The Vibrational Spectrum of a Strong O–H · · · F Hydrogen Bond: Infrared and Raman Spectra of the Potassium Fluoride–Succinic Acid Adduct †

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The crystalline potassium fluoride–succinic acid adduct contains strong hydrogen bonds, O–H · · · F^-. The i.r. spectra of $KF\cdot(CH_2CO_2H)_2$ and $KF\cdot(CH_2CO_2D)_2$ in the range 3 500—250 cm^{-1}, and the Raman spectrum of the protonated adduct between 3 000 and 20 cm^{-1} are analysed in terms of the site symmetry in the crystal and are discussed according to current theories of the strong hydrogen bond.

Few examples of strong hydrogen bonds formed between heteroatomic donor and acceptor centres A–H · · · B are known, compared with the vast literature concerning O · · · O or N · · · N hydrogen bonds.[1,2] In particular, compounds containing strong or medium-strong O–H · · · F bonds have been obtained in a form suitable for diffraction experiments in only a handful of cases,[3] with little published concerning their vibrational spectra.[4]

Succinic, $(CH_2CO_2H)_2$, and malonic, $CH_2(CO_2H)_2$, acids form crystalline adducts with caesium or potassium fluorides when mixed in equimolar proportions in aqueous solution.[5] The single-crystal *X*-ray study of $KF\cdot(CH_2CO_2H)_2$ has shown the succinic acid units to be linked into infinite chains by fluoride ions with, owing to the crystal symmetry, a single O–H · · · F distance of 2.441 Å[6] (Figure). This simple arrangement allows a detailed vibrational spectroscopic analysis, providing an interesting example of the vibrational spectrum produced by strong O–H · · · F bonds. In addition, since the *X*-ray investigations have included that of the deuteriated adduct, $KF\cdot(CH_2CO_2D)_2$,[7] it is instructive to compare the spectral manifestations in the i.r. of deuterium substitution with the isotope effect observed in the single-crystal diffraction experiment.

A vibrational analysis of the i.r. spectrum in terms of group frequency and symmetry co-ordinates has already been published.[6] However, in the light of several recent publications,[8] it is clear that such a specific assignment is only appropriate for certain bands in the i.r. spectra of hydrogen-bonded compounds. We thus felt justified in reinterpreting the spectrum, particularly with respect to the stretching vibrations of the hydrogen bond and the assignment of the hydrogen-bond bending modes. The present study includes, in addition, the Raman spectrum of the protonated compound in the range 3 000—20 cm^{-1}.

Experimental

The adducts $KF\cdot(CH_2CO_2H)_2$ and $KF\cdot(CH_2CO_2D)_2$ were prepared as in refs. 6 and 7 respectively. The i.r. spectra were recorded using a Perkin-Elmer 457 instrument with CsBr plates for Nujol and hexachlorobutadiene mulls. The Raman spectrum of a large single crystal of the protonated compound was recorded using a Dilor spectrometer, and the data processed through a Tracor TN1710 modular multichannel computer (Northern Instruments). A Spectraphysics argon laser was used (5 145 Å, 150 mW). Spectral resolution was 0.5—1.0 cm^{-1} over the entire spectral range.

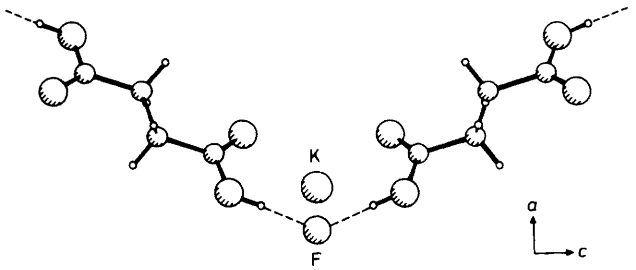

Figure. Structure of $KF\cdot(CH_2CO_2H)_2$ projected down the *b* axis

Results

The i.r. spectra in the frequency range 3 500—250 cm^{-1} of $KF\cdot(CH_2CO_2H)_2$ and $KF\cdot(CH_2CO_2D)_2$ and also the Raman spectrum of $KF\cdot(CH_2CO_2H)_2$ (between 3 000 and 20 cm^{-1}) are available as supplementary publication No. SUP 23941. The vibrational frequencies and their assignments are collected for the protonated and deuteriated compounds in Table 1.

Discussion

X-Ray diffraction has determined the structure to consist of chains of alternating succinic acid molecules and fluoride ions held together by strong hydrogen bonds and extending in the *c* direction (Figure). The compound crystallizes in the space group *Pnam* (D_{2h}) with four molecules per unit cell. Potassium and fluoride ions lie on mirror planes perpendicular to the *c* axis and to the plane of the hydrogen bonds. The succinic acid molecules lie on inversion centres. An isolated infinite chain · · · F^- · · · $(CH_2CO_2H)_2$ · · · F^- · · · conforms to the C_{2h} factor group. The correlation between the site symmetry of the O–H · · · F · · · H–O group and the succinic acid moieties, and the different factor groups, are available in SUP 23941.

The OHFHO group bears some resemblance to the poly-

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† *Supplementary data available* (No. SUP 23941, 5 pp.): i.r. spectra of $KF\cdot(CH_2CO_2H)_2$ and $KF\cdot(CH_2CO_2D)_2$ (3 500—250 cm^{-1}), Raman spectrum of $KF\cdot(CH_2CO_2H)_2$ (3 000—20 cm^{-1}), correlation diagram for $KF\cdot(CH_2CO_2H)_2$. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Infrared and Raman spectra of $KF{\cdot}(CH_2CO_2H)_2$ and the i.r. spectrum of $KF{\cdot}(CH_2CO_2D)_2$ [a,b]

$KF{\cdot}(CH_2CO_2H)_2$			$KF{\cdot}(CH_2CO_2D)_2$	
I.r.	Assignment	Raman	I.r.	Assignment
		2 986w		
		2 969w		
2 950w	SA, CH_2	2 951m	2 950w	SA, CH_2
		2 935w		
		2 924w		
		2 500vw, br		
2 460m,br				
			2 420w,br	
2 240m,br	ν(OH)			
			2 200w,br	ν(OH) [c]
		1 978vw,br		
1 920s,br				
			1 890w,br	
		1 739s		
1 720s			1 725s,br	
	SA, ν(C=O)	1 697w		SA, ν(C=O)
1 695s			1 665s,br	
1 545m,br	δ(OH)			
		1 523w		
		1 457w		SA, ν(OD) [d]
1 425s	SA		1 425s (sh)	
		1 418s		
1 410s	SA		1 410s (sh)	
			1 365s,br	
1 350m,br	SA, ν(C–O)	1 343s		
1 300m,br	SA	1 299w	1 295m (sh)	
1 280m (sh)	SA		1 270m (sh)	
1 250m	SA	1 249w	1 250m (sh)	
1 210m (sh)	SA	1 205w	1 200s	
1 195s	SA		1 195s	
1 175s	SA	1 177w		
1 085m,br		1 088w	1 085m (sh)	
	γ(OH)		1 078s	δ(OD)
1 050m,br		1 057vw	1 055m (sh)	
			1 005w (sh)	
990w	SA	994s	980w (sh)	
		956m (sh)		
950w	SA	945s	945w (sh)	
895m	SA	898m	900w	
			865m	
855		850vs		
845m			840m (sh)	
			818m	
810s	SA			
			775m	γ(OD)
740w		742w	735w	
		685vw		
		681vw		
645m (sh)		655vw		
635s	SA	640vw	630m	
585w (sh)	SA	593m		
562s		559w	565s	
542w (sh)		538m	545s (sh)	
480w				
440w (sh)	SA	440m		
415w	SA	420m		
		350m		
330s,br	ν(K–F)	ν(HFH)	330s,br	ν(K–F)
		252m		
		160m (sh)		
		132vs		
		109vs		
		72m (sh)		
		56vs		
		38vs		

[a] Values are reported in cm^{-1}. [b] Abbreviations used: weak, w; medium, m; strong, s; very, v; shoulder, sh; broad, br; SA = succinic acid mode. [c] Due to small amounts of residual $KF{\cdot}(CH_2CO_2H)_2$. [d] SA modes superimposed on the very broad ν(OD).

Table 2. Classification of co-ordinates *

Group vibration	Symmetry co-ordinates	Irreducible representation		
		C_{2v}	C_s	
ν(OH); symmetric (in-phase) stretching	$\frac{1}{\sqrt{2}}(r_1 + r_2)$	A_1	A'	ν_1
ν(OH); antisymmetric (out-of-phase) stretching	$\frac{1}{\sqrt{2}}(r_1 - r_2)$	B_1	A''	ν_3
ν(HFH); symmetric stretching	$\frac{1}{\sqrt{2}}(R_1 + R_2)$	A_1	A'	ν_2
ν(HFH); antisymmetric stretching	$\frac{1}{\sqrt{2}}(R_1 - R_2)$	B_1	A''	ν_4

* r and R are the internal co-ordinates for bonds O–H and H · · · F respectively.

fluoride ion $H_2F_3^-$. This ion has C_{2v} symmetry and strong asymmetric hydrogen bonds. However, in the OHFHO system the angle O–F–O is more acute (126°) than the corresponding angle in $H_2F_3^-$, being determined as 134° by *X*-ray diffraction [9a] and 147° by *ab initio* calculations.[9b]

For the five-atom system considered as having ideal C_{2v} symmetry, the co-ordinates of the stretching of the bonds can be classified as in Table 2. The site symmetry in the crystal being lower than this, the irreducible representation should be changed to that for C_s. However, the crystal symmetry has little effect on the activity in i.r. and Raman and the possible factor group splitting is expected to be unimportant, especially for the broad absorptions associated with the strong hydrogen bonding.

In the previous study [6] of $KF\cdot(CH_2CO_2H)_2$, each of the group vibrations in Table 2 was assigned to a particular band in the i.r. spectrum: for ν_1 2 240, ν_2 1 545, ν_3 2 460, and ν_4 1 920 cm^{-1}. Since this five-atom hydrogen-bonded system is probably highly asymmetric, with the hydrogen lying much closer to its parent oxygen atom than to the fluoride acceptor, the H · · · F vibrator behaves essentially as O · · · F. We propose that the ν(HFH) symmetric and antisymmetric modes, ν_2 and ν_4, should be assigned to lower frequencies.

If this system is compared with, for example, $H_2F_3^-$, the analogous modes for ν(HFH) have been found at frequencies <500 cm^{-1}.[10] For a stronger hydrogen-bonded system like HF_2^-, the symmetric stretch is found at *ca.* 600 cm^{-1} in the Raman spectrum (KHF_2,[11,12] $NaHF_2$[11]). The intense band at 330 and the weak band at 415 and 440 cm^{-1} in the i.r. spectra are possible candidates for these ν(HFH) modes, although they have been otherwise assigned in ref. 6. The latter two bands, however, also appear in the i.r. spectrum of pure succinic acid. In the Raman spectrum a further two lines are observed, at 350 and 252 cm^{-1}. K–F (or K–O) stretching modes are expected in this frequency range, possibly mixed with the symmetric stretch of the hydrogen bonds. This symmetric stretch is expected to be stronger in the Raman than in the i.r., whereas the ionic character of the K^+–F^- bond would cause it to be weak in the Raman and strong in the i.r. From the relative intensities of the low-frequency bands observed in the i.r. and Raman, we propose the following assignments: K–F (or K–O), possibly mixed with ν(HFH), at 330 cm^{-1}, ν(HFH) at 350 and 252 cm^{-1}. The assignment of the K–F stretch to the somewhat high-frequency band at 330 cm^{-1} is justified by the short K–F distance in the crystal of 2.684 Å.

Although it is agreed that the two high-frequency bands at 2 460 and 2 240 cm^{-1} arise from ν(OH) stretching vibrations, it is felt that coupling of the OH vibrators would be weak and insufficient to give large band splitting. It is suggested instead that the broad continuous absorption over several hundred wavenumbers ~3 000—1 500 cm^{-1} is mainly due to the ν(OH) absorption. This band culminates at *ca.* 1 920 cm^{-1}. It is well known that for strong and medium-strong hydrogen bonds the broad ν(OH) band presents some structure,[13] and recent explanations in terms of Fermi resonance between the ν(OH) fundamental and overtones and combinations of γ and δ(OH) have been given for these sub-maxima.[8c,13,14] In initial studies, no good agreement was found between the maxima and the frequency overtones and combinations. More recently it has been suggested that the minima and not the maxima must match the frequency overtone or combination frequency.[8a,8d,8e]

The unusual band profile for hydrogen bonds results from the particular interaction between a broad level ν(OH) and a narrow overtone 2γ or 2δ. A similar explanation has been given by Evans [15] to explain 'transmission windows' in the spectra of very strong hydrogen bonds. In the present case, an Evans hole is observed at *ca.* 2 150 cm^{-1}, which almost exactly matches the frequency of the overtone of the hydrogen-bond bending vibration γ(OH) at 1 085 cm^{-1}.

There are important changes in the i.r. spectrum of the deuteriated compound which are entirely consistent with the crystallographic result,[7] which indicated a small positive isotope effect, and with a single minimum potential for the hydrogen. Although some absorption due to O–H stretching is seen in the high-frequency region >1 800 cm^{-1}, the main ν(OD) stretch lies between 1 200 and 1 800 cm^{-1}, with a maximum at *ca.* 1 520 cm^{-1}. This gives an isotopic ratio ν(OH) : ν(OD) of ~1.25 : 1.

The strong broad i.r. absorption at 1 545 cm^{-1}, assigned to δ(OH), is absent in the deuteriated spectrum. This mode should shift upon deuteriation with an isotopic ratio close to $\sqrt{2}$. The δ(OD) vibration is therefore expected in the region of 1 100 cm^{-1}. The only change in this region concerns the pair of bands observed at 1 050 and 1 085 cm^{-1} in the protonated compound, which have been assigned to the γ(OH) vibrations. A single peak occurs in the spectrum of the deuteriated compound at 1 078 cm^{-1}, which is the only possibility for δ(OD). Although this represents an isotopic ratio of 1.43 : 1, higher than expected, the in-plane modes are known to be frequently not pure, but mixed with other vibrations.[16] In the present case, the high isotopic ratio may result from kinematic coupling of δ(OH) with the ν(C=O) stretch.

The out-of-plane mode, γ(OD), is now observed at 775 cm^{-1}, representing an isotopic ratio of 1.40 : 1 for γ(OH) : γ(OD). Such values of ν and γ isotopic ratios have frequently been found in asymmetric OHO systems.[16]

As for the protonated case, the structure of the broad ν(OD) band is caused by Fermi resonance. The transmission window at 1 550 cm^{-1} is due to the interaction of the ν(OD) level with the first overtone of the γ(OD) vibration at 775 cm^{-1}.

It should be noted that the protonated and deuteriated compounds both present the same band pattern in the ν(OH) and ν(OD) regions, that is, a broad band split into two components. Although this suggests the possibility of assigning a specific vibrational mode to each component, a different isotopic ratio between the components of the band is found. The different isotopic ratios are more consistent with the explanation in terms of Fermi resonance since ν(OH) and γ(OH) have significantly different isotopic shifts, mainly due to the strong anharmonicity of the ν(OH) vibration. Additional band structure as usually observed in strong hydrogen bonds arises from coupling of the symmetric stretch of the hydrogen bond with ν(OH); this is found in particular for acid salts of the polyfluoride ions.

A broad i.r. band, with two barely discernible maxima at 1 725 and 1 665 cm^{-1} is attributed to the symmetric and antisymmetric stretches of the C=O group, the lower frequency band being shifted to lower wavenumbers relative to that of the protonated complex, indicating a probable mixing of ν(C=O) with ν(OH).

The strong absorption at 330 cm^{-1} is unaffected by deuteriation and confirms its assignment as an M–F or M–O mode.

From the point of view of the present theories of the hydrogen bond, the rest of the spectrum is of less significance, and it will simply be mentioned that sharp CH$_2$ vibrations due to the succinic acid framework may be easily recognised by comparison with the spectrum of the pure acid, and are denoted SA in Table 1.

Since the succinic acid group lies on an inversion centre, there is no coincidence in i.r. and Raman frequencies.

The Raman spectrum in the low-frequency range ($<$250 cm^{-1}) is characterised by a series of intense lines which arise from rotational motion of the succinic acid groups, which may be described equally well as deformation modes of the hydrogen bond (including bending of the HFH angle), and internal vibrations of the succinic moiety. For instance, in the Raman spectrum of succinic acid, bands at 157, 135, 96, and 77 cm^{-1} have been assigned to twisting and rocking vibrations of the carbon chain and CO groups, and hydrogen-bond vibrations coupled with these intramolecular vibrations.[17]

Conclusions

The presence of very strong hydrogen bonding in the KF adduct leads to an important lowering of the ν(OH) [or ν_{asym}(OHF)] frequency from 2 900 cm^{-1} in pure succinic acid [17] to *ca.* 1 900 cm^{-1} in the adduct. This result is consistent with the very short O–H $\cdots$ F distance of 2.441 Å observed in the *X*-ray diffraction study,[6] compared with the O $\cdots$ O distance of 2.66 Å in crystalline succinic acid.[18] This stretching frequency is, however, significantly higher than that observed for symmetric centred hydrogen bonds, which for OHO systems is lower than 1 000 cm^{-1} [13,16] and for ν_{asym}(FHF) in HF$_2^-$ is found at 1 400 cm^{-1}.[11]

It therefore appears that the H atom is not centred in the hydrogen bond but lies closer to the oxygen atom.* Furthermore the strength of the hydrogen bond manifests itself by the higher frequencies of the bending modes δ(OH) and γ(OH) at 1 545 and 1 085 cm^{-1} respectively, which are *ca.* 100 cm^{-1} higher than the corresponding modes in the pure acid.[17]

The doublet structure of the ν(OH) and ν(OD) bands is explained in terms of Fermi resonance with the γ(OH) [or γ(OD)] overtone. The low-frequency Raman spectrum has provided useful complementary information about the strength of the hydrogen bond, in particular ν(H $\cdots$ F $\cdots$ H) modes have been identified at 252 and 350 cm^{-1}.

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* Confirmed by recent neutron-diffraction data, D. J. Jones, M. S. Lehmann, and J. Rozière, unpublished work.

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