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The K X-Ray Absorption Structure of Cl_2 and HCl

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The fine structure on the short wavelength side of the K x-ray absorption edge of chlorine in Cl_2 and in HCl has been measured with a vacuum double crystal spectrometer using Geiger counter registration. Pronounced structure was obtained which agreed well with structure previously detected using lower resolution and photographic registration. However, the structure does not agree with the theory. Some reasons for the discrepancy in terms of the optical levels and the different types of binding in the two cases are discussed.

INTRODUCTION

THERE is a fine structure to be observed on the short wavelength side of the x-ray absorption edges of certain gases. For monatomic gases and vapors this structure is limited to a region within the ionization potential of the atom of next higher atomic number and is brought about when an electron, removed from some inner shell in the absorption process, goes into one of the optical levels for a final state. For molecular gases and vapors one finds, however, an extended fine structure which may reach out several hundred volts on the short wavelength side of the edge and which can be ascribed to final energy states characteristic of the molecule caused by the scattering of the ejected electron by the neighboring atom or atoms in the molecule.

The best known polyatomic molecule from an extended fine structure point of view is $GeCl_4$. The theory for this molecule has been worked out[1-3] and measurements have been made both by photographic[4,5] and by double crystal spectrometer[6-8] methods. The double crystal method with its greater resolution brought out certain discrepancies between theory and experiment both as to position and intensity of the structure near the edge. Now it would seem that the best chance of obtaining agreement between theory and experiment in extended fine structure would come for the simplest possible case for which such extended structure is expected, namely, the case of the diatomic molecule; for this purpose, bromine and chlorine offer the best possibilities. The K absorption edge of Br_2 and the region adjacent to it on the short wavelength side have been studied thoroughly and with high resolution.[9-11] It may be regarded as well established that there is a very pronounced absorption minimum on the high energy side of the edge extending from about 2 volts to 12 volts with the actual minimum about 5–6 volts from the edge. There is no structure of magnitude greater than experimental error at distances further from the edge. The theory of secondary fine structure as applied to this particular molecule[12] gives the position of the first minimum of the absorption coefficient with acceptable accuracy but predicts this structure to be less pronounced than is actually the experimental case. The theory also predicts structure still further from the edge which is not observed at all. One reason for the lack of agreement may be that the scattering fields and phases have not been worked out in detail for bromine, hence approximate expressions derived from krypton were used in the calculations.

The most accurate application of the theory should be in the case of chlorine for which the fields and phases have been worked out[2] in detail. However, predictions concerning the structure[12,13] do not agree with the only experimental work on Cl_2.[14] Since the experiments were carried out with a photographic spectrograph of only 18 cm radius, the resolution was not as great as one would hope for. Therefore, it was thought worthwhile to study the K absorption edge of Cl_2 using a vacuum double crystal Geiger counter spectrometer to insure high resolution, thus rendering feasible an accurate and independent comparison between theory and experiment for the simplest possible case yet worked out in detail. Furthermore, Geiger counter registration should yield more accurate data on intensity relationships than photographic registration. In addition another question was raised by the observation that HCl[14] has a pronounced secondary structure. Other observers have failed to find such structure for HBr[10,11] and Peterson[12] has suggested that hydrogen is too low in atomic number to scatter the electron wave sufficiently to cause a structure in molecules such as HCl and HBr. Therefore, the present paper presents also a double crystal study of the Cl K-edge in HCl.

EXPERIMENTAL

The vacuum double crystal instrument and associated equipment have already been described in some detail.[15]

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[1] R. de L. Kronig, Z. Physik **75**, 468 (1932).

[2] Hartee, Kronig, and Peterson, Physica **1**, 895 (1934).

[3] E. M. Corson, Phys. Rev. **70**, 645 (1946).

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

[5] T. Drynski and R. Smoluchowski, Physica **6**, 929 (1939).

[6] C. H. Shaw, Phys. Rev. **70**, 643 (1946).

[7] S. T. Stephenson, Phys. Rev. **71**, 84 (1947).

[8] H. Glaser, Phys. Rev. **82**, 616 (1951).

[9] S. T. Stephenson, Phys. Rev. **50**, 790 (1936).

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

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

[12] T. M. Snyder and C. H. Shaw, Phys. Rev. **57**, 881 (1940).

[13] H. Peterson, Z. Physik **80**, 258 (1933); **76**, 768 (1932).

[14] A. E. Lindh and A. Nilsson, Arkiv. Mat, Astron. Fysik, **29A** 27, 1 (1943).

[15] S. T. Stephenson and F. W. Mason, Phys. Rev. **75**, 1711 (1949).

The double crystal arrangement is of the Ross[16] type using calcite crystals whose faces had been lightly etched with HCl. These crystals gave a $(1, -1)$ rocking curve having a full width at half-maximum of 50 seconds at the wavelength of the chlorine *K*-edge. The scales on crystal *B* do not allow absolute determinations of wavelength but relative settings may be made to 10 seconds of arc. X-ray intensities were measured with a Geiger counter having a Cellophane covered window; the counters were filled with neon to 9 cm pressure and with 1 cm of alcohol vapor. The counting rates varied from 23 counts per second on the low absorption side to 9 counts per second on the high absorption side including a natural count of 0.8 count per second. From 5000 to 10,000 counts were taken at each point in a run and three different runs were made on Cl_2 and three on HCl in the final studies.

Many preliminary runs were made while testing absorption cells and using gases of different degrees of purity. The cells finally used were glass bubbles blown out as thin as could be done without collapsing mechanically and having a diameter of 4 to 5 cm. These bubbles were fastened to an all glass system using three stopcocks in such a way that the bubble could be pumped down with the spectrometer system and then sealed off from the bell jar. The gas was then admitted from a glass vessel previously filled with Cl_2 or HCl, the relative volumes of the vessel and the bubble having been calculated so that the final pressure in the bubble was about 10 cm. The bubbles would withstand this pressure indefinitely but, of course, shattered immediately if for any reason, in preparation, the pressure outside the bubble exceeded that inside. The gases were taken from cylinders freshly obtained from The Matheson Company and having a purity of 99.8 percent. These gases were entirely satisfactory. One has to be particularly careful about HCl as an impurity in Cl_2. In the runs on Cl_2 the increase of an HCl impurity could be noted after several hours of operation, and this was ascribed to reaction of the Cl_2 with residual water vapor on the walls of the glass container and with the grease on the three small bore stopcocks which were used. Blank runs of the background were made without any gas in the glass bubble.

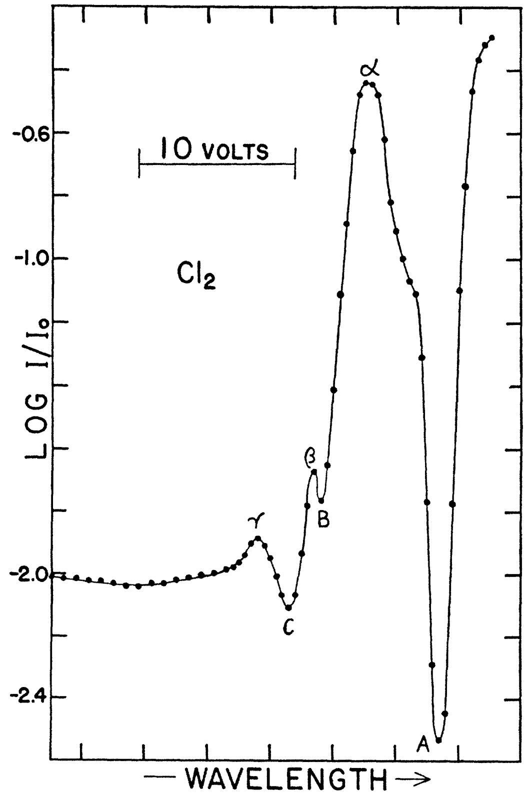

FIG. 1. *K* x-ray absorption edge of chlorine in Cl_2.

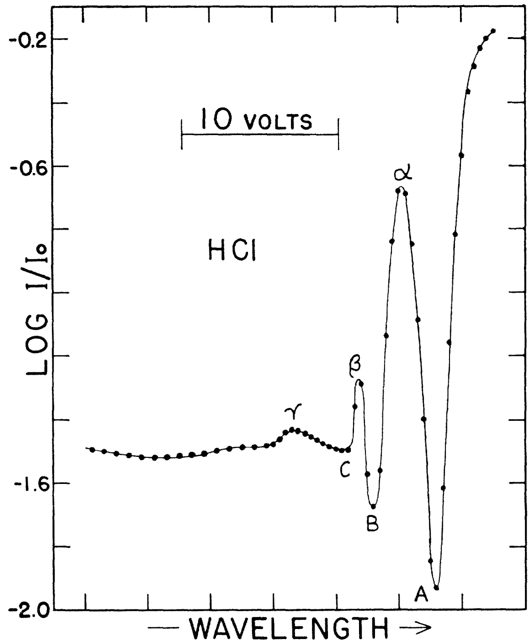

FIG. 2. *K* x-ray absorption edge of chlorine in HCl.

The x-ray tube was operated at 5.5 kv and 250 ma. The target was a tungsten button in a hollow copper block through which the cooling water circulated. In order to prevent reflected electrons from passing out of the x-ray tube into the bell jar, the hole in the x-ray tube was covered by a grid fastened electrically to the cathode support. The power supply, pumping system and other details are as previously described[15] except that the glass bell jar has been replaced with a steel bell jar.

RESULTS

A typical individual run over Cl_2 is shown in Fig. 1, and a typical run for HCl is given in Fig. 2. The structure feature in Cl_2 between *A* and *α* comes at the same position as the main *K*-edge of HCl. This feature became more and more pronounced as long as the Cl_2 was left

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[16] P. A. Ross, Rev. Sci. Instr. 3, 253 (1932).

TABLE I. Energy separations in volts of fine structure maxima and minima as measured from the point of inflection of the main edge.

	Cl_2				HCl	
Structure	Present work	Previous experiment[a]	Theory[b,c]		Present work	Previous experiment[a]
A	1.2	1.1	3.5		0.8	1.1
α	6.0	5.1	12	6.5	3.0	3.1
B	8.6	8.3	17	13	4.8	4.8
β	9.2	9.0		23	5.8	5.7
C	10.6	10.6			6.6	
γ	13.2				10.0	

[a] See reference 14. [b] See reference 12. [c] See reference 13.

in the cell but practically disappeared upon admitting fresh Cl_2. It was, therefore, ascribed to an increase of HCl in the cell as mentioned above; similar effects of HCl impurity are described by Lindh.[14] The feature α comes at the same absolute wavelength for both HCl and Cl_2 within the experimental error of perhaps 0.5 volt and the features B, β, C, γ, and D are at the same absolute position within a volt. The center of the main K-edge (defined for the purposes of this article as the point of inflection of the edge of longest wavelength) for HCl was shifted $3.0^{\pm 0.5}$ volts to a shorter wavelength than the Cl_2 K-edge. Lindh's[14] value for the shift was 2.6 volts.

The distances in volts from the center of the main edge of the structure observed are presented in Table I together with other experimental results and theoretical predictions.

DISCUSSION

It is apparent at once after inspecting Table I that the present experimental results with a double crystal x-ray spectrometer and Geiger counter registration are in excellent agreement with the single crystal results using photographic registration, although comparison of Figs. 1 and 2 with Lindh's[14] work indicates that the double crystal spectrometer gives better resolution. It is also apparent that there is no agreement between theory and experiment.

The situation from the standpoint of theory within 10 to 15 volts of the main K-edge is really quite complicated in the case of a molecule as can be seen from the following considerations: 1. Certainly the atomic optical levels are important in this region giving rise to a structure which, in the case of monatomic gases, can be related to the optical levels of the atom of atomic number one greater. Thus argon[17] shows a structure characteristic of the atomic levels; however, krypton[11] does not show such a structure because of the increased width of the K level, the closeness of the optical levels one to another, and the poorer energy resolution obtainable in this wavelength region. 2. In a molecule the atomic optical levels are changed by the presence of the other atom or atoms in the molecule; just what these changes are would be very difficult to calculate. No doubt the effect of the H atom in HCl which is chiefly heteropolar in character would be quite different from the effect of a Cl atom in Cl_2 which is homopolar. 3. At some energy, which should really characterize the series limit for the molecular-atomic optical levels, the electrons become essentially free, and for this and larger energies scattering of the ejected electron by the neighboring atom or atoms becomes the main consideration in the calculation of extended structure. But the position of this series limit is not readily calculable as indicated under 2.

HCl (Fig. 2) shows a pronounced structure, and yet one supposes that any scattering of the ejected electron by the H atom would be so small as to give rise to no extended structure from this source. Consequently all the structure must be ascribed to atomic levels essentially like those of argon but modified by the presence of the H atom. A comparison of the structure with the known optical atomic energy states of argon shows no detailed agreement, so the presence of the H atom must cause considerable modification. During the course of a private conversation on this topic, Parratt pointed out that if the structure close to the edge, as obtained in HCl, is characteristic of the chlorine ion rather than the molecule, it might bear some relation to the close-in structure of the chlorine ion in KCl.[18] A comparison does in fact show remarkable agreement for the features A, α, B, β, and C as though these features may be characteristic of the Cl ion from which a K electron is being lifted. At first it appears surprising that HBr[10,11] yielded no structure similar to HCl but it is probable that the reasons are the same as those which caused Kr to show no structure although A does.

In the case of Cl_2 one supposes that the scattering of the ejected electron by the Cl atom would give rise to a structure. However, close to the edge this structure will be complicated by atomic optical levels modified by homopolar binding with the other Cl atom. Thus the position of the absorption maxima and minima with respect to the initial increase in absorption is quite different in the two cases HCl and Cl_2 because of the different types of binding. It is quite pertinent to note that the pronounced A, α, for Cl_2 are very similar to the pronounced A, α reported for Br_2,[9-11] and for N_2[19] and consequently that the pronounced absorption maximum A and minimum α may be characteristic of diatomic homopolar molecules. Out beyond 15 volts from the edge, where one could suppose that electron scattering is the only factor giving rise to an extended structure, there is no structure pronounced enough to be measured, although fluctuation of the absorption coefficient great enough to be detected is predicted by the theory.

CONCLUSION

Both Cl_2 and HCl yield a pronounced fine structure close to the edge, for which earlier measurements with

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

[18] J. W. Trischka, Phys. Rev. 67, 318 (1945).

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

photographic registration have been checked with higher resolution and Geiger counter registration of intensities. This structure is all so close to the edge as to be affected by, if not governed entirely by, atomic optical levels modified by heteropolar (HCl) and homopolar (Cl_2) binding. Extended structure solely dependent upon electron scattering was not observed.

There is no agreement between theory and experiment in the case of Cl_2 for which the best chance of checking theory and experiment is expected. This serves to point up other discrepancies cited in the Introduction and to indicate that the theory of the structure to be found for absorption in molecular gases, within several tens of volts immediately on the short wavelength side of the main edge, is unsatisfactory.

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A Note on the Propagation of Excitation in an Idealized Crystal*†

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It is shown that, in insulators, overlapping of the electronic wave functions of near-by crystal constituents is not necessary for effective transfer of excitation energy by the "exciton" mechanism. The electromagnetic interaction of the "virtual" dipoles of the transition is sufficient to give rise to such transfer characterized in cubic crystals by a wave number **k**, and an anisotropic effective mass, given in order of magnitude by the ratio electronic mass/oscillator strength of transition. Implications and limitations of the calculation are discussed.

I. INTRODUCTION

During the past year, a basic advance has been made in the understanding of the processes of migration of energy in ionic crystals,[1] through the experimental work of Apker and Taft. Although these workers dealt with photoelectric emission, an inescapable conclusion from their results is that part of the emitted electrons derive their energy only by some intermediate transfer process from the energy of the incident photons. Since the energy distribution of this group of electrons (called the *S*-group by Apker and Taft) does not display the characteristics one would expect if the electrons were directly released by absorption of light, one is led to the hypothesis that, in an intermediate stage, the energy is carried by what have been called "excitons." These entities were first introduced as a theoretical concept by Frenkel,[2] and signify a moving state of electronic excitation energy in the lattice. That electronic states of this kind must in general be characterized by a wave number, rather than by a label corresponding to the atom on which they reside, is a consequence of the strong coupling between adjacent constituents of the lattice; in the alkali halides the participating units may presumably be considered to be the halide ions.

An important purpose of the present paper is to show that the use of the term "exciton" (for electronic excitation energy traveling in an insulating solid) is appropriate to a situation in which there is "strong coupling" of any type between an excited atom and its neighbors. In particular, appreciable overlapping of their electronic wave functions is not necessary to insure "strong coupling" of the crystal constituents. It will be seen as a principal result, that energy transfer by electromagnetic "near zone" interactions may take place very quickly in certain crystals.[3] Thus, because of this interaction alone, one must characterize the wave functions of the excitation by a wave number (and hence one is obliged to use the term exciton), rather than view the excitation as well localized on single atoms or molecules. This does not require the appearance of a new band in the spectrum of atoms when they are placed into condensed systems. The structure in absorption spectra due to the doublet levels characteristic of the bromide and iodide ions, for example, is observed also in the solid state. The work of the present paper demonstrates that one has every reason to believe that these levels become typical exciton levels when the ions mentioned are made the anions of ionic crystals.

Further discussion of the implications of our calculation will be given in later publications. The authors wish to thank Professor Frederick Seitz for suggesting that a suitably simplified model of an insulating crystal

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* A preliminary report of this work was given at the New York meeting of the American Physical Society, February, 1951, Phys. Rev. **82**, 315 (1951).

† Supported by the ONR.

[1] L. Apker and E. Taft, Phys. Rev. **82**, 814 (1951); **81**, 698 (1951); **72**, 964 (1950); M. Hebb, Phys. Rev. **81**, 702 (1951).

[2] J. Frenkel, Phys. Rev. **37**, 17 (1931); **37**, 1276 (1931); Physik. Z. Sowjetunion **9**, 158 (1936).

[3] This is analogous to the mechanism of "sensitized fluorescence" in gases. G. Cario and J. Franck, Z. Physik **17**, 202 (1923), and many later papers.