

THE RAMAN SPECTRA OF ORGANIC COMPOUNDS : ANILINE

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THE complete Raman spectrum of aniline $C_6H_5 \cdot NH_2$ has not so far been obtained owing to the fact that it is highly photosensitive and turns yellow on continued exposure to light. A very intense spectrum of this substance is photographed in the present investigation by adopting a simple technique of replacing the liquid as soon as it develops a yellow tinge by freshly distilled material. The polarisation characters of the Raman lines are also obtained.

Results

The frequency shifts of the observed Raman lines and their polarisation values are listed in Table I. The spectrum and the polarisation pictures are reproduced in Plate XVII.

Aniline has been investigated previously by Bonino and Brül (1929), Ganesan and Thatte (1931), Pal and Sen Gupta (1930), Dadieu and Kohlrausch (1931), Dupont and Reymond Dulow (1936) and Vitale (1936). The results obtained by Dadieu and Kohlrausch, being more complete than of the others, are included in the table for comparison. Besides confirming the spectrum obtained by the latter authors, twenty-five new lines have been identified. The data given within brackets against the polarisation ratios are those obtained by Cabannes and Rousset (1933).

Discussion

Aniline is one of the simplest of the monosubstituted derivatives of benzene, in which the D_{6h} symmetry of benzene changes over to C_{2v} symmetry. The character table for the molecule is given in Table II.

According to this analysis, all the normal modes are single and Raman-active. It may be recalled that on account of the high order of symmetry of the benzene molecule, ten frequencies are doubly degenerate and thirteen are forbidden in the Raman effect. As the substitution of one of the hydrogen atoms by a simple group may not alter the frequency shifts of the benzene

TABLE I

No.	Authors $\Delta\nu$ in cm.^{-1}	ρ	Kohlrausch $\Delta\nu$ in cm.^{-1}	Infra-red absorption (Coblentz)
1	234 (4)	.71	234 (5)	
2	280 (0 d)	D		
3	330 (0 b)	D		
4	387 (4 b)	.63	388 (2)	
5	408 (1)	..		
6	532 (5)	.62	532 (3)	
7	619 (5)	.62		
8	700 (1 b)	..		
9	757 (3)	.71	755 (2)	
10	775 (0)	..		
11	810 (8)	.26	812 (15)	804
12	830 (8)	.30	822 (5 b)	
13	888 (0)	P		888
14	938 (1 b)	P		930
15	987 (0 d)	..		
16	996 (10)	.26 (P)	996 (10)	994
17	1029 (5)	.28	1029 (5)	1027
18	1060 (0)	..		1058
19	1110 (0)	..		
20	1149 (3)	.78		1158
21	1168 (2)	.55		
22	1200 (0)	P		
23	1230 (0)	P		
24	1272 (4 b)	.33 (.40)	1272 (4 b)	1269
25	1340 (1)	D		
26	1388 (1)	D		
27	1456 (2)	.62		
28	1499 (2)	P		1492
29	1538 (2)	P		
30	1590 (2)	D		
31	1601 (10)	.69 (.75)	1601 (10)	
32	1612 (2)	P		1626
33	2922 (2)	P		
34	3020 (1)	D		
35	3046 (10)	.53	3046 (10)	
36	3066 (4)	P		
37	3190 (1)	D		3115
38	3362 (3 b)	P	3362 (3 b)	3378
39	3423 (2 b)	D	3423 (2 b)	

TABLE II. Character Table for $C_6H_5 \cdot NH_2$

C_{2v}	E	C_2	σ_v	σ_v'	n_i	n_i'	Raman	Infra-red
A_1 ..	1	1	1	1	14	13	P	<i>a</i>
A_2 ..	1	1	-1	-1	5	4	D	<i>ia</i>
B_1 ..	1	-1	1	-1	10	8	D	<i>a</i>
B_2 ..	1	-1	-1	1	13	11	D	<i>a</i>
U_R ..	14	4	6	12				
$h_i\phi_j'$..	42	-4	6	12				
$h_j\psi_j'$..	36	-2	6	12				

ring greatly, the spectrum of the derivatives provides a means of finding out these frequencies directly. The vibrations of the ring in the derivative may be classified under five groups: (1) ω (C—C)—vibrations of the carbon ring which are symmetric with respect to the plane, (2) γ (C—C)—anti-symmetric vibrations of the ring in which the movement of the carbon ring is normal to the plane, (3) ν (C—H)—the valence oscillations of C—H groups, (4) δ (C—H)—the deformation oscillations of C—H in the plane and γ (C—H)—the deformation oscillations of C—H in which the hydrogen atoms move normal to the plane of the ring. The frequencies of aniline are assigned to these groups by comparing its spectrum with those of benzene and some of its monosubstituted derivatives, viz., toluene, phenol, and chlorobenzene (see Table III).

It will be observed that ν_1 , the breathing frequency of benzene molecule at 993 cm.^{-1} , appears at 810 in aniline, the corresponding frequency for toluene being 788, for phenol 812 and for chlorobenzene 708. ν_{12} which is forbidden in benzene but appears weakly at 1006, is one of the strongest lines in the derivatives. It will also be noticed all the doubly degenerate lines in benzene are split into two lines in the latter compounds. ν_8 in benzene is a doubly degenerate frequency, which is generally attributed to the ethylenic linkage C=C. On account of an accidental degeneracy $\nu_1 + \nu_6 = \nu_8$, this is split into two nearly equally intense lines 1584 and 1605. In the derivatives, since ν_1 is lowered, this type of coincidence does not exist and hence the two lines having the above frequency shifts should be explained as due to the splitting up of ν_8 . The forbidden vibration ν_{14} of benzene appears at 1612 in aniline. There are five Raman-active frequencies belonging to ν (C—H) which have been identified.

The infra-red absorption of aniline has been studied by Coblentz (1905) and the frequencies given by him are given in Table I. The infra-red absorptions at 804, 994, 1492, 1269 and 1626 coincide with ω (C—C) frequencies at 810, 996, 1499, 1272 and 1612 respectively. The Raman frequencies γ (C—H), viz., 888 and 938 coincide with the infra-red bands at 888 and 930, δ (C—H) at 1029, 1060 and 1149 coincide with 1027, 1058, and 1158, and ν (C—H) at 3066 and 3190 together appear as a single absorption band at 3115. This coincidence between the infra-red and the Raman spectrum is to be expected from the characteristic vibrations of the C_{2v} symmetry.

According to the group-theoretical analysis, twenty-three out of the thirty-six vibrations should be depolarised. However it has been observed that no line is completely depolarised. The highest degree of depolarisation is .78 for 1149, and the lowest is .26 for 810 and 996 cm.^{-1}

TABLE III

Reference to vibration forms of C_6H_6	Benzene	Aniline	Toluene	Phenol	Chlorobenzene	Assignment
ν_4	<i>f</i>	234 (3)	218 (6 b)	243 (5 b)	196 (6 b)	γ (C-C)
ν_{16}^*	<i>f</i>	280 (0) 330 (0)	334 ($\frac{1}{2}$)	..	270 ($\frac{1}{2}$) 295 (2)	γ (C-C) γ (C-C)
ν_5	400 (0)	387 (4) 408 (1)	..	507 ($\frac{1}{2}$)	420 (6)	δ (C-N) γ (C-H)
ν_6^*	606 (5)	532 (5) 619 (5)	523 (5) 622 (4 b)	532 (4) 620 (4)	615 (3)	ω (C-C) ω (C-C)
ν_{18}	688 ($\frac{1}{2}$) 788 (0) <i>f</i>	700 (1) 757 (3) 775 (0)	730 (0) ..	655 (0) 756 (3) 787 (0 b)	..	γ (C-H)
ν_9^*	850 (2)	830 (8) 888 (1 b) 938 (1 b)	813 (0 b) 978 (0)	830 (3)	830 (0)	γ (C-N) γ (C-H)
ν_1	993 (10)	987 (0)	993 ($\frac{1}{2}$)	991 (0)	989 (0)	γ (C-H)
ν_{12}	1006 ($\frac{1}{2}$)	810 (8) 996 (10)	788 (10) 1005 (10)	812 (8) 1001 (10) 1013 (0)	708 (6) 1003 (10) 1013 (0)	ω (C-C) ω (C-C)
ν_{11}^*	1035 (0) <i>f</i>	1029 (5) 1060 (0)	1030 (8) ..	1027 (8) 1072 (1)	1024 (7) 1121 ($\frac{1}{2}$)	δ (C-H) δ (C-H)
ν_{15}	<i>f</i>	1110 (0)	..	1113 (0)	1158 ($\frac{1}{2}$)	δ (C-H)
ν_{10}^*	1175 (2)	1149 (3) 1168 (2) 1200 (0) 1230 (0)	1157 (2) 1181 (1)	1155 (3) 1170 (4)	1165 (0) 1176 ($\frac{1}{2}$)	δ (C-H) δ (C-H)
ν_{17}^*	<i>f</i>	1340 (1) 1388 (1)	1348 (0) 1381 (1)	..	1372 (0)	γ (C-H) γ (C-H)
ν_3	1445 (0) <i>f</i>	1456 (2)	1402 (0) 1434 (0) 1455 (0)	1425 (0) 1464 (0)	1443 (0)	δ (C-H)
ν_{19}^*	1480 (0) <i>f</i>	1272 (4 b) 1499 (2) 1538 (2)	1212 (0) 1499 (0)	1253 (2 b) 1498 ($\frac{1}{2}$)	1084 (5) 1565 (0)	ω (C-C) ω (C-C) δ (NH ₂)
ν_8^*	1584 (3)	1590 (2)	1588 (0)	1595 (5)	1584 (4)	ω (C-C)
ν_{14}	1605 (2) <i>f</i>	1601 (10) 1612 (2)	1606 (3) 1630 (0)	1605 (5)	..	ω (C-C) ω (C-C)
ν_{13}	<i>f</i>	2922 (2)	2868 (3 b) 2922 (6 b)	ν (C-H)
ν_7^*	3048 (4)	3020 (1) 3046 (10)	3037 (4 b) 3058 (8)	3017 ($\frac{1}{2}$) 3051 (5)	3008 (0) 3028 (0)
ν_2	3062 (8)	3066 (4 b)	3070 (4 b)	3064 (8)	3068 (10b)	..
ν_{20}^*	<i>f</i>	3190 (1 d) 3362 (3 b) 3423 (2 b)	..	3085 ($\frac{1}{2}$) 3150 (0)	3140 (0) 3165 (1)
						} NH ₂

Note.—The notations employed in column one are those given by Wilson (1935).

* Denotes doubly degenerate frequencies.

The frequencies of the NH₂ group.—The NH₂ group in aniline has three normal modes of vibrations, ω_1 , ω_2 and ω_3 , if we assume that it possesses the form of a bent triatomic molecule. ω_2 and ω_3 come under the symmetric class and should be highly polarised, and ω_1 is antisymmetric and hence depolarised. All the three are active in the Raman and the infra-red spectra; but while ω_2 is the strongest in the former, it is the weakest in the latter. From our knowledge of the spectra of H₂O and H₂S, we should expect ω_1 and ω_2 to appear in the region 3300 and ω_3 to be nearly half of ω_2 . Indeed there are two lines observed at 3362 and 3423, the former being polarised and the more intense of the two and the latter depolarised. 3423 has therefore to be assigned to ω_1 , and 3362 to ω_2 . The infra-red absorption at 3398 reported by Coblenz has to be attributed to ω_1 . The Raman line at 1538 which does not belong to the benzene ring is obviously ω_3 . A similar line at 1537 in urea CO (NH₂)₂ is attributed by Ananthakrishnan (1937) to the same mode of vibration in NH₂ group. Applying the formula given by Dennison (1926) and assuming the above frequencies for ω_1 , ω_2 and ω_3 , we get the force-constant for N—H as 6.3×10^5 dynes/cm. and the angle HNH as $104^\circ 48'$.

The C—N frequencies.—Besides the frequencies of the benzene ring and the NH₂ group we should expect three Raman frequencies, *viz.*, one valence oscillation of the C—N linkage, one deformation oscillation of C—N in the plane and one deformation oscillation perpendicular to the plane. Assuming the force-constant of C—N as 4.85×10^5 dynes/cm. (Hibben, 1939) the valence frequency comes out as 1040 cm.⁻¹ Venkateswaran and Bhagavantam (1930) from their studies on methyl and ethyl amines conclude that the line at 1050 is due to this linkage. According to Médard (1935) this frequency varies from 910 to 850 in nitro-compounds. In compounds CH₃NH₂, (CH₃)₂NH and CH₃N, it falls at 1047 (7), 930 (5), and 850 (5) respectively. Thus we see that the Raman frequency characteristic of the C—N linkage is very much influenced by the constituent group. From the analysis of the spectrum of aniline given in Table III, we have to conclude that the polarised line 830 (8) is the valence and the line 408 (1) is the deformation frequency in the plane of the ring.

Besides the lines assigned above, there are five other lines, *viz.*, 700 (1), 775 (0), 987 (1), 1200 (0) and 1230 (0) which require explanation. 987 is presumably due to ν_1 vibration of the carbon isotope C₁₃, 775 due to $2\nu_5$ and the others due to combinational frequencies.

In conclusion the authors wish to thank Sir C. V. Raman for his keen interest in the work.

Summary

An intense Raman spectrum of aniline has yielded thirty-nine lines. They are: 234 (4, .71), 280 (0, D), 330 (0, D), 387 (4, .63), 408 (1), 532 (5, .62), 619 (5, .62), 700 (1,), 757 (3, .71), 775 (0), 810 (8, .28), 830 (8, .30), 888 (0, P), 938 (1, P), 987 (0), 996 (10, .26), 1029 (5, .28), 1060 (0,), 1110 (0), 1149 (3, .78), 1168 (2, .55), 1200 (0, P), 1230 (0, P), 1272 (4, .33), 1340 (1, D), 1388 (1, D), 1456 (2, .62), 1499 (2, P), 1538 (2, P), 1590 (2, D), 1601 (10, .69), 1612 (2, P), 2922 (2, P), 3020 (0, D), 3046 (10, .53), 3066 (4, P), 3190 (1, D), 3362 (3, P), and 3423 (2, D). Thirty of these are assigned to the benzene ring by comparing these frequencies with those of benzene and its monosubstituted derivatives. 3362 (3 P), 3423 (3 D,) and 1538 (2 P) are assigned to the NH₂ group and 830 (8, .30) and 408 (1) to the C—N linkage.

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