THE SELECTIVE DISPERSION OF MERCURY VAPOR AT THE λ2536 ABSORPTION LINE

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Abstract

By means of a Rayleigh's gas refractometer, measurements were made on the interference fringes in seven iron lines extending about 3 A.U. on both sides of the mercury absorption line at λ2536.7. The mercury vapor pressures used ranged from 0.0015 to 0.113 mm of mercury. Shifts of fringes for the line closest to λ2536.7 were found to be proportional to the density of the vapor, while farther from the absorption line, the displacements of the fringes increased less rapidly than the density of the vapor. This is probably due to the increasing width of the absorption line and not to complex mercury molecules as has been previously suggested. *The molecular refractive indices for the wave-lengths* 2536.9, 2538.4, and 2535.6 were found to be respectively 1.068, 1.006, and 0.988. Selective dispersion in the vicinity of λ2536.7 was demonstrated by means of crossed prisms.

Data by Cuthbertson and Metcalfe on refractive indices of mercury vapor indicate an absorption band somewhere between λ6560 and λ6900. Since no evidence of selective dispersion was found in this region, it was concluded that their value for the index at λ6560 is about three percent low.

A QUANTITATIVE determination of the selective dispersion of mercury vapor at the λ2536 absorption line was made a number of years ago by Professor Wood.[1] The method used was to place in one of the paths of a Michelson interferometer a quartz tube 10 cm long with end plates of the same material fused on. The tube contained a drop of mercury and was highly exhausted and sealed. An iron arc was used as a source of illumination and the interference fringes formed in the region of wave-length 2536A were photographed with a small quartz spectrograph. The shifts of the fringes in the several iron lines close to the λ2536 line were observed, and were found to increase less rapidly than did the vapor pressure as the temperature was increased. It was supposed that this indicated that the absorption is due not to the simple mercury molecule but to some more complex structure, the percentage of which varies with the density of the vapor.

It has since been shown that the nature of the absorbed region depends upon the density of the mercury vapor, the absorption band increasing in width as the density is increased. This means, of course, that it is not necessary to have a complex structure of mercury molecules to explain the changes in the refractivity. To measure the refractivity it

[1] R. W. Wood, Phil. Mag. April, 1913.

was thought advisable, however, to repeat the experiment, the original experiment being not entirely satisfactory inasmuch as the optical path through the mercury vapor was only 20 cm and the fringes were not distinct at temperatures above 60°. Furthermore, the spectrograph used was one of rather low dispersion and a quartz spectrograph of much greater dispersion is now available.

In repeating the experiment, I used two glass tubes, as shown in Fig. 1, each 1.3 cm in diameter and 50 cm long. The tubes were fastened together and the ends ground flat with emery and water. Plane parallel plates of quartz were sealed over each end of the double tube with "Rock Cement" which forms a tight seal and does not soften at tem-

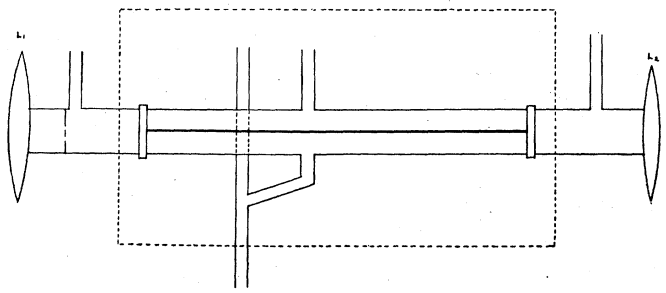

Fig. 1. Diagram of experimental tube.

peratures to which it was desired to carry the work. The lower tube was attached to a long vertical tube which terminated in a mercury reservoir of adjustable height. The other arm, extending higher than the tube, was joined directly to a McLeod gauge and the pump. After the apparatus was exhausted to a very low pressure with the mercury reservoir in such position that the mercury did not rise enough to seal off the lower side of the tube, the reservoir was raised just far enough to form a shallow layer of mercury in the lower tube. The upper tube and the two larger end tubes to be described presently were connected to the pump with a liquid air trap intervening to remove mercury vapor.

A horizontal slit S_1, Fig. 2, was placed at the principal focus of the quartz lens L_1, which was sealed directly to the large end tube. The lens L_1 had a focal length of 80 cm. The two horizontal slits S_2, made by fastening strips of black paper with edges cut straight over the end of a glass tube, were previously inserted in the end tube in such position that one of the beams of light from the slit passed through the upper tube and the other beam through the lower tube. The slits S_2 were each 2 mm wide with a separation of 3 mm between the inner edges. An iron spark was placed behind the slit S_1 and the two beams of light from

S_2 focused on the slit of the spectrograph by means of the lens L_2 sealed directly to the second large end tube. The focal length of this second lens was 140 cm and the spectrograph was therefore placed at that distance from the lens. An exposure now made with the slit S_1 opened quite wide showed two spectra, one from each beam, slightly inclined to each other because of the variation with wave-length of the focal

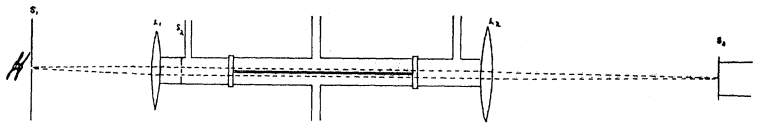

Fig. 2. Arrangement of apparatus.

length of the lenses. The spectrograph was then moved a short distance to bring the intersection of the spectra at λ2536. The slit S_1 was then narrowed and a fifteen minute exposure made, showing excellent fringes from λ2400 to λ2650, those near λ2536 being the best.

The heating arrangement was very simple. A large wooden box which could be tightly closed occupied the position shown by the dotted line in Fig. 1. A wooden frame fitting into the bottom of the box had resistance wire wound upon it, the wire being connected to the laboratory mains through variable resistance coils on the outside of the box. Small heating coils, to correct for the end cooling effect, were placed in the ends of the box on a circuit separate from the large heating coil. Thermometers were placed in the top of the box with the bulbs of the thermometers at the same level as the tube containing the mercury vapor and as close to it as possible. The stems of the thermometers in this position extended sufficiently far to allow the temperature to be read without opening the box. By adjusting the variable resistances any desired temperature could be obtained and kept constant to within less than a half degree as long as one might wish. It was necessary to wait a considerable time, however, before exposures were begun as the temperature of the mercury in the thick walled tubing changed very slowly. The end tubes to which reference was made were used to eliminate convection currents, which would otherwise destroy the interference fringes when the temperature was only a few degrees above room temperature. The tubes used were each about 20 cm long.

To determine the wave-lengths of the iron lines near λ2536, comparison spectra were made with the iron spark and mercury arc. It was found that when the exposure was continued long enough to show the weaker mercury line, the stronger mercury line was broadened to such an extent that accurate measurements were impossible. Therefore,

two photographs were made, one in which the mercury arc when cold was exposed a very short time so that only the stronger line appeared; the other, one in which the time of exposure was increased to show the weaker line also. The separation of the stronger mercury line from the nearest iron line on the first photograph and that of the weaker mercury line from the same iron line on the second photograph gave the wave-lengths of the iron line in terms of the wave-lengths of the mercury lines which were taken from the tables by Eder and Valenta. Beginning on the shorter wave-length side (left) of the group of lines in Fig. 3, the wave-lengths are:

Iron:	2533.7	2534.5	2535.6	2536.9	2538.4	2538.7	2539.1
Mercury:			2534.9	2536.7			

Exposures were made at temperatures ranging from 22.4° to 83.2°C. In Fig. 4 are shown enlargements of several of the photographs for this temperature range. The displacements of the fringes in the several iron lines were measured with a comparator microscope and are given in Table I, the displacements being recorded in fringe widths.

TABLE I

The displacements of the fringes in the several iron lines.

Temp. °C	Vapor Press. mm	2533.7	2534.5	2535.6	2536.9	2538.4	2538.7	2539.1
22.4	.0015				.27			
26.5	.0022				.40			
33.0	.0037		.10	.22	.64			
39.4	.0060	.08	.15	.33	1.02	.12		
44.5	.0087	.11	.20	.46	1.49	.17	.14	.11
52.4	.0153	.17	.29	.71	——	.25	.20	.17
60.5	.027	.23	.38	.96	——	.44	.34	.28
70.5	.052	.38	.57	1.75	——	.84	.64	.54
76.5	.076	.50	.80	2.42	——	1.23	.93	.75
83.2	.113	.70	1.18	3.53	——	1.82	1.40	1.07

It will be seen from the table that the shifts in the fringes for the line closest to the λ2536.7 mercury line, that is, the λ2536.9 line, is within experimental error, proportional to the density of the mercury vapor. As the separation from this line increases the shift increases more slowly than does the vapor pressure of the mercury at the lower temperatures. As the temperature increases the absorption band becomes wider, and since the total energy absorbed is proportional to the density, the absorption for a line near the edge of the band cannot increase as rapidly as does the density, and hence the shift of the fringes, which measures the refractivity, is not proportional to the density of

the vapor. For the higher temperatures at which observations were made, the shift of fringes in the lines closest to the middle of the absorption band increases at nearly the same rate as does the density. These lines are now well within the absorption band and most of the energy absorbed is in this central part. It is therefore to be expected that the shift should increase at a rate more nearly equal to the rate of increase of the density.

Cuthbertson and Metcalfe[2] have measured the refractive index of mercury vapor for wave-lengths ranging from 6900A to 4900A. If the same rate of change takes place as far as λ2536 as we have from λ6900 to λ4900 we would find that a saturated column of mercury vapor 50 cm long and at a temperature of 50° would give a retardation of one-thirtieth of a wave-length, or a shift of one-thirtieth fringe width in the interference pattern. Any superimposed effect may, of course, be ascribed to the λ1849 line and since the separation from this line is still quite large, it is not expected that the shift would greatly exceed the above amount, which is small in comparison with the shifts observed for the same density in several of the iron lines and may therefore be omitted. The molecular refractive indices for the wave-lengths affected by the absorption may then easily be determined and in the cases calculated are found to be for the λ2536.9 line 1.068, for the λ2538.4 line 1.006 and for the λ2535.6 line 0.988, where only the determinations at higher temperature have been taken into account. The well known Sellmeier dispersion formula cannot be applied in this case since the refractivities determined are those for wave-lengths within the absorbed region.

As a subsequent experiment, I observed the dispersion by the method of "crossed prisms." A large glass tube, 2 inches in diameter and 3 feet long, was bent slightly near each end and mounted horizontally, bent ends upward, with enough mercury placed in it to form a shallow pool in the middle of the tube. Over the ends had been sealed glass plates through which holes had been ground and quartz windows fitted. A small hole near the top of each plate was used for sealing in a glass tube of about one-fourth inch diameter, through which cold water was circulated. A spark operating under water was placed at the principal focus of a quartz lens at one end of the tube and the parallel beam of light was focused upon the slit of the spectrograph by means of a second quartz lens at the other end of the tube. A gas burner made by drilling small holes in a gas pipe at intervals of an inch for the full length of 24

[2]Cuthbertson and Metcalfe, Proc. Roy. Soc. **A(80)**, 406 (1908); **A(83)**, 151 (1909).

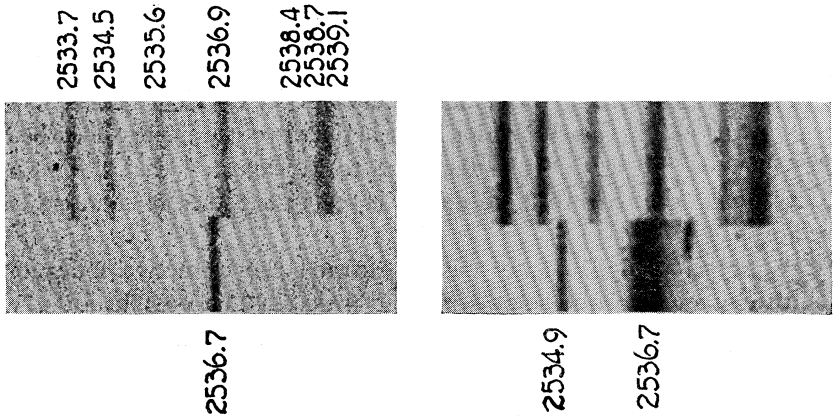

Fig. 3.

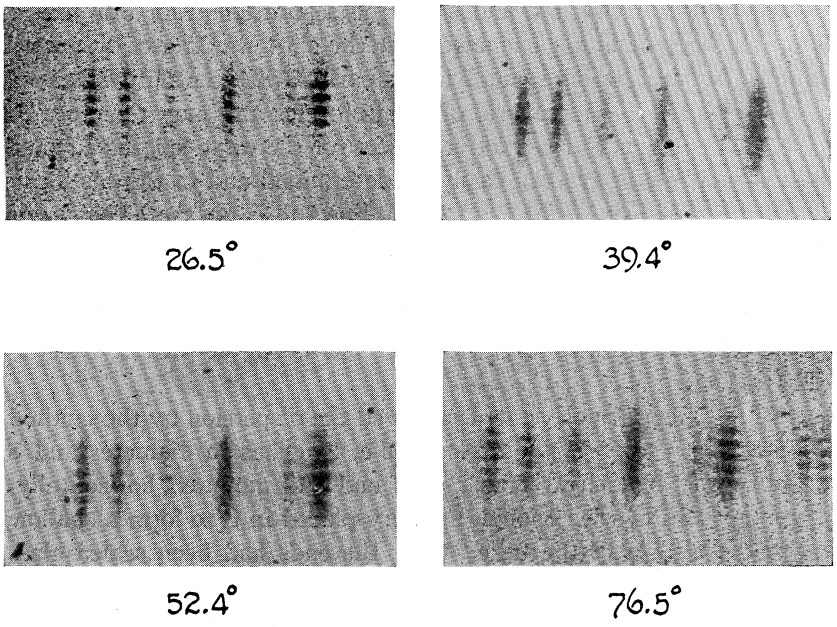

Fig. 4.

Fig. 5.

inches was placed beneath the tube which was now exhausted to about one cm pressure. The photographs obtained, one of which is reproduced in Fig. 5, shows the continuous changes in refractivity near the λ2536 absorption line. Measurements of this curve are of no interest, since the density of the vapor is not known, but it does give a very good picture of how the refractivity changes on either side of the absorption band.

The values of the refractivity given by Cuthbertson and Metcalfe indicate that an absorption band should be present somewhere between the wave-lengths 6560 and 6900A. I observed this region closely by focussing the red region from the carbon arc lamp, after passing through the tube, upon the slit of a spectroscope and found no evidence of a dispersion curve such as at the λ2536.7 line, whereas calculation shows that if such an absorption band is present the displacement of the spectrum formed would easily be distinguishable. We may conclude, therefore, that the refractive index obtained by Cuthbertson and Metcalfe for the λ6560 line is about three percent too low; that is, the value of it should be intermediate between the values obtained for the wave-lengths greater and those less than λ6560.

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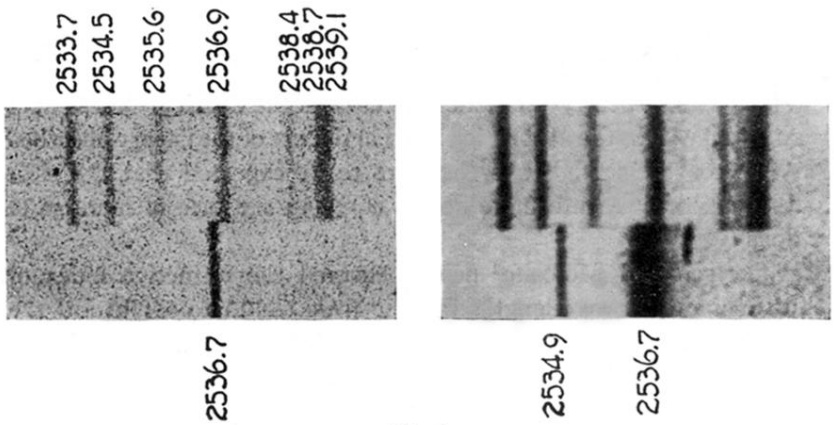
2533.7
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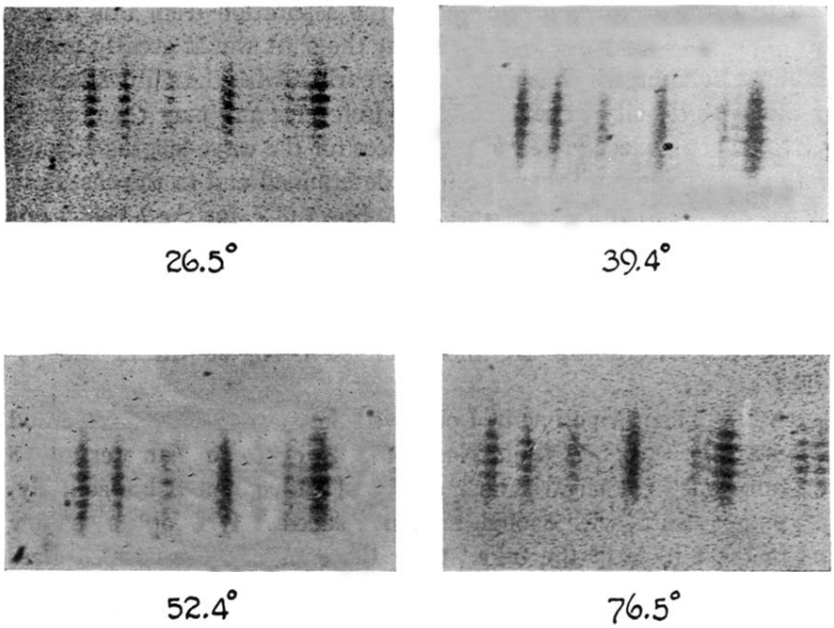
Fig. 3.



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