

# Intermolecular multiple scattering of electrons. I. Theory

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Coherent intramolecular multiple scattering by free molecules has been investigated extensively in the literature. Scant attention has been paid to incoherent intermolecular multiple scattering, however, a potentially serious problem under some circumstances. Therefore, a treatment of this problem has been carried out, taking advantage of simplifications afforded by the predominance of forward scattering. Explicit expressions of elementary form are derived for the differential cross sections corresponding to double, triple, and higher scatterings, and for the fractional contribution of each to the total intensity. Illustrative calculations are presented for electrons diffracted at various sample pressures encountered in a recent diffraction study of collisionally assisted laser pumping of SF<sub>6</sub>.

## I. INTRODUCTION

Electrons are scattered by matter many orders of magnitude more strongly than are x rays or neutrons. This is sometimes a great advantage in diffraction studies of atomic and molecular structure (e.g., of low density vapors or exceedingly thin films) but it may also be a source of difficulty. Coherent intrasample multiple scattering effects observed with x-rays only when crystalline samples approach macrodimensions<sup>1</sup> can be seen in the scattering of electrons by individual molecules.<sup>2,3</sup> Although a large body of literature exists on this subject including practical treatments<sup>3</sup> for gas-phase electron diffraction, little attention has been given to the potentially serious problem of incoherent intermolecular multiple scattering in gas-phase diffraction. Although some experimental and theoretical work has been published on small angle electron multiple scattering in delocalized gas samples,<sup>4</sup> we are aware of no general treatment applicable to, and assessing potential errors in, gas-phase studies of molecular structure. A useful beginning was made by the Karles three decades ago<sup>5</sup> based on empirical measurements applicable to a particular nozzle and sample. Since that time experimentalists have continued to be guided by rules-of-thumb checked by only occasional comparisons between structures determined by gas-phase electron diffraction and structures derived by spectroscopy.

It turns out that a substantial amount of multiple scattering can be encountered under conditions not differing radically from those sometimes used. Therefore it is appropriate to examine theoretically and experimentally the degree of multiple scattering to be expected under specified conditions and to establish the influence of this scattering on the molecular parameters derived by the standard procedures. The theoretical information needed to carry out such a study has long been known. It consists of atomic cross sections, differential<sup>6</sup> and integrated,<sup>7</sup> for electrons in the energy range normally used. The incentive prompting the present research was the desirability of probing laser-

pumped molecules by electron diffraction,<sup>8,9</sup> under collisional conditions with vapor densities exceeding those normally adopted in structure studies.

A practical theoretical treatment of intermolecular multiple scattering is developed in the present paper in a form convenient for comparing with experiment. An experimental test is reported in the following paper.<sup>10</sup>

## II. THEORETICAL DEVELOPMENT

### A. Single scattering

For the present purposes effects of chemical binding on charge distribution can be disregarded and the expectation value of the differential cross section for electrons singly scattered by a free molecule can be expressed in terms of the independent atom model as

$$d\sigma/d\Omega = g_A^s(s) + g_M^s(s), \quad (1)$$

where the superscript denotes single scattering and  $s = (4\pi/\lambda) \sin(\theta/2)$ . Atomic scattering can be written, in the semikinematic approximation,<sup>11</sup> as

$$g_A^s(s) = \sum_i [ |f_i|^2 + (4/a_0^2 s^4) S_i ] \quad (2)$$

in the usual notation, and molecular scattering, as

$$g_M^s(s) = \sum_{i \neq j} \sum_j |f_i| |f_j| \cos \Delta\eta_{ij} \exp(-l_{ij}^2 s^2 / 2) \times (\sin sr_{ij}) / sr_{ij}. \quad (3)$$

To simplify the treatment, we absorb the phase shift factor  $\cos \Delta\eta_{ij}$  into an effective mean-square amplitude  $l_n^2$ , taking

$$\cos \Delta\eta_{ij} \exp(-l_{ij}^2 s^2 / 2) \approx \exp(-l_n^2 s^2 / 2) \quad (4)$$

if  $\Delta\eta_{ij}$  is not large.

In the case of vapor molecules the average intermolecular distances are so large and random that the above asymptotic (Fraunhofer) expressions can be used to describe radiation scattered by upstream molecules and encountering downstream molecules. Near-field (Fresnel diffraction) effects need not be considered. A full treatment, then, would begin by following the course of radiation scattered once and incident upon other molecules. Each scattered ray would be followed

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as it experienced a rescattering by a new molecule through a new angle  $\theta'$  with a probability distribution governed by Eqs. (1)–(4). Keeping a quantitative account of the net intensity distribution after these and subsequent scatterings would be an undertaking of enormous complexity. The problem can be considerably simplified, however, when it is recognized that the scattering is predominantly in the forward direction and that the diffraction information sought occurs at scattering angles that are not large. It is reasonable to adopt a small angle approximation, used also by the Karles,<sup>5</sup> in which the Cartesian coordinates  $x$  and  $y$  of an electron striking the detector after experiencing a single scattering can be related to the momentum transfer components  $s_x$  and  $s_y$  by

$$x = (\lambda L/2\pi)s_x \quad (5a)$$

and

$$y = (\lambda L/2\pi)s_y, \quad (5b)$$

where  $s^2 = s_x^2 + s_y^2$  and  $L$  is the sample-to-detector distance. In the following we shall regard the connection between the Cartesian coordinates and components of  $s$  to be so direct that we shall lay aside precision in notation and use  $s(x, y)$  and  $s(x, y)$  interchangeably.

A further device (which, while complicating the single-scattering equations, greatly simplifies the multiple-scattering integrals) is to represent the terms in Eqs. (2) and (3) as sums over Gaussians, or

$$s_A^s \approx \sum_n L_n \exp(-c_n s^2) \quad (6a)$$

$$\approx \sum_n L_n \exp[-b_n(x^2 + y^2)] \quad (6b)$$

and

$$|f_i| |f_j| \approx \sum_m M_m \exp(-d_m s^2) \quad (7a)$$

$$\approx \sum_m M_m \exp[-g_m(x^2 + y^2)], \quad (7b)$$

where the forms of  $s_A^s(s)$  and  $|f_i| |f_j|$  are well approximated if enough Gaussians are involved. According to Eqs. (5a) and (5b) the constants in Eqs. (6) and (7) are related by

$$b_n = (2\pi/\lambda L)^2 c_n \quad (8a)$$

and

$$g_m = (2\pi/\lambda L)^2 d_m. \quad (8b)$$

## B. Multiple scattering integrals

Inspection of Fig. 1 should make it clear that if an electron scattered by molecule 1 and on its way to  $(x_i, y_i)$  at the detector strikes a second molecule, the expectation value of the intensity scattered by molecule 2 is proportional to

$$[s_A^s(x_j - x_i, y_j - y_i) + s_M^s(x_j - x_i, y_j - y_i)]_1$$

in our small-angle approximation. [Note that indices  $i$  and  $j$  bear no relation to those of Eqs. (2)–(4).] Accordingly, the differential cross section for double scattering, averaged over the incident directions of the ini-

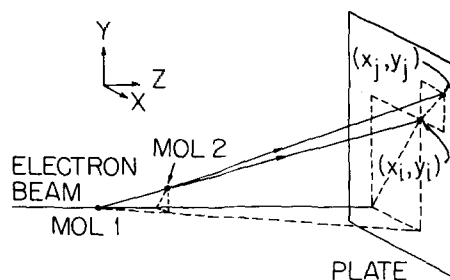


FIG. 1. Schematic illustration of a ray scattered by molecule 1 and rescattered by molecule 2. In the absence of a second scattering, the ray would have struck the detector (photo plate) at  $x_i, y_i$ .

tial scattering, is proportional to the integral

$$I^D(s) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} [s_A^s(x_i, y_i) + s_M^s(x_i, y_i)]_1 \times [s_A^s(x_j - x_i, y_j - y_i) + s_M^s(x_j - x_i, y_j - y_i)]_2 dx_i dy_i, \quad (9)$$

where the integration limits, while nonphysical, are consistent with the small angle model in its Gaussian representation. When the multiplication expressed in the integrand of Eq. (9) is carried out, it is apparent that the integral can be written as

$$I^D(s) = I_{A_1 A_2} + I_{A_1 M_2} + I_{M_1 A_2} + I_{M_1 M_2}. \quad (10)$$

Component  $I_{A_1 A_2}$  is a smooth, double scattered atomic background falling less steeply than  $s_A^s(s)$ , while  $I_{A_1 M_2}$  and  $I_{M_1 A_2}$  contribute molecular interference features that are weaker than those of  $s_M^s(s)$ . The last term  $I_{M_1 M_2}$ , which should be minor, is hereafter neglected. Integration of the first term immediately yields

$$I_{A_1 A_2} = \pi \sum_m \sum_n \frac{L_m L_n}{(b_m + b_n)} \exp - \left[ \frac{b_m b_n (x_i^2 + y_i^2)}{(b_m + b_n)} \right] = \pi \left( \frac{\lambda L}{2\pi} \right) \sum_m \sum_n \frac{L_m L_n}{(c_m + c_n)} \exp - \left[ \frac{c_m c_n s^2}{(c_m + c_n)} \right]. \quad (11)$$

The cross terms are

$$I_{A_1 M_2} = I_{M_1 A_2} = \sum_k \sum_m \sum_n M_m L_n G_{mn}^k, \quad (12)$$

where

$$G_{mn}^k = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp(-\xi_k) (\sin SR_k) / SR_k dx_i dy_i \quad (13)$$

for the  $k$ th internuclear distance  $r_k \equiv r_{ij}$  of Eq. (13), with

$$\xi_k = [g_m + (2\pi/\lambda L)^2 I_n^2 / 2]_k (x_i^2 + y_i^2) + b_m [(x_j - x_i)^2 + (y_j - y_i)^2] \quad (14)$$

and

$$SR_k = (2\pi/\lambda L) (x_i^2 + y_i^2)^{1/2} r_k. \quad (15)$$

Integral  $G_{mn}^k$  can be evaluated with the aid of auxiliary formulas published elsewhere<sup>12</sup> with the result

$$G_{mn}^k = \pi \left( \frac{\lambda L}{2\pi} \right)^2 \exp \left[ \frac{c_n(Q_{mn}^k - c_n)s^2}{Q_{mn}^k} \right] \times \exp \left[ - \frac{r_k^2(1 + Q_{mn}^k/2c_n s^2 + \dots)}{4Q_{mn}^k} \right] \times (c_n s r_k)^{-1} \sin \left[ \frac{c_n s r_k}{Q_{mn}^k} - \frac{r_k}{2c_n s} - \frac{Q_{mn}^k r_k}{c_n^3 s^3} + \frac{r_k^3}{24c_n^3 s^3} + \dots \right], \tag{16}$$

where  $Q_{mn}^k = (c_n + d_m + \frac{1}{2}l_n^2)_k$ .

Higher-order scatterings can be treated in exactly analogous ways. For example, the principal triple scattering integrals are

$$I_{A_1 A_2 A_3}(x_k, y_k) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} I_{A_1 A_2}(x_j, y_j) g_A^s(x_k - x_j, y_k - y_j) dx_j dy_j \tag{17}$$

or

$$I_{A_1 A_2 A_3}(s) = \pi^2 \left( \frac{\lambda L}{2\pi} \right)^4 \sum_l \sum_m \sum_n \frac{L_l L_m L_n}{c_l c_m + c_l c_n + c_m c_n} \times \exp \left[ \frac{-c_l c_m c_n s^2}{c_l c_m + c_l c_n + c_m c_n} \right] \tag{18}$$

and

$$I_{A_1 A_2 M_3}(x_k, y_k) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} I_{A_1 A_2}(x_j, y_j) g_M^s(x_k - x_j, y_k - y_j) dx_j dy_j \tag{19}$$

or

$$I_{A_1 A_2 M_3}(s) = \sum_k \sum_l \sum_m \sum_n [L_m L_n M_l / (c_m + c_n)] G_{imn}^k, \tag{20}$$

where

$$G_{imn}^k = \pi^2 \left( \frac{\lambda L}{2\pi} \right)^4 \exp \left[ \frac{c_{mn}(Q_{imn}^k - c_{mn})s^2}{Q_{imn}^k} \right] \times \exp \left[ - \frac{r_k^2(1 + Q_{imn}^k/2c_{mn}s^2 + \dots)}{4Q_{imn}^k} \right] \times (c_{mn} s r_k)^{-1} \sin \left[ \frac{c_{mn} s r_k}{Q_{imn}^k} - \frac{r_k}{2c_{mn} s} + \dots \right], \tag{21}$$

with

$$c_{mn} = c_m c_n / (c_m + c_n)$$

and

$$Q_{imn}^k = (c_{mn} + d_l + \frac{1}{2}l_n^2)_k.$$

### C. Cross sections for multiple scattering

In the previous section we established the integrals governing the angular dependence of the differential cross sections for multiple scattering. In this section we evaluate  $K_2, K_3$ , etc., the constants converting the integrals into differential cross sections. According to

$$g_A^D(s) = K_2 I_{A_1 A_2}(s), \tag{22}$$

$$g_A^T(s) = K_3 I_{A_1 A_2 A_3}(s), \text{ etc.}, \tag{23}$$

where superscripts  $D$  and  $T$  refer to double and triple scattering. It is taken for granted that each scattering, whether first, second, ...,  $n$ th, etc., has the same

integrated atomic cross section, or

$$\int g_A^n(s) d\Omega \equiv \int (d\sigma_n/d\Omega)_A d\Omega \equiv \sigma_n \equiv \sigma, \tag{24}$$

where

$$d\Omega = \sin \theta d\theta d\phi = (\lambda/2\pi)^2 s ds d\phi$$

and where, via Eq. (6),

$$\sigma = \pi(\lambda/2\pi)^2 \sum_n L_n / c_n. \tag{25}$$

Accordingly, the  $K_n$  are

$$K_2 = \int_0^\infty g_A^s(s) s ds / \int_0^\infty I_{A_1 A_2}(s) s ds = (\sigma L^2)^{-1}, \tag{26}$$

$$K_3 = \int_0^\infty g_A^s(s) s ds / \int_0^\infty I_{A_1 A_2 A_3}(s) s ds = (\sigma L^2)^{-2}, \tag{27}$$

etc., where  $\sigma$  can be evaluated from Eq. (25). Obviously,  $K_1$  is unity.

Differential cross sections for molecular multiple scattering can be written as

$$g_M^D(s) = 2K_2 I_{A_1 A_2}(s), \tag{28}$$

$$g_M^T(s) = 3K_3 I_{A_1 A_2 M_3}(s), \tag{29}$$

etc., where the multiplicities 2, 3, etc., arise because

$$I_{A_1 A_2} = I_{M_1 A_2},$$

$$I_{A_1 A_2 M_3} = I_{A_1 M_2 A_3} = I_{M_1 A_2 A_3}$$

which equalities can be demonstrated by changing variables, e.g.,  $x_j - x_l = X_l$ , etc. in the integrands involved, and noting the equivalence of form.

### D. Apportionment of multiple scattering

In the foregoing we have developed the differential cross sections for successive scatterings, all of which lead to the same ratio of integrated  $n$ th-scattered flux to incident [( $n - 1$ )th scattered] flux. At a given point in the sample, however, the flux of once-scattered electrons is different from that of unscattered electrons, and the flux of twice-scattered electrons is yet different. Furthermore, the apportionment of flux incident upon a given point in the sample between unscattered, once-scattered, twice-scattered, etc., radiation varies with position in the sample. The most elementary way to take this into account and to maintain flux conservation (which is *not* maintained in the usual Born kinematic approximation) is to take advantage of further simplifications offered by the small angle approximation. Let us consider the attenuation of the unscattered radiation as the beam progresses through the sample, and the attenuation of the singly scattered radiation by a second scattering, and of doubly scattered radiation by a third scattering, etc. as functions only of  $z$ , along

the incident directions. Ultimately, of course, after many scatterings, an electron has lost a sense of the direction from which it came and the  $z$  direction has no more relevance than any other direction. Suppose then, at any distance  $z$ , that  $f_0(z)$  is the fraction of electrons having reached that point that have suffered no scattering, that  $f_1(z)$  is the fraction having suffered one scattering,  $f_2(z)$  the fraction having suffered two scatterings, and so on. Conservation requires that

$$\sum_{n=0}^{\infty} f_n(z) = 1. \quad (30)$$

The differential equations governing the fractions  $f_n(z)$  are

$$df_0/dz = -\sigma_1 \rho f_0, \quad (31)$$

$$df_1/dz = \sigma_1 \rho f_0 - \sigma_2 \rho f_1, \quad (32)$$

$$df_2/dz = \sigma_2 \rho f_1 - \sigma_3 \rho f_2, \quad (33)$$

etc., where the  $\sigma_n$  are the scattering cross sections of Eq. (24), all henceforth taken as equal, and  $\rho$  stands for the number density of gas molecules at  $z$ . To simplify notation let us write  $\rho z$  in place of  $\int_{-\infty}^z \rho(z) dz$  (a substitution that would be rigorous if the gas density were a step function).

The solutions of the above differential equations are

$$f_0(z) = e^{-\sigma \rho z}, \quad (34)$$

$$f_1(z) = \sigma \rho z e^{-\sigma \rho z}, \quad (35)$$

⋮

$$f_n(z) = [(\sigma \rho z)^n / n!] e^{-\sigma \rho z}, \quad (36)$$

which satisfy Eq. (30), as well. Upon leaving the sample the fractions are

$$f_n = [N_t^n / n!] e^{-N_t}, \quad (37)$$

where

$$N_t = \sigma \int_{-\infty}^{\infty} \rho(z) dz. \quad (38)$$

The total number of scatterings, on the average, experienced by a given electron in traversing the sample is, then,

$$\begin{aligned} \sum_{n=0}^{\infty} n f_n &= \sum_{n=0}^{\infty} n [N_t^n / n!] e^{-N_t} \\ &= N_t. \end{aligned} \quad (39)$$

Atomic cross sections are available<sup>7</sup> and, hence,  $\sigma$  is calculable for molecules. Moreover,  $\rho(z)$  is readily measurable for gas jets. Therefore it is simple to determine  $N_t$ . In order for the conventional kinematic treatment to apply it might seem necessary for  $N_t$  to be much smaller than unity. It turns out that, in practice,  $N_t$  is often not that small. Nevertheless, as we shall see, the application of kinematic equations to structure analysis may lead to reasonably satisfactory results even in some cases with  $N_t$  as high as several scatterings per electron.

Putting the foregoing relations together, we obtain for the combined intensity distribution

$$\begin{aligned} (d\sigma/d\Omega)_{\text{net}} &\equiv \mathcal{I}(s) \\ &= (1-f_0)^{-1} [f_1 \mathcal{I}^S(s) + f_2 \mathcal{I}^D(s) + f_3 \mathcal{I}^T(s) + \dots], \end{aligned} \quad (40)$$

where the factor  $(1-f_0)^{-1}$  enters to recover the integrated cross section from Eq. (40) inasmuch as the sum of  $f_n$  from 1 to  $\infty$  is  $(1-f_0)$ .

Finally, the quantity corresponding most closely to that determined experimentally in practical structure determinations is  $M(s)$ , the ratio of the "molecular" interference terms  $\mathcal{I}_M(s)$  to the smooth "atomic" background  $\mathcal{I}_A(s)$  drawn through the interference oscillations. In the present treatment, this "reduced intensity function" is evidently

$$M(s) = \frac{f_1 \mathcal{I}_M^S + f_2 \mathcal{I}_M^D + f_3 \mathcal{I}_M^T + \dots}{f_1 \mathcal{I}_A^S + f_2 \mathcal{I}_A^D + f_3 \mathcal{I}_A^T + \dots}. \quad (41)$$

It is convenient to express this quotient as  $M^S(s)$ ,  $M^{SD}(s)$ ,  $M^{SDT}(s)$ , etc., depending upon whether the sums are truncated at single, double, or triple, etc., scattering. Physical intuition (confirmed by numerical calculations) leads one to expect that higher-order molecular terms  $\mathcal{I}_M(s)$  become weaker and more chaotic the higher the order while the atomic terms  $\mathcal{I}_A(s)$  begin to become less strongly peaked in the forward direction.

### III. NUMERICAL ILLUSTRATIONS

We report here some illustrative results based on conditions encountered in a study of laser-pumped SF<sub>6</sub>. The nozzle chosen, with an i.d. of 0.012 cm, is substantially finer than that of conventional studies (i.d. of, say, 0.036 cm) and gives a throughput at a given pressure roughly 1 to 2 orders of magnitude lower, depending upon whether the flow is supersonically choked (high pressure limit) or viscous. The distribution  $\rho(z)$  of the gas jet at the electron beam was measured as described elsewhere<sup>8</sup> and found to be very nearly of the form

$$\rho(z) = \rho_m (1 + bz^2)^{-2} \quad (42)$$

with  $b$  approximately  $[1270 - 0.138 P(\text{Torr})] \text{ cm}^{-2}$  0.041 cm from the nozzle tip where the electron beam crosses the jet. From Eq. (42) can be calculated the "area density" of molecules,

TABLE I. Cross sections and constants for differential cross sections<sup>a</sup> for 40 kV electrons scattered by an SF<sub>6</sub> molecule.

$n$	$L_n/c_n$	$10^3 c_n$	$M_n^{\text{SF}}/d_n$	$10^3 d_n^{\text{SF}}$	$M_n^{\text{FF}}/d_n$	$10^3 d_n^{\text{FF}}$
0	753.90	$10^4$	49.94	155.58	4.93	202.98
1	170.88	753.94	49.10	45.02	25.08	78.60
2	279.12	155.91	24.17	10.81	25.71	28.00
3	328.13	44.42	7.48	2.20	10.56	7.68
4	165.20	8.74	1.61	0.40	3.48	1.39
			$\sigma_{\text{total}} = 0.19 \text{ \AA}^2$		$\sigma_{\text{inel}} = 0.29 \text{ \AA}^2$	

<sup>a</sup> $L_n$  in  $\text{\AA}$ ,  $M_n$  in  $\text{\AA}^2$ ,  $c_n$ ,  $d_n$  in  $\text{\AA}^{-2}$ . Constants based on scattering factors of Ref. 6. Total elastic and inelastic cross sections are from Ref. 7. Coefficients  $L_0$  and  $c_0$  are highly arbitrary. They do not influence differential cross sections in the observable range of scattering angles but augment the other constants to reproduce the total cross section.

TABLE II. Mean number of scatterings  $N_t$  per electron and fractions of electrons having undergone 0, 1, 2, and 3 scatterings at various sample pressures inside 0.012 cm nozzle.

$P$ (Torr)	$N_t^a$	$N_t'^b$	$f_0^b$	$f_1^b$	$f_2^b$	$f_3^{b,c}$
760	0.44	0.24	0.789	0.190	0.023	0.002
2000	0.98	0.55	0.579	0.316	0.086	0.016
4000	1.72	0.96	0.385	0.368	0.176	0.056

<sup>a</sup>From Eq. (38) with total  $\sigma = 0.486 \text{ \AA}^2$  from Ref. 7.

<sup>b</sup>Based on  $\sigma = 0.270 \text{ \AA}^2$  calculated by deleting the very small angle  $L_0$  component. See the text.

<sup>c</sup>Tabulated value based on Eq. (37) but value used in calculations for Figs. 1-4 was  $1 - f_0 - f_1 - f_2$  because treatment was only carried through triple scattering.

$$\int_{-\infty}^{\infty} \rho(z) dz = \pi \rho_m / 2b^{1/2}. \quad (43)$$

Center-line density  $\rho_m$  can be determined from measurements of the gas throughput  $Q$  through the nozzle with the aid of the expression

$$\rho_m \approx 3.09 \times 10^{-9} (4bx^2 + 1) Q / x^2 v(x), \quad (44)$$

where  $\rho_m$  is in molecules/cm<sup>3</sup>,  $x$  is the distance from the nozzle tip in cm,  $Q$  is in Torr cm<sup>3</sup>/s, and  $v(x)$  is the velocity of the gas jet in cm/s. An algorithm to compute  $Q$  from nozzle dimensions and gas pressures is reported elsewhere.<sup>9</sup> It gave results in close accord with our experiments.

In this preliminary investigation of multiple scattering no effort was made to obtain Gaussian fits of great precision for Eqs. (6) and (7) and only a few terms were resorted to. Constants for the molecule SF<sub>6</sub> are listed in Table I. They yield accuracies for  $\mathcal{J}_A(s)$  of  $\pm 4\%$  inside  $s = 12$ , and of  $\pm 10\%$  inside  $s = 17.5$ . The products  $|f_i| |f_j|$  are accurate to  $\pm 4\%$  inside  $s = 19$  and  $\pm 10\%$  inside  $s = 35$ . Ratios  $L_n/c_n$  and  $M_n/d_n$  are tabulated in place of  $L_n$  and  $M_n$  to give a better indication of relative contributions to cross sections.

The mean number of scatterings  $N_t$  per electron is

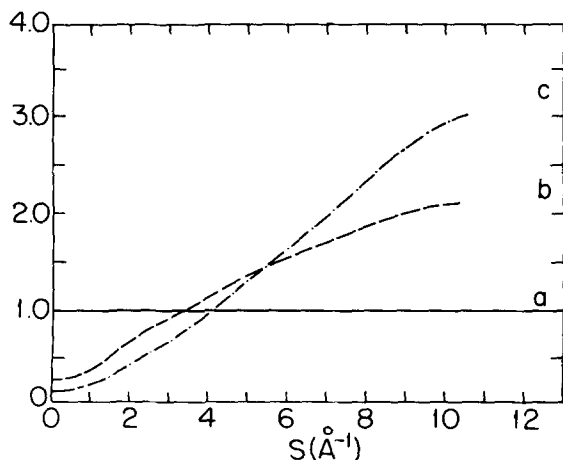


FIG. 2. Atomic intensity distributions  $\mathcal{J}_A^s(s)$  for (a) single scattering, (b) double scattering, and (c) triple scattering, each divided by  $\mathcal{J}_A(s)$  for single scattering to convey distinctions more clearly. Constant  $L_0$  has been deleted.

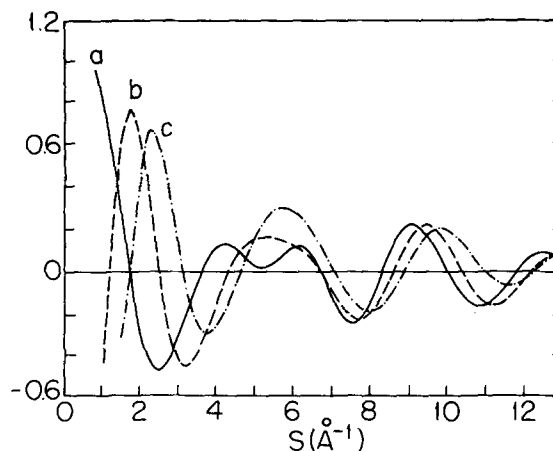


FIG. 3. Molecular differential cross sections  $\mathcal{J}_M^s(s)$  for (a) single scattering, (b) double scattering, and (c) triple scattering, each divided by  $\mathcal{J}_A(s)$  for single scattering to make visual assessment simpler. Double-scattering and triple-scattering curves are multiplied by 8 and 64, respectively, to render them easily visible in the same plot.

shown in Table II as a function of sample pressure applied to the micronozzle. A second number of scatterings  $N_t'$  is also tabulated. It is calculated by deleting the component  $L_0$  which is predominantly inelastic and of consequence only at extremely small scattering angles. Effects of  $L_0$ , then, are almost indistinguishable from those of the incident unscattered beam and serve only to augment  $N_t$  and the  $f_n$  in an unimportant way. Fractions of unscattered, once scattered, twice scattered, etc., electrons based on  $N_t'$  are also listed.

Atomic and molecular differential cross sections, all divided by  $\mathcal{J}_A^s(s)$  to make comparisons more readily comprehensible, are plotted in Figs. 2 and 3. From this information it is immediately obvious what effect multiple scattering will have on the reduced molecular intensity curve,

$$M(s) = \sum f_n \mathcal{J}_M^n / \sum f_n \mathcal{J}_A^n.$$

As the sample pressure and, hence, the higher-order  $f_n$  fractions increase, the denominator will grow relative to the numerator, and will grow at large scattering angles relative to smaller scattering angles. This will tend to wash out the molecular interference terms (reducing the so-called "index of resolution") and increase their damping as if by increased amplitudes of molecular vibration. Small phase shifts to the interference oscillations will also be introduced.

Whether an approach as simplified as the present treatment can give a realistic representation of the actual effect of multiple scattering is tested with experimental data in the following paper.

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<sup>1</sup>See, for example, W. H. Zachariasen, *Theory of X-Ray Diffraction in Crystals* (Dover, New York, 1967).

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<sup>3</sup>See B. R. Miller and L. S. Bartell, *J. Chem. Phys.* **72**, 800 (1980), and citations therein.

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<sup>11</sup>For a brief review of the full dynamic vs semikinematic treatment of multiple scattering of molecules, see Ref. 3. For a review of the standard notation in the present paper, see L. S. Bartell, in *Physical Methods of Chemistry*, 4th ed., edited by A. Weissberger and B. W. Rossiter (Interscience, New York, 1973).

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