistry and the use of conformer interchange to drive molecular motions and shapes in nano-chemistry. Specifically the conformation of organoamines is currently at work in every human alive with this arising from the amino acids in proteins and the substituted bases in DNA and RNA. The importance of conformational stability is further demonstrated in biological systems by enzyme binding where the conformational changes of the protein can change the binding site either enhancing or deactivating the enzyme.

One of the early utilizations of rare gas solutions was of small molecules to study their rotational energy changes in solution. These studies indicated that there was very little interaction of the solute with the solvent molecules so the frequencies observed in the solution were shifted very little from those observed in the gas [1]. Also, the bands were relatively narrow particularly when the data was recorded at relatively low temperatures. Thus, it was possible to resolve relatively close frequency fundamentals so individual bands could be assigned for very complex gas phase contours. Also, relative intensities of bands which were extensively overlapped in the gas were obtainable when they were recorded in low temperature rare gas solutions. Therefore, these solutions are very good for making vibrational assignments particular for molecules where more than one conformer is present and many fundamentals are closely spaced. Also, the rare gas solutions are ideally suited for making conformational determinations of the enthalpy changes since a very wide temperature range is available. There are several other advantages of the rare gas solutions for making conformational stability determinations and these will be

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demonstrated by the examples that follow. The advantages and disadvantages of rare gas solutions will be summarized in the conclusion.

2 Experimental and Computational Methods

The mid-infrared spectra of the gas were obtained from 4000 to 250 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 theoretical resolution used to obtain the spectrum of the gas was 0.5 cm^{-1} . One hundred twenty eight interferograms were added and transformed with a boxcar truncation function.

The mid-infrared spectra (4000 to 400 cm^{-1}) of the sample dissolved in liquefied xenon were recorded on a Bruker model IFS-66 Fourier transform spectrometer equipped with a globar source, a Ge/KBr beamsplitter and a DTGS detector. In all cases, 100 interferograms were collected at 1.0 cm^{-1} resolution, averaged and transformed with a boxcar truncation function. For these studies, a specially designed cryostat cell was used. It consists of a copper cell with a path length of 4 cm with wedged silicon windows sealed to the cell with indium gaskets. The copper cell was enclosed in an evacuated chamber fitted with KBr windows. The temperature was maintained with boiling liquid nitrogen and monitored by two Pt thermo resistors. The complete cell was connected to a pressure manifold to allow for the filling and evacuation of the cell. After the cell was cooled to the designated temperature, a small amount of the sample was condensed into the cell. Once the cell was cooled, the manifold and the cell were pressurized with xenon, which immediately starts condensing in the cell, thus allowing the compound to dissolve.

The Raman spectra were recorded on a Spex model 1403 spectrometer equipped with a Spectra-Physics model 2017 argon laser operating on the 514.5 nm line. The laser power used was 0.5 W with a spectral bandpass of 3 cm^{-1} . The spectrum of the liquid was recorded with the sample sealed in a Pyrex glass capillary. The measurements of the Raman frequencies are expected to be accurate to $\pm 2 \text{ cm}^{-1}$.

To support the vibrational assignments contained herein *ab initio* calculations were performed with the Gaussian-03 program [2] using Gaussian-type basis functions. The energy minima with respect to nuclear coordinates were obtained by the simultaneous relaxation of all geometric parameters using the gradient method of Pulay [3]. The Møller-Plesset perturbation method [4] to the second order MP2 with full electron correlation was used with the 6-31G(d) basis set, as well as with the density functional theory by the B3LYP method in some cases, to obtain predicted infrared frequencies, infrared intensities, Raman activities, and depolarization ratios.

To further support the vibrational assignments, we have simulated the Raman spectra from the *ab initio* MP2(full)/6-31G(d) results. The evaluation of Raman activity by using the analytical gradient methods has been developed [5-8]. The activity S_j can be expressed as: $S_j = g_j (45 \alpha_j^2 + \beta_j^2)$, 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. To obtain the polarized Raman scattering cross sections, the polarizabilities are incorporated into S_j by multiplying S_j with $(1-\rho_j)/(1+\rho_j)$, where ρ_j is the depolarization ratio of the j^{th} normal mode. The Raman scattering cross sections and calculated wavenumbers obtained from the Gaussian 03 program were used together with a Lorentzian function to obtain the simulated Raman spectra. The predicted spectrum of the mixture should be compared to that of the Raman spectrum of the liquid.

The infrared spectra were predicted from the MP2(full)/6-31G(d) calculations. The predicted scaled frequencies were used together with a Lorentzian function to obtain the calculated spectra. Infrared intensities determined from MP2(full)/6-31G(d) calculations were obtained based on the dipole moment derivatives with respect to Cartesian coordinates. The derivatives were transformed with respect to normal coordinates by $(\partial\mu_u/\partial Q_i) = \sum_j (\partial\mu_u/\partial X_j)L_{ij}$, where Q_i is the i^{th} normal coordinate, X_j is the j^{th} Cartesian displacement coordinate, and L_{ij} is the transformation matrix between the Cartesian displacement coordinates and the normal coordinates. The infrared intensities were then calculated by $[(N\pi)/(3c^2)] [(\partial\mu_x/$

$\partial Q_i)^2 + (\partial \mu_y / \partial Q_i)^2 + (\partial \mu_z / \partial Q_i)^2$. The predicted spectrum of the mixture should be compared to the infrared spectra of the gas or xenon solutions.

3 Results and Discussion

Three-membered hydrocarbon ring molecules substituted with an asymmetric internal rotor are of interest to scientists to determine molecular structures because there is the possibility of the presence of conformations at ambient temperature and, when they are present, which form is the more stable conformer. For the halomethylcyclopropanes, $c\text{-C}_3\text{H}_5\text{CH}_2\text{X}$, where $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{and I}$, initially there was considerable controversy as to whether more than one conformer of chloromethylcyclopropane was present at room temperature [9-11]. However, later studies [12-14] conclusively showed that the predominant form was the *gauche* conformer and from variable temperature studies of the infrared spectra of xenon solutions [15] the enthalpy difference was determined to be $274 \pm 21 \text{ cm}^{-1}$ ($3.28 \pm 0.25 \text{ kJ/mol}$) with only 12% of the *cis* form present at room temperature. With other X substituents such as cyano $-\text{CN}$ [16,17], and ethynyl $-\text{C}\equiv\text{CH}$ [18,19] groups the percent of the *gauche* form present at ambient temperature dropped to 72 and 52%, respectively. Initially, it was proposed [18] that the electronegativity of the substituent has the most pronounced effect on the relative amounts of the conformational isomers present since the substitution of the ethynyl and cyano-groups had a relatively larger amount of the *cis* (syn) form present compared to the amount of the *gauche* conformers. These groups have considerably larger electronegativities [20] i.e. 3.1 and 3.2 than the other substituents such as CH_3 (2.9) and Cl (3.0). However, the determination [21] of the enthalpy difference of the two conformers of fluoromethylcyclopropane clearly showed that electronegativity was not the most significant factor since fluorine has the largest electronegativity (4.0) yet there was a relatively small amount of the *cis* form present ($12 \pm 1\%$) at ambient temperature. The factor which seems to have the most pronounced effect on the amount of *cis* rotamer present is the distance of the carbon atom of the methyl group to the carbon atom of the ring [21].

In contrast, the corresponding silyl molecules, $c\text{-C}_3\text{H}_5\text{SiH}_2\text{X}$ where $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{and I}$ are predicted by molecular mechanics [22] to have the *cis* conformer as the most stable form. These predictions have been found to be correct for chloro- [23] and bromosilylcyclopropane [24] where the enthalpy differences have been found to be $126 \pm 25 \text{ cm}^{-1}$ ($1.50 \pm 0.30 \text{ kJ/mol}$) and $98 \pm 10 \text{ cm}^{-1}$ ($1.17 \pm 0.12 \text{ kJ/mol}$), respectively, with the *cis* form the more stable conformer. These experimental results were consistent with predictions from MP2/6-311+G(2d,2p) calculations with values of 48 cm^{-1} [23] and 73 cm^{-1} [24], respectively, but not from DFT calculations by B3LYP where the conformational energy differences were 123 cm^{-1} and 130 cm^{-1} , respectively, with the *gauche* form the more stable conformer [23-24].

Since the methyl group has nearly the same size as the chloride atom and ethylcyclopropane has only approximately 8% of the *cis* form present at ambient temperature [25], an investigation [26] of the structure and conformational stability of methylsilylcyclopropane, $c\text{-C}_3\text{H}_5\text{SiH}_2\text{CH}_3$, was initiated to determine if the *gauche* conformer was the more stable form. Also of interest was the enthalpy difference between the two conformers for comparison to the two halosilylcyclopropanes as well as to the corresponding carbon compound which could possibly provide some information on the major factors contributing to the stability of the more stable forms. Therefore, the infrared and/or Raman spectra were recorded of the gas, liquid and solid phases of methylsilylcyclopropane from which complete vibrational assignments were made [26].

In order to obtain the enthalpy difference between the two conformers a vibrational assignment needs to be made for the spectral region from which the conformer pairs will be selected for the enthalpy determination. For the best result the lowest frequency fundamentals should be used for the conformer pairs since they have the lowest probability to have intensity contributions from overtones or combination bands. The bands selected should be well resolved and well separated with relatively straight baselines and without predicted underlying bands from the other conformer(s).

There are other reasons why a complete vibrational assignment for a molecule may be desirable, such as, for analytical purposes. The vibrational spectrum of a molecule is frequently used to verify purity or to

identify impurities in samples. The infrared spectra are used for this purpose much more frequently than Raman spectra at the current time. Therefore, the emphasis in this article will be mainly on the infrared spectrum as the utilization of Raman spectra in Xe solutions is very new.

Table 1. Calculated^a and observed frequencies (cm⁻¹) for gauche methylsilylcyclopropane.

Vib. No.	Approx. Description	<i>ab initio</i>	scaled ^t	IR Int.	Raman Act.	dp ^c	dp ^d	IR			Raman liquid ^f	Band Contour		
								gas	in xenon solution	in liquid ^f		A	B	C
v ₁₁	CH ₂ deformation	157	1490	1.3	5.2	0.74	-	-	1457	-	77	10	13	
v ₁₂	CH ₂ deformation	153	1456	1.8	10.	0.75	0.4	1443	1441	1458	7	86	6	
v ₁₃	CH ₃ antisym. deformation	152	1448	2.6	14.	0.73	0.7	-	1435	1438	40	60	-	
v ₁₄	CH ₃ antisym. deformation	152	1446	4.8	14.	0.75	0.3	1433	1421	(1420)	-	3	97	
v ₁₅	CH ₃ sym. deformation	137	1300	35.8	1.6	0.29	0.4	1290	1286	(1282)	1284	74	23	3
v ₁₆	CH wag in-plane	136	1299	7.6	4.7	0.56	0.0	1258	1252	1254	39	42	19	
v ₁₇	ring breathing	126	1200	3.7	19.	0.11	0.1	1187	1185	1187	85	3	12	
v ₁₈	CH ₂ rock	124	1177	0.4	6.2	0.75	0.2	1177	1173	(1176)	7	72	21	
v ₁₉	CH ₂ twist	117	1117	3.5	0.7	0.67	0.5	1097	1099	(1096)	(1100)	20	73	7
v ₂₀	CH ₂ wag	112	1062	3.9	0.2	0.61	0.6	1061	1055	(1057)	4	91	6	
v ₂₁	CH ₂ wag	111	1058	12.2	1.9	0.51	0.3	1041	1037	(1035)	1038	48	-	52
v ₂₂	CH ₂ twist	108	1028	4.6	5.9	0.74	0.7	1022	1018	(1015)	1018	5	10	85
v ₂₃	SiH ₂ deformation	996	945	117.	14.	0.73	0.6	950	946	(955)	950	12	76	12
v ₂₄	ring deformation	971	921	59.6	8.0	0.73	-	-	-	(926)	94	-	6	
v ₂₅	SiH ₂ wag	954	906	250.	5.9	0.73	0.2	906	899	(890)	902	98	-	2
v ₂₆	CH ₃ rock	934	887	26.6	12.	0.74	0.7	873	870	871	3	4	93	
v ₂₇	ring deformation	922	877	25.8	5.7	0.74	0.6	852	847	847	19	49	31	
v ₂₈	CH bend out-of-plane	871	827	21.5	4.2	0.73	0.4	824	822	823	15	81	4	
v ₂₉	CH ₂ rock	840	797	5.5	1.7	0.73	-	802	800	(797)	(807)	29	6	65
v ₃₀	CH ₃ rock	776	738	46.0	4.4	0.48	0.1	738	734	736	67	31	2	
v ₃₁	CSiC antisym. stretch	737	700	14.7	7.1	0.65	0.3	713	713	713	26	8	66	
v ₃₂	SiH ₂ twist	704	669	5.2	13.	0.57	0.3	682	682	686	-	-	100	
v ₃₃	CSiC sym. stretch	620	588	6.2	14.	0.28	0.1	598	599	(592)	599	61	26	12
v ₃₄	SiH ₂ rock	511	486	13.7	1.1	0.29	0.3	503	502	(511)	505	10	27	63

^aMP2(full)/6-31G(d) *ab initio* calculations, scaled frequencies, infrared intensities (km/mol), Raman activities (Å⁴/u), and depolarization ratios (dp).

^bScaled *ab initio* calculations with factors of 0.9 for all modes shown except torsions and heavy atom bends using MP2(full)/6-31G(d) basis set.

^cValues predicted from *ab initio* calculations.

^dExperimentally determined values.

^eValues in parenthesis are for the *cis* conformer.

^fValues in parenthesis are from Raman solid.

Variable-temperature infrared studies of methylsilylcyclopropane dissolved in liquid xenon were recorded. To aid in the vibrational assignment MP2(full)6-31G(d) calculations were used to predict the force constants, vibrational frequencies, infrared and Raman intensities, and conformational stabilities and these data are listed in Table 1 for the spectral region where the conformer pairs will be chosen for the

determination of the enthalpy difference. Of major interest is the frequency region of 1000 to 500 cm^{-1} and there are 12 fundamentals predicted for the *gauche* conformer in this region. However, in the infrared spectrum of the gas from 800 to 1000 cm^{-1} there are only two pronounced bands at 950 and 906 cm^{-1} with the lower frequency bands having a very broad low frequency shoulder with some very weak Q-branches and possibly a B-type contour for one of the bands (Fig. 1A). However, in the infrared spectrum of the xenon solution there are five well determined bands resolved for this shoulder (Fig. 1B). For the 950 cm^{-1} band in the gas it is split into two relatively resolved bands at 955 cm^{-1} and 946 cm^{-1} (Fig. 1B) from the xenon solution and the predicted frequency for the SiH_2 deformation is 945 cm^{-1} with an intensity of 117.8 km/mol which makes it easily assigned to this band. The next higher frequency band for the *gauche* conformer is at 1028 cm^{-1} where a band is clearly observed at 1022 cm^{-1} . Therefore, the 955 cm^{-1} band must be due to the *cis* conformer for which a fundamental is predicted at 956 cm^{-1} with a predicted intensity of 98.3 km/mol which allows for the confident assignment of the 955 cm^{-1} band to the *cis* form. Since these two bands are separated by 9 cm^{-1} they provide a conformer pair that can be used to obtain the enthalpy difference.

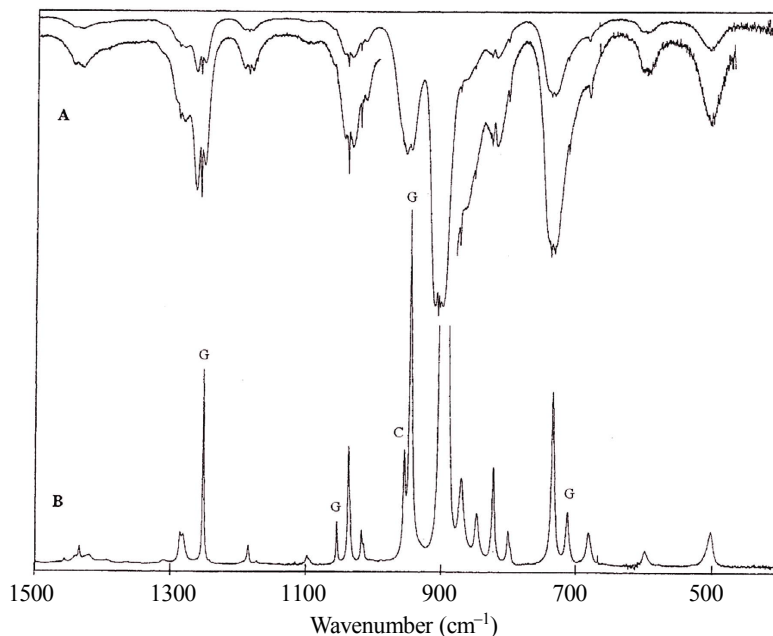


Fig. 1. Mid-infrared spectra (400-1500 cm^{-1}) of methylsilylcyclopropane [26]: (A) gas in transmittance; (B) liquid xenon solution at -95°C in absorbance, bands used in enthalpy determination: *Ggauche*, *C-cis*.

In continuation the 906 cm^{-1} band with its shoulder which extends to 800 cm^{-1} results in six fundamentals in this region which can be assigned from the infrared spectrum of the xenon solution (Table 1). The six fundamentals are predicted for the *cis* form in this same spectral region so these bands are overlapped by the fundamentals for the two conformers that none of them can be used for the enthalpy determinations. A similar problem exists for the *gauche* bands at 599, 682, and 734 cm^{-1} but the 713 cm^{-1} (ν_{31} , CSiC antisymmetric stretch) is well displaced ($\sim 30 \text{ cm}^{-1}$) from the corresponding mode for the *cis* conformer so the 713 cm^{-1} band can be used for the enthalpy determination. Thus only one fundamental for the *cis* conformer and two fundamentals for the *gauche* form are available in the frequency range from 1000 to 500 cm^{-1} . However, it should be noted that by combining the infrared spectra of the gas and xenon solutions with predictions from the MP2(full)/6-31G(d) calculations most of the fundamentals for the conformer in greater abundance can be assigned.

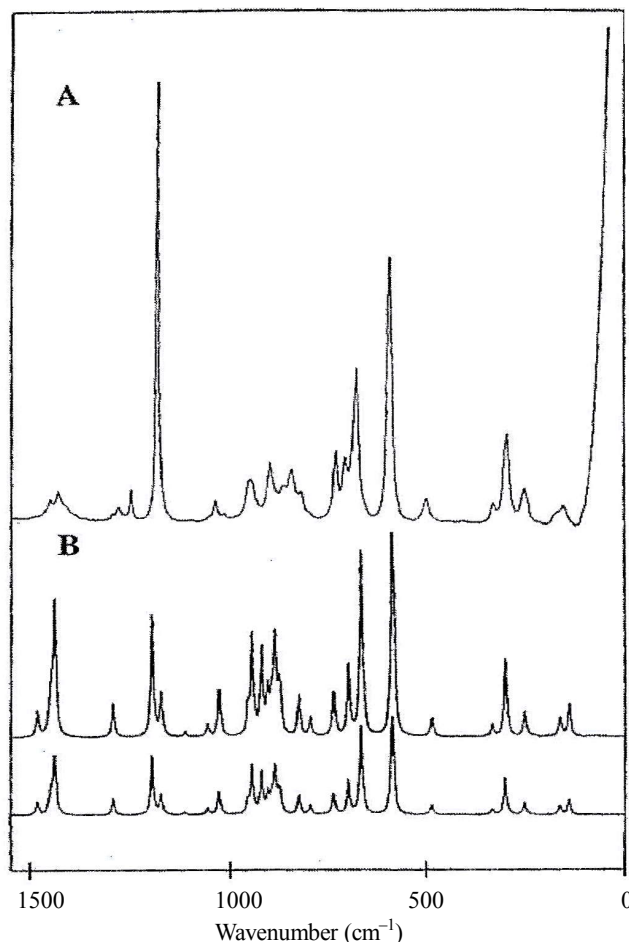


Fig. 2. Comparison of experimental and calculated Raman spectra of methylsilylcyclopropane [26]: (A) observed Raman spectrum of the liquid; (B) simulated Raman spectrum of a mixture of *gauche* and *cis* conformers at 25°C with $\Delta H = 98 \text{ cm}^{-1}$

If the goal of the research is to provide a complete vibrational assignment for a molecule it is essential for most cases that the Raman data are available along with the infrared spectrum. Usually the Raman spectrum is obtained for the liquid or the solid and if for the liquid then the depolarization data along with the predicted Raman activity can be very valuable for making the vibrational assignment. This will be demonstrated for the vibrational assignment of methylsilylcyclopropane.

In Fig. 2A the observed Raman spectrum of the liquid is shown from 1600 to 100 cm^{-1} and the "rich" spectral region from 800 to 1000 cm^{-1} provides some data for aiding the vibrational assignment when it is compared to the predicted spectrum, which is the combined spectrum of the two conformers by utilizing the experimentally determined enthalpy difference for the two conformers. In general the predicted intensities of the Raman lines are helpful for making the assignments. Additionally the depolarization values can often support some of the assignments and in Table 1 the predicted values along with the experimentally determined depolarization values are listed. As can be seen from these data the predictions are quite good when one considers that the predicted values are for the pure liquid of the *gauche* conformer and but the liquid contains $23 \pm 6 \%$ of the *cis* form. With a confident vibrational assignment made the bands to be used for the conformational stability determination may be chosen.

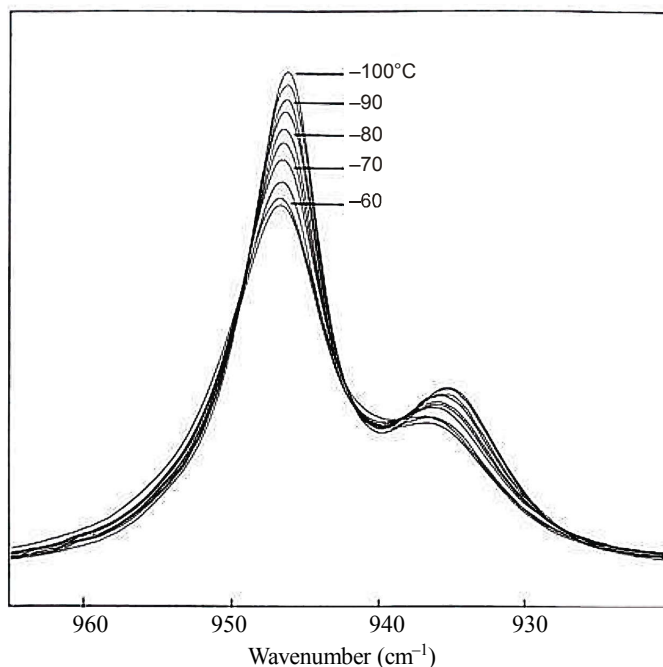


Fig. 3. Temperature (-55 to -100°C) dependent mid-infrared spectrum in the $925\text{--}965\text{ cm}^{-1}$ region of methylsilylcyclopropane dissolved in liquid xenon [26].

As indicated earlier there is only one band (955 cm^{-1}) of the *cis* conformer in the infrared spectrum of the xenon solution which could be used for the conformational stability determination. However, there are four bands at 1252 , 1055 , 946 and 712 cm^{-1} of the *gauche* conformer which are reasonably isolated and of the approximate intensities which were used along with the band of the *cis* conformer for the conformational studies. The intensities of the infrared bands were measured as a function of temperature (Fig. 3) and their ratios were determined. By application of the van't Hoff equation $\ln K = \Delta H/(RT) - \Delta S/R$, the enthalpy difference was determined from a plot of $\ln K$ versus $1/T$, where, $\Delta H/R$ is the slope of the line and K is substituted with the appropriate intensity ratios, i.e. I_{cis} / I_{gauche} . It was assumed that ΔH is not a function of temperature in the small temperature range studied.

By combining the four *gauche* bands and one *cis* conformer band, four pairs of bands (Fig. 1) were utilized for the determination of the enthalpy difference. The resulting values with statistical uncertainties are listed in Table 2. The average of these four values is 9813 cm^{-1} where the error limit is derived from the statistical standard deviation of one sigma of the measured intensity data where the data from all four pairs were taken as a single set.

The values for each set are also shown. These error limits do not take into account small associations with the liquid xenon or the interference of overtones and combination bands in near coincidence with the measured fundamentals. The variations are undoubtedly due to these types of interferences but by taking four pairs of bands the effect of such interferences should cancel. The abundance of the less stable *cis* form present at ambient temperature is $23 \pm 6\%$.

We also obtained the enthalpy difference in the liquid by using the Raman spectra where a pair of bands at 333 cm^{-1} (*cis*) and 299 cm^{-1} (*gauche*) were sufficiently separated and confidently assigned. The intensities of these two bands were measured as a function of temperature over nine different values from 2 to -126°C . Again by the application of the van't Hoff equation the enthalpy difference of $101 \pm 37\text{ cm}^{-1}$ ($1.21 \pm 0.44\text{ kJ/mol}$) was obtained. This value is in excellent agreement with the value obtained

from the xenon solution. Also, the interferences from overtones or combination bands is limited to two possibilities so the uncertainties for this determination in the liquid is mainly due to the difficulty in obtaining reproducible intensities from the Raman lines. Nevertheless, it appears that any interaction in the liquid which affects the enthalpy difference is relatively small.

Table 2. Temperature and intensity ratios of the conformational bands of methylsilylcyclopropane from the infrared spectra of the liquid xenon solution phase.

	T(°C)	1/T ($\times 10^3$ K $^{-1}$)	I ₉₅₅ / I ₉₄₆	I ₉₅₅ / I ₁₀₅₅	I ₉₅₅ / I ₁₂₅₂	I ₉₅₅ / I ₇₁₂
Liquid xenon	-55.0	4.584	0.2314	3.0660	0.6372	2.1779
	-60.0	4.692	-	2.8521	0.5969	1.9757
	-65.0	4.804	0.2221	2.7990	0.5968	2.0434
	-70.0	4.923	0.2341	2.8582	0.5949	2.0796
	-75.0	5.047	0.2277	2.7634	0.5888	2.0917
	-80.0	5.177	-	2.4804	0.5506	1.9708
	-85.0	5.315	0.2303	2.5326	0.5642	1.9750
	-90.0	4.460	0.2082	2.4215	0.5353	1.9708
	-95.0	5.613	0.2134	2.2505	0.5223	1.9312
	-100.0	5.775	0.2200	2.2639	0.5084	1.9974

ΔH^a

44 ± 22 cm $^{-1}$

178 ± 17 cm $^{-1}$

119 ± 11 cm $^{-1}$

42 ± 17 cm $^{-1}$

^aAverage value: $\Delta H = 98 \pm 13$ cm $^{-1}$ (1.17 \pm 0.16 kJ/mol) with the gauche conformer the more stable form and the statistical uncertainty (σ) obtained by utilizing all of the data as a single set.

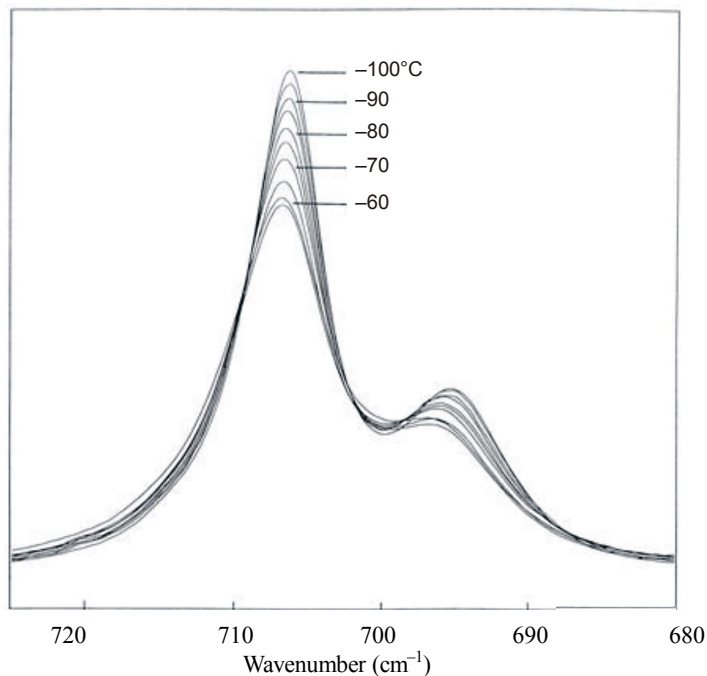


Fig. 4. Temperature (-55 to -100°C) dependent mid-infrared spectrum in the 680-725 cm $^{-1}$ region of methylsilylcyclopropane dissolved in liquid xenon.

In general, the enthalpy differences obtained from variable temperature infrared studies frequently have large variations in the individually determined values. Part of the reason can be due to having only a single band available for one conformer as well as by using higher frequency fundamentals where the probability is much higher of interferences from combination or overtone bands. Nevertheless, the value obtained statistically by using all of the data as a single set gives a value with a reasonable uncertainty.

As a continuation of our structural and spectroscopic studies of mono-substituted cyclopropanes we were also interested in methylgermylcyclopropane, $c\text{-C}_3\text{H}_5\text{GeH}_2\text{CH}_3$ for a comparison to the conformational stability results of our investigation [26] of methylsilylcyclopropane, $c\text{-C}_3\text{H}_5\text{SiH}_2\text{CH}_3$, as well as to the corresponding carbon analogue which we investigated some years ago [25]. Therefore, the infrared and/or Raman spectra of the gas, liquid and solid phases of methylgermylcyclopropane [27] were recorded and additionally, we recorded variable temperature studies of the infrared spectra (Fig. 4) of the sample dissolved in liquid xenon. The force constants, vibrational frequencies, infrared and Raman intensities, and conformational stabilities were predicted from the *ab initio* calculations. By utilizing the predicted frequencies as well as the infrared intensities and band contours, the fundamentals for the *gauche* conformer were assigned rather straightforwardly.

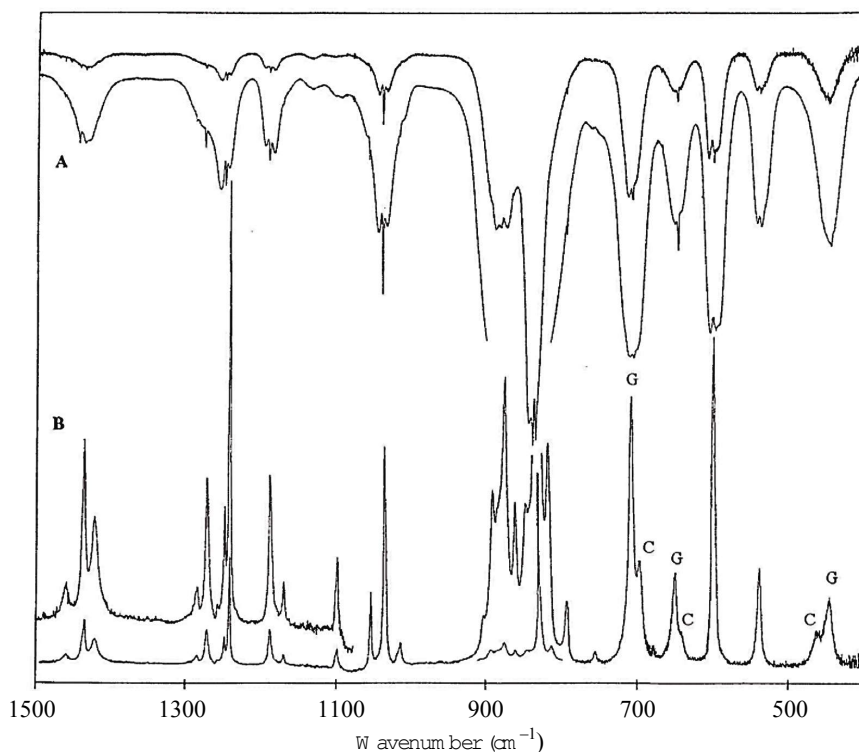


Fig. 5. Mid-infrared spectra ($400\text{-}1500\text{ cm}^{-1}$) of methylgermylcyclopropane: (A) gas in transmittance; (B) liquid xenon solution at -95°C in absorbance [27], bands based in enthalpy determination: G – *gauche*, C – *cis*.

With confident assignments for the fundamentals of the *gauche* conformer it was possible to assign many fundamentals for the *cis* conformer, particularly for those arising from the GeH_2 modes which are relatively strong and should be most sensitive to the different conformers. Of particular aid was the comparison of the infrared spectrum of the xenon solution with the spectrum of the gas (Fig. 5). For several of these fundamentals the spectrum of the gas had a shoulder or an unsymmetrical band shape (597 , 705 , 837 cm^{-1}) whereas the band was relatively sharp in the low temperature xenon liquid so it could be readily identified. With these data it was possible to assign eleven fundamentals of the *cis* conformer in the

“fingerprint” region (Table 3). The frequencies for these fundamentals are very similar to those of the corresponding modes of the *gauche* conformer (Table 3). Nevertheless, with the significant number of fundamentals identified for the less stable conformer it was possible to obtain enthalpy values for several pairs of bands. There are three pairs of bands at 707/696, 649/640, and 446/464 cm^{-1} which are the GeH₂ wags, GeH₂ twists and GeH₂ rocks, respectively, which meet the criteria that they are not expected to have adverse interference from the overtone or combination bands. These fundamentals are expected to be some of the most sensitive to the conformational interchange along with the CGeC stretches and ring-GeH₂ bends. Unfortunately, the two CGeC antisymmetric stretches are predicted to be only separated by 2 cm^{-1} and they appear as a single band at 598 cm^{-1} in the infrared spectrum of the xenon solution. Although the GeH₂ twists are predicted to be separated by 17 cm^{-1} they are only separated by 9 cm^{-1} which makes their intensity measurements a little difficult. Nevertheless, we used this pair which made it possible to have nine experimentally determined enthalpy differences.

Table 3. Calculated^a and observed frequencies (cm^{-1}) for *gauche* methylgermylcyclopropane

Vib. No.	Approx. Description	<i>ab initio</i>		IR Int.	Raman Act.	B3LYP cc-PVDZ	B3LYP PVQZ	IR Int.	IR		Raman liquid ^d	Band Contour		
		<i>initio</i>	scaled ^b						gas	xenon solution ^c		A	B	C
v ₁₁	CH ₂ deformation	1569	1471	1.1	5.0	1482	1508	0.5	146	1459	1461	51	1	37
v ₁₂	CH ₃ antisym.	1538	1443	1.5	11.5	1444	1481	2.0	143	1435	(1454)	39	4	18
v ₁₃	CH ₃ antisym.	1537	1442	3.3	12.8	1439	1469	3.0	143	1435	1437	5	1	80
v ₁₄	CH ₂ deformation	1533	1438	1.7	10.3	1438	1469	1.6	142	1421	1420	9	8	5
v ₁₅	CH bend in-plane	1356	1287	4.9	3.6	1289	1303	3.4	127	1272 (1285)	1273	22	1	77
v ₁₆	CH ₃ sym. deformation	1352	1268	7.5	2.2	1251	1276	4.9	124	1243 (1249)	1243	49	5	1
v ₁₇	Ring breathing	1266	1202	5.9	19.1	1214	1218	5.0	119	1189	1190	91	1	8
v ₁₈	CH ₂ rock	1235	1172	0.7	6.3	1182	1200	0.5	117	1170	1174	4	8	14
v ₁₉	CH ₂ twist	1177	1117	2.3	0.4	1117	1134	0.8	110	1099 (1101)	1099	13	8	6
v ₂₀	CH ₂ wag	1118	1060	3.5	0.2	1069	1091	2.3	105	1053 (1051)	1052	2	5	43
v ₂₁	CH ₂ wag	1113	1056	11.2	1.5	1051	1066	11.4	103	1035	1034	32	5	63
v ₂₂	CH ₂ twist	1072	1017	2.5	6.1	1027	1039	1.2	101	1013 (1017)	1013	36	3	61
v ₂₃	Ring deformation	960	911	25.9	7.0	912	907	19.6	887	890 (903)	888	78	-	21
v ₂₄	Ring deformation	939	892	1.7	9.9	897	896	14.9	883	883	882	1	9	4
v ₂₅	CH ₃ rock	905	859	29.7	8.0	871	875	39.1	872	874 (861)	875	12	3	85
v ₂₆	GeH ₂ deformation	897	851	29.0	14.4	854	862	23.6	841	843 (847)	862	16	8	2
v ₂₇	CH ₃ rock	884	840	130.4	4.6	838	847	139.7	837	833 (830)	848	77	1	4
v ₂₈	CH bend out-of-plane	865	821	33.1	3.7	819	832	20.9	-	818	818	44	4	8
v ₂₉	CH ₂ rock	833	791	5.1	1.4	793	804	3.8	793	792 (754)	791	50	5	45
v ₃₀	GeH ₂ wag	725	689	60.7	7.6	697	706	62.4	705	707 (696)	708	76	2	1
v ₃₁	GeH ₂ twist	669	636	25.5	7.0	638	645	16.0	646	649 (640)	650	45	9	45
v ₃₂	CGeC antisym. stretch	641	608	24.6	12.7	581	585	28.3	598	597 (599)	597	65	3	1
v ₃₃	CGeC sym. stretch	571	542	11.5	12.6	522	527	13.7	537	538	537	74	5	21

^aMP2(full)/6-31G(d) *ab initio* calculations, scaled frequencies, infrared intensities (km/mol) and Raman activities ($\text{\AA}^4/\text{u}$).

^bScaled *ab initio* calculations with factors of 0.9 for all modes shown except torsions and heavy atom bends using MP2(full)/6-31G(d) basis set.

^cValues in parenthesis are for the *cis* form.

^dValue in parenthesis is from Raman solid.

By combining the intensities from three of the bands for the *gauche* conformers with the intensities of three bands for the *cis* form six pairs of bands (Fig. 4) were obtained for the determination of the enthalpy difference. The band pair at 649/696 cm^{-1} had an uncertainty larger than the determined value so it was not used for the determination of the enthalpy difference. The values obtained for each of the six pairs are listed in Table 4 with each of the individual uncertainties which, for the most part, are relatively small although the range of the values of the enthalpy difference is rather large. Nevertheless, by using all of the data as a single set, the determined enthalpy difference is $60 \pm 13 \text{ cm}^{-1}$ ($0.72 \pm 0.16 \text{ kJ/mol}$) where the uncertainty is the statistical standard deviation of one sigma, with the *gauche* conformer the more stable form. These error limits do not take into account possible associations with the liquid xenon which could have different effects on different fundamentals.

Table 4. Temperature and intensity ratios of the conformational bands of methylgermylcyclopropane from the infrared spectra of the liquid xenon solution phase.

T(°C)	1/T ($\times 10^3 \text{ K}^{-1}$)	I_{649} / I_{640}	I_{707} / I_{640}	I_{707} / I_{464}	I_{649} / I_{464}	I_{446} / I_{696}	I_{446} / I_{640}
-55.0	4.584	4.7000	5.4000	-	-	0.9649	-
-60.0	4.692	4.5455	5.1818	-	-	0.8714	4.6654
-65.0	4.804	4.3333	5.0000	8.4233	2.6981	0.8788	-
-70.0	4.923	4.2308	4.9231	9.0493	2.9276	0.8568	4.9562
-75.0	5.047	4.3846	5.1538	9.0549	2.9702	0.8888	4.5064
-80.0	5.177	4.2143	5.0000	9.1279	2.9646	0.8750	4.4255
-85.0	5.315	4.0667	4.8667	9.4780	3.0713	0.7690	4.2583
-90.0	4.460	3.9375	4.7500	-	-	0.7848	4.1728
-95.0	5.613	4.0625	4.8750	9.6399	3.1764	0.7894	4.1515
-100.0	5.775	3.9412	4.7059	-	2.9919	0.7749	4.2129
$\Delta H^{\circ} (\text{cm}^{-1})$		95 ± 14	63 ± 13	101 ± 23	71 ± 30	113 ± 23	101 ± 26

^aAverage value: $\Delta H = 60 \pm 13 \text{ cm}^{-1}$ ($0.72 \pm 0.16 \text{ kJ/mol}$) with the *gauche* conformer the more stable form and the statistical uncertainty (σ) obtained by utilizing all of the data as a single set.

In the initial investigation [27] the reported enthalpy difference value was $43 \pm 11 \text{ cm}^{-1}$ from nine band pairs and this was mainly due to the band pairs at I_{707} / I_{696} with a enthalpy value of $33 \pm 7 \text{ cm}^{-1}$, I_{446} / I_{464} with a enthalpy value of $40 \pm 17 \text{ cm}^{-1}$ and I_{538} / I_{696} with a enthalpy value of $22 \pm 5 \text{ cm}^{-1}$. The above mentioned band pairs did not have more than six temperature measurements and hence it would be interesting to go back and reinvestigate the spectrum to see if we can come up with more possibilities. It needs to be noted that the band pair at I_{649} / I_{464} with an enthalpy difference value of $71 \pm 30 \text{ cm}^{-1}$ has large uncertainty and which can be attributed to the fact that the band pair measurement was taken from intensity measurements and not by the area of the band. Nevertheless if we disregard this band pair and it's enthalpy value by using only five band pairs data as a single set, then the determined enthalpy difference is $78 \pm 12 \text{ cm}^{-1}$ ($0.93 \pm 0.14 \text{ kJ/mol}$).

Also, there is possible interference of the combination band of $\nu_{26} + \nu_{37}$ of the *gauche* conformer with the ν_{30} fundamental of the *cis* conformer or $2 \nu_{36}$ with the *gauche* form with ν_{34} of the *cis* form. There is also possible interference of the overtone (three possibilities) and combination bands (two possibilities) of the *cis* form being in near coincidence with the ν_{34} fundamental of the *gauche* form. The variations are undoubtedly due in part to these types of interferences as well as the measurements of the band intensities. As further support, the relative intensities of several pairs of conformer bands at a single temperature were measured and the predicted *ab initio* intensities were then used to obtain the enthalpy

differences. The arithmetic average of these values was consistent with the experimentally determined value. The abundance of the less stable *cis* form present at ambient temperature is $30 \pm 3\%$.

The determined enthalpy difference of $60 \pm 13 \text{ cm}^{-1}$ is consistent with the value of $98 \pm 13 \text{ cm}^{-1}$ obtained for the ΔH for the corresponding silicon molecule where the *ab initio* MP2(full) predicted a value of $65 \pm 8 \text{ cm}^{-1}$ from eight different basis sets. A similar calculation with the same basis sets from density functional theory calculations by the B3LYP method gave a value of $207 \pm 6 \text{ cm}^{-1}$. This difference of about 150 cm^{-1} higher by density functional theory calculations is similar to what has been observed for the germanium compound where the predicted value of $162 \pm 5 \text{ cm}^{-1}$ is about 150 cm^{-1} higher than the MP2 predicted value of $13 \pm 22 \text{ cm}^{-1}$. This larger predicted value from density functional theory calculation for the enthalpy difference has been found for most of the conformational determinations made when the enthalpy difference is relatively small.

The predicted frequencies for the fundamental vibrations with two scaling factors compare very favorably with the observed values with an average error of 9 cm^{-1} which represents a percentage error of 0.7% for the *gauche* conformer. This error cannot be obtained for the *cis* conformer since many of the vibrations of this conformer seem to have nearly the same frequency as the corresponding vibrations for the *gauche* form; thus, only limited number of fundamentals for this conformer was clearly identified. Nevertheless, there is strong evidence from the few normal modes that were assigned for the *cis* form that the error is probably similar to that found for the *gauche* form for the predicted frequencies.

The depolarization values were obtained from *ab initio* calculations for both the *gauche* and the *cis* conformers. The depolarization values from the MP2 basis set calculations and the density functional theory calculations are essentially the same and, in general, the predicted values are in agreement with the experimentally determined ones. In fact, out of the thirty-nine depolarization values predicted for the fundamentals only three of them were inconsistent with the experimental values. The CH_2 wags and the ring- GeH_2 out-of-plane bend were predicted to be significantly polarized (~ 0.50) but the values from the experimental measurements showed these vibrations to be depolarized. This small number of incorrect predictions can be considered relatively minor when assessing the reliability of the *ab initio* predicted depolarization values which can be very useful when making vibrational assignments.

There are many advantages as well as disadvantages for the utilization of liquid rare gases as solvents for enthalpy determinations. The ten advantages are: (1) The bands are very narrow. (2) Very accurate measurement of the temperature is possible. (3) The temperature range is fairly large. (4) There is normally little interaction of solvent with solute molecules. (5) Small enthalpy changes can be measured. (6) Band areas are easily measured. (7) Paths lengths for the liquids are long so very dilute solutions can be used. (8) The xenon solvent has no absorption bands. (9) Several conformer pairs can usually be measured. (10) The statistical uncertainty of the determined values is very low. The most common disadvantages are: (1) Limited solubility of many polar molecules. (2) It is difficult to have very dry xenon so water can interfere. (3) At low temperatures the sample may deposit on the window. Also, the infrared spectrum of rare gas solutions can aid greatly in the determination of the centers of bands in the gas phase and can distinguish closely spaced bands that are badly overlapped. Thus, such solutions can significantly aid the assignment of fundamentals of a molecule.

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