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XXXIX. The fluorescence, magnetic rotation, and temperature emission spectra of iodine vapour

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Results.

(1) The insulating liquids do not differ very much from one another in power of resisting discharge, the strength lying between the limits 110 volts per micron and 70 volts per micron, though some liquids seem to have slightly less strength. The range of voltage here spoken of is between 25 and 400.

(2) Some liquids have a peculiar variation in potential gradient for distances between 1μ and 2μ . Castor oil, olive oil, and paraffin are cases in point.

(3) All insulating liquids have greater strength than air for P.D. greater than 300 volts; for less P.D. liquids have much less strength than air.

(4) The results for a homologous series of hydrocarbons do not indicate any simple connexion between composition and power of resisting discharge; the differences found are as likely to be due to accidental impurities as to specific qualities of the liquids.

But these simple substances have specially great dielectric strength. It may be that simplicity of composition makes for strength.

(5) Whereas in the case of gases there is always a horizontal portion in the curve, in liquids there is no such distinct break in the curve between 25 and 400 volts, unless the region at about 60 volts in castor oil, olive oil, and paraffin is of this nature.

(6) No simple connexion can be observed between power of resisting discharge and specific inductive capacity, in liquids.

(7) The temperature throughout was from 15° C. to 18° C.

XXXIX. *The Fluorescence, Magnetic Rotation, and Temperature Emission Spectra of Iodine Vapour.* By R. W. WOOD, Professor of Experimental Physics, Johns Hopkins University*.

[Plate IV.]

THE fluorescence of iodine vapour has been observed by Wiedemann and Schmidt, and also by Konen, but the luminosity appeared to be too feeble to allow a study, either visual or photographic, to be made of its spectrum. By studying the conditions under which the fluorescence manifests itself to the best advantage, it has been found possible to photograph its spectrum with a large three-prism spectrograph, with its slit narrowed to such a degree that the

* Communicated by the Author.

distance between the D lines of sodium was fully three times their width.

The magnetic-rotation spectrum which was discovered last year, which manifests itself when polarized white light is passed in succession through magnetized iodine vapour and a Nicol prism, set originally for extinction, has been photographed with a concave grating of twelve feet radius, so that a very perfect knowledge of its nature is now at our command. As is the case with the analogous magnetic-rotation spectrum of sodium vapour, many of its bright lines coincide in position with the dark lines of the absorption spectrum, though the one is by no means the complement of the other.

The remarkable emission of light which occurs when iodine is raised to a temperature of 700° or over has been carefully studied, and the condition found under which its spectrum is very distinctly discontinuous. Its spectrum is remarkably like the fluorescence spectrum, though the heads of the bands do not appear to coincide, due possibly to a difference in the densities in the two cases.

The three types of spectra enumerated above will now be considered in detail.

The Fluorescence Spectrum.

The fluorescence of iodine vapour manifests itself to the best advantage when the vapour is formed in a moderately high vacuum. A glass bulb from 5 to 10 cms. in diameter, and containing a few flakes of iodine, is exhausted on a mercurial pump and sealed. The fluorescence at once appears when a beam of sun- or arc-light is focussed at the centre of the bulb by means of a large condensing-lens, no heating of the bulb being necessary. The cone of fluorescent light is yellowish green and of considerable intensity, and can be shown to a large audience in a darkened room. If the bulb contains air at atmospheric pressure, there is absolutely no trace whatever of fluorescence. Not until the pressure has been reduced to about 15 cms. does the luminous cone appear, and it is then so feeble that only close inspection reveals its presence. The intensity gradually increases as the pressure is further reduced, the most rapid change occurring between 1 cm. and the high vacuum. The presence of air also destroys the magneto-rotatory power of the vapour, though to a less degree at fairly low pressures; in other words, the fluorescence seems to be more sensitive than the magnetic rotation. I was at first inclined to agree with Professor Larmor that the effects might be due to collisions, the phenomena requiring

time for their development. The heating of a gas by absorption of radiant energy must in some way result from a transformation of the energy stored in the molecule during absorption (which we may regard as potential) into kinetic energy at the moment of collision. That is, the velocity of the rebound is increased by actions or motions going on within the molecule. If we consider that the molecule is capable of storing up energy to a certain point after which further absorption results in a re-emission of radiant energy (fluorescence), and if we further assume that at the moment of collision the stored energy is liberated, or spent in increasing the molecular velocity, it is clear, if the time-interval between collisions is sufficiently small, that the internal energy of the molecule cannot be increased up to the point at which fluorescence manifests itself. At atmospheric pressure, however, the average time-interval between two collisions is sufficient for the passage of about 130,000 light-waves. It may appear at first sight improbable that fluorescence would be excited at all if the passage of such an enormous number of waves failed to awaken any response. The capacity of a molecule for storing energy may be, and probably is, very great; and it is by no means unlikely that a molecule can absorb the energy of many thousand light-waves before being brought to the unstable condition at which a re-emission of radiant energy commences. If molecular impacts are responsible for the suppression of the fluorescence, it would appear probable that a light gas, such as hydrogen, would be less detrimental. Bulbs were accordingly filled with hydrogen, and the fluorescence of the iodine vapour examined as the pressure was gradually reduced. Faint traces of fluorescence appeared at a pressure of 30 cms., much higher than was the case with air; but at lower pressures there did not seem to be very much difference, the intensity of the fluorescence in air and hydrogen at 2 cms. pressure being about the same. It was found, moreover, that if a bulb containing just enough air to prevent the fluorescence were warmed, the fluorescence at once appeared. This circumstance may perhaps be taken as evidence against the theory of molecular collisions, and we may adopt as an alternative what may be termed a solution theory. I have been of the opinion for many years that we may speak with perfect correctness of a solution of a gas in a gas. Experiments made in 1896 on the absorption spectrum of iodine and bromine mixed with the vapours of bisulphide of carbon, showed that a portion of the iodine was in a state of solution, giving an absorption spectrum devoid of lines or bands, while a portion

existed in the state of a gas, giving the fine-line absorption spectrum. With a given density of the vapour, a certain amount of iodine could be vaporized without showing its gas absorption spectrum: if a little more were added, however, the fine lines at once appeared. This experiment appears to me to be analogous to the one in which the fluorescence of iodine in air at moderately low pressure can be brought about by the vaporization of an excess of iodine. In other words, we may say that at room temperature, air at 15 cms. pressure will dissolve all of the iodine which will vaporize at this temperature, but if the temperature is raised the excess of iodine remains undissolved, and it is this portion only which fluoresces. Further evidence confirming this theory has been recently found by one of my students, Mr. T. S. Elston, who has been working on the fluorescence of anthracene. The vapour of this substance emits a brilliant blue-violet fluorescent light when it is formed in a vacuum, or in hydrogen, nitrogen, or carbonic acid at atmospheric pressure, but when formed in oxygen, sulphur dioxide, or cyanogen at atmospheric pressure, there is absolutely no trace of fluorescence. Heated to a higher temperature in any one of these gases, it reacts chemically with them, and we may if we choose use the term incipient chemical action instead of solution. That the union is only of a temporary nature was shown by vaporizing the anthracene in the oxygen, cooling the bulb until the anthracene had crystallized on the walls, and then opening the bulb. The oxygen was found to be at atmospheric pressure, indicating that none of it had been consumed, and on filling the bulb with hydrogen and vaporizing the anthracene, the fluorescence at once appeared again with undiminished intensity. Probably interesting results will be obtained by measuring the vapour-pressure of mixtures of anthracene and oxygen. If equal volumes at the same pressure and temperature are mixed, it seems probable that a diminution in the pressure will result.

The fluorescence was bright enough to record its spectrum on an isochromatic plate with an exposure of seven hours. The spectrum is reproduced on Pl. IV. (upper figure). The dispersion of the three-prism spectrograph was insufficient to show the structure of the bands, which extend from the orange-red well down into the greenish-blue. I feel certain that I shall be able to photograph the spectrum with the 12-foot concave grating, although it will require a very long exposure.

The magnetic-rotation spectrum and the temperature-

emission spectrum are shown in register with the fluorescence spectrum. The dark bands of the latter appear to be pushed further towards the red end than in the magnetic-rotation spectrum, while in the temperature spectrum they are still further displaced. The magnetic spectrum shows much more structure than either of the other two.

Some visual observations were made of the fluorescence of the vapour when stimulated with fairly homogeneous light furnished by the monochromatic illuminator. The colour of the fluorescent light changed in a marked manner when the wave-length of the exciting radiation was altered. It was bluish-green when stimulated with blue light, yellow-green with green stimulation, and orange with yellow stimulation. It was only with great difficulty that the spectrum could be observed under these conditions, and about all that can be said at present is that the fluorescence spectrum covers the exciting region and extends to a short distance on the red side of it.

The Magnetic-Rotation Spectrum.

A glass bulb, 3 cms. in diameter, containing a small flake of iodine, was exhausted, sealed, and mounted in a small section of brass tubing placed between the poles of a powerful magnet. Two small holes in the brass tube permitted the passage of light, along the lines of force, through the bulb. Parallel light from an arc was passed in succession through a Nicol prism, the bulb, and a second nicol. When the latter was set at extinction, the crater of the arc could be barely seen, and appeared of a faint grey colour. On exciting the magnet, an intense blaze of emerald-green light at once appeared, wholly different in colour from that of the fluorescent light.

The spectrum of this light was photographed without difficulty with the 12-foot concave grating, with an exposure of eight hours. The absorption spectrum and the iron arc are shown on the same Plate, together with a scale of wave-lengths. These spectra are reproduced on Plate IV. (lower figure), the upper absorption spectrum taken with dense, the lower with rare vapour. At certain points the magnetic spectrum appears to be the complement of the absorption spectrum, the bright lines of the former coinciding with the dark lines of the latter. This is especially noticeable at wave-length 5125. Below this point the magnetic spectrum shows more structure than the absorption, though both were taken with the same width of slit. The absorption-lines in this

region were too fine and close together to be completely resolved, which makes it difficult to draw conclusions. In the region around wave-length 5200, the bright magnetic lines usually coincide with dark absorption-lines, though there appears to be no relation between their relative intensities. Above wave-length 5300 the spectra at first sight appear to be the same. This is only true, however, if we confine ourselves to the general appearance of the fluted bands, careful inspection showing that the bright lines coincide with the dark.

Theoretical considerations make it seem probable that all of the magnetic lines are close doubles, since the rotation of the plane of polarization has its maximum value on *each* side of every absorption-line. The double lines have only been observed, however, in the case of the D lines of sodium. Photographs of the magnetic effects seen with sodium vapour of varying density were reproduced in connexion with an earlier paper ("Magneto-Optics of Sodium Vapour" *). It is clear that two absorption-lines very close together may under certain conditions give rise to a magnetic triplet, the rotation midway between the absorption-lines having a value of 90° , with a similar condition just above one absorption-line, and just below the other. I have been unable to find any evidence of such an effect in the iodine spectrum, though it can be observed without difficulty at the D lines, the components of the triplet being very broad in this case. With very dense sodium vapour, as I have already shown, we may have a multiplex magnetic line, the rotations at the components being 90° , 270° , 360° , 450° , &c. In the case of iodine, and also in the case of sodium in the region of the channelled absorption spectrum, the magnetic lines appear single with all resolving powers used up to the present time. Possibly the employment of an echelon or some such instrument would reveal their duplicity. The line 5001 of the magnetic spectrum of sodium would be the best one to begin with, as it is isolated and fairly bright. If the nicols were set parallel, instead of crossed, it is possible that the appearance of the lines in the absorption spectrum would be altered. We should expect the lines to appear doubled, with two fainter and very close components between them. Probably, however, this system would not be resolved with a 12-foot grating, and we should notice only a slight broadening of the line. Bromine gives a fairly bright magnetic-rotation spectrum, which has been photographed with the three-prism spectrography, but not with the grating. It does not, however, exhibit the slightest trace of fluorescence under any conditions.

* Phil. Mag. [6] x. p. 408.

On the theory proposed, this indicates that the bromine molecule has a greater capacity for storing energy than the molecule of iodine: in other words, it takes care of the absorbed energy, without re-emission, during the interval between collisions.

The magnetic rotatory power appears to be less easily affected by molecular impacts.

The Temperature Emission Spectrum.

The temperature emission of iodine vapour can be most beautifully shown by means of a quartz bulb provided with a short tubular stem. A small flake of iodine is introduced into the bulb, which is then highly exhausted and sealed with an oxy-hydrogen flame. The bulb is supported with a stiff iron wire, and heated with a blast-lamp as shown in fig. 1. In

Fig. 1.

a dark room it will be observed that, even at the high temperature of the blast-lamp, the quartz bulb radiates little or no light, on account of its small absorption coefficient. If now a small flame is applied to the stem containing the iodine, the vapour enters the white-hot bulb, which instantly appears filled with a highly luminous red cloud, which flashes into view like a red flame. The spectrum of this light appeared almost continuous in the three-prism spectrograph. There was, however, a faint suggestion of bands in the orange region, which made it appear probable that the continuity of the spectrum might be due to too great depth of the radiating layer. As is well known, the theory of radiation shows that an absorbing vapour, when radiating a discontinuous spectrum, will emit a continuous spectrum, if the thickness of the radiating layer be sufficient. On heating the stem as well as the bulb and projecting its image on the slit of the spectro-

graph, the bands appeared much more distinct. The layer of vapour in this case was only a millimetre or two in thickness. The bulb was now opened, and the stem drawn down to a very fine capillary, with a bore of perhaps 0.1 mm. It was then re-exhausted and sealed. The capillary was placed in the hottest part of the flame of the blast-lamp and the remainder of the bulb heated with a small Bunsen flame. The vapour in the capillary immediately became highly luminous and almost white in colour, owing doubtless to the higher temperature possible with this arrangement.

The spectrum of the capillary light was found to exhibit strong bands, and resembled closely the fluorescence spectrum. It was photographed with an exposure of 8 hours, the blast-lamp being operated with an improvised water-blower. The bands were not resolved into lines, and it is of great importance to study it under higher dispersion. It can doubtless be photographed with the large concave grating, since an exposure of several days can be given if necessary, the apparatus requiring no attention. The fluorescence will give more trouble, as a powerful beam of sun- or arc-light is necessary, either of which requires more or less constant attention.

The temperature-emission spectrum is reproduced on Pl. IV. between the fluorescence and absorption spectrum.

The bands will be seen to be shifted towards the red, with respect to the corresponding bands in the fluorescence spectrum.

XL. Leakage Currents in the Moisture condensed on Glass Surfaces. By Prof. FRED. T. TROUTON, *F.R.S.*, and C. SEARLE*.

THE leakage currents over the surfaces of non-conductors exposed to ordinary atmospheric conditions behave often in a most perplexing way. The current is not only very different on different occasions, but in addition may be very different on the same occasion according to the direction it is applied. This latter effect was exhibited by one of us to the Physical Society during last Session, when it was shown that the current may be many times greater when sent in one direction over the surface of glass, than when sent

* Communicated by the Authors.