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Raman and Infrared Spectra, Conformational Stability, Normal Coordinate Analysis, Vibrational Assignment, and AB Initio Calculations of Difluoromethylcyclopropane

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The Raman spectra (3300 to 10 cm^{-1}) of gaseous, liquid, and solid difluoromethylcyclopropane, c-C_3H_5-CF_2H, and the infrared spectra (3400 to 60 cm^{-1}) of the gas and solid have been recorded. The spectra of the fluid phases are consistent with two stable conformers in equilibrium at ambient temperature. These spectral data have been interpreted on the basis that the cis conformer (H atom of the difluoromethyl group is cis to the three-membered ring) is more stable than the gauche form in both the gaseous and liquid phases, and it is the only rotamer present in the solid. The mid-infrared spectra of the sample dissolved in liquid xenon as a function of temperature (−100 to −60 °C) have been recorded. Utilizing two conformer pairs, the enthalpy difference has been determined to be 102 ± 8 cm^{-1} (1.22 ± 0.10 kJ/mol) with the cis conformer the more stable form. The enthalpy difference has also been determined to be 145 ± 48 cm^{-1} (1.73 ± 0.57 kJ/mol) for the liquid from the temperature-dependent Raman spectra. The potential function governing the asymmetric torsion has been obtained and the determined potential constants are $V_1 = 229 \pm 5$, $V_2 = 40 \pm 4$, $V_3 = 1270 \pm 3$, and $V_4 = -136 \pm 2$ cm^{-1}. The cis to gauche barrier is 1255 cm^{-1} (15.01 kJ/mol) and the gauche to gauche barrier is 1399 cm^{-1} (16.74 kJ/mol). A vibrational assignment for the 30 normal modes for the cis conformer is proposed and several of the fundamentals for the gauche conformer have been identified. The structural parameters, dipole moments, conformational stability, vibrational frequencies, and infrared and Raman intensities have been determined from ab initio calculations. The predicted conformational stability is at variance with the experimental results even from the MP2/6-311+G(2d,2p) calculations. These experimental and theoretical results are compared to the corresponding quantities of some similar molecules.

Introduction

Three-membered ring hydrocarbon molecules substituted with an asymmetric internal rotor, such as a halomethyl group, are of interest to structural chemists since there are two or three possible conformations depending on the three-membered ring. For the halomethylcyclopropane molecules at room temperature in the gas phase, there is a mixture of two equivalent gauche conformers and a cis form with the gauche rotamer the dominant conformer for the chloride and bromide.[1−6] Apparently the relative abundance of the cis conformer increases with decreased size of the halogen atom.[1,2,5] However, from the initial microwave studies[7,8] of chloromethylcyclopropane it was proposed that only the gauche rotamer was present at ambient temperature. For fluoromethylcyclopropane the most stable conformer is predicted[9] from ab initio calculations at the MP4(SDQ)/6-311G(d,p)(SDQ)/6-311G(d,p) level to be the gauche form (H atom over the three-membered ring) by 70 cm^{-1} (0.84 kJ/mol). However, molecular mechanics calculations indicate that the cis conformer is the low energy rotamer for this molecule.[9] There are no experimental measurements of this energy difference since the fluoromethylcyclopropane molecule has been reported as being relatively unstable at ambient temperature,[10] although it was proposed from some preliminary vibrational data that the gauche conformer is the more stable form. As a continuation of our studies of halomethyl substituted cyclopropanes we have prepared difluoromethylcyclopropane, c-$C_3H_5CF_2H$, for conformational stability determinations.

There have not been any previous spectroscopic studies of the dihalomethylcyclopropane molecules so we have recorded the Raman spectra of the gas, liquid, and solid phases and the infrared spectra of the gas and solid phases and in xenon solutions at variable temperatures. We have also carried out ab initio calculations employing the 6-31(d)G basis set at levels of restricted Hartree−Fock (RHF) and Moller−Plesset (MP) to second order[11] to obtain equilibrium geometries, force constants, vibrational frequencies, infrared and Raman intensities, and conformational stabilities. Structural parameters and conformational stabilities have also been obtained from larger basis sets, i.e., MP2/6-311+G(d,p), MP2/6-311++G(d,p), and

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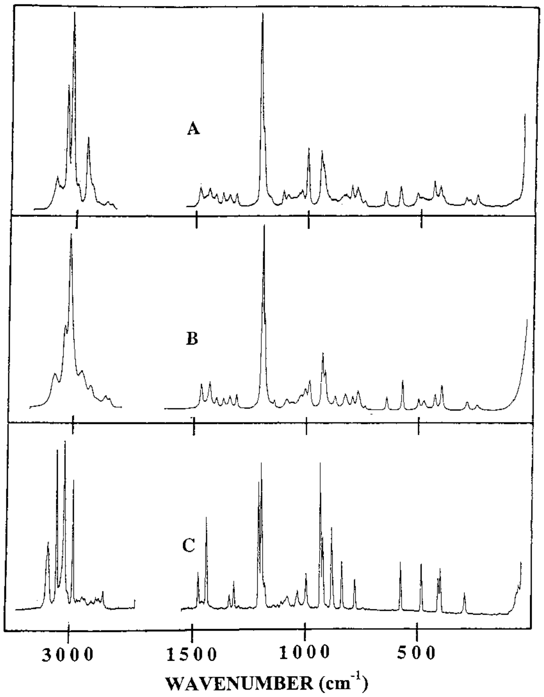

Figure 1. Raman spectra of difluoromethylcyclopropane: (A) gas, (B) liquid, and (C) annealed solid.

MP2/6-311+G(2d,2p). The results of this vibrational spectroscopic and theoretical study are reported herein.

Experimental Section

The difluoromethylcyclopropane sample was provided by Bayer Corp., Charleston, SC. The sample was purified by using a low-temperature, low-pressure fractionation column, and the sample was stored at low temperature under vacuum until used.

The Raman spectra were recorded on a Cary model 82 Raman spectrometer with a Spectra-Physics model 171 argon ion laser operating on the 5145 Å line. The laser power at the sample was 1−4W. The spectrum of the gaseous sample was recorded by using a standard Cary multipass accessory. The reported frequencies are expected to be accurate to ±1.5 cm^{-1} for sharp lines. The spectrum of the liquid was recorded from the sample sealed in a glass capillary that contained a spherical bulb on the end.[12] The spectrum of the crystalline solid was recorded from the capillary contained in a Cryogenic Technology, Inc., Cryostat model 20/70 equipped with quartz windows and a Lakeshore Cryotronics, Inc., model DTC-500 high precision temperature controller. The spectrum of the crystalline solid was obtained from a sample held at 30 K, and representative Raman spectra of all three phases are shown in Figure 1.

The mid-infrared spectra of the gas and the amorphous and crystalline solids were obtained from 3250 to 400 cm^{-1} on a Digilab model FTS-14C Fourier transform interferometer equipped with a Ge/KBr beam splitter and a TGS detector. The gaseous sample was contained in a 10 cm cell equipped with CsI windows, and the spectrum was obtained by recording the interferograms of the sample and the empty reference cell 500 times. The spectrum was obtained at 0.5 cm^{-1} resolution and transformed with a boxcar truncation function. The spectrum of the solid was obtained by condensing the sample onto a CsI plate contained in an evacuated cell equipped with CsI windows. This spectrum was also collected for both the sample and reference with 300 interferograms at 1.0 cm^{-1} resolution and then transformed with a boxcar truncation function. The crystalline solid sample was annealed until no further changes in the spectrum were observed, and the final spectrum was recorded with the sample cooled with boiling liquid nitrogen. Typical infrared spectra of the gas phase and amorphous and crystalline solids are shown in Figure 2.

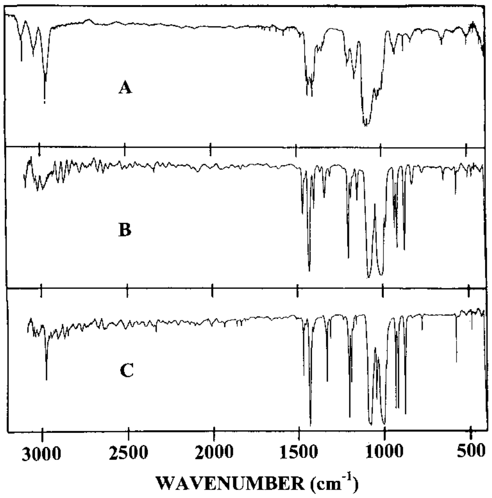

Figure 2. Mid-infrared spectra of difluoromethylcyclopropane: (A) gas, (B) amorphous solid, and (C) annealed solid.

The far-infrared spectrum of the gas (Figure 3) was recorded from 340 to 60 cm^{-1} on a Nicolet model 200 SXV Fourier transform interferometer equipped with a vacuum bench and a liquid helium cooled Ge bolometer containing a wedged sapphire filter and a polyethylene window. A 6.25 μm Mylar beam splitter was employed, and the sample was contained in a 1 m cell. The effective resolution was 0.10 cm^{-1}, and 256 interferograms were taken for both the sample and empty reference cell. The interferograms were averaged and transformed using a boxcar truncation function, and the measured frequencies are expected to be accurate to ±0.05 cm^{-1} (Table 1S).

The mid-infrared spectra of the sample dissolved in liquified xenon (Figure 4A) were recorded on a Bruker model IFS-66 Fourier transform interferometer equipped with a Globar source, Ge/KBr beam splitter, and a DTGS detector. The spectra were recorded at variable temperatures ranging from −60 to −100 °C with 100 scans at a resolution of 1.0 cm^{-1}. The temperature studies in the liquified noble gas were carried out in a specially designed cryostat cell, which is composed of a copper cell with a 4 cm path length and wedged silicon windows sealed to the cell with indium gaskets. The temperature is monitored by two Pt thermoresistors and the cell is cooled by boiling liquid nitrogen. The complete cell is connected to a pressure manifold to allow for the filling and evacuation of the cell. After the cell is cooled to the desired temperature, a small amount of sample is condensed into the cell. Next, the pressure manifold and the cell are pressurized with xenon, which immediately starts condensing in the cell, allowing the compound to dissolve.

Conformational Analysis

From the comparison of the Raman spectra of the gas and solid, Raman lines observed in the spectrum of the gas (Figure 1A) at 1408, 1377, 803, 655, 515, 440, 236 and 252 cm^{-1} all disappear from the spectrum of the solid (Figure 1C). This observation clearly indicates the presence of two conformers in the gas. Additionally, lines occurring at 1404, 1373, 802, 651, 513, and 255 cm^{-1} in the spectrum of the liquid (Figure 1B) disappear with solidification, which shows the presence of

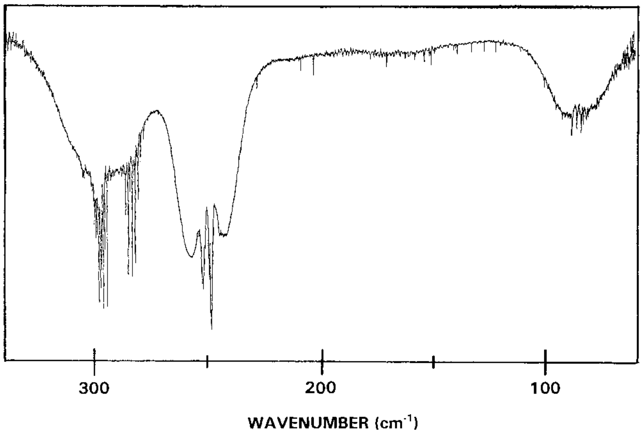

Figure 3. Far infrared spectrum of gaseous difluoromethylcyclopropane in the region of the 350 to 60 cm^{-1}.

TABLE 1: Temperature and Intensity Ratios from Conformational Study of Difluoromethylcyclopropane

T(°C)	1000/T(K)	I_{876}/I_{513}	I_{826}/I_{834}
−60	4.69	2.604	0.299
−65	4.80	2.646	0.306
−70	4.92	2.636	0.308
−75	5.05	2.718	0.315
−80	5.18	2.708	0.319
−85	5.31	2.796	0.331
−90	5.46	2.869	0.334
−95	5.61	2.982	0.348
−100	5.78		0.353
ΔH^a		97 ± 10 cm^{-1}	108 ± 5 cm^{-1}

[a] Average value is 102 ± 8 cm^{-1} with the cis conformer the more stable rotamer.

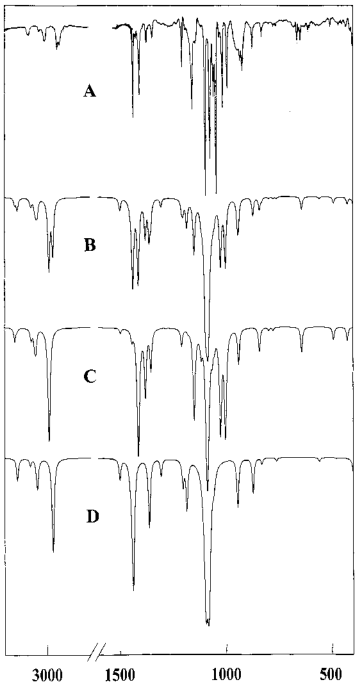

Figure 4. Infrared spectra of difluoromethylcyclopropane: (A) xenon solution at −55 °C, (B) calculated spectrum of the mixture of both conformers, (C) calculated spectrum of the gauche conformer, and (D) calculated spectrum of the cis conformer.

two conformers in the liquid phase. The disappearance of the Raman line at 651 cm^{-1} is the key in identifying the conformer remaining in the solid since only the gauche conformer is predicted from ab initio calculations to have a fundamental in this spectral region. Therefore, all of the Raman lines persisting in the spectrum of the solid are attributed to the cis conformer which indicates that this rotamer is the stable form in this phase.

To gain information about the enthalpy difference between the two conformers similar to what is expected for the gas, a variable temperature study in liquified xenon was carried out. The sample was dissolved in liquified xenon and the spectra were recorded at different temperatures varying from −60 to −100 °C. Only small interactions are expected to occur between the dissolved sample and the surrounding xenon atoms, and consequently, only small frequency shifts are anticipated when passing from the gas phase to the liquified noble gas solutions.[13,14] A significant advantage of this temperature study is that the conformer bands are better resolved in comparison with those in the infrared spectrum of the gas (Figures 2A and 4A). This is particularly important since most of the conformer bands for this molecule are expected to be observed within a few wavenumbers of each other. Also the areas of the conformer peaks are more accurately determined than those from the spectrum of the gas.

The bands used for the conformational stability studies from the infrared spectrum of the xenon solution are those assigned to the CH_2 rocks at 876 cm^{-1} ($\nu_{13,\mathrm{cis}}$), 834 cm^{-1} ($\nu_{27',\mathrm{gauche}}$) and 826 cm^{-1} ($\nu_{27,\mathrm{cis}}$) along with the CF_2 deformation at 513 cm^{-1} ($\nu_{15',\mathrm{gauche}}$). The corresponding mode (ν_{15}) for the cis conformer could not be used because it is too weak and there is a similar problem with ν_{13}' of the gauche form. Nine sets of spectral data were obtained for these two pairs of conformer bands (Figures 5 and 6). The intensities of the infrared bands were measured as a function of temperature and their ratios were determined. By application of the van't Hoff equation $-\ln K = (\Delta H/RT) - (\Delta S/\mathrm{R})$, where ΔS is the entropy change, ΔH was determined from a plot of $-\ln$ K versus $1/T$, where $\Delta H/R$ is the slope of the line and K is the appropriate intensity ratio. It is assumed that ΔH is not a function of temperature.

From a plot of the natural logarithm of the ratio I_{826}/I_{834} as a function of the reciprocal of the absolute temperature the ΔH value is determined to be 108 ± 5 cm^{-1} with the cis form the more stable rotamer. Similarly, the pair at 876 (cis) and 513 (gauche) cm^{-1} gives a ΔH value of 97 ± 10 cm^{-1} again with the cis conformer the more stable form (Table 1). The average of these two values is 102 ± 8 cm^{-1} where the error limits are given by the standard deviation of the measured areas of the intensity data. These error limits do not take into account small associations with the liquid xenon or other experimental factors such as the presence of overtones or combination bands in near coincidence with the measured fundamentals.

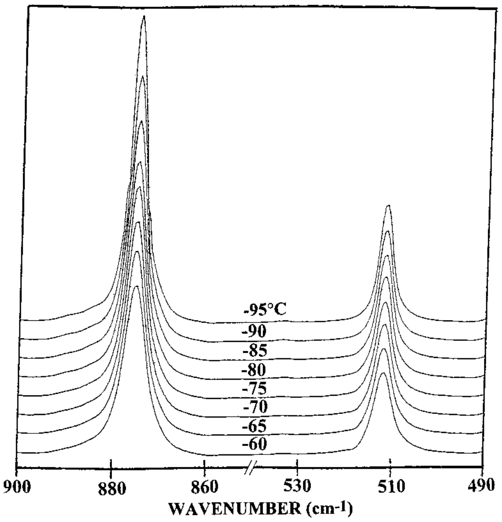

Figure 5. Temperature dependence of infrared spectra in the region 490−540 and 850−900 cm^{-1} of difluoromethylcyclopropane in xenon solution.

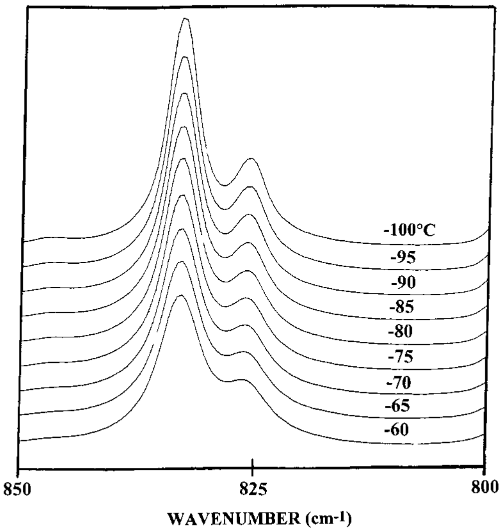

Figure 6. Temperature dependence of infrared spectra in the region 800−850 cm^{-1} of difluoromethylcyclopropane in xenon solution.

Variable temperature studies of the Raman spectrum of the gas were also carried out over the range of temperature of 25 to 50 °C where decomposition began. These data clearly indicate that Raman lines due to the gauche conformer are increasing in intensity with increased temperature. The conformer doublets at 1408/1349, 1377/1317, and 655/587 cm^{-1} have been used to determine the enthalpy difference of the conformers in the gas phase by using their relative intensities and correcting for the differences in activities using the values obtained from the ab initio calculations. The value of ΔH has been determined to be 119 ± 22 cm^{-1} (1.42 ± 0.26 kJ/mol) with the cis rotamer the more stable form which is in agreement with the results from the xenon solution. From the relative intensities of the doublets at 1373/1315, 651/583, and 513/412 cm^{-1}, and again correcting for the predicted differences from the ab initio activities, ΔH has been determined for the liquid to be 145 ± 48 cm^{-1} (1.73 ± 0.57 kJ/mol) with the cis conformer the more stable rotamer for this state. Therefore, the cis conformer is the more stable form in all three physical states.

Ab Initio Calculations

To provide additional information with regard to the structural parameters, conformational stability, and the potential energy distribution of the normal vibrational modes of difluoromethylcyclopropane, we have carried out ab initio calculations. These calculations were performed with the Gaussian-94 program[15] at the restricted Hartree−Fock level, RHF/6-31G(d), and with full electron correlation by the perturbation method[11] to second order, MP2/6-31G(d), for obtaining the optimized geometries, conformational stabilities, and frequencies for both the cis and gauche conformations. The energy minima with respect to the nuclear coordinates were obtained by the simultaneous relaxation of all the geometric parameters using the gradient method of Pulay.[16,17] The calculated parameters are given in Table 2S for the cis and gauche conformations. Since the MP2/6-31G(d) calculation predicts the gauche conformer is more stable than the cis form by 440 cm^{-1} (5.26 kJ/mol), which is at variance with the experimental results where the cis rotamer is found to be the more stable conformer, we carried out ab initio calculations with the much larger basis sets of 6-311+G(d,p) (168 basis functions, gauche more stable by 105 cm^{-1}), 6-311++G(d,p) (174 basis functions, gauche more stable by 27 cm^{-1}), and 6-311+G(2d,2p) (216 basis functions) with electron correlation to second order. The energy difference between the conformers was drastically reduced to 15 cm^{-1} (0.18 kJ/mol) with the largest basis set but still the gauche conformer is predicted to be more stable. However, the energy difference is quite small and possibly higher level ab initio calculations would predict the experimental results that the cis rotamer is the more stable form.

For the normal coordinate analysis, the following procedure was used to transform the ab initio results into the form required for our iterative normal coordinate programs. The Cartesian coordinates obtained for the optimized structure were input into the **G**-matrix program together with the complete set of thirty-four internal coordinates (Figure 7). This complete set of internal coordinates was used to form the symmetry coordinates with the four redundancies. The output of this **G**-matrix program consists of the **B**-matrix and the unsymmetrized **G**-matrix.

The **B**-matrix was used to convert the ab initio force field in Cartesian coordinates to a force field in the desired internal coordinates for the cis and gauche conformers which can be obtained from the authors. All diagonal elements of the obtained force fields in internal coordinates were assigned scaling factors. The force field was then input, along with the unsymmetrized **G**-matrix and scaling factors, into the perturbation program written by Schachtschneider.[18] Initially, all scaling factors were kept fixed at a value of 1.0 to produce the pure ab initio calculated vibrational frequencies and the potential energy distributions (PED) which are given in Table 2. Subsequently, scaling factors of 0.9 for all of the coordinates except the carbon−fluorine bends and the asymmetric torsion were utilized. The geometric average of scaling factors for the interaction force constants were used to obtain the scaled force field for both conformers and the resultant frequencies are listed in Table 2.

To aid the vibrational assignment the theoretical infrared spectra of both the cis and gauche conformers were calculated as well as mixtures of the two conformers with various enthalpy differences between them. The infrared intensities were calculated based on the dipole moment derivatives with respect to the Cartesian coordinates. The derivatives were taken from the ab initio calculations transformed to normal coordinates by

TABLE 2: Observed and Calculated Frequencies (cm^{-1}) for Difluoromethylcyclopropane

			cis						gauche					
species	vibrational no.	fundamental	ab initio[a]	fixed scaled[b]	IR int.[c]	Raman act[d]	obs[e]	PED[f]	ab initio[a]	fixed scaled[b]	IR int[c]	Raman act[d]	obs[e]	PED[f]
A′	ν_1	CH_2 antisymmetric stretch	3310	3140	7.9	33.99	3100	$98S_1$	3322	3152	4.4	30.14	3105	$95S_1$
	ν_2	C_1H stretch	3245	3079	2.4	81.24	3054	$98S_2$	3241	3075	3.8	133.96		$96S_2$
	ν_3	CH_2 symmetric stretch	3214	3049	4.3	165.67	3033	$98S_3$	3224	3059	4.9	95.01		$75S_3$,$21S_{19}$
	ν_4	C_4H stretch	3133	2973	41.8	38.42	2967	$100S_4$	3152	2991	56.8	86.63		$100S_4$
	ν_5	C_1H bend	1580	1499	6.9	3.40	1478	$68S_5$, $19S_8$	1577	1496	1.5	3.94		$70S_5$, $19S_9$
	ν_6	CH_2 deformation	1516	1438	77.1	5.64	1436	$18S_6$, $24S_7$, $22S_5$, $16S_9$	1490	1413	74.1	7.63	1407	$24S_6$, $20S_9$, $16S_5$, $10S_{16}$
	ν_7	C_4H bend	1377	1306	6.5	3.29	1316	$36S_7$, $23S_{16}$, $16S_9$	1427	1354	14.0	6.83		$31S_7$, $36S_{21}$
	ν_8	ring breathing	1268	1203	8.1	13.10	1206	$54S_8$, $16S_{14}$	1274	1209	6.9	21.67		$47S_8$, $27S_9$, $10S_{14}$
	ν_9	CC stretch	1249	1185	19.5	12.85	1192	$48S_9$, $24S_6$	1213	1150	39.1	9.30		$10S_9$, $16S_{10}$, $12S_{14}$, $12S_{24}$, $11S_6$
	ν_{10}	CF_2 symmetric stretch	1154	1095	49.9	2.92	1108	$64S_{10}$, $10S_{15}$	1146	1088	153.5	6.20		$36S_{10}$, $37S_{22}$
	ν_{11}	CH_2 wag	1108	1051	1.5	0.65	1039	$83S_{11}$, $15S_{12}$	1112	1055	4.6	0.61		$91S_{11}$
	ν_{12}	ring deformation	996	945	8.1	14.56	937	$50S_{12}$, $14S_6$, $10S_{14}$	991	940	13.5	10.25		$27S_{12}$, $43S_{26}$
	ν_{13}	CH_2 rock	919	872	12.4	7.35	878	$31S_{13}$, $28S_{12}$	840	797	1.0	4.30		$28S_{13}$, $18S_{12}$, $14S_{27}$, $13S_6$
	ν_{14}	CH_2 twist	801	760	1.1	4.01	(767)	$47S_{14}$, $44S_{13}$	818	776	6.1	0.31	(776)	$30S_{14}$, $40S_{13}$, $13S_{12}$
	ν_{15}	CF_2 wag	588	558	1.3	1.40	588	$46S_{15}$, $22S_{10}$, $13S_{16}$	517	491	4.2	1.53	513	$50S_{15}$, $18S_{28}$, $12S_{17}$
	ν_{16}	CF_2 deformation	413	392	17.4	2.73	410	$27S_{16}$, $36S_{15}$, $13S_6$, $13S_7$	675	641	8.4	2.40	652	$26S_{16}$, $16S_{10}$, $11S_{17}$, $10S_{14}$
	ν_{17}	ring-CHF_2 bend	294	279	4.3	0.47	296	$82S_{17}$	262	249	4.5	0.14	252	$35S_{17}$, $30S_{29}$, $14S_{16}$, $10S_7$
A″	ν_{18}	CH_2 antisymmetric stretch	3299	3130	0.1	89.44	3087	$98S_{18}$	3311	3141	0.9	81.64		$95S_{18}$
	ν_{19}	CH_2 symmetric stretch	3210	3045	7.9	21.14	3011	$99S_{19}$	3219	3053	6.8	35.39		$78S_{19}$, $21S_{20}$
	ν_{20}	CH_2 deformation	1529	1451	3.1	7.48	1455	$100S_{20}$	1521	1443	3.0	3.89		$100S_{20}$
	ν_{21}	C_4H bend	1435	1362	27.6	3.47	1346	$96S_{21}$	1454	1380	26.4	3.08	1375	$56S_{21}$, $19S_7$
	ν_{22}	CF_2 antisymmetric stretch	1235	1172	0.1	7.34	1166	$42S_{22}$, $46S_{27}$	1241	1178	0.9	2.84		$45S_{22}$, $44S_{27}$
	ν_{23}	CH_2 twist	1173	1113	1.2	1.15	1121	$62S_{23}$, $31S_{22}$	1176	1117	6.1	0.31		$56S_{23}$, $30S_{22}$
	ν_{24}	C_1H bend	1143	1084	173.4	3.13	1086	$88S_{24}$	1082	1026	53.9	2.73		$28S_{24}$, $21S_{14}$, $16S_{13}$, $10S_9$
	ν_{25}	CH_2 wag	1116	1059	4.4	0.34	1065	$98S_{25}$	1122	1065	5.7	0.52		$97S_{25}$
	ν_{26}	ring deformation	995	944	10.1	8.73	927	$70S_{26}$	1057	1003	46.9	12.66	998	$13S_{26}$, $14S_6$, $11S_{16}$
	ν_{27}	CH_2 rock	874	830	2.1	6.35	(826)	$34S_{27}$, $21S_{23}$, $21S_{26}$, $16S_{22}$	886	841	7.6	6.89	(834)	$18S_{27}$, $35S_{26}$, $12S_{23}$
	ν_{28}	CF_2 twist	502	476	0.2	2.93	480	$49S_{28}$, $25S_{29}$	449	426	4.3	2.53	438	$24S_{28}$, $31S_{15}$, $15S_{29}$
	ν_{29}	ring-CHF_2 bend	201	191	0.005	0.02	200	$57S_{29}$, $38S_{28}$	243	231	0.1	0.10	236	$28S_{29}$, $41S_{28}$, $26S_{17}$
	ν_{30}	CHF_2 torsion	85	85	0.7	0.02	88	$90S_{30}$	102	102	0.7	0.10	96	$85S_{30}$

[a] Calculated values are obtained by ab initio calculations with the MP2/6-31G* basis set. [b] Calculated using scaling factors of 0.9 except for the CHF_2 torsion. [c] Infrared intensities are in km/mol. [d] Raman activities in Å^4/u. [e] Frequencies are from the spectrum of the gas except those in parentheses which are taken from the xenon solution. [f] Potential energy distribution predicted by ab initio calculations.

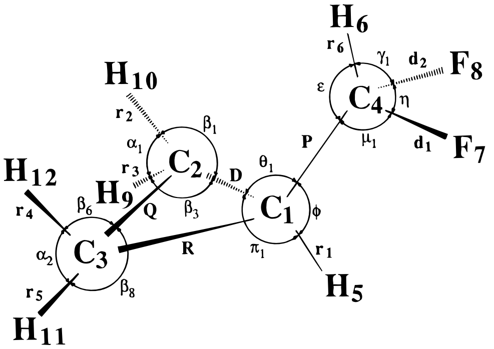

Figure 7. Geometric model and internal coordinates for the cis conformer of difluoromethylcyclopropane.

$$\left(\frac{\partial \mu_u}{\partial Q_i}\right) = \sum_j \left(\frac{\partial \mu_u}{\partial X_j}\right) L_{ij}$$

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 normal coordinates. The infrared intensities were then calculated by

$$I_i = \frac{N\pi}{3c^2}\left[\left(\frac{\partial \mu_x}{\partial Q_i}\right)^2 + \left(\frac{\partial \mu_y}{\partial Q_i}\right)^2 + \left(\frac{\partial \mu_z}{\partial Q_i}\right)^2\right]$$

In Figure 4D the predicted infrared spectrum of the more stable cis conformer is shown and Figure 4C that for the gauche conformer. The predicted infrared spectrum of the mixture is shown in Figure 4B with an enthalpy difference of 100 cm^{-1} with the cis conformer the more stable rotamer. The experimental infrared spectrum of difluoromethylcyclopropane dissolved in liquid xenon at −55 °C is also shown for comparison in Figure 4A. The agreement between the observed and calculated spectra is excellent, and these data were quite valuable for making the vibrational assignment.

Vibrational Assignment

Since there are no previous vibrational assignments proposed for this molecule, the presently obtained Raman and infrared spectra have been used to provide a complete assignment for the normal modes for the cis conformer. The assignment is based on the frequencies obtained from the ab initio calculations along with relative intensities and the band contours. The assignments made for the fundamentals associated with the carbon−hydrogen modes should be considered tentative in the absence of selective deuteration studies. These assignments are summarized in Table 2.

The cis conformer of difluoromethylcyclopropane has C_s symmetry and the fundamental vibrations span the irreducible representations: $17A' + 13A''$. From a reasonable set of structural parameters (Table 2S) it can be shown that the *a* principal axis is perpendicular to the symmetry plane for the cis conformer. Therefore, the out-of-plane modes are expected to give rise to A-type infrared band contours and the in-plane modes should be B-, C-, or B/C-hybrid type contours. The gauche form has C_1 symmetry and gives rise to A-, B-, C− or any hybrid-type infrared band contour.

Carbon−Hydrogen Modes. In the carbon−hydrogen stretching region of the Raman spectrum of the gas, four strong sharp lines are observed at 3100, 3054, 3033, and 2967 cm^{-1}. These lines can readily be assigned to the four A′ carbon hydrogen stretching motions in the decreasing wavenumber order of CH_2 antisymmetric stretch, C_1H stretch, CH_2 symmetric stretch, and C_4H stretch as predicted from the ab initio calculations. Two additional lines appear as shoulders at 3087 and 3007 cm^{-1} and they have been assigned as the CH_2 antisymmetric stretch and the corresponding symmetric stretch for the A″ species. The lines observed at 2945, 2875, and 2855 have been considered as overtones or combination bands of the carbon−hydrogen bending modes.

The assignments of the CH_2 bending modes are consistent with those of the corresponding modes for the similar molecules.[2,5,6] Between 1500 and 1330 cm^{-1} we observe C-type bands at 1478 and 1436 cm^{-1}, an A-type band at 1346 cm^{-1}, and a very weak Q transition at 1316 cm^{-1} in the infrared spectrum of the gas. All of these bands are also observed as sharp lines in the Raman spectrum of the gas at 1477, 1439, 1349, and 1317 cm^{-1} and they have been assigned to the C_1H bend (A′), CH_2 deformation (A′), C_4H bend (A″), and C_4H bend (A′), respectively. The ab initio calculation predicts that the CH_2 deformation of the A′ species has a higher frequency than that for the corresponding A″ mode, which is consistent with the infrared intensity and line shape of the Raman spectrum for the higher frequency band being the CH_2 deformation of the A′ species. Sharp Q transitions at 998, 882, and 782 cm^{-1} are observed in the Raman spectrum of the gas and they have been assigned as the CH_2 wag, CH_2 rock, and CH_2 twist of A′ symmetry, respectively, with the frequency order consistent with that predicted from the ab initio calculations. The very weak lines at 1059 and 1039 cm^{-1} and the moderately intense line at 842 cm^{-1} in the Raman spectrum of the solid do not appear as sharp Q transitions in the Raman spectrum of the gas. Therefore, these transitions should be modes of A″ symmetry and they have been assigned as the C_1H bend, CH_2 wag, and CH_2 rock of A″ symmetry, respectively.

Skeletal Modes. The assignments of the three ring modes are consistent with those given previously for the corresponding modes in similar molecules.[2,5,6] In the previously reported studies, the ring breathing vibration is assigned to the Raman line at ∼1200 cm^{-1} which has relatively strong intensity. For this molecule, the ring breathing fundamental has been assigned to the strongest Raman line observed at 1207 cm^{-1} in the spectrum of the gas. For the other ring modes, the lines at 940 and 929 cm^{-1} in the Raman spectrum of the gas have been assigned to the ring deformational modes of A′ and A″, respectively.

For the $C(H)F_2$ group, there are three sharp Q branches at 587, 414, and 300 cm^{-1} in the Raman spectrum of the gas, and these lines are due to the CF_2 wag, CF_2 deformation, and ring-CHF_2 bend of A′ symmetry, respectively. The B-type transition at 480 cm^{-1} and Q transitions at 86 cm^{-1} in the far-infrared spectrum of the gas (Figure 3), which do not appear as sharp Q branches in the Raman spectrum of the gas, have been assigned as the CF_2 twist and CHF_2 torsion, respectively. The ring-CHF_2 bend is assigned to a very weak Raman line at 200 cm^{-1} in the spectrum of the solid.

Asymmetric Torsion

The far-infrared spectrum of a gaseous molecule, which has an internal rotor, can be a source of detailed information about the barrier to conformational interchange.[19] The far-infrared spectrum of difluoromethylcyclopropane is shown in Figure 3. In the region of asymmetric torsion well-defined Q branches occur at 88.2, 86.3, 84.2 and 81.9 cm^{-1}, with additional weaker Q branches at 96.3, 94.0, 92.0, and 89.8 cm^{-1}. The three pronounced Q transitions at 88.2, 86.3, and 84.2 cm^{-1} appear to form a reasonable series and have been assigned as the first

TABLE 3: Observed and Calculated (cm^{-1}) Asymmetric Torsional Transition for Difluoromethylcyclopropane

transition	obs	calcd (cm^{-1})	Δ[a]
cis			
1 ← 0	88.20	87.62	0.58
2 ← 1	86.30	86.02	0.28
3 ← 2	84.20	84.37	−0.17
4 ← 3	81.90	82.66	−0.76
gauche			
1∓ ← 0±	96.30	96.12	0.18
2± ← 1∓	94.00	94.11	−0.11
3∓ ← 2±	92.00	92.04	−0.04

[a] Values from potential parameters listed in Table 4.

three transitions of the torsional mode for the more stable cis conformer (Table 3). For an assignment for the higher energy conformer, the Q branches at 96.3, 94.0, 92.0, and 89.8 cm^{-1} have been chosen as the transitions for this conformer.

With these assignments, a potential function governing internal rotation has been calculated for this molecule. The torsional potential is represented by a Fourier cosine series in the internal rotation angle ϕ:

$$V(\phi) = \sum_{i=1}^{6} \left(\frac{V_i}{2}\right)(1 - \cos i\phi)$$

where ϕ and i are the torsional angle and foldness of the barrier, respectively. It is assumed that V_5 and V_6 are relatively small, and they are not included in the series. The potential coefficients, V_1, V_2, V_3, and V_4 are calculated from the input of the frequencies for the two torsional transitions, the ΔH value, the gauche dihedral angle, and the internal rotation constants $F(\phi)$. The internal rotation constants also vary as a function of the internal rotation angle, and this is approximated by another Fourier series

$$F(\phi) = F_0 + \sum_{i=1}^{6} F_i \cos i\phi$$

The relaxation of the structural parameters $B(\phi)$ during the internal rotation can be incorporated into the above equation by assuming them to be small periodic functions of the torsional angle of the general type

$$B(\phi) = a + b \cos \phi + c \sin \phi$$

The series approximating the internal rotation constants for difluoromethylcyclopropane was determined by using structural parameters from the MP2/6-31G(d) ab initio calculation. In the initial calculation of the potential parameters the transitions assigned as the 1 ← 0, 2 ← 1, and 3 ← 2 transitions for the cis and ±1 ← ∓0 transition for the gauche (Table 3) were used along with the value of 102 cm^{-1} for ΔH and a dihedral angle of 121.6 for the gauche rotamer. As the values for the potential parameters converged, one additional torsional transition for the cis conformer and two more for the gauche rotamer were added to the calculation. The final resulting values for the potential coefficients are listed in Table 4 and the potential function is shown in Figure 8.

Discussion

From the study of the vibrational spectra of gaseous, liquid and solid difluoromethylcyclopropane, the cis conformer has been identified as the stable form in all three physical states. This is the conformer one would predict to be more stable on the basis of the relative steric interaction of the hydrogen and fluorine atoms with the three-membered ring. However, the ab initio calculations predict the gauche conformer to be the more stable form but by only 15 cm^{-1} from the MP2/6-311++G(2d,2p) calculations. As the size of the basis sets was increased the difference in energy between the two rotamers decreased. Nevertheless, it was disappointing that the correct conformer stability could not be predicted from the MP2/6-311+G(d,p) calculations. These results cast doubt on the prediction of Saebo and Kavana[9] that the gauche conformer of fluoromethylcyclopropane is the more stable form from the MP4(SDQ)/6-311G(d,p) calculation. The ab initio calculations should be carried out with larger basis sets, and the conformational stability should be determined experimentally for comparison. Therefore, further ab initio calculations with much larger basis functions should be carried out to see if the correct conformer stability could eventually be predicted.

TABLE 4: Potential Function Coefficients (cm^{-1}) for the Asymmetric Torsion of Difluoromethylcyclopropane and Barriers to Interconversion (cm^{-1})

coefficient	experimental value[a]	MP2/6-311+G(d,p)
V_1	229 ± 5	−139
V_2	40 ± 4	31
V_3	1270 ± 3	1200
V_4	−136 ± 2	−30
V_6		−73
gauche dihedral angle	121.6	121.2
ΔH	102 ± 8	−105
cis to gauche barrier	1255	1165
gauche to cis barrier	1155	1272
gauche to gauche barrier	1399	1168

[a] Calculated using $F_0 = 0.787\,625$, $F_1 = 0.024\,293$, $F_2 = 0.010\,932$, $F_3 = 0.000\,451$, $F_4 = 0.000\,180$, $F_5 = 0.000\,015$, $F_6 = 0.000\,002$ cm^{-1} and the transitions listed in Table 3.

The value obtained for ΔH from the temperature dependent study of the xenon solutions is expected[13,14] to be similar to the value for the gas since the dipole moments of the two conformers are predicted to have similar values and the molecular sizes of the two rotamers are nearly the same. Since the ΔH value for the liquid was similar to that obtained for the xenon solution, one does not expect the xenon solvent to significantly effect the ΔH. Thus, we believe the enthalpy value from the rare gas solution should be close to the value in the gas.

The calculated structural parameters are very similar for the two conformers except for the C_1-C_4 bond distance which is predicted to be 0.007 Å longer for the gauche conformer compared to the corresponding distance in the cis rotamer. Also the $C_4C_1C_2$ angle opens about 1.8° when one of the fluorine atoms (gauche) is over the ring. Because of the similarity of all the remaining parameters one might expect the force constants to be very similar for the two rotamers. However, there are some significant differences which should be noted.

Although the C_1-C_4 distance for the gauche conformer is predicted to be 0.007 Å longer than the corresponding bond of the cis form, the stretching force constant for this bond is slightly larger for the gauche conformer than the corresponding force constant for the cis rotamer. However, the major difference between the force constants for the two conformers is for the C_1C_4F bending force constant when the fluorine atom is over the ring which results in the force constant (μ_1) increasing from 0.893 to 1.086 mdyn/Å for the cis form. With this increase in the μ_I force constant, the force constant associated with the $C_3C_1H_5$ bend (π) decreases about 7% for the cis conformer since there is less interaction with the fluorine atom. The bending

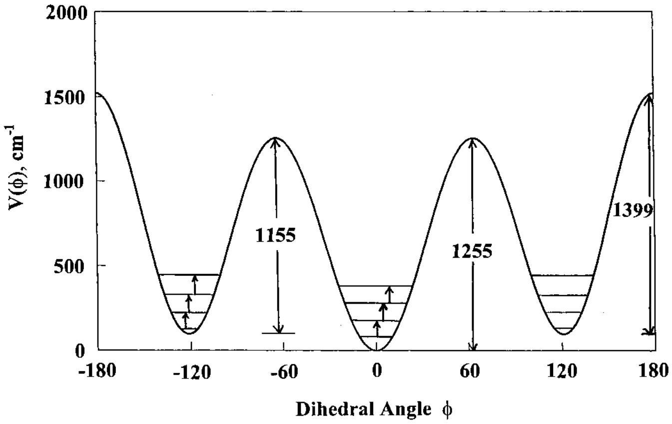

Figure 8. Asymmetric torsional potential function for difluoromethylcyclopropane as determined from far-infrared spectral data. The torsional dihedral angle of 0° corresponds to the cis conformer.

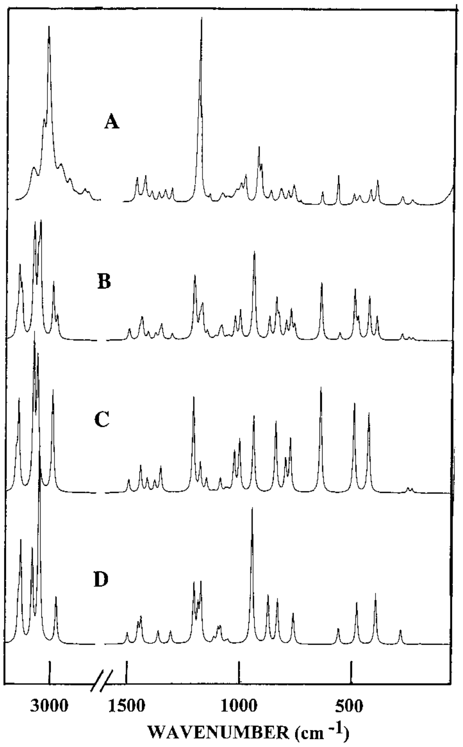

Figure 9. Raman spectra of difluoromethylcyclopropane: (A) liquid (B) calculated spectrum of the mixture of both conformers, (C) calculated spectrum of the gauche conformer, and (D) calculated spectrum of the cis conformer.

force constant for the $C_2C_1C_4$ angle (θ) increases by about 12% for the gauche conformer. These changes in the bending force constants result in large changes in the bending modes associated with the CHF_2 moiety. For example, the CF_2 twist (ν_{28}) shifts from 480 cm^{-1} in the cis conformer to 438 cm^{-1} for the gauche rotamer. Similarly, the ring-CHF_2 bend (ν_{29}) shifts from 200 cm^{-1} for the cis form to 236 cm^{-1} for the gauche conformer. For this reason, the bending modes are much more indicative of the presence of conformers for these types of molecules than the stretching modes.

For the cis conformer the PEDs for the A″ modes are usually greater than 50% from the major contributors from the indicated motions except for the CH_2 rock which has contributions from four different symmetry coordinates. However, for the A′ block the mixing is extensive with some vibrations having no contributions of more than 31% from any one symmetry coordinate, i.e., ν_6 and ν_{14}. As expected, the mixing is even more extensive for the gauche conformer which has no symmetry. Therefore, the approximate descriptions of the fundamentals are simplified expressions, which are more for bookkeeping than to give the molecular motions, nevertheless many have the major contributions from that particular symmetry coordinate

The potential parameters obtained from the torsional transitions, the enthalpy difference and the gauche dihedral angle have statistical uncertainties which only reflect the fit of the torsional frequencies and not the uncertainty of the value of the enthalpy which would mainly affect the V_1 term. Also, the uncertainties do not take into account the approximation of the one-dimensional model to the conformer interconversion. For comparison purposes, we have obtained the potential parameters from the torsional motion from the MP2/6-311+G(d,p) calculation and these parameters are listed in Table 4. The V_1 term will be different since the ab initio calculation predicts the gauche conformer to be more stable by 105 cm^{-1} rather than the cis conformer as found experimentally. Nevertheless, the V_3 term, which is essentially the barrier to conformer interchange, is nearly the same ($V_3 = 1200$ cm^{-1}) as the 1270 ± 3 cm^{-1} value obtained from the far-infrared data. The gauche to gauche barrier is predicted to be higher from the experimental data as expected for the two C−F bonds crossing the two C−C bonds of the ring, whereas only one such crossing is necessary for the cis to gauche transition. Therefore, the larger gauche to gauche barrier is consistent with predictions based on steric interactions.

The V_3 term is similar to the value for the barriers of 3-fold CF_3 rotors.[20] The replacement of a hydrogen atom by a fluorine atom raises the ethane barrier by about 270 cm^{-1} for fluoroethane.[21,22] The addition of a second fluorine atom, i.e., 1,1-difluoroethane, has little effect on the barrier.[23] Therefore, a barrier around 1250 cm^{-1} would be expected for the CHF_2 rotor based on the earlier values obtained for the CF_3 3-fold rotors.[20−24]

Although we used a single scaling factor of 0.9 with the MP2/6-31G(d) calculations, the predicted frequencies are in excellent agreement with the observed values. Excluding the frequencies for the six carbon−hydrogen stretches the average error in the frequency predictions for the normal modes are less than 10 wavenumbers on an average. Thus, multiple scaling factors are not warranted for aiding in the vibrational assignments for the fundamental modes.

For the sake of completeness, we have also predicted the Raman and infrared spectra from the ab initio data. The evaluation of Raman activity by using the analytical gradient methods has been developed.[25,26] The activity S_j can be expressed as

$$S_j = g_j(45\alpha_j^2 + 7\beta_j^2)$$

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. 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 wavenumbers for each normal mode using the relationship:[27,28]

$$\frac{\partial\sigma_j}{\partial\Omega} = \left(\frac{2^4\pi^4}{45}\right)\left(\frac{(\nu_0 - \nu^j)^4}{1 - \exp\left[\frac{-hc\nu_j}{kT}\right]}\right)\left(\frac{h}{8\pi^2 c\nu^j}\right) S_j$$

where ν_0 is the exciting wavenumber, ν_j is the vibrational wavenumber of the jth normal mode, and S_j is the corresponding Raman scattering activity. To obtain the polarized Raman scattering cross sections, the polarizabilities are incorporated into S_j by $S_j[(1 - \rho_j)/(1 + \rho_j)]$, where ρ_j is the depolarization ratio of the jth normal mode. The Raman scattering cross sections and calculated wavenumbers obtained from the standard Gaussian program were used together with a Lorentzian function to obtain the calculated spectra. Since the calculated wavenumbers are approximately 10% higher than those observed, the wavenumber axis of the theoretical spectrum was compressed by a factor of 0.9.

The predicted Raman spectra of the pure cis and gauche conformers are shown in Figures 8D and 8C, respectively. In Figure 8B, the mixture of the two conformers is shown with the theoretically determined ΔH value of 102 cm^{-1} with the cis conformer the more stable rotamer. The experimental Raman spectrum of the liquid is shown in Figure 8A for comparative purposes and the agreement is considered satisfactory but not as good as normally found. For example, the 583 cm^{-1} line (ν_{15}) for the cis conformer is predicted to be significantly less intense than the 490 and 412 cm^{-1} lines whereas it is nearly twice as intense as either of these Raman lines. Similarly the Raman line at 651 cm^{-1} for the gauche conformer is predicted to be about twice as intense as the observed lines. Therefore, the predicted intensity of the Raman lines is sufficient for distinguishing between those due to the cis and gauche conformers but they could not be used for predicting enthalpy differences between the conformers.

Since this is the first dihalomethylcyclopropane studied for the determination of conformer stabilities, there are only a few other molecules with which to compare the results. The corresponding ethylenic molecules are frequently compared to the three-membered ring molecules so a study of the conformational stability of 3,3-difluoropropene, CH_2CHCHF_2, should be of interest for comparison with the results of difluoromethylcyclopropane. We[29] have some preliminary enthalpy data for the 3,3-difluoropropene molecule and the value from the xenon solution is 82 ± 10 cm^{-1} (0.98 ± 0.12 kJ/mol) with the cis conformer the more stable rotamer. Therefore, this value is very similar to the enthalpy value for the corresponding ring. We[30] have also reported the vibrational spectra and conformational stability of cyclopropyldifluorosilane and determined that the cis conformer is the more stable rotamer with an enthalpy difference of 73 ± 10 cm^{-1} (0.87 ± 0.12 kJ/mol). However, the ab initio calculations at the level of MP2/6-311+G(d,p) predicts the gauche conformer to be the more stable form by 97 cm^{-1} (1.16 kJ/mol). Therefore, the ab initio calculations at this level fail to predict the more stable conformer for these three-membered rings. It would be of interest to see what size basis set was needed to correctly predict the stability of these ring molecules by ab initio calculations.

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Supporting Information Available: Supporting Information available Table 1S, observed infrared and Raman frequencies (cm^{-1}) for difluoromethylcyclopropane and Table 2S, structural parameters, rotational constants, dipole moments, and total energies for difluoromethylcyclopropane (7 pages). Ordering information is given on any current masthead page.

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