ELECTRON DIFFRACTION AND THE MOLECULAR STRUCTURE OF GASES

THE CRYSTAL STRUCTURE OF CHALCOPYRITE

THESIS

by

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CONTENTS

ABSTRACT

An apparatus has been developed for the study of the molecular structure of gases by the electron diffraction method. A number of improved features in the construction are described.

The method has been applied to an investigation of the resonance among the possible electronic structures of the Lewis type and also of the atomic configurations in certain molecules.

Diacetylene and cyanogen are found to be linear, contrary to a published report of evidence for a model with 150° bond angles.

Methyl azide is found to have a linear azide group. The ring model which has been proposed is shown to be eliminated. The ring model for carbon suboxide has also been eliminated in favor of a linear model.

Chlorine dioxide shows evidence for the existence of the three-electron bond, and this fact explains its lack of tendency to polymerize to Cl_2O_4.

The hexafluoride of sulfur, selenium and tellurium are found to have structures which may be represented by a regular octahedron with six atoms at the corners surrounding the central atom.

The interatomic distances for all of the above compounds are reported.

The crystal structure of chalcopyrite has been re-investigated and the correct structure is reported.

INTRODUCTION

Interference effects in the scattering of a beam of electrons were first obtained by Davisson and Germer[1] in 1927 when they obtained well-defined maxima and minima in the angular distribution of electrons scattered at the surface of a single crystal of nickel. Their observations were of greatest interest at that time because of the evidence which they supplied for the wave properties of propagated particles. The application of electron diffraction to a study of the structure of metals was made by G.P. Thomson[2] who prepared thin foils of gold, silver, aluminum and other metals and, by projecting a beam of electrons through the foil onto a photographic plate, obtained photographs which are analogous to the powder photographs obtained under similar conditions with X-radiation. Analysis of the photographs leads to precisely the same evidence for the structure of the metal with both electron and X-ray diffraction experiments. Other experiments[3] on the scattering of electrons by solids have been performed to determine the relation between the wave-length associated with the electrons and the accelerating difference of potential and also to find any polarization effect (orientation of the axis of spin) which may be introduced by the scattering process.

The first observation of interference effects in the scattering of electrons by gases was made by Mark and Wierl.[4] Their work was undoubtedly inspired by the experiments of Debye[5] on the diffraction of X-radiation by gases, who in 1915 derived a theoretical relation between the intensity of the scattered radiation and the angle of scattering. His formula (the derivation of which is given in the following section) is valid for the scattering by single gas molecules of any kind of radiation which is capable of showing interference phenomena. The characteristic differences between x-radiation and electron beams appear in their respective atomic scattering factors, since the mechanism of scattering is not the same in both cases. The advantages of experiments in scattering by gases for the study of molecular structure lie in the independent action of the single molecules on the x-ray (or electron) beam. The interference effects observed in the photographs arise entirely from the interaction of the radiation scattered by the atoms of a single molecule, and an interpretation on this basis leads directly to a knowledge of the structure of the molecule. The work of Debye with x-radiation and that of Mark and Wierl with electron beams have accordingly led to a determination of the structures of a number of molecules.

The present work was undertaken as part of a program of study of the nature of the chemical bond. Since the interatomic distances are one of the important criteria[6] of the character of the bonds between atoms in a given molecule the determination of the structures of a number of related molecules constitutes an important part of such a study. Specific applications are given with the detailed discussion of the results.

The development of the experimental technic has received considerable attention in this work, and the present arrangement for obtaining usable photographs is described in detail.

THEORY

The de Broglie Wave-length. Of great historical interest is the following relation proposed by de Broglie[7] between the "associated" wave-length and the velocity of the electrons in the beam:

$$\lambda = \frac{h}{mv} \tag{1}$$

in which λ is the wave-length, h is Planck's constant, m is the mass and v the velocity of the electron. De Broglie's derivation depended upon the two equations of Einstein, relating energy to frequency and to mass,

$$E = h\nu$$

$$E = mc^2$$

and also upon the relation between the wave-length and the wave-velocity V of a monochromatic plane wave,

$$\lambda = \frac{V}{\nu}$$

in which $V = \frac{c^2}{v}$. v is the group velocity and here is the velocity of the electron. Then,

$$\lambda = \frac{V}{\nu} = \frac{c^2}{\nu v} = \frac{mc^2}{mv\nu} = \frac{h}{mv}$$

This relation is also obtained very simply from the wave equation for a free electron. In one dimension,

$$\frac{\partial^2\psi}{\partial x^2} + \frac{8\pi^2 m}{h^2} E \psi = 0$$

$$\psi = A \cos a x \qquad \text{where} \quad a^2 = \frac{8\pi^2 m E}{h^2}$$

But if this solution represents a wave, $a = \frac{2\pi}{\lambda}$ and substituting $\frac{1}{2} m v^2 = E$, equation (1) is again obtained.

A more immediately useful expression is obtained by transformation to a relation between λ and the accelerating difference of potential, V. Since the useful range of potential difference lies between forty thousand and one hundred thousand volts the relativistic relation between velocity and voltage must be used; namely,

$$\frac{eV}{300} = \frac{m_0 c^2}{\sqrt{1 - v^2/c^2}} - m_0 c^2$$

in which e is the electronic charge, V is the accelerating potential in volts, m_o is the rest mass of the electron and c is the velocity of light. By use of this expression the velocity may be eliminated from the following relativistic form of equation (1),

$$\lambda = \frac{h}{m_0 v}\sqrt{1 - v^2/c^2}$$

The result is

$$\lambda = \sqrt{\frac{150}{V}} \cdot \frac{h}{\sqrt{e m_0}} \frac{1}{\left\{1 + \frac{eV}{600 m_0 c^2}\right\}^{1/2}}$$

or

$$\lambda \text{ in Ångstrom units} = \sqrt{\frac{150}{V}} \frac{1}{\left\{1 + 9.834 \times 10^{-7}\, V\right\}^{1/2}} \qquad (2)$$

The approximate expression corresponding to equation (1) is

$$\lambda' = \sqrt{\frac{150}{V}}$$

The following table contains a number of values of λ and λ', and also of the relative velocity, β $(= \frac{v}{c})$ and β', corresponding to given accelerating potentials.

Table of Wave-Lengths and Relative Velocities

V	λ	λ'	β	β'
0	∞	∞	0	0
10	3.873	3.873	0.0063	0.0063
100	1.225	1.225	0.0198	0.0198
1000	0.3871	0.387	0.0626	0.0627
10000	0.1219	0.122	0.1955	0.1983
20000	0.08576	0.0866	0.2725	0.280
30000	0.06968	0.0707	0.3291	0.343
40000	0.06006	0.0613	0.3749	0.397
50000	0.05347	0.0548	0.4136	0.443
60000	0.04858	0.0500	0.4472	0.486
70000	0.04477	0.0463	0.4768	0.525
80000	0.04169	0.0433	0.5034	0.561
90000	0.03913	0.0408	0.5270	0.595
100000	0.03695	0.0387	0.5493	0.627
1000000	0.008696	0.0122	0.9414	1.983
10000000	0.001177	0.00387	0.9988	

λ' and β' are the non-relativistic values of wave-length and relative velocity.

The foregoing discussion of the wave-length of electrons might seem to impute some physical reality to "electron waves"; but, although this point of view found favor for a time, it is being displaced by the view that these waves are no more than a mathematical abstraction. Although the analogies to wave motion are convenient to use in the treatment of diffraction problems there are many electron problems which are not susceptible to such considerations.

The quantum mechanics, which aspires to provide a treatment of all problems of physical science, may be applied to the diffraction problem in that form which takes for its starting point the Schrödinger "wave" equation (the designation "wave" being unfortunate and having no general significance). In the special case of the free electron, which corresponds to the situation in diffraction experiments, the solution of the Schrödinger equation may be represented by a sinusoidal wave; but it must be emphasized that the wave appears in the quantity ψ (the solution of the equation), which has no physical significance, and not in the electron beam. ψ is regarded as a probability amplitude such that the product of ψ with its complex conjugate is a function of the appropriate coordinates and represents the probability of a scattered electron's being at any specified point in the diffraction pattern. For a large number of electrons this function may be said to represent the distribution of intensity, as it is convenient to do in the present case of photographically recorded electrons. Since the Schrödinger equation in this case is very similar to the classical wave equation there is a quantity appearing in its solution which may be called a wave-length by analogy, but this analogy is scarcely a satisfactory basis for identifying the electron beam with a propagated wave. The analogy is good enough, however, that in the region of high accelerating potentials the wave-length derived as in the preceding paragraphs may be substituted in the formulas which describe the scattering of X-radiation from single crystals, powders and gases and which then give correctly the positions of the interference maxima observed in the corresponding experiments with electrons.

Scattering by a Single Atom. The derivation of the scattering equation may be divided into two parts; the first considering the interaction of an electron beam with a single atom, and the second treating the interaction with a group of molecules. The derivation given below is due in the first part chiefly to Born[8], Mott[9], and Wentzel[10] and in the second part to Debye.[11]

The problem starts with the assumption of an unidirectional beam of electrons traveling with a uniform velocity in a field-free space, which falls upon a stationary atom. In a very small region around the atom there is a perturbing potential due to the electrostatic field of force set up by the charges of which the atom is composed. The energy of the atom itself is to be regarded as unchanged by the encounter so that the result will apply only to the elastically scattered electrons.

The solution of the following Schrödinger equation must be chosen in a form to give the phase and amplitude of the "probability wave" for any point of observation:

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2}(E - V_1)\psi = 0 \qquad (3)$$

E is the kinetic energy of the electrons in the beam and V_1 is the perturbing potential function representing the field of force around the scattering center. If we let

$$\frac{8\pi^2 m}{h^2} E = k^2$$

then $\frac{2\pi}{k} = \lambda$, the deBroglie wave-length.

Rearranging (3),

$$(\nabla^2 + k^2)\psi = \frac{8\pi^2 m}{h^2} V_1 \psi \equiv f(x, y, z) \qquad (4)$$

The most general solution of (4) is

$$\psi = \psi_0 + \psi_1 \qquad \psi_1 = \frac{1}{4\pi}\iiint \frac{e^{ik|\bar{r}-\bar{r}'|}}{|\bar{r}-\bar{r}'|} f(x', y', z')\, dx'\, dy'\, dz' \qquad (5)$$

ψ_0 is the complementary function of (4) and ψ_1 is the particular integral, the form given being known from potential theory. The integration is carried out over the primed coordinates, and since $f(x, y, z) = 0$ when $V_1 = 0$ the integral covers the region in space occupied by the field of force. With the origin of coordinates at the center of the atom, $\bar{r}$ is the vector representing the point of observation.

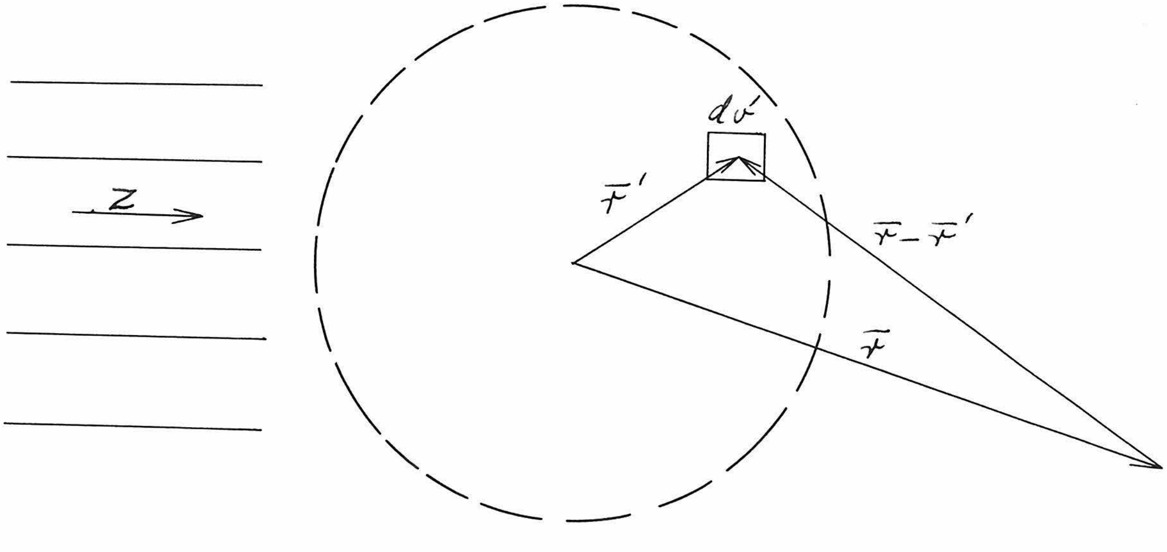
For large r the integral tends to $A\frac{e^{ikr}}{r}$ where A depends only on $\frac{\bar{r}}{|\bar{r}|}$ (i.e., the direction of observation) so that ψ_1 is the probability amplitude for the scattered electrons. ψ_0 then represents the incident beam and as a solution of the equation

$$(\nabla^2 + k^2)\psi_0 = 0$$

we may write

$$\psi_0 = e^{ikz} \qquad (6)$$

where the z axis has been chosen as the direction of the incident beam.



The problem has been reduced to the evaluation of the integral

$$\psi_1 = \frac{1}{4\pi}\iiint \frac{e^{ik|\bar{r}-\bar{r}'|}}{|\bar{r}-\bar{r}'|}\,\frac{8\pi^2 m}{h^2}\,V_1(x',y',z')\,\psi(x',y',z')\,dv' \qquad (7)$$

Now we assume that in

$$\psi(x',y',z') = \psi_0' + \psi_1'$$

ψ_1' may be neglected so that

$$\psi(x',y',z') = e^{ikz'} \qquad (8)$$

This is equivalent to the assumption that the scattered wave inside the atom is negligible in comparison to the incident wave. Then

$$\psi_1 = \frac{2\pi m}{h^2}\iiint \frac{e^{ik(|\bar{r}-\bar{r}'|+z')}}{|\bar{r}-\bar{r}'|}\,V_1(x',y',z')\,dv' \qquad (9)$$

If our observations are made at great distqnces from the atom, a

$$r \gg r'$$

and

$$|\bar{r}-\bar{r}'| \approx r - r'\{\alpha\alpha' + \beta\beta' + \gamma\gamma'\}$$

in which α, β, γ and α', β', γ' are the respective direction cosines. Since $z' = \gamma' r'$,

$$\psi_1 = \frac{2\pi m}{h^2}\,\frac{e^{ikr}}{r}\iiint e^{-ikr'\{\alpha\alpha'+\beta\beta'+\gamma'(\gamma-1)\}}\,V_1\,dv' \qquad (10)$$

Now we introduce a vector A with components α , β and $\gamma - 1$ and magnitude $A = \sqrt{\alpha^2+\beta^2+(\gamma-1)^2} = \sqrt{2(1-\gamma)}$. If θ is the angle between the incident beam (along z) and r, then $\theta = \cos^{-1}\gamma$ and

$$A = \sqrt{2(1-\cos\theta)} = 2\sin\theta/2$$

The exponent in the factor under the integral sign is the scalar product of $\bar{r}'$ and $\bar{A}$. Therefore,

$$\psi_1 = \frac{2\pi m}{h^2}\frac{e^{ikr}}{r}\iiint e^{-2ikr'\sin\theta/2\cos\eta}\,V_1\,dv' \qquad (11)$$

where η is the angle between $\bar{r}'$ and $\bar{A}$.

For convenience let $\mu = 2k\sin\theta/2 = 4\pi\frac{\sin\theta/2}{\lambda}$

We may integrate over the volume containing the field of force after transforming to polar coordinates with the polar axis in the direction of $\bar{A}$. The further assumption is made that V_1 is a function of r' only. Then with

$$dx'dy'dz' = r'^2\sin\eta\,d\eta\,d\phi\,dr'$$

$$\psi_1 = \frac{2\pi m}{h^2}\frac{e^{ikr}}{r}\int_0^\infty\int_0^{2\pi}\int_0^\pi e^{-i\mu r'\cos\eta}\,V_1\,r'^2\sin\eta\,d\eta\,d\phi\,dr'$$

$$= \frac{4\pi^2 m}{h^2}\frac{e^{ikr}}{r}\int_0^\infty\left[\frac{e^{-i\mu r'\cos\eta}}{i\mu r'}\right]_0^\pi V_1\,r'^2\,dr'$$

$$= \frac{8\pi^2 m}{h^2}\frac{e^{ikr}}{r}\int_0^\infty\frac{\sin\mu r'}{\mu r'}\,V_1\,r'^2\,dr' \qquad (12)$$

By definition

$$V_1 = -\varepsilon\int_\infty^{r'}K(r')\,dr' \qquad (13)$$

In this case **K**, the field strength, is given by the following expression:

$$K(r') = \frac{\varepsilon}{r'^2}\left[Z - \int_0^{r'}|\phi(r')|^2\,4\pi r'^2\,dr'\right] \qquad (14)$$

in which $\varepsilon|\phi(r)|^2 = \rho$, the charge density at r' from the nucleus and $\phi(r')$ is the radial part of the solution of the Schrödinger equation for the atom. The expression above for K may be deduced from the fact that the field inside a charged spherical shell is zero and the field outside is just that which would be produced by the total charge concentrated at the center.

A two stage integration by parts leads to the following result,

$$\psi_1 = \frac{8\pi^2 m}{h^2}\,\frac{e^{ikr}}{r}\,\frac{\epsilon^2}{\mu^2}\left\{Z - 4\pi\int_0^\infty \frac{\sin\mu r'}{\mu r'}\,|\phi(r')|^2\, r'^2\, dr'\right\} \qquad (15)$$

Let $F = 4\pi\int_0^\infty \frac{\sin\mu r'}{\mu r'}\,|\phi(r')|^2\, r'^2\, dr'$

F is identical with the atomic scattering factor for X-radiation and values have been tabulated as a function of μ (or $\frac{\sin\theta/2}{\lambda}$) with the aid of expressions for $\phi(r')$.

On substitution of the expression for μ, (15) becomes

$$\psi_1 = \frac{m\epsilon^2}{2h^2}\,\frac{e^{ikr}}{r}\,\frac{Z-F}{\frac{\sin^2\theta/2}{\lambda^2}} \qquad (16)$$

With incident intensity I_0 the intensity is

$$I = I_0\,\frac{m^2\epsilon^4}{4h^4}\,\frac{1}{r^2}\,f^2$$

where $f = \frac{Z-F}{\frac{\sin^2\theta/2}{\lambda^2}}$,

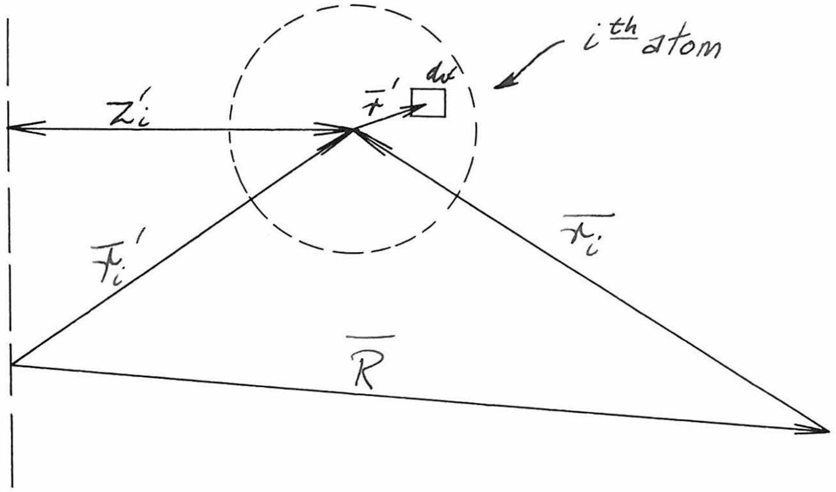
the atomic scattering factor for electrons. I_0 represents the number of electrons crossing a disc of unit area in the incident beam per unit time; and I is the number of electrons crossing per unit time a disc of area $r^2 d\omega$ which subtends a solid angle $d\omega$ and is r distant from the origin.

Scattering by a Group of Molecules. The problem of scattering by group of molecules may be attacked by the consideration first of a single molecule in a fixed orientation. This result is averaged over all possible orientations of the molecule and the final expression will be valid for the effect produced by the simultaneous scattering from a large number of randomly oriented molecules.

Let the molecule consist of n atoms with atomic scattering factors, f_1, f_2, f_3, ... f_n.

$$f_i = \frac{Z_i - F_i}{\sin^2\theta/2/\lambda^2}$$

The origin of coordinates may be taken at any fixed point in the molecule. In general the individual atoms will lie in some position with their centers away from the origin, and the form of equation (16) must be altered a little.



In equation (8) Z' must be replaced by $Z'+Z_i'$ where Z_i' is the z displacement of the center of the i^{th} atom from the new origin. This introduces a factor $e^{ikz_i'}$ into the integral which has already been evaluated, but since it is constant for a given atom the factor does not alter the integration. (16) then becomes

$$\psi_1 = \frac{m\varepsilon^2}{2h^2} \frac{e^{ik(r_i + z_i')}}{r_i} f_i \qquad (17)$$

Now if the fields of force belonging to the individual atoms do not overlap, the probability amplitude for the molecule is just the sum of those for the individual atoms; that is

$$\Psi = a \sum_i' \frac{e^{ik(r_i + z_i')}}{r_i} f_i \qquad \text{where} \quad a = \frac{m\varepsilon^2}{2h^2} \tag{18}$$

If $\overline{R}$ is the vector to the point of observation and $\overline{r}_i'$ to the center of the i^{th} atom, $\overline{r}_i = \overline{R} - \overline{r}_i'$. Since R is always much larger than r_i',

$$r_i \simeq R - r_i'\{\alpha\alpha_i' + \beta\beta_i' + \gamma\gamma_i'\} \tag{19}$$

Substituting this in (18) and noting that $z_i' = \gamma_i' r_i'$

$$\Psi = a \frac{e^{ikR}}{R} \sum_i' e^{-ikr_i\{\alpha\alpha_i + \beta\beta_i + (\gamma-1)\gamma_i\}} f_i \tag{20}$$

The primes have been dropped since the subscripts denote the quantities referring to atoms.

Since there are no phase relations between the several molecules which simultaneously scatter the electron beam, equation (20) is squared to obtain the expression for intensity before the averaging process is carried out.

$$I = \Psi\Psi^* = \frac{a^2}{R^2} \left| \sum_i' e^{-ikr_i\{\alpha\alpha_i + \beta\beta_i + \gamma_i(\gamma-1)\}} f_i \right|^2 \tag{21}$$

Transforming the square into a double summation,

$$I = \frac{a^2}{R^2} \sum_i' \sum_j' f_i f_j e^{ik\{r_i[\alpha\alpha_i + \beta\beta_i + (\gamma-1)\gamma_i] - r_j[\alpha\alpha_j + \beta\beta_j + (\gamma-1)\gamma_j]\}} \tag{23}$$

As in equation (10)

$$r_i[\alpha\alpha_i + \beta\beta_i + (\gamma-1)\gamma_i] = \overline{r}_i \cdot \overline{A}$$

where $\overline{A}$ has the components α, β, $\gamma-1$ and $|\overline{A}| = 2\sin\theta/2$

Then

$$I = \frac{a^2}{R^2} \sum_i \sum_j' f_i f_j e^{ik\overline{r}_{ij}\cdot\overline{A}} \qquad \text{where } \overline{r}_i - \overline{r}_j = \overline{r}_{ij}$$

and as before

$$I = \frac{a^2}{R^2} \sum_i' \sum_j' f_i f_j e^{i\mu r_{ij}\cos\eta_{ij}} \tag{24}$$

Each element of this double summation is averaged by multiplying by $d\Omega \ (= \sin\eta_{ij}\, d\eta_{ij}\, d\phi)$, integrating and dividing by 4π. This process depends upon the assumption that all spatial orientations of the molecule are equally probable.

$$\left[e^{i r_{ij}\mu\cos\eta_{ij}}\right]_{av.} = \frac{1}{4\pi}\int_0^{\pi}\int_0^{2\pi} e^{i\mu r_{ij}\cos\eta_{ij}} \sin\eta_{ij}\, d\eta_{ij}\, d\phi$$

$$= \frac{\sin\mu r_{ij}}{\mu r_{ij}}$$

Therefore,

$$I = \frac{m^2\varepsilon^4}{4h^2}\frac{1}{R^2}\sum_i\sum_j f_i f_j \frac{\sin x_{ij}}{x_{ij}} \qquad (25)$$

where

$$x_{ij} = 4\pi r_{ij}\frac{\sin\theta/2}{\lambda}$$

The double summation is carried out as indicated over all the atoms in the molecule. r_{ij} is the separation of the i^{th} and j^{th} atoms, θ is the scattering angle and λ is the de Broglie wave-length.

This is the equation (except for the constant factor) which was developed by Debye for the scattering of X-radiation by gases, and since it is now shown to be equally applicable to electron diffraction it is the fundamental description of the elastic scattering of electrons by gases.

EXPERIMENTAL PROCEDURE

Apparatus. The experiment is carried out by causing a well defined beam of electrons all traveling with the same velocity to intersect a jet of the vapor of the substance to be studied, the scattered electrons being recorded on a photographic film set at right angles to the direction of the initial beam.

The source of electrons is a cathode of the hot filament type. Plate I gives the constructional details of the cathode. The filament of 0.007" tungsten wire is shaped like a hairpin with the two limbs at an angle of about 70°. The ends are supported by a pair of clamps, one of which is fastened to a 1/8" Monel metal rod, the other to a 3/8" thin walled tube. The rod and the tube form the two filament leads and are insulated from each other by a short section of Pyrex tubing at the filament end and mica sleeves and washers at the other end. The tube is in two parts, the right half in the photograph is thin walled Monel metal and the left half is thick walled copper which conducts heat through the vacuum joint to the radiator at the extreme left.

The filament holder is supported in a circular brass plate by a pair of nuts, the joint being insulated by mica and made vacuum tight with shellac. The plate is supported by a three-armed dural casting. A second casting and brass plate support a one inch Monel tube which encloses the filament holder and terminates in a focussing cup, which lies at the extreme right in the illustration. By virtue of the insulated joint supporting the filament this cup may be placed at any desired potential with respect to it.

The whole arrangement is supported on a brass plate which is bolted to the plate on the end of the large glass tube. The glass is shown in broken section. The joint between the two plates is made by a rubber gasket so that the complete cathode is very easily removed.

Because of the two ball and socket joints, which appear at the lower edge of the illustration, and the two sylphon connections the filament may be moved around inside the cup; and as a second independent movement the filament and cup together may be moved with respect to the anode. The bolts through which these movements are controlled are turned with the aid of <u>insulated</u> handles in order that, with the high potential on, the effect of these adjustments on the focussing of the electron beam may be observed directly on the fluorescent screen. The saving in time and effort through the direct observation of the focussing adjustments cannot be over-emphasized.

Plate II shows the anode arrangement. The anode itself is a $\frac{1}{2}$" steel tube with a two inch disc facing the cathode an inch away. The steel tube carries the collimating device which consists of a four inch copper tube having a 0.2 mm. hole and a platinum foil with a 0.4 mm. hole, supported by a short copper cylinder. The copper tube was made by milling a scratch in each half of a longitudinally split cylinder while the hole in the foil was punched with a needle. The cone subtended by this arrangement of holes has a two millimeter cross-section at the position of the photographic film thirty centimeters away; but the long fine hole has a focussing effect on the beam which reduces the central image diameter to less than one millimeter.

The gas is introduced from below through a 0.1 by 1.0 mm. jet supported on a tapered brass joint. The position of the nozzle over the brass taper is slightly eccentric to allow for accurate alignment with the electron beam. On the opposite side of the beam is a copper

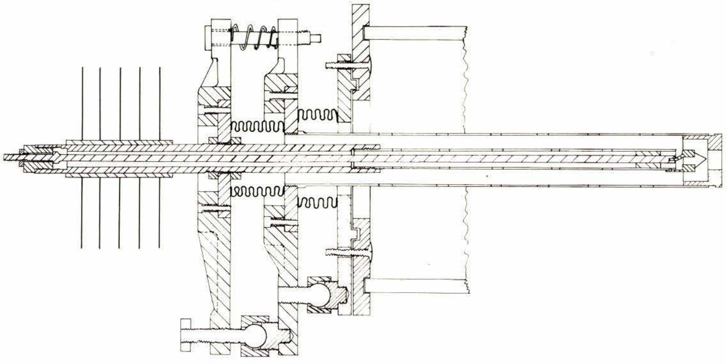


Plate I

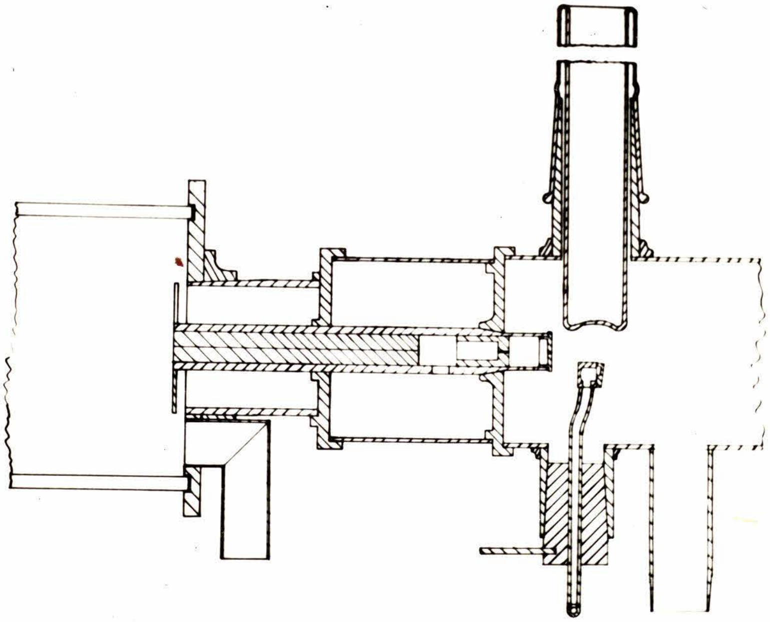


Plate II

surface cooled by liquid air from the outside so that much of the gas introduced is condensed there. Separate two stage diffusion pumps are used to maintain the vacuum in the electron tube and in the observation chamber. Introduction of gas into a space which must be kept at very low pressure (to prevent extraneous film fog) necessitates the use of a large charcoal tube as an aid to the pump. This tube is not shown in Plate II.

The photographic film is mounted on a vertical circular disc which rotates inside a vacuum tight container just slightly larger than the film holder. The film holder carries a willemite screen for visual observation as well as film for three exposures. These are brought into position by a magnetic control from the outside. A door and a window on the back allow respectively for loading the camera and for observing.

The electrons are accelerated with about fifty thousand volts taken from the secondary of a high voltage transformer. The slow electrons which are produced through part of each cycle are effectively prevented from leaving the cathode by a two hundred volt negative potential on the focussing cup around the filament. This value for the negative bias was determined by observing on the willemite screen the influence of a strong magnetic field on the central electron beam. The potential, which was taken from batteries, was increased until the central image was deflected by the field without the appearance of a "tail" of slow electrons. The homogeneity of the beam is also indicated by the sharpness of the rings obtained in scattering experiments with gold foils.

Exposures are made by opening the stop-cock which connects the gas reservoir with the nozzle and simultaneously closing the primary circuit of the high potential transformer. The time of an exposure is of the order of one-half second, though for some substances as many as five exposures are made on the same film. The gas pressure in the reservoir should be about one-half atmosphere. With these conditions and the collimating device described above a space current of fifty to one hundred microamperes is sufficient.

A calibration of the wave-length furnished by the accelerating potnetial was obtained with the aid of photographs of gold. The structure of gold determined by electrons was checked by Thomson with the generally accepted one determined by X-radiation; hence, measurements of gold photographs constitutes a convenient method of standardization. The wave-length used in most of the following experiments was 0.0566 Å.

The photographs obtained show from two to six rings whose shapes and positions are used in the analysis for the structure of the molecules of the gas.

Interpretation of Photographs. The photographs are interpreted by comparison with theoretical intensity curves calibrated with the aid of the following formula derived above:

$$I = k \sum_i \sum_j f_i f_j \frac{\sin x_{ij}}{x_{ij}} \qquad x_{ij} = 4\pi l_{ij} \frac{\sin \theta/2}{\lambda}$$

Since $f_i \left(= \frac{Z_i - F_i}{\sin^2\theta/2/\lambda^2}\right)$ is a function of $\frac{\sin \theta/2}{\lambda}$, an approximate calculation is made using Z_i in place of f_i. A sample formula is the following one for the tetrahedral model for carbon tetrachloride:

$$I = Z_C^2 + 8 Z_C Z_{Cl} \frac{\sin x}{x} + Z_{Cl}^2 \left(4 + 12 \frac{\sin \sqrt{8/3}\, x}{\sqrt{8/3}\, x}\right)$$

For a given substance such cruves are prepared for all of the probable models corresponding to different relative positions of the atoms. The most probable model is that leading to the curve which permits the best correlation of maxima and minima with the apparent maxima and minima seen on visual examination of the film. This correlation must be satisfactory both qualitatively and quantitatively; that is, the general appearance of the theoretical curve (such as the presence of a double maximum) must be reproduced in the photograph, and in addition the interatomic distances as calculated from the measured diameters of all of the rings must be consistent. A detailed discussion of the comparison between theory and experiment is given for each substance in the following section.

The necessity of a standardized procedure for measuring the photographs must be emphasized. The negatives are laid against a five by seven inch ground glass screen in an Eastman Safelight illuminated by a sixty watt bulb. The points of a pair of dividers are placed at the positions of greatest apparent density on opposite sides of a ring and the separation is measured on a steel millimeter scale. The diameter is measured this way in several directions, and the average of the results is used in the subsequent calculation. Any variation from this procedure, especially in the matter of illumination while measuring, has always led to inconsistent results.

The measurement of an asymmetric ring (such as one of a pair of rings close together or one ring with a very different rate of decline in apparent density on the inside and outside) always gives a value for the interatomic distance which is different from that calculated from any sharp, well-defined ring. The discrepancy between the position of an asymmetric spectral line as measured subjectively with a filar micrometer and objectively by a recording micro-photometer has been thoroughly investigated by St. John and Ware.[12] They show that the apparent maximum of such a line measured subjectively is always shifted toward the side of greater contrast, and the effect on the measurement of a doublet is such that the apparent separation is greater than the true. The cause for this shift lies in the psychological effect of the difference in brightness of the background on the two sides of the line. A particularly clear example of this effect in the measurement of electron diffraction photographs has been found in the case of sulfur hexafluoride; here the inner component of a double ring is shifted in by six percent and the outer is shifted out by six percent as determined by a comparison of the corresponding interatomic distances with those calculated from two sharp single rings lying farther out in the photograph. While the general appearance of the asymmetric characteristics of such a photograph is very useful in the qualitative comparison with theoretical curves, good quantitative agreement among all the rings is impossible. The exact size of the correction to be applied can not be predicted, but an allowance for the effect may be made by determining the interatomic distance only from the sharply defined single rings.

The measurement of the positions of minima on the photograph also involves the St. John effect. This is particularly apparent in the first minimum because of the extreme density in the central image. Measurement of the photographs of fifteen different compounds taken with various intensities shows that the position of the first minimum is always shifted out (or toward the side of the lower contrast) by from eight to ten percent.

The observed values for interatomic distances are found to be somewhat dependent on the apparent density of the photograph. A small correction (1 or 2%) is sometimes applied as the result of comparison with standard intensity photographs of carbon tetrachloride. This process is explained in the published material on the hexafluorides included below.

A complete interpretation of the photograph would require recalculation of the theoretical intensity curve with the use of the f values corresponding to the interatomic distances given by the simpler treatment, and the quantitative comparison of this curve with the observed intensity curve. The very rapid decrease of intensity with increasing angle θ, which is explained theoretically by the presence of the factor $\sin^4 \theta/2$ in the denominator of the intensity formula, makes an accurate knowledge of the behaviour of photographic emulsions toward electrons necessary for the interpretation of microphotometer records of diffraction photographs. While this knowledge is still lacking the simpler treatment may be justified by the self-consistence of the results to which it leads and their agreement with the results of x-ray diffraction and band spectral investigations. The probable error in distance determined by the simpler treatment is ±2%, which is the same order of accuracy claimed by Wierl.

APPLICATIONS

Cyanogen and Diacetylene. Cyanogen and diacetylene have been the subject of both band spectral and electron diffraction investigations. They have been studied again here because the relative complexity of the spectroscopic method has prevented a complete analysis and the previous electron diffraction work led to unsatisfactory results.

The general considerations which lead to a choice of possible models for cyanogen are applicable to a large class of compounds and accordingly will be outlined in some detail for the case of cyanogen.

The possible electronic structures which may be written for C_2N_2 in accordance with the quantum mechanical rules for the formation of electron pair bonds[13] and which do not correspond to high lying energy states are represented as follows:

$:N:::C:C:::N:$ I

$:N:::C:\overset{+}{C}::\overset{\cdot\cdot -}{N}:$ II

$:\overset{\cdot\cdot -}{N}::\overset{+}{C}:C:::N:$ III

$:\dot{N}::C::C::\dot{N}:$ IV

$:\overset{\cdot\cdot -}{N}::C::C::\overset{+}{N}:$ V

$:\overset{+}{N}::C::C::\overset{\cdot\cdot -}{N}:$

Only the electrons in incomplete shells are indicated. The charges for the atoms are obtained on dividing the electrons of the shared pairs.

The choice of one of these structures as the correct representation of the molecule in its normal state depends upon the result of theoretical calculations of the energy. If the value obtained for one should lie considerably below the values for all of the others that structure would be correct. No one of the above structures can be assigned to the molecule, however, if two or more of them have close-lying energy values. The method for determining how many different structures are to be considered and the relative importance of their contributions to the true structure is provided by quantum mechanics. A linear combination of the wave functions representing all of the possible structures is used in the energy integral,

$$E = \int \Psi H \Psi^* d\tau$$

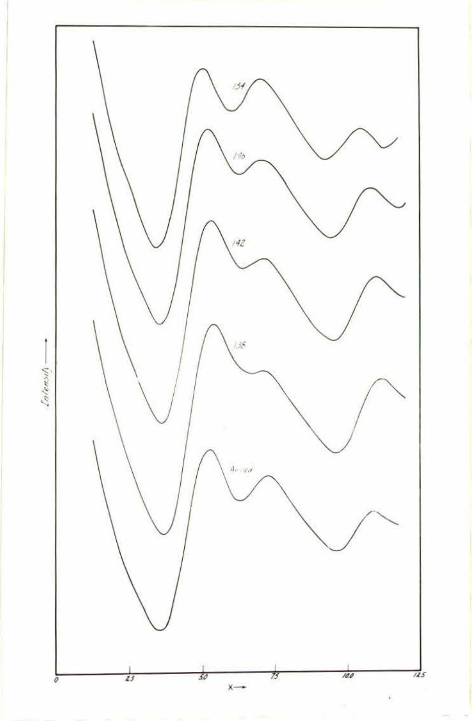
and the integral is minimized with respect to variation of the coefficients with which the separate wave functions appear. According to the well-known theorem due to Eckart the combined wave function which gives the lowest theoretical value for the energy is the most nearly correct representation of any system; accordingly, the relative values of the coefficients of the simple functions appearing in the minimized integral represent the criterion for choice among the elementary structures given above.

The effect on interatomic distances of including more than one electronic structure of the Lewis type in the representation of the of the structure of a molecule must be known since the observation of the interatomic separations is the experimental test to be applied here to the foregoing considerations. It has been pointed out by Pauling[14] that in such a case the observed distance between two atoms corresponds to that of the strongest type of bond involved in the resonating structure and not to a mean (if the elementary structures are of equal importance, i.e., if their respective wave functions have equal coefficients). Values for the interatomic distances which are intermediate between those corresponding to two different types of bond will be observed only when the structure containing the weaker type is relatively more important than the other. Accordingly, with the aid of a table of covalent radii[14] based upon observed distances in non-resonating molecules the observed distances in resonating structures lead to an analysis of the contributing elements.

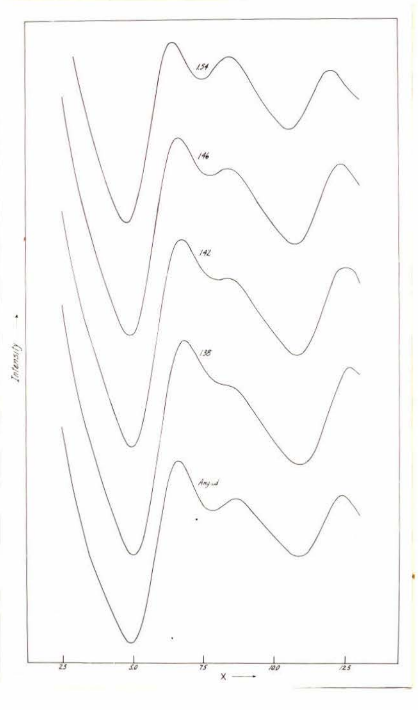
The foregoing rule makes it possible to predict probable atomic configurations in cyanogen. The contribution of I is certainly as important as any single structure above because of the two strong bonds which it contains; therefore, the only necessary consideration is the effect of combining the others with I. II and III would have no effect on distances. IV, V and VI would tend to decrease the carbon-carbon distance toward that of a double bond. Of these latter three, IV is the most important because each atom is electrically neutral and the molecule has a lower energy value than V or VI.

Four theoretical intensity curves have been calculated in which the ratio of carbon-carbon to carbon-nitrogen distance has the values 1.54/1.16, 1.46/1.16, 1.42/1.16 and 1.38/1.16. In the accompanying figure the curves are designated with the numerators of these fractions. The first corresponds to I alone, the fourth to complete resonance of I with IV, and the second and third to two stages of partial resonance. The most important qualitative feature of these curves is the disappearance of the second maximum in going from the first to the fourth curve.

The photographs of cyanogen are characterized by a sharp first ring with a broad "shelf" slowly falling off toward the outside edge. This is followed further out by a maximum which is sharply defined on both sides. This qualitative appearance eliminates the single bond model since our experience with the hexafluorides[15] indicates that such a double maximum is duplicated in the appearance of the photograph.



Cyanogen



Diacetylene

The experience of Wierl[16] with cyanogen supports the elimination of the same model. His unwillingness, however, to alter the two bond distances from the chosen values, 1.52 and 1.20, led him to a very improbable conclusion. He relinquished the linearity of the molecule and assumed an angle of 150° between the carbon-carbon and carbon-nitrogen bonds and claimed thereby to find satisfactory quantitative agreement with his photographs.

Three objections must be brought against the conclusion of Wierl. The first is that in no other case has a compound containing a triple bonded carbon atom been measured by any method and found to have the single bond not in a straight line with the triple bond. The second is that in view of the foregoing discussion of resonance between several electronic structures and the abundant evidence adduced by Pauling[14] and furnished by the results of this investigation there is no need to consider non-linear models. The third objection is to be found in the appearance of the fifth curve in the illustration. In this the second maximum is only a little less prominent than in the first curve. The fifth curve was calculated from the 150° model but using the bond distances 1.54 and 1.16 taken from the table of covalent radii mentioned above. The discrepancy with Wierl's curve is probably due to his use of somewhat different bond distances which appear to correspond to the case of diacetylene. His use of the same curves for cyanogen and diacetylene is open to the objection that it neglects the difference in the carbon-nitrogen and carbon-carbon triple bond distances in the two compounds. This leads to different values for the central carbon-carbon bond distances in the two compounds, a result which is highly improbable because of the identical electronic arrangement. Wierl's support of the model with the 150° angle is, therefore, the result of incorrect interpretation of the photographs.

The quantitative comparison of the photographs is shown in the following table:

	$\frac{\sin\theta/2}{\lambda}$	1.46		1.42		1.38	
		x	a	x	a	x	a
1st min.	.352	4.77	1.08	4.85	1.10	4.88	1.10
1st max.	.427	6.45	1.20	6.55	1.22	6.63	1.24
2nd min.	.718	10.63	1.18	10.82	1.20	10.85	1.21
2nd max.	.831	12.03+	1.15	12.23	1.17	12.45	1.19

The values in the first column are the averages from two photographs. The x values are taken from the theoretical curves for the respective models. The a values correspond to the carbon-nitrogen triple bond distance for which 1.16 is the expected value.

Comparison with the standard photograph shows that no density correction is to be applied.

The values for the first minimum are from eight to ten percent low as is to be expected on the basis of theexplanation given above. The first maximum is of the type which shows the St.John effect and hence the corresponding a value is larger than the correct one. The sharp second maximum affords a correct estimation of the value of a. The "1.38" model is not satisfactory, but the other two can scarcely be distinguished The most probable values are chosen as follows:

C-N = 1.16 ± 0.02 Å

C=C = 1.43 ± 0.03 Å

These results show that the single bond models are somewhat more important than the double bond models in the resonating structure which represents the structure of cyanogen.

The theoretical discussion for diacetylene is exactly the same as for cyanogen. The models calculated again vary from 1.54 to 1.38 for the central bond distance while the triple bond distance is 1.22 and the carbon-hydrogen bond is 1.06 throughout. It will be noticed that the subsidiary maximum in the angled model is relatively less prominent than in the case of cyanogen.

The qualitative comparison as before eliminates the single bond model; the quantitative comparison is indicated in the table.

	$\frac{\sin \theta/2}{\lambda}$	1.46		1.42		1.38	
		$\bar{x}$	$\bar{a}$	$\bar{x}$	$\bar{a}$	$\bar{x}$	$\bar{a}$
1st min.	.356	4.90	1.10	4.90	1.10	5.03	1.12
1st max.	.430	6.63	1.23	6.70	1.24	6.80	1.26
2nd min.	.753	10.75	1.14	10.80	1.14	10.90	1.15
2nd max.	.833	12.32	1.18	12.53	1.20	12.65	1.21

Comparison with the intensity standards indicates about 1% correction. The values calculated from sharp second maximum become 1.19, 1.21 and 1.22, respectively. The most probable values are

C-C at end = 1.21 ± 0.02

C-C in center = 1.43 ± 0.03

This agrees satisfactorily with the result for cyanogen.

Normal Electron-Pair-Bond Radii of Atoms

SINGLE-BOND RADII

H
0.29 Å (0.375 Å in H_2)

B	C	N	O	F
0.89	0.77	0.70	0.66	0.64
	Si	P	S	Cl
	1.17	1.10	1.04	0.99
	Ge	As	Se	Br
	1.22	1.21	1.17	1.14
	Sn	Sb	Te	I
	1.40	1.41	1.37	1.33

DOUBLE-BOND RADII

B	C	N	O
0.80	0.69	0.63	0.59
			S
			0.94

TRIPLE-BOND RADII

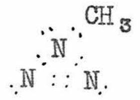
C	N	O
0.61	0.55	0.52

Methyl Azide. The study of methyl azide is particularly interesting because two quite different formulas have been proposed; in one the nitrogens form a three membered ring, in the other they have a linear arrangement.

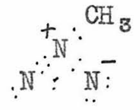
$CH_3 - N - N - N$

Crystal structure analysis of sodium and potassium azides[17] shows that the azide ion has the linear arrangement.

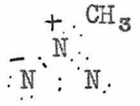
The possible electronic arrangements in which the nitrogens form a ring are as follows:



I



II

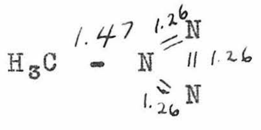


III

Since these structures have the same total number of bonds and none of the atoms are doubly charged, the contribution of each of these three should be the same. The inclusion of II and III in the group of resonating structures would require the methyl group to be coplanar with the ring.

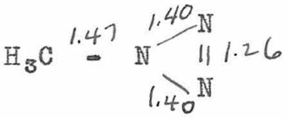
Four intensity curves corresponding to the ring model are shown in the first of the following illustrations. The corresponding models may be indicated as follows:

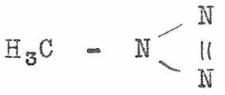
A



Coplanar

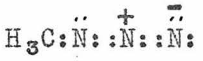
Complete resonance between I, II and III

B  Coplanar I alone

C  Non-coplanar I alone
Angle between C-N and N-N bonds 133½°

D Same as C except that bond angle = 110½°

The linear arrangement of nitrogen atoms is compatible with the following electronic structures:

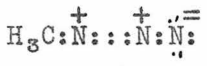


$H_3C{:}\overset{..}{N}{::}\overset{+}{N}{::}\overset{-}{\overset{..}{N}}{:}$

IV

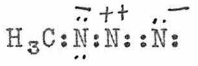
$H_3C{:}\underset{..}{\overset{..\,-}{N}}{:}\overset{+}{N}{:::}N{:}$

V



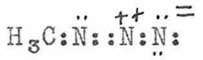
$H_3C{:}\overset{+}{N}{:::}\overset{+}{N}{:}\underset{..}{\overset{..\,=}{N}}{:}$

VI



$H_3C{:}\underset{..}{\overset{-}{\overset{..}{N}}}{:}\overset{++}{N}{::}\overset{..\,-}{N}{:}$

VII



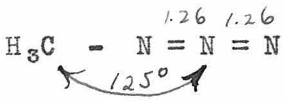
$H_3C{:}\overset{..}{N}{::}\overset{++}{N}{:}\underset{..}{\overset{..\,=}{N}}{:}$

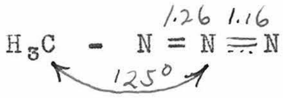
VIII

In this group IV and V should contribute equally since the total number of bonding electron pairs is the same and the arrangement of formal charges is nearly the same. VI should be considerably less important since it has two adjacent atoms with charges of the same sign. VII and VIII undoubtedly make some contribution but they would have no effect on the interatomic distances in any set of structures in which IV is prominent.

Intensity curves corresponding to the following models were calculated:

E $H_3C \overset{1.47}{-} N \overset{1.10}{\equiv} N \overset{1.10}{\equiv} N$ Collinear Complete resonance between IV, V + VI

F  Linear azide group IV alone

G  " Partial resonance between IV and V

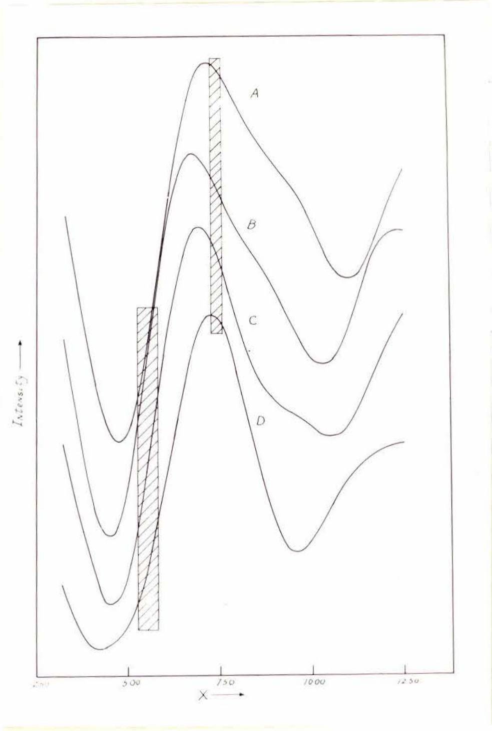
H - 100°	$\underset{\curvearrowright 100^\circ}{H_3C - N} \overset{1.26}{=} N \overset{1.10}{\equiv} N$	Linear azide group	Complete resonance between IV and V
H - 125°	Same as H-100° except for indicated angles	"	"
H = 129°10'			
H - 136° 41'			
H = 150°			

In all of the calculations the carbon-hydrogen distance was taken as 1.06 and the carbon-nitrogen as 1.47. Interference effects between the hydrogen and nitrogen atoms were neglected.

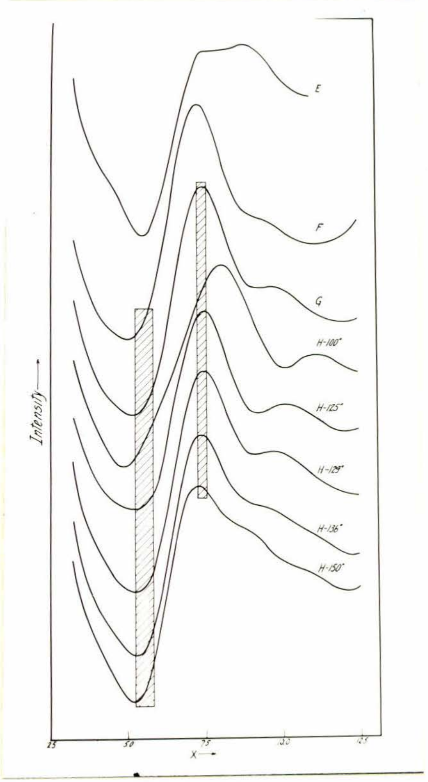
Five photographs of methyl azide show only one maximum in the 6° range of angles allowed by the dimensions of the apparatus. This maximum is exceedingly sharp and distinct, and is susceptible to measurements of greater than the usual accuracy.

Qualitative comparison with all of the curves leads immediately to the elimination of E. Since VI has the most highly charged atoms of all of the three structures which make up model E, the elimination of this model means that VI makes a negligible contribution to the true structure of methyl azide. It may be pointed out that the isoelectronic structure of N_2O, $:\overset{=}{\underset{\cdot\cdot}{\ddot{N}}}:\overset{+}{N}::\overset{+}{O}:$ which also has charges of the same sign on adjacent atoms, has been found to make only a very small contribution to the true structure of the compound.[18]

The quantitative comparison may conveniently be made in a somewhat different manner than before because of the large number of different models. The assumed interatomic distances are combined with the observed values of $\frac{\sin \theta/2}{\lambda}$ for the first minimum and maximum to obtain "observed" values of x for the first minimum and maximum of the theoretical curves. The reliability of this procedure is entirely



Ring Model

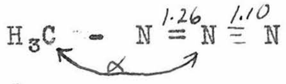


Linear Model

satisfactory because the atomic radii taken from the table have been tested for a variety of compounds; and any analysis taking into account the effect of resonance on interatomic distances which gave values appreciably different from those obtained with the aid of the table would be rejected. The observed X values are indicated on the curves together with the limits of uncertainty. It will be noticed that the limits for the first minimum are very broad to allow for the ten percent shift which is always observed. The indicated limits for the first maximum are ±2%. It is very certain that any model corresponding to a curve whose first minimum and maximum do not both fall within the indicated ranges must be neglected.

No ring model is acceptable since all of the first minima are well outside of the allowable range. A choice must therefore be made among the models which have a linear azide group. Among the corresponding curves H = 100° is eliminated by the position of its maximum and F by the position of its minimum. This leaves G, which represents partial resonance between IV and V, and the remaining H curves representing complete resonance with variation in angle. While the experimental agreement with G is almost as good as with the H curves, the probability of complete resonance between IV and V seems very high since it is observed in the cases of N_3^-, CO_2 and N_2O[14,18] whose structures are isoelectronic with that of methyl azide.

The most probable configuration is the following:



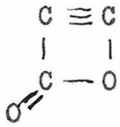
$$H_3C - N \overset{1.26}{=} N \overset{1.10}{\equiv} N$$

with $\alpha = 133 \pm 15°$. The uncertainty in the experimental determination of the distances is not larger than ±2%.

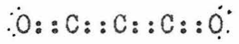
The value of the angle is not determined very accurately. 125° would be expected for the case of a tetrahedral atom having one double and two single bonds, as in the case of ethylene. In methyl azide the angle is probably a little larger since the extra electron pair on the nitrogen atom is not bonded to a third atom.

Carbon Suboxide. Another compound which lends support to the resonance considerations is carbon suboxide. It, too, has had a linear and a ring formula proposed.*

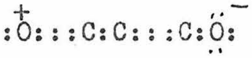
$O = C = C = C = O$



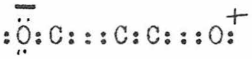
The electronic structures for the linear model are:



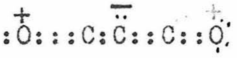
$:\ddot{O}::C::C::C::\ddot{O}:$ I



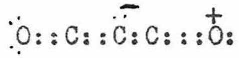
$:\overset{+}{O}:::C:C:::C:\overset{-}{\ddot{O}}:$ II



$:\overset{-}{\ddot{O}}:C:::C:C:::\overset{+}{O}:$ III



$:\overset{+}{O}:::C:\overset{=}{C}::C::\overset{+}{\ddot{O}}:$ IV



$:\ddot{O}::C::\overset{-}{\ddot{C}}:C:::\overset{+}{O}:$ V

III is the reverse of II and V that of IV.

Resonance among all five would give a model whose distances corresponded to triple bonds throughout. The same result would follow from a combination of II and III with I. Only one calculation is needed for the representation of all models in which the bond type is the same throughout the molecule since the ratio of carbon-carbon to carbon-oxygen distance is constant under that restriction. The curve A, therefore, may represent the resonance of all five, the resonance of I, II and III; I alone; or any intermediate state of resonance of I with II and III. The curve B represents resonance of I with IV and V.

The photographs show two quite distinct rings. There is no indication of the step-wise decrease in intensity following the first maximum as shown in B; therefore, this model is eliminated. The following table is given for A:

---

*The ring structure is very highly improbable, however, because bonds of the type indicated can not assume the angles which are necessary for the formation of a four-membered ring. For that reason it is not considered in the following discussion.

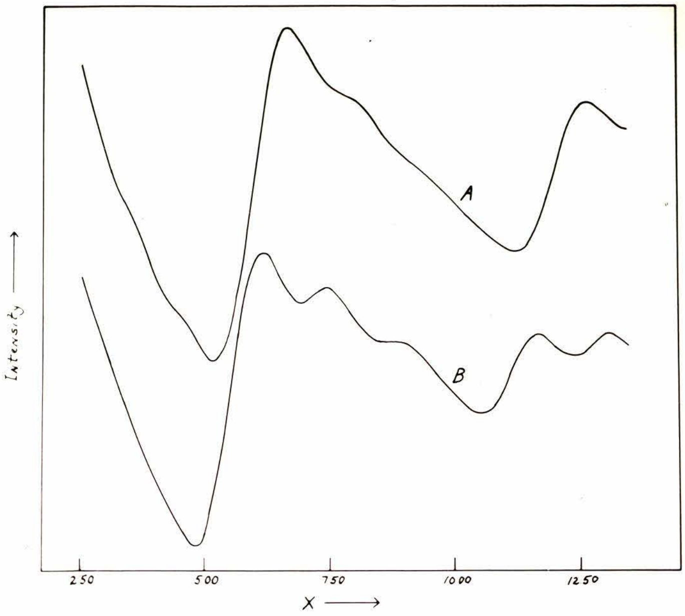
	$\frac{\sin \theta/2}{\lambda}$	x	a
1st min.	.367	5.18	1.12
1st max.	.438	6.66	1.21
2nd min.	.756	11.22	1.18
2nd max.	.849	12.70	1.19

The average value of a is 1.193 (with the usual neglect of the first minimum). The small correction required by comparison with the density standard raises this value to 1.20. Accordingly,

C-O distance = 1.20 ± .02 Å

C-C distance = 1.28 ± .02 Å

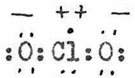
It should be pointed out that elimination of B signifies only that the contribution of II and III is at least as important as that of IV and V. The carbon-oxygen triple bond is 1.13, the double bond is 1.28; the intermediate value which is observed indicates that some resonance occurs but that I is more important than any of the others.



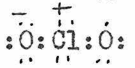
Carbon Suboxide

Chlorine Dioxide. Chlorine dioxide is one of a small class of compounds which show an exceptional stability for molecules having an odd number of electrons. Evidence is obtained in the electron diffraction investigation of ClO_2 which supports the explanation of these unusual properties based upon the formation of the three-electron bond.

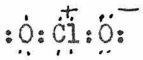
In accordance with the procedure used in the foregoing discussions all of the possible structures involving electron pair bonds are formulated.


$:\overset{-}{O}:\overset{++}{Cl}:\overset{-}{O}:$

I


$:\overset{-}{O}:\overset{+}{Cl}:O:$

II


$:O:\overset{+}{Cl}:\overset{-}{O}:$

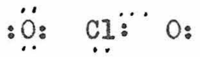
III

The unsymmetrical arrangement Cl-O-O is improbable for chemical reasons.

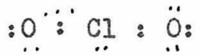
Normal chlorine and oxygen are rather near to each other on the electronegativity scale[19] and the electronegativity of positive chlorine is greater than that of neutral chlorine, and may be nearly equal to that of oxygen, so that the transfer of one electron from oxygen to chlorine in ClO_2 may well involve only a small change in the energy of the molecule. Structures I, II and III above would then correspond to energy levels near to one another.

The criterion for the formation of a three-electron bond is that two structures, in one of which there is an unshared pair of electrons on one atom and a single electron on the other, and in the other the single electron and the pair are interchanged, have nearly the same energy. It has been shown[20] that in this case a lower (and hence more nearly correct) value for the energy is obtained by taking a linear combination of the wave functions representing the two structures than corresponds to the use of either function alone. This extra resonance energy which serves to stabilize the molecule may be ascribed to the formation of a bond with the three electrons in the same way that the interchange of two single electrons on two atoms affords a resonance energy which is the principal energy of the electron-pair bond. The formation of the two kinds of bonds may be indicated diagrammatically in the same manner, that is, by placing two dots between the atoms for the electron-pair and three dots for the three electron bond.

Since structures I and II or I and III taken together meet the conditions for the formation of a three-electron bond, a better representation of ClO_2 is given by the two formulas:



$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:\ \underset{\cdot\cdot}{Cl}\overset{\cdot\cdot\cdot}{:}\ O:$ IV



$:\underset{\cdot\cdot}{O}\overset{\cdot\cdot\cdot}{:}\underset{\cdot\cdot}{Cl}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:$ V

In both IV and V one oxygen atom is bonded to chlorine by an electron-pair bond and a three-electron bond, and the other by an electron-pair bond alone. IV and V have exactly the same energy since one is the reverse of the other; accordingly, the observed chlorine-oxygen separation will be the same for both bonds and should correspond to the combined electron-pair-three-electron bond distance.

In the investigation[20] of helium molecule ion He_2^+ the three-electron bond is found to have the same energy as a one-electron bond and about two-thirds of the energy of an electron-pair bond; and the distance is about half again as large as that of the corresponding electron-pair bond. On this basis the combination indicated here in ClO_2 should be roughly equivalent to one and one-half single bonds or a little more than midway between a single and a double bond.

A further comparison may be made with nitric oxide which has the structure:

$$\mathrm{N} \overset{\cdot\cdot\cdot}{::} \mathrm{O}$$

Here the compound bond consists of one three-electron and two electron-pair bonds. The observed distance[21] is 1.15 Å which is midway between the double and triple bond distances taken from the table, 1.22 Å and 1.07 Å, respectively. Since the single and double bond distance for Cl-O are 1.65 Å and 1.48 Å, a reasonable estimate for the bond distance in ClO_2 is 1.56 Å.

Theoretical intensity curves for six molecular models corresponding to a range of bond angles from 50° to 180° are reproduced in the figure. It will be noted that thepositions of the maxima and minima change very slightly throughout the range. This is explained by the large scattering power of chlorine relative to that of oxygen; the interference effects observed arise almost exclusively from the chlorine-oxygen separation so that the effect of the change of the oxygen-oxygen separation with variation of the bond angle is scarcely detectable. In the following table are given the results of the observations as interpreted with the use of each of the theoretical models.

	$\frac{\sin \theta/2}{\lambda}$ observed	180°		150°		125°		110°		90°		50°	
		x	a	x	a	x	a	x	a	x	a	x	a
1st min.	0.282	4.72	1.335	4.75	1.343	4.60	1.300	4.35	1.230	4.25	1.201	4.63	1.309
1st max.	0.397	7.55	1.514	7.60	1.524	7.80	1.564	7.92	1.588	7.72	1.548	7.90	1.584
2nd min.	0.556	11.13	1.592	11.12	1.590	10.65	1.524	10.80	1.545	11.20	1.603	11.15	1.595
2nd max.	0.737	13.85	1.496	13.90	1.502	14.30	1.545	13.90	1.502	14.15	1.528	14.30	1.545
3rd min.	0.921	17.45	1.508	17.40	1.504	17.10	1.478	17.40	1.504	17.05	1.474	17.30	1.495
Mean value			1.528		1.530		1.528		1.535		1.538		1.555
Average deviation			.033		.030		.027		.032		.037		.035

Final value Cl-O = 1.53 ± 0.03 Å

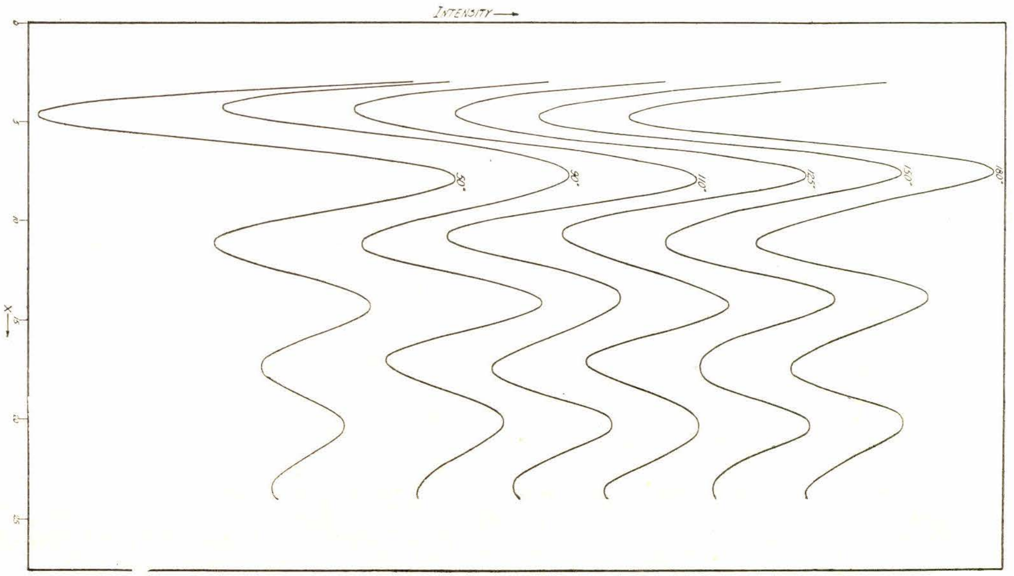


FIGURE 1

The most probable model is considered to be the one giving the most consistent a-values. Since in this case the deviation in the least consistent set is only a little larger than the experimental error no very definite conclusion in regard to the bond angle is afforded by the results. An angle near 120° is expected from theoretical considerations. The uncertainty in the value of the angle, however, does not affect the determination of the Cl-O separation. The most probable value for the Cl-O distance is thus found to be 1.53 ± 0.03 Å.

This observed value shows that no model with single bonds is satisfactory. Since it is impossible to write any structure with double bonds which does not involve high-lying energy states the experimental result substantiates the type of resonating structure which is represented in IV and V. The separation in the combined bond (1.53 Å) is nearer the double bond (1.48 Å) than to the single bond distance (1.65 Å).

The published[22] result of this work contained a numerical error which led to the incorrect value of 1.58 Å. This has been corrected.

Hexafluorides of Sulfur, Selenium and Tellurium. Reference[15] has already been made to the published results of the work on the hexafluorides. Attention may be called to the explanation of the density correction which appears as the first part of the following excerpt.

> It was found for a series of photographs made with carbon tetrachloride that the measured maxima and minima on any one photograph gave consistent values for the C-Cl separation, but that the value depended somewhat on the apparent density of the photograph. Thus the light film No. 123 and the dark film No. 126, for which data are included in table 1, lead to C-Cl = 1.79 and 1.76 Å, respectively, while very dark films lead to values as low as 1.73 Å, 4% smaller than the value C-Cl = 1.80 Å which we assume to be correct. In interpreting photographs of the hexafluorides we have compared the apparent density of each film with that of CCl_4 photographs, and have then made a corresponding correction in the interatomic distances, which, however, was always less than 3%.

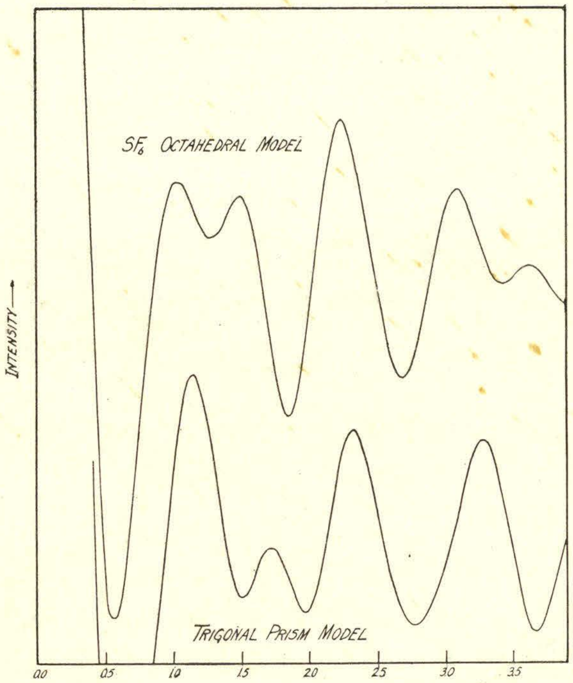


FIGURE 1

> Interatomic distances obtained in this way from rather indistinct photographs made with Br_2 and Cl_2 lay within 2% of the values known from band-spectral data.
>
> Two models were considered for each of the hexafluorides, in one the fluorine atoms being placed at the corners of a regular octahedron about the central atom, and in the other at the corners of a right trigonal prism with axial ratio unity; these were shown by Hultgren[5] to be the only

TABLE 1

CARBON TETRACHLORIDE

MAXIMUM	MINIMUM	x	FILM NO. 123, LIGHT $\sin \theta/_2/\lambda$	a = C-Cl	FILM NO. 126, DARK $\frac{\sin \theta/_2}{\lambda}$	a
1		0.765	0.212	1.80 Å	0.220	1.74 Å
	2	1.04	0.292	1.778	0.290	1.795
2		1.35	0.376	1.798	0.385	1.752
	3	1.69	0.474	1.784	0.484	1.746
3		2.01	0.558	1.801	0.569	1.766
	4	2.31	0.648	1.809	0.659	1.754
4		2.58	0.730	1.767	0.735	1.756
	5	2.90			0.826	1.756
5		3.215	0.905	1.777	0.905	1.777
			Weighted mean	1.788 Å		1.761 Å

SULFUR HEXAFLUORIDE

MAXIMUM	MINIMUM	x	FILM NO. 66, DARK $\sin \theta/_2/\lambda$	a = S-F
1		1.05	0.310	1.69 Å
	2	1.29	0.417	1.548
2		1.51	0.506	1.491
	3	1.86	0.619	1.502
3		2.255	0.729	1.547
	4	2.70	0.907	1.49
4		3.10	1.027	1.51

Corrected value S-F = 1.58 ± 0.03 Å

SELENIUM HEXAFLUORIDE

Second maximum $x = 2.250$

	FILM NO. 70, DARK	FILM NO. 71, DARK
$\sin \theta/_2/\lambda$	0.685	0.676
a = Se-F	1.643 Å	1.666
Corrected a	1.69 Å	1.71 Å

Average Se-F = 1.70 ± 0.03 Å

TELLURIUM HEXAFLUORIDE

Second maximum $x = 2.248$

	FILM NO. 80, DARK	FILM NO. 81, MEDIUM	FILM NO. 82, DARK
$\sin \theta/_2/\lambda$	0.618	0.620	0.628
a = Te-F	1.819	1.812	1.789
Corrected a	1.86	1.84	1.83

Average Te-F = 1.84 ± 0.03 Å

probable structures for molecules containing a central atom with six equivalent bonds. The intensity formulas used are illustrated by the following one, for the octahedral model of SF_6:

$$I/k = 2\pi Z_S^2 + 12 Z_S Z_F \frac{\sin x}{x} + Z_F^2 \left(12\pi + 24 \frac{\sin \sqrt{2}x}{\sqrt{2}x} + \frac{6 \sin 2x}{2x} \right)$$

with

$$x = 2a \frac{\sin \theta/2}{\lambda}$$

in which a is the S-F distance. The two curves for SF_6 are shown in figure 1.

The photographs from all three substances eliminate the prismatic models, the shapes and relative positions of the maxima and minima of the curves being in pronounced disagreement with the observed rings. Good agreement is obtained for the octahedral models, however. The two close inner maxima of the SF_6 curve appear as two distinct rings in the photograph. In SeF_6 and TeF_6 the increased scattering factors of the central atoms modify these two into a single broad maximum, and the photographs also show correspondingly a broad inner ring. The relative positions of maxima and minima when correlated with observed ring diameters lead to consistent values for the interatomic distances, as shown for SF_6 in the table. The error shown by the first maximum is probably due to the effect of the close second ring in causing low estimates of the ring diameter. The value 1.55 Å given by the sharp third maximum is the most reliable; this corrected by the factor 1.02 for the dark photograph leads to an S-F separation of 1.58 ± 0.03 Å. Measurements of the same sharp maximum on the SeF_6 and TeF_6 films lead to Se-F = 1.70 ± 0.03 Å and Te-F = 1.84 ± 0.03 Å.

The interatomic distances agree very well with those expected for an ionic structure. The sums of ionic radii[6] are 1.65, 1.78 and 1.92 Å, respectively, and these sums are expected to be somewhat larger than the equilibrium distances between small highly charged cations and large anions. The differences, 0.07, 0.08 and 0.08 Å, are very close to that between the observed Si-F distance 1.68 ± 0.02 Å in the crystal $(NH_4)_2SiF_6$ and the ionic radius sum 1.77 Å.

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[5] Hultgren, R., *Phys. Rev.*, **40,** 891 (1932).

[6] Pauling, L., *J. Am. Chem. Soc.*, **49,** 765 (1927).

Further work in the electron diffraction method of studying the structure of molecules is planned with two main objectives. The first is the development of experimental technic for the purpose of attaining a completely objective interpretation of the photographs and also for the purpose of extending the work to include the study of a large number of very interesting molecules which have very low scattering powers. The second objective is the assembling of sufficient data on resonating compounds to allow the formulation of a set of rules which will be the basis for predicting most probable structures among this very large class of substances.

I wish to acknowledge my indebtedness to Professor Linus Pauling for the inspiration and assistance which has made the research possible, and to Professor R.M.Badger for his invaluable aid during the design and construction of the apparatus. For the preparation of the hexafluorides I am indebted to Professor D.M.Yost, for diacetylene, cyanogen and methyl azide to Dr. G.W.Wheland, and for carbon suboxide to Dr. W.E.Vaughan.

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15. L.O.Brockway and Linus Pauling, ibid., 19, 68 (1933).

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20. Linus Pauling, ibid., 53, 3225 (1931);
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    Jenkins, Barton and Mulliken, Phys.Rev., 30, 150 (1927).

22. L.O.Brockway, Proc.Nat.Acad., 19, 303 (1933).

The Crystal Structure of Chalcopyrite $CuFeS_2$.

By

Linus Pauling and **L. O. Brockway** in Pasadena.

(With 3 figures.)

An investigation of the crystal structure of chalcopyrite was made in this Laboratory in 1917 by Burdick and Ellis[1]), who measured the angles and intensities of reflection in successive orders of the palladium K-doublet from seven different faces ground on a sphenoidal crystal. Their observations were completely explained by an atomic arrangement based on a pseudo-cubic unit of structure, with $a_0 = 5.24$ Å and $c_0 = 5.15$ Å (calculated from their reported angles of reflection by using the wavelength 0.5857 Å for $Pd\,K_\alpha$). No odd-order reflections were observed except from planes with all indices odd, showing that the structure must approximate a face-centered arrangement. Burdick and Ellis suggested a structure closely similar to that of sphalerite, the atomic positions being

$$2\,Cu \text{ at } 0\,0\,0,\ \tfrac{1}{2}\,\tfrac{1}{2}\,0$$
$$2\,Fe \text{ at } \tfrac{1}{2}\,0\,\tfrac{1}{2},\ 0\,\tfrac{1}{2}\,\tfrac{1}{2}$$
$$4\,S \text{ at } \tfrac{1}{4}\,\tfrac{1}{4}\,u,\ \tfrac{3}{4}\,\tfrac{3}{4}\,u,\ \tfrac{3}{4}\,\tfrac{1}{4}\,\bar{u},\ \tfrac{1}{4}\,\tfrac{3}{4}\,\bar{u}, \text{ with } u = \tfrac{1}{4}.$$

This structure is described on pages 280—281 of the Strukturbericht of Ewald and Hermann.

Burdick and Ellis had assumed u to be $\frac{1}{4}$ without discussion. A later study[2]) of data obtained from Laue photographs was said to lead to a value of 0.21. In neither of these investigations were any reflections reported except those corresponding to a face-centered arrangement, so that the assumed structure could hardly be considered to be very well substantiated by experiment, inasmuch as any structure derived from that of sphalerite by replacing half the zinc atoms by copper and the other half by iron would account for the data equally well.

Because of our interest in interatomic distances, we began the study of chalcopyrite with the idea of evaluating the parameter accurately.

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1) C. L. Burdick and J. H. Ellis, J. Am. chem. Soc. **39**, 2518. 1917.

2) R. Gross and N. Gross, N. Jb. Min. **48**, 113. 1923.

Using crystals from Joplin, Missouri, we prepared oscillation photographs and Laue photographs. On analyzing the Laue photographs, we found that the previously accepted structure is not correct. The true unit is twice as large as the pseudo-cubic unit described above, and the distribution of copper and iron atoms is completely different.

Unit of Structure and Space-group Symmetry.

A Laue photograph taken with the incident beam parallel to the *c*-axis of a thin crystal slip showed a four-fold axis and four symmetry planes; this together with the sphenoidal development of the crystals determines the point-group symmetry to be that of D_{2d}. The conventional arrangement of axes for this point-group places the *a* and *b* axes 45° from the vertical symmetry planes. Adopting this convention, data from oscillation photographs (45° oscillation of the crystal) of molybdenum radiation reflected from (001) and (111) of chalcopyrite led to a unit with $a_0 = 5.24$ Å and $c_0 = 5.15$ Å, as found by Burdick and Ellis. On assigning indices to the spots on the Laue photographs with the aid of a gnomonic projection, and calculating values of $n\lambda$ on the basis of this unit, it was found that most of the reflections, but not all, gave $n\lambda$ values greater than 0.24 Å, the short wave-length limit of x-rays in the incident radiation. On Laue Photograph No. 1, with the incident beam 5° from the *c*-axis, the forms {861} and {821} gave distinct reflections at $n\lambda$ values of 0.17 to 0.18 Å, while the forms {421} and {601} provided similar evidence by reflecting strongly at $n\lambda = 0.25$ to 0.30 Å and very weakly or not at all at $n\lambda = 0.40$ Å. Similar reflections with low $n\lambda$ values were observed on other Laue photographs; for example, Photograph No. 7, with the incident beam normal to a developed (111) face, showed definite reflections from the forms {861} and {645} at $n\lambda = 0.16$ to 0.18 Å. *These reflections eliminate the unit with* $a_0 =$ *5.24 Å and* $c_0 = 5.15$ *Å*, and all units with this value of c_0. They are accounted for, however, by the unit obtained by doubling c_0. This unit, with

$$a_0 = 5.24 \text{ Å}$$
$$c_0 = 10.30 \text{ Å}$$

accounts for all the data obtained from the five Laue photographs analyzed, and may be accepted as the true unit in the absence of any evidence requiring a still larger one. All indices used in the remainder of this paper are referred to this unit.

The unit contains 4 *CuFeS*$_2$, corresponding to a calculated density of 4.28, in good agreement with the observed value of 4.1—4.3.

On assigning indices and calculating $n\lambda$ values on the basis of this unit, it was found that forms such as $\{431\}$ give first-order reflections, eliminating the face-centered and end-centered lattices. No such reflections from forms with $h + k + l$ odd were observed, however; accordingly the lattice was assumed to be the body-centered lattice $\Gamma_t'\,(b)$. The only two space groups based on this lattice and isomorphous with the point-group D_{2d} are $D_{2d}^{11} - I\,\bar{4}\,2\,m$ and $D_{2d}^{12} - I\,\bar{4}\,2\,d$. Of these D_{2d}^{12} does not permit any reflections from forms $\{hhl\}$ with $\frac{1}{2}(2h+l)$ odd, whereas D_{2d}^{11} permits such reflections. No such reflections were observed, though several planes of this type were in positions favorable to reflection. Accordingly we have assumed the space group to be

$$D_{2d}^{12} - I\,\bar{4}\,2\,d.$$

We recognize that on account of the low intensity of all reflections except those corresponding to a face-centered pseudo-cubic arrangement the evidence for this space group is not overwhelming. We have found, however, that a structure based on this space group can be derived which accounts satisfactorily for all the x-ray data obtained, and so we believe this space group to be correct.

The Atomic Arrangement.

Reference to Wyckoff's tabulation of the results of the theory of space groups shows the following sets of equivalent positions to be available.

4a: $0\,0\,0,\ \frac{1}{2}\,0\,\frac{1}{4},\ \frac{1}{2}\,\frac{1}{2}\,\frac{1}{2},\ 0\,\frac{1}{2}\,\frac{3}{4};$
4b: $0\,0\,\frac{1}{2},\ \frac{1}{2}\,0\,\frac{3}{4},\ \frac{1}{2}\,\frac{1}{2}\,0,\ 0\,\frac{1}{2}\,\frac{1}{4};$
8c: $0\,0\,u,\ 0\,0\,\bar{u},\ \frac{1}{2}\,0\,\frac{1}{4}-u,\ \frac{1}{2}\,0\,\frac{1}{4}+u,$
$\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}+u,\ \frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}-u,\ 0\,\frac{1}{2}\,\frac{3}{4}-u,\ 0\,\frac{1}{2}\,\frac{3}{4}+u;$
8d: $\frac{1}{4}\,u\,\frac{1}{8},\ u\,\frac{3}{4}\,\frac{7}{8},\ \frac{3}{4}\,\bar{u}\,\frac{1}{8},\ \bar{u}\,\frac{1}{4}\,\frac{7}{8},$
$\frac{3}{4}\,\frac{1}{2}+u\,\frac{5}{8},\ \frac{1}{2}+u\,\frac{1}{4}\,\frac{3}{8},\ \frac{1}{4}\,\frac{1}{2}-u\,\frac{5}{8},\ \frac{1}{2}-u\,\frac{3}{4}\,\frac{3}{8}.$

The observed greater intensity of reflection of (400) over (200) eliminates the structure with $8\,S$ in 8c and $4\,Fe$ and $4\,Cu$ in 4a and 4b, leaving as the only possibility that with $4\,Cu$ in 4a, $4\,Fe$ in 4b, and $8\,S$ in 8d. The sulfur parameter u is easily seen to be required to lie in the neighborhood of $\frac{1}{4}$ by the observed intensities.

An oscillation photograph was taken from the ground face (112), using molybdenum radiation filtered through zirconia. The crystal was oscillated through 45°. The slits used were so wide that the incident divergent beam was permitted reflection from all parts of the face. Under these conditions the theoretical expression for the integrated intensity of reflection from $(n \cdot n \cdot 2n)$ is

$$I_{n \cdot n \cdot 2n} = \text{Constant} \cdot n \cdot \frac{1 + \cos^2 2\theta}{2 \sin 2\theta} \left| 4 (f_{0\,Cu} + f_{0\,Fe}) + (-i)^n \cdot 8 f_{0\,S} \sin 2\pi n u \right|^2 e^{-0.075\, n^2}. \quad (1)$$

Here the factor n results from the experimental conditions, under which the effective intensity of radiation impinging on the reflecting face increases linearly with the order of reflection. The temperature factor is calculated from the Waller expression[1]) with the use of an estimated characteristic temperature of 540°. In fig. 1 calculated values of I for four orders are given, obtained by introducing Pauling and Sherman's[2]) f_0-values in Equation (1). The observed intensities $n = 1$, very strong; $n = 2$, weak; $n = 3$, medium weak; $n = 4$, weak, require u to lie in the region between 0.204 and 0.296. The parameter can be further limited with the aid of data from Laue photographs. The estimated intensities of some Laue spots with λ-values between 0.36 and 0.40 Å

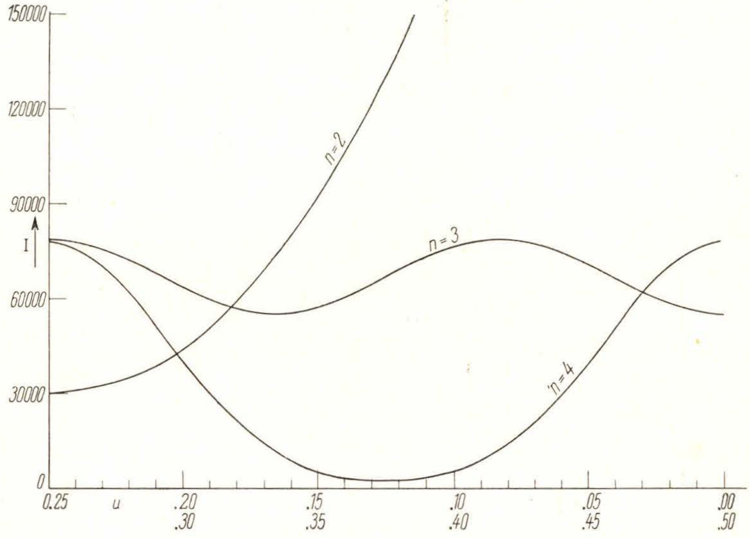

Fig. 1. Calculated intensities of reflections $\{n \cdot n \cdot 2n\}$ as functions of u. The curve for $n = 1$ lies above the top of the figure for all values of u.

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1) See R. W. James and G. W. Brindley, Proc. Roy. Soc. (A) **121**, 159. 1928.

2) Linus Pauling and J. Sherman, Z. Krist. **81**, 1. 1932.

are the following: {411}, 0.02; {325}, 0.05; {422}, 0.00; {501}, 0.00; {431}, 0.05; {5·5·14}, 0.15; in order of decreasing interplanar distance.

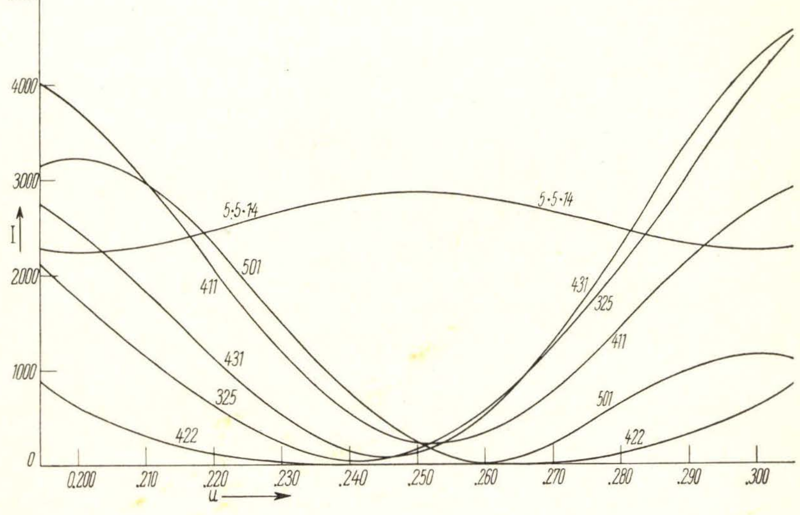

Fig. 2. Calculated intensities of reflection for various forms as functions of u.

In fig. 2 there are given intensities of reflection for these forms, calculated from the equation

$$I_{hkl} = \text{Constant} \cdot \frac{1 + \cos^2 2\theta}{2 \sin 2\theta} \cdot f_{0hkl}^2 \, e^{-\frac{0.122}{d^2_{hkl}}} \qquad (2)$$

with $f_{0hkl} = \sum_j f_{0j} \, e^{2\pi i (h x_j + k y_j + l z_j)}$

(The polarization and Lorentz factor given here do not correspond exactly to the Laue technique, but it is probable that the error introduced is not great.) It is seen from this figure that the comparisons {5·5·14} > {431} and {431} > {411} limit u to the region between 0.254 and 0.282. We accordingly chose as the value of the parameter

$$u = 0.27 \pm 0.01.$$

Description of the Structure.

The structure found, shown in fig. 3, is closely related to that of sphalerite, *ZnS*. Each sulfur atom is closely surrounded by four metal atoms, two copper and two iron, located at the corners of a nearly regular tetrahedron, and each metal atom is similarly surrounded by four sulfur atoms. The copper-sulfur distance of 2.32 ± 0.03 Å is somewhat greater than the iron-sulfur distance, 2.20 ± 0.03 Å.

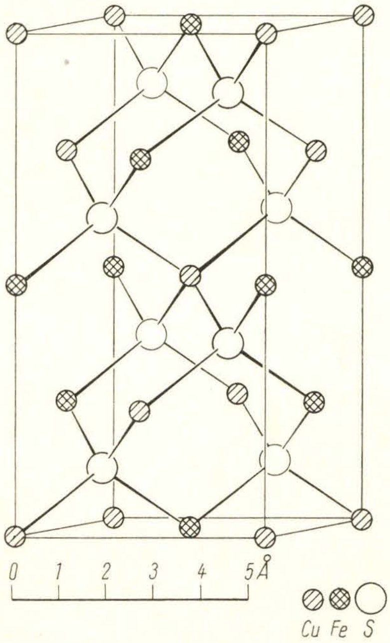

Fig. 3. The arrangement of atoms in the unit of structure of chalcopyrite. The sulfur atoms are drawn in the positions for $u = 0.25$.

The bonds in this crystal probably approach the shared-electron-pair type, as in other sulfides of transition metals. The question might be asked as to what the valences of the metal atoms are; that is, whether the formula of chalcopyrite should be wirtten $Cu^{I}Fe^{III}S_2$ or $Cu^{II}Fe^{II}S_2$. Some evidence is provided by a comparison of the observed interatomic distances and the radii of the elements. The tetrahedral electron-pair-bond radii effective in other crystals are[1]: S, 1.04 Å; Cu^{I}, 1.35 Å; Fe^{II}, 1.19 Å; Fe^{III}, 1.13 Å, with no value available for Cu^{II}, which, however, would be expected to be somewhat smaller than Cu^{I}. The radius sums $Cu^{I} - S = 2.39$ Å and $Fe^{III} - S = 2.17$ Å are seen not to be in good agreement with observation, so that the formula $Cu^{I}Fe^{III}S_2$ probably is not correct. It is probable that in chalcopyrite the atoms do not have fixed valences, but instead fluctuate between the two states $Cu^{I}Fe^{III}S_2$

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1) Linus Pauling and M. L. Huggins, Z. Krist., to be published.

and $Cu^{II}Fe^{II}S_2$. The interatomic distances are compatible with such a structure.

Summary.

Investigation of the tetragonal crystal chalcopyrite with the use of oscillation and Laue photographs has shown that the previously accepted structure is incorrect, and has resulted in the determination of a new structure. The unit of structure, containing $4CuFeS_2$, has $a_0 = 5.24$ Å and $c_0 = 10.30$ Å. The atomic arrangement, isomorphous with the space group $D_{2d}^{12} - I\,\bar{4}\,2\,d$, has

$$\begin{array}{lll} 4\,Cu & \text{in} & 0\,0\,0,\ \tfrac{1}{2}\,0\,\tfrac{1}{4},\ \tfrac{1}{2}\,\tfrac{1}{2}\,\tfrac{1}{2},\ 0\,\tfrac{1}{2}\,\tfrac{3}{4}; \\ 4\,Fe & \text{in} & 0\,0\,\tfrac{1}{2},\ \tfrac{1}{2}\,0\,\tfrac{3}{4},\ \tfrac{1}{2}\,\tfrac{1}{2}\,0,\ 0\,\tfrac{1}{2}\,\tfrac{1}{4}; \\ 8\,S & \text{in} & \tfrac{1}{4}\,u\,\tfrac{1}{8},\ u\,\tfrac{3}{4}\,\tfrac{7}{8},\ \tfrac{3}{4}\,\bar{u}\,\tfrac{1}{8},\ \bar{u}\,\tfrac{1}{4}\,\tfrac{7}{8}, \\ & & \tfrac{3}{4}\,\tfrac{1}{2}+u\,\tfrac{5}{8},\ \tfrac{1}{2}+u\,\tfrac{1}{4}\,\tfrac{3}{8},\ \tfrac{1}{4}\,\tfrac{1}{2}-u\,\tfrac{5}{8},\ \tfrac{1}{2}-u\,\tfrac{3}{4}\,\tfrac{3}{8}, \end{array}$$

with $u = 0.27 \pm 0.01$. The structure is a tetrahedral one, resembling that of sphalerite. Smallest interatomic distances are $Cu\text{-}S = 2.32 \pm 0.03$ Å, $Fe\text{-}S = 2.20 \pm 0.03$ Å.

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