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The *K*-Absorption Edges of Br (35) and Kr (36)*

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The absorption of monochromatic x-rays as a function of the wave-length has been measured for gaseous krypton, bromine and hydrogen bromide in the region of the absorption edges. The data were taken with a double crystal spectrometer with a G-M counter to measure the x-ray intensities. The structure for krypton is considerably different from that previously obtained for argon. The data for Br_2 and HBr are of sufficient accuracy so that they may be used to check the Kronig-Petersen theory quantitatively.

FINE structure on the short wave-length side of the *K*-absorption edge of gaseous absorbers has been found to be of two kinds. The first is typified by argon, in which the structure is produced by transitions from the *K* state to discrete optical states allowed by the selection rules.[1] The second kind of structure is exhibited by polyatomic gases.[2] That the latter structure is a property of the molecule rather than the atom is demonstrated by the fact that the structure completely disappears when light atoms such as hydrogen are substituted for all but the absorbing atom in the molecule.

The present work is a quantitative determination of the shape and fine structure of the *K*-absorption edges of krypton and of bromine in Br_2 and in HBr. In the following paper comparisons are made with theory.

Experimental

The Societé Génevoise double crystal spectrometer has been described in a previous communication.[3] The accessories, with the exception of the intensity recorder, have remained essentially unchanged.

The x-ray intensity was recorded by a Geiger-Mueller counter especially designed for the purpose. The counter briefly described below is suitable for x-rays of wave-length between 0.7 and 2.5A. The cathode was of copper about 10 cm long and with an inside diameter of 2 centimeters. The thin entrance window was of the glass bubble type about 7 microns thick. It was placed at the end of the cathode so that the x-rays traversed the length of the counter and thus had ample chance for absorption. Since the central wire must be supported entirely from one end of the counter, it should be stiff enough to prevent undue sagging. A straight piece of ground tungsten wire 30 mils in diameter was selected and polished with crocus cloth until it was bright and smooth. Since it was not possible because of its large area to use the usual glass bead on the end of the counter wire, the end was merely rounded off carefully by grinding and likewise polished smooth. About one percent of the beam was intercepted by the wire. The rounded end of the central wire was allowed to approach within two or three millimeters of the glass window when the former was sealed into the glass envelope. The forward end of the cathode was kept about a centimeter away from the glass window to eliminate spurious discharges between the cathode and the end of the central wire. The counter was filled to about 45 centimeters of mercury pressure with 99.98 percent pure argon and 12 millimeters pressure of ethyl alcohol vapor.[4] The addition of the alcohol vapor, besides quenching metastable states in the argon gas, lowers the operating voltage of the counter considerably over those in which hydrogen or air is used. The counter operated at 1600 volts with about an 80-volt-wide plateau.

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[1] D. Coster and J. H. van der Tuuk, Zeits. f. Physik **37**, 367 (1926); J. D. Hanawalt, Phys. Rev. **37**, 715 (1931); L. G. Parratt, Phys. Rev. **56**, 295 (1939).

[2] A. E. Lindh, Dissertation, University of Lund, 1923; J. D. Hanawalt, Phys. Rev. **37**, 715 (1931); J. A. Prins, Physica **1**, 1174 (1934); D. Coster and G. H. Klamer, Physica **1**, 889 (1934); S. T. Stephenson, Phys. Rev. **50**, 790 (1936); B. Cioffari, Phys. Rev. **51**, 630 (1937); T. Drynski and R. Smoluchowski, Physica **6**, 929 (1939).

[3] J. A. Bearden and C. H. Shaw, Phys. Rev. **48**, 18 (1935).

[4] A. Trost, Zeits. f. Physik **105**, 399 (1937).

Calculations show that about 80 percent of the radiation at 1.5A is absorbed in the counter. The residual background count was approximately 50 counts per minute. The Getting type of multivibrator,[5] thyratron scale of sixteen[6] and Cenco high impedance impulse counter were used to record the counts. The intensity recorder was linear to one or two percent up to 8000 random counts per minute. The intensities recorded in the present work were far below this—usually not more than 2500 per minute.

The Geiger counter has certain advantages and some disadvantages over the ionization chamber for measuring intensities. Statistical considerations indicate that 10,000 particles must be counted to bring the accuracy to ±1 percent. Actually because of variations in the x-ray output from the tube, about 20,000 are needed. In recording absorption edges the intensity of the continuous spectrum using the double crystal spectrometer is rarely more than 2000 per minute, so that at least 30 minutes aggregate time must be spent for each point—twenty minutes with absorber in and ten minutes with absorber out. Of course, if plenty of intensity is available, this difficulty disappears, especially if a very fast counter and circuit are used.[7]

There are some rather impressive advantages of the counter over the ionization chamber and Pliotron tube. With the Pliotron tube circuit, there are always residual drifts in the base line which may change in magnitude from day to day inexplicably. This is especially true when high sensitivities are used, as is necessary when working with the continuous spectrum. The unsteadiness of the base line seems to always be more than the Brownian motion limit would indicate. This is probably due to variations in the high resistance leak, emission of positive ions from the filament and variations of the batteries. A long period galvanometer is oftentimes used to decrease the wanderings of the galvanometer spot due to statistical variations and alpha-particles from radioactive contamination of the ionization chamber. Sudden large deflections are produced, with a consequent loss of time and temper.

The counter is not subject to these limitations. It is stable and dependable over long periods of time. Since the action of the Geiger counter is a type of "trigger action" the effect of a highly ionizing alpha-particle is exactly the same as a weakly ionizing beta-particle. Both merely produce a count and the circuit has recovered in 10^{-4} second. The counter has been found to be simple in operation and more dependable than the Pliotron and galvanometer for the measurement of small x-ray intensities.

The calcite crystals used on the spectrometer were fairly good. The $(1-1)$ width at half-maximum was 3 or 4 percent wider than that for theoretically perfect crystals in the wavelength region used. Comparisons of $(1+1)$ and $(1-1)$ widths indicated that they were class I[8] crystals.

The absorption chambers were made by blowing a bubble glass window at either end of a glass tube about 15 mm in diameter. The actual length of the gas column was about 7 centimeters. A drop of liquid bromine was introduced into the tube, the end of the tube placed in a dry ice mixture to freeze the bromine, and the tube pumped out and sealed off. The vapor pressure of the bromine gas during the course of the experiment, then, was determined by its temperature. For this reason the ambient temperature was recorded to 0.1°C at short intervals while the absorption data were being taken. A similar cell contained spectroscopically pure krypton to approximately two-thirds atmospheric pressure.

In order to compare the absorption by the bromine molecule with that by the bromine atom the absorption of atomic bromine is required. The dissociation temperature of the bromine molecule is so high that it is not practical to observe the absorption in dissociated bromine gas. The alternative is to use a molecule composed of a bromine atom and another very light atom such as hydrogen. The interaction between the photoelectron ejected from the bromine atom and the hydrogen atom is negligible, so the absorption of this molecule is

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[5] I. A. Getting, Phys. Rev. **53**, 103 (1938).

[6] J. Giarratana, Rev. Sci. Inst. **8**, 390 (1937).

[7] John Strong, *Procedures in Experimental Physics*, p. 270.

[8] L. G. Parratt, Rev. Sci. Inst. **6**, 387 (1935).

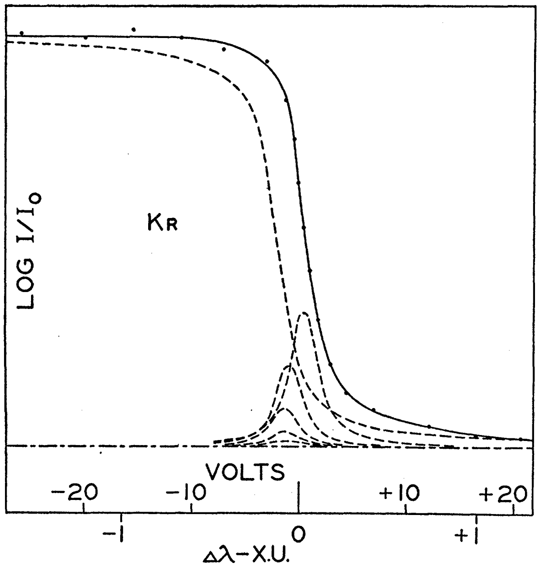

FIG. 1. Absorption in krypton as a function of x-ray wave-length near the absorption edge. The dots are experimental points; the broken lines are main absorption edge and absorption lines.

essentially the same as that of the bromine atom alone. Vapor from heated HBr solution was passed through phosphorus pentoxide, which removed most of the water vapor, and then into a liquid-air trap to which the absorption cell was connected and which had previously been exhausted. When dry ice and alcohol mixture was substituted for the liquid air, the HBr filled the cell, while the water and any Br_2 remained in the trap. The cell was thus filled to about 50 cm pressure with dry HBr.

The absorption cell was mounted on a slide between the crystals of the spectrometer in such a manner that it could be moved in and out of the x-ray beam. Because of the fact that the in-blown glass windows are curved, care was taken that the cell was always introduced into the x-ray beam accurately in the same position. The curvature of the window introduces an uncertainty in the actual length of the absorption path, but this was not serious in the present work, since the absolute values of the absorption coefficients were not of interest.

The procedure in taking data was then to record the number of counts with absorber removed in a two-minute period, the number of counts in four minutes with absorber in the beam. This was repeated four times and an average taken for each point on the curve. In the case of the bromine, the ambient temperature was then read. The whole curve was repeated three times, and parts four times to reduce the random error.

Since the temperature changed slowly from time to time, a correction due to the change in effective thickness of bromine gas was necessary. The absorption in the glass windows was measured. Allowance was made for both these factors in the accompanying plots of log I/I_0 *versus* wave-length.

RESULTS

Krypton

In Fig. 1 is shown a graph of log I/I_0 as a function of the wave-length. For convenience a voltage scale is also included. In contrast with the observations on argon,[9] it is apparent that no Kossel structure is resolved in the case of the krypton edge. However, the fact that the absorption edge is not symmetrical suggests that the structure may be present but washed out. Such washing out for krypton is to be expected when it is considered that the width of the *K* state in energy units is greater for krypton than for argon, and the separation in energy units of the *p* levels is less.

The theory of Richtmyer, Barnes and Ramberg[10] for the shape of an absorption edge unfortunately cannot be applied directly to the present observations. Ideally the arc tangent form of the absorption edge applies to the case where the electron is ejected into a continuum of energy states or into energy states which are close together and whose distribution on an energy scale is uniform. Neither of these conditions is satisfied even approximately for the first few empty *p* levels of krypton.

For energies of the ejected electron greater than that of the *K*-ionization potential, there is a continuum of energy states and the R.B.R. theory may be applied. A very rough estimate of the *K*-level width may be obtained in the usual way by measuring the width between $\frac{1}{4}$ and $\frac{3}{4}$ of the height of the limit. Such a measurement gives 2.07 volts, corrected for the resolving power of the crystals.[8] In dealing with problems

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[9] L. G. Parratt, Phys. Rev. **56**, 295 (1939).

[10] Richtmyer, Barnes and Ramberg, Phys. Rev. **46**, 843 (1934).

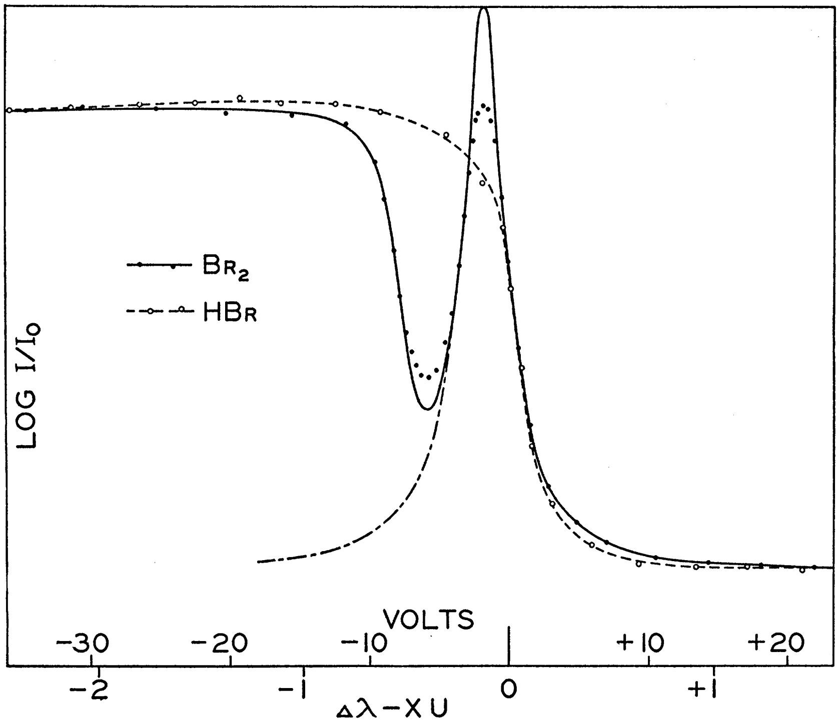

FIG. 2. Absorption in bromine gas (solid line) and HBr (broken line) near the absorption limit. Experimental points are indicated. The line — — — — — is the mirror image of the initial absorption edge used in correcting for the finite resolving power of the spectrometer.

of the present kind, it is convenient to make a distinction between the *initial* absorption edge as observed, in which absorption takes place to the first empty states allowed by the selection rules, and the *main* absorption edge, in which absorption takes place into a continuum of energy levels. This distinction has less meaning in the case of solids—particularly metals.

The position of the main absorption edge for krypton may be located approximately by adding the energy difference between the 5*p* level and the series limit for rubidium[11] (atomic number 37) to the energy corresponding to the position of the initial absorption edge. The unpredictable influence of the *K*-level width will make the position uncertain to perhaps half a volt.

The analysis into the component absorption lines can be done in the present case with only an indifferent degree of accuracy. Such a "reasonable" resolution into components is shown in the figure. In drawing the curves it was assumed that the intensity of the components would continually decrease as the main absorption edge is approached. Perhaps the most noteworthy feature is the difference in intensity of the first absorption line as compared to that for argon.[9]

Bromine

The two curves shown in Fig. 2 are for absorption in Br_2 and in HBr. The dots represent the experimental data. The solid line is the Br_2 curve as corrected for the resolving power of the crystals.[8] The most striking feature is the single sharp and intense region of high transmission to the high frequency side of the initial absorption edge for Br_2. The energy separation of this minimum from the absorption edge (the "position of the absorption edge" is here taken to be that of the inflection point in the initial absorption edge) is approximately 5.9 volts. The Kossel structure is completely washed out by the large width of the *K* state.

The previous observations by Cioffari[12] have indicated that the structure for Br_2 is limited to

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[11] Bacher and Goudsmit, *Atomic Energy States*, p. 377.

[12] B. Cioffari, Phys. Rev. **51**, 630 (1937).

the one band of transmission and that within the limits of accuracy of the experiment there was no structure further from the edge. The present results show that the intensity of any remaining structure less than 50 volts from the initial absorption edge is not greater than 2 percent of the first absorption minimum.

This result is in sharp contrast with those of Coster and Klamer on $GeCl_4$.[13] Here several maxima and minima were observed of gradually decreasing intensity on the high frequency side of the initial absorption edge. As shown in the succeeding paper, the best theory[14] at the present time indicates that several maxima and minima should likewise be observed for bromine. As there suggested, some of the washing out may be due to molecular vibrations and the consequent variation of the interatomic distance. However, the calculations indicate that only part of the effect may be due to this factor. Since the Hartree fields and scattering phases have not been worked out for bromine, it was necessary to use those for krypton.[15] The several approximations and omissions from the theory including the above one introduce rather serious uncertainties, so the form of the theoretical intensity curve is subject to revision when these corrections are finally applied. For this reason the comparison with theory of such secondary characteristics as the width of the transmission band is meaningless.

The author wishes to express his appreciation to Professor J. A. Bearden for his interest during the progress of the work and his cooperation in the development of the Geiger counter.

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[13] D. Coster and G. H. Klamer, Physica **1**, 889 (1934).

[14] H. Petersen, Zeits. f. Physik **80**, 258 (1933).

[15] J. Holtsmark, Zeits. f. Physik **66**, 49 (1930).

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The Fine Structure of the X-Ray Absorption Limits of Bromine and Chlorine*

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The ratio of the absorption coefficient of the bromine atom in Br_2 to that in HBr for monochromatic x-rays is calculated as a function of the x-ray wave-length in the region of the K-absorption edge according to the theory as given by Petersen. A predicted minimum at about 5.9 volts on the high frequency side of the absorption edge agrees satisfactorily with the experimental findings in position but not in intensity. A predicted broad maximum at about 15 volts from the absorption edge is not found experimentally. The structure for chlorine is recalculated from the Hartree self-consistent field for the chlorine atom and is compared with previous photographic measurements.

X-RAY absorption by an atom takes place when a deep-lying electron can be lifted past all the filled atomic levels into either an unoccupied discrete level or completely outside the atom into the continuum. As a result the x-ray absorption coefficient as a function of the frequency rises initially with a series of absorption lines extending to higher energies which converge to a series limit in a few volts. Absorption to still higher frequencies is continuous. Argon[1] and krypton[2] are excellent examples of this type of absorption.

In polyatomic gases, on the other hand, structure is found which extends for a distance of several hundred volts on the high frequency side of the absorption threshold. The explanation of this phenomenon was given by Kronig,[3] who called attention to the important rôle played by the ejected photoelectron because of its scattering by the partner atoms in the molecule.

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* This research was supported by a grant-in-aid made to Professor J. A. Bearden from the Penrose Fund of the American Philosophical Society.

[1] L. G. Parratt, Phys. Rev. **56**, 295 (1939).

[2] C. H. Shaw, preceding paper.

[3] R. de L. Kronig, Zeits. f. Physik **75**, 468 (1932).