

# RAMAN EFFECT IN DIBASIC ACIDS IN CRYSTALLINE STATE.

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## Abstract.

A TECHNIQUE for studying Raman Spectra of crystalline and amorphous solids is described. The results of the study of the first three members of the oxalic acid series are given. Malonic and succinic acids have been tried for the first time. Possible modes of vibration of the molecules corresponding to the observed Raman frequencies are discussed. The characteristic frequencies for the acids in the crystalline state are found to be:—

Oxalic acid, 1658, 1590, 1522, 840, 692, 533, 457  $\text{cm.}^{-1}$

Malonic acid, 1658, 1471, 1261, 1029, 879, 682, 508  $\text{cm.}^{-1}$

Succinic acid, 1654, 1420, 1200, 1153, 927  $\text{cm.}^{-1}$

Frequencies 1660 and 1450  $\text{cm.}^{-1}$  are ascribed to C = O, and

$\begin{array}{c} \text{H} \\ | \\ \text{---C---} \\ | \\ \text{H} \end{array}$  bindings respectively and those between 1200 and 1000  $\text{cm.}^{-1}$  to

$\begin{array}{c} \text{H} \\ | \\ \text{C---C} \\ | \\ \text{H} \end{array}$ , while lower frequencies correspond to the vibrations of the two main

groups of atoms of the various molecules.

## Introduction.

The experimental investigation of Raman effect has been of very great service in explaining the internal structure of various molecules. The characteristic frequencies and the modes of vibration about the various kinds of chemical bonds were the subject of study of workers all over the world for the substances available in the liquid state or large crystals. Menzies<sup>1</sup> for the first time showed that small crystal aggregates, *i.e.*, crystalline, and even amorphous, powders could be used to find the Raman spectrum of these substances. He employed a small flask as the container for the

substance under examination. The light of a quartz mercury-vapour lamp was concentrated on the flask, the scattered radiation being observed in a perpendicular direction. Bär<sup>2</sup> used a rectangular plate-glass cell for holding the crystalline powder and corroborated the results of Menzies. Although the regular reflection from the crystals produced a continuous background which masked all but the strongest modified lines, their discovery showed that single crystals were not essential for studying the molecular scattering. P. Krishnamurti<sup>3</sup> improved the experimental technique by using a triangular cell, two sides of which were silvered and near the third side a quartz mercury lamp was placed. A concentrated solution of didymium chloride was used to absorb the continuous background.

For some time past we have been trying in this laboratory to develop a technique suitable for studying the Raman spectrum in crystal aggregates using the apparatus at our disposal.

*Experimental Arrangements.*

The substance contained in a hollow plate-glass cube was illuminated on three sides by a specially designed arc of pyrex-glass, as shown diagrammatically in Fig. 1. The arc was generally run at about 3 amperes and could work continuously for very long periods without any attention. With

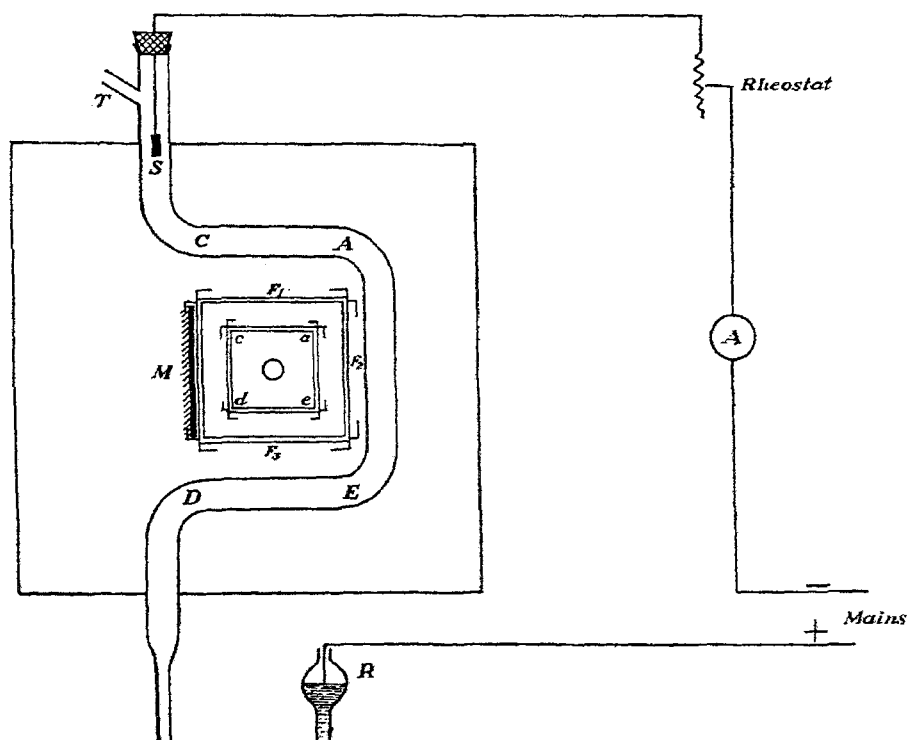


FIG. 1.

this arrangement the intensity of scattered light in case of naphthalene crystals was sufficient for the strongest Raman lines to be observed visually while a few minutes' exposure gave all the modified lines on a plate. The ease in the construction and manipulation of the lamp, its low cost and longer life as compared to the commercial quartz mercury lamp are some of the redeeming features of the arrangement. It is specially suited for substances which require very long exposures.

For holding amorphous substances and fine crystalline powders a slightly different device was used. It consisted of a glass tube of 1.8 cm. bore fitted centrally in the glass cube. Saturated sodium nitrite solution as suggested by Pfund<sup>4</sup> was used as a filter which cuts off effectively the light below  $\lambda$  4358 Å and in addition absorbed a good deal of the continuous radiation.

The Raman spectra of the first three members of the oxalic acid series (Kahlbaum's and British Drug House Analytic reagents) were photographed in the usual manner using a Carl Zeiss Spectrograph of great light-gathering power with a large equilateral prism giving a dispersion of about 70 Å per mm. in the region  $\lambda$  4358. A Hilger comparator reading upto 1/1000 of a mm. was used for measurement. Backed ortho-special Kodak plates and supersensitive Ilford Iso-zenith plates were used.

Using a set of standard sieves the available chemical was graded into crystals of various sizes. Crystals which passed through 1.5 mm. but not through 1 mm. diameter mesh yielded best results.

#### *Results.*

The results of measurements on the different plates are summarised in Tables I, II and III. Table I is for oxalic acid dihydrate and also includes the results of previous workers.

Table II gives the frequencies observed for malonic acid which has been tried for the first time in solid state. The results of Ghosh and Kar on saturated solution of malonic acid in ultra-violet region are given for comparison.

Table III gives the results for succinic acid in the crystalline state which had not been tried before. The exciting line in all cases was  $\lambda = 4358.3$  Å.

TABLE I.

*Oxalic acid dihydrate*  $\begin{matrix} \text{COOH} \\ \text{COOH} \end{matrix} 2\text{H}_2\text{O}$

No.	Wave-length of Raman line in I.A. $\lambda$	Intensity I	Wave number in vacuum $\nu$	Frequency shift $\Delta\nu$	$\Delta\nu$ as observed by other authors			
					Krishnamurti <sup>5</sup>	Siva Rao <sup>6</sup>	Hibben <sup>7</sup>	Angus and Leckie <sup>8</sup>
1	4447	1s	22481	457		473		495
2	4462	1s	22405	533				
3	4494	1s	22246	692				
4	4524	2s	22098	840	855	851	847 1365	854
5	4668	1s	21416	1522		1506	1470	1471
6	4683	0d	21348	1590				
7	4698	1s	21280	1658		1640 ± 20 1758		1661 1759

TABLE II.

*Malonic acid*  $\text{H}_2\text{C} \begin{matrix} \text{COOH} \\ \text{COOH} \end{matrix}$

No.	$\lambda$	I	$\nu$	$\Delta\nu$	$\Delta\nu$ as observed by Ghosh and Kar <sup>9</sup> in saturated solution of malonic acid
1	4457	1s	22430	508	
2	4492	1s	22256	682	
3	4532	1s	22059	879	
4	4563	1s	21909	1029	908 960
5	4602	0d	21677	1261	
6	4657	1s	21467	1471	
7	4698	1s	21280	1658	1737 2935

TABLE III.

Succinic acid  $\begin{matrix} H_2C \cdot OOOH \\ H_2\dot{C} \cdot COOH \end{matrix}$

No.	$\lambda$	I	$\nu$	$\Delta\nu$
1	4542	1 <sub>s</sub>	22011	927
2	4589	2 <sub>s</sub>	21785	1153
3	4599	2 <sub>s</sub>	21738	1200
4	4646	1 <sub>s</sub>	21518	1420
5	4697	1 <sub>s</sub>	21284	1654

$\nu = 22938 \text{ cm.}^{-1}$  Letters *s*, *b* and *d* denote respectively sharp, broad and diffuse lines.

#### Discussion.

In dibasic acids each molecule consists of two main groups of atoms. The smaller frequencies, namely, 457, 533, 692 and 840 in case of oxalic acid, 508, 682 and 879 for malonic acid and 927 for succinic acid are ascribed to the vibrations of these main groups of their respective molecules.

In oxalic acid the frequency at  $840 \text{ cm.}^{-1}$  is the strongest and has been observed by all the authors. Corresponding to the frequency  $473 \text{ cm.}^{-1}$  as found by Siva Rao, and  $495 \text{ cm.}^{-1}$  as found by Angus and Leckie, the author found two frequencies at 457 and  $533 \text{ cm.}^{-1}$ . Another frequency at  $692 \text{ cm.}^{-1}$  has also been observed by the author.

In malonic acid, in the crystalline state the frequency observed at  $879 \text{ cm.}^{-1}$  might correspond to the frequency  $908 \text{ cm.}^{-1}$  in saturated solution of the acid as reported by Ghosh and Kar.

The larger frequencies are ascribed to the vibrations of the various radicals within each one of the main groups of the various molecules. The frequencies between 1200 and  $1000 \text{ cm.}^{-1}$  are attributed primarily to the vibrations of the carbon atoms, within these main groups. Morris<sup>10</sup> gives for C—C binding a frequency at  $1024 \text{ cm.}^{-1}$ , while Collins<sup>11</sup> gives two frequencies at 1192 and  $1152 \text{ cm.}^{-1}$ . The results of the dibasic acids also point towards the same conclusion. Oxalic acid does not show any line between 1000 and

$1200 \text{ cm.}^{-1}$  and its structure shows no  $\begin{matrix} H \\ | \\ C-C \\ | \\ H \end{matrix}$  group. On the other hand,

both malonic and succinic acids show one or two of these frequencies showing

the presence of  $\begin{array}{c} \text{H} \\ | \\ \text{C}-\text{C} \\ | \\ \text{H} \end{array}$  groups.

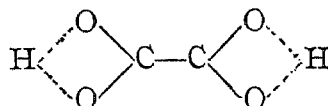
The conclusion of Siva Rao, that the Raman line at about  $1450 \text{ cm.}^{-1}$  observed in a series of aliphatic compounds is due to the OH group does not appear to be justified, because as is well known, this frequency occurs prominently in the saturated aliphatic hydrocarbons. Available data would tend to show that its origin is to be traced most probably to the  $\delta$  (C—H) vibration of the  $\text{CH}_2$  group. This view is supported by the fact that this frequency is absent in oxalic acid whose structure shows no  $\text{CH}_2$  group while it is present in the other two acids which are known to contain one or more  $\text{CH}_2$  groups.

Frequency  $1660 \text{ cm.}^{-1}$  is considered to be the characteristic frequency of the carbonyl (C=O) group. It is shown by all compounds containing this group, such as fatty acids, aldehydes, ketones, esters, anhydrides, etc. The corresponding wave-length also appears in the infra-red absorption spectra of compounds containing this group. The fatty acids have a frequency at about  $1660 \text{ cm.}^{-1}$ , their derivatives have, as a rule, slightly higher frequency which may go up to  $1798$  in acid chlorides. Thus the replacement of a hydrogen atom in the acid by an alkyl or a halogen group tends to increase the frequency of the carbonyl binding.

Siva Rao found two frequencies, at  $1650$  and  $1750 \text{ cm.}^{-1}$ , in oxalic acid, the intensity of the latter being greater than that of the former. Hibben has not been able to record any one of these frequencies. Angus and Leckie have found both these frequencies and support Rao's result. The present writer has observed the frequency at  $1650 \text{ cm.}^{-1}$  but failed to observe the higher frequency in any one of the three dibasic acids studied.

The important work of Kohlrausch and Pongratz<sup>12</sup> on dimethyl and diethyl esters of oxalic, malonic and succinic acids definitely points to the presence of only one frequency for both the carbonyl groups. Even in tri- and tetracarboxylic acids no doubling of frequency occurred. In tautomeric forms such a doubling of frequency may be possible and has been observed. But in non-tautomeric compounds like oxalic acid and succinic acid no such doubling is conceivable. This supports the contention of the present author that in dibasic acids the two carboxylic groups are similarly situated giving rise to only one characteristic Raman frequency.

Recently J. Gupta<sup>13</sup> has proposed for oxalic acid in anhydrous state the structure



while retaining for solution the normal structure  $\begin{array}{c} \text{OH} \\ | \\ -\text{C}=\text{O} \end{array}$ . B. C. Ray and P. B. Sarkar<sup>14</sup> have proposed a  $\left( \begin{array}{c} \text{O} \\ // \\ \text{C} \\ \backslash \\ \text{OH} \end{array} \right)^{-}$  structure for the formate

ion in solution retaining the normal structure  $\begin{array}{c} \text{O} \\ // \\ -\text{C} \\ \backslash \\ \text{OH} \end{array}$  for the acid and its

ester in the crystalline state. Small and Wolfenden<sup>15</sup> have opposed such a hypothesis. So far as the present work goes, it shows that there is only one frequency corresponding to carbonyl groups indicating normal structure for both the COOH groups in oxalic, malonic and succinic acids in the crystalline state.

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