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Small-angle Electron Scattering by Gases. CS_2 and CCl_4

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The small-angle scattering intensity of 40 keV electrons by CS_2 and CCl_4 molecules has been measured by the use of a counting unit. The experimental intensities have been compared with the theoretical values for the independent-atom-model, and an analysis of the comparison has shown the consistency of the present results with Tavard's energy relation. The difference intensity, $\Delta\sigma(s)$, of CCl_4 has shown oscillatory behavior resulting from the distortion of charge distribution due to chemical-bond formation.

The study of the charge distribution of atoms and molecules by means of a small-angle scattering experiment of high-energy (~40 keV) electrons has been shown to be feasible and promising by several recent works.[1-6] In most of them, molecules consisting of light atoms were investigated and the results interpreted in terms of the effect of the chemical binding and electron correlation on the charge distribution. Since the theoretical scattering intensity calculated from the exact molecular wave function is not available except for a few very simple cases, a direct comparison of the experimental results with the theoretical intensity is generally impossible at present. The theoretical relationship between the scattering intensity and the electronic energy of the molecular system given by Tavard and co-worker[7] has been useful for a semi-quantitative discussion of the experimental results. The difficulty in intensity measurements in the small-angle region was largely decreased by the use of a new diffraction unit with the scintillation-counting system in place of the photographic plate.[4,6]

The following atom and molecules have so far been successfully investigated by the counting technique; Ne,[2] CH_4,[3] CO_2,[4,8] N_2O,[4] and N_2[5] by Bonham and co-workers, and H_2O[6] by Konaka. All of them consist of atoms in the first row of the periodic table. The present study is an extension of these previous works along the same line of interest to molecules which contain atoms in the second row of the periodic table. For these atoms, the correlation energy is fairly large. To see how far the observed scattering intensity is consistent with the correlation energy estimated by Clementi[10] was the main purpose of the present study. However, the quantitative discussion of the result has been obscured by the uncertainty in our knowledge of the relativistic effect, which can not be ignored for the second-row atoms.

Experimental

The diffraction experiment was carried out on a counting unit which was reported elsewhere.[6] The experimental conditions were as follows: accelerating voltage, 41 kV, stabilized within 0.01%; camera length, 107 cm; pressure in the diffraction chamber, 2.0×10^{-6} Torr without sample gas injection and 3.5×10^{-6} Torr during measurement. A liquid nitrogen cold trap was placed close to the nozzle. The accumulated count was in the range of 2000—600000, and the time of measurement for a single data-point was 20 s. The data covered the range of $s=0.6-9$ Å^{-1} at intervals of 0.5 Å^{-1}.

The residual gas correction was carried out by the method of Fink and Bonham.[4] However, the second nozzle for the background measurement was not placed close to the main nozzle; rather, it was in between the nozzle and the detector, about 30 cm from the main nozzle and close to the wall of the diffraction chamber. This modification was made simply because of the difficulty in doing additional machine work for the small specimen-chamber. The amount of gas-injection through the second nozzle was adjusted so that the reading of the vacuum gauge was the same as that of the first run of the scattering measurements for a gas sample from the main nozzle. The present method is effective enough to make the residual gas correction for the background scattering from the almost uniformly-distributed gas in the scattering chamber, which is the major portion of the residual gas in the present unit for condensable samples.

The measured electron counts were first corrected for the counting loss due to the finite resolving time of the scaler. Then the normalized relative intensity, I_{exp}, was obtained by;

$$I_{\text{exp}} = C\left(N_{\text{G}}^{\text{D}}\frac{N_{\text{G}}^{\text{M}_0}}{N_{\text{G}}^{\text{M}}} - N_{\text{B}}^{\text{D}}\frac{N_{\text{B}}^{\text{M}_0}}{N_{\text{B}}^{\text{M}}}\right) \tag{1}$$

where $N_{\text{G,B}}^{\text{D,M,M}_0}$ are the corrected counts of the scanning detector (D) and monitor (M) for the sample gas (G) and background (B). The superscript M_0 indicates the reference value of the monitor count, and C is the normalization constant. This equation is valid on the assumption that the variation in the scattering intensity from the sample gas is proportional to the variation due to background scattering. The incident beam current was not monitored during measurements in the unit of the present study. However, an independent observation of the scattering count from a solid specimen indicated that the stability of the beam current was within

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[1] D. A. Kohl and R. A. Bonham, *J. Chem. Phys.*, **47**, 1634 (1967) and references cited therein.

[2] M. Fink and R. A. Bonham, *Phys. Rev.*, **187**, A114 (1969).

[3] M. Fink, D. A. Kohl, and R. A. Bonham, *J. Chem. Phys.*, **52**, 5487 (1970).

[4] M. Fink and R.A. Bonham, *Rev. Sci. Instrum.*, **41**, 389 (1970).

[5] R. A. Bonham, M. Fink and D. A. Kohl, *Chem. Phys. Lett.*, **4**, 349 (1969).

[6] S. Konaka, *Japan. J. Appl. Phys.*, **11**, 1199 (1972).

[7] a) C. Tavard and M. Roux, *C. R. Acad. Sci. Paris*, **260**, 4933 (1965); b) C. Tavard, *Cahiers Phys.*, **20**, 397 (1966).

[8] In Ref. 4, difficulty in the normalization of CO_2 and N_2O data to the theoretical intensity was reported. However, it was found recently that there were errors in the calculated values of the theoretical curve and the experimental data showed sufficient consistency with the Tavard's relation. Similar result for CO_2 was obtained also by the present authors.[9]

[9] S. Konaka, International Symposium of the Application of Quantum Mechanics, Florida (January, 1973).

[10] a) E. Clementi, *J. Chem. Phys.*, **38**, 2248 (1963); b) E. Clementi, *ibid.*, **39**, 175 (1963); c) A. Veillard and E. Clementi, *ibid.*, **49**, 2415 (1968).

Table 1. Experimental and theoretical (IAM) scattered intensities for CS_2 and CCl_4 at 41 kV

CS_2				CCl_4			
s(Å^{-1})	I_{exp}[a]	σ/I_{exp}[b]	I_{IAM}	s(Å^{-1})	I_{exp}	σ/I_{exp}	I_{IAM}
0.658	1.453×10^1	2.2%	1.706×10^1	0.676	3.436×10^1	2.2%	3.497×10^1
0.955	8.122×10^0	1.5	9.706×10^0	0.973	1.683	1.5	1.784
1.350	4.235	1.0	5.133	1.468	4.796×10^0	1.0	5.462×10^0
1.744	2.698	0.9	3.176	1.962	3.074	0.9	3.492
2.139	1.956	0.9	2.210	2.457	3.184	0.8	3.540
2.534	1.377	0.8	1.531	2.951	2.295	0.7	2.484
2.929	9.246×10^{-1}	0.7	1.008	3.446	1.278	0.8	1.361
3.324	6.520	0.7	6.920×10^{-1}	3.940	9.490×10^{-1}	0.8	9.779×10^{-1}
3.719	5.314	0.8	5.549	4.435	8.807	0.8	9.081
4.114	4.660	0.8	4.827	4.930	6.807	0.8	7.060
4.509	3.941	0.8	4.009	5.424	4.188	0.9	4.256
4.904	3.031	0.8	3.069	5.915	2.576	0.9	2.595
5.299	2.212	0.9	2.257	6.413	2.216	1.0	2.223
5.693	1.685	0.9	1.710	6.908	2.069	1.0	2.098
6.088	1.347	0.9	1.367	7.402	1.683	1.1	1.683
6.483	1.082	1.0	1.108	7.897	1.240	1.2	1.227
6.878	8.836×10^{-2}	1.0	8.844×10^{-2}	8.391	9.891×10^{-2}	1.3	9.941×10^{-2}
7.273	7.240	1.0	7.136	8.886	8.813×10^{-2}	1.5	8.948×10^{-2}
7.668	6.125	1.1	6.124				
8.063	5.613	1.2	5.572				
8.458	5.054	1.3	5.076				
8.853	4.059×10^{-2}	1.5	4.436×10^{-2}				

a) Normalized to I_{IAM} at $s=6.5-8$

b) The symbol σ denotes the estimated standard error of I_{exp}, which include the error resulting from the uncertainty in s. The relative errors σ/I_{exp} are shown in percentage unit.

5%. Therefore, a systematic error of 5% may be included in the second term of Eq. (1); this error is, fortunately, smaller than the random error of $N_G{}^D$.

The scale factor, $L\lambda$, was calibrated by Debye-Scherrer rings of gold-foil.[11]

Results and Discussion

The experimental intensity, I_{exp}, was normalized to the theoretical intensity for the independent-atom-model,[1] I_{IAM}, in the s-range of 6.5—8. The final values of I_{exp} were obtained as the average of six sets of data from three independent measurements. Two sets of data were obtained for each measurement by scanning both sides of the main beam. The values of I_{exp} and I_{IAM} are shown in Table 1, together with the estimated uncertainties evaluated in much the same way as in Ref. 6.

The theoretical I_{IAM} value was calculated by the use of the elastic and inelastic scattering factors[12] based on the Hartree-Fock wave functions and by the use of the structure parameters[13] taken from the literature. The elastic scattering factor is the partial wave amplitude, even though Tavard's equation is valid only for the Born amplitude. The necessity and meaning of this treatment were discussed by Kohl and Bonham.[1]

The s^2I_{exp} and s^2I_{IAM} curves are compared in Figs. 1 and 2 for CS_2 and CCl_4 respectively. The difference intensities, $\Delta\sigma(s)=s^4[I_{exp}-I_{IAM}]$, are shown in Figs. 3 and 4.

Analysis of the Results by Means of Tavard's Energy Relation. In the present scheme of analysis, where I_{IAM} is calculated on the basis of the Hartree-Fock wave functions of the atoms, the energy relation given by Tavard and co-worker[7] can be reduced to the following expression;[1]

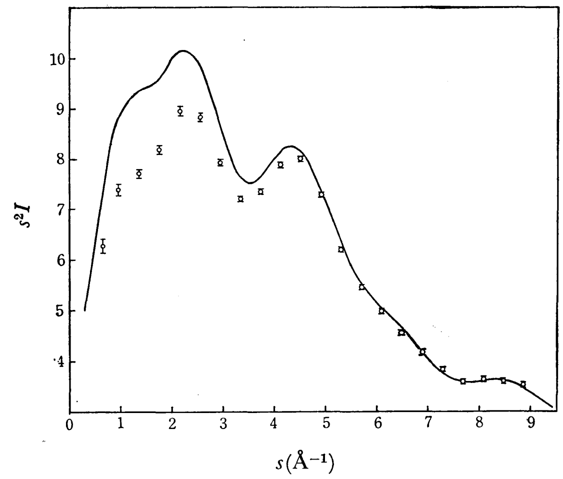

Fig. 1. Comparison between the experimental and theoretical (IAM) s^2I intensities for CS_2. ——: Theoretical intensity curve calculated using partial wave amplitude. ○: Experimental intensity. The vertical bar of experimental intensity shows the experimental standard error.

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[11] The lattice constant 4.078Å was used.

[12] a) M. Kimura, S. Konaka, and M. Ogasawara, *J. Chem. Phys.*, **46**, 2599 (1967); b) C. Tavard, D. Nicolas, and M. Rouault, *J. Chim. Phys.*, **64**, 540 (1967).

[13] a) Y. Morino and T. Iijima, This Bulletin, **35**, 1661 (1962); b) Y. Morino, Y. Nakamura, and T. Iijima, *J. Chem. Phys.*, **32**, 643 (1960).

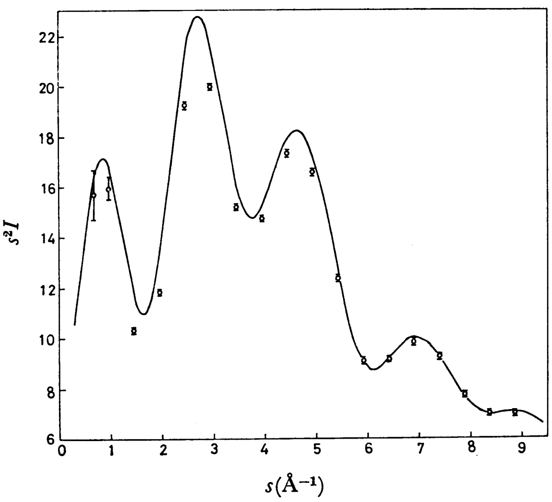

Fig. 2. Comparison between the experimental and theoretical (IAM) s^2I intensities for CCl_4. ——: Theoretical intensity curve calculated using partial wave amplitude. ○: Experimental intensity. The vertical bar of experimental intensity shows the experimental standard error.

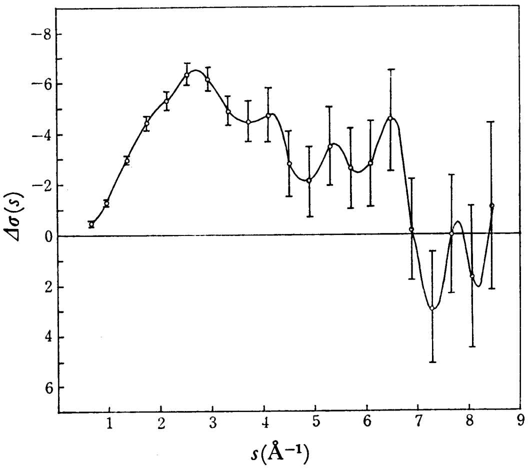

Fig. 3. Plot of $\Delta\sigma(s)$ for CS_2. The vertical bar shows the experimental standard error.

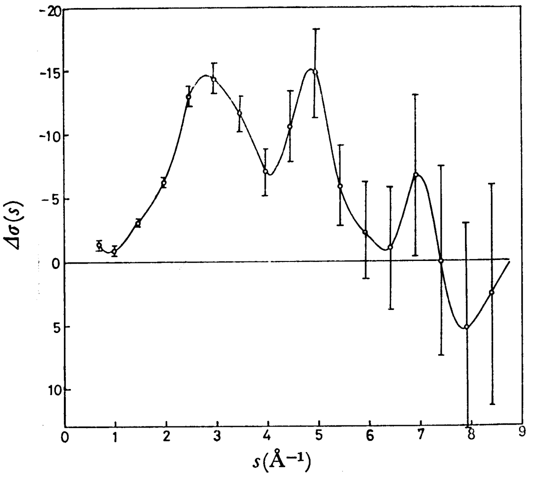

Fig. 4. Plot of $\Delta\sigma(s)$ for CCl_4. The vertical bar shows the experimental standard error.

$$E_b = \Delta E + E_1 - E_{corr} - E_{rel}, \qquad (2)$$

where;

$$\Delta E = \frac{1}{2\pi}\int_0^\infty \sigma(s)\mathrm{d}s.$$

In this equation, E_b is the binding energy of the molecule, E_1 is one-half of the lowering of the potential energy of the IAM molecule from that of the separated atoms, and E_{corr} and E_{rel} are the sum of the correlation energies for all the atoms and that of the relativistic energies respectively. All the terms in this expression have negative values.[14] The contribution to the first integral from the s-region beyond the normalization point was assumed to be zero.

According to the theoretical estimations,[10c,15] the relativistic energy, E_{rel}, is comparable to E_{corr} for the present molecules. Since the relativistic Hamiltonian contains terms other than the Coulomb interaction between charged particles, Tavard's equation in the form of Eq. (2) becomes invalid. According to Bonham and Cox,[16] a modified version of Tavard's equation can be obtained by putting a factor of 1.5—2.0 to E_{rel} for the K-shell electrons of He-like ions,[17] where the relativistic effect appears as the charge contraction due to an increase in the effective mass of electrons. However, the decrease in scattering intensity corresponding to the relativistic effect confined in the charge distribution of the inner core should show up in a wide s-range extending to large scattering angles. The integral of $\Delta\sigma(s)$, which is obtained from a rather limited s-range, could not contain the contribution from the E_{rel} term of at least K-shell electrons. By a similar argument, the K-shell correlation energy is most probably excluded from the integration of $\Delta\sigma(s)$. Although the charge contraction by the mass-effect in outer cores may be very small, the contribution of the relativistic energy of outer cores to Tavard's equation can not necessarily be assumed to be negligible. In the present stage of knowledge, it seems to be most reasonable to regard the relativistic energy of the outer cores as a theoretical uncertainty in Tavard's relation. Equation (2) was modified by this conjecture to:

$$\Delta E + E_1 = E_b + E^*_{corr} \quad \text{with} \pm E^*_{rel}, \qquad (3)$$

where E^* means that the contribution from the K-shell is not included; this equation was tested by the experimental data. The results were satisfactory, as is shown in Table 2. By considering that the radius of the L-shell of S and Cl is smaller than those of the first-row atoms, it is worth comparing the experimental values with the theoretical energies, where both the K- and L-shell energy are excluded for S and Cl. This is also shown in Table 2, where the energies without the contribution of the K- and L-shells are denoted by E^{**}. The agreement is poor. The exclusion of the whole L-shell seems, therefore, to be too extreme.

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14) Note that in Eq. (11) of Ref. 1 the correlation energy E_{corr} is taken as a positive quantity and the relativistic energy is neglected.

15) a) E. Clementi, *J. Mol. Spectrosc.*, **12**, 18 (1964); b) H. Hartmann and E. Clementi, *Phys. Rev.*, **133**, A1295 (1964).

16) R. A. Bonham and H. L. Cox, Jr., *J. Chem. Phys.*, **47**, 3508 (1967).

17) R. A. Bonham, *ibid.*, **43**, 1434 (1965).

Table 2. Result of the analysis by Tavard's relation (Energies in a.u.)

	$\Delta E^{a)}$	E_1	$\Delta E+E_1$	$E_b+E^{*}_{corr}$	$E_b+E^{**}_{corr}$	$E_b{}^{b)}$
CS_2	-1.67 ± 0.6	-0.32	-2.0 ± 0.6	-1.69	-0.92	-0.41
CCl_4	-3.58 ± 1.5	-0.41	-4.0 ± 1.5	-3.28	-1.69	-0.51
	$E_{corr}{}^{c)}$	$E^{*}_{corr}{}^{d)}$	$E^{**}_{corr}{}^{e)}$	$E_{rel}{}^{f)}$	$E^{*}_{rel}{}^{d)}$	$E^{**}_{rel}{}^{e)}$
CS_2	-1.42	-1.28	-0.51	-2.12	-0.56	-0.03
CCl_4	-3.01	-2.78	-1.19	-5.51	-1.53	-0.08

a) Experimental values obtained by the integration of $\Delta\sigma(s)$
b) Calculated from the values of enthalpy of formation in Ref. 26.
c) Ref. 10.
d) The K-shell energy is excluded.
e) The K-shell energy for C and the K- and L-shell energy for S and Cl are excluded.
f) Ref. 10c, 15.

Further correction for the vibrational effect,[18] which is of the order of the zero-point energy (a few hundredth of an a.u.), was neglected in the present analysis.

Comparison of I_{exp} and I_{IAM} in the Large s-Region by Means of Photographic Data. Since the s-range covered by the present counting experiment is rather limited, it is often uncertain whether or not the normalization at s=6.5—8 might have introduced a systematic error, thus leading to an underestimation of the absolute value of ΔE. In order to be sure that there is no such systematic error, the scattering intensity of CS_2 was carefully examined in the larger s-region by the use of the best photographic plate which has so far been obtained by the diffraction unit for the precise determination of the molecular structure.[19]

The s^4I_{exp} values up to $s=12$ are compared with s^4I_{IAM} in Fig. 5, where the counting data are also shown. The agreement of the counting data with the photographic intensity in the overlapping region, especially in the $7<s<9$ region is satisfactory. The agreement of the photographic data with the IAM intensity in the larger s-region up to $s=19$ is almost perfect, although the data beyound $s=12$ are not shown in the figure. The slight discrepancy between the counting and photographic data in $4.5<s<7$ seems to show an experimental imperfection still existing in the photographic data, because the increase in the intensity in this region has been experienced to be most sensitive to a slight misalignment of the slit system and/or the nozzle assembly. The photographic data in the $s<5$ region are not reliable enough because of the uncertainty in the effective sector correction and possible extraneous scattering from the main-beam stopper.

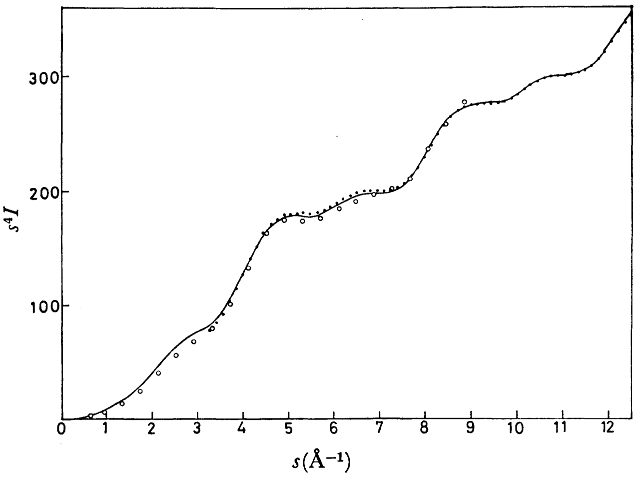

Fig. 5. Comparison of the photographic experimental, counting experimental and theoretical (IAM) s^4I intensities for CS_2. ——: Theoretical (IAM) curve calculated using partial wave amplitude.
● : The photographic experimental intensity.
○ : The counting experimental intensity.

The comparison leads to the conclusion that there can be no better alternative for the normalization of the counting data in the present study, unless the precision of the intensity measurement is greatly improved.

Effect of Multiple Scattering. It has been pointed by several recent studies[20–23] that the effect of intramolecular multiple scattering appears in two ways: the double scattering, which reduces the atomic background intensity in the small s-region, and the triple scattering, which leads to a correction term containing a geometric factor. The first effect may be important in the interpretation of the experimental scattering intensity in terms of the binding and correlation energies, as in the present paper. The second one is related to the structure determination and also to the oscillatory behavior of the $\Delta\sigma(s)$ curve, as will be discussed in the next section.

The double-scattering contribution was, therefore, calculated for CCl_4 by means of Eq. (11) of Ref. 22. Also, one of the present authors (S.K) calculated the multiple effect for CCl_4 by means of the formalism of the eikonal approximation.[24] Both of these results indicated that the amount of the multiple effect for s^4I_T is less than 2 in the scale of Fig. 4, which is well within the limits of experimental uncertainty. Furthermore, the multiple effect for the atomic back-

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[18] R. A. Bonham, *J. Phys. Chem.*, **71**, 856 (1967).

[19] M. Nagashima, H. Fujii, and M. Kimura, This Bulletin, to be published.

[20] A. C. Yates and A. Tenney, *Phys. Rev.*, **5**, A2474 (1972).

[21] L. S. Bartell and T. C. Wong, *J. Chem. Phys.*, **56**, 2364 (1972).

[22] R. A. Bonham and E. M. A. Peixoto, *ibid.*, **56**, 2377 (1972).

[23] A. C. Yates, *ibid.*, **57**, 1686 (1972).

[24] a) D. P. Duncan, F. H. Tuley, Jr. and D. A. Kohl, *ibid.*, **56**, 3766 (1972); b) F. H. Tuley, Jr., Doctral Dissertation, The University of Texas at Austin, (1972); c) S. Konaka, unpublished.

ground of $s^4 I_T$ is found to be a monotonously increasing function within the s-range of 0—9; therefore, if one is to normalize the experimental intensity at $s=6.5$—8 to the IAM intensity which is corrected for the multiple effect, the ΔE value becomes almost equivalent to that obtained without the multiple correction, the difference being less than 0.1 a.u. Thus, the effect of multiple scattering seems to be safely ignorable in the present scheme of analysis.

Oscillatory Behavior of $\Delta\sigma(s)$. As is shown in Fig. 4, the $\Delta\sigma(s)$ curve of CCl_4 shows oscillatory behavior which is very similar to the interference pattern of diffraction pictures. In fact, the difference in s-values for the first and second maxima corresponds to that of the interference pattern for the Cl···Cl atom-pair in the CCl_4 molecule. This result can be reasonably understood in the light of the theoretical study of molecular Hartree-Fock cross sections for diatomic molecules performed by Kohl and Bartell.[25)]

The oscillatory part of $\Delta\sigma(s)$ is primarily attributable to the interference of scattered electrons where the scatterers are a nucleus and the distorted part of the electron cloud around other nuclei produced by the chemical-bond formation, and it is denoted by $\Delta\sigma_{ne}$. Although the distortion of the charge density is generally not simple, it may be more or less described by an expansion around each nucleus in the Legendre polynomials, with radial function as coefficients. Then, the Fourier transform gives $\Delta\sigma_{ne}$, which consists of terms of the spherical Bessel functions, $j_n(sr_{AB})$, where r_{AB} is a nucleus-nucleus separation in the molecule. The $j_n(sr_{AB})$ can show up in a limited range of s as an oscillatory function with the characteristic distance of r_{AB}, irrespective of the order n. In general, $\Delta\sigma_{ne}$ is only a small portion of the total $\Delta\sigma$. However, the multiplicity of Cl···Cl separation due to the high symmetry of this molecule and the large scattering power of the Cl atom seem to have made the $\Delta\sigma_{ne}$ detectable, while the $\Delta\sigma_{ne}$ of CS_2 is perhaps of the order of the uncertainty of the total $\Delta\sigma$.

A similar oscillatory contribution can also be expected from the intramolecular multiple scattering. According to a preliminary calculation on the basis of the eikonal approximation,[24c)] the peak-to-peak difference in the oscillatory multiple effect for CCl_4 is 1.2 or less in the scale of Fig. 4, which is only a small fraction of the observed oscillatory part of the $\Delta\sigma(s)$ curve.

The $\Delta\sigma_{ne}$ forms a part of the elastically-scattered intensity and is a one-electron property. Thus, the molecular Hartree-Fock wave function can be a satisfactorily good description for the calculation of $\Delta\sigma_{ne}$, and, conversely, the oscillatory part of the observed $\Delta\sigma$ curve can be an observable for testing a computed charge distribution of molecules. The usefulness of Tavard's equation is limited to a great extent by the uncertainties in the intensity measurement, which are amplified by the multiplication of s^4 for large s-values. A comparison of I_{exp} itself with the theoretical descriptions over all the observed region seems to be more fruitful for the future program of the small-angle scattering study, as the computation of molecular cross-sections becomes more familiar to experimentalists as well as to theoreticians.

Added Discussion. Relativistic-Hartree-Fock (RHF) calculations of atoms have been performed by several authors. The most extensive ones were obtained by Coulthard[27)] and more recently by Malý and Hussonnois.[28)] The first Born scattering factors were calculated by Doyle and Turner[29)] on the basis of Coulthard's RHF atomic potentials; they are available for atoms from He through U. In these calculations, the Hamiltonian is expressed as:

$$\mathscr{H} = \mathscr{D} + \mathscr{B},$$

where $\mathscr{D}$ is the sum of the one-electron Dirac Hamiltonians for all the electrons plus the Coulomb interaction terms of the $1/r_{12}$ type and $\mathscr{B}$ is the sum of the relativistic two-electron terms, *viz.*, the Gaunt term and the retardation term. The wave function is made self-consistent with respect to $\mathscr{D}$, and the $\mathscr{B}$ term is neglected. The charge distribution used in the calculation of the scattering factors then corresponds to the $\mathscr{D}$ term.

By integrating $\Delta=(Z-f_X)^2_{RHF}-(Z-f_X)^2_{HF}$ for Ne up to $s=60$ Å^{-1}, where the integrand almost coverges to zero, it was found that the integrated value was nearly 15% larger than E_D-E_{HF}, where E_D means the eigen value of the $\mathscr{D}$ term, in absolute value. The difference, Δ, for Cl extends to more than $s=60$ Å^{-1}, with a small but appreciable magnitude. However, if $(Z-f_X)^2_{RHF}$ is normalized to $(Z-f_X)^2_{HF}$ at $s=8$ Å^{-1}, as in the present scheme of analysis, the energy obtained by integrating the differences in the $s<8$ Å^{-1} range amounts to -0.026 a.u., that is, -0.10 a.u. for four Cl atoms.

Theoretical uncertainty still remains concerning the effect of the $\mathscr{B}$ term on the charge distribution. Since the energy correction due to the $\mathscr{B}$ term is only 10% of E_D-E_{HF} for atoms heavier than Ne,[30)] the uncertainty, $\pm E_{rel}$, mentioned in the text might be too pessimistic. Another uncertainty arises from the neglect of the inelastic scattering intensity in the discussion mentioned above. The inelastic part is probably important in the small-angle region investigated in the present study. The calculation of the inelastic scattering factors on the RHF basis is very much awaited.

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25) a) D. A. Kohl and L. S. Bartell, *J. Chem. Phys.*, **51**, 2891 (1969); b) *idem, ibid.*, **51**, 2896 (1969).

26) The Chemical Society of Japan, "Kagaku-Binran," Maruzen Co., Ltd., Tokyo (1966), p. 819.

27) a) M. A. Coulthard, *Proc. Phys. Soc.*, **91**, 44 (1967); b) M. A. Coulthard, unpublished, cited in Ref. 29.

28) J. Malý and M. Hussonnois, *Theoret. Chim. Acta*, **28**, 363 (1973).

29) P. A. Doyle and P. S. Turner, *Acta Crystallogr*, **A24**, 390 (1968).

30) J. B. Mann and W. R. Johnson, *Phys. Rev.*, **4**, A41 (1971).