NOTE ON THE RELATION BETWEEN THE EMISSION SPECTRUM OF A COMPOUND AND ITS ABSORPTION SPECTRUM IN SOLUTION.

BY ALBERT K. CHAPMAN.

IT is the intention of this note to call attention to a certain relation which appears to exist between the spectrum of a compound, excited by the ordinary vacuum tube discharge, and the absorption band which the same compound exhibits when in solution. In every case the compound was introduced into a spectrum tube of the usual form, fitted with aluminum electrodes, exhausted, sealed off and excited by the discharge from an induction coil. The tube was heated in order to vaporize the compound; the compounds used having been selected simply on account of their low melting points.

In the case of mercuric iodide the pressure was reduced to about 0.08 mm. when sealed off. Before heating, when the discharge was allowed to pass, the spectrum showed the lines of mercury and iodine, beside those due to the residual air. After the tube had been sufficiently heated to vaporize the mercuric iodide to a considerable extent, the character of the discharge was radically changed, becoming an intense violet in color. In addition to the lines of mercury and iodine there appeared a brilliant band, shading off toward both the red and the violet, extending from about λ 4420 to λ 4450 as seen visually: on the photographic plate it is shown broader. All measurements were taken by means of a Hilger constant deviation spectrometer. For making the photographs the telescope was replaced by the usual camera of 21-inch focal length. In observing the absorption spectrum the following solution was used:

KI	11.18 gr.
HgI_2	10.60 gr.
Water	100.0 gr.
Thickness of absorbing layer	12.32 cm.

The observations were made at room temperature with a Nernst glower as the source of continuous spectrum. It was necessary to use the potassium iodide in order to get the mercuric iodide into solution: a separate solution of potassium iodide was examined for absorption but none was found.

Fig. 1 shows: (*a*) Continuous spectrum of Nernst glower. (*b*) Absorption spectrum of mercuric iodide solution. (*c*) Mercuric iodide spectrum. (*d*) Mercuric iodide spectrum (shorter exposure). (*e*) Iodine spectrum. (*f*) Mercury arc spectrum. (*g*) Oxygen spectrum.

It will be observed that the emission and absorption bands correspond, although it is to be remembered, of course, that the width of the absorption band may be changed by varying the concentration, thickness of absorbing layer, etc. As no photographic scale was available for comparison, a few of the prominent lines are marked.

A similar set of observations was made on stannic iodide, the tube having been exhausted to 0.07 mm. In this case it was not necessary to heat the tube as it became hot enough from the discharge to vaporize the compound. In addition to the lines for tin, iodine, oxygen and nitrogen, the spectrum showed a band extending from about λ 5160 to the violet limit of visibility. The following is the absorption solution used:

SnI_4	0.1790 gr.
Ethyl alcohol	100 c.c.
Thickness of absorbing layer	1.95 cm.

Fig. 2 is as follows: (*a*) Continuous spectrum. (*b*) Absorption spectrum of solution. (*c*) SnI_4 in vacuum tube, 25 min. exposure. (*d*) SnI_4 in vacuum tube, 15 min. exposure. (*e*) SnI_4 in vacuum tube, 7 min. exposure. (*f*) Tin spark with capacity. (*g*) Iodine spectrum. (*h*) Oxygen spectrum.

The absorption covers the region from the extreme violet to about λ 5330, while the emission band extends from the violet to λ 5160, giving fair agreement between the emission and absorption bands.

In the case of ferrous iodide the spectrum was very faint and difficult to photograph; pressure 0.01 mm.

SOLUTION.

FeI_2	1.075 gr.
Sugar	10.00 gr.
Water	600 c.c.
Thickness of absorbing layer	1.93 cm.

Fig. 3 is as follows: (*a*) Continuous spectrum. (*b*) Absorption spectrum of solution. (*c*) FeI in vacuum tube. Here again the emission band corresponds to the absorption band but does not extend so far into the violet. The main emission band extends from about λ 4550 to λ 4850, but there is also a faint emission band at λ 4150. Longer exposure might have shown this to be wider.

It is interesting to note, in this connection, that mercurous chloride

gives a very strong emission band from λ 5350 to λ 5750, while the salt itself is white and insoluble except in very small quantities. The emission spectrum is shown in Fig. 4.

It is seen that a wide emission band, shading off toward both the violet and red, is characteristic of the compounds investigated. When the absorption spectrum of the compound is available, there seems to be a definite relation existing between the absorption and emission bands. It would seem, therefore, that the vibrating system responsible for the emission is also effective in producing absorption in solution.

These experiments were carried on at the Physical Laboratory of the Ohio State University under the direction of Dr. A. W. Smith, to whom my thanks are due for his help and interest at all times.

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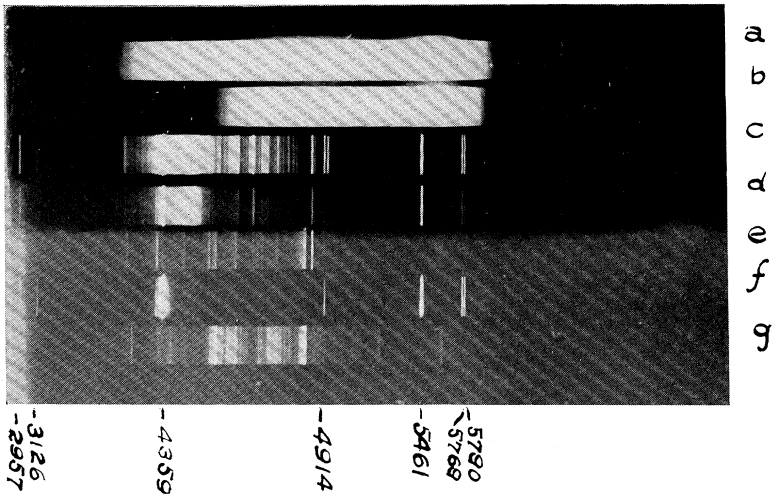

Fig. 1.

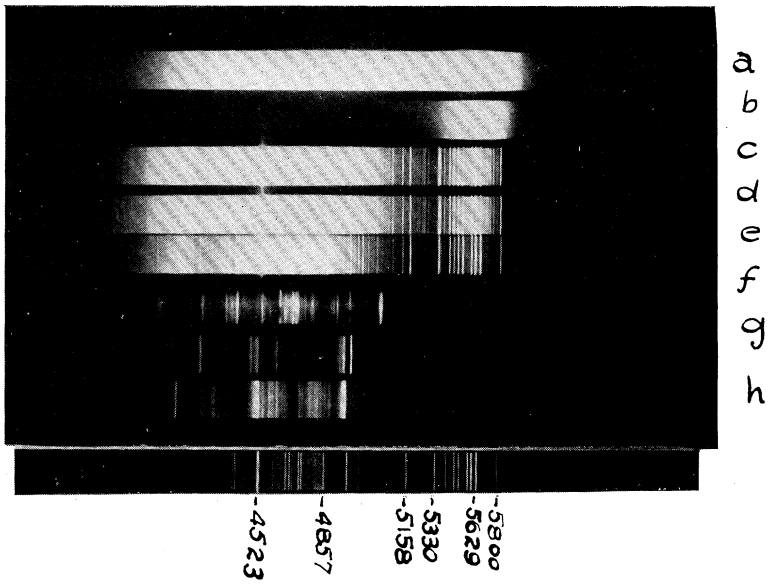

Fig. 2.

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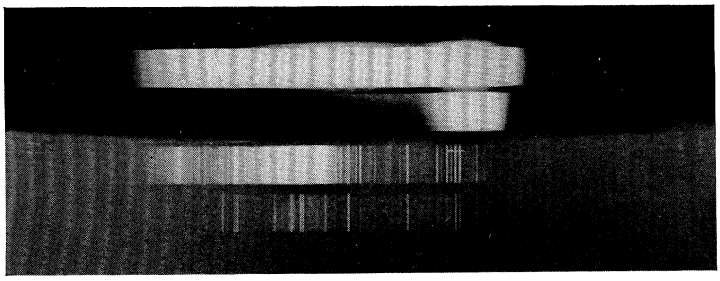

Fig. 3.

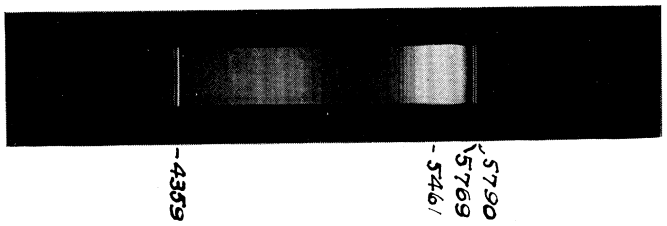

Fig. 4.

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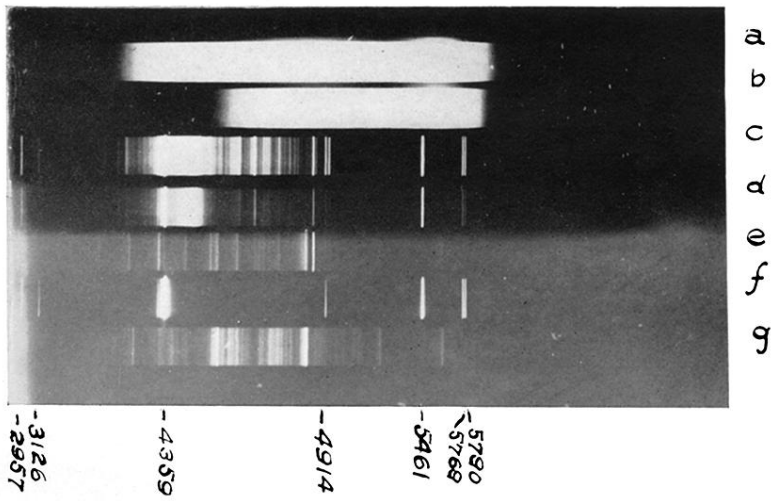

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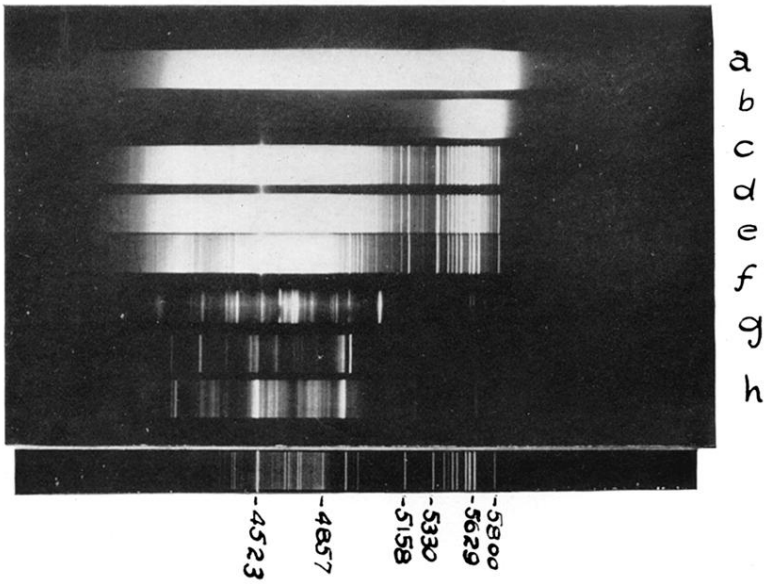

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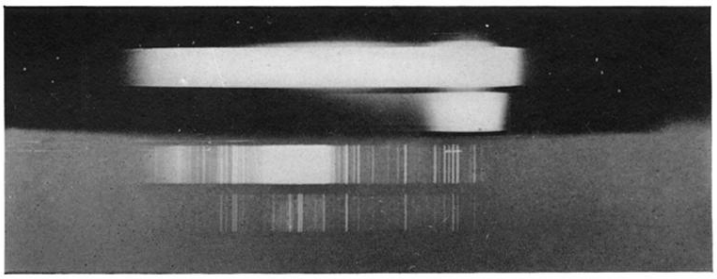

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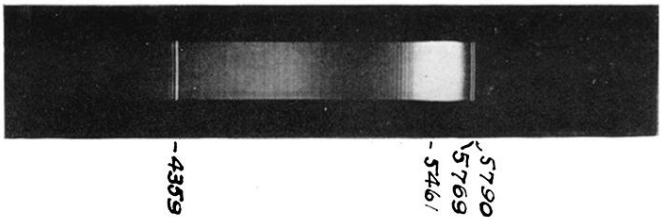

Fig. 4.