

Infrared spectrum of anhydrous citric acid in the solid state—I

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The infrared spectra of anhydrous citric acid in mull and in KBr matrix have been recorded in the range 700-4000 cm^{-1} with a Perkin-Elmer Infrared Spectrophotometer, model 221 equipped with sodium chloride optics. The observed frequencies are assigned tentatively to their respective characteristic groups. The frequencies due to the hydrogen bonds in the unit cell, are assigned with reference to the data known from Hadzi (1965). The results are reported in this communication.

INTRODUCTION

There are only a few investigations that are to be found in the literature on the infrared and Raman spectra of citric acid either in solution or in the solid state. Passorini (1935) and Duval (1955) have recorded the infrared spectrum in the solid state without presenting any analysis. There is no investigation reported on the infrared spectrum of citric acid in solution. Edsall (1937) has investigated the Raman spectrum in solution and has reported the Raman frequencies without any analysis except indicating the C=O and CH₂ frequencies. Nisi (1931), Thatte *et al* (1936) and Canal *et al* (1938) have investigated the Raman spectrum of citric acid monohydrate in the solid state. Nisi has confined himself to the region of water of crystallization only and reported the same. Thatte *et al* have photographed the Raman spectrum in the molten state and discussed the O=C—O group frequencies only. Canal *et al* have photographed the spectrum using powder technique and reported the data without any analysis. The authors have attempted to analyse the vibrational spectrum of this molecule in the solid state. Thus they have recorded the infrared spectrum of anhydrous citric acid in mull and in KBr matrix and have assigned the frequencies to their respective characteristic groups.

EXPERIMENTAL

Citric acid monohydrate of AR grade from S. Merck & Co. was procured and purified by repeated recrystallization. A hot saturated solution of the substance in distilled water at about 70°C was cooled slowly to room temperature over several days. It is known that citric acid becomes anhydrous above the temperature 36.7°C and so we have obtained the crystals of anhydrous citric acid by the

above process of cooling. This anhydrous citric acid was used to record the spectra in mull as well as with a KBr pellet. The spectra are reproduced in figures 1 and 2.

RESULTS

The observed frequencies with assignments are given in table 1. Also a pictorial diagram of anhydrous citric acid molecule is given in figure 3a. The Raman frequencies of citric acid in the polycrystalline state from Landolt and Bornstein tables (1951) are also given for comparison.

DISCUSSION

Anhydrous citric acid with the chemical formula $C_6H_8O_7$, is a tribasic acid with an OH group attached to the middle carbon atom. There is no data available on the molecular symmetry of this molecule in the free state. The crystal structure has been fully worked out by Nordman *et al* (1960).


To facilitate understanding of the assignment of observed frequencies to their functional groups, a few salient details on the structure of the anhydrous citric acid molecule are given here. The aliphatic chain C_1-C_5 is approximately planar, but is slightly bent away from the carboxyl $O_5C_6O_6$. All the carboxyls are coplanar with their α -carbons. The carboxyl group $O_1C_1O_2$ is at an angle of 3.3° , while the carboxyl $O_3C_3O_4$ is approximately at right angles to that plane. There is approximate parallelism between the carboxyl $O_5C_6O_6$ to the plane $C_6C_3O_7$, containing the α -hydroxyl. In the unit cell the carboxyl group $O_1C_1O_2$ is connected by two equivalent hydrogen bonds to an equivalent group across a centre of symmetry, i.e., the bonding is of the dimer type.

The free state symmetry of the molecule is only C_1 and the site symmetry is also C_1 although we could consider C_s to be the approximate site symmetry from the view point of the structural details already given above. Since in the present work we have aimed at only the characteristic group frequency assignments and not the assignment of symmetry species of the modes of vibration, the site symmetry has not been discussed further. The observed frequencies are discussed below in terms of their functional groups.

CH_2 frequencies

The antisymmetric stretching frequencies of this group appear in the region 2920–2948 cm^{-1} as a broad region of absorption and the symmetric stretching frequencies appear in the region 2885–2895 cm^{-1} in the mull spectrum. These frequencies are absent in the KBr pellet spectrum and this may be so because the pressure applied might be too high and some solid state reaction might take place between KBr and the substance. The region 1100–1400 cm^{-1} is a little bit complicated, in the case of carboxylic acids having a number of COOH groups and because of waggings of CH_2 group some of the skeletal frequencies and carboxyl group frequencies appear in this region. So in this region assignments

TABLE I Infrared frequencies of anhydrous citric acid from mull and KBr pellet spectra, with tentative assignments, 700-4000 cm^{-1} region.

Raman freqs. from Landolt & Bornstein (1951)		Infrared freqs. present authors		Assignment
Freq cm^{-1}	Intensity	Freq. cm^{-1}	Intensity	
419	(1)	—	—	
—		687	$w \rightarrow$	 Angle deformation
—		775	m	CH_2 rocking
870	(1)	928 } 937 }	w } w }	C-C bending and OH out of plane bending.
—		960	w	CH_2 rocking
—		1044 } 1073 }	w } w }	C-O stretches of C-OH
1071	(1)	1207	m	C-C stretching.
—		1280	m	C-O stretching of carboxyl
—		1307	vw	CH_2 wagging
—		1328 } 1342 }	$m \rightarrow$	OCO bending of COOH
—		1407 } 1413 }	m } $m.br$ }	CH_2 scissoring
1442	(1)	1425	$m.br \rightarrow$	C-O stretching
—		1430	m	C-OH deformation
—		1460	m	CH_2 scissoring
—		1689 } 1695 } 1704 }	m } vs }	C = O stretching
—		1715	vs	—
1739	(0)	1730 } 1741 } 1740 }	$vs \rightarrow$	OH stretching lowered due to hydrogen bonding.
—		2325 } 2340 }	$kinks$ }	—
—		2630 } 2650 }	$vw br \rightarrow$	OH frequencies lowered due to hydrogen bonding
—		2734 } 2776 }	$vw.br$	—
—		2845 } 2860 }	$s.br$	—
—		2885	s	CH_2 stretching
2984	(b)	2920 } 2948 }	\rightarrow $m.br$	CH_2 stretching
—		3203 } 3277 } 3343 } 3367 } 3485 }	$m.br$ } s } m } vw } $s.sh$ }	O-H stretchings (fundamentals and overtones and combinations)

are made in comparison with the assignments for adipic acid due to Anantanarayanan (1964). The other frequencies of this group appear at 1460, 1413, 1407 cm^{-1} assigned to CH_2 scissoring modes and at 1307 cm^{-1} a broad band assigned to CH_2 wagging modes. The rocking vibrations of this group appear at 960 and 775 cm^{-1} .

COOH frequencies

The frequencies at 1689, 1694 and 1704 cm^{-1} are attributed to $\text{C}=\text{O}$ stretchings of this group. These frequencies are in accordance with the fact that there is dimerization in the unit cell. From the literature it is known that the dimer type molecule will give $\text{C}=\text{O}$ stretching frequencies in the range 1690–1720 cm^{-1} . The other frequencies of this group, namely $\text{C}-\text{O}$ stretchings appear at 1280, 1425 cm^{-1} , the COO angle bendings of COOH group appear at 1328, 1342 cm^{-1} and the angle deformation frequencies appear at 687 cm^{-1} . The assignments are given in table 1.

C—OH frequencies

$\text{C}-\text{O}$ stretchings of this group appear at 1073, 1044 cm^{-1} and the $\text{C}-\text{OH}$ in plane bending appears at 1430 cm^{-1} . These are given the assignments in comparison with other compounds containing $\text{C}-\text{OH}$ group.

C—C frequencies

It is known from the anhydrous citric acid molecular structure given in figure 3a that the molecule consists of a zig-zag chain of carbon atoms and so one should expect the CC group to give rise to stretchings and bendings. The frequency at 1207 cm^{-1} is attributed to the stretching vibration of this group and the band at 928 cm^{-1} is attributed to the bendings of this group.

Hydrogen bond frequencies

The range of these frequencies is identified using the details available from Hadzi (1965). According to Hadzi these bands form a characteristic trio near 2800, 2500 and 1900 cm^{-1} , if the carboxyl groups act as proton donors but they are somewhat lower (about 2700, 2200, 1600 cm^{-1}) for hydrogen phosphate and similar groups. Thus the frequencies in the range 2776 to 2325 cm^{-1} and the frequencies at 1749 to 1730 cm^{-1} assigned to the OH stretches are lowered due to hydrogen bonding. Except for identifying the range of these frequencies, any other discussion is difficult in the absence of studies on single crystals.

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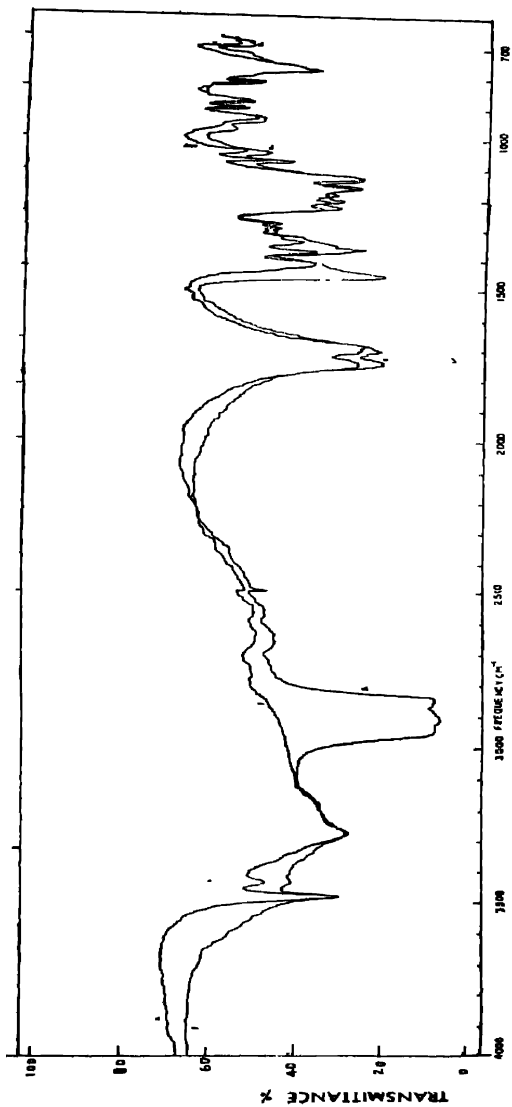


Figure 1. Infrared spectrum of anhydrous citric acid :

(1) KBr pellet spectrum (2) mull spectrum, 700—4000 cm^{-1} ; NaCl optics, PE IRS—Model 221.

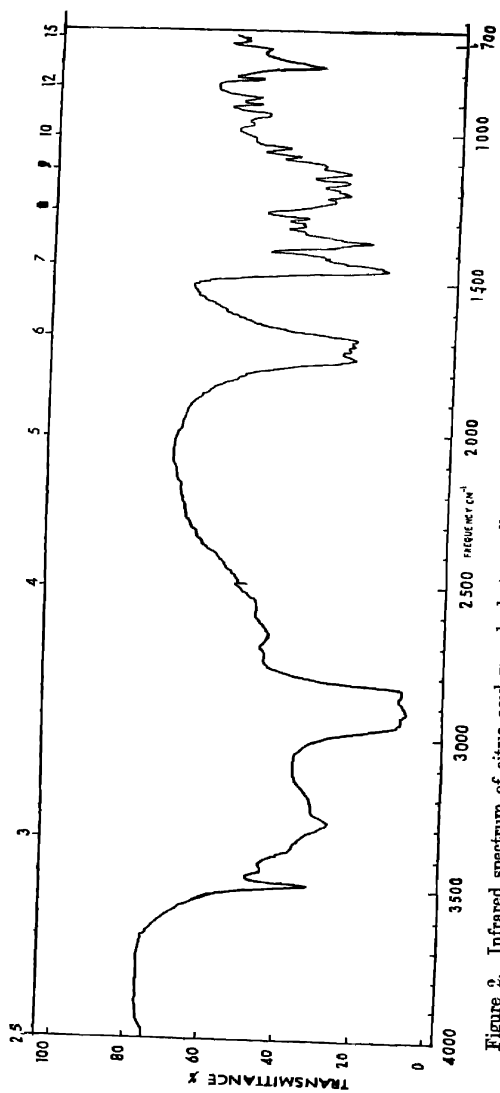


Figure 2. Infrared spectrum of citric acid monohydrate, mull spectrum ; 700-4000 cm^{-1} , NaCl optics PE IRS-Model 221.

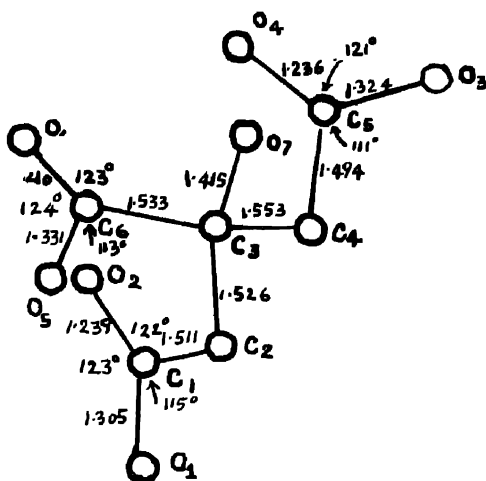


Figure 3a, Anhydrous citric acid molecule with H atoms removed.

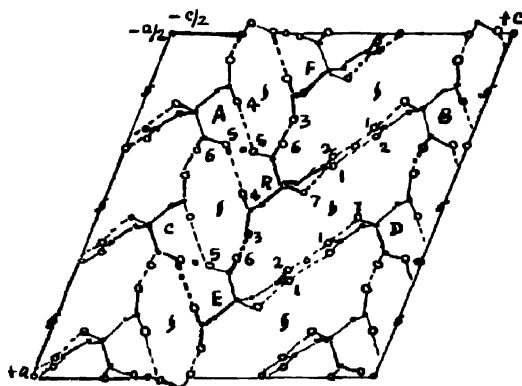


Figure 3b. Hydrogen bonding and molecular packing in anhydrous citric acid unit cell. Unit cell-dimensions : $a = 12.82\text{\AA}$, $b = 5.62\text{\AA}$, $c = 11.54\text{\AA}$, $\beta = 111.2^\circ$ space group C_{2h}^{22} , $Z = 4$ molecules.