

Differential cross sections for elastic scattering of electrons by CH₄ in the energy range of 3 to 20 eV

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Received 14 April 1982, in final form 7 June 1982

Abstract. Differential, integral and momentum transfer cross sections have been determined for the elastic scattering of electrons by CH₄. With the help of a crossed electron beam, molecular beam apparatus using the relative flow technique, the ratios of the elastic differential cross sections (DCS) of CH₄ to those of He were measured at electron impact energies of 3, 5, 6, 7.5, 9, 10, 15, and 20 eV for scattering angles from 30 to 140°. From the ratios, the absolute DCS were determined by utilising the known DCS of He. Because pure rotational excitation could not be resolved, the elastic DCS are the sum of elastic and pure rotational excitations at room temperature. Integral and momentum transfer cross sections were calculated from the DCS. The CH₄ DCS are similar in size and in angular behaviour to those of Ar at impact energies below 7.5 eV, and also agree approximately with a close-coupling calculation for electron scattering from polyatomic molecules. A broad maximum in the integral and momentum transfer cross sections is located at 7.5 eV. The angular distributions at energies up to about 7.5 eV are characteristic of a d-wave type of resonance.

1. Introduction

Methane is the simplest of all organic compounds and thus has attracted much attention. It is known (Massey *et al* 1969) that the total cross section for scattering of slow electrons by CH₄ exhibits the Ramsauer–Townsend minimum at 0.4 eV, followed by a broad maximum centred near 7 eV. Interest in these features has generated extensive experimental studies since the early 1930's. There remains, however, considerable uncertainty about the magnitude of the total cross section, the value of the electron energy at the minimum (however, see Sohn *et al* 1982), and the possible existence of resonances. For theoretical models, as well as for practical applications, absolute DCS as a function of electron impact energy are needed.

Recent direct total cross section measurements by Barbarito *et al* (1979) showed that the position of the minimum and also the cross section itself over the whole energy range from 0 to 16 eV are lower than the values found in the literature. Mathur (1980) reported that the electron transmission function of CH₄ shows a broad minimum at 7.8 eV, a shallow structure at 12 eV and a resonance at 18.5 eV.

Quantitative electron impact DCS measurements on CH₄ are less extensive and less precise than studies of the total absorption cross sections from transmission experiments (cf Brode 1925, Brüche 1927, 1930, Ramsauer and Kollath 1930) or momentum transfer cross sections from diffusion experiments (e.g. Cottrell and Walker 1965, 1967, Pollock 1968, Duncan and Walker 1972, 1974, McCorkle *et al* 1978).

Angular distributions of elastically scattered electrons were measured by Bullard and Massey (1931), Arnot (1931), Mohr and Nicoll (1932), and Hughes and McMillen (1933). More recently, normalised absolute DCS were obtained by Rohr (1980) in the energy range below 10 eV for scattering angles between 20 and 120°. He found a broad resonance structure at about 5 eV, not 7 eV, for a scattering angle of 80°.

Theoretically, Gianturco and Thompson (1976) calculated the total cross section for $e + \text{CH}_4$ scattering in a fixed-nuclei approximation including both exchange and polarisation effects. The Ramsauer–Townsend minimum at low energies (0.4 eV) and the broad T_2 symmetry (mainly d-wave) resonance at higher energies (7 eV) were both correctly described. Recently, they have extended their calculation of differential cross sections to other polarisation cut-offs ($r_0 = 0.92, 0.88$, and 0.84 ; Gianturco and Thompson 1980).

As a first step in a systematic study of the paraffin series, we report extensive, normalised absolute values of the DCS for CH_4 at impact energies from 3 to 20 eV for the angular range from 30 to 140° as well as the corresponding integral and momentum-transfer cross sections. Specifically, we do not discuss the Ramsauer–Townsend minimum at lower energies and the temporary negative-ion states (cf Sanche and Schulz 1973, Botz and Glick 1975, Marmet and Binette 1978), but are concerned here only with the broad resonance at higher energies. In § 2, we briefly describe the methods employed in the measurements. In § 3, the experimental results are presented and compared with other available measurements, with the DCS of Ar and with the close-coupling calculation mentioned before. Estimates of accuracy and an explanation of the empirical fitting procedure can be found in appendix 1.

2. Apparatus and method

The apparatus used in the measurements has been described previously (Tanaka *et al* 1981). An energy-selected electron beam of the required impact energy from a cylindrical electrostatic monochromator is collimated and focused onto the target beam at right angles. The molecular beam of CH_4 with a density corresponding to a pressure of about 10^{-3} Torr is formed by effusion from a nozzle with a backing pressure of about 0.2 Torr. The electrons scattered at angle θ are energy selected by an analyser and counted with a channeltron detector. The analyser can be rotated through the angular range of 30 to 140°.

The overall resolution during these measurements was approximately 50 meV. This is sufficient to separate the elastic scattering clearly from the $\nu_{1,3}$ (ν_1 and ν_3 not resolved; at 0.37 eV) and $\nu_{2,4}$ (0.17 eV) vibrational excitations, but insufficient to resolve any rotational structures (Tanaka 1979). The electron energy scale was calibrated by measuring the 19.3 eV resonance of He; the view cone angle of detection was about $\pm 2^\circ$.

First, the intensity of the electrons scattered by CH_4 was measured and immediately followed by a measurement of the intensity of electrons scattered from He under exactly the same experimental conditions and the same impact energy. Thus the ratio of the two intensities is related to the ratio of the cross sections by

$$\begin{aligned} \sigma(\text{CH}_4, \theta) / \sigma(\text{He}, \theta) \\ = (N_e(\text{CH}_4) / N_e(\text{He})) (m(\text{CH}_4) / m(\text{He}))^{0.5} (N_b(\text{He}) / N_b(\text{CH}_4)) \end{aligned} \quad (1)$$

$$= (N_e(\text{CH}_4)/N_e(\text{He}))(P(\text{He})/P(\text{CH}_4))$$

$$\equiv R_0 \quad (2)$$

where $N_e(\text{CH}_4)$ and $N_e(\text{He})$ are the experimentally determined intensities (integrated peak counts) of the elastically scattered electrons, $m(\text{He})$ and $m(\text{CH}_4)$ are the atomic and molecular weights, $N_b(\text{He})$ and $N_b(\text{CH}_4)$ are the flow rates of the two gases through the nozzle, and $P(\text{He})$ and $P(\text{CH}_4)$ are the pressures of the gases behind the nozzle. The pressure was determined with a Baratron capacitance manometer. The quantities of equations (1) and (2) and their derivations are described in detail in Srivastava *et al* (1975). As a check on the correct performance of our apparatus, we measured the DCS of Ne which is isoelectronic with CH₄ and found excellent agreement with the data of Williams (1979) in the energy range of 3 to 20 eV.

From the ratio of the differential cross sections (equation (2)) the absolute value of $\sigma(\text{CH}_4, \theta)$ was calculated by multiplying R_0 by the absolute values of $\sigma(\text{He}, \theta)$ as recently reported by Register *et al* (1980). Thus, the cross sections $\sigma(\text{He}, \theta)$ are used as secondary standards. As in all previous studies, precautions were taken to minimise all sources of known systematic experimental errors. They have been discussed in detail in Srivastava *et al* (1975, 1981).

3. Results and discussion

Over a span of almost two years, with various settings and readjustments of the instrument, but using the relative flow technique described above, we have obtained the ratios R_0 at incident energies of 3, 5, 6, 7.5, 9, 10, 15, and 20 eV for the angles from 30 to 140° in steps of 10° repeatedly. The averaged cross sections are presented in table 1 which also gives a fit described in the appendix, R_0 and an estimate of the

Table 1. Differential cross sections. M and F are the measured and fitted cross sections, respectively, in units of $10^{-16} \text{ cm}^2 \text{ sr}^{-1}$. $R_0 = F/\sigma(\text{He})$ and SD are the standard deviations of the repeated measurements in the same units as the measurements.

Angle (deg)		Incident energy (eV)							
		3	5	6	7.5	9	10	15	20
30	M	0.81	1.51	1.88	3.02	3.13	3.14	3.93	3.37
	F	0.61	1.40	1.86	2.95	3.09	3.28	3.90	3.46
	R_0	3.56	5.73	6.87	9.69	9.36	9.65	10.00	8.65
	SD	0.53	0.37	0.67	0.62	0.05	1.19	0.12	0.42
40	M	0.53	1.04	1.52	2.46	2.70	3.02	2.42	1.77
	F	0.60	1.22	1.56	2.37	2.39	2.44	2.29	1.77
	R_0	3.07	4.51	5.34	7.52	7.33	7.29	6.76	5.36
	SD	0.21	0.15	0.28	0.17	0.25	0.41	0.41	0.24
50	M	0.51	1.16	1.47	1.98	1.79	2.07	1.57	1.03
	F	0.63	1.14	1.39	1.97	1.94	1.93	1.47	1.03
	R_0	2.82	3.87	4.38	6.19	6.06	6.07	4.98	3.81
	SD	0.05	0.14	0.33	0.28	0.01	0.15	0.12	0.06

Table 1. (continued)

Angle (deg)		Incident energy (eV)							
		3	5	6	7.5	9	10	15	20
60	<i>M</i>	0.86	1.21	1.20	1.46	1.42	1.37	0.94	0.72
	<i>F</i>	0.72	1.20	1.36	1.71	1.61	1.56	1.02	0.70
	<i>R</i> ₀	2.25	3.83	4.46	5.71	5.54	5.46	4.03	3.14
	SD	0.15	0.14	0.28	0.14	0.15	0.20	0.05	0.13
70	<i>M</i>	0.81	1.42	1.41	1.55	1.32	1.14	0.67	0.51
	<i>F</i>	0.80	1.30	1.41	1.54	1.35	1.26	0.73	0.53
	<i>R</i> ₀	2.34	3.81	4.15	4.74	4.38	4.25	2.98	2.65
	SD	0.19	0.18	0.16	0.09	0.02	0.15	0.03	0.02
80	<i>M</i>	0.94	1.39	1.50	1.43	1.22	1.05	0.52	0.45
	<i>F</i>	0.82	1.32	1.40	1.35	1.10	1.00	0.52	0.42
	<i>F</i>	2.02	3.46	3.78	3.91	3.42	3.07	2.14	2.15
	SD	0.12	0.09	0.21	0.15	0.09	0.13	0.02	0.02
90	<i>M</i>	0.68	1.09	1.19	1.20	0.94	0.80	0.41	0.35
	<i>F</i>	0.75	1.17	1.21	1.07	0.83	0.74	0.38	0.33
	<i>R</i> ₀	1.79	2.93	3.08	2.89	2.41	2.24	1.52	1.78
	SD	0.06	0.07	0.26	0.17	0.01	0.04	0.07	0.04
100	<i>M</i>	0.57	0.84	0.89	0.68	0.50	0.49	0.27	0.29
	<i>F</i>	0.59	0.85	0.85	0.70	0.55	0.48	0.29	0.28
	<i>R</i> ₀	1.15	1.83	1.95	1.78	1.56	1.45	1.21	1.56
	SD	0.09	0.10	0.09	0.07	0.02	0.02	0.04	0.04
110	<i>M</i>	0.41	0.48	0.46	0.32	0.35	0.27	0.26	0.25
	<i>F</i>	0.40	0.48	0.46	0.34	0.34	0.28	0.26	0.27
	<i>R</i> ₀	0.77	0.96	0.94	0.76	0.84	0.75	1.00	1.47
	SD	0.14	0.10	0.08	0.10	0.02	0.02	0.04	0.03
120	<i>M</i>	0.25	0.26	0.23	0.21	0.30	0.26	0.29	0.32
	<i>F</i>	0.26	0.25	0.24	0.21	0.31	0.25	0.31	0.31
	<i>R</i> ₀	0.46	0.46	0.46	0.44	0.72	0.63	1.14	1.59
	SD	0.07	0.06	0.06	0.04	0.03	0.03	0.03	0.05
130	<i>M</i>	0.24	0.29	0.43	0.50	0.64	0.51	0.47	0.42
	<i>F</i>	0.22	0.31	0.40	0.48	0.59	0.50	0.42	0.39
	<i>R</i> ₀	0.36	0.53	0.71	0.96	1.31	1.21	1.47	1.95
	SD	0.05	0.10	0.09	0.18	0.07	0.06	0.02	0.04
140	<i>M</i>	0.31	0.77	0.94	1.15	1.14	1.01	0.56	0.50
	<i>F</i>	0.32	0.74	0.99	1.21	1.19	1.04	0.58	0.52
	<i>R</i> ₀	0.51	1.19	1.65	2.28	2.56	2.45	2.00	2.52
	SD	0.08	0.17	0.13	0.22	0.14	0.04	0.05	0.06
Number of repetitions		3	4	6 [†]	5	2	3	3	3

[†] Near ends of range 6, otherwise 3.

experimental errors obtained from the standard deviations of the repetitions. An analysis of further errors is given in the appendix.

Figure 1 shows $\sigma(\text{CH}_4)$ as a function of the scattering angles and incident energies. Also shown are previous experimental values of Bullard and Massey (1931), Hughes and McMillen (1933), Newell *et al* (1979), and of Rohr (1980) for 5 eV. All these experimental data except the last one have been published only in relative units; they were normalised to the present measurements at $\theta = 90^\circ$. Within the limits of the

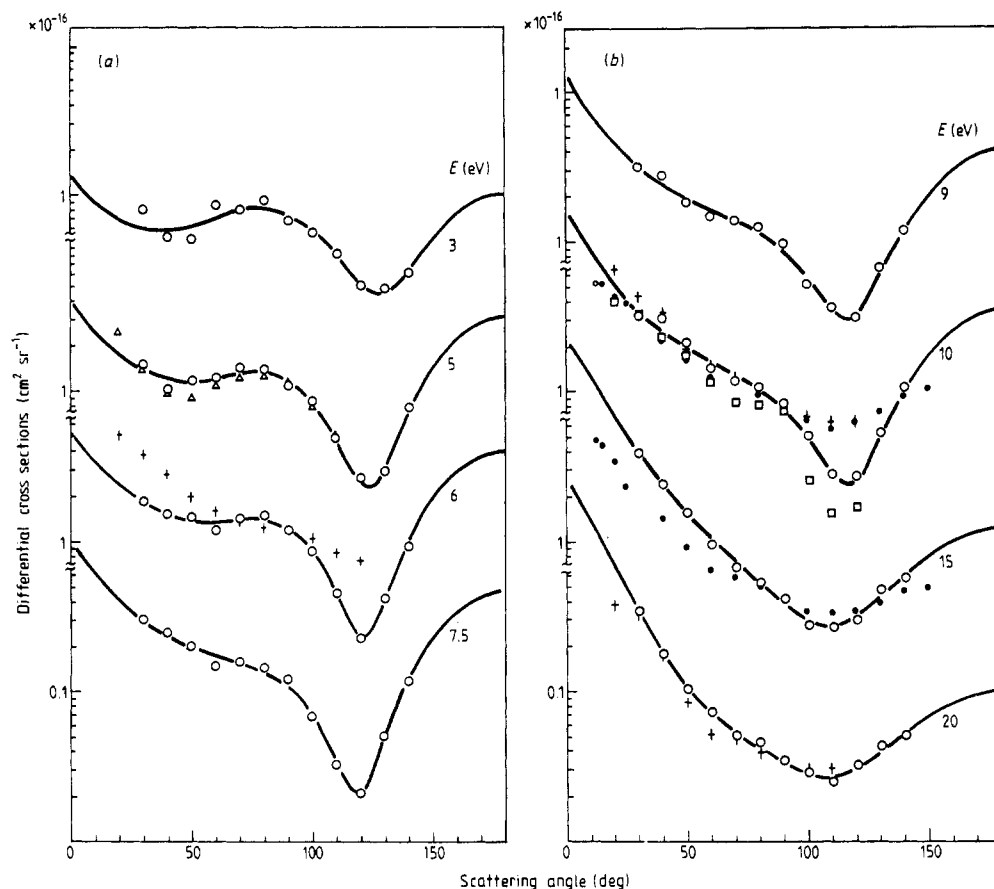


Figure 1. Differential cross sections for elastic scattering of electrons by CH_4 . The full curves are fits to the measurements (open circles). Experimental data: Δ , Rohr (1980); +, Bullard and Massey (1931); \square , Newell *et al* (1979), \bullet , Hughes and McMillen (1933).

experimental errors, all normalised DCS are in satisfactory agreement with the present results, both in shape and magnitude, except for the depth of the minimum at 10 eV. The shape of the 3 and 5 eV curves indicates a fairly large contribution from d-wave scattering (number of peaks; maximum near 90° ; minima near 60° and 120°). As the impact energy increases, the influence of the d-wave scattering ($l = 2$) diminishes, the minimum at 60° changes into a plateau (7.5 and 10 eV) and then into a small deformation at higher energies. When the differential cross sections are drawn as a function of impact energy, a rather broad peak becomes visible, the position of which decreases from about 15 eV at 30° to 5 eV at 110° , cf figure 2. At 120° either the weak signal of the minimum in the angular distributions is too inaccurate to allow an indication of the peak or, more likely, there is no peak, since for yet higher angles, 130° and 140° , the peak reappears and now tends towards higher energies.

Figure 3 compares the present angular distribution observed for CH_4 with those of Ar as reported by Srivastava *et al* (1981). As first observed by Bullard and Massey (1931), there is a surprising similarity between the two sets of DCS for electron energies below 10 eV, except for the location of the first minimum, and for the deeper and sharper minimum in Ar. It seems that the molecular structure of CH_4 has little effect on the elastic scattering as long as the energy of the molecular field is comparable

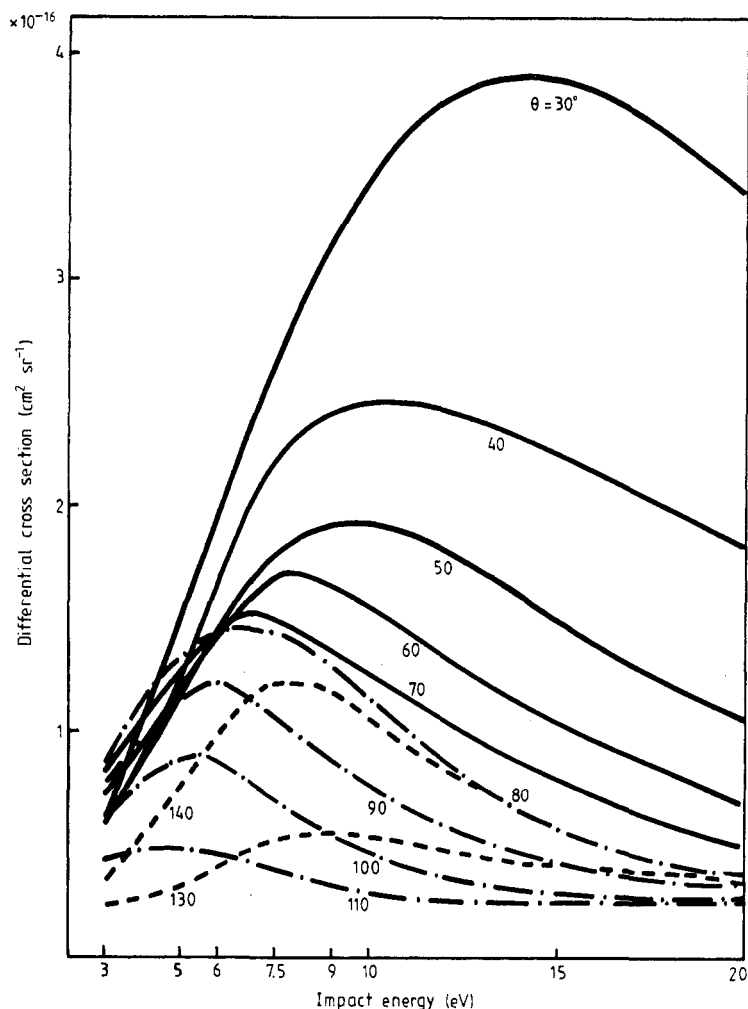


Figure 2. Approximate shape of the differential cross sections of figure 1 as a function of impact energy and scattering angle (θ). The curve for 120° has not been drawn because of too much superimposed noise.

with the impact energy. There is, however, no resemblance for electrons with energies greater than 10 eV.

Comparison with the theoretical results of Gianturco and Thompson (1980) is shown in figure 4. They have recently extended their close-coupling DCS calculations within a fixed-nuclei approximation to 10 eV. Methane belongs to the symmetry group T_d and has a ground-state configuration $1a_1^2 2a_1^2 1t_x^2 1t_y^2 1t_z^2$, yielding an 1A_1 ground state. Their results contained contributions from the scattering states A_1 , T_2 , and E (from the possible states A_1 , A_2 , T_1 , T_2 and E). Exchange was included by orthogonalising to the bound orbitals, and polarisation by a cut-off potential. Our measurements agree quite well with the calculation with a cut-off r_0 of 0.92. Gianturco and Thompson (1976) also calculated the total cross sections for $e + CH_4$ and showed that the partial waves for the T_2 wavefunction are $l = 1, 2, 3, 4, 5$ and that the shape resonance exhibits a strong $l = 2$ behaviour at 7 eV. Based on group theory, Read (1968) has given general expressions for the angular distribution for resonant scattering of electrons by the cubic T_d molecules. According to his table, the dominant

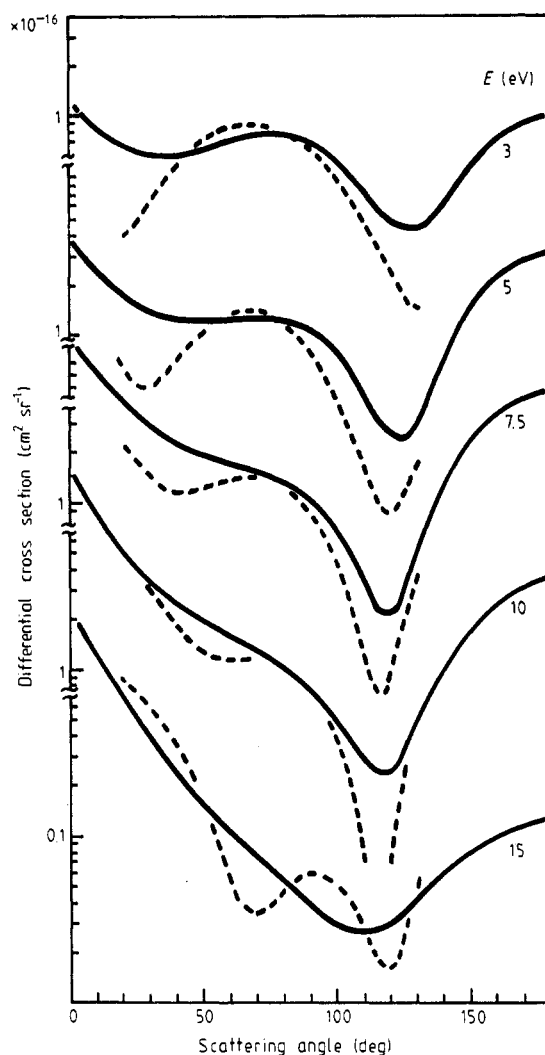


Figure 3. Comparison of the differential cross sections of figure 1 with those of argon (Srivastava 1981, broken curves).

partial waves for this experiment are expected to be p and d waves, the latter characterising the present angular distribution in the low-energy range.

In figure 5, we compare the present DCS at various electron impact energies for the scattering angle 80° with the results of Rohr (1980). The electron energy of the maximum in our measurements (approximately 6 eV) is higher than that reported by Rohr. It becomes evident from an inspection of figure 2 that the position of the peak is consistent with the curves for different scattering angles. Rohr did not use the relative flow technique.

In table 2, the integral (σ_I) and momentum transfer (σ_M) cross sections calculated from the equations

$$\begin{aligned}\sigma_I &= 2\pi \int_0^\pi \sigma(\text{CH}_4, \theta) \sin \theta \, d\theta \\ \sigma_M &= 2\pi \int_0^\pi \sigma(\text{CH}_4, \theta) (1 - \cos \theta) \sin \theta \, d\theta\end{aligned}\tag{3}$$

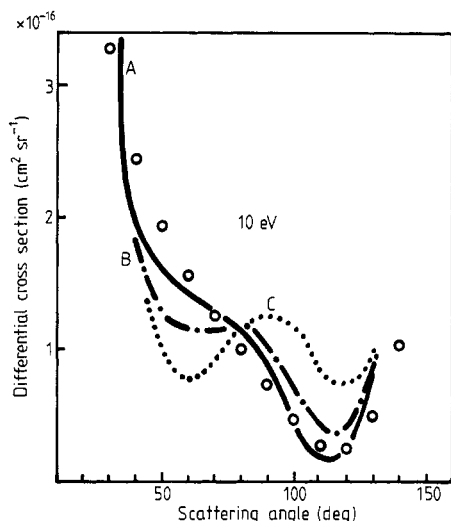


Figure 4. Comparison of the differential cross sections of figure 1 (fits) with the theoretical results of Gianturco and Thompson (1980) for various cut-off parameters: A, $r_0 = 0.92$; B, $r_0 = 0.88$; C, $r_0 = 0.84$.

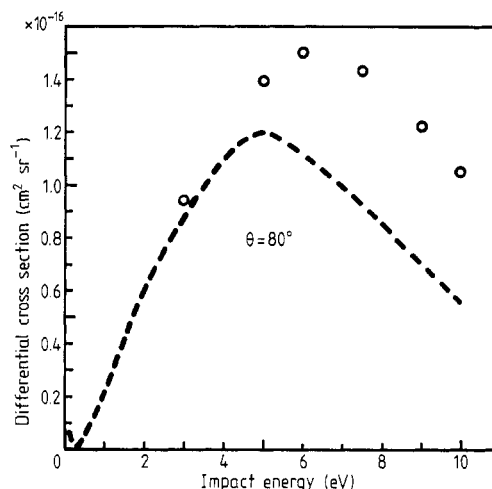


Figure 5. Differential cross sections of figure 1 for a scattering angle of 80° as a function of impact energy. The peak of our data (fits) appears at higher impact energies than that of Rohr (1980), broken curve.

are given together with some error estimates based on the repetitions. The error estimates, of both tables 1 and 2, should not be misread as final error estimates, cf the appendix. In the present experiments, measurements were done only in the range from 30 to 140° . To carry out the integrations in equations (3), the DCS had to be extrapolated between 0 to 30° and 140 to 180° . There are no theoretical DCS calculations for $e + \text{CH}_4$ elastic scattering in these energy ranges, except at 10 eV. Various methods of fitting were tried and evaluated as shown in the appendix. It turned out that a modified partial-wave fitting, including polarisation corrections (CH_4 polarisability = 17.5 au) and the Born approximation for higher partial waves (Thompson 1971), gave the most consistent and optimum fits, and this was used not only for the integrations but also for a smoothing of the observed angular DCS curves. The integral cross sections and momentum transfer cross sections are given in figure 6 and compared with earlier total cross section measurements by Brode (1925), Brüche (1927, 1930), Ramsauer and Kollath (1930) and recent direct total cross section measurements by Barbarito *et al* (1979), and theoretical calculations (Gianturco and Thompson 1976). The present measurements confirm the general trend found for the total cross sections: from a maximum around 7.5 eV the cross section decreases rapidly toward lower energies. As pointed out by Barbarito *et al*, in the whole energy range investigated, the cross sections are lower than the values found in the earlier literature and lower than previous theoretical calculations. Within the error limits, the agreement of the present results with Barbarito *et al* is excellent. A pronounced broad peak appears at an impact energy of approximately 7.5 eV which agrees well with the location of the broad resonance in the transmission function observed by Mathur (1980) at 7.8 eV. The main features of figure 6, the steep decline at the left towards the Ramsauer–Townsend minimum at lower energies (0.4 eV) and the broad T_2 symmetry resonance (mainly d wave, $l = 2$) at around 7 eV have both been described theoretically. A further indication of a broad resonance peak at 7.5 eV could come

Table 2. Integral σ_I and momentum transfer σ_M cross sections. σ_I and σ_M are in units of 10^{-16} cm^2 from the fits. The errors (%) are the propagated mean errors (statistical errors only, cf appendix) expressed as percentages.

E (eV)	σ_I	Error (%)	σ_M	Error (%)
3	7.4	8	6.6	26
5	13.7	5	12.4	24
6	16.1	6	14.5	20
7.5	19.6	2	16.0	14
9	18.9	2	14.4	7
10	18.4	7	13.1	7
15	15.7	2	7.6	13
20	14.3	3	6.5	13

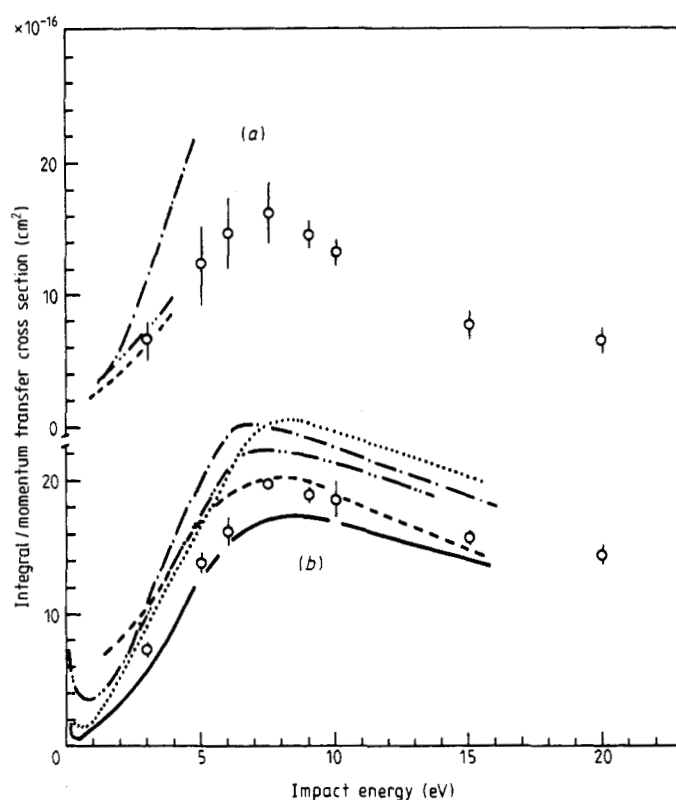


Figure 6. Integral (b) and momentum transfer (a) cross sections calculated from the fits of figure 1 together with estimates of the propagated standard deviation errors. The lower part of the graph also contains the total cross sections of: - - - -, Brode (1925); ·····, Ramsauer and Kollath (1930); — · — · —, Brüche (1927, 1930); —, Barbarito *et al* (1979); as well as the theoretical calculation of — · — · —, Gianturco and Thompson (1976). In (a), the momentum transfer cross sections of — · — · —, Duncan and Walker (1972, 1974); — · — · —, Pollock (1968); - - -, Cottrell and Walker (1965, 1967) have been inserted.

from a measurement of the vibrational excitation. The coupling between electronic and vibrational motion, induced by resonant scattering, enhances the vibrational excitation relative to that induced by direct scattering. Enhanced vibrational excitation of the $\nu_{2,4}$ (0.37 eV) and $\nu_{1,3}$ (0.17 eV) modes was observed at 7.5 eV and will be reported elsewhere (Tanaka *et al* 1982).

In figure 6, the corresponding momentum transfer cross sections (σ_M) are also shown together with other data which, unfortunately, are available only at 5 eV and below. A great deal of less precise information, mainly about momentum transfer cross sections, is available from swarm experiments at lower energies (Cottrell and Walker 1965, 1967, Pollock 1968, Duncan and Walker 1972, 1974, McCorkle *et al* 1978). However, the full analysis of data on electron transport properties obtained in this way is more complicated than for atoms because of the occurrence of inelastic collisions with molecules that leads to the excitation of molecular vibrations and rotations.

4. Conclusion

The present measurements provide a broad range of quantitative data for the elastic scattering of electrons by CH₄ over an angular range from 30 to 140° and an energy range of 3 to 20 eV, together with the corresponding integral and momentum transfer cross sections. There is a broad peak near 7.5 eV in the integral and momentum transfer cross sections; however, in the DCS curves, the position of the peak shifts with scattering angle. It could be experimentally confirmed that the angular distribution in the energy region of 3 to 7.5 eV is dominated by a d-wave scattering as was theoretically predicted and also established experimentally at 5 eV. The agreement between the present measurements and the theoretical calculations seems to indicate that the single-centre expansion method with model exchange and polarisation potentials is capable of yielding relatively good results for CH₄. A more detailed experiment, including the investigation of the Ramsauer-Townsend minimum at much lower energies (Ferch and Ehrhardt 1982), and the temporary negative-ion states at 12 and 18.5 eV, is in preparation and should help us to gain a better understanding of the resonances of CH₄.

Acknowledgments

One of the authors (HT) would like to express his deep gratitude to Professors W Raith and G Baum for their kind hospitality during his stay as a Deutscher Akademischer Austauschdienst (DAAD) guest Professor at the University of Bielefeld between July and September 1981 where the first version of this manuscript was written. Also gratefully acknowledged is the receipt of a visiting scientist fellowship of DAAD. We are greatly indebted to Drs J Ferch and K Rohr for many helpful comments and clarifying discussions, and to Dr S Trajmar and his co-workers for their stimulating and generous advice during the final stages of this experiment. We also wish to acknowledge the technical assistance provided by Sophia University Krupp Hall.

Appendix 1. Fitting procedure and error analysis

For CH₄, there exists no unified theory which can be used throughout the range of 3 to 20 eV, and the theories which do exist rely heavily on numerical calculations (e.g. Gianturco and Thompson 1980). On the other hand, the experimenter is often in need of a curve-fitting function which allows him to smooth out the experimental curves and to interpolate or extrapolate from limited data. An empirical fitting function is described here which we have found consistent and fairly stable with respect to the number of parameters not only for CH₄ up to an impact energy of 20 eV but also for Ar up to almost 100 eV, well beyond the opening of inelastic channels.

An error analysis with such an empirical fitting function must consider the following sources of errors: (a) statistical errors connected with the counting of events (Poisson errors), (b) other statistical errors connected with the experiment (standard deviations and mean errors), (c) systematic experimental errors and (d) 'errors' connected with the choice of the fitting function and the number of parameters used (stability of fit). We will treat each of these in turn.

A1.1. Poisson-type errors and mean errors

Since the number of counts is known for each measurement, it is easy to work out via equation (1) the propagated cumulative effect of the Poisson errors on the final cross sections. However, when these errors were compared with the mean errors (equal to the standard deviations of the repeated measurements divided by the square root of the number of repetitions) obtained from experiments on different days and with different adjustments of the spectrometer, it was found that, on the average, the mean errors were roughly twice as large as the Poisson errors. It can also be seen in table 1 that these errors fluctuated very much (small sample estimates). Hand drawn smoothed error curves were constructed and used in one series of fittings, but were found to overemphasise the minima of the curves in figure 2. To emphasise this minimum less and to eliminate the arbitrariness of the hand smoothing, the propagated Poisson errors (multiplied by ten) were used in the fitting procedure. However, the final values of the statistical errors shown in table 2 were obtained from the propagated mean standard deviations as shown below. We attribute the large mean errors mostly to an inexact, machine-bound procedure to remove the background signals (estimated from the non-smoothed counts near the edges of the peak). Other factors were non-reproducible manual settings of some lens controls and, possibly, some variations in the collision volume with varied gases and angles.

To estimate the influence of the standard deviations (mean errors) on the final cross sections, a kind of numerical differentiation including the fitting procedure was used. Each of the twelve average cross sections entering a single fit was increased in turn by 1%, the parameters were re-obtained by a new fitting, and the resulting deviations in the parameters, divided by the cross section deviations, were interpreted as numerically obtained partial derivatives (PD). The resulting propagated mean errors are then

$$(\text{mean error})^2 = \sum_{\theta=30^\circ}^{\theta=140^\circ} [(\text{PD})(\text{SD}(\theta))]^2 / n$$

where SD stands for standard deviations and n gives the number of repetitions. These errors can only be called 'reasonable error estimates' (cf Bevington 1969), since they

have been obtained neither by analytical derivation nor by true numerical differentiation.

A1.2. Systematic errors

Systematic errors have been discussed by Srivastava *et al* (1975, 1982). We will not list them again. The He cross sections, claimed to be accurate within about 5%, will of course influence our results in terms of absolute cross sections. The overall systematic errors are assumed to be smaller than 15%.

A1.3. Fitting procedure

A scattering experiment removes the azimuthal angular component so that a series expansion in Legendre polynomials

$$\sigma(\text{CH}_4) = \sum_l a_l P_l(\cos \theta)$$

with fitting parameters a_l could be considered appropriate. Here, use was made of the fact that the square of an infinite polynomial series can itself be expressed as a simple polynomial series. The fit was tried in the usual fashion by searching for the minimum of

$$\chi^2 = \sum \left(\frac{\text{fit} - \text{data}}{\text{error}} \right)^2 n^{-1}$$

where n is the number of degrees of freedom. The fit obtained in this way was then extrapolated to 180 and 0°. However, the fitted cross sections for higher impact energies always became negative, no matter how many parameters were fitted. Of course, this unexpected result may be because the fitting procedure can handle only a restricted number of parameters.

Next, we attempted to restrict the cross section to positive values by using

$$\sigma(\text{CH}_4) = \sum_l (a_l P_l(\cos \theta))^2.$$

Now, the fits were more realistic at low energies but showed a peak near 150° for higher energies. Some stronger connection between the fitting parameters seems to be required. Since the differential cross sections of CH₄ and Ar look fairly similar at low energies, a modified partial-wave expansion was tried including polarisation and the Born approximation for higher phaseshifts. After some trials, the fit became

$$\begin{aligned} d\sigma(\theta)/d\Omega &= N|f(\theta)|^2 \\ f(\theta) &= \sum_{l=0}^L \{(2l+1)[\exp(2i\delta_l) - 1]P_l(\cos \theta)\} + C_L(\theta) \\ C_L(\theta) &= 2i\pi\alpha k^2 \left(\frac{1}{3} - \frac{1}{2} \sin \left(\frac{1}{2}\theta \right) - \sum_{l=1}^L \frac{P_l(\cos \theta)}{(2l+3)(2l-1)} \right). \end{aligned} \quad (4)$$

where the symbols have their usual meaning (α is the polarisability), and atomic units are used. N is defined as

$$N = 2\left(\frac{1}{4k^2}\right)N'$$

Table 3. Summary of fitting parameters and their variations. The figures in the five-parameter rows are the values of the various fitting parameters found. The values in the four- and six-parameter rows are the percentage changes in the parameters when four and six fitting parameters are used, respectively. The values in the p rows are the propagated mean errors (as percentages), cf explanation in the appendix.

E (eV)	Number of parameters	δ_0	δ_1	$-\delta_2$	δ_3	N	σ_1	σ_M
3	5	0.975	0.221	0.176	0.022	0.595	7.4	6.6
	4	-0.1	+5	+2		-1	+2	+3
	6	+0.3	-8	-49		+10	-2	-12
	p	± 2	± 19	± 9		± 2	± 8	± 26
5		1.054	0.355	0.244	0.049	0.754	13.7	12.4
	4	+1	+2	+1		-2	-11	+1
	6	-8	-21	+88		-14	+13	+27
	p	± 2	± 5	± 4		± 1	± 5	± 24
6	5	1.153	0.417	0.260	0.061	0.752	16.1	14.5
	4	+2	+1	-1		-1	+1	+2
	6	-0.3	+1	-14		+2	-2	-6
	p	± 2	± 9	± 5		± 0.5	± 6	± 20
7.5	5	1.311	0.561	0.210	0.086	0.749	19.6	16.0
	4	+2	-1	-6		+2	+1	+1
	6	-2	+2	-22		-0.3	-2	-10
	p	± 1	± 1	± 3		± 1	± 2	± 14
9	5	1.491	0.590	0.115	0.102	0.715	18.9	14.4
	4	± 2	-2	-20		+3	+1	+1
	6	-1	+3	-27		+3	-1	-9
	p	± 1	± 1	± 13		± 1	± 2	± 7
10	5	1.502	0.640	0.085	0.119	0.652	18.4	13.1
	4	+2	-3	-28		+3	+1	+0
	6	+0.1	+1	-12		-1	+0	-3
	p	± 0.3	± 4	± 9		± 0.3	± 7	± 7
15	5	2.249	1.127	0.335	0.216	0.311	15.7	7.6
	4	-6	-11	-10		+5	-5	-6
	6	-1	+2	+1		-2	-1	-2
	p	± 0.4	± 0.3	± 3		± 2	± 2	± 13
20	5	2.483	1.146	0.424	0.268	0.259	14.3	6.5
	4	-4	-11	-7		+3	-5	-6
	6	-1	+3	-1		-4	-3	-1
	p	± 0.2	± 0.1	± 2		± 3	± 3	± 13
Average of (4/6) fitting deviations (%)		2	5	18		4	3	6
Average of propagated mean errors (%)		1.1	4.9	6		1.4	4.4	15.5

and contains the $(1/2ik)^2$ normally found in $f(\theta)$. N' is a further fitting parameter to allow an overall normalisation of experiment and fit. The modification of the partial-wave expansion consists in the inclusion of N which should be $1/2k^2$ if the molecule were spherically symmetric. Fitting the Ar data of Srivastasa *et al* (1981) gave a value of $2N'$ close to one for lower energies, and also produced excellent fits for higher energies provided $2N'$ was allowed to drift away from one. In the fitting procedure N , not N' is used as the parameter.

Without C_L , two types of fit have been found which cannot be transformed into one another by the symmetries inherent in the fitting function ($\text{fit}(\delta) = \text{fit}(\delta \pm \pi)$); the sign of *all* δ_l can be inverted simultaneously without affecting the fit. These two types can easily be distinguished by the sign pattern of the phaseshifts. When C_L is introduced, each fit further splits into two, because, depending on the choice of the signs of the phaseshifts, C_L adds or subtracts. The four fits have been sorted out by drawing graphs of the parameters against the impact energy and looking for smooth curves, followed by an inspection of chi-squared which removed two of the fits, and finally by inspecting the behaviour of the fits near 0 and 180°. Up to ten parameters were tried, but too many parameters only follow the noise of the data. The fitting program uses a line search along the gradient which is found with the help of the Boyden–Fletcher–Goldfarb–Fannon algorithm for an approximation of the inverse Hessian (Tone 1981; the program given there was extensively modified).

Fits of the cross section of CH₄ with five parameters have been included in table 1 and generally agree quite well with the measurements.

To check the stability of the fits against variations in the number of parameters, the percentage shift in the fitting parameters and the integrals were worked out for four and six parameters and generally found to be sufficiently small. Fitting parameters and their deviations with the number of parameters as well as the propagated mean errors are given in table 3. The phaseshifts of table 3 would change if N were removed as a fitting parameter, the more so the larger l is. We feel hesitant to combine the last two averaged 'error' rows of table 3 because they can hardly be considered independent. If they are treated as uncorrelated and absolute averages over all impact energies of the two errors are formed as in table 3, the combined averaged statistical errors would become $\delta_0 = 2\%$, $\delta_1 = 7\%$, $\delta_2 = 19\%$, $N = 4\%$, $\sigma_1 = 5\%$ and $\sigma_M = 17\%$. To these the systematic errors would have to be added. Maximum errors can be found in the table. All error estimates should be read as implying 'supposing the fit, equation (4), can be used'. Because of this, no overall combined error estimate has been given. Whether the separation into a partial-wave factor and a size factor N can be supported theoretically is by no means clear, but the consistency of the fits over all angular and impact ranges is surprisingly good.

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