The Absorption Bands of Benzene and Its Derivatives in Visible Region

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Benzene is known to show four absorption bands at 1850 Å., 2070 Å., 2590 Å. and 3400Å., the one at the shortest wave-length being the strongest. According to the theory proposed by Goeppert-Mayer and Sklar[1], the molecule of benzene has one ground level $^1A_{1g}$ and six lower excited levels $^3B_{1U}$, $^3E_{1U}$, $^3B_{2U}$, $^1B_{2U}$, $^1B_{1U}$ and $^1E_{1U}$, with the energies increasing progressively in the given order. The strongest absorption band at 1850 Å. was attributed to the transition $^1A_{1g}-^1E_{1U}$, and the bands at 2070 Å. and 2590 Å. were ascribed to the transition $^1A_{1g}-^1B_{1U}$ and $^1A_{1g}-^1B_{2U}$, respectively. As to the band at 3400 Å., an interpretation was given in the paper of the authors named, but later it was assumed by Sklar[2] to be due to the forbidden $^1A_{1g}-^3E_{1U}$ transition. This theory, however, cannot be regarded as being quite satisfactory, especially in so far as it restricts

(1) M. Goeppert-Mayer and A. L. Sklar, *J. Chem. Phys.*, **6**, 645 (1938).

(2) A. L. Sklar, *Rev. Mod. Phys.*, **14**, 232 (1942).

the considerations only to the transition to the triplet states. Indeed, it has been criticized by London,[3] Mulliken[4] and Shull[5] from various points of view; but even when we take into account the opinions of these authors, we cannot explain why the singlet-triplet transition would not yield the corresponding absorption bands, which may lie in the visible region. Apart from these considerations, it seemed worth while to scrutinize the spectroscopic properties of benzene and its derivatives in the visible region. It was found that, besides the four bands hitherto known, benzene and some of its derivatives show a weak, but distinct, absorption band in the vicinity of 5200-5300 Å., which, strangely enough, has escaped observations by the earlier workers.

The measurements were made by photoelectric method, using a multiplier photo-tube RCA 931 A. The samples were purified by the method described in "Organic Solvent"[6] with the greatest possible care. The observations were made with a pure substance without using any solvent. The thickness of the liquid in the cell was 20 cm.

The maximum of the band shown by benzene was situated at 5200 Å. with the intensity of about 5×10^{-6} in molar extinction coefficient unit. The corresponding absorption was also found in toluene, monochlorobenzene and tetralin with the maximum at 5290 Å., 5250 Å. and 5280 Å., respectively. In the cases of benzene, monochlorobenzene and tetralin, the curves of absorption spectrum showed a smooth protrusion in the said spectral region, while that of toluene was split into two crests. It may be reasonable to assume that these bands are due to the singlet-triplet transitions, although the numerical agreement, with the calculated energy difference found in earlier reports, is not satisfactory.

In addition to the new finding described above, it is of great interest to note that there is a nice simple rule governing the location of absorption bands observed in benzene. Namely, if we divide the wave-numbers (in cm^{-1} unit) corresponding to the absorption maxima with 9653 cm^{-1}, we obtain almost the round numbers 2, 3, 4 and 5, except for the band at 1850 Å. which gave the figure 5.6 (see Table 1). We

Table 1

λ in Å.	ν in cm^{-1}	1/9653
1850	54054	5.600
2070	48356	5.009
2590	38612	4.000
3400	29412	3.047
5200	19231	1.992

are not in a position at present to give an explanation of this interesting rule, but it is doubtless that it involves a problem which awaits theoretical elucidation in the future.

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(3) A. London, *J. Chem. Phys.*, **13**, 396 (1945).
(4) R. S. Mulliken, *J. Chem. Phys.*, **16**, 118 (1948).
(5) Shull, *J, Chem. Phys.*, **17**, 295 (1949).
(6) A. Weissberger and E. Proskauer, "Organic Solvents."