atomic numbers. The base line for germanium absorption is the abscissa of Fig. 1.

Since no GeH_4 was available, it was not possible to determine the shape of the absorption edge for the germanium atom directly, but there is no reason to expect that it would be much different from that for the bromine or krypton atom. On the assumption that the true absorption edge width for the germanium atom is 2.10 volts, the average of those for bromine and krypton,[4] the dashed curve in Fig. 1 was constructed. The relative positions of the absorption edges were fixed arbitrarily. It is obvious that the large absorption peak introduces uncertainty in the position of the edge. In fact if a shift of the initial rise for the molecule of about 6 volts toward lower energies were assumed, the discrepancy between experiment and theory for the major peak intensity (following paper) disappears without very much affecting the remainder of the structure. Had GeH_4 been available, a measure of the shift would have been made experimentally.

Because of the high resolving power, structure appears which has not been detected previously. This structure, of finer detail than the remainder, appears within some 15 volts of the absorption edge.

The ratio of the absorption coefficient of the germanium atom in $GeCl_4$ to that of the free atom is given in Fig. 1 of the following paper to an ejection energy of 180 volts, together with the theoretical results of HKP and the theoretical modification of Corson. Experiment and theory agree for the position of the fine structure from 80 to 180 volts. In contrast with the results of Coster and Klamer[2] the experimental and predicted positions of the absorption minimum α fail to coincide by practically 20 volts. A decrease in resolving power would have the effect of shifting the observed absorption minimum α to larger voltages, which would account for these authors' better agreement with theory.

The following paper reconsiders the Kronig-Petersen theory in the light of different assumptions for the distribution of the chlorine atoms in the molecule.

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The Theory of the Fine Structure of X-Ray Absorption Limits in Polyatomic Molecules†

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The theory of the fine structure of x-ray absorption limits in polyatomic molecules is developed in a form which takes molecular configuration into account, and it is found that the Petersen formula represents a limiting case. The fine structure of the K-absorption limit is calculated for several molecular models, in particular that of Ge in $GeCl_4$, for which comparison is made with the previous calculation of Hartree, Kronig, and Petersen, and the newer experimental results obtained by Shaw.

INTRODUCTION

X-RAY fine structure, which in the case of polyatomic molecules may extend over a region of several hundred volts on the high frequency side of the edge, was first explained by Kronig[1] on the basis of the interference between the direct wave representing the ejected photoelectron, and the components scattered by the partner atoms. This interference modifies the amplitude of the wave, and thereby the transition

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

probability, with the result that the absorption coefficient increases or decreases as the interference is constructive or destructive.

The direct problem involves certain difficulties, both with respect to the physical picture which one must consider, and the mathematical formulation. Therefore, instead of calculating the Einstein absorption coefficient $B_{jj'}$ directly, Kronig[1] considered the inverse process, i.e., the emission of a photon when an electron is captured by an atom with an empty K-level, which amounts to the simpler problem of calculating $A_{j'j}$, where

$$A_{j'j}=\frac{8\pi h\nu^3{}_{j'j}}{c^3}B_{j'j}=\frac{64\pi^4\nu^3{}_{j'j}}{3hc^3}\times\{|M_x(j'j)|^2+|M_y(j'j)|^2+|M_z(j'j)|^2\}\qquad(1)$$

in the usual notation. The problem is further simplified by calculating not the absorption coefficient itself, but the absorption coefficient ratio $\chi(W)$, namely, the ratio of the absorption coefficient for the atom in question, when bound in the molecule to the absorption coefficient of the same atom when free. This device achieves a twofold simplification, in that it avoids an explicit representation of the final state, the K-level in question, permitting a symbolic treatment, and eliminates arbitrary constants in making comparison with experiment.

In this picture of the inverse process, it is readily evident that the probability of absorption of the electron in the K-level, with accompanying photon emission, is dependent upon the resultant amplitude at the atom in question, which varies with the phase difference between the direct and scattered electron waves. The phase difference depends upon the following factors: (1) the interatomic distance ρ, (2) the energy W of the electron, (3) the angle θ between the axis of the atom-pair considered and the incident wave-normal, (4) the phase difference δ_l between the asymptotic solutions

$$R_0\sim\sin\left(Kr-\frac{l\pi}{2}\right);\quad R_1\sim\sin\left(Kr-\frac{l\pi}{2}+\delta_l\right)$$

of the equation

$$\frac{d^2R}{dr^2}+\left[K^2-\frac{8\pi^2m}{h^2}V(r)-\frac{l(l+1)}{r^2}\right]R=0\qquad(2)$$

for the field free case, and when $V(r)$ corresponds to the field of the scattering partner atom.

For the diatomic case Kronig[2] obtained

$$\begin{aligned}\frac{A_{j'j}(\text{bound})}{A_{j'j}(\text{free})}&=|1+q\cos\theta|^2+|q\sin\theta|^2\\&=1+qq^*+(q+q^*)\cos\theta\end{aligned}\qquad(3)$$

and

$$\chi(W)-1=\tfrac{1}{2}\int_0^\pi[qq^*+(q+q^*)\cos\theta]\sin\theta d\theta,\qquad(4)$$

where $q=C(\rho,\theta)e^{i\tau(1-\cos\theta)}/\rho$ in which $C(\rho,\theta)$ is the amplitude of the scattered spherical wave, and $\tau=2\pi\rho(2mW)^{\frac{1}{2}}/h$ or $(2W)^{\frac{1}{2}}\rho$ in atomic units.

To obtain $\chi(W)$ explicitly, q must be evaluated. Using a technique similar to that developed by Faxen and Holtsmark[3] in another connection, Petersen[4] obtained

$$q_s=\sum_{l=0}^{\infty}(2l+1)\sin\delta_l[(-1)^lf_{-l-1}(\tau)+if_l(\tau)]\times P_l(\mu_s)\exp\left[-i\left(2\pi\alpha\rho\mu_s-\delta_l-\frac{l\pi}{2}\right)\right]\qquad(5)$$

where $f_l(\tau)=(\pi/2\tau)^{\frac{1}{2}}J_{l+\frac{1}{2}}(\tau)$; $\alpha=(2mW)^{\frac{1}{2}}/h$;

$$\mu_s=\cos\theta_s,$$

and

$$\begin{aligned}\chi_s(W)-1=\sum_{l=0}^{\infty}\{&(2l+1)\sin^2\delta_l[f_{-l-1}{}^2+f_l{}^2]\\&+2\sin\delta_l[(-1)^lf_{-l-1}\sin\delta_l+f_l\cos\delta_l]\\&\times[(l+1)f_{l+1}-lf_{l-1}]\}.\end{aligned}\qquad(6)$$

Corresponding to Eqs. (3) and (4) Petersen[5] found in the polyatomic case

$$\begin{aligned}1+\textstyle\sum_s[q_sq_s^*+(q_s+q_s^*)\cos\theta_s]&\\+\sum\sum_{s\neq t}(q_sq_t^*+q_s^*q_t)\cos(\theta_s-\theta_t)&\\=A_{j'j}(\text{bound})/A_{j'j}(\text{free}),&\end{aligned}\qquad(7)$$

s, $t=1, 2, \cdots n$, where n is the number of partner atoms (e.g., $n=4$ for $GeCl_4$) and

$$\chi(W)-1=\textstyle\sum_s[\chi_s(W)-1]=n[\chi_s(W)-1]\qquad(8)$$

under the assumption that the terms in the

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

[3] H. Faxen and J. Holtsmark, Zeits. f. Physik **45**, 307 (1927).

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

[5] H. Petersen, Dissertation. Groningen Arch. Neerl **14**, 165 (1933).

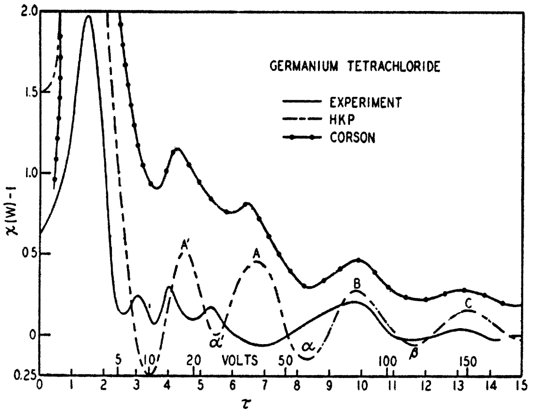

FIG. 1. $\chi(W)-1$ as a function of the energy separation from the absorption edge in units of $\tau=2\rho W^{\frac{1}{2}}$. The maximum ordinate for the H.K.P. curve is 9.2, while that for the author's is 12.5.

double sum, and the angular interdependence, may be neglected in Eq. (8).

GERMANIUM TETRACHLORIDE

Hartree, Kronig, and Petersen[6] (referred to as H.K.P.) calculated the fine structure for the K-absorption of Ge in $GeCl_4$, assuming $\chi(W)-1=4[\chi_s(W)-1]$ with the above-mentioned restrictions. Their result was considered in fairly good agreement with the experiments of Coster and Klamer,[7] but more recent and accurate experiments performed by Shaw[8] indicate that there is considerable disagreement between theory and experiment both as to positions of maxima and minima, and the general character of the $\chi(W)-1$ curve from about 100 volts down to the edge. (See Fig. 1.)

Among the several factors which might contribute to this discrepancy perhaps the most obvious is the assumption of angular independence, which was made in deriving Eq. (8). This amounts to saying that all molecules with the same interatomic distances and number of atoms will give the same result for $\chi(W)-1$ regardless of structure. This can hardly be the case, and in the following $\chi(W)-1$ is calculated, taking molecular structure into account.

CALCULATIONS FOR $GeCl_4$

According to Wierl[9] the Cl-atoms are located at the apices of a regular tetrahedron, with the Ge-atom at the center and $\rho_{\text{Ge—Cl}}=2.10\text{A}$.

The immediate problem is to obtain the $\cos\theta_s$ where the angles are those between the unit vectors to the four Cl-atoms and the incident wave normal, in a form which will automatically satisfy the constraints imposed by the model, and facilitate integration.

The most convenient choice of body fixed axes is the set of symmetry axes, and relative to these the unit vectors to the four Cl-atoms are

$$\begin{aligned} r_1&=\frac{1}{\sqrt{3}}(i+j-k),\\ r_2&=\frac{-1}{\sqrt{3}}(i+j+k),\\ r_3&=\frac{1}{\sqrt{3}}(-i+j+k),\\ r_4&=\frac{1}{\sqrt{3}}(i-j+k). \end{aligned} \tag{9}$$

Relative to wave axes whose Z' direction is that of the wave normal, and whose origin coincides with that of the symmetry axes, the same unit vectors are

$$\begin{aligned} r_1&=(\sin\theta_1\cos\varphi_1 i'+\sin\theta_1\sin\varphi_1 j'+\cos\theta_1 k'),\\ r_2&=(\sin\theta_2\cos\varphi_2 i'+\sin\theta_2\sin\varphi_2 j'+\cos\theta_2 k'), \end{aligned} \tag{10}$$

etc.

The most convenient specification of direction cosines between the two systems of axes is by means of Euler's angles. In which case, the usual relations are:

$$\begin{aligned} i&=(\cos\theta\cos\psi\cos\varphi-\sin\varphi\sin\psi)i'-(\cos\theta\cos\varphi\sin\psi+\sin\varphi\cos\psi)j'+\sin\theta\cos\varphi k',\\ j&=(\cos\theta\cos\psi\sin\varphi+\cos\varphi\sin\psi)i'+(\cos\psi\cos\varphi-\cos\theta\sin\varphi\sin\psi)j'+\sin\theta\sin\varphi k',\\ k&=-\cos\theta\cos\psi i'+\sin\psi\sin\theta j'+\cos\theta k'. \end{aligned} \tag{11}$$

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[6] D. R. Hartree, R. de L. Kronig, and H. Petersen, Physica **1**, 895 (1934).

[7] D. Coster and G. H. Klamer, Physica **1**, 890 (1934).

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

[9] R. Wierl, Ann. d. Physik **8**, 521 (1931).

From these relations it follows with $\mu=\cos\theta$:

$$\begin{aligned}
\cos\theta_1&=\frac{1}{\surd 3}[(1-\mu^2)^{\frac{1}{2}}(\cos\varphi+\sin\varphi)-\mu],\\
\cos\theta_2&=\frac{-1}{\surd 3}[(1-\mu^2)^{\frac{1}{2}}(\cos\varphi+\sin\varphi)+\mu],\\
\cos\theta_3&=\frac{-1}{\surd 3}[(1-\mu^2)^{\frac{1}{2}}(\cos\varphi-\sin\varphi)-\mu],\\
\cos\theta_4&=\frac{1}{\surd 3}[(1-\mu^2)^{\frac{1}{2}}(\cos\varphi-\sin\varphi)+\mu].
\end{aligned}\tag{12}$$

The Legendre polynomials $P_l(\cos\theta_s)$ $(s=1, 2, 3, 4)$ will also be required and for this purpose we consider the addition theorem for spherical harmonics.

$$P_l(\cos\gamma)=P_l(\cos\theta)P_l(\cos\theta')+\sum_{m=1}^{l}\frac{(l-m)!}{(l+m)!}P_l^m(\cos\theta)P_l^m(\cos\theta')\times[e^{im(\varphi-\varphi')}+e^{-im(\varphi-\varphi')}],$$

where

$$\cos\gamma=\sin\theta\sin\theta'\cos(\varphi-\varphi')+\cos\theta\cos\theta'.$$

The relations for $\cos\theta_s$ are of this form if the following values are assigned to θ' and φ', with $\cos\lambda=1/\surd 3$. For:

$$\begin{array}{lll}
\cos\theta_1, & \theta'=\lambda+\pi, & \varphi'=-3\pi/4,\\
\cos\theta_2, & \theta'=\lambda+\pi, & \varphi'=\pi/4,\\
\cos\theta_3, & \theta'=\lambda, & \varphi'=3\pi/4,\\
\cos\theta_4, & \theta'=\lambda, & \varphi'=-\pi/4.
\end{array}\tag{13}$$

λ above is half the angle between any pair of unit vectors. Then one finds, with $P_l^m(\pm)=P_l^m(\pm 1/\surd 3)$

$$P_l(\mu_1)=P_l(\mu)P_l(-)+\sum_{m=1}^{l}\frac{(l-m)!}{(l+m)!}P_l^m(\mu)P_l^m(-)\times[e^{im(\varphi+3\pi/4)}+e^{-im(\varphi+3\pi/4)}]\tag{14}$$

with similar relations for μ_2, μ_3, μ_4.

As an illustration q_1 takes the form

$$q_1=\sum_{l=0}^{\infty}(2l+1)\sin\delta_l[(-)^lf_{-l-1}+if_l]P_l(\mu)P_l(-)e^{-i\gamma}+\sum_{l=1}^{\infty}\sum_{m=1}^{l}(2l+1)\frac{(l-m)!}{(l+m)!}$$
$$\times\sin\delta_l[(-)^lf_{-l-1}+if_l]P_l^m(\mu)P_l^m(-)[e^{i\{m(\varphi+3\pi/4)-\gamma\}}+e^{-i\{m(\varphi+3\pi/4)+\gamma\}}],\tag{15}$$

where

$$\gamma=2\pi\alpha\rho\mu_1-\delta_l-\tfrac{1}{2}l\pi.$$

From Bauer's formula

$$e^{2\pi i\alpha\rho\mu_1}=\sum_{l=0}^{\infty}(2l+1)i^lf_lP_l(\mu_1)\tag{16}$$

and

$$q_1+q_1^*=2\sum_{l=0}^{\infty}(2l+1)\sin\delta_lP_l(\mu)P_l(-)[(-)^lf_{-l-1}\cos\gamma+f_l\sin\gamma]+2\sum_{l=1}^{\infty}\sum_{m=1}^{l}(2l+1)\frac{(l-m)!}{(l+m)!}$$
$$\times\sin\delta_lP_l^m(\mu)P_l^m(-)[(-)^lf_{-l-1}(\cos k_1+\cos k_2)+f_l(\sin k_2-\sin k_1)],\tag{17}$$

where

$$k_1=m(\varphi+3\pi/4)-\gamma,\quad k_2=m(\varphi+3\pi/4)+\gamma.$$

Evidently, $\chi(W)-1$ takes the form

$$\chi(W)-1=\frac{1}{4\pi}\sum_{s=1}^{4}\int_{-1}^{1}\int_{0}^{2\pi}[q_sq_s^*+(q_s+q_s^*)\mu_s]d\mu d\varphi.\tag{18}$$

The actual integrations are rather lengthy, and must necessarily be omitted here, except for a brief illustrative sketch of the method for q_1.

The integral

$$\frac{1}{4\pi}\int_{-1}^{1}\int_{0}^{2\pi} q_1 q_1^* d\mu d\varphi$$

is fairly straightforward, and requires no amplification.

For the integral involving $(q_1+q_1^*)\mu_1$ consider just the first summation as given in (18). Then the explicit integral of this part is

$$\frac{2}{4\pi\sqrt{3}}\sum_{l=0}^{\infty}(2l+1)\sin\delta_l P_l(-)\int_{-1}^{1}\int_{0}^{2\pi} P_l(\mu)\{(-)^l f_{-l-1}\cos\gamma+f_l\sin\gamma\}$$
$$\times\left\{\frac{(1-\mu^2)^{\frac{1}{2}}}{2}[(1+i)e^{-i\varphi}+(1-i)e^{i\varphi}]-\mu\right\}d\mu d\varphi, \tag{19}$$

where the value of μ_1 is given in (12). This integral may be written as

$$\frac{2}{4\pi\sqrt{3}}\sum_{l=0}^{\infty}(2l+1)\sin\delta_l P_l(-)[(-)^l f_{-l-1}A^{11}+f_l A_{12}], \tag{20}$$

where

$$A_{12}^{11}=\frac{Re}{Im}\left[e^{-i(\delta_l+l\pi/2)}\int_{-1}^{1}\int_{0}^{2\pi} P_l(\mu)e^{2\pi i\alpha\rho\mu_1}\left\{\frac{(1-\mu^2)^{\frac{1}{2}}}{2}[(1+i)e^{-i\varphi}+(1-i)e^{i\varphi}]-\mu\right\}d\mu d\varphi\right]. \tag{21}$$

The value of $\exp(2\pi i\alpha\rho\mu_1)$ as given in (16) may be inserted, and the integral evaluated using recursion formulae for the ordinary and associated Legendre polynomials. Proceeding in this manner, one finally obtains:

$$\chi(W)-1=4\sum_{l=0}^{\infty}\sum_{m=-l}^{l}(2l+1)\frac{(l-|m|)!}{(l+|m|)!}[f_{-l-1}^2+f_l^2]\left[P_l^{|m|}\left(\frac{1}{\sqrt{3}}\right)\right]^2\sin^2\delta_l\frac{-8}{\sqrt{3}}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\left[\frac{(l-|m|)!}{(l+|m|)!}\right]$$
$$\times P_l^{|m|}(+)\sin\delta_l[(-)^l f_{-l-1}\sin\delta_l+f_l\cos\delta_l]$$
$$\times[(l+|m|)f_{l-1}P_{l-1}^{|m|}(+)-(l-|m|+1)f_{l+1}P_{l+1}^{|m|}(+)]. \tag{22}$$

The corresponding expression used by H.K.P. is:

$$\chi(W)-1=4\sum_{l=0}^{\infty}(2l+1)\sin^2\delta_l[f_{-l-1}^2+f_l^2]-8\sum_{l=0}^{\infty}\sin\delta_l[(-)^l f_{-l-1}\sin\delta_l+f_l\cos\delta_l][lf_{l-1}-(l+1)f_{l+1}]. \tag{23}$$

These expressions are plotted with the experimental curve in Fig. 1.

It is evident that, although the new curve maintains much the same trend as the experimental, there is still considerable disagreement at the principal maximum ($\tau=1.2$) as regards amplitude, and a section of the experimental curve between 5 and 7 on the τ scale appears to have been shifted laterally away from the edge by about one unit. In addition, the first minimum of the experimental curve is entirely absent.

A clearer picture of configuration dependence, and the additional factors which contribute to these differences, is obtained if we consider first, several intermediate structures leading to Petersen's limiting case.

Case I

According to Coster and Klamer[10] the molecule $AsCl_3$ is a regular pyramid, with the As-atom at the top, and the three Cl-atoms at equal distances from it. It is estimated that ρ_{As-Cl} is about 2.20A.

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[10] D. Coster and G. H. Klamer, Physica **1**, 890 (1934).

Proceeding as for $GeCl_4$, but with the changes appropriate to this model, there results

$$\begin{aligned}\chi(W)-1=3\sum_{l=0}^{\infty}\Bigg\{&(2l+1)\sin^2\delta_l[f_{-l-1}^2+f_l^2][P_l(-)]^2+\frac{2}{3\sqrt{3}}\sin\delta_lP_l(-)\\&\times[(-)^lf_{-l-1}\sin\delta_l+f_l\cos\delta_l][f_{l+1}P^1{}_{l+1}(-)+f_{l-1}P^1{}_{l-1}(-)]\\&+2(\tfrac{2}{3})^{\frac{1}{2}}\sin\delta_lP_l(-)[(-)^lf_{-l-1}\sin\delta_l+f_l\cos\delta_l][lf_{l-1}P_{l-1}(-)-(l+1)f_{l+1}P_{l+1}(-)]\Bigg\}\\&+6\sum_{l=1}^{\infty}\sum_{m=1}^{l}\Bigg\{(2l+1)\frac{(l-m)!}{(l+m)!}\sin^2\delta_l[f_{-l-1}^2+f_l^2][P_l^m(-)]^2+\frac{1}{3\sqrt{3}}\frac{(l-m)!}{(l+m)!}\sin\delta_lP_l^m(-)\\&\times[(-)^lf_{-l-1}\sin\delta_l+f_l\cos\delta_l][f_{l+1}P_{l+1}^{m+1}(-)+f_{l-1}P_{l-1}^{m+1}(-)\\&-(l+m)(l+m-1)f_{l-1}P_{l-1}^{m-1}(-)-(l-m+1)(l-m+2)f_{l+1}P_{l+1}^{m-1}(-)]\\&+2(\tfrac{2}{3})^{\frac{1}{2}}\frac{(l-m)!}{(l+m)!}\sin\delta_lP_l^m(-)[(-)^lf_{-l-1}\sin\delta_l+f_l\cos\delta_l]\\&\qquad\times[(l+m)f_{l-1}P_{l-1}^m(-)-(l-m+1)f_{l+1}P_{l+1}^m(-)]\Bigg\},\end{aligned}\tag{24}$$

where $P_l^m(-)=P_l^m[-(2/3)^{\frac{1}{2}}]$.

The curve for $AsCl_3$ is not drawn since the only experimental curve available appears to be that of Coster and Klamer[10] which gives the absorption coefficient for $AsCl_3$ rather than the ratio $\chi(W)$, and is therefore unsuitable for comparison with the theoretical result.

The interesting feature of the result for $AsCl_3$ is the relation one finds between $\chi(W)-1$ of $GeCl_4$ and $AsCl_3$, which will be denoted by $\chi(G)-1$ and $\chi(A)-1$, respectively.

$$\frac{\chi(A)-1}{\chi(G)-1}=\frac{3}{4}+8\sum_{l=0}^{\infty}\frac{\sin\delta_l[f_{-l-1}\sin\delta_l+f_l\cos\delta_l][(l+1)f_{l+1}-lf_{l-1}]}{3[\chi(G)-1]},\tag{25}$$

where ρ AsCl has been taken as 2.10A to simplify the relation.

Petersen's equation would predict just the constant term.

Case II

Imagine a flat model YCl_4, with the Cl atoms located by the unit vectors, i, j, $-i$, $-j$. This case approaches the physical conditions corresponding to Petersen's average over independent angles. Then

$$\begin{aligned}\chi(W)-1=4\sum_{l=0}^{\infty}\{&(2l+1)\sin^2\delta_l[f_{-l-1}^2+f_l^2](P_l)^2+2\sin\delta_lP_l[(-)^lf_{-l-1}\sin\delta_l+f_l\cos\delta_l]\\&\times[f_{l+1}P^1{}_{l+1}+f_{l-1}P^1{}_{l-1}]\}+8\sum_{l=1}^{\infty}\sum_{m=1}^{l}\Bigg\{(2l+1)\frac{(l-m)!}{(l+m)!}\sin^2\delta_l[f_{-l-1}^2+f_l^2][P_l^m]^2\\&+\frac{(l-m)!}{(l+m)!}\sin\delta_lP_l^m[(-)^lf_{-l-1}\sin\delta_l+f_l\cos\delta_l][f_{l+1}P_{l+1}^{m+1}+f_{l-1}P_{l-1}^{m+1}\\&\qquad-(l+m)(l+m-1)f_{l-1}P_{l-1}^{m-1}-(l-m+1)(l-m+2)f_{l+1}P_{l+1}^{m-1}]\Bigg\},\end{aligned}\tag{26}$$

where the argument of P_l^m is 0. The resultant curve is practically identical with the curve obtained by H.K.P.

Case III

The limiting case is obtained when one considers all the scattering atoms placed at one point, and the atom in question at the origin. From Eqs. (9)–(11), it is evident that with the assumed choice of axes this corresponds to locating all the atoms by the unit vector **k**, in which case one simply obtains a linear superposition amounting to four diatomic molecules.

In each of the cases considered, the inclusion of the constraints imposed by the molecular model has introduced a characteristic parameter of the molecule as argument of the Legendre polynomials in the expression for $\chi(W)$. Thus for the tetrahedral model of $GeCl_4$ the argument is $1/\sqrt{3}$, which is the cosine of half the angle between unit vectors, whereas the flat model (Case II) introduces the cosine of the angle between unit vectors as argument. Comparison of the results for the different models indicates that the configuration dependence has considerable influence on the magnitude of the $\chi(W)$ curve, but does not affect the position of the maxima and minima appreciably.

We note in passing that the configuration dependence of the fine structure may, in certain cases, decide between possible molecular structures, although this application will depend to some extent on how well the remaining discrepancies can be explained.

SOURCES OF ERROR

It need hardly be mentioned that an accurate determination of the phases δ_l with a truly representative field is vital to all such calculations. In the present case, the phases were determined by H.K.P. for the Hartree field of Cl by direct numerical integration of Eq. (2), which in atomic units becomes

$$\frac{d^2R}{dr^2}+\left[2(E-V)-\frac{l(l+1)}{r^2}\right]R=0. \qquad (27)$$

For $E=V=0$, the solution of (27) goes to zero at the origin as r^{l+1} (no nodes), and the value of $\delta_l/\pi(E=0)$ is therefore given by the number of nodes present when $V=V(r)$, i.e., the number of half-waves which pass a fixed radius as V is increased from zero to its final value.

Inasmuch as a bound $(3p)$ wave function in the Cl atom tends asymptotically to the r-axis and has only one node, one might expect $\delta_1(E=0)$ to be 2π. This would certainly be the case if the field used for calculating the wave function for the limiting case of an incident electron of energy $E_i=0$, $l=1$ were the same as that for the bound $(3p)$ electron $(E_b<0)$. If Eq. (27) is written in the form

$$\left[-\frac{R''}{R}=2(E-V)-\frac{l(l+1)}{r^2}\right],$$

it is evident that in passing from the bound to the free case $(E_b<0\leq E_i)$ the curvature increases with E, and R cuts the axis to form a second node. However, this picture is incomplete because the free electron interacts with one more electron than does a member of the Cl $(3p)^5$ group.

If the potential energies of a bound and free electron be denoted by V_b, V_i, respectively, then V_i-V_b is positive—so that in going from V_b to V_i, the effect on the curvature of the wave function is opposite in direction to that caused by the corresponding increase in E. In the present case, the change in V is greater than that in E, and the radial function for the incident electron has only one node for $E_i=0$.

The huge peak at low energies appears to be caused by this rather unexpected shift of $\delta_1(E=0)$ from 2π to π. On the other hand, we can readily see that the polarization effect will tend to reduce the difference between V_i and V_b so that $\delta_1(E=0)$ may return to 2π.

In the absence of a corrected Hartree field for Cl, we may use the following device to estimate the polarization effect, although it must be emphasized that the result can only be indicative of the trend.

Henneberg[11] showed on the basis of the W.J.B.K. method and the Fermi-Thomas field that, with some restrictions, the phases δ_l for any atom could be obtained from the known values for some one atom. Taking Holtsmark's[12] values of the δ_l for the polarization corrected Hartree field of Kr, it is found that the correction to $\delta_1(\mathrm{Cl})$ is of the order of π.

The absence of the first minimum which appears in the experimental curve perhaps is caused

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[11] W. Henneberg, Zeits. f. Physik **83**, 555 (1933).

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

by this same effect, but more generally the above result emphasizes the fact that the uncorrected Hartree field is not sufficiently accurate for such calculations, particularly at small energies.

The almost uniform vertical displacement of the theoretical curve is probably due to the neglect of the double summation terms in Eq. (7) which take into account the secondary interference between the electron waves scattered by the different partner atoms. It is important to distinguish this effect from the primary interference between the direct wave and the wave scattered by each partner atom taken separately, as described by the single summation in (7), and multiple scattering which is entirely neglected in this treatment.

An exact evaluation of these terms is extremely difficult, but approximate calculation indicates that their contribution will be small, and mainly negative. It would be of interest to obtain a complete expression for these terms since mixed factors such as $f_l f_{l'} \sin \delta_l \sin \delta_{l'} \cos (\delta_l - \delta_{l'})$ will appear, and might affect the positions of maxima and minima to some degree. Physically it is quite clear that the secondary terms $q_s^* q_t$ must be much less important than the terms $q_s q_s^*$ because $q_s q_s^*$ is always positive while $q_s^* q_t$ will change sign, and the factors $q_s^* q_t$ do not attain their maxima simultaneously. It is only necessary to visualize the tetrahedral model of $GeCl_4$ to see that at least one atom of a given pair s, t will be scattering through a large angle, which results in a correspondingly small amplitude.

In the discussion of Case III it was shown that the H.K.P. calculation of $\chi(W)$ is formally equivalent to a superposition of four diatomic molecules, and it is clear that the secondary interference terms cannot be neglected in this limiting case. In fact, all q's become identical, and every term $q_s^* q_t$ is positive and equal to $q_s^* q_s$. If these cross terms are included the first maximum of the H.K.P. curve ($\tau = 1.2$, $\chi(W) - 1 = 9.26$) increases to approximately 50, and the curve is distorted and shifted vertically off the scale of Fig. 1. Starting from this oversimplified model, the scattering atoms may be rearranged in various more complex models, and as the actual physical configuration is approached, the contribution from the secondary terms decreases until the closest approximation to the experimental curve is obtained.

Thus, when the atoms are separated as in Case II, the secondary terms contribute an amount of the order of that due to the primary terms, and the first maximum drops to about half the value found above.

Electron exchange has not been considered because of the additional complication introduced, and the fact that the various approximations, including the several implicit in Kronig's original formulation, would make such considerations of doubtful significance.

CONCLUSION

Figure 1 indicates that the relative amplitudes of Corson's curve agree better with experiment than do those of the H.K.P. curve, which vary too sharply. This is also true of the absolute amplitudes if one takes into account the secondary terms, as indicated in the discussion. However, the most significant result of the present investigation is that the molecular configuration plays an important role in determining the absorption fine structure.

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