THE SPECTRUM OF THE NEUTRAL MERCURY ATOM IN THE WAVE-LENGTH RANGE FROM 1 TO 2μ

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Abstract

New information on the near infra-red spectrum of mercury has been obtained with a specially constructed thermocouple in connection with an automatic recording spectrograph. Fourteen new lines predicted by the combination principle and eight unclassified lines have been found in this region. Intensity relations for the triplet $1^3S_1-2^3P_{0,1,2}$, which extends over 2700A, have been found to follow rather closely the summation rule as refined by R. H. Fowler for wide multiplets.

Very little has been done on the infra-red spectrum of mercury since Paschen's[1] excellent work. By taking advantage of the concentration of energy in a prismatic spectrum and using a vacuum thermocouple of minute dimensions and high sensitivity (constructed by the writer) the number of classified lines in the region from 1 to 2μ has been nearly doubled. The source used was a 300–watt quartz vacuum arc. The spectroscope is automatic recording.

I. Calibration of the Spectroscope

(1) *Wave-length.* A dispersion curve, *A* Fig. 1, (wave-length against position on the film) for the spectroscope was obtained from two sources, (a) observations on several of the more intense classified lines of the mercury spectrum whose wave-lengths have been accurately measured by Paschen[1] with a grating, and (b) observations on lines in the absorption bands of water vapor in this region—these having been accurately measured with a grating by Sleator and Phelps.[2] One of these bands extends from 1.8002 to 1.9326μ—another from 1.3480 to 1.4234μ. Sleator's wave-lengths are reduced to vacuum and by taking the vacuum wave-length for the mercury lines (i.e. reciprocals of calculated wave-numbers) the dispersion curve gives the wave-lengths of the new lines in vacuum. The lines marked with a dash (—) in Table I are those used for the dispersion curve. Sleator's wave-lengths fall very nicely upon the curve drawn through the mercury lines, the largest discrepancy being 3A. The spectrum from one to two μ covers 43 cm on the film. Reading positions on the film to 0.1 mm gives an accuracy of 2.5A. More accurate readings are not justified because of uneven shrinking of the film upon development. Most of the wave-lengths in Table I are thought to be of this accuracy, especially those near a standard line.

[1] Paschen, Ann. d. Physik **29**, 662 (1909); **30**, 750 (1909); **35**, 869 (1911).
[2] Sleator and Phelps, Astrophys. J. **62**, 28 (1925).

(2) *Intensity.* Since there is absorption and reflection over this region due mainly to the flint prisms the spectroscope was calibrated for relative intensities over the region used by observing the emission from a tungsten

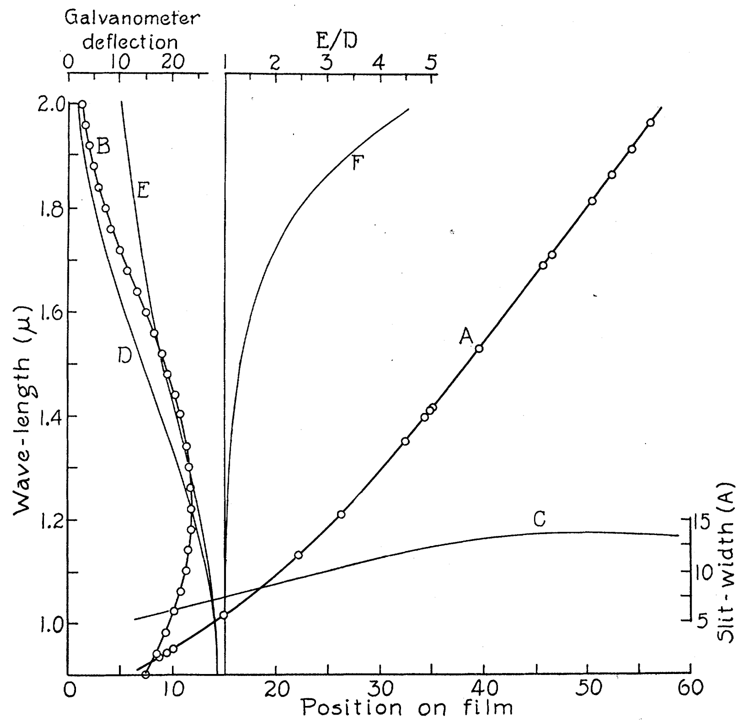

Fig. 1. Calibration curves for spectroscope.

filament at 3050°K, Fig. 2, giving curve B (wave-length against galvanometer deflection) on Fig. 1. To obtain the galvanometer zero the light was occulted for fifteen seconds every twenty minutes and to cover this region two revolutions of the drum are required. At this high temperature tungsten

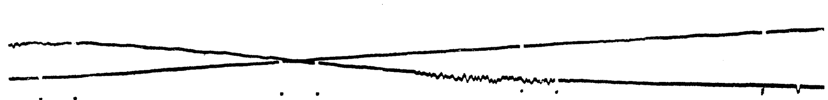

Fig. 2. Radiation from tungsten filament, visible to 2μ.

radiates somewhat as a black body. It is observed by Coblentz[3] that as the temperature of tungsten is raised it approaches the behavior of a black body. Extrapolating his curves to 3000°K gives the constant "a" in

[3] Coblentz, Bull. Bur. Standards **5**, 373 (1908).

Planck's radiation formula approximately the black body value of 5. In the calibration it is assumed that tungsten radiates as a black body at the high temperature used. The temperature of the filament was observed with an "F and F" optical pyrometer and found to be 200°C below that calculated from the maximum of curve D by Wien's Law. The optical measurement of this temperature is not very reliable as it was obtained by a doubtful extension of the range of the instrument which is designed to operate only up to 2500°K. Curve D Fig. 1 (wave-length against galvanometer deflection) is curve B corrected for variations in the spectral range covered by the slit. Points on the slit-width curve C, Fig. 1 (slit-width against position on the film) are obtained by dividing the slope at a corresponding point on curve A by one-half of the basal width of a sharp spectral line. Curve E Fig. 1 (wave-length against galvanometer deflection) is the theoretical black body emission for a temperature of 3050°K calculated from Planck's radiation formula. Curve F Fig. 1 (intensity-correction-factor, E/D, against wave-length) which gives the intensity-correction-factor for different wave-lengths is obtained by dividing abscissae of curve E by the corresponding abscissae on curve D. The relative intensities (corrected) given in Table I are obtained by multiplying the observed intensity by an appropriate correction factor taken from curve F.

II. The Spectrum Obtained

Figures 3 and 4 are two automatic records of the mercury spectrum from 1 to 2μ—Fig. 3 with the arc operating at 76 volts and 3.7 amps, and Fig. 4 at 86 volts and 3.8 amps. Several of the weak lines cannot be seen on the

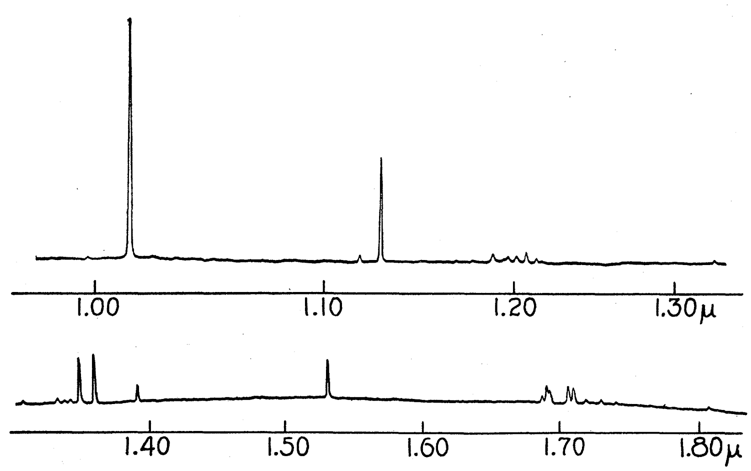

Fig. 3. Mercury spectrum in the range from 1 to 2μ. Arc operating at 76 volts.

reduced reproduction of the original record. Fig. 5 is a plot of the 86-volt record on a frequency scale, the height of a line is proportional to its corrected relative intensity. Underneath this plot the lines are grouped as follows: 1st row, the principal triplet $1^3S_1-2^3P_{0,1,2}$; 2d row, the second sharp triplet $2^3P_{0,1,2}-3^3S_1$; 3d row, two fundamental triplets $2^3D_{1,2,3}-4^3F, -3^3F$;

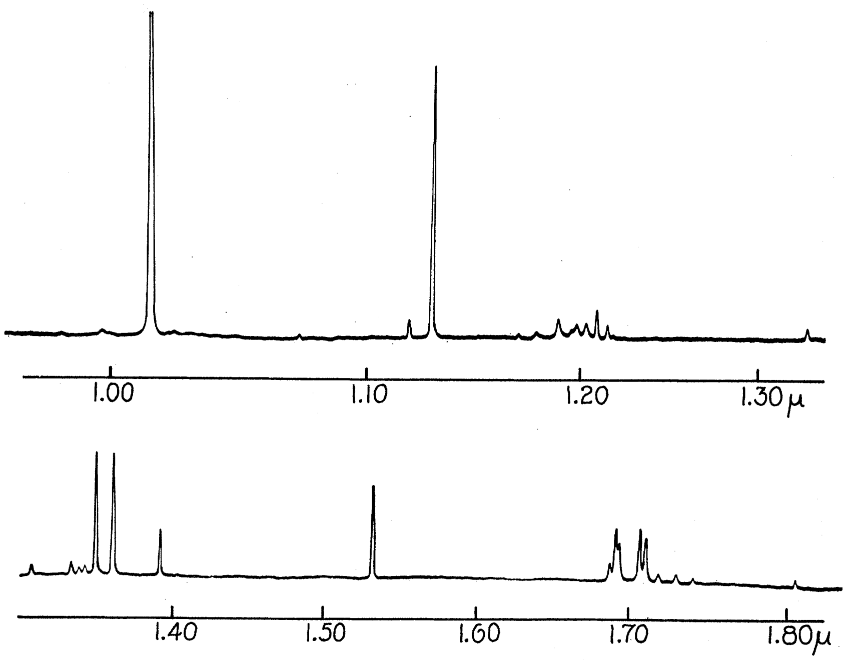

Fig. 4. Mercury spectrum in the range from 1 to 2μ. Arc operating at 86 volts.

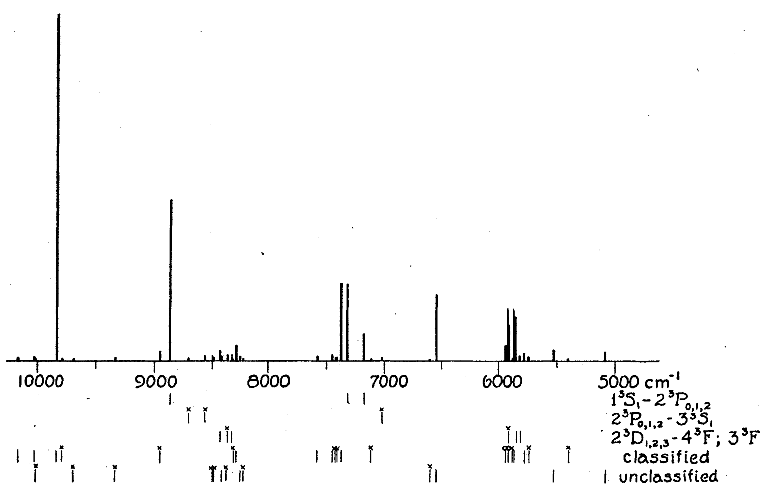

Fig. 5. Mercury spectrum in the range from 1 to 2μ plotted on a frequency scale.

4th row, classified singlets and combination lines; and 5th row, unclassified lines some of which may be mercury spark lines. Lines that have not been reported previous to this are marked on Fig. 5 with a cross. Those marked with a circle are reclassified.

Table I gives the wave-length (in vacuum), relative intensity, classification, and frequency of the lines observed. No lines are given here that did

TABLE I. *Wave-length, relative intensity, and classification of mercury spectrum in the range from 1 to 2μ.*

Line No.	λ (vacuum) in microns	Intensity mm defl.	Intensity corrected	Classification	ν	ν (calc.)
1	0.9842	0.5	0.5	$2^3P_0-4^3D_1$	10161	10162
2	0.9975 —	1.0	1.0	$1^3P_2-1^1P_1$	10025	10025
3	0.9996	0.3	0.[illegible]		10004	
4	1.0142 —	152.2	153.[illegible]	$1^1P_1-2^1S_0$	9860	9860
5	1.0224	0.8	0.8	$2^1P_1-5^3D_1$	9781	9781
6	1.0332	0.4	0.4		9679	
7	1.0711	1.1	1.1		9336	
8	1.1187	4.2	4.3	$1^3S_1-2^1P_1$	8939	8940
9	1.1289 —	68.2	71.0	$1^3S_1-2^3P_2$	8858	8858
10	1.1497	0.3	0.3	$2^3P_0-3^3S_1$	8698	8700
11	1.1692	1.0	1.1	$2^3P_1-3^3S_1$	8553	8554
12	1.1781	1.3	1.4		8488	
13	1.1798	0.5	0.5		8476	
14	1.1889 —	4.5	4.9	$2^3D_1-4^3F$	8411	8411
15	1.1899	1.3	1.4		8404	
16	1.1957	1.4	1.5		8363	
17	1.1978	2.5	2.7	$2^3D_2-4^3F$	8349	8351
18	1.2024 —	2.5	2.7	$2^3D_3-4^3F$	8316	8316
19	1.2034	1.0	1.1	$2^3D_3-4^1F_2$	8310	8312
20	1.2075	6.8	7.4	$1^1P_1-1^3S_1$	8282	8282
21	1.2131	3.0	3.3		8243	
22	1.2159	0.3	0.3		8224	
23	1.3208	2.2	2.5	$2^3P_0-3^3D_1$	7571	7568
24	1.3434	3.0	3.5	$2^3P_1-3^3D_2$	7444	7446
25	1.3489	1.7	2.0	$2^3D_2-3^1P_1$	7414	7417
26	1.3512	2.0	2.3	$2^3P_1-3^1D_1$	7401	7402
27	1.3572	30.1	35.1	$2^1S_0-2^1P_1$	7368	7362
28	1.3676 —	29.1	33.9	$1^3S_1-2^3P_1$	7312	7312
29	1.3955 —	11.0	12.9	$1^3S_1-2^3P_0$	7166	7166
30	1.4064	0.3	0.3	$2^3S_1-5^3D_1$	7110	7110
31	1.4273	0.3	0.3	$2^3P_2-3^3S_1$	7006	7008
32	1.5186	0.4	0.5		6585	
33	1.5298 —	22.7	29.6		6537	
34	1.6878	4.7	8.2	$2^3P^2-3^3D_3$	5925	5922
35	1.6919	12.9	23.0	$2^1D_2-3^3F$	5910	5908
36	1.6935	9.0	16.2	$2^3D_1-3^3F$	5905	5905
37	1.7014	0.2	0.4	$2^3P_2-3^3D_1$	5878	5877
38	1.7073	12.9	23.8	$2^3P_2-3^1D_1$	5857	5856
39	1.7108 —	10.9	20.3	$2^3D_2-3^3F$	5845	5845
40	1.7210	1.9	3.6	$2^3D_3-3^3F$	5811	5810
41	1.7320	2.0	3.9	$2^1P_1-3^1D_1$	5774	5774
42	1.7445	1.3	2.7	$2^1D_2-3^1D_1$	5731	5731
43	1.8131	1.9	4.8		5515	
44	1.8539	0.2	0.6	$2^3D_3-3^3P_3$	5394	5392
45	1.9705	1.0	4.2		5075	

not appear on four different films. Some doubt may legitimately be expressed for classifications where the observed frequency deviates more than two units (cm^{-1}) from the calculated frequency. The calculated frequencies are obtained from Fowler's[4] term values.

[4] Fowler, "Report on Series in Line Spectra," Fleetwood Press.

III. Relative Intensities in the Principal Triplet $1^3S_1-2^3P_{0,1,2}$

The summation rule gives a theoretical relative intensity relationship of 1, 3, 5, for the members of the principal triplet $1^3S_1-2^3P_{0,1,2}$. Since this triplet extends over considerable frequency range the observed relative energies must be corrected[5] for the size of the quanta involved in each transition. Table II gives these intensities under varying conditions of excitation (E = voltage across the arc). Since these intensities rest on the assumption

Table II. *Relative intensities in the triplet* $1^3S_0-2^3P_{0,1,2}$.

Film No.	λ (microns)	Intensity observed	Intensity corrected	No. of transitions	Relative numbers
I	1.1289	15.0	15.6	176	50
$E=55.0$	1.3676	7.2	8.4	115	33
	1.3955	2.4	2.8	39	11
II	1.1289	28.9	30.1	340	50
$E=76.1$	1.3676	13.3	15.5	212	31
	1.3955	4.3	5.0	70	10
III	1.1289	53.3	55.6	628	50
$E=83.8$	1.3676	23.4	27.3	374	30
	1.3955	8.8	10.3	144	11
IV	1.1289	68.2	71.0	802	50
$E=86.3$	1.3676	29.4	34.2	468	29
	1.3955	11.0	12.9	180	11

that tungsten radiates as a black body at high temperatures—the close agreement between observed and theoretical intensities may be considered to offer information either as to the validity of this assumption or as to the applicability of Fowler's[5] refinement of the intensity rule. In this type of intensity measurement there is always the question of selective absorption by the luminous vapor. The intensity that is observed may be regarded as dependent on the algebraic sum of the energy radiating transitions plus the energy absorbing transitions.

The fundamental series of mercury lies well into the infra-red. Consequently no Zeeman pattern upon which the theoretical intensities depend has been observed. Thus no theoretical values are available to compare with experiment. The relative intensities of the lines in the two triplet members observed do not check each other because they are not resolved from lines due to transitions from other levels of $3F$ and $4F$ which are undoubtedly triple levels.

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[5] Fowler, Phil. Mag. **50**, 1079 (1925).