RAMAN EFFECT IN BINARY LIQUID MIXTURES: PART II

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This paper describes the results obtained from a study of the effect of concentration on the Raman spectra of three liquid mixtures. One component, namely pyridine, is common to all the mixtures. The second component is a fatty acid. Some interesting results have been obtained which confirm the existence of complexes of the type $4RCOOH\text{-}C_5H_5N$ in these mixtures.

1. Introduction

In a previous publication* (Lakshmanan, 1954), the author reported the results obtained from a study of the effect of concentration on the Raman spectrum of the binary system: pyridine-acetic acid. The Raman spectrum of the mixture was found to be slightly different from that of the individual components. The observed variations were accounted for on the basis of complex formation between the reacting molecules. This investigation has now been extended to three more binary liquid mixtures, namely, pyridine-formic acid, pyridine-propionic acid and pyridine-butyric acid.

2. Experimental

The conventional Wood's tube arrangement was employed to photograph the Raman spectra. The substances used were either pure Merck's or pure Kahlbaum's. They were further purified by distillation. Using a Fuess spectrograph and zenith plates, an exposure of 6 hours was found to be sufficient for recording a fairly complete Raman spectrum of the components. Unfiltered mercury light was used for illumination, while the scattered light was filtered through a cell containing dilute sodium nitrite solution. For mixtures of varying concentrations, the time of exposure was adjusted to be inversely proportional to the concentration of pyridine. Besides the spectra of the individual components, the Raman spectra of mixtures containing 20, 30, 40, 50, 70 and 80 mol. per cent. pyridine were recorded.

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* Hereafterwards this will be referred to as Part I.

3. Results

The Raman spectra of the mixtures of pyridine and the respective fatty acids are reproduced in Figs. 1, 2 and 3 on Plates (XVIII–XX). The observed results are summarised below:—

Pyridine-Formic Acid

1. With the addition of formic acid, the most important change that is noticed is the appearance of a faint Raman line with a frequency shift 1010 cm.$^{-1}$ in between the two strong lines 990 cm.$^{-1}$ and 1029 cm.$^{-1}$ which are due to the C-C oscillations of the pyridine molecule. The existence of this new line is clearly discernible in the spectrum taken with 70 per cent. pyridine mixture. As the concentration of the acid is increased, the new line increases in intensity while the 990 line becomes progressively faint and diffuse. When the concentration of pyridine is reduced to 30 per cent. a second line with a frequency shift of 1024 also appears. At a concentration of 20 per cent. pyridine the two new lines are very intense and almost merge into one another, while the original C–C lines 990 and 1029 are scarcely to be seen.

2. The strong line (3054 cm.$^{-1}$) arising from the C–H oscillation of the pyridine molecule remains as such in mixtures containing 40 and more per cent. of pyridine. When the concentration of pyridine is reduced to 30 per cent., another strong line with a frequency shift of 3098 cm.$^{-1}$ appears in the photograph forming a doublet with 3054. When the concentration of pyridine is decreased further, the 3054 line disappears while the 3098 line increases in intensity. Owing to the lack of sensitivity of zenith plates in the region 4916–5461 A.U., this hydrogen line excited by λ 4358 is not as clear as the line excited by λ 4047 in the region 4358–4916 A.U.

3. In pure pyridine, the line at 1572 cm.$^{-1}$ is brighter than 1594 cm.$^{-1}$ both being slightly broad. This continues to be the case even at 80 and 70 per cent. concentrations. At 50 per cent., the line 1594 gains intensity at the expense of the 1572 line. At 40 per cent. both are of equal intensity and sharp. From here onwards, both gradually fade in intensity till at 20 per cent., they entirely disappear.

4. In the spectrum of pure pyridine, two faint lines appear with frequency shifts 602 and 652 cm.$^{-1}$, the one with the greater shift being brighter than the other. These two lines alter little in intensity and separation as the concentration of pyridine is decreased to 40 per cent. When the concentration of pyridine is decreased below this value, the 652 line exhibits

a shift as well as increase in intensity. For a mixture containing 20 per cent. pyridine the high frequency line appears at 642 cm.$^{-1}$

5. In the spectrum of pure formic acid there are two broad lines with frequency shifts 1672 cm.$^{-1}$ and 1730 cm.$^{-1}$ With the addition of pyridine, the 1730 line becomes more well-defined and intense. The 1672 line disappears at 20 per cent. concentration and in its place two sharp lines 1616 and 1639 appear. The line at 1639 is much more intense than the 1616 line. For a mixture containing more than 30 per cent. pyridine the lines in this region are hardly to be seen.

6. The frequency shift of the 2962 cm.$^{-1}$ line corresponding to the C-H oscillation of the acid molecule is reduced by the addition of pyridine. At about 20 per cent. concentration of pyridine, this line has a frequency shift of 2924 cm.$^{-1}$

7. In the spectrum of the mixture two new lines appear at 1252 cm.$^{-1}$ and 1357 cm.$^{-1}$ which are completely absent in the spectra of the individual components. These two lines could be clearly seen in the spectra of the mixtures containing 20 and 30 per cent. pyridine. The two low frequency lines 189 and 675 cm.$^{-1}$ of the acid, which are broad in the spectrum of the pure acid, get sharper with the addition of pyridine.

PYRIDINE-PROPIONIC ACID

1. As in the case of the pyridine-formic acid system, the spectrum of pyridine-propionic acid mixture exhibits a new line of frequency shift 1007 cm.$^{-1}$ (in addition to the very faint line 1000 cm.$^{-1}$ due to the acid in this region) approximately in the centre of the strong doublet 990 and 1029 due to pyridine. This line goes on increasing in intensity with decreasing concentration of pyridine and is of practically constant maximum intensity at 30 and 20 per cent. concentrations.

2. The 3054, 1572 and 1594 lines of pyridine suffer exactly similar changes as described for the previous mixture except that the line 3054 shifts to 3068 cm.$^{-1}$ at 40 per cent. and continues to be so till 20 per cent.

3. On propionic acid being mixed with pyridine a new line of frequency shift 1716 cm.$^{-1}$ [or perhaps the 1710 (0) line reported by Seshadri (1942) getting broader and brighter] appears close to the 1665 cm.$^{-1}$ corresponding, to the C=O oscillations of the acid. At 20 and 30 per cent. concentration these are of maximum breadth and intensity. At 40 per cent. concentration itself the 1665 line is scarcely visible whereas the 1716 cm.$^{-1}$ line is not visible in the photograph only beyond 70 per cent.

Pyridine-Butyric Acid

1. Here again, there is a new line for this mixture in between the 990 and 1029 lines, the frequency shift in this case being 1001 cm.$^{-1}$, and is of maximum intensity at 20 per cent. Both 990 and 1029 fall in intensity at 40 per cent. From here 990 gradually fades away till at 20 per cent. it is scarcely visible. 1029 line also behaves in a similar way; but, surprisingly enough, it brightens up considerably at 20 per cent. concentration. The only explanation for this seems to be that at this concentration the line 1038 cm.$^{-1}$ due to the acid shifts to 1029 and together with the now feeble 1029 line gives a fairly strong line at that position.

2. The 3054, 1572 and 1594 lines of pyridine change in character in almost the same way as they do in the other two mixtures, the 3054 line shifting to 3073 cm.$^{-1}$

3. The 602 and 652 cm.$^{-1}$ lines of pyridine: There is a feeble broad line at 602 cm.$^{-1}$ for the acid as well. At 20 per cent. concentration, the line 602 is scarcely discernible, while 652 brightens up considerably. Since the time of exposure has been adjusted such that this time is inversely proportional to the concentration of pyridine in the mixture, one has to attribute such a change only to an alteration in the physical structure of the scattering substances. Such a change is seen at all concentrations but is most evident only at 20 per cent.

4. In pure butyric acid there is a slight broad line of frequency 1657 cm.$^{-1}$ corresponding to its C=O oscillation. The changes experienced by this oscillation at different concentrations are similar to that of the C=O oscillation of propionic acid.

5. The lines 862, 881, 1413, 1449, 2912, 2937 and 2973 cm.$^{-1}$ of the acid: the first two are sharp lines in the pure acid and preserve their nature at 80, 70, 50 and 40 per cent. concentrations. But at 30 per cent. and 20 per cent., they broaden up considerably. The rest of the lines are broad and strong lines in the pure acid and are so at all concentrations except at 20 per cent., where they are very much broader than they are in the pure acid.

4. Discussion

While discussing the results listed above, we shall also take into account the results obtained with pyridine-acetic acid mixture and described in Part I. A critical examination of these results clearly indicates that the changes that are observed in the Raman spectra of these mixtures with variations in

concentration are similar in character for the various fatty acids, the differences being only in degree depending on the nature of the acid. The changes are much more striking in formic acid than in the other acids.

The second interesting result that emerges out of the present investigation is the fact that the changes that are noticed in the Raman spectrum are most pronounced for a mixture containing 20 mol. per cent. pyridine and 80 mol. per cent. acid. This holds good irrespective of the nature of the acid. This was further confirmed by recording the Raman spectra of these mixtures containing 12½ per cent. pyridine when it was observed that the changes were not as prominent as for 20 per cent. concentration but were more like that recorded at 30 per cent.

The appearance of new Raman lines in mixtures of pyridine and one of the fatty acids clearly indicates the formation of a complex compound between pyridine and the fatty acid. Since the changes are most prominent when the concentration of pyridine in the mixture is 20 mol. per cent., one is led to the conclusion that the molecular formula of this complex is of the form $4RCOOH \cdot C_5H_5N$. The frequency shifts of the characteristic C–C, C=O, C–H oscillations of these complexes can be tabulated as follows:

TABLE I

	Complex	C-C vibration (in $cm.^{-1}$)	C=O (in $cm.^{-1}$)	C–H (in $cm.^{-1}$)
4	$HCOOH–C_5H_5N$ ..	1010, 1024	1616, 1639, 1725	3098
4	$CH_3COOH–C_5H_5N$ ..	1006	1707, 1750	3070
4	$C_2H_5COOH–C_5H_5N$ ..	1007	1665, 1716	3068
4	$C_3H_7COOH–C_5H_5N$ ..	1001	1657, 1716	3073

Such a complex formation as revealed by the present investigation, finds support from other physico-chemical data. These include the vapour pressure versus concentration curves of Zawidzki (1900), the viscosity *versus* concentration curves of Yajnik *et al.* (1925), the density determination of Tsakalatos (1908), the compressibility curve of Balachandran (1954) and the determination of refractive indices by Matavalj and Khojman (1939) for these mixtures. The results on refractive index measurements in particular reveal the formation of compounds containing 1 molecule of pyridine

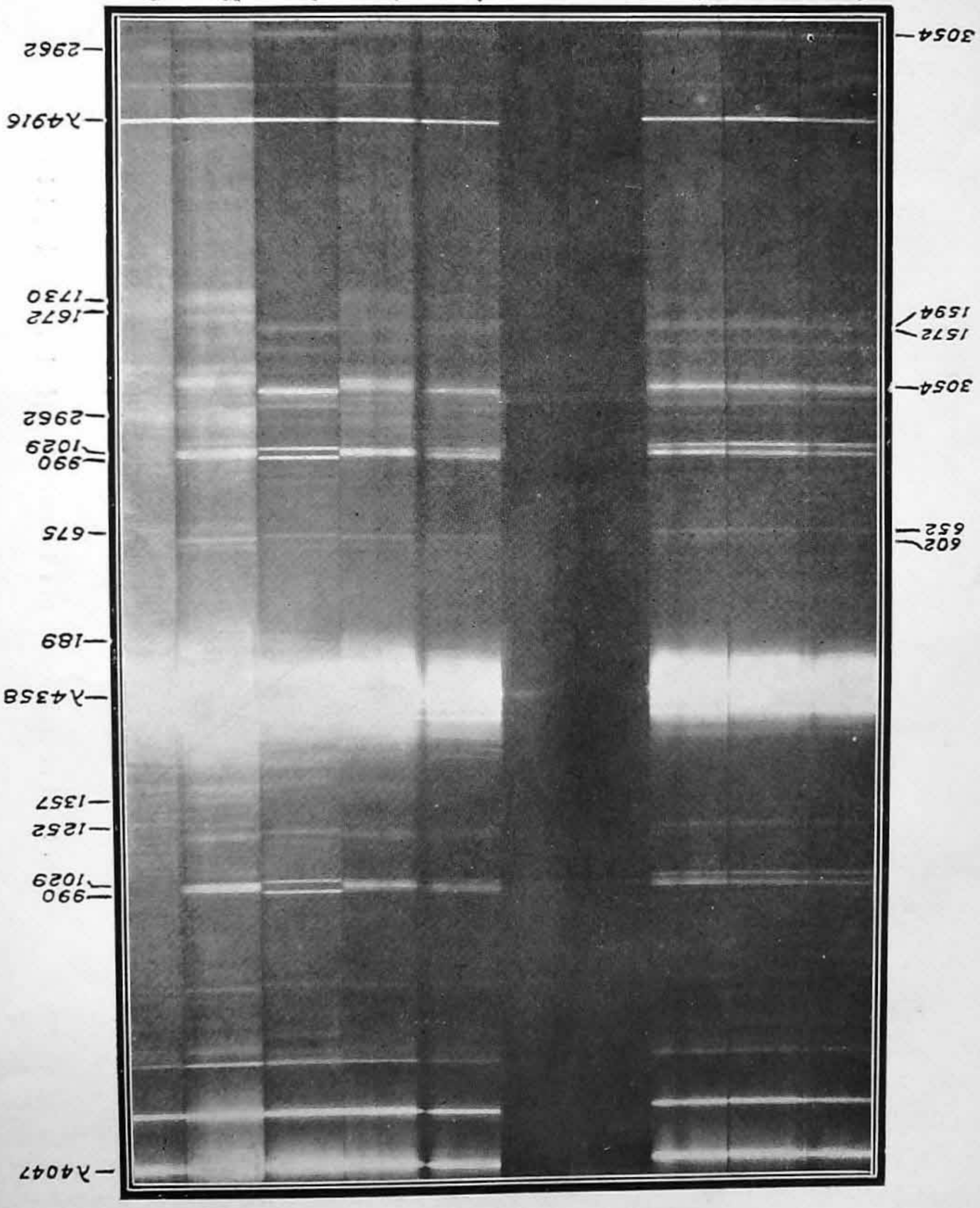

FIG. 1. Raman spectrum of a mixture of formic acid and pyridine

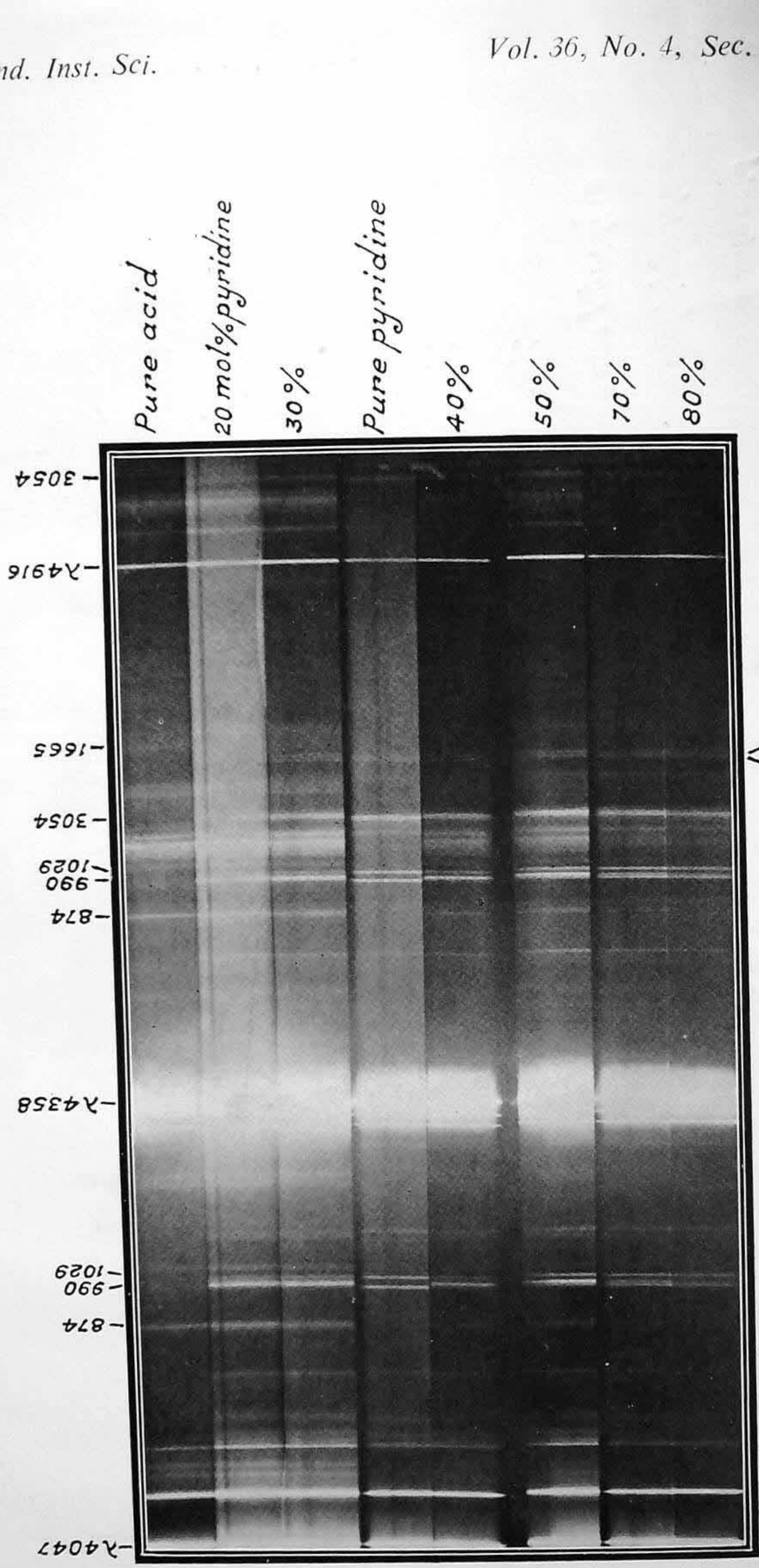

FIG. 2. Raman spectrum of a mixture of propionic acid and pyridine

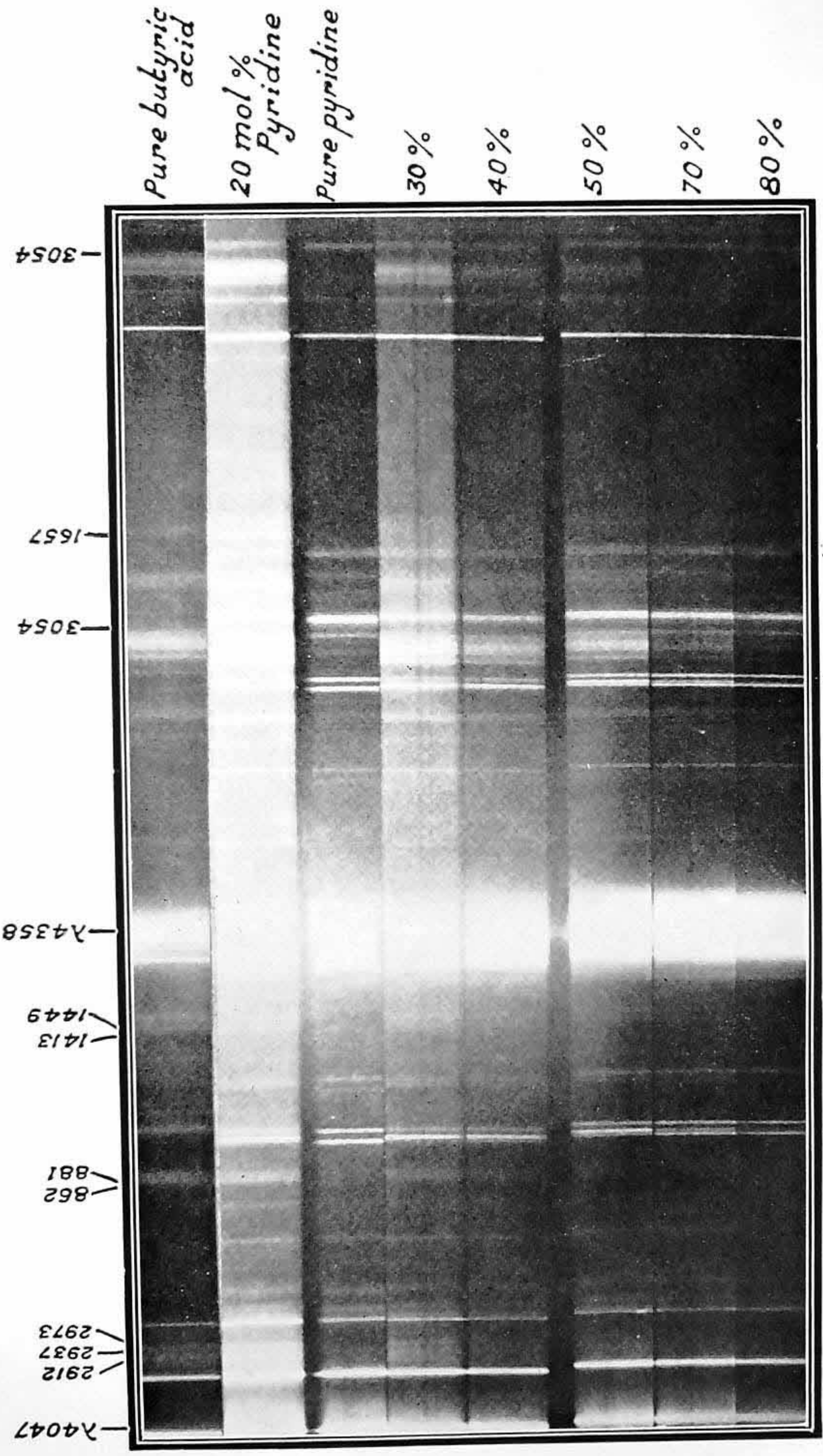

Fig. 3. Raman spectrum of a mixture of butyric acid and pyridine

and 3 molecules of acid, that is, for 75 mol. per cent. concentration, a value close to 80 given by this investigation.

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References

1. Lakshmanan .. *J. Ind. Inst. Sci.*, 1954, **36**, 97.
2. Murty and Seshadri .. *Proc. Ind. Acad. Sci.*, 1942, **16**, 264.
3. Zawidzki .. *Z. Physik Chem.*, 1900, **35**, 129.
4. Tsakalatos .. *Bull. Soc. Chim.*, 1908, **3**, 234.
5. Balachandran .. *J. Ind. Inst. Sci.*, 1954, **36**, 10.
6. Yajnik *et al.* .. *Z. Physik. Chem.*, 1925, **118**, 305.
7. Matavalj and Khojman .. *Bull. Soc. Chim. Roy.* Yugoslav, 1939, **10**, 43.