X-RAY ABSORPTION COEFFICIENTS OF MERCURY VAPOR IN THE REGION OF ITS L-ABSORPTION DISCONTINUITIES

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Abstract

An apparatus is described which is suitable for absorption measurements up to 2 or more angstroms. The absorber, which was in the form of superheated vapor whose density could be calculated on the assumption of perfect gas behavior, was contained in an all-glass chamber. The windows were constructed of thin glass films in such a way as to withstand atmospheric pressure from either side. The mass absorption coefficients, μ/ρ, of mercury in the wave-length region 0.74 to 1.4A were determined by an ionization method. They were found to obey the relation $\mu/\rho = A\lambda^c$, where the constants A and c vary from branch to branch of the μ/ρ, λ curve. The value of c is 2.56 on the short and 2.66 on the long wave-length side of the L discontinuities. The magnitudes, δ, of the three L absorption discontinuities, where δ is defined as the ratio of μ/ρ (the scattering coefficient being neglected) on the short and long wave-length sides of an absorption limit, are

$$\delta L_{\mathrm{I}} = 1.18 \qquad \delta L_{\mathrm{II}} = 1.39 \qquad \delta L_{\mathrm{III}} = 2.45$$

Introduction

THE magnitude, δ, of an absorption discontinuity (in case the absorption due to scattering is relatively small and may be neglected in comparison with the true or fluorescent absorption) is defined as the ratio of the mass absorption coefficients on the short and long wave-length sides of an absorption limit. Values for the magnitude of the K discontinuity have been determined for a large number of elements by Richtmyer,[1] Allen,[2] Jönsson,[3] and others. These have been found to decrease with increasing atomic number. Few researches have been published on the magnitudes of the three L discontinuities. Dauvillier[4] worked on gold, Kellström[5] on silver, and Backhurst[6] on gold and platinum.

Such paucity of data in this wave-length region is due to the lack of x-ray intensity and to the difficulties involved in preparing and measuring uniform absorbing screens of 0.0005 cm thickness. These difficulties have been obviated in the present research by the design of the apparatus and by using mercury in the vapor state, the latter making it possible to obtain the equivalent thickness of the absorber from accurate temperature and pressure measurements.

[1] F. K. Richtmyer, Phys. Rev. **27,** 1 (1926); **30,** 755 (1927).
[2] S. J. M. Allen, Phys. Rev. **28,** 907 (1926).
[3] E. Jönsson, Upsala Universitets Arsskrift, 1928, Mathematik och Naturvetenskap 1.
[4] A. Dauvillier, C. R. **178,** 476 (1924).
[5] G. Kellström, Zeits. f. Physik **44,** 269 (1927).
[6] Ivor Backhurst, Phil. Mag. (7) **7,** 353 (1929).

Apparatus

The high potential for operating the x-ray tube was furnished by a transformer-kenetron-capacity set, to which 500 cycle current was supplied from a 5 kw motor-generator. The field current for the generator was supplied by storage batteries. The tube voltage was read on an electrostatic voltmeter of the repulsion type, calibrated by using the short wave-length limit of the continuous x-radiation.

The x-ray tube and absorption chamber were of Pyrex glass and were combined into a single unit as shown in Fig. 1. All three compartments of the system were evacuated through a liquid air trap at the same time by a mercury diffusion pump. The target holder *W* was fitted on a ground glass joint

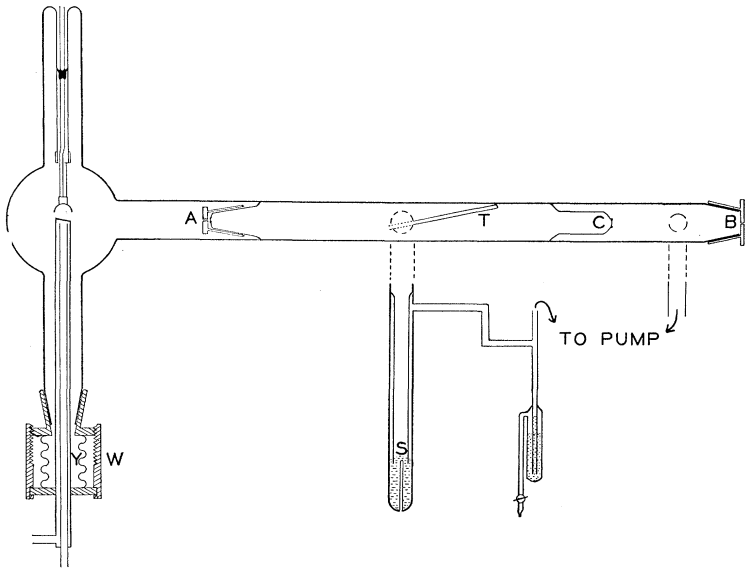

Fig. 1. Horizontal cross section of the x-ray tube and absorption chamber, and vertical cross section of the tube containing the liquid mercury.

to the x-ray tube and was made vacuum tight with deKhotinsky cement. The water-cooled tungsten target was made adjustable by the use of corrugated extensible copper tubing at *Y* so that the focal spot could be lined up with the fixed slits. The anticathode being grounded, the position of the target could be varied while the tube was in operation. The constancy of the focal spot was assured by using a cone-type filament holder at a distance of 1 cm from the face of the target, the latter making an angle of 12 degrees with the slit system. The current through the tungsten filament was supplied by storage batteries and was controlled by a continuously variable mercury resistance of the Kirkpatrick[7] type.

The x-ray beam was defined by two steel slits, *A* and *B*, each being 0.2 by 10 mm, placed 65 cm apart, giving an angular width to the beam of ap-

[7] P. Kirkpatrick, J.O.S.A. and R.S.I. **7**, 195 (1923).

proximately 2′ of arc. The corresponding spreads in wave-length were 0.45 and 0.25 percent at 0.8 and 1.4 A respectively. The resolution obtained was ample for separating the L_{III} edge of mercury and the γ_4 line of tungsten, which have an angular separation of 11′.

The absorption chamber was 3.5 cm in diameter and 40.4 cm in length. The windows were also made of Pyrex by sealing glass films 0.0025 cm thick on narrow glass slits. Glass tubing was flattened at one end to make a slit 0.1 by 1.5 cm. With the edge of this slit heated to incandescence, a thin glass film was pressed gently against it—there being sufficient heat present to fuse the two together. A small flame was used to melt in thoroughly the edges of the film and to give a finished appearance to the product. Satisfactory pieces of nearly curvature free film were obtained by blowing large glass bulbs. Skillfully prepared windows would withstand atmospheric pressure in either direction. The liquid mercury was contained in a tube 2 cm in diameter and 22 cm in depth, which projected from the bottom of the vapor chamber. After evacuation the absorption chamber was closed off by driving in sufficient mercury from a side tube to fill the trap at S. The temperature of the liquid at S, then, determined the vapor pressure of the system. This temperature was measured by inserting a thermocouple in the small tube just below the surface of the mercury. A thermocouple in the upper tube at T, as shown in the figure, measured the temperature of the vapor. To secure steady temperatures, the absorption tube was surrounded with a layer of 1.5 mm copper, which projected about 10 cm beyond the glass windows in order to prevent condensation. Heat insulation was provided by a large cylindrical furnace of 22 cm internal diameter and 62 cm length made of magnesium oxide. Four heating coils were strung lengthwise in this air space and maintained a temperature of 270°C. The liquid mercury container was insulated in a similar manner and electrically heated with current supplied by storage batteries.

The e.m.f. of the copper-constantan thermocouples was read on a potentiometer whose smallest scale division was 5 microvolts, which corresponds to a temperature difference of 0.1°C. A Weston standard cell was used for the reference voltage. The thermocouples were calibrated and used with the cold end in ice shavings. Fixed points for calibration were checked with thermometers recently certified by the U. S. Bureau of Standards. The boiling point of naphthalene was taken as 217.95°C from the Smithsonian Physical Tables. In practice, temperatures were determined by using a deviation curve in conjunction with a standard e.m.f.-temperature curve for copper-constantan, the latter being plotted from data in the International Critical Tables.[8] Data from the same source[9] were used in plotting on the same graph the vapor pressure-temperature curve of mercury. Each millimeter scale division on the chart corresponded to 0.1 degree or to 4 microvolts.

The ionization chamber followed in design and operation the descriptions of Williams and Allison[10] and of Hicks[11]. It was of Pyrex glass 3.5 cm

[8] International Critical Tables, Vol. I, p. 58.
[9] International Critical Tables, Vol. III, p. 206.
[10] J. H. Williams and S. K. Allison, J.O.S.A. and R.S.I. **18,** 473 (1929).
[11] Victor Hicks, Phys. Rev. **36,** 1273 (1930).

in diameter and 35 cm in length and was filled with methyl iodide and argon at partial pressures of 14 and 62 cm of mercury respectively. The window of the chamber, 2 by 20 mm, was covered with thin mica and was at a distance of 5 cm from the axis of the spectrometer table. The scale of the Bragg-type spectrometer could be read to 30″ of arc. The Compton electrometer was used heterostatically with a voltage sensitivity of 3500 mm/volt at a scale distance of 3 meters. The calcite crystal was one previously used by Allison for relative intensity measurements of x-ray measurements.

Method

The absorption tube was kept always at a temperature of about 270°C. Several hours before each series of measurements the liquid mercury was raised to a steady temperature which ranged from 205 to 230°C, depending on the wave-length region being investigated. The corresponding vapor pressures ranged from 25 to 40 mm of mercury. Temperature changes were always in one direction and were not greater than one degree per hour.

The voltage applied to the x-ray tube varied from 17 to 24 kv, in each case being sufficiently low to prevent excitation of radiation which would reflect in the second order. Tube currents ranged from 6.5 to 17.5 m.a. Both current and voltage could be kept constant to within one percent. The tube was operated for a period of two hours before any readings were recorded. Each series of readings consisted of from 8 to 12 positions of the crystal and required about two hours. Electrometer deflections were timed over the same range of the scale for a distance of 10 cm for all crystal positions. Individual readings varied from their average by about one percent. The temperature of the liquid mercury was read for each electrometer deflection. Then the furnace was removed and the liquid mercury cooled to below room temperature. Rates of deflection for the unweakened beam were measured for the same angular settings of the crystal and ranged from 2 to 7 mm/sec. From 0.4 to 0.8 of the original intensity was absorbed.

Calculations and Results

The mass absorption coefficient is given by the equation

$$\frac{\mu}{\rho} = \frac{\ln (I_0/I)}{\rho x}$$

where I_0 is the original intensity of the monochromatic beam of x-rays and I is the intensity after penetrating to a depth x in an absorbing medium of density ρ. Assuming that superheated mercury vapor behaves as a perfect gas, we will make use of the equation

$$pV = (m/M)RT$$

so that

$$\rho = \frac{m(\text{grams})}{V(\text{cm}^3)} = \frac{M(\text{grams/mole})p(\text{mm of } Hg.)A_n(\text{dynes/cm}^2)}{R(\text{ergs/deg/mole})(T_0 + t)760}$$

where A_n is the normal atmosphere. The constants used have the values: $A_n = 1.01325 \times 10^6$ dynes/cm^2, $R = 8.3136 \times 10^7$ ergs/deg/mole, $M = 200.61$ grams/mole = at. wt. of mercury, $T_0 = 273.18$ C, $x = 40.4$ cm = length of absorbing column, giving now as our final equation

$$\frac{\mu}{\rho} = \frac{T \ln (I_0/I)}{0.12997 p} \text{ or}$$

$$\log \frac{\mu}{\rho} = \log T + \log (\log (I_0/I)) - \log p + 1.24870$$

I_0 and I are proportional to the rates of deflection of the electrometer due to the ionization produced. T is the absolute temperature of the absorbing vapor and p its pressure in mm of mercury as determined from the vapor pressure-temperature curve of the liquid.

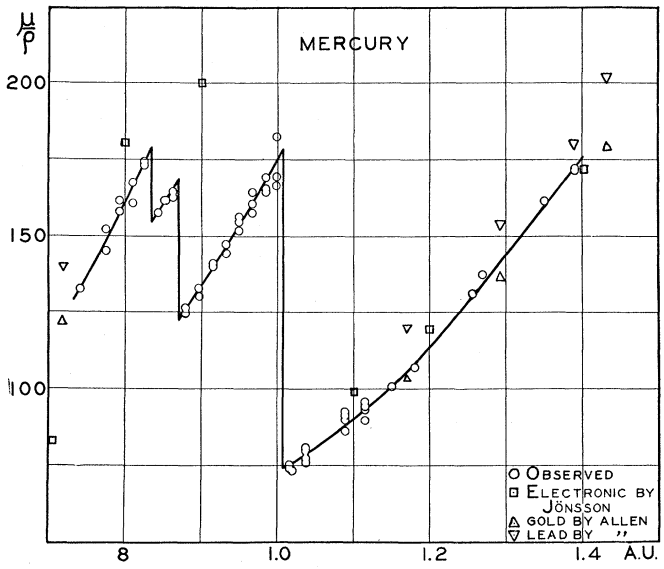

Fig. 2. The variation of the mass absorption coefficient of mercury with wave-length.

The observed points are plotted in Figs. 2 and 3. The wave-length corresponding to each position of the crystal has been obtained by interpolation from the tables in Siegbahn's Spectroscopy of X-rays. When several points are indicated for the same wave-length, they refer to observations made on different days under varying conditions of temperature, pressure, and perhaps current and voltage also. Edvin Jönsson[3] has proposed a universal formula for x-ray absorption which is based on the average absorption per electron. He finds this electronic absorption coefficient to be a function of $N\lambda$ for all elements, where N is the atomic number. Several values of μ/ρ for mercury, calculated from the tables of Jönsson, have been plotted for comparison in Fig. 2. There is no particular agreement except on the long wave-length side. The

mass absorption coefficients for gold and lead from the results of Allen[2] are seen to be consistent with the data for mercury.

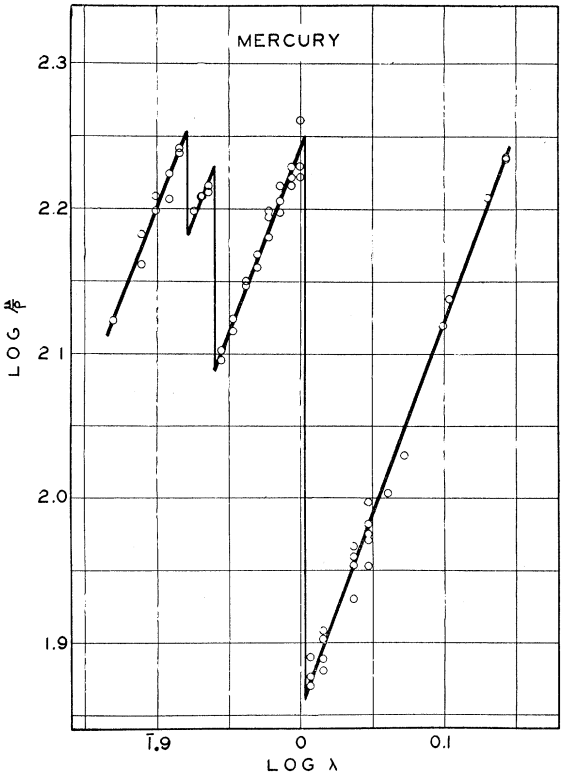

Fig. 3. Log μ/ρ as a function of log λ for mercury.

Within the limits of experimental error, the mass absorption coefficients have been found to obey the empirical law:

$$\frac{\mu}{\rho} = A\lambda^c$$

where A and c are constants whose values change from branch to branch of the absorption curve. In Fig. 3, log μ/ρ is plotted against log λ and the resulting equations for the four straight lines are

$$\log\left(\frac{\mu}{\rho}\right)_{L_{\mathrm{I}}} = 2.456 + 2.557 \log \lambda$$

$$\log\left(\frac{\mu}{\rho}\right)_{L_{\mathrm{II}}} = 2.384 + 2.557 \log \lambda$$

$$\log\left(\frac{\mu}{\rho}\right)_{L_{\mathrm{III}}} = 2.242 + 2.586 \log \lambda$$

$$\log\left(\frac{\mu}{\rho}\right)_{M_{\mathrm{I}}^{\infty}} = 1.856 + 2.656 \log \lambda$$

where λ is in Angstroms. The L_{II} branch has been assigned the same slope as L_I. Corresponding slopes for other elements are given in Table I. These slopes give good agreement with each other except for the short wave-length branch of gold. Allen finds that his data fit best a $c=2.92$ curve for L_I and a $c=2.6$ curve for M_I absorption for the elements W, Au, Pt, and Pb. Wingardh,[12] on the other hand, obtains 2.58 for Pb on the L_I branch. There is need for more experimental data.

TABLE I. *Slopes of the log μ/ρ, log λ curve for several elements.*

Element	Branch of curve				Observer
	L_I	L_{II}	L_{III}	M_I	
Silver (47)	2.6	2.6	2.6	2.6	Kellström[5]
Platinum (78)	2.6	2.6	2.6	2.64	Backhurst[6]
Gold (79)	2.91	2.91	2.64	2.61	Backhurst[6]
Mercury (80)	2.56	2.56	2.59	2.66	The author

The total mass absorption coefficient is the sum of two components—the fluorescence coefficient, τ/ρ, and the scattering coefficient, σ/ρ. The absorption due to scattering is supposed to be a continuous function of the wave-length and is believed to be relatively slight at long wave-lengths for elements of high atomic number, probably not greater than unity. Since μ/ρ is large under such conditions, σ/ρ is generally considered as negligibly small in comparison. It is τ/ρ that suffers a discontinuity at the absorption limits and so we define the magnitude of an absorption discontinuity as the ratio of τ/ρ on the short and long wave-length sides of a limit. If we neglect σ/ρ, then δ becomes equal to the corresponding ratio of the total mass absorption coefficients. The wave-lengths of the L limits of mercury, as recently measured by Sandström,[13] are

$$L_I = 0.8342A \quad L_{II} = 0.8708A \quad L_{III} = 1.0075A.$$

Values taken from the curve in Fig. 3 give the following for the magnitudes of the three L absorption discontinuities,

$$\log \delta L_I = 0.072 \quad \text{or} \quad \delta L_I = 1.183$$
$$\log \delta L_{II} = 0.142 \quad \text{or} \quad \delta L_{II} = 1.387$$
$$\log \delta L_{III} = 0.390 \quad \text{or} \quad \delta L_{III} = 2.455.$$

The discontinuity magnitudes for mercury are compared with those for other elements in Table II. Dauvillier used a photographic method and assumed a λ^3 law in arriving at his results. The only striking singularity in the atomic number sequence 78, 79, 80 is δL_I of mercury, which is decidedly lower than the corresponding values for gold and platinum. δL_{III} is also somewhat lower. One would expect a decrease in δ with increasing atomic number from an analogy with the K discontinuities. There are not sufficient data available, however, to allow conclusions to be drawn for the L absorption spectrum.

[12] K. A. Wingardh, Dissertation at Lund, 1923.
[13] Arne Sandström, Zeits. f. Physik **66**, 784 (1930).

Edvin Jönsson[3] has found that δK and δL obey the relation

$$\delta K = E_K/E_{L_1} \quad \text{and} \quad \delta L = E_{L_1}/E_{M_I}$$

where E represents the ν/R value of the designated absorption limit and δL is the product of the three separate magnitudes δL_I, δL_{II} and δL_{III}. How well this holds for mercury and several other elements can be seen from Table II also.

TABLE II. *Magnitudes of the L absorption discontinuities for several elements.*

Element	E_{L_I}/E_{M_I}	δL	δL_I	δL_{II}	δL_{III}	Observer
Silver (47)	5.24	5.82	1.25	1.47	3.17	Kellström[5]
Platinum (78)	4.22	4.26	1.25	1.37	2.47	Backhurst[6]
Gold (79)	4.20	4.20	1.24	1.39	2.48	Dauvillier[4]
	4.20	4.25	1.26	1.36	2.53	Backhurst[6]
Mercury	4.16	4.02	1.18	1.39	2.45	The author

As has been pointed out frequently in the literature,[1,2] none of the classical theories of x-ray absorption,—as formulated by Thomson, Compton, Kramers and deBroglie, represents satisfactorily the experimental data. The λ^3 law, which is contained in all of them, gives fair agreement for certain wave-length regions, however. The quantum-theoretical treatments of the problem by Oppenheimer[14] and Wentzel[15] allow more latitude in the value of the exponent of λ, but they are unable to predict definite values for a given wave-length region. More recently, Nishina and Rabi[16] and Roess[17] have worked out formulas on the basis of the Schrödinger and Dirac mechanics, respectively, but with only fair agreement with experiment. All these later theories, however, were developed for the K electrons, so that the L absorption still remains practically untouched from the theoretical viewpiont.

The original suggestion and mode of attack of this problem are due to Professor Samuel K. Allison, to whom the author wishes to express his sincere gratitude. The willing cooperation of Professor Robert B. Brode in furthering the experimental work is worthy of my heartiest thanks. I am also indebted to the University of California for the appointment to a Harold Whiting Fellowship in Physics during the course of the investigation.

[14] J. R. Oppenheimer, Zeits. f. Physik **41,** 268 (1926).
[15] G. Wentzel, Zeits. f. Physik **40,** 574 (1926).
[16] Y. Nishina and Rabi, Verh. d. D. Phys. Ges. (3) **9,** 6 (1928).
[17] L. C. Roess, Phys. Rev. **37,** 532 (1931).