The Raman Spectra of Oxalic Acid

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The Raman spectra of anhydrous oxalic acid, its aqueous and alcoholic solutions, and oxalic acid dihydrate were determined. The spectra from the aqueous solution and anhydrous oxalic acid show that the two carboxyl groups do not behave identically. Peculiarities in the spectrum of the dihydrate are indicated. In the alcoholic solution both carboxyl groups behave similarly. The magnitude of the force constants in the carbonyl groups are consistent with the strength of this acid. Various explanations of these anomalies are discussed briefly.

OXALIC acid is one of the strongest organic acids. From the point of view of classical organic chemistry the simple structural formula

$$
\begin{array}{cc}
\text{O} & \text{O} \\
\diagdown & \diagup \\
\text{C} & - \text{C} \\
\diagup & \diagdown \\
\text{OH} & \text{OH}
\end{array}
$$
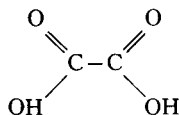
does not explain all its properties. It has been suggested[1] that a tautomeric rearrangement of the acid is possible in conformity with the scheme

or
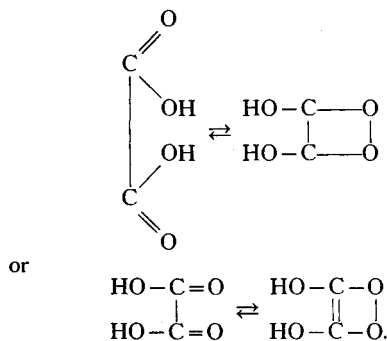
It is further supposed that the crystal hydrate might exist as the poly-hydroxy compound[2]

$$
\begin{array}{c}
\text{C (OH)}_3 \\
| \quad\cdot \\
\text{C (OH)}_3
\end{array}
$$

The Raman spectra of the anhydrous acid, the crystal hydrate, and the aqueous and alcoholic solutions of the acid were therefore determined in order to define more clearly the constitution of the molecule, and as illustrative of the method.

TABLE I. *Raman spectra of oxalic acid.*

(COOH)$_2$ in CH$_3$OH Hibben	(COOH)$_2$·2H$_2$O Hibben	Aqueous Solution (COOH)$_2$ Rao	Aqueous Solution (COOH)$_2$ Hibben	(COOH)$_2$ Rao	(COOH)$_2$ Hibben
		248 (?)			
403$_m$			395$_m$		
			453$_m$		
		480$_m$		473$_m$	
		673 (?)			
850$_s$	847 ·	845$_s$	842$_s$	851$_s$.	848$_s$
			1310$_w$		
	1365	1430$_{wd}$*			1370$_d$
	1471		1460$_d$		
				1506$_w$	
	1656$_d$	1645$_d$		1640$_d$	1651$_m$
1755$_s$	1744$_s$	1740$_m$		1758$_w$	1740 (?)

s (strong), w (weak), d (diffuse), m (medium)   * ±30

Krishnamurti[3] observed one frequency shift for the hydrate, $\Delta\bar{\nu}$ (cm^{-1}) 855. Recently Siva Rao[4] examined oxalic acid and its aqueous solution. The results were in partial agreement with those obtained by the author. There are, however, some pertinent points of disagreement. Table I summarizes these results.

So far as the solution is concerned, the difference lies in the two lower frequency shifts and the shift between $\Delta\bar{\nu}$ 1310 and $\Delta\bar{\nu}$ 1460. In Fig. 1
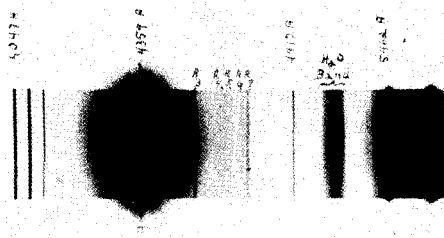
FIG. 1. Raman spectra of oxalic acid in aqueous solution.

[1] Tschitschibabin, J. Prakt. Chem. (2) **120**, 214 (1928).
[2] Noyes, *Organic Chemistry* (Henry Holt & Co., second edition).

[3] Krishnamurti, Ind. J. Phys. **6**, 309 (1931).
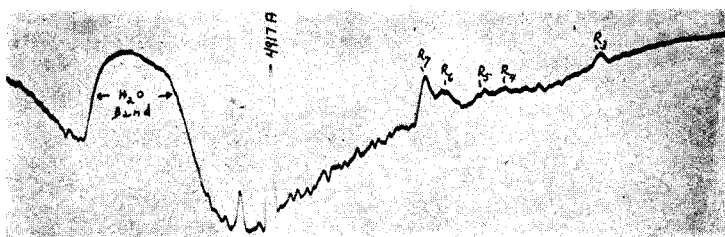[4] Rao, Zeits. f. Physik **94**, 546 (1935).

FIG. 2. Microphotometer tracing of the Raman spectra of aqueous oxalic acid.

is shown the positive spectrogram of the aqueous solution with the 4359A mercury line as a source of excitation with $NaNO_2$ and $Co(SCN)_2$ solutions as filters. The two lower shifts are hidden in the print behind the general scattering. The $\Delta\bar{\nu}$ 1460 and 1310 shifts, however, are clearly apparent. Fig. 2 is a microphotometer tracing of the same plate. Fig. 3 is a similar tracing of a positive contact plate made from the same spectrum. The frequencies $\Delta\bar{\nu}$ 395 and 453 are thus easily made discernible. The frequency $\Delta\bar{\nu}$ 248 is too close to the exciting line for its existence to be at all certain. It is possible that the frequency designated as $\Delta\bar{\nu}$ 480 by Rao is the same as $\Delta\bar{\nu}$ 453. The discrepancy of 27 wave numbers is greater, however, than the accuracy of measurement. The questionable frequency at $\Delta\bar{\nu}$ 673 is apparently nonexistent.

For the anhydrous acid the principal frequencies near $\Delta\bar{\nu}$ 850 and $\Delta\bar{\nu}$ 1650 are in reasonable agreement with Rao's results, but his lines corresponding to $\Delta\bar{\nu}$ 1506 and $\Delta\bar{\nu}$ 473 were not recorded and $\Delta\bar{\nu}$ 1370 not observed by him was clearly readable. The shift at $\Delta\bar{\nu}$ 1740 is very difficult to estimate correctly using the unfiltered mercury spectrum employed by Rao. This nearly overlaps the mercury line at 4730A.

In the crystal hydrate the principal shift $\Delta\bar{\nu}$ 847 is accompanied by $\Delta\bar{\nu}$ 1365 analogous to the anhydrous acid but with the addition of a weaker shift at $\Delta\bar{\nu}$ 1471. No shifts corresponding to those at approximately $\Delta\bar{\nu}$ 1650 and $\Delta\bar{\nu}$ 1750 of the anhydrous acid were observed in the hydrate. This does not preclude the possibility that they may be extant but if so they are very much weaker than the same shifts in the dehydrated acid. The water band which extends from

$\Delta\bar{\nu}$ 3415 to $\Delta\bar{\nu}$ 3531 in the hydrate is much sharper than the corresponding water band in aqueous solution which is nearly four times as broad.

It is to be admitted that the exact measurements of diffuse and weak lines is difficult against the strong background scattering of the exciting radiation. This is particularly true of the Raman spectra from small crystals.

In Fig. 4 is given the microphotometer tracing of the alcoholic solution of oxalic acid in comparison with alcohol in which the upper curve represents methyl alcohol. The results are independent of the amount of water which may be present up to 10 percent. The lower frequency shift $\Delta\bar{\nu}$ 403 is not discernible in the tracing. Nevertheless it is easily measurable on the original plate. There is no evidence of a shift corresponding to approximately $\Delta\bar{\nu}$ 1650, which is one of the characteristic lines in the aqueous solution of the acid. The frequency at $\Delta\bar{\nu}$ 1740 in water solution becomes $\Delta\bar{\nu}$ 1755.

The above are all the experimental observations so far obtained. There appear, however, from these results certain salient facts that are beyond any experimental rationalization, namely, there are apparently two definite frequencies in the aqueous solution of oxalic acid which are normally attributed to the $C=O$ oscillation and which become a single frequency in the alcoholic solution, and these same frequencies are radically diminished in intensity, if not extinct, in the hydrated crystal. The interpretation of these observations is a matter of opinion. A consideration of the Raman spectra of some other organic compounds containing carbonyl groups would be of value in arriving at any conclusion.
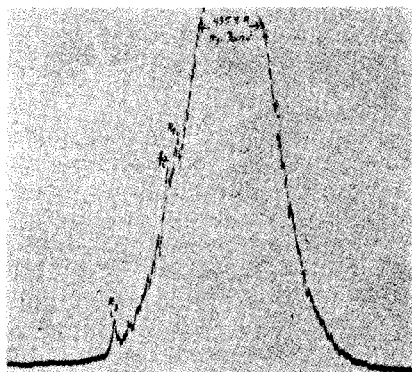
FIG. 3. Microphotometer tracing indicating Raman shifts 395 and 453 in aqueous oxalic acid.
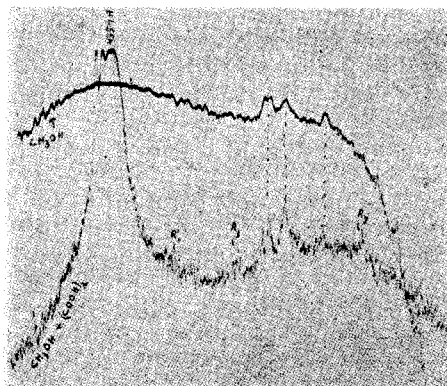

FIG. 4. The Raman spectra of oxalic acid dissolved in CH_3OH and the spectra of CH_3OH. The upper curve represents the pure alcohol.

Siva Rao correctly points out that, in the aliphatic series, $C=O$ frequencies between $\Delta\bar{\nu}$ 1712 and 1760 are confined to the higher homologues of the esters and the aldehyde and ketone derivatives of the aliphatic hydrocarbons. Ordinarily the acid derivatives of the simple hydrocarbons have a shift which falls within the region $\Delta\bar{\nu}$ 1640 and 1660. This would account for the frequency shift in the region of $\Delta\bar{\nu}$ 1650 observed in the aqueous solution of oxalic acid and with the powdered anhydrous acid.

Only one other saturated dicarboxylic acid has been studied. This is malonic acid.[5] The observed shifts were $\Delta\bar{\nu}$ 908; 960; 1737; 2935. The only other acid which shows a comparable displacement is pyruvic acid[6, 7] yielding $\Delta\bar{\nu}$ 1735 with a very weak component at $\Delta\bar{\nu}$ 1769. Pyruvic acid, like oxalic acid, has two carbonyl groups in juxtaposition. From this meager evidence it is impossible, however, to extrapolate with definiteness as to the expected characteristic frequency shift of the carbonyl groups in a saturated dicarboxylic acid.

Siva Rao has suggested that the frequency shift $\Delta\bar{\nu}$ 1430 is characteristic of the OH group—presumably present in oxalic acid—on the ground that other organic hydroxy compounds (containing CH_2 groups) have such a displacement. This precise designation does not seem to be tenable. In the first place the frequency is measured by him only to within ± 30 wave numbers. On the assumption that this is correct, it is to be noted that the frequency falls within the region of frequency shifts observed with all the saturated aliphatic hydrocarbons from ethane to decane. This has been ordinarily ascribed by Kohlrausch[8, 9] and Andrews[10] to the bending moment of the hydrogen in the CH_2 groups. With oxalic acid, however, this assignment is impossible because of the complete lack of CH_2 groups. Nevertheless, $\Delta\bar{\nu}$ 1430±30 cannot be used as evidence of the OH grouping when CH_2 groups are present. On the contrary, possibly the most characteristic frequency of $C\leftrightarrow O$ is in the region of $\Delta\bar{\nu}$ 1015 to 1050. This is present in methylene glycol and ethylene glycol. Venkateswaran and Bhagavantam[11] attribute, in addition to the approximate $\Delta\bar{\nu}$ 1025, also $\Delta\bar{\nu}$ 1225 and 1365, to the $C-OH$ grouping. This is supported by the work of Bolla,[12, 13] who records 56 lines

[5] Ghosh and Kar, J. Phys. Chem. **35**, 1735 (1931).
[6] Dadieu and Kohlrausch, Monatsh. **55**, 379 (1930).
[7] Dadieu and Kohlrausch, Sitzber. Akad. Wiss. Wien, (IIa) **139**, 77 (1930).

[8] Kohlrausch, *Der Smekal Raman Effekt* (Julius Springer, Berlin, 1931), p. 304.
[9] Kohlrausch, Naturwiss. **22**, 161 (1934).
[10] Andrews, Phys. Rev. **34**, 1626 (1929).
[11] Venkateswaran and Bhagavantam, Ind. J. Phys. **5**, 129 (1930).
[12] Bolla, Zeits. f. Physik **89**, 513 (1934).
[13] Bolla, Zeits. f. Physik **90**, 607 (1934).

for each of the simpler alcohols. Those between $\Delta\bar{\nu}$ 1050 and 1090 are considered fundamental frequencies among fourteen others. The frequency which may be used with the most certainty to identify an OH group is the one attributed to the O↔H oscillation and which occurs near $\Delta\bar{\nu}$ 3400. With the anhydrous oxalic acid this shift is not clearly apparent. In aqueous solution, alcoholic solution and with the hydrated acid any O↔H vibration originating in the organic acid is lost in the O↔H vibration of the solvent or of the water of crystallization. The net result of these observations is that there is no definite evidence in favor of a C—OH linkage although its presence is not precluded.*

These considerations together with the experimental data lead to the conclusion that the tautomeric form of oxalic acid as suggested by Tschitschibabin is not present. There are no lines which could be ascribed to C=C or to a true ring structure. The poly-hydroxy form of the hydrated acid is not clearly demonstrated although the lack of C=O frequencies in the hydrate would indicate at least a profound modification in the normal structure. In aqueous solution one carboxyl group behaves normally but the interaction between two closely situated carbonyl groups results in one carbonyl group having more nearly the characteristics of an aldehyde ketone or ester carbonyl than that of the usual acid. In alcoholic solution both carbonyl groups behave abnormally. In any case, in solution the influence of one carboxyl group on the other is to increase the force constant between the carbon and oxygen atoms of at least one carbonyl group. This is similar to the action of any other negative substituent group and is direct evidence for the classical explanation of the strength of this acid.

There are two other hypotheses which may be considered in connection with the structure of oxalic acid. Pauling[14] has suggested that organic acids owe their acidity to carboxyl groups which may exist in resonance in two forms, namely,

$$R : C : O : H \qquad R : C : : \overset{..}{O} : H$$
$$\;\;\; :: \quad \cdot\cdot \qquad\qquad\quad \cdot\cdot$$
$$\;\;\; O : \qquad\qquad\qquad\quad : \overset{}{O} :$$
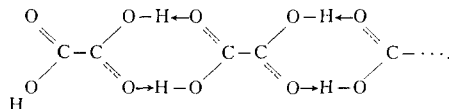$$\;\;\; \cdot\cdot \qquad\qquad\qquad\qquad\; \cdot\cdot$$
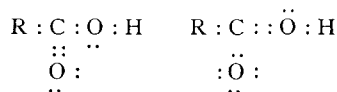
so that the hydrogen atom is attached to an oxygen atom which forms a double bond with the carbon atom half the time. There is no obvious method of determining the validity of this hypothesis or what would be the effect of the adjacent carboxyl groups in oxalic acid.

There remains the possibility of chelation or "hydrogen bond" to explain some of this behavior. It has been pointed out by Hilbert, Wulf, Hendricks and Liddel[15] that chelation may exist between some organic compounds of the type postulated by Sidgwick.[16] In this type of compound a stable ring may be formed between a donor and a possible acceptor. The case of complex ions containing anions of dibasic acids possibly belongs to a rare but existing species. For compounds consisting of larger rings it is assumed that the enolic form of aceto-acetic ester may exist, thus,

$$CH_3 - C - O$$
$$\qquad\quad \| \qquad\quad \diagdown$$
$$\qquad\quad CH \qquad H.$$
$$\qquad\quad | \qquad\quad \diagup$$
$$C_2H_5 - O - C = O$$
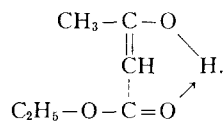
It has been shown[15] that in some more complicated aromatic organic compounds possessing both an O—H and a C=O group in the ortho position the O—H group is not present as such but rather the hydrogen of the OH is chelated with the C=O. Other results, however, indicate that the C=O in normally chelated compounds such as methyl salicylate is unaffected.[17] From the chelate point of view crystalline oxalic acid possibly would have the partial structure

$$O\diagdown \qquad\quad O-H\leftarrow O \qquad\quad O-H\leftarrow O$$
$$\quad\; C-C\diagup \qquad\quad \diagdown C-C\diagup \qquad\quad \diagdown C-\cdots.$$
$$O\diagup \qquad\quad O\rightarrow H-O\diagdown \qquad\quad O\rightarrow H-O\diagdown$$
$$H$$

If these chains were relatively short and incomplete this might account for the presence of

* An exciting frequency of 4359A does not yield a frequency shift corresponding to $\Delta\bar{\nu}$ 3500 as readily as an exciting frequency in the ultraviolet. Strong absorption in the ultraviolet prevents the use of high frequency radiation as a source of excitation.

[14] Pauling, Proc. Nat. Acad. Sci. **18**, 293 (1932).

[15] Hilbert, Wulf, Hendricks and Liddel, Nature **135**, 148 (1935).

[16] Sidgwick, *The Electronic Theory of Valency* (Oxford University Press, 1929), p. 240.

[17] Unpublished results.

the weak C=O frequency and the absence of a normally strong O↔H vibration. The hydrated oxalic acid would have larger aggregates interspersed with normal water of crystallization. It is not inconsistent to suppose that on solution these loose chelate structures would break down into individual molecules showing some residual abnormality

It can be generally stated that while the evidence is not conclusive that the crystal hydrate contains no C=O oscillations, such shifts if present are certainly far weaker than to be expected in comparison with the anhydrous form or the aqueous solution.

Whatever may be the explanation of the be-

havior of anhydrous oxalic acid, aqueous oxalic acid solutions or solutions in methyl alcohol, it is quite evident that the two carboxyl groups do not behave the same except in organic solvents. The abnormality of oxalic acid is amply confirmed by spectroscopic measurements.

Finally, it may be mentioned that experiments with sodium salts of oxalic acid lead to very weak or no shifts characteristic of the C=O. This is in accordance with the observation of Krishnamurti[3] with ammonium oxalate and of Ghosh and Kar[5] with sodium formate, sodium acetate and sodium malonate. This work is being continued.

The Reaction Rate of Acetic Anhydride and Water

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The infrared absorption of acetic acid and acetic anhydride has been measured from 1μ to 6.5μ. A number of bands were observed below 5μ which were similar for the two substances, and were attributed to CH bonds. An intense band was found in acetic anhydride at 5.45μ and in acetic acid at 5.75μ. By measuring the intensity of these bands at different times, the reaction velocities of equivalent amounts of anhydride and water were determined. This method offers a new and independent means of

determining reaction velocities and related constants. The reaction was approximately unimolecular for any concentration. The reaction constant decreased as the time increased. A different value of the constant was obtained when different concentrations were used. The reaction constant was also determined for three different temperatures. The values of the reaction constant and other constants are tabulated. The error is estimated to be 10 percent.

THE infrared absorption spectra of acetic acid have been measured by Coblentz[1] and its Raman spectra determined by Gansean and Venkateswaran.[2] In the region from 1μ to 5μ the bands are similar to those found in other CH compounds. Acetic anhydride also had the characteristic spectra of CH compounds to 5μ. In order to find bands for the anhydride, which were due to the difference in structure from the acid, it was necessary to work in the 6μ region. Good resolution was obtained by using a fluorite prism,

the effective slit width being 0.02μ at 6μ. The method of measurement was similar to that used by Plyler and Barr[3] in a previous paper. In Fig. 1 is shown a comparison of the spectra of acetic acid, acetic anhydride and a mixture of the two substances. The acetic acid had absorption bands at 1.1, 2.25, 2.5, 2.8, 3.35, 3.9 and 5.75μ. These bands are similar to the bands found by Coblentz except those in the region below 3.4μ, where thicker cells than those used by him are necessary to bring out the bands. In the Raman spectra other bands were found at longer wave-lengths than the upper limit of this

[1] Coblentz, *Investigations of Infrared Spectra* (Carnegie Institution of Washington, 1905).
[2] Gansean and Venkateswaran, Ind. J. Phys. **4**, 195 (1929).

[3] Plyler and Barr, J. Chem. Phys. **2**, 306 (1934).