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Conformational stability, *r*⁰ structural parameters, and vibrational assignments of mono-substituted cyclobutanes: Fluorocyclobutane

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ABSTRACT

Variable temperature (-55 to -100 °C) studies of the infrared spectra (3500-400 cm⁻¹) of fluorocyclobutane, c-C₄H₇F, dissolved in liquid xenon have been carried out as well as the infrared spectra of the gas. By utilizing eight pairs of conformers at 10 different temperatures, the enthalpy difference between the more stable equatorial conformer and the axial form has been determined to be 496 ± 40 cm⁻¹ (5.93 \pm 0.48 kJ/mol). The percentage of the axial conformer present at ambient temperature is estimated to be $8 \pm 1\%$. The *ab initio* MP2(full) average predicted energy difference from a variety of basis sets is 732 ± 47 cm⁻¹ (9.04 ± 0.44 kJ/mol) and the average value of 602 ± 20 cm⁻¹ from density functional theory predictions by the B3LYP method are significantly larger than the experimentally determined enthalpy value. By utilizing previously reported microwave rotational constants for the equatorial and axial conformers combined with ab initio MP2(full)/6-311+G(d,p) predicted structural values, adjusted r_0 parameters have been obtained. The determined heavy atom structural parameters for the equatorial [axial] conformer are: distances (Å) C-F=1.383(3) [1.407(3)], C_{α} -C_B=1.543(3) [1.546(3)], $C_{\beta}-C_{\gamma}=1.554(3)$ [1.554(3)] and angles (°) $\angle C_{\alpha}C_{\beta}C_{\gamma}=85.0(5)$ [89.2(5)], $\angle C_{\beta}C_{\alpha}C_{\beta}=89.3(5)$ [89.2(5)], $\angle F - (C_B C_\alpha C_B) = 117.4(5)$ [109.2(5)] and a puckering angle of 37.4(5) [20.7(5)]. The conformational stabilities, harmonic force fields, infrared intensities, Raman activities, depolarization ratios and vibrational frequencies have been obtained for both conformers from MP2(full)/6-31G(d) ab initio calculations and compared to experimental values where available. The results are discussed and compared to the corresponding properties of some other monosubstituted cyclobutanes with halogen and pseudohalogen substituents.

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1. Introduction

The cyclobutane molecule is puckered in the ground vibrational state which results from the steric forces being larger than the ring strain forces. The structural parameters of cyclobutane have been determined from a microwave investigation of four different deuterated isotopomers and the puckering angle was determined [1] to be $29.55(9)^\circ$. Prior to this study only the structural parameters of the equatorial chlorocyclobutane had been reported [2] from a microwave study but the reported *A* rotational constants were found to differ significantly from those parameters obtained by the weighted least-squares adjusted method from *ab initio* predicted

* Corresponding author. Tel.: +1 816 235 6038; fax: +1 816 235 2290. *E-mail address*: durigj@umkc.edu (J.R. Durig). values [3]. However, from a more recent microwave investigation of both the equatorial and axial conformers of chlorocyclobutane [4] it has been possible to obtain the complete structural parameters [5] from the revised rotational constants of the equatorial conformer along with those for axial conformer combined with those predicted from the *ab initio* MP2(full)/6-311+G(d,p) calculations. By utilizing the *ab initio* predicted parameters in combination with previously reported microwave rotational constants it has been possible to obtain complete r_0 structural parameters in addition to chlorocyclobutane for cyclobutylamine [6], bromocyclobutane [7], cyanocyclobutane [8], and cyclobutanol [9]. All of these molecules have at least two conformers present at ambient temperature. By variable temperature infrared investigations of rare gas solutions [5-9] the enthalpy differences have been determined after confident vibrational assignments have been made by using ab initio predicted frequencies, infrared band contours and intensities, along with Raman activities and depolarization values. From far infrared and low frequency Raman spectra of the gases it has been possible to obtain the potential function governing the conformational interchange for many of these molecules. A comparison of the dif-

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ferent values of the heavy atom structural parameters and the barrier to inversion and enthalpy differences has been made along with predicted energy differences.

As a continuation of our conformational and structural determination of monosubstituted cyclobutanes with halogen and pseudo-halogen substituents we have investigated the temperature dependent infrared spectra of fluorocyclobutane in xenon solutions to obtain the enthalpy difference between the two conformers. In the initial study [2] of the microwave spectrum of fluorocyclobutane the structural parameters could not be obtained from the three experimentally obtained rotational constants. Therefore, corresponding parameters from chlorocyclobutane were used for fluorocyclobutane along with an estimated C–F bond distance of 1.37 Å. These parameters were sufficient to provide rotational constants which satisfactorily agreed with the experimentally determined ones [2].

Later by weighted least-squares adjustment method the C–F distance and the angle of the fluorine atom to the plane of the ring were determined [10], by utilizing the three experimentally determined rotational constants from the initial microwave study [2] along with the remaining parameters, to be the same as the corresponding parameters obtained for chlorocyclobutane [3]. Therefore, to obtain a more complete structural parameter determination for fluorocyclobutane we have combined the *ab initio* MP2(full)/6-311+G(d,p) predicted parameters with the six experimentally determined rotational constants [4] for the two forms to obtain the complete structural parameters for both conformers of fluorocyclobutane.

2. Experimental

The fluorocyclobutane sample was prepared by replacing the chlorine atom in chlorocyclobutane (Sigma–Aldrich Chemical Co., with stated purity of 97%) with a fluorine atom by allowing the chlorocyclobutane to drip onto powdered AgF_2 which had been dried under vacuum at 110 °C for 24 h. The sample was purified by a low-temperature, low-pressure fractionation column and the purity of the sample was verified by comparing the infrared spectrum with that previously reported [11].

The mid-infrared spectrum of the gas (Fig. 1B) was obtained from 4000 to $250 \,\mathrm{cm^{-1}}$ on a Perkin-Elmer model 2000 Fourier transform spectrometer equipped with a Ge/CsI beamsplitter and a DTGS detector. Atmospheric water vapor was removed from the spectrometer housing by purging with dry nitrogen. The theoretical resolution used to obtain the spectrum of the gas was $0.5 \,\mathrm{cm^{-1}}$. One hundred twenty-eight interferograms were added and transformed with a boxcar truncation function. The frequencies for the predicted and observed fundamentals are listed in Tables 1 and 2.

The mid-infrared spectra $(4000-400 \text{ cm}^{-1})$ of the sample dissolved in liquefied xenon (Fig. 1C) were recorded on a Bruker model IFS-66 Fourier transform spectrometer equipped with a globar source, a Ge/KBr beamsplitter and a DTGS detector. In all cases, 100 interferograms were collected at 1.0 cm^{-1} resolution, averaged and transformed with a boxcar truncation function. For these studies, a specially designed cryostat cell was used. It consists of a copper cell with a path length of 4 cm with wedged silicon windows sealed to the cell with indium gaskets. The copper cell was enclosed in an evacuated chamber fitted with KBr windows. The temperature was maintained with boiling liquid nitrogen and monitored by two Pt thermo resistors.

3. Ab initio calculations

The *ab initio* calculations were performed with the Gaussian-03 program [12] using Gaussian-type basis functions. The energy minima with respect to nuclear coordinates were obtained by the



Fig. 1. Comparison of experimental and predicted mid-infrared spectra of fluorocyclobutane: (A) simulated spectrum of equatorial conformer; (B) observed infrared spectrum of the gas, asterisk denotes an impurity and (C) Xe solution at $-70 \,^{\circ}$ C.

simultaneous relaxation of all geometric parameters using the gradient method of Pulay [13]. A variety of basis sets as well as the corresponding ones with diffuse functions were employed with the Møller–Plesset perturbation method [14] to the second order MP2 with full electron correlation as well as with the density functional theory by the B3LYP method. The predicted conformational energy differences are listed in Table 3.

In order to obtain descriptions of the molecular motions involved in the fundamental modes of fluorocyclobutane, a normal coordinate analysis was carried out. The force field in Cartesian coordinates was obtained with the Gaussian 03 program at the MP2(full) level with the 6-31G(d) basis set. The internal coordinates used to calculate the **G** and **B** matrices are given in Table 4 with the atomic numbering shown in Fig. 2. By using the **B** matrix [15], the force field in Cartesian coordinates was converted to a force field in internal coordinates. Subsequently, 0.88 was used as the scaling factor for the CH stretches and CH₂ scissors whereas 0.90 was used as the scaling factor for all other modes to obtain



Fig. 2. Fluorocyclobutane showing atomic numbering.

Table 1
Observed ^a and calculated ^b frequencies for the <i>equatorial</i> conformer of fluorocyclobutane.

		Fundamental	Ab initio	Fixed scaled ^c	IR int.	Raman act.	dp ratio	Gas ^d	Gas ^f	Gas	Xe	P.E.D. ^h	Band o	contour					
													A	В	С				
A'	ν_1	β-CH ₂ antisymmetric stretch	3214	3015	38.3	41.5	0.74	3006	2992	3003	2995	52S ₁ ,47S ₂	52S ₁ ,47S ₂ –						
	ν_2	γ-CH ₂ antisymmetric stretch	3199	3001	5.3	81.8	0.51	2992	2 2970 2991 - 50S ₂ ,44S ₁		50S ₂ ,44S ₁	93	-	7					
	ν_3	γ-CH ₂ symmetric stretch	3141	2947	18.7	142.9	0.10	2950	2961	2947	2950	90S ₃	88	-	12				
	ν_4	β -CH ₂ symmetric stretch	3138	2944	8.9	117.4	0.21	2912	2950	2910	2895	92S4	27 – 7		73				
	v_5	CH stretch	3131	2937	27.1	83.7	0.28	2861*	2934	2892	2878	91S ₅	17 –		83				
	ν_6	β -CH ₂ scissors	1578	1480	6.4	6.4	0.66	1472	1471	1473	1466	56S ₆ ,38S ₇	84	-	16				
	v_7	γ -CH ₂ scissors	1553	1457	4.7	15.4	0.75	1453	1453	1454	1446 60S ₇ ,39S ₆		-	-	100				
	ν_8	CH in-plane bend	1449	1375	44.8	8.3	0.66	1361	1361	1361 1362 1358		49S ₈ ,27S ₁₇	100	-	-				
	ν_9	β -CH ₂ wag	1314	1247	16.4	2.5	0.74	1242	1242	1244	1240	61S ₉ ,16S ₁₄	96	-	4				
	v_{10}	β -CH ₂ twist	1279	1213	3.1	9.2	0.74	1140	1221	1222	1218	72S ₁₀ ,12S ₁₅	85	-	15				
	v_{11}	β -CH ₂ rock	1199	1137	25.2	1.9	1.9 0.67 1098 1140 1141 1136		41S ₁₁ ,16S ₁₇ ,15S ₁₂ ,15S ₁₅ ,11S ₁₈	83	-	17							
	v_{12}	C–F stretch	1168	1108	58.9	8.0	0.22	1079*	1098	1099	1090	39S ₁₂ ,40S ₁₃	96	-	4				
	v_{13}	Ring breathing	1016	964	14.4	15.2	0.11	959	959	961	954	46S ₁₃ ,17S ₁₂ ,14S ₁₆	79	-	21				
	v_{14}	Ring deformation 1	955	906	1.8	1.3	0.74	783*	851	914	911	40S ₁₄ ,19S ₁₆ ,17S ₁₅ ,12S ₉	99 –		1				
	v_{15}	γ -CH ₂ rock	792	751	3.5	1.9	0.32	750	750	750	750	44S ₁₅ ,25S ₁₄ ,16S ₁₀	13 –		87				
	v_{16}	Ring deformation 2	618	586	2.3	3.0	0.49	599	599	599	599	62S ₁₆ ,14S ₁₁ ,12S ₁₂	94	-	6				
	v_{17}	C-F in-plane bend	474	450	7.2	0.4	0.49	456	456	455	454	32S ₁₇ ,27S ₈ ,14S ₁₈ ,13S ₁₁	80	-	20				
	v_{18}	Ring puckering	202	192	1.6	0.1	0.02	166	166	(166) ^g	-	72S ₁₈ ,13S ₈ ,11S ₁₇	28	-	72				
<i>A</i> ″	v_{19}	β-CH ₂ antisymmetric stretch	3204	3006	20.1	61.6	0.75	2988	2988	2993	2986	99S ₁₉	-	100	-				
	v_{20}	β -CH ₂ symmetric stretch	3135	2941	29.4	0.1	0.75	2966*	2914*	2941	2940	99S ₂₀	-	100	-				
	v_{21}	β -CH ₂ scissors	1537	1442	3.1	7.8	0.75	1441	1441	1441	1435	99S ₂₁	-	100	-				
	v_{22}	CH out-of-plane bend	1359	1289	1.4	3.7	0.75	1263	1246	1260	1257	60S ₂₂ ,16S ₂₃	-	100	-				
	v_{23}	γ -CH ₂ wag	1294	1228	1.5	0.1	0.75	1221	1263	1223	1221	58S ₂₃ ,17S ₂₇ ,16S ₂₂	-	100	-				
	v_{24}	γ -CH ₂ twist	1282	1216	0.3	5.0	0.75	1161	1216	1218	1215	42S ₂₄ ,43S ₂₅	-	100	-				
	v_{25}	β -CH ₂ wag	1221	1158	0.3	8.6	0.75	1049	1161	1159	1161	46S ₂₅ ,21S ₂₄	-	100	-				
	v_{26}	Ring deformation 1	1102	1045	8.5	1.5	0.75	1057 ^e	1026	1050	1048	24S ₂₆ ,29S ₂₈ ,26S ₂₇ ,10S ₃₀	-	100	-				
	v_{27}	β -CH ₂ twist	974	924	2.8	1.1	0.75	921	921	926	921	42S ₂₇ ,18S ₂₄ ,17S ₂₂ ,14S ₂₆	-	100	-				
	v_{28}	Ring deformation 2	957	908	0.5	12.6	0.75	899	843	897	893	57S ₂₈ ,26S ₂₆	-	100	-				
	v_{29}	β -CH ₂ rock	821	779	0.3	1.2	0.75	835*	783*	781	774	79S ₂₉ ,13S ₂₄	-	100	-				
	v_{30}	C-F out-of-plane bend	374	355	3.4	1.1	0.75	371	371	-	-	81S ₃₀ ,12S ₂₆	-	100	-				

^a Observed spectra: gas and Xe are IR.

^b MP2(full)/6-31G(d) *ab initio* calculations, scaled frequencies, infrared intensities (km/mol), Raman activities (Å⁴/u), depolarization ratios (dp) and potential energy distributions (P.E.D.s).

 c Scaled frequencies with scaling factors of 0.88 for the CH stretches, β -CH₂ and γ -CH₂ scissors and 0.90 for all other modes.

^d Frequencies listed are taken from Ref. [11], values marked with an asterisk (*) are from the Raman spectrum, all others are from the IR spectrum of the gas.

^e Frequency taken from the IR spectrum of the solid.

^f Frequencies listed are taken from Ref. [10].

^g Frequency taken from far infrared of the gas.

^h Symmetry coordinates with P.E.D. contribution less than 10% are omitted.

Table 2			
Observed ^a and calculated	^b frequencies for the axia	l conformer of fluorocy	clobutane.

		Fundamental		Fixed scaled ^c	IR int.	Raman act.	dp ratio	Gas ^d	Gas	Xe	P.E.D. ^f	Banc	contour	
												A	В	С
A'	ν_1	γ -CH ₂ antisymmetric stretch	3217	3018	32.2	41.3	0.74				69S ₁ ,30S ₂	53	_	47
	ν_2	β -CH ₂ antisymmetric stretch	3198	3000	4.9	71.6	0.62	67S ₂ ,30S ₁		67S ₂ ,30S ₁	-	-	100	
	ν_3	CH stretch	3152	2957	45.1	179.1	0.07	79S ₃ ,17S ₅				19	-	81
	ν_4	γ -CH ₂ symmetric stretch	3146	2951	41.8	62.1	0.15				95S4	56	-	44
	ν_5	β -CH ₂ symmetric stretch	3131	2937	3.0	121.6	0.37	80S ₅ ,16S ₃			80S ₅ ,16S ₃	98	-	2
	ν_6	γ -CH ₂ scissors	1566	1469	3.1	5.8	0.65	64S ₆ ,34S ₇			64S ₆ ,34S ₇	100	-	-
	ν_7	β -CH ₂ scissors	1538	1443	3.9	18.2	0.75	64S ₇ ,35S ₆				30	-	70
	ν_8	CH in-plane bend	1425	1352	27.6	2.6	0.72		1348 1348 47S ₈ ,29S ₁₇ ,11S ₁₀				-	2
	ν_9	β -CH ₂ wag	1336	1267	11.7	1.4	0.55	5 78S ₉ ,14S ₁₃				81	-	19
	v_{10}	β -CH ₂ twist	1276	1211	5.8	16.4	0.74 63S ₁₀ ,11S ₁₆				63S ₁₀ ,11S ₁₆	60	-	40
	v_{11}	β -CH ₂ rock	1194	1133	24.1	0.9	0.43	35S ₁₁ ,23S ₁₅ ,15S ₁₇			35S ₁₁ ,23S ₁₅ ,15S ₁₇ ,15S ₁₆ ,12S ₁₈	38	-	62
	v_{12}	Ring breathing	1095	1039	17.5	19.4	0.16		1039 1037		70S ₁₂ ,13S ₁₅	89	-	11
	v_{13}	Ring deformation 2	970	920	14.4	5.5	0.09				36S ₁₃ ,19S ₁₅ ,15S ₁₂ ,10S ₁₀	72	-	28
	v_{14}	Ring deformation 1	927	879	7.5	4.0	0.42				26S ₁₄ ,26S ₁₆ ,20S ₁₃	98	-	2
	v_{15}	C–F stretch	895	849	16.2	4.4	0.50	825	832	832	27S ₁₅ ,28S ₁₄ ,20S ₁₁ ,10S ₁₃	45	-	55
	v_{16}	γ-CH ₂ rock	708	672	1.7	0.6	0.60				39S ₁₆ ,27S ₁₄ ,16S ₁₁	10	-	90
	v_{17}	C–F in-plane bend	403	382	1.8	0.3	0.14				30S ₁₇ ,18S ₈ ,16S ₁₈ ,15S ₁₁ ,13S ₁₄	100	-	-
	v_{18}	Ring puckering	180	171	1.5	0.1	0.19	131	(131) ^e		69S ₁₈ ,13S ₈ ,10S ₁₇	60	-	40
<i>A</i> ″	v_{19}	β -CH ₂ antisymmetric stretch	3204	3006	9.3	72.4	0.75				97S ₁₉	-	100	-
	v_{20}	β -CH ₂ symmetric stretch	3131	2937	26.7	0.8	0.75				97S ₂₀	-	100	-
	v_{21}	β -CH ₂ scissors	1523	1429	4.4	6.5	0.75				99S ₂₁	-	100	-
	v_{22}	CH out-of-plane bend	1344	1275	0.8	1.5	0.75				46S ₂₂ ,29S ₂₃ ,19S ₂₈	-	100	-
	v_{23}	γ -CH ₂ wag	1303	1236	2.4	6.4	0.75				31S ₂₃ ,33S ₂₅ ,15S ₂₆ ,11S ₂₂	-	100	-
	v_{24}	β -CH ₂ wag	1292	1226	0.3	0.1	0.75				65S ₂₄ ,15S ₂₃ ,11S ₂₂	-	100	-
	v_{25}	γ -CH ₂ twist	1217	1155	5.2	5.5	0.75				31S ₂₅ ,20S ₂₇ ,16S ₂₄ ,14S ₂₃	-	100	-
	v_{26}	β -CH ₂ twist	1098	1042	2.3	6.1	0.75				63S ₂₆ ,10S ₂₅	-	100	-
	v_{27}	Ring deformation 1	979	929	0.8	14.6	0.75				64S ₂₇ ,13S ₂₄	-	100	-
	ν_{28}	Ring deformation 2	953	904	5.8	0.6	0.75				57S ₂₈ ,10S ₂₂ ,10S ₂₉	-	100	-
	ν_{29}	β -CH ₂ rock	779	739	0.2	0.2	0.75	63S ₂₉ ,19S ₂₈ ,11S ₂₅			63S ₂₉ ,19S ₂₈ ,11S ₂₅	-	100	-
	v_{30}	C-F out-of-plane bend	397	377	3.2	0.7	0.75				83S ₃₀ ,10S ₂₉	-	100	-

^a Observed spectra: gas, Xe, are IR.

^b MP2(full)/6-31G(d) *ab initio* calculations, scaled frequencies, infrared intensities (km/mol), Raman activities (Å⁴/u), depolarization ratios (dp) and potential energy distributions (P.E.D.s).

 c Scaled frequencies with scaling factors of 0.88 for the CH stretches, β -CH₂ and γ -CH₂ scissors and 0.90 for all other modes.

^d Frequencies listed are taken from Ref. [10].

^e Frequency taken from far infrared of the gas.

^f Symmetry coordinates with P.E.D. contribution less than 10% are omitted.

Table 3

Calculated energies in H and energy differences (cm⁻¹) for the two conformers, and transition state of fluorocyclobutane.

Method/basis set	Energy ^a , E	Energy differences	, $arDelta$	
	Equatorial	Axial ^b	Planar ring ^b	Planar ring ^c
RHF/6-31G(d)	0.952938	583		
MP2(full)/6-31G(d)	1.661929	658	1189	531
MP2(full)/6-31+G(d)	1.682782	668		
MP2(full)/6-31G(d,p)	1.719525	722		
MP2(full)/6-31+G(d,p)	1.739104	712		
MP2(full)/6-311G(d,p)	1.906145	779		
MP2(full)/6-311+G(d,p)	1.915779	793	1377	584
MP2(full)/6-311G(2d,2p)	1.976511	694		
MP2(full)/6-311+G(2d,2p)	1.984410	730		
MP2(full)/6-311G(2df,2pd)	2.065639	762	1279	516
MP2(full)/6-311+G(2df,2pd)	2.073066	794	1236	443
MP2(full)/aug-cc-pVTZ	2.087353	740		
Average MP2(full)	-	732 ± 47	1270 ± 69	518 ± 50
B3LYP/6-31G(d)	2.447881	643	659	15
B3LYP/6-31+G(d)	2.465403	585		
B3LYP/6-311G(d,p)	2.524013	600		
B3LYP/6-311+G(d,p)	2.531097	596	555	41
B3LYP/6-311G(2d,2p)	2.533492	577		
B3LYP/6-311+G(2d,2p)	2.539708	587		
B3LYP/6-311G(2df,2pd)	2.539411	612	584	29
B3LYP/6-311+G(2df,2pd)	2.545645	612	566	46
B3LYP/aug-cc-pVTZ	2.554573	605		
Average B3LYP	-	602 ± 20	591 ± 47	33 ± 14

^a Energy of conformer is given as -(E+254) H.

^b Difference is relative to *equatorial* form and given in cm⁻¹.

^c Difference is relative to *axial* form and given in cm⁻¹.

the fixed scaled force field and resultant wavenumbers. A set of symmetry coordinates was used similar to those used for chlorocyclobutane [5] to determine the corresponding potential energy distributions (P.E.D.s). A comparison between the observed and calculated wavenumbers, along with the calculated infrared intensities, Raman activities, depolarization ratios and potential energy distributions for the *equatorial* and *axial* conformers of fluorocyclobutane, is given in Tables 1 and 2, respectively.

Table 4

Structural parameters (Å and degrees), rotational constants (MHz) and dipole moments (Debye) for equatorial and axial fluorocyclobutane.

Structural parameters	Int. coor.	MP2(full)/6-3	11+G(d,p)	B3LYP/6-311+	G(d,p)	Microwave ^a	Adjusted r_0^{b}	
		Equatorial	Axial	Equatorial	Axial	Equatorial	Equatorial	Axial ^c
rC _α -F	R_1	1.386	1.398	1.398	1.407	1.386(2)	1.383(3)	1.407(3)
$rC_{\alpha}-C_{\beta},C_{\beta'}$	R_2	1.530	1.534	1.536	1.541	1.535	1.543(3)	1.546(3)
$rC_{\gamma}-C_{\beta},C_{\beta'}$	R ₃	1.551	1.552	1.557	1.557	1.548	1.554(3)	1.554(3)
$rC_{\alpha}-H$	r_1	1.094	1.092	1.093	1.091	1.092	1.094(2)	1.092(2)
$rC_{\beta}-H_1$, $C_{\beta'}-H_1$	r_2	1.093	1.092	1.092	1.091	1.094	1.093(2)	1.092(2)
$rC_{\beta}-H_2, C_{\beta'}-H_2$	r_3	1.091	1.094	1.091	1.092	1.093	1.091(2)	1.094(2)
$rC_{\gamma}-H_1$	r_4	1.090	1.091	1.090	1.091	1.092	1.090(2)	1.091(2)
$rC_{\gamma}-H_2$	r_5	1.093	1.091	1.092	1.091	1.094	1.093(2)	1.091(2)
$\angle C_{\beta}C_{\alpha}F$	ϕ_1	117.3	109.6	116.6	111.2	116.9	117.4(5)	109.2(5)
$\angle C_{\beta}C_{\alpha}C_{\beta}$	θ_1	89.4	88.9	90.0	89.9	89.7	89.3(5)	89.2(5)
$\angle C_{\gamma}C_{\beta}C_{\alpha}$	θ_2	86.4	88.0	87.4	89.3	87.1	85.0(5)	89.2(5)
$\angle C_{\beta}C_{\gamma}C_{\beta}$	θ_3	87.8	87.6	88.4	88.7	88.7	88.6(5)	88.6(5)
$\angle HC_{\alpha}C_{\beta}$	σ_1	112.1	120.2	113.2	118.8	112.5	112.1(5)	120.4(5)
$\angle HC_{\alpha}F$	σ_2	107.7	107.2	106.7	106.4	107.7	107.7(5)	107.2(5)
$\angle H_1 C_\beta C_\alpha$	λ_1	109.3	116.3	110.0	114.8	109.9	109.3(5)	116.3(5)
$\angle H_1 C_\beta C_\gamma$	λ_2	110.4	119.1	111.3	117.6	109.7	112.8(5)	123.3(5)
$\angle H_2 C_\beta C_\alpha$	λ_3	118.8	110.4	118.0	111.9	118.2	118.8(5)	110.4(5)
$\angle H_2 C_\beta C_\gamma$	λ_4	119.6	111.4	119.0	113.1	117.9	118.5(5)	105.8(5)
$\angle H_1 C_{\beta} H_2$	λ_5	110.2	109.9	109.4	109.0	109.3	110.2(5)	109.9(5)
$\angle H_1 C_{\gamma} C_{\beta}$	π_1	117.7	111.3	117.1	112.7	116.1	116.4(5)	108.3(5)
$\angle H_2 C_{\gamma} C_{\beta}$	π_2	111.4	117.8	112.2	116.5	111.2	112.4(5)	120.1(5)
$\angle H_1 C_{\gamma} H_2$	π_3	109.4	109.6	108.8	108.6	108.6	109.4(5)	109.6(5)
$\tau C_{\gamma} C_{\beta} C_{\beta} C_{\alpha}$	$ au_1$	34.0	29.2	28.0	17.6	20	37.4(5)	20.7(5)
A (MHz)		10392.071	8463.98	10204.376	8762.20	10250.412(7)	10250.620	8628.79
B(MHz)		4271.121	4848.58	4247.106	4619.90	4274.930(3)	4275.419	4726.22
C (MHz)		3411.111	4109.91	3380.445	3815.67	3402.614(3)	3402.568	3939.20
$ \mu_{a} $		1.968	1.819	2.066	1.802	1.870(5)		1.61(5)
$ \mu_{ m b} $		0.000	0.000	0.000	0.000	0.000		0.0000
$ \mu_{\rm c} $		0.553	1.314	0.599	1.116	0.52(2)		1.22(22)
$ \mu_{ m t} $		2.044	2.244	2.151	2.120	1.94(1)		2.02(17)

^a Proposed structural parameters from Ref. [10], equatorial dipole moments from Ref. [2] and rotational constants [4].

^b Adjusted parameters using the microwave data from Ref. [4] for the given ground states.

^c Experimental rotational constants A = 8628.77(7) MHz, B = 4726.25(6) MHz, and C = 3939.16(8) MHz and dipole moments taken from Ref. [4].

The infrared spectra were predicted from the MP2(full)/6-31G(d) calculations. The predicted scaled frequencies were used together with a Lorentzian function to obtain the calculated spectra. Infrared intensities determined from MP2(full)/6-31G(d) calculations were obtained based on the dipole moment derivatives with respect to Cartesian coordinates. The derivatives were transformed with respect to normal coordinates by $(\partial \mu_u / \partial Q_i) = \sum_j (\partial \mu_u / \partial X_j) L_{ij}$, where Q_i is the *i*th normal coordinate, X_i is the *j*th Cartesian displacement coordinate, and L_{ij} is the transformation matrix between the Cartesian displacement coordinates and the normal coordinates. The infrared intensities were then calculated by $[(N\pi)/(3c^2)]$ $[(\partial \mu_x/\partial Q_i)^2 + (\partial \mu_y/\partial Q_i)^2 + (\partial \mu_z/\partial Q_i)^2]$. In Fig. 1 a comparison of the experimental and simulated infrared spectra of fluorocyclobutane is shown for the spectral region from 900 to 1500 cm⁻¹. The predicted spectrum is in relatively good agreement with the experimental spectrum which shows the utility of the scaled predicted frequencies and intensities for supporting the vibrational assignment.

4. Vibrational assignment

In order to obtain the enthalpy difference between the two stable conformers of fluorocyclobutane it is necessary to confidently identify a vibrational mode for the axial conformer which is expected to be a very small percentage of the sample at ambient temperature. This requires confident assignments of all the fundamentals of the more stable equatorial conformer. There have been two extensive vibrational assignments [10,11] for fluorocyclobutane where in the earlier study [11] the assignment was made by using the infrared vapor phase band contours, Raman depolarization data, expected infrared and Raman intensities and "group frequencies". In the more recent study [10] ab initio calculations with the 3-21G(d) basis set with two scaling factors of 0.88 for stretches and 0.90 for the bends were used to predict frequencies for the fundamentals and potential energy distributions. These new data resulted in some significant changes in a few of the descriptions of the motions contributing to some of the bands. In particular, two ring deformations were reassigned to lower frequency bands. There was also a few major changes in the vibrational assignment where the C-H out-of-plane bend was reassigned as nearly accidently degenerate with the β -CH₂ wag at 1242 cm⁻¹. The more accurately predicted fundamental frequencies along with the predicted infrared intensities and Raman activities as well as the relatively sharp bands in the spectrum from the xenon solution provides considerably more spectral information for making the vibrational assignment.

With the confident assignment for the fundamentals of the equatorial conformer a search was made for bands arising from the axial conformer. As expected the C–F stretch should be the most intense band in the spectral "fingerprint" region. Unfortunately there is mixing of this mode with both ring deformations along with the β -CH₂ rock. Nevertheless, the band at 832 cm⁻¹ is quite pronounced and it can be assigned as a fundamental of the axial conformer. There is also a band at 1348 cm⁻¹ which undoubtedly is due to the axial conformer. There is another band at 1037 cm⁻¹ which is probably due to the axial conformer but it is partly overlaid by the equatorial band at 1048 cm⁻¹. Therefore, there are only two bands of the axial conformer which could be considered for the determination of the enthalpy difference for the two conformers.

5. Conformational stability

To determine the enthalpy difference between the two conformers, the mid-infrared spectra of fluorocyclobutane dissolved in liquefied xenon as a function of temperature from -55 to -100 °C were 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. A significant advantage of this study is that the conformer bands are better resolved in comparison with those in the infrared spectrum of the gas. From *ab initio* calculations, the dipole moments of the two conformers are predicted to have similar values and the molecular sizes of the two conformers are nearly the same, so the ΔH value obtained from the temperature dependent FT-IR study is expected to be close to that for the gas [16–22].

As indicated earlier only the two bands at 832 and 1348 cm⁻¹ were confidently assigned for the axial conformer. The fundamental at 1348 cm⁻¹ could not be resolved in the spectra of the xenon solution due to the close proximity of the v_8 equatorial conformer fundamental. Therefore, only the band at 832 cm⁻¹ could be used for intensity measurements for the axial conformer. The choice of the bands to be used for the equatorial conformer was also a little difficult since they must be sufficiently separated from any interfering bands. Also, for best results they should have comparable intensity to the band being used for the axial conformer and preferably be in the lower frequency range to minimize interference of overtone and combination bands. From the inspection of the various possible bands the fundamentals at 954, 1090, 1136, and 1240 cm⁻¹ were selected for the equatorial conformer bands to be use in the determination of the enthalpy difference.

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 $-\ln K = \Delta H/(RT) - \Delta S/R$, 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, *i.e.* $I_{equatorial}/I_{axial}$. It was assumed that ΔH , ΔS , and α are not a function of temperature in the temperature range studied.

By combining the axial band and the four equatorial conformer bands, four pairs were utilized for the determination of the enthalpy difference, and the resulting values with statistical uncertainties are listed in Table 5. As can be seen from the data in this table there is a fair spread of values but each one has a relatively small uncertainty. However, this spread is expected when measuring band intensities for bands with shoulders and considerable potential for underlying overtones and combination bands. Nevertheless, the statistical uncertainty is quite small and the statistical average obtained by using all eight pairs as a single set gives a value of $496 \pm 9 \text{ cm}^{-1}$. This error limit is derived from the statistical standard deviation of one sigma of the measured intensity data. This error limit does not take into account small associations with the liquid xenon or the interference of overtones and combination bands in near coincidence with the measured fundamentals. The variations in the individual values are undoubtedly due to these types of interferences, but by taking several pairs, the effect of such interferences should cancel. Nevertheless, we expect the error is probably significantly larger than the statistical uncertainty obtained so we believe the determined ΔH value is 496 ± 40 cm⁻¹. Thus, the abundance of the less stable axial conformer present at ambient temperature is $8 \pm 1\%$.

6. Structural parameters

We have [21] shown that *ab initio* MP2(full)/6-311+G(d,p) calculations predict 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 are compared [22] to previously determined values from earlier microwave studies. Thus, all of the carbon–hydrogen r_0 parameters can be taken from the MP2(full)/6-311+G(d,p) pre-

Table	5
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Temperature and intensity ratios of the equatorial and axial bands of fluorocyclobutane.

	<i>T</i> (°C)	$1/T(\times 10^{-3} \mathrm{K}^{-1})$	I_{1240}/I_{832}	I_{1136}/I_{832}	I_{1090}/I_{832}	I ₉₅₄ /I ₈₃₂
Liquid xenon	-55.0	4.584	28.047	21.816	73.347	20.196
-	-60.0	4.692	30.335	22.479	82.453	21.944
	-65.0	4.804	34.427	25.001	91.191	24.540
	-70.0	4.923	37.342	26.659	99.334	25.717
	-75.0	5.047	42.126	30.737	107.541	29.125
	-80.0	5.177	45.832	31.483	120.126	32.373
	-85.0	5.315	51.851	36.427	132.261	35.535
	-90.0	5.460	55.804	37.080	144.495	39.539
	-95.0	5.613	64.312	42.029	156.716	43.091
	-100.0	5.775	69.057	44.885	176.726	47.951
ΔH^{a} (cm ⁻¹)			536 ± 14	439 ± 18	499 ± 14	508 ± 11

^a Average value $\Delta H = 496 \pm 9 \text{ cm}^{-1} (5.93 \pm 0.11 \text{ kJ mol}^{-1})$ with the equatorial conformer the more stable form and the statistical uncertainty (1 σ) obtained by utilizing all of the data as a single set.

dicted values for fluorocyclobutane. Also, we have found [23] that we can obtain good structural parameters by adjusting the structural parameters from the *ab initio* calculations to fit the rotational constants obtained from the microwave experimental data. In order 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 which results in only two heavy atoms distances, *i.e.* C–C and C–F, for fluorocyclobutane. Also, the 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. Thus, it is possible to reduce the number of heavy atom independent structural parameters to five with the CC and CF bond lengths, and the angles of FCC, CCC and the ring puckering angle. Therefore, if the CH parameters are taken from the MP2(full)/6-311+G(d,p) calculations, then it should be possible to obtain "adjusted r_0 " structural parameters for the equatorial and axial conformers of fluorocyclobutane by utilizing the previously reported [4] six rotational constants from the microwave study.

These determined adjusted r₀ parameters are listed in Table 4 and the final fit of the rotational constants is shown in Table 6. The differences are quite small with those for the *B* and *C* rotational constants fit to better than 0.5 MHz. The largest adjustment for the angles is associated with the ring puckering angle which changes from 34.0° to 37.4° for the equatorial conformer and from 29.2° to 20.7° for the axial conformer and the largest distance change is the C_{α} – C_{β} ($C_{\beta'}$) bond which increased from 1.530 to 1.543 Å for the equatorial conformer and 1.534 to 1.546 Å for the axial conformer. The C-F bond distance in the axial conformer also exhibits a significant change from 1.398 to 1.407 Å. The remaining changes were relatively small. It is somewhat difficult to estimate the uncertainties in these structural parameters, but it is believed those for the CH distances should be no more than ± 0.002 Å and for the heavy atom distances ± 0.003 Å, whereas the uncertainties in the angles is estimated to be $\pm 0.5^{\circ}$. These parameters are expected to be more

Table 6

Comparison of rotational constants (MHz) obtained from modified *ab initio*, MP2(full)/6-311+G(d,p) structural parameters and the experimental values from the microwave spectra of *equatorial* and *axial* fluorocyclobutane.

Isotopomers	Rotational constant	Experimental ^a	Calculated	$ \Delta $
eq-C ₄ H ₇ F	A	10250.412(7)	10250.620	0.208
	B	4274.930(3)	4275.419	0.489
	C	3402.614(3)	3402.568	0.046
ax-C ₄ H ₇ F	A	8628.77(7)	8628.79	0.02
	B	4726.25(6)	4726.22	0.03
	C	3939.16(8)	3939.20	0.04

^a Ref. [4].



Fig. 3. Low frequency spectra of gaseous fluorocyclobutane: (A) background; (B) far infrared and (C) Raman.

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Ob	oserved	and	cal	cu	ated	l frequencies	(cm ⁻	1)	for the r	ing-puc	kering vi	brat	ions o	of f	luorocycl	obutane.
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Conformer	Transition	Observed ^a		Calculated ^b	Obs. – Calc.	Weight
		Infrared	Raman			
Equatorial	1 ← 0	166.44	167	166.92	-0.48	1.0
	2 ← 1	157.25	157	157.29	-0.04	1.0
	4 ← 2	146.50	147	145.51	0.99	1.0
	$6 \leftarrow 4$	129.04		129.46	-0.42	1.0
Axial	5 ← 3	130.94		132.03	-1.09	1.0

^a The infrared were utilized preferentially over the Raman [10] in the calculations.

^b Calculated by using a potential of the form $V(cm^{-1}) = (8.46 \pm 0.12) \times 10^5 X^4 - (4.05 \pm 0.18) \times 10^4 X^2 + (6.01 \pm 0.11) \times 10^4 X^3$ with a reduced mass of 214 amu.

accurate than those that could be obtained from electron diffraction or microwave study alone or a microwave study with all atoms substituted to obtain r_s parameters.

7. Discussion

The determined enthalpy difference of $496\pm40\,cm^{-1}$ is a reasonable value compared to the relative values obtained for bromocyclobutane ($\Delta H = 291 \pm 22 \text{ cm}^{-1}$ [7]) and chlorocyclobutane $(\Delta H = 361 \pm 17 \text{ cm}^{-1} \text{ [5]})$ as compared to the predicted values from the MP2(full) calculations with a relatively large number of basis sets. For the bromide the ΔE value was $560 \pm 46 \text{ cm}^{-1}$ and for the chloride the ΔE value was $646 \pm 73 \text{ cm}^{-1}$ where the calculations include basis sets up to aug-cc-pVTZ. Therefore, the ab initio calculations predicted considerably large energy differences than the experimentally determined enthalpy difference for both the chloride and bromide. For the fluoride the predicted energy difference is 732 ± 47 cm⁻¹ which is about 230 cm⁻¹ larger than the experimental determined enthalpy difference. However, from the microwave study of fluorocyclobutane [4] the energy difference was determined to be 620 ± 30 cm⁻¹ which is significantly larger than the ΔH value obtained herein. Nevertheless it is clear that the enthalpy difference for the fluoride is much larger than the value for the other two halocyclobutanes.

In the present study the experimentally determined enthalpy difference was larger at 496 cm⁻¹ than the 413 cm⁻¹ enthalpy difference used in the previous study [10] for determining the ring-puckering potential function. With the higher and more reliable ΔH value, we have again obtained the potential function governing the conformational interchange for fluorocyclobutane. By using

the far infrared and low frequency Raman (Fig. 3) data the "hot bands" series for the equatorial conformer as well as the first transition in the axial well were assigned (Table 7) and the assignment used matches the previous spectral study [10]. With this assignment the potential function (Fig. 4) was determined to have a ΔH of 450 cm⁻¹ with a barrier of 774 cm⁻¹ as compared to the previous study where the potential function gave a barrier slightly smaller at 713 cm⁻¹. This ΔH value is on the low side of the experimentally determined value for this study. This potential function is not significantly different from the potential function from the previous study [10].

The three parameters which show significant differences from the previous study [10] of this molecule are the puckering angle, as well as the $C_{\alpha}\text{-}C_{\beta}$ $(C_{\beta'})$ and $C_{\gamma}\text{-}C_{\beta}$ $(C_{\beta'})$ bond distances. In the previous study these parameters were all assumed with values of 20°, 1.535 Å, and 1.548 Å, respectively; however for this study we obtained values of $37.4(5)^\circ$ for the puckering angle along with 1.543(3) and 1.554(3)Å for the $C_{\alpha}-C_{\beta}$ ($C_{\beta'}$) and $C_{\gamma}-C_{\beta}$ ($C_{\beta'}$) bond distances in the equatorial conformer. We found that there are two parameters which were very sensitive to the A rotational constant, with those being the C_{α} - C_{β} ($C_{\beta'}$) bond distance and the puckering angle for the equatorial and axial conformers. We also found that the C-F distance in the axial conformer was very sensitive to even small changes in the A rotational constant and to a lesser extent the B and C rotational constants so that even a relatively small change of 0.001 Å would change the fit of the rotational constants by one to two MHz for each rotational constant. This lead to the 1.407 Å C-F bond distance where even a small change would drastically alter the rotational constant fit. Therefore, the determined C-F distance has a very small uncertainty.



Fig. 4. Potential function governing the ring-puckering vibration of fluorocyclobutane. $V(cm^{-1}) = (8.46 \pm 0.12) \times 10^5 X^4 - (4.05 \pm 0.18) \times 10^4 X^2 + (6.01 \pm 0.11) \times 10^4 X^3$ with a reduced mass of 214 amu.

Table 8

Structural parameters (Å and degrees) of cyclobutane^a and some fluoroalkanes and fluoroalkenes.

Parameters	Fluoromethane Fluoro		ethane Fluoroethene		hene	cis-3-Fluoropropene		Isoprop	Isopropyl fluoride		gauche-1-Fluoropropane	
	MP2 ^b	Exp. ^c	MP2 ^b	Exp.d	MP2 ^b	Exp. ^e	MP2 ^b	Exp. ^f	MP2 ^b	Exp. ^g	MP2 ^b	Exp. ^h
$rC_{\alpha}-F$	1.387	1.383(1)	1.396	1.387(3)	1.346	1.342(4)	1.399	1.388(4)	1.406	1.398(13)	1.398	1.390(5)
$rC_{\alpha}-C_{\beta}$			1.510	1.512(2)			1.492	1.495(4)	1.512	1.522(7)	1.512	1.506(2)
$rC_{\gamma}-C_{\beta}$											1.526	1.526(3)
$rC_{\alpha}-H$	1.091	1.087(1)	1.093	1.094(1)	1.084	1.080*	1.094	1.098(2)	1.095	1.092*	1.093	1.097(1)
Parameters	gauche-1-Fluoro-2- methylpropane			<i>eq</i> -Fluorocyclobutane <i>ax</i> -Fluo		ocyclobutane Ch		Chair eq-flu	air eq-fluorocyclohexane		Chair ax-fluorocyclohexane	
	MP2 ^b	Exp. ⁱ		MP2 ^b I	Exp. ^j	MP2 ^b	Exp. ^j	I	MP2 ^b	Exp. ^k	MP2 ^b	Exp. ^k
rC _a -F	1.396	1.398(13)	1.386	1.383(3)	1.398	1.407(3	3) 1	1.403	1.399(2)	1.408	1.4021(14)
$rC_{\alpha}-C_{\beta}$	1.515	1.525(5)		1.530	1.543(3)	1.534	1.546(3	3) 1	1.515	1.5346(1)	1.518	1.5348(1)
$rC_{\gamma}-C_{\beta}$	1.528	1.536*		1.551 1	1.554(3)	1.552	1.554(3	3) 1	1.532	1.5358(1)	1.530	1.5359(1)
$rC_{\alpha}-H$				1.094	1.094(2)	1.092	1.092(2	2)				

^a Structural parameters [1]: rC-C 1.555(2), rC-H 1.0910(6), and puckering angle 29.55(3).

^b From *ab initio* MP2(full)/6-311+G(d,p).

^c Ref. [24]: *r*_e structural parameters.

^d Ref. [25]: *r*_e structural parameters.

^e Ref. [26]: *r*₀ structural parameters; value with asterisk is assumed.

^f Ref. [27]: adjusted r_0 structural parameters.

^g Ref. [28]: r₀ structural parameters; value with asterisk is from isolated C-H stretch.

^h Ref. [29]: *r*₀ structural parameters.

ⁱ Ref. [30]: *r*₀ structural parameters; value with asterisk is assumed.

^j This study.

^k Ref. [31] *r*₀ structural parameters.

Table 9

Structural parameters of the ring for a few four-membered ring molecules (Å and degree).

Structural parameters	Cyclobutane ^a	Chlorocyclobut	Chlorocyclobutane ^b		ane ^c	Fluorocyclobutane ^d		
		Equatorial Axial		Equatorial	Axial	Equatorial	Axial	
$rC_{\alpha}-X$		1.783(5)	1.803(5)	1.942(3)	1.952	1.383(3)	1.407(3)	
$rC_{\alpha}-C_{\beta}$	1.5555(2)	1.539(3)	1.547(3)	1.541(3)	1.548	1.543(3)	1.546(3)	
$rC_{\beta} - C_{\gamma}$	1.5555(2)	1.558(3)	1.557(3)	1.552(3)	1.546	1.554(3)	1.554(3)	
Puckering angle	28.58(9)	30.7(5)	22.3(5)	29.8(5)	24.0	37.4(5)	20.7(5)	

^a Ref. [1].

We have compared the heavy atom and C–F distances of a number of fluoroalkanes and alkenes (Table 8) in order to demonstrate the effect of fluorine atom on the structural parameters of a molecule. The *ab initio* MP2(full)/6-311+G(d, p) predicted C–F distances for all the fluoroalkanes and alkenes is predicted to be larger than the experimentally determined values. Whereas the $C_{\alpha}-C_{\beta}$ ($C_{\beta'}$) bond distance is on average predicted 0.010 Å shorter than its corresponding experimental value. It is also of interest that the $C_{\gamma}-C_{\beta}$ ($C_{\beta'}$) distance for *gauche*-1-fluoropropene is predicted to be equal to the experimentally determined value.

The heavy atom structural parameters for the halogen substituted four member rings also shows some interesting trends (Table 9). The $C_{\gamma}-C_{\beta}$ ($C_{\beta'}$) distances for the conformers of chlorocyclobutane differ by only 0.001 Å and for the $C_{\gamma}-C_{\beta}$ ($C_{\beta'}$) distance in fluorocyclobutane they are equal but 0.004 Å shorter than those for the chloride. The most pronounced effect of a substituent on four membered rings can be visualized by comparing the puckering angle between the conformers. The largest difference of ~16° is obtained for the case of fluorocyclobutane for the halogens. The C_{α} - C_{β} ($C_{\beta'}$) bond also exhibits interesting behavior in the presence of a halogen substituent as the bond is significantly shorter for the halogen substituted molecules than the corresponding bond for the cyclobutane without substitution. This bond also is significantly longer in the axial conformers of chlorocyclobutane and fluorocyclobutane than in their equatorial conformers.

The centrifugal distortion constants obtained for the asymmetric reduced Hamiltonian for both conformers are listed in Table 10

Table 10

Quadratic centrifugal distortion constants (kHz) for equatorial and axial conformers of fluorocyclobutane.

	Equatorial					Axial					
	MP2(full)/ 6-31G(d)	MP2(full)/ 6-311+G(d,p)	B3LYP/6- 31G(d)	B3LYP/6- 311+G(d,p)	Exp. ^a	MP2(full)/ 6-31G(d)	MP2(full)/ 6-311+G(d,p)	B3LYP/6- 31G(d)	B3LYP/6- 311+G(d,p)	Exp. ^a	
$\Delta_{\rm J}$	0.68	0.68	0.73	0.76	0.72(2)	2.6	2.6	3.7	5.4	-2.(2)	
$\Delta_{\rm JK}$	1.93	1.967	1.59	1.388	1.74(7)	-6.0	-5.9	-12.2	-23.3	10.(1)	
$\Delta_{\rm K}$	3.4	3.4	4.8	5.4	4.4(2)	8.9	8.9	18.5	37.3	-27.(1)	
δ_{I}	0.122	0.124	0.131	0.135	0.138(4)	-0.02	-0.02	-0.2	-0.5	0.7(1)	
$\delta_{\rm K}$	1.8	1.8	1.8	1.8	1.7(1)	1.3	1.3	1.9	3.5	-7.(3)	

^a Values taken from Ref. [4].

^b Ref. [5], X = Cl.

^c Ref. [7], X=Br.

^d This study, X = F.

along with the values obtained from the force constants that were predicted from the *ab initio* MP2(full)/6-31G(d) and 6-311+G(d, p) calculations and from the density functional theory calculations by the B3LYP method with both the 6-31G(d) and the 6-311+G(d,p) basis sets. In general the fit is much better with the larger basis set from the B3LYP calculations where the differences between the predicted and experimental values is quite small for all the constants for the equatorial conformer. However for the axial conformer the difference from the predicted values from the MP2(full) and B3LYP calculations are significantly different from the values reported from the microwave study [4]. The magnitude of the constants is in fair agreement but the signs of the constants are all different for the experimentally determined values compared to the predicted values.

We recently obtained the enthalpy difference for the equatorial and axial conformers of cyanocyclobutane [8] and the determined experimental value was 254 ± 12 cm⁻¹ (3.03 ± 12 kJ/mol) with the equatorial conformer more stable, which indicates that there is $23 \pm 1\%$ of the axial form present at ambient temperature. This value is smaller than the corresponding values for the halocyclobutanes and the question arises what are the factors of the substitute species that control the relative amounts of the two forms. The ab initio MP2(full) calculations predicted an enthalpy difference for the cyanide of 238 ± 23 cm⁻¹ which is consistent with the experimentally determined value. Thus it would be of interest to investigate the conformational stability of ethynylcyclobutane, as it is isoelectronic with cyanide, to determine the enthalpy difference for the two conformers for this molecule. Another molecule of interest is silvlcyclobutane where the axial form is predicted more stable by *ab initio* MP2(full) calculations using relatively large basis sets, whereas, by using the smaller basis sets the equatorial form is predicted more stable. Also of interest would be the isocyanocyclobutane which is expected to have trans and cis forms in addition to the equatorial and axial conformers. Therefore, the conformational study of these and similar molecules might be used to determine the factors which control the relative stability of these types of molecules.

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