

111. Hydrogen Bonding in Aqueous Solutions of Some Dicarboxylic Acid Salts.

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The infrared spectra of maleic, fumaric, phthalic, malonic, di-n-propyl-malonic, and salicylic acid and their mono- and di-alkali-metal salts have been examined in aqueous solution and are considered in relation to intramolecular hydrogen bonding in the acid anions.

The origin of a difference between the results of infrared and thermodynamic methods for assessing the symmetry of the hydrogen bond in the hydrogen malonate ion is discussed.

THE crystals of the acid salts of dicarboxylic acids have been shown by a variety of techniques, including infrared, X-ray, and nuclear magnetic resonance (n.m.r.) spectroscopy, to contain strong hydrogen bonds.¹ In some cases these bonds are particularly strong and are described by symmetrical, single-minimum, potential-energy curves. Others give a double-minimum curve, with a small barrier, whilst others are of the unsymmetrical type.

We have examined some of these acids and salts in aqueous solution, using infrared spectroscopy to see whether a strong intramolecular hydrogen bond persists in water. We contrast their behaviour in water with that in the crystal and in some cases in dimethyl sulphoxide. The infrared evidence is also briefly considered in relation to the kinetics of proton transfer obtained from relaxation measurements.²

EXPERIMENTAL

The potassium salts of maleic, fumaric, phthalic, malonic and di-n-propyl-malonic acid were prepared from alcoholic or aqueous-alcoholic solutions of the acids and potassium carbonate.

Infrared spectra were recorded on a Perkin-Elmer model 21, double-beam, infrared spectrometer equipped with a sodium chloride prism. Capillary films of the solution in water or deuterium oxide between fluorite plates were examined. Disodium salicylate was prepared by dissolving the acid in an excess of sodium hydroxide. "AnalaR" benzoic acid and its sodium salt were used directly.

Basis of Interpretation.—The most characteristic absorption frequencies in the infrared spectra of carboxylic acids and their salts are those due to the stretching frequency, $\nu(\text{C}=\text{O})$ of the carboxyl group or the asymmetric stretching frequency, ν_{as} , of the carboxylate anion. These bands occur in a region of the spectrum (about 1750—1550 cm^{-1}) in which ordinary water absorbs strongly, but heavy water does not, so that heavy-water solutions of the acids and their salts may be used for studies in this region. The symmetrical stretching frequency of the CO_2^- group is usually found at about 1400 cm^{-1} (this band disappears on protonation and is replaced by a number of bands in the 1200 cm^{-1} region).

The change of the asymmetric frequency of the carboxylate group on protonation to carboxyl is so large ($\sim 140 \text{ cm}^{-1}$) that this is by far the best diagnostic test of whether or not a proton is associated with a carboxylate group. The effects of hydrogen bonding on these frequencies have been examined for various carboxylic acids. A hydrogen-bonded carboxyl group has a lower $\nu(\text{C}=\text{O})$ frequency than when it is not so bonded (1725—1705 cm^{-1});³ correspondingly the asymmetric frequency of the carboxylate group⁴ (1550—1610 cm^{-1}) increases when hydrogen bonding is present.* This is supported by data from which this conclusion was not explicitly

* A case,⁵ $\text{CF}_3\cdot\text{CO}_2\text{Na}, 2\text{CF}_3\cdot\text{CO}_2\text{H}$, in which the asymmetric frequency is lowered, is exceptional in that both oxygen atoms of the CO_2^- group are thought to be hydrogen-bonded. The symmetric and asymmetric frequencies will be moved further apart from each other by any influence inducing asymmetry into the CO_2^- groups (*e.g.*, H-bonding, as in this work, or covalent bonding to a metal atom.^{6,7}). A symmetrical influence upon the two oxygen atoms will cause the two frequencies to change together.¹

¹ Hadzi and Novak, "Infrared Spectra of and Hydrogen Bonding in Some Acid Salts of Carboxylic Acids," University of Ljubljana, 1960; Speakman, *J.*, 1949, 3357; Blinc and Hadzi, *Spectrochim. Acta*, 1960, **16**, 852.

² Eigen and Kruse, personal communication.

³ Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd edn., Methuen, London, 1958, p. 167.

⁴ Ref. 3, p. 175.

⁵ Klemperer and Pimentel, *J. Chem. Phys.*, 1954, **22**, 1399.

⁶ Sawyer and Paulsen, *J. Amer. Chem. Soc.*, 1958, **80**, 1597.

⁷ Nakamoto, Morimoto, and Martell, *J. Amer. Chem. Soc.*, 1961, **83**, 4528.

drawn. Thus, in a recent study⁸ of substituted succinic acids and their acid salts it was shown that certain of the salts have very strong intramolecular hydrogen bonding, whereas others have no detectable hydrogen bonding. The infrared spectra were examined also in heavy-water solution.⁹ From these results two effects may be seen: first, the asymmetric frequency of a strongly hydrogen-bonded CO_2^- group is uniformly about 35 cm^{-1} higher than that of a non-hydrogen-bonded CO_2^- group; secondly, the frequency of a strongly hydrogen-bonded CO_2H group is about 30 cm^{-1} lower than that of a "free" CO_2H group. Similar shifts are found in the spectra of some of the compounds described here and these shifts are considered to be ascribable to intramolecular hydrogen bonding.

Spectra of Hydrogen Carboxylate Salts.—The main features of the spectra of the dicarboxylic acids and their salts are recorded in the Table; the Figure shows the frequency shifts, in ν_{as} , of the carboxylate vibration on monodeuteration of the bare anion, A^{2-} to AD^- , and the frequency shifts in $\nu(\text{C}=\text{O})$ of the carbonyl vibration of the carboxylic acid group on deuteriation from D_2A to DA^- . Where the frequency shift is small, say, $0-10 \text{ cm}^{-1}$, the hydrogen bonding in DA^- is considered to be relatively weak and the spectrum of this ion is essentially a superposition of the spectra of D_2A and A^{2-} . Shift limits of 35 cm^{-1} for ν_{as} and 30 cm^{-1} for $\nu(\text{C}=\text{O})$ are marked in the Figure: shifts of this order indicate strong hydrogen bonding. Also given are $\Delta(\Delta\nu)$ values, the changes in frequency difference $\Delta\nu = \nu_{\text{as}} - \nu_{\text{sym}}$ in passing from DA^- to A^{2-} . These values will next be considered *per se* and in relation to other structural data for each acid anion, DA^- , in turn.

Wavelengths (cm^{-1}) of infrared absorption peaks of dibasic acids and their derivatives.

Acid	No. of ionisable protons	CO_2H	$\text{C}=\text{C}$	$\text{CO}_2^-(\text{as})$	$\text{CO}_2^-(\text{sym})$	$\Delta\nu$
Maleic	D_2A 2	1705	1640			
	DA^- 1	1698	1620	1570	1430	140
	A^{2-} 0		1646w	1563	1435	128
Fumaric	D_2A 2	1695	*			
	DA^- 1	1690	1640w	1577	1360	217
	A^{2-} 0		*	1572	1360	192
Phthalic	D_2A 2	1696	1590			
	DA^- 1	1692	1586sh	1570	1409	161
	A^{2-} 0		1609w	1571	1409	162
Malonic	D_2A 2	1707				
	DA^- 1	1698	—	1588	1418	170
	A^{2-} 0			1573	1425	158
Di-n-propylmalonic	DA^- 1	1677		1586	1410	176
	A^{2-} 0			1553	1414	139
	D_2A 2	1662	1596			
Salicylic	DA^- 1		1593	1621	1377	244
	A^{2-} 0		1596	1536	1400	136
	DA 1	1687	1606			
Benzoic	A^- 0		1602	1553	1395	158

Hydrogen Fumarate Ion.—This ion, by virtue of its geometry, cannot contain an intramolecular hydrogen bond. The observed shifts are small: the spectrum of potassium hydrogen fumarate in heavy water can be regarded as a superposition of the acid and of the dipotassium salt in the $1750-1400 \text{ cm}^{-1}$ region. This feature appears also in the hydrogen maleate system.

Hydrogen Maleate Ion.—Crystalline potassium hydrogen maleate has been studied by a variety of techniques including X-ray,^{9a} n.m.r.,¹⁰ infrared,¹¹ and neutron spectroscopy,¹² and shown to possess a strong intramolecular and symmetrical hydrogen bond. In solution in dimethyl sulphoxide the acid salt is considered to retain this symmetrical hydrogen bond.¹³ A previous infrared study of the salt has been made by Dodd *et al.*¹⁴ with water and heavy-water

⁸ Eberson, *Acta Chem. Scand.*, 1959, **13**, 203, 211.

⁹ Eberson, *Acta Chem. Scand.*, 1959, **13**, 224.

^{9a} Darlow, "Hydrogen Bonding," Pergamon Press, London, 1959.

¹⁰ Forsen, *J. Chem. Phys.*, 1959, **31**, 852.

¹¹ Cardwell, Dunitz, and Orgel, *J.*, 1953, **3740**.

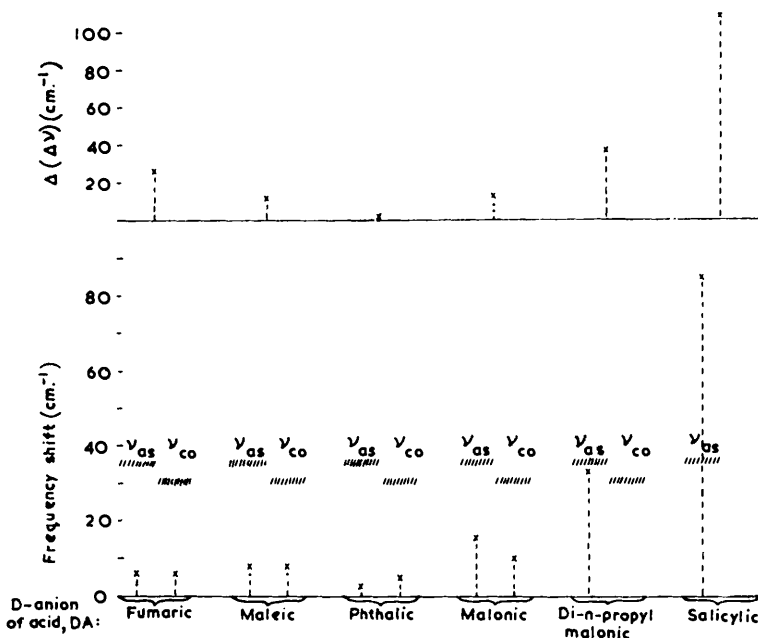
¹² Peterson and Levy, *J. Chem. Phys.*, 1958, **29**, 948.

¹³ Hadzi and Novak, *Spectrochim. Acta*, 1962, **18**, 1059.

¹⁴ Dodd, Miller, and Wynne-Jones, *J.*, 1961, 2790.

solutions, but although our experimental results for heavy-water solution are in good agreement we differ from them in our interpretation. We have also examined the spectrum of the dipotassium salt.

The frequencies of bands in the 1750—1400 cm^{-1} region are shown in the Table for heavy-water solutions of the appropriate compounds. The band at 1698 cm^{-1} assigned to the carboxyl group is weaker than that at 1570 cm^{-1} , but this effect appears to be quite common with acid salts in heavy-water solution. The band at 1620 cm^{-1} assigned to the C=C stretching vibration is of medium intensity, whilst in the spectrum of the dipotassium salt in heavy-water solution the band is very weak. The spectrum of the potassium hydrogen salt in the solid state also shows that this band is weak. This is consistent with the highly symmetrical character of the acid salt in the solid and of the dipotassium salt in heavy-water but also with an unsymmetrical



Upper diagram: change in the difference ($\nu_{as} - \nu_{sym}$) of the CO_2^- group [$\Delta(\Delta\nu)$] on loss of a proton from the DA^- ion.

Lower diagram: frequency shifts in ν_{as} on monoprotection of the A^{2-} ion and in $\nu(\text{C}=\text{O})$ for loss of one proton from D_2A .

character for the acid salt in heavy water.* The spectrum of the potassium hydrogen salt in heavy-water is also almost a superposition of that of the acid and the dipotassium salt, in contrast to the spectra of the solids.

We suggest that this evidence points to the existence of an unsymmetrical hydrogen bond in the potassium hydrogen salt in aqueous solution. Relaxation measurements, while showing that proton transfer from the hydrogen maleate ion is slower than with normal typical monocarboxylic acids, also show that the rate for the potassium salt is much faster than that observed for, say, monosodium salicylate² which, as will be shown below, contains a strong hydrogen bond which persists in aqueous solution. This is consistent with the presence of a weaker, less symmetrical, hydrogen bond in the hydrogen maleate ion. The structure of this ion in the solid salt, determined by the X-ray method, shows that there is considerable strain in the planar ring

* S. Nagakura (Conference on Intermolecular Forces, Communication No. 27, Paris, 1963) has observed that aqueous potassium hydrogen maleate has an absorption band at $\sim 211 \text{ m}\mu$ which he suggests arises from "a charge transfer process characteristic of the δ -electron of the symmetrical hydrogen bonding." We have confirmed that such a band occurs both in water and in heavy water at 2107 Å. The band may arise from a $\pi \rightarrow \pi^*$ transition.

of the symmetrical hydrogen-bonded structure.⁸ By way of contrast, in dimethyl sulphoxide⁷ the loss of hydrogen-bond energy is presumably not counterbalanced by twisting of the carboxyl groups out of the plane, whereas the greater possibilities for hydrogen bonding in aqueous systems may make such twisting energetically favourable in aqueous solution.

Hydrogen Phthalate Ion.—In the solid state, potassium hydrogen phthalate has been shown by infrared and n.m.r. spectroscopy to contain hydrogen bonds of the double-minimum type with a low potential barrier.¹ In dimethyl sulphoxide the hydrogen bonding changes to the intramolecular symmetrical type.⁷ The frequency of the bands for heavy-water solutions of the salt in the range 1850—1400 cm^{-1} are given in the Table. The evidence suggests that any hydrogen bonding in this medium is of the unsymmetrical rather than of the symmetrical type.

Hydrogen Malonate and Di-n-propylmalonate Ions.—The evidence here suggests that a strong symmetrical hydrogen bond is not present in aqueous solutions of potassium hydrogen malonate. The spectrum of the monoprotonated anion is not very different from a simple superposition of that of the acid and the dipotassium salt. The conclusion differs from that based on thermodynamic data on the basis of which it was suggested that a symmetrical hydrogen bond is present.¹⁵ The origin of this difference is considered briefly in the appendix to this paper.

On the basis of pK measurements it has been suggested¹⁶ that there is appreciable hydrogen bonding in the hydrogen di-n-propylmalonate ion in aqueous solution. The infrared spectra of the acid, and of the mono- and di-potassium salt, in heavy-water, give the frequencies shown in the Table and the frequency shifts in the Figure. The ν_{as} shift is substantial and the spectrum of the potassium hydrogen salt cannot be regarded as a simple superposition of the spectra of the acid and the dipotassium salt. This is consistent with the occurrence of hydrogen bonding, the hydrogen atom shared between carboxyl and carboxylate groups raising the carboxylate (asymmetric) frequency some 33 cm^{-1} .

Salicylate Ion.—The infrared spectra of crystalline salicylic acid and monosodium salicylate show that strong intramolecular hydrogen bonding occurs between the phenolic proton and an oxygen atom of the carboxylic group.¹⁷ The results of pK measurements of aqueous solutions of the acid and the monosodium salt are consistent with retention of this strong intramolecular hydrogen bond in solution.¹⁸ We have obtained the infrared spectra of the acid and its mono- and di-sodium salt in water and heavy water (see Table).

The frequency of the C=O stretching vibration of the acid is low if we compare it with that for benzoic acid. On the other hand, the frequency of the CO_2^- (asym) vibration for the monosodium salt is as high as that found in some α -amino-acids and much higher than that of sodium benzoate in heavy water (see Table). The frequency of this vibration for disodium salicylate is much lower, by $\sim 85 \text{ cm}^{-1}$. These facts confirm the view that strong hydrogen bonding occurs with both the acid and the monosodium salt in aqueous solution.

Some additional confirmation is provided by the presence of a very broad, complex absorption with a maximum at 2050 cm^{-1} for the acid and at 2120 cm^{-1} for the sodium salt in heavy water. The band is also observed with aqueous solutions of the monosodium salt, but shifted to 2720 cm^{-1} . This frequency is the same as that for the solid. The ratio of the frequency of these bands with water and deuterium oxide is 1.33 : 1 and probably corresponds to substitution of deuterium for hydrogen in the molecule.

The hydrogen bonding with sodium salicylate appears to be about as strong in aqueous solution as in the crystal. This is in contrast to the situation with maleic acid. Relaxation measurements show that the loss of the second proton from salicylic acid is a hundred times slower than for other carboxylic acids, behaviour consistent with the presence of a strong hydrogen bond.³

Values of the Frequency Difference, $\Delta(\Delta\nu)$.—The differences, $\Delta\nu$, in frequency between the symmetric and antisymmetric carboxylate vibrations are included in the Table. They have been previously used as a measure of the covalent character of metal-bonding to carboxylate groups¹⁹ and, if this is correct, $\Delta(\Delta\nu)$ values may also be of use in indicating hydrogen-bonding tendencies. Indeed, with salicylate salts this quantity is 108 cm^{-1} and for di-n-propylmalonate

¹⁵ Das and Ives, *Proc. Chem. Soc.*, 1961, 373; Lloyd and Prince, *Proc. Chem. Soc.*, 1961, 464.

¹⁶ Levy and Magoulas, *J. Amer. Chem. Soc.*, 1962, 84, 1345.

¹⁷ Eigen, *Z. Elektrochem.*, 1960, 64, 115.

¹⁸ MacDougall and Long, *J. Phys. Chem.*, 1962, 66, 429.

¹⁹ Sawyer and McKinnic, *J. Amer. Chem. Soc.*, 1960, 82, 4191.

salts it is about 40 cm.^{-1} . However, the $\Delta(\Delta\nu)$ value for hydrogen fumarate and fumarate is 25 cm.^{-1} , much greater than occurs with malonic (12 cm.^{-1}), maleic (12 cm.^{-1}) or phthalic salts (1 cm.^{-1}). It is clear that, while large differences in $\Delta(\Delta\nu)$ values may at times be useful for indicating the degree of hydrogen bonding, small differences should be interpreted with care: various other factors can affect the values, *e.g.*, changes in coupling between the vibrations.

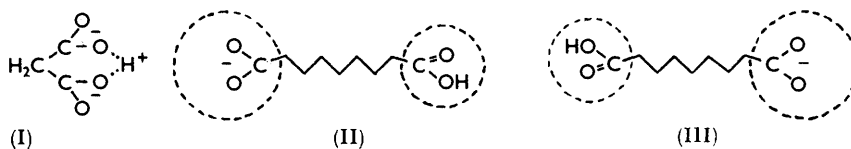
APPENDIX

We shall here discuss the origin of a difference between the results of infrared and thermodynamic methods for assessing the symmetry of the hydrogen bond in the hydrogen malonate ion.

An investigation²⁰ of the thermodynamic quantities associated with the dissociation of malonic acid showed that, although the value of ΔG° for the first ionisation allows the acid to be placed in a series of substituted acetic acids $\text{R}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ between the acid where $\text{R} = \text{I}$ and that when R is an organic residue, the values of ΔH° , ΔS° , and ΔC_p are not those expected for an acid at this position. The only reasonable interpretation of the hydration effects is that there is such a close association of the carboxylic acid and carboxylate groups in the half-salt that the ion apparently becomes symmetrical. This, it was suggested, is evidence for a strong intramolecular hydrogen bond as in (I). The infrared spectra of the acid and its salts in solution should then be similar to those of substituted succinic acids which have been shown to contain internal hydrogen bonds. We have seen, however, that this similarity is not found and that there is only a relatively small change in frequency shifts and in $\Delta(\Delta\nu)$ for the addition of one proton to the "bare" anion. The small changes observed, though in the expected direction for hydrogen bonding, are much too small to be ascribable to a symmetrical hydrogen bond.

A possible explanation of the discrepancy between the infrared and the thermodynamic results lies in the time scales of the two experimental methods: the period of a carbonyl vibration is of the order of 10^{-14} sec. whereas a time-averaged property is observed in a thermodynamic measurement such as an e.m.f. Such a measurement could indicate an average of two proton positions, one for each carboxylate group, and therefore an averaged hydration effect such as would be expected for the ion (I).

To investigate the effect of this wide difference in time scale, consider first a long-chain dicarboxylic acid. Solvation of the hydrocarbon chain is ignored, so that the instantaneous picture of the half salt will be as in (II), the negative charge of the carboxylate group having the



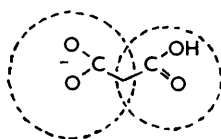
larger orientating effect on the surrounding water molecules. The process occurring to produce the situation in (III) will be (a) proton dissociation from CO_2H , (b) proton transfer through the intervening water molecules, (c) proton association with CO_2^- , (d) formation of the new hydration sphere of the CO_2^- , and (e) the collapse of the "old" hydration sphere. The rates of (a) and (c) are known from relaxation work on the protolytic kinetics of acids.¹⁷ The half-life of process (a) will be about 10^{-5} sec., whereas that for (c) is much smaller (second-order constant, $k \approx 5 \times 10^{-10}$ l. mole⁻¹ sec.⁻¹). Process (b) will proceed by a type of Grotthuss conduction for which the half-life is very small¹⁷ ($\sim 10^{-13}$ sec.). The rate-controlling step for proton transfer is thus (a). Processes (d) and (e) will be assumed to occur at similar rates. An accurate estimate of the time required to form a hydration sphere does not seem to be available, but limits may be placed upon it. The time cannot be less than the relaxation time of a water molecule in an oscillating electric field. In water at 20° this is about 10^{-11} sec.,²¹ in ice at 0° it is about 2×10^{-5} sec. The time to build up the hydration sphere is unlikely to be more than 100 times larger than this.

Since the carboxyl and the carboxylate group are assumed to be well removed from each

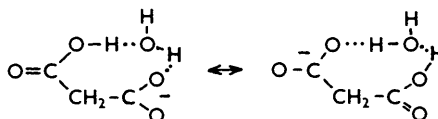
²⁰ Darlow and Cochran, *Acta Cryst.*, 1961, **14**, 1250; Darlow, *ibid.*, p. 1257.

²¹ See data summarised by Davies, *Quart. Rev.*, 1954, **8**, 254.

other their hydration spheres will be well separated and the time to re-form the hydration sphere ($10^{-11} < t_{\frac{1}{2}} < 10^{-9}$ sec.) is much less than that for proton transfer ($t_{\frac{1}{2}} \sim 10^{-5}$ sec.). Therefore, thermodynamic quantities which are controlled by the size of the hydration sphere of both groups will be those expected in the absence of interaction between them (*e.g.*, the absence of hydrogen bonding). In the case of malonic acid, however, the above analysis is no longer valid: the carboxyl and carboxylate groups are close to one another and there will be considerable overlapping of the hydration spheres (IV). As a result, when the proton is transferred from



(IV)



(V)

carboxyl to carboxylate, the newly formed carboxylate ion must make up its hydration sphere very largely from water molecules which are still orientated towards the carboxyl group. The relaxation time for water molecules in an ordered structure is much larger than for molecules in bulk liquid water. In many respects the structure of water in a hydration sphere is similar to that of ice. It is reasonable, then, to take the relaxation time in ice as an approximate lower limit to that of the formation of the new hydration sphere. This limit (10^{-5} sec. $< t_{\frac{1}{2}} < 10^{-3}$ sec.) is now greater than the time required to transfer a proton from one carboxylate group to the other. As a result, the hydration sphere will be unable to rearrange as fast as the proton interchanges positions and so the water molecules will take up an average orientation, *i.e.*, as they would if the proton was equidistant from the carboxylate groups. The resulting hydration sphere will be small and the thermodynamic effects observed will be the same as those expected for the hydrogen-bonded structure (I).*

In a modification of this scheme²² it has been suggested that primary hydration is reduced to one water molecule which is hydrogen-bonded between the carboxylate and carboxyl groups (V). Models show that such a structure is possible for malonic acid, but with increasing C-substitution it becomes more difficult to orientate the carboxylate groups correctly. This is consistent with the observed direct hydrogen bonding when the substitution increases sufficiently. However, the infrared evidence for unsubstituted malonic acid shows that the carboxylate symmetry is but little affected by any hydrogen bonding that may be present. Consequently, it must be supposed that the distribution of charge in the carboxylate group is much the same as in a non-hydrogen-bonded group, so there will be more than one water molecule orientated by the field of the carboxylate group. It is to these water molecules that the argument in terms of changing orientation applies. The infrared evidence, however, does not eliminate structure (V) since hydrogen bonding to solvent water molecules seems not to affect the carboxyl or carboxylate frequency to any great extent. This may be seen by comparing the crystal and solution spectra.

It is concluded that there is no essential discordance between the results of the thermodynamic and infrared studies of malonic acid in solution. The apparent discordance arises because the two are measuring different properties of the system especially in regard to time scales.

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* Essentially, the infrared measurements "see" one or other of two asymmetrical hydrogen bonds, whereas thermodynamic measurements detect an averaged hydration effect.

²² Ives, personal communication.