

THE RAMAN SPECTRA OF CRYSTAL POWDERS.

IV. Some Organic and Inorganic Compounds.

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1. Introduction.

IN several previous communications, the author has pointed out that the new technique of complementary filters described by him has opened out for the study of Raman effect an extensive array of crystalline compounds in the domain of organic as well as of inorganic chemistry whose investigation by the method of light-scattering has till now remained extremely meagre, incomplete or inadequate for reasons of a technical nature. The procedure sometimes adopted in such cases, of studying the substance in solution or in the molten state, has several limitations, and is attended with difficulties, into which it is not necessary to enter at great length. Suffice it to remark that, as the first two papers of this series have made it clear, profound spectral changes—even the complete washing out of the entire spectrum—can and sometimes do occur when a substance is dissolved in water. Again, in the case of a large number of crystalline solids of high melting point, prolonged maintenance of the substance above this temperature during the exposure causes partial or total decomposition of the substance itself, a difficulty which has been already pointed out by Kohlrausch (1936). These difficulties are all overcome by the powder technique, and in favourable cases, comparison of the Raman spectrum of the solid substance with the spectrum of the same substance in solution or in the molten state, can be expected to furnish important conclusions. The present paper is an attempt in this direction, and embodies the results of the author's investigation on the Raman spectra of crystalline naphthalene, oxalic acid, urea, guanidine hydrochloride, acetamide, propionamide, amino-acetic acid, phenyl acetic acid, phosphorous acid, sodium phosphite, phosphoric acid and boric acid.

2. *Experimental.*

All the crystalline solids were Kahlbaum's purest chemicals, and were mostly used directly without any preliminary treatment. A Hilger two-prism spectrograph of high light-gathering power and a Fuess spectrograph of somewhat larger dispersion than the Hilger instrument were employed to photograph the Raman spectra. The duration of exposure varied with the nature of the substance, and was minimum in the case of naphthalene which yielded a very intense spectrum on the Hilger instrument in about 10 hours. λ 4046 was the exciting line in all cases.

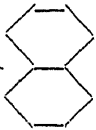
3. *Results.*

The results are contained in Table I. The notations employed have the following significance:

t = time of exposure in hours; n = total number of observed lines.

F = Fuess spectrograph; H = Hilger two-prism spectrograph.

TABLE I.

1. <i>Naphthalene</i> ,  $t = 10; n = 18; H$	511 3s	764 5s	1019 5s	1144 3s	1168 1s	1240 2s	1280 $\frac{1}{2}$	1328? 0	1379 15s	1440 1s	1460 5s	1573 7s	1623 $\frac{1}{2}$ s	3001 1s	3025 0	3054 12s
2. <i>Oxalic acid</i> , $(COOH)_2 \cdot 2H_2O$ $t = 70; n = 5; H$	485 0s	854 6s	1360 $\frac{1}{2}$	1486 2d	3432 6	3467 4bd										
3. <i>Urea</i> , $OC(NH_2)_2$ $t = 72, n = 10; H$	1012 10s	1171 $\frac{1}{2}$ d	1465 $\frac{1}{2}$ d	1537 2	1576 $\frac{1}{2}$	3243 2d	3324 4d	3353 5d	3434 5							
4. <i>Guanidine Hydrochloride</i> , $\left[\begin{array}{c} NH_2 \\ \\ HN = C \\ \\ NH_2 \end{array} \right] \cdot HCl$ $t = 72; n = 10; F$	526 0	1006 10s	1554 5	1624 0d	3172 1d	3238 1d	3279 1d	3338 4d	3430 1d							
5. <i>Acetamide</i> , $H_3C \cdot CO \cdot NH_2$ $t = 40; n = 13; H$	455 1s	875 8s	1147 5s	1354 3	1397 3d	1594 1d	2933 10s	2970 0d	3020 0d	3150 6bd	3286 1d	3351 4d				
6. <i>Propionamide</i> , $H_3C_2 \cdot CO \cdot NH_2$ $t = 48; n = 12; H$	820 4s	1145 5s	1418 2d	1456 2d	1594 1d	2743 $\frac{1}{2}$ d	2850? 0	2897 3s	2942 8s	2997 4s	3173 4bd	3356 3bd				
7. <i>Amino-acetic acid</i> , $H_2N \cdot CH_2 \cdot COOH$ $t = 48; n = 17; H$	507 1	893 5s	1047 2s	1121 1s	1132 $\frac{1}{2}$ d	1319 4d	1336 6d	1397 4b	1437 4s	1499 1bd	1577 1d	1650 $\frac{1}{2}$ d	2592 1d	2959 1d	2999 10	3113 8s 3bd

8. <i>Phenyl acetic acid</i> , $C_6H_5 \cdot CH_2 \cdot COOH$ $t = 48$; $n = 20$; F	624 748 840 890 925 1003 1032 1188 1234 1338 1402 1432 1585 1600 2920 2952 2986 3013 3035 3063 1s 3s 4s $\frac{1}{2}$ $\frac{1}{2}$ d 10s 6s 4s 3 1 1 $\frac{1}{2}$ d 2 3 6 1 $\frac{1}{2}$ $\frac{1}{2}$ 12
9. <i>Phosphorous acid</i> , H_3PO_3 $t = 12$; $n = 6$; H	961 990 1038 1104 2485 2511 6s 3d 2 1d 8s 7s
10. <i>Sodium phosphite</i> , Na_2HPO_3 $t = 72$; $n = 4$; H	969 1046 1057 2338 3s 1 1 6s
11. <i>Phosphoric acid</i> , H_3PO_4 $t = 24$; $n = 2$; H	919 1100 (?) 10s 1d
12. <i>Boric acid</i> , $B(OH)_3$ $t = 70$; $n = 3$; F	880 3172 3256 5s 3d 2d

4. Discussion of Results.

1. *Naphthalene*. The Raman spectrum of naphthalene in the crystal line state was reported by Bär (1929) in his very first communication which he pointed out the possibility of obtaining Raman spectra with crystal powders instead of single crystals. The spectrum of the molten substance has been studied by Petrikaln and Hochberg (1929), Ziemecki (1932), and Gockel (1935); Dadiou and Kohlrausch (1929) have photographed the spectrum of the solution of naphthalene in CCl_4 . It is of interest to compare the results of the previous authors with the frequencies recorded in the present investigation. Table II gives such a comparison.

TABLE II.

Dadiou and Kohl. (1929) Soln. in CCl_4	Petrikaln and Hoch. (1929) molten	Ziemecki (1932) molten	Gockel (1935) molten	Bär (1929) Cryst.	Author (1937) Cryst.
505 (2)	516 (4)	511 (3)	512 (5)	514	511 (3s)
610 (0)
..	..	742 (2)
..	762 (4)	763 (3)	761 (5)	761	764 (5s)
936 (0)
1023 (2)	1029 (4)	1026 (3)	1026 (4)	1025	1019 (5s)
1142 (0)	1157 (1)	..	1153 ($\frac{1}{2}$)	..	1144 (3s)
..	1168* (1s)
1245 (0)	1251 (0)	..	1240 (2s)
..	1293 (4) ?	1280* ($\frac{1}{2}$)
..	..	1323 (0)	1323 (1)	..	1328 (0) ?
1377 (4)	1381 (5)	1377 (10)	1379 (8)	1391	1379 (15s)
1412 (0)
..	1440* (1s)
..	1463 (3)	1460 (4)	1462 (4)	..	1460 (5s)
1573 (3)	1580 (3)	1575 (4)	1572 (3)	..	1573 (7s)
..	1623* ($\frac{1}{2}$ s)
..	3001* (1s)
..	3025* (0)
3046 (1b)	3064 (4)	3058 (4)	3062 (4b)	3068	3054 (12s)

* Frequencies noticed for the first time.

An inspection of the table reveals at once that many new frequencies have been recorded in the spectrum of this substance. Comparison of the author's results with those of Bär shows the vast improvement effected by the technique of complementary filters in the photography of the Raman spectra of crystal powders. A characteristic feature of the Raman spectrum of naphthalene crystals is the extreme sharpness of all the modified lines. Some difference between the spectra of the substance in the solid and molten states is noticed in the region of the hydrogen frequencies above 3000 cm^{-1} . In the crystals, three sharp lines are present in this region, while Gockel and others have found only a single broad line.

the spectrum of molten naphthalene. This difference is very significant in the case of a non-polar substance, because it shows that the hydrogen frequencies are very susceptible to temperature and the state of aggregation of the substance even in such cases. Influence of change of state and presumably also of temperature on the C-H frequencies was noticed by the author (1936) in the case of cyclopropane, and recently Bhagavantam and Rao (1937) observed intensity and frequency changes for the hydrogen lines of benzene on passing from the liquid to the vapour state. The 1379 line of naphthalene is the most intense line in the whole spectrum, and does not seem to undergo any appreciable change on passing from the solid to the molten state. It might be of interest to note that it is also a very prominent line in the spectra of the α - and β - mono-derivatives of naphthalene.

2. *Oxalic Acid*, $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$. Rao (1935), Hibben (1935) and Angus and Leckie (1936) have examined the Raman spectrum of crystalline oxalic acid. Aqueous solutions of the acid have also been studied by the above authors and more recently by Gupta (1936). Some controversy appears to have arisen between Hibben on the one hand and Angus and Leckie on the other as to the presence or otherwise of frequencies near 1700 cm^{-1} corresponding to $\text{C}=\text{O}$ in the Raman spectrum of oxalic acid dihydrate. Unfortunately, as only $\lambda 4046$ excitation was employed in the present investigation, frequencies in the 1700 region, even if present, could not have been observed because of the presence of the $\lambda 4358$ group of mercury lines. Comparison of the Raman frequencies of oxalic acid dihydrate observed by the author with those reported by Hibben and Angus and Leckie is given below :—

TABLE III.

Hibben	847	1365	1470			
Angus and Leckie	495	854		1471	1661(b)	1759
Author	485 0	854 6s	1360 $\frac{1}{2}$	1486 2d	3432 6	3467 4bd

The frequencies of crystalline oxalic acid reported in a recent paper by Balmokand Anand (1936) appear to be entirely false. A new feature of the present investigation is that it shows the presence of two strong Raman frequencies in the 3400 region which presumably originate from the oscillations of the water molecules.

3. *Urea*, $OC.(NH_2)_2$. The Raman spectrum of this substance has been studied in the aqueous solution by Pal and Sen Gupta (1930), Krishnamurti (1931), Kohlrausch and Pongratz (1934), and recently by Edsall (1936). Krishnamurti also studied the Raman spectrum of the crystalline substance by the powder technique and recorded two frequencies 1006 (strong) and 1134 (weak). The broad water-band in the 3μ region renders the complete elucidation of the N-H frequencies which fall practically in the same region very difficult indeed in the case of aqueous solutions, and it is, therefore, of interest to compare the spectrum of the crystalline substance recorded by the author with the previous results on aqueous solutions.

TABLE IV.

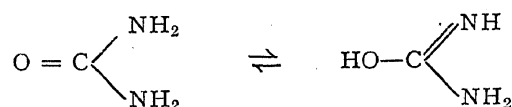
Kohlrausch and Pongratz (aq. soln.)	525 2b	585 1b	1000 8	1157 1b	1350 $\frac{1}{2}$	1458 0	1593 2b	1665 0	3218 1b	3383 3vb	3462 2vb	
Edsall (aq. soln.)	521 1	584 1	1000 6	1170 1vb		1468 0	1580 0	1666 1b	1768 ?	3230 1	3380 3b	3489 1b
Author (crystal)			1012 10s	1171 $\frac{1}{2}$ d		1465 $\frac{1}{2}$ d	1537 2	1576 $\frac{1}{2}$	3243 2d	3324 4d	3353 5d	3434 5

It is seen that the frequency near 1000 cm.^{-1} is the most prominent one in the crystal as well as in the aqueous solution. Its magnitude shows a distinct diminution on passing from the crystal to the aqueous solution, a feature which has been also noticed by Krishnamurti. A significant difference between the spectrum of the crystal and of the solution is the absence in the latter of the frequency near 1537 cm.^{-1} which is a very prominent line in the crystal spectrum, and which probably arises from a δ (N-H) oscillation. Differences seem to exist even in the region of the N-H valence oscillations, as can be seen from Table IV. These differences are, of course, due to the large influence of the highly polar solvent on the solute molecules. Failure to observe the frequencies in the 500 and 1700 region in the crystal spectrum does not mean their non-existence.

The usually written chemical formula of urea is $O = C \begin{matrix} \nearrow NH_2 \\ \searrow NH_2 \end{matrix}$. If we regard the C, O and N atoms as being in the same plane, the molecule has the symmetry C_{2v} . On this basis, Kohlrausch and Pongratz have attempted to discuss the spectrum of this substance by comparing it with the Raman spectra of presumably similar molecules such as acetone,

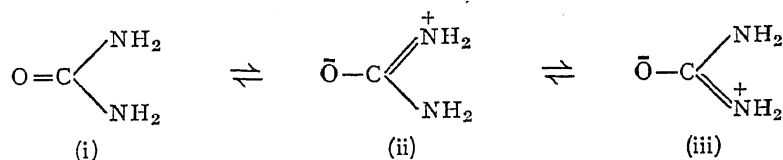
$\text{O} = \text{C} \begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix}$ and phosgene, $\text{O} = \text{C} \begin{matrix} \text{Cl} \\ \text{Cl} \end{matrix}$. Nevertheless, as far as the present author can see, the resemblance between the spectra of these substances in the spectral region concerned (below 1800 cm^{-1}) is by no means of a very striking character, and polarisation measurements are necessary before any definite classification of the frequencies can be attempted.

Krishnamurti has suggested the possibility that urea might exist in two tautomeric forms :



However, it appears very difficult to decide this issue by the evidence furnished by the Raman spectrum of urea.

During the last few years, Pauling and his collaborators have attacked the problem of the nature of chemical valence from the standpoint of the quantum theory, and have published a series of interesting papers in which they have adduced very strong evidence in favour of resonance between the various possible configurations in the case of those molecules in which the normal electronic state can be represented by more than one Lewis structure. According to Pauling's view (1935), resonance exists in the case of urea between the three alternative structures,



the resonance being of sufficient importance to give each C-N bond 28 per cent double bond character. The influence of such resonance on the Raman spectrum of the molecule concerned is rather a complicated problem; nevertheless, if we are justified in regarding the simultaneous existence of the two different types of molecules represented by (i) and (ii), [forms (ii) and (iii) are not essentially different] we might expect to find certain characteristic features in the region of the N-H valence frequencies. In a previous paper (1937) the author pointed out that a change in the co-valency of nitrogen from three to four causes an appreciable diminution of the N-H frequencies. Kohlrausch (1936) has tabulated the N-H valence frequencies observed in the Raman spectra of a series of primary amines of the type

$\text{R} \cdot \text{N} \begin{matrix} \text{H} \\ \text{H} \end{matrix}$ and has found the mean values 3313 and 3367 cm^{-1} for the two

frequencies observed in this region. The departure from the mean values does not exceed 10 or 15 wavenumbers in individual cases. The author's previous investigations showed that the N-H frequencies of the ions $[\text{NH}_4]^+$, $[\text{H}_3\text{N}\cdot\text{OH}]^+$ and $[\text{H}_3\text{N}\cdot\text{NH}_3]^{++}$ observed in the Raman spectra of their crystalline salts are well below the values given above, and extend over the spectral range 2500–3200 wavenumbers. If we are to accept the Pauling resonance structure of urea, it is probable that the bands 3243 (2d) and 3324(4d) owe their origin primarily to the $=\overset{+}{\text{N}}\text{H}_2$ group, and the bands 3353(5d), 3434(5) primarily to the $-\text{NH}_2$ group. The increase above the normal values of these frequencies could then be attributed to the influence of the resonating double bond.

4. *Guanidine Hydrochloride*, $\left[\text{HN} = \text{C} \begin{array}{l} \text{NH}_2 \\ \text{NH}_2 \end{array} \right] \cdot \text{HCl}$. The Raman spec-

trum of the guanidonium ion in aqueous solutions of its salts has formed the subject-matter of a recent investigation by Gupta (1936). The spectrum of the aqueous solution obtained by him and that of the crystalline salt reported in the present investigation differ in certain important respects as can be seen from the following table.

TABLE V.

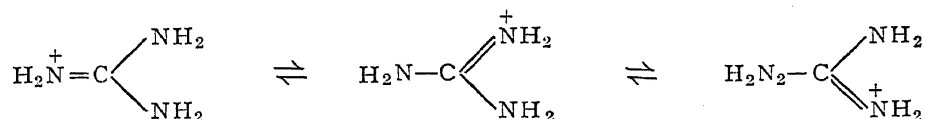
Gupta (aq. soln.)	522 1	995 4	1620 $\frac{1}{2}\text{b}$						
Author (crystal)	526 0	1006 10s	1554 5	1624 0d	3172 1d	3238 1d	3279 1d	3338 4d	3430 1d

Besides showing a large number of frequencies in the N-H region, the spectrum of the crystalline salt exhibits a strong line at 1554 cm^{-1} which is absent in the aqueous solution. We notice, moreover, a definite fall in the frequency of the most intense Raman line near 1000 cm^{-1} on dissolving the substance in water. In these respects, there is a very close similarity between the guanidonium ion and urea. It is also very significant that the frequency of the strongest Raman line is practically the same in the two cases.

The structure of the guanidonium ion has been discussed by Theilacker (1931, 1935) in connection of his X-ray investigation of the crystal structure of the guanidonium halides. His results show that from the crystallographic standpoint, all the three nitrogen atoms of the guanidonium ion are equivalent. This result is, however, insufficient to decide between the two alternative structures of this ion :

(i) the non-resonating structure $\text{H}_2\text{N}-\overset{+}{\text{C}}\begin{matrix} \text{NH}_2 \\ \text{NH}_2 \end{matrix}$

(ii) the resonating structure



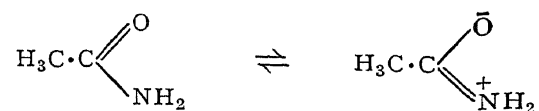
Theilacker has concluded in favour of the formula (i), while Pauling and Sherman (1933) postulate for the guanidonium ion a double bonded resonance structure with three-fold degeneracy as is shown by formula (ii).

Gupta has stated that the low value of the strongest Raman frequency of the guanidonium ion, *viz.*, 1000 cm.^{-1} rules out the possibility of the Pauling double-bond resonance structure and lends every support to the Theilacker non-resonating structure. The present author, however, fails to see the force of this argument because, as has been already pointed out, we find an identical and equally intense frequency in the spectrum of urea the molecule of which certainly contains a double bond. On the other hand, if we bear in mind that the masses of NH_2 and O are identical, and that the C-N and C-O force constants are not appreciably different, the Pauling resonance structure enables us at once to understand the close coincidence of the frequencies observed in the Raman spectrum of the guanidonium ion and of urea. The N-H frequencies in the 3000 region are of interest in this connection. We find N-H frequencies greater and less than 3300 wavenumbers in the spectrum of guanidine hydrochloride. This is probably an indication of the presence of $=\overset{+}{\text{N}}\text{H}_2$ as well as of $-\text{NH}_2$ groups in the guanidonium ion. In any case, the arguments adduced by Gupta in favour of the symmetric non-resonating model of the ion—the low value of the frequency of the strongest Raman line, and its high degree of polarisation—are not sufficient to rule out the Pauling structure.

The strong Raman frequency at 1554 cm.^{-1} in the crystal which is apparently non-existent in the solution represents probably a $\delta(\text{N-H})$ frequency. Disappearance of such sharp and intense $\delta(\text{N-H})$ frequencies in aqueous solutions has been noticed by the author in the case of hydroxylamine and hydrazine hydrochlorides. The reason for this is not clear.

5. *Acetamide*, $\text{H}_3\text{C}\cdot\text{CO}\cdot\text{NH}_2$. The Raman spectrum of this substance is of great interest because the phenomenon of resonance predicted by Pauling and Sherman (1933) in the case of amides appears to have been confirmed from several different sources such as the measurement of dipole

moment (by Kunler and Porter, 1934), from the magnetic susceptibility (by Clow and Thompson, 1936), etc., and some evidence for the same might be expected from the Raman spectrum. In the case of acetamide, the expected resonance is between the structures



As far as the author is aware, the Raman spectrum of acetamide has not been examined in the crystalline state. The spectrum of the molten substance has been studied by Kohlrausch and Pongratz (1934) and by Thatte and Joglekar (1935). As the results of the latter authors are incomplete, we shall not consider them here. Kohlrausch and Pongratz have found the surprising result that the Raman frequencies characteristic of the NH_2 group are completely absent in the spectrum of this substance. In this and other respects, the author's results on the Raman spectrum of acetamide crystals forms a striking contrast as can be seen from Table VI.

TABLE VI.

Kohlrausch and Pongratz (molten, 92°)	236 0	448 3	564 3	862 7b	1119 3b	1344 3b	1387 3b	1422 $\frac{1}{2}$	1611 2	1660 ± 9 3b	2933 6b	2998 2
Author (crystal)	..	455 1s	..	875 8s	1147 5s	1354 3	1397 3d	..	1594 1d	..	2933 10s	2970 0d
									3020 0d	3150 6b	3286 1d	3351 4d

The absence of the N-H frequencies in the molten substance, if genuine, is indeed very significant, in view of the fact that they come out quite strongly in the crystals; the matter, however, requires re-examination. The N-H frequencies of the solid consist of three diffuse bands of which the one of lower frequency at 3150 is more intense than the others of higher frequency. In acetamide, if we are to postulate the co-existence of two types of molecules in equal proportion, then, excepting in the region of the N-H frequencies, we cannot expect any appreciable differences between the vibrational frequencies of the two forms, since the vibrating masses and the force constants concerned are nearly identical. For reasons which have been already explained, it seems justifiable to attribute the N-H band at 3150 to

the $\text{R} \cdot \text{C} \begin{smallmatrix} \text{O} \\ \diagup \\ \text{NH}_2^+ \end{smallmatrix}$ type and the bands of higher frequency to the $\text{R} \cdot \text{C} \begin{smallmatrix} \text{O} \\ \diagup \\ \text{NH}_2 \end{smallmatrix}$ type of molecules.

Kohlrausch and Pongratz have suggested the possible occurrence of the tautomeric forms $\text{R} \cdot \text{C} \begin{smallmatrix} \text{O} \\ \diagup \\ \text{NH}_2 \end{smallmatrix}$ and $\text{R} \cdot \text{C} \begin{smallmatrix} \text{OH} \\ \diagup \\ \text{NH} \end{smallmatrix}$ in acetamide, on the ground that two Raman frequencies are observed in the 1600 region instead of one (see Table VI).

6. *Propionamide*, $\text{H}_5\text{C}_2 \cdot \text{CO} \cdot \text{NH}_2$. The crystals employed were somewhat fluorescent and hence the spectrum showed an appreciable background. Even so, the N-H frequencies in the 3000 region were very clearly recorded, the spectrum differing in this respect from that reported by Kohlrausch and Pongratz (1934) for the molten substance.

TABLE VII.

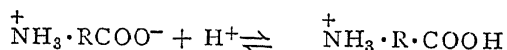
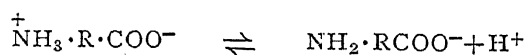
Kohlrausch and Pongratz (molten, 80°)	269	453	555	807	997	1056	1131	1244	1291	1413
	2b	3b	2b	8b	3b	3b	4b	2b	1	4b
	1453	1606	1664 ± 13	1691	2848	2913	2942			
	4b	2b	4b	2	2	5	5b			
Author (crystal)	820	1145	1418	1594	2742	2850?	2897	2942	3173	3356
	4s	5s	5s	1d	½d	0	3s	8s	4d	3d

The N-H bands are practically in the same position as in acetamide, and suggest resonance of a similar nature in this case also. The agreement between the C-H frequencies of the solid with those of the molten substance is fairly good, although their relative intensities seem to be somewhat different in the two states.

7. *Amino-acetic acid (Glycocoll)*, $\text{H}_2\text{N} \cdot \text{CH}_2 \cdot \text{COOH}$. This is the simplest member of a homologous series of acids characterised by very exceptional properties. All the compounds of this series belong to the so-called class of *amphoteric electrolytes*, *i.e.*, substances that possess both basic and acidic properties. Study of the dielectric constants of aqueous solutions of these acids has furnished the most crucial evidence in favour of the view originally put forth by Bjerrum (1922) that the aliphatic-amino-acids in the undissociated state exist practically entirely as salt-like "zwitter ions" or dipolar ions, $\text{NH}_3^+ \cdot \text{R} \cdot \text{COO}^-$. They are therefore characterised by the

possession of large permanent electric moments. According to Bjerrum, the amino-acids are far from being acids in the usual sense of the term; they are more correctly pictured as ammonium salts.

When an amino-acid is dissolved in water, the reactions taking place are as follows:



We see that the acid character of the amino-acid is supplied by the substituted ammonium group, while the carboxyl end of the molecule is responsible for its basic nature.

Because of the many interesting properties of the amino-acids outlined above, their Raman spectra in the solid state and as aqueous solutions are of great interest. Some results in this connection have been published recently by Edsall (1936). He has studied a number of amino-acids in aqueous solution, and has found that in all cases the characteristic carbonyl group frequency in the 1700 region is absent in them. The corresponding frequency, however, appeared strongly in the spectra of aqueous solutions of the hydrochlorides of all the amino-acids studied by him. From this Edsall has

concluded that the carbonyl group $\text{—C} \begin{smallmatrix} \nearrow \text{O} \\ \searrow \text{OH} \end{smallmatrix}$ is absent in the free acid, which

shows that neutral amino-acids in aqueous solution exist as "zwitter ions" $^+\text{NH}_3 \cdot \text{R} \cdot \text{COO}^-$. The hydrochlorides, on the other hand, have the configuration $\text{Cl}^- \cdot ^+\text{NH}_3 \cdot \text{R} \cdot \text{COOH}$ so that the carbonyl group frequency comes out in the spectra of the amino-acid cations. Edsall has also examined the Raman spectrum of amino-acetic acid in the crystalline state; his results do not show any striking difference between the spectrum of the crystals and that of the aqueous solution.

In a more recent communication, Kahovec and Kohlrausch (1936) have reported the Raman spectra of the aqueous solution and crystals of amino-acetic acid. They have found certain discrepancies between their results and those of Edsall. It is therefore of interest to compare the results obtained in the present investigation with the frequencies observed by the previous workers.

TABLE VIII.

Aqueous solution		Crystalline		
Edsall	Kahovec and Kohlrausch	Edsall	Kahovec and Kohlrausch	Author
..	236 (0)
508 (2b)	498 (1)	507 ($\frac{1}{2}$)	..	507 (1)
590 (1)	587 (1)	598 (1)
665 (1)	709 ($\frac{1}{2}$)
..	800 (0)
897 (3)	891 (2)	891 (2)	870 (4)	893 (5s)
1033 (1)	1029 (2)	1033 (1)	1020 (2)	1047 (2s)
1122 (1)	1099 (3)	1112 ($\frac{1}{2}$)	1130 (2)	{ 1121 (1s)
..	1210 (0)	{ 1132 ($\frac{1}{2}$ d)
1331 (3)	1348 (3)	1323 (3)	1320 (7)	{ 1319 (4d)
1412 (3)	1407 (3b)	1404 (3)	1400 (4)	{ 1336 (6d)
1491 (0)	..	1436 (3)	1440 (2)	1397 (4b)
..	1510 (1)	1437 (4s)
..	1570 (1)	1499 (1bd)
1630 (1vb)	1624 ($\frac{1}{2}$) (doublet)	..	1650 ($\frac{1}{2}$)	1577 (1d)
..	1650 ($\frac{1}{2}$ d)
..	2592 ($\frac{1}{2}$ d)
2978 (3b)	2972 (00)	2968 (3)	2960 (3)	2870 (1d)
3018 (1)	..	3002 (1)	..	2959 (10)
..	2999 (8s)
..	3113 (3bd)

Table VIII brings out a number of interesting features. In the first place, we see that the crystal frequencies reported previously are very incomplete indeed. Kahovec and Kohlrausch explained the discrepancy between their results and those of Edsall by pointing out the extreme difficulty of obtaining good photographs of the Raman spectra of crystal powders. The technique of complementary filters completely overcomes all these difficulties, and it is therefore not surprising that both in the matter of the relative intensities of the lines as well as in their total number, the author's results differ from those of Edsall and of Kohlrausch.

Edsall in a recent note (1936) on the Raman spectra of amines and methylated ammonium ions, has pointed out that while the free primary and secondary amines $R \cdot NH_2$ and $RR' \cdot NH$ give one or two intense Raman lines between 3300 and 3400 cm^{-1} , presumably associated with the unionised N-H bond, the corresponding ammonium chlorides $[R \cdot NH_3]^+ Cl^-$, $[RR' \cdot NH_2]^+ Cl^-$, $[RR'R'' \cdot NH]^+ Cl^-$ in which the amino group has acquired a proton show no Raman frequencies above 3050 cm^{-1} . He appears to have arrived at this conclusion by the study of the spectra of the aqueous solutions of the chlorides. Conversely, he has concluded that since the isoelectric

amino-acids show no Raman frequencies above 3030 cm.^{-1} , it clearly follows that the amino group in these acids is electrically charged.

As has been already explained, the author found from a study of the spectra of the crystalline salts of ammonium, hydroxylamine and hydrazine that the N-H frequencies observed in these compounds in which the covalency of nitrogen is four, are much lower compared with the N-H frequencies observed in the amines wherein nitrogen is trivalent. The N-H frequencies of crystalline amino-acetic acid are of interest in this connection. The three diffuse bands $2592(\frac{1}{2}d)$, $2870(1d)$ and $3133(3bd)$ observed in the spectrum of this substance are presumably N-H frequencies, and fall within the limit (2500 to 3200 cm.^{-1}) of the N-H frequencies formerly observed by the author in the case of compounds in which the covalency of nitrogen is four. *This is therefore positive evidence that there is no free amino group in crystalline amino-acetic acid, and that the constitution of the free acid is*

$$H_3\overset{|}{N}\cdot CH_2\cdot COO^-.$$

The failure of Edsall and of Kahovec and Kohlrausch to observe any of the above N-H frequencies in the spectrum of crystalline amino-acetic acid is in all probability due to the inferior quality of the powder photographs obtained by them. On the other hand, the absence of the N-H frequencies in aqueous solutions of this acid is of significance. In a series of papers Freymann and Freymann (1936) have recently reported the interesting result of what they call 'the dissimulation of the N-H frequencies in the case of tetra-covalent nitrogen compounds'. From their investigation of the Raman spectra as well as the near infra-red absorption spectra of aqueous solutions of a number of nitrogen compounds, these authors arrived at the very general conclusion that the N-H frequencies in the 3μ region, while quite intense in all those compounds wherein nitrogen is three-covalent, are completely absent in all those compounds in which nitrogen is four-covalent. They also pointed out that on account of the quite general nature of this result, the presence or absence of the 3μ N-H bands in a nitrogen compound can be expected to furnish important information regarding its constitution. These conclusions are practically identical with those of Edsall.

We have, however, to bear in mind the important fact noticed by the present author, that the N-H frequencies are actually lowered from their normal values in the primary and secondary amines, in the tetra-covalent nitrogen compounds. In a previous paper (1937) the author also remarked that these lowered frequencies in four-covalent nitrogen compounds are considerably weakened or otherwise perturbed in aqueous solutions. Their

complete disappearance is a point about which the author is not quite certain. Freymann and Freymann assume the entire disappearance of the N-H frequencies in aqueous solutions of four-covalent nitrogen compounds such as NH_4Cl , and postulate that this result can probably be only explained by assuming that the N-H bonds which are covalent in the crystalline state, become electrovalent in solution. This is a point which the author shall not go into in the present communication. It might be of interest to point out that the frequency 1577 observed in the crystal is absent in the aqueous solution. This is presumably a δ (N-H) frequency.

8. *Phenyl acetic acid*, $\text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{COOH}$. As far as the author is aware, the Raman spectrum of this substance has been studied only by Kohlrausch and Pongratz (1934). These authors have reported the spectrum of the molten substance, which agrees reasonably well with the author's frequencies for the crystalline solid.

TABLE IX.

Kohlrausch and Pongratz (molten)	245 3b	470 2	616 4	751 4	845 4	893 1b	—	998 10	1029 4	1161 1	1188 4	—	—
Author (crystal)	—	—	624 1s	748 3s	840 4s	890 $\frac{1}{2}$	925 $\frac{1}{2}$ d	1003 10s	1032 6s	—	1188 4s	1234 3	1338 1
Kohlrausch and Pongratz	1400 1b	—	1593 6b	1662 \pm 7 1b	—	2924 1	—	2981 0	—	—	—	3055 3	—
Author	1402 1	1432 $\frac{1}{2}$ d	1585 2	1600 3	—	2920 6	2952 1	2986 $\frac{1}{2}$	3013 $\frac{1}{2}$	3035 $\frac{1}{2}$	3063 12	—	—

However, many new frequencies have been observed in the solid spectrum, and we notice also remarkable differences between the spectra of the solid and molten substance in the region of the hydrogen frequencies. This emphasises once again the susceptibility of the hydrogen frequencies to external influences such as change of state, temperature, etc., which is presumably much more pronounced here on account of the polar nature of the substance.

9, 10. *Phosphorous acid and Sodium phosphite*, H_3PO_3 and Na_2HPO_3 . The information furnished by the Raman spectra of these two substances relating to the question of the constitution of phosphorous acid and the phosphites, has already been briefly reported by the author in a recent note in *Nature* (1936). Before going into the question in somewhat greater detail

it might be of interest to compare the author's results on the Raman spectra of these two substances with the frequencies observed by Ghosh and Das (1932) for the corresponding aqueous solutions.

TABLE X.

Ghosh and Das (H ₃ PO ₃ aq.)	672 5b	940 4	1012 2			
Author (H ₃ PO ₃ crystal)	961 6s	990 3d	1038 2	1104 1d	2485 8s	2511 7s
Ghosh and Das (Na ₂ HPO ₃ aq.)	978 3		1030 1			
Author (Na ₂ HPO ₃ crystal)	961 3s		1046 1	1057 1	2338 6s	

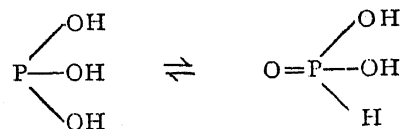
The strong Raman frequency 672(5b) reported by the latter authors in the spectrum of H₃PO₃ solution is most probably incorrect since there is not even a trace of it in the spectrum of the crystalline acid. The author is inclined to believe that there is a mistake in the assignment of Ghosh and Das in the case of this line. The wavenumber as reported by them is 22265, and if the line is assumed to originate from λ 4046 excitation instead of λ 4358 as these authors suppose, the corresponding frequency shift works out as $\Delta\nu = 2440 \text{ cm.}^{-1}$, which is near the frequency shift of the Raman doublet observed by the author in the crystal spectrum. Ghosh and Das do not seem to have observed the most intense Raman frequency at 2338 cm.^{-1} observed by the author in the case of sodium phosphite.

From the chemical standpoint, the constitution of phosphorous acid has been a long-disputed problem. This is because of the rather conflicting nature of the chemical evidence in this case. The mode of formation of the acid from PCl₃ and water as represented by the equation

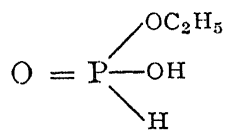


suggests that the acid is tri-basic, and that all the three -OH groups are identically linked to the phosphorus atom. Nevertheless, it has been known from long since that the acid is only dibasic, *i.e.*, only two atoms of hydrogen can be replaced by metals to form salts (NaH₂PO₃ and Na₂HPO₃). In order to explain this apparent anomaly, it has been generally assumed that

in the process of formation of the acid from PCl_3 and H_2O , it undergoes the tautomeric change

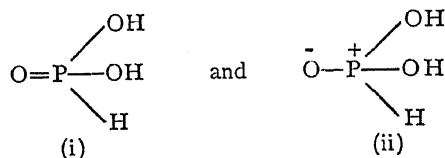


While the existence of two ethyl phosphorous acids $\text{O} = \text{P} \begin{array}{l} \diagup \text{OH} \\ \diagdown \text{C}_2\text{H}_5 \end{array}$ and



supports the asymmetric formula of the acid, normal esters of phosphorous acids of the type $\text{P}(\text{OC}_2\text{H}_5)_3$ are also known, which can be adduced as evidence in favour of the symmetric form.

The Raman spectra of phosphorous acid and sodium phosphite furnish valuable evidence regarding the constitution of the acid. In both these compounds, Raman frequencies are observed in the 2400 region, which can presumably arise only from a P-H oscillation. Thus, *the presence of a P-H linkage in phosphorous acid is definitely established, so that the symmetric configuration of the acid has to be ruled out.* We have only to decide between the two alternative Lewis structures



It is probable that formula (i) gives the correct picture. According to Pauling (1933), the molecules of oxygen acids can be represented as containing either covalent bonds or ionic bonds, and their properties are best understood by considering both the extreme cases. Pauling has also remarked that the ionic extreme can be considered to be more closely approached in the case of those oxygen acids in which the highest valency of the element comes into play such as H_2SO_4 , H_3PO_4 , etc., while in oxygen acids of elements in their lower valency states such as H_3PO_3 , H_2SO_3 , etc., the covalent character of the bonds is more pronounced. The present investigation, however, clearly shows that phosphorus in H_3PO_3 is certainly in its highest valency state.

Recently, Redlich, Kurz and Stricks (1936) have examined the Raman spectrum of the hypophosphite ion $(\text{H}_2\text{PO}_2)^-$ in aqueous solutions of sodium hypophosphite. Unfortunately, the author has been unable to see

their original paper, but from the brief summary of their results in *Physikalische Berichte* (1936, **17**, 2075), there appears to exist some similarity between the spectrum of this ion with the spectra of phosphorous acid and sodium phosphite reported in the present paper. This is probably due to the fact that the constitution of hypophosphorous acid is represented by the

formula
$$\text{O} = \text{P} \begin{array}{c} \diagup \text{H} \\ \text{---} \text{OH} \\ \diagdown \text{H} \end{array}$$
 Two frequencies 2358(4b) and 2450(1) have been

observed by the above authors in the spectrum of the hypophosphite ion which indicates the existence of two P-H linkages. While only one Raman line is observed in the 2400 region in the spectrum of sodium phosphite a sharp and well-separated doublet appears in the spectrum of crystalline phosphorous acid. Since these compounds contain only one P-H linkage this can only mean that the P-H frequency is split up in the case of the acid.

11. *Phosphoric acid, H_3PO_4* . The crystalline acid was badly fluorescent so that the spectrum showed an intense background. Only two Raman lines could be distinguished whose frequency shifts are given in Table I. In the case of the 1100 frequency, there is a partial superposition of the Raman line 919 due to $\lambda 4078$ excitation. Since the spectrum of this acid has been discussed previously by various authors, it is not necessary to consider it any further.

12. *Boric acid, $\text{B}(\text{OH})_3$* . The Raman spectrum of an aqueous solution of boric acid was examined by the author on a former occasion; because of the intense fluorescence, only one frequency 875 cm^{-1} could be identified. The spectrum of the crystalline acid shows in addition to this line two rather diffuse bands at 3172 and 3256 cm^{-1} , presumably arising from the O-H oscillations. This is of interest in connection with a recent paper of Rein and Megaw (1935) dealing with the function of hydrogen in intermolecular forces. They have distinguished between two kinds of bonds between hydrogen and oxygen, the *hydrogen bond* and the *hydroxyl bond*. In oxyacids of the type $\text{XO}_n(\text{OH})_m$, e.g., H_2SO_4 , the bond between O and H is the hydrogen bond so that the hydrogen ion can migrate to a neighbouring oxygen atom. This possibility of migration does not exist in hydroxyacids of the type $\text{X}(\text{OH})_m$, so that the bond in such cases is a hydroxyl bond. The above authors have pointed out the absence of the O-H frequency in Raman spectra of the acids of the former type as evidence for the presence of the hydrogen bond in them. They have also remarked that hydroxy bonds should be present in crystalline boric acid; the present investigation

confirms this view. It is, however, noteworthy that the O-H frequencies observed in this case are somewhat lower than those generally observed in the alkali hydroxides.

In conclusion, the author's grateful thanks are due to Professor Sir C. V. Raman for his kind interest in the present work.

Summary.

Employing the technique of complementary filters recently described by the author, the Raman spectra of naphthalene, oxalic acid dihydrate, urea, guanidine hydrochloride, acetamide, propionamide, amino-acetic acid, phenyl acetic acid, phosphorous acid, sodium phosphite, phosphoric acid, and boric acid have been studied in the crystalline state. The results are discussed at some length in relation to the work of previous investigators on the Raman spectra of these compounds in solution or in the molten state. Naphthalene crystals give an intense spectrum consisting of very sharp lines. Many new frequencies have been observed in the spectrum of the crystals. The crystal spectrum shows certain differences in the region of the C-H frequencies when compared with the spectrum of molten naphthalene. Two strong bands in the 3400 region have been recorded in the spectrum of oxalic acid dihydrate in addition to the frequencies hitherto reported for this substance. These bands are due to the O-H oscillation of the water molecules.

The spectrum of crystalline urea shows certain characteristic differences when compared with the spectrum of its aqueous solution. An intense sharp line at 1012 cm.^{-1} in the crystal shifts to 1000 cm.^{-1} in the solution. A frequency at 1537 which is strong in the crystal spectrum is absent in the spectrum of the aqueous solution. Since disappearance of such sharp and intense lines in this frequency region has been formerly noticed by the author in the case of the crystalline salts of hydroxylamine and hydrazine on dissolving them in water, it is concluded that this is a $\delta(\text{N-H})$ frequency. The N-H valence frequencies of crystalline urea consist of four bands $3243(2d)$, $3324(4d)$, $3353(5d)$ and $3434(5)$. The spectrum of the guanidonium ion in guanidine hydrochloride crystals shows a close similarity with the spectrum of urea. The intense Raman line at 1006 cm.^{-1} in the crystal shifts to 995 cm.^{-1} in solution. A strong frequency $1554(5)$ in the crystal apparently disappears on dissolving the substance in water. This is therefore considered as a $\delta(\text{N-H})$ frequency. The N-H valence frequencies in the crystal consist of a number of bands extending from 3170 to 3430 wave-numbers. It is pointed out that the Pauling double bond resonance

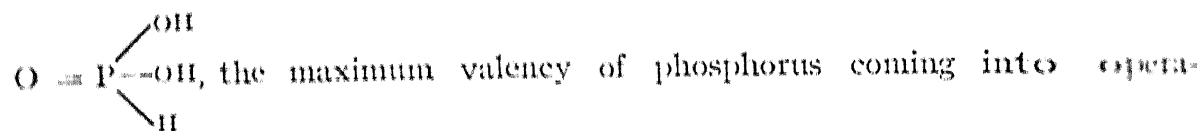
structure of urea and the guanidonium ion enables one to understand the observed similarity between their spectra.

The N-H frequencies are strongly recorded in the spectra of crystalline acetamide and propionamide. This is an interesting result in view of the fact that Kohlrausch and Pongratz have reported the complete absence of N-H frequencies in the Raman spectra of these amides in the molten state. The N-H frequencies are practically identical in the spectra of acetamide and propionamide, and consist mainly of two intense bands 3150(6*b*), and 3350(4*b*). While the frequency shift of the second band falls in the region of the N-H frequencies observed in the case of primary and secondary amines, the frequency of the first one is much less, and falls in the frequency interval (2005 to 3200 cm.⁻¹) of the N-H frequencies observed by the author in the tetra-covalent nitrogen compounds. It is pointed out that this fact lends strong support to the resonance structure in the case of amides

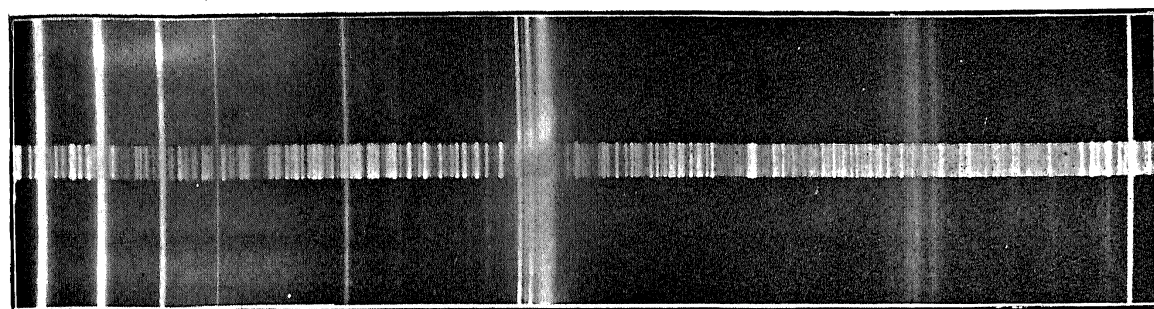


The spectrum of crystalline amino-acetic acid reported here differs in certain important respects from the spectra of the crystalline acid and its aqueous solution reported by previous investigators. No N-H frequencies are observed in the 3300 region in the spectrum of this substance, but three diffuse bands 2592($\frac{1}{2}$ *d*), 2870(1*d*), 3113(3*d*) are observed in the spectrum of the crystalline acid, which presumably arise from N-H oscillations. This shows that nitrogen is tetra-covalent in crystalline amino-acetic acid, and hence that the molecules of the crystalline acid exist as "zwitter ions" (Bjerrum), $\text{NH}_3^+ \cdot \text{CH}_2 \cdot \text{COO}^-$ —a result amply confirmed from various other sources.

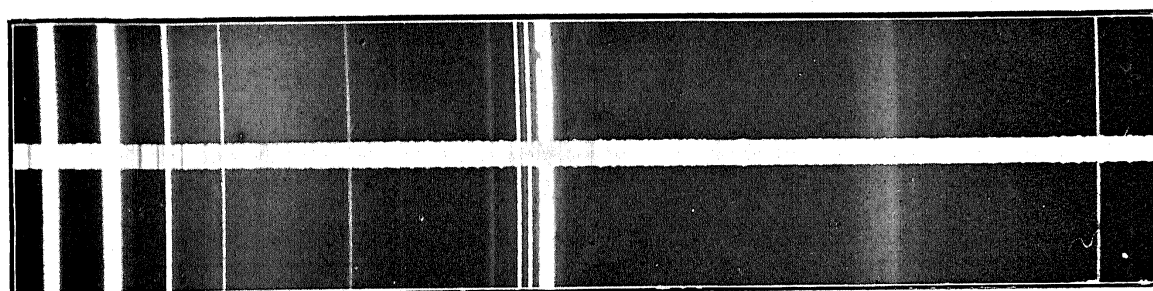
Phosphorous acid and sodium phosphite show P-H frequencies in the 2400 region, from which it is concluded that the constitution of the acid is



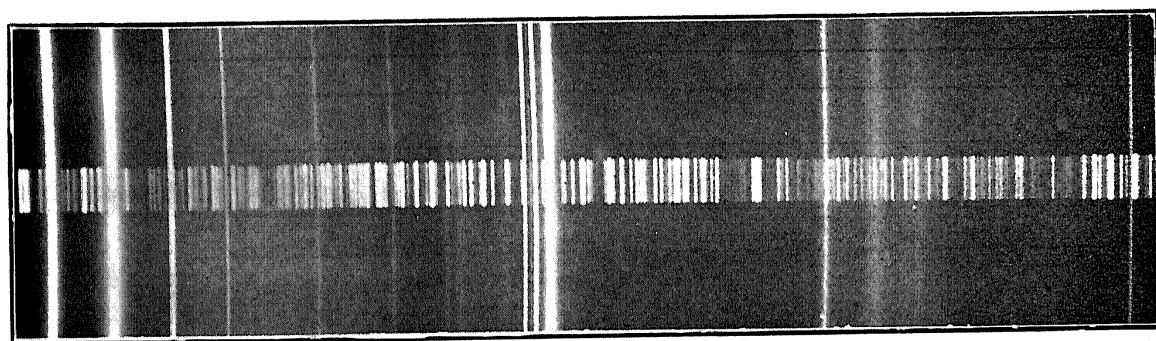
In contrast to the numerous oxy-acids, boric acid shows O-H frequencies in the 3200 region. This confirms the view of Bernal and Megaw that the bonds between O and H in acids of the former type are hydrogen bonds, while in hydroxy-acids such as B(OH)₃, hydroxyl bonds are present.



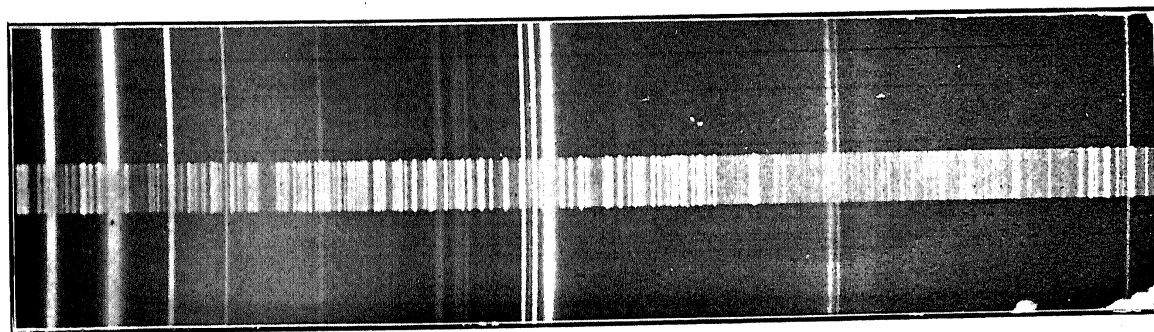
Urea
 $\text{OC} \cdot (\text{NH}_2)_2$



Guanidine hydro-
chloride.
 $\left[\text{HN}=\text{C} \begin{array}{l} \nearrow \text{NH}_2 \\ \searrow \text{NH}_2 \end{array} \right] \cdot \text{HCl}$



Acetamide
 $\text{H}_3\text{C} \cdot \text{CO} \cdot \text{NH}_2$



Glycocoll
 $\text{H}_2\text{N} \cdot \text{CH}_2 \cdot \text{COOH}$

FIG. 1. Raman Spectra of Crystal Powders.