RAMAN AND FAR-INFRARED SPECTRA OF GASEOUS 1,1,1,3,3,3-HEXAFLUORO-2-PROPANOL, CONFORMATIONAL STABILITY AND BARRIERS TO INTERNAL ROTATION

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ABSTRACT

The Raman (4000-50 cm⁻¹) and far-infrared (370-50 cm⁻¹) spectra of gaseous 1,1,1,3,3,3-hexafluoro-2-propanol, (CF₃),CHOH, and of the O-D compound have been recorded. Particular attention is given to the O-H stretching and low frequency spectral regions, where evidence is found for the existence of both the trans and gauche conformers. From simulations of observed gas phase IR band profiles, it is possible to assign the O-H stretch at 3666 cm⁻¹ to the gauche conformer and the one at 3626 cm⁻¹ to the trans conformer (the O-H bond trans to the C-H bond). From relative intensities of the corresponding Raman lines as a function of temperature, the enthalpy difference in the gas phase is found to be 336 ± 132 cm⁻¹ (961 ± 377 cal mol⁻¹) with the *trans* conformer being more stable. The fundamental O-H torsion is observed at 331.7 cm⁻¹ for the trans conformer and at 288.9 cm⁻¹ for the gauche conformer with both bands being identified from their shift with deuteration. From these data an asymmetric potential function is calculated which gives a trans/gauche barrier of 937 cm⁻¹ (2.68 kcal mol⁻¹) and a gauche/ gauche barrier of 360 cm⁻¹ (1.00 kcal mol⁻¹). One of the CF₃ torsional modes has been observed at 90 cm^{-1} from which the barrier to internal rotation is estimated to be in the range and 5-6 kcal mol⁻¹. All these data are compared to the corresponding quantities for some similar compounds.

INTRODUCTION

The conformational preference of 1,1,1,3,3,3-hexafluoro-2-propanol has been the subject of some controversy. Although the vibrational work suggests that the *trans* conformer (O-H bond *trans* to the C-H bond) is the more stable form [1, 2], Truax et al. [3] have suggested that, based on CNDO calculations, the *gauche* conformer should be the more stable form. The vibrational spectra of 1,1,1,3,3,3-hexafluoro-2-propanol in various solvents have been previously reported [4, 5]. Barnes and Murto [1] have published

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the matrix isolated IR spectra of $(CF_3)_2$ CHOH and its deuterated analogs in the region above 500 cm⁻¹. Additionally, the IR spectra of $(CF_3)_2$ CHOH and its three deuterated analogs in the gaseous, liquid, and solid states in the region above 200 cm⁻¹ have been reported [2]. A normal coordinate analysis of bands assigned to the *trans* conformer in that study has also been reported [6]. In all of these studies, the assignment is based on the increased stability of the *trans* conformer relative to the *gauche* conformer.

Recently, the two conformers of ethanol and 2-propanol have been assigned utilizing gas phase IR band contour simulations of the O-H stretches of both conformers [7]. We felt that a study of this type, which allows for the assignment of conformer bands based on information obtained directly from the rotation-vibration contours in the IR spectra, would be interesting to confirm the previous assignment of the O-H stretching modes of the two conformers of 1,1,1,3,3,3-hexafluoro-2-propanol. Additionally, no Raman data for the gaseous phase or high resolution far-IR spectrum of this compound have been reported. The Raman study of this molecule in the vapor phase should be useful because, unlike data from the liquid and solid phase which are complicated by hydrogen bonding and dimer formation, only intramolecular interactions should be present. Finally, the higher resolution far-IR spectrum should allow for the assignment of the CF_3 and O-Htorsions, the latter of which was observed as a very strong band in a study of 2,2,2-trifluoroethanol [8], and should be observable for both conformers. In an effort to provide a definitive determination of the conformational stability of 1,1,1,3,3,3-hexafluoro-2-propanol, we have obtained these data for both $(CF_3)_2$ CHOH and $(CF_3)_2$ CHOD. It was hoped that these data would allow for the assignment of the low frequency torsional modes and the determination of their respective barriers to internal rotation.

EXPERIMENTAL

The sample of 1,1,1,3,3,3-hexafluoro-2-propanol was obtained commercially from Fairfield Chemical Co., Blythewood, SC. The deuterated analog, $(CF_3)_2CHOD$, was prepared by exchange with excess D_2O , followed by distillation under nitrogen to separate the compound from the D_2O . Each compound was further purified using a low temperature, low pressure fractionating column. When handling the deuterated compound, all glassware and appropriate apparatus were flushed several times with D_2O vapor to prevent exchange. Traces of water were removed by repeatedly passing the gaseous samples through activated Linde 3 Å molecular sieves.

The far-IR spectra of the gaseous compounds (Fig. 1) were collected on a Nicolet model 200 SXV Fourier transform interferometer equipped with a vacuum bench, a liquid helium cooled Ge bolometer with a wedged sapphire filter and a polyethylene window, a high pressure Hg arc source, and 6.25 and 25 μ Mylar beamsplitters. The samples were contained in a 10 cm gas cell at their ambient vapor pressure. Interferograms for both the sample and



Fig. 1. Far-IR spectra of gaseous 1,1,1,3,3,3-hexafluoro-2-propanol: (A) (CF₃)₂CHOH (H₂O vapor insert); (B) (CF₃)₂CHOD (D₂O vapor insert). The asterisks indicate (CF₃)₂CHOH impurities in the spectrum of the O-D compound.



Fig. 2. Raman spectra of 1,1,1,3,3,3-hexafluoro-2-propanol-O-H: (A) gas phase; (B) liquid phase.



Fig. 3. Raman spectra of 1,1,1,3,3,3-hexafluoro-2-propanol-O-D: (A) gas phase; (B) liquid phase. The asterisk indicates residual D_2O in the spectrum.

empty reference cells were recorded 256 times, with an effective resolution of 0.10 cm^{-1} , averaged, and transformed with a boxcar truncation function.

The Raman spectra (Figs. 2 and 3) from $4000-50 \text{ cm}^{-1}$ were recorded using a Cary model 82 spectrophotometer equipped with a Spectra-Physics model 171 argon ion laser operating on the 5145 Å line. The laser power was varied from 0.5 to 1 W, depending on the physical state of the sample being investigated. The spectra of the vapor were recorded using a standard Cary multipass accessory. Spectra of the liquids were measured with the samples sealed in glass capillaries. Spectra of the gaseous compounds were recorded with a spectral bandwidth of 5 cm⁻¹, whereas those of the liquid were recorded with a 4 cm⁻¹ spectral bandwidth. Measured frequencies are expected to be accurate to $\pm 2 \text{ cm}^{-1}$.

The mid-IR spectra of the gaseous compounds from 4000 to 400 cm⁻¹ were obtained using a Digilab model FTS-14C Fourier transform interferometer equipped with a Ge/KBr beamsplitter, a nichrome wire source element, and a TGS detector. The spectra were recorded with an effective resolution of 0.5 cm^{-1} , with the sample contained in a 10 cm cell fitted with CsI windows. The spectra (Figs. 4 and 5), from which the sum and difference bands (4500 to 1500 cm⁻¹) with the O-H stretch were obtained, were recorded using a Bomem model DA3.002 Fourier transform interferometer equipped with a KBr beamsplitter, a globar source and a Cu doped Ge bolometer cooled to liquid helium temperature. Both the sample and empty reference cells were recorded 200 times, with an effective resolution of 0.10 cm^{-1} , averaged and transformed with a boxcar truncation function. The samples were contained in a 20 cm cell fitted with CsI windows.



Fig. 4. Mid-IR spectra of gaseous 1,1,1,3,3,3-hexafluoro-2-propanol in the OH stretching region at various concentrations.



WAVENUMBER (cm⁻¹)

Fig. 5. Comparison of the sum and difference modes associated with the *gauche* OH stretch: (A) difference region from 3000 cm^{-1} to 3665 cm^{-1} ; (B) sum region from 4300 cm^{-1} to 3665 cm^{-1} .

RESULTS

Conformational stability

Band contour analysis

In a series of papers [7, 9–11] we have shown that the simulated IR band contours can be useful for assigning specific bands to their respective conformations when more than one conformer is present in the gaseous phase. The a priori knowledge of the orientation of $d\vec{\mu}/dQ$ for the simulation of gas phase band contours restricts the fundamentals which can be used in the simulation to those which are sufficiently characteristic normal modes. For conformer identification, the number of fundamentals which can be used is limited by the restriction that the contours predicted for the various conformations must be sufficiently different from one another to allow for their distinction.

The two expected conformers of 1,1,1,3,3,3-hexafluoro-2-propanol in the principal coordinate axis system are shown in Fig. 6, and are generated by the rotation of the C—O bond. The relative masses of the atoms involved result in the orientation of the heavy atom skeleton in the principal axis system being quasi-identical for both conformers. The orientation of the O—H bond, therefore, is substantially different in the *gauche* and *trans* conformations, which satisfies one of the requirements discussed in the previous paragraph. As a result of the different orientations of the O—H bond in the two



Fig. 6. Projection of 1,1,1,3,3,3-hexafluoro-2-propanol in the principal coordinate axis system: (A) trans conformer; (B) gauche conformer.

conformers, only modes which are localized in the O-H bond can give rise to rotation-vibration bands which result in different band contours for the O-H stretch of each conformer. This highly characteristic O-H stretching mode should have the dipole moment vector, $d\mu/dQ$, oriented along the O-H bond, and therefore, should have a band contour which can be reliably predicted. For the simulations performed in this study, the O-H stretching modes were treated as harmonic vibrations where the rotational constants of the upper and ground states were assumed to be identical.

The gas phase pure type A, B, and C infrared band contours of both conformers were calculated using the rotational constants calculated from the structural parameters utilized by Murto et al. [2] and Truax et al. [3] in their studies. All of the pure type contours were calculated using the rigid rotor approximation, at 298 K, with a maximum J level of 120. A Gaussian slit function of 1 cm⁻¹ was used, and the intensities were calculated every 0.5 cm^{-1} for the region extending approximately 25 cm⁻¹ in each direction from the band center. The simulated band contours for the hybrid band types were constructed from the values for the direction cosines for the O—H bond in the principal coordinate axis system (Table 1). An extra convolution of the theoretical hybrids was used to account for the thermally excited states, which broaden the observed bands in the IR spectrum. The full width at half height of the calculated Q-branch was used as the criterion for determining the width of the slit function used in the extra convolution.

Both the IR and Raman spectra of the gas in the O–H stretching region show two bands centered at 3666 and 3626 cm⁻¹, the latter of which is considerably more intense than the former, and therefore, will be treated first. The Q-branch of this band is rather broad, indicating there is a substantial influence from the thermally excited states. In Fig. 7(A), the experimental contour is compared with the theoretical contours of the *trans* and *gauche* conformers, shown in parts (B) and (C), respectively, for the band observed at 3626 cm⁻¹ in the IR spectrum. It is quite clear that the agreement between the observed and calculated band contour for the *trans* conformer is much better than for the *gauche* conformer, which is considerably more intense in the area near the Q-branch in the center and less intense in the wings of the band. On this basis, the 3626 cm⁻¹ band is assigned as the O–H stretch of the *trans* conformer.

The high frequency absorption appears as a doublet with maxima at 3665.5 and 3668.5 cm⁻¹, and a very shallow minimum between them. This is

TABLE 1

Unit vector along $\partial \ddot{\mu} / \partial Q$ for the O–H stretch of 1,1,1,3,3,3-hexafluoro-2-propanol

	x	у	z
gauche	0.8363	0.3929	-0.3817
trans	0.0	0.0388	0.9992



Fig. 7. Comparison of the experimental and simulated band contour profiles for the low frequency O-H stretching mode: (A) experimental; (B) *trans* conformer simulation; (C) *gauche* conformer simulation.



Fig. 8. Comparison of the experimental and simulated band contour profiles for the high frequency doublet: (A) experimental; (B) gauche conformer simulation; (C) trans conformer simulation.

similar to the high frequency absorption observed for isopropanol [7], where two well defined Q-branches were observed and found to arise from two transitions of the *gauche* conformer. The simulations performed in this study were done in a similar manner.

In Fig. 8(A) the experimental contour for the high frequency doublet is compared to the theoretical contours for the *gauche* and *trans* conformers, shown in parts (B) and (C), respectively. Both transitions in the theoretical traces were given the same relative intensity. Extra convolutions, using a Gaussian function, were performed to reproduce the experimental maxima and minimum. A 5.0 cm^{-1} slitwidth was used for the extra convolutions of the *gauche* hybrid, whereas a 4.5 cm^{-1} slitwidth was applied to the convolutions of the *trans* hybrid.

No definitive P, Q, and R structure is observed on the high frequency O—H stretch. This is probably due to not only the strong overlap of the two transitions, but also the thermal broadening effects. As a result, making a definitive assignment based on the band contour simulations of this band is difficult. However, with the lower frequency band assigned to the *trans* conformer, the assignment of the high frequency band to the *gauche* conformer follows indirectly. These assignments are consistent with those which were previously reported [1, 2].

ΔH Values

Raman spectra of gaseous and liquid 1,1,1,3,3,3-hexafluoro-2-propanol are shown in Figs. 2 and 3 for the O-H and O-D compounds, respectively. One advantage of using Raman spectroscopy in the gaseous phase to do conformational studies of fluorinated alcohols which undergo intermolecular hydrogen bonding in other phases can be seen in Fig. 2. Evidence for two conformers in the vapor phase can be found in the O-H, C-H, and C-O stretching regions. Based on the band contour analysis discussed earlier, the strong band observed in the Raman spectrum of the gas at 3626 cm⁻¹ is assigned as the O-H stretch of the *trans* conformer, whereas the weaker band at 3666 cm⁻¹ is the corresponding stretch of the *gauche* conformer.

As for the O-H stretch, two bands are observed for the C-H stretch at 2988 and 2945 cm⁻¹ The relative intensity of the 2945 cm⁻¹ band suggests it must be assigned to the same conformer that gives rise to the high frequency O-H stretch, whereas the 2988 cm⁻¹ band has to be correlated with the low frequency O-H stretch. This is substantiated from the temperature dependence study (vide infra). In the *gauche* conformer the C-H bond is weakened by the overlap of one of the oxygen free electron pairs with the antibonding σ^* (C-H) orbital [12-14]. Consequently, the C-H stretch of the *trans* conformer must absorb at higher frequency than that for the corresponding band in the *gauche* conformer. Hence, the 2988 cm⁻¹ band is assigned to the *trans* C-H stretch of the conformer, and the one at 2945 cm⁻¹ to the *gauche* conformer. In view of the above intensity correlation, this confirms the conformer assignment obtained from the contour simulation of the bands for the O-H stretches.

The C—O stretching mode of the "light" compound also exhibits a conformer doublet in the Raman spectrum of the gas at 847 and 834 cm⁻¹. Additionally, the CC₂ symmetric stretch appears as a conformer doublet at 735 and 728 cm⁻¹ in the Raman spectrum of the O—D compound in the vapor phase. Of these four pairs of conformer bands, two are well resolved and were used to obtain the ΔH value between the conformers.

First, a variable temperature study of the two bands observed in the Raman spectrum of the gas at 3666 and 3626 cm⁻¹ was performed to see if there was any variation in relative intensity of the two bands with increasing temperature. Several sets of data were taken at five temperatures ranging from 23 to 84°C. Utilizing the equation $-\ln K = (\Delta H/RT) - (\Delta S/R)$, where ΔS is the entropy change, one can evaluate the enthalpy change, ΔH , by plotting $-\ln K$ versus T^{-1} which gives $\Delta H/R$ as the slope of the line. In this equation, K is the ratio I(high energy conformer)/I(low energy conformer), where I represents the relative intensity of a particular line. If the enthalpy difference is sufficient, the relative intensity of the band associated with the higher energy conformer will increase as the temperature is increased. It is assumed that ΔH is not a function of temperature. The natural log of the ratios of the two bands observed at 3666 and 3626 cm⁻¹ was plotted as a function of the reciprocal of the absolute temperature, and values of 336 ± 132 cm⁻¹ $(0.96 \pm 0.38 \text{ kcal mol}^{-1})$ and $1.7 \pm 0.6 \text{ cal mol}^{-1} \text{ K}^{-1}$ were obtained for ΔH and ΔS , respectively. The lower energy conformer in the gaseous phase was found to be the trans conformer. This value is significantly higher in the gaseous phase than the value of 100 cal mol⁻¹ previously reported in dilute CCl_4 solution [4]. However, it is in agreement with the value of 1.1 kcal mol⁻¹ previously reported for the gaseous phase [2], but that value was quoted from a private communication, and no details are available regarding the experimental conditions under which it was obtained or the error limits associated with the quoted value.

To check our measured value of ΔH , a second set of data over the same temperature range was obtained for the conformer bands observed at 2988 and 2945 cm⁻¹. This variable temperature study resulted in values of 506 ± 231 cm⁻¹ (1.44 ± 0.66 kcal mol⁻¹) and 2.13 ± 1.16 cal mol⁻¹ K⁻¹ for ΔH and ΔS , respectively. Both of these values (and their uncertainties) are higher than those obtained from the measurements of the O–H stretching bands. However, there are two factors which probably contribute to these results. The two bands at 2988 and 2945 cm⁻¹ are not as well resolved as those at 3666 and 3626 cm⁻¹, and there appears to be some asymmetry on the high frequency side of the 2945 cm⁻¹ band, which results in the broadening of this band which makes intensity measurements more difficult. It should be mentioned, however, that the *trans* conformer was found to be the more stable form in both studies.

Low frequency fundamentals

Several fundamental vibrations are expected to have frequencies which fall in the region below 700 cm^{-1} . Vibrations which are associated with the

trans conformer, which has C_s point group symmetry, will either be motions which preserve the molecular symmetry plane and therefore belong in the A' symmetry block, or A'' modes which destroy the symmetry plane. The vibrations which belong to the A' symmetry block will give rise to sharp Qbranches in the Raman spectrum of the gas, polarized lines in the corresponding spectrum of the liquid, and type B, C, or B/C hybrid band contours in the IR spectrum of the vapor phase. The A'' vibrations will exhibit very weak, broad lines in the Raman spectrum of the gas, depolarized lines in the Raman spectrum of the liquid, and A-type IR band contours in the vapor phase. The proposed assignment for this region is summarized in Tables 2 and 3 for the O—H and O—D compounds, respectively.

TABLE 2

Observed^a IR and Raman frequencies below 700 cm⁻¹ and their assignment for $(CF_3)_2CHOH$

Infrared		Ram	an	Assignment		
Gas	Relative intensity	Gas	Relative intensity	Liquid	Relative intensity and depolarization	Approximate description
694 R						
689 Q	s	690	vw	689	vw, dp	CF_3 def. A''
685 P						
		612	w	614	m	$\mathbf{CF}_{\mathfrak{z}}$ def. A'
		606	sh			
555 Q	w			549	sh, dp	CF_3 def. A''
539 R						
534 Q	mw			536	vw, dp	CF_3 def. A''
530 P						
523	sh					
517 Q	mw			519	mw	CF_3 def. A'
462 Q	mw					
458 Q	mw	460	m	465	m	CC_2 in-plane wag
356 R					_	~~
351.9 Q	m	350	sh	350	mw, dp	CC ₂ twist
346 P						
$331.7 \ Q$	s					$1 \leftarrow 0 \text{ O} - \text{H torsion},$
						trans conformer
330.6 Q	s	328	S	330	8	CC_2 def.
				299	w, dp	CF_3 rock, A''
294 <i>R</i>						
288.9 Q	ms					$1^{-} \leftarrow 0^{-} O - H$ torsion,
						gauche conformer
285.6 P		0.05		0.45	,	
233	mw, br	235	vw	245	vw, br	CF ₃ rock, A
Z11	w, br	100		100		OF_3 rock, A'
00	1	163	vw	109	vw	OF_3 rock, A
~90	vw, br					OF ₃ torsion

^aAbbreviations used: s, strong; m, medium; w, weak; dp, depolarized; br, broad; sh, shoulder; def., deformation; P, Q, and R refer to vibrational-rotational branches.

TABLE 3

Infrared		Ram	an	Assignment		
Gas	Relative intensity	Gas	Relative intensity	Liquid	Relative intensity and depolarization	Approximate description
693 R					· · · · · · · · · · · · · · · · · · ·	
689 Q 684 P	S	69 0	vw, br	687	vw, dp	CF_3 def. A''
608	vw	608	w	613	mw	CF_{a} def. A'
554 Q 539 R	vs			552	sh, dp	CF_3 def. A''
534 Q	vw			538	vw. dp	CF_{\bullet} def. A''
514	vw			519	W	CF_{\bullet} def. A'
456 Q	w	456	m	464	mw	CC, in-plane wag
355 R						• • •
350.1 Q 347 P	mw	350	sh	348	mw, dp	CC ₂ twist
329 308 R	mw, br	328	s	330	m	CC ₂ def.
301.9 Q	w			299	w. dp	CF, rock A''
266.4 Q	S				···, -r	$1 \leftarrow 0$ O-D torsion, trans conformer
		225	vw	240	vw, br	CF_3 rock, A'
222 R						
215.5 Q	vs					$1^- \leftarrow 0^+$ O—D torsion, gauche conformer
212 P						0
		162	vw	169	vw	CF_3 rock, A'
154 ~90	mw, br vw, br					CF_3 rock, A' CF_3 torsion

Observed^a IR and Raman frequencies below 700 cm⁻¹ and their assignment for $(CF_3)_2CHOD$

^aAbbreviations used: s, strong; m, medium; w, weak; v, very; br, broad; dp, depolarized; sh, shoulder; def., deformation; P, Q, and R refer to vibrational—rotational branches.

In the region below 700 cm⁻¹, normal modes are expected for six CF₃ deformations; four CF₃ rocks; the CC₂ wag (in-plane), twist, and deformation; two CF₃ torsions; and the O–H torsion. Our assignment of the CF₃ deformations, and CC₂ wag and twist is consistent with that previously proposed [2]. Based on sum and difference bands with the O–H stretching mode of the *trans* conformer. Murto et al. [2] previously assigned the CC₂ deformation and O–H torsion to the bands centered at 327 and 287 cm⁻¹, respectively, in the IR spectrum of the gas. In the Raman spectra of both the O–H and O–D species, a band is observed at 329 cm⁻¹ which is the CC₂ deformation. However, there is a significant difference in the relative intensity of this band in the IR spectra of the O–H and O–D compounds (Fig. 1). In the spectrum of the "light" compound, this band is twice the intensity of the CC₂ twist, and is clearly the strongest band in this spectral region. Upon

deuteration of the O-H group, the intensity of this band decreases to the point where it is one of the weakest in this spectral region, the intensity of which varies depending upon the extent of deuteration. The higher resolution spectrum of the "light" compound obtained in this study shows this band to be composed of at least two overlapping bands, one with a minimum around 329 cm^{-1} , and the second exhibiting a Q-branch at 331.7 cm^{-1} with a series of hot bands falling to higher frequency. This band appears to shift down in frequency upon deuteration of the O-H group which accounts for the decreased intensity of this band in the spectrum of the O–D compound. A new band is observed in the spectrum of the "heavy" compound at 266.4 $\rm cm^{-1}$ which exhibits a Q-branch series similar to the 331.7 cm⁻¹ band in the spectrum of the "light" compound. This band at 266.4 cm⁻¹ has previously been assigned as a CF_2 rocking mode [2], but the fact that it is not observed in the spectrum of the "light" compound suggests that it may be a different fundamental. Since only the O-H torsion (in the low frequency region) should show any appreciable shift upon deuteration of the hydroxyl group. we have assigned the bands at 331.7 and 266.4 cm⁻¹ as the $1 \leftarrow 0$ transitions of the asymmetric torsion of one conformer for the O-H and O-D rotors. respectively. Likewise, we have assigned the band at 288.9 cm⁻¹ in the spectrum of the "light" compound, which shifts to 215.5 cm⁻¹ upon deuteration of the hydroxyl group, as the $1 \leftarrow 0$ transition of the asymmetric torsion of the second conformer. Since the variable temperature study indicates that the *trans* conformer is more stable in the gaseous phase, we have assigned the 331.7 cm⁻¹ band to this conformer and the 288.9 cm⁻¹ band to the gauche conformer. Additionally, the broad band observed at 211 cm⁻¹ in the IR spectrum of the "light" compound, which appears to shift to 154 cm^{-1} upon deuteration of the hydroxyl group, was tentatively assigned as the $1^+ \leftarrow 0^$ transition of the asymmetric torsion of the gauche conformer; this assignment was eventually discarded.

Our assignment of the two $A' \operatorname{CF}_3$ rocking modes and one of the A'' rocking modes is consistent with that of Murto et al. [2]. The remaining $A'' \operatorname{CF}_3$ rock was eventually assigned to the 211 cm⁻¹ band in the light compound. The broad band at 154 cm⁻¹ in the O–D spectrum was assigned to the $A' \operatorname{CF}_3$ rock of the *gauche* conformer. A very broad band is observed in both IR spectra near 90 cm⁻¹. We have assigned this band as one of the CF₃ torsional modes, although both CF₃ torsions may lie in this region of the spectrum. However, one would expect potential and kinetic coupling between the rotors so that the two CF₃ torsions are expected to have significantly different frequencies.

As an aid in the assignment of the low frequency fundamentals, the IR spectrum of 1,1,1,3,3,3-hexafluoro-2-propanol in the OH stretching region was observed in the vapor phase at various concentrations and shows several distinctive bands on either side of the *trans* and *gauche* OH stretching fundamentals (Fig. 4). At higher concentrations, a broad featureless band is observed centered at ca. 3400 cm⁻¹.

These satellite bands have been assigned as sum and difference modes of the monomer OH stretches associated with the low frequency fundamentals. As a result, it was felt that an investigation of these side bands would clarify the assignment of the low frequency fundamentals.

Barnes et al. [1, 15] reported the observation of a few of these bands for 1,1,1,3,3,3-hexafluoro-2-propanol, although the spectra were poorly resolved and little conclusive information was gained. It was also reported [15] that similar sum and difference bands were observed for 2,2,2-trifluoroethanol, ethanol and similar alkanols. These authors also noticed a broad featureless band in the difference region at high concentrations and attributed it to the OH absorption of the dimer compound.

The majority of the sum and difference modes are shown to be associated with the gauche OH stretch at 3665 cm⁻¹ (Fig. 5) and are assigned on this basis (Table 4). Eleven of the low frequency fundamentals are identified in this manner, the resulting calculated frequencies of these modes indicating vibrational fundamentals of the gauche conformation. This conclusion is drawn from the disparity between the observed low frequency vibrations and the frequencies calculated from the sum and difference spectra.

Obviously, any sum and difference modes arising from an association with the OH stretching of the *trans* conformer must agree quite closely with the observed low frequency vibrations. As shown in Table 5, the $1 \leftarrow 0$ trans OH torsion was the only fundamental associated with the *trans* OH stretch that fulfilled this criterion. The bands observed at 3913, 3872, 3340 and 3384 cm⁻¹ have approximately equal spacing around the *trans* OH stretch but the calculated fundamentals do not agree as well with the proposed A''CF₃ rock at 299 cm⁻¹ nor the A' CF₃ rock at 233 cm⁻¹; see Table 5. It should be noted, however, that the sum and difference bands are rather broad and the assigned frequencies may be ± 5 cm⁻¹. These assignments also support the

TABLE 4

Transition	νi	^v sum	$\nu_{sum} - \nu_{OH}$	^ν diff	$\nu_{\rm OH} - \nu_{\rm diff}$
CF ₃ def. A"	689	4302	637	3019	646
CF, def. A'	612	4254	589	3075	590
CF_3 def. A'' CF_3 def. A''	555 5 34	4193	528	3124	541
CF_{1} def. A'	517	4135	470	3184	481
CC_2 in-plane wag	460	4095	430	3235	430
CC ₂ twist	351.9	4025	360	3298	367
CC ₂ def.	330.6	3977	312	3340	325
CF ₃ rock, A'	233	3913	248	3405	260
CF_3 rock, A''	211	3873	218	3459	206
CF ₃ rock, A'	163	3813	148	3513	152
CF ₃ τ	90	3758	93	3570	95

Sum and difference bands of 1,1,1,3,3,3-hexafluoro-2-propanol associated with the gauche OH stretch (3665 cm⁻¹)

Transition	νi	^v sum	$\nu_{sum} - \nu_{OH}$	^ν diff	^v OH ^{- v} diff
τ_{OH} trans, $1 \leftarrow 0$	331.7	3957	330	3298	329
CF_{a} rock A''	299	3913	285	3340	287
CF_3 rock A'	233	3872	246	3384	243

Sum and difference bands of 1,1,1,3,3,3-hexafluoro-2-propanol associated with the *trans* OH stretch (3627 cm⁻¹)

greater intensity of the sum and difference bands associated with both conformers as compared to the bands associated with only one conformer.

A number of side bands were also observed in the spectrum of the O–D isotope but were quite distorted by the C–H stretching fundamentals. As a result, no conclusive identification of these particular sum and difference modes could be reached, and this information was not utilized.

Barriers to internal rotation

A potential function for the asymmetric torsion was calculated based on the assignment of the fundamental torsional transitions at 331.7 and 288.9 cm⁻¹ for the *trans* and *gauche* conformers, respectively. Using the structural parameters utilized by Murto et al. [2] and Truax et al. [3], the reduced internal rotation constant was calculated as a function of the angle of internal rotation, α , by

$$F(\alpha) = F_{\theta} + \sum_{i=1}^{6} F_i \cos i\alpha$$

where α is defined as zero for the *trans* conformer. The observed frequencies were fitted to a potential function varying in α as

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

by supplying values for the V_1 , V_2 , and V_3 potential coefficients only. Several iterations of the potential coefficients were performed to minimize the difference between the observed and calculated frequencies; a satisfactory fit was achieved without resorting to the V_4 , V_5 or V_6 potential coefficients. A similar calculation was performed for the "heavy" compound using the 266.4 and 215.5 cm⁻¹ bands as the fundamental torsional transitions of the trans and gauche conformers, respectively. In these calculations, the gauche transition was input as a $1^- \leftarrow 0^+$ transition. Initially, the transitions for each conformer were input, and values for V_3 and V_2 were calculated. However, the calculated value for ΔH was 185 cm⁻¹, which is slightly below the lower limit of uncertainty for the experimentally measured ΔH . The inclusion of the 211 cm⁻¹ band as the $1^+ \leftarrow 0^-$ gauche transition drove the ΔH increasingly

TABLE 6

(CF ₃) ₂ CHOH		(CF ₃) ₂ CHOD		
Coefficient Value		Coefficient	Value	
	-117	V,	-186	
V,	396	V,	453	
V.	657	V_3	780	
ΔH	150	ΔH	150	
Barrier		Barrier		
trans/gauche	937	trans/gauche	1085	
gauche/gauche	360	gauche/gauche	430	

Calculated potential coefficients and barriers (cm⁻¹) for the asymmetric torsion

downward. For this reason, the ΔH was held at 150 cm⁻¹. Subsequent calculations included this fixed value for ΔH and a V_1 potential coefficient. The final calculated values for the potential coefficients and the gauche/gauche and trans/gauche barrier heights are listed in Table 6 for both the O-H and O-D potential functions.

Coupling of the two CF₃ rotors would result in two bands in the IR spectrum, but only one broad band is observed around 90 cm⁻¹. A threefold periodic barrier to internal rotation was calculated assuming that the two CF_3 rotors are at least kinetically coupled. Utilizing the theoretical treatment given by Groner and Durig [16] for two coupled C_{3v} rotors where the frame has a plane of symmetry, the internal Hamiltonian for the $C_{3v}(T)-C_s(F)$ - $C_{3v}(T)$ semi-rigid model (T = top, F = frame) is $H_{I} = (1/2)(g^{44}\hat{p}_{0}^{2} + 2g^{45}\hat{p}_{0}\hat{p}_{1} + 2g^{45}\hat{p}_{0}\hat{p}_{1})$ $g^{55}\hat{p}_1^2$ + $V(\tau_0, \tau_1)$ where the potential energy term of $V(\tau_0, \tau_1)$ is in standard form. From the structural parameters previously given, the g^{44} (g^{55}) is calculated to have a value of 0.60765 cm^{-1} and the g^{45} term is -0.18088 cm^{-1} . With a value of 88 cm^{-1} for one of the CF₃ torsional modes, an upper limit of 7.2 kcal mol⁻¹ is calculated for the barrier to internal rotation. Assuming the two torsional modes are split by 10 cm⁻¹ results in a barrier of 5.8 kcal mol⁻¹ whereas a splitting of 20 cm⁻¹ gives a barrier of 5.3 kcal mol⁻¹. Certainly some splitting is expected so we estimate that the CF_3 internal rotational barrier is in the range of 5–6 kcal mol⁻¹.

DISCUSSION

The calculated barrier to internal rotation for the CF₃ rotors is rather high. The assignment of the CF₃ torsion, however, is consistent with other assignments of perfluoromethyl torsions. In 2,2,2-trifluoroethylmethyl ether [17] and 2,2,2-trifluoroethanol [8], the CF₃ torsions were observed at 102 and 106 cm⁻¹, respectively. The F number, $h^2/8\pi^2 I_r$ where I_r is the reduced moment of inertia for internal rotation, which is $g^{44}/2$ shows a significant variation depending on the mass of the substituents on the frame and the relative orientation of the CF₃ rotor. In 2,2,2-trifluoroethanol [8] and trans-2,2,2-trifluoroethylmethyl ether [17] the calculated F numbers are 1.116 cm⁻¹ and 0.918 cm⁻¹, respectively. However, the calculated F number for the gauche form of 2,2,2-trifluoroethylmethyl ether is 0.442 cm⁻¹. We also considered that the broad band observed in this study at 90 cm⁻¹ could be an overtone of the CF₃ torsion, but no band was observed around 40-50 cm⁻¹ which could be assigned as the fundamental. The resulting barrier of 5–6 kcal mol⁻¹ is significantly higher than those reported for 2,2,2-trifluoroethylmethyl ether [17] which are 3.72 and 3.78 kcal mol⁻¹, respectively. However, the addition of the second CF₃ rotor is expected to significantly raise the barrier but it is not possible to predict the amount. The barriers to internal rotation for two CF₃ groups attached to the same carbon atom have not been determined. Therefore, such a study would be of interest to determine the effect of adding a CF₃ rotor to the same carbon atom which already has one CF₃ rotor attached.

The possibility that the assignment of the bands at 331.7 and 288.9 cm⁻¹ to the trans and gauche conformers should be reversed was considered. This assignment would imply that the gauche conformer is more stable, unless the gauche well in the potential function was extremely narrow and the trans well very broad. Assuming the gauche conformer to be the more stable form, a potential function was calculated in the same manner as described earlier based on the above assignment. The final values calculated for the potential coefficients were -159, -143 and 782 cm⁻¹ for the V_1 , V_2 and V_3 terms, respectively. The resulting barrier heights were 849 and 867 cm^{-1} for the gauche/gauche and gauche/trans barriers, respectively. A similar calculation for the O-D compound, using the bands at 266.4 and 215.5 cm^{-1} , resulted in significantly different values for the potential coefficients and the barrier heights as well. The final values for the potential coefficients were 220, -492 and 888 cm⁻¹ for the V_1 , V_2 and V_3 terms, respectively. The calculated values for the gauche/gauche and gauche/trans barrier heights were 1348 and 823 cm⁻¹, respectively. This assignment was rejected because of the unrealistic differences in the calculated barriers for the isotopic species as well as the requirement that the assignment of the O-H stretching modes be interchanged.

Based on the assignment proposed in this study, the calculated potential functions for the internal rotation of the O-H and O-D groups show significant agreement. The calculated gauche/gauche barrier height is approximately 20% lower, and the trans/gauche barrier height 16% lower, in the potential function for the O-H group as compared to the O-D group. This result is caused by the minor differences in the V_1 and V_2 potential coefficients, which were necessary to accommodate the different shift factors for the O-H torsion upon deuteration for the two conformers. If either the 1.25 or 1.34 shift factor for the trans and gauche conformers is assumed for the other conformer, no suitable bands are observed in the spectra.

A series of potential functions were calculated including the 211 cm⁻¹ band

as the $1^+ \leftarrow 0^-$ transition of the gauche O—H torsion. It was observed that a potential function including this transition required a much lower ΔH and high gauche/gauche barriers. In view of this fact, the 211 cm⁻¹ band was assigned to the A'' CF₃ rock and the final potential function was calculated using only the transitions at 331.7 and 288.9 cm⁻¹. The resulting potential function of the O—H compound also agreed with the final potential function of the O—D isotope, a discussion of which follows.

If the shift factor of 1.34, as found for the $\Gamma \leftarrow 0^+$ transition upon deuteration, is assumed for the 211 cm⁻¹ of the "light" compound, a band at 157 cm⁻¹ is calculated for the "heavy" compound. Thus, the potential function for the O-D compound was also calculated with the inclusion of a $1^+ \leftarrow 0^-$ transition corresponding to 154 cm⁻¹ in the far-IR spectrum of $(CF_3)_2CHOD$. This resulted in unacceptable values for the ΔH and the gauche/gauche barrier heights of the "heavy" compound, however, and this transition was not included in the final calculations.

Thus, the band at 154 cm^{-1} in the spectra of the O–D compound is assigned to the $A' \text{ CF}_3$ rock of the *gauche* conformer, the band being intensified in the O–D compound due to mixing with the *gauche* O–D torsional mode. These were tentative conclusions, at best, and could not be confirmed either way as the confirmation offered by sum and difference modes could not be extended to the "heavy" compound.

There are a number of possible sources of error in these potential function calculations. The "F series" has a critical dependence on the initial structural parameters (bond lengths, angles and dihedral angles) used, and in the case of this molecule where no overall structural determination has been reported, these values are taken from similar molecules. Additionally, it is also quite possible that there may be some structural relaxation as the torsional angle changes, which implies that more structural parameters than just the dihedral angle change in going from the *trans* to the *gauche* conformer. Indeed, positive adjustments of 10% to the "F series" increased the calculated ΔH towards the experimental values. However, because more extensive structural data were not available for this molecule, the structural parameters for both conformers were assumed to be the same.

Finally, it is difficult to propose a unique assignment of all of the low frequency fundamentals based on gas phase data alone. However, data obtained in the liquid and solid phases are of little value for identifying torsional fundamentals because dimer formation causes a dramatic shift in these frequencies, which makes correlation with data taken in the vapor phase impossible. Furthermore, the calculation of an asymmetric potential function for the rotation of a hydroxyl group is very difficult. Generally, the observation of more than one torsional transition for each conformer increases the accuracy of the calculated potential function [18]. When considering alcohols, this is not likely to be the case, because the F numbers are very large and the frequencies of the torsional fundamentals are quite high with relatively low barriers. Because of these effects, the spacing between successive energy levels within a given potential well are very large, which results in only two or three energy levels being localized below the top of the barrier. Due to the lack of multiple torsional transitions, we have discussed alternative assignments which were considered but finally rejected. Further studies on 1,1,1-trifluoro-2-propanol, ethanol, 2,2,2-trifluoroethanol, and 2-propanol are currently in progress in our laboratory in an effort to determine the barriers to internal rotation for their respective rotors.

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