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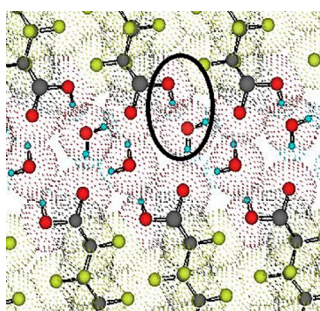
## Infrared spectra of hydrogen bond network in lamellar perfluorocarboxylic acid monohydrates

Urban Novak, Jože Grdadolnik\*

National Institute of Chemistry, Hajdrihova 19, SI-1000 Ljubljana, Slovenia



## GRAPHICAL ABSTRACT



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## ABSTRACT

The infrared spectra of the long-chain perfluorocarboxylic acid monohydrates differ markedly from those of the anhydrous dimers. Consequently, the structure of the solid perfluorocarboxylic acid monohydrates must differ from any known dimer-containing carboxylic acid crystals. Consideration of the significant features of the infrared spectra of the long-chain perfluorocarboxylic acid monohydrates, supplemented by their Raman spectra, and comparison with the spectra of auxiliary substances have led us to conclude that the rather strong neutral carboxyl-hydroxyl to water bonding can best explain the observations. The infrared spectra indicate the presence of fairly short hydrogen bonds connecting the water molecules to the carbonyl groups. In the construction of the hydrogen bonding pattern of the perfluorocarboxylic acid monohydrates, the oxalic acid dihydrate plays the key role. The striking similarity between the infrared spectra of the oxalic acid dihydrates and the perfluorocarboxylic acid monohydrates in the regions characteristic of water and O—H...O vibration suggests that the structure of the hydrated carboxyl groups is the same in both crystals. These regions are characterized by the sharp doublet at  $3539\text{ cm}^{-1}$  and  $3464\text{ cm}^{-1}$ , which is due to the  $\text{H}_2\text{O}$   $\nu_1$  and  $\nu_3$  stretching vibrations, respectively, and the broad absorption between  $3000\text{ cm}^{-1}$  and  $1500\text{ cm}^{-1}$  with the intense band at  $1970\text{ cm}^{-1}$ , both associated with the vibration of the O—H...O group. The later peak consists of two band components at near  $1980\text{ cm}^{-1}$  and  $2020\text{ cm}^{-1}$ . These band components show different behaviour when the temperature, polarization or deuteration is changed. In general, the infrared spectra of long-chain perfluorocarboxylic acids represent the system with very short hydrogen bonds connecting the water molecules to the carboxylates. This hydrogen bond pattern should be very similar to that found in the crystals of  $\alpha$ -oxalic acid dihydrate.

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**Abbreviations:** PFCA, long chain perfluorocarboxylic acid; PFB, perfluorated butyric acid; PFT, tridecafluoroheptanoic acid; PFP, pentadecafluorooctanoic acid; PFH, heptadecafluorononanoic acid; PFN, nonadecafluorodecanoic acid; TFAM, trifluoroacetic acid monohydrate; TFAT, trifluoroacetic acid tetrahydrate; OXAD,  $\alpha$ -oxalic acid dihydrate.

\* Corresponding author.

E-mail addresses: [urban.novak@ki.si](mailto:urban.novak@ki.si) (U. Novak), [joze.grdadolnik@ki.si](mailto:joze.grdadolnik@ki.si) (J. Grdadolnik).

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## 1. Introduction

Hydrogen bonds play a crucial role in many biological and chemical systems [1] and are therefore the subject of numerous experimental and theoretical studies. Although hydrogen bonding is a phenomenon that can be detected and studied by almost all methods of physical chemistry, diffraction and spectroscopies, infrared spectroscopy plays a central role in its study. Indeed, the infrared spectra contain complete information about the electronic and consequently nuclear dynamic effects of the hydrogen bonds, encoded in the band shape and frequencies of the bands associated with the hydrogen bonds. The most obvious effect of the formation of hydrogen bonds  $X-H \cdots Y$  is the redshift of the high-frequency stretching mode, its intensity increase and band broadening [2–7]. The red shift of the stretching vibration reflects a decrease in the effective force constant of the hydrogen stretching oscillator [8,9]. While the origin of red shift of  $X-H$  frequency upon formation of hydrogen bond is well understood, the proposed numerous broadening mechanisms, especially ones connected to a medium and strong hydrogen bonds, are still under discussion [2,5,7,10–26].

The other unresolved question relates to the influence of the environment on the hydrogen bonding property and hence on the characteristic pattern of the same in the vibrational spectra. The hydrates of oxalic acid (OXAD) and perfluorated fatty acids (PCFA) represent an ideal system for such studies. While the former compound has been extensively studied [27–31], the vibrational analysis of perfluorated fatty acids is still incomplete with respect to the spectral characteristics of formatted hydrogen bonds (see Fig. 1).

In contrast to the extensive studies of the surfactant and aggregation properties of long-chain perfluorocarboxylic acid [32–35] there is little information on the general physicochemical properties of its crystalline monohydrates. In particular, we have not been able to obtain spectroscopically or diffraction-derived structural information on water binding. However, given the tendency of PFCA to form layered structures [33,36–38] and the strength of these acids, the formation of an extensive network of strong hydrogen bonds within the bilayers is to be expected. That relatively strong hydrogen bonds are present, involving carboxylic groups and probably also neutral water, is already readily apparent from the overview spectra. However, the spectra do not show features that would allow classification into typical groups of hydrogen-bonded materials, which in turn would give an indication of the type of the one-dimensional potential function gov-

erning the proton dynamics and hydrogen bonding pattern. The rather peculiar spectral density of PFCA invites further investigation in light of recent developments in the theories of spectral densities of crystalline solids with short hydrogen bonds; relevant examples could be very useful for further developments and discrimination of the underlying physical models. This has led us to investigate the infrared spectra of a number of PFCA, including perfluorobutyric acid, heptanoic acid, octanoic acid, nonanoic acid and decanoic acid.

The colloidal properties of amphiphilic long-chain PFCA and its salts have been extensively studied [39–42], but little was known about the structure of PFCA and its salts in the solid state or in molecular solution. Only recently has the structure of pentadecafluorooctanoic acid monohydrate been elucidated by X-ray powder studies using DFT periodic calculation [38]. The accompanying experimental and theoretical study shows that the structure of the hydrogen bonding network found in the polycrystalline sample of PFCA monohydrate is very similar to that defined in the crystals of OXAD. However, the surrounding molecules are packed differently in the unit cells. This change in environment gives us a unique opportunity to study the effects of the neighbourhood on the physicochemical properties of the established hydrogen bonds. Although the structure of the hydrogen bond network appears to be similar to OXAD, the question arises whether ionic forms are also part of the network.

The infrared spectra of the anhydrous solid PFCA show features characteristic of carboxylic acid dimers. However, the anhydrous solids exposed to atmospheric moisture readily absorb water and form monohydrates. The infrared spectra of the perfluorocarboxylic acid monohydrates (PFCA monohydrate) are clearly different from those of the anhydrous dimers, indicating that the structure of solid FCAM must be different from all known dimers containing carboxylic acid crystals. Therefore, a more detailed investigation seemed worthwhile.

It is obvious that for any discussion of the spectral properties of hydrogen bonds, the hydrogen-bonded moieties must first be identified, which in this example means distinguishing between neutral and ionic bonding partners. The phase diagram of the related trifluoroacetic acid-water system, showing two crystalline phases with different composition and ionicity, suggests the possible existence of both. The monohydrate (TFAM, melting point =  $-43.73$  °C) is neutral; the carboxylic hydroxyl group is bonded to the oxygen of water via a moderately strong hydrogen bond ( $R_{O \cdots O} = 2.605$  Å). The tetrahydrate (TFAT, melting point =  $-16.06$  °C) contains two ionic species:  $(H_5O_2)^+$  and  $(CF_3COO)_2H^-$  with formally symmetric hydrogen bonds. However, the deuterium analog of the latter has a different structure containing neutral species. Apparently, the tendency of fluoroacetic acids to donate protons to water is very sensitive to medium and crystal dynamic effects in the solid state.

The detailed structure of the hydrogen bonding pattern of PFCA hydrate prediction, which includes the distinction between neutral and charged entities, requires comparisons with the spectra of model systems such as the corresponding neutral and acid salts; comparisons with the spectra of substances with established diffraction structure such as OXAD [43], trifluoroacetic acid hydrates [44] are particularly useful.

The paper is organized as follows. In the experimental section, we briefly describe the properties of PFCA that suggest the sampling protocol. In describing the spectra in the Results and Discussion section, we focus on features that characterize hydrogen bond. In discussing the assignment of these features, we will exploit the similarity (or dissimilarity) with related systems. In this regard, particular attention will be paid to the spectra of oxalic acid dihydrate. The features related to the strong hydrogen bonding in PFCA

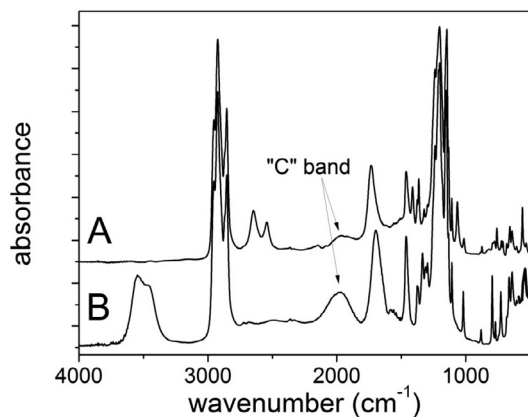


Fig. 1. The infrared spectra of PFP monohydrate in nujol mull; A. hydrated with  $D_2O$  and B. hydrated with  $H_2O$ .

and the latter systems will be discussed together in the last paragraph of this section. The experimental results and their interpretation are summarized in the Conclusions.

## 2. Experimental

The substances were of commercial origin (Fluka) and purified by recrystallization from water. Perfluorated butyric acid (PFB,  $\text{CF}_3(\text{CF}_2)_3\text{COOH}$ , 97%), tridecafluoroheptanoic acid (PFT,  $\text{CF}_3(\text{CF}_2)_5\text{COOH}$ , 97%), pentadecafluorooctanoic acid (PFP,  $\text{CF}_3(\text{CF}_2)_6\text{COOH}$ , 95%), heptadecafluorononanoic acid (PFH,  $\text{CF}_3(\text{CF}_2)_7\text{COOH}$ , 97%) and nonadecafluorodecanoic acid (PFN,  $\text{CF}_3(\text{CF}_2)_8\text{COOH}$ , 97%) were twice recrystallized from  $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$ . The crystals contain one water molecule per acid (TGA,  $^1\text{H}$  NMR). The hydrates loose water at melting but also are dehydrated under vacuum at room temperature. Rehydration occurs at exposure to room atmosphere. X-ray powder diffraction shows lamellar structure with the long spacing of 21.4 Å, 22.9 Å, 25.9 Å and 27.4 Å in PFT, PFP, PFH and PFN crystals, respectively. Anhydrous PFCA were prepared by recrystallization from dry  $\text{CHCl}_3$ . Solvent residues were removed under reduced pressure ( $p = 10^{-2}$  torr). IR and Raman spectra were recorded using a Bruker Vertex 80 and Ram II spectrometers. IR spectra were recorded as Nujol mulls, KBr pellets, or oriented films. Liquid samples were measured in a Harrick liquid cell with Teflon spacers. Temperature measurements were made with a Specac low-temperature transmission cell using liquid nitrogen and a home-made temperature controller. A DPY laser with an excitation wavelength of 1064 nm and a nominal power of 100–250 mW was used throughout. The nominal resolution was 4  $\text{cm}^{-1}$ . Typically 256 (IR) and 2048 (Raman) interferograms were recorded, averaged and apodized with a triangular function. Spectra were processed using commercial OPUS and Grams software.

## 3. Results and discussion

The studied infrared spectra of PFCA show very similar properties (see SI Fig. 1). We will therefore mainly present and discuss a representative PFCA, namely PFP monohydrate (Fig. 1), mentioning the minor differences in the characteristics related to hydrogen bonding. These then do not include the bands due to the fluorinated carbon chain.

### 3.1. Weakly hydrogen bonded OH groups

A doublet broadened at room temperature (RT) appears near 3500  $\text{cm}^{-1}$ , with the higher-frequency component in the mull spectra being more intense. On cooling to  $-150$  °C the peaks become sharper. The position (Table 1) of the higher frequency component varies between 3500  $\text{cm}^{-1}$  and 3440  $\text{cm}^{-1}$  and that of the second component (between 3412  $\text{cm}^{-1}$  and 3423  $\text{cm}^{-1}$ ); both are shifted  $\sim 50$   $\text{cm}^{-1}$  in red upon cooling (Fig. 2). The corresponding bands of the deuterated acids are already well resolved at RT. The small peaks on the inside of this doublet, indicated at RT, are well separated at low temperatures. They are due to the uncoupled HOD strains corresponding to incomplete deuteration [45]. The doublet is obviously due to vibrations  $\nu_1$  and  $\nu_3$  of the water.

The water molecules can be neutral in principle as in the example of TFAM [44] and OXAD [43,46] or they can be part of the oxonium dihydrate  $\text{H}_5\text{O}_2^+$  as in the example of TFAT [44,47]. However, the latter alternative requires the formation of negatively charged hydrogen dicarboxylate counterions. Fluorinated carboxylic acids are quite strong acids, and in the crystalline state proton transfer to water can occur; the crystal structure of TFAT is a good example. This acid is formed by the action of three fluorine atoms on the  $\alpha$

**Table 1**

The most significant vibrational frequencies of the PFCA in various forms in high frequency region.

	$\nu_1$ and $\nu_3$ OH ( $\text{cm}^{-1}$ )	carboxylic $\nu\text{OH}$ ( $\text{cm}^{-1}$ )	$\nu$ C=O ( $\text{cm}^{-1}$ )
dimer		$\sim 3050$ broad	1757
monohydrate	3545, 3458	$\sim 2465$ very broad	1695
$\text{H}_2\text{O}$			
$T = \text{RT}$			
monohydrate	3487, 3406	$\sim 2500$ very broad	1660
$\text{H}_2\text{O}$			
$T = -150$ °C			
monohydrate	2647, 2543	$\sim 1500$ very broad and strongly overlapped	1736
$\text{D}_2\text{O}$			
$T = \text{RT}$			
monohydrate	2597, 2530, 2509	$\sim 1500$ very broad and strongly overlapped	1722
$\text{D}_2\text{O}$			
$T = -150$ °C			
solution in $\text{CHCl}_3$		$\sim 3000$ very broad	1782
K neutral salt			1686, 1670, 1654
K H acid salt		$\sim 1100$	1770, 1724
Raman	3528, 3440		1746, 1690
monohydrate			
$\text{H}_2\text{O}$			
Raman	2614, 2552		1740, 1705
monohydrate			
$\text{D}_2\text{O}$			

carbon atom of a carboxylic acid of excellent strength. It is therefore surprising that in the crystal form only the tetrahydrate is in ionic form [44]. The lattice consists of the ionised acid and the cations  $\text{H}_5\text{O}_2^+$  or  $\text{H}_2\text{O} \cdot \text{H}_3\text{O}^+$  and the  $2\text{H}^-$  anions  $\text{CF}_3(\text{COO})$ . The ions are formed by strong hydrogen bonds, both of which are the shortest in the crystal structure. The cations and anions are connected by further hydrogen bonds to form an extended chain. Two more hydrogen bonds connect these chains to the water layer, which consists of the water molecules connected by hydrogen bonds in tetra- and sextamer rings.

Thus, at least four different classes of hydrogen bonds are found in the crystal of TFAT.

The distinction between water as a neutral proton donor and water enveloped by the  $\text{H}_5\text{O}_2^+$  ion requires the examination of the rest of the spectrum for the presence of bands attributable to the  $\text{H}_5\text{O}_2^+$  and  $\text{H}(\text{PFCA})_2$  ions. Both ions are known to cause strong, very broad absorptions, ranging from 3000  $\text{cm}^{-1}$  to the far infrared region. Such absorption is indeed observed in the spectra of hydrated PFP, and we need to look at it in more detail.

Characteristics related to strong hydrogen bond. While the anhydrous PFP shows bands characteristic of carboxylic dimer (broad complex  $\nu$  OH absorption culminating near 3000  $\text{cm}^{-1}$ ,  $\nu$  C=O at 1757  $\text{cm}^{-1}$  in the infrared and 1718  $\text{cm}^{-1}$  in the Raman spectrum, in-plane deformation mixed with C—O stretching at 1430  $\text{cm}^{-1}$ , out-of-plane  $\gamma$  OH deformation at 870  $\text{cm}^{-1}$ ), the monohydrate shows features indicative of much stronger hydrogen bonding. In particular, this is the broad absorption extending from the water band to above 1000  $\text{cm}^{-1}$  with superimposed absorption windows.

The extended absorption, which can also be considered as a “continuum” according to Zundel [48], is poorly defined, but with interpretation deuteration gives rise to a better defined OD stretching; it is around 1500  $\text{cm}^{-1}$ . The extended  $\nu$  OH -absorption shows dichroic properties; this becomes clear when comparing the mull spectra with those obtained by evaporating methanolic solutions onto ZnSe plates, and even better with the ATR spectra (Fig. 4). Although it is rather difficult to interpret polarization spectra in more detail, they provide us with accurate evidence that the struc-

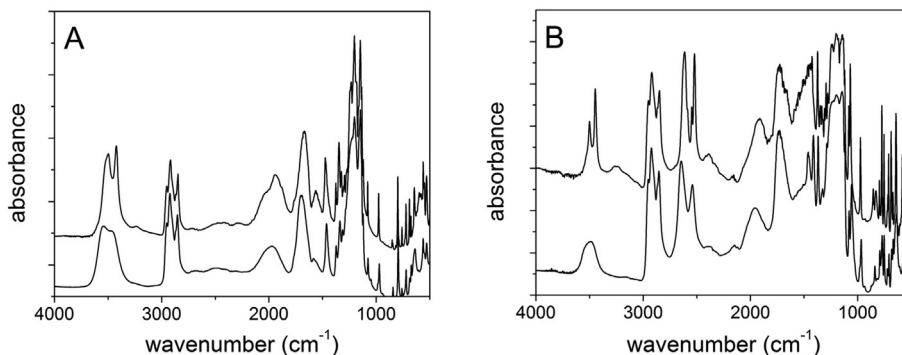


Fig. 2. The infrared spectra of PFP monohydrate in nujol mull at  $T = \text{RT}$  (bottom spectra) and  $T = -150\text{ }^{\circ}\text{C}$  (upper spectra); A. Hydrated with  $\text{H}_2\text{O}$  and B. Hydrated with  $\text{D}_2\text{O}$ .

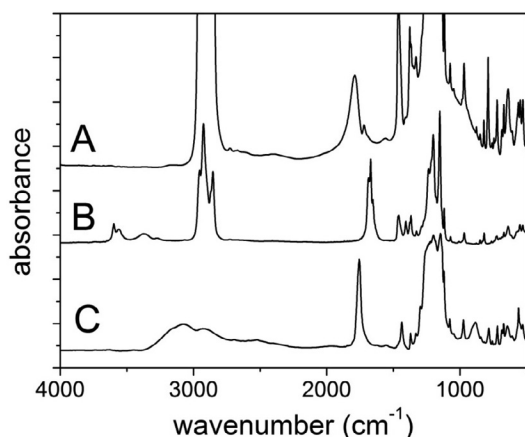


Fig. 3. A. The infrared spectrum of potassium acid salt of di-PFP (KH acid salt), B. The infrared spectrum of potassium salt of PFP and C. The infrared spectrum of PFP in dimer form.

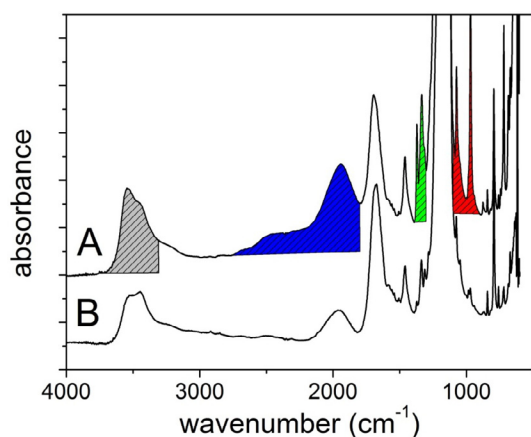


Fig. 4. The ATR infrared spectra of PFN monohydrate film using, A. perpendicular polarization, and B. parallel polarization.

ture of band C is complex and that different regions of broad OH absorption exhibit different polarization. Cooling reduces the level of extended absorption. Unfortunately, attempts to perform reliable quantitative absorption measurements failed due to the properties of the material, namely the production of layers with controlled thickness. The continuum-like OH stretching is supported by a medium-strong feature at  $1970\text{ cm}^{-1}$ , besides some smaller submaxima at higher frequencies. The absorption at  $1970\text{ cm}^{-1}$  is striking even in thin samples, where the continuum

is barely perceptible. Therefore, it could be considered as the peak of elongation of OH stretching.

It is well known that medium and strong hydrogen bonds give rise to broad band(s) in the vibrational spectrum extending over several hundred wavenumbers. In the case where this broad absorption culminates in three distinct, still broad subpeaks, it is often referred to as the Hadži ABC structure of OH stretching [8,14,49,50]. The existing of sub-bands originates in Fermi resonances of the in-plane bend, out-of-plane bend, and combination of these bends [15]. To take advantage of this assignment, a closer examination reveals that the origin of the  $1970\text{ cm}^{-1}$  band-we will call it "b and C" (see Fig. 1) because of its obvious similarity to the last member of the ABC trio [49]- is more complex. Indeed, the band C consists of two components. This is already indicated at room temperature by the example of PFP monohydrate. The respective peaks are located in the vicinity of  $1980\text{ cm}^{-1}$  and  $2020\text{ cm}^{-1}$ , with the former gaining intensity upon cooling (Fig. 2A). The increase in intensity of the low-frequency peak is much more pronounced for longer-chain acids, so that the higher-frequency component becomes a broad shoulder. Deuteration removes the higher frequency component while the lower frequency component remains at the frequency of the center of the former. At room temperature, the effect of deuteration appears to be negligible, but upon cooling, the peak remaining after deuteration continuously shifts to lower frequencies; the shift is  $50\text{ cm}^{-1}$  (Fig. 2B).

The components of band C appear to have different polarizations, as suggested by the frequency changes at different polarizer settings in the ATR spectra (Fig. 4).

Localization of the analogue of band C in the spectra of deuterated acids is complicated by the presence of a rather broad absorption near  $1560\text{ cm}^{-1}$ , which is weak at room temperature but well pronounced at low temperatures. It appears to disappear during deuteration, while broad shoulders develop on the low-frequency side of the carbonyl band and on the high-frequency side of the band at  $1430\text{ cm}^{-1}$ . The connection between these absorptions and the deuteration-sensitive band of the protic material at  $\sim 1980\text{ cm}^{-1}$  is not clear. Band C is separated from the  $\nu\text{C=O}$  band by a deep gap with a bottom at  $\sim 1800\text{ cm}^{-1}$ . This is apparently an Evans-type transmission window. The depth of the gap is somewhat reduced upon deuteration. More important for identifying its origin is the redshift of the minimum on cooling [51,52].

In the context of the analysis of spectral features associated with strong hydrogen bonding, it is useful to locate the two OH deformation vibrations. Comparison of the protic and deuterium acid spectra suggests the band at  $1461\text{ cm}^{-1}$  as a candidate for in-plane deformation. It is then very close to one in the dimeric carboxylic acids. However, the disappearance of this and the band at  $1330\text{ cm}^{-1}$  and the formation of new bands at  $1427\text{ cm}^{-1}$  and



$1065\text{ cm}^{-1}$  is very similar to the behaviour of the dimeric carboxylic acids. Actually, this is surprising given the strong hydrogen bonding in PFCA compared to the dimeric acids, but there is simply no other possibility. Moreover, we observed very similar frequencies for the analogous modes in crystalline trifluoroacetic acid hydrates (Fig. 5). In the spectra of the protonic acids, there is no obvious candidate for out-of-plane COH deformation. However, in the case of the deuterium acids, there is a new absorption centred at  $\sim 720\text{ cm}^{-1}$ . It is weak, broad, and overlaid by C-F bands. Its appearance is supported by two Evans windows. The protic analogue is probably obscured by the strong  $\text{CF}_2$  stretchings and is therefore unidentifiable.

### 3.2. Carbonyl stretching

The frequency range  $1705\text{ cm}^{-1}$  to  $1690\text{ cm}^{-1}$ , where the strong and quite broad band is found, appears somewhat low compared to the dimers ( $1759\text{ cm}^{-1}$ ) and the neutral potassium salts ( $\sim 1660\text{ cm}^{-1}$ ). Even more surprising is the large low-temperature shift to  $1650\text{ cm}^{-1}$ . However, the explanation for these unexpected features is provided by the effects of deuteration: the  $\nu\text{C}=\text{O}$  band now appears at  $1730\text{ cm}^{-1}$  with a red shift on cooling of only  $4\text{ cm}^{-1}$ . The reason for the unusual behaviour of the  $\nu\text{C}=\text{O}$  band must be sought in the dynamical interaction of this mode with that causing the deuteration-sensitive component of the C band. The interaction pushes the  $\nu\text{C}=\text{O}$  to lower frequencies; removal of the  $\text{C}=\text{O}$  component by deuteration allows the  $\nu\text{C}=\text{O}$  mode to assume the unperturbed higher frequency of  $1730\text{ cm}^{-1}$ . The large temperature effect on the  $\nu\text{C}=\text{O}$  frequencies is most likely also associated with a similar effect on the C band. Before discussing the properties of strong hydrogen bond, it is necessary to identify at least the molecular species involved.

### 3.3. Molecular species that form the strong hydrogen bond

Two hydrogen bonding patterns must be considered: (i) neutral carboxyl groups bonded to water, and (ii) the doubly homoconju-

gated ions  $\text{H}(\text{PFCA})_2^-$  and  $\text{H}_5\text{O}_2^+$ . Both patterns were found with trifluoroacetic acid hydrates and their X-ray structures were determined. We will first consider the second possibility. The assignment of the bands that could be used to identify the  $\text{H}_5\text{O}_2^+$  ion is not promising, since the complex spectra are rich in broad features, while those of the  $\text{H}_5\text{O}_2^+$  bands are not really characteristic for crystalline acid hydrates.

On the other hand, the spectra of hydrogen dicarboxylates differ strongly depending on the geometrical constraints imposed by the crystal structure. The symmetric or nearly symmetric arrangements of carboxylates with extremely short hydrogen bonds can be eliminated because they characteristically absorb at much lower frequencies. We have studied the spectra of potassium hydrogen bisperfluorooctanoate; its characteristic OH stretching is at  $1100\text{ cm}^{-1}$ . Acid salts of trifluoroacetic acid show this absorption at even lower frequencies. However, acid salts with significantly different metric parameters of the carboxyl groups show spectra with ABC bands. A typical example is acid salt of potassium phthalate (K-H-phthalate) [53], where band C is striking in its intensity. This band also has a complex origin, but the temperature and deuteration effects are not the same as those observed for band C in the PFCA example. The same is true for the carbonyl stretchings. However, before the presence of ionic forms can be completely ruled out, it is advisable to investigate model systems for neutral molecular bonds; these are the TFAM and the OXAD.

The spectrum of TFAM shows some characteristic features similar to those of PFCA monohydrate (Fig. 5); these are the broad absorption starting at the lower frequency rise of the  $\nu\text{H}_2\text{O}$  band and extending beyond the boundary of the studied region, and the band C at  $\sim 2000\text{ cm}^{-1}$ , the intensity of the latter only slightly exceeding that of some submaxima at higher frequencies, but being much lower compared to  $\nu\text{C}=\text{O}$  at  $1710\text{ cm}^{-1}$ . The  $\nu\text{H}_2\text{O}$  absorption has a strong peak at  $3450\text{ cm}^{-1}$  and a shoulder at the high frequency flank. The intensity ratio between the symmetric and antisymmetric modes suggests dichroic effects. Unfortunately, the low melting point ( $-45\text{ }^\circ\text{C}$ ) precludes any form of sampling other than freezing in the low-temperature cell. The spectrum of

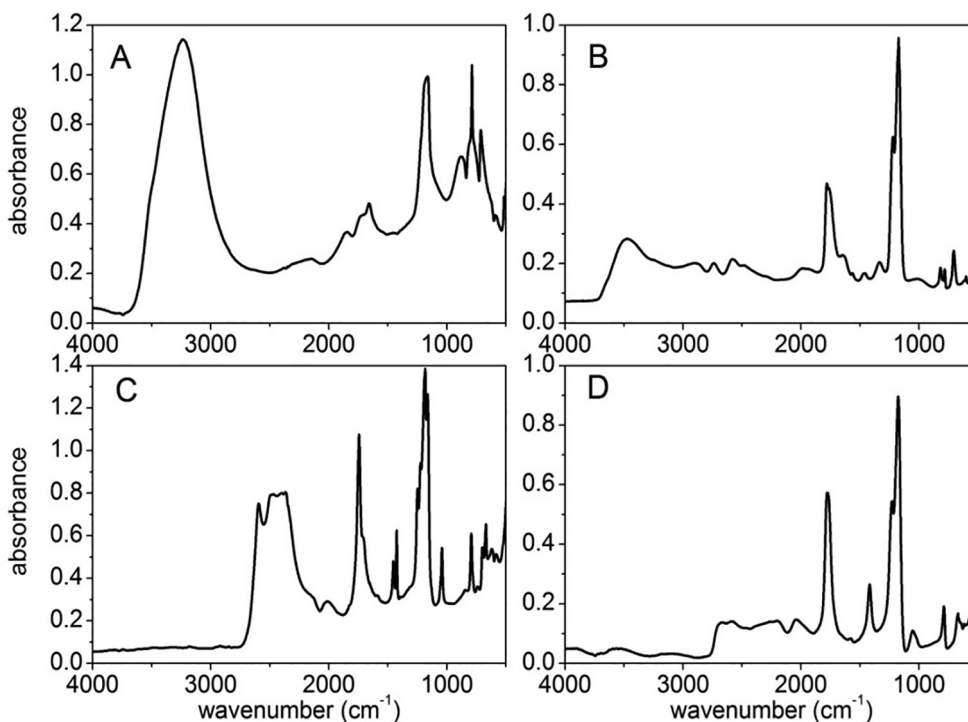


Fig. 5. The infrared spectra of TFAM (B, D) and TFAT (A, C) at  $T = -50\text{ }^\circ\text{C}$ . A. TFAT ( $\text{H}_2\text{O}$ ), B. TFAM ( $\text{H}_2\text{O}$ ), C. TFAT ( $\text{D}_2\text{O}$ ) and D. TFAM ( $\text{D}_2\text{O}$ ).

this model system is quite similar to the PFCA monohydrate, except for the water stretching bands. However, the differences between the spectra of the deuterated hydrates are much more pronounced. Since the crystal structure of deuterated TFAM is not known, comparisons with PFCA monohydrate are not meaningful.

The spectrum of  $\alpha$ -oxalic acid dihydrate (Fig. 6) seems more attractive for comparison with the hydrogen bonding properties of PFCA. Remarkably similar in every respect are the  $\nu\text{H}_2\text{O}$  bands. These include the frequencies of the two bands in the range  $3450\text{--}3540\text{ cm}^{-1}$ , their large shifts at low temperatures, and the frequencies of the partially deuterated and decoupled HOD bands.

These observations are sufficient to identify the ionization state of the hydration water, which is obviously neutral. However, the strong hydrogen bonding characteristics in the spectrum of OXAD push the comparison in the direction of the similarity of such bonds in both materials. OXAD crystallizes in two forms, designated as  $\alpha$  and  $\beta$ . Besides the differences in unit cell dimensions, the main difference is related to the structure of the water molecules. In the water molecule, one of the orbitals of the  $\alpha$  type with one of the lone pairs is directed toward the hydrogen bond donor group, while the other lone pair is not specifically directed toward adjacent groups. On the other hand, the water molecule in the  $\beta$  type has the bisection of the lone pair directed towards the hydrogen bond donor group [46]. The neutron diffraction studies show that the hydrogen bonds between the carboxylic proton and the oxygen of the water molecule are  $1.480\text{ \AA}$ , which corresponds to a distance of  $2.506\text{ \AA}$   $R_{\text{O}\cdots\text{O}}$  distance. The  $R_{\text{H}\cdots\text{O}\cdots\text{C}}$  distances of water to adjacent neighbour oxalic oxygen atoms are  $1.917\text{ \AA}$  and  $1.979\text{ \AA}$ , respectively. The most striking feature in the infrared spectrum of OXAD is the rather strong absorption near  $1900\text{ cm}^{-1}$ , which appears to be the peak of a broad absorption that extends over virtually the entire range of this study; we will again briefly refer to the absorption at  $1900\text{ cm}^{-1}$  as band C. It appears to be composite, as in the PFCA monohydrate example, and the components also show similar sensitivity to temperature and interpreta-

tion. However, there is also a notable difference: the gap between band C and the  $\nu\text{C}=\text{O}$  does not look like Evans-type transmission, and this difference becomes even more apparent upon cooling and after deuteration. We believe that the similarities between the spectra of PFCA monohydrate and OXAD are sufficient under all circumstances to predict similar hydrogen bonding of water to the carbonyl group and fairly strong bonding of the carboxylic OH group to hydrogen oxygen. The similarity in water expansion suggests that the metric parameters of the water molecules in both hydrates are also very similar. The  $R_{\text{O}\cdots\text{O}}$  distance in the strong hydrogen bond is expected to be close to  $2.5\text{ \AA}$ . Later, this was recently demonstrated by powder X-ray experiments and theoretical calculations [38].

#### 4. Conclusions

The infrared spectra of long-chain perfluorocarboxylic acids represent the system with very short hydrogen bonds connecting the water molecules to the carboxylates. Consideration of the significant features of the infrared spectra of the long-chain perfluorocarboxylic acid monohydrates, supplemented by their Raman spectra, and comparison with the spectra of auxiliary substances have led us to conclude that the rather strong neutral carboxyl-hydroxyl to water bonding can best explain the observations. The infrared spectra indicate the presence of fairly short hydrogen bonds connecting the water molecules to the carbonyl groups. In the construction of the hydrogen bonding pattern of the perfluorocarboxylic acid monohydrates, the oxalic acid dihydrate plays the key role. The striking similarity between the infrared spectra of the oxalic acid dihydrates and the perfluorocarboxylic acid monohydrates in the regions characteristic of water and  $\text{O-H}\cdots\text{O}$  vibration suggests that the structure of the hydrated carboxyl groups is the same in both crystals. These regions are characterized by the sharp doublet at  $3539\text{ cm}^{-1}$  and  $3464\text{ cm}^{-1}$ , which is due to the  $\text{H}_2\text{O}$   $\nu_1$  and  $\nu_3$  stretching vibrations, respectively, and the broad

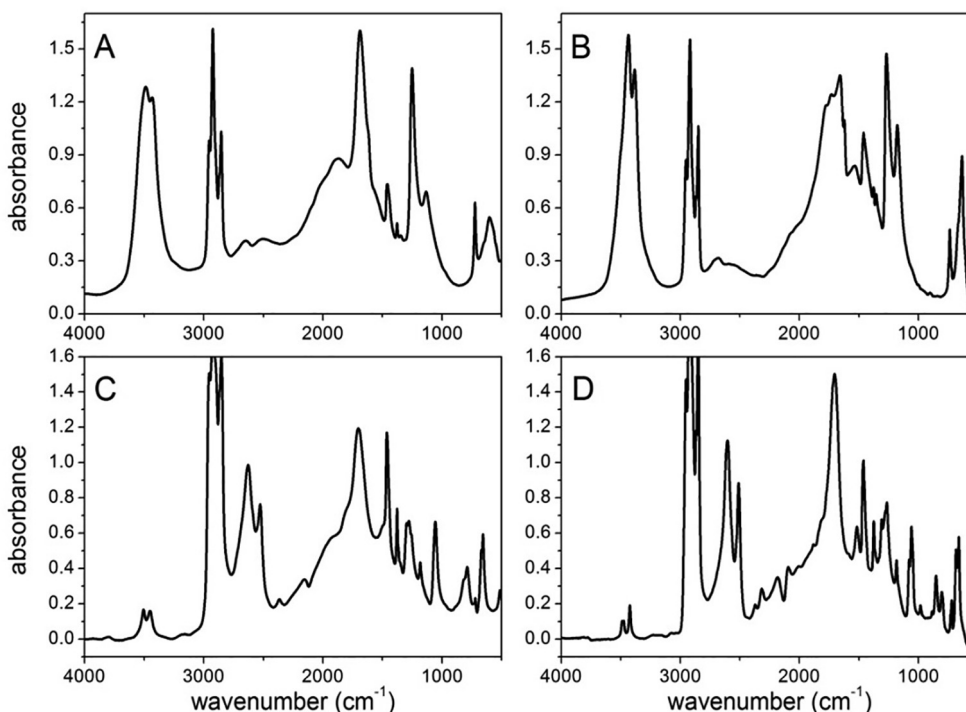


Fig. 6. Oxalic acid dihydrate at  $T = \text{RT}$  (A, C) and  $T = -150\text{ }^\circ\text{C}$  (B, D) A and B oxalic acid dihydrate ( $\text{H}_2\text{O}$ ); C and D oxalic acid dihydrate ( $\text{D}_2\text{O}$ ).

absorption between  $3000\text{ cm}^{-1}$  and  $1500\text{ cm}^{-1}$  with the intense band at  $1970\text{ cm}^{-1}$ , both associated with the vibration of the O—H...O group. The later peak consists of two band components at near  $1980\text{ cm}^{-1}$  and  $2020\text{ cm}^{-1}$ . These band components show different behaviour when the temperature, polarization or deuteration is changed. No clear indicators were found that differ between the two acid hydrates and can be attributed to environmental influences.

The infrared spectra of the acid hydrates shown differ markedly from those known to be typical of acid dimers (Fig. 3). The position, band shape, and especially the bandwidth of the OH stretching band(s) of the OH groups involved in the strongest hydrogen bonds are completely altered. The band position is largely red-shifted, indicating the formation of stronger hydrogen bonds. The explanation for the change in band shape and width is not so clear. It has been proven that many different mechanisms that have origin in formation of hydrogen bonds have influence on the infrared band shapes [2,3,7,12,15,18,54–56]. And it is quite possible that different mechanisms contribute to the shaping of the O–H stretching band in different hydrogen-bonded systems. Furthermore, the interpretation of the origin of the A, B, and C bands in the spectra of materials with relatively short hydrogen bonds (RO...O 2.5 Å) is not clear. The still most frequently mentioned role of Fermi resonances with resulting Evans transmission and submaxima. It is therefore interesting to study systems that help to differentiate between the possible band formation mechanisms. This is particularly desirable for band C, which has been discussed in detail by Hofacker et al [20] and where, on the other hand, some questions have been left open in the explanation based on the Fermi resonance [11,57]. The spectra of PFCA monohydrate with the prominent band C promise to be helpful in this regard. With respect to the role of large-amplitude proton motion in the possible band shaping mechanisms, it is necessary to first consider the probability of proton tunnelling. This is because the related example of OXAD tunnelling does not seem likely after neutron diffraction; this refers at least to the fundamental vibrational state. If we now consider band C in the spectra of PFCA monohydrate, we recall that it is composed of two bands, one of which is deuteration sensitive while the other is not. The high-frequency shift of  $\nu_{\text{C=O}}$  associated with the removal of this component of band C suggests that it is a normal mode of protonic origin. The origin of the second component is currently unclear.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.saa.2021.119551>.

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