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INFRARED AND RAMAN SPECTRA OF PENTAFLUOROPROPIONIC ACID

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SUMMARY

Infrared and Raman spectra have been obtained for CF_3CF_2COOH showing the acid to be completely associated in the liquid state at room temperature, but partially dissociated in the vapor state. All the carboxyl group vibrational frequencies differ in the associated and monomeric forms, but all other frequencies are the same in both forms. The stronger hydrogen bonding in this acid as compared to CF_3COOH indicates group electronegativities in the order of $CF_3 > CF_3CF_2$.

INTRODUCTION

The interpretation of the vibrational spectra of trifluoroacetic acid has been the subject of several papers [1-3]. It has been shown that this compound exists predominantly as the hydrogen-bonded dimer in the liquid state at room temperature, although there is some monomer present, and that the vibrational frequencies of the COOH group (O–H stretch, C=O stretch, C–O stretch, O–H in-plane deformation, O–H out-of-plane deformation, and O–C=O deformation) are different in the associated and monomeric forms. In the vapor state at room temperature the associated form is slightly predominant, but at 100° the acid is present mainly in the monomeric form.

Infrared and Raman spectra have been obtained for pentafluoropropionic acid to compare the associative behavior of that compound with trifluoroacetic acid, and to study the effect of hydrogen bonding on the vibrational frequencies. Substitution of a CF_3 group for F in CF_3COOH may change the strength of the hydrogen bond and the carboxyl group frequencies because of the difference in electronegativities of the CF_3 and CF_3CF_2 groups.

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EXPERIMENTAL

The sample of pentafluoropropionic acid (PFPA) was obtained from PCR, Inc., and was used without further purification. The infrared spectra were obtained with a Beckman IR-12 spectrophotometer, and the Raman spectrum was obtained with a Jarrell–Ash 25-100 dual monochromator photon-counting spectrometer by Dr. J. Paul Devlin.

RESULTS AND DISCUSSION

Infrared spectra of PFPA in the vapor state as determined at 30° and 75° are shown in Figure 1. The wavenumbers are listed in Table 1, including liquid-state infrared and Raman values. The liquid-state infrared spectrum shows only one carbonyl stretching band and a broad O–H stretching band indicative of hydrogen bonding, whereas there are two carbonyl bands and two O–H stretching bands present in the vapor-state spectra. The frequency and sharpness of the vapor-state band at 3579 cm^{-1}, which is completely absent in the spectrum of the liquid, identifies it as the O–H stretch of the free molecule. Therefore, PFPA exists completely in the associated form in the liquid state at room temperature. However, enough heat is absorbed on vaporization at room temperature that a little less than one-half (comparing the C=O band intensities) of the dimer dissociates.

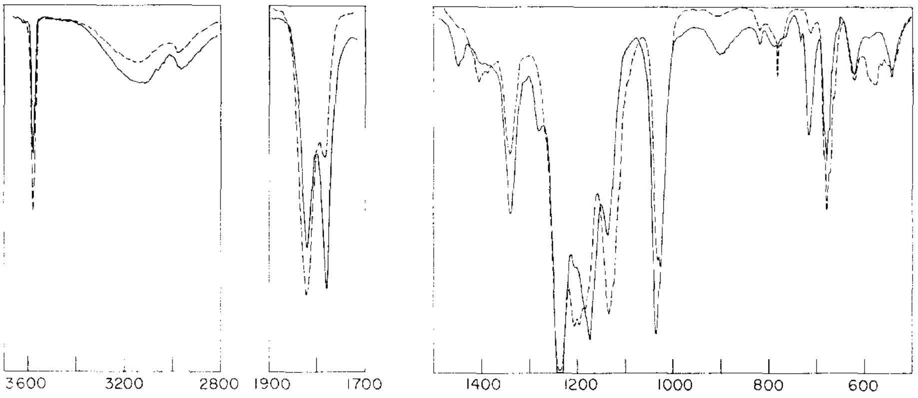

Fig. 1. Infrared spectra of pentafluoropropionic acid vapor. Solid curve at 30°; dashed curve at 75°. Abscissa in cm^{-1}; ordinate in per cent transmittance.

Vibrational assignments; carboxyl group frequencies

The O–H stretching frequency of the associated and monomeric forms of PFPA can be assigned with certainty to the bands observed at *ca.* 3150 cm^{-1} (associated) and 3579 cm^{-1} (monomeric), with the band due to the associated form being very broad. These values are in good agreement with the corresponding frequencies[1] in CF_3COOH (TFAA), at 3134 and 3587 cm^{-1}.

TABLE 1

INFRARED AND RAMAN SPECTRA (cm^{-1}) OF CF_3CF_2COOH

IR(vap.)	IR(liq.)	R(liq.)	Form	IR(vap.)	IR(liq.)	R(liq.)	Form
3579			m	782			m
3150	$\sim$3180		a	716	715		a
1822			m		705	698	a
1783	1778	$\sim$1745	a	678			m
1450	1445	1441	a	620			m
1405			m	580	582		m,a
1340	1337	1343	m,a	545	543	540	m,a
1280	$\sim$1270		a	456	444		m,a
1237	1228	1225	m,a	400	400	407	m,a
1205	1200		m,a	388	388	379	m,a
1196			m,a			354	m ?,a
1176	1165		a	288	297	290	m,a
1135			m			264	m ?,a
1028	1034	1034	m,a	225	227		m,a
900	900		a			169	a
817	800	780	m,a				

m = monomer, a = associated.

The C=O stretching frequencies can also be assigned without ambiguity to the bands observed at 1783 cm^{-1} (associated) and 1822 cm^{-1} (monomer). The C–O stretching frequencies of PFPA can be assigned by analogy with TFAA to the bands at 1450 cm^{-1} (a) and 1405 cm^{-1} (m).

The O–H in-plane bending vibration can be assigned to the bands at 1280 cm^{-1} (a) and 1135 cm^{-1} (m). In TFAA, these vibrations are assigned to bands at 1297 and 1122 cm^{-1}, respectively. The O–H out-of-plane bends (torsions) can be assigned to bands at 900 cm^{-1} (a) and 782 cm^{-1} (m).

The remaining fundamental vibration of the carboxyl group that was assigned is the O–C=O deformation, which can be assigned to bands at 716 cm^{-1} (a) and 678 cm^{-1} (m) in PFPA.

Infrared spectra of PFPA in the vapor state were determined at several temperatures up to 90°. At that temperature, the dimer is perhaps 80–85% dissociated and the intensities of the infrared bands assigned in this section to the associated form (1783, 1450, 1280, 900, and 716 cm^{-1} respectively) decrease as the temperature increases, and are very weak or absent in the 90° spectrum. At the same time, the intensities of the other bands, assigned to the monomer, increase as the temperature increases, as shown in Figure 1. Some of the bands due to both forms have a lower intensity at the higher temperature because the overall absorption was lower.

It can be seen from Table 1 that only the frequencies assigned to vibrations of the carboxyl group differ in the associated and monomeric forms. This is also true for most of the vibrations of TFAA, with the exception of two of the CF_3

deformations[1]. However, these assignments are questionable, and the only low-frequency band assignable separately to the two forms may be the C–CO_2 out-of-plane bend which was not assigned. Table 2 lists the frequencies of the carboxyl group that were assigned for PFPA and TFAA.

TABLE 2

CARBOXYL GROUP FREQUENCIES (cm^{-1}) OF CF_3COOH AND CF_3CF_2COOH

CF_3COOH*	CF_3CF_2COOH	Assignment
3587	3579	O–H stretch, m
3134	3150	O–H stretch, a
1830	1822	C=O stretch, m
1792	1783	C=O stretch, a
1466	1450	C–O stretch, a
1415	1405	C–O stretch, m
1297	1280	O–H in-plane bend, a
1122	1135	O–H in-plane bend, m
903	900	O–H out-of-plane bend, a
781	782	O–H out-of-plane bend, m
706	716	O–C=O bend, a
665	678	O–C=O bend, m

* From ref. 1.
m = monomer, a = associated.

It is interesting to note that only for the O–H and C=O stretching vibrations does the monomer have a higher frequency than the dimer. In every case except the C=O stretch, the difference between frequencies of the two forms is greater for TFAA. For both acids, this difference is greater for vibrations that involve the hydrogen atom.

Cullen, Sams and Waldman have suggested from the results of their Mössbauer studies that the electronegativity of the CF_3 group is less than that of the CF_3CF_2 group[4]. If this is true, we might expect the carbonyl bond in CF_3CF_2COOH to possess a little more double-bond character than in CF_3COOH, which would decrease the strength of the hydrogen bond. However, the hydrogen bond must certainly be stronger in PFPA than in TFAA because PFPA is completely associated in the liquid state at room temperature and TFAA is partially dissociated. A 1% solution of PFPA in the non-polar solvent CS_2 is only about 20% dissociated.

If the order of electronegativities is $CF_3 > CF_3CF_2$, the carbonyl bond in PFPA would have a little less double-bond character than in TFAA, and this would explain the relative strengths of the hydrogen bonding in the two compounds. It would also explain the fact that the carbonyl frequency in PFPA is lower than in TFAA.

Skeletal frequencies

The C–F stretching frequencies are normally assigned to intense infrared bands that lie in the 1100–1300 cm^{-1} region, but the CF_3CF_2 group gives rise to a band near 1350 cm^{-1} [5]. The two C–C stretching modes can only be assigned to the infrared liquid-state bands at 1034 and 800 cm^{-1} for both associated and monomeric forms of PFPA. The assignment of the 800 cm^{-1} band is verified by the high intensity of the corresponding Raman band, which is highly polarized.

No attempt has been made to assign the skeletal bending vibrations to bands in the region below 700 cm^{-1} because of the uncertainty in such an assignment and because the normal modes are very likely highly mixed. However, the 169 cm^{-1} Raman band can be assigned to a stretching vibration involving the hydrogen bond (O——H).

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