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Conformational Studies of Fluoromethylcyclopropane from Temperature-Dependent FT-IR Spectra of Xenon Solutions and Ab Initio Calculations

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Variable-temperature (−55 to −100 °C) studies of the infrared spectra (3500 to 400 cm^{-1}) of fluoromethylcyclopropane, *c*-$C_3H_5CH_2F$, dissolved in liquefied xenon have been carried out, and the Raman (liquid and solid) and infrared (gas and solid) spectra have been recorded from 3500 to 60 cm^{-1}. By utilizing four conformer pairs, an enthalpy difference of 262 ± 26 cm^{-1} (3.13 ± 0.31 kJ/mol) was obtained, with the gauche rotamer the more stable conformer and the only form present in the solid. The abundance of cis conformer present at ambient temperature is 12 ± 1%. On the basis of the far-infrared spectral data along with the experimental enthalpy and gauche dihedral angle, the potential function governing conformational interchange has been obtained, and the determined potential constants are $V_1 = -245 \pm 23$, $V_2 = -414 \pm 17$, $V_3 = 1263 \pm 6$, $V_4 = 272 \pm 17$, and $V_5 = 101 \pm 2$ cm^{-1}, with the cis-to-gauche barrier of 1223 cm^{-1} (14.63 kJ/mol) and the gauche-to-gauche barrier of 1362 cm^{-1} (16.29 kJ/mol). From MP2 ab initio calculations with triple-ζ basis sets with diffuse functions, the gauche conformer is predicted to be the more stable rotamer by about 320 cm^{-1}, which is consistent with the experimental results, but without diffuse functions the two conformers are predicted to have nearly the same energy. Similar results are predicted from density functional theory by the B3LYP method. The complete vibrational assignment for the gauche conformer is proposed, and several fundamentals for the cis conformer have been identified. The structural parameters, dipole moments, conformational stability, vibrational frequencies, and infrared and Raman intensities have been predicted from ab initio calculations. These experimental and theoretical results are compared to the corresponding quantities of some similar molecules.

Introduction

For some time, the relative stabilities of the rotamers of halomethylcyclopropane[1−7] have been investigated along with those of methyl-,[8] cyano-,[9,10] and ethynyl (acetenyl)-substituted[11−13] molecules. These compounds are of interest because, for molecules which contain an asymmetrical monosubstituted methyl group bonded to a symmetrical three-membered (cyclopropane) ring, two staggered conformers of cis (syn) and gauche structure are possible, whereas the eclipsed forms have been predicted to be unstable.[1−13] The conformational stability of fluoromethylcyclopropane has not been determined experimentally, apparently because of its instability.[14] From theoretical investigations, both the cis and gauche rotamers have been predicted to be the more stable conformer.[14,15] On the basis of molecular mechanics calculations,[15] the cis rotamer was predicted to be the lower energy conformer by 190 cm^{-1}, whereas from MP4(SDQ)/6-311G(d,p) calculations it has been concluded that the gauche (skew) rotamer is more stable by 70 cm^{-1}. For the other three halomethylcyclopropane molecules, the gauche form is predominant in chloromethylcyclopropane,[7] with 88% of this conformer present at ambient temperature, the corresponding bromo[7] and iodo[6] molecules having 92% and 100% gauche form present at ambient temperature, respectively, in the gas phase. Thus, it has been proposed[6] that as the size of the halogen atom increases, the abundance of the cis conformer decreases.

As a continuation of these studies on the effect of the substituent on the monosubstituted methylcyclopropane molecules, spectroscopic and theoretical studies of methyl,[8] cyano[9,10] and ethynyl[12] groups as substituents have been carried out, with the abundance of the gauche conformer in the gas phase at ambient temperature determined experimentally to be 92%, 72%, and 52%, respectively. These experimental results are in good agreement with ab initio calculations from the MP2/6-31G(d) basis set. From a microwave study[11] of cyclopropylmethylacetylene (ethynylmethylcyclopropane), the energy difference was determined to be 64 ± 30 cm^{-1}, with the cis conformer more stable; the conformational stability order is in agreement with our more recent experimental result[12] of 147 ± 14 cm^{-1}, a significantly larger value obtained from infrared spectra of variable-temperature studies of xenon solutions. Since the values for the electronegativity[16] of I, Br, Cl, CH_3, C≡N, and C≡CH are 2.5, 2.8, 3.0, 2.9, 3.2, and 3.1, these investigators[11] concluded that the abundance of the cis form parallels the increase of electronegativity of the substituents for the monosubstituted methylcyclopropane molecules.

To provide a test of the effect of the electronegativity of the substitution on the monosubstituted methylcyclopropane molecules, a conformational study of fluoromethylcyclopropane became of interest because of the large value of the electronegativity of the fluorine atom. First, ab initio calculations with a variety of basis sets at the level of restricted Hartree−Fock

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TABLE 1: Calculated Energies (Hartrees) and Energy Differences (cm^{-1}) for the Gauche and Cis Conformers of Fluoromethylcyclopropane

method/basis set	gauche	cis	ΔE^a
RHF/6-31G(d)	−254.944445	−254.944824	−83
RHF/6-31+G(d)	−254.954936	−254.953779	254
RHF/6-311G(d,p)	−255.012959	−255.012695	58
RHF/6-311+G(d,p)	−255.017639	−255.016433	265
MP2/6-31G(d)	−255.652957	−255.654060	−242
MP2/6-31+G(d)	−255.676310	−255.675171	250
MP2/6-311G(d,p)	−255.897879	−255.897857	5
MP2/6-311+G(d,p)	−255.908546	−255.907089	320
MP2/6-311G(2d,2p)	−255.968529	−255.968488	9
MP2/6-311+G(2d,2p)	−255.977076	−255.975584	327
MP2/6-311G(2df,2pd)	−256.058669	−256.058631	8
MP2/6-311+G(2df,2pd)	−256.066621	−256.065145	324
B3LYP/6-31G(d)	−256.438232	−256.438902	−147
B3LYP/6-31+G(d)	−256.457763	−256.456178	348
B3LYP/6-311G(d,p)	−256.516844	−256.516797	10
B3LYP/6-311+G(d,p)	−256.524640	−256.523019	356
B3LYP/6-311G(2d,2p)	−256.526255	−256.526201	12
B3LYP/6-311+G(2d,2p)	−256.533134	−256.531558	346
B3LYP/6-311G(2df,2pd)	−256.533157	−256.533111	10
B3LYP/6-311+G(2df,2pd)	−256.540001	−256.538396	352

[a] Negative value of energy difference indicates that the cis conformer is the more stable form.

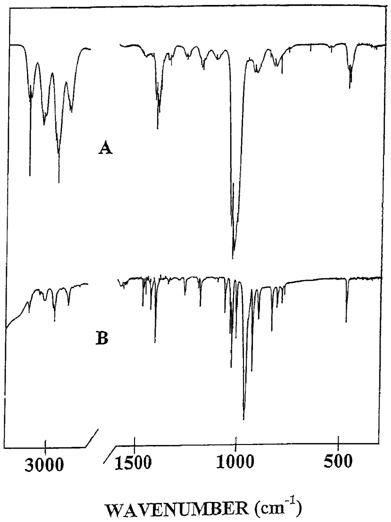

Figure 1. Mid-infrared spectra of fluoromethylcyclopropane: (A) gas and (B) annealed solid.

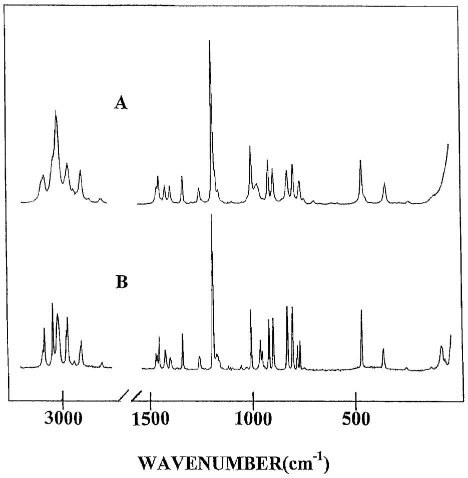

Figure 2. Raman spectra of fluoromethylcyclopropane: (A) liquid and (B) annealed solid.

(RHF) and with full electron correlation by the perturbation method to second order (MP2) were carried out. These calculations, with basis sets without diffuse functions, predicted the cis form to be the more stable conformer or the two conformers to have nearly the same energy (Table 1). Similar results were also obtained from density functional theory calculations. Since it has been shown[17] that ab initio calculations with most of the basis sets with diffuse functions predict the gauche conformer of 3-fluoropropene (allyl fluoride), $CH_2{=}CHCH_2F$, to be the more stable form, whereas the cis rotamer has been experimentally determined[18] to be the more stable conformer, the theoretical predictions for fluoromethylcyclopropane cannot be relied on to provide the correct conformer stability. Due to the importance of determining the conformational stability for this molecule, an investigation of fluoromethylcyclopropane from temperature-dependent FT-IR spectra of xenon solutions has been carried out. Additionally, we have recorded the infrared and Raman spectra of the liquid and solid phases. The conformational stability, optimized geometry, force constants, vibrational frequencies, infrared intensities, Raman activities, and depolarization ratios have been calculated for comparison with the experimental quantities when appropriate. The results of these vibrational spectroscopic and theoretical studies are reported herein.

Experimental Section

The fluoromethylcyclopropane molecule was prepared by the reaction of cyclopropylmethanol with (diethylamino)sulfur trifluoride (DAST), obtained from Aldrich Chemical Co., in diglyme at −50 °C for 1 h. The volatile portion was collected and purified by using a low-temperature, low-pressure fractionation column, and the sample was stored in liquid nitrogen under vacuum until use. The purity of the sample was checked by comparing the mid-infrared spectrum to the ab initio predictions and mass spectral data. All sample transfers were carried out under vacuum to avoid contamination.

The mid-infrared spectra (Figure 1) of the gas and the annealed solid from 3500 to 300 cm^{-1} were recorded on a Perkin-Elmer model 2000 Fourier transform spectrometer equipped with a Nichrome wire source, Ge/CsI beam splitter, and DTGS detector. The spectrum of the gas was obtained with the sample contained in a 12 cm cell equipped with CsI windows. Atmospheric water vapor was removed from the spectrometer chamber by purging with dry nitrogen. For the annealed solid, the spectrum was recorded by depositing a solid sample film onto a CsI substrate cooled by boiling liquid nitrogen and housed in a vacuum cell fitted with CsI windows. The sample was annealed until no further change was observed in the spectrum. Interferograms obtained after 256 scans for the gas and reference as well as 128 scans for the amorphous, annealed solid and reference were transformed by using a boxcar truncation function with theoretical resolutions of 0.5 and 1.0 cm^{-1} for the gaseous and solid samples, respectively.

The Raman spectra of fluoromethylcyclopropane from 3200 to 40 cm^{-1} (Figure 2) were recorded on a SPEX Ramalog spectrophotometer equipped with a Spectra-Physics model 171 argon ion laser operating on the 5145 Å line. The liquid sample was sealed in a glass capillary, and the spectrum was recorded at −10 °C due to the instability of the sample at ambient temperature. The spectrum of the solid was then recorded by inserting the capillary into a Miller−Harvey[19] jacket cooled by N_2 gas obtained from liquid N_2. The temperature of the solid was maintained at about −105 °C by controlling the rate of the nitrogen boiling off from the liquid. The frequencies for the observed lines are listed in Table 1S.

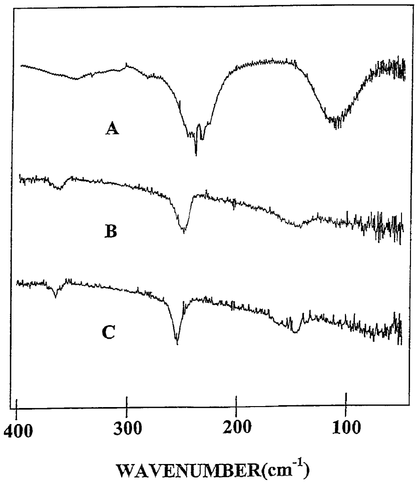

Figure 3. Far-infrared spectra of fluoromethylcyclopropane: (A) gas, (B) amorphous, and (C) annealed solid.

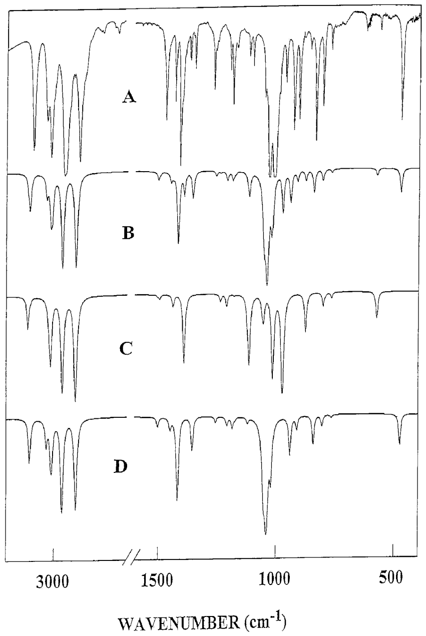

Figure 4. Infrared spectra of fluoromethylcyclopropane: (A) xenon solution at −100 °C, (B) calculated spectrum of the mixture of the two conformers, (C) calculated spectrum of the cis conformer, and (D) calculated spectrum of the gauche conformer.

The far-infrared spectra (600 to 50 cm^{-1}) of the annealed solid (Figure 3C) and gas (Figure 3A) were obtained with the Perkin-Elmer model 2000 Fourier transform spectrometer equipped with a far-infrared grid beam splitter and DTGS detector. The spectrum of the solid was obtained by condensing the sample onto a silicon plate held in a cell equipped with polyethylene windows and cooled with boiling liquid nitrogen at an effective resolution of 1.0 cm^{-1}. The sample was annealed until no further change was observed in the spectrum. The spectrum of the gas was obtained from the sample contained in a 10 cm path cell equipped with polyethylene windows with an effective resolution of 0.5 cm^{-1}. Typically, 256 scans were used for both the sample and reference to give a satisfactory signal-to-noise ratio.

The mid-infrared spectra of the sample dissolved in liquefied xenon (Figure 4A) were recorded on a Bruker model IFS-66 Fourier interferometer equipped with a Globar source, Ge/KBr beam splitter, and DTGS detector. The spectra were recorded at variable temperatures ranging from −55 to −100 °C with 100 scans at a resolution of 1.0 cm^{-1}. The temperature studies in the liquefied 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 was monitored by two Pt thermoresistors, and the cell was cooled by boiling liquid nitrogen. 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 desired temperature, a small amount of sample was condensed into the cell. Next, the pressure manifold and the cell were pressurized with xenon, which immediately started condensing in the cell, allowing the compound to dissolve. The frequencies observed for the fundamentals are listed in Tables 2 and 3.

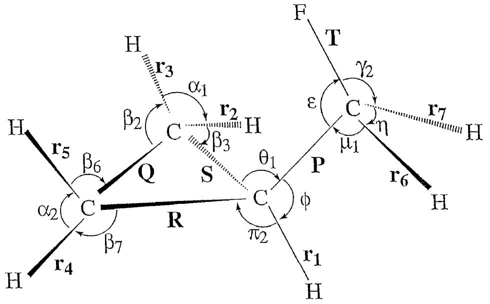

Figure 5. Geometric model and internal coordinates for the gauche conformer of fluoromethylcyclopropane.

Ab Initio Calculation

The geometry optimization of fluoromethylcyclopropane was performed by the LCAO-MO-SCF restricted Hartree−Fock calculations RHF/6-31G(d) and electron correlation calculations with Møller−Plesset perturbation to the second order, i.e., MP2/6-31G(d), MP2/6-311+G(d,p), MP2/6-311++G(d,p), and MP2/6-311+G(2d,2p), with the program Gaussian 98 using a Gaussian-type basis set.[20] The energy minimum with respect to the nuclear coordinates was obtained by the simultaneous relaxation of all geometric parameters using the gradient method of Pulay.[21] These optimized parameters are listed in Table 2S. RHF/6-31G(d) and MP2/6-31G(d) calculations predict the cis conformer to be the more stable rotamer, and even with much larger basis sets the gauche form is favored by only a few wavenumbers, i.e., 5−9 cm^{-1}. However, by using diffuse functions, the gauche form is predicted to be more stable by about 320 cm^{-1} (Table 1). Similar density functional theory (DFT) calculations by the B3LYP method with the same basis sets predict the same results: without diffuse functions the gauche conformer is predicted to be more stable by about only 10 cm^{-1}. However, the corresponding calculations with basis sets with diffuse functions predict the gauche conformer to be more stable by about 350 cm^{-1}.

The intramolecular harmonic force fields were calculated with the Gaussian 98 program at the MP2/6-31G(d) levels. Internal coordinates were defined as shown in Figure 5, and they were used to form the symmetry coordinates listed in Table 3S. The Cartesian coordinates obtained from the optimized geometry were used to calculate the **B**-matrix elements. These **B**-matrix elements were used to convert[22] the ab initio force fields in Cartesian coordinates to force fields in desired internal coordinates, and the resulting force constants can be obtained from the authors. These force fields were used to reproduce the ab initio vibrational frequencies without a scaling factor. Scaling factors of 0.88 for all of the C−H stretching modes, 0.90 for all the heavy-atom stretches and C−H bending modes, and 1.0

TABLE 2: Observed and Calculated Frequencies (cm^{-1}) and Potential Energy Distribution for *gauche*-Fluoromethylcyclopropane

vib. no.	fundamental vibration	ab initio[a]	fixed scaled[b]	IR int.[c]	Raman act.[c]	dp ratio	obsd[d]	PED[e]
ν_1	CH_2 antisymmetric stretch	3307	3102	11.5	36.2	0.57	3096	$97S_1$
ν_2	CH_2 antisymmetric stretch	3295	3092	0.4	90.2	0.74	3084	$98S_2$
ν_3	C−H stretch	3232	3032	8.0	125.4	0.07	3042	$97S_3$
ν_4	CH_2 symmetric stretch	3212	3014	6.2	104.5	0.20	3018	$92S_4$
ν_5	CH_2 symmetric stretch	3207	3009	10.6	28.9	0.52	3004	$93S_5$
ν_6	$CH_2(F)$ antisymmetric stretch	3163	2967	38.0	71.2	0.71	2956	$97S_6$
ν_7	$CH_2(F)$ symmetric stretch	3102	2910	35.8	85.1	0.10	2898	$99S_7$
ν_8	$CH_2(F)$ deformation	1584	1503	2.2	6.6	0.72	1477	$70S_8$, $24S_9$
ν_9	CH_2 deformation	1574	1493	0.1	6.5	0.62	1465*	$51S_9$, $28S_8$, $13S_{14}$
ν_{10}	CH_2 deformation	1529	1451	2.6	7.9	0.75	1438	$100S_{10}$
ν_{11}	CH in-plane bend	1496	1419	29.7	3.0	0.59	1412	$21S_{11}$, $40S_{12}$, $14S_{21}$, $13S_9$
ν_{12}	$CH_2(F)$ wag	1425	1353	8.3	6.2	0.54	1348	$56S_{12}$, $19S_{11}$
ν_{13}	$CH_2(F)$ twist	1320	1254	1.4	7.6	0.71	1266	$68S_{13}$, $12S_{26}$
ν_{14}	ring breathing	1271	1206	2.0	15.6	0.20	1200	$50S_{14}$, $28S_{11}$
ν_{15}	CH_2 twist	1243	1184	2.6	8.9	0.64	1186	$12S_{15}$, $31S_{23}$, $14S_{21}$, $13S_{11}$, $10S_{13}$
ν_{16}	CH_2 twist	1235	1173	0.6	9.9	0.33	1170*	$38S_{16}$, $46S_{25}$, $11S_{17}$
ν_{17}	CH out-of-plane bend	1178	1119	1.2	0.7	0.73	1099	$60S_{17}$, $32S_{16}$
ν_{18}	CH_2 wag	1113	1057	1.9	0.2	0.74	1053	$79S_{18}$
ν_{19}	CH_2 wag	1108	1051	24.4	1.2	0.61	1042	$65S_{19}$, $16S_{18}$, $11S_{20}$
ν_{20}	C−F stretch	1093	1040	90.5	4.2	0.70	1025	$68S_{20}$, $15S_{19}$
ν_{21}	C−C stretch	1071	1021	16.3	7.8	0.31	1010	$16S_{21}$, $23S_{23}$, $11S_{24}$, $10S_{14}$
ν_{22}	ring deformation	989	940	9.9	12.4	0.49	930	$31S_{22}$, $25S_{24}$
ν_{23}	$CH_2(F)$ rock	958	911	3.0	5.4	0.74	907	$22S_{23}$, $23S_{26}$, $18S_{24}$
ν_{24}	ring deformation	885	841	7.0	10.3	0.74	834	$39S_{24}$, $18S_{25}$, $12S_{22}$, $10S_{16}$, $10S_{17}$
ν_{25}	CH_2 rock	846	804	2.5	7.6	0.57	804	$17S_{25}$, $27S_{22}$, $11S_{21}$, $11S_{26}$
ν_{26}	CH_2 rock	805	764	0.6	5.9	0.61	768	$43S_{26}$, $45S_{15}$
ν_{27}	C−F bend	485	475	7.4	3.7	0.57	477	$41S_{27}$, $22S_{29}$
ν_{28}	ring-CH_2F in-plane bend	363	356	0.6	0.9	0.18	358	$79S_{28}$
ν_{29}	ring-CH_2F out-of-plane bend	237	236	3.4	0.06	0.70	237	$52S_{29}$, $33S_{27}$
ν_{30}	CH_2F torsion	109	109	2.5	0.02	0.50	113	$79S_{30}$, $11S_{29}$

[a] Calculated values are obtained by ab initio calculations at the MP2/6-31G(d) level. [b] Calculated using scaling factors of 0.88 for C−H stretches, 0.90 for C−H bends and heavy atom stretches, and 1.0 for heavy atom bends and torsional mode. [c] Infrared intensities are in km/mol; Raman activities in Å^4/μ. [d] Frequencies from infrared spectrum of the gas and xenon solutions except for those marked with asterisks, which are from the Raman spectrum of the solid. [e] Potential energy distribution predicted by ab initio calculations; contributions less than 10% are omitted.

for the heavy-atom bending modes and asymmetric torsion were input along with the force fields into a perturbation program to obtain the “fixed scaled” force field, vibrational frequencies, and potential energy distributions (PEDs). These data are listed in Tables 2 and 3.

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

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

where Q_i is the ith normal coordinate, X_j is the jth 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 is shown the predicted infrared spectrum of the more stable gauche conformer, and Figure 4C shows that for the cis conformer. The predicted infrared spectrum of the mixture at −100 °C is shown in Figure 4B with the enthalpy difference of 262 cm^{-1} (experimentally determined value), with the gauche conformer the more stable rotamer. The experimental infrared spectrum of fluoromethylcyclopropane dissolved in liquid xenon at −100 °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.

Also to support the vibrational assignment, we have predicted the Raman spectra from the ab initio calculation results. The evaluation of Raman activity using analytical gradient methods has been developed.[23,24] 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[25,26]

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

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 multiplying S_j by $(1 - \rho_j)/(1 + \rho_j)$, where ρ_j is the depolarization ratio of the jth normal mode. The Raman scattering cross sections and calculated wavenumbers obtained from the Gaussian 98 program[20] were used together with a Lorentzian function to obtain the calculated spectra.

TABLE 3: Observed and Calculated Frequencies (cm^{-1}) and Potential Energy Distribution for *cis*-Fluoromethylcyclopropane

species	vib. no.	fundamental vibration	ab initio[a]	fixed scaled[b]	IR int.[c]	Raman act.[c]	dp ratio	obsd[d]	PED[e]
A′	ν_1	CH_2 antisymmetric stretch	3316	3110	8.0	28.7	0.75		$99S_1$
A″	ν_2	CH_2 antisymmetric stretch	3305	3100	0.3	84.7	0.75		$99S_2$
A′	ν_3	C−H stretch	3215	3015	9.3	25.3	0.61		$51S_3$, $48S_4$
A′	ν_4	CH_2 symmetric stretch	3221	3022	5.2	208.6	0.06	3029	$51S_4$, $48S_3$
A″	ν_5	CH_2 symmetric stretch	3214	3015	10.6	25.3	0.75		$100S_5$
A″	ν_6	CH_2(F) antisymmetric stretch	3162	2967	40.3	81.2	0.75	2932	$100S_6$
A′	ν_7	CH_2(F) symmetric stretch	3104	2912	51.6	114.4	0.13	2916	$100S_7$
A′	ν_8	CH_2(F) deformation	1585	1505	0.4	9.9	0.62		$84S_8$
A′	ν_9	CH_2 deformation	1575	1496	0.9	4.1	0.73		$60S_9$, $17S_{14}$, $15S_8$
A″	ν_{10}	CH_2 deformation	1519	1441	2.6	8.1	0.75		$100S_{10}$
A′	ν_{11}	CH in-plane bend	1462	1388	0.5	4.4	0.50	1362	$31S_{11}$, $28S_{12}$, $24S_9$
A′	ν_{12}	CH_2(F) wag	1465	1391	20.9	5.2	0.75	1392	$60S_{12}$, $19S_{21}$
A″	ν_{13}	CH_2(F) twist	1301	1235	1.6	8.0	0.75	1222	$91S_{13}$
A′	ν_{14}	ring breathing	1273	1209	2.7	22.9	0.17		$46S_{14}$, $25S_{11}$, $13S_{15}$
A′	ν_{15}	CH_2 twist	1110	1015	5.6	0.8	0.34		$23S_{15}$, $33S_{20}$, $16S_{26}$, $12S_{11}$
A″	ν_{16}	CH_2 twist	1240	1177	0.4	8.9	0.75		$47S_{16}$, $45S_{25}$
A″	ν_{17}	CH out-of-plane bend	1173	1114	3.0	1.3	0.75	1119	$58S_{17}$, $19S_{16}$, $15S_{23}$
A″	ν_{18}	CH_2 wag	1142	1060	0.1	0.4	0.75		$90S_{18}$
A′	ν_{19}	CH_2 wag	1117	1054	2.8	1.0	0.75		$86S_{19}$
A′	ν_{20}	C−F stretch	1174	1120	21.3	1.5	0.71	1141	$44S_{20}$, $12S_{15}$, $10S_{11}$
A′	ν_{21}	C−C stretch	1025	973	43.8	12.4	0.29	965	$25S_{21}$, $30S_{22}$, $12S_{19}$, $10S_{20}$
A′	ν_{22}	ring deformation	807	765	1.2	15.7	0.53		$40S_{22}$, $22S_{15}$, $22S_{21}$, $11S_{26}$
A″	ν_{23}	CH_2(F) rock	1142	1089	0.1	0.4	0.75		$54S_{23}$, $15S_{16}$, $10S_{29}$
A″	ν_{24}	ring deformation	924	876	9.9	17.2	0.75	861	$86S_{24}$, $10S_{25}$
A″	ν_{25}	CH_2 rock	843	801	3.0	2.2	0.75		$42S_{25}$, $26S_{17}$, $19S_{16}$
A′	ν_{26}	CH_2 rock	832	790	0.3	1.1	0.75		$59S_{26}$, $12S_{15}$, $12S_{21}$, $12S_{22}$
A′	ν_{27}	C−F bend	585	574	6.2	1.7	0.68	564	$48S_{27}$, $28S_{28}$, $11S_{15}$
A′	ν_{28}	ring-CH_2F in-plane bend	249	245	3.6	0.2	0.17	243	$60S_{28}$, $37S_{27}$
A″	ν_{29}	ring-CH_2F out-of-plane bend	350	348	1.0	0.3	0.75	334	$86S_{29}$
A″	ν_{30}	CH_2F torsion	154	154	2.0	0.02	0.75	150	96_{30}

[a] Calculated values are obtained by ab initio calculations at the MP2/6-31G(d) level. [b] Calculated using scaling factors of 0.88 for C−H stretches, 0.90 for C−H bends and heavy atom stretches, and 1.0 for heavy atom bends and torsional mode. [c] Infrared intensities are in km/mol; Raman activities in $Å^4/\mu$. [d] Frequencies from infrared spectrum of the gas or xenon solutions. [e] Potential energy distribution predicted by ab initio calculations; contributions less than 10% are omitted.

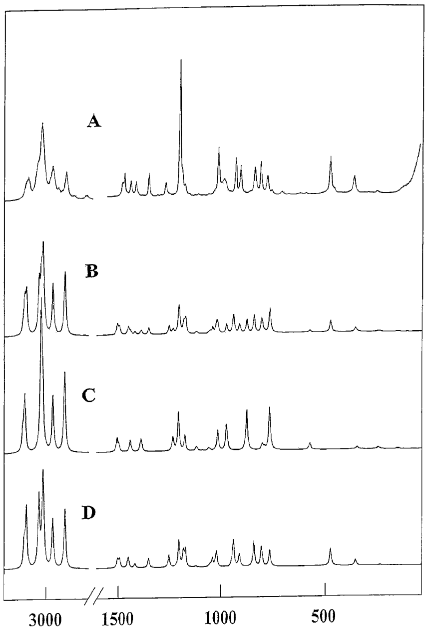

Figure 6. Raman spectra of fluoromethylcyclopropane: (A) liquid, (B) calculated spectrum of the mixture of both conformers, (C) calculated spectrum of the cis conformer, and (D) calculated spectrum of the gauche conformer.

The predicted Raman spectra of the pure gauche and cis conformers are shown in Figure 6D and Figure 6C, respectively. In Figure 6B the mixture of the two conformers is shown with the experimentally determined ΔH value of 262 cm^{-1}, with the gauche conformer the more stable form. The experimental Raman spectrum of the liquid is shown in Figure 6A for comparison, and the agreement is considered satisfactory but not nearly as good as the agreement of the simulated infrared spectrum due to the significant extent of intermolecular association in the liquid phase.

Vibrational Assignments

To determine the conformational stability of fluoromethylcyclopropane, it is necessary to correctly identify fundamentals for each conformer. Additionally, the bands chosen for the stability study should not have any accidental fundamentals, overtone, and combination bands of the other conformer at the same frequency. Therefore, the vibrational assignment needs to be made for each conformer, which was aided by the ab initio predictions for the fundamentals. The cis conformer has C_s symmetry, and the fundamental vibrations span the irreducible representation 17A′ + 13A″. Based on the prediction of structural parameters from ab initio calculations (Table 2S), the c principal axis is perpendicular to the symmetry plane for the cis conformer. Therefore, the out-of-plane modes are expected to give rise to C-type infrared band contours and the in-plane modes should be A, B, or A/B hybrid-type contours. The A″ vibrations of the cis conformer will yield depolarized Raman lines in the spectrum of the liquid, whereas the A′ vibrations should give rise to polarized Raman lines. The gauche form has C_1 symmetry and gives rise to A, B, C, and any hybrid-type infrared band contours. The data from the solid phase are also helpful in identifying conformer bands, as only one conformer should remain upon annealing. For fluoromethylcyclopropane, it will be shown that the form in the annealed solid is the gauche conformer, and all of the bands which are observed in the fluid phases and disappear in the crystal have been assigned to the cis conformer.

Carbon−Hydrogen Modes. In the infrared spectrum of the solid, five pronounced bands were observed at 3089, 3081, 3039, 2968, and 2901 cm^{-1}, as well as one broad band with two maxima at 3016 and 3009 cm^{-1}. Since there should be seven carbon−hydrogen stretching fundamentals for the gauche conformer in this region, and the C−H stretching modes on the ring are predicted to have higher frequencies than those at the $CH_2(F)$ group, by comparison to the spectra of similar molecules,[2,5,6] the bands at 3089, 3081, and 3039 cm^{-1} have been assigned as CH_2 antisymmetric stretches and C−H stretch with the broad band as CH_2 symmetric stretches, and the two bands of medium intensity at 2968 and 2901 cm^{-1} should be assigned as $CH_2(F)$ antisymmetric and symmetric stretches, respectively, which agrees with the predicted wavenumbers and infrared intensities from ab initio calculations.

The assignment of the carbon−hydrogen bending modes on the ring for the gauche conformer compares favorably with the corresponding modes of similar molecules. The $CH_2(F)$ deformation has been assigned to the highest frequency band at 1436 cm^{-1} in the region of 1500 to 1300 cm^{-1} according to the prediction from ab initio calculations. And the $CH_2(F)$ wag, $CH_2(F)$ twist, and $CH_2(F)$ rock have been assigned to the bands observed at 1351, 1269, and 906 cm^{-1} in the Raman spectrum of the solid, in good agreement with the corresponding modes for 3-fluoropropene at 1367, 1244, and 918 cm^{-1} from a previous study.[18,27]

Skeletal Modes. The ab initio calculations predict that the C−F stretch has the highest infrared intensity in the spectrum of the gas of the gauche conformer. Therefore, the strongest band, observed at 1025 cm^{-1} in the infrared spectrum of the gas, is assigned to this mode, with the C−F bending mode assigned to another strong band at 477 cm^{-1}. For the cis conformer, the C−F bending mode is predicted to be at 555 cm^{-1} with almost an A-type band contour. Therefore, the A-type band at 564 cm^{-1} in the infrared spectrum of the gas, which disappeared under annealing, is assigned to this mode. This assignment gives strong evidence that only the gauche conformer remains in the annealed solid.

The ring breathing mode for the gauche conformer has been assigned to the strongest band at 1201 cm^{-1} in the Raman spectrum, which is typical of three-membered-ring molecules. For the other ring modes, the strong Raman lines at 927 and 836 cm^{-1} in the spectrum of the solid have been assigned to the ring antisymmetric and symmetric deformational modes of the gauche conformer, respectively, consistent with the predictions from the ab initio calculations and the observed frequencies for similar molecules.

For the ring−CH_2F bending modes, the ab initio calculations predict similar wavenumbers for the two conformers in this low-frequency region, and the bands in the spectra of the solid have significant shifts toward higher frequency compared to those in the spectra of the fluid phases. For these modes, the infrared band contours become very important for identification of the conformer giving rise to the band. The ring−CH_2F in-plane bend for the gauche conformer is expected to be at 356 cm^{-1} with 95% B-type band contour, and the ring−CH_2F out-of-plane bend for the cis conformer is expected to be at 348 cm^{-1} with a pure C-type band. In the far-infrared spectrum of the gas, a B-type band is observed at 358 cm^{-1} and assigned as the ring−CH_2F in-plane bend for the gauche form, whereas a weak C-type band at 334 cm^{-1} is assigned as the ring−CH_2F out-of-plane bend for the cis rotamer. Similarly, the ring−CH_2F out-of-plane bend for the gauche conformer has been assigned to the A-type band at 237 cm^{-1}.

TABLE 4: Temperature Dependence and Intensity Ratios from Conformational Study of Fluoromethylcyclopropane

T (°C)	1000/T (K^{-1})	I_{927g}/I_{961c}	I_{904g}/I_{961c}	I_{1100g}/I_{1115c}	I_{769g}/I_{565c}
−55.0	4.584	2.872	2.192	1.052	1.581
−60.0	4.692	2.920	2.251	1.123	1.663
−65.0	4.804	3.051	2.322	1.093	
−70.0	4.922	3.174	2.423	1.253	1.837
−75.0	5.047	3.312	2.548	1.310	2.147
−80.0	5.177	3.445	2.619	1.394	1.851
−85.0	5.315	3.668	2.797	1.458	2.063
−90.0	5.460	3.861	2.911	1.580	
−95.0	5.613	4.055	3.062	1.590	2.368
−100.0	5.775	4.352	3.294	1.694	2.619
ΔH^a (cm^{-1})		250 ± 5	237 ± 5	288 ± 19	272 ± 38

[a] Average value is 262 ± 16 cm^{-1} (3.13 ± 0.19 kJ/mol), with the gauche conformer the more stable rotamer.

Asymmetric Torsions. The ab initio calculations predict the frequencies of the asymmetric torsional mode of the cis and gauche conformers at 154 and 109 cm^{-1}, respectively. A significant series of strong Q-branches are observed at 113.02, 111.52, 109.53, 107.38, 105.13, and 102.78 cm^{-1}, with a weak, sharp Q-branch at 149.78 cm^{-1} in the far-infrared spectrum of the gas. Because of the relatively large enthalpy difference between the two conformers along with the predicted band contours and intensities, the Q-branches are assigned to the ground-state and first five excited-state transitions of the CH_2F torsional mode for the gauche conformer, whereas the Q-branch at 149.78 cm^{-1} is assigned as the fundamental torsional mode for the cis form.

Conformational Stability

To obtain the enthalpy difference between the two conformers, the mid-infrared spectra of fluoromethylcyclopropane dissolved in liquefied xenon as a function of temperature from −55 to −100 °C have been recorded. 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 liquefied noble gas solutions.[27−31] 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, and the temperature of the solution is easily maintained for high-accuracy measurements. 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.

In the xenon solutions of fluoromethylcyclopropane, the major intermolecular force is the dipole−induced dipole interaction between this molecule and surrounding xenon atoms. From ab initio calculations, the dipole moments of the two conformers are predicted to have similar values (Table 2S), and the molecular sizes of the two rotamers are nearly the same, so the ΔH value obtained from the temperature-dependent FT-IR study is expected to be close to the value for the gas.[28−32]

The bands used for the conformational stability study are those assigned to the CH_2 rock at 769 cm^{-1} (gauche), C−F bend at 565 cm^{-1} (cis), $CH_2(F)$ rock at 904 cm^{-1} (gauche), ring deformation at 927 cm^{-1} (gauche), C−C stretch at 961 cm^{-1} (cis), and CH out-of-plane bend at 1115 (cis) and 1100 cm^{-1} (gauche). Ten sets of spectral data were obtained for four pairs of conformer bands (Table 4). The intensities of the infrared

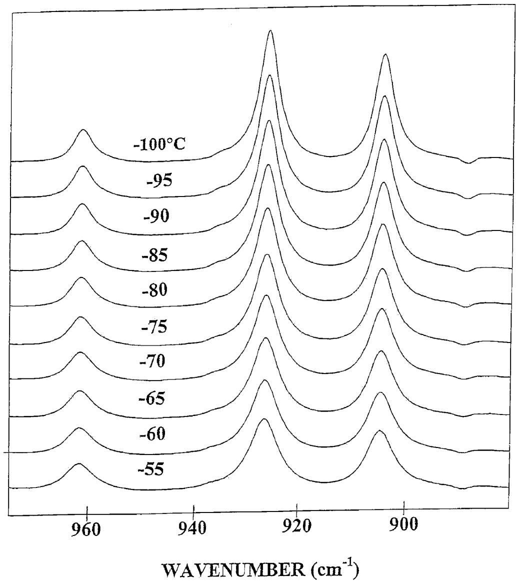

Figure 7. Temperature dependence of infrared spectra in the region 880−980 cm^{-1} of fluoromethylcyclopropane.

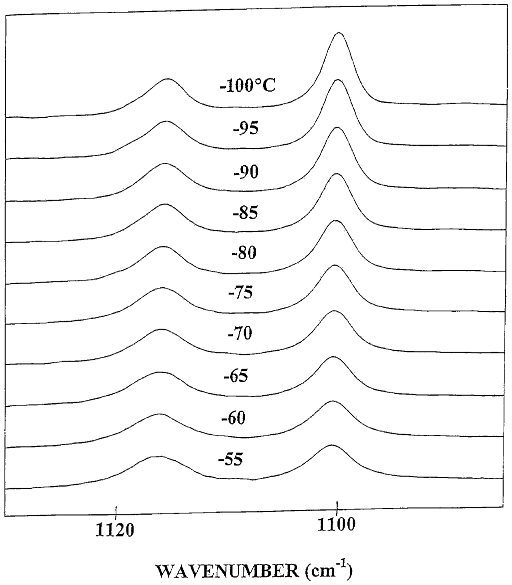

Figure 8. Temperature dependence of infrared spectra in the region 1080−1130 cm^{-1} of fluoromethylcyclopropane in xenon solutions.

bands were measured as a function of temperature, and their ratios were determined. By application of the van't Hoff equation, $-\ln K = \Delta H/(RT) - \Delta S/R$, 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 substituted with the appropriate intensity ratios. It was assumed that ΔH is not a function of temperature in the temperature range studied.

From a plot of the natural logarithm of the ratio I_{769}/I_{565} as a function of the reciprocal of the absolute temperature, the ΔH value was determined to be 272 ± 38 cm^{-1}, with the gauche form the more stable rotamer. Similarly, the pairs of I_{927}/I_{961}, I_{904}/I_{961}, and I_{1100}/I_{1115} (Figures 7 and 8) gave the ΔH values of 250 ± 3, 237 ± 5, and 288 ± 19 cm^{-1}, respectively, again with the gauche conformer the more stable form (Table 4). The average of these four values is 262 ± 16 cm^{-1}, where the error limit is given by the standard statistical 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. A more reasonable uncertainty is at least 10% to provide a more realistic error value. Thus, a final value of 262 ± 26 cm^{-1} (3.13 ± 0.31 kJ/mol) is reported for the enthalpy difference between the two conformers.

Discussion

Two scaling factors of 0.88 and 0.90 have been used with the MP2/6-31G(d) calculations to obtain the predicted vibrational frequencies, which are in good agreement with the observed values. The average error in the frequency predictions for the normal modes of the gauche conformers is 8.4 cm^{-1}, which represents a percentage error of 0.6, with the largest errors on the CH$_2$ deformations. Thus, multiple scaling factors are not needed for predicting the wavenumbers of the normal modes aiding in the vibrational assignments for the fundamentals, particularly for distinguishing those for the two different conformers.

There are five modes, ν_{11}, ν_{15}, ν_{21}, ν_{23}, and ν_{25}, where the described vibration contributes 22% or less to the atomic motion for the gauche form as indicated by the PEDs (Table 2). These include two of the CH$_2$ rocks, the C−C stretch, the CH$_2$ twist, and the C−H bend, which are vibrations where one usually finds such mixing for the monosubstituted methylcyclopropane molecules, particularly when there are no symmetry elements present. The mixing is less extensive for the cis rotamer, but ν_{11}, ν_{15}, and ν_{21} still are extensively mixed (Table 3).

The major differences in the structural parameters (Table 2S) between the two conformers are those about the CH$_2$F group; for example, the C−F distance for the gauche conformer is predicted to be 0.004 Å longer than that for the cis form. Therefore, it is reasonable to expect that there will be significant differences in the normal-mode frequencies between the two conformers for those fundamentals involving the CH$_2$F group. The C$_1$−C$_4$ distance for the cis conformer is predicted to be 0.010 Å longer than that for the gauche conformer; accordingly, the stretching force constant for this mode is larger by about 10% for the gauche conformer than the corresponding force constant for the cis form. As a result, the C$_1$−C$_4$ stretching mode (ν_{21}) is observed at 1010 cm^{-1} for the gauche conformer and shifts to 965 cm^{-1} for the cis form. However, the largest differences in the force constants are the bending force constants associated with the CH$_2$F group; for example, the bending force constant for the CCF angle (ϵ) increases by 30% when the angle increases by only 0.4° for the cis conformer. For this reason, the CCF bending mode shifts from 477 cm^{-1} for the gauche rotamer to 564 cm^{-1} for the cis conformer. Another large difference is found in the torsional force constant (τ), which increases by 50% for the cis conformer and results in the torsional fundamental frequency shifting from 113 cm^{-1} for the gauche conformer to 150 cm^{-1} for the cis form. Because of the structural parameter change of the CH$_2$F group, all the normal modes associated with this group have some remarkable shifts between the conformers. In fact, for the gauche conformer, the CH$_2$(F) wag and twist modes have been assigned to the bands at 1348 and 1266 cm^{-1}, whereas the corresponding modes for the cis conformer are found at 1392 and 1222 cm^{-1}, respectively. Therefore, the bending modes are much more indicative of the presence of the conformers for these types of molecules than the stretching modes.

For fluoromethylcyclopropane, molecular mechanics calculations indicated that the cis conformer is the more stable rotamer.[15] From the present study of the vibrational spectra of the fluid and solid phases, the gauche conformer has been

TABLE 5: Observed Asymmetric Torsional Transitions of Fluoromethylcyclopropane

transition	obsd (cm^{-1})	calcd[a] (cm^{-1})	Δ (cm^{-1})
gauche			
∓1 ← ±0	113.02	113.10	0.08
±2 ← ∓1	111.52	111.39	−0.13
∓3 ← ±2	109.53	109.51	−0.03
±4 ← ∓3	107.38	107.45	0.07
∓5 ← ±4	105.13	105.20	0.07
±6 ← ∓5	102.78	102.72	−0.05
cis			
1 ← 0	149.78	149.78	0.00

[a] Calculated using $F_0 = 1.426842$, $F_1 = 0.018681$, $F_2 = 0.013713$, $F_3 = -0.000816$, $F_4 = 0.000108$, $F_5 = -0.000010$ cm^{-1}.

identified as the more stable form in all three physical states. The enthalpy value determined from the xenon solutions is consistent with the ab initio calculations with diffuse functions. However, the RHF/6-31G(d) and MP2/6-31G(d) ab initio calculations predict the cis conformer to be the more stable form by 83 and 242 cm^{-1}, respectively. Also, it should be noted that the MP2 calculations without diffuse functions give the gauche more stable than the cis form by only a few wavenumbers (5−9 cm^{-1} from the 6-311G(d,p) to 6-311(2df,2pd) basis sets). Similar results were obtained from the B3LYP calculations, where with the larger basis sets without diffuse functions the gauche conformer is predicted to be more stable than the cis form by only 10−12 cm^{-1}.

With the assignment of the torsional fundamental for the gauche conformer along with several excited-state transitions as well as the torsional fundamental of the cis form, it is possible to obtain the experimental potential function governing the conformational interchange. The torsional potential is represented by a Fourier cosine series in the internal rotation angle θ:

$$V(\theta) = \sum_{i=1}^{6}((V_i/2))(1 - \cos i\theta)$$

where θ and i are the torsional angle and foldedness of the barrier, respectively. The potential coefficients V_1 through V_6 were initially calculated from the input of the frequencies for the two torsional transitions, the experimental ΔH value, the gauche dihedral angle, and the internal rotation kinetic constant, $F(\phi)$. The internal rotation constant also varies as a function of the internal rotation angle, and it is approximated by another Fourier series:

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

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

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

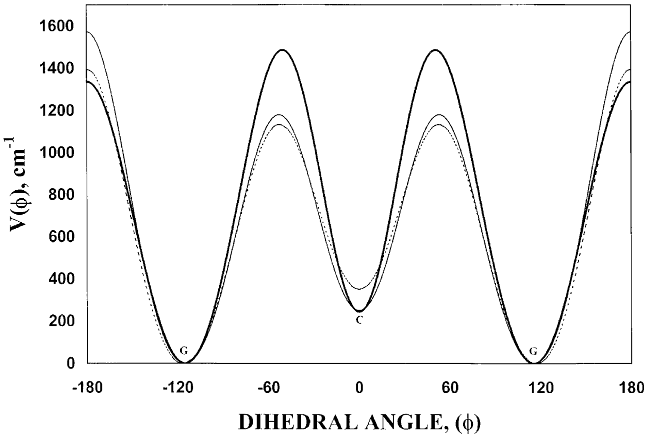

Figure 9. Asymmetric torsional potential function for fluoromethylcyclopropane, with the dark solid curve the experimentally determined potential function, the thin solid curve from MP2/6-31+G(d) calculations, and the dotted curve from B3LYP/6-31+G(d) calculations. Torsional dihedral angle of 0° corresponding to the cis conformer.

The series approximating the internal rotation constants for fluoromethylcyclopropane were determined by using structural parameters from the MP2/6-311+G(d,p) ab initio calculations. In the initial calculation of the potential parameters, the transitions assigned as the 1 ← 0 transition for the cis form and the ±1 ← ∓0 transition for the gauche form (Table 5) were used with the value of 262 cm^{-1} for ΔH and a dihedral angle of 113.7° for the gauche rotamer. As the values for the potential parameters converged, five additional torsional transitions for the gauche rotamer were added to the calculation. However, it was soon learned that the V_6 term was very small and the uncertainty was larger than its value. Therefore, the V_6 term was dropped, and the final potential function was obtained with reliably small uncertainties for each of the terms. The final resulting values for the potential coefficients are listed in Table 6, and the potential function is shown in Figure 9. The MP2 calculations with the 6-31G(d) basis set were used to predict the potential surface for conformational interchange. The dihedral angle of the internal rotation for the CH_2F moiety was allowed to vary every 30° increment, while the structural parameters were optimized at each position. From the resulting potential surface, only two minima (gauche and cis positions) were predicted, and the maxima correspond to the transition states of interconversion between the two stable conformers. The barriers predicted from those calculations were 929, 1179, and 1572 cm^{-1} for the cis-to-gauche, gauche-to-cis, and gauche-to-gauche transitions, respectively, with the transition states at the dihedral angles of 53.0° and 180.0°, respectively. The experimentally determined barriers are as follow: cis-to-gauche barrier, 1223 cm^{-1}; gauche-to-cis barrier, 1465 cm^{-1}; and gauche-to-gauche barrier, 1362 cm^{-1}. The values for the coefficients are $V_1 = -245 \pm 23$ cm^{-1}, $V_2 = -414 \pm 17$ cm^{-1}, $V_3 = 1263 \pm 6$ cm^{-1}, $V_4 = 272 \pm 17$ cm^{-1}, and $V_5 = 103 \pm 2$ cm^{-1}. The relatively large values of the V_2, V_4, and V_5 terms indicate that the asymmetric torsional mode of fluoromethylcyclopropane is not a restricted harmonic motion, probably because of the highly nonspherical electron distribution caused by the three-membered ring. From the vibrational study of 3-fluoropropene,[18] V_1 and V_3 were determined to be -162 ± 9 and 860 ± 5 cm^{-1}, while the cis-to-gauche, gauche-to-cis, and gauche-to-gauche barriers were determined to be 1117, 958, and 526 cm^{-1}, respectively (Table 6). The large difference in the gauche-to-gauche barriers between the two molecules indicates that there is a much stronger attractive interaction between the fluorine atom and the vicinal hydrogen atom in fluoromethylcyclopropane than in 3-fluoropropene. It is interesting to compare the potential function of fluoromethylcyclopropane to that of difluoromethylcyclopropane (Table 6).[36] The potential function coefficients of V_1, V_2, and V_3 difluoromethylcyclopropane were determined to be 229 ± 5, 40 ± 4, and 1270 ± 3 cm^{-1}, respectively. The difference in the conformational stability between the two molecules gives rise to different V_1 and V_2

TABLE 6: Potential Function Coefficients (cm^{-1}) for the Asymmetric Torsion of Fluoromethylcyclopropane and Barriers to Interconversion (cm^{-1})

coefficients	experimental value[a]	MP2/6-31+G(d)	$CH_2{=}CHCH_2F$[b]	c-$C_3H_5CHF_2$[c]
V_1	−245 ± 23	42	−162 ± 9	229 ± 5
V_2	−414 ± 17	−494	333 ± 12	40 ± 4
V_3	1263 ± 6	1190	860 ± 5	1270 ± 3
V_4	272 ± 17	46	65 ± 2	−136 ± 2
V_5	101 ± 2	90	−13 ± 5	−
V_6	−	−48	−35 ± 2	−
gauche dihedral angle (°)	113.7	115.2	124.6	121.6
ΔH (ΔE) (cm^{-1})	262 ± 16	250	−130 ± 25	−102 ± 8
cis-to-gauche barrier	1223	929	1117	1255
gauche-to-cis barrier	1465	1179	958	1155
gauche-to-gauche barrier	1362	1572	526	1399

[a] Calculated using the F numbers given in Table 7. [b] Reference 34. [c] Reference 35.

terms. The V_3 term, which is the dominating term in the barrier to conformer interconversion, indicates clearly that substitution of the second fluorine atom for hydrogen in the CH_2F group of fluoromethylcyclopropane has little effect on the barrier, as was previously found for 1,1-difluoroethane.[37]

According to a previous theoretical study of internal rotation potential functions,[38] the V_1 term is related to a simple dipole−dipole interaction, which for fluoromethylcyclopropane favors the trans form, having the opposed dipole compared to the cis form with reinforced dipoles. As to the V_2 term, it involves σ electron withdrawal and π electron donation.[39] In this case, attraction of electrons along the C−F bond partially empties the carbon 2p orbitals and thus facilitates donation from the corresponding 2p orbital of the nearby carbon atoms on the ring. From Walsh's molecular orbital theory on cyclopropane,[33] there should be a preference for the C−F bond to be coplanar with the axis of the 2p orbital of the carbon atom on the ring rather than perpendicular to it. Accordingly, we find a relatively large value of V_2 for fluoromethylcyclopropane, and it is probably for this reason that this molecule has an enthalpy difference similar to that for chloromethylcyclopropane.

Due to the relative steric interaction of the hydrogen and fluorine atoms with the three-membered ring, the gauche conformer would be expected to be more stable than the cis form for fluoromethylcyclopropane. The enthalpy differences of chloromethylcyclopropane and bromomethylcyclopropane are reported[7] to be 274 ± 21 and 383 ± 29 cm^{-1}, respectively, with the gauche rotamer the more stable form for both molecules. Since the enthalpy differences increase with decreasing electronegativity of the halogen atom, it is predicted[11] that the cis conformer would be more stable than the gauche form for fluoromethylcyclopropane. However, according to the present study, this prediction is found to be in error. Therefore, the steric effect may be one of the main reasons that the gauche conformer is favored for the halomethylcyclopropanes.

On the basis of Walsh−Hoffmann theory,[33−35] the corresponding ethylenic molecules are frequently compared to the three-membered-ring molecules, and consequently the conformational stability of 3-fluoropropene, $CH_2{=}CHCH_2F$, is of interest for comparison with the results of fluoromethylcyclopropane. The enthalpy for 3-fluoropropene from the xenon solutions has been determined[18] to be 60 ± 8 cm^{-1}, with the cis conformer the more stable rotamer. This result should be contrasted to the theoretical predictions[17] for 3-fluoropropene, where the predicted stability from ab initio calculations from basis sets with diffuse functions gives mainly the gauche conformer as the more stable rotamer, whereas the experimentally determined more stable conformer is the cis form,[18] with values ranging from 60 ± 8 cm^{-1} in liquid xenon to 81 ± 1 cm^{-1} in liquid argon. On the basis of these results, the ab initio calculations should be carried out with relatively larger basis sets with diffuse functions for substituted three-membered rings, but the conformational stability should be determined experimentally when the predicted energy differences are small.

TABLE 7: Calculated Energies (Hartrees) and Energy Difference (cm^{-1}) for the Cis and Gauche Conformers of Cyanomethylcyclopropane

method/basis set	cis	gauche	ΔE[a]
MP2/6-31G(d)	−248.654934	−248.654234	154
MP2/6-31+G(d)	−248.668826	−248.668644	40
MP2/6-311G(d,p)	−248.879396	−248.878587	178
MP2/6-311+G(d,p)	−248.885680	−248.885221	101
MP2/6-311G(2d,2p)	−248.944098	−248.943173	203
MP2/6-311+G(2d,2p)	−248.949336	−248.948725	134
MP2/6-311G(2df,2pd)	−249.039464	−249.038432	226
MP2/6-311+G(2df,2pd)	−249.043722	−249.043000	158
B3LYP/6-31G(d)	−249.449442	−249.449720	−61
B3LYP/6-31+G(d)	−249.459403	−249.460125	−158
B3LYP/6-311G(d,p)	−249.517131	−249.517528	−87
B3LYP/6-311+G(d,p)	−249.520432	−249.521072	−140
B3LYP/6-311G(2d,2p)	−249.525674	−249.525951	−61
B3LYP/6-311+G(2d,2p)	−249.529045	−249.529635	−129
B3LYP/6-311G(2df,2pd)	−249.533967	−249.534276	−68
B3LYP/6-311+G(2df,2pd)	−249.537006	−249.537607	−132

[a] Negative value of energy difference indicates that the gauche conformer is the more stable form.

To further demonstrate the need for diffuse functions for the ab initio predictions of the conformational stabilities of the monosubstituted methylcyclopropane molecules, we carried out calculations to estimate the conformer stability of cyanomethyl- and ethynylmethylcyclopropane with a variety of basis sets at the MP2 level and by density functional theory by the B3LYP method with the same basis sets. The predicted energy differences for the c-$C_3H_5CH_2CN$ molecule are listed in Table 7, and those for the c-$C_3H_5CH_2C{\equiv}CH$ molecule are listed in Table 8. For both of these molecules, the predicted energy differences between the two rotamers give the cis conformer to be the more stable form from the MP2 calculations, with energy differences of approximately 130 cm^{-1} for the cyano molecule and 175 cm^{-1} for the ethynyl molecule when diffuse functions are used and about 70 cm^{-1} larger without diffuse functions. The predicted value agrees well with the experimentally determined value of 147 ± 14 cm^{-1} (1.76 ± 0.17 kJ/mol) for c-$C_3H_5CH_2C{\equiv}CH$, which was obtained from infrared spectra from variable-temperature xenon solutions.[12] However, similar experimental studies[10] for the cyanide gave the gauche conformer more stable by 54 ± 4 cm^{-1} (0.65 ± 0.05 kJ/mol), which was consistent with the results from an earlier microwave investigation.[40] Therefore, differences between the isoelectric C≡CH and C≡N groups do not appear to be predicted from the MP2 calculations with basis sets up to 6-311+G(2df,2pd).

TABLE 8: Calculated Energies (Hartree) and Energy Difference (cm^{-1}) for the Cis and Gauche Conformers of Ethynylmethylcyclopropane

method/basis set	cis	gauche	ΔE^a
MP2/6-31G(d)	−232.560629	−232.559479	252
MP2/6-31+G(d)	−232.574664	−232.574298	80
MP2/6-311G(d,p)	−232.787134	−232.786029	243
MP2/6-311+G(d,p)	−232.792227	−232.791476	165
MP2/6-311G(2d,2p)	−232.849579	−232.848444	249
MP2/6-311+G(2d,2p)	−232.853676	−232.852881	174
MP2/6-311G(2df,2pd)	−232.943338	−232.942117	268
MP2/6-311+G(2df,2pd)	−232.946542	−232.945624	201
B3LYP/6-31G(d)	−233.348014	−233.347806	46
B3LYP/6-31+G(d)	−233.358710	−233.359306	−89
B3LYP/6-311G(d,p)	−233.414566	−233.414782	−47
B3LYP/6-311+G(d,p)	−233.416925	−233.417449	−115
B3LYP/6-311G(2d,2p)	−233.423332	−233.423530	−43
B3LYP/6-311+G(2d,2p)	−233.425729	−233.426261	−117
B3LYP/6-311G(2df,2pd)	−233.431476	−233.431734	−57
B3LYP/6-311+G(2df,2pd)	−233.433527	−233.434080	−121

[a] Negative value of energy difference indicates that the gauche conformer is the more stable form.

From the density functional B3LYP calculations with all of the basis sets (except 6-31G(d)), the predictions are that the gauche conformer is the more stable form for both the cyano and ethynyl molecules. Only small differences are predicted in the values with successively larger basis sets, and the difference with diffuse functions is about 60 cm^{-1}, with those with the diffuse functions having the larger values of about 130 cm^{-1} for the cyano and about 120 cm^{-1} for the ethynyl molecule, with the gauche conformer the more stable form. This result is in contrast to the predictions from the MP2 calculations, where the cis form was predicted to be more stable. Therefore, the DFT calculations do not predict significant differences in conformer stabilities between the cyanide and ethynyl molecules. At this point it does not appear possible to predict the conformational stability of the monosubstituted methylcyclopropanes from either MP2 or B3LYP calculations if the energy differences between the conformers are less than 200 cm^{-1}.

We[41] have recently shown that MP2/6-311+G(d,p) calculations predicted the r_0 structural parameters for more than 50 carbon−hydrogen distances better than 0.002 Å compared to the experimentally determined values from isolated CH stretching frequencies, which were compared[42] to previously determined values from earlier microwave studies. It has also been shown[43] that similar calculations predict the C−C distances very well for cyclopropane and methylcyclopropane. Finally, we have found[18] that we can obtain good structural parameters by adjusting the structural parameters obtained from the ab initio calculations to fit the rotational constants (computer program A&M, Ab initio and Microwave, developed in our laboratory) obtained from the microwave experimental data. To reduce the number of independent variables, the structural parameters are separated into sets according to their types. Bond lengths in the same set keep their relative ratio, and bond angles and torsional angles in the same set keep their differences in degrees. This assumption is based on the fact that the errors from ab initio calculations are systematic. Therefore, it should be possible to obtain “adjusted r_0” structural parameters for $c\text{-}C_3H_5CH_2C{\equiv}CH$ from the six previously reported rotational constants as well as those for the corresponding cyanide, particularly since the distance of the triple bond is nearly the same irrespective of the substituent.[44] Such parameters are expected to be more accurate than those obtained from the electron diffraction study[45] with microwave rotational constant[11] restraints.

The adjusted r_0 parameters for the ethynyl molecule obtained by the ab initio MP2/6-311+G(d,p)-predicted parameters and the fit of the six microwave rotational constants[11] are listed in Table 9, along with the ab initio values and those reported from the electron diffraction study.[45] First, it should be noted that the parameters reported for the heavy atoms, except for the triple bond obtained from the ED investigation, have very large uncertainties, with those for the two carbon distances from the methylene (CH_2) moiety and the $C_2{-}C_3$ distance in the three-membered ring being exceptionally large, ranging from 0.013 to 0.028 Å. The adjusted r_0 distances for these parameters certainly do not exceed 0.005 Å as uncertainties and are probably slightly less. Also, the previously reported C−H distances for the “ring” bonds, with values of 1.107 ± 0.006 Å, are significantly longer than the methylene C−H distances of 1.095 ± 0.005 Å, which are inconsistent with the shorter C−H bonds for those on the three-membered rings, with the r_0 values of 1.084−1.086 ± 0.002 Å, consistent with the expected values. The heavy-atom angle parameters previously reported[45] have very small uncertainties, and they agree very well with the r_0 parameters for these angles found in this study, whereas the ∠HCH values given earlier have rather large uncertainties (2.4°), whereas the r_0 values should be accurate to ±0.5° or better. Thus, it is believed that the adjusted r_0 parameters obtained from the combined ab initio predicted values and the microwave data for ethynylmethylcyclopropane[11] are much more accurate and reliable than the parameters previously reported for this molecule.

For the cyanide, since only three experimental rotational constants are available for structural determinations for the gauche conformer, the C≡N bond distance was fixed at the value of 1.159 Å from this bond distance in methyl cyanide.[46] The fit of the rotational constants is better than 1 MHz, and the determined parameters similar to those of the ethynyl molecule differ by only very small amounts, i.e., 0.002 Å or less. The major parameter to note for both of these molecules is the $C_1{-}C_4$ distance, which is a very short distance of 1.465 Å for the gauche conformer of the −C≡CH molecule (1.467 Å for the cyanide) and an even shorter value of 1.463 Å for the cis form. This is in contrast to the ab initio predicted $C_1{-}C_4$ distance in fluoromethylcyclopropane of 1.492 Å for the gauche conformer and the much longer value of 1.502 Å for this bond in the cis form. Similarly, much longer $C_1{-}C_4$ distances have been obtained[43] for chloromethylcyclopropane (1.495 Å for the gauche form and 1.507 Å for the cis form). For ethylcyclopropane, where the substitution is a methyl group, the $C_1{-}C_4$ distance is even longer, with values[47] of 1.510 Å for the gauche form and 1.518 Å for the cis rotamer. For this latter molecule, the methyl group has a relatively small electronegativity compared to the chlorine atom but similar van der Waals radii, but both have small amounts of the cis conformer present at ambient temperature. Therefore, the electronegativity must have a very minor effect on the amount of the cis form present in these monosubstituted methylcyclopropanes, which is in contrast to the previous suggestion[11,45] that electronegativity a major factor for determining the conformational stability of these molecules as well as an earlier suggestion for similar cyclobutanes.[48,49] The current results for fluoromethylcyclopropane, coupled with those for the corresponding ethynyl and cyanide analogues, strongly indicate that the major factor contributing to the large amount of the cis conformer present at ambient temperature for these molecules is through-bond interactions between the substituent and the carbon bond to the three-membered ring. This results in a shortening by 0.030 Å or more

TABLE 9: Structural Parameters (Bond Lengths in Angstroms, Angles in Degrees), Rotational Constants, Dipole Moments, and Energies for Substituted Methylcyclopropane Molecules

	c-$C_3H_5CH_2C{\equiv}CH$						c-$C_3H_5CH_2C{\equiv}N$			
	MP2/6-311+G(d,p)		MW + ED[a]		adjusted r_0		MP2/6-311+G(d,p)		adjusted r_0	
parameter	gauche	cis	gauche	cis	gauche	cis	gauche	cis	gauche[b]	cis[c]
$r(C_1-C_2)$	1.507	1.506	1.506(14)	1.509(9)	1.507(5)	1.505(5)	1.506	1.506	1.507(5)	1.506(5)
$r(C_1-C_3)$	1.505	1.506	1.509(9)	1.509(9)	1.505(5)	1.505(5)	1.505	1.506	1.506(5)	1.506(5)
$r(C_2-C_3)$	1.513	1.513	1.516(14)	1.517(14)	1.513(5)	1.513(5)	1.512	1.513	1.511(5)	1.512(5)
$r(C_1-C_4)$	1.515	1.521	1.517(28)	1.518(28)	1.516(5)	1.522(5)	1.514	1.519	1.514(5)	1.519(5)
$r(C_4-C_5)$	1.464	1.463	1.450(13)	1.450(13)	1.465(5)	1.463(5)	1.466	1.463	1.467(5)	1.463(5)
$r(C_5{\equiv}C_6,N_6)$	1.219	1.219	1.215(3)	1.215(3)	1.209(3)	1.210(3)	1.174	1.174	1.159(3)	1.160(3)
$r(C_1-H_1)$	1.086	1.086	1.107(6)	1.107(6)	1.086(2)	1.086(2)	1.085	1.086	1.085(2)	1.086(2)
$r(C_4-H_2)$	1.097	1.097	1.095(5)	1.095(5)	1.097(2)	1.097(2)	1.096	1.096	1.096(2)	1.096(2)
$r(C_4-H_3)$	1.096	1.097	1.095(5)	1.095(5)	1.096(2)	1.097(2)	1.095	1.096	1.095(2)	1.096(2)
$r(C_2-H_4)$	1.085	1.084	1.107(6)	1.107(6)	1.085(2)	1.084(2)	1.085	1.084	1.085(2)	1.084(2)
$r(C_3-H_5)$	1.085	1.084	1.107(6)	1.107(6)	1.085(2)	1.084(2)	1.085	1.084	1.085(2)	1.084(2)
$r(C_2-H_6)$	1.084	1.084	1.107(6)	1.107(6)	1.084(2)	1.084(2)	1.083	1.083	1.083(2)	1.083(2)
$r(C_3-H_7)$	1.083	1.084	1.107(6)	1.107(6)	1.083(2)	1.084(2)	1.083	1.083	1.083(2)	1.083(2)
$r(C_6-H_8)$	1.064	1.065	1.065(5)	1.065(5)	1.064(2)	1.065(2)	−	−	−	−
$\angle C_3C_1C_2$	60.3	60.3	60.4(3)	60.3(2)	60.3(3)	60.3(3)	60.3	60.3	60.2(3)	60.2(3)
$\angle C_1C_2C_3$	59.8	59.9	59.9(3)	59.9(1)	59.8(3)	59.9(3)	59.9	59.9	59.8(3)	59.9(3)
$\angle C_1C_3C_2$	59.9	59.9	59.7(3)	59.8(1)	59.9(3)	59.9(3)	59.8	59.9	60.0(3)	59.9(3)
$\angle C_3C_1C_4$	118.9	121.0	118.9(17)	121.0(7)	119.2(5)	121.2(5)	118.8	121.0	118.8(5)	121.4(5)
$\angle C_1C_4C_5$	111.9	113.2	114.1(8)	114.1(8)	112.1(5)	113.8(5)	111.5	112.3	111.7(5)	112.9(5)
$\angle C_4C_5C_6,N_6$	179.1	179.3	180.0	180.0	178.9(5)	179.5(5)	178.9	178.6	178.8(5)	178.9(5)
$\angle H_4C_2H_6$	115.0	115.6	117.2(24)	115.5(24)	115.0(5)	115.6(5)	115.1	115.4	115.1(5)	115.4(5)
$\angle H_5C_3H_7$	115.1	115.6	117.2(24)	115.5(24)	115.1(5)	115.6(5)	115.0	115.4	115.0(5)	115.4(5)
$\angle H_2C_4H_3$	106.8	107.0	111.6(33)	106.9(33)	106.8(5)	107.0(5)	107.3	107.6	107.3(5)	107.6(5)
$\angle H_1C_1$ring	121.1	120.2	121.7(33)	120.2(25)	121.1(5)	120.2(5)	121.3	120.5	121.3(5)	120.5(5)
$\angle C_4C_1$ring	124.2	126.5	123.5(26)	126.5(9)	124.3(5)	126.8(5)	123.9	126.6	124.1(5)	127.0(5)
$\tau C_4C_1C_3C_2$	109.1	110.4	107.7(24)	110.4(19)	108.9(5)	110.6(5)	108.6	110.4	108.5(5)	110.7(5)
$\tau C_3C_1C_4C_5$	151.6	35.9	149.6(16)	35.9(4)	153.6(5)	36.0(5)	150.9	35.9	152.6(5)	36.0(5)
$\tau C_5C_4C_1H_1$	63.0	180.0	61.3(17)	180.0	61.0(5)	180.0	63.9	180.0	62.2(5)	180.0
$\lvert\mu_a\rvert$ (D)	0.733	0.407					4.043	3.156		
$\lvert\mu_b\rvert$ (D)	0.331	0.575					1.882	2.841		
$\lvert\mu_c\rvert$ (D)	0.033	−					0.306	−		
$\lvert\mu_t\rvert$ (D)	0.805	0.704					4.471	4.246		
A (MHz)	10545.6	6835.0	10690.7(11)	6895.8(5)	10690.5	6895.1	10670.7	6944.6	10800.5	7019.6
B (MHz)	2001.8	2650.4	1984.990(5)	2621.43(1)	1984.9	2621.7	2026.0	2705.4	2014.8	2674.6
C (MHz)	1817.4	2283.8	1808.226(6)	2268.91(1)	1808.5	2269.0	1840.8	2337.2	1835.9	2322.0

[a] Reference 45. [b] Microwave rotational constants for *gauche*-c-$C_3H_5CH_2C{\equiv}N$: $A = 10800.703 \pm 1.639$ MHz, $B = 2014.942 \pm 0.006$ MHz, $C = 1835.685 \pm 0.006$ MHz. Dipole moments: $|\mu_a| = 3.77(3)$ D, $|\mu_b| = 0.63(19)$ D, $|\mu_c| = 0.72(8)$ D, $|\mu_t| = 3.89(8)$ D.[40] [c] Estimated parameters; no microwave data for *cis*-c-$C_3H_5CH_2C{\equiv}N$ have been published.

of the C_1-C_4 bond compared to the corresponding bond in the fluoride and an even larger difference for the chloride and methyl substituents (ethylcyclopropane). A similar effect is also expected for the corresponding molecules where the halogen atom is replaced by a pseudo-halogen substituent, such as NCO or NCS, and a study of one or both of these molecules would be of interest for comparison. A conformational stability study of 2-butynylcyclopropane, where the H atom on the triple bond of ethynylmethylcyclopropane is replaced by a methyl group, would also be of interest, because this molecule would be expected to have the cis form more stable if the primary controlling factor is the C_1-C_4 distance from the through-bond interaction.

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Supporting Information Available: Table 1S, observed infrared and Raman frequencies for fluoromethylcyclopropane; Table 2S, calculated structural parameters, rotational constants, dipole moments, and energies for fluoromethylcyclopropane; and Table 3S, symmetry coordinates for fluoromethylcyclopropane. This material is available free of charge via the Internet at http://pub.acs.org.

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