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Hydrogen bond patterns in solid state carboxylic acids. Vibrational study of the hydrogen bond patterns in oxamic, malonamic and succinamic acid

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Abstract—The vibrational spectra of oxamic, malonamic and succinamic acid are reported. Although these molecules exhibit identical functional groups, their solid state hydrogen bond patterns can be divided in two different types, which can be clearly distinguished through the combination of infrared and Raman spectroscopy at variable temperatures and through the vibrational behaviour of the deuterated compounds. Oxamic acid behaves as a linear hydrogen bonded polymer with cyclic acid-acid and cyclic amide-amide dimers while the other discussed carboxylic acid derivatives exhibit a cyclic acid-amide hydrogen bond pattern. A model is proposed to investigate the peculiar vibrational behaviour of oxamic acid theoretically. Spectroscopic studies of the cyclic heterogenic acid-amide hydrogen bond pattern are studied for the first time.

INTRODUCTION

The molecules under investigation are derivatives of dicarboxylic acids in which one acid function is substituted by a primary amide function. This class of molecules offers good hydrogen bond perspectives as they exhibit NH and OH proton donating groups and C=O proton accepting groups. Introducing other proton donating and/or accepting groups in a carboxylic acid molecule gives a variety of possible hydrogen bond patterns. Among these hydrogen bond patterns we can distinguish between cyclic acid dimers, acid-acid catamers and heterogenic associations. The last exhibits hydrogen bonds between the carboxylic acid function and another functional group. The purpose of this series of articles is to show that vibrational analysis is an ideal tool to study different hydrogen bond associations observed in solid carboxylic acids.

TRIPATHI and KATON proved that oxamic acid behaves as a hydrogen bonded polymer with cyclic acid-acid and cyclic amide-amide dimers [1]. This hydrogen bond pattern is shown in figure 1. The hydrogen bond pattern in succinamic acid is somewhat different. LEISEROWITZ concludes that succinamic acid exhibits cyclic acid-amide intermolecular associations as shown in figure 2 [2]. These intermolecular associations are strongly resemblant to those in fumaramic acid [2,3].

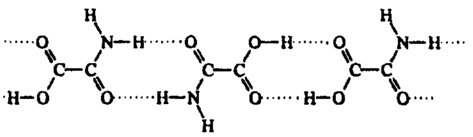

Figure 1: hydrogen bond pattern in oxamic acid.

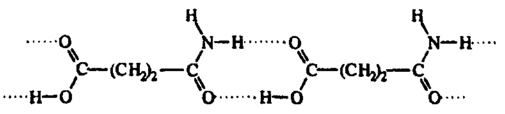

Figure 2: hydrogen bond pattern in succinamic acid.

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In the present study we report on the vibrational analysis of succinamic acid for the first time. Comparison of the vibrational behaviour of malonamic acid with that of oxamic acid and succinamic acid will lead to a decision concerning the solid state hydrogen bond pattern exhibited by malonamic acid. To the best of our knowledge malonamic acid has not yet been studied neither spectroscopically nor by diffraction methods.

Recently Neuheuser et al. calculated the geometries and interaction energies for the cyclic formic acid dimer, the cyclic formamide dimer and the cyclic formic acid formamide dimer [4]. The vibrational behaviour of simple model molecules is calculated in the present publication in order to get a better understanding of the experimental vibrational behaviour of the studied hydrogen bonded molecules on cooling.

EXPERIMENTAL AND COMPUTATIONAL METHODS

Oxamic acid is commercially available. A sample of 99% purity was obtained from Janssen Chimica (O920-4). Malonamic acid was prepared by hydrolysis of the commercially available monoethyl malonamide ester (Fluka 63403), and succinamic acid is available from Aldrich (13.437-6). Oxamic acid was purified by vacuum sublimation, while malonamic and succinamic acid were purified by successive recrystallisations respectively from $CHCl_3$ and from water.

The infrared spectra were recorded on a Bruker IFS 113v Fourier Transform spectrometer, using a liquid nitrogen cooled MCT (4000-500 cm^{-1}) or a DTGS (500-50 cm^{-1}) detector with a resolution of 1 cm^{-1}. The low temperature measurements were performed with a self-designed liquid nitrogen cooled cryostat, consisting of a copper sample holder with a small container which can be filled with liquid nitrogen. This is surrounded by a jacket with KBr (4000-500 cm^{-1}) or polyethylene (500-50 cm^{-1}) windows and placed under vacuum, avoiding condensation on the sample when cooled. From the sample a pellet with KBr or polyethylene as a matrix was made, and this was mounted firmly upon the sample holder.

The solid state Raman spectra of oxamic and succinamic acid were recorded on a SPEX model 1403 - 0.85m double monochromator - Raman spectrometer. The spectra were excited by the 514.5 nm line of a Spectra Physics model 2020 Argon ion laser operating at 500 mW. For these products the scanning range was between 50 cm^{-1} to 4000 cm^{-1}. The spectra were recorded at 1 cm^{-1} intervals with a two second time constant at a spectral slith width of 4 cm^{-1}. The Raman spectra of malonamic acid were recorded on a Bruker IFS 66v interferometer equipped with a FT-Raman FRA 106 module. The spectra where excited by the 1064 nm line of a Nd-YAG laser operating at 200 mW. The scanning range was between 50 cm^{-1} to 3500 cm^{-1}. The spectra were recorded with a spectral slith width of 4 cm^{-1} and for each spectrum 250 scans where recorded and averaged.

For the ab initio calculations Gaussian 92 [5] was executed on an IBM RS-6000 system. Geometry optimisations were performed using restricted Hartree-Fock calculations with the standard 6-31G basis set [6] augmented with a polarisation function.

For the determination of the geometry we employed the gradient techniques implemented in Gaussian 92, calculating analytical gradients at the SCF level. The ab initio harmonic force constants in Cartesian coordinates were computed as analytical second derivatives of the total energy. In order to estimate the fundamental frequencies, the obtained frequencies were scaled through a uniform scale factor of 0.89. We are aware that this scaling method is less quantitative than a differentiated scaling method of the force constants [7], but the results are sufficient for the purposes in this publication.

The program MolVib [8] running on a 486 DX personal computer was used for calculating the B-matrices and for obtaining the PED of the normal coordinates.

RESULTS AND DISCUSSION

The compounds under investigation all exhibit the carboxylic acid and the primary amide group. The CH_2 and CC frequencies are given in the tables without any further discussion as the behaviour of these vibrations is sufficiently well known. Deuteration and low temperature infrared spectra make the assignments of both acid and amide fundamentals more obvious.

Oxamic acid

Oxamic acid is the simplest molecule exhibiting both a primary amide and a carboxylic acid functional group. Therefore it is an ideal model to investigate the vibrational behaviour of both the primary amide and the carboxylic acid groups, as well as their hydrogen bond capabilities.

Earlier vibrational studies of oxamic acid show that this compound exhibits linear hydrogen bonded chains with alternating cyclic acid-acid and cyclic amide-amide dimers [1,9,10]. The vibrational behaviour of a carboxylic acid associated in the cyclic dimer hydrogen bond pattern is well known [11,12] and the local inversion centres in both cyclic dimers can be proved through the clear non coincidence of infrared and Raman bands, as can be observed in table 1. We can easily show that the non coincidence also holds for the primary amide group in oxamic acid, so the hydrogen bond pattern as given in figure 1 can be adopted.

Table 1 : characteristical fundamentals for oxamic acid and its deutero analogue.

$HOOC-CONH_2$			$DOOC-COND_2$			Assignment
IR		Raman	IR		Raman	
20 °C	-196 °C	20 °C	20 °C	-196 °C	20 °C	
3361 vs	3346 vs					$\nu_{as}NH_2$, B_u
		3346 (1)				$\nu_{as}NH_2$, A_g
			3306 mw	3291 mw		νNH
3242 vs	3234 vs					ν_sNH_2, B_u
		3228 (2)				ν_sNH_2, A_g
2764 w	2769 w					νOH
2679 w	2676 w					
2538 w	2543 w					
			2528 s	2518 s		$\nu_{as}ND_2$, B_u
					2521 (2)	$\nu_{as}ND_2$, A_g
			2448 w	2439 w		νND
			2381 s	2370 s		ν_sND_2, B_u
					2372 (4)	ν_sND_2, A_g
			2159 w,br	2154 w,br		νOD
			1969 m,br	1967 m,br		
		1759 (4)				Acid I, A_g
					1751 (4)	Acid I', A_g
1735 vs	1734 vs	1725 (1)				Acid I, B_u
			1732 vs	1727 vs		Acid I', B_u
1677 vs	1681 vs,br					$\nu C=O$, B_u
		1660 (2)				$\nu C=O$, A_g
			1644 vs	1635 vs		$\nu C=O(d)$, B_u
					1625 (3)	$\nu C=O(d)$, A_g
1593 w	1597 sh					δNH_2, B_u
		1590 (1)				δNH_2, A_g

Table 1 : continued

			1508 w	1507 w		Am II'
		1479 (5)				νCN, A_g
1468 m	1475 m					νCN, B_u
					1457 (8)	νCN(d), A_g
			1448 s	1453 s		νCN(d), B_u
		1406 (1)	1401 vvw	1406 vvw		
		1371 (4)				Acid II, A_g
1361 m	1367 m					Acid II, B_u
			1304 s	1310 s	1307 (1)	Acid II'
1235 vs	1241 vvs					Acid III, B_u
			1132 w	1138 mw	1135 (2)	δND_2
		1089 (10)				ρNH_2, A_g
1084 s	1083 s					ρNH_2, B_u
			1064 s	1067 s	1063 (3)	Acid III'
961 m,br	979 m,br					Acid IV, A_u
			926 vs	926 vs	925 (10)	ρND_2, A_g
833 w	834 mw	835 (3)				
			829 mw	831 mw	830 (3)	νCC
		826 (7)				δNCO, B_g
813 m	817 m					δNCO, A_u
			794 w	798 w		
		749 (1)				ωNH_2, B_g
741 m,br	753 m,br					ωNH_2, A_u
			742 m	747 m	751 (4)	δNCO(d)
			715 m,br	724 m,br		Acid IV', A_u
683 s	687 s					Acid V
		672 (2)				
661 sh	662 mw					ρNCO
			656 vw	659 w		Acid V'
			640 m	644 m		
					630 (2)	
			609 w,br	618 mw		ωND_2, A_u
		555 (3)				
548 m,br	560 m,br					τCN
	530 mw	533 (3)				πNCO
		486 (5)				
475 m	476 mw					
					468 (4)	Acid VII/
454 mw	457 mw		445 m	447 m		Acid VII'
329 w	331 w					
		310 (3)	311 mw	311 mw		
					293 (1)	
		194 (3)				
175 w	175 w		175 mw	175 w	180 (3)	ν_σ
						lattice
		144 (20)			141 (25)	vibrations
		112 (10)				and
					106 (20)	librations

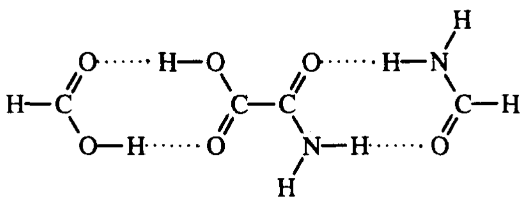


Figure 3 : chosen model for the oxamic acid calculations.

The strong hydrogen bonds exhibited by solid state oxamic acid makes the isolated molecule a bad model to investigate the vibrational behaviour theoretically. Therefore we propose a model that exhibits similar hydrogen bonds as the solid state oxamic acid molecule. The model used in our calculations is given in figure 3, and is constructed from an oxamic acid molecule, hydrogen bonded through a cyclic dimer pattern with a formic acid molecule on the carboxylic acid side and with a formamide molecule on the primary amide side. We expect that this model will describe the vibrational behaviour of the solid state oxamic acid sufficiently well. One exception has to be made for the NH vibrations, since the model does not account for hydrogen bonding at the trans oriented N-H bond.

During the geometry optimisation at the HF/6-31G* level we imposed planarity to our supermolecule, the calculated geometry was, however, at a minimum of the potential surface since the harmonic frequencies, obtained for this geometry are all positive.

The geometric parameters for the model are given in table 2, and are compared to the HF/6-31G* theoretical geometric parameters for the non hydrogen bonded oxamic acid molecule.

A comparison of the theoretical geometry of the isolated oxamic acid molecule to the theoretical geometry of the hydrogen bonded molecule shows that the OH, C=O and NH bond distances lengthen while the CN and C-O bond distances shorten on hydrogen bonding, as predicted by Gutmanns donor-acceptor theory (figure 4). Indeed, pile-up and spill-over effects act in the same sense in this cyclic dimer, resulting in the above described changes in bond distances.

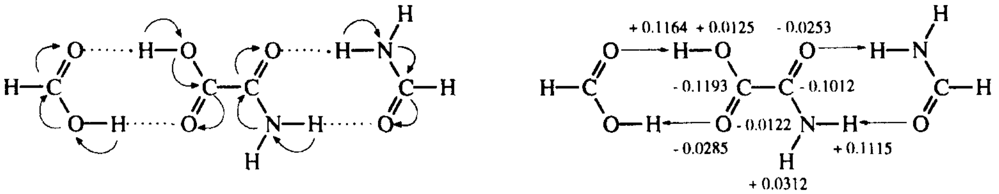


Figure 4 : pile-up and spill-over effects in the chosen model (left) and the theoretical changes (HF/6-31G*) in fractional nuclear charges on hydrogen bond formation (right).

Table 2 : some computed HF/6-31G* geometric parameters for the non hydrogen bonded oxamic acid (monomer) compared to the computed HF/6-31G* parameters for the hydrogen bonded oxamic acid molecule (H-bond) (in pm and °).

Parameter	monomer	H-bond	Parameter	monomer	H-bond
rCC	153.7	154.0	αCO_2	124.7	125.6
rC=O	118.8	120.1	αCOH	108.6	110.9
rC-O	131.1	129.0	αNCO	126.3	126.7
rOH	95.3	96.6	αCNH(cis)	118.9	119.6
rC=O	119.1	120.1	αHNH	120.1	120.3
rCN	134.0	132.5			
rNH(cis)	99.5	100.6	rO·····O		279.9
rNH(trans)	99.4	99.4	rN·····O		298.7

The clear changes in geometry on hydrogen bond formation will influence the force constants for the various vibrations resulting in different vibrational frequencies. Table 3 compares the theoretical frequencies of the monomer oxamic acid with the frequencies of oxamic acid in the proposed supermolecule.

Cooling of the crystalline product results in a shortening of the intermolecular distances and consequently stronger hydrogen bonding. The fundamentals are given in table 3 clearly follow the sequence : free molecule → hydrogen bonded molecule → hydrogen bonded molecule at low temperature.

Table 3 : some HF/6-31G* calculated vibrational frequencies for the monomeric (mono) and for the hydrogen bonded oxamic acid molecule (H-bond) compared to the uniformly scaled quantum mechanical frequencies (scaled) and the experimental ones (exp).

	mono	H-bond	scaled	exp (20 °C)	exp (-196 °C)
νOH	4050	3940 *R*	3507		
		3931 *IR*	3499		
Acid I	2047	2007 *R*	1786	1759	
		1986 *IR*	1767	1735	1734
Acid II	1589	1644 *R*	1463	1371	
		1503 *IR*	1338	1361	1367
Acid III	1213	1410 *IR*	1255	1235	1241
		1355 *R*	1206	n.o.	
Acid IV	714	961 *IR*	855	961	979
		901 *R*	802	n.o.	
$\nu_{as}NH_2$	3976	3833 *IR*	3411	3361	3346
		3769 *R*	3354	3346	
$\nu_{s}NH_2$	3843	3744 *IR*	3332	3242	3234
		3670 *R*	3266	3228	
νC=O	2008	1955 *IR*	1740	1677	1681
		1937 *R*	1724	1660	
δNH_2	1786	1818 *R*	1618	1593	
		1813 *IR*	1614	1590	1597
νCN	1445	1534 *R*	1365	1479	
		1435 *IR*	1277	1468	1475

The typical carboxylic acid fundamentals are assigned according to the previously defined nomenclature, namely Acid I to VII [11].

In the infrared spectrum the νOH vibration is observed as an extremely broad band, consisting of various subbands, which are distinctly sharpened on cooling, while the intensity of the Raman active νOH is rather weak as can be observed from figures 5 and 6.

The carbonyl stretching region is somewhat peculiar. The carboxylic acid carbonyl stretching vibration, Acid I, which is expected in the 1700 cm^{-1} region in the infrared spectrum, and due to local inversion symmetry at lower wavenumbers in the Raman spectrum, is observed as a strong band at 1738 cm^{-1} in the infrared spectrum. The corresponding Raman active Acid I vibration is observed as a splitted band at 1756 cm^{-1} and at 1727 cm^{-1} (figure 6). The splitting is probably due to crystal effects, but it is very unusual for the symmetric carbonyl stretch of a cyclic dimer associated carboxylic acid to be situated above 1700 cm^{-1} [13]. Taking a closer look at the theoretical frequencies we also calculate the Raman active Acid I vibration at higher wavenumbers than the corresponding infrared vibration (table 3).

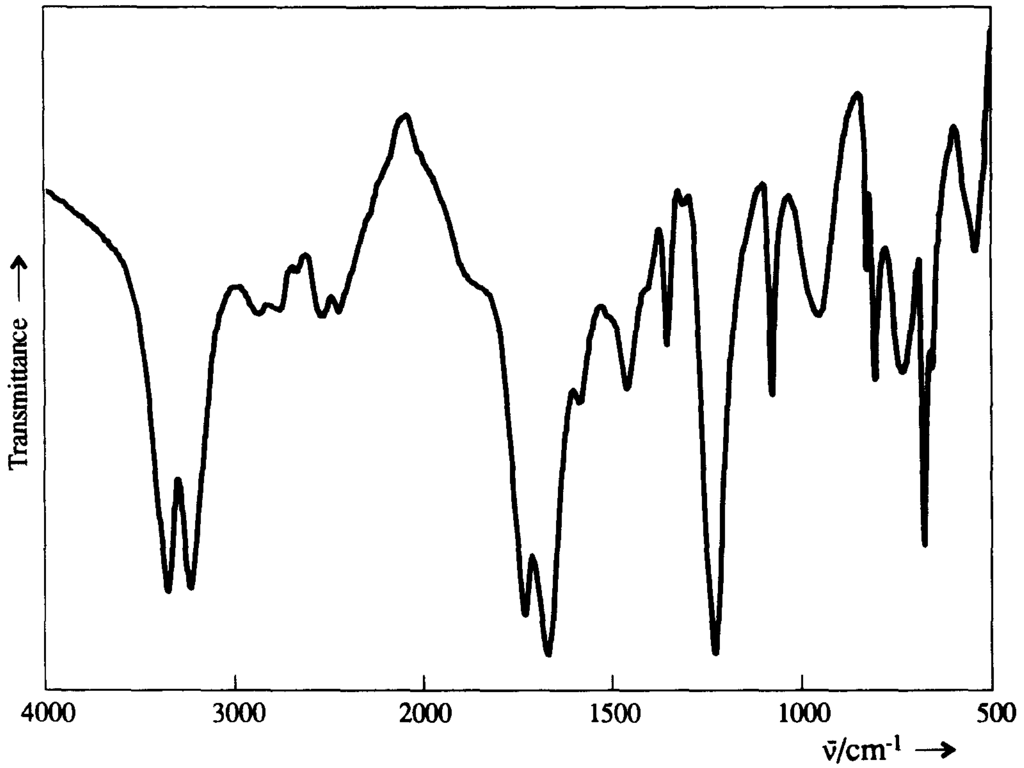


Figure 5 : mid infrared spectrum of oxamic acid.

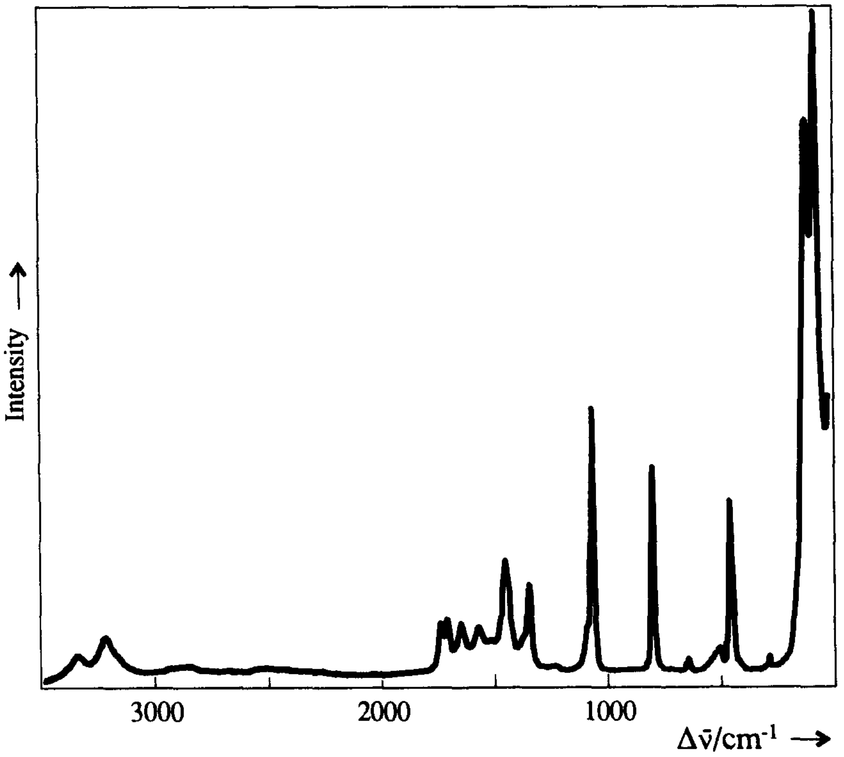


Figure 6 : Raman spectrum of oxamic acid.

The Acid II and Acid III bands, with mixed νC-O and δOH character are observed respectively in the 1300 cm^{-1} and 1400 cm^{-1} region. Both the donor acceptor theory and the calculated values indicate an increased frequency on hydrogen bonding. This proposed increased frequency is confirmed by the experimental higher values obtained for these

fundamentals at low temperature. Acid II', with nearly pure νC-O character, is observed at 1304 cm^{-1} (1310 cm^{-1} at -196 °C) while Acid III', with mainly δOD character, is observed at 1062 cm^{-1} (1067 cm^{-1} at -196 °C) in the infrared spectra of the deuterated compound.
Acid IV is observed as a broad infrared band of medium intensity at 961 cm^{-1}, this band is shifted nearly 20 cm^{-1} to higher wavenumbers on cooling, indicating stronger hydrogen bonds on cooling, as expected for our model. On deuteration the corresponding πOD or Acid IV' is observed at 741 cm^{-1}. A corresponding Ramanband is not observed, this phenomenon is probably due to the minor polarisability of the OH bond.
The CO_2 deformational vibrations are assigned as previously proposed for the dicarboxylic acids [11], these assignments are gathered in table 1.

In the room temperature infrared spectrum of the normal oxamic acid we observe two intense bands in the high frequency region at 3361 cm^{-1} and 3242 cm^{-1} respectively. On deuteration these bands dissappear and two new bands are observed at 2528 cm^{-1} and 2381 cm^{-1}. In the normal product as well as in the deuterated product the bands shift to lower wavenumbers on cooling, and can thus be assigned to the antisymmetrical and the symmetrical NH_2 stretching vibrations. The primary amide function is thus intermolecularly hydrogen bonded as evidenced through their position and the νNH_2 shifts on cooling [14].
The C=O stretching vibration is expected in the 1680 cm^{-1} region for a primary amide in the solid state [15,16], therefore we can assign the infrared band at 1677 cm^{-1} to this vibration, the band shifts to 1644 cm^{-1} on deuteration indicating a decoupling of δNH_2. The corresponding Raman bands are observed at 1660 cm^{-1} and 1625 cm^{-1}, where the clear difference between the infrared and the Raman frequencies can be attributed to local inversion symmetry, as previously mentioned.
The NH_2 deformational vibrations can be easily assigned since they undergo a clear mass effect on deuteration, resulting in a shift to lower wavenumbers. On cooling we expect these vibrations to shift to higher frequencies, as predicted by Gutmanns donor-acceptor theory and through the theoretical results (table 3). The δNH_2 vibrations are observed at 1593 cm^{-1} (infrared) and 1590 cm^{-1} (Raman). On cooling we observe a clear shift to higher frequencies. The δND_2 fundamentals are observed at 1132 cm^{-1} in the room temperature infrared spectrum and at 1135 cm^{-1} in the Raman spectrum. The ρNH_2 fundamental is expected in the 1100 cm^{-1} region and shifts to the 950 cm^{-1} region on deuteration, therefore we can assign the NH_2 rocking vibration to the 1084 cm^{-1} infrared band and to the 1089 cm^{-1} Raman band. The ωNH_2 fundamentals are assigned to the 741 cm^{-1} infrared band and to the 749 cm^{-1} Raman band. The CN torsional vibration, which is usually assigned as τNH_2, is expected in the 600 cm^{-1} region and shifts to the 500 cm^{-1} region on deuteration, the resulting assignments are gathered in table 1.
The CN stretching vibration is observed at 1468 cm^{-1} in the room temperature infrared spectrum, on cooling this band shifts to higher wavenumbers, a direct consequence of the delocalised π-bond in the NCO group. On cooling the hydrogen bond becomes stronger, resulting in a longer C=O bond and a shorter CN bond, as the total electron density does not change.
Also for the amide fundamentals we can follow the shift of the fundamentals by increasing hydrogen bond strength on going from : monomer → calculated model → hydrogen bonded molecule at low temperatures.

Succinamic and malonamic acid

The monoamide derivative of malonamic acid has not yet been studied by diffraction or spectroscopic methods. Therefore no hydrogen bond pattern is known for malonamic acid. The intermolecular interactions in succinamic acid are known and since these associations are totally different from those in oxamic acid a different vibrational behaviour is expected.
The total coincidence of infrared and Raman bands rules out any local inversion symmetry. When comparing the vibrational characteristics for malonamic acid with those of succinamic acid several similarities can be observed (figures 7 and 8). Local inversion symmetry and thus

a hydrogen bond pattern as observed in oxamic acid can be ruled out when analysing the infrared and Raman frequencies for both molecules as given in tables 4 and 5.

The OH stretching vibration of the carboxylic acid function in malonamic and succinamic acid is observed as a very broad and structured band with several subbands in the 3000 cm^{-1} region. The typical structure of this fundamental can be observed in figure 7 for malonamic acid and in figure 8 for succinamic acid. The νOH fundamental has a very low intensity in the Raman spectrum, since it is overlapped by the intense CH stretching vibrational bands in the Raman spectrum. The position and profile of the νOH band indicate that the hydrogen bond is medium strong [17].

Table 4 : carboxylic acid fundamentals for malonamic and succinamic acid.

	$HOOC-CH_2-CONH_2$			$HOOC-(CH_2)_2-CONH_2$		
	IR		Raman	IR		Raman
	20 °C	-196 °C	20 °C	20 °C	-196 °C	20 °C
νOH	2910 w	2912 w				
	2815 mw	2815 mw	2816 (1)	2850 vw	2840 w	2822 (1)
				2770 w	2772 w	
	2692 mw	2699 mw		2677 w	2682 w	
	2570 m	2564 m	2572 (1)	2592 mw	2579 mw	2596 (1)
	2505 m	2491 m	2504 (1)	2537 mw	2520 m	
		2342 mw				
	1942 vw,br	1950 mw			1941 mw	
		1919 w				
Acid I	1728 vs	1728 vs	1728 (6)	1727 ms	1723 s	1731 sh
				1709 vs	1704 vs	1709 (4)
Acid II	1323 s,br	1329 vs,br	1328 (1)	1363 ms	1369 s	1365 (2)
Acid III	1186 vvs	1187 vvs	1186 (4)	1204 vvs	1209 vvs	1206 (2)
Acid IV	985 m,br	1009 ms,br	n.o.	970 mw,br	1004 m	n.o.
Acid V	610 ms	614 ms	605 (2)	Overlap with τCN		611 (2)
Acid VI	430 m	432 m	429 (5)	390 mw	391 mw	393 (9)
Acid VII	393 m	394 m	386 (4)	229 m	231 ms	227 (2)
νOD	2188 mw	2180 mw	2175 (1,br)	2196 mw	2186 m	2194 (1,br)
	2028 mw	2000 m	2034 (1,br)	2060 m,br	2026 ms	2059 (2,br)
	1938 w	1930 m			1973 mw	
				1947 w	1952 mw	
Acid I'	1718 vs	1714 vs	1719 (9)	1701 vs	1696 vs	1699 (5)
Acid II'	1348 s,br	1356 s,br	1333 (1)	1319 m	1324 ms	1325 (3)
Acid III'	1072 s	1080 s	1073 (4)	1082 m	1088 m	1086 (6)
				1066 m	1071 m	
Acid IV'	707 m,br	737 m	n.o.	711 m,br	729 m	n.o.
Acid V'	490 m	494 m	479 (2)	482 m	481 m	n.o.
Acid VI'	417 m	424 m	419 (3)	368 mw	368 mw	372 (8)
Acid VII'	386 m	384 m	377 (4)	217 m	227 ms	220 (1)

The carboxylic acid carbonyl stretching vibration is observed as a very strong band in the infrared spectrum. For succinamic acid both infrared and Raman bands are splitted and since no overtones and/or combination bands are expected in the 1730 cm^{-1} region, Fermi resonance can be ruled out. This splitting is then probably due to crystal effects. On deuteration νC=O shifts to lower wavenumbers, as can be explained through a decoupling of δOH. For malonamic acid the Acid I fundamental is observed in the 1730 cm^{-1} region as a non splitted band and no shift is observed on cooling, indicating a strong coupling of νC=O, δOH and νC-O, indeed, on deuteration a shift to 1718 cm^{-1} is observed, which is probably due to a decoupling of δOH. The shift of Acid I' compared with the Acid I, on cooling proves the higher νC=O character of this band.

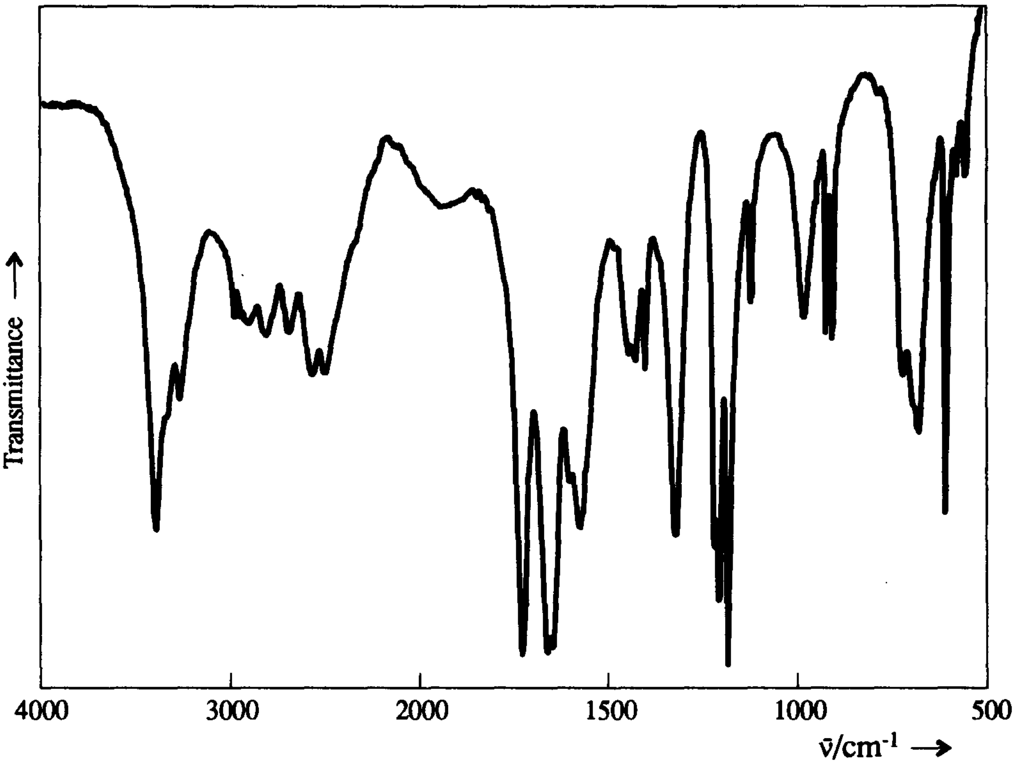


Figure 7 : mid infrared spectrum of malonamic acid.

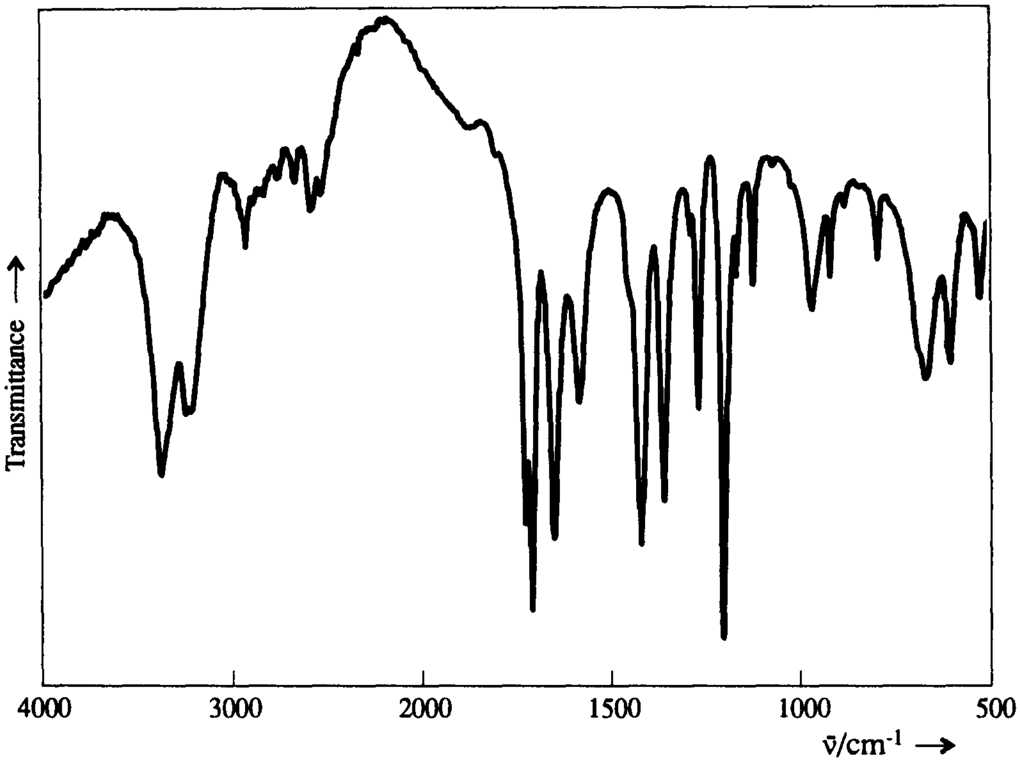


Figure 8 : mid infrared spectrum of succinamic acid.

The frequencies of the Acid II and III vibrations are unusually low. For succinamic acid we observe a medium strong infrared band at 1363 cm^{-1} which is shifted to 1369 cm^{-1} on cooling from room temperature to -196 °C, on deuteration this band dissappears and a new one can be observed at 1319 cm^{-1} which is also shifted to higher wavenumbers on cooling. Acid III is observed at a rather low frequency, normally we expect this vibration in the 1300 cm^{-1} region, the Acid III vibration in succinamic acid is observed at 1204 cm^{-1} as the most intense infrared band. The coupled character of νC-O and δOH in the Acid II and Acid III bands can be clearly proved through deuteration experiments. In the vibrational spectra of malonamic acid, the Acid II, III, II' and III' fundamentals have a very peculiar behaviour. Acid II and III are at even lower wavenumbers than the corresponding bands in succinamic acid. Acid II, with coupled νC-O and δOH character, is observed at 1323 cm^{-1} while Acid III is observed at 1186 cm^{-1} as the most intense infrared band. On deuteration Acid II' and III' are observed at respectively 1348 cm^{-1} and 1072 cm^{-1}, proving the mixed character of Acid II and III.

Acid IV, which represents τC-O as explained in a previous publication [11], is observed as a medium and broad infrared band which shifts to higher wavenumbers and clearly sharpens on cooling, a corresponding Raman band is as usual not observed.

Table 5 : primary amide fundamentals for malonamic acid and succinamic acid.

	$HOOC-CH_2-CONH_2$			$HOOC-(CH_2)_2-CONH_2$		
	IR		Raman	IR		Raman
	20 °C	-196 °C	20 °C	20 °C	-196 °C	20 °C
$\nu_{as}NH_2$	3397 s	3378 s	3392 (2,br)	3382 m,br	3360 m	3370 (2,br)
						3335 (2,br)
$\nu_{s}NH_2$	3269 m	3261 ms	3245 (2)	3251 mw,br	3242 mw	3247 (2,br)
				3224 mw,br	3217 m,br	3212 (2,br)
$\nu C=O$	1663 vs	1664 vs	1673 (1)			
	1647 vs	1648 vs	1646 (1)	1651 s	1654 s	1649 (1)
δNH_2	1578 ms	1557 m	1576 (4,br)	1586 m	1587 m	1588 (4)
νCN	1450 mw	1452 mw	1450 (4)	1419 sh	1415 ms	1418 (6)
ρNH_2	1125 mw	1132 m	1126 (6)	1126 mw	1127 m	1129 (9)
ωNH_2	725 m,br	737 ms	723 (3)	685 sh	695 m	685 (4)
τCN	685 m,br	701 s	n.o.	606 m,br	611 m	611 (2)
δNCO	703 sh	717 m	n.o.	669 m,br	671 mw	n.o.
πNCO	582 w	583 w	582 (2)	525 m,br	555 w	540 (1)
ρNCO	559 w	562 mw	558 (3)	525 m	529 m	540 (1)
$\nu_{as}ND_2$	2557 s	2546 s	2558 (4)	2546 s	2537 s	2550 (4)
$\nu_{s}ND_2$	2407 ms	2400 s	2408 (7)	2389 ms	2372 ms	2391 (6)
$\nu C=O(d)$	1615 vvs,br	1613 vvs,br	1632 (2)	1593 vs	1587 vs	1591 (5)
$\nu CN(d)$	1466 m	1472 m	1457 (9)	1461 ms	1469 ms	1464 (7)
δND_2	1150 mw	1153 mw	1130 (1)	1162 w	1160 w	1163 (4)
ρND_2	965 m	970 m	969 (7)	966 m	968 m	969 (8)
ωND_2	576 mw	589 m	569 (2)	581 ms	581 ms	584 (2)
τCN	512 m,br	526 ms	518 (2)	502 ms	515 ms	509 (2)
$\delta NCO(d)$	604 mw	612 mw	601 (2)	636 mw	640 m	641 (6)

The low frequencies observed for the Acid II and III fundamentals in both malonamic acid and succinamic acid seem rather peculiar. Indeed, νOH and Acid IV are observed at comparable frequencies as the corresponding fundamentals in the vibrational spectra of the dicarboxylic acids and of oxamic acid, indicating comparable hydrogen bond strengths. The low frequencies of Acid II and III could be due to couplings with the amide νCN and δNH_2 modes.

In order to investigate this phenomenon we calculated the normal modes for the cyclic formic acid formamide dimer as given in figure 9.

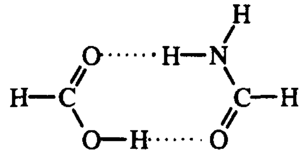


Figure 9 : cyclic formic acid formamide dimer.

The ab initio calculated frequencies and their PED's are given in table 6. From these theoretical results we conclude that there is no coupling between the carboxylic acid and amide vibrations and that the low frequency for the Acid II and III vibrations is inherent to the heterogenic hydrogen bond pattern exhibited by the products under investigation, since the calculated frequencies are lower than the mean calculated frequencies for the carboxylic acids associated in the cyclic dimer pattern

Table 6: HF/6-31G* frequencies (calc) and the uniformly scaled frequencies (scaled) for the cyclic formic acid formamide dimer (figure 9).

calc	scaled	PED
3943	3509	85% $\nu_{as}NH_2$ + 14% ν_sNH_2
3760	3346	71% ν_sNH_2 + 14% νOH + 13%$\nu_{as}NH_2$
3710	3301	84% νOH + 11% ν_sNH_2
3310	2946	98% νCH
3250	2893	99% νCH
1994	1775	61% $\nu C{=}O$ (ac) + 12% $\nu C{=}O$ (am) + 9% $\nu C\text{-}O$ + 8% δCH
1937	1724	49% $\nu C{=}O$ (am) + 13% $\nu C{=}O$ (ac) + 12%νCN + 11% δCH + 7% δNH_2
1804	1606	82% δNH_2 + 11% $\nu C{=}O$
1573	1400	59% δCH + 17% δOH + 10% δCH + 9% $\nu C{=}O$ (ac)
1563	1391	69% δCH + 13% δCH + 9% $\nu C{=}O$ (am)
1529	1361	45% δOH + 21% δCH + 18% $\nu C\text{-}O$ + 10% $\delta CO2$
1440	1282	56% νCN + 23% ρNH_2 + 13% δNCO
1361	1211	63% $\nu C\text{-}O$ + 21% δOH + 5% δCH + 5% $\delta CO2$
1211	1078	94% γCH
1199	1067	58% ρNH_2 + 24% νCN + 8% $\nu C{=}O$ (am) + 6% δCH
1197	1065	89% γCH + 8% τCN
976	869	62% πOH + 21% ν_γ + 8% ν_α + 6% γCH
829	738	60% τCN + 17% ν_β+ 7% γCH + 7% ωNCO
745	663	86% δCO_2 + 8% $\nu C\text{-}O$
656	584	73% δNCO + 18% ρNH_2
470	418	48% ωNCO + 39% τCN + 10%
228	203	89% ν_δ + 7% ν_σ
220	196	39% πOH + 35% ν_γ + 12% ωNCO + 9% ν_β
170	151	77% ν_σ + 17% ν_δ
150	134	76% ν_ε + 15% δOH
143	127	35% ν_β + 31% ωNCO + 15% ν_α + 8% ν_γ + 7% πOH
63	56	57% ν_α + 21% ν_γ + 10% ν_β + 7% ωNCO

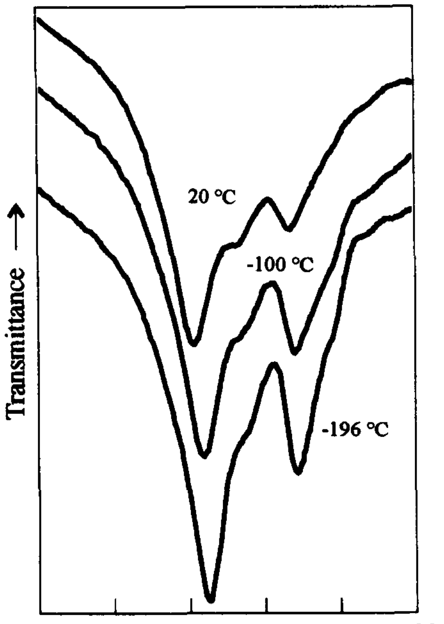
The fundamentals describing a vibration of the NH bonds, can easily be assigned through deuteration. Care has to be taken when interpreting the vibrational spectra of the deuterated products, incomplete deuteration can be the reason for wrong assignments. The methylene group in malonamic acid can be deuterated too since the CH_2 hydrogen atoms are relatively acidic. The CH_2 frequencies will therefore shift to lower wavenumbers on deuteration.

The NH_2 stretching vibrations are expected for a primary amide function in the solid state in the 3400 cm^{-1} and 3200 cm^{-1} region. In the infrared spectrum of malonamic acid we observe $\nu_{as}NH_2$ at 3397 cm^{-1} (3378 cm^{-1} at -196°C), ν_sNH_2 is observed at 3269 cm^{-1} (3261 cm^{-1} at -196 °C), the temperature shift of the NH_2 stretching vibration on cooling can be observed in figure 10. For succinamic acid we observe these fundamentals at respectively 3382 cm^{-1} (3360 cm^{-1} at -196°C) and at 3251 cm^{-1} (3245 cm^{-1} at -196 °C).

The vibrational behaviour of the primary amide function is somewhat peculiar. The antisymmetric and symmetric NH_2 stretching vibrations are observed at the well known positions [15], indicating a normal hydrogen bonded primary amide function. These positions are comparable with the νNH_2 frequencies in simple amides, indicating amide-amide hydrogen bonds [15,18].

The amide C=O stretching vibration, which is usually expected in the 1680 cm^{-1} region, is observed at 1651 cm^{-1} for succinamic acid. On deuteration a shift of this vibration to an even lower wavenumber of 1593 cm^{-1} is observed, while we expect the C=O stretching vibration of a deuterated primary amide in the 1660 cm^{-1} region. This extremely low frequency is probably the result of the strong hydrogen bond that C=O exhibits, the (carboxylic acid) O-H·······O (primary amide) hydrogen bond is, indeed, much stronger than the hydrogen bond between two primary amide functions and is nearly as strong as the hydrogen bond in a carboxylic acid dimer. These assumptions are clearly proved through the normal position of the νOH, $\nu_{as}NH_2$ and ν_sNH_2 frequencies and the very low amide $\nu C=O$ frequency. The above described peculiar behaviour of the amide $\nu C=O$ is also observed in the spectra of malonamic acid, as can be observed in table 4. The calculated normal modes of the cyclic formic acid formamide dimer show a significant mixing between the $\nu C=O$ modes of the carboxylic acid and amide functional group.

The δNH_2 fundamental is expected as a medium to medium weak infrared band in the 1600 cm^{-1} region. In the room temperature infrared spectrum of succinamic acid (figure 8) δNH_2 is observed at 1586 cm^{-1}, on deuteration δND_2 is observed at 1162 cm^{-1} while these fundamentals are observed at respectively 1578 cm^{-1} and 1150 cm^{-1} for malonamic acid.



<u>Figure 10:</u> behaviour of $\nu_{as}NH_2$ and ν_sNH_2 in the infrared spectrum of malonamic acid on cooling.

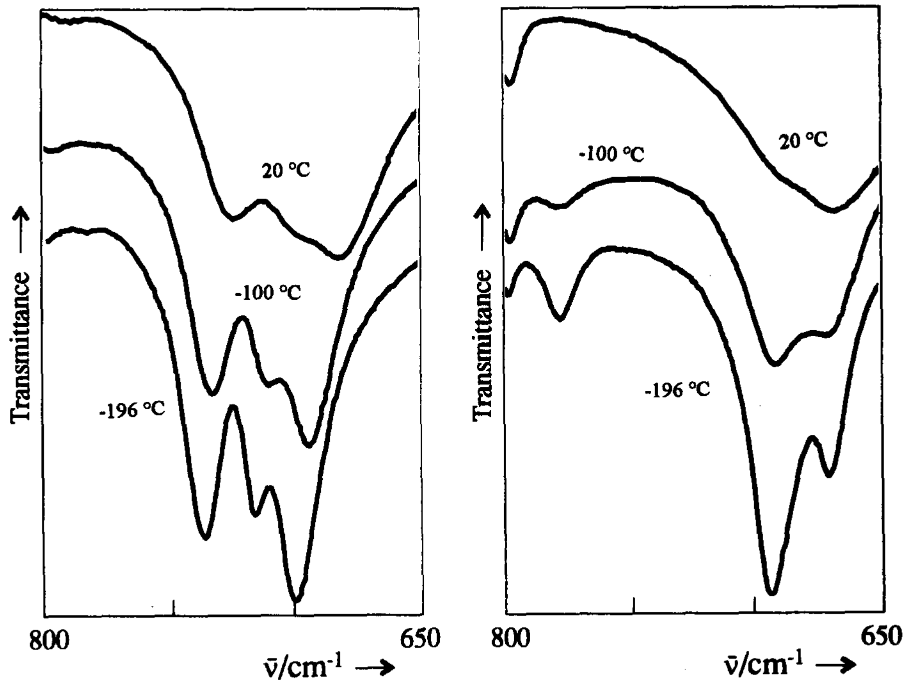


Figure 11 : behaviour of ωNH_2 and τCN on cooling in the infrared spectra of malonamic acid (left) and succinamic acid (right).

The CN stretching vibration is usually expected in the 1400-1350 cm^{-1} region. This fundamental is observed at higher wavenumbers for both acids, what can be explained by assuming a considerable contribution of the polar form in the real amide structure. Indeed, since the $\nu C{=}O$ frequency is observed at lower wavenumbers than normally expected for a primary amide functional group, the νCN frequency should be at higher wavenumbers than expected. ρNH_2, ωNH_2 and τCN are observed as medium intense infrared bands at respectively 1126 cm^{-1}, 685 cm^{-1} and 606 cm^{-1} for succinamic acid and at 1125 cm^{-1}, 725 cm^{-1} and 685 cm^{-1} for malonamic acid.. These bands clearly shift to higher wavenumbers on cooling, as can be observed in figure 11 for ωNH_2 and τCN. Strong coupling between NCO and CO_2 deformations in both acids occurs, these modes can only be described as zone frequencies and are consequently not useful for characterisation. The assignments of these normal coordinates will therefore be omitted from this discussion, their positions can be observed in tables 4 and 5.

CONCLUSIONS

The vibrational behaviour of oxamic acid clearly indicates that this simple acid-amide is intermolecularly hydrogen bonded through alternating cyclic acid-acid and cyclic amide-amide dimers. The proposed supermolecule models the peculiar behaviour of the carboxylic acid carbonyl stretching vibrations of oxamic acid sufficiently well, and can be used in further theoretical calculations on the vibrational behaviour of the hydrogen bonded oxamic acid molecule.

As expected, through the known hydrogen bond pattern, the vibrational behaviour of succinamic acid is different from the oxamic acid behaviour. The absence of any local inversion symmetry is reflected in the total coincidence of the infrared and Raman frequencies. The typical behaviour of the primary amide and carboxylic acid fundamentals indicate acid-amide hydrogen bonds. The theoretical values for some fundamentals such as the low values obtained for Acid II and Acid III and the relatively low amide $\nu C{=}O$ and high νCN are typical for these acid-amide dimers and are confirmed by the experiment.

Since malonamic acid behaves very similar as succinamic acid we propose an analogue hydrogen bond pattern for this compound.

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REFERENCES

[1] G. N. R. Tripathi, J. E. Katon, *Spectrochim. Acta* **35A**, 401 (1979).

[2] L. Leiserowitz, *Acta Cryst.* **B32**, 775 (1976).

[3] V. Benghiat, H. W. Kaufmann, L. Leiserowitz, G. M. J. Schmidt, *J. Chem. Soc. Perkin II*, 1758 (1972).

[4] T. Neuheuser, B. A. Hess, C. Reutel, E. Weber, *J. Phys. Chem.* **98**, 6459 (1994).

[5] Gaussian 92, Revision E. 3, M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, J. A. Pople, Gaussian, Inc. Pittsburgh PA (1992).

[6] W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **56**, 2257 (1972).

[7] G. Fogarasi, P. Pulay in *Vibrational Spectra and Structure*, Vol. **14**, ed. J. R. Durig, Elsevier Amsterdam, 125 (1985).

[8] T. Sundius, *J. Mol. Struct.* **218**, 321 (1990).

[9] F. Wallace, Ph. D. thesis, Washington State University (1975).

[10] F. Wallace, E. Wagner, *Spectrochim. Acta* **34A**, 589 (1978).

[11] I. Wolfs, H. O. Desseyn, submitted to *Appl. Spectrosc.*.

[12] I. Wolfs, H. O. Desseyn, accepted for publication in *J. Mol. Struct. (Theochem)*.

[13] J. Dybal, T. C. Cheam, S. Krimm, *J. Mol. Struct.* **159**, 183 (1987).

[14] B. Slootmaekers, H. O. Desseyn, *Appl. Spectrosc.* **45**, 118 (1991).

[15] H. O. Desseyn in *The Chemistry of Acid Derivatives*, ed. S. Pataï (1992).

[16] H. O. Desseyn, B. J. van der Veken, M. A. Herman, *Spectrochim. Acta* **33A**, 633 (1977).

[17] S. Bratos, H. Ratajczak, P. Viot in *Hydrogen Bonded Liquids*, eds. J. C. Dore, J. Teixeira, Kluwer, p. 221 (1991).

[18] I. Wolfs, H. O. Desseyn, S. P. Perlepes, *Spectrochim. Acta* **50A**, 1141 (1994).