ON THE X-RAY ABSORPTION FREQUENCIES CHARACTERISTIC OF THE CHEMICAL ELEMENTS.

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SYNOPSIS.

Object.—The object of this paper is to record in some detail the data presented to the American Physical Society at its meeting on April 27, 1918.[1]

Blake and Duane[2] had determined the critical absorption wave-lengths associated with the K series of x-rays for most of the chemical elements from bromine (atomic number 35) to cerium (atomic number 58) by measuring the currents in an ionization chamber attached to an x-ray spectrometer. The research reported in this paper extends the measurements to chemical elements of lower atomic number, as far as manganese (atomic number 25). The same apparatus was used as in the previous research, except that the x-ray tube employed had a long glass tube attached to it carrying a thin glass window at its end. This window lay close to the spectrometer slit, and the device materially reduced the absorption of the long x-rays by the air and glass.

Importance in Theory.—These critical absorption wave-lengths have considerable importance in connection with the theories of the structure of matter and the mechanism of radiation, for they represent frequencies of vibration that are the highest x-ray frequencies definitely known to be characteristic of the chemical elements.

Results.—From the experiments it appears that the square root of the critical absorpion frequency is not quite a linear function of the atomic number.

If we calculate the velocity v of an electron in the x-ray tube required to produce the radiation from the equation

$$\frac{1}{2}\frac{m_0 v^2}{\sqrt{1-\frac{v^2}{c^2}}} = h\nu \qquad (1)$$

using for ν the critical absorption frequency, we find that v is a linear function of N, namely

$$v = v_0\,(N - 3/2),\ v_0 = .00678xc \qquad (2)$$

for all the chemical elements from manganese to cerium.

Further equation (2) gives the critical velocity for the chemical elements as far as magnesium, if we use data obtained from emission spectra.

It will be noticed that equation (1) contains the expression for the *transverse* mass of the electron.

IN Moseley's classical experiments[3] on x-rays he showed that the square roots of the frequencies, ν, of corresponding lines in the characteristic emission spectra of the chemical elements are very nearly linear functions of the atomic number, N, of those elements. Recent researches have confirmed and extended these results. The wave-lengths of about fifteen

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[1] PHYS. REV., June, 1918, p. 488.

[2] PHYS. REV., Dec., 1917, 697.

[3] Phil. Mag., April, 1914, p. 703.

lines in each of the emission spectra of a large number of chemical elements have been measured and tabulated. The graphs[1] representing $\sqrt{\nu}$ for corresponding lines in these spectra as functions of N are not quite straight. They bend slightly upward, the curvature becoming more marked as the frequency increases.

Attempts have been made to deduce empirical formulas for ν in terms of N, and some of these,[2] with four arbitrary constants, seem to fit the data very well.

The equations[3] in Bohr's theory of radiation contain the mass m of the electron. Since m varies with the electron's velocity the square roots of these expressions for the frequencies of rotation and vibration are not quite linear functions of N. The deviation from the straight line law is much the same as that which appears in the graphs representing experimental data.

It might be expected that the critical absorption frequencies associated with the emission series of x-rays would bear the most fundamental and, perhaps, the simplest relations to the atomic numbers; for they appear to be the most important frequencies characteristic of the chemical elements. Their importance rests upon the following facts. (*a*) A critical absorption frequency equals the critical ionization frequency associated with the same x-ray emission series.[4] The latter probably means the critical frequency for the characteristic emission of electrons with definite energy from the atom. (*b*) The difference between two critical absorption frequencies equals the frequency of one of the emission lines characteristic of the chemical element.[5] (*c*) A critical absorption frequency, substituted in the quantum equation, $Ve = h\nu$, gives the voltage V required to produce the emission series associated with it.[6] (*d*) A K critical absorption frequency is the highest x-ray frequency known to be characteristic of its chemical element. It lies very close to, but slightly above, the highest frequency in the corresponding emission series.[7]

De Broglie has made a series of interesting and important experiments, in which he measured the critical absorption wave-lengths characteristic of a large number of chemical elements. He used an x-ray spectrometer with a rock salt crystal, and determined the position of the beam of rays reflected from the crystal by means of a photographic plate.

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[1] Friman, Phil. Mag., Nov., 1916, p. 497.

[2] Uhler, Phys. Rev., April, 1917, p. 325.

[3] Phil. Mag., September, 1913, p. 476.

[4] Duane and Hu, Phys. Rev., June, 1918, p. 489; Dec., 1919.

[5] Duane and Shimizu, Phys. Rev., April, 1919, p. 306; July, 1919.

[6] Webster, Phys. Rev., June, 1916, p. 599; and Duane and Hu, *l.c.*

[7] Duane and Hu, *l.c.*

Owing to the difficulty of estimating by this method the effect due to the penetration of the x-ray into the reflecting crystal, and that due to the widths of the spectrometer's slits, Prof. F. C. Blake and one of us[1] decided to undertake a series of measurements using the ionization method of detecting the reflected beam. The data obtained in these experiments include the critical absorption wave-lengths associated with the K series of x-rays for all but two of the known chemical elements from bromine ($N = 35$) to cerium ($N = 58$).

The equation $\nu = \nu_0 \, (N - 3.5)^2$, in which ν_0 is the Rydberg fundamental frequency, namely 109,675 multiplied by the velocity of light, approximately represents the critical absorption frequencies ν corresponding to these wave-lengths. There appears to be, however, a small systematic variation from the law represented by the equation.

The object of the research reported in this paper has been to extend the measurements to chemical elements of lower atomic number than that of bromine, and we have succeeded in obtaining the critical absorption wave-lengths associated with the K series for all the chemical elements from bromine ($N = 35$) to manganese ($N = 25$).

The magnitudes of the frequencies belonging to chemical elements having small values of N give us the best determinations of the quantity k in formulas of the general form

$$\nu = \nu_0(N - k).$$

The x-rays in the K series of chemical elements of low atomic numbers are comparatively long; and, since the coefficient of absorption of x-rays varies approximately as the cube of the wave-length, the absorption of the rays of long wave-length by the glass walls of the x-ray tube itself becomes of great importance. In order to allow as much radiation of long wave-length to emerge from the tube as possible we designed, and had constructed an x-ray bulb with a long glass side tube attached to it. This tube extended out toward the x-ray spectrometer, and carried at its end a thin glass window, which lay close to the spectrometer's slit. The device markedly reduced the absorption of the x-rays by the glass and air.

Except for this side tube attached to the x-ray bulb the apparatus used in the experiments on chemical elements from manganese to bromine was exactly the same as that employed in the experiment on chemical elements from bromine to cerium. A detailed description of this apparatus may be found in the PHYSICAL REVIEW for December, 1917, on page 624.

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[1] PHYS. REV., December, 1917, p. 697.

The electric current exciting the x-ray tube came from a high-tension storage battery containing 20,000 cells, and the voltage across the tubes terminals was kept constant by slowly changing a water resistance in series with it. An electrostatic voltmeter, calibrated by means of a measured current from the storage battery flowing through a known metallic resistance of 890,000 ohms, served to measure the voltage. The current through the tube, amounting to several milliamperes was measured by a milliameter. Two slits in lead blocks placed between the x-ray tube and the reflecting crystal defined the beam of rays and the third slit, in front of the ionization chamber, was wide enough to allow all the reflected rays to pass. This arrangement eliminates a correction for the penetration of the rays into the crystal. This correction, however, is very small for x-rays of long wave-lengths.

The absorbing screen consisted of a thin layer of the chemical element, or of one of its salts, and lay between the x-ray tube and the first slit.

We made measurements on both sides of the zero line of the spectrometer, and obtained curves for each chemical element representing the ionization currents as functions of the readings of the verniers attached to the crystal table, similar to the curves shown on page 701 of the Physical Review for December, 1917. The sharp drops in these curves correspond to the critical absorption wave-lengths, the angular breadths of the drops representing the effects due to the widths of the slits.

To determine the grazing angles of incidence θ to substitute in the formula for the wave-length

$$\lambda = 2a \sin \theta = 6.056 \times \sin \theta \times 10^{-8} \text{ cm}.$$

we measured from the mid-points in the drops. The breadths of the drops amount to a few minutes of arc, and the grazing angles of incidence to several degrees. The positions of the mid-points can be estimated to within 1/10 per cent. of the values of the grazing angles.

The slopes of the curves above and below the drops depend upon the setting of the instrument, the thickness of the absorbing layer, the relation between the voltage applied to the x-ray tube and that required to produce x-rays as short as the critical rays, etc.

The following Table I. contains the critical absorption data for the K series of all the known chemical elements from manganese ($N = 25$) to cerium ($N = 58$), except the two gases xenon and krypton. The critical absorption wave-lengths appear in the third column, and the square roots of the corresponding vibration frequencies, in the fourth. The $\sqrt{\nu}$ cannot quite be represented by a linear function of N. The values of $\sqrt{\nu}$ differ from such a function by several per cent.

TABLE I.[1]

Chemical Element.	Automic Number.	$\lambda \times 10^8$.	$\sqrt{\nu} \times 10^{-9}$.	Ratio $\beta = v/c$.	$\beta_0 \times 1{,}000$.
Cerium	58	.3068	3.127	.3828	6.775
Lanthanum	57	.3188	3.068	.3761	6.778
Barium	56	.3307	3.012	.3698	6.785
Cæsium	55	.3444	2.952	.3629	6.783
Iodine	53	.3737	2.833	.3494	6.784
Tellurium	52	.3896	2.775	.3426	6.783
Antimony	51	.4065	2.717	.3358	6.784
Tin	50	.4242	2.659	.3291	6.786
Indium	49	.4434	2.601	.3223	6.786
Codnium	48	.4632	2.545	.3157	6.790
Silver	47	.4850	2.488	.3089	6.789
Palladium	46	.5075	2.431	.3023	6.794
Rhodium	45	.5330	2.373	.2953	6.790
Ruthenium	44	.5584	2.319	.2889	6.797
Molybdenum	42	.6180	2.203	.2751	6.794
Niobium	41	.6503	2.149	.2685	6.797
Zirconium	40	.6872	2.089	.2614	6.791
Yttrium	39	.7255	2.034	.2547	6.792
Strontium	38	.7696	1.974	.2475	6.783
Rubidium	37	.8143	1.919	.2408	6.784
Bromine	35	.9179	1.808	.2272	6.783
Selenium	34	.9790	1.751	.2202	6.775
Arsenic	33	1.0435	1.696	.2135	6.776
Germanium	32	1.1146	1.639	.2067	6.780
Gallium	31	1.1902	1.590	.2002	6.785
Zinc	30	1.2963	1.521	.1922	6.759
Copper	29	1.3785	1.475	.1863	6.774
Nickel	28	1.4890	1.420	.1793	6.766
Cobalt	27	1.6018	1.369	.1730	6.784
Iron	26	1.7396	1.313	.1661	6.780
Manganese	25	1.8892	1.260	.1595	6.787

It is interesting to inquire whether some other quantity connected with x-radiation may not be a linear function of N. If we calculate the velocity of the electron in the x-ray tube required to produce the K emission series from the quantum equation.

$$\tfrac{1}{2}mv^2 = h\nu, \tag{1}$$

assuming that m varies with the velocity according to the law

$$m = \frac{m_0}{\sqrt{1-\beta^2}}, \qquad \beta = \frac{v}{c}, \tag{2}$$

where c is the velocity of light, we find that the values of v do not differ

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[1] We wish to express our sincere thanks to Professor C. James and to Professor J. L. Howe for sending us some of the rare elements.

from those given by the linear equation

$$v = v_0(N - 3/2), \qquad v_0 = .006783c \tag{3}$$

by as much as 1/5 per cent.

The fifth column in the table contains the values of β, and the sixth, of $\beta_0 = v_0/c$. None of the values of β_0 differ from .006783 by as much as 1/5 per cent., except that for zinc.

We have shown by experiment (*l.c.*) that the critical absorption frequency of rhodium does not differ from the highest frequency in its K emission series by more than about 1/4 per cent. If we calculate the critical velocity v from equations (1) and (2) using for ν the highest frequencies given in Siegbahn's tables of emission lines in the K series, we find that equation (3) represents the velocities with considerable precision for all the chemical elements as far down as and including magnesium ($N = 12$).

The following table contains the data for these chemical elements:

Chemical Element.	**Atomic Number.**	$\lambda \times 10^8$.	$\sqrt{\nu} \times 10^{-9}$.	**Ratio** $\beta = v/c$.	$\beta_0 \times 1{,}000$.
Chromium........	24	2.067	1.205	.1526	6.782
Titanium.........	22	2.490	1.097	.1391	6.785
Calcium..........	20	3.072	.9880	.1253	6.773
Potassium........	19	3.446	.9437	.1185	6.771
Chlorine..........	17	4.391	.8265	.1050	6.774
Sulphur..........	16	5.014	.7734	.09829	6.779
Phosphorus.......	15	5.804	.7188	.09137	6.768
Silicon...........	14	6.755	.6663	.08475	6.778
Aluminum........	13	7.982	.6131	.07797	6.778
Magnesium.......	12	9.471	.5627	.07158	6.817

In conclusion we wish to call attention to the fact that $\frac{1}{2}mv^2$ is not the *relativity* expression for the kinetic energy of the electron. The fact that equation (2) gives the *transverse* mass of the electron suggests that possibly v may represent the velocity of an electron travelling in an orbit. These points will be discussed in another paper.