

ON THE RAMAN SPECTRA AT LOW TEMPERATURES. BENZENE DERIVATIVES

By S. C. SIRKAR* AND B. M. BISHUI

ABSTRACT The Raman spectra of benzylamine, benzyl alcohol and benzoyl chloride have been investigated in the solid state at about -170°C and in the liquid state at the room temperature. The polarisation of the Raman lines of all these liquids has also been studied. From the observed depolarisation of some of the Raman lines it has been concluded that the molecules of these three compounds in the liquid state possess a plane of symmetry. In the case of benzyl amine in the solid state some of the Raman lines undergo changes in frequency and intensity and some new lines appear in the low frequency region, and it is concluded that in the liquid state the molecules are only loosely associated, but in the solid state they are strongly associated and form polymeric groups. In the case of benzyl alcohol and benzoyl chloride such Raman lines in the low frequency region appear even in the liquid state and no appreciable changes in the frequencies of the other prominent Raman lines take place with the solidification of the liquids at the low temperature. It is concluded from these facts that even in the liquid state the molecules of these two compounds exist as polymers

It was observed by Mizushima and Morino (1938) and by the present authors (1943, 1945, 1946) that the Raman spectra of some aliphatic compounds undergo some changes when these compounds are solidified at low temperatures. As pointed out previously by the present authors (1945), the explanation offered by the previous workers regarding such changes in the lines due to intramolecular vibrations is not quite satisfactory. As regards the origin of the new Raman lines, which appear in the low frequency region in the Raman spectra of many aliphatic and aromatic compounds, the view is held by many workers that these lines are due to lattice oscillations in which only intermolecular electrostatic field takes part. Sirkar (1937), however, pointed out some difficulty in such an interpretation, because in the case of centrosymmetrical molecules the intensity of the lines due to such intermolecular oscillations is expected to be negligible. He put forward the view that some secondary bonds may be formed between neighbouring molecules to form small polymeric groups, and the oscillations of constituent single molecules against each other in such groups may give rise to Raman lines in the low frequency region. Experimental results regarding such new lines in the case of different types of molecules may be helpful in understanding the true origin of such lines and therefore, a programme has been undertaken to study the Raman spectra of a large number of aromatic and aliphatic compounds in the solid state at low temperatures. The present investigation deals with such spectra of three benzene derivatives, each having an aliphatic side chain.

The substances studied in the present investigation are benzylamine, benzyl alcohol and benzoyl chloride. Liquids from Kahlbaum's original packing were used after being redistilled in vacuum. The technique

* Fellow of the Indian Physical Society

Benzylamine. The Raman spectrum of benzylamine was studied formerly by Dadiou and Kohlrausch (1930) and by Reitz and Stockmair (1935). The results obtained by the latter authors are more recent and have been included in Table I. These results agree fairly well with those obtained by the present authors, which are given in column 2 of Table I, but there are some minor discrepancies. The weak lines 579 cm^{-1} , 895 cm^{-1} , 1176 cm^{-1} , 2973 cm^{-1} and 3385 cm^{-1} observed by them have not been observed by the present authors. Also the frequencies of some of the lines reported by them are a little lower than those observed in the present investigation.

The lines 175 cm^{-1} , 628 cm^{-1} , 1458 cm^{-1} , 1590 cm^{-1} and 1605 cm^{-1} are found in the present investigation to be totally depolarised. This fact suggests that the molecule has a symmetry element which is most probably a plane of symmetry passing through the plane of the benzene ring. The carbon and nitrogen atoms in the CH_2NH_2 group then also lie in this plane, and two of the four hydrogen atoms are above and the other two below this plane. No other alternative symmetry element of the single molecule is more probable than this plane of symmetry.

In the solid state at about -170°C the substance yields two new Raman lines at 92 cm^{-1} and 124 cm^{-1} respectively and some of the prominent Raman lines of the single molecule undergo changes in frequency and intensity at this low temperature. Thus the band at 175 cm^{-1} is split up into two lines at 160 cm^{-1} and 207 cm^{-1} and the lines 786 cm^{-1} , 1207 cm^{-1} , 1590 cm^{-1} , 1605 cm^{-1} and 2935 cm^{-1} shift to 774 , 1138 , 1584 , 1596 and 2901 cm^{-1} respectively at the low temperature. Also the relative intensities of the lines 1590 cm^{-1} and 1605 cm^{-1} are reversed in the solid state. The line 3063 cm^{-1} , which has a diffuse wing in the lower frequency side in the liquid state, becomes sharper and is accompanied by a faint component at 3050 cm^{-1} in the solid state at the low temperature. As the Rayleigh line due to the liquid at the room temperature is accompanied by a wing extending upto about 125 cm^{-1} from its centre it is difficult to say whether the lines 92 cm^{-1} and 124 cm^{-1} observed in the solid state are also present in the spectrum due to the liquid. It is doubtful whether any intramolecular vibration of the single molecule can have such low frequencies. The diminution in the frequencies of the prominent Raman lines with the solidification of the liquid at the low temperature suggests that the molecules become strongly associated in the latter case and the new lines 92 cm^{-1} and 124 cm^{-1} may be due to vibrations of such groups of associated molecules. The fact that the C-H frequencies are lowered in the solid state shows that the association takes place through the hydrogen atoms of the molecules.

Benzyl alcohol. The Raman spectrum of this liquid was studied previously by Dadiou and Kohlrausch (1929), Howlett (1931) and Reitz and Stockmair (1935). The results reported by the last two authors being comparatively recent have been included in Table II. A comparison of the data given in the first two columns of Table II shows that the weak lines

585 cm^{-1} , 900 cm^{-1} , 1176 cm^{-1} , 1358 cm^{-1} and 3414 cm^{-1} have not been observed by the present authors. Also the frequencies of some of the hydrogen lines, e.g., 2870 cm^{-1} , 2923 cm^{-1} and 2975 cm^{-1} reported by them are much lower than those observed in the present investigation.

The second and third columns of Table II show that with the solidification of the liquid at the low temperature the wing accompanying the Rayleigh line disappears and a line at 91 cm^{-1} is observed. It is not unlikely that this line may be present also in the Raman spectrum due to the liquid, but being masked by the intense wing, which extends upto 120 cm^{-1} from the centre of the Rayleigh line, it can not be detected. Fox and Martin (1940) concluded from the results of investigation of the absorption spectrum of benzyl alcohol in the near infra-red region at the room temperature that the molecules are present even in the dilute solution of the liquid as dimers and in the concentrated solution there is an equilibrium between dimers and tetramers. Although these conclusions were drawn from the observed structure of the band at 2.75μ , the Raman lines 91 cm^{-1} and 155 cm^{-1} , which correspond to bands in the extreme infra-red region, may also, be due oscillations in such dimers and polymers. In the solid state also probably the molecules exist as dimers and polymers, and therefore only the rotational wing is absent and the lines 91 cm^{-1} and 155 cm^{-1} due to vibrations in these polymers persist. It is significant that in the case of benzylamine the band at 175 cm^{-1} splits up into two lines at 160 cm^{-1} and 207 cm^{-1} in the solid state, while in the case of benzylalcohol even the liquid at the room temperature yields two lines at 165 cm^{-1} and 210 cm^{-1} . It is further observed that the prominent Raman lines of benzyl alcohol do not undergo any appreciable change with the solidification of the liquid, while in the case of benzylamine the lines undergo changes with the solidification. These facts clearly point out that in the case of benzyl alcohol the molecules are already strongly associated in the liquid state and the strength of the association does not further increase appreciably with the solidification of the substance at the low temperature, while in the case of benzyl amine such association is not so strong in the liquid state, but it becomes much stronger in the solid state.

Some of the Raman lines due to the liquid are observed in the present investigation to be totally depolarised, as can be seen from Table II. Hence the molecule possesses probably a plane of symmetry, which is more probable than a two-fold axis of rotation.

Benzoyl chloride.—The data given in the first two columns of Table III show that some of the Raman lines due to this liquid at the room temperature observed by the present authors have not been observed by Thompson and Norris (1936). The Raman spectrum of the liquid had also been studied, previously by Dadiou and Kohlrausch (1929), Matsuno and Han (1933), Thatte and Ganesan (1931) and Kohlrausch and Pongratz (1934), and the polarisation of the lines was studied by Simons (1932). The results obtained by Thompson and Norris being latest have been included in Table III. The

lines observed by Kohlrausch and Pongratz but not observed by Thompson and Norris are 1317 cm^{-1} , 2610 cm^{-1} , 2649 cm^{-1} and 3012 cm^{-1} . These lines have not been observed in the present investigation also. The line 846 cm^{-1} observed in the present investigation was not observed by Kohlrausch and Pongratz, but it was recorded as a line 840 cm^{-1} by Thompson and Norris, and the line 1164 cm^{-1} observed by the latter authors but not recorded by the former authors has not been observed in present investigation. The line 201 cm^{-1} observed in the present investigation and also by Kohlrausch and Pongratz was not recorded by Thompson and Norris.

It can be seen from the third column of Table II that no remarkable change takes place in the frequencies of the prominent Raman lines when the liquid is solidified at about -170°C . The line 98 cm^{-1} observed at the low temperature is probably also present in the Raman spectrum of the liquid, and is masked by the strong wing accompanying the Rayleigh line and extending upto about 120 cm^{-1} from its centre. In this case also two lines at 161 cm^{-1} and 231 cm^{-1} are yielded by the liquid at the room temperature as in the case of benzyl alcohol. From these facts it may be concluded that just like the molecules of benzyl alcohol those of benzoyl chloride also are strongly associated to form polymeric groups in the liquid state. As in the previous cases some of the Raman lines due to the liquid are observed to be totally depolarised both by the present authors and by Simons (1932). Hence the single molecule has a plane of symmetry.

From the above discussions it can be concluded that the lines in low frequency region observed in the Raman spectra of these three benzene derivatives in the solid state at about -170°C are not due to lattice oscillations in which only the intermolecular electrostatic field takes part, but they are due to vibrations in polymeric groups which are present even in the liquid state in two of the derivatives and are formed in the solid state in the case of benzylamine.

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PHYSICS DEPARTMENT,
CALCUTTA UNIVERSITY,
92, UPPER CIRCULAR ROAD,
CALCUTTA.

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