[12] R. C. Gunton and T. M. Shaw, Phys. Rev. 140, A756 (1965).

[13] L. J. Puckett, M. D. Kregel, and M. W. Teague, Phys. Rev. Abstr. 2, 11 (1971).

[14] B. H. Mahan and I. C. Walker, J. Chem. Phys. 47, 3780 (1967).

[15] E. E. Ferguson, D. B. Dunkin, and F. C. Fehsenfeld (unpublished results).

[16] C. Lifshitz, B. M. Hughes, and T. O. Tiernan, Chem. Phys. Letters 7, 479 (1970).

[17] D. A. Parkes and T. M. Sugden, "Electron Attachment and Detachment in Nitric Oxide," Trans. Faraday Soc. (to be published).

[18] D. A. Parkes (private communication).

[19] D. C. Conway and L. E. Nesbit, J. Chem. Phys. 48, 509 (1968).

[20] J. L. Moruzzi and A. V. Phelps, J. Chem. Phys. 45, 4617 (1966).

[21] J. Billingsley and A. B. Callear, Trans. Faraday Soc. 67, 589 (1971).

[22] D. Spence and G. J. Schulz, Phys. Rev. A 3, 1968 (1971).

[23] F. C. Fehsenfeld, E. E. Ferguson, and D. K. Bohme, Planetary Space Sci. 17, 1759 (1969).

[24] J. D. Payzant, R. Yamdagni, and P. Kebarle, Can. J. Chem. 49, 3308 (1971).

[25] J. Berkowitz, W. A. Chupka, and D. Gutman, J. Chem. Phys. 55, 2733 (1971).

[26] N. G. Adams, D. K. Bohme, F. C. Fehsenfeld, and E. E. Ferguson, J. Chem. Phys. 52, 3133 (1970).

[27] F. Bloch and N. E. Bradbury, Phys. Rev. 48, 689 (1935).

[28] A. Herzenberg, J. Chem. Phys. 51, 4942 (1969).

[29] E. E. Ferguson, F. C. Fehsenfeld, and A. L. Schmeltekopf, J. Chem. Phys. 47, 3085 (1967).

[30] F. C. Fehsenfeld, D. L. Albritton, J. A. Burt, and H. I. Schiff, Can. J. Chem. 47, 1793 (1969).

Three-Atom Scattering in Gas-Phase Electron Diffraction: A Tractable Limiting Case*

L. S. BARTELL AND T. C. WONG

Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48104

(Received 15 October 1971)

The contribution of intramolecular multiple scattering in electron diffraction patterns of gas molecules is investigated by Glauber's method. An analytical expression for three-atom scattering is derived for the limiting case in which the distance between atoms is large compared with atomic radii. This expression accounts well for the discrepancies between observed and conventionally calculated scattered intensities reported by Jacob and Bartell in the case of ReF_6. The analogous four-atom scattering is found to be very small.

Electron diffraction patterns of free molecules give Fourier transforms with peaks corresponding to internuclear distances. Observed peaks deviate systematically from peaks calculated by current theoretical expressions, the discrepancy increasing as atomic number increases. If heavy atoms are present this discrepancy may seriously interfere with structure analyses.[1,2] The principal failure of kinematic diffraction theory was treated many years ago by Schomaker and Glauber[3] and others,[4] who showed that phase shifts on scattering may split radial distribution peaks into two components, symmetrically (neglecting small effects of anharmonicity). Observed peak splittings are often decidedly asymmetric, however, by an amount far in excess of random errors in current experiments, and other anomalies occur.

Observed asymmetries cannot be accounted for by adjusting atomic scattering factors unless the atoms are made markedly aspherical. They can be explained, however, by intramolecular multiple scattering, a topic treated previously by several workers.[5,6] Since previous treatments have involved difficult multiple numerical integrations as well as approximations of uncertain validity, it seemed worthwhile to explore a method susceptible of quite rigorous treatment yet capable of analytical evaluation of scattered intensities. The present paper is a preliminary note to illustrate the method in a limiting case yielding a simple but fairly accurate

result even for real molecules. A later communication will offer a more general and detailed account applicable to all cases.

The three-atom system in Fig. 1 will be considered, assuming that the atoms M, 2, and 3 all present spherical, nonoverlapping, static potential energies to an incident electron. A convenient treatment is a partial
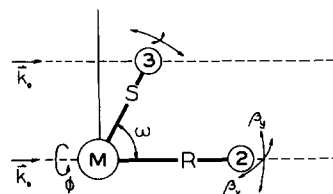

FIG. 1. Three-atom system. Wave incident along the dashed lines. The three orientational variables β_x, β_y, and ϕ do not constitute a proper Eulerian set but they are satisfactory coordinates for the orientational averaging in view of the small range of β_x and β_y over which effective eclipsing of atoms M and 2 occurs.

wave expansion modified to handle systems without spherical symmetry with phases evaluated by Glauber's approximation.[7] To introduce the method it is convenient to start with the familiar partial wave expansion and progress to a semiclassical expression associating the quantum angular momentum $[l(l+1)]^{1/2}\hbar \approx (l+1/2)\hbar$ with the classical angular momentum $mvp = \hbar k p$, where p is the impact parameter. The scattering

factor for an axially symmetric system may be expressed as[8]

$$f(\mathbf{s}) = (2ik)^{-1} \sum_l (2l+1)[\exp(2i\delta_l)-1]P_l(\cos\theta)$$

$$\approx (2ik)^{-1} \int_0^\infty (2l+1)[\exp(2i\delta_l)-1]$$
$$\times J_0[2(l+\tfrac{1}{2})\sin\tfrac{1}{2}\theta]dl$$

$$= (2ik)^{-1} \int_0^\infty 2kp\{\exp[2i\delta(\mathbf{p})]-1\}J_0(sp)kdp$$

$$= (-ik) \int_0^{2\pi}\int_0^\infty \{\exp[2i\delta(\mathbf{p})]-1\}(2\pi)^{-1}$$
$$\times \exp(i\mathbf{s}\cdot\mathbf{p})pdpd\phi$$

$$= (-ik/2\pi) \iint \exp(i\mathbf{s}\cdot\mathbf{p})$$
$$\times \{\exp[2i\delta(x,y)]-1\}dxdy, \quad (1)$$

with $\mathbf{s}=\mathbf{k}_{\text{inc}}-\mathbf{k}_{\text{scatt}}$ and in which the final expression, which is mathematically equivalent to the second expression in the case of axial symmetry, is also applicable to general systems within the restrictions outlined by Glauber.[7] The phases $\delta(x,y)$ may be evaluated according to the semiclassical approximation[7,8]

$$\delta(x,y) = -\frac{m_{\text{el}}}{2\hbar^2 k} \int_{-\infty}^\infty V(x,y,z)dz. \quad (2)$$

Since $V(x,y,z)$ is a sum of atomic contributions, the phases $\delta(x,y)$ can be represented as a sum of atomic contributions. In the event that one atom eclipses another in the course of molecular rotation, the pair will generate an augmented scattering for that orientation, according to Eq. (1). It turns out that the interference between this augmented scattered wave and a wavelet scattered by some other atom gives rise to the principal discrepancies between observed and calculated diffraction patterns referred to in the introductory paragraph. Referring to the three-atom system in Fig. 1, we note when atom 3 is not eclipsing (or eclipsed by) atoms M and 2 that

$$\exp(2i\delta)-1 = \exp[2i(\delta_M+\delta_2+\delta_3)]-1$$
$$\approx \{\exp[2i(\delta_M+\delta_2)]-1\}+[\exp(2i\delta_3)-1]$$
$$(3)$$

since for any given impact parameter, $\mathbf{p}$, either $(\delta_M+\delta_2)$ or δ_3 is zero by virtue of nonoverlap of the projections of the potential energy functions on the x, y plane. Further, we note that since

$$\exp[2i(\delta_M+\delta_2)]-1 = [\exp(2i\delta_M)-1]+[\exp(2i\delta_2)-1]$$
$$+[\exp(2i\delta_M)-1][\exp(2i\delta_2)-1], \quad (4)$$

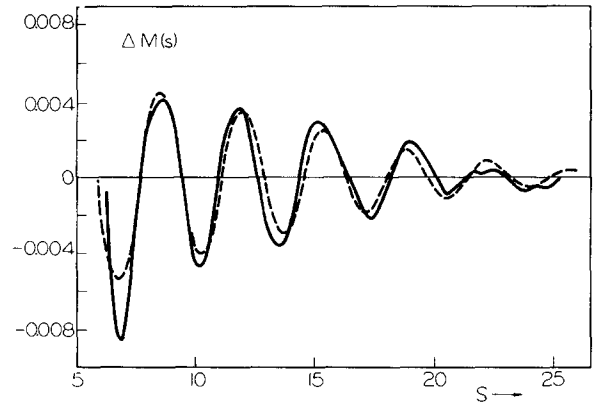FIG. 2. The solid curve represents the difference between the reduced intensity observed for ReF$_6$ by Jacob and the reduced intensity calculated by the conventional two-atom expression. The dashed curve represents the $\cos sr$ component of the three-atom scattering calculated according to Eqs. (17) and (21).

it follows that

$$f_{M,2}(\mathbf{s}) = (-ik/2\pi) \iint \exp(i\mathbf{s}\cdot\mathbf{p})$$
$$\times \{\exp[2i(\delta_M+\delta_2)]-1\}dxdy$$
$$= f_M(s)\exp(i\mathbf{s}\cdot\mathbf{p}_M)+f_2(s)\exp(i\mathbf{s}\cdot\mathbf{p}_2)+f_{M2}(\mathbf{s})$$
$$(5)$$

in which the $\mathbf{p}_i$ are components of the radial vectors $\mathbf{r}_i$ in the x, y plane, in which $f_M(s)$ and $f_2(s)$ are conventional partial wave atomic scattering factors as defined by Eq. (1) for isolated atoms at the origin, and the "eclipse amplitude" f_{M2} is

$$f_{M2}(\mathbf{s}) = (-ik/2\pi) \iint \exp(i\mathbf{s}\cdot\mathbf{p})[\exp(2i\delta_M)-1]$$
$$\times [\exp(2i\delta_2)-1]dxdy. \quad (6)$$

Accordingly, we may write the scattering factor for the three-atom system as

$$f(\mathbf{s}) = f_M\exp(i\mathbf{s}\cdot\mathbf{p}_M)+f_2\exp(i\mathbf{s}\cdot\mathbf{p}_2)$$
$$+f_3\exp(i\mathbf{s}\cdot\mathbf{p}_3)+f_{M2}(\mathbf{s})+\cdots \quad (7)$$

and the elastic differential cross section averaged over all orientations as

$$\langle d\sigma/d\Omega\rangle_\Omega = \langle f^*(\mathbf{s})f(\mathbf{s})\rangle_\Omega$$
$$= \sum_i\sum_j f_i^*f_j\langle\exp[i\mathbf{s}\cdot(\mathbf{p}_j-\mathbf{p}_i)]\rangle_\Omega$$
$$+2\,\text{Re}\langle f_3^*\exp(-i\mathbf{s}\cdot\mathbf{p}_3)f_{M2}(\mathbf{s})\rangle_\Omega+\cdots, \quad (8)$$

in which the first term on the right hand side is the conventional two-atom expression and the next is the three-atom interference term we seek. Analogous three-atom terms with $f_i^*\exp(-i\mathbf{s}\cdot\mathbf{p}_i)f_{jk}$ will occur for every combination with $j\neq k$. They will contribute significantly only when j and k are nearly eclipsed. The treatment remains valid if $i=j$ or $i=k$. Since it is impossible with a nonzero angle ω (see Fig. 1) for

i, j, and k to be eclipsed simultaneously, the formally allowed combinations f_i, f_{ijk} and f_{ij}, f_{jk} are negligible.

It is very simple to evaluate the three-atom spherical average in Eq. (8) in the event that the internuclear distance R is large in comparison with the atomic radii. This average involves integration over three Eulerian angles[9] α, β, and γ or, in our limiting case, over the three variables β_x, β_y, and ϕ of Fig. 1. Let us assume that atom M is at the origin and that, at $\alpha=\beta=\gamma=0$, atom 2 is on the z axis in the direction of the incident momentum while atom 3 is in the yz plane. For large R, we may envision the spherical average simply as the averaging over β_x and β_y angles of Fig. 1 while holding $\phi=0$, followed by an average over ϕ. If R is large, $\delta_M(x, y)$ and $\delta_2(x, y)$ eclipse each

other effectively over such a small range of β_x and β_y that the integrand in $\langle f_3{}^* \exp(-i\mathbf{s}\cdot\mathbf{p}_3)f_{M2}\rangle_\Omega$ is very small unless β_x and β_y are very small in which case the component of $\mathbf{p}_3$ along $\mathbf{s}$ is very little changed from its value at perfect eclipsing of atoms M and 2. Therefore we may write

$$\langle f_3{}^* \exp(-i\mathbf{s}\cdot\mathbf{p}_3)f_{M2}\rangle_\Omega \approx f_3{}^* \langle \exp(-i\mathbf{s}\cdot\mathbf{p}_3)\rangle_\phi \langle f_{M2}\rangle_{sph},$$
(9)

where

$$\langle \exp(-i\mathbf{s}\cdot\mathbf{p}_3)\rangle_\phi = (2\pi)^{-1}\int_0^{2\pi} \exp[-i(sS\sin\omega)\cos\phi]d\phi$$
$$= J_0(sS\sin\omega)$$
(10)

and

$$\langle f_{M2}\rangle_{sph} = \langle(-ik/2\pi)\iint \exp(i\mathbf{s}\cdot\mathbf{p})[\exp(2i\delta_M)-1][\exp(2i\delta_2)-1]dxdy\rangle_{sph},$$
(11)

which simplifies to

$$\langle f_{M2}\rangle_{sph} \approx [(-ik/2\pi)\iint \exp(i\mathbf{s}\cdot\mathbf{p})[\exp(2i\delta_M)-1]dxdy]\langle \exp[2i\delta_2(0, 0)]-1\rangle_{sph}$$
$$= f_M(s)\langle \exp[2i\delta_2(0, 0)]-1\rangle_{sph}$$
(12)

since a little reflection shows that, when atom 2 is delocalized in a spherical shell of large radius, the phase $\delta_2(x, y)$ averaged over the orientation of atom 2 is virtually constant in the x, y range near zero where the localized $\delta_M(x, y)$ is significant and, hence, the δ_2 term can be factored as shown. That is, designating the coordinates of atom 2 as $x_2 = R\cos\phi_2\sin\theta_2$ and $y_2 = R\sin\phi_2\sin\theta_2$, by definition

$$\langle \exp(2i\delta_2)-1\rangle_{sph} = (4\pi R^2)^{-1}\iint\{\exp[-(2im/2k\hbar^2)\int V_2(x-x_2, y-y_2, z)dz]-1\}R^2\sin\theta_2 d\theta_2 d\phi_2$$

$$= 2i\langle\delta_2(x, y)+i\delta_2{}^2(x, y)+\cdots\rangle_{sph}$$

$$= 2i\langle\delta_2(0, 0)+i\delta_2{}^2(0, 0)+\cdots\rangle_{sph}\{1+[(x^2+y^2)/2R^2]+\cdots\}$$

$$\approx 2i\langle\delta_2(0, 0)+i\delta_2{}^2(0, 0)+\cdots\rangle_{sph}$$
(13)

at small x and y. Moreover, it is apparent that Eq. (13), for $s_0=0$ and $x=y=0$, can be written as

$$\langle \exp(2i\delta_2)-1\rangle_{sph} = [2/(4\pi R^2)](2\pi/-ik)\{(-ik/2\pi)\iint \exp(i\mathbf{s}_0\cdot\mathbf{p})[\exp(2i\delta_2)-1]dx_2dy_2\}$$

$$= (i/kR^2)f_2(s_0)$$

$$\equiv (i/kR^2)f_2(0),$$
(14)

where the first factor of 2 in the rhs represents the two eclipsing conformations, M by 2, and 2 by M. Moreover, the accuracy of Eq. (10) can be improved by (a) shrinking the effective vertical distance $S\sin\omega$ to atom 3 to

$$(S\sin\omega)_{eff} \approx S\sin\omega[1-\tfrac{1}{2}\langle\beta_y{}^2\rangle_{Av}-\tfrac{1}{2}\langle(\Delta\omega)^2\rangle_{Av}] = S\sin\omega[1-\tfrac{1}{4}\langle\beta^2\rangle_{Av}-\tfrac{1}{2}\langle(\Delta\omega)^2\rangle_{Av}] \equiv S\sin\omega(1-\epsilon)$$
(15)

by incorporating the effect of foreshortening due to motion over an arc in displacements over the mean square Eulerian eclipsing angle $\langle\beta^2\rangle_{Av}$ and over the angular molecular vibrations, and (b) by multiplying by the vibrational temperature factor $\exp(-l_s{}^2s^2/2)$ where

$$l_s{}^2 = l^2\sin^2\omega + S^2\langle(\Delta\omega)^2\rangle_{Av}\cos^2\omega,$$
(16)

in which l^2 and $\langle(\Delta\omega)^2\rangle_{Av}$ represent mean square bond stretch and bend amplitudes of vibration. Neither ϵ nor $l_s{}^2$ can be ignored in real cases if accuracy is desired. Since $\langle\beta^2\rangle_{Av}$ is perforce very small in our limiting case of very large R, the present treatment does not lead to a useful evaluation of the correction ϵ. The eclipsing latitude $\langle\beta^2\rangle_{Av}$ decreases with s as the broader components of the atomic $V(r)$ become less effective in scattering, and a full treatment[10] is required for numerical evaluation of ϵ.

Collecting the above terms together, the three-atom differential cross section of Eq. (8) becomes

$$\langle d\sigma/d\Omega\rangle_{M2,3} = 2 \, \mathrm{Re}\langle f_3^* \exp(-i\mathbf{s}\cdot\mathbf{p_3})f_{M2}\rangle_\Omega$$

$$= 2 \, \mathrm{Re}(i/kR^2)f_3^*(s)f_M(s)f_2(0)[\exp(-l_s^2 s^2/2)]J_0(sS \sin\omega[1-\epsilon])$$

$$= -(2/kR^2) \, |f_3(s)| \, |f_M(s)| \, |f_2(0)| \, \sin[\eta_M(s)+\eta_2(0)-\eta_3(s)]\times[\exp(-l_s^2 S^2/2)]J_0(sS \sin\omega[1-\epsilon])$$

$$(17)$$

if the imaginary part of ϵ is neglected.

Identical reasoning in which atom 2 is made the center of the sphere gives the analogous result in which the product $f_M(s)f_2(0)$ of Eq. (17) is reversed to $f_M(0)f_2(s)$. A more rigorous treatment[10] reveals that the correct leading term contains, in general, neither of these quite similar quantities, but rather is as follows:

$$\langle d\sigma/d\Omega\rangle_{M2,3} = 2 \, \mathrm{Re}\{(i/kR^2)f_3^*(s)f_M(s_M)f_2(s_2)[\exp(-l_s^2 s^2/2)](1+\epsilon)J_0(sS \sin\omega[1-\epsilon])\}, \qquad (18)$$

where

$$s_M = [1-(S/R)\cos\omega]s, \qquad (19a)$$

$$s_2 = [(S/R)\cos\omega]s, \qquad (19b)$$

and

$$\epsilon(s) = \frac{1}{2R^2}\left[-\frac{f_M''(s_M)}{f_M(s_M)} + 2\frac{f_M'(s_M)f_2'(s_2)}{f_M(s_M)f_2(s_2)} - \frac{f_2''(s_2)}{f_2(s_2)}\right] + \tfrac{1}{2}\langle(\Delta\omega)^2\rangle_{Av}. \qquad (20)$$

In electron diffraction analyses, Eq. (18) is applicable if the distance $S \sin\omega$ corresponds to no true, major internuclear distances. If $\omega=90°$, however, $S \sin\omega$ is a bond distance and the $(\pi sS)^{-1/2} \sin sS$ component of $J_0(sS)$ is at least partially absorbed into the experimental scale factor in the $(sS)^{-1}\sin sS$ term in conventional analyses. Indeed, in one of the most definitive studies to date involving a heavy atom, Jacob[2] found in the case of ReF_6 that the unexplained residual in $\langle d\sigma/d\Omega\rangle$ was an almost pure $\cos sS$ component for $S=r(Re-F)$, modulated by a smooth envelope. If the $\sin sS$ term is removed from $J_0(sS[1-\epsilon])$, the coefficient of the $\cos sS$ term can be deduced from

$$J_0(sS[1-\epsilon]) \approx (\pi sS)^{-1/2}\{\cos(sS[1-\epsilon])$$

$$+\sin(sS[1-\epsilon])\}$$

$$= (\pi sS)^{-1/2}\{[\cos sS\epsilon+\sin sS\epsilon] \sin sS$$

$$+[\cos sS\epsilon-\sin sS\epsilon] \cos sS\}. \qquad (21)$$

The agreement between the "reduced intensity" three-atom $\cos sS$ component of $\langle d\sigma/d\Omega\rangle_{ReF,F}/\langle d\sigma/d\Omega\rangle_{tot}$ for the 24 ReF, F eclipsing combinations in ReF_6 calculated according to Eqs. (17) and (21) and the reduced intensity residuals observed by Jacob is shown in Fig. 2. The agreement confirms that three-atom interatomic intramolecular scattering accounts for the principal effect observed. Similar conclusions arrived at by different routes have been drawn by Bonham, Piexoto, and Liu[11] and by Yates.[12]

Four-atom scattering can be studied by an approach analogous to that outlined above. If the four atoms are all different, the associated intensity is negligible unless two pairs or three individual atoms eclipse simultaneously. Rhenium hexafluoride, with parallel pairs

of fluorines and with linear F–Re–F groups which can interfere with a fourth atom, contains the atomic arrangements required for optimum four-atom scattering. The magnitude of the four-atom effect is much less than that of the three-atom effect, however [by a factor the order of $f_F(0)/kR^2$], in the case of ReF_6 with 40 kV electrons.

ACKNOWLEDGMENT

* This research was supported by a grant from the National Science Foundation.

[1] See, for example, R. M. Gavin, Jr. and L. S. Bartell, J. Chem. Phys. 48, 2460, 2466 (1968); E. J. Jacob and L. S. Bartell, ibid. 53, 2235 (1970); E. J. Jacob, H. B. Thompson, and L. S. Bartell, J. Mol. Struct. 8, 383 (1971); W. J. Adams, H. B. Thompson, and L. S. Bartell, J. Chem. Phys. 53, 4040 (1970); H. M. Seip and R. Seip, Acta Chem. Scand. 20, 2698 (1966); H. M. Seip and R. Stölevik, ibid. 20, 385 (1966); S. P. Arnesen and H. M. Seip, ibid. 20, 2711 (1966).

[2] E. J. Jacob and L. S. Bartell, J. Chem. Phys. 53, 2231 (1970).

[3] V. Schomaker and R. Glauber, Nature 170, 291 (1952).

[4] J. A. Hoerni and J. A. Ibers, Phys. Rev. 91, 1182 (1953); Acta Cryst. 7, 405 (1954). R. A. Bonham and T. Ukaji, J. Chem. Phys. 36, 72 (1962).

[5] J. A. Hoerni, Phys. Rev. 102, 1530 (1956); P. J. Bunyan, Proc. Roy. Soc. (London) 82, 1051 (1963); J. Gjønnes, Acta Cryst. 13, 1075 (1964).

[6] R. A. Bonham, J. Chem. Phys. 43, 1103 (1965); Am. Cryst. Assoc. 2, 165 (1966).

[7] R. Glauber, Lectures in Theoretical Physics (Interscience, New York, 1959), Vol. 1.

[8] N. F. Mott and H. S. W. Massey, The Theory of Atomic Collisions (Oxford U. P., London, 1965), 3rd edition, pp. 19–25, 346–349.

[9] Notation follows H. Margenau and G. M. Murphy, The Mathematics of Physics and Chemistry (D. Van Nostrand, Princeton, 1956), 2nd edition, pp. 286–289.

[10] L. S. Bartell and T. C. Wong (unpublished research).

[11] R. A. Bonham and E. M. A. Peixoto (unpublished); J. W. Liu and R. A. Bonham (unpublished).

[12] A. C. Yates (private communication).