

ON THE RAMAN SPECTRUM OF SOLUTION OF BENZOYL
CHLORIDE IN BENZENE*

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Plate III

ABSTRACT. The Raman spectra of solutions of benzoyl chloride in benzene of different concentrations have been investigated and the relative intensities of the lines 162 cm^{-1} and 316 cm^{-1} observed in the case of solutions have been compared with those for the pure liquid at room temperature. It is found that the ratio of the intensity of the line 162 cm^{-1} to that of the line 316 cm^{-1} diminishes gradually as the concentration of the solution decreases. It is concluded from these results that the line 162 cm^{-1} may be due to inter-molecular vibration in a dimer and that in the pure liquid such dimers are predominant while in the solution some of them break up into monomers. The relative intensities of the two lines, however, are found to diminish very slightly even at 150°C .

I N T R O D U C T I O N

It is wellknown that in the Raman spectra of some substituted benzene compounds in the liquid state there is a Raman line with frequency-shift having a value in the range, $160 - 200\text{ cm}^{-1}$. For instance, benzoyl chloride in the liquid state yields a line at 161 cm^{-1} which is totally depolarised, as observed by previous workers (Sirkar and Bishui, 1946). This line is reported to be only slightly less intense than the line 316 cm^{-1} when the intensity at the peak is concerned, but when the integrated intensity is taken into account the former line is more intense than the latter, because it is much wider than the line 316 cm^{-1} . The origin of this line is not clearly understood. The deformation oscillation of the C-Cl group will be totally depolarised, but its frequency is expected to be a little higher. Also acetophenone, in which there is no C-Cl group, yields such a line. Hence it may be due to some other mode of oscillation. The line, however, may not be due to a monomer at all and in that case its intensity should alter with the rise of temperature of the liquid and also with the concentration of solution of this liquid in some suitable solvent. In order to find out actual origin of this line the Raman spectra of solutions of benzoyl chloride in benzene having concentrations of 1:3 and 1:5 by volume and also of the pure liquid at 25°C and 150°C have been studied in the present investigation.

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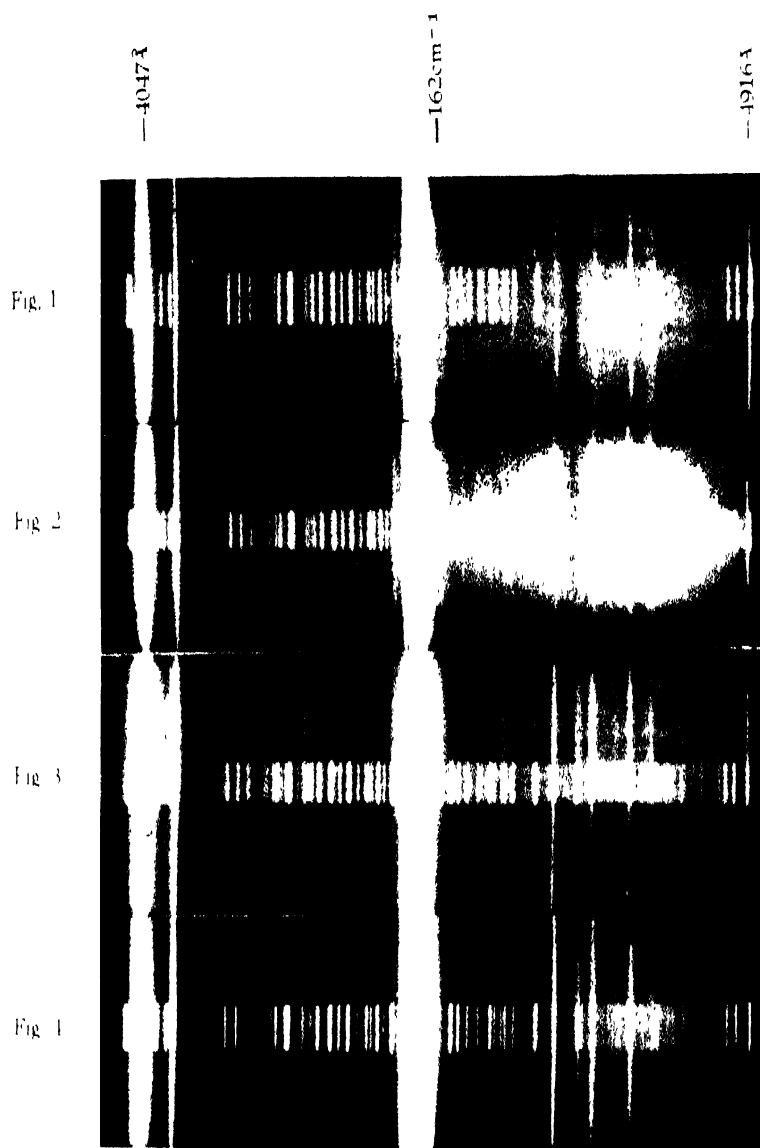
EXPERIMENTAL

The liquid was obtained from the old stock and it was of Kahlbaum's chemically pure quality. It was distilled very carefully in an evacuated and sealed double bulb in order to get rid of fluorescence and continuous background. Chemically pure benzene was also distilled in the same way and when mixed with the liquid in the proportions mentioned above the solutions were found to be quite homogeneous without showing any trace of opalescence. A Fuess glass spectrograph having a dispersion about 12 Å per mm. in the region of 4046 Å was used to photograph the Raman spectra. Iron arc comparison spectrum was also photographed on each plate in order to find out whether any of the lines change their positions with the change of concentration of the solution. A very dilute solution of sodium nitrite in distilled water was used as a filter in order to cut off rays of wavelengths shorter than 4000 Å, which were found to decompose the liquid and thereby to produce continuous background in the visible region of the Raman spectrum. Spectrograms with very clear backgrounds were obtained when the filter was used. Ilford special rapid plates were used for photographing the Raman spectra and plates from the same packet were used to photograph the Raman spectra of solutions of different concentrations and they were developed under identical conditions. The Raman spectrum of the liquid at 150°C was also photographed to see if any changes take place in the intensities or positions of the lines with rise of temperature of the liquid.

RESULTS AND DISCUSSIONS

The spectrograms for the pure liquid at 25°C and 150°C and those for the solutions of benzoyl chloride in benzene of concentrations 1:3 and 1:5 (by volume) are reproduced in figures 1-4 in Plate III. The lines observed in the case of pure liquid and the solutions are listed in Table I.

It can be seen from Table I that the lines of benzoyl chloride do not shift appreciably from their original positions when the liquid is dissolved in benzene except the line 1204 cm^{-1} . There are, however, changes in the intensities of some of the lines. Most of such changes occur due to superposition of Raman lines of benzene on those of benzoyl chloride. Benzene, however, does not yield any Raman line below 400 cm^{-1} , and therefore, the change in the intensity of the line 162 cm^{-1} observed in the present case with dissolution of the substance in benzene is due to a different cause. It can be easily seen from Plate III and Table I that the line 162 cm^{-1} is much broader and slightly more intense than the line 316 or 510 cm^{-1} in the case of the pure liquid, but in the case of the solution of concentration 31% by weight the line 162 cm^{-1} is quite sharper and less intense than the line 316 cm^{-1} and in case of solution of concentration 22% by weight the line 162 cm^{-1} diminishes further in intensity. These facts definitely prove that this line, in spite of being totally depolarised, may not be due to any mode of vibration of



Raman spectra of benzoyl chloride

- Fig. 1 Pure liquid at 25 C
- Fig. 2 „ „ at 150 C
- Fig. 3. Solution in benzene, 1:3 by volume
- Fig. 4. „ „ 1:5 „ „

Raman Spectrum of Solution of Benzoyl Chloride in Benzene 117

TABLE I

Benzoyl chloride

Pure liquid at 25°C	Solution in benzene (31% by wt)	Solution in benzene (22% by wt)
162(5b)	162(3)	162(2)
202(1)	202(1)	202(0)
316(5)	316(4)	318(4)
418(3b)	418(3b)	418(2b)
510(5)	510(4)	510(4)
618(5)	618(6)	618(6)
672(6)	672(5)	672(4)
774(1)	774(0)	
	855(4)	855(4)
1000(10)	995(20)	995(20)
1028(3)	1028(2)	1028(2)
1168(3)	1168(3)	1168(3)
1176(6)	1176(5)	1176(6)
1204(6)	1200(3)	1200(2)
1450(1)		
1480(0)		
1593(15)	1593(15)	1593(15)
1728(3)	1728(3)	1728(3)
1772(10)	1772(10)	1772(10)
3070(10)	3070(10)	3070(10)

the single molecule, because in that case its intensity with respect to that of any other line would not diminish with dissolution of the liquid in benzene. Hence it has to be concluded that in the liquid state some of the molecules form dimers without thereby changing the frequencies of the Raman lines of the monomer and in the solution the number of dimers diminish gradually as the concentration is diminished. It is not surprising that the formation of such dimers keeps the frequencies of other Raman lines unchanged, because it is known from the results obtained by Kojima (1949) that when methylmethacrylate is polymerised only the intensity of the line due to C=C vibration diminishes while the frequencies of the other lines remain unchanged. It is further seen from Table I that the intensity of the line 1204 cm^{-1} relative

to that of the line 1028 cm^{-1} is smaller in the case of the 22% solution than that in the case of the pure liquid. This may be due the superposition of the faint line 1034 cm^{-1} of benzene on the 1028 cm^{-1} line of benzoyl chloride. Similar superposition also affects the intensities of the lines 1000, 1176 and 3070 cm^{-1} .

A comparison of the spectrograms for the pure liquid at 25°C and 150°C reproduced in Plate III shows that the intensities of the lines 162 and 202 cm^{-1} with respect to those of the lines 316 or 418 cm^{-1} diminish very slightly with the rise of temperature. This fact shows that the molecules in this liquid are too strongly associated to be affected by temperature. Only large change in the intermolecular field caused by non-polar molecules of the solvent breaks the dimers into monomers. The fact that the width of the lines 162 and 202 cm^{-1} are not very large also indicates that the bond is fairly strong so that its strength is not affected appreciably during the modes of vibration giving these lines.

An attempt may be made to assign this line to a particular mode in a dimer. An examination of the published data shows that such a strong line occurs in the Raman spectra of acetophenone and other substances having the $\text{C}=\text{O}$ group in the molecule. The mode in which the whole benzene nucleus executes bending oscillation against the remaining portion of a dimer may give rise to a line of frequency below 200 cm^{-1} and such a line should be depolarised. Investigations undertaken with other similar liquids to test the correctness of the above hypothesis are in progress.

A C K N O W L E D G M E N T

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R E F E R E N C E S

- Sirkar, S. C. and Bishui, B. M., 1946, *Ind. J. Phys.* **20**, 111.
Kojima, J. K. 1949, *J. Chem. Soc. Japan. Pure. Chem. Sec* **70**, 147.