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Raman Spectra of Amino Acids and Related Compounds
I. The Ionization of the Carboxyl Group

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Raman spectra have been determined for four amino acids and their hydrochlorides; for three fatty acids and chloracetic acid, and their sodium salts; and for several related compounds. The influence of the solvent water on the Raman spectra of aqueous solutions is discussed. The "carbonyl" frequency, lying near 1670 cm^{-1} in the pure fatty acids, shifts to 1720 cm^{-1} when they are dissolved in water. No shift is found for the corresponding frequency in methyl acetate or acetone. The presence of a charged NH_3^+ group on the carbon α to the carboxyl increases this frequency by about 20 cm^{-1}. On ionization of the carboxyl group it is found that: (1) The "carbonyl" frequency vanishes in all cases investigated. The behavior of the amino acids in this respect is entirely consistent with their structure as zwitterions. (2) A group of lines in the region 1200–1420 cm^{-1} undergoes characteristic changes in position and intensity. (3) In most cases there is a powerful line in the region 750–930 cm^{-1} whose frequency increases by 20–40 cm^{-1} on ionization. The frequency of this line is decreased by about 50 cm^{-1} for each additional methyl group on the carbon atom adjoining the carboxyl. (4) Ionization markedly decreases the C—H frequency in formic acid, and also certain strong frequencies in methyl and ethyl amine.

INTRODUCTION

THE amino acids form an important class of compounds, containing a wide variety of organic radicals, but especially distinguished by the presence of electrically charged ammonium ($-NH_3^+$) and carboxylic (COO^-) groups, even when the molecule as a whole is electrically neutral. Because of this structure, the amino acids possess very large permanent electric moments, and in some properties they are closely akin to the inorganic salts, especially in their high melting points, relatively great solubility in water, and nearly complete insolubility in most organic solvents.[1]

With the aim of obtaining further insight into their structure, an extensive study of the Raman spectra of amino acids and related compounds has been undertaken in this laboratory. This first communication is concerned particularly with the changes in Raman spectrum accompanying ionization of the carboxyl group. For an amino acid cation ($^+H_3N \cdot R \cdot COOH$) the reaction may be written:

$$^+H_3N \cdot R \cdot COOH \rightleftharpoons {}^+H_3N \cdot R \cdot COO^- + H^+. \quad (1)^2$$

The study of the spectra of four amino acids, and their hydrochlorides, has provided a basis for the consideration of this reaction; four other carboxylic acids and their sodium salts have also been studied for comparison, as well as a number of related compounds. Since the salts studied are virtually completely dissociated in water, the sodium or chloride ions present do not contribute to the observed Raman spectrum.[3]

[1] Bjerrum, Zeits. f. physik. Chemie **104**, 147 (1923); Cohn, Ergeb. Physiol. **33**, 781 (1931); Ann. Rev. Biochem. **4**, 93 (1935).

[2] Edsall and Blanchard, J. Am. Chem. Soc. **55**, 2337 (1933).

[3] See Krishnamurti, Ind. J. Phys. **5**, 113 (1930); Kohlrausch, Naturwiss. **22**, 196 (1934).

Experimental Methods and Materials

The experimental arrangement for exciting the Raman spectra was based on that of Wood.[4] A cylindrical tube 30 mm in diameter, containing a filter solution, was interposed between the mercury arc and the Raman tube, and served as a combined lens and filter. The axes of the tubes and the arc were horizontal and parallel. Filter tube and Raman tube were supported in a wooden frame which rested on the housing of the mercury lamp. When desired, an additional filter in the form of a suitable type of glass plate could be introduced between the filter tube and the Raman tube. The mercury arc was cooled by a blast of compressed air directed horizontally across the aperture between the arc and the filter tube. An aluminum reflector was placed over the Raman tube to increase the light intensity.

The spectra were photographed with a Hilger E-439 glass spectrograph (aperture ratio of camera *f* 3, dispersion about 70A/mm at 4600A), and Eastman spectroscopic plates (generally the plates were type I−O; in special cases type I−H or I−J). The instrument was calibrated by using an argon lamp as the source of a standard spectrum. The slit width was generally 0.07 mm.

Filters

To remove the mercury *e* line[5] (4358A) and transmit the *k* line (4047A) Corning red purple ultra glass 2 mm thick[6] was found very satisfactory. Simultaneous elimination of the *o*, *p*, *q* triplet is accomplished by a dilute solution of sodium nitrite (2 to 4 cc of saturated solution in 125 cc of water) in the filter tube. We have found this combination preferable to the noviol-iodine filter used by Wood.

To transmit the *e*, *f* and *g* lines, removing all those of higher frequency, a solution of sodium nitrite (0.4 saturated) in the filter tube was employed.[7]

Glycine crystals were studied in the powder form, by using the method of complementary filters.[8] The details of the method, and of the filters used, will be reported in a subsequent communication.

In dilute aqueous solutions, such as those frequently employed in these investigations, there is great danger that the continuous background in the spectrum of the mercury arc may be so intense as to mask the Raman lines of the solute. The intensity of the continuous background was greatly diminished by two procedures: (1) The mercury arc was run at low intensity (40–50 volts) and cooled at the same time by a strong blast of compressed air. This low intensity (in combination with the filters used) made long exposures necessary (18 to 24 hours or more with the red purple ultra glass) but enormously decreased the continuous background. Such a procedure is only practicable with a spectrograph of high luminosity; otherwise the exposures would become intolerably long. (2) Solutions of the salts and amino acids, which could not be purified by distillation, were shaken with norit (highly purified charcoal) and heated for ten or fifteen minutes, with stirring, to 60° or 70°. They were then filtered through a fine-pore filter paper, the filtrate being collected and poured on to the filter again repeatedly for five or ten minutes, to wash out dust particles in the filter system. The filtrate was then allowed to flow directly into the Raman tube. This technique removed almost all the suspended particles in the liquid. It was particularly effective in the acid solutions, appreciably less so (although still valuable) when the solution was neutral. It proved unsuitable for alkaline solutions, as the norit then gave rise to a fluorescent impurity in the solution. Control experiments with norit in pure water and in 3 normal HCl showed no Raman lines or bands not found in pure distilled water.

The amino acid hydrochlorides studied (also chloracetic acid in water) contained an excess of hydrochloric acid (0.5 to 1 normal) to repress the ionization of the carboxyl group, and to make sure that the form R·COOH was alone present. As stated above, control experiments showed that HCl, even in concentrations higher than this, gives rise to no Raman lines (as would be

[4] R. W. Wood, *Physical Optics* (1934), third edition, Chapter XIV.

[5] The notation of the mercury lines is that of Kohlrausch, *Der Smekal-Raman-Effekt* (Berlin, 1931), p. 19.

[6] Murray and Andrews, J. Chem. Phys. **1**, 406 (1933).

[7] Pfund, Phys. Rev. **42**, 581 (1932).

[8] For references see Kohlrausch, *Der Smekal-Raman-Effekt*, p. 37.

expected, since it is virtually completely ionized at this concentration in water). The fatty acids in water did not require addition of HCl, since their dissociation constants are much lower than those of the carboxyl groups in the amino acids.

In preparing the salts of the fatty acids and of chloracetic acid, the *p*H was calculated (from the known dissociation constant of the acid) at which there would be 50 to 100 moles of salt present per mole of acid. Concentrated c.p. sodium hydroxide solution was then added (slowly and with cooling) to the concentrated aqueous solution of the acid, until the *p*H (tested by a suitable indicator)[9] had reached the desired value. In this way the amount of free acid present was made so small that it could scarcely contribute to the Raman spectrum, and the solutions were at the same time maintained slightly on the acid side of neutrality, thereby avoiding absorption of carbon dioxide and other complications.

Discussion

Since the great majority of the spectra here reported were obtained from aqueous solutions, it is important to differentiate the Raman lines (or bands) due to water from those due to the solute. The principal (double or triple) water band in the region 3250–3600 cm^{-1} is so intense and so characteristic that it is scarcely likely to be confused with anything else. It can, however, obscure the presence of other Raman lines lying in the same region of the spectrum, notably frequencies due to the N−H vibration, which lie in the region 3200–3400 cm^{-1}. Except in urea we have found no such frequencies in aqueous solutions which could be attributed to the solute, but the possibility that they exist cannot of course be excluded. In unfiltered light, some Raman lines of low frequency excited by the mercury *e* line will be obscured by the water band excited by the *k* and *i* lines, and some lines of low frequency excited by *k* or *i* are covered by the water band due to the *o*, *p*, *q* triplet. These complications are eliminated by the use of suitable filters, as described above under experimental methods.

Besides this very intense water band, a number of fainter bands have been reported by various authors. Notably Bolla[10] has reported bands at 60, 172, 510, 780, 1645, 2150 and 3990 cm^{-1}. We

[9] Clark, *The Determination of Hydrogen Ions* (Baltimore, 1928), third edition.

[10] Bolla, Nuovo cimento (N. S.) **9**, 290 (1932); **10**, 101 (1933).

Table I. *Frequencies in the range 1200–1750 cm^{-1}.* (The estimated intensity of each line is given in parenthesis following its frequency.)

Substance	Form	(1)	(2)	(3)	(4)	(5)
Formic acid	R COOH	1214 (2*b*)	1400 (3)			1727 (4*b*)
	R COO^-	—	1351 (6)			—
			1386 (1)			
Acetic acid	R COOH	1272 (1)	1370 (1)		1436 (2)	1720 (4*b*)
	R COO^-	—	1347 (2*b*)		1413 (6*b*)	—
Propionic acid	R COOH	1263 ($\frac{1}{2}b$)	—	1424 (3)	1459 (3)	1719 (2*b*)
	R COO^-	1257 (2)	1300 (2)	1417 (4)	1464 (2)	—
			1368 (1)			
Chloracetic acid	R COOH	—			1413 (4)	1729 (4*b*)
	R COO^-	1263 (1)			1404 (5)	—
Glycine	R COOH	1260 (1)	1315 (2)		1436 (3)	1743 (3*vb*)
	R COO^-	—	1331 (3)		1412 (3)	—
Alanine	R COOH	1240 (0)	1356 (0)	—	1460 (2*b*)	1738 (2*vb*)
	R COO^-	1310 (1)	1358 (2)	1416 (2)	1467 (2)	—
α-amino-*n*-butyric acid	R COOH	1316 (1)	1363 (1)	—	1450 (4*b*)	1746 (3*vb*)
	R COO^-	1258 (2)	1358 (4)	1413 (3)	1459 (3)	—
α-amino-isobutyric acid	R COOH	1273 (0)	1359 (0)	—	1452 (3*b*)	1729 ($\frac{1}{2}b$)
					1467 (2*b*)	
	R COO^-	1264 (1*vb*)	1374 (3*b*)	1411 (3)	1444 (2*b*)	—
					1465 (3*b*)	

All values tabulated are for the substances dissolved in water.

TABLE II. *The "sensitive frequency" (intensities given in parentheses).*

SUBSTANCE	R COOH	R COO^-	Δ
Glycine	871 (4)	897 (3)	26
Alanine	823 (5)	846 (5)	23
Aminoisobutyric acid	765 (5*b*)	795 (6*b*)	30
Acetic acid	898 (5)	928 (7)	30
Propionic acid	845 (6)	886 (4)	41
Chloracetic acid	906 (3*b*)	928 (3)	22

have observed bands corresponding in position to the first two of these, lying very close to the exciting mercury line. They do not overlap, however, with any of the Raman lines with which we are here concerned, and need not be considered further.

The bands near 510 and 780 are very broad and extremely faint, and could not possibly be confused with the relatively very sharp Raman lines given by the solutes studied in this range. The bands at 2150 and 3990 were not observed in these studies. That at 1645, however, appeared in most of the aqueous solutions studied. Though broad, it is sharper than most of the water bands, and it might readily be confused with Raman lines due to the solute. Its distinctive breadth and appearance, however, render it easy to identify, and its probable origin is indicated in the spectra for which it is listed in Table IV.

Having examined the influence of the solvent, we may now consider the spectra of the amino acids and fatty acids themselves, with special reference to the ionization of the carboxyl group. The complete Raman spectra are listed in Table IV, at the end of the paper; sets of lines which appear particularly significant in connection with the problem of ionization are listed in Tables I and II. A number of systematic empirical correlations between Raman frequencies and chemical structure can be readily derived from the observed data.

(1) The "carbonyl" frequency in the fatty acids and their salts [Table I, column (5)]

A frequency in the range 1650–1800 cm^{-1} is known to be present in all compounds containing the C=O group (esters, aldehydes, ketones, carboxylic acids, urea, etc.).[11] In the pure fatty acids this line is broad and lies at the lower limit of this range (1650–1670), far below the typical values for the esters (1730), aldehydes (1720) or ketones (1710). However, when the three fatty acids here studied were dissolved in water, it was found that this frequency was increased by some 50 cm^{-1}, from about 1670 to about 1720 (see data in Table IV).[12] Pure anhydrous formic acid possesses two frequencies in this range, a powerful one at 1672 and a weak one near 1730. In aqueous solution the strong line has shifted to 1727, and the weaker line has vanished or is covered up. The "carbonyl" frequency in methyl acetate and in acetone, however, was found (within the limits of experimental error) to be the same in aqueous solution as in the pure liquid (Table IV, Nos. 26–29). This shift, therefore, appears to be characteristic of the carboxyl group, and is not found for the C=O frequency in an ester or ketone.

A shift of this magnitude in a Raman frequency strongly suggests the possibility of an actual chemical change in the structure of the substance concerned. It appears probable that most of the fatty acids (acetic acid may be taken as typical) exist largely as double molecules in the pure state. Smyth and Rogers[13] conclude from several lines of evidence that acetic acid in benzene solution exists mainly as double molecules. This is also probably true of the pure acid; while in ether both double and single molecules appear to be present. In aqueous solutions, freezing-point measurements indicate that the single molecules greatly predominate.[14] Correspondingly Dadieu and Kohlrausch[15] have found the C=O frequency for acetic acid in benzene (1656) to be very slightly lower than that for the pure acid. In ether solution the frequency splits into two (at 1664 and 1750) while our measurements in water indicate one high frequency at 1720. It appears at present a tenable hypothesis that the high frequency (near 1720) arises from single molecules,

[11] Kohlrausch and Pongratz, Zeits. f. physik. Chemie **B27**, 176 (1934).

[12] This is in accord with the finding of Krishnamurti, Ind. J. Phys. **6**, 401 (1931–32) on acetic acid in water.

[13] Smyth and Rogers, J. Am. Chem. Soc. **52**, 1824 (1930); also Smyth, *Dielectric Constant and Molecular Structure* (New York, 1931), p. 173; see also Pauling and Brockway, Proc. Nat. Acad. Sci. **20**, 336 (1934).

[14] See for instance Lewis and Randall, *Thermodynamics* (New York, 1923), p. 290.

[15] Dadieu and Kohlrausch, Physik. Zeits. **31**, 514 (1930).

and the low frequency (near 1670) from double molecules of the acid.[16]

When the fatty acids are ionized, the "carbonyl" frequency vanishes. No trace of it could be detected in the spectrum of sodium formate, acetate, propionate or chloroacetate. This effect of ionization has been reported by Ghosh and Kar[17] and by Krishnamurti[18] but the spectra reported here are considerably richer in lines than those given in either of the above-mentioned papers. In conjunction with the data on the amino acids (discussed below), these findings furnish very powerful additional evidence for the validity of the view originally put forward by Ghosh and Kar.

It cannot, of course, be proved that the "carbonyl" frequency vanishes completely in the ionized carboxyl group, but it must in any case be extremely weak. It might lie in the region covered by the water band near 1640 cm^{-1}, but the appearance of the spectra gave no indication of such overlapping.

(2) The "carbonyl" frequency in the amino acids and their hydrochlorides

In the amino acid cations ($^{+}H_3N \cdot R \cdot COOH$) this frequency (Table I, column 5) is strongly present. In the free amino acids, however, as in the sodium salts of the fatty acids, it vanishes. Therefore it is clear that when an amino acid cation is titrated with base, it is the carboxyl group which dissociates (Eq. (1)). This may be taken as the fundamental hypothesis of the theory that the neutral amino acids exist as zwitterions ($^{+}H_3N \cdot R \cdot COO^{-}$); and these findings from the Raman spectrum could be used (in the absence of other evidence) as virtually conclusive proof of the validity of that theory. They also suggest that the Raman spectrum might be used in the titration of a substance containing several dissociable groups, to determine which group was reacting at a given stage in the titration.

The "carbonyl" frequency in the amino acid cations appears to be appreciably higher than in the fatty acids. The average value for the four amino acid cations is 1739 cm^{-1}, that for acetic and propionic acids is 20 cm^{-1} lower. This effect is presumably due to the positively charged $-NH_3^{+}$ group attached to the α carbon atom. It is interesting to note that the effect of the uncharged $-NH_2$ group is in the opposite direction. Thus in ethyl formate ($H \cdot COOC_2H_5$)[19] the C=O frequency is 1715; in ethyl carbamate ($H_2N-COOC_2H_5$)[19] it decreases to 1692. In urea $CO(NH_2)_2$ (Table IV, No. 25) it is still lower, namely 1666. This effect is apparent only when the amino group is directly attached to the C=O group. An intervening CH_2 group virtually abolishes the effect; thus the C=O frequency in the amino acid esters (Table IV, Nos. 23 and 24) is virtually identical with the typical value for the fatty acid esters. Since the effect of the charged $-NH_3^{+}$ group is still appreciable when this group is separated by a CH_2 group from the carboxyl it may be concluded that its effect is more powerful than that due to the uncharged $-NH_2$ group.

(3) The lines in the range 1200–1420 cm^{-1}

A group of lines in this region (Table I, columns 1–3) appears to undergo characteristic changes when the form $R \cdot COOH$ is transformed into the form $R \cdot COO^{-}$. All the amino acids but glycine, in the form $R \cdot COO^{-}$, show strong lines near 1360 and near 1412. The former of these lines becomes extremely weak, and the latter vanishes completely, when these amino acids are converted into their hydrochlorides. The lines at 1300 and 1368 in the propionate ion, and that at 1263 in the chloracetate ion (none of which appear in the form $R \cdot COOH$) may be analogous. The relation of these lines to ionization is the converse of that of the carbonyl frequency.

In contrast, the strong frequency in the range 1450–1470 (Table I, column 4) remains essentially unaltered by ionization in all the substances in which it occurs. This probably represents a deformational frequency of the methylene or methyl group,[20] and its constancy indicates that this type of vibration is not measurably affected by ionization of the carboxyl group, unless the CH_2 or CH_3 group involved is directly attached

[16] Dadieu and Kohlrausch reported a frequency of only 1676 in an acetic acid-water solution, but in their experiment the mole ratio acid : water was 1 : 1, whereas in ours it was approximately 1 : 10. See also Krishnamurti, Ind. J. Phys. **6**, 401 (1931–32).

[17] Ghosh and Kar, J. Phys. Chem. **35**, 1735 (1931).

[18] Krishnamurti, Ind. J. Phys. **6**, 309 (1931–32).

[19] Kohlrausch, Köppl and Pongratz, Zeits. f. physik. Chemie **B22**, 359 (1933).

[20] Reference 8, pp. 190, 206.

to the carboxyl. If it is so attached, as in glycine or acetic acid, this characteristic frequency is lowered to 1436 in the form R·COOH, and is still further lowered to 1412 by the ionization of the carboxyl group. The line at 1413 in chloracetic acid, which shifts to 1404 on ionization, doubtless represents the same type of vibration. Certain other lines in this range are listed for consideration in Table I, although it seems premature as yet to attempt a discussion of them.

The close similarity of glycine and acetic acid is notable in Table I. They resemble each other in Raman spectrum far more closely than either one resembles its higher homologs.

(4) The "sensitive frequency" in the range 750–930 cm^{-1}

In this range all the acids investigated (except formic and α-amino n-butyric acids) show a powerful line, which always increases in frequency on ionization of the carboxyl group (Table II).

It is possible that the line at 708 in aqueous formic acid, shifting to 772 in the formate ion, is analogous to those listed in Table II; but this appears dubious, as formic acid contains no C−C bond.

Regarding this frequency, it may be noted that: (a) In all the substances listed in Table I except chloracetic acid, it is by far the most powerful Raman line in the range 600–1000 cm^{-1}. (b) It is unaltered by change of state, being the same for glycine crystals as for glycine in solution, the same for aqueous solutions of acetic and propionic acids as for the pure acids. (c) Its frequency invariably increases (by 20–40 cm^{-1}) on ionization of the carboxyl group (column headed Δ in Table II). (d) The substitution of a methyl group for a hydrogen atom, on the carbon α to the carboxyl group, decreases this frequency by approximately 50 cm^{-1}. (See the progressive decrease in the series glycine → alanine → aminoisobutyric acid, in Table II; also the shift from acetic to propionic acid.)

This last-mentioned characteristic suggests a close relationship between this frequency and a very strong Raman line found in certain aldehydes, ketones, fatty acids and amides, studied by Kohlrausch and his collaborators (Table III). In every substance (except acetaldehyde) listed in Table III, the indicated line is by far the most powerful in the spectrum, in the range 600–1000 cm^{-1}, and the decrease in frequency for each additional methyl group on the α carbon atom is similar to that shown in Table II. It seems a reasonable inference that all these lines belong to the same family and have their origin in a similar type of molecular vibration.[21]

Compounds containing extended hydrocarbon chains show no one outstandingly powerful frequency in this range, but a large number of relatively weak lines. (See for instance α-amino-n-butyric acid, Table IV, Nos. 6 and 7.)

TABLE III. *The "sensitive frequency" in the range 600–900 cm^{-1} for molecules of the form* $R\cdot C(=O)X$.

R	Aldehydes X=H	Acids X=OH	Amides X=NH_2	Ketones X=CH_3
CH_3^-	887 (1)	893 (9)	862 (7*b*)	787 (8)
$CH_3CH_2^-$	846 (6)	844 (7)	807 (8*b*)	763 (7)
$(CH_3)_2CH^-$	796 (6)	800 (10)		724 (8)
$(CH_3)_3C^-$	762 (7)	753 (10)		671 (10)
$(CH_3)_2(C_2H_5)C^-$	749 (4)	736 (8)		660 (6)

References: (1) Aldehydes and ketones: Kohlrausch and Köppl, Zeits. f. physik. Chemie **B24**, 370 (1934). (2) Acids: Kohlrausch, Köppl and Pongratz, ibid. **B21**, 242 (1933). (3) Amides: Kohlrausch and Köppl, ibid. **B27**, 176 (1934).

(5) Other effects of ionization

Just as the loss of a proton by the carboxyl group increases the frequency of the "sensitive line" discussed above, so the acquisition of a proton by the amino group in methyl or ethylamine decreases the frequency of a strong line in the same range. In methylamine[22] the shift is from 1038 in the free amine to 995 in its hydrochloride; in ethylamine[23] from 1092 to 1047. A systematic study of the ionization of the amino group is now being undertaken.

A striking effect of ionization is the decrease of the principal C−H vibrational frequency from 2947 in formic acid to 2823 in the formate ion. In this case, the shift may reasonably be taken as reflecting an actual change in the strength of the C−H bond, and a similar interpretation

[21] For similar sets of lines in other types of compounds, and their possible interpretation, see Dadieu, Pongratz and Kohlrausch, Ber. Wien Akad. (II a) **141**, 267 (1932); Kohlrausch and Köppl, Monatsch. f. Chem. **63**, 255 (1933).

[22] Reference 8, p. 311; and Table IV (this paper, No. 21).

[23] Reference 8, p. 312; and Table IV, No. 22.

might be offered of some of the other effects of ionization discussed above.

I am indebted to Mr. Joseph Shack for valuable assistance in the carrying out of the experimental work.

In the following list of spectra there is listed for each Raman line: first, its frequency in cm^{-1}; second, in parenthesis, its intensity as estimated by direct observation; third, in parenthesis, the mercury lines (Kohlrausch's notation) exciting it. The letter "*b*" following the number indicating the intensity, signifies a broad line (*vb* = very broad). In some cases an approximate numerical estimate of the breadth of the line (in cm^{-1}) is given. The band near 1630 cm^{-1} is marked "water" to indicate the probable origin (see discussion in text above). The principal water band, in the region 3200–3600 cm^{-1}, was observed in all aqueous solutions, but is not listed here. In general, the presentation in this table closely follows that of Kohlrausch.[24]

Reference may be made to the literature regarding substances previously studied.[25]

Since this paper was written, Wright and Lee[26] have reported Raman spectra for glycine and alanine (as also for the hydrochlorides of tyrosine and cystine). In general, their frequency values agree with ours within the limits of experimental error. They report a line at 1445 cm^{-1} in glycine, and one at 1715 in alanine, which we have not observed (although the hydrochlorides of these substances give rise to lines very close to these values). Conversely, several of the fainter lines in glycine and alanine, here reported, were not observed by Wright and Lee.

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

1. *Glycine*, $^{+}H_3N\cdot CH_2\cdot COO^{-}$ (Eastman product, three times recrystallized from water) (aqueous solution, 22 percent): 508 (2*b*) (*k*, *g*, *f*, *e*); 590 (1) (*e*); 665 (1) (*e*); 897 (3) (*k*, *g*, *f*, *e*); 1033 (1) (*k*, *e*); 1122 (1) (*k*, *e*); 1331 (3) (*k*, *e*); 1412 (3) (*k*, *e*); 1491 (0) (*e*?); 1630±60 (1*b*) (*e*) (water); 2978 (3*b*) (*k*); 3018 (1) (*k*).

2. *Glycine* (*crystalline*): 507 ($\frac{1}{2}$) (*e*); 589 (1) (*e*); 891 (2) (*k*, *e*); 1033 (1) (*e*); 1112 ($\frac{1}{2}$) (*e*); 1323 (3) (*k*, *e*); 1404 (1) (*k*, *e*); 2968 (3) (*k*, *e*); 3002 (1) (*k*).

3. *Glycine hydrochloride*, $Cl^{-}NH_3^{+}\cdot CH_2COOH$ (aqueous solution 20 percent, with added HCl): 504 (2*b*) (*k*, *e*); 559 (0) (*e*?); 654 (1) (*k*, *e*); 871 (4) (*k*, *e*); 1049 (2) (*k*, *e*); 1111 (1) (*k*, *e*); 1260 (1) (*k*, *e*); 1315 (2) (*k*, *e*); 1436 (3) (*k*, *e*); 1516 (0) (*e*?) 1630±45 (2) (*e*) (water); 1743±27 (3) (*e*); 2973 (4) (*q*, *p*, *k*, *e*); 3014 (1) (*q*, *k*).

4. *dl-Alanine*, $^{+}H_3N\cdot CH(CH_3)\,COO^{-}$ (Eastman product, twice recrystallized) (aqueous solution, 13 percent): 421 (1) (*e*); 533 (2*b*) (*f*, *e*); 846 (5) (*k*, *f*, *e*); 920 (1) (*k*, *e*); 1003 (1) (*k*, *e*); 1125 (2*b*) (*k*, *e*); 1310 (1) (*k*, *e*); 1358 (2) (*k*, *e*); 1416 (2) (*k*, *e*); 1467 (2) (*k*, *e*); 1636±40 (1) (*e*) (water); 2893 (1) (*k*); 2949 (4) (*k*, *i*, *e*); 3003 (1) (*k*).

5. *dl-Alanine hydrochloride*, $Cl^{-}\,^{+}H_3N\cdot CH(CH_3)COOH$ (aqueous solution containing 20 percent of alanine by weight, and excess HCl): 401 (1*b*) (*e*); 520 (1*b*) (*k*, *e*); 620 (0*b*) (*e*); 680 (00) (*e*?); 747 (1) (*k*, *e*); 823 (5) (*k*, *e*); 920 (1*b*) (*k*, *e*); 1008 (1*b*) (*k*, *e*); 1120 (1*b*) (*k*, *e*); 1240 (0) (*k*, *e*); 1356 (0) (*k*, *e*); 1460 (2*b*) (*k*, *e*); 1619±30 (1*vb*) (*e*) (water); 1738±18 (2) (*e*); 2893 (2*b*) (*k*); 2953 (5*b*) (*q*, *p*, *k*); 3007 (3*b*) (*q*, *k*).

6. *dl-α-Amino-n-butyric acid*, $^{+}H_3N\cdot CH(C_2H_5)COO^{-}$ (Eastman product, once recrystallized) (aqueous solution, 17 percent): 542 (2) (*e*); 772 (1) (*e*); 842 (1) (*e*); 872 (1) (*e*); 914 (2) (*k*, *e*); 980 (2) (*k*, *e*); 1043 (3) (*k*, *e*); 1120 (2) (*k*, *e*); 1258 (2) (*e*); 1358 (4) (*k*, *e*); 1413 (3) (*k*, *e*); 1459 (3) (*k*, *e*); 1637±40 (1) (*e*) (water); 2900 (3) (*k*); 2954 (6*b*) (*k*, *e*); 2995 (2*b*) (*k*).

7. *dl-α-Amino-n-butyric acid hydrochloride*, $^{-}Cl^{+}H_3N\cdot CH(C_2H_5)\cdot COOH$ (aqueous solution containing 25 percent of amino acid, and excess HCl): 365 (2) (*e*); 429 ($\frac{1}{2}$*vb*) (*e*); 538 (3) (*k*, *e*); 659 (1*b*) (*e*); 745 (1) (*k*, *e*); 790 (1) (*k*, *e*); 831 (2) (*k*, *e*); 859 (2) (*k*, *e*); 913 (2) (*k*, *e*); 993 (2) (*k*, *e*); 1043 (3*b*) (*k*, *e*); 1127 (2*b*) (*k*, *e*); 1194 (1*vb*) (*k*?); 1316 (1) (*k*, *e*); 1363 (1) (*k*, *e*); 1450 (4*b*) (*k*, *e*); 1634±30 (1) (*e*) (water); 1746±15 (3) (*e*); 2894 (1) (*k*); 2953 (3) (*q*, *k*, *i*, *e*); 2995 (1) (*q*, *k*).

8. *α-Aminoisobutyric acid*, $^{+}H_3N\cdot C(CH_3)_2COO^{-}$ (Eastman product, once recrystallized) (aqueous solution, 12 percent): 353 (0) (*e*); 400 (0) (*e*); 600 (4) (*k*, *f*, *e*); 795 (6*b*) (*k*, *g*, *f*, *e*); 886 (1) (*k*, *e*); 948 (2*b*) (*k*, *i*, *e*); 1066 (1*vb*) (*e*); 1193 (0*b*) (*k*, *e*); 1264 (1*vb*) (*k*, *e*); 1374 (3*b*) (*k*, *e*); 1411 (3) (*k*, *e*); 1444 (2*b*) (*k*); 1465 (3*b*) (*k*, *e*); 1630±40 (1) (*e*) (water); 2880 (1*b*) (*k*); 2937 (4*b*) (*q*, *k*); 2998 (4*b*) (*q*, *k*).

9. *α-Aminoisobutyric acid hydrochloride*, $Cl^{-}\,^{+}H_3N\cdot C(CH_3)_2COOH$ (aqueous solution containing 16 percent of amino acid and excess HCl): 258 (2) (*e*); 358 (1*b*) (*e*); 407 (1*b*) (*e*); 538 (1) (*e*); 594 (2*b*) (*k*, *e*); 765 (5*b*) (*k*, *i*, *e*); 880 (1) (*k*, *e*); 951 (3) (*k*, *i*, *e*); 1066 (0*b*) (*k*, *e*); 1195 (0) (*k*, *e*); 1273 (0) (*e*); 1359 (0) (*e*); 1452 (3*b*) (*k*, *e*); 1467 (2) (*k*); 1623±40 (0) (*e*) (water); 1729 ($\frac{1}{2}$*b*) (*e*); 2879 (1) (*k*); 2945 (6*vb*) (*q*, *k*); 2998 (6*vb*) (*q*, *k*).

10. *Formic acid*, $H\cdot COOH$ (Eastman b. p. 99.8–100.2° at 755 mm): 180±35 (1*vb*) (*e*); 678 (3) (*k*, *e*); 873 ($\frac{1}{2}$) (*k*?); 1065 (1) (*k*, *e*); 1204 (2*b*) (*k*, *e*); 1396 (5) (*k*, *i*, *e*); 1670±20 (3*b*) (*e*); 1731 (1*b*) (*e*); 2148 ($\frac{1}{2}$) (*k*); 2598 ($\frac{1}{2}$*vb*) (*k*); 2787 (1) (*k*); 2961 (6*b*) (*k*, *i*, *e*).

11. *Formic acid* (aqueous solution, 35 percent): 170±30 (*e*); 708 (1*b*) (*e*); 1065 (0*b*) (*k*, *e*); 1214 (2*b*) (*k*, *e*); 1400 (3) (*k*, *i*, *e*); 1727 (4*b*) (*e*); 2792 ($\frac{1}{2}$*b*) (*k*); 2947 (6*b*) (*k*, *i*, *e*).

12. *Sodium formate*, $H\cdot COO^{-}Na^{+}$ (aqueous solution containing 35 percent of formic acid, neutralized with c.p. sodium hydroxide): 159 (band) (*e*); 503 (0) (*k*?); 772 (1)

[24] Kohlrausch, Köppl and Pongratz, Zeits. f. physik. Chemie **B21**, 242 (1933) and later papers in Zeits. f. physik. Chemie and Monatsch. f. Chem.

[25] Formic, acetic, propionic and chloracetic acids: Kohlrausch, Köppl and Pongratz, reference 24. Also for acetic acid, pure and in water, Krishnamurti, Ind. J. Phys. **6**, 367, 401 (1931–32). Sodium formate, sodium acetate, sodium chloracetate: Ghosh and Kar, J. Phys. Chem. **35**, 1735 (1931). (For sodium acetate also Kohlrausch, reference 8, p. 317.) Methyl acetate: Kohlrausch, Köppl and Pongratz, Zeits. f. physik. Chemie **B22**, 359 (1933). Acetone: Kohlrausch and Köppl, Zeits. f. physik. Chemie **B24**, 370 (1934). Urea: Kohlrausch and Pongratz, Zeits. f. physik. Chemie **B27**, 176 (1934). All these papers give references to the earlier literature.

[26] Wright and Lee, Nature **136**, 300 (1935).

(*k, e*); 1072 (1) (*k, e*); 1351 (6) (*k, i, g, f, e*); 1386 (1) (*k*); 1611 (0*vb*) (*e*) (water); 2123 (1*b*) (*k*); 2734 (2*b*) (*k*); 2823 (6*b*) (*k, i*).

13. *Acetic acid*, CH_3COOH (Baker's Glacial): $\Delta\nu=452$ (3) (*k, e*); 563 (0) (*k*); 623 (4) (*k, e*); 895 (5) (*k, i, e, f, g*); 1015 ($\frac{1}{2}$) (*e*); 1150 ($\frac{1}{2}$) (*k*); 1291 ($\frac{1}{2}$) (*e*); 1366 (3) (*k, e*); 1433 (4) (*k, e*); 1670 (4) (*e*); 2858 (0) (*k*?); 2946 (6) (*k, e*); 3017 ($\frac{1}{2}$*vb*) (*k*).

14. *Acetic acid*, CH_3COOH (aqueous solution, 33 percent from Baker's Glacial c.p.): 470 (1*b*) (*e*); 630 (3*b*) (*e*); 898 (5) (*k, i, e*); 1026 (1) (*e*); 1272 (1) (*k, e*); 1370 (1) (*k, f, e*); 1436 (2) (*k, f, e*); 1720 (4*b*) (*e*); 2936 (6) (*q, p, k, i, e*); 2994 (0) (*k*); 3026 (0) (*k*).

15. *Sodium acetate*, $CH_3COO^-Na^+$ (saturated aqueous solution of Sterling's c.p., once recrystallized): 475 (2) (*k, e*); 613 (0) (*k*); 652 (3) (*k, e*); 928 (7) (*k, i, g, f,* $\pm e$); 1011 (0) (*e*); 1347 (2*b*) (*k, e*); 1413 (6*b*) (*k, e*); 1542 (00*b*) (*e*); 1648 (00*b*) (*e*) (water); 2851 (0) (*k*); 2930 (5*b*) (*k, e*).

16. *Propionic acid*, C_2H_5COOH (Eastman, once distilled b.p. 140.2°): 290 (1*b*) (*e*); 480 (3*b*) (*k, e*); 606 (2) (*k, e*); 844 (6) (*k, i, f, e*); 1005 (3*b*) (*k, e*); 1078 (5) (*k, e*); 1256 (2) (*k, e*); 1424 (5) (*k, e*); 1462 (4) (*k, e*); 1665±8 (3) (*e*); 2753 (3) (*k*); 2900 (6) (*q, k, e*); 2950 (6) (*q, k, i, e*); 2998 (6) (*k, i*).

17. *Propionic acid* (aqueous solution, 35 percent, Eastman product, once distilled): 268 (2*b*) (*e*); 492 (3*b*) (*k, e*); 603 (1*b*) (*e*); 845 (6) (*k, e*); 998 (1*b*) (*k, e*); 1079 (2) (*k, e*); 1219 (0) (*e*?); 1263 ($\frac{1}{2}$*b*) (*k, e*); 1424 (3) (*k, e*); 1459 (3) (*k, e*); 1719±12 (2*b*) (*e*); 2749 (1) (*k*); 2891 (1) (*k*); 2950 (5) (*q, k*); 2991 (2) (*q, k*).

18. *Sodium propionate*, $C_2H_5COO^-Na^+$ (aqueous solution containing 30 percent distilled propionic acid+a very slight excess of sodium hydroxide): 294 (1) (*e*); 512 (2*b*) (*k, e*); 630 (2*b*) (*k, e*); 886 (4) (*k, g, f, e*); 1014 (3) (*k, e*); 1078 (3) (*k, e*); 1257 (2) (*k, e*); 1300 (2) (*k, e*); 1368 (1) (*k, e*); 1417 (4) (*k, e*); 1464 (2) (*k, e*); 2888 (1) (*k*); 2950 (2) (*k, e*); 2984 (1) (*k*).

19. *Chloracetic acid*, $CH_2ClCOOH$ (aqueous solution, 40 percent, Eastman Product m.p. 62–64°): $\Delta\nu=244$ (3) (*k, e*); 430 (4*vb*) (*k,* $\pm e$); 573 (1*vb*) (*k, e*); 676 (1*vb*) (*k, e*); 794 (6) (*k, i,* $\pm e$); 906 (3*b*) (*k, i, e*); 1185 (2) (*k, i, e*); 1413 (4) (*k, e*); 1729±29 (4*b*) (*e*); 2964 (6) (*k, e*); 3009 (2) (*k*).

20. *Sodium chloracetate*, $CH_2Cl\cdot COO^-Na^+$ (aqueous solution containing 33 percent acid, and equivalent sodium hydroxide): $\Delta\nu=255$ (1) (*k, e*); 433 (5) (*k,* $\pm e$); 584 (1) (*e*); 690 (1) (*e*); 780 (5) (*k, i, e*); 928 (3) (*k, e*); 1186 (1) (*k, e*); 1263 (1) (*k, e*); 1404 (5) (*k, i, e*); 1624±40 (1*b*) (*e*) (water); 2969 (5) (*k, e*); 3021 (1) (*k*).

21. *Methylamine hydrochloride*, $CH_3NH_3^+Cl^-$ (aqueous solution, 50 percent, containing excess HCl. Eastman product, once recrystallized from alcohol): $\Delta\nu=995$ (6) (*k, i, f, e*); 1268 (1) (*k, e*); 1466 (3) (*k, e*); 2833 (2) (*k*); 2914 (2) (*k, i*); 2975 (6) (*k, i, e*); 3032 (3) (*k, e*).

22. *Ethylamine hydrochloride*, $C_2H_5NH_3^+Cl^-$ (aqueous solution, 50 percent, with excess HCl. Eastman product, once recrystallized from alcohol): $\Delta\nu=411$ (2) (*k, e*); 873 (5) (*k, f, e*); 1047 (4) (*k, f, e*); 1205 (2) (*k, e*); 1335 (3) (*k, e*); 1458 (5) (*k, f, e*); 2883 (2) (*k, e*); 2946 (3) (*q, k, e*); 2986 (3) (*q, k, e*).

23. *dl-Alanine ethyl ester*, $H_2N\cdot CH(CH_3)\cdot COOC_2H_5$ (prepared from *dl*-alanine by the method of Fischer[27] twice distilled, b.p. 48.0° to 48.4° at 11–12 mm): $\Delta\nu=353$ (2) (*e*); 501 (2) (*k, e*); 628 (0) (*k, e*); 670 (0) (*k, e*); 757 ($\frac{1}{2}$) (*k, e*); 794 (1) (*k, e*); 860 (5*b*) (*k, g, f, e*); 934 (2) (*k, e*); 1021 (3) (*k, e*); 1107 (3) (*k, e*); 1268 (1) (*e*); 1319 (1) (*k, e*); 1456 (5) (*k, e*); 1740 (3) (*e*); 2880 (1) (*k, i*); 2937 (6) (*k, i, e*); 2987 (6) (*k, i*); 3003 (6) (*k, e*); 3318 (3) (*k, e*); 3395 (2) (*k*).

24. *dl-a-Amino-n-butyric acid ethyl ester*, $H_2NCH(C_2H_5)COOC_2H_5$ (prepared from *dl-a*-amino-*n*-butyric acid by method of Fischer; twice distilled, b.p. 66.5° at 17 mm): $\Delta\nu=334$ (5*b*) (*e*±); 512 (3*b*) (*e*±); 646±25 ($\frac{1}{2}$) (*e*); 788 (0) (*e*); 867 (6*b*) (*k, e, g*); 934 (1*b*) (*e*); 1003 (2) (*e*); 1034 (2) (*e*); 1111 (3*b*) (*e*); 1276 (1) (*e*); 1309 (1) (*e*); 1454 (6*b*) (*k, e*); 1740 (3) (*e*); 2876 (3) (*k*); 2932 (6) (*k*); 2982 (3) (*k*); 3324 (3*b*) (*k*); 3389 (2) (*k*).

25. *Urea*, H_2NCONH_2 (aqueous solution—saturated, about 60 percent urea): $\Delta\nu=521$ (1) (*e*); 584 (1) (*e*); 1000 (6) (*k, e*); 1170 (1*vb*) (*k, e*); 1468 (0) (*k*); 1580 (0) (*k, e*); 1666 (1*b*) (*e*); 1768 (*e*?) (*e*); 3230 (1) (*k*); 3380 (3*b*) (*k*); 3489 (1*b*) (*k*).

The very broad line at 3380 is probably due, at least in part, to water; but the two lines at 3230 and 3489 are sharply distinct from this central band, and appear very differently from the bands in pure water. The line at 1666 is probably due to urea, not to water, since even the strong water bands appear relatively weak in the spectrum of this solution.

This spectrum is in good agreement with those reported by Kohlrausch and Pongratz,[25] and by Schneider (see reference 25).

26. *Methyl acetate*, (CH_3COOCH_3) (Eastman, b.p. 56.3°) anhydrous: $\Delta\nu=304$ (3) ($\pm e$); 433 (5) (*k,* $\pm e$); 639 (6) (*k, g, f,* $\pm e$); 843 (6) (*k, g, f,* $\pm e$); 983 (1) (*e*?); 1042 (4) (*k, f, e*); 1191 (1*b*) (*e*); 1254 ($\frac{1}{2}$*b*) (*e*); 1374 (1) (*e*); 1451 (5*vb*) (*k, e*); 1741 (5) (*e*); 2850 (3) (*k, e*); 2948 (6*b*) (*k, i, f, e*); 3023 (4*vb*) (*k*).

27. *Methyl acetate*, (20 percent in water): $\Delta\nu=303$ (1) (*e*); 436 (2) (*k, e*); 640 (3) (*k, e*); 855 (4) (*k, e*); 1046 (1*b*) (*k, e*); 1453 (1*b*) (*k, e*); 1730 (2*b*) (*e*); 2863 (2) (*k*); 2956 (5) (*k, e*); 3039 (2*vb*) (*k*).

28. *Acetone*, (CH_3COCH_3) (Eastman, from bisulfite compound b.p. 56.2°) anhydrous: $\Delta\nu=385$ (3) (*e*); 488 (1) (*k, e*); 527 (4) (*k, i, e*); 783 (7*b*) (*k, i, g, f,* $\pm e$); 903 (1*b*) (*k, e*); 1061 (3) (*k, e*); 1217 (4) (*k, e*); 1356 (1) (*k, e*); 1426 (6*vb*) (*k, i, e*); 1703 (5) (*e*); 2698 (2) (*k*); 2846 (1) (*k*); 2921 (6*vb*) (*k*); 3011 (3*b*) (*k, i*).

29. Acetone in water (30 percent): $\Delta\nu=399$ (2) (*e*); 499 ($\frac{1}{2}$) (*k, e*); 542 (3) (*k, e*); 797 (6*b*) (*k, i, e*); 1068 (2) (*k, e*); 1236 (3) (*k, e*); 1363 (2) (*k, e*); 1425 (5*b*) (*k, e*); 1702 (6*b*) (*e*); 2860 (1) (*k*); 2934 (7*vb*) (*q, p, i, e*); 2975 (3) (*q, k*); 3018 (3) (*q, k*).

Several frequencies appear to be 10 to 20 cm^{-1} higher in aqueous acetone than in the anhydrous liquid. The line at 1703, however, is unchanged in frequency.

[27] Fischer, Sitzungsber. Preuss. Akad. Wiss. 1062 (1900).