The Scattering of Electrons by Hydrocarbon Films

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Several formulae are derived expressing the intensity of electron scattering for a variety of orientations of hydrocarbon films on a solid surface. Intensity contour maps may be constructed from these formulae for arbitrarily chosen models. These maps are helpful for determining the structure of a film and are being prepared for future publication.

CONSIDERABLE attention has been given to the study of the unusual properties of long chain hydrocarbon films on various solid surfaces. An example is the field of boundary lubrication where proper significance has been given to the importance of the strong adhesive forces between an oil film and the metal surface being lubricated.[1] These films are at times perhaps only one molecule thick, oriented so that their long molecular axes are vertical or almost so. Electrons are ideal for studying such films because of their low penetrating power. As a result the major portion of the scattering arises from the outermost layers of atoms when the beam strikes at a glancing angle. Murison,[2] using fast electrons, performed the first experiments on long chain organic compounds. A study of lubricating oils was subsequently made using electron diffraction by Andrew[3] who obtained a correlation between the lubricating qualities of the oils and their corresponding patterns. Another interesting study of surface films has been made by Germer and Storks.[4] They investigated the structure of monomolecular and multimolecular films of barium stearate and stearic acid prepared by the Langmuir-Blodgett technique.

Thus far an expression for the intensity of scattering has been given only for the case where the molecules are distributed randomly about their axes and these axes are normal to the surface of attachment.[2,4] The expressions to be derived below give the intensity of scattering for more general spatial arrangements and by means of these, more detailed information concerning the structure of surface films may be obtained.

MATHEMATICAL DEVELOPMENT

We wish to obtain the intensity of coherent scattering of fast electrons (*ca.* 30,000 volt electrons) by long hydrocarbon chains in arbitrary orientations relative to the surface of attachment. It is assumed that a chain is composed of two parallel rows of carbon atoms in a staggered configuration, and that the contribution from hydrogen atoms and end groups, such as

[1] For a general discussion containing many references one is referred to the book by N. K. Adam, *The Physics and Chemistry of Surfaces* (Oxford University Press, New York, 1941). See also *The Chemical Background for Engine Research* (Interscience Publishers, Inc., New York, 1943), "Lubrication," by O. Beeck, page 265.
[2] C. A. Murison, Phil. Mag. **17**, 201 (1934).
[3] L. T. Andrew, Trans. Faraday Soc. **32**, 607 (1936).
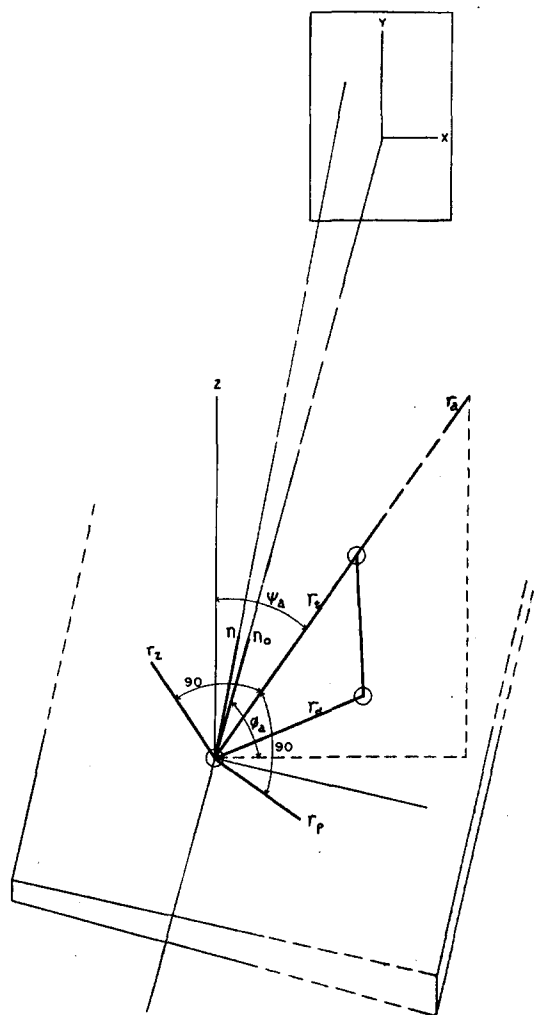[4] L. H. Germer and K. H. Storks, J. Chem. Phys. **6**, 280 (1938).

carboxyl, may be neglected. The distribution of the chains is considered to be sufficiently dilute so that each one scatters independently.

In order to discuss the various spatial arrangements which will be considered, we define a set of parameters in terms of which the orientation of the carbon chain may be completely determined. We place the carbon atom closest to the supporting surface at the origin and define the row in which it occurs as the axis of the molecule, vector $\mathbf{r}_a$ (see Fig. 1). The other row of atoms may be free to rotate about this axis and the angle of rotation, δ, is measured relative to a vertical plane containing axis $\mathbf{r}_a$. By fixing the position of

$\mathbf{r}_a$ in space and the value of angle δ, the orientation of the carbon chain is determined.

Expressions for the intensity of scattering will be obtained for the following cases:

I. The molecules are fixed in space. Thus, angles ψ_a and ϕ_a, the angles which determine the position of $\mathbf{r}_a$, and angle δ which determines the orientation of the plane of the carbon chain assume specific arbitrary values.[5]

II. The axes of the molecules are arbitrarily fixed in space but the planes of the carbon chains are considered to have random orientations about these axes.[6]

III. The tilt of the molecular axis and the orientation of the plane of the chain are arbitrarily chosen. However, the molecules are randomly oriented about axis z.

IV. The tilt of the molecular axis is arbitrarily fixed. However, the molecules are randomly oriented about the vertical, z, and also about their own axes.

Our next step is to obtain an expression for the amplitude of electron scattering for a generalized molecule consisting of i atoms, bearing in mind that the intensity is equal to the square of the absolute magnitude of the amplitude. The general expression is then applied to the above listed cases for the staggered carbon chain.

We describe by $\mathbf{r}_i$ the vector from the origin to the atom i (see Fig. 2). As an electron beam
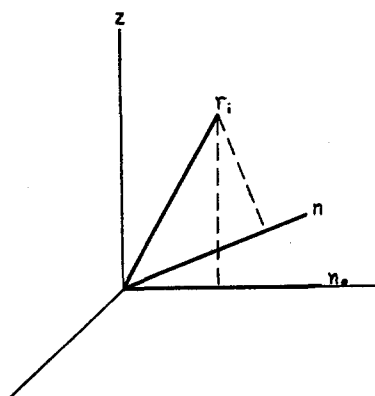
FIG. 2. Vectors defining path difference, $\mathbf{n} \cdot \mathbf{r}_i - \mathbf{n_0} \cdot \mathbf{r}_i$.

[5] Angle ψ_a is the tilt of $\mathbf{r}_a$ from the vertical axis, z, and angle ϕ_a is the clockwise rotation (when looking down on the surface) of the $\mathbf{r}_a z$ plane from the plane bounded by z and the incident beam after traversing the origin, $\mathbf{n_0} z$.

[6] The case of free rotation about an axis cannot be distinguished from fixed random orientations among the many molecules.

strikes the molecule, each atom scatters a wavelet; and the path difference between the wavelets scattered by the atom at the origin and the atom i is $(\mathbf{n}-\mathbf{n}_0)\cdot\mathbf{r}_i$, where $\mathbf{n}$ and $\mathbf{n}_0$ are unit vectors in the direction of the scattered wave and the incident wave, respectively. If the phase of the wavelet scattered at the origin is considered to be zero, the amplitude of the wave scattered by the carbon chain in the direction $\mathbf{n}$ is proportional to

$$\frac{f_c}{r}\sum_{i=1}^{N}\exp\left[ik(\mathbf{n}-\mathbf{n}_0)\cdot\mathbf{r}_i\right], \quad (1)$$

where f_c is the scattering factor for carbon, a function of $\mathbf{n}$ and $\mathbf{n}_0$, r is the radial coordinate of the scattered beam measured from the origin to any reference point in space (in our case points on the photographic plate), $k=2\pi/\lambda$ where λ is the electron wave-length and N is the number of carbon atoms. The regularity of the structure of the hydrocarbon chain allows one to sum expression (1) as a power series before squaring its absolute value to obtain the intensity of scattering. Cases I and II are then obtained in a compact form. However, for Cases III and IV there is no gain in summing the series and so instead, a general expression for the intensity is obtained from (1) by multiplying it by its complex conjugate. The result is

$$\frac{f_c{}^2}{r^2}\sum_{i=1}^{N}\sum_{j=1}^{N}\exp\left[ik(\mathbf{n}-\mathbf{n}_0)\cdot\mathbf{r}_{ij}\right], \quad (2)$$

where $\mathbf{r}_{ij}$ is a vector connecting the ith and jth atoms. Expression (2) is used for deriving formulae III and IV, resulting in less compact expressions than those of the first two cases.

Case I

The plan of this section is (a) to write expression (1) in the form of a power series and sum it, (b) to obtain the path differences included in (a) in terms of the internal structural parameters of the chain γ_d, r_d, and r_t (defined below), functions of the polar coordinates of the scattered beam, and the orientation parameters ψ_a, ϕ_a, and δ, and (c) to insert the results of (b) into (a) and arrive at an expression for the intensity. Finally the relations between the polar coordinates of the scattered beam and the functions thereof are
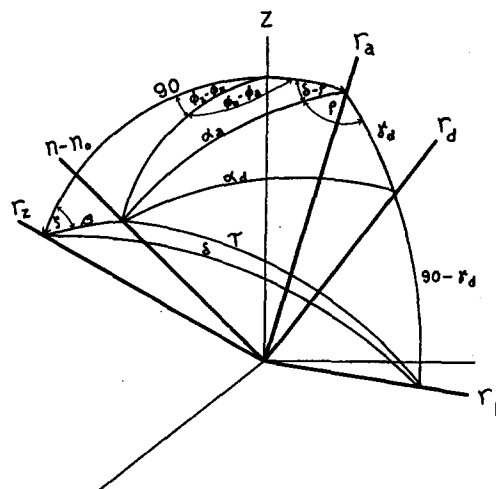

FIG. 3. Trigonometric details at point of scattering.

given. We thus may express the intensity in terms of the internal structural parameters, the orientation parameters, and the coordinates of the scattered beam.

(a) We may write expression (1), for a chain containing an even number of carbon atoms, N, in the form of a power series as follows:

$$\frac{f_c}{r}\sum_{g=0}^{N/2-1}\exp\left[ikg(\mathbf{n}-\mathbf{n}_0)\cdot\mathbf{r}_t\right]$$
$$\times(1+\exp\left[ik(\mathbf{n}-\mathbf{n}_0)\cdot\mathbf{r}_d\right]), \quad (3)$$

where $\mathbf{r}_d$ is the vector which connects the carbon atom at the origin to the nearest one and $\mathbf{r}_t$ is the vector which connects the carbon atom at the origin to the nearest one in the same row. The sum of (3) is

$$\frac{1-\exp\left[iNk(\mathbf{n}-\mathbf{n}_0)\cdot\mathbf{r}_t/2\right]}{1-\exp\left[ik(\mathbf{n}-\mathbf{n}_0)\cdot\mathbf{r}_t\right]}$$
$$\times(1+\exp\left[ik(\mathbf{n}-\mathbf{n}_0)\cdot\mathbf{r}_d\right]). \quad (4)$$

(b) The angle between $\mathbf{n}-\mathbf{n}_0$ and $\mathbf{r}_t$ is α_a and the angle between $\mathbf{n}-\mathbf{n}_0$ and $\mathbf{r}_d$ is α_d (see Fig. 3). We proceed to relate these angles to the structural and orientation parameters and functions of the coordinates of the scattered beam: Let us define the following quantities:

$\mathbf{r}_p =$ a vector perpendicular to $\mathbf{r}_a$ in the plane of the carbon chain and placed at the origin.

$\mathbf{r}_z =$ a vector perpendicular to $\mathbf{r}_a$ in the $\mathbf{r}_a z$ plane and placed at the origin,

The angle of rotation of the chain, δ, is clearly the angle between r_z and r_p.

β = angle between $n - n_0$ and r_z.

τ = angle between $n - n_0$ and r_p.

γ_d = angle between r_a and r_d.

ρ = angle between planes defined by r_a and r_d and r_a and $n - n_0$.

ζ = angle between planes defined by r_a and r_z and r_z and $n - n_0$.

ψ_n = angle of tilt of $n - n_0$ from the vertical axis, z.

ϕ_n = angle of rotation of $n - n_0$ from the $n_0 z$ plane.[7]

ψ_z = angle of tilt of r_z from the vertical axis, z.

ϕ_z = angle of rotation of r_z from the $n_0 z$ plane.[7]

From the sine and cosine laws of spherical trigonometry, the following relations are obtained:

$$\cos \alpha_d = \cos \alpha_a \cos \gamma_d + \sin \alpha_a \sin \gamma_d \cos \rho,$$
$$\cos \tau = \sin \alpha_a \cos \rho,$$
$$\cos \tau = \cos \delta \cos \beta + \sin \delta \sin \beta \sin \zeta, \qquad (5)$$
$$\sin \zeta = \sin \alpha_a \sin (\delta - \rho)/\sin \beta,$$
$$\cos \alpha_a = \cos \psi_n \cos \psi_a$$
$$\qquad\qquad + \sin \psi_n \sin \psi_a \cos (\phi_a - \phi_n),$$

and

$$\cos \beta = \cos \psi_n \cos \psi_z + \sin \psi_n \sin \psi_z \cos (\phi_z - \phi_n),$$

where

$$\phi_z = \pi + \phi_a \quad \text{and} \quad \psi_z = 90 - \psi_a.$$

By combining the first four expressions in (5) we get[8]

$$\cos \alpha_d = k_0 + k_1 \cos \delta \pm k_2 \sin \delta, \qquad (6)$$

where

$$k_0 = \cos \alpha_a \cos \gamma_d, \quad k_1 = \sin \gamma_d \cos \beta,$$

and

$$k_2 = \sin \gamma_d \sin \psi_n \sin (\phi_a - \phi_n).$$

(c) We multiply (4) by its complex conjugate, introduce the expressions for $\cos \alpha_a$ and $\cos \alpha_d$ obtained in (5) and (6), and find the intensity

proportional to[9]

$$2 \frac{f_c{}^2 \sin^2 (Nsr_t \cos \alpha_a/4)}{r^2 \sin^2 (sr_t \cos \alpha_a/2)}$$
$$\times [1 + \cos (sr_d \cos \alpha_d)], \quad (7)$$

where $s = k |n - n_0|$.

We denote the angular coordinates of the scattered beam, n, by ψ, the tilt from the vertical axis, z, and by ϕ the rotation from the $n_0 z$ plane using the same conventions as apply to angle ϕ_a. The following readily obtained relations enable us to express (7) and the subsequent expressions in II, III, and IV, in terms of these coordinates.

$$s = 4\pi [1 - \cos \phi \sin \psi/2]^{\frac{1}{2}}/\lambda,$$
$$s \cos \psi_n = 2\pi \cos \psi/\lambda,$$
$$s \sin \psi_n = 2\pi [2(1 - \cos \phi \sin \psi) - \cos^2 \psi]^{\frac{1}{2}}/\lambda, \quad (8)$$
$$s \sin \psi_n \cos \phi_n = -2\pi (1 - \cos \phi \sin \psi)/\lambda,$$
$$s \sin \psi_n \sin \phi_n = \pm 2\pi [2(1 - \cos (\pm\phi) \sin \psi) - \cos^2 \psi - (1 - \cos (\pm\phi) \sin \psi)^2]^{\frac{1}{2}}/\lambda.[10]$$

The scattering factor, f_c, may also be expressed in terms of the angular coordinates of the scattered beam since it is equal to $6 - F_c/s^2$ where F_c is the x-ray scattering factor for carbon atoms.[11]

Cartesian coordinates may be defined for the photographic plate in terms of the main beam as the origin, an x axis parallel to the plane of the supporting surface and a y axis parallel to the surface normal, z. Since

$$\sin \phi = x/(L^2 + x^2)^{\frac{1}{2}} \qquad (9)$$

and

$$\cos \psi = y/(L^2 + x^2 + y^2)^{\frac{1}{2}},$$

where L is the distance from the point of scattering to the origin of the photographic plate, the relations in (8) may be expressed as accurately as desired in terms of x and y. The fact that L is much larger than x or y allows one to make

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[7] These angles are measured by the same convention as applies to angle ϕ_a.

[8] The ambiguity regarding the sign may be resolved by defining δ as increasing when the rotation of Γ_d about the axis of the chain, r_a, appears counterclockwise to one observing the tip of r_a and facing the origin. Then a numerical check shows that the negative sign must be taken.

[9] Note that N is even. When N is odd an expression much less compact than (7) is obtained. Because of the rarity of occurrence of odd chains, it does not seem worth while to discuss this case further at present.

[10] We are interested in the scattered intensities occurring in the solid angle above the undeviated beam included by a photographic plate. Thus, only small values of ϕ are involved. If we mean by $+\phi$ a small clockwise rotation from the $n_0 z$ plane and $-\phi$ a small counterclockwise rotation, the method for choosing the correct sign of the square root is clear.

[11] See *Internationale Tabellen Zur Bestimmung von Kristallsstrukturen* (J. W. Edwards, Ann Arbor, Michigan, 1944), revised edition, Vol. II, p. 571.

greatly simplifying approximations. Also in practice the change in r may be neglected over the area of a photographic plate ordinarily considered.

Case II

For Case II, an average of the contributions from all positions of the molecule about axis r_a is required. This is accomplished by integrating (7) with respect to δ, from 0 to 2π, the probability of the chain occurring in any interval δ and $\delta + d\delta$ is $d\delta/2\pi$. We note in (6) that $\cos \alpha_d$ is a function of δ and rewrite it as

$$\cos \alpha_d = k_0 + A \cos (\delta + B), \qquad (10)$$

where

$$A = \pm (k_1{}^2 + k_2{}^2)^{\frac{1}{2}} \quad \text{and} \quad B = \tan^{-1} \frac{k_2}{k_1}.$$

Expression (10) replaces the expression for $\cos \alpha_d$ in (7) and we find that the contribution from all positions about axis r_a may be obtained from considering the real part of the integral,

$$\exp [isr_d k_0]$$

$$\times \int_0^{2\pi} \exp [isr_d A \cos (\delta + B)] d\delta/2\pi \quad (11)$$

which has the value,

$$\cos (sr_d k_0) J_0(sr_d A), \qquad (12)$$

where J_0 represents the Bessel function of zero order. We thus have from (7) and (12) the desired formula II,

$$2 \frac{f_c{}^2 \sin^2 (Nsr_t \cos \alpha_a/4)}{r^2 \sin^2 (sr_t \cos \alpha_a/2)}$$

$$\times [1 + \cos (sr_d \cos \gamma_d \cos \alpha_a)$$

$$\times J_0(sr_d \sin \gamma_d \sin \alpha_a)], \quad (13)$$

where $\cos \alpha_a$ is defined in (5) and N is even. The relations required for writing (13) in terms of the angular coordinates of the scattered beam, ψ and ϕ are found in (8). The term $s \sin \alpha_a$ can be expressed in terms of ψ and ϕ using s and $s \cos \alpha_a$. Since $J_0(x) = J_0(-x)$, no difficulty results from the ambiguity of sign arising from deriving the sine of an angle from its cosine.

Case III

In order to obtain formulae III and IV we work with expression (2). The vector r_d in the above analysis can be replaced by the general interatomic vector r_{ij} and then α_d is replaced by α_{ij} and γ_d by γ_{ij}. We may write instead of expression (6),

$$\cos \alpha_{ij} = H_0 + H_1 \cos \delta - H_2 \sin \delta, \qquad (14)$$

where

$$H_0 = \cos \alpha_a \cos \gamma_{ij}, \quad H_1 = \sin \gamma_{ij} \cos \beta,$$

and

$$H_2 = \sin \gamma_{ij} \sin \psi_n \sin (\phi_a - \phi_n).$$

We substitute (14) into (2) and find the intensity proportional to[12]

$$\frac{f_c{}^2}{r^2} \sum_{i=1}^{N} \sum_{j=1}^{N}$$

$$\times \exp [isr_{ij}(H_0 + H_1 \cos \delta - H_2 \sin \delta)]. \quad (15)$$

To obtain formula III an average is taken of the contribution from all values of ϕ_a from 0 to 2π. The expressions for $\cos \alpha_a$ and $\cos \beta$ given in (5) are substituted into (15) and we find that we must consider the integral

$$\int_0^{2\pi} \exp [isr_{ij} C \cos (\phi' + D)] d\phi'/2\pi, \quad (16)$$

where

$\phi' = \phi_a - \phi_n$,
$C = \pm([\cos \gamma_{ij} \sin \psi_n \sin \psi_a$
$\qquad - \sin \gamma_{ij} \sin \psi_n \cos \psi_a \cos \delta]^2$
$\qquad\qquad + [\sin \gamma_{ij} \sin \psi_n \sin \delta]^2)^{\frac{1}{2}}$

and D is an arc tangent function which disappears, as previously, in the integration. The value of (16) is

$$J_0(sr_{ij} C). \qquad (17)$$

Next let us break up the summation over the interatomic distances into two groups, one over the distances along the two rows of atoms and the other over the distances across the rows. If we consider N even, it can be shown that there are.

[12] Note that since $r_{ij} = -r_{ji}$, expression (2) is real and thus so is (15). It will be convenient henceforth, however, to consider only the contribution from r_{ij} (when $i \neq j$) and obtain our final result by multiplying the real part of this contribution by 2.

2ν distances of length $(N/2-\nu)r_t$ along the two rows where ν goes from 1 to $(N-2)/2$. Across the rows there are μ distances projected by the cosines of their respective angles γ_{ij}, and have the projected length $([N+1]/2-\mu)r_t$ where μ goes

from 1 to $N/2$ and also λ distances of projected length $-([N-1]/2-\lambda)r_t$ as λ goes from 1 to $(N-2)/2$. All the distances across the rows, multiplied by $\sin \gamma_{ij}$, give the inter-row distance.[13] We get for Case III

$$Nf_c^2/r^2 + 2\frac{f_c^2}{r^2}\sum_{\nu=1}^{(N-2)/2} 2\nu \cos \left[(N/2-\nu)r_t \cos \psi_a s \cos \psi_n\right] J_0\left[(N/2-\nu)r_t \sin \psi_a s \sin \psi_n\right]$$

$$+2\frac{f_c^2}{r^2}\sum_{\mu=1}^{N/2} \mu \cos \left[([N+1]/2-\mu)r_t \cos \psi_a s \cos \psi_n + r_0 \sin \psi_a s \cos \psi_n \cos \delta\right]$$

$$\times J_0\{s \sin \psi_n([([N+1]/2-\mu)r_t \sin \psi_a - r_0 \cos \psi_a \cos \delta]^2 + [r_0 \sin \delta]^2)^{\frac{1}{2}}\}$$

$$+2\frac{f_c^2}{r^2}\sum_{\lambda=1}^{(N-2)/2} \lambda \cos \left[-([N-1]/2-\lambda)r_t \cos \psi_a s \cos \psi_n + r_0 \sin \psi_a s \cos \psi_n \cos \delta\right]$$

$$\times J_0\{s \sin \psi_n([-([N-1]/2-\lambda)r_t \sin \psi_a - r_0 \cos \psi_a \cos \delta]^2 + [r_0 \sin \delta]^2)^{\frac{1}{2}}\}, \quad (18)$$

where r_0 is the inter-row distance. The factor 2 appears since all interatomic distances are counted twice in the double summation. By using (8), expression (18) may be given in terms of the angular coordinates of the scattered beam, ϕ and ψ.

Case IV

It would seem natural to obtain formula IV from formula III directly by integrating with respect to δ to get the average contribution from random positions about $\mathbf{r}_a$. However, a formula which appears more simple to calculate is obtained if one reverses the order of integrating, that is to derive the average contribution from random positions about $\mathbf{r}_a$ first and then the average contribution from random positions about z. We note that (14) may be written

$$\cos \alpha_{ij} = H_0 + E \cos (\delta + F), \quad (19)$$

where

$$E = \pm(H_1^2 + H_2^2)^{\frac{1}{2}} \quad \text{and} \quad F = \tan^{-1}(H_2/H_1).$$

We have by substituting this into (2)

$$\frac{f_c^2}{r^2}\sum_{i=1}^{N}\sum_{j=1}^{N} \exp \left[isr_{ij}(H_0 + E \cos [\delta + F])\right]. \quad (20)$$

The average over all values of δ is obtained from considering the integral,

$$\int_0^{2\pi} \exp \left[isr_{ij}E \cos (\delta + F)\right]d\delta/2\pi, \quad (21)$$

whose value is $J_0(sr_{ij}E)$. The contribution from the rotation of the chain about axis $\mathbf{r}_a$ is then

$$\frac{f_c^2}{r^2}\sum_{i=1}^{N}\sum_{j=1}^{N} \exp \left[isr_{ij} \cos \gamma_{ij} \cos \alpha_a\right] J_0(sr_{ij} \sin \gamma_{ij} \sin \alpha_a). \quad (22)$$

[13] The case when N is odd is readily considered. There are $2\nu-1$ distances of length $([N+1]/2-\nu)r_t$ along the two rows where ν goes from 1 to $(N-1)/2$. Across the rows there are μ distances projected by the cosines of their respective angles, γ_{ij}, and have the projected length $(N/2-\mu)r_t$ as μ goes from 1 to $(N-1)/2$ and also λ distances of projected length $-(N/2-\lambda)r_t$ as λ goes from 1 to $(N-1)/2$.

Let us now split the above summation among distances along the two rows of atoms and those across the rows (neglecting for the present terms for which $i = j$, the atomic scattering). We get

$$2\frac{f_c^2}{r^2}\sum_{\nu=1}^{(N-2)/2} 2\nu \exp\left[i(N/2-\nu)r_t s \cos\alpha_a\right] + 2\frac{f_c^2}{r^2}\sum_{\mu=1}^{N/2}\mu\exp\left[i([N+1]/2-\mu)r_t s \cos\alpha_a\right]J_0(sr_0\sin\alpha_a)$$

$$+2\frac{f_c^2}{r^2}\sum_{\lambda=1}^{(N-2)/2}\lambda\exp\left[-i([N-1]/2-\lambda)r_t s \cos\alpha_a\right]J_0(sr_0\sin\alpha_a). \quad (23)$$

We now wish to obtain the average contribution from all possible values of ϕ_a. The expression for $\cos\alpha_a$ is substituted into the first summation in (23) and it is found that we must consider the integral,

$$\int_0^{2\pi}\exp\left[i(N/2-\nu)r_t s \sin\psi_n\right.$$
$$\left. \times \sin\psi_a\cos(\phi_a-\phi_n)\right]d\phi_a/2\pi. \quad (24)$$

Its value is

$$J_0([N/2-\nu]r_t\sin\psi_a s \sin\psi_n). \quad (25)$$

For the second and third summations in (23) we must obtain a useful expansion for $J_0(sr_0\sin\alpha_a)$. We have

$$\sin\alpha_a = (1-\cos^2\alpha_a)^{\frac{1}{2}}$$
$$= (P-Q\cos(\phi_a-\phi_n) \qquad (26)$$
$$-R\cos^2(\phi_a-\phi_n))^{\frac{1}{2}},$$

where

$$P = 1-\cos^2\psi_n\cos^2\psi_a,$$
$$Q = 2\cos\psi_n\cos\psi_a\sin\psi_n\sin\psi_a,$$
$$R = \sin^2\psi_n\sin^2\psi_a.$$

The above expression may be approximated by neglecting R. This imposes a strict limitation on the applicability of the final formula. An estimate may be made of this limitation by setting $\phi_a-\phi_n$ equal to 0° or 180° and calculating the values of $P, Q,$ and R for some typical cases. It is found that if one assumes a value of 20° for angle ψ_a, the area enclosed in $-1.5 < x < 1.5$ cm and $1 < y < 4$ cm may be covered with an error in the intensity probably not greater than 10 percent in the vicinity of the main maxima, and usually much less. In the region mentioned the approximation improves with larger y and smaller x since $\sin\psi_n$ is very nearly $x/(x^2+y^2)^{\frac{1}{2}}$.

We may write

$$\sin\alpha_a = [a^2+b^2-2ab\cos(\phi_a-\phi_n)]^{\frac{1}{2}}, \quad (27)$$

where

$$a^2 = [P+(P^2-Q^2)^{\frac{1}{2}}]/2$$

and

$$b^2 = Q^2/[2P+2[P^2-Q^2]^{\frac{1}{2}}].$$

From the addition theorem for J_0, we get

$$J_0(sr_0\sin\alpha_a)$$
$$= \sum_{m=0}^{\infty}\epsilon_m J_m(sr_0 a)J_m(sr_0 b)\cos m(\phi_a-\phi_n), \quad (28)$$

where ϵ_m is equal to unity when $m=0$ and is equal to 2 for all other values of m.[14] By substituting (28) into the second summation of (23) the following integral arises from considering the contribution from all values of ϕ_a,

$$\int_0^{2\pi}\exp\left[i([N+1]/2-\mu)r_t\sin\psi_a s \sin\psi_n\right.$$
$$\left.\times\cos(\phi_a-\phi_n)\right]\cos m(\phi_a-\phi_n)d\phi_a/2\pi. \quad (29)$$

Its value is

$$(i)^m J_m[([N+1]/2-\mu)r_t\sin\psi_a s \sin\psi_n]. \quad (30)$$

Clearly, a similar integral arises for the third summation whose value is

$$(i)^m J_m[-([N-1]/2-\lambda)r_t\sin\psi_a s \sin\psi_n]. \quad (31)$$

From the results, (25), (30), and (31) and the terms in (23) which were constant with respect to the integration over ϕ_a, we may now write down formula IV. (The contributions from the second and third summations in (23) may be combined since $J_\nu(-z) = -J_\nu(z)$ if ν is odd and $J_\nu(-z) = J_\nu(z)$ if ν is even.[13])

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[14] My thanks to Professor Otto Laporte for suggesting this expansion.

$$N\frac{f_c^2}{r^2}+2\frac{f_c^2}{r^2}\sum_{\nu=1}^{(N-2)/2}2\nu\cos\left[(N/2-\nu)r_t\cos\psi_a s\cos\psi_n\right]J_0\left[(N/2-\nu)r_t\sin\psi_a s\sin\psi_n\right]$$

$$+\frac{2f_c^2}{r^2}\sum_{\mu=1}^{N/2}(2\mu-1)\cos\left[([N+1]/2-\mu)r_t\cos\psi_a s\cos\psi_n\right]$$

$$\times\sum_{m=0}^{\infty}(-1)^m\epsilon_m J_{2m}(sr_0 a)J_{2m}(sr_0 b)J_{2m}\left[([N+1]/2-\mu)r_t\sin\psi_a s\sin\psi_n\right]\ .$$

$$+\frac{2f_c^2}{r^2}\sum_{\mu=1}^{N/2}(2\mu-1)\sin\left[([N+1]/2-\mu)r_t\cos\psi_a s\cos\psi_n\right]$$

$$\times\sum_{m=0}^{\infty}(-1)^{m+1}2J_{2m+1}(sr_0 a)J_{2m+1}(sr_0 b)J_{2m+1}\left[([N+1]/2-\mu)r_t\sin\psi_a s\sin\psi_n\right].\quad(32)$$

Expression IV, though quite complex, permits calculation of the intensity distribution from a chosen structure. Examination shows that, within the range of validity mentioned above, the arguments $sr_0 a$ and $sr_0 b$ are sufficiently small to cause the infinite series to converge very rapidly.

Because of the small value of $\sin\psi_n$ for points along the y axis, formulae III and IV will be indistinguishable from formulae I and II, respectively. In other words the intensity along the y axis is virtually independent of the variable ϕ_a.

Additional Remarks

The intensity from a molecule with r_a vertical has been previously obtained.[2,4] For the case when the plane of the molecule is rotated ϕ_d degrees from the $n_0 z$ plane (measured according to previous conventions) we have

$$\frac{f_c^2\sin^2(Nr_t s\cos\psi_n/4)}{r^2\sin^2(r_t s\cos\psi_n/2)}$$

$$\times(1+\cos[r_d s\cos\psi_n\cos\gamma_d$$

$$+r_d s\sin\psi_n\sin\gamma_d\cos(\phi_n-\phi_d)]).\quad(33)$$

By integrating (33) with respect to ϕ_d from 0 to 2π we get

$$\frac{f_c^2\sin^2(Nr_t s\cos\psi_n/4)}{r^2\sin^2(r_t s\cos\psi_n/2)}$$

$$\times(1+\cos[r_d\cos\gamma_d s\cos\psi_n]$$

$$\times J_0[r_d\sin\gamma_d s\sin\psi_n])\quad(34)$$

for the intensity when there is free rotation about r_a. Expression (34) agrees with the result of Germer and Storks when given in terms of the

coordinates of the photographic plate, making suitable approximations.

DISCUSSION

For the purpose of interpreting diffraction patterns produced by chains tilted away from the normal, the effect on scattering of only one of the two rows of carbon atoms in a hydrocarbon chain has been used. This has been successful in locating the main maxima. However, subtle effects on the intensity of the interaction of the two rows of the staggered chain could not be anticipated. The formulae obtained above which take into account the effect of both rows give the scattered intensity for some of the more interesting spatial orientations. They are, of course, not exhaustive. For instance, expressions were not obtained for the average effect of a variation in angle ψ_a, the tilt from the vertical, through a small angle range.

It was previously noted that fixed random positions of the molecules about an axis is mathematically indistinguishable from the case of free rotation of each molecule about this axis. Thus the same pattern can be expected from both cases. Another situation which appears at first glance indistinguishable from the previous two is the case in which there are small patches on a surface in which all the molecules have the same orientation, but the orientation varies from patch to patch. This case, however, would probably arise when the density of packing approaches that present in a crystal. Thus, such an arrangement of the molecules could affect the intensity of scattering because of their repeated intermolecular distances. This effect is not included in the above formulae. Instead, the latter are

derived on the assumption that the distribution of molecules is sufficiently dilute to make intermolecular interaction negligible. A lack of agreement, therefore, between the scattered intensity calculated from the theoretical formulae and that actually found may be caused by a close packing of the molecules. This effect has already been suggested.[4]

When making calculations for contour maps of the intensity, it is very helpful to know the region in which the main maxima occur. The formulae for the intensity, conveniently expressed in terms of the plate coordinates, x and y, may then be considered in fairly restricted areas.[15] Such calculations are being made at present in this laboratory for future publication.

[15] The following useful tables are available: (a) Tables of Sines and Cosines for Radian Arguments, Federal Works Agency Work Projects Administration, Project No. 765-97-3-10, New York, 1940. (b) Hague, Proc. Phys. Soc. 29, 211 (1917). (c) Gray, Mathews, and MacRobert, A Treatise on Bessel Functions (The Macmillan Company, New York, 1931), p. 286.

An improvement in interpretation can be expected from a method of photographing which would allow for quantitative measurements of the intensity. P. P. Debye[16] has suggested the use of a rotating sector in gas diffraction to eliminate the effect of the scattering factors. In our case only one occurs, f_c. It would appear that hydrocarbon films are unusually suited for use by the sector method since one sector would suffice for all films, the radiation allowed to pass through being inversely proportional to $(6 - F_c)^2/s^4$. In addition the difficulty of vapors diffusing into the camera on long exposure, as occurs in gas diffraction, does not arise.

[16] P. P. Debye, Physik. Zeits. 40, 66 and 404 (1939).

A Relation between Bond Force Constants, Bond Orders, Bond Lengths, and the Electronegativities of the Bonded Atoms

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A relation of the form

$$k = aN(x_A x_B/d^2)^{\frac{3}{4}} + b$$

has been found to hold accurately for a large number of diatomic and simple polyatomic molecules in their ground states. (The average deviation of k calculated from k observed for seventy-one cases is 1.84 percent.) Here k is the bond-stretching force constant, d the bond length, N the bond order, and x_A and x_B are the electronegativities of the bonded atoms. If k is measured in dynes/cm$\times 10^{-5}$ and d in Angstrom units, a and b have the values 1.67 and 0.30, respectively, for stable molecules exhibiting their normal covalencies, except those in which both bonded atoms have only one electron in the valence shell; for diatomic molecules of the alkali metals, Na_2, NaK, etc., a and b are 1.180 and -0.013, respectively; for hydrides of elements having a single electron in the valence shell, 1.180 and 0.040, respectively; and for diatomic hydrides of elements having two to four electrons in the valence shell, 1.42 and 0.08, respectively. Numerous applications of the relation are made and certain exceptions are pointed out.

DESCRIPTION OF THE RELATION

SEVERAL relations[1,2] between force constants or vibrational frequencies and bond distances have been found to hold approximately for a limited number of molecules. They, in general,

[1] P. M. Morse, Phys. Rev. 34, 57 (1929); D. Clark, Phil. Mag. 18, 459 (1934); H. S. Allen and A. K. Longair, Phil. Mag. 19, 1032 (1935); M. L. Huggins, J. Chem. Phys. 3, 473 (1933); 4, 308 (1936); J. J. Fox and A. E. Martin, J. Chem. Soc. 884 (1939); G. B. B. M. Sutherland, J. Chem. Phys. 8, 161 (1940); J. W. Linnett, Trans. Faraday Soc. 36, 1123 (1940); C. K. Wu and Chang-Tsing Yang, J. Phys. Chem. 48, 295 (1944).

[2] R. M. Badger, J. Chem. Phys. 2, 128 (1934); 3, 710 (1935).