Raman Effect in Some Organic and Inorganic Substances

By

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(Plates II and III).

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ABSTRACT.

The paper describes the results of a study of the Raman spectra of several organic and inorganic substances, namely urea, ethyl formate, ethyl malonate, ethyl acetoacetate, ethyl monochloroacetate, ethyl carbonate, potassium and ammonium thiocyanates, phenyl isothiocyanate, potassium cyanide, potassium cyanate, double cyanide of silver and potassium, methyl cyanide, aniline, phenylhydrazine, hydrazine hydrate, benzaldehyde and formaldehyde.

Aniline and phenyl hydrazine darken in air under the action of light, thus rendering the study of the scattering of light in them extremely difficult. The difficulty has been successfully overcome by distilling these liquids into the observation tube in vacuo. Under these conditions, the liquids do not develop colour and the Raman lines come out strongly, unaccompanied by a continuous spectrum. Other liquids, e.g., benzaldehyde, give a continuous spectrum even in the absence of air.

The cyanides give two Raman frequencies of about 836 and 2080 which are presumably characteristic of the cyanogen ion. It is remarkable that

the frequency 756 appearing in phenyl isothiocyanate which may be attributed to C=S does not differ appreciably from that of C-S in the thiocyanates, viz., 741.

It is suggested that the production of continuous spectrum accompanying the Raman lines is due to the photochemical action of the light causing the molecules themselves (or their reaction products) to dissociate into parts having a distributed range of kinetic energies.

1. Introduction.

The discovery of the Raman Effect, apart from its theoretical importance, has opened up a new method of investigating molecular spectra in the infra-red region with comparative ease and accuracy. A large number of substances has already been investigated for their Raman scattering and an attempt has been made to determine the influence of chemical structure upon the Raman spectra. It has been found that, although each substance shows its own characteristic Raman spectrum, certain similarities are noticeable in the spectra of compounds having similar chemical composition. tance, it has been found that all aromatic compounds containing a carbon-hydrogen linkage, show prominently a modified line in identically the same position, corresponding to the frequency shift 3060 wave numbers, which has therefore been identified to be the natural frequency of the aromatic C-H bond. Similarly the frequency 2940 has been identified as due to the oscillation of the aliphatic C-H bond. and Venkateswaran, and recently Dadieu and Kohlrausch have carried out elaborate investigations of the Raman spectra of a large number of substances from this point of view and have been able to isolate the oscillation frequencies of a number of chemical bonds.

¹ Ind. Journ. Phys., Vol. IV, p. 195, 1929.

Sitz. Akd. Wiss. Wien, Vol. 188, pp. 41, 335, 419, 607, 635.

The present paper describes an investigation of the Raman spectra of ā number of organic and inorganic substances and a discussion of the results in relation to their chemical structure. The paper also contains a description of a new method of studying the Raman spectra of liquids that rapidly darken in air under the action of light.

2. Experimental Method.

The investigation was carried out by an arrangement similar to the one described by Wood. A quartz mercury vapour lamp of 3000 C.P., made by Heraus, was used as the source of illumination and the spectrum of the scattered light was taken with a Constant Deviation Spectrograph, using Ilford's Iso-Zenith (H &D 700) or Soft-Gradation Panchromatic plates. The time of exposure varied from one to six hours for different substances. Kahlbaum's pure substances and in some cases Merck's extra pure chemicals were used. Further purification was made, wherever found necessary, in the way indicated later on. The wave lengths were calculated by Hartmann's simplified interpolation formula, using the mercury lines as standards for reference and in some cases by means of a copper comparison spectrum.

3. Results.

Urea. (TABLE I).

Saturated solution of urea in water was investigated for its Raman scattering. It gives a number of lines, of which those corresponding to the frequency shift of 1000 wave numbers are very prominent. The origin of this frequency is not understood.

¹ R. W. Wood. Phil. Mag., Vol. VI, p. 729, Oct. 1928.

Esters. (TABLES II-VI).

Five esters have been studied, namely, ethyl formate, ethyl malonate, ethyl acetoacetate, ethyl monochloroacetate and ethyl carbonate. In all of them the modified lines corresponding to the Raman shifts 2930 and 2970 come out very prominent. As a close companion of this group there also appears a weak line corresponding to the shift 2878. There is a small continuous spectrum present in the scattering by most of the esters; which is particularly marked in ethyl malonate and ethyl acetoacetate.

Potassium and Ammonium Thiocynates and Phenyl Isothiocyanates.

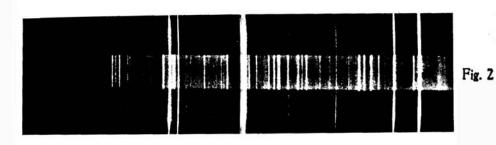
(TABLES VII AND VIII.)

Saturated aqueous solutions of potassium and ammonium thiocyanates have been investigated. Both of them show eight modified lines in exactly the same positions, corresponding to the frequency shifts 2060 and 738; which are evidently due to the -S-C-N ion. The lines corresponding to the shift of 2060 come out to be very prominent; in fact the one excited by 4358 A.U. is even stronger than the mercury line 4916 A.U. appearing on the plate.

In order to investigate the influence of isomerism of the SCN group on its Raman frequencies, freshly distilled phenyl mustard oil was studied. As many as 24 lines have been obtained some of which are sufficiently strong to be seen visually through the spectroscope. Several of them coincide in position with the lines of the benzene spectrum, and are evidently due to the phenyl group. Among the other Raman radiations of this liquid, the broad band corresponding to a shift of about 2056 wave numbers, and the line shifted by 756 may be specially mentioned as they seem to have their origin in the -N = C = S group.

Raman Spectra





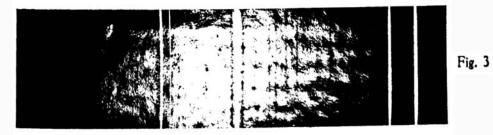


Fig. 1-Potassium thiocyanate

Fig. 2-Acetonitrile

Fig. 3-Aniline.

Cyanides and Cyanates (Tables IX-XII)

Potassium cyanide and cyanate were studied in solution in water, and double cyanide of silver and potassium in solution containing slight excess of KCN; one organic cyanide was also investigated viz., methyl cyanide.

Potassium cyanide gives two Raman frequencies 836 and 2080 which are presumably due to the CN ion; these frequencies appear also in the scattering by the other substances, but in slightly different positions. Potassium cyanate has, in addition two other frequencies, 1229 and 1314, while methyl cyanide shows several.

Aniline (Table XIII)

The fact that aniline quickly darkens in air under the action of light with the consequent absorption in the violet, renders the study of its Raman scattering extremely difficult. Owing to this cause, Fujioka was not able to obtain any Raman lines at all with this liquid. Dadieu and Kohlrausch and Bonino and Brull used freshly purified aniline and changed the liquid every fifteen minutes. Even with these precautions the Raman lines which they obtained were very faint. On the other hand we find that if the liquid is distilled and studied for its scattering in vacuum, it does not show any appreciable tendency to darken even after several hours exposure to the light of the mercury arc. In our investigations with this and other similar liquids, a distilling flask was attached to the horn end of the Wood's tube. After introducing the necessary amount of liquid the apparatus

Inst. Phys. Chem. Research, Tokyo, Vol. 11, pp. 205-222, 1923.

Sitz- Akd. Wiss. Wien., Vol. 138, p. 341, 1929

Gazetta Chemica Italiana, Vol. 59 p. 668, 1929

was connected to a pump and while it was being exhausted, the liquid was kept boiling vigorously to drive off traces of air from the apparatus; it was then sealed off from the pump. The liquid was then distilled over 'to the Wood's tube and after washing the latter with the distillate once or twice and transferring back to the flask it was allowed to fill it up. The distilled aniline was perfectly colourless, and remained so even after three hours exposure to the intense light of the arc used for the investigation of its scattering. Under these conditions the Raman lines of aniline came out very prominently with no trace of the continuous spectrum, which is so conspicuous in the scattering of aniline when it is kept exposed to air.

Phenyl Hydrazine (Table XIV)

Like aniline phenyl hydrazine also quickly gets coloured in air under the action of light. We therefore, studied its scattering by the same method as described in the case of aniline. The liquid was distilled in vacuum at about 150-155°C. and a slightly straw coloured liquid was obtained in the Wood's tube. A good spectrogram was obtained on a three hours exposure, with no appreciable amount of continuous spectrum. The liquid did not darken even on a very long exposure. As many as 18 lines have been obtained some of which are very prominent and coincide in positions with those in aniline.

Hydrazine Hydrate (Table X V)

A 90% solution of hydrazine in water was studied. A few lines which are more or less diffuse, have been obtained upon a continuous background. There is a close doublet corresponding to frequency shifts 3215-75 wave numbers.

Benzaldehyde (Table XVII)

Benzaldehyde offered the same difficulties as experienced in the case of aniline, and the same method was therefore adopted for its investigation. The liquid was distilled in vacuo at 120°C., and a perfectly colourless distillate was collected in the Wood's tube. We have obtained as many as 37 lines which are very sharp and some of them very intense. The sharpness of the modified lines seems to be a remarkable characteristic of this liquid. In this particular case, however, the exclusion of all traces of air does not seem to prevent completely the darkening of the liquid under the influence of the intense light of the arc. There is always an appreciable continuous background in the scattered spectrum, which seems to get more and more prominent as the liquid darkens.

Formaldehyde (Table XVI)

An 80% aqueous solution of formaldehyde was used for the investigation. A number of lines have been obtained which are more or less diffuse.

4. Discussion of Results.

It has already been mentioned in the introduction that associated with each type of chemical bond, there appear in the various molecules containing such a bond certain well-defined Raman frequencies characteristic of it. Probably, the best example of such a persistence of the frequencies in different compounds where the same group appears, is afforded by a study of the various derivatives of benzene. Almost all the lines appearing in the scattering by benzene liquid are

Sitz. Akd. Wiss. Wien., Vol. 138 p. 340, 1929

also present in general in that of all the aromatic compounds, as can be easily seen from the Tables given in the previous section.

An equally striking example is the prominent group of three frequencies, 2878, 2930 and 2970, which are common to all the ethyl esters. This group has been identified by Ganesan and Venkateswaran as due to the aliphatic C-H linkage and they further point out that as we proceed to higher members in any series of aliphatic compounds containing hydrogen this group becomes more complex, splitting in some cases into as many as five components more or less equally spaced. In connection with this remark it is significant that in the case of the simple compounds like methyl cyanide and formaldehyde which have been investigated by us there is only one line representative of this group. The frequency 1440 always accompanies the above group of lines and is presumably also to be attributed to the same origin.2 Corresponding to the above group of lines in the aliphatic series, the aromatics also show a line at about 3060 due to the aromatic C-H bond.

In view of the appreciable difference in frequency of oscillation of the aliphatic and aromatic carbon atoms, we would naturally expect the frequencies corresponding to a linkage between any two given atoms to be widely different, according as the bond between them is single, double or triple. But the results obtained with $-S-C\equiv N$ and $S=C\equiv N$ - gives us a pause here. The frequency 756 in phenyl mustard oil which is presumably due to $C\equiv S$ bond, as is evidenced by its appearance also in CS_2 , does not differ appreciably from that of the C-S bond in the thiocyanates, viz., 741. Regarding the linkage between the C and N atoms, however, though the

Ind. Journ. Phys., Vol. IV, pp. 195-280, 1989.

[†] Sitz. Akd. Wiss. Wien. Vol. 138, p. 607, 635, 1929.

Ind. Journ. Phys., Vol. IV, p. 253, 1929.

absolute value of the frequency does not seem to depend on whether the bond is triple or double, the spectral characters of the radiations corresponding to the two bonds seem to be quite different; whereas in the former case, i.e., $C \equiv N$, the radiation is very sharp, (not only in the case of the thiocyanates but also in the scattering by the cyanides and cyanates investigated by us) the double bonded C = N of phenyl mustard oil gives a very broad band extending over nearly 120 wave numbers.

The statements made in the previous paragraphs may suggest that the Raman lines corresponding to C=N appear in the same position in the various cyanides cyanates, and thiocyanates. Strictly speaking, it is far from being the case. They vary to some extent from compound to compound which is probably what is to be expected, since the oscillation of a bond will not be quite unaffected by the positions and masses of the neighbouring atoms of the molecule. But if this were the explanation, we should further find that in the simplest case of the C=N ion in potassium cyanide solution, the frequency should be the one really characteristic of the bond, and that in other cases, e.g., Ag(CN)2 ion, due to the loading of either of the atoms C and N by the neighbouring ones, the frequency of oscillation must be diminished. But as a matter of fact the reverse is the case. The frequency of the C≡N bond is almost a minimum in the case of KCN and greatest in the case of acetonitrile, KAg(CN)₂ coming intermediate. The exact significance of this order is difficult to understand.

Finally we come to the N-H bond. The frequency 3358 in aniline, that of the doublet 3215, 3275 in hydrazine hydrate, and 3226 and 3374 in urea are attributable to it. In support of this assignment of frequencies we may evidence the results obtained by Carelli. Pringsheim, and Rosen¹ on light scattering by solution of ammonia in water which gives also two

¹ Zeits. f. Phys. Vol. 51, p. 511, 1928.

frequencies in comparable positions, viz., 3331 and 3389. The singlet value of this frequency in some compounds, e.g., aniline, and its duplexity in others are probably to be attributed to the same cause which determines the complexity or otherwise of the analogous C—H bond in the different aliphatic compounds discussed in an earlier part of this section.

5. Continuous Spectrum.

We should add a few words regarding the continuous spectrum that generally appears in the scattered spectra of most of the substances studied for their Raman scattering. That it is really a characteristic of the substance and not due to impurities is evident from the fact that it is exhibited by even the purest liquid, purified by a slow distillation in vacuum. Venkateswaran 1 tried to connect it with the viscosity of the substance. During our investigations with aniline, phenyl hydrazine, benzaldehyde, guanidine, etc., we have been led to form a different view of the phenomena. We have observed that the continuous spectrum is markedly developed in substances which are sensitive to light; the presence of photochemical changes being in most cases evident by the change of colour of the substance during an exposure. In some cases the induced changes require the presence of air and the continuous spectrum in those cases increases in intensity with time, i.e., with the increase of concentration of the intermediate compound. There is, however, a further category in which light can act on the substance directly and changes seem to proceed even in vacuum. We have observed that in certain cases the continuous spectrum may be almost completely suppressed by removing air, as in the case of aniline and phenyl hydrazine. In the case of benzaldehyde, however, we have found that the changes in colour go on even in vacuum and

¹ Ind. Journ. Phys., Vol. III, p. 105, 1028.

we have convinced ourselves, by taking different exposures, that the continuous spectrum does actually increase with time, *i.e.*, with the increased concentration of the product of photochemical reaction.

In the case of aqueous solutions of certain substances which are not appreciably viscous we have also found the continuous spectrum developed in considerable intensity. The case of guanidine is very characteristic: even a moderate concentration introduces an intense continuous spectrum.

We suggest a mechanism of the production of the continuous spectrum, somewhat on the same lines as the explanation of the continuous spectrum in hydrogen given by Blackett and Franck.¹ Either the molecule itself or the product of the photochemical reaction can go to an excited state involving large electronic energy change; the total energy thus absorbed exceeds the energy of molecular dissociation by a large amount. It is then clear that the final state may be a dissociated molecule with parts having various kinetic energies relative to one another. The initial state is discrete, whereas, the final state corresponds to continuously distributed energy levels. The resultant radiation will thus have a sharp violet edge and will continue far in the red end, which is usually observed in most cases.

The absence of continuous spectrum in aniline, etc. may be explained by saying that it is the first product of reaction which further breaks down under the action of light. The absence of air suppresses the first chemical reaction and suppresses the continuous spectrum also. In other molecules, the action of light may consist in an immediate partial disintegration of the molecules even in vacuum, or the photochemically sensitive product may not depend upon the presence of air at all for its formation. In this connection it is interesting to note the similarity of our

Zeits. f. Phys., Vol. 34, p. 889, 1925.

explanation with the ideas of Perrin¹ about the origin of fluorescence.

Since the paper was sent to press we have been studing in detail the Raman Spectra of liquids like benzaldehyde which darken under the action of light even in vacuum. By maintaining a continual flow of distilled liquid through the Wood tube (which is done with the help of a specially constructed distillation apparatus) we have been able to completely eliminate the continuous spectrum. The details of the experimental arrangement and the significance of the results obtained to the explanation of the continuous spectrum briefly outlined in this paper, are reserved for separate publication.

In conclusion we wish to express our sincerest thanks to Prof. S. N. Bose for his kindly suggesting the problem and helpful guidance during the progress of the work. Our thanks are also due to Mr. K. S. Krishnan for his many valuable suggestions and kind interest in the work.

Physics Laboratory Dacca University, 8th April, 1930.

TABLE I.

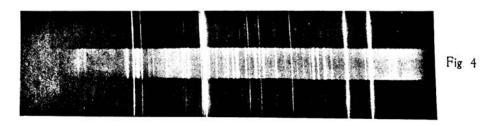
Urea.
$$O = C < \frac{NH_2}{NH_2}$$

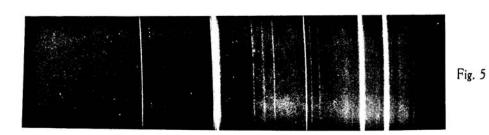
Int.	Wave no. of the Raman iines (Vac.)	Wave no. of the exciting lines (Vac.)	Diff. △ν
(2)	21331	24705	3374
(1)	21479	,,	3226
(0)	21774	22938	1164
(5)	21938	,,	1000
(2)	22108	,,	830
(0)	23545	24705	1160
(5)	23702	,,	1003

Δν: 880, 1002, 1162, 3226, 3374.

¹ Ann de Phys. Series 9, Vol. 10, page 133, 1918.

Raman Spectra





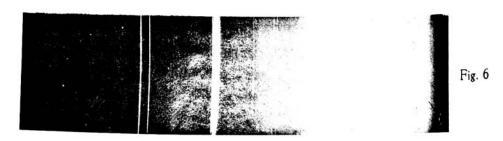


Fig. 4-Phenyl Mustard Oil.

Fig. 5-Phenyl hydrazine.

Fig. 6-Benzaldehyde.

Int.	Wave no. of the Raman lines (Vac.)	Wave no. of the exciting lines (Vac).	Diff.
(2)d	19960	22938	2978
(8)d	19998		2940
(2)	21188		1750
(2)	21282	,,	1656
(2)	21488	,.	1450
(2)	21600		1888
(8)	21781	24705	2974
(8)	21775	,,	2930
(0)	21829	,,	2876
(1)	22900	22938	638

Δν: 638, 1338, 1450, 1656, 1750, 2876, 2935, 2976.

TABLE III

				-
(1)	19963	22938	2975	
(1)	19999	,,	2989	
(1)	21482	,,	1456	
(8)d	21736	24705	3969	
(4)d	21777	,,	2928	
(00)	21830	"	2875	
(1)	24412	27389	2977	
(1)	24453	,,	2936	
	(1) (1) (8)d (4)d (00) (1)	(1) 19999 (1) 21482 (8)d 21736 (4)d 21777 (00) 21890 (1) 24412	(1) 19999 ,, (1) 21482 ,, (8)d 21736 24705 (4)d 21777 ,, (00) 21830 ,, (1) 24412 27389	(1) 19999 ,, 2989 (1) 21482 ,, 1456 (3)d 21736 24705 2969 (4)d 21777 ,, 2928 (00) 21830 ,, 2875 (1) 24412 27389 2977

Δν: 1456, 2875. 2984, 2974.

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TABLE IV.

Ethyl Carbonate
$$O = C \left(\begin{array}{c} O \ C_2 \ H_5 \\ O \ C_2 \ H_5 \end{array} \right)$$

Int.	Wave no. of the Raman lines (Vac.)	Wave no. of the exciting lines (Vac.)	Diff.
(1)	19964	22938	2974
(1)	19998	,,	2940
(2)	21485	.,	1453
(4)	21729	24705	2976
(5)	21778	.,	2932
(1)	21829	,,	2876
(2)	28606	,,	1099
(2)	23807	.,	898
(2)	24411	27389	2978
(2)	24450	.,	2939

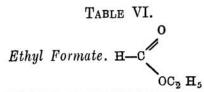
Δν: 898, 1099, 1453, 2876, 2937, 2976.

TABLE V.

Ethyl Monochloroacetate H₂C-C-OC₂H₅

(2)	19962	22938	2976
(1)	19999	11	2939
(2)	21509	**	1429
(6)	21729	24705	2976
(7)	21771	,,	2934
(1)	21825	**	2880
(2)	22059	22938	879
(2)	22148	,,	790
(2)	23832	24705	873
(2)	23922		789
(2)	24412	27389	2977
(2)	24451	11	2938

Δν: 786, 876, 1429, 2880, 2987, 2976



Int.	Wave no. of the Raman lines (Vac.)	Wave no. of the exciting lines (Vac.)	Diff.
(1) (2)	19963	22938	2975
(2)	19999		2939
(2)	21221	,,,	1717
(2)	21479	,,	1459
(2) d	21560		1378
(5)	21738	24705	2972
(8)	21775	,,	2980
(1)	21827	1220	2878
(8) (1) (1)	21941	22938	997
(2)	22096		842
(2)	23250	24705	1455
(2) (2) (2)	23330	11	1375
		1	
(00)	23416	24516	1100
(00)	23516	,	1000
(1)	23606	24705	1099
(1)	23703	,,	1002
(2)	23872	1	833
(3)	24411	27389	2978
(3)	24450	.,	2938

 $\Delta \nu$: 837, 1000, 1100, 1377, 1457, 1717, 2878, 2938, 2975.

Table VII. Potassium and Ammonium Thiocyanates. $K-S-C\equiv N,\ NH_4-S-C\equiv N$

Int.	Wave no. of the Raman lines (Vac.)	Wave no. of the exciting lines (Vac.)	Diff, △ν
(12)	20871	22938	2067
(4)	22193		745
(4) (1)	22451	24516	2065
(10)	22641	24705	2064
(3)	23964	,, ,	741
(2)	2522	27290	2064
(2)	215	27354	2069
(3)	25324	27389	2065

 $\Delta \nu$: 748, 2066.

Table VIII. $\label{eq:continuous_phonon} Phonyl~Isothiocyanate~C_6H_5-N=C=S.$

Int.	Wave no. of the Raman lines (Vac.)	Wave no. of the exciting lines (Vac.)	Diff. Δν
(8)	15243	18308	8065
(2)	15676	17274	1598
(2)	15742	17887	1595
(5)	16714	18308	1594
(5)	19882	22938	3056
(6) band	20869		2069
(10)	21846	1	1592
(0)	21404	22995	1591
(8)	21449	22988	1489
(1)	21648	24705	3062
(10)	21695	22988	1249
(2)	21767		1171
(4)	21984		1004
(0)	22182		756
(0)	22248	,.	695
(o)	22312		626
(0)	22587	.,	351
(2) band	22640	24705	2065
(1)	22695	22938	248
(4)	28112	24705	1598
(1)	28212		1493
(6)	28459	, ,	1246
(1)	28536	,,	1169
(2)	28659	.,	1010

 $\Delta \nu: \textbf{248, 351, 626, 695, 756, 1007, 1170, 1245, 1491, 1594, 2067. 3061}.$

Cyanides and Cyanates

Table IX. $\label{eq:potassium Cyanide} \ \, \mathbf{K} - \mathbf{C} = \mathbf{N}.$

Int.	Wave no. of the Raman lines (Vac.)	Wave no. of the exciting lines (Vac.)	Diff. Δν
(2)	20857	22938	2081
(<u>}</u>)	22103	, ,	835
(2)	2 2626	24705	2 79
(<u>1</u>)	23867		888
(0)	25209	27290	2081
(0)	25276	27854	2078
(4)	25309	27389	2080

Δν: 887, 2080.

TABLE X.

Double Cyanide of Potassium and Silver KAg (C=N),

Int.	Wave no. of the Raman lines (Vac.)	Wave no. of the exciting lines (Vac.)	Diff. △r
(2)	20829	22938	2109
(<u>1</u>)	22079	,,	855
(2)	22600	24705	2105
(0)	25181	27290	2109
(0)	25245	27854	2109
(1)	25279	27389	2110

 $\Delta \nu$: 855, 2109.

Int.	Wave no. of the Raman lines (Vac.)	Wave no. of th exciting lines (Vac.)	Diff.
(1)	20755	22938	2183
(0)	21624		1314
(0)	21709		1229
(1)	22100	.,	888

Δν: 838, 1229, 1314, 2183.

TABLE XII. Acetonitrile $CH_3 - C \equiv N$.

Int.	Wave no. of the Raman lines (Vac.)	Wave no. of the exciting lines (Vac.)	Diff. Δν
(2)	15859	18308	2949
(6)	19995	22938	2943
(6)	20681	,,	2257
(2)	21568		1370
(1)	21705	.,	1233
(8)	21759	24705	2946
(2)	22016	22938	922
(1)	22260	24516	2256
(6)	22452	24705	2253
(1)	22559	22938	379
(2)	23330	24705	1375
(2)	28782	24705	928
(0)	24134	24516	382
(2)	24344	27290	2946
(8)	24407	27854	2947
(5)	24443	27389	2946
(2)	25035	27290	2255
(—) Hg	25093	27354	2261
(8)	25133	27889	2256

Δv: 380, 922, 1288, 1872. 2256, 2946.

TABLE XIII.

Aniline. C.H.-NH.

Int.	Wave no. of the Raman lines (Vac.)	Wave no. of the exciting lines (Vac.)	Diff. △ν
(1)	15244	18308	3064
(1)	16704	,,	1604
(1)	19580	22938	8358
(5)	19888	(22938	3050
(8) br.	21338	22938 24705	1600 } 3367 }
(0)	21463	24516	3053
(10) br.	21657	{ 22938 } 24705 }	{ 1281 } { 3048 }
(1)	21780	22938	1158
(2)	21910	,,,	1028
(4)	21942	,,	996
(4) br.	22118		820
(0)	22181	2 2995	814
$(\frac{1}{2})$	22317	22938	621
(1)	22408	,,	530
(1)	22553		385
(1)	22705		233
(2)	23101	24705	1604
(1)	23432	"	1273
(1)	23542	,,	1163
(2)	23678	,,	1027
(3)	23708	.,	997
(3)	23889	,	816
(1)	24031	27389	3358
(0)	24165	24705	540
(0)	24327	{ 24705 { 27389	378 } 3062 }

 $\Delta \nu: 233,\ 381,\ 535,\ 817,\ 997,\ 1028,\ 1160,\ 1277.\ 1603,\ 3055,\ 3361.$

TABLE XIV.

Phenyl Hydrāzine

$$C_0H_5-N-H$$

Int.	Wave no. of the Raman lines (Vac.)	Wave no. of the excit- ing lines (Vac.)	Diff. Δυ
(1)	15249	18308	3059
(1)	16705	18308	1603
(4)	19889	22938	3048
(6) br.	21839	22938 24705	1599 3866 }
(0)	21465	24516	3051
(6)	21659	{ 22938 24705	1279 } 3048 }
(1)	21780	22938	1158
(2)	21909	,,	1029
(3)	21940	.,	998
(3)	22120		818
(0)	22679	,,	259
(0)	22505	.,	433
(0)	22380	24705	2325
(00)	22180	22995	815
(2)	23099	24705	1606
(1)	23678		1027
(2)	23706	,,	999
(2)	23 892		813

 $\Delta \nu: 259, \, 433, \, 815, \, 999, \, 1028, \, 1158, \, 1279, \, 1603, \, 2825, \, 3051, \, \, 3368, \,$

Int.	Wave no. of the Raman lines (Vac.)	Wave no. of the exciting lines (Vac.)	Diff. △ν
(2)	19563	22938	3275
(3)	21426	24705	3279
(1)	21490	,,	3215
(1)	21820	22938	1118
(1)	22032	,,	906
(0)	23595	24705	1110
(0)	23795		910
(0)	24078	27354	3276
(1)	24112	27389	3277

 $\Delta \nu$: 908, 1114, 3215, 3277.

Aldehydes.

TABLE XVI.

Formaldehyde $H-C \stackrel{\bigcirc}{\downarrow}_H$

(1) diff.	21170	22938	1768
(1)	21477	311	1461
(1) br.	21760	24705	2945
(0)	23666	33	1039
(0)	23788	12	917

 $\Delta \nu$: 917, 1039, 1461, 1768, 2945.

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TABLE XVII

Benzaldehyde CoH5-C

Int.	Wave no. of the Raman lines (Vac,)	Wave no, of the ex- citing lines (Vac,)	Diff. Δν.
(1)	15242	18308	3066
(1)	16606		1702
(1)	16711	"	1597
(1)	10/11		
(3)	19872	22938	3066
(10)	21237	100	1701
(0)	21290	22995	1705
(10)	21339	29938	1599
	h-average average	(22938	{ 1493
(1)	21445	24516	3071
(0)	21481	22938	1457
(1)	21546	.,	1392
(5)	21641	24705	3064
(6)	21731	22938	1207
(5)	21773	,,	1165
(1)	21914	;;	1024
(8)	21936	,.	1002
(4)	22108	,,	830
(0)	22186	:;	752
(1)	22285	.,	653
(3)	22323		615
(4)	22499	.,	439
(1)	22709	"	229
(2)	22814	24516	1702
(6)	23109	24705	1596
(0)	23209	,,	1496
(0)	23248	1920	, 1457
2450	10 marga	(24705	1200
(1)	23313	24516	1332
(0)	23353	24516	1163
(4)	23502	24705	1203
(3)	23542	"	1163
(0)	23634	;	1021
(5)	23703	24705	1003
(1)	23880	,,	825
(00)	23947	90	758
(0)	24054	451	651
(i)	24090	"	615
(i)	24271		434
(0)	24474	"	231

Δν: 230, 437, 615, 652, 755, 828, 1002, 1023, 1164, 1205, 1392, 1457, 1495. 1598, 1703. 065.