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The Fluorescence Spectrum of Benzene in Solution at 77°K

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The fluorescence spectrum of benzene in methylcyclohexane at 77°K has been analyzed in detail. The forbidden 0–0 band appeared weakly, and all the bands were interpreted as allowed bands except for the 0–992 band. The fluorescence spectrum has also been studied in carbon tetrachloride; the anomalous vibrational structure has been found in solutions as dilute as 10^{-3} M, irrespective of the cooling procedure. The correlation with the absorption and with the phosphorescence spectrum of benzene reported previously has been discussed.

Ivanova and Sveshnikov1) studied the fluorescence spectrum of benzene in an alcoholic solution at 77°K and gave a tentative vibrational analysis. The 0–0 band was not observed, and the 992-cm^{-1} progression appeared from bands separated by 606 and 1178 cm^{-1} from the assumed position of the 0–0 band. The $606+n\times992$ series was much stronger in intensity than the $1178+n\times992$ cm^{-1} series. Wolf2) also gave a simple analysis of the fluorescence spectrum of crystalline benzene at 77°K. The forbidden 0–0 band appeared weakly, while the $606+n\times992$ series appeared strongly. The 992-cm^{-1} progression was also seen to start from the 0–0 band with quite a strong intensity. The crystal spectrum at 77, 20.4, and 4.2°K has also been reported on by Shpak, Solov'ev, and Sheremet3) and by Vatulev, Sheremet, and Shpak.4)

We studied the fluorescence spectrum of benzene in solutions in ethanol, cyclohexane, and methylcyclohexane and of the crystal at 77°K in order to check if all the analyses previously reported were correct.

We also studied the fluorescence spectrum in carbon tetrachloride at 77°K. In previous papers5) we have found anomalous vibrational structures in the phosphorescence spectrum of benzene in carbon tetrachloride and in the absorption spectrum in a rapidly-cooled carbon tetrachloride solution. Here we experimented in order to check if any anomalous feature was also present in the fluorescence spectrum.

Experimental

Benzene was purified according to a method previously described.5) In the course of study toluene was found to be an impurity in benzene, since it emitted a characteristic fluorescence spectrum overlapping the benzene spectrum. The toluene in the benzene was therefore removed through oxidation with a potassium permanganate solution acidified with sulfuric acid. This operation was repeated several times before the ordinary purification operation of benzene.

Ethanol, cyclohexane, methylcyclohexane, and carbon tetrachloride were purified by methods previously described.6) A super-high vapor pressure mercury arc lamp of the ORC 1 kW type, CHM-621, was used as the light source, and Hg 2537 Å was introduced into the cell through a filter system.7) A RIKEN medium quartz spectrograph corresponding to a Hilger E2 was used throughout the work. The optical setup was exactly the same as that described previously except for a phosphoroscope.5) Here it was unnecessary. The surface of a frozen sample was oblique to the incident light. The concentration was fixed at 10^{-3} M for all the solutions. The slit-width was 50 μ, and Eastman Kodak plates 103a-0 were used. Exposure

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1) T. V. Ivanova and B. Ya. Sveshnikov, *Opt. Spectry.*, **11**, 332 (1961).

2) H. C. Wolf, "Solid State Physics," Vol. IX, ed. by F. Seitz and D. Turnbull, Academic Press, New York and London (1959), p. 1.

3) M. T. Shpak, A. V. Solov'ev and N. I. Sheremet, *Opt. Spectry.*, **13**, 393 (1962).

4) V. N. Vatulev, N. I. Sheremet and M. T. Shpak, *ibid.*, **15**, 315 (1964).

5) Y. Kanda and R. Shimada, *Spectrochim. Acta*, **17**, 7 (1961); Y. Kanda, Y. Gondo and R. Shimada, *ibid.*, **17**, 424 (1961).

6) Y. Kanda and R. Shimada, *ibid.*, **15**, 211 (1959); Y. Kanda, R. Shimada and Y. Sakai, *ibid.*, **17**, 1 (1961).

7) C. L. Braga and M. D. Lumb, *J. Sci. Instrum.*, **43**, 341 (1966).

times ranged from 2 to 15 h. The accuracy of measurement was about ±3 $\mathrm{cm^{-1}}$ for sharp bands and about ±20 $\mathrm{cm^{-1}}$ for broader bands.

Results and Discussion

The fluorescence spectrum of benzene in solutions in ethanol, methylcyclohexane, cyclohexane, carbon tetrachloride and in the crystal was studied at 77°K; some of the tracing curves are shown in Figs. 1 and 2. The spectrum in ethanol appears broad in comparison with that in methylcyclohexane; the vibrational analysis has been made with the latter at the beginning. The results are given in Table 1. A band at 37820 $\mathrm{cm^{-1}}$ is ascribed to the 0–0 band of the spectrum, a band which is forbidden by symmetry but which is allowed weakly by solvent perturbation. The 992-$\mathrm{cm^{-1}}$ progressions appear, perturbed by vibrations of $606(e_{2g})$, $405\times2(e_{2u}\times e_{2u})$, $405+671$ $(e_{2u}\times a_{2u})$, $1178(e_{2g})$, $405\times2+606(e_{2u}\times e_{2u}\times e_{2g})$, $849\times2(e_{1g}\times e_{1g})$, $970\times2(e_{2u}\times e_{2u})$ or $606+1326$ $(e_{2g}\times a_{2g})$, and $606+703\times2(e_{2g}\times b_{2g}\times b_{2g})$, and $606+849\times2(e_{2g}\times e_{1g}\times e_{1g})$. Therefore, all the bands in the progressions are allowed except for two bands, those at 37820 (0–0) and 36830 $\mathrm{cm^{-1}}$ (0–992). The spectrum in ethanol looks smoothed out of that in methylcyclohexane. The progression assigned to $1178+n\times992$ by Ivanova and Sveshnikov must be interpreted as the overlap of the $405\times2+n\times992$, $405+671+n\times992$, $1178+n\times992$, $970\times2+n\times992$ *etc.*, series. They did not find the 0–0 band of the fluorescence spectrum and assumed an unobserved position at 37780 $\mathrm{cm^{-1}}$ as the band origin. That the differences between the observed and calculated values are greater for the $1178+n\times992$ series than those for the $606+n\times992$ series means that their assignment, $1178+n\times992$, was not complete enough.

The fluorescence spectrum of benzene in cyclohexane was analyzed in the same way as that in methylcyclohexane. Cyclohexane undergoes a phase transition at −87°C, and the spectrum of a rapidly frozen sample contains bands from the high- and low-temperature phases. By the use of a careful annealing technique, the low-temperature-phase spectrum (the 0–0 band at 37705 $\mathrm{cm^{-1}}$) was separated from the high-temperature one (the 0–0 band at 37790 $\mathrm{cm^{-1}}$). Only the low-temperature spectrum is shown in Fig. 1.

The fluorescence spectrum of crystalline benzene was analyzed in comparison with the solution spectra. A weak band at 37713 $\mathrm{cm^{-1}}$ looked like the band origin of the spectrum. However, reabsorption must be taken into account, and an unobserved position at 37814 $\mathrm{cm^{-1}}$ was assumed here to be the 0–0 band of the spectrum. This really corresponds to the band at 37811 $\mathrm{cm^{-1}}$, one of the components of the 0–0 band of the absorption spectrum of the benzene crystal at 90°K suggested by Bronde, Medvedev, and Prikhot'ko.[8] The spectrum photographed at 77°K

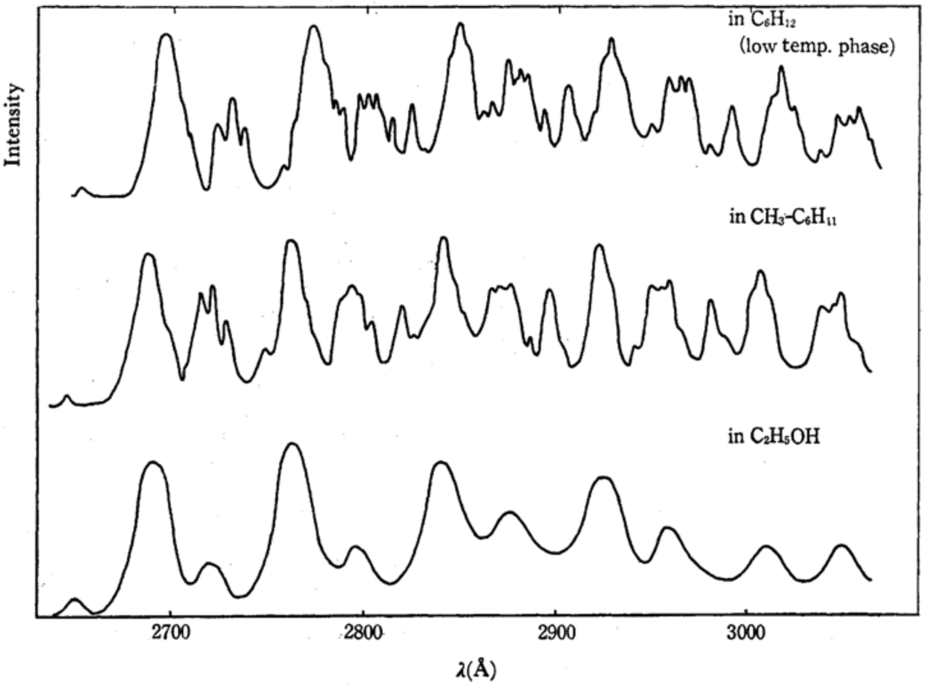

Fig. 1. Fluorescence spectra of benzene in various matrices at 77°K.

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[8] V. L. Broude, V. S. Medvedev and A. F. Prikhot'ko, *Zhur. Exptl. Teoret. Fiz.*, **21**, 665 (1951).

TABLE 1. FLUORESCENCE SPECTRUM OF BENZENE IN ETHANOL AND METHYLCYCLOHEXANE MATRICES AT 77°K

in Ethanol			in Methylcyclohexane			Assignment
$\tilde{\nu}$(cm^{-1})	Rel. int.	$\Delta\tilde{\nu}$(cm^{-1})	$\tilde{\nu}$(cm^{-1})	Rel. int.	$\Delta\tilde{\nu}$(cm^{-1})	
37735	1	0	37820	4	0	0, 0
37145	9	590	37210	10	610	0−606 (e_{2g})
			37030	5	790	0−405 (e_{2u})×2
36745	3	990	36830	6	990	0−992 (a_{1g})
			36745	6	1075	0−405(e_{2u})−671(a_{2u})
			36645	3	1175	0−1178(e_{2g})
			36410	2	1410	0−405(e_{2u})×2−606(e_{2g})
36180	10	1555	36215	10	1605	0−606−992
			36135	8	1685	0−849(e_{1g})×2
			36025	6	1795	0−405×2−992 0−606(e_{2g})−1178(e_{2g})
			35885	7	1935	0−970(e_{2u})×2 0−606(e_{2g})−1326(a_{2g})
35745	4	1990	35810	7	2010	0−606(e_{2g})−703(b_{2g})×2
			35745	7	2075	0−405−671−992
			35660	5	2160	0−1178−992
			35520	6	2300	0−606(e_{2g})−849(e_{1g})×2
			35420	4	2400	0−405×2−606−992
35170	9	2565	35225	10	2595	0−606−992×2
			35145	8	2675	0−849×2−992
			35025	6	2795	0−405×2−992×2
			34885	8	2935	0−970×2−992
34760	6	2975	34820	8	3000	0−606−703×2−992
			34765	8	3055	0−405−671−992×2 0−3047(e_{2g})
			34670	6	3150	0−1178−992×2
			34525	7	3295	0−606−849×2−992
			34425	5	3395	0−405×2−606−992×2
34175	8	3560	34240	10	3580	0−606−992×3
			34165	8	3655	0−849×2−992×2
			34010	6	3810	0−405×2−992×3
			33900	8	3920	0−970×2−992×2
33790	5	3945	33830	7	3990	0−606−703×2−992×2
			33785	8	4035	0−405−671−992×3
			33685	5	4135	0−1178−992×3
			33535	6	4285	0−606−849×2−992×2
			33455	4	4365	0−405×2−606−992×3
			33300	7	4520	
33195	4	4540	33250	8	4570	0−606−992×4
			33180	6	4640	0−849×2−992×3
32785	4	4950	32915	6	4905	0−970×2−992×3
			32830	6	4990	0−606−702×2−992×3
			32800	6	5020	0−405−671−992×4
			32705	2	5115	0−1178−992×4
			32550	2	5270	0−606−849×2−992×3
			32470	1	5350	0−405×2−606−992×4
32220	2	5515	32300	3	5520	
			32260	4	5560	0−606−992×5
			32195	1	5625	0−849×2−992×4
31795	2	5940				

in this experiment is essentially the same as that reported by Shpak, Solov'ev, and Shermet³⁾ and will not be reproduced here. It is to be discussed elsewhere.⁹⁾ However, we would like to propose here a suggestion concerning the interpretation of the 0–0 band of the fluorescence spectrum of the benzene crystal they studied.

If we use the data in Fig. 2 in Ref. 3 and add the vibrational frequencies of 607 and 990 cm^{-1} to 37221 and 36838 cm^{-1} respectively, we obtain 37828 cm^{-1} for both cases. This must be the band origin; it corresponds to one of the 0–0 bands of the absorption spectrum. The band at 37775 cm^{-1} may be a band from a trap or a remainder band due to reabsorption. The same interpretation can be applied to the spectra at 20.4 and 4.2°K in Fig. 1 in the paper by Vatulev, Sheremet, and Shpak.⁴⁾

No bands corresponding to the III series in Figs. 1 and 2 of Ref. 8 were found in our spectrum. They were not in Fig. 1 in Ref. 10 either and so must be ascribed to an impurity.

The fluorescence spectrum of benzene was also studied in carbon tetrachloride. In previous papers⁵⁾ we have reported an anomalous vibrational structure in the phosphorescence spectrum of benzene in carbon tetrachloride and have examined the absorption spectrum of benzene in carbon tetrachloride with rapidly- and slowly-cooled samples. The spectrum of a rapidly-cooled solution has a strong and broad 0–0 band, while that of a slowly-cooled solution gives weak and split 0–0 bands. No difference was found between the phosphorescence spectra of rapidly- and slowly-cooled samples; this phenomenon may tentatively be ascribed to the mixing of the rapidly-cooled phase in the slowly-cooled phase. The phosphorescence spectrum of weak intensity of the slowly-cooled sample might have been overshadowed by the phosphorescence spectrum of strong intensity of the rapidly-cooled sample. In the absorption experiment, the concentration was as high as 10 mol% since a thin-layer sample had to be used. For the phosphorescence spectrum the concentration was of the order of 10^{-3} M and the volume was about 2 m*l*. These incoincidences in concentrations and in the sample mounting may sometimes be crucial for the interpretation of the spectrum. Therefore, it is necessary to study the fluorescence spectrum at various concentrations. Concentrations were chosen according to a phase diagram of the CCl_4-Benzene System. While a phase diagram designed by Kapustinskii and Drakin¹⁰⁾ was used in the previous papers,⁵⁾ a new diagram recently suggested by Ott, Goates and Gudge¹¹⁾ has been used in this work. Samples were mounted as thin layers between quartz plates at 77°K. The results are shown in Fig. 2.

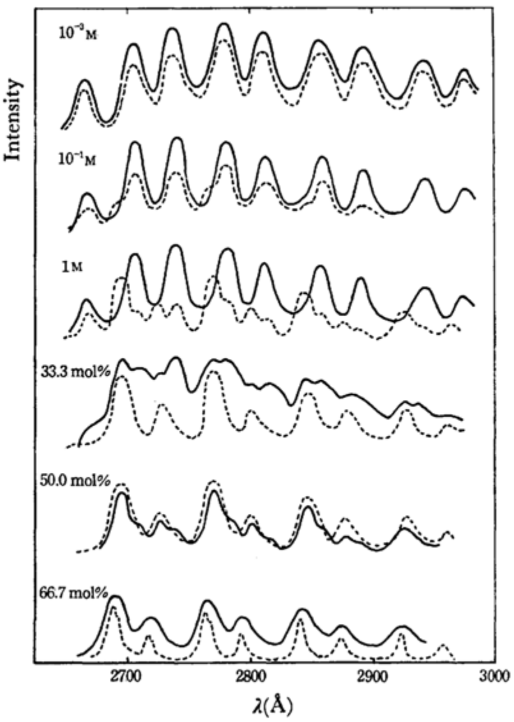

Fig. 2. Fluorescence spectra of benzene in carbon tetrachloride at 77°K.
——: Rapid cooling ……: Slow cooling

It is interesting to see that there is no difference between the fluorescence spectra of the rapidly- and slowly-cooled solutions at 10^{-3} M; this is in agreement with the results in the phosphorescence spectrum. In one of our previous papers⁵⁾ we assumed the mixing of the rapidly-cooled phase in the slowly-cooled phase, but this interpretation proves untenable. At such a low concentration both samples have the same phase and give an anomalous vibrational structure due to a strong environmental effect. At concentrations such as 33.3 and 50.0 mol%, the fluorescence spectrum of the slowly-cooled samples gives a weak 0–0 band (hereafter we will call this the H-spectrum), unlike the spectrum at concentrations as low as 10^{-3} M, which has a strong 0–0 band (hereafter we will call this the L-spectrum). A question arose whether the H-spectrum of the slowly-cooled samples of 33.3 and 50.0 mol% solutions could be the spectrum of the benzene crystal crystallized out of the solution during the cooling processes. However, this is not the case, since the wavelength of each band was different from that of the benzene crystal.

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9) A. Nakahara, M. Koyanagi, Y. Murakami, T. Edamura and Y. Kanda, to be published.

10) A. F. Kapustinskii and S. I. Drakin, *Bull. acad. sci. U.S.S.R. classe sci. chim.*, 475 (1947); *Chem. Abstr.*, **42**, 1902 (1948).

11) J. B. Ott, J. R. Goates and A. H. Gudge, *J. Phys. Chem.*, **66**, 1387 (1962).

The spectra of the slowly-cooled samples at 10^{-3} and 1 M (the latter corresponding to about 10 mol%) and that of the rapidly-cooled samples at 33.3 and 50.0 mol% show an overlapping of the L- and H-spectra. The species giving the H-spectrum is considered to be C_6H_6-$2CCl_4$ on the basis of the finding that the H-spectrum appears in the slowly-cooled samples over the wide range from 10^{-1} M to 50.0 mol% (of benzene) and the results of the study of the molecular complex of carbon tetrachloride with benzene from the far infrared spectrum by Chantry, Gebbie, and Mirza.[12]

The spectrum of the slowly-cooled sample at much higher concentrations, such as 66.7 mol%, is the same as the spectrum of the benzene crystal, and the spectrum of the rapidly-cooled sample is an overlapping of the H-spectrum and the spectrum of the benzene crystal. These results show that benzene was crystallized out of the solution during the cooling process; the presence of the C_6H_6-CCl_4 complex, which is indicated by the freezing-point method, is not clearly shown in the fluorescence spectrum.

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12) G. W. Chantry, H. A. Gebbie and H. N. Mirza, *Spectrochim. Acta*, **23A**, 2749 (1967).