

viscosity resulting from a rise in temperature when the heat input is applied. An attempt to observe a thermomechanical effect directly, with apparatus similar to that used in the quantitative measurements on helium<sup>2</sup>, also gave a negative result. Landau<sup>3</sup> has stated that a thermomechanical effect in water is to be expected; but from our results it is clear that any such effect, if it exists, must certainly be less than one ten-thousandth of that observed in helium.

We must conclude that the flow of water through very narrow channels of the order of  $10^{-6}$  cm. in width exhibits no very unusual features. The leakage of water vapour which is observed to occur into evacuated apparatus through such narrow channels must therefore be presumed to be due to surface tension action alone. Further, so long as the apparatus is maintained in a normally humid atmosphere, it will not be possible to detect any air leakage unless excess pressures are used exceeding that due to the surface tension, which can, of course, in channels of this width, reach very high values.

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<sup>1</sup> Allen and Misener, *Proc. Roy. Soc., A*, **172**, 467 (1939).

<sup>2</sup> Allen and Reekie, *Proc. Camb. Phil. Soc.*, **35**, 114 (1939); *Nature*, **144**, 475 (1939).

<sup>3</sup> Landau, *J. Phys. U.S.S.R.*, **5**, No. 1, 71 (1941).

### Near Ultra-Violet Emission Bands of Benzene

In the course of a study of the high-frequency discharge in benzene vapour, a set of bands in the spectral region 3000–2475 Å. is obtained using oscillations in the frequency range 1765–1200 kc./sec. to excite the flowing vapour of benzene (pressure  $\sim 0.1$  mm. mercury). These oscillations were produced in a modified Hartley circuit using a Mullard PM4DX valve. A Hilger medium quartz spectrograph was used as the resolving instrument to photograph the spectrum. The bands, which are degraded towards longer wave-lengths, occur in several distinct groups, six such being obtained in the present experiments. Measurements of the wave-lengths of the band heads show that they are identical with the bands obtained in the Tesla discharge in benzene vapour<sup>1,2</sup>.

It has been possible to analyse most of the bands observed into five series designated as *A*, *B*, *C*, *D* and *F*, in all comprising about 76 band heads, in accordance with the nomenclature adopted by Sponer *et al.*<sup>3</sup>, in their analysis of the near ultra-violet absorption bands of benzene. It may be recalled that these absorption bands of benzene are, according to Sklar<sup>4</sup>, due to the forbidden electronic transition  ${}^1A_{1g} \rightarrow {}^1B_{2u}$  which can only be made possible in the presence of a superposed non-totally symmetrical vibration of the type  $\epsilon_g^+$ . In agreement with this deduction, all of these five series in emission, except the *F* series, involve the ( $606 \text{ cm.}^{-1}$ )  $\epsilon_g^+$  vibration, either in the final state or in the initial state where its frequency falls down to  $520 \text{ cm.}^{-1}$  exactly as in absorption or fluorescence spectra. The present data on the *F* series, however, are better represented if a frequency of  $1610 \text{ cm.}^{-1}$  instead of  $1596 \text{ cm.}^{-1}$  is assumed for the second  $\epsilon_g^+$  vibration which is also present in the ground state. The average discrepancy

between observed and calculated values is  $5 \text{ cm.}^{-1}$ , which is equivalent to about 0.4 Å. in this region and is within the limits of experimental error. About twenty band heads the intensity of which is low do not afford unambiguous classification. They fit in fairly well as members of one or other of the above series, involving frequencies both in the excited and the ground states; but it is also possible that they may involve some other new series altogether.

Whereas in absorption the positive members of the various series, that is, those involving frequencies of the excited state, are naturally predominant, in high-pressure fluorescence it is the negative members involving vibration frequencies of the ground state which form the bulk of the spectrum. Indeed, a rearrangement of the data of Ingold and Wilson<sup>5</sup> on the fluorescence spectrum of benzene clearly shows this expected difference between absorption and high-pressure fluorescence. The emission spectrum, which ought to contain both types of members of the series and hence present a much more complicated structure is, however, surprisingly simple. This is due to the circumstance that although both negative and positive members of the series are present, they are not loaded with more than 3 or 4 quanta of  $160 \text{ cm.}^{-1}$ , which is the difference between  $(\alpha^{1_{2g}})''$  (400) and  $(\alpha^{1_{2g}})'$  (240) non-totally symmetrical frequency. In contrast to this, it may be noted that most of the series observed in fluorescence are loaded with high quanta (in some cases up to 26) of this difference frequency.

The intensity distribution in each series of bands is roughly the same as that observed in the fluorescence spectrum, namely, an almost regular decrease with increasing quantum numbers of vibration in each series. The intensity of the various series is, however, in the following order: *B*, *F*, *D*, *A* and *C*. This may be contrasted with the intensity of the fluorescence series, which from the data of Ingold and Wilson gives the following order: *C*, *A*, *B*, *E* and *D*.

This analysis shows that the bands observed are, as in fluorescence, to be attributed to the electronic transition  ${}^1B_{2u} \rightarrow {}^1A_{1g}$  in the benzene molecule.

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<sup>1</sup> McVicker, Marsh and Stewart, *Phil. Mag.*, **48**, 628 (1924).

<sup>2</sup> Austin and Black, *Phys. Rev.*, **35**, 452 (1930).

<sup>3</sup> Sponer, Nordheim, Sklar and Teller, *J. Chem. Phys.*, **7**, 207 (1939).

<sup>4</sup> Sklar, *J. Chem. Phys.*, **5**, 669 (1937).

<sup>5</sup> Ingold and Wilson, *J. Chem. Soc.*, 941 (1936).

### The 'Green Flash' at Sunset with a Near Horizon

THE observation of the 'green flash' with a near horizon, presumably at Harrow, recorded by Mr. D. R. Barber in *Nature* of August 4, p. 146, recalls one of which I gave an account in the *Meteorological Magazine* of October 1926. In this case the artificial 'horizon' was a building some miles off, and the colour of the flash was "a smoky white with a faint tinge of green". Mr. Barber also comments on the small saturation of the colours which he observed; it is possible that this is due, not to the nearness of the 'horizon', but to the smoky atmosphere of London.

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