J. Phys. B: At. Mol. Opt. Phys. 24 (1991) 2747-2754. Printed in the UK

Absolute total cross sections for electron scattering on CH_4 molecules in the 1–4000 eV energy range

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Received 21 December 1990, in final form 27 February 1991

Abstract. Absolute total cross sections for electron–methane scattering have been measured in the energy range from 0.9 to 4000 eV in two separate experiments. The present results, the first available above 500 eV, are in good agreement with other recent experimental and theoretical data. The low energy scattering is dominated by a shape resonance; a broad hump has been detected centred around 100 eV. A short critical review of previous measurements is given.

1. Introduction

The considerable interest in electron scattering on methane molecules is closely related to several practical applications. Due to its electron-attachment features, CH_4 is frequently used as an admixture in gas radiation counters (Schultz and Gresser 1978) and discharge diffuse switches (Hunter *et al* 1985). It is also an important constituent of comets, atmospheres of major planets (Wallace and Hunten 1978, Belton and Hayes 1975) and interstellar space (Smith and Adams 1989). Its influence on the greenhouse effect is often stressed (Hansen *et al* 1981).

Due to the symmetry of the molecule, the relative simplicity in the theoretical treatment of the $e^- + CH_4$ scattering problem enables the testing of different models and forms of electron-target interaction (see Gianturco and Jain 1986 for an extensive review). For these reasons methane is, along with noble gases' atoms, one of the most extensively studied targets, both experimentally and theoretically.

Electron total scattering on methane was first investigated at low energies by Brode (1925) and Brüche (1927). The measurements of Ramsauer and Kollath (1930) brought into evidence a pronounced minimum in the total cross section at a collision energy of about 0.4 eV.

Very intensive measurements of total cross sections were performed during the last decade. Most of them concerned the low energy (see Jones 1985) and the very low energy scattering (Ferch *et al* 1985, Lohmann and Buckman 1986). Results of these experiments are consistent concerning the existence of the Ramsauer minimum, but differ marginally about its width. More recent experiments on total cross sections cover the low and intermediate energy range up to 500 eV, both for electron and positron scattering (Floeder *et al* 1985, Sueoka and Mori 1986, Dababneh *et al* 1988). The main

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aim of these latter works was to make comparative studies between the two different projectiles. All of the recent measurements were made by the time-of-flight technique, conceptually different from the pioneer works. The energy coverages of all total $e^- + CH_4$ cross section measurements are shown in figure 1.

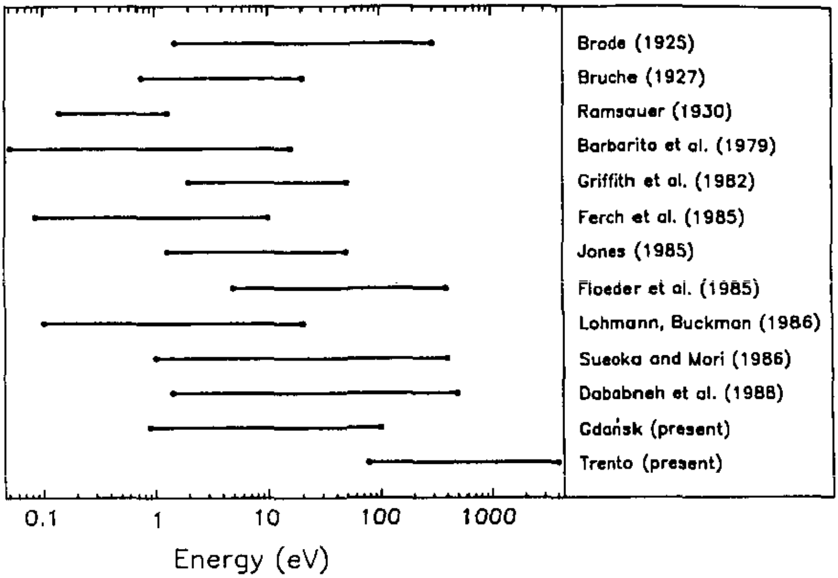

Figure 1. Energy coverage of the available total cross section measurements for electron-CH_4 scattering.

In the present joint work, performed in two laboratories (Gdańsk and Trento), total cross sections for $e^- + CH_4$ scattering in the 0.9–4000 eV energy range are presented. An electrostatic analyser (Szmytkowski *et al* 1984) has been used to select the electron beam in the low energy experiment ($\leqslant 100$ eV) and a modified Ramsauer-type spectrometer (Zecca *et al* 1987) at energies above 75 eV.

2. Experimental method

The experimental procedure was based on the relation between the total cross section $Q(E)$ at a given energy E and the attenuation of an electron beam passing through the target under study (Beer-Lambert law):

$$I_g(E) = I_0(E) \exp[-nLQ(E)].$$

I_0 is the primary beam intensity, I_g is the intensity of the beam leaving the scattering chamber, L is the length of the beam's path in the scattering chamber and n is the target density.

Both apparatuses used in the present experiment have been employed for a number of absolute total cross section measurements. A more detailed description of the set-ups and the data taking procedures can be found in Szmytkowski *et al* 1984, Zecca *et al* 1987.

In the low-energy experiment, an electrostatic cylindrical deflector of 70 meV resolution was used to form the beam. A scattering chamber of 30.5 mm length, rectangular entrance and exit apertures (0.3×0.7 mm^2 and 0.35×0.7 mm^2, respectively) was followed by a Faraday cup. The angular resolution of the experiment was 2×10^{-3} sr. No retarding potential was applied before the collector. The electron energy scale was calibrated with an accuracy of 60 meV against the oscillatory resonant structure in the transmission current at around 2.3 eV in N_2 (Kennerly 1980).

In the intermediate-energy measurements the electron beam was formed in the 180° sector of the transverse magnetic field. The length of the electron's path in the gas volume was 140.2 mm. The angular acceptance of the collector amounted to 3.4×10^{-4} sr. No retarding field was applied. However, due to the magnetic field, the apparatus performs screening against electrons inelastically scattered into small angles, with a mean resolution of $E/25$. In Ramsauer's method both the intensities I_s of scattered and I_c of transmitted electrons are measured. The total cross section was evaluated with a modified formula

$$I_{c_1}/(I_{c_1}+I_{s_1}) = I_{c_2}/(I_{c_2}+I_{s_2}) \exp[-(n_1-n_2)LQ(E)],$$

where n_1 and n_2 are the target densities corresponding to currents I_1 and I_2, respectively.

In the course of both experiments, special precautions were taken to minimize the effects of exposure of the electron optics to the measured gas. The effects of gas effusion from the scattering chamber on the total cross sections values were negligible. The number density n of the target vapour was determined through absolute pressure measurements by MKS-Baratron capacitance manometers. The pressures used varied between 0.1 and 0.5 Pa at low energies and between 0.1 and 5 Pa in the intermediate-energy experiment. These values were chosen for each measurement energy in order to satisfy the single scattering conditions. In the low-energy experiment, corrections of the pressure readings due to the thermal transpiration effect (Poulter *et al* 1983) were used; in the intermediate-energy experiment the manometer head temperature was stabilized to trace within 0.1 °C the gas cell temperature.

Each experimental value is the mean of about 30–40 measurements performed for different pressures. An averaging procedure with weights depending on the statistical errors was applied to the low energy data. The intermediate-energy experiment was controlled by a computer; post-measurement statistic procedures were employed to reveal possible systematic errors.

The overall systematic uncertainty does not exceed 4% in the low energy experiment and 2.5% in the intermediate-energy measurements. Statistical errors (one standard deviation of the mean value) over the entire energy range did not exceed 3%. The angular resolution error due to the elastic scattering into near-to-zero angles amounted to 0.8% at 100 eV in the Gdańsk experiment and to 1.0% at 4000 eV in the Trento measurements. To evaluate these errors we used the experimental differential cross sections of Sakae *et al* (1989); according to the Born approximation (Szabo and Ostlund 1974), the value of the angle DCS at 4000 eV was assumed to be equal to that at 700 eV. No appropriate data exist for inelastic scattering. The gas purities were 99.95%.

3. Results

Absolute total electron-scattering cross sections for CH_4 obtained in both reported experiments are given in table 1. They are compared with other recent absolute measurements in figure 2*a* and with selected theoretical calculations in figure 2(*b*). Our set of results agree within experimental errors in the overlapping energy range.

Table 1. Absolute total cross sections for electron–methane scattering (10^{-20} m^2).

Energy (eV)	TCS	Energy (eV)	TCS
0.90	2.0	77.5	10.75
1.00	2.3	80	10.63
1.20	2.9	83	10.16
1.40	4.0	88	10.12
1.70	4.9	90	10.12
2.00	6.3	92.5	9.74
2.50	8.2	98	9.51
3.00	10.3	100	9.61
3.50	12.6	110	8.83
4.00	15.1	125	8.16
4.50	17.9	150	7.35
5.00	19.9	165	7.12
5.50	21.8	175	6.93
6.00	23.9	190	6.51
6.50	25.0	200	6.31
7.00	26.5	215	6.04
7.50	26.5	225	5.70
8.00	27.4	240	5.54
8.50	26.8	250	5.36
9.00	26.5	264	5.27
9.50	26.1	276	5.03
10.00	25.8	292	4.84
10.50	25.2	300	4.76
11.00	25.0	326	4.46
13.00	23.9	350	4.28
15.00	23.0	400	3.90
17.00	21.1	450	3.53
20.00	19.6	500	3.18
23.00	18.3	600	2.71
25.00	17.5	700	2.49
30.00	16.1	800	2.21
35.00	14.6	900	1.98
40.00	13.6	1000	1.78
45.00	12.8	1250	1.45
50.00	12.3	1500	1.21
60.00	11.7	1750	1.03
70.00	11.0	2000	0.894
75.00	10.8	2250	0.803
80.00	10.3	2500	0.717
90.00	9.6	2750	0.647
100.00	9.0	3000	0.588
		3250	0.554
		3500	0.517
		4000	0.441

The most prominent feature in the cross section is a broad structureless maximum centred near 8 eV where the cross section reaches a value of 27.4×10^{-20} m^2. The existence of this maximum is partly related to the presence of a very deep Ramsauer minimum (Ferch *et al* 1985, Lohmann and Buckman 1986) below the investigated energy range, but in part it may be due to a number of resonances in this energy region.

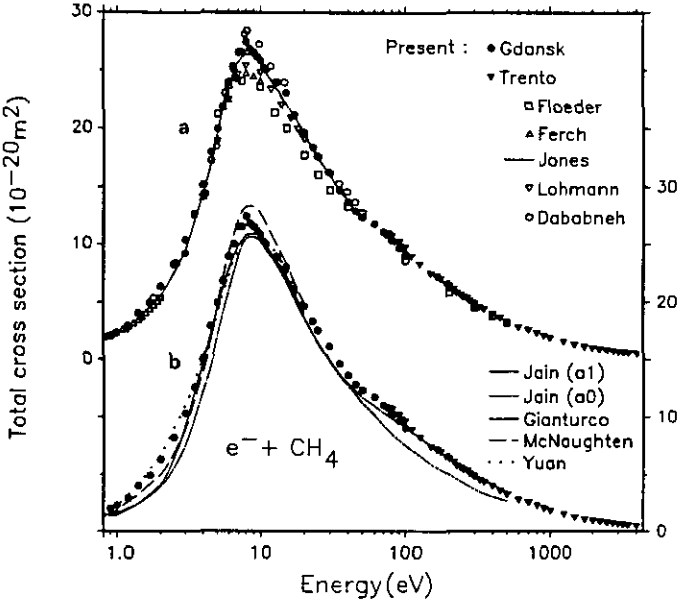

Figure 2. Comparison of the present absolute total cross sections with other experimental (*a*) and theoretical (*b*) data. (*a*) ●, present (Gdańsk); ▼, present (Trento); □, Floeder *et al* 1985; △, Ferch *et al* (1985) (below 2 eV only selected points are shown for clarity); ▽, Lohmann and Buckman (1986) (below 2 eV only selected points are shown for clarity); ○, Dababneh *et al* (1988); ——, Jones (1985). (*b*): Experimental points as in figure 2(*a*); —·—, Jain (1986b) with distorted-wave absorption; —··—, Jain (1986b) with non-distorted-wave absorption; ——, Gianturco and Scialla (1987); — — —, McNaughten *et al* (1990); · · · ·, Yuan (1988a). Details of the theoretical models are given in text.

Their existence between 7–9 eV has already been observed in the vibrationally elastic as well as the inelastic cross sections by Rohr (1980) and Tanaka *et al* (1982, 1983). The angular distributions at these energies are characteristic of a d-wave resonance which is in agreement with earlier predictions of Gianturco and Thompson (1976). The results of the dissociative attachment experiment of Sharp and Dowell (1967) also indicate the presence of a resonant process in the region of the total cross section maximum. The same broad resonance at 7.8 eV and two additive resonant structures at 12 eV and between 17–19 eV were observed by Mathur (1980) in a transmission experiment. These latter resonances are probably very weak and are not observed in the total cross section measurements.

In the region of a few hundreds of eV a number of processes, including Auger transitions and inner-shell ionization (Tronc *et al* 1979), are energetically accessible. Evidence of inner-shell resonances for $e^- + CH_4$ scattering has been reported in the differential elastic (Mathur *et al* 1984) and energy loss (Tronc *et al* 1976, Hitchcock *et al* 1977) spectra. In the previous measurements of the Trento group for CO_2 (Szmytkowski *et al* 1987), a broad structure between 200 and 600 eV was distinguishable over the smoothly descending energy dependence of the total cross section. Therefore, special attention has been devoted to this energy region during the present experiment. However, within our experimental accuracy we did not resolve any structure in methane. Probably, the inner-shell resonances in CH_4 are too weak to manifest themselves in the total cross section. In order to give an explanation of the different behaviours of the two total cross sections, the knowledge of at least relative values of the probabilities for corresponding inner-shell processes in CO_2 and CH_4 would be required.

Some changes in the slope of the total cross section energy dependence can be noticed at about 100 eV, i.e. near the maximum of the total ionization cross section. According to the most recent measurements (Orient and Srivastava 1987), the ionization cross section amounts to 42% of the total cross sections at 100 eV. This contribution rises to 66% at 1000 eV (Rapp and Englander-Golden 1965).

In the high energy limit of our measurements, the total cross section falls monotonically and at 4000 eV reaches a value about three times smaller than in the Ramsauer minimum (Ferch *et al* 1985, Lohmann and Buckman 1986).

Our results are generally in good agreement with the most recent experimental data. In the low energy region, the best agreement (less than 5% below 5 eV and 2% at the maximum of the total cross section) is between the present data and the results of Jones (1986). The results of very low-energy experiments (Ferch *et al* 1985, Lohmann and Buckman 1986) are, at the cross section maximum, slightly lower than the present data (about 5%). Our data also agree very well in the whole energy range up to 500 eV with the results of Dababneh *et al* (1988). Some systematical differences can be noticed at the resonant region where the data of Dababneh *et al* are slightly higher than the present ones and over 100 eV where they are lower by 2–5%. These minor discrepancies are similar in value and sign to those observed for CO_2 (see Szmytkowski *et al* 1987); the high-energy difference lies within the angular resolution error declared by Dababneh *et al* (1988). No other measurements are available above 500 eV.

Somewhat more serious differences exist between the present data and those of Floeder *et al* (1985), which are lower in the whole energy range, by about 10% at 10 eV to 5% at 400 eV. A similar discrepancy is with the normalized data of Sueoka and Mori (1986) (not presented in figure 2), which are also lower than the present results by 5–15%. The discrepancy is outside the combined claimed experimental errors. It is worth mentioning that the experimental set-ups of both Floeder *et al* (1985) and Sueoka and Mori (1986) work in a linear geometry and use a longitudinal magnetic field to guide electrons/positrons. In some circumstances this can lead to an underestimation of the total cross sections (Kauppila *et al* 1977). The data of Barbarito *et al* (1979) as well as of Griffith *et al* (1982) are essentially lower than other experimental results in their whole energy range (cf Lohmann and Buckman 1986).

In figure 2(*b*) we compare the present data with some theoretical results. Since the recent review of Gianturco and Jain (1986), in a number of works (Brescansin *et al* 1989, Gianturco and Jain 1986, Gianturco *et al* 1987, Gianturco and Scialla 1987, Jain *et al* 1989, Lima *et al* 1989, McNaughten and Thompson 1988, McNaughten *et al* 1990, Yuan 1988a, b) different forms of interaction have been tested for $e^- + CH_4$ scattering. The major part of these works concerned the energy range below the electronic excitation threshold. The calculations of Jain (1986b) are the only ones extending from 0.1 eV up to 500 eV. For comparison we have used only selected results from the most recent calculations.

Jain (1986b) used three different effective potentials separately for the Ramsauer minimum, the shape resonance and the intermediate energy regions. In figure 2(*b*) we present the results of a model with an asymptotically adjusted free-electron-gas exchange and parameter-free polarization potentials (Jain and Thompson 1982) for the region of the shape resonance. In the energy range below the maximum of the total cross section, the results of Jain are slightly lower than the present ones. Above 20 eV two models were tested by Jain: with an absorption potential obtained from fully deformed (non-adiabatic) and non-deformed wavefunctions of the target. The non-adiabatic model gives results in good agreement with the present data in the whole energy range: at 100 eV, the difference between the results of Jain and the present data is only −5%; at 500 eV it rises to +8%. The model neglecting deformation of the wavefunctions does not reproduce the experimentally observed hump at about 100 eV and in the whole 100-500 eV energy range gives total cross sections which are by about 25% lower than the present results.

Below the total cross section maximum, a somewhat better agreement is observed between the present data and the results of Gianturco and Scialla (1987). They used the semiclassical exchange potential and the correlation-polarization potential of Gianturco *et al* (1986). However, this model gives the position of the Ramsauer minimum at an energy slightly higher than the experimentally observed value (Lohmann and Buckman 1986).

In the whole 1-20 eV energy range, the model of Yuan (1988a) shows the best agreement with the present data. Yuan used a free-electron-gas exchange and the correlation-polarization potentials of O'Connell and Lane (1983). The recent model of McNaughten *et al* (1990), with exact exchange and parameter-free polarization potentials, agrees also very well with the present data but it slightly overestimates the total cross section at its maximum. A common feature of all considered models is that they give the position of the total cross section maximum shifted by about 0.5-1 eV towards higher energies with respect to the experimental value.

The available experimental results allow establishing the values of the total cross section for $e^- + CH_4$ scattering in the 0.1-4000 eV energy range within a few per cent. Larger discrepancies, both among theoretical and experimental data, still remain for scattering at near-to-zero energies. The scattering length of $-2.48\,a_0$ (where a_0 is the Bohr radius) obtained from experimental total cross sections by Ferch *et al* (1985) is in good agreement with the swarm results of Haddad (1985), but disagrees somehow with the theoretical value of $-3.41\,a_0$ obtained by Jain (1986a). On the other hand, from the swarm data of Duncan and Walker (1972) and of Bowman and Gordon (1967), an absolute value of the scattering length of about $5.4\,a_0$ can be derived, and this is in serious disagreement with the most recent results. Further experimental swarm and beam experiments as well as further theoretical work would be necessary to resolve these discrepancies.

Acknowledgment

The research carried out in Trento has been supported by the Ministero della Universita' e della Ricerca Scientifica e Tecnologica. The research in Gdańsk has been supported in part by Polish Ministry of National Education (MEN) within Programme CPBP 01.06, Project 3.01.

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