Application of Quantum Mechanics to Molecular Structure

Electron Diffraction Investigation of the Structure of Gas Molecules and

The Dependence of Interatomic Distance on Single Bond-Double Bond Resonance

Thesis by

John Y. Beach

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Contents

PROPOSITIONS

1. The electron diffraction method is the most generally applicable method for determining the structure of gas molecules.

2. The molecular structures of the chloroethylenes afford evidence for the resonance of molecules among different electronic structures.

3. The van der Waals forces between hydrogen atoms can be conveniently calculated by the use of a set of ortho-normal functions which are different from the hydrogen atom wave functions.

4. The molecule-ion, HeH^+, is stable, the stability being due to the partial formation of a covalent bond and to the polarization of the helium atom.

5. The molecule-ion HeH^{++}, is unstable. The molecule-ion HeH_2^{++} is probably stable if constrained to the symmetrical linear configuration but is probably unstable with respect to dissociation into HeH^+ and H^+.

6. The group V pentahalide molecules are trigonal bipyramids.

7. In spite of the general applicability of Pauling's theory of bond directions it does not lead to unambiguous results in the case of the group VI tetrahalide molecules and ions isoelectronic with them.

8. The treatment of double bonds by double bond orbitals is simple analytically but faces serious theoretical difficulties and, in the case of $POCl_3$, is in disagreement with experiment.

9. The existence of covalent compounds and ions containing the inert pair is due to the utilization of excited orbitals for bond formation.

10. In the $Al(OH)_3$ sol and the $Cr(OH)_3$ polymerization products the oxygen bonds should be equivalent, contrary to the picture given by Thomas[1].

11. It is time to stop writing nitrogen with five covalent bonds.

12. The explanation of Lessheim and Samuel[2] for the increase in dissociation energy of NO upon excitation is incorrect.

13. The "lambda point" of liquid helium and other similar phenomena are neither second order nor third order phase equilibria but exhibit some of the characteristics of both.

14. Chemistry 1 at C.I.T. would be improved if the lectures and text books placed more emphasis on writing chemical equations in the ionic form.

15. The railroad companies should speed up the service between Los Angeles and San Francisco by operating buses between Los Angeles and Bakersfield which would meet the trains at Bakersfield.

Application of Quantum Mechanics to Molecular Structure

Introduction

The first of the quantum mechanical calculations of the stability of molecules was the treatment by Burrau1) in 1927 of the hydrogen molecule ion, H_2^+. Previous classical treatment of this problem by Pauli2) and Niessen3) had failed to give results compatible with experiment. Burrau's calculation showed that the potential energy of the system for all finite internuclear distances greater than about 0.6 A was less than the energy of the hydrogen atom. The potential energy curve possessed a minimum of .2053 Rhc at an internuclear distance of 1.06 A. This result was obtained by a numerical integration of the wave equation after separation of variables in confocal elliptic coordinates. Other treatments were given by Hylleraas4) and Jaffe5) who, while using different methods, arrived at the same results. The value obtained for the dissociation energy after taking into account the zero point vibrational energy is 2.639 ± .002 v.e. which is in complete agreement with and probably more accurate than the existing experimental value. This calculation was the first theoretical justification of the concept of the electron bond, in this case a one electron bond. A less precise but much simpler discussion of this molecule was given by Pauling6) who treated the problem by the variation method using a variation function of the following form: $\Psi = a + b$. a denotes an electron occupying a hydrogen ground state wave function on proton A and b denotes an electron occupying a hydrogen ground state wave function on proton B. This calculation gives a dissociation energy of about two thirds the observed value , agreeing qualitatively with experiment. An obvious interpretation of this result is that to a fair approximation the stability of the molecule is due to the resonance or exchange of the electron between the two positions given in the variation function. The variation method, due to Ritz7) before the advent of quantum mechanics, will be described in some detail in the section on the helium hydride molecule-ion; its distinctive feature, however, is that it gives an upper limit for the energy of the system. The only restrictions on the variation function are that it obey the boundary conditions and that it permit the evaluation of the necessary integrals. Other treatments of intermediate precision have been given this molecule by Finkelstein and Horowitz8), Guillemin and Zener9) and Dickinson10). This triumph of quantum mechanics within a year of its inception foreshadowed the subsequent success it was to meet in treating other more complicated molecules where the classical theory invariably failed.

In the same year of the appearance of Burrau's paper on the hydrogen molecule-ion the first treatment of the hydrogen molecule was started by Heitler and London11). This calculation was completed, also during 1927, by Sugiura12) who evaluated an integral only estimated by Heitler and London. The Heitler London Sugiura treatment of the hydrogen molecule was much less accurate than the Burrau treatment for the hydrogen molecule-ion, being a variation treatment using a variation function similar to the one mentioned above, used in 1928 by Pauling in discussing the hydrogen molecule-ion. This calculation showed that the potential energy of the system for all finite internuclear distances greater than about .5 A was less than the energy of two isolated hydrogen atoms. The minimum in the potential energy curve was found to be 3.14 e.v. at an internuclear distance of .80 A. This derivation of the existence of the non polar bond, never realized by classical mechanics, made the electron pair bond, which up to that time had merely been an assertion made reasonable by chemical evidence and bearing no relation to physical laws, a natural consequence of a generally applicable mechanics. This dissociation energy, 3.14 e.v., is only about two thirds of the observed value, 4.72 e.v., and the internuclear distance, 80 A, is somewhat greater than the observed distance, .74 A. The variation function used was Ψ = a(1) b(2) + b(1) a(2); a and b have the same significance as above. 1 and 2 refer to the two electrons. This result admits a qualitative interpretation analogous to the one made in the case of the hydrogen molecule-ion; that is, that to a fair degree of approximation the stability of the molecule is due to the resonance of the molecule between the two equivalent configurations given in the variation function. More detailed treatments approaching more closely the correct value for the dissociation energy of the molecule have been given by Wang[13)], Hund[14)], Rosen[15)], Mulliken[16)] and Weinbaum[17)]. The desired accuracy in the hydrogen molecule calculation was obtained by James and Coolidge[18)]. Introducing the interelectronic distance explicitly into the variation function, not done by any of the other investigators, they obtained a value for the dissociation energy coincident with the experimental value.

The interpretation made above that the bond formation in the hydrogen molecule and the hydrogen molecule-ion is due to the resonance of the molecule between two electronic structures is of no theoretical significance. In the detailed calculation for these two molecules nothing appears that suggests that it is true. The interpretation was based on the variation treatments of the hydrogen molecule by Heitler, London and Sugiura and the hydrogen molecule-ion by Pauling to which no unique theoretical significance can be ascribed. In spite of its qualitative nature, however, it provides an extremely valuable and practically indispensable language for discussing the large number of molecules where rigorous treatment is impossible.

Accuracy comparable to that in the two calculations just described has not been realized for any other molecule. Several other molecules have, however, been treated by the variation method using variation functions of varying complexity and upper limits for their energy have been obtained. The molecules for which these calculations have been made are: H_3^+ 19), H_3 20), He_2^{++} 21), HeH^+ 22), LiH^+ 23), LiH 23), Li_2^+ 24), Li_2 25), He_2^+ 26). Li_2 is the most complicated molecule for which a variation treatment has been made. Many other molecules have been treated by more approximate methods but will not be mentioned here. In the following section the variation treatment for HeH^+ will be given.

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QUANTUM MECHANICAL TREATMENT OF HELIUM HYDRIDE MOLECULE-ION, HeH^+.

QUANTUM MECHANICAL TREATMENT OF HELIUM HYDRIDE MOLECULE-ION HeH^+

Singly charged helium hydride molecule-ion has been known$^{1)}$ for many years from mass spectroscopic investigations of helium hydrogen mixtures. Its position with respect to that of $H^2H^2H^{1+}$ in the mass spectrograph has been used to determine accurately the mass of the deuteron$^{2)}$. Spectroscopic work has not shown the existence of this ion.

The only previous quantum mechanical discussion of HeH^+ is a variation treatment made by Glockler and Fuller$^{3)}$. They consider two problems: (1) the interaction of a proton with an excited helium atom, the wave functions for the electrons being $\psi_1 = ae^{-\alpha r_1}$ and $\psi_2 = (b + er_2)e^{\beta r_2}$, and (2) the interaction of a hydrogen atom with a singly ionized helium atom, the wave functions for the electrons being $\psi_1 = ae^{-\alpha r_{a1}}$ and $\psi_2 = be^{-\beta r_{b2}}$. When in the first case α and β are put equal to 2 and 0.7 respectively the interaction is repulsive at all distances. The functions ψ_1 and ψ_{22} are the <u>1s</u> and <u>2s</u> hydrogenlike wave functions, the helium atom being approximately in the first excited state. In case two α and β are put equal to 2 and 1, the resulting potential energy curve has a minimum of 8.1 e.v. at 1.3 a_0. In this calculation the unsymmetrical Sugiura type integral was neglected. As pointed out by Glockler and Fuller, including this integral will raise the energy by an undetermined amount.

The above calculation is not evidence for the existence of HeH^+. The dissociation energy, 8.1 e.v., obtained by making the above approximation, is with respect to the dissociation products hydrogen atom and helium ion, while the difference in the ionization potentials of hydrogen and helium is 10.9 e.v. Under these conditions the molecule would be unstable with respect to dissociation into a helium atom and a hydrogen ion. To prove the stability of the molecule it is necessary to show that for some intermediate internuclear distance the energy of the molecule is less than the energy of the helium atom.

The variational integral $W = \int \Psi^* H \Psi d\tau \Big/ \int \Psi^* \Psi d\tau$ gives an upper limit for the energy of a system. $\bar{\Psi}$ is an approximate wave function. H is the Hamiltonian operator and in this case is

$$H = -\frac{h^2}{8\pi^2 m}\nabla_1^2 - \frac{h^2}{8\pi^2 m}\nabla_2^2 - \frac{2e^2}{r_{a2}} - \frac{2e^2}{r_{a1}} - \frac{e^2}{r_{b1}} - \frac{e^2}{r_{b2}} + \frac{e^2}{r_{12}} + \frac{2e^2}{R}$$

When a variation function of the form $\bar{\Psi} = \sum_{n=1}^{m} c_n \Psi_n$ is used, the condition that W be a minimum with respect to the constants c_n is that the determinantal equation $\left| H_{ij} - \Delta_{ij} W \right| = 0$ (eq. 1) be satisfied$^{4)}$, where $H_{ij} = \int \psi_i^* H \psi_j d\tau$ and $\Delta_{ij} = \int \psi_i^* \psi_j d\tau$.

The approximate energy for the ground state will be the lowest root of this equation. The constants, c_n, are obtained by solving the set of linear equations $\sum_{j=1}^{m} c_j(H_{ij} - \Delta_{ij}W)$, $i = 1,2\ldots m$. Most of the integrals required in evaluating H_{ij} and Δ_{ij} were used by Rosen$^{5)}$ and Weinbaum$^{6)}$ in discussing the hydrogen molecule. Dr. Weinbaum has not published his integrals but kindly placed them at my disposal. The integrals used in this calculation, not tabulated by Rosen$^{5)}$, are given in the appendix.

The variation functions used here are composed of the following functions: $a(1) = \left(\frac{Z^3}{\pi a_0^3}\right)^{\frac{1}{2}} e^{-\frac{Z r_{a1}}{a_0}}$, $b(1) = \left(\frac{Z^3}{\pi a_0^3}\right)^{\frac{1}{2}} e^{-\frac{Z r_{b1}}{a_0}}$ eq.(2)

$a'(1) = \left(\frac{Z^5}{\pi a_0^5}\right)^{\frac{1}{2}} r_{a1} \cos\theta_{a1} e^{-\frac{Z r_{a1}}{a_0}}$ and the same functions for electron (2). Each function is normalized to unity. $a(1)$ is the ground state wave function for a hydrogenic atom of nuclear charge Z, and satisfies the equation $\left(-\frac{h^2}{8\pi^2 m}\nabla_1^2 - \frac{Ze^2}{r_{a1}}\right)a(1) = -Z^2W_Ha(1)$ where $W_H = \frac{e^2}{2a_0}$. $a'(1)$ is a first excited wave function for a hydrogenic atom of nuclear charge $2Z$ and satisfies the equation

$\left(-\frac{h^2}{8\pi^2 m}\nabla_1^2 - \frac{2Ze^2}{r_{a1}}\right)a'(1) = -Z^2W_Ha'(1)$. This form of $a'(1)$ was used by Rosen$^{5)}$ in introducing polarization into the hydrogen molecule calculation. It is very convenient as it leaves the exponents in $a(1)$ and $a'(1)$ identical making the calculation of integrals much simpler. In the present calculation the same effective nuclear charge, Z, is used in each term of the variation functions. This is done to eliminate the necessity of calculating the unsymmetrical Sugiura integral and other integrals. This procedure was adopted by Pauling7) in treating the helium molecule-ion $He_2{}^+$.

It is evident that the stable state of the molecule is a singlet state so we shall require the variation function to be symmetric in the spatial coordinates of the two electrons (and antisymmetric in the spin coordinates). In the following paragraphs we shall calculate the energy of the systems for several such variation functions. It will be found possible, by taking a linear combination of the lowest lying states for simple wave functions, to obtain a calculated value of the energy of the molecule that is lower than the experimental value for the helium atom.

1. Normal helium atom and proton.

The most stable state for the system for a single wave function of the type we are considering, eq. (2), is the state helium atom and proton. It will therefore be necessary, if the lowest value of the energy is desired, to include this state in the calculations. Taking as the electronic wave function of the system $\Psi = a(1)\, a(2)$, equation (1) for the energy becomes

$$W = \int \Psi^* H \Psi \, d\tau = \left\{ 2Z^2 - 2Z \left[\frac{27}{8} - 2\, e^{-2\rho} \left(1 + \frac{1}{\rho} \right) \right] \right\} W_H \quad \text{where}$$

$\rho = \frac{ZR}{a_o}$. This interaction is repulsive at all distances and is shown by curve C, Fig. 1 for the case that $Z = \frac{27}{16}$. When ρ equals infinity this expression becomes the familiar expression for the energy of a helium atom for hydrogenlike wave functions with variable effective nuclear charge, $W = (2Z^2 - \frac{27}{4} Z)W_H$. This energy is a minimum when $Z = \frac{27}{16}$ then $W = -5.695\ W_H$. The experimental value and the value calculated by Hylleraas[8)] for the helium atom is $-5.807\ W_H$.

2. Hydrogen atom and helium ion.

The symmetric variation function, $\Psi = a(1)\ b(2) + a(2)\ b(1)$, corresponds to an electron pair bond between the two atoms. The energy is shown by curve B in Fig. 1 for the case that $Z = 27/16 = 1.69$. This energy can be minimized with respect to Z for each value of ρ. When this is done a value of W only 0.04% lower than that for $Z = 27/16$ is obtained, the effective charge then being equal to 1.72. When equals infinity the energy becomes $W = (2Z^2 - 6Z)W_H$ which is a minimum when $Z = 3/2$ and $W = -4.5W_H$. The correct value for the sum of the energies of a hydrogen atom and a helium ion is $-5\ W_H$. This discrepancy is due to the fact that we have taken the same effective charge on the two atoms.

This calculation is the same as that made by Glockler and Fuller except that here the same effective nuclear charge is used on both atoms and consequently all the integrals can be calculated. This curve indicates the existence of a metastable attractive state for HeH^+.

3. Excited helium atom and proton.

The variation function $\bar{\Psi} = a(1)a'(2) + a'(1)a(2)$ in conjunction with $a(1)a(2)$, will be used to represent a polarized helium atom. The potential energy corresponding to the variation function $a'(1)a(2) + a(1)a'(2)$ alone is shown by curve A in Fig. 1 for the case that $Z = 27/16$. This curve is higher than that for the corresponding triple state, $a'(1)a(2) - a(1)a'(2)$, but the triplet state does not combine with the more important singlet states, non-diagonal matrix elements being equal to zero, so cannot be used. When the energy for the singlet state is minimized with respect to the effective nuclear charge, the enefgy curve is lowered by about 0.35 W_H, the corresponding value of the effective nuclear charge at the minimum being 1.26.

4. Combination of 1 and 3.

Using $\Psi = a(1)a(2) + k(a'(1)a(2) + a(1)a'(2))$ as a variation function, the energy appears as a root of a quadratic secular equation, equation (1). The result of solving the equation is shown by curve B in Fig. 2 for the case that the effective nuclear charge is 27/16. It is not possible to minimize easily with respect to the effective nuclear charge so the quadratic is merely solved for several values of the effective charge. It is found that the energy is worse for any value of the effective charge much different than 27/16. The minimum energy for this curve is $W = -5.750$ at $R = 1.60\ a_o$. The normalized function is $\Psi = 0.99\ a(1)a(2) + 0.13(a(1)a(2) + a(1)a'(2))$. The best value of the energy of the system at ρ equals infinity for this type of variation function is $-5.695\ W_H$, giving for the dissociation energy of the molecule $0.055\ W_H$ or 0.74 v.e. The stabilization resulting from the use of this variation function can be attributed to a polarization of the helium atom.

5. Combination of 1 and 2.

The energy corresponding to the variation function $\Psi = a(1)a(2) + k(a(1)b(2) + b(1)a(2)$ is shown in curve C in Fig. 2 for the case that $Z = 27/16$. The normalized function is $\Psi = 0.97a(1)a(2) + 0.24(a(1)b(2) + h(1)a(2))$. It is not easy to minimize with respect to the effective charge so again the quadratic secular equation is solved for several values of the effective charge, the calculated energy being much higher when the effective charge is much different than 27/16. The lowest value obtained is $W = -5.805$ at $R = 1.60\ a_o$, which when subtracted from the value $-5.695\ W_H$ for the helium atom, gives a dissociation energy of $0.110\ W_H$ or 1.49 v.e. The form of the variation function suggests that this is due to the partial formation of a covalent bond.

6. Combination of 1, 2 and 3.

The best variation function used is of the form

$$\Psi = a(1)a(2) + k\,(a'(1)a(2) + a(1)a'(2)) + k_2(a(1)b(2) + b(1)a(2)).$$

On the basis of calculations 5 and 6, in which it was found that the best value of the effective charge was not far from 27/16, calculations were made only for the case that $\underline{Z} = 27/16$. The energy appears as a root of a cubic secular equation and is shown by curve D, Fig. 2 and by curve D, Fig. 1. The normalized function is $\Psi = 0.97a(1)a(2) + 0.20(a'(1)a(2) + a(1)a'(2)) + 0.10(a(1)b(2) + b(1)a(2))$. The lowest energy obtained is $-5.844\ W_H$ at $R = 1.57\ a_0$. This, when subtracted from the helium atom value of $-5.695\ W$, gives a value for the dissociation energy of $0.149\ W_H$ or 2.02 v.e. This dissociation energy is obtained by using the energy of the helium atom calculated from a variation function of the same type as the one used for the undissociated molecule. This procedure assumes that the error in the energy is the same at the equilibrium distance and at infinity. A lower limit for the dissociation energy is obtained by subtracting the minimum energy for the molecule from the experimental value, $-5.807\ W_H$, for the helium atom. The result is $0.037\ W_H$ or .50 v.e. This positive result proves conclusively that the molecule is stable. The value 2.02 e.v. however, is probably much closer to the actual value of the dissociation energy.

Fitting a parabola to the bottom part of the curve leads to a value for the force constant of 0.43 megadynes/cm. as a fundamental vibration frequency of 2800 cm^{-1}.

The Molecule-Ion HeH^{++}

Doubly charged helium hydride molecule-ion was treated by the same type of variation function, $\Psi = a(1) + k_1 b(1) + k_2 a'(1)$. The resulting potential energy curve shows no minimum and differs only slightly from $-4W_H + \frac{e^2}{R}$. The one electron bond between the two atoms is not sufficiently strong to overcome the coulomb repulsion. Another molecule in which there is coulomb repulsion between the atoms, the helium molecule ion, He_2^{++}, has been treated by Pauling including ionic terms in the variation function. In this case the electron pair bond formed is strong enough to overcome the coulomb repulsion of the two atoms, there being a minimum in the potential energy curve. The instability of HeH^{++} is due to the lack of degeneracy of the two states $\overset{\cdot}{\mathrm{He}}^{+}\ \mathrm{H}^{+}$ and $\mathrm{He}^{++}\ \overset{\cdot}{\mathrm{H}}$.

Discussion

From a comparison of curves B and C, Fig. 2, it is seen that the introduction of polarization into the variation function is about half as effective in stabilizing the molecule as the introduction of the covalent bond. It is therefore qualitatively correct to say that two thirds of the stabilization is due to the formation of a covalent bond and one third is due to polarization of the helium atom. The strength of the bond, 2.02 e.v., is surprisingly great in view of the small coefficients of the covalent bond terms and the polarization term, 0.20 and 0.10, in the variation function given in section 6. It is roughly half as strong as the bond in the hydrogen molecule, 4.10 e.v., calculated[6)] from the same type of variation function.

I wish to thank Professor Linus Pauling for making many valuable suggestions during the preparation of this paper.

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Appendix

The simpler integrals are omitted. The integrals, $M_{001,0}$ and $M_{010,0}$, are evaluated by the use of the Neumann expansion in confocal elliptic coordinates. The functions H(m,n,) and S(m,n) are defined by Rosen5).

$$M_{000,0} = \int \frac{a^2(1)\ a(2)\ b(2)}{r_{12}}\, dv_1\, dv_2 = \frac{Z}{a_o} \left\{ e^{-\rho}\left(\frac{5}{16\rho} + \frac{1}{8} + \rho\right) - e^{-3\rho}\left(\frac{5}{16\rho} + \frac{1}{8}\right) \right.$$

$$\begin{aligned} M_{001,0} = \int \frac{a^2(1)\ a'(2)\ b(2)}{r_{12}}\, dv_1\, dv_2 = \frac{\rho}{2} M_{000,0} + \frac{Z}{a_o} \frac{\rho^6}{480} \Big[A \Big\{ &- 225\ H(5,4,\rho) + \\ &+ 135\ H(5,2,\rho) + 195\ H(3,4,\rho) - 117\ H(3,2,\rho) + 225\ S(3,5,\rho) - \\ &- 60\ S(1,5,\rho) + 225\ S(4,4,\rho) - 120\ S(2,4,\rho) - 195\ S(3,3,\rho) + \\ &+ 72\ S(1,3,\rho) - 135\ S(4,2,\rho) + 72\ S(2,2,\rho) \Big\} + B \Big\{ 375\ H(5,4,\rho) - \\ &- 225\ H(5,2,\rho) - 195\ H(1,4,\rho) + 117\ H(1,2,\rho) - 375\ S(3,5,\rho) + \\ &+ 100\ S(1,5,\rho) - 375\ S(4,4,\rho) - 125\ S(2,4,\rho) + 120\ S(0,4,\rho) + \\ &+ 225\ S(4,2,\rho) + 75\ S(2,2,\rho) - 728(0,2,\rho) + 195\ S(3.1,\rho) - \\ &- 72\ S(1,1,\rho) \Big\} + C \Big\{ - 375\ H(3,4,\rho) + 225\ H(1,4,\rho) + \\ &+ 225\ H(3,2,\rho) - 135\ H(1,2,\rho) + 375\ S(2,4,\rho) - 100\ S(0,4,\rho) + \\ &+ 375\ S(3,3,\rho) - 225\ S(3,1,\rho) - 100\ S(1,3,\rho) - 225\ S(2,2,\rho) + \\ &+ 60\ S(0,2,\rho) + 60\ S(1,1,\rho) \Big\} \Big] \end{aligned}$$

$$M_{010,0} = \int \frac{a(1)\ a'(1)\ a(2)\ b(2)}{r_{12}}\, dv_1\, dv_2 = \frac{\rho}{2} M_{000,0} + \frac{Z}{a_o} \frac{\rho^6}{96} \Big[A \Big\{ 9\ H(5,2,\rho) -$$

$$- 3\ H(5,0,\rho) + 9\ H(3,2,\rho) - 3\ H(3,0,\rho) - 9\ S(4,2,\rho) +$$

$$+ 3\ S(4,0,\rho) - 9\ S(1,5,\rho) + 3\ S(2,0,\rho) \Big\} + B \Big\{ -27\ H(5,2,\rho) +$$

$$+ 9\ H(5,0,\rho) - 9\ H(1,2,\rho) + 3\ H(1,0,\rho) + 27\ S(4,2,\rho) -$$

$$- 9\ S(4,0,\rho) + 9\ S(2,2,\rho) - 3\ S(2,0,\rho) + 27\ S(1,5,\rho) -$$

$$- 3\ S(1,1,\rho) \Big\} + C \Big\{ 27\ H(3,2,\rho) - 9\ H(3,0.\rho) - 9\ H(1,2,\rho) +$$

$$+ 3\ H(1,0,\rho) - 27\ S(2,2,\rho) + 9\ S(2,0,\rho) - 27\ S(1,3,\rho) +$$

$$+ 9\ S(1,1,\rho) \Big\} \Big]$$

where

$$A = \int_{-1}^{+1} x e^{-\rho x} dx, \quad B = \int_{-1}^{+1} x^3 e^{-\rho x} dx, \quad \text{and} \quad C = \int_{-1}^{+1} x^5 e^{-\rho x} dx$$

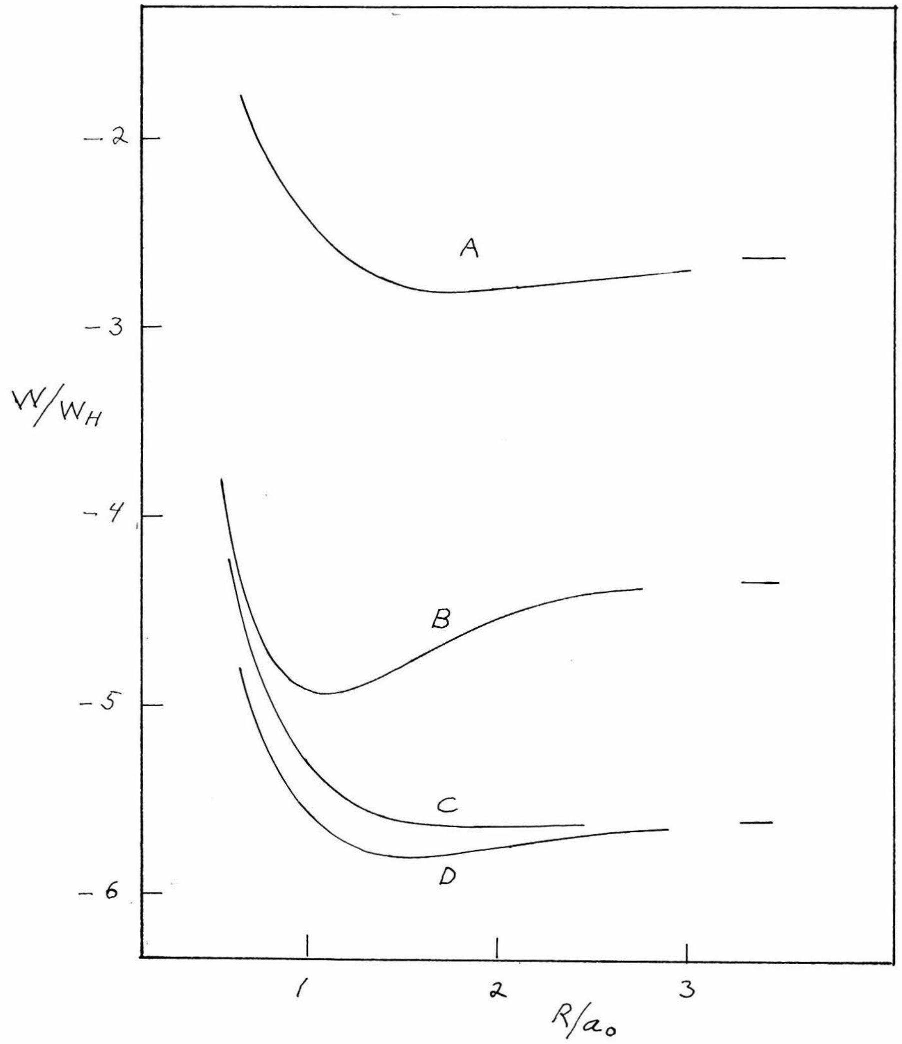

Fig. 1. Potential energy curves. A, $\Psi = a(1)a'(2) + a'(1)a(2)$; B, $\Psi = aa(1)b(2) + b(1)a(2)$; C, $\Psi = a(1)a(2)$; D, $\Psi = a(1)a(2) + K\big(a(1)b(2) + b(1)a(2)\big) + K_2\big(a(1)a'(2) + a'(1)a(2)\big)$

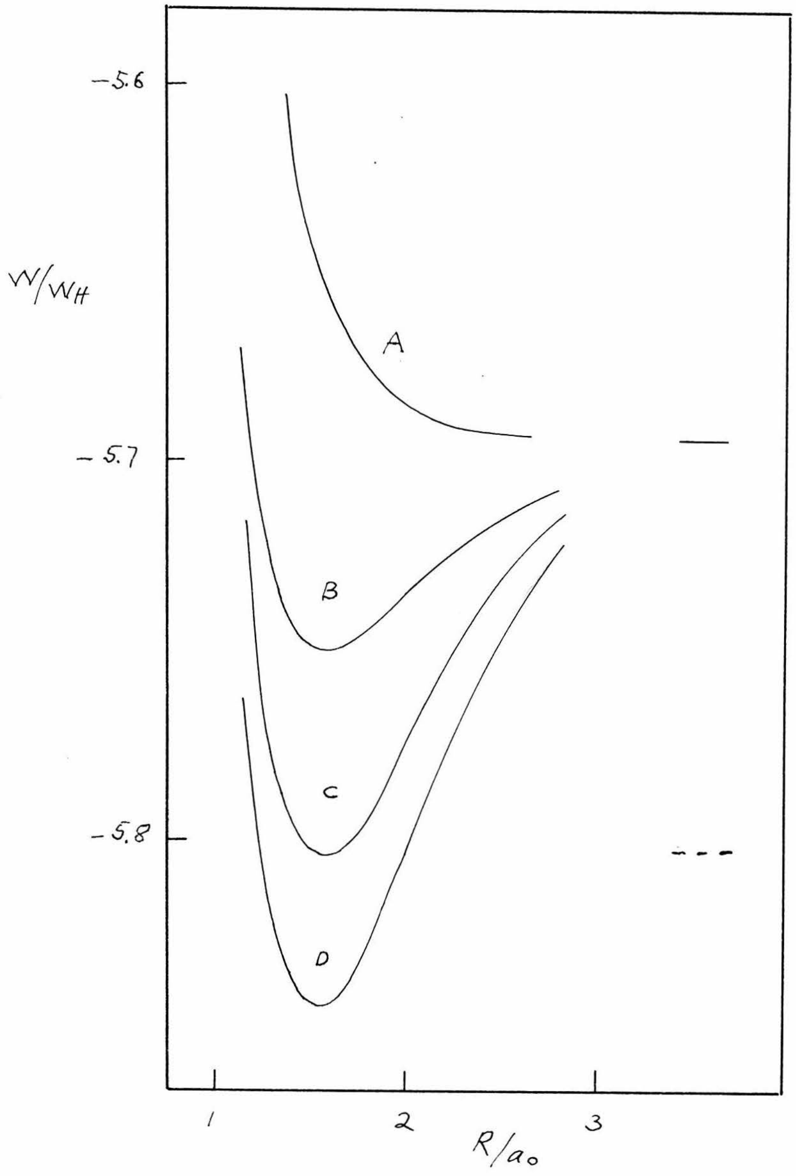

Fig. 2. Potential energy curves. A, $\Psi = a(1)a(2)$;

B, $\Psi = a(1)a(2) + K \ a(1)a'(2) + a'(1)a(2)$;

C, $\Psi = a(1)a(2) + K(a(1)b(2) + b(1)a(2))$;

D, $\Psi = a(1)a(2) + K\ (a(1)b(2) + b(2)a(1)) + K_2(a(1)a'(2) + a'(1)a(2))$

VAN DER WAALS INTERACTION OF HYDROGEN ATOMS

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The van der Waals Interaction of Hydrogen Atoms

LINUS PAULING AND J. Y. BEACH, *Gates Chemical Laboratory, California Institute of Technology*

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The van der Waals interaction energy of two hydrogen atoms at large internuclear distances is discussed by the use of a linear variation function. By including in the variation function, in addition to the unperturbed wave function, 26 terms for the dipole-dipole interaction, 17 for the dipole-quadrupole interaction, and 26 for the quadrupole-quadrupole interaction, the interaction energy is evaluated as

$$W''=-\frac{6.49903\,e^2}{a_0\,\rho^6}-\frac{124.399\,e^2}{a_0\,\rho^8}-\frac{1135.21\,e^2}{a_0\,\rho^{10}}-\cdots,$$

in which $\rho=R/a_0$, with R the internuclear distance. Some properties of the functions $F_{\nu\lambda\mu}(\xi,\vartheta,\varphi)$, which are orthogonal for the volume element $\xi d\xi \sin\theta d\theta d\varphi$, are discussed, and their usefulness in atomic problems is pointed out.

INTRODUCTION

An approximate second-order perturbation treatment of the inverse sixth power interaction energy of two hydrogen atoms a large distance apart (corresponding to the so-called dipole-dipole van der Waals attraction) was given in 1930 by Eisenschitz and London.[1] This treatment led to the result $W''=-e^2A/a_0\rho^6$, with $\rho=r_{AB}/a_0$ (r_{AB} being the internuclear distance for the two atoms), A being evaluated as 6.47. Applications of the variation method by Hassé[2] and by Slater and Kirkwood[3] verified this result essentially, the constant A being shown to be equal to or greater than 6.4976.

As early as 1927 this problem had been attacked by Wang,[4] using the method developed by Epstein[5] for the treatment of the Stark effect. Wang claimed to have obtained an exact solution; it was, however, pointed out by Eisenschitz and London that Wang's result is necessarily in error. It seemed to us possible that Wang's work might have contained only a numerical error, and that the method might actually be capable of giving an exact solution. Because of the usefulness which a method of exact solution of problems of this sort would have, we thought it worth while to study the problem thoroughly. We have found that the method used by Wang does not give an exact solution,[6] but that it can be extended to give as closely approximate a solution as is desired. The results of the treatment are communicated in this paper.

A rough treatment of the dipole-quadrupole and quadrupole-quadrupole interactions of two hydrogen atoms has been published by Mar-

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[1] R. Eisenschitz and F. London, Zeits. f. Physik **60**, 491 (1930).

[2] H. R. Hassé, Proc. Camb. Phil. Soc. **27**, 66 (1931).

[3] J. C. Slater and J. G. Kirkwood, Phys. Rev. **37**, 682 (1931).

[4] S. C. Wang, Physik. Zeits. **28**, 663 (1927).

[5] P. S. Epstein, Phys. Rev. **28**, 695 (1926).

[6] Wang does not present the final steps in his calculation in detail, but states that he set up a sixth degree secular equation from which he obtained an accurate value for the energy. We believe that the error in his treatment occurs at this point.

genau.[7] We have applied our method to obtain reasonably accurate expressions for these interactions also.

Formulation of the Problem

In the wave equation for two hydrogen atoms $H\psi = W\psi$ let us put $H = H^0 + H'$, H^0 being the part of the Hamiltonian corresponding to two isolated hydrogen atoms and H' representing the interaction of the two hydrogen atoms. In order to do this we neglect the resonance phenomenon (which is unimportant at large distances), taking as the unperturbed wave function the product function $\psi_{100}(A1)\ \psi_{100}(B2)$; that is, we consider electron 1 to be attached to nucleus A and electron 2 to nucleus B. We also write $W = W^0 + W''$ (W', the first-order perturbation energy, being equal to zero). We shall consider only the interaction of two normal hydrogen atoms, so that W^0 is equal to $-e^2/a_0$. Making the substitutions $\xi_1 = 2r_{A1}/a_0$ and $\xi_2 = 2r_{B2}/a_0$, the wave equation becomes

$$\left(\nabla_1^2 + \frac{1}{\xi_1} - \frac{1}{4}\right)\psi + \left(\nabla_2^2 + \frac{1}{\xi_2} - \frac{1}{4}\right)\psi - \frac{a_0}{2e^2} H'\psi = \lambda\psi, \quad (1)$$

in which $\lambda = -W''a_0/2e^2$.

The interaction H' is equal to

$$-e^2/r_{A2} - e^2/r_{B1} + e^2/r_{AB} + e^2/r_{12}.$$

If $R(=r_{AB})$ is large, this can be expanded[7] in inverse powers of R to give the expression

$$\begin{aligned} H' = {} & (e^2/R^3)(x_1x_2 + y_1y_2 - 2z_1z_2) \\ & + (3/2)(e^2/R^4)\{r_1^2z_2 - r_2^2z_1 \\ & + (2x_1x_2 + 2y_1y_2 - 3z_1z_2)(z_1 - z_2)\} \\ & + \tfrac{3}{4}(e^2/R^5)\{r_1^2r_2^2 - 5r_2^2z_1^2 - 5r_1^2z_2^2 \\ & - 15z_1^2z_2^2 + 2(x_1x_2 + y_1y_2 + 4z_1z_2)^2\} + \cdots. \quad (2) \end{aligned}$$

In this expression $x_1y_1z_1$ are Cartesian coordinates of electron 1 relative to nucleus A, and $x_2y_2z_2$ those of electron 2 relative to nucleus B, the z axis for each being directed towards the other nucleus. The first term represents the mutual energy of two dipoles; this term alone is important for large values of R. The second and third terms represent the dipole-quadrupole and quadrupole-quadrupole interactions, respectively. It can be easily shown that in the calculation of the second-order perturbation energy the terms can be considered separately, their contributions being additive.

In the solution of the problem we shall make use of the functions $F_{\nu\lambda\mu}$ $(\xi, \vartheta, \varphi)$ discussed in the appendix. Each of these functions can be made identical with a hydrogen-like wave function ψ_{nlm} (r, ϑ, φ) by choosing a suitable linear relation between r and ξ; the functions $F_{\nu\lambda\mu}$ all contain the same exponential function, in contradistinction to the functions ψ_{nlm}. We have defined ξ_1 and ξ_2 in such a way that F_{100} $(\xi_1, \vartheta_1, \varphi_1)$ and F_{100} $(\xi_2, \vartheta_2, \varphi_2)$ are identical with ψ_{100} $(r_1, \vartheta_1, \varphi_1)$ and ψ_{100} $(r_2, \vartheta_2, \varphi_2)$, respectively; that is, the unperturbed wave function can be written as F_{100} (ξ_1) F_{100} (ξ_2). We now apply the variation method in treating the perturbed wave equation, using as the variation function a linear combination of the product functions $F_{\nu_1\lambda_1\mu_1}$ $(\xi_1, \vartheta_1, \varphi_1)$ $F_{\nu_2\lambda_2\mu_2}$ $(\xi_2, \vartheta_2, \varphi_2)$, with arbitrary coefficients. It can be seen that the second-order perturbation energy for the perturbation function

$$\begin{aligned} H' = {} & -(2e^2/a_0)\{\alpha\xi_1\xi_2 \cos\vartheta_1 \cos\vartheta_2 \\ & + \beta\xi_1\xi_2^2 \cos\vartheta_1(3\cos^2\vartheta_2 - 1) \\ & + \gamma\xi_1^2\xi_2^2(3\cos^2\vartheta_1 - 1)(3\cos^2\vartheta_2 - 1) \\ & + \cdots\}, \quad (3) \end{aligned}$$

in which

$$\alpha = (6)^{\frac{1}{2}}a_0^3/8R^3, \quad \beta = (30)^{\frac{1}{2}}a_0^4/32R^4, \quad \text{and} \quad \gamma = (70)^{\frac{1}{2}}a_0^5/128R^5, \quad (4)$$

is identical with that for the function of Eq. (2), and, moreover, that to obtain the first-order perturbed wave function and the second-order perturbation energy, the variation function used need contain, in addition to the unperturbed part F_{100} (ξ_1) F_{100} (ξ_2), only the terms $F_{\nu_1 10}$ (ξ_1, ϑ_1) $F_{\nu_2 10}$ (ξ_2, ϑ_2) (for the dipole-dipole term in α), $F_{\nu_1 10}$ (ξ_1, ϑ_1) $F_{\nu_2 20}$ (ξ_2, ϑ_2) (for the term in β), and $F_{\nu_1 20}$ (ξ_1, ϑ_1). $F_{\nu_2 20}$ (ξ_2, ϑ_2) (for the term in γ).[8]

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[7] H. Margenau, Phys. Rev. **38**, 747 (1931).

[8] On application of the ordinary methods of perturbation theory, it is seen that the first-order perturbed wave function for a normal hydrogen atom with perturbation function $f(r)T(\vartheta, \varphi)$, where T is a tesseral harmonic, has the form $\Psi_{100}(r) + \Phi(r)T(\vartheta, \varphi)$, the perturbed part involving the same tesseral harmonic as the perturbation function. The statements in the text can be verified by an extension of this argument.

For a linear variation function $\sum_l a_l\Phi_l$ (where Φ_l represents the product functions $F_{\nu_1\lambda_1\mu_1}(\xi_1, \vartheta_1, \varphi_1)\, F_{\nu_2\lambda_2\mu_2}(\xi_2, \vartheta_2, \varphi_2)$) the secular equation corresponding to the wave equation (1) is the determinantal equation[9]

$$|\mathcal{H}_{jk}{}^0+\mathcal{H}_{jk}{}'-\Delta_{jk}\lambda|=0, \tag{5}$$

in which

$$\mathcal{H}_{jk}{}^0=\int\int\Phi_j{}^*(\nabla_1{}^2+(1/\xi_1)-\tfrac{1}{4}+\nabla_2{}^2+(1/\xi_2)-\tfrac{1}{4})\Phi_k d\tau_1 d\tau_2,$$

$$\mathcal{H}_{jk}{}'=\int\int\Phi_j{}^*(-(a_0/2e^2)H')\Phi_k d\tau_1 d\tau_2,$$

and

$$\Delta_{jk}=\int\int\Phi_j{}^*\Phi_k d\tau_1 d\tau_2,$$

$d\tau_1$ being equal to $\xi_1{}^2 \sin\theta_1 d\xi_1 d\vartheta_1 d\varphi_1$ (with $d\tau_2$ differing only in the subscripts) and the integrals extending over the configuration space of the system. It is to be noted that the volume element $d\tau_1 d\tau_2$ is not such as to make the functions Φ mutually orthogonal. The integrals can be evaluated with the help of the relations given in the appendix. To obtain the second-order perturbation energy we need introduce the term in λ in the row and column corresponding to the wave function for the unperturbed system only.

THE DIPOLE-DIPOLE INTERACTION

The secular equation for the dipole-dipole interaction is

$$\begin{array}{c|cccccccccc c|}
\nu_1\lambda_1\mu_1\nu_2\lambda_2\mu_2 & & & & & & & & & & & \\
100100 & -4\lambda & 32\alpha & -16\alpha & -16\alpha & 8\alpha & 0 & 0 & 0 & 0 & 0 & \cdots \\
210210 & 32\alpha & -8 & 2 & 2 & 0 & 0 & 0 & 0 & 0 & 0 & \cdots \\
210310 & -16\alpha & 2 & -14 & 0 & 4 & \sqrt{(10)} & 0 & 0 & 0 & 0 & \cdots \\
310210 & -16\alpha & 2 & 0 & -14 & 4 & 0 & \sqrt{(10)} & 0 & 0 & 0 & \cdots \\
310310 & 8\alpha & 0 & 4 & 4 & -24 & 0 & 0 & 2\sqrt{(10)} & 2\sqrt{(10)} & 0 & \cdots \\
210410 & 0 & 0 & \sqrt{(10)} & 0 & 0 & -20 & 0 & 6 & 0 & 0 & \cdots \\
410210 & 0 & 0 & 0 & \sqrt{(10)} & 0 & 0 & -20 & 0 & 6 & 0 & \cdots \\
310410 & 0 & 0 & 0 & 0 & 2\sqrt{(10)} & 6 & 0 & -34 & 0 & 3\sqrt{(10)} & \cdots \\
410310 & 0 & 0 & 0 & 0 & 2\sqrt{(10)} & 0 & 6 & 0 & -34 & 3\sqrt{(10)} & \cdots \\
410410 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 3\sqrt{(10)} & 3\sqrt{(10)} & -48 & \cdots \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot &
\end{array}=0, \tag{6}$$

the rows and columns corresponding to the values of $\nu_1\cdots\mu_2$ shown at the left. We obtain successive approximations to the solution of this equation by neglecting rows and columns beyond the nth. This process has been carried out for $n=2$, 5, 10, 17 and 26. Some simplification is achieved by combining rows (and columns) with ν_1 and ν_2 interchanged, the corresponding functions having the same coefficient. The results of the calculation are given in Table I, in terms of the constant A in the expression $W''=-Ae^2/a_0\rho^6$, with $\rho=R/a_0$ (A being equal to $3\lambda/16\alpha^2$).

TABLE I. *The dipole-dipole interaction constant A.*

Degree of approx.	Terms included		A
2	$\nu_1\leq 2$,	$\nu_2\leq 2$	6
5	3	3	6.4822
10	4	4	6.4984
17	5	5	6.49899
26	6	6	6.49903

TABLE II. *The dipole-quadrupole interaction constant B.*

Degree of approx.	Terms included		B
2	$\nu_1\leq 2$,	$\nu_2\leq 3$	115.7
5	3	4	124.10
10	4	5	124.386
17	5	6	124.399

TABLE III. *The quadrupole-quadrupole interaction constant C.*

Degree of approx.	Terms included		C
2	$\nu_1\leq 3$,	$\nu_2\leq 3$	1063.1
5	4	4	1132.6
10	5	5	1134.35
17	6	6	1135.12
26	7	7	1135.21

It is seen that the convergence is rapid, the final value of A, 6.49903, being trustworthy to within one unit in the last decimal place.

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[9] See, for example, L. Pauling and E. B. Wilson, Jr., *Introduction to Quantum Mechanics, with Applications to Chemistry*, McGraw-Hill Book Co., **1935**, Chap. VII.

THE DIPOLE-QUADRUPOLE INTERACTION

The secular equation for the dipole-quadrupole interaction is

$$\begin{array}{l|cccccccccc c|l}
\nu_1\lambda_1\mu_1\nu_2\lambda_2\mu_2 & & & & & & & & & & & & \\
100100 & -4\lambda & -192\sqrt{(3)}\beta & 96\sqrt{(3)}\beta & 96\sqrt{2}\beta & -48\sqrt{2}\beta & 0 & 0 & 0 & 0 & 0 & \cdots & \\
210320 & -192\sqrt{(3)}\beta & -14 & 4 & \sqrt{(6)} & 0 & 0 & 0 & 0 & 0 & 0 & \cdots & \\
310320 & 96\sqrt{(3)}\beta & 4 & -24 & 0 & 2\sqrt{(6)} & 2\sqrt{(10)} & 0 & 0 & 0 & 0 & \cdots & \\
210420 & 96\sqrt{2}\beta & \sqrt{(6)} & 0 & -20 & 6 & 0 & \sqrt{(14)} & 0 & 0 & 0 & \cdots & \\
310420 & -48\sqrt{2}\beta & 0 & 2\sqrt{(6)} & 6 & -34 & 0 & 0 & 3\sqrt{(10)} & 2\sqrt{(14)} & 0 & \cdots & \\
410320 & 0 & 0 & 2\sqrt{(10)} & 0 & 0 & -34 & 0 & 3\sqrt{(6)} & 0 & 0 & \cdots & \\
210520 & 0 & 0 & 0 & \sqrt{(14)} & 0 & 0 & -26 & 0 & 8 & 0 & \cdots & =0. \quad (7) \\
410420 & 0 & 0 & 0 & 0 & 3\sqrt{(10)} & 3\sqrt{(6)} & 0 & -48 & 0 & 3\sqrt{(14)} & \cdots & \\
310520 & 0 & 0 & 0 & 0 & 2\sqrt{(14)} & 0 & 8 & 0 & -44 & 4\sqrt{(10)} & \cdots & \\
410520 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 3\sqrt{(14)} & 4\sqrt{(10)} & -62 & \cdots & \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & & \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & & \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & &
\end{array}$$

We have solved this equation approximately, the results being given in Table II in terms of the constant B in the energy expression $-Be^2/a_0\rho^8$.

The error in the final value of B we estimate to be less than one unit in the last figure quoted.

THE QUADRUPOLE-QUADRUPOLE INTERACTION

The secular equation for the quadrupole-quadrupole interaction is

$$\begin{array}{l|cccccccccc c|l}
\nu_1\lambda_1\mu_1\nu_2\lambda_2\mu_2 & & & & & & & & & & & & \\
100100 & -4\lambda & 3456\gamma & -576\sqrt{(6)}\gamma & -576\sqrt{(6)}\gamma & 576\gamma & 0 & 0 & 0 & 0 & 0 & \cdots & \\
320320 & 3456\gamma & -24 & 2\sqrt{(6)} & 2\sqrt{(6)} & 0 & 0 & 0 & 0 & 0 & 0 & \cdots & \\
320420 & -576\sqrt{(6)}\gamma & 2\sqrt{(6)} & -34 & 0 & 3\sqrt{(6)} & 2\sqrt{(14)} & 0 & 0 & 0 & 0 & \cdots & \\
420320 & -576\sqrt{(6)}\gamma & 2\sqrt{(6)} & 0 & -34 & 3\sqrt{(6)} & 0 & 2\sqrt{(14)} & 0 & 0 & 0 & \cdots & \\
420420 & 576\gamma & 0 & 3\sqrt{(6)} & 3\sqrt{(6)} & -48 & 0 & 0 & 3\sqrt{(14)} & 3\sqrt{(14)} & 0 & \cdots & \\
320520 & 0 & 0 & 2\sqrt{(14)} & 0 & 0 & -44 & 0 & 4\sqrt{(6)} & 0 & 0 & \cdots & \\
520320 & 0 & 0 & 0 & 2\sqrt{(14)} & 0 & 0 & -44 & 0 & 4\sqrt{(6)} & 0 & \cdots & =0. \quad (8) \\
420520 & 0 & 0 & 0 & 0 & 3\sqrt{(14)} & 4\sqrt{(6)} & 0 & -62 & 0 & 4\sqrt{(14)} & \cdots & \\
520420 & 0 & 0 & 0 & 0 & 3\sqrt{(14)} & 0 & 4\sqrt{(6)} & 0 & -62 & 4\sqrt{(14)} & \cdots & \\
520520 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 4\sqrt{(14)} & 4\sqrt{(14)} & -80 & \cdots & \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & & \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & & \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & &
\end{array}$$

The results of the approximate solution of this equation, in terms of the constant C in the energy expression $-Ce^2/a_0\rho^{10}$, are given in Table III.

The final value, $C=1135.21$, is reliable except for the last figure.

DISCUSSION OF RESULTS

We have thus found for the interaction energy of two normal hydrogen atoms at the large distance $R=\rho a_0$ the expression

$$W''=-\frac{6.49903\,e^2}{a_0\rho^6}-\frac{124.399\,e^2}{a_0\rho^8}-\frac{1135.21\,e^2}{a_0\rho^{10}}-\cdots. \tag{9}$$

It is interesting to note that the value $A=6.4976$ found by Hassé for the dipole-dipole coefficient by the use of a variation function $\psi_{100}\,(r_1)\;\psi_{100}\,(r_2)\;\{1+H'(A+Br_1r_2+Cr_1^2r_2^2+Dr_1^3r_2^3)\}$ is very close to our value for $\nu_1\leq 4$, $\nu_2\leq 4$, which is based on a variation function involving all terms (unsymmetric as well as symmetric) out to $r_1^3r_2^3$. This indicates that the unsymmetric terms are of minor importance.

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[10] We use here shortened symbols, such as $F_{\nu_1}F_{\nu_2}$ for $F_{\nu_1\lambda_1\mu_1}(\xi_1,\vartheta_1,\varphi_1)F_{\nu_2\lambda_2\mu_2}(\xi_2,\vartheta_2,\varphi_2)$, etc.

The approximate second-order perturbation energy $W_0'' = (H_{00}')^2/W_0^0$, with $W_0^0 = -e^2/a_0$, leads to the values $A = 6$, $B = 135$, and $C = 1417.5$, the last two values being given by Margenau.[7] It is seen that the value of A is too low, and those of B and C are too high. This means that the dipole-dipole interaction is due more to excited states with negative energy (less than e^2/a_0 above the normal state of the system of two hydrogen atoms) than to excited states with positive energy, whereas the dipole-quadrupole and quadrupole-quadrupole interactions are due more to the latter than to the former states.

As has been pointed out by earlier authors, the van der Waals forces are more important than exchange forces for values of R greater than about $7a_0$. At this distance the dipole-quadrupole force is about one-half as large as the dipole-dipole force, and the quadrupole-quadrupole force is about one-eighth as large, the dipole-dipole attraction becoming relatively still more important at larger distances. This van der Waals calculation, based on product wave functions, is not significant for values of R much less than $7a_0$ because of neglect of the resonance phenomenon and because of failure of the expansion given in Eq. (2).

While our treatment has not led to an exact solution of our problem, the use of the functions $F_{\nu\lambda\mu}(\xi, \vartheta, \varphi)$ has permitted the reasonably accurate approximate solution to be made with considerable ease, and we feel that these functions may be found useful in the treatment of other problems of atomic and molecular structure.[11]

APPENDIX

The functions $F_{\nu\lambda\mu}(\xi, \vartheta, \varphi)$

We define

$$F_{\nu\lambda\mu}(\xi, \vartheta, \varphi) = \Lambda_{\nu\lambda}(\xi)\Theta_{\lambda\mu}(\vartheta)\Phi_\mu(\varphi),$$

with

$$\Lambda_{\nu\lambda}(\xi) = \{(\nu-\lambda-1)!/[(\nu+\lambda)!]^3\}^{\frac{1}{2}} e^{-\xi/2}\xi^\lambda L_{\nu+\lambda}^{2\lambda+1}(\xi),$$

L being an associated Laguerre polynomial,

$$\Theta_{\lambda\mu}(\vartheta) = \{[(2\lambda+1)(\lambda-\mu)!]/2(\lambda+\mu)!\}^{\frac{1}{2}} P_\lambda^{|\mu|}(\cos\vartheta),$$

P being an associated Legendre function, and

$$\Phi_\mu(\varphi) = (2\pi)^{-\frac{1}{2}} e^{i\mu\varphi}.$$

The functions are orthogonal and normalized for the weight function $\xi \sin\vartheta$, satisfying the equation

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} F'_{\nu'\lambda'\mu'}(\xi, \vartheta, \varphi) F_{\nu\lambda\mu}(\xi, \vartheta, \varphi)\xi \sin\vartheta d\varphi d\vartheta d\xi = \delta_{\nu'\nu}\delta_{\lambda'\lambda}\delta_{\mu'\mu}.$$

$F_{\nu\lambda\mu}(\xi, \vartheta, \varphi)$ satisfies the differential equation

$$(\nabla^2 + 1/\xi - \tfrac{1}{4})F_{\nu\lambda\mu} = -[(\nu-1)/\xi]F_{\nu\lambda\mu}.$$

The following relations involving the Λ's can be easily derived from the properties of the associated Laguerre polynomials:

$$\xi\Lambda_{\nu\lambda} = -\{(\nu-\lambda)(\nu+\lambda+1)\}^{\frac{1}{2}}\Lambda_{\nu+1,\,\lambda} + 2\nu\Lambda_{\nu\lambda} - \{(\nu+\lambda)(\nu-\lambda-1)\}^{\frac{1}{2}}\Lambda_{\nu-1,\,\lambda}.$$

$$\begin{aligned}\xi^2\Lambda_{\nu\lambda} = &-\{(\nu-\lambda)(\nu+\lambda+1)(\nu+\lambda+2)(\nu+\lambda+3)\}^{\frac{1}{2}}\Lambda_{\nu+2,\,\lambda+1}\\ &+2(2\nu-\lambda)\{(\nu+\lambda+1)(\nu+\lambda+2)\}^{\frac{1}{2}}\Lambda_{\nu+1,\,\lambda+1} - 6\nu\{(\nu+\lambda+1)(\nu-\lambda-1)\}^{\frac{1}{2}}\Lambda_{\nu,\,\lambda+1}\\ &+2(2\nu+\lambda)\{(\nu-\lambda-1)(\nu-\lambda-2)\}^{\frac{1}{2}}\Lambda_{\nu-1,\,\lambda+1} - \{(\nu+\lambda)(\nu-\lambda-1)(\nu-\lambda-2)(\nu-\lambda-3)\}^{\frac{1}{2}}\Lambda_{\nu-2,\,\lambda+1}.\end{aligned}$$

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[11] *Added in proof:* Professor J. H. Van Vleck has pointed out to us that the functions were used in the treatment of dispersion by hydrogen-like atoms by B. Podolsky, Proc. Nat. Acad. Sci. **14**, 253 (1928).

$$
\begin{aligned}
\xi^3\Lambda_{\nu\lambda}=&-\{(\nu-\lambda)(\nu+\lambda+1)(\nu+\lambda+2)(\nu+\lambda+3)(\nu+\lambda+4)(\nu+\lambda+5)\}^{\frac{1}{2}}\Lambda_{\nu+3,\,\lambda+2}\\
&+2(3\nu-2\lambda)\{(\nu+\lambda+1)(\nu+\lambda+2)(\nu+\lambda+3)(\nu+\lambda+4)\}^{\frac{1}{2}}\Lambda_{\nu+2,\,\lambda+2}\\
&-5(3\nu-\lambda)\{(\nu-\lambda-1)(\nu+\lambda+1)(\nu+\lambda+2)(\nu+\lambda+3)\}^{\frac{1}{2}}\Lambda_{\nu+1,\,\lambda+2}\\
&+20\nu\{(\nu+\lambda+1)(\nu+\lambda+2)(\nu-\lambda-1)(\nu-\lambda-2)\}^{\frac{1}{2}}\Lambda_{\nu,\,\lambda+2}\\
&-5(3\nu+\lambda)\{(\nu+\lambda+1)(\nu-\lambda-1)(\nu-\lambda-2)(\nu-\lambda-3)\}^{\frac{1}{2}}\Lambda_{\nu-1,\,\lambda+2}\\
&+2(3\nu+2\lambda)\{(\nu-\lambda-1)(\nu-\lambda-2)(\nu-\lambda-3)(\nu-\lambda-4)\}^{\frac{1}{2}}\Lambda_{\nu-2,\,\lambda+2}\\
&\qquad-\{(\nu+\lambda)(\nu-\lambda-1)(\nu-\lambda-2)(\nu-\lambda-3)(\nu-\lambda-4)(\nu-\lambda-5)\}^{\frac{1}{2}}\Lambda_{\nu-3,\,\lambda+2}.
\end{aligned}
$$

From these we obtain similar relations in the F's. The following special cases are needed in evaluating the matrix elements in Eqs. (6), (7) and (8):

$$
\begin{aligned}
\xi F_{100}&=-\sqrt{2}F_{200}+2F_{100},\\
\xi^2\cos\vartheta F_{100}&=-2\sqrt{2}F_{310}+4\sqrt{2}F_{210},\\
\xi^3(3\cos^2\vartheta-1)F_{100}&=-24F_{420}+24\sqrt{(6)}F_{320}.
\end{aligned}
$$

The evaluation of the matrix elements

In order to illustrate the method of construction of the matrices in Eqs. (6), (7) and (8), we shall evaluate some of the integrals. Let us first consider the integral[10]

$$\mathcal{H}^0{}_{\nu_1'\nu_2'\nu_1\nu_2}=\int\int F^*{}_{\nu_1'}F^*{}_{\nu_2'}\{\nabla_1{}^2+1/\xi_1-\tfrac{1}{4}+\nabla_2{}^2+1/\xi_2-\tfrac{1}{4}\}F_{\nu_1}F_{\nu_2}d\tau_1d\tau_2.$$

By using the differential equation for $F_{\nu\lambda\mu}$ (ξ,ϑ,φ), the equation becomes

$$
\begin{aligned}
\mathcal{H}^0{}_{\nu_1'\nu_2'\nu_1\nu_2}&=\int\cdots\int F^*{}_{\nu_1'}F^*{}_{\nu_2'}\{-(\nu_1-1)/\xi_1-(\nu_2-1)/\xi_2\}F_{\nu_1}F_{\nu_2}\xi_1{}^2\xi_2{}^2\sin\vartheta_1\sin\vartheta_2d\xi_1d\vartheta_1d\varphi_1d\xi_2d\vartheta_2d\varphi_2\\
&=\int\cdots\int F^*{}_{\nu_1'}F^*{}_{\nu_2'}\{-(\nu_1-1)\xi_2-(\nu_2-1)\xi_1\}F\nu_1F_{\nu_2}\xi_1\xi_2\sin\theta_1\sin\theta_2d\xi_1d\vartheta_1d\varphi_1d\xi_2d\vartheta_2d\varphi_2.
\end{aligned}
$$

For Eq. (6) $(\lambda_1=\lambda_2=1,\ \mu_1=\mu_2=0)$ this becomes

$$
\begin{aligned}
\mathcal{H}^0{}_{\nu_1'\nu_2'\nu_1\nu_2}=\int\cdots\int F^*{}_{\nu_1'}F^*{}_{\nu_2'}&[(\nu_2-1)\{(\nu_1-1)(\nu_1+2)\}^{\frac{1}{2}}F_{\nu_1+1}F_{\nu_2}+(\nu_1-1)\{(\nu_2-1)(\nu_2+2)\}^{\frac{1}{2}}F_{\nu_1}F_{\nu_2+1}\\
&-2(2\nu_1\nu_2-\nu_1-\nu_2)F_{\nu_1}F_{\nu_2}+(\nu_2-1)\{(\nu_1+1)(\nu_1-2)\}^{\frac{1}{2}}F_{\nu_1-1}F_{\nu_2}\\
&+(\nu_1-1)\{(\nu_2+1)(\nu_2-2)\}^{\frac{1}{2}}F_{\nu_1}F_{\nu_2-1}]\xi_1\xi_2\sin\vartheta_1\sin\vartheta_2d\xi_1d\vartheta_1d\varphi_1d\xi_2d\vartheta_2d\varphi_2,
\end{aligned}
$$

and hence we obtain

$$
\begin{aligned}
\mathcal{H}^0{}_{\nu_1+1,\,\nu_2,\,\nu_1,\,\nu_2}&=(\nu_2-1)\{(\nu_1-1)(\nu_1+2)\}^{\frac{1}{2}},\\
\mathcal{H}^0{}_{\nu_1,\,\nu_2+1,\,\nu_1,\,\nu_2}&=(\nu_1-1)\{(\nu_2-1)(\nu_2+2)\}^{\frac{1}{2}},\\
\mathcal{H}^0{}_{\nu_1-1,\,\nu_2,\,\nu_1,\,\nu_2}&=(\nu_2-1)\{(\nu_1+1)(\nu_1-2)\}^{\frac{1}{2}},\\
\mathcal{H}^0{}_{\nu_1,\,\nu_2-1,\,\nu_1,\,\nu_2}&=(\nu_1-1)\{(\nu_2+1)(\nu_2-2)\}^{\frac{1}{2}},
\end{aligned}
$$

and

$$\mathcal{H}^0{}_{\nu_1,\,\nu_2,\,\nu_1,\,\nu_2}=-2(2\nu_1\nu_2-\nu_1-\nu_2),$$

all others being equal to zero.

In Eq. (7) we have

$$\mathcal{H}'_{\nu_1\nu_2,\,11}=\beta\int\cdots\int F_{\nu_1}{}^*F_{\nu_2}{}^*\xi_1\xi_2{}^2\cos\vartheta_1(3\cos^2\vartheta_2-1)F_1F_1\xi_1{}^2\xi_2{}^2\sin\vartheta_1\sin\vartheta_2 d\xi_1 d\vartheta_1 d\varphi_1 d\xi_2 d\vartheta_2 d\varphi_2$$

$$=\beta\int\cdots\int F_{\nu_1}{}^*F_{\nu_2}{}^*\{48\sqrt{2}F_{310}F_{420}-96\surd(3)F_{310}F_{320}-96\sqrt{2}F_{210}F_{420}$$

$$+192\surd(3)F_{210}F_{320}\}\xi_1\xi_2\sin\vartheta_1\sin\vartheta_2 d\xi_1 d\vartheta_1 d\varphi_1 d\xi_2 d\vartheta_2 d\varphi_2,$$

and hence

$$\mathcal{H}'_{23,11}=192\surd(3)\beta,\qquad \mathcal{H}'_{33,11}=-96\surd(3)\beta,\qquad \mathcal{H}'_{24,11}=-96\sqrt{2}\beta,$$

and $\mathcal{H}'_{34,\,11}=48\sqrt{2}\beta$, all others being equal to zero.

To illustrate the evaluation of the integral Δ let us consider $\Delta_{11,\,11}$:

$$\Delta_{11,\,11}=\int\cdots\int\{F_{100}(\xi_1)F_{100}(\xi_2)\}^2\xi_1{}^2\xi_2{}^2\sin\vartheta_1\sin\vartheta_2 d\xi_1 d\vartheta_1 d\varphi_1 d\xi_2 d\vartheta_2 d\varphi_2$$

$$=\int\cdots\int F_{100}(\xi_1)F_{100}(\xi_2)\{2F_{200}(\xi_1)F_{200}(\xi_2)-2\sqrt{2}F_{200}(\xi_1)F_{100}(\xi_2)-2\sqrt{2}F_{100}(\xi_1)F_{200}(\xi_2)$$

$$+4F_{100}(\xi_1)F_{100}(\xi_2)\}\xi_1\xi_2\sin\vartheta_1\sin\vartheta_2 d\xi_1 d\vartheta_1 d\varphi_1 d\xi_2 d\vartheta_2 d\varphi_2,$$

or, making use of the orthogonality and normalization of the F's, $\Delta_{11,\,11}=4$.

Electron Diffraction Investigation of the Structure of Gas Molecules

[Reprint from the Journal of the American Chemical Society, 57, 2693 (1935).]

[Contribution from the Gates Chemical Laboratory, California Institute of Technology. No. 508]

The Electron Diffraction Investigation of Phosgene, the Six Chloroethylenes, Thiophosgene, α-Methylhydroxylamine and Nitromethane[1]

By L. O. Brockway, J. Y. Beach and Linus Pauling

Introduction

The importance of the use of interatomic distances as a test for resonance of molecules among several valence-bond structures has been mentioned in earlier papers,[2] in which it was pointed out that the interatomic distance for two bonded atoms in a resonating molecule is determined mainly by the strongest of the bonds between the two atoms provided by the resonating structures. We have now obtained evidence regarding the quantitative dependence of interatomic distance on bond type for resonance between a single bond and a double bond, and have made use of this relation in the discussion of the electronic structure of a number of molecules involving single bond–double bond resonance. The investigation is based largely on the determination of the atomic configuration of molecules by the diffraction of electrons; the description of this work is given in this paper, and the interpretation and discussion of results in the following one.

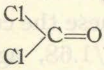
Electron diffraction photographs of the gas molecules investigated were prepared in the usual way,[3] with film distances of about 12, 20 or 30 cm., the electron wave lengths being about 0.06 Å. The photographs were measured on a comparator and interpreted both by the radial distribution method[4] and the usual visual method.[5] The results are given below; in each case the interatomic distances and bond angles are provided with estimated probable errors, which indicate the extent to which we consider them to be reliable.

We are indebted to Dr. S. Weinbaum and Dr. J. Sherman for aid in connection with the extensive calculations involved in the interpretation of the photographs.

Phosgene.—The phosgene used was prepared by the action of fuming sulfuric acid on carbon tetrachloride in the presence of a catalyst (infusorial earth), and was purified by distillation.

The photographs show eight rings, with values of $s = (4\pi \sin \Theta/2)/\lambda$ (averages for eleven photographs measured by two observers) and estimated intensities given in Table I.

The eight-term radial distribution function (Fig. 1) shows two peaks, the first, with maximum at 1.79 Å., representing C–Cl, and the second, a broad peak with maximum at 2.74 Å., representing Cl–Cl and Cl–O (unresolved).

In applying the usual visual method we calculated curves for sixteen plane symmetric models. Three parameters are involved, the Cl–C–Cl angle, the C–O distance, and the C–Cl distance, the qualitative appearance of the curves being dependent on the angle and the ratio of the distances. The angle was varied from 110 to 125° and the ratio C–Cl/C–O from 1.23 to 1.60. Most of the models are eliminated at once by qualitative comparisons. The model corresponding to the valence bond structure  $\mathrm{Cl_2C{=}O}$, with C–Cl = 1.76, C–O = 1.28, and the angle Cl–C–Cl = 110°, leads to curve A of Fig. 2, which is unsatisfactory in regard to the fourth and sixth rings, each of which is observed to be close to the preceding one. Curve B of Fig. 2 represents the model (with C–O = 1.12, C–Cl = 1.80, angle Cl–C–Cl = 110°) reported by Dornte[6] as the result of the study of electron diffraction photographs showing only four rings; it is seen that this curve is unsatisfactory, showing no maximum corresponding to our observed fourth ring.

It was found that models with the Cl–C–Cl angle equal to about 117° and the ratio of distances C–O/C–Cl equal to about 1.28/1.66 lead to curves in reasonably good qualitative agreement with experiment, all other models tried being unsatisfactory. Thus in Fig. 3 the curve for α = 117° (C) is reasonably satisfactory, the fourth and sixth rings being represented by humps rather than maxima; the curve for α = 115° (D) shows no sign of the sixth ring, and that for 120° (B) is unsatisfactory with regard to the clearly ob-

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[1] Some of the results communicated in this paper were presented at the meeting of the A. A. A. S. in Berkeley, June, 1934.

[2] L. Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293, 498 (1932); L. O. Brockway, *ibid.*, **19**, 860 (1930); L. O. Brockway and L. Pauling, *ibid.*, **19**, 868 (1933); L. Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934).

[3] R. Wierl, *Ann. Physik*, **8**, 521 (1931); L. O. Brockway and L. Pauling, *Proc. Nat. Acad. Sci.*, **19**, 69 (1933).

[4] L. Pauling and L. O. Brockway, This Journal, **57**, 2684 (1935).

[5] See L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 867 (1934).

[6] R. W. Dornte, This Journal, **55**, 4126 (1933).

TABLE I

PHOSGENE, $COCl_2$

Max.	Min.	I	s	Values of x C	D	F	Values of C–Cl C	D	F
1		20	3.00	2.88	2.84	2.90	(1.574 Å.)	(1.590 Å.)	(1.605 Å.)
	2		3.95	3.88	3.83	3.88	(1.610)	(1.629)	(1.631)
2		15	5.05	5.15	5.07	5.11	1.672	1.687	1.680
	3		6.33	6.50	6.35	6.40	1.684	1.685	1.678
3		10	7.44	7.70	7.66	7.74	1.697	1.730	1.727
	4		8.53	8.90		8.87	1.711		1.726
4		2	9.34	9.63		9.30	1.691		1.653
	5		10.33	10.76	10.25	10.50	1.708	1.667	1.687
5		5	11.51	12.25	11.75	11.95	1.745	1.715	1.723
	6		12.54						
6		1	13.51[a]						
	7		14.52	14.50	14.25	14.40	1.638	1.649	1.646
7		3	15.70	16.00	15.62	15.76	1.671	1.671	1.666
	8		16.94	17.38	16.88	17.12	1.683	1.674	1.678
8		1	18.10	18.25	17.80	18.00	1.654	1.652	1.651
						Average	1.687 Å.	1.681 Å.	1.683 Å.

Model C: Cl–C–Cl = 117° C–O = 1.28 Å. C–Cl = 1.64 Å
D: Cl–C–Cl = 117° 1.28 1.68
F: Cl–C–Cl = 118° 1.28 1.66

Results: C–Cl = 1.68 ± 0.02 Å.
Cl–Cl = 2.87 ± .02 Å.
C–O = 1.28 ± .03 Å.
Angle Cl–C–Cl = 117 ± 2°
Angle Cl–C–O = 121°30′ ± 1°

[a] This ring or shelf does not appear as a maximum on the simplified theoretical curves for these models.

served fourth ring. The effect of changing the C–O/C–Cl ratio is shown by the lower four curves in Fig. 2. Of these the curves for 117°, 1.28/1.64, and 117°, 1.28/1.68, agree very well with the photographs in qualitative appearance except that the sixth ring is not quite so well represented as expected, appearing only as a shelf on the curves.

In the figures of this paper showing intensity curves the observed values of s for apparent maxima and minima are indicated by small vertical lines. In comparing these with the calculated intensity curves it must be borne in mind that a linear change of scale may be made; the indicated s values are shown in each case for the x/s ratio determined by quantitative comparison for the model finally accepted.

The results of the quantitative comparison of the photographs with the curves for three models are given in Table I. Bearing in mind the qualitative comparison, we write as the probable configuration of the phosgene molecule $\alpha = 117 \pm 2°$ (angle Cl–C–Cl), C–Cl = 1.68 ± 0.02 Å., C–O = 1.28 ± 0.03 Å., and Cl–Cl = 2.87 ± 0.02 Å.

The values of Dornte (whose work has been referred to above), $\alpha = 110 \pm 5°$, C–Cl = 1.80 ± 0.04 Å., and C–O = 1.12 ± 0.02 Å., we believe to be less accurate than the errors assigned to them indicate.

Vinyl Chloride.—Photographs of vinyl chloride (from the Carbide and Carbon Chemical Company) were taken with a film distance of 12.19 cm. (the same distance being used also for the other chloroethylenes). The photographs show about six rings: the first very weak, the second strong, the third and fourth medium, the fifth weak and the sixth very weak. In addition there is apparent a very weak ring or shelf be-

TABLE II

VINYL CHLORIDE

Max.	Min.	I	s	x for model D	C–Cl
2		30	5.19	5.14	1.663 Å.
	3		6.45	6.48	1.687
3		20	7.61	7.77	1.714
Shelf		5	9.84		
	4		10.76	10.76	1.680
4		15	12.15	12.21	1.687
	5		13.51	13.48	1.676
5		10	15.27	15.01	1.653
6		5	19.10	19.40	1.707
				Average	1.683 Å.

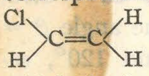
Results: C–C = 1.38 Å. (assumed)
C_1–Cl = 1.69 ± 0.02 Å.
C_2–Cl = 2.70 ± .02 Å.
α = 122 ± 2°

tween the third and fourth rings, somewhat closer to the third than to the fourth. Measured values of *s* obtained by two observers from nine photographs are given in the fourth column of Table II and estimated intensities for the rings in the third column.

The six-term radial distribution curve is given in Fig. 1. It shows two pronounced peaks, with maxima at 1.695 and 2.69 Å., with indication of a subsidiary peak at 1.35 or 1.40 Å. The first two we associate with the two carbon–chlorine interactions, and the last with carbon–carbon. If we accept the value 1.38 Å. for C–C, the distances 1.695 and 2.69 Å. lead to the value 121° for the C–C–Cl bond angle α.

In applying the usual visual method, we have found that the photographs do not provide enough information to permit us to evaluate simultaneously the two distances C–Cl and C–C and the angle Cl–C–C with much accuracy. Accordingly we have assumed the C–C distance to have the double bond value 1.38 Å., and have calculated curves for C–Cl = 1.68, C–C = 1.38 and the angle α = 130, 125, 122.5 and 120°. These are shown as B, C, D and E in Fig. 4. Of these B and C are qualitatively unsatisfactory in that the hump corresponding to the faint ring or shelf observed between the third and fourth rings is too large, and E in that the hump is too small. Comparison of measured values of *s* with the *x* values for model D (Table II) leads to the carbon–chlorine distances 1.683 and 2.70 Å.

Combining the results of the two methods, we write C–C = 1.38 Å. (assumed), C_1–Cl = 1.69 ± 0.02 Å., C_2–Cl = 2.70 ± 0.02 Å., α = 122 ± 2°. No earlier electron diffraction work on this substance has been reported.

It is of interest to consider also the model with C_1–Cl = 1.76, C–C = 1.38 and α = 125°, corresponding to the non-resonating structure . This gives the curve A of Fig. 4, which is in satisfactory qualitative agreement with the photographs. The quantitative comparison leads to the distances C–Cl = 1.68 Å. and C–C = 1.32 Å., however, and since the latter distance should not fall below 1.38 Å., the experimentally established value for the carbon–carbon double bond, the non-resonating structure is unsatisfactory.

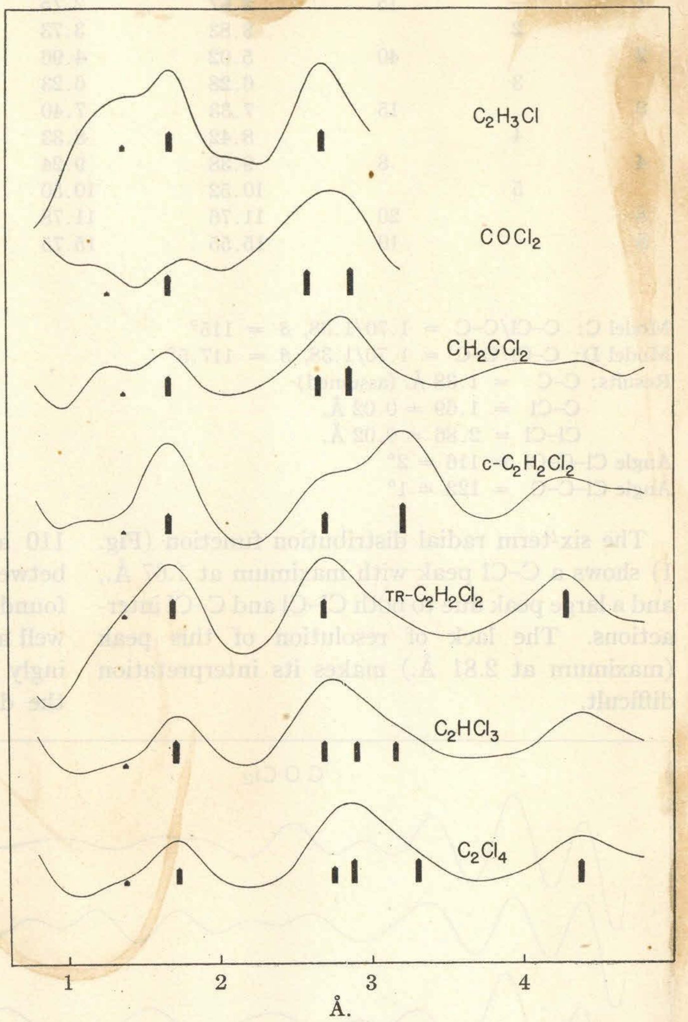


Fig. 1.—Radial distribution curves for phosgene and the six chloroethylenes.

1,1-Dichloroethylene.—The substance was prepared by treating 1,1,2-trichloroethane (made by passing vinyl chloride into antimony pentachloride) with alcoholic potassium hydroxide, and was purified by fractional distillation.

The photographs, showing seven well-defined rings, have the following qualitative appearance: the first medium, the second strong, the third medium, the fourth weak and the fifth medium weak, these five being about equally spaced; then a wide minimum and a weak ring, and another wide minimum and weak ring. Measured values of *s* (averages for four photographs) and estimates of *I* are given in Table III.

TABLE III

1,1-DICHLOROETHYLENE

Max.	Min.	I	s	x for Model C	x for D	C–Cl for Model C	C–Cl for D
1		15	2.87	2.75	2.74	(1.629 Å.)	(1.623 Å.)
	2		3.83	3.73	3.67	(1.656)	(1.629)
2		40	5.02	4.96	4.95	1.679	1.676
	3		6.28	6.23	6.20	1.687	1.679
3		15	7.33	7.40	7.34	1.717	1.702
	4		8.42	8.33	8.22	1.681	1.660
4		8	9.38	9.24	9.15	1.674	1.659
	5		10.52	10.50	10.33	1.697	1.670
5		20	11.76	11.78	11.73	1.703	1.696
6		10	15.55	15.75	15.56	1.722	1.701
					Average C–Cl =	1.695 Å.	1.680 Å.
					Cl–Cl =	2.858 Å.	2.870 Å.

Model C: C–Cl/C–C = 1.70/1.38, β = 115°
Model D: C–Cl/C–C = 1.70/1.38, β = 117.5°
Results: C–C = 1.38 Å. (assumed)
C–Cl = 1.69 ± 0.02 Å.
Cl–Cl = 2.86 ± 0.02 Å.
Angle Cl–C–Cl = 116 ± 2°
Angle Cl–C–C = 122 ± 1°

The six-term radial distribution function (Fig. 1) shows a C–Cl peak with maximum at 1.67 Å., and a large peak due to both Cl–Cl and C–Cl interactions. The lack of resolution of this peak (maximum at 2.81 Å.) makes its interpretation difficult.

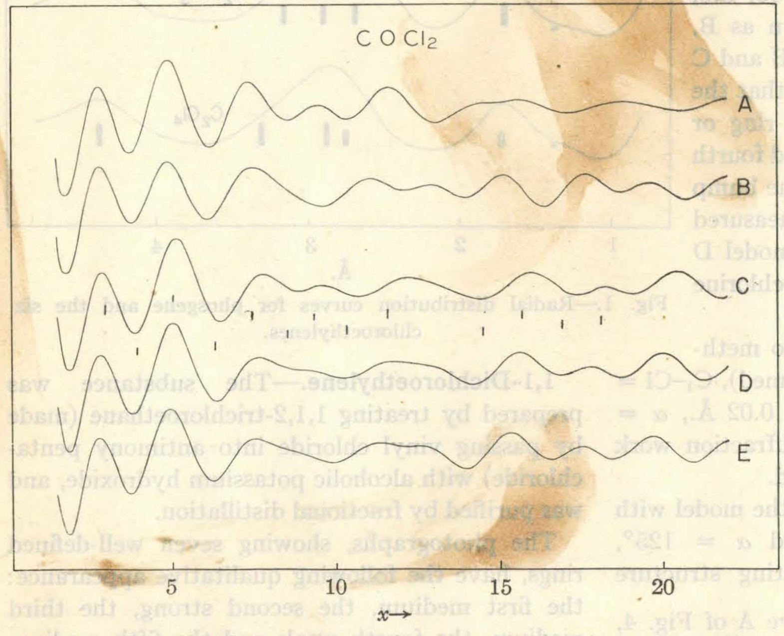
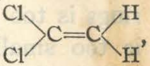


Fig. 2.—Simplified intensity curves for phosgene. A, α (angle Cl–C–Cl) = 110°, r (ratio C–O/C–Cl) = 1.28/1.76; B, α = 110°, r = 1.12/1.80; C, α = 117°, r = 1.28/1.64; D, α = 117°, r = 1.28/1.68; E, α = 117°, r = 1.28/1.72.

We have calculated intensity curves for twelve models, with the Cl–C–Cl angle β varied between 110 and 125° and the C–Cl/C–C ratio varied between 1.76/1.38 and 1.64/1.38. It was not found possible to evaluate the C–Cl/C–C ratio as well as the angle β with much accuracy; accordingly we have assumed the C–C distance to have the double bond value 1.38 Å. Of the models tried, only those with β equal to about 115° agree qualitatively with the photographs. For example, the model with C–Cl = 1.76 Å., C–C = 1.38 Å., and β = 110°, corresponding to the valence-bond structure , is unsatisfactory in that the fourth maximum on the curve (curve A of Fig. 5) is higher than the third, whereas the fourth ring is observed to be much weaker than the third and fifth. Quantitative comparison with this and other curves shows the C–Cl distance to be about 1.70 Å. Curves B, C, D and E of Fig. 5 are calculated for C–Cl = 1.70, C–C = 1.38, and the angle β = 112.5, 115, 117.5 and 120°, respectively. Of these curve B is unsatisfactory in that it shows an additional maximum between those corresponding to the fifth and sixth rings, and curve E in that the fourth maximum is too high. Curves C and D are satisfactory, and we accordingly accept for the Cl–C–Cl angle the value $\beta = 116 \pm 2°$.

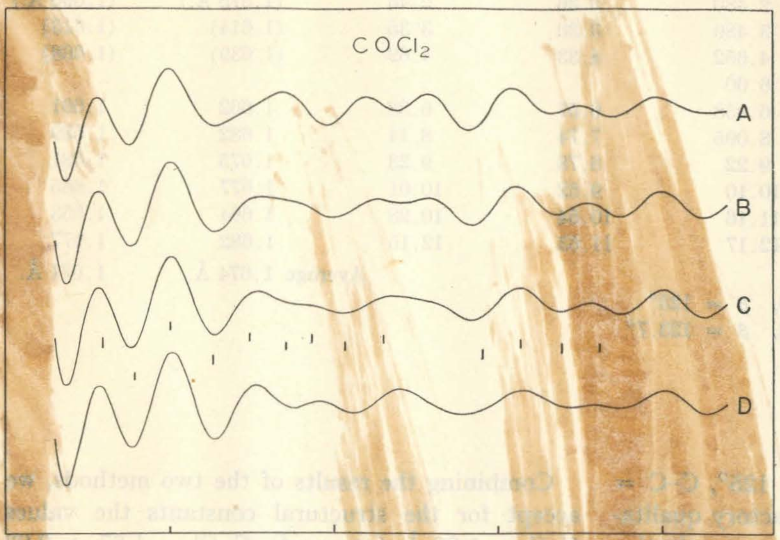


Fig. 3.—Intensity curves for phosgene, with $r = 1.28/1.68$, and $\alpha = 125$, 120, 117 and 115° for A, B, C and D, respectively.

The quantitative comparison of the measured values of s and the x values for models C and D, given in Table III, leads to the interatomic distances C–Cl = 1.69 ± 0.02 Å., Cl–Cl = 2.86 ± 0.02 A., with the angle Cl–C–Cl = 116 ± 2° and C–C = 1.38 Å. (assumed).

The only previous investigation of this substance, that of Wierl[7] by electron diffraction, gave the value Cl–Cl = 2.9 ± 0.3 Å.

cis-Dichloroethylene.—The sample of *cis*-dichloroethylene used was obtained from a mixture of the *cis* and *trans* compounds by fractional distillation with a 90-cm. column.

The photographs show five well-defined rings, with the following qualitative appearance: the first ring medium; the second strong, with an outer shelf; the third medium; the fourth weak, and somewhat closer to the third than to the fifth; the fifth medium weak. Observed values of s (averages for nine photographs) and estimated intensities are given in Table IV.

The six-term radial distribution function is shown in Fig. 1. It shows two well-defined peaks, with maxima at 1.67 Å. (C–Cl) and 3.21 Å. (Cl–Cl). These correspond to the value 123°15′ for the angle Cl–C–C, and to another C–Cl distance of 2.69 Å., some indication of which is visible in the curve.

On calculation of theoretical intensity curves it was found that all models giving rough qualitative agreement with the photographs lead to a Cl–Cl distance close to 3.23 Å. In order to determine the C–Cl distance, curves were calculated for a series of models with C–C = 1.38 and Cl–Cl = 3.23, the value of C–Cl being varied. It was found that the shelf beyond the second ring changes rapidly in this series; only for C–Cl = 1.68 (curve C in Fig. 6) does the shelf correspond to its appearance on the photograph (about one-fourth as pronounced as the second ring). Decrease by 3% wipes it out entirely. We accordingly accept model C. The comparison of observed s values and x values for this model, given in Table IV, leads to C–Cl = 1.671 Å., Cl–Cl = 3.223 Å.

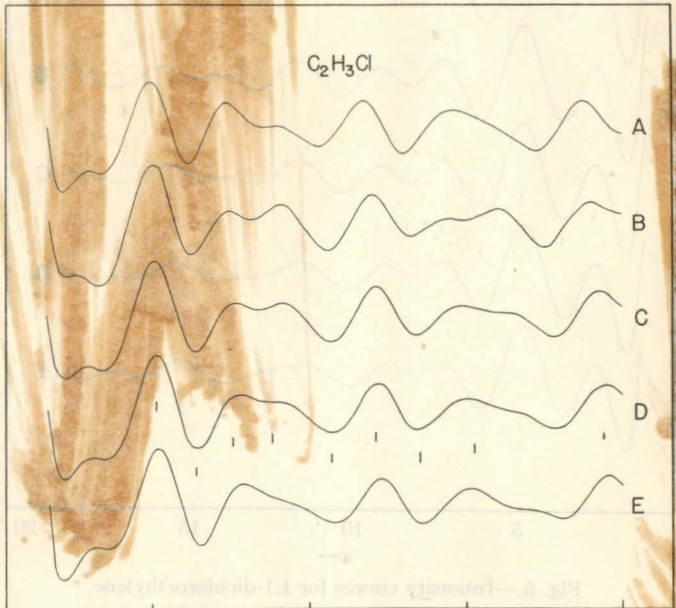


Fig. 4.—Intensity curves for five models of vinyl chloride.

Curve A, calculated for the non-resonating

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[7] R. Wierl, *Ann. Physik*, **13**, 453 (1932).

TABLE IV

cis-DICHLOROETHYLENE

Max.	Min.	I	s	x for Model A	x for C	C–Cl for Model A	C–Cl for C
1		10	2.480	2.36	2.46	(1.675 Å.)	(1.666 Å.)
	2		3.489	3.20	3.35	(1.614)	(1.613)
2		30	4.652	4.33	4.62	(1.639)	(1.668)
Shelf		8	6.00				
	3		6.958	6.57	6.88	1.662	1.661
3		20	8.095	7.74	8.14	1.682	1.689
	4		9.22	8.78	9.23	1.675	1.681
4		3	10.10	9.62	10.01	1.677	1.665
	5		11.16	10.54	10.98	1.664	1.653
5		10	12.17	11.63	12.15	1.682	1.677
					Average	1.674 Å.	1.671 Å.

Model A: C–C = 1.38, C–Cl = 1.76, β = 125°
Model C: C–C = 1.38, C–Cl = 1.68, β = 123.7°
Results: C–C = 1.38 Å. (assumed)
C–Cl = 1.67 ± 0.03 Å.
Cl–Cl = 3.22 ± 0.02 Å.
Angle Cl–C–C = 123.5 ± 1°

model with the Cl–C–C angle β = 125°, C–C = 1.38, and C–Cl = 1.76, is in satisfactory qualitative agreement with the photographs, quantitative comparison, however, giving C–Cl = 1.674 Å. and Cl–Cl = 3.233 Å. (Table IV), the only essential difference from the results for model C being in the C–C distance, for which the low value 1.30 Å. is obtained. Curve D, calculated for β = 130°, C–Cl = 1.72, and C–C = 1.38, shows the extreme qualitative disagreement caused by a relatively small change in model.

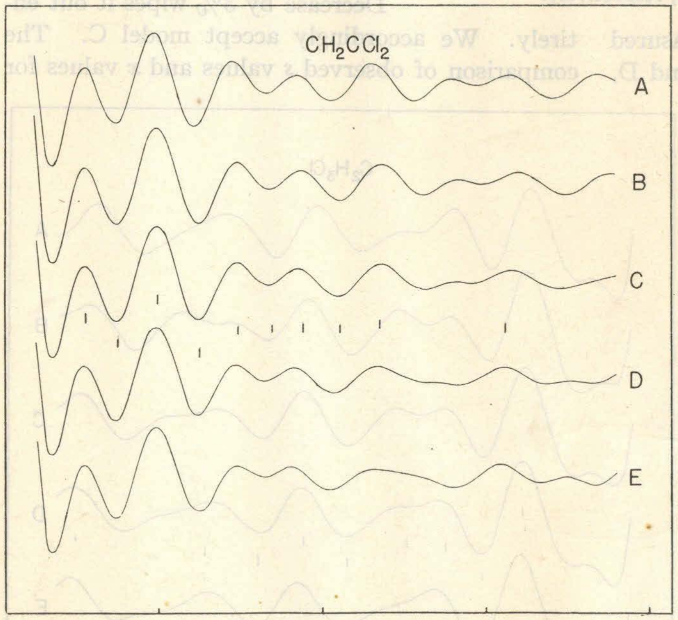

Fig. 5.—Intensity curves for 1,1-dichloroethylene.

Combining the results of the two methods, we accept for the structural constants the values C–C = 1.38 Å. (assumed), C–Cl = 1.67 ± 0.03 Å., Cl–Cl = 3.22 ± 0.02 Å., β (angle Cl–C–C) = 123.5 ± 1°. Previous investigations have given the less accurate values Cl–Cl = 3.30 ± 0.1 Å. (Wierl,[7] electron diffraction) and Cl–Cl = 3.6 Å. (Debye,[8] x-ray diffraction).

trans-Dichloroethylene.—The sample of *trans*-dichloroethylene was separated from a mixture with the *cis* compound by fractional distillation.

The photographs show seven measurable rings, with apparent intensities as given in Table V (the second ring showing an outer shelf). Values of s (averages for ten photographs) are also given in the table for the features which could be measured with accuracy.

The eight-term radial distribution function, given in Fig. 1, shows three well-defined peaks, with maxima at 1.675, 2.70 and 4.27 Å. These we correlate with the two C–Cl interactions and the Cl–Cl interaction, the three interactions being of about equal importance. The distances correspond to the values C–C = 1.38 Å., β (angle Cl–C–C) = 123°.

In applying the usual visual method we observed that the quantitative comparison with the photographs of all the models tried gave values close to 4.27 Å. for the Cl–Cl distance. We then

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(8) P. Debye, *Physik. Z.*, **31**, 142 (1930).

TABLE V

trans-DICHLOROETHYLENE

Max.	Min.		s	x for Model C	x for D	C–Cl for Model C	C–Cl for D
1		5	3.11	3.25	3.26	(1.777 Å.)	(1.803 Å.)
	2		3.98	3.95	3.95	1.687	1.707
2		20	4.90	4.87	4.87	1.690	1.716
Shelf		5	5.68				
	3		6.78	6.71	6.77	1.682	1.717
3		10	7.74	7.75	7.74	1.702	1.720
4		1	9.18	9.17	9.18	1.698	1.720
5		1	10.59	10.63	10.62	1.706	1.724
6		5	12.11	12.10	12.11	1.699	1.720
7		2	14.97	15.05	15.02	1.709	1.725
					Average C–Cl	1.697 Å.	1.719 Å.
					Cl–Cl	4.272 Å.	4.277 Å.

Results:
C–C = 1.38 Å. (assumed)
C–Cl = 1.69 ± 0.02 Å.
Cl–Cl = 4.27 ± 0.02 Å.
Angle Cl–C–C = 122.5 ± 1°

calculated curves for models with Cl–Cl = 4.28, C–C = 1.38, and C–Cl = 1.68, 1.70, 1.72 and 1.76 (curves B, C, D and E, respectively, of Fig. 7). All of these agree qualitatively with the photographs except in so far as the weak fourth and fifth rings are concerned; the approximate equality of these rings is best represented by curve D. The results of the quantitative comparison for C and D are given in Table V; it is seen that the value of the Cl–Cl distance is essentially independent of the model.

Averaging the results of the two methods, with about equal weights, we assign to the structural parameters the values C–C = 1.38 Å. (assumed), C–Cl = 1.69 ± 0.02 Å., Cl–Cl = 4.27 ± 0.02 Å., β (angle Cl–C–C) = 122.5 ± 1°. Previous studies gave the values Cl–Cl = 4.33 ± 0.1 Å. (Wierl,[7] electron diffraction) and Cl–Cl = 4.1 Å. (Debye,[8] x-ray diffraction). In addition a note has been published by de Laszlo[9] in which the C–Cl distance in this molecule is given as 1.74 Å.

Trichloroethylene.—The photographs of trichloroethylene (Eastman) show six rings, with intensities weak, strong, medium, weak, medium weak, weak. Characteristic features are that there is some indication of a small shelf between the second and third rings (closer to the second than to the third) and that the weak fourth ring is closer to the third than to the fifth. The measured values of s (average for three photographs, two observers) are given in Table VI.

The five-term radial distribution function (Fig. 1) shows three peaks, with maxima at 1.73, 2.85 and 4.37 Å., the first corresponding to the small C–Cl distances, the second to the larger C–Cl distances and to two Cl–Cl distances, and the third to the *trans* Cl–Cl distance. The lack of resolution of the second peak makes it of little value.

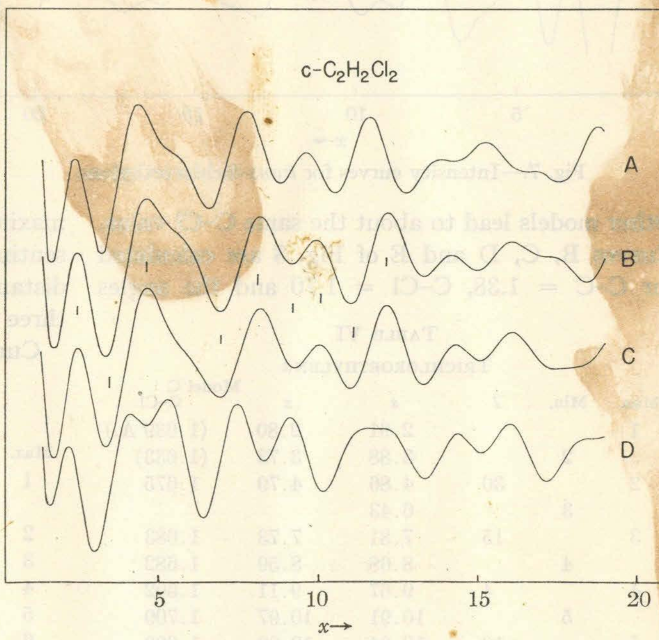

Fig. 6.—Intensity curves for *cis*-dichloroethylene.

In discussing the possible molecular models we have restricted ourselves mainly to those in which

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(9) H. de Laszlo, *Nature*, **135**, 474 (1935).

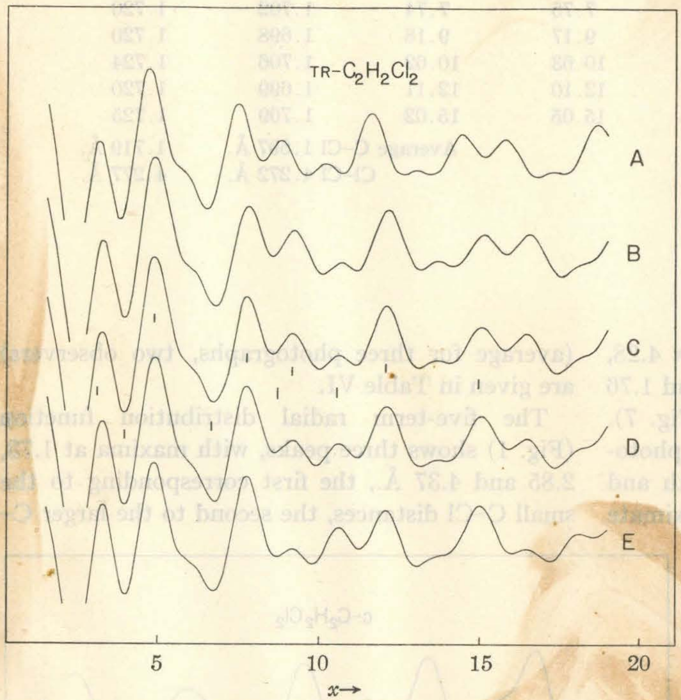

Fig. 7.—Intensity curves for *trans*-dichloroethylene.

the three Cl–C–C angles are equal. Curve A (Fig. 8) is calculated for C–C = 1.38, C–Cl = 1.76 and the angles Cl–C–C = 125° for the CCl_2 group and 123° for the CHCl group. This curve agrees with the photographs qualitatively, and leads on quantitative comparison to the value 1.69 Å. for C–Cl (and hence 1.32 Å. for C–C). Other models lead to about the same C–Cl value. Curves B, C, D and E of Fig. 8 are calculated for C–C = 1.38, C–Cl = 1.70 and the angles Cl–C–C = 125, 122.5, 121.5 and 120°, respectively. Of these curves C alone is in satisfactory qualitative agreement with the photographs. Quantitative comparison (Table VI) leads to the values C–Cl = 1.69 Å., Cl–Cl = 2.85, 3.19 and 4.27 Å. Giving somewhat more weight to these than to the radial distribution values, we accept as representing the configuration of the molecule the values C–C = 1.38 Å. (assumed), C–Cl = 1.71 ± 0.03 Å., Cl–Cl = 2.72 ± 0.04 Å. (in the CCl_2 group), and Cl–Cl = 3.23 ± 0.05 Å. and 4.33 ± 0.05 Å. (between CCl_2 and CHCl), with the angles Cl–C–C = 123 ± 2°.

TABLE VI

TRICHLOROETHYLENE

Max.	Min.	*I*	*s*	*x*	Model C C–Cl
1			2.91	2.80	(1.639 Å.)
	2		3.88	3.73	(1.633)
2		30	4.86	4.79	1.675
	3		6.43		
3		15	7.81	7.73	1.683
	4		8.68	8.59	1.682
4		4	9.67	9.11	1.602
	5		10.91	10.97	1.709
5		10	12.04	12.03	1.699
6		4	15.49	16.20	1.778
				Average	1.690 Å.

Results: C–C = 1.38 Å. (assumed)
C–Cl = 1.71 ± 0.03 Å.
Cl–Cl = 2.72 ± 0.04 Å.
3.23 ± 0.05 Å.
4.33 ± 0.05 Å.
Angles Cl–C–C = 123 ± 2°

Trichloroethylene previously has been studied by this method by Dornte,[10] who reported the values C–C = 1.32 ± 0.08 Å., C–Cl = 1.82 ± 0.08 Å., Cl–Cl = 3.41 ± 0.08 Å., and Cl–Cl = 4.52 ± 0.08 Å., in approximate agreement with our values.

Tetrachloroethylene.—The rather weak photographs of tetrachloroethylene (Eastman) obtained at room temperature show six rings, the first medium, the second strong, the third medium, the fourth weak, the fifth medium weak and the sixth weak. Averaged values of *s* (for four photographs) and estimated intensities are given in Table VII.

The six-term radial distribution function (Fig. 9) shows three peaks, with maxima at 1.72, 2.86 and 4.37 Å., the first representing a C–Cl distance, the third the *trans* Cl–Cl distance, and the large second peak representing three distances.

Curves A, B, C and D of Fig. 9 are calculated

TABLE VII

TETRACHLOROETHYLENE

Max.	Min.	*I*	*s*	*x* for model B	C–Cl
1		15	2.78	2.70	(1.69 Å.)
	2		3.81	3.68	(1.68)
2		30	4.76	4.63	1.691
3		10	7.46	7.52	1.753
4		3	9.00	9.12	1.761
5		8	11.84	11.72	1.722
6		3	15.17		
				Average	1.732 Å.

Results: C–C = 1.38 Å. (assumed)
C–Cl = 1.73 ± 0.02 Å.
Cl–Cl = 2.87 ± 0.03 Å.
3.30 ± 0.03 Å.
4.28 ± 0.03 Å.
Angle Cl–C–C = 123° 45′ ± 1°

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(10) R. W. Dornte, *J. Chem. Phys.*, **1**, 566 (1933).

for models with C–C = 1.38, C–Cl = 1.74 and the angles Cl–C–C = 125°, 123°45′, 122°30′ and 121°15′, respectively. It is seen that the curves change very rapidly with change in angle. The appearance of the photograph is closely reproduced by curve B, and not so well by C or A; the latter is unsatisfactory only in that the fourth peak is not sufficiently displaced toward the third. We accordingly accept for the Cl–C–C angle the value 123°45′ ± 1°.

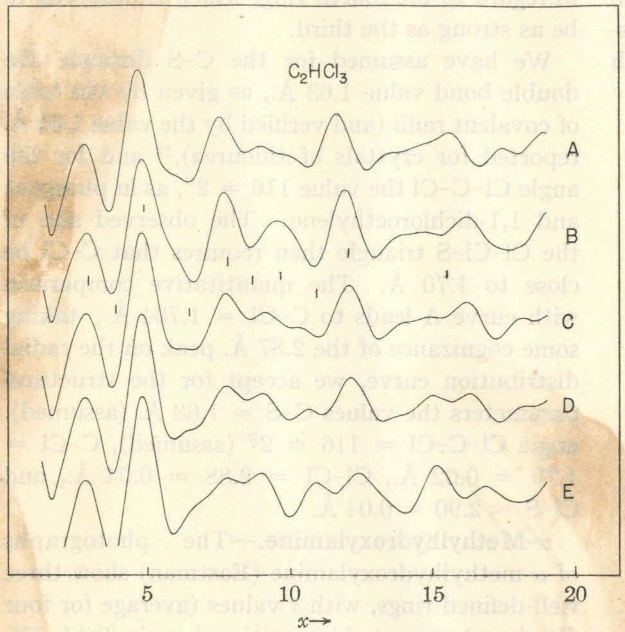

Fig. 8.—Intensity curves for trichloroethylene.

TABLE VIII

THIOPHOSGENE

Max.	Min.	*I*	*s*	*x* for model B	C–Cl
1		10	2.84	2.67	(1.598 Å.)
	2		3.75	3.67	(1.664)
2		25	5.00	4.84	(1.646)
	3		6.08	6.04	1.689
3		12	7.16	7.13	1.693
	4		8.10	8.06	1.692
4		12	9.17	9.09	1.685
	5		10.25	10.29	1.707
5		6	11.40	11.49	1.713
	6		12.43	12.51	1.711
6		3	13.41	13.48	1.709
	7		14.51	14.56	1.706
7		3	15.56	15.75	1.721
	8		16.78	16.88	1.710
8		1	17.79	17.90	1.711
	9		18.90	18.87	1.697
9		1	19.90	19.97	1.706
				Average	1.704 Å.

Results: C–S = 1.63 Å. (assumed)
Angle Cl–C–Cl = 116 ± 2° (assumed)
C–Cl = 1.70 ± 0.02 Å.
Cl–Cl = 2.88 ± 0.04 Å.
Cl–S = 2.90 ± 0.04 Å.

The quantitative comparison leads to C–Cl = 1.732 Å. and Cl–Cl (*trans*) = 4.38 Å., in essential agreement with the results of the radial distribution treatment. We accordingly accept for the structural parameters of the molecule the values C–C = 1.38 Å. (assumed), C–Cl = 1.73 ± 0.02 Å., Cl–Cl = 2.87 ± 0.03 Å. (in the same CCl_2 group), and Cl–Cl = 3.30 ± 0.03 Å. and 4.28 ± 0.03 Å. (between CCl_2 groups), with the angle Cl–C–C = 123°45′ ± 1°.

A previous electron diffraction investigation by Dornte[10] gave the values C–C = 1.32 ± 0.08 Å., C–Cl = 1.82 ± 0.08 Å., and Cl–Cl = 3.41 ± 0.08 Å. and 4.52 ± 0.08 Å., in approximate agreement with our results. De Laszlo has also reported the value C–Cl = 1.74 Å. in a preliminary note.[9]

Thiophosgene.—The thiophosgene used was prepared by the chlorination of carbon disulfide and subsequent reduction, and purified by fractional distillation.[11]

The photographs show nine rings, for which measured *s* values and estimated intensities are given in Table VIII (averages for four photo-

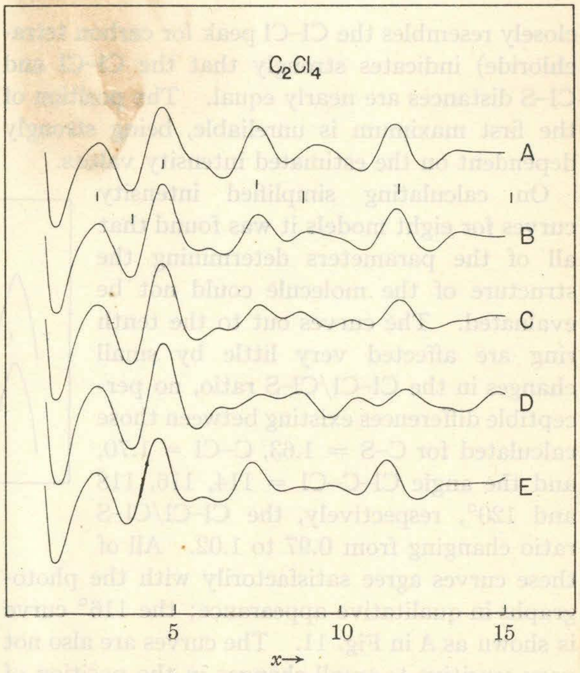

Fig. 9.—Intensity curves for tetrachloroethylene.

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[11] "Organic Syntheses," John Wiley and Sons, Inc., New York City Coll., Vol. I, p. 493.

graphs[12]). The nine-term radial distribution curve (Fig. 10) shows two well-defined peaks, the first, with maximum at 1.59 Å., corresponding to the C–S and C–Cl distances, and the second, with maximum at 2.87 Å., to the Cl–Cl and Cl–S distances. The sharpness of the second peak (which closely resembles the Cl–Cl peak for carbon tetrachloride) indicates strongly that the Cl–Cl and Cl–S distances are nearly equal. The position of the first maximum is unreliable, being strongly dependent on the estimated intensity values.

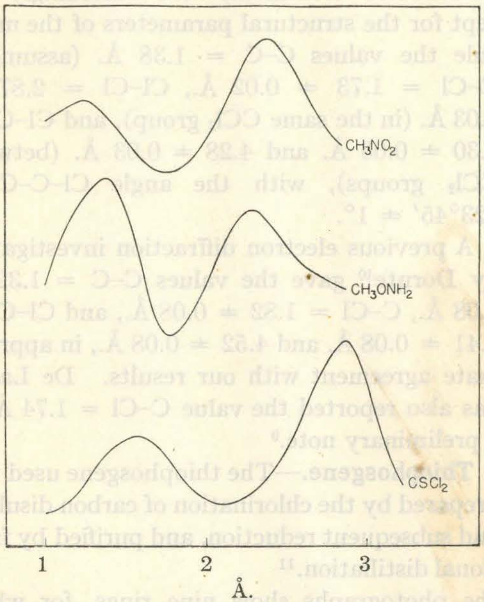

Fig. 10.—Radial distribution curves for nitromethane, α-methylhydroxylamine and thiophosgene.

On calculating simplified intensity curves for eight models it was found that all of the parameters determining the structure of the molecule could not be evaluated. The curves out to the tenth ring are affected very little by small changes in the Cl–Cl/Cl–S ratio, no perceptible differences existing between those calculated for C–S = 1.63, C–Cl = 1.70, and the angle Cl–C–Cl = 114, 116, 118 and 120°, respectively, the Cl–Cl/Cl–S ratio changing from 0.97 to 1.02. All of these curves agree satisfactorily with the photographs in qualitative appearance; the 116° curve is shown as A in Fig. 11. The curves are also not very sensitive to small changes in the position of the light carbon atom; however, the curve for C–Cl = 1.76, C–S = 1.44 and the angle Cl–C–Cl = 110° (B of Fig. 11) is qualitatively unsatisfactory in regard to the fourth ring, which is observed to be as strong as the third.

We have assumed for the C–S distance the double bond value 1.63 Å., as given by the table of covalent radii (and verified by the value 1.64 Å. reported for crystals of thiourea),[13] and for the angle Cl–C–Cl the value 116 ± 2°, as in phosgene and 1,1-dichloroethylene. The observed size of the Cl–Cl–S triangle then requires that C–Cl be close to 1.70 Å. The quantitative comparison with curve A leads to C–Cl = 1.704 Å.; taking some cognizance of the 2.87 Å. peak on the radial distribution curve, we accept for the structural parameters the values C–S = 1.63 Å. (assumed), angle Cl–C–Cl = 116 ± 2° (assumed), C–Cl = 1.70 ± 0.02 Å., Cl–Cl = 2.88 ± 0.04 Å., and Cl–S = 2.90 ± 0.04 Å.

α-Methylhydroxylamine.—The photographs of α-methylhydroxylamine (Eastman) show three well-defined rings, with *s* values (average for four films) and estimated intensities given in Table IX. The three-term radial distribution function (Fig. 10) shows peaks with maxima at 1.39 and 2.31 Å. The first we interpret as showing the C–O and O–N distances, unresolved, the table of covalent radii giving for them the values 1.43 and 1.36 Å., respectively. The C–N distance 2.31 Å. then leads to the value 112° for the C–O–N angle.

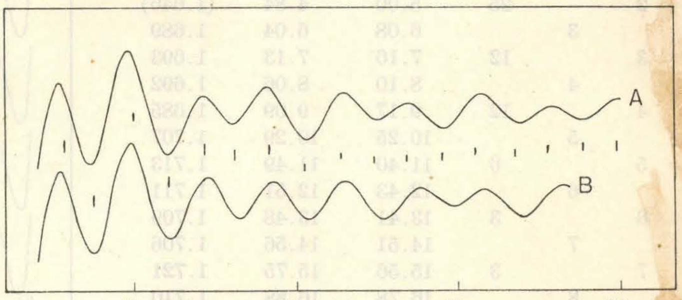

Fig. 11.—Intensity curves for thiophosgene.

Intensity curves were calculated for the following values of the angle: 114, 110 and 106°. In these the ratio of the O–N and C–O distances was taken as 1.36/1.43. The curves for the first two are shown in Fig. 12 and the *x* values in Table IX. Model A (110° angle) is superior to Model B (114° angle) as indicated by the poor agreement between the *x* and *s* values for the second maxi-

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(12) Some measurements made on five rings of very weak photographs, disagreeing with those in the table by about 2%, were discarded.

(13) R. W. G. Wyckoff and R. B. Corey, *Z. Krist.*, **81**, 386 (1932).

TABLE IX

α-METHYLHYDROXYLAMINE

Max.	Min.	I	s	Model A x	Model A N–O	Model B x	Model B N–O
1		5	6.00	6.10	1.383 Å.	6.04	1.369 Å.
	2		7.95	7.93	1.357	7.88	1.349
2		2	9.49	9.93	1.418	10.20	(1.461)
	3		12.13	12.20	1.367	12.17	1.362
3		1	13.94	14.30	1.393	14.18	1.381
				Average	1.384 Å.		1.365 Å.

Results: N–O = 1.37 ± 0.02 Å.
C–O = 1.44 ± 0.02 Å.
C–N = 2.31 ± 0.03 Å.
Angle C–O–N = 111 ± 3°

mum in Model B. The 106° model was rejected because it leads to widely fluctuating values for the size of the molecule as calculated from the various maxima and minima. The quantitative comparison for Model A leads to N–O = 1.38 Å., C–O = 1.45 Å. and C–N = 2.31 Å.

Combining the results of the two methods we obtain the values N–O = 1.37 ± 0.02 Å., C–O = 1.44 ± 0.02 Å., angle C–O–N = 111 ± 3°, C–N = 2.31 ± 0.03 Å.

Nitromethane.—The photographs of nitromethane (Eastman) show four well-defined rings followed by a very wide minimum and two more very faint maxima. The s values averaged from six photographs and the estimated intensities are given in Table X. The six-term radial distribution function (Fig. 10) shows two peaks with maxima at 1.19 and 2.18 Å., the first corresponding to the N–O distance with the N–C distance unresolved and the second to the O–O and C–O distances.

TABLE X

NITROMETHANE

Max.	Min.	I	s	x	N–O$_{125°}$
1		10	3.65	3.27	(1.09 Å.)
	2		5.04	4.43	(1.07)
2		30	6.50	6.26	1.175
	3		7.96	8.00	1.226
3		12	9.29	9.28	1.219
	4		10.54	10.17	1.178
4		12	11.75	11.83	1.228
	5		13.47	13.61	1.231
5		3	17.77	17.21	1.181
	6		19.37	19.50	1.227
6		2	21.02		
				Average	1.208 Å.

Results: N–O = 1.21 ± 0.02 Å.
C–N = 1.46 ± 0.02 Å.
Angle O–N–O = 127 ± 3°

The photographs do not permit the evaluation of all the structural parameters. We expect, however, that the C–N distance has the single bond value 1.47 Å. and the N–O distances approximately the double bond value 1.22 Å. The three curves in Fig. 13 correspond to models having the relative dimensions determined by the above distances and the three values of the O–N–O angle, 120, 125 and 130°, respectively. The qualitative features of the photographs fix the angle at about 127°. Thus, the prominence of the third maximum relative to the fourth and the position and character of the fifth minimum as observed on the photograph eliminate the 120° model. In the 130° curve the position of the seventh maximum is a little better than in the one for 125° but the hump following the fifth minimum is too pronounced. The quantitative comparison (Table X) leads to the values C–N = 1.46 ± 0.02 Å. and N–O = 1.21 ± 0.02 Å., with the angle O–N–O = 127 ± 3°.

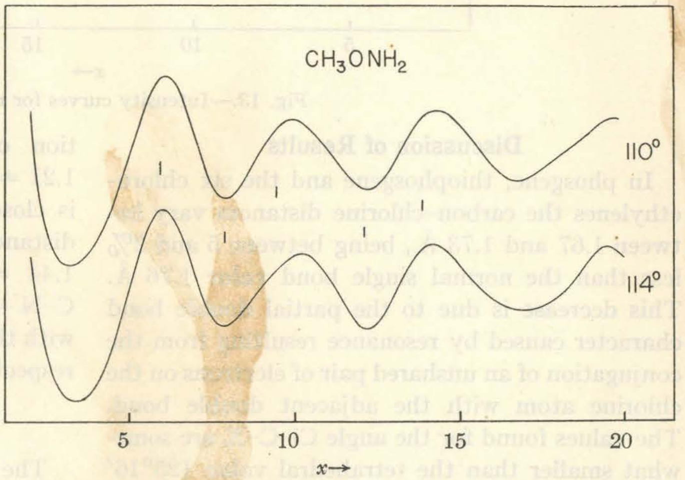


Fig. 12.—Intensity curves for α-methylhydroxylamine.

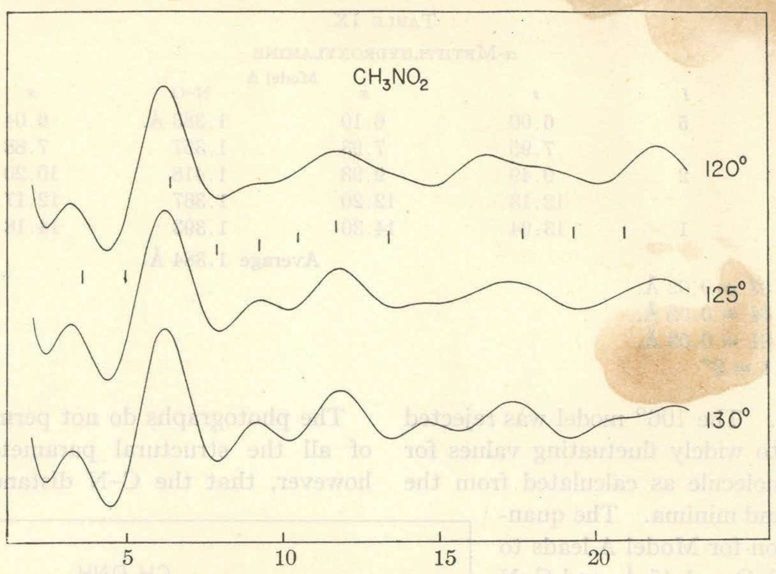


Fig. 13.—Intensity curves for nitromethane.

Discussion of Results

In phosgene, thiophosgene and the six chloroethylenes the carbon–chlorine distances vary between 1.67 and 1.73 Å., being between 5 and 2% less than the normal single bond value 1.76 Å. This decrease is due to the partial double bond character caused by resonance resulting from the conjugation of an unshared pair of electrons on the chlorine atom with the adjacent double bond. The values found for the angle Cl–C–X are somewhat smaller than the tetrahedral value 125°16′ for the angle between a single bond and a double bond, as a result of the same phenomenon. A detailed discussion of these effects is given in the following paper.

For the other interatomic distances the values found are in good agreement with the table of covalent radii. In phosgene the carbon–oxygen distance has the double bond value 1.28 ± 0.02 Å. (1.28 Å. from the table), and for thiophosgene the double bond value 1.63 Å. for the carbon–sulfur distance leads to a satisfactory interpretation of the photographs. The N–O distance 1.21 ± 0.02 Å. for the nitro group in nitromethane is close to the double bond value 1.22 Å. The distances N–O = 1.37 ± 0.02 Å. and C–O = 1.44 ± 0.02 Å. in α-methylhydroxylamine and C–N = 1.46 ± 0.02 Å. in nitromethane agree well with the single bond values 1.36, 1.43 and 1.47 Å., respectively, given by the table of radii.

Summary

The arrangements of atoms in molecules of phosgene, the six chloroethylenes, thiophosgene, α-methylhydroxylamine and nitromethane have been determined by the use of electron diffraction photographs, interpreted both by the radial distribution method and the usual visual method, with the following results. (Values given without attached probable errors were assumed to be correct in the investigation.)

Phosgene: C–Cl = 1.68 ± 0.02 Å.; C–O = 1.28 ± 0.02 Å.; angle Cl–C–O = 121.5 ± 1°.

	C—C	C—Cl	Angle Cl—C—C
Vinyl chloride	1.38 Å.	1.69 ± 0.02 Å.	122 ± 2°
1,1-Dichloroethylene	1.38	1.69 ± 0.02	122 ± 1°
cis-Dichloroethylene	1.38	1.67 ± 0.03	123.5 ± 1°
trans-Dichloroethylene	1.38	1.69 ± 0.02	122.5 ± 1°
Trichloroethylene	1.38	1.71 ± 0.03	123 ± 2°
Tetrachloroethylene	1.38	1.73 ± 0.02	123.75 ± 1°

Thiophosgene: C–Cl = 1.70 ± 0.02 Å.; C–S = 1.63 Å.; angle Cl–C–S = 122°.

α-Methylhydroxylamine: N–O = 1.37 ± 0.02 Å.; O—C = 1.44 ± 0.02 Å.; angle C–O–N = 111 ± 3°.

Nitromethane: N–O = 1.21 ± 0.02 Å.; C–N = 1.46 ± 0.02 Å.; angle O–N–O = 127 ± 3°.

The discussion and interpretation of these results are given in the following paper.

PASADENA, CALIFORNIA RECEIVED SEPTEMBER 24, 1935

The Dependence of Interatomic Distance on Single Bond-Double Bond Resonance

[Reprint from the Journal of the American Chemical Society, **57**, 2705 (1935).]

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 509]

The Dependence of Interatomic Distance on Single Bond–Double Bond Resonance[1]

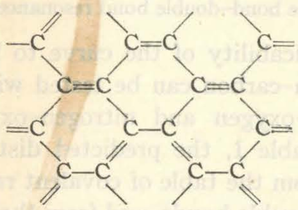
BY LINUS PAULING, L. O. BROCKWAY AND J. Y. BEACH

Introduction

Three years ago it was pointed out[2] that observed values of interatomic distances provide useful information regarding the electronic structures of molecules, and especially regarding resonance between two or more valence bond structures. On the basis of the available information it was concluded that resonance between two or more structures leads to interatomic distances nearly as small as the smallest of those for the individual structures.[3] For example, in benzene each carbon–carbon bond resonates about equally between a single bond and a double bond (as given by the two Kekulé structures); the observed carbon–carbon distance, 1.39 Å., is much closer to the carbon–carbon double bond distance, 1.38 Å., than to the single bond distance, 1.54 Å.

In benzene the two Kekulé structures contribute equally. In general, however, the coefficients of the functions corresponding to different structures in the approximate wave function of a molecule may have arbitrary values, and a bond between two atoms may have any intermediate character between the extremes of a pure single bond and a pure double bond. For a series of bonds covering the range between a pure single bond and a pure double bond we expect the interatomic distance to change continuously from the single bond value to the double bond value. In this paper we present evidence regarding the nature of the function expressing the dependence of interatomic distance on single bond–double bond resonance, and then make use of the function in order to obtain information regarding the electronic structures of resonating molecules for which experimental interatomic distance values are available. The effect of resonance on bond angles is also discussed.

The Interatomic Distance Function for Single Bond–Double Bond Resonance.—The carbon–carbon single bond distance is 1.54 Å. (diamond, aliphatic compounds). For the carbon–carbon double bond distance we shall use the value 1.38 Å. given by the table of covalent radii;[4] some support for this is given by Badger's value[5] 1.37 Å. for ethylene. These give the two extreme points of the interatomic distance function for single bond–double bond resonance. The midway point, for fifty per cent. double bond character, is provided by the value 1.39 Å. for benzene;[6] the electronic structure of benzene is represented in the main by resonance between the two Kekulé structures (the contribution of excited structures being small[7]), and this makes each bond resonate equally between a double and a single bond. Another point on the curve is provided by graphite (C–C = 1.42 Å.), in which each bond has one-third double bond character, corresponding to resonance among many structures such as



Through these four points we draw a smooth curve, as shown in Fig. 1, which we accept as representing the dependence of carbon–carbon interatomic distance on double-bond character for single bond–double bond resonance. We believe that by a suitable translation and a change of vertical scale (to give the correct end-points) the same function can be used for bonds between other atoms, and probably also for double bond–triple bond resonance. This use of the curve will be illustrated below.

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[1] Part of the material in this paper was presented at the meeting of the A. A. A. S. in Berkeley, June, 1934.

[2] L. Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293 (1932).

[3] The following argument, suggested by Professor P. M. Morse, shows that this conclusion is reasonable. Of two potential functions corresponding to two structures, the one with the smaller value of the equilibrium internuclear distance will have the greater curvature in the neighborhood of the minimum [see for example, R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1934)]. Hence the more stable of the two resultant potential functions corresponding to resonance between these two structures will tend to have its minimum in the position determined by the original curve of greater curvature, that is, near the smaller value of the internuclear distance.

[4] L. Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293 (1932); L. Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934).

[5] R. M. Badger, *Phys. Rev.*, **45**, 648 (1934).

[6] L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 867 (1934).

[7] A possibly more accurate value for the double bond character of the bonds in benzene (0.46) is obtained by considering all five canonical structures with weights equal to the squares of their coefficients in the wave function. There is some uncertainty as to the significance of this, however, because of the non-orthogonality of the wave functions for the canonical structures, and for chemical purposes it is sufficiently accurate to follow the simple procedure adopted above.

It is seen that a small amount of double bond character causes a large decrease in interatomic distance below the single bond value, whereas only a small change from the double bond value is caused by even as much as fifty per cent. single bond character.[8] In consequence, the interatomic distance criterion for resonance provides quantitative information only through about one-half of the bond character region.

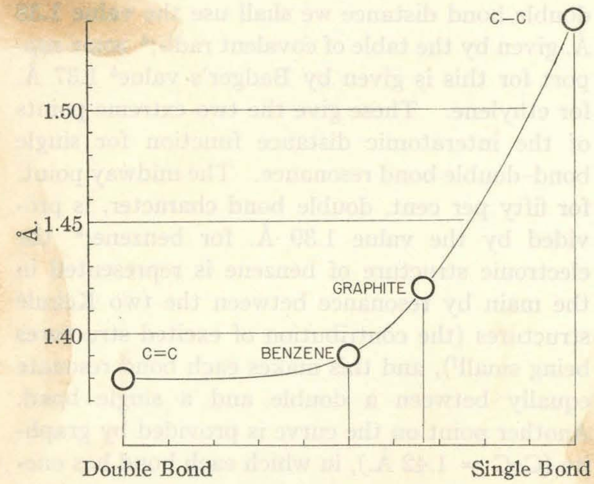

Fig. 1.—The empirical function expressing the dependence of carbon–carbon interatomic distance on bond character for single bond–double bond resonance.

The applicability of the curve to bonds other than carbon–carbon can be tested with the data for carbon–oxygen and nitrogen–oxygen bonds given in Table I, the predicted distances being obtained from the table of covalent radii for pure single and double bonds, and from the curve (with end-points determined by the table) for bonds of intermediate type. The carbonate and nitrate ions resemble graphite in that the double bond resonates among three positions, whereas in the carboxyl and nitro groups, as in benzene, the double bond resonates between two positions. It is seen that there is approximate agreement between predicted and observed values.

The Use of the Interatomic Distance Function in Discussing the Electronic Structure of Molecules.—The observed interatomic distances listed in Table II are interpreted with the aid of the curve of Fig. 1 to lead to the assignment of fractional double bond character as given in the last column. It is seen that a single bond between conjugated double bonds (cyclopentadiene) or conjugated benzene rings (biphenyl) *p*-diphenylbenzene, has about 15 or 20% double bond character,[9] whereas a single bond between conjugated

TABLE I

COMPARISON OF PREDICTED AND OBSERVED INTERATOMIC DISTANCES

Carbon–Oxygen Bonds

Amount of double bond character	Predicted distance	Observed distance
0	1.43 Å.	1.42 Å. in $(CH_3)_2O$[a] 1.44 in CH_3ONH_2[a]
$^1/_3$	1.32	1.31 (1.26) in $(CO_3)^{=}$[b]
$^1/_2$	1.29	1.29 in $(HCOOH)_2$[c]
1	1.28	

Nitrogen–Oxygen Bonds

Amount of double bond character	Predicted distance	Observed distance
0	1.36 Å.	1.37 Å. in CH_3ONH_2[a]
$^1/_3$	1.26	1.22 (1.26) in $(NO_3)^-$[b]
$^1/_2$	1.23	1.21 in CH_3NO_2[a]
1	1.22	

[a] Preceding papers. [b] Preliminary values obtained through redetermination of parameters in crystals (calcite and sodium nitrate) by Mr. Norman Elliot. The values in parentheses are based on older parameter determinations. [c] L. Pauling and L. O. Brockway, *Proc. Nat. Acad. Sci.*, **20**, 336 (1934). The value 1.25 Å. reported in crystals of oxalic acids and oxalates is probably less reliable.

TABLE II

INTERATOMIC DISTANCES AND BOND TYPE

Molecule	Bond	Observed distance	Amount of double bond character
Cyclopentadiene	C—C	1.46 Å.[a]	0.20
p-Diphenylbenzene	C—C	1.48[b]	.14
Biphenyl	C—C	1.48[c]	.14
Cyanogen	C—C	1.43[d]	.29
Diacetylene	C—C	1.43[d]	.29
Urea	C—N	1.37[e]	.28
Thiourea	C—N	1.37[f]	.28
Cyanuric triazide	C—N	1.38[g]	.25
Carbon suboxide	C=C	1.30[h]	.20[i]
	C=O	1.20[h]	.20[i]

[a] Preliminary result of electron diffraction study in this Laboratory. [b] L. W. Pickett, *Proc. Roy. Soc.* (London), **A142**, 333 (1933). [c] J. Dhar, *Indian J. Phys.*, **7**, 43 (1932). [d] L. O. Brockway, *Proc. Nat. Acad. Sci.*, **19**, 868 (1933). [e] R. W. G. Wyckoff and R. B. Corey, *Z. Krist.*, **89**, 462 (1934). [f] R. W. G. Wyckoff and R. B. Corey, *ibid.*, **81**, 386 (1932). [g] I. E. Knaggs, *Proc. Roy. Soc.* (London), **A150**, 576 (1935). [h] L. O. Brockway and L. Pauling, *Proc. Nat. Acad. Sci.*, **19**, 860 (1933). [i] Triple-bond character.

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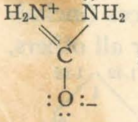
[8] Verification of the shape of the curve has been obtained with the collaboration of Dr. J. Sherman by the theoretical treatment of a somewhat similar problem (the effect of *s-p* hybridization of bond orbitals on interatomic distance).

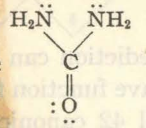
[9] The comparison of these results with the simple theory of conjugated systems [Pauling and Sherman, *J. Chem. Phys.*, **1**, 679 (1933)] is not straightforward because of non-orthogonality of the canonical structures. If we assume that the double bond character is given by the square of the coefficient of the structure — = — in the normalized wave function for a system of two conjugated double bonds the simple theory leads to the value 0.25. in approximate agreement with the experimental result.

triple bonds (cyanogen, diacetylene) has about 30% double bond character. In cyanuric triazide the reported distance for the bond linking an azide group to the cyanuric ring corresponds to about 25% double bond character.

In urea and thiourea the ionic structures such as are of sufficient importance to give each C–N bond about 28% double bond character.

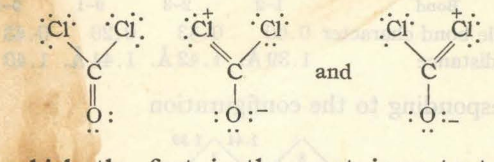


In case these structures were equivalent to the structure giving complete resonance, each bond would have one-third double bond character, as in the carbonate, nitrate, and guanidonium ions. The experimental result shows that resonance is nearly complete.



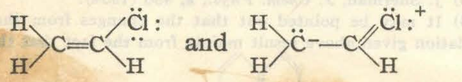
In carbon suboxide, for which the structure $:\ddot{O}=C=C=C=\ddot{O}:$ is most important, structures such as $^{-}:\ddot{O}-C\equiv C-C\equiv O:^{+}$ contribute about 20% triple bond character to each bond.

Resonance of a Carbon–Chlorine Bond and an Adjacent Double Bond.—We expect the phosgene molecule to resonate among the structures



of which the first is the most important, the second and third making only small contributions to the normal state of the molecule. The value 1.68 ± 0.02 Å. for the C–Cl distance, reported in the preceding paper,[10] corresponds to 17% double bond character for the carbon–chlorine bonds, calculated with the curve of Fig. 1, with end points C–Cl = 1.76 Å. and C=Cl = 1.58 Å. The value C–Cl = 1.70 ± 0.02 Å. in thiophosgene leads to 12% double bond character, indicating that the ionic structures make a smaller contribution for this molecule than for phosgene.

We might predict that of the six chloroethylenes the C–Cl distance would be smallest in vinyl chloride, which resonates between the structures



and largest in tetrachloroethylene, in which the effect of the double bond is divided among four carbon–chlorine bonds. This is found experimentally (Table III), except that the distance reported for *cis*-dichloroethylene is about 0.02 Å. smaller and that for vinyl chloride somewhat larger than expected. The amounts of double bond character shown in the table are reasonable—about 15% for mono- and dichloroethylenes, 10% for trichloroethylene, and 6% for tetrachloroethylene.

TABLE III

INTERATOMIC DISTANCES AND BOND TYPE FOR CARBON–CHLORINE BONDS

Molecule	C–Cl distance	Double bond character
Phosgene	1.68 ± 0.02 Å.	0.17
Thiophosgene	1.70 ± .02	.12
CH_2CHCl	1.69 ± .02	.14
CH_2CCl_2	1.69 ± .02	.14
cis-CHClCHCl	1.67 ± .03	.20
trans-CHClCHCl	1.69 ± .02	.14
$CHClCCl_2$	1.71 ± .03	.10
C_2Cl_4	1.73 ± .02	.06

The effect of this partial double bond character on the chemical properties of chlorine atoms conjugated to double bonds is well known; it corresponds in the main to a diminution in reactivity. The correlation with bond angles is discussed in a later section of this paper.

Inasmuch as the conjugation properties of a double bond and a benzene ring are closely similar,[11] we expect for the halogen substituted benzenes interatomic distances similar to those for the halogen ethylenes. De Laszlo[12] has reported the values C–Cl = 1.69 Å., C–Br = 1.88 Å., and C–I = 2.05 Å., corresponding to 14, 6, and 10% double bond character, respectively.[13]

The Dependence of Bond Angles on Single Bond–Double Bond Resonance.—In a molecule such as phosgene or 1,1-dichloroethylene the value 125°16′ for the angle Cl–C–O (β) is predicted by the theory of the tetrahedral carbon atom in case that the C–Cl bonds have no double bond character. If the double bond resonates equally among all three positions, giving the Cl–C bond one-third double bond character, we expect from symmetry

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(10) Brockway, Beach and Pauling, THIS JOURNAL, **57**, 2693 1935).

(11) L. Pauling and J. Sherman, *J. Chem. Phys.*, **1**, 679 (1933).

(12) H. de Laszlo, *Proc. Roy. Soc.* (London), **A146**, 690 (1934).

(13) The interatomic distance values given are stated to hold for hexahalogen, *sym*-trihalogen and *p*-dihalogen benzenes. We expect the distances in these different compounds to be different, however; and investigation of these and other halogen compounds is under way in this Laboratory. De Laszlo has also reported values of C–Br and C–I distances in ethylenic and acetylenic compounds in a letter to *Nature*, **135**, 474 (1935).

the value 120° for β. Between these limits the dependence of β on the amount of double bond character of the C–Cl bonds may be postulated to be given by a curve similar in shape to the interatomic distance curve of Fig. 1. If this is so, there would be a linear relation connecting the angle β and the C–Cl distance, between the points β = 125°16′, C–Cl = 1.76 Å. and β = 120°, C–Cl = 1.64 Å. (as given by the curve for one-third double bond character). From a similar discussion, the other chloroethylenes (except vinyl chloride) would be expected to fall roughly on the same line.

A test of this relation is shown in Fig. 2, the seven points being those determined experimentally for phosgene and the six chloroethylenes.

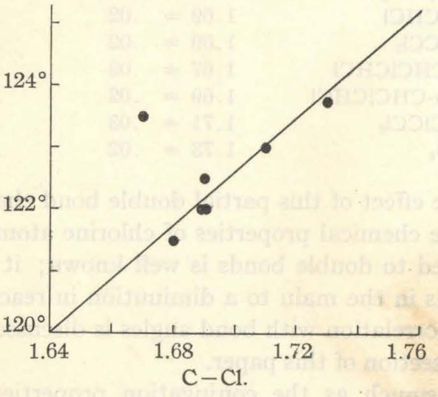
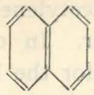
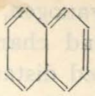
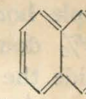
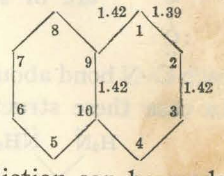


Fig. 2.—The relation between bond angle and carbon-chlorine distance for phosgene and the chloroethylenes.

It is seen that, with one exception, the points lie very close to the straight line drawn according to our assumptions, the displacements being much less than the probable errors of the experimental values. The exceptional point is that for *cis*-dichloroethylene, the discrepancy confirms the suggestion made in the preceding section that our results for this substance are slightly in error.[14] It is surprising that vinyl chloride obeys the same relation, as there is no apparent reason for the angle to be much different from 125°16′.

Interatomic Distances in Polynuclear Aromatic Hydrocarbons.—As a further example of the use of the interatomic distance function we shall discuss the polynuclear aromatic hydrocarbons.

For naphthalene there are three unexcited structures   and  Giving these equal weights, we obtain the result that the 1–2 bonds have $^2/_3$ double bond character and all others $^1/_3$. These correspond to the values 1.39 Å. for the 1–2 interatomic distances (including 3–4, 5–6 and 7–8), and 1.42 Å. for all others, giving the configuration



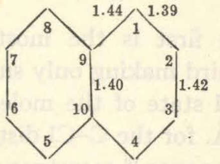
A possibly more reliable prediction can be made on the basis of Sherman's wave function for naphthalene,[15] by considering all 42 canonical structures. The fractional double bond character of a bond can be considered to be given approximately (neglecting non-orthogonality of the canonical wave functions) by the expression

$$\sum\nolimits_i' a_i^2 \Big/ \sum\nolimits_i a_i^2$$

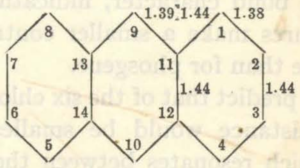
in which a_i represents the coefficient for the ith structure; the unprimed sum includes all structures of the set of 42, and the primed sum those for which the bond in question is a double bond. The results of this calculation are the following:[16]

Bond	1–2	2–3	9–1	9–10
Double bond character	0.60	0.33	0.26	0.43
C–C distance	1.39 Å.	1.42 Å.	1.44 Å.	1.40 Å.

corresponding to the configuration



The four unexcited structures for anthracene, given equal weights, lead to $^3/_4$ double bond character for the 1–2 bonds, $^1/_2$ for the 9–11 bonds and $^1/_4$ for others, the predicted configuration being



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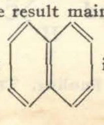
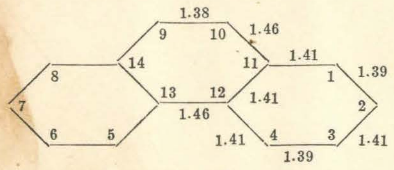
[14] The discrepancies are removed by increasing the C–Cl distance by 0.02 Å., to 1.69 Å., and decreasing the angle by 1°, to 122°30′. These changes are within the estimated probable errors of our determination, ±0.03 Å. and ±1°, respectively.

[15] J. Sherman, *J. Chem. Phys.*, **2**, 488 (1934).

[16] It may be pointed out that the changes from the simple calculation given above result mainly from the fact that the coefficient for the structure  is larger than that for the other unexcited structures.

For phenanthrene the five unexcited structures lead to $^4/_5$ double bond character for the 9–10 bonds, $^3/_5$ for the 1–2 bonds, $^2/_5$ for the 1–11, 11–12 and 4–12 bonds, and $^1/_5$ for the 10–11 and 12–13 bonds, and the predicted configuration is



Similar prediction can be made for larger molecules. It must be pointed out that the contributions of excited structures become important for bonds with small double bond character, inasmuch as in conjugated systems excited structures alone may lead to as much as 20% double bond character; it is probable that the maximum carbon–carbon bond distance in aromatic hydrocarbons is about 1.46 Å., the minimum being the double bond distance 1.38 Å.

The predicted average interatomic distance is 1.41 Å. in naphthalene, anthracene and phenanthrene, this value being somewhat larger than the benzene value (1.39 Å.). With increase in size of the hydrocarbon the carbon–carbon distances should all approach the graphite value 1.42 Å.

The only experimental values of sufficient accuracy to permit a test of the predicted values are those obtained by Robertson in his careful and thorough x-ray investigations of the structure of crystals of naphthalene[17] and anthracene.[18] In each of these molecules Robertson reports the value 1.41 Å. for the average carbon–carbon bond distance, in complete agreement with the predicted value.[19] He does not discuss individual variations from the average; however, measurements made on his reproduced electron distribution projections (Fig. 2 for naphthalene, Fig. 2 for anthracene) show differences of 2 or 3% in the predicted directions.[20]

Summary

Using experimental values for carbon–carbon bonds, a function is plotted showing the dependence of interatomic distance on bond character for single bond–double bond resonance. This function is tested with data for other bonds, and used in the discussion of the electronic structure of molecules containing conjugated double or triple bonds or aromatic nuclei and of molecules containing carbon–chlorine bonds adjacent to double bonds. The dependence of bond angles on single bond–double bond resonance is discussed. Values of carbon–carbon bond distances in polynuclear aromatic hydrocarbons are predicted and compared with the existent experimental data.

PASADENA, CALIFORNIA RECEIVED SEPTEMBER 24, 1935

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(17) J. M. Robertson, *Proc. Roy. Soc.* (London), **A142**, 674 (1933).

(18) J. M. Robertson, *ibid.*, **A140**, 79 (1933).

(19) The data for chrysene [J. Iball, *ibid.*, **A146**, 140 (1934)] are also compatible with this value.

(20) The value 1.41 Å. has also been reported for the carbon–carbon distance in benzene derivatives. We think it probable that this is 0.02 Å. too large.