RELATIVE INTENSITIES OF SOME LINES IN THE MERCURY SPECTRUM

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Abstract

Intensities of the most intense spectrum lines associated with transitions to and from the $2p_2$ state in mercury were measured by means of a photographic method. The spectrum of the vapor was excited by electron impact above the ionization potential. Variations in the line intensities due to changes in the accelerating potentials and vapor pressures were observed. At 22°C and with 50 volt electrons, there were about 1.7×10^{12} quanta of λ2537 radiation emitted per cubic centimeter per second for a current density of 4.75×10^{15} electrons per square centimeter per second. From the intensities of the other lines relative to λ2537, it was found that there are apparently more transitions to $2p_2$ than down from $2p_2$, as given by measurements of the radiation. This made it impossible to determine the probability of excitation of resonance from the intensities of the spectrum lines. A comparison is made between the relative intensities in the experimental tube and in a commercial arc.

THIS work was undertaken for the purpose of obtaining a measurement of the intensities of some of the lines in the mercury spectrum, using different electron speeds and vapor pressures. Lines associated with transitions to and from the $2p_2$ state were chosen with the original intention of obtaining a measure of the excitation of this state. A summary of the technique of line intensity measurements has lately been given by Dorgelo,[1] while the theory of the intensities of spectral lines has been recently discussed by Bartels.[2] In the latter paper it is shown how the intensities of emission lines depend on both the distribution of the various Einstein probabilities of emission and the relative probabilities of excitation of the various states from without the atom. This makes the intensity relations of emission lines difficult to interpret theoretically until one of these sets of probability coefficients is known. However, as suggested by Bartels, one might expect that the probability of excitation of the first resonance level could be obtained by measuring the intensities of lines emitted by transitions to and from this state and comparing the number of transitions to the resonance level with the number obtained from the intensity of the resonance line.

A diagram showing the disposition of the more essential parts in the tube used is given in Fig. 1. The grid G was close to the filament F, so that most of the collisions took place in the space between the grid and the plate P, which were kept at the same potential. The source of electrons was an oxide coating on a platinum surface which was heated by a tungsten filament. The latter was insulated from the platinum except at one end where they

[1] Dorgelo, Phys. Zeits., **26,** 756, (1925).
[2] Bartels, Zeits. f. Physik **37,** 35 (1926).

were connected together. Various accelerating potentials were applied between the platinum sheath and the grid by means of a potentiometer device. The grid and the plate were coated with soot to reduce the number of secondary electrons. The plate current was kept constant at 5 milliamperes throughout the series of observations recorded here. An electric heater wound around the tube made it possible to vary the pressure of the mercury contained inside. The radiation was transmitted to the spectrograph by a re-entrant quartz window Q, 1.28 cm in diameter, and sufficiently off the axis of the cylinder to be out of line with the filament. The window darkened because of a sputtered deposit as the tube was operated, but this effect was corrected for by repeating some of the exposures after a definite interval of time. A sooted nickel surface B, 3.2 cm behind the quartz window, served

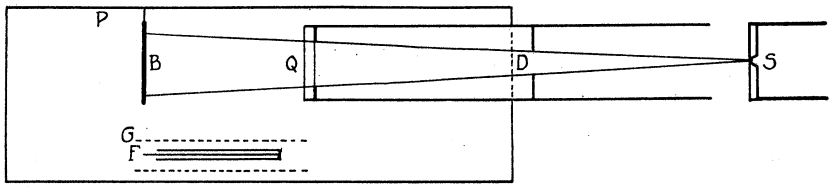

Fig. 1. Diagram of the experimental tube.

as a background. A diaphragm D kept the light reflected from the cylindrical surface from reaching the slit of the spectrograph at S. Since it has been found by R. W. Wood, that mercury vapor even at room temperature absorbs λ2537 quite strongly, the room and spectrograph were ventilated, but this did not seem to produce any appreciable change in the results.

Since most of the lines were in the ultra-violet, the intensities of the spectrum lines were measured by a photographic method. The photographic density of each line was measured with a Moll (thermoelectric) microphotometer. The density is defined as the common logarithm of the ratio of the intensity of the light transmitted by an unblackened portion of the plate adjacent to the line, to the intensity of the light transmitted by the blackened portion. In making the exposures, the slit of the spectrograph was made wide enough so that the center of each line was blackened uniformly over a width greater than that of the microphotometer beam. A series of four or five exposures was made for each voltage and temperature. These were for two different times of exposure (either ten and one hundred seconds, or one hundred and one thousand seconds), with and without blackened calibrated wire screens interposed. The transmission factors of the screens used were measured photometrically and also with a Hilger selenium cell. It was assumed that their transmissions were non-selective over the range used.

The relation of the photographic density, D, to the common logarithm of the intensity, log I, is given by the familiar Hurter-Driffield curve, which is straight over a fairly wide range of densities. The straight line is defined by

means of its slope, called the contrast, γ, and the intercept on the log intensity axis which is called the log inertia. The reciprocal of the inertia is called the speed, σ. We have then:

$$\log I = D/\gamma - \log \sigma$$

This formula applies only to the straight region of the characteristic curve, and it is simplest to discard all readings that are too light or too dense to be included in this region. For dim lines, a longer exposure must be given and a different pair of values of γ and σ must be used. Harrison[3] has published values of γ and σ for a number of emulsions for exposures of ten seconds, and for wave-lengths between 4360 and 2144A. From these it is easy empirically to obtain values of these constants for other times of exposure by the use of the calibrated wire screens. Thus no assumption is made regarding the validity of the reciprocity law or of Schwartzchild's law. However, it is best not to rely on these published values too much, for variations may occur in development or in the emulsion itself. Of the two constants, it is the more important to know the value of gamma accurately and it is, fortunately, easy to measure gamma for each plate by the use of a few calibrated wire screens. To obtain $\log \sigma$, on the other hand, is not so easy for its measurement necessitates a set of standard spectrum lines of known intensities. However, if the variation of $\log \sigma$ with wave-length is known, a slight error in its value introduces an error of the same percentage in all the measurements. This will not affect the relative intensities. In calculating the results here presented, Harrison's values of $\log \sigma$ for ten seconds exposure were used, but the values of gamma and $\log \sigma$ for other times of exposure were independently determined for each plate. The plates were developed for five minutes at 21°C in the following developer:

Distilled water	2300 grams	Hydrochinon	12.9 grams
Elon	3.2 "	Potassium bromide	1.84 "
Sodium sulphite	48.7 "	Sodium carbonate	69.0 "

When used, the developer was diluted with three volumes of distilled water to one of developer. The stock solution will keep for several months when kept in a well stoppered bottle.

From the intensities of the lines, one can immediately find how many quanta of each frequency strike the plate per unit area per second. From the light losses in the instrument and the areas of the images and of the slit, one can calculate how many quanta enter the spectrograph per second. Assuming that the fraction of the total number of emissions entering the slit is proportional to the solid angle subtended by the slit, and knowing the portion of the glow which will be within the angular aperture of the instrument, one can calculate the average number of transitions of each kind per cubic centimeter of glow. The factor for converting intensities in quanta per square centimeter of photographic plate to the number of emissions per cubic centimeter of the glow was found to be 2.2×10^3.

[3] Harrison, J.O.S.A. & R.S.I., **11**, 341, (1925).

The relative number of transitions per cubic centimeter per second as compared with the number for λ2537 is plotted in Figs. 2(a) and 2(b) against, respectively, the temperature of the vapor and the accelerating voltage.

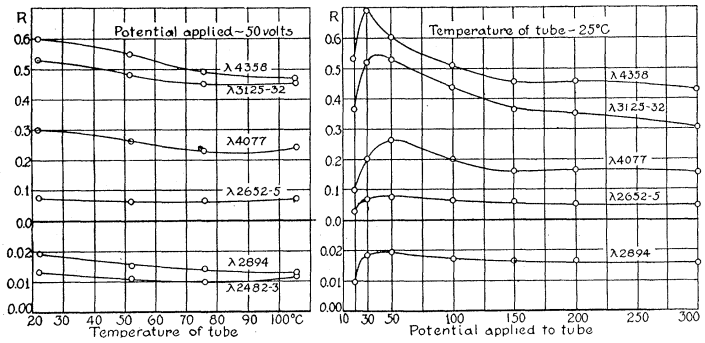

Fig. 2. Numbers of emissions relative to the number for λ2537, (a) Variation with temperature of the vapor; (b) Variation with accelerating potential.

There are no marked changes in the intensities of the lines relative to λ2537 under the conditions of these experiments except at the lower voltages.

The intensity of λ2537 is plotted in Fig. 3 against the same variables. These curves are, of course, not as accurate as those of relative intensities; still they will serve to give the order of magnitude of the intensities and the

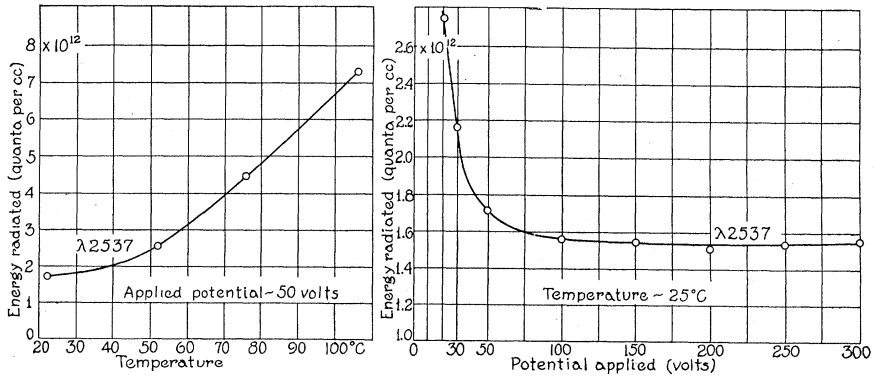

Fig. 3. Number of emissions per cubic centimeter for λ2537, (a) Variation with temperature of the vapor; (b) Variation with accelerating potential.

manner of variation with voltage and temperature. These changes are of the general nature that one would expect. The average current density through the region of the glow photographed was 4.75×10^{15} electrons per square centimeter per second, as measured by a cage having a cross-section equal to that of the glow.

The intensities of the same lines emitted by a commercial "Lab-arc" were also measured. The relative intensities are entirely different from those

in the experimental tube. Table I gives a comparison of these two spectra in terms of the relative number of emissions compared to the number for λ2537.

TABLE I

Comparison of relative number of emissions.

Wave-length	Notation	"Lab-arc"	Exper. Tube 50ν.
4358	$2p_2-2s$	8.9	0.60
4078	$2p_2-2S$	0.76	0.30
3126−32 sum	$2p_2-3Dd_{23}$	3.61	0.53
2894	$2p_2-3s$	0.11	0.02
2652−5 sum	$2p_2-4Dd_{23}$	0.91	0.07
2537	$1S-2p_2$	1.00	1.00
2482−3 sum	$2p_2-5Dd_{23}$	0.21	0.01

The data show that there are apparently more transitions to $2p_2$ than from it, at least when one considers only the transitions giving rise to radiation. Therefore it is not possible with either type of source to determine the "external excitation" probability of the $2p_2$ state by taking the difference between the number of transitions from that state and the number to that state as suggested by Bartels. Apparently there are many radiationless transfers down from $2p_2$. The very high current densities in the lab-arc would then be expected to enhance the subordinate series lines as compared with the resonance line.

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