APRIL 1 AND 15, 1942 PHYSICAL REVIEW VOLUME 61

The *K*-Absorption Edges of Metal Ions in Aqueous Solution*

W. W. BEEMAN, *Department of Physics, University of Wisconsin, Madison, Wisconsin*
AND
J. A. BEARDEN, *The Johns Hopkins University, Baltimore, Maryland*

(Received January 29, 1942)

The x-ray *K*-absorption edges of Ni^{++}, Cu^{++}, Zn^{++}, $Cu(NH_3)_4^{++}$ and $Cu_2(CN)_4^{--}$ in aqueous solution have been measured with a double crystal spectrometer. Ni^{++}, Cu^{++}, and Zn^{++} have similar edges. Each consists of two absorption maxima which arise from the excitation of *K* electrons into the empty 4*p* and 5*p* levels of the ion. The final levels are broadened by the fields of the coordinated water molecules. Quite different edge structures were found in the complex ions. They probably arise from the scattering of the photoelectron by the other atoms of the ion, the same process which takes place in polyatomic gases.

VERY little has been published on the x-ray absorption edges of dissolved substances. The reason for this fact appears to lie in the complexity and disorder of liquid structure which make impossible any interpretation of the experimental results unless structure very close to the main absorption edge can be resolved. In the latter region, as the present research shows, simple explanations can be given because the absorption structure is determined by final states in which the excited electron remains bound to the parent ion. Most of the earlier work[1] has been done with single crystal spectrometers incapable of resolving the interesting structure close to the absorption edge.

The only previous double crystal measurements are those of Cioffari[2] on the Br *K* edge in bromine water and in a solution of KBr. He was not primarily concerned with solutions, however, and indeed found only slight differences between the above edges and those of liquid bromine and solid KBr, respectively.

EXPERIMENTAL

The double crystal spectrometer used in this research and the technique of taking readings have been completely described in previous publications.[3-5]

In work with solutions some complications are introduced by the absorption of the solvent. In one mm of H_2O at the wave-length of the Cu *K* edge, this amounts to half the incident intensity. Absorption cells are thus limited to a thickness of one or two mm. At the same time there must be enough of the absorbing ion present to give good edge contrast, therefore very dilute solutions may not be used. Most of the present work was done with 1.0 normal solutions and measurements could probably be extended to 0.1 normal without too great difficulty. We made tests with 0.5 and 1.0 normal solutions of $CuSO_4 \cdot 5H_2O$ and found no dependence of the absorption edge on concentration.

The absorption cell was made by drilling a 1-cm diameter hole through the center of a brass plate 1 mm thick and about 4 cm square. Both Cellophane and mica proved satisfactory as entrance and exit windows, the mica rather more so, as it is stiffer and gives a cell of uniform thickness. Cellophane will sometimes bulge out when the cell is filled. The windows were almost as large as the brass plate and were easily attached to its faces with a low melting paraffin. The paraffin also prevented contact between the brass and the solution. Before attaching the windows, the plate was cut with a hacksaw from the outside to the center. The completed cell was filled through this opening with a thin drawn glass tube.

We measured the Cu^{++} edge in each of three solutions, $CuSO_4 \cdot 5H_2O$, $Cu(NO_3)_2 \cdot 6H_2O$, and $CuCl_2 \cdot 2H_2O$ with identical results, indicating that the dissociation was almost complete in each

---

* This research was supported by a grant made to one of the authors (J. A. B.) by the American Philosophical Society.

[1] B. B. Ray, S. R. Das, and N. Bagchi, Ind. J. Phys. **14**, 37 (1940); N. Bagchi, Ind. J. Phys. **14**, 61 (1940).

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

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

[4] W. W. Beeman and H. Friedman, Phys. Rev. **56**, 392 (1939).

[5] C. H. Shaw, Phys. Rev. **57**, 877 (1940).

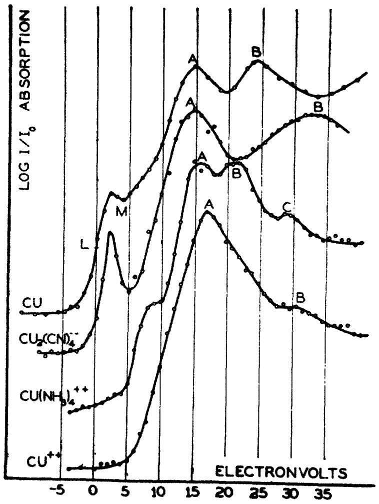

FIG. 1. K-absorption edges of Cu^{++}, $Cu(NH_3)_4{}^{++}$, $Cu_2(CN)_4{}^{--}$, and Cu metal, the latter taken from reference 4.

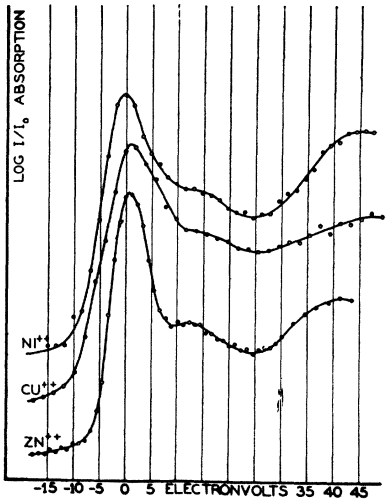

FIG. 2. K-absorption edges of Ni^{++}, Cu^{++}, and Zn^{++}.

solution. $Cu(NH_3)_4{}^{++}$ was measured in an ammoniacal solution of $CuSO_4 \cdot 5H_2O$ and $Cu_2(CN)_4{}^{--}$ in a solution of $Cu(CN)_2$ in KCN. Zn^{++} and Ni^{++} were both observed in solutions of the sulphates. All were approximately normal solutions of the absorbing ion. The absorption edges are shown in Figs. 1 and 2. The Cu curve of Fig. 1 is reproduced from reference 4. The four curves of Fig. 1 are on the same frequency scale so that shifts of structure from one curve to the next are accurately portrayed.

DISCUSSION

The K-absorption edges of metallic Ni, Cu, and Zn have been measured[4] and the structure qualitatively explained on the basis of the electron bands to be expected for these solids. Band calculations[6, 7] were available only for Cu, and in this case good quantitative agreement was found between the observed maxima and minima of absorption and the calculated density of states curve. In particular, point L on the Cu curve of Fig. 1 gives the energy necessary to excite the K electron into the first empty level at the top of the Fermi distribution, the minimum of absorption at M is due to the small overlap of the $4s$ and $4p$ bands, and the maximum at A to absorption into a high density of states in the $4p$ band.

The absorption edge structure of the ions could also be explained if the energy distribution of final states and the transition probabilities to these states were known. Only for the atomic ions does this appear feasible without detailed calculation. Here the great similarity of the Ni^{++}, Cu^{++}, and Zn^{++} edges and the presence in each of two absorption maxima some 14 to 16 ev apart suggest the hypothesis that the ions are absorbing about as they would in vacuum and that the structure is due to excitation of the K electron into the optical levels of the ion. The transitions allowed by the selection rules are to the various p orbits beginning with $4p$. In Table I we have compared the observed structure and that predicted on the above hypothesis. The optical $4p-5p$ separations in the first column are for the ion of next higher atomic number. The data were taken from Bacher and Goudsmit, *Atomic Energy States*, and a paper by K. C. Mazumder[8] on the Zn III spectrum. The slight uncertainty in the optical separations is due to the splitting of the terms entering into the $4p$ and $5p$ configurations. Not enough of the higher Cu III terms are known to permit any predictions for Ni^{++}.

The observed absorption peak separations are somewhat poorly defined because of the broadness of the second absorption maximum. An attempt has been made to locate its center to within 1 or 2 ev. This is, however, not a matter of great importance, as exact agreement between

---

[6] H. Krutter, Phys. Rev. **48**, 664 (1935).

[7] E. Rudberg and J. C. Slater, Phys. Rev. **50**, 150 (1936).

[8] K. C. Mazumder, Ind. J. Phys. **10**, 171 (1936).

the observed and predicted separations cannot be expected for the following reason. We have resolved only two absorption maxima. Therefore the second one must contain contributions not only from the $1s-5p$ transition but also from transitions to $6p$, $7p$ and higher levels. The latter will shift the center of the absorption line to higher frequencies, and the observed separation will be greater than the predicted. The magnitude of this shift is hard to estimate, since it depends not only upon the separations of successive absorption lines but also upon their relative intensities. Very rough extrapolations from the spectra of similar but less highly ionized atoms indicate that $6p$ is about 4 ev above $5p$ and $7p$ about 2 ev above $6p$ for Ni^{++}, Cu^{++}, and Zn^{++}. The intensity of absorption falls off rapidly with increasing total quantum number. In argon, intensity ratios of about 4 : 2 : 1 have been found[9] for the $5p$, $6p$, and $7p$ absorption lines. If we take an average of the positions of these three lines weighting them in the above ratios, it is found that the average lies 2.5 ev above the $5p$ position. This agrees nicely with the data of Table I, where the observed $A-B$ separations are 2 or 3 ev greater than the optical $4p-5p$ separations.

Parratt has recently investigated the K-absorption spectrum of argon gas[9] which is of the simple type postulated for the ions. Because of the greater wave-length, he obtained somewhat greater energy resolving power and was able to separate three absorption maxima. They agreed perfectly with the optical terms of potassium.

A second, and quantitatively more satisfactory, comparison can be made between the observed structure and that predicted on the above hypothesis that the ions are absorbing as if they were in a vacuum. From the curves of reference 4 and the present data we can determine the shift from point L of the metal edge (indicating absorption into the first empty level at the top of the Fermi distribution) to point A of the corresponding ion absorption edge. This quantity can also be calculated from optical data with the help of the following cycle, if we assume, of course, that absorption maximum A is caused by a transition to the $4p$ level of the ion. The cycle will be illustrated for copper.

1. Remove a Cu atom from the Cu lattice and use the binding energy S_{Cu}.
2. Remove two outer electrons from the Cu atom and use energy corresponding to the first two ionization potentials of Cu.
3. Excite a $1s$ electron of Cu^{++} to the $4p$ orbit of Zn^{++} by using the energy $h\nu_{\mathrm{ion}}$.
4. Return this electron to the $3d$ orbit, and obtain the energy difference $3d^9\,4p-3d^{10}$ of Zn^{++}.
5. Return two electrons to Zn^{++}, and obtain the energy corresponding to the first two ionization potentials of Zn.
6. Place the zinc-like atom at the vacant Cu lattice point and obtain the binding energy S_{Zn}.
7. Allow an electron at the top of the Fermi distribution to return to the K shell of the zinc-like atom and thus obtain the energy $h\nu_{\mathrm{metal}}$ and return the system to its original condition.

This cycle gives the energy equation:

$$h\nu_{\mathrm{ion}}-h\nu_{\mathrm{metal}}=(17.2\pm0.6\ \mathrm{ev})+(S_{\mathrm{Zn}}-S_{\mathrm{Cu}}).$$

All the optical terms involved are summed in the first parenthesis. They were taken from Bacher and Goudsmit. The second parenthesis is the difference between the binding energy of a zinc atom and a copper atom in the copper lattice. It is difficult to estimate accurately the magnitude of this term. However, it can be shown that it is less numerically than the difference between the lattice energy per atom of pure Zn and pure Cu unless the heat of formation of a low zinc brass is negative. Actually the heats of formation of the brasses are positive[10] so we may say that the term in parentheses is numerically less than the approximately 2.0 ev per atom difference in the binding energy of pure Cu and pure Zn. It might, of course, be considerably less depending upon the actual value of the heat of formation. The corresponding term in the cycle for Ni^{++} is probably less than 1.0 ev since Ni and Cu have the same lattice energy to within this amount.

We have evaluated the edge shift for Ni^{++} and Zn^{++} using the same cycle and collected the data

TABLE I.

Edge	$4p-5p$ separation from optical data	Observed $A-B$ separation
Ni^{++}		15–16 ev
Cu^{++}	10.9–12.6 ev	14–16 ev
Zn^{++}	11.8–12.1 ev	13.5–14.5 ev

---

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

[10] W. Biltz, Zeits. f. Metallkunde **29**, 73 (1937).

TABLE II.

Edges	*L* to *A* shift Calculated from optical data	Observed
Ni-Ni^{++}	17.7–18.2 ev	17.9 ev
Cu-Cu^{++}	16.6–17.9 ev	16.7 ev
Zn-Zn^{++}	7.3– 7.5 ev	8.7 ev

in Table II. In each case the term in the second parenthesis has been omitted from the energy equation, since it is likely that the mistake thus made is less than the experimental accuracy of about 1.0 ev. Some of the terms of Cu^{++} were taken from a paper of L. Bloch and E. Bloch.[11] The numerical agreement between the observed and calculated separations is seen to be quite good, and there can be but little doubt that the correct transitions have been assigned to the two absorption maxima in the ion edges.

The great difference between the optical levels in metals and in solution, then, appears to be that a transition to the *sd* band is allowed in metals, but a transition to the corresponding *s* and *d* states is not allowed in solutions. This is understandable since the exchange of electrons between atoms in metals destroys the meaning of the angular momentum quantum number while the Stark effect and other non-exchange forces exerted on the metal ion by the associated water molecules in solution do not, leaving the *l*-selection rules in force as in free atoms.

Although the positions of the absorption maxima are not affected by the solvent, the absorption lines are broadened considerably. Earlier work with the same instrument indicates that a transition to a sharp optical level should give an absorption line 2 or 3 ev wide at half maximum at these wave-lengths. This width is partly instrumental and partly due to the short lifetime of the excited state. The first absorption maxima of the atomic ions of Fig. 2 are very much broader. It is not possible to define accurately their half maximum width, since the lines are not symmetric, but a minimum value may be found by measuring, at half maximum intensity, the distance from the center of the line to its low frequency side and then doubling the result to get the half maximum width. Calculating in this way, one finds widths of 11.5 ev for Ni^{++}, 13 ev for Cu^{++}, and 8 ev for Zn^{++}. These widths are not caused by any contributions from the tails of the $1s-5p$, or higher absorption lines, since the $4p-5p$ separation is about 11 or 12 ev, three or four times the half maximum width predicted for sharp optical levels. Neglecting the influence of the coordinated water, one might put an upper limit of 4.5 ev on the line width for the $1s-4p$ transition, since in Ni^{++} and Cu^{++} the $4p$ level splits about 1.5 ev because of interaction with the unfilled $3d$ shell. The difference between 4.5 ev and the observed widths must be due to the fields of water molecules. Six molecules are attached permanently[12] to each atomic ion and they subject the ion to a perturbing field of cubic symmetry. This field causes an over-all splitting of the ground states of ions having an unfilled $3d$ shell (amounting to about 2.0 ev).[13] Probably the fact that Zn^{++} has a filled $3d$ shell while Ni^{++} and Cu^{++} do not, explains the narrower $4p$ absorption line of the former, although nothing very quantitative can be said.

The edge structure of $Cu_2(CN)_4^{--}$ seems to be of the same type as that found in polyatomic molecules, the theory of which has been given by R. de L. Kronig.[14] Evidence for this view is furnished by the shape of the initial absorption line (at 2.0 ev in Fig. 1) of the $Cu_2(CN)_4^{--}$ edge. The line fits accurately an inverse square curve, indicating that the absorption is into final states occupying an energy range small compared to the width of the *K* state plus crystals. Similar initial absorption lines are observed in the edges of most polyatomic molecules. The final states involved are states of positive energy, since the molecule or complex ion is not generally stable after the absorption.

The case for $Cu(NH_3)_4^{++}$ is not so convincing, as there are no sharp absorption lines. This result may be related to the fact that the binding in $Cu_2(CN)_4^{--}$ and in the polyatomic molecules which have been investigated is largely homopolar while the binding of the NH_3 groups to the Cu^{++} is largely ionic.

---

[11] L. Bloch and E. Bloch, Comptes rendus **200**, 2017 (1935).

[12] J. D. Bernal and R. H. Fowler, J. Chem. Phys. **1**, 515 (1933).

[13] W. G. Penney, Trans. Faraday Soc. **36**, 627 (1940).

[14] For a simplified explanation of the theory and references to the original work, see T. M. Snyder and C. H. Shaw, Phys. Rev. **57**, 881 (1940).