Raman Spectra of Amino Acids and Related Compounds IV. Ionization of Di and Tricarboxylic Acids

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which depends largely, if not wholly, on the properties of the molecules as electric dipoles. This electric force depends on the charge and on the separation of the dipoles, and would be expected to be independent of the mass. Since the molecular volume of deuterium oxide is slightly greater than that of water the slight decrease in surface tension which is found experimentally may be ascribed to the greater separation of the dipoles. The facts may therefore be accounted for without ascribing any direct influence of the mass on the surface tension.

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Raman Spectra of Amino Acids and Related Compounds

IV. Ionization of Di- and Tricarboxylic Acids

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A systematic study of Raman spectra has been made for a large number of carboxylic acids and their salts dissolved in water. In particular, malonic acid and its two sodium salts, and malonic-d_2 acid-d_2 and its disodium salt, have been studied in detail. The substitution of deuterium in this molecule permits the vibrations arising primarily from the $-CH_2$ group to be distinguished from those arising primarily from the carboxyl groups. The Raman spectrum of deuterium oxide has been redetermined in connection with these studies. The following general conclusions have been reached: (1) The powerful "carbonyl" frequency near 1700 cm^{-1} is always found when an un-ionized carboxyl group is present, and always vanishes on ionization of the carboxyl. (2) One or more intense Raman lines near 1400 cm^{-1} can always be found in a substance containing an ionized carboxyl group. Such lines are definitely polarized, and presumably correspond to a symmetrical valence oscillation of the COO^- group. Like the "C=O" frequency near 1700, these lines are almost unaffected by deuterium substitution. Deformation frequencies arising from $-CH_2$ or $-CH_3$ groups commonly lie in the same range; the marked effect of deuterium substitution, however, clearly differentiates these from the vibrations of the $-COO^-$ group. (3) Other Raman lines, near 1330 and 1580 cm^{-1}, are frequently but not invariably found in substances containing ionized carboxyl groups. (4) Most of the substances studied show strong Raman lines between 700 and 950 cm^{-1}, which increase in frequency by 30 to 50 cm^{-1} on ionization. These lines are strongly polarized, and in malonic acid are noticeably depressed in frequency by deuterium substitution. (5) Certain frequencies below 600 cm^{-1} are virtually unaffected either by ionization or by deuterium substitution. These presumably represent bending or twisting vibrations of the heavy molecular framework. The "C=C" frequency near 1650 in crotonic and maleic acids is unchanged by the ionization of a neighboring carboxyl group. The Raman spectra of *d*-tartaric acid and of mesotartaric acid, although very similar, show definite differences which are well beyond the experimental error. The structure of the ionized carboxyl group is undoubtedly closely related to that of the nitro group. Both show intense polarized Raman lines near 1400, probably corresponding to the same type of oscillation in both cases; and the bond strength in the two groups is probably nearly the same.

INTRODUCTION

A SYSTEMATIC study of the effect of ionization of the carboxyl group on the Raman spectrum of fatty acids and amino acids has already been begun.[1] This study has now been extended to a considerable number of acids containing two or three carboxyl groups. Malonic acid has been studied with particular attention, the effect of ionization and also of deuterium substitution having been examined in detail. The large number of carboxylic acids which has now been studied permits certain definite generalizations concerning the effect of ionization, and furnishes a basis for an analysis of the structure of the carboxyl group.

EXPERIMENTAL

The methods used were essentially the same as those described in the previous studies of this series.[2,3] It may be noted, however, that, in studying the salts of the acids, it is important to maintain the solution slightly acid to neutrality

[1] J. T. Edsall, J. Chem. Phys. **4**, 1 (1936).

[2] J. T. Edsall, J. Phys. Chem. **41**, 133 (1937).
[3] J. T. Edsall, J. Chem. Phys. **5**, 225 (1937).

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or, in any case, not more alkaline than *p*H 8. In solutions more alkaline, the Norit used as a clarifying agent in filtration gives off a fluorescent impurity which renders it almost impossible to obtain clear Raman spectra. The acidity of the solutions, therefore, was always tested by means of a suitable indicator before filtration was carried out.

Malonic-d_2 acid-d_2 was prepared by treating malonic acid (m.p. 134–135°) with 99.5 percent D_2O, evaporating off the heavy water after a few hours' standing, repeating the process, again dissolving the acid in D_2O and filtering directly into the Raman tube. Halford and Anderson[4] have shown that all the hydrogens in malonic acid are readily replaced by deuterium under these circumstances, and the Raman spectra entirely confirm their conclusion, since the C–H frequencies above 2900 cm^{-1} had quite disappeared from the spectrum after this treatment.

Disodium malonate-d_2 was similarly prepared from disodium malonate (a sample previously

[4] J. O. Halford and L. C. Anderson, J. Am. Chem. Soc. **58**, 736 (1936).

TABLE II. *Characteristic frequencies of the CH_2 and CD_2 groups in the malonic acids.*

	$-CH_2$	$-CD_2$	RATIO
ν_1	2956(6)	2159(5)	1.368
ν_2	3003(3)	2258(3)	1.332
δ	1417(4*b*)	1050(4)	1.349

TABLE I. *Raman spectra of malonic acid, malonic-d_2 acid-d_2, and the ions derived from them.*

1	2	3	4	5	
H, COOH, C, H, COOH	H, COOH, C, H, COO^-	H, COO^-, C, H, COO^-	D, COOD, C, D, COOD	D, COO^-, C, D, COO^-	
427(4*b*)	434(5)	427(3*b*)	412(3)	414(1*b*)	*A*
590(2*b*)	586(2*b*)	590(3*b*)	538($\frac{1}{2}b$)	573±35(1*b*)	*B*
660(2*b*)	664(3*b*)	698(1*b*)	607(1)	654($\frac{1}{2}$)	*C*
773(4*b*)	802(2*b*)	828(3*b*)	733(3) 790($\frac{1}{2}$)	810(2)	*D*
919(8*b*)	923(8*vb*)	935(6) 956(3)	845(3)	873(3) 910(2)	*E*
1031(0*b*)			940(0)	940(1)	*F*
1181(2*b*)	1193(1*vb*)	1181(3)	1106($\frac{1}{2}$)	1106(1)	*G*
1308(0)	1278($\frac{1}{2}$)	1260(2*b*)	1360(1)		*H*
	1372(5)	1361(6)		1367(4)	*I*
1417(4*b*)	1408(5*b*)	1413(6)	1050(4)	1054(4)	*J*
		1439(6)		1427(7)	*K*
		1587(1*vb*)		1573(2*b*)	*L*
	1639(0*vb*)[H_2O?]		1209($\frac{1}{2}b$)[D_2O?]	1228($\frac{1}{2}vb$)[D_2O?]	*M*
1738(8*b*)	1730(2*b*)		1719(7*b*)		*N*
2956(6)	2943(6)	2947(6*b*)	2159(5)	2153(5)	*O*
3003(3)	2987(1)	2984(2*b*)	2258(3)	2238(3)	*P*

The frequencies in the row marked *M* probably arise from the solvent. Observations on deuterium oxide gave the spectrum: 1209±20 (1/2)(*K*, *e*); 1383 (0)(*e*?); 2370 (8)(*K*, *e*); 2517 (12)(*K*, *e*); 2679 (4)(*K*?). The doubtful line at 1383 (due possibly to HDO?) has not been reported by others. Compare R. Ananthakrishnan, Proc. Indian Acad. Sci. **A2**, 291 (1935); **3**, 201 (1936) and E. Bauer and M. Magat, Comptes rendus **201**, 667 (1935). The very faint Raman bands near 350 and 500 cm^{-1}, reported by the latter authors, are clearly too weak and broad to disturb the observation of the malonic acid spectrum.

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TABLE III. *Raman frequencies shifted by ionization in the range 700–1000 cm⁻¹.*

SUBSTANCE	UN-IONIZED ACID	COMPLETELY IONIZED ACID
Crotonic Acid	690(2*b*)	730(2*b*)
Glycolic Acid	898(6)	932(6)
Oxalic Acid	852(6)	902(6)
Malonic Acid	773(4) 919(8*b*)	828(3*b*) 935(6); 956(3)
Malonic-d_2 Acid-d_2	733(3) 845(3)	810(2*b*) 873(3*b*); 910(2*b*)
Succinic Acid	837(6) 935(2)	873(6) 957(6)
d-Tartaric Acid	754(6)	805(4)
l-Aspartic Acid	822(4)	858(4)
d-Glutamic Acid	917(2)	937(4*b*)
Maleic Acid	869(6)	903(4)
Tricarballylic Acid	930(4)	948(5*b*)
Citric Acid	800(5) 939(6)	845(4) 956(5)

The data for glycolic and succinic acids are taken from I. Pèyches, Bull. Soc. Chim. [5] **2**, 2195 (1935).

employed for determination of Raman spectrum) and D_2O.

DISCUSSION

The malonic acids

The study of malonic acid, malonic-d_2 acid-d_2, and the ions derived from them, reveals particularly clearly the types of Raman frequencies encountered in carboxylic acids and their salts. The data are set forth in Table I, frequencies which appear to correspond being placed in the same row. (In a few cases, as in the rows marked *F* and *H*, it is dubious whether the frequencies grouped together actually correspond.) Several criteria have been employed in establishing such correspondence: relative intensity of the lines, relative polarization (in the case of malonic acid

TABLE IV. *Effect of ionization on frequencies in the range 1300 to 1750 cm⁻¹.*

		(1)	(2)	(3)	(4)	(5)
1. Oxalic Acid	$R\cdot(COOH)_2^-$	1310(0)	1460($\frac{1}{2}$)		1645(2)	1750(3)
	$R\cdot(COO)_2^{--}$	1311(4)	*1457(4) *1489(7)		*1580(1*b*) 1647(2*vb*)	
2. Malonic Acid	$R\cdot(COOH)_2$		1417(4*b*)			1738(8*vb*)
	$R\cdot COOH\cdot(COO)^-$	*1372(5)	1408(5*b*)			1730(2*b*)
	$R\cdot(COO)_2^{--}$	*1361(6)	1413(6)	*1439(6)	*1587(1*vb*)	
3. Malonic-d_2 Acid-d_2	$R\cdot(COOD)_2$	1360(1)				1719(7*b*)
	$R\cdot(COO)_2^{--}$	*1367(4*b*)		*1427(7)	*1573(2*b*)	
4. Succinic Acid	$R\cdot(COOH)_2$	1339(0)	1409(3)		1637(3*b*)	1702(3)
	$R\cdot(COO)_2^{--}$	*1330(3)	*1410(6)		*1555(3*b*) 1640(3*b*)	
5. Crotonic Acid	$R\cdot COOH$	1302(6)	1383(3)	1451(4)	1658(5)	1700(2)
	$R\cdot COO^-$	1297(5)	*1396(4*vb*)	1450(4)	1661(7*b*)	
6. Maleic Acid	$R\cdot(COOH)_2$	1325(1*b*)	1390(1*vb*)		1654(6*b*)	1725(6*vb*)
	$R\cdot(COO)_2^{--}$	1306(2)	*1400(6) *1434(2)		*1570(1*vb*) 1647(6)	
7. *d*-Tartaric Acid	$R\cdot(COOH)_2$		1413(1)	1442(2)		1740(5*b*)
	$R\cdot(COO)_2^{---}$	*1310(2*b*) *1370(5*b*)	*1418(6*b*)		*1617(1*vb*)	
8. *l*-Aspartic Acid	$R\cdot(COOH)_2$	1376($\frac{1}{2}$)	1418(1)		1634($\frac{1}{2}$)	1743(4*vb*)
	$R\cdot(COO)_2^{--}$	*1330(1) *1355(2)	*1411(5*b*)		1620±50(1*vb*)	
9. *d*-Glutamic Acid	$R\cdot(COOH)_2$	1347($\frac{1}{2}$)	1433(3)		1649($\frac{1}{2}$*vb*)	1736(4*vb*)
	$R\cdot(COO)_2^{--}$	*1345(2*b*)	*1410(4*b*)		*1625(2*vb*)	

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and disodium malonate), similarity in the effects of ionization for the hydrogen and deuterium compounds. Furthermore, the studies of Angus, Leckie and Wilson[5] and of Engler[6] on CH_3COOH, CH_3COOD and CD_3COOD furnish a very valuable set of comparative data for testing the reasonableness of the assignments made. Thus the lines 1359 and 1436 in CH_3COOH go over into 1025 and 1093, respectively, in CD_3COOD. Likewise, the line at 1417 in $CH_2(COOH)_2$ goes over into 1050 in $CD_2(COOD)_2$.

Apart from the frequency marked *M*, which probably arises from the solvent, only three Raman lines are shifted as much as ten percent by deuterium substitution. These three (*J*, *O* and *P* in Table I) are shifted by more than thirty percent. Hence they must arise primarily from the $-CH_2$ or $-CD_2$ group. Such a group, considered as a separate entity (a "pseudo-triatomic molecule") should give rise to three fundamental frequencies: two valence oscillations (ν_1 and ν_2) and one symmetrical deformation (δ) (Table II).[7] Although polarization measurements have not been carried out on ν_1 and ν_2, it is

[5] W. R. Angus, A. H. Leckie and C. L. Wilson, Proc. Roy. Soc. **A, 155**, 183 (1936).
[6] Engler, Zeits. f. physik. Chemie **B32**, 471 (1936).

[7] Other modes of vibration in these molecules undoubtedly exist, in which the hydrogens of the CH_2 or CD_2 groups play an important part (for instance, a bending frequency involving a motion of the hydrogens approximately parallel to the plane of the three carbon atoms). Such frequencies, however, if they do give rise to any of the observed Raman lines, are much less affected by deuterium substitution than the three listed in Table II. Raman lines arising from the carboxylic O—H and O—D groups might be expected to appear, but have not been found. Quite probably they coincide with the intense bands arising from the solvent H_2O or D_2O.

TABLE IV.—*Continued.*

		(1)	(2)	(3)	(4)	(5)
10. Tricarballylic Acid	$R\cdot(COOH)_3$		1420(5*b*)			1724(6*b*)
	$R\cdot(COO)_3^{---}$	*1333(3*b*)	*1419(8*b*)		*1571(1*b*)	
11. Citric Acid	$R\cdot(COOH)_3$		1403(3)	1438(2)		1731(6*b*)
	$R\cdot(COO)_3^{---}$	*1302(0)	*1415(8*b*)		*1580($\frac{1}{2}$*b*)	
12. Lactic Acid	$R\cdot COOH$	1381(1)	1446(3)			1710(3)
	$R\cdot COO^-$	1380(1)	*1411(5)		*1605—30(3)	
13. Glycolic Acid	$R\cdot COOH$	1372(1*b*)	1449(5)			1733(5*b*)
	$R\cdot COO^-$	1355(2*b*)	*1434(5*b*)		*1596(3*b*) 1632(3*b*)	
14. Sarcosine	$R\cdot COOH$	1284(1)	1429(2)	1464(3)	1622($\frac{1}{2}$*vb*)	1732(1*b*)
	$R\cdot COO^-$	*1320(3*b*)	*1408(5*b*)	1468(4)	1633(2*vb*)	
15. Betaine	$R\cdot COOH$	1337($\frac{1}{2}$)	1419($\frac{1}{2}$)	1453(4)		1751(1*b*)
	$R\cdot COO^-$	*1335(2)	*1403(2)	1453(2)	1638(0*b*)	
16. Di-Methyl Phenyl Betaine	$R\cdot COOH$	1327(0*b*)		1468(3*b*)		1750(0*vb*)
	$R\cdot COO^-$	*1330(3*b*)	*1404(3*b*)	1465(3*b*)		
17. β-Alanine	$R\cdot COOH$	1328(2*b*)	1413(3*b*)	1472(1*b*)	1630(1*vb*)	1730(4*b*)
	$R\cdot COO^-$	1338(1)	*1410(5*b*)	1471($\frac{1}{2}$)	1630(1*vb*)	
18. β-Amino-*n*-Butyric Acid	$R\cdot COOH$	1380(2*b*)	1419(2)	1461(4)	1637(2*vb*)	1726(4*vb*)
	$R\cdot COO^-$	1366($\frac{1}{2}$)	*1408(7*b*)	1457(3)	1641(1*vb*)	

The data for succinic, glycolic and lactic acids and their salts are taken from I. Peychès (Bull. Soc. Chim. (5) **2**, 2195 (1935)), who has also studied *d*-tartaric acid and its salts in detail; the data here presented on tartaric acid and the tartrates are in close accord with those of Peychès. The complete Raman spectra of the substances numbered 14–18, inclusive, will be published later.
This table may be regarded as a continuation of Table I in reference 1, except that the grouping of frequencies into columns is somewhat different.
Lines marked * appear to be closely associated with the ionized carboxyl group. Lines near 1630, listed in column 4, may arise largely from the water used as solvent.

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probable that the more intense line (ν_1) represents a symmetric, and the weaker (ν_2) an antisymmetric, valence vibration. Angus, Leckie and Wilson[5] have suggested that the ratio of corresponding frequencies for the $-CH_3$ and $-CD_3$ groups should roughly be equal to the reciprocal of the square root of the ratio of the reduced masses of the C−H and C−D atomic pairs, or 1.36. Although this conception is undoubtedly over-simplified, it does give a fair approximation to the facts for the $-CH_2$ and $-CD_2$ groups (see Table II).[8]

We may now consider the other Raman lines in Table I. The lowest frequency (*A*) is unaffected by ionization and almost unaffected by deuterium substitution; its depolarization factor is high. It probably corresponds to an asymmetrical bending or twisting of the heavy framework of the molecule. The line *B* is strongly polarized, and may arise from a symmetrical deformation, which probably largely involves the carboxyl groups. The lines *D* and *E* are also strongly polarized; they are markedly increased in frequency by ionization, and depressed by deuterium substitution. In this they are very similar to the strong line at 895 in acetic acid, which is highly polarized, which increases in frequency to 928 on ionization[1] and falls to 800 in CD_3COOD.[5, 6] A great number of other carboxylic acids (see reference 1, and Table III of this paper) show Raman lines of apparently similar nature. Their character is further discussed below, in connection with Table III.

The lines *I*, *K*, *L* and *N* evidently arise from the carboxyl group. Whether they appear or not depends on the state of ionization of this group; deuterium substitution affects them very little. Thus the very intense and polarized line at 1738 in $CH_2(COOH)_2$ (the "C=O frequency") is decreased only to 1719 in $CD_2(COOD)_2$.[9] On the other hand, ionization of one carboxyl group greatly weakens its intensity (although scarcely diminishing the frequency) and ionization of both carboxyl groups abolishes it altogether. This behavior is typical of all carboxylic acids hitherto investigated (see Table IV).

The lines *I*, *K* and *L*, on the other hand, arise primarily from the *ionized* carboxyl group. The line near 1370 appears at the first step in ionization; those near 1430 and 1580 at the second. The 1430 line is strongly polarized; the other two less markedly so.

The lines near 1400 happen to coincide very nearly with the deformation frequencies of the $-CH_2$ and $-CH_3$ groups. The effect of deuterium substitution, however, clearly differentiates the two types of vibration. In disodium malonate, the three lines 1361, 1413, and 1439 are almost equally intense. In disodium malonate-d_2, 1413 is completely gone, its place being taken by 1054; while the other two lines are virtually unchanged, and must, therefore, be associated primarily with the ionized carboxyl group.

Raman Lines of Other Carboxylic Acids and Their Salts

Most of the characteristic features of the spectra of the malonic acids and their salts are also found in the other acids studied. Most of the molecules studied possess one or more Raman frequencies in the region below 600 cm^{-1}, which remain essentially unaffected by ionization, like the lines at 430 and 590 in malonic acid (see Table V). These presumably correspond to deformations of the molecular framework.

The "sensitive frequency" between 700 and 1000 cm^{-1}

In this region, practically all the acids studied show one or two powerful Raman lines which are increased in frequency by 20 to 50 cm^{-1} on ionization of the carboxyl group (Table III). Exactly similar lines have already been reported in several fatty acids and amino acids (reference 1, Table II). Where polarization measurements have been made (as in acetic and malonic acids, and dipotassium oxalate) these lines have all been found to be very strongly polarized. They fall in the same frequency range as the totally symmetric vibrations of the methylated methanes[10] and ammonium ions;[3] and in all cases this type of frequency is depressed by the replacement of hydrogen by a methyl group on

[8] Another very weak frequency near 2075 was found in malonic-d_2 acid-d_2 and its disodium salt (see Table V).

[9] Similarly the "C=O frequency" which lies near 1670 in CH_3COOH, decreases only to 1657 in CD_3COOD (reference 5).

[10] K. W. F. Kohlrausch and F. Koppl, Zeits. f. physik. Chemie **B26**, 209 (1934).

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the central carbon atom.[1] Probably then this type of vibration in the carboxylic acids is similar to that found in the other compounds mentioned, being of course modified in detail by the presence of the carboxyl group. The increase in the frequency on ionization, and the decrease on deuterium substitution, suggest that the change of mass involved in both cases is primarily responsible for the shift. Thus for acetic acid[1, 5] we have the series:

CH_3COO^-	CH_3COOH	CH_3COOD	CD_3COOD
928 cm^{-1}	898	850	800

In this case, certainly, increase in mass of the vibrating groups is directly correlated with the decrease in frequency (for the malonic acids, see rows *D* and *E* in Table I).

d-Tartaric acid and mesotartaric acid

These isomers (Table V no. 13 and 15) have very similar Raman spectra, as might be expected, but the differences between them are well beyond the magnitude of the experimental error. Particularly is this true for the frequencies in the region 700–1100 cm^{-1}, where the mutual orientation of the $-OH$ and $-COOH$ groups evidently induces significant differences. A further study of some optically active and meso isomers will be undertaken later.

Raman lines between 1300 and 1750 cm^{-1}

We may now consider the frequencies in this range (arising probably for the most part from the C–H linkages and the carboxylic group). The data available are given in Table IV, which is essentially a continuation of data previously reported (see reference 1, Table I).

The "carbonyl" frequency, between 1700 and 1750 cm^{-1}, (Table IV, column 5) is found invariably in un-ionized carboxylic acids, and invariably vanishes on complete ionization of the carboxyl group. No exception to this rule has been found among the twenty-six carboxylic acids tabulated in this and the previous investigation.[1] For a saturated fatty acid, dissolved in water,[1] this frequency is very near 1720 cm^{-1}. Crotonic acid shows a lower value of 1700; this depressing effect of an adjoining double bond on the carbonyl frequency is well known for other compounds.[11] The C=O frequency in lactic acid is also rather low; in all the other compounds reported, however, it is higher than in the fatty acids. The influence of an adjoining carboxyl group, like that of a charged $-NH_3^+$ group, is thus to increase the C=O frequency.

The presence of one or more strong frequencies near 1400 cm^{-1} is apparently characteristic of the *ionized* carboxyl group. In the case of the malonic acids, already discussed, this fact stands forth with particular clarity. In many other carboxylic acids, these frequencies are less easily recognized, because of the presence of other lines in the same region of the spectrum, arising from different modes of vibration (commonly from $-CH_2$ and $-CH_3$ groups). The effect of ionization, however, is always shown by a great increase of intensity (and often a shift of frequency) of one or more lines near 1400 cm^{-1} (see Table IV, column 2, lines marked *, also some of the lines listed in columns 1 and 3). In the formate, malonate and oxalate ions, these lines are strongly polarized, and must correspond to a symmetrical oscillation. Probably the same is true for the other ionized carboxylic acids.

A typical example of the effect of ionization is shown in Fig. 1. Maleic acid in solution shows the two adjoining powerful frequencies, 1654 and 1725. There is only one faint line near 1400 (not clearly visible on the microphotometer tracing). In disodium maleate, the 1650 line is virtually unchanged in frequency or intensity, but the 1725 line has vanished, being replaced by a very powerful line at 1400, with a weaker satelite at 1434. In Fig. 2 (crotonic acid and sodium crotonate) the effect of ionization is also unmistakable, although less obvious. The free acid shows three strong lines at 1302, 1383 and 1451. On ionization of the carboxyl group, the first and third appear essentially unchanged, but the middle line—formerly the weakest of the three—becomes much broader and decidedly more

[11] A. Dadieu, A. Pongratz and K. W. F. Kohlrausch, Ber. Wiener Akad. Wiss IIa, **140**, 353, 647 (1931) studied the Raman spectrum of pure crotonic acid above its melting point and found one frequency in this range at 1654, while we obtain two frequencies (1658 and 1700) in the aqueous solution. In pure liquid fatty acids, the C=O frequency is about 50 cm^{-1} lower than in their aqueous solutions (reference 1). Similarly the C=O frequency in pure crotonic acid should lie near 1650, where it will coincide with the "C=C" frequency and not be observed. This probably explains the difference between Kohlrausch's observations and ours.

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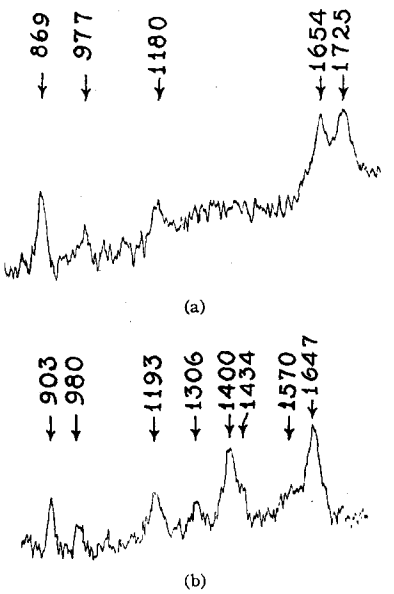

FIG. 1. Microphotometer tracings of Raman spectra of (a) maleic acid and (b) disodium maleate in water in the region 800–1750 cm^{-1}. These spectra were excited by Hg 4358A.

intense, its maximum also being displaced to 1396.

Such changes as this are typical of all carboxylic acids investigated. Acetic acid,[1] for instance, gives a fairly strong and depolarized line at 1430, which as the effect of deuterium substitution shows,[5] arises from the methyl group. Sodium acetate shows a rather similar line at 1413, which was formerly attributed to the same origin.[1] The latter line, however, is very much more intense than that in the free acid: probably it represents two different frequencies which accidentally coincide—one arising from the methyl and one from the carboxyl group. The latter component should be definitely polarized (in contradistinction to the 1430 line in acetic acid), and in sodium acetate-d_3 it should remain nearly unchanged while the component arising from the methyl group should be shifted to a value near 1100.[12]

A frequency near 1400 is thus apparently as characteristic of the ionized carboxyl group as the frequency near 1700 is of the same group when un-ionized. In the formate ion, this frequency has the unusually low value 1351; in the oxalate ion, it corresponds to the doublet, 1457 and 1489; in the malonate ion to the doublet, 1370 and 1439. In most of the other substances studied this frequency lies at 1405 ± 10.[13]

In many, but not all, of the substances studied, a strong line near 1340 makes its appearance on ionization of the carboxyl group (Table IV, column 1). Another line near 1580 (column 4) is also frequently found under the same circumstances. The fact that this line appears with almost identical frequency in disodium malonate and in disodium malonate-d_2 indicates its probable association with the ionized carboxyl group. Polarization measurements on dipotassium oxalate and disodium malonate solutions indicate that this line has a high depolarization factor (nearly, if not quite, 6/7).

The structure of the carboxyl group

It is well known that the "carbonyl" frequency near 1700 cm^{-1} is nearly independent of the length of the attached hydrocarbon chain;[13] likewise, both in acetic acid[5, 6] and in acetone,[6] it is almost unaffected by the substitution of deuterium for hydrogen in adjoining groups of the molecule. It appears probable, then, that this frequency really does correspond to a normal

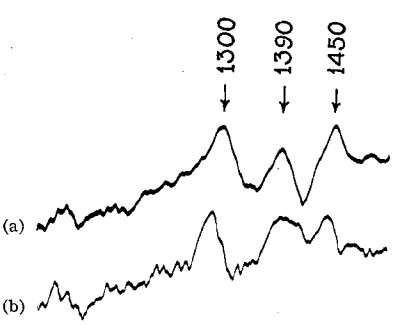

FIG. 2. Raman spectrum of (a) crotonic acid (b) sodium crotonate, in the region 1200–1450 cm^{-1}, excited by Hg 4047A. Note the increase in breadth and intensity of the line near 1390 in sodium crotonate as compared with crotonic acid.

[12] In addition to the data given in Table IV, J. C. Ghosh and B. C. Kar, J. Phys. Chem. **35**, 1735 (1931) have reported a very strong Raman line at 1402 in sodium benzoate, although benzoic acid shows no frequency in this range. This line also may therefore be attributed to the ionized carboxyl group.

[13] K. W. F. Kohlrausch, F. Köppl and A. Pongratz, Zeits. f. physik. Chemie **B21**, 242 (1933) and **22**, 359 (1933) have concluded that a frequency near 1410 is characteristic of the *un-ionized* carboxyl group in the fatty acids. This frequency is much weaker than the 1400 line arising from the ionized group; its polarization character is not yet known. Whether both frequencies arise from a fundamentally similar mode of vibration is a question that cannot yet be answered.

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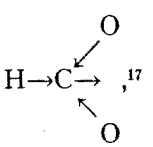
mode of vibration which is essentially an oscillation of the C=O bond; other parts of the molecule undergoing little displacement relative to one another. The recent x-ray studies of Robertson and Woodward[14] on oxalic acid dihydrate show a definite difference in the two C−O bonds of the un-ionized carboxyl group. The longer bond (1.30A) is presumably that to which the hydrogen is attached; the shorter one (1.24A) is undoubtedly the stronger, and corresponds to the C=O linkage of the classical formula. It is presumably the vibration of this latter linkage which gives rise to the "carbonyl" frequency.

The ionized carboxyl group, as might be expected because of resonance, shows a much nearer approach to complete equivalence of the two C−O bonds[15] which probably do not differ in length by more than 0.02A. Thus the COO^- group is closely similar to a bent symmetric triatomic molecule. In electronic structure, it is very intimately related to the nitro group. The latter is found to possess two very characteristic Raman frequencies: one near 1380, which is very intense and polarized, the other near 1560, less intense and depolarized.[16] The intense polarized frequency near 1400, which we have found to be characteristic of the ionized carboxyl group, is thus probably analogous to the 1380 frequency of the nitro group. In the formate ion, the simplest carboxylate ion[1, 2] this frequency (1351 cm^{-1}) presumably corresponds to the normal mode of vibration



which is essentially a symmetrical valence vibration of the COO^- group.[18] In the more complex substances studied, a similar mode of oscillation in the COO^- groups is almost certainly involved.

The asymmetrical valence vibration, which should also be characteristic of the ionized carboxyl group, is less easy to identify. By analogy with the nitro group, it might be identified with the moderately intense line near 1580 (Table IV) found in many, but not all of the ionized carboxylic acids. This line has a high depolarization ratio, as would be expected for such a frequency, but since it has not been found in all the substances studied, final interpretation of its nature must be postponed.

Such a triatomic group as the COO^- group should also give rise to a third, symmetrical deformation frequency, much lower than either of the other two. No such frequency has yet been definitely identified; it might correspond to the polarized line at 590 in the malonate ion, and to similar lines in other compounds studied. Here again interpretation must be postponed.

One very definite point emerges, however, from the comparison of the nitro and the ionized carboxyl group. The masses of the atoms in the two groups are very similar; the principal symmetrical frequencies near 1400 are nearly identical. Hence the force constants of the bonds in the two groups must be nearly alike. They approach values characteristic of double rather than single bonds.[19] On this point the evidence from Raman spectra is entirely consistent with the x-ray diffraction data, and with the relations which have been found to hold between bond character and interatomic distance[20] in these and other groups.

I am indebted to Mr. Joseph Shack for valuable aid in the measurement and tabulation of spectra and to Dr. James H. Hibben for the microphotometer tracings reproduced in Figs. 1 and 2.

[14] J. M. Robertson and I. Woodward, J. Chem. Soc. 1817 (1936).

[15] S. B. Hendricks and M. E. Jefferson, J. Chem. Phys. **4**, 102 (1936).

[16] J. Cabannes and A. Rousset, Ann. de physique **19**, 269 (1933).

[17] See G. B. B. M. Sutherland and D. M. Dennison, Proc. Roy. Soc. **A148**, 250 (1935) for the normal modes of vibration of a molecule of this type (formaldehyde). The vibration shown above is ν_1 in their notation.

[18] This interpretation of the 1351 line in the formate ion has already been proposed by J. Gupta, Indian J. Phys. **10**, 313 (1936), who has found the line to be highly polarized ($\rho=0.16$). Gupta has also (Indian J. Phys. **10**, 199, 465 (1936)) attempted an interpretation of the spectrum of the oxalate ion, whose structure is closely related to that of ethylene. He attributes the intense doublet near 1470 in this ion to what is essentially a symmetrical valence oscillation of the two COO^- groups, in agreement with the view adopted here.

[19] A group of three similar masses held together by single bonds has a much lower characteristic frequency for this type of symmetric oscillation. Thus the value for propane is 867, and for dimethyl amine, 931 (3).

[20] L. Pauling, L. O. Brockway and J. Y. Beach, J. Am. Chem. Soc. **57**, 2705 (1935).

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TABLE V. *Complete list of observed Raman spectra.*

The notation used in recording these spectra is the same previously employed.[1-3]

A number of the substances here studied have been previously observed. Detailed studies have been made of *d*-tartaric acid and its salts (footnote, Table III), of oxalic acid[21,18] and of dipotassium oxalate[18] in water, of crotonic acid in the pure molten state,[11] and of citric acid[23] in water. Other more fragmentary data have been obtained for malonic acid, disodium malonate, disodium maleate and disodium fumarate.[23] The agreement of our own with the earlier data is in general very satisfactory.

1. *Oxalic acid*, HOOC·COOH. 8 percent solution in water. $\Delta\nu$: 464 (3*b*) (*k*, *e*); 852 (6) (*k*, *e*); 1395 (00*b*) (*k* ?); 1476 ($\frac{1}{2}$*b*) (*k*, *e*); 1652±35 (2*vb*) (*e*); 1753 (6*b*) (*e*).

2. *Dipotassium oxalate*, $K^+ {}^-OOC\cdot COO^- K^+$. 25 percent solution in water (prepared from Merck's reagent oxalic acid and two equivalents of concentrated c.p. KOH). $\Delta\nu$: 317 (2) (*e*); 456 (3) (*k*, *e*); 902 (6) (*k*, *e*); 1311 (4) (*k*, *e*); 1457 (4) (*k*, *e*); 1489 (7) (*k*, *e*); 1580 (1*b*) (*e*); 1647 ($\frac{1}{2}$*b*) (*e*).

3. *Malonic acid*, HOOC·CH_2·COOH (Eastman) 40 percent solution in water, +0.4 *N* HCl. $\Delta\nu$: 427 (4*b*) (*k*, ±*e*); 590 (2*b*) (*e*); 660 (2*b*) (*k*, *e*); 773 (4*b*) (*k*, *i*, *e*); 919 (8*b*) (*k*, *i*, *e*); 1031 (0*b*) (*e*); 1181 (2*b*) (*k*, *e*); 1308 (0) (*k*, *e*); 1417 (4*b*) (*k*, *i*, *e*); 1738 (8*vb*) (*e*); 2956 (6) (*k*, *e*); 3003 (3) (*k*).

4. *Monosodium malonate*, $Na^+ {}^-OOC\cdot CH_2\cdot COOH$. Aqueous solution containing 33 percent Eastman malonic acid, +1 equivalent c.p. NaOH. *p*H 4.2 to brom cresol green. $\Delta\nu$: 434 (5) (*k*, ±*e*); 586 (2*b*) (*e*); 664 (3*b*) (*k*, *e*); 802 (2*b*) (*k*, *e*); 923 (8*vb*) (*k*, *e*); 1193 (1*vb*) (*k*, *e*); 1278 ($\frac{1}{2}$) (*e*); 1372 (5) (*k*, *e*); 1408 (5*b*) (*k*, *e*); 1639 (0*vb*) (*e*) (water?); 1730 (2*b*) (*e*); 2943 (6) (*k*, *e*); 2987 (1) (*k*).

5. *Disodium malonate*, $Na^+\cdot {}^-OOC\cdot CH_2\cdot COO^-\cdot Na^+$. Aqueous solution containing 35 percent Eastman malonic acid, +2 equivalents NaOH. *p*H 7.2 (by brom thymol blue). $\Delta\nu$: 427 (3*b*) (*k*, *e*); 590 (3*b*) (*k*, *e*); 698 (1*b*) (*k*, *e*); 828 (3*b*) (*k*, *i*, *e*); 935 (6) (*k*, *i*, *e*); 956 (3) (*k*, *e*); 1181 (3) (*k*, *e*); 1260 (2*b*) (*k*, *e*); 1361 (6) (*k*, *e*); 1413 (6) (*k*, *e*); 1439 (6) (*k*, *e*); 1587 (1*vb*) (*k*, *e*); 2947 (6*b*) (*k*); 2984 (2*b*) (*k*).

6. *Malonic-d_2 acid-d_2*, DOOC·CD_2·COOD; 40 percent solution in D_2O. (For method of preparation see experimental section.) $\Delta\nu$: 412 (3) (*k*, *e*); 538 ($\frac{1}{2}$*b*) (*e*); 607 (1) (*k*, *e*); 733 (3) (*k*, *e*); 790 ($\frac{1}{2}$) (*k*, *e*); 845 (3) (*k*, *e*); 940±15 (0) (*k*, *e*); 1050 (4) (*k*, *e*); 1106 ($\frac{1}{2}$) (*k*); 1209 ($\frac{1}{2}$*b*) (*k*, *e*) (D_2O ?); 1360 (1) (*k*, *e*); 1719 (7*b*) (*e*); 2073 ($\frac{1}{2}$) (*k*); 2159 (5) (*k*, *e*); 2258 (3) (*k*, *e*).

7. *Disodium malonate-d_2*, $Na^+ {}^-OOC\cdot CD_2\cdot COO^{--} Na^+$; 35 percent solution in D_2O. (For method of preparation see experimental section.) $\Delta\nu$: 414 (1*b*) (*e*); 573±35 (1*vb*) (*e*) (double ?); 654 ($\frac{1}{2}$) (*e*); 810 (2) (*k*, *e*); 873 (3) (*k*, *e*); 910 (2) (*k*, *e*); 940 (1) (*k*, *e*); 1054 (4) (*k*, *e*); 1106 (1) (*k*, *e*); 1228 ($\frac{1}{2}$*vb*) (*k*, *e*) (D_2O ?); 1367 (4) (*k*, *e*); 1427 (7) (*k*, *i*, *e*); 1573 (2*b*) (*k*, *e*); 2076 (0) (*k*); 2153 (5) (*k*, *e*); 2238 (3) (*k*, *e*).

8. *Crotonic acid*, $CH_3CH{:}\,CH\cdot COOH$. (Eastman, m.p. 70–72°) 8 percent solution in water, +0.2 *N* HCl. $\Delta\nu$: 415 (1*b*) (*e*); 513 (1*b*) (*k*, *e*); 690 (2*b*) (*k*, *e*); 850 (1*b*) (*k*, *e*); 916 (1*b*) (*k*, *e*); 994 (1*b*) (*k*, *e*); 1053 (1) (*k*, *e*); 1110 (1) (*k*, *e*); 1223 ($\frac{1}{2}$*b*) (*k*, *e*); 1302 (6) (*k*, *e*); 1383 (3) (*k*, *e*); 1451 (4) (*k*, *e*); 1658 (5) (*e*); 1700 (2) (*e*); 2939 (6) (*k*, *e*); 3061 (2) (*k*, *e*).

9. *Sodium crotonate*, $CH_3CH : CH\cdot COO^- Na^+$; aqueous solution containing 22 percent Eastman crotonic acid, +0.96 equivalent NaOH. *p*H 6.2–6.3. $\Delta\nu$: 403 (3) (±*e*); 518 (1) (*k*, ±*e*); 730 (2*b*) (*k*, *e*); 865 (1) (*k*, *e*); 915 (1) (*k*, *e*); 1001 ($\frac{1}{2}$) (*k*, *e*); 1050 (1) (*k*, *e*); 1109 (1) (*k*, *e*); 1297 (5) (*k*, *e*); 1396 (4*vb*) (*k*, *e*); 1450 (4) (*k*, *e*); 1564 (0*vb*) (*e*?); 1661 (7*b*) (*e*); 2939 (4) (*k*, *e*); 3041 (2*b*) (*k*, *e*).

10. *Maleic acid* HOOC·CH : CHCOOH [*cis*]. 30 percent in water plus 0.5 *N* HCl. $\Delta\nu$ = 260 (2*b*) (*e*); 329 (1*b*) (*e*); 513 (1*vb*) (*k*, *e*); 624 (0*vb*) (double ?) (*k*, *e*); 750 (0) (*k*, *e*); 810 ($\frac{1}{2}$) (*k*, *e*); 869 (6) (*k*, *i*, *e*); 977 (2) (*k*, *e*); 1049 (1) (*k*, *e*); 1180 (5) (*k*, *e*); 1280 (0) (*k* ?); 1325 (1*b*) (*k*, *e*); 1390 (1*vb*) (*k*, *e*); 1654 (6*b*) (*e*); 1725 (6*vb*) (*e*); 2976 (4) (*k*, *e*).

11. *Disodium maleate* $Na^+ {}^-OOC\cdot CH : CHCOO^- Na^+$ [*cis*]. Aqueous solution, containing 36 percent maleic acid + two equivalents NaOH. $\Delta\nu$ = 258 (1*b*) (*e*); 339 (1*b*) (*e*); 482 (0) (*e*); 535 (0) (*e*); 903 (4) (*k*, *i*, *e*); 980 (2) (*k*, *e*); 1044 (0*b*) (*k*); 1193 (5) (*k*, *e*); 1306 (2) (*k*, *i*, *e*); 1400 (6) (*k*, *i*, *e*); 1434 (2) (*k*, *e*); 1570 (1*vb*) (*e* ?); 1647 (6) (*k*, *e*); 3038 (4) (*k*, *e*).

12. *Disodium fumarate* $Na^+ {}^-OOC\cdot CH : CH\cdot COO^- Na^+$ [*trans*]. Solution containing 18 percent fumaric acid [Eastman, twice recryst.] + two equivalents of NaOH. $\Delta\nu$: 235 (1) (*e*); 307 (1) (*e*); 775 (0) (*k*, *e*); 905 (2) (*k*, *e*); 981 (2) (*k*, *e*); 1279 (5) (*k*, *i*, *e*); 1403 (6) (*k*, *i*, *e*); 1573 (1*b*) (*k*, *e*); 1657 (7*b*) (*e*); 3053 (4) (*k*).

13. *d-Tartaric acid*, HOOC·CHOH·CHOH·COOH (Eastman), m.p. 167–168°. 50 percent solution in water, +0.4 *N* HCl. $\Delta\nu$ = 367 (3) (*e*); 517 (3) (*k*, *e*); 601 (2) (*e*); 690 ($\frac{1}{2}$) (*k*, *e*); 754 (6) (*k*, *i*, *e*); 838 (1) (*k*, *e*); 894 (5) (*k*, *e*); 993 (3) (*k*, *e*); 1091 (2) (*k*, *e*); 1140 (2) (*k*, *e*); 1279 (4*vb*) (doublet ?) (*k*, *i*, *e*); 1413 (1) (*k*); 1442 (2) (*k*, *e*); 1630 (1*vb*) (*e*) (water ?); 1740 (5*b*) (*e*); 2950 (6*vb*) (*k*, *i*, *e*).

14. *Disodium d-tartrate*, $Na^+ {}^-OOC\cdot CHOH\cdot CHOH\cdot COO^- Na^+$; made from Eastman *d*-tartaric acid and 2 equivalents of c.p. NaOH. Solution contains 30 percent of tartaric acid, in water (Approx. 2 molar). $\Delta\nu$ = 239 ($\frac{1}{2}$*b*) (*e*); 378 (1*b*) (*e*); 491 (0) (*e*); 532 (2*b*) (*k*, *e*); 618 (1*b*) (*k*, *e*); 719 ($\frac{1}{2}$*b*) (*k*, *e*); 805 (4) (*k*, *e*); 844 ($\frac{1}{2}$) (*k*); 893 (4) (*k*, *e*); 992 (6) (*k*, *i*, *e*); 1068 (3*b*) (*k*, *e*); 1121 (3*b*) (*k*, *e*); 1224 (2*vb*) (*k*, *e*); 1310 (2*b*) (*k*, *e*); 1370 (5*b*) (*k*, *e*); 1418 (6*vb*) (*k*, *i*, *e*); 1617 (1*vb*) (*e*); 2936 (8*vb*) (*k*).

15. *Meso-tartaric acid*, HOOC·CHOH·CHOH·COOH (Eastman). 45 percent in water, +0.25 *N* HCl. $\Delta\nu$ = 233 (1*b*) (*e*); 376 (2*b*) (*e*); 532 (2*b*) (*k*, *f*, *e*); 669 (1*b*) (*k*, *e*); 739 (3*b*) (*k*, *e*); 817 (1) (*k*, *e*); 870 (3) (*k*, *i*, *e*); 937 (1) (*k*, *e*); 1009 (1) (*k*, *e*); 1119 (2*vb*) (*k*, *e*); 1252 (3*vb*) (*k*, *e*); 1432 ($\frac{1}{2}$*vb*) (*k*, *e*); 1632 (1*vb*) (*e*) (water ?); 1732 (5*vb*) (*e*); 2936 (6*vb*) (*k*, *e*).

16. *l-Aspartic acid hydrochloride*, HOOC·CH_2CH(NH_3^+-Cl^-)·COOH. (Aqueous solution, containing 30 percent by weight of Hoffman-LaRoche aspartic acid, + equivalent HCl, and excess HCl to 1.2 *N*.) $\Delta\nu$ = 393 (1*b*) (*e*); 533 (1*b*) (*k*, *e*); 624 ($\frac{1}{2}$) (*e*); 822 (4) (*k*, *f*, *e*); 898 ($\frac{1}{2}$) (*e*); 928 (3*b*) (*k*, *e*); 1007 (1) (*k*, *e*); 1087 ($\frac{1}{2}$) (*k*, *e*); 1151 ($\frac{1}{2}$) (*k*, *e*); 1258 (1*vb*) (*k*, *e*); 1367 ($\frac{1}{2}$) (*k*, *e*); 1418 (1) (*k*, *e*); 1634 ($\frac{1}{2}$) (*e*) (water); 1743 (4*vb*) (*e*); 2961 (4*vb*) (*k*, *i*, *e*) (double ?).

17. *Sodium l-aspartate*, $Na^+[^-OOC\cdot CH_2\cdot CH(NH_3^+)\cdot COO^-]$. Made from Hoffman-LaRoche aspartic acid and c.p. NaOH. Solution contained 26 percent of *l*-aspartic acid. *p*H 6.3±0.2 by indicators. $\Delta\nu$ = 533 ($\frac{1}{2}$) (*e*); 608 ($\frac{1}{2}$) (*e*); 732 (0) (*e*?); 858 (4) (*k*, *f*, *e*); 939 (4) (*k*, *e*); 983 ($\frac{1}{2}$) (*k*); 1085 (1*vb*) (*k*, *e*); 1140 (1*vb*) (*k*, *e*); 1227 (1*vb*) (*k*, *e*); 1330 (1) (*k*, *e*); 1355 (2) (*k*, *e*); 1411 (5*b*) (*k*, *i*, *e*); 1620±50 (1*vb*) (*e*) (water ?); 2935 (5*b*) (*k*, *e*); 2993 (2) (*k*).

18. *d-Glutamic acid hydrochloride*, HOOC·CH_2·CH_2·CH($NH_3^+Cl^-$)·COOH. (From Eastman *d*-glutamic acid, once recrystallized from hot water.) Solution containing 21 percent glutamic acid +HCl. Excess HCl to 0.5 *N*. $\Delta\nu$ = 345 (0) (*e*); 504 (0) (*k*, *e*); 639 (0) (*e*); 751 ($\frac{1}{2}$) (*k*, *e*); 804 ($\frac{1}{2}$) (*k*, *e*); 857 (2) (*k*, *e*); 917 (2) (*k*, *e*); 1098 ($\frac{1}{2}$) (*k*, *e*); 1347 ($\frac{1}{2}$) (*k*, *e*); 1433 (3) (*k*, *e*); 1649 ($\frac{1}{2}$*vb*) (*e*) (water ?); 1736 (4*vb*) (*e*); 2953 (6*b*) (*k*, *e*).

19. *Sodium d-glutamate*, $[^-OOC\cdot CH_2\cdot CH_2\cdot CH(NH_3^+)\cdot COO^-]Na^+$. Solution containing 32 percent Eastman *d*-glutamic acid (once recryst.) + one equivalent c.p. NaOH. *p*H 7.2±0.2 by brom thymol blue and phenol red. $\Delta\nu$: 655 (0*vb*) (*k*); 777 (0*b*) (*k*); 877 ($\frac{1}{2}$*b*) (*k*, *e*); 937 (4*b*) (*k*, *e*); 999 ($\frac{1}{2}$) (*k*, *e*); 1080 ($\frac{1}{2}$) (*k*, *e*); 1145 ($\frac{1}{2}$) (*k*, *e*); 1283 ($\frac{1}{2}$) (*k*); 1345 (2*b*) (*k*, *e*); 1410 (4*b*) (*k*, *i*, *e*); 1625±50 (2*vb*) (*e*) (water ?); 2943 (5*vb*) (*k*, *e*) (double ?).

20. *Tricarballylic acid*, $C_3H_5(COOH)_3$. (Eastman, m.p. 161–163°) 30 percent solution in water, +0.4 *N* HCl. $\Delta\nu$: 342 (0) (*e*); 424 (2*b*) (*e*); 540 ($\frac{1}{2}$) (*e*); 612 ($\frac{1}{2}$*b*) (*k*, *e*); 837 (3)

[21] J. H. Hibben, J. Chem. Phys. **3**, 675 (1935).

[22] H. Nisi, Jap. J. Phys. **7**, 1 (1931).

[23] For a complete list of references up to the end of 1935, see J. H. Hibben, Chem. Rev. **18**, 1 (1936). References and complete tables of Raman spectra up to about the same period are given by J. Weiler in Landolt-Börnstein's *Tabellen*, fifth edition, 3rd Ergänzungsband, Part II.

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(*k, f, e*); 874 (2) (*k, e*); 930 (4) (*k, i, e*); 998 (0) (*k*); 1059 ($\frac{1}{2}$) (*k, e*); 1245 (1*vb*) (*k, e*); 1420 (5*b*) (*k, i, e*); 1724 (6*b*) (*e*); 2938 (6*b*) (*k, i, e*).

21. *Trisodium tricarballylate*, $Na_3^{+++}[C_3H_5(COO)_3]^{---}$. Solution containing 45 percent Eastman tricarballylic acid and three equivalents NaOH. *p*H 7.6±0.2 to phenol red. $\Delta\nu$: 327 ($\frac{1}{2}$) (*e*); 428 (2*b*) (*e*); 802 (1*b*) (*k, e*); 883 (4) (*k, e*); 948 (5*b*) (*k, e*); 1009 (2) (*k, e*); 1050 (1) (*k, e*); 1105 (1) (*k, e*); 1164 (1) (*k, e*); 1207 (1) (*k, e*); 1333 (3*b*) (*k, e*); 1419 (8*b*) (*k, i, e*); 1571 (1*b*) (*k, e*); 2934 (9*vb*) (*k, i, e*).

22. *Citric acid*, $C_3H_4(OH)(COOH)_3$, (Merck). 50 percent solution in water, with 0.4 *N* HCl. $\Delta\nu$: 253 (1*b*) (*e*); 396 (3*b*) (*e*); 525 (1*b*) (*e*); 605 (1*b*) (*e*); 723 (1) (*k, e*); 800 (5) (*k, i, f, e*); 903 (1) (*k, e*); 939 (6) (*k, e*); 1056 (3) (*k, e*); 1130 (1*b*) (*k, e*); 1200 (1) (*k, e*); 1403 (3) (*k, e*); 1438 (2) (*k, e*); 1731 (6*b*) (*e*); 2948 (6) (*k, i, e*); 3001 (1) (*k*).

23. *Trisodium citrate*, $Na_3^{+++}[C_3H_4(OH)(COO)_3]^{---}$. Solution containing 30 percent Merck's citric acid in water, with 3 equivalents NaOH. *p*H 7.4−7.6 by phenol red. $\Delta\nu$: 233 ($\frac{1}{2}$) (*e*); 317 (0) (*e*); 409 (1*b*) (*e*); 583 ($\frac{1}{2}$*vb*) (*e*); 845 (4) (*k, e*); 956 (5) (*k, i, f, e*); 1045 (1*b*) (*e*); 1100 (1*b*) (*k, e*); 1210 ($\frac{1}{2}$) (*e*); 1302 (0) (*e*); 1415 (8*b*) (*k, i, e*); 1580 ($\frac{1}{2}$*b*) (*e*); 2929 (5) (*k, e*); 2982 (1) (*k*).

Polarization Studies: Examination by the technique previously described[3] showed the following lines to be strongly polarized ($\rho \ll 6/7$) malonic acid: 590, 773, 919, 1738. Disodium malonate: 590, 828, 935, 1361(?), 1439. Dipotassium oxalate: 902, 1457, 1489.

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The Rotation and Vibration of Linear Triatomic Molecules

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The rotation and vibration of a linear molecule cannot be treated by the method of rotating axes if it contains more than three atoms. The definition of the axes for the triatomic case may be based on the fact that the three atoms always determine a plane. The relation of this definition to that for the nonlinear molecules is discussed, and the appropriate normal coordinates are introduced. The wave equation of the problem is derived and its approximate solution is discussed. The fact that the Eulerian angles do not enter into the zero- and first-order terms of the Hamiltonian makes it possible to calculate some of the second order terms of the expression for the energy values with complete generality. These are the terms that arise from the rotation and from the coupling between the rotation and vibration. They are found to be

$$\hbar^2[J(J+1)-l^2]/2A+C,$$

where A is the value of the moment of inertia at equilibrium, and

$$C=[\hbar^2(V_2+1)/2A]\{s^2(V_1+\tfrac{1}{2})[(\omega_1/\omega_2)+(\omega_2/\omega_1)] +c^2(V_3+\tfrac{1}{2})[(\omega_3/\omega_2)+(\omega_2/\omega_3)]\}-\hbar^2/2A.$$

In this expression, the V's are the vibrational quantum numbers and the ω's are the natural frequencies. The index 2 refers to the perpendicular vibration. The quantities c and s are determined by the potential energy function and are related by $c^2+s^2=1$. For symmetric molecules, $X-Y-X$, their values are $c=1$, $s=0$. If the natural frequencies are commensurable, the derivation ceases to be valid, but it appears likely that the result is essentially the same in this case.

INTRODUCTION

THE general theory of the interaction of the rotation and vibration of normal polyatomic molecules has been discussed by Eckart[1] and by Wilson and Howard.[2] They found it convenient to exclude linear molecules by their definition of normality. In an investigation preliminary to this one, it was found that the method developed by these authors cannot be extended, in general, to apply to linear molecules. More general schemes are needed, such as those considered by Welker.[3] These methods are also applicable to other anomalous molecules, such as ethane.

However, the method of rotating axes can still be used for the particular case of a triatomic linear molecule. The definition of the axes is then essentially that used by Dennison.[4] In the first part of this paper, it will be shown how this this definition is related to that given in references 1 and 2 for the nonlinear molecules. The Hamiltonian will be derived in the second part and in the third, the solution of the wave equation and calculation of the energy values will be discussed. In the concluding part, this calcu-

* The first and second parts of this paper are based on a master's thesis entitled "The Quantum Mechanical Hamiltonian for Triatomic Linear Symmetric Molecules" submitted to the University of Chicago by A. W.

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[4] D. M. Dennison, Rev. Mod. Phys. **3**, 292 (1931).

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