4

OPTICALLY CATALYTIC ACTION OF ANTHRACENE AND PHENANTHRENE IN GIVING RAMAN SHIFTS OF SOME ORGANIC COMPOUNDS*

By S. P. SINHA

(*Received for publication, January 20, 1944*)

ABSTRACT. By taking the wavelengths of the absorption bands of anthracene in benzene, methyl alcohol, hexane, toluene and chlorobenzene and those of phenanthrene in benzene and methyl alcohol as giving the exciting frequencies the differences between these and the frequencies of the fluorescent bands have been calculated. These have been found to agree well with most of the Raman frequencies of the solvents. Some shifts observed in the present case which do not agree with any known Raman shift have been shown to be capable of being built up by the combinations of Raman shifts observed by the present or other authors.

INTRODUCTION

In a paper published Prosad and Bhattacharyya (1939) have described a new technique for the production of Raman effect. Compounds like $Er(NO_3)_3$ and $KMnO_4$ having sharp absorption bands are dissolved in small quantities in substances whose Raman spectra are to be obtained and the absorption and fluorescent spectra of the solutions are photographed. The latter are obtained in the usual way for getting Raman spectra. The differences between the frequencies of the absorption and fluorescent bands have been correlated with the Raman frequencies of the solvents with remarkable agreement. Some Raman shifts (*cf.* 3956cm.$^{-1}$ in case of water) by Collins (1939) obtained by the new method only have later on been discovered by the direct method and this stresses the importance of the technique.

The action of small quantities of salts like $Er(NO_3)_3$ and $KMnO_4$ which do not affect the Raman spectra of the solvents has been described as optically catalytic and the salts have been called optical catalysers by Prosad and Bhattacharyya (1936) and by Hartley (1937).

Earlier Prosad, Bhattacharyya and Chatterji (1935) had shown that by taking the wavelengths of the absorption bands of didymium glass as giving the exciting frequencies, the differences between these and the frequencies of the fluorescent bands observed with the same glass agreed well with most of the values of Raman shifts for different varieties of glass as measured by others. Working on the same lines, Banerji and Mishra (1937) had found the relation to hold good in case of a few organic liquids using anthracene as optical catalyser.

* (Communicated by K. Prosad).

This new technique for the production of Raman spectra has also been referred to by Hibben (1939) and by Glockler (1943).

Sambursky and Wolfsohn (1940) have studied the absorption and fluorescent spectra of anthracene and phenanthrene in different solvents but unaware of the work of Prosad and Bhattacharyya which was published later on, they did not make any attempt to verify the conclusions drawn by them.

In the present paper an attempt has been made to justify the optically catalytis action of anthracene and phenanthrene by calculating the Raman shifts from the absorption aud fluorescent spectra of some organic compounds and comparing them with those found by others by the direct method. The data of the absorption and the flurescent bands have been taken from the paper of Sambursky and Wolfsohn (*loc cit*).

CALCULATIONS AND DISCUSSIONS

Benzene.—Table I below gives the wavelengths and corresponding wavenumbers of the absorption and fluorescent bands obtained in the case of benzene with anthracene and phenanthrene as optical catalysers.

TABLE I

Benzene

Optical Catalyser	Absorption bands		Fluorescent bands	
	λ_{air} in Å.U.	ν_{vac} in cm.$^{-1}$	λ_{air} in Å.U.	ν_{vac} in cm.$^{-1}$
Phenanthrene	3095	32301(a)	3405	29360(A)
	3162	31636(b)	3480	28727(B)
	3237	30883(c)	3573	27980(C)
	3308	30221(d)	3656	27344(D)
	3392	29473(e)	3758	26602(E)
	3469	28818(f)	3852	25953(F)
	—	—	4068	24575(G)
Anthracene	3790	26378(g)	3828	26116(H)
	3596	27801(h)	4042	24733(I)
	3420	29231(i)	4280	23358(J)
	3261	30657(j)	4547	21986(K)

Table II compares the Raman Shifts calculated with the help of Table I with those given by other authors. The agreement is fairly satisfactory.

TABLE II

Benzene

Some Raman shifts for Benzene calculated from the observed values of Table I.

$d\nu$ in cm.$^{-1}$ by other authors Hibben (1939)	$d\nu$ in cm.$^{-1}$ from Table I	$d\nu$ in cm.$^{-1}$ by other authors	$d\nu$ in cm.$^{-1}$ from Table I
	91 (f—B)	1693	1685 (h—H)
	262 (g—H)	2128	2129 (e—D)
781	746 (e—B)	2925	2603 (c—C)
849	838 (f—C)	—	—
	861 (d—A) mean 849.3	3047	3020 (g—J)
1473	1474 (f—D	3062	3068 (h—I)
	1494 (d—B)	—	—
	1493 (e—C)	—	—
	mean 1487	—	—

TABLE III

Benzene

Some combination shifts built up by the Raman shifts compared with the observed shifts in the present case.

$d\nu$ by other authors Hibben (1939)	$d\nu$ by other[10]	Shifts observed	Shifts by combination	Shifts observed	Shifts by combination
ν_1 606	ν_{11} 2358	2216 (f—E) 2241 (d—C)		4930 (c—F)	$\nu_6+\nu_{18}$ 4916
ν_2 824	ν_{12} 2454	mean 2229	$\nu_2+\nu_5$ 2228	5873 (i—J)	$\nu_{14}+\nu_{15}$ 5873
ν_3 979	ν_{13} 2618	2877 (d—D) 2865 (f—F)		5924 (j—I) 6815 (h—K)	$\nu_{12}+\nu_{18}$ 5924 $\nu_{19}+\nu_{14}$ 6841
ν_4 1030	ν_{14} 2925	2871 (e—E)			
ν_5 1404	ν_{15} 2948	mean 2871	$\nu_5+\nu_7$ 2882		
ν_6 1449	ν_{16} 3047	4268 (d—F)	$2\nu_{10}$ 4256		
ν_7 1478	ν_{17} 3116	4392 (g—K)	$\nu_9+\nu_{11}$ 4388		
ν_8 1585	ν_{18} 3467	4443 (h—J)	$\nu_3+\nu_{18}$ 4446		
ν_9 2030	ν_{19} 3916	4498 (i—I)	$\nu_6+\nu_{16}$ 4496		
ν_{10} 2128	—	4541 (j—H)	$\nu_5+\nu_{15}$ 4533		

TABLE IV

Methyl alcohol

Optical catalyser	Absorption bands		Fluorescent bands	
	λ_{air} in Å.U.	ν_{vac} in cm^{-1}	ν_{air} in Å.U.	ν_{vac} in cm^{-1}
Phenanthrene	3458	28910(a)	3464	28858(A)
	3381	29568(b)	3556	28113(B)
	3298	30313(c)	3637	27487(C)
	3228	30970(d)	3740	26730(D)
	3151	31727(e)	3829	26101(E)
Anthracene	3088	32374(f)	3778	—
	3753	26638(g)	3988	26461(F)
	3561	28074(h)	4220	25074(G)
	3388	29507(i)	4220	23690(H)
	3231	30941(j)	4480	22315(I)

TABLE V

Some Raman shifts for methyl alcohol calculated from Table V

$d\nu$ by other authors Hibben (1939)	$d\nu$ calculated from Table IV	$d\nu$ by other authors	$d\nu$ calculated from Table IV
	42 (a—A)		1455 (b—B)
	177 (g—F)		1445 (c—A)
	700 (b—A)	1458	1423 (a—C)
	797 (a—B)	2942	mean 1441
	2809 (a—E)		2948 (g—H)
	2838 (b—D)		
	2859 (e—A)		3506 (f—A)
	2857 (d—B)		4240 (d—D)
2837	mean 2838		4240 (e—C)

TABLE VI

Methyl alcohol

Some combination shifts built up by the Raman shifts compared with observed shifts in the present case.

$\Delta\nu$ by other authors Hibben (1939)		Shifts observed	Shifts by combination	Shifts observed	Shifts by combination
ν_1 1029	ν_{10} 2914	2081 ($b-c$)	$\nu_1+\nu_2$ 2085	4887 ($f-c$)	$\nu_6+\nu_{13}$ 4876
ν_2 1056	ν_{11} 2942	2102 ($d-$A)	$2\nu_2$ 2112	4997 ($c-$D)	$2\nu_1+\nu_{11}$ 5000
ν_3 1111	ν_{12} 2987	2180 ($a-$D)	$\nu_1+\nu_4$ 2182	5626 ($c-$E)	$\nu_6+\nu_{14}$ 5610
ν_4 1153	ν_{13} 3506*	2200 ($c-$B)	$\nu_1+\nu_5$ 2200	5759 ($h-$I)	$\nu_9+\nu_{10}$ 5751
ν_5 1171	ν_{14} 4240*	3614 ($e-$B)	$\nu_1+\nu_8$ 3617	5817 ($i-$H)	$2\nu_{10}$ 5828
ν_6 1370	—	4212 ($c-$E)	$\nu_6+\nu_9$ 4207	7192 ($i-$I)	$\nu_{11}+\nu_{14}$ 7182
ν_7 1458	—	4323 ($g-$I)	$\nu_6+\nu_{11}$ 4312	7251 ($j-$H)	$2\nu_{11}+\nu_9$ 7254
ν_8 2588	—	4384 ($h-$H)	$\nu_7+\nu_{10}$ 4372	8626 ($j-$I)	$\nu_7+\nu_{10}+\nu_{14}$ 8612
ν_9 2837	—	4433 ($i-$G)	$\nu_7+\nu_{12}$ 4445	—	—

Two frequencies ν_{13} and ν_{14}, *i.e.*, 3506 and 4240 which have not been noted by previous workers have been included in the above list on the basis of calculations shown in Table V. One of these has occurred twice in Table V and three times in Table VI. It may further be noted that 2838 cm^{-1} which has been reported as one of the most intense Raman shift of the substance has occurred in four different combinations in Table V.

TABLE VII

Toluene

Optical catalyser	Absorption bands		Fluorescent bands	
	λ_{air} in Å.U.	ν_{vac} in cm^{-1}.	λ_{air} in Å.U.	ν_{vac} in cm^{-1}.
Anthracene	3787	26398(a)	3820	26170(A)
	3593	27824(b)	4032	24794(B)
	3417	29257(c)	4270	23412(C)
	3258	30685(d)	4536	22040(D)

TABLE VIII

Toluene

Some Raman shifts built up with the help of Table VII compared with those given by other authors.

$d\nu$ by others	$d\nu$ from Table VII	$d\nu$ by others	$d\nu$ from Table VII
218	228(a—A)	3070	3087(c—A)
1603	1604(a—B)	3026	3030(b—B)
1630	1654(b—A)	5848	5845(c—C)
2994	2986(a—C)	—	—

TABLE IX

Toluene

Some combination shifts built up by the Raman shifts compared with observed shifts in the present case.

$d\nu$ by other authors Ananthakrishnam (1936)		Shifts observed	Shifts by combination	Shifts observed	Shifts by combination
ν_1 519	ν_8 3002	4412 (b—C)	$\nu_4+\nu_7$ 4414	4358 (a—D)	$\nu_3+\nu_7$ 4356
ν_2 1377	ν_9 3205				
ν_3 1434	ν_{10} 2865	4463 (c—B)	$\nu_6+\nu_{10}$ 4468	7273 (d—C)	$\nu_3+\nu_{12}$ 7282
ν_4 1492	ν_{11} 2941				
ν_5 1588	ν_{12} 5848	4515 (d—A)	$\nu_5+\nu_7$ 4510	5784 (b—D)	$\nu_7+\nu_{10}$ 5787
ν_6 1603	ν_{13} 4586				
ν_7 2922	—	5891 (d—B)	$2\nu_{11}$ 5882	7217 (c—D)	$\nu_2+\nu_{12}$ 7225

TABLE X

Chlorobenzene

Optical catalyser	Absorption bands		Fluorescent bands	
	λ_{air} in Å. U.	ν_{vac} in cm^{-1}.	λ_{air} in Å.U.	ν_{vac} in cm^{-1}.
Anthracene	3795	26343(a)	3845	26068(A)
	3600	27770(b)	4050	24684(B)
	3424	29197(c)	4290	23303(C)
	3265	30619(d)	4561	21917(D)

TABLE XI

Chlorobenzene

Some Raman shifts built up with the help of Table X compared with those due to other authors.

$d\nu$ by others	$d\nu$ from Table X	$d\nu$ by others	$d\nu$ from Table X
275	275 (*a*—A)	3068	3086 (*b*—B)
3028	3040 (*a*—C)	3129	3129 (*c*—A)

TABLE XII

Chlorobenzene

Some combination shifts built up by Raman shifts compared with those observed in the present case.

$d\nu$ by other Anantakrishnam		Shifts observed	Shifts by combination	Shifts observed	Shifts by combination.
ν_1 702	ν_8 1443	1659 (*a*—B)	$2\nu_2$ 1660	5853 (*b*—D)	$2\nu_7+2\nu_9$ 5874
ν_2 830	ν_9 1565	1702 (*b*—A)	$\nu_1+\nu_4$ 1705	5894 (*c*—C)	$2\nu_8+\nu_{10}$ 5894
ν_3 989	ν_{10} 3008	4426 (*a*—D)	$\nu_5+\nu_{12}$ 4435	5935 (*d*—B)	$2\nu_5+\nu_{11}$ 5954
ν_4 1003	ν_{11} 3068	4467 (*b*—C)	$\nu_6+\nu_{13}$ 4461	7280 (*c*—D)	$\nu_4+2\nu_{13}$ 7283
ν_5 1295	ν_{12} 3140	4513 (*c*—B)	$\nu_8+\nu_{11}$ 4511	7316 (*d*—C)	$\nu_3+2\nu_{13}$ 7319
ν_6 1321	ν_{13} 3165	4551 (*d*—A)	$\nu_7+\nu_{13}$ 4537	8702 (*d*—D)	$\nu_6+\nu_7+2\nu_{10}$ 8709
ν_7 1372	—	—	—	—	—

TABLE XIII

Hexane

Optical catalyser	Absorption bands		Fluorescent bands	
	λ_{air} in Å.U.	ν_{vac} in cm^{-1}.	λ_{air} in Å.U.	ν_{vac} in cm^{-1}.
Hexane	3748	26673 (*a*)	3770	26517 (A)
	3558	28097 (*b*)	3978	25131 (B)
	3386	29524 (*c*)	4210	23746 (C)
	3230	30950 (*d*)	4470	22365 (D)

It may be noted here that the Raman shift calculated in this case agrees only in one instance (2966 cm.$^{-1}$ (*b*—B) and 2927^{-1}cm. (*a*—C) with mean value 2946 cm.$^{-1}$ agrees with 2940 cm.$^{-1}$ as given in Table XIV) with the values of others. This may be either due to the particular substance not being an effective catalyser or else due to conditions more favourable for the production of large shifts only. The agreement between the values calculated and those built up by combinations as given in Table XIV is however quite satisfactory.

TABLE XIV

Hexane

Some combination shifts built up by the Raman shifts compared with those observed in the present case.

$d\nu$ by other authors Andant etc. (1934)		Shifts observed	Shifts by combination	Shifts observed	Shifts by combination
ν_1 320	ν_8 1442	156 (*a*—A)	—	4432 (*d*—A)	$\nu_3+\nu_6+\nu_{10}$ 4445
ν_2 355	ν_9 2865	1542 (*a*—B)	$\nu_4+2\nu_1$ 1540	5732 (*b*—D)	$2\nu_9$ 5730
ν_3 825	ν_{10} 2940	1580 (*b*—A)	$\nu_4+\nu_2+\nu_1$ 1575	5778 (*c*—C)	$2\nu_8+\nu_9$ 5749
ν_4 900	—	3007 (*c*—A)	$\nu_3+\nu_5+\nu_6$ 3016	5819 (*d*—B)	$\nu_9+\nu_{10}$ 5805
ν_5 1041	—	4308 (*a*—D)	$\nu_1+\nu_5+\nu_{10}$ 4301	7159 (*c*—D)	$2\nu_9+\nu_8$ 7172
ν_6 1150	—	4351 (*b*—C)	$\nu_2+\nu_5+\nu_{10}$ 4336	7204 (*d*—C)	$\nu_7+2\nu_{10}$ 7195
ν_7 1315	—	4393 (*c*—B)	$\nu_8+\nu_{10}$ 4382	8585 (*d*—D)	$3\nu_9$ 8595

CONCLUSIONS

The results included in the above Tables indicate the fruitfulness of the new technique in obtaining Raman frequencies of the solvents in presence of some suitable substances which might act as optical catalysers. The agreement between the Raman frequencies obtained in the present case and those by direct method due to other authors is quite satisfactory. Prosad and Bhattacharyya have however obtained still better agreement which may be due to the fact that the optical catalyser used by them *viz.*, $Er(NO_3)_3$ and $KMnO_4$ have sharper absorption bands than anthracene and phenanthrene.

It may be worthwhile adding here that the existence of the phenomenon of optical catalysis has been supported by Hartley from the considerations of the classical theory of Raman effect. He has further predicted the effect of temperature and irradiating frequencies on the efficiency of the optically catalytic action of a particular substance. More work remains to be done in order to bring out the exact picture of the mechanism involved in the process and substantiate the predictions made by Hartley referred to above.

In the end, I would like to record my gratefulness to Principal K. Prosad, O.B.E., I.E.S., for his valuable suggestions.

PHYSICS DEPARTMENT,
SCIENCE COLLEGE, PATNA.

REFERENCES

Anantakrishnam, 1936, *Indian Acad. Sci. Proc.*, **3**, 70.
Andant, Lambert and Lecomte, 1934, *Comptes Rendus*, **198**, 1316.
Banerji and Mishra, 1937, *Zeits. f. Phys.*, **106**, 669.
Collins, 1939, *Phys. Rev.*, **55**, 470.
Glockler, 1943, *Reviews of Modern Physics*, **15**, 160.
Hartley, 1937, *Nature*, **139**, 329.
Hibben, 1939, *The Raman effect and its chemical applications*
Prosad and Bhattacharyya, 1939, *Zeits. f. Phys.*, **113**, 637.
Prosad and Bhattacharyya, 1936, *Nature*, **138**, 510.
Prosad, Bhattacharyya and Chatterji, 1935, *Zeits. f. Phys.*, **98**, 324.
Sambursky and Wolfsohn, 1940, *Faraday Soc. Trans.*, **36**, 423.