Structure of the X-Ray K Absorption Limits of Bromine, Iodine, and Some of Their Compounds

BERNARD CIOFFARI

Pupin Physics Laboratories, Columbia University, New York, N. Y.

The double crystal spectrometer has been used to investigate the structure, width, and relative positions of the K absorption limits of bromine in the vapor, liquid, and solid states; of iodine in the vapor and solid states; and of some compounds of these elements. Curves of these absorption limits are presented. Tables are given of the widths of these limits, of the relative displacements of the limits in compounds, and of the positions of secondary structure. The absorption limit of bromine vapor possesses a pronounced structure near the short wave-length side. This structure does not appear in the absorption limit of either the liquid or solid, or of any of the compounds investigated, except iodine monobromide vapor. The absorption limit of solid iodine shows a faint structure near the short wave-length side. A similar structure is found in the absorption limit of the vapor, but no shift is detected. The iodine K absorption limits of the compounds investigated show no measurable shifts.

INTRODUCTION

IN recent years, the double crystal x-ray spectrometer has been used by Barnes,[1] Ross,[2] Richtmyer and Barnes,[3] Zinn,[4] and Stephenson[5] for investigating the structure and width of K absorption limits, and by Hull[6] and Semat[7] for L absorption limits. The suitability of this instrument for such investigations was previously demonstrated by Bergen Davis and Harris Purks.[8] The effect of physical state and chemical combination on the absorption limits has been studied in the above investigations and also with the single crystal spectrograph by Hanawalt,[9] Coster and Veldkamp,[10] Lindsay,[11] Kawata,[12] and Lindh.[13]

This investigation was undertaken to study the effect of physical state and chemical combination upon the structure, width, and position of an absorption limit. The elements used were bromine in the vapor, liquid, and solid states, and iodine in the vapor and solid states. The compounds used were HBr, CH_3Br, KBr (solid), KBr (solution), IBr (solid), IBr (vapor), bromine water, CdI_2, HgI_2, KI, KIO_3 and SnI_4.

APPARATUS

The double crystal x-ray spectrometer was of the type described by Bergen Davis and Harris Purks.[8] A water-cooled x-ray tube with a tungsten target and a thin glass window was used in this investigation. The tube was operated at 26 kv and 31 ma for the bromine absorption edge, and at 45 kv and 20 ma for the iodine absorption edge. The beam was limited by slits 0.4 cm wide and 1.0 cm high. The ionization chamber was 7 cm long and 2.5 cm in diameter. It was filled with methyl bromide gas at atmospheric pressure for the study of the iodine absorption edge. Methyl iodide was used for the study of the bromine absorption edge. The ionization current was amplified by an FP-54 Pliotron and was read on a Leeds and Northrup type R galvanometer having a sensitivity of 10,000 megohms. The voltage sensitivity was about 10,000 mm/volt. Rates of deflection of the galvanometer were observed.

The cells for the vapors were made of Pyrex. They were 22 cm long, with thin windows at the ends and a side tube at the center. In all cases,

[1] A. H. Barnes, Phys. Rev. 44, 141 (1933).
[2] P. A. Ross, Phys. Rev. 44, 977 (1933).
[3] F. K. Richtmyer and S. W. Barnes, Science 77, 459 (1933); Phys. Rev. 45, 754 (1934).
[4] W. H. Zinn, Phys. Rev. 46, 659 (1934).
[5] S. T. Stephenson, Phys. Rev. 44, 349 (1933); 49, 495 (1936); 50, 790 (1936).
[6] H. L. Hull, Phys. Rev. 40, 676 (1932).
[7] H. Semat, Phys. Rev. 46, 688 (1934).
[8] Bergen Davis and Harris Purks, Proc. Nat. Acad. Sci. 13, 419 (1927); Phys. Rev. 32, 336 (1928).
[9] J. D. Hanawalt, Phys. Rev. 37, 715 (1931); Zeits. f. Physik 70, 293 (1931).
[10] D. Coster and J. Veldkamp, Zeits. f. Physik 70, 306 (1931); 74, 191 (1932).
[11] G. A. Lindsay, Zeits. f. Physik 71, 735 (1931); B. Kievit and G. A. Lindsay, Phys. Rev. 36, 648 (1930).
[12] S. Kawata, Kyoto Coll. Sci. Mem. 14, 55 (1931); Phys. Math. Soc. Japan Proc. 17, 89 (1935).
[13] A. E. Lindh, Comptes rendus 172, 1175 (1921); Dissertation, Lund, 1923.

the amount of material contained in the cell was such that when it was all vaporized, the transmission curve showed optimum contrast. The temperature of the bromine cell was kept at 125°C, which is above the boiling point of bromine; that of the iodine cell was kept at 237°C, which is above the boiling point of iodine. Under these conditions the substances were completely vaporized, hence a small variation in temperature caused no change in the absorption. The temperature of the iodine monobromide cell was kept at 50°C. This was below the boiling point, but it was done to prevent excessive dissociation of the bromide into its elements. The heating coils were so arranged that the regions near the windows were kept at a higher temperature than the rest of the furnace, so as to prevent any condensation of vapor on the windows. The hydrogen bromide cell and the methyl bromide cell were kept at room temperature.

A cell of liquid bromine was made by using Pyrex capillary tubes filled with bromine and sealed off at both ends. These tubes were about 5 cm long and had an outside diameter of 1/10 mm, several hundred of them being used to form a single screen. To insure a reasonably uniform thickness of bromine, two screens were superimposed, each of which was made up of two layers of capillary tubes closely packed together. The cell of solid bromine was obtained by lowering the temperature of the liquid bromine cell by means of carbon dioxide snow. This was done by placing the absorption cell in a copper container provided with thin mica windows and enclosed in a wooden box in which the carbon dioxide snow was placed. The windows were kept clear of frost by blowing warm air over them. The bromine water and the KBr solution were contained in thin-walled paraffin cells. A screen of solid IBr was made by embedding the substance in paraffin. A screen of solid iodine was obtained by spraying an ether solution of iodine upon a microscope cover glass by means of an atomizer. As the ether evaporated, it left behind a fine-grained, uniform deposit of iodine. A similar cover glass was superimposed on the first, and the cell was sealed with paraffin. Substances in powder form were ground as fine as possible and sifted onto

cigarette paper coated with a thin layer of castor oil. The thickness of screen used was that which gave maximum contrast in transmitted energy on the two sides of the absorption limit.

The absorbing screens were placed either between the crystals and the x-ray tube, or between the second crystal and the ionization chamber. With the exception of the vapor cells and of the solid bromine cell, the screens were oscillated several times per second in a direction perpendicular to the x-ray beam, in order to smooth out any effects due to nonuniformities in the screens.

In order to make sure that the transmission curves represented changes in energy due to the absorbing material and not fluctuations in the primary radiation, the following procedure was adopted: for each setting of the second crystal, observations were taken of the rates of deflection of the galvanometer, first with the absorber in place, and then with the absorber removed. Each transmission curve is thus accompanied by the corresponding curve of the primary radiation. In a like manner, the relative displacement of the absorption limit of a compound with respect to that of the element was determined by taking observations of the rates of deflection for the unfiltered energy, for the energy transmitted through the element, and for the energy transmitted through the compound, at each setting of the second crystal.

EXPERIMENTAL RESULTS

The structure of the absorption limits of the substances investigated is shown in Figs. 1 to 5. These curves are the results of individual runs; but they are typical of several curves obtained for each substance. Each point on a curve represents the average of about ten readings. The ordinates represent the ratio I/I_0, where I is the x-ray energy transmitted through the absorber, and I_0 is the incident energy; the abscissae represent wave-lengths in x units. The values of the abscissae in volts and in seconds of arc are also indicated. The transmission curves of the compounds, plotted to the same scale as the elements, are shown displaced an arbitrary amount above the curve of the free element. The values of the ordinates correspond-
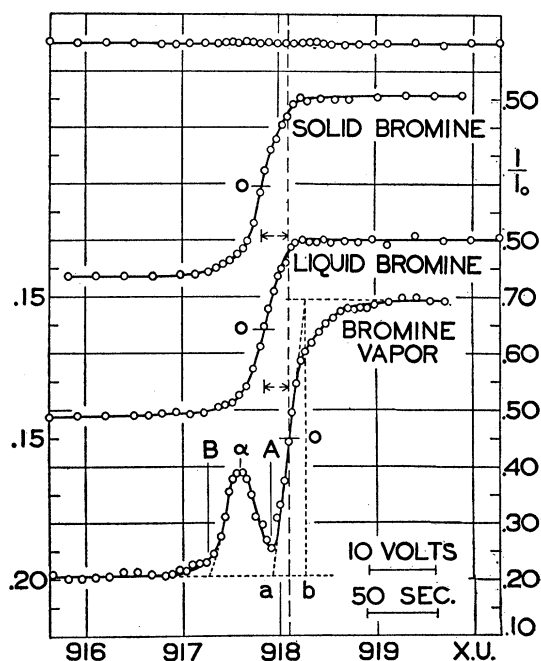
FIG. 1. The absorption limit of bromine for the vapor, liquid, and solid states. The broken vertical line shows the position of the absorption limit of bromine vapor. The center of each limit is marked by the letter O. The shift is indicated by the small arrows.

FIG. 2. The absorption limits of HBr, CH₃Br, and bromine water. The broken vertical line shows the position of the absorption limit of bromine vapor. The center of each limit is marked by the letter O. The shift is indicated by the small arrows.
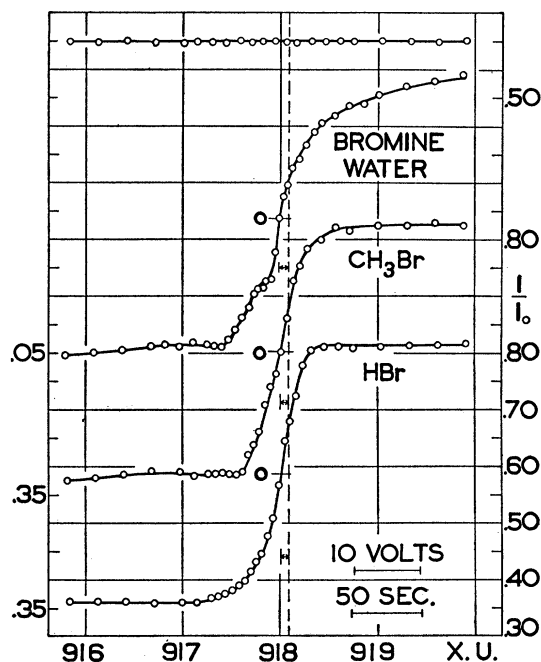
ing to each individual curve are shown at the two ends of each curve. The scale units are the same for all curves. At the top of each figure is shown the plot of the incident energy.

The width of the absorption limit was obtained by drawing a straight line tangent to the curve at the point of greatest slope and determining its intersections with the ordinates of maximum and minimum energy. (a–b in Fig. 1.) The width of the rocking curve for the crystals
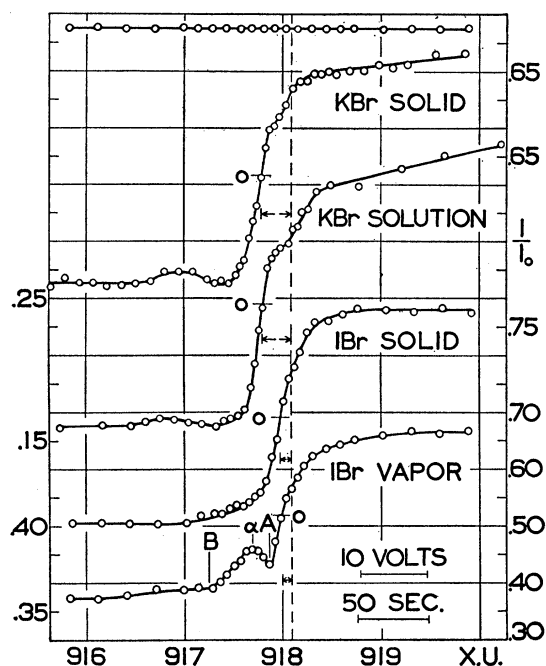

FIG. 3. The absorption limits of IBr vapor, IBr solid, KBr solution, and KBr solid. The broken vertical line shows the position of the absorption limit of bromine vapor. The center of each limit is marked by the letter O. The shift is indicated by the small arrows.

in the (1, −1) position was found to be 7.0 seconds. Different corrections for the crystal width have been proposed by Ehrenberg and Mark,[14] Schwarzschild,[15] Ross,[2] Barnes and Palmer,[16] Richtmyer, Barnes and Ramberg,[17] and Parratt.[18] The Ehrenberg-Mark-Schwarzschild equation gives a negligible correction.

[14] W. Ehrenberg and H. Mark, Zeits. f. Physik 42, 807 (1927).
[15] M. M. Schwarzschild, Phys. Rev. 32, 162 (1928).
[16] S. W. Barnes and L. D. Palmer, Phys. Rev. 43, 1050 (1933).
[17] F. K. Richtmyer, S. W. Barnes and E. Ramberg, Phys. Rev. 46, 843 (1934).
[18] L. G. Parratt, Rev. Sci. Inst. 6, 387 (1935).

However, the other corrections proposed are quite appreciable. Since there appears to be, as yet, no general agreement regarding the correction to be used, the uncorrected values for the widths of the absorption edges have been given.

The wave-length position of the absorption limit is taken as that of the midpoint of the main edge. No attempt was made to measure this wave-length position, but the center of the limit was fixed on the wave-length scale at the best value given in Siegbahn's *Spektroskopie der Röntgenstrahlen*. The shift is obtained by measuring the displacement of the midpoint of the edge of the compound with respect to that of
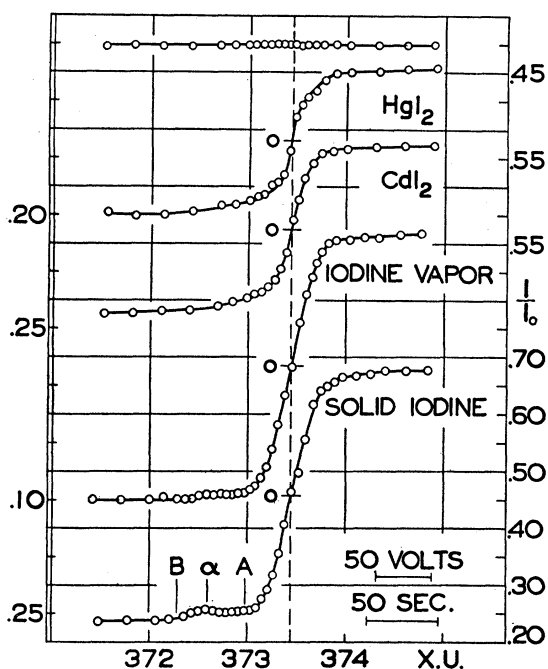

FIG. 4. The absorption limits of solid iodine, iodine vapor, CdI₂, and HgI₂. The broken vertical line shows the position of the absorption limit of iodine vapor. The center of each limit is marked by the letter *O*.

the element. For the bromine curves, all shifts are measured with respect to the absorption limit of the vapor.

Table I gives the widths of the absorption limits in seconds, in x units, and in volts. The values given are the averages obtained from all the curves taken, uncorrected for crystal width. Table II gives the displacements of the absorption limits of the compounds with respect to the absorption limit of the element. All of the shifts

are to the short wave-length side of the absorption limit of the element. Table III shows the position, in volts, of the secondary structure with respect to the center of the absorption limit. The convention of Coster and Veldkamp[10] of labeling the minima of the transmission curves by *A*, *B*, *C*, and the maxima by α, β, γ is followed.

DISCUSSION

Secondary structure

The absorption limit of bromine vapor possesses a pronounced structure near the short wave-length side. (See Fig. 1.) The first minimum occurs at 2.7 volts, the first maximum at 6.6 volts, and the second minimum at 13.0 volts from the center of the edge. The structure found for the vapor does not appear either in the absorption limit of the liquid or of the solid. Bromine water does not show this structure, but it does show a break in the curve corresponding very nearly to the first minimum of the absorption limit of the vapor. (See Fig. 2.) Neither HBr nor CH_3Br shows any fine structure. The
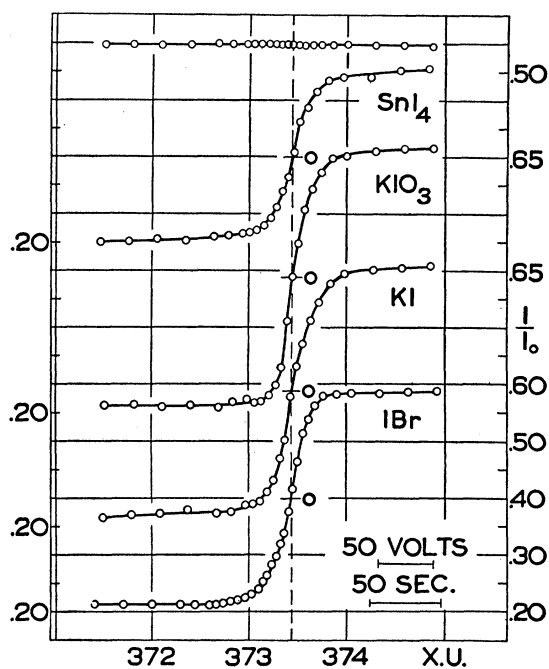

FIG. 5. The absorption limits of IBr, KI, KIO₃, and SnI₄. The broken vertical line shows the position of the absorption limit of iodine vapor. The center of each limit is marked by the letter *O*.

TABLE I. *Width of K absorption limits.*

SUBSTANCE	SECONDS	X.U.	VOLTS
Bromine vapor	24.9±1.0	0.362±0.015	5.3±0.2
Liquid bromine	32 ±3.0	0.46 ±0.04	6.8±0.6
Solid bromine	32 ±3.0	0.46 ±0.04	6.8±0.6
Bromine water	31 ±3.0	0.45 ±0.04	6.6±0.6
HBr	34 ±3.0	0.49 ±0.04	7.2±0.6
CH_3Br	48 ±3.0	0.70 ±0.04	10.2±0.6
KBr (solid)	34 ±3.0	0.49 ±0.04	7.2±0.6
KBr (solution)	33 ±3.0	0.48 ±0.04	7.0±0.6
IBr (solid)	34 ±3.0	0.49 ±0.04	7.2±0.6
IBr (vapor)	27 ±3.0	0.39 ±0.04	5.7±0.6
Solid iodine	35 ±3.0	0.51 ±0.04	45 ±3.9
Iodine vapor	36 ±3.0	0.53 ±0.04	46 ±3.9
CdI_2	26 ±3.0	0.38 ±0.04	34 ±3.9
IBr	31 ±3.0	0.45 ±0.04	40 ±3.9
HgI_2	25 ±3.0	0.37 ±0.04	33 ±3.9
KIO_3	25 ±3.0	0.37 ±0.04	33 ±3.9
SnI_4	30 ±3.0	0.44 ±0.04	39 ±3.9
KI	31 ±3.0	0.45 ±0.04	40 ±3.9

TABLE II. *Displacement of the K absorption limits.*

SUBSTANCE	VOLTS	SUBSTANCE	VOLTS
Bromine vapor	0	CH_3Br	1.3±0.3
Liquid bromine	3.6±0.3	KBr (solid)	4.5±0.3
Solid bromine	3.9±0.3	KBr (solution)	4.2±0.3
Bromine water	1.4±0.3	IBr (solid)	1.7±0.3
HBr	1.2±0.3	IBr (vapor)	1.3±0.3

TABLE III. *Position (in volts) of secondary structure.*

SUBSTANCE	A	α	B
Bromine vapor	2.7	6.6	13.0
KBr (solid)	6.5	13.4	22.4
KBr (solution)	7.5	14.8	21.8
IBr (vapor)	1.7	5.1	11.0
Solid iodine	41	79	103
Iodine vapor	41	75	101

absorption limits of the KBr solution and of the solid are identical within the limits of experimental error. (See Fig. 3.) The vapor IBr is the only one that shows a structure similar to that found for bromine vapor. Solid IBr does not show any structure.

The absorption limit of solid iodine shows a faint structure near the short wave-length side. (See Fig. 4.) The absorption limit of iodine vapor is very nearly the same as that of the solid, both with respect to position and with respect to structure. The compounds of iodine show some indications of fine structure at the base of the edge, but the structure is of the same order of magnitude as the experimental error, hence no attempt was made to investigate it thoroughly.

None of the compounds of iodine investigated shows a measurable shift. Since a shift of two seconds of arc could have been detected, it is concluded that if any shifts are present, they must be less than about 2.5 volts.

Ross[2] has examined iodine with the double crystal spectrometer, employing iodine powder with beeswax binder. For the maxima α and β he obtained 77 volts and 120 volts respectively. The first maximum agrees with the value given in Table III. The second maximum was not resolved in this investigation, probably because the intensity was too low. The value of the uncorrected width reported in this paper is a little lower than the value reported by Ross.[2]

Since the absorption limit of bromine vapor was chosen for reference, the number of bromine vapor curves obtained was large, a total of 36. This accounts for the small probable error shown in Table I. Both the bromine vapor and the solid bromine were examined over a region of about 125 volts on the short wave-length side of the absorption limit. No conclusive evidence of any further structure was found. Stephenson[5] finds a structure in the absorption limit of bromine vapor that is very similar to the one reported here, but he finds slightly smaller values, both for the width of the edge and for the position of the secondary structure. An attempt was made to determine whether the structure found for the vapor disappears at higher temperatures. Data on the absorption limit were taken with the vapor held at 180°C and also with the vapor held at 350°C. No noticeable change in the appearance of the structure was observed. This result is to be expected if it is assumed that the structure should disappear for monatomic bromine, for at these temperatures, less than 0.2 percent of the bromine vapor is dissociated.

Structure of the type found for bromine vapor has been found by Prins[19] in the K absorption limit of nitrogen vapor and in the chlorine L_{III} absorption limit of CCl_4. It has been found by Lindh[13] in the K absorption limit of chlorine. Hanawalt[9] pointed out that polyatomic gases or vapors in general show fluctuations in the absorption coefficient extending to quite a distance from the absorption edge. Coster and

[19] J. A. Prins, Physica 1, 1174 (1934).

Klamer[20] made accurate measurements of this structure for polyatomic gases. They investigated the *K* absorption limits of Ge and As in the vapors $GeCl_4$ and $AsCl_3$. An interpretation of this structure was given by Kronig[21] on the basis of the wave theory of matter. Hartree, Kronig, and Petersen[22] calculated the *K* absorption coefficient of Ge in $GeCl_4$. The positions of maxima and minima agree very well with the calculated values. However, the first maximum of Coster and Klamer's[20] experimental curve corresponds to the third maximum of the theoretical curve. The explanation given was that the first two theoretical maxima and minima were too close together to be resolved by the single crystal x-ray spectrometer, hence they appeared merely as an irregularity in the slope of the first maximum.

The structure found in the absorption edge of bromine vapor may be explained in a similar manner on the basis of Kronig's theory for polyatomic gases. The observed maximum is the same as the first maximum predicted by theory, for it is very readily resolved by the double crystal spectrometer. The following maxima and minima do not appear in the curve because their intensity is relatively small compared to that of the first, smaller than the experimental error. No attempt was made to calculate the position of the structure for bromine vapor. But an estimate was made of the order of magnitude to be expected, by taking the values found by Hartree, Kronig and Petersen[22] for $GeCl_4$, and calculating the values appropriate to the distance between atoms of the bromine molecule, which is given as 2.28 ± 0.06A by Wierl.[23] This could be readily done, for by Kronig's theory, the distances of the corresponding maxima and minima from the edge are inversely proportional to the square of the atomic distances. The values obtained in this manner were: $A = 0.9$ volt, $\alpha = 6.9$ volts, and $B = 12.0$ volts. These values are of the same order of magnitude as those found experimentally for bromine vapor. (See Table III.)

From x-ray diffraction experiments with water and mercury, Danilow[24] was led to the view that the liquid state approximates in arrangement more closely the solid than the gaseous state. A comparison of the curves for the liquid, solid and vapor states of bromine, in Fig. 1, shows that the results of the present investigation support this conclusion. It is seen that the absorption edge of the liquid is nearly similar to that of the solid, but it is different from that of the vapor, both with respect to structure and to the position of the limit. The absence of structure for the liquid and solid may be explained by assuming that the different interatomic distances in the crystalline structure of the solid and in the closely-packed molecular arrangement of the liquid give rise to maxima and minima which overlap and cannot be resolved. The absorption edge of bromine water was investigated to see whether the pronounced structure found for the vapor appeared for the solution. The faint structure found may be explained by assuming the existence, in the bromine water, of a large fraction of undissociated molecules with a gaseous distribution. No noticeable difference was found between the absorption edges of solid KBr and of the solution; the same structure appeared in both edges. Yost[25] found similar results: he found no detectable difference in the *K* absorption of manganous and chromate ions in crystals and in water solutions. The fine structure found in the chromate edge of the solid salts was also observed in the spectra of the solutions.

The absorption limit of solid IBr does not show any structure. It is similar to that of solid bromine, although it is not displaced quite as much as the latter. The absorption limit of the vapor IBr does show a structure of the type found for bromine vapor, but it is less intense. The presence of this structure may be explained by the fact that there is some dissociation of the IBr vapor into iodine vapor and bromine vapor. No fine structure was found by Hanawalt[9] for molecules containing hydrogen, as AsH_3, HBr and HCl. Petersen[26] explains this as due to the

[20] D. Coster and G. H. Klamer, Physica **1**, 889 (1934).
[21] R. de L. Kronig, Zeits. f. Physik **70**, 317 (1931); **75**, 191 (1932); **75**, 468 (1932).
[22] D. R. Hartree, R. de L. Kronig and H. Petersen, Physica **1**, 895 (1934).
[23] R. Wierl, Ann. d. Physik **8**, 521 (1931).

[24] V. Danilow, Acta Physicochimica **3**, 725 (1935).
[25] D. M. Yost, Phil. Mag. **8**, 845 (1929).
[26] H. Petersen, Zeits. f. Physik **76**, 768 (1932); **80**, 258 (1933); **98**, 569 (1936).

fact that the hydrogen atom scatters very little on account of its small nuclear charge. In this investigation, similar results were obtained for HBr and CH_3Br.

Width of edges

Zinn[4] has presented a curve showing that the volt width of the K absorption limit increases as the fourth power of the atomic number for elements above atomic number 32. The values of the widths of the bromine and of the iodine absorption limits obtained in this investigation fit the curve reasonably well, although in each case the value is somewhat lower than that given by the curve. It is reasonable to expect some fluctuations, in the values of the widths, about the values given by the curve, if consideration is given to the type of transition involved in the absorption, for the width of the edge may be considerably influenced by it. Thus, differences will arise between edges in which the absorption is produced mostly by a transition to a single incomplete level, and those in which the transitions are to any one of a large number of optical levels. The absorption edge of elements which possess either an incomplete outer level or an incomplete inner level seems to be produced mostly by transitions to the incomplete level. Thus, it was shown by Barnes[1] that for the elements Mn to Zn, the initial increase in absorption in the K absorption edge occurs at the same wave-length as the K_{β_2} line of the element, within the limits of experimental error. The K_{β_2} lines of these elements are produced by transitions from the inner incomplete level $M_{IV, V}$ to the K level. This seems to indicate that the absorption limit, in this case, is due to a transition from the K level to the incomplete inner level $M_{IV, V}$. Similarly, Sandström[27] has shown that the wave-length position of many absorption limits is the same as that of certain emission lines. For example, the initial increase in absorption in the K absorption limits of the elements Zn to Br occurs at the same wave-lengths as the K_{β_2} lines of the elements. This seems to indicate that the absorption

limit, in this case, is due to a transition from the K level to the incomplete outer level $N_{II, III}$, since the K_{β_2} line is produced by a transition in the reverse direction between the same limits. It appears, then, that an absorption transition to the first incomplete level is more probable than a transition to higher levels of the atom, provided that such a transition is allowed by the selection rules. This allows some latitude to the widths of absorption edges. For in the case where most of the absorption takes place by a transition to an incomplete level, the initial large increase in the absorption is due to such a transition. If the width of the edge is equal to the sum of the widths of the energy levels involved in the transition, then in this case the edge will be relatively narrow, for the K level will supply practically the entire width. This circumstance might explain the narrow width found in bromine. If the width of the edge, measured by the triangle method, were equal to the sum of the widths of the K level and of the combined optical levels, as pointed out by Semat,[7] then the width of the bromine edge should be not less than 12.8 volts, which is the width of the combined optical levels of bromine. Actually, the width of the edge is 5.3 volts. It is thus concluded that the absorption limit represents a transition from the K level to the $N_{II, III}$ level of bromine.

In general, then, it seems that the width of the edge should depend on the type of transition involved in the absorption. If most of the absorption is due to a transition from the K level to the first unoccupied level, the edge will be relatively narrow and its width will be practically the same as the width of the K level. If the transition is from the K level to any one of a large number of optical levels, the width of the edge will be given by the sum of the widths of the K level and of the combined optical levels. The fine structure found in the edge itself, or very close to the edge, is produced by transitions to various permissible unoccupied optical levels, as predicted by Kossel.[28] The secondary structure found at a greater distance from the edge is produced by transitions to crystal lattice levels, as predicted by Kronig's theory.[21]

[27] A. E. Sandström, Nova Acta Regiae Soc. Scient. Upsal., Ser. 4, Vol. 9, No. 11 (1935); Phil. Mag. 22, 497 (1936).

[28] W. Kossel, Zeits. f. Physik 1, 119 (1920).

Effect of chemical combination

Chemical combination seems to have very little effect on the width of the K absorption edge. Most of the compounds of iodine investigated show a width nearly equal to that of the element. The compounds of bromine have very nearly the same width. The only exceptions are the IBr vapor, which has a slightly narrower width, and CH_3Br, which has a larger value for its width. The absorption edge of bromine vapor is the narrowest bromine edge found.

The shift found for HBr, 1.2 volts, compares favorably with that found by Hanawalt,[9] 1.5 volts, using photographic methods. The value of the shift found for CH_3Br, 1.3 volts, agrees with the value found by Stephenson,[5] 1.1 volts. The shift found for KBr, 4.5 volts, is of the same order of magnitude as that found by Hanawalt[9] for AgBr, 4.1 volts. Stephenson[5] finds a lower value for KBr and remarks that the effect of chemical combination on the position of the bromine edge seems to be less than that indicated by Hanawalt's data. Our data support Hanawalt's results.

It was thought desirable to check the effect of the thickness of the screen on the position and width of an absorption edge. Data were obtained on three different screens of solid iodine in which the transmission on the long wave-length side of the edge varied from 0.70 to 0.40. It was found that there is no change either in the position of the absorption limit or in its width, as the thickness of the screen is varied between these limits. Richtmyer and Barnes[3] show that the position and the width of an edge should vary with the thickness of the screen, but for the magnitude of variation of the thickness of the screens used for measurements of absorption limits, the change to be expected is too small to measure.

In conclusion, the writer wishes to thank Professor Bergen Davis for suggesting this problem, and for his interest and advice throughout the course of the investigation.

X-Ray Fluorescence Yields

R. J. STEPHENSON
Ryerson Physical Laboratory, University of Chicago, Chicago, Illinois
(Received February 17, 1937)

The x-ray fluorescence yield for the K shell of atoms has been measured for a number of elements ranging from nickel to tin by an ionization chamber method similar to that developed by A. H. Compton. The results show an increase in the fluorescence yield with atomic number and are compared with those calculated by Massey and Burhop using relativistic wave mechanics and also with those calculated by Burhop from nonrelativistic wave mechanics. The fluorescence yield for the L_{III} shell of lead, thorium and uranium has been determined using suitable exciting radiation. An increase in the yield with atomic number is found.

INTRODUCTION

THE x-ray fluorescence yield, w_K, for the K shell of an assemblage of similar atoms is defined as the ratio of the number of fluorescence K quanta emitted per unit time to the number of atoms ionized in the K shell per unit time. Similar definitions may be applied to any one of the shells of an atom. It might be expected from the simple Bohr atomic theory that every atom ionized in the K shell would necessarily emit a K series quantum of radiation and that therefore this ratio would be unity. However, experiments have shown that this ratio is always less than unity although it increases with increase in the atomic number of the emitting atom. This phenomenon may be explained in either of two ways; first, by assuming that every atom ionized in the K shell emits a K series quantum but that in some of the atoms these quanta are photoelectrically absorbed in the parent atom with the ejection of an electron from an outer shell. The second explanation is