

The Complete Raman Spectrum in Relation to Infra-red Absorption. Part I—Pyridine and Acetic Acid.

BY

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(Plate X)

ABSTRACT.

The infra-red spectra of liquids show a large number of absorption maxima, of which only a few have found counterparts in Raman spectra. A careful examination with a new filter technique of the Raman spectra of pyridine and acetic acid has revealed a host of new lines, and the complete spectrum reproduces in a striking way all the infra-red absorption maxima recorded by Coblenz. It can be therefore inferred that in these complex molecules there cannot be any completely 'inactive' frequencies. Some very strong absorption maxima are represented by extremely faint Raman lines; and the present technique enables one to observe such faint lines.

Each liquid is studied with two filters: (1) a dilute solution of o-cresolphthalein (sodium salt) to weaken the 4046 group; (2) a dilute solution of uranine to weaken the 4358 group. A visual comparison of the relative intensities of the lines on the two plates gives their proper assignment. A third filter consisting of o-cresolphthalein followed by a quinine solution cuts off the 4046 group *completely* and is useful in some special cases. These filters should be used in conjunction with a spectrograph of moderately large dispersion. A spectrum of the iron arc taken on each plate facilitates comparison and gives accurate values for the frequencies.

The following is a list of the observed Raman frequencies:—

Pyridine:— $\Delta\nu=371, 404, 553(?), 603, 652, 717, 747, 806, 885, 942, 992, 1029, 1067, 1145, 1218, 1439, 1483, 1571, 1581, 1597, 2368, 2455, 2651, 2867, 2913, 2952, 2985, 3024, 3054, 3089, 3144, 3175 \text{ cm.}^{-1}$

Acetic acid:— $\Delta\nu=444, 603, 621, 869, 893, 942, 1014, 1221, 1276, 1370, 1431, 1667, 1726, 1771, 2943, 2996, 3033 \text{ cm.}^{-1}$

A noteworthy feature in the spectrum of pyridine is the presence of wings on either side of 305 μ line, stronger on the violet side than on the red, and the number of nearly equally spaced lines on either side of the principal line.

1. Introduction.

The infra-red absorption spectra of a large number of organic liquids in the region from 2 μ to 14 μ formed the subject of careful study by W. W. Coblentz¹ and later on by a few other workers who confined their attention only to some special cases. A great interest attaches to Coblentz's studies since the discovery of the Raman effect. Each Raman line, in fact, represents a characteristic infra-red absorption frequency and as such should be capable of being observed directly in the infra-red. In the case of a symmetrical oscillation, however, the 'inactive' frequency appears strongly in Raman spectra, but fails to appear in the infra-red as it involves no change in the electric moment of the molecule. On the other hand, it is also equally clear from experiment that strong infra-red absorption maxima may be associated with extremely weak Raman lines. This explains why a satisfactory agreement between the two sets of results has not been found in many cases. It is only by a careful study of the fainter Raman lines that a real comparison becomes possible as is shown clearly by pyridine and acetic acid which have now been examined with a new and improved technique.

It is the usual practice with many workers to use the total light of the mercury arc as exciting radiation. This procedure can only enable the more prominent frequencies to be observed and often leads to errors in assignment. The reasons for this can be briefly stated as follows :

(1) A fluorescence of some kind mainly arising from the shorter wave-lengths is superposed on the Raman spectrum and hides faint lines.

¹ Coblentz, Investigations of Infra-red Spectra (Carnegie Inst. Wash., 1905).

(2) The mercury spectrum itself has a faint background, which becomes pronounced if the arc works at a high temperature.

(3) The Raman lines excited by 4046, of about 1600—2200 wave numbers, fall in the region of the 4358 group with their accompanying wings and halation.

(4) The lines excited by the 4358 group greater than 1800 wave-numbers fall in a region which contains numerous faint mercury lines, and hence difficult to observe unless they are pretty strong. In tables of Raman spectra it is usual to find a gap in the region between 1800 to 2800, most probably due to the difficulty of detecting such lines even if they are present.

(5) After 2200 cm^{-1} , especially in the case of complex molecules, the lines excited by 4046 fall in a region already containing numerous lines excited by 4358. Hence overlapping occurs frequently with the attendant possibility of the lines being overlooked. The corresponding lines excited by 4358 not only fall in a region full of mercury lines but is also one which is photographically less sensitive.

(6) Every strong line excited by the 4046 is also excited by its companion 4077. Similarly the two faint components of the 4358 line also excite in some cases. If these happen to fall on other lines, it leads to some confusion in assignment. The anti-Stokes lines from 4358 also give similar trouble.

(7) Finally, want of sufficient resolution and under-exposure of the spectrum may explain why faint lines have been overlooked in many cases.

Thus, when the mercury arc is used it becomes obvious that a filter of some kind should be used to overcome all the above difficulties.

2. Filter Methods in Use.

The importance of isolating a particular line of the mercury arc for excitation was recognised by Raman and Krishnan,² who used a quinine sulphate solution followed by a Corning Blue Filter for getting the 4358 group. This combination weakens the exciting line very considerably, hence necessitating long exposures. The quinine solution gets rapidly coloured under the action of light and has to be changed frequently. On account of these difficulties this method has not come into common use.

In a recent paper,³ R. W. Wood has examined the whole question of filter technique in detail. He suggests principally the use of the following filters :

(1) Praseodymium and quinine sulphate solutions for isolating the 4358 group.

(2) Cobalt sulphocyanide solution for the 4046 group.

These filters suffer from some disadvantages, praseodymium salts being rather costly and rare, while quinine and cobalt sulphocyanide get decomposed under intense illumination and have to be changed often. As will be seen later, it is not necessary to cut out either of these lines *completely* in order to identify the frequencies, though this may be necessary in a few special cases for confirmatory evidence.

The present author has already used with success a dilute solution of the sodium salt of o-cresolphthalein⁴ for liquid work which is better in many respects than a quinine filter, since it not only weakens the 4046 group sufficiently but also absorbs all the mercury lines after 4358. It is further less affected by continued exposure to the light of the mercury arc. Being a dyestuff, small quantities are sufficient and the solution can be circulated through the outer jacket of

² Raman and Krishnan. *Ind. J. Phys.*, **2**, 399 (1928).

³ Wood, *Phys. Rev.*, **36**, 1421 (1930).

⁴ Krishnamurti. *Ind. J. Phys.*, **5**, 651 (1930) ; **6**, 7 (1931).

a Wood tube. Similarly, a dilute solution of uranine (sodium salt of fluorescein) has been found very useful since it transmits the 4046 line freely and at the same time cuts off the 4916 and neighbouring mercury lines completely.

3. The Present Technique.

The new method essentially consists in taking two separate spectrograms, one with a dilute solution of *o*-cresolphthalein and the other with a solution of uranine as filter. The former weakens the 4046 group while the latter weakens the 4358 group, and a careful comparison of both spectrograms with regard to the positions and relative *intensities* of the lines will give all the frequencies without any possibility of doubt. The essence of the method consists in *weakening* rather than completely eliminating the lines not required for excitation, so that good spectra are obtained with reasonable exposures. Moreover, each of these filters clears up the region around 4916 in a remarkable manner, so that a real chance is given for observation of faint lines in that region.

The apparatus used in this investigation is shown in section.

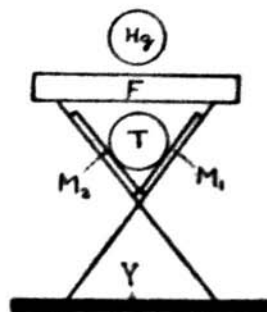


FIG. 1.

The Wood tube T containing the liquid is supported on a triangular stand Y between two inclined mirrors M_1 and M_2 . The filter solution is contained in a rectangular cell F with plane glass sides, about $15 \times 7 \times 1$ cm. This cell can be prepared by fitting two glass plates 15×7 cms. into a brass frame and cementing the sides with sealing-wax. The shorter side is provided with a neck which is closed by a stopper after the solution is poured in. F rests on the top of Y over the Wood tube. The source of illumination is a Cooper-Hewitt lamp of the flat type which is supported just above the filter cell. It is worked at 220 volts and $3\frac{1}{2}$ amps., but cooled by a slow current of air from a neighbouring table fan. An exposure of about 20 hours is usually necessary with either of the filters mentioned above. In order that the filter solutions may not be more concentrated than what is actually necessary, each solution is put into the cell and its transmission range examined with a direct-vision spectroscope in white light. Good results are obtained when the absorption band for *o*-cresol-phthalein starts from $\lambda 5000$, and for uranine from $\lambda 4600$ approximately.¹

The special utility of the filters.—The difficulties enumerated at the outset when using the total light of the mercury arc largely disappear by the use of these two filters :

(1) The cresolphthalein cuts out radiations of short wave-lengths, and hence the fluorescence.

(2) Both uranine and cresolphthalein have strong absorption in the region of Hg 4916 and hence clear up the background of the mercury spectrum, which is however very feeble since the arc is cooled.

¹The uranine solution should be changed after each exposure as it is slowly decolorised under the action of light.

(3, 4) The region from 1800-3200 wave-numbers ($\Delta\nu$) from the 4358 line is entirely freed from mercury lines, the 4916 line and its companion appearing very feebly. Hence even faint Raman lines excited by 4358 falling in this region can be detected easily.

(5) The lines >2200 cm^{-1} excited by the 4046 can be recognised independently by a comparison of the spectra taken with cresolphthalein and that with uranine respectively. The relative intensities give strong evidence for their assignment.

(6) Since each spectrogram is well-exposed, one after the 4046 and the other after the 4358 line, some frequencies which cannot be found with only either excitation (due to superposition on other lines) could be discovered.

(7) A high-dispersion instrument has been used and the exposure given is that beyond which the continuous spectrum would begin to hide the faint lines. An iron arc comparison spectrum is invariably photographed in the middle of each spectrum so that the positions of the Raman lines could be recognised at a glance, after some acquaintance with the iron arc spectrum.

Other filters.—In some cases, an independent verification of the frequencies obtained is necessary. In such a case, a dilute solution of *o*-cresolphthalein followed by a quinine sulphate solution (in a glass container) was found to be very efficient in completely removing the 4046 group. The quinine even then gets coloured after about 24 hours, but lasts easily for one exposure. This filter has been used in the case of benzene which will be reported later.

Assignment of Raman lines.—The region between the 4046 and 4358 lines includes 1767 wave numbers. In this region, the excitation is mostly by 4046. Each strong Raman line excited by the latter will have a faint companion due to 4077. In addition, with uranine filter we can expect the 3μ

Raman lines excited by the 3650 group. We should not also ignore the anti-Stokes lines from 4358.

The region from 4358 to 4916 comprises of 2602 wave numbers. Here, in addition to the principal lines due to 4358, we have their faint components excited by 4347 and 4339. Moreover, all the 3μ frequencies excited by the 4046 group fall in this region. Usually, by using either of the two filters, the 4916 and its faint companion appear very faintly, and in general all the lines in that region except these could be taken as Raman lines.

For assignment of the lines, the two plates, one taken with the cresolphthalein filter (A) and the other with the uranine filter (B) should be visually compared, preferably with a hand-lens. The following method of comparison is satisfactory.

(a) The lines after 4358 in A should have corresponding lines after 4046 in B, having the same relative intensities.

(b) The lines before 4358 in A, if they are actually stronger than in B denote anti-Stokes lines of 4358.

(c) The lines after 4358 in plate A should have the same relative intensities as the same lines in B. If any line in the latter is stronger, it is a line excited by the 4046 group which may or may not coincide with a line excited by 4358. Both the possibilities should be examined by searching for similar lines excited by 4358 and 4046 respectively.

(d) When any Raman line is strong, the two companions of 4358, as well as 4077 will also excite feebly. These faint lines should be eliminated by measurement.

In this way, we can get *all* the possible frequencies, even including very weak ones by a comparison of the two plates. The assignments can seldom go wrong since each frequency is either verified with two different excitations, or if observed with only one, suitable evidence is forthcoming for the existence of the other excitation.

4. *Experimental.*

Pyridine and acetic acid were the two liquids investigated by this method. They had a special interest in connection with the spectra of their aqueous solutions which have also been examined and will be published later. The liquids were Kahlbaum's reagents and they were purified before use. Pyridine was left over solid KOH for a day and then distilled, the middle portion having the correct boiling point being collected separately. Acetic acid was first distilled, and the middle fraction was frozen by placing it in ice. It was then allowed to re-melt partially and the liquid portion rejected. The liquids were examined in a wood tube closed by a ground stopper.

The spectrograph used in this as well as in the previous experiments was a Fuess glass instrument of moderately large dispersion with a Rutherford prism, giving about 20 Å per mm. at $\lambda 4400$. After each exposure, a wedge was inserted in the slit, and an iron arc spectrum taken without disturbing the arrangement. The Raman lines were measured with a Hilger comparator, and the wave-lengths calculated by linear interpolation from two neighbouring iron lines not more than 20 Å apart. Very faint lines were only visually estimated from their positions with respect to the iron lines as shown by a hand lens, and the values given are probably accurate to within 1 Å.

5. *Results for Pyridine.*

A list of all the observed pyridine frequencies, their approximate intensities as well as infra-red absorption maxima recorded by Coblentz are given in Table I. The values given for the frequencies are not *averages* of those given by all the exciting lines, but only those have been taken which from

considerations of dispersion and intensity appear to represent the best values. Complete tables for the 4046 and 4358 excitations are given at the end of the paper.

TABLE I.

Pyridine Frequencies.

| No. | $\Delta\nu$ | Inten- sity. | Values in μ | Corr. infra-red max. in μ | Inten- sity. | Unidentified in- fra-red max. in μ . |
|------|-------------|-----------------|-----------------|----------------------------------|-----------------|---|
| 1 | 371 | 0 | 26.95 | | | |
| 2 | 403.6 | 1 | 24.78 | | | |
| (?)3 | 553 | 0 | 18.08 | | | |
| 4 | 603 | 1½ | 16.56 | | | |
| 5 | 651.9 | 3 | 15.34 | | | |
| 6 | 717 | 0 | 13.95 | 14.1 | 10 | |
| 7 | 747 | 0 | 13.39 | 13.3 | 7 | |
| 8 | 806 | 0 | 12.41 | 12.4 | 1 | |
| | ... | | ... | ... | | 11.7, 11.9(½) |
| 9 | 885 | 1 | 11.30 | 11.28 | 1 | |
| | ... | | ... | ... | | 10.85(½) |
| 10 | 942 | 0 | 10.62 | 10.53 | ½ | |
| 11 | 992 | 10 | 10.08 | 10.08 | 5½ | |
| 12 | 1029.4 | 10 | 9.714 | 9.73 | 4½ | |
| 13 | 1067 | 1 | 9.372 | 9.35 | 3½ | |
| 14 | 1145 | 1 | 8.734 | 8.78 | 3 | |
| 15 | 1218 | 3 | 8.210 | 8.26 | 2½ | |
| | ... | | ... | ... | | 7.75(½) |
| | ... | | ... | ... | | 7.30(1) |
| 16 | 1439 | 0 | 6.949 | 6.95 | 6 | |
| 17 | 1483 | 1½ | 6.743 | 6.75 | 5 | |
| 18 | 1571.4 | 4 | 6.364 | ... | | |
| 19 | 1580.8 | 2 | 6.326 | ... | | |

| No. | $\Delta\nu$ | Inten- sity. | Values in μ | Corr. Infra-red max. in μ | Inten- sity. | Unidentified in- fra-red max. in μ . |
|-----|-------------|-----------------|-----------------|----------------------------------|-----------------|---|
| 20 | 1506.7 | 1 | 6.263 | 6.25 | 5½ | |
| | ... | | ... | ... | | 5.2(1) |
| | ... | | ... | ... | | 5.8(1) |
| 21 | 2368 | ½ | 4.2230 | | | |
| 22 | 2455 | ½ | 4.0733 | | | |
| 23 | 2651 | 0 | 3.7722 | | | |
| 24 | 2867 | ½ | 3.4880 | | | |
| 25 | 2913 | ½ | 3.4329 | | | |
| 26 | 2952.2 | 1 | 3.3841 | | | |
| 27 | 2985 | ½ | 3.3501 | | | |
| 28 | 3024 | 1 | 3.3069 | | | |
| *29 | 3054 | 10 | 3.2744 | 3.25 | 3½ | |
| 30 | 3089 | ½ | 3.2373 | | | |
| 31 | 3144.1 | 1½ | 3.1776 | | | |
| 32 | 3175 | ½ | 3.1496 | | | |

* Has a wing on either side limited by (28) and (30), stronger on the violet side.

All the frequencies in the above table were obtained with both 4046 and 4358 excitations except 1, 3, 6 and 7 which were obtained only with cresolphthalein filter, but that their origin is not due to 4046 seems to follow from the fact that they could not be detected when the intensity of 4046 is increased by the uranine filter. 3 is the only one left doubtful. 29 has wings on either side, stronger on the violet side than on the red, both terminating in the two lines 28 and 30 respectively. This is very interesting in view of the fact that the unmodified lines show abnormally strong wings on either side.

The lines previously recorded for pyridine⁵ have the following values :

$$\Delta\nu = 606, 651, 884, 990, 1029, 1155, 1220, 1379, 1480, 1580, 3058.$$

It will be seen that these represent only the strongest lines in its spectrum. There is, however, no 1379 frequency for pyridine, this line arising from the 4046 line, its actual value being 3144. This moderately strong line can be observed also with 4358 excitation.

Comparison with Infra-red data.—We have the accurate data of Coblenz⁶ for comparison in the region between $2\ \mu$ and $14\ \mu$. The curve given by Spence⁷ is probably not so good. From Table I it can be seen that all the strong infra-red frequencies recorded by Coblenz within the error of observation coincide in position with the lines in the Raman spectrum. Their relative intensities, however, have widely different values. While the strong Raman lines at $10\cdot03$ and $9\cdot71\ \mu$ have strong maxima of absorption, the strong line at $3\cdot27\ \mu$ as well as the medium strong lines at $8\cdot2$ and $6\cdot36\ \mu$ have less absorption. But some of the fainter lines, notably those at $13\cdot4$, $6\cdot95$ and $6\cdot25\ \mu$ show exceptionally strong absorption maxima. Hence it should be recognised that it is only by a careful study of the fainter Raman lines that we can hope to get some of the very prominent infra-red maxima.

It is to be expected from general considerations that a complicated molecule cannot have anything like an entirely 'inactive' frequency, in which case of course we cannot have any corresponding absorption in the infra-red. Hence every Raman line should find a counterpart in infra-red spectra, as has now been found to be the case.

⁵ Petrikaln and Hochberg, *Z. Phys. Chem. (B)*, **3**, 217, 405 (1929); Ganesan and Venkateswaran, *Ind. J. Phys.*, **5**, 196 (1929).

⁶ Coblenz, *loc. cit.*, p. 272.

⁷ Spence, *Astrophys. J.*, **39**, 249 (1914).

It is also common to find that frequencies associated with large changes in electric moment of the molecule appear very strongly in the infra-red, but very faintly in Raman spectra. The present experiments show that while this is so in many cases, the reverse is not always true, since some strong Raman lines have also corresponding strong infra-red maxima.

A point of great interest is the frequency at 3.27μ . While the Raman spectrum shows a number of lines of varying intensity, but separated by a more or less constant difference of about 30 cm^{-1} on both sides of the strong line, the infra-red maximum is only broad without showing any such resolution. Probably, much higher resolution as has recently been employed by Barnes⁸ in the case of benzene, may show such a structure demanded by Raman spectra.

There are a few infra-red maxima, usually not all prominent, for which no Raman lines have been found. It is difficult to say whether they are too faint to be observed in Raman spectra or whether these small peaks represent overtones and combinations.

6. *Results for Acetic Acid.*

This liquid was also investigated in the same way as pyridine. The results are summarised in the following table, together with the infra-red absorption data of Coblentz. Complete tables of the Raman lines will be found at the end of the paper.

⁸ Barnes, *Phys. Rev.*, **36**, 226 (1930).

TABLE II.
Acetic Acid Frequencies.

| No. | $\Delta\nu$ | Inten- sity. | Ra i.r. in μ . | Corr. infra- red max. in μ . | Inten- sity. | Unidentified infra-red max. in μ . |
|-----|-------------|-----------------|--------------------|--|-----------------|--|
| 1 | 444.2 | 1 | 22.51 | | | |
| 2 | 603.1 | 0 | 16.58 | | | |
| 3 | 620.7 | 2 | 16.11 | | | |
| 4 | 869 | 0 | 11.51 | 11.5 | 9½ | 13.9 (2) |
| 5 | 893.1 | 4 | 11.20 | 11.2 | 9* | |
| 6 | 942 | 0 | 10.62 | 10.7 | | |
| 7 | 1014 | ½ | 9.86 | 9.9 | 9 | 9.6 (6)** |
| 8 | 1221 | 0 | 8.19 | 8.15 | 10 | |
| 9 | 1276 | ½ | 7.84 | * | | |
| 10 | 1370.3 | ½ br. | 7.30 | 7.2 | 10 | |
| 11 | 1430.9 | 2v. br. | 6.99 | | | |
| 12 | 1667 | 2v. br. | 5.999 | 5.86 | 9½ | |
| 13 | 1726 | 0 | 5.794 | | | |
| 14 | 1771 | 0 | 5.647 | | | |
| 15 | 2943.1 | 6 br. | 3.3978 | 3.45 | 10 | |
| 16 | 2996 | ½ | 3.3378 | | | |
| 17 | 3033 | ½ | 3.2971 | | | |

In the above table, all the frequencies have been obtained with both 4046 and 4358 excitations except 1, 6, 12, 13 and 14 which have been obtained only with the latter, while 8 was obtained only with 4046. Several frequencies have been observed for the first time, only the following frequencies having been recorded for this liquid :⁹

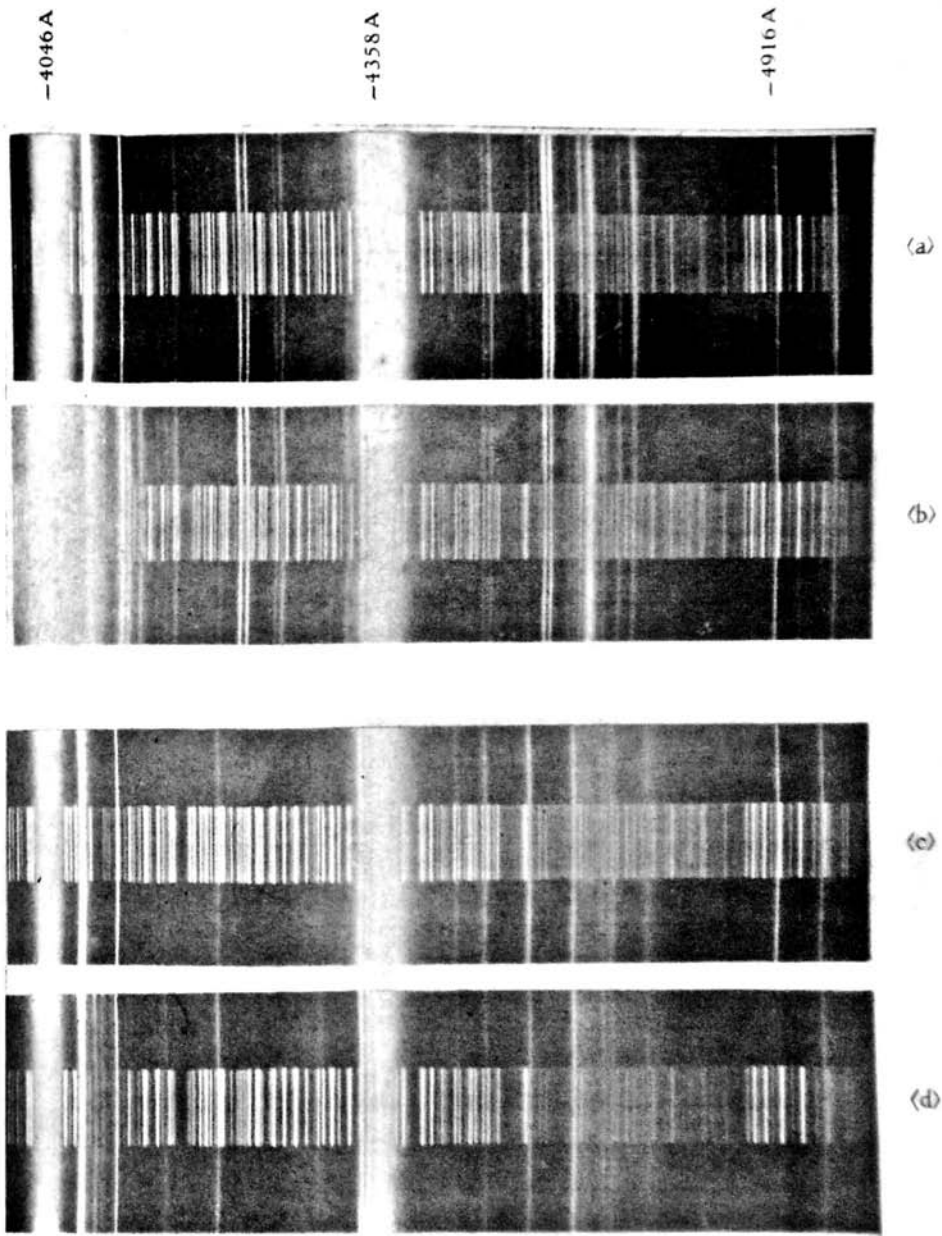
$$\Delta\nu = 441, 618, 895, 1277, 1360, 1431, 1666, 2942$$

* Though there is strong absorption, there is no distinct maximum between these limits.

** Unresolved from 9.9 μ maximum.

⁹ Dadiou and Kohlrausch, Wien. Ber., 139, 77 (1930).

Deure, Ann. de Phys., 12, 375 (1929).



(a) Pyridine, Cresolphthalein filter.
 (b) Pyridine, Uranine filter.

(c) Acetic Acid, Cresolphthalein filter.
 (d) Acetic Acid, Uranine filter.

Raman Spectra of Pyridine and Acetic Acid.

Comparison with Infra-red data.—Here as in the previous instance, we find a beautiful confirmation of the infra-red spectra obtained by Coblenz. We notice a very strong absorption corresponding to the strong Raman line at 3.4μ . The other strong absorption maxima at 5.8 , 7.2 , 8.2 , 9.9 and 11.5μ are represented by weak Raman lines. The very strong absorption at 8.2μ is in fact represented by a just detectable Raman line. The strong Raman line at 11.2μ has a rather flat maximum in the infra-red, though the faint line next to it has a maximum. This frequency is associated with the C—C oscillation, and its symmetrical character probably renders it less active, in which case it will not show very strong absorption in the infra-red.

In order to bring out these relationships clearly, the Raman lines as well as the infra-red absorption maxima from 2 — 14μ are diagrammatically represented on the same scale in Fig. 2.

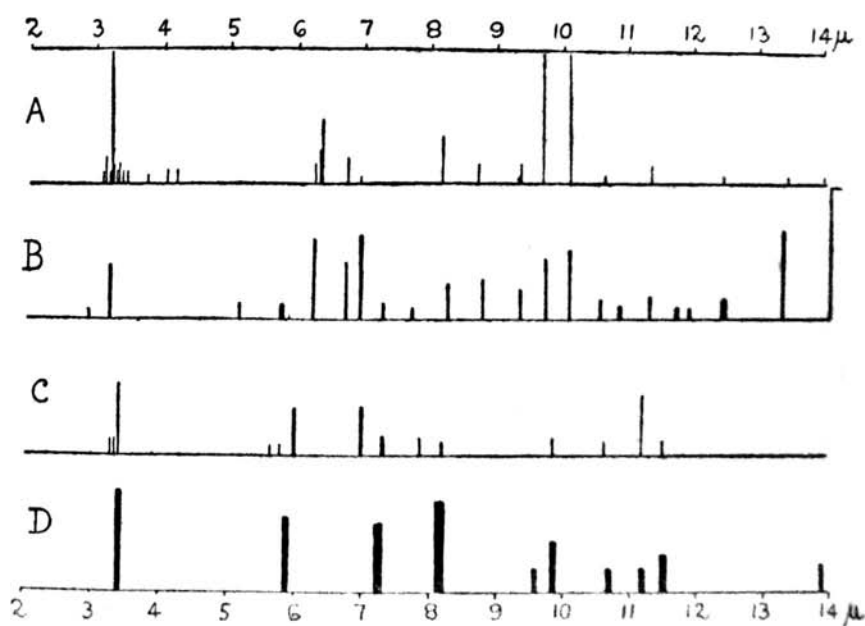


FIG. 2.

A—Raman Spectrum of Pyridine.

C—Raman Spectrum of Acetic Acid.

B—Infra-red Spectrum of Pyridine.

D—Infra-red Spectrum of Acetic Acid.

The agreement in the positions of the lines is brought out very clearly though their intensities are sometimes markedly different.

7. *Conclusion.*

It will be clear from what has been stated above that this new technique opens up a wide field for further research. Most of the substances which have already been examined have to be reinvestigated with suitable filters to bring out the fainter lines and settle the assignment for the stronger ones. The exact location of faint lines is a necessary preliminary to an accurate comparison with infra-red spectra. Indeed, as has been frequently emphasised by Sir C. V. Raman, all the vibration frequencies which come out in Raman spectra are really fundamentals, and should find their counterparts in infra-red spectra. The present results afford a beautiful confirmation of his ideas in the case of complex molecules. A reinvestigation of benzene by the author has yielded all the frequencies required by infra-red data, and a full report on this and some typical aliphatic liquids is reserved for a future communication.

In conclusion, the author's warmest thanks are due to Sir C. V. Raman, F.R.S., for suggesting this problem for investigation, and for constant help and guidance during its progress.

TABLE III
Pyridine with O-cresolphthalein Filter.

| Wavelength of Raman line in I. A. | Wave No. ν | $\Delta \nu$ | Inten- sity. | Assign- ment. | Wave-length of Raman line in I. A. | Wave-number ν | $\Delta \nu$ | Inten- sity. | Assign- ment. |
|-----------------------------------|----------------|--------------|--------------|----------------|------------------------------------|-------------------|--------------|--------------|----------------|
| 4430 | 22567 | 371 | 0 | A | 4649 | 21504 | 1434 | 0 | A |
| 4436.4 | 22534.5 | 403.6 | 1 | A | 4658.6 | 21469 | 1479 | 2 | A |
| 4466 | 22385 | 553 | 0 | A | | | 3056 | | b ₁ |
| | | 654 | | a ₂ | 4678.86 | 21366.7 | 1571.4 | 5 | A |
| 4476.0 | 22335 | 603.0 | 1½ | A | 4680.94 | 21357.3 | 1580.8 | | |
| 4485.82 | 22296.2 | 651.9 | 3 | A | 4684.41 | 21341.4 | 1596.7 | 1 | A |
| 4499 | 22221 | 717 | 0 | A | 4860 | 20570 | 2368 | ½ | A |
| 4505 | 22191 | 747 | 0 | A | 4880 | 20486 | 2452 | ½ | A |
| 4517 | 22132 | 806 | 0 | A | 4928 | 20287 | 2651 | 0 | A |
| 4553.13 | 22063.2 | 884.9 | 1½ | A | 4980 | 20075 | 2863 | 0 | A |
| | | 986 | | a ₂ | 4992 | 20026 | 2912 | ½ | A |
| 4542.82 | 22006.6 | 968.7 | 1 | a ₁ | 5002 | 19986 | 2952 | | A |
| 4545 | 21996 | 942 | 0 | A | | | 3053 | 1 | a ₂ |

(Continued overleaf)

TABLE III—(contd.)
Pyridine with O-cresolphthalein Filter.

| Wave-length of Raman line in I.A. | Wave-number ν | $\Delta \nu$ | Inten-sity. | Assign-ment. | Wave-length of Raman line in I.A. | Wave-number ν . | $\Delta \nu$ | Inten-sity. | Assign-ment. |
|-----------------------------------|-------------------|--------------|-----------------|--------------|-----------------------------------|---------------------|--------------|---------------|--------------|
| 4554.7 | 21949.1 | 989 | 10 | A | 5012 | 19946 | 3049 | $\frac{1}{2}$ | A |
| 4568.3 | 21908 | 1080 | 10 | A | | | 2992 | | A |
| 4571.0 | 21871 | 1067 | 1 | A | *5027.7 | 19884 | 3054 | 8 | A |
| 4578 | 21838 | 2867 | 0 | B | 5050 | 19796 | 3142 | 1 | A |
| 4587.4 | 21792.8 | 1145 | 1 $\frac{1}{2}$ | A | 5060 | 19757 | 3161 | 0 | A |
| | | 2913 | | B | | | | | |
| 4596.3 | 21750 | 2955 | $\frac{1}{2}$ | B | 4171.5 | 23965 | -1027 | 1 | A |
| 4602.95 | 21719 | 1219 | 3 | A | 4178 | 23928 | -990 | 1 | A |
| *4617.55 | 21650.5 | 3055 | 4 | B | 4288 | 23589 | -651 | $\frac{1}{2}$ | A |
| 4637 | 21559 | 3146 | 1 | B | 4282.4 | 23345 | -407 | 0 | A |
| 4643.3 | 21530 | 3175 | 0 | B | | | | | |

* Has wings on either side each terminating in a line.

TABLE IV.
Pyridine with Uranine Filter.

| W. l. of Raman line in I. A. | Wave No. ν | $\Delta\nu$ | Intensity. | Assignment. | W. l. of Raman line in I. A. | Wave No. ν | $\Delta\nu$ | Intensity. | Assignment. |
|------------------------------|----------------|----------------------|---------------|-------------|------------------------------|----------------|-------------|-------------------|-------------|
| 4148 | 24101 | 604 | 1 | B | *4476.0 | 22335 | 2370 | 1 | B |
| 4156.2 | 24053.7 | 651.7 | 3 | B | | | 603 | | A |
| 4189.5 | 23862 | 654 | 0 | b_1 | 4493 | 22250 | 2455 | $\frac{1}{2}$ | B |
| 4197 | 23820 | 885 | 1 | B | 4533 | 22053 | 885 | 1 | A |
| 4207 | 23763 | 942 | 0 | B | | | 986 | | a_2 |
| 4215.7 | 23714 | 991 | 10 | B | | | 2652 | | B |
| 4222.5 | 23676.0 | 1029.4 | 10 | B | 4578 | 21838 | 2867 | $\frac{1}{2}$ | B |
| 4229.5 | 23637 | 1068 | $\frac{1}{2}$ | B | 4587.4 | 21792.8 | 2913 | 2 br. | B |
| 4243 | 23562 | 1143 | $\frac{1}{2}$ | B | | | 1145 | | A |
| 4249.4 | 23526 | 990 | 3 | b_1 | 4595.74 | 21753.2 | 2952.3 | $1\frac{1}{2}$ | B |
| 4256.4 | 23487.4 | 1028.5 } 1218.0 } | 5 | b_1 | 4602.68 | 21720.4 | 1218 | 3 | A |
| 4292 | 23293 | 1223 | $\frac{1}{2}$ | b_1 | 4611 | 21681 | 2985 | | B |
| 4337 | 23266 | 1439 | 0 | B | 4617.55 | 21650.5 | 3024 | 1 br. | B |
| 4365 | 23222 | 1483 | 1 | B | 4625 | 21616 | 3054.9 | 10 | B |
| **4321.6 | 23133 | 1572 | 4 | B | 4636.6 | 21561.3 | 3089 | $\frac{1}{2}$ br. | B |
| | | | | | 4643.3 | 21530 | 3141.1 | $1\frac{1}{2}$ | B |
| | | | | | 4658.0 | 21462 | 3175 | $\frac{1}{2}$ | B |
| | | | | | | | 3054 | 2 | b_1 |

** Resolution into two lines not clear. * Raman lines separately excited by 4365 not considered in this table.

TABLE V

Acetic Acid with O-cresolphthalein Filter.

| Wave-length of Raman line in I. A. | Wave-number. ν | $\Delta \nu$. | Intensity. | Assignment. |
|------------------------------------|--------------------|------------------|-------------------|-------------|
| 4444.41 | 22493.9 | 444.2 | 1 | A |
| 4476.02 | 22335 | 603 | 0 | A |
| 4479.55 | 22317.4 | 620.7 | 2 | A |
| 4530 | 22069 | 869 | 0 | A |
| 4534.91 | 22045.0 | 893.1 | 4 | A |
| 4545 | 21996 | 942 | 0 | A |
| 4560 | 21924 | 1014 | $\frac{1}{2}$ | A |
| 4593.83 | 21762.3 | 2943.1 | 4 br. | B |
| 4605 | 21709 | 2996 | 0 | B |
| 4615 | 21662 | 1276 | $\frac{1}{2}$ | A |
| 4635.2 | 21568 | 1370 } 2948 } | $1\frac{1}{2}$ br | A b_1 |
| 4648.3 | 21507.2 | 1430.9 | 3v. br. | A |
| 4700 | 21271 | 1667 | 2 br. | A |
| 4713 | 21212 | 1726 | 0 | A |
| 4723 | 21167 | 1771 | 0 | A |
| *5000 | 19994 | 2944 | 4 | A |

* Two faint components towards longer wave-length observed but were not measured.

TABLE VI

Acetic Acid with Uranine Filter.

| W. l. of Raman line in I. A. | Wave No. ν | $\Delta \nu$ | Intensity | Assignment. |
|------------------------------|----------------|------------------|-------------------|-------------|
| 4148 | 24101 | 604 | 0 | B |
| 4151 | 24084 | 621 | $1\frac{1}{2}$ | B |
| 4184 | 23894 | 622 | 0 | b_1 |
| 4194 | 23837 | 868 | 0 | B |
| 4198.5 | 23811 | 894 | 4 | B |
| 4220 | 23690 | 1015 | 0 | B |
| 4232 | 23623 | 893 | $\frac{1}{2}$ | b_1 |
| 4257 | 23484 | 1221 | 0 | B |
| 4267 | 23429 | 1276 | $\frac{1}{2}$ br | B |
| 4284 | 23336 | 1369 | 1 br. | B |
| 4295 | 23276 | 1429 | 2 br. | B |
| *4593.83 | 21762.3 | 2943.1 | 8 | B |
| 4605 | 21709 | 2996 | $\frac{1}{2}$ | B |
| 4613 | 21672 | 3033 | $\frac{1}{2}$ br. | B |
| 4634.4 | 21572 | 2944 } 1366 } | $1\frac{1}{2}$ | b_1 A |

* Starting from this line there is a background which gradually falls off with increasing wave-length.

TABLE VII
Exciting Lines.

| Symbol used. | Wave-length in. I.A. | Wave-number. | Intensity. |
|--------------|----------------------|--------------|------------|
| A | 4358.34 | 22938.1 | 10,000 |
| a_1 | 4347.50 | 22995.3 | 600 |
| a_2 | 4339.24 | 23039.1 | 300 |
| b_3 | 4140.4 | 24145 | 10 |
| b_2 | 4108.5 | 24333 | 100 |
| b_1 | 4077.84 | 24515.9 | 400 |
| B | 4046.56 | 24705.4 | 4,000 |

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