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Low-energy electron scattering from methane

Birgit Lohmann and Stephen J Buckman

Atomic and Molecular Physics Laboratories, Research School of Physical Sciences, Australian National University, Canberra, ACT, Australia

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Abstract. A low-energy time-of-flight electron spectrometer has been used to measure total collision cross sections for methane in the energy range 0.1-20 eV. Agreement with two recent experiments and with the pioneering work of Ramsauer and co-workers from the 1930s is excellent.

There has been considerable recent interest in experimental investigations of electron scattering from methane including both the measurement of absolute scattering cross sections and the study of collisional effects such as threshold resonances. Despite the increasing sophistication of these measurements, there are still quite significant discrepancies between the most recent results for the simplest of all direct measurements, the total collision cross section. The two most recent measurements of the low-energy total cross section in methane are those of Barbarito *et al* (1979) and Ferch *et al* (1985b). The magnitude of the Ramsauer minimum in methane as measured in the latter experiment is about a factor of 3 higher than that measured in the former. There is also a discrepancy of almost 0.2 eV in the position of the minimum. However, the data of Ferch *et al* are in good agreement with the early measurements of Ramsauer and Kollath (1930).

At higher energies (1 eV or more), where the experimental difficulties are in principle reduced, the situation is also unclear. The measurements of Ferch *et al* (1985b) and Barbarito *et al* (1979) differ in magnitude by up to 30%, although the data of Ferch *et al* are in fair agreement with those of Brüche (1930), Griffith *et al* (1982) and Jones (1985). Recent theoretical calculations (Gianturco and Thompson 1976, 1980, Jain and Thompson 1982) have not clarified the situation, particularly at low energies where there is a large variation in both the shape and magnitude of the calculated cross sections.

Further information on electron-methane scattering is available from the differential measurements of various groups (Rohr 1980, Sohn *et al* 1983, Tanaka *et al* 1982, 1983, Vusković and Trajmar 1983). The energy discrimination for both incident and scattered electrons in these experiments enables the measurement of both differential and total vibrationally elastic cross sections. Comparison has been made (Sohn *et al* 1983) between these total elastic cross sections and the total cross section of Barbarito *et al* (1979). However, such a comparison and the subsequent conclusions drawn from it may be erroneous, particularly at low energies (below 1.0 eV) where the ground-state vibrational excitation cross sections appear to make a significant contribution to the total cross section (Haddad 1985) and at higher energies (above 9 eV) where the contribution from electronic excitation becomes significant (Vusković and Trajmar

1983). As a result, care must be exercised when making a comparison between the available experimental cross sections.

In addition to the single-collision experiments described above, there have also been several electron-swarm studies in methane (Cottrell and Walker 1967, Duncan and Walker 1972, Haddad 1985). Haddad (1985) has employed a multiterm solution of the Boltzmann equation to derive momentum transfer (σ_m) and total vibrational cross sections from measurements of electron drift velocities and lateral diffusion coefficients. Ferch *et al* (1985b) have used modified effective-range theory (MERT) to enable a comparison between their total cross section and that of Haddad. Their MERT derived σ_m is in good agreement with the latter at energies up to 0.5 eV, the upper limit of the MERT analysis.

A detailed description of the apparatus used for this study will be given in a forthcoming publication (Buckman and Lohmann 1986). Briefly, it is a linear transmission time-of-flight spectrometer similar in many respects to that of Ferch *et al* (1985a). A well defined high-energy (typically 150 eV) electron beam is pulsed by sweeping it across a small aperture with an RF square-wave pulse (100–200 kHz) applied to a pair of deflection plates. The pulsed electron beam is retarded by a series of electrostatic lenses to the required low energy before it enters a 255 mm long attenuation cell. Those electrons not scattered within the cell are reaccelerated and detected by a channeltron. The energy of the electrons within the scattering cell is determined from their time of flight and the total cross section is derived by performing measurements with and without the target gas in the cell and applying the Lambert–Beer relationship. The absolute number density of the target gas is measured with a spinning rotor viscosity gauge. Unlike the apparatus of Ferch *et al* (1985a), no magnetic steering or energy selection is used in the present system.

Our measured total cross sections are given in table 1 and comparison with previous results is made in figures 1 and 2. At low energies (figure 1) the overall agreement with the data of Ramsauer and Kollath (1930) and Ferch *et al* (1985b) is excellent both in the shape and absolute magnitude of the cross section. In the region of the Ramsauer minimum, however, we observe a feature that is not evident in either of the other two cross sections. This feature, a slight enhancement of the total cross section, appears in the energy region 0.4–0.5 eV. Numerous investigations of possible experimental sources of this structure were carried out. Its presence was not pressure dependent, nor did it depend on electron optical conditions. The gas (Matheson UHP grade, 99.97%) was independently analysed using a gas chromatograph and the impurity levels were found to be within those specified by the manufacturer. We believe this structure is a real feature of the electron–methane total cross section and that its position and magnitude are in fact consistent with several recent studies of vibrational excitation in methane.

Both Rohr (1980) and Sohn *et al* (1983) have demonstrated that ground-state vibrational excitation in methane is significantly enhanced near threshold and they postulate that this is due to the existence of short-lived compound states. The swarm experiments of Duncan and Walker (1972) result in a derived momentum transfer cross section that exhibits a broad structure in the energy region of the Ramsauer minimum. Haddad (1985) used a more sophisticated analysis of his own transport data than that employed by Duncan and Walker (1972) and found that, while such a structure was compatible with the transport data, it was not uniquely so, and his derived total momentum transfer cross section was chosen to be smooth in the region of the Ramsauer minimum. However, both of these analyses resulted in total vibrational

Table 1. Measured total cross section in methane.

Energy (eV)	σ_T (10^{-16} cm^2)	Error, $\pm 1\sigma$ (%)
0.10	4.179	5.3
0.11	3.474	4.3
0.12	3.312	4.1
0.13	3.109	3.8
0.18	2.246	3.0
0.20	2.051	3.0
0.25	1.751	3.0
0.28	1.527	3.1
0.30	1.462	3.0
0.32	1.405	3.1
0.34	1.358	3.1
0.36	1.314	3.1
0.38	1.327	3.0
0.40	1.343	3.0
0.42	1.371	3.0
0.44	1.387	3.0
0.46	1.396	3.0
0.48	1.398	3.0
0.50	1.403	3.0
0.52	1.422	3.0
0.55	1.451	3.0
0.60	1.489	3.0
0.65	1.555	3.0
0.70	1.618	3.0
0.75	1.713	3.0
0.80	1.794	3.0
0.85	1.859	3.0
0.90	1.942	3.0
0.95	2.006	3.0
1.00	2.134	3.0
1.2	2.544	3.6
1.5	3.536	3.0
2.0	5.242	3.0
3.0	9.057	3.0
4.0	14.07	3.0
5.0	18.81	3.0
6.0	22.40	3.0
7.0	24.56	3.0
8.0	25.31	3.0
9.0	25.17	3.0
10.0	24.68	3.0
12.0	23.27	3.0
14.0	21.89	3.0
16.0	20.79	3.0
18.0	19.86	3.0
20.0	18.97	3.0

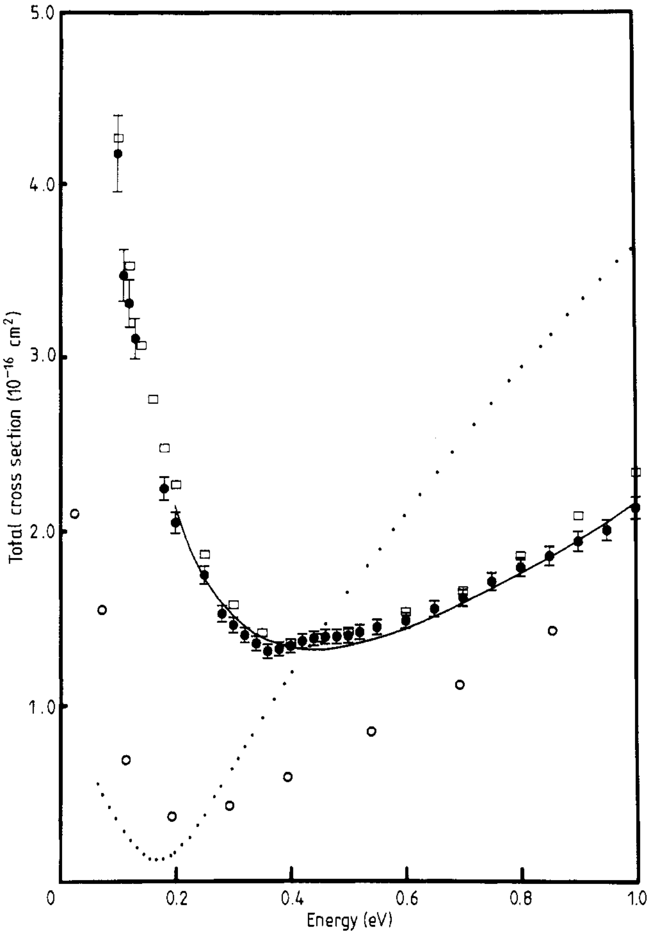

Figure 1. Low-energy (1 eV or less) total cross sections for electron–methane scattering: ●, present results; ——, Ramsauer and Kollath (1930); ○, Barbarito *et al* (1979); □, Ferch *et al* (1985b); · · · ·, Jain and Thompson (1982).

excitation cross sections that were peaked near threshold and whose magnitudes (approximately 0.35 Å^2) are only slightly smaller than that reported for the total *elastic* cross section (Sohn *et al* 1983) in the energy region 0.4–0.5 eV.

The most plausible explanation for this structure is that it is due to the onset of excitation of the essentially degenerate vibrational modes ν_1 and ν_3 of methane at an energy of 0.37 eV. The position of the feature is consistent with this threshold energy and its magnitude and width are consistent with the proposed vibrational cross sections of Haddad (1985) and the observed features and cross sections of Sohn *et al* (1983). We note that we do not observe a series of such structures as reported by Barbarito *et al* (1979), and that the magnitude of our cross section in the region of the minimum is almost a factor of three larger than theirs (see figure 1). This discrepancy has been discussed in some detail by Ferch *et al* (1985b); the excellent agreement between the present data and their data lends strong support to their conclusions. However, the

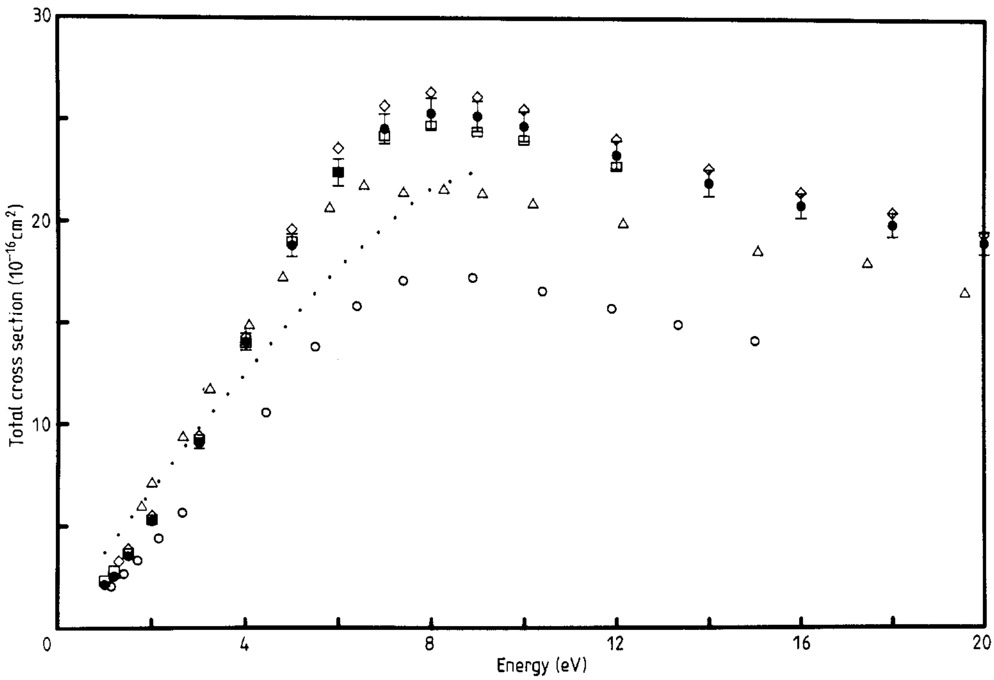

Figure 2. Total cross sections for electron-methane scattering 1-20 eV: ●, present results; ○, Barbarito *et al* (1979); △, Griffith *et al* (1982); □, Ferch *et al* (1985b); ◇, Jones (1985); · · · ·, Jain and Thompson (1982).

broad structure observed by us in the Ramsauer minimum is not present in the data of Ferch *et al.* This is particularly surprising given that our apparatus is very similar to theirs.

At energies above 1.0 eV (figure 2) the present results are in best agreement with the measurements of Ferch *et al* (1985b) and Jones (1985). Between 3.0 and 20 eV the agreement is excellent, with substantial overlap in the quoted error bars on each data set. Below 3.0 eV the maximum disagreement is 10%, which is outside the combined uncertainties. The agreement between the present results and those of Griffith *et al* (1982) is only fair, with discrepancies of the order of 15% over the whole energy range. As was the case at low energies, the data of Barbarito *et al* (1979) are considerably lower than all the other experimental results.

We have also included in figures 1 and 2 a comparison with the elastic plus rotationally inelastic cross section calculated by Jain and Thompson (1982) using a parameter-free polarisation potential. This comparison extends only to the threshold for electronic excitation at about 9 eV. At low energies, the fact that vibrational excitation is not included in the calculation may account for the poor agreement with the present results, particularly in the region of the Ramsauer minimum. At higher energies, the agreement is somewhat better, although the discrepancies are still of the order of 20-50%, with the calculated cross section lying below the experimental results. It is unlikely that these discrepancies can be attributed to the non-inclusion of vibrational excitation and dissociative attachment in the calculation.

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