Electron scattering from CF_4 and CCl_4. Total cross section measurements

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Absolute total cross sections for e^-–CF_4 and e^-–CCl_4 scattering were measured using the linear transmission technique with energy ranging from 0.5 to 200 eV. A comparison is made with other measurements and calculations.

1. Introduction

An important motivation for the measurements of total electron scattering cross sections for different targets stems from the ever-increasing need for reliable cross-section data in such diverse fields as plasma physics, chemistry and physics of the atmosphere, gaseous electronics, radiation physics and space sciences. Accurate electron-scattering data are also of great importance for testing current theoretical models. It should be emphasized that most of the applications primarily require absolute cross sections over a wide energy range.

Increasing interest in the electron-impact phenomena on CF_4 molecules, mainly related to technological applications of this compound as an etching agent [1–3], began in the mid seventies. Since that time a great deal of experimental effort has been devoted to the study of e^-–CF_4 scattering processes [4–37].

The total cross section for e^-–CF_4 scattering was first determined by Tice and Kivelson [28] at thermal energies with the use of the cyclotron resonance technique. The variation of the total cross section below 0.5 eV was studied by Field et al. [29], but their results were not on an absolute scale. Mori et al. [30] and Sueoka [31] [#1] presented normalized data for energies ranging from 1 to 400 eV. Absolute total cross sections have been measured by Jones (1–50 eV) [32] and recently by Zecca et al. [33] at intermediate and high energies, and by Nishimura [#2].

The only total e^-–CF_4 cross-section calculations available in the literature were performed by Baluja et al. [37] over a very wide energy range from 10 to 5000 eV.

Although the first experiments on electron scattering from the CCl_4 molecule date from the early 1930s [38], this compound has only received a moderate amount of interest [4,6,24,31–34,38–48] and most work was concerned with low energies.

The absolute e^-–CCl_4 total cross section has been measured by Holst and Holtsmark (0.25–25 eV) [38], Jones (1–50 eV) [32] and Zecca et al. [33] (75–4000 eV). Normalized data for energies that range from 1 to 400 eV were derived by Sueoka [31].

Most of the afore-cited total cross-section experiments employed a magnetic field.

Both CF_4 and CCl_4 low-energy results reveal big disagreements in the magnitude of the measured cross sections. Part of our motivation for the present work is to resolve the discrepancies between data taken in different laboratories. This work is one in a series from this laboratory which deals with the upgrading of quantitative knowledge of electron impact data. Current measurements are devoted to five-atom molecules.

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[#1] See also fig. 17 in ref. [6].

[#2] See fig. 3 in ref. [26].

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2. Experimental

The present total cross-section measurements were made using a transmission method [49] in linear configuration. In this technique, energy-selected electrons enter the field-free collision chamber filled with a target under study. The measured attenuation of the electron beam of given energy E, due to the presence of the target can be, to the first approximation, related to the total cross section $\sigma(E)$ by the formula

$$\sigma(E)=\frac{k(T_t T_m)^{0.5}}{pL}\ln[I_0(E)/I_p(E)]\,,$$

where I_p and I_0 are intensities of the electron beam transmitted through the scattering volume of length L in the presence of the target of pressure p or in its absence, respectively. T_t is the temperature of the target (scattering cell), T_m is the temperature of the manometer head and k is the Boltzmann constant.

The experimental apparatus and procedure are basically the same as those used in our recent experiments [50,51]. A beam of quasimonoenergetic electrons ($\Delta E \leqslant 70$ meV, fwhm) was produced by an electrostatic cylindrical dispersing element and a system of electron lenses. Electrons of the desired energy were projected into a scattering chamber of 30.5 mm in length. Electrons leaving the scattering volume through the exit orifice were selected with a retarding field analyzer while on their way to the Faraday cup collector.

The energy calibration of our data was carried out by reference to the oscillatory resonance structure visible in the transmission current when, together with the investigated compound, some amount of N_2 was admitted to the collision cell. This procedure gives us the ability to determine the impact energy with an accuracy that could be up to about 50 meV. Repetitive energy scaling revealed, however, that the once fixed energy scale may shift in the course of the experiment, most probably due to the influence of the target on electron optics. As a result, the uncertainty of the impact energy can be as high as 80 meV.

The target absolute pressure in the collision chamber was measured with the baratron. Since the temperature of the manometer head ($T_m=322$ K) was usually higher (by up to 12 K) than that of the scattering cell, a correction of the pressure readings due to the thermal transpiration effect [52] was necessary.

One of the serious experimental problems encountered in transmission measurements arises from the inability to discriminate against electrons which are scattered elastically through small angles in the forward direction. Basing ourselves on available angular distributions of scattered electrons that are of interest to this experiment [20,26,27,36,47], we estimated that the lack of the mentioned discrimination tends to lower our measured cross sections by less than 1% for all applied energies in CF_4 and not more than 2% at 75 and 200 eV in CCl_4. The data are, however, not corrected for this effect.

Statistical uncertainties (one standard deviation of the weighted mean values) are usually below 1.5% over almost the entire impact energy range studied, excluding the lowest and the highest applied energies, where they reach 2%. The direct sum of all potential individual systematic uncertainties in the CF_4 experiment is estimated to be 4% below 1 eV, gradually decreasing to 3% near 20 eV and increasing again to 4% at higher energies. For CCl_4 it is as high as 8% below 2 eV, about 5.5% in the range 2–10 eV, decreasing to 4.5% at the highest applied energies. Relatively high errors in CCl_4 at low energies are mainly related to the shape of the total cross-section function.

We have checked that in the limits of statistical uncertainties our results were independent of the target pressure applied in the scattering cell (90–300 mPa for CF_4 and 40–160 mPa for CCl_4), the background pressure in the electron optics region (100–200 μPa), electron beam intensity (0.1–100 pA) and voltage settings on electron optics.

The final total cross sections at particular energies are the weighted means of the average from different measurement series.

The tetrafluoromethane was 99.95% pure. This compound has been used without further purification. Vapour of tetrachloromethane was obtained from the 99.6% pure liquid. Several freeze–pump–thaw cycles were used to remove gases dissolved in CCl_4.

3. Results

Absolute total cross sections for electrons of energy ranging from 0.5 to 200 eV colliding with tetrafluoromethane and tetrachloromethane molecules have been measured.

3.1. CF_4

The present e^-–CF_4 absolute total cross section is plotted in fig. 1 in comparison with the values available in literature: the absolute experimental data of Jones [32] and the normalized results of Sueoka [30,31]. For comparison at the highest-used energies we included the very recent, lowest-energy absolute data of Zecca et al. [33].

According to the observed features in the measured total cross-section function, the whole of the investigated energy range can be divided into three regions.

In the first, ranging from 0.45 to about 6 eV, the total cross section smoothly increases with impact energy. The analysis of swarm [6–10] and electron beam experiments [11,25–27] points out that in the lower part of this energy range a vibrational excitation of the CF_4 molecule (mainly ν_3 asymmetric stretch mode) makes an appreciable contribution to the scattering. The explicitly direct character of this excitation is related to optically allowed transitions. The resonant effects predicted in calculations near 3 eV [34] were not observed in those experiments.

To complement the present data, it is worth noting that at energies lower than the range of this experiment, the total cross section continuously decreases to about 0.2 eV [10,11,26] where a deep Ramsauer–Townsend minimum [6–10,26] appears. The total cross section increases again towards much lower energies [26,28].

The second energy region, spanned between 6 and 50 eV, is characterized by the broad structureless enhancements of the cross section. The distinct peak centered around 9 eV with a maximum value of 22×10^{-20} m^2 is related to resonant scattering phenomena which involve the formation of short-lived negative-ion states. The first evidence for the existence of the resonances in the vicinity of 7 eV was found in experiments on the dissociative electron at-

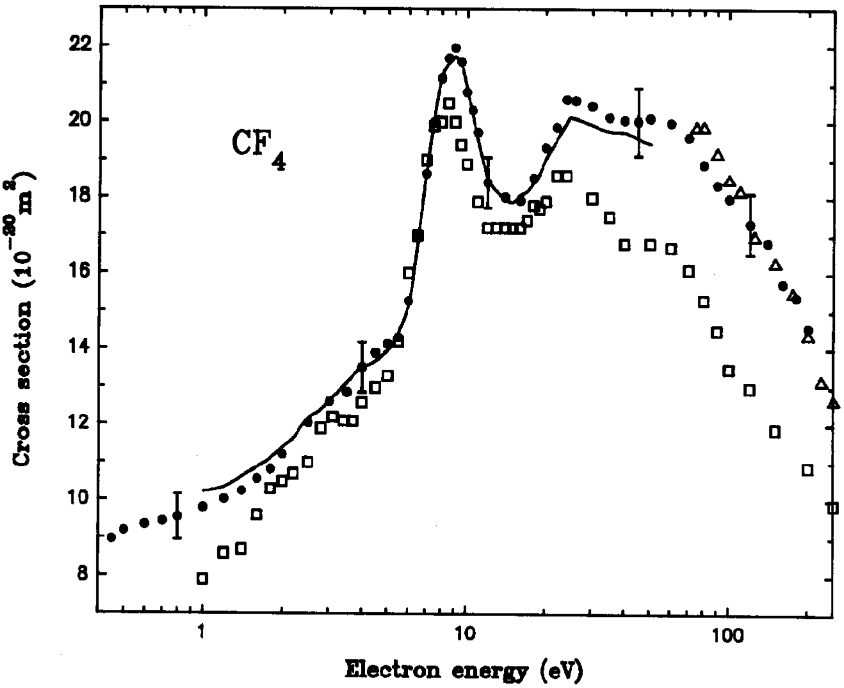

Fig. 1. Absolute e^-–CF_4 scattering total cross sections. The error bars correspond to the overall experimental uncertainties estimated at some selected points. (●) Present, absolute; (□) refs. [30,31], normalized; (—) ref. [32], absolute; (△) ref. [33], absolute.

tachment to the CF_4 molecule [4,11,22,24,25]. The cross sections for negative ion formation have broad maxima near 6.8 and 7.7 eV [4,11,22,24]. Recently, Mann and Linder [26] and Boesten et al. [27] observed a strong enhancement of the electron-impact-induced vibrational excitation of the CF_4 molecule between 6 and 11 eV. An analysis of angular distributions of scattered electrons led in both cases to the conclusion that this feature is mainly connected to a shape resonance, of T_2 symmetry, localized at around 8 eV. Mann and Linder, however, suggested the presence of a second compound state (A_1) close to 9 eV. Feshbach resonances near 11 eV were deduced from experiments of Verhaart et al. [25] and Curtis and Walker [11].

The MS-Xα calculations of Tossell and Davenport [34] predicted two maxima in the low-energy electron elastic scattering cross section. These maxima, in the t_2 channel at 3.2 eV and in a_1 near 5.2 eV, were localized, however, at markedly lower energies than observed experimentally. At the same time, the energy position of the T_2 resonance appeared to be very sensitive to the C–F distance. Two low-energy resonances, T_2 and A_1, were also found in the variational calculations of Huo [35]. Their estimated energy positions in elastic scattering are 6.6 and 11.7 eV, respectively, and are consistent with experiment.

A second, broad hump in the experimental total cross section is centered near 24 eV. This structure seems to be the product of weak resonant phenomena and of a number of direct processes allowed at these energies. Boesten et al. [27] reported only the presence of a very broad resonance of T_2 symmetry around 21 eV, while theoretical studies of Huo [35] indicate another resonant state, E, centered near 28 eV.

One of the features which distinguish CF_4 from other investigated compounds, except SF_6, is that the systematic fall of the total cross section does not start before 50 eV.

Experiments on the electron-induced fragmentation of the CF_4 molecule gave values of cross sections for ionization [14–16] and dissociation [13] which, at around their maxima near 100 eV, constitute almost 30% of the gross total cross section.

In regard to the general shapes, the experimental e^-–CF_4 total cross sections obtained in different laboratories are quite similar. Our results are also in excellent quantitative agreement with those of Jones [32]. Only for energies below 1.5 eV and above 30 eV do the present data differ from the results of Jones by slightly more than 3%. Instead, substantial quantitative discrepancies are visible between the present results and the indirect cross sections of Mori et al. [30] and Sueoka [31]. Below 1.5 eV, and particularly above 20 eV, discrepancies reach about 25% and are outside the combined claimed uncertainties of both experiments. Recent experiments, e.g. refs. [53–56], indicate that the lowering of Sueoka's results (at intermediate energies on average by a factor 0.85)

Table 1
Measured absolute total cross sections (TCS) for electron impact of CF_4 and CCl_4 in units of 10^{-20} m^2

Energy (eV)	TCS		Energy (eV)	TCS	
	CF_4	CCl_4		CF_4	CCl_4
0.45	8.96		8.0	21.2	70.2
0.50	9.19	36.1	8.5	21.7	66.2
0.60	9.35	39.9	9.0	22.0	64.9
0.70	9.44	44.0	9.5	21.6	64.4
0.80	9.55	50.0	10.0	20.8	64.2
0.90		59.0	10.5	20.3	64.5
1.0	9.80	65.2	11.0	19.7	64.1
1.1		69.0	12.0	18.4	63.5
1.2	10.0	72.0	14.0	18.0	61.0
1.3		72.1	16.0	17.9	57.8
1.4	10.2	68.1	18.0	18.5	54.8
1.5		65.5	20.0	19.3	52.9
1.6	10.6	64.2	22	19.9	50.6
1.8	10.8	58.7	24	20.6	
2.0	11.2	53.0	25		48.1
2.2		47.6	26	20.6	
2.4		45.4	27		47.4
2.5	12.0		30	20.4	46.0
2.6		42.4	35	20.1	43.9
2.8		40.9	40	20.1	42.6
3.0	12.6	39.7	45	20.0	41.9
3.2		39.9	50	20.1	41.3
3.5	12.9	40.8	60	20.0	41.0
4.0	13.5	44.3	70	19.6	39.3
4.5	13.9	47.1	80	18.9	37.5
5.0	14.1	51.6	90	18.3	36.2
5.5	14.3	55.6	100	18.0	35.2
6.0	15.3	60.2	110		33.7
6.5	17.0	66.1	120	17.3	32.4
7.0	18.6	70.1	140	16.8	30.0
7.3		71.3	160	15.7	28.2
7.5	20.0	72.4	180	15.4	26.7
7.7		71.6	200	14.6	25.7

is also needed for other molecules and might be partially related to the normalization procedure applied in Sueoka's experiments. Above 100 eV, the present measurements are in good agreement with results of Zecca et al. [33], while below 100 eV their points are higher by about 4%.

The theoretical total (elastic plus inelastic) cross sections of Baluja et al. [37] are noticeably larger than ours in the whole overlapping energy range. A particularly serious difference, in average above 60%, is visible below 100 eV. It should be noted, however, that above 200 eV agreement of the theory with experiment is good [33,37]. It is the common feature of elastic [34–36] as well as total [37] CF_4 cross-section calculations that at the lower-energy limit they tend to be higher than the measured total cross section.

In table 1 our e^-–CF_4 absolute total cross sections are provided in numerical form.

3.2. CCl_4

Fig. 2 compares the present absolute electron scattering cross section for CCl_4 with old absolute data of Holst and Holtsmark [38], recent results of Jones [32] and Zecca et al. [33] and with normalized results of Sueoka [31]. Our numerical data are listed in table 1.

The general energetic dependence of all cross sections displayed in fig. 2 is similar, but striking discrepancies in absolute values of the results obtained in some laboratories are visible. Our results agree fairly well (generally within 5%) with the measurements of Jones [32]. Meanwhile, disaccord with the results of Zecca et al. [33] increases with energy, and at 200 eV equals 8%. As in CF_4, there is a large disagreement with the normalized data of Sueoka [31]. The Sueoka results are on average about 30% lower than present data for the whole energy range com-

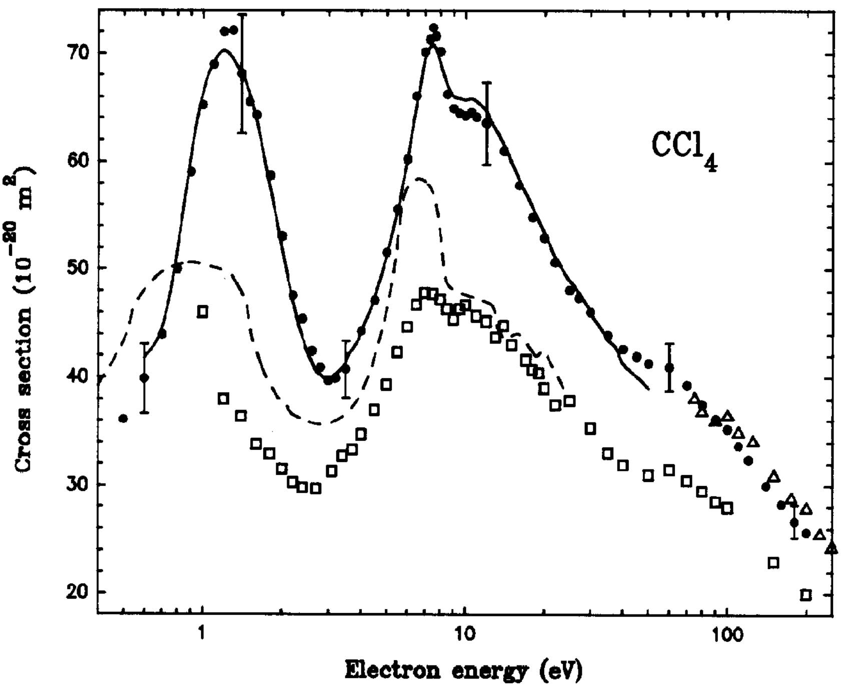

Fig. 2. Absolute e^-–CCl_4 scattering total cross sections. The error bars correspond to the overall experimental uncertainties at selected points. (●) Present, absolute; (---) ref. [38], absolute; (□) ref. [31], normalized; (—) ref. [32], absolute; (△) ref. [33], absolute.

mon to both experiments. Such a large discrepancy suggests the possible existence of an unrecognized factor in Sueoka's experiments which drastically lowers his results.

Two distinct features appear in the low-energy total cross section of CCl_4. The single peak is centered near 1.2 eV while a second, broad peak at 7.5 eV is located on the low-energy side of a much broader maximum.

Experiments on the dissociative attachment of slow electrons to CCl_4 [24,39,42,46] and electron transmission spectroscopy [24,45] indicate a resonant character of scattering slightly above 1 eV. Chu and Burrow [46] attributed the structure near 1.2 eV to the resonant state of T_2 symmetry. In contrast with CF_4, calculations of Tossell and Davenport [34] for CCl_4 gave the energy position of the T_2 resonance in agreement with experiment, but in turn the shape of their cross section in the vicinity of the resonance differs substantially from the measurements. The magnitude of the calculated low-energy elastic cross section [34] is substantially higher than the total cross section measured.

The analysis of negative ion formation above 5 eV [4,24,42,46] also suggests that the peak at 7.5 eV may partly result from resonant electron capture processes.

Above 15 eV the total cross section decreases steadily along with the energy. A change in the slope of the cross section function between 50 and 150 eV coincides with the maximum in the ionization cross section [48]. At higher energies the contribution of ionization processes to the scattering increases, and above 100 eV the total ionization cross section in CCl_4 [48] constitutes at least one third of the total scattering cross section.

No calculations of the total electron scattering cross section by CCl_4 are available which could enable comparison with the present experiment.

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