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Conformational stability, far-infrared spectra, barriers to internal rotation, vibrational assignment and RHF/STO-3G* calculations of 1-bromo-2-fluoroethane

J.R. Durig, Jian Liu† and T.S. Little

Department of Chemistry, University of South Carolina, Columbia, SC 29208 (USA)

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Abstract

The far-IR spectrum (350-35 cm^{-1}) of gaseous 1-bromo-2-fluoroethane, $BrCH_2CH_2F$, has been recorded at a resolution of 0.10 cm^{-1}. The fundamental asymmetric torsional frequencies of the more stable trans (two halogen atoms oriented trans) and high energy gauche conformers have been observed at 125.3 cm^{-1} and 111.3 cm^{-1}, respectively, and the asymmetric torsional potential function governing internal rotation about the C-C bond has been determined. This potential function gives values for the torsional potential coefficients of $V_1 = 584 \pm 6$, $V_2 = -147 \pm 4$, $V_3 = 1217 \pm 11$, $V_4 = 138 \pm 2$, and $V_6 = -21 \pm 4$ cm^{-1}, and a dihedral angle (∠FCCBr) of 67° for the gauche conformer. The trans to gauche, gauche to gauche, and gauche to trans barriers have been determined to be 1356 cm^{-1}, 1418 cm^{-1} and 973 cm^{-1}, respectively, with an energy difference between the conformations of 383 ± 21 cm^{-1} (1.09 ± 0.06 kcal mol^{-1}). From studies of the Raman spectra at variable temperatures the conformational energy difference has been determined to be 350 ± 87 cm^{-1} (1.00 ± 0.25 kcal mol^{-1}) with the trans more stable and 300 ± 46 cm^{-1} (0.86 ± 0.13 kcal mol^{-1}) with the gauche more stable for the gas and liquid, respectively. A complete assignment of the vibrational spectra including the IR (3500-400 cm^{-1}) spectra of the gas and solid and the Raman (3200-10 cm^{-1}) spectra of the gas, liquid and solid is proposed. The structural parameters, conformational stabilities, barriers to internal rotation and fundamental vibrational frequencies which have been determined from experiment, are compared to those obtained from ab initio Hartree-Fock gradient calculations and to the corresponding quantities obtained for some similar molecules.

INTRODUCTION

Rotational isomerism for the haloethanes has been of interest for many years with some of the earliest experimental studies addressing internal rotation being carried out for this series of molecules [1-9]. Although the experimental techniques used for these studies have varied, the potential functions governing internal rotation for many of these molecules have remained undefined. For the 1,2-dihaloethane series, XCH_2CH_2Y (where X and Y are the same or

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different halogens), it has been found that both the gauche and trans conformers exist at ambient temperature in the gaseous and liquid states [2]. For some of the molecules in this series, results regarding the relative stability of the two forms have been ambiguous, and this has prompted the more recent investigations of the electron diffraction patterns [10], microwave [11] and far-IR spectra [12], and ab initio calculations [13] for these molecules.

From an investigation of 1-bromo-2-fluoroethane of the mid-IR spectra in the gas, liquid and solid, and Raman spectrum of the liquid, it has been determined that the trans conformation is more stable in the gas, but for the liquid the gauche form is preferred and is the only form present in the spectrum of the solid [2]. An assignment of the rotational transitions arising from the ^{79}Br and ^{81}Br species of the gauche conformer observed in the microwave spectrum, enabled the determination of six rotational constants from which a structure was determined [11]. However, the transitions arising from the trans conformer were not assigned. More recently, the structures of the two conformations and the rotameric composition in the gas phase have been investigated by the electron diffraction technique [10]. The molecule was determined to have the trans configuration in greater abundance than the gauche form at room temperature. The abundance of the trans conformer was shown to decrease with increasing temperature, which is consistent with the results obtained from the earlier study of the vibrational spectra where it was concluded that the trans conformer is thermodynamically preferred in the vapor [2]. A potential function based on the value of the gauche dihedral angle, the conformational energy difference, and the previously reported [2] value of the gauche torsional frequency for the liquid was determined [10].

Thus, different structural and vibrational studies including electron diffraction [10], IR, Raman [2] and microwave spectroscopy [11] have previously been carried out for the identification of the rotational isomers of 1-bromo-2-fluoroethane, but no one has attempted to observe and assign the torsional transitions in the far-IR or low frequency Raman spectra of the gas. These data have presently been obtained from which a potential function for the interconversion of the two conformations has been determined. We have also carried out variable temperature studies of the Raman spectra of the gas and liquid in order to determine the energy difference between the rotameric forms. Finally, we have included ab initio calculations at the STO-3G* basis set level for comparison of theoretically obtained values of the energy difference, barriers to internal rotation and vibrational frequencies to the corresponding values obtained from experiment.

EXPERIMENTAL

The sample of 1-bromo-2-fluoroethane was prepared by the reaction of 2-fluoroethanol (Aldrich) with phosphorus tribromide (Aldrich) under reduced

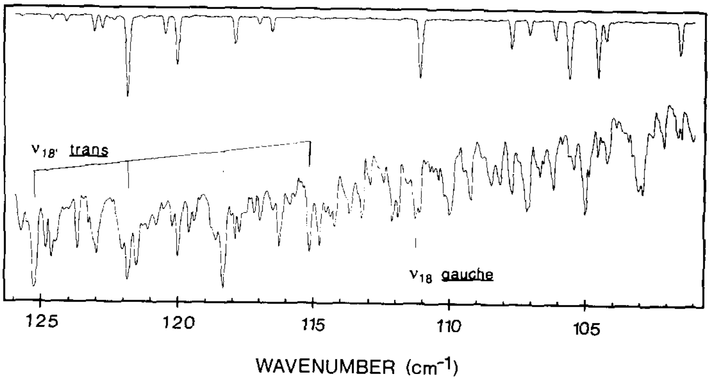

Fig. 1. Far-IR spectra of gaseous 1-bromo-2-fluoroethane in the region of the asymmetric torsional mode.

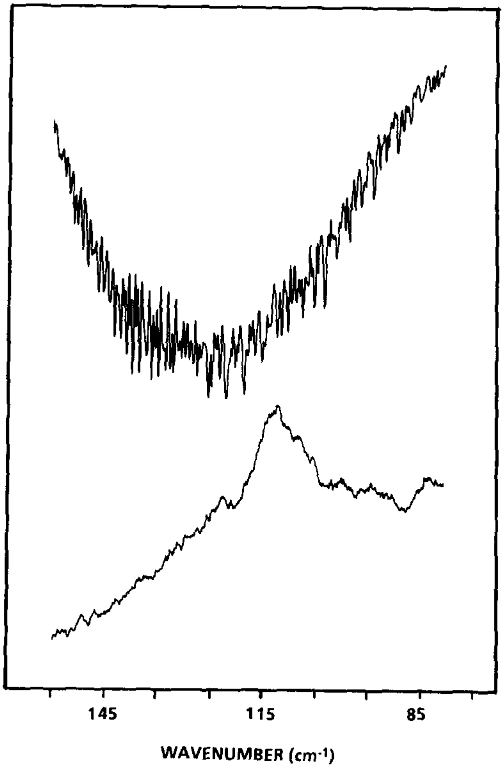

Fig. 2. Far-IR (upper) and Raman (lower) spectra of 1-bromo-2-fluoroethane in the region of the asymmetric torsional mode.

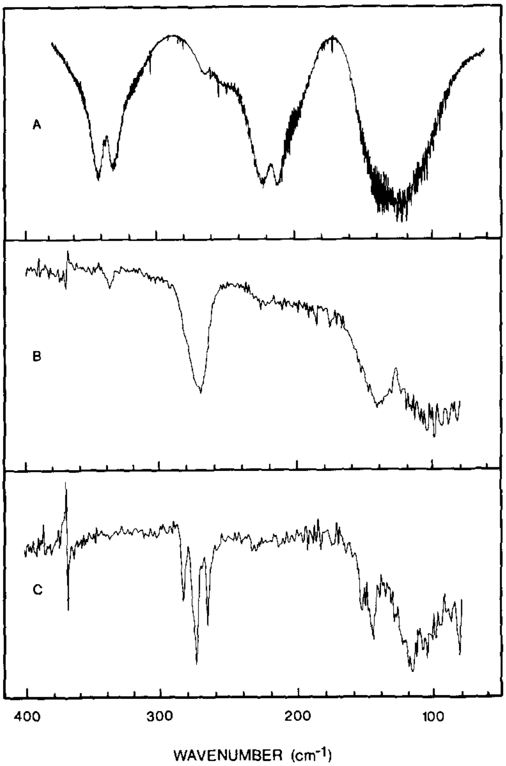

Fig. 3. Far-IR spectra of 1-bromo-2-fluoroethane in the A, gas; B, solid (amorphous); and C, solid (annealed). The sharp feature observed in C at 375 cm^{-1} is an instrumental artifact.

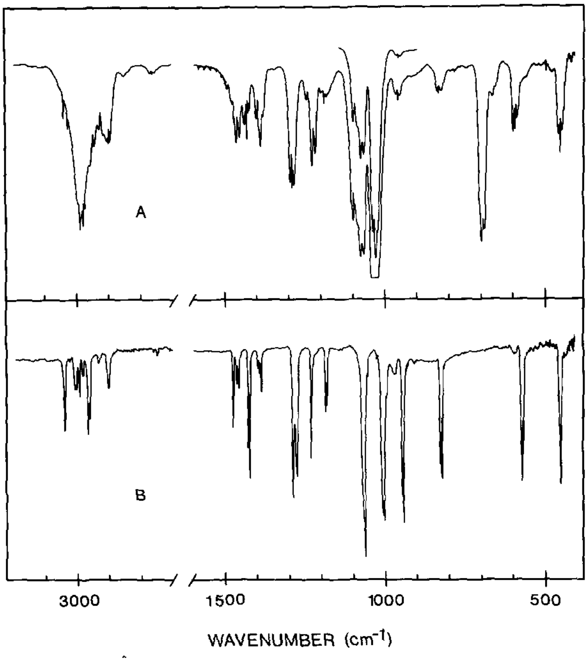

Fig. 4. Mid-IR spectra of 1-bromo-2-fluoroethane in the A, gas; and B, annealed solid.

pressure. Purification was carried out with a low temperature vacuum fractionation column and the pure 1-bromo-2-fluoroethane was stored under vacuum in a slush of ethanol and Dry Ice.

The far-IR spectra (Figs. 1 and 2) of gaseous 1-bromo-2-fluoroethane, from which the torsional transitions were measured, were recorded with a Nicolet model SXV 200 Fourier transform interferometer from the sample contained in a 1 m cell fitted with polyethylene windows. This instrument is equipped with a vacuum bench and a liquid helium cooled germanium bolometer. The spectra were collected at 0.10 cm^{-1} resolution with 6.25, 12.5 and 25 μm Mylar beamsplitters. The far-IR spectrum (Fig. 3) of the annealed solid was obtained with a Digilab model FTS-15B Fourier transform interferometer equipped with a 6.25 μm Mylar beamsplitter and a TGS detector. The sample was deposited onto a silicon plate which was maintained under vacuum and cooled with boiling liquid nitrogen.

The mid-IR spectra (Fig. 4) of the gas and annealed solid from 3200 to 400

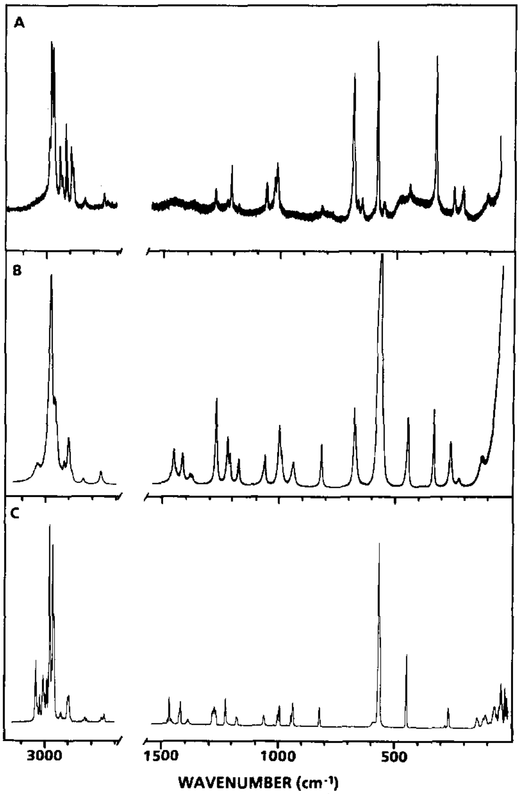

Fig. 5. Raman spectra of 1-bromo-2-fluoroethane in the A, gas; and B, liquid; and C, annealed solid.

cm^{-1} were recorded on a Digilab model FTS-14C Fourier transform interferometer equipped with a Ge/KBr beamsplitter and a TGS detector. For the gaseous sample, a 12 cm cell equipped with CsI windows was employed. The spectrum of the annealed solid was obtained by depositing the sample onto a CsI plate cooled by boiling liquid nitrogen and housed in a cell fitted with CsI windows.

The Raman spectra (Fig. 5) were recorded on a Cary model 82 spectrophotometer equipped with a Spectra-Physics model 171 argon ion laser operating on the 5145 Å line. The spectrum of the gas, as well as the variable temperature study of the vapor, were recorded by using a standard Cary multipass accessory. The reported wavenumbers are expected to be accurate to ±2 cm^{-1}. The spectrum of the liquid was obtained from the sample sealed in a glass capillary. The variable temperature study of the liquid was carried out by using a Cryogenic Technologies, Inc. cryostat connected to a model DTC-500 cryogenic temperature controller by Lake Shore Cryotronics, Inc. The Raman spectrum of the annealed solid was recorded by depositing the sample onto a blackened brass block which was maintained in a cell fitted with quartz windows and cooled by boiling liquid nitrogen.

CONFORMATIONAL ANALYSIS

We are in agreement with the conclusions from the previous study of the IR and Raman spectra [2] as well as from the analysis of the electron diffraction

TABLE 1

Temperature and intensity ratios for the conformational study of gaseous and liquid 1-bromo-2-fluoroethane

	T(°C)	1000(1/T) (K^{-1})	$K=I_1/I_2$[a]	ln$K$
Gas	26	3.34	1.211	0.191
	39	3.21	1.295	0.258
	52	3.08	1.368	0.313
	60	3.00	1.433	0.360
	68	2.93	1.499	0.405
	79	2.84	1.568	0.450
	90	2.75	1.611	0.477
	100	2.68	1.729	0.547
	114	2.58	1.868	0.625
Liquid	−70	4.92	0.143	−1.946
	−55	4.58	0.160	1.830
	−44	4.36	0.183	−1.697
	−35	4.20	0.197	−1.627
	−15	3.87	0.221	−1.507

[a] For the gas the trans conformer is more stable and K is the intensity ratio of 587/691 cm^{-1} lines. For the liquid the gauche conformer is more stable and K is the intensity ratio of 683/573 cm^{-1} lines.

pattern [10] of 1-bromo-2-fluoroethane in that the trans conformation is thermodynamically preferred in the vapor whereas the gauche form is more stable in the liquid and the only form present in the solid. The value of the enthalpy difference between the more stable trans and high energy gauche conformers determined from relative IR band areas of the C–Br stretch as a function of temperature was reported to be 105 ± 28 cm^{-1} (0.3 ± 0.08 kcal mol^{-1}) [2]. This value is within the experimental uncertainty of the value of 199 ± 126 cm^{-1} (0.57 ± 0.36 kcal mol^{-1}) obtained from the electron diffraction data at variable temperatures [10], but the value from the electron diffraction study has a relatively high uncertainty. The listed uncertainty of the ΔH value from the IR data is probably too small.

The enthalpy difference between the two conformers of 1-bromo-2-fluoroethane, for both the gas and liquid, can be determined from studies of the appropriate Raman spectra at variable temperatures. For the gas, the intensities of the Raman lines observed at 691 and 587 cm^{-1}, which have been assigned to the C–Br stretch of the trans and gauche conformers, respectively, were measured as a function of temperature. The "conformer pair" arising from the CCBr bend (ν_{11}) is also well resolved in the Raman spectrum of the gas, 257 and 218 cm^{-1}, and the ratio of the intensities of these two lines were also measured as a function of temperature. The Raman lines observed in the spectrum of the liquid at 683 and 573 cm^{-1} were similarly measured. By application of the van't Hoff isochore, $-\ln K = (\Delta H/RT) - (\Delta S/R)$, where ΔS is the entropy change, we have determined ΔH by making a plot of $-\ln K$ versus $1/T$ where $\Delta H/R$ is the slope of the line and K is the appropriate intensity ratio. It is assumed that ΔH is not a function of temperature.

Nine sets of spectral data were obtained for the 691/587 cm^{-1} pair from the gaseous sample ranging from 26 to 114°C (Table 1). The ratio of the intensities of these two lines were plotted as a function of the reciprocal of the absolute temperature. Similar measurements were made for the conformer pair observed at 257 and 218 cm^{-1}. All of these data are consistent with a value of 350 ± 87 cm^{-1} (1000 ± 250 cal mol^{-1}) for ΔH. Five sets of spectral data were obtained for the two lines observed at 683 and 573 cm^{-1} for the liquid at various temperatures ranging from −70 to −15°C and a value of 300 ± 46 cm^{-1} (0.9 ± 0.1 kcal mol^{-1}) for ΔH was obtained.

TORSIONAL POTENTIAL FUNCTION

The observed torsional transition frequencies for the more stable trans and high energy gauche conformers taken from the spectrum for the vapor are listed in Table 2. The assignments given in this table have been made based on both the far-IR and Raman spectra (Figs. 1 and 2).

The broad band centered at about 130 cm^{-1} in the far-IR spectrum of gaseous 1-bromo-2-fluoroethane is undoubtedly due to the torsional modes for

TABLE 2

Observed and calculated (cm^{-1}) asymmetric torsional transitions for 1-bromo-2-fluoroethane[a]

	Transition	Obs.	Calc.	Obs. − Calc.
Trans	$1 \leftarrow 0$	125.29	125.18	0.11
	$2 \leftarrow 1$	121.89	121.95	−0.06
	$3 \leftarrow 2$	118.35	118.57	−0.22
	$4 \leftarrow 3$	115.18	115.01	0.17
	$5 \leftarrow 4$		111.26[a]	
Gauche	$\pm 1 \leftarrow \pm 0$	111.25 (111)[b]	111.25	0.00
	$\pm 2 \leftarrow \pm 1$		108.88[a]	

[a] Calculated by using the potential coefficients given in Table 3.

[b] The value given in parentheses is from the Raman spectrum of the gas.

both the trans and gauche forms. The close proximity of the torsional fundamentals and associated excited state transitions results in an extremely complicated band envelope. Expansion of the far-IR spectrum indicates a series of sharp, regularly spaced Q-branches on the high frequency side of the band between 150 and 130 cm^{-1}. This series is assigned as arising from vibrational–rotational fine structure but the Q-branch at 125.29 cm^{-1} is of considerably stronger relative intensity and appears to be followed by a series of similar Q-branches (i.e. also of stronger intensity relative to the fine structure), which proceed to lower frequency. This series of Q-branches is assigned to the torsional fundamental and associated torsionally excited state transitions of the more stable trans conformer. The complexity of the overall band envelope obscures the assignment of the fundamental and associated excited state transitions for the gauche conformer. This rotamer has C_1 symmetry compared to C_s for the trans form, and all of the normal vibrations are totally symmetric and are expected to give rise to Q-branches in the Raman spectrum of the vapor. A distinct Q-branch is observed at about 111 cm^{-1} in the Raman spectrum of the vapor which has a corresponding Q-branch in the far-IR spectrum of the gas at 111.25 cm^{-1} (Fig. 2). This band is assigned to the torsional fundamental of the high energy gauche conformer. All of the assigned transitions are listed in Table 2.

A potential function governing internal rotation about the C–C bond can be proposed which is based on the torsional transitions observed in both the far-IR and low frequency Raman spectrum of the gas and a combination of structural information obtained from the investigation of the microwave spectrum [11], electron diffraction data [10] and presently obtained ab initio calculations which will be discussed later.

The torsional dihedral angular dependence of the internal rotation constant, $F(\phi)$, can be represented as a Fourier series

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

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

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

Structural parameters obtained from optimized geometries for both the trans and gauche conformers can be used to determine $F(\phi)$. Alternatively, structures for the two conformations can be taken from the electron diffraction study [10].

The torsional potential is also represented as a Fourier cosine series in the internal dihedral angle (ϕ)

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

With the aforementioned F series, the asymmetric torsional frequencies given in Table 2, and the experimentally obtained energy difference for the gas, the torsional potential function can be determined (Fig. 6) using a program developed in our laboratory [14]. Several exploratory calculations indicated a strong dependence of the gauche to gauche barrier on the value of the torsional dihedral angle of the gauche conformer. For example, the observed torsional transitions could be reasonably fit using either the value of about 63°, deter-

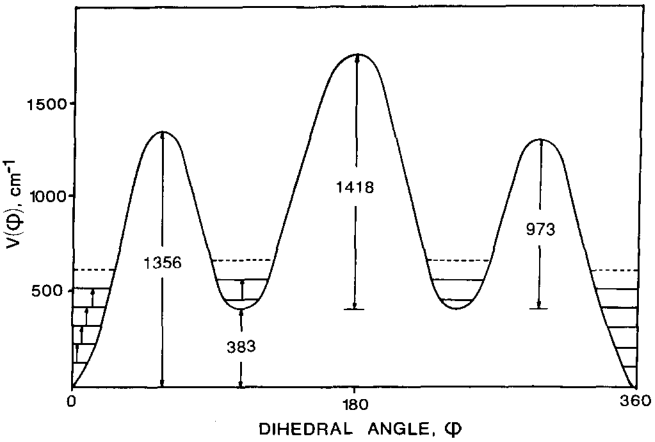

Fig. 6. Asymmetric torsional potential function for 1-bromo-2-fluoroethane as determined from far-IR spectral data. The torsional dihedral angle of 0° corresponds to the trans conformer.

TABLE 3

Potential coefficients and barriers to interconversion (in cm^{-1}) for 1-bromo-2-fluoroethane

Parameter	Value[a]	Ab initio (STO-3G*)	Electron diffraction[b]
V_1	584±6	271	588±40
V_2	−147±4	−115	−199±40
V_3	1217±11	997	1077±47
V_4	138±2		
V_6	−21±4		
Trans to gauche barrier	1356	979	
Gauche to gauche barrier	1418	1156	1665±83
Gauche to trans barrier	973	867	
Enthalpy difference	383±21	112	199±126
Dihedral angle ∡FCCBr	67	63	68

[a] Parameters as determined from the assignment given in Table 2, and $F_0 = 1.458678$, $F_1 = -0.361951$, $F_2 = 0.283363$, $F_3 = -0.082409$, $F_4 = 0.038087$, $F_5 = -0.013794$ and $F_6 = 0.005790$ cm^{-1}.

[b] Values are from ref. 10 and are based on a torsional frequency from the Raman spectrum of the liquid given in ref. 2. The enthalpy difference and gauche dihedral angle are from ED results given in ref. 10.

mined from the STO-3G* calculations, or the value of 73°, determined from the investigation of the microwave spectrum [11]. The gauche to gauche barrier, however, was determined to be about 1163 cm^{-1} from the former calculations but a barrier height of 1562 cm^{-1} was determined for the latter. Therefore, we have combined all of the experimental and theoretically obtained results from the electron diffraction data [10], the analysis of the microwave spectrum [11], and ab initio calculations to obtain an r_0 structure for the gauche conformer of 1-bromo-2-fluoroethane. The resulting r_0 structural parameters will be discussed later but it should be noted that a value of 67° was obtained for the gauche dihedral angle. This value, when used as a constraint on the subsequent calculations, gives a fit of the torsional transitions as shown in Table 2, and this fit is consistent with the potential constants and barrier heights given in Table 3.

VIBRATIONAL ASSIGNMENT

The Raman spectra of the gas and solid and Raman spectrum of the liquid in the C–H stretch region have not been previously reported for 1-bromo-2-fluoroethane. These data are particularly helpful in concluding to which symmetry species the observed bands belong and which conformer is more stable.

The present study also includes an analysis of the depolarization ratios measured for the Raman spectrum of the liquid. These data, when used concomitantly with the vibrational frequencies obtained from the ab initio calculations allow for a more definitive assignment to the fundamental vibrational modes of the trans and gauche conformations.

The presently proposed vibrational assignment of the C–H stretching modes for 1-bromo-2-fluoroethane are more complete than those given earlier [2]. Only two bands were previously observed [2] in the C–H stretching region of the IR spectrum of the gas, 2978 and 2898 cm^{-1}, and both were assigned to fundamentals. Presently, only the former of these two is assigned to a fundamental vibration and this results in the assignments of the remaining three CH_2 stretching modes being completely revised as shown in Table 4. All of these fundamentals are assigned to frequencies above 2900 cm^{-1} and the assignment of one of the two CH_2 antisymmetric stretching modes is to a frequency previously unobserved and above 3000 cm^{-1}.

The assignment of the CH_2 deformation modes are straightforward and occur between 1400 and 1500 cm^{-1}. One of the two deformational modes is conformer sensitive and assigned for the trans and gauche conformers to the two bands of A-type contour observed at 1467 and 1456 cm^{-1}, respectively, in the IR spectrum of the gas. The assignments for the CH_2 wag, rocking and twisting motions follow the general trend of decreasing frequency order given by the CH_2 wag, CH_2 twist and CH_2 rock. Additionally, for a given CH_2 bending mode, the vibration arising from the CH_2 group to which the bromine is bonded occurs lower in frequency than that to which the fluoride is bonded. This general order is in agreement with that given in the previous study; however, some of the specific assignments presently given are different. For example, we have assigned the four bands observed at 1391, 1381, 1231 and 1217 cm^{-1} as the two A' CH_2 wagging vibrations of both conformers. All of these features correspond to either Q-branches in the Raman spectra of the gas or polarized lines in the spectrum of the liquid. It should be mentioned that the latter two frequencies were previously assigned as an A'' twisting mode [2].

The assignment of the C–F and C–C stretching fundamentals is reversed from that given earlier [2]. We have assigned the C–F stretch for the trans and gauche conformers to the frequencies of 1091 and 1068 cm^{-1}, respectively, and the C–C stretch to the lower frequencies of 1032 and 1020 cm^{-1} in the IR spectrum of the gas. This reassignment is based on our ab initio calculations.

The assignment of the remainder of the fundamentals (i.e. the C–Br stretch, FCC and BrCC bending vibrations), are consistent with those given earlier [2]. Each of these fundamentals show very clear "conformer pairs" and they have all been well predicted by ab initio calculations which will be discussed in the ensuing text. The assignment of the torsional mode for the gauche conformer to the weak line observed at 127 cm^{-1} in the Raman spectrum of the liquid is in agreement with the corresponding assignment previously given [2].

TABLE 4

Observed[a] IR and Raman frequencies (cm^{-1}) and vibrational assignment for 1-bromo-2-fluoroethane

IR				Raman						Assignment	
Gas	Rel. int.	Solid	Rel. int.	Gas	Rel. int.	Liquid	Rel.int. and depol.	Solid	Rel. int.	ν_i^{b}	Approximate description
3039 Q,C	m	3036	s			3028	w,dp	3036	s	ν_{12}, ν_{12}'	*CH$_2$ antisymmetric stretch
								3018	m		
3025 Q,C	m									ν_{13}'	CH$_2$ antisymmetric stretch
		3003	m					3004	s		
2989 Q	vs	2999	m	2991	s			2988	s	ν_{13}	CH$_2$ antisymmetric stretch
		2989	m								
2979 Q	vs			2982	vs					ν_1'	*CH$_2$ symmetric stretch
2972 Q	vs	2980	m	2972	vs	2973	vs,p	2975	vs	ν_1	*CH$_2$ symmetric stretch
		2976	m								
2956 R		2963	s								
2948 Q,A	m	2957	s	2948	s	2952	s,p	2962	vs	ν_2, ν_2'	CH$_2$ symmetric stretch
2942 P											
		2929	w	2939	sh			2928	vw		
2928 R											
2922 min,B	m			2922	s	2914	w,p				$2\nu_3$
2915 P											
2904 R											
2899 Q,A	s	2897	m	2900	s	2893	m,p	2896	m		
2895 P				2893	sh						
2848	bd,vw			2842	w	2830	vw,p	2835	vw		$2\nu_4$
								2819	vw		
2766 R											
2760 Q,A	w	2744	w	2759	w	2753	v,p	2756	vw		$2\nu_5$
2753 P								2744	vw		

1490 R											
1483 min,B	sh										
1474 P											
1475 R											
1467 Q,A	m									ν_3'	CH_2 deformation
1461 P											
				1460	bd,vw	1462	m,p				
1461 R		1472	s								
1456 Q,A	m	1461	m					1469	m	ν_3	CH_2 deformation
1451 P		1454	m					1460	w		
1434 R		1425	s					1426	sh		
1428 Q,A	m	1420	s			1424	m,p	1420	m	ν_4, ν_4'	*CH_2 deformation
1423 P											
		1394	sh								
1398 R		1389	sh								
1391 Q,A	m	1385	m			1388	vw,p	1387	w	ν_5	CH_2 wag
1385 P		1383	m								
				1380	bd,vw						
1385 R											
1381 Q,A	m					1379	vw,p			ν_5'	CH_2 wag
1376 P											
1290 R								1283	sh		
1285 Q,A	s	1285	s	1284	m	1280	s,p	1274	m	ν_{14}, ν_{14}'	CH_2 twist
1279 P		1272	s					1268	sh		
1240 R											
1231 Q,A	w	1228	s	1234	vw	1231	s,p	1228	m	ν_6	*CH_2 wag
1223 R										ν_6'	*CH_2 wag
1217 Q,A/B	s			1217	m	1220	m,p				
1213 P											
1195 Q,C	w									ν_{15}'	*CH_2 twist
1186 Q,A/C	w	1183	m	1185	vw	1181	m,p	1180	w	ν_{15}	*CH_2 twist
		1178	m								
1095 R											
1091 Q,A	vs									ν_7'	
1084 P											

TABLE 4 (continued)

IR				Raman						Assignment	
Gas	Rel. int.	Solid	Rel. int.	Gas	Rel. int.	Liquid	Rel.int. and depol.	Solid	Rel. int.	$\nu_i{}^b$	Approximate description
1072 R		1065	vs								
1068 Q,A	vs	1061	vs	1065	m	1067	m,p	1063	w	ν_7	CF stretch
1063 P		1051	sh								
1036 R		1004	s					1005	sh		
1032 min,B	vs	1002	s	1030	m	1004	m,p	996	m	ν_8	CC stretch
1027 Q		998	s								
		991	sh								
1020	sh			1021	m	994	sh,p			ν_8'	CC stretch
959 R		942	s					946	sh		
953 Q,A	m	938	s			944	m,dp(?)	940	m	ν_{16},ν_{16}'	CH_2 rock
946 P								936	sh		
830 R		826	m								
826 Q,A	m	824	s	824	w	822	m,p	823	m	ν_{17}	*CH_2 rock
817 P		820	s								
776 Q,C	vw									ν_{17}'	*CH_2 rock
694 R											
691 ctr,A/B	s			691	s	683	s,p			ν_9'	C–Br stretch
686 P											
658 R											
652 min,B	w			652	w						
648 P											
594 R		575	s					593	sh		
588 Q,A	m	572	s	587	vs	573	vs,p	573	vs	ν_9	C–Br stretch
582 P		568	s					567	sh		
554	bd			558	vw						Combination or overtone
				490	bd,vw						Glass
455 R		457	s								

449 Q,A	m	455	s	448	w	451	s,p	454	s	ν_{10}	FCC bend
443 P		451	s								
340 R											
335 Q,A/B	m			335	s	338	s,p			ν_{10}'	FCC bend
343 P											
264 R		286	vw					286	m		
258 Q,A	w	272	m	257	w	264	m,p	272	m	ν_{11}	BrCC bend
252 P											
222 R											
216 min,B	m			218	w	224	vw,p			ν_{11}'	BrCC bend
210 P											
125 Q,C	m									ν_{18}'	Asymmetric torsion
111 Q	m	145	m	111	w	127	w,dp(?)	149	w	ν_{18}	Asymmetric torsion

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[a] Abbreviations used: s, strong; m, moderate; w, weak; v, very; sh, shoulder; bd, broad; p, polarized; dp, depolarized; Q, P and R refer to vibrational-rotational branches; A, B and C refer to IR band contours.

[b] ν' refers to the assignments made for the trans conformer. The asterisk (*) denotes the carbon atom to which the bromine atom is bonded. For convenience, the vibrations for the gauche conformer have been numbered according to a molecule with a plane of symmetry.

TABLE 5

Structural parameters (bond lengths in Å, bond angles in degrees, rotational constants in MHz, and dipole moments in Debye) for 1-bromo-2-fluoroethane[a]

Parameters	Microwave[b] gauche	Electron diffraction[c]		r_0[d] gauche	STO-3G*	
		trans	gauche		trans	gauche
$r(C_1-F)$	1.394	1.393 ± 0.004	1.393 ± 0.004	1.390 (fixed)	1.384	1.383
$r(C_1-C_2)$	1.535	1.509 ± 0.007	1.509 ± 0.007	1.502 ± 0.006	1.557	1.555
$r(C_2-Br)$	1.950	1.937 ± 0.004	1.937 ± 0.004	1.940 ± 0.004	1.880	1.881
$r(H_1-C_1)$	1.087	1.084 ± 0.008	1.084 ± 0.008	1.092 (fixed)	1.098	1.100
$r(H_2-C_1)$	1.087	1.084 ± 0.008	1.084 ± 0.008	1.089 (fixed)	1.098	1.098
$r(H_3-C_2)$	1.087	1.084 ± 0.008	1.084 ± 0.008	1.088 (fixed)	1.091	1.091
$r(H_4-C_2)$	1.087	1.084 ± 0.008	1.084 ± 0.008	1.087 (fixed)	1.091	1.091
$\angle(C_1C_2F)$	107.80	107.6 ± 0.8	110.1 ± 0.6	110.8 ± 0.3	109.90	111.30
$\angle(H_1C_1C_2)$	108.30	110.0 ± 0.19	110.0 ± 0.19	109.01 (fixed)	109.38	108.08
$\angle(H_2C_1C_2)$	108.30	110.0 ± 0.19	110.0 ± 0.19	111.46 (fixed)	109.38	109.41
$\angle(BrC_2C_1)$	110.0	109.9 ± 0.7	112.0 ± 0.5	111.83 ± 0.23	111.14	112.15
$\angle(H_3C_2C_1)$	112.55	110.0 ± 0.19	110.0 ± 0.19	110.23 (fixed)	110.00	109.25
$\angle(H_4C_2C_1)$	112.55	110.0 ± 0.19	110.0 ± 0.19	110.48 (fixed)	110.00	109.94
$\angle HC_1H$	109.83	108.05	108.05	109.45 (fixed)	108.02	108.01
$\angle HC_2H$	110.13	108.05	108.05	109.54 (fixed)	108.39	108.51
$\tau(FC_1C_2Br)$	73.17	180.0	67.8 ± 5.3	67.32 ± 0.34	180.00	62.59
A	12541.7	29732.8	12548.6	12547.0	29460	12376
B	2296.4	1605.1	2205.6	2218.1	1613	2268
C	1997.5	1552.0	1989.9	1998.4	1559	2028
μ_a					0.460	1.004
μ_b					0.138	1.949
μ_c					0.000	0.159
μ_t					0.480	2.198
$-E+2720$ (Hartree)					0.529361	0.528848

[a] The structural parameters reported from ab initio calculations and the r_0 structure are from this study.

[b] Values are from ref. 11. Experimental rotation constants for ^{79}Br are $A = 12547.013 \pm 0.044$, $B = 2218.112 \pm 0.007$, and $C = 1998.444 \pm 0.007$ MHz.

[c] Values are from ref. 10 and, for comparison, the reported gauche dihedral angle is 112.2 ± 5.3° based on a dihedral angle for the trans conformer of 0°.

[d] This study by determining r_0 values using rotational constants from ref. 11. For the trans conformer, it is expected that the C–F = 1.395 Å, C–Br = 1.940 Å and C–C = 1.507 Å with the other parameters about the same as those predicted from the 6-31G* basis set of 1-chloro-2-fluoroethane [18].

The structural parameters obtained for the trans and gauche conformers of 1-bromo-2-fluoroethane from optimized geometries utilizing the STO-3G* basis set are summarized in Table 5. These restricted Hartree–Fock calculations were performed with the Gaussian-86 program [15]. The energy minima with respect to the nuclear coordinates were obtained by simultaneous relaxation of all the geometric parameters using the gradient method of Pulay [16]. Also given in Table 5 are the structural parameters determined from the investigations of the microwave spectrum [11] and the electron diffraction data [10].

From a comparison of the structural parameters obtained for the two conformers with the STO-3G* basis set, several structural differences can be found. For example, both the FCC and BrCC angles open by 1.4° and 1.0°, respectively, as the molecule changes from the trans to the gauche conformer. Such a trend was also determined from the analysis of the electron diffraction pattern but of greater magnitude. Other than these two angles and the torsional dihedral angle, ∡ FCCBr, all other parameters are calculated to be essentially equivalent and have been assumed to be the same in the analysis of the electron diffraction pattern [10].

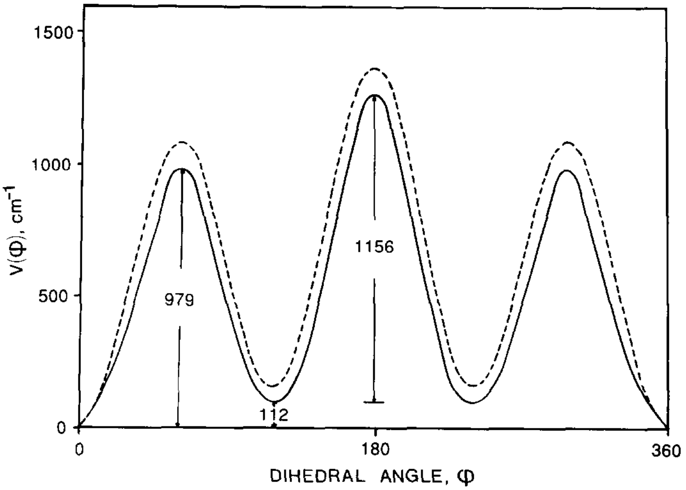

Fig. 7. The potential function governing internal rotation of 1-bromo-2-fluoroethane as determined by ab initio calculations with the STO-3G* basis set. The torsional dihedral angle of 0° corresponds to the trans conformer. The potential surface given by the dashed line was obtained by allowing the torsional dihedral angle to vary by 10° increments, while all other structural parameters were fixed at the optimized value obtained for the trans conformer. The potential surface given by the bold line was calculated by allowing for optimization at the transition state, and at the trans minimum by relaxation of all the geometric parameters.

Potential surface

The final optimized geometry for the trans conformer (Table 5) was used to obtain a potential surface scan in which only the FCCBr torsional dihedral angle was allowed to vary from 180° (trans) to 0° (cis). The potential function obtained in this way with the STO-3G* basis set is shown by the dashed line

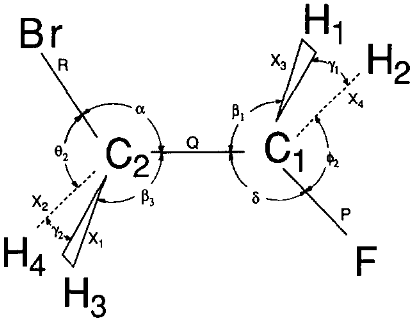

Fig. 8. Internal coordinates for 1-bromo-2-fluoroethane.

TABLE 6

Symmetry coordinates for 1-bromo-2-fluoroethane

Species	Approximate description[a]	Symmetry coordinate[b]
A'	*CH_2 symmetric stretch	$S_1 = X_1 + X_2$
	CH_2 symmetric stretch	$S_2 = X_3 + X_4$
	CH_2 deformation	$S_3 = (\sqrt{6}+2)\gamma_1 - (\sqrt{6}-2)\delta - \beta_1 - \beta_2 - \phi_1 - \phi_2$
	*CH_2 deformation	$S_4 = (\sqrt{6}+2)\gamma_2 - (\sqrt{6}-2)\alpha - \beta_3 - \beta_4 - \theta_1 - \theta_2$
	CH_2 wag	$S_5 = \beta_1 + \beta_2 - \phi_1 - \phi_2$
	*CH_2 wag	$S_6 = \beta_3 + \beta_4 - \theta_1 - \theta_2$
	CF stretch	$S_7 = P$
	CC stretch	$S_8 = Q$
	CBr stretch	$S_9 = R$
	CCF bend	$S_{10} = (\sqrt{6}+2)\delta - (\sqrt{6}-2)\gamma_1 - \beta_1 - \beta_2 - \phi_1 - \phi_2$
	CCBr bend	$S_{11} = (\sqrt{6}+2)\alpha - (\sqrt{6}-2)\gamma_2 - \beta_3 - \beta_4 - \theta_1 - \theta_2$
	Redundancy	$S_{1R} = \delta + \beta_1 + \beta_2 + \gamma_1 + \phi_1 + \phi_2$
	Redundancy	$S_{2R} = \alpha + \beta_3 + \beta_4 + \gamma_2 + \theta_1 + \theta_2$
A''	*CH_2 antisymmetric stretch	$S_{12} = X_1 - X_2$
	CH_2 antisymmetric stretch	$S_{13} = X_3 - X_4$
	CH_2 twist	$S_{14} = \beta_1 - \beta_2 - \sigma_1 + \phi_2$
	*CH_2 twist	$S_{15} = \beta_3 - \beta_4 - \theta_1 + \theta_2$
	CH_2 rock	$S_{16} = \beta_1 - \beta_2 + \phi_1 - \phi_2$
	*CH_2 rock	$S_{17} = \beta_3 - \beta_4 + \theta_1 - \theta_2$
	Torsion	$S_{18} = \tau$

[a] The asterisk (*) denotes the carbon atom to which the bromime atom is bonded.
[b] Not normalized.

TABLE 7

Comparison of observed and calculated frequencies (cm^{-1}) for the trans and gauche conformers of 1-bromo-2-fluoroethane

Species	Fundamental[a]	trans				gauche			
		Ab initio[b]	Fixed scaled[c]	Obs.[d]	P.E.D.[e]	Ab initio	Fixed scaled	Obs.	P.E.D.
A'	*CH_2 symmetric stretch	3603	3121	2979	$100S_1$	3602	3120	2972	$99S_1$
	CH_2 symmetric stretch	3558	3082	2948	$99S_2$	3548	3073	2948	$99S_2$
	CH_2 deformation	1810	1516	1467	$85S_3$	1804	1510	1456	$92S_3$
	*CH_2 deformation	1782	1492	1428	$82S_4$	1768	1480	1428	$96S_4$
	CH_2 wag	1684	1417	1381	$53S_5,17S_7,11S_8$	1683	1418	1391	$68S_5,14S_7$
	*CH_2 wag	1493	1251	1217	$72S_6,19S_5$	1570	1317	1231	$71S_6,13S_{14}$
	CF stretch	1356	1168	1091	$82S_7,12S_5$	1346	1145	1068	$52S_7,24S_{15},12S_8$
	CC stretch	1197	1031	1032	$82S_8$	1128	961	1021	$38S_8,25S_{16},12S_9,11S_6$
	CBr stretch	918	789	691	$78S_9,12S_{10}$	796	686	587	$74S_9$
	FCC bend	381	322	335	$64S_{10},20S_9$	500	419	449	$58S_{10},16S_{11},14S_{17}$
	BrCC bend	244	205	218	$73S_{11},23S_9$	263	230	257	$50S_{11},24S_{10},16S_{18}$
A''	*CH_2 antisymmetric stretch	3725	3227	3039	$99S_{12}$	3725	3226	3039	$99S_{12}$
	CH_2 antisymmetric stretch	3671	3180	3025	$99S_{13}$	3662	3171	2989	$99S_{13}$
	CH_2 twist	1512	1266	1285	$61S_{14},30S_{15}$	1454	1221	1285	$52S_{14},18S_{15}$
	*CH_2 twist	1389	1164	1195	$41S_{15},38S_{14}$	1406	1189	1186	$36S_{15},24S_{15},12S_8$
	CH_2 rock	1194	1000	953	$41S_{16},31S_{15},27S_{17}$	1207	1020	953	$42S_{16},17S_{17},16S_{15},15S_8$
	*CH_2 rock	881	743	776	$54S_{17},31S_{16}$	976	822	826	$66S_{17}$
	Torsion	111	110	125	$93S_{18}$	97	93	111	$72S_{18},19S_{11}$

[a] The asterisk (*) denotes the carbon atom to which the bromine atom is bonded.
[b] Calculated using the STO-3G* basis set.
[c] Calculated using scaling factors of 0.75 for stretches, 0.70 for bends and 1.0 for torsion.
[d] Raman and/or IR frequencies from the gas.
[e] Potential energy distribution.

in Fig. 7. This calculation is consistent with another minimum at the gauche position. The structures corresponding to the cis position (i.e. the gauche to gauche transition state) and the trans to gauche transition state were optimized by relaxation of all of the geometric parameters (solid line in Fig. 7). From the optimized geometries, the total energies for the trans and gauche conformers were found to be −2720.52936054 and −2720.52884784 Hartree (1 Hartree = 219474 cm^{-1}), respectively. Therefore, at this level of calculation the trans conformer is found to be more stable than the gauche form by 112 cm^{-1} (320 cal mol^{-1}) and the trans to gauche, gauche to trans and gauche to gauche barriers are 979 cm^{-1}, 867 cm^{-1} and 1156 cm^{-1}, respectively.

Normal coordinate analysis

In order to obtain a more complete description of the molecular motions involved in the fundamental modes of 1-bromo-2-fluoroethane, we have presently carried out a normal coordinate analysis. The force field in Cartesian coordinates was calculated by the Gaussian-86 program [15] with the STO-3G* basis set. The following procedure was used to transform the ab initio results, which are in terms of Cartesian coordinates, into the form usually found for normal coordinates. The Cartesian coordinates obtained for the optimized structure were input into the **G**-matrix program together with the complete set of twenty internal coordinates (Fig. 8). This complete set of internal coordinates was used to form the symmetry coordinates, with two redundancies, and they are listed in Table 6. The output of this **G**-matrix program consists of the **B**-matrix and the unsymmetrized **G**-matrix. The **B**-matrix was used to convert the ab initio force field in Cartesian coordinates to a force field in the desired internal coordinates. The resulting force fields for the trans and gauche conformers are available from B.L.L.D. as Supplementary Publication number SUP 26423 (2 pages). All diagonal elements of the force fields in internal coordinates were assigned scaling factors. This force field was then used as input, along with the unsymmetrized **G**-matrix and scaling factors, in the perturbation program written by Schachtschneider [17]. Initially, all scaling factors were kept fixed at 1.0 to produce the pure ab initio calculated vibrational frequencies. Subsequently, scaling factors of 0.75 for stretching coordinates, 0.7 for bending coordinates, 1.0 for torsional coordinates, and the geometric average of scaling factors for the interaction constants were used to obtain the "fixed scaled" force field and resultant frequencies along with the potential energy distributions (P.E.D.) which are given in Table 7.

STRUCTURE

Structural parameters for 1-bromo-2-fluoroethane determined from microwave spectroscopy [11], the electron diffraction technique [10] and ab initio calculations employing STO-3G* basis set are given in Table 5. A comparison of all of these values reveals a number of discrepancies between the values determined from the two experimental techniques. For example, the value of 1.535 Å for the C–C distance reported from the investigation of the microwave spectrum of the gauche conformer [11] is much longer than the value of 1.509 ± 0.007 Å determined from analysis of the electron diffraction data [10]. Also, the ∡FCCBr dihedral angle for the gauche conformer of 73° is too large based on all other values given in Table 5. It should be mentioned that the C–F and C–C distances were previously reported [11] to be 1.535 Å and 1.394 Å, respectively, and we have assumed that these two values were reversed accidentally and are corrected in Table 5. From the electron diffraction structure the C–H distances and CCH angles were given as equivalent values for the two conformers, which does not reflect the effect of the position of the hydrogen atoms relative to the heavy atoms. Because ab initio calculations can be useful for elucidating subtle structural changes we have used a combination of the available experimental and theoretical results to determine an r_0 structure for the gauche conformer. Rotational constants, determined from experiment, are not available for the trans conformer and, thus, a similar structure for this rotamer cannot be provided.

With only six rotational constants available for the gauche conformer it is not possible to obtain all of the r_0 structural parameters but the values of the heavy atom parameters can be obtained. From the recent results [18] for 1-chloro-2-fluoroethane, the C–F distance was estimated to be 1.388 Å, which is close to the 1.393 ± 0.004 Å value from the electron diffraction data [10], and thus we have fixed the C–F distance at 1.390 Å. Based on results obtained for related molecules we have added 0.008 Å to each of the C–H distances determined from the 6-31G* calculation values for the gauche conformer of 1-chloro-2-fluoroethane [18]. Additionally, all of the angles associated with the hydrogen atoms were fixed at the values from the same calculations [18]. With these fixed parameters, we then varied the remaining five heavy atom parameters to determine the r_0 parameters by the method of weighted least-squares described [19] previously to fit the six rotational constants. The values of these parameters are listed in Table 5. The calculated C–C distance of 1.502 ± 0.006 Å is in excellent agreement with the value of 1.509 ± 0.007 Å determined from the electron diffraction study [10]. From the r_0 structure the CCF angle is determined to be 110.8° which is larger by 0.7° and 3.0° than the values obtained from electron diffraction study [10] and that previously reported from the microwave data [11], respectively. The torsional dihedral angle with the value of 67.3° from the r_0 structure agrees well with the electron diffraction value but is much smaller, i.e. 5.8°, than that previously given from the microwave data. The CBr distance is consistent with the electron diffraction value [10]. It is believed that these structural parameters with the indicated uncertainties which are listed in Table 5 represent reliable values for the structural parameters for the gauche conformer of 1-bromo-2-fluoroethane.

DISCUSSION

In the present study, the enthalpy difference for the gas phase has been determined to be 350 ± 87 cm^{-1} from the variable temperature study of the Raman spectrum of the gas. This value is considerably different from the previously reported values of 105 ± 28 cm^{-1} and 199 ± 126 cm^{-1} determined from the investigations of the IR spectra [2] and the electron diffraction data [10], respectively. The uncertainty in our value is reported at a 95% confidence level and, in general, we have found the values determined from variable temperature studies of Raman spectra to be more reliable than those from the corresponding studies of IR spectral features.

Using a more reliably determined value for the enthalpy difference and dihedral angle for the gauche conformer, from the r_0 structure in this study, a more definitive potential function can be determined. Of course, the calculation of the potential function is largely dependent on the observed torsional transitions. In the present study several transitions have been identified as arising from the trans conformer, whereas only the fundamental for the gauche conformer, has been used in the calculations. This results in the trans potential well being more completely defined. The gauche to gauche barrier is dependent on the spacing of successive gauche transitions occurring higher in the potential well. Several additional Q-branches have been observed at progressively lower frequencies than the assigned fundamental (111.25 cm^{-1}) in the far-IR spectrum of the gas (Fig. 1), but a specific assignment to upper level transitions is not possible. In fact, identification of the fundamental for the gauche conformer would not have been possible in the absence of the low frequency Raman spectrum of the gas. From this spectrum only a single Q-branch having a full width at half height (FWHH) of about 10 cm^{-1} and centered at about 111 cm^{-1} has been observed. It is possible that the $\pm 2 \leftarrow \mp 1$, and possible other upper level gauche transitions occur near this frequency. Therefore, we have carried out several exploratory calculations utilizing a variety of spacings between successive gauche transitions. Calculations were carried out assuming spacings of 0.4, 1.0, 2.0 and 3.0 cm^{-1} between the fundamental and $\pm 2 \leftarrow \mp 1$ transitions and the resulting gauche to gauche barriers are 1614 cm^{-1}, 1545 cm^{-1}, 1450 cm^{-1} and 1361 cm^{-1}, respectively. Spacings greater than 3 cm^{-1} seem unlikely with a single Q-branch being observed in the Raman spectrum of the gas. The best fit of the observed transitions, torsional dihedral angle and energy difference was obtained with a spacing of about 2 cm^{-1}. Therefore, although additional transitions for the gauche conformer could not be assigned, the value of the gauche to gauche barrier given in Table 3 should be reasonably well determined.

The potential coefficients reported from the investigation of the electron diffraction pattern are listed in Table 3. Although these potential coefficients were determined from a frequency from the spectrum of the liquid phase they are relatively good. The fundamental transition of the gauche conformer used in the potential function calculation from the electron diffraction study is 126 cm^{-1} which is considerably higher than the value of about 111 cm^{-1} from the IR and low frequency Raman spectra of the gas. A more accurate determination of the fundamental frequency of the gauche conformer, energy difference between the two conformers and dihedral angle, results in a rather well determined potential function.

The vibrational assignment reported herein differs from that proposed [2] previously and is more definitive with the inclusion of the Raman spectra of the solid and gas. Furthermore, our assignment is supported by the normal coordinate analysis utilizing the scaled ab initio force constants with the STO-3G* basis set. Also in agreement with the ab initio calculations is our conclusion that both the gauche and trans conformers exist in the fluid phases, and the trans conformer is preferred in the vapor. Although the values of the dipole moments determined from ab initio calculations are unreliable, their relative magnitudes should be similar. The increased stability of the gauche conformer ($\mu = 2.20$ D) relative to the trans conformer ($\mu = 0.48$ D) as one proceeds from the gas to the condensed phase is consistent with some of the earliest work on conformational analysis [1] which showed that the conformation having the larger dipole moment becomes stabilized in the liquid due to intermolecular dipole–dipole interaction.

The structural parameters previously reported from the earlier microwave study [11] were given without any uncertainties, but it is clear that the carbon–carbon bond distance is entirely too long for a 1,2-dihalogen substituted ethane molecule. The C–C, C–F and C–Br distances are correlated so the longer C–Br distance of 1.950 Å results in a longer C–C bond in order to obtain only fair agreement between the experimental and calculated rotational constants, i.e. the *A* constant differs by 6 MHz, the *B* constant by 22 MHz, and the *C* constant by 1 MHz for the ^{79}Br isotopic species with similar agreement between the experimental and calculated values for the ^{81}Br species. Also, it should be noted that the dihedral angle previously reported differs by 5.8° from the one obtained by the weighted least-squares fit to the experimental rotational constants. The structural parameters which we report are now in excellent agreement with those obtained from the electron diffraction data and trends expected from the series CH_2FCH_2F [20], CH_2FCH_2Cl [10,18] and CH_2FCH_2Br. Finally, it should be noted that the calculated dipole moment components are so small for the trans conformer that it would be extremely difficult to assign the microwave spectrum of this rotamer with conventional techniques but the proposed structural parameters listed in Table 5 should be close to the actual values.

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