A Note on the Intensities of the Lines of the Balmer Series of Hydrogen

By

Masamichi Kimura aud Mitsuharu Fukuda

(Received May 28, 1921)

In a course of the study of the iodine spectrum containing a trace of water vapour, one of us noticed that the line Hα of hydrogen was very intense in comparison with the lines of the higher member of the Balmer series. This suggested that the iodine vapour suppresses higher members of the Balmer lines and led us to the further study of the phenomena. Examining the literatures, it was found that Holtzmark[1] has studied the influence of iodine vapour upon the intensity ratio of Hβ to Hγ of the lines of the Balmer series of hydrogen. He concluded that an addition of iodine vapour to hydrogen has no appreciable influence upon the intensity ratio of these lines, when the mixture of these gases was excited by cathode rays. But the phenomena would depend upon the vapour density of iodine, and consequently the following experiments were performed to see how the behaviour of iodine vapour varies with its densities.

The spectral tubes first used in this experiment were of the form of an ordinary Geissler tube having two side tubes. In one of the tubes a piece of metallic sodium free from oil was put and a small quantity of an iodine crystal was placed in the other. The air in the tube was pumped out with a Gäde pump, and then a proper amount of hydrogen was driven out from the sodium by heating it gently with

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1 Ann. d. Phy. **55**, 245 (1918).

a fine jet of gas flame. The vapour density of the iodine was controlled by changing the temperature of a side tube containing it, but both the hydrogen and iodine were soon used up, and a satisfactory result was not obtained. Next, the hydrogen spectrum emitted by hydrogen iodine was photographed at various pressures, and these were compared with that of pure hydrogen at the same pressures. By such a procedure the influence of iodine vapour upon the spectrum of hydrogen can be studied.

In the study of the spectrum of hydrogen emitted from a tube containing hydrogen iodide, the gas chemically prepared was constantly passed slowly through the discharge tube, which was excited by an uncondensed discharge from an induction coil. The light emitted from the side of the capillary portion was analysed with a small spectrograph having a constant deviation prism. The spectrum was taken at the pressure of ½, 3, 7, 10, and 14 mm. of the hydrogen iodide. The spectrum of pure hydrogen was also photographed at the corresponding pressures. For each of these pressures, the times of exposure were varied, and two plates having almost equal intensity for $H\alpha$ were selected from the spectrograms of hydrogen and hydrogen iodide. By these two plates, the intensities of the remaining members of the Balmer lines were compared. The result obtained in this way is not of course quantitative. But this affords us a qualitative idea about the influence of iodine vapour upon the intensity distribution of the Balmer lines.

We now proceed to describe the result. On the spectrum emitted by the hydrogen iodide at the pressure of ½ mm., lines of the Balmer series and the spectra of iodine appeared pretty strong, while the secondary spectrum was very faint. As the vapour pressure was raised, both the hydrogen and iodine spectra got stronger and the secondary spectrum appeared distinctly. The intensity distribution among the lines of the Balmer series emitted from such tube remained almost the same as that of pure hydrogen up to the pressure of 7 mm. But at the pressure of 10 mm. $H\beta$, $H\gamma$, $H\delta$, etc. became distinctly less intense in the hydrogen iodide tube than in the pure hydrogen at the same pressure. This difference came out more distinctly with the spectrum taken at the higher pressure of 14 mm. (Fig. 3).

According to Holtzmark, as stated before, an addition of iodine to hydrogen has no appreciable influence upon the intensity ratio of the lines $H\beta$ to $H\gamma$ when the mixture of these gases was excited by cathode rays, and this intensity ratio depends upon the partial pressure of hydrogen. As regards the partial pressure of iodine in the gas mixture, he did not give an exact statement but only supposed it was very small. In our experiments, however, intensities of higher members of the Balmer lines are reduced decidedly in comparison with Hα when a certain amount of iodine vapour was added to hydrogen.

A similar experiment was also performed with chlorine. In this case, vapour of hydrogen chloride chemically prepared was passed slowly through a discharge tube, and the lights emitted from the side of the capillary at various pressures were photographed through the same spectrograph. The spectrum thus obtained was compared with that of hydrogen taken at the corresponding pressure. The result is that the lines of higher members in the former spectrum were weaker than those in the latter, the intensities of Hα being made almost equal for the both spectra. In Fig. 2, "a" shows the spectrum emitted by HCl gas at the pressure of 15 mm, "b" that of pure hydrogen at the same pressure, and "c" the spectrum emitted by a tube having NaCl-electrodes and containing a small amount of hydrogen. In these three spectrograms, the intensity of Hα from hydrogen tube is little less than those of the remaining ones, but the intensity of Hδ from the pure hydyogen is clearly stronger than the other.

Addition of vapour of sulphur, mercury (Fig. 4) or sodium separately to hydrogen gave similar results. Thus all of the results obtained tell us that the presence of a certain amount of vapoür of external gas either electro-positive or electro-negative in hydrogen at a small pressure reduces the intensity of higher members of the lines of the Balmer series.

Lastly, the influence of the raise of hydrogen pressure upon the intensity distribution under consideration was studied, and the result is shown by the two spectra (Fig. 1): "a" represents hydrogen spectrum taken at a low vapour density, while "b" that of higher density. The lines Hγ and Hδ in "a" are evidently stronger than those in "b", Hα being nearly equal in the both spectra.

Merton[1] has already found that in a water vapour tube intensities of Hβ, Hγ and Hδ were reduced in comparison with those of pure hydrogen in the ratio of $\frac{1}{2}$, $\frac{1}{3}$ and $\frac{1}{4}$ respectively, while those emitted by a trace of hydrogen in helium at a high pressure were reduced

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[1] Proc. Roy. Soc. **96**, 112 (1920).

only to 3/4, 2/5, 1/4 and 2/13. The results are very interesting, but he did not exactly give the pressures of his tubes.

Our results show that the intensity distribution among the lines of the Balmer series is greatly affected by the pressure of hydrogen, and that the presence of a certain amount of external gases such as iodine, chlorine, mercury, etc. has much larger influence than hydrogen itself at the same pressure. The phenomena described above will partly be due to the pressure effect and partly to certain specific action of foreign atoms or atomions toward hydrogen atoms. Indeed, the fact that the higher members of the Balmer series were suppressed in the case of the present experiment might be expected if we simply accept the so-called Bohr's Theory.

Summary

1. Influence of the vapour pressure of hydrogen, and that of presence of chlorine, iodine or mercury in hydrogen tubes upon the intensities of the lines of the Balmer series were studied.
2. It was found that the presence of certain amounts of the vapours in hydrogen at a small pressure reduces selectively the intensities of higher members of the lines of the Balmer series.

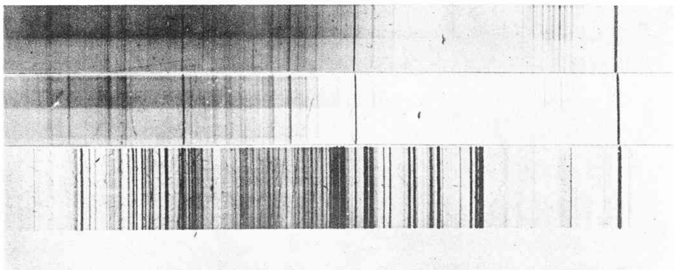
In conclusion, the writers wish to express their thanks to Prof. T. Mizuno for the interest he has taken in this work.

Fig. 1.

a Hydrogen: press: low

b Hydrogen: press: high

Fig. 2.

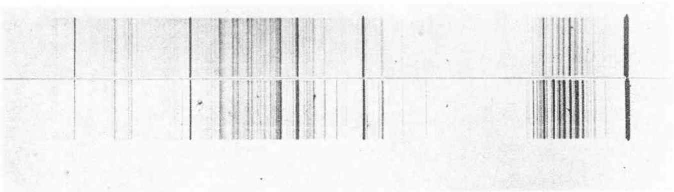


a HCl. press. 15 mm.

b H_2 press 15 mm.

c H_2 in chlorine tube.

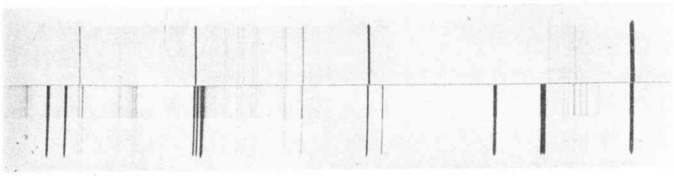
Fig. 3.



Hydrogen.

Hydrogen iodide.

Fig. 4.



Hydrogen.

Hydrogen with Mercury.