RAMAN EFFECT AND CHEMICAL CONSTITUTION.

Influence of Constitutive and Other Factors on the Double Bonds in Organic Compounds.

Part I—Coumarin.

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The large amount of existing data on the Raman spectra of organic substances indicate considerable variations in the C = O and C = C frequencies depending upon the location of the groups in compounds which are differently constituted. These seem to correspond in a general way to the well-known differences in the chemical behaviour of these groups in different situations. Whereas chemical reactions are capable of indicating only larger differences, the physical method using Raman spectra seems to be capable of indicating even small changes in the nature of these groups. It is therefore proposed to examine in detail the C = O and C = C frequencies of suitable organic compounds of various types.

With the above end in view the Raman spectra of coumarin and dimethyl-γ-pyrone in carbon tetrachloride solution were studied by us more than a year ago. Meanwhile Venkateswaran[1] published a note in *Current Science* recording the Raman spectrum of coumarin in the solid state and in the molten condition. Though there was a general agreement between our results obtained with the solution and his relating to the solid, there were certain noteworthy differences particularly in regard to the carbonyl frequency. With a view to clarify the position we have now examined the Raman spectrum of coumarin in the solid state and in solution in various solvents and present the important features of the results in this paper.

As the exciting radiation Venkateswaran employed the 4046 Å.U. and 4077 Å.U. lines, the 4358 Å.U. of the mercury are being almost completely cut off by means of a filter of iodine in carbon tetrachloride. Since the Raman lines characteristic of the ethylenic and carbonyl double bonds fall within the region 1500 to 1800 cm.$^{-1}$, we were interested in that part of the spectrum and therefore employed the 4358 Å.U. line as the more suitable one using a filter of a saturated solution of sodium nitrite. However, in order to check the results, pictures have been taken without using any filter and lines occurring within the region 1000 to 1800 cm.$^{-1}$ noted. The solvents were rendered dust-free by repeated slow distillation and a pure sample of

coumarin was used for the experiments. The same slit width was employed in all cases so as to facilitate comparison of the diffuse lines.

The Raman lines obtained by us and those recorded by Venkateswaran in the region 1000 to 1800 cm.$^{-1}$ are given in the following table. The numbers within brackets indicate visual estimates of the intensities.

*TABLE I.

Coumarin in CCl_4	Coumarin in $CHCl_3$	Coumarin Solid (Authors)	Coumarin Solid (Venkateswaran)
1030 (1)	1030 (3)	1030 (1)	1031 (7)
1102 (3)	1096 (3)	1100 (3)	1098 (6)
1125 (3)	1123 (3)	1128 (3)	1120 (7)
1158 (3)	1156 (3)	1156 (3)	1152 (6)
1178 (10)	1181 (10)	1181 (10)	1173 (8)
1228 (4)	1229 (4)	1228 (4)	1228 (6)
1257 (2)	1262 (4)	1260 (4)	1259 (4)
1330 (4)	1332 (8)	1328 (6)	1324 (8 *b*)
..	..	..	1361 (6)
..	..	..	1396 (3)
..	..	..	1415 (3)
1457 (2)	1460 (1)	1457 (2)	1451 (7)
1492 (2)	1493 (4)	1486 (4)	1483 (7)
1570 (8)	1569 (8)	1567 (8)	1562 (10)
1610 (6)	1609 (6)	1604 (6)	1610 (6)
1625 (6)	1631 (6)	1620 (6)	1623 (6)
..	..	1708 (6)	1709 (8)
..	1720 (6 *b*)	1731 (6)	1729 (8)
1742 (6)	..	..	..

*The lines corresponding to the solvents have appeared unaltered in the solutions.

It will be noticed that there is a fair general agreement between the four sets of results. The following points are however noteworthy :—

(1) In our pictures the lines 1361, 1396, 1415 cm.$^{-1}$ that were observed by Venkateswaran were absent. They were definitely absent when 4358 Å.U. excitation was employed. On the other hand when 4046 Å.U. line was used it was difficult to observe Raman lines 1361 and 1415 cm.$^{-1}$ because in the same places the fairly powerful lines 1178 and 1228 cm.$^{-1}$ excited by 4077 Å.U. fall.

(2) Of the three lines 1570, 1610 and 1625 the first two could be attributed to the C = C linkage in the benzene ring and the last to the ethylene linkage present in the pyrone ring, since benzene gives the Raman shifts 1585 and 1606 and ethylene the shift 1620. Though the pyrone double bond is situated in a ring it is highly reactive for addition reactions like ethylene and hence its resemblance to ethylene in the Raman frequency is justifiable.

(3) The Raman frequency attributable to the carbonyl group is highly interesting. In carbon tetrachloride solution it is 1742 cm.$^{-1}$, in chloroform it comes down to 1720 and is rather diffuse whereas in the solid it is clearly resolved into a doublet equally spaced on either side of 1720. The C = O frequencies of a few closely allied compounds are given below :—

Methyl cinnamate ..	1712	Benzylidine acetone	1666
Ethyl cinnamate ..	1706	Benzylidine acetophenone ..	1668
Coumarin	1742	Dimethyl-γ-pyrone	1678†

The C = O in coumarin which is a typical example of an α-pyrone differs markedly from that present in dimethyl-γ-pyrone. The former belongs to the ester or lactone type chemically and the latter to the ketones. The grouping of the γ-pyrone along with the unsaturated ketones is therefore quite acceptable. Coumarin exhibits a rather high C = O frequency as compared with the unsaturated esters. This increased strength of the C = O bond is probably due to its existence in the ring which exhibits a far greater stability than ordinary esters and lactones. For this comparison we have taken the frequency of the C = O of coumarin obtained in CCl_4 solution since as explained below we consider that in this solution the coumarin molecule exists in the normal state.

In order to get more data with a view to explain the variation in Raman frequencies of the double bonds of coumarin, the Raman spectra of the compound in benzene, carbondisulphide, acetone and methyl alcohol have also

† Our unpublished work.

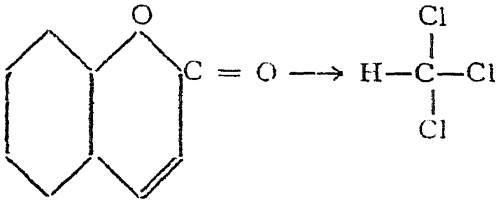
been studied. The C = O and C = C frequencies obtained with the solution using the different solvents and in the solid state are given below :—

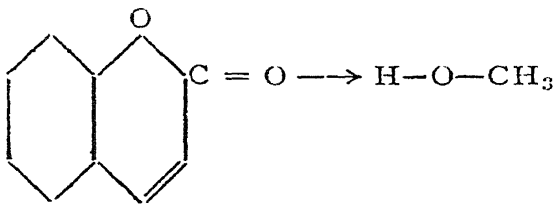
TABLE II.

Coumarin in	C = C	C = O
CCl_4 ..	1570, 1610, 1625	1742
C_6H_6 ..	1569, 1610, 1624	1736
CS_2	1568, 1610, 1626	1740
$CH_3CO \cdot CH_3$ ..	1568, 1611, 1625	1738
$CHCl_3$* ..	1569, 1609, 1621	1720
CH_3OH ..	1571, 1609, 1624	1721
Solid ..	1567, 1604, 1620	1708, 1731

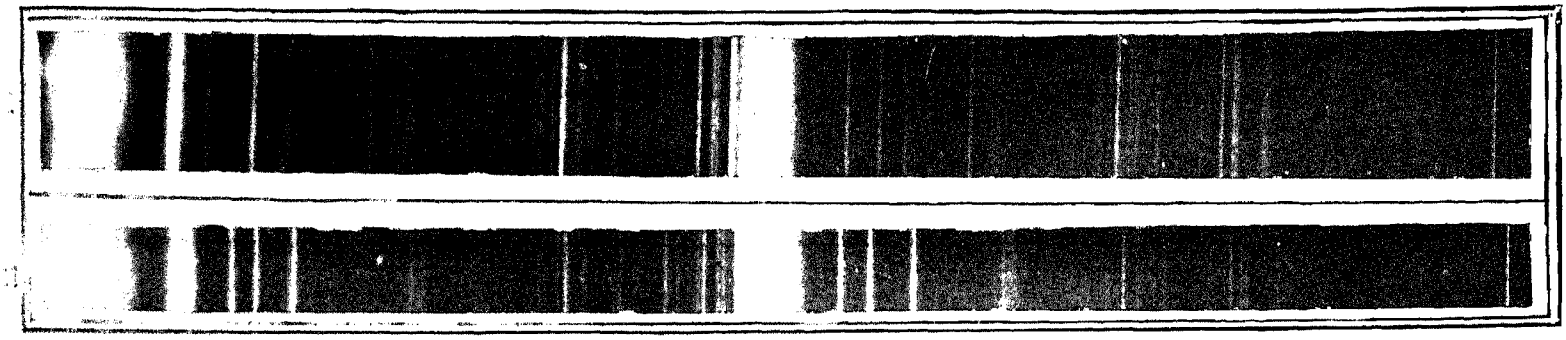
* Coumarin is more soluble in chloroform than in any of the solvents employed and hence the Raman spectrum in this solvent was studied at three different concentrations. It was found that the concentration has no effect on the frequencies of the Raman lines.

It will be noticed that the ethylenic C = C frequencies are practically uneffected in the different states whereas the C = O frequency is considerably influenced. The first four agree amongst themselves and differ from the second group of readings. The results obtained with the non-polar solvents like CCl_4, C_6H_6 and CS_2 may be taken as representing the normal state of the molecule practically unaffected by neighbouring molecules of coumarin or of the solvent. The lowering of the frequencies in polar solvents like $CHCl_3$ and methyl alcohol seems to be due to the weakening of the C = O bond by combination with the solvent molecules as represented below through the

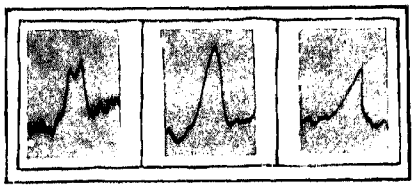




formation of a co-ordinate bond. Though acetone is a polar solvent it is similar in behaviour to carbon tetrachloride, etc., since it cannot affect the C = O bond in coumarin. It was noted in this case that the C = O frequencies of the solvent and of the solute were quite independent of each other and quite definite.



III



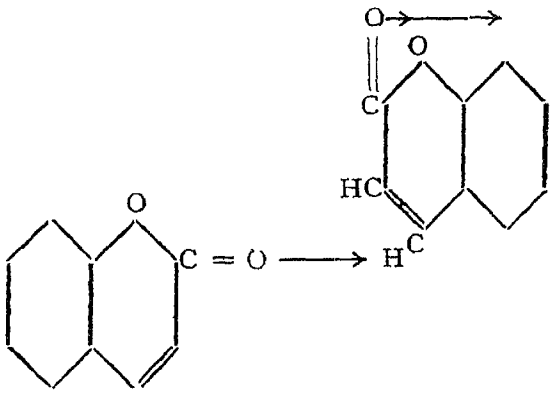
A B C

Fig. I. Coumarin in chloroform.

Fig. II. Coumarin in carbon tetrachloride.

Fig. III. Microphotometric records of the C = O frequency: (A) Solid, (B) Chloroform solution; (C) Carbon tetrachloride solution.

The splitting of the C = O frequency in the spectrum of the solid is rather difficult to explain. A similar splitting was observed by Bonino[2] in the case of hydroxymethylene camphor and he suggested that it may be due to the existence of resonance in the molecule. Though resonance exists in the coumarin molecule also as shown by Govinda Rao,[3] the above explanation cannot hold good in the present case of coumarin since in the solutions in non-polar solvents where resonance is not prohibited the phenomenon is absent. Obviously this splitting is not due to the free molecule itself but arises as due to intermolecular effects. If we take the average of the two split components the single line for the solid should be in 1720 cm.$^{-1}$ and this is the C = O frequency given by the solutions in polar solvents. The lowering of the frequency and diffused nature or splitting seem to occur together. In the solid state the C = O bond may be weakened by the mechanism given below :



All chemical reactions indicate that the position 4 in the pyrone ring has a positive charge thus indicating deficiency of electrons and the possible point of attack for the C = O bond of the neighbouring molecule.

Summary.

The Raman spectrum of coumarin in the solid state and when dissolved in various solvents has been examined with reference to (1) the C = C and (2) the C = O frequencies. Of the three frequencies belonging to (1) which are fairly constant throughout, the two lower ones represent the aromatic double bonds of the benzene ring and the third represents the ethylene double bond of the pyrone ring. The C = O frequency is considerably low in the solid state as well as in the solutions with certain polar solvents. This is attributed to the weakening of the C = O bond by the formation of hydrogen bonds through co-ordination.

REFERENCES.

1. Venkateswaran, C. S. .. *Curr. Sci.*, 1938, **6**, 328.
2. Bonino .. *Ric. Sci. tec.*, 1935, **6**, II, 181–82.
3. Govinda Rau, M. A. .. *Curr. Sci.*, 1936, **5**, 13.