

# Dimerization of Carboxylic Acids and Salts: An IR Study in Perfluoropolyether Media

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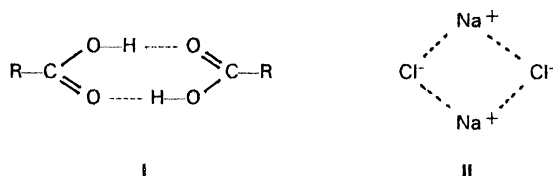
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**Abstract:** It was found that perfluoropolyethers (PFPE) with carboxylic acid end groups, PFPE-COOH, and their sodium salts, PFPE-COONa, afford an anhydrous fluid medium in which the direct pair-wise interaction of these end groups may be examined. An IR study (of the carbonyl band) of these materials revealed not only the dimerization of acid units, but also the formation of salt dimers, (salt)<sub>2</sub>, and *mixed dimers*, (acid)(salt). The carbonyl spectra of PFPE-acid/salt mixtures exhibit temperature-dependent broadening, shift, and, in some cases, coalescence of the bands which are attributed to the *pseudocoalescence phenomenon* stemming from the presence of relatively low energy cation exchange passages among the three possible dimers. Examination of the corresponding CH<sub>3</sub>COOH/CH<sub>3</sub>COONa system by ab initio calculations (6-31G) yielded the heat of dimerization of ~20, ~50, and ~35 kcal/mol for the acid–acid, the salt–salt, and the acid–salt dimers, respectively. The calculated dimer structures are shown and discussed. The calculations also yielded the carbonyl stretching frequencies in good accord, and in support of the analyses/postulates made for the PFPE-acid/salt system.

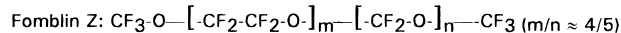
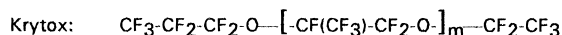
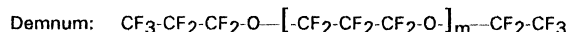
## Introduction

It is well-known that (organic) carboxylic acids, R-COOH, in a fluid state (liquid or vapor) primarily exist in the hydrogen-bonded dimeric form, **I**.<sup>1</sup> It is also well-known that the vapor phase in equilibrium with solid NaCl at elevated temperature ( $T \geq 500$  °C) is dominated by the dimeric species, **II**.<sup>2</sup> The formation and stability of the latter are attributed to the pair-wise Coulombic interaction of the constituent ions.



The heat of dimerization for the acetic acid dimer has been measured to be 15 kcal/mol,<sup>3,4</sup> and that for (NaCl)<sub>2</sub> to be 48 kcal/mol.<sup>5</sup> On account of experimental difficulties, the corresponding pair-wise interaction between salt molecules of carboxylic acid, e.g. CH<sub>3</sub>COONa, has not been reported.

Perfluoropolyethers (PFPEs) are currently in use as lubricants in a variety of high-performance applications. PFPEs are commercially available in several distinct structural forms. Representative formulae of such PFPEs known by the brand names Demnum, Krytox, and Fomblin Z, respectively, are as follows.



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<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, October 1, 1997.

(1) Karle, J.; Brockway, L. O. *J. Am. Chem. Soc.* **1944**, *66*, 574.

(2) Miller, R. C.; Kusch, P. *J. Chem. Phys.* **1956**, *25*, 860.

(3) Taylor, M. D. *J. Am. Chem. Soc.* **1951**, *73*, 315.

(4) Weltner, W. Jr. *J. Am. Chem. Soc.* **1955**, *77*, 3941.

Krytox is made by base-catalyzed polymerization of hexafluoropropylene oxide.<sup>6</sup> Demnum is made similarly but starting with 2,2,3,3-tetrafluorooxetane; the hydrogen atoms in the resulting polymers are replaced by fluorine atoms by subsequent contact with F<sub>2</sub> in solution.<sup>7</sup> Fomblin Z is synthesized by photooxidation of tetrafluoroethylene and is a linear, random copolymer of ethylene oxide and methylene oxide units as indicated.<sup>8</sup> PFPE fractions employed in lubricant applications have molecular weight of 2000–10000 corresponding to the number of monomer units in each chain of 12–60.

All of the PFPEs listed above are also available with carboxylic acid end groups. The excellent lubricity of PFPEs stems partly from their exceptionally weak intermolecular cohesive force. The weakness of such interaction is evidenced in the fluid range persisting from the decomposition point (ca. +400 °C) down to –100 °C. Also, abundantly present ethereal oxygen notwithstanding, PFPEs are extremely hydrophobic and are soluble only in Freon or other highly fluorinated solvents. It follows that PFPEs with carboxylic end groups may provide an anhydrous fluid medium wherein the naked, pair-wise interaction of not only the carboxylic acid group, RCOOH, but also the corresponding salt group, RCOO<sup>–</sup>M<sup>+</sup>, may be examined.

We report here the result of our IR study (of the carbonyl band) of PFPEs with carboxylic acid end groups and their Na salts. The study revealed the following: (1) Long, perfluorinated polyether chains notwithstanding, PFPEs with carboxylic acid end groups and their Na salts both exist in the dimeric form at ambient condition. (2) In a mixture of PFPE acid and salt, the mixed dimer (RCOOH)(RCOO<sup>–</sup>M<sup>+</sup>) is also formed. (3) The IR carbonyl bands of PFPE acid/salt mixtures exhibit temperature dependent shift, broadening, and (partial) coalescence. The latter result uniquely observed from the mixture is ascribed to the *pseudocoalescence phenomenon*<sup>9</sup> stemming from

(5) Bauer, S. H.; Diner, R. M.; Porter, R. F. *J. Chem. Phys.* **1958**, *29*, 991.

(6) Gumprecht, W. H. *ASLE Trans.* **1966**, *9*, 24.

(7) Ohsaka, Y. *Petrotech (Tokyo)* **1985**, *8*, 840.

(8) Sianesi, D.; Pasetti, A.; Fontanelli, R.; Bernardi, G. C.; Caporiccio, G. *Chim. Ind.* **1973**, *55*, 208.

the presence of relatively low energy cation exchange passages among the three possible dimers.

We also report here the result of theoretical examination of the dimerization of carboxylic groups. Ab initio SCF calculations (6-31G) were performed for monomers and dimers of the  $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$  system. The calculations predicted the heat of dimerization of  $\sim 20$ ,  $\sim 50$ , and  $\sim 35$  kcal/mol for the acid–acid, the salt–salt, and the acid–salt dimers, respectively. The calculations also revealed that, while the acid dimers are indeed formed through hydrogen bonding, the salt dimers are formed by Coulombic interactions of charged constituents. The ab initio calculations also yielded the carbonyl stretching frequencies of the monomers and the homo- and mixed-dimers in good accord and in support of the analyses/postulates made for the PFPE carboxylic system.

### Experimental Sections and Computational Method

PFPEs with carboxylic acid end groups, Demnum-SH, Krytox-H, and Fomblin Z-DIAC, were obtained from Daikin Industries of Japan, DuPont Co. of the United States, and Montefluos S.p.A. of Italy, respectively. The  $^{19}\text{F}$  NMR analyses yielded the number-averaged molecular weight of  $\sim 3000$  for Demnum-SH,  $\sim 5000$  for Krytox-H, and  $\sim 2000$  for Z-DIAC. In Demnum-SH and Krytox-H the acid end group is present only at the propagation end (the ethoxy side) of the chain. Fomblin Z-DIAC has acid end groups at both ends. The structural formulae of the acid terminal units are:



Hereinafter, for the sake of brevity, the notations D-COOH, K-COOH, and Z-COOH will be used to denote these PFPEs with acid end groups.

The Na salts of the PFPE acids were prepared as follows: (1) Equal weights (5 g) of PFPE acid and 5 M NaOH solution were vigorously shaken until uniform gelation was complete. (2) The emulsion was transferred into a separatory funnel containing trifluoroethanol and methanol (5 g each). (3) From the mixture in the separatory funnel, PFPE-COONa was extracted with a chlorine-free fluorocarbon solvent FC72 (of 3M Corp.). (4) Upon evaporation of the solvent, PFPE-COONa was obtained with  $\sim 100\%$  purity and  $\sim 95\%$  yield. The Na salts of PFPE acids thus obtained are much more viscous than the starting acids.

The IR spectra were obtained with an IBM IR/44 FTIR spectrometer. The PFPE samples were smeared over a NaCl window or, for variable temperature experiments, sandwiched between two NaCl plates which were imbedded in a heatable metal block. Unless mentioned otherwise, the reported spectra are those obtained at room temperature.

The ab initio calculations were performed on IBM RS/6000 work stations using a chemical computation package, Mulliken.<sup>10</sup> The 6-31G basis set was used. Pacansky et al. reported earlier that the vibrational spectra (frequencies and intensities) of model (short) PFPE molecules computed with the 3-21G basis set were in reasonable agreement with the observed spectra.<sup>11</sup>

### IR Spectra and Analyses

(a) **PFPE Acids, the OH Band.** The IR spectrum ( $4000\text{--}500$   $\text{cm}^{-1}$ ) observed from D-COOH is shown in Figure 1. A series

(9) Wood, K. A.; Strauss, H. L. *J. Phys. Chem.* **1990**, *94*, 5677 and references cited therein.

(10) Mulliken is a computational quantum chemistry program for the calculation of molecular structure, property and reactivity, developed at Almaden Research Center, IBM Research Division, San Jose, California by Rice, J. E.; Horn, H.; Lengsfeld, B. H.; McLean, A. D.; Carter, J. T.; Replogle, E. S.; Barnes, L. A.; Maluendes, S. A.; Lie, G. C.; Gutowski, M.; Rudge, W. E.; Sauer, S. P. A.; Lindh, R.; Anderson, K.; Chevalier, T. S.; Widmark, P. O.; Bouzida, D.; Pacansky, G.; Singh, K.; Gillan, C. J.; Carnevali, P.; Swope, W. C.; Liu, B.

(11) Pacansky, J.; Miller, M.; Hatton, W.; Liu, B.; Schoiner, A. *J. Am. Chem. Soc.* **1991**, *113*, 329.

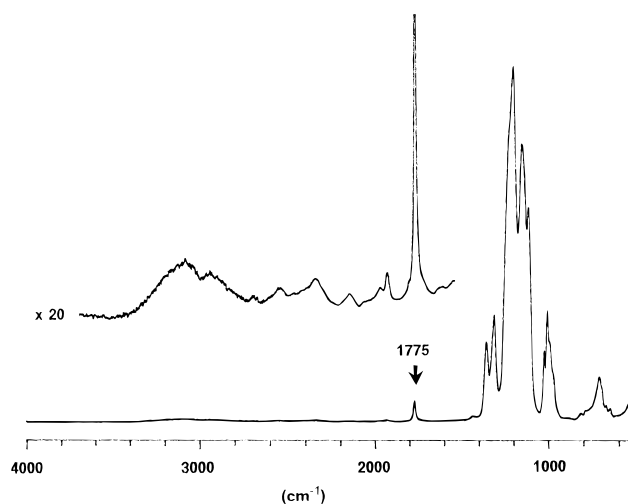


Figure 1. An IR spectrum of D-COOH.

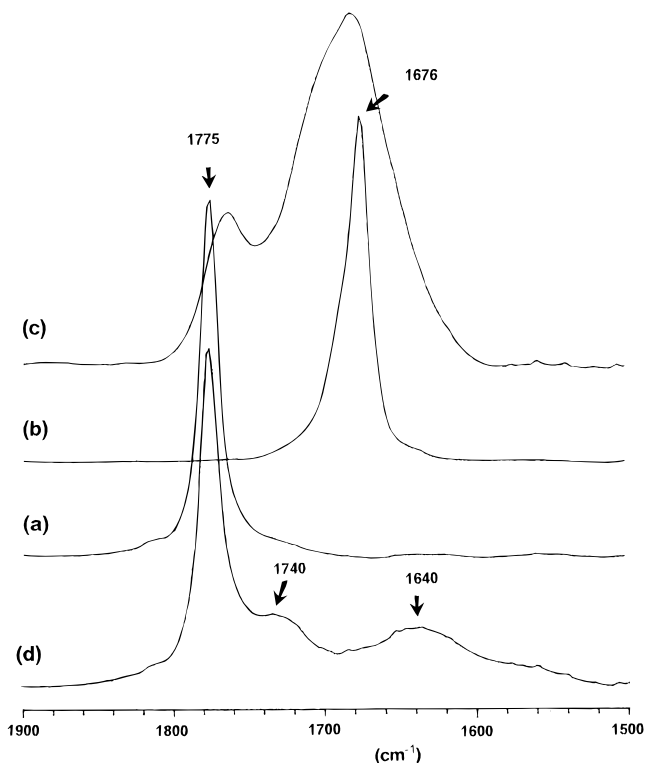
of strong bands in the  $1400\text{--}900$   $\text{cm}^{-1}$  range are due to C–F stretch and other modes involving skeletal atoms.<sup>11</sup> The carboxylic acid units give rise to the carbonyl band at  $1775$   $\text{cm}^{-1}$ , and the OH band broadened across the  $3500\text{--}2500$   $\text{cm}^{-1}$  range. A carboxylic acid of monomeric form is known to give a sharp band at  $\sim 3600$   $\text{cm}^{-1}$ . The contour of the broad OH band observed here is exactly the same as that reported earlier for cyclic dimers **I** of  $\text{CF}_3\text{COOH}$ .<sup>12</sup> Broad OH bands of essentially identical contours were also observed from K-COOH and Z-COOH. It is thus concluded that, long perfluorinated polyether chains notwithstanding, the carboxylic ends of PFPE acids all exist in the hydrogen bonded dimeric form **I**.

(b) **D-COOH and D-COONa, the Carbonyl Band.** Spectra a and b in Figure 2 show the carbonyl sections ( $1900\text{--}1500$   $\text{cm}^{-1}$ ) observed from D-COOH and D-COONa, respectively. The carbonyl band of D-COOH at  $1775$   $\text{cm}^{-1}$  thus shifts to  $1676$   $\text{cm}^{-1}$  on conversion to the Na salt. We then prepared an intimate, equimolar mixture of D-COOH and D-COONa (by dissolution in solvent FC72, followed by solvent evaporation). The spectrum (the carbonyl section) observed from the mixture is shown in Figure 2c. It is clearly not a superposition of the bands of the constituents; it comprises two bands which are much broader than those of the constituents and are shifted inward. The anomalous pattern of the mixture might be ascribed to shifts in the monomer–dimer equilibrium (of both the acid and salt forms). However, the carbonyl band of the acetic acid monomer has been observed at  $31$   $\text{cm}^{-1}$  above that of the dimer species.<sup>4</sup> Since the band at  $1775$   $\text{cm}^{-1}$  observed from neat D-COOH (Figure 2a) is that of the dimer, it is unlikely that the anomalous, inward-shifted pattern of the mixture can be accounted for by the equilibrium shifts.

We examined concurrently the  $^{19}\text{F}$  NMR spectra of the D-COOH/D-COONa system. Figure 3a shows the  $^{19}\text{F}$  NMR spectrum of D-COOH (mixed with an equal volume of  $\text{C}_6\text{F}_6$ ). The spectrum had been assigned earlier as indicated.<sup>13</sup> The  $^{19}\text{F}$  spectrum of D-COONa revealed that only peaks 7 and 8 (due to fluorine nuclei attached to the first and second carbons following the carbonyl group) are affected by the conversion to the Na salt. Figure 3b compares, in an expanded frequency scale, the peak 8 sectors observed from D-COOH, D-COONa, and their 1:1 mixture. The extra wide line width of D-COONa is attributed to the increased viscosity, hence longer rotational correlation time, of the fluid. Here it is clearly shown that, in the time scale corresponding to the NMR frequency difference

(12) Redington, R. L.; Lin, K. C. *J. Chem. Phys.* **1971**, *54*, 4111,

(13) Kasai, P. H. *Appl. Surf. Sci.* **1991**, *52*, 91.



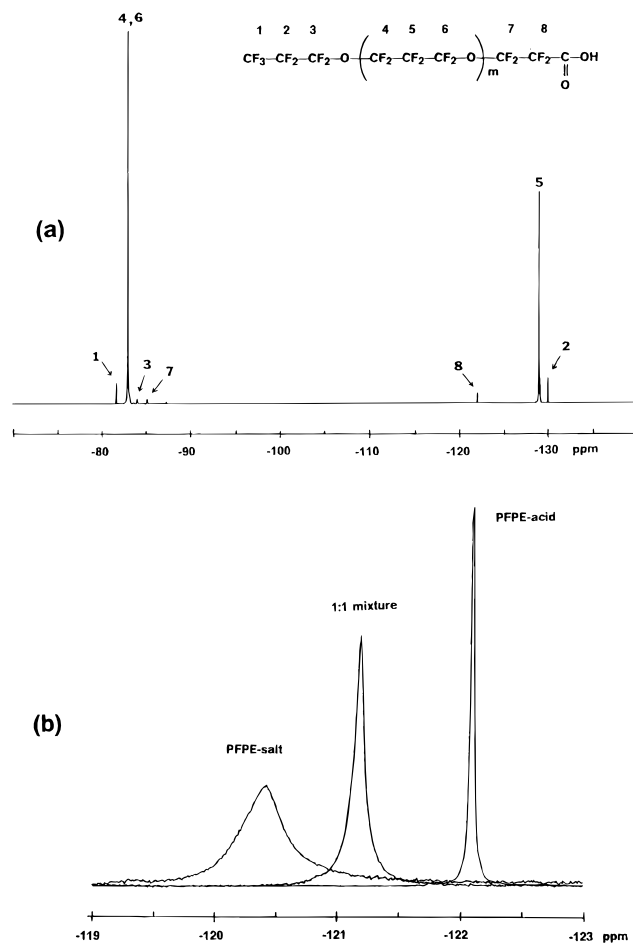
**Figure 2.** IR spectra (the carbonyl section) observed from (a) D-COOH, (b) D-COONa, (c) an intimate 1:1 mixture of D-COOH and D-COONa, and (d) lightly stir-mixed D-COOH and D-COONa of 3:1 proportions.

( $\sim 2$  ppm, or  $\sim 10^{-3}$  s), the carbonyl units in the mixture are completely averaged through the cation exchange process.

It is well-known that chemical-shift resolved NMR peaks would be broadened and/or coalesced if the chemical environment of the nuclei in question changes between two or more different states, by such processes as proton exchange or isomerization, *at the rate comparable to the difference in the chemical shifts for the totally static situation*. The effect of such exchange motion upon vibrational spectra has been extensively examined by Strauss and his co-workers.<sup>9</sup> It has been shown that such exchange motion which would bring about broadening and coalescence of NMR peaks would not be, in most cases, rapid enough to affect the relevant vibrational bands in exactly the same manner. However, it has been further shown and demonstrated that, if the potential function along the reaction coordinate for the exchange reaction is sufficiently low, the relevant vibrational bands may become broadened and shifted inward (for the two site case) without attaining actual exchange.<sup>9</sup> The phenomenon is termed pseudocollapse. If the temperature is sufficiently high, and/or if the separation between the component bands is sufficiently small, and/or if the mass motion required for the exchange process is sufficiently small, the band collapse due to real exchange may occur along with pseudocollapse.<sup>9,14</sup> The carbonyl spectrum of Figure 2c shown by the mixture is indeed very much like that expected from the constituent bands affected by pseudocollapse.

We thence performed a theoretical examination (SCF ab initio calculations) of the energetics of pair-wise interactions of CH<sub>3</sub>-

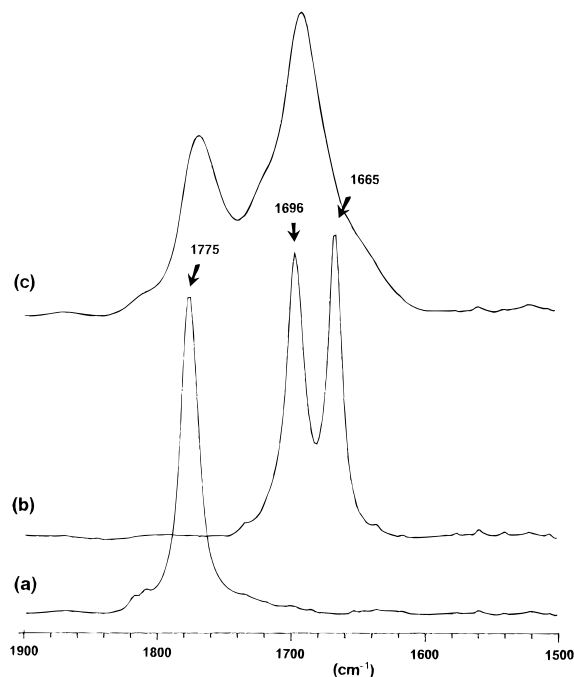
(14) For NMR peaks affected by the exchange process, the transient time (the time required for the exchange) is effectively zero; thus, as the exchange rate increases, the constituent peaks become broader and broader with no discernible shift in their positions. The inward shift (for the two-site case) becomes apparent only when the exchange rate becomes comparable to the difference of the original positions. Eventually a new band appears centered at the averaged position. IR bands, if affected by the pseudocollapse mechanism, show symptomatically not only broadening but also conspicuous inward shift (for the two-site case) *immediately*. See ref 9.



**Figure 3.** (a) <sup>19</sup>F NMR spectrum of D-COOH. The chemical shifts are measured in reference to CFCl<sub>3</sub>. (b) Peak 8, shown in an expanded scale, of D-COOH, D-COONa, and their 1:1 mixture.

COOH and CH<sub>3</sub>COONa molecules. The theoretical study (details presented later) predicted the formation and stability of not only the acid dimer but also the salt dimer and the *mixed dimer* (between the acid and salt molecules). The calculations also predicted the following for the carbonyl stretching frequencies. (1) The carbonyl band of the salt dimer is  $\sim 100$  cm<sup>-1</sup> below that of the acid dimer. (2) The carbonyl band of the acid monomer is  $\sim 50$  cm<sup>-1</sup> above that of its dimer, while the carbonyl band of the salt monomer is  $\sim 60$  cm<sup>-1</sup> below that of its dimer. (3) The acid-salt mixed dimer has two carbonyl bands, the acid sector showing its carbonyl band at  $\sim 40$  cm<sup>-1</sup> below that of the acid dimer, and the salt sector showing its carbonyl band also at  $\sim 40$  cm<sup>-1</sup> below that of the salt dimer (see Figure 10). The observed spectra would hence be in accord with the calculated features if we postulate that the carbonyl bands at 1775 and 1676 cm<sup>-1</sup> observed from D-COOH and D-COONa, respectively, are those of <acid-acid> and <salt-salt> dimers, and the spectrum of the mixture is due to those peaks and possibly those of <acid-salt> *mixed dimers* broadened and shifted by the pseudocollapse mechanism stemming from the cation exchange passages.

We then prepared a *lightly stir-mixed mixture* of D-COOH and D-COONa of 3:1 weight proportions. The mixing ratio ensures (essentially) total conversion of D-COONa to the mixed form, while coarse mixing would curtail/eliminate the exchange reaction passage. The IR spectrum (the carbonyl section) of the resulting material is shown in Figure 2d. The unperturbed carbonyl band of the <acid-acid> dimer is prominently seen, while the band due to the <salt-salt> dimer is essentially absent, as expected. The spectrum is further characterized by two new



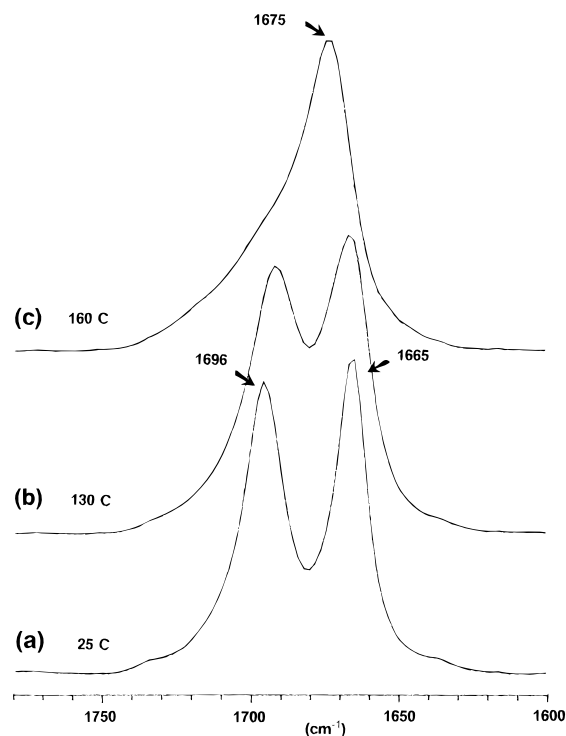
**Figure 4.** IR spectra (the carbonyl section) observed from (a) K-COOH, (b) K-COONa, and (c) an intimate 1:1 mixture of K-COOH and K-COONa.

bands centered at  $\sim 1740$  and  $\sim 1640$   $\text{cm}^{-1}$ , respectively, as indicated. These two bands are most consistent with those predicted above by the ab-initio calculation for the  $\langle \text{acid-salt} \rangle$  mixed dimer. The extreme broadness of these bands may be ascribed to the "intramolecular exchange" of the carbonyl states (between the acid-sector and the salt sector). Both the true exchange and the pseudocollapse mechanism may be operative here.

**(c) K-COOH and K-COONa, the Carbonyl Band.** Figure 4 shows the IR spectra of the carbonyl section observed from K-COOH, K-COONa, and their 1:1 mixture. The peak at  $1775$   $\text{cm}^{-1}$  observed from K-COOH is assigned to the  $\langle \text{acid-acid} \rangle$  dimers. The doublet at  $1696$  and  $1665$   $\text{cm}^{-1}$  observed from K-COONa is most intriguing; the two peaks are of equal intensity and more or less symmetrically displaced from the position of the carbonyl band of the  $\langle \text{salt-salt} \rangle$  dimers of D-COONa ( $\sim 1676$   $\text{cm}^{-1}$ ).

In the formation of cyclic dimers of type I, if the rotation about the  $\text{C}_\alpha\text{-C}_\beta$  bond becomes restricted due to bulky substituents at the  $\text{C}_\beta$  position, the cis and trans type isomerism is possible for the resulting cyclic dimers. K-COOH is unique in that its  $\beta$  carbon has a pendant  $\text{CF}_3$  substituent. The doublet at  $1696$  and  $1665$   $\text{cm}^{-1}$  observed from K-COONa is thus attributed to the existence of the  $\langle \text{salt-salt} \rangle$  dimers in two such isomeric forms. The sharpness of the doublet indicates that the stability of the  $\langle \text{salt-salt} \rangle$  dimer is such that the interconversion between the two isomers does not occur at the ambient condition. For the  $\langle \text{acid-acid} \rangle$  dimers of K-COOH, it must be that the interconversion occurs effected most likely by the dimer-monomer equilibrium process.

The spectrum observed from the mixture (Figure 4c) is much like that of the intimate mixture of D-COOH and D-COONa (Figure 2c). We must conclude that, though the interconversion of the two isomers of  $\langle \text{salt-salt} \rangle$  dimers does not occur at room temperature in neat K-COONa, presence of the  $\text{H}^+/\text{Na}^+$  cation exchange process in the mixture results in broadening, shifts, and partial coalescence of the component bands via the pseudocollapse mechanism. As in the case of D-COOH/D-COONa, the spectrum of lightly stir-mixed K-COOH/K-COONa



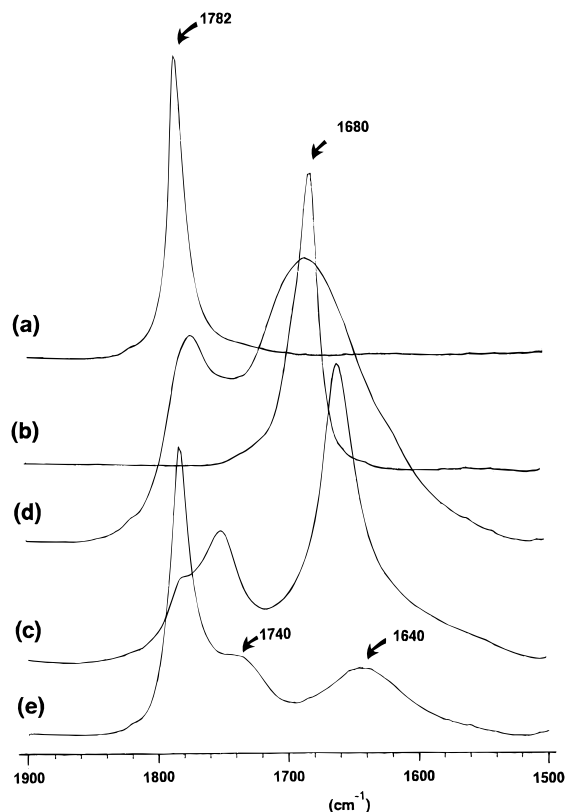
**Figure 5.** IR spectra (the carbonyl section) of K-COONa observed at (a) 25, (b) 130, and (c) 160 °C. The temperature dependence is reversible.

of 3:1 proportions revealed the broad bands attributable to  $\langle \text{acid-salt} \rangle$  dimers at  $1735$  and  $1645$   $\text{cm}^{-1}$ .

Figure 5 shows, in an expanded frequency scale, the carbonyl band of neat K-COONa observed at 25, 130, and 160 °C, respectively. The observed temperature effect was reversible. The broadening and partial coalescence observed here at elevated temperature are ascribed to the combined effect of the true exchange between the two isomeric forms (most likely via the rotation about the  $\text{C}_\alpha\text{-C}_\beta$  bond) and pseudocollapse stemming from such reaction. The skewed shape of the "coalesced spectrum" (Figure 5c) is attributed to heterogeneity of the process and/or the sample material. The mobility of individual polymer chains depends on the chain length. A dispersity of  $\pm 30\%$  has been measured for the molecular weight of K-type perfluoropolyethers with the number averaged molecular weight of  $\sim 5000$ .<sup>15</sup> We should also note that the  $\text{C}_\beta$  carbon in K-COOH/K-COONa is an asymmetric carbon. Thus the diastereomerism should occur for the dimers. The diastereomerism may have little effect on the carbonyl stretching frequency, but may influence significantly the height and shape of the barrier for the rotation about the  $\text{C}_\alpha\text{-C}_\beta$  bond.

**(d) Z-COOH and Z-COONa, the Carbonyl Band.** Spectra a and b in Figure 6 show the carbonyl bands observed from Z-COOH and Z-COONa, respectively. The carbonyl band of Z-COOH at  $1782$   $\text{cm}^{-1}$  and that of Z-COONa at  $1680$   $\text{cm}^{-1}$  are assigned to the respective  $\langle \text{acid-acid} \rangle$  and  $\langle \text{salt-salt} \rangle$  dimers. Spectra c and d in Figure 6 show the carbonyl bands of an intimate equimolar mixture of Z-COOH and Z-COONa observed at 25 and 60 °C, respectively. The temperature dependency of the spectrum was completely reversible (including the shoulder at  $1782$   $\text{cm}^{-1}$ ). Figure 6e shows the carbonyl spectrum observed from a lightly stir-mixed mixture of Z-COOH and Z-COONa of 3:1 weight proportions. Following the case of the stir-mixed D-COOH/D-COONa mixture, the broad bands at  $1740$  and  $1640$   $\text{cm}^{-1}$  (both  $40$   $\text{cm}^{-1}$  red shifted from the respective constituent

(15) Kasai, P. H. *Macromolecules* **1992**, *25*, 6791.



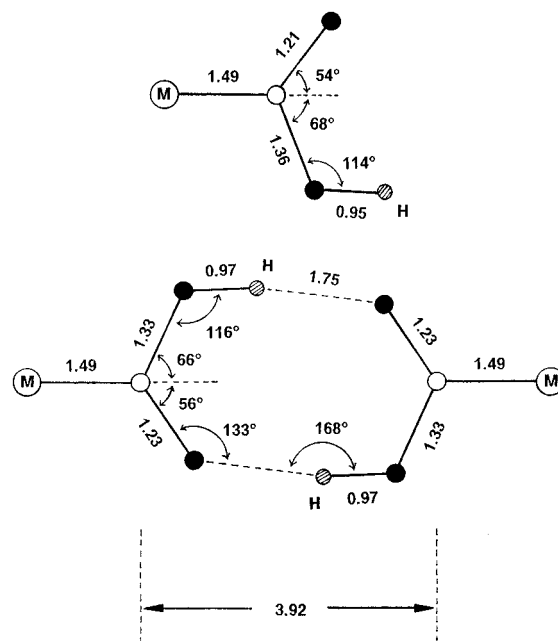
**Figure 6.** IR spectra (the carbonyl section) observed from (a) Z-COOH, (b) Z-COONa, (c) an intimate 1:1 mixture of Z-COOH and Z-COONa at 25 °C, (d) the same mixture at 60 °C, and (e) lightly stir-mixed Z-COOH and Z-COONa of 3:1 proportions.

bands) are assigned to ⟨acid–salt⟩ mixed dimers. It appears that, for the intimate mixture of Z-COOH and Z-COONa, coalescence occurs at room temperature between the carbonyl band of ⟨acid–acid⟩ dimers and that of the acid sector of ⟨acid–salt⟩ mixed dimers, and between the carbonyl band of ⟨salt–salt⟩ dimers and that of the salt sector of ⟨acid–salt⟩ mixed dimers (Figure 6c). The much broader, inward-shifted pattern observed at 60 °C (Figure 6d) is attributed to pseudocollapse due to the cation exchange passages among all three dimers. The shoulder at 1782  $\text{cm}^{-1}$  seen in Figure 6c is attributed to a fraction of ⟨acid–acid⟩ dimers phasing out at this temperature. Slightly different temperature dependence of the carbonyl bands shown by the Z-COOH/Z-COONa system is not unexpected; unlike the other systems, the molecular chains of Z-COOH and Z-COONa have the carboxylic group at both ends.

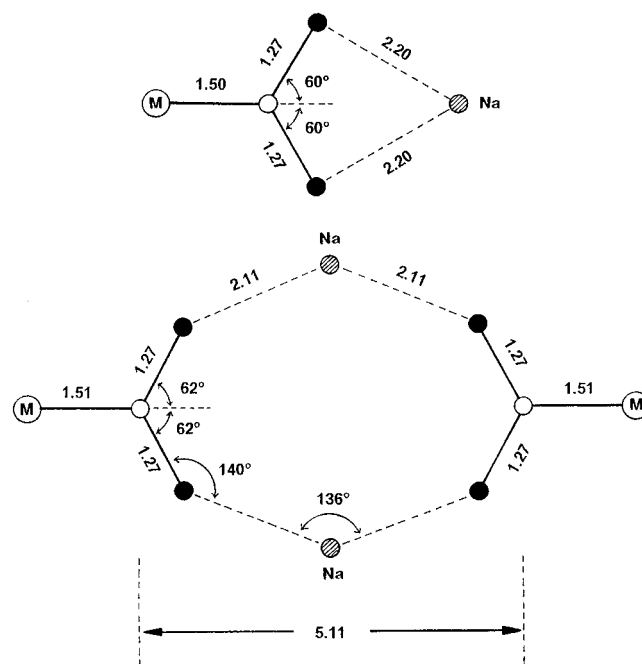
Excepting the special case of K-COONa where the cis and trans isomerism affected the carbonyl band, the carbonyl bands of all the PFPE acids and their Na salts studied above remained sharp and unaltered when heated individually (up to  $\sim 150$  °C).

### Theoretical Study and Discussions

The formation of the ⟨acid–acid⟩, ⟨acid–salt⟩, and ⟨salt–salt⟩ dimers observed here must be the consequence of the interaction inherent to the carboxylic sectors,  $-\text{COOH}$  and  $-\text{COONa}$ . To gain further insight into such interaction, to ascertain the structures and stabilities of the dimers, and to complement the spectral assignments presented above, we performed ab initio SCF calculations (with geometry optimization and vibrational frequency calculations) of the monomers and dimers of the  $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$  system. The 6-31G basis set was chosen for the calculation. The structures thus obtained are shown in Figures 7–9. The structures of the monomer and the dimer of acetic acid in vapor had been



**Figure 7.** The structures of the acetic acid monomer and dimer given by ab initio SCF calculations (6-31G). The bond distances are given in Å. The open and solid circles represent carbons and oxygens, respectively. For the methyl group, only the carbon position is shown.

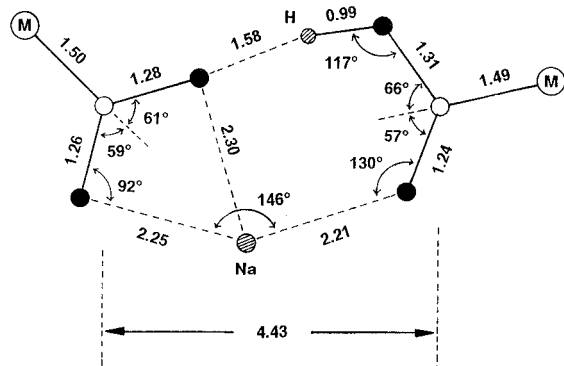


**Figure 8.** The structures of the sodium acetate monomer and dimer given by ab initio SCF calculations (6-31G). The open and solid circles represent carbons and oxygens, respectively. For the methyl group, only the carbon position is shown.

determined earlier from the electron diffraction patterns.<sup>16</sup> The bond distances and angles given in Figure 7 for these species are all within  $\pm 1\%$  of the experimental values, thus giving credence to the reliability of the theoretical method.

Excepting the methyl protons, the calculations thus predicted completely planar structures for the three dimers. The ⟨acid–acid⟩ dimer (Figure 7) has a  $C_{2h}$  symmetry, and though perturbed slightly, the integrity of the monomer constituents is retained. The ⟨salt–salt⟩ dimer (Figure 8) has a  $D_{2h}$  symmetry, and all four oxygen atoms are equivalent as are the two oxygen atoms

(16) Derissen, J. L. *J. Mol. Struct.* **1971**, *7*, 67.



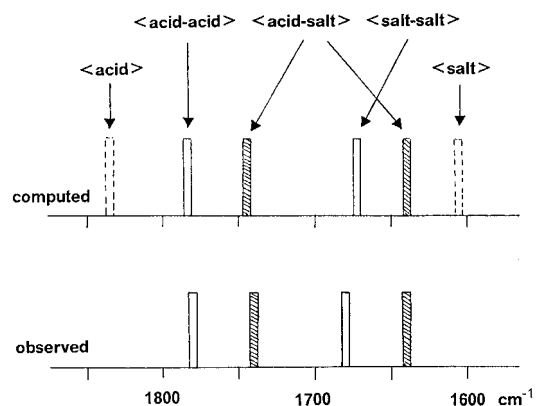
**Figure 9.** The structure of the acetic acid/sodium acetate mixed dimer given by an ab initio SCF calculation (6-31G). The open and solid circles represent carbons and oxygens, respectively. For the methyl group, only the carbon position is shown.

in the salt monomer. The Na–O distance in the dimer (2.11 Å) is also close to that in the monomer (2.20 Å). The ⟨acid–salt⟩ dimer (Figure 9) has a  $C_s$  symmetry, and though slightly perturbed, the respective integrities of the constituent monomers are clearly retained. The Na atom, however, is positioned equidistantly from three oxygen atoms, the third oxygen being the carbonyl oxygen of the acid sector. Also the length of the hydrogen bond (1.58 Å) is significantly shorter than that in the ⟨acid–acid⟩ dimer (1.75 Å), due certainly to the increased negative charge of the oxygen involved. The dimension of the cyclic structure of a given dimer (as measured by the  $C_\alpha$ – $C'_\alpha$  distance) increases from 3.92 Å of the ⟨acid–acid⟩ dimer to 4.43 and 5.11 Å for the ⟨acid–salt⟩ and the ⟨salt–salt⟩ dimers, respectively.

The calculations yielded the heats of dimerization of 19.5, 34.1, and 53.1 kcal/mol for the ⟨acid–acid⟩, ⟨acid–salt⟩, and ⟨salt–salt⟩ dimers, respectively. That the heat of formation of the mixed dimer is close to the average of those of the ⟨acid–acid⟩ and ⟨salt–salt⟩ dimers accounts for the presence of three species in the mixture. From vapor density measurements the heat of dimerization of the acetic acid dimer has been determined as 15.3 kcal/mol.<sup>3,4</sup> The much larger heat of dimerization predicted for the ⟨salt–salt⟩ dimer is attributed to the Coulombic interaction of the ionic constituents. The net atomic charges in the ⟨salt–salt⟩ dimer given by the calculation are such that 0.81 electron charges of alternating signs are placed on the eight contiguously connected atoms of the ring structure. It is perhaps not entirely accidental that the predicted heat of dimerization of  $(\text{CH}_3\text{COONa})_2$  is essentially the same as that of  $(\text{NaCl})_2$ . While two isomeric forms of ⟨salt–salt⟩ dimers of K–COONa are observed, only one carbonyl band is seen from the ⟨acid–acid⟩ dimers of KCOOH. The rapid isomerization indicated for the latter is attributed to the dimer–monomer equilibrium process facilitated by its smaller heat of dimerization.

It has been shown that stretching vibrational frequencies computed by ab initio calculations (using medium size basis sets) are generally ~10% larger than the observed values.<sup>17</sup> The carbonyl stretching band of acetic acid dimers in vapor has been

(17) Seeger, D. M.; Korzeniewski, C.; Kowalchuk, W. *J. Phys. Chem.* **1991**, *95*, 6871.



**Figure 10.** The carbonyl stretching frequencies of PFPE acid/salt monomers and dimers given by ab initio calculations (6-31G) are shown in comparison with the observed frequencies. See text for detail.

experimentally observed at 1739  $\text{cm}^{-1}$ .<sup>4</sup> The ab initio calculation performed above for acetic acid dimers yielded the carbonyl band at 1870  $\text{cm}^{-1}$ ; the scaling factor appropriate for the vibrational frequencies computed for this set of molecules was thus set as 0.930. It is also known that, upon fluorination of the carbon adjacent to a carbonyl group, the carbonyl stretching frequency increases by ~45  $\text{cm}^{-1}$ .<sup>18</sup> The carbonyl stretching frequencies of the PFPE acid/salt monomers and dimers presently observed may thus be estimated from the values computed for the acetic acid/salt system ( $\nu_{\text{pfpe}} = 0.93\nu_{\text{comp}} + 45$ ). Figure 10 shows diagrammatically the values thus estimated in comparison with the observed values. The agreements between the observed and "computed" frequencies are quite reasonable in strong substantiation of the assignments. The computed frequencies rule out the possibility that the ⟨acid⟩ or ⟨salt⟩ monomers contribute to the spectra affected by exchange. Their contribution would result in outward shifts of peaks contrary to the observed trend.

It is intriguing that the intergroup interactions much like those expected in vapor phase are observed for the carboxylic acid and their Na salt units tethered to PFPE chains. The PFPE chains proper, owing to their exceptionally weak intermolecular cohesive force, provide an inert fluid medium; an extensive aggregation of the active sectors, however, is prevented by the entropic factor of long polymeric chains. It is enticing to explore the possibility of examining the intergroup interactions of other groups similarly attached to the PFPE system.

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(18) See, for example: Cooper, J. W. *Spectroscopic Techniques for Organic Chemists*; John Wiley & Sons: New York, 1980; Chapter 2.