THE ABSORPTION OF THE $K\alpha$ LINE OF CARBON IN VARIOUS GASES AND ITS DEPENDENCE UPON ATOMIC NUMBER

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Abstract

A description is given of the apparatus and methods used in a photographic investigation of absorption coefficients for the $K\alpha$ line of the carbon ($\lambda=44.6$A) in different gases and in gold leaf. The mass absorption coefficients, μ/ρ, found were as follows: He, 3600: CO_2, 4780: N_2, 3850: O_2, 5765: Ne, 13100: A, 45700: Kr, 31800: Xe, 6740: Au, 12500. Some of the atomic absorption coefficients (μ_a) derived from these values on the assumption that the absorption is independent of chemical combination are as follows: C, 0.44×10^{-19}: N, 0.89×10^{-19}: O, 1.52×10^{-19}: Ne, 4.36×10^{-19}: The wave-length of the $K\alpha$ line of carbon lies between the K and L_I absorption limits of these elements. The values of log μ_a when plotted against log Z fall upon a straight line whose slope is 4.4. Hence in this wave-length region this should be the value of p in the equation $\tau_a = C\lambda^n Z^p$, provided that $\lambda_K < \lambda < \lambda_L$. The results of extrapolating current x-ray formulas to this wave-length are given and the values of μ_a so obtained are, in general, considerably too large. Since the exponent of Z in the above equation is found experimentally to be as large or larger than in the case of ordinary x-rays it appears that the proper exponent of λ may be considerably less than 3.

Introduction

THIS investigation was undertaken to determine absorption coefficients for soft x-rays over as great a range of wave-lengths and absorbing elements as might be possible with the use of ruled gratings to isolate single wave-lengths and a photographic method to measure intensities. The present report deals only with data obtained with the use of one wave-length, that of the $K\alpha$ line of carbon (44.6A). As will be shown in a following paper the reflecting power of a mirror for these rays is intimately related to the absorption of the radiation by the mirror. Hence it was necessary first to investigate the laws of absorption applicable to such soft x-rays in order to determine the exact role played by absorption in modifying the intensity of reflection of x-rays from mirrors and gratings.

The x-ray absorption coefficient of an atom of any element is usually considered to consist of two terms as may be expressed in the following equation, $\mu_a = \tau_a + \sigma_a$ in which μ_a is the total atomic absorption coefficient and τ_a and σ_a are the atomic fluorescence and scattering absorption coefficients respectively. For radiations longer than 1A, σ_a becomes quite small in comparison to τ_a.

In the case of ordinary x-rays the atomic fluorescence absorption coefficient was early found to be very well represented by the formula $\tau_a = C\lambda^n Z^p$ in which C is a constant depending upon the absorption region considered, λ the

wave-length and Z the atomic number. For wave-lengths less than 1A the values of the exponents n and p are very nearly 3 and 4 respectively. For longer wave-lengths there is considerable evidence that n decreases and p increases with increasing wave-length. A number of methods have been proposed for theoretically evaluating the above constants. These will not be discussed here. From a consideration of experimental data, Richtmyer and Warburton[1] found empirically the values, $C = 2.24 \times 10^{-26}$ for wave-lengths shorter than the K limit and $C = 0.33 \times 10^{-26}$ for those between the K and L_I limits, n and p being taken as 3 and 4 respectively and λ expressed in Angstrom units. Allen[2] with data extending in some instances to 4A found the corresponding values of C to be 2.18×10^{-26} and 0.299×10^{-26} respectively while reducing the value of n to 2.92. Gray[3] summarized the existing data and proposed a more complicated formula for the K region, namely:

$$\tau_a = 1.92(1 + 0.008Z)(1 - \lambda/4\lambda_K - \lambda/50\lambda_K{}^2)Z^4\lambda^3 \times 10^{-26}.$$

The factors in parenthesis are introduced empirically to compensate for the reduction found in n with increasing wave-length. Between the K and L_I absorption limits Gray finds the simpler formula $\tau_a = 0.255Z^4\lambda^{2.7} \times 10^{-26}$.

An important investigation by Jönsson[4] extended absorption measurements for some metals to nearly 12A. He concluded that the absorption per K electron, for all elements, could be represented by the same function, $f(Z\lambda)$ of the product of the atomic number and the wave-length. This is made applicable to the case of wave-lengths longer than that of the K limit by multiplying $f(Z\lambda)$ by the ratio of the wave-length of the K limit to that of the nearest absorption limit having a wave-length greater than that of the absorbed radiation. This latter step depends for its justification upon the experimental fact as shown by Richtmyer[5] that the magnitude of the absorption discontinuity at the K limit is very nearly equal to the ratio of the wave-length of the L_I limit to that of the K limit. Jönsson tabulates values of $f(Z\lambda)$ obtained from experiment for values of $Z\lambda$ between 8 and 790. With the aid of these tables one may compute absorption coefficients by Jönsson's method for various elements and wave-lengths provided $8 < Z\lambda < 790$.

Woernle[6] has investigated the absorption of certain gases for wave-lengths ranging from 2.3A to 9.9A and found some variation from the law proposed by Jönsson. His results indicate that the exponent of Z is greater in the L than in the K absorption region.

All of the above formulas were deduced from a consideration of data relating to wave-lengths less than 12A and one should not expect them to hold for wave-lengths as long as that of the carbon $K\alpha$ line. Nevertheless, since they furnished previous to this investigation about the only means of estimat-

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[1] Richtmyer and Warburton, Phys. Rev. 18, 13 (1921).

[2] Allen, Phys. Rev. 27, 266 (1926).

[3] Gray, International Critical Tables 6, 12 (1929).

[4] Jönsson, Dissertation, Uppsala, (1928).

[5] Richtmyer, Phys. Rev. 27, 1 (1926).

[6] Woernle, Ann. d. Physik 5, 475 (1930).

ing the order of magnitude of the absorption to be expected, it is of some
interest to calculate absorption coefficients by the use of these formulas and
to compare the results with those obtained experimentally. These results are
given in Table II.

APPARATUS AND METHODS

A sketch of the apparatus is shown in Fig. 1. A beam of x-rays passed
upward from the water-cooled x-ray tube X, through the slit S_1 which was
covered with a thin film of celluloid, then through the slit S_2 onto the grating
G. This was a plane glass grating having 600 lines per mm and gave a very
intense first "inside order" of the $K\alpha$ line of carbon when the glancing angle
of incidence was about $4°40'$. The shield S_3 was so placed as to cut out all
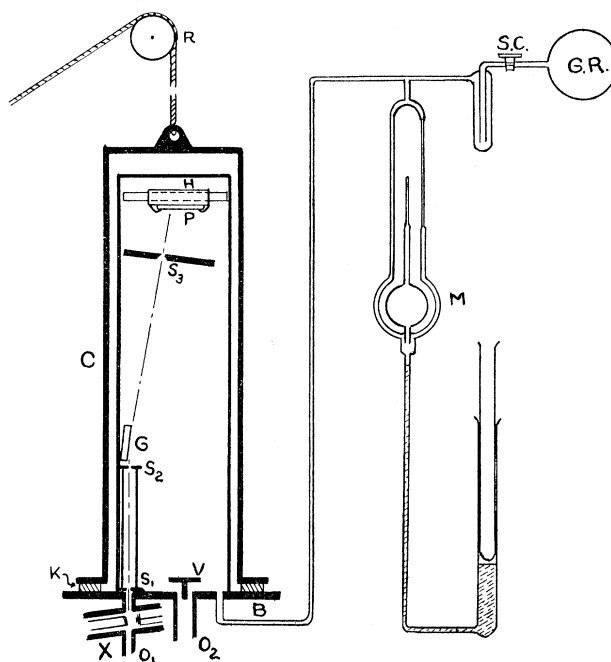

Fig. 1. Diagram of apparatus.

other wave-lengths while letting the $K\alpha$ line of carbon pass through a narrow
slit and fall upon the photographic plate P which was carried by the sliding
plate holder H. The latter could be given a step-by-step motion across the
path of the x-ray beam by means of an electromagnet which is not shown in
the sketch but which could be operated at will by pressing a button outside
the spectrograph. The apparatus could be opened for adjustments or the
changing of plates by raising the cylinder C with the aid of the rope and pul-
ley R. When closed the bottom flange of this cylinder rested on the sulphur-
free gasket K which made a vacuum tight seal between the cylinder and the
base plate B. The x-ray tube and spectrograph were evacuated by mercury
diffusion pumps connected to the outlets O_1 and O_2. The valve V could be

either opened or closed by a ratchet device actuated by another electromagnet controlled from outside.

When in operation the apparatus was used as follows: With the valve V open the spectrograph was evacuated to a pressure of about 2×10^{-5} mm Hg. Several photographs of the $K\alpha$ line were then taken with different times of exposure. The valve V was then closed and such an amount of gas admitted from the gas reservoir GR as was estimated to absorb one half or more of the radiation. Several exposures were then made with varying time of exposure. These times of exposure were so chosen as to produce blackenings intermediate between the lightest and darkest lines obtained in the vacuum. Pressures were measured with the calibrated McLeod gauge M, which was provided with two compression chambers in order to measure a large range of pressures. Readings were taken repeatedly during a run to check against pressure changes. Finally the valve V was opened, the gas swept out and another series of exposures similar to the first were made.

The power input to the tube was kept constant during a run. Ordinarily a current of 22 milliamperes and an effective voltage of 2.7 kv were used. Lines of the desired density were usually secured in one to three minutes when the chamber was evacuated. This varied somewhat from time to time due to variations in the amount of carbon adhering to the target of the x-ray tube, but no sudden changes in the intensity of the carbon line were ever noted. However, continuous variations of five or ten percent per hour were common. It was found that by rubbing a small quantity of stopcock grease on the stem supporting the filament of the x-ray tube that some portion of the stem would remain at just the right temperature to cause a slow evaporation of carbon compounds which would maintain a quite constant amount of carbon deposit on the target provided the energy input to the tube did not exceed that noted above.

Eastman x-ray plates and x-ray developer were used, care being taken to avoid over-development and to keep the plates rotating while in the developer. The densities of the lines were then compared with the aid of a photoelectric photometer recently constructed in this laboratory. In this instrument, which will be described in more detail elsewhere, a beam of light from a small bulb was directed upon a fine slit so placed that the light passing through the slit fell upon a potassium hydride photoelectric cell connected to a string electrometer. The photographic plate was then placed with the film side very close to the slit and moved across the beam of light by means of a graduated screw. The time for a given reflection of the string of the electrometer was noted when the various lines and intervening clear spaces were in front of the slit. Repeated measures of the same lines gave variations in electrometer readings of much less than one percent. The time required for the electrometer string to move a certain number of divisions with a line before the slit minus the time for the same deflection with the adjacent clear portion of the plate in front of the slit was taken as a measure of the relative density of the line.

The noble gases used were obtained from the Air Reduction Sales Company and were guaranteed to be spectroscopically pure. This was verified by

tests with a small direct vision spectroscope which gave no evidence of lines other than those belonging to the gas in question. Carbon dioxide was obtained by heating magnesium carbonate, nitrogen by heating sodium azide and oxygen by the electrolysis of barium hydroxide. These gases were dried by phosphorus pentoxide. Such gases as would not be condensed were further purified by passing through a liquid air trap. For those of higher boiling points carbon dioxide snow in acetone was used to cool the trap. The data for gold were obtained with the use of gold leaf. The thickness of the latter was determined by weighing.

Results and Calculations

The mass absorption coefficients were determined from the equation $I/I_0 = e^{-(\mu/\rho)\rho x}$ in which x is the length of path through the gas from the celluloid window on the slit S_1 to the photographic plate. This distance was 57.7 cm. The density ρ, was computed from the density at standard conditions and the experimental values of temperature and pressure.

The ratio I/I_0 was obtained from the photographic density measurements and the times of exposure of the lines with and without gas in the chamber. Several methods of determining this ratio from density measurements were tried. In one method four lines having different exposure-times were photographed near one end of the plate with the chamber evacuated, followed by seven lines through the gas, the latter exposure-times being lengthened to give densities intermediate between the extremes of those obtained without gas in the chamber. The chamber was then again evacuated and the first four lines repeated on the other end of the plate. Curves were drawn with the photometer densities of the lines in vacuum plotted against exposure-time. In case the curves obtained at the beginning and end of the run were not identical, the densities of the lines through the gas were corrected on the assumption that the radiation from the tube had varied uniformly in intensity throughout the time of the complete operation. The time which would have been required in vacuum to produce a blackening equal to that of any line through the gas could be read from these curves. The ratio of this time to the actual exposure time of the line through the gas is, from the reciprocity law, the desired ratio of intensities, I/I_0. Each line taken through the gas thus gave a measure of this ratio.

In some cases in which a sufficient number of lines in vacuum had not been secured to give a suitable curve of blackening against time, auxiliary plates with variable time of exposure were taken and curves of blackening against exposure-time were drawn for each of these. Let T_v be the exposure time of a line in vacuum and T_{va} the time to produce the same blackening on the auxiliary plate. Also let T_g be the exposure time of a line in gas and T_{ga} the time to produce the same blackening on the auxiliary plate. Then

$$\frac{I}{I_0} = \frac{T_v}{T_g} \times \frac{T_{ga}}{T_{va}}.$$

Experience showed that the two methods led to identically the same result when the average of a considerable number of comparisons were taken.

The results of these measurements are summarized in Table I. The large number of observations taken in some cases reduced the mathematical probable error but the actual error is perhaps considerably larger. This comes from

TABLE I. *Mass, molecular and atomic absorption coefficients of the carbon Kα line in various gases and gold leaf.*

Absorber	μ/ρ	$\mu_m \times 10^{19}$	$\mu_a \times 10^{19}$	Number of observations	Percent probable error
He	3600		0.238	104	1.0
CO_2	4780	3.49		23	1.4
N_2	3850	1.78		20	1.0
O_2	5765	3.05		14	2.8
Ne	13100		4.36	84	0.8
A	45700		30.1	52	0.6
Kr	31800		43.4	112	0.5
Xe	6740		14.5	139	1.0
Au	12500		40.7	5	10.
Air	5350			76	
C			0.44		
N			0.89		
O			1.52		

the fact that not all of the variations are due to chance errors. The absorption coefficient for carbon is derived from that of carbon dioxide on the assumption that absorption is independent of chemical combination. This assumption appears justified when we consider the relatively enormous effect of atomic
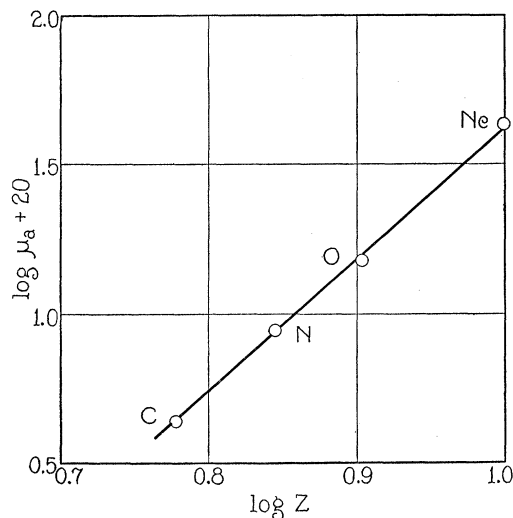

Fig. 2.

number as contrasted with the number of electrons in a molecule. For example, the absorption by an atom of neon with 10 electrons is considerably greater than that of a molecule of carbon dioxide with 22 electrons. Fig. 2 shows the logarithm of atomic absorption coefficient plotted against loga-

rithm of atomic number for the elements carbon, nitrogen, oxygen and neon. The straight line thus obtained indicates that μ_a is a function of the atomic number only, or that its dependence upon any other factor is relatively small, since the atomic absorption coefficients derived from measurements on molecules of CO_2, N_2, O_2 and atoms of Ne are thus shown to be proportional to the atomic number raised to the same power. Some measures of the absorption of sulphur dioxide were made. When corrected for the probable impurity the gas was found later to contain, the value of μ_a so obtained for sulphur agreed fairly well with a continuation of the straight line of Fig. 2 and strengthened our conviction that this line represents the true law of absorption for this wave-length in the elements from carbon to sulphur. However it was thought best to repeat these measures with other samples of gas before publication of final values for the absorption of sulphur.

From the slope and intercepts of the line of Fig. 2 the following formula for the atomic absorption coefficient of an element in which $\lambda_K < 44.6A < \lambda_{LI}$ is easily deduced.

$$\mu_a = 1.65Z^{4.4} \times 10^{-23}.$$

This equation may then be used to determine the absorption coefficients of the other elements in this region of atomic number.

The experimental values of the absorption coefficients for the elements investigated are given in Table I. Except for the elements represented in Fig. 2 these all fall in different absorption regions. It may be noted that the mass absorption coefficient of argon is greater than that of krypton, xenon or gold while the absorption by an atom of krypton is greater than that of any other atom in the list. This is readily explained by the fact that with increasing atomic number of the absorber the K, L, M and N absorption limits pass in turn to the high frequency side of the incident radiation and the electrons belonging to these levels cease to absorb. Nevertheless this decrease is, perhaps, more than might be expected. For example, in the case of an atom of xenon there remain 26 electrons with natural frequencies less than that of the incident radiation yet these absorb only about one half as much as the 14 electrons in an argon atom whose natural frequencies are such as to permit absorption.

Conclusions

The experimental results indicate a probable value of 4.4 for p in the equation $\tau_a = C\lambda^n Z^p$ when it is applied to the L absorption region of the absorbing element and to wave-lengths in the neighborhood of the $K\alpha$ line of carbon. A value of n cannot be deduced directly, since only one wave-length was investigated. Nevertheless there is indirect evidence that n for this region may be considerably less than 3. It may be noted that the values of τ_a listed in Table II which are computed from the formulas of Richtmyer and Warburton, Allen, and Gray are considerably too large. This indicates that either C or n or both have smaller values in this soft x-ray region than is the case for ordinary x-rays. The numerical value of $C\lambda^n$ for some of these elements has

TABLE II. *Experimental and calculated values of atomic absorption coefficients for the Kα line of carbon. τ_a should equal μ_a at this wave-length.*

Absorber	$\mu_a \times 10^{19}$ Experimental	$\tau_a \times 10^{19}$ Richtmyer and Warburton	$\tau_a \times 10^{19}$ Allen	$\tau_a \times 10^{19}$ Gray	$\tau_a \times 10^{19}$ Jönsson
He	0.238	3.2	2.28	2.7	0.19
C	0.44	3.8	2.54	0.94	1.05
N	0.89	7.0	4.7	1.74	1.44
O	1.52	11.9	8.0	2.97	1.61
Ne	4.36	29.3	19.6	7.24	2.63

been shown experimentally to be 1.65×10^{-23}. If we assume a value of C equal to that of the Richtmyer and Warburton formula we obtain $n = 2.24$. With the values of C taken from the formulas of Allen and Gray we find $n = 2.27$ and $n = 2.31$ respectively. This does not yield a trustworthy value of n since the value of C is quite uncertain. In fact we do not know that an equation of the assumed form can represent absorption coefficients in this region. On the other hand the method of Jönsson is shown to lead to values of the right order of magnitude. This appears at first somewhat difficult to understand, since his assumption that the absorption is a function of λZ is equivalent to assuming that the exponents of λ and Z are the same. If, however, the exponent of Z increases and the exponent of λ decreases with increase of λ at such rates that the changes in one approximately compensate for the changes in the other, it would be possible to secure an apparent but quite fortuitous agreement with experiment by assuming the absorption to be a function of λZ raised to some intermediate power. In view of the fact that all investigations indicate that the exponent of Z is always greater than the exponent of λ and also that this difference probably increases with increase of wave-length, it seems probable that the results achieved by Jönsson's method are to be explained in this way.

It is planned to continue this investigation with the use of other wave-lengths in an endeavor to find the law relating absorption to wave-length in this region and to test further the dependence of absorption upon atomic number.

NOTE ADDED IN PROOF:

It has been called to the author's attention that Kurtz[7] used the entire beam of x-radiation from a carbon target and measured its absorption in several of these gases. Substituting his values of the constants in the equation $\tau_a = C\lambda^n z^p$ we obtain $\tau_a = 1.7 \ z^{4.4} \times 10^{-23}$. Considering the uncertainty regarding the homogeneity of his radiation the results are in remarkable agreement with those obtained in the present investigations.

[7] Kurtz, Ann. d. Physik **85**, 529 (1928).