Potassium Fluoride–Succinic Acid Adduct: A Fully Refined *X*-Ray Crystal-structure Determination, *Ab Initio* Calculations of a Model System, and the Infrared Spectrum of a Very Strong Hydrogen-bonded System

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The title complex $KF{\cdot}(CH_2CO_2H)_2$, grown from aqueous solution, is orthorhombic, space group *Pnam*, with a = 7.0680(1), b = 5.5710(1), c = 16.846(2) Å, and Z = 4. Its structure, determined by *X*-ray diffraction techniques and refined to R 0.035, consists of infinite chains of fluoride ions joined to two succinic acid molecules by very short hydrogen bonds of $R(O \cdots F)$ = 2.441(3) Å. The complex $[F(HCO_2H)_2]^-$ has been used as a model for the purpose of *ab initio* calculations on this doubly hydrogen-bonded fluoride, and these show a theoretical hydrogen-bond energy of 179 kJ mol^{-1} for each bond. The i.r. spectrum of $KF{\cdot}(CH_2CO_2H)_2$ shows eight very broad bands in several regions of the spectrum and these are assigned to the vibrational modes of this unique $O{-}H \cdots F^- \cdots H{-}O$ hydrogen-bonded system.

AMONG the growing number of very strong hydrogen bonds those of the type O–H–F are relatively few.[1,2] Where crystals with such bonds have been investigated, as with metal fluoride hydrates, they have shown $R(O \cdots F)$ distances in the range 2.60—2.86 Å.[3] Although these bonds qualify as hydrogen bonds, by being less than the sum of the van der Waals radii of oxygen and fluorine (2.90 Å), they do not show a shortening of 0.3 Å which is taken to indicate a very short (and consequently very strong) hydrogen bond.[2] However, some fluoride hydrates show $R(O \cdots F)$ distances that put them in this category: $RbVF_4{\cdot}2H_2O$, 2.56;[4] $ZnF_2{\cdot}4H_2O$, 2.57;[5] $[NH_4]_2[Cr(H_2O)_6]F_5$, 2.53—2.57 (several bonds);[6] $Te(OH)_6{\cdot}2KF$ and $Te(OH)_6{\cdot}NaF$, 2.58 Å.[7] The only compounds with unquestionably very short OHF hydrogen bonds are $KH_2PO_3{\cdot}HF$ (2.38 Å)[8] and the compound under discussion here, $KF{\cdot}(CH_2CO_2H)_2$ (2.44 Å) in both its H and D forms.[9]

Since the discovery that alkali-metal fluorides, with the exception of LiF, are very soluble in carboxylic acids,[10] it had been claimed that the unusual properties of these solutions arise from $F^- \cdots H{-}O$ hydrogen bonding. Their high viscosities,[11] large enthalpies of solution,[12] the chemical shift of the acid proton,[13] and the i.r. spectra of the $MF{\cdot}RCO_2H$ solvates[14] have been explained in terms of a very strong hydrogen bond.

Previous *ab initio* calculations on the systems HCO_2HF^- and $CH_3CO_2HF^-$ have shown hydrogen-bond energies of 105 kJ mol^{-1} relative to the separated species $HCO_2^- + HF$ and $CH_3CO_2^- + HF$ respectively.[15] These calculations showed short $R(O \cdots F)$ distances of 2.37—2.39 Å with the proton located near the fluoride, and hence the energy is defined with respect to the carboxylate anion and HF.[16] Bond energies have been measured experimentally by ion cyclotron resonance methods for these gaseous hydrogen-bonded ions and show E = 82 kJ mol^{-1}.[17]

From KF solution in acetic acid, a solvate $KF{\cdot}2CH_3CO_2H$ can be obtained.[11] On exposure to air some CH_3CO_2H is readily lost and no crystal suitable for *X*-ray diffraction analysis has been found. Potassium fluoride in acetic acid–water mixtures yields KHF_2 crystals.[18] However, from KF solutions in succinic acid and water, *anhydrous* crystals of $KF{\cdot}(CH_2CO_2H)_2$ grow. These are held together by a framework of very strong O–H–F hydrogen bonds which we have investigated by *X*-ray, *ab initio*, and i.r. methods.

Succinic acid is a biochemically important acid of the Krebs (tricarboxylic acid) Cycle. That it will form a strong attachment of a fluoride ion, even under aqueous conditions, comes as a surprise. This is further evidence that this simple ion is far from inert towards organic components in the living cell, as is commonly supposed.

EXPERIMENTAL AND RESULTS

Preparation of $KF{\cdot}(CH_2CO_2H)_2$.—Potassium fluoride (2.02 g, 0.035 mol) was dissolved in water (50 cm^3) and succinic acid (4.05 g, 0.035 mol) added in stages with stirring. The solution was evaporated on a hot water-bath until saturated and then allowed to cool slowly to yield crystals of the product, m.p. 153 °C (Found: C, 27.3; H, 3.45; F, 10.6. Calc. for $C_4H_6FKO_4$: C, 27.25; H, 3.40; F, 10.8%). Titration of the acid content showed two acid protons per formula unit.

The solubility of succinic acid in water (68 g dm^{-3} at 20 °C)[19] is greatly enhanced by the addition of KF. In fact the solubility of the acid increases in direct proportion to the molarity of KF, *i.e.* each fluoride ion induces the solution of an extra succinic acid molecule. The solubility of succinic acid in KF solution of molarity c_{KF} is given by the equation below.

$$\text{Solubility of } (CH_2CO_2H)_2 = 0.45 + 1.00c_{KF}/\text{mol dm}^{-3}$$

The adduct $KF{\cdot}(CH_2CO_2H)_2$ crystallises from solutions having excess of acid up to a mol ratio of KF : $(CH_2CO_2H)_2$ of 1 : 2. At higher ratios of acid the solid phase which first crystallises from solution is the acid itself.

Crystal Data.—$C_4H_6FKO_4$, M = 176.19, Orthorhombic, space group *Pnam*, a = 7.0680(1), b = 5.5710(1), c = 16.846(2) Å, U = 663.3 Å^3, Z = 4, D_c = 1.764 g cm^{-3}, $F(000)$ = 360, $\mu(\text{Cu-}K\alpha)$ = 69.73 cm^{-1}, λ = 1.5418 Å.

The adduct $KF{\cdot}(CH_2CO_2H)_2$ formed clusters of clear, colourless flattened prisms with good morphology. One such crystal (maximum dimension 0.036 cm) was mounted for data collection about *b* and lattice parameters were calculated from θ values of high-angle axial reflections measured on a Siemens off-line, four-circle diffractometer.

Intensities of 651 reflections ($\theta_{max.} = 70°$) were measured with the diffractometer in five-value mode, 14 of these being classed as unobserved [$I < 2.58\sigma(I)$]. The data were corrected for Lorentz-polarisation factors, and the structure was solved by the heavy-atom method using the program SHELX-76 of Professor G. M. Sheldrick.

TABLE 1

Fractional atomic co-ordinates ($\times 10^4$) for $KF\cdot(CH_2CO_2H)_2$, with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
K	2 221(1)	4 096(1)	2 500(0)
F	5 792(3)	5 733(4)	2 500(0)
O(1)	7 840(3)	1 610(4)	−1 202(1)
O(2)	5 769(2)	−1 337(3)	−1 380(1)
C(1)	6 451(3)	231(4)	−972(1)
C(2)	5 813(3)	781(5)	−137(1)
H(1)	8 209(50)	1 247(65)	−1 666(22)
H(21)	5 405(40)	2 553(57)	−119(17)
H(22)	6 880(30)	581(52)	202(17)

The intensity characteristics of preliminary photographs indicated that the structure was probably centrosymmetric, and this was confirmed during the early stages of refinement by markedly superior performance in *Pnam*. Anisotropic refinements of all non-hydrogen atoms gave an *R* factor of 0.078; methylene hydrogen atoms (with co-ordinates calculated by the program) were included in further cycles of least squares, after which the *R* value was 0.066. The position of the hydroxy hydrogen was very clearly shown by a weighted difference map, and was subsequently included with co-ordinates calculated by the difference program. The data were then corrected for absorption using a program based on that by Coppens *et al.*[20] and 14 reflections suspected of extinction were withdrawn from the final stages of refinement. The final *R* value was 0.035, and the difference-Fourier map showed no peaks greater than *ca.* 0.25 e Å^{-3}. Coefficients required by the SHELX-76 program for the calculation of K^+ and F^- scattering factors were taken from ref. 21. Two sets of special positions are utilised in this structure with fluorine and potassium lying on the mirror planes and succinic acid on centres of symmetry.

Table 1 lists the atomic co-ordinates and Table 2 the bond lengths and angles. Thermal parameters for the non-hydrogen atoms and the structure factors are listed in Supplementary Publication No. SUP 23244 (5 pp.).* Figure 1 shows the ORTEP diagram of the molecule, Figure 2 the hydrogen-bond environment around the fluoride ion, and Figure 3 the environment around potassium within a radius of 3 Å. The interatomic distances surrounding K^+ are given in Table 2. Each potassium ion has two fluorides and four carbonyl oxygens as nearest neighbours in a distorted octahedral arrangement.

The *X*-ray crystallographic determination clearly shows each fluoride ion to be involved in two very short O–H · · · F^- hydrogen bonds which are also highly asymmetric with the hydrogen atoms still covalently near their parent oxygens. This does not accord with the position of the proton as calculated for RCO_2HF^-.[15]

Ab Initio *LCAO-MO-SCF Calculations*.—The species $[F(CH_2CO_2H)_2]^-$ is unfortunately too large for a sufficiently accurate *ab initio* treatment, and so $[F(HCO_2H)_2]^-$ was chosen as a model and its molecular configuration and hydrogen-bond energy were calculated. *Ab initio* LCAO–MO–SCF calculations have been performed on $[F(HCO_2H)_2]^-$ using a version of the program GAUSSIAN 76.[22] This program has recently been modified to perform level-shifting of the Hartree–Fock Hamiltonian [23] directly in the atomic orbital basis to guarantee the convergence of the iterative SCF calculations.[24]

TABLE 2

Bond lengths (Å) and angles (°) for $KF\cdot(CH_2CO_2H)_2$, with e.s.d.s in parentheses

F–H(1)	1.598(30)	H(1)–O(1)–C(1)	111.3(2)
F–O(1)	2.441(3)	C(2)–C(1)–O(1)	112.4(2)
H(1)–O(1)	0.849(28)	C(2)–C(1)–O(2)	123.8(2)
C(1)–O(1)	1.305(3)	O(1)–C(1)–O(2)	123.8(2)
C(1)–O(2)	1.211(3)	H(21)–C(2)–C(1)	107.8(16)
C(1)–C(2)	1.509(3)	H(22)–C(2)–C(1)	107.4(16)
C(2)–H(21)	1.029(31)	H(21)–C(2)–H(22)	108.4(23)
C(2)–H(22)	0.953(29)	H(1)–F–H(1)	123(3)
C(2)–C(2′)	1.514(5)	O(1)–H(1)–F	171(2)
K–F(1)	2.874(3)		
K–F(2)	2.684(3)		
K–O(21)*	2.843(3)		
K–O(22)	2.843(3)		
K–O(23)	2.818(3)		
K–O(24)	2.818(3)		

* The oxygen atoms are related in pairs O(21),O(22) and O(23),O(24) by the crystallographic mirror plane through F(1)KF(2).

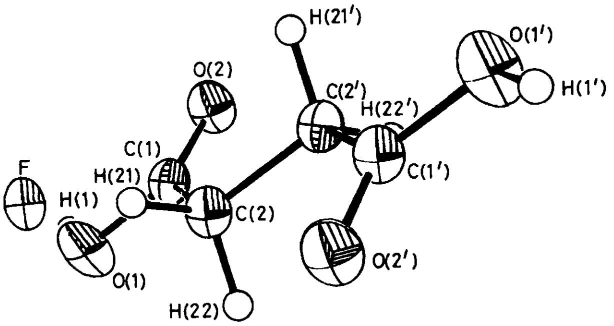

FIGURE 1 ORTEP diagram of $KF\cdot(CH_2CO_2H)_2$

The complex $[F(HCO_2H)_2]^-$ was assumed planar and a preliminary optimisation was carried out on the bond lengths *R*(C–O), *R*(C=O), and *R*(C–H) and angles H–C=O, O–C=O, and H–C–O of the formic acid units, using the split-valence 4-31G basis set [25] and univariate quadratic interpolation techniques. These geometrical parameters were subsequently held fixed at *R*(C–O) = 1.313, *R*(C=O) = 1.214, *R*(C–H) = 1.085 Å, H–C=O 119.8, H–C–O 111.3, and O–C=O 129.1°.

Geometry optimisations of *R*(O–H), *R*(H · · · F), O–H–F, and H–F–H (bond lengths to within 0.005 Å, bond angles to within 1°) were then performed in the 4-31G basis set. Figure 4 shows the six conformations with their optimised bond lengths and angles. In all six cases the protons prefer to remain near the oxygen atoms, as in the actual crystal. These conformations can be classified as *cis* or

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

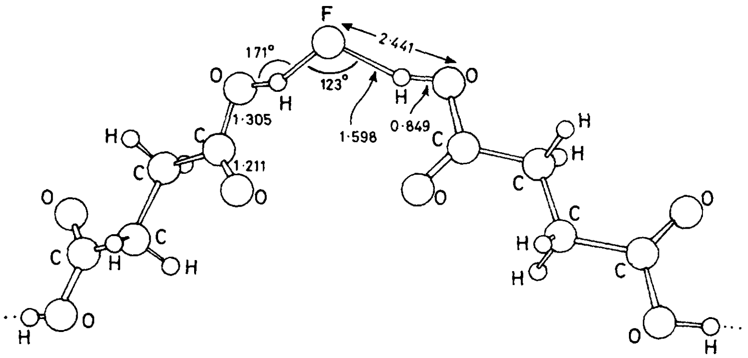

FIGURE 2 Hydrogen-bond environment around the fluoride in $KF{\cdot}(CH_2CO_2H)_2$

trans with respect to the placings of the formic acid molecules about the fluoride ion, and within this classification there are three possible arrangements of the two formyl protons and the two carbonyl oxygens with respect to one another. In (I) and (II) both of the formyl protons are nearer the fluoride site, in (III) and (IV) one formyl proton and one carbonyl oxygen are nearer F^-, and in (V) and (VI) both carbonyl oxygens are so arranged. The 4-31G energies show that these arrangements are more important in determining the energy or the conformation than is the *cis* or *trans* arrangement.

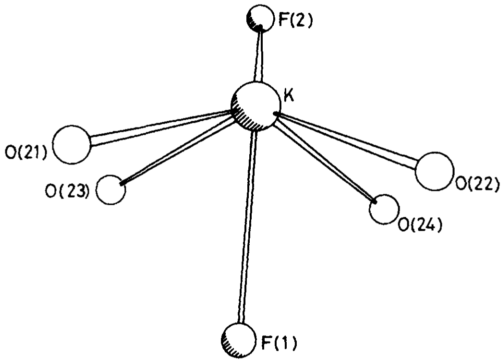

FIGURE 3 Potassium environment

It is most gratifying to find that structure (I) is the most stable since this *cis* arrangement resembles the actual structure of the crystals in terms of the hydrogen bonding. However, it differs in the actual angle at F^-, which is observed as 123°, and in the arrangement of the carbonyl oxygens, which are placed in the crystal so as to form part of the co-ordination sphere of the potassium ions.

In a previous paper,[18] two possible ways of defining the hydrogen-bond energy of multiple hydrogen-bonded systems were discussed and applied to polyfluorides. The hydrogen-bond dissociation energy of $[F(HCO_2H)_2]^-$ is defined with respect to whichever of the two possible alternative pairs of component molecules (either HCO_2HF^- and HCO_2H or HCO_2HFH and HCO_2^-) is energetically closer to the complex.[15,16] The energies of the optimised geometries for HCO_2H, HCO_2^-, and HCO_2HF^- in the 4-31G basis set are already available,[16] and the energy of the 4-31G optimised geometry of $HCO_2H \cdots FH$ [$R(H \cdots F) = 1.829$, $R(F{-}H) = 0.923$ Å] was determined as $-288.373\,14$ Hartree.* Thus, at the 4-31G level, the former pair of components is energetically closer to the complex than the latter pair by 112 kJ mol^{-1}, demonstrating that the hydrogen-bond dissociation energy should be defined with respect to the pair HCO_2HF^- and HCO_2H.

The *mean* hydrogen-bond energy of $[F(HCO_2H)_2]^-$ is defined with respect to either $2HCO_2H$ and F^- or $2HCO_2^-$ and H_2F^+, whichever is energetically closer to the complex.[15,16] The 4-31G energy for H_2F^+ was computed to be $-100.075\,14$ Hartree using the optimised geometry of Diercksen and Kraemer.[26] Thus, at the 4-31G level the former set of components is energetically closer to the complex than the latter set by 840 kJ mol^{-1}, demonstrating that the mean hydrogen-bond energy should be defined with respect to $2HCO_2H$ and F^-.

The total energy of the most stable conformation, (I), was finally computed to be $-476.993\,78$ Hartree using the extended [$4s2p/2s1p$] basis set of Dunning[27] with an s-orbital scaling factor of $\sqrt{2}$ and a p-orbital exponent of 0.7 for the acidic protons, and the scaling factors and p-exponents of the other protons set to unity, using the ATMOL3 program system.[28] This basis set has previously been shown to be sufficiently complete to yield hydrogen-bond energies which are stable against further basis-set extensions [18,29] and against 'ghost orbital' corrections.[30] Single-determinant wavefunctions are generally adequate for calculations of the energies of strong hydrogen bonds between closed-shell molecules since the molecular extra correlation energy and the zero-point vibrational corrections are both small, *ca.* 5%.[31] The [$4s2p/2s1p$] energies of the components HCO_2HF^-, HCO_2H, and F^- were similarly computed (using the 4-31G optimised geometries for HCO_2HF^- and HCO_2H of Bouma and Radom) [16] to be $-288.234\,55$, $-188.721\,69$, and $-99.414\,06$ Hartree respectively. The hydrogen-bond dissociation energy, defined with respect to HCO_2HF^- and HCO_2H, is thus computed to be 99 kJ mol^{-1}. The mean hydrogen-bond energy of each of the $H \cdots F$ bonds in $[F(HCO_2H)_2]^-$, defined with respect to the pair $2HCO_2H$ and F^-, is calculated to be 179 kJ mol^{-1} using the [$4s2p/2s1p$] basis set; the total hydrogen-bond energy of the system is 358 kJ mol^{-1}.

For multiple strong hydrogen bonds about F^- the best definition of bond energies is with respect to F^- and the neutral hydrogen-bond donors. The same was found to be the case with the polyfluorides, $H_nF_{n+1}^-$.[18] However, for single hydrogen bonds the definition producing the minimum energy is with respect to HF and the conjugate base of the hydrogen-bond donor.[15,16,32] In this way the hydrogen-bond energy of HCO_2HF^- is reported [15] to be 105 kJ mol^{-1}

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* Throughout this paper: 1 Hartree = 2 625.5 kJ mol^{-1}.

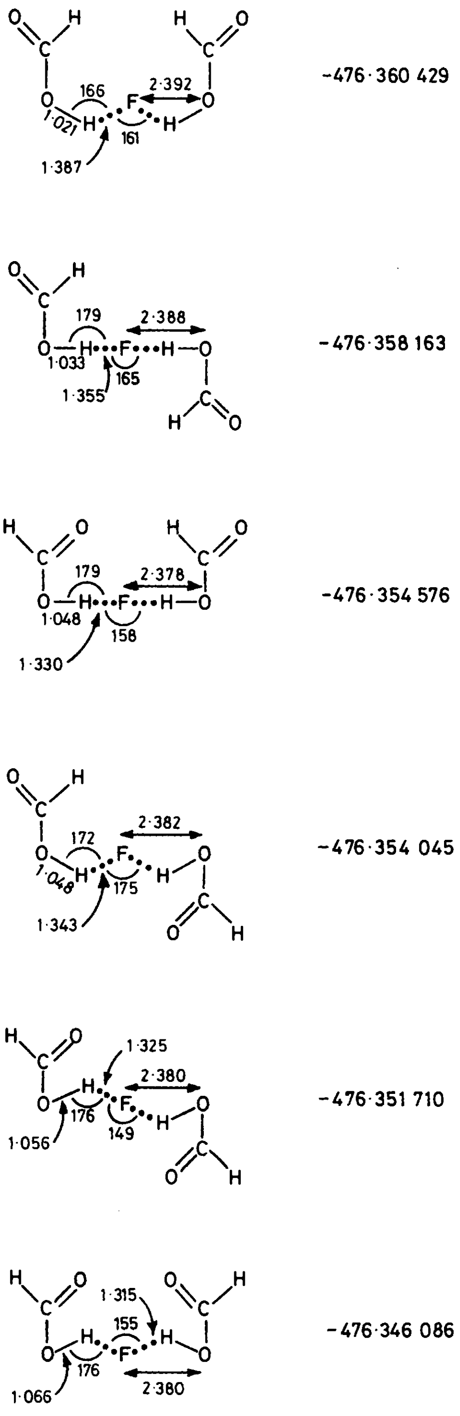

FIGURE 4 Structures [bond lengths (Å) and angles (°)] and total energies (Hartree) of six possible conformations of $[F(HCO_2H)_2]^-$, calculated with the 4-31 G basis set

(as opposed to 249 kJ mol^{-1} with respect to F^- and HCO_2H[29]). Bouma and Radom reoptimised the structure of HCO_2HF^- and calculated the hydrogen-bond energy as 139 kJ mol^{-1} in the 4-31G basis set.[16] Using the [4s2p/2s1p] basis set we have recalculated the energy of their reoptimised structure as −288.234 55 Hartree, which together with the corresponding energies for HCO_2^- (−188.147 88) and HF (−100.038 47) yields a hydrogen-bond energy of 127 kJ mol^{-1} with respect to HCO_2^- and HF (259.5 kJ mol^{-1} with respect to HCO_2H and F^-). It is with these energies that the hydrogen-bond energy of $[F(HCO_2H)_2]^-$ should be compared, showing that the formation of a second such bond to F^- still produces a bond that can be defined as very strong. It is thus reasonable to suppose that in $KF\cdot(CH_2CO_2H)_2$ the array of interlinked F^- and succinic acid molecules will also be held by very strong hydrogen bonds of the order of 150 kJ mol^{-1}.

TABLE 3

I.r. data (cm^{-1}) for $KF\cdot(CH_2CO_2H)_2$ with assignments *

330s (br)	ρ(OH) out-of-plane bend A_1, O–H···$\bar{F}$···H–O
412w	SA
542w	
562s	ν(KO)
585w	SA
635s	SA
740w	
810s	SA
840m	
895s	SA
950w	SA
990w	SA
1 050m (br)	δ(OH) in-plane, in-phase, A_1, symmetric bend
1 085m (br)	δ(OH) in-plane, out-of-phase, B_1, asymmetric bend
1 175s	SA
1 195s	SA
1 210 (sh)	SA } CH_2
1 250m	SA
1 280 (sh)	SA
1 300m	SA, ν(CO_2)
1 350 (br, sh)	ν(HFH), B_1, symmetric bend H···$\bar{F}$···H
1 410s	SA δ(CH_2)
1 425s	SA ν(C–O)
1 545m (br)	ν(HFH), A_1, symmetric stretch ←H···F···H→
1 695s	SA } ν(C=O) in- and out-of-phase
1 720s	SA
1 920s (br)	ν(HFH), B_2, asymmetric stretch H···→F···H→
2 240m (br)	ν(OH), A_1, in-phase stretch
2 460m (br)	ν(OH), B_1, out-of-phase stretch
2 950w	SA, ν(CH_2)

* SA = Succinic acid mode.

The total hydrogen-bond energy for $[F(HCO_2H)_2]^-$ of 358 kJ mol^{-1} can also be compared to the total [4s2p/2s1p] hydrogen-bond energy of 354 kJ mol^{-1} for $H_2F_3^-$ with its two hydrogen bonds to F^-.[18] This shows OHF and FHF hydrogen bonds to be equally strong in these two complexes.

Infrared Spectrum of $KF\cdot(CH_2CO_2H)_2$.—The i.r. spectrum was recorded on a Perkin-Elmer 457 instrument with CsBr plates for Nujol and hexachlorobutadiene mulls. The principal features of the spectrum are the many very broad bands due to the hydrogen bonding. The succinic acid framework modes are sharp and are readily distinguished. The spectrum is listed in Table 3.

The structure of $KF\cdot(CH_2CO_2H)_2$ with its unique double, strong hydrogen bonding permits a close analysis of the bands hydrogen bonding would give rise to. Applying group theory to the C_{2v} symmetry of the five-atom OHFHO system in isolation shows that the $3n - 6$ (*i.e.* nine) vibrational modes will be as follows: $4A_1$ (i.r.-active), A_2 (inactive), $3B_1$ (i.r.-active), and B_2 (i.r.-active). Thus there should be eight broad hydrogen-bonding bands in the i.r. spectrum and these are observed.

Three of the vibrational modes are principally the motion of the F^- ion in three perpendicular directions. Two of these are in the plane of the OHFHO system and are the symmetric (A_1) and asymmetric (B_2) $H\cdots\overset{-}{F}\cdots H$ stretching modes; the out-of-plane motion is the bending mode (B_1). There are three directions of motion for each OH group, one of which represents the in-plane stretching mode, while the others represent the in- and out-of-plane bending modes. These three OH vibrations can be in- or out-of-phase with the same mode on the other OH group, giving rise to six modes in all. However, one of these, the torsion mode (A_2) is i.r.-inactive. The bands in Table 3 are assigned on the basis that the $O\underline{H}$ stretching modes are of higher frequency than the $H\cdots\overset{-}{F}\cdots H$ stretching modes because of their relative bond lengths. A similar assumption was made for the bending modes.

In succinic acid itself, hydrogen bonding gives rise to three broad bands in its spectrum at *ca.* 2 900 (ν_{OHO}), 1 300 ($\nu_{bending}$), and 915 cm^{-1} ($\nu_{torsional}$). These are the stretching and in- and out-of-plane bending modes respectively. Some of the bands in the spectrum of $KF{\cdot}(CH_2CO_2H)_2$ can be related to these modes and show shifts of several hundred wavenumbers.

The spectrum of a saturated solution of KF in glacial acetic acid and of the solvate $KF{\cdot}2CH_3CO_2H$ show marked similarities to the spectrum of $KF{\cdot}(CH_2CO_2H)_2$.[11] The solvate $KF{\cdot}2CH_3CO_2H$ has broad bands at 2 425, 2 040, 1 840, 1 560, 1 490, 1 325, 1 165, and 995 cm^{-1}. Previously only the bands at 1 490, 1 165, and 995 cm^{-1} were assigned to OHF hydrogen bonding on the assumption that there was only one such bond in the substance $KF{\cdot}2CH_3CO_2H$. The other bands were left unassigned. In the light of the spectrum of $KF{\cdot}(CH_2CO_2H)_2$ it seems likely that $KF{\cdot}2CH_3CO_2H$ is also a doubly hydrogen-bonded, OHFHO system. Its spectrum also contains a low-frequency band at 463 cm^{-1} which was linked to the adjacent peak at 483 cm^{-1} and assigned as δ(CCO). A more likely assignment is ρ(OH) (A_1).

The disolvate was originally postulated to be $KF{\cdot}CH_3CO_2H{\cdot}CH_3CO_2H$ [11] with the second acid molecule weakly hydrogen bonded to the carbonyl oxygen of the first acid molecule (the one that is strongly hydrogen bonded to the F^- ion). This seemed reasonable since one of the acid molecules can be removed by warming to 50 °C whereas the other is not lost completely until 150 °C. A more logical prediction of the structure of this disolvate would now be $K^+[CH_3CO_2H\cdots F\cdots HO_2CCH_3]^-$ and this further supports the nuclear Overhauser effect reported for fluoride solutions in glacial acetic acid which was interpreted in terms of there being two acid molecules strongly hydrogen bonded to each fluoride ion.[33]

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