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A Reinvestigation of Small-angle Electron Scattering by CS_2 and CCl_4 Molecules[†]

Makoto Nagashima,[††] Shigehiro Konaka, and Masao Kimura*
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

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A small-angle electron-diffraction unit (*Jpn. J. Appl. Phys.*, **11**, 1199 (1972)) has been improved by enlarging the scattering chamber and installing a new nozzle system and a better counting unit. The intensities of 50 keV electrons scattered by CS_2 and CCl_4 molecules have been measured with a $\approx 1\%$ precision in the s-range from 1 to 11.5 $Å^{-1}$. Theoretical intensities have been calculated for the independent-atom model by taking into account the intramolecular double-scattering effect, and those intensities have been compared with the experimental intensities. The oscillatory feature appearing in the difference function, $\Delta\sigma(s) = s^4(I_{\text{exptl}} - I_{\text{IAM}})$, of CCl_4 has been ascribed mainly to the deformation of the one-electron density in chlorine atoms by chemical binding.

A small-angle electron-diffraction unit equipped with a scintillation counting device was used by the present authors and their collaborators to measure the total (elastic plus inelastic) intensities of electrons scattered by gas molecules.[1–3] An observed decrease in the total scattered intensity from the theoretical value for the independent-atom model (IAM) was interpreted as the effect of chemical-bond formation. However, the qualities of the above data were limited mainly by the counting loss due to the poor resolving time of the counting system and by the uncertainties associated with the correction for the delocalization of the sample gas. The purpose of the present study is to offer refined data on the total scattered intensities for CS_2 and CCl_4 by improving these weaknesses.

Intramolecular multiple scattering is known to decrease the small-angle intensities and to produce a characteristic oscillation depending on the molecular geometry.[4–9] In the previous studies of CS_2 and CCl_4,[2] the effect of the intramolecular multiple scattering was concluded to be negligible by calculating the two-atom double-scattering cross-section for CCl_4 using the formula proposed by Bonham and Peixoto[4] and by comparing it with the single-scattering cross-section. Since then, the theory of multiple scattering has further advanced.[6,8,9] At the present stage, therefore, it seems necessary to reexamine the validity of the conclusion that multiple scattering was negligible by utilizing recent theories. In the present study, the multiple-scattering cross-sections have been calculated for CS_2 and CCl_4 and incuded in the IAM intensities, which were then used for extracting the net chemical-binding effect from the experimental data.

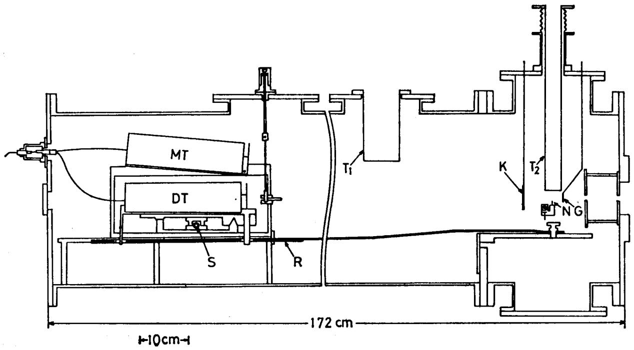

Fig. 1. Cross-sectional view of the scattering chamber. The sample chamber on the right-hand side was remodelled in this work. N, nozzle; T_1, T_2, cold traps; K, phosphorescent screen; G, gold-foil for adjusting the nozzle position; DT, detector; MT, monitor; R, arm; S, screw. Ref. 1 should be referred for the other details.

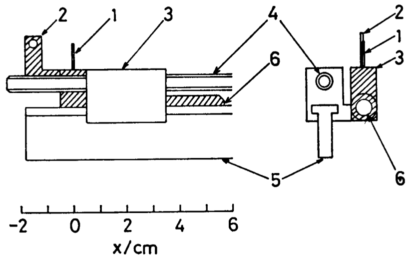

Fig. 2. Front and side view of the nozzle system. 1, Nozzle; 2, gold-foil holder; 3, nozzle-base; 4, screw; 5, a base for sliding the nozzle-base; 6, inlet of the sample gas.

Improvements of the Apparatus

The main improvements are as follows: (1) the enlargement of the scattering chamber for rarefying delocalized sample gas near the scattering center, (2) the employment of a new nozzle system, and (3) the introduction of a counting system with a shorter resolving time.

Figure 1 shows a cross-sectional view of the sample chamber. The inner diameter of the chamber, 347 mm, is about five times as large as that of the old one. The two camera lengths, 1168 and 815 mm, cover a wider range of scattering angles. A cylindrical mu-metal case placed close to the inside wall of the whole chamber shields the inside from the terrestrial magnetism. The residual magnetic field inside the case is less than 10 mG.

The construction of the nozzle system is shown in Fig. 2. The nozzle is made of non-magnetic stainless steel (SUS304). The inner and outer diameters are 0.2 and 0.6 mm respectively, and the length is 10 mm. The nozzle can be shifted in a plane perpen-

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[†] Throughout this paper 1 Å$=10^{-10}$ m and 1 Torr$\approx$ 133.322 Pa are used.

[††] Present address: Japan IBM Co., Ltd., Kusatsu 525.

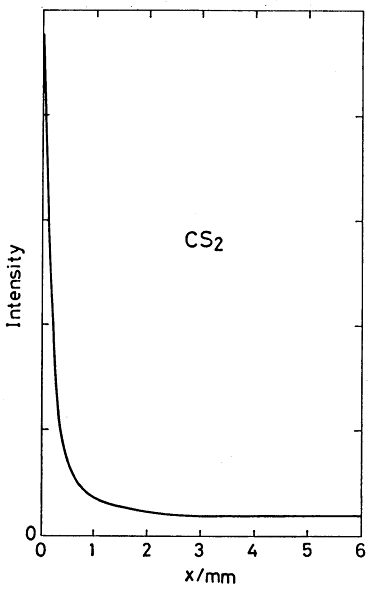

Fig. 3. Plot of the intensity of electrons scattered by carbon disulfide *versus* the nozzle position, x. The nozzle was moved along the x-direction shown in Fig. 2. The ordinate scale is arbitrary.

dicular to the incident electron beam. The interval between the nozzle tip and the incident electron beam was chosen to be about 0.5 mm. When the nozzle tip approaches the beam, the ratio of the background scattering to the main one decreases, but the reflection of scattered electrons by the nozzle increases.

Figure 3 shows the change in the intensity of electrons scattered by the sample gas when the nozzle is shifted on a horizontal plane in the direction perpendicular to the incident electron beam. Scarcely any change was found when the nozzle was placed more than 3 mm from the incident electron beam. In order to exclude a contribution corresponding to the tail of this curve, the background scattering was measured by shifting the nozzle by 5 mm and was subtracted from the scattering measured with the nozzle placed at its original position. The proportion of the background scattering to the total one varied with the molecular species as well as with the sample pressure. In the present measurement for CCl_4, the ratio was about 5% at s-values greater than 5 Å^{-1}, but it increased gradually with a decrease in the s-values, rising to 14—18% at $s=1\ \text{Å}^{-1}$.

Previously, an extra nozzle for the background measurement was placed between the nozzle and the detector, about 30 cm from the nozzle and close to the wall of the diffraction chamber. With this arrangement, however, the distribution of gas injected from the extra nozzle will not reproduce successfully that of gas in the sample measurement, particularly in the neighborhood of the nozzle. In fact, systematic discrepancies of about 3% or more had previously been observed between the scattered intensities measured on both sides of the primary electron beam.[2] In the refined data, such discrepancies were reduced to about 1% or less and had no systematic feature. This refinement was achieved by enlarging the scattering chamber and by using the new nozzle system. Thus, the background correction could be made more accurately than in the previous study, and consequently, more reliable data were obtained.

The old counting system used for the detector was replaced by a new one composed of a preamplifier (ORTEC 9301), a pulse-height analyzer (9302), and a counter (770). This replacement improved the resolving time of the counting system from 3.6 μs to about 10 ns and made the statistical error in the present study one order of magnitude lower than in the previous study. After all, the limits of error for the final data could be reduced to about one-third of the estimated errors in the previous study.**

Measurement of Scattered Intensities

The ultimate vacuum pressure was about 3×10^{-6} Torr, while the pressure during the measurement on the sample gas was 1×10^{-5} Torr. By using gold foil, the product of the camera length and the electron wavelength*** and the central position of the electron beam were determined with precisions of 0.05% and 0.02 mm respectively. No change in the position or wavelength of the electron beam was detected during a continuous measurement for four hours. The beam current was about 0.05 μA, and it changed monotonously by 13% during four hours. The accelerating voltage was about 50 kV. The camera length was 815 mm, and the range of s covered by the present measurement was from 1 to 11.5 Å^{-1}. The room temperature was about 20 °C. Spectroscopic-grade reagents of the Merck Co., with the minimum assays of 99.9 and 99.7% for CS_2 and CCl_4 respectively, were used without further purification.

The counting rate in the present measurement was about 50 times that in the previous measurement. The counting-loss correction was made by using the following equation:

$$n = n'(1+n'\tau),$$

where n' is the apparent counting rate and τ is the resolving time.

The scannings were performed first for the sample gas. After the last data on the sample gas, $I_G^M(s_0)$, had been taken at the turning point s_0, the nozzle was shifted quickly by 5 mm to observe $I_B^M(s_0)$, and then the background measurement was performed. The scattered intensities were calculated as follows:

$$I_{\text{exptl}}(s) = C\left\{\frac{I_G^D(s)}{I_G^M(s)}I_G^M(s_0)-\frac{I_B^D(s)}{I_B^M(s)}I_B^M(s_0)\right\}, \tag{1}$$

where the superscripts D and M denote the intensities measured by the detector and the monitor respectively, and where the first and second terms in the brackets are the intensities observed on the sample and the background respectively. The normalization constant, C, was determined by comparison with the theoretical intensities to be described in the next section.

** The errors listed in Table 1 of Ref. 2 were the standard errors, not the limits of error.

*** The lattice constant of 4.078 Å was used.

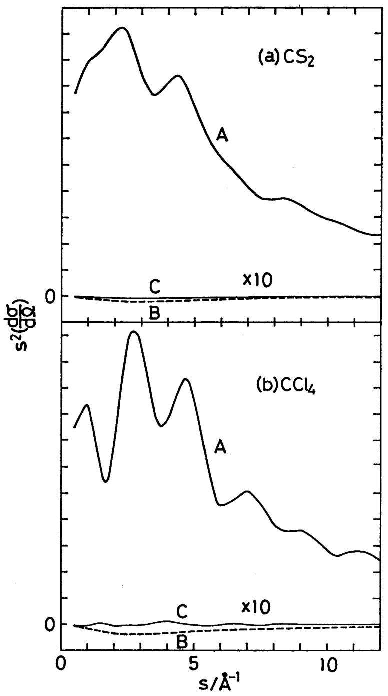

Fig. 4. Comparison of single and double scattering terms. Curves A, B, and C show $s^2\left(\frac{d\sigma}{d\Omega}\right)_{MB}$, $s^2\left(\frac{d\sigma}{d\Omega}\right)_{12}$, and $s^2\left(\frac{d\sigma}{d\Omega}\right)_{123}$, respectively. The ordinate scale is arbitrary.

Calculation of the IAM Intensities

According to the Glauber approximation,[5,6] the first-order multiple-scattering correction of the elastically scattered intensity is given by the sum of $\left(\frac{d\sigma}{d\Omega}\right)_{12}$ and $\left(\frac{d\sigma}{d\Omega}\right)_{123}$, which are two-atom and three-atom double-scattering terms respectively.

The three-atom double-scattering term was calculated by the use of the analytical expression given by Bartell.[6] It has been comfirmed by Kohl and Arvedson[8,9] that Bartell's expression reproduces very well the result of an exact numerical calculation for $s < \approx 20$ Å^{-1}. The two-atom double-scattering term was calculated according to the following formula:[10]

$$\left(\frac{d\sigma}{d\Omega}\right)_{12} = -\mathrm{Im}\sum_{i\neq j}\sum \frac{1}{ka_{ij}^2}[|f_i(s)|^2 f_j(0) + |f_j(s)|^2 f_i(0)] + \mathrm{Im}\sum_{i\neq j}\sum \frac{1}{ka_{ij}^4}[\alpha_{ij}(s) + \alpha_{ji}(s)], \qquad (2)$$

where a_{ij} is the distance between i and j atoms; k, the propagation number $(2\pi/\lambda)$ of the incident electrons; $f_i(s)$, the complex scattering factor, and

$$\alpha_{ij}(s) = f_i^*(s)\left[f_j(0)\left(f_i'(s)\frac{\cos\theta}{s} + f_i''(s)\frac{\cos^2(\theta/2)}{s}\right) + 2f_i(s)\lim_{s\to 0}\frac{f_j'(s)}{2s}\right]. \qquad (3)$$

The two terms in the first brackets on the right-hand side of Eq. 2 are the formulas given by Yates[5] and by Bonham and Peixoto[4] on the basis of the Glauber and second Born approximations respectively, while the terms in the second brackets are corrections derived on the basis of the second Born approximation.[10] The contribution of these correction terms to $(d\sigma/d\Omega)_{12}$ was less than 5% for CS_2 and CCl_4. The numerical values were obtained by using the scattering factors[11] based on the RHFS wave functions, the structural parameters[12,13] and the parallel and perpendicular mean amplitudes[12,14] taken from the literature. Figure 4 compares the results multiplied by s^2 with $s^2\left(\frac{d\sigma}{d\Omega}\right)_{MB}$, which is the total intensity given by the modified first Born approximation. The $\left(\frac{d\sigma}{d\Omega}\right)_{MB}$ is written as:

$$\left(\frac{d\sigma}{d\Omega}\right)_{MB} = \sum_i [|f_i(s)|^2 + (2/as^2)^2 S_i] + 2\mathrm{Re}\sum_{i<j}\sum f_i^*(s) f_j(s)\frac{\sin(sa_{ij})}{sa_{ij}}\exp\left(-\frac{1}{2}s^2 l_{ij}^2\right), \qquad (4)$$

where a is the relativistic Bohr radius, and l_{ij}, the mean amplitude. The inelastic scattering factors, S_i, were taken from the literature.[11] The anharmonicity correction was omitted because it was negligible in

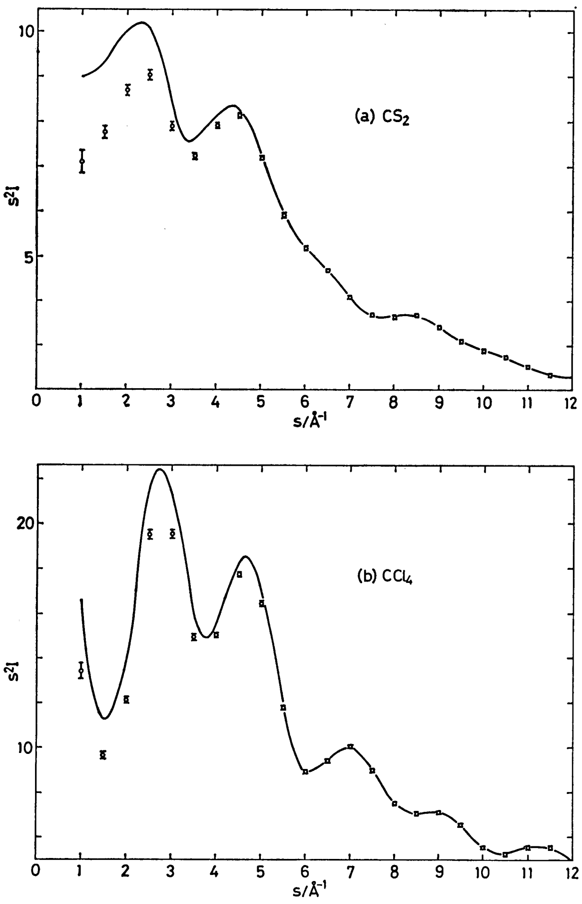

Fig. 5. Comparison between the experimental and theoretical (IAM) s^2I intensities, (a) CS_2, (b) CCl_4. —: Theoretical intensity, ○: experimental intensity, the vertical bar of experimental intensity shows the limit of experimental error.

TABLE 1. EXPERIMENTAL AND THEORETICAL (IAM) SCATTERED INTENSITIES FOR CS_2 AND CCl_4 AT 50 kV

$s/\text{Å}^{-1}$	CS_2			CCl_4		
	I_{exptl}[a)]	$\varepsilon/I_{\text{exptl}}$[b)]	I_{IAM}	I_{exptl}[a)]	$\varepsilon/I_{\text{exptl}}$[b)]	I_{IAM}
1.0	7.113×10^{0}	3.5%	8.981×10^{0}	1.344×10^{1}	2.5%	1.659×10^{1}
1.5	3.453	1.5	4.143	4.293×10^{0}	1.5	5.008×10^{0}
2.0	2.174	1.0	2.510	3.037	1.0	3.448
2.5	1.445	1.0	1.606	3.126	1.1	3.472
3.0	8.783×10^{-1}	1.1	9.387×10^{-1}	2.176	0.8	2.349
3.5	5.921	0.6	6.219	1.220	1.0	1.291
4.0	4.955	0.6	5.082	9.409×10^{-1}	0.4	9.693×10^{-1}
4.5	4.032	0.6	4.089	8.781	0.5	9.015
5.0	2.878	0.9	2.894	6.594	0.7	6.750
5.5	1.958	0.7	1.974	3.897	0.9	3.948
6.0	1.446	0.7	1.458	2.486	0.5	2.497
6.5	1.108	0.7	1.116	2.221	0.7	2.238
7.0	8.337×10^{-2}	0.7	8.382×10^{-2}	2.052	0.4	2.074
7.5	6.567	0.7	6.572	1.600	0.5	1.608
8.0	5.698	0.7	5.741	1.173	0.5	1.172
8.5	5.099	0.8	5.098	9.768×10^{-2}	0.5	9.784×10^{-2}
9.0	4.231	1.2	4.249	8.810	0.5	8.825
9.5	3.437	0.8	3.436	7.276	0.5	7.250
10.0	2.886	0.9	2.894	5.591	0.5	5.575
10.5	2.501	0.9	2.488	4.769	0.6	4.769
11.0	2.094	1.0	2.094	4.580	0.6	4.589
11.5	1.786×10^{-2}	1.0	1.783×10^{-2}	4.186×10^{-2}	0.6	4.182×10^{-2}

a) Normalized to I_{IAM} at $s=9$—11.5. b) The symbol ε denotes the estimated limits of error of I_{exptl}. The relative errors, $\varepsilon/I_{\text{exptl}}$, are shown in percentage units.

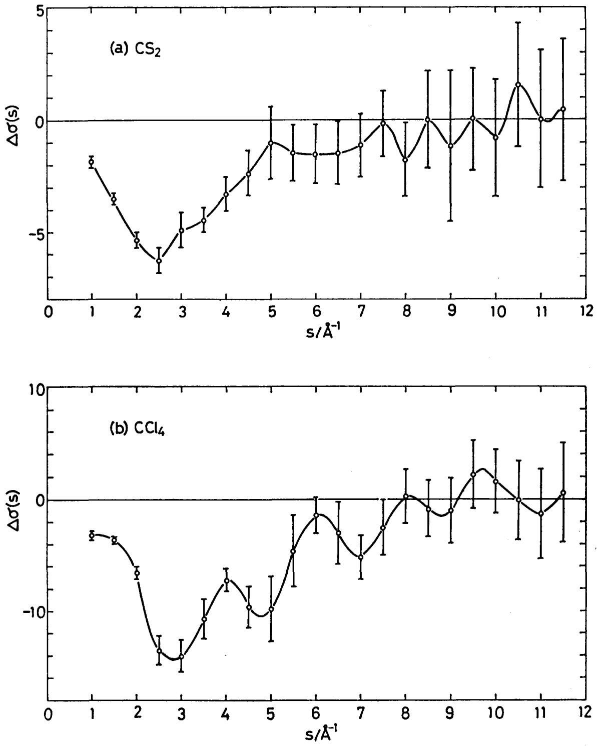

Fig. 6. Plots of $\Delta\sigma(s)$ for CS_2 (a) and CCl_4 (b). The vertical bar shows the limit of experimental error.

the s-range covered by the present work. As may be seen in Fig. 4, the double-scattering terms are insignificant for CS_2 and CCl_4, although such terms cannot be ignored for every molecule. In the present study, the I_{IAM} values defined by $(a/2)^2[(d\sigma/d\Omega)_{\text{MB}}+(d\sigma/d\Omega)_{12}+(d\sigma/d\Omega)_{123}]$ were employed; they are listed in Table 1.

Results and Discussion

The experimental intensites were normalized to I_{IAM} at s-values from 9 to 12 Å^{-1}. Four runs of measurements were performed for each sample. The experimental errors were estimated from the reproducibility of the data and the uncertainties in the s-values. Table 1 lists the experimental intensities, I_{exptl}, and the estimated limits of error. The values of s^2I_{exptl} are compared with those of s^2I_{IAM} in Fig. 5.

Figure 6 shows the $\Delta\sigma(s)$ defined by $s^4(I_{\text{exptl}}-I_{\text{IAM}})$. As in the previous work,[2)] a significant oscillation is found in the $\Delta\sigma$ of CCl_4, while the oscillation in that of CS_2 is within the range of experimental error. As has been shown elsewhere,[15)] the following integral relationship holds between the $\Delta\sigma$ and one-electron and two-electron deformation densities, $\Delta\rho$ and $\Delta\rho_c$.

$$\begin{aligned}\Delta j(r') &= \frac{2}{\pi}\int_0^{\infty} ds\Delta\sigma(s)sr'\sin(sr') \\ &= -2\sum_{i}(r')^2Z_i\langle\int d\Omega_{r'}\Delta\rho(\boldsymbol{r}'+\boldsymbol{r}_i)\rangle_{\text{vib}} \\ &\quad+(r')^2\langle\int d\Omega_{r'}\Delta\rho_c(\boldsymbol{r}')\rangle_{\text{vib}}.\end{aligned} \tag{5}$$

Here, the notations follow those given in Ref. 15. Errors in $\Delta j(r')$ were also calculated from the ex-

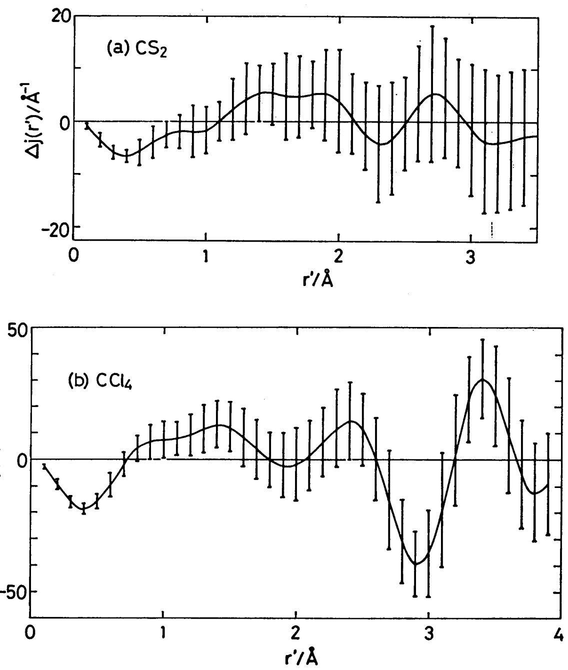

Fig. 7. Plot of $\Delta j(r')$ for CS_2 (a) and CCl_4 (b). The vertical bar corresponds to the limit of experimental error of $\Delta\sigma(s)$.

perimental errors by assuming the propagation-law of error,**** The contribution to the integral from the s-region beyond 9 $Å^{-1}$ was neglected. The results are shown in Fig. 7. The second term of Eq. 5 can be expected to be smaller than the first one.[16,17] The significant negative portion in the $\Delta j(r')$ of CS_2 at r' values of less than 1 Å corresponds to an increase in the one-electron density in the bonding region. No other conclusion can be drawn for CS_2 because of the large experimental errors. The $\Delta j(r')$ of CCl_4 has a significant valley at ≈2.9 Å. The position of the minimum is consistent with the Cl–Cl distance, 2.885 Å, within the range of experimental error. This valley can be ascribed to an increase in the one-electron density around chlorine atoms. This is consistent with the large electronegativity of chlorine. The other significant valley found in the small r'-region is due to an increase in the one-electron density in the C–Cl bonds. The significant positive portion at ≈3.4 Å can be related to the change in the distribution of the lone-pair electrons of chlorine.

In a previous paper,[2] we analysed the experimental results by the use of Tavard's energy relation. Since the relativistic atomic wave functions are used in the present study, Tavard's relation can be written as:

$$\Delta E + E_1 = E_b + E^*_{\text{corr}}, \tag{6}$$

where

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

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} denotes the sum of the correlation energies for all the atoms without the contribution from the K-shell. The exclusion of the K-shell contribution is necessary because of the normalization at comparatively small s-values.[2] The contribution to the integral from the s-region beyond 9 $Å^{-1}$ was assumed to be zero. The values of $\Delta E + E_1$ are -2.0 ± 0.6 and -4.5 ± 1.4 au for CS_2 and CCl_4 respectively. These values are in good agreement with the previously reported values, -2.0 ± 0.6 and -4.1 ± 1.5 au.[2] It should be noted that the uncertainties, ε, in the present results denote the limits of error, while those quoted in the previous paper were the estimated standard errors. The present $\Delta E + E_1$ values are consistent with the calculated values of $E_b + E^*_{\text{corr}}$, -1.69 and -3.28 au for CS_2 and CCl_4 respectively.[2]

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